

Orientalional/translational relaxation in aqueous electrolyte solutions: a molecular model for microwave/far-infrared ranges

V. I. Gaiduk,^{*a} B. M. Tseitlin^a and J. K. Vijb

^a Institute of Radio Engineering & Electronics, Russian Academy of Sciences, Vvedensky sq. 1, Fryazino, Moscow Region, 141190, Russia. E-mail: gvil69@ire216.msk.su

^b Advanced Materials Laboratory, Trinity College Dublin, Dublin 2, Ireland

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A model is given where the complex permittivity of an electrolyte solution is calculated as a superposition of the contributions due to the translation of ions and the reorientation of water molecules, which occur in intermolecular potential wells during the lifetime of local order in liquids. Simple analytical expressions are found for the contributions of cations and anions to the linear-response spectral function. The one-dimensional rectangular potential well with perfectly elastic walls is considered. The contribution of water molecules to the orientational relaxation was calculated in terms of a hybrid model using the approach given recently in a book by Gaiduk (*Dielectric Relaxation and Dynamics of Polar Molecules*, World Scientific, Singapore, 1999). A modification of this model is also suggested in which the walls of the potential well undergo rather slow vibration. If the angular frequency ω is much less than the plasma frequency ω_p of an ion, then the theory yields a nearly constant real part σ' of the complex ionic conductivity $\sigma(\omega)$, while its imaginary part σ'' is very small. Large variations with ω of both parts of σ are predicted to occur at millimetre/submillimetre wavelengths, when ω approaches ω_p . Wideband (up to 1000 cm^{-1}) theoretical spectra of the complex permittivity and absorption coefficient are calculated for NaCl–water and KCl–water solutions. The theory predicts that an additional loss/absorption could arise in the far-infrared (FIR) spectral range, if the mean ionic lifetime τ_{ion} is much longer than the lifetime τ of the bulk water molecules.

1. Introduction

This paper is concerned with the modelling of the ionic conductivity and the dielectric dispersion of aqueous electrolyte solutions and employs a semi-phenomenological approach to this problem. Using analytical formulae, we describe the wideband (up to 1000 cm^{-1}) dielectric response due to the translation of ions and the reorientation of H_2O polar molecules. The fundamental problem of the dielectric response of water is important in physical chemistry and biology. During the last three decades several works have appeared^{1–6} in the literature about the microwave and far-infrared (FIR) spectra of pure water, and the low-frequency Raman spectrum of water has also been considered.^{2,5,6} A few works have appeared on the wideband spectra of electrolyte solutions.^{7–11} Theoretical developments usually have explained the low-frequency response, but so far there has been no unified theory, except possibly ref. 12, that explains the wideband dielectric/FIR spectra, in particular those of aqueous electrolyte solutions.

In this paper, we present such a unified theory applied to the wideband (from dc to a wavenumber ν range of 1000 cm^{-1}) spectra of electrolytes at rather low salt concentrations, calculated with account taken of the dispersion $\sigma(\nu)$ of the complex ionic conductivity, $\nu = \omega/c$, c being the velocity of light in vacuum (ν is later termed ‘frequency’). We start from a version^{12–14} of a linear-response analytical theory, based on a classical theory applicable to fluids. Then we generalise the theory in order to apply it to the calculation of the ionic dispersion $\sigma(\nu)$. A preliminary consideration was given in ref. 15, where more complex analytical expressions were used.

It is suggested that dipoles reorient in a rectangular potential box, where molecules, termed ‘librators’, move freely, but exert regularly instantaneous reflections from the rectangular

walls of the well. The well presents a rough model of neighbouring molecules, as a one-particle approximation is employed in our theory. The librators contribute mostly to the librational absorption band situated at around $\nu = 700\text{ cm}^{-1}$. A small percentage (about 10% or less) of dipoles, termed ‘rotators’, perform a complete rotation. In aqueous media these rotators determine the translational absorption band around the frequency $\nu = 200\text{ cm}^{-1}$. Both molecular groups contribute to the complex dielectric permittivity in the Debye relaxation region, observed at microwave frequencies.

In order to apply the dynamic method^{12,13} for ions we consider the dielectric response in the same manner as was previously assumed for dipoles. The main cause of the ionic response comes from the oscillations of ions inside the potential box during some lifetime τ_{ion} . This box again is chosen to be rectangular, similar to that for polar fluids. For simplicity, we use the one-dimensional approximation and in accordance with the estimations made in ref. 15 we set the well to be infinitely deep. In Sections 2 and 3 (see also Appendix A) we derive a general expression (27) for the complex conductivity $\sigma(\omega)$ suitable for further calculations. The dynamic method is reformulated so that it becomes applicable for an ensemble of ions. Here we arrive at a particular form of the Kubo linear-response theory, in which $\sigma(\omega)$ is determined by the auto correlation function (ACF) spectrum of the translational motion performed by charges. A rough model of the ionic conductivity $\sigma(\omega)$ is presented in Sections 3 and 4, where we also examine the dependences of the static conductivity σ_s and the dispersion $\sigma(\omega)$ on the parameters of the ionic model. In Section 5 the model is applied to the important aqueous solutions of NaCl and KCl, which in particular determine biological functions in living organisms at the basic level of cells. The contributions of cations (Na^+ or K^+) and of the anions

(Cl⁻) to σ are added up, while the resulting complex permittivity $\varepsilon(\omega)$ is found by summing up the contributions of ions and dipoles:

$$\varepsilon(\omega) = \varepsilon_{\text{dip}}(\omega) + \Delta\varepsilon_{\text{ion}}; \quad \Delta\varepsilon_{\text{ion}} = \chi_{\text{ion}}(\omega), \quad (1)$$

where χ is the complex susceptibility due to ions.

Note: Relative permittivity ε is a dimensionless parameter; it is the same in the MKS system of units used here and in the CGS one, which was used in previous works.^{12–15,24}

To find $\varepsilon_{\text{dip}}(\omega)$ we employ the hybrid model (ref. 12, ch. 9), according to which dipoles librate/rotate during some lifetime τ in a rectangular potential, having finite well depth U_0 . The parameters of the ionic and dipolar models are fitted by proceeding from the assumption that the calculated steady-state parameters and Debye/FIR spectra agree with the main features of the observed spectra in aqueous 1–1 electrolyte solutions.

2. Transformation of the non-homogeneous wave equation

We consider the Maxwell equations for a non-magnetic isotropic medium with current sources, comprising moving charges (ions) and polar molecules (dipoles) in a vacuum. We write down the wave equation for the electric component $\mathbf{E}(t)$ of the electromagnetic field (ref. 13, sec. II):

$$\nabla(\nabla \cdot \mathbf{E}) - (\nabla \cdot \nabla)\mathbf{E} = -\frac{1}{c^2} \frac{\partial}{\partial t} \left(\frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{J}}{\varepsilon_0} \right). \quad (2)$$

Here SI units are used, in which ε_0 is the dielectric constant of vacuum:

$$\varepsilon_0 = [36\pi \times 10^9]^{-1} \text{ F m}^{-1}.$$

Assuming that a homogeneous plane wave propagates in the medium, we express field \mathbf{E} and current density \mathbf{J} , which arise from both the ions and the dipoles, in terms of complex amplitudes $\hat{\mathbf{E}}$, $\hat{\mathbf{J}}$, propagation constant $\mathbf{k} = \mathbf{k}' - i\mathbf{k}''$ and 'initial' phase γ :

$$\mathbf{E} = \text{Re}\{\hat{\mathbf{E}} \exp[i(\omega t - \mathbf{k} \cdot \mathbf{r} + \gamma)]\};$$

$$\mathbf{J} = \text{Re}\{\hat{\mathbf{J}} \exp[i(\omega t - \mathbf{k} \cdot \mathbf{r} + \gamma)]\}; \quad (3)$$

$$\mathbf{J} = \mathbf{J}_{\text{ion}} + \mathbf{J}_{\text{dip}}. \quad (4)$$

We introduce the complex susceptibility $\chi^* = \chi' + i\chi''$ as related to the scalar quantity k^{*2}

$$k^{*2} = (\omega^2/c^2)(\chi^* + n_\infty^2). \quad (5)$$

Here the asterisk means the complex conjugate, so that $\chi^* = \chi' + i\chi''$ [we remark that for the $\exp(i\omega t)$ dependence in eqn. (3) the susceptibility χ should be $\chi' - i\chi''$]; and n_∞^2 is the permittivity in the IR range (in the low/FIR frequency ranges, to which our study is applied, we may regard n_∞^2 to be independent of frequency ω). On dividing χ^* in accordance with eqn. (4) and transforming eqn. (2) in the same manner as was given in ref. 13, sec. II, we have:

$$\chi^* = \chi_{\text{ion}}^* + \chi_{\text{dip}}^*, \quad (6)$$

$$\chi_{\text{ion}}^* = \frac{i}{\varepsilon_0 \pi \hat{\mathbf{E}}^*} \int_{N_{\text{ion}}} \delta N \int_0^{t_v} e v_E(t) \exp(i\omega t + i\gamma) dt, \quad (7)$$

$$\chi_{\text{dip}}^* = \frac{i}{\varepsilon_0 \pi \hat{\mathbf{E}}^*} \int_{N_{\text{dip}}} \delta N \int_0^{t_v} \frac{d\mu_E(t)}{dt} \exp(i\omega t + i\gamma) dt. \quad (8)$$

Here in the exponents we have omitted the $\mathbf{k} \cdot \mathbf{r}$ product, since we neglect the spatial dispersion (it can be shown that the correction, related to it, is negligible); e is the charge of an ion (which is the same as that of an electron); v_E and μ_E are the projections of the ion's velocity and of the dipole moment, respectively, in the direction of the HF \mathbf{E} field. The inner inte-

gration is carried out over time t in the interval $[0, t_v]$, where t_v is the lifetime of a molecule between strong consecutive collisions. The external integration is carried out over all particles contained in a unit volume of the medium and over phases γ , varying in the interval $[0, 2\pi]$, corresponding to the field period $2\pi/\omega$. Finally, N_{ion} and N_{dip} are the number densities of charges and dipoles, respectively. We suppose that the distribution functions of the ions and the dipoles are independent of each other, just as are the translations and reorientations of molecular motions.

3. Transformation of integrals for the orientational and ionic susceptibilities

According to the linear-response approach, χ_{dip}^* is expressed^{12–14} through the spectral function (SF) $L(z)$ characterising the dielectric response of dipoles, librating/rotating without friction under the effect of a specific intermolecular potential well; the expression for $L(z)$ will be given in Section 5. We apply the isothermal collision model, and then in accord with ref. 12, p. 195 or ref. 13, p. 191 we shall have

$$\chi_{\text{dip}}^*(x) = \frac{gGzL(z)}{gx + iy(1 + gxz)L(z)}, \quad (9)$$

where

$$z = x + iy, \quad x = \eta\omega, \quad y = \eta/\tau,$$

$$\eta \equiv \sqrt{\frac{I}{2k_B T}}, \quad \mu = \mu_0 k_\mu \left(\frac{n_\infty^2 + 2}{3} \right), \quad (10)$$

i.e. z is the normalised complex frequency; g is the Kirkwood correlation factor; $G = \mu^2 N_{\text{dip}} / (3\varepsilon_0 k_B T)$ is the normalised density of dipoles; k_B is the Boltzmann constant; T is temperature; I is the moment of inertia of a molecule; μ and μ_0 are the dipole moment of a molecule in a liquid and that of an isolated molecule; k_μ is the correction factor for μ (k_μ is about 1); and τ is a mean over ensemble value of lifetime t_v , further termed simply 'lifetime'.

In view of ref. 13, eqn. (4.34), the first term $\varepsilon_{\text{dip}}(\omega)$ of eqn. (1) is related to χ_{dip}^* in eqn. (9) as the root of the quadratic equation

$$\frac{[\varepsilon_{\text{dip}}^*(\omega) - n_\infty^2][2\varepsilon_{\text{dip}}^*(\omega) + n_\infty^2]}{3\varepsilon_{\text{dip}}^*(\omega)} = \chi_{\text{dip}}^*(\omega). \quad (11)$$

For $\omega \rightarrow 0$, $\varepsilon^*(\omega)$ tends to the static value ε_s . It follows from eqns. (1) and (11) that the Kirkwood correlation factor g is related to the static permittivity ε_s and to the static ionic susceptibility $\chi_{\text{ion}}(0)$:

$$g = \frac{[\varepsilon_s - \chi_{\text{ion}}(0) - n_\infty^2][2\varepsilon_s - 2\chi_{\text{ion}}(0) + n_\infty^2]}{3G[\varepsilon_s - \chi_{\text{ion}}(0)]}. \quad (12)$$

Therefore the static parameters of the dipolar and ionic subensembles are interrelated. However, if the condition

$$\chi_{\text{ion}}(0) \ll \varepsilon_s \quad (12a)$$

holds, then eqn. (12) yields the usual formula for g :

$$g \approx \frac{(\varepsilon_s - n_\infty^2)(2\varepsilon_s + n_\infty^2)}{3G\varepsilon_s}. \quad (13)$$

We replace δN in eqn. (7) by the expression (2.13) in ref. 13:

$$\delta N = \frac{N_{\text{ion}}}{\omega\tau_{\text{ion}}} W(\Gamma) d\Gamma F(\gamma) d\gamma \exp\left(-\frac{t_v}{\tau_{\text{ion}}}\right) \frac{dt_v}{\tau_{\text{ion}}}. \quad (14)$$

Here Γ denotes phase variables, $W(\Gamma)$ and $F(\Gamma)$ are the normalised Boltzmann and induced distribution functions, such

that

$$\int_r W(\Gamma) d\Gamma = 1, \quad \langle f(\Gamma) \rangle \equiv \int_r f(\Gamma) W(\Gamma) d\Gamma,$$

$$W = C \exp\left(-\frac{H(\Gamma)}{k_B T}\right) \equiv C \exp(-h), \quad (15)$$

and $\langle \square \rangle$ means the average over the ensemble of particles, H is the energy of a particle. It follows from eqns. (7) and (15) after integration by parts over t that

$$\chi_{\text{ion}}^*(\omega) = \frac{2iN_{\text{ion}} e}{\varepsilon_0 \hat{E}^* \omega \tau} \times \left\langle \int_0^{2\pi} F(\gamma) \exp(i\gamma) \frac{d\gamma}{2\pi} \int_0^\infty v_E(t) \exp(i\hat{\omega}t) dt \right\rangle, \quad (16)$$

$$\hat{\omega} = \omega + i/\tau. \quad (17)$$

In eqn. (16) the law of motion $v_E(t)$ corresponds to the trajectory of an ion, *perturbed* by the propagating wave. We set $F(\gamma) \equiv 1$. Thus for $\omega \neq 0$ the induced distribution function is taken to be the same (Boltzmann) as for the steady state. As shown in Appendix A for $\mu|\hat{E}| \ll k_B T$, eqn. (16) can be reduced to

$$-i\omega r_D^2 \chi_{\text{ion}}^*(\omega) = \left\langle v_E(0) \int_0^\infty v_E(t) \exp(i\hat{\omega}t) dt \right\rangle$$

$$\equiv \int_r W v_E(0) d\Gamma \int_0^\infty v_E(t) \exp(i\hat{\omega}t) dt$$

$$\equiv C \int_r \exp(-h) v_E(0) d\Gamma \int_0^\infty v_E(t) \exp(i\hat{\omega}t) dt,$$

$$r_D = \sqrt{\frac{\varepsilon_0 k_B T}{e^2 N_{\text{ion}}}}; \quad C^{-1} = \int_r \exp(-h) d\Gamma; \quad (18)$$

and r_D is the Debye radius for charges in vacuum. The ionic conductivity $\sigma^*(\omega)$ is proportional to $\chi_{\text{ion}}^*(\omega)$; omitting the asterisk (*viz.* we denote hereafter $\sigma \equiv \sigma' + i\sigma''$), we have (see Appendix A):

$$\sigma(\omega) = -i\varepsilon_0 \omega \chi_{\text{ion}}^*(\omega), \quad (19)$$

$$\sigma(\omega) = \frac{C\varepsilon_0}{r_D^2} \int_r \exp(-h) v_E(0) d\Gamma \int_0^\infty v_E(t) \times \exp(i\hat{\omega}t) dt. \quad (20)$$

Now the ionic susceptibility/conductivity is a function of the trajectories of the charges at *equilibrium*, *viz.* $\chi_{\text{ion}}^*(\omega)$ is proportional to the ac field spectrum of the E projection of the steady-state velocity \dagger . One may regard eqn. (20) as a convenient (for numerical calculations) form of the Kubo formula¹⁶ for the diagonal component of the conductivity tensor

$$\sigma_{xx}(\omega) = (k_B T N)^{-1} \text{Re} \int_0^\infty \langle J_x(t) J_x(0) \rangle \exp(-i\omega t) dt. \quad (21)$$

In Appendix B we prove that χ_{ion}^* , found from eqns. (19) and (20), satisfies the sum rule for the integrated absorption. An estimation given in Appendix C shows that a pair of electrostatic interactions between ions can approximately be neglected.

4. Formula for the complex conductivity

We may substantiate the necessity of using a potential barrier for ions starting from the rarefied plasma theory, in which the intermolecular potential U_{plasma} can be taken as zero. Then,

\dagger Analogously, the orientational susceptibility χ_{dip}^* is proportional (ref. 13, p. 150) to the spectrum of the normalised projection $q = \mu_E/\mu$ of the dipole moment; in an isotropic medium the SF $L(z)$ is given by

$$L(z) = iz \left\langle q_0 \int_0^\infty [q(t/\eta) - q(0)] \exp(izt/\eta) dt \right\rangle.$$

neglecting spatial dispersion in accordance with ref. 17, p. 52, we have:

$$\chi(\omega) = -\frac{\omega_p^2}{\hat{\omega}\omega}; \quad \sigma(\omega) = i \frac{\varepsilon_0 \omega_p^2}{\hat{\omega}}, \quad (22)$$

where the complex frequency $\hat{\omega}$ is defined by eqn. (17), the plasma frequency $\omega_p = \sqrt{e^2 N / (m\varepsilon_0)}$, $m = m_H M_{\text{ion}}$ is the mass of an ion, and m_H is the mass of a proton. Eqns. (22) also follow from eqn. (6.24) in ref. 18, if one neglects the spatial dispersion but generalises the theory for a finite lifetime τ_{ion} . If $\omega \rightarrow 0$, the second of eqns. (22) yields

$$\sigma_s = \varepsilon_0 \omega_p^2 \tau_{\text{ion}}. \quad (23)$$

Summing the contributions due to cations (Na^+) and anions (Cl^-) we can make an estimate of the static conductivity of NaCl-water solution. Since $N = 1000 N_A C_M$, where N_A is the Avogadro number and C_M (mol l^{-1}) is molar concentration, eqn. (23) yields:

$$\sigma_s = \frac{1000 e^2 N_A C_M \tau_{\text{ion}}}{m_H} \left(\frac{1}{M^+} + \frac{1}{M^-} \right);$$

$$M^+ = M_{\text{Na}} \approx 23, \quad M^- = M_{\text{Cl}} \approx 35.5.$$

For $C_M \sim 1 \text{ mol l}^{-1}$ this relation gives the observed¹⁹ conductivity ($\sigma_s \sim 10 \text{ ohm}^{-1} \text{ m}^{-1}$) for τ_{ion} of about 0.01 ps. This lifetime seems to be unreasonably short, since the τ -values typical for water are (ref. 12, ch. 15) of the order of 0.5 ps. We can substantially improve the situation, *viz.* to make τ_{ion} about 0.5 ps or more, by introducing an intermolecular potential well. \ddagger

For simplicity we regard the one-dimensional ensemble ($v_E \rightarrow v$). We assume that a charged particle oscillates during the lifetime τ_{ion} inside a rectangular infinitely deep potential well, having width $2l_{\text{cell}}$ (see Fig. 1), from the walls of which an ion performs elastic reflections. We consider the equations of motion for a *point* particle (ion) having mass m and charge e . Since, as we shall show, the width $2l_{\text{cell}}$ is only slightly greater than the diameter $2R_{\text{ion}}$ of an ion, the centre O' of mass of an ion shifts only a little relative to the centre O of the cell. Let l be the maximum distance OO' between these two centres; then the maximal and minimal distances between the surface of an ion and the wall of the well are $2l$ and 0, respectively (see Fig. 1). Therefore, the centre of mass O oscillates inside a fictitious slot having width $2l$, such that $l \ll l_{\text{cell}}$. During the lifetime τ_{ion} the absolute value $|v|$ of the ion's velocity is constant:

$$|v| = \sqrt{2H/m} = v_T \sqrt{2h} \quad \text{at} \quad |r| \leq l,$$

where r is the translational shift (we set $r = 0$ in the middle of the well); H is the energy of an ion; the averaged velocity of

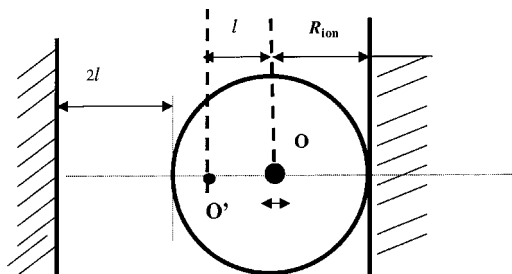


Fig. 1 The scheme of a hydration cell, having width $2R_{\text{ion}} + 2l$. The centre O of an ion undergoes small oscillations inside a fictitious thin layer, having width $2l$; O' lies on the symmetry axis of this layer. In the diagram the position of an ion is shown at the instant when the ion exerts an elastic reflection from the right wall of the potential well. Dashed areas show the hydration sheath.

\ddagger The analogous situation was met previously (ref. 13, p. 357), when the self-diffusion coefficient $D(T)$ of polar molecules was calculated for liquids.

an ion $v_T = \sqrt{(k_B T/m)}$; and $h = H/(k_B T)$ is the dimensionless energy. The time dependence of the velocity of an oscillating ion can be expressed as a series, containing only odd harmonics, having the oscillation period Θ :

$$v(t) = \sum_{n=1}^{\infty} v_{2n-1} \cos \left[\frac{2\pi}{\Theta} (2n-1)(t+t_0) \right];$$

$$\Theta(h) \equiv \frac{4l}{v_T \sqrt{2h}}. \quad (24)$$

The constant t_0 in eqn. (24) and the energy H of a particle are canonically conjugated constants, the phase-volume element then being $d\Gamma = dH dt_0 \equiv mv_T^2 dh dt_0$. Integration over t_0 is carried out in the interval $t_0 \in [0, \Theta(h)/4]$, corresponding to the interval of distances $r \in [0, l]$. Then the velocity autocorrelation function is given by

$$\langle v(t)v(0) \rangle \equiv mv_T^2 C \int_0^{\infty} \exp(-h) dh \int_0^{\Theta(h)} v(t)v(0) dt_0$$

$$= mv_T^2 \frac{C}{8} \int_0^{\infty} \sum_{n=1}^{\infty} v_{2n-1}^2$$

$$\times \cos \left[2\pi(2n-1) \frac{t}{\Theta(h)} \right] \Theta(h) \exp(-h) dh. \quad (25)$$

According to eqn. (24)

$$v_{2n-1} = \frac{8}{\Theta} v_T \sqrt{2h} \int_0^{\Theta/4} \cos \left[2\pi(2n-1) \frac{t}{\Theta(h)} \right] dt$$

$$dt = \frac{4(-1)^{n+1}}{\pi(2n-1)} v_T \sqrt{2h}.$$

To calculate the normalisation constant C it is convenient to take r and v as the phase variables:

$$d\Gamma = m dr dv;$$

$$C^{-1} = \int_r \exp(-h) d\Gamma$$

$$= m \int_0^l dr \int_0^{\infty} \exp\left(-\frac{v^2}{2v_T^2}\right) dv$$

$$= \sqrt{\frac{\pi}{2}} v_T ml.$$

Now, using eqn. (20) we can calculate the normalised conductivity S as a function of two dimensionless parameters: complex frequency Z and width d of the fictitious well. We get

$$S \equiv \frac{\sigma}{4\pi\epsilon_0 \omega_p}; \quad Z = X + iY = \frac{\hat{\omega}}{\omega_p};$$

$$X \equiv \frac{\omega}{\omega_p}; \quad Y \equiv (\omega_p \tau_{ion})^{-1}, \quad (26a)$$

$$d \equiv l/(\sqrt{2} r_D); \quad (26b)$$

$$S(Z) = \frac{1}{4\pi r_D v_T} \left\langle v(0) \int_0^{\infty} v(t) \exp(i\omega_p Zt) dt \right\rangle \quad (27)$$

$$= -\frac{8iZ}{\pi^3 \sqrt{\pi}} \int_0^{\infty} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2}$$

$$\times \frac{\exp(-\xi^2) \xi^2 d\xi}{\left[\frac{\pi}{2d} (2n-1) \xi \right]^2 - Z^2} \quad (28a)$$

$$= \frac{i}{4\pi Z} \left[1 - \frac{4}{\sqrt{\pi} Z d} \int_0^{\infty} \tan\left(\frac{Zd}{\xi}\right) \right.$$

$$\left. \times \exp(-\xi^2) \xi^3 d\xi \right]. \quad (28b)$$

For rather rare ionic collisions ($Y \ll 1$) we have the simple formula:

$$S(Z, d) \approx -\frac{iZd^2}{6\pi} \quad \text{for } |Zd^2| \ll 1. \quad (29a)$$

Representing $\tan(\cdot)$ in eqn. (28b) as $\sin(\cdot)\cos(\cdot)/[1 - \sin^2(\cdot)]$ and noting that the imaginary component of the denominator reduces in the limit $Y \rightarrow 0$ to a δ -function, we deduce from eqn. (28b):

$$\lim_{Y \rightarrow 0} \text{Re}\{S(Z)\} \equiv S'(X)$$

$$= \frac{16X^2 d^3}{\pi^5 \sqrt{\pi}} \exp[-(2Xd/\pi)^2]. \quad (29b)$$

In view of eqn. (19) the ionic susceptibility χ^* and the contribution $\Delta\epsilon_{ion}^*$ of ions to the complex permittivity are given by:

$$\chi_{ion}^* = i\epsilon_0 \sigma/\omega = 4\pi i S/X, \quad (30)$$

$$\Delta\epsilon_{ion}^* = \chi_{ion}^* = 4\pi i S/X. \quad (31)$$

The normalised static conductivity is given by:

$$S_s(Y, d) = S(iY, d)$$

$$= \frac{8Y}{\pi^3 \sqrt{\pi}} \int_0^{\infty} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2}$$

$$\times \frac{\exp(-\xi^2) \xi^2 d\xi}{\left[\frac{\pi}{2d} (2n-1) \xi \right]^2 + Y^2} \quad (32a)$$

$$= \frac{1}{4\pi Y} \left[1 - \frac{4}{\sqrt{\pi} Y d} \int_0^{\infty} \tanh\left(\frac{Yd}{\xi}\right) \right.$$

$$\left. \times \exp(-\xi^2) \xi^3 d\xi \right]; \quad (32b)$$

$$S_s \approx Yd^2/(6\pi) \quad \text{for } Yd^2 \ll 1. \quad (32c)$$

In accordance with eqn. (24) the frequency Ω of ionic oscillations is

$$\Omega = \frac{2\pi}{\Theta} = \frac{\pi v_T}{l} \sqrt{\frac{h}{2}}.$$

The corresponding normalised quantity p , which is also the resonance frequency of the first Lorentz-like denominator in eqn. (28a), is given by:

$$p \equiv \frac{\Omega}{\omega_p} = \frac{\pi \sqrt{h}}{2d}.$$

The mean oscillation frequency $\langle p \rangle$ is about the reverse value of the d -parameter of the model:

$$\langle p \rangle = \left\langle \frac{\Omega}{\omega_p} \right\rangle = \frac{C}{\omega_p} mv_T^2 \frac{\pi}{2} \int_0^{\infty} \exp(-h) dh = \frac{\sqrt{\pi}}{2d}. \quad (33)$$

We shall show below that this parameter d has the order of magnitude 1. Therefore, the mean oscillation frequency in electrolytes is about the plasma frequency. From Fig. 2(a) we see that the static conductivity S_s decreases with decreasing width of the well d , since for smaller d the ion velocity changes its direction more frequently. For $d \rightarrow \infty$ we have just the case of a rarefied plasma. Indeed, as follows from eqn. (22) as well as from eqns. (32a,b),

$$S_{s, \text{plasma}} = (4\pi Y)^{-1}; \quad (34a)$$

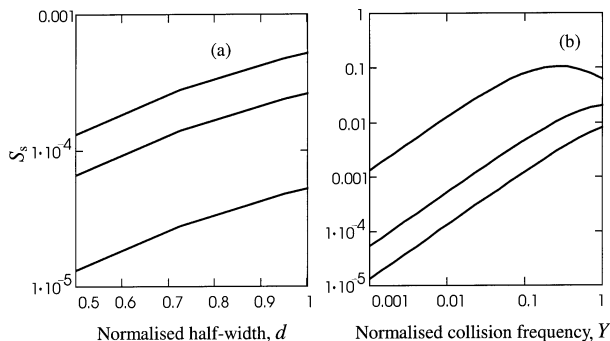


Fig. 2 Normalised static conductivity vs. normalised half-width of a fictitious slot (a) or collision frequency (b). (a) $Y = 0.001, 0.005$ and 0.01 ; (b) $d = 0.5, 1$ and 5 (from bottom to top).

$$S_s(Y, 0) = \frac{8}{\pi^3 \sqrt{\pi} Y} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \int_0^{\infty} \xi^2 \exp(-\xi^2) d\xi$$

$$= \frac{8}{\pi^3 \sqrt{\pi} Y} \frac{\pi^2 \sqrt{\pi}}{8 \cdot 4} = \frac{1}{4\pi Y}. \quad (34b)$$

Consequently, for $d \rightarrow \infty$ the static conductivity tends to infinity, if $Y \rightarrow 0$. On the contrary, if the half-width d is finite, then $S_s \rightarrow 0$ for $Y \rightarrow 0$. This is the principal distinction of our model from that corresponding to a rarefied plasma.

Now let Y be finite. If $Y = 0.005$ and $d = 1$, then we find: $S_{s, \text{plasma}} \approx 15.9$ and $S_s(Y, d) \approx 2.64 \times 10^{-4}$. For the same Y and $d = 0.5$, $S_s(Y, d) \approx 6.6 \times 10^{-5}$. Consequently, for a deep potential well the static conductivity decreases by several orders of magnitude, when the pure translations in a rarefied plasma are replaced by small-amplitude oscillations inside a local potential well introduced for the liquid state.

Fig. 2(a) illustrates how S_s increases with d for three different values of the normalised collision frequency Y . The increase of Y results in the increase of the static conductivity, if Y is small [Fig. 2(b)]; for larger Y , the $S_s(Y)$ function goes through a maximum. We remark that in polar fluids the static permittivity ϵ_s decreases with the rise of the normalised colli-

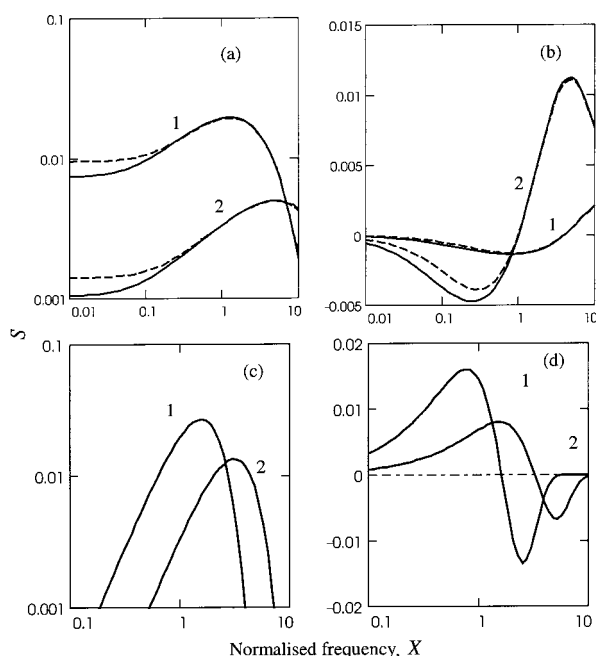


Fig. 3 Real (a,c) and imaginary (b,d) parts of the normalised complex susceptibility S vs. the normalised frequency X ; curves 1—for $d = 1$; curves 2—for $d = 0.5$. (a,b) Normalised collision frequency $Y = 0.05$ (solid lines) and 0.1 (dashed lines); (c,d) long lifetime limit ($Y \rightarrow 0$).

sion frequency $y = \eta/\tau$ for all y -values [see eqn. (10), where y is introduced].

Figs. 3(a) and (b) demonstrate the frequency dependences of the real and imaginary parts of the normalised conductivity (28). For the chosen set of parameters ($Y = 0.05$ and 0.1 ; $d = 0.5$ and 1), which are more or less typical for electrolytes under consideration:

(a) in the low-frequency region the real part S' is almost independent of frequency X , while the imaginary part S'' decreases from zero with increase of X , so that it is negative; a noticeable change of S' with X occurs for $X \approx 0.1$, viz. when ω approaches one-tenth of the plasma frequency ω_p ;

(b) in the high-frequency region S' goes through a maximum, while the imaginary part S'' goes through a minimum and then a maximum;

(c) these quasi-resonance curves shift to higher frequencies, if the width of the well decreases;

(d) the increase of the collision frequency Y results in the change of only the low-frequency part of these X -dependences.

For the zero- Y case, use of eqn. (29) yields narrower quasi-resonance $S'(X)$ and $S''(X)$ curves, their dependence on the parameter d being qualitatively the same, as was described for $Y > 0$ [cf. Figs. 3(c) and (d) with Figs. 3(a) and (b), respectively].

5. Dielectric permittivity/absorption spectra of NaCl and KCl aqueous solutions

The plateau-like region of $S'(X)$ seen in Fig. 3(a) at small X implies the idea that for moderate X -values the formula

$$\epsilon^*(\nu) = \epsilon_{\text{dip}}^*(\nu) + \frac{i\sigma_s}{2\pi\epsilon_0 c\nu} \quad (35)$$

can be a rather good approximation to the exact formula $\epsilon^*(\nu)$ given by eqns. (1), (19), (26) and (27). The corresponding ionic contribution to the total loss is

$$\Delta\epsilon''_{\text{ion}}(\nu) = \frac{\sigma_s}{2\pi\epsilon_0 c\nu}. \quad (36)$$

Further calculations will be performed in two stages: (1) ionic loss will be found for a constant conductivity, viz. for σ , equal to the experimentally measured static value σ_s , while the ionic contribution $\Delta\epsilon'_{\text{ion}}(\nu)$ to the real part of the permittivity will be neglected; the parameters of the dipolar reorientation will be determined for the hybrid model at this stage; (2) then the rigorous formula (28) for the ionic frequency-dependent conductivity will be applied and after that the complex dielectric permittivity of the solutions under consideration will be calculated from eqn. (1).

The first stage

The response of water (*i.e.* of the dipolar component of the solution) is calculated using the hybrid model, just as was done in refs. 12 and 15. The complex permittivity $\epsilon_{\text{dip}}^*(\nu) = \epsilon'_{\text{dip}}(\nu) + i\epsilon''_{\text{dip}}(\nu)$ of the water component is related, in view of eqn. (11), to the orientational susceptibility $\chi_{\text{dip}}^*(\nu)$ as

$$\epsilon_{\text{dip}}^*(\nu) = \frac{1}{4} \{ n_{\infty}^2 + 3\chi_{\text{dip}}^* + [(n_{\infty}^2 + 3\chi_{\text{dip}}^*)^2 + 8n_{\infty}^4]^{1/2} \}^{1/2}; \quad (37)$$

χ_{dip}^* is determined by eqn. (9). The spectral function $L(z)$ of the hybrid model is (ref. 12, sec. 9.2)

$$L(z) = \check{L}_{\parallel}(z) + \check{L}_{\perp}(z) + \check{L}(z); \quad (38)$$

$$\check{L}_{\parallel} = C_{\parallel} \int_0^u \frac{h \exp(-h) dh}{h - (\beta z/\pi)^2},$$

$$\check{L}_{\perp} = C_{\perp} \int_0^u \frac{h \exp(-h) dh}{h - (2\beta z/\pi)^2},$$

$$\check{L} = C_0 \exp(-u) \int_0^{\infty} \frac{h \exp(-h) dh}{h - z^2};$$

$$C_{\parallel} = \frac{C_0}{\pi^5} (2\beta^2 \sin \beta)^2; \quad C_{\perp} = \frac{C_0}{\pi^5} (8\beta^2 \cos \beta)^2;$$

$$C_0 = \frac{1}{1 - \exp(-u) \cos \beta}.$$

Subscripts \parallel and \perp refer to the symmetry axes of the potential wells, directed along and perpendicular to the radiation field, respectively; the last term in eqns. (38) is due to the dipoles performing complete rotation; β is the amplitude of libration, measured in angular units; the normalised well depth $u = U_0/(k_B T)$; the complex frequency z is determined by eqn. (10). Setting $x = 0$ in eqns. (9) and (38), one can estimate the Debye relaxation time as

$$\tau_D^{\text{est}} \approx \eta g [1 - y^2 L(iy)] / [y L(iy)]. \quad (39)$$

Experimental^{19,20} values ϵ_s , σ_s , τ_D , ϵ_{∞} , ρ_{eff} and the fitted parameters of the hybrid model are presented in Table 1 for two concentrations C_M (mol l⁻¹). For liquid water, *viz.* at $C_M = 0$, we used experimental data given in refs. 12 and 21. The number density N_{dip} of water molecules is found from the formula

$$N_{\text{dip}} = \frac{N_A \rho_{\text{eff}}}{M_{\text{ion}}}; \quad \rho_{\text{eff}} = \rho - 1000 C_M M_{\text{ion}},$$

where M_{ion} is the molecular mass of an ion (M_{NaCl} or M_{KCl} in our case); ρ_{eff} (g cm⁻³) is the effective density of water in the electrolyte solution; and ρ is the density of the solution.

When the electrolyte concentration C_M is changed, the wideband spectra are controlled only by one parameter (τ) of the hybrid model. Other parameters of this model—the normalised well depth u , libration amplitude β and μ -correcting coefficient k_{μ} in eqn. (10)—may be set independent of C_M and therefore may be fitted when the spectra, calculated for water, are compared with the recorded^{21,25} ones (see Table 1).

The second stage

A more rigorous theory will now be applied, for which σ_s in eqn. (35) is replaced by $\sigma(v)$:

$$\epsilon^*(v) = \epsilon_{\text{dip}}^*(v) + i\sigma(v)/(2\pi\epsilon_0 cv); \quad (40)$$

$$\Delta\epsilon_{\text{ion}}''(v) = \sigma/(2\pi\epsilon_0 cv). \quad (41)$$

Let the values corresponding to the cations (*viz.* Na⁺, K⁺) and to the anions (*viz.* Cl⁻) be marked respectively by signs + and -. In our case of 1-1 electrolytes we have $N^+ = N^- = N_{\text{ion}}$. We write the expressions for the ionic complex conductivity/susceptibility as the superposition of the corre-

sponding contributions of the cations and anions:

$$\chi_{\text{ion}}^*(\omega) = 4\pi i \left(\frac{S^+}{X^+} + \frac{S^-}{X^-} \right);$$

$$\sigma(\omega) = 4\pi\epsilon_0 (S^+ \omega_p^+ + S^- \omega_p^-), \quad (42a)$$

$$S^{\pm} \equiv S(X^{\pm}); \quad X^{\pm} \equiv \omega/\omega_p^{\pm}, \quad (42b)$$

$$\Delta\epsilon_{\text{ion}}^*(\omega) = \chi_{\text{ion}}^*(\omega) = 4\pi i (S^+/X^+ + S^-/X^-). \quad (43)$$

Then the resulting permittivity ϵ^* and the absorption coefficient α can be found as

$$\epsilon^* = \epsilon_{\text{dip}}^*(v) + \Delta\epsilon_{\text{ion}}^*(v) \\ = \epsilon_{\text{dip}}(v) + 4\pi i (S^+/X^+ + S^-/X^-), \quad (44)$$

$$\alpha(v) = 4\pi v \text{Im} \sqrt{\epsilon^*(v)}, \quad (45)$$

where $\epsilon_{\text{dip}}^*(v)$ and S are given by eqns. (37) and (28), respectively.

In further estimations we neglect the distinction between hydrated and bulk water; and we take the lifetimes τ_{ion} to be equal for anions and cations, *viz.* for Cl⁻ and Na⁺ or Cl⁻ and K⁺. Consequently, the normalised collision frequency Y is related to τ_{ion} as $Y^+ = (\omega_p^+ \tau_{\text{ion}})^{-1}$; $Y^- = (\omega_p^- \tau_{\text{ion}})^{-1}$. The ionic lifetime will be set equal to or much longer than that (τ), fitted above for water molecules: (a) $\tau_{\text{ion}} \equiv \tau$, and (b) $\tau_{\text{ion}} \equiv 10\tau$. In order to fit the half-width l of the fictitious slot, in which an ion's centre of mass moves, we consider l to be proportional to the sum of the radii of an ion and of the water molecule:

$$l^{\pm} = (R^{\pm} + R_w)\psi,$$

so that

$$d^{\pm} = (R^{\pm} + R_w)\psi/(\sqrt{2}r_D). \quad (46)$$

The coefficient ψ can be determined from the condition that the static conductivity of the solution should be equal to the experimental value σ_s . This condition yields the equation for ψ after we put $\omega = 0$ in eqn. (42):

$$\sigma_s = 4\pi\epsilon_0 [S_s^+(Y^+, d^+)\omega_p^+ + S_s^-(Y^-, d^-)\omega_p^-]; \quad (47)$$

$S_s(Y, d)$ is determined by eqn. (32).

In Tables 2-4 we present the fitted/calculated parameters of our model for ions: the plasma frequency ω_p^{\pm} ; the static ionic conductivity σ_s^{\pm} ; the mean distance between ions, estimated using the formula

$$\Delta R_{\text{ion}} = (2 \times 1000 N_A C_M)^{-1/3}, \quad (47a)$$

where the multiplier 2 accounts for the doubling of the concentration of ions in the solution; the fitted parameters d^{\pm} ; and the corresponding *mean distances* l^{\pm} between the walls and the surface of an ion. We see that l^{\pm} has the order of a part of an angstrom; this result looks reasonable. We remark that the mean distance ΔR_w between water molecules weakly depends on C_M , *viz.*

Table 1 Experimental and fitted parameters for NaCl-water and KCl-water solutions; $T = 20^\circ\text{C}$. Concentration C_M in mol l⁻¹; density ρ_{eff} of water in the solution in g cm⁻³; static conductivity σ_s in (ohm m)⁻¹; relaxation time τ_D and mean lifetime τ in ps^a

C_M	NaCl-water						KCl-water					
	ρ_{eff}	σ_s	ϵ_s	τ_D	τ	m_{dip}	ρ_{eff}	σ_s	ϵ_s	τ_D	τ	m_{dip}
0.0	0.998	0	80	9.8	0.42	7.6	0.998	0	80	9.8	0.42	7.6
0.5	0.988	3.89	71	9.2	0.44	8.0	0.984	5.11	74	9.0	0.41	7.4
1	0.980	7.22	63	8.8	0.47	8.5	0.969	9.78	69	8.3	0.40	7.2

^a Notes: $k_{\mu} = 1.12$, $I = 1.483 \times 10^{-47}$ kg m², $n_{\infty}^2 = 1.7$, $\epsilon_{\infty} \approx 5$, $u = 5.575$, $\mu_0 = 1.48$ D, $\beta = 19.4^\circ$, $M_{\text{NaCl}} = 58.44$, $M_{\text{KCl}} = 74.55$, $M_w = 18$. Note that 1 D = 3.333×10^{-30} C m; in CGS system of units

$$[\sigma] = \text{s}^{-1} \quad \text{and} \quad \sigma_{[\text{SI}]} = \frac{1}{9 \times 10^9} \sigma = [\text{CGS}].$$

Table 2 Experimental and fitted parameters for the molecular model of the static conductivity σ_s ; $T=20^\circ\text{C}$. Plasma frequency ω_p^\pm in 10^{-12} rad s^{-1} , σ_s in $(\Omega\text{ m})^{-1}$, ΔR_{ion} in \AA^a

$C_M/\text{mol l}^{-1}$	NaCl-water					KCl-water				
	ω_p^-	ω_p^+	σ_s^-	σ_s^+	ΔR_{ion}	ω_p^-	ω_p^+	σ_s^-	σ_s^+	ΔR_{ion}
0.5	3.84	4.77	9.0	3.0	11.8	3.65	4.77	1.6	3.0	11.8
1	5.43	6.74	17	5.6	9.4	5.17	6.74	3.3	5.8	9.4

^a Notes: $R^+ = 1.8 \text{ \AA}$, $R_w = 1.5 \text{ \AA}$, $\Delta R_w \approx 3.13 \text{ \AA}$. For NaCl-water: $R^- = 0.95 \text{ \AA}$. For KCl-water: $R^- = 1.33 \text{ \AA}$.

$$\Delta R_w = (N_A \rho_{\text{eff}}/M_w)^{-1/3} \approx 3.13 \text{ \AA}$$

In Figs. 4 and 5 we illustrate the effect of the σ dispersion in terms of the ionic contribution to the $\epsilon^*(\nu)$ spectrum, calcu-

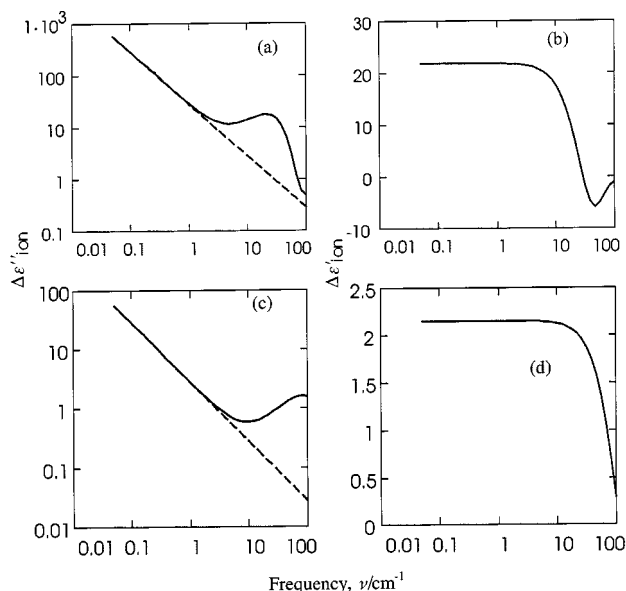


Fig. 4 Calculated contributions of the ionic permittivity for the imaginary (a,c) and real (b,d) parts of the total complex permittivity (solid lines); dashed lines refer to the calculation, neglecting the ionic dispersion. (a,b) For NaCl-water solution; (c,d) for KCl-water solution. $C_M = 0.5 \text{ mol l}^{-1}$, $\tau_{\text{ion}}/\tau = 10$.

lated for the lowest concentration 0.5 mol l^{-1} . From Figs. 4(a), (c) and 5(a), (c) we see that an additional loss $\Delta\epsilon''_{\text{ion}}(\nu)$ arises due to this dispersion: the effect is larger (especially for NaCl) for longer ionic lifetime τ_{ion} , for which it appears at millimetre waves, while for $\tau_{\text{ion}} = \tau$ it is at submillimetre waves. The ionic zero-frequency contribution $\Delta\epsilon'_{\text{ion}}(0) = \chi'_{\text{ion}}(0)$ to the static permittivity ϵ_s of the total permittivity is small at $\tau_{\text{ion}} = \tau$ [see Figs. 5(b) and (d)], so that we may indeed neglect the ionic term $\chi_{\text{ion}}(0)$ in eqn. (12) in comparison with the static

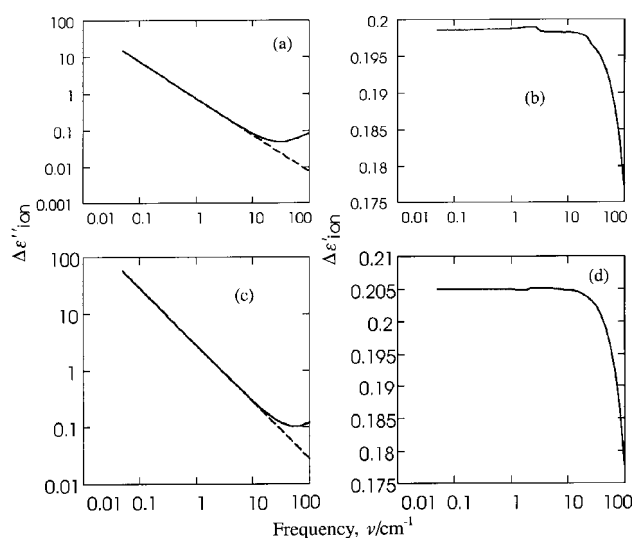


Fig. 5 The same as in Fig. 4 but for $\tau_{\text{ion}}/\tau = 1$.

Table 3 The fitted parameters of the model; lifetimes are given in ps

$C_M/\text{mol l}^{-1}$	NaCl-water				KCl-water			
	$\tau_{\text{ion}} = 10\tau$		$\tau_{\text{ion}} = \tau$		$\tau_{\text{ion}} = 10\tau$		$\tau_{\text{ion}} = \tau$	
	d^+	d^-	d^+	d^-	d^+	d^-	d^+	d^-
0.5	1.51	0.82	0.48	0.26	1.47	1.10	0.47	0.35
1	2.13	1.16	0.69	0.37	2.01	1.50	0.65	0.49
	Y^+		Y^-		Y^+		Y^-	
0.5	0.0102	0.0082	0.102	0.082	0.0123	0.0130	0.123	0.130
1	0.0096	0.0077	0.096	0.077	0.0129	0.0136	0.129	0.136

Table 4 The mean distance l (in \AA) between the surface of an ion and the hydrated layer

$C_M/\text{mol l}^{-1}$	NaCl-water				KCl-water			
	$\tau_{\text{ion}} = 10\tau$		$\tau_{\text{ion}} = \tau$		$\tau_{\text{ion}} = 10\tau$		$\tau_{\text{ion}} = \tau$	
	l^+	l^-	l^+	l^-	l^+	l^-	l^+	l^-
0.5	0.25	0.14	0.080	0.043	0.275	0.205	0.088	0.066
1	0.35	0.19	0.11	0.062	0.379	0.283	0.123	0.092

permittivity ϵ_s . For $\tau_{\text{ion}} = 10\tau$, the value $\Delta\epsilon'_{\text{ion}}(0)$ is rather large for NaCl [Fig 4(b)] and noticeable for [Fig. 4(d)].

The calculated loss $\epsilon''(\nu)$ and absorption $\alpha(\nu)$ spectra are pictured for NaCl–water solution in Figs. 6 and 7. Again we take $C_M = 0.5 \text{ mol l}^{-1}$. At microwave frequencies the $\epsilon''(\nu)$ curve [see Figs. 6(a) and 7(a)] comprises a shoulder, while in the submillimetre range it shows two maxima. They correspond to the translational (near 200 cm^{-1}) and librational (near 700 cm^{-1}) peaks of the absorption frequency dependence $\alpha(\nu)$, shown in Figs. 6(b) and 7(b). At low frequencies (up to $\nu \approx 10 \text{ cm}^{-1}$ for $\tau_{\text{ion}}/\tau = 1$ or up to $\nu \approx 2 \text{ cm}^{-1}$ for $\tau_{\text{ion}}/\tau = 10$) the

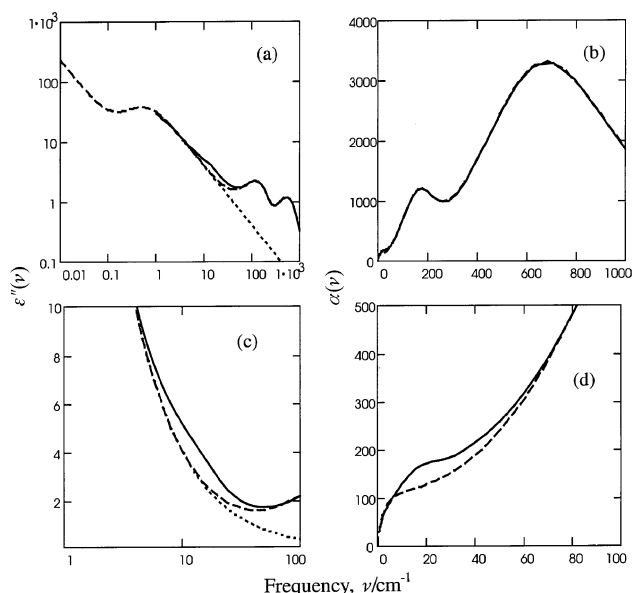


Fig. 6 Frequency dependences of dielectric loss (a,c) and of absorption coefficient (b,d) calculated for NaCl–water solution at $C_M = 0.5 \text{ mol l}^{-1}$, $T = 20^\circ\text{C}$, $\tau_{\text{ion}}/\tau = 10$. Solid and dashed lines refer, respectively, to account for and to neglect of ionic dispersion $\sigma(\nu)$; dotted line is the calculation from eqn. (48). For $\nu < 1 \text{ cm}^{-1}$ all three curves (solid, dashed and dotted) coincide.

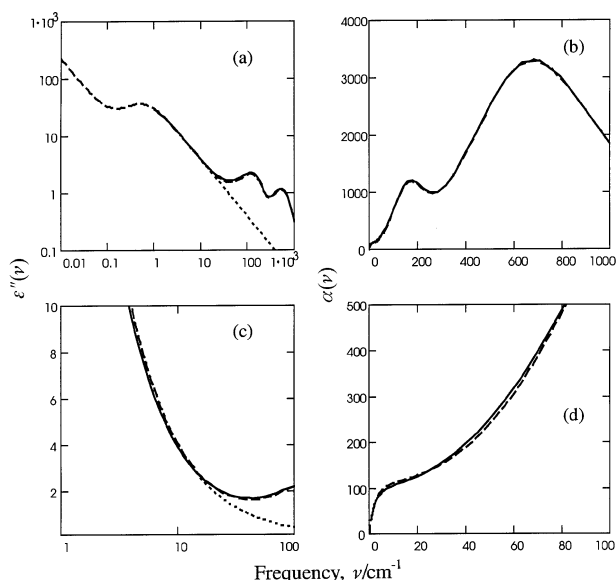


Fig. 7 The same as in Fig. 6 but for $\tau_{\text{ion}} = \tau$.

§ It can also be shown that if $C_M \rightarrow 0$ then the $\alpha(\nu)$ curve becomes rather close for low frequencies to that described in ref. 21 by an empirical formula; for the concentrated NaCl electrolyte the theoretical $\alpha(\nu)$ dependence is similar in the FIR region to the observed⁸ curve.

rigorous $\epsilon''(\nu)$ solid curve is well approximated (*cf.* the dotted curve) by the formula composed of the Debye term and the ionic term for $\sigma \equiv \sigma_s$:

$$\epsilon^*(\nu) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 - 2\pi i c \nu \tau_D} + \frac{i\sigma_s}{2\pi\epsilon_0 c \nu}. \quad (48)$$

However, for $\nu > 10 \text{ cm}^{-1}$, eqn. (48) does not hold.

It is also interesting to compare the exact $\epsilon^*(\nu)$ and $\alpha(\nu)$ dependences (44) and (45) with those based on the formula (35), in which the first dipolar term is rigorous but in the second one the effect of ionic dispersion is neglected (*cf.* dashed and solid curves in Figs. 6 and 7). It is seen in Figs. 6(a), (c) and (d) that a noticeable distinction between the spectra calculated with or without the account of the $\sigma(\nu)$ dispersion may arise at millimetre/submillimetre wavelengths, if the ratio τ_{ion}/τ is large (*viz.*, 10 in Fig. 6). However, if $\tau_{\text{ion}} \approx \tau$, the effect of the $\sigma(\nu)$ dispersion on the $\epsilon^*(\nu)$ and $\alpha(\nu)$ dependences disappears (see Fig. 7). In any case, the simplified formula (35) works well not only at low frequencies but also in the FIR range, if $\nu > 70 \text{ cm}^{-1}$.

6. Potential well with vibrating walls

We discuss the situation in which the width of the well changes harmonically with time. This idea could be reasonable, since all molecules of the medium are in motion. Using the hybrid model, we shall apply the new consideration only for liquid water. Thus we replace the constant half-width β of the rectangular well by the following time-varying quantity:

$$\beta(\Phi) = \beta_0 + \beta_1 \sin \Phi(t); \quad \Phi(t) \equiv \Omega t + \Phi_0; \quad \Omega \tilde{T} \ll 1, \quad (49)$$

where \tilde{T} is the mean reorientation period of dipoles. The inequality in (49) means that the direction of a dipole moment changes many times during the vibration period $2\pi/\Omega$ this Ω should not be confused with Ω from eqn. (33). We regard the well to be ‘almost conservative’. Since the SF L depends on β , in view of (49) it depends also on the phase $\Phi(t)$, thus $L = L\{z, \beta[\Phi(t)]\}$. Consequently, for a slow time dependence $\beta[\Phi(t)]$, the corrected orientational spectral function (SF) $L(z)$ is found as the average over Φ :

$$L(z) \rightarrow \bar{L}, \quad \bar{L} \equiv \langle L\{z, \beta[\Phi(t)]\} \rangle_\Phi, \quad (50)$$

This average will be found in two ways, differing in the value of $\Omega\tau_D$. First, we consider *very low* vibration frequency Ω , such that $\Omega \ll \tau_D^{-1}$, *i.e.* $\Omega\tau_D \ll 1$, and we have

$$\bar{L} = \frac{1}{2\pi} \int_0^{2\pi} L\{z, \beta_0 + \beta_1 \sin(\Phi_0)\} d\Phi_0$$

so that

$$\bar{L} = \bar{L}(x, y, \beta_0, \beta_1). \quad (51a)$$

Eqn. (51a) is actually the average over different β -values distributed homogeneously. Second, we take a greater vibration frequency, but still restricted by the inequality $\Omega\tilde{T} \ll 1$. We consider that τ_D is the *longest time* pertinent to molecular processes in a polar liquid. We employ here the exponential distribution over lifetimes t_{long} between ‘rare’ collisions, occurring, on average, after the Debye time τ_D : $\langle t_{\text{long}} \rangle = \tau_D$. During each time interval t_{long} , the β -value changes, in accord with eqn. (49), harmonically in time t . Therefore, now $\Omega\tau_D > 1$, and we have

$$\bar{L} = \int_0^\infty L\{z, \beta_0 + \beta_1 \sin \Omega t\} \exp(-t/\tau_D) \frac{dt}{\tau_D}$$

$$\bar{L} = \bar{L}(x, y, \beta_0, \beta_1, \Omega\tau_D). \quad (51b)$$

Using the calculation Scheme (51b) we first find the average over ‘short’ time t with the mean lifetime value τ (which is much shorter than τ_D) in order to get the SF $L\{z, \beta[\Phi(t)]\}$.

The second averaging yields \bar{L} , eqn. (50), and is carried out for a 'long' time t_{long} with the mean value τ_D . Eventually, the orientational susceptibility $\chi^*(x)$ is found from eqn. (9), where we replace L by \bar{L} . Further calculations are made in the 'first stage' manner, described in Section 3, eqns. (9)–(13) and in Section 5, eqns. (37)–(39).

Both calculation schemes are applied for liquid water at $T = 27^\circ\text{C}$. We consider an example of a rather large libration amplitude by setting $\beta_1 \equiv 0.8\beta_0$. We also set: (a) $\Omega\tau \ll 1$ and (b) $\Omega\tau = \pi$. It is seen from Table 5 that the fitted β_0 and u values are the same for both cases but the values of the lifetime τ are different. Therefore, for the vibrating well the mean angle β_0 and lifetime τ decrease and the well depth u increases in comparison with the well at rest. Our modified model yields a better description of the FIR spectral region in the vicinity of the translational peak ($\nu_T = 200\text{ cm}^{-1}$), see Fig. 8. The comparison of Fig. 8(a) with Fig. 8(b) leads to the conclusion that the Scheme (51b) gives a better result than the Scheme (51a).

Table 5 Results from the various calculation schemes

Calculation scheme	Libration amplitude	Normalised well depth, u	Lifetime, τ/ps
For the hybrid model (with the walls at rest)	$\beta = 19.9^\circ$	5.1	0.475
For the average (51a), $\Omega\tau \ll 1$	$\beta_0 = 12.9^\circ$	5.4	0.45
For the average (51b), $\Omega\tau = \pi$	$\beta_0 = 12.9^\circ$	5.4	0.39

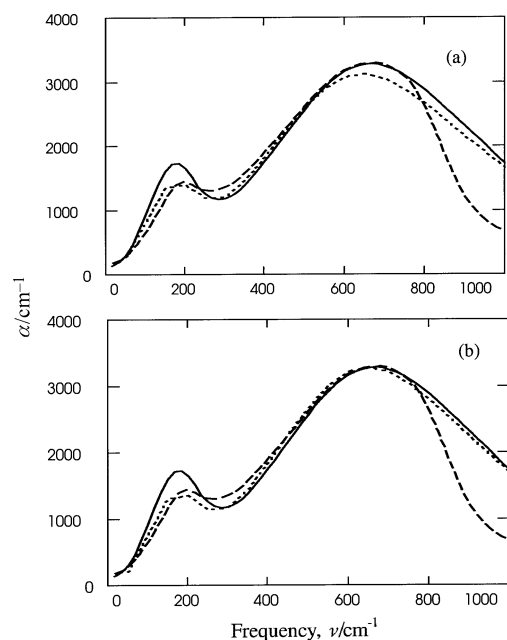


Fig. 8 Absorption coefficient of liquid water vs. frequency; $T = 27^\circ\text{C}$. The hybrid model, calculation for the potential well at rest (solid line) and for the well with vibrating walls (dotted line). (a) Integration over phases Φ_0 , eqn. (51a); (b) integration over long time between strong collisions, eqn. (51b). Dashed lines: experimental data.²⁵

We remark that if $\Omega\tau_D > 2\pi$, then the 'internal' lifetime τ can be approximately set to a quarter of the vibration period $2\pi/\Omega$, since the configuration of the well remains approximately unchanged during $T_{\text{vibr}}/4 = \pi/(2\Omega)$; thus, $\tau = \pi/(2\Omega)$. Consequently, one can estimate the vibration frequency as

$$f_{\text{vibr}} \approx \Omega/(2\pi) = 1/(4\tau). \quad (52)$$

The 'lifetime' may actually have an 'oscillatory origin'. For water at 20°C , $f_{\text{vibr}} \approx 500\text{ GHz}$; the relaxation time τ_{vis} of the volume viscosity is approximately the same as the fitted τ (ref. 14) (about 0.5 ps). It seems reasonable that the dynamic behaviour of the suggested molecular system is closely related to some frequency corresponding to a molecular process in a liquid.

7. Discussion

It is useful to characterise (ref. 12, pp. 316, 540) the molecular dynamics/structure of a solution by the mean number m_{dip} of reorientation cycles performed by a water molecule in the solution during its mean lifetime τ :

$$\langle p \rangle = \frac{\sin \beta [\frac{1}{2}\sqrt{\pi} \operatorname{erf} \sqrt{u} - \sqrt{u} \exp(-u)] + \frac{1}{2}\sqrt{\pi} \exp(-u)}{1 - [1 - \exp(-u)] \cos \beta}, \quad (53)$$

where $\operatorname{erf}(\)$ is the error function. From Table 6 we see that m_{dip} is about 15. This means that the structure of each liquid is rather rigid. For $\text{NaCl-H}_2\text{O}$, m_{dip} increases with concentration C_M , while for $\text{KCl-H}_2\text{O}$ it decreases, in accordance with the strengthening or, respectively, weakening of the water structure. Using eqn. (24), we can calculate the mean number m^\pm of ionic translation cycles, occurring in the well during the lifetime τ_{ion} :

$$m^\pm \approx \frac{\langle \Omega^\pm \rangle}{\tau_{\text{ion}}} = \frac{\sqrt{\pi}}{2d} \omega_p^\pm \tau_{\text{ion}} = \sqrt{\frac{\pi}{2}} \frac{v_T^\pm \tau_{\text{ion}}}{l^\pm}. \quad (54)$$

This number m^\pm depends on the ionic lifetime τ_{ion} . In view of Table 6 for $\tau_{\text{ion}} = 10\tau$, m^\pm is much greater than m_{dip} , but for $\tau_{\text{ion}} = \tau$ it is commensurable with m_{dip} .

Recently the ionic dispersion $\sigma(v)$ has been discussed using a linear-response theory in conjunction with a molecular dynamics simulation.^{9,10} Thus, Wei and Patey concluded⁹ on the basis of a mean-field approximation that the dispersion of the ionic conductivity is negligible in electrolytes. However, later¹⁰ such a dispersion was discovered. Yet the problem remained unsolved, since the results of ref. 10 cannot take into account the specific properties of the solvent (water). Using the formulae (27)–(29) we have shown that the dispersion $\sigma(v)$ should appear when the normalised frequency $X = \omega/\omega_p$ exceeds approximately 0.1, see Fig. 3(a). In view of Figs. 4–6 if the aqueous sheath around an ion lives much longer than a local order cell in bulk water (*viz.* if $\tau_{\text{ion}} \gg \tau$), then the dispersion $\sigma(v)$ of the conductivity may cause an additional dielectric loss/absorption in the ranges of millimetre and submillimetre wavelengths. From Table 6 we see that in this case an ion should perform at $C_M = 0.5\text{ mol l}^{-1}$ about 50 or more cycles of translational motion inside the sheath. The question is whether such a situation is possible. On the other hand, as

Table 6 The mean number of ion and dipole reflections performed during their lifetimes in corresponding potential wells

$C_M/\text{mol l}^{-1}$	NaCl–water				m_{dip}	KCl–water				m_{dip}
	$\tau_{\text{ion}} = 10\tau$		$\tau_{\text{ion}} = \tau$			$\tau_{\text{ion}} = 10\tau$		$\tau_{\text{ion}} = \tau$		
	m^+	m^-	m^+	m^-		m^+	m^-	m^+	m^-	
0.5	58	132	18	41	16	49	62	19	19	15
1	44	99	13	31	17	34	44	13	13	14

seen from Fig. 7, if $\tau_{\text{ion}} \approx \tau$, then the phenomenon of *ionic dispersion* actually should not affect the calculated spectra. In this case the simplified equation (35) holds, where $\sigma \equiv \sigma_s$ is set. It would be interesting to find experimentally which of two controversial inequalities ($\tau_{\text{ion}} \ll \tau$ or $\tau_{\text{ion}} \approx \tau$) is more realistic.

In a recent article²² self-consistent expressions were derived for the frequency-dependent electrolyte friction and the conductivity. Unlike our approach, the effect of the surrounding solvent (water) was described using the phenomenological coefficients. However, no oscillatory component $\sigma'(\omega)$ or $\sigma''(\omega)$ of the ionic motion was discovered in ref. 22, while our Figs. 3(a) and (b) show *damped oscillations*, typical for the resonance phenomena occurring in a condensed state.

The intermolecular interactions are strong in the condensed state. The key assumption, used as the basis of our models, is that the motion of particles occurs in rather deep and narrow potential wells. Comparing the parameters obtained for NaCl–water and KCl–water solutions, we can distinguish the solutions with positive (for NaCl) and negative (for KCl) hydration, to which the strengthening or weakening of the water structure correspond.²³ These properties are inherently confirmed in our calculations by the fitted $\tau(C_M)$ dependences, which are *increasing* for NaCl and *decreasing* for KCl.

A recent study²⁴ of translation of ions *in space*, made in terms of the spherical hydration sheath, confirms qualitatively the main results of this work. However, the theory given here is much simpler than in ref. 24, where double integrals appear for the complex conductivity instead of ordinary integrals in eqns. (28).

The drawback of our dipolar model is that the librational band, placed in the FIR range, is wider than the recorded one. We intend to solve this problem in the near future.

In this article we have neglected (1) ion–ion interaction, (2) the cross-correlation between the ionic and dipolar subensembles and (3) the finiteness of the potential well depth for ions. The study²⁶ of aqueous NaCl solutions, using a molecular dynamics simulation, and our estimations show that at low salt concentration C_M these assumptions cause only a small effect on the calculated spectra.¶ It is important that the interrelation between the ionic and dipolar subensembles appears in our theory already in the first approximation, if τ_{ion} is rather long and/or C_M is rather high, so that the zero-frequency contribution $\chi_{\text{ion}}(0)$ is noticeable in comparison with the static permittivity ϵ_s of the solution. This interrelation can be accounted for within the framework of our calculation scheme, if we employ eqn. (12) for the Kirkwood correlation factor instead of eqn. (13) (the latter was used in this work).

One can get from the simulation results²⁶ some additional information about the residence times of bulk water molecules and about those in the hydration sheaths arising around the cations Na^+ and the anions Ca^- . In ref. 26 the following ratios were given in Table 7:

$$\frac{\tau(\text{H}_2\text{O}-\text{Na})}{\tau(\text{H}_2\text{O}-\text{H}_2\text{O})} \approx \frac{21 \text{ ps}}{4.4 \text{ ps}} \approx 4.8; \quad \frac{\tau(\text{H}_2\text{O}-\text{Cl})}{\tau(\text{H}_2\text{O}-\text{H}_2\text{O})} \approx \frac{10.4 \text{ ps}}{4.7 \text{ ps}} \approx 2.2. \quad (55)$$

These data show that the hydrated layer indeed lives longer than the bulk water molecules. Let us identify the ratios (55) with τ_{ion}/τ . Then we conclude that the additional loss/absorption, predicted in our work, due to movement of ions inside the hydration sheath, should be *less pronounced* for NaCl, than is shown in Fig. 6. One may also expect that for KCl this effect should be negligible. The detailed information,

¶ We remark that our theory is not applicable to very low frequencies when the effect of the ionic atmosphere may cause a *very small* increase in the real part of σ' .

given in ref. 26, can be used for a further elaboration of our ionic model. Namely, in future it will be possible to account for: (a) the formation of contact ion pairs, which is substantial for concentrations C_M greater than 1 mol l^{-1} ; (b) the specific values of the lifetimes [similar to those given by eqns. (55)]; (c) the distinction between the properties of bulk water and water in the hydration sheaths; (d) the distinction between the properties of the cations and anions; (e) the interrelation of type (12), when the inequality (12a) does not hold; and (f) the finiteness of the potential well depth for the ionic subensemble. But if the salt concentration is rather small ($C_M \leq 1 \text{ mol l}^{-1}$), one may consider this work to give a qualitative picture and the relevant time/space scales of the molecular events.

In conclusion, we shall discuss some results of new experiments.^{27–29} The interaction between ions in concentrated electrolyte solutions and FIR ($10\text{--}40 \text{ cm}^{-1}$) was studied by Dodo *et al.*²⁷ It was shown there that the absorption coefficient for high concentration ($\sim 13 \text{ mol l}^{-1}$) is small because the conductivity of highly concentrated electrolyte solutions decreases in spite of the increase of ion number. It would be interesting to investigate such phenomena theoretically, since our calculation scheme is applicable only to low electrolyte concentration. We remark that, if we are to account for the experimental error, then the measured absorption coefficient for LiCl aqueous solution at the frequency 10 cm^{-1} slightly exceeds that calculated for contributions of both the electrical (static) conductivity and Debye relaxation. This fact may indirectly confirm the result of our work that additional absorption due to $\sigma(\nu)$ frequency dependence indeed arises. However for a definite conclusion about this matter an additional more precise experimental investigation would be very useful. Recent experiments²⁸ in the $5\text{--}100 \text{ cm}^{-1}$ band, where the absorption coefficient of liquid water was compared with that of LiCl and NaCl aqueous solutions, show a number of interesting phenomena. Their preliminary qualitative interpretation was given²⁸ in terms of network breaking and restricted H_2O molecule motion. The reverse of examined effects was found for HCl in water, where the water network structure is enhanced, collective dynamics become more important and there is a huge increase in proton polarisability, giving a large fluctuating transition dipole and extreme broadening of the whole FIR spectrum. In ref. 29 the phenomenon of ‘ion rattling’ motions was supposed to influence the recorded absorption band at $\nu > 200 \text{ cm}^{-1}$. It seems that without a theory capable of describing the whole $0\text{--}1000 \text{ cm}^{-1}$ band it is hardly possible to assign the measured alteration of absorption due to a number of specific physical factors. The model presented above can be used as a basis for this purpose. However, to achieve this aim a few important factors should additionally be accounted for: (i) change of the dielectric response of water molecules trapped inside the hydration sheath and (ii) development of a model to describe the specific mechanism due to vibration of H-bonded molecules. Such development of our theoretical approach is under way.

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Appendices

A. Derivation of the linear-response formula (27)

The integral in eqns. (19)–(21), containing the velocity projection $v_E(t)$, does not vanish only due to the radiation-induced

perturbation v_E of the steady-state velocity $v_E^0(t)$, to which $v_E(t)$ reduces for $E(t) = 0$: $\langle v_E(t) \rangle_\gamma = \langle v_E^0(t) + \delta v_E \rangle_\gamma = \langle \delta v_E \rangle_\gamma$, where $\langle \rangle_\gamma$ denotes integration over the initial phases γ , the disturbance δv_E being proportional to the radiation amplitude $|\hat{E}|$. We apply the average perturbation theorem (ref. 13, pp. 148, 374). Noting that $dW/dh = -W/(k_B T)$, and omitting the superscript 0, we rewrite eqns. (3.10c) and (3.10d) of ref. 13 in terms of this paper:

$$\begin{aligned} \langle \delta v_E(t) \rangle &= (k_B T)^{-1} \langle v_E^0(t) h(t) \rangle, \\ h(t) &= e \int_0^t E(t') v_E(t') dt', \end{aligned} \quad (\text{A1})$$

$h(t)$ being the work done by the ac field in moving charge e during time interval t ; now $v_E(t)$ denotes the *unperturbed* velocity projection. The time dependence $E(t)$, eqn. (3), is represented as the sum of two complex-conjugate quantities. Neglecting the spatial dispersion ($\mathbf{k} \cdot \mathbf{r}$ is omitted), we find that the term proportional to $\exp[i(\omega t + \gamma)]$ vanishes after averaging over γ_0 :

$$\langle \delta v_E \rangle = \left\langle \frac{e \hat{E}^*}{2k_B T} \int_0^t v_E \exp(-i\omega t' - i\gamma) dt' \right\rangle. \quad (\text{A2})$$

Substituting into eqn. (16), where we set $F(\gamma) \equiv 1$, and taking account of eqn. (18) we derive

$$\begin{aligned} \chi^* &= \frac{i \langle s \rangle}{r_D^2 \omega \tau}; \\ s &\equiv \int_0^\infty v_E(t) \exp(i\hat{\omega} t) dt \int_0^t v_E(t') \exp(-i\omega t') dt'. \end{aligned} \quad (\text{A3})$$

This expression is applied to such a model potential, in which velocity $v_E(t)$ varies periodically; let $\mathcal{O}(h)$ be the period of this dependence. An ensemble averaging includes integration over energy-time variables h, t_0 . By analogy with eqn. (3.15) in ref. 13, we write:

$$\left\langle \frac{dv_E(t)}{dt} v_E(t') + v_E(t) \frac{dv_E(t')}{dt'} \right\rangle = 0. \quad (\text{A4})$$

Indeed, here the integral over t_0 vanishes because of this periodicity, as it is equal to

$$\int_0^{\mathcal{O}(h)} \frac{d}{dt_0} v_E(t') v_E(t) dt_0.$$

Using eqn. (A4), we may reduce the expression for s to an ordinary integral. First, we take the integral over t' and then by parts over t from

$$[dv_E(t)/dt] \exp(i\hat{\omega} t) \int_0^t v_E(t') \exp(-i\omega t') dt'$$

to obtain:

$$\begin{aligned} s &= \frac{i}{\omega} \int_0^\infty v_E(t) e^{i\hat{\omega} t} \left[v_E(t) e^{-i\omega t} - v_E(0) \right. \\ &\quad \left. - \int_0^t \frac{dv_E(t')}{dt'} e^{-i\omega t'} dt' \right] dt \\ &= \frac{i}{\omega} \left\{ v_E(t) e^{i\hat{\omega} t} [v_E(t) e^{-i\omega t} - v_E(0)] \right. \\ &\quad \left. + \frac{dv_E(t)}{dt} e^{i\hat{\omega} t} \int_0^t v_E(t') e^{-i\omega t'} dt' \right\} \\ &= \frac{i}{\omega} \int_0^\infty v_E(t) e^{i\hat{\omega} t} \left[v_E(t) e^{-i\omega t} - v_E(0) - i\hat{\omega} \right. \\ &\quad \left. \times \int_0^t v_E(t') e^{-i\omega t'} dt' - v_E(t) e^{i\omega t} \right] dt. \end{aligned}$$

Second, comparing with the definition of s in eqn. (A3), we finally derive:

$$\begin{aligned} \left(1 - \frac{\hat{\omega}}{\omega} \right) s &= -\frac{is}{\omega \tau} \\ &= -\frac{iv_E(0)}{\omega} \int_0^\infty v_E \exp(i\hat{\omega} t) dt; \\ s &= \tau v_E(0) \int_0^\infty v_E(t) \exp(i\hat{\omega} t) dt. \end{aligned}$$

Inserting this into χ^* in eqn. (A3), we get eqn. (27).

B. The integrated absorption Π

In view of eqns. (19) and (20),

$$\begin{aligned} \Pi &= \int_{-\infty}^{+\infty} \omega \chi''(\omega) d\omega \\ &= \frac{1}{r_D^2} \left[\int_{-\infty}^\infty d\omega v_E(0) \int_0^\infty v_E(t) \cos(\omega t) \exp\left(-\frac{t}{\tau}\right) dt \right]. \end{aligned}$$

We change the order of integration and introduce the dimensionless parameters $X = \omega/\omega_p$ and $Y = (\omega_p \tau)^{-1}$:

$$\begin{aligned} r_D^2 \Pi &= \omega_p \left[v_E(0) \int_0^\infty v_E(t) \right. \\ &\quad \left. \times \exp(-\omega_p Y t) dt \int_{-\infty}^\infty \cos(\omega_p X t) dX \right] \\ &= 2 \left\langle v_E(0) \int_0^\infty v_E(t) e^{-\omega_p Y t} \right. \\ &\quad \left. \times \lim_{X \rightarrow \infty} \left[\frac{\sin(\omega_p X t)}{t} \right] dt \right\rangle \\ &= 2\pi \left\langle v_E(0) \int_0^\infty v_E(t) \exp(-\omega_p Y t) \delta(t) dt \right\rangle. \end{aligned}$$

We employ a model potential such that $\langle v_E(0) v_E(t) \rangle$ is an even function of t . Then

$$\begin{aligned} r_D^2 \Pi &= \pi \left[v_E(0) \int_{-\infty}^\infty v_E(t) \right. \\ &\quad \left. \times \exp(-\omega_p Y |t|) \delta(t) dt \right] = \pi \langle v_E^2 \rangle. \end{aligned} \quad (\text{B1})$$

For an ensemble of particles having one degree of freedom

$$\begin{aligned} \langle v_E^2 \rangle &= \int_0^\infty \exp\left(-\frac{mv^2}{k_B T}\right) v^2 dv \int_0^\infty \exp\left(-\frac{mv^2}{k_B T}\right) dv = v_T^2; \\ v_T &\equiv \sqrt{\frac{k_B T}{m}}. \end{aligned} \quad (\text{B2})$$

The same result is obtained also for a *spatial* ensemble of charges since: (1) we may take v_E as one of the phase variables; and (2) other variables do not depend on the averaged quantity (on v_E^2). Combining eqns. (B1) and (B2) with eqn. (18) for r_D , we obtain the standard value

$$\begin{aligned} \Pi &= \int_{-\infty}^\infty \omega \chi''(\omega) d\omega \equiv \int_{-\infty}^\infty \sigma'(\omega) d\omega \\ &= \pi \omega_p^2 = \pi e^2 N / (m \epsilon_0). \end{aligned} \quad (\text{B3})$$

C. Estimation of pair electrostatic interaction between ions

It follows from Table 2 that the criterion $\Delta R_{\text{ion}} > \Delta R_w$, which means that the solution is dilute, holds for all ranges of concentration in σ_s -values. Let the mean energy $U_E =$

|| Note a misprint in eqn. (1.65) of ref. 17, where the multiplier 1/3 should be omitted.

$e^2/(4\pi\epsilon_0 \epsilon_s \Delta R_{\text{ion}})$ of the pair electrostatic ionic interaction be small in comparison with the potential barrier U_{ion} . We introduce the parameter ζ of the electrostatic interaction, defined as the ratio of these two energies. Taking into account eqn. (47a), we have

$$\zeta = \frac{U_E}{U_{\text{ion}}} = \frac{e^2(2 \times 1000 N_A C_M)^{1/3}}{4\pi\epsilon_0 \epsilon_s k_B T u_{\text{ion}}},$$

where $u = U_{\text{ion}}/(k_B T)$, U_{ion} being the well depth of the well in which the ions move. Then

$$U_E \ll U_{\text{ion}}, \quad \text{if } \zeta \ll 1. \quad (\text{C1})$$

In this work we employ the approximation $u_{\text{ion}} \rightarrow \infty$, so that this inequality holds; it also holds for the estimation¹⁵ given for $U_{\text{ion}} \approx 10k_B T$.

D. Relation of ionic susceptibility χ_{ion}^* to conductivity $\sigma(\omega)$

We start from eqn. (2.4a) in ref. 13. For wave vector \mathbf{k} perpendicular to electric field \mathbf{E} this equation is given by

$$k^{*2} - \frac{\omega^2}{c^2} = \frac{\omega^2}{c^2} (n^{*2} - 1) \hat{\mathbf{E}}^* = \frac{i\omega}{\epsilon_0 c^2} \hat{\mathbf{J}}^*, \quad (\text{D1})$$

where n^* is the complex refractive index, $n^{*2} = \epsilon^*$. Projecting this equation onto the direction of the electric field and averaging over the ensemble we have:

$$n^{*2} - 1 = \frac{i}{\omega\epsilon_0} \frac{\langle \hat{\mathbf{J}}_E^* \rangle}{\hat{\mathbf{E}}^*}.$$

For an ensemble of ions in a vacuum we have in accordance with the definition: $n^{*2} = \Delta\epsilon_{\text{ion}}^* = 1 + \chi_{\text{ion}}^*$. Then

$$\chi_{\text{ion}}^* = \frac{i}{\omega\epsilon_0} \frac{\langle \hat{\mathbf{J}}_E^* \rangle}{\hat{\mathbf{E}}^*}. \quad (\text{D2})$$

If conductivity does not depend on frequency, then in accord with Ohm's law the mean current density is: $\langle \hat{\mathbf{J}}_E^* \rangle = \sigma \mathbf{E}$. Generalisation for $\sigma = \sigma(\omega)$ yields: $\langle \hat{\mathbf{J}}_E^* \rangle = \sigma(\omega) \hat{\mathbf{E}}^*$. Therefore, it follows from eqn. (D2):

$$\chi_{\text{ion}}^* = \frac{i\sigma(\omega)}{\epsilon_0 \omega} = \frac{i\sigma(\nu)}{2\pi\epsilon_0 c\nu},$$

so that

$$\Delta\epsilon_{\text{ion}}'' = \frac{\sigma'(\nu)}{2\pi\epsilon_0 c\nu}. \quad (\text{D3})$$

Thus we have got relations (19), (30), (36), (40), (41) and (48), and the second term of eqn. (35)

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