Theory and simulation of polar and nonpolar polarizable fluids

Jianshu Cao[a] and B. J. Berne
Department of Chemistry and Center for Biomolecular Simulation, Columbia University, New York, New York 10027

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The theory of polarizable fluids is developed on the basis of a model fluid consisting of anisotropic Drude oscillators with embedded permanent dipoles. A matrix Monte Carlo method is used to simulate these fluids and to compare their dielectric properties with the predictions of the mean spherical approximation (MSA) theory. Simple identities are used in conjunction with the matrix expressions to derive mean spherical approximations to the screening functions for charges and permanent multipoles in polarizable fluids. This is useful in the theory of the solvated electron.

I. INTRODUCTION

It is becoming increasingly clear that electrical induction has an important effect in fluids. In liquid water induced dipoles can be 50% as large as the permanent dipoles. Large scale quantum chemical calculations show that polarizability and hyperpolarizability play a very important role in the properties of molecular aggregates and clusters.[1,2] A model that incorporates induction is the well studied Drude oscillator model, an isotropic harmonic oscillator with a frequency ω_0, mass μ, and charges $+q$ and $-q$ connected by a harmonic spring. If the electrostatic interaction between the Drude oscillators is treated in the dipole–dipole approximation the problem reduces to a matrix problem. This simplification provides an excellent platform for studying the dielectric and spectral properties of many-body systems[3–9] and because linear response theory then holds exactly in the dipole–dipole approximation many physical quantities can be easily formulated and calculated. In addition, the classical and the quantum linear response to an external field are the same so that, although the problem of electrical induction is intrinsically quantum mechanical, most of the results derived for the classical Drude model need little modification when adapted for quantum systems.[10,11]

The Drude oscillator model has been used to study fluids of either nonpolar–polarizable or polar polarizable molecules.[3,12–14] Pratt[13] and independently Hoye and Stell[4] have studied a classical fluid of isotropic Drude oscillators. Using the mean spherical approximation (MSA) they derived a self-consistent theory of the renormalized polarizability, a quantity that increases with fluid density. Hoye and Stell[15,16] and independently Chandler[11] applied the MSA to the path integral representation of the quantum Drude oscillators. This simple generalization leads to a theory of quantum polarizable fluids. Analytical continuation of the MSA theory gives the absorption spectrum of the polarization fluctuations.[8,9,17–21] Although an approximation, the MSA model has played an important role in the present understanding of electrostatic interactions in dielectrics. More recently, Stratt and co-workers proposed a nonlinear theory which gives better agreement with simulation than the MSA approximation.[22–24]

In polar fluids the major contribution to the dielectric constant comes from the permanent dipoles. In this paper we study both kinds of fluids. In fluids containing polar molecules that are also polarizable the molecules are modeled as anisotropic Drude oscillators in which the electronic motion along the direction of the permanent dipole and perpendicular to it have different force constants, or equivalently different polarizabilities along the parallel and perpendicular directions.[4] The molecules can then be treated using a polarizability matrix or tensor in the lab fixed coordinate frame. In nonpolar fluids the molecules can either be optically spherical or optically anisotropic. In the latter case one can assign anisotropic harmonic Drude oscillators as we have recently to study the optical birefringence of smectic and nematic liquid crystals.[25]

The most general Hamiltonian for polar–polarizable fluids consisting of molecules with anisotropic polarizabilities acted upon by an inhomogeneous electric field is treated in Sec. II. Because the internal motions of the Drude oscillators are fast compared to the molecular translations and rotations the Born–Oppenheimer approximation is invoked. The fluctuating degrees of freedom of the Drude oscillator are integrated out to yield a matrix expression for the Drude oscillator partition function as well as the potential of mean force for the nuclear configurations. All relevant physical properties, such as the polarization energy of a solvated charge or permanent multipole, the dielectric constant, and the electronic adsorption spectrum can all be simulated using matrix techniques. In addition many of the previous theoretical results based on the MSA theory can be derived from a matrix formulation as has been pointed out earlier.[8,9] The derivations are analogous to the Greens function formalism in solid state theory.[26,27] The renormalized polarizability and the dielectric constant can be expressed in terms of the polarization matrix. A straightforward diagrammatic expansion of the matrix leads to a mean field theory equivalent to the MSA.[8,19,20,28] Furthermore, by identifying the off-diagonal elements as the dipolar correlation function, one can derive the equations for the renormalized polarizability, for the

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[a] In partial fulfillment of the Ph.D. in the Department of Physics, Columbia University.

screening functions for a point dipole and point charge dissolved in the fluid, and for the dielectric constant. An easy extension of the matrix analysis gives us the spectral line shapes in the MSA. Several of these points have been made in other papers[8,9,17,19,20,24] but we feel that the reader will have an easier time if we repeat some of this in our notation.

Recently, Felderhof and Cichocki[6,7,29] have developed a numerical scheme to calculate the electronic spectrum of nopolar hard sphere fluids. They were able to determine the spectral density in the Stieltjes representation of the dielectrical constant. This method is based on the determination of moments using Monte Carlo or molecular dynamics simulations and using these moments in Padé approximates of continued fraction representations. This method is not easily generalized to clusters, solutions or anisotropic fluids; moreover, it is not a general procedure for determining other thermal properties of polarizable fluids by simulation.

The approach we pursue in this paper and elsewhere[25,30,31] is based on the fact that all the equilibrium and dynamical properties of systems composed of Drude oscillators can be formulated as a matrix theory. Usually the dispersion oscillator frequency ω_0 is assumed to be high compared to the characteristic time scale of the nuclear motion so that the varing dipole can quickly respond to the changing environment, and a Born–Oppenheimer approximation is valid. We apply matrix techniques to the simulation of fluids and clusters and to the determination of the polarization spectrum in a variety of complicated circumstances. We call this the matrix Monte Carlo method. The numerical solution of the absorption spectrum reduces to an eigenvalue problem. The method of matrix diagonalization is very general and versatile. One can treat clusters, mixtures, and anisotropic liquids (discussed in another paper) by matrix operations, systems that do not lend themselves to the Felderhof treatment. Not only is this scheme practical but it should also lends itself to parallel algorithms.

In Sec. III we use the matrix formulation to derive the generalized Clausius–Mossotti equation for the dielectric constant of polarizable–dipolar fluids. In Sec. IV an approximate expression for the the dielectric constant of polar–polarizable systems is derived. Section V A establishes a simple identity which is used to derive the self-consistent equation for the renormalized polarizability, the screening function of charges and permanent multipole solutes, and the dielectric constant (see Secs. V B–V E). In Sec. VI methods are introduced, based on the matrix formulation, for performing Monte Carlo Simulations of polarizable fluids. In Sec. VII A the results of the MSA theory are compared with matrix Monte Carlo simulations. It is found that the MSA theory dielectric constant of polar polarizable fluids at high molecular polarizability deviates significantly from the simulation. Finally in Sec. VII C comparison of theory and simulation for the nonpolar polarizable fluids is discussed.

II. MATRIX FORMULATION OF A THEORY OF POLAR POLARIZABLE FLUIDS

Consider an axially symmetric molecule. In the body-fixed coordinate frame in which the principal axis (the direction of the permanent dipole) is labeled z and the two other orthogonal axes are labeled x and y, the dimensionless polarizability tensor, $\mathscr{C}'$, is

$$\mathscr{C}'=\frac{1}{\alpha}\begin{pmatrix}\alpha_{xx} & 0 & 0\\ 0 & \alpha_{yy} & 0\\ 0 & 0 & \alpha_{zz}\end{pmatrix}, \tag{2.1}$$

where $\alpha_{zz}=\alpha_{\parallel}$ and $\alpha_{xx}=\alpha_{yy}=\alpha_{\perp}$, and the polarizability matrix in the body-fixed frame is $\alpha\mathscr{C}'$. In the laboratory fixed coordinate frame the polarizability matrix of a Drude molecular ellipsoid labeled i is $\alpha\mathscr{C}_i$ in which matrix $\mathscr{C}_i$ is related to $\mathscr{C}'$ through a transformation $\mathscr{C}_i=\mathscr{R}_i^T\mathscr{C}'\mathscr{R}_i$, where the rotational matrix $\mathscr{R}_i$ is

$$\mathscr{R}_i(\theta_i,\phi_i)=\mathscr{R}(\theta_i)\mathscr{R}(\phi_i)=\begin{bmatrix}\cos(\phi_i) & \sin(\phi_i) & 0\\ -\cos(\theta_i)\sin(\phi_i) & \cos(\theta_i)\cos(\phi_i) & -\sin(\theta_i)\\ -\sin(\theta_i)\sin(\phi_i) & \sin(\theta_i)\cos(\phi_i) & \cos(\theta_i)\end{bmatrix} \tag{2.2}$$

in which θ_i and ϕ_i are the Euler angles formed by the body-fixed reference frame of molecule i with respect to the lab-fixed reference frame.

The internal Hamiltonian of one Drude molecule with an embedded permanent dipole, $\mathbf{m}_i$, in an electrical field, $\mathbf{E}^0$, is then

$$\begin{aligned}H&=H_0(\mathbf{p}_i,\boldsymbol{\pi}_i)-(\mathbf{p}_i+\mathbf{m}_i)\cdot\mathbf{E}_i^0\\&=\alpha\omega_0^2\frac{\boldsymbol{\pi}_i\cdot\mathscr{C}_i\cdot\boldsymbol{\pi}_i}{2}+\frac{\mathbf{p}_i\cdot\mathscr{C}_i^{-1}\cdot\mathbf{p}_i}{2\alpha}-(\mathbf{p}_i+\mathbf{m}_i)\cdot\mathbf{E}_i^0,\end{aligned} \tag{2.3}$$

where $\mathbf{p}_i$ is the instantaneous dipole and $\boldsymbol{\pi}_i$ is its conjugate momentum defined as $\boldsymbol{\pi}_i=\mathscr{C}_i^{-1}\cdot\dot{\mathbf{p}}_i/\alpha\omega_0^2$, and where $\mathbf{m}_i=m\mathbf{u}_i$ is the permanent dipole where m is the permanent dipole moment and $\mathbf{u}_i$ is a unit vector specifying the orientation of the permanent dipole. The expectation value of the dipole vector in an applied field is easily found to linear terms in the field,

$$\langle(\mathbf{p}_i+\mathbf{m}_i)\rangle=\alpha\mathscr{C}\mathbf{E}_i^0+\beta\frac{m^2}{3}\mathbf{E}_i^0, \tag{2.4}$$

where the total dipole is simply the sum of the induced dipole and the average field oriented permanent moment as if these contributions contribute independently, a result which is valid in the gas phase.

The Hamiltonian for a fluid composed of N axially symmetric Drude molecules is then

$$\begin{aligned}H=&\sum_{i=1}\left(\frac{P_i^2}{2M_i}+\frac{J_i^2}{2I_i}\right)+\sum_{i>j}U_0(\mathbf{R}_{ij},\mathbf{u}_i,\mathbf{u}_j)\\&+\sum_i H_0(\mathbf{p}_i,\boldsymbol{\pi}_i)-\sum_{i>j}(\mathbf{p}_i+\mathbf{m}_i)\cdot\mathscr{T}_{ij}\cdot(\mathbf{p}_j+\mathbf{m}_j)\\&-\sum_i(\mathbf{p}_i+\mathbf{m}_i)\cdot\mathbf{E}_i^0,\end{aligned} \tag{2.5}$$

where $\{P_i,J_i\}$ are, respectively, the linear and angular momenta of the molecule, $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$ is the vector connecting particle i to particle j, $U_0(\mathbf{R}_{ij},\mathbf{u}_i,\mathbf{u}_j)$ is the short range interaction potential between atoms i and j, arising from the overlap interactions between the atoms, and where the dipole–dipole propagator is

$$T_{ij}^{\mu\nu}=\frac{3R_{ij}^{\mu}R_{ij}^{\nu}-\delta^{\mu\nu}R_{ij}^2}{R^5}. \tag{2.6}$$

Tensors and matrices in this paper are represented by calligraphic symbols; $\mathscr{I}$ is the identity tensor or matrix; the upper indices $\mu\nu$ stand for coordinate components; the lower indices i or j stand for particles.

The dielectric response of polar polarizable fluids reflects two time scales, a slow time scale characterizing the reorientations of the permanent dipoles and a fast time scale characterizing the response of the embedded Drude oscillators. Thus the frequency dependent dielectric constant will reflect this separation of time scales by having low frequency bands arising from the reorientation of the permanent dipoles (rotational relaxation) and high frequency bands corresponding to charge redistribution in the molecules. The zero frequency (static) dielectric constant will of course have contributions from both of these time scales but usually the contribution from the permanent dipoles will dominate. Given the separation in time scales, the charge redistribution should rapidly follow changes in the nuclear positions and changes in the orientations of the permanent dipoles. The system should be well approximated by the adiabatic approximation, that is, the Born–Oppenheimer approximation.[32,31]

In the adiabatic approximation, the nuclear degrees of freedom need not be treated as dynamical variables. Thus the conjugate momenta of the nuclear positions and orientations in Eq. (2.5) are omitted giving the Born–Oppenheimer Hamiltonian

$$H_{\mathrm{BO}}=\sum_{i>j}U_0(\mathbf{R}_{ij},\mathbf{u}_i,\mathbf{u}_j)+H_{\mathrm{DO}}, \tag{2.7}$$

where the Drude oscillator Hamiltonian is,

$$\begin{aligned}H_{\mathrm{DO}}=&\sum_i H_0(\mathbf{p}_i,\boldsymbol{\pi}_i)-\sum_{i>j}(\mathbf{p}_i+\mathbf{m}_i)\cdot\mathscr{T}_{ij}\cdot(\mathbf{p}_j+\mathbf{m}_j)\\&-\sum_i(\mathbf{p}_i+\mathbf{m}_i)\cdot\mathbf{E}_i^0.\end{aligned} \tag{2.8}$$

The first term U_0 in Eq. (2.7) determines the distribution function of the nuclear configurations and the second term H_{DO} determines the dynamics of the system. The dynamics of the instantaneous dipoles for each nuclear configuration is averaged over all the possible configurations. This gives the heterogeneous band shape.

The expectation value of the observable, $O(\{R_i\},\{u_i\},\{p_i\},\{\pi_i\})$ is

$$\langle O\rangle=\frac{\int d\{R_i\}d\{u_i\}d\{p_i\}d\{\pi_i\}O(\{R_i\},\{u_i\},\{p_i\},\{\pi_i\})e^{-H_{\mathrm{BO}}/kT}}{\int d\{R_i\}d\{u_i\}d\{p_i\}d\{\pi_i\}e^{-H_{\mathrm{BO}}/kT}}, \tag{2.9}$$

where the denominator in Eq. (2.9) is the canonical partition function, Z_{BO} in the BO approximation. It is a simple matter to express Z_{BO} as

$$\begin{aligned}Z_{\mathrm{BO}}=&\int d\{R_i\}d\{u_i\}Z_{\mathrm{DO}}(\{R_i\},\{u_i\})\\&\times\exp\left[-\beta\sum_{i>j}U(\mathbf{R}_{ij},\mathbf{u}_i,\mathbf{u}_j)\right],\end{aligned} \tag{2.10}$$

where $Z_{\mathrm{DO}}(\{R_i\},\{u_i\})$ is the partition function of the Drude oscillators for a fixed nuclear configuration.

Because H_{DO} is quadratic in both $\{p_i\}$ and $\{\pi_i\}$, the multivariate Gaussian integral can be evaluated exactly giving,

$$\begin{aligned}&Z_{\mathrm{DO}}(\{R_i\},\{u_i\})\\&\quad=\int d\{p_i\}d\{\pi_i\}\exp[-\beta H_{\mathrm{DO}}]\\&\quad=Z'\left(\frac{1}{\det\mathscr{C}\mathscr{A}}\right)^{1/2}\exp\left\{\frac{\beta}{2\alpha}[(\mathbf{m}\mathscr{C}^{-1}+\alpha\mathbf{E}^0)\cdot\mathscr{A}^{-1}\right.\\&\quad\quad\left.\cdot(\mathscr{C}^{-1}\mathbf{m}+\alpha\mathbf{E}^0)-\mathbf{m}\mathscr{C}^{-1}\mathbf{m}]\right\},\end{aligned} \tag{2.11}$$

where Z' is an irrelevant prefactor, $\mathscr{C}$ is a $3N\times 3N$ matrix with each diagonal block given by $\mathscr{C}^{\mu\nu}_{ij}=\mathscr{C}^{\mu\nu}_{i}\delta_{ij}$, and $\mathscr{A}$ is a $3N\times 3N$ matrix defined as

$$\mathscr{A}=\mathscr{C}^{-1}-\alpha\mathscr{T}. \tag{2.12}$$

This definition of $\mathscr{A}$ will be particularly convenient for the calculation of the electronic absorption spectrum of liquid crystals, a subject addressed in another paper. For spherical particles, $\mathscr{A}$ takes the form of $\mathscr{A}=\mathscr{I}-\alpha\mathscr{T}$ which is useful in the matrix formulation of the MSA theory, a subject discussed later.

It is simple to show that the potential of mean force for the nuclear coordinates in the BO approximation is[31]

$$\begin{aligned} W(R_i,u_i)= & \sum_{i>j} U_0(\mathbf{R}_{ij},\mathbf{u}_i,\mathbf{u}_j)+\frac{1}{2}kT\ln[\det(\mathscr{A})] \\ & -\frac{1}{2\alpha}\sum_{i,j}[(\mathbf{m}\mathscr{C}^{-1}+\alpha\mathbf{E}^0)\cdot\mathscr{A}^{-1} \\ & \cdot(\mathscr{C}^{-1}\mathbf{m}+\alpha\mathbf{E}^0)-\mathbf{m}\mathscr{C}^{-1}\mathbf{m}], \end{aligned} \tag{2.13}$$

where the second term arises from the prefactor $[\det\mathscr{A}]^{1/2}$ in Eq. (2.11).

The second term in Eq. (2.13) gives the classical many-body dispersion energy of the system which is small because the vibrational amplitudes of the Drude oscillators are very small, $O(\sqrt{kT})$. Zero point fluctuations in quantum systems give large amplitudes and correspondingly much larger dispersion interactions (see Ref. 30). In most simulations only the two-body part of the dispersion interaction is usually included by incorporating it into the simple pairwise potentials but it should be recognized that the above expression contains many-body effects to all orders.

The last term is the polarization energy of the system in the external field. For a given nuclear configuration, we can calculate the polarization energy. This expression has been used in simulations of an electron in polarizable fluids like water and xenon. Although the electron is a quantum particle, the use of Eq. (2.13) can be justified if the quantum Drude oscillators are high frequency oscillators. This topic will be discussed in the context of the screening function in a forthcoming paper.[31]

As can be seen here and later on, all the relevant quantities can be determined by applying proper matrix techniques. In this paper and other papers[25,30,31] these matrices are evaluated both analytically and numerically.

III. THE DIELECTRIC CONSTANT

Because the molecular reorientational relaxation is much slower than the electronic relaxation, the high frequency dielectric response is only determined by the spontaneous fluctuations of the Drude oscillators. The static response is determined by both the fluctuating dipoles and the permanent dipoles. In the rest of the paper, we focus our attention on the calculation of the static response, the dielectric constant ϵ.

Linear response theory gives the average dipole in a weak inhomogeneous static electric field. Expanding Eq. (2.11) to linear order in the external field $\mathbf{E}^0$ yields

$$\langle\mathbf{p}_i+\mathbf{m}_i\rangle=\alpha\langle\mathscr{A}^{-1}\rangle_{ij}\mathbf{E}^0_j+\beta\langle\delta\mathbf{m}'\delta\mathbf{m}'\rangle_{ij}\mathbf{E}^0_j, \tag{3.1}$$

where

$$\begin{aligned} \mathbf{m}' &=\mathscr{A}^{-1}\mathscr{C}^{-1}\mathbf{m}, \\ \delta\mathbf{m}' &=\mathbf{m}'-\langle\mathbf{m}'\rangle, \end{aligned} \tag{3.2}$$

is the polarizability renormalized permanent dipole vector and the corresponding fluctuation. For an orientational disorder system, we have $\langle\mathbf{m}'\rangle=\langle\mathbf{m}\rangle=0$ when the external field is absent. As usual repeated indices are to be summed over. The matrix $\alpha\langle\mathscr{A}^{-1}\rangle_{ij}$ in Eq. (3.1) defines a polarizability response matrix to the external static field. The angular bracket denotes an average over the nuclear configurations specified by the Boltzmann distribution function of the nuclear positions and molecular orientations, $\exp[-\beta U]$, where the total potential energy of a particular configuration is

$$U=\sum_{i>j} U_0(\mathbf{R}_{ij},\mathbf{u}_i,\mathbf{u}_j)-\frac{1}{2}\sum_{ij}\mathbf{m}_i(\mathscr{T}\cdot\mathscr{A}^{-1}\cdot\mathscr{C}^{-1})_{ij}\mathbf{m}_j \tag{3.3}$$

which is the potential of mean force for the nuclear configuration when the external field is absent.

In general, the dielectric permittivity ϵ is defined as

$$\epsilon\mathbf{E}=\mathbf{E}+4\pi\mathbf{P}, \tag{3.4}$$

where the polarization density is

$$\mathbf{P}(\mathbf{r})=\left\langle\sum_i(\mathbf{p}_i+\mathbf{m}_i)\delta(\mathbf{r}-\mathbf{r}_i)\right\rangle. \tag{3.5}$$

For a homogeneous isotropic fluid, the polarization density becomes a constant vector $\mathbf{P}=\rho\langle(\mathbf{p}+\mathbf{m})\rangle$ directed along the external field. In anisotropic fluids (liquid crystals) the dielectric permittivity will be an axially symmetric tensor and the polarization density can be directed along a direction different than the external field.

The Maxwell field $\mathbf{E}$ differs from the applied external field $\mathbf{E}^0$ because it includes the electric field of the induced dipoles. Consider a large spherical sample of polarizable material immersed in a medium of dielectric constant ϵ_0.[4,29] It is a standard exercise to solve the Maxwell equations for this system and obtain an expression for the dielectric constant of the material,

$$\frac{(\epsilon-1)(2\epsilon_0+1)}{(\epsilon+2\epsilon_0)}=4\pi\rho\left(\alpha g_1+\frac{\beta m^2}{3}g_2\right) \tag{3.6}$$

in which α is the average of the trace of the polarizability matrix $\alpha\mathscr{C}$ given by

$$\alpha=\frac{\alpha_{xx}+\alpha_{yy}+\alpha_{zz}}{3}, \tag{3.7}$$

and g_1 and g_2 are the Kirkwood g-factors defined individually as

$$g_1(\epsilon_0)=\lim_{N\to\infty}\left\langle\frac{\Sigma_\mu\Sigma_{ij}(A^{-1})^{\mu\mu}_{ij}}{3N}\right\rangle, \tag{3.8}$$

and

$$g_2(\epsilon_0)=\lim_{N\to\infty}\left\langle\frac{\Sigma_\mu\Sigma_{ij}\delta m_i'^\mu\delta m_j'^\mu}{Nm^2}\right\rangle. \tag{3.9}$$

In this matrix formulation the polarizability α does not only contribute to the first term of Eq. (3.6) but also modulates the permanent dipole **m** by Eq. (3.2). Just as many-body interactions yield a renormalized polarizability which is larger than the original bare polarizability it is also expected that these interactions will lead to a larger effective interaction of two permanent dipoles which depends nonlinearly on the polarizability.

The expression for the dielectric constant, Eq. (3.6), is very general. In the limit $\alpha\to 0$ it reduces to the dielectric constant of a nonpolarizable dipolar fluid; in the limit $m\to 0$ it reduces to the dielectric constant of a polarizable nonpolar fluid. For an isotropic fluid, the matrix $\mathscr{C}$ reduces to the identity matrix $\mathscr{I}$ and the intermolecular potential, $U_0(\mathbf{R}_{ij},\mathbf{u}_i,\mathbf{u}_j)$, becomes a central potential.

It is important to note that the left-hand side of Eq. (3.6) has factors dependent on the boundary conditions, whereas the right-hand side seemingly does not. Obviously, since Eq. (3.6) relates the macroscopic quantities on the left-hand side to the microscopic quantities on the right-hand side, the dependence on boundary conditions must appear in the matrix formulation.[14,29,33]

IV. AN APPROXIMATE THEORY FOR POLAR–POLARIZABLE FLUIDS

Pratt and Hoye and Stell introduced the MSA theory for nonpolar polarizable fluids based on a Drude oscillator with dipole–dipole interactions.[13,15,16] The dipole moment fluctuation was treated using classical statistical mechanics. The graph theoretical studies of the internal degrees of freedom, pioneered by Pratt and Chandler,[34–36] prove to be very useful for treating this problem and related problems such as the calculation of the electronical band structure and phonon spectrum in liquids as was already recognized by Stratt.[21,28,37] We have shown that these systems can also be investigated both numerically and analytically using a matrix formulation. The matrix method is a direct and simple alternative. The two approaches are essentially equivalent and complementary in many aspects.

Here we generalize Pratt's approach to polar–polarizable fluids. Both the permanent dipole and the fluctuating dipole contribute to the dielectric constant. In the mean spherical approximation theory the fluid molecules are assumed to have an effective dipole moment. For a particular molecule, the probability distribution of the fluctuating dipole is described by the excess chemical potential of an intramolecular degree of freedom solvated in the effective polar fluid. However because this particular molecule is no different from the rest of molecules in the fluid, the average of the fluctuating total dipole moment is set equal to the effective dipole moment. This strategy leads to a self-consistent equation for the effective dipole moment. If m_e is the effective dipole moment in a homogeneous, isotropic fluid, the excess chemical potential of the molecule solvated in the dipolar solvent can be calculated by the standard charging method,

$$\Delta\mu_p=\int_m^{p+m}dp_1\left\langle\frac{\partial\phi}{\partial p_1}\right\rangle, \tag{4.1}$$

where ϕ is the interaction energy between the chosen molecule and the rest of the particles in the fluid, that is,

$$\phi=-\sum_{i=2}^{N}\mathbf{p}_1\cdot\mathscr{T}_{1i}\cdot\mathbf{p}_i. \tag{4.2}$$

In the mean spherical approximation, the quantity $\langle\partial\phi/\partial p_1\rangle$ can be related to the average dipolar interaction energy by

$$\left\langle\frac{\partial\phi}{\partial p_1}\right\rangle=\frac{2p_1}{m_e^2}\langle U/N\rangle_e, \tag{4.3}$$

where $\langle U/N\rangle_e$ is the average dipolar energy in the effective dipolar fluid.

In Appendix A the internal energy was identified as Σ, the sum of the simply connected diagrams, that is,

$$\Sigma=-\frac{2}{3}\left\langle\frac{\beta U_e}{N}\right\rangle \tag{4.4}$$

in which Σ is then approximated by the first two diagrams

$$\Sigma\approx\frac{t_2}{1-t_3/t_2}, \tag{4.5}$$

where t_2 and t_3 are discussed in the Appendix. Also the effective polarizability α_e is related to the effective dipole moment by the well-known expression $\alpha_e=\beta m_e^2/3$. Now, it is a simple matter to integrate Eq. (4.1) to find that

$$\Delta\mu_p=-\frac{p^2+2pm}{2\alpha_e}\Sigma. \tag{4.6}$$

According to Chandler and Pratt,[34,35] the distribution function of the fluctuating dipole is

$$f(p)=\exp\left[-(\beta)\left(\frac{p^2}{2\alpha}+\Delta\mu_p\right)\right]\Bigg/\int dp\exp\left[-(\beta)\left(\frac{p^2}{2\alpha}+\Delta\mu_p\right)\right] \tag{4.7}$$

in which the denominator is the normalization factor. From this it follows that the effective dipole moment is

$$\langle(m+p)^2\rangle=\int dpf(p)(m+p)^2=m_e^2. \tag{4.8}$$

Combining Eqs. (4.6), (4.7), and (4.8) leads to self-consistent equations for the effective polarizability α_e,

$$\bar{\alpha}_i=\left(\frac{\alpha_i'}{\alpha_i}\right)m_i^2\beta+\alpha_i', \tag{4.9}$$

where α_i' is given by

$$\frac{1}{\alpha_i'}=\frac{1}{\alpha_i}-\frac{\Sigma}{\alpha_e}, \tag{4.10}$$

and the effective polarizability is the average of the trace

$$\alpha_e = \frac{\Sigma_i \bar{\alpha}_i}{3}. \tag{4.11}$$

The index i refers to the three components in the body-fixed frame in which $m_1 = m_2 = 0$, $m_3 = m$, and $\alpha_1 = \alpha_2 = \alpha_\perp$, $\alpha_3 = \alpha_\parallel$. The above equations will reduce to the self-consistent equation of Pratt if the permanent dipole m_i vanishes.

Alternative formulations of the theory of polar–polarizable fluids are available.[10,38] Hoye and Stell[3] have presented a more sophisticated dielectric theory of polar molecules with fluctuating polarizability. These authors showed that the dielectric constant can be calculated in the mean spherical approximation and that the single superchain approximation and the results for polar–polarizable fluids are equivalent to an effective dipolar fluid. More details can be found in their paper and other references cited in this section.

The method we present here is a simple extension of the work on nonpolar polarizable fluids. Moreover the matrix formulation makes it possible to perform a simulation of the full spectrum for comparison with MSA theory.

The self-energy term Σ of Eq. (4.5) is calculated using the effective dipole moment m_e. Because Σ is a positive monotonically increasing function of the density, $\alpha_i' > \alpha_i$, and the contribution from the permanent dipole as well as the contribution from the fluctuating dipole is magnified. The effective dipole moment and hence the dielectric constant thus increases strongly with the density and the polarizability. Furthermore the polarizability anisotropy, $\alpha_\parallel > \alpha_\perp$, will further increase the dielectric constant.

Once Eq. (4.9) is solved for m_e, Wertheim's expression for the dielectric constant of polar fluids is used to determine the dielectric constant of polar–polarizable fluids.[4,14,39]

V. MATRIX FORMULATION OF NONPOLAR POLARIZABLE FLUIDS

The above results simplify considerably when applied to a nonpolar fluid of isotropic Drude oscillators. Then $\mathbf{m}_i = 0$, $\mathscr{C}' = \mathscr{I}$, $\mathscr{A} = \mathscr{I} - \alpha\mathscr{T}$. The Drude oscillator Hamiltonian of fluid is then

$$H_{\mathrm{DO}} = \sum_i \frac{\dot{\mathbf{p}}_i^2}{2\alpha\omega^2} + \sum_i \frac{\mathbf{p}_i^2}{2\alpha} - \sum_{i>j} \mathbf{p}_i \cdot \mathscr{T}_{ij} \cdot \mathbf{p}_j - \sum_i \mathbf{p}_i \cdot \mathbf{E}_i^0, \tag{5.1}$$

where $\mathbf{E}^0$ is the external field, $\{\mathbf{p}_i, \dot{\mathbf{p}}_i\}$ are the instantaneous dipoles and their associated velocities, the dipole–dipole propagator $\mathscr{T}$ is given in Eq. (2.6).

The response of particle i to an external field field $\mathbf{E}_j^0$ applied at j, given by Eq. (2.4), becomes

$$\mathbf{p}_i = \alpha \mathscr{A}_{ij}^{-1} \cdot \mathbf{E}_j^0, \tag{5.2}$$

where the matrix $\mathscr{A}$ in Eq. (2.12) becomes

$$\mathscr{A} = \mathscr{I} - \alpha\mathscr{T}. \tag{5.3}$$

This contains effects due to the interacting Drude oscillator system. In a neat isotropic nonpolar fluid all of the particles are identical so that the thermal average of $\mathscr{A}$ matrix [see Eq. (5.3)] over nuclear positions is such that all $3N$ diagonal elements must be equal. If these elements are summed and divided by $3N$ one obtains the average effective polarizability of an atom in the fluid. This is the renormalized polarizability $\bar{\alpha}$,

$$\bar{\alpha} = \lim_{N \to \infty} \frac{1}{3N} \alpha \langle \mathrm{Tr}\, \mathscr{A}^{-1} \rangle = \alpha \langle\langle \mathscr{A}_{11}^{-1} \rangle\rangle, \tag{5.4}$$

where the $\langle\langle \cdots \rangle\rangle$ designates an average over the N particles and where the limit is the thermodynamic limit. In an isotropic fluid $\bar{\alpha}$ is a spherical tensor and the renormalized polarizability is then proportional to the trace of the polarizability matrix over particle indices and Cartesian components. It is important to note that this renormalized molecular polarizability is not an observable. It is of interest because in MSA it satisfies a self-consistent equation from which it can be determined.[13] In the Appendix A we present a detailed diagrammatic study of the renormalized polarizability.

All the results for the classical Drude system can be easily transformed into the quantum mechanical version with the help of a normal mode transformation. Full quantum mechanical analysis leads to the calculation of the many-body dispersion interaction[30] and the quantum solvation of an electron in the polarizable fluid which will be discussed in a forthcoming paper.[31]

Section V A establishes two simple identities which are then used to derive the self-consistent equation for the renormalized polarizability in Sec. V B. Section V C gives the screening function of charges and permanent multipole solutes, and the dielectric constant is given in Sec. V D. Finally in Sec. V E we show how to determine the dynamics and spectral line shapes in MSA fluids.

A. Simple identities

Wertheim found an analytical solution to the MSA theory of a fluid of hard spheres with embedded permanent dipoles.[14] Although the MSA theory is not a quantitatively satisfactory theory, Wertheim's work has had a great influence on later work in the field. Pratt[13] then showed that in the MSA a nonpolar polarizable fluid with renormalized polarizability $\mathscr{A}$ is equivalent to a polar fluid in which the spheres have embedded permanent dipole moments of magnitude,

$$|\mathbf{p}|^2 = 3\frac{\bar{\alpha}}{\beta} \tag{5.5}$$

that is with permanent moments equal to the root mean square dipole moment of the induced dipole in the nonpolar fluid.

In this section we exploit Pratt's observation to establish a formal connection between the matrix theory for $\mathscr{A}^{-1}$ and the MSA. This connection proves to be particularly fruitful. It leads to a simple method for deriving self-consistent equations, deriving expressions for screening functions for charges in polarizable fluids, and for determining the dielectric constant. This approach is particularly simple and rewarding.

If a tagged particle, labeled 0 has a fixed dipole $\mathbf{p}_0$, what is the average induced dipole of another oscillator at another position? The induced dipoles satisfy a set of field equations,

$$\mathbf{p}_i=\alpha(\mathscr{T}_{i0}\mathbf{p}_0+\mathscr{T}_{ij}\mathbf{p}_j), \tag{5.6}$$

where $\mathscr{T}_{i0}\mathbf{p}_0$ is the field at i due to the permanent dipole $\mathbf{p}_0$ and $\mathscr{T}_{ij}\mathbf{p}_j$ is the field due to all the other induced dipoles (repeated indices imply summation). The matrix solution for $\mathbf{p}_i$ is

$$\mathbf{p}_i=(\mathscr{I}-\alpha\mathscr{T})^{-1}_{ij}\alpha\mathscr{T}_{j0}\mathbf{p}_0, \tag{5.7}$$

where the matrix $(\mathscr{I}-\alpha\mathscr{T})$ differs from $\mathscr{A}$ of Eq. (5.3) because the index zero is excluded from the matrix. Thus $(\mathscr{I}-\alpha\mathscr{T})$ is a $(3N-3)\times(3N-3)$ matrix where none of the indices can be the index for particle 0. Now from Wertheim's MSA theory of polar hard sphere fluids a dipole $\mathbf{p}_0$ on one particle gives an aligned dipole

$$\langle\mathbf{p}_i\rangle=\tfrac{1}{3}\mathscr{H}_{i0}\mathbf{p}_0 \tag{5.8}$$

on another particle in which $\mathscr{H}$ is the dipolar pair correlation function for the equivalent dipolar fluid. The tensor $\mathscr{H}$ has the explicit form,[14]

$$\mathscr{H}=h^{\Delta}\mathscr{I}+h^{D}\mathscr{D}, \tag{5.9}$$

where $\mathscr{D}$ is the tensor defined as

$$\mathscr{D}^{\mu\nu}_{ij}=(3R^{\mu}_{ij}R^{\nu}_{ij}-R^2_{ij}\delta_{\mu\nu})/R^2_{ij} \tag{5.10}$$

and where h^{Δ} and h^{D} are given in closed form by Wertheim.[14]

Eliminating $\mathbf{p}_i$ between Eqs. (5.8) and (5.7) gives

$$\langle(\mathscr{I}-\alpha\mathscr{T})^{-1}\alpha\mathscr{T}\rangle=\tfrac{1}{3}\mathscr{H}. \tag{5.11}$$

The matrix $\mathscr{A}$ includes the zero index particle because the sites associated with both endings are polarizable. In the MSA this factor is accounted for by replacing the bare polarizability α of particle 0 by the renormalized polarizability $\bar{\alpha}$. Thus the off-diagonal element (O.D.) of $\mathscr{A}$ can be identified as

$$\langle\alpha\mathscr{A}^{-1}\rangle_{\text{O.D.}}=\tfrac{1}{3}\bar{\alpha}\mathscr{H}. \tag{5.12}$$

This identity has been used by Chen and Stratt[9] to obtain the off-diagonal contribution of polarization matrix to the absorption spectrum.

These two identities establish a connection between the dipolar MSA and the matrix solution to the polarizable fluid. Some interesting results follow from this identity.

B. Self-consistent equation for renormalized polarizability

Equations (5.12) and (5.11) provide a simple means for deriving the self-consistent equation of Pratt. The diagonal element of the $\mathscr{A}^{-1}$ matrix can be expressed in terms of the off-diagonal elements by using simple operator identities like $(\mathscr{I}-\alpha\mathscr{T})^{-1}(\mathscr{I}-\alpha\mathscr{T})=\mathscr{I}$. For example,

$$(\mathscr{I}-\alpha\mathscr{T})^{-1}_{11}=1+\alpha\mathscr{T}_{1i}\cdot(\mathscr{I}-\alpha\mathscr{T})^{-1}_{i1} \tag{5.13}$$

which can be expressed as

$$\alpha\mathscr{A}^{-1}_{11}=\alpha+\alpha\sum_{j}\mathscr{T}_{1j}\cdot\alpha\mathscr{A}^{-1}_{j1}. \tag{5.14}$$

Substitution of Eqs. (5.12) and (5.9) into Eq. (5.14) followed by contraction of the tensors then allows this to be written in integral form,

$$\frac{\bar{\alpha}}{\alpha}=1+\rho\int g(r)\mathscr{T}\langle\alpha\mathscr{A}^{-1}\rangle_{\text{O.D.}}d\mathbf{r}. \tag{5.15}$$

On substituting Eq. (5.12), one easily obtains,

$$\frac{\bar{\alpha}}{\alpha}=1+\rho\frac{\bar{\alpha}}{3}\int g(r)\frac{2}{r^3}h^{D}d\mathbf{r} \tag{5.16}$$

which is exactly the equation for $\bar{\alpha}$ obtained by Pratt.

Thus in a very simple and straightforward way, the self-consistency of the matrix expansion leads to the self-consistent equation for the renormalized polarizability which can otherwise be determined only from a lengthy graphical reduction procedure as discussed in the Appendix.

C. The screening function for solvated permanent multipoles

A problem of recent interest is that of electron or ion solvation in a polarizable fluid. It has been found that, if the polarizability is large enough, the electron solvation process is greatly affected by many-body polarization effects.[40,41] Here we consider the classical theory. If one of the Drude oscillators is replaced by a point charge or a point dipole or any multipole, what is the electrostatic field in the fluid? The field equations are then[12]

$$\mathbf{E}=\mathbf{E}^0+\alpha\mathscr{T}\cdot\mathbf{E}, \tag{5.17}$$

where $\mathbf{E}^0$ is the bare field introduced by the electrical source, be it a charge or permanent multipole, and the term $\alpha\mathscr{T}\cdot\mathbf{E}$ is the field due to induced dipoles. The solution of Eq. (5.17) can be substituted back into itself to give,

$$\mathbf{E}=\mathbf{E}^0+(\mathscr{I}-\alpha\mathscr{T})^{-1}\cdot\alpha\mathscr{T}\cdot\mathbf{E}^0. \tag{5.18}$$

By combining the above solution and Eq. (5.11), we calculate the average electric field at the point $\mathbf{r}$ with respect to the permanent multipole,

$$\langle\mathbf{E}(\mathbf{r})\rangle=\mathbf{E}^0(\mathbf{r})+\frac{\rho}{3}\int\mathbf{E}^0(\mathbf{r}')g(\mathbf{r}')\cdot\mathscr{H}(\mathbf{r}-\mathbf{r}')d\mathbf{r}'. \tag{5.19}$$

This is a self-consistent equation for the average electric field. Here $\rho g(\mathbf{r}')$ is the radial distribution of the atoms at $\mathbf{r}'$ from the multipole. Substitution of Eq. (5.9) gives an equation for the electric field in terms of the functions h^{Δ} and h^{D}. The detailed calculation of the field $\mathbf{E}$ involves Fourier transformation of vectors and tensors and is best left for the Appendix.

Because the quantities are averaged over fluid configurations, the average Maxwell field $\langle\mathbf{E}\rangle$ must be along the same direction as the bare field of the charge. The ratio of the magnitudes of the local to the bare field is defined to be the screening function $f(r)$,

$$f(r)=\frac{|\langle\mathbf{E}\rangle|}{|\mathbf{E}^0|}. \tag{5.20}$$

The polarization energy of the system, Φ_P, in the external field can be found in Ref. 31. A simple approximation is to average this over nuclear configurations keeping particles i and j fixed, that is to replace $A_{i,j}^{-1}$ by its average value $\langle A_{i,j}^{-1}\rangle$. The resulting polarization energy can be expressed in terms of $f(r)$ as follows:

$$\Phi_P=-\frac{1}{2}\sum\alpha\mathbf{E}_i^0\langle\mathscr{A}_{ij}^{-1}\rangle\mathbf{E}_j^0\approx-\frac{1}{2}\sum\alpha f(r_i)(\mathbf{E}_i^0)^2. \tag{5.21}$$

The approach is valid if the polarization field is weak and the many-body correlation functions alter little due to the present of the external field.

D. MSA theory of the dielectric constant

The methods outlined in the previous sections can be used to derive an expression for the dielectric constant of a polarizable fluid. In a constant external field the column vector of induced dipoles is

$$\mathbf{p}=\alpha\mathscr{A}^{-1}\cdot\mathbf{E}^0. \tag{5.22}$$

Taking the average, $\langle\Sigma_{i=1}^N\mathbf{p}_i\delta(\mathbf{r}-\mathbf{r}_i)\rangle$, of the above equation, and applying Eq. (5.12) yields,

$$\mathbf{P}(\mathbf{r})=\langle\mathbf{p}(\mathbf{r})\rangle=\bar{\alpha}\rho\left[\mathbf{E}^0+\frac{\rho}{3}\int\mathscr{H}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{E}^0d\mathbf{r}'\right]. \tag{5.23}$$

Fourier transformation of Eq. (5.23) gives

$$\hat{P}_k=\rho\mathscr{A}\left(1+\frac{1}{3}\rho\hat{\mathscr{H}}_k\right)\cdot\hat{\mathbf{E}}_k^0, \tag{5.24}$$

where all of the quantities with a ^ on them are Fourier transforms of the corresponding spatial properties. According to the definition of the susceptibility $\hat{p}_k=\hat{\chi}_k^0\mathbf{E}_k^0$ we obtain the longitudinal and transverse components of the Fourier transform of the response function,

$$\hat{\chi}_\parallel^0(k)=\rho\bar{\alpha}\left[1+\frac{\rho}{3}(\hat{h}_k^\Delta+2\hat{h}_k^{\mathscr{D}})\right] \tag{5.25}$$

and

$$\hat{\chi}_\perp^0(k)=\rho\bar{\alpha}\left[1+\frac{\rho}{3}(\hat{h}_k^\Delta-\hat{h}_k^{\mathscr{D}})\right]. \tag{5.26}$$

For a homogeneous isotropic fluid, the static susceptibility is,

$$\chi^0=\lim_{k\to0}\frac{1}{3}[2\hat{\chi}_\perp^0(k)+\hat{\chi}_\parallel^0(k)]=\bar{\alpha}\rho\left(1+\frac{\rho\hat{h}^\Delta}{3}\right). \tag{5.27}$$

Finally, combining with Eq. (3.6) and letting $\epsilon_0=\epsilon$, we find

$$\frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon}=\frac{4\pi}{3}\mathscr{A}\rho g_k, \tag{5.28}$$

where g_k is the Kirkwood g-factor given by[14]

$$g_k=1+\frac{1}{3}\rho\hat{h}_{k=0}^\Delta. \tag{5.29}$$

This is the MSA expression for the dielectric constant of polarizable fluid.[14] The Kirkwood g-factor arises from the dipole–dipole interaction between different particles. In the low density limit, $g_k\to1$, the correlation between particles vanishes, and the dielectric constant reduce to a linear summation of contributions from each particles in the fluid.

E. Dynamics and absorption spectrum in the MSA

Chandler *et al.*[17] employed analytical continuation of the Euclidean time quantum response response function to extend Pratt's equilibrium MSA theory[13] to the dynamics and spectrum of a fluid of quantum dispersion oscillators. We follow a similar path to study a system described by a quadratic Hamiltonian. In such systems, the quantum and classical response functions are the same. Since the subject has been explored by several authors,[8,9,17] this section serves as a natural extension of the equilibrium studies and provides an interesting comparison with simulation.

All the operations used in deriving the results of MSA are still valid for the frequency-dependent response functions.[25] Thus, it is a simple matter to generalize the self-consistent equation Eq. (A5) to determine a renormalized frequency dependent polarizability $\bar{\alpha}(\omega)$,

$$\bar{\alpha}(\omega)=\frac{\alpha(\omega)}{1-\frac{\alpha(\omega)}{\bar{\alpha}(\omega)}\Sigma[\bar{\alpha}(\omega)]}, \tag{5.30}$$

where $\alpha(\omega)=\alpha/[1-(\omega/\omega_0)^2]$ is the frequency dependent polarizability of a single Drude oscillator. If the function $\Sigma[\bar{\alpha}(\omega)]$ is again approximated by Eq. (A6), Eq. (5.30) reduces to a quadratic equation. The singularities of $\bar{\alpha}(\omega)$ are simple in a finite system, but turn into a branch cut in the thermodynamic limit. The line spectrum of a finite system is then smeared into a continuous spectrum in the thermodynamic limit. The imaginary part, $\bar{\alpha}(\omega)$ gives the spectrum of polarization fluctuations.

To obtain the frequency dependent dielectric response function $\epsilon(\omega)$, we insert the renormalized polarizability $\bar{\alpha}(\omega)$ into the Kirkwood expression Eq. (5.28). The imaginary part of $\epsilon(\omega)$ is the electronic absorption spectrum due to dipolar excitations in the MSA approximation.

One can immediately recognize the similarity of Eq. (5.30) to the self-consistent equation in the Green function analysis which can be easily recovered by interpreting $\bar{\alpha}$ as the average of the trace, ω^2 as the energy spectrum, Σ and as the self-energy term.[19,20,27,28,37] Essentially, both approaches are equivalent to the random matrix problem which arises because from topological disorder or thermal disorder. The resulting mean field equation always leads to a continuous and broadened spectrum.

We now treat a binary mixture in which the resonant frequencies and the static polarizabilities of the two components are different. This system was not treated before. The average renormalized polarizability $\bar{\alpha}(\omega)$ then becomes the weighed sum of the two components, and the self-consistent equation reads

$$\bar{\alpha}(\omega)=X_1\frac{\alpha_1(\omega)}{1-\frac{\alpha_1(\omega)}{\bar{\alpha}(\omega)}\Sigma[\bar{\alpha}(\omega)]}+X_2\frac{\alpha_2(\omega)}{1-\frac{\alpha_2(\omega)}{\bar{\alpha}(\omega)}\Sigma[\bar{\alpha}(\omega)]},\tag{5.31}$$

where X_1 and X_2 are the mole fractions of the two components and $\alpha_1(\omega)$ and $\alpha_1(\omega)$ are the frequency-dependent polarizabilities of a single Drude oscillator for the two components,

$$\alpha_i(\omega)=\frac{\alpha_i}{1-(\omega/\omega_\zeta)^2}\tag{5.32}$$

in which $\zeta=1,2$ stand for the two components.

VI. MONTE CARLO METHOD FOR SIMULATING POLARIZABLE FLUIDS

The frequency response of a system of Drude oscillators to a time dependent electric field is the same for classical and quantum systems because the Hamiltonian is quadratic.[9,17] A fluid of Drude oscillators driven by a monochromatic electromagnetic field $\mathbf{E}_i(\omega)e^{-i\omega t}$ obeys the set of linear equations of motion,

$$\frac{\ddot{\mathbf{p}}_i}{\omega_i^2}+\mathbf{p}_i-\alpha\mathscr{T}_{ij}\mathbf{p}_j=\alpha\mathbf{E}_i(\omega)e^{-i\omega t},\tag{6.1}$$

where ω_i is the intrinsic frequency of the harmonic oscillator and α is the static polarizability.

The particular solution of Eq. (6.1) gives the frequency dependent response function, or the susceptibility matrix,[6,7,9,17]

$$\chi_{ij}(\omega)=\omega_i\left\langle\frac{\rho\alpha}{\mathscr{W}-\omega^2\mathscr{I}}\right\rangle_{ij}\omega_j,\tag{6.2}$$

where ρ is the density, α is the static polarizability, and the matrix $\mathscr{W}$ is defined as

$$\mathscr{W}_{ij}=\omega_i^2\delta_{ij}-\omega_i\alpha\mathscr{T}_{ij}\omega_j.\tag{6.3}$$

Diagonalization of the matrix $\mathscr{W}$ gives

$$\chi_{ij}(\omega)=\omega_i\left\langle\mathscr{S}\frac{\rho\alpha}{\Lambda-\omega^2\mathscr{I}}\mathscr{S}^{-1}\right\rangle_{ij}\omega_j,\tag{6.4}$$

where $\Lambda_{ij}=\lambda_i\delta_{ij}$ is the diagonal matrix, λ_i is the ith eigenvalue and $\mathscr{S}$ is the transformation matrix. Thus we obtain the power spectrum

$$I(\omega)=\frac{\Sigma_{ij}^{\mu,\nu}\omega\chi''(\omega)}{3N},\tag{6.5}$$

where $\chi''(\omega)$ is the imaginary part of the response matrix. The dielectric constant can be obtained in a similar fashion. The details of the matrix Monte Carlo method for evaluating the susceptibility are given in a previous paper.[25]

Because the dipole–dipole interaction is long ranged, the calculations will be very sensitive to the system size and geometry and thus to the boundary conditions.[14,29,33] The dipole propagator defined in Eq. (2.6) has to be modified depending on the cavity size, L, and the value of dielectric constant of the surrounding medium, ϵ_0. We adopt the Ewald summation technique of deLeeuw, Perram, and Smith.[33] The modified dipole propagator is then,

$$\mathscr{T}_{12}=\frac{1}{L^3}\nabla\nabla\phi_{\text{ew}}(R_{12}/L)-\frac{3}{2\epsilon_0+1}\frac{4\pi}{L^3}\mathscr{I},\tag{6.6}$$

where L is the edge of the cubic system studied and ϕ_{ew} is the Ewald summation,

$$\phi_{\text{ew}}=\sum_{\mathbf{n}\neq 0}\frac{1}{\pi n^2}e^{-(\pi\mathbf{n}/c)^2+i2\pi\mathbf{n}\mathbf{r}}+\sum_{\mathbf{n}'}\frac{\operatorname{erfc}(c|\mathbf{r}+\mathbf{n}'|)}{|\mathbf{n}'+\mathbf{r}|}\tag{6.7}$$

in which c is an arbitrary constant, and erfc is complementary error function. The choice of constant c and the convergence of the series have been discussed in the paper by de Leeuw *et al.* The constant c in our simulations is taken to be $c=4.0$ which is sufficiently large that the only term contributing in the real space part in Eq. (6.7) is $n'=0$, the conventional minimum image term, and the number of reciprocal vectors $\mathbf{n}$ used in the first term of Eq. (6.7) is 124.

To assure the convergence, systems of both 108 particles and 256 particles are simulated were compared and no difference was found at the densities reported here. The step size of the MC move was adjusted to yield a 50% acceptance rate. Initially the system was placed on a fcc lattice and was then equilibrated for 10^5–10^6 configurations. Matrix diagonizations were performed for more than 10^3 noncorrelated liquid configurations to obtain the dielectric constant and spectrum.

VII. RESULTS

A. Polar polarizable fluids

In this section we calculate the dielectric constant of polar–polarizable fluid using an approximate theory and compare the results of this theory to simulations of the fluid.

de Leeuw *et al.*[33] have discussed the Ewald summation technique in great detail. The dielectric constant of the fluid should be invariant to the choice of the dielectric constant ϵ_0 of the surrounding medium. Nevertheless the choice $\epsilon_0=1$ suppresses the dipolar fluctuation more efficiently than other choices of ϵ_0. As long as α and βm^2 are not too large, we run simulations in a surrounding vacuum, $\epsilon_0=1$. In this case Eq. (3.6) reduces to the generalized Clausius Mossotti formula. Fluids consist of hard sphere molecules with dimensionless polarizability, $\alpha^*=\alpha/\sigma^3$, and dimensionless dipole moment defined such that

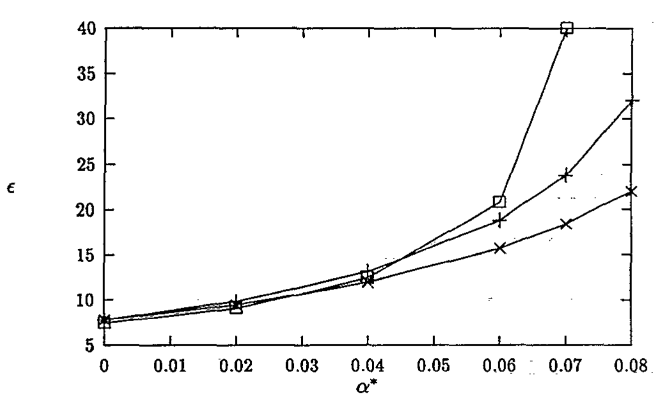

FIG. 1. The dielectric constant of a polar–polarizable fluid plotted as a function of the reduced polarizability α^*. The parameters of the fluids are given in the text. (a) □, the Monte Carlo simulation result for a spherical polar polarizable fluid with $\theta=1.0$ and $\rho^*=0.8$; (b) ×, the MSA result for the same isotropic fluid as in curve (a); (c) +, the MSA result for the anisotropic fluid with $\theta=1.0$ and $\rho^*=0.8$ but with $\alpha_{\parallel}/\alpha_{\perp}=1.44$ where $(\alpha_{\parallel}+2\alpha_{\perp})/3$ is the same as the spherical polarizability used in curve (a).

$\theta=m^2\beta/\sigma^3$, where σ is the hard sphere diameter. For purposes of calibration we simulate the nonpolarizable polar fluid, $\alpha=0$, under the same conditions as in the paper of de Leeuw *et al.*, that is $\rho^*=0.8$ and $\theta=1.0$. The system consists of 108 particles. The nuclear configurations are sampled using metropolis Monte Carlo sampling. The maximum step sizes of tentative moves of the spatial coordinates and the two Euler angles are adjusted to yield an acceptance rate of 50%. The system is equilibrated after 10^6 configurations. In Fig. 1, curve (a) is the dielectric constant for several different values of the polarizability α^*. We observe that the dielectric constant increases quickly at large values of polarizability. This nonlinearly demonstrates the importance of many-body effects in polar–polarizable fluids.

Even though Eq. (3.6) is formulated for the general polarization matrix $\mathscr{C}$, implementation of Monte Carlo simulations is limited by computer capacity. If the polarizability is isotropic as in the above simulation, the matrix $\mathscr{A}$ is independent of molecular reorientations and changes when the nuclear positions are moved. This allows us to invert the matrix approximately 10^3 times during the whole run to attain convergence in reasonable cpu time. For anisotropic polarizability, the matrix $\mathscr{A}^{-1}$ must be updated whenever both the position and orientation are moved because the matrix $\mathscr{A}$ now depends on both the spatial and angular coordinates. The simulation now requires that the matrix be inverted 10^5–10^6 times, a feat requiring the use of a massively parallel computer.

The solution of the Eqs. (4.9), (4.10), and (4.11) gives the predictions of the approximation theory. For comparison, we plot the analytical results for the same conditions as the simulations in curve (b). At low polarizability, the two curves agree reasonably well; at high polarizability, the simulation results are much larger than those predicted by the theory. The discrepancy of the analytical results and simulation results is expected at high polarizability because the mean spherical approximation underestimates the strong coupling between the induced dipoles and permanent dipoles. Curve (c) is the approximation solution for anisotropic polarizability tensor. All the parameters are the same as for curves (a) and (b) except that $\alpha_{\parallel}/\alpha_{\perp}=1.44$. Obviously, curve (c) increases with α much faster than curves (a) and (b). As can be seen from Eq. (3.2), it is mainly the polarizability along the direction of the permanent dipole, $\alpha_{\parallel}$, that renormalizes the permanent dipole moment and thus increases the polarization field. Therefore, it is expected that the larger $\alpha_{\parallel}/\alpha_{\perp}$ is at fixed value of $(\alpha_{\parallel}+2\alpha_{\perp})/3$ the larger will be the dielectric constant ϵ.

From the perspective of the approximation theory, a polar polarizable fluid is equivalent to a polar fluid with an effective dipole moment determined by Eq. (4.8). This indicates that the dielectric constant of a polar–polarizable fluid can be mapped to a corresponding nonpolarizable polar fluid at the same density and temperature but with an effective dipole moment.

All atoms and molecules have induced dipoles due to the electronic fluctuations. The dielectric properties of atoms or spherical molecules are completely determined by fluctuations in the induced dipoles. Strictly speaking, all polar fluids are polarizable but because such fluids are difficult to treat they are often approximated by the rigid dipole approximation. We show here both numerically and analytically how the dielectric constant for polarizable polar fluids increases with polarizability and thereby demonstrate the significance of many-body polarization in polar fluids. Only nonspherical molecules can have a permanent dipole. Strictly speaking, the polarizability of such molecules is anisotropic, that is, charge fluctuations have different amplitudes along and perpendicular to the molecular symmetry axis. Nevertheless if the polarizability is small, its anisotropy can be ignored. Here we present the general formulation for molecules with anisotropic polarizability but we carry out the numerical simulations for the case where the polarizability is isotropic. To assess the importance of polarizability anisotropy we present the analytical results for the more general situation. The calculations of the approximation theory show that the dielectric constant increases with polarizability anisotropy $\alpha_{\parallel}/\alpha_{\perp}$ for fixed value of the trace of the polarizability tensor. This observation gives further convincing evidence of the importance of many-body polarization in the liquid phase.

B. The screening functions

The screening function defined by Eq. (5.20) (and detailed expressions given in the Appendix) is calculated for (a) a permanent point charge and (b) a permanent point dipole in a polarizable hard sphere fluid of reduced density $\rho^*=\rho\sigma^3=0.8$ and reduced polarizability $\alpha^*=\alpha/\sigma^3=0.2$. ($\sigma$ is the hard sphere diameter.) In Fig. 2 curves of the screening functions are plotted vs the distance from the charge or the dipole.

Notice that curve (a) is much lower than curve (b), in other words, the screening function of a point charge is much stronger than that of a point dipole. Obviously the

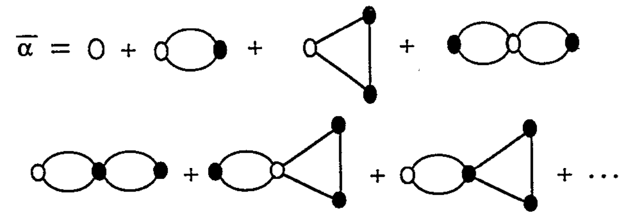

FIG. 2. The screening function defined by Eq. (5.20) for (a) a permanent point charge (the solid curve) and (b) a permanent point dipole (the bold curve) in a polarizable hard sphere fluid of reduced density $\rho^*=\rho\sigma^3=0.8$ and reduced polarizability $\alpha^*=\alpha/\sigma^3=0.2$. ($\sigma$ is the hard sphere diameter.)

screening function for higher order multipoles is successively weaker because each in turn is less capable to polarizing the solvent. On the other hand, the locations of peaks are similar for the two curves because these screening functions are determined by the structure of the solvent. The amplitudes of the screening functions, on the other hand, are determined by the charge distribution of the electrical source.

It should be noted that this MSA theory of screening is different than Lekner's.[42] Lekner's theory is essentially equivalent to applying a superposition approximation to all of the spatial many-body correlation functions of the nuclear coordinates. It only includes chain diagrams whereas the MSA theory includes higher order diagrams and should thus be more accurate than Lekner's.[31] Berne *et al.* have applied the Lekner theory to polarization calculations of the quantum solvation of electrons[40] and compare these to full many-body calculations without the superposition approximation.[43] They show that the Lekner theory is good to within 10%.

C. Results for nonpolar polarizable fluids

For the sake of comparison, we simulate an equimolar hard-sphere fluid mixture ($X_1=X_2=0.5$) at a reduced density of $\rho^*=\rho\sigma^3=0.382$ and a reduced polarizability of $\alpha^*=\alpha/\sigma^3=0.06$ where σ is the hard sphere diameter. The Ewald summation is applied with the surrounding medium taken as a perfect conductor. Power spectra are plotted along with the with MSA predictions in Fig. 3 for $\omega_1=\omega_0$ and $\omega_2=1.2\omega_0$ and in Fig. 4 for $\omega_1=\omega_0$ and $\omega_2=1.5\omega_0$.

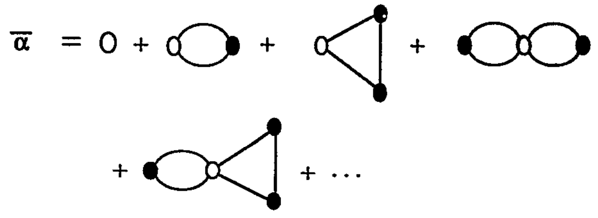

FIG. 3. The power spectrum of a hard sphere mixture containing equal size sphere at a reduced density of $\rho^*=0.384$. The mole fractions of the two components are the same, that is, $X_1=X_2=0.5$. The polarizability is the same for the two components, $\alpha^*=0.06$, but the frequencies are different, $\omega_1=\omega_0$, $\omega_2=1.2\omega_0$. The solid curve is the simulation result and the bold curve is the MSA result.

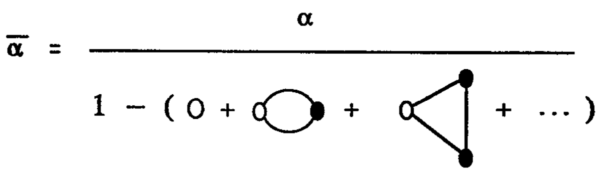

FIG. 4. The same plot as Fig. 7 except for $\omega_1=\omega_0$ and $\omega_2=1.5\omega_0$.

Notice that the MSA predicts the correct bandwidths but fails to give the detailed shape of the spectrum. In both the simulation and MSA results the separation between the two bands in the mixture is larger than the separation between the bands of neat fluids of these two different molecules at the same density because of the dipolar interaction between the two components.[9,18]

The Padé approximate Eq. (A6) when used with Eq. (A5) yields a cubic equation whose solution gives the absorption spectrum of the mixture. In the limit of infinite dilution the dilute component can be regarded as an impurity. It is then found that if the impurity frequency lies above the spectral band of the solvent the impurity resonance is blue shifted whereas if the frequency lies below the spectral band of the solvent the impurity resonance is red shifted. This agrees with the analysis of Chandler *et al.*[17] Our approach is to take a very small but nonzero impurity concentration. We are able to determine the dielectric absorption spectrum for the system in which the impurity manifests itself as a very narrow band outside the main spectral band of the solvent. In the approach taken by Chandler *et al.*, the impurity is a single particle in an infinite solvent. The impurity spectrum is then a delta function.

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APPENDIX A: THE MATRIX THEORY AND DIAGRAMMATICS

The renormalized polarizability $\bar{\alpha}$ defined by Eq. (5.4) can be Taylor expanded as

$$\bar{\alpha}=\alpha\langle\langle(\mathscr{I}-\alpha\mathscr{T})^{-1}\rangle\rangle=\sum_{n=1}^{n=\infty}\alpha^n\langle\langle\mathscr{T}^{n-1}\rangle\rangle. \quad \text{(A1)}$$

This can be represented by diagrams in which white circles represent tagged particles, black circles represent particles being summed over, the coupling between particles, given by the dipolar propagator $\mathscr{T}$, is represented by a line, an α is assigned wherever a line passes through a circle and an extra α is assigned to the white circles. In the following we give a brief and somewhat cursory description of the diagrammatic analysis.

The value of each diagram is the product of all the elements composing the diagram. This expansion is given

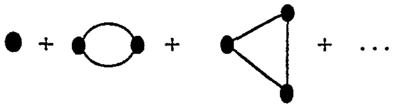

FIG. 5. The Taylor expansion of the renormalized polarizability $\bar{\alpha}$. The white circle represents the tagged particle, each black circle represents a dummy particle being integrated, and lines connecting the circles represent dipolar propagator.

in Fig. 5. Because $\bar{\alpha}$ is a trace, the diagrams are closed chains or cycles. Each diagram represents an average as, in Eq. (A1), and thus contains a many-body correlation function. For example, the second diagram in Fig. 5 corresponds to

$$\left\langle \alpha^3 \sum_{i\neq 1} \mathcal{T}_{1i}^2 \right\rangle = \alpha^3 \rho \int \mathcal{T}_{12}^2\, g(r_1,r_2)\,dr_2, \tag{A2}$$

whereas the third diagram corresponds to

$$\left\langle \alpha^4 \sum_{i\neq j\neq 1} \mathcal{T}_{1i}\mathcal{T}_{ij}\mathcal{T}_{j1} \right\rangle = \alpha^4 \rho^2 \int\int g(r_1,r_2,r_3)\,\mathcal{T}_{12}\mathcal{T}_{23}\mathcal{T}_{31}\,dr_2\,dr_3, \tag{A3}$$

where $g(r_1,r_2)$ and $g(r_1,r_2,r_3)$ are the pair and three-body correlation functions, respectively, and ρ is the number density.

Whenever circles connect two or more otherwise separated sub-diagrams it is possible to approximate this by reducing it to a product of two parts. For example, the fourth diagram of Fig. 5 can be approximated by

$$\alpha^5 \rho^2 \int g(r_1,r_2,r_3)\,\mathcal{T}_{12}^2 \mathcal{T}_{13}^2\,dr_2\,dr_3 \approx \alpha \left[\int \rho \alpha^2 g(r_1,r_2)\,\mathcal{T}_{12}^2\,dr_2 \right]^2 \tag{A4}$$

and most of the many-body diagram can be decomposed into a set of smaller diagrams. This approximation leads to a renormalization of the diagrams. A general diagram is constructed by summing all possible decorations of each circle. The decorations attached to a black circle are equivalent to an $\bar{\alpha}$ expansion series starting and terminating at that black circle. One can thus remove these decorations by assigning the renormalized $\bar{\alpha}$ to each black circle in place of the bare α. The results are given in Fig. 6. The set of diagrams generated by adding decorations to the white circle can be grouped according to the number of decorations thus yielding the results given in Fig. 7. Finally, we can express this as the self-consistent equation,[27]

$$\bar{\alpha} = \frac{\alpha}{1 - \frac{\alpha}{\bar{\alpha}}\Sigma(\bar{\alpha})}, \tag{A5}$$

where Σ is the infinite sum of the simply connected diagrams given in Fig. 8. It is a simple matter to show that $\bar{\alpha} \geqslant \alpha$.

The limit $N \to \infty$ makes it possible to have an infinite number of combinations of diagrams. This allows a topological reduction in which α is replaced by $\bar{\alpha}$. In Sec. V E, where the absorption spectrum is discussed, it is noted that the thermodynamic limit gives a continuous spectrum instead of discretized absorption lines.

Except for the first two terms of the Σ series, the many-body correlation function is difficult to calculate analyti-

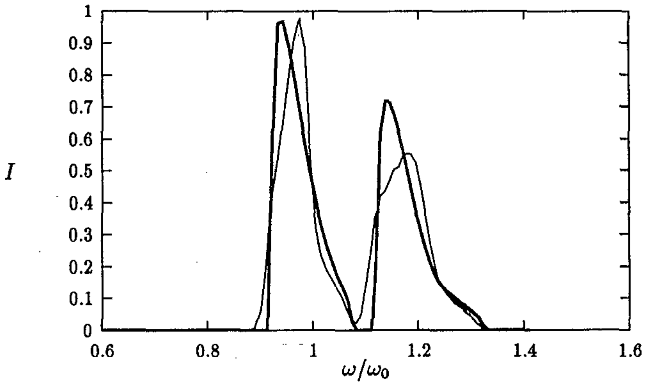

FIG. 7. Further reduction of Fig. 3 which leads to the self-consistent equation (A5).

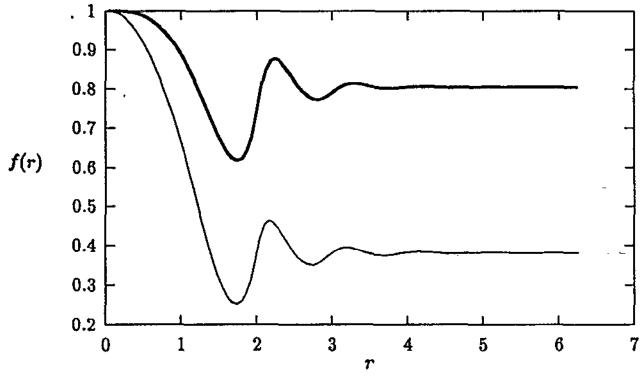

FIG. 6. The topological reduction of Fig. 2. Each black circle now represents the summation of diagrams in Fig. 2.

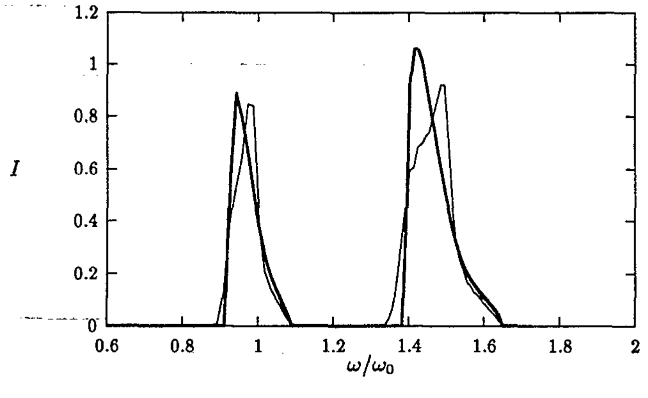

FIG. 8. The infinite series of the simple connected diagrams which defines Σ used in Eq. (A5).

cally. Fortunately, a simple argument based on Onsager's saturation property[44] allows us to construct a Padé approximate from the first two terms,[39]

$$\Sigma=t_2+t_3+\cdots\approx\frac{t_2}{1-t_3/t_2}, \tag{A6}$$

where t_2 and t_3 are given by Eqs. (A2) and (A3) and can be evaluated numerically (see Appendix B).

The above analysis[1] is similar to that used in the topological reduction in the Green function theory of electronic states in solids.[27,26] (On revising this paper, we noticed that much of the diagrammatic expansion used here is very close to the work done by Chen *et al.*) In solid state theory, the Green function depends on the crystal structure, in liquids, where there is topological disorder of the nuclear configurations, it depends on the correlation functions. In the equilibrium theory of classical fluids similar methods have been employed to derive diagrammatic expansions of thermodynamic functions, such as the free energy and chemical potential.[34–36]

Pratt[13] derived a self-consistent equation for the renormalized polarizability based on a Padé approximation to the free energy. This is the same as Eq. (A5) with $\Sigma(\bar{\alpha})$ given by Eq. (A6). Pratt's work is based on diagrammatic reduction of the free energy of the intramolecular degree of freedom, an analysis similar to our procedure. However, in order to get the excess chemical potential due to the dipole fluctuations, a MSA is applied. This does not effect the first two diagrams in Eq. (A5), but the next order diagram in our summation has a term with two circles connected by four lines, a term ignored in Pratt's MSA.

Logan and Winn have applied the similar strategy to a calculation of the electronic band structure.[19,20,45] The density of states (DOS) was evaluated for a tight-binding Hamiltonian with off-diagonal randomness due to spatial disorder. Stratt studied the same problem by adding artificial degrees of freedom.[21,28,37,46] Both authors show that on the MSA level both theories are identical to the effective medium approximation proposed by Ruth.[47] Therefore the methods and results here are similar to what appears in previous publications.[8,9,19] and we include this section for clarity.

APPENDIX B: EVALUATION OF THE TWO INTEGRALS

The two integrals in Eq. (A6) are all that is needed in the MSA equation. t_2 is,

$$t_2=\alpha^2\rho\int\frac{\operatorname{tr}\mathscr{T}^2}{3}g(r)d\mathbf{r}=\alpha^2\rho\int\frac{2}{r^6}g(r)d\mathbf{r}, \tag{B1}$$

where $g(r)$ is the pair correlation function. If $g(r)$ is taken as a step function (the dilute hard-sphere gas phase limit) t_2 becomes

$$t_2=\alpha^2\rho\frac{8\pi}{3d^3} \tag{B2}$$

in which d is hard sphere diameter.

The second integral is

$$t_3=\alpha^3\rho^2\int\mathscr{T}(\mathbf{r}_1-\mathbf{r}_2)\mathscr{T}(\mathbf{r}_2-\mathbf{r}_3)\times\mathscr{T}(\mathbf{r}_3-\mathbf{r}_1)g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_2d\mathbf{r}_3, \tag{B3}$$

where g_3 is the three-body correlation function. In the superposition approximation g_3 is the product of three two-body pair correlation function,

$$g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=g(\mathbf{r}_1,\mathbf{r}_2)g(\mathbf{r}_2,\mathbf{r}_3)g(\mathbf{r}_3,\mathbf{r}_1). \tag{B4}$$

Thus the integrand of Eq. (B3) can be written as the product of the tensor

$$\mathscr{T}(\mathbf{r}_1-\mathbf{r}_2)g(\mathbf{r}_1-\mathbf{r}_2)=\frac{g(r_{12})}{r_{12}^3}\mathscr{D}, \tag{B5}$$

where $\mathscr{D}$ is the second order tensor given by Eq. (5.10). Performing a Fourier transform of the integral, gives

$$t_3=\alpha^3\rho^2\frac{2}{(2\pi)^3}\int\hat{q}^3d\mathbf{k} \tag{B6}$$

in which the factor 2 comes from tr $\mathscr{D}^3/3$ and $\hat{q}$ is the scalar part of the Fourier transformation of the tensor $\mathscr{T}g$ given by

$$\hat{q}=-\int j_2(kr)\frac{g(r)}{r^3}d\mathbf{r}, \tag{B7}$$

where j_2 is the second order spherical Bessel function.

Again, we can calculate the integral explicitly for the case of the step-function dilute hard-sphere gas correlation function,

$$\hat{q}=4\pi\left[\frac{\cos(kd)}{(kd)^2}-\frac{\sin(kd)}{(kd)^3}\right]. \tag{B8}$$

Substitution of Eq. (B8) into Eq. (B6) yields

$$t_3=-\frac{5\pi^2}{3d^3}\rho^2\alpha^3. \tag{B9}$$

In general, t_2t_3 can be evaluated numerically according to Eqs. (B1) and (B6) if the pair correlation function is given.

APPENDIX C: SCREENING FUNCTION OF A CHARGE AND A DIPOLE

Equation (5.19) is a general expression of the field induced by an electrostatic charge in a polarizable fluid.

First we introduce a general Fourier transformation. Any function can be expanded in the spherical harmonic functions,

$$q(\mathbf{r})=\sum q_{lm}(r)Y_{lm}(\theta,\phi). \tag{C1}$$

Each q_{lm} transforms according to

$$\hat{q}_{lm}(k)=(-i)^l\int q_{lm}(r)j_l(kr)d\mathbf{r}, \tag{C2}$$

where $j_l(kr)$ is the lth order spherical Bessel function. Thus the full transformation of $q(\mathbf{r})$ is

$$\hat{q}(\mathbf{k}) = \sum \hat{q}_{lm}(k) Y_{lm} \tag{C3}$$

and the inverse Fourier transformation is

$$q_{lm}(r) = \frac{(i)^l}{(2\pi)^3} \int d\mathbf{k} \hat{q}_{lm}(k) j_l(kr). \tag{C4}$$

We have made use of the transformation given by Eq. (B7).

Consider a point charge. The bare field is

$$\mathbf{E}^0 = \frac{\mathbf{n}}{r^2}, \tag{C5}$$

where **n** is the unit vector. The convolution integral in Eq. (5.19) can be evaluated by Fourier transformation. First the function f_1 can be expressed as

$$q_1 = \frac{g(r)}{r^2} \tag{C6}$$

which transforms as a vector,

$$\hat{q}_1 = (-i) \int q_1 j_1(kr) d\mathbf{r}. \tag{C7}$$

Also the dipole pair correlation function transforms as

$$\hat{\mathscr{H}} = \hat{h}_\Delta \mathscr{I} + \hat{h}_D \mathscr{D}, \tag{C8}$$

where h^Δ transforms as a scalar and h^D transforms as a tensor. Then, Eq. (5.19) reads as

$$\mathbf{E} = \frac{\mathbf{n}}{r^2} + \frac{i}{3} \frac{\rho}{(2\pi)^3} \int \hat{q}_1 \mathbf{n} \hat{\mathscr{H}} j_1(kr) d\mathbf{k}. \tag{C9}$$

As $\mathbf{n}\mathscr{D} = 2\mathbf{n}$, we finally arrive at the expression for the screening function of a point charge,

$$f(r) = 1 + \frac{i}{3} \frac{r^2 \rho}{(2\pi)^3} \int \hat{q}_1 (\hat{h}^\Delta + 2\hat{h}^D) d\mathbf{k}. \tag{C10}$$

A similar analysis leads to the screening function for a point dipole which has been discussed by Pratt.

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