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WIDE-BAND DIELECTRIC SPECTROSCOPY OF SMALL-

MOLECULE GLASS-FORMING LIQUIDS AND INSULATING THIN

FILMS

Ph.D Thesis

presented to the faculty of Engineering, University of Dublin.

by

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February 2005

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Declaration

Declaration

I declare that this thesis is entirely my own work and has not previously been submitted as a whole or in part as an exercise for a degree at the University of Dublin, Trinity College Dublin (TCD), or at any other university. The research described in this thesis was carried out under the supervision of Professor J. K. Vij of the Department of Electronic and Electrical Engineering, Trinity College, University of Dublin from September 2000 to February 2005. I give my consent to the library of TCD to lend or copy this thesis on request.

Gerard Cower.

Gerard Power

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Abstract

Abstract

This thesis describes the application of broadband dielectric spectroscopy in the frequency range 1 mHz - 1.8 GHz to two main topics; (i) the glass transition and relaxation features of supercooled liquids and glasses, and; (ii) the characterisation of insulator films for use as low dielectric constant (low-k) dielectrics. The first two chapters provide background information on dielectric theory of materials and the glass transition. The remainder of the thesis covers four main areas of study. The dielectric spectra of pure and 1.0 mol% LiClO₄ solutions of supercooled liquid and glassy 1-propanol and 0.5-1.0 mol% LiClO₄ solutions of 5-methyl-2-hexanol were measured. Analysis of the spectra showed three relaxations (process I, II, and III) in the frequency range 1 mHz - 1 MHz which persist on addition of the salt. The effect of ions on the dielectric properties is discussed. Arguments against the assignment in the literature of process II as the α -relaxation (with process I being unrelated to viscous flow) are given. The crystallisation of supercooled liquid D-sorbitol was investigated by holding samples isothermally for several hours at different temperatures, and observing the evolution of the dielectric spectra. Changes in the ε^* spectra are used to argue that D-sorbitol crystallises to an orientationally disordered form. The Johari Goldstein (JG) β -relaxation in four small-molecule glassformers is studied. D-Sorbitol glasses are prepared with varying cooling rates. ε^* spectra are measured as the glasses are either heated through T_g at a constant rate or isothermally annealed. Stabilisation is shown to lead to a minimum in the plot of $\Delta \varepsilon_{JG}$ against temperature and a more negative slope in the Arrhenius plot of $f_{m,JG}$ at low temperatures as the glass is heated. An analogy is drawn with the effect on thermodynamic properties such as the molar volume V, enthalpy H, and entropy S. The main properties of the JG β -relaxation described in the literature are confirmed here. The Coupling Model is used to explain a change in temperature dependence in $f_{m,JG}$ of diethyl phthalate observed above T_g . SiO₂ and SiOF films on Si wafers were studied by FTIR and dielectric spectroscopy. Circuit models were proposed to account for relaxation processes seen in the ε^* spectra. Poly(ether) samples were evaluated as potential low-k dielectrics using TGA, DSC, and FTIR techniques and by measuring the ε^* spectra of freestanding films at several temperatures.

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Abbreviations

2d	2-dimensional
3 <i>d</i>	3-dimensional
а-	amorphous
ac	alternating current
AG	Adam and Gibbs
AIS	Analytical Instrument Systems GmbH
APC-7	Amphenol Precision connector, 7mm
BDS	broadband dielectric spectrometer
BMPC	1,1'-bis(p-methoxyphenyl)cyclohexane
BNC	British Naval connector
CC	Cole-Cole
CDI	Chelsea Dielectric Interface
Ch. 1	channel 1
Ch. 2	channel 2
СМ	Coupling Model
CRR	co-operatively rearranging region
C-V	capacitance-voltage
CVD	chemical vapour deposition
CZ	Czochralski
DC	Davidson-Cole
dc	direct current
DH	Dissado-Hill
DIN	Deutsche Industrie Norm
DSC	differential scanning calorimetry
DVM	digital multimeter
FLD	Frustrated Limited Domain
FRA	Frequency Response Analyser
FTES	fluorotriethoxysilane
FTIR	Fourier transform infrared
FWHM	full width at half maximum
FZ	float-zone

GD glow discharge

GEN	generator
GPIB	general-purpose interface bus
HDP	high density plasma
HN	Havriliak-Negami
HO	Hubbard-Onsager
HP	Hewlett-Packard
ILD	interlevel dielectric
IR	infrared
I-V	current-voltage
JG	Johari-Goldstein
KWW	Kohlrausch-Williams-Watts
MC	Mode-Coupling
MCM	MOBIL TM Composition of Matter
<i>m</i> -	meta
MOS	metal-oxide-silicon
MSD	mean square deviation
n-	normal
NMR	nuclear magnetic resonance
0-	ortho
<i>p</i> -	para
PID	proportional integral derivative
RC	resistance-capacitance
RDF	radial distribution function
RF	radiofrequency
SB	Souletie-Bertrand
SiOF	fluorinated silica
TEOS	tetraethoxysilane
TFS	tetrafluorosilane
TGA	thermogravimetric analysis
TPMT	GE triphenylolmethane triglicidyl ether
VFT	Vogel-Fulcher-Tammann
w/v	weight-over-volume
WLF	Williams-Landell-Ferry

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List of Symbols

- *a* radius, circuit terminal
- A area, nucleation rate equation pre-exponential constant, geometric constant in Avrami equation
- A_{AG} Adam and Gibbs equation pre-exponential constant

Arrhenius equation pre-exponential constant

 A_{cal}^* calibration coefficient (Agilent 4291 B)

- A_{compen}^{*} dielectric cell compensation coefficient (Agilent 4291 B)
- A_{Dyre} Dyre equation pre-exponential constant
- A_{mc} Mode-Coupling equation pre-exponential constant
- A_{SB} Souletie-Betrand equation pre-exponential constant
- A_{VFT} Vogel-Fulcher-Tammann equation pre-exponential constant
- *b* circuit terminal
- B_{ARR} Arrhenius equation constant
- B_{cal}^* calibration coefficient (Agilent 4291 B)

 B_{compen}^{*} dielectric cell compensation coefficient (Agilent 4291 B)

 B_{VFT} Vogel-Fulcher-Tammann equation constant

C Williams-Landel-Ferry equation constant, Adam and Gibbs equation constant,

interface growth rate equation pre-exponential constant

- C_0, C_1 capacitors in equivalent circuit (Fig. 6.4)
- *C*1 capacitor representing oxide film permittivity (Fig. 6.12)
- C2 capacitor representing Si wafer permittivity (Fig. 6.12)
- C^* complex capacitance
- C_{cal}^* calibration coefficient (Agilent 4291 B)
- C^*_{compen} dielectric cell compensation coefficient (Agilent 4291 B)
- C_{eff}^{*} effective complex capacitance
- C' real part of complex capacitance
- *C*["] imaginary part of complex capacitance

C_d depletion layer capacitance

- C_{diode} MOS diode capacitance
- C_{diode.min} minimum MOS diode capacitance
- C_i oxide capacitance
- *C_m* measuring capacitor (Chelsea Dielectric Interface/Solartron)
- C_p specific heat capacity at constant pressure
- $C_{p, glass}$ specific heat capacity of the glass
- $C_{p,lia}$ specific heat capacity of the liquid
- $C_{p,xtal}$ specific heat capacity of the crystal
- C_{vac} vacuum capacitance
- d film thickness
- dr radius element
- dt time element
- *dT* temperature element
- *D* Williams-Landel-Ferry equation constant, strength parameter
- D_R rotational diffusion constant
- D_{T} translational diffusion constant
- dA vector area element
- **D** electric flux density
- E_A activation energy
- $E_{A,\beta}$ β -relaxation activation energy
- $\hat{E}(\omega)$ Fourier transform of electric field magnitude
- E external electric field
- E_d directing field
- E_i internal field
- E_{i.I.} Lorentz field
- *f* linear frequency, factor related to molecular radius
- f_0 Coupling Model primitive relaxation frequency
- $f_{m,\alpha}$ α -relaxation frequency of maximum loss

- $f_{m,i}$ frequency of maximum loss of the *i*th process
- $f_{m,JG}$ Johari-Goldstein β -relaxation frequency of maximum loss

F force

 $F_{1/2}$ $F_{1/2}$ fragility

- g Kirkwood Correlation Factor
- g_1 oxide thickness
- g_2 Si wafer thickness
- $g(\phi)$ function representing phase errors in the measuring circuit (Chelsea Dielectric Interface/Solartron)
- G molar Gibbs free energy
- G_{∞} limiting high frequency value of the shear modulus of the liquid
- G_{melt} molar Gibbs free energy of the melt
- G_{xtal} molar Gibbs free energy of the crystal
- h height of multiplate capacitor (Fig. A.7)
- *H* molar enthalpy
- *H* potential energy barrier
- H_n potential energy barrier for viscous flow
- *I*₀ maximum current amplitude

I^{*} current phasor

 $j \quad \sqrt{-1}$

k dielectric permittivity

- k_A Avrami equation kinetic parameter
- *K* strength of interaction between oscillators in the Coupling Model
- K' strength of interaction between oscillator arrays in the Coupling Model
- K_{g} strength of interaction between oscillators in the Coupling Model at large

 $\tau_{\rm KWW}$

- *m* kinetic fragility, mass
- m_{\min} minimum kinetic fragility
- M molar mass

- *n* real refractive index, number density of species in the melt, Avrami equation nucleation parameter
- n_c number density of critical nuclei
- n_D refractive index at wavelength of Na-D line
- N number density, number of co-operatively rearranging regions, number of molecules, number density of heterogeneous nucleation sites
- N_D dopant concentration of n-type Si wafer
- $N_{e}(t)$ number density of growth nuclei
- **n** unit vector
- *p* hydrodynamic constant, pressure
- p_f fictive pressure
- *P* probability that a heterogeneous nucleation site becomes a stable nucleus
- P polarisation
- **P**_a atomic polarisation
- **P**_e electronic polarisation
- P_{ion} ionic polarisation
- **P**_o orientational polarisation
- q charge, heating rate
- Q charge
- Q_{encl} charge enclosed by a Gaussian surface
- $Q_{f.encl}$ free charge enclosed by a Gaussian surface
- r radius
- r_c radius of the critical nucleus

R cooling rate

- R_1, R_2 resistors in equivalent circuit (Fig. 6.4)
- *R2* resistor representing Si wafer loss (Fig. 6.12)
- R_n nucleation rate
- R_m measuring resistor (Chelsea Dielectric Interface/Solartron)
- r displacement
- **R** reaction field

- s_c configurational entropy of a co-operatively rearranging region
- s_c^* configurational entropy of the smallest co-operatively rearranging region
- *S* molar entropy
- S_0 molar residual entropy of a glass at 0 K
- S(t) step function
- S_c molar configurational entropy
- $S_{c,IG}$ molar configurational entropy of the Johari-Goldstein β -relaxation
- S_{exc} molar excess entropy of the supercooled liquid over the crystal phase
- S_{lia} molar entropy of the liquid
- S_{xtal} molar entropy of the crystal
- t time
- t_0 start time of phase transition
- *t_c* Coupling Model crossover time
- *T* absolute temperature
- T_0 Vogel-Fulcher-Tammann equation temperature constant
- $T_{1/2}$ half-way temperature on the dielectric relaxation plot ($\tau_{\alpha} = 10^{-6}$ s)
- T_2 temperature of 2nd order phase transition underlying the glass transition
- T_A Stickel plot upper crossover temperature
- T_B Stickel plot lower crossover temperature
- T_{β} β -relaxation merging temperature
- T_c crystallisation temperature, temperature of phase transition, temperature constant in the Mode-Coupling and Souletie-Bertrand equations
- T_e temperature of equilibrium between melt and crystal phases
- T_f fictive temperature
- T_{g} glass transition temperature
- T_{g}^{o} orientational glass transition temperature
- T_{κ} Kauzmann temperature
- *u* rate of advance of crystal-melt interface

- U potential energy
- v_x x-component of velocity
- V molar volume, voltage
- V_0 maximum voltage amplitude
- V_c specific volume of old phase at phase transition temperature, characteristic volume in Shoving Model equation
- V_m factor related to molecular volume
- V_T total volume
- \mathbf{V}^* voltage phasor
- V1^{*} channel 1 vector sample voltage (Chelsea Dielectric Interface/Solartron)
- $V1_r^*$ channel 1 vector reference voltage (Chelsea Dielectric Interface/Solartron)
- **V2**^{*} channel 2 vector sample voltage (Chelsea Dielectric Interface/Solartron)
- $V2_r^*$ channel 2 vector reference voltage (Chelsea Dielectric Interface/Solartron)
- V_{ref}^* vector voltage reflected from sample (Agilent 4291 B)
- V_s^* vector source voltage (Agilent 4291 B)
- *w* full width at half maximum normalised to Debye value
- *W* energy of dipole in an electric field
- W(T) probability of transition as a function of temperature
- x displacement magnitude, transformed volume fraction, mole fraction of sample involved in the Johari-Goldstein β -relaxation
- x_e extended volume fraction
- x displacement
- $y(\tau)$ distribution function for relaxation time
- z number of species in a co-operatively rearranging region
- z^* minimum number of species in a co-operatively rearranging region
- z(t) unnormalised quantity depending on volume fraction of uncrystallised melt
- Z^* complex impedance
- Z' real part of complex impedance
- Z" imaginary part of complex impedance
- Z_0 characteristic impedance of the measuring circuit (Agilent 4291 B)

 Z_{cal}^{*} complex impedance of calibration termination (Agilent 4291 B)

- Z_{eff}^{*} effective complex impedance
- $Z_{LOAD.corr}^{*}$ corrected complex impedance of LOAD termination (Agilent 4291 B)
- $Z_{lowloss,corr}^{*}$ complex impedance of low loss termination corrected by calibration (Agilent 4291 B)
- $Z'_{lowloss,corr}$ real part of complex impedance of low loss termination corrected by calibration (Agilent 4291 B)
- $Z''_{lowloss,corr}$ imaginary part of complex impedance of low loss termination corrected by calibration (Agilent 4291 B)
- Z_m^* Chelsea Dielectric Interface measuring circuit complex impedance (Chelsea Dielectric Interface/Solartron)
- Z_{mes}^* uncorrected measured complex impedance (Agilent 4291 B)
- Z_r^* reference capacitor complex impedance (Chelsea Dielectric Interface/Solartron)
- α polarisibility, volume coefficient of thermal expansion
- $\alpha(t)$ step response function
- α_{α} α -relaxation symmetric broadening parameter
- α_a atomic polarisibility
- α_{cc} Cole-Cole distribution parameter
- α_e electronic polarisibility
- α_{e}^{*} complex electronic polarisibility
- α'_{e} real part of electronic polarisibility
- α''_{e} imaginary part of electronic polarisibility
- α_i Havriliak-Negami symmetric broadening parameter of the *i*th process
- α_{ion} ionic polarisibility
- α_{IG} Johari-Goldstein β -relaxation symmetric broadness parameter

- α_o orientational polarisibility
- α_{T} total induced polarisibility
- α_{T}^{*} complex total induced polarisibility
- β_{α} α -relaxation asymmetric broadening parameter
- β_{DC} Davidson-Cole distribution parameter
- β_i Havriliak-Negami asymmetric broadening parameter of the *i*th process
- β_{JG} JG β -relaxation asymmetric broadening parameter

 β_{KWW} Kohlrausch-Williams-Watts stretched exponential parameter

- γ damping coefficient, exponent in Nagel wing, co-operative length scale, exponent in the Mode-Coupling and Souletie-Bertrand equations, interfacial tension at the crystal-melt interface, power law exponent for JG β -relaxation
- **Γ** voltage reflection coefficient (Agilent 4291 B)

 δ loss angle

- $\delta \varepsilon$ dielectric decrement
- $\delta \varepsilon_{HO}$ Hubbard-Onsager dielectric decrement
- $\delta \varepsilon_{KDD}$ kinetic dielectric decrement
- ΔC_{eff} difference between low and high frequency effective capacitance
- ΔC_p change in specific heat capacity on phase transition, specific heat capacity difference between equilibrium supercooled liquid and glass
- ΔG molar Gibbs free energy of crystallisation
- ΔG_c molar Gibbs free energy barrier to transport of species within the crystal
- ΔG_I molar Gibbs free energy barrier to transport of species across the crystal-melt interface
- ΔG_m molar Gibbs free energy barrier to transport of species within the melt
- ΔG_n molar Gibbs free energy of formation of the cluster
- $\Delta G_{n,c}$ molar Gibbs free energy of formation of the critical nucleus
- ΔG_{ν} molar Gibbs free energy of crystallisation per unit volume
- ΔH molar enthalpy of crystallisation
- ΔS molar entropy of crystallisation

ΧХ

- ΔT undercooling of melt
- $\Delta \alpha$ change in volume coefficient of thermal expansion on phase transition
- $\Delta \varepsilon$ dielectric strength
- $\Delta \varepsilon_{\alpha}$ α -relaxation dielectric strength
- $\Delta \varepsilon_{\beta} = \beta$ -relaxation dielectric strength
- $\Delta \varepsilon_i$ dielectric strength of the *i*th relaxation process
- $\Delta \varepsilon_{JG}$ Johari-Goldstein β -relaxation dielectric strength
- $\Delta \theta$ difference between actual and measured phase angles of low loss termination (Agilent 4291 B)
- $\Delta \kappa$ change in compressibility on phase transition
- $\Delta \mu$ per species energy barrier to rearrangement of a co-operatively rearranging region
- ε^* complex permittivity
- ε' dielectric permittivity
- ε'' dielectric loss
- ε_1^* oxide complex permittivity
- ε'_1 oxide permittivity
- ε_2^* Si wafer complex permittivity
- ε'_2 Si wafer permittvity
- ε_2'' Si wafer loss
- \mathcal{E}_{∞} limiting high frequency permittivity
- $\varepsilon_{\infty i}$ limiting high frequency permittivity of the *i*th process
- ε'_{IG} Johari-Goldstein β -relaxation contribution to permittivity
- $\varepsilon_{IG}^{"}$ Johari-Goldstein β -relaxation contribution to loss
- ε_{o}^{*} orientational complex permittivity
- ε_r dielectric permittivity
- ε_s static permittivity
- ε_{si} limiting low frequency permittivity of the *i*th process
- $\varepsilon_{s, pure}$ static permittivity of pure alcohol

- ε'_{α} α -relaxation contribution to permittivity
- ε_{α}'' α -relaxation contribution to loss

 η viscosity

- θ angle between vectors
- $\theta_{lowloss}$ actual phase angle difference between current and voltage for low loss termination (Agilent 4291 B)
- $\theta_{lowloss,mes}$ measured phase angle difference between current and voltage for low loss termination corrected by calibration (Agilent 4291 B)
- *κ* compressibility
- λ width of crystal-melt interface
- μ dipole moment
- $\mu_{ind,a}$ induced atomic dipole moment
- $\mu_{ind,e}$ induced electronic dipole moment
- $\mu_{ind,ion}$ induced ionic dipole moment
- μ_{p} permanent dipole moment
- v wavenumber
- ξ frictional constant
- ρ resistivity, density
- σ surface charge density
- σ^* complex conductivity
- σ' real part of complex conductivity
- σ'' imaginary part of complex conductivity
- σ_b bound surface charge density
- σ_{dc} dc conductivity
- σ_f free surface charge density
- τ relaxation time
- τ_0 Coupling Model primitive relaxation time
- $au_{\infty,ARR}$ Arrhenius equation high temperature relaxation time
- $\tau_{\infty,\beta}$ β -relaxation high temperature relaxation time

 $\tau_{\infty,VFT}$ Vogel-Fulcher-Tammann equation high temperature relaxation time

- τ_c rotational correlation time
- au_{cc} Cole-Cole relaxation time
- τ_D Debye relaxation time
- $\tau_{\scriptscriptstyle DC}$ Davidson-Cole relaxation time
- τ_{g} α -relaxation time at glass transition in Williams-Landel-Ferry equation
- $\tau_{HN\alpha}$ α -relaxation Havriliak-Negami relaxation time
- τ_{HNi} Havriliak-Negami relaxation time of the i^{th} process
- τ_{HNJG} JG β -relaxation Havriliak-Negami relaxation time
- τ_{JG} Johari-Goldstein β -relaxation relaxation time
- τ_{KWW} Kohlrausch-Williams-Watts relaxation time
- τ_{vis} viscosity relaxation time
- τ_{α} α -relaxation time
- τ_{β} β -relaxation relaxation time
- ϕ phase difference between ac current and voltage
- $\phi(t)$ decay function
- ϕ_{ms} metal-Si workfunction difference
- χ_e dielectric susceptibility
- Ψ_{b} potential difference between Fermi levels of extrinsic and intrinsic Si
- Ψ_s surface potential
- ω angular frequency
- ω_0 resonance frequency
- Ω_c number of configurations
- $\Omega_{c,JG}$ number of configurations for species taking part in the Johari-Goldstein β -relaxation

Constants

е	electronic charge	1.6 🗙 1	0 ⁻¹⁹ C	
k	Boltzmann constant	1.38×	10 ⁻²³ J	K ⁻¹
n _i	intrinsic carrier conce	ntratior	n of Si	$1.45 \times 10^{16} \text{ m}^{-3}$
N_A	Avogadro number		6.02 🗴	$(10^{23} \text{ mol}^{-1})$
R	Universal gas constan	it	8.314.	J K ⁻¹ mol ⁻¹
\mathcal{E}_0	permittivity of free sp	ace	8.854	$\times 10^{-12} \mathrm{F m^{-1}}$
$\mathcal{E}_{s,Si}$	static permittivity of S	Si	12	
\mathcal{E}_{s,SiO_2}	static permittivity of S	SiO ₂	4	

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Compound	Formula	Supplier	Purity
chlorobenzene	ÇI	Lancaster	99 %
<i>cis-</i> decalin	H H	Fluka AG	98% (purum)
5-methyl-2- hexanol	OH	Fluka AG	98 % (purum)
D-sorbitol	ОН	Fluka AG	99.5 % (puriss.)
diethyl		Fluka AG	99.5 %
phthalate	ſ		(puriss.)
lithium perchlorate	LiCIO ₄	Fluka AG	99 %
1-propanol	ОН	Fluka AG	99.5 % (puriss.)
5-methyl-2- hexanol	OH	Fluka AG	98 % (purum)

Chapter 1

Theory of Dielectric Properties of Materials

1.1 Definition of a Dielectric

The application of an external electric field to a material can have two main effects (the following assumes the field is not so large as to have any nonlinear effects). The first is the transport of charge in the material resulting in a current density \mathbf{J} given by $J = \sigma_{dc} E$ where E is the applied electric field. This is observed in materials where there may be charges free to move (metals, semiconductors, ionic conductors etc). A second effect of an external electric field is charge separation within the material, which occurs irrespective of whether there are free charges or not. When this occurs, the material is said to be polarised, having a net dipole moment per unit volume called its polarisation, **P**. If the material already contains dipoles that are oriented randomly due to thermal motions (so overall $\mathbf{P} = 0$ in the absence of an external electric field), the distribution of these dipoles may be altered so that they are preferentially ordered in a certain direction, also giving rise to a net polarisation. Finally, if a material is ferroelectric, it will have randomly oriented domains in which there is already a net polarisation (so again overall $\mathbf{P} = 0$ in the absence of an external electric field). Domains with polarisation oriented in a certain direction may grow at the expense of the others in the presence of the field, again resulting in a net polarisation. These effects are responsible for the dielectric properties of materials, and materials in which these effects are more important than charge transport are called dielectrics. The term 'dielectric' is generally interchangeable with 'insulator' [1] (in a perfect insulator no

1

charge transport occurs) but even semiconductors have 'dielectric properties'. Dielectric effects in poor insulators are obscured by conduction.

1.2 Polarisation and Bound Charge

A typical dielectric can be considered as a neutral assembly of charges (unless charge has been injected into the dielectric in some way). This is reasonable when one considers that the simplest model of an atom is a positive point charge nucleus surrounded by a negatively charged region in which the electrons are found [2]. The dipole moment of a neutral collection of charges is

$$\boldsymbol{\mu} = \sum_{i} q_{i} \mathbf{r}_{\mathbf{i}0,} \tag{1.1}$$

where \mathbf{r}_{i0} is the vector from the origin to the *i*th charge q_i . $\boldsymbol{\mu}$ is independent of the choice of origin when the total charge $Q = \sum_i q_i = 0$ [2, 3]. When a field is applied, the overall centres of positive and negative charge are displaced by a vector \mathbf{r} and the dipole moment for the assembly becomes $\boldsymbol{\mu} = Q\mathbf{r}$

If the assembly consisted of a number density N of equal elementary charges q per unit volume, then the dipole moment per unit volume (polarisation) of the material is

$$\mathbf{P} = Nq\mathbf{r}.\tag{1.2}$$

An alternative way to look at this [4] is to consider a surface inside the dielectric. When a field is applied, if charge separation occurs, the charge crossing an area element dA (with a normal area vector dA) on the surface is **P.dA**. If dA were on the surface of the dielectric it would result in a bound surface charge density of

$$\sigma_b = \mathbf{P}.\hat{\mathbf{n}},\tag{1.3}$$

where $\hat{\mathbf{n}}$ is a unit vector normal to the surface of the dielectric.

Although Eq. (1.3) was arrived at by considering a particular model, it is valid regardless of the actual microscopic origins of the polarisation.

Chapter 1

1.3 Polarisation and Relative Permittivity

The electric field between the plates of an empty parallel plate capacitor, area A, with plate separation d is found from Gauss' law

$$\int_{\mathbf{A}} \mathbf{E}.\mathbf{dA} = \frac{\mathcal{Q}_{encl}}{\varepsilon_0},\tag{1.4}$$

where Q_{encl} is the charge enclosed by the Gaussian surface (a cylinder with one end in the metal plate and the other in the free space between the plates). **dA** is a vector normal to the area element *dA* on the cylinder ends of the Gaussian surface. ε_0 is the permittivity of free space (8.854 x 10⁻¹² F m⁻¹ – the constant used here just depends on the units used [3]) For $d \ll A$ this leads to a field

$$E = \frac{\sigma}{\varepsilon_0},\tag{1.5}$$

where σ is the surface charge density on the plates.

Using V = Ed for the potential between the plates, and since the charge Q on the plates is σA the capacitance is given by

$$C_{vac} = \frac{Q}{V} = \frac{\varepsilon_0 A}{d}.$$
 (1.6)

The vac suffix stresses that the capacitor is empty. If we put a dielectric between the plates and in contact with them, the charge on the plates is reduced by σ_b [5] [see Eq. (1.3)] and we have

$$E = \frac{\sigma_f - \sigma_b}{\varepsilon_0}.$$
 (1.7)

Here we introduce σ_f , the free surface charge density on the plates – the surface charge density that would result from field **E** if no dielectric were present. If we now define a new field **D**, the electric flux density, such that $\int_A \mathbf{D.dA} = Q_{f,encl}$ then $D = \sigma_f$ in the case where no dielectric is present between the plates. Substituting into Eq. (1.7) – in vector terms we have

$$\mathbf{D} = \mathcal{E}_0 \mathbf{E} + \mathbf{P}. \tag{1.8}$$

We could also express the drop in field strength when the dielectric is placed between the plates using the relative permittivity (also called the 'dielectric constant') of the
material between the plates as a factor in Eq. (1.5) assuming the charge on the plates stays the same:

$$E = \frac{\sigma_f}{\varepsilon_0 \varepsilon_r} \tag{1.9}$$

so that the capacitance with a dielectric between the plates becomes

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}.$$
 (1.10)

Since $D = \sigma_f$, Eq. (1.9) leads to the equation for **D** in terms of **E**:

$$\mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E}. \tag{1.11}$$

Inserting into Eq. (1.8) gives

$$\mathbf{P} = \varepsilon_0 (\varepsilon_r - 1) \mathbf{E} = \varepsilon_0 \chi_e \mathbf{E}, \qquad (1.12)$$

where χ_e is called the dielectric susceptibility. Fig. 1.1 is a diagram of the capacitors and a summary of the results obtained. Eq. (1.11) and (1.12) contain the implicit assumption that **P** and hence **D** are linear in **E**, which will be true except for very large fields. Using a scalar for ε_r implies the dielectric is isotropic and homogeneous – if the polarisation caused by **E** were different in different directions ε_r would be a tensor [4].



Fig. 1.1 The electric field **E** and electric flux density **D** vectors between two empty charged metal plates. When the dielectric is placed between the plates, the flux density is increased to a new value \mathbf{D}_{diel} and electric field is decreased to \mathbf{E}_{diel} . The polarisation **P** of the dielectric is also shown.

1.4 Microscopic Mechanisms of Polarisation

The microscopic origins of polarisation were alluded to in Sect. 1.1. They are described in more detail here. There are three main processes [2-6], which will be described in turn:

- (i) Electronic polarisation
- (ii) Atomic/Ionic Polarisation
- (iii) Orientational Polarisation

The first two types all involve charge separation caused by the electric field and are often grouped as various types of 'displacement polarisation' [7].

(i) Electronic Polarisation

When an electric field is applied to the simple model of the atom described above, there is a relative displacement of the equilibrium positions of the nucleus and centre of charge of the electron cloud by a small distance, x. This results in an induced dipole moment of magnitude $\mu_{ind,e} = Zex$ where Z is the atomic number and e is the electron charge. The subscript e identifies the type of polarisation. A simple calculation [3, 6] can then show that for the model

$$\boldsymbol{\mu}_{\text{ind},e} = \boldsymbol{\alpha}_e \mathbf{E},\tag{1.13}$$

where α_e is the electronic polarisibility of the atom. In general, polarisibilities are dipole moments per unit electric field. Such an equation could also be applied to an assembly of atoms (usually a molecule, but may be a crystal basis or unit cell for a covalent or ionic crystal) but unless the assembly has spherical symmetry,

 μ_{ind} and E will not be collinear and α_e becomes a tensor. In a material, each of the induced dipoles will contribute to the electronic polarisation, which is given by their vector sum. If the number density of induced dipoles is *N*, then the electronic polarisation is

$$\mathbf{P}_{\mathbf{e}} = N\alpha_{e}\mathbf{E}_{\mathbf{i}}.\tag{1.14}$$

There are several differences between Eq. (1.13) and (1.14). The electronic polarisibility becomes an average quantity $\overline{\alpha_e}$ as it may be different for different moieties in the assembly depending on their orientation to the field. E_i is average field

experienced by an induced dipole inside the material, excluding its own field. This field is called the 'internal field' [3, 5, 6, 7], and it may be different from the external electric field **E** in circumstances where the interaction of the induced dipoles with each other must be considered (condensed phases). The distinction between **E** and \mathbf{E}_i is discussed further in Sect. 1.6 and 1.7. Electronic polarisation is present in all materials. Since electrons respond very quickly and remain in phase with the field, electronic polarisation can contribute to ε_r of a material, even at optical frequencies.

(ii) Atomic/Ionic Polarisation

In molecules that contain more than one atom type, there will be an electronegativity difference between different atoms that are covalently bonded. It will be more probable that electrons will be found nearer to the atom of higher electronegativity. Formally, this atom has a slight negative charge, while the other atom has a slight positive charge. This gives the bond a permanent dipole moment in the absence of a field. The net dipole moment for the molecule will be the vector sum of those for its bonds. If the molecule has a centre of symmetry there will be no net dipole moment. Diatomic molecules AB such as HCl always have a dipole moment [3, 5], triatomic ones will too unless they are linear of form ABA (e.g. CO₂) [3, 5]. Even when the molecule has no net dipole moment, the fact that the atoms in the bonds have small apparent charges means that their equilibrium positions can be adjusted slightly by the application of a field resulting in an induced dipole moment. As for electronic polarisation we can express this as

$$\boldsymbol{\mu}_{\text{ind},\mathbf{a}} = \boldsymbol{\alpha}_a \mathbf{E},\tag{1.15}$$

where α_a is the atomic polarisation, which may or may not be a scalar. If there are N species with an average atomic polarisation $\overline{\alpha_a}$ then in analogy with Eq. (1.14) we write

$$\mathbf{P}_{\mathbf{a}} = N\alpha_a \mathbf{E}_{\mathbf{i}},\tag{1.16}$$

where \mathbf{P}_{a} is the atomic polarisation. The larger size of atoms means that they will not respond to electric fields with frequencies beyond the infrared, so that atomic polarisation only makes an important contribution to ε_{r} below these frequencies. An extreme form of atomic polarisation (ionic polarisation) occurs in an ionic crystal, where charge is transferred from one atom to another to create ionic bonds. The

anions and cations can be displaced from their equilibrium positions in the presence of an electric field to create a net induced dipole moment in a single unit cell of

$$\boldsymbol{\mu}_{\text{ind,ion}} = \boldsymbol{\alpha}_{ion} \mathbf{E}, \tag{1.17}$$

which, when extended to the bulk as before (N unit cells per unit volume) gives

$$\mathbf{P}_{\rm ion} = N\alpha_{\rm ion}\mathbf{E}_{\rm i}.\tag{1.18}$$

 α_{ion} , the ionic polarisibility, should be the same for all unit cells in an ideal crystal with perfect translational symmetry so it is not averaged (it would be for a polycrystalline material), but it may be a tensor rather than a scalar. In essence, ionic polarisation is just a special case of atomic polarisation, and contributes to ε_r over the same frequency range.

(iii) Orientational Polarisation

It was outlined above how a polyatomic molecule with more than one atom type (or a unit cell in a crystal) may come to possess a net permanent dipole moment, which we will call $\mu_{\rm p}$, as a result of its symmetry. If a material possesses such dipoles it is said to be polar and has orientational polarisation in an electric field - otherwise it is nonpolar and only possesses displacement polarisation in an electric field. Polar materials will also have displacement polarisation. Here we consider the contribution of permanent dipoles to the observed polarisation of a material. If no field is applied, random thermal reorientations of the dipoles will ensure that the system as a whole has no net dipole moment and no polarisation. Another way of saying this is that the probability of finding the dipole in any orientation is equal to it being found in any other orientation. This assumes that the temperature is high enough to allow these reorientations to occur. When an external electric field is applied, the field direction becomes preferred. The probability of finding a dipole in a certain range of angles $d\theta$ where θ is the angle the dipole makes with the field is given by the Boltzmann distribution. The important energy in this case is the potential energy of a single dipole in an electric field:

$$W = -\boldsymbol{\mu}_{p} \cdot \mathbf{E}_{d} = -\boldsymbol{\mu}_{p} E_{d} \cos \theta.$$
(1.19)

A subscript *d* is included on the field as this field is the "directing field", which tends to orient the dipoles [7]. In the case of condensed phases of polar molecules, this will be different from both the external electric field, \mathbf{E} , and the internal field, \mathbf{E}_i . The distinction between these fields in discussed in more detail in Sect. 1.6-1.8.

We must now obtain the average $\cos\theta$ for all the dipoles, which is given by [3, 5-7]

$$\overline{Cos\theta} = \frac{\int_{0}^{\pi} \cos\theta \sin\theta \exp\left[\frac{-W}{kT}\right] d\theta}{\int_{0}^{\pi} \sin\theta \exp\left[\frac{-W}{kT}\right] d\theta} = \frac{\int_{-a}^{a} z \exp[z] dz}{a \int_{-a}^{a} \exp[z] dz},$$
(1.20)

where $z = \frac{\mu_p E_d}{kT} \cos \theta$ and $a = \frac{\mu_p E_d}{kT}$. *T* is the absolute temperature and *k* is the

Boltzmann constant.

The result is $\overline{\cos \theta} = L(a) = \coth a - 1/a$, which saturates to 1 at large *a*. When *a* is small (which will be the case at 300 K if the electric field is less than about 10 MV m⁻¹, even if the dipole moment is a relatively large 4 Debye Units (D) [7] i.e. 4 x 3 x 10⁻³⁰ C m⁻¹), $L(a) \sim a/3$ and we may write for the effective dipole moment $\overline{\mu_p}$ of a molecule averaged over all orientations [3, 5-7]

$$\overline{\boldsymbol{\mu}_{\mathbf{p}}} = \boldsymbol{\mu}_{p} \overline{\cos\theta} = \frac{\boldsymbol{\mu}_{p}^{2} \mathbf{E}_{\mathbf{d}}}{3kT}, \qquad (1.21)$$

and if there are *N* molecules per unit volume then we can write the orientational polarisation as

$$\mathbf{P}_{\mathbf{O}} = N\overline{\mathbf{\mu}_{\mathbf{p}}} = \frac{N\mu_{p}^{2}\mathbf{E}_{\mathbf{d}}}{3kT} = N\alpha_{o}\mathbf{E}_{\mathbf{d}}, \qquad (1.22)$$

where $\alpha_o = \frac{\mu_p^2}{3kT}$ is the orientational polarisibility of the material, in analogy with the electronic, atomic, and ionic polarisibilites. The orientational polarisation of a material contributes to the permittivity only at relatively low frequencies (up to the microwave region) as it involves rearrangements of entire groups of atoms (generally molecular rotations). Although the derivation above deals with molecular rotation, orientational polarisation can also arise from the rearrangement of point defect aggregations in ionic crystals, which would be better considered by a derivation exploring the probabilities of ionic jumps on the crystal lattice [5]. Fig. 1.2 gives an overview of the four polarisation processes.



Fig. 1.2 Diagram illustrating the (A) electronic (B) atomic (C) ionic, and (D) orientational polarisation processes in dielectric materials. The upper part of each section shows the situation in zero electric field, the lower part the situation when field **E** is applied. **x** is the relative displacement of the positive and negative charge centres.

1.5 Permittivity of a Material

We can now write a general equation for the polarisation of a material combining Eq. (1.14), (1.16), (1.18), and (1.22). If there are *N* species per unit volume, the total polarisation, omitting complexities of inhomogeneous and anisotropic materials is

$$\mathbf{P} = \mathbf{P}_{\mathbf{e}} + \mathbf{P}_{\mathbf{a}} + \mathbf{P}_{\mathbf{ion}} + \mathbf{P}_{\mathbf{O}} = N[\alpha_T \mathbf{E}_{\mathbf{i}} + \alpha_O \mathbf{E}_{\mathbf{d}}], \qquad (1.23)$$

where $\alpha_T = \alpha_e + \alpha_a + \alpha_{ion}$ is the sum of the various induced polarisibilities. Using Eq. (1.12) we now have an equation expressing the permittivity, ε_r , and external electric field **E** (the bulk parameters) in terms of the polarisibilities and the internal and directing fields (microscopic quantities),

$$\varepsilon_0 (\varepsilon_r - 1) \mathbf{E} = N [\alpha_T \mathbf{E}_i + \alpha_o \mathbf{E}_d]$$
(1.24)

The fact that **E** cannot be used as the electric field experienced inside the material is a result of the influence of interactions between the constituent particles of the dielectric material. These can be grouped into two classes [5]; (i) Short range ('local') interactions such as covalent bonds, Van Der Waals forces (including Hydrogen Bonds), which are strong but need only be considered for nearest-neighbours, and; (ii) Dipolar interaction forces - the forces between the induced and permanent dipoles themselves. These are long range and must be accounted for even at macroscopic distances. Exact calculation of the effect of dipole interaction forces on any given dipole quickly becomes intractable due to the large numbers of particles involved unless simplifications are made. Approaches to the problems of internal and directing fields inside dielectrics are described in Sect. 1.6-1.10. There are two main ways to tackle the problem. In a continuum approach [5, 7] we may consider the dielectric as a continuous medium and try to determine the fields experienced by single molecule by creating cavities in the material and isolating the various contributions to the field inside the cavity. In a statistical mechanical approach [5, 7], the various interactions between the molecules are considered in as exact a way as possible. Simplifications like considering part of the dielectric beyond outside some boundary as a continuum must be made (the Lorentz field in the next section is an early example of this). There is one class of materials for which the distinction between the three fields above can

be ignored because all of the interaction forces between the particles are small - low pressure gases [3, 5, 7]. In this case we can equate and cancel the external, internal, and directing fields in Eq. (1.24) to give:

$$\varepsilon_0(\varepsilon_r - 1) = N \left[\alpha_T + \frac{\mu_p^2}{3kT} \right]. \tag{1.25}$$

This can be further simplified if the gas is non-polar as μ_p is 0 and $\varepsilon_0(\varepsilon_r - 1) = N\alpha_r$.

1.6 The Lorentz Calculation of Internal Field

The first (and simplest) attempt to include the dipolar interaction forces and calculate E_i is due to Lorentz [8] and is described in most dielectric texts [5-7]. The basic method applied here can also be adapted for use in more complex treatments of dielectrics, including a statistical mechanical treatment. A spherical region inside the dielectric is considered, large enough so that it has the properties of the bulk. The region inside the sphere can be treated exactly using a microscopic model, while the rest of the dielectric is approximated as a continuous medium of relative permittivity ε_r . The field at a dipole inside the sphere will contain contributions from the polarised medium both inside and outside the sphere. In certain special cases, the contribution from inside can be shown to be zero. Two such cases were considered by Lorentz; (i) A cubic lattice of 'atoms' with a positive point charge nucleus and a negatively charged electron cloud and; (ii) Randomly oriented molecules. The first may be a reasonable model for some non-polar solids while the second may describe gases at reasonable pressures, which were already covered by Eq. (1.25). The Lorentz field (Lorentz's estimate for the internal field E_i) can be found by replacing the inner sphere by a cavity, while leaving the polarisation and electric field in the material unaltered (the cavity is only 'virtual'). The problem is shown graphically in Fig. 1.3. If we consider an area element dA with normal vector dA pointing out then the charge on dA is **P.dA**. All components of electric field due to this charge not collinear with the external field E will cancel when integrated over the whole surface of the sphere (the field is radial). If θ is the angle between dA and E then the field due to the bound charge on the sphere is

$$E_s = \int_{A} \frac{\mathbf{P}.\mathbf{d}\mathbf{A}\cos\theta}{4\pi\varepsilon_0 r^2} = \int_{0}^{\pi} \frac{P\cos^2\theta}{4\pi\varepsilon_0 r^2} dA.$$
 (1.26)

Since $dA = 2\pi r^2 \sin \theta d\theta$ and θ varies from 0 to π over the sphere

$$E_{s} = \frac{P}{2\varepsilon_{0}} \int_{0}^{\pi} \sin \theta \cos^{2} \theta d\theta = \frac{P}{3\varepsilon_{0}}.$$
 (1.27)



Fig. 1.3 Lorentz calculation of the internal field. A spherical cavity, radius r, is created in the dielectric. The field due to the bound surface charge on the inside of the cavity is then considered.

The direction of \mathbf{E}_s is the same as that of the external field so Lorentz's value for the internal field (the 'Lorentz field') is [using Eq. (1.12)]

$$\mathbf{E}_{\mathbf{i},\mathbf{L}} = \mathbf{E} + \frac{\mathbf{P}}{3\varepsilon_0} = \frac{\varepsilon_r + 2}{3} \mathbf{E}.$$
 (1.28)

We can now use Eq. (1.28) to write an equation for the permittivity of a non-polar [5] material ($\mu_p = 0$) by substituting **E**_{i,L} for **E**_i in Eq. (1.24):

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\alpha_T}{3\varepsilon_0}.$$
(1.29)

This is the Clausius-Mossotti equation. It will also apply for polar dielectrics at higher frequencies where only atomic or ionic, and electronic polarisation is important and $\varepsilon_r = \varepsilon_{\infty}$, the limiting high frequency permittivity. At optical frequencies (or neglecting atomic/ionic polarisation contributing to ε_{∞}), ε_r can be replaced by the square of the real refractive index, n^2 [5]. If we assumed $\mathbf{E}_{i,L}$ and the directing field \mathbf{E}_d were equal, as Debye [9] did, we could now write an equation for polar materials using Eq. (1.25):

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N}{3\varepsilon_0} \left[\alpha_T + \frac{\mu_p^2}{3kT} \right].$$
(1.30)

However this is only the case in gases at normal pressures (for which we already have a satisfactory equation since $E_i \sim E$ also) because of a further effect of the interaction of a dipole with its surroundings described below and first discussed by Onsager [7, 10].

1.7 Reaction Field of a Molecule, Cavity field, and the Internal Field

Molecules with dipole moments create an electric field. This field polarises the environment of the molecule. If the molecule is polar, this effect occurs even if there is no external field – if the molecule is non-polar, the effect only occurs when there is an external field. This polarisation of its surroundings results in a contribution to E_i at the dipole, which is called the reaction field **R** of the dipole [7]. A suitable model for calculating the reaction field for a molecule with a dipole moment μ_p was proposed by Bell [11] and applied to the problem of polar dielectrics by Onsager [10]. The

molecule is considered as a polarisible point dipole (a dipole in the limit of zero separation between the positive and negative centres of charge) with polarisibility α inside a cavity of radius *a* in the material of permittivity ε_r [7] (Fig 1.4). Onsager [10] chose *a* so that the sphere is equivalent to a single molecular volume:

$$\frac{4}{3}\pi a^3 = \frac{1}{N},\tag{1.31}$$

where N is the number density of molecules. The reaction field induced by the dipole is given by a recursive relation in **R**

$$\mathbf{R} = f\left(\boldsymbol{\mu}_{\mathbf{p}} + \alpha \mathbf{R}\right) = \frac{f}{1 - \alpha f} \,\boldsymbol{\mu}_{\mathbf{p}}.$$
 (1.32)

Fig. 1.4 Bell and Onsager's model for calculating the reaction field of a point dipole (After Ref. [7]).

The reaction field is proportional to the total dipole moment in the sphere (which includes an induced portion $\alpha \mathbf{R}$) with a factor f. Solving the Laplace equation $\nabla^2 V = 0$ for the potential in the simplified situation where $\alpha = 0$ [7] allows the factor f to be determined as

$$f = \frac{1}{4\pi\varepsilon_0 a^3} \frac{2(\varepsilon_r - 1)}{2\varepsilon_r + 1}.$$
(1.33)

The above analysis allows us to write the internal field at a particular molecule in a new way, which is more useful when dealing with polar substances. We can decompose E_i into two parts:

$$\mathbf{E}_{i} = \mathbf{E}_{c} + \mathbf{R}. \tag{1.34}$$

R was defined above. Another field \mathbf{E}_{c} , the cavity field is introduced here. This is the field in a *real* cavity inside a dielectric [7] (not a *virtual* one such as in Lorentz's derivation) so it takes account of changes in the material's polarisation due to the void (in other words, **R** is excluded from it by definition, whereas the Lorentz field implicitly takes account of **R**). An electrostatic calculation [7] shows that if the external field is **E** then

$$\mathbf{E}_{c} = \frac{3\varepsilon_{r}}{2\varepsilon_{r}+1}\mathbf{E}.$$
(1.35)

In a non-polar material, \mathbf{R} will depend on the induced dipole moment alone so that Eq. (1.32) becomes:

$$\mathbf{R} = f\alpha \mathbf{E}_{i} = f\alpha (\mathbf{E}_{c} + \mathbf{R}). \tag{1.36}$$

Using Eq. (1.33), (1.34), (1.35), (1.36), and Onsager's value of the radius of the cavity a [Eq. (1.31)], expression of the internal field in terms of the external field leads back to the Clausius-Mossotti equation [Eq. (1.29) with $\alpha_T = \alpha$] when the macroscopic and microscopic expressions for the polarisation are equated [7].

1.8 Onsager Equation for Polar Dielectrics

Now consider the situation in a polar dielectric where Eq. (1.24) applies, viz

$$\varepsilon_0(\varepsilon_r-1)\mathbf{E}=N\left[\alpha\mathbf{E}_{\mathbf{i}}+\frac{\mu_p^2}{3kT}\mathbf{E}_{\mathbf{d}}\right].$$

In this case we can still use Eq. (1.34) for the internal field but a part of the reaction field on a given molecule will be a result of the permanent dipole moment μ_p of the molecule. This part of the reaction field will have to be in the same direction as the dipole itself at all times so it *cannot* contribute to the directing field that orients the

dipoles. If $\overline{\mathbf{R}_{p}}$ is the reaction field of the permanent dipoles averaged over all of the possible orientations then we have for the directing field [7],

$$\mathbf{E}_{d} = \mathbf{E}_{i} - \overline{\mathbf{R}_{p}}.$$
 (1.37)

The directing field can be found as follows [7] – if the permanent dipole moment of the molecule in the cavity were removed without affecting its polarisibility and the molecule then removed from the cavity without changing the charge distribution (virtual cavity situation), the field inside the cavity would be the directing field because it would not include the component of the reaction field due to the permanent dipole moment. In analogy with Eq. (1.36),

$$\mathbf{E}_{\mathbf{d}} = \mathbf{E}_{\mathbf{c}} + f \boldsymbol{\alpha} \mathbf{E}_{\mathbf{d}}. \tag{1.38}$$

which, using Eq. (1.35) for the cavity field and leads to in terms of the external field E:

$$\mathbf{E}_{\mathbf{d}} = \frac{1}{1 - f\alpha} \frac{3\varepsilon_r}{2\varepsilon_r + 1} \mathbf{E}.$$
 (1.39)

Next we must find $\overline{\mathbf{R}_{p}}$ so that Eq. (1.37) can be applied to find the internal field. If $\overline{\mathbf{\mu}_{p}}$ is the averaged permanent dipole of the molecule then:

$$\overline{\mathbf{R}_{p}} = \frac{f}{1 - f\alpha} \overline{\boldsymbol{\mu}_{p}}.$$
(1.40)

Since from Eq. (1.21) $\overline{\mu_p} = \frac{\mu_p^2 \mathbf{E_d}}{3kT}$ we can now write an expression for the internal field in terms of $\mathbf{E_d}$, and then in terms of \mathbf{E} using Eq. (1.37)and Eq. (1.40):

$$\mathbf{E}_{i} = \left(1 + \frac{f}{1 - f\alpha} \frac{\mu_{p}^{2}}{3kT}\right) \left(\frac{1}{1 - f\alpha} \frac{3\varepsilon_{r}}{2\varepsilon_{r} + 1}\mathbf{E}\right).$$
 (1.41)

With both E_d and E_i expressed in terms of E, an equation relating the permanent dipole moment and the permittivity for a polar substance is obtained from

$$\varepsilon_0(\varepsilon_r - 1)\mathbf{E} = N\left[\alpha \mathbf{E}_i + \frac{\mu_p^2}{3kT}\mathbf{E}_d\right]$$
 by substitution of Eq. (1.41) for \mathbf{E}_i and Eq. (1.39) for

E_{d} [7, 12].

Using the Onsager approximation [Eq. (1.31)], the expression for f [Eq. (1.33)], and the Clausius-Mossotti equation for high frequencies, i.e. $\frac{\varepsilon_{\infty} - 1}{\varepsilon_{\infty} + 2} = \frac{N\alpha}{3\varepsilon_0}$, we can eliminate both *f* and α to obtain the Onsager equation [5, 7, 10, 12] for polar substances:

$$\mu_p^2 = \frac{9kT\varepsilon_0}{\varepsilon_r N} \frac{(\varepsilon_r - \varepsilon_\infty)(2\varepsilon_r + \varepsilon_\infty)}{(\varepsilon_\infty + 2)^2},$$
(1.42)

which can be considered as a correction to the Clausius-Mossotti equation [12], which is itself a correction to the Debye equation [Eq. (1.25)] [12].

This equation will apply for the special case of spherical polar molecules. Also the equation neglects interactions between the molecules other than the long-range dipolar interaction. For this reason, it cannot be applied to polar materials in which there are local interactions between molecules such as pure hydrogen bonded liquids [5, 7, 12].

1.9 Kirkwood-Onsager-Fröhlich Equation

Statistical mechanics can be applied to take account of the local interactions between polar molecules in a more explicit way. This involves solving two main problems – (i) finding the field experienced in the material as a result of the external field and the field due to both local and dipolar interactions between the molecules, which is similar to finding the internal field in the continuum model and (ii) finding the average sum of all the dipole moments of all molecules. The usual way the problem is approached is to treat all the molecules inside a certain region that is large enough to have bulk properties in an exact way while the rest of the material is treated as a continuum. It emerges after much work [5, 7] that it is possible to approximately include the effects of local interactions by introducing the Kirkwood Correlation Factor, g, into the Onsager equation to obtain what is called the Kirkwood-Onsager-Fröhlich [5, 7, 12, 13] equation

$$g\mu_p^2 = \frac{9kT\varepsilon_0}{\varepsilon_r N} \frac{(\varepsilon_r - \varepsilon_\infty)(2\varepsilon_r + \varepsilon_\infty)}{(\varepsilon_\infty + 2)^2}.$$
(1.43)

g represents the effects of local interactions on the observed average dipole moment of the material. If g = 1, local interactions result on average in no specific directing effect on the molecules. If g > 1, local interactions orient the molecules so that the average observed moment is greater than expected on the basis of the Onsager equation. If g < 1, the local interactions result in a decrease in the average observed moment. This equation is often applied to pure polar liquids where there are strong forces between the molecules ('associating liquids'). Examples include water, alcohols, and acids, in all of which there are hydrogen bonds between the molecules. Eq. (1.43) can also be adapted to describe situations such as polar molecules mixed in a non-polar solvent (where the polar molecules may associate in multimer groups) and ideal polymer chains in melts and solution (where the various polar segments can be considered as separated molecules correlated as a result of covalent bonds). The adapted equation [7] can also be applied to some pure polar liquids (monohydric alcohols, mono-carboxylic acids) as a result of the tendency of their molecules to form ring or chain multimer species (see Chap. 3 of this thesis).

In general, the specifics of the molecular interactions may not be known, so g is often determined from Eq. (1.43) as an empirical constant using a value of μ_p obtained in some other way. If a model describing the specifics of local interaction between molecules is available then parameters in the model may be found from g values obtained empirically. We now have several equations, which can be used to estimate the permittivity of a material from its molecular properties or vice versa.

1.10 Complex Permittivity

If we consider the empty parallel plate capacitor again [12] (see Sect. 1.3) and apply an alternating electric field $\mathbf{E}(t) = \mathbf{E}_0 \exp(j\omega t)$ where $j = \sqrt{-1}$, whose angular frequency is $\omega = 2\pi f$ (*f* being the linear frequency) the charge density on the plates is $\sigma = \varepsilon_0 E(t)$, which results in a current density:

$$\mathbf{J} = \frac{d\sigma}{dt}\hat{\mathbf{n}} = j\omega\varepsilon_0 \mathbf{E}(t), \qquad (1.44)$$

where $\hat{\mathbf{n}}$ is a unit vector in the direction of the electric field. In the empty capacitor case, \mathbf{J} leads the field by $\frac{\pi}{2}$. When a dielectric is included there may also be a component of \mathbf{J} in phase with the field. This is a result of dissipation of energy in the

dielectric arising from either dc conduction or polarisation currents associated with the finite time required for reorientation of bound charge associated with polarisation in the dielectric. In order to account for this, the permittivity is included in Eq. (1.44) as a complex quantity giving

$$\mathbf{J} = \frac{d\sigma}{dt}\hat{\mathbf{n}} = j\omega\varepsilon_0\varepsilon^* \mathbf{E}(t), \qquad (1.45)$$

where $\varepsilon^* = \varepsilon' - j\varepsilon''$ is the complex permittivity (or "complex dielectric constant") with real and imaginary parts of ε' and ε'' respectively. ε' (the real permittivity, or just permittivity, equivalent to the relative permittivity ε_r , discussed until now) is associated with energy stored in the electric field, while ε'' (the dielectric loss, or simply loss) is associated with energy absorbed by the dielectric. It should be noted that we expect that $\lim_{\omega \to 0} \varepsilon^* = \varepsilon_s$, the static value of the permittivity. Also, $\lim_{\omega \to \infty} \varepsilon^* = 1$, when ω is so high that no polarisation processes can contribute to the real or imaginary permittivity.

1.11 Superposition and Decay Functions

If a dielectric is linear, then the superposition principle will apply to its polarisation and electric flux density in a time-dependent electric field [12]. If the applied field can be written as a sum of several functions $\mathbf{E}(t) = \mathbf{E}_1(t) + \mathbf{E}_2(t)$ then the electric flux density at some time *u* can be expressed as the sum $\mathbf{D}(u) = \mathbf{D}_1(u) + \mathbf{D}_2(u)$ where $\mathbf{D}_1(u)$ and $\mathbf{D}_2(u)$ are the flux densities due to the components $\mathbf{E}_1(t)$ and $\mathbf{E}_2(t)$ of the electric field. The superposition principle allows the polarisation caused by a time dependent electric field to be expressed using response functions. If a constant electric field of magnitude *E* [see Fig. 1.5(A)], is applied to a sample at some time *u*, it would be expected that *P* and *D* would take some time to reach a constant value as the microscopic processes that result in polarisation cannot respond instantly to the change in the field. We can write the field as E(t) = ES(t-u) where S(t-u) is a step-function with S(t < u) = 0 and $S(t \ge u) = 1$. In this case the flux density is:

$$D(t) = \varepsilon_0 \varepsilon_r E \alpha (t - u). \tag{1.46}$$

 $\alpha(t-u)$ is called the step-response function. For the situation in Fig. 1.5(A), $\lim_{t\to\infty} \alpha = 1$, and $\alpha(t \le u) = 0$. The induced (electronic, atomic, and ionic) polarisation responds to changes in the electric field much more much rapidly than orientational polarisation since the dipoles take a relatively long time to reorient. As a result, the induced polarisation can be considered to respond instantly over timescales of interest in orientational polarisation [12]. If ε_{∞} is the limiting permittivity due to these processes, and ε_s is the permittivity approached at long times (the static permittivity) then,

$$D(t) = \varepsilon_0 \varepsilon_\infty ES(t-u) + \varepsilon_0 [\varepsilon_s - \varepsilon_\infty] E\alpha(t-u).$$
(1.47)

If the field were a block function as in Fig. 1.5(B), so that it has a magnitude E between the times u and $u + \Delta u$, and outside this time interval the field vanishes, the flux density is now given by the superposition of

$$D_{1} = \varepsilon_{0}\varepsilon_{\infty}ES(t-u) + \varepsilon_{0}[\varepsilon_{s} - \varepsilon_{\infty}]E\alpha(t-u)$$
(1.48)

due to the rising step [12] and

$$D_2 = -\varepsilon_0 \varepsilon_\infty ES(t - u - \Delta u) - \varepsilon_0 [\varepsilon_s - \varepsilon_\infty] E\alpha(t - u - \Delta u)$$
(1.49)

due to the falling step [12] that make up the block. Since any time varying field $\mathbf{E}(t)$ can be considered as an integral sum of such functions with an infinitesimal width *du* on the time axis we can integrate from all times in the past up to time *t* to obtain a complete expression for *D*, so

$$\mathbf{D}(t) = \varepsilon_0 \varepsilon_\infty E + \varepsilon_0 [\varepsilon_s - \varepsilon_\infty] \int_{-\infty}^{t} \mathbf{E}(u) \phi(t-u) du, \qquad (1.50)$$

where $\phi(t-u) = -\dot{\alpha}(t-u)$ is called the decay function for the electric flux density. If the substitution t' = t - u is made for the time then the integral is simplified to $\int_{0}^{\infty} E(t-t')\phi(t') dt'$ The integral term is called the "convolution product" of the decay function and the field. Using t as the time, when the one-sided Fourier transform $F(\omega) = \int_{0}^{\infty} E(t)\phi(t)\exp(-i\omega t)dt$ to the frequency domain of such a convolution product is performed the result is a simple product, which in this case is $\varepsilon_{o}^{*}(\omega)\hat{E}(\omega)$ where $\varepsilon_{o}^{*}(\omega)$ is the orientational component [12] of the complex permittivity. A carat is used to distinguish the field as a function of angular frequency from the field as a function of time.



Fig. 1.5 Plots against time for (A) a step function and (B) a block function **E**field. The corresponding change in **D** with time is shown in red. When the field switches there is a delay before **D** achieves a steady-state value.

1.12 Relaxation – Debye Equations

It can be shown using Eq. (1.50) and the above discussion on convolution integrals [12] that

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + [\varepsilon_s - \varepsilon_{\infty}] \int_0^{\infty} \phi(t) \exp(-j\omega t) dt, \qquad (1.51)$$

where the integral is the one-sided Fourier transform of the decay function i.e. $\varepsilon_o^*(\omega)$ [12].

If we use

$$\phi(t) = \frac{1}{\tau_D} \exp\left(\frac{-t}{\tau_D}\right)$$
(1.52)

for the decay function we obtain for the complex permittivity:

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{s} - \varepsilon_{\infty}}{1 + j\omega\tau_{D}} = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1 + j\omega\tau_{D}}$$
(1.53)

 $\Delta \varepsilon$ is sometimes called the dielectric relaxation strength (it is actually a susceptibility) and τ_D is referred to as the Debye [9] relaxation time. The real and imaginary parts are given by

$$\varepsilon'(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1 + \omega^2 \tau_D^2}$$
(1.54)

$$\varepsilon''(\omega) = \frac{\omega\tau\Delta\varepsilon}{1+\omega^2\tau_D^2} \tag{1.55}$$

Eq. (1.53) - (1.55) are collectively called the "Debye equations" [2, 3, 5-7, 9, 12]. These equations are plotted in Fig. 1.6. There is an alternative, more direct derivation in Ref. [3] that doesn't use the abstract idea of a decay function and a Laplace transform and proceeds from the idea of the polarisation decaying exponentially when an electric field is removed.



Fig. 1.6 The Debye equations. The graphical relationships between the various parameters are shown. The loss has a peak value of $\Delta \varepsilon / 2$ at $\omega = \frac{1}{\tau_D}$. The full width at half maximum (FWHM) is 1.14 decades.

Fig. 1.6 The Debye equations. The graphical relationships between the various parameters are shown. The loss has a peak value of $\Delta \varepsilon / 2$ at $\omega = \frac{1}{\tau_D}$. The full width at half maximum (FWHM) is 1.14 decades.

1.13 Simple Models Leading to the Debye Equations

The important assumption made in deriving the Debye equations is that the decay function has an exponential form. Such a decay function can arise from several possible physical models. The common feature in all is that the dipoles can be considered individually and effects of direct interactions between them can be ignored [5]. One such model [5] is that of a charged particle having two possible equilibrium positions separated in space by some distance. The potential energy function is a double well with minima A and B at each position (Fig. 1.7), separated by a barrier of height *H*. In thermal equilibrium the particles have thermal energy $kT \ll H$ and the fraction of particles having sufficient energy to jump from one minimum to the other

is $\exp\left(\frac{-H}{kT}\right)$. There are equal numbers of particles in each well so the probability of a particle being found in one well is equivalent to its probability of being found in the other. Applying an electric field (Fig. 1.7) alters the equilibrium positions slightly, and the relative depth of the wells by an amount *qdE* if q is the charge, *d* the distance between the equilibrium positions, and *E* the field component parallel to *d*. The fraction of particles in A that have enough energy to jump from A to B will be larger that the fraction in B having enough energy to make the equivalent jump. This alters the transition probabilities for particles jumping from one well to another. The numerical difference between the number of particles in B and A is found to approach its equilibrium value in the presence of the field exponentially [5].



Fig. 1.7 Two well potential model resulting in an exponential relaxation equation and Debye relaxation (After Ref. [5]).

Since this number is proportional to the polarisation, the decay function will also be exponential in form, leading to the Debye equations. Such a model may be applied to the polarisation due to point defects in ionic crystals [14]. The model can also be adapted to polar solids at high temperatures where interaction between the dipoles is weak [5] or at low temperatures for an ordered solid [5]. In the latter case, even though the dipoles interact strongly, most of the dipoles are ordered in a particular way so that each reorienting dipole experiences a similar potential and can be treated as independent of the other reorienting dipoles [5]. In an ordered solid, a dipole may have a limited number of equilibrium directions and can jump potential barriers to reorient itself. In a liquid however, there is no long-range order. Taking two extremes, we can either conceive of; (i) a similar situation to a solid in which the local arrangement of molecules may be fixed over the timescale of a dipole reorientation, or; (ii) the dipole may reorient infrequently in concert with rearrangement of its surroundings [5].

Debye himself [9] showed that the equations could also be applied to polar liquids in the latter case. The dipoles are considered as equivalent to one another and independent (non-interacting). In the light of (ii) above, the molecules that surround the dipoles are considered as a continuous fluid with viscosity η . The inertia of the dipole is neglected. In Debye's model, the polar molecules are spherical and experience frictional forces as they reorient in the viscous fluid due to the combined effects of an applied electric field and rotational Brownian motion (bombardment by the molecules that surround them). Based on these assumptions, it can then be shown that the result is an exponential decay function for the polarisation [5, 9]. The assumptions above mean that the Debye equations have limited applicability to polar fluids. They may apply when [5]; (i) The polar molecules are diluted by a non-polar solvent, or the temperature is high, to satisfy the non-interaction requirement; (ii) The molecules are axially symmetric, and; (iii) The liquid is isotropic (satisfying the requirement that all dipoles are equivalent). In addition, Debye found for the relaxation time of the dipoles [5, 9],

$$\tau_D = \frac{\xi}{2kT},\tag{1.56}$$

where ξ is a "frictional constant" associated with the resistance of the fluid to reorientation of the dipole. For a macroscopic sphere of radius *a* in a fluid of viscosity η , ξ is given by Stokes' law:

$$\xi = 8\pi\eta a^3. \tag{1.57}$$

So within the limits of Debye's assumptions

$$\tau_D = \frac{4\pi\eta a^3}{kT}.\tag{1.58}$$

Since, in order to derive Eq. (1.58) the molecules around the dipole were considered as a fluid, the dipole is considered as relatively fixed relative to its surroundings (case (ii) above for the motion of the dipole in the liquid – the dipole may reorient infrequently). Large angle jumps are unlikely [5]. This implies a low energy barrier for viscous flow of molecules in the fluid relative to the energy barrier for reorientation i.e.; (iv) $H >> H_{\eta}$ where H_{η} is the potential energy barrier for viscous flow.

It should be stressed that *a* cannot be assumed to be related to molecular dimensions in any simple way [15] and will depend on the solvent also [5, 15].

1.14 Empirical Equations

In the dielectric spectroscopy of polar liquids and particularly glasses it is usually found that the Debye equations do not describe the observed relaxations. This is not surprising given the restrictions imposed when deriving the equations. Typically, the decay of polarisation on removal of the external field is less rapid than predicted by an exponential decay function. In the frequency domain, the peak in ε'' is broadened relative to the Debye FWHM of 1.14 Decades. One approach is to describe the relaxation by a continuous distribution of Debye relaxations with various relaxation times [5, 12]. The distribution function is $y(\tau)$ normalised so that

 $\int_{0}^{\infty} y(\tau) d\tau = 1 \text{ (integrating over all possible relaxation times). The function represents the probability of a given species having a Debye relaxation time of <math>\tau$. The decay function is now $\phi(t) = \int_{0}^{\infty} \frac{y(\tau)}{\tau} \exp\left(\frac{-t}{\tau}\right) d\tau$ and the complex permittivity becomes: $\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \Delta \varepsilon \int_{0}^{\infty} \frac{y(\tau)}{1+i\omega\tau} d\tau.$ (1.59)

This equation can be written in other ways, and has been used with a distribution function of $\ln(\tau)$ rather than τ itself. Obviously, if the dipoles interact, as in a pure polar liquid or glass, then the main assumption in the derivation of the Debye equations is invalidated and a distribution of relaxation times is expected. However, it is possible in some cases to have a distribution of relaxation times even for non-interacting dipoles such as polar molecules dissolved in a nonpolar solvent or as a solid solution in a nonpolar amorphous solid [5]. In arriving at an exponential decay function for a polar liquid, it was considered that the dipole reoriented infrequently relative to its surroundings so that the latter could be treated as a viscous fluid, and a diffusion approach applied [5]. If the opposite is the case and the dipole reorients more rapidly than a relatively fixed surrounding (as may apply in a very viscous fluid or a glass) then the situation may be better described by jumping over a potential barrier as for a crystalline polar solid. However, unlike the ordered solid, in

an amorphous solid or liquid the local arrangement will vary for dipoles at different positions, the potential energy barriers, *H*, will vary too, resulting in a distribution of transition probabilities and relaxation times [5]. This theme is taken up in Chap. 3. A number of empirical equations have been used to analyse relaxations that depart from the Debye equations. These are used as an aid to systematising parameters such as strength, relaxation time, and broadness for a relaxation without appeal to theories. These equations are generally defined in the frequency domain as most measurements are made as frequency spectra. Among the earliest of these is the Cole-Cole (CC) equation [16]

$$\varepsilon^*(\omega) = \varepsilon_{\omega} + \frac{\Delta\varepsilon}{1 + (j\omega\tau_{cc})^{1-\alpha_{cc}}}.$$
(1.60)

 α_{cc} is the Cole-Cole distribution parameter such that $0 < \alpha_{cc} < 1$ and τ_{cc} is the Cole-Cole relaxation time.. Eq. (1.60) results in a peak in ε'' which is symmetrically broadened relative to the Debye relaxation. Fig. 1.8(A) and (B) show ε' and ε'' spectra of the Cole-Cole distribution with $\alpha_{cc} = 0.5$ in comparison to the Debye equations. On a log-log plot of ε'' against frequency, the low and high frequency sides of the peak have slopes of $1 - \alpha_{cc}$ and $-(1 - \alpha_{cc})$ respectively (as compared to 1 and -1 for the Debye equations). ε'' follows power laws in frequency with these exponents in the limit of low and high frequency. The frequency of maximum loss, f_m , is the same as for the Debye equation. The CC equation is often used for description of the β -relaxations in glassforming liquids. Another early equation is that of Davidson and Cole (DC) [17]:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left(1 + j\omega\tau_{DC}\right)^{\beta_{DC}}}$$
(1.61)

with β_{DC} and τ_{DC} being the Davidson-Cole distribution parameter (obeying $0 < \beta_{DC} < 1$) and relaxation time respectively. A DC distribution with $\beta_{DC} = 0.5$ is shown in Fig. 1.8(A) and (B). In this case, the peak in ε'' is non-symmetrically broadened relative to the Debye peak and the limiting high frequency slope on a loglog plot of ε'' against frequency is $-\beta_{DC}$. An extension of these equations which is often used is that of Havriliak and Negami (HN) [18], which combines both symmetric and asymmetric broadening in a single relaxation equation, at the cost of an extra parameter,

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left[1 + (j\omega\tau_{HN})^{\alpha_{HN}}\right]^{\beta_{HN}}}.$$
(1.62)

 α_{HN} and β_{HN} are the HN distribution parameters. The former specifies the symmetric and the later the asymmetric broadening of the peak in ε'' relative to the Debye relaxation. τ_{HN} is the Havriliak-Negami relaxation time. ε'' obeys the power laws $\varepsilon'' \propto \omega^{\alpha_{HN}}$ and $\varepsilon'' \propto \omega^{-\alpha_{HN}\beta_{HN}}$ at low and high frequencies respectively. This equation reduces to the CC form when $\alpha_{HN} = 1 - \alpha_{CC}$ and $\beta_{HN} = 1$ and the DC form when $\alpha_{HN} = 1$ and $\beta_{HN} = \beta_{DC}$. A HN distribution with $\beta_{HN} = 0.5$ is shown in Fig. 1.8(A) and (B).

It is clearly seen that f_m is different for the DC and HN equations than for the CC and Debye equations. It can been shown for the HN equation that f_m is given by Eq. (1.63) [19],

$$f_m = \left(2\pi\tau_{HN}\right)^{-1} \left[\sin\left(\frac{\alpha_{HN}\pi}{2+2\beta_{HN}}\right)\right]^{\frac{1}{\alpha_{HN}}} \left[\sin\left(\frac{\alpha_{HN}\beta_{HN}\pi}{2+2\beta_{HN}}\right)\right]^{\frac{-1}{\alpha_{HN}}},$$
(1.63)

which is of course applicable to the DC equation as a special case. It should be noted that if β_{HN} is 1, f_m as given by this equation is independent of α_{HN} .

A historically very useful representation for permittivity data is an Argand diagram of ε' and ε'' on equivalent scales (a "Cole-Cole plot" [16]). The Cole-Cole plot for the Debye, CC, DC, and HN equations is shown in Fig. 1.8(C). The Debye equations describe a semicircle, the CC equation gives a depressed circular arc, and the DC equation gives an arc skewed at high frequency values (as one approaches ε_{∞} on the real axis). The HN equation gives a combination of these effects. In all cases, the real (ε') axis is intersected at ε_{∞} and ε_s . A tangent to the arc at ε_{∞} makes an angle of $\pi(1-\alpha_{CC})/2$ with the real axis for the CC equation [16], $\pi\beta_{DC}/2$ for the DC equation, and $\pi\alpha_{HN}\beta_{HN}/2$ for the HN equation. The depression of the arc for the CC equation is also given by $\pi\alpha_{cC}/2$ [16].

Prior to the advent of cheap computing power and common nonlinear fitting programs capable of minimisation of several variables, various graphical methods were used to extract parameters such as $\Delta \varepsilon$, τ , and the broadness parameters of the various empirical equations. The Cole-Cole plot quantifies the broadness of the relaxation and

can be used to determine ε_{∞} and ε_s from the intercepts on the real axis and the broadness parameters of the CC, DC, and HN equations from construction of the tangents at the intercepts. If a Debye equation applies, a plot of $\omega \varepsilon''$ vs. ε' has a slope

 $-\frac{1}{\tau}$ and intercept $\frac{\varepsilon_s}{\tau}$ while a plot of $\frac{\varepsilon''}{\omega}$ vs. ε' has a slope of τ and an intercept of $(\tan^{-1}[\sigma'' / (\sigma' - \sigma)])$

$$-\tau \varepsilon_{\infty}$$
. If a DC equation applies, a plot of $\tan\left\{\frac{\tan^{-1}\left[\varepsilon''/(\varepsilon'-\varepsilon_{\infty})\right]}{\beta_{DC}}\right\}$ vs. ω gives

 τ_{DC} [17]. Nonlinear curve fitting has now replaced such graphical methods and the fitting program used for analysis of dielectric relaxation spectra in this thesis is discussed in later chapters and in Appendix B.

Another often-used empirical equation defined in the time domain [since the expression (the Fourier transform of the derivative of the time domain expression) is more complex in the frequency domain] is the Kohlrausch [20]-Williams-Watts [21] (KWW) stretched exponential function

$$\phi(t) = \exp\left(\frac{-t}{\tau_{KWW}}\right)^{\beta_{KWW}}$$
(1.64)

which leads to an asymmetrically broadened ε'' peak when transformed to the frequency domain. β_{KWW} is the KWW stretched exponential parameter and τ_{KWW} is the KWW relaxation time. This discussion of empirical relaxation equations is not exhaustive and others such as those of Fouss-Kirkwood [22] and Jonscher [1, 23] have all been used in the description of relaxations.



Fig. 1.8 Plots of the (A) ε' and, (B) ε'' spectra for the Debye, CC with $\alpha_{CC} = 0.5$, DC with $\beta_{DC} = 0.5$, and HN with $\alpha_{HN} = \beta_{HN} = 0.5$ distributions are compared. (C) Cole-Cole plot of the Debye, CC, DC, and HN equations with the same parameters as above. The thin lines indicate the tangents to the DC equation and HN equation data at ε_{∞} . The tangent to the CC distribution data is the same as that to the DC distribution. The slopes of these tangents in terms of the relaxation parameters are indicated.

1.15 Resonance



Fig. 1.9 Plot of α'_e and α''_e against $\log \omega$ for the case of dielectric resonance as described by Eq. (1.69). The relationship between important points on the plots and the various parameters in the equation is shown.

Consider an electronic charge (-e) bound elastically so that it can oscillate about an equilibrium position (a simple model for a single electron in an atom) [3, 5, 12, 24]. If $\mathbf{r}(t)$ is the displacement of the charge from equilibrium then

$$\frac{d^2 \mathbf{r}}{dt^2} = -\omega_0^2 \mathbf{r} \tag{1.65}$$

is the classical equation of motion for the charge, which undergoes simple harmonic oscillation with a resonance frequency of $\omega_0 = \sqrt{a/m}$ where *a* is the force constant and *m* is the mass of the charge (the electron mass). Eq. (1.65) implicitly ignores interaction of the charge with its surroundings and implies it oscillates with a constant energy so that thermal equilibrium cannot be established [5, 12]. When an alternating external electric field $\mathbf{E}_0 \exp(j\omega t)$ is applied, this exerts a driving force on the charge. This also requires that a damping term $m\gamma \frac{d\mathbf{r}}{dt}$ be included to account for energy loss due to emission, and in condensed matter, interactions with the surroundings. The equation of motion becomes [3, 12, 24]:

$$\frac{d^2\mathbf{r}}{dt^2} + \gamma \frac{d\mathbf{r}}{dt} + \omega_0^2 \mathbf{r} = \frac{-e\mathbf{E}_0}{m} \exp(j\omega t).$$
(1.66)

The solution of this is of the form $\mathbf{r} = \mathbf{A}^* \exp(j\omega t)$ [3]. Inserting this into Eq. (1.66) gives for the value of the complex pre-exponential \mathbf{A}^* ,

$$\mathbf{A}^* = \frac{e\mathbf{E}_0 / m}{\omega^2 - \omega_0^2 - j\gamma\omega}.$$
(1.67)

The displacement is thus:

$$\mathbf{r} = \frac{e\mathbf{E}_0}{m} \exp(j\omega t)$$
(1.68)

The associated induced dipole moment is $-e\mathbf{r}$. Using Eq. (1.13) gives a complex electronic polarisibility, α_e^* [3] (and thence expressions for ε^* [12, 24]):

$$\alpha_e^* = \frac{\frac{e^2}{m}}{\omega_0^2 - \omega^2 + j\gamma\omega}.$$
(1.69)

This real (α'_e) and imaginary (α''_e) parts of this expression are plotted against $\log \omega$ in Fig. 1.9. The equation can be extended to the case of a multi-electron atom or non-polar molecule [24]. The term on the right-hand-side becomes a summation over all electrons, f_n of which have a given characteristic frequency ω_{0n} , and damping term γ_n .

$$\alpha_{e}^{*} = \frac{e^{2}}{m} \sum_{n} \frac{f_{n}}{\omega_{0n}^{2} - \omega^{2} + j\gamma_{n}\omega}.$$
(1.70)

In a quantum mechanical treatment, which would result in a similar equation, the ω_{0n} would be frequencies of radiation emitted an absorbed by the system as a result of energy transitions and the f_n would be the corresponding transition probabilities [24]. Eq. (1.14) will now give the electronic polarisation. It is possible to consider the atomic and ionic polarisations in an analogous manner to obtain a similar equation to Eq. (1.70). Since the field in the above discussion is really the internal field in the material when we cease to consider an isolated atom, we can use an adapted version of Eq. (1.25) in a gas, or Eq. (1.29) (Clausius-Mossotti equation) for condensed matter in which the Lorentz approximation for the internal field applies.

$$\varepsilon_0(\varepsilon^* - 1) = N\alpha_T^* \tag{1.71}$$

$$\frac{\varepsilon^* - 1}{\varepsilon^* + 2} = \frac{N\alpha_T^*}{3\varepsilon_0} \tag{1.72}$$

The total induced polarisibilities α_T^* have now become complex in accordance with Eq. (1.70), as has the permittivity ε^* itself. It is also possible to arrive at an expression for the permittivity when resonance occurs by using an oscillating decay function and a similar method to the derivation of the Debye equations [5].

1.16 Dielectric Spectra of Materials

Finally, to give a general overview, Fig. 1.10 shows a typical ε' and ε'' spectrum for a material over the frequency range from sub-Hz up to the visible light region (~ $10^{14} - 10^{15}$ Hz) [6, 12]. Orientational polarisation results in peaks in the radiofrequency (1 kHz – 1GHz) [24] and microwave (1 GHz – ~ 0.1 THz) [24] regions. These peaks can have their origin in different relaxation processes depending on the material in question and the frequency range. In a supercooled liquid, the reorienting species are molecules. In a semiconductor, they may be defects with trapped charges or excitons. In an ionic crystal, they may be caused by ion hopping resulting in the reoreintation of point defect pairs. Into the infrared and visible, there are resonances associated with rotational and electronic transitions, which also appear in the complex refractive index.



Fig. 1.10 Dielectric dispersion in the ε' and ε'' spectra of a material in different frequencies. Relaxation associated with orientational polarisation processes occurs in the radiofrequency range. Above this there are resonance processes (Adapted from Ref. [6]).

1.17 References

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Glasses

2.1 Levels of Disorder in Matter

A perfect crystal has a basis of atoms, ions, or molecules associated with an infinite periodic lattice [1]. With a real crystal, things are not so ordered. The crystal will have surfaces so it is finite, and it will have defects of various dimensions too. The disorder is further increased in a mixed crystal such as Ge_xSi_{1-x} [2], where the atoms can occupy sites in the crystal randomly with a probability determined by the composition of the crystal. The crystal has compositional disorder [2] or substitutional disorder [3]. In a "plastic crystal", like cyclohexane, the orientations of the molecules associated with the crystal lattice may be random (see Chap. 4) and the crystal has orientational or "rotational disorder" [2]. A more fundamental type of disorder is the inability to associate the overall structure with one of the Bravais lattices, which occurs in quasicrystalline metallic alloys, for example Al₈₆Mn₁₄ [1, 3, 4]. Such materials have been shown by comparing the x-ray diffraction patterns they produce with simulations to possess long-range order based on five-fold symmetry axes ("icosahedral symmetry") that do not occur in any of the space lattices [5]. Penrose [1, 3, 6] tilings with two tile types are an example of 2d analogues of quasicrystalline structures (see Fig. 2.1).





The most extreme type of disorder in the solid-state occurs in amorphous (or noncrystalline) solids. In such solids, there is no long-range order, and the disorder is topological [2, 3], or intrinsic to the structure. This does not preclude a large extent of short range ordering in such solids. Given a particular atom in the amorphous solid, the nature, numbers and positions of the surrounding atoms may be quite predictable in a statistical sense and various stochastic models of the structure of a glass have been developed [2]. A liquid at any instant may have a structure quite similar to an amorphous solid [2]. However, in contrast to the amorphous solid in which the positions of the atoms or molecules are constant in time apart from jumps associated with defects, the atoms and molecules in the liquid may make large excursions from their original positions as time passes. The liquid structure is transient, while that of the amorphous solid is relatively fixed [2, 3] so that it is a true "solid". This difference can be illustrated by a plot of the locus of a species over time in a solid or a liquid as in Fig 2.2.



Fig. 2.2 Locus of a species in (A) a solid and (B) a liquid. The species in the solid cannot move a large distance from its equilibrium position whereas in the liquid translations of quite long distance are possible (After Ref. [2]).

Such trajectory plots are available from molecular dynamics experiments [2] and experiments in which suspensions of small polymer spheres are used to simulate the liquid-glass transition [7]. The species in the liquid are still closely bound to each other and there are large attractive forces between them. In an ideal gas, these species are separated from each other. Their positions are random in time and there is no long- or short-range order. The only interactions are rare elastic collisions. Diffraction experiments allow the construction of a radial distribution function (RDF) for material [2]. If a random species is chosen as the origin of a sphere of radius r, the RDF is the probability of finding another species between r and r + dr. Its integral over the entire sample should be 1.



Fig. 2.3 RDF of (A) a crystalline solid, (B) an amorphous solid, and (C) a gas (After Ref. [2]).

The RDF of a crystalline and an amorphous solid, and a gas are compared in Fig. 2.3. The crystal has a large number of sharp peaks corresponding to the various coordination spheres that are associated with the different points on the lattice. These are encountered as the shell of thickness dr is swept outwards from the origin. In reality, the peaks are not perfectly sharp because of thermal motions (zero point vibrational energy would still broaden the peaks at 0 K [2]) so at some distance out they begin to overlap. The amorphous solid still retains the first two to three peaks, which is evidence of the extensive short-range order. The gas has a broad RDF that increases according to the volume of the shell described by r and r + dr. This is indicative of a constant number density of particles in the gas, N so that the RDF is $4\pi r^2 / V_T$ where V_T is the total volume of the sample [2].

2.2 Preparation of Amorphous Solids

There are many ways to prepare an amorphous solid, and the same composition amorphous solid can be prepared by a variety of routes resulting in materials with
different properties [3]. Most prominent among these methods, (which are discussed at length in Chap. 1. of Ref. [3]) are:

- (i) Evaporation
- (ii) Sputtering
- (iii) Glow Discharge (GD)
- (iv) Chemical Vapour Deposition (CVD)
- (v) Melt quenching
- (vi) Sol-Gel techniques.

The first four of these are gas phase techniques and the last two involve the liquid phase. Amorphous solids may also be produced by electrolytic deposition processes [3, 8], by reaction (precipitates in solution reactions may be amorphous) [3, 8], by application of high pressures [3, 8] [explosive shockwaves (without fusion), grinding and milling etc. [9] to cause a solid-state phase change], by irradiation (in semiconductor wafer processing amorphous layers are often created in Si during ion implantation steps which then require annealing [10]), and by solid state diffusion processes amongst the layers of crystalline metal stacks [11]. A very short summary of each of the six main methods is given below. Melt quenching is discussed in most detail because of its connection to the glass transition, which is the main subject of this chapter.

(i) Evaporation

In this technique, the material is vaporised in a resistively heated boat made from a tungsten wire coil or basket and condensed on a substrate to give an amorphous thin film. The process is carried out at high vacuum (10^{-6} Torr) to avoid contamination. The process can be used to make amorphous semiconductor (*a*-Si, *a*-Ge) and insulator (*a*-SiO_x) films [3]. It is necessary to use a very cold (4 K) substrate to produce amorphous rather than polycrystalline metal films (for example Ga and Bi) [3].

(ii) Sputtering

Sputtering is similar to evaporation in that it involves transport of atoms from a source to a substrate under vacuum. In this case atoms or atom clusters are blasted from a target by an ionic plasma and are subsequently deposited on the substrate. In dc sputtering a negative voltage is applied to the target to attract ions from the plasma. This can be used only for a conducting target. Alternatively, an alternating radiofrequency (RF) field can be applied. This allows insulating targets to be used

because the only requirement is that there is a capacitance in the circuit formed by the plasma, target, and source [3]. This process is also carried out under a high vacuum. An inert gas is introduced at low pressure (1- 20 mTorr [3]) to strike the plasma. Sputtering can be used to create similar amorphous films to evaporation. Introduction of trace gases like H_2 into the chamber allows reactive sputtering to occur and doped amorphous films to be produced [3]. Sputtering is also better for multicomponent films because the complication of different vapour pressures for the various constituent elements is no longer a problem.

(iii) GD

In this technique [3], a plasma is created in a low-pressure gas (like sputtering) but the film is deposited as a result of decomposition of the gas and reactions at the substrate. An inert gas (Ar) may be used as carrier. The plasma can be generated by capacitive coupling to the field (as in sputtering) or inductive coupling. The technique can be used to produce hydrogenated amorphous silicon (a-Si:H) films with silane (SiH₄) as the reactive gas. There is great flexibility for introduction of dopants like boron, phosphorous, and fluorine etc into the silicon by adding appropriate gases such as diborane (B₂H₆), phosphine (PH₃), and tetraflourosilane (SiF₄). Many other amorphous semiconductors, oxide, and polymer films can be produced using the GD technique.

(iv) CVD

In CVD, the amorphous film is also deposited as a result of decomposition of source gases. In this case the decomposition is thermal (the substrate is hot). Applied RF fields can also be used as a means to heat the substrate. Again *a*-Si:H can be deposited by CVD. Doping can be achieved by introduction of phosphorous and boron bearing gases.

(v) Melt-Quenching

Melt-Quenching, the rapid cooling of a liquid (the melt) until it solidifies continuously (passes the glass transition) without forming a crystal, is the oldest method of preparing amorphous solids [2, 3]. Solids produced in this way have traditionally been called glasses or "vitreous solids". Many of the earliest hominid tools were fashioned from naturally quenched obsidian [8]. Much later, the first manmade silica (SiO₂) based glasses were produced in this way in Mesopotamia about 4500 B.C. [8], with early moulded glass objects being produced in Egypt by 3000

B.C. [8]. Blown glass objects were not produced until later (100 B. C.) and were traded across the Roman Empire [8]. Moving to the present time vast quantities of common, or soda-lime "glass" (mixed oxide glass of SiO₂, Na₂O, and CaO) quite similar to the earliest man-made glasses are manufactured for use as a structural material, for packaging, containers etc. The addition of Na₂O lowers the melting point so that the glass is easier to work and requires less energy to produce [8]. CaO improves chemical stability [8]. More specialised mixed oxide glasses containing other additives are also widely produced by this method such as Pyrex (with B₂O₃ as an additive), and lead crystal (with PbO). Various transition metal oxides can be added to colour the glass [8]. Common thermosetting plastics such as polystyrene are also produced in their final form by melt quenching through extrusion or pressure and blow moulding processes [12]. All of the above are quite easy to vitrify, as the rate of the quench required to avoid crystallisation is not very high. Oxide glasses will form at rates as low as 10^{-5} K s⁻¹ [2, 3] so they are difficult to crystallise. Since for a long time the only known substances to form glasses were such oxides and some other organic liquids (e.g. glycerol), it was assumed that they belonged to a special "glassformer" class of materials that would form a glass on cooling [2, 13]. New melt quenching techniques [2, 3] (Fig. 2.4) like splat quenching, melt spinning, and melt extraction permit high cooling rates of up to 10^6 K s⁻¹ (a quench to a glass in a cold liquid may give a maximum rate of about 10^3 K s⁻¹). This has allowed metal alloy "glasses" to be made such as Au₇₅Si₂₅ [14]. Laser glazing (small parts of a block of material are fused by a laser and rapidly cooled by the surrounding material acting as a heatsink) can achieve even higher rates [2]. In some ways, the gas phase methods of preparing amorphous solids, particularly evaporation, can be considered as an extreme form of very fast "quenching" from a vapour [2, 3]. In the real world, finite thermal conductivity acts as a limit to quenching rates attainable – for example the metallic glasses are prepared as thin ribbons in melt spinning so that conduction of heat through the metal itself is as fast as possible [3]. In the virtual world of a computer simulations, quenching rates of 10¹² K s⁻¹ are possible and even noble gases like Ar can be vitrified [13]. Glass formation is better considered as a fundamental physical process that will occur over different timescales rather than a property of some restricted set of materials. As a result of these developments, glass is now often used as a synonym for amorphous solid [2, 13]. Some prefer to restrict "glass" to those

amorphous solids that can be cycled through the glass transition [3, 8]. This definition would exclude the metallic "glasses" [3, 13] as they are often called, and thin semiconductor films [8] because they crystallise before they can be heated through a glass transition. The melt quenching technique is intimately connected to the glass transition concept, which will be discussed in the following section. Table 2.1 summarises the cooling rate for various melt-quenching techniques (includes evaporation and sputtering).



Fig. 2.4 Chill block techniques for preparation of glassy metals. (A) A splat quench technique in which a drop of molten metal is quenched between a laser triggered piston and an anvil to produce a film of glassy metal [2]. The drop can also be fired at a cooled metal sheet (this method has been used to vitrify water [15]). (B) Melt spinning – a molten stream of metal is dispensed onto a rapidly turning cooled rotor to form a glassy metal ribbon (max thickness ~ $30 \ \mu m$ [3]) at a rate of up to 1 km min⁻¹ [2]. (C) Melt extraction – a glassy metal ribbon is extracted from a crucible containing the melt by a cold rotor spinning at the melt surface. In a related technique, a fed rod of metal can replace the injection system in (B), with the rod being melted by an induction heater just before it touches the rotor [3].

Malt O and Table in a	Casting Data [K -1]	Matariala	
Meit-Quench Technique	Cooling Rate [K s]	Materials	
Anneal	$10^{-5} - 10^{-2} [2, 3, 8]$	Optical glasses – ordinary glass	
Air Quench	1 – 10 [3]	Ordinary glass, lead crystal, polymers	
Liquid Quench	$10^2 - 10^3$ [2, 3]	Some Glassy Metal alloys (Pd-Ni-P)	
Chill-Block			
Splat Quench	10 ⁵⁻⁸ [2, 3]	Glassy Metal Alloys	
Extraction/Spinning	$10^{6} [2, 3]$		
Evaporation/Sputtering	> 10 ⁹ (uncertain) [2, 3]	Amorphous semiconductor films,	
		glassy metal films	
Laser Glazing	$\sim 10^{10} - 10^{12}$ (uncertain) [2]	¹² (uncertain) [2] Amorphous semiconductor films,	
		glassy metal films	

Table 2.1Overview of melt-quenching techniques for forming glasses.

(vi) Sol-Gel techniques

These techniques are used to produce silica-based glasses. They are described extremely briefly here, omitting many details, which can be found elsewhere (See Ref. [8], Chap. 18 and Ref. [3], Chap. 1 and references therein). The basic approach is to use condensation polymerisation reactions between compounds of silicon, aluminium etc. in a solution to form a colloid (sol) of amorphous particles. Crosslinking between the particles (without flocculation) then results in an increase of viscosity to give a wet gel. This is then dried (giving a xerogel) and sintered to a solid glass. The final product is quite similar to that produced by melt quenching. It is a low temperature process and allows an easier route to preparation of very pure and homogeneous silica based glasses whose melts would have very high temperatures. The chemicals needed (commercial silica sols or organometallics depending on whether a water or alcohol based preparation route is chosen) are more expensive than for melt-quenching, and the process can be tricky to control [8]. Variations in the drying/sintering procedure allow production of porous glasses [8]. Glass films can also be prepared by spin or dip coating in the wet gel stage. It is even possible to control the pore size and geometry precisely by use of an appropriate templating surfactant as in MCM (MOBILTM Composition of Matter) materials [16, 17]. Finally, Table 2.2 gives an overview of the main classes of amorphous materials with sample materials and applications for each class. The small-molecule organic glassformers

like sorbitol that are studied in this thesis have been omitted from the table. Such materials are less technologically useful but some do have some applications in the food industry and in the stabilisation/packaging of drugs in the pharmaceutical industry. They are easy to vitrify over temperature ranges readily accessible in the laboratory so have often been used as model systems for studying the glass transition itself. It is notable that glass transitions have been observed for materials with all classes of bonding (metallic, ionic, covalent, Van der Waals, and hydrogen bonds).

Туре	Example	Applications	Useful Properties
Oxide Glass	(SiO ₂) _{0.8} (Na ₂ O) _{0.2}	Windows, Containers	Transparent, isotropic,
		etc.	rigid, formable as large
			sheets, low cost
Oxide Glass	$(SiO_2)_{0.9}(GeO_2)_{0.1}$	Fibre Optic waveguides	Ultratransparent, very
		(graded index type)	pure, formable as long,
			thin fibres with
			composition variable
			along the diameter.
Organic Polymers	Polystyrene	Structural materials,	Strong, easily processed
		packaging etc.	(transparent in some
			cases), low cost, low
	H		weight
Chalcogenide Glass	Se, As_2Se_3	Xerography	Photoconductive,
			formable as large area
			films.
Amorphous	$Te_{0.8}Ge_{0.2}$	Non-volatile memory	E-field induced glass
Semiconductor			transition (See Ref. [2],
			p. 30)
Amorphous	Si _{0.9} H _{0.1}	Photocells	Photovoltaic optical
Semiconductor			properties, formable as
			large area thin films
Metallic Glass	Fe _{0.8} B _{0.2}	Transformer Cores	Ferromagnetic, low
			loss, ribbons formed

Table 2.2Applications of Amorphous solids (Adapted from Ref. [2], p. 24).

2.3 The Glass Transition



Fig. 2.5 Plot of molar volume against temperature for the cooling of a liquid showing two paths for the formation of a solid. The crystallisation temperature T_c and fictive temperature T_f of the melt are indicated. The glass transition temperature T_g occurs within the transformation range. As temperature decreases, the relaxation time τ increases as indicated by the arrow at the top of the plot.

Consider the experiment of cooling a liquid and monitoring its molar volume, V, as it is cooled [2, 8] (Fig. 2.5). One could also construct a similar plot by measuring other first-order thermodynamic variables (such as molar entropy, S, and enthalpy, H) [8]. To simplify things, the cooling rate and the pressure are constant. The volume decreases with temperature. At the crystallisation temperature, T_c , the liquid and crystal have equal chemical potential. Below T_c , the liquid is expected to crystallise

with a sharp change in volume (usually negative, but may also be positive as in the case of water ice). However, it may be possible to supercool the liquid below T_c without crystallisation occurring (red line in Fig. 2.5). In this region the liquid is in metastable equilibrium with respect to the crystal, and adopts a configuration of minimum free energy. If the liquid is then cooled further, at some point the volume curve begins to bend so that it has similar temperature dependence to the crystal and a glass, which is not in equilibrium, has been formed. It should be noted that the glass is still in thermal equilibrium (vibrational degrees of freedom of molecules) [8] and we refer to the arrangements of the molecules here. The temperature range over which the bending occurs (and over which changes occur in other properties such as enthalpy and entropy) is called the transformation range or interval [8, 13]. The glass transition temperature, T_g [2, 3, 8, 13], will lie inside this range but it will vary somewhat depending on the measurement technique, as will be discussed shortly. A more precise temperature applicable to the volume curve above is the fictive temperature, T_f [3], which is the temperature coordinate of the intersection of the volume lines extrapolated from the glass and the liquid.

Experimentally, it is found that if a faster cooling rate is used, the transformation range, T_g , and T_f are all increased. This is a result of the temperature dependence of molecular relaxation times. Various theories (such as the early example of Zachariasen's "rules" for the oxide glassformers [18]) based on the structure and bonding of the material [2, 3, 8] and on the kinetics of crystallisation [3, 8, 13] (since glasses form when the melt avoids crystallisation) have been developed to explain why particular materials make easy glassformers that can be vitrified with a low cooling rate. From the theory of Turnbull [19] based on nucleation and growth kinetics, which allow estimation of the cooling rate needed to form the glass (avoid nucleation and growth of the crystal phase) if the melt properties are well known, the intuitive result emerges that it is liquids with T_g close to T_c (high viscosity near T_c) that are the easiest to vitrify [3, 8, 13].

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2.4 Relaxation and the Glass Transition

Molecules may have several different relaxation times associated with various types of motion within the molecule or involving the molecule as a whole. These may be differently probed depending on the relaxation experiment chosen. An example discussed earlier is the dielectric relaxation time associated with reorientation of molecules in an electric field. The viscosity can also be considered a related quantity [see the Debye equation for the relaxation time, Eq. (1.56) in Chap. 1]. In addition, there will be a distribution of relaxation times in the glass so that we can speak of either an average or a most probable relaxation time, the latter usually being quoted for dielectric experiments [20]. The relaxation time and viscosity increase as the temperature of the liquid is reduced (see the arrow at the top of Fig. 2.5). At higher temperatures the relaxation time in the liquid follows the Arrhenius equation,

$$\tau_{\alpha} = \tau_{\infty,ARR} \exp(B_{ARR} / T), \qquad (2.1)$$

where τ_{α} is the structural, or α -relaxation time, and $\tau_{\infty,ARR}$ and B_{ARR} are constants. If a real activated process is involved (which is thought to be the case for liquids at a high temperature), $B_{ARR} = E_A / k$ where E_A is the activation energy. At such temperatures, (assuming the molecules are polar), the dielectric relaxation spectra would be expected to show a single peak in ε'' and dispersion in ε' and follow the Debye equation (however, some results suggest that there is still departure from exponential relaxation at high temperatures [21]. A constant high temperature value of the stretch parameter β_{KWW} of the relaxation is required by the Mode-Coupling theory [21]). The loss peak and ε' dispersion are the dielectric signature of the α -relaxation associated with reorientations of the molecules allowing flow of the material. As the liquid is cooled towards T_g , the α -relaxation time dependence on temperature becomes stronger than Arrhenius. Around T_g , a popular empirical equation used to describe this temperature dependence is the Vogel-Fulcher-Tammann (VFT) [22-24] equation,

$$\tau_{\alpha} = \tau_{\infty, VFT} \exp[B_{VFT} / (T - T_0)], \qquad (2.2)$$

where T_0 is a new constant. Another empirical equation of related form known as the Williams-Landell-Ferry (WLF) [25] equation,

$$-\ln\left(\frac{\tau_{\alpha}}{\tau_{g}}\right) = \frac{C(T - T_{g})}{D + (T - T_{g})},$$
(2.3)

where *C*, and *D* are constants and τ_g is the relaxation time at T_g has also been used for polymers around the glass transition. Such equations can of course be applied to measured quantities that are directly related to the relaxation time such as the viscosity and dc conductivity. In addition, the α -relaxation observed in dielectric spectroscopy is usually broadened considerably (alcohols are an exception, see Chap. 3 of this thesis), so that it is now best described by one of the empirical relaxation formulae given in Sect. 1.14 of Chap. 1. The DC function [Chap. 1, Eq. (1.61)] and the Fourier transform of the derivative of the KWW function [See Chap. 1, Eq. (1.64) for the time domain form] are generally used. There are departures at high frequencies from both these equations, which are discussed in terms of additional relaxation processes in the glass and supercooled liquid in Sect. 2.13. The KWW equation is sometimes considered preferable because it has less parameters [20].

A useful method of determining the temperature dependence was suggested by Stickel

[26-30]. Plotting $\left[\frac{d(\log \tau_{\alpha})}{d(1/T)}\right]^{-1/2}$ vs 1/T will linearise the VFT equation, while an Arrhenius temperature dependence becomes a horizontal line. Such plots have been made for τ_{α} in several substances including Salol [28], *o*-terphenyl [29], 1-propanol [29], and propylbenzene [30]. Stickel et al. [26-30] have found that there are three distinct regions over the range of relaxation times and viscosities from deep in the liquid phase to below T_g . At high temperatures, there is an Arrhenius region, crossing over at T_A to the 1st VFT region, with a second crossover to a shallower VFT dependence at a temperature T_g . Dixon [31] alternatively tested the applicability of the VFT equation by dividing the relaxation data into 3-decade segments and comparing the value of T_0 obtained from the fit of the VFT equation for each segment. He found that the VFT equation only applied near T_g (as judged by a constant value of T_0 holding for relaxation times from below to slightly above T_g) [20, 31]. More recent results of Lunkenheimer et al. [21] on glycerol and propylene carbonate suggest that there are no clear-cut "regions" and the slope of the Stickel plots varies continuously

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[21]. As the glass transition is approached, the temperature dependence of au_{lpha} and the viscosity η become very strong and they increase to very large values below T_g . The above discussion allows an explanation of the dependence of T_g on the cooling rate. When a slower cooling rate is used the molecules in the liquid will have more time to attain an internal equilibrium (or relax) at a given temperature. The falling out of equilibrium that occurs over the transformation range is postponed to a lower temperature and T_g and T_f are reduced. If a faster cooling rate is used, the supercooled liquid will have less time to equilibrate and T_g and T_f are increased. T_g is thus dependent on the timescale of the measurement and will vary depending on how it is measured [differential scanning calorimetry (DSC), dilatometry, viscosity measurements, mechanical spectroscopy etc.] - the frequency of the experimental probe relative to the cooling rate (these are combined in a DSC measurement) determines how long the supercooled liquid will be allowed to equilibrate. It has been noted that we might choose a different value of T_g if we lived longer or shorter lives [21]. Often, a relaxation time for the α -relaxation of between 100 –10000 s [2, 8, 13, 20, 21] (or sometimes $f_m = 10^{-4}$ Hz if frequency of maximum loss is used instead of relaxation time [32]) is chosen to define T_g . In viscosity measurements $\eta = 10^{13}$ Pa s (behaves as a solid) defines the T_g [3, 8].



Fig. 2.6 Volume-Temperature plots for glasses cooled at different rates and heated at the same rate. If the rates are the same, there is no hysteresis in the volume-temperature plots. If they are different there is hysteresis as indicated by the dotted lines as the glasses attempt to relax towards the equilibrium liquid. The vertical dotted line shows the effect of isothermal annealing on the volume of glass 3. (see Ref. [8], p. 29).

A further result of the above discussion is that glasses formed with different cooling rates will have different properties [8] (this includes dielectric and optical properties as well as the different volumes and other thermodynamic properties). Fig. 2.6 shows the volume-temperature plot again, for three glasses (1, 2, and 3) formed by cooling at different rates $R_1 < R_2 < R_3$, so that $T_{f1} < T_{f2} < T_{f3}$ [8]. If we have a glass at the point represented by the dot, holding it isothermally (annealing or aging) will result in a reduction of the volume of the glass with time along the path shown, with a corresponding fall in T_f . Other properties of the glass including dielectric ones will also change as the glass structurally relaxes toward the equilibrium liquid at that temperature (the extrapolation of the volume line for the supercooled liquid). Glasses

that have attained the state of the equilibrium-supercooled liquid are said to be "stabilised" [8]. This is only possible in the transformation range. Deep in the glassy phase, there will never be enough time for stabilisation. Structural relaxation also causes hyteresis effects when a glass prepared with a given cooling rate is heated through the transformation range with a different rate [8, 13]. The dotted lines in Fig. 2.6 are the change in volume around the transformation range for glasses 1 and 3 as they are heated with a rate equal to the cooling rate R_2 of glass 2. Glass 1 is heated at a quicker rate than it was cooled so its T_f and volume are too low and it structurally relaxes *upwards* toward the equilibrium liquid line. Glass 3 is heated at a slower rate than it was cooled and it structurally relaxes downwards to a lower T_f and volume, resulting in a minimum in the volume-temperature plot. Glass 2 is heated at the same rate as it was originally cooled and follows its cooling volume curve exactly. The hook that is seen in the specific heat capacity at constant pressure (C_n) curves of glasses 1 and 3 corresponding to the "softening temperature" signifies that they have reached the same state [8]. Tool [33] proposed empirical equations for the relation of the rate of change of T_f given the difference between T_f and the actual temperature. These effects are discussed in Chap. 5. for the dielectric properties of glasses cooled and heated at different rates in terms of competing effects of structural relaxation and heating on the dielectric properties of a glass.

2.5 Second Order Phase Transitions and the Glass

Transition

In the Ehrenfest scheme [34], a first order phase transition is continuous in the molar Gibbs Free-Energy G, while the first derivatives are not continuous. A second order phase transition is continuous in both but the second derivatives of G are not continuous. Since molar entropy is $S = -(\partial G/\partial T)_p$ and molar volume is $V = (\partial G/\partial P)_T$, these are discontinuous for 1st order phase transitions (see the crystallisation path for V in Fig. 2.5). For a second order phase transition $(\partial S/\partial T)_p$, $(\partial V/\partial T)_p$, $(\partial S/\partial P)_T$, $(\partial V/\partial P)_T$ are all discontinuous. As a result, the specific heat

capacity at constant pressure, $C_p = T(\partial S / \partial T)_p$, the volume coefficient of thermal expansion $\alpha = (1/V)(\partial V / \partial T)_p$ and the compressibility $\kappa = -(1/V)(\partial V / \partial P)_T$ are all discontinuous for a 2nd order phase transition [34]. Discontinuities in these quantities are found for the glass transition [2, 3, 8, 13]. Fig. 2.7 shows a typical plot of C_p for a glass heated through the transformation range. The discontinuity visible near T_g suggested a relationship with 2nd order phase transitions. These are "rounded" however [3, 13] (as expected from the continuous change of slope of V over the transformation range in Fig. 2.5), and not precise as would be if the glass transition were a real 2nd order phase transition. Given that T_g depends on the cooling rate (a dynamic quantity), it would not be expected that T_g could be the transition temperature for a proper phase change either [3, 13].



Fig. 2.7Specific heat capacity, C_p , of a glass heated through its glass transition.The small peak is a structural relaxation effect similar to those in Fig. 2.6.

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The continuity of *S* and *V* at the boundary T_c of a 2nd order phase transition lead to the Ehrenfest relations [3, 8, 13, 34]:

$$\left. \frac{dT}{dP} \right|_{T=T_c} = T_c V_c \frac{\Delta \alpha(T_c)}{\Delta C_p(T_c)}$$
(2.4)

$$\left. \frac{dT}{dP} \right|_{T=T_c} = \frac{\Delta \kappa(T_c)}{\Delta \alpha(T_c)}.$$
(2.5)

Experimentally, it has been found that Eq. (2.4) applies to the glass transition in at least some cases [3, 8, 13] but Eq. (2.5) does not. If the phase transition occurs at T_c with a volume V_c then the ratio of Eq. (2.5) and (2.4) (the Prigogine-Defay ratio [3, 8, 13]) at T_c should be 1 i.e.

$$\frac{\Delta C_p(T_c)\Delta\kappa(T_c)}{T_c V_c [\Delta\alpha(T_c)]^2} = 1.$$
(2.6)

If T_g is used as the transition temperature, the ratio is found to be > 1 for glasses [3, 8 13] (2 – 5 being typical values [13]) so that a single "ordering parameter" [3, 8, 13] (defined as an internal parameter whose value becomes fixed on passing through the transition [13]) cannot describe the glass transition. At least two such parameters, a fictive pressure p_f , as well as T_f must be given [3, 13]. Finally, there is the difficulty of defining a real "order parameter" [13] for the resultant amorphous solid if the glass transition is to be considered as a thermodynamic phase transition.

2.6 The Kauzmann Plot



Fig. 2.8 Plot of the excess entropy S_{exc} of the supercooled liquid and glass over the crystal for a typical glassformer. Two different glasses, 1 and 2, are shown. Glass 2 has a slower cooling rate than glass 1 and vitrifies at $T_{g2} < T_{g1}$ as it remains in equilibrium longer. The Kauzmann temperature, T_K , is the extrapolation of the supercooled liquid line to the point where $S_{exc} = 0$ (After Ref. [8]).

The difference in entropy between the supercooled liquid and crystal phases is given by:

$$S_{exc} = S_{liq} - S_{xtal}.$$
 (2.7)

If this is plotted against the temperature (Fig. 2.8) it is found to decrease rapidly as T_g is approached and then level off beyond T_g to a value above that of the crystal [2, 3, 8, 13]. In Kauzmann's plot, S_{exc} was scaled by the entropy of melting and T by the melting temperature [35-37]. By applying slower cooling rates in a DSC experiment one can reduce T_g and measure the heat capacity of the equilibrium liquid, $C_{p,liq}$ at progressively lower temperatures. S_{liq} is found from the area under the $C_{p,liq}$ vs.

 $\ln T$ curve. If the S_{liq} curve is extrapolated below T_g to a temperature T_K (the Kauzmann Temperature [35]), the entropy of the equilibrium liquid will fall below that of the crystal, which would imply that the crystal will not be the phase of lowest entropy at 0 K in violation of the 3rd law of thermodynamics, which states that the entropy of all perfect crystals or any equilibrium phases is equal at 0 K and taken to be zero. To attain the equilibrium liquid in a real experiment at T_K would require an extremely long time and most liquids would crystallise well before then. There are however atactic polymers whose molecular structure precludes crystalline packing [13]. In order to avoid the scenario of a negative S_{exc} , it has usually been suggested that a 2nd order phase transition intervenes at T_K to halt the decrease in S_{liq} . This cannot be observed because of the real glass transition (a postulated phase transition at T_K is sometimes termed an "ideal glass transition" [3, 13]). However, there is no reason why the equilibrium liquid's entropy could not gradually fall off towards 0 at 0 K rather than invoke the idea of a 2^{nd} order phase transition at T_K [8, 38, 39]. It would thus be similar to metastable crystalline allotropes that persist to T = 0 K for kinetic reasons but have zero entropy because they are trapped in a single configuration [38, 39]. When the τ_{α} or η temperature dependence is fitted with the VFT equation around T_g , it is found that the parameter T_0 (the temperature of an infinitely large relaxation time or viscosity) is close to T_K , which has also been considered suggestive of the idea of an unobservable 2^{nd} order phase transition at T_K .

2.7 Configurational Entropy Theory

In 1958 Gibbs and DiMarzio [40] published a paper in which the statistics of arrangement of system of long polymer chains on a set of lattice points corresponding to low energy arrangements of the bonds (which is a subset of another lattice of voids where there is no segment) [40] was used to demonstrate the existence of a 2^{nd} order phase transition at temperature T_2 (as defined above in terms of changes in thermodynamic properties at T_2) for the polymer on cooling. The configurational entropy of the system (entropy associated with arrangement of the chain segments) is given by:

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$$S_c = R \ln \Omega_c, \qquad (2.8)$$

where Ω_c is the number of possible configurations of the system. High above T_2 there are many configurations available for the system and the system can freely change between them. As the temperature falls the number of available configurations is reduced and the dynamics become slower until the system is fixed in a minimum free energy one at T_2 and $S_c = 0$ [40]. Factors that change T_g in a real amorphous polymer system were then shown to have a similar effect on T_2 [40]. The calculation thus related the dynamics observed around T_g to a thermodynamic transition at T_2 , seeming to validate the Kauzmann extrapolation and the idea of a 2nd order phase transition underlying the glass transition [40].

Adam and Gibbs then generalised the idea of the configurational entropy controlling the dynamics to glasses in general [41]. The following discussion is a summary of the arguments in their paper. They assumed that the liquid consisted of a number, N, of "co-operatively rearranging regions" (CRRs) at a given temperature and pressure. A CRR was the smallest region capable of independently changing its configuration given enough enthalpy [41]. Each CRR contains z species, monomeric chain segments in a polymer, and molecules in a small-molecule glassformer. The probability of a transition from one configuration to another for a CRR at temperature T is,

$$W(T) = A \exp(-z\Delta\mu/kT).$$
(2.9)

 $\Delta \mu$ is the free energy barrier per segment/molecule required for the rearrangement. The theory assumes this is independent of *T* and *z*. To obtain an average transition probability, $\overline{W}(T)$ a minimum size for the CRR, z^* , is defined. It can be shown that [41]

$$\overline{W}(T) = \overline{A} \exp\left(-z^* \Delta \mu / kT\right).$$
(2.10)

Most of the rearrangements involve the smallest CRRs. Calculation of z^* then allows the relaxation time-temperature dependence to be obtained.

All the CRRs are independent so the total configurational entropy of the sample is just

$$S_c = N s_c, \qquad (2.11)$$

where s_c is the configurational entropy of a single CRR. Using Eq. (2.8) leads to

$$s_c = k \ln \Omega_c^{1/N}. \tag{2.12}$$

For a mole (= Avogadro's number N_A) of segments or molecules (molar sample):

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$$s_c = k \ln \Omega_c^{z/N_A}. \tag{2.13}$$

We can write this equation for the special case of a CRR with the minimum size as

$$s_c^* = k \ln \Omega_c^{z'/N_A}, \qquad (2.14)$$

so that we have for z^* ,

$$z^* = N_A s_c^* / S_c. (2.15)$$

Given that the transition probability is inversely proportional to the relaxation time, this is given by an equation of the form:

$$\tau_{\alpha} = A_{AG} \exp(C/TS_c). \tag{2.16}$$

 A_{AG} and C are constants, while S_c is temperature dependent. Adam and Gibbs [41] then attempted to link Eq. (2.16) to the empirical temperature dependence of τ_{α} and η as described by the WLF [41] or VFT equation. The link to the VFT equation is obtained as follows [8]:

If ΔC_p is the specific heat capacity difference between the equilibrium liquid and the glass then,

$$S_{c}(T) = S_{c}(T_{2}) + \int_{T_{2}}^{T} \frac{\Delta C_{p}}{T} dT.$$
 (2.17)

Further, if ΔC_p is constant with temperature and $S_c(T_2) = 0$ in accordance with Gibbs' and DiMarzio's calculations on polymers then,

$$S_c(T) = \Delta C_p \ln\left(\frac{T}{T_2}\right). \tag{2.18}$$

If $\left(\frac{T-T_2}{T_2}\right)^2 <<1$ then it can be shown that the VFT equation is obtained for the

relaxation time-temperature dependence [8]. By comparison with the WLF rather than VFT equation, Adam and Gibbs estimated T_g/T_2 for several glassformers and found a mean value of $1.30 \pm 8.4 \%$ [41]. They also used a calorimetric method to estimate the ratio. Assuming that the vibrational entropies in the glass and crystal are similar, the entropy difference between the glass and crystal at T = 0 K should be equal to the configurational entropy frozen in the glass at T_g , i.e. $S_{exc}(T = 0 \text{ K}) \sim S_c(T_g)$. Note that residual entropy for a glass doesn't violate the 3rd law because the glass is not in equilibrium [34]. This can be estimated from calorimetric measurements on the glass

near T = 0 K. This quantity is given by the same integral $S_c(T_g) = S_c(T_2) + \int_{T_2}^{T_g} \frac{\Delta C_p}{T} dT$.

Making the same approximation as before for ΔC_p and the same assumption $S_c(T_2) = 0$ allows T_2 to be calculated from Eq. (2.18) with $T = T_g$. Calorimetric values of 1.26 for polypropylene [42] and 1.29 \pm 10.9 % for the average of 11 glassformers [43] are quoted in Ref. [41].

Recently, Johari [39] has advanced lengthy and detailed arguments against the Kauzmann extrapolation and the need for (or evidence of) a 2nd order transition associated with the glass transition at some temperature between T_g and 0 K. He has emphasised that $S_c(T_2) = 0$ [used to obtain Eq. (2.18) from Eq. (2.17)] was an assumption (based on Gibb's and DiMarzio's work) to obtain agreement with the VFT temperature dependence and is not part of the configurational entropy theory itself, which makes no comment on the value of S_c at a given temperature [39]. In addition, it is argued that ΔC_p may not be taken outside the integral in Eq. (2.17) because $C_{p,liq}$ is not temperature invariant near T_g [39]. The original polymer chain calculation of T_2 [40] is also criticised [38, 39] on the grounds that; (i) later work (see Ref. [44] and other references in Ref. [38] and [39]) shows that S_c may not decrease as rapidly as Gibbs and DiMarzio suggested; (ii) the Flory-Huggins approximations used may not be valid [45, 46], and (iii) calculations by Stillinger [47] have shown that a molecular liquid will not reach a point of entropy crisis (i.e. a temperature T_K where the liquid phase entropy falls below that of the crystal phase). T_2 and T_K must be different in any case because S_c and S_{exc} are not the same [39]. S_{exc} will include any vibrational entropy differences of the equilibrium liquid from the crystal, as well as entropy differences arising from other relaxations [Johari-Goldstein (JG) β relaxations and excess wings, discussed in a Sect. 2.12 and 2.13], and the short time tail of the structural relaxation. These objections [and the points related to Eq. (2.18)] invalidate Adam and Gibbs calorimetric method for estimation of T_g/T_2 [39]. These other relaxations should also preclude the vanishing of S_{exc} at T > 0 K. It is stressed that there must still be a considerable relation between the thermodynamics and dynamics of the glass transition because the relation between T_K and the empirical T_0 of the VFT equation still stands in many glassformers. S_c must be related to the form

of the VFT equation around T_g [36, 39] even if the Kauzmann extrapolation and conclusions from it concerning a 2nd order phase transition are invalid. The interpolation of C_p for an equilibrium liquid below T_g such that its 0 K entropy is 0 is compared to the expectation given a 2nd order transition at T_K in Fig 2.9. The configurational entropy theory has other weaknesses. One of these is that there is no way to determine a size for a CRR [10]. Johari has mentioned the fact that the theory allows no escape mechanism for species within a CRR [39]. In addition, $T_0 \neq T_K$ for many polymeric substances.





Ngai [48] has discussed some experimental facts such as dynamical heterogeneity, finite-size effects (both discussed in the next section), and the rheological behaviour of polymers that seem to conflict with the Adam and Gibbs (AG) theory and how these could be resolved by introduction of ideas from the Coupling Model (CM) dynamical theory of the glass transition [48, 49] (see Sect. 2.12).

2.8 Non-Exponential Relaxation

In Chap. 1, Sect. 1.14, some ways in which a non-exponential decay function could arise in dielectric relaxation were outlined. This is discussed in more detail with a concentration on molecular processes in liquids and glasses.

The idea of CRR's and cooperative motion in general has become a useful concept in the study of glasses independent of the configurational entropy theory. An associated idea is that of "dynamical heterogeneity" [50] - that in the supercooled liquid and glass there are subgroups of species with different relaxation times selectable by experiment. This would result in a non-exponential overall relaxation even if the individual units relaxed exponentially. Given enough time, the fast and slow species may exchange. The alternative extreme is a dynamically homogeneous liquid or glass with intrinsically non-exponential relaxation – both scenarios and combinations will produce similar dielectric spectra or similar results in any extensive experiment in which average properties of a large ensemble of molecules are measured (see Fig. 2.10). There is support for dynamical heterogeneity from NMR experiments [51], from non-resonant dielectric hole burning [52, 53], and solvation dynamics [54] as well as other methods (see Ref. [50]). Other indirect evidence from experiments on supercooled liquids (see below) and more direct evidence from the "glass transition" that occurs in colloids as the volume fraction of spherical particles increases [7], as well as computer simulation results [55] seem to suggest that groups of faster and slower particles are also spatially related, connecting with Adam and Gibbs' idea of CRR's. However, the AG theory doesn't include the idea of different relaxation rates for the CRR's [48].



Fig. 2.10 Illustration of how the same stretched exponential (KWW) relaxation function can result from (A) a sum of stretched exponentials with the same time constant or (B) from a sum of exponential relaxations with different time constants (After Ref. [54]).

Experiments allow an indirect estimation of a so-called "cooperative length scale" γ [50]. One approach involves confining a liquid to small pores (e.g. by filling a vycor or controlled pore sol-gel glass under reduced pressure) with functionalised walls, which do not interact with the liquid's molecules. Relaxation can then be studied by a variety of techniques including dielectric spectroscopy [56], NMR [57], and solvation dynamics [58, 59]. When the pores are small enough, it is found in dielectric measurements that the τ_{α} shows less departure from the Arrhenius equation and T_g is decreased [56]. When the pores are not coated, there may be strong surface effects at the pore walls that must be taken into account in any analysis [60]. These cause additional relaxations in dielectric loss spectra associated with a layer near the pore wall where relaxation is retarded, and T_g may be increased [60]. Such experiments can be extended to the very small pore sizes offered by zeolites to try to see how many interacting molecules are required for liquid-like behaviour [61, 62]. Interestingly, the AG theory can be used to argue for both an increase and a decrease of T_g [37]. Looking at Eq. (2.16), S_c should be smaller at a given temperature because of the smaller liquid volume in the pore leading to a higher T_g . However, going back to the

possibly more fundamental equation based on the CRR idea, which contains $\exp(z^*\Delta\mu/kT)$ instead of $\exp(C/TS_c)$ we see that as the size of the CRR's increases with the fall in temperature there may come a temperature where they match the pore size. τ_{α} and η will be lower than in the bulk liquid below this temperature [37]. However, z^* has been estimated to be only a few molecules at temperatures around T_B ($\tau_{\alpha} \sim 1$ MHz) [37], which is where departures from bulk behaviour begin [37, 56]. By confining to pores, Arndt et al. [56] put an upper limit of 7 nm on γ in salol around T_g . In an experiment with uncoated pores the same group [60] estimated γ to be less than 1 nm in glycerol. Recently, new NMR experiments that attempt to associate a length-scale with dynamical heterogeneities [63, 64] have been used to estimate $\gamma \sim 3$ nm in poly(vinyl acetate) without confining the liquid to pores. Finally, it should be noted again that the extent of non-exponentiality, as measured for example by β_{KWW} depends on temperature, with β_{KWW} approaching a constant value near 1 in liquids at high temperatures as discussed in Chap. 1, Sect. 1.13 concerning the applicability of the Debye equation.

2.9 Fragility of a Glassformer

The idea of fragility [3, 20, 36, 37, 65-67] has proved to be a useful concept for grouping different classes of glassfromers and linking their thermodynamic and dynamic properties. If $\log \eta$ or $\log \tau_{\alpha}$ is plotted against a reduced inverse temperature (multiplied by T_g), an interesting plot results in which glassformers are arranged in order of departure from Arrhenius behaviour, which is a straight line on the plot. An example of such a plot is shown for the viscosity of several glassformers of various types in Fig. 2.11. It is seen that glassformers of similar chemistry such oxides, ionic salts, and small-molecule liquids tend to group together on the plot. The inorganic oxides show the least departure from Arrhenius behaviour, the small-molecule organic liquids generally show the most. Excluded from this plot are polymeric materials.

A plot with τ_{α} is to be preferred for these because viscosity depends on the molecular weight and polydispersity [37, 68]. These are found to show a wide range of different extents of departure from the Arrhenius equation on the plot [68]. Oldekop [69] and Laughlin and Uhlmann [70] were the first to use this type of plot to classify glassformers.

Later, Angell [65-67] introduced the terms "strong" and "fragile" to categorise liquids that show very little or extensive departure from the Arrhenius line (i.e. curvature) on the plot. This type of plot is sometimes called an Angell plot [65-67] or alternatively an Oldekop-Laughlin-Uhlmann-Angell (OLUA) plot [37]. The "fragility" of a liquid is usually quantified by the extent of curvature on the Angell plot at T_g given by:

$$m = \frac{d\log \tau_{\alpha}}{d(T_g/T)}\Big|_{T=T_g}.$$
(2.19)

m is usually called the kinetic fragility [71] or steepness index [72]. For the case of VFT temperature dependence it can be shown that [68, 73]:

$$m = \frac{B_{VFT} T_g}{\ln 10 (T_g - T_0)^2}.$$
 (2.20)



Fig. 2.11 Plot of $\log \eta$ vs. T_g/T for several glassformers. The positions of strong and fragile glassformers are marked on the plot. It is seen in the inset that the strong liquids have a small heat capacity change (using $C_{p,liq}/C_{p,xtal}$ as a measure) at T_g and the fragile liquids have a large change. Data is from Ref. [66] and Ref. [67] and the figure itself is taken from Ref. [68].

Other definitions of fragility have been used when the VFT equation applies such as a "strength parameter" [73],

$$D = B_{VFT} / T_0, (2.21)$$

which is small (< 10) for fragile liquids, and large (~ 100) for a strong liquid [72]. *D* is related to *m* by [73]

$$m = \left(\frac{D}{\ln 10}\right) \left(\frac{T_0}{T_g}\right) \left(1 - \frac{T_0}{T_g}\right)^{-2}.$$
(2.22)

If the Arrhenius equation describes the temperature dependence then [71, 73],

$$m = \frac{B_{ARR}}{T_g \ln 10}.$$
(2.23)

If we define $\tau_{\alpha} = 100$ s at T_g , the minimum possible value of the kinetic fragility is $m_{\min} \sim 16$ (the other intersection point on the relaxation time Angell plot is at $\tau_{\alpha} \sim 10^{-14}$ s giving an overall straight line slope of 16) [73]. Another measure of fragility is the so-called $F_{1/2}$ fragility [74, 75], given by

$$F_{1/2} = 2(T_g / T_{1/2} - 0.5), \tag{2.24}$$

where $T_{1/2}$ is the temperature at which τ_{α} is half-way between that of the high temperature liquid limit of 10⁻¹⁴ s and the glass transition value of 10² s. Examination of Fig. 2.11 shows that $T_{1/2}$ is lower for a more fragile liquid so that $F_{1/2}$ increases with fragility.

The original idea of Angell [66, 67] concerning fragility was that the strong liquid has a stable structure that doesn't change much with cooling below T_g . The activation energy is constant with temperature. Properties should not change much on passing through the transformation interval. A fragile liquid on the other hand would show large changes in its properties. The configurational entropy S_c is the major property depending on the liquid structure, so the idea of fragility is intimately related to the links between the thermodynamics of glasses and their dynamics and whether the former controls the latter, as suggested by the AG theory. From the above, a large change in S_c would be expected for the fragile liquid as it is cooled – a small change for the strong liquid. This should result in the fragile liquids showing a larger step in the heat capacity at T_g than the strong liquids. Angell [66, 67] demonstrated a correlation between the heat capacity step (a thermodynamic measure of fragility) and the kinetic fragility for the limited set of liquids in Fig. 2.11 as shown in the inset of that figure. As with the AG equation it is found that polymers seem not to fall into this scheme. More recent work [68] in which a similar measure of thermodynamic fragility, $C_{p,liq}/C_{p,xtal}$ (or $C_{p,liq}/C_{p,glass}$ for the amorphous polymers) was compared to m for a large number of inorganic, small-molecule organic (Van der Waals and hydrogen bonded), and polymeric glassformers showed a positive correlation only for the inorganic glassformers which constitute most of those studied originally by Angell. An almost negligible positive correlation was found for the small-molecule

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glassformers and a *negative* correlation was found for the polymers (large m values were associated with smaller heat capacity steps) [68]. Roland et al. [76] have pointed out that adding bulky groups to a polymer chain will decrease S_{exc} , and thus the heat capacity step, but has been shown to increase m. Scaled excess entropy $S_{exc}(T_g)/S_{exc}(T)$ vs. T_g/T plots are a more successful attempt to correlate a thermodynamic and kinetic fragility measure. An example is shown in Fig. 2.12 [77]. This plot is superficially very similar to the Angell plot (see Fig. 2.11) [77], with the substances occupying similar positions in it. SiO₂ appears to be much more fragile on the scaled entropy plot than on the original Angell plot (where it is the strongest liquid). This can be explained by the fact that $S_{exc} \neq S_c$. Rather it includes contributions from vibrational entropy also. Martinez and Angell [77] point out that the vibrational entropy of the glass is less than that of the crystalline forms for SiO_2 resulting in a low S_{exc} . Thermodynamic fragilities from the entropy plot and kinetic fragility do not seem to be as well correlated for polymers [76]. Ngai has questioned the existence of such a direct relationship between measures of kinetic and thermodynamic fragility [78], even in the small-molecule glassformers.



Fig. 2.12 $S_{exc}(T_g)/S_{exc}(T)$ vs. T_g/T for a variety of glassforming liquids taken from Ref. [77]. Note the superficial similarity to Fig. 2.11. SiO₂ appears to be a much more fragile liquid on this plot than on the Angell plot.

It has also been established that there is a relationship between the broadness of the α -relaxation observed in for example, dielectric spectroscopy of supercooled liquids and m [73]. The broadness is generally specified by the value of the KWW stretch parameter, β_{KWW} at T_g . β_{KWW} is generally largest for the strong liquids. The relationship is clearest when the plot is confined to particular classes of glassformer [37, 73]. Ngai [79] has attempted to explain this within the CM, which is described in Sect. 2.12. Some possible exceptions to the correlation (pressure may alter m and not β_{KWW}) have been described recently [80].

2.10 Energy Landscape

The energy landscape construct may act as a general concept to explain the link between dynamics and thermodynamics of glassformers. The energy landscape is the total potential energy of a glass (or other system) as a function of the positions of its constituent atoms/molecules. Goldstein [81] was the first to articulate the idea of a potential energy landscape as an aid for simply describing the dynamics around the transformation interval and in the glass while Stillinger [82, 83] has expounded on it mathematically. A simple molecule may have three degrees of freedom associated with its translational motion. If there are N such molecules, the potential U will be a 3N variable function that defines a hypersurface in 3N + 1 dimensional space. The internal energy (and so called state point [36]) of the sample is a function of the arrangement of the molecules (configurations). In this discussion, the term "inherent structure" [36, 82, 83] is used to mean those configurations corresponding to local minima in U. In the crystal the molecules have well defined positions in space such that U is a sharp deep minimum about which there are only small fluctuations in energy, since the crystal is solid and molecules rarely change their positions. When a glass is formed by quenching a liquid a variety of solids (in the dynamic sense of Sect. 2.1) with differing thermodynamic properties and final arrangements of the atoms may result. This suggests that for a glass there must be a large number of inherent structures corresponding to minima of different depths on the potential energy landscape [81]. We now consider the glass transition in the opposite direction to most of the introduction (heating the solid). At T = 0 K, the glass will be trapped in one of these minima. If T > 0 K, there will be thermal energy available (kT/2 per degree of freedom) for transitions over the barriers in the landscape between different minima providing a mechanism for relaxation and viscous flow [81]. The height of the barriers controls these processes. These transitions correspond to changes in the configuration of the entire system [81]. However, only a small local group of molecules will be affected when the change is from one minimum to a nearby one over a small barrier [81]. As kT approaches the barrier height (in the supercooled liquid), the system will spend more time in the process of changing from one configuration to another so it will be near a minimum rather than occupying one at

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most times [81]. At temperatures where kT is much larger than the depth of the minima the energy landscape has a minimal influence on relaxation time and viscosity. Goldstein [81] went on to ascribe maximum relaxation times and viscosities for which one could assume that the landscape idea is relevant. He estimated a limit below which the landscape idea should be useful of 1 ns - 1 ps in several different ways [81]. In addition he also described a minimum length scale for such changes in configuration, which can be related to the CRR idea [81]. Any distance associated with such a change should be distinguishable from the amplitude of molecular vibrations in the glass or supercooled liquid for the landscape idea to be meaningful in the same way that the timescales for the two processes must be resolvable. Since the AG theory is concerned with numbers of configurations and S_c it seems that there should be some link between the AG theory and the energy landscape (internal energy associated with different configurations). Evidence for this comes from molecular dynamics computer simulations on models of glassforming liquids (Lennard-Jones binary mixtures with several hundred particles) [84]. Different configurations are generated and the potential energy minimised to obtain the associated inherent structures. It is found that the average energy of these (averaged over a minimum of 60 structures in Ref. [84]), which can be seen in Fig. 2.13, is pretty constant at high temperatures, begins to decrease at some temperature, and levels off to a plateau at a lower temperature.



Fig. 2.13 Schematic of potential energy, *U*, as a function of temperature for inherent structures produced in a molecular dynamics simulation in which a 256-particle Lennard-Jones binary mixture (two types of atoms with the interaction being a Lennard-Jones potential) was cooled at different rates (After Ref [36] and Ref [84]).

This can be rationalised in terms of the energy landscape as follows: At high temperatures the liquid is able to sample all the minima in the landscape because there is plenty of thermal energy available to overcome even the highest potential barriers and change to a new configuration. Most of these minima are shallow (the deep minima or "megabasins" [36] which themselves contain local minima are rare overall) so the inherent structure energy is higher. Indeed, the landscape idea is not so useful at such temperatures as described above [81]. As the temperature is reduced, the liquid will become stuck in the deeper minima so that the inherent structure energy is lowered and the liquid's properties are landscape-influenced. At still lower temperatures, the liquid becomes trapped near the bottom of one of the megabasins

with almost constant low inherent structure energy. The change of slope of the energy at the higher temperature is shown [84] to correspond to the onset of non-exponential relaxation and the start of the landscape-influenced region – above this temperature the relaxation is exponential [36, 84]. The change in slope at the lower temperature corresponds to the glass transition. Below $T \sim 0.45$ there is a small increase with temperature in the mean square distance travelled per particle during the minimisation to the nearest inherent structure [84] – above this temperature there is a sharp increase suggesting that changes to neighbouring basins can occur above this while below it only vibrations within the same basin are possible. $T \sim 0.45$ is described as the onset of the landscape-dominated regime. The authors [84] relate it to the temperature of the avoided singularity T_c in the Mode-Coupling theory [85-88]. One further point should be stressed here. It is *not* the landscape itself that changes since the landscape includes all possible arrangements of the molecules. What changes is the way in which the liquid samples it at different temperatures [36].

This reduction in available inherent structures with an onset above the glass transition temperature also ties in well with the AG idea of a fall in configurational entropy as the temperature of the supercooled liquid is reduced resulting in non-Arrhenius temperature dependence of the relaxation time. It has also been speculated that the distinction between strong and fragile behaviour of supercooled liquids and glasses may lie in differences in the topology of the energy landscapes as discussed in Ref. [36]. In both liquid types, the activation energy is low at high temperature and most changes of inherent structure involve transitions over low energy barriers. In a strong liquid, the activation energy remains constant as the temperature is reduced. The processes involved in transition from one inherent structure to another remain the same at all temperatures (e.g. breaking and reforming of covalent bonds in the SiO₂ melt). In a fragile liquid, the activation energy increases with temperature. At the lower temperatures changes of inherent structure involve more molecules and higher potential barriers. A strong liquid like molten SiO₂ would have a relatively simple landscape that has a single deep megabasin while a fragile one like the smallmolecule glassformer o-terphenyl has a complex energy landscape with a series of deep megabasins [36] (Fig 2.14). Simulations employing the energy landscape approach may be the most correct way to treat the complex many-body interactions

between the molecules that become important as the temperature of the liquid falls [20].



Fig. 2.14The Potential energy landscapes of strong and fragile liquids (afterRef. [36]).

2.11 Stokes-Einstein and Debye-Stokes-Einstein Equations in supercooled Liquids and Glasses

In a liquid, an equation of Stokes relates the force F required to move a spherical particle with radius a at velocity v_x in the x-direction through a fluid with viscosity η is $F = 6\pi\eta a v_x$. Such a particle may diffuse due to the translational Brownian motion caused by impingement of the liquid molecules. The mean square displacement (time-averaged) of the particle in the x-direction will be $\langle x^2 \rangle = 2D_T t$ where D_T is the translational diffusion constant and t is the time that the particle diffuses for. We can write a translational Langevin equation for the particle in the x-direction at any instant as [89],

$$m\frac{d^2x}{dt^2} = -6\pi\eta a\frac{dx}{dt} + F_B,$$
(2.25)

where F_B is a force included to account for random forces on the particle due to the liquid molecules. Since the factor for the viscous drag on the particle is a continuum approximation it will include effects due to these forces. This does not matter as F_B cancels later in the derivation. v_x at any instant is due to collisions of molecules with the particle, then the equipartition principle gives the kinetic energy of the particle in terms of the absolute temperature of the fluid:

$$\frac{1}{2}kT = \frac{1}{2}m\langle v_x^2 \rangle.$$
(2.26)

The aim is to use the equation of motion to find $\langle v_x^2 \rangle$ and eliminate it from Eq. (2.26). This can be done by multiplying Eq. (2.25) by x and taking a time-average to get:

$$m\left\langle x\frac{d^{2}x}{dt^{2}}\right\rangle = -6\pi\eta a\left\langle x\frac{dx}{dt}\right\rangle + \left\langle xF_{B}\right\rangle.$$
(2.27)

 $\langle xF_B \rangle = 0$, since these are not correlated over time. Eq. (2.27) can be rewritten as,

$$m\left[\frac{d\langle xdx/dt\rangle}{dt} - \left\langle \left(\frac{dx}{dt}\right)^2 \right\rangle \right] = -6\pi\eta a \left[\frac{1}{2}\frac{d\langle x^2\rangle}{dt}\right].$$
(2.28)

 $\langle xdx/dt \rangle$ also vanishes because $v_x = dx/dt$ and x are not correlated either. Rearranging Eq. (2.28) and inserting Eq. (2.26) gives,

$$\frac{d\langle x^2 \rangle}{dt} = \frac{kT}{3\pi\eta a}.$$
(2.29)

Integration, and replacing the mean square displacement with the Diffusion Constant from $\langle x^2 \rangle = 2D_T t$ gives the Stokes-Einstein equation [37]:

$$D_T = \frac{kT}{6\pi\eta a} = \frac{kT}{f\eta}.$$
(2.30)

One can obtain the Debye-Stokes-Einstein expression for a rotational diffusion constant D_R from Chap. 1, Eq. (1.58) [37]:

$$D_R = \frac{kT}{8\pi\eta a^3}.$$
(2.31)

These equations imply the same viscosity and temperature dependence for both D_T and D_R . It is found that Eq. (2.30) is a valid description of the temperature dependence for liquids at high temperatures. However, if a probe molecule of a similar size to that of the glassformer [37] is used to measure translational and rotational diffusion below ~ 1.2 T_g it is found that D_T doesn't depend on the viscosity according to Eq. (2.30). D_T is found to be enhanced at the lower temperatures, equivalent to a change in viscosity dependence to $D_T \propto \eta^{-\xi}$ where $\xi < 1$. This is usually called the "breakdown" of the Stokes-Einstein relation in supercooled liquids and glasses. Experiments are usually performed by measuring diffusion and reorientation of a probe molecule dissolved in the glassformer. The results are

presented as plots of $\log \frac{(D_T \tau_c)_{MES}}{(D_T \tau_c)_{SE,DSE}}$ where the subscripts *SE,DSE* refer to the

predictions of the Stokes-Einstein and Debye-Stokes-Einstein equations and the subscript MES to the measured values [37]. τ_c is a rotational correlation time for the probe molecule. Plots of $\log(\tau_c/\eta)$ and $\log(1/D_T\eta)$ are also used to illustrate the breakdown [90]. These should have a slope of the same sign at all temperatures but the latter has a negative slope below some temperature while the former has a positive slope [90]. The effect disappears when the probe molecules become large compared to the glassformer molecules where $\tau_c / \tau_\alpha >> 1$ (the probe relaxes much more slowly than the glassformer so the latter appears as a continuous viscous fluid). The effect is strongest for a probe with a slow decay of its rotational correlation function (low stretched exponential parameter β_{KWW}) [91, 92], which also correlates with small τ_c / τ_{α} [93]. The enhancement effect has also been demonstrated in glasses by comparing η and self-diffusion coefficients obtained from NMR, dc conductivity or crystallisation rate measurements rather than using the properties of probe molecules (see Ref. [37] and references therein). The temperature at which the breakdown in the Stokes-Einstein equation occurs is similar to T_B on the Stickel plot (and T_β , the merging temperature for the α - and JG β -relaxations to be discussed in the next section). These property changes that occur at a similar temperature have been related to the critical temperature, T_c , of a dynamic transition that is avoided, as predicted by Mode-Coupling theories [85-88]. This temperature doesn't seem to correspond to the temperature at which the inherent structure energy per molecule begins to fall in computer simulations of the glass transition analysed with potential energy landscape ideas however [20, 84].
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2.12 Relaxations in the glass – Johari-Goldstein β -relaxations

Most of this chapter on glasses has discussed the α -relaxation that is seen to "freeze out" below T_g as this is the major feature observed in the dielectric spectra of supercooled liquids and glasses. There are molecular relaxations still occurring in the glass, which have been observed in dielectric spectroscopy as well as other techniques. These relaxations, called secondary or β -relaxations, which often persist above T_g as a peak above the α -relaxation in frequency or as a shoulder on the α relaxation, are usually weaker, and have an Arrhenius temperature dependence of their relaxation time $\tau_{\beta} = \tau_{\infty,\beta} \exp(E_{A,\beta}/kT)$ where $E_{A,\beta}$ and $\tau_{\infty,\beta}$ are the activation energy and high temperature relaxation time for the β -relaxation. These two parameters are compatible in magnitude with molecular processes [37]. The ε'' spectra peaks of β -relaxations in the glass are very broad and the Cole-Cole function often provides a good fit. The broadness decreases as the temperature increases. Such relaxations were first found in polymers [94]. It was assumed that they arose from intramolecular degrees of freedom such as side chain motions that were not entirely arrested below T_g and so were not really an intrinsic part of glass phenomenology. Later, Johari and Goldstein demonstrated their existence in a number of rigid smallmolecule glassformers, which did not possess internal degrees of freedom such as mixtures of chlorobenzene in cis-decalin [95-97], in glasses of non-rigid molecules such as *i*-propylbenzene [95], various aliphatic alcohols and phthalates [98], some fused salts [95], and some plastic crystals [97]. The occurrence of β -relaxation in glasses is thus widespread but not universal (see the next section). Secondary relaxations in glasses occurring with no obvious intramolecular origin are designated Johari-Goldstein (JG) β -relaxations and are generally thought to be a fundamental property of glasses [37, 95, 99]. Polymers with no carbon side chains (such as polyvinyl chloride) will also show such relaxations [94]. We will now discuss the phenomenology of the JG β -relaxations without reference to intramolecular ones. Things are not so clear-cut in reality. It can be difficult to distinguish JG β -relaxations from intramolecular motions because the two types have many of the same properties [99]. We will return to this point later.

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JG β -relaxations grow in strength as the temperature increases [95-98] and persist well into the liquid [96]. They become submerged under the α -relaxation in dielectric spectra [95] and progressively more difficult to resolve as the temperature increases. The merging temperature T_{β} is often estimated by extrapolation of the β -relaxation to higher temperatures [37]. This has been found to be close to the temperature T_B from the Stickel plot [29] and the temperature at which the Debye-Stokes-Einstein relation breaks down [90] suggesting a close link between the α - and JG β -relaxations. Recent measurements have shown that the temperature dependence of JG β -relaxations may change around T_g but this point is still controversial. Some of the new results on Dsorbitol for example are contradictory to some extent, with those of Olsen [100] showing a maximum and subsequent decrease in the frequency of maximum loss $f_{m,JG}$, above T_g while others [101-105] in general show an increase in the magnitude of the slope of an $f_{m,JG}$ vs. inverse temperature plot. Similar results to those found for D-sorbitol by Olsen have also been found by the same group for the pyridine-toluene mixture [106] and tripropylene glycol [107] systems. At temperatures above T_g , the window over which the two relaxation processes can be correctly resolved in the spectra is rather narrow. Nevertheless, an increase in the slope above T_g has been observed (i.e. separate peaks) for D-sorbitol by applying pressure [105], and for picoline-tri-styrene mixtures [108], and more tentatively by fitting procedures alone for copolyesters of poly(ethylene terephthalate) and poly(ethylene isophthalate) [109]. In many cases, it is also seen that $f_{m,JG}$ becomes temperature independent over a small temperature range around T_g [100, 103-109].

The older measurements of Johari suggested that the Arrhenius temperature dependence was maintained through T_g [96] but these had less measurement points than the newer data. It has been pointed out by Fujima et al. [101, 102] that a change in temperature dependence around T_g would imply a new position for the merging temperature since previous estimates were based on the extrapolation of data in or close to the glassy phase. Another controversial point is whether the ultimate relaxation at high temperatures in the liquid should be associated with the JG β relaxation [37]. Johari [96] showed that microwave relaxation data for 8.2 mol% chlorobenzene in *cis*-decalin at high temperatures agreed with the extrapolation of the JG β -relaxation Arrhenius line for 17.2 mol% solution data. A similar point was made

much later by Nozaki et al. concerning extrapolations of all the properties of the JG β relaxation in D-sorbitol [110]. Another property of the JG β -relaxation, its dielectric strength $\Delta \varepsilon_{IG}$ does undergo a change in temperature dependence above T_g . As a glass is heated $\Delta \varepsilon_{JG}$ increases slowly with temperature below T_g , and then more rapidly above it [111]. In addition, the broadness of the relaxation is decreased as the temperature rises [95-98], as already mentioned for β -relaxations in general. It has been found that the $\Delta \varepsilon_{JG}$ in dielectric experiments is higher for a glass formed by fast as opposed to slow cooling [95-97] and decreases with time as a glass is isothermally annealed [112]. The JG β -relaxation time τ_{JG} has also been shown to decrease as a glass is annealed [100] in a similar manner to which properties of a glass stabilise (see Sect. 2.4). The behaviour of the JG β -relaxation with quench rate and annealing time is investigated for several small-molecule glassforming systems in Chap. 5. A glassformer may have several relaxation peaks at frequencies above the α relaxation in its ε'' spectra, with only one (generally the slower one) assigned as the JG β -relaxation while the others are intramolecular in origin. An example is triepoxy triphenylolmethane triglicidyl ether (TPMTGE) [99, 113], which has a slower JG β relaxation and another, faster side group relaxation. Relaxations beyond a secondary relaxation are often named in order as γ -, δ - etc. relaxations Ngai [99] has discussed the ways in which a real (intermolecular) JG β -relaxation is distinguished from the intramolecular relaxations in dielectric measurements. This topic is very important since it is only the JG type that is thought to be a general property important for understanding the glass transition. The basis of the discrimination is the assumption that there must be a relationship between the α - and

the higher frequency relaxation in order for a β -relaxation to be considered a true JG one. This relationship is defined through the Coupling Model of Ngai [79, 114-117], which will now be outlined briefly.

In the CM, the supercooled liquid and glass are modelled as an assembly of interacting arrays of coupled anharmonic oscillators. The general result for relaxation (towards incoherence) in such a system is an exponential decay according to $\exp(-t/\tau_0)$ where τ_0 is the "primitive relaxation time" (the relaxation time over all times for a single oscillator array [115], i.e. the non-interacting case) at short times

gives:

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and a non-exponential decay at long times that can be approximated well by the KWW form $\exp(-t/\tau_{KWW})^{\beta_{KWW}}$. There is a crossover between these regimes at some time t_c which is found to decrease with increasing interaction strength between the arrays. Continuity of the KWW and exponential forms at t_c results in the relation [115-117]

$$\tau_0 = t_c^{1-\beta_{KWW}} \tau_{KWW}^{\beta_{KWW}}.$$
(2.32)

The departure from exponentiality (as measured by β_{KWW}) also depends on the strength of the interaction between the arrays. When the arrays are independent the exponential decay is found to persist at long times. This has been compared to some of the features of the α -relaxation [79]. Decrease in the strength of interactions between the individual oscillators, K, in an array is found to act similarly to a decrease in temperature in a glassforming liquid in that $\beta_{\rm KWW}$ decreases and $\tau_{\rm KWW}$ increases [79]. The strength of interactions between the oscillator arrays K' (the analog of intermolecular interaction strength) correlates with the kinetic fragility (strong liquids with small m have large K'). It is possible [79] to calculate an analogue of the steepness index in analogy with Eq. (2.19) from a plot of $\log \tau_{KWW}$ vs. $\log(1/K)/\log(1/K_g)$ where K_g is the strength of interaction between the oscillators when τ_{KWW} is some arbitrarily large value for fixed K'. Ngai and Tsang [79] chose $\tau_{KWW} = 10^{2.3} \,\mathrm{s}$. This index increases with K' and is approximately proportional to $1 - \beta_{KWW}(K_g)$ for various K'. This is similar to the relationship between the kinetic fragility and $1 - \beta_{KWW}(T_g)$ found for glassformers [73] (see Sect. 2.9). Ngai [118] has found that there is a general relationship between $\tau_{JG}(T_g)$ and β_{KWW} for quite a large group of glassfomers of various classes, attempting to exclude intramolecular relaxations. The CM provides such a relationship between the primitive relaxation time and the α -relaxation. Replacing τ_{KWW} with τ_{α} in Eq. (2.32)

$$\tau_0 = t_c^{1-\beta_{KWW}} \tau_\alpha^{\beta_{KWW}}.$$
(2.33)

If $t_c \sim 2$ ps is assumed, which has been estimated in various ways [116, 118], it can be shown that $\tau_{JG}(T_g) \sim \tau_0$ [118] so,

$$\tau_{JG}(T_g) = t_c^{1-\beta_{KWW}} \tau_a^{\beta_{KWW}}. \qquad (2.34)$$

The primitive relaxation is by definition a local relaxation as is the JG β -relaxation by virtue of the Arrhenius temperature dependence of τ_{JG} . However, they are not the same [116]. Eq. (2.34) now provides the means for a number of tests of whether a secondary relaxation is a true JG one or not. First, it would be expected that Eq. (2.34) would predict the rough relaxation time for the JG β -relaxation if we know β_{KWW} and τ_{α} . Relaxation times at T_g for a β -relaxation much shorter than that predicted by Eq. (2.34) would be unreasonable. An example cited in Ref. [99] is the highest frequency relaxation in tripropylene glycol [119]. Second, if τ_{α} and β_{KWW} are the same at two temperature-pressure conditions then τ_{JG} should also be the same at these conditions [99, 120] for a JG β -relaxation. β -relaxations that are not pressure sensitive should not be JG β -relaxations. 1,1'-bis(*p*-methoxyphenyl)cyclohexane (BMPC) has been given as an example [121].

Third, rearranging Eq. (2.34) gives [98, 117]:

$$\log \tau_{\alpha} - \log \tau_{\beta} (T_s) = (1 - \beta_{KWW}) (\log \tau_{\alpha} - \log t_c), \qquad (2.35)$$

which has been found to be a reasonable predictor of the α - and JG β -relaxation separation for the polyalcohol homologuous series threitol, xylitol, and sorbitol in order of increasing molecular weight and decreasing β_{KWW} [99, 122, 123].

Finally, the equation suggests that the change in temperature dependence of τ_{JG} around T_g is to be expected if the equation applies above T_g (since the α -relaxation doesn't follow the Arrhenius equation), and would act as a criterion distinguishing the JG β -relaxation from intramolecular relaxations (which are Arrhenius with the same activation energy at all temperatures e.g. *m*-fluoroaniline [124]). Several of the other experimental features of the JG β -relaxation have been found in β -relaxations that do not satisfy the criteria above and may be intramolecular [99]. These include merging with the α -relaxation at some temperature, change in $\Delta \varepsilon_{\beta}$ on annealing (this is stronger for a true JG β -relaxation), the temperature dependence of $\Delta \varepsilon_{\beta}$ and of course the Arrhenius temperature dependence at low temperatures.

There have been two main theories as to the origin of the JG β -relaxation [125]. Goldstein in his exposition of the energy landscape [80] proposed that there could be

local regions of a glass where transitions between several accessible minima in the potential energy landscape could still occur with most molecules being fixed due to large potential barriers to motion. These "islands of mobility" [80] could "give rise to mechanical or dielectric loss phenomena in the glassy condition" [80] which would be "inherent in the packing together of molecules in the amorphous state" [80]. Johari and Goldstein [95] then went on to assign the β -relaxations they observed in the dielectric spectra of rigid small-molecule glassformers to these regions of fast dynamics. Such a scheme can explain the majority of experimental properties of the JG β -relaxation [95-98, 112]. An alternative idea proposed by Williams and Watts [126] is that the JG β -relaxation is a small-angle reorientation undergone by *all* molecules in the sample prior to the α -relaxation be spatially heterogeneous while the other requires that it be homogenous. There has been some evidence for this idea from NMR results [127, 128]. These theories and evidence for or against them are discussed further in Chap. 5.

2.13 Excess (Nagel) Wings and the JG β -relaxation

Some small-molecule glassformers (e.g. glycerol, propylene carbonate) and the plastic crystalline states of cyclohexanol and cyclooctanol show only a single main relaxation peak in their ε'' spectra [37]. This peak cannot be fitted by the usual functions described in Chap. 1, Sect. 1.14. It may be fitted by the sum of the Fourier transform of the derivative of a KWW decay function that describes the region around the frequency of maximum loss and a power law for higher frequencies such that $\varepsilon'' \propto \omega^{-\gamma}$ [31]. The region of this power law is often called the Nagel [129] wing or the excess wing. Such glassformers are sometimes categorised as a special type (type A) having no JG β -relaxation, as opposed to those that display a JG β -relaxation peak (type B). Also, the ε'' spectra for such a glassformer can be scaled onto a single master curve by plotting $(1/w)\log(\varepsilon''f_m/\Delta\varepsilon f)$ vs. $(1/w)(1+1/w)\log(f/f_m)$ where w is the FWHM of the ε'' peak normalised by the Debye FWHM of 1.14 decades, f_m is

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the frequency of maximum loss, and $\Delta \varepsilon = \varepsilon_s - \varepsilon_{\infty}$. Indeed, data from several materials can be reduced to the same curve (see Fig. 2.15) [21].



Fig. 2.15 Nagel Scaling plot for ε'' of glycerol (at 195 K, 223 K and 363 K) and propylene carbonate (at 158 K, 173 K, and 253 K). The inset shows the small deviations from the scaling relationship at high *x*-coordinate values, which correspond to high frequencies (Adapted from Ref. [21]).

It has been argued that this shows that the excess wing is an integral part of a single α -relaxation with an unusual form [31, 129].

A more likely explanation of the wing is it constitutes a submerged JG β -relaxation that cannot be resolved because $\log \tau_{\alpha}$ and $\log \tau_{JG}$ are too close and/or the ratio of the α - and JG β -relaxation strengths is small [37, 99]. It is possible to fit the dielectric spectra of an excess wing glassformer with two relaxation peaks [130-132]. Also, given the empirical relationship between $\tau_{JG}(T_g)$ and β_{KWW} [118] expressed in Eq.

(2.35) it would be expected that glassformers with large β_{KWW} will have excess wings rather than JG β -relaxation. This is found to be the case (e.g. glycerol has $\beta_{KWW} = 0.7$) while the other polyalcohols of the series such as sorbitol have smaller β_{KWW} and resolved JG β -relaxations [122, 123].

It has been shown that isothermally annealing an excess wing glassformer for a long time [133] can expose a shoulder on the peak which could be explained as the JG β relaxation emerging from beneath the α -relaxation peak when the latter shifts to lower frequencies as the fictive temperature is reduced. Increasing the molecular weight as in the polyalcohol series [122, 123] mentioned above and for the case of the various propylene glycol oligomers $[H_3C-O-(C_3H_6O)_N-CH_3]$ with various values of N [131] could also be considered a way of exposing the JG β -relaxation peak but the demonstration is less conclusive because the chemical structure of the glassformer has been altered. Another way to expose a JG β -relaxation peak in an extended wing glassformer is to prepare mixtures of a very polar small-molecule excess wing glassformer (like picoline) in an almost non-polar glassformer with a higher T_g (e.g. tristyrene) [99, 108]. The latter will only make a small contribution to the polarisation and the measured dielectric spectra, but β_{KWW} is reduced so that the separation between the α - and the JG β -relaxation is increased. The conclusion that the excess wing is a submerged JG β -relaxation does not conflict with the Nagel scaling plot or the invariance of the lineshape of the peak of an excess wing glassformer when measured at two pressure-temperature conditions where τ_{α} is the same because the relationship between the α - and JG β -relaxations implied by Eq. (2.35) ensures that the gap between these will not change if τ_{α} and β_{KWW} remain constant.

2.14 Final Words on the Glass Transition

In this chapter, an attempt has been made to give a general overview of amorphous solids and the glass transition, concentrating on areas most relevant to the data presented in this thesis. There are some omissions here. The summary of glass transition theories in particular is by no means complete as the area is extensive with

many competing approaches. There is also a vast amount of experimental and computer simulation data, both of which can be difficult to systematise into a coherent picture. Three omissions need to be highlighted. These are: (i) The Free Volume theory of the glass transition [134-137], which considers "free volume", meaning volume available for rearrangements of molecules to be the thermodynamic variable that controls the glass transition (as opposed to configurational entropy) and also leads to a VFT temperature dependence of the viscosity, (ii) The idealised [85-88] and extended [138] (includes hopping processes) Mode-Coupling theories of liquids mentioned previously that try to predict a glass transition from purely dynamical point of view (a feedback occurring as a result of another relationship between the relaxation time and the viscosity apart from the Debye-Stokes-Einstein equation) and their attendant "fast" relaxation processes at high frequencies [21] and (iii) the Frustrated Limited Domain (FLD) model [139, 140] that considers the glass transition as a result of the liquid having a local preferred structure that cannot tile space and so becomes "frustrated" as the temperature is lowered. The important point is that both of these theories predict some critical temperature where a transition is avoided in the liquid as it is cooled [139, 140]. This has been related to the important changes in properties that begin to occur in the liquid at some point above T_g as temperature is reduced (viz non-exponentiality of relaxation, departure of τ_{α} from Arrhenius behaviour, emergence of the JG β -relaxation peak or the extended wing, and the decoupling of the relationship between rotational and translational diffusion).

2.15 References

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Dielectric Properties of Alcohol-LiCIO₄ Solutions

3.1 Introduction

In this chapter, the dielectric properties of supercooled liquid and glassy 1-propanol and 5-methyl-2-hexanol containing various concentrations of ions are investigated. It is expected that the presence of ions, in addition to increasing the dc conductivity, will alter the rate of molecular relaxation processes and the static permittivity, ε_s . The following sections briefly describe the theory of the effect of ions on ε_s of solvents, the interpretation of ε_s of alcohols in terms of hydrogen-bonding (H-bonding) between their molecules and the factors affecting this, and the various relaxations observed in the dielectric spectra of supercooled liquid and glassy alcohols and their origin.

3.1.1 Dielectric Decrement

The addition of an ionic salt to a dielectric solvent will alter ε_s of the solution relative to the original solvent depending on the amount of salt added and the properties of both components of the ionic solution. Several different effects contribute to the change in ε_s . These can be broadly grouped as; (i) static and (ii) dynamic effects. The latter depend on the motion of ions in the solution. The dynamic effects caused by the motion of ions under the influence of the field should vanish at long times, but the effects will still appear in the measured ε_s of a salt solution

[1, 2]. First, we must be clear about what we mean by ε_s in such a case [2]. When an electric field is applied to a conducting solution, ionic drift will eventually screen the

field completely so that the ionic solution has an infinite permittivity. However it is possible to extend this argument to pure solvents since these will always contain ionic impurities or ions arising from the acidic or alkaline nature of the solvents themselves. We can define an apparent static permittivity for the solution, ε_s , which is the quantity actually measured in experiments, as the finite part of the permittivity in the zero frequency limit [2]:

$$\varepsilon_s = \lim_{\omega \to 0} \varepsilon^*(\omega) = \varepsilon_{s,pure} + \delta \varepsilon.$$
(3.1)

 $\varepsilon_{s,pure}$ is the static permittivity of the pure solvent and $\delta\varepsilon$ is the change on addition of the salt, often called the dielectric decrement for reasons apparent below. There are two static effects on $\delta\varepsilon$. At low salt concentrations it has been found that $\delta\varepsilon$ is positive and proportional to the square root of the salt concentration. This is the Debye-Falkenhagen effect [3]. In addition, it would be expected that solvation of ions would result in rotationally bound solvent molecules which would no longer contribute to the polarisation causing a reduction in ε_s [2]. This was assumed to be the reason for the linear decrease in ε_s at higher salt concentrations.

Additional dynamical effects on ε_s were first postulated by Hubbard and Onsager [1]. In their continuum theory of the dielectric properties of ionic solutions they calculated that excluding the Debye-Falkenhagen effect, the static permittivity of the solution should be reduced upon addition of ions by an amount

$$\delta \varepsilon_{HO} = -\frac{1}{2\varepsilon_0} \left(p + 1 \right) \left(\frac{\varepsilon_{s,pure} - \varepsilon_{\infty}}{\varepsilon_{s,pure}} \right) \tau_D \sigma_{dc} - \frac{\tau_{vis} \sigma_{dc}}{\varepsilon_0}.$$
(3.2)

 $\delta \varepsilon_{HO}$ is the Hubbard-Onsager dielectric decrement. *p* is a constant whose value depends on the flow condition at the ion surface – 1 for stick and 2/3 for slip. τ_{vis} is the viscosity relaxation time, which should be close to τ_D . The other symbols have their usual meaning. The first term in this equation contains contributions from two distinct processes occurring in the ionic solution, which were described by Hubbard and Onsager [1]. First, when an electric field is applied, a force is exerted on the ions, which move through the solution. As they move, they tend to cause rotation of the polarised molecules in a direction opposite to that due to the external electric field resulting in a reduction in the polarisation while the ion is moving. The reduction in

the measured static permittivity is given by
$$-\frac{p}{2\varepsilon_0}\left(\frac{\varepsilon_{s,pure}-\varepsilon_{\infty}}{\varepsilon_{s,pure}}\right)\tau_D\sigma_{dc}$$
. Second, the

polarised molecules retard the effect of the electric field on the ion. The force exerted by the field on an ion takes time to reach its full value because it depends on the

polarisation. This results in a reduction of $-\frac{1}{2\varepsilon_0} \left(\frac{\varepsilon_{s,pure} - \varepsilon_{\infty}}{\varepsilon_{s,pure}}\right) \tau_D \sigma_{dc}$ in the static

permittivity – the first term in Eq. (3.2). These two contributions are termed the kinetic dielectric decrement, $\delta \varepsilon_{KDD}$ and

$$\delta \varepsilon_{KDD} = -\frac{(p+1)}{2\varepsilon_0} \left(\frac{\varepsilon_{s,pure} - \varepsilon_{\infty}}{\varepsilon_{s,pure}} \right) \tau_D \sigma_{dc}.$$
(3.3)

In a later paper, Hubbard, Colonomos, and Wolynes [2] derived a microscopic theory of the kinetic dielectric decrement, generalising it to include the effect of ion size and the ion-dipole interaction strength. They also clarified the molecular origin of the two contributions to the kinetic dielectric decrement, showing that they are complementary effects, which should be equal in magnitude, correcting a small error in the original continuum theory. Kusalik and Patey [4] have also attempted to derive a microscopic theory of the dielectric properties of ionic solutions and the kinetic dielectric decrement.

Comparisons have been made between the predictions of these theories and actual static permittivity measurements on ionic salts such as NaCl and LiCl dissolved in polar liquids such as H_2O and methanol adjusted for the Debye-Falkenhagen effect. It is found that the dielectric decrement is larger than that predicted by either the continuum or microscopic theories [3]. However, Windsor and Cole [5] found that the theory of Kusalik and Patey predicts a larger total dielectric decrement for aqueous NaCl solutions than is observed. However, this involved extrapolation of their model to much higher salt concentrations than those used in deriving it.

3.1.2 Hydrogen Bonding and Alcohol Static Permittivity

The generally very large ε_s of hydrogen bonded polar liquids such as aliphatic alcohols, amines, carboxylic acids, and water are explained in terms of the Kirkwood-Onsager-Frohlich [6-8] equation [Eq. (1.43) in Chap. 1] which can be rearranged as:

$$\Delta \varepsilon = \varepsilon_s - \varepsilon_{\infty} = \frac{3\varepsilon_s}{2\varepsilon_s + \varepsilon_{\infty}} \left(\frac{\varepsilon_{\infty} + 2}{3}\right)^2 \frac{N_A \rho}{3\varepsilon_0 kTM} g\mu_p^2, \qquad (3.4)$$

where M is the molar mass and ρ is the density of the liquid. μ_p is the permanent dipole moment of the isolated molecule. The size of the factor g (the Kirkwood Correlation factor [6]) in this equation depends on whether there are any local correlations in the direction of neighbouring molecular dipoles in the liquid giving rise to a change in ε_s from the value expected from the Onsager Equation (g = 1). If g > 1, such correlations result in a greater than expected average dipole moment and value of ε_s , while if g < 1 there are correlations resulting in a reduced average dipole moment and reduced ε_s . The value g = 1 does not always imply that correlations between neighbouring dipoles do no exist - they may exist, but their overall effect is not detectable by a change in ε_s relative to the Onsager value. In aliphatic alcohols, on time average the molecules may associate to form linear chains so that the dipole moments of individual molecules are parallel [9]. If these predominate, g > 1. They may also form ring structures [9] in which molecules have antiparallel dipoles and g < 1 if these structures predominate. The equilibrium between these two types of association and thus the value of g depend strongly on the temperature and pressure, and the structure of the alcohol [10-14]. The structure of the alcohol also controls the manner in which g varies with temperature and pressure (increases or decreases over particular ranges) [10, 11]. The main structural determinant is the steric hindrance of the hydroxyl (OH) group. For example, 2-octanol has a large g-value of > 3 at low temperature and high pressure due to association of the molecules into chains [10]. At high temperatures, g decreases towards 1 as the chains dissociate. The isomer 2methyl-3-heptanol, where the OH group is nearer to the middle of the carbon chain (on the carbon atom adjacent to the carbon to which the methyl group is attached) has g < 1 at most temperatures and pressures due to the presence of low dipole moment rings [10]. At high temperatures, g tends to 1 for the same reason as the 2-octanol isomer. Low temperatures and high pressures result in breaking of the rings in favour of chains or individual molecules and an increase in g. Similar trends have also been observed for other octanol isomers [11] and other alcohol homologues – isomeric heptanols [10], butanols [13], and pentanols [14]. The equilibrium between chains and rings also has implications for the density of the alcohols [10, 12]. The alcohols with large g in which chain structures occur (generally simple isomers with the OH group

near the carbon chain end) have a higher density than those with ring structures and g < 1 (generally branched isomers).

Several types of interactions can reduce the extent of H-bonding in a liquid or a solid and thereby affect the dielectric behaviour. One of these is the formation of a solvation layer on ions, which decreases the extent of intermolecular H-bonds by selectively aligning the molecular dipole vector. This occurs in ionic solutions. A decrease in the number of H-bonds alters the orientational correlation of dipoles and also the rate of H-bond breaking and reforming. This in turn suggests that the nature of the interactions that alter the H-bonds populations may be studied by measuring the dielectric properties by dielectric spectroscopy. Investigated here is the effect of solvation on the extent of H-bonding in 1-propanol and 5-methyl-2-hexanol, and on their dielectric relaxation.

3.1.3 Relaxation Processes in Alcohols

The following is intended as a brief summary of the dielectric relaxation processes observed in the radiofrequency (1 mHz - 1 GHz) range in supercooled liquids and glasses in general and their comparison with alcohols in particular. More detailed information on these processes is provided in Chap. 2. In a dipolar liquid at high temperatures well above its melting point a single relaxation process is observed by dielectric spectroscopy, corresponding to the rotational Brownian motion of the molecules, influenced by the electric field (which increases the probability that a molecular dipole will be colinear with the field direction at any time). As explained in the Chap. 1, such a relaxation process can often be described by the Debye equation, and is connected with the viscosity of the liquid. It may also be observed by other techniques such as mechanical spectroscopy, light scattering measurements etc. Relaxation times follow an Arrhenius temperature dependence. In the supercooled liquid, there are two important relaxation processes related to the dynamics of molecules. (There may be other relaxation processes detectable by dielectric spectroscopy at higher frequencies but associated with intramolecular motions.) The larger one, which occurs at lower frequencies, is the α -relaxation. At higher frequencies is the smaller Johari-Goldstein (JG) β -relaxation, which is broad, has an Arrhenius temperature dependence, and persists below T_g . As the liquid is cooled

below the glass transition temperature, T_g , the α -relaxation becomes slower than the experimental timescale (frequency of electric field, mechanical stimulation etc) and the substance behaves as a solid. The α -relaxation is associated with structural relaxation and viscosity but the dynamics are different to those in the liquid at high temperatures. The relaxation is broader than Debye, and relaxation times follow a non-Arrhenius temperature dependence.

Most supercooled alcohols however have three relaxations in their dielectric spectra a large Debye relaxation at low frequencies, a broader relaxation as a shoulder on this loss peak at intermediate frequencies, and another relaxation at high frequencies. These have been observed in 1-propanol [15-18] and 5-methyl-2-hexanol [19], as well as other alcohols [20] and alcohol mixtures [21, 22]. In general, in earlier papers [15, 22], only the largest relaxation was isolated due to measurement limitations. It is now commonly accepted that the highest frequency relaxation is the JG β -relaxation. It should be noted that there are relaxations beyond the JG β -relaxation but these are not observed in the frequency range under discussion here. The other two relaxations both have non-Arrhenius temperature dependence of their relaxation times and their origin is more controversial. It has been suggested by Hansen et al. [23] and Kudlik et al. [24] that the shoulder rather than the Debye relaxation is the α -relaxation signature in dielectric measurements, and the Debye relaxation is caused by the breaking and reforming of H-bonds. The reasons given [23] are; (i) The Debye relaxation is not observed in the light scattering and photon correlation measurements on 1-propanol; (ii) the shape and temperature dependence of the shoulder are similar to the relaxation observed in these measurements, and; (iii) the viscosity itself has similar temperature dependence to the shoulder relaxation frequency. This idea is also appealing because it removes a peculiar feature of the alcohols – a α -relaxation with a Debye lineshape and non-Arrhenius relaxation time temperature dependence, which is not compatible with most theories of relaxation [25-33]. It is argued in this chapter that the Debye relaxation may still contribute to the structural relaxation, and that the α -relaxation may have a Debye lineshape.

3.2 Experimental

Table 3.1 gives a list of the substances used and their stated purity. All substances were used as is without any further purification.

Table 3.1	Summary	of	substances	used.
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Substance	Formula/Structure	Supplier	Stated Purity
lithium perchlorate	LiClO ₄	Fluka AG	99 %
1-propanol	ОН	Fluka AG	99.5 % (puriss.)
5-methyl-2- hexanol	ОН	Fluka AG	98 % (purum)

The alcohols are both liquids at room temperature. Lithium Perchlorate (LiClO₄) was supplied as small granules. It was chosen as a salt for studying the effect of ions on hydrogen bonding and relaxation because of its excellent solubility in alcohols [34]. The dielectric cell used in all cases was a miniature capacitor with 24 plates, and a nominal capacitance of 27 pF in air (see Appendix A p. 285 for a full description of this capacitor). The exact empty capacitance was accurately measured prior to each experiment.

Table 3.2 shows the Lithium Perchlorate concentrations used with the various alcohols, given as mol % (number of moles of salt per 100 moles of the solution). All solutions were prepared by weighing in a volumetric flask, sealed and stored in a fridge.

Table 3.2 Salt concentration of alcohol solutions in mol % (and mol L^{-1}).

Alcohol	LiClO ₄ Concentrations in mol % (mol L ⁻¹)			
1-propanol	0 % (pure)	0.98 % (0.132)	-	
5-methyl-2-hexanol	0 % (pure)	0.50 % (0.035)	1.03 % (0.073)	

The data for pure 5-methyl-2-hexanol was not measured in this work and is taken with permission from a paper of Kalinovskaya et al. [19]. The pure 5-methyl-2-hexanol used to prepare the solutions is from the same supply used in that work. Liquid samples were prepared for measurement as follows:

The capacitor was inserted in a small glass vial (10 mm diameter, 33 mm length) holding the liquid to be studied. Care was taken to ensure that no air bubbles were trapped in the capacitor plates. A 100 Ω platinum resistance temperature sensor was also inserted into the cell. This was connected to the four terminals of a Keithley 195A digital multimeter allowing accurate sample temperature monitoring (see Appendix A). The sample was quenched to a glass by plunging in liquid nitrogen. It was then transferred to a liquid nitrogen-filled cryostat (Oxford Instruments Spectrostat DN) at base temperature (77.3 K). An Oxford ITC502 temperature controller allowed sample temperatures to be maintained to within a maximum error of ± 0.1 K for the several hours required for a single measurement at millihertz frequencies. Changing of the sample temperature and waiting for stabilisation was carried out manually. Labelled diagrams of the dielectric cell with capacitor, sample cell holder, and cryostat can be found in Appendix A. Generally, it was impossible to measure all temperatures for a given sample in a single run as the cryostat needs to be replenished with liquid nitrogen every few hours. In this case the capacitor, sensor, and vial were cleaned with acetone and n-hexane, dried, and a new dielectric cell was prepared as described for each set of measurements from fresh pure liquid or stock salt solution. Dielectric measurements of complex permittivity, $\varepsilon^* = \varepsilon' - j\varepsilon''$, were made using a Solartron FRA1255A frequency response analyser (FRA) connected to a Chelsea Dielectric Interface (CDI), which are described in Appendix A.

3.3 Results and Analysis

The temperature ranges over which the ε' and ε'' spectra of pure 1-propanol and 1propanol containing 1.0 mol% LiClO₄ were measured were 88.6 K to 160.2 K and 88.7 K to 161.0 K respectively. Examples of these ε' and ε'' spectra (at higher temperatures where the large relaxation peak is visible) can be seen in Fig. 3.1(A) and (B) for pure 1-propanol and Fig. 3.2(A) and (B) for 1.0 mol% LiClO₄ in 1-propanol. In addition, Fig. 3.3(A) and (B) show the evolution with temperature of the fastest relaxation in the ε' and ε'' spectra of pure 1-propanol in the frequency range studied, which was 1 mHz - 1 MHz. The insets in both panels of Fig. 3.3 show the same process, this time for the 1-propanol salt solution. The corresponding temperatures for each spectra are given on the right-hand side of the figures. ε' and ε'' spectra were also measured for solutions of LiClO₄ in 5-methyl-2-hexanol at two concentrations: 0.5 mol% and 1.0 mol%. The 0.5 mol% solution was measured over a temperature range of 116.6 K to 229.5 K. For the 1.0 mol% solution a temperature range of 114.1 K to 231.7 K was used. Several ε' and ε'' spectra for the 0.5 mol% solution are shown in Fig. 3.4(A) and (B) respectively, illustrating the evolution of the slowest relaxation with temperature. Similar spectra for the 1.0 mol% solution are plotted in Fig. 3.5(A) and (B). The spectra for low temperatures deep inside the glass where the highest frequency relaxation is most apparent are shown for the 0.5 mol% solution of LiClO₄ in 5-methyl-2-hexanol in Fig. 3.6(A) and (B) and for the 1.0 mol% solution in the insets of the same figure. The temperatures at which the corresponding spectra are measured are indicated in the figures in all cases.

The dielectric relaxation spectra of both the pure alcohols and salt solutions share several common features, which are typical for supercooled liquid alcohols. At higher temperatures (see Fig. 3.1, 3.2, 3.4, and 3.5) there is a large relaxation peak in the loss spectrum [panel (B) of the figures], with a corresponding dispersion in the permittivity spectrum [panel (A)]. This will be denoted throughout as Process I. A shoulder in ε'' at higher frequencies indicates the presence of a second, higher frequency relaxation peak, which we will call Process II. At low frequencies the loglog plot of ε'' vs. frequency becomes linear with a slope of -1 indicating the presence

of a contribution from dc conductivity. This conductivity is due to mobile ions, which are present both as a result of impurities in the alcohols themselves, and the dissociation of the salt into solvated Li⁺ and ClO₄⁻ ions in the solutions. At low temperatures, well below the glass transition another relaxation peak and dispersion are visible in the ε'' and ε' spectra respectively (Fig. 3.3 and 3.6). We will refer to this as Process III. It is much smaller than the other two processes. There are also some differences between the spectra of the pure alcohols and the salt solutions. In the ε'' spectra of some of the salt solutions, the effect of dc conductivity becomes so large that the loss peak may become partially hidden and appears as a high frequency shoulder [Fig. 3.2(B), 3.4(B), and 3.5(B)]. The addition of salt changes the ε' spectra of the solution somewhat, resulting in scatter and large permittivity at low frequencies [for example, see Fig. 3.2(A) and 3.5(A)]. This effect is due to electrode polarisation. The following description of the procedure followed for analysing the spectra applies to all measurements on all samples. It was assumed that each complex permittivity spectra is the sum of several contributions from the different relaxation processes. Each one of these can be described by a Havriliak-Negami (HN) [35] term. There are three relaxation processes, and so three HN terms are required in any function to describe the complex permittivity. Based on these assumptions, the following function was fitted to the complex permittivity, $\varepsilon^*(\omega)$:

$$\varepsilon^{*}(\omega) = \varepsilon' - j\varepsilon'' = \varepsilon_{\infty} + \sum_{i=1}^{III} \frac{\Delta\varepsilon_{i}}{\left(1 + \left(j\omega\tau_{HNi}\right)^{\alpha_{i}}\right)^{\beta_{i}}} - \frac{j\sigma_{dc}}{\varepsilon_{0}\omega}.$$
(3.5)

 $\omega = 2\pi f$ and ε_0 are the angular frequency and permittivity of free space respectively. The subscript *i* denotes the *i*th relaxation process in order of increasing frequency. $\Delta \varepsilon_i = \varepsilon_{si} - \varepsilon_{\infty i}$ is the dielectric relaxation strength of this process. This is the difference between the limiting low frequency permittivity, ε_{si} , and the high frequency permittivity, $\varepsilon_{\infty i}$ for that relaxation. τ_{HNi} is the characteristic (HN) relaxation time for the *i*th process. α_i and β_i are the symmetric and asymmetric broadening parameters. There are two other terms included in the equation. The term $\frac{-j\sigma_{dc}}{\varepsilon_0\omega}$ takes account of ionic conduction losses, which become important at low

frequencies and high temperatures. σ_{dc} is the dc conductivity. The ε_{∞} term represents remaining permittivity contributions at high frequency. This is mainly due to the ionic

and electronic polarisations but there may also be a contribution from orientational polarisation at high temperatures where relaxation due to the faster processes appears above 1 MHz (the highest frequency used in these measurements). In order to extract the values for the parameters from the spectra, Eq. (3.5) was fitted to the spectra using the WinFit dielectric fitting program (Novocontrol), which has been used successfully for such analysis [19, 23, 36, 37] (see Appendix B). It was not necessary to include all terms of Eq. (3.5) in each case. For spectra measured well into the glass, dc conductivity and also in some cases Processes I and II could be neglected. For spectra measured at high temperatures, Process III and on occasion Process II may be excluded. Tables 3.3 to 3.6 (given after the figures) contain lists of the fit parameters of Eq. (3.5) obtained for 1-propanol, its 1.0 mol% salt solution, and the 0.5 mol% and 1.0 mol% salt solutions of 5-methyl-2-hexanol respectively. The solid lines in Fig. 3.1 to 3.6 were drawn using the parameters obtained via fits of Eq. (3.5) to the data. In general, the fits to the data are good. Some points must be noted however. At low frequencies, the ε' spectra of higher concentration salt solutions [1.0 mol% LiClO₄ in 1-propanol and 5-methyl-2-hexanol – see Fig. 3.2(A) and 3.5(A)] show large deviations from the fit curve. As mentioned previously, this discrepancy is the result of electrode polarisation. There is also quite a lot of scatter in the spectra of process III in the 5-methyl-2-hexanol salt solutions (Fig. 3.6). The maximum loss for these curves is low and the measurements approach the limits of resolution for the setup. Three figures serve to illustrate the fitting of Eq. (3.5) to the data in order to resolve the various relaxation regions. Fig. 3.7(A) and (B) show the ε' and ε'' spectra for pure 1-propanol at 123.3 K (open circles) The heavy lines are the ε' and ε'' fit curves calculated with the parameters: $\sigma_{dc} = 4.04 \text{ x } 10^{-11} \text{ S m}^{-1}$, $\Delta \varepsilon_I = 64.8$, $\alpha_I = 0.998$, β_I = 0.999, τ_{HNI} = 9.80 ms, $\Delta \varepsilon_{II}$ = 1.91, α_{II} = 0.947, β_{II} = 0.502, τ_{HNII} = 0.190 ms, $\Delta \varepsilon_{III} = 1.16, \ \alpha_{III} = 0.518, \ \beta_{III} = 0.851, \ \tau_{HNIII} = 3.37 \ \mu s, and \ \varepsilon_{\infty} = 2.68.$ The contributions of the various terms in Eq. (3.5) to the overall fit are indicated by thin dashed and dotted lines. The ε_{∞} term is included in the process I contribution to ε' . Fig. 3.8(A) and (B) show similar data for the 1.0 mol% salt solution of 1-propanol at 124.0 K. Again, measured data is compared to the fit curve (heavy line) generated from Eq. (3.5) with the following parameters: $\sigma_{dc} = 3.84 \text{ x } 10^{-8} \text{ S m}^{-1}$, $\Delta \varepsilon_1 = 30.7$, α_1 = 1.00, $\beta_I = 0.970$, $\tau_{HNI} = 7.29$ ms, $\Delta \varepsilon_{II} = 2.15$, $\alpha_{II} = 0.863$, $\beta_{II} = 0.581$, $\tau_{HNII} =$

0.231 ms, $\Delta \varepsilon_{III} = 1.22$, $\alpha_{III} = 0.471$, $\beta_{III} = 1.00$, $\tau_{HNIII} = 2.74 \,\mu$ s, and $\varepsilon_{\infty} = 2.74$. The overall fit is also resolved into the contribution from each term as in Fig. 3.7. Fig. 3.9(A) and (B) compare ε' and ε'' spectra for 1-propanol and its salt solution at approximately the same temperature (99.5 K and 99.7 K respectively). Also shown is the resolution of the spectra into their relaxation regions. Although process II is included in the fitting to account for the low frequency wing in the loss spectra, reliable parameters are only obtained for process III. Only contributions from the process III terms are shown as solid lines through the data in Fig. 3.9. These curves were generated from Eq. (3.5) with the following parameters for process III in 1-propanol: $\Delta \varepsilon_{III} = 0.504$, $\alpha_{III} = 0.399$, $\beta_{III} = 0.800$, $\tau_{HNIII} = 1.71$ ms, and $\varepsilon_{\infty} = 2.61$, while for the salt solution the parameters were: $\Delta \varepsilon_{III} = 0.433$, $\alpha_{III} = 0.328$, $\beta_{III} = 1.00$, $\tau_{HNIII} = 1.09$ ms, and $\varepsilon_{\infty} = 2.59$.

Values of ε_s can be obtained either from the low frequency plateau of the ε' spectra or using the fit parameters ($\varepsilon_s = \varepsilon_{\infty} + \sum_{i=1}^{HI} \Delta \varepsilon_i$) in cases where there is large electrode polarisation. ε_s of 1-propanol and its 1.0 mol% salt solution are plotted against the temperature in Fig. 3.10(A).Values of $\Delta \varepsilon_i$ are shown in Fig. 3.10(B), while those of $\Delta \varepsilon_{II}$ and $\Delta \varepsilon_{III}$ are shown in Fig. 3.10(C). Literature ε_s data for 1-propanol, after Denney and Ring [17], is also plotted for comparison in Fig. 3.10(A). Fig. 3.11(A), (B), and (C) show ε_s , $\Delta \varepsilon_i$, and $\Delta \varepsilon_{II}$ and $\Delta \varepsilon_{III}$ for the 0.5 mol% and 1.0 mol% 5methyl-2-hexanol salt solutions. Also included in this figure is data of Kalinovskaya and Vij [19] for the pure alcohol. Since these measurements were carried out in our group, they were made with the same apparatus, and the alcohol sample was from the same source and was prepared in the same way, and the spectra analysed similarly. For these reasons, a direct comparison of the fitting parameters obtained from the dielectric data is admissible. This is the data that was used wherever reference is made to any results for pure 5-methyl-2-hexanol.

When Eq. (3.5) has been fitted to the data, we can use the HN parameters to find the frequency of maximum loss f_m of a given relaxation process. For the i^{th} process:

$$f_{m,i} = \left(2\pi\tau_{HNi}\right)^{-1} \left[\sin\left(\frac{\alpha_i\pi}{2+2\beta_i}\right)\right]^{\frac{1}{\alpha_i}} \left[\sin\left(\frac{\alpha_i\beta_i\pi}{2+2\beta_i}\right)\right]^{\frac{-1}{\alpha_i}}.$$
(3.6)

 f_m serves as a standard measure of the rate of relaxation processes when examining their temperature dependence. The frequencies of maximum loss, $f_{m,I}$, $f_{m,II}$, and $f_{m,III}$ of the three relaxation processes in 1-propanol are plotted against inverse temperature (1000/T) on a logarithmic scale in Fig. 3.12 (an "Arrhenius" plot). The three temperature points for $f_{m,I}$ of the salt solution are also included on this plot. In this figure, the fits of the Vogel-Fulcher-Tammann (VFT) equation [38-40],

$$f_m = A_{VFT} \exp[-B_{VFT} / (T - T_0)]$$
(3.7)

to the process I data of the pure alcohol and salt solution are drawn as a solid line through the data according to $f_{m,l} = 10^{11.91} \exp[-1734/(T - 52.68)]$ while the curve through the solution data (dashed line) is $f_{m,l} = 10^{12.11} \exp[-1755/(T - 53.22)]$. $f_{m,l}$, $f_{m,ll}$, and $f_{m,lll}$ vs. inverse temperature for pure 5-methyl-2-hexanol and its salt solutions are plotted in Fig. 3.13, together with the VFT fits to process I plotted according to $f_{m,l} = 10^{13.63} \exp[-2775/(T - 79.8)]$ for the pure alcohol (solid line), $f_{m,l} = 10^{12.92} \exp[-2494/(T - 84.70)]$ for the 0.5 mol% salt solution (dashed line), and $f_{m,l} = 10^{12.60} \exp[-2309/(T - 89.53)]$ for the 1.0 mol% solution (dotted line). These parameters can also be found in Table 3.7.

The temperature dependence of the broadening parameters, α , and β , for the various relaxation processes in the ε' and ε'' spectra of 1-propanol and its salt solution are shown in Fig. 3.14. The values of α_1 and β_1 , α_n and β_n , and α_m and β_m are plotted in Fig. 3.14(A), (B), and (C) respectively. As discussed in Chap. 1, the Debye [41], Davidson-Cole [15, 16], and Cole-Cole [42] distributions are all special cases of the HN [35] distribution in which constraints are put on the values of α and β . For a Debye Distribution $\alpha = \beta = 1$, for a Davidson-Cole distribution with skewed-arc parameter β_{Dc} , $\alpha = 1$ and $\beta = \beta_{Dc} < 1$, while for a Cole-Cole distribution with a broadness parameter of α_{cc} , $\alpha = 1 - \alpha_{cc} < 1$ [43]. In pure 1-propanol, $\alpha_1 = \beta_1 = 1$ making this a Debye relaxation process. For the salt solution, β_1 is reduced somewhat to ~ 0.97. This reduction in β_1 is found for all of the salt solutions studied here. Both process II and process III follow the HN distribution ($\alpha < 1$, $\beta < 1$) in the pure substance. In the salt solution, process II is HN and process III is Cole-Cole. Fig. 3.15 contains similar data to the previous two figures for pure 5-methyl-2-hexanol and its

0.5 mol% and 1.0 mol% salt solutions. α_1 and β_1 are graphed against temperature in Fig. 3.15(A). α_{II} and β_{II} are plotted in Fig. 3.15(B), while α_{III} and β_{III} are plotted in Fig. 3.15(C). For 5-methyl-2-hexanol, $\alpha_1 = 1$ and $\beta_1 \sim 0.96$ (Davidson-Cole). The values are similar for the 0.5 mol% solution. As for 1-propanol, $\alpha_1 = 1$ and $\beta_1 \sim 0.9$ in the 1.0 mol% solution, which is somewhat lower than in the pure alcohol itself. Process II is HN for pure 5-methyl-2-hexanol and the solutions. A definite trend is seen the parameters for the 2nd relaxation. As salt concentration increases from 0 mol% to 1 mol%, α_{μ} increases from ~ 0.6 to ~ 0.9 and β_{μ} decreases from ~ 0.7 to ~ 0.5. Similarly to 1-propanol, process III is HN in 5-methyl-2-hexanol, and appears to change to a Cole-Cole distribution in the salt solutions. Fig. 3.16 shows an Arrhenius plot for σ_{dc} of 1-propanol and its salt solution in S m⁻¹ scaled by a factor of 10¹⁰. The solid and dashed lines through the pure 1-propanol and 1.0 mol% salt solution data respectively are the fits of the VFT equation to the data according to $\sigma_{dc} = 10^{-10}$ $^{1.129} \exp[-1285/(T - 62.65)]$ for pure 1-propanol and $\sigma_{dc} = 10^{2.338} \exp[-1400/(T - 62.65)]$ 61.66)] for the salt solution. Fig. 3.17 shows a similar plot for 5-methyl-2-hexanol and its salt solutions. The lines are also VFT fits to the data. All relaxation fitting parameters obtained by fitting of the VFT equation to processes I and II and the Arrhenius equation to process III in the pure alcohols and their solutions are summarised in Table 3.8.



Fig. 3.1 (A) ε' spectra of pure 1-propanol measured at selected temperatures above the glass transition temperature, T_g , as indicated on the right hand side of the figure. (B) The corresponding ε'' spectra for the same temperatures. The relaxation peak of the slowest process (process I) is clearly visible. The solid lines in both panels are the fits of Eq. (3.5) to the data. The fit parameters so obtained are listed in Table 3.3.



Fig. 3.2 (A) ε' spectra of 1.0 mol% LiClO₄ in 1-propanol measured at selected temperatures above T_g , as indicated on the right hand side of the figure (B) The corresponding ε'' spectra. The relaxation peak of the slowest process (process I) is masked by dc conductivity but can be seen as a shoulder. The solid lines in both panels are the fits of Eq. (3.5) to the data. The fit parameters so obtained are listed in Table 3.4.



Fig. 3.3 (A) ε' spectra of pure 1-propanol measured at selected temperatures below and near T_g , as indicated on the right hand side of the figure. The ε' spectra for the 1.0 mol% LiClO₄ solution at several temperatures are shown in the inset. (B) The corresponding ε'' spectra. ε'' spectra for the 1.0 mol% LiClO₄ solution corresponding to the ε' spectra in the inset of panel A are shown in the inset. The relaxation peak of the fastest process (process III) is visible in both cases. The solid lines in both panels are the fits of Eq. (3.5) to the data. The fit parameters so obtained are listed in Table 3.3 (pure) and 3.4 (salt solution).



Fig. 3.4 (A) ε' spectra of 0.5 mol% LiClO₄ in 5-methyl-2-hexanol measured at selected temperatures above T_g , as indicated on the right hand side of the figure (B) The corresponding ε'' spectra. The relaxation peak of the slowest process (process I) is visible. The solid lines in both panels are the fits of Eq. (3.5) to the data. The fit parameters so obtained are listed in Table 3.5.



Fig. 3.5 (A) ε' spectra of 1.0 mol% LiClO₄ in 5-methyl-2-hexanol measured at selected temperatures above T_g , as indicated on the right hand side of the figure (B) The corresponding ε'' spectra. The relaxation peak of the slowest process (process I) is only visible as a shoulder. The solid lines in both panels are the fits of Eq. (3.5) to the data. The fit parameters so obtained are listed in Table 3.6.



Fig. 3.6 (A) ε' spectra of 0.5 mol% LiClO₄ in 5-methyl-2-hexanol measured at selected temperatures below and near T_g , as indicated on the right hand side of the figure. The ε' spectra for the 1.0 mol% LiClO₄ solution at several temperatures are shown in the inset. (B) The corresponding ε'' spectra. ε'' spectra for the 1.0 mol% LiClO₄ solution corresponding to the ε' spectra in the inset of panel A are shown in the inset here. The relaxation peak of the fastest process (process III) is visible in both cases despite the scatter in the data. The solid lines in both panels are the fits of Eq. (3.5) to the data. The fit parameters so obtained are listed in Table 3.5 (0.5 mol%) and 3.6 (1.0 mol%).



Fig. 3.7 (A) Resolution of the of the ε' spectra of pure 1-propanol at 123.3 K (open circles) into the contribution made by the real part of the HN terms in Eq. (3.5) for the processes I, II, and III to the total fit curve (shown as heavy solid line through the measured data). The limiting permittivity at high frequency, ε_{∞} , has been added to the process I term. (B) Resolution of the of the ε'' spectra into the contribution made by the imaginary part of the HN terms in Eq. (3.5) for the processes I, II, and III to the total fit curve (heavy solid line). The contribution of σ_{dc} to the loss is also shown.


Fig. 3.8 (A) Resolution of the ε' spectra of 1.0 mol% LiClO₄ in 1-propanol at 124.0 K (filled circles) into the contributions made by the HN terms in Eq. (3.5) to the total fit curve (heavy solid line), as in Fig. 3.7. (B) Resolution of the ε'' spectra into its various components, again as in Fig. 3.7. The total fit curve is shown as a heavy solid line.



Fig. 3.9 (A) Comparison of ε' spectra of 1-propanol (open circles) and its 1.0 mol% LiClO₄ solution (filled circles) at similar temperatures of 99.5 K and 99.7 K respectively. The lines through the data are the real part of the HN fit term in Eq. (3.5) corresponding to process III. (B) The corresponding ε'' spectra, together with the imaginary part of the process III fit terms for each.



Fig. 3.10 Plots of (A) ε_s , (B) $\Delta \varepsilon_I$, and (C) $\Delta \varepsilon_{II}$ and $\Delta \varepsilon_{III}$ against the temperature for pure 1-propanol (open symbols) and 1.0 mol% LiClO₄ in 1-propanol (filled symbols). Crossed squares in panel A are literature data for ε_s of pure 1-propanol measured by Denney and Ring [17]. Lines are a guide to the eye only.



Fig. 3.11 Plots of (A) ε_s , (B) $\Delta \varepsilon_I$, and (C) $\Delta \varepsilon_{II}$ and $\Delta \varepsilon_{III}$ against the temperature for pure 5-methyl-2-hexanol (open symbols) adapted from the data of Kalinovskaya and Vij [19], 0.5 mol% LiClO₄ in 5-methyl-2-hexanol (crossed symbols), and 1.0 mol% LiClO₄ in 5-methyl-2-hexanol (filled symbols). Lines are a guide to the eye only.



Fig. 3.12 Arrhenius plots of $f_{m,I}$, $f_{m,II}$, and $f_{m,III}$ on a logarithmic scale against inverse temperature (1000/*T*, where *T* is the absolute temperature) for pure 1-propanol (open symbols), and 1-propanol containing 1.0 mol% LiClO₄ (filled symbols). The solid line and dashed lines are generated from the fits of the VFT equation to the 1propanol $f_{m,I}$ data and LiClO₄ in 1-propanol $f_{m,I}$ data respectively with fit parameters given in Table 3.7.



Fig. 3.13 Arrhenius plots of $f_{m,I}$, $f_{m,II}$, and $f_{m,III}$ for pure 5-methyl-2-hexanol [19] (open symbols), 0.5 mol% LiClO₄, and 1.0 mol% in 5-methyl-2-hexanol (crossed and filled symbols). The solid, dashed, and dotted lines are generated from the fits of the VFT equation to the $f_{m,I}$ data of the pure alcohol and the 0.5 mol% and 1.0 mol% solutions respectively with fit parameters given in Table 3.7.



Fig. 3.14 Plots of (A) α_I and β_I (B) α_{II} and β_{II} , and (C) α_{III} and β_{III} , against the temperature for pure 1-propanol (open symbols) and LiClO₄ in 1-propanol (filled symbols). Lines are guides for the eye.



Fig. 3.15 Plots of (A) α_1 and β_1 , (B) α_{11} and β_{11} , and (C) α_{111} and β_{111} , against the temperature for pure 5-methyl-2-hexanol [19] (open symbols) and 0.5 mol% and 1.0 mol% LiClO₄ in 5-methyl-2-hexanol (crossed and filled symbols). Lines are guides for the eye.



Fig. 3.16 Arrhenius plots of σ_{dc} for pure 1-propanol (open circles) and 1propanol containing 1.0 mol% LiClO₄ (filled circles). The solid line through the 1propanol data and the dashed line through the salt solution data are obtained from fits of the VFT equation to the conductivity data in each case. The fit parameters are given in Table 3.8.



Fig. 3.17 Arrhenius plots of σ_{dc} for pure 5-methyl-2-hexanol [19] (open circles) and 5-methyl-2-hexanol containing 0.5 mol% and 1.0 mol% LiClO₄ (crossed and filled circles). The solid line through the pure alcohol data and the dashed and dotted lines through the 0.5 mol% and 1.0 mol% salt solution datasets are obtained from fits of the VFT equation to the conductivity data in each case. These fit parameters are given in Table 3.8.

Table 3.3	Parameters of Eq. (3.5) obtained by fitting to the 1-propanol dielectric
spectra.	

Odc [S cm ⁻¹]	ΔEI	THNI [S]	αi	Bi	ΔεΠ	[S] IINH1	αII	Bu	AEm	THINIII [S]	01III	Bui	T[K]
									0.3595	0.03102	0.2987	1	88.56
									0.3423	0.00704	0.3023	1	91.68
and the same and the constraints of the same									0.3373	0.00326	0.3662	0.8754	93.93
				the same series of the same series					0.3784	0.00224	0.3662	0.8754	95.91
									0.4235	0.002	0.3899	0.8	97.75
									0.504	0.00171	0.3992	0.8	99.51
and the second second second									0.5241	5.47E-04	0.4177	0.8351	101.92
	75.16	136.2	1	1	2.901	3.503	1	0.4467	0.5751	3.89E-04	0.4336	0.8102	103.61
at many a strength of the stre	75.49	37.96	0.9913	1	2.776	0.793	0.988	0.4553	0.6478	2.52E-04	0.442	0.8139	105.4
2.76E-16	70.83	9.095	0.99998	1	2.795	0.1946	0.9653	0.4617	0.7127	1.40E-04	0.4565	0.8141	107.72
4.28E-16	70.64	2.976	1	1	2.649	0.05734	0.9487	0.4817	0.8311	9.01E-05	0.452	0.8507	109.72
6.44E-15	70.64	1.22	0.9995	1	2.545	0.02166	0.9313	0.4921	0.882	5.37E-05	0.4632	0.8665	111.44
4.06E-15	68.83	0.4576	1	0.9995	2.376	0.00784	0.941	0.4909	0.9738	3.58E-05	0.4715	0.8575	113.43
5.15E-14	67.79	0.1703	0.9964	1	2.264	0.00269	0.9325	0.4927	0.9862	1.78E-05	0.5011	0.8513	115.54
1.17E-13	66.6	0.07411	0.9959	1	2.076	0.00112	0.9475	0.4932	1.077	1.17E-05	0.509	0.8503	117.45
2.12E-13	65.8	0.01898	0.9967	0.99996	2.008	3.72E-04	0.9481	0.4955	1.1	5.09E-06	0.5122	0.8501	121.35
4.04E-13	64.76	0.0098	0.9979	0.9993	1.912	1.90E-04	0.9473	0.5015	1.158	3.37E-06	0.5175	0.8513	123.27
7.79E-13	63.85	0.00507	0.9984	7666.0	1.842	1.01E-04	0.9453	0.4906	1.225	2.24E-06	0.507	0.8514	125.18
1.53E-12	62.41	0.0026	0.999	1	1.744	5.04E-05	0.938	0.5038	1.274	1.36E-06	0.5133	0.8571	127.25
2.82E-12	61.25	0.00141	1	1	1.635	2.77E-05	0.9361	0.5066	1.356	1.01E-06	0.5145	0.8582	129.21
5.00E-12	59.37	7.88E-04	0.9994	0.9998	1.536	1.53E-05	0.9413	0.4957	1.393	6.64E-07	0.5097	0.8579	131.2
7.96E-12	60.29	4.45E-04	0.9987	0.9993	1.504	9.32E-06	0.9568	0.4751	1.456	5.20E-07	0.5049	0.8477	133.38
1.30E-11	58.66	2.71E-04	0.9993	7666.0	1.426	5.51E-06	0.9433	0.487	1.488	3.52E-07	0.501	0.8759	135.25
2.06E-11	55.68	1.65E-04	0.9994	1	1.221	3.38E-06	0.9499	0.4704	1.6	3.30E-07	0.4883	0.9183	137.22
3.39E-11	57.01	9.88E-05	1	1									139.21
5.17E-11	55.74	6.49E-05	1	1						and many in the second state of the second state of the			141.03
7.73E-11	54.22	4.30E-05	1	0.9964							A TATA A REPORT OF		142.87
1.72E-10	52.62	1.91E-05	7799.0	1						Name and Address	-		146.81
2.54E-10	52.44	1.32E-05	0.9967	1									148.69
3.59E-10	51.61	9.30E-06	0.9969	1						and the second sec	No. of the second second second	a contraction of the state	150.61
5.79E-10	50.41	5.74E-06	0.9984	1									153.36
7.93E-10	49.58	4.17E-06	0.9989	1									155.34
1.08E-09	48.86	3.03E-06	0.9984	1									157.38
1.63E-09	47.8	1.99E-06	1	1									160.24

[S cm ⁻¹]	$\Delta \epsilon_I$	[S] INH ₂	αI	Bi	$\Delta \epsilon_{II}$	THINII [S]	σII	BII	$\Delta \epsilon_{III}$	[S] IIINH1	0, III	Bill	T[K]
									0.306	0.02086	0.3362	1	88.72
									0.3264	0.00739	0.3105	1	92.13
									0.3508	0.00447	0.3044	1	94.25
									0.3868	0.00186	0.3147	1	97.38
									0.4332	0.00109	0.3279	- 1	99.7
									0.4963	3.65E-04	0.3669	. 1	102.52
									0.5419	1.88E-04	0.3911	-	104.4
									0.6929	1.96E-04	0.4253	0.8744	107.37
				and a second sec					0.7988	1.16E-04	0.4318	0.8744	109.75
1E-13	45.11	3.925	1	1	3.181	0.2023	0.8819	0.5377	0.763	1.01E-04	0.4054	0.9447	109.69
1E-12	42.22	1.025	0.9892	0.9652	2.564	0.03517	0.8957	0.5147	0.823	4.16E-05	0.4178	1	112.2
5E-12	39.1	0.3612	0.9965	0.9728	2.651	0.01355	0.8865	0.5157	0.8542	2.36E-05	0.4341	1	114.41
1E-11	37.29	0.08835	0.9912	0.9747	2.491	0.00299	0.8884	0.5155	0.9107	1.07E-05	0.4622	0.9822	117.62
0E-11	35.89	0.04891	0.9919	0.9811	2.447	0.00161	0.8567	0.5732	1.037	8.31E-06	0.4591	0.9995	118.92
0E-10	32.49	0.0139	1	0.9695	2.261	4.50E-04	0.86	0.5813	1.179	4.18E-06	0.4675	1	122.22
4E-10	30.7	0.00729	1	0.9695	2.146	2.31E-04	0.8632	0.5813	1.223	2.74E-06	0.4707	1	123.98
5E-10	29.59	0.00381	1	0.9698	2.019	1.18E-04	0.8728	0.5822	1.299	1.82E-06	0.4714	0.9955	125.96
6E-09	28.64	0.00195	0.9992	0.9693	1.955	5.96E-05	0.8743	0.5715	1.347	1.07E-06	0.4647	0.9929	128.09
0E-09	27.2	0.00109	0.99999	0.9829	2.007	3.76E-05	0.8542	0.5619	1.462	6.73E-07	0.4275	1	129.93
[E-09	26.01	5.05E-04	1	0.9807	1.947	1.68E-05	0.8497	0.5622					132.53
IE-09	25.47	3.29E-04	1	0.969	2.007	9.71E-06	0.8492	0.5629					134.15
7E-08	24.48	1.98E-04	1	0.969									136.08
E-08	23.73	1.20E-04	0.9939	0.969									138.1
E-08	22.03	6.02E-05	1	0.9632									141.04
DE-08	21.56	3.70E-05	1	0.9699									143.24
2E-07	20.81	2.16E-05	1	0.9699									145.79
5E-07	20.08	1.47E-05	1	0.9694									147.53
2E-07	19.76	8.35E-06	1	0.9648									150.59
5E-07	19.54	6.14E-06	0.9995	0.9629									152.48
8E-07	17.86	3.48E-06	1	0.9674				Water and the second second second					155.58
E-06	15.94	2.73E-06	1	0.9674						to the second seco			157.66
E-06	16.53	1.41E-06	1	0.96									161.03

Table 3.4Parameters of Eq. (3.5) obtained by fitting to the dielectric spectra ofthe 1.0 mol% solution of LiClO4 in 1-propanol.

ode [Scm-1]	Δ57	THNI [S]	ai	Bi	Δ <i>E</i> _{II}	THNII [S]	an	Bii	Asm	THNIII [S]	am	Bill	T [K]
									0.08726	0.0016	0.3047	1	116.6
-									0.08446	6.74E-04	0.3182	1	119.59
									0.08463	3.09E-04	0.3186	1	122.64
									0.08095	1.48E-04	0.3433	1	125.75
									0.08062	8.13E-05	0.3508	1	128.38
									0.07877	5.26E-05	0.362	1	131.42
									0.07809	2.87E-05	0.3739	1	134.36
									0.07752	1.69E-05	0.3829	1	137.4
									0.07442	1.08E-05	0.4088	1	140.15
									0.07458	6.83E-06	0.42	1	143.07
									0.07538	4.69E-06	0.4287	1	146.13
									0.08847	2.85E-06	0.4237	1	150.99
									0.09823	2.13E-06	0.4363	1	153.94
									0.1055	1.74E-06	0.4508	1	156.8
									0.1113	1.32E-06	0.4802	1	159.81
									0.1162	1.03E-06	0.5032	1	162.82
1.22E-13	27.76	4.592	1	0.9569	0.7952	0.09269	0.8939	0.4992	0.102	1.07E-06	0.5241	1	160.63
5.01E-13	27.26	1.097	1	0.9569	0.7918	0.01972	0.8939	0.4992	0.1071	7.99E-07	0.5402	1	163.74
1.37E-12	26.99	0.4384	1	0.9569	0.7785	0.00706	0.8939	0.4992	0.1097	6.10E-07	0.5402	-	165
2.73E-12	26.53	0.199	1	0.9408	0.7754	0.00286	0.8253	0.5477	0.108	5.70E-07	0.56	1	167.91
7.40E-12	26.29	0.07221	1	0.9294	0.7056	8.68E-04	0.8743	0.5076	0.1059	5.01E-07	0.56	1	170.82
1.85E-11	25.64	0.02751	0.999	0.9382	0.7457	3.41E-04	0.8053	0.5614	0.09509	4.36E-07	0.6	1	173.72
4.29E-11	24.98	0.01146	1	0.9301	0.7202	1.32E-04	0.8107	0.5573	0.094	4.10E-07	0.5975	1	176.72
1.07E-10	24.43	0.00432	0.999	0.9323	0.6916	4.70E-05	0.8024	0.5702	0.1025	2.48E-07	0.5634	1	180.11
2.23E-10	23.94	0.00195	1	0.9289	0.6443	2.15E-05	0.8584	0.5271	0.09646	3.30E-07	0.6185	1	183.2
4.54E-10	23.38	8.83E-04	0.9921	0.9516	0.8532	1.26E-05	0.7125	0.5441					186.4
8.78E-10	22.89	4.26E-04	0.9905	0.9533	0.8452	6.05E-06	0.7034	0.563					189.62
1.56E-09	22.36	2.29E-04	1	0.931	0.8059	3.71E-06	0.796	0.417					192.58
3.19E-09	21.66	1.01E-04	1	0.934									196.57
6.35E-09	21.05	4.55E-05	1	0.934									200.76
9.92E-09	20.55	2.73E-05	1	0.9315									203.64
1.53E-08	20.26	1.71E-05	1	0.8989									206.63
2.33E-08	19.74	9.47E-06	0.9845	0.9585									209.64
3.44E-08	19.02	5.63E-06	0.9777	1									212.65
4.98E-08	18.44	3.57E-06	0.9794	1									215.64
7.12E-08	18.44	2.53E-06	1	0.8926									218.73
8.43E-08	18.46	2.02E-06	0.9939	0.8982									220.28
1.19E-07	18.14	1.26E-06	0.9852	0.9099									223.46
1.58E-07	17.84	8.85E-07	0.9882	0.8911									226.29
2.15E-07	17.76	5.25E-07	0.9598	0.9509									229.52

Table 3.5Parameters of Eq. (3.5) obtained by fitting to the dielectric spectra ofthe 0.5 mol% solution of LiClO4 in 5-methyl-2-hexanol.

0138 0.3031 1 116.85 0E-04 0.3134 1 119.86 6E-04 0.3269 1 123.66 1E-04 0.3223 1 126.59 3E-05 0.3463 1 129.46	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	01.38 0.5031 1 116.85 0E-04 0.3134 1 119.86 6E-04 0.3259 1 123.66 3E-05 0.3463 1 126.59 3E-05 0.3463 1 123.66 7E-05 0.35349 1 125.42 7E-05 0.3533 1 125.42 7E-05 0.3533 1 132.41 1E-05 0.3632 1 132.41 1E-05 0.3632 1 135.26 8E-06 0.4025 1 135.25 8E-06 0.4056 1 135.26 5E-06 0.4996 1 142.48 5E-07 0.5707 1 168.18 5E-07 0.5707 1 168.18 5E-07 0.5707 1 168.18 5E-07 0.5707 1 171.02 8E-07 0.5707 1 176.03 4E-07 0.5579 1	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
0.08721 6.10E-04 0.3134 0.08633 2.56E-04 0.3265 0.08752 1.31E-04 0.3223 0.08315 6.53E-05 0.3463	0.08721 6.10E-04 0.3134 0.08653 2.56E-04 0.3269 0.088633 2.55E-04 0.3229 0.08752 1.31E-04 0.3223 0.088753 1.31E-04 0.3223 0.088753 1.31E-04 0.3223 0.088753 1.31E-05 0.3463 0.088776 3.57E-05 0.3463 0.088776 3.57E-05 0.3463 0.088776 3.57E-05 0.3463 0.08877 1.08E-05 0.4996 0.07387 4.98E-06 0.4996 0.07387 4.98E-06 0.4996 0.07038 1.36E-06 0.4996 0.1006 1.36E-06 0.4996 0.102 8.73E-07 0.5707 0.103 5.95E-07 0.5707 0.1044 5.35E-07 0.5707	0.08721 6.10E-04 0.3134 0.08633 2.56E-04 0.3269 0.08633 2.55E-04 0.3259 0.08752 1.31E-04 0.3223 0.08315 6.53E-05 0.3269 0.08751 3.57E-05 0.3463 0.08276 2.11E-05 0.3632 0.0783 1.08E-05 0.4056 0.07387 4.98E-06 0.4056 0.07387 4.98E-06 0.4096 0.1048 1.05E-06 0.525 0.1048 1.05E-06 0.5707 0.102 8.73E-07 0.5707 0.103 5.95E-07 0.5707 0.1073 3.84E-07 0.5707 0.1073 3.84E-07 0.5775	0.08721 6.10E-04 0.3134 0.08633 2.56E-04 0.3269 0.08653 2.55E-04 0.3259 0.08752 1.31E-04 0.3223 0.08753 5.31E-05 0.32463 0.08753 5.55E-05 0.32463 0.08753 1.31E-05 0.3463 0.08276 3.57E-05 0.3463 0.08276 3.57E-05 0.3463 0.08276 3.57E-05 0.3463 0.0783 1.08E-05 0.4996 0.07387 4.98E-06 0.4096 0.07387 4.98E-06 0.4996 0.1004 1.36E-06 0.4996 0.1003 5.95E-07 0.5707 0.103 5.95E-07 0.5707 0.1044 5.35E-07 0.5707 0.1073 3.84E-07 0.5707 0.1073 3.84E-07 0.5779 0.1073 3.84E-07 0.5779	0.08721 6.10E-04 0.3134 0.08633 2.56E-04 0.3269 0.08633 2.55E-04 0.3229 0.08752 1.31E-04 0.3223 0.08753 5.37E-05 0.3463 0.08754 3.57E-05 0.3463 0.08751 5.51E-05 0.3463 0.08753 1.31E-05 0.3463 0.08753 1.08E-05 0.3463 0.08751 5.57E-05 0.3463 0.07387 1.08E-05 0.4996 0.07387 4.98E-06 0.4068 0.07387 1.35E-07 0.5707 0.1002 8.73E-07 0.5707 0.1044 5.35E-07 0.5707 0.1043 5.35E-07 0.5707 0.1073 3.84E-07 0.5707 0.1073 3.84E-07 0.5777 0.1073 3.84E-07 0.5779 0.1073 3.84E-07 0.5779 0.1073 3.84E-07 0.5779	0.08721 6.10E-04 0.3134 0.08633 2.56E-04 0.3269 0.08633 2.55E-04 0.3229 0.08752 1.31E-04 0.3223 0.08753 1.31E-05 0.3269 0.08753 1.31E-05 0.3263 0.087515 6.53E-05 0.3463 0.08753 1.08E-05 0.3463 0.08753 1.08E-05 0.4966 0.07387 4.98E-06 0.4068 0.07387 4.98E-06 0.4966 0.1004 1.36E-06 0.4966 0.1048 1.05E-06 0.4966 0.1048 1.05E-06 0.575 0.1043 5.35E-07 0.5707 0.1044 5.35E-07 0.5707 0.1073 3.84E-07 0.5707 0.1073 3.84E-07 0.5707 0.1073 3.84E-07 0.5779 0.1073 3.84E-07 0.5779 0.1073 3.84E-07 0.5779 0.1073 3.84E-07 0.5779
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	0 0 0 0 0 0.4716 0 0.4717 1 0.4726 1 0.4746	0 0.4716 0 5 0.4716 0 6 0.4716 0 7 0.4726 0 1 0.4726 0 1 0.4726 0 2 0.4726 0 9 0.4726 0 1 0.4726 0 1 0.4726 0 2 0.4726 0 3 0.4726 0 4 0.4756 0	0 0.4716 0 9 0.4716 0 5 0.4717 0 2 0.4717 0 1 0.4746 0 1 0.4746 0 5 0.4755 0 6 0.4755 0 7 0.4755 0 9 0.4755 0 0.4755 0 0 1 0.4755 0 0 0.4755 0 0.4755 0 0 0.4755 0 0 0.4755 0 0 0.4755 0 0 0.4755 0 0 0.466 0 0 0.466 0 0 0.466 0 0	0.4716 0 0.4716 0 0.4717 0 1 0.4717 2 0.4717 2 0.4726 1 0.4755 0 0.475 0 0.475 0 0.475 0 0.475 0 0.475 0 0.475 0 0.475 0.46 0.46 0.46 0.46	0.4716 0.4716 0.4716 0.4717 0.4717 0.4717 0.475 0.4755 0.475 0.475 0.475 0.475 0.475 0.475 0.475 0.475 0.475 0.475 0.475 0.475 0.466 0.466
	0.9199 0.9199 0.9345 0.9332 0.9332 0.9291	0.9199 0.9199 0.9332 0.9332 0.9332 0.9117 0.9117 0.9117 0.9117	0.9199 0.9199 0.9335 0.9335 0.9332 0.9117 0.9117 0.9117 0.882 0.81 0.81 0.81	0.9199 0.9345 0.9332 0.9332 0.9117 0.9117 0.9117 0.9117 0.81 0.81 0.81 0.81 0.81 0.81	0.9199 0.9345 0.9332 0.9332 0.9117 0.9117 0.9117 0.81 0.81 0.81 0.81
	0.4293 0.4293 0.4293 0.0.26268 0.0.00288 0.0000000000	0.4293 0.4293 0.4293 0.4293 0.4293 0.4293 0.4293 0.4293 0.56268 0.505268 0.505268 0.505269 0.5052604 0.555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555204 0.5555504 0.5555504 0.55555504 0.55555504 0.5555555555	0.4293 0.4293 0.4293 0.4293 0.01666 0.4293 0.01666 0.01666 0.00288 0.00288 0.00288 0.002880 0.02804 0.628-04 0.628-04 0.558-04 0.028-05 0.338-05 0.0228-05 0.028-05 0.028-05 0.028-05 0.028-05 00000	0.4293 0.4293 0.4293 0.4293 0.0268 0.01666 0.00288 0.00288 0.00288 0.00288 0.00288 0.00288 0.00280 0.028-04 0.028-04 0.028-05 0.028-05 0.37E-05 0.37E-05	0.4293 0.4293 0.4293 0.0268 0.002888 0.00288 0.00288 0.00288 0.00288 0.00288 0.00288 0.00288 0
	7244 0.4 6939 0.0 77295 0.0	7244 0.4 6939 0.0 65939 0.0 77295 0.0 7237 9.65 66944 4.65 6819 1.74 6606 7.80 6605 3.55	7244 0.4 6939 0.0 6939 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 77295 0.0 7737 9.6 6606 7.8 6502 3.5 7792 1.0 7792 2.3 7742 2.3	7244 0.4 6939 0.0 6939 0.0 7295 0.0 7295 0.0 7295 1.7 6606 7.8 6592 3.5 805 2.3 7742 2.3 77237 2.6 6592 3.5 7742 2.3	77244 0.4 6939 0.0 6939 0.0 7295 0.0 7295 0.0 77295 1.7 6606 7.8 6592 3.5 77237 9.6 6592 3.5 7742 2.3 7742 2.3
	91 0.77 079 0.66 074 0.77 0741 0.77 071 0.77	91 0.7 079 0.6 0741 0.7 0411 0.7 0335 0.66 003 0.66 003 0.66 003 0.66	91 0.77 079 0.66 0741 0.77 0742 0.77 0741 0.77 0735 0.66 903 0.66 91 0.86 91 0.73 91 0.71 91 0.75 91 0.76 91 0.77 91 0.77 91 0.77 91 0.77 91 0.77	91 0.77 077 0.07 077 0.06 074 0.77 0741 0.77 035 0.66 903 0.66 91 0.76 91 0.77 91 0.77 91 0.76 91 0.77 91 0.77 91 0.77 91 0.77 91 0.77	91 0.77 077 0.79 077 0.77 077 0.77 077 0.77 077 0.77 077 0.77 077 0.77 077 0.77 079 0.66 903 0.66 91 0.77
	0.907 0.907 0.907 0.904 0.904	0.907 0.907 0.904 0.903 0.903 0.903 0.903 0.903 0.903	0.904 0.904 0.904 0.903 0.903 0.903 0.903 0.903 0.903 0.903 0.903 0.903 0.903 0.904 0.905 0.906 0.907 0.903 0.903 0.904 0.905 0.905 0.906 0.907 0.907 0.907 0.907 0.907 0.907 0.907 0.907 0.907 0.907 0.907 0.907 0.907 0.907	0.900 0.900 0.900 0.900 0.900 0.900 0.900 0.900 0.900 0.900 0.910 0.9000 0.90000 0.90000 0.90000 0.90000 0.90000 0.90000 0.90000 0.900000 0.90000000000	0.900 0.900 0.900 0.900 0.900 0.9100 0.9100 0.9100 0.9100 0.9100 0.9100 0.910000000000
	1 0.9996 1 1 1	1 1 1 1 1 1 1 1 1 1 1	960		
	20.76 4.069 1.243 0.2183 0.07793	20.76 20.76 20.76 2183 2183 2183 07793 07793 07793 07793 07793 001568		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 1 1 0.9996 0 1 0 1 0 1 1 0 1 0 1 1 0 1 0 1 1 1 1 1 1 1 1 1 0
	6.01 6.01 5.14 4.51 4.33	<u> </u>	20.76 1 20.76 1 4.069 0.95 1.243 1 0.2183 1 0.07793 1 0.07793 1 0.01568 1 0.00682 1 0.00155 1 0.00155 1 1.796E-04 1 1.776E-04 1	20.76 1 20.76 1 4.069 0.9990 1.243 1 0.01868 1 0.01568 1 0.00582 1 0.0032 1 0.00155 1 0.00155 1 1.756E-04 1 1.756E-05 1 2.15E-05 1 0.055 1	20.76 1 20.76 1 4.069 0.9996 1.243 1 0.02183 1 0.02183 1 0.01568 1 0.0032 1 0.0032 1 0.001558 1 0.001558 1 0.00155 1 1.756E-04 1 1.756E-05 1 2.15E-05 1 2.51E-06 0.9855 0.152E-06 0.9865 0.152E-06 0.9865
	00000	26.01 2 24.79 4 25.14 1 25.13 0 24.51 0 24.53 0 23.69 0 23.29 0 23.29 0 23.29 0	26.01 20.76 1 24,79 4.069 0.95 25.14 1.243 1 24.51 0.2183 1 24.51 0.2183 1 24.53 0.07793 1 24.33 0.07793 1 23.59 0.0411 1 23.59 0.01568 1 23.29 0.001568 1 23.29 0.00155 1 23.09 0.00155 1 21.97 7.96E-04 1 21.19 1.77E-04 1 21.19 1.77E-04 1	26.01 20.76 1 24.79 4.069 0.9990 25.14 1.243 1 24.51 0.2183 1 24.51 0.2183 1 24.53 0.07793 1 24.33 0.07793 1 23.59 0.0411 1 23.29 0.01568 1 23.23 0.00155 1 23.03 0.00155 1 21.97 7.96E-04 1 21.97 7.56E-05 1 20.77 7.66E-05 1 20.77 7.56E-05 1 20.77 7.66E-05 1 20.78 9.05E-06 0.985 19.96 2.15E-05 1 19.96 2.15E-05 1	26.01 20.76 1 24.79 4.069 0.9996 0 24.51 0.2183 1 0 25.14 1.243 1 0 24.51 0.2183 1 0 24.33 0.07793 1 0 23.55 0.01568 1 0 23.02 0.00682 1 0 23.02 0.00582 1 0 23.02 0.00155 1 0 21.97 7.96E-04 1 1 21.19 1.77E-04 1 1 20.77 7.66E-05 1 0 21.19 1.77E-04 1 1 20.26 3.74E-05 1 0 19.96 2.15E-06 1 0 0 19.33 4.55E-06 1 0 0 19.33 1.52E-06 0.9884 0 0

Table 3.6Parameters of Eq. (3.5) obtained by fitting to the dielectric spectra ofthe 1.0 mol% solution of LiClO4 in 5-methyl-2-hexanol.

Table 3.7Values of the parameters of four empirical and theoretical relaxationequations obtained by fitting to the relaxation data for 1-propanol, 5-methyl-2-hexanol, and their salt solutions. Data for process II are given in parentheses andthose for process III are marked with an asterisk.

	LiClO ₄ Concentration	Model	A	B, Y	T_0, T_c
	[mol%]	Equation	[Hz]	[K]	[K]
1-propanol	0	Arrhenius	10 ^{15.01*}	2901*	
		(Eq. 3.12)			
	"	VFT	$10^{11.91}$	1734	52.68
		(Eq. 3.7)	$(10^{11.74})$	(1146)	(64.59)
		Mode	10 ^{5.943}	12.05	87.59
		Coupling			
		(Eq. 3.10)	10.50		
		Souletie-	1012.58	28.57	73.83
		Bertrand			
		(Eq. 3.11)	15.05*		
	1.0	Arrhenius	10 ^{15.05+}	2942	
		VFT	10 ^{12.11}	1755	53.22
			$(10^{12.43})$	(1314)	(63.00)
		Mode	$10^{6.314}$	11.55	90.36
		Coupling			
		Souletie-	1012.73	28.15	75.15
		Bertrand	12.91*		
5-methyl-2-	0	Arrhenius	1012.01	2874	
пеханог	"	VFT	10 ^{13.63}	2775	79.80
			$(10^{12.40})$	(1325)	(112.25)
		Mode	10 ^{7.3}	12.33	133.9
		Coupling			
		Souletie-	10 ^{14.24}	29.59	112.7
		Bertrand			
	0.5	Arrhenius	10 ^{12.52*}	2744*	
		VFT	10 ^{12.92}	2494	84.70
			$(10^{11.31})$	(1119)	(115.48)
		Mode	10 ^{7.362}	12.08	135.16
		Coupling			
		Souletie-	10 ^{13.70}	26.76	116.63
		Bertrand			
	1.0	Arrhenius	10 ^{12.79*}	2831*	
	"	VFT	10 ^{12.60}	2309	89 53
			$(10^{11.63})$	(1198)	(113.93)
		Mode	107.454	11.93	136.54
		Coupling		11.75	100.01
		Souletie-	10 ^{13.47}	24.79	120.72
		Bertrand			

	LiClO ₄ Concentration [mol%]	A _{VFT} [S m ⁻¹]	B _{VFT} [K]	T ₀ [K]
1-propanol	0	10 ^{-1.129}	1285	62.65
	1.0	10 ^{2.338}	1400	61.66
5-methyl-2-	0	10 ^{-3.351}	913.1	124.32
nexanol	0.5	10 ^{0.4529}	1490	103.29
	1.0	10 ^{0.6963}	1457	105.35

Table 3.8Summary of parameters of the fit of the VFT equation to the dcconductivity of 1-propanol, 5-methyl-2-hexanol, and the LiClO4 solutions.

3.4 Discussion

3.4.1 Effect of lons on Es

For 1-propanol at a temperature of 117.5 K, Eq. (3.3) leads to an estimate for the reduction in ε_s smaller in size than the actual reduction of 40 % [from 72.4 in pure 1-propanol to 43.4 in the salt solution as can be seen in Fig. 3.10(A)], without any compensation for the Debye-Falkenhagen effect. The value of g for pure 1-propanol at this temperature has been estimated using Eq. (3.4) and data measured here to be 4.3, implying association of the 1-propanol molecules in H-bonded linear chains on time average. This estimate of g uses $\mu_p = 1.68$ D (the vapor phase dipole moment of an OH group), and $\varepsilon_{\infty} = 1.1n_D^2$ where n_D is the refractive index of the Na-D line (1.385), and the standard density at 298.2 K, so it is somewhat unrealistic. Johari et al. [44] and Kalinovskaya et al. [45] have shown that using the refractive index value may result in an underestimation of ε_{∞} and suggest that the limiting high frequency permittivity of process I, $\varepsilon_{\infty I}$, be used instead for calculation of $\Delta \varepsilon$, which will give a lower value for g. If $\varepsilon_{\infty} = 2.98$ as found from fitting is used instead, g = 3.31. Addition of LiClO₄ will reduce g and hence ε_s of 1-propanol by disrupting the H-bonded chains, accounting for any reduction in ε_s in excess of that resulting from the

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dielectric decrement. The addition of the salt also affects g in two other ways. First, the density of the solution is increased, and second, ε_{∞} is increased both by the change in density itself (through the Clausius-Mossotti equation), and as a result of the additional infrared polarisibility of the ions.

The effect of the addition of salt to 5-methyl-2-hexanol on its ε_s can be seen in Fig. 3.11(A). At lower temperatures, it seems that the addition of ions has reduced \mathcal{E}_s while at higher temperatures (above ~ 203 K) ε_s is larger in the solutions. To quantify this, at 177.3 K, the pure liquid has $\varepsilon_s \sim 28.6$. The 0.5 mol% LiClO₄ solution has $\varepsilon_s \sim 28.2$ at the similar temperature of 176.7 K (1.1 % reduction), and at 176.0 K the 1.0 mol% solution has $\varepsilon_s \sim 26.5$ (7.1 % reduction). At 223.8 K, $\varepsilon_s \sim 18.7$ for pure 5methyl-2-hexanol. For the 0.5 mol% salt solution, $\varepsilon_s \sim 20.8$ at 223.5 K (11 % rise) while for the 1.0 mol% solution, $\varepsilon_s \sim 21.0$ at 222.6 K (12 % rise). ε_s values are not available for all three LiClO₄ concentrations at the same temperatures so direct comparisons cannot be made without interpolation. At 176.7 K for the 0.5 mol% solution the kinetic dielectric decrement $\delta \varepsilon_{\rm KDD}$ estimated from the continuum theory with stick conditions (p = 1) and using $\varepsilon_s \sim 28.6$ at 177.3 K for the pure liquid is – 4.8. For the 1.0 mol% solution at 176 K $\delta \varepsilon_{KDD} = -8.6$. Both values are larger than the observed decreases in \mathcal{E}_s . At higher temperatures, \mathcal{E}_s increases rather than decreases. The smaller than expected decreases in \mathcal{E}_s at low temperatures and the increases at high temperatures cannot be explained by a reduction in g due to the dissociation of H-bonded ring structures on addition of LiClO₄. This is because there is strong evidence that pure 5-methyl-2-hexanol has considerable association of molecules in chains despite its lower ε_s compared to 1-propanol. Using $n_D = 1.417$, g is estimated in the same somewhat unrealistic way as for 1-propanol to be 4.5 at 177.3 K, while if $\varepsilon_{\infty} = 2.44$ is used g = 4.0 implying the presence of chains in the pure liquid. Also, the main relaxation in 5-methyl-2-hexanol is approximately Debyelike – in phenyl substituted propanols where H-bonding is disrupted by steric hindrance [44, 45] (eg. $g \sim 1$ for 1-phenyl-1-propanol [44]), the main relaxation broadens to a Davidson-Cole distribution as is observed for non-H-bonded liquids. If 5-methyl-2-hexanol contained both ring and chain structures it seems unlikely that the addition of ions would reduce H-bonding in rings preferentially. The two salt

concentrations seem to cause a similar increase in ε_s at higher temperatures. It has been found for aqueous alkali nitrates and sulphates that at high salt concentrations \mathcal{E}_s may remain constant or increase slightly with temperature [46]. This temperature independence was attributed to the inclusion of water molecules in the hydration spheres of ions, or additional contributions to \mathcal{E}_s from ion-ion complexes [47] present at higher concentrations. At some temperature, this could cause a crossover where ε_s becomes greater than that of the solvent or lower concentration solutions, especially if the orientation of such ion-ion pairs were prevented at temperatures closer to T_{g} by the larger viscosity. It should be noted however that molalities of 1.35 mol kg^{-1} (2.4 mol%) and above were required to observe this effect in aqueous solutions of LiSO₄ [46]. Even higher concentrations (5 mol kg⁻¹) were needed to see the same effect in nitrate and sulphate solutions of other alkali metals [46]. Another possibility is that there was a reduction in \mathcal{E}_s of the pure 5-methyl-2-hexanol sample as a result of a small amount of crystallisation occurring above T_g . In terms of moles of LiClO₄ per unit volume, it is seen in Table 3.2 that both concentrations are much lower than that of the LiClO₄ in 1-propanol solution. The concentrations used here may not have been large enough to significantly affect intermolecular H-bonding in 5-methyl-2-hexanol.

3.4.2 Relative Dielectric Strengths and the Nature of Dielectric Relaxation Processes

In the most recent and comprehensive study made of liquid, supercooled liquid, and glassy 1-propanol, Hansen et al. [23] have measured its dielectric spectra in the frequency range 10 mHz to 20 GHz between 65 K and 350 K. They also made photon correlation spectroscopy and Brillouin light scattering measurements at several temperatures. Similar to the results here, they found three relaxation processes in the dielectric spectra. The relaxation time, temperature dependence, and shape of process II in the dielectric loss corresponded to the α -relaxation as observed in the light scattering while process I was not observed in the light scattering data at all. The authors conclude that process II is the α -relaxation and as such is responsible for structural relaxation and viscosity in the supercooled liquid. They also illustrate that literature viscosity data corresponds more closely to process II. Process III is classified as a Johari-Goldstein β -relaxation. Since there are many alcohols that have

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three relaxation processes analogous to those in 1-propanol, one can speculate that these assignments apply to these also.

However, several arguments can be made against this assignment of the relaxation processes. In pure 1-propanol at 117.5 K, $\Delta \varepsilon_1 = 66.6$, $\Delta \varepsilon_{11} = 2.1$, and $\Delta \varepsilon_{111} = 1.1$. This means that at this temperature, 95.5 % of the polarisation relaxes by process I, while processes II and III account for only 4.5 %. If this is suggestive of the populations of molecules involved in these processes [see Eq. (3.4)] it is hard to understand how a process involving such few molecules can be responsible for the structural relaxation and, conversely, how a process that involves many molecules doesn't contribute to it at all. In 1-propanol containing 1.0 mol% LiClO₄ at 117.6 K, $\Delta \varepsilon_1 = 37.3$, $\Delta \varepsilon_{11} = 2.5$, and $\Delta \varepsilon_{111} = 0.9$. There is a 44.0 % reduction in $\Delta \varepsilon_1$, $\Delta \varepsilon_{II}$ increases by 20.0 %, and $\Delta \varepsilon_{III}$ decreases by 15.4 %. The increase in $\Delta \varepsilon_{III}$ is clearly visible in Fig. 3.10(C). Process I is substantially reduced in strength on addition of salt and this is partly due to reduction in H-bonding. The combined strength of the other two processes has hardly changed at all, which is not what would be expected if these were due to rotational diffusion of the 1-propanol molecules not involved in hydrogen bonding, which is implicit in the claim that process I does not contribute to the structural relaxation.

Measurements on the substituted propanols 1-phenyl-1-propanol [44] and 1-phenyl-2propanol [45] also provide evidence against the conclusions of Hansen et al. *g* is found to be approximately unity in 1-phenyl-1-propanol and the main relaxation in 1propanol is Davidson-Cole rather than Debye, so that there is little H-bonding in this alcohol. However, the main relaxation (which presumably involves rotational diffusion of non-H-boded molecules as for the α -relaxation in a non-H-bonded liquid) has $\Delta \varepsilon \sim 12$ at 198.7 K, which is much larger than the contribution of process II and III to the relaxation of 1-propanol, which is hard to reconcile with these two processes being solely responsible for viscosity and structural relaxation in that alcohol. Similar arguments were made for 1-phenyl-2-propanol with reference to both 1-propanol and 2-propanol. $\Delta \varepsilon_{II} + \Delta \varepsilon_{III}$ of 1-propanol at a given temperature is much smaller than the strength of the main relaxation in 1-phenyl-2-propanol, scaling for temperature and molar mass differences, than can be accounted for by the quite low *g* value of this highly sterically hindered alcohol (*g* = 2.3 at 211.6 K) [45]. This alcohol also has a non-Debye main relaxation. Finally, proton transfer between H-bonds has been suggested [19] as one mechanism that could account for process I in 1-propanol. This would fulfil the requirement that process I should not contribute to the structural relaxation. However, the relaxation time of this process would not depend on pressure [48], as has been found for process I in many alcohols [49].

The molecular population argument against Hansen's assignment of the relaxations in 1-propanol has been made previously when discussing 5-methyl-2-hexanol [19]. From the data at 172.6 K, $\Delta \varepsilon_1 = 26.5$, $\Delta \varepsilon_2 = 0.76$, and $\Delta \varepsilon_{11} = 0.05$ and 97.0 % of the polarisation relaxes by process I. It is evident from Fig. 3.11(C) that addition of 0.5 mol% and 1.0 mol% LiClO4 to 5-methyl-2-hexanol had minimal effect on both $\Delta \varepsilon_{\mu}$ and $\Delta \varepsilon_{III}$. There is little change in $\Delta \varepsilon_{III}$, which is 0.095 at 173.7 K in the 0.5 mol% solution, and 0.093 at 172.9 K in the 1.0 mol% solution. The large difference between these values and the value of 0.049 for the pure alcohol obtained at 172.6 K may be explained by a difference in fitting procedure. A Cole-Cole function was used for the fit of the salt solution data while a HN function was used for the pure alcohol. In any case, process III in 5-methyl-2-hexanol is difficult to resolve, particularly below T_g , as it has quite a low strength. $\Delta \varepsilon_{\mu}$ decreases slightly from 0.76 to 0.75 in the 0.5 mol% LiClO₄ solution and then to 0.69 in the 1.0 mol% solution. The changes in $\Delta \varepsilon_1$ have been explained above without implying any large changes in the H-bonding between the alcohol molecules, so nothing novel can be concluded about the origin of the relaxations in 5-methyl-2-hexanol from the relaxation strengths of these processes in the salt solutions. In order to test the assignments of the processes made by Hansen further, Brillouin light scattering and photon correlation spectroscopy measurements must be made on the salt solutions of 1-propanol and 5-methyl-2-hexanol, and the phenyl substituted 1-propanols for which dielectric data exists [45].

3.4.3 Assignment of the Relaxation Processes in 1-propanol and 5methyl-2-hexanol

As mentioned above, it has been suggested that process II in 1-propanol (and by extension perhaps in other alcohols) is the α -relaxation found in non-H-bonded supercooled liquids [23, 24]. Process I was associated with breaking and reforming of H-bonds by an unspecified mechanism, which does not contribute to the structural relaxation. It has long been considered that this process is related to H-bonding in

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alcohols. Process III was classified as a JG- β relaxation. The assignment of process II as the α -relaxation and exclusion of process I is appealing because process II, unlike process I, is broader than Debye, having a distribution of relaxation times consistent with current theories of the α -relaxation. Cooperative motion of molecules is thought to be responsible for both the broadening of the relaxation spectrum and the curvature of the Arrhenius plot of the relaxation rate in supercooled liquids. Process I in 1propanol and 5-methyl-2-hexanol is problematic because it has a Debye relaxation spectrum whose relaxation rate has a non-Arrhenius temperature dependence. However it is still possible that process I is the α -relaxation and contributes to the viscosity and structural relaxation. The fluctuating environment model of Anderson and Ullman [50] describes the conditions in which the various spectral lineshapes defined by the Debye equations, and the Davidson-Cole, and Cole-Cole empirical equations may occur. Different relative rates of dipolar reorientation and structural relaxation may result in either a single Debye relaxation or a distribution of relaxation times. If a dipole reorients more slowly than the relaxation of its surroundings, then the potential energy it experiences is the same on average (over time and spatially) resulting in a Debye relaxation. If the dipole reorients more rapidly than the surroundings (the dipolar relaxation time is less than the structural relaxation time), the reorientation of the dipole occurs in a system that is changing its position on, to use Goldstein's term, a "potential energy landscape" [51] as the dipole reorients. A distribution of relaxation times would be observed because of these angle-dependent barriers to reorientation and the fact that different molecules reorient in different environments. In such a model, there is no set shape for a dielectric spectrum - it depends only on a set of conditions for the rate of environmental fluctuations and dipolar reorientation. This idea is basically similar to the original ideas of Dannhauser [20] and Johari and Dannhauser [49] concerning the main Debye relaxation, equivalent to process I here, observed in several octanols as well as some of the ideas of Fröhlich discussed in Chap. 1. The process responsible for the dipolar reorientation is a non-H bonded alcohol molecule rotating to form a new H-bond, a process that occurs more slowly than the structural relaxation and as a result occurs in an environment that is the same throughout the liquid on average. The breaking of the Hbond is not part of the activating step since the activation energy depends on the isomeric structure. Johari and Dannahuser [49] also argue that since the molecules in

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these alcohols are ordered in chains on time average, the dipolar reorientation must occur in one step. These arguments have also been used by Kalinovskaya et al. [19] in assigning the relaxation process I in 5-methyl-2-hexanol.

We must now explain the origin of process II in 1-propanol and 5-methyl-2-hexanol. First we note that the addition of 1.0 mol% LiClO₄ appears to decrease the relaxation rate of this process in 1-propanol slightly (see Fig. 3.12). However, the addition of salt has no effect on this process' rate in 5-methyl-2-hexanol (Fig. 3.13). This is reasonable given that there appears to be no change in ε_s of 5-methyl-2-hexanol or the strengths of its relaxation processes caused by changes in the structure of the supercooled liquid.

Hassion and Cole [21] assigned this process in ethanol-2-propanol mixtures to the reorientation of the –OR group about the –OH bond, as have Dannhauser [20] and Johari and Dannhauser [49] for octanols.

An argument against process II being a result of rotation of non-H-bonded 1-propanol molecules as suggested originally by Garg et al. [18] from analysis of microwave dielectric spectra of several primary alcohols and implied by Hansen [23] is the temperature dependence of this process' dielectric strength. $\Delta \varepsilon_{II}$ decreases with increasing temperature for 1-propanol, as is seen in Fig. 3.10(C). Since the extent of H-bonding increases with decreasing temperature as shown by the increase of g [15], the opposite trend would be expected. This analysis is also valid for $\Delta \varepsilon_{II}$ of 5methyl-2-hexanol [Fig. 3.11(C)].

In Fig. 3.3(B) and (A) respectively, it is clear that for 1-propanol at temperatures far below the glass transition, relaxation process III is distinct peak in ε'' , rather than a wing, and a dispersion in ε' . It increases in strength with temperature. However, it is unusual that the rate of increase with temperature appears to remain constant through the glass transition, which is estimated to be 100.0 K at $f_{m,I} = 10^{-4}$ Hz using the VFT parameters of process I in pure 1-propanol. $f_{m,III}$ has an Arrhenius temperature dependence and will merge with $f_{m,I}$ and $f_{m,II}$ on the inverse temperature plot at some temperature. These are the usual characteristics of a JG β -relaxation in a glassforming liquid [52], as concluded previously for 1-propanol [23]. Process III in 5methyl-2-hexanol has similar features. A curious difference between $\Delta \varepsilon_{III}$ in the pure 5-methyl-2-hexanol and the 0.5 mol% and 1.0 mol% LiClO₄ solutions can be seen in Fig. 3.11(C). For the pure alcohol $\Delta \varepsilon_{III}$ is constant below T_g (148.1 K at $f_{m,I} = 10^{-4}$ Hz), and appears to decrease slightly above T_g By contrast, for the salt solutions it falls with temperature below T_g and then increases sharply above T_g . This increase in slope above T_g is typical for JG β -relaxations and is discussed further in Chap 1 and Chap. 5. The negative slope below T_g is found in quenched glasses where structural relaxation has not occurred and is also discussed in Chap. 5. The reason why these trends are not seen in the data of the pure alcohol may be a result of fitting procedures rather than any physical difference. This is borne out in the differences seen in the broadness parameters for process III in Fig. 3.15(C). The pure alcohol has been fitted using a HN distribution (α_{III} , $\beta_{III} < 1$) while a Cole-Cole distribution ($\alpha_{III} < 1$, $\beta_{III} = 1$) was assumed in fitting of the salt solutions. It is worth noting again that process III in this alcohol is very weak which may result in errors in its fitting.

For both 1-propanol and 5-methyl-2-hexanol there is no appreciable change in the rate of the JG β -relaxation, which suggests that the presence of low concentrations of ions does not affect the energy landscape picture in the supercooled liquid and glass so as not to affect the dynamics of the JG β -relaxation.

3.4.4 Temperature Dependence of the Relaxation Rates

The relaxation rate of the α -relaxation in supercooled liquids has been fitted by a variety of equations – semiempirical ones such as the VFT equation and equations based on various theories of relaxation in supercooled liquids. Three aspects of the temperature dependence of the relaxation dynamics are considered. These continue to be a subject of debate [53, 54] and are used to support one theory over the other. A brief description and comparative analysis of several of the equations is given here, and has been discussed elsewhere [44, 45]. First, the variation of f_m of the α -relaxation with T and its interpretation in terms of the configurational entropy theory of Adam and Gibbs [55] [see Chap. 2, Eq. (2.10)] is written in terms of f_m :

$$f_m = A_{AG} \exp\left(-z^* \Delta \mu / RT\right), \qquad (3.8)$$

where z^* is the number of molecules forming a co-operatively re-arranging region, $\Delta \mu$, is, according to Adam and Gibbs, using polymer terminology ".....largely the energy barrier resisting the cooperative rearrangement per monomer segment." [55]. Here, a "monomer segment" corresponds to an individual alcohol molecule hydrogen bonded to neighbours in the co-operatively re-arranging region, and the molar quantity is used. $R = N_A k$ is the gas constant. The data in Fig. 3.12 and Fig. 3.13 can be described by the VFT equation as discussed in Sect. 3.3, p. 101-102. The best-fit values for the various parameters, A_{VFT} , B_{VFT} , and T_0 of the fit of the VFT equation to the process I relaxation data of 1-propanol, 5-methyl-2-hexanol, and their LiClO₄ solutions are given in the results section and in Table 3.7. It can be seen that there are definite trends in the values of these parameters for this process. The parameters are almost unchanged for addition of 1.0 mol% LiClO₄ to 1-propanol. All parameters of the VFT equation increase slightly. In 5-methyl-2-hexanol, A_{VFT} and B_{VFT} decrease, while T_0 increases with increasing salt concentration. Using the parameters of the VFT equations to calculate T_g at 10⁻⁴ Hz gives values of 100.0 K and 100.5 K for 1propanol and its salt solution, and 148.1 K, 148.7 K and 149.9 K for 5-methyl-2hexanol in order of increasing salt concentration. Addition of salt increases T_g marginally in both substances. As has been shown previously [56], the data may also be analysed on the premise that the curved shape of the configurational entropy against T plot above T_g extrapolates to zero at T_0 , where f_m also becomes formally zero, and that doing so does not imply that the configurational entropy of an equilibrium liquid in fact becomes zero at T_0 . In this analysis, the pre-exponential term in Eq. (3.7) became identical to the pre-exponential term in Eq. (3.8). Without implying that the temperature T_0 has a thermodynamic significance, the identification of these terms [56] had led to: $\Delta \mu = 8.314 B_{VFT}$ and $z^* = [T/(T - T_0)]$. By using the values of B_{VFT} and T_0 given above, we obtain, $\Delta \mu = 14.4$ kJ mol⁻¹ and $z^*(T_g \text{ for } f_m =$ 10^{-4} Hz) = 2.11 for 1-propanol, and $\Delta \mu = 14.6$ kJ mol⁻¹ and $z^*(T_g \text{ for } f_m = 10^{-4} \text{ Hz}) =$ 2.13 for its 1 mol% LiClO₄ solution. These are compiled, together with the values for 5-methyl-2-hexanol, in Table 3.9. These values may be compared with those for other alcohols as described in [44]. A comparison between Eq. (3.7) and Eq. (3.8) requires only the matching of the shapes of the plots of $\ln f_m$ against T at $T > T_g$. This matching has been done by using the available values of the parameters B_{VFT} and T_0 . Therefore the estimates of z^* and $\Delta \mu$ depend sensitively on the values of B_{VFT} and T_0 , which themselves in turn are obtained by using a relatively long extrapolation.

Dyre and coworkers [57, 58] have preferred an alternative interpretation of the temperature dependence of relaxation rate in terms of a "shoving model" [58]. Accordingly,

$$f_m = A_{Dyre} \exp(-G_{\infty}V_c / RT), \qquad (3.9)$$

where G_{∞} is the temperature-dependent high frequency shear modulus of a liquid and V_c a characteristic volume. It leads to $G_{\infty}V_c = z^*\Delta\mu$ when the quantities are represented in mole units. For 1-propanol at its T_g (or T for $f_m = 10^{-4}$ Hz), we calculate: $G_{\infty}V_c = 30.5$ kJ mol⁻¹ (or, $z^*(T_g)\Delta\mu = 2.11$ x 14.4 kJ mol⁻¹). For its 1 mol% LiClO₄ solution, we calculate: $G_{\infty}V_c = 31.0$ kJ mol⁻¹. For 5-methyl-2-hexanol, $G_{\infty}V_c = 50.0$ kJ mol⁻¹, for its 0.5 mol% salt solution $G_{\infty}V_c = 48.2$ kJ mol⁻¹, and for the 1.0 mol% solution, $G_{\infty}V_c = 47.6$ kJ mol⁻¹. These values are also given in Table 3.9 and may be compared against the values for other liquids given earlier [56]. It should be noted that these earlier values should be multiplied by 2.303 so that they are consistent with the values here because base 10 rather than natural logarithm versions of the relaxation equations were used (see note about Ref. 56). Two more equations are currently used to fit the *T*-dependence of f_m . The first is

based on the Mode-Coupling theory [59, 60]:

$$f_m = A_{mc} [(T - T_c) / T_c]^{\gamma}, \qquad (3.10)$$

where $A_{\rm mc}$, T_c and γ are empirical parameters. The second is an empirical equation provided by Dissado and Hill [61, 62], namely, $f_m \propto (T - T_c)^{\gamma}$. These two equations admit to the same form, namely, that f_m varies as $(T - T_c)^{\gamma}$. But Souletie and Bertrand [63] have provided a somewhat different form:

$$f_m = A_{SB} [(T - T_c)/T]^{\gamma}, \qquad (3.11)$$

where A_{SB} , T_c and γ are also empirical constants. Eq. (3.10) and (3.11) were fitted to the data for the relaxation rates. For 1-propanol, the values of the parameters obtained by fitting these equations to the α -relaxation data are: $A_{mc} = 10^{5.943}$ Hz, $T_c =$ 87.59 K and $\gamma = 12.05$ for Eq. (3.10), and $A_{SB} = 10^{12.58}$ Hz, $T_c = 73.83$ K and $\gamma =$ 28.57 for Eq. (3.11). For its 1 mol% LiClO₄ solution, the parameters obtained by fitting are, $A_{mc} = 10^{6.314}$ Hz, $T_c = 90.36$ K and $\gamma = 11.55$ for Eq. (3.10), and $A_{SB} =$ $10^{12.73}$ Hz, $T_c = 75.15$ K and $\gamma = 28.15$ for Eq. (3.11). The values of the parameters of the fit of the equations to the $f_{m,l}$ vs. 1/T data for 1-propanol and 5-methyl-2hexanol, and their salt solutions are given in Table 3.7. For comparison of the three fitting equations for the process I relaxation data, Fig. 3.18 shows a plot of the $f_{m,l}$ data of pure 1-propanol against the temperature, together with the fit of the VFT, Mode-Coupling, and Souletie-Bertrand equations to the data.

Table 3.9 Glass transition temperatures (calculated using $f_{m,l} = 10^{-4}$ Hz) and the parameters of the Adam-Gibbs equation and the Dyre model calculated from the VFT fit parameters of process I in 1-propanol, 5-methyl-2-hexanol, and their LiClO₄ solutions.

	LiClO ₄ Conc.	$T_{g} (10^{-4} \text{ Hz})$	z*(T _g)	Δμ	$G_{\infty}V_{c} = z^{*}\Delta\mu$
				[KJ mol]	[KJ mol]
1-propanol	0	100.0	2.11	14.4	30.5
	1.0	100.5	2.13	14.6	31.0
5-methyl-2- hexanol	0	148.1	2.17	23.1	50.0
	0.5	148.7	2.32	20.7	48.2
	1.0	149.9	2.48	19.2	47.6



Fig. 3.18 Pot of $f_{m,l}$ vs *T* for pure 1-propanol. Also plotted are the fits of the VFT [Eq. (3.7)], Mode-Coupling (MC) [Eq. (3.10)], and Souletie-Bertrand (SB) [Eq. (3.11)] equations to the data. The fits are all good, and value of T_g (intercept on temperature axis) predicted is almost identical in each case.

Figures with equally good fit could have been drawn for process I in pure 5-methyl-2hexanol and the salt solutions if desired. At first sight, the excellence of the fit seen here would indicate that the theories on which Eq. (3.10) and Eq. (3.11) are based are valid for 1- propanol. However, according to these theories, the critical exponent γ must be between 2 and 4, and usually the high temperature part of the curves is fitted to the mode-coupling theory and deviations occur at low temperatures. The values of γ observed here are 3 to 4-times as high. It seems that in view of the requirement of the fits, no preference for one or other type of the power law equations can be made on the basis of the fits in Fig. 3.18. It also seems unsatisfactory to divide the entire temperature range in an *ad hoc* manner with the power laws obeying one temperature range and the Vogel-Fulcher-Tammann equation the other.

For completeness, the VFT equation has also been fitted to process II and the simple Arrhenius equation:

$$f_m = A_{ARR} \exp(-B_{ARR} / T),$$
 (3.12)

to process III. The parameters obtained for both alcohols and their salt solutions are also given in Table 3.7.

3.4.5 Ionic Effects on Relaxation Time and dc Conductivity

We consider two more aspects of addition of ions on the relaxation kinetics of 1propanol and 5-methyl-2-hexanol. Fig. 3.12 and 3.13 have shown the effect of the ions on the relaxation rate for both alcohols. The similarity between the relaxation rate of 1-propanol and its 1 mol% LiClO₄ solution is remarkable in view of the fact that the extent of intermolecular H-bonding that leads to a parallel correlation of dipoles in the former is reduced in the latter, as discussed earlier. If H-bonding is reduced, the viscosity should also be reduced leading to an increase in the rate of relaxation processes. The relaxation rates of processes I and III are unchanged and that of process II is reduced. A possible explanation is the solvation of 1-propanol by the ions restricting reorientation. The fact that there is little change in the relaxation rates of the processes in 5-methyl-2-hexanol is less surprising given the lack of effect of ions on H-bonding, as evidenced by the ε_s results.

Fig. 3.16 shows the effect on the dc conductivity, σ_{dc} , in 1-propanol. It shows that σ_{dc} increases by about three orders of magnitude on the addition of 1 mol% LiClO₄.

The values may be fitted to a VFT type equation for the dc conductivity in S m⁻¹: σ_{dc} (1-propanol) = 10^{-1.129}exp[-1285/(T – 62.65)] and σ_{dc} (LiClO₄ solution) = 10^{2.338}exp[-1400/(T – 61.66)]. Fig. 3.17 is a similar plot for 5-methyl-2-hexanol. The parameters obtained from the fit of the same VFT equation to σ_{dc} data in 5-methyl-2-hexanol and its 0.5 mol% and 1.0 mol% solutions are given, together with the parameters for 1-propanol and its salt solution in Table 3.8.

 σ_{dc} is directly proportional to the population of the charge carriers and their mobility. The 5-methyl-2-hexanol data indicates the proportionality of σ_{dc} to the number density of ions. It is seen that there is a large increase in σ_{dc} on addition of 0.5 mol% LiClO₄ as ionic concentration is raised from an initially very low level in the pure alcohol. Doubling the concentration then raises the conductivity by a relatively small amount. In liquids, the mobility, which is proportional to the translational diffusion constant D_T , is inversely related to the viscosity according to the Stokes-Einstein equation (See Chap. 2, Eq. 2.30):

$$D_T = \frac{kT}{f\eta},\tag{3.13}$$

where f is *related* to the molecular radius. Thus, if no other effects were present, the ratio of σ_{dc} of 1-propanol to σ_{dc} of 1 mol% LiClO₄ solution would remain constant with changing temperature. The data in Fig. 3.16 and Fig. 3.17 show that this ratio increases with temperature (for example, from ~ 250 at 117.5 K to ~ 900 at 150.6 K for 1-propanol). If the viscosity were to vary similarly in the two cases, this would imply that the number density of ions increases significantly with temperature. The relaxation rate itself is seen as proportional to the viscosity according to the Debye-Stokes-Einstein equation (Chap. 1, Eq. 1.58), which can be rearranged as:

$$f_{m,I} = kT / 6\pi V_m \eta \,, \tag{3.14}$$

where V_m is *related* to the molecular volume.

It is important to note that both the Stokes-Einstein and Debye-Stokes-Einstein relations are derived by considering a macroscopic sphere immersed in a viscous fluid. Their extension to molecules involves assuming that the fluid can be treated as a continuum and that it is useful to apply a macroscopic concept such as viscosity to such small species. The parameters f and V_m in the equations do not bear a direct

relation to molecular radii and volumes in any case [64]. Rössler has shown that Eq. (3.13) is inadequate for describing the dynamics of supercooled liquids [65]. However, discussion on the applicability of hydrodynamics has been continued by Hansen, et al. [66], who suggest that the dielectric relaxation time is proportional to η/T , and not proportional just to η , as suggested previously by Macedo and Litovitz [67]. Since *T* differs by usually no more than 50% in the extreme temperatures of measurements, the maximum difference arising from this revision would be by factor of 1.5. The similarity of $f_{m,l}$ of 1-propanol and its 1 mol% LiClO₄ solution, and 5-methyl-2-hexanol and its 0.5 mol% and 1.0 mol% LiClO₄ solutions suggests that the ratio of the product $V_m\eta$ of the two be equal to 1. Further it should remain so over the entire temperature range of the study, which it does. This would seem to be consistent with relation provided by Hansen, et al. [66].

3.5 Summary

Addition of Li⁺ and ClO₄⁻ ions to 1-propanol causes no change in the relaxation rate and only a small change in the distribution parameters of its principal relaxation, which is asymmetrically broadened to a Davidson-Cole distribution. The zero frequency conductivity increases ~ 900 fold and ε_s decreases by ~ 55 %, both at 150.6 K. The decrease in the permittivity is more than anticipated by the continuum theory of the kinetic dielectric decrement due to ions [1] and is attributed to a decrease in the orientational correlation caused by intermolecular H-bonds. The decrease in ε_s is mostly due to a large decrease in $\Delta \varepsilon_I$. $\Delta \varepsilon_{II}$ increases and $\Delta \varepsilon_{III}$ decreases, while their sum remains approximately the same. The decrease in Hbonding is expected to decrease the viscosity of 1-propanol and thereby increase the dipolar relaxation rate. No increase was found in the relaxation rate of any of the three relaxation processes – indeed, that of process II decreased. Thus, either the relaxation shell decreases the relaxation rate. The latter may be responsible for the observed decrease in the relaxation rate of process II. Addition of Li⁺ and ClO₄⁻ ions to 5-methyl-2-hexanol also leaves the relaxation rate of its primary relaxation process unchanged, while broadening it to a Davidson-Cole distribution. This broadening increases with LiClO₄ concentration. The dc conductivity is raised by a factor of ~ 250 on addition of 0.5 mol% LiClO₄ (comparing the pure 5-methyl-2-hexanol and 0.5 mol% solution at 225.7 K and 226.3 K respectively). It is then raised by a further factor of 1.8 (at 225.7 K relative to the 0.5 mol% solution at 226.3 K) on doubling the salt concentration at 225.7 K. The decrease in \mathcal{E}_s is less than anticipated by the continuum theories of kinetic dielectric decrement at both concentrations below ~ 203 K, while above this temperature \mathcal{E}_s increases by an amount that is similar for both salt concentrations. It is suggested that presence of ions has had little effect on H-bonding in 5-methyl-2-hexanol and the increase in \mathcal{E}_s may be a result of the formation of ion-pairs in the salt solution, which become free to orient as the viscosity falls. $\Delta \varepsilon_1$ decreased below 203 K and increased above it as LiClO₄ was added, just as ε_s did. $\Delta \varepsilon_{II}$ decreases slightly. $\Delta \varepsilon_{III}$ was difficult to resolve above T_g due to its low strength. A change in the temperature dependence of $\Delta \varepsilon_{III}$ (which shows a large increase above T_g in the salt solutions and a decrease in pure 5-methyl-2-hexanol) is an artifact due to a difference in the fitting procedure used for process III in the pure alcohol.

The spectra corresponding to the α -relaxation process contributes ~ 95% of the total polarisation in 1-propanol and ~ 97 % in 5-methyl-2-hexanol. In both cases, process I is identified as the α -process and process II is assigned to the rotation of the -OR group, where R is C₃H₇ in the case of 1-propanol, and C₇H₁₅ in the case of 5-methyl-2-hexanol. Both processes in each of the alcohols follow the VFT equation as both are intimately connected with the vitrification process. T_g at 10⁻⁴ Hz for process I is 100 K in pure 1-propanol and 100.5 K in the solution. It is 148.1 K, 148.7 K, and 149.0 K for process I in pure 5-methyl-2-hexanol, and its 0.5 mol% and 1.0 mol% LiClO₄ solutions respectively. Process I is approximately Debye in the pure alcohols (in 5-methyl-2-hexanol it is very slightly asymmetrically broadened) and it is therefore concluded that a non-Debye process is not a prerequisite for the α -process. Process III can be separated, follows the Arrhenius equation, and persists below T_g , and will merge with the lower frequency relaxation process at some temperature. It is therefore assigned to the Johari-Goldstein process in both alcohols.

A discussion in terms of the configurational entropy (without implying an underlying thermodynamic transition in the equilibrium liquid below T_g) allowed estimation of the size of the cooperatively arranging region and the height of the constant potential energy barrier in 1-propanol, 5-methyl-2-hexanol, and their LiClO₄ solutions at T_g (see Table 3.8). The model of Dyre et al [57, 58] for a temperature-dependent activation energy leads to a set of parameters whose product can be estimated from the values given in Table 3.9. However, uncertainty in the extrapolation of the parameters of the VFT equation may lead to an inconsistency in the evaluated parameters. The power (or scaling) law based equations fit the data well in all cases, but the critical exponents for 1-propanol and its 1.0 mol% LiClO₄ solution, and 5-methyl-2-hexanol and its 0.5 mol% and 1.0 mol% solutions were 4 times the value expected from these laws. This indicates that fitting of such power-laws is ambiguous.

3.6 References

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Fulcher-Tammann equation. This was also mentioned in Ref. 44 and 45)

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Chapter 4

Dielectric Spectroscopy Study of the Crystallisation of D-Sorbitol

4.1 Introduction

D-sorbitol is a polyhydric alcohol with a permanent dipole moment of ca. 3.3 D and is a typical glass-forming liquid. Its dilatometric glass-softening temperature T_g is 265.3 \pm 1.5 K [1, 2], and its dielectric relaxation time is 100 s at 268 K [3]. Glassy and supercooled liquid D-sorbitol has been studied by a large number of groups [1-20] by both dielectric [1, 3-11, 13-15, 17, 18, 20] and other techniques. Further dielectric measurements on the JG β -relaxation of D-sorbitol are presented in Chap. 5 of this thesis. In some cases, conflicting results have been reported, such as varying values of $\mathcal{E}_{s}[3, 4-7]$ and unusual relaxation features [7, 10, 14, 15]. The reason seems to lie in the material itself: Firstly, D-sorbitol at room temperature is a crystalline solid in the form of a white powder whose melting temperature is ~ 370 K [21], but its melting is slow and takes a very long time. In order to completely melt the crystals, D-sorbitol is heated well above the melting temperature, typically to 400 K or above for at least 2-3 h, until the entire melt becomes transparent. Incomplete melting leads to lower values of dielectric strength for the Johari-Goldstein (JG) β -relaxation, and particularly the α -relaxation [3]. The two relaxation processes are broad and their rates are not well separated close to T_g . This tends to introduce errors in resolving the α -relaxation from the JG β -relaxation.

The supercooled state of liquid D-sorbitol also crystallises slowly. It has been found previously that D-sorbitol has two crystalline forms, as characterised by calorimetry and x-ray diffraction [21]. Since some of the unusual findings in earlier dielectric

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studies may have been caused by crystallisation, it seemed necessary to study the general effects of crystallisation on molecular relaxations in D-sorbitol. A real-time study by dielectric spectroscopy of the crystallisation of supercooled liquid D-sorbitol kept at 271.1 K (3 K above T_g), 298.5 K (31 K above T_g), 332.4 K and 332.8 K (65 K above T_g) is presented here. This provides evidence that D-sorbitol crystallises into an ordered or disordered crystalline phase depending on conditions. The results are compared with measurements performed by Minoguchi and Nozaki at 303 K [6], in which $\Delta \varepsilon$ for both the α - and the JG β -relaxation processes had been found to decrease as crystallisation progressed. Before the results are presented, the theory of crystallisation and growth is developed, and a background discussion of rotationally disordered crystalline states is given.

4.1.1 Crystal Nucleation and Growth

Crystallisation is a very complex process. Typically, crystallisation from the melt will involve; (i) Generation of critical nuclei of the crystalline phase as a result of undercooling; (ii) Growth of the stable nuclei by transport of species to the interface between the crystal and the melt, followed by; (iii) incorporation into the new phase. Any of the steps may control the rate at which the melt crystallises, as expressed in terms of the rate of change of the volume fraction, x, which has been transformed after a certain time, t. The aim is to derive an equation that relates x and t.

The driving force for the crystallisation of the melt at temperature T (and constant pressure) is the molar difference in Gibbs free energy, ΔG between the two phases (free energy of crystallisation) [22],

$$\Delta G = G_{xtal} - G_{melt} = \Delta H - T\Delta S, \qquad (4.1)$$

where ΔH is the molar enthalpy of crystallisation and where ΔS is the molar entropy of crystallisation. If there is equilibrium at some temperature T_e and the chemical potential/molar Gibbs free energy of the two phases are equal, $\Delta G = 0$ then $\Delta S = \Delta H / T_e$. We can then write

$$\Delta G = \frac{\Delta H \, \Delta T}{T_e}.\tag{4.2}$$

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 ΔT is the extent of undercooling, $T_e - T$, at temperature T. ΔH is negative in general, so the larger the undercooling, the more favourable is crystallisation of the melt. Before the new phase can grow, it must be nucleated. The theory of nucleation of new phases was originally developed by Volmer and Weber [23] and Becker and Doring [24] for the problem of condensation of a liquid from a vapour. It is thus often referred to as Volmer-Weber-Becker-Doring theory even when dealing with different systems [25]. The nuclei are the centres from which the phase transition starts. Their formation may be entirely due to local statistical fluctuations which bring the building blocks of the new phase together in the right configuration (Homogeneous nucleation), or it may happen at some sites which are particularly favourable for formation of the nuclei such as foreign substrates, inclusions etc (Heterogeneous nucleation). Theoretically, the latter can be treated as an extension of the former [25]. Formation of the nucleus is initially opposed by a surface free energy associated with the creation of the interface between the phases, but once the nucleus attains a critical size, the negative volume term associated with the formation of the new phase dominates. The nucleus is now said to be stable and will continue to grow. The free energy change for forming a critical nucleus can be found as follows [22-25]: If we consider a spherical cluster of species, which may become a critical nucleus if it grows large enough, the molar Gibbs free energy change ΔG_n on forming it is,

$$\Delta G_n = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_{\nu}, \qquad (4.3)$$

where r is the radius of the cluster, γ is an interfacial tension term (a free energy per unit area for creation of the interface between the phases), and ΔG_{ν} is the molar Gibbs free energy per unit volume for crystallisation. ΔG_n is a maximum when $\frac{d\Delta G_n}{dr} = 0$. This gives a value for the critical radius r_c of the nucleus above which ΔG_n begins to decrease, of

$$r_c = \frac{-2\gamma}{\Delta G_{\nu}}.$$
(4.4)

This corresponds to a critical value of ΔG_n of

$$\Delta G_{n,c} = \frac{16\pi\gamma^3}{3\Delta G_{\nu}^2}.$$
(4.5)

Fig. 4.1 shows the variation of ΔG_n with r, with the maximum $\Delta G_{n,c}$ occurring at r_c .



Fig. 4.1 Cluster free energy vs. cluster radius for nucleation of the crystal phase. The radius r_c and free energy of formation $\Delta G_{n,c}$ of the critical nucleus are indicated (dashed lines). At r = 0, $\Delta G_n = 0$.

Another assumption made here is that there is no strain due to volume differences between the two phases [25]. All such derivations imply that bulk thermodynamic quantities can be applied to the small number of species in the cluster. The number density of critical nuclei, n_c , can be approximated

by $n_c = n \exp\left(\frac{-\Delta G_{n,c}}{RT}\right)$ where *n*, is the number density of species in the melt and *R* is the Gas constant. The rate of nucleation R_n is the number of critical nuclei appearing per unit volume of the melt per unit time. The probability that a species can be transferred to the cluster is proportional to $\exp\left(\frac{-E_A}{RT}\right)$ where E_A is the molar activation energy for a species to move from the melt to the cluster. Thus the nucleation rate is [25]

$$R_n = A \exp\left(\frac{-\Delta G_{n,c} - E_a}{RT}\right)$$
(4.6)

A is related to the number density and frequency of jump of the species in the melt. In the case of heterogeneous nucleation, the nuclei form at favourable sites in the melt. The number of these sites is reduced by two processes, the birth of the stable growth nuclei of the crystalline phase and the ingestion of as yet inactive sites as the crystalline phase grows into the melt [26]. If the second process is neglected, the number density of growth nuclei at time t, $N_g(t)$ in terms of the number density of these sites N is $N_g(t) = N[1 - \exp(-Pt)]$ [27], where P is the probability that a site will become a stable nucleus. This is proportional to R_n , the rate of generation of critical nuclei, given above. Typically, two special cases are considered, that of large P, where $N_g(t) \sim N$ and small P, where $N_g(t) \sim NPt$. These are respectively the cases of instantaneous and progressive nucleation.

The other steps in the crystallisation process comprise the expansion of the stable nuclei into the melt to form the crystal. How this is dealt with depends to some extent on the nature of the growing crystal surface, or growth face [22]. For the purposes of crystal growth, faces can be classified as either singular or rough [22]. A perfect singular face is atomically smooth. Such a face has a minimum in its surface free energy change with filling of available surface sites when the fraction of filled sites tends to 0 or 1 [22]. As a result when material is transported from the melt it will only incorporate at favourable sites where it will be well bound to other species (as defined by the number of nearest neighbours on the surface as a ratio of the coordination number in the bulk crystal). These sites can occur either as the result of formation of 2d nuclei on the growth face (which is treated in a very similar way to the nucleation problem above [22]) or because of defects in the growth face. An example is the presence of steps that are singular (the overall crystal face is then described as vicinal). These may be formed even on a perfect singular face if the nucleation rate is faster than the completion of each layer. Another example is a defect – especially screw dislocations, as these are not destroyed by growth, unlike the ledges in a vicinal face. All of this assumes that species can arrive at the crystal face and then move to the preferred sites.

A face is rough if there are no preferred sites and species arriving from the melt are incorporated randomly without the nucleation of new layers. Such a face has a minimum in the free energy change on filling a site if half of available sites are full. If there is no motion of species after they arrive at the growth face (they stick where they land) then the growth face will always be rough even if the surface free energy suggests the face is singular. We will deal with rough faces here [22]. Rough faces occur when growth is controlled by mass transport [22].

The kinetically controlled rate at which the phase interface advances into the melt can be estimated by modelling the interface as a free energy barrier [22, 25], lower on the melt than on the crystal side, and determining the net flux of species from the melt to the crystal across the interface. Such a model for the interface is shown in Fig. 4.2 [22]. The rate of advance of the interface is found to depend on the extent of undercooling through ΔG according to (ΔG is defined to be negative for crystallisation as above):

$$u = C \exp\left(\frac{-\Delta G_I}{RT}\right) \left(\exp\left(\frac{-\Delta G}{RT}\right) - 1\right), \quad (4.7)$$

where ΔG_I is the molar free energy barrier for transfer of molecules across the crystal-melt interface and *C* is a frequency factor depending on the frequency of motion of species near the interface, the probability that motion is in the right direction, and the increase in volume of the crystalline region on addition of a single species from the melt [25]. An accommodation factor to account for the fact that all sites may not be suitable for species incorporating in the nucleus could also be included in the prefactor [25]. The derivation assumes that all these factors are similar for the flux to and from the growing nucleus.

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Fig. 4.2 Simple model of the crystal-melt interface [after Ref. 22] showing the various molar free energy barriers. ΔG_I is the free energy barrier associated with transporting a species from the crystal to the melt. λ is the width of the interface. ΔG_m and ΔG_c are the free energy barriers for motion of species in the melt and crystal. ΔG is the free energy of crystallisation, which was defined to be negative. The others are positive.

4.1.2 The Avrami Equation

When theoretical equations for the rate of formation of critical nuclei and the rate of growth have been determined, an equation for the rate of transformation of the melt, dx/dt, can be found in terms of the growth rate. Integration gives the transformed volume fraction, x. The final complication is the overlap of the various growth nuclei at long times. This was accounted for by Avrami [26] using the "extended volume" concept. If x is the transformed volume fraction, and x_e is the volume fraction the crystalline phase would occupy if the growth nuclei didn't overlap (the extended volume fraction), then [25, 26]:

$$x = 1 - \exp(-x_e). \tag{4.8}$$

In general, combining these concepts, x can now be found as shown by the derivation in Rao [25]. For example if there is instantaneous nucleation of N nuclei per unit volume that grow with a constant rate u in all 3 dimensions then the extended volume fraction they occupy at time t if they started to grow at t = 0 is

$$x_e = NAu^3 t^3. ag{4.9}$$

A depends on nucleus geometry. Using Avrami's relation for the extended volume fraction in terms of the real volume fraction gives for the special case of 3d instantaneous nucleation with a constant growth rate a transformed volume fraction of:

$$x = 1 - \exp(-NAu^{3}t^{3}).$$
 (4.10)

In general, the transformed volume fraction is given by [25]

$$x = 1 - \exp\left(-k_A t^n\right) \tag{4.11}$$

As we have seen, k_A is a kinetic parameter related to the numbers of nuclei and the rates of nucleation and growth, with factors dependent on nucleus geometry. The power, n, depends on whether the nucleation is instantaneous or progressive (or something in between), and whether transport from the melt to the growth nucleus, or kinetics of incorporation [as in Eq. (4.7)], controls the growth rate. It is often non-integral for mass transport controlled growth.

4.1.3 Orientationally Disordered Crystals

In orientationally (or rotationally) disordered crystals, the structure (position of the molecules in space) has the same translational symmetry as a normal crystal and can be described by a lattice and a basis. Unlike an ordinary crystal, the molecules may assume random orientations on their sites in the crystal. Since this results in a higher plasticity than is typical for a crystalline solid such materials are also known as plastic crystals [27]. These are molecular crystals, and the molecules tend to be spherical or disk-shaped [27], for example *m*-carborane and cyclohexanol. An interesting feature of such materials is that they have similar phenomenology to glassforming liquids. At high temperatures, the molecules in an orientationally disordered crystal can reorient rapidly. If the material is cooled rapidly enough, avoiding the formation of an orientationally ordered crystal, these reorientations will slow continuously until an

orientational glass transition temperature T_g^o is reached. Below T_g^o , reorientations are slower than the experimental timescale. The plastic crystal becomes a glassy crystal or "orientational glass" [27, 28]. This is analogous to the glass transition in an ordinary structural glassformer without the complications of spatial disorder and random translational motion. Since orientationally disordered crystals are simpler in this respect than glassformers, the glass transition in orientationally disordered crystals could be of help in understanding the glass transition in liquids. Fig. 4.3 [27] shows the interrelationships between the various phases that may be obtained when a liquid is cooled.

If the molecules have a dipole moment the dynamics of the orientationally disordered crystal can be studied by dielectric spectroscopy in the same way as the dynamics of a supercooled liquid or a glass. The characteristic peak in ε'' and dispersion in ε' associated with the α -relaxation are also observed in plastic crystals. JG β -relaxation has also been found in several plastic crystals (e.g. cyanoadamantane) at low temperatures. The JG β -relaxation is hidden beneath the α -relaxation above T_{ϵ}^{o} [27].



Fig. 4.3 Map [taken from Ref. 27] showing how various phases are obtained from the liquid phase. Upon cooling, the liquid may crystallise to either an orientationally ordered or disordered phase. The orientationally disordered or plastic crystal can undergo an orientational glass transition on further cooling. Alternatively, the liquid can be supercooled through its T_g to a structural glass and avoid crystallisation altogether.

4.2 Experimental

D-sorbitol (99.5 % – puriss.) in crystalline powder form was obtained from Fluka AG and used without further purification. The D-sorbitol molecule is shown in Fig. 4.4. It is has a total of six hydroxyl groups.



Fig. 4.4 Structure of D-sorbitol.

The D-sorbitol samples were prepared by heating to ~ 408 K in a vacuum oven. They were held at this temperature for about 24 h [6]. This both ensured that any adsorbed moisture was driven off and that the D-sorbitol crystals were thoroughly melted prior to measurements. Multiplate capacitors of similar design to those described in Chap. 3, but with a lower nominal empty capacitance of 17 pF were used (see Appendix A). The capacitor was cleaned by washing in heated water, and rinsing with deionised water, acetone, and *n*-hexane. A fresh capacitor was used after 2-3 measurements. The empty capacitance was measured prior to each measurement. The dielectric cell was filled with molten D-sorbitol, and the capacitor and a Pt-100 Ω temperature sensor quickly inserted while the D-sorbitol viscosity was still low, ensuring that no air bubbles remained trapped between the capacitor plates. The dielectric cell containing the liquid was maintained at a fixed temperature by using the Heto thermostatic bath system described in Appendix A. For measurements at temperatures below the room temperature, isopropyl alcohol was used as the working fluid in the cryobath. The sample was held at 298.5 \pm 0.1 K for a period of 92.7 h. Dielectric measurements were made, as in Chap. 3, using a Solartron FRA1255A frequency response analyser connected to a CDI, with both instruments controlled by Novocontrol WinDETA software. The ε' and ε'' spectra in the frequency range 1 Hz to 1 MHz were measured at 30 min intervals. After a certain period of maintaining the sample at a constant temperature and observing the changes in the spectra, the water in the bath was drained and replaced with isopropyl alcohol, and the ε' and ε'' spectra of the transformed state of the D-sorbitol sample were measured at several temperatures in the range 255.8 K to 280.5 K, on both sides of its liquid's T_g of 268 K. Dielectric measurements on D-sorbitol liquid kept at 271.1 ± 0.2 K, 332.4 ± 0.2 K, and at 332.8

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 \pm 0.2 K were carried out in a similar manner for periods of 138.5 h, 108.8 h, and 138.3 h respectively. The sample temperature was measured as in Chap. 3 by using a Keithley 195A digital multimeter to measure the resistance of the Pt-100 Ω resistor immersed in the D-sorbitol sample. The sample's temperature was measured at 1 min intervals during the course of the isothermal studies. The maximum deviation from a set temperature was found to be \pm 0.2 K, as noted above. The time for the beginning of the isothermal measurements was taken from the instant the temperature stabilised after the molten D-sorbitol had been removed from the oven. The stabilisation time was 5 min for the 298.5 K and 30 min for the 271.1 K, 332.4 K, and 332.8 K experiments. The sample's temperature was measured at 20 sec intervals during the course of obtaining the dielectric spectra over the indicated frequency range for the transformed state.

A simple Visual Basic computer program was written with Microsoft Visual Basic 6.0 during this study to allow complete computer control of all of the instruments used. The program could set the temperature on the cryobath, wait for stabilisation and then call the WinDETA software application (which was already set up and open) to measure and save dielectric spectra. The temperature during the spectra would then be monitored with the Keithley multimeter and saved to a text file. The measurements made on the transformed state produced by keeping the sample at 298.5 K were made using this program.

4.3 Results

Fig. 4.5(A) and (B) show ε' and ε'' spectra for supercooled liquid D-sorbitol measured at selected times during the period it was kept at 298.5 K. Several features and trends can be seen. Initially, the ε' spectra shows a plateau-like static permittivity, ε_s , at low frequencies and an inverted sigmoid-shape decrease to a lower value characteristic of dielectric dispersion. In the ε'' spectra, there is a corresponding broad peak at ~ 33 kHz. This broad peak has been seen as a merger of the α relaxation peak with the JG-relaxation peak, which are close to each other both in the ε'' intensity [3, 6, 7, 15] and relaxation rate of D-sorbitol liquid at 298.5 K [3, 6, 7,

13-15, 17]. The dispersion in the ε' spectra and the peak in the ε'' spectra measured at short times are thus typical of a supercooled liquid [3, 6, 7, 14, 15], containing contributions from both the α - and the JG β -relaxation processes. However at ~ 30 K above T_{e} , these are quite close in relaxation time and of comparable strength. It was impossible to resolve them by fitting so no detailed information is available about the behaviour of each as the state of the sample changes isothermally. Measurements over a wider frequency range as performed by others [6] and/or measurements at increased pressure [29] are required to separate the α - and JG β -relaxations this far above T_{ϱ} . At frequencies lower than 10² Hz, the ε'' spectra shows an increase in ε'' , which is attributable to the dc conductivity. However, since ε' does not rise rapidly at frequencies below 10^2 Hz, this dc conductivity does not cause an interfacial polarisation. As the sample is kept for a longer period at 298.5 K, both the low frequency plateau in the ε' spectra and the height of the peak in the ε'' spectra decrease. The dispersion in ε' and the ε'' peak become somewhat broader and do not entirely vanish even after keeping the sample for 92.7 h. At first sight, the relatively slow rise in ε'' at frequencies below 10 Hz indicates that the dc conductivity of the sample may have decreased by a factor of 11.8 on keeping the sample for 92.7 h at 298.5 K. But since the ε' spectra shows a slow rise in ε' in this frequency range, and the slope of the ε'' spectra is much less than unity, this rise in ε'' is to be seen as the high frequency range of a relaxation peak appearing at frequencies much lower than 1 Hz. It is indirectly concluded that supercooled D-sorbitol liquid crystallised to an orientationally disordered phase at 298. 5 K. The crystals formed have two characteristic relaxations, one large relaxation whose ε'' peak is at a frequency less than 10 Hz and the other whose peak is observed in the 40 - 80 kHz range. The depth of the minimum in the ε'' spectra at ~ 80 Hz initially decreases as crystallisation occurs and then increases. This cannot be a result of an increase in the dc conductivity because ε'' at 1 Hz decreases as crystallisation occurs. Instead, it is due to a decrease in the dc conductivity and the emergence of a second relaxation process at frequencies below 1 Hz at 298.5 K in the orientationally disordered state. The limiting high frequency permittivity, ε_{∞} , after 92.7 h is 5.1. This is the upper-bound value of ε_{∞} due to orientation polarisation. The ε' spectra measured at different times during the course of crystallisation of D-sorbitol show a large decrease in the plateau value, \mathcal{E}_{s} ,

and at long times even a loss of plateau-like region [compare the plot at 0.42 h with that at 92.7 h in Fig. 3.5(A)]. This also indicates that there is a second dispersion region at frequencies below ca. 10^2 Hz.

Fig. 4.6(A) and (B) show ε' and ε'' spectra measured at several temperatures for the sample which had been kept at a constant temperature of 298.5 K for 92.7 h. The general form of the spectra is very similar to those of the JG β -relaxation in glassy and supercooled D-sorbitol liquid reported earlier [1, 3, 11. 15, 17]. There is a peak in ε'' , and a corresponding broad and inverted sigmoid shape decrease in ε' . The increase in ε' with decrease in frequency at temperatures above 271.0 K and the low-frequency wing in ε'' are due to contributions from a relaxation peak, which is outside the spectral window. These spectra were analysed by the method described in more detail in Appendix B. The imaginary part of a two-term Havriliak-Negami [30] equation was fitted to the ε'' data. The equation for the complex permittivity, $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$, is thus:

$$\varepsilon^{*}(\omega) = \varepsilon_{\omega} + \frac{\Delta\varepsilon_{I}}{\left(1 + (j\omega\tau_{HNI})^{\alpha_{I}}\right)^{\beta_{I}}} + \frac{\Delta\varepsilon_{II}}{\left(1 + (j\omega\tau_{HNII})^{\alpha_{I}}\right)^{\beta_{II}}}, \qquad (4.12)$$

where the parameters are as described in Chap. 3. The subscript *I* refers to the low frequency relaxation, while the subscript *II* refers to the high frequency relaxation. In general, best fits to the data were found in all cases when $\beta_{II} = 1$ (Cole-Cole distribution). As in Chap. 3, the width parameters and the relaxation times for some process *i*, are related to the frequency of maximum loss, f_{mi} , by [31],

$$f_{m,i} = \left(2\pi\tau_{HNi}\right)^{-1} \left[Sin\left(\frac{\alpha_i\pi}{2+2\beta_i}\right)\right]^{1/\alpha_i} \left[Sin\left(\frac{\alpha_i\beta_i\pi}{2+2\beta_i}\right)\right]^{-1/\alpha_i}, \quad (4.13)$$

and $f_{m,i}$ is often used as a measure of the relaxation rate of the corresponding process. Representative ε' and ε'' spectra calculated from the values of the fit parameters in Eq. (4.12) at one temperature of 255.8 K are shown in Fig. 4.6. The quantities $\Delta \varepsilon_{II}$, α_{II} , and $f_{m,II}$ are also plotted against the temperature in Fig. 4.7(A), (B), and (C), respectively. These quantities refer to the localised motions and will henceforth be written as $\Delta \varepsilon_{JG}$, α_{JG} , and $f_{m,JG}$. For the sample of D-sorbitol crystallised for 92.7 h at 298.5 K, the values are shown by open data points, and the corresponding values for the JG β -relaxation in liquid D-sorbitol taken from data presented in Chap. 5 are shown, for comparison, by filled data points. The dashed vertical line indicates the dielectric T_g (268 K) of D-sorbitol.

The ε' and ε'' spectra of supercooled D-sorbitol liquid kept at 332.8 K were also measured at various times. At this temperature, the ε'' spectra showed no peak appearing in the frequency window, as expected on the basis of earlier studies [3, 5, 7, 11, 14, 15, 17]. Therefore, only the ε' spectra are shown in Fig. 4.8(A). The spectra show that ε' remains almost constant over a wide frequency range (0.1 kHz – 10^2 kHz) before crystallisation began. After 35.7 h, its value decreases rapidly at high frequencies and increases rapidly at low frequencies. The increase in ε' at low frequencies and the appearance of a progressively more rapid rise to very high values (in excess of 100 at 10 Hz) indicates strong effects due to interfacial polarisation as crystallisation occurs.

The ε' spectra for a liquid D-sorbitol sample kept at 332.4 K are shown in Fig. 4.8(B). The spectra differ from those of the sample kept at 332.8 K in Fig. 4.8(A) in two respects; (i) the interfacial polarisation effects on the ε' spectra are lesser in magnitude and discerned at a lower frequency and; (ii) the magnitude of ε' decreases to the lower value of ~ 5.6 after 108.1 h of crystallisation. The lower value of ε_s was also observed in the study of crystallisation of several other D-sorbitol samples near this temperature, and as will be discussed later here, this lower value indicated contamination of the liquid by small crystals because melting of the powdered Dsorbitol crystals requires a long time. The contamination inevitably produced an ordered crystalline phase.

Finally, a sample of D-sorbitol liquid was kept for 138.5 h at 271.1 K. It showed little change in its spectra over this period. Typical ε' and ε'' spectra obtained after 0.13 h and after 138.5 h are shown in Fig. 4.9(A) and (B). In the same figure are ε' and ε'' spectra for the sample held isothermally at 298.5 K after 83.8 h and 92.7 h. The latter spectra are very similar showing that the sample has almost completed the change to a disordered crystalline phase. To indicate the number of spectra collected and analysed in the case of the sample held isothermally at 271.1 K, the values of $\Delta \varepsilon_{JG}$ and α_{JG} obtained from the fit of Eq. (4.12) to the ε'' spectra, and $f_{m,JG}$ calculated from the fit parameters with Eq. (4.13), are plotted against annealing time in Fig. 4.10(A), (B), and (C) respectively. These values remain unchanged with time, which shows that the

sample of D-sorbitol liquid at 271.1 K showed no crystallisation discernable by dielectric spectroscopy in \sim 140 h (about 6 days).





Fig. 4.5 (A) The ε' spectra of supercooled liquid D-sorbitol kept at 298.5 K and measured at various times during a period of 92.7 as shown on the figure. (B) The corresponding ε'' spectra measured at these same times.



Fig. 4.6 (A) The ε' spectra of the D-sorbitol sample, which had been kept at 298.5 K for 92.7 h, measured at various temperatures. Also shown, as heavy lines are the fits of Eq. (4.12) to the data. The contributions, ε'_{α} , and ε'_{JG} , of the α -, and JG β -relaxation terms, are also shown for the fit to the 255.8 K spectra. Included in ε'_{JG} is the frequency independent term, ε_{∞} . (B) The corresponding ε'' spectra for these temperatures. The heavy lines are the fits of Eq. (4.12) to the spectra. The contributions of the α -, and the JG β -relaxation terms are shown for the fit to the 255.8 K spectra by dashed and dotted lines.



Fig. 4.7 (A) The dielectric strength parameter, $\Delta \varepsilon_{JG}$, is plotted against the temperature for the disordered crystalline state after the D-sorbitol sample had been kept for 92.7 h at 298.5 K (open symbols), and for the liquid state (filled symbols). Data for the liquid state is from Chap. 5. (B) The corresponding plots of the parameter, α_{JG} . (C) The corresponding plots of $f_{m,JG}$. The dashed line at 268 K denotes T_{g} of liquid D-sorbitol.



Fig. 4.8 (A) The ε' spectra of a liquid D-sorbitol kept at 332.8 K measured at various times during the period of 138.3 h, crystallised to a disordered phase. (B) The corresponding spectra of a new liquid D-sorbitol sample kept at 332.4 K and measured over a period of 108.1 h crystallised to an ordered phase.



Fig. 4.9 (A) Two ε' spectra for a D-sorbitol sample kept at 271.1 K. One was recorded after 0.13 h, and the second after 138.5 h. Also shown are two ε' spectra for a D-sorbitol sample kept at 298.5 K. One was recorded after 83.8 h and the second after 92.7 h, both of disordered crystalline phase (B) The corresponding ε'' spectra at the two times for each of the two different samples.



Fig. 4.10 (A) $\Delta \varepsilon_{JG}$ is plotted against time for the sample kept at 271.1 K. The solid line shows the mean value of 5.55. (B) The corresponding plot of α_{JG} . The solid line shows the mean value of 0.341. (C) The corresponding plot of $f_{m,JG}$ at 271.1 K. The solid line shows the mean value of 15.2. The dashed lines in all panels indicate the standard deviation from the mean. These parameters did not change with time showing that the structure of the supercooled liquid (as it is rather close to its T_g) does not change appreciably with time.

4.4 Discussion

4.4.1 Changes in Relaxation Processes During Crystallisation

Minoguchi and Nozaki have also followed the crystallisation of D-sorbitol at 303 K for 90 h by dielectric spectroscopy [6]. The use of a broader frequency range (100 μ Hz to 0.5 GHz for the final spectrum, with a higher minimum frequency of 0.1 Hz for the other spectra) allowed fitting of the α - and JG β -relaxation with Davidson-Cole and Cole-Cole dispersions respectively. The evolution of the fitting parameters with time could then be followed. They found that; (i) $\Delta \varepsilon_{\alpha}$ and $\Delta \varepsilon_{IG}$ begin to decrease with time about 40 h after the start of the isothermal anneal, the decrease in $\Delta \varepsilon_{\alpha}$ being more than 3 times the decrease in $\Delta \varepsilon_{JG}$; (ii) $f_{m,\alpha}$ and $f_{m,JG}$ also decrease with time by three and one decade respectively, with an onset time of 10 h; (iii) the Cole-Cole parameter, $\alpha_{CC} = 1 - \alpha_{HN}$, increases with time for both relaxations, also with an onset time of 10 h and; (iv) a new relaxation, which the authors called the α' relaxation appears at a frequency below that of the α -relaxation at about 4 h. As a result of contribution from this relaxation process, it was concluded that \mathcal{E}_s remains constant during the crystallisation, and even increases slightly at ~ 100 h [6]. This conclusion was based on the results of fitting only. This fitting equation has a large number of parameters, with up to 4 relaxation terms (the α - and JG β -relaxations, the α' -relaxation and a very low frequency relaxation for electrode polarisation), as well as dc conductivity loss term.

The decreases in $\Delta \varepsilon_{\alpha}$ and $\Delta \varepsilon_{JG}$ were assigned to a reduction in the volume fraction of the liquid phase as crystallisation proceeds. The α -relaxation involves co-operative motion of more than one molecule so this is more affected by the reduction in the volume of liquid than the JG β -relaxation, which is assumed to be local (not involving co-operative motion). The decrease in $f_{m,\alpha}$ and $f_{m,JG}$ occurs after the change in dielectric strength because the latter is more sensitive to the number of species involved. The slow α -relaxation process [6] was tentatively attributed to polarisation of molecules in the crystal-liquid interface or the in the crystal itself. However, the ε'

spectra of D-sorbitol in Fig. 2 of Ref. 6 do not show the low frequency plateau indicating ε_{e} corresponding to this polarisation. The decrease in the dc conductivity and the broad low frequency wing in the ε'' spectra of the sample kept at 298.5 K for 92.7 h [Fig. 4.5(B)] shows that the α -relaxation contribution from a small amount of uncrystallised liquid remains. Using the data of Wagner and Richert [3], and data from Chap. 5, one can extrapolate to 298.5 K and estimate the ratio $\Delta \varepsilon_{IG} / \Delta \varepsilon_{\alpha}$ to be 0.7 at this temperature. If, after crystallisation, the amount of residual liquid were ~ 2 %, it would be expected that $\Delta \varepsilon_{JG} \sim 0.28$ (2 % of 0.7 x $\Delta \varepsilon_{\alpha}$, where $\Delta \varepsilon_{\alpha} \sim 20$ [3]). The value of $\Delta \varepsilon_{JG}$ is actually about 3.2 at 280.5 K [see Fig. 4.7(A)] and $\Delta \varepsilon_{JG}$ should be larger still at 298.5 K. This is about 11 times the value of $\Delta \varepsilon_{JG}$ expected on the basis of an estimate of 2 % uncrystallised sample. It shows that the broad relaxation in the spectra after 92.7 h in Fig. 4.5 is not solely due to remaining liquid phase as implied previously. Rather, it is largely due to the new JG β -relaxation in the orientationally disordered crystalline state of D-sorbitol. Generally, $\Delta \varepsilon_{JG} / \Delta \varepsilon_{\alpha}$ is found to be smaller in the orientationally disordered crystal than in the liquid phase [27], so observations here are consistent with this.

It is found for a glass that $\Delta \varepsilon_{JG}$ increases more rapidly with temperature above the glass transition than below it [3, 32, 33]. The plot of $\Delta \varepsilon_{JG}$ vs. *T* for glassy and supercooled liquid D-sorbitol shows just such a change of slope around its T_g . This can be seen clearly in Fig. 5.12(A) of Chapter 5. In Fig. 4.7(A), it seems that for the orientationally disordered crystal there is a change in the slope of $\Delta \varepsilon_{JG}$ at the higher temperature of 279 K. Since there is only one data point above this temperature, it is not possible to be certain here. This would mean that the α -relaxation in the orientationally disordered crystal is at a lower frequency that that of the liquid, as was already suggested by an examination of Fig. 4.5(B) in the Results (Sect. 4.2).

4.4.2 Orientationally Ordered and Disordered Crystalline Phases

In Fig. 4.8, it is seen that the sample crystallised at 332.8 K [panel (A)] had an initially larger ε_s than the sample crystallised at the quite similar temperature of 332.4 K [panel (B)]. ε' of the 332.8 K sample does not attain as low a value of ε_s as

the 332.4 K sample, despite the fact it was maintained isothermally for a longer period. It is possible to explain the initial discrepancy in ε_s by the presence of air bubbles in the 332.4 K sample. The initial difference in ε_s is 8.3 % of the ε_s value for the 332.8 K sample (31.4). After 108.1 h, ε_s of the sample kept at 332.4 K has fallen to 5.5, while ε_s of the sample kept at 332.8 K is still 14.1 after 138.3 h. The percentage difference is now 61.0 %. It would be expected that this difference would remain quite similar if it were due entirely to air bubbles in the sample. Such discrepancies were also observed in other crystallisation runs not reported here. The explanation is that the liquid D-sorbitol sample crystallised at 332.4 K had been contaminated with some of the original crystals that were not entirely melted despite the precautions taken. More such crystals formed on cooling the melt to 332.4 K. Such crystals acted as seeds for the recrystallisation of the molten D-sorbitol to the original ordered crystalline phase resulting in a lower permittivity of 5.5. When the Dsorbitol was uncontaminated with such crystals, it transformed to the orientationally disordered crystal phase (Fig. 4.5).

4.4.3 Kinetics of D-sorbitol Crystallisation

D-sorbitol is an example of a liquid that is quite difficult to crystallise. It is very easy to supercool and as we have seen here will only crystallise slowly, even when in contact with its own crystals. Glycerol is another example of this type of liquid, while chlorobenzene is an example of the opposite type – a liquid that is hard to supercool and easy to crystallise. Some basic theory of nucleation and growth applicable to crystallisation from a melt was outlined in the Introduction (Sect. 4.1), and this led to an equation for the transformed volume fraction, *x* at time *t*:

$$x = 1 - \exp\left[-k_A \left(t - t_0\right)^n\right].$$

which can be rearranged as,

$$1 - x = \exp\left[-k_{A}(t - t_{0})^{n}\right].$$
 (4.14)

This equation is often used for solid-state phase transformations [25]. The time is offset by the time t_0 at which the phase transformation begins. In Eq. (4.11), $t_0 = 0$ is assumed. As we have seen, k_A is a temperature-dependent rate-constant related to the

numbers of nuclei, the rate of nucleation and growth, and nucleus geometry. The parameter *n* indicates whether the nucleation is instantaneous or progressive and whether mass transport or incorporation is the rate-controlling step. According to Eq. (4.14), a plot of 1 - x, which represents the volume fraction of melt remaining, against $log(t - t_0)$ will be an inverted sigmoid decreasing from 1 when crystallisation starts to 0 at an infinitely long time. The position of the inverted sigmoid shifts with k_A and as the temperature is decreased, k_A also decreases, and the inverted sigmoid shifts to longer times. The shape of the plot varies with *n*.

It is also possible to use for x in Eq. (4.11) and (4.14) any quantity which depends directly on the volume fraction of the crystalline phase provided it is normalised to be zero at the start $(t = t_0)$ and 1 at the end $(t = \infty)$ of the phase transformation. As a corollary, it is possible to use for 1 - x any quantity that is directly proportional to the amount of liquid phase remaining. The quantity must be normalised to be 1 at the start and 0 at the end of the transformation. If normalised quantities are not used, then if z is the unnormalised quantity that depends on 1 - x, Eq. (3.14) must become:

$$z(t) = z(t = \infty) + [z(t = t_0) - z(t = \infty)] \exp[-k_A(t - t_0)^n].$$
(4.15)

It would be expected that the slow crystallisation of the D-sorbitol melt would be controlled by mass transport because the melt is unstirred and its viscosity is high. It is also expected that Eq. (4.11) and Eq. (4.14) can be applied here, with ε_s as an appropriate parameter to represent the extent of crystallisation of the sample. At $t = t_0$, ε_s is that of the liquid D-sorbitol, while as the volume fraction of liquid phase decreases during the phase transformation, ε_s decreases towards the limiting value of the crystal phase. The normalised value of ε_s is thus a suitable quantity to use for 1 - x. A plot of ε_s against $\log(t)$ [or $\log(t - t_0)$] is thus expected to have an inverse sigmoid shape. Such plots are shown for the D-sorbitol samples crystallised at 332.8 K, 332.4 K, and 298.5 K in Fig. 4.11(A), (B), and (C) respectively. Some points should be noted concerning the determination of ε_s for these figures. Since there are very large contributions from interfacial polarisation in the ε' spectra at low frequencies at 332.8 K and 332.4 K, ε_s was estimated for these samples using ε' at 123 kHz and 112 kHz respectively. These frequencies fall in the plateau region of the ε' plots in Fig. 4.8(A) and (B). For the data for the sample crystallised at 298.5 K,

the interfacial polarisation (polarisation caused by ions collecting near the electrodes) contribution to ε_s is not as high and ε' at 10 Hz is used. This is exactly ε_s in the early measurements but becomes an approximation in the later measurements. Two interesting features of the crystallisation of D-sorbitol can be seen when the plots in Fig. 4.11(A), (B), and (C) are compared; (i) Crystallisation onset occurs more slowly when the liquid is contaminated with original crystal phase than when it is not, i.e., crystallisation to the orientationally-disordered crystal phase is faster in the beginning than for the ordered phase. Also, the shape of the plots differs in the two cases. (ii) The plot at 298.5 K has bodily shifted to shorter times relative to the plot at 332.8 K since it reaches a plateau sooner, thereby indicating that not only has the crystallisation onset decreased to a shorter time at a lower temperature but also the crystallisation rate constant k_A has increased.

The first feature is expected in view of the fact that D-sorbitol crystallises into two different phases, an ordered-phase at 332.4 K and an orientationally disordered phase at 332.8 K. The second feature is surprising because a decrease in temperature from 332.8 K to 298.5 K increases the viscosity, which in turn slows the rates of nucleation and crystal growth. A decrease in temperature also generally decreases the value of k_A thereby tending to shift the crystallisation kinetics curves to longer times. This may occur if the liquid's hydrogen-bonded structure changes at a low temperature. Such a change in the structure is expected to occur after the α -relaxation process has emerged from the JG β -relaxation process. For D-sorbitol this occurs at a temperature near 298.5 K. It would be significant to determine whether a similar change in the crystallisation kinetics is observable for other slowly crystallising liquids. Crystallisation of triphenylethylene has been observed to be accelerated close to T_g as a result of the JG β -relaxation [34]. However, crystallisation for D-sorbitol is found to be very slow just above T_g , as shown by the fact that the parameters of the JG β -relaxation vertime for the sample kept at 271.1 K (Fig. 4.10).



Fig. 4.11 (A) The magnitude of ε_s for a liquid D-sorbitol sample at 332.8 K taken as equal to its ε' value at ~ 10⁵ Hz is plotted against the logarithm of time allowed for crystallisation to the orientationally disordered phase. (B) The magnitude of ε_s for liquid D-sorbitol at 332.4 K taken as equal to its ε' value at ~ 10⁵ Hz is plotted against the logarithm of time allowed for crystallisation leading to orientationally ordered phase. (C) The magnitude of ε_s for liquid D-sorbitol at 298.5 K taken as its ε' value at 10 Hz is plotted against the logarithm of time allowed for crystallisation leading to crystallisation leading to an orientationally disordered crystalline phase.

4.4.4 Quantitative Analysis of Crystallisation Kinetics

It is possible to obtain the *n* and k_A parameters of Eq. (4.14) in two ways; (i) by nonlinear fitting of Eq. (4.14) directly to a plot of 1 - x vs. $\log(t - t_0)$ or (ii) from a plot of $\ln[-\ln(1-x)]$ vs. $\ln(t-t_0)$, which will be linear if Eq. (4.14) applies [25]. The slope of such a plot is *n*, while the intercept is $\ln(k_A)$. The first step is to normalise ε_s so that it represents the volume fraction of untransformed liquid remaining using

$$1 - x(t) = \frac{\varepsilon_s(t) - \varepsilon_s(t = \infty)}{\varepsilon_s(t = t_0) - \varepsilon_s(t = \infty)}.$$
(4.16)

In any case, such plots cannot be constructed for the ε_s data of D-sorbitol crystallised at 332.8 K and 332.4 K because the plateau value of ε_s at long times was not attained over the course of the crystallisation. It was attempted to fit Eq. (4.15) to the data instead [$\varepsilon_s(t = \infty)$ being an extra fitting parameter, $\varepsilon_s(t = t_0)$ is known] but results were not satisfactory. For the sample crystallised at 298.5 K the plateau value of ε_s is attained at long times and the phase transformation is almost complete. Eq. (4.16) could be used to normalise the ε_s data. The position of t_0 and $\varepsilon_s(t = t_0)$ are indicated in Fig. 4.12(A), which is equivalent to Fig. 4.11(C). The inset of Fig. 4.12(A) shows the plot of 1 - x against $\log(t - t_0)$. The heavy line in the inset is the fit of Eq. (4.14) to the data with n = 1.78 and $k_A = 2.12 \times 10^{-9}$. Fig. 4.12(B) is the plot of $\ln[-\ln(1-x)]$ vs. $\ln(t-t_0)$. From the slope and intercept of the straight-line fit to the data n = 1.58and $k_A = 1.87 \times 10^{-8}$. The difference between the parameter values obtained suggests that Eq. (4.14) is not entirely adequate to describe the crystallisation process. It can be seen in Fig. 4.12(B) that the data are not linear over the whole range and the slope seems to change with time. A value of n = 1.58 would correspond to the mass transport controlled growth with instantaneous nucleation of spherical particles with n = 1.5 theoretically (see p. 93 of Ref. [25]).

The liquid D-sorbitol sample held at 271.1 K provides further evidence of transport limitation on crystal growth rates. 271.1 K is the lowest temperature studied, and so it is the temperature at which crystallisation is most energetically favoured according to Eq. (4.2). However the sample is quite close to T_g , so its viscosity is high. As a result, the sample appears not to crystallise at all over 138.5 h. Spectra recorded at the

beginning and end of the anneal at 271.1 K superimpose well (Fig. 4.9), and the fitting parameters for the JG β -relaxation are approximately constant (Fig. 4.10).





Fig. 4.12 (A) Plot of ε_s of the D-sorbitol sample crystallised at 298.5 K against $\log(t)$. The offset time t_0 at which crystallisation starts (ε_s begins to decrease) is indicated. The dashed line is ε_s at this time. The inset shows the normalised value 1 - x obtained from ε_s with Eq. (4.16), plotted against $\log(t - t_0)$. The heavy line is the fit of Eq. (4.14) to the data. (B) Plot of $\ln[-\ln(1-x)]$ against $\ln(t - t_0)$. A straight line is fitted to the data. The value of *n* and k_A were obtained from the slope and intercept.

4.5 Summary

It is found that supercooled liquid D-sorbitol can transform to either an orientationally ordered or disordered crystal when held at a constant temperature below its melting point. The orientationally ordered form is obtained if the melt is contaminated by crystalline D-sorbitol. The evidence for existence of the orientationally disordered form is; (i) ε_s remains at ~ 14-15 after keeping a D-sorbitol sample for almost 6 days at a temperature of 332.8 K; (ii) the strength of the JG β -relaxation in a sample crystallised at 298.5 K for ~ 4 days is considerably larger than can be explained by the residue of a small amount of uncrystallised liquid phase, and; (iii) the presence of a new relaxation (α -relaxation of the orientationally disordered crystal) below 1 Hz in the sample crystallised at 298.5 K suggested by changes in the slope of the low frequency wing of the ε' spectra [Fig. 4.5(B)].

The strength of the Johari-Goldstein β -relaxation for the orientationally disordered crystal phase of D-sorbitol is less than half of that for the liquid, the spectra are considerably broader, and the relaxation rate is higher (Fig. 4.7). The rate of increase of this strength with temperature changes at a temperature of *ca*. 279 K, indicating that orientational glass transition in the disordered crystalline phase occurs at a higher temperature than T_g of the supercooled liquid, and that the rate of its α -relaxation process is lower.

If ε_s is considered proportional to the extent of crystallisation, then curves of ε_s against $\log(t)$ show a sigmoid shape, which is expected if the kinetics of crystallisation are described qualitatively by the Avrami equation. The sample crystallised at 298.5 K is the only sample for which ε_s attains a plateau value indicating a complete transformation. A quantative analysis with the Avrami equation was performed for the crystallisation at 298.5 K by normalising ε_s so that it corresponded to the volume fraction of liquid remaining, 1 - x. The slope and intercept of a plot of $\ln[-\ln(1-x)]$ vs. $\ln(t-t_0)$ gave for the parameters of the Avrami equation n = 1.58 (i.e. mass transport controlled growth with instantaneous nucleation of 3d nuclei) and $k_A = 1.85 \times 10^{-8}$. However, the slope of the plot changed with time indicating that the Avrami equation is not an exact description of the crystallisation kinetics.

Finally, the onset of crystallisation of D-sorbitol in the orientationally-disordered phase occurs at an earlier time at 298.5 K than at 332.8 K (Fig. 4.11), and the crystallisation rate is faster, which is opposite to what is expected given that cooling decreases both the crystallisation rate constant and the nucleation rate. This suggests that there is a structural change in the liquid at 298.5 K, which enhances the crystallisation rate. Thus it seems that deviation from the usual temperature dependence of crystallisation kinetics occurs in the temperature range of emergence of the α -relaxation from the Johari-Goldstein β -relaxation. At 271.1 K (3 K above its T_g), high viscosity again prevents crystallisation.

4.6 References

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Chapter 5

Johari-Goldstein β -relaxation in Small-Molecule Glassformers

5.1 Introduction

Two important properties of glasses are: (i) Stabilisation [1] or structural relaxation – the tendency of physical properties of the glass to approach those of the equilibrium liquid at the same temperature at a rate that increases as T increases toward T_g , and; (ii) β -relaxations. The "equilibrium liquid" is the supercooled liquid phase that would exist below T_g and the melting point if the glass transition or crystallisation did not intervene. It could also be attained if there were infinite time for the glass to stabilise. As discussed in detail in Chap. 2, Sect. 2.12, β -relaxations are local, occur at higher frequency than the structural α -relaxation, and persist below T_g . JG β -relaxations are β -relaxations that are intermolecular in origin rather than involving a motion of part of a molecule. Goldstein [2] postulated that intermolecular relaxations associated with local viscous flow processes may persist in discrete "islands of mobility" [2, 3] in the glass, and would involve transitions between neighbouring minima in a small region of the energy landscape. Johari and Goldstein [3] expanded on this idea and used it to explain β -relaxations in the dielectric spectra of rigid molecule glassformers. In this chapter, several small-molecule glassformers with β -relaxation thought to be of the JG type (there is debate in the case of diethyl phthalate [4, 5]) are studied by dielectric spectroscopy during heating at a constant rate and isothermal annealing. In the case of rapidly quenched glasses, these treatments expose the stabilisation

behaviour of the JG β -relaxation. The variation of the main properties (dielectric strength $\Delta \varepsilon_{JG}$, frequency of maximum loss $f_{m,JG}$, and symmetric broadness α_{JG}) of the JG β -relaxation with temperature and structural relaxation are examined below and above T_g and compared with the thermodynamic properties. Arguments are made against the Williams and Watts mechanism [6] of the JG β -relaxation (as a smallangle reorientation of *all* molecules, with a temperature independent small angle suggested by $_1^2$ H NMR experiments [7-9]), as opposed to the original idea of Johari and Goldstein (JG β -relaxation only involves some molecules and occurs in certain regions of a glass). The results for diethyl phthalate are also examined using the Coupling Model.

5.2 Experimental

Table 5.1Substances used in investigation of JG β -relaxation in small-moleculeglassformers.

Substance	Formula	Supplier	Purity
chlorobenzene	CI	Lancaster	99 %
<i>cis-</i> decalin	H	Fluka AG	98% (purum)
5-methyl-2-	ŎН	Fluka AG	98 %
hexanol			(purum)
D-sorbitol	ОН	Fluka AG	99.5 %
	ОН НО		(puriss.)
diethyl	/	Fluka AG	99.5 %
phthalate			(puriss.)

Table 5.1 gives a list of the substances, their structural formulae, supplier, and stated purity. All were used without further purification. JG β -relaxation in four small-molecule organic glassforming systems (one mixture and three pure liquids) was studied:

- (i) 16.6 mol% chlorobenzene in *cis*-decalin (i.e. 16.6 molecules of chlorobenzene per 100 solution molecules prepared by weighing).
- (ii) 5-methyl-2-hexanol
- (iii) D-sorbitol
- (iv) diethyl phthalate.

These glassformers all show α - and JG β -relaxations. 5-methyl-2-hexanol has three relaxations in the glass and supercooled liquid over the frequency range of interest (1 Hz – 10 MHz).

The dielectric cell used is the same as described before, consisting of a multiple plate capacitor with a nominal capacitance of 27 pF and a Pt 100 Ω platinum resistor sensor immersed in a small vial containing the liquid sample. The resistor allows direct monitoring of the temperature of the cell (see Chap. 3 and 4, and Appendix A). In each case, while preparing the cell, care was taken to ensure the absence of air bubbles between the capacitor plates. A different capacitor was used for each liquid studied and the capacitor was cleaned with acetone and *n*-hexane between measurements with the same liquid. In the case of D-sorbitol, warm deionised water was used to clean the capacitor first. D-sorbitol, unlike the other three glassformers is a solid at room temperature (melting point is ~ 368 K) and must be melted prior to filling of the cell. The D-sorbitol was heated to 400 K for 2-3 hr until its melt became transparent. The thermal treatment and dielectric measurements performed for each glassformer are now described in turn.

The chlorobenzene/*cis*-decalin solution ($T_g = 133$ K for a similar solution [3]) was vitrified by immersion in liquid N₂ at 77 K. The dielectric cell was transferred to the temperature-controlled Oxford cryostat (see Chap. 3 and Appendix A) and heated to ~ 103 K. The sample was then heated at a nominal rate of 0.08 K min⁻¹ to above T_g . Dielectric permittivity ε' , and loss ε'' , spectra between 10 Hz and 1 MHz were continuously recorded using a CDI and Solartron FRA-1255A frequency response analyser (Appendix A). 4-6 temperature measurements were made during each

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frequency scan, which lasted, on average 194 s. The maximum temperature rise over a scan was 0.33 K.

5-methyl-2-hexanol was also quenched in liquid N₂. Two different thermal treatments were followed. In the first, the sample was transferred to the cryostat and heated quickly to 105 K, and then heated slowly through its T_g ($f_{m,\alpha} = 10^{-4}$ Hz) of 148 K at 0.1 K min⁻¹. During the slow temperature increase, the dielectric spectra were measured continuously between 10 Hz and 1 MHz as for chlorobenzene/*cis*-decalin. These scans took an average of 218 s over which the temperature rose by at most 0.36 K. 4-6 temperature measurements were made during each scan. In the second, the sample was heated to 131.6 K and the temperature allowed to stabilise for ~ 30 min, after which the sample was isothermally annealed for 14.6 ks (4.1 h). Again, dielectric spectra were measured continuously over the same frequency range. The maximum temperature deviation was ± 0.1 K over the course of annealing.

For D-sorbitol ($T_g = 268$ K for $\tau_{\alpha} = 100$ s [10]), after filling of the dielectric cell, it was transferred to a cryostat at ~ 390 K. When the temperature had stabilised above the melting temperature, five glasses (A-E) were prepared using different rates of cooling as follows. The cooling curves for the preparation of the quenched glasses A, and C-E are shown in Fig. 5.1.

Sample A was cooled in the cryostat from 391.8 K to 221.1 K at 10 K min⁻¹. The sample was then heated at 0.1 K min⁻¹ through T_g . Dielectric spectra in the frequency range 10 Hz – 1 MHz were measured continuously during heating. Sample B was cooled from 392.9 K to 281.3 K at 5 K min⁻¹, and slowly cooled at 0.1 K min⁻¹ to 221.6 K.

Sample C was quenched from 390.6 K in liquid N₂. It was then heated rapidly in the cryostat to 220.4 K. Dielectric spectra were again measured continuously during heating at 0.1 K min⁻¹ through T_g .

The average time required to measure a spectra for samples A to C was 206 s, corresponding to a 0.34 K temperature rise or fall over the course of a measurement. Sample D was quenched from 399.3 K in liquid N₂. It was heated rapidly to 205.3 K. Dielectric spectra, this time in a narrower frequency range of 1 Hz – 10 kHz were measured in the course of slow heating to 234.3 K at 0.1 K min⁻¹. The temperature rose by 0.31 K in the 186 s required for measurement of a single spectra.
D-sorbitol sample E was heated to 396.7 K, quenched in liquid N₂, and annealed in the cryostat at 221.1 K for 16.0 ks (4.5 h). The maximum temperature deviation was \pm 0.1 K. Unlike for 5-methyl-2-hexanol, most of the temperature stabilisation time of ~ 30 min is included in the duration of the anneal.

The dielectric properties of the diethyl phthalate (Calorimetric $T_g = 180$ K [11]) samples was measured using a different temperature control system (a cryostat cooled by a nitrogen gas jet system whose temperature is adjusted by a Novocontrol Quattro controller) and broadband dielectric spectrometer (Novocontrol Alpha with active sample head). The gas jet also provides an inert atmosphere around the sample. This system is described in detail in Appendix A. The dielectric cell was similar to that used in the other measurements but requiring an extra connection to the sample head, which causes a small additional lead impedance that is not considered. The system controls the temperature using a sensor close to the sample inside the cryostat. The actual temperatures used in the results were determined instead via the sensor inserted in the dielectric cell and the multimeter, as for the other substances. The maximum cooling rate of the system was used so that the sample cooling rate slowed as the base temperature of 119.5 K, which is below the rated minimum temperature for the system of 123.2 K [12], was approached in ~ 1 h. A portion of this cooling curve is shown in Fig. 5.2. The sample was then heated to 226.3 K at 0.08 K min⁻¹, which is well above T_g and allows α -relaxation data for the liquid to be presented. During heating the dielectric spectra in the frequency range 1 Hz - 10 MHz were measured continuously. In practice, the higher frequency limit was not always attained due to lead impedance contributions to the measured capacitance above 1 MHz. These become significant when the capacitance of the sample is low (i.e. during low temperature measurements in the glassy state). Several temperature measurements (6-7) were made during each scan and the average of these was taken as the temperature for that scan. The mean time for each scan was 135 seconds, which equates to a temperature rise of ~ 0.18 K over the course of a scan.

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Fig. 5.1 Cooling curves for D-sorbitol glasses. Glass A was quenched at 10 K min⁻¹ and glasses C, D, and E were quenched in liquid N_2 (77 K).





5.3 Results

The results for each glassformer are given in turn below. The extraneous effects of measuring the dielectric spectra while heating at a constant rate are discussed first. Since the dielectric spectra take a finite time to measure, a temperature rise occurs which means that the broadness, $\Delta \varepsilon$, ε_{∞} , and ε'' peak position of any relaxation (i.e., the quantities that describe the dielectric spectra) have changed in the interval between recording the first and last frequency points. The changes in the peak frequency would also affect the shape of the spectra. The largest temperature rises

over the course of a frequency scan were ~ 0.4 K. Taking the example of D-sorbitol, Gangasharan and Murthy [13] found that the temperature dependence of $f_{m,JG}$ in the glass could be described by an Arrhenius equation with an activation energy, E_A , of 55.35 kJ mol⁻¹ and $A_{ARR} = 10^{14.98}$ Hz, which would mean that log $f_{m,JG}$ would change by 0.024 decades at 221.1 K given a 0.4 K temperature increase to 221.5 K. If the temperature dependence of $f_{m,JG}$ becomes stronger above T_g (slope of the plot of log $f_{m,JG}$ vs inverse temperature becomes more negative) as has been found by some workers and is suggested by the Coupling Model (see Chap. 2), the temperature rise will have a greater effect on the peak position. Above T_g , $\Delta \varepsilon_{JG}$ increases more rapidly with temperature so the temperature rise should also have more effect on dielectric strength in this region. Data above T_g may thus be more affected by the temperature increase and less reliable.

The effect of peak frequency change can be quantified more easily for the case deep in the glass where α_{JG} and $\Delta \varepsilon_{JG}$ are approximately temperature independent and only $f_{m,JG}$ changes as the temperature increases over the course of a scan. The high frequency tail of the α -relaxation should not change much with temperature here either, so temperature effects on this are neglected too.

The complex permittivity $\varepsilon^*(\omega)$, where $\omega = 2\pi f$ is the angular frequency if f is the frequency, for D-sorbitol at 221.1 K may be fitted by an equation similar to Eq. (4.12) used in Chap. 4 for the plastic crystalline state of D-sorbitol, *viz* two Havriliak-Negami (HN) terms [14]:

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon_{\alpha}}{\left(1 + (j\omega\tau_{HN\alpha})^{\alpha_{\alpha}}\right)^{\beta_{\alpha}}} + \frac{\Delta\varepsilon_{JG}}{\left(1 + (j\omega\tau_{HNJG})^{\alpha_{JG}}\right)^{\beta_{JG}}},$$
(5.1)

where ε_{∞} is the limiting high frequency permittivity, $\Delta \varepsilon_{\alpha}$ is the dielectric strength of the α -relaxation, $\tau_{HN\alpha}$ is the HN relaxation time of the α -process, α_{α} is the symmetric broadness parameter, and β_{α} the asymmetric broadness parameter. The JG subscript denotes the same parameters for the JG β -relaxation.

The best fit is obtained with $\beta_{JG} = 1$ (Cole-Cole dispersion [15]). This means that $\tau_{HNJG} = \tau_{JG}$, the JG β -relaxation time corresponding to the frequency of maximum

loss. The change in the form of the JG β -relaxation term during a ramped measurement is shown by comparing the JG β -relaxation fitting curve for constant τ_{IG} to that when τ_{IG} varies during the scan as a result of a temperature ramp (see Fig. 5.3). The important quantities here are the rates of the frequency scan (assumes 206 s to cover 5 decades of frequency – 0.024 decades s⁻¹) and the temperature ramp (0.1 K min⁻¹ = 1.67 mK s⁻¹). The parameters $\Delta \varepsilon_{IG}$ and α_{IG} for the Cole-Cole JG β relaxation term are taken from those for the first D-sorbitol spectra recorded after temperature stabilisation during anneal of sample E at 221.1 K. τ_{IG} is calculated at each temperature from $f_{m,IG} = A_{ARR} \exp(-E_A/RT)$ and the values for A_{ARR} and E_A of Gangasharan and Murthy [13]. It is seen in Fig. 5.3 that the Cole-Cole terms overlap almost exactly.



Fig. 5.3 (A) ε' and (B) ε'' components of the JG β -relaxation term of the fit of Eq. (5.1) to dielectric data for D-sorbitol sample E annealed at 221.1 K (solid line). The components of the same term are shown (dashed line) calculated when the temperature is increased at 0.1 K min⁻¹ from the start of the dielectric spectra, measured at 0.024 decades s⁻¹.

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5.3.1 Chlorobenzene/cis-decalin Mixture

cis-decalin is an easy glassformer in the sense discussed in Chap. 2. Its molecular dipole moment is low however, so in order to study *cis*-decalin glasses by dielectric spectroscopy, Johari and Smyth [16] and Johari and Goldstein [3] added chlorobenzene, which crystallises easily but has a large dipole moment, to create polar glasses consisting of rigid small molecules that may be studied by dielectric techniques.

 ε' and ε'' spectra for 16.6 mol% chlorobenzene in *cis*-decalin quenched in liquid nitrogen and heated at 0.08 K min⁻¹ are shown in Fig. 5.4 (A) and (B) for several temperatures. There is a broad step in ε' and peak in ε'' , which is the JG β -relaxation [3]. On the low frequency side, a wing appears as the temperature increases. This is the emergence of the α -relaxation into the frequency window as the temperature increases. The evolution of the dielectric spectra with temperature is analysed using the values of the parameters of Eq. (5.1), which is fitted to the dielectric spectra. The other important quantity is the frequency of maximum loss of a relaxation, which can be obtained using Eq. (1.63) [17] as discussed in Chap. 1. For the *i*th relaxation:

$$f_{m,i} = \left(2\pi\tau_{HNi}\right)^{-1} \left[Sin\left(\frac{\alpha_i\pi}{2+2\beta_i}\right)\right]^{\frac{1}{\alpha_i}} \left[Sin\left(\frac{\alpha_i\beta_i\pi}{2+2\beta_i}\right)\right]^{\frac{-1}{\alpha_i}}.$$
(5.2)

Since only the high frequency wing of the α -relaxation extends into the frequency window, reliable values are obtained only for the JG β -relaxation parameters. Best fits were obtained when $\beta_{JG} = 1$ was used at all temperatures. Fig. 5.4 also shows the deconvolution of the total fit curve into the contribution of the α -relaxation and JG β -relaxation terms to ε' and ε'' for the temperature of 135.0 K. The values of the fit parameters for the JG β -relaxation in chlorobenzene/cis-decalin at this temperature are: $\Delta \varepsilon_{JG} = 0.321$, $\tau_{JG} = 3.44 \,\mu$ s, and $\alpha_{JG} = 0.340$.



Fig. 5.4 The (A) ε' and (B) ε'' spectra of 16.6 mol% chlorobenzene in *cis*decalin quenched in liquid N₂ measured at various temperatures below and above T_g during slow heating at 0.08 K min⁻¹. Thin continuous lines through the data for the first four temperatures are guides only. The contribution of the α -relaxation and JG β relaxation terms to the overall fit at 135.0 K (heavy line) are shown as solid and dashed lines in both panels.

FIG 5.5



Fig. 5.5 Plot against the temperature of the parameters (A) α_{JG} and (B) $\Delta \varepsilon_{JG}$ obtained from the fits of Eq. (5.1) to the dielectric spectra of 16.6 % chlorobenzene/*cis*-decalin. T_g of 133 K for a 16.5 mol% mixture [3] is also indicated on the plots.

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Fig. 5.6 Plot of $f_{m,JG}$ on a log scale for the chlorobenzene/*cis*-decalin mixture against inverse temperature. T_g is indicated on the plot. The straight line is the fit of the Arrhenius equation to the data.

Fig. 5.5(A) and (B) show a plot of α_{JG} and $\Delta \varepsilon_{JG}$ against the temperature respectively. These both increase with the temperature, which corresponds to the narrowing and increase in the loss peaks clearly seen in Fig. 5.4(B) as *T* increases. At a temperature of 133 K, which is close to the expected T_g of such a glass as indicated on the plot, $\Delta \varepsilon_{JG}$ begins to increase more rapidly. There is a change in the slope of the $\Delta \varepsilon_{JG}$ vs. *T* plot for the glass. Fig. 5.6 shows the plot on a log scale of $f_{m,JG}$ against inverse temperature (1000/*T*). The data is linear both in the glass and above T_g , as found previously by Johari and Goldstein [3] for this glassformer, and can be described by the Arrhenius equation $f_{m,JG} = A_{ARR} \exp(-B_{ARR}/T)$ [Chap. 3, Eq. (3.12)], with an activation energy $E_A = B_{ARR}$. *R* in J mol⁻¹ where *R* is the gas constant. For chlorobenzene/*cis*-decalin $A_{ARR} = 10^{15.37}$ Hz and $B_{ARR} = 3331$ K. These values are also given together with those of the JG β -relaxations in the other glassformers in Table 5.2 at the end of Sect. 5.3.

5.3.2 5-methyl-2-hexanol

Typical ε' and ε'' spectra for the pure 5-methyl-2-hexanol sample which was quenched in liquid N₂ and heated slowly at 0.1 K min⁻¹ are shown in Fig. 5.7(A) and (B). The form of the spectra is similar to those of chlorobenzene/*cis*-decalin in Fig. 5.4. There is a broad peak in ε'' , a corresponding dispersion in ε' and a wing in ε'' that becomes more prominent as the temperature increases. As discussed in Chap. 3, 5-methyl-2-hexanol has, in common with many aliphatic alcohols, three relaxations in the dielectric spectra of its supercooled liquid and glassy phases in the radiofrequency and low microwave regions. In the current temperature range, the loss peak corresponds to process III in the terminology of Chap. 3. This has been assigned as a JG β -relaxation [18]. The low frequency wing corresponds to the high frequency edges of processes II and I, which were shown to emerge into the frequency window in pure 5-methyl-2-hexanol [18], and for 5-methyl-2-hexanol solutions in Chap. 3 as the temperature increases. It should be noted therefore that this wing cannot be due to any dc conductivity contribution to ε'' . In any case, the slope of the wing on a log-log plot of ε'' vs. ω is not – 1 as it should be for a dc conductivity contribution. These points also apply to the similar low frequency wings observed in the spectra of the other glassformers discussed here. Since both these processes lie outside the frequency window they may be represented by one general HN term as for the α -relaxation in chlorobenzene/*cis*-decalin. This allows Eq. (5.1) to be used to fit the dielectric spectra. The parameters of this term will not contain any useful information about processes I and II. Only the ε'' peak of process III appears in the frequency window, and may be fitted by the 2nd term of Eq. (5.1) for extraction of parameters associated with the JG β -relaxation. The fit of Eq. (5.1) to the data is shown for a single temperature of 149.5 K in Fig. 5.7. As for chlorobenzene/*cis*-decalin it was found that the best fits were obtained when a Cole-Cole dispersion was used to fit the JG β -relaxation at all temperatures for both the slowly heated and annealed samples. The values of the parameters for the JG β -relaxation at 149.5 K are: $\Delta \varepsilon_{JG} = 0.0791$,

 $\tau_{JG} = 3.00 \,\mu \text{s}$, and $\alpha_{JG} = 0.439$.

Fig. 5.8(A) shows the variation of α_{IG} with the temperature for the slowly heated sample. As for chlorobenzene/cis-decalin, α_{IG} increases and the broadness of the spectra decreases monotonically as the temperature increases. The evolution of the strength parameter for the JG β -relaxation of the slowly heated sample is interesting. The plot of $\Delta \varepsilon_{IG}$ vs. T [Fig. 5.8(B)] shows an initial decrease with temperature from 0.105 at 115.3 K to 0.073 at 145.6 K and a subsequent increase to 0.106 at 159.1 K. The JG β -relaxation in the quenched chlorobenzene/cis-decalin mixture did not show this behaviour as it was heated. Fig 5.9 shows the Arrhenius plot of $f_{m,IG}$ calculated using Eq. (5.2). It is clearly visible that unlike chlorobenzene/cis-decalin, the data depart from an Arrhenius straight line. This departure takes the form of a stronger temperature dependence below ~ 140 K (a more negative slope at lower temperatures). There may be a small region around T_g where $f_{m,JG}$ becomes less dependent on temperature, and a suggestion of a region above T_g where the temperature dependence changes again but the frequency range is too limited and the α - and JG β -relaxation peaks too close to be certain of this. An Arrhenius equation has been fitted to the high temperature data with $A_{ARR} = 10^{12.54}$ Hz and $B_{ARR} = 2690$ K, excluding the highest temperature data where the dependence may change again.

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The evolution of the parameters of the JG β -relaxation with time for the sample annealed at 131.6 K for 14.6 ks is also shown. Fig. 5.10(A), (B) and (C) are plots of α_{JG} , $\Delta \varepsilon_{JG}$, and $f_{m,JG}$ against annealing time in ks (the initial 30 min stabilisation period is not included in this time). α_{JG} and $f_{m,JG}$ appear to be fairly constant with annealing time. There is a suggestion that α_{JG} and $f_{m,JG}$ may increase slightly during the anneal since the values before ~ 2 ks are generally below the values later in the anneal. It is clear that $\Delta \varepsilon_{JG}$ decreases as the anneal progresses from 0.083 to 0.074 according to an exponential decay: $\Delta \varepsilon_{JG}(t) = 0.0736 + 0.00825.\exp(-t/3463)$. t is the time in seconds since the stabilisation of the temperature.



Fig. 5.7 The (A) ε' and (B) ε'' spectra of 5-methyl-2-hexanol quenched in liquid N₂ and heated slowly at 0.1 K min⁻¹ at several temperatures. Curves through the data for the first four temperatures are guides to the eye only. The heavy solid line through the ε' and ε'' data at 149.5 K is generated from the real and imaginary parts of Eq. (5.1) with appropriate fit parameters. This is decomposed into the contributions from the α - and JG β -relaxation HN terms (solid and dashed lines) as indicated on the plot.



Fig. 5.8 (A) α_{JG} and (B) $\Delta \varepsilon_{JG}$ against the temperature for the slowly heated 5methyl-2-hexanol sample obtained from the fit of Eq. (5.1) to the data. T_g of 148 K is indicated on the plot.



Fig. 5.9 Plot of $f_{m,JG}$ on a log scale for 5-methyl-2-hexanol against inverse temperature. T_g is indicated on the plot. The straight line is the fit of the Arrhenius equation to the data in the limited temperature range of 134.2 K – 154.2 K. The lower temperature data are excluded as these depart from the Arrhenius line due to relaxation effects while the higher temperature data are excluded because these may depart from the Arrhenius line due to a change in the temperature dependence of the JG β -relaxation as discussed in connection with the Coupling Model in Chap. 2.



Fig. 5.10 (A) α_{JG} , (B) $\Delta \varepsilon_{JG}$, and (C) $f_{m,JG}$ for the 5-methyl-2-hexanol sample, which was quenched in liquid N₂ and annealed at 131.6 K, plotted as a function of the annealing time in ks. The dashed line through the $\Delta \varepsilon_{JG}$ data is a fit of the exponential decay function $\Delta \varepsilon_{JG}(t) = 0.0736 + 0.00825 \cdot \exp(-t/3463)$, where t is the elapsed time in seconds.

5.3.3 D-Sorbitol

D-sorbitol has been extensively studied by many groups as a model small-molecule glassformer using a battery of techniques including dielectric [10, 13, 18-33], NMR [7, 8, 30, 31, 34], solvation dynamics [26], dielectric hole burning [35], mechanical spectroscopy and viscosity measurements [27], DSC [13, 36, 37], and dilatometry [38]. One of these studies was of its crystallisation [22]. Its large dipole moment and ease of preparation as a glass make it very popular for use in dielectric spectroscopy studies. The large number of –OH groups mean that D-sorbitol glasses will have complicated network structures of molecules linked by H-bonds.

Fig. 5.11(A) and (B) show the ε' and ε'' spectra of D-sorbitol sample A (cooled at 10 K min⁻¹ and heated at 0.1 K min⁻¹) at selected temperatures. Dielectric spectra for the other thermal treatments were qualitatively similar. The spectra have the same form as for the other glassformers – a peak in ε'' due to a JG β -relaxation and a wing at low frequencies due to the α -relaxation. The spectra are analysed in the same way as before by fitting of Eq. (5.1) to the data to extract the dielectric strength, broadness, and frequency of maximum loss [from Eq. (5.2)] of the JG β -relaxation. The fitting equation and its decomposition into α - and JG β -relaxation terms is shown for 265.4 K in Fig. 5.11. As before, a Cole-Cole dispersion provides the best fit to the JG β -relaxation peak in ε'' . The fit parameters of the JG β -relaxation at this temperature were: $\Delta \varepsilon_{JG} = 4.64$, $\tau_{JG} = 14.9 \,\mu$ s, and $\alpha_{JG} = 0.336$.

The plots of $\Delta \varepsilon_{JG}$ against *T* for D-sorbitol samples A – C are shown in Fig. 5.12(A). As observed for the chlorobenzene/*cis*-decalin mixture in Fig. 5.5(B), $\Delta \varepsilon_{JG}$ of states A and B increases slowly initially and, then as the glass softens near T_g , it increases rapidly. For D-sorbitol, this rapid increase begins at ~ 265 K. In contrast, Nozaki et al. [21] have found that its $\Delta \varepsilon_{JG}$ increased smoothly from 270 K to 288 K. A change similar to that seen in Fig 5.8(B) and Fig. 5.12(A) had been observed for D-sorbitol [10, 13], and other liquids [39], as well as for a polymer [40]. In Fig. 5.12(A), $\Delta \varepsilon_{JG}$ of sample C decreases on heating from 220 K to 230 K, showing a shallow minimum before $\Delta \varepsilon_{JG}$ begins to increase. This is similar to the feature observed for 5-methyl-2-hexanol, for which the minimum was more pronounced [see Fig. 5.8(B)]. This can be

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seen more clearly in Fig. 5.12(B) where the value of $\Delta \varepsilon_{JG}$ of D-sorbitol sample D is plotted against *T*. It decreases with increase in *T* and appears to reach a broad local minimum.

 α_{JG} of the samples A – D is plotted against *T* in Fig. 5.13. For samples A – D, α_{JG} increases on heating. Data for sample A and C agree within the errors, those for sample B (the sample cooled slowly at 0.1 K min⁻¹) are slightly higher at low temperatures, while those for sample D (quenched in liquid N₂) are *ca.* 4.1% higher than that of sample A at 221.1 K. For all samples A – D, α_{JG} increases with increase in *T*, from 0.253 at 221.1 K to 0.346 at 271.2 K for sample A, from 0.256 at 221.6 to 0.371 at 276.1 K for sample B, from 0.247 at 220.4 K to 0.351 at 274.4 K for sample C, and from 0.232 at 205.3 K to 0.299 at 234.3 K for sample D.



Fig. 5.11 The (A) ε' and (B) ε'' spectra of D-sorbitol sample A (cooled from 391.8 K to 221.1 K at 10 K min⁻¹ and heated slowly at 0.1 K min⁻¹ as spectra were measured) at several temperatures. Curves through the data for the first eight temperatures are fits of Eq. (5.1). The heavy solid line through the ε' and ε'' data at 265.4 K is generated from the real and imaginary parts of Eq. (5.1) with appropriate fit parameters. This is decomposed into the contributions from the α - and JG β -relaxation HN terms (solid and dashed lines) as indicated on the plot.



Fig. 5.12 (A) $\Delta \varepsilon_{JG}$ of the glassy and liquid states of D-sorbitol is plotted against the temperature. The dielectric T_g at 100 s [10] is marked on the plot. Notations used for samples A – C are as indicated. (B) The $\Delta \varepsilon_{JG}$ of glassy D-sorbitol sample D, which was obtained by quenching in liquid N₂, is plotted against the temperature.



Fig. 5.13 α_{JG} of D-sorbitol is plotted against the temperature. Notations for different samples A – D, which were prepared as described in the text are indicated. The position of T_g is also shown.

The plots of $f_{m,JG}$ on a log scale against inverse temperature are shown in Fig. 5.14. The plots for samples A – D lie close to each other, showing that the sample history has a relatively small effect on $f_{m,JG}$. This sample history dependence of $f_{m,JG}$ is consistent with the effect of density increase observed by Naoki and Ujita [20]. They had found that $f_{m,IG}$ of D-sorbitol vitrified under a pressure of 785 bar and studied at 1 bar was 23 % higher than $f_{m,JG}$ of the sample that had been vitrified at 1 bar by cooling at 0.2 K/min and at 2.0 K/min rates. However, Naoki and Ujita [20] also found that several features of the Johari-Goldstein relaxation in D-sorbitol are distinguished from those of other small-molecule and polymeric glasses. In particular; (i) $\Delta \mathcal{E}_{JG}$ of a 0.6 % higher density D-sorbitol glass obtained by vitrifying under 785 bar pressure was found to be larger and the distribution of relaxation times narrower than those of the glass obtained by vitrifying at 1 bar pressure and; (ii) $\Delta \varepsilon_{JG}$ of both the higher and lower density glasses was found to increase slightly with increase in pressure [20]. Similar effects have been observed in ion-containing alcohols and attributed to the hydrogen-bond breaking effects and electrostriction [41]. However, Nozaki et al. [21] also reported that ε_s of liquid D-sorbitol decreases with decrease in T, and $\Delta \varepsilon_{JG}$ increases, which means that contribution to $\Delta \varepsilon$ from the α -relaxation process decreases with decrease in T. In contrast, more recent studies have shown that $\Delta \varepsilon$ of the α -relaxation process *increases* with decrease in T (Fig. 7 in Ref. [10]) Since such inconsistencies can also arise if samples of D-sorbitol used by different groups were contained different impurities and/or their respective data analysis differed, the observations on $\Delta \varepsilon_{JG}$ in relation to ε_s are not discussed. There does not appear to be any temperature independent region in $f_{m,JG}$ around T_g or change in temperature dependence for the data above T_g . The former [23, 33] and the latter [10, 23, 28, 29, 33] have both been found for JG β -relaxation in D-sorbitol. Neither is a broad maximum observed as was found by Olsen [25] for $f_{m,JG}$ of Dsorbitol. The observation of a minimum has not been confirmed by others. The results here should not be seen as conclusive as the data here do not extend far above T_g due to the limited frequency range and difficulty of separation of the α - and JG β -

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relaxation above T_g where they are similar in strength and relaxation time. An

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Arrhenius equation has been fitted to the high temperature data of sample C (above 250 K) with $A_{ARR} = 10^{14.29}$ Hz and $B_{ARR} = 6311$ K and is shown by a dashed line in Fig. 5.14. In common with the 5-methyl-2-hexanol sample (Fig. 5.9), data for the rapidly quenched samples C and D shows a departure from this line, having lower then predicted $f_{m,JG}$ and a more negative slope at low temperatures. Sample A (cooled at 10 K min⁻¹) shows less departure from the line while the slowly cooled sample B shows the least departure. The data converge at higher temperatures. Fig. 5.15 shows how the parameters of the JG β -relaxation of the quenched D-sorbitol sample E change with time during an anneal for 16.0 ks at 221.1 K. Fig. 5.15(A), (B) and (C) are plots of α_{JG} , $\Delta \varepsilon_{JG}$, and $f_{m,JG}$ against the elapsed annealing time in ks. α_{JG} appears to be almost constant with time. The values below ~ 6 ks are somewhat lower that the average value of 0.253 as shown by the dashed line in the plot. It is clear that $\Delta \varepsilon_{IG}$ decreases with time as was found for 5-methyl-2-hexanol. As before, an exponential decay describes the decrease well. If t is the time in seconds: $\Delta \varepsilon_{IG}(t) = 3.58 + 0.649 \cdot \exp(-t/4731)$. Unlike for 5-methyl-2-hexanol, a clear increase in $f_{m,JG}$ with annealing time is observed, a feature of the JG β -relaxation that has only been demonstrated relatively recently [25, 42, 43]. This is in contrast to the behaviour of the frequency of maximum loss for the structural relaxation $f_{m,\alpha}$, which decreases on annealing a glass. An inverted exponent described the increase:

 $f_{m,JG}(t) = 71.9 - 28.8.\exp(-t/4933)$ with t in s. The time constant is similar to that for the decay of $\Delta \varepsilon_{IG}$.

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Fig. 5.14 $f_{m,JG}$ in glassy D-sorbitol is plotted logarithmically against the reciprocal temperature. The symbols used for the data corresponding to the various states are indicated. The solid line is a fit of the Arrhenius equation to the data of sample C at T > 250 K. T_g is also marked on the plot.



Fig. 5.15 (A) α_{JG} , (B) $\Delta \varepsilon_{JG}$ and (C) $f_{m,JG}$ for D-sorbitol sample E which was quenched in liquid N₂ and annealed at 221.1 K, plotted as a function of the annealing time in ks. The dashed line through the α_{JG} data is the mean value, that through the $\Delta \varepsilon_{JG}$ data is a fit of the exponential decay function

 $\Delta \varepsilon_{JG}(t) = 3.58 + 0.649 \cdot \exp(-t/4731), \text{ where } t \text{ is the elapsed time in seconds, while}$ that through the $f_{m,JG}$ curve is a fit to the data according to $f_{m,JG}(t) = 71.9 - 28.8 \cdot \exp(-t/4933).$ Chapter 5

5.3.4 Diethyl Phthalate

Diethyl Phthalate is another well-studied small molecule glassformer. Interest in this substance (and in the other phthalate esters) has stemmed from their importance as plasticisers [44]. Fig. 5.16(A) and (B) show ε' and ε'' spectra at several temperatures below T_g of ~ 180 K, which are similar to the results for the other glasses. A relaxation peak is seen in ε'' with an accompanying step in ε' . There is also a wing in ε'' at low frequencies, which increases with increasing temperature. In Fig. 5.17(A) and (B), which contain spectra at several temperatures above 180 K, the wing emerges into the frequency window to become a loss peak, and corresponding decrease in ε' . In the last spectra shown, which was measured at 205.7 K, ε'' begins to increase at low frequencies again due to ionic conductivity. As for the other glasses, the lower frequency wing and peak are the α -relaxation while the higher frequency peak is assigned here to the JG β -relaxation.

In order to extract such parameters as the frequency of maximum loss f_m , broadness of loss peaks, and dielectric strength, the empirical equation with HN terms was fitted to the data as for the other glassformers. In addition to a HN term for each relaxation an imaginary term proportional to the dc conductivity σ_{dc} is included, which accounts for losses due to ionic conduction. The complex permittivity $\varepsilon^*(\omega)$, is thus

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon_{\alpha}}{\left(1 + (j\omega\tau_{HN\alpha})^{\alpha_{\alpha}}\right)^{\beta_{\alpha}}} + \frac{\Delta\varepsilon_{JG}}{\left(1 + (j\omega\tau_{HNJG})^{\alpha_{JG}}\right)^{\beta_{JG}}} - j\frac{\sigma_{dc}}{\varepsilon_{0}\omega}.$$
 (5.3)

The dc conductivity is neglected until it appears at about 20 K above T_g , so Eq. (5.1) is used below this. Parameters obtained for the α -relaxation are not reliable until the peak appears in the frequency window at about 192 K. f_m of each relaxation process is found as before from Eq. (5.2). As for the other glassformers, $\beta_{JG} = 1$ provides the best fit over all temperatures (so $\tau_{HNJG} = \tau_{JG}$). The contribution of each term is shown at 179.1 K for Fig. 5.16 and 205.7 K for Fig. 5.17. The values of the parameters for the JG β -relaxation Cole-Cole term in Eq. (5.1) at 179.1 K are: $\Delta \varepsilon_{JG} = 0.195$, $\tau_{JG} = 4.61 \,\mu$ s, and $\alpha_{JG} = 0.418$. The values of the parameters of Eq. (5.3) at 205.7 K are: $\Delta \varepsilon_{\alpha} = 7.10$, $\tau_{\alpha} = 0.154 \,\mathrm{ms}$, $\alpha_{\alpha} = 0.992$, and $\beta_{\alpha} = 0.463$ for the α -relaxation

term and $\Delta \varepsilon_{JG} = 0.188$, $\tau_{JG} = 0.111 \mu s$, $\alpha_{JG} = 0.675$ for the JG β -relaxation term, with $\sigma_{dc} = 1.82 \text{ pS m}^{-1}$ and $\varepsilon_{\infty} = 3.06$.

Reliable parameters for the JG β -relaxation were obtained for diethyl phthalate at 21 K above T_g – much higher than for any other glassformer studied here (e.g. 5-methyl-2-hexanol data only extends to 11 K above T_g). This was because of the wider frequency range and greater sensitivity of the dielectric spectrometer used. Reliable here means that a shoulder was detectable on the high frequency wing of the α -relaxation and the final value obtained for $f_{m,JG}$ was > ~ 0.5 decades from the highest frequency point in the spectra.



Fig. 5.16 The (A) ε' and (B) ε'' spectra of diethyl phthalate (heated slowly at 0.08 K min⁻¹ as spectra were measured) at several temperatures below T_g . Curves through the data for the first eight temperatures are fits of Eq. (5.1). The heavy solid line through the ε' and ε'' data at 179.1 K is generated from the real and imaginary parts of Eq. (5.1) with appropriate fit parameters. This is decomposed into the contributions from the α - and JG β -relaxation terms (solid and dashed lines) as indicated on the plot.



Fig. 5.17 Plots showing the (A) ε' and (B) ε'' spectra of diethyl phthalate at several temperatures above T_g . Solid lines through the data in both panels are fits of Eq. (5.1) or Eq. (5.3) to the data. The decomposition of the fit is shown for 205.7 K. The α -relaxation contribution is shown as a solid line, and the β -relaxation as a dashed line. The dc conductivity contribution to ε'' is shown as a dotted line.

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Figure 5.18(A) shows α_{IG} , plotted against the temperature. It is seen that α_{IG} has unusual temperature dependence. It increases from a value of 0.27 (very broad relaxation) at 120.4 K to 0.42 at 180.4 K. There is a shallow minimum at ~ 185.7 K before α_{IG} increases more sharply to 0.55 at 201.1 K. In the temperature ramp measurements made on chlorobenzene/cis-decalin, 5-methyl-2-hexanol, and Dsorbitol, α_{IG} was observed to increase continuously with temperature. Others have observed changes in slope in the exponent obtained of a power-law fitted to the high frequency wing of the JG β -relaxation in 2-picoline/tri-styrene mixtures [45]. This exponent γ is directly comparable to α_{JG} since $\gamma = \alpha_{JG}\beta_{JG}$ (= α_{JG} here). As can be seen in Fig. 5.18 (B), $\Delta \varepsilon_{IG}$ at first follows the typical behaviour for the JG β -relaxation seen for chlorobenzene/cis-decalin and slowly cooled D-sorbitol here and as has been observed previously [39, 40]. $\Delta \varepsilon_{IG}$ increases slowly with temperature from 0.17 at 120.4 K to 0.19 at 178.1 K. Above T_g it increases more rapidly – there is a change of slope in the plot of $\Delta \varepsilon_{JG}$ vs. T around the glass transition. However, at 195.2 K, $\Delta \varepsilon_{JG}$ reaches a maximum value and begins to decrease. Also shown in Fig. 5.18(B) is the excess entropy $S_{exc} = S - S_{xtal}$ of the glass/supercooled liquid over the crystal at various temperatures. This was obtained from entropy data for an annealed glass and the crystalline phase tabulated in Ref. [11]. This was then scaled by a factor 0.0122 K mol J⁻¹ chosen so that the $\Delta \varepsilon_{JG}$ and S_{exc} data points at 190 K coincide. S_{exc} also begins to increase more rapidly around T_g . The correspondence between the trends of the $\Delta \varepsilon_{JG}$ and S_{exc} data shows that $\Delta \varepsilon_{JG}$ depends on temperature in a similar way to thermodynamic properties of glasses. However, S_{exc} and $\Delta \varepsilon_{JG}$ do not coincide either above or below the glass transition because the JG β -relaxation is only one of a number of factors that contribute to S_{exc} . Others include the difference between the vibrational entropy of the glass and the crystal and the remaining configurational entropy of the disordered arrangement of molecules in the glass excluding the JG β relaxation.

In Fig. 5.19(A), the distribution parameters for the α -relaxation are plotted against the temperature. At 192.1 K, $\alpha_{\alpha} = 0.90$ and $\beta_{\alpha} = 0.58$ (HN distribution). α_{α}

increases to ~1, while β_{α} decreases to 0.45 at 221.9 K (Davidson-Cole distribution [46]). A plot of $\Delta \varepsilon_{\alpha}$ against temperature is shown in Fig. 5.19(B). There is an abrupt change in slope at ~ 209 K and $\Delta \varepsilon_{\alpha}$ begins to decrease more sharply. This is probably due to the onset of crystallisation in the diethyl phthalate sample [11]. ε_s is also observed to decrease more rapidly above ~ 217 K, also due to crystallisation of the sample.

Figure 5.20 shows $f_{m,\alpha}$ and $f_{m,JG}$ on a logarithmic scale vs. inverse temperature. Our data for both the α - and JG β -relaxations agrees with published data [5] in the frequency range in which they overlap. The solid line through the $f_{m,\alpha}$ data in this figure is the fit K to the α -relaxation frequency data of the VFT equation [47-49]

$$f_m = A_{VFT} \exp[-B_{VFT} / (T - T_0)], \qquad (5.4)$$

with fit parameters $A_{VFT} = 10^{16.69}$ Hz, $B_{VFT} = 2268$ K, and $T_0 = 132.16$. The departure of the data of Pawlus et al. [5] from this curve shows that in common with most glassformers, the α -relaxation in diethyl phthalate cannot be described by a single VFT equation over its entire range. Features not observed for the JG β -relaxation before in this substance are the temperature-independent region around T_g and increase in the magnitude of the slope of $f_{m,JG}$ to more closely follow the α relaxation above T_g . Fits of the Arrhenius equation have been made to the JG β relaxation frequency data at and below 180 K and between 193.6 K and 201.1 K, the temperature ranges over which the Arrhenius plot of $f_{m,JG}$ appears to be linear. At low temperatures, as for the other slowly cooled glasses, there is no curvature of the relaxation data. The values of the fit parameters were $A_{ARR} = 10^{12.97}$ Hz and $B_{ARR} =$ 3462 K below T_g and $A_{ARR} = 10^{21.89}$ Hz and $B_{ARR} = 7506$ K above T_g .

FIG. 5.18



Fig. 5.18 Plots of (A) α_{JG} and (B) $\Delta \varepsilon_{JG}$ of the JG β -relaxation of diethyl phthalate against temperature. Also plotted (filled triangles) is S_{exc} of a diethyl phthalate glass calculated from glass, supercooled liquid, and crystal entropies in Table 6 of Ref. [11]. The values are scaled so that S_{exc} and $\Delta \varepsilon_{JG}$ are numerically equal at 190 K.

FIG. 5.19



Fig. 5.19 Plot showing the variation of (A) α_{α} and β_{α} , and (B) $\Delta \varepsilon_{\alpha}$ for the α - relaxation of diethyl phthalate with temperature. ε_s data (filled triangles) is also shown.

FIG. 5.20



Fig. 5.20 f_m for the α -relaxation and JG β -relaxation is plotted against 1000/T. Also shown, are selected relaxation rate data from Fig. 2 in Ref. [5] (filled triangles). Values of the primitive frequency f_0 estimated from the Coupling Model [Eq. (5.10)] are shown (crosses) for comparison with the $f_{m,JG}$ values above T_g . The solid line through the $f_{m,\alpha}$ data is the fit of the VFT equation [Eq. (5.4)] to the data, while the two dashed lines through the $f_{m,JG}$ data are the fits of the Arrhenius equation below and above T_g .

Table 5.2Parameters of the fits of the Arrhenius and VFT equations to the $f_{m,\alpha}$ and $f_{m,JG}$ vs. T data of the glassformers studied.

Glassformer	Relaxation	Model Equation	Temperature Range	A [Hz]	B [K]	<i>T</i> ₀ [K]
Chlorobenzen	JG B	Arrhenius	All data	10 ^{15.37}	3331	
e/cis-decalin						
5-methyl-2-	JG β	Arrhenius	134.2 K –	10 ^{12.54}	2690	
hexanol			154.2 K			
D-sorbitol	JG β	Arrhenius	> 250 K	10 ^{14.29}	6311	
(Sample C)						
diethyl	$JG\beta$	Arrhenius	< 180 K	10 ^{12.97}	3462	
phthalate	(below T_g)					
	$JG\beta$	Arrhenius	193.6 K –	$10^{21.89}$	7506	
	(above T_g)		201.1 K			
	α	VFT	All data	$10^{16.69}$	2268	132.16

5.4 Discussion

5.4.1 $\Delta \varepsilon_{JG}$ and its Mimicry of the Thermodynamic Properties of Glasses

As discussed in Chap. 2, when a liquid is cooled, there is a bend in the molar volume V, entropy S, and enthalpy H curve over some range where the temperature dependence continually changes from the stronger one of the liquid to the weaker one of the glass. The glass transition occurs in this range and the fictive temperature T_f is defined by the intersection of the extrapolated liquid and glass volume-temperature lines. T_f depends on the cooling rate of the liquid, the faster the cooling rate the higher is T_f .

During annealing at a constant temperature, the properties of the glass approach those of the equilibrium liquid (they stabilise). When a quenched glass is heated at a constant rate, which is less than the quench rate, stabilisation causes an initial decrease in *V*, *H*, and *S* towards a minimum followed by an increase with temperature.
It is seen through the experiments here that the dielectric properties of the JG β -relaxation mimic the behaviour of the thermodynamic properties. This is clearly seen for $\Delta \varepsilon_{JG}$ in particular because its rate of change with time and temperature have the same sign as those of *V*, *H*, and *S* of most glasses. The significance of this is made clear in the next section.

For all the glasses here, $\Delta \varepsilon_{JG}$ shows a more rapid increase for $T > T_g$ than for $T < T_g$, like V, H, and S [Fig. 5.5(B), 5.8(B), 5.12(A), and 5.18(B)]. This is best illustrated for diethyl phthalate [Fig. 5.18(B)] where the temperature dependence of scaled value of the excess entropy S_{exc} of the liquid and glass over the crystal is compared with $\Delta \varepsilon_{JG}$. $d\Delta \varepsilon_{JG}/dT$ depends on temperature in a similar way to the 2nd order thermodynamic quantities such as C_p and the volume coefficient of thermal expansion α . This has been observed by others for the polymer tetramethyl-bisphenol A-polycarbonate [40], and the small molecule glassformer toluene [39], as well as for D-sorbitol itself [10] but the connection was not made to the thermodynamic properties of glasses. $\Delta \varepsilon_{JG}$ also decreases during annealing for 5-methyl-2-hexanol and D-sorbitol [Fig. 5.10(B) and 5.15(B)] – which has again been observed previously by Johari for other glassformers [50]. Finally, a minimum in $\Delta \varepsilon_{JG}$ is seen for rapidly quenched glasses as they are heated slowly at a constant rate [5-methyl-2-hexanol in Fig. 5.8(B) and Dsorbitol sample C in Fig. 5.12(A)]. $\Delta \varepsilon_{JG}$ has a value and temperature dependence that itself depends on the thermal history below ~ 270 K in the case of D-sorbitol, as do the other parameters of the JG β -relaxation of D-sorbitol. This has also been observed for the value of $\Delta \varepsilon_{IG}$ for other glasses previously [3, 51, 52].

5.4.2 Time and Temperature Effects on $\Delta \varepsilon_{JG}$

The effect of structural relaxation on V, H, and S of a rapidly quenched glass as it is heated at a lower rate is explained in terms of changes in the fictive temperature of the glass [53]. An equivalent way to quantify the effect on $\Delta \varepsilon_{JG}$ of structural relaxation during heating is to express $\Delta \varepsilon_{JG}$ as a function of both time (structural relaxation) and temperature (heating) effects. Its total derivative is

$$d\Delta\varepsilon_{JG} = \left(\frac{\partial\Delta\varepsilon_{JG}}{\partial t}\right)_T dt + \left(\frac{\partial\Delta\varepsilon_{JG}}{\partial T}\right)_t dT, \qquad (5.5)$$

where the first term represents the effect of structural relaxation at a fixed temperature while the latter represents the effect of heating without structural relaxation. If the heating rate is q = dT / dt, then

$$\frac{d\Delta\varepsilon_{JG}}{dT} = \left(\frac{\partial\Delta\varepsilon_{JG}}{\partial t}\right)_T \frac{1}{q} + \left(\frac{\partial\Delta\varepsilon_{JG}}{\partial T}\right)_t.$$
(5.6)

We have found here that $(\partial \Delta \varepsilon_{JG} / \partial t)_T$ is negative and $(\partial \Delta \varepsilon_{JG} / \partial T)_t$ has been shown to be positive. At some point $d\Delta \varepsilon_{JG} / dT = 0$, corresponding to a minimum in the $\Delta \varepsilon_{JG}$ -T plot. This minimum, which can be seen for 5-methyl-2-hexanol in Fig. 5.8(B) and D-sorbitol sample C in Fig 5.12(A) as they are heated will occur when $q^{-1}(\partial \Delta \varepsilon_{JG} / \partial t)_T = -(\partial \Delta \varepsilon_{JG} / \partial T)_t$. The minimum will occur at a lower temperature when q is low and at a higher temperature when q is high. The condition is satisfied at ~ 146 K for 5-methyl-2-hexanol and at 230 ± 4 K for D-sorbitol sample C. Below the minimum temperature, changes in $\Delta \varepsilon_{JG}$ are dominated by structural relaxation effects while above it the effect of temperature dominates.

5.4.3 Quantifying Time and Temperature Effects on $f_{m,JG}$

It has been shown unambiguously here for D-sorbitol that $f_{m,JG}$ increases as a glass is annealed at a constant temperature [Fig. 5.15(C)], which is opposite to the behaviour of $f_{m,\alpha}$, which decreases as the density of the glass increases upon annealing. However, an increase in $f_{m,JG}$ was not observed for the anneal of 5-methyl-2-hexanol [Fig. 5.10(C)]. The increase in $f_{m,JG}$ on annealing has however been observed recently for D-sorbitol [25] as well as for other glassformers [42, 43], so it appears to be another general feature of the JG β -relaxation.

It is also possible to infer the effect of annealing on $f_{m,JG}$ by applying a similar equation to Eq. (5.6) to $f_{m,JG}$ of a quenched glass as it is heated at a constant rate q:

$$\frac{d\log(f_{m,JG})}{dT} = \left(\frac{\partial\log(f_{m,JG})}{\partial t}\right)_T \left(\frac{1}{q}\right) + \left(\frac{\partial\log(f_{m,JG})}{\partial T}\right)_t.$$
(5.7)

An alternative form in terms of 1/T is

$$\frac{d\log(f_{m,JG})}{d(1/T)} = \left(\frac{\partial\log(f_{m,JG})}{\partial t}\right)_T \left(\frac{dt}{d(1/T)}\right) + \left(\frac{\partial\log(f_{m,JG})}{\partial(1/T)}\right)_t.$$
 (5.8)

As for the analogous equations for $\Delta \varepsilon_{JG}$, the first term on the RHS in Eq. (5.7) and (5.8) represents the effect of structural relaxation and the second term the effect of thermal energy. Thus during measurements on a quenched sample with increasing T, the slope of the plot of $\log(f_{m,JG})$ against inverse temperature will be affected by the structural relaxation until a temperature is reached where the equilibrium state has been attained during the time of heating. Consequently, a change in the slope of the plot from the Arrhenius equation would be a reflection of a time-dependence of $f_{m,JG}$ during the course of the dielectric measurements, when the first term on the RHS in Eq. (5.8) is significant.

For 5-methyl-2-hexanol, the magnitude of (1/q) in the first term in RHS of Eq. (5.7) is fixed at 600 s K⁻¹, and $dt/d(1/T) = -T^2/q$ in the first term on RHS of Eq. (5.8) decreases from -7.88×10^6 s K at 114.6 K, to -1.52×10^7 s K at 159.1 K. For D-sorbitol sample C, 1/q = 600 s K⁻¹ and dt/d(1/T) decreases from -2.915×10^7 s K at 220.4 K, to -4.518×10^7 s K at 274.4 K. Therefore, even a very small rate of increase in $f_{m,JG}$ on spontaneous relaxation at a fixed T would be substantially increased in magnitude on multiplication by the large value of 600 s K⁻¹ in Eq. (5.7) and of -10^7 s K in Eq. (5.8) leading to noticeable effects.

An examination of the change in the slope of the plot in Fig. 5.14 shows that $f_{m,JG}$ for D-sorbitol sample C is lower than that of sample B, the more structurally relaxed sample, even thought the density of the latter is higher. Similarly, the $f_{m,JG}$ data for quenched 5-methyl-2-hexanol at lower temperatures in Fig. 5.9 is below the Arrhenius line followed by the high temperature data. This indicates that the term $[\partial \log(f_{m,JG})/\partial t]_T$ is positive. Since dt/d(1/T) is negative, the product of the two terms is negative, which adds to the negative second term in Eq. (5.8). The net result is that the slope of the Arrhenius plot is more negative when structural relaxation occurs during the measurements.

Eq. (5.8) allows an estimation of $\left|\partial \log(f_{m,JG})/\partial t\right|_{T}$ to be made for 5-methyl-2-hexanol and D-sorbitol sample C. To estimate its value for 5-methyl-2-hexanol at 131.6 K from Fig. 5.9, we extend the Arrhenius fit to the data from high temperatures to 131.6 K as shown by the dashed line. Knowing dt/d(1/T) from the heating rate, $\left|\partial \log(f_{m,JG})/\partial(1/T)\right|_{t}$ from the slope of the extended line, and $d \log(f_{m,JG})/d(1/T)$ from an estimate of the actual slope in Fig. 5.9 at 131.6 K (the most uncertain quantity in the calculation), $\left|\partial \log(f_{m,JG})/\partial t\right|_{T}$ at 131.6 K can be calculated. Its value is ~ 2.139 x 10⁻⁵ s⁻¹ where the unit of frequency is Hz. For D-sorbitol sample C at 221.1 K, we can similarly estimate $\left|\partial \log(f_{m,JG})/\partial t\right|_{T}$ as ~ 7.54 x 10⁻⁵ s⁻¹. The illustration that the downwards bending of the $\log(f_{m,JG})$ against 1/T plots is a result of structural relaxation is also important because this effect has

been observed for several glasses before, and attempts have been made to fit empirical equations to such data in the same manner as for the α -relaxation process observed in the equilibrium state of a liquid.

5.4.4 The Effect of Structural Relaxation on $f_{m,JG}$ During Annealing and Heating at a Constant Rate

For 5-methyl-2-hexanol, a comparison of the actual $f_{m,JG}$ values with those expected from extrapolation of the high temperature Arrhenius line at 131.6 K shows that $f_{m,JG}$ should increase on annealing from ~ 3.81 kHz (from extrapolation of smoothed data used to find the slope at 131.6 K) at the time the spectra was measured to an expected 4.56 kHz at formally infinite time, when spectra could be measured in the equilibrium state. This means that $\log(f_{m,JG})$ must increase by ~ 7.804 x 10⁻² which should take roughly 3.6 ks, *if* $[\partial \log(f_{m,JG})/\partial t]_T$ *is constant*. This is far shorter than the time scale of the isothermal anneal at 131.6 K, which lasted 14.6 ks, yet during the anneal $f_{m,JG}$ remained almost constant at 3.9 kHz. However, the stabilisation time before the commencement of measurements was ~ 1.8 ks so $f_{m,JG}$ should have achieved a constant value after only about 1.8 ks of annealing. Re-examining the $f_{m,JG}$ data in the light of this, the $f_{m,JG}$ values obtained from spectra recorded before about 2 ks seem to be slightly below average but the data is very scattered. According to the annealing experiment at 131.6 K, the equilibrium value of $f_{m,JG}$ should be at most 4.2 kHz. This suggests that the higher value obtained from extrapolation of the equilibrium line is unreliable for estimating $f_{m,JG}$ after annealing.

In summary, there are several possible reasons why an expected rise in $f_{m,JG}$ was not observed during the anneal of 5-methyl-2-hexanol. Firstly, in the glassy state of 5methyl-2-hexanol at 131.6 K, the equilibrium was reached quickly and therefore its consequences on $f_{m,JG}$ were unobservable. In addition, the broadness of the ε'' peak at low temperatures contributes significantly to the observed fluctuations in the fitting parameters, which obscure small time dependencies in $f_{m,JG}$. Unfortunately, at T <120 K where $f_{m,JG}$ deviates increasingly more from the Arrhenius temperature

dependence in Fig. 5.9, the time-dependence of the spectra at a fixed temperature was not investigated.

Finally, it is likely that the increase in $f_{m,JG}$ with time in this study was of the order of the changes in $f_{m,JG}$ caused by a temperature instability of 0.1 K at T = 131.6 K (~ 0.07 kHz estimated with the Arrhenius line), and again this would tend to obscure any changes in $f_{m,JG}$ with time.

Now considering D-sorbitol sample C, $f_{m,JG}$ at 221.1 K is 43.4 Hz (from data measured at that temperature), while the value of $f_{m,JG}$ estimated from the Arrhenius line at high temperatures extrapolated to 221.1 K is 78.6 Hz. This is a difference of 0.258 decades, which should require a total annealing time of 3.4 ks. This is much *less* than the time taken for $f_{m,JG}$ to reach an almost constant value of 71.0 Hz during the anneal of D-sorbitol sample E at 221.1K. This can be explained by the fact that the rate of change of $f_{m,JG}$ during structural relaxation is found to be time dependent [as seen for D-sorbitol in Fig. 5.15(C)]. It is initially fast and becomes extremely slow after long annealing. This also provides a possible explanation of the difference seen in both 5-methyl-2-hexanol and D-sorbitol between the values of $f_{m,JG}$ as predicted by extrapolation of the Arrhenius line and those attained after annealing. It may be

impossible when the glass is far below T_g for $f_{m,JG}$ to attain the high value suggested by extrapolation of the high temperature data in any reasonable time. This is sensible given that the glass is a non-equilibrium state. Equilibrium can only be reached in a reasonable time (defined subjectively) when one is in the transformation region.

5.4.5 Origin and Mechanism of the JG β -relaxation

A premise of some theories of the JG β -relaxation is that it is the precursor of the α -relaxation [54, 55]. JG β -relaxation facilitates viscous flow (the α -relaxation) and must occur before the latter can occur. In such theories, the narrow dielectric relaxation peak seen in the GHz frequency range at high temperatures in the ε'' spectra of polar liquids is associated with processes similar to the JG β -relaxation observed at low temperatures. As the liquid is cooled, the peak broadens and shifts to lower frequencies. A new peak (the α -relaxation) emerges from the low frequency side of this peak once some density and viscosity are reached. As the liquid is further cooled, this peak broadens and grows in strength at the expense of the original peak and rapidly moves to very low frequencies at $T < T_g$. The original peak (now the JG β -relaxation) doesn't move to low frequencies as rapidly as the α -relaxation peak. At low viscosity there is a single relaxation, which is narrow while at high viscosity there one persists and has a similar origin to the single relaxation observed at high frequencies.

This idea cannot be verified by supercooling a liquid but it is supported by dielectric measurements on monomeric liquids as they polymerise [56-59]. On polymerisation, macromolecules grow in the liquid so that covalent bonds replace weaker Van der Waals interactions. The state of the liquid changes irreversibly with time at a constant temperature. As the macromolecules grow, the viscosity and density increase. It is found that the GHz relaxation process observed in the monomeric liquid begins to decrease in strength while its position is not significantly changed. An α -relaxation evolves from this peak, increases in strength, and shifts to lower frequency as the viscosity increases. The decrease in $\Delta \varepsilon$ with time for the high frequency peak as

polymerisation occurs has the same form as the decrease in $\Delta \varepsilon_{JG}$ as structural relaxation occurs during isothermal annealing [58, 59].

Two main mechanisms have been proposed for the JG β -relaxation as was touched on in Chap. 2, Sect. 2.12. The older of these, described in several papers by Goldstein [2], Johari and Goldstein [3], and Johari [51, 52], is the idea that the JG β -relaxation arises from localised motions in regions of loose packing that remain in the glass below T_g . These decrease in size as the glass density increases on cooling and structural relaxation. This causes a decrease in $\Delta \varepsilon_{JG}$. Given that $f_{m,JG}$ has an

Arrhenius temperature dependence at least for $T < T_g$, it appears that unlike the α -relaxation [60], the configurational entropy arising from the localised motions doesn't affect their rate.

In another mechanism proposed by Williams and Watts [6], all the molecules would contribute to the JG β -relaxation by undergoing a small-angle rotational diffusion, after which the larger angle one corresponding to the α -relaxation would occur. Recent measurements using ²₁H NMR [7-9] and solvation dynamics [26] techniques have supported this mechanism. Several arguments against it can be made however. The mechanism implies that the rotational diffusion of a molecule occurs in two steps, a small angle reorientation followed by a large angle reorientation. This is inconsistent with observations from a study of metallic glasses.

It is well known that $\Delta \varepsilon$ for a polar material is proportional to the number density of dipoles *N*, and inversely proportional to the temperature i.e. $\Delta \varepsilon \propto N/T$. During isothermal annealing, if all molecules contribute to the JG β -relaxation, *N* will increase because of the increase in the density of the glass, leading to an increase in $\Delta \varepsilon_{JG}$. During cooling *N* increases and *T* decreases, again leading to an expected increase in $\Delta \varepsilon_{JG}$. This is the opposite of what is observed. A decrease in $\Delta \varepsilon_{JG}$ requires that either the rotation angle decreases or the fraction of molecules involved in the JG β -relaxation decreases (so *N* falls). The NMR measurements suggest that the angle is independent of temperature. However, if the fraction of molecules involved in the JG β -relaxation were to decrease, it would leave some molecules without the precursor motion required for the α -relaxation. One would then expect $\Delta \varepsilon_{\alpha}$ to decrease as the temperature is decreased, which is not observed, so it does not seem

likely that at high temperatures all molecules contribute to the JG β -relaxation while at low temperatures only some do. To summarise, there are three possible ways $\Delta \varepsilon_{JG}$ may be reduced on cooling:

- The angle of rotation decreases, while the population of molecules involved is unchanged,
- (ii) The angle and molecular population both decrease, and
- (iii) The molecular population only decreases.

Only (iii) seems plausible if the angle is temperature independent as suggested by NMR measurements.

The extrapolation of an equilibrium liquid's entropy to temperatures below T_g also has implications for the mechanism of the JG β -relaxation. Newer extrapolations avoiding a fall to zero at some T > 0 K [61] imply that the entropy of the equilibrium liquid decreases continuously from its value for the supercooled liquid at $T > T_g$ to 0 at 0 K, and the number of accessible minima in the potential energy landscape (the number of inherent structures) decreases to 1 at 0 K. Since the JG β -relaxation also contributes to configurational entropy of the glass [55] and is a precursor to the α -relaxation, configuration changes between the local minima in its portion of the landscape should also become inaccessible as T $\rightarrow 0$ K and any associated entropy should be 0 at 0 K. This cannot be the case if *all* molecules reorient with a *temperature-independent* small angle to produce the JG β -relaxation.

The size of the contribution of the JG β -relaxation to the configurational entropy can be estimated and used to argue that a mechanism in which all molecules take part is implausible. The JG β -relaxation configurational entropy per mole is given by

$$S_{c,JG} = xN_A k \ln \Omega_{JG} = xR \ln \Omega_{c,JG}, \qquad (5.9)$$

where x is the mole-fraction of species involved in the JG β -relaxation and $\Omega_{c,JG}$ is the number of accessible configurations per species partaking in the JG β -relaxation, and the other symbols have their usual meanings. If all molecules contribute and x = 1 and assuming the simplest possible case of $\Omega_{c,JG} = 2$, $S_{c,JG} = 5.76 \text{ J K}^{-1} \text{ mol}^{-1}$. This implies that the excess entropy of the glass over the crystal, S_{exc} , less the residual entropy at 0 K, S_0 , should have at least this value. Since $S_{exc} - S_0$ is less than this for

many liquids (e.g. 4.3 J K⁻¹ mol⁻¹ for toluene [62]), a simple two-site model with the assumption of all molecules contributing cannot explain the entropy of these glasses. In the mechanism of Johari and Goldstein supported by dielectric results, the JG β -relaxation is spatially heterogeneous, while in the Williams-Watts mechanism supported by ${}^{2}_{1}$ H NMR it is homogeneous. Ngai and Paluch [4] attempt to reconcile the conflicting results by assuming that at a given instant only some molecules participate in JG β -relaxation but if the glass is studied for sufficiently long time all molecules will participate in JG β -relaxation.

5.4.6 Diethyl Phthalate Results Above T_g and the Coupling Model

The measurements made on diethyl phthalate provide information about the JG β -relaxation properties further above T_g than the other studies. These other studies on heating glasses at constant rates, which only extend a few K above T_g , do not imply that major changes occur in the temperature dependence of α_{JG} , $\Delta \varepsilon_{JG}$, or $f_{m,JG}$. There may be a small fall off in the rate of increase of $\Delta \varepsilon_{JG}$ above T_g for 5-methyl-2-hexanol and D-sorbitol, and 5-methyl-2-hexanol may show a small region around T_g where $f_{m,JG}$ depends less strongly on the temperature. This fall off in the rate of increase of $\Delta \varepsilon_{JG}$ above T_g has also been observed by Wagner and Richert for D-sorbitol [10].

As was discussed in Chap. 2, Sect. 2.12, many new dielectric measurements on smallmolecule glassformers and polymers that use the very broad frequency ranges available with modern dielectric spectrometers show changes in the temperature dependence of $f_{m,JG}$ occurring around and above the glass transition. This typically takes the form of a small temperature-independent region near T_g followed by a stronger temperature dependence (more negative slope on a log scale plot of $f_{m,JG}$ vs. 1/T). Results (on D-sorbitol for example [10, 23, 28, 29], or on copolyesters of poly(ethylene terephthalate) and poly(ethylene isophthalate) [63] relied on fitting to separate the JG β -relaxation shoulder from the α -relaxation in the ε'' spectra (since these are almost merged at temperatures above T_g), but some studies have used pressure [33], or mixtures of glassformers [45] to ensure that the two relaxations are well separated above T_g . As mentioned in Sect. 5.3.3, the anomaly of a broad maximum in $f_{m,JG}$ has also been found by Olsen [25] for D-sorbitol and by the same group for other glassformers [42, 43] but has not been observed by others, so it is not discussed further here.

The behaviour of $f_{m,JG}$ above T_g shows that the α - and JG β -relaxations are coupled. These observations can be explained by the Coupling Model [64-66], in which the supercooled liquid is modelled as an assembly of interacting arrays of coupled anharmonic oscillators [65]. At times shorter than some crossover time, t_c , relaxation is exponential, decaying according to $\exp(-t/\tau_0)$ where τ_0 is the "primitive relaxation time" [65]. At times longer than t_c , the relaxation function becomes non-exponential. It may be approximated by $\exp(-t/\tau_{\alpha})^{\beta_{KWW}}$ where τ_{α} is the α -relaxation time, and β_{KWW} is the stretch parameter. Continuity implies that τ_0 in the coupling model is related to τ_{α} , by [65]

$$\tau_0 = t_c^{1-\beta_{KWW}} \tau_\alpha^{\beta_{KWW}}.$$
(5.10)

 $t_c = 2$ ps is a good estimate for the crossover time in a supercooled liquid [67]. The model suggests that the JG β -relaxation is the precursor of the α -relaxation, since the JG β -relaxation time τ_{JG} at T_g has been shown to be approximately equal to τ_0 for several glass-formers [54, 67, 68], and correlates with β_{KWW} in the same way. The primitive relaxation and the JG β -relaxation are not identical however [67], but must be related. Since α -relaxation is only measurable above T_g , this equation only has a useful purpose above this temperature. The position of the JG β -relaxation above T_g should depend only on the position and the shape of the α -relaxation. We can use Eq. (5.10) to calculate τ_0 and from this a primitive relaxation frequency $f_0 = 1/2\pi\tau_0$ and compare this with $f_{m,JG}$ above T_g . The values of β_{KWW} at each temperature are estimated using the numerical relationship between the broadness parameters of the HN and KWW equations derived by Alvarez, Alegría, and Colmenero [69],

$$\beta_{KWW} = \left(\alpha_{\alpha}\beta_{\alpha}\right)^{\frac{1}{1.23}}.$$
(5.11)

As seen in Fig. 5.20, the f_0 values obtained from Eq. (5.11) are quite close to $f_{m,JG}$ for diethyl phthalate obtained by fitting above T_g , as has been observed for copolyesters [63].

In $\Delta \varepsilon_{JG}$ as a function of temperature above T_g , the coupling gives rise to larger fluctuations or co-operativity in the relaxation of the individual molecules responsible for the JG β -relaxation. This behaviour is similar to an order among the individual molecules. At a temperature of ~ 195 K, this coupling or order is lost, and the system reverts to a disordered state for the β -relaxation. The maximum in $\Delta \varepsilon_{JG}$ is connected with the coupling of the JG β -relaxation and the transition between couplingdecoupling is similar to the order-disorder transition observed in condensed systems. In the glassy state, the JG β -relaxation is observed to be Arrhenius as the activation energy is connected with the dipole jumping local potential barriers in the energy landscape [2, 3]. The change in the temperature dependence of α_{JG} above T_g must also be connected to the features observed in $f_{m,JG}$ and $\Delta \varepsilon_{JG}$.

Ngai and Paluch [4] and Pawlus et al. [5] have claimed that the β -relaxation in diethyl phthalate may not be a "true" JG β -relaxation but may have an intramolecular origin. They claim that the critical criterion is that a β -relaxation at and above T_g must be related to the α -relaxation through the Coupling Model [Eq. (5.10)]. This implies that a "true" JG β -relaxation must involve non-co-operative motion of entire molecules (or entire chain segments in a polymer). Eq. (5.10) suggests that for a supercooled liquid at two pressure-temperature states where the α -relaxation is superimposable, $f_{m,JG}$ is the same in each case. Pawlus et al. [5] have applied this test to diethyl phthalate and found that there is a change in the position of the β -relaxation. This is used as evidence that it is not a true JG β -relaxation, despite the fact that it behaves in as one in all other respects. However, the correspondence between $f_{m,JG}$ above T_g and f_0 clearly shows that the relationship between the α - and JG β -relaxations implied by the Coupling Model is valid for the β -relaxation in diethyl phthalate. The β -relaxation in diethyl phthalate is thus a JG one.

5.5 Summary

The JG β -relaxation of four small-molecule glassformers (a chlorobenzene/cis-decalin mixture, 5-methyl-2-hexanol, D-sorbitol, and diethyl phthalate) has been studied by a technique in which the glass is heated at a slow constant rate as dielectric spectra were measured.

For D-sorbitol, several glasses (A, C, and D) were formed at different rates and heated, and one glass (B) was prepared by slow cooling (0.1 K min⁻¹) as its dielectric spectra were measured during cooling.

For 5-methyl-2-hexanol and D-sorbitol (E), samples of rapidly quenched glass were annealed isothermally as their dielectric spectra were measured continuously. The typical features of the JG β -relaxation found in all cases – an Arrhenius temperature dependence of $f_{m,JG}$ below T_g , a decrease in broadness with increasing T, and $\Delta \varepsilon_{JG}$ increasing more strongly for $T > T_g$ than $T < T_g$. The temperature dependence of $\Delta \varepsilon_{JG}$ is shown to be similar to that of the thermodynamic properties of glasses (V, H, S).

Structural relaxation (or stabilisation) effects were observed for $\Delta \varepsilon_{JG}$ and $f_{m,JG}$ of rapidly quenched 5-methyl-2-hexanol and D-sorbitol glasses as they were heated at a constant rate. The plot of $\Delta \varepsilon_{JG}$ vs. *T* showed a minimum (again similar to plots of thermodynamic properties for a rapidly quenched glass as it is heated at a slower rate), and the log scale plot of $f_{m,JG}$ vs. 1/*T* had a more negative slope at low temperatures (departure from the Arrhenius line extrapolated from high temperatures). These features were quantified in terms of a total derivative of $\Delta \varepsilon_{JG}$ and $f_{m,JG}$, the time and temperature dependent rates of change of $\Delta \varepsilon_{JG}$ and $f_{m,JG}$, and the heating rate.

For rapidly quenched glasses, $\Delta \varepsilon_{JG}$ was confirmed to decrease with structural relaxation during annealing while for D-sorbitol $f_{m,JG}$ increased. The change of $f_{m,JG}$ on structural relaxation was also deduced from the Arrhenius plots for both 5-methyl-2-hexanol and D-sorbitol sample C. At temperatures far below T_g , the value of $f_{m,JG}$ expected on the basis of extrapolation of the Arrhenius behaviour of the high temperature data is inaccessible in finite annealing times.

It has been established from a nonlinear fitting analysis of dielectric spectra that the temperature dependence of $f_{m,JG}$ on an Arrhenius plot undergoes a change at T_g for diethyl phthalate. Below T_g , the dependence is Arrhenius, around T_g the relaxation frequency becomes temperature independent, and above T_g the slope magnitude increases and becomes closer to the α -relaxation. These features can be explained by a coupling between the α - and JG β -relaxations above T_g . The prediction for τ_0 of the Coupling Model provides a reasonable estimate for the JG β -relaxation time above T_g , showing that the β -relaxation in diethyl phthalate is a true JG β -relaxation as defined recently [4]. A maximum in $\Delta \varepsilon_{JG}$ above T_g is reminiscent of an order-disorder transition.

5.6 References

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Characterisation of Low Permittivity Materials for use in

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6.1 Introduction

SiO₂ is commonly used in the electronics industry, both for masking and as an interlevel dielectric (ILD). There is a need however to reduce the real part of the permittivity ε' , (or the dielectric constant, k), of ILDs from the value of 4.2 for SiO₂ grown by chemical vapour deposition (CVD) to below 2 for use in future device generations. As devices shrink below 0.25 µm (Intel's newest processors are based on a 90 nm feature size, and so are already entering the size range covered by nanotechnology), cross talk effects become more pronounced and capacitive propagation delays in interconnects become exponentially larger, dominating intrinsic device delay [1]. A further problem associated with an increase in capacitance due to the fall in the separation of the lines is an increase in the power dissipated in interconnects as a proportion of the total power used [2]. Reductions in interconnect delay can be achieved in two main ways. Firstly, the resistance of the metal lines can be reduced, by adoption of optimised connection schemes with shorter lines or by use of Cu instead of Al as the metallisation material (Cu has a lower resistivity). Secondly, the capacitance can be reduced by using a low permittivity material between the lines. This will also resolve the power loss problem. There are a very

large number of criteria, particularly thermal and mechanical ones, that such a material will have to satisfy, apart from possession of a low ε' value [3]. Some examples of these properties are given in Table 6.1.

Table 6.1 Ideal properties for a low ε' ILD.

Property Class	Thermal	Chemical	Physical	Electrical
	Thermally stable	Resists moisture	High Planarity	Low ε' value
	Withstands Thermal cycling	Withstands process chemicals + conditions	Good gap-filling and adhesion	Low loss ε''
	Low Coefficient of Thermal Expansion α	Etchable	Low Stress	Low Leakage Current
	Good thermal conductivity	Stable to materials in contact with it	Withstands Chemical Mechanical Polishing	High Breakdown Voltage
	High T_g			

As described in Chap. 1, there are there are three main types of polarisibility – electronic, ionic/atomic, and orientational, and each is caused by a particular molecular process. The first is induced by the E-field by shift of the electrons relative to the nuclei and the second by shifts of the atoms in an electronegative bond in a covalent solid. The 1st and 2nd can be reduced by using a material with non-polarisible atoms and non-polarisible bonds. The third is due to permanent dipoles in the material and can be reduced by eliminating these. It also occurs at lower frequencies than the other two. Organic polymer materials generally have the lowest ε' values but other properties (especially thermal and mechanical) make most of them unsuitable for use as ILDs.

Many possible candidates for low-relative permittivity (commonly known as low dielectric constant and abbreviated as low-k) materials suitable for integration into electronic devices have been suggested in the literature such as some polymeric materials [4], fluorinated amorphous carbon [5], and silsesquioxanes [6]. Reviews

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listing several of the candidate ILD materials and their properties have been published [2-4]. Typically, for ease of integration in processing, these materials would be either deposited by a chemical vapour deposition (CVD) process or by spincoating. The minimum value of ε' that can be achieved for a solid material is about 2.2 (Teflon). Most suitable non-porous low-k materials under investigation would have ε' above this. Further reductions in ε' require incorporation of voids (air has $\varepsilon' \sim 1$) into the material, all the while ensuring that the properties outlined earlier are not compromised. Examples of possible porous materials for use as ILDs are various solgel produced porous silicas (xerogels [7], ordered mesoporous aluminosilicates [8] etc), porous silsesquioxane based materials [9, 10], and foamed polyimides [4, 11]. The size of the pores, which must be much smaller than the device size, the pore volume, which must be as large as possible to reduce ε' , while not deleteriously affecting other properties, the interconnectedness of the porous structure, and the affinity of water for the pores are all critical properties for such materials. Since, however, there is no ideal low- ε' material to switch to at present, Industry has persevered with CVD produced SiO₂ and derivatives as ILDs. The ε' -value of CVD SiO₂ can be reduced somewhat from 4.2 [12] by doping with species such as fluorine [3, 13-16], or methyl groups [17]. It has been found that upon fluorinating the SiO₂ during its formation, to form a so-called "SiOF" film, the ε' -value can be reduced to below 4, depending on the amount of fluorine added. Fluorine can be introduced into CVD SiO₂ films by adding fluorine-containing substances such as CF₄ or C₂F₆ etc to the reaction mixture of the silicon bearing compound [silane, tetraethoxysilane (TEOS)] and an oxidant (typically N_2O with silane, O_2 , or O_3 with TEOS), or by including the fluorine in the silicon bearing substance itself [tetrafluorosilane (TFS), fluorotriethoxysilane (FTES) etc.]. In this chapter, results of infrared and dielectric

measurements of SiO_2 and SiOF films that were deposited by proprietary techniques used by Intel Ireland are presented.

The dielectric properties of Si and SiO_2 systems have been reported recently in two publications [18, 19], where the measurements were made using an Agilent dielectric probe [20] in the microwave (GHz) frequency range. Results are also compared with those obtained by the probe method, and its possible limitations are commented on.

In addition, some thermal and dielectric properties of polymer samples with high decomposition temperatures are evaluated to see if the polymers could serve as low- ε' ILDs.

6.2 Experimental

Samples were obtained from two 8" <100> n-type Si wafers, provided by Intel Ireland, with fresh samples being cut for measurements made using different techniques. The wafers were polished on one side and were approximately 0.7 mm thick. On one of the wafers had been deposited a pure SiO_2 film (wafer 1). A SiO_2 film into which some fluorine had been incorporated during formation to give a SiOF film had been deposited on the other wafer (wafer 2). The films were formed by highdensity plasma (HDP) CVD using a silane (SiH₄), O₂ and Ar reaction mixture in the case of the SiO_2 film. TFS (SiF₄) was added to the reaction mixture to deposit the SiOF film. Pressures of ~ 6 mTorr and RF powers of between 2.5 kW and 4.8 kW were used. The resistivity, ρ , of the wafers was measured with a Jandel 4-point probe used on the rough side of each, and was found to be 13.8 Ω cm for wafer 1 and 56.4 Ω cm for wafer 2. The average percentage of bound fluorine (fluorine incorporated as Si-F, % F) in the SiOF film on wafer 2 was determined using FTIR measurements at 9 points on the wafer. The mean value and standard deviation over the 9 points on wafer 1 was 3.85 ± 0.27 %. The thickness of the SiOF film was determined at the same 9 points and the mean taken. This was $1.649 \pm 0.020 \,\mu\text{m}$. Only an average thickness of 1.666 μ m was specified for the SiO₂ film on wafer 1.

The infrared (IR) spectra of pieces sectioned from the wafers were measured using a Biorad FTS-6000 FTIR spectrometer. Spectra were measured at a resolution of 2 cm^{-1} in the range 6500 cm⁻¹ to 500 cm⁻¹.

All IR spectra were recorded in transmission mode with IR radiation incident normally to the specimen. The thickness and refractive indices of the films were also measured using a Rudolph ellipsometer. For this purpose, large segmental samples

were cut from each wafer, a selection of points from wafer edge to wafer centre measured, and average values and maximum deviations were taken. For dielectric measurements, several 3 x 3 cm square samples were cut from the wafers. Circular Al electrodes of nominal diameter 20 mm were deposited by evaporation onto both sides of each sample. Measurements in the frequency range 1 Hz – 1 MHz were made by mounting the wafer pieces in the active sample holder of Analytical Instrument Systems GmbH (AIS) Alpha-S high-resolution dielectric analyser. At higher frequencies, from 1 MHz to 1.8 GHz, dielectric measurements were performed with an Agilent 4291B impedance analyser, which measures impedance using a reflectance technique. As the sample cell of this instrument only has an internal diameter of 14 mm, small pieces were cut from larger samples prepared in the same manner as for low frequency measurements. These instruments are described in Appendix A.

The polymeric materials were obtained from T. Pakula at the Max Planck Institute for Polymer Research, Mainz, Germany in the form of amorphous granules with the labels T8007 and T6013. Details of the composition and molecular weight of these polymers are not known other than they are poly(ethers) [21].

Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris TGA on small samples of both polymers by heating between room temperature and 900 °C at 10 K min⁻¹ under air and N₂. Differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris DSC was performed by heating at a rate of 20 K min⁻¹ to estimate T_g for the polymers.

10 % w/v solutions of T8007 and T6013 were prepared by dissolving weighed amounts in 10 mL volumes of chloroform. The solutions were then filtered through 0.45 μ m syringe filters. After filtering, the solution was dropcast onto 25 x 32 mm pieces of glass slide. The glass pieces were prepared by washing in detergent, rinsing with deionised (DI) water, and drying at 60 °C. The glass was also wiped with acetone prior to dropcoating.

The T8007 dropcast films were dried in ambient for 1.5 days, and then heated to 130 °C at 2 K min⁻¹ and held at that temperature for 2 h. The samples were then cooled

slowly. A similar heat treatment was found to cause bubbles in the T6013 films, so these were heated to 60 $^{\circ}$ C under vacuum for 1 day to complete solvent evaporation. The polymer films were removed from the glass by immersion in DI water. The freestanding films were dried for 3 h under vacuum at 60 $^{\circ}$ C.

A T8007 and a T6013 film were selected for dielectric measurements. The film thickness was measured at several places on each film using a micrometer. The films were found to be considerably thicker at the edges. 40 nm thick Al films with a nominal diameter of 20 mm were evaporated onto the film through a mask to serve as the bottom contact. Concentric 10 mm Al films with a thickness of 53 nm were evaporated for the top contact. Fig. 6.1 shows the electrode arrangement. The vacuum capacitance C_{vac} was found from the area of the top contact and the film thickness. Dielectric measurements were made between 10 mHz and 10 MHz using the AIS Alpha-S with an ac voltage of 0.2 V. The film was secured between the electrodes of the sample holder, which was heated in a cryostat with a N₂ gas jet controlled by a Novocontrol Quatro temperature controller. The ε' and ε'' spectra of the T6013 film were measured at 2 K intervals at temperatures from 30 °C to 156 °C and the T8007 film was also measured at 2 K intervals between 30 °C and 110 °C.

FTIR spectra of a further two freestanding films were taken in transmission mode with normal incidence between 6500 and 650 cm⁻¹ with a 1 cm⁻¹ resolution using a Biorad FTS-60A spectrometer.





6.3 Results – Si Wafers with SiO₂ and SiOF Films

6.3.1 IR Refractive Index Measurements

Fig. 6.2 shows the transmission IR spectra of pieces sectioned from wafer 1 (SiO₂), and wafer 2 (SiOF). The typical spectral features of SiO₂ are plainly visible in the spectrum of wafer 1, such as the stretching bands at 814 cm⁻¹ (symmetric) and 1090 cm⁻¹ (antisymmetric). These are also seen in the spectrum of wafer 2, shifted to the slightly higher frequencies of 816 cm⁻¹ and 1096 cm⁻¹ respectively. This effect of the doping of SiO₂ with F has been observed before. [13, 14, 16] An additional band at 937 cm⁻¹ is also seen in the SiOF spectra, which is attributed to stretching of the Si-F bond. The band at 610 cm⁻¹, present in both spectra, corresponds to the phonon mode of the Si substrate. The broad features visible in the region from approx. 2000 cm⁻¹ to 6500 cm⁻¹ are interference fringes. If the film thickness is well known, the maxima/minima of these fringes can be used to estimate the film refractive index, *n*. Given the positions in cm⁻¹, v_1 , and v_2 , of two consecutive minima in the absorbance spectrum, the refractive index may be found from

$$n = \frac{1}{2d(v_2 - v_1)},\tag{6.1}$$

where *d* is the film thickness in cm⁻¹. If this analysis is applied to the SiO₂ spectrum we obtain n = 1.467. This value is close to the typical value of 1.46 for CVD SiO₂. [3, 12–16]

Applying Eq. (6.1) to the position of the interference fringe minima in the SiOF spectrum, we obtain n = 1.416, which represents a reduction of 3.5 % compared to the CVD SiO₂ film. The reduction in n is slightly greater than that observed in Ref. [15] where at a fluorine concentration of 3.5 % (determined by FTIR, relative to the O-Si-O antisymmetric stretch peak area) a refractive index of 1.425 was found.



Fig. 6.2 The normal IR transmission spectrum of a piece of Si wafer 1 (0.705 mm thick with a 1.666 μ m SiO₂ film) (-----), and of wafer 2 (0.725 mm thick with a 1.649 μ m SiOF film) (-----) in the range 6500 – 500 cm⁻¹. The positions of the interference fringes, v_1 , and v_2 , used to determine the refractive index of the films are indicated, as are the Si-O stretching bands associated with SiO₂ bonding, the Si-F stretch indicating the presence of bound fluorine in the SiOF film, and the phonon mode of the Si substrate.

Ellipsometry measurements gave thickness and refractive index values of $d = 1.65 \pm 0.04 \ \mu\text{m}$, and $n = 1.455 \pm 0.002$ for the SiO₂ film. The values for the SiOF film were $d = 1.63 \pm 0.04 \ \mu\text{m}$, and $n = 1.441 \pm 0.003$, a reduction of only 0.96 %. The thickness values agree roughly, within error, with those measured at Intel (Ireland), but the refractive index of the SiOF film measured by ellipsometry is higher than that estimated from the FTIR spectra. There are three possible explanations for this. The refractive index of the SiOF film depends on the percentage of fluorine, which varies from point to point over the wafer, and will be different for different samples. However, this effect seems too small to give rise to the difference observed. The

second possible explanation is that the SiOF film absorbed water in the time interval between the FTIR and ellipsometry measurements, raising the refractive index. SiOF is quite hygroscopic [3, 12, 14]. Finally, a calculation of n made from FTIR spectra depends on a precise measurement of the film thickness, which varies by about $\pm 2\%$ across the wafers. The thickness measured using ellipsometry is therefore considered more reliable as it is an average value for the entire wafer.

6.3.2 Dielecric Results

Fig. 6.3 shows a plot of the complex capacitance, $C^*(\omega) = C' - jC''$, for wafer 1 (SiO₂) and wafer 2 (SiOF) samples over the frequency range 1 Hz – 1.8 GHz. The real component, C', is plotted in Fig. 6.3(A) while the imaginary component, C'', is plotted in Fig. 6.3(B). If the system is a homogeneous sample (non-layered) between an arrangement of electrodes, then $C^*(\omega)$ can be related to the complex permittivity, $\varepsilon^*(\omega)$, of the sample material by $\varepsilon^*(\omega) = C^*(\omega)/C_{vac}$, where C_{vac} , the empty capacitance of the electrode arrangement, depends on the geometry of the sample and electrodes.

Since the area of the sample capacitance for the high frequency samples could not be determined accurately, the real and imaginary parts of the measured capacitance may differ by a constant from their actual values. The plot was thus constructed by multiplying the data from a high frequency measurement (1 MHz – 1.8 GHz) on a sample from each wafer by a constant factor to match the limiting capacitance at 1 MHz obtained from a low frequency measurement (1 Hz – 1 MHz). This gives complete C' and C'' spectra for both the SiO₂ and SiOF coated wafers over the whole frequency range of 1 Hz – 1.8 GHz, with adjustment for the different sample and electrode geometry used in the high frequency measurements. The C'' plot shows two relaxations for wafer 1, one centred at 0.94 kHz, and another at 66 MHz, while C' shows dispersion corresponding to these. Wafer 2 also shows two peaks. The low frequency one is at approximately the same frequency (0.85 kHz), but the high frequency one is shifted to a lower frequency of 16 MHz. C' approaches zero in the limit of high frequency in both plots. The form of these dielectric spectra suggested

that the equivalent circuit [22] shown in Fig. 6.4 could be used to describe the data. The circuit has a capacitance, C_0 , in parallel with a series resistance-capacitance (*RC*) pair, R_1 and C_1 . These elements are in series with another resistor R_2 . The effective impedance $Z_{eff}^*(\omega)$ between the terminals of such a circuit is given by

$$Z_{eff}^{*}(\omega) = R_{2} + \frac{1}{j\omega C_{0} + \frac{1}{R_{1} + \frac{1}{j\omega C_{1}}}},$$
(6.2)

corresponding to a complex capacitance, $C_{eff}^*(\omega)$ of

$$C_{eff}^{*}(\omega) = \frac{C_{0} + \frac{C_{1}}{1 + j\omega\tau_{1}}}{1 + j\omega\tau_{2}\left(1 + \frac{C_{1}}{C_{0}(1 + j\omega\tau_{1})}\right)},$$
(6.3)

where $\tau_1 = R_1 C_1$ and $\tau_2 = R_2 C_0$. These times correspond to the low and high frequency maxima in C'' respectively. From Eq. (6.3) it can be seen that the limiting low and high frequency values of C' should be $C_{\omega=0} = C_0 + C_1$, and $C_{\omega\to\infty} = 0$. This equation has been fitted to the wafer 1 and wafer 2 C'' data. The C' and C'' curves generated from the values of C_0 , C_1 , R_1 , and R_2 resulting from fits to the SiO₂ and SiOF (wafer 1 and 2) C'' data are shown as heavy solid lines in Fig. 6.3(A) and (B) respectively. The vertical lines indicate the values of frequency f_1 , and f_2 , corresponding to τ_1 and τ_2 , where $f = 1/2\pi\tau$, obtained from the fits to the SiOF wafer 2 data. Horizontal dotted lines indicate the values of C_0 and $C_0 + C_1$. The parameters C_0 , C_1 , R_1 , and R_2 , of the fits to data in Fig. 6.3 are given in Table 6.2. As can be seen in Fig. 6.3(A) and (B), the fit of the empirical model to the data is reasonable for both wafers. Deviations from the response of the model circuit are seen in the regions between the low and high frequency dispersion/peak in both wafers, and for the high frequency side of the high frequency dispersion/peak in the complex capacitance data of wafer 2. The deviations arise from the fact that a simple equivalent circuit, as is being proposed, can not exactly model the complex SiO₂/SiOF-Si systems.

Fig. 6.3



Fig. 6.3 (A) C' of wafer 1 (SiO₂ film) (\Box) and wafer 2 (SiOF film) (\circ) is plotted against the frequency. The solid lines through the data are the curves obtained when the parameters in Eq. (6.3) take the values shown in Table 6.2. The values of the parameters used for the curves were obtained by the fitting of Eq. (6.3) to the C'' data of the two wafers as described in the text. (B) C'' of wafer 1 and wafer 2 together with the C'' curves. Also indicated on the plot are the relationships between features of $C^*(\omega)$ of wafer 2 and the parameters in Eq. (6.3). The mid and low frequency plateau capacitances correspond to C_0 and $C_0 + C_1$, while the low and high frequency relaxation peak positions are given by $f_1 = 1/2\pi\tau_1 = 1/2\pi R_1 C_1$ and

 $f_2 = 1/2\pi\tau_2 = 1/2\pi R_2 C_0$. For each wafer, the data above 1 MHz have been matched to the data below 1 MHz by multiplying each point by a constant factor.



Fig. 6.4 A diagram of the equivalent circuit, whose effective complex impedance, $Z_{eff}^*(\omega)$, and complex capacitance, $C_{eff}^*(\omega)$, between terminals *a* and *b* are given by Eq. (6.2) and Eq. (6.3) respectively.

Table 6.2 Parameters for the fitting of the equivalent circuit of Fig. 6.4, whose $C_{eff}^*(\omega)$, is given by Eq. (6.3), to the $C^*(\omega)$ data measured for wafer 1 (SiO₂ film) and wafer 2 (SiOF film).

Wafer	C ₀ (nF)	C ₁ (nF)	$\mathbf{R}_{1}\left(\mathbf{k}\Omega ight)$	$\mathbf{R}_{2}\left(\Omega ight)$
1 (SiO ₂)	5.14	2.47	68.2	0.465
2 (SiOF)	4.70	1.75	107	2.06

6.4 Results – Polymer Samples

6.4.1 TGA/DSC Measurements

Fig. 6.5(A) and (B) show the TGA results for the polymer T8007 in air and in a N_2 atmosphere. The % weight remaining and its derivative are shown for both cases. Decomposition occurs in two steps in air, with a small weight loss occurring as low as 265 °C. The main onset is at 430.9 °C, with a maximum rate at 449.6 °C. The second decomposition is fastest at 537.3 °C. Under N_2 there is a single decomposition single step with onset at 453.8 °C and reaching a maximum rate at 479.1 °C.

Fig. 6.6(A) and (B) shows TGA scans for the T6013 polymer sample in air and under N_2 . Decomposition also occurs in two steps in air. The main decomposition onsets at 423.1 °C and is most rapid 441.6 °C. The second decomposition step is fastest at 527.0 °C. Under N_2 , decomposition occurs in a single step at 454.2 °C, reaching a maximum rate at 479.6 °C. TGA for both polymer samples gives similar results, especially under an inert atmosphere.

Fig. 6.7 shows the DSC results for both samples. The T_g of the T8007 sample cannot be determined from the DSC as it does not extend to low enough temperatures. The T_g is below 88 °C. The T_g of the T6013 sample is 149.7 °C. These glass transition temperatures are quite low.

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Fig. 6.5



Fig. 6.5 TGA of polymer sample T8007 between 30 $^{\circ}$ C and 900 $^{\circ}$ C with a 10 K min⁻¹ heating rate in (A) air and (B) N₂. Percentage weight remaining (-----) and its derivative (-----) are shown. Onset and maximum rate temperatures are indicated.

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Fig. 6.6



Fig. 6.6 TGA of polymer sample T6013 between 30 $^{\circ}$ C and 900 $^{\circ}$ C with a 10 K min⁻¹ heating rate in (A) air and (B) N₂. Percentage weight remaining (-----) and its derivative (-----) are shown. Onset and maximum rate temperatures are indicated.



Fig. 6.7 DSC scans for T8007 and T6013 samples. T_g for T6013 is estimated to be 149.7 °C. T_g for T8007 cannot be estimated, but must be less than the peak in the heat capacity (87.8 °C).

6.4.2 Dielectric Results

Table 6.3 shows the results of micrometer thickness measurements on the two dropcast freestanding films used for dielectric measurements. Nine measurements were made for each film in the pattern shown. Position e corresponds to the place where the Al top contact was evaporated and thickness measurements from this position were used to calculate C_{vac} for the polymer samples.

Table 6.3Thickness of T8007 and T6013 freestanding films for dielectricmeasurements, showing sample layout. e corresponds to the position of the top Alcontact.

Position	Sample Layout	T8007 Thickness (mm)	T6013 Thickness (mm)
а		0.070	0.196
Glass Slide		0.047	0.103
Sample	Label	0.167	0.205
a D 32	DC	0.070	0.174
[™] d	e f	0.047	0.091
a	h i	0.164	0.151
h	25 mm	0.127	0.193
		0.167	0.178
i		0.230	0.189

Fig. 6.8(A) and (B) show the ε' and ε'' spectra respectively of the T8007 and T6013 films measured at 30 °C. Data above ~ 1 MHz are unreliable and not shown. The two samples have similar ε'' . Both have almost constant ε' . For T8007, $\varepsilon' = 3.23$ at 0.95 MHz and for T6013 $\varepsilon' = 3.43$ at 0.68 MHz (6.2 % larger).

Fig. 6.9(A) and (B) and Fig. 6.10(A) and (B) show the spectra for the T8007 and T6013 films at a selection of temperatures. ε' decreases with temperature in both cases. However, for the T8007 film, ε' at 110 °C is higher than at 90 °C perhaps due

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to the softening of the film and a reduction in its thickness under the pressure of the sample holder electrodes. For the T6013 film, measurements become scattered above ~ 130 °C indicating that the film has flowed from between the electrodes.

Fig. 6.8



Fig. 6.8 (A) ε' and (B) ε'' spectra of the T8007 and T6013 freestanding polymer films measured at 30 °C.

Fig. 6.9



Fig. 6.9 (A) ε' and (B) ε'' spectra of the T8007 freestanding polymer film measured at several temperatures.

Fig. 6.10



Fig. 6.10 (A) ε' and (B) ε'' spectra of the T6013 freestanding polymer film measured at several temperatures.
6.4.3 Infrared Results

Fig. 6.11 shows the FTIR spectra of freestanding films of the two polymers. The spectra are almost identical. Combined with the similarity of the TGA results, this suggests that the polymers are very similar in structure, perhaps only differing in molecular weight.





X

6.5 Discussion – Si Wafers with SiO₂ and SiOF Films

6.5.1 The High Frequency Peak

The wafer 1 (SiO₂) and 2 (SiOF) samples with aluminium electrodes can be considered as parallel plate capacitors containing two dielectrics (the oxide and the underlying Si substrate) in a layered structure as in figure 6.12(A). The effective complex capacitance (between terminals *a* and *b*), $C_{eff}^*(\omega)$, for such a structure with two capacitors in series will be given by [23]:

$$C_{eff}^{*}(\omega) = \frac{1}{\frac{g_1}{\varepsilon_1^* \varepsilon_0 A} + \frac{g_2}{\varepsilon_2^* \varepsilon_0 A}},$$
(6.4)

where g_1 and g_2 are the oxide and Si thickness, ε_1^* and ε_2^* are their respective complex permittivity, A is the overlap area of the aluminium electrodes, and ε_0 is the permittivity of free space. $C_{eff}^*(\omega)$ [or equivalently the complex impedance, $Z_{eff}^*(\omega)$], is the quantity measured in the dielectric spectroscopy experiments. The equation can also be written in the form:

$$C_{eff}^{*}(\omega) = C_{vac} \frac{g_{1} + g_{2}}{\frac{g_{1}}{\varepsilon_{*}^{*}} + \frac{g_{2}}{\varepsilon_{*}^{*}}},$$
(6.5)

where the factor $C_{vac} = \varepsilon_0 A / (g_1 + g_2)$ is the vacuum capacitance of the structure (the capacitance between *a* and *b* if the dielectric layers are removed).

Since the oxide film has negligible dc conductivity, we can assume that its loss, ε_1'' is small and $\varepsilon_1^* = \varepsilon_1' - j\varepsilon_1''$ becomes $\varepsilon_1^* = \varepsilon_1'$, where ε_1' is the real part of the oxide permittivity.

The Si wafer is a semiconductor however so we must include its loss, ε_2'' due to dc conductivity and so $\varepsilon_2^* = \varepsilon_2' - j\varepsilon_2''$ becomes $\varepsilon_2^* = \varepsilon_2' - j\sigma_{dc} / \varepsilon_0 \omega$ where ε_2' is the real



part of the Si substrate permittivity and σ_{dc} is its dc conductivity.

Fig. 6.12 (A) The layer structure of Si wafer samples used in the dielectric measurements. g_1 and g_2 are the oxide film and wafer thickness. A is the electrode area. (B) An equivalent circuit for a wafer sample with a dielectric film. The oxide with dielectric permittivity ε'_1 is represented as the pure capacitance C1. This is in series with a parallel combination of a capacitance, C2, and a resistance R2, associated with the permittivity, ε'_2 , and conductivity, σ_{dc} , of the Si substrate.

Substitution of these values for the complex permittivity of the oxide and the Si wafer into Eq. (6.5) gives the following:

$$C_{eff}^{*}(\omega) = C_{vac} \frac{g_1 + g_2}{\frac{g_1}{\varepsilon_1'} + \frac{g_2}{\varepsilon_2' - j\sigma_{dc}/\varepsilon_0\omega}},$$
(6.6)

which may be written as:

$$C_{eff}^{*}(\omega) = C_{vac} \frac{(g_1 + g_2)(\sigma_{dc} / \varepsilon_0 + i\omega\varepsilon_2')}{g_1\sigma_{dc} / \varepsilon_1'\varepsilon_0 + j\omega(\varepsilon_2'g_1 / \varepsilon_1' + g_2)}.$$
 (6.7)

To get some idea of the behaviour of the structure at different frequencies we can examine what happens at the low and high frequency limits.

As $\omega \rightarrow 0$, and using $C_{vac} = \varepsilon_0 A / (g_1 + g_2)$,

$$C_{eff}(0) = \varepsilon_0 \varepsilon_1' A / g_1. \tag{6.8}$$

In other words, in the low frequency limit, $C_{eff}^*(\omega)$ reduces to the capacitance of the oxide film alone.

As $\omega \rightarrow \infty$

$$C_{eff}(\infty) = \varepsilon_0 A / (g_1 / \varepsilon_1' + g_2 / \varepsilon_2').$$
(6.9)

In the high frequency limit, $C_{eff}^{*}(\omega)$ is equivalent to the capacitance of the oxide film and the Si substrate in series. $C_{eff}(0)$ and $C_{eff}(\infty)$ are both real quantities.

Eq. (6.7) models the samples with an equivalent circuit consisting of a pure capacitance (representing the oxide film) in series with a parallel resistance-capacitance (*RC*) combination (representing the Si substrate) [see figure 6.12(B)]. It can also be shown that the frequency dependence of $C_{eff}^*(\omega)$ for the structure will be Debye-like by rearranging Eq. (6.6) using Eq. (6.8) and Eq. (6.9), as follows [23]:

$$C_{eff}^{*}(\omega) = C_{eff}(\infty) + \frac{\left[C_{eff}(0) - C_{eff}(\infty)\right]}{\left[1 + j\omega\frac{\left(\varepsilon_{2}^{\prime}g_{1}/\varepsilon_{1}^{\prime} + g_{2}\right)}{\left(g_{1}\sigma_{dc}/\varepsilon_{2}^{\prime}\varepsilon_{0}\right)}\right]} = C_{eff}(\infty) + \frac{\Delta C_{eff}}{\left[1 + j\omega\tau_{D}\right]}, \quad (6.10)$$

where τ_D , the characteristic 'Debye relaxation time', is given by:

$$\tau_{D} = \frac{\varepsilon_{2}'g_{1}/\varepsilon_{1}' + g_{2}}{g_{1}\sigma_{dc}/\varepsilon_{1}'\varepsilon_{0}}.$$
(6.11)

We can obtain an approximate expression for τ_D so that it may be estimated for the samples. Rearranging gives

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$$\tau_D = \frac{g_2(\varepsilon_2'g_1/g_2\varepsilon_1'+1)}{g_1\sigma_{dc}/\varepsilon_1'\varepsilon_0},$$
(6.12)

and since g_1/g_2 will be small in all cases (in our case, the wafer is 3 orders of magnitude thicker than the oxide film), we have [23]

$$\tau_D = \frac{g_2 \mathcal{E}'_1 \mathcal{E}_0}{g_1 \sigma_{dc}}.$$
(6.13)

Using the parameters of wafer 1, $\sigma_{dc} = 7.25 \text{ Sm}^{-1}$ (corresponding to $\rho = 13.8 \Omega \text{ cm}$), $g_1 = 1.666 \,\mu\text{m}, g_2 = 0.705 \text{ mm}$, and assuming $\varepsilon'_1 = 4.0$ we obtain $\tau_D = 2.07 \text{ ns}$, corresponding to a frequency, f = 77.0 MHz.

In addition, the high frequency capacitance for this model must approach zero because of the large thickness difference between the oxide film and the wafer.

In summary, three features are expected – a Debye dependence of $C^*(\omega)$ on ω , with a relaxation peak centred at ~ 10-100 MHz in C'', depending on sample geometry etc. and a vanishing of C' at high frequencies.

The high frequency relaxation observed in the wafer 1 samples (SiO₂ film) exhibits all of these features, while the high frequency peak observed in wafer 2 (SiOF) shows two of them (the high frequency edge of the peak deviates from the model curve).

6.5.2 Estimating ε' of the Dielectric Films

The above analysis suggests a number of possible ways of estimating the permittivity, ε'_1 of the SiO₂ or SiOF film from the $C^*_{eff}(\omega)$ data obtained from measurements on the thin films of dielectrics deposited on Si wafers. First, an estimate for the film permittivity, ε'_1 , can be obtained using the position of the high frequency peak and Eq. (6.13). Second, the C' data for the samples at the central plateau region of 10 kHz – 1 MHz [see Fig. 6.3(A)], which corresponds to $C_{eff}(0)$ for the high frequency relaxation, can be used with Eq. (6.8) if the oxide thickness, g_1 and the electrode area, A are known. This capacitance corresponds to the value C_0 in the equivalent circuit model of Eq. (6.3). Estimates for ε'_1 obtained from the first method, using the

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values of $\tau_2 = R_2 C_0$ are given for wafer 1 (SiO₂) and 2 (SiOF) in Table 6.4. The values obtained from Eq. (6.8) using C_0 are also given. The values obtained using τ_2 found from Eq. (6.3) for both wafer 1 and wafer 2 samples are roughly in the range expected, showing that the suggested origin of the high frequency peak is reasonable.

Table 6.4	\mathcal{E}_1'	for the	SiO ₂	and	SiOF	films.
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Wafer	$ au_2$ (ns)	\mathcal{E}'_1 (from τ_2)	\mathcal{E}'_1 (from C_0)	ε'_1 (from $C_0 + C_1$)
1 (SiO ₂)	2.39	4.65	3.10	4.58
2 (SiOF)	9.68	4.42	2.82	3.87

There appears to be little discrimination between the SiO₂ and SiOF wafers, the ε'_1 value for the latter being reduced by only 4.9 % relative to the SiO₂ film. This could be due to inaccuracies in the resistivity measurements or film thickness variations. It would be expected that the SiOF film on wafer 2 would have ε'_1 of ~ 3.6-3.8 as compared to ε'_1 ~ 4.2 for the CVD SiO₂ film on wafer 1. The estimates of ε'_1 obtained from the mid-frequency plateau capacitance show a considerably greater reduction in ε'_1 for the SiOF film on wafer 2. The value is 3.10 for the SiO₂ film and 2.82 for the SiOF film, a 9.0 % reduction, which is reasonable for the fluorine concentration given. However, these values are much lower than the expected values for the films. If we use the low frequency (1 Hz – 100 Hz) plateau capacitance value $C_0 + C_1$ then values of 4.58 for the SiO₂ film and 3.87 for the SiOF film are obtained, (16 % reduction) which are closer to the expected values but are too large in this case.

6.5.3 Metal-Oxide-Silicon (MOS) Diodes and the Low Frequency Peak

The departure of the calculated ε'_1 from the known values of permittivity for SiO₂ and SiOF films exposes the limitations of the simple model circuits of Fig. 6.4 and 6.12(B) outlined above. However, this fact, together with the presence of the low frequency peak in C" and the corresponding dispersion in C' in both the wafer 1 and wafer 2 samples (1 kHz) can be explained by consideration of the samples as MOS diodes with thick oxide layers. All of the samples consist of a metal contact to which voltage is applied evaporated onto an oxide film on a semiconductor substrate with an ohmic back contact i.e. a MOS diode [24, 25].

An "ideal" MOS diode is one with a flatband voltage of 0 V (a metal-silicon workfunction difference, ϕ_{ms} , of 0 V at an applied voltage of 0 V), no uncompensated charges except on the top contact and in the semiconductor, and a perfectly insulating oxide. The flatband voltage for all MOS diodes (ideal and real) is the voltage applied to the oxide contact when the surface potential, Ψ_s , (the potential difference between the intrinsic Fermi level in the silicon on the oxide-silicon interface and in the bulk semiconductor) is 0 V. Ψ_s essentially quantifies how much and in what direction (down is positive, up is negative) the Si energy bands are bent near the oxide-silicon interface with reference to the bulk. If we consider the properties of an ideal MOS diode with n-type Si, three distinct regimes of behaviour are seen depending on the value of Ψ_s (changed via the applied voltage). When $\Psi_s > 0$, the MOS diode will be in accumulation. The majority carriers (electrons) accumulate near the oxide creating a layer with very high capacitance, C_d , close to the interface. This capacitance C_d is in series with but much greater than the oxide capacitance C_i so that the overall observed capacitance of the MOS diode is ~ C_i . When $\Psi_s < 0$ but $\Psi_s > \Psi_b$ where Ψ_{b} is the potential difference between the intrinsic and extrinsic Fermi Levels of Si, we have the depletion condition where the majority carriers are "depleted" from a region (the depletion layer) near the oxide-silicon interface. The capacitance C_d falls

to approach C_i and the capacitance of the MOS diode, C_{diode} , is given by the series value:

$$C_{diode} = \frac{C_i C_d}{C_i + C_d},\tag{6.14}$$

which will be lower than C_i , eventually reaching a minimum value, $C_{diode,min}$. At more negative $\Psi_s < \Psi_b$ inversion occurs (when $\Psi_s < 2\Psi_b$ the charge in Si builds up more rapidly and we enter strong inversion) with an excess of the minority carriers (holes) within a thin layer close to the interface (the inversion layer). This causes the MOS diode capacitance to increase towards C_i again. With knowledge of the physical properties of the oxide and the silicon substrate, we can calculate the entire capacitance-surface potential curve for an ideal MOS diode by applying the Poisson equation to the charge in the Si [24]. An important point on this curve is the minimum capacitance of the MOS diode, which is given by [24]

$$C_{diode,\min} = \frac{\varepsilon_0 \varepsilon'_1 A}{g_1 + \frac{\varepsilon'_1}{\varepsilon'_2} \sqrt{\frac{4\varepsilon'_2 \varepsilon_0 kT \ln\left(\frac{N_D}{n_i}\right)}{e^2 N_D}}}$$
(6.15)

where ε'_1 is the oxide relative permittivity, A is the diode area, g_1 is the oxide thickness, ε'_2 is the relative permittivity of silicon, k is Boltzmann's constant, T is the absolute temperature (taken as 300 K), N_D is the dopant concentration of the n-type wafer (estimated to be 4 x 10^{20} m⁻³), n_i is the intrinsic carrier concentration, and e is the electron charge. Using the parameters of our SiO₂ low frequency sample we obtain $C_{diode,min} = 5.25$ nF, which is close to C_0 suggesting that some of the reduction in capacitance is due to the effect of the interface layer (depletion/inversion) capacitance, $C_d \cdot C_{diode,min}$ is still a large fraction of the expected oxide capacitance (~ 80 %) because the effect is greatly reduced as the oxide becomes thicker. In a real MOS structure, there are various charges [24] located at the SiO₂-Si interface (interface trapped charge), fixed near the interface within the oxide (fixed oxide charge), distributed in the oxide (oxide trapped charge), or free to travel through the oxide (mobile ionic charges). The interface-trapped charge may arise from the

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disruption of the Si lattice at the SiO₂-Si interface, resulting in the creation of energy levels in the bandgap of Si. The fixed oxide charge is composed of unreacted Si ions and incompleted bonds close to SiO₂-Si interface and it cannot be charged or discharged. The oxide-trapped charges are associated with defects (e.g. impurity atoms) in the oxide itself. The mobile charges are alkali ions (typically Na⁺). The main effect of the oxide charges is to just to shift the position of the Capacitance-Voltage (*C-V*) curve and the flatband voltage by requiring compensation before Ψ_s itself can be changed. The interface trapped charges however as well as shifting the *C*-*V* curve can give rise to dispersion in the *C'*, and a peak in the *C''* spectra (or Conductance spectra) of a MOS diode, and such effects have been modelled by *RC* circuits [24]. The interface-trapped charge could thus contribute to the peak observed here at low frequencies for both wafer samples.

As can be seen above, the system is very complicated and full *C*-*V* curve measurements at various frequencies as well as dielectric spectra would be required to establish exactly which physical processes contribute to the parameters of the empirical circuit represented in Fig. 6.4 and Eq. (6.2) and (6.3). In any case, a more complicated circuit may be needed to take account of the MOS diode effects (depletion layer). However, it seems clear that R_2 corresponds to the resistance of the silicon wafer. The product of R_1 and C_1 may be associated with the lifetime of the interface traps [24]. If this were so then C_1 could be used to estimate the number of traps [24] but it is possible that C_1 here is not purely associated with the traps but is also related to the depletion layer capacitance, $C_d \cdot C_0$ seems to correspond to the minimum capacitance of the MOS diode itself.

6.5.4 Comparison with Other Results

Dielectric measurements in the microwave frequency range have been made on bare Si wafers by Fannin et al. [19] and by Ding et al. [18], and on Si wafers with deposited dielectric films (thermally grown SiO₂ and spin-on dopant glasses) by Fannin et al. [19]. Fannin et al. have measured two bare Czochralski (CZ) n-type Si

wafers; (i) a <100> orientation wafer with $\rho = 9 - 15 \Omega$ cm and; (ii) another with <111> orientation and $\rho = 3 - 5 \Omega$ cm, as well as; (iii) a sample of the second type on which was deposited a 0.250 µm film of thermally grown SiO₂, while Ding et al. [18] measured; (ia) a 60 x 50 x 40 mm piece cut from a <100> CZ ingot ($\rho = 18.4 \Omega$ cm), and; (iia) a 2mm thick <100> Float-Zone grown (FZ) n-type Si wafer ($\rho = 500$ Ω cm). The ε'' spectra of all the CZ-grown Si samples (see Fig. 2 in Ref. [18], and Fig. 1 in Ref. [19]) in the GHz frequency range show large relaxation peaks (dielectric strength, $\Delta \varepsilon \sim 20$), which are roughly Debye like (slightly skewed), at frequencies of 1.2 GHz and 2.8 GHz for samples (i) and (ii) in Ref. [19] and at 1.35 GHz for sample (ia) in Ref. [18]. Sample (iii) with the thermally grown SiO₂ [19] had a peak at 3.6 GHz, with a suggestion of another one at higher frequencies. There is dispersion in ε' corresponding to the peak, from ~ 70 at low frequencies to ~ 12 at high frequencies, in all these samples except sample (iii) of Ref. [19] (with oxide film), where the low frequency static value of ε' is only about 50. These values of ε' are too large to be meaningful for Si and especially for SiO₂-Si systems.

It is interesting to note that samples for dielectric measurements with the dielectric probe system must fulfil certain requirements before the ε' and ε'' data obtained can be considered to be reliable. The technique requires that the thickness of the dielectric sample on which measurements are made be sufficiently large to appropriately reflect the signal for measurement by the network analyser. Specifically, the sample thickness in mm must be $>20/|\varepsilon^*|$ [20]. If we assume that ε^* , is given by

 $\varepsilon^* = 12 - i(\sigma_{dc} / \varepsilon_0 \omega)$, then at 1 GHz, the thickness is 0.2 mm for sample (ia), and 1.6 mm for sample (iia) of [18]. This condition is satisfied in the case of sample (ia) and just about satisfied for the wafer sample (iia). For sample (i) and (ii) in [19], the limiting values for thickness at 1 GHz are respectively, 0.17 mm and 0.06 mm, which may not have been satisfied in the measurements made. However, the oxide film ($\varepsilon^* \sim 3.9$) of sample (iii) at 0.250 µm thick could definitely not satisfy this requirement at all. Hence, the results for ε' of Si and Si-SiO₂ systems using the dielectric probe kit cannot be relied upon. Our results on the other hand are much closer to those expected for the SiO₂ and SiOF thin films.

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6.6 Summary

FTIR measurements indicate that the refractive index, n, of the SiO₂ film is ~ 1.467 and that of the SiOF film is 1.416– a reduction of 3.5 %, which is reasonable given the fluorine content of the SiOF film. Ellipsometry measurements of the film thickness compare well with those given by Intel, while measurements of n give 1.455 for the SiO₂ film and 1.441 for the SiOF film (0.96 % reduction). The difference between FTIR and ellipsometry measurements may be explained by variations in the film thickness between different samples, or the water vapour absorbed by the SiOF film.

 $C^*(\omega)$ of SiO₂ and SiOF CVD dielectric films deposited onto Si wafers between Al electrodes has been found to vary in a complicated way with the frequency in the range 1 Hz – 1.8 GHz. C' shows two steps, and decreases towards negligible values at high frequency, while C" has two relaxation peaks, the first centred in the kHz region and the other centred in the 10-100 MHz region. An equivalent circuit model has been suggested which explains the position of the high frequency peak in terms of the resistance and capacitance of the wafer and the capacitance of the dielectric film. The model also predicts a Debye relaxation profile and negligible C' at high frequencies. In the case where the dielectric film capacitance is much greater than that of the underlying substrate, this reduces to Eq. (6.13), in which the relaxation time, τ_D of the peak is found to depend on ε_1' of the oxide, the resistivity, ρ , of the wafer, and the ratio of the wafer and oxide thickness, g_2 and g_1 . Given the values of ε_1' , ρ , g_2 , and g_1 for the wafer 1 (SiO₂) samples, the model approximately predicts the peak position.

An empirical equivalent circuit model [Eq. (6.3), and Fig. 6.4] has been fitted to the $C^*(\omega)$ data, which allowed the estimation of ε'_1 of the SiO₂ and SiOF films from the relaxation time of the high frequency peak using Eq. (6.13), and the mid and low frequency plateau capacitances in C' using Eq. (6.8). The model provides a reasonably good fit to the $C^*(\omega)$ data for both wafers, with departures observed

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between the low and high frequency peaks for both wafer 1 and 2, and for the high frequency edge of the high frequency C'' peak and C' dispersion for wafer 2. The relaxation time method gives only a rough estimate of ε'_1 . The average central plateau ε'_1 value is 3.10 for the SiO₂ film samples and 2.82 for the SiOF film, a 9.0 % reduction. If we use the low frequency plateau capacitance value, we find average values of ε'_1 of 4.58 for the SiO₂ film and 3.87 for the SiOF (16 % reduction), which are closer to but larger than the expected values. The peak in C'' and dispersion in C'observed at low frequencies may be caused partly by trapped charge at the Si-SiO₂ interface, and the fact that the sample forms an MOS diode with a depletion layer capacitance, C_d . Some limitations associated with the use of a dielectric probe for measuring ε' of Si wafers and films deposited on them have been outlined. The variation in $C^*(\omega)$ measured at different frequencies shows that it may be desirable to evaluate the behaviour of MOS structures over a range of frequencies and voltages rather than obtaining C' at one frequency using a C-V meter to determine ε' from the sample geometry, as is usually done – especially in cases where ρ of the Si substrate is not negligible. It should be noted that all the unusual features observed in the dielectric spectra of the oxide films coated onto Si wafers are the result of the layered nature of the samples used. If the moderately doped semiconductor wafer were replaced by a metal, then typical dielectric spectra of an insulator would be obtained. Finally, the T8007 and T6013 polymers were found to have ε' values of 3.23 and 3.43. Such ε' values are quite low for solid materials, but are close to the ε' values of CVD films now being used as ILDs. Much lower ε' values (< 2) are required in the future that can only be achieved by using porous materials. The onset decomposition temperatures of T8007 and T6013 determined by TGA are 430.9 °C and 423.1 °C under air and 453.8 °C and 454.2 °C under N2. The TGA and FTIR measurements suggest that the polymers are very similar in composition. DSC measurements, and the behaviour on heating film samples during dielectric measurements indicate T_g below 150 °C for T6013 and below 110 °C for T8007, which implies that they may not be useful for microelectronic applications.

6.7 References

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Conclusions

Discrete conclusions (A - D) are given in sequence for each area covered in this thesis. This material is similar to the summaries at the end of Chap. 3-6.

(A) The three dielectric relaxation processes (I – III) observed in the aliphatic alcohols 1-propanol and 5-methyl-2-hexanol are also found in dilute solutions of LiClO₄ in these. Addition of 1.0 mol% LiClO₄ to 1-propanol and 0.5 mol% and 1.0 mol% to 5-methyl-2-hexanol causes no change in the relaxation rate and only a small change in the distribution parameters of process I, which is asymmetrically broadened to a Davidson-Cole distribution. The extent of this broadening is greater at the higher salt concentration in 5-methly-2-hexanol.

A larger decrease in the ε_s of 1-propanol is observed than expected from continuum theory of the kinetic dielectric decrement due to ions. It is attributed to a decrease in orientational correlation caused by intermolecular H-bonds. Decrease in ε_s is mostly due to a decrease in $\Delta \varepsilon_I$. The decrease in H-bonding is expected to decrease the viscosity of 1-propanol and thereby increase the dipolar relaxation rate. No increase is found in the relaxation rate of any of the relaxation processes – that of process II decreases. Thus, either the relaxation rate is not related to the viscosity or the iondipole interaction in the solvation shell decreases the relaxation rate. The decrease in ε_s of 5-methyl-2-hexanol is less than that anticipated by the continuum theories of kinetic dielectric decrement at both concentrations below ~ 203 K, while above this temperature ε_s increases by an amount that is similar for both

salt concentrations. It is suggested that the presence of ions has little effect on Hbonding in 5-methyl-2-hexanol and the increase in ε_s may be a result of the formation of ion-pairs in the salt solution, which become free to orient as the

Conclusions

viscosity falls. $\Delta \varepsilon_1$ decreases below 203 K and increases above it as LiClO₄ is added, as does ε_s .

In both alcohols, process I is identified as the α -relaxation and process II is assigned to the rotation of the –OR group, where R is C₃H₇ in the case of 1-propanol, and C₇H₁₅ in the case of 5-methyl-2-hexanol. Both processes in each of the alcohols follow the VFT equation. It had been argued that process I cannot be associated with structural relaxation because it doesn't appear in light scattering measurements, and viscosity data correspond more closely to process II. Here, it is concluded that process I is involved in structural relaxation in alcohols. The dielectric strength (process I contributes > 90% of the total polarisation), and comparisons with results from alcohols where H-bonding is sterically hindered (process I is larger than expected) are used to support this.

Process I is approximately Debye in the pure alcohols (in 5-methyl-2-hexanol it is slightly asymmetrically broadened) and it is therefore concluded that a non-Debye process is not a prerequisite for the α -process. This can be explained by the idea of differences in the rate at which individual dipoles and their environment relax. Process III in both alcohols can be separated, follows the Arrhenius equation, and persists below T_g , and will merge with the lower frequency relaxation processes at some temperature. It is thus classified as a Johari-Goldstein process.

(B) It was found that supercooled liquid D-sorbitol transforms to either an orientationally ordered or disordered crystal when held at a constant temperature below its melting point. The orientationally ordered form is obtained if the melt is contaminated by crystalline D-sorbitol. The evidence for existence of the orientationally disordered form is; (i) ε_s remains at ~ 14-15 after keeping a D-sorbitol sample for almost 6 days at a temperature of 332.8 K; (ii) the strength of the JG β -relaxation in a sample crystallised at 298.5 K for ~ 4 days is larger than can be explained by the residue of a small amount of uncrystallised liquid phase, and; (iii) the presence of a new relaxation (α -relaxation of the orientationally disordered crystal) below 1 Hz in the sample crystallised at 298.5 K suggested by changes in the slope of the low frequency wing of the ε' spectra.

The strength of the JG β -relaxation for the orientationally disordered crystal phase of D-sorbitol is found to be less than half of that for the liquid, the spectra are considerably broader, and the relaxation rate was higher. The orientational glass

transition in the disordered crystalline phase occurs at a higher temperature than T_g of the supercooled liquid, and the rate of its α -relaxation process is lower.

A quantative analysis with the Avrami equation was performed for the crystallisation at 298.5 K by normalising ε_s so that it corresponded to the volume fraction of liquid remaining, 1 - x. The slope and intercept of a plot of $\ln[-\ln(1-x)]$ vs. $\ln(t-t_0)$ gave for the parameters of the Avrami equation n = 1.58 (i.e. mass transport controlled growth with instantaneous nucleation of 3*d* nuclei) and $k_A = 1.85 \times 10^{-8}$.

The onset of crystallisation of D-sorbitol to the orientationally disordered phase occurs at an earlier time at 298.5 K than at 332.8 K, and the crystallisation rate is found to be faster, which is opposite to what is expected given that cooling decreases both the crystallisation rate constant and the nucleation rate. This suggests that there is a structural change in the liquid at 298.5 K, which enhances the crystallisation rate.

(C) Stabilisation effects are observed for $\Delta \varepsilon_{JG}$ and $f_{m,JG}$ of rapidly quenched 5methyl-2-hexanol and D-sorbitol glasses as they are heated at a constant rate. The plot of $\Delta \varepsilon_{JG}$ vs. *T* shows a minimum like plots of thermodynamic properties for a rapidly quenched glass as it is heated at a slower rate, and the log scale plot of $f_{m,JG}$ vs. 1/Thas a more negative slope at low temperatures. It is shown that this behaviour could be explained in terms of a total derivative of $\Delta \varepsilon_{JG}$ and $f_{m,JG}$ that depends on the time and temperature dependent rates of change of $\Delta \varepsilon_{JG}$ and $f_{m,JG}$, and on the heating rate.

For rapidly quenched glasses, $\Delta \varepsilon_{JG}$ is confirmed to decrease with structural relaxation during annealing while for D-sorbitol $f_{m,JG}$ is shown to increase. The change of $f_{m,JG}$ on structural relaxation was also deduced from the Arrhenius plots for both 5-methyl-2-hexanol and D-sorbitol sample C. At temperatures far below T_g , the value of $f_{m,JG}$ expected on the basis of extrapolation of the Arrhenius behaviour of the high temperature data was found to be inaccessible in finite annealing times. It has been established from a nonlinear fitting analysis of dielectric spectra that the temperature dependence of $f_{m,JG}$ on an Arrhenius plot undergoes a change at T_g for diethyl phthalate. Below T_g , the dependence is Arrhenius, around T_g the relaxation frequency becomes temperature independent, and above T_g the slope magnitude increases and becomes closer to the α -relaxation. The slope change can be explained

Conclusions

by a coupling between the α - and JG β -relaxations above T_g . The prediction for τ_0 of the Coupling Model provides a reasonable estimate for the JG β -relaxation time above T_g .

The typical features of the JG β -relaxation were confirmed in all glasses – an Arrhenius temperature dependence of $f_{m,JG}$ below T_g , a decrease in broadness with increasing T, and $\Delta \varepsilon_{JG}$ increasing more strongly for $T > T_g$ than $T < T_g$. The temperature dependence of $\Delta \varepsilon_{JG}$ was shown to be similar to that of the thermodynamic properties of glasses (V, H, S).

FTIR measurements show that the refractive index, n, of a sample of an SiOF (D)CVD film on an Si wafer is 3.5 % less than that of a SiO₂ film, as would be expected. Ellipsometry measurements of the film thickness compare well with those given by the supplier of the wafer samples (Intel), while values of n give only a 0.96 % reduction for the fluorinated film. It is concluded that differences between FTIR and ellipsometry measurements is due to either variations in the film thickness between samples, or water vapour absorbed by the SiOF film between the measurements. The complex capacitance, $C^*(\omega) = C' - jC''$, of samples of Si wafers with deposited SiO₂ and SiOF films and evaporated Al electrodes has been found to vary in a complicated way with the frequency in the range 1 Hz - 1.8 GHz. C' shows two steps, and decreases towards negligible values at high frequency, while C'' has two relaxation peaks, the first centred in the kHz region and the other centred in the 10-100 MHz region. An equivalent circuit model with parallel resistor and capacitor terms for the loss and permittivity of the wafer and a series capacitance for the permittivity of the dielectric film explains the position of the high frequency peak. The model also predicts a Debye relaxation profile and negligible C' at high frequencies. In the case where the dielectric film capacitance is much greater than that of the substrate, a simple relationship between the relaxation time, τ_D of the peak and ε'_1 of the oxide, the resistivity, ρ , of the wafer, and the ratio of the wafer and oxide thickness, g_2 and g_1 , is found. Given the values of ε'_1 , ρ , g_2 , and g_1 for wafer sample with the SiO_2 film, the model roughly predicts the peak position. An empirical equivalent circuit model that covers the entire spectrum is also suggested. This has been fitted to the $C^*(\omega)$ data, which allowed the estimation of ε'_1 of the SiO₂ and SiOF films from both the relaxation time of the high frequency peak

and the mid and low frequency plateau capacitances in C'. The relaxation time method gives only a rough estimate of ε'_1 . The average central plateau ε'_1 value is 3.10 for the SiO₂ film samples and 2.82 for the SiOF film, a 9.0 % reduction. If we use the low frequency plateau capacitance value, we find average values of ε'_1 of 4.58 for the SiO₂ film and 3.87 for the SiOF (16 % reduction), which are closer to but larger than the expected values. The peak in C'' and dispersion in C' observed at low frequencies may be caused partly by trapped charge at the Si-SiO₂ interface, and the fact that the sample forms an MOS diode with a depletion layer capacitance, C_d . It is concluded that a dielectric probe is not suitable for measuring ε' of Si wafers and films deposited on them.

The T8007 and T6013 polymers were found to have ε' values of 3.23 and 3.43. High decomposition temperatures are found for T8007 and T6013. However, DSC measurements, and heating film samples during dielectric measurements indicate T_g below 150 °C for T6013 and below 110 °C for T8007 It is concluded that the polymers are not useful as low-k dielectrics for microelectronic applications.

Appendix A Apparatus

A.1 Oxford Instruments Cryostat and Temperature Controller

A.1.1 General

For the dielectric measurements made with the Solartron FRA-1255A frequency response analyser (Solartron FRA) [1] and Chelsea dielectric interface (CDI) [2], the temperature of the sample was controlled with one of the two following systems; (i) Oxford cryostat and temperature controller, and; (ii) Heto cryobath with temperature controller. The second of these is described in Sect. A.2.

A schematic of the Oxford Instruments Spectrostat DN cryostat [3] is shown in Fig. A.1, with the important parts labelled descriptively. The cryostat can operate between 77 K and 500 K. The sample is loaded through a central port in the top on an armature (shown in Fig. A.2).

The cryostat has a metal body, inside which is an evacuated space that provides thermal insulation. This contains a sorb for removing gas when the cryostat vacuum chamber is not connected to a vacuum pump. In the body of the cryostat is a reservoir for coolant (liquid N_2). The tapered part at the bottom contains a cylindrical sample space 20 mm in diameter and 50 mm long. Below this is a heat exchanger. Liquid N_2 is fed to the heat exchanger from the reservoir through a capillary tube. The flow is controlled by the needle valve at the top of the cryostat. Further valves can be used to isolate both the sample space and the vacuum chamber from ambient. There are also two ports for filling the reservoir and venting evaporated N_2 from the cryostat. A DIN style plug at the top of the cryostat allows connection of the Oxford ITC502 temperature controller [4]. There are two heaters, one in the heat exchanger for sample temperature control, and another in the body for activating the sorb in the vacuum chamber. A Pt 100 Ω resistance sensor measures the temperature in the heat exchanger.



Fig. A.1 Oxford Spectrostat DN cryostat with important features labelled (after [3]).

A.1.2 Preparing for Cooldown

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The sorb is activated before using the cryostat as follows. A rotary oil pump is connected to the vacuum chamber, which is pumped down. The ITC502 is connected to the cryostat via an adapter cable. This arranges for the ITC502 to control the power supplied to the heater in the body of the cryostat. The manual setting of the temperature controller is used with a voltage of 18 V. The sorb is then left to outgas overnight (manual recommends at least 4 h). A pressure of at least 5 x 10^{-2} mbar (measured via a Pirani gauge connected to the vacuum pump) is attained after this time. After this, the ITC502 can be disconnected and the sorb allowed cool before closing the vacuum chamber valve and disconnecting the pump.

A.1.3 Cooldown

Once the vacuum chamber is evacuated and sealed, the sample space is fitted with a cap and the pump connected to it. Once this has been pumped down for a few minutes to a reasonable vacuum (not as high as the vacuum chamber), the sample space valve is shut and the pump reconnected to the vacuum chamber. The vacuum chamber valve can be opened again without breaking the vacuum once the tubing has been evacuated. In most cases, the pump was allowed to run for the duration of the measurement as this maintained a better vacuum for groups of measurements lasting several days without needing to recharge the sorb. The ITC502 is reconnected without the adapter cable so that it controls the heat exchanger heater. The voltage is set to 0 V, with the temperature controller in manual mode.

The cryostat can then be cooled down its base temperature of 77 K by opening the needle valve ~ 4 turns and filling with liquid N₂ through one of the ports on the top. These ports have pieces of stiff polythene tubing attached to them to minimise icing of the vents (an explosion hazard) and prevent cold gas from the vents damaging the seals and connections on the top of the cryostat. When the cryostat has reached the base temperature (or the desired temperature), the needle valve can be set almost closed to slow the evaporation rate of the liquid N₂ through the valve and the ports. The cryostat can maintain stable temperatures for ~ 3 - 5 h (longer times at lower temperatures) before refilling with coolant is required.

A.1.4 Sample Loading

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Before loading the sample, a rubber bladder is filled with N₂ gas by dipping a metal tube in liquid N₂. This bladder is then connected to the sample space. A small amount of N₂ is allowed into the sample space from the bladder to break the vacuum. The cap can then be removed from the port. The sample cell holder (Fig. A.2), to which is attached the dielectric sample cell vial containing the liquid, is inserted into the cryostat. Thin coaxial cable connects the multiplate capacitor to two male BNC terminals on top of the sample holder. These are connected to the sample BNC terminals on the CDI via coaxial cable. The Pt 100 Ω resistance sensor immersed in the cell is connected to a plug on top of the sample holder. This is then connected to a Keithley 195 A digital multimeter (DVM), which allows 4-wire measurement of the temperature. The digital multimeter is also connected to the computer via a general-purpose interface bus (GPIB) or IEEE-488 interface for control and the recording of sample temperatures.

When the sample has been loaded, the remaining N_2 in the bladder is released into the sample space. Although the sample holder has an o-ring seal where it mates with the cryostat, the connections at the top of the holder are not perfectly sealed and air can enter slowly. The N_2 in the bladder can maintain an inert atmosphere for some time if it is replenished.

A.1.5 ITC502 Temperature Controller

The ITC502 is a PID temperature controller supplied with the cryostat. The PID settings are correctly set at factory for the system so they are not discussed. The controller is calibrated for use with the temperature sensor in the cryostat. When in auto mode with a set temperature > 77 K, the ITC502 controls power supplied to the heater in the heat exchanger cooled by liquid N₂ from the reservoir. The coolant flow is independently controlled by setting the position of the needle valve.

The controller is capable of executing temperature ramps at a set rate, or holding a temperature for a set time, or any sequence of both.

The ITC502 can be adjusted manually from its front panel or it can be sent commands by and output data to a computer using its RS-232 serial port connector.



Fig. A.2Sample holder for insertion into the Oxford cryostat. Main parts arelabelled.

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A.1.6 Temperature Stability of the Oxford Cryostat

The standard deviation of sample temperature (measured with the temperature sensor in the sample) from the mean value over several hours is ± 0.1 K. This temperature can be as much as 2.5 K above the set temperature range near the lower temperature limit for the cryostat, and is below the set temperature at temperatures above ambient. The magnitude of the difference increases at the limits of the cryostat's working temperature range. If the cryostat is not refilled regularly (every 3 h) the mean temperature will begin to increase over time and the maximum deviation will obviously become much larger.

A.2 Heto Cryobath and Temperature Controller

A.2.1 Features of the Heto Bath Setup

The Oxford cryostat is not suitable for some situations.

At temperatures above 0°C but not much higher than ambient, the Oxford Instruments cryostat maintains a stable sample temperature only if it is filled with cryogen. The capillary supplying cryogen to the heat exchanger often becomes iced up when operating the cryostat at these temperatures. In addition, the liquid N₂ reservoir must be replenished regularly, which is awkward for measurements lasting several days. Both of these problems applied to the dielectric measurements on the crystallisation of D-sorbitol in Chap. 4, so a Heto 8-30 cryobath [5] with a HMT 200 thermostat [6] was used. This system consists of a refrigerated bath capable of cooling 8 L of liquid to 243.2 K (-30 °C). With the thermostat fitted, the bath temperature can be controlled between 243.2 K and 393.2 K (120 °C) [temperatures > 373.2 K (100 °C) cannot be used continuously]. Different liquids with appropriate freezing, boiling, and flash points are used in the bath depending on the temperature. The temperature controller on the thermostat can maintain the set temperature for the liquid to ± 0.1 K, and is capable of computer control and data collection via a serial port connector.

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A.2.2 Sample Holder for use with Heto Bath

The thermostat and the bath have fittings that allowed the liquid to be recirculated through an external sample holder, custom built by the Department of Civil, Structural and Environmental Engineering, which contains the dielectric cell. The body and lid of the sample holder are shown in Fig. A.3 and A.4. The sample holder and lid were lagged with pipe insulation foam and placed in a foam bucket. Polythene tubing with pipe insulation was used to pipe the liquid to and from the bath.

The sample holder is a double wall brass cylinder, with an isolated inner sample chamber 25 mm in diameter and 75 mm deep. The liquid circulates in the gap between the walls of the cylinder to control the temperature of the dielectric cell, which was contained in a close fitting brass inset. The aluminium lid has an o-ring seal for the sample chamber, two coaxial cables with female BNC terminals for connection of the multiplate sample capacitor to the Chelsea dielectric interface, and a copper capillary N₂ gas inlet to ensure an inert atmosphere inside the sample chamber. The 4 wire connections between the Pt 100 Ω temperature sensor and the Keithley DVM are also incorporated in the lid. The lid can be secured with two screws.



Fig. A.3 Dielectric sample cell holder for use with the Heto bath and thermostat.



Fig. A.4 Lid of the sample cell holder showing connections to the capacitor and temperature sensor.

A.3 Solartron Frequency Response Analyser and Chelsea Dielectric Interface (1 mHz – 1 MHz)

Two main apparatus were used for measuring dielectric spectra. The first is the Solartron FRA and CDI, used with the above temperature control systems; the second is a Broadband dielectric spectrometer (BDS) (Novocontrol GmbH), discussed in Sect. A.4.

A.3.1 Principle of an Impedance Measurement with the Solartron FRA and CDI

The basic principle of measurement of the complex permittivity $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$ using the Solartron FRA and CDI is to apply a sinusoidal voltage to the dielectric

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sample and measure the current that flows through the sample in some way. Using the phasor notation for frequency dependent voltage V^* and current I^* (the real part of the exponent is the actual voltage or current), the applied voltage is:

$$\mathbf{V}^* = V_0 \exp(j\omega t) \tag{A.1}$$

where *t* is the time.

The current has a constant angular phase difference ϕ from the voltage so

$$\mathbf{I}^* = I_0 \exp[j(\omega t + \phi)]$$
(A.2)

The frequency dependent complex impedance $Z^*(\omega) = Z' + jZ''$ is [7]

$$Z^*(\omega) = \mathbf{V}^* / \mathbf{I}^* = \frac{V_0}{I_0} \exp(-j\phi).$$
(A.3)

Defining a complex capacitance as $C^*(\omega) = C' - jC'' = \varepsilon^*(\omega)C_{vac}$ where C_{vac} is the vacuum capacitance of the empty cell, the complex permittivity is given by [7]

$$\varepsilon^*(\omega) = \frac{1}{j\omega C_{vac} Z^*(\omega)}.$$
 (A.4)

The FRA and CDI allow for calculation of the ratio of the vector voltage and current as will be described.

A.3.2 FRA and CDI Setup

Fig. A.5 is a diagram showing the overall setup of the FRA/CDI dielectric measurement system. The dielectric cell, temperature control system with sensor (Oxford or Heto), and the DVM and temperature sensor for sample temperature measurements are all shown. The FRA and CDI are controlled by a computer via a GPIB interface using Novocontrol WinDETA software. The Solartron FRA also has front panel control; the CDI may only be controlled by sending commands over the GPIB bus.



Fig. A.5 Solartron FRA/CDI measurement setup showing connections, temperature control system, sample temperature measurement via digital multimeter (DVM), and dielectric cell.

A circuit diagram [2] for the Chelsea dielectric interface and its connections to the Solartron FRA is shown in Fig. A.6.

The frequency response analyser generator (GEN) output and correlator channel 1 (Ch. 1) and 2 (Ch. 2) inputs are connected to the GEN input and Ch. 1 and 2 outputs of the CDI. The CDI is connected to the dielectric sample cell through terminals 11 and 12, and to a known reference capacitor through terminals 21 and 22. The generator output terminal has 50 Ω impedance and the two channels have input impedance of 1 M Ω . All connections are made with coaxial cables to BNC terminals. For all measurements with this system reported in this thesis a reference capacitance of 100 pF was used. The FRA generator outputs a sinusoidal voltage of a given frequency and amplitude. V1^{*} and V2^{*} are the vector voltages on Ch. 1 (which measures the generator voltage applied to the reference and sample) and Ch. 2 [measures the output from the current-voltage (*I-V*) converter of the CDI] of the Solartron FRA, all with respect to ground. The channels select the component of input and output voltage at the same frequency as the generator and measure the magnitudes and relative phase.





The CDI has a number of operating modes depending on the positions of S1 and S2, and the earth switches. In Mode 0, S1 and S2 are open and the terminals 12 and 22 are grounded. This is the power on mode in which the *I-V* converter is isolated. In addition, a 200 Ω protective resistor is placed in the feedback loop of the *I-V* converter on powerup. In Mode 1 (sample circuit measurement), S1 is closed, S2 is open and 22 is grounded. The sample output 12 is connected to the *I-V* converter. In Mode 2 (reference circuit measurement), S1 is open with 12 grounded and S2 is closed connecting 22 (reference output) to the *I-V* converter. In mode 3 (not used here), both S1 and S2 are shut, with the earth switches both open. The feedback loop of the *I-V* converter has 23 resistors R_m from 10 Ω to 1 T Ω (~ 2 per decade) and 2 capacitors C_m of 100 and 1000 pF. Any *RC* parallel pair of these can be selected by

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setting switches in the CDI. Fig. A.7 shows a close-up of the dielectric cell itself, a capacitor and temperature sensor in a glass vial 33 mm long and 10 mm in diameter. A detailed schematic of the multiplate capacitor (Alfred Tronser GmbH) used in the liquid measurements is also shown in the figure. The capacitor plates are silver-plated brass and the capacitor base is ceramic. The capacitor plates are arrayed alternately on a rotor and stator with 0.2 mm gap between plates allowing tuning of the capacitance by turning the shaft to separate the plates. Each plate is approximately semicircular with a radius of ~ 4 mm. The capacitors either have 18 plates (13.8 mm high) and a capacitance of 17 pF or 24 plates (16.5 mm high) and a capacitance of 27 pF. The cell was used for measurements on small-molecule liquid and glassy samples. The air capacitance of the system comprising the cell connected to the sample holder for the Oxford cryostat or the lid of the sample holder for the Heto cryobath is accurately measured prior to filling the cell with liquid. The cell is shielded in a metal container during this measurement. The glass vial can then be filled with the liquid to be studied.



Fig. A.7 The dielectric sample cell for small-molecule liquids and glasses. This is connected to the sample holder for the cryostat or lid of the sample holder for the cryobath. A schematic of the multiplate capacitor is also shown. The height, h, is either 13.8 mm for the 18 plate or 16.5 mm for the 24 plate capacitor.

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A.3.3 Measurement of Z^{*}

In order to measure the impedance of the sample $Z^*(\omega)$, a sinusoidal voltage at some angular frequency ω of suitable amplitude is output from the generator of the FRA. The CDI provides a high impedance buffer between the sample or reference and the FRA, and it converts the current to a voltage. The resistor and capacitors in the *I-V* converter are selected so that the voltage output at Ch. 2 is in a suitable range for the frequency response analyser. The magnitude and phase of this voltage relative to the Ch. 1 voltage allow calculation of the sample impedance, Z^* if the measurement resistor and capacitor are known from [2]

$$Z^* = \frac{-\mathbf{V}\mathbf{1}^*}{\mathbf{V}\mathbf{2}^*} Z_m^*,\tag{A.5}$$

where $\frac{1}{Z_m^*} = \frac{1}{R_m} + j\omega C_m$ gives the inverse complex impedance (admittance) of the

feedback circuit.

However, this measurement will be inaccurate for two reasons [2].

(i) R_m and C_m are not well specified. Their values are calibrated at a single frequency and may change over time.

(ii) Voltage phase lags in the CDI and FRA may cause phase errors. For this reason, an alternative procedure involving measurements on a reference capacitor as well as the sample is used to calculate Z^* [2]. Eq. (A.5) can be rewritten to include the effects of linear phase errors in the analogue parts of the circuit:

$$Z^{*} = \frac{-g(\phi)\mathbf{V}\mathbf{1}^{*}}{\mathbf{V}\mathbf{2}^{*}}Z_{m}^{*},$$
 (A.6)

where $g(\phi)$ represents these phase errors.

If the reference measurement circuit is enabled (mode 2 described above), the measured impedance for a known reference capacitance is

$$Z_r^* = \frac{-g(\phi)\mathbf{V}\mathbf{1}_r^*}{\mathbf{V}\mathbf{2}_r^*} Z_m^*.$$
(A.7)

These equations can be used to remove the factor $g(\phi)Z_m^*$ to give [2]

$$Z^{*} = \frac{\mathbf{V1}^{*}\mathbf{V2}_{r}^{*}}{\mathbf{V2}^{*}\mathbf{V1}_{r}^{*}}Z_{r}^{*}.$$
 (A.8)

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This eliminates both of the problems with the measurement method without a reference capacitor. ε^* can be found using Eq. (A.4).

A.3.4 Capabilities of the Solartron FRA and CDI System

The frequency range of the Solartron FRA-1255A is $10 \ \mu\text{Hz} - 20 \ \text{MHz}$. The generator is capable of supplying sinusoidal voltages between 0 and 3 V. The two correlator channels can measure voltages of up to 3 V ac. It can also apply a dc bias voltage of up to $\pm 40 \ \text{V}$. For all measurements with this setup, the default generator voltage of 1 V was used. dc bias was not used in any measurements.

The *I-V* converter of the CDI can respond to currents from 0.1 pA to 100 mA given appropriate selection of R_m and C_m . It has a specified frequency range of 10 μ Hz – 50 MHz and a loss angle, δ , resolution of 50 μ rad. The CDI is most accurate when a well-known reference capacitance with impedance close to that of the sample is used. A difference of not more than 20 % between sample and reference capacitance is desirable [2]. 100 pF was chosen as a reasonable size reference capacitance for the dielectric samples measured here.

The upper frequency limit of the setup is limited by the sample cell connections and cabling. Since the capacitive impedance of the low loss sample is falling as the frequency increases, while the inductive impedance of the cabling is rising, the latter may become larger than the former. The pairs of cables connecting the reference and sample to the CDI are as short as possible to minimise this effect. The GEN, Ch. 1, and Ch. 2 cables and the reference and sample cables are the same length so cable phase errors should cancel when the reference measurement is made. The highest frequency used was 1 MHz.

Accurate measurements take at least the period of the applied voltage, so the measurement time can become very long at low frequencies. The lowest frequency used here was 1 mHz.

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A.4 Novocontrol Broadband Dielectric Spectrometer (3 μHz – 1.8 GHz)

The Novocontrol Broadband Dielectric Spectrometer (BDS) is a complete system for measuring the complex permittivity of materials from 3 μ Hz up to 1.8 GHz in the temperature range 123.2 K to 673.2 K. The system has two impedance analysers to cover this range; (i) An AIS Alpha-S analyser [7] with active sample holder, and; (ii) an Agilent 4291B impedance analyser [8]. The first covers the subradiofrequency and radiofrequency range from 3 μ Hz up to 10 MHz, the second from 1 MHz to 1.8 GHz in the microwave region. These are described in detail in their respective sections. An overview of the Novocontrol BDS showing the Alpha-S and active sample holder is given in Fig. A.8. The Quatro temperature controller [9], which runs the temperature control system and the two dielectric measurement systems are computer controlled over a GPIB bus using Novocontrol WinDETA software. The Agilent 4291B and the temperature controller also allow front panel operation.



Fig. A.8 Novocontrol BDS, showing the temperature control system, the Alpha-S frequency response analyser and active sample holder (inside cryostat).

Each analyser has its own sample holder system. These are inserted into the same cryostat and the temperature is maintained by the same temperature control system during measurements.

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A.4.1 Quatro Temperature Control System of Novocontrol BDS

The sample temperature is controlled inside a double wall cryostat (7 cm in diameter and 30 cm deep). The sample temperature is maintained by a heated N₂ jet produced by evaporating liquid nitrogen inside a 50 L dewar (Apollo 50 by Messer Griesheim GmbH). The pressure produced expels gas from the dewar. It is then heated by the gas heater before flowing through the cryostat. The gas both maintains the sample temperature and provides an inert atmosphere inside the cryostat when a sample holder is fully inserted. There is an o-ring seal on the lip of the cryostat. The Quatro Temperature controller controls the power supplied to the dewar and gas heater by monitoring the pressure and temperature in the dewar, the gas temperature at the gas heater and the sample temperature (both the low and high frequency sample holders have a fitted Pt 100 Ω resistance temperature sensor in contact with the electrodes). The temperature controller can execute ramps and hold the temperature for specified times.

A.4.2 Alpha-S Analyser and Active Sample Holder

The Alpha-S analyser [7] operates on a similar principle to the Solartron FRA/CDI combination discussed in Sect. A.3.

The Alpha-S analyser consists of two parts. The first is the Alpha-S frequency response analyser mainframe, which performs the same function as the Solartron FRA. It outputs the sinusoidal ac voltage through the generator (GEN output) to a dielectric interface, which provides a high impedance sample connection and a current-voltage converter. The V1 and V2 channels measure the magnitude and relative phase of the applied voltage and the voltage output of the *I-V* converter in the interface respectively as for the Solartron FRA/CDI system. The GEN terminal has an output impedance of 50 Ω , and the V1 and V2 channels have a 1 M Ω input impedance. The GEN terminal can output up to 3 V ac between 3 µHz and 20 MHz with up to ± 40 V dc bias voltage. The V1 and V2 channels can measure to 3 V ac with a 4 V ac and ± 45 V dc input limit. Unlike the FRA/CDI, the dielectric interface is located in the sample holder, which is shown in Fig. A.9 [7].


Fig. A.9 Active sample holder of the Alpha-S analyser (from Ref. [7]). The GEN input and the V1 and V2 output terminals are connected to the GEN output and V1 and V2 inputs on the frequency response analyser (mainframe) part of the Alpha-S analyser system.

A| 25-pin D-connector (the mainframe connector) supplies power and control signals to the sample head. This setup means that the sample is closer to the interface. Also, the connections between the sample cell electrodes and the interface are made with special air insulated lines built into the sample holder rather than coaxial cables and BNC terminals. This all means that the inductive impedance of the cables at high frequency is less of a problem with this system, allowing measurements to be made up to 10 MHz. The sample is placed between two brass electrodes. The upper electrode can be screwed down to clamp the sample. The current is sensed at the upper electrode and the voltage applied at the lower one. The lower electrode has a Pt 100Ω temperature sensor inside it. Alternatively, the electrodes can be disconnected and the sample cell for measuring liquids already described (see Fig. A.7) attached to the electrode connectors with suitable plugs.

Another difference between the FRA/CDI system and the Alpha-S analyser is that a selection of reference capacitors are built into the active sample holder section, rather than a single external reference being used. There are 64 of these between 25 pF and 2 nF. The reference capacitance closest to the sample capacitance at a given frequency is selected, ensuring optimum accuracy.

The Alpha-S analyser can measure a very broad impedance range of 0.01 Ω to $10^{14} \Omega$, which is required for wide frequency measurements on low loss (mainly capacitive) dielectric samples, which have high impedance at low frequency and low impedance at high frequency. The analyser can also measure tan δ values of 10^{-5} , which requires a resolution in δ of < 18 µrad.

A.4.3 Agilent 4291B Impedance Analyser

Fig. A.10 shows the Agilent 4291B analyser system. This comprises a sample holder (by Novocontrol), which is inserted into the cryostat. A brass dielectric sample cell (also Novocontrol), with a Pt 100 Ω sample temperature sensor is connected via a coaxial line to the high impedance test head, which is locked into the test station. A cable connects the test station to the analyser mainframe. A close-up of the dielectric cell is shown in Fig. A.11. The sample is inserted between two flat brass electrodes and secured with a moveable rod. This type of cell only permits measurement of solid samples between the electrodes. Connections between the cell and the line and line and test head are made with APC-7 connectors rather than BNC, as the latter are not suitable for higher frequencies.

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Fig. A.10 Agilent 4291B impedance analyser system showing the mainframe, test station and head, and the dielectric sample holder and cell.



Fig. A.11 High frequency dielectric sample cell (for Agilent 4291B).

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A.4.4 Theory of Measurement with Agilent 4291B

The Agilent 4291B measures the sample impedance, Z^* , by a voltage reflection technique. If V_{ref}^* is the voltage reflected from the sample and V_s^* is the source voltage, then the reflection coefficient, Γ , of the sample is [8]

$$\Gamma^* = \mathbf{V}_{\mathrm{ref}}^* / \mathbf{V}_{\mathrm{s}}^*. \tag{A.9}$$

It can be shown that if Z_0 is the characteristic impedance of the measuring circuit containing the sample then [8],

$$Z^* = Z_0 \frac{1 + \Gamma^*}{1 - \Gamma^*}.$$
 (A.10)

For the 4291B, $Z_0 = 50 \Omega$. ε^* can then be obtained using Eq. (A.4), with C_{vac} being calculated from the sample geometry.

Error terms in the measurement circuit up to the point where the dielectric sample cell is connected can be eliminated by performing a calibration using several terminations of known impedance on the coaxial line. The dielectric sample cell is replaced by the OPEN, SHORT, and LOAD (50 Ω) terminations. If Z_{cal}^* is the known impedance of one of these terminations, then [8]

$$Z_{cal}^{*} = \frac{A_{cal}^{*} Z_{mes}^{*} - B_{cal}^{*}}{1 - C_{cal}^{*} Z_{mes}^{*}}.$$
 (A.11)

where Z_{mes}^* is the measured value of the impedance of the termination, and A_{cal}^* , B_{cal}^* , and C_{cal}^* are the calibration coefficients. The three simultaneous equations are solved to obtain the calibration coefficients. This procedure is repeated at each frequency at which the sample is to be measured. An additional calibration is performed with a low loss capacitor termination to improve the phase accuracy of the measurement. For the low loss calibration we have [8]:

$$Z_{lowloss,corr}^{*} = \frac{A_{cal}^{*} Z_{mes}^{*} - B_{cal}^{*}}{1 - C_{cal}^{*} Z_{mes}^{*}},$$
(A.12)

where $Z_{lowloss,corr}^* = Z_{lowloss,corr}' + j Z_{lowloss,corr}''$ is the actual impedance of the low loss capacitor corrected by the calibration coefficients determined in the OPEN, SHORT, and LOAD calibrations. The phase delay of the current for the low loss capacitor is a

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well-known value $\theta_{lowloss}$. The phase delay can also be estimated from the impedance measurement,

$$\arg(Z_{lowloss,corr}^{*}) = \tan^{-1} \frac{Z_{lowloss,corr}^{\prime\prime}}{Z_{lowloss,corr}^{\prime\prime}} = \theta_{lowloss,mes}.$$
 (A.13)

The difference between the phase angles is

$$\Delta \theta = \theta_{lowloss} - \theta_{lowloss,mes}. \tag{A.14}$$

This is the phase error made in any corrected measurement. This can now be used to make a correction to the impedance of the 50 Ω LOAD termination [8]:

$$Z_{LOAD,corr}^* = 50 \exp(j\Delta\theta). \tag{A.15}$$

This value in turn can be used to calculate new values of the three calibration constants A_{cal}^* , B_{cal}^* , and C_{cal}^* .

There is no need to introduce an electrical length [8] parameter to account for the coaxial line connected to the test head. This is because all calibrations are made at the end of this line rather than at the test head connector in accordance with the Novocontrol instructions for the system (rather than Agilents' instructions for the 4291B instrument).

Finally, the dielectric sample cell itself has parasitic impedances that can introduce errors in the measurement. An open-short compensation is performed using the cell electrodes separated by a very high resistance, low ε' insulator to create an open circuit or touching to create a short. It can be shown that [8] for measurements of the impedance of a sample Z^* ,

$$Z^{*} = A_{compen}^{*} \frac{Z_{mes,corr}^{*} - B_{compen}^{*}}{1 - C_{compen}^{*} Z_{mes,corr}^{*}},$$
 (A.16)

where $Z_{mes,corr}^*$ is the measured impedance corrected by calibration, and A_{compen}^* , B_{compen}^* , and C_{compen}^* are the dielectric sample cell compensation coefficients. For an openshort calibration $A_{compen}^* = 1$ and the other two coefficients can be found. Like the calibration coefficients, the compensation coefficients are calculated at the frequencies at which the sample is to be measured. Appendix A

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A.5 References

- [1] *1255 H.F. Frequency Response Analyser Operating Manual* (Schlumberger Technologies, Farnborough, 1989)
- [2] *Chelsea Dielectric Interface User Guide* (Dielectric Instrumentation, Worcester; England)
- [3] *Variable temperature cryostat Spectrostat^{DN} Operator's Handbook* (Oxford Instruments, Abingdon; England, 1997).
- [4] *Temperature Controller ITC502 Operator's Handbook* (Oxford Instruments, Abingdon; England, 1996).
- [5] Instruction Manual Heto CBN 8/18/28-30 -30 °C Cooling Baths (Jouan Nordic A/S, Denmark, 2003).
- [6] Instruction Manual HMT 200 (Jouan Nordic A/S, Denmark, 2003).
- [7] *Alpha High Resolution Dielectric Analyzer Users Manual* (AIS Analytical Instrument Systems GmbH, Germany, 2000).
- [8] Agilent 4291B RF Impedance/Material Analyzer Operation Manual (Agilent Technologies, Japan, 1999).
- [9] *Quatro Cryosystem Owner's Manual* (Novocontrol GmbH, Germany, 1997)

Appendix B WinFit Dielectric Fitting Program

B.1 Use of the WinFit Program

A brief description of the procedure for fitting ε^* spectra using WinFit is given in this Appendix. This is not a comprehensive description of the program. An extensive hardcopy manual for WinFit [1] contains additional information. In this Appendix, menu options and **DIALOG BOX BUTTONS** are denoted by the respective fonts and "dialog box names" are denoted by quotes.

WinFit is a program supplied by Novocontrol for nonlinear fitting of dielectric spectroscopy data and impedance measurements generally. The program can fit either dielectric relaxation functions or equivalent circuit models to the material properties of a sample such as $\varepsilon^*(f) = \varepsilon' - j\varepsilon''$ or $\sigma^*(f) = \sigma' - j\sigma''$ or to circuit properties for samples or devices such as $Z^*(f) = Z' + jZ''$ or $C^*(f) = C' - jC''$.

After starting WinFit, the data to be fitted may be loaded as spectra using File \rightarrow Load WinDETA Result from files in the WinDETA format (*.eps) produced by the program used to control the various dielectric analysers. Alternatively, ASCII files formatted as columns of data in the order frequency f, real quantity, imaginary quantity can be loaded with Load Ascii Data in the File menu (Fig. B.1).





Fig. B.2 Data List Menu.

If a WinDETA *.eps file is loaded, the various spectra contained in the file can be added to the data list to be fitted using Data List \rightarrow Add or Select Curves (Fig. B.2). This brings up a dialog box in which the data can be added to the data list with ADD TO DATA LIST (Fig. B.3). If ASCII data is used, this dialog box will be opened directly from the File menu and ADD ASCII TO DATA LIST (Fig. B.3) can be used to add the ASCII data to the list from the file. One also selects from the list what type of data (permittivity, impedance etc) is contained in the ASCII file. Once data has been added to the list it is highlighted, indicating that it is selected. It appears graphically as points in the Actual Fit window. The EDIT button opens the "Limits and Parameters for Actual Data Curve" dialog shown in Fig. B.4 where the limits over which the fit will be performed may be selected and the temperature for the data set entered (if it was not already contained in the *.eps file). Other options in the Data List menu allow the left and right limits for all the fit curves to be set in sequence graphically on the actual fit window. The next and preceding data set in the list can also be selected with Select Next Fit and Select Preceding Fit. Initialize from Preceding Fit sets the fitting parameters of the current data to those of the preceding data.

WinDETA Results Free : Frequency Fix	Ascii Files Lines Comment 1 Temperature 2	ns ency 1 Real 2
	Data Start 3	mag 3
	Data List	st
	1-phenyl-1-propanol, 208K, 1 1-phenyl-1-propanol, 210K, 1	MHz to 1Hz MHz to 1Hz
Fix	I-phenyi-I-propanol, 212K, I 1-phenyi-1-propanol, 215K, I 1-phenyi-1-propanol, 217K, 1 1-phenyi-1-propanol, 220K 1	MHz to 1Hz MHz to 1Hz MHz to 1Hz MHz to 1Hz
Fix	1-phenyl-1-propanol, 222K, 1	MHz to 1Hz
	Edit Delete	Clear
Add to Data List		

Fig. B.3 "Add or Select Curves to the Data List" dialog.

Free : Fr	Results equency	Ascii Files Lines Comment Temperature Data Start	Columns Frequency 2 3 Imag
		Read Data as	Dielectric Function Eps
Fix Fix Add to	Title 1-p Temperate Multi Plot Show Show	henyl-1-propanol, 2 ure 207.50 Windows Data Curves Fit Curve Single Fit Terms	208K, 1MHz to 1Hz Do Not Use Temperature Fit Limits Lowest Frequency Highest Frequency 1.230e+00 Hz Mouse Select Mouse Select

Fig. B.4 "Limits and Parameters for Actual Data Curve" dialog.

Once the list of data for fitting has been prepared, one of the two fitting modes Select Relaxation Fit Function or Select General Fit Function can be chosen (Fig. B.5) from the Frequency Fit menu.



Fig. B.5 Frequency Fit menu.

In the Select Relaxation Fit Function mode, up to three Havriliak-Negami (HN) or Dissado-Hill (DH) functions and a dc conductivity term can be fitted to the data (Fig. B.6). This mode is usually used for material properties. The dielectric function (typically Eps^{*}, i.e. $\varepsilon^*(f) = \varepsilon' - j\varepsilon''$) for fitting is selected from the list of options in the dialog box. For complex quantities, the program allows fitting of the imaginary or real parts as functions of frequency, the imaginary part as a function of the real part (Cole-Cole type plot) or the inverse, and the absolute value as a function of frequency. It will *not* allow both the imaginary and real parts to be fitted simultaneously. In addition, a log scale or linear scale f and y axis can be chosen. In the Select General Fit Function mode, a circuit consisting of resistor, capacitor, inductor, and relaxation function elements (Debye, HN etc) is created by entering an equation for its total impedance or other quantity. The dielectric function for fitting is selected in the same way as for the other mode. The settings chosen in these dialogs also control the display in the Actual Fit window.

1. Term	Havriliak Negami	Conductivity
2. Term	Havriliak Negami	-
3. Term	None	-
Fit and A	ctual Fit Window —	
	Variable	Complex
Dielectri	c Function Eps'	Imag(Frequency)
Show	Single Terms	✓ Log Fit and Y Axis
60 F	it Function Points	Log X Axis
		Negative

Fig. B.6 "Select Dielectric Relaxation Fit Function" dialog.

The Fit Parameter Limits option in the Frequency Fit menu opens a dialog where the values of the independent fitting parameters can be constrained within limits. The fitting parameters can also be constrained to have a constant value for a fixed number of iterations.

it Stability Conditions	1
Number of Fit Iterations	
Maximum 500 Minimum 3	
Terminate if MSD is Relative Stable to 1e-07 Over 20 Iterations	
Fit Procedure	
C Gauss	
Gauss then Newton	
C Newton	
Use 90 % of System Time for Fit	
Dissado Hill Numerical Function Precision	
Max number of terms for 2F1 200	
Terminate if term//2F11 is / 1e.06	
- <i>Novocontrol</i> Help Cancel OK	-
	-

Fig. B.7 "Fit Stability Conditions" dialog.

WINFIT Dielectric Fitting program

The Fit Stability Conditions menu option opens the "Fit Stability Conditions" dialog (Fig. B.7) where the conditions that must be met for the nonlinear fit routine to halt are set. The maximum and minimum number of iterations can be specified, as can the minimum value of the change in the mean square deviation (MSD) of the fit curve from the data over a set number of iterations that defines a stable fit. Once the MSD becomes constant to this precision over a given number of iterations, fitting is halted.

Other options in the Frequency Fit menu allow the editing, deletion etc of data points contained in the selected spectrum shown in the Actual Fit window. To begin nonlinear least squares fitting of the data in the window, the Frequency Fit \rightarrow Start Single Fit command is selected, which opens the "Fit Parameters" dialog box. Fig. B.8 shows an example of the dialog for fitting of two HN terms to ε'' at a single temperature with log f and log ε'' scales. In this dialog, initial values can be set for the fit parameters. A tick in the box beside a parameter means it will be optimised during fitting. The parameter is activated. Clicking SHOW redraws the total fit curve and its component terms on the Actual Fit window and calculates the MSD for the fit with these parameters. This easy visualisation of the fit allowing a quick gauge of its quality is the major advantage of the WinFit program. **STORE** saves the current values of the fit parameters in the memory. **RESTORE** recalls previously stored values. To begin minimisation, **OPTIMIZE** is selected. This stops when the conditions set in the "Fit Stability Conditions" dialog are met. When the fit is acceptable, OK closes the dialog and stores the values of the fit parameters for the spectrum. CANCEL restores the values to the previously saved ones and closes the dialog.

In this thesis, for ε^* spectra, the procedure was to fit ε'' for each temperature generally using a log scale f axis. A log scale ε'' axis was used when the loss changes by several orders of magnitude during measurements. Then ε' was fitted on a linear scale with all parameters constant except for a single ε_{∞} (eps_i) term. When all spectra have been fitted, the entire set of fit parameters can be saved in WinFit's own format with File \rightarrow Save Data List. In addition, the fit parameters and their standard deviations, fit function points, and the data itself can be saved as ASCII using options in the File menu.

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	Fit Paramet	ers		
10.161	1-phenyl MSD = 8	-1-propanol, 2	08K, 1MHz	o 1Hz
. 10 1112	Havrilia	k Negami	Havrili	ak Negami
<u> </u>	▼ 🔽 d_eps	9.855e+00	✓ d_eps	1.079e+00
	🔽 tau s	6.103e-02	🔽 tau s	5.729e+00
	I eps_i	3.000e+00	₩ eps_i	1.000e+00
	🔽 alpha	1.000e+00	🔽 alpha	3.373e-02
	✓ beta	5.732e-01	₩ beta	1.000e+00
	Destroy	1	Chan	OK
	Hestore	Store	Snow	Canad
	-DOVO	notrol	Optimize	Lancel
	110000			Help
		a franciska star	STREET OF	
				1

Fig. B.8 "Fit Parameters" dialog with Actual Fit window showing ε'' data, total fit curve (in white), and HN components (pink) corresponding to these parameters.

The Frequency Fit \rightarrow Start Fit Series command is used for consecutively fitting large numbers of curves where the parameters are almost the same from one curve to the next in the series. The command opens the same dialog box as the Start Single Fit command but the **OPTIMIZE** button now starts a sequence of fits from the currently selected data set to the final one in the data list. The fit limits, selection of the active parameters of the fit and parameter values of each fit can be initialised from the one before it in the list. This is controlled with the Frequency Fit \rightarrow Series Fit Parameters menu command, which opens the "Initialization of Series Fits" dialog, shown in Fig. B.9.



Fig. B.9 "Initialization of Series Fits" dialog.

B.2 References

[1] WinFit Manual (Novocontrol GmbH, Germany)

Appendix C Visual Basic Control Program

C.1 Summary of Program Features

This Appendix describes a Visual Basic 6.0 program (on CDROM), which allows the Oxford ITC502 temperature controller, the Keithley 195A digital multimeter (DVM), and Solatron FRA-1255A frequency response analyser and Chelsea Dielectric Interface to be controlled by a computer for ε^* measurements. A similar program was

written for the Heto thermostat but is not described here.

The ITC502 is connected by a serial port and Microsoft's own Serial Port routines built into Visual Basic 6.0 can be used to control it.

The FRA and CDI are connected to a National Instruments GPIB card. These are operated by sending command keystrokes to Novocontrol WinDETA. This is set up before starting the program. The DVM is connected to a Hewlett-Packard (HP) GPIB card.

The program has three modes. It can perform frequency scans of ε^* at several temperatures separated by a step, it can perform many frequency scans at constant temperature, and it can ramp the temperature as frequency scans are performed. These are executed by the three main subroutines measure, measuresteady, and measureramp. The program waits for cryostat and sample temperature stability before calling the WinDETA program to start ε^* measurements at a given temperature in the step mode, the constant temperature of the steady mode, or the start temperature of the ramp.

The sample temperatures are measured by the DVM and saved to an ASCII text file. These are the temperatures for each frequency scan in the step mode, and the temperatures for the whole run in the other two modes. The program listing given in the text file on the disc is complete except for the properties of the forms and controls and the sicl4.bas module. This module is available from the libraries on the Agilent (formerly HP) website [1] and incorporates the routines for control of the HP GPIB card and sending commands to instruments connected to it.

C.3 References

[1] <u>http://www.agilent.com/find/iolib</u>.

Appendix D List of Publications

D.1 Letters and Papers

Most of the research described in this thesis has been published previously.

Chap. 3 is partly based on work reported in: G. Power, G. P. Johari, and J. K. Vij, J. Chem. Phys. **116**, 4192 (2002).

Chap. 4. is based on work reported in:

G. Power and J. K. Vij, J. Chem. Phys. 120, 5455 (2004).

Chap. 5 is partly based on work reported in:
G. P. Johari, G. Power, and J. K. Vij, J. Chem. Phys. 116, 5908 (2002).
G. P. Johari, G. Power, and J. K. Vij, J. Chem. Phys. 117, 1714 (2002).
G. Power, G. P. Johari, and J. K. Vij, J. Chem. Phys. 119, 435 (2003).

Chap. 6 is partly based on work reported in:G. Power, J. K. Vij, and M. Shaw, J. Phys. D: Appl. Phys. 37, 1362 (2004).