

A molecular Debye-Hückel theory of solvation in polar fluids: An extension of the Born model

Tiejun Xiao¹ and Xueyu Song²

¹Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Synergetic Innovation Center of Scientific Big Data for Advanced Manufacturing Technology, Guizhou Education University, Guiyang 550018, People's Republic of China and Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA

²Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA

(Received 29 July 2017; accepted 7 November 2017; published online 6 December 2017)

A dielectric response theory of solvation beyond the conventional Born model for polar fluids is presented. The dielectric response of a polar fluid is described by a Born response mode and a linear combination of Debye-Hückel-like response modes that capture the nonlocal response of polar fluids. The Born mode is characterized by a bulk dielectric constant, while a Debye-Hückel mode is characterized by its corresponding Debye screening length. Both the bulk dielectric constant and the Debye screening lengths are determined from the bulk dielectric function of the polar fluid. The linear combination coefficients of the response modes are evaluated in a self-consistent way and can be used to evaluate the electrostatic contribution to the thermodynamic properties of a polar fluid. Our theory is applied to a dipolar hard sphere fluid as well as interaction site models of polar fluids such as water, where the electrostatic contribution to their thermodynamic properties can be obtained accurately. *Published by AIP Publishing.* <https://doi.org/10.1063/1.4998255>

I. INTRODUCTION

Solvation in polar fluids is a fundamental problem in nature and is widely used in the description of many processes such as crystallization processes^{1–3} and electron transfer processes.^{4–6} A widely used theory for the polar fluid is the Born model of solvation,^{7,8} where a polar fluid is treated as a dielectric continuum with relative dielectric constant ϵ_r , while an ion is characterized by a charge q and a radius a . According to the Born model, the electrostatic contribution to the solvation energy of an ion is $\beta\mu^{ele} = -\frac{\beta q^2}{2\epsilon_0 a} \left(1 - \frac{1}{\epsilon_r}\right)$. This theory is also extended to fluids with dispersion interactions to include quantum corrections.^{9–11} However, the Born model has several limitations. First, the Born model overestimates the solvation energy as long as a is interpreted as the cavity size of the solute-solvent interaction. To alleviate this problem, the generalized Born model takes the size a as a tunable parameter so that one can match the solvation energies from experiments.^{12,13} The size parameter a determined in this way is always smaller than the cavity size and hence its physical significance is not very clear. Second, the Born model cannot predict the oscillatory decay charge density profile around an ion in dense polar fluids.^{14,15} To this end, a theory that could accurately account for both the solvation energy and the microscopic structure of polar fluids, and at the same time preserving the linear feature of the model, will be useful to our understanding of solvation in polar fluids.

In recent years, there have been extensive studies on the theory of dense fluids with Coulomb interactions.^{16–27} Due to the universality of Coulomb interactions, one may expect that there are common properties shared by ionic fluids and polar fluids. As demonstrated by Kjellander and co-workers in the dressed ion theory^{22,23} and the dressed molecule

theory,²⁴ the Poisson equation for the electric potential of a solute in a solvent can always be reformulated as a linearized Debye-Hückel (DH)-like theory by an exact charge renormalization process. The difference between ionic fluids and polar fluids is known to appear in the root structure of the dielectric function,^{18,25,26} which can be understood from the dispersion relations in electrodynamics.^{25,26} The dressed molecule theory indicates that the electric potential around an ion in a polar fluid decays as $\phi_i(r) \simeq \frac{q_i}{\epsilon_b r} + \sum_n \frac{q_{in} e^{-k_n r}}{\epsilon_{bn} r}$. Motivated by the fact that one can use the DH-like modes to reproduce the multi-Yukawa potential in ionic fluids accurately,²⁶ a combination of Born response mode and DH response modes to build an extended theory for the polar fluids should be possible, i.e., the term of $\phi(r) \sim \frac{1}{\epsilon_b r}$ in the electric potential is resulted from the Born response mode $\nabla^2 \phi(r) = 0$, while the term of $\phi(r) \sim \frac{e^{-k_n r}}{r}$ comes from a DH response mode with $\nabla^2 \phi(r) = k_n^2 \phi(r)$.

In this paper, we focus on such a dielectric response theory of polar fluids. In general, there are two widely used models for polar fluids. One is the classic dipolar hard sphere fluid, where a spherical polar molecule carries a point dipole at its center. The other is the interaction site model of polar fluids, where a polar molecule carries several point charges at various positions of the molecule. As the dressed molecule theory is valid for these two kinds of polar fluids, we demonstrate that the electric response of a general polar fluid can always be expressed as a combination of a Born response mode and multi-DH response modes, where all the parameters can be determined from the dielectric function of the pure solvent. The electrostatic contribution to the solvation energy can be calculated accurately from this approach. As the Born response mode can be treated as a special DH response mode with $k_n = 0$, such a dielectric response theory is called a molecular

Debye-Hückel (MDH) theory of polar fluids. For the special case of dipole and ion solvation in a polar fluid, the electric potential, the induced charge density, and the electrostatic contribution to the thermodynamic properties are discussed. Applications of the theory to the interaction site model, such as water, are also discussed.

This paper is organized as follows. In Sec. II, we develop the MDH theory for dipole hard sphere fluids, based on which the induced charge density about a solute, the bulk dielectric function, and the excess thermodynamic properties are derived analytically. In Sec. III, the MDH theory applications to the interaction site model of dipole fluids are presented. A brief summary is given in Sec. IV and some of the details of the theoretical formulation are presented in Appendixes A and B.

II. A MOLECULAR DEBYE-HÜCKEL THEORY FOR DIPOLE HARD SPHERE FLUIDS

A. Model description of a polar fluid

We first consider an one-component dipole hard sphere fluid that serves as the simplest model of polar fluids. The particle number density of the polar species is n_d , the reduced inverse temperature is $\beta = \frac{1}{k_B T}$ with k_B being the Boltzmann constant and T being the temperature; the permittivity of the vacuum is ϵ_0 . It is known that one can use the orientation-dependent molecule interaction potential $u_{12}(\mathbf{r}_{12}, \omega_1, \omega_2)$ and orientation-dependent correlation function $h_{12}(r_{12}, \omega_1, \omega_2)$ to describe such a molecular fluid,^{24,28} where the solid angle ω_i denotes the orientation of the molecule i . Denote σ and μ as the hard sphere diameter and the dipole moment of the polar species. The pair potential between one dipole at \mathbf{r}_1 and another dipole at \mathbf{r}_2 is $u_{dd}(1, 2) = u_{dd}^{hs}(r_{12}) - \frac{\mu^2}{\epsilon_0 r_{12}^3} D(1, 2)$, where $u_{dd}^{hs}(r_{12})$ is the hard sphere potential, $D(1, 2) = -\hat{\mu}_1 \cdot \hat{\mu}_2 + 3(\hat{\mu}_1 \cdot \hat{r}_{12})(\hat{\mu}_2 \cdot \hat{r}_{12})$. \hat{r}_{12} is a unit vector defined as $\hat{r}_{12} \equiv \mathbf{r}_{12}/|\mathbf{r}_{12}|$. $\hat{\mu}_i = \hat{\mu}(\omega_i)$ with $i = 1, 2$ is the unit vector in the direction of i th dipole. A dimensionless parameter $y = \frac{4\pi\beta\mu^2 n_d}{9\epsilon_0}$ can be introduced to measure the strength of the electrostatic interaction.²⁹

B. A MDH theory for a dipole hard sphere fluid

To build a molecular dielectric response theory for a polar fluid, a tagged molecule labeled o at the origin is taken as a solute, while the surrounding molecules are taken as the solvent. Let $h_{od}(\mathbf{r}, \omega_1, \omega_2) = g_{od}(\mathbf{r}, \omega_1, \omega_2) - 1$ be the correlation function between the solute o with solid angle ω_1 and the solvent dipole species d with solid angle ω_2 . Denote $\Phi_o(\mathbf{r}, \omega)$ as the electric potential of the solute o with bare charge density $\rho_o^b(\mathbf{r}, \omega)$. The Poisson equation for the solute reads $\nabla^2 \Phi_o(\mathbf{r}, \omega) = -\frac{4\pi}{\epsilon_0} \rho_o^b(\mathbf{r}, \omega) = -\frac{4\pi}{\epsilon_0} [\rho_o^b(\mathbf{r}, \omega) + \rho_o^{ind}(\mathbf{r}, \omega)]$, where $\rho_o^{ind}(\mathbf{r}_{12}, \omega_1) = \frac{1}{4\pi} \int d\mathbf{r}_3 d\omega_2 n_d h_{od}(\mathbf{r}_{13}, \omega_1, \omega_2) \rho_d^b(\mathbf{r}_{32}, \omega_2)$ is the induced charge density, $\rho_d^b(\mathbf{r}, \omega) = -\mu \hat{\mu}(\omega) \cdot \nabla \delta(\mathbf{r})$ is the bare charge density for a dipolar solvent molecule.^{24,30}

Let $f(\mathbf{k}, \omega) \equiv \int f(\mathbf{r}, \omega) e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r}$ be the three-dimensional Fourier transform of a function $f(\mathbf{r}, \omega)$. As indicated by the dressed molecular theory, a rigorous charge renormalization process can be applied to the total charge density so that the Poisson equation in k -space can be rewritten as

$k^2 \epsilon_l(k) \Phi_o(\mathbf{k}, \omega) = 4\pi \theta_o(\mathbf{k}, \omega)$,²⁴ where $\epsilon_l(k)$ is the dielectric response function of the solvent and $\theta_o(\mathbf{k}, \omega)$ is an effective charge density of the dressed solute. The main results of the dressed molecule theory of a dipolar fluid are summarized in Appendix A. For the case of the solute being an ion, the electric potential depends only on $r = |\mathbf{r}|$ such that $\Phi_o(\mathbf{r}, \omega) = \Phi_o(r)$, the electric potential in r -space can be evaluated^{24,26}

$$\begin{aligned} \Phi_o(r) &= \frac{1}{2\pi^2 r} \int_0^\infty dk [k \Phi_o(k)] \sin(kr) \\ &= \frac{1}{2\pi^2 r} \int_0^\infty dk \left[\frac{4\pi \theta_o(k)}{\epsilon_l(k) k} \right] \sin(kr). \end{aligned} \quad (1)$$

Pole analysis yields that $\Phi_o(r) \approx \frac{q_0}{\epsilon_b r} + \sum_n \frac{q_n e^{-k_n r}}{\epsilon_{bn} r}$ ²⁴ and hence motivates us to expand the dielectric response of a polar fluid with a Born mode and multiple DH modes.

In general, one can expand the electric potential $\Phi_o(\mathbf{r}, \omega)$ with a Born mode ($l = 0$) and multi-DH-like modes, i.e.,

$$\Phi_o(\mathbf{r}, \omega) = \sum_{l=0}^L C_l \phi_l(\mathbf{r}, \omega), \quad (2)$$

where L is the number of DH response modes and $\{C_l\}$ s are the linear combination coefficients to be determined.

The dielectric constant of the bulk polar fluid is $\epsilon_b \equiv \lim_{k \rightarrow 0} \epsilon_l(k)$, and then the relative dielectric constant is defined as $\epsilon_r = \epsilon_b / \epsilon_0$. The electric potential $\phi_0(\mathbf{r}, \omega)$ is the solution of the Born response mode with dielectric constant ϵ_r , i.e.,

$$\begin{aligned} \nabla^2 \phi_0(\mathbf{r}, \omega) &= -\frac{4\pi}{\epsilon_0} \rho_o^b(\mathbf{r}, \omega), & r \leq a_o, \\ \epsilon_r \nabla^2 \phi_0(\mathbf{r}, \omega) &= 0, & r > a_o, \end{aligned} \quad (3)$$

where a_o is the cavity radius of the solute-solvent interaction. When the solvent and solute molecules are described by hard spheres with diameters σ and σ_o , one can find that $a_o = (\sigma + \sigma_o)/2$. It is easy to check that the dielectric constant inside and outside the spherical cavity is set to be ϵ_0 and $\epsilon_r \epsilon_0$.

The electric potential $\phi_l(\mathbf{r}, \omega)$ with $l = 1, 2, \dots, L$ is the solution of a linearized Poisson-Boltzmann equation with a Debye screening length k_l , i.e.,

$$\begin{aligned} \nabla^2 \phi_l(\mathbf{r}, \omega) &= -\frac{4\pi}{\epsilon_0} \rho_o^b(\mathbf{r}, \omega), & r \leq a_o, \\ \nabla^2 \phi_l(\mathbf{r}, \omega) &= k_l^2 \phi_l(\mathbf{r}, \omega), & r > a_o, \end{aligned} \quad (4)$$

where k_l are the non-zero roots of $\epsilon_l(k)$ and the dielectric constants inside and outside the spherical cavity are all set to be ϵ_0 for simplicity as the effective dielectric constant and the renormalized charge can be combined to be represented by the linear combination coefficient.

Equations (2)–(4) are the main working equations for the molecular Debye-Hückel (MDH) theory of polar fluids. According to the above equations, the dielectric response of a polar solvent is described by a Born response mode with an effective dielectric constant ϵ_r and a set of DH-like response modes with decay parameter $\{k_l\}$, while a solute is characterized by the cavity size and its bare charge density distribution. Such a physical picture is hidden behind any integral equation theories or computer simulations such as molecular dynamics

simulations and Monte Carlo simulations. In general, the linear combination coefficient $\{C_l\}$ depends on the solute size, the solute bare charge density, and the solute-solvent correlation function. Even though the potential terms $\frac{e^{-k_l r}}{r}$ from DH modes are short-ranged potentials, the DH response modes actually take the non-local response of Coulomb interactions into account.

C. The electric potential of a dipole hard sphere solute

When the solute molecule is chosen as a solvent dipole molecule, one can expect that the MDH theory naturally leads to a self-consistent description for the polar fluid. Let us consider the solvation of a dipole hard sphere in a dipole hard sphere fluid. The solute is the same as the solvent molecules so the solute diameter is σ and the solute dipole moment is μ . In this case, it is found that $a_0 = \sigma$. The electric potential $\Phi_d(\mathbf{r}, \omega)$ around the dipole solute is expanded as $\Phi_d(\mathbf{r}, \omega) = \sum_{l=0}^L C_l \phi_l(\mathbf{r}, \omega)$. The solution of the Born mode with $l = 0$ reads

$$\begin{aligned} \phi_0(\mathbf{r}, \omega) &= \left(\frac{\mu}{\epsilon_0 r^2} + A_0 r\right) \hat{\mu}(\omega) \cdot \hat{r}, & r \leq \sigma \\ \phi_0(\mathbf{r}, \omega) &= \frac{\mu}{\epsilon_0 \epsilon_r r^2} \hat{\mu}(\omega) \cdot \hat{r}, & r > \sigma, \end{aligned} \quad (5)$$

where $A_0 = -\frac{2(\epsilon_r - 1)}{2\epsilon_r + 1} \frac{\mu}{\sigma^3}$ is an induced electric field. The solution of the DH mode with $l \geq 1$ reads

$$\begin{aligned} \phi_l(\mathbf{r}, \omega) &= \left(\frac{\mu}{\epsilon_0 r^2} + A_l r\right) \hat{\mu}(\omega) \cdot \hat{r}, & r \leq \sigma, \\ \phi_l(\mathbf{r}, \omega) &= \frac{3\mu}{3 + k_l \sigma + k_l^2 \sigma^2} \frac{(1 + k_l r) e^{-k_l(r - \sigma)}}{\epsilon_0 r^2} \hat{\mu}(\omega) \cdot \hat{r}, & r > \sigma, \end{aligned} \quad (6)$$

where $A_l = -\frac{k_l^2 \sigma^2}{(k_l^2 \sigma^2 + 3k_l \sigma + 3)} \frac{\mu}{\sigma^3}$ is an induced electric field. Then the total electric potential inside the cavity can be written as $\Phi_d(\mathbf{r}, \omega) = \left(\frac{\mu}{\epsilon_0 r^2} + E_d r\right) \hat{\mu}(\omega) \cdot \hat{r}$, where $E_d = \sum_{l=0}^L C_l A_l$ is the total induced electric field.

The Fourier transform of $\Phi_d(\mathbf{r}, \omega)$ is $\Phi_d(\mathbf{k}, \omega) = \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} \Phi_d(\mathbf{r}, \omega) = i\hat{\mu}(\omega) \cdot \hat{k} \int_0^\infty dr 4\pi r^2 \frac{\sin(kr) - kr \cos(kr)}{(kr)^2} \Phi'_d(r)$, where $\Phi'_d(r)$ is $\Phi_d(\mathbf{r}, \omega) / (\hat{\mu}(\omega) \cdot \hat{r})$. According to the Poisson equation, the total charge density $\rho'_d(\mathbf{r}, \omega)$ of the dipole solute can be evaluated as $\rho'_d(\mathbf{r}, \omega) = -\frac{\epsilon_0}{4\pi} \nabla^2 \Phi_d(\mathbf{r}, \omega)$ or equivalently $\rho'_d(\mathbf{k}, \omega) = \frac{\epsilon_0}{4\pi} k^2 \Phi_d(\mathbf{k}, \omega)$. Now the Fourier transform of $\rho'_d(\mathbf{r}, \omega)$ is $\rho'_d(\mathbf{k}, \omega) = i\epsilon_0 \hat{\mu}(\omega) \cdot \hat{k} \int_0^\infty dr [\sin(kr) - kr \cos(kr)] \Phi'_d(r)$. Using the $\Phi_d(\mathbf{r}, \omega)$ expression from the MDH theory, some straightforward calculations yield

$$\rho'_d(\mathbf{k}, \omega) = i\hat{k} \cdot \hat{\mu}(\omega) k \mu \sum_{l=0}^L C_l f_l(k\sigma), \quad (7)$$

where the function $f_l(x)$ is defined as $f_0(x) = 1 + \frac{6(\epsilon_r - 1)}{2\epsilon_r + 1} \frac{x \cos x - \sin x}{x^3}$ and $f_l(x) = 1 - \frac{\sin x}{x} + \frac{k_l^2 \sigma^2}{(k_l^2 \sigma^2 + 3k_l \sigma + 3)}$ $\frac{3x \cos x + (x^2 - 3) \sin x}{x^3} + \frac{3}{(k_l^2 \sigma^2 + 3k_l \sigma + 3)} \left(\frac{\sin x}{x} + \frac{-k_l^2 \cos x + x k_l \sin x}{x^2 + k_l^2}\right)$ for $l \geq 1$. Similar to the case of ionic fluids, the normalization condition reads $\sum_{l=0}^L C_l = 1$.²⁶

D. The dielectric response function of the dipole hard sphere fluids

In this part, the charge density $\rho'_d(\mathbf{k}, \omega)$ from the MDH theory is used to build the dielectric response function of the polar fluid. We introduce $\chi(k) \equiv 1 - \epsilon_s / \epsilon_l(k)$ as the dielectric response function. Note that $\rho'_d(\mathbf{k}, \omega) = \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} (-\hat{\mu}(\omega) \cdot \nabla \delta(\mathbf{r})) = -ik \hat{\mu}(\omega) \cdot \hat{k}$, $\chi(k) = \frac{\beta n_d}{\epsilon_0 k^2} \int \rho'_d(\mathbf{k}, \omega) \rho'_d(-\mathbf{k}, \omega) d\omega$, and $\int [\hat{\mu}(\omega) \cdot \hat{k}]^2 d\omega = \frac{4\pi}{3}$.^{24,31} The response function can be evaluated as

$$\begin{aligned} \chi(k) &= \frac{\beta n_d}{\epsilon_0 k^2} \int [ik \hat{\mu}(\omega) \cdot \hat{k}] [-ik \hat{\mu}(\omega) \cdot \hat{k}] \sum_{l=0}^L C_l f_l(k\sigma) d\omega \\ &= \frac{4\pi \beta \mu^2 n_d}{3\epsilon_0} \sum_{l=0}^L C_l f_l(k\sigma) = 3y \sum_{l=0}^L C_l f_l(k\sigma). \end{aligned} \quad (8)$$

Note that $f_0(0) = \frac{3}{2\epsilon_r + 1}$ and $f_l(0) = 0$ for $l \geq 1$, the DH modes have no contribution to the bulk dielectric constant $\epsilon_r \equiv \lim_{k \rightarrow 0} \frac{\epsilon_l(k)}{\epsilon_0}$. Then the bulk dielectric constant is determined by the Born mode, i.e., $\chi(0) = 1 - \frac{1}{\epsilon_r} = 3y C_0 f_0(0) = C_0 \frac{9y}{2\epsilon_r + 1}$ or equivalently

$$C_0 = \frac{(\epsilon_r - 1)(2\epsilon_r + 1)}{9y\epsilon_r}. \quad (9)$$

An interesting observation is that C_0 can also be evaluated with the Kirkwood g-factor g_K . When comparing Eq. (9) with the Kirkwood fluctuation formula $\frac{(\epsilon_r - 1)(2\epsilon_r + 1)}{9\epsilon_r} = yg_K$,^{32,33} one can find that $C_0 = g_K$. As noted by Pollock and co-workers,³³ the electric field of a dipole hard sphere immersed in a dipole fluid decays as $\lim_{r \rightarrow \infty} E(r) = \frac{\mu_{eff}}{r^3}$, where $\mu_{eff} = g_K \mu_0$ is the effective dipole moment and μ_0 is the bare dipole moment. One can recognize C_0 as the ratio of effective dipole moment over the bare dipole moment as $C_0 = \frac{\mu_{eff}}{\mu} = g_K$. Note that $g_K \geq 1$ in general and $g_K = 1$ holds only for dilute polar fluids when $n_d \rightarrow 0$. One can conclude that the conventional Born result $C_0 = 1$ is valid only in the dilute limit.³³

Now the dielectric response function can be evaluated as

$$\chi(k) = \frac{(\epsilon_r - 1)(2\epsilon_r + 1)}{3\epsilon_r} f_0(k) + 3y \sum_{l=1}^L C_l f_l(k\sigma), \quad (10)$$

where the normalization condition reads $\sum_{l=1}^L C_l = 1 - \frac{(\epsilon_r - 1)(2\epsilon_r + 1)}{9y\epsilon_r}$. Given the charge density $\rho'_d(\mathbf{k}, \omega)$ or equivalently $\chi(k)$ with Eq. (10) will lead to a set of coefficient $\{C_l\}$ for the solvent. One may note that the results similar to Eq. (10) have been discussed in previous studies on polar fluids, for example, based on a phenomenological polarization model for polar fluids, the response function can be expanded as $\frac{1}{\epsilon_l(k)} = \frac{1}{\epsilon_\infty} - \frac{C_1}{1 + \lambda_1^2 k^2} - \frac{C_2(1 + l^2 k^2)}{(1 + l^2 k^2)(1 + l^2 k^2 - L^2 k^2)}$.³⁴⁻³⁷

E. Excess thermodynamic properties of the dipole hard sphere fluids

As long as the mean electric potential $\Phi_d(\mathbf{r}, \omega)$ of a solvent molecule is determined, one can calculate electrostatic contribution to the excess thermodynamic properties. In the following parts of this study, the thermodynamic properties are timed by the reduced temperature β so that the properties would be dimensionless.

According to the previous discussion, the total induced electric field is $E_d = \sum_{l=1}^L C_l A_l$, then the excess internal energy u_d^{ele} for a dipolar molecule can be evaluated as^{38,39}

$$\begin{aligned} \beta u_d^{\text{ele}} &= \frac{\beta \mu E_d}{2} \\ &= -\frac{\beta \mu^2}{\epsilon_0 \sigma^3} \frac{C_0(\epsilon_r - 1)}{2\epsilon_r + 1} - \frac{\beta \mu^2}{2\epsilon_0 \sigma} \sum_{l=1}^L \frac{C_l k_l^2}{k_l^2 \sigma^2 + 3k_l \sigma + 3}. \end{aligned} \quad (11)$$

As a comparison, the excess internal energy from the conventional Born model is given by

$$\beta u_d^{\text{ele}} = -\frac{\beta \mu^2}{\epsilon_0 \sigma^3} \frac{\epsilon_r - 1}{2\epsilon_r + 1}, \quad (12)$$

where the contributions of DH modes are absent. As one can expect, the Born model is valid only for weak dipolar interaction limit where the effect of DH modes can be neglected.

The excess chemical potential μ of the dipole hard sphere can be expressed as^{40,41}

$$\beta \mu_d^{\text{ex}} = \beta \mu_d^{\text{hs}} + \beta \mu_d^{\text{ele}}, \quad (13)$$

where $\beta \mu_d^{\text{hs}}$ is the cavity formation energy and can be evaluated from the integral equation theories,³¹ while $\beta \mu_d^{\text{ele}}$ is the electrostatic contribution to the excess chemical potential. Using the Kirkwood charging process, one can find that

$$\beta \mu_d^{\text{ele}} = \beta \int_0^1 \mu E(\xi \mu) d\xi = \frac{\beta \mu E_d}{2}, \quad (14)$$

where $E(\xi \mu)$ is the induced electric field for a solute with dipole moment $\xi \mu$, where we assume that the coefficients of the MDH theory is independent of the dipole moment so that $E(\xi \mu) = \xi E_d$. Equation (14) implies that the electrostatic part of the excess chemical potential equals to the electrostatic excess internal energy, a feature of linear models.

F. Excess thermodynamic properties of an ion in polar fluids

Our MDH theory is also applicable to the solvation of an ion in a dipole solvent. The diameter and charge of the ion are denoted as σ_i and q_i . The pair potential between an ion and a dipole molecule is $u_{id}(\mathbf{r}, \omega) = u_{id}^{\text{hs}}(r) - \frac{q_i \mu}{\epsilon_0 r^2} \hat{\mu}(\omega) \cdot \hat{r}$, where $u_{id}^{\text{hs}}(r)$ is a hard sphere potential. The bare charge density of the solute ion is $\rho_i^b(r) = q_i \delta(\mathbf{r})$. The electric potential around the ion depends only on r and is denoted as $\Phi_i(r)$.

According to Eqs. (2)–(4), the mean electric potential $\Phi_i(r)$ outside the cavity is found to be

$$\Phi_i(r) = \frac{q_i C_0}{\epsilon_0 \epsilon_r r} + \sum_{l=1}^L \frac{q_i C_l}{\epsilon_0 (1 + k_l a_i)} \frac{e^{-k_l(r-a_i)}}{r}, \quad r > a_i, \quad (15)$$

where $a_i = (\sigma_i + \sigma)/2$ is the cavity radius. Inside the cavity, Eq. (4) can be solved with appropriate boundary conditions

$$\Phi_i(r) = \frac{q_i}{\epsilon_0 r} + \psi_i, \quad r \leq a_i, \quad (16)$$

where the induced electric potential ψ_i is defined as

$$\psi_i = -\frac{q_i C_0}{\epsilon_0 a_i} \left(1 - \frac{1}{\epsilon_r}\right) - \frac{q_i}{\epsilon_0} \sum_{l=1}^L \frac{C_l k_l}{1 + k_l a_i}. \quad (17)$$

According to the Poisson equation, the induced charge density $\rho_i^{\text{ind}}(r)$ about a central ion can be evaluated as $\rho_i^{\text{ind}}(r) = -\frac{\epsilon_0}{4\pi} \nabla^2 \Phi_i(r)$. After some straightforward calculations, the induced charge density $\rho_i^{\text{ind}}(k) = \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} \rho_i^{\text{ind}}(r)$ in k -space reads

$$\begin{aligned} \rho_i^{\text{ind}}(k) &= -q_i C_0 \frac{\sin(ka_i)}{ka_i} \left(1 - \frac{1}{\epsilon_r}\right) \\ &\quad - \sum_{l=1}^L q_i \frac{C_l k_l^2}{k_l^2 + k^2} \frac{\cos(ka_i) + k_l \sin(ka_i)/k}{1 + k_l a_i}. \end{aligned} \quad (18)$$

It would be convenient to introduce the polarization density $P_i(r) \equiv \frac{nd}{4\pi} \int d\omega h_{id}(r, \omega) [\mu(\omega) \cdot \hat{r}]$ to measure the response of the dipole fluid to an ion.¹⁵ The polarization about the ion leads to an induced charge density, which can be evaluated as $\rho_i^{\text{ind}}(k) = \frac{nd}{4\pi} h_{id}(r, \omega) * \sigma_d(k, \omega)$. According to Eq. (A21) of Appendix A, this induced charge density can be evaluated as

$$\rho_i^{\text{ind}}(k) = k \int_0^\infty P_i(r) j_1(kr) 4\pi r^2 dr, \quad (19)$$

where $j_1(x) = (\sin x - x \cos x)/x^2$ is a spherical Bessel function. It is found that the macroscopic polarization density $P_{i,\text{mac}}(r) = -\frac{q_i}{4\pi r^2} (1 - \frac{1}{\epsilon_r})$ with $r \geq a$ leads to an induced charge density $\rho_{i,\text{mac}}^{\text{ind}}(k) = -q_i \frac{\sin(ka)}{ka} (1 - \frac{1}{\epsilon_r})$.¹⁵

Note that the linear response coefficients $\{C_l\}$ depend on the solute-solvent interactions, then the determination of $\{C_l\}$ relies on the availability of the induced charge density or polarization density. Using the polarization density from other accurate theories as input, we can evaluate the induced charge density $\rho_i^{\text{ind}}(k)$ according to Eq. (19). By fitting $\rho_i^{\text{ind}}(k)$ with Eq. (18), the set of $\{C_l\}$ can be determined. As demonstrated by the dressed molecule theory, the electric potential of an ion in a polar fluid always decays as $\lim_{r \rightarrow \infty} \Phi_i(r) = \frac{q_i}{\epsilon_0 \epsilon_r r}$.²⁴ When we compare this relation with Eq. (15), one can find that that $C_0 = 1$ and hence the normalization condition reads $\sum_{l=1}^L C_l = 0$. With the induced potential ψ_i from our MDH theory, the excess electrostatic internal energy u_i^{ele} can be determined as

$$\beta u_i^{\text{ele}} = \frac{\beta q_i \psi_i}{2} = -\frac{\beta q_i^2}{2\epsilon_0 a_i} \left(1 - \frac{1}{\epsilon_r}\right) - \frac{\beta q_i^2}{2\epsilon_0} \sum_{l=1}^L \frac{C_l k_l}{1 + k_l a_i}. \quad (20)$$

In the weak electrostatic coupling case, one can expect that the contribution from DH modes is negligible and then Eq. (20) reduces to the familiar Born results⁷

$$\beta u_i^{\text{ele}} = -\frac{\beta q_i^2}{2\epsilon_0 a} \left(1 - \frac{1}{\epsilon_r}\right). \quad (21)$$

It is worth to point out that there are other choices of the size parameter in the Born model, such as the Pauling radii, Shannon-Prewitt's crystal radii,⁴² or the modified radii from MSA theory.¹⁵ In the generalized Born model, the Born radius is chosen by matching the Born energy function Eq. (21) to the experimental chemical potentials.^{12,13} In general, these solute radius parameters differ from the true cavity sizes. In this study, the cavity size of a solute is used both in the Born model and the MDH theory as it is natural to interpret the solute size in a continuum model as a cavity to accommodate the solute.^{26,43} It is also important to note that the size of a molecule is not

well defined just with respect to electrostatic interactions, a general definition for the size of a molecule should account for other type of interactions, which is still an open question.

As both the MDH theory and Born model are continuum models, the MDH theory and the Born model can be easily extended to solvation of complex solutes, i.e., when specific solute information, such as molecule surface and charge distribution, is used in the continuum model, one can solve the electrostatic boundary problem to find the induced potential and thus the electrostatic solvation energy, which is another major motivation for such theoretical development.

The excess chemical potential of the ion reads

$$\beta\mu_i^{\text{ex}} = \beta\mu_i^{\text{hs}} + \beta\mu_i^{\text{ele}}, \quad (22)$$

where μ_i^{hs} is the cavity formation energy of the ion and can be evaluated from the integral equation theories.³¹ μ_i^{ele} is the electrostatic contribution to the excess chemical potential and can be evaluated with the Kirkwood charging process, i.e.,

$$\beta\mu_i^{\text{ele}} = \beta \int_0^1 q_i \psi(\xi q_i) d\xi = \frac{\beta q_i \psi_i}{2} = \beta u_i^{\text{ele}}, \quad (23)$$

where $\psi(\xi q_i)$ is the induced electric potential for an ion with charge ξq_i , and it is assumed that the coefficients of the MDH theory are independent of the ion charge so that $\psi(\xi \mu) = \xi \psi_i$. Equation (23) implies that the electrostatic part of the excess chemical potential equals to the electrostatic excess internal energy. One can see that such a physical picture is also valid in our MDH theory of ionic fluids²⁶ and the mean spherical approximation of ionic fluids,⁴⁴ again a feature of a linear theory.

G. Applications of the MDH theory to the dipole hard sphere fluids

The mean spherical approximation (MSA) of dipole hard sphere fluids leads to analytical dielectric function and thermodynamic properties and has been widely used in the studies of polar fluids.^{15,29,45–49} In this section, we will use the MSA results to demonstrate how our MDH theory can be used. It can be shown that the Born mode and typically two or four DH modes are capable of evaluating the dielectric response function and the excess internal energies accurately. Similar to the case of ionic fluids, when the electrostatic coupling of a polar system becomes very strong, more DH modes in the MDH calculation are required as long as there is no higher order poles or branch cut in the dielectric response function.

Before our discussion, the main MSA results are summarized here for convenience.^{15,47,49} The model description of the dipole hard sphere fluids can be found in the Sec. II A. MSA is a linear theory where all thermodynamic properties depend on a dimensionless parameter $y = \frac{4\pi\beta\mu^2 n_d}{9\epsilon_0}$. Let $q(x) = \frac{(1+2x)^2}{(1-x)^4}$, one can solve $q(\eta) - q(-\eta/2) = 3y$ to find a reference hard sphere packing fraction η_* . The bulk dielectric constant from the MSA is $\epsilon_r = \frac{(1+2\eta_*)^2(1+\eta_*/2)^4}{(1-\eta_*)^6}$. Using packing fraction of the dipole system $\eta_d = \frac{\pi\sigma^3 n_d}{6}$ and let $K = \eta_*/(2\eta_d)$, the excess internal energy of the dipole fluid can be evaluated as $\beta u_d^{\text{ex}} = -3yK$.⁴⁷ Using the direct correlation function $c(k; \rho_*)$ for a hard sphere fluid with particle number density

$\rho_* = 6\eta_*/(\pi\sigma^3)$, a correlation function $h(k; \rho_*)$ can be evaluated via the Ornstein-Zernike (OZ) equation as $[1 + \rho_* h(k; \rho_*)][1 - \rho_* c(k; \rho_*)] = 1$. The dielectric response function can then be evaluated as $\chi(k) = 3y[1 + \rho_* h(k; \rho_*)] = 3y/[1 - \rho_* c(k; \rho_*)]$. The decay parameters k_l of the dielectric response function can be evaluated by $\chi(ik_l)^{-1} = 0$ or equivalently $1 - \rho_* c(ik_l; \rho_*) = 0$. According to the MSA, one can also study ion solvation in a polar fluid. Using the solution of an ion-dipole mixture from the MSA, one can find the polarization density $P_i(r)$ around an ion in a polar fluid.⁴⁸ $P_i(r)$ can be used to evaluate the induced charge density $\rho_i^{\text{ind}}(k)$ from Eq. (19). The excess electrostatic internal energy of an ion in a dipole hard sphere fluid reads $\beta u_i^{\text{ele}} = -\frac{\beta q_i^2}{2\epsilon_0[(\sigma_i + \sigma)/2 - \delta]} \left(1 - \frac{1}{\epsilon_r}\right)$, where $\delta = \frac{3\eta_*}{1+2\eta_*} \frac{\sigma}{2}$, q_i is the ion charge and σ_i is the ion diameter.^{15,48} Note that the MSA theory implies that $\beta\mu_i^{\text{ele}} = \beta u_i^{\text{ele}}$; hence, the results for the excess electrostatic chemical potential $\beta\mu_i^{\text{ele}}$ can also be obtained.

To show how our MDH theory can be applied to dipole fluids, we consider a dipole fluid with $\sigma = 1.0$, $\beta = 1.0$, $n_d = 1.0$, $\mu = 1.0$, $\epsilon_0 = 1$. The packing fraction of the system is $\eta_d = 0.524$ and the dimensionless parameter is $y = 1.396$. One can find that $\eta_* = 0.196$, $K = \eta_*/(2\eta_d) = 0.187$, and the bulk dielectric constant $\epsilon_r = 10.41$. The first four decay parameters are $k_{1,2} = 2.141 \pm 5.587i$ and $k_{3,4} = 3.662 \pm 11.988i$. Using the MDH theory, we find that $C_0 = 1.570$, $C_{1,2} = -0.232 \pm 0.555i$, and $C_{3,4} = -0.053 \pm 0.551i$. The excess internal energy from MDH theory is $\beta u_d^{\text{ex}} = -0.763$, which can be compared with the MSA results $\beta u_d^{\text{ex}} = -3yK = -0.784$. On the other hand, the traditional Born model from Eq. (12) leads to $\beta u_d^{\text{ex}} = -0.431$, which is 44% off. With those $\{k_l\}$ and $\{C_l\}$, one can evaluate the dielectric response function $\chi(k)$ according to Eq. (10) of our MDH theory. $\chi(k)$ from the MDH theory and that from the MSA theory are shown in Fig. 1. As one can see, our MDH theory is in good agreement with the MSA results, a demonstration that our MDH theory can provide a self-consistent description of a dipolar fluid.

In order to see how the decay parameters $\{k_l\}$ of the DH modes depend on the parameter y , we calculate the first two Debye parameters $k_{1,2}$ in the parameter range of $0.014 < y \leq 2.51$, where the bulk dielectric constant is found

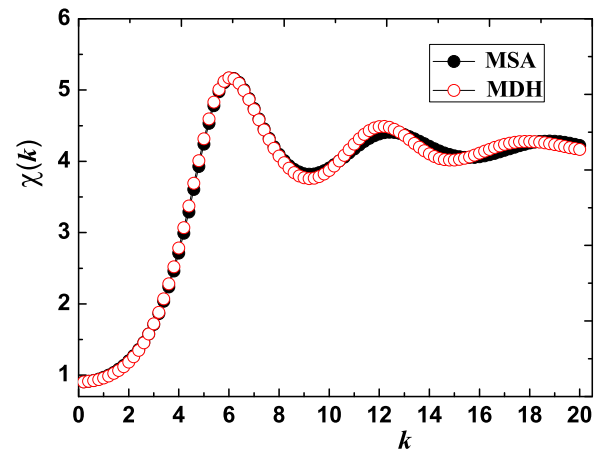


FIG. 1. A typical dielectric response function $\chi(k)$ for a dipole hard sphere fluid. The results from MSA are denoted by filled cycle, while results from our MDH theory are denoted by hollow circle. The lines are guides to the eye.

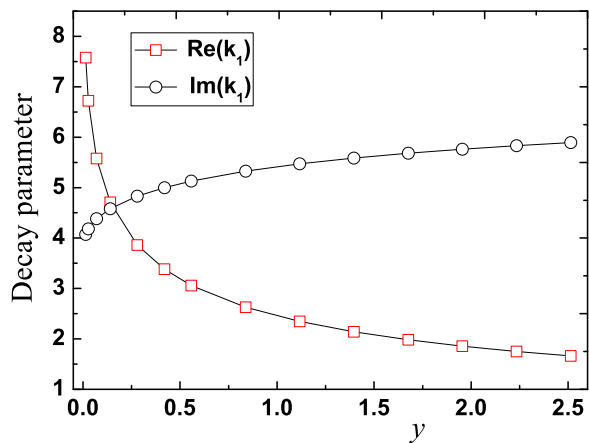


FIG. 2. The first two decay parameters as a function of the coupling parameter y . The real parts $\text{Re}(k_1)$ are denoted by squares, while the imaginary parts $\text{Im}(k_1)$ are denoted by circles. The lines are guides to the eye.

to be $1.04 < \epsilon_r \leq 23.72$. Note that $k_{1,2}$ appears in complex conjugates, the real and imaginary parts of $k_{1,2}$ are shown in Fig. 2. One can see that $\text{Re}(k_1)$ decreases as y increases, while $\text{Im}(k_1)$ increases as y increases, which are physically transparent, namely as y increases, the screening becomes better while the packing oscillations become denser slightly.

The excess internal energy βu_d^{ex} as a function of y is shown in Fig. 3. We use 2 DH modes for $y \leq 0.28$ and 4 DH modes for $y > 0.28$. Our MDH theory is in good agreement with MSA results, where the maximum difference is about 4% at $y = 2.51$. As a comparison, the Born theory is inaccurate especially for the strong coupling case, for example, the Born theory overestimates the excess internal energy by 55% at $y = 2.51$.

With the discussion in Sec. II F, ion solvation in a dipolar fluid can also be addressed using our MDH theory. The solvent parameters are fixed as $\sigma = 1.0$, $\beta = 1.0$, $n_d = 1.0$, $\mu = 1.0$, and $\epsilon_0 = 1$. In this case, the dielectric constant is $\epsilon_r = 10.41$, the first four decay parameters are $k_{1,2} = 2.141 \pm 5.587i$ and $k_{3,4} = 3.662 \pm 11.988i$. For a solute with $q_i = 1$ and $\sigma_i = 1$, the induced charge density from the MSA is fitted to Eq. (18) and then it is found that $C_0 = 1$, $C_{1,2} = -0.196 \pm 0.414i$, $C_{3,4} = 0.196 \pm 0.721i$. The excess internal energy from our MDH

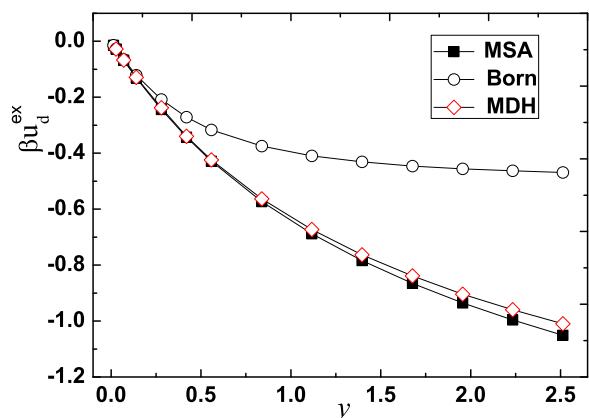


FIG. 3. Excess internal energy βu_d^{ex} as a function of the coupling parameter y . The MSA results are denoted by filled squares, the Born results are denoted by hollow circles, and the MDH results are denoted by hollow diamonds. The lines are guides to the eye.

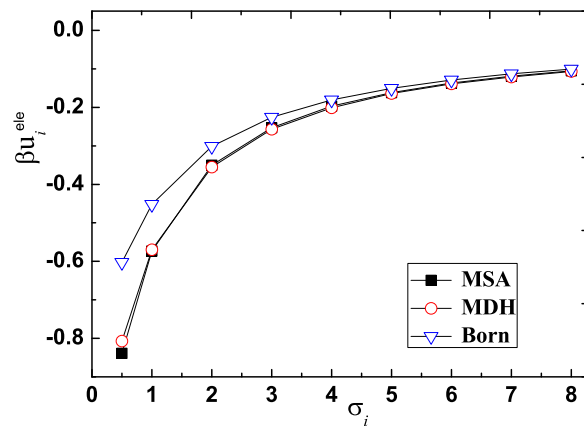


FIG. 4. Excess electrostatic internal energy βu_i^{ele} as a function of the solute diameter σ_i . The MSA results are denoted by filled squares, the MDH results are denoted by hollow circles, the Born results are denoted by hollow triangles. The lines are guides to the eye.

theory is $\beta u_i^{\text{ele}} = -0.570$, which can be compared with the MSA results $\beta u_i^{\text{ele}} = -0.573$, while the traditional Born result is $\beta u_i^{\text{ele}} = -0.452$ from Eq. (21).

In general, the coefficients $\{C_l\}$ are solute-dependent so that the solute with different sizes will have different coefficients. Our numerical calculations show that $\{C_l\}$ is a slow varying function of the solute size as long as the solute size is larger than the size of the solvent molecules. Such an observation implies that it would be a good approximation to use $\{C_l\}$ of an ion with a size comparable to the solvent to predict the solvation energy of ions with other sizes or solutes with general geometry. Using $\{C_l\}$ for the ion with $\sigma_i = 1$, the excess internal energies of solutes with other sizes or solutes with general geometry are evaluated with Eq. (20), and the results are shown in Fig. 4. The traditional Born results are also shown. As one can see, our MDH theory leads to excess internal energies which are in good agreement with the MSA results, for example, the difference between our MDH theory and the MSA result is no more than 4% in the range of $0.5 \leq \sigma_i \leq 8$. In contrast, the Born theory is not very accurate, for example, the difference between the Born theory and the MSA theory could be more than 25% for $\sigma_i = 0.5$.

III. A MOLECULAR DEBYE-HÜCKEL THEORY FOR THE INTERACTION SITE MODEL OF POLAR FLUIDS

Another type of polar fluid models is the interaction site model (ISM),³¹ where a polar molecule is described by multiple sites and each site carries a point charge. As the ISM is widely used in the molecular simulations, it would be of special interest to see how the MDH theory can be applied to such systems. In Appendix B, the details of the dressed molecular theory formulation for ISM molecular fluids are presented to facilitate the following discussion.

A. A MDH theory for ISM polar fluids

Consider the solvation of an ion in a single component ISM polar fluid. The central ion is tagged by i and its charge is denoted as q_i . The surrounding polar molecules with M sites are taken as the solvent. The pair potential between the ion i and a site j in the polar molecule is $u_{ij}(r) = u_{ij}^s(r) + \frac{q_i q_j}{\epsilon_0 r}$, where

$u_{ij}^s(r)$ is a short-ranged potential. The particle number density of the polar molecules is ρ .

Denote $\Phi_i(r)$ as the electric potential around the solute ion i . The Poisson equation for the electric potential reads $\nabla^2\Phi_i(r) = -\frac{4\pi}{\epsilon_0}[q_i\delta^{(3)}(\mathbf{r}) + \rho_i^{\text{ind}}(r)]$, where $\rho_i^{\text{ind}}(r) = \rho \sum_{j=1}^M q_j h_{ij}(r)$ is the induced charge density around the central ion and $h_{ij}(r) = g_{ij}(r) - 1$ is the correlation function between the solute i and the j th site of the solvent molecules. Using the formulation presented in Appendix B, the Poisson equation in k -space can be reformulated to $k^2\epsilon_l(k)\Phi_i(k) = 4\pi\theta_i(k)$. Following the discussions in Sec. II, the asymptotic analysis also leads to $\Phi_i(r) \simeq \frac{q_i}{\epsilon_b r} + \sum_n \frac{q_n e^{-knr}}{\epsilon_{bn} r}$,^{18,24} which implies that the dielectric response of an ISM polar fluid can also be expanded with the Born response mode and multi-DH response modes.

When $\Phi_o(r, \omega)$ in Eqs. (2)–(4) is replaced by $\Phi_i(r)$, we get the main working equations for the MDH theory of ISM polar fluids. Assume that the solvent site and solute ion are hard spheres with diameters σ and σ_i , the cavity radius can be evaluated as $a_i = (\sigma + \sigma_i)/2$. The solution of the electric potential around the ion is already shown in Sec. II, and the reader can refer to Eqs. (15)–(18).

Using the induced charge density $\rho_i^{\text{ind}}(k)$ from other methods, such as molecular simulations or integral equation theories, as input, one can fit $\rho_i^{\text{ind}}(k)$ with Eq. (18) and find the linear coefficients $\{C_l\}$, and then the excess electrostatic energy βu_i^{ele} can be evaluated using Eq. (20). Furthermore, it is also possible to evaluate the electrostatic contribution to the excess chemical potential $\beta\mu_i^{\text{ele}}$. In general, the chemical potential $\beta\mu_i^{\text{ele}}$ can be evaluated with the Kirkwood charging process and relies on the availability of $\{C_l\}$ as a function of the solute charge. When the polar solvent is symmetric in charge and size (the simplest case is a diatomic polar fluid with the same site size), our numerical calculation implies that the linear coefficients $\{C_l\}$ are insensitive to the solute charge. In such cases, one can assume that $\{C_l\}$ is independent of the solute charge and then one can easily find that $\beta\mu_i^{\text{ele}} = \beta u_i^{\text{ele}}$. However, when the polar fluid is asymmetric in charge or size, the dependence of coefficients $\{C_l\}$ on the solute charge could be evident and then $\beta\mu_i^{\text{ele}}$ could differ quite bit from βu_i^{ele} .

B. Applications to ion solvation in ISM polar fluids

In this section, we show how the MDH theory can be applied to ion solvation in ISM polar fluids. The validation of our MDH approach is tested for ion solvation in two ISM polar fluids.

1. Application to a symmetric diatomic polar fluid

Consider a solution consists of 510 polar molecules and one pair of conjugate solutes $j = 3, 4$ with charges $q_{3,4} = \pm q_o$. In this case, the solute particle number density is much smaller than that of the polar molecules and hence can be treated as in the dilute limit. A polar molecule consists of two atoms labeled 1 and 2, and each atom carries a charge $q_{1,2} = \pm q_s$. The solvent charges are fixed at $q_s = 0.5e_0$, where e_0 is the elementary charge. In the Gaussian unit, one can set $e_0 = 1$. The bond length between atom 1 and 2 is fixed at $l_{12} = 1.44 \text{ \AA}$. The pair additive potential between two atoms reads $u_{ij}(r) = \frac{q_i q_j}{\epsilon_0 r} + u_{ij}^s(r)$, where ϵ_0 is the dielectric

constant of the vacuum, $u_{ij}^s(r) = 4E_{ij} \left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^6 \right]$ is the van der Waals (vdw) interaction described by a Lennard-Jones potential. The parameters for the solvent species are $\sigma_{i'j'} = \sigma_s = 3.166 \text{ \AA}$ and $E_{i'j'} = E_s = 0.65 \text{ kJ/mol}$ ($i, j' = 1, 2$). The solute-solute interaction parameters are $\sigma_{jj'} = \sigma_o$ and $E_{jj'} = E_o = 0.41 \text{ kJ/mol}$ ($j, j' = 3, 4$). The parameters for the solute-solvent interactions are $\sigma_{ij} = \sigma_{so} = (\sigma_o + \sigma_s)/2$ and $E_{ij} = E_{so} = \sqrt{E_s E_o} = 0.5162 \text{ kJ/mol}$ ($i = 1, 2; j = 3, 4$). As one can see, the system is symmetric so that the excess electrostatic energy u_j^{ele} is the same for $j = 3, 4$. In the dilute limit, the excess electrostatic energy u_j^{ele} is insensitive to the solute-solute interaction potential $u_{jj'}(r)$, given σ_o is not much smaller than σ_s .

Molecular dynamics (MD) simulations are performed with the DL-POLY program.⁵⁰ NVT ensemble with periodic boundary conditions at temperature $T = 300 \text{ K}$ is used. The length of the cubic simulation box is $d = 30.397 \text{ \AA}$ and then the total number density is found to be $\rho = 0.0182/\text{\AA}^3$. The time step in the simulations is about 1.2 fs, and a trajectory of 0.48 ns was collected after an equilibrium run of 0.48 ns. Truncation of the van der Waals interaction is at 10 \AA . Ewald summation is used to find the excess electrostatic energies, where particles in the image cells are treated as part of the solvent, which contribute to the electrostatic energy of the solute. When 20 000 equilibrium configurations of the system are used, the typical uncertainty of the excess electrostatic energy u_j^{ele} is about 1 kJ/mol. One may note there are many corrections that need to be made to single ion solvation energies in simulations.⁵¹ When $q_o = 1$, one can treat the system as a dilute electrolyte solution, and then there is an electrostatic contribution due to the ion interactions. This contribution can be evaluated from the DH theory, which reads $\Delta u = -\frac{q^2}{2\epsilon_0\epsilon_r} k_D$, with $k_D = \sqrt{\frac{4\pi\beta q_o^2 n}{\epsilon_0\epsilon_r}}$, the inverse Debye length. Note that the total electrostatic energy from Ewald summation contains contribution from both the polar species and ionic species. We subtract the DH energy contribution from the total electrostatic energy and use it as the electrostatic energy of a single ion in polar fluids.

When 510 polar molecules and one pair of neutral solutes with $q_o = 0$ are used in the simulations, the dipole moment fluctuations of the bulk system are collected to evaluate the dielectric constant, which is found to be $\epsilon_r = 97$. The dielectric response function $\chi(k) \equiv 1 - \frac{\epsilon_0}{\epsilon_l(k)}$ from MD simulation is fitted to a half empirical function

$$\chi(k) = \frac{(1 - \frac{1}{\epsilon_r})(a_1 + a_3 b_1 + a_2 b_1^2 + a_4 \sin(b_2 k))k^2}{k^4 + (a_1 k^2 - a_2) \cos(b_1 k) + a_3 k \sin(b_1 k) + a_2},$$
^{52–54} which is the function form of the MSA response function for a dipolar hard sphere fluid. The fitted parameters are found to be $a_1 = 7.1953$, $a_2 = 120.58$, $a_3 = 10.431$, $a_4 = -619.04$, $b_1 = 3.2588$, and $b_2 = 0.30096$. The Debye parameters $\{k_l\}$ can be determined from the pole structure of the response function, i.e., $\chi^{-1}(ik_l) = 0$, where the first four Debye parameters are $k_{1,2} = (0.232 \pm 1.824i) \text{ \AA}^{-1}$ and $k_{3,4} = (0.576 \pm 3.442i) \text{ \AA}^{-1}$.

As the first test case, we set $q_o = 1$ and $\sigma_{so} = 3.483 \text{ \AA}$. With the correlation function $h_{ij}(r)$ from simulations, the induced charge density around the ion j is evaluated as $\rho_j^{\text{ind}}(r) = \sum_{i=1,2} q_i n_i h_{ij}(r)$. Due to the symmetry of the system, one can find that $\rho_4^{\text{ind}}(r) = -\rho_3^{\text{ind}}(r)$ and $u_4^{\text{ele}} = u_3^{\text{ele}}$, so hereafter we

only show the results for solute 3. The first valley position $r_1 = 3.05 \text{ \AA}$ of $\rho_3^{\text{ind}}(r)$ is taken as the effective solvent-solute cavity size a_3 . The induced charge density $\rho_3^{\text{ind}}(k)$ in k -space is fitted to Eq. (18), where the first five linear coefficients are $C_0 = 1$, $C_{1,2} = -0.414 \pm 0.788i$ and $C_{3,4} = 0.414 \pm 0.385i$. The excess internal energy from MDH theory is $u_3^{\text{ele}} = -305 \text{ kJ/mol}$, which can be compared with $u_3^{\text{ele}} = -311 \text{ kJ/mol}$ from MD simulations. As a comparison, the Born model leads to $u_3^{\text{ele}} = -225 \text{ kJ/mol}$ which overestimates the excess electrostatic energy by 28%. We also did calculations for solutes with other sizes, it is found that our theories can always lead to accurate electrostatic energies.

As the second test, we consider the solute charge dependence of the excess electrostatic energies. The solute size is fixed at $\sigma_{so} = 3.483 \text{ \AA}$ and q_o is taken as a parameter. By assuming that the response coefficients $\{C_l\}$ are insensitive to the solute charge, we can predict the excess internal energies of solutes with different charges. Using $\{C_l\}$ and a_3 for solute 3 with $q_o = 1$ and $\sigma_{so} = 3.483 \text{ \AA}$, u_3^{ele} for solutes with different charges q_o is evaluated with Eq. (20). The results for u_3^{ex} are shown in Fig. 5. As one can see, the MDH theory is in good agreement with the MD simulations, where the energy difference is no more than 7% in the range of $0.5 \leq q_o \leq 3$, which can be improved if the $\{C_l\}$ dependence on the solute charge is accounted for. As a comparison, the Born theory always overestimates the energy more than 21% and hence is not reliable.

As the third test, we consider the size dependence of the excess electrostatic energies. The solute charge is fixed at $q_o = 1$ and the solute size σ_{so} is taken as a parameter. Using the charge density $\rho_3^{\text{ind}}(r)$ from MD simulations, the location r_1 of the first valley of $\rho_3^{\text{ind}}(r)$ can be found. r_1 can be well fitted to σ_{so} with a linear function $r_1 = 0.984\sigma_{so} - 0.349 \text{ \AA}$ and is used as the effective size in the MDH theory. Using $\{k_l\}$ and $\{C_l\}$ from the first test case, the energies u_3^{ele} for solutes with different sizes can be evaluated with Eq. (20) and are presented in Fig. 6. In the range of $2.5 \text{ \AA} \leq \sigma_{so} \leq 6.0 \text{ \AA}$, the predicted excess internal energies from MDH theory are in good agreement with the MD results, where the difference is no more than 4%. The Born results are also shown. Again, one

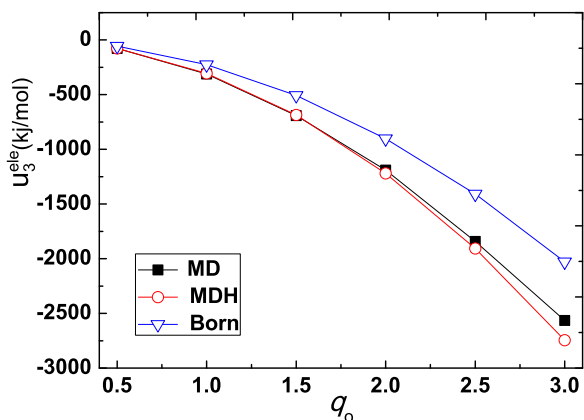


FIG. 5. Excess electrostatic internal energy u_3^{ele} as a function of the solute charge q_o . The MD results are denoted by filled squares, the MDH results are denoted by hollow circles, and the Born results are denoted by hollow triangles. The lines are guides to the eye.

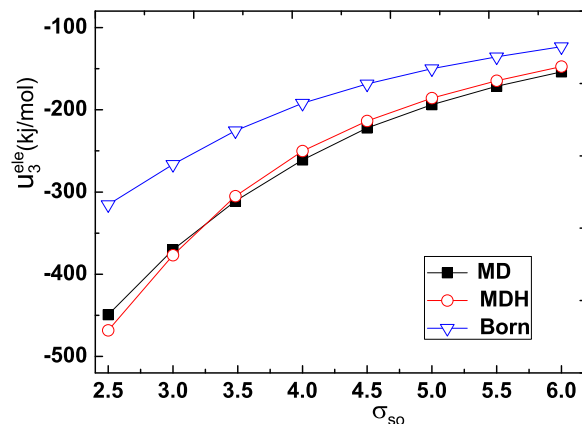


FIG. 6. Excess electrostatic internal energy u_3^{ele} as a function of the solute-solvent diameter σ_{so} . The MD results are denoted by filled squares, the MDH results are denoted by hollow circles, and the Born results are denoted by hollow triangles. The lines are guides to the eye.

can see that the Born theory is inaccurate and overestimates the electrostatic energies by 20% to 30%.

2. Application to ion solvation in a water model

Using the SPC/E water model,⁵⁵ a mixture of 510 water molecule and one pair of conjugate solute with charge $q_{3,4} = \pm e_0$ is simulated using the DL-POLY program.⁵⁰ The van der Waals (vdw) interaction between two atoms is the Lennard-Jones potential $u_{ij}^s(r) = 4E_{ij}[(\frac{\sigma_{ij}}{r})^{12} - (\frac{\sigma_{ij}}{r})^6]$. The O atom and H atom in water molecule are labeled as species 1 and 2. The vdw interaction between H atom and other atoms is neglected in the SPC/E model and the other parameters used for our studies are $E_{11} = 0.65 \text{ kJ/mol}$, $\sigma_{11} = 3.166 \text{ \AA}$, $E_{34} = E_{33} = E_{44} = 0.41 \text{ kJ/mol}$, $\sigma_{34} = \sigma_{33} = \sigma_{44} = 3.8 \text{ \AA}$, $E_{41} = E_{31} = \sqrt{E_{11}E_{33}} = 0.5162 \text{ kJ/mol}$, and $\sigma_{41} = \sigma_{31} = (\sigma_{33} + \sigma_{11})/2 = 3.483 \text{ \AA}$. NVT ensemble with periodic boundary conditions is used, where the temperature is $T = 300 \text{ K}$ and the total number density is $\rho = 0.0336/\text{\AA}^3$. The dielectric constant $\epsilon_r = 71$ from previous literatures⁵⁶ is adopted in this study. Using the dielectric response function $\chi(k)$ from simulations as input, the first four Debye parameters k_l are found to be $k_{1,2} = (0.512 \pm 3.021i) \text{ \AA}^{-1}$ and $k_{3,4} = (1.056 \pm 5.340i) \text{ \AA}^{-1}$. Using the location r_1 of the first valley (or the first peak) of the induced charge density around the solute 3 (or solute 4), the effective size for the solute-solvent interaction is $a_j = 3.03 \text{ \AA}$ for ion 3 (or $a_j = 1.92 \text{ \AA}$ for ion 4). Using the induced charge density $\rho_{3,4}(k)$ as input, the coefficients are found to be $C_0 = 1$, $C_{1,2} = -0.273 \mp 0.542i$, and $C_{3,4} = 0.273 \mp 0.554i$ for ion 3 and $C_0 = 1$, $C_{1,2} = -0.647 \mp 0.771i$ and $C_{3,4} = 0.647 \pm 0.312i$ for ion 4.

Since we insert a pair of ions into the system, there is an electrostatic energy due to interaction between ionic species. Following the same idea as used for diatomic polar fluids in Sec. III B 1, the electrostatic energy contribution from ionic species is evaluated from DH theory and is subtracted from the total electrostatic energy. The excess internal energies from MDH theory are found to be $u_{3,4}^{\text{ele}} = -268 \text{ kJ/mol}$, -435 kJ/mol , which differ the MD results, $u_{3,4}^{\text{ele}} = -281 \text{ kJ/mol}$, -459 kJ/mol , by 5%. As a comparison, the Born model leads to $u_{3,4}^{\text{ele}} = -226 \text{ kJ/mol}$, -357 kJ/mol which overestimates the excess

internal energies by about 20%. It is worth to note that the accuracy of our MDH theory could be improved by a refined choice of the effective solute cavity size a_j , for example, using $a_j = r_1 - 0.1 \text{ \AA}$, one can find a new set of coefficients $\{C_l\}$ and further reduce the energy difference between MDH theory and MD simulations to about 2%. One may note that the Born results can also be improved by tuning the size parameter. When using $a_j = r_1 - 0.1 \text{ \AA}$, the Born energy results can also be improved by 2%-3% but are still much less satisfactory than the MDH theory. If one tries to match the Born energy to the MD values, the Born radius needs to be tuned to $a = 2.42 \text{ \AA}$ (or $a = 1.49 \text{ \AA}$) for the cation (or the anion) used in this study and hence is significantly smaller than r_1 . To this end, further work would be interesting to find better ways to determine the effective solute size with soft interactions. In addition, our MDH can discriminate the solvation energy asymmetry of cations and anions in water.

As our formulation is a linear theory and hence it would be straightforward to apply our theory to the solvation of solutes with general charge distribution and geometry, which can be done in four steps. First, one can determine ϵ_r and $\{k_l\}$ with the bulk dielectric function of the polar fluids. Second, one can use the induced charge density of a test ion with size comparable to the solvent species to determine the coefficients $\{C_l\}$. Third, one can replace the charge density and the boundary condition in Eqs. (3) and (4) by that of the solute of interest and then solve the dielectric boundary problem for each response mode. Finally, one can sum up the energy contribution from all response modes to get the excess chemical potential just as in the case of solvation in ionic fluids.²⁶ One may also note that our discussion is based on the assumption that the molecules are hard objects. For polar fluids with soft interactions, the effective cavity size may need to be determined with a perturbation theory or free energy minimization process.⁵⁷⁻⁵⁹ Note that the application of the MDH theory to ion solvation requires the solute-solvent correlation functions $h_{so}(r)$ as input. However, the exact correlation functions in general cases are not easy to find. One may use the Gaussian field model^{60,61} or the mean spherical approximation as the closure in the integral equation theory and then the correlation functions can be determined, which deserves further studies.

IV. CONCLUDING REMARKS

In summary, a molecular Debye-Hückel theory for the polar fluids is developed. The dielectric response of a dipole fluid is described by a Born mode and a linear combination of Debye-Hückel modes. The Born mode is characterized by the bulk dielectric constant ϵ_r , while the nonlocal dielectric response is characterized by several Debye-Hückel modes with Debye parameter k_l . When the bulk dielectric function is known, one can determine the bulk dielectric constant and the Debye parameters. In the current formulation, the linear coefficients of the response modes are determined by the correlation function between the solute and its solvent. Then the electrostatic contribution to the thermodynamic properties of a polar fluid can be obtained analytically. The validity of our theory is demonstrated by applications to dipole hard sphere

fluids and various interaction site models of polar fluids such as water.

ACKNOWLEDGMENTS

T. Xiao acknowledges the financial support from the National Natural Science Foundation of China (NSFC) (Grant No. 21403041), the Natural Science Foundation of the Education Department of Guizhou Province (Nos. ZDXK[2014]18 and QJHKY[2015]329), and a startup package from Guizhou Education University. X. Song was supported by the Division of Material Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC02-07CH11358 with Iowa State University.

APPENDIX A: THE DRESSED MOLECULE THEORY OF DIPOLE HARD SPHERE FLUIDS

The key idea in the dressed molecule theory is that the Poisson equation for the electric potential can be rewritten as a linearized Poisson-Boltzmann form after a charge renormalization process.²⁴ Even though a quite general formulation is given by Ramirez and Kjellander,²⁴ some of the key results are presented here for two widely used models of molecular fluids, a mixture of dipole/charge hard spheres and an interaction site model (ISM), to facilitate the development of our molecular Born-Debye-Hückel theory.

Consider a fluid mixture with one dipole species and two ionic species. The dipole species is tagged by d and the ionic species are tagged by $i = 1, 2$. The hard sphere diameter and the particle number density of the j species are denoted as b_j and n_j . The dipole moment of the dipole molecule is denoted as μ . The charge of the i th ionic species is denoted as q_i . Due to the charge neutrality condition, one can expect that $\sum_i q_i n_i = 0$. Let $\sigma_j(\mathbf{r}, \omega)$ be the charge density of the j species. It is known that $\sigma_i(\mathbf{r}, \omega) = q_i \delta(\mathbf{r})$ and $\sigma_d(\mathbf{r}, \omega) = -\mu \hat{\mu} \cdot \nabla \delta(\mathbf{r})$, where $\delta(\mathbf{r})$ is the Dirac delta function and $\hat{\mu} = \hat{\mu}(\omega)$ is the unit vectors in the direction of the dipole.

The pair potential between species j with orientation ω_1 and the species l with orientation ω_2 reads

$$u_{jl}(\mathbf{r}, \omega_1, \omega_2) = u_{jl}^{\text{hs}}(r) + u_{jl}^{\text{ele}}(\mathbf{r}, \omega_1, \omega_2), \quad (\text{A1})$$

where $u_{jl}^{\text{hs}}(r)$ is a hard sphere potential with radius $\sigma_{jl} = (\sigma_j + \sigma_l)/2$ and $u_{jl}^{\text{ele}}(\mathbf{r}, \omega_1, \omega_2)$ is the electrostatic interaction that reads^{15,48}

$$\begin{aligned} u_{dd}^{\text{ele}}(\mathbf{r}, \omega_1, \omega_2) &= -\frac{\mu^2}{\epsilon_0 r^3} D_{12}, \\ u_{id}^{\text{ele}}(\mathbf{r}, \omega_2) &= -\frac{q_i \mu}{\epsilon_0 r^2} E_2, \quad (i = 1, 2), \\ u_{ii'}^{\text{ele}}(\mathbf{r}) &= \frac{q_i q_{i'}}{\epsilon_0 r}, \quad (i, i' = 1, 2), \end{aligned} \quad (\text{A2})$$

where ϵ_0 is the permittivity of the vacuum, $D_{12} \equiv 3\hat{\mu}(\omega_1) \cdot \hat{r} \hat{r} \cdot \hat{\mu}(\omega_2) - \hat{\mu}(\omega_1) \cdot \hat{\mu}(\omega_2)$, $E_2 \equiv \hat{\mu}(\omega_2) \cdot \hat{r}$, and $\hat{r} \equiv \mathbf{r}/r$ is a unit vector. In general, one can introduce the correlation function $h_{jl}(\mathbf{r}, \omega_1, \omega_2) = g_{jl}(\mathbf{r}, \omega_1, \omega_2) - 1$ between a species j and a species l to describe the equilibrium property of the mixtures. Naturally, for the charged species, there is no orientational dependence.

Denote $\Phi_j(\mathbf{r}, \omega)$ as the mean electric potential of a dipole molecule ($j = d$) or the mean electric potential of an ion ($j = 1, 2$). The Poisson equation for the electric potential in the r -space reads²⁴

$$\begin{aligned}\nabla^2\Phi_j(\mathbf{r}, \omega_1) &= -\frac{4\pi}{\epsilon_0}\rho_j^t(\mathbf{r}, \omega_1) \\ &= -\frac{4\pi}{\epsilon_0}[\sigma_j(\mathbf{r}, \omega_1) + \rho_j^{\text{ind}}(\mathbf{r}, \omega_1)],\end{aligned}\quad (\text{A3})$$

where $\rho_j^{\text{ind}}(\mathbf{r}_{12}, \omega_1) = \sum_l \frac{n_l}{4\pi} \int d\mathbf{r}_3 d\omega_2 h_{jl}(\mathbf{r}_{13}, \omega_1, \omega_2) \sigma_l(\mathbf{r}_{32}, \omega_2)$ is the induced charge density and $\int d\omega = 4\pi$ for a dipole or a charge angular integration.

Introduce $f(\mathbf{k}, \omega_1) = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}, \omega_1)$ as the three-dimensional Fourier transform of a function $f(\mathbf{r}, \omega_1)$ in the r -space. It is easy to find that $\sigma_i(\mathbf{k}, \omega_1) = q_i$, $\sigma_d(\mathbf{k}, \omega_2) = -ik\mu\hat{E}_2$ where $\hat{E}_2 = \hat{\mu}(\omega_2) \cdot \hat{k}$.^{29,40} In k -space, the Poisson equation reads

$$\begin{aligned}k^2\Phi_j(\mathbf{k}, \omega_1) &= \frac{4\pi}{\epsilon_0}[\sigma_j(\mathbf{k}, \omega_1) \\ &+ \sum_l \frac{n_l}{4\pi} \int d\omega_3 h_{jl}(\mathbf{k}, \omega_1, \omega_2) \sigma_l(\mathbf{k}, \omega_2)], \\ &= \frac{4\pi}{\epsilon_0} \sigma_l(\mathbf{k}, \omega_2) * [\delta(\omega_{12}) + \sum_l \frac{n_l}{4\pi} h_{jl}(\mathbf{k}, \omega_1, \omega_2)],\end{aligned}\quad (\text{A4})$$

where $\delta(\omega)$ is an angle Dirac delta function and the $*$ symbol denotes the convolution integration over the angle variable ω_2 . Let Φ and \mathbf{p} be vectors with elements $\Phi_j(\mathbf{k}, \omega)$ and $\sigma_l(\mathbf{k}, \omega)$. In the matrix form, the Poisson equation reads

$$k^2\Phi^\dagger = \frac{4\pi}{\epsilon_0} \mathbf{p}^\dagger * [\mathbf{I} + \mathbf{NH}],\quad (\text{A5})$$

where \mathbf{H} , \mathbf{N} , and \mathbf{I} are matrixes with element $H_{jl} = h_{jl}(\mathbf{k}, \omega_1, \omega_2)$, $N_{jl} = \frac{n_l}{4\pi} \delta_{jl}$, and $I_{jl} = \delta(\omega_{12})$, respectively, δ_{jl} is the Kronecker delta function, the superscript “ \dagger ” denotes a combination of matrix transpose and complex conjugate operations (Hermitian conjugation) so that the element of the row vector Φ^\dagger is $\Phi_l^\dagger = \Phi_l(-\mathbf{k}, \omega_1)$.

Denote \mathbf{C} as a matrix with elements $c_{jl}(\mathbf{r}, \omega_1, \omega_2)$, which is the direct correlation function between species j and l . In k -space, the Ornstein-Zernike (OZ) equation reads²⁴

$$(\mathbf{I} + \mathbf{NH}) * (\mathbf{I} - \mathbf{NC}) = \mathbf{I}.\quad (\text{A6})$$

Note that $\lim_{r \rightarrow \infty} c_{jl}(\mathbf{r}, \omega_1, \omega_2) = -\beta u_{jl}^{\text{ele}}(\mathbf{r}, \omega_1, \omega_2)$, $\beta u_{dd}^{\text{ele}}(\mathbf{k}, \omega_1, \omega_2) = \frac{4\pi\beta}{\epsilon_0 k^2} \sigma_d(\mathbf{k}, \omega_1) \sigma_d(-\mathbf{k}, \omega_2)$, $\beta u_{id}^{\text{ele}}(\mathbf{k}, \omega_2) = \frac{4\pi\beta}{\epsilon_0 k^2} \sigma_i(\mathbf{k}) \sigma_d(-\mathbf{k}, \omega_2)$, $\beta u_{i'i'}^{\text{ele}}(\mathbf{k}) = \frac{4\pi\beta}{\epsilon_0 k^2} \sigma_i(\mathbf{k}) \sigma_{i'}(-\mathbf{k})$,²⁴ and $\phi(k) = \frac{4\pi}{\epsilon_0 k^2}$, then one can introduce short ranged direct correlation function \mathbf{C}^s as²⁴

$$\mathbf{C}^s = \mathbf{C} + \beta\phi(k)\mathbf{pp}^\dagger,\quad (\text{A7})$$

where the element of the row vector \mathbf{p}^\dagger is $p_l^\dagger = \sigma_l(-\mathbf{k}, \omega)$.

A short-ranged correlation function \mathbf{H}^s can be defined via the OZ equation²⁴

$$(\mathbf{I} + \mathbf{NH}^s) * (\mathbf{I} - \mathbf{NC}^s) = \mathbf{I}.\quad (\text{A8})$$

Define the effective charge density Θ as²⁴

$$\Theta^\dagger \equiv \mathbf{p}^\dagger * [\mathbf{I} + \mathbf{NH}^s],\quad (\text{A9})$$

one can times Eq. (A8) by $(\mathbf{I} + \mathbf{NH})\mathbf{N}^{-1}$ from the right-hand side, then using Eqs. (A6) and (A7), it is found that²⁴

$$\mathbf{H}^s - \beta[\mathbf{I} + \mathbf{H}^s\mathbf{N}] * \mathbf{p}\phi(k)\mathbf{p}^\dagger * [\mathbf{I} + \mathbf{NH}] = \mathbf{H}.\quad (\text{A10})$$

Using Eqs. (A5) and (A9), Eq. (A10) can be rewritten as²⁴

$$\mathbf{H}^s - \beta\Theta\Phi^\dagger = \mathbf{H}.\quad (\text{A11})$$

Then the Poisson equation, Eq. (A5), can be rewritten as²⁴

$$k^2\Phi^\dagger = \frac{4\pi}{\epsilon_0} \Theta^\dagger - \alpha(k)\Phi^\dagger,\quad (\text{A12})$$

where $\alpha(k) \equiv \frac{4\pi\beta}{\epsilon_0} \mathbf{p}^\dagger * \mathbf{N}\Theta$ is a local response function. The bulk dielectric function $\epsilon_l(k)$ can be evaluated as^{21,24}

$$1 - \frac{\epsilon_0}{\epsilon_l(k)} = \frac{4\pi\beta}{\epsilon_0 k^2} \sum_l \frac{n_l}{4\pi} \sigma_l(\mathbf{k}, \omega_1) * \rho_l^t(-\mathbf{k}, \omega_1).\quad (\text{A13})$$

It is known that $\epsilon_l(k)$ relates to the local response function $\alpha(k)$ via $\epsilon_l(k) = \epsilon_0 + \alpha(k)/k^2$;^{21,24} hence, Eq. (A12) leads to

$$k^2\epsilon_l(k)\Phi^\dagger = 4\pi\Theta^\dagger,\quad (\text{A14})$$

which is the key result of the dressed molecular theory and also the starting point of our MDH development.

It would be of interest to see how the current formulation of correlation functions can be used to evaluate the dielectric function so that a connection can be made with the conventional results. It is known that the correlation function can be expanded as²⁹

$$\begin{aligned}h_{dd}(\mathbf{r}, \omega_1, \omega_2) &= h_{dd}^0(r) + h_{dd}^D(r)D_{12} + h_{dd}^\Delta(r)\Delta_{12}, \\ h_{id}(\mathbf{r}, \omega_1, \omega_2) &= h_{di}(\mathbf{r}, \omega_2, \omega_1) \\ &= h_{id}^0(r) + h_{id}^E(r)E_2, \quad (i = 1, 2), \\ h_{i'i'}(\mathbf{r}, \omega_1, \omega_2) &= h_{i'i'}^0(r), \quad (i, i' = 1, 2),\end{aligned}\quad (\text{A15})$$

where $\Delta_{12} = \hat{\mu}(\omega_1) \cdot \hat{\mu}(\omega_2)$ and the functions $h_{jl}^0(r)$, $h_{dd}^D(r)$, $h_{id}^E(r)$, and $h_{dd}^\Delta(r)$ can be determined analytically from the mean spherical approximation.²⁹ After the Fourier transform, it is found that the correlation functions in k -space read

$$\begin{aligned}h_{dd}(\mathbf{k}, \omega_1, \omega_2) &= h_{dd}^0(k) + \hat{h}_{dd}^D(k)\hat{D}_{12} + h_{dd}^\Delta(k)\Delta_{12}, \\ h_{id}(\mathbf{k}, \omega_1, \omega_2) &= h_{di}(\mathbf{k}, \omega_2, \omega_1) = h_{id}^0(k) + h_{id}^E(k)\hat{E}_2, \\ h_{i'i'}(\mathbf{k}, \omega_1, \omega_2) &= h_{i'i'}^0(k),\end{aligned}\quad (\text{A16})$$

where $h_{dd}^0(k) = \int_0^\infty dr 4\pi r^2 j_0(kr) h_{dd}^0(r)$, $h_{dd}^\Delta(k) = \int_0^\infty dr 4\pi r^2 j_0(kr) h_{dd}^\Delta(r)$, $\hat{h}_{dd}^D(k) = \int_0^\infty dr 4\pi r^2 j_2(kr) h_{dd}^D(r)$, $h_{id}^0(k) = \int_0^\infty dr 4\pi r^2 j_0(kr) h_{id}^0(r)$, $\hat{h}_{id}^E(k) = -i \int_0^\infty dr 4\pi r^2 j_1(kr) h_{id}^E(r)$, $h_{i'i'}^0(k) = \int_0^\infty dr 4\pi r^2 j_0(kr) h_{i'i'}^0(r)$ and $j_n(x)$ is the spherical Bessel function. Note that the angle convolution rule leads to $\hat{D}_{12} * \hat{E}_2 = 8\pi\hat{E}_1/3$, $\Delta_{12} * \hat{E}_2 = 4\pi\hat{E}_1/3$, $\hat{E}_2 * 1 = 0$, $\hat{E}_1 * 1 = 4\pi\hat{E}_1$, and $\hat{E}_2 * \hat{E}_2 = 4\pi/3$,⁴⁸ then the total charge density about the dipole molecule $\rho_d^t(\mathbf{k}, \omega_1) = \sigma_d(\mathbf{k}, \omega_1) + \frac{n_0}{4\pi} h_{dd}(\mathbf{k}, \omega_1, \omega_2) * \sigma_d(\mathbf{k}, \omega_2) + \sum_{i'} \frac{n_{i'}}{4\pi} h_{di'}(\mathbf{k}, \omega_1, \omega_2) * \sigma_{i'}(\mathbf{k}, \omega_2)$ can further be

evaluated as

$$\begin{aligned}\rho_d^i(\mathbf{k}, \omega_1) &= -ik\mu\hat{E}_1 + \frac{n_d}{4\pi} [h_{dd}^0(k) + \hat{h}_{dd}^D(k)\hat{D}_{12} \\ &\quad + h_{dd}^\Delta(k)\Delta_{12}] * (-ik\mu\hat{E}_2) \\ &\quad + \sum_{i'} \frac{n_{i'}}{4\pi} (h_{i'd}^0(k) + \hat{h}_{i'd}^E(k)\hat{E}_1) * q_i \\ &= -ik\mu\hat{E}_1 (1 + \frac{n_d}{3} [2\hat{h}_{dd}^D(k) + h_{dd}^\Delta(k)]) \\ &\quad + \sum_{i'} n_{i'} q_{i'} [h_{i'd}^0(k) + \hat{h}_{i'd}^E(k)\hat{E}_1]. \quad (\text{A17})\end{aligned}$$

The total charge density around an ion $\rho_i^t(\mathbf{k}, \omega_1)$ = $\sigma_i(\mathbf{k}, \omega_1) + \frac{n_d}{4\pi} h_{id}(\mathbf{k}, \omega_1, \omega_2) * \sigma_d(\mathbf{k}, \omega_2) + \sum_{i'} \frac{n_{i'}}{4\pi} h_{i'i}(\mathbf{k}, \omega_1, \omega_2) * \sigma_{i'}(\mathbf{k}, \omega_2)$ reads

$$\begin{aligned}\rho_i^t(\mathbf{k}, \omega_1) &= q_i + \frac{n_d}{4\pi} [h_{id}^0(k) + \hat{h}_{id}^E(k)\hat{E}_2] * (-ik\mu\hat{E}_2) \\ &\quad + \sum_{i'} \frac{n_{i'}}{4\pi} h_{i'i}^0(k) * q_{i'} \\ &= q_i - ik\mu \frac{n_d}{3} \hat{h}_{id}^E(k) + \sum_{i'} n_{i'} q_{i'} h_{i'i}^0(k). \quad (\text{A18})\end{aligned}$$

It would also be of interest to see how the polarization density is related to the induced charge density. The polarization density $P_i(r) = \frac{n_d}{4\pi} \int d\omega_2 h_{id}(\mathbf{r}, \omega_2) \mu[\hat{\mu}(\omega_2) \cdot \hat{r}]$ around an ion reduces to

$$P_i(r) = \frac{n_d}{4\pi} \int d\omega_2 [h_{id}^0(r) + h_{id}^E(r)E_2] \mu E_2 = \frac{n_d \mu}{3} h_{id}^E(r), \quad (\text{A19})$$

which further leads to

$$\frac{n_d \mu}{3} \hat{h}_{id}^E(k) = -i \int_0^\infty dr 4\pi r^2 j_1(kr) P_i(r). \quad (\text{A20})$$

Note that the polarization response to the ion leads to an induced charge density of $\rho_i^p(k) \equiv \frac{n_d}{4\pi} h_{id}(\mathbf{k}, \omega_1, \omega_2) * \sigma_d(\mathbf{k}, \omega_2) = ik\mu \frac{n_d}{3} \hat{h}_{id}^E(k)$. One can find that

$$\rho_i^p(k) = k \int_0^\infty dr 4\pi r^2 j_1(kr) P_i(r). \quad (\text{A21})$$

Equation (A21) can be used to evaluate the induced charge density for a given polarization density.

Now with Eqs. (A17), (A18), and Eq. (A13), the dielectric response function $\chi(k) \equiv 1 - \frac{\epsilon_0}{\epsilon(k)}$ of the mixture can be evaluated analytically. In the special case of pure dipole fluids where the ionic species vanishes, the dielectric response function can be evaluated as²⁸

$$\begin{aligned}\chi(k) &= \frac{\beta n_d}{\epsilon_0 k^2} \sigma_d(\mathbf{k}, \omega) * \rho_d^t(-\mathbf{k}, \omega) \\ &= \frac{4\pi \beta n_d \mu^2}{3\epsilon_0} (1 + \frac{n_d}{3} [2\hat{h}_{dd}^D(k) + h_{dd}^\Delta(k)]), \quad (\text{A22})\end{aligned}$$

which agrees with the results in the literature, for example, Eq. (12.5.21) of Ref. 31.

APPENDIX B: THE DRESSED MOLECULE THEORY OF ISM MOLECULAR FLUIDS

In this section, the dressed molecule theory is presented using the interaction site model of molecular fluids, which is widely used in molecular simulations. A molecule of type M has L_M interaction sites and its i th site carries a charge

q_{Mi} , so the net charge of the M molecule is $q_M = \sum_{i=1}^{L_M} q_{Mi}$. When $q_M = 0$, the M molecule is a neutral species. The particle number density of the M molecule is n_M , the reduced inverse temperature is $\beta = \frac{1}{k_B T}$ with k_B being the Boltzmann constant and T being the temperature; the dielectric constant of the vacuum is ϵ_0 . The pair potential between two molecules is $u_{MM'} = \sum_{i=1}^{L_M} \sum_{j=1}^{L_{M'}} u_{ij}(r_{ij})$, where $u_{ij}(r_{ij}) = u_{ij}^s(r_{ij}) + \frac{q_i q_j}{\epsilon_0 r_{ij}}$ is the pair additive potential between the i th site in the M molecule and the j th site in the M' molecule; and $r_{ij} = |\mathbf{r}_M^i - \mathbf{r}_{M'}^j|$ is the distance between the two sites, \mathbf{r}_M^i is the position of the i th site in the M molecule, and $u_{ij}^s(r_{ij})$ is the short ranged potential.

Denote $\Phi_{iM}(r)$ as the electric potential of a site i in the M molecule. The Poisson equation in the r -space reads⁶²

$$\begin{aligned}\nabla^2 \Phi_{iM}(r) &= -\frac{4\pi}{\epsilon_0} \rho_{iM}^t(r) \\ &= -\frac{4\pi}{\epsilon_0} [q_{iM} \delta(\mathbf{r}) + \rho_{iM}^{\text{intra}}(r) + \rho_{iM}^{\text{inter}}(r)], \quad (\text{B1})\end{aligned}$$

where $\rho_{iM}^t(r)$ is the total charge density, $\rho_{iM}^{\text{intra}}(r) = \sum_{jM \neq iM} q_{jM} w_{ijM}(r)$ is the charge density from intra-molecular interaction, $\rho_{iM}^{\text{inter}}(r) = \sum_{jM'} n_{M'} q_{jM'} h_{iMjM'}(r)$ is the charge density from inter-molecular interaction. $w_{ijM}(r) = \delta_{ij} \delta(\mathbf{r}) + (1 - \delta_{ij}) \delta(r - l_{ij}) / (4\pi l_{ij}^2)$, l_{ijM} is the bond length between the i th site and j th site in the M molecule, and δ_{ij} is the Kronecker delta function. $h_{iMjM'}(r) = g_{iMjM'} - 1$ is the correlation function between the i th site in the M molecule and the j th site in the M' molecule.

Let us introduce $f(k) = \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} = \int_0^\infty f(r) 4\pi r^2 \frac{\sin(kr)}{kr} dr$ as the three-dimensional Fourier transform of a function $f(r)$ in the r -space. In the k -space, the Poisson equation reads

$$k^2 \Phi_{iM}(k) = \frac{4\pi}{\epsilon_0} [\sum_{jM} q_{jM} w_{ijM}(k) + \sum_{jM'} n_{M'} q_{jM'} h_{iMjM'}(k)], \quad (\text{B2})$$

where $w_{ijM}(k) = \delta_{ij} + (1 - \delta_{ij}) \sin(kl_{ijM}) / (kl_{ijM})$.

Define $\Psi(k)$ and \mathbf{q} as vectors with element $\Phi_{iM}(k)$ and q_{iM} , and define $\mathbf{W}(k)$, $\mathbf{H}(k)$, and \mathbf{N} as matrixes with element $w_{iMjM'}(k) = \delta_{MM'} w_{ijM}(k)$, $h_{iMjM'}(k)$, and $N_{iMjM'} = \delta_{ij} \delta_{MM'} n_{M'}$, respectively. Now the Poisson equation in k -space reads

$$k^2 \Psi^T(k) = \frac{4\pi}{\epsilon_0} \mathbf{q}^T [\mathbf{W}(k) + \mathbf{N}\mathbf{H}(k)], \quad (\text{B3})$$

where the superscript "T" denotes the transpose of the vector.

As the Ornstein-Zernike (OZ) equation is crucial for the derivation of dressed molecular theory, we introduce $c_{iMjM'}(r)$ as the direct correlation function between the i th site in the M molecule and the j th site in the M' molecule. In k -space, the OZ equation for the interaction site model reads^{31,63}

$$\begin{aligned}\mathbf{H}(k) &= \mathbf{W}(k)\mathbf{C}(k)[\mathbf{W}(k) + \mathbf{N}\mathbf{H}(k)] \\ &= [\mathbf{I} - \mathbf{W}(k)\mathbf{C}(k)\mathbf{N}]^{-1} \mathbf{W}(k)\mathbf{C}(k)\mathbf{W}(k), \quad (\text{B4})\end{aligned}$$

where $\mathbf{C}(k)$ is a matrix with element $c_{iMjM'}(k)$.

Using the asymptotic behavior $\lim_{r \rightarrow \infty} c_{iMjM'}(r) = -\frac{\beta q_{iM} q_{jM'}}{\epsilon_0 r}$, one can introduce a short ranged correlation function as

$$c_{iMjM'}^s(r) = c_{iMjM'}(r) + \frac{\beta q_{iM} q_{jM'}}{\epsilon_0 r}. \quad (\text{B5})$$

The Fourier transform of this equation leads to

$$\mathbf{C}(k) = \mathbf{C}^s(k) - \frac{4\pi \beta}{\epsilon_0 k^2} \mathbf{q} \cdot \mathbf{q}^T, \quad (\text{B6})$$

where $\mathbf{C}^s(k)$ is a matrix with element $C_{iMjM'}^s(k)$. Furthermore, one can introduce a short-ranged correlation function $h_{iMjM'}^s(k)$ via the OZ equation

$$\begin{aligned} \mathbf{H}^s(k) &= \mathbf{W}(k)\mathbf{C}^s(k)[\mathbf{W}(k) + \mathbf{N}\mathbf{H}^s(k)] \\ &= [\mathbf{I} - \mathbf{W}(k)\mathbf{C}^s(k)\mathbf{N}]^{-1}\mathbf{W}(k)\mathbf{C}^s(k)\mathbf{W}(k), \end{aligned} \quad (\text{B7})$$

where $\mathbf{H}^s(k)$ is a matrix with element $h_{iMjM'}^s(k)$. We define an effective charge density vector $\Theta(k)$ as

$$\Theta(k) \equiv [\mathbf{W}(k) + \mathbf{N}\mathbf{H}^s(k)]\mathbf{q}. \quad (\text{B8})$$

Note that the OZ equation, Eq. (B7), can also be rewritten as $[\mathbf{I} - \mathbf{N}\mathbf{W}(k)\mathbf{C}^s(k)][\mathbf{W}(k) + \mathbf{N}\mathbf{H}^s(k)] = \mathbf{W}(k)$, the charge density vector reads

$$\Theta(k) = [\mathbf{I} - \mathbf{N}\mathbf{W}(k)\mathbf{C}^s(k)]^{-1}\mathbf{W}(k)\mathbf{q}. \quad (\text{B9})$$

Using Eqs. (B3), (B4), and (B6), one can find that

$$\begin{aligned} \mathbf{H}(k) &= \mathbf{W}(k)[\mathbf{C}^s(k) - \frac{4\pi\beta}{\epsilon_0 k^2}\mathbf{q}\mathbf{q}^T][\mathbf{W}(k) + \mathbf{N}\mathbf{H}(k)] \\ &= \mathbf{W}(k)\mathbf{C}^s(k)[\mathbf{W}(k) + \mathbf{N}\mathbf{H}(k)] - \beta\mathbf{W}(k)\mathbf{q}\Psi^T(k). \end{aligned} \quad (\text{B10})$$

This equation can be rewritten as

$$\begin{aligned} \mathbf{H}(k) &= [\mathbf{I} - \mathbf{W}(k)\mathbf{C}^s(k)\mathbf{N}]^{-1}\mathbf{W}(k)\mathbf{C}^s(k)\mathbf{W}(k) \\ &\quad - \beta[\mathbf{I} - \mathbf{W}(k)\mathbf{C}^s(k)\mathbf{N}]^{-1}\mathbf{W}(k)\mathbf{q}\Psi^T(k) \\ &= \mathbf{H}^s(k) - \beta\Theta\Psi^T(k), \end{aligned} \quad (\text{B11})$$

where Eq. (B7) has been used in the second equality. Now the Poisson equation, Eq. (B3), can be evaluated as

$$\begin{aligned} k^2\Psi^T(k) &= \frac{4\pi}{\epsilon_0}[\mathbf{q}^T\mathbf{W}(k) + \mathbf{q}^T\mathbf{N}\mathbf{H}^s(k)] - \frac{4\pi\beta}{\epsilon_0}\mathbf{q}^T\mathbf{N}\Theta\Psi^T(k) \\ &= \frac{4\pi}{\epsilon_0}\Theta^T(k) - \frac{\alpha(k)}{\epsilon_0}\Psi^T(k), \end{aligned} \quad (\text{B12})$$

where $\alpha(k) \equiv 4\pi\beta\mathbf{q}^T\mathbf{N}\Theta = 4\pi\beta\sum_{iM}n_Mq_{iM}\theta_{iM}(k)$ is a local response function, $\theta_{iM}(k) \equiv \sum_{jM}q_{jM}w_{ijM}(k) + \sum_{jM'}q_{M'}n_{M'}h_{iMjM'}^s(k)$ is the element of $\Theta(k)$ and can be interpreted as an effective charge density of the site i . This equation leads to

$$k^2[\epsilon_0 + \alpha(k)/k^2]\Psi^T(k) = 4\pi\Theta^T(k). \quad (\text{B13})$$

The bulk dielectric function $\epsilon_l(k)$ can be evaluated as^{18,21}

$$1 - \frac{\epsilon_0}{\epsilon_l(k)} = \frac{4\pi\beta}{\epsilon_0 k^2} \sum_{iM} n_M q_{iM} \rho_{iM}^l(k), \quad (\text{B14})$$

and it is related to the local response function $\alpha(k)$ via $\epsilon_l(k) = \epsilon_0 + \alpha(k)/k^2$.^{18,21} The scalar form of Eq. (B13) reads

$$k^2\epsilon_l(k)\Phi_{iM}(k) = 4\pi\theta_{iM}(k). \quad (\text{B15})$$

Equation (B15) is the same as the dressed molecule theory for polar fluids with angle-dependent interaction.²⁴

Some remarks on the dressed molecule theory are in order. When different models are used, the bulk dielectric function $\epsilon_l(k)$ should be evaluated with different prescriptions, e.g., when the angle-dependent pair interaction potential or the site-site interaction potential is used, $\epsilon_l(k)$ would be evaluated with Eq. (A13) or Eq. (B14). When the charge distribution function used in Appendix A is taken as the same as that in

Appendix B, one can expect the Poisson equation in these two cases should be equivalent. So even though the detailed derivation of the dressed molecule theory in Appendix A seems to be different quite bit from that in Appendix B, the final results, Eqs. (A14) and (B15), are actually equivalent. As noted by Ohba and Arakawa¹⁸ and by Ramirez and Kjellander,²⁴ the dielectric function $\epsilon_l(k)$ for molecule fluids can be expanded as $\frac{\epsilon_l(k)}{\epsilon_0} = k_{\text{DH}}^2/k^2 + E_0 + O(k^2)$. For non-neutral molecules such as ionic liquids, the first term is non-zero and the DH results $\frac{\epsilon_l(k)}{\epsilon_0} \approx k_{\text{DH}}^2/k^2 + \epsilon_r$ with $k_{\text{DH}}^2 = \frac{4\pi\beta\sum_M n_M q_M^2}{\epsilon_0}$ can be recovered in the dilute limit. When the molecules are neutral, it is found that $k_{\text{DH}} = 0$ and then the Born results $\frac{\epsilon_l(k)}{\epsilon_0} \approx \epsilon_r$ are recovered in the dilute limit. Due to such differences in the dielectric response function, the electric potential of an ion in an ionic fluid decays asymptotically as $\Phi(r) \sim \sum_{n \geq 1} \frac{q_{\text{eff},n}}{\epsilon_{\text{eff},n}} \frac{e^{-knr}}{r}$, while electric potential of an ion in a polar fluid decays asymptotically as $\Phi_j(r) \sim \frac{q}{\epsilon_r r} + \sum_{n \geq 1} \frac{q_{\text{eff},n}}{\epsilon_{\text{eff},n}} \frac{e^{-knr}}{r}$.^{18,24} Since no constraints on the molecule charge distribution is used in the above derivation, the net charge q_M of the molecule could be either zero or nonzero. Then one can expect that the dressed molecule theory is applicable to both the ionic liquids (at least two $q_M \neq 0$) and the polar liquid (all $q_M = 0$). In the special case of a primitive model of electrolyte solutions, the dressed molecule theory reduces to the dressed ion theory.²⁴

¹A. George and W. Wilson, *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **50**, 361 (1994).

²A. Onufriev, D. Bashford, and D. A. Case, *Proteins: Struct., Funct., Bioinf.* **55**, 383 (2004).

³N. E. Chayen and E. Saridakis, *Nat. Methods* **5**, 147 (2008).

⁴R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956).

⁵J. K. Hwang and A. Warshel, *J. Am. Chem. Soc.* **109**, 715 (1987).

⁶A. Rosspeintner, B. Lang, and E. Vauthey, *Annu. Rev. Phys. Chem.* **64**, 247 (2013).

⁷M. Born, *Z. Phys.* **1**, 45 (1920).

⁸C. J. Cramer and D. G. Truhlar, *Chem. Rev.* **99**, 2161 (1999).

⁹C. Amovilli and B. Mennucci, *J. Phys. Chem. B* **101**, 1051 (1997).

¹⁰T. T. Duiignan, D. F. Parsons, and B. W. Ninham, *J. Phys. Chem. B* **117**, 9412 (2013).

¹¹T. T. Duiignan, D. F. Parsons, and B. W. Ninham, *J. Phys. Chem. B* **117**, 9421 (2013).

¹²D. Bashford and D. A. Case, *Annu. Rev. Phys. Chem.* **51**, 129 (2000).

¹³H. Nguyen, D. R. Roe, and C. Simmerling, *J. Chem. Theory Comput.* **9**, 2020 (2013).

¹⁴D. Y. C. Chan, D. J. Mitchell, B. W. Ninham, and B. A. Pailthorpe, *J. Chem. Phys.* **69**, 691 (1978).

¹⁵S. L. Carnie and D. Y. C. Chan, *J. Chem. Phys.* **73**, 2949 (1980).

¹⁶C. W. Outhwaite, *J. Chem. Phys.* **50**, 2277 (1969).

¹⁷C. W. Outhwaite, *Chem. Phys. Lett.* **5**, 77 (1970).

¹⁸M. Ohba and K. Arakawa, *J. Phys. Soc. Jpn.* **50**, 743 (1981).

¹⁹P. Attard, D. J. Mitchell, and B. W. Ninham, *J. Chem. Phys.* **88**, 4987 (1988).

²⁰A. McBride, M. Kohonen, and P. Attard, *J. Chem. Phys.* **109**, 2423 (1998).

²¹L. M. Varela, M. García, and V. Mosquera, *Phys. Rep.* **382**, 1 (2003).

²²R. Kjellander and D. J. Mitchell, *J. Chem. Phys.* **101**, 603 (1994).

²³R. Kjellander, *J. Phys. Chem.* **99**, 10392 (1995).

²⁴R. Ramirez and R. Kjellander, *J. Chem. Phys.* **119**, 11380 (2003).

²⁵X. Song, *J. Chem. Phys.* **131**, 044503 (2009).

²⁶T. Xiao and X. Song, *J. Chem. Phys.* **135**, 104104 (2011).

²⁷T. Xiao, *ChemPhysChem* **16**, 833 (2015).

²⁸F. O. Raineri, H. Resat, and H. L. Friedman, *J. Chem. Phys.* **96**, 3068 (1992).

²⁹M. S. Wertheim, *J. Chem. Phys.* **55**, 4291 (1971).

³⁰D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, Evanston, San Francisco, London, 1976).

³¹J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

³²J. G. Kirkwood, *J. Chem. Phys.* **7**, 919 (1939).

- ³³E. Pollock, B. Alder, and L. Pratt, *Proc. Natl. Acad. Sci. U. S. A.* **77**, 49 (1980).
- ³⁴A. A. Kornyshev and G. Sutmann, *J. Chem. Phys.* **104**, 1524 (1996).
- ³⁵A. Kornyshev, S. Leikin, and G. Sutmann, *Electrochim. Acta* **42**, 849 (1997).
- ³⁶I. G. Medvedev, *Electrochim. Acta* **49**, 207 (2004).
- ³⁷J. P. Bardhan, *J. Mech. Behav. Mater.* **22**, 169 (2013).
- ³⁸V. C. Weiss and W. Schroer, *J. Chem. Phys.* **108**, 7747 (1998).
- ³⁹J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, Inc., 1998).
- ⁴⁰E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **56**, 3086 (1972).
- ⁴¹E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **56**, 3093 (1972).
- ⁴²W. R. Fawcett, *J. Phys. Chem. B* **103**, 11181 (1999).
- ⁴³H. S. Ashbaugh and L. R. Pratt, *Rev. Mod. Phys.* **78**, 159 (2006).
- ⁴⁴L. Blum, *Theoretical Chemistry: Advances and Perspectives* (Academic, New York, 1980), Vol. 5, pp. 1–66.
- ⁴⁵G. S. Rushbrooke, G. Stell, and J. Høye, *Mol. Phys.* **26**, 1199 (1973).
- ⁴⁶L. Blum, *J. Chem. Phys.* **61**, 2129 (1974).
- ⁴⁷G. Patey, *Mol. Phys.* **34**, 427 (1977).
- ⁴⁸D. Y. C. Chan, D. J. Mitchell, and B. W. Ninham, *J. Chem. Phys.* **70**, 2946 (1979).
- ⁴⁹F. Vericat and L. Blum, *J. Stat. Phys.* **22**, 593 (1980).
- ⁵⁰I. T. Todorov, W. Smith, K. Trachenko, and M. T. Dove, *J. Mater. Chem.* **16**, 1911 (2006).
- ⁵¹M. A. Kastenholz and P. H. Hünenberger, *J. Chem. Phys.* **124**, 579 (2006).
- ⁵²T. Xiao and X. Song, *J. Chem. Phys.* **138**, 114105 (2013).
- ⁵³T. Xiao and X. Song, *J. Chem. Phys.* **141**, 134104 (2014).
- ⁵⁴T. Xiao, *Electrochim. Acta* **178**, 101 (2015).
- ⁵⁵H. Berendsen, J. Grigera, T. Straatsma *et al.*, *J. Phys. Chem.* **91**, 6269 (1987).
- ⁵⁶P. G. Kusalik, I. M. Svishchev *et al.*, *Science* **265**, 1219 (1994).
- ⁵⁷J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971).
- ⁵⁸H. C. Andersen, J. D. Weeks, and D. Chandler, *Phys. Rev. A* **4**, 1597 (1971).
- ⁵⁹F. Lado, *Mol. Phys.* **52**, 871 (1984).
- ⁶⁰D. Chandler, *Phys. Rev. E* **48**, 2898 (1993).
- ⁶¹X. Song, D. Chandler, and R. Marcus, *J. Phys. Chem.* **100**, 11954 (1996).
- ⁶²N. Bagatella-Flores and P. González-Mozuelos, *J. Chem. Phys.* **117**, 6133 (2002).
- ⁶³D. Chandler, *J. Chem. Phys.* **59**, 2742 (1973).