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Dielectric relaxation of dipolar liquids

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An approximate expression is derived for the dielectric function $\epsilon(\mathbf{k}, \omega)$. The theory includes inertial and non-Markovian effects and is free of adjustable parameters. For the $k=0$ case, detailed comparisons are made with computer simulation results for dipolar soft-sphere and Stockmayer fluids, and the theory is shown to be qualitatively sound at both low and high frequencies. The present approximation should be very useful in developing a theory of solvation dynamics which properly includes important inertial effects.

I. INTRODUCTION

This article is concerned with the frequency dependent dielectric relaxation of dipolar liquids. The dielectric behavior of dense fluids is a subject of long standing interest and there has been a good deal of recent progress.^{1,2} Microscopic theories based upon diffusional models of orientational relaxation have been developed³⁻⁷ and these predict a simple Debye (or, at nonzero wave vectors, a multi-Debye) form for the frequency and wave vector dependent dielectric function. The importance of inertial and non-Markovian effects has also been explored and these factors introduce non-Debye behavior at high frequency.⁸⁻¹² There have also been several detailed computer simulation studies¹³⁻¹⁵ of model dipolar fluids and these have contributed significantly to the present understanding of dielectric relaxation. However, despite these efforts there remains a need for a general microscopic theory which is valid at both high and low frequencies and which does not strongly depend upon empirical parameters. The present paper is a contribution towards this end.

Here we derive microscopic expressions for the dielectric function $\epsilon(\mathbf{k}, \omega)$. Linear response theory provides formal expressions for the longitudinal and transverse com-

ponents of $\epsilon(\mathbf{k}, \omega)$ in terms of the van Hove space-time correlation function.^{6,7} In the present theory we use the Kerr approximation for the total van Hove function together with a non-Markovian equation of motion for the self-contribution in order to obtain closed expressions for the components of $\epsilon(\mathbf{k}, \omega)$. Explicit numerical results are given for the long wavelength limit [i.e., $\epsilon(\omega) \equiv \epsilon(0, \omega)$] and we compare with computer simulations for simple dipolar fluids. It is shown that the present theory gives a relatively good description of the high frequency deviations from Debye behavior which are associated with the fast inertial motion of the dipolar particles.

II. THE KERR APPROXIMATION

In this section we briefly summarize the application of the Kerr theory to fluids of nonspherical particles and introduce the notation used in this paper. We consider a homogeneous isotropic fluid of rigid nonspherical molecules and let the vector $\mathbf{r}_i(t)$ and the Euler angles, denoted by $\Omega_i(t)$, describe the position and orientation of particle i at time t . The Kerr approximation relates the total van Hove correlation function $G(\mathbf{r}, \Omega_0, \Omega, t)$ to the self-part $G_s(\mathbf{r}, \Omega_0, \Omega, t)$ and can be written in the form^{6,7}

$$G(\mathbf{r}, \Omega_0, \Omega, t) = G_s(\mathbf{r}, \Omega_0, \Omega, t) + \frac{\rho}{\Omega} \int d\mathbf{r}' d\Omega' g(\mathbf{r} - \mathbf{r}', \Omega_0, \Omega') G_s(\mathbf{r}', \Omega', \Omega, t) - \frac{\rho}{\Omega^2} \int_0^t dt' \int d\mathbf{r}' d\mathbf{r}'' d\Omega' d\Omega'' G(\mathbf{r} - \mathbf{r}', \Omega_0, \Omega', t - t') c(\mathbf{r}' - \mathbf{r}'', \Omega', \Omega'') \frac{\partial G_s(\mathbf{r}'', \Omega'', \Omega, t')}{\partial t'}, \quad (2.1)$$

where ρ is the number density, g and c are the equilibrium pair distribution function and the direct correlation function, respectively, and $\Omega = \int d\Omega$. The van Hove function gives the probability density of finding a particle at (\mathbf{r}, Ω) at time t , given that there was a particle at $(\mathbf{0}, \Omega_0)$ initially. The self part gives the probability density of finding a particle at (\mathbf{r}, Ω) at time t , given that the same particle was at $(\mathbf{0}, \Omega_0)$ initially.

Equation (2.1) can be solved^{6,7} by expanding the van Hove function in a complete set of rotational invariants according to the equation

$$G(\mathbf{r}, \Omega_0, \Omega, t) = \sum_{\substack{mnl \\ \mu\nu}} G_{\mu\nu}^{mnl}(r, t) \Phi_{\mu\nu}^{mnl}(\Omega_0, \Omega, \Omega_r), \quad (2.2)$$

where the rotational invariants are defined by^{6,16}

$$\Phi_{\mu\nu}^{mnl}(\Omega_0, \Omega, \Omega_r) = f^{mnl} \sum_{\mu', \nu', \lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} R_{\mu'\mu}^m(\Omega_0) R_{\nu'\nu}^n(\Omega) R_{\lambda'0}^l(\Omega_r). \quad (2.3)$$

Here $R_{\nu'\nu}^n(\Omega)$ is a Wigner generalized spherical harmonic,¹⁷ Ω_r denotes the orientation of the vector \mathbf{r} , f^{mnl} represents a nonzero constant and we have used standard notation for the 3- j symbol. For the convenient choice^{6,16}

$$f^{mnl} = \sqrt{(2m+1)(2n+1)}, \quad (2.4)$$

Eq. (2.1) yields sets of coupled equations which can be expressed in the form

$$\begin{aligned} \bar{G}_{\mu\nu\chi}^{mn}(k, \omega) = & \bar{G}_{s\mu\nu\chi}^{mn}(k, \omega) + \rho \sum_{n_1\nu_1} (-)^{\chi+\nu_1} \bar{g}_{\mu\nu_1\chi}^{mn_1}(k) \bar{G}_{s-\nu_1\nu\chi}^{n_1n}(k, \omega) + \rho \sum_{n_1\nu_1} (-)^{\chi+\nu_1} \bar{G}_{\mu\nu_1\chi}^{mn_1}(k, \omega) \bar{c}_{-\nu_1\nu\chi}^{n_1n}(k) \\ & + i\omega\rho \sum_{\substack{n_1n_2 \\ \nu_1\nu_2}} (-)^{\nu_1+\nu_2} \bar{G}_{\mu\nu_1\chi}^{mn_1}(k, \omega) \bar{c}_{-\nu_1\nu_2\chi}^{n_1n_2}(k) \bar{G}_{s-\nu_2\nu\chi}^{n_2n}(k, \omega). \end{aligned} \quad (2.5)$$

The “tilde” and “bar” denote the Hankel and Hankel-Laplace transforms defined by^{6,7}

$$\tilde{G}_{\mu\nu}^{mnl}(k, t) = 4\pi t^l \int dr r^2 j_l(kr) G_{\mu\nu}^{mnl}(r, t), \quad (2.6a)$$

$$\bar{G}_{\mu\nu}^{mnl}(k, \omega) = \int_0^\infty dt e^{i\omega t} \tilde{G}_{\mu\nu}^{mnl}(k, t), \quad (2.6b)$$

where $j_l(kr)$ is a spherical Bessel function of order l . Also, in Eq. (2.5) we have introduced the χ transforms^{6,16}

$$\bar{G}_{\mu\nu\chi}^{mn}(k, \omega) = \sum_{l=|m-n|}^{m+n} \begin{pmatrix} m & n & l \\ \chi-\chi & 0 & 0 \end{pmatrix} \bar{G}_{\mu\nu}^{mnl}(k, \omega). \quad (2.7)$$

In the remainder of this paper we will restrict our discussion to fluids of axially symmetric particles and hence only terms for which the lower indices $\mu=\nu=0$ occur in the various rotational invariant expansions. Therefore, we will drop these indices and adopt the simpler notation $\bar{G}^{mnl}(k, \omega) = \bar{G}_{00}^{mnl}(k, \omega)$, $\bar{G}_\chi^{mn}(k, \omega) = \bar{G}_{00\chi}^{mn}(k, \omega)$ and similar conventions are used for analogous quantities.

III. THE DIELECTRIC FUNCTION

For a polar-nonpolarizable fluid the exact expressions for the longitudinal (L) and transverse (T) components of the dielectric tensor $\epsilon(k, \omega)$ in terms of the van Hove function are given by^{3,6}

$$\epsilon_L(k, \omega) - 1 = \frac{3y[\tilde{S}_0^{11}(k) + i\omega\bar{G}_0^{11}(k, \omega)]}{1 - 3y[\tilde{S}_0^{11}(k) + i\omega\bar{G}_0^{11}(k, \omega)]}, \quad (3.1a)$$

$$\epsilon_T(k, \omega) - 1 = 3y[\tilde{S}_1^{11}(k) + i\omega\bar{G}_1^{11}(k, \omega)], \quad (3.1b)$$

where

$$\tilde{S}_\chi^{11}(k) = 1 + (-)^{\chi} \rho \tilde{h}_\chi^{11}(k), \quad (3.1c)$$

and $y = 4\pi\rho\beta\mu^2/9$ (μ is the molecular dipole moment and $\beta = 1/k_B T$). Since here we will deal only with simple dipolar fluids, for the sake of simplicity we restrict the

rotational invariant basis set to the three terms defined by $(mnl) = (000), (110), (112)$. Subject to this restriction, Eq. (2.5) reduces to the simplified form⁷

$$\bar{G}_\chi^{11}(k, \omega) = \frac{[\tilde{S}_\chi^{11}(k)]^2 \bar{G}_{s\chi}^{11}(k, \omega)}{1 + [1 - \tilde{S}_\chi^{11}(k)] i\omega (-)^{\chi} \bar{G}_{s\chi}^{11}(k, \omega)}, \quad (3.2)$$

where we have used the Ornstein-Zernike relationship

$$\tilde{S}_\chi^{11}(k) = [1 - (-)^{\chi} \rho \tilde{c}_\chi^{11}(k)]^{-1} \quad (3.3)$$

valid for this restricted basis set. We emphasize that this simplification is by no means essential and that one could retain more general (but more cumbersome) expressions for $\bar{G}_\chi^{11}(k, \omega)$.⁷ However, Eq. (3.2) is consistent with the mean spherical approximation for dipolar hard spheres¹⁸ and we would expect it to be a good general approximation for simple dipolar fluids. Furthermore, at $k=0$, Eq. (3.2) represents the *exact* solution of the Kerr approximation for all particles where the dipole moment is along the symmetry axis.⁶

We next construct an approximate form for the frequency dependent self van Hove function. Formally, we can write $\bar{G}_{s\chi}^{11}(k, \omega)$ in the form

$$\bar{G}_{s\chi}^{11}(k, \omega) = \frac{(-)^{\chi}}{-i\omega + 2\Theta(\omega) + D(\omega)k^2}, \quad (3.4)$$

where $\Theta(\omega)$ and $D(\omega)$ are frequency dependent rotational and translational diffusion coefficients which include the inertial and non-Markovian effects. Equation (3.4) reduces to the usual Fick-Debye diffusion equation when the frequency dependence of $\Theta(\omega)$ and $D(\omega)$ is neglected. In recent papers^{19,20} we have derived approximate expressions for $D(\omega)$ and $\Theta(\omega)$.

In the absence of any rotation-translation cross coupling $D(\omega)$ can be described by the expression¹⁹

$$D(\omega) = \frac{(k_B T/m) [-i\omega + D\langle F^2 \rangle / 3(k_B T)^2]}{-\omega^2 - i\omega D\langle F^2 \rangle / 3(k_B T)^2 + \langle F^2 \rangle / 3mk_B T}, \quad (3.5)$$

where m is the mass of a particle, F is the total force acting on a particle, $\langle \cdots \rangle$ denotes an equilibrium average, and

D is the zero frequency translational diffusion coefficient. The details of the derivation of Eq. (3.5) are given in Ref. 19. Therefore, here we simply note that this expression for $D(\omega)$ was obtained from an approximate form of the memory function of the velocity autocorrelation function.

This approximation ensures that the second frequency moment of the velocity autocorrelation function is given correctly.

In a similar manner, the frequency dependence of the rotational diffusion coefficient can be described by²⁰

$$\Theta(\omega) = \frac{(k_B T/I) [-i\omega + 2\Theta(1 + \langle L^2 \rangle / 4(k_B T)^2)]}{-\omega^2 - 2i\omega\Theta[1 + \langle L^2 \rangle / 4(k_B T)^2] + (2k_B T/I)[1 + \langle L^2 \rangle / 4(k_B T)^2]}, \quad (3.6)$$

where I is the molecular moment of inertia, L is the total torque acting on a particle, and Θ is the zero frequency rotational diffusion coefficient. Again, this expression for $\Theta(\omega)$ was derived by using an approximate form of the rotational memory function which satisfies the second frequency moment of the angular velocity autocorrelation function and the fourth frequency moment of the self dipole-dipole reorientational correlation function.^{20,21} The details of the derivation of Eq. (3.6) are given in Ref. 20.

Equations (3.1)–(3.6) can be combined to obtain

$$\epsilon_L(k, \omega) - 1 = \frac{\epsilon_L(k) - 1}{1 - i\omega\tau_{DL}(k, \omega)}, \quad (3.7a)$$

$$\epsilon_T(k, \omega) - 1 = \frac{\epsilon_T(k) - 1}{1 - i\omega\tau_{DT}(k, \omega)}, \quad (3.7b)$$

where the static dielectric functions, $\epsilon_L(k)$ and $\epsilon_T(k)$, are given by

$$\epsilon_L(k) = \frac{1}{1 - 3y\tilde{S}_0^{11}(k)}, \quad (3.8a)$$

$$\epsilon_T(k) = 1 + 3y\tilde{S}_1^{11}(k), \quad (3.8b)$$

and the frequency dependent relaxation times, $\tau_{DL}(k, \omega)$ and $\tau_{DT}(k, \omega)$, are of the form

$$\tau_{DL}(k, \omega) = \epsilon_L(k)\tilde{S}_0^{11}(k)/[2\Theta(\omega) + D(\omega)k^2], \quad (3.9a)$$

$$\tau_{DT}(k, \omega) = \tilde{S}_1^{11}(k)/[2\Theta(\omega) + D(\omega)k^2], \quad (3.9b)$$

with $D(\omega)$ and $\Theta(\omega)$ given by Eqs. (3.5) and (3.6). At $k=0$, we have $\epsilon_L(0, \omega) = \epsilon_T(0, \omega) \equiv \epsilon(\omega)$, and $\epsilon(\omega)$ can be written as

$$\epsilon(\omega) - 1 = \frac{\epsilon - 1}{1 - i\omega\tau_D(\omega)}, \quad (3.10)$$

where ϵ is the static dielectric constant and $\tau_D(\omega)$ is a frequency dependent Debye time defined by

$$\tau_D(\omega) = \frac{\epsilon - 1}{3y} \left\{ \frac{1}{2\Theta(\omega)} \right\}. \quad (3.11)$$

We note that Eq. (3.10) reduces to the standard Debye form if the frequency dependence of $\tau_D(\omega)$ is ignored. It is shown below that the frequency dependence of $\tau_D(\omega)$ plays an important role in the dielectric dispersion at high frequency.

The frequency dependent dielectric function can be divided into real and imaginary parts to obtain

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega), \quad (3.12)$$

where

$$\epsilon_1(\omega) = 1 + \frac{(\epsilon - 1)[1 + \omega\tau_{D2}(\omega)]}{[1 + \omega\tau_{D2}(\omega)]^2 + [\omega\tau_{D1}(\omega)]^2}, \quad (3.13a)$$

$$\epsilon_2(\omega) = \frac{\omega(\epsilon - 1)\tau_{D1}(\omega)}{[1 + \omega\tau_{D2}(\omega)]^2 + [\omega\tau_{D1}(\omega)]^2}. \quad (3.13b)$$

Here $\tau_{D1}(\omega)$ and $\tau_{D2}(\omega)$ are the real and imaginary parts of $\tau_D(\omega)$ and are given by

$$\tau_{D1}(\omega) = \frac{\epsilon - 1}{3y(k_B T/I)} \left\{ \frac{2\Theta(k_B T/I)[1 + \langle L^2 \rangle / 4(k_B T)^2]^2}{[2\Theta(1 + \langle L^2 \rangle / 4(k_B T)^2)]^2 + \omega^2} \right\}, \quad (3.14a)$$

$$\tau_{D2}(\omega) = \frac{\omega(\epsilon - 1)}{3y(2k_B T/I)} \left\{ \frac{[(k_B T/I)(1 + \langle L^2 \rangle / 4(k_B T)^2) - \omega^2] - [2\Theta(1 + \langle L^2 \rangle / 4(k_B T)^2)]^2}{[2\Theta(1 + \langle L^2 \rangle / 4(k_B T)^2)]^2 + \omega^2} \right\}. \quad (3.14b)$$

IV. COMPARISON WITH COMPUTER SIMULATIONS

We have carried out constant temperature molecular dynamics (MD) simulations²² for dipolar soft-sphere^{15,20} and Stockmayer¹⁴ fluids. These systems can be described by specifying the reduced parameters, $\rho^* = \rho\sigma^3$, $T^* = k_B T / \epsilon_{ss}$, $\mu^* = (\mu^2 / \epsilon_{ss} \sigma^3)^{1/2}$ and $I^* = I / m\sigma^2$, where ϵ_{ss} and σ are parameters characterizing the spherically symmetric (ss) soft-sphere or Lennard-Jones potential. For the dipolar soft-sphere system the values of the reduced parameters employed were $\rho^* = 0.8$, $T^* = 1.25$, $\mu^* = 1.65$ and $I^* = 0.025$. For the Stockmayer fluid we used $\rho^* = 0.822$, $T^* = 1.15$, $\mu^* = 1.732$ and $I^* = 0.025$ which define a system previously considered by Neumann *et al.*¹⁴ The MD calculations were carried out with 256 particles and periodic boundary conditions with $\epsilon' = \infty$ ²³ were employed. The reduced time step $\Delta t^* = \Delta t (\epsilon_{ss} / m\sigma^2)^{1/2} = 0.0025$ was used and the simulations were continued 400 000 time steps for the dipolar soft-sphere system and 100 000 time steps for the Stockmayer fluid. The results obtained for the Stockmayer system were in excellent agreement with those of Neumann *et al.*¹⁴ The values of the diffusion constants, mean square force and mean square torque which enter into the theory are summarized in Table I.

At $k=0$, $\tilde{G}_{s0}^{11}(0,t) = -\tilde{G}_{s1}^{11}(0,t)$ and both are given by the self-dipole-dipole reorientational time correlation function $\langle \hat{\mu}_i(0) \cdot \hat{\mu}_i(t) \rangle$, where $\hat{\mu}_i(t)$ denotes a unit vector along $\mu_i(t)$. The simulation and theoretical results for $\tilde{G}_{sX}^{11}(0,t)$ are compared in Fig. 1. We emphasize that the present approximation guarantees that the results must agree at short and long times and it is clear from the plots that these constraints are obeyed. Overall, the agreement is reasonably good considering that no adjustable parameters are involved and, as we would anticipate, the largest discrepancies occur at intermediate times.

The real and imaginary parts of $\epsilon(\omega)$ together with Cole-Cole plots are shown in Figs. 2–4. However, before discussing these results it is useful to note that discrepancies between the theory and computer simulations may arise from two sources; specifically, from $\tilde{G}_{sX}^{11}(0,t)$ itself or through the Kerr approximation relating the total van Hove function to the self part. It is possible to partially correct for inaccuracies in the Kerr theory in the following manner.

In general, the static Debye time τ_D can be related to the self time τ_s (i.e., $\tau_s = 1/2\Theta$ in the present context) by the equation^{1,15}

$$\tau_D = \frac{\epsilon - 1}{3\nu(1+f)} \tau_s, \quad (4.1)$$

where $(1+f)$ is a dynamical factor. In the Kerr theory $(1+f) = 1$ and one obtains⁶ an expression equivalent to the static limit of Eq. (3.11). However, it is well known¹⁵ that for many systems this is not the case and, indeed, for the dipolar soft-sphere and Stockmayer systems considered here we find that $(1+f)^{-1} = 0.668$ and 0.554 , respec-

TABLE I. Values of the quantities which enter into theory.

System	D^{*a}	Θ^{*a}	$\langle F^2 \rangle^b$	$\langle L^2 \rangle^b$
Dipolar soft-sphere	0.0506	3.335	1440.1	18.17
Stockmayer	0.0714	2.18	1324.1	21.63

$$^a D^* = D(m/\epsilon_{ss}\sigma^2)^{1/2}, \Theta^* = \Theta(m\sigma^2/\epsilon_{ss})^{1/2}.$$

$$^b F^* = F\sigma/\epsilon_{ss}, L^* = L/\epsilon_{ss}.$$

tively. Therefore, in Figs. 2–4 we have also included “corrected Kerr” results obtained by replacing Eq. (3.11) with the expression

$$\tau_D(\omega) = \frac{\epsilon - 1}{3\nu(1+f)} \left[\frac{1}{2\Theta(\omega)} \right], \quad (4.2)$$

where $(1+f)$ is taken to be the static value.

In Figs. 2–4 we compare both the Kerr and corrected Kerr versions of the present treatment with simple Debye theory and with simulation results. It can be seen that both the Kerr and corrected Kerr approximations include characteristic inertial features not present at the Debye level. In particular, we note the high frequency minima in $\epsilon_1(\omega)$ [Figs. 2(a) and 3(a)] and the deviations from semicircular shape evident in the Cole-Cole plots (Fig. 4). Quantitatively, it is obvious that the corrected Kerr theory is significantly better than the uncorrected approximation. The corrected version is in fact in reasonably good agreement with the molecular dynamics results. The remaining discrepancies occur at intermediate frequencies and in all likelihood reflect the intermediate time inaccuracies of the self-

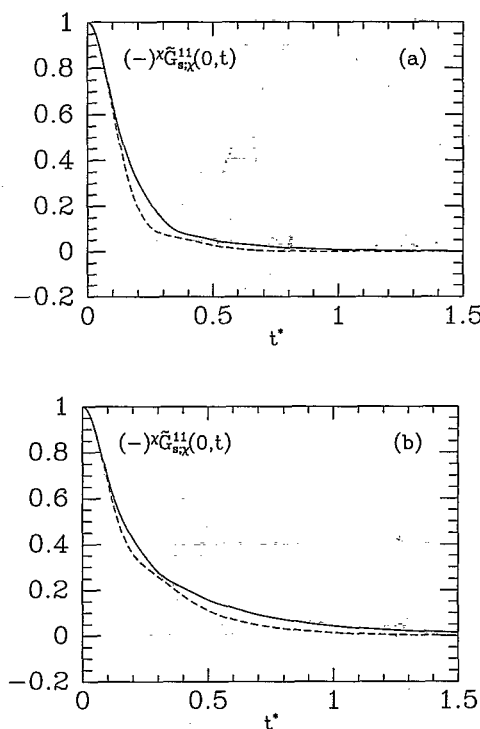


FIG. 1. The time dependence of $(-)\tilde{G}_{sX}^{11}(0,t) \equiv \langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle$ for the (a) dipolar soft-sphere and (b) Stockmayer fluids. The solid and dashed curves are MD and theoretical results, respectively.

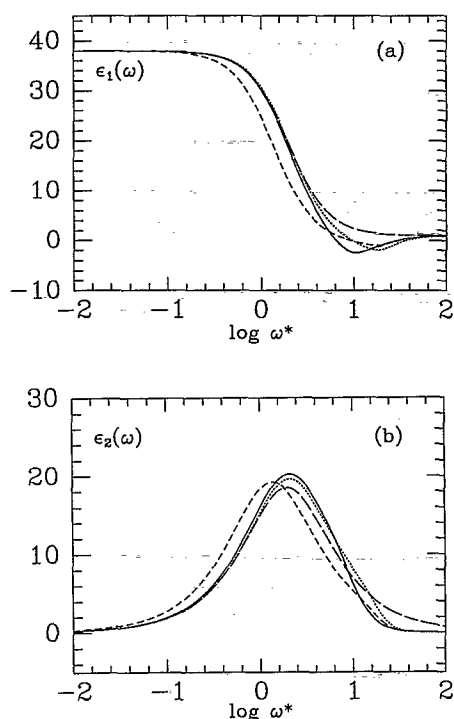


FIG. 2. The (a) real and (b) imaginary parts of the dielectric function for the dipolar soft-sphere system. The solid curves are the MD results. The curves drawn with long dashes were obtained from the simple Debye formula using MD values of τ_D . The curves drawn with short dashes and dots are given by the present theory employing, respectively, the Kerr and corrected Kerr approximations.

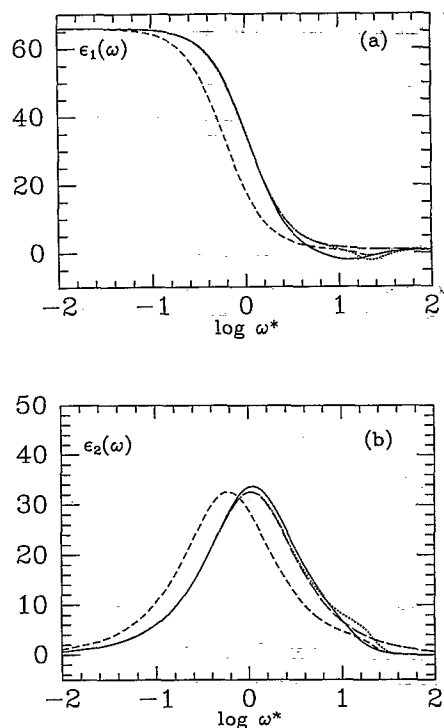


FIG. 3. The (a) real and (b) imaginary parts of the dielectric function for the Stockmayer system. The curves are as in Fig. 2.

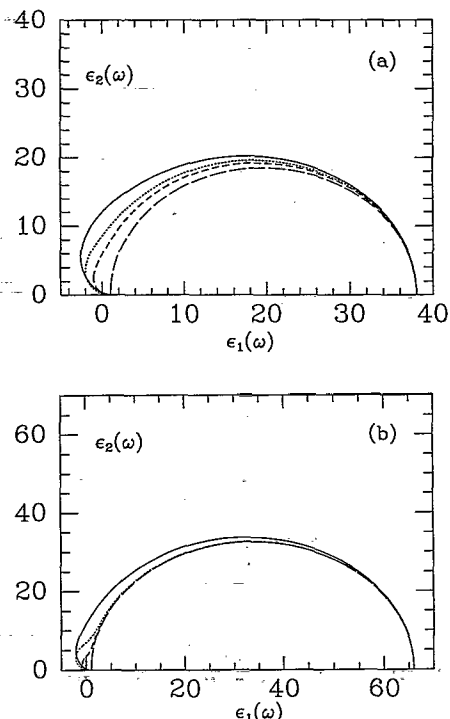


FIG. 4. Cole-Cole plots for the (a) dipolar soft-sphere and (b) Stockmayer systems. The curves are as in Fig. 2.

van Hove function as discussed above. It should be emphasized that the present approximation approaches the exact result at high frequencies, and we shall show in a subsequent paper that this is very important in theoretical treatments of ion solvation dynamics. Further, we note that the inertial contribution is larger for the dipolar soft sphere fluid than for the Stockmayer system. This is likely simply because the Stockmayer particles we consider have a larger dipole moment and the stronger interactions increase the relative importance of diffusional motion.

V. SUMMARY AND CONCLUSIONS

In this paper we have given approximate expressions for some frequency and wave vector dependent projections of the self-van Hove function. Explicit results are obtained only for simple dipolar fluids, but the ideas could be readily generalized to more complex models. The theory includes both inertial and diffusional effects, and at zero wave vector the approximate form is constrained to be correct at both short and long times. We have carried out computer simulations for dipolar soft-sphere and Stockmayer fluids in order to test the theory, and the agreement was found to be reasonably good over the entire time domain. As expected, discrepancies do occur at intermediate times but these are not large, particularly in view of the fact that the theory contains no adjustable parameters.

We have also employed the present approximation for the self-van Hove function together with Kerr theory in order to obtain an expression for the dielectric function $\epsilon(\mathbf{k}, \omega)$. Comparison with the simulations shows that this

theory includes inertial effects in a qualitatively correct manner, although there is certainly still room for quantitative improvement.

Finally, we remark that one of our principal motivations for developing this theory was the need for a good dielectric function in the theory of dynamic solvation.^{2,7} Preliminary calculations show that the present dielectric function greatly improves upon the current theoretical descriptions of ion solvation dynamics. In fact it includes the very fast inertial contribution which accounts for about 70%–80% of the ion-solvent energy,²⁴ but which has proven difficult to include in earlier theoretical treatments.

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