LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2002 issue.

NOTES

Localized relaxation's strength and its mimicry of glass-softening thermodynamics

G. P. Johari[a)]
Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, L8S 4L7, Canada

G. Power and J. K. Vij
Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Ireland

(Received 23 October 2001; accepted 8 January 2002)

[DOI: 10.1063/1.1456030]

There has been a wide interest in understanding the nature of the β relaxation[1–8] and of its role in viscous flow and vitrification[9–12] since 1970, when a dielectric study[13] of rigid molecular glasses had shown that β relaxation is (i) intrinsic to a disordered structure,[14,15] (ii) a property of the viscous liquid,[14] (iii) a precursor of the α relaxation,[9,10,12,14] (iv) affected by the cooling rate used for vitrifying a liquid and the ageing time of a glass,[13,14] and (v) connected to the non-Debye behavior of the heat capacity, C_p, at $T<1$ K.[15] The dielectric relaxation strength, $\Delta\varepsilon_\beta$, of this process, which is now called the Johari–Goldstein relaxation, is determined by the number of molecules capable of reorienting in a local region of a glass' or viscous liquid's structure, and its relaxation rate, $f_{m,\beta}$, decreases on cooling according to the Arrhenius equation.[4,5,7,14] Here we report a new phenomenon in the disordered structure: The change in $\Delta\varepsilon_\beta$ on heating through the glass-softening temperature, T_g, mimics the changes observed in the enthalpy, *H*, entropy, *S*, and volume, *V*, of a glass. This indicates that kinetic *unfreezing* of density fluctuations at T_g, which raises its C_p and expansion coefficient, also raises $(d\Delta\varepsilon_\beta/dT)$, but it has no effect on $f_{m,\beta}$.

Chlorobenzene (99% Lancaster) and *cis*-decalin (purum, Fluka AG. Switzerland) were used to prepare 16.6 mol % chlorobenzene *cis*-decalin mixture. The dielectric cell was a miniature parallel plate condenser with 18 plates and a nominal capacitance of 27 pF in air. The sample was contained in a vial of 10 mm diameter, 33 mm length in which the PT-100 sensor and the condenser were immersed. The assembly was mounted inside a cryostat. The temperature was programmed for heating at a rate of 0.08 K/min, and the ε' and ε'' spectra were obtained in the frequency range of 10 Hz–1 MHz by means of a Solartron FRA-1255A frequency response analyzer interfaced with a Chelsea dielectric interface. The spectra were taken in a period of around 218 s, during which the temperature increased by at most ~0.36 K. The mean value is used. Typical spectra of ε' and ε'' are shown in Fig. 1. Their shapes show a broad step-like decrease in ε' and a broad peak in ε''. The spectra at each temperature were analyzed by fitting the sum of two empirical Havriliak and Negami type equations,[16]

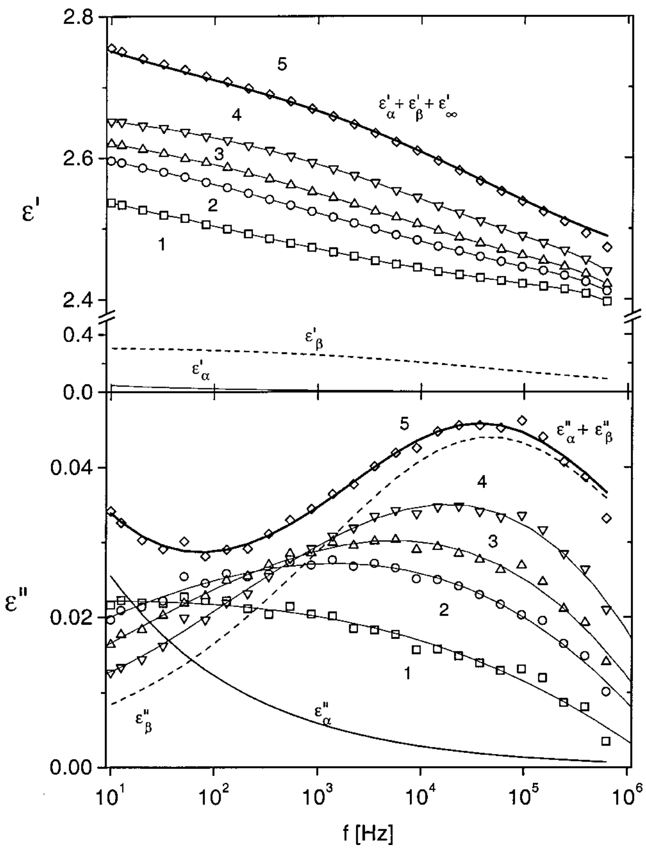

FIG. 1. The ε' and ε'' spectra of 16.6 mol % chlorobenzene–decalin mixture at several temperatures below its T_g. Curves 1–5 are for 106.8, 117.7, 122.7, 129.0, and 135.0 K. Resolution of a typical spectra for obtaining $\Delta\varepsilon_\beta$, $f_{m,\beta}$, and α_2, and β_2 parameters is shown for curve 5 (at 135.0 K).

[a)]Electronic mail: joharig@mcmaster.ca

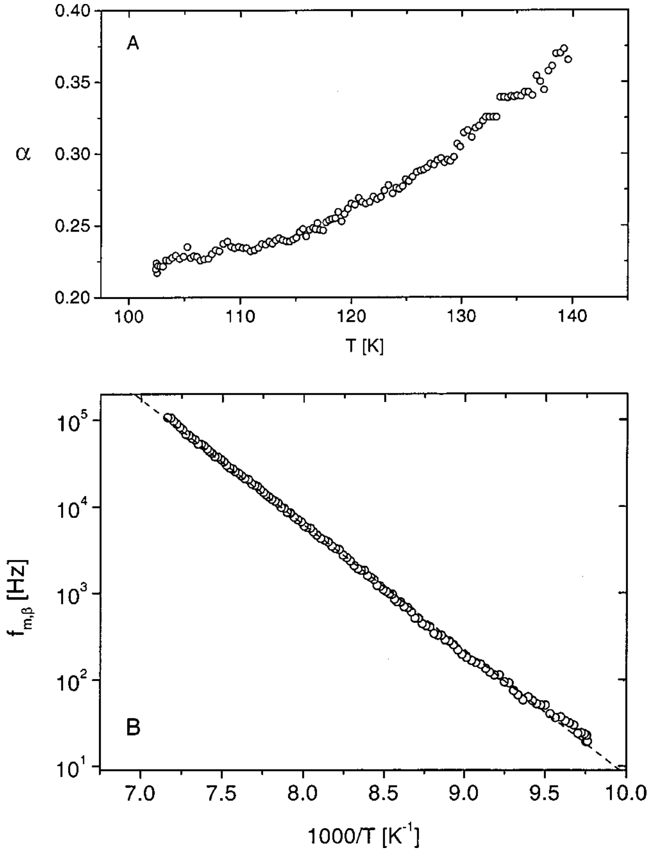

FIG. 2. (a) Plot of the distribution parameter against T for the β relaxation. (b) Plot of $f_{m,\beta}$ against $1/T$.

$$\varepsilon^*(\omega)=\varepsilon_\infty+\frac{\Delta\varepsilon_\alpha}{(1+(j\omega\tau_\alpha)^{\alpha_1})^{\beta_1}}+\frac{\Delta\varepsilon_\beta}{(1+(j\omega\tau_\beta)^{\alpha_2})^{\beta_2}}, \qquad (1)$$

where $\Delta\varepsilon_\alpha$ and $\Delta\varepsilon_\beta$ are the dielectric relaxation strengths of the α and β relaxations, respectively, and τ_α and τ_β are the relaxation times, $\omega=2\pi f$ (f is the frequency in Hz), $j=(-1)^{1/2}$, and α_1 and β_1 are the parameters of the Cole–Cole and Cole–Davidson distribution functions for the α relaxation, and α_2 and β_2 are those for the β relaxation.

A typical fit of Eq. (1) to the ε' and ε'' spectra measured at 135.0 K is shown in Fig. 1 by thick lines, and the ε' and ε'' contributions from the α and β relaxations are indicated. Values of $\Delta\varepsilon_\beta$, τ_β, α_2, and β_2 were thus determined from the ε' and ε'' spectra measured for more than 110 temperatures. The parameter β_2 remained constant at 1.00, but α_2, which is plotted against T in Fig. 2(a), increased from 0.22 at 102.5 K to 0.37 at 140 K. The plot of $f_{m,\beta}[=(2\pi\tau_\beta)^{-1}]$ against $1/T$, shown in Fig. 2(b), follows the Arrhenius equation, $f_{m,\beta}=10^{15.37}\exp(-27700/RT)$.

Figure 3 shows the plot of $\Delta\varepsilon_\beta$ against T. It has an elbow-shape bend at ~133 K, the calorimetric T_g of 16.5 mol % chlorobenzene–decalin mixture.[13] For comparison, characteristic changes in H, S, and V of a glass spontaneously relaxing at $T<T_g$ and then softening to a liquid at $T>T_g$ are schematically shown in the Fig. 3 inset. The $\Delta\varepsilon_\beta$ plot is clearly similar to the H, S, and V plots. Therefore, unfreezing of density fluctuations at T_g has similar effects on $(d\Delta\varepsilon_\beta/dT)$, C_p, and thermal expansivity.

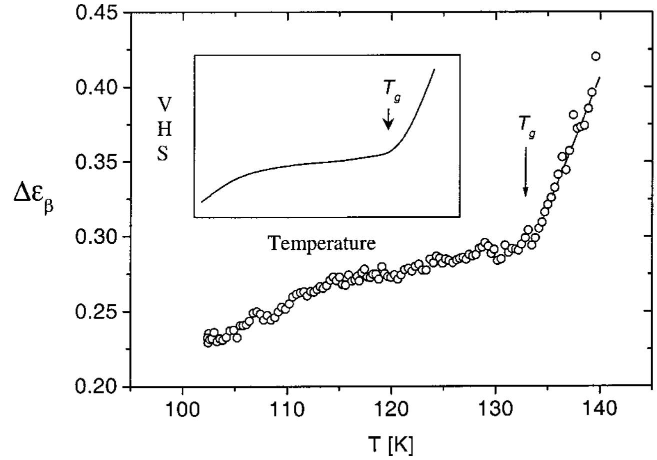

FIG. 3. Plot of $\Delta\varepsilon_\beta$ against T. Decrease in the slope in the 115–125 K range is due to spontaneous structural relaxation. Inset is a schematic plot of H, S, and V of a glass heated through its T_g.

Configurational entropy, S_{conf}, and free volume, V_f, of a liquid decrease on cooling toward T_g. Therefore, $\Delta\varepsilon_\beta$ contains the effects of decreasing S_{conf} and V_f, but $f_{m,\beta}$ is not effected. This has consequences for the recently proposed[17] entropy extrapolation: If $\Delta\varepsilon_\beta$ and S_{conf} of an equilibrium liquid were to decrease together on cooling then its $\Delta\varepsilon_\beta\to 0$ as its $S_{\text{conf}}\to 0$ at 0 K.

G.P.J. is grateful for the hospitality of Trinity College, Dublin, Ireland, during his stay. Support from Enterprise Ireland under the International Collaboration Program is gratefully acknowledged.

[1] C. J. Reid and J. K. Vij, J. Chem. Phys. **79**, 4624 (1983).
[2] L. Wu and S. R. Nagel, Phys. Rev. B **46**, 11198 (1992).
[3] N. B. Olsen, J. Non-Cryst. Solids **235–237**, 399 (1998).
[4] See Symposia volume issues of J. Non-Cryst. Solids **172, 173**, (1994); **235–237**, (1998).
[5] A. Kudlik, S. Benkhof, T. Blochowicz, C. Tschirwitz, and E. Rössler, J. Mol. Struct. **479**, 201 (1999).
[6] J. Perez, J. Y. Cavaille, and L. David, J. Mol. Struct. **479**, 183 (1999).
[7] S. Kahle, E. Hempel, M. Beiner, R. Unger, K. Schröeter, and E. Donth, J. Mol. Struct. **479**, 149 (1999).
[8] T. Hikima, M. Hanaya, and M. Oguni, J. Mol. Struct. **479**, 245 (1999).
[9] J. Y. Cavaille, J. Perez, and G. P. Johari, Phys. Rev. B **39**, 2411 (1989).
[10] K. L. Ngai, Phys. Rev. E **57**, 7346 (1998); J. Non-Cryst. Solids **257**, 7 (2000).
[11] B. Bagchi, A. Chandra, and S. A. Rice, J. Chem. Phys. **93**, 8991 (1990).
[12] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
[13] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).
[14] G. P. Johari, J. Chem. Phys. **58**, 1766 (1973); Ann. N.Y. Acad. Sci. **279**, 117 (1976).
[15] G. P. Johari, Phys. Rev. B **33**, 7201 (1986).
[16] S. Havriliak and S. Negami, J. Polym. Sci., Part C: Polym. Symp. **14**, 99 (1966).
[17] G. P. Johari, J. Chem. Phys. **113**, 751 (2000); Chem. Phys. **265**, 217 (2001).