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Yukawa hard-sphere fluid**

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Abstract

Thermodynamic perturbation theory for central-force associating potentials and Monte Carlo simulations are used to study the phase behaviour of the dipolar Yukawa hard- sphere fluid over a wide range of the particle dipole moment, μ. Liquid-vapour coexistence is found to exist for values of μ far in excess of a `threshold' value found in earlier simulation studies. The predictions of the present theory are found to be in reasonably good agreement with computer simulation results, all the way up to the highest dipole moment studied.

Introduction

The dipolar Yukawa hard-sphere (DYHS) fluid is a simple and convenient molecular model which can be used to describe the properties of polar molecular fluids. It consists of hard spheres interacting via *attractive* Yukawa and point-dipolar potentials. Liquid-vapour coexistence in the non-polar model – the Yukawa hard-sphere (YHS) fluid – has been studied to high precision using the self-consistent Ornstein-Zernike approxi- mation and computer simulations[1]. The polar model with a *repulsive* Yukawa potential can be used to model charge-stabilised colloidal ferro fluids[2]. Recently, liquid-vapour coexistence in the DYHS fluid was studied both theoretically and via computer simulations by Szalai *et al.*[3, 4]. According to the computer simulation data[4] the liquid-vapour phase equilibrium disappears beyond a large, threshold dipole moment. As the dipole moment is increased, the role of the Yukawa interaction diminishes, and the properties of the DYHS fluid should approach those of the dipolar hard-sphere (DHS) fluid. Estimates of the critical parameters for the DHS fluid have recently been published[5]; one might therefore expect the transi- tion to survive in the DYHS fluid to very high values of the dipole moment, and that the critical parameters will approach those of the DHS fluid.

In this paper we present new theoretical and computer simulation results for the liquid-vapour coexistence envelope of the DYHS fluid, and compare them against existing theoretical and computer simulation predictions. We provide results for dipole interaction strengths more than twice as high as those studied previously[4]. Theoretical results are generated using an extension of a recently proposed thermodynamic perturbation theory designed to treat associating fluids with central forces[6].

The model

We consider a one-component fluid at a temperature T and a number density ρ, with the particles interacting via the following pair potential

$$U(12) = U_{hs}(r) + U_y(r) + U_{dd}(12), \tag{1}$$

where $U_{hs}(r)$ is the hard-sphere potential, $U_y(r)$ is the Yukawa potential

$$U_y(r) = -\epsilon_y \left(\frac{\sigma}{r}\right) e^{-z(r-\sigma)}, \tag{2}$$

and $U_{dd}(12)$ is the dipole-dipole potential

$$U_{dd}(12) = -\frac{\mu^2}{r^3} \left[2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2)\right]. \tag{3}$$

Here '12' denotes the relative positions and orientations of particles 1 and 2, σ is the hard-sphere diameter, ϵ_y and z are the Yukawa potential energy and range parameters, respectively, μ is the dipole moment, θ_1 and θ_2 denote the angles between the dipole vectors and the pair-separation vector r, and ϕ_1 and ϕ_2 are the azimuthal angles about r. We set $z = 1:8 = \sigma$ as in previous studies[1,3,4]. We define reduced units in terms of the potential parameters and the thermal energy $k_B T$ as follows: number density $\rho^* = \rho\sigma^3$; dipole moment $\mu^* = \sqrt{\mu^2/\epsilon_y\sigma^3}$; 'Yukawa' temperature $T_y^* = k_B T/\epsilon_y$; and 'dipolar' temperature $T_d = k_B T \sigma^3/\mu^2$.

Theory

The theoretical description of the DYHS fluid is carried out using thermodynamic perturbation theory for central-force (TPT-CF) associating potentials, developed earlier[6, 7]. In the TPT-CF approach, the total pair potential is represented as a sum of reference $U_{ref}(12)$ and associating $U_{ass}(12)$ parts:

$$U(12) = U_{ref}(12) + U_{ass}(12). \tag{4}$$

Following earlier studies[6], we define $U_{ref}(12)$ and $U_{ass}(12)$ as

$$\begin{aligned} U_{ref}(12) = U_{hs}(r) + U_y(r) \\ + \left(\sin^{2n}\theta_1 \sin^{2n}\theta_2\right) U_{dd}(12), \end{aligned} \tag{5}$$

$$U_{ass}(12) = \left(1 - \sin^{2n}\theta_1 \sin^{2n}\theta_2\right) U_{dd}(12). \tag{6}$$

With these definitions, the global potential energy minimum, corresponding to the "nose-to-tail" parallel configuration of the dipoles ($\theta_1 = \theta_2 = 0$, $\theta_1 = \theta_2 = \pi$), is included in $U_{ass}(12)$; this minimum is responsible for the formation of chains in the system[8]. In eqs. (5) and (6) n plays the role of a potential-splitting parameter, since it controls the distribution of $U_{dd}(12)$ between $U_{ref}(12)$ and $U_{ass}(12)$. According to previous studies[6] the optimal choice is $n = 3$, and we adopt this value here.

Given $U_{\text{ref}}(12)$ and $U_{\text{ass}}(12)$, the Helmholtz free energy A of the system can also be represented as a sum of reference and associating parts:

$$A = A_{\text{ref}} + A_{\text{ass}}. \tag{7}$$

For the associative part A_{ass} we have[6]

$$\frac{\beta A_{\text{ass}}}{N} = \ln\left(\frac{\sigma_0}{\rho}\right) + \frac{\sigma_1(\sigma_1 - \sigma_0)}{2\rho\sigma_0}, \tag{8}$$

where $\beta = 1/k_B T$, $\sigma_0 = \rho/(\frac{1}{2}x^2 + x + 1)$, $\sigma_1 = (1+x)\sigma_0$, and x satisfies the equation

$$\frac{1}{2}x^3 + x^2 + (1 - \rho K)x - \rho K = 0 \tag{9}$$

in which

$$K = \int g_{\text{ref}}(12)\left(e^{-\beta U_{\text{ass}}(12)} - 1\right)\text{d}2 \tag{10}$$

and $g_{\text{ref}}(12)$ is the radial distribution function (RDF) of the reference system. The properties of the reference system are calculated using the scheme developed by Rushbrooke, Stell, and Høye[9]. The Helmholtz free energy of the reference system A_{ref} is expressed using the Padé approximation,

$$A_{\text{ref}} = A_{\text{ref}}^{(0)} + \frac{(\mu^*)^4 A_{\text{ref}}^{(2)}}{1 - (\mu^*)^2 A_{\text{ref}}^{(3)}/A_{\text{ref}}^{(2)}}, \tag{11}$$

where $A_{\text{ref}}^{(0)}$ is the Helmholtz free energy of the YHS fluid, which we calculate using the equation of state developed for that system by Henderson $et\ al.$[10]. The terms $A_{\text{ref}}^{(2)}$ and $A_{\text{ref}}^{(3)}$ are given by

$$\frac{\beta A_{\text{ref}}^{(2)}}{N} = -\frac{1}{4}\rho \int w_2(r)g_{\text{yhs}}(r)\text{d}r, \tag{12}$$

$$\frac{\beta A_{\text{ref}}^{(3)}}{N} = \frac{1}{6}\rho^2 \int w_3(r_{12}, r_{13}, r_{23})$$
$$\times g_{\text{yhs}}(r_{12})g_{\text{yhs}}(r_{13})g_{\text{yhs}}(r_{23})\text{d}\boldsymbol{r}_{12}\text{d}\boldsymbol{r}_{13}, \tag{13}$$

where $g_{\text{yhs}}(r)$ is the RDF of the YHS fluid, and the expressions for $w_2(r)$ and $w_3(r_{12}, r_{13}, r_{23})$ are given in the appendix. Finally, for the RDF of the reference system $g_{\text{ref}}(12)$ in eq. (10) we used the approximation

$$g_{\text{ref}}(12) = y_{\text{yhs}}(r)\exp\left[-\beta U_{\text{ref}}(12)\right], \tag{14}$$

where $y_{yhs}(r)$ is the YHS fluid cavity distribution function. $y_{yhs}(r)$ and $g_{yhs}(r)$ are calculated by solving modified hypernetted chain approximation with hard-sphere bridge function due to Malijevsky and Labik[11]. The TPT-CF scheme yields the total Helmholtz free energy of the system (7). All other thermodynamic quantities, and in particular those required for the determination of phase equilibrium (pressure and chemical potential), are calculated using standard relations.

Computer simulations

We used Wang-Landau, flat-histogram Monte Carlo (MC) simulations in the grand-canonical ensemble to determine the canonical partition function $Q(N, V, T)$, up to an irrelevant factor C, as a function of particle number N in a fixed cubic volume $V = L^3 = 1000\sigma^3$ at temperature T. From $C \times Q(N, V, T)$ one can determine the number-density distribution at fixed chemical potential, and hence solve the conditions for phase coexistence; the complete procedure is described in ref.[12]. The long-range dipolar interactions were handled using the Ewald summation[13] with conducting boundary conditions, real-space screening parameter $\alpha = 6/L$, and 552 reciprocal-space wavevectors. In order to enhance the efficiency of particle insertions and deletions, rotational biasing of the dipole orientations was performed as described in ref.[14]. The coexistence results reported here are from averages over five independent runs. To estimate the critical temperature T_c and critical density ρ_c, we fitted the coexistence densities to the standard scaling relation[15]

$$\rho_\pm = \rho_c \pm (A_0 t^\beta + A_1 t^{\beta+\Delta}) + (B_0 t^{1-\alpha} + B_1 t) + \dots, \qquad (15)$$

where $\alpha = 0.11$, $\beta = 0.326$, and $\Delta = 0.52$ are the usual Ising critical exponents, ρ_+ and ρ_- are the liquid and vapour coexistence densities, respectively, and $t = |T - T_c|/T_c$. In practice, B_0 could not be fitted with a relative uncertainty < 100%, and so it was set to zero.

Results and discussion

We first compare liquid-vapour coexistence envelopes in the ρ^*-T_y^* plane, computed from theory and from MC simulations. In fig. 1 we present results for $(\mu^*)^2 = 4, 9, 16, 25,$ and 36. For comparison we also include the computer simulation and mean spherical approximation (MSA) results of Szalai *et al.*[3, 4]; we do not show results of the perturbation theory proposed by these authors, since its predictions for the phase behaviour are less accurate than those of the MSA. According to the *NPT* + test particle insertion simulation results of Szalai *et al.*[4], liquid-vapour coexistence is absent for $(\mu^*)^2 \geqslant 16$. However, our computer simulation results show that liquid-vapour coexistence persists up

to at least $(\mu^*)^2 = 36$. The fact that Szalai *et al.*'s constant-pressure simulations indicate no transition at high μ^* may be due to the characteristic chaining in dipolar systems, which strongly suppresses volume fluctuations and hence precludes simulation convergence. For $(\mu^*)^2 = 4$ the predictions of both computer simulation studies almost coincide; however, for $(\mu^*)^2 = 9$ one can already see differences between the critical temperatures of about 8%, and between the critical densities of about 18%. These apparent discrepancies might arise from the difficulty in extrapolating sub-critical data to the critical region; note that neither we nor Szalai *et al.* performed finite-size scaling studies.
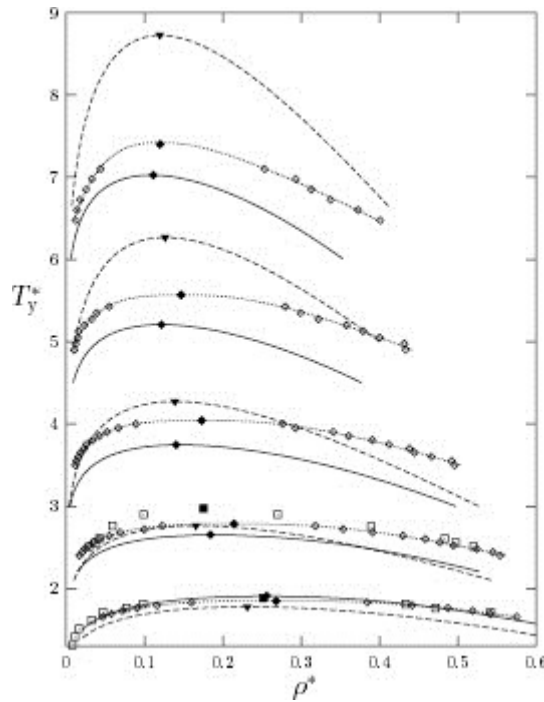
Figure 1. Liquid-vapour coexistence curves for the DYHS fluid in the ρ^*-T_y^* plane. Simulation results are shown for, from bottom to top, $(\mu^*)^2 = 4, 9, 16, 25,$ and 36. Circles and dotted lines: MC and fit from eq.(15); squares: MC[4]; filled symbols indicate critical points. Theoretical results are shown for, from bottom to top, $(\mu^*)^2 = 4, 9, 16, 25,$ and 36. Solid lines: TPT-CF; dashed lines: MSA[3]; filled symbols indicate critical points.

For $(\mu^*)^2 = 4$, the theoretical results are in a good quantitative agreement with simulation results. As μ^* is increased, the accuracies of both the MSA and TPT-CF decrease, with the MSA being substantially less accurate for the larger dipole values, $(\mu^*)^2 \geqslant 25$. While for $(\mu^*)^2 = 9$ both theories underestimate the critical temperature, for $(\mu^*)^2 \geqslant 16$ MSA overestimates it and for $(\mu^*)^2 \geqslant 9$ TPT-CF underestimates it. In all cases TPT-CF reproduces the overall shape of the phase diagrams more faithfully than does the MSA.

In figs. 2 and 3 we compare theoretical and computer simulation predictions for the critical Yukawa/dipolar temperatures and critical density as functions of $(\mu^*)^2$ (upper panels) and $1/(\mu^*)^2$ (lower panels). While TPT-CF predictions are in relatively good agreement with simulation estimates of the critical temperature at all values of $(\mu^*)^2$, the MSA is accurate only at low values. For the critical density both theories give results which are in a good qualitative agreement with simulation estimates.
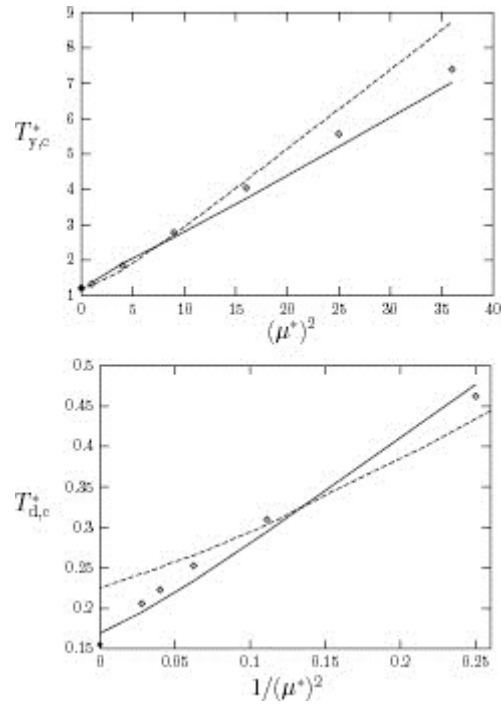
Figure 2. Critical Yukawa temperature $T_{y,c}^*$ as a function of $(\mu^*)^2$ (upper panel), and critical dipolar $T_{d,c}^*$ as a function of $1/(\mu^*)^2$ (lower panel). Open circles: MC; solid lines: TPT-CF; dashed lines: MSA[3]; filled circle, upper panel: MC (YHS fluid)[1]; filled circle, lower panel: MC (DHS fluid)[5].
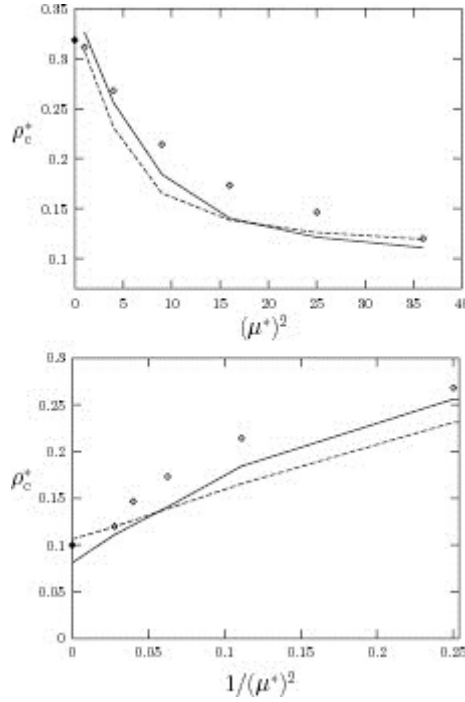
Figure 3. Critical density ρ_c^* as a function of $(\mu^*)^2$ (upper panel) and $1/(\mu^*)^2$ (lower panel). Open circles: MC; solid lines: TPT-CF; dashed lines: MSA[3]; filled circle, upper panel: MC (YHS fluid)[1]; filled circle, lower panel: MC (DHS fluid)[5].

In the limiting case $1/(\mu^*)^2 \to 0$, the DYHS critical temperature $T_{d,c}^*$ and critical density ρ_c^* should approach the corresponding values for the dipolar hard-sphere fluid. The extrapolation of $T_{d,c}^*$ to the DHS limit seems straightforward and a linear fit to the simulation results for $(\mu^*)^2 = 16$, 25, and 36 gives $T_{d,c}^* = 0.1693(3)$, 10% above the DHS value $T_{d,c}^* = 0.153(1)$[5]. The extrapolation of ρ_c^* to the DHS limit seems far more difficult, and should depend crucially on what happens above $(\mu^*)^2 = 36$. (Two of us—GG and PJC—are currently exploring this question.) However, it is not inconceivable that ρ_c^* would approach the DHS value of $\simeq 0.1$[5]. Determining ρ_c^* is always difficult due to the critical region of the coexistence envelope being very 'flat'. In addition, simulations with $(\mu^*)^2 = 36$ are near the limits of our computational ability, due to the extent of chaining and the associated finite-size effects[12]. As a result, the coexistence curve in fig. 1 looks unusual in shape.

Conclusions

New theoretical and computer simulation results for the phase behaviour of the DYHS fluid are presented and compared against existing theoretical and computer simulation predictions. Theoretical results are generated using an extension of a recently proposed thermodynamic perturbation theory for

associating fluids with central interaction potentials. In previous simulation work, it was claimed that liquid-vapour coexistence disappears above a threshold value of the dipole moment, $(\mu^*)^2 \geqslant 16$. In contrast, our simulations show that the transition persists up to at least $(\mu^*)^2 = 36$. (We note that in the case of the Stockmayer fluid, a similar conflict has arisen between early simulations using the Gibbs ensemble technique[16, 17] and recent simulation work[12, 18].) In the limiting case of infinitely large dipole moment, the phase diagram of the dipolar Yukawa hard-sphere fluid should approach that of the dipolar hard-sphere fluid; the DYHS results are at least consistent with this expectation. The present theory performs very well against simulation results, and is generally more accurate than the MSA, especially for large values of the dipole moment.

Appendix

For $w_2(r)$ and $w_3(r_{12}, r_{13}, r_{23})$, which enter eqs. (12) and (13), we have

$$w_2(r) = \frac{A}{r^6} \quad \text{and} \quad w_3(r_{12}, r_{13}, r_{23}) = \frac{27B(\alpha_1, \alpha_2)}{(r_{12}r_{13}r_{23})^3}, \tag{A.1}$$

where $A = 17825792/225450225$,

$$B(\alpha_1, \alpha_2) = \sum_{i=1}^{85} \frac{k_i}{l_i} \cos\left(m_i^{(1)}\alpha_1 + m_i^{(2)}\alpha_2\right), \tag{A.2}$$

and α_1 and α_2 are the interior angles at particles 1 and 2, respectively, in the triangle formed by particles 1, 2, and 3. The values of the integer numbers k_i, l_i, and m_i can be obtained from the corresponding author upon request.

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