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Polarization relaxation, dielectric dispersion, and solvation dynamics in dense dipolar liquid

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A unified treatment of polarization relaxation, dielectric dispersion and solvation dynamics in a dense, dipolar liquid is presented. It is shown that the information of solvent polarization relaxation that is obtained by macroscopic dielectric dispersion experiments is not sufficient to understand dynamics of solvation of a newly created ion or dipole. In solvation, a significant contribution comes from intermediate wave vector processes which depend critically on the short range (nearest-neighbor) spatial and orientational order that are present in a dense, dipolar liquid. An analytic expression is obtained for the time dependent solvation energy that depends, in addition to the translational and rotational diffusion coefficients of the liquid, on the ratio of solute-solvent molecular sizes and on the microscopic structure of the polar liquid. Mean spherical approximation (MSA) theory is used to obtain numerical results for polarization relaxation, for wave vector and frequency dependent dielectric function and for time dependent solvation energy. We find that in the absence of translational contribution, the solvation of an ion is, in general, nonexponential. In this case, the short time decay is dominated by the longitudinal relaxation time but the long time decay is dominated by much slower large wave vector processes involving nearest-neighbor molecules. The presence of a significant translational contribution drastically alters the decay behavior. Now, the long-time behavior is given by the longitudinal relaxation time constant and the short time dynamics is controlled by the large wave vector processes. Thus, although the continuum model itself is conceptually wrong, a continuum model like result is recovered in the presence of a sizeable translational contribution. The continuum model result is also recovered in the limit of large solute to solvent size ratio. In the opposite limit of small solute size, the decay is markedly nonexponential (if the translational contribution is not very large) and a complete breakdown of the continuum model takes place. The significance of these results is discussed.

I. INTRODUCTION

Recently, several theoretical¹⁻¹⁴ and experimental¹⁵⁻²⁴ studies on dynamics of solvation of a newly created charge or a dipole in a polar liquid have been carried out. These studies have raised several important questions on the role of solvent polarization relaxation in determining the rates of several important chemical reactions. It has become clear that short-range (for example, nearest-neighbor) intermolecular correlations play an important role in the dynamics of solvation,^{1,5,9-13,15-22} although the details are yet to be understood. This is to be contrasted with the earlier continuum model theories^{2,3} which considered only the long-range polar forces, but neglected contributions from the short-range molecular interactions. Thus, the continuum model of solvation in a dipolar liquid predicts that solvation of an ion proceeds with a time constant τ_L given by¹

$$\tau_L = \left(\frac{\epsilon_\infty}{\epsilon_0} \right) \tau_D. \quad (1)$$

The same theory predicts that the solvation of a dipole proceeds with a slightly larger time constant τ_L^d which is given by^{2,3}

$$\tau_L^d = \left(\frac{2\epsilon_\infty + \epsilon_c}{2\epsilon_0 + \epsilon_c} \right) \tau_D. \quad (1')$$

Here ϵ_0 and ϵ_∞ are, respectively, the static and the infinite

frequency dielectric constants of the polar solvent and ϵ_c is the dielectric constant of the (assumed) spherical cavity that contains the polar solute molecule. τ_D is the Debye relaxation time of the polar solvent, as measured in dielectric relaxation experiments. The continuum model thus includes all the information on solvent polarization relaxation that is contained in the frequency dependent zero wave vector dielectric constant, but the microscopic structure of the dense liquid around the solute molecule is totally neglected. Also neglected is the contribution of the translational diffusion in the solvent polarization relaxation. Surprisingly, in some cases, these simple expressions seem to agree rather well with experiments,¹⁶⁻¹⁸ but in some others significant deviations have been observed.¹⁹⁻²² This raises the important question as to what extent the polarization relaxation involved in the solvation process is accurately represented by the dielectric relaxation of the pure dipolar solvent. In fact, several recent theoretical studies^{5,9} seem to imply a close relation between the two. In these studies an expression for the frequency dependent dielectric constant $\epsilon(\omega)$ is used in the calculation of the solvation energy $E_{\text{solv}}(t)$. The time dependent solvation energy is related to solvent polarization relaxation by the following expression

$$E_{\text{solv}}(t) = -\frac{1}{2} \int d\mathbf{r} \mathbf{D}_{\text{ion}}(\mathbf{r}) \cdot \mathbf{P}(\mathbf{r}, t), \quad (2)$$

where $\mathbf{D}_{\text{ion}}(\mathbf{r})$ is the bare electric field of the ion (or the dipole) whose solvation is being studied and $\mathbf{P}(\mathbf{r}, t)$ is the time dependent solvent polarization fluctuation that couples with solvation. Equation (2) suggests that polarization relaxation at intermediate wavelengths may be important in solvation. The dielectric relaxation, on the other hand, contains information only of the long wavelength ($k \rightarrow 0$) processes. Thus, the relaxation processes that contribute to $\epsilon(\omega)$ may not be the dominant one in $\mathbf{P}(\mathbf{r}, t)$. This point has been recognized earlier by several others.^{4,6,10-13} Our objective in this paper is somewhat different. First, we would like to explore the extent to which the two relaxation spectra overlap in the $k \rightarrow 0$ limit. Second, we investigate the behavior of these two relaxations at intermediate wave vectors. Since the effects of translational diffusion are important at intermediate wave vectors, we have also made a detailed study of the role of translational diffusion. Third and most importantly, we present a microscopic expression of the time dependent solvation energy of an ion in a dipolar liquid. This expression is novel in several respects. It is based on a hydrodynamic description of density fluctuations that pays proper attention to the microscopic structure, especially the short range spatial and orientational order, of a dense dipolar liquid. Second, this expression includes the contribution of translational diffusion in the solvation process. We shall show that, in some cases, the translational diffusion plays a very important role in the solvation dynamics.

The work reported in this article is based on the following generalized Smoluchowski equation (GSE) for the position (\mathbf{r}) and orientation (ω) dependent number density, $\rho(\mathbf{r}, \omega, t)$

$$\begin{aligned} \frac{\partial}{\partial t} \delta\rho(\mathbf{r}, \omega, t) = & D_R \nabla_\omega^2 \delta\rho(\mathbf{r}, \omega, t) + D_T \nabla^2 \delta\rho(\mathbf{r}, \omega, t) \\ & - D_R \nabla \omega \cdot \rho_{\text{eq}}(\mathbf{r}, \omega) \nabla_\omega \\ & \times \int d\mathbf{r}' d\omega' c(\mathbf{r}, \omega, \mathbf{r}', \omega') \delta\rho(\mathbf{r}', \omega', t) \\ & - D_T \nabla \cdot \rho_{\text{eq}}(\mathbf{r}, \omega) \nabla \int d\mathbf{r}' d\omega' \\ & \times c(\mathbf{r}, \omega, \mathbf{r}', \omega') \delta\rho(\mathbf{r}', \omega', t), \end{aligned} \quad (3)$$

where

$$\delta\rho(\mathbf{r}, \omega, t) = \rho(\mathbf{r}, \omega, t) - \rho_{\text{eq}}(\mathbf{r}, \omega). \quad (4)$$

Here D_T and D_R are, respectively, the translational and rotational diffusion coefficients of the solvent, $\rho_{\text{eq}}(\mathbf{r}, \omega)$ is the equilibrium number density of the liquid in the presence of the polar solute, ∇ and ∇_ω are the usual spatial and angular gradient operators. $c(\mathbf{r}, \omega, \mathbf{r}', \omega')$ is the two particle direct correlation function.²⁵ A derivation of this equation, along with the assumptions and the approximations that are involved, is given in a previous paper.¹¹ The advantage of this Smoluchowski equation is twofold. Firstly, it includes the influence of the liquid structure through a mean-field force term. Second, the effects of translational diffusion is included in a self-consistent manner. The Smoluchowski equation with a mean-field force term is known to provide a reliable description of number density fluctuations at intermediate wave vectors.²⁶ In the limit of long wavelength ($k \rightarrow 0$), Eq.

(3) gives the required dominance of the orientational motions in the decay of the density fluctuations.

The role of translational modes in the solvation dynamics has also been discussed by van der Zwan and Hynes²⁷ who used continuum model to derive an expression of the reaction field. We have discussed elsewhere^{11,12} that translational effects are important for large wave vector processes for which continuum model is inappropriate. We must include the details of microscopic structure in order to treat the translational effects in a dense liquid. The experimental indication of a probable role of translational motion in the solvation dynamics comes from the observation that the solvation times of excited LDS 50 in methanol and butanol are substantially smaller than the longitudinal relaxation time.^{18,19} These solvents have appreciably larger ratio of translational to rotational diffusion coefficients than the other alcohol solvents where the solvation times are, in general, larger than τ_L .¹⁹⁻²²

We use the generalized Smoluchowski equation to develop a unified theoretical treatment of polarization relaxation, dielectric dispersion and solvation dynamics in a dense, dipolar liquid. We have obtained exact expressions for polarization relaxation and for wave vector and frequency dependent dielectric function. An analytic expression of the time dependent solvation energy is obtained within linear response theory. Thus, the present theory explores the interrelationship between polarization relaxation, dielectric dispersion, and solvation dynamics without using any external result. The calculations are thus self-consistent. We find that translational diffusion becomes important at large wave vectors where nearest-neighbor correlations are important. We find that the translational contribution can not only accelerate the solvation process, but it may also render the process nearly single exponential in situations where the rotational contribution proceeds on a large number of time scales. Since translational contribution is important for short range processes, it is especially important when the solute-solvent size ratio is small. In this limit, we find that the continuum limit breaks down completely.

The organization of the rest of the paper is as follows. In Sec. II, we present theoretical results on polarization relaxation. In Sec. III, we present analytical expressions of wave vector and frequency dependent dielectric constant. In Sec. IV, we present the analytic expression of time dependent solvation energy. Section V contains numerical results and discussion of their significance. Section VI summarizes the main results of this paper.

II. POLARIZATION RELAXATION IN A PURE DIPOLAR LIQUID

The polarization fluctuation in a pure dipolar liquid is given by the following expression¹

$$\delta\mathbf{P}(\mathbf{r}, t) = \int d\omega \hat{a}(\omega) \delta\rho(\mathbf{r}, \omega, t), \quad (5)$$

where $\hat{a}(\omega)$ is a unit vector with the orientation ω . Since we now consider pure, unperturbed, liquid, $\rho_{\text{eq}}(\mathbf{r}, \omega) = \rho_0/4\pi$, where ρ_0 is the average number density of the liquid. Because of mathematical convenience, we work in the Fourier space.

The forward and inverse Fourier transforms are defined by

$$f(\mathbf{k}) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) f(\mathbf{r}),$$

$$f(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{k} \exp(-i\mathbf{k} \cdot \mathbf{r}) f(\mathbf{k}).$$

Use of Eq. (5) in Eq. (3) and simple mathematical manipulations lead to the following equation of motion of the k -dependent polarization fluctuation $\delta\mathbf{P}(\mathbf{k}, t)$

$$\frac{\partial}{\partial t} \delta\mathbf{P}(\mathbf{k}, t) = -(2D_R + D_T k^2) \delta\mathbf{P}(\mathbf{k}, t) + \frac{\rho_0}{3} (2D_R + D_T k^2) \mathbf{C}(\mathbf{k}) \cdot \delta\mathbf{P}(\mathbf{k}, t), \quad (6)$$

where the tensor $\mathbf{C}(\mathbf{k})$ is defined by the following expansion^{1,25}

$$c(\mathbf{k}, \omega, \omega') = c_{\text{iso}}(k) + \hat{\alpha}(\omega) \cdot \mathbf{C}(\mathbf{k}) \cdot \hat{\alpha}(\omega') + \dots, \quad (7)$$

where $c_{\text{iso}}(k)$ is the Fourier transform of the isotropic part of the two-particle direct correlation function. As clear from Eq. (7), the tensor $\mathbf{C}(\mathbf{k})$ contains the anisotropic part of the direct correlation function. In the next step, we divide $\delta\mathbf{P}(\mathbf{k}, t)$ into the usual longitudinal (P_L) and transverse (P_T) components, then Eq. (6) can be solved to obtain

$$P_L(\mathbf{k}, t) = P_L(\mathbf{k}) \exp[-t/\tau_L(k)], \quad (8)$$

$$P_T(\mathbf{k}, t) = P_T(\mathbf{k}) \exp[-t/\tau_T(k)], \quad (9)$$

with

$$\tau_L(k) = (2D_R)^{-1} \left\{ 1 + p'(k\sigma)^2 - \frac{\rho_0}{3} \times [1 + p'(k\sigma)^2] (C_\Delta + 2C_D) \right\}^{-1}, \quad (10)$$

$$\tau_T(k) = (2D_R)^{-1} \left\{ 1 + p'(k\sigma)^2 - \frac{\rho_0}{3} \times [1 + p'(k\sigma)^2] (C_\Delta - C_D) \right\}^{-1}, \quad (11)$$

where $p' = D_T/(2D_R\sigma^2)$, is a dimensionless solvent parameter that characterizes the relative importance of translational modes, and σ is the molecular diameter of a solvent molecule. C_Δ and C_D are the usual MSA anisotropy functions.²⁵ Note that the solvent parameter p' is related to the van der Zwan-Hynes²⁷ parameter p by $p = p'(\sigma/a)^2$, where a is the radius of the solute molecule whose solvation is being studied.

In deriving Eqs. (10) and (11), it is assumed that $\mathbf{C}(\mathbf{k})$ can be decomposed into C_Δ and C_D in the way it is usually done in MSA. We have shown elsewhere²⁸ that such a decomposition is also possible when $c(\mathbf{r}, \omega, \mathbf{r}', \omega')$ is evaluated by an alternative perturbative method. Actually, the decomposition is expected to be reliable for not too strongly polar liquid. In this work we assume for convenience that C_Δ and C_D are given by MSA.

From Eqs. (8)–(11), we see that the two components of the polarization vector relax with different time constants and the theory also predicts that polarization relaxation is multiexponential because $\tau(k)$'s are wave vector dependent. Numerical results are given in Sec. V.

III. DIELECTRIC RELAXATION IN A PURE DIPOLAR LIQUID

Analytic expressions for wave vector and frequency dependent dielectric constant $\epsilon(k, \omega)$ can be obtained by combining linear response theory with the explicit expressions for time dependence of polarization fluctuations derived in the preceding section. Formal expressions for the longitudinal dielectric constant $\epsilon_L(k, \omega)$ and the transverse dielectric constant $\epsilon_T(k, \omega)$ are given recently by Loring and Mukamel⁶ in terms of the polarizabilities α_L and α_T . These are given by the following equations:

$$\epsilon_L(k, \omega) = [1 - 4\pi\alpha_L(k, \omega)]^{-1}, \quad (12)$$

$$\epsilon_T(k, \omega) = [1 + 4\pi\alpha_T(k, \omega)], \quad (13)$$

where,

$$\alpha_L(k, \omega) = \frac{\beta}{V} [C_{ML}(k, 0) - i\omega\tilde{C}_{ML}(k, \omega)], \quad (14)$$

$$\alpha_T(k, \omega) = \frac{\beta}{V} [C_{MT}(k, 0) - i\omega\tilde{C}_{MT}(k, \omega)], \quad (15)$$

with

$$\tilde{C}_{ML}(k, \omega) = \hat{k} \cdot \tilde{\mathbf{C}}_M(k, \omega) \cdot \hat{k},$$

$$\tilde{C}_{MT}(k, \omega) = \hat{u} \cdot \tilde{\mathbf{C}}_M(k, \omega) \cdot \hat{u},$$

where \hat{k} is a unit vector parallel to \mathbf{k} and \hat{u} is a unit vector perpendicular to \mathbf{k} . $\tilde{\mathbf{C}}_M(k, \omega)$ is the Laplace transform of $\mathbf{C}_M(k, t)$. V is the volume of the system, $\beta = (k_B T)^{-1}$ and $\mathbf{C}_M(k, t)$ is given by

$$\mathbf{C}_M(k, t) = \mu^2 \langle \delta\mathbf{P}(\mathbf{k}) \delta\mathbf{P}(-\mathbf{k}, t) \rangle, \quad (16)$$

where μ is the dipole moment of a solvent molecule. In the next step, we use the time evolution of the polarization fluctuation as given by Eqs. (8)–(11) in Eqs. (14) and (15) to obtain the polarizabilities which are then substituted in Eqs. (12) and (13) to obtain the following two expressions for $\epsilon_L(k, \omega)$ and $\epsilon_T(k, \omega)$,

$$\epsilon_L(k, \omega) = \frac{1 + i\omega\tau_L(k)}{[1 - A(k)] + i\omega\tau_L(k)}, \quad (17)$$

$$\epsilon_T(k, \omega) = 1 + \frac{B(k)}{1 + i\omega\tau_T(k)}, \quad (18)$$

where

$$A(k) = \frac{4\pi\beta\mu^2}{V} \langle P_L(\mathbf{k}) P_L(-\mathbf{k}) \rangle = \frac{4\pi\beta\mu^2\rho_0}{3} \left\{ 1 + \frac{\rho_0}{3} [h_\Delta(k) + 2h_D(k)] \right\}, \quad (19)$$

$$B(k) = \frac{4\pi\beta\mu^2}{V} \langle P_T(\mathbf{k}) P_T(-\mathbf{k}) \rangle = \frac{4\pi\beta\mu^2\rho_0}{3} \left\{ 1 + \frac{\rho_0}{3} [h_\Delta(k) - h_D(k)] \right\}, \quad (20)$$

where h_Δ and h_D are the usual MSA anisotropy functions of the total pair correlation function $h(k, \omega, \omega')$.²⁵

From Eqs. (17) and (18), it is clear that longitudinal dielectric relaxation occurs with a time constant $\tau_{DL}(k) = \epsilon_0(k)\tau_L$. Transverse dielectric relaxation occurs with a time constant $\tau_T(k)$. In the limit $k \rightarrow 0$, $\epsilon_L(\omega) = \epsilon_T(\omega)$. Thus, $\epsilon(\omega)$ contains a single relaxation time, $\tau_T (= \epsilon_0\tau_L)$.

It is important to note at this juncture that the present theory predicts that at $k = 0$, the dielectric function, $\epsilon(\omega)$, is of simple Debye form with a relaxation time τ_T ($= \tau_D$) given by

$$\tau_T = (2D_R)^{-1} \left\{ 1 - \frac{\rho_0}{3} \times [C_\Delta(k=0) - C_D(k=0)] \right\}^{-1}. \quad (21)$$

Thus, τ_T contains many-body effects through C_Δ and C_D . Numerical study shows that the dielectric relaxation time depends rather strongly on the static dielectric constant ϵ_0 . In the limit $\epsilon_0 \rightarrow 1$, $\tau_T \rightarrow (2D_R)^{-1}$, and in the limit of large ϵ_0 , τ_T approaches a limiting value (which depends on the density of the liquid) significantly larger than $(2D_R)^{-1}$. It is also important to note that the continuum model of $\epsilon(k, \omega)$ recently proposed by van der Zwan and Hynes²⁷ and by Hubbard *et al.*²⁹ is valid only near $k = 0$.

If we separate the real and imaginary parts of $\epsilon_L(k, \omega)$ and $\epsilon_T(k, \omega)$ in the following manner:

$$\epsilon_L(k, \omega) = \epsilon'_L(k, \omega) - i\epsilon''_L(k, \omega), \quad (22)$$

$$\epsilon_T(k, \omega) = \epsilon'_T(k, \omega) - i\epsilon''_T(k, \omega), \quad (23)$$

then explicit expression for those real and imaginary parts can be obtained from Eqs. (17)–(20).

The numerical results, along with wave vector dependent Cole–Cole plots, will be presented in Sec. V.

IV. SOLVATION DYNAMICS

We shall now consider time dependence of $E_{\text{solv}}(t)$ as it evolves towards its equilibrium value. The time-dependent solvation energy is given by Eq. (2), with $\delta\mathbf{P}(\mathbf{r}, t)$ now the deviation of the time dependent solvent polarization from its equilibrium value $\mathbf{P}_{\text{eq}}(\mathbf{r})$. Thus $\delta\mathbf{P}(\mathbf{r}, t)$ evolves towards zero as solvation progresses and it has the highest magnitude at time $t = 0$. The right-hand side of this expression can be Fourier transformed to obtain

$$E_{\text{solv}}(t) = -\frac{1}{2} (2\pi)^{-3} \int d\mathbf{k} \mathbf{D}_{\text{ion}}(\mathbf{k}) \cdot \delta\mathbf{P}(\mathbf{k}, t), \quad (24)$$

where $\mathbf{D}_{\text{ion}}(\mathbf{k})$ is the Fourier transform of the bare electric field due to the ion (or the dipole). Equation (24) is an exact expression of time dependent solvation energy. However, in order to proceed further, we need to make certain approximations on $\delta\mathbf{P}(\mathbf{k}, t)$. We assume that the time dependence of the polarization fluctuation can be given by Eqs. (8) and (10). This assumption is actually based on two other assumptions. First, it is assumed that the two particle direct correlation function, $c(\mathbf{r}, \omega, \mathbf{r}', \omega')$, in the presence of the polar solute molecule, is given by that of the pure liquid. This approximation is necessary because little is known about $c(\mathbf{r}, \omega, \mathbf{r}', \omega')$ in an inhomogeneous state. Second, it is assumed that $\rho_{\text{eq}}(\mathbf{r}, \omega) = \rho_0/4\pi$. This assumption may not be too bad if the liquid around the solute is not distorted to a large extent. Note that because of the last approximation, the dynamics and statics are dealt at two different levels. This is because we assume that the polarization of the final, equilibrium state is nonzero (because otherwise there is no solvation), yet the dynamics is that of the pure liquid. Thus, we

assume a linear response of the dipolar liquid. This is, of course, true for other treatments^{1–14} of solvation as well. Such descriptions will be reliable if the perturbation is not too strong. It will be shown below that this description reproduces many qualitative features correctly; the quantitative accuracy can only be tested by developing a better theory.

With the use of Eq. (8) in Eq. (24), we obtain the following expression for the time dependent solvation energy

$$E_{\text{solv}}(t) = -\frac{1}{2} (2\pi)^{-3} \int d\mathbf{k} \times \mathbf{D}_{\text{ion}}(\mathbf{k}) \cdot \delta\mathbf{P}(\mathbf{k}, 0) e^{-t/\tau_L(k)}. \quad (25)$$

In order to evaluate $E_{\text{solv}}(t)$ completely, we need an explicit expression for $\delta\mathbf{P}(\mathbf{k}, 0)$. As noted by Calef and Wolynes,¹ $\delta\mathbf{P}(\mathbf{r}, 0)$ is related to equilibrium polarization $\mathbf{P}_{\text{eq}}(\mathbf{r})$ by the following relation

$$\delta\mathbf{P}(\mathbf{r}, 0) = -\mathbf{P}_{\text{eq}}(\mathbf{r}) = -Ze \left(\frac{\epsilon_0 - 1}{\epsilon_0} \right) \frac{\hat{\mathbf{r}}}{r^2}, \quad (26)$$

where Ze is the charge of the solvating ion. Equation (26) is strictly valid if perturbation of the solvent is small and there are no saturation effects. Equation (26) is now Fourier transformed to obtain

$$\delta\mathbf{P}(\mathbf{k}, 0) = -\frac{Ze(\epsilon_0 - 1)}{\epsilon_0 k} \int_{ka}^{\infty} dx \frac{\sin x}{x}, \quad (27)$$

where a is the radius of solute particle. The Fourier transform of the bare electric field of an ion is given by

$$\mathbf{D}_{\text{ion}}(\mathbf{k}) = \frac{4\pi Ze}{k} \int_{ka}^{\infty} dx \frac{\sin x}{x}. \quad (28)$$

The time dependent solvation energy is now given by

$$E_{\text{solv}}(t) = \frac{(Ze)^2}{\pi\sigma} \left(1 - \frac{1}{\epsilon_0} \right) \int_0^{\infty} dq \times e^{-t/\tau_L(q)} \left[\int_{Rq}^{\infty} dx \frac{\sin x}{x} \right]^2, \quad (29)$$

where

$$q = k\sigma, \quad (29a)$$

$$R = 2a/\sigma. \quad (29b)$$

Equation (29) is the principal result of this section. This equation gives the time evolution of the solvation energy of a newly created ion of charge Ze and radius a in a dipolar liquid of static dielectric constant ϵ_0 and molecular diameter σ . Several comments on this expression are in order. First, we have assumed that the dynamic response of the solvent is that of the pure, unperturbed solvent. Thus, the influence of the solute on the dynamics of the solvent is neglected. Thus, in our “linear response theory,” the zeroth order system does not contain the solute. The hard sphere part of the solute–solvent interactions is introduced through a cutoff in the spatial integration [see Eq. (27)]. This approximation introduces certain ambiguity and may overestimate the importance of the intermediate wave vector processes. It is not difficult to treat the static part [$\mathbf{P}_{\text{eq}}(\mathbf{k})$] more rigorously by using density functional theory; the results are not expected to differ much from what is obtained from a nonlocal elec-

trostatics. However, a similar improvement on dynamic part requires considerable amount of numerical work and much of the simplicity of the theory is lost. We show later that the choice of cutoff employed in Eq. (27) leads to Born expression of solvation energy [see Eq. (33)]. A better description may be obtained if the full nonlocal electrostatics with $\epsilon(k)$ is used in Eqs. (26)–(29) because large wave vector processes will then be properly screened [$\epsilon(k) \rightarrow 1$ as k becomes large]. Alternatively, we can make the cutoff radius a a function of solvent as well. This may be useful in complex liquids and is a well-established (although phenomenological) practice.³¹ We plan to explore some of these possibilities in a future publication.³² Second, an attractive feature of Eq. (29) is that it contains the contributions of the translational modes in the polarization relaxation. We should mention that this is the first calculation that includes the role of translational modes in a microscopic theory. We have shown below that translational motions can be quite important at large wave vectors if the value of the parameter p' is comparable to or larger than unity. Thirdly, GSE is accurate for intermediate wave vector processes. It may become unreliable at very large wave vectors ($k\sigma \gg 2\pi$), but this limit is not relevant in the present problem as Eq. (29) shows that contribution to solvation energy from large k is negligibly small.

It is straightforward to evaluate Eq. (29) numerically. Further simplification results from the observation that the integral within the parentheses in Eq. (29) is related to well-known sine integral³⁰ by

$$\int_{\frac{1}{2}Rq}^{\infty} dx \frac{\sin x}{x} = \frac{\pi}{2} - \text{Si}(\frac{1}{2}Rq). \quad (30)$$

The properties of sine integral are well documented and extensive tables of $\text{Si}(z)$ exist.³⁰ Because of Eq. (30), we can now easily study the limiting properties of $E_{\text{sol}}(t)$ analytically as a function of the solute-solvent size ratio R . In the limit of large R ($a \gg \sigma/2$), $\text{Si}(0.5 Rq)$ is very close to $\pi/2$ unless $q = 0$. So, in this limit, $E_{\text{sol}}(t)$ is virtually single exponential with time constant equal to τ_L . Thus, in the limit of large R , we recover the continuum model result, as expected. In the opposite limit of very small R ($a \ll \sigma/2$), Eq. (29) simplifies to

$$E_{\text{sol}}(t) \sim \frac{(Ze)^2 \pi}{4} \left(1 - \frac{1}{\epsilon_0}\right) \int_0^{\infty} dq e^{-t/\tau_L(q)}. \quad (31)$$

Equation (31) is obtained by observing that $\tau_L(q)$ is very small at large q where $\text{Si}(0.5 Rq)$ differs significantly from $\pi/2$. Thus, in the limit of small R , $E_{\text{sol}}(t)$ is nonexponential because a large number of relaxation modes contribute to solvation. However, if the translational contribution is significant, then the picture changes drastically because modes in the intermediate to large wave vector regime now relaxes very fast and the relaxation is dominated by the $k \simeq 0$ wave vector processes. This can be seen clearly from Fig. 1 where $\tau_L(k)$ is plotted against k for several values of the parameter p' . In such situations, we predict a fast short time decay followed by a nearly exponential slower decay with rate constant again given by τ_L .

We now present numerical results of the analytical expressions obtained in the preceding three sections.

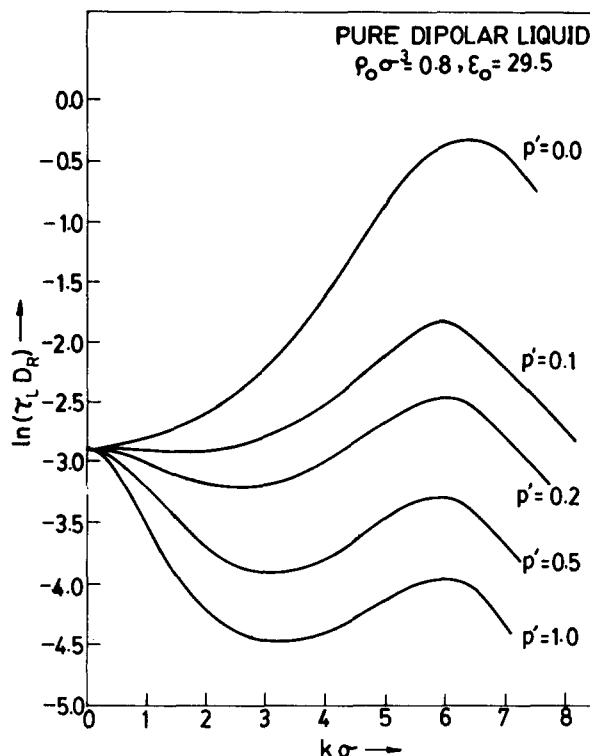


FIG. 1. The dependence of the longitudinal polarization relaxation time on wave vector k and on translational diffusion. The calculated values of $\tau_L(k)$ are plotted against wave vector k for several different values of the dimensionless solvent parameter p' ($= D_T/2D_R \sigma^2$). The values of the static dielectric constant and the density of the solvent are indicated on the figure.

V. NUMERICAL RESULTS

A. Polarization relaxation

It is seen from Eqs. (5) and (6) that polarization relaxation is characterized by two k -dependent relaxation times: one is the longitudinal relaxation time τ_L and the other is the transverse relaxation time τ_T . In Fig. 1, we have plotted the dependence of $\tau_L(k)$ on wave vector k and on translational diffusion. It is seen clearly that translational diffusion plays an important role in the intermediate values of the wave vector ($k\sigma \simeq 6.3$). In a previous publication,¹¹ we have presented a detailed study of both $\tau_L(k)$ and $\tau_T(k)$ and we refer to that paper for further information.

B. Dielectric dispersion

In Fig. 2 we have plotted $\epsilon_L''(k, \omega)$ vs $\epsilon_L'(k, \omega)$ (evaluated at different frequencies) for several different values of the wave vector k . These are the so-called Cole-Cole plots. It is seen that as the value of the wave vector is changed even by a small amount, these plots change drastically. At $k = 1.0$, the Cole-Cole plot for $\epsilon_L(k, \omega)$ shows that ϵ_L' approaches the limiting value unity at high frequency from negative side and here, τ_{DL} is negative. This rather surprising behavior occurs because the wave vector dependent dielectric constant is negative at intermediate wave vectors. We have shown elsewhere that this behavior does not violate any stability conditions of the system.²⁸ In fact, negative values of $\epsilon(k)$ have also been found in molten salt³³ and in hydrogen plasma.³⁴ As discussed by Dolgov *et al.*,³⁵ negative $\epsilon(k)$ at intermedi-

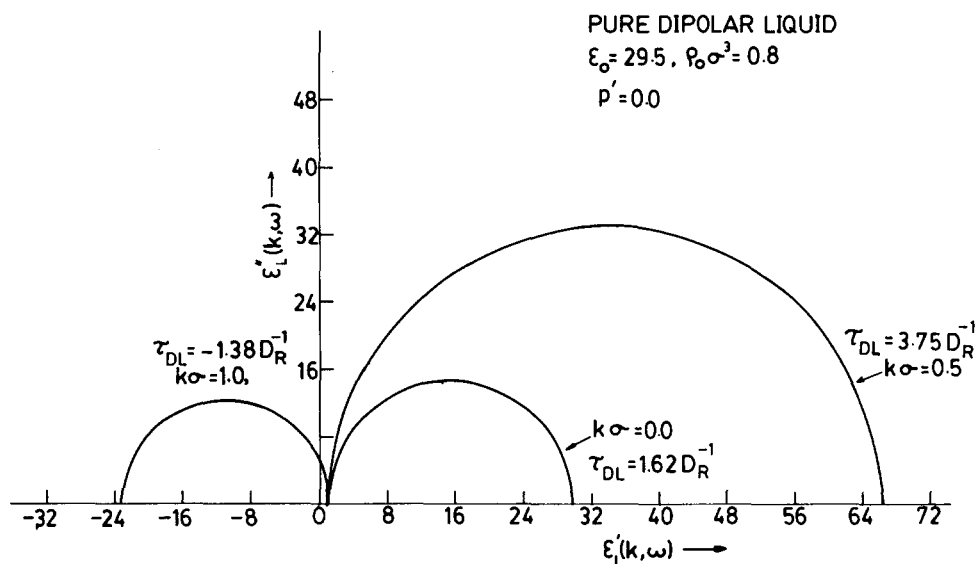


FIG. 2. The wave vector dependent Cole-Cole plots of $\epsilon_L(k, \omega)$. The imaginary part of the longitudinal dielectric function is plotted against the real part for several values of wave vector k . The values of k and p' are given on each figure. We have also indicated the values of the longitudinal dielectric relaxation times on the figure. The values of the other parameters remain the same as in Fig. 1.

ate wave vector is more of a rule than an exception. The physical reason for negative $\epsilon(k)$ is as follows. As the system is subjected to an electrostatic field of wave vector k , the response of the system, measured by $\epsilon(k)$, is determined by interparticle correlations of length $2\pi/k$. Thus, a local electric field probes the "local correlations," unlike the $k = 0$ field that probes only the macroscopic response. Now, in a strongly interacting dipolar (or charged) system, the linear response of the system may be in a direction opposite to the applied field. This is expected if the weak field attempts a local rearrangement that would lead to an increase in the energy of the system. This is seen most dramatically in the study of molten salt.³³

In Fig. 3 we have plotted $\epsilon_T''(k, \omega)$ vs $\epsilon_T'(k, \omega)$ (evaluated at different frequencies) for several different values of the wave vector k . We see that the Cole-Cole plot changes with change in the value of the wave vector. However, the change is less drastic than that in the case of $\epsilon_L(k, \omega)$.

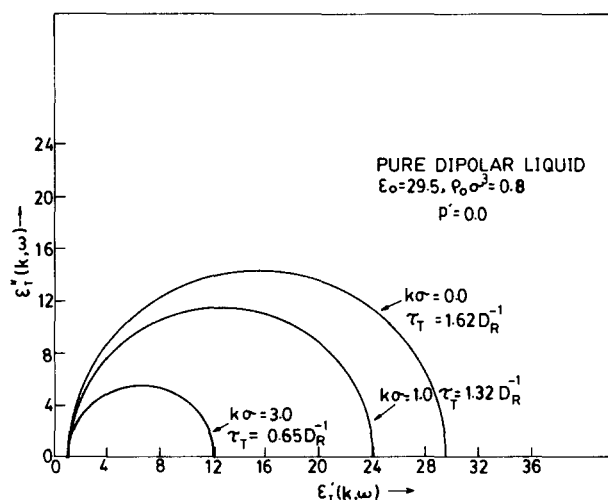


FIG. 3. The wave vector dependent Cole-Cole plots of the transverse dielectric function $\epsilon_T(k, \omega)$ for several values of the wave vector k . The values of k and p' are indicated on the figures. The other parameter values remain the same as in Fig. 2.

C. Solvation dynamics

The experimental and theoretical results on the dynamics of polar solvation are usually analyzed in terms of solvation time correlation function $C_s(t)$ defined by the following expression:

$$C_s(t) = \frac{E_{\text{solv}}(t)}{E_{\text{solv}}(t=0)}. \quad (32)$$

The initial value of the solvation energy can be obtained by evaluating the integral in Eq. (29) and the result is

$$E_{\text{solv}}(t=0) = \frac{(Ze)^2}{2a} \left(1 - \frac{1}{\epsilon_0}\right), \quad (33)$$

which is the well-known Born expression for the solvation energy of an ion of radius a and charge Ze in a dipolar liquid of dielectric constant ϵ_0 . Therefore, the final expression of the solvation energy correlation function is given by

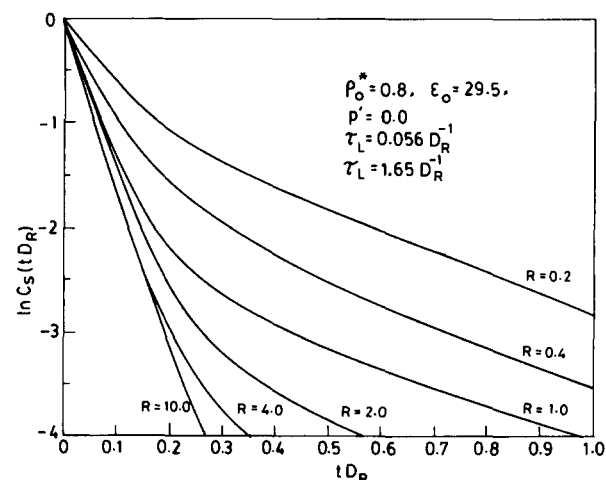


FIG. 4. The time dependence of the solvation time correlation function $C_s(t)$ in the absence of translational contribution, as a function of the solute-solvent size ratio R . $C_s(t)$ is plotted against time for several values of R which are indicated on the figures. The other parameter values are also indicated. $\rho_0^* = \rho_0\sigma^3$ and $\tau_D = 1.65 D_R^{-1}$.

$$C_s(t) = \frac{R}{\pi} \int_0^\infty dq e^{-t/\tau_L(q)} \left[\int_{Rq}^\infty dx \frac{\sin x}{x} \right]^2. \quad (34)$$

We now present numerical results of $C_s(t)$. In Fig. 4, we have plotted the time dependence of the solvation time correlation function in the absence of the translational contribution (that is, $p' = 0$). As can be seen from the graphs, the decay is, in general, nonexponential, especially at low values of the solute-solvent size ratio R . As R is increased, the results approach the continuum model prediction. We find that for all practical purposes continuum model result is recovered near the value $R = 5$. This result can be understood easily from Fig. 1 where the wave vector dependent longitudinal relaxation time is plotted against wave vector. When the solute is smaller than the solvent ($R < 1$), then a significant contribution to solvation comes from the near molecules and, as a result, the ion probes more of the short range (large wave vector) dynamics of the solvent. In the absence of translational contribution, the large wave vector polarization relaxation of the solvent is much slower [especially near k_M , where k_M is the value of the wave vector at the first maximum of $\tau_L(k)$] than that at $k = 0$, as can be seen from Fig. 1. This large wave vector relaxation proceeds at a rate not too different from the Debye relaxation time of the solvent [although, qualitatively, τ_D and $\tau_L(k = k_M)$ are very different and have different dependences on solvent properties]. Thus, the long time decay will now be dominated by these slow structural relaxation times at large wave vector. This result is not too different from the nonequilibrium MSA solvation model of Wolynes⁵ and of Rips, Klafter, and Jortner.⁹ Note that at $p' = 0$, the decay can be approximately described as a biexponential process with two time constants, τ_L and $\tau_L(k = k_M)$. As can be seen from Fig. 1, this biexponential nature of the solvation is a consequence of the existence of two disparate time scales in the polarization relaxation of the solvent. The collective polarization relaxation of the distant molecules proceeds at a rate given correctly by the continuum model, whereas, the polarization relaxation of the near molecules, although still collective because $\tau_L(k = k_M)$ involves contribution from the solvent, proceeds at a much smaller rate. Crudely speaking, the nearest-neighbor molecules (probed at large wave vectors) are less collective simply because they involve less number of molecules. As the size of the solute molecule increases (R increases), the less of the short range solvent structure and dynamics are probed, so we recover continuum model result. This is clearly reflected in Fig. 4.

The conclusions reached in the above paragraphs undergo a qualitative change when translational contribution to solvent polarization relaxation is significant. In Fig. 5, we have plotted the time dependence of the solvation energy for different values of the parameter p' ($= D_T/(2D_R\sigma^2)$) and for solute-solvent ratio $R = 2.0$. It is seen that the solvation is considerably accelerated by translational contribution, which is to be expected from Fig. 1. The reason for such behavior is as follows. The slow long time decay in the absence of translational contribution comes from the processes at large wave vectors (which means the contributions of the near molecules) which relax slowly (see Fig. 1). The translational contribution accelerates these large wave vector

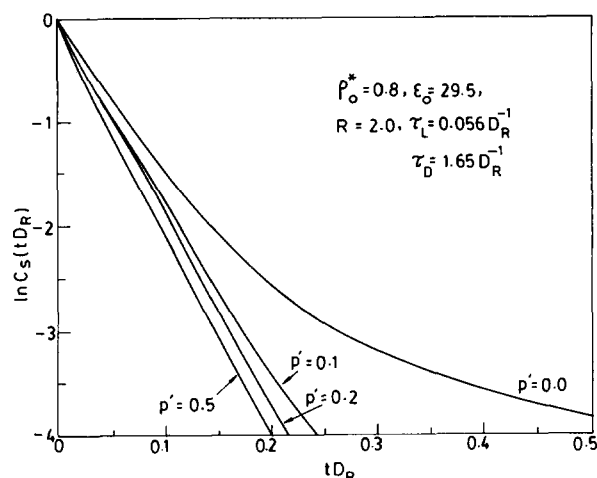


FIG. 5. The effects of translational modes on the time dependence of the solvation time correlation function $C_s(t)$. $C_s(t)$ is plotted against time for several values of the parameter p' for a fixed size ratio $R (= 2.0)$. The other parameter values are given on the figure.

processes most. Thus, the slowly relaxing components of solvation disappears from long time, but they show up at short times as transients. As can be seen from Fig. 5, we approach an exponential decay at large p' , except at short times, with the long time rate constant now given by τ_L^{-1} . Thus, we recover continuum limit result at large p' , but for a very different reason.

We are presently carrying out a detailed analysis of Eq. (34) to compare it with the available experimental results. A detailed comparison of the predictions of this paper with those of the nonequilibrium MSA^{5,9} will be considered in a future publication.³² Our preliminary calculations show that at $p' = 0$ (which is the only limit for which nonequilibrium MSA is available) our theory gives somewhat faster decay than MSA; the qualitative features, especially the dependence on the solute-solvent size parameter R and on the static dielectric constant ϵ_0 are quite similar (which is a bit surprising considering the rather different approaches that are involved). It is also of interest to compare the present treatment with that of Calef and Wolynes¹ who used a similar approach. First, Calef and Wolynes did not consider the effects of the translational modes. Second, they adopted a more realistic description of the statics of solute-solvent interaction but they had to carry out the entire calculation numerically. We have shown that much simplicity and insight can be gained if the pure solvent is treated as a zeroth order system. This, however, necessitates a consistent perturbative scheme. We believe that the calculations presented in this paper constitute a step in the correct direction because a microscopic theory of dynamics of solvation must be based on a kinetic equation as has been done here.

VI. CONCLUSION

In this paper, we presented a unified treatment of the polarization relaxation, dielectric dispersion, and solvation dynamics in a dense dipolar liquid. The relevant theoretical quantities for all these three processes are calculated from

the same starting point—the generalized Smoluchowski equation. It has thus been possible to explore the interrelationship without appealing to external results. We found that the zero-wave vector dielectric function $\epsilon(\omega)$ is of simple Debye form with the Debye relaxation time given by Eq. (23). We derived a closed-form analytic expression for the time dependent solvation energy. For small solute–solvent size ratio (R), the solvation is markedly nonexponential, if the translational contribution is not significant. For large R , we recover the continuum model result. We have shown that the translational contribution can render the solvation process nearly single exponential with the long time rate constant given by τ_L ; all the large wave vector processes show up as transients at early times. Thus, our theory seems to explain the anomalous experimental results on solvation of LDS 50 in alcohol solvents.^{18,19}

The main limitation of the present work is the use of MSA result for the anisotropy functions C_A and C_D . Thus, the detailed numerical predictions are applicable to not too strongly polar solvents. Also, a better description of the direct correlation function is necessary for hydrogen-bonded solvents. Recent computer simulations of Maroncelli and Fleming³⁶ indicate that the first solvation shell of the polar solute may be structured in hydrogen-bonded solvents. To account for this, we not only need an appropriate direct correlation function, but also a nonlinear dynamic theory. However, we believe the general conclusions reached here will retain some validity even in the hydrogen-bonded solvents.

The present study leads to several interesting problems. First, a detailed comparison of the present theory with the nonequilibrium MSA theory of Wolynes⁵ needs to be carried out. The general features of the two theories seem to be similar when translational component is neglected, but they may differ quantitatively. Second, we should now be able to develop a nonlinear dynamic theory where effects of solvent distortion by the polar solute molecule will be included. A better description of the direct correlation function is, of course, warranted. Maroncelli and Fleming³⁷ have recently carried out a detailed comparison of nonequilibrium MSA with the available experimental results. Such an analysis with the present theory will also be welcome. We hope to address some of these problems in future.

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- ¹D. F. Calef and P. G. Wolynes, *J. Chem. Phys.* **78**, 4145 (1983).
- ²B. Bagchi, D. W. Oxtoby, and G. R. Fleming, *Chem. Phys.* **86**, 257 (1984).
- ³G. van der Zwan and J. T. Hynes, *J. Phys. Chem.* **89**, 4181 (1985).
- ⁴V. Friedrich and D. Kivelson, *J. Chem. Phys.* **86**, 6425 (1987).
- ⁵P. G. Wolynes, *J. Chem. Phys.* **86**, 5133 (1987).
- ⁶R. F. Loring and S. Mukamel, *J. Chem. Phys.* **87**, 1272 (1987).
- ⁷R. F. Loring, Y. J. Yan, and S. Mukamel, *J. Chem. Phys.* **87**, 5840 (1987).
- ⁸E. W. Castner, G. R. Fleming, and B. Bagchi, *Chem. Phys. Lett.* **143**, 270 (1988).
- ⁹I. Rips, J. Klafter, and J. Jortner, *J. Chem. Phys.* **88**, 3246 (1988).
- ¹⁰B. Bagchi and A. Chandra, *Proc. Indian Acad. Sci.* **100**, 353 (1988).
- ¹¹A. Chandra and B. Bagchi, *Chem. Phys. Lett.* **151**, 47 (1988); **155**, 533 (1989).
- ¹²B. Bagchi, E. W. Castner, and G. R. Fleming, *J. Mol. Struct.* (in press).
- ¹³E. W. Castner, G. R. Fleming, B. Bagchi, and M. Maroncelli, *J. Chem. Phys.* **89**, 3519 (1988).
- ¹⁴A. L. Nichols III and D. F. Calef, *J. Chem. Phys.* **89**, 3783 (1988).
- ¹⁵M. Maroncelli, E. W. Castner, S. P. Webb, and G. R. Fleming, in *Ultrafast Phenomena V*, edited by G. R. Fleming and A. E. Seigmann (Springer, Berlin, 1986), p. 303.
- ¹⁶S.-G. Su and J. D. Simon, *J. Phys. Chem.* **90**, 6475 (1986); **91**, 2693 (1986).
- ¹⁷V. Nagarajan, A. M. Brearley, T.-J. Kang, and P. F. Barbara, *J. Chem. Phys.* **86**, 3183 (1987).
- ¹⁸E. W. Castner, M. Maroncelli, and G. R. Fleming, *J. Chem. Phys.* **86**, 1090 (1987).
- ¹⁹M. Maroncelli and G. R. Fleming, *J. Chem. Phys.* **86**, 6221 (1987).
- ²⁰M. A. Kahlou, T. J. Kang, and P. F. Barbara, *J. Phys. Chem.* **91**, 6452 (1987); *J. Chem. Phys.* **88**, 2372 (1988).
- ²¹J. D. Simon and S.-G. Su, *J. Chem. Phys.* **87**, 7016 (1987).
- ²²S.-G. Su and J. D. Simon, *J. Chem. Phys.* **89**, 908 (1988).
- ²³F. Heisel and J. A. Mische, *Chem. Phys. Lett.* **128**, 323 (1986).
- ²⁴J. D. Simon, *Acc. Chem. Phys.* **21**, 128 (1988).
- ²⁵C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids, Vol. I* (Clarendon, Oxford, 1984).
- ²⁶B. Bagchi, *J. Chem. Phys.* **82**, 5677 (1985); *Physica A* **145**, 273 (1987).
- ²⁷G. van der Zwan and J. T. Hynes, *Physica A* **121**, 227 (1983).
- ²⁸(a) A. Chandra and B. Bagchi, *J. Chem. Phys.* (to be published); (b) **90**, 1832 (1989).
- ²⁹J. B. Hubbard, R. F. Kayser, and P. J. Stiles, *Chem. Phys. Lett.* **95**, 399 (1983); P. J. Stiles and J. B. Hubbard, *Chem. Phys.* **84**, 432 (1984).
- ³⁰M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972), p. 231–244.
- ³¹See, for example, A. A. Kornyshev, in *The Chemical Physics of Solvation Part A: Theory of Solvation* (Elsevier, Amsterdam, 1985).
- ³²A. Chandra and B. Bagchi, *J. Phys. Chem.* (submitted).
- ³³A. Fasolino, M. Parrinello, and M. P. Tosi, *Phys. Lett. A* **66**, 119 (1978).
- ³⁴J. P. Hansen and I. R. McDonald, *Phys. Rev. Lett.* **41**, 1379 (1978).
- ³⁵O. V. Dolgov, D. A. Kirzhnits, and E. G. Maksimov, *Rev. Mod. Phys.* **53**, 81 (1981).
- ³⁶M. Maroncelli and G. R. Fleming, *J. Chem. Phys.* **89**, 5044 (1988).
- ³⁷M. Maroncelli and G. R. Fleming, *J. Chem. Phys.* **89**, 875 (1988).