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NONLINEAR DIELECTRIC EFFECT OF TWO-COMPONENT DIPOLAR FLUIDS

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We studied the linear and nonlinear dielectric effects in two-component dipolar hard sphere mixtures. In our approach the hard spheres differ by their dipole moments but their diameters are the same. Within the framework of the mean spherical approximation we extended the results of our previous work and realized that the formulas which apply to one-component case are readily applicable to mixtures. We performed canonical Monte Carlo (MC) simulations for three different binary mixtures for various compositions of the components. The theoretical results are in good agreement with the corresponding MC simulation data. The linear and the nonlinear dielectric permittivities obtained from MC simulations are determined from the fluctuation formulas of the total dipole moment of the system in the absence of an applied electric field.

Keywords: nonlinear dielectric permittivity, linear dielectric permittivity, two-component dipolar mixture, mean spherical approximation, fluctuation formula, Monte Carlo simulation, dipolar hard sphere

Introduction

The nonlinear dielectric effect (NDE) is extremely sensitive to intermolecular (interparticle) interactions, therefore, it is widely used to study the structure of simple (e.g. dipolar molecular) and comlex (e.g. electrorheological) fluids [1, 2, 3, 4]. As shown in our previous paper [5], the NDE of one-component dipolar fluids can be described by the mean spherical approximation (MSA). In this paper we extend our theory to two-component dipolar-dipolar and dipolar-apolar mixtures. The dielectric permittivity of simple and complex fluids is a function of the internal electric field:

$$\varepsilon_E = \varepsilon_0 + \varepsilon_2 E^2 + ..., \tag{1}$$

where ε_E – field dependent dielectric permittivity;
ε_0 – linear dielectric permittivity;
ε_2 – nonlinear dielectric permittivity;
E – internal electric or Maxwell field.

The relation between the polarization **P** and the Maxwell field **E** [1] is

$$4\pi\mathbf{P} = (\varepsilon_E - 1)\mathbf{E}. \tag{2}$$

For simple liquids, the assumption that the dielectric is linear is usually reasonable for small electric fields [1]. From Eqs. (1) and (2) we obtain that

$$\varepsilon_0 = 1 + 4\pi\left(\frac{\partial P}{\partial E}\right)_{E=0}. \tag{3}$$

In strong electric fields, we have to take into account the second term in Eq. (1). Substituting Eq. (1) into Eq. (2) the third order derivative yields

$$\varepsilon_2 = \frac{4\pi}{3!}\left(\frac{\partial^3 P}{\partial E^3}\right)_{E=0}. \tag{4}$$

Wertheim [6] reported the MSA solution for the linear dielectric permittivity of the dipolar hard sphere (DHS) fluid. Within this approximation the linear dielectric constant of the DHS fluid is

$$\varepsilon_0 = \frac{q(2\xi(y))}{q(-\xi(y))}, \tag{5}$$

where $\xi(y)$ is a parameter without any physical meaning. This parameter is determined by the following equations:

$$3y = q(2\xi) - q(-\xi), \tag{6}$$

$$q(x) = \frac{(1+2x)^2}{(1-x)^4}, \tag{7}$$

where y is the dipole strength function defined as

$$y = \frac{4\pi}{9}\frac{m^2\rho}{k_B T}, \tag{8}$$

where m – dipole moment of particles;
k_B – Boltzmann constant;
T – temperature;
ρ – density;
$q(x)$ – reduced inverse compressibility factor of the hard sphere fluid.

The MSA has been extended [7] to finite external fields on the basis of a density functional theory (DFT). The field dependence of the polarization can be given as

$$P = m\rho L\left[\beta m\left(E + \frac{4\pi\left(1-q(-\xi)\right)}{3y}P\right)\right], \tag{9}$$

where: Langevin function $L(x) = \coth(x) - 1/x$;
$\beta - 1/k_B T$.

In our previous work [5] we proposed a formula for the nonlinear dielectric permittivity on the basis of Eq. (9):

$$\varepsilon_2 = -\frac{m^2\beta^2}{5}\frac{y}{q^4(-\xi)} = -\frac{4\pi}{45}\frac{\beta^3}{q^4(-\xi)}m^4\rho . \tag{10}$$

It has been found that Eq. (10) is in good agreement with the corresponding simulation data.

In this paper, we extend our theory to the nonlinear dielectric constant of DHS mixtures. Adelman and Deutch [8] have given the solution of the MSA for the linear dielectric constant of this system. In their theory, the particles differ by their dipole moments, while their diameters are the same. In this restricted case, the same equations apply (Eqs. (6-7)), but using the dipole strength function of the mixture defined as

$$y' = \frac{4}{9k_B T}\sum_{i=1}^{2} m_i^2\rho_i , \tag{11}$$

where m_i – dipole moment of component i,
ρ_i – density of component i.

Similarly, the resulting quantity ξ' for the mixture is introduced and denoted by prime.

Theory

Microscopic model

We examine the linear and nonlinear dielectric effects in binary mixtures that consist of dipolar hard spheres characterized by parameters σ, m_1 and m_2 interacting via a dipolar interaction between point dipoles embedded at the centers of the particles:

$$u_{DHS} = \begin{cases} -\dfrac{m_1 m_2}{r_{12}^3}D, & r_{12} \ge \sigma \\ \infty, & r_{12} < \sigma \end{cases} , \tag{12}$$

$$D = 3\left(\hat{\mathbf{m}}_1 \cdot \hat{\mathbf{r}}_{12}\right)\left(\hat{\mathbf{m}}_2 \cdot \hat{\mathbf{r}}_{12}\right) - \left(\hat{\mathbf{m}}_1 \cdot \hat{\mathbf{m}}_2\right), \tag{13}$$

where σ – diameter of particles;
r_{12} – distance between the centers;
$\mathbf{r}_{12}$ – difference vector between the centers;
$\hat{\mathbf{r}}_{12}$ – unit vector along $\mathbf{r}_{12}$ vector;
$\hat{\mathbf{m}}_i$ – unit vector of dipole moments.

Linear dielectric permittivity of binary mixtures

In order to obtain the dielectric permittivities of the DHS fluids, the field dependence of the polarization has to be known. This function can be obtained from DFT methods [9] using the MSA results of Adelman and Deutch [8]:

$$P = \sum_{i=1}^{2} m_i\rho_i L\left[\beta m_i\left(E + \frac{4\pi\left(1-q(-\xi')\right)}{3y'}P\right)\right]. \tag{14}$$

To calculate the permittivities, we need to know the derivatives of the Langevin function up to the third order:

$$\left.\frac{dL(x)}{dx}\right|_{x=0} = \frac{1}{3},\quad \left.\frac{d^2L(x)}{dx^2}\right|_{x=0} = 0,\quad \left.\frac{d^3L(x)}{dx^3}\right|_{x=0} = -\frac{2}{15} . \tag{15}$$

From the first order derivative of the implicit polarization function (Eq. (14)) one obtains

$$\left(\frac{\partial P}{\partial E}\right)_{E=0} = \frac{1}{4\pi}\frac{3y'}{q(-\xi')} . \tag{16}$$

Equations (3) and (16) lead to

$$\varepsilon_0 = 1 + \frac{3y'}{q(-\xi')} = \frac{q(2\xi')}{q(-\xi')}, \tag{17}$$

where the relation between the dipole strength function y' and the inverse compressibility $q(x)$ (Eq. (6)) was used.

Nonlinear dielectric permittivity of binary mixtures

In order to obtain ε_2, we have to calculate the third order derivative of the polarization (Eq. (4)). From Eqs. (14) and (15) we obtain:

$$\left(\frac{\partial^3 P}{\partial E^3}\right)_0 = -\frac{2}{15}\left(\frac{\beta}{q(-\xi')}\right)^3 \sum_{i=1}^{2} m_i^4\rho_i + \left(\frac{\partial^3 P}{\partial E^3}\right)_0 \left(1-q(-\xi')\right) . \tag{18}$$

After further rearrangement on the basis of Eq. (4) one finds

$$\varepsilon_2 = -\frac{4\pi}{45}\frac{\beta^3}{q^4(-\xi')}\sum_{i=1}^{2} m_i^4\rho_i . \tag{19}$$

We note that if we reduce the number of components to one, Eqs. (17) and (19) reproduce the corresponding pure fluid results, Eqs. (5) and (10).

Monte Carlo Simulations

We have performed canonical (*NVT*) ensemble Monte Carlo (MC) simulations to verify our theoretical results. We used *N = 512* particles, and the simulations were started from a simple cubic lattice configuration with randomly oriented dipoles. Boltzmann sampling, periodic boundary conditions, and the minimum image convention [10] were applied. In order to take into account the long-ranged part of the dipolar interaction the reaction field method was used.

We used the following formulas to calculate the linear and nonlinear dielectric permittivities, respectively, according to [5] and [11]:

$$\varepsilon_0 = 1 + \frac{4\pi\beta}{3V}\left\langle \mathbf{M}^2 \right\rangle, \qquad (20)$$

$$\varepsilon_2 = \frac{4\pi\beta^3}{90V}\left(3\left\langle \mathbf{M}^4 \right\rangle - 5\left\langle \mathbf{M}^2 \right\rangle^2\right), \qquad (21)$$

where

$\mathbf{M} = \sum_{j=1}^{N} \mathbf{m}_i$ – the total dipole moment of the system;

V – volume of the simulation box.

The advantage of the application of these fluctuation formulas is that we didn't need to apply any external field during the simulation. The triangular bracket denote the ensemble averages of the corresponding total dipole moments in zero external field. The statistical uncertainty of Eq. (21) is quite large due to the fourth exponent. Therefore we performed $10^7 - 2\cdot 10^7$ production cycles (after 10^5 equilibration cycles) to obtain resonable results. The statistical errors were calculated from the standard deviations of subaverages containing one million cycles.

Results and discussion

In the following we shall use reduced quantities: $\rho^* = \rho\sigma^3$ is the reduced density and $(m_i^*)^2 = m_i^2/(kT\sigma^3)$ is the reduced dipole moment of component i. *Figs. 1a* and *1b* show the linear and nonlinear dielectric permittivities as functions of the mole fraction of the first component ($x = N_1/(N_1 + N_2)$) for $(m_1^*)^2 = 0.5$ and $(m_2^*)^2 = 1$. (The various curves and symbols correspond to reduced densities $\rho^* = 0.2$; 0.4; 0.6 and 0.8 from bottom to top.) The MSA results (lines) are in good agreement with the simulation data (symbols). For the linear dielectric constant the statistical errors are smaller than the size of the symbols.

Figs. 2a and *2b* show the results for mixtures where the first component is non-polar (hard spheres): the dipole moments are $(m_1^*)^2 = 0$ and $(m_2^*)^2 = 1$. The linear dielectric permittivity, therefore, converges to 1 and the nonlinear dielectric permittivity converges to 0 at $x = 1$. The values for $x = 0$ in Figs. 2a and 2b are the same as the $x = 0$ values in Figs. 1a and 1b.

Figs. 3a and *3b* show the results for a dipolar – nonpolar mixture with a smaller dipole moment of the dipolar component ($(m_2^*)^2 = 0.5$). Now, the $x = 0$ values in Figs. 3a and 3b agree with the $x = 1$ values of Figs. 1a and 1b. The MSA theoretical data are in very good agreement with the corresponding simulation data. These results show that for moderate dipole moments ($(m_2^*)^2 \le 1$) our MSA based theory is valid for two component mixtures as well. In a subsequent publication we extend the present theory to the investigation of chain formation in electrorheological fluids.

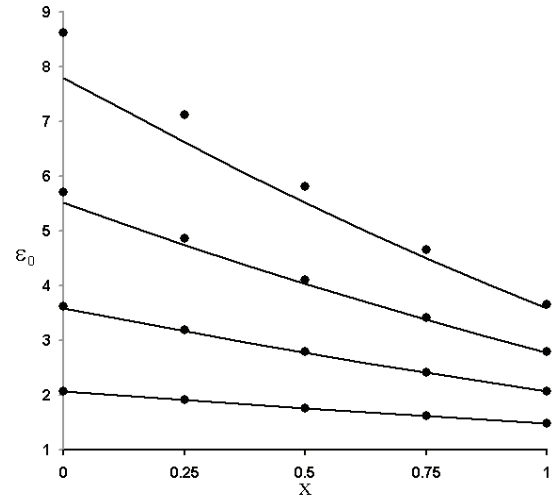

Figure 1a: Linear dielectric permittivities of a two-component DHS fluid mixture with $(m_1^*)^2 = 0.5$ and $(m_2^*) = 1$ reduced dipole moments at various densities

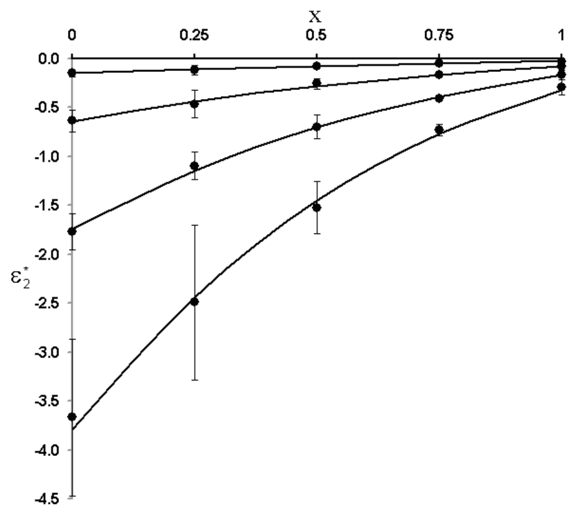

Figure 1b: Nonlinear dielectric permittivities with $(m_1^*)^2 = 0.5$ and $(m_2^*) = 1$

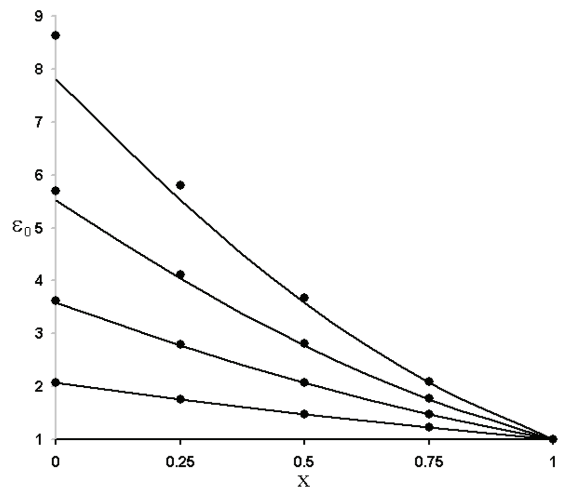

Figure 2a: Linear dielectric permittivities with $(m_1^*)^2 = 0$ and $(m_2^*)^2 = 1$

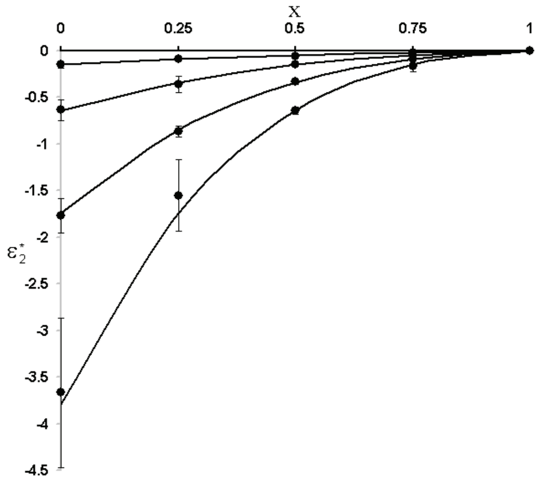

Figure 2b: Nonlinear dielectric permittivities with $(m_1^*)^2 = 0$ and $(m_2^*)^2 = 1$

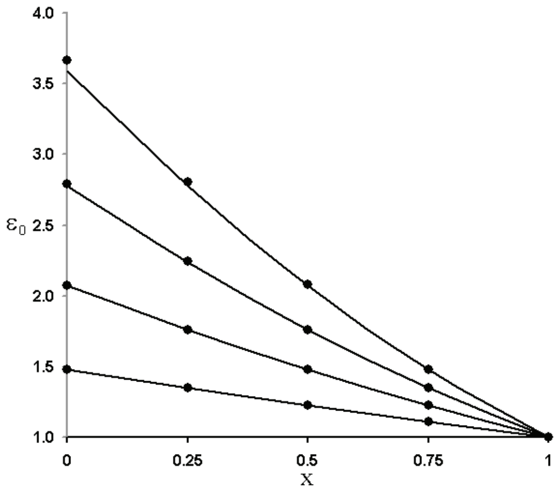

Figure 3a: Linear dielectric permittivities with $(m_1^*)^2 = 0$ and $(m_2^*)^2 = 0.5$

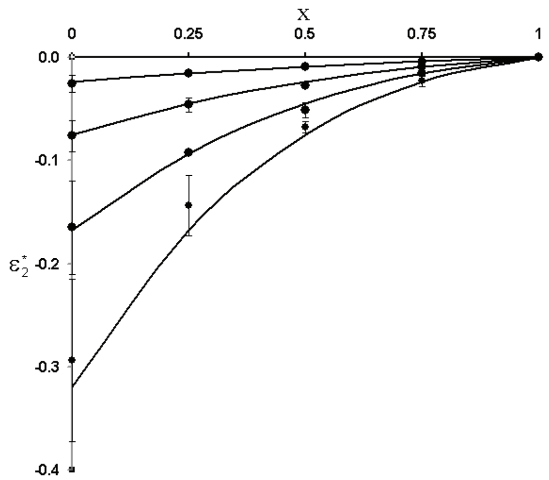

Figure 3b: Nonlinear dielectric permittivities with $(m_1^*)^2 = 0$ and $(m_2^*)^2 = 0.5$

Summary

In the present study of the NDE for DHS mixtures, the following main results have been obtained:

1) From the electric field dependence of the polarization analytical equations have been obtained for the linear and the nonlinear dielectric constants of two-component DHS fluids. Our results for the linear dielectric permittivity reproduce the corresponding results of Adelman and Deutch [8].
2) NVT ensemble Monte Carlo simulations have been performed to determine the linear and nonlinear dielectric permittivities for various two-component DHS mixtures.
3) We have compared our theoretical results with the corresponding simulation data and obtained very good agreement verifying the validity of our theoretical approximations.

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