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Electric multipole moment fluctuations in polar liquids

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A general expression for the distribution of the fluctuating 2^ℓ -pole moment M_ℓ of a spherical sample of dielectric material is derived on the basis of dielectric theory combined with statistical mechanics. The formulas are compared with results from computer simulations of a weakly coupled Stockmayer fluid and the agreement is shown to be excellent. Furthermore, we calculate the size of the coupling, quantified through the free energy of solvation A_{solv} , of the fluctuating electric moments to a surrounding dielectric medium. It turns out that the contribution to A_{solv} from each fluctuating electric moment actually *increases* with increasing order ℓ of the moment, resulting in a formally infinite free energy of solvation. We also present a correction to A_{solv} for molecular media, which shows that the molecular nature of the surrounding medium effectively suppresses the divergence in the solvation free energy. © 2009 American Institute of Physics.

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I. INTRODUCTION

The investigation of structural and thermodynamical properties of liquids composed of molecular dipoles is a problem of long-standing interest due to both the high abundance of such liquids in nature and their interesting thermodynamic properties. In particular, a lot of effort has been put into understanding the dielectric properties of polar fluids and developing theoretical and computational methods for calculating their static dielectric constant ϵ .^{1,2} The use of computer simulation methods to calculate dielectric properties of polar liquids has proven highly demanding due to the long-ranged nature of the dipole-dipole interaction. A number of different computational methods has been suggested to overcome these problems; two of the most popular are the Ewald summation method³ and the reaction field (RF) approach.⁴ In the former method, the central simulation box is duplicated in all directions to form an infinite lattice embedded either in vacuum or in a conducting environment that solvates the dipole moment of the simulating box, so-called tin-foil boundary conditions.⁵ In the RF method, each particle explicitly interacts with all neighbor particles within a cutoff radius R_c , as well as with the reaction field \mathbf{E}_R , given by Onsager's⁶ formula

$$\mathbf{E}_R = \frac{2(\epsilon - 1)}{(2\epsilon + 1)R_c^3} \mathbf{M}_S, \quad (1)$$

where \mathbf{M}_S is the total dipole of the cutoff sphere and ϵ is the dielectric constant of the surrounding dielectric.

The most common method to calculate ϵ from computer simulations of dipolar fluids is to use the fluctuations of the total dipole moment M of the simulation box. Formulas relating the mean-square dipole moment $\langle M^2 \rangle$ to ϵ have been

derived by Neumann⁷ for a number of different boundary conditions. Furthermore, Kusalik⁸ derived expressions for the probability distribution $P(M)$ for dielectric media. To our knowledge, however, no study of how the fluctuating multipole moments of higher order reflect the dielectric properties of the liquid has been made. In the present paper, we will derive a general expression for the distribution of the 2^ℓ -pole moment M_ℓ of a dielectric sphere. Furthermore, we will calculate the electrostatic coupling between these fluctuating moments and the fluctuating potential of a surrounding dielectric medium using an approach similar to that used by Karlström and Halle⁹ to calculate solvation free energies.

II. THEORY

A. Induced multipole moments in a dielectric medium

In the following section, we will solve a standard dielectric boundary value problem to obtain the induced multipole moments in a dielectric sphere subject to an external electric potential. The methodology is identical to that described in, for example, Ref. 6 and the derivation is included here to provide a suitable background and to highlight the underlying approximations and assumptions.

We consider a dielectric sphere with radius R and dielectric constant ϵ surrounded by vacuum ($\epsilon=1$). We then apply an external electric potential given by

$$\phi_{\text{ext}} = - \sum_{\ell=1}^{\infty} A_\ell r^\ell P_\ell(\cos \theta) \quad (2)$$

onto the dielectric sphere, where $P_\ell(\cos \theta)$ is the ℓ :th order Legendre polynomial and A_ℓ is an arbitrary constant. The electric potential of the system is then divided into two parts, $\phi_1(r, \theta)$ and $\phi_2(r, \theta)$, representing the electric potential outside ($r > R$) and inside ($r < R$) the sphere, respectively. Since

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the space inside as well as outside the sphere does not contain any charges, we can solve Laplace's equation,

$$\Delta\phi = 0, \quad (3)$$

independently for ϕ_1 and ϕ_2 . In the case of rotational symmetry about the z -axis, the general solution to Laplace's equation is given by⁶

$$\phi = \sum_{m=0}^{\infty} \left(a_m r^m + \frac{b_m}{r^{m+1}} \right) P_m(\cos \theta), \quad (4)$$

where a_m and b_m are arbitrary constants. It is now a straightforward task to identify the proper coefficients in Eq. (4) using the standard boundary conditions

$$(\phi_1)_{r \rightarrow \infty} = - \sum_{\ell=1}^{\infty} A_{\ell} r^{\ell} P_{\ell}(\cos \theta), \quad (5a)$$

$$(\phi_1)_{r=R} = (\phi_2)_{r=R}, \quad (5b)$$

$$\left(\frac{\partial \phi_1}{\partial r} \right)_{r=R} = \varepsilon \left(\frac{\partial \phi_2}{\partial r} \right)_{r=R}, \quad (5c)$$

$$(\phi_2)_{r=0} < \infty. \quad (5d)$$

The resulting potential functions become

$$\phi_1(r, \theta) = - \sum_{\ell=1}^{\infty} A_{\ell} \left[r^{\ell} - \frac{\ell(\varepsilon - 1)}{\ell(\varepsilon + 1) + 1} \frac{R^{2\ell+1}}{r^{\ell+1}} \right] P_{\ell}(\cos \theta), \quad (6)$$

$$\phi_2(r, \theta) = - \sum_{\ell=1}^{\infty} A_{\ell} \frac{(2\ell + 1)}{\ell(\varepsilon + 1) + 1} r^{\ell} P_{\ell}(\cos \theta). \quad (7)$$

We can now calculate the contribution $\phi_{1,p}$ to ϕ_1 from the polarization charge distribution of the sphere, i.e.,

$$\phi_{1,p} = \phi_1 - \phi_{\text{ext}} = \sum_{\ell=1}^{\infty} A_{\ell} \frac{\ell(\varepsilon - 1)}{\ell(\varepsilon + 1) + 1} \frac{R^{2\ell+1}}{r^{\ell+1}} P_{\ell}(\cos \theta). \quad (8)$$

$\phi_{1,p}$ can be identified as the potential originating from a collection of ideal multipoles located at the origin, possessing the axial 2^{ℓ} -pole moments M_{ℓ} given by

$$M_{\ell} = A_{\ell} \frac{\ell(\varepsilon - 1)}{\ell(\varepsilon + 1) + 1} R^{2\ell+1}. \quad (9)$$

B. Statistical-mechanical calculation of $\langle M_{\ell} \rangle$

We will now use a statistical-mechanical approach to calculate the expectation value $\langle M_{\ell} \rangle$ of M_{ℓ} , which can be compared to the "classical" value of Eq. (9). We start by using the fact that the probability distribution $P(M_{\ell})$ in vacuum of the multipole moment component M_{ℓ} can be described by a Gaussian function

$$P(M_{\ell}) = a e^{-\alpha M_{\ell}^2}, \quad (10)$$

where a and α are positive constants. It is a straightforward task to show that a Gaussian distribution is the only distri-

bution consistent with linear response, see for example Ref. 9.

The 2^{ℓ} -pole interacts with the external potential given by Eq. (2) according to (Appendix A)

$$U_{\text{ext}}^{\dagger}(M_{\ell}) = -A_{\ell} M_{\ell}. \quad (11)$$

The resulting reweighted distribution $\hat{P}(M_{\ell})$ is thus given by

$$\hat{P}(M_{\ell}) = \hat{a} P(M_{\ell}) e^{-\beta U_{\text{ext}}^{\dagger}}, \quad (12)$$

where $\beta = (kT)^{-1}$, k being Boltzmann's constant and T the absolute temperature, and \hat{a} is a normalization constant. The resulting expectation value $\langle M_{\ell} \rangle$ can now be calculated through the statistical-mechanical average

$$\langle M_{\ell} \rangle = \frac{\int_{-\infty}^{\infty} M_{\ell} \hat{P}(M_{\ell}) dM_{\ell}}{\int_{-\infty}^{\infty} \hat{P}(M_{\ell}) dM_{\ell}} = \frac{\beta A_{\ell}}{2\alpha}. \quad (13)$$

By equating M_{ℓ} and $\langle M_{\ell} \rangle$ of Eqs. (9) and (13), we can identify the exponent α of Eq. (10) as

$$\alpha = \frac{\beta[\ell(\varepsilon + 1) + 1]}{2\ell(\varepsilon - 1)} \frac{1}{R^{2\ell+1}}. \quad (14)$$

This value of α represents the width of the multipole moment distribution *in vacuo*.

C. Coupling with a surrounding dielectricum

We will now proceed to a statistical-mechanical calculation of the distributions of the multipole moments when the dielectric sphere is immersed in a dielectric medium of the same dielectric constant ε . The probability distribution $P(M_{\ell})$ given by Eqs. (10) and (14) will be reweighted by the coupling between the sphere and its dielectric surroundings. For now, we will assume that the dielectric discontinuity has zero width, i.e., that the dielectric response of the surroundings is fully developed at $r=R$. The case of a dielectric discontinuity of nonzero width will be treated briefly in Sec. V. Using this, the reweighted probability distribution is given by

$$\tilde{P}(M_{\ell}) \equiv \tilde{a} e^{-\tilde{\alpha} M_{\ell}^2} = P(M_{\ell}) e^{-\beta U^{\dagger}}, \quad (15)$$

where

$$U^{\dagger}(M_{\ell}) = -\frac{1}{2} \chi_{\ell} M_{\ell}^2 \quad (16)$$

is the interaction energy of a 2^{ℓ} -pole with moment M_{ℓ} with the dielectric surroundings, χ_{ℓ} is the susceptibility of the surrounding medium, given by^{9,10}

$$\chi_{\ell} = \frac{(\ell + 1)(\varepsilon - 1)}{(\ell + 1)\varepsilon + \ell} \frac{1}{R^{2\ell+1}}, \quad (17)$$

and \tilde{a} is a normalization constant. Using Eq. (10) and Eq. (15)–(17), we obtain the exponent $\tilde{\alpha}$, representing the reweighted probability distribution,

$$\tilde{\alpha} = \alpha - \frac{1}{2} \beta \chi_{\ell} = \frac{\beta(2\ell + 1)^2 \varepsilon}{2(\varepsilon - 1)\ell[(\ell + 1)\varepsilon + \ell]} \frac{1}{R^{2\ell+1}}. \quad (18)$$

It should be noted that the leading ε -dependence of Eq. (18) is different from that of Eq. (14), indicating that for high

TABLE I. Values of A_ℓ^{solv} as calculated from Eq. (19) for $\varepsilon \gg 1$.

ℓ	$\beta A_\ell^{\text{solv}}$	$(2\ell+1)\beta A_\ell^{\text{solv}}$
1	$-\varepsilon/9$	$-\varepsilon/3$
2	$-3\varepsilon/25$	$-3\varepsilon/5$
3	$-6\varepsilon/49$	$-6\varepsilon/7$
4	$-10\varepsilon/81$	$-10\varepsilon/9$
\vdots		
∞	$-\varepsilon/8$	$-\infty$

values of ε the multipole moment distribution becomes considerably wider when the system is immersed in a dielectric medium, compared to that in vacuum. Furthermore, for $\ell=1$, Eq. (18) is identical to the expression derived by Kusalik⁸ for the dipole moment probability distribution. It should furthermore be noted that to this point, the only assumptions we made in the derivations of Eqs. (14) and (18) are (i) that the medium exhibits dielectric behavior and (ii) that the multipole moment distributions are described by Gaussian functions.

D. Free energy of solvation

Using the reweighted probability distribution $\tilde{P}(M_\ell)$ of Eq. (15), we may now calculate the free energy A_ℓ^{solv} associated with the interaction between the fluctuating 2^ℓ -pole and the surrounding dielectric. Integrating using Eqs. (15) and (16), and the subsequent use of Eqs. (17) and (18) yields

$$\begin{aligned} \beta A_\ell^{\text{solv}} &= \frac{\int_{-\infty}^{\infty} U^\dagger(M_\ell) \tilde{P}(M_\ell) dM_\ell}{\int_{-\infty}^{\infty} \tilde{P}(M_\ell) dM_\ell} \\ &= -\frac{1}{4} \frac{\chi_\ell}{\alpha} \\ &= -\frac{\ell(\ell+1)(\varepsilon-1)^2}{2(2\ell+1)^2\varepsilon}. \end{aligned} \quad (19)$$

Since a 2^ℓ -pole has $2\ell+1$ independent components, the total solvation free energy is given by

$$A_{\text{solv}} = \sum_{\ell=1}^{\infty} (2\ell+1) A_\ell^{\text{solv}}. \quad (20)$$

Values of A_ℓ^{solv} for some values of ℓ are given in Table I, the value for $\ell=1$ being identical with that derived in Ref. 9. In Table I, we also present values of $(2\ell+1)A_\ell^{\text{solv}}$, i.e., the total contribution from all $2\ell+1$ independent components of the 2^ℓ -pole. There are three interesting features that can be noted about the values of Table I, namely, that (i) the free energy of solvation is independent of the size R of the sphere, (ii) for $\varepsilon \gg 1$, A_{solv} is large compared to kT , and (iii) its magnitude *increases* with ℓ , which implies that this ‘‘multipole expansion’’ of the free energy A_{solv} diverges. We will try to shed some more light on this fact in Sec. V.

E. Multipole fluctuations of randomly oriented molecular dipoles

We will now derive an expression for the mean-square 2^ℓ -pole moment of a spherical and homogenous molecular

system composed of randomly oriented ideal dipoles. The mean-square 2^ℓ -pole moment $\langle M_\ell^2 \rangle$ of the sphere expanded about its center is given by the integral

$$\langle M_\ell^2 \rangle = \rho \int_V \left[\frac{1}{4\pi} \int_{\Omega_\mu} M_\ell^2 d\Omega_\mu \right] dV, \quad (21)$$

where M_ℓ is the 2^ℓ -pole moment of a dipole with the magnitude μ and orientation Ω_μ located at \mathbf{r} in the spherical volume V with the radius R and where ρ is the number density of the dipoles. Using the formalism of Appendix B, one arrives at the result

$$\langle M_\ell^2 \rangle = \frac{4\pi\rho\mu^2}{3} \frac{\ell}{(2\ell+1)} R^{2\ell+1}. \quad (22)$$

This relation can also be obtained by inserting the Debye relation⁶

$$\varepsilon = 1 + \frac{4\pi\rho\mu^2}{3kT} \quad (23)$$

into Eq. (14) for α , taking the limit $\mu \rightarrow 0$, and then calculating

$$\langle M_\ell^2 \rangle = (2\alpha)^{-1}. \quad (24)$$

III. MODEL AND METHODS

A. Model

For the simulation studies, we consider a model system composed of N particles in a cubic volume V at a temperature T . The potential energy U of the system is assumed to be pairwise additive according to

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u_{ij}(r_{ij}). \quad (25)$$

The interaction between molecules i and j , u_{ij} , is composed of a Lennard-Jones (LJ) and a dipole-dipole potential (also referred to as a Stockmayer potential) according to

$$u_{ij}(r_{ij}) = u_{ij}^{\text{LJ}}(r_{ij}) + u_{ij}^{\text{dip}}(r_{ij}), \quad (26)$$

with

$$u_{ij}^{\text{LJ}}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (27)$$

$$u_{ij}^{\text{dip}}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \left[\frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r_{ij}^3} - \frac{3(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right], \quad (28)$$

where the size parameter σ and interaction parameter ϵ characterize the LJ interaction, $\boldsymbol{\mu}_i$ denotes the dipole vector of particle i , \mathbf{r}_{ij} is the vector between particle i and j , and $r_{ij} = |\mathbf{r}_{ij}|$.

In this study, we used the LJ parameters $\sigma=2.8863 \text{ \AA}$ and $\epsilon=1.97023 \text{ kJ mol}^{-1}$. The magnitude of the molecular dipole moments equals $\mu=0.10584 \text{ e \AA}$ and the number density was held fixed at $\rho=0.038446 \text{ \AA}^{-3}$ (corresponding to 0.2 a.u.). The temperature was kept constant at $T=315.8 \text{ K}$. In reduced units, the system can be characterized by the quantities $\rho^* = \rho\sigma^3 = 0.9244$, $T^* = kT/\epsilon = 1.333$, and

$\mu^* = \mu / (4\pi\epsilon_0\epsilon\sigma^3)^{1/2} = 0.5732$. These physical parameters of the system are identical to those used in Ref. 11.

B. Simulation aspects

The properties of the model systems were determined by performing molecular dynamics (MD) simulations at constant number of particles, volume, and temperature. The particles were enclosed in a cubic box with length $L=63.833$ Å and periodical boundary conditions were applied. The number of particles in the system equaled $N=10\,000$.

The long-range dipole-dipole interactions were treated using the Ewald summation adapted to dipolar systems³ using conducting boundary conditions. This approach formally involves an infinite periodic system where the dipole-dipole interaction energy is divided into several terms. An Ewald convergence parameter $\alpha=3.2/R_{\text{cut}}$ was used in conjunction with the spherical cutoff distance $R_{\text{cut}}=19$ Å in real space and the spherical cutoff $n_{\text{cut}}=11$ in reciprocal space. The LJ interactions were subjected to the same spherical cutoff as the dipole-dipole interaction in real space.

The MD simulations were performed using the velocity Verlet algorithm with the orientations described by quaternions using a time step $\Delta t=0.001$ ps, corresponding to a reduced time step $\Delta t^* = \Delta t / (m\sigma^2/\epsilon)^{1/2} = 0.0011$, where the mass $m=18$ g mol⁻¹ has been used. The particles were treated as spherical tops with the components of the moment of inertia $I_{xx}=I_{yy}=I_{zz}=1$ g Å² mol⁻¹. Each simulation involved 10^5 time steps, hence extending over $t_{\text{sim}}=100$ ps or 115 reduced time units. The approach of Berendsen *et al.*¹² of coupling the system to an external bath to preserve the temperature was used, with a time coupling constant of $100\Delta t$. This weak coupling only suppresses the potential energy drift and does not affect the dynamics of the system. The integrated Monte Carlo/molecular dynamics/Brownian dynamics simulation package MOLSIM (Ref. 13) for molecular systems was employed throughout.

C. Fluctuating multipole moment analyses

The magnitude of the fluctuating multipole moments M_ℓ was evaluated after every 100th time step using Eq. (B1). For each evaluated configuration, the value of M_ℓ , $\ell=1, 2, 3$, and 4 was sampled for spheres of radii $R=10, 15$, and 20 Å. Every particle was taken as the origin of a sphere of each of the three radii, meaning that for each value of R , 10 000 values of M_ℓ were sampled for each configuration. The values of $\tilde{\alpha}$ were then obtained by fitting a Gaussian function to the probability distributions obtained.

To obtain a reasonable value of ϵ for calculating the theoretical values of $\tilde{\alpha}$ according to Eq. (18), Neumann's⁷ formula

$$\epsilon = 1 + \frac{4\pi\langle M^2 \rangle}{3VkT}, \quad (29)$$

relating ϵ to the mean-square dipole moment $\langle M^2 \rangle$ of the entire simulation box for a system treated using Ewald summation with conducting boundaries was used.

TABLE II. Calculated and simulated reduced mean-square multipole moments $R^{-(2\ell+1)}\langle M_\ell^2 \rangle$ for different moments ℓ and radii R . Calculated values were obtained from Eq. (18) using $\epsilon=2.3$ obtained from $\langle M_\ell^2 \rangle_{\text{calc}}=(2\tilde{\alpha})^{-1}$ and Eq. (29). Estimated relative uncertainties are $\approx 7\%$ for the theoretical values and $\approx 1\%$ for the simulated values.

ℓ	R (Å)	$R^{-(2\ell+1)}\langle M_\ell^2 \rangle_{\text{calc}}$ ($10^{-4} e^2 \text{Å}^{-1}$)	$R^{-(2\ell+1)}\langle M_\ell^2 \rangle_{\text{sim}}$ ($10^{-4} e^2 \text{Å}^{-1}$)	$\langle M_\ell^2 \rangle_{\text{sim}}/\langle M_\ell^2 \rangle_{\text{calc}}$
1	10	6.65	6.49	0.98
1	15	6.65	6.61	1.00
1	20	6.65	6.79	1.02
2	10	7.62	7.36	0.96
2	15	7.62	7.32	0.96
2	20	7.62	7.28	0.96
3	10	7.98	7.74	0.97
3	15	7.98	7.74	0.97
3	20	7.98	7.80	0.98
4	10	8.18	7.99	0.98
4	15	8.18	7.94	0.97
4	20	8.18	7.97	0.97

IV. RESULTS

In Table II, we present values of the mean-square multipole moment $\langle M_\ell^2 \rangle = (2\tilde{\alpha})^{-1}$, where $\tilde{\alpha}$ has been calculated from Eq. (18) using the value $\epsilon=2.3(\pm 0.1)$ obtained from Eq. (29). These values are compared to the corresponding values determined from molecular dynamics simulations of a weakly dipolar Stockmayer fluid, whose details are described in Sec. III. Furthermore, in Fig. 1 the simulated probability distribution for the quadrupole moment ($\ell=2$) for a sphere with $R=20$ Å is compared to the results of Eqs. (14), (18), and (22).

V. DISCUSSION AND FUTURE PERSPECTIVES

A. Comparison between theoretical and simulation data

As can be seen from Fig. 1, the simulated probability distribution very accurately obeys the predicted Gaussian be-

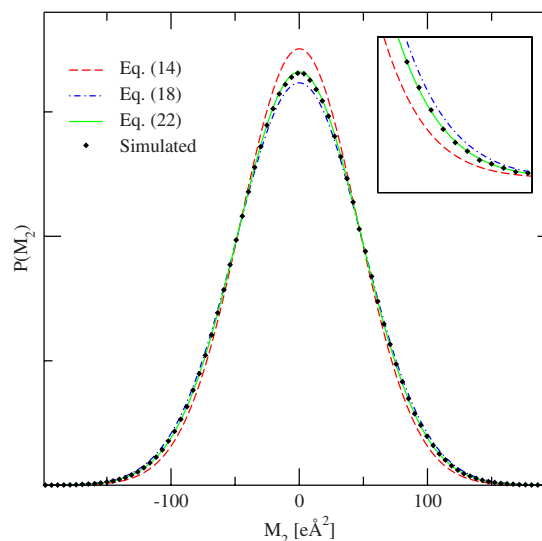


FIG. 1. (Color online) Probability distribution of the quadrupole moment for a sphere of radius $R=20$ Å obtained from Eqs. (14), (18), and (22) as well as from simulation.

havior. Furthermore, the quantitative correspondence between the simulated and the theoretical curves is very good. The theoretical curve obtained from Eq. (14) is clearly the one which shows the least correspondence with the simulated data. This fact should be expected, since Eq. (14) gives the exponent for a sphere in vacuum, whereas the simulated data correspond to a solvated sphere. The reason that the correspondence between the curves obtained from simulation and from Eq. (18), obtained from dielectric theory, is not perfect is mainly due to the uncertainty in the value of ϵ used for the calculation of $\tilde{\alpha}$. Nevertheless, the values of Table II show correspondence well within the estimated uncertainties between the theoretical and simulated values of $\tilde{\alpha}$ for all simulated values of ℓ and R , further indicating that the behavior of the system is indeed very close to being dielectric. As expected, the curve obtained using Eq. (22) provides excellent correspondence with the simulated data, since the simulated system is only weakly dipolar and the particles are therefore expected to adopt in practice fully random orientations.

B. Solvation free energies

The seemingly disturbing fact that Eq. (20) diverges independently of the value of R can be explained by the deviation from dielectric behavior when $\ell \rightarrow \infty$. All liquids are composed of discrete units (atoms or molecules) and one effect of this discreteness of the medium is that the width of the dielectric “discontinuity” has to be given a positive value. This means that the radius R of Eq. (17) should be slightly larger than R of Eq. (14). In other words, the formula for χ_ℓ of Eq. (17) should instead be written as

$$\chi_{\ell,\delta} = \frac{(\ell+1)(\epsilon-1)}{(\ell+1)\epsilon+\ell} \frac{1}{(R+\delta)^{2\ell+1}}. \quad (30)$$

This effect comes from the fact that, due to the finite size of the molecules, the reaction field of the surrounding medium cannot be applied directly at the boundary between the inner sphere and the surroundings. The displacement δ , at which the response of the medium has been fully developed, should therefore be of the order of a molecular radius, and thus the value $\delta=0$ corresponds to a system composed of infinitely small molecules. It turns out that replacing χ_ℓ with $\chi_{\ell,\delta}$ leads to an effective damping of the higher order terms. Furthermore, this damping becomes less effective as the value of R increases, which means that the magnitude of A_{solv} increases as the size of the sphere increases, just as expected. A numerical calculation, using $\epsilon=100$ and $\delta=1 \text{ \AA}$ gives a total free energy of solvation of $\approx -0.4 kT$ per particle in the outermost layer (2 \AA) of the sphere, whereas $\delta=0.5 \text{ \AA}$ yields a free energy of $\approx -1.7 kT$ per particle. This “surface free energy” should be interpreted as the electrostatic interaction free energy over the imaginary spherical surface separating the inner sphere from its dielectric surroundings. The value is hardly affected as the value of R is varied between 1 nm and 1 dm. Furthermore, the values of A_{solv} are very reasonable, indicating that this effect is indeed the dominant factor behind the suppression of the higher order terms of A_{solv} .

Even though the mechanism described above is successful in removing the divergence of A_{solv} for real liquids, two rather remarkable facts still remain, namely, that (i) the free energy of solvation of a perfectly dielectric sphere of finite size in a medium of the same dielectric constant is *infinite* and (ii) the importance of the higher order multipoles (i.e., $\ell > 1$) regarding the energetics of the system is *larger* than that of the dipole. The latter fact should have a profound effect on the simulation techniques used to model the long-range behavior of systems containing charges or dipoles, e.g., Ewald summation and RF techniques. In the latter approach, the liquid outside the cutoff radius is regarded as a dielectric medium, which responds to the total dipole moment of the primary system. Considering the results of the present paper, one may expect this to be a rather bad approximation, since in fact only the *smallest* contribution to the interaction free energy is included. Given the importance of the fluctuating electric moments of higher order that we demonstrated in the present paper, the neglect of these effects should be expected to have a significant impact on the structure of the system.

C. Future perspectives

In the simulations described in the present study, we have deliberately chosen to study a system which should clearly be expected to exhibit dielectric properties even on relatively short length scales. For this reason, we chose to model a Stockmayer fluid with a small reduced dipole moment ($\mu^* \approx 0.6$). Furthermore, the radii of the spheres for which we sampled the fluctuating multipole moments were considerably smaller than $L/2$ of the simulation box to avoid any effects from the conducting boundaries. These choices were made to be able to effectively assess the validity of the equations derived in this paper. In forthcoming papers, however, we intend to use these formulae to investigate strongly coupled Stockmayer fluids, and particularly, in which ways, if any, the behavior of these deviate from dielectric behavior. Using the tools developed in this study, we hope to be able to reveal interesting facts about the physical behavior of dipolar fluids, as well as highlighting some of the strengths and drawbacks of using different simulation methods for these systems.

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APPENDIX A: INTERACTION BETWEEN A CHARGE DISTRIBUTION AND AN EXTERNAL POTENTIAL

The interaction energy U_{ext} between a general charge distribution $\rho(\mathbf{r})$ in a volume V and an external electric potential $\phi(\mathbf{r})$ is given by

$$U_{\text{ext}} = \int_V \rho(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r}. \quad (\text{A1})$$

The potential $\phi(\mathbf{r})$ is now expanded around a point inside V according to

$$\phi(\mathbf{r}) \equiv \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \phi_{\ell m} r^{\ell} C_{\ell m}^*(\Omega), \quad (\text{A2})$$

where $C_{\ell m}$ represents Racah's un-normalized spherical harmonics and $\phi_{\ell m}$ are expansion coefficients. Insertion of Eq. (A2) in Eq. (A1) gives the following expression for U_{ext} :

$$U_{\text{ext}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \phi_{\ell m} \int_V \rho(\mathbf{r}) r^{\ell} C_{\ell m}^*(\Omega) d\mathbf{r}. \quad (\text{A3})$$

With the definition

$$Q_{\ell m} \equiv \int_V \rho(\mathbf{r}) r^{\ell} C_{\ell m}(\Omega) d\mathbf{r} \quad (\text{A4})$$

of the spherical multipole moment $Q_{\ell m}$, we get

$$U_{\text{ext}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \phi_{\ell m} Q_{\ell m}^*. \quad (\text{A5})$$

Applying this formula to the case of an axial field for which $\phi_{\ell m} = 0$ for $m \neq 0$, using the identity $C_{\ell 0} = P_{\ell}$ and making the identification $\phi_{\ell 0} = -A_{\ell}$, it follows that the interaction (free) energy between the polarization 2^{ℓ} -pole and the external potential in our particular case is given by

$$U_{\text{ext}}^{\dagger}(M_{\ell}) = -A_{\ell} M_{\ell}. \quad (\text{A6})$$

APPENDIX B: DERIVATION OF EQ. (22)

We will here derive Eq. (22) expressing the mean-square 2^{ℓ} -pole moment of a spherical system of randomly oriented molecular dipoles. The contribution to the axial 2^{ℓ} -pole moment M_{ℓ} from an ideal dipole $\boldsymbol{\mu} \equiv (\mu, \Omega_{\mu})$ located at $\mathbf{r} \equiv (r, \Omega) \equiv (r, \theta, \varphi)$ is given by

$$M_{\ell} = \boldsymbol{\mu} \cdot \nabla [r^{\ell} P_{\ell}(\cos \theta)], \quad (\text{B1})$$

where P_{ℓ} is the Legendre polynomial of ℓ :th order. Inserting the following relation:¹⁴

$$\nabla_m [r^{\ell} P_{\ell}(\cos \theta)] = (-1)^{\ell+m} [\ell(2\ell-1)(2\ell+1)]^{1/2} \times \begin{pmatrix} \ell-1 & \ell & 1 \\ m & 0 & -m \end{pmatrix} r^{\ell-1} C_{\ell-1, m}, \quad (\text{B2})$$

where index $m \in \{-1, 0, 1\}$ represents vector components in the standard basis, into Eq. (21), one obtains after some manipulations

$$\begin{aligned} \langle M_{\ell}^2 \rangle &= \frac{\rho}{4\pi} [\ell(2\ell-1)(2\ell+1)] \\ &\times \int_V \left[r^{2\ell-2} \sum_{m=-1}^1 \sum_{m'=-1}^1 (-1)^{m+m'} \begin{pmatrix} \ell-1 & \ell & 1 \\ m & 0 & -m \end{pmatrix} \right. \\ &\times \begin{pmatrix} \ell-1 & \ell & 1 \\ m' & 0 & -m' \end{pmatrix} C_{\ell-1, m} C_{\ell-1, m'}^* \\ &\left. \times \int_{\Omega_{\mu}} \mu_m^* \mu_{m'} d\Omega_{\mu} \right] dV. \end{aligned} \quad (\text{B3})$$

Using the standard integrals

$$\int_{\Omega_{\mu}} \mu_m^* \mu_{m'} d\Omega_{\mu} = \frac{4\pi}{3} \mu^2 \delta_{mm'}, \quad (\text{B4})$$

and

$$\int_{\Omega} C_{\ell-1, m} C_{\ell-1, m'}^* d\Omega = \frac{4\pi}{2\ell-1} \delta_{mm'}, \quad (\text{B5})$$

as well as carrying out the integration over r , the following expression is obtained:

$$\langle M_{\ell}^2 \rangle = \frac{4\pi\rho\mu^2}{3} \ell R^{2\ell+1} \sum_{m=-1}^1 \begin{pmatrix} \ell-1 & \ell & 1 \\ m & 0 & -m \end{pmatrix}^2. \quad (\text{B6})$$

Inserting explicit expressions for the $3j$ -symbols,¹⁴ we arrive at the final result

$$\langle M_{\ell}^2 \rangle = \frac{4\pi\rho\mu^2}{3} \frac{\ell}{(2\ell+1)} R^{2\ell+1}. \quad (\text{B7})$$

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