Correction to the Clausius-Mosotti equation: the dielectric constant of non-polar fluids from Monte Carlo simulations

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Abstract

We examine the dielectric constant of non-polar fluids by direct Monte Carlo simulations on the basis of the polarizable hard sphere (PHS) model where the spheres carry molecular polarizabilities. Point dipoles are induced in the spheres partly by an external electric field and partly by other molecules. It has been known that the Clausius-Mosotti equation needs a correction due to mutual polarization between molecules. We reproduce the qualitative behavior found in experiments: the correction increases with increasing density, reaches a maximum, and decreases at high densities. We show that the classic theory of Kirkwood and Yvon is quantitatively correct for the PHS model.

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I. INTRODUCTION

It has been known since the first measurements for carbon dioxide[1], argon[2], and carbon disulfide[3,4] that the Clausius-Mosotti (CM) formula[5,6] for the dielectric constant, ϵ, of non-polar fluids is not strictly valid at high pressures. The CM equation in its corrected form can be expressed as

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}\alpha\rho(1 + S) \tag{1}$$

where α is the molecular polarizability, $\rho = N/V$ is the density, and S is the correction factor. When $S = 0$, the CM equation is recovered, which is the low density limit. Measurements showed that S first increased with increasing density, reached a maximum, then decreased at high densities (high pressures).

The CM equation is based on the Lorentz formula[7] for the internal field and ignores the fact that a molecule is also polarized by other molecules not only by the external field[8]. Kirkwood[9] and Yvon[10] developed a molecular theory (KY) for the dielectric constant of non-polar fluids. Their equations used second and third order correlation functions that were not available at that time.

Böttcher[11,12] developed an approximate formula based on Onsager's treatment. It was critically reviewed by Brown[13] stating that the apparent success of the formula may be a consequence of cancellation of errors. The theory of KY was further analyzed and developed by Van Vleck[14] and de Boer *et al.*[15].

As modern theories of liquids raised in the 60s and 70s[16], the KY theory was revisited and the dielectric constant was computed using the correlation-functions now available. Stell and Rushbrooke[17] used the hard sphere (HS) potential, while Graben *et al.*[18] used the Lennard-Jones potential as the basic model for the non-polar fluid. Wertheim[19] developed a theory for the dielectric constant of non-polar fluids on the basis of graph theoretical techniques. He considered a sample of arbitrary shape and expressed the relation of the external field to polarization as a sum of graphs. Approximations resulted in analytic expressions similar to those of the mean spherical approximation of polar fluids.

In this paper, we simulate dielectric constant of non-polar fluids directly, to our knowledge, for the first time. We use Monte Carlo (MC) simulations to study systems of HS molecules that carry molecular polarizabilities – the so called polarizable hard sphere (PHS) model – in an external electric field. We calculate the correction to the CM equation and

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compare our results to the theoretical data of Stell and Rushbrooke[17] and show that the KY theory is accurate for the PHS model. We also discuss the deviations of the MC results from experimental data.

II. MODEL AND METHOD

We use the PHS model to represent non-polar fluids. This is the simplest model in which the particles have finite size. In the absence of a polarizing external electric field, this system reduces to the HS fluid:

$$u_{HS}(r) = \begin{cases} \infty & \text{for} \quad r \leq d \\ 0 & \text{for} \quad r > d \end{cases}, \tag{2}$$

where d is the diameter of the sphere (we consider a one-component system).

When a uniform external electric field, $\mathbf{E}$, is applied, a dipole moment with magnitude $\boldsymbol{\mu}_0 = \alpha \mathbf{E}$ is induced on each molecule, where α is the molecular polarizability of the molecules We assume that the molecular polarizability is a scalar. The dipole moments point to the direction of the electric field so we use scalar quantities from now on.

We simulated this system with the MC simulation method in the canonical ensemble, where the temperature T, the volume V, and the number of molecules N is fixed (we used $N = 256$ in our simulations). We used a cubic simulation cell with periodic boundary conditions. We applied the minimum image convention without any long range correction, which practically corresponds to using a reaction field with $\epsilon_{\mathrm{RF}} = 1$. Because the dielectric constant is close to unity in our systems, this assumption is reasonable. (We performed a few simulations with the CM value for ϵ_{RF} and found little effect on the correction.) The dipoles induced by other dipoles were computed by an iteration procedure[20,21]. The details of our simulation methodlgy can be found in other papers[22–24].

The dielectric constant can be computed from the following polarization formula derived by Neumann[25]:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \frac{\langle P \rangle}{E}, \tag{3}$$

where P is the polarization density. The total polarization of the N-particle system is a sum of the dipoles $\mu_0 = \alpha E$ induced directly on a particle by the external field and the average induced dipoles $\langle \mu_{\mathrm{ind}} \rangle$ (induced by other molecules):

$$V \langle P \rangle = N\mu_0 + N \langle \mu_{\mathrm{ind}} \rangle \tag{4}$$

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The brackets denote ensemble averages. Eqs. 3 and 4 results in

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}\alpha\rho\left(1 + \frac{\langle\mu_{\text{ind}}\rangle}{\mu_0}\right),$$ (5)

which is the corrected CM equation and the correction S can be computed as the average induced dipole due to other molecules normalized by the dipole due to the external field.

The classical theory of nonpolar fluids as developed by Kirkwood[9] and Yvon[10] can be summarized as

$$
\begin{aligned}
S = \alpha^2 \Bigg[& 8\pi\rho \int \frac{g_2(r)}{r^4}dr \\
& + 2\rho^2 \int \frac{g_3(r,s) - g_2(r)g_2(s)}{r^3 s^3} P_2(\cos\theta)\,dr\,ds \Bigg] \\
& + O(\alpha^3)
\end{aligned}
$$ (6)

The term proportional to α^2 can be given as

$$S^{(2)} = \left(\frac{4\pi}{3}\alpha^*\right)^2\left[\frac{3}{2\pi}\rho^* I_2(\rho^*) - \frac{15}{16}(\rho^*)^2 J_3(\rho^*)\right]$$ (7)

where the reduced polarizability $\alpha^* = \alpha d^{-3}$ and density $\rho^* = \rho d^3$ were introduced.

The integrals $I_2(\rho^*)$ and $J_3(\rho^*)$ depend on the pair and triplet correlation functions $g_2(r)$ and $g_3(r,s)$ and can be found in the paper of Stell and Rushbrooke[17]. Stell and Rushbrooke also analyzed the graph-theory of Wertheim[19] that provides a closed formula for the dielectric constant. They showed that Wertheim's equations recovered Eq. 7 when $I_2(\rho^*)$ and $J_3(\rho^*)$ were replaced by 1 (their low density limits).

III.   RESULTS AND DISCUSSION

First, we analyze our results as a function of the strength of the external field. We present our results in terms of the dipole moment $\mu_0 = \alpha E$ induced by the external field in reduced unit $(\mu^*)^2 = \mu_0^2/kTd^3$. Figure 1 shows the correction S as a function of $(\mu^*)^2$ for a fixed value of the polarizability $\alpha^* = 0.06$ at various densities $\rho^* = 0.05$, 0.5, and 0.8. The correction increases with increasing fixed dipole moment because stronger dipoles can polarize each other more strongly.

The figure shows the results for experimentally unattainable, very large dipole moments to demonstrate different behavior at low and high densities. At high densities, S increases

linearly with $(\mu^*)^2$, while at low density ($\rho^* = 0.05$) a clearly nonlinear behavior is observed. This is a consequence of chain-formation that was found in low-density highly polar dipolar fluids[26]. There, the molecules spontaneously form chains with dipoles in head-to-tail position. Here, the dipoles already point in the same direction and chain-formation is more likely. When the dipoles are in a chain, they are in a low-energy configuration, and their mutual polarizing effect is maximal. Thus, the correction increases non-linearly as longer chains form because the second neighbor in the chain has a considerable polarizing effect. At high densities this non-linearity vanishes because energetically less favorable (parallel) positions are also present due to close packing.

These high-field results might be irrelevant for ordinary non-polar molecular fluids, but they represent attainable states for electrorheological fluids that are suspensions of fine non-conducting particles in an electrically insulating fluid. In an external electric field, dipoles are induced on the particles because they have a dielectric constant different from that of the fluid. Properties of the system (for example, viscosity) change in an external field because of chain formation of the suspended particles.

For ordinary non-polar fluids, we should use the zero-field limit. The values at very small dipole moments converge to a well defined limit (see the inset of Fig. 1). From now on, we use $(\mu^*)^2 = 0.005$ in our simulations.

The theoretical works of KY and others imply that the dominant term in the expansion of S as a function of α is the second order term (see Eq. 7). In Fig. 2, we demonstrate that MC simulations reproduce this result at least for the PHS model, where the elecrostatic forces dominate the problem: S varies linearly with $(\alpha^*)^2$. This result is a strong support for the KY theory.

Therefore, we plot $S/(\alpha^*)^2$ in Fig. 3, where we compare our simulation results to theoretical data taken from the paper of Stell and Rushbrooke[17]. The two simulation curves for $\alpha^* = 0.04$ and 0.06 practically coincide; the small differences are due to statistical uncertainties of the simulations. The three curves without symbols show results computed from Eq. 7 using various approximations. The dotted line represents the approximation that the pair-correlation function is a step function ($e(r) = 0$ for $r < d$, $e(r) = 1$ for $r > d$). In this case, $I_2(\rho^*) = I_2(0) = 1$, namely, we replace the integral by its low density limit. The other integral is also 1, $J_3(\rho^*) = J_3(0) = 1$, if we use the superposition approximation (SA) where the triplet correlation function is a product of the three pair functions. This curve

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underestimates the simulation results and becomes negative at higher densities.

The next approximation uses computed data for $I_2(\rho^*)$ (we show the results of Stell and Rushbrooke[17] who use unpublished MC data of Verlet and Schiff for $g_2(r)$), while still uses the approximation $J_3(\rho^*) = 1$ for the other integral (green dashed line). The agreement with MC data is much better indicating the importance of the correct calculation of $I_2(\rho^*)$. Deviations from simulations appear above $\rho^* = 0.4$.

A better approximation is to apply the SA for $g_3(r, s)$ using simulation data for $g_2(r)$ and to compute $J_3(\rho^*)$ accordingly (magenta dot-dashed line). This approximation works well up to $\rho^* = 0.55$ and it overestimates the simulation data above that. This implies that a correct calculation of the integral $J_3(\rho^*)$ is necessary.

Stell and Rushbrooke[17] used a direct MC estimate by Alder et al.[27] for $J_3(\rho^*)$ at the density $\rho^* = 0.884$. The result using this value is shown by a red square in the figure. The agreement with our simulation results is excellent. This agreement is an even stronger support of the KY theory for the PHS model and indicates that higher order terms in the series expansion of S (Eq. 6) are really negligible.

Finally, we discuss the ability of the PHS model to reproduce experimental data. It is advantageous to plot S against the dielectric constant when we compare to experiments. Figure 4 shows the results for various polarizabilities. The inset shows the experimental data for carbon dioxide[1]. Comparison of the two plots (the range of ϵ) implies that the reduced polarizability that roughly corresponds to CO_2 is about $\alpha^* = 0.06$. The experimental correction at the maximum point is about 2 %. For $\alpha^* = 0.06$, the MC value is less than 1 %. The simplistic PHS model can only partially reproduce the experimental correction to the CM equation in the case of CO_2 but the qualitative behavior is correct.

IV. DISCUSSION

The qualitative shape of the S vs. ρ^* (and also the S vs. ϵ) curves can be reproduced by the PHS model. The quantitative disagreement with experiments may be due to various approximations of the model. It ignores the attractive dispersion potential between the molecules. The theoretical calculations of Graben et al.[18] for the polarizable Lennard-Jones fluid show that the correction is slightly larger than in the case of the PHS model, but the difference is not decisive. The shape of the molecules might also be important at high

densities, but not at $\rho^* \approx 0.5$, where the maximum appears.

The PHS model uses idealized point dipoles to treat electrostatic interactions so it ignores higher order terms in the multipole expansion. The non-ideality of the charge distribution of the molecule is probably an important issue that captured the attention of several researchers over the years who modified the KY theory by including quadrupole[28–35] and octopole moments[36]. All these authors conclude that the effect of higher order terms is not negligible (supported by the experimental result that the correction is larger for CO_2 than for Ar).

With the improvement of experimental techniques[37,38], the density dependence of the dielectric constant of various gases were measured and analyzed in term of the dielectric virial expansion, which is the density expansion of the CM function $(\epsilon - 1)/(\epsilon + 2)\rho$. The results were fitted to theories and higher order multipole moments were estimated. Examples include the quadrupole moment of CO_2[39], C_2H_4[40], and N_2[41] on the basis of the theory of Buckinhgam and Pople[32,34]. The octopole moments of He, Ar, N_2, and CH_4[36] as well as CH_4 and CF_4[42] were computed on the basis of the theory of Johnston *et al.*[36]. All these measurements, nevertheless, were conducted for relatively low densities where the underlying theories can be assumed to be valid. Reliable models – studied either by simulations or theories – that are able to describe the dielectric anomalies of non-polar gases even at high densities are desirable in order to understand the internal structure of the molecules and to obtain accurate values for the multipole moments.

Jansen *et al.*[28–31] raised the possibility that the molecular polarizability, α, is no longer a well defined molecular quantity, but it depends on the density. At high densities, the molecules can modify each others' structure and the apparent polarizability of colliding molecules can be different from that of the isolated molecules. The difference, the incremental polarizability can be studied by collision-induced light scattering[43,44]. The effect of anisotropic, tensorial polarizability can also be important at high densities[45].

A heuristic explanation of the maximum in the S vs. ρ^* curve can be the following. Increasing the density, the molecules tend to be closer to each other in average. Furthermore, they tend to polarize each other strongly and ion pairs (sometimes triplets) form in head-to-tail positions. As density increases, the positive polarizing effect of the head-to-tail configurations is gradually diminished by parallel configurations that necessarily appear at high densities. These are repulsive configurations with an opposite polarizing effect, but

this effect is smaller than that of the head-to-tail configurations, so the correction is never negative.

We have presented direct MC simulations for the dielectric constant of non-polar fluids and showed that the KY theory is correct in second order in α in describing the behavior of the PHS model. Experimental corrections to the CM equations are reproduced partially, so consideration of other effects will be necessary.

Acknowledgments

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Captions of figures

Figure 1 MC results for the correction to the CM equation as a function of $(\mu^*)^2$ for $\alpha^* = 0.06$ at various densities. The inset shows the results for small dipole moments.

Figure 2 MC results for the correction to the CM equation as a function of $(\alpha^*)^2$ for $(\mu^*)^2) = 0.005$ at various densities.

Figure 3 The correction to the CM equation normalized by $(\alpha^*)^2$ as a function of the density as obtained from simulations (symbols with lies) and the KY theory (Eq. 7) using different approximations as described in the text.

Figure 4 MC results for the correction to the CM equation as a function of the dielectric constant for different polarizabilities. The inset shows experimental data for carbon dioxide[1].
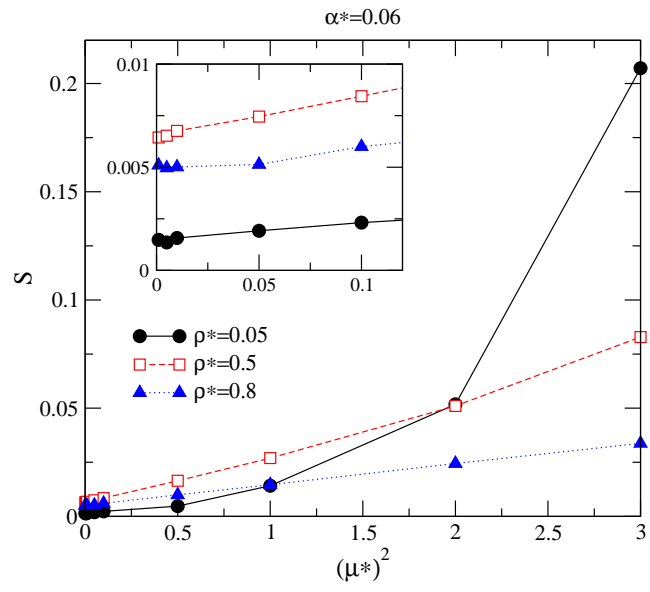
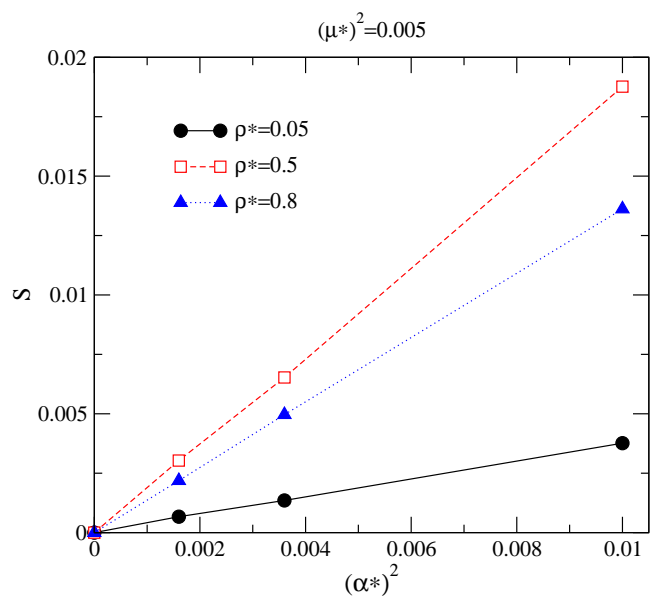FIG. 1: Valiskó and Boda, *J. Chem. Phys.*
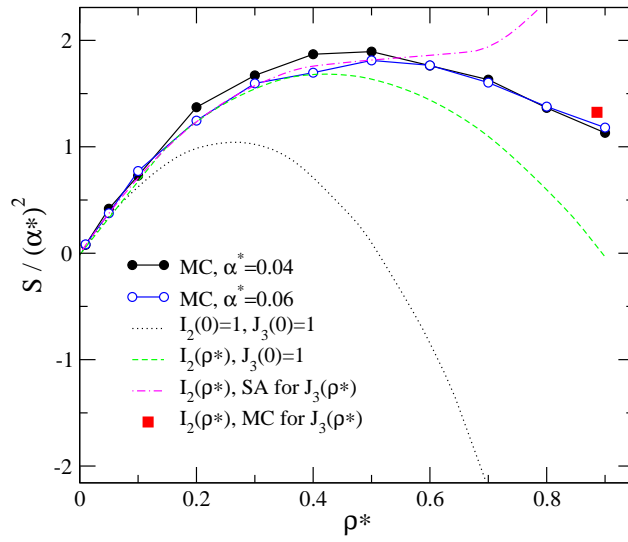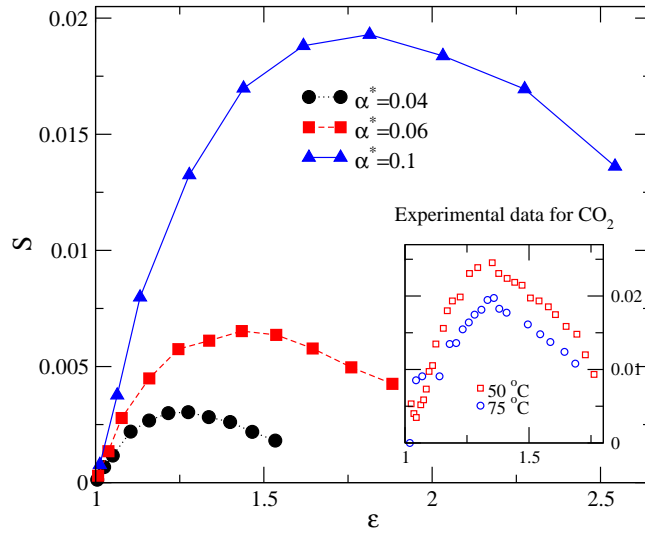
FIG. 2: Valiskó and Boda, *J. Chem. Phys.*

FIG. 3: Valiskó and Boda, *J. Chem. Phys.*

FIG. 4: Valiskó and Boda, *J. Chem. Phys.*