FLUID OF HARD SPHERES WITH A MODIFIED DIPOLE: SIMULATION AND THEORY

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Received December 14, 2007
Accepted April 3, 2008

Dedicated to Professor William R. Smith on the occasion of his 65th birthday.

A model fluid made up of hard spheres with a modified point dipole, resulting from application of a perturbation theory to general molecular fluids, is studied by both molecular simulations and theory. Molecular simulations at 64 state points have been performed for two different types of modification. Two variants of Rushbrooke's Padé approximant are used to describe the system theoretically. No satisfactory theoretical results are obtained due to tendencies of the modified dipolar systems to form ferroelectric ordering.

Keywords: Molecular simulation; Monte Carlo method; Perturbation theory; Dipolar hard spheres; Ferroelectric phase.

Molecular simulations have become the indispensable tool in modern science and engineering. Based on intermolecular interaction potential models, they provide not only insight into molecular mechanisms governing the behavior of macroscopic samples but also information/data otherwise inaccessible by laboratory experiments. Nonetheless, most engineering applications require the properties of matter in close analytic forms. In this case molecular simulations play only an auxiliary or supporting role, typically, verifying theoretical computations and/or approximations, or providing 'experimental' data for models (in many cases unrealistic ones) resulting from theoretical considerations.

Concerning complex fluids, the perturbation theory seems at present to be the only method available to develop a molecular-based equation of

Collect. Czech. Chem. Commun. 2008, Vol. 73, No. 4, pp. 541–557

doi:10.1135/cccc20080541

state in an analytic form. It consists in decomposition of the intermolecular interaction potential into reference and perturbation parts, which leads to an expression for the Helmholtz energy in the form of the sum of the reference term and perturbation corrections. Regardless of the level of rigor of the approach[1], the correction terms commonly include contributions due to dispersion forces and long-range Coulombic interactions, with the latter typically in the form of the dipole–dipole interaction. Whereas for the first contribution a number of various results is available, the determination of the electrostatic contribution is still unsatisfactory.

When implementing the perturbation expansion one should always keep in mind that the correction terms are functionals of the reference system. The problem of practically all applications of the perturbation expansion to polar fluids is that this fact has been, for various reasons, ignored. Consequently, the available results are unsatisfactory. Regardless of the choice of the reference, the dipole–dipole contribution over the reference has been commonly described by the Padé approximant for dipolar hard spheres developed by Rushbrooke et al.[2], who approximated the perturbation expansion, to a high degree of accuracy, by the sum of an infinite geometrical series using the second and third perturbation terms derived by the SRN [3] perturbation theory. A simplified, low-density version of Rushbrooke's expression (corresponding to Wertheim's solution[4] of the mean spherical approximation) has been used, e.g., in molecular-based equations of state for water[5,6] and in SAFT equations of state[7], though it fails even in the case of dipolar hard spheres themselves.

To approximate the dipole–dipole contribution for complex fluids by means of that for dipolar hard spheres is a too crude approximation. Starting from the rigorous formulation of the perturbation expansion[1], one obtains expressions in which the dipole–dipole interaction is averaged over the configurations of a short-range reference system[8]. To accomplish this averaging, the reference system is conveniently approximated by an appropriate primitive model[9]. Consequently, one gets a model the properties of which should be known to estimate the correction term(s) resulting from the dipole–dipole interaction. In this paper we thus consider such a simple non-continuous potential which consists of a hard core and the point dipole switched off at short distances to model the effect of the long-range part of the electrostatic interactions. Monte Carlo simulations are performed for this potential at various conditions. Two theoretical methods, based on those due to Rushbrooke et al.[2], are proposed to describe the system: (i) scaling the reduced density and the reduced dipole moment, as used in molecular-based equations of state[5,6,10] (the method hereafter referred to as the “scaled Rushbrooke’s method”) and (ii) computing the perturbation integrals using the modified potential (denoted as the “modified Rushbrooke’s method”). Theoretical results are critically compared with the simulation ones. Finally, a few remarks are made on the structural differences between the ‘true’ dipolar hard spheres and the considered system with modified dipoles.

THEORY

The Model

Any perturbation theory starts from decomposition of the full intermolecular potential model, $u(\mathbf{1},\mathbf{2})$, into reference and perturbation parts

$$u(\mathbf{1},\,\mathbf{2}) = u_{\mathrm{ref}}(\mathbf{1},\,\mathbf{2}) + u_{\mathrm{pert}}(\mathbf{1},\,\mathbf{2}) \tag{1}$$

where $\mathbf{1} \equiv (\mathbf{r}_1, \boldsymbol{\omega}_1)$ and $\mathbf{2} \equiv (\mathbf{r}_2, \boldsymbol{\omega}_2)$ denote positions, $\mathbf{r}_i$, and orientations, $\boldsymbol{\omega}_i$, of respective particles. Following the latest development revealing the relation between the range of the interaction and the structure[8], the reference potential should include all short-range interactions (i.e., both repulsive and attractive) and the perturbation comes then from the long-range part of u. Since the long-range part is dominated by the dipole–dipole interaction, a theoretically tractable decomposition may thus read as follows:

$$u_{\mathrm{ref}}(\mathbf{1},\,\mathbf{2}) = u(\mathbf{1},\,\mathbf{2}) - S(\mathrm{r}_{12};\,R_1,\,R_2)u_{\mathrm{DD}}(\mathbf{1},\,\mathbf{2}) \tag{2}$$

where S is a switch function monotonically changing from 0 to 1 within the interval (R_1,R_2), $r_{12} = |\mathbf{r}_{12}| = |\mathbf{r}_2 - \mathbf{r}_1|$, and $u_{\mathrm{DD}}(\mathbf{1},\mathbf{2})$ is the interaction energy between two point dipoles μ_i, $i = 1, 2$, of magnitude $\mu = |\mu_i|$,

$$u_{\mathrm{DD}}(\mathbf{1},\,\mathbf{2}) = \frac{1}{4\pi\varepsilon_0}\frac{1}{r_{12}^3}\left[\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2 - 3\frac{(\boldsymbol{\mu}_1\cdot\mathbf{r}_{12})(\boldsymbol{\mu}_2\cdot\boldsymbol{\nu}_{12})}{r_{\mathbf{12}}^2}\right]. \tag{3}$$

Using decomposition (*2*), the perturbation correction to the Helmholtz energy, which is a functional of the reference distribution functions (of all orders) and the perturbation potential, assumes a form

$$A - A_{\mathrm{ref}} = F[g_{\mathrm{ref}}^{(i)}, Su_{\mathrm{DD}}] = A_1 + A_2 + \ldots \tag{4}$$

where for the first-order term the following relationship holds

$$A_1 \sim \int g_{\mathrm{ref}}^{(2)}(\mathbf{1},\mathbf{2}) S(r_{12};R_1,R_2)\, u_{\mathrm{DD}}(\mathbf{1},\mathbf{2})\, \mathrm{d}\mathbf{1}\, \mathrm{d}\mathbf{2}\,. \tag{5}$$

Evaluation of the above integral in an analytic form is, in general, practically impossible and in the case of higher orders one finds even more complex expressions. The crudest approximation would be to estimate the expansion (*4*) by the expression developed by Rushbrooke et al.[2] for the system of dipolar hard spheres of a certain effective diameter $D \in (R_1,R_2)$. This route was followed in previous studies on water[5,6,10].

A typical range of the intermolecular separations in which the dipole–dipole interaction is completely switched off covers at least the first coordination shell. This means that the range which would give the most important contribution from the correlation function $g_{\mathrm{ref}}^{(2)}$ does not contribute to A_1 at all. Beyond this shell the pair correlations are not so pronounced and the pair correlation function tends to fluctuate around unity. It is thus reasonable to assume that in the region where $Su_{\mathrm{DD}} \neq 0$ the function $g_{\mathrm{ref}}^{(2)}$ is radially symmetric, $g_{\mathrm{ref}}^{(2)}(\mathbf{1},\mathbf{2}) \equiv g_{\mathrm{ref}}(r_{12})$. The first-order term in Eq. (*4*) will then vanish

$$A_1 \sim \int g_{\mathrm{ref}}(r_{12}) S(r_{12})\, u_{\mathrm{DD}}(\mathbf{1},\mathbf{2})\, \mathrm{d}\mathbf{1}\, \mathrm{d}\mathbf{2} = 0 \tag{6}$$

and the second- and third-order terms simplify, respectively, to[3]

$$A_2 \sim \int g_{\mathrm{ref}}(r_{12}) [S(r_{12})\, u_{\mathrm{DD}}(\mathbf{1},\mathbf{2})]^2\, \mathrm{d}\mathbf{1}\, \mathrm{d}\mathbf{2} \tag{7}$$

and

$$A_3 \sim \int g_{\mathrm{ref}}^{(3)}(\mathbf{1},\mathbf{2},\mathbf{3}) S(r_{12})\, u_{\mathrm{DD}}(\mathbf{1},\mathbf{2}) S(r_{13})\, u_{\mathrm{DD}}(\mathbf{1},\mathbf{3}) S(r_{23})\, u_{\mathrm{DD}}(\mathbf{2},\mathbf{3})\, \mathrm{d}\mathbf{1}\, \mathrm{d}\mathbf{2}\, \mathrm{d}\mathbf{3}\,. \tag{8}$$

Finally, we will assume that functions $g_{\mathrm{ref}}^{(i)}$ are approximated by the correlation functions, $g_{\mathrm{HS}}^{(i)}$ of hard spheres of some effective diameter d. Thus, the expressions (*7*) and (*8*) will be formally identical to the exact perturbation terms for the total pair potential defined as

$$\begin{aligned} u_{\mathrm{MDD}}(\mathbf{1},\mathbf{2}) &= +\infty && \text{for } r_{12} \le d \\ &= S(r_{12};R_1,R_2)\,u_{\mathrm{DD}} && \text{for } r_{12} > d\ . \end{aligned} \tag{9}$$

In general, the switch function S turns on gradually the dipole–dipole interaction within the range (R_1,R_2). For the purpose of this paper we will consider the switch function in the form of the Heaviside function, $S(r;R_1,R_2) \equiv H(r - D)$, where D is a distance at which the dipole is switched on. The model we are going to investigate in this paper reads thus as

$$\begin{aligned} u_{\mathrm{MDD}}(\mathbf{1},\mathbf{2}) &= +\infty && \text{for } r_{12} \le d \\ &= 0 && \text{for } d < r_{12} \le D \\ &= u_{\mathrm{DD}}(\mathbf{1},\mathbf{2}) && \text{for } r_{12} > D\ . \end{aligned} \tag{10}$$

Original Rushbrooke's Method

An expression for the Helmholtz energy of dipolar hard spheres of diameter σ has been developed long time ago by Rushbrooke et al.[2]:

$$\frac{A - A_{\mathrm{HS}}}{Nk_{\mathrm{B}}T} = -\frac{\dfrac{2\pi}{9}\tilde{\mu}^4\tilde{\rho}I_2(\tilde{\rho})}{1 + \dfrac{5\pi}{36}\tilde{\mu}^2\tilde{\rho}\dfrac{I_3(\tilde{\rho})}{I_2(\tilde{\rho})}} \tag{11}$$

where $\tilde{\mu}^2 = \mu^2/4\pi\varepsilon_0\sigma^3k_{\mathrm{B}}T$ and $\tilde{\rho} = \rho\sigma^3$. Integrals I_2 and I_3 are defined as follows:

$$I_2(\tilde{\rho}) = \frac{3\sigma^3}{4\pi}\int g_{\mathrm{HS}}(r;\tilde{\rho})\frac{1}{r^6}\,\mathrm{d}\mathbf{r} \tag{12}$$

and

$$I_3(\tilde{\rho}) = \frac{3\sigma^3}{5\pi^2}\int g^{(3)}_{\mathrm{HS}}(\mathbf{1},\mathbf{2},\mathbf{3};\tilde{\rho})\,u(\mathbf{1},\mathbf{2},\mathbf{3})\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3 \tag{13}$$

where $g_{\mathrm{HS}}(r;\tilde{\rho})$ and $g^{(3)}_{\mathrm{HS}}(\mathbf{1},\mathbf{2},\mathbf{3};\tilde{\rho})$ are the pair and the triplet correlation function of hard spheres at the specified reduced density, respectively, and

$$u(\mathbf{1},\mathbf{2},\mathbf{3}) = \frac{1 + 3\cos\alpha_1 \cos\alpha_2 \cos\alpha_3}{(r_{12} r_{23} r_{13})^3} \tag{14}$$

is the Axilrod–Teller three-body interaction, where α_1, α_2, α_3 are the interior angles of triangle 123.

Rushbrooke[2] approximates the integrals by a rational parametrization

$$I_2(\tilde\rho) = \frac{1 - 0.3618\tilde\rho - 0.3205\tilde\rho^2 + 0.1078\tilde\rho^3}{(1 - 0.5236\tilde\rho)^2} \tag{15}$$

and

$$I_3(\tilde\rho) = \frac{1 + 0.62378\tilde\rho - 0.11658\tilde\rho^2}{1 - 0.59056\tilde\rho + 0.20059\tilde\rho^2} \, . \tag{16}$$

Note that I_2 has a pole at $\tilde\rho = 1/0.5236 \approx 1.91$. The low-density limit for both I_2 and I_3 is unity. If we set $I_2 \equiv I_3 \equiv 1$ in Eq. (*11*) we obtain the Padé approximant corresponding to the mean spherical approximation (MSA)[2]

$$\frac{A - A_{\mathrm{HS}}}{N k_{\mathrm{B}} T} = - \frac{\frac{2\pi}{9}\tilde\mu^4 \tilde\rho}{1 + \frac{5\pi}{36}\tilde\mu^2 \tilde\rho} \tag{17}$$

that is simple and possesses no singular values.

Scaled Rushbrooke's Method

Let us assume that we want to approximate our modified potential (*10*) by 'true' dipolar hard spheres in order to estimate the dipolar correction to the Helmholtz energy. This can be done adopting the approach used in molecular-based equations of state[5,6,10]. We replace our model by a dipolar sphere of diameter σ, equal to the switching distance, D. Both potentials will be thus different only for $r \in (d,D)$.

Let us define new reduced variables: the density, $\rho^* = \rho d^3$, and the squared dipole moment, $\mu^{*2} = \mu^2/4\pi\varepsilon_0 d^3 k_{\mathrm{B}} T$. If we set now $\sigma \equiv D = Kd$, the original reduced variables in Eq. (*11*) will transform in this way: $\tilde\rho = \rho D^3 = K^3\rho^*$ and $\tilde\mu^2 = \mu^{*2}/K^3$. Expression (*11*) for the spheres of diameter D reads, in the new variables, as

$$\frac{A - A_{\mathrm{HS}}}{Nk_{\mathrm{B}}T} = -\frac{\dfrac{2\pi}{9K^3}\mu^{*4}\rho^* I_2(K^3\rho^*)}{1 + \dfrac{5\pi}{36}\mu^{*2}\rho^* \dfrac{I_3(K^3\rho^*)}{I_2(K^3\rho^*)}} \tag{18}$$

and this is our working approximation for the dipolar contribution. Note that for $K = 1$ the expression for dipolar hard spheres (*11*) with $\sigma = d$ is recovered. The corresponding MSA version of Eq. (*18*) reads

$$\frac{A - A_{\mathrm{HS}}}{Nk_{\mathrm{B}}T} = -\frac{\dfrac{2\pi}{9K^3}\mu^{*4}\rho^*}{1 + \dfrac{5\pi}{36}\mu^{*2}\rho^*}\,. \tag{19}$$

Modified Rushbrooke's Method

The method of Rushbrooke et al. is in fact more general. Instead of applying to dipolar hard spheres, we can apply it also directly to the potential defined by Eq. (*10*) and the only modification appears in integrals I_2 and I_3. The Helmholtz energy then reads

$$\frac{A}{Nk_{\mathrm{B}}T} = -\frac{\dfrac{2\pi}{9}\mu^{*4}\rho^* I'_2(\rho^*)}{1 + \dfrac{5\pi}{36}\mu^{*2}\rho^* \dfrac{I'_3(\rho^*)}{I'_2(\rho^*)}} \tag{20}$$

where

$$I'_2(\rho^*) = \frac{3\sigma^3}{4\pi}\int g_{\mathrm{HS}}(r;\rho^*)\,H(r - D)\,\frac{1}{r^6}\,\mathrm{d}\mathbf{r} \tag{21}$$

and

$$I'_3(\rho^*) = \frac{3\sigma^3}{5\pi^2}\int g^{(3)}_{\mathrm{HS}}(\mathbf{1},\mathbf{2},\mathbf{3};\rho^*)H(r_{12} - D)H(r_{23} - D)H(r_{13} - D)\,u(\mathbf{1},\mathbf{2},\mathbf{3})\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\,. \tag{22}$$

Similarly as in the preceding subsection, the reduced density and the reduced squared dipole moment are here defined as $\rho^* = \rho d^3$ and $\mu^{*2} = \mu^2/4\pi\varepsilon_0 d^3 k_{\mathrm{B}}T$, respectively. It is clear that for the special case where $d = D$

(K = 1) the expressions are again equal to those for the dipolar hard spheres with diameter $\sigma = d$.

RESULTS AND DISCUSSION

Simulation

Standard Metropolis *NVT* Monte Carlo simulations are performed in a cubic box with $N = 216$ particles interacting via modified dipolar potential (*10*). Periodic boundary conditions are applied. Two values for $K = D/d$ are used: 1.5 and 2. For each of them, the residual internal energy (the ensemble average of the potential energy), $\Delta U = \langle E \rangle$, is measured at 64 state points differing in $\rho^* = \rho d^3$ and $\mu^{*2} = \mu^2/4\pi\varepsilon_0 d^3 k_B T$ (Fig. 1). The potential cutoff is set to one half of the simulation box, and the reaction field method with water-like relative permittivity ($\varepsilon'_r = 80$) is used for the dielectric continuum to handle the long-range electrostatics. For each state point, 5×10^6 configurations are generated at the equilibration stage, and 16×10^6 configurations in the production runs. Every 1000th configuration is used to compute en-

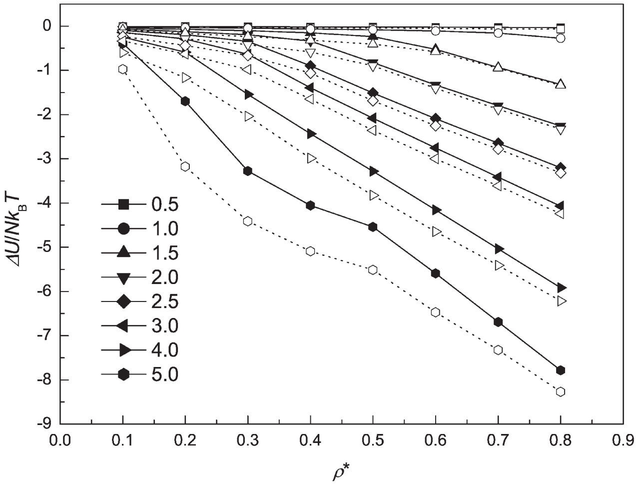

FIG. 1

Simulation results for the residual internal energy of the fluid of hard spheres with the modified dipole as a function of the reduced density, ρ^*, for eight values of the squared reduced dipole moment, μ^{*2} (numbers in the legend); $\varepsilon'_r = 80$. Open symbols and dotted line: $K = 1.5$; filled symbols and full line: $K = 2.0$

semble averages. Parameters of the random moves are set so as to have the acceptance ratio ca. 0.3 for the translational and 0.5 for the rotational moves (it may be higher at low densities). To keep the development of the system during simulations under control, various control quantities were monitored[11]. Standard deviations of the data plotted in Fig. 1 are smaller than 1%, and therefore no error bars are shown.

Scaled Rushbrooke's Method

In Fig. 2 we can see how Eq. (*18*) performs for dipolar hard spheres (i.e., K = 1.0). In this case the expression is equivalent to original Rushbrooke's Padé approximant (*11*) and it is thus not surprising that the agreement with pseudoexperimental data is excellent. Figure 2 also shows results for the MSA version of the Padé approximant, Eq. (*17*), which turns out to be inaccurate, especially at the higher density, $\rho^* = 0.8$.

Considering now the case of $K = 1.5$ and $K = 2.0$ systems, the situation is a bit more complicated. Since in Eq. (*18*) the density is multiplied by K^3, the singularity of I_2 now moves from nonphysical densities to reachable

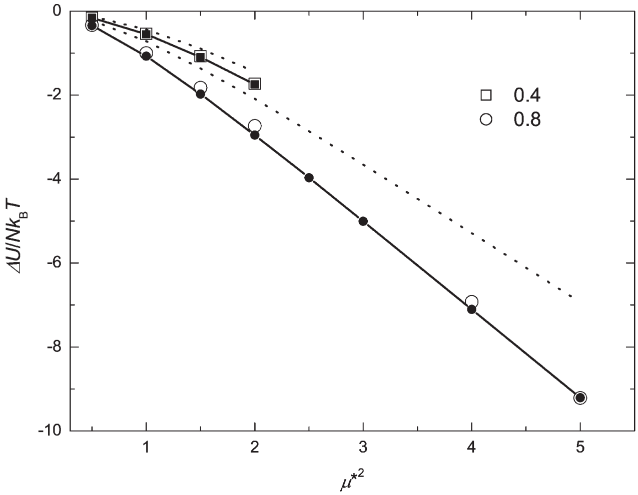

FIG. 2

Comparison of simulation (open symbols) and theoretical results for the residual internal energy of the fluid of dipolar hard spheres (K = 1.0) as a function of the squared reduced dipole moment, μ^{*2}, for two values of the reduced density, ρ^* (numbers in the legend). Filled symbols: Rushbrooke's Padé approximant, Eq. (*11*); dotted line: MSA, Eq. (*17*)

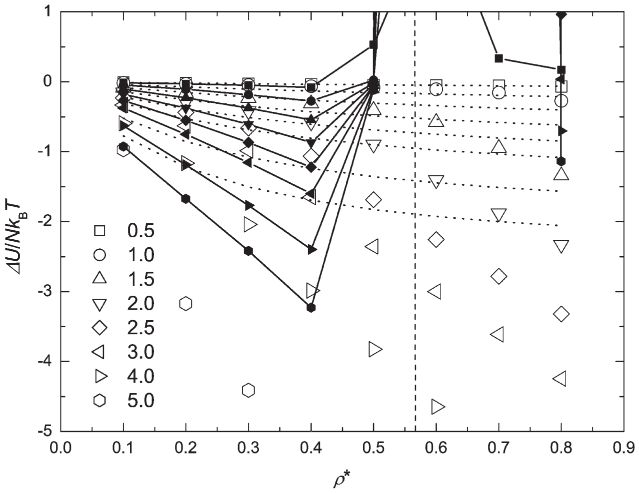

FIG. 3
Comparison of simulation (open symbols) and theoretical results for the residual internal energy of the system of hard spheres with the modified dipole, $K = 1.5$, as a function of the reduced density, ρ^*, for eight values of the squared reduced dipole moment, μ^{*2} (numbers in the legend). Filled symbols: Rushbrooke's Padé approximant for $\sigma = D$, Eq. (*18*); dotted lines: MSA, Eq. (*19*). Lines have been drawn to guide the eyes; the vertical dashed line indicates the location of the singularity of $I_2(K^3\rho^*)$

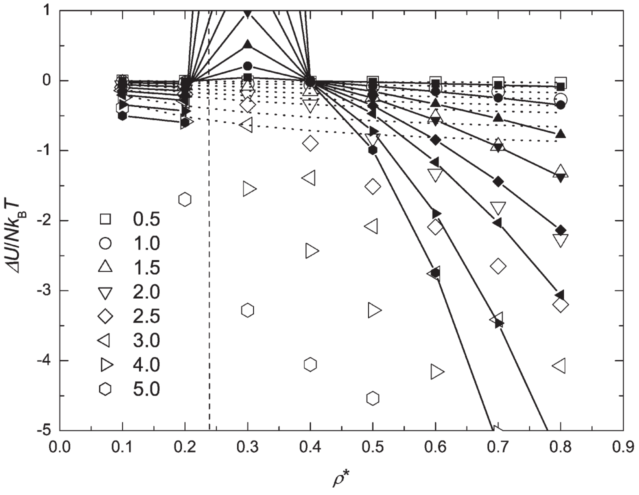

FIG. 4
The same as Fig. 3 for $K = 2.0$

lower values. For K = 1.5 and 2.0, the singular density is, approximately, 0.566 and 0.239, respectively. Above these values the results from Eq. (*18*) are useless; however, Figs 3 and 4 show that quite large discrepancies are present even at the densities below the mentioned limits. It turns out that the only expression applicable to real computations in this case is the MSA expression (*19*), which is, however, very inaccurate.

Modified Rushbrooke

Figures 5 and 6 show the residual internal energies, ΔU, of the modified dipolar system computed employing Eq. (*20*). Integrals (*21*) and (*21*) are evaluated by means of an *NVT* Monte Carlo simulation on 1000 hard spheres using the following formulas:

$$I_2' = \frac{3d^6}{2\pi N\rho^*}\left\langle \sum_{i<j} H(r_{ij} - D)/r_{ij}^6 \right\rangle_{\mathrm{HS}} \qquad (23)$$

and

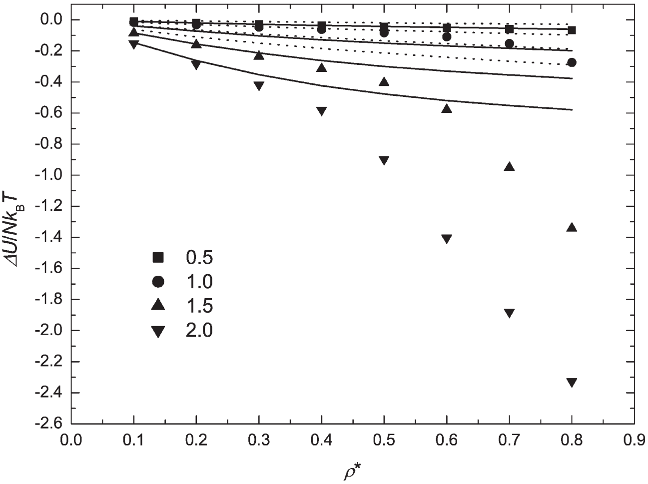

FIG. 5

Comparison of simulation (symbols) and theoretical results for the residual internal energy of the system of hard spheres with the modified dipole, K = 1.5, as a function of the reduced density, ρ^*, for four values of the squared reduced dipole moment, μ^{*2} (numbers in the legend). Full lines: modified Rushbrooke's expression, Eq. (*20*); dotted lines: MSA, Eq. (*19*)

$$I'_3 = \frac{18d^9}{2\pi^2 N\rho^{*2}} \left\langle \sum_{i<j<k} H(r_{ij} - D)\, H(r_{jk} - D)\, H(r_{ik} - D)\, u(\mathbf{i},\mathbf{j},\mathbf{k}) \right\rangle_{\mathrm{HS}} \qquad (24)$$

where $\langle\cdot\rangle_{\mathrm{HS}}$ denotes the canonical ensemble average over the configurations of hard spheres.

As regards the accuracy of the approach, it must be quite surprising that the performance of the method is as poor as shown in Figs 5 and 6. One would assume that if the method performs well for dipolar hard spheres, it should do so for the modified potential as well. A possible explanation comes from an analysis of the structure discussed in the following subsection.

In Figs 5 and 6, the results from the MSA scaled Padé approximant (*19*) is added for comparison with the modified Rushbrooke method. One can see that for $K = 2.0$ the corresponding curves lie very close each to other.

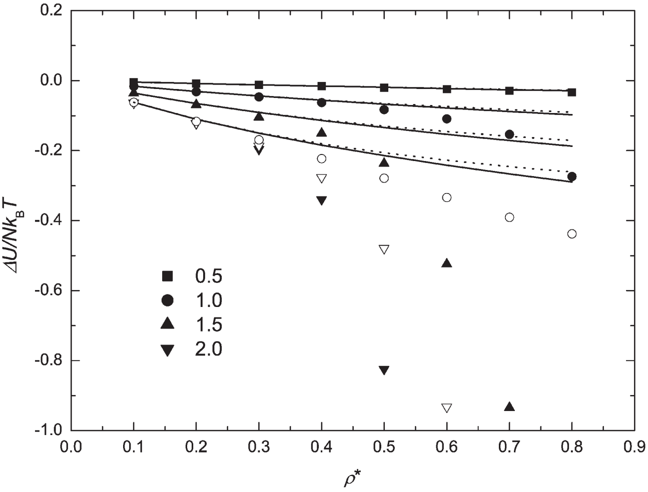

FIG. 6

Lines and filled symbols: the same as Fig. 5 for $K = 2.0$. Open symbols: preliminary simulation results for $\mu^{*2} = 2.0$; △ $\varepsilon'_r = 10$, ○ $\varepsilon'_r = 1$

Structure

As regards the translational structure, there is practically no difference between the modified and true dipolar systems as witnessed by the radial distribution functions, $g(r)$, shown in Fig. 7 for dense, strongly polar systems ($\rho^* = 0.8$, $\mu^{*2} = 5.0$) with $K = 1.0$ and 2.0. The curves are similar; however, the contact value is smaller for $K = 2.0$ and the phase is slightly shifted. The coordination number, n_c, defined by

$$n_c = 4\pi\rho \int_0^{r_{\min}} g(r) r^2 \, \mathrm{d}r \qquad (25)$$

where $r_{\min}$ is the location of the first minimum of $g(r)$, is 11.9 for $K = 1.0$ compared with 12.2 for $K = 2.0$ ($\rho^* = 0.8$, $\mu^{*2} = 5.0$). The difference, however, is observed in the orientational structure. At higher reduced densities and dipole moments, the orientational structure of systems with $K > 1.0$ significantly differs from that of the dipolar hard spheres (i.e., for $K = 1.0$). In simulations we have computed also the average squared dipole moment

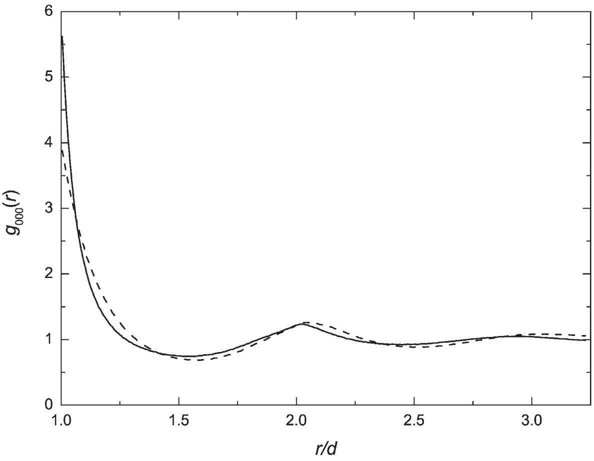

FIG. 7
The radial distribution function, $g(r)$, as a function of the center-to-center distance, r. Full line: dipolar hard spheres; dashed line: hard spheres with the modified dipole and $K = 2.0$. Both at $\rho^* = 0.8$ and $\mu^{*2} = 5.0$

of the simulation box, $\langle M^2 \rangle$, and noticed that in the case of the modified-dipole systems ($K > 1.0$) the value of $\langle M^2 \rangle$ is much larger compared with the corresponding system of the dipolar hard spheres. High values of $\langle M^2 \rangle$ imply that the dipole vectors tend to align to form a ferroelectric phase. The presence of the ferroelectric transition at different densities can also be inferred from a sigmoidal shape of the $\langle M^2 \rangle^{1/2}$ vs μ^{*2} curves shown in Fig. 8.

In comparison with the fluid of dipolar hard spheres[12], the ferroelectric transition occurs at lower values of μ^{*2}; weaker interactions are therefore sufficient to maintain a long-range orientational order in the fluid phase. This shift can be explained by the absence of the short-range dipole–dipole interaction which would prevent neighboring dipoles from forming parallel configurations. Moreover, interactions with the surrounding dielectrics, which remain intact by switching, favor the parallel alignment of the sample.

To eliminate the influence of the initial conditions (where all dipoles point to the same direction) on the orientational order, we have also equilibrated first the system of dipolar hard spheres (isotropic phase) with K = 1.0, and then we have substituted the dipole–dipole interaction potential

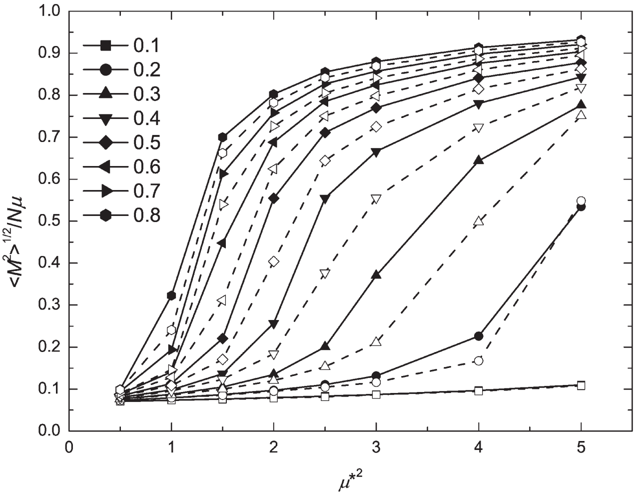

FIG. 8
The root-mean-square net dipole moment of the simulation cell, $\langle M^2 \rangle^{1/2}$, as a function of the squared reduced dipole moment, μ^{*2}, at eight distinct reduced densities (numbers in the legend). Full symbols and full line: K = 2.0; open symbols and dotted line: K = 1.5. Lines are drawn to guide the eyes

by the modified one, $K = 2.0$, and continued the simulation. The result of this experiment is shown in Fig. 9: as soon as we change the potential, the dipole vectors start aligning parallel giving rise to a rapid increase in the net dipole moment. The strong polarization of the sample is also apparent from snapshots shown in Fig. 9. Whereas M changes dramatically, the potential energy increases only slightly as the loss of the preferable short-range interactions (from antiparallel pairs and chain configurations) is compensated by the reaction field.

The simulation results are influenced also by the chosen relative permittivity, ε'_r, of the surrounding dielectrics. Wei and Patey[13] found that for dipolar hard and soft spheres the ferroelectric phase is stable only above a certain value of ε'_r. Since we have employed in simulations a relatively high value, $\varepsilon'_r = 80$, we have used also lower values to potentially suppress the occurrence of the transition. Preliminary results using $\varepsilon'_r = 10$ ($\mu^{*2} = 2.0$), however, have showed qualitatively the same picture as with $\varepsilon'_r = 80$, al-

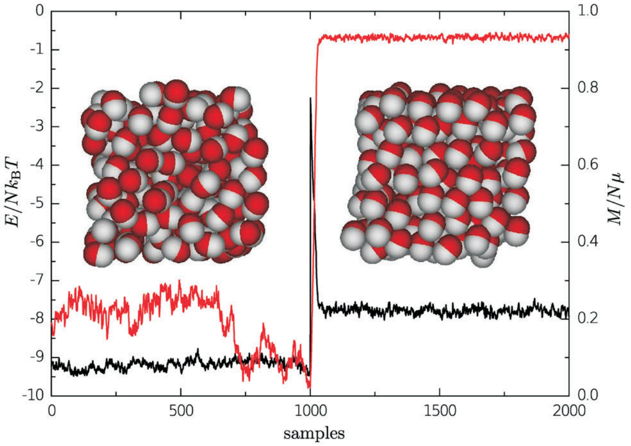

FIG. 9

The instantaneous potential energy (black curve), E, left axis, and the magnitude of the net dipole moment of the simulation box (red curve), M, right axis. Samples were taken after every 1000 configurations. First 10^6 configurations (1000 samples) have been generated using the true dipolar hard-sphere potential. Then the potential has been changed to the modified one, Eq. (*10*), with $K = 2.0$ and further 10^6 configurations have been generated. The inserted snapshots visualize the typical structure of the fluid in the corresponding phases of the simulation. Grey spheres correspond to hard cores, whereas the centers of the red spheres are displaced by $0.25d$ along the direction of the dipole vector. Conditions: $\rho^* = 0.8$ and $\mu^{*2} = 5.0$

though the deviations from the theory are quantitatively a bit smaller (see Fig. 6). Fair agreement has been found when we have set $\varepsilon'_r = 1$ (vacuum) to turn the reaction field completely off (see again Fig. 6 for preliminary results, $K = 2.0$ and $\mu^{*2} = 2.0$). In this case, the net dipole moment fluctuates near zero.

CONCLUSIONS

In this paper we have considered a specific dipolar fluid resulting from application of a perturbation theory. Computer simulations have been performed and an attempt has been made to describe the results theoretically using available methods. The results do not show satisfactory agreement.

The orientational anisotropy of the system may explain the failure of the modified Rushbrooke method to reproduce the simulation results for $\varepsilon'_r = 80$. Comparison of Figs 5 and 6 with Fig. 8 reveals a rough correspondence between the polarization of the sample and the discrepancy between the theory and simulation. Preliminary results with (unphysical) $\varepsilon'_r = 1$ show that the modified Rushbrooke expression can give a reasonable approximation for the internal energy of an isotropic fluid phase and bring further evidence that the orientational ordering plays the crucial role for the applicability of the proposed theory. In contrast to realistic models of complex fluids, our modified potential does not contain short-range directional forces the effect of which is qualitatively similar to the interactions of two dipoles and which would, in most cases, prevent the occurrence of the isotropic–nematic transition. The system with unphysical $\varepsilon'_r = 1$ may thus yield a dipole–dipole contribution closer to an appropriate correction for realistic fluid models.

Further research should be devoted to the examination of the isotropic case in a broader range of thermodynamic conditions in order to assess thoroughly the accuracy of modified Rushbrooke's method. As regards the realistic fluids, it is quite possible that, in some cases, the simple MSA variant of the Padé approximant due to Rushbrooke et al.[2] will finally turn out to be an acceptable approximation to a rigorously derived dipole–dipole contribution, and its so far intuitive use will become theoretically justified.

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. IAA400720710), by the Czech National Research Program "Information Society" (project No. 1ET400720409), and by the Czech Science Foundation (Grant No. 203/05/H001).

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