RESEARCH NOTE

Phase diagram for the dimerizing hard-core Yukawa fluid

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(Received 13 June 1995; accepted 26 July 1995)

The liquid–gas phase diagram for the dimerizing hard-core Yukawa fluid is calculated. The model consists of the one-site hard-sphere dimerizing model of Wertheim with an additional Yukawa attraction included into the non-associating part of the interaction. The thermodynamic properties of the model are obtained from the analytical solution of the associative mean spherical approximation. Predictions of the theory are consistent with qualitative trends in the behaviour of the phase equilibrium of associating liquids.

1. Introduction

The hard-core Yukawa fluid (HCYF) has been the subject of renewed interest in recent years (see 1 and references therein). Most of the interest in this model stems from the fact that, on the one hand, its pair potential takes into account the basic elements of the interparticle interaction, i.e. short-range repulsion and long-range attraction, while on the other hand, it can be described analytically using the mean spherical approximation (MSA). Although there are no real systems which have the interparticle interaction of the form used in the HCYF model, it can be utilized to study a variety of physical phenomena. In particular, the thermodynamical properties of a system with a more realistic Lennard–Jones (LJ) potential can be successfully described by a correspondent HCYF model 2–4. In 3, 4 it was demonstrated that the liquid–gas phase diagram for the LJ fluid can be reproduced by the Monte Carlo (MC) simulation 3 and by the MSA 4 applied for the corresponding HCYF model.

In this study we present the liquid–gas phase diagram for the dimerizing HCYF system, a model for associating fluids. The model is an extension of the dimerizing model of Wertheim 5 to the case when the non-associating part of the potential involves the Yukawa attractive interaction in addition to the hard-sphere repulsion. In several recent papers 6–8 the liquid–gas phase diagrams for associating fluids modelled by the dimerizing LJ systems have been investigated by both theoretical and computer simulation methods. The theoretical approach used in these studies is based on the thermodynamic perturbation theory (TPT) of Wertheim 5 in which the LJ system is considered as the reference system, while the effects of association are taken into account as a perturbation. In the present report we utilize an integral equation theory for associating fluids which was developed concurrently with TPT 5. The theory consists of the two-density Ornstein–Zernike (OZ) equation together with an approximate closure condition. Because of the availability of an analytical solution,

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we have chosen here to use the two-density version of the MSA, the so-called associating mean spherical approximation (AMSA) \cite{9,10}.

The paper is organized as follows. In section 2 we discuss the model and AMSA closure conditions. Since the analytic solution of the AMSA for the more general model of dimerizing ionic HCYF has been obtained in \cite{10}, in section 3 we simply quote the results of the solution for the model at hand. Expressions for thermodynamical quantities which are needed to calculate the phase envelope are presented in section 4 and in section 5 we briefly discuss the results of our calculations.

## 2. The model and AMSA closure conditions

The model consists of the HSYF with hard-core diameter $\sigma = 1$ with an additional associative interaction due to the site–site square-well potential of the depth $\varepsilon_A$ and width $a$. Each particle contains one off-centre site located at a distance $d$ from the centre of the hard sphere. The values of the parameters $a$ and $d$ satisfy the following inequality

$$1 - 2d < a \leq 1 - \sqrt{3d}, \quad (1)$$

which guarantees saturation of the associative interaction at the dimer level. The pair potential $U(12)$ for this model has the form

$$U(12) = U_{HS}(r) + U_Y(r) + U_A(12), \quad (2)$$

where 1 and 2 stand for the spatial and orientational coordinates of the two particles, $U_{HS}$ is the hard-sphere potential, $U_A$ is the associative potential and $U_Y$ is the Yukawa potential

$$U_Y(r) = \frac{1}{2} \sum_{l=1}^{\infty} \frac{B_n}{r} \exp(-iz_n). \quad (3)$$

Here $B_n = \Re z_n$, $z_n = -\bar{z}_n$. Im $z_n < 0$, $z^*$ denotes the complex conjugate of $z$ and the term with $n = 0$ is not included into the summation. The summation of the complex conjugated pairs in (3) results in a potential which is purely real.

As in \cite{11,9} we are using here an orientationally averaged version of the theory in which the associative potential $U_A(12)$ appears via its orientationally averaged Mayer function

$$\bar{f}_A(r) = (\exp(\beta \varepsilon) - 1) \frac{(a+2d-r)^2(2a-2d+r)}{24d^2r} \quad (4)$$

where $\beta = 1/k_B T$.

To make the model analytically solvable we consider it in the so-called sticky limit, in which we let $a \to 0$ and $\varepsilon \to \infty$ so, that the volume integral

$$K_0 = 4\pi \int_1^{2d+a} \bar{f}_A(r) r^2 \, dr \quad (5)$$

is held constant. This is equivalent to holding the contribution of the associating interaction to the second virial coefficient constant during the limiting process.
The AMSA closure conditions for the model in question are thus read

\[ c_{ij}(r) = -\beta U_y(r) \delta_{i0} \delta_{j0} + \delta_{i1} \delta_{j1} \frac{K}{4\pi} g_{00} \delta(r-1), \quad r > 1 \]

\[ h_{ij}(r) = -\delta_{i0} \delta_{j0} \quad r < 1 \]  

(6)

where \( g_{ij} = h_{ij} + \delta_{i0} \delta_{j0}, g_{00} = g_{00} \) is the OZ equation \{5, 11\}

\[ \hat{h}(k) = \hat{c}(k) + \hat{c}(k) \rho \hat{h}(k), \]  

(7)

where \( \hat{h} \) and \( \hat{c} \) are the matrices with the elements being the Fourier transforms of \( h_{ij} \) and \( c_{ij} \), respectively, \( \rho \) is the matrix with the elements

\[ \{\rho\}_{ij} = \rho \delta_{i0} \delta_{j0} + \rho \delta_{i1} \delta_{j1} + \delta_{i0} \delta_{j1} \].

Here the monomer density \( \rho_0 \) is related to the total number density of the system \( \rho \) by

\[ \rho_0 = \frac{-1 + (1 + 4K_{n}g_{00}\rho)^{1/2}}{2K_{n}g_{00}}. \]  

(8)

The set of the OZ equations (7) together with closure conditions (6) and (8) form a closed set of equations to be solved.

**3. Solution of the AMSA for the dimerizing hard-core Yukawa fluid**

As was already noted in the previous section, the solution of the AMSA for the more general model, which in addition to the Yukawa and associative interactions involves a Coulombic interaction, was obtained by Kalyuzhnyi and Holovko \{10\}. Therefore we shall omit here the details of this solution and present only the final results relevant to the special case here, i.e., no Coulombic interaction.

As a result of the factorization of the OZ equation (7) the partial total correlation functions are written in terms of Baxter \( q \)-functions as

\[ -r h_{ij}(r) = q_{ij}(r) - 2\pi \sum_{lm} \int_{0}^{\infty} q_{lm}(t) \rho_{lm}(r-t) h_{mj}(|r-t|) \, dt \]

where

\[ q_{ij}(r) = (\frac{4}{2} + b \frac{b}{1} + r^2) \delta_{ij} + c_{ij} + 2\pi \frac{1}{2} \sum_{n=N}^{\infty} A_{n} \chi^{(n)}_{i} G_{j}^{(n)} \exp(-iz_{n} r), \quad r < 1 \]

\[ q_{ij}(r) = \delta_{ij} \frac{1}{2} \sum_{n=N}^{\infty} A_{n} \chi^{(n)}_{i} \exp(-iz_{n} r), \quad r > 1 \]  

(9)

and \( A_n = \beta B_n \),

\[ c_{ij} = - (\frac{4}{2} + b \frac{b}{1} \delta_{ij} + 2\pi \frac{1}{2} \sum_{n=N}^{\infty} A_{n} \chi^{(n)}_{i} (\delta_{ij} - 2\pi \frac{G_{j}^{(n)}}{iz_{n}}) \exp(-iz_{n} r) + \delta_{ij} \frac{K_{n}}{4\pi} g_{00} \].

(10)
The unknown coefficients $a_i$, $b_i$, $\chi_i^{(n)}$ and $G_i^{(n)}$ follow from the solution of a set of algebraic equations, which can be written as a set of four linear equations

\[
(1 - \frac{4}{3} \pi \rho) a_i - \pi \rho b_i = \delta_{ij} + R_i(\chi_i^{(n)}, G_i^{(n)}, g_{00}) \quad i = 0, 1
\]

\[
\frac{1}{3} \pi \rho a_i + (\frac{4}{3} \pi \rho + 1) b_i = E_i(\chi_i^{(n)}, G_i^{(n)}, g_{00}) \quad i = 0, 1
\]

(11)

and $4N+1$ nonlinear equations

\[
z_n \chi_i^{(n)} = iQ^T (-z_n, G_i^{(n)}, \chi_i^{(n)}, g_{00}) \rho_{n0}^1, \quad i = 0, 1; \quad n = 1, \ldots, N
\]

\[
G_i^{(n)} = -Q^1 (-z_n, G_i^{(n)}, \chi_i^{(n)}, g_{00}) F(iz_n, G_i^{(n)}, \chi_i^{(n)}, g_{00}) \delta_{i0}, \quad i = 0, 1; \quad n = 1, \ldots, N
\]

(12)

\[
g_{00} = a_0 + b_0 + \frac{1}{2} \sum_{n=1}^{N} A_n \chi_n^{(n)} (iz_n - 2\pi G_0^{(n)}) \exp (-iz_n).
\]

(13)

Here $R_i(\chi_i^{(n)}, G_i^{(n)}, g_{00})$, $E_i(\chi_i^{(n)}, G_i^{(n)}, g_{00})$ and the elements of the matrices $Q(k, G_i^{(n)}, \chi_i^{(n)}, g_{00})$ and $F(s, G_i^{(n)}, \chi_i^{(n)}, g_{00})$ are presented in the Appendix.

We utilize an iterative method to solve the set of equations (11)–(14). As an initial input in our iteration scheme we assume that $\chi_i^{(n)} = 0$, $G_i^{(n)} = 0$ and use the estimate for $a_i$, $b_i$, $g_{00}$ and $\rho_0$ which follows from the solution of the set of equations (11) and (14) at $B_n = 0$ \{5, 9\}. On the subsequent iteration loop, the previous result for the set of unknowns is used to calculate the elements of the matrices $Q(-z_n, G_i^{(n)}, \chi_i^{(n)}, g_{00})$ and $F(iz_n, G_i^{(n)}, \chi_i^{(n)}, g_{00})$, which are used then to get new estimates for $\chi_i^{(n)}$ and $G_i^{(n)}$ from (12) and (13) and for $a_i$, $b_i$, $g_{00}$ and $\rho_0$ from (8), (11) and (14). The convergency of this scheme is rather fast: about 20 to 25 iteration loops was sufficient to obtain the solution with an accuracy of up to six digits.

4. Liquid–gas phase diagram

The calculation of the liquid–gas phase diagram requires knowledge of the chemical potential $\mu$ and pressure $P$ of the system. These quantities can be obtained from the expression for the Helmholtz free energy $A$ \{5\}

\[
\frac{\beta[A - A_{\text{non}}]}{V} = \rho \ln \left( \frac{\rho_0}{\rho} \right) - \frac{1}{2} \rho_0 + \frac{1}{2} \rho
\]

(15)

where $A_{\text{non}}$ is the Helmholtz free energy for the HCYF, which is the limiting case of the present model at $K_0 = 0$. It was calculated following the method of Høye and Stell \{12\}, in which the Carnahan–Starling expression for the Helmholtz free energy of the corresponding hard-sphere system is used. The monomer density $\rho_0$ follows from the present solution of the AMSA.

Differentiating (15) with respect to the density $\rho$ we obtain at the following expression for the pressure of the system

\[
\frac{\beta P}{\rho} = \frac{\beta P_{\text{non}}^{(CS)}}{\rho} + \frac{\beta P_{\text{non}}^{(CS)}}{\rho} + \left( \frac{\rho - \rho_0}{\rho_0} \right) \left( \frac{1}{\Delta} + \frac{1 - \Delta}{2K_0 \rho g_{00}} \right) \left( 1 + \frac{\rho}{g_{00}} \frac{\partial g_{00}}{\partial \rho} \right).
\]

(16)

Here $\Delta = (1 + 4\rho K_0 g_{00})^{1/2}$, $P_{\text{non}}^{(CS)}$ is the excess pressure of the HCYF calculated via the
Figure 1. Liquid–gas phase diagram for dimerizing HCY fluid at $\varepsilon_A = 0$ (4), $\varepsilon_A = 10\varepsilon_Y$ (3), $\varepsilon_A = 15\varepsilon_Y$ (2) and $\varepsilon_A = 20\varepsilon_Y$ (1).

Høye–Stell method \cite{12}, and $P^{cs}$ is the Carnahan–Starling equation of state. In (16) the derivative $\partial g_{00}/\partial \rho$ was calculated numerically. The chemical potential $\mu$ follows from the well known relation

$$A/V = \mu \rho - P.$$  \hspace{1cm} (17)

Finally, the liquid–gas phase envelope was obtained solving the Gibbs phase equilibrium conditions.

$$P(\beta, \rho_l) = P(\beta, \rho_g)$$

$$\mu(\beta, \rho_l) = \mu(\beta, \rho_g)$$  \hspace{1cm} (18)

where $\rho_l$ and $\rho_g$ are the equilibrium liquid and gas densities, respectively.

5. Results and discussion

The liquid–gas phase diagram, presented in figure 1, was calculated for the dimerizing HCYF with the following values for the parameters of the model: $N = 1$, Im $B_1 = 0$, Re $z_1 = 0$, Im $z_1 = -1.8$, $\varepsilon_A/\varepsilon_Y = 10, 15$ and $20$, $a = 0.1$ and $d = 0.5$, where $\varepsilon_Y = \text{Re} B_1 \exp(-iz_1)$. This choice for the value of $z_1$ makes the Yukawa fluid qualitatively similar to the LJ fluid \cite{13}. The ratio between the Yukawa potential and associative potential wells depths, $\varepsilon_A$ and $\varepsilon_Y$, is chosen to be the same as that of the LJ potential and associative potential used in \cite{6–8}. In figure 1 we also show the liquid–gas phase diagram for the present model at $\varepsilon_A = 0$. It can be seen that associative interaction causes the shift of the phase diagram in the direction of higher temperatures. This results in the change of the critical temperatures from $T^* = 1.237$ at $\varepsilon_A = 0$, to $T^* = 1.312$ at $\varepsilon_A = 10\varepsilon_Y$, $T^* = 1.476$ at $\varepsilon_A = 15\varepsilon_Y$ and $T^* = 1.585$ at $\varepsilon_A = 20\varepsilon_Y$. The corresponding changes in the critical density are not as pronounced:
Figure 2. Fraction of monomers \( x = \rho_c / \rho \) along the liquid–gas coexistence curve at \( \varepsilon_A = 10\varepsilon_Y \) (3), \( \varepsilon_A = 15\varepsilon_Y \) (2) and \( \varepsilon_A = 20\varepsilon_Y \) (1).

\[ \rho_c = 0.320 \ (\varepsilon_A = 0), \ \rho_c = 0.328 \ (\varepsilon_A = 10\varepsilon_Y), \ \rho_c = 0.322 \ (\varepsilon_A = 15\varepsilon_Y) \] and \( \rho_c = 0.315 \ (\varepsilon_A = 20\varepsilon_Y) \). Here \( T^* = k_B T / \varepsilon_Y \) and \( \rho^* = \rho \sigma^3 \).

In figure 2 we show the equilibrium fraction of monomers \( x = \rho_c / \rho \) in liquid and vapour phases. As was found in \( \{6–8\} \), for \( \varepsilon_A = 10\varepsilon_Y \) the vapour phase consists mostly of the unbonded particles and the fraction of bonded particles is around 0.1. Close to the critical point the fraction of monomers is still high \( (x \approx 0.9) \), which makes the present model of associating fluid in this region quite similar to the unassociated HCYF. With the increase of the ratio between \( \varepsilon_A \) and \( \varepsilon_Y \) the mole fraction of monomers in both phases decreases and for \( \varepsilon_A = 20\varepsilon_Y \) \( x \) does not exceed 0.2.

This behaviour of the phase equilibrium at different values of \( \varepsilon_A \) is in qualitative agreement with the corresponding behaviour of the phase diagram for the dimerizing LJ fluid as predicted by MC simulation and TPT \( \{6–8\} \).

6. Concluding remarks

In this report, the analytical solution of the associative MSA for the dimerizing HCYF is used to calculate the liquid–gas phase diagram. The model is an extension of the one-site dimerizing hard-sphere model of Wertheim to the case where the non-associative interaction, in addition to the hard-sphere interaction, involves the Yukawa attraction. Although the model was not designed to reproduce the phase behaviour of a certain particular associating liquid, its pair potential involves all three types of interaction peculiar to associating fluids, i.e. short-range repulsive interaction modeled by the hard-sphere potential, short-range highly directional attractive interaction represented by the site–site square-well potential, and long-range dispersive interaction described by the Yukawa potential. Taking into account all three types of interaction, results in modifications in the phase diagram which are consistent with what has been observed in the case of associating liquids.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy.
Appendix

Here we present the expressions for the elements of the matrices, which are involved in the set of equations (11), (12) and (13):

\[
R_{ij}(G^{(i)}, \chi^{(i)}, g_{00}) = 2 \pi \rho \frac{1}{2} \sum_{n=-N}^{N} A_n \chi^{(i)}(n) \left[ \frac{1}{1 - i z_n} - 2 \pi G^{(i)}_0 \left( \frac{1}{z_n^2} + \frac{1}{i z_n} \right) \exp(-iz_n) + \frac{2 \pi}{z_n^2} G^{(i)}_0 \right] - 4 \pi^2 \rho \frac{1}{2} \sum_{n=-N}^{N} A_n \chi^{(i)}(n) \left( \frac{1}{z_n^2} + \frac{1}{i z_n} \right) \exp(-iz_n) - \frac{1}{z_n^2} \delta_{ij} \rho \delta_0 K_0 g_{00}, \quad (A1)
\]

\[
E_{ij}(G^{(i)}, \chi^{(i)}, g_{00}) = 2 \pi \rho \frac{1}{2} \sum_{n=-N}^{N} A_n \chi^{(i)}(n) \left[ \frac{2 \pi G^{(i)}_0}{i z_n} \left( \frac{1}{z_n^2} + \frac{1}{i z_n} \right) \exp(-iz_n) - \frac{1}{z_n^2} \right]
\]

\[
- \left( \frac{1}{z_n^2} + \frac{1}{i z_n} \right) \exp(-iz_n) + 4 \pi^2 \rho \frac{1}{2} \sum_{n=-N}^{N} A_n \chi^{(i)}(n) G^{(i)}_1 \exp\left(\frac{z_n}{s+i z_n}\right) + \delta_{i1} \rho \delta_0 K_0 g_{00}. \quad (A2)
\]

\[
Q_{ij}(k, G^{(i)}, \chi^{(i)}, g_{00}) = \rho \frac{1}{2} \left[ \sum_{n=-N}^{N} \left( \frac{1}{ik} + \frac{1}{k^3} \right) \exp(ik) \delta_{ij} + \frac{1}{ik} \exp(ik) - 1 \right] + b \left[ \frac{1}{ik} \exp(ik) - 1 \right] \delta_{ij} + c \frac{1}{ik} \exp(ik) - 1
\]

\[
- 2 \pi \rho \frac{1}{2} \sum_{n=-N}^{N} A_n \chi^{(i)}(n) \left( \frac{1}{ik} \exp(ik) - 1 \right) \delta_{ij} \left[ \frac{1}{i k^2} \right] + \frac{1}{ik} \exp(ik) - 1
\]

\[
F_{ij}(s, G^{(i)}, \chi^{(i)}, g_{00}) = -2 \pi a_1 \delta_{ij} \left( \frac{1}{s} + \frac{1}{s^3} \right) \exp(-s) - 2 \pi b_i \delta_{ij} \frac{1}{s} \exp(-s)
\]

\[
- \frac{1}{2} i k \left( \frac{1}{k} \right) \exp(-s) - 2 \pi \frac{1}{2} \sum_{n=-N}^{N} A_n \chi^{(i)}(n) \frac{i z_n}{s + i z_n} \exp\left(\frac{-s + i z_n}{s + i z_n}\right) + 4 \pi^2 \frac{1}{2} \sum_{n=-N}^{N} A_n \chi^{(i)}(n) \frac{i z_n}{s + i z_n}. \quad (A4)
\]

References
