RESEARCH NOTE

Phase diagram for the Lennard-Jones fluid modelled by the hard-core Yukawa fluid

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The liquid–gas phase diagram for the Lennard-Jones (LJ) fluid model is obtained using the mean spherical approximation (MSA) for the corresponding hard-core Yukawa fluid. The calculated phase diagram is compared with the phase diagrams for the LJ fluid predicted by the Gibbs ensemble Monte Carlo simulation, and by the Percus–Yevick (PY) and reference hypernetted chain (RHNC) theories. The accuracy of the MSA is comparable with the accuracy of the PY approximation. Although the MSA is less accurate than the RHNC approximation, it has an important advantage of being solvable along the whole liquid–gas coexistence curve, including the vicinity of the critical point.

Recently there has been growing interest in studying hard-core Yukawa (HCY) fluids and their application for the description of a variety of physical phenomena (see [1] and references therein). Although there are no real systems which have the interparticle potential of the form used in the HCY fluid, it is of interest because it takes into account the basic elements of the interparticle interaction in fluids, i.e., short-range repulsion and long-range attraction. Together with the availability of the analytical description via the mean spherical approximation (MSA), these are the main reasons for the considerable interest in the HCY fluids. In particular, the ability of the Yukawa fluid to describe thermodynamic properties of the system with a realistic Lennard-Jones (LJ) potential has been demonstrated by Rudisill and Cummings [2]. In this study the LJ potential was approximated by the two-Yukawa potential and the liquid–gas phase diagram of the model was calculated by the Monte Carlo (MC) simulation method. Excellent agreement was obtained between the phase diagram of the two-Yukawa fluid and MC phase diagram of the corresponding LJ fluid.

In the present study we demonstrate the abilities of the MSA to predict the liquid–gas phase diagram for the LJ fluid modelled by the corresponding HCY fluid. With this aim the initial LJ potential is separated into short-range repulsive and long-range attractive parts using the Weeks–Chandler–Andersen method [3]. The short-range part was substituted by the hard core potential with the hard-sphere diameter $\sigma_{HS}$ calculated via the Barker–Henderson formula [4], while the long-range part was approximated by the two-tail Yukawa potential. The resulting HCY potential can be written in the following form.

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Figure 1. Pair potentials of the interparticle interaction for the LJ fluid (dotted line) and for the HCY fluid (solid line).

\[ U_Y(r) = \begin{cases} \infty & r < \sigma_{HS}^y \\ \frac{Ae_{LJ}}{r} \exp[-a(r-\sigma_{LJ}^y)] + \frac{Be_{LJ}}{r} \exp[-b(r-\sigma_{LJ}^y)] & r > \sigma_{HS}^y \end{cases} \]  

(1)

where \( \epsilon_{LJ} \) and \( \sigma_{LJ} \) are the energy and the distance parameters of the LJ potential, respectively, \( A = 1.6438 \sigma_{LJ}^y \), \( a = 14.7 \sigma_{LJ}^y \), \( B = 2.03 \sigma_{LJ}^y \) and \( b = 2.69 \sigma_{LJ}^y \). Here the values of the last three parameters are the same as those used in [5] to fit the LJ potential, while the value of \( A \) was chosen to correct HCY potential (1) for the difference between the original LJ potential and WCA choice for its long range part in the region \( \sigma_{HS} < r < 2^{1/6} \sigma_{LJ} \). This value was calculated using the condition of the equality of the second virial coefficient for the HCY potential (equation (1)) and for the hard-core potential of the same diameter supplemented by the WCA long range part of the LJ potential at \( T^* = 1.3 \). Here \( T^* = k_B T/\epsilon_{LJ} \), where \( T \) is the absolute temperature and \( k_B \) is Boltzmann’s constant. In figure 1 we present a comparison between the original LJ potential and HCY potential (1).

The MSA for this model has been solved using the general scheme developed by Blum and Hoye [6]. The resulting set of nonlinear algebraic equations was solved using the numerical method proposed by Cummings and Smith [7]. The liquid–gas phase diagram has been calculated utilizing the Maxwell construction

\[ P(T^*, \rho^*_l) = P(T^*, \rho^*_g) \]
\[ \mu(T^*, \rho^*_l) = \mu(T^*, \rho^*_g) \]  

(2)

where \( \rho^*_l \) and \( \rho^*_g \) denote the equilibrium reduced densities \( \rho^* = \rho_{LJ} \) of liquid and gas, respectively, and \( P \) and \( \mu \), the pressure and chemical potential, respectively, were obtained via the energy route utilizing the method of Hoye and Stell [8].

In figure 2 we demonstrated the liquid–gas diagram as predicted by the MSA for the present HCY fluid. For the same of comparison we show also the liquid–gas phase diagram for the LJ fluid obtained by MC simulation [9], via the energy route from the
Figure 2. Liquid–gas phase diagram for the LJ model fluid calculated from the MSA for the HCY fluid (solid line), from the PY approximation using the energy role [10] (dashed line), from the RHNC approximation [11] (dotted line) and from the MC simulation [9] (diamonds).


In general the MSA results and the results of MC simulation show reasonably good agreement and are comparable with those of the PY and RHNC approximations, except for the liquid branch of the phase diagram at relatively high densities and low temperatures. Here the PY and RHNC approximations give better agreement with the MC results. However, MSA gives better prediction for the critical density ($\rho_c^\infty = 0.293$, $T_c^\infty = 1.34$) than the PY approximation ($\rho_P^* = 0.34$, $T_P^* = 1.34$). We remark in passing that MC simulation gives $\rho_c^\infty = 0.304 \pm 0.006$ and $T_c^\infty = 1.316 \pm 0.006$. As one would expect, the most accurate is RHNC theory, at least in the region where its solution is possible. Thus it appears, that the accuracy of the MSA is the lowest among the three theories discussed here. However, there are several important inadequacies of the PY and RHNC theories, which make their application in studying the phase behavior of simple fluids rather difficult. Although the RHNC theory is more accurate, it is not able to predict the high-temperature near-critical part of the phase diagram, since in this region RHNC approximation does not have real solutions [1]. On the other hand, the PY approximation suffers from the well known problem of thermodynamic inconsistency, i.e., different routes to thermodynamical properties will give different values for the pressure and chemical potential. This results in an inconsistency between the structure and thermodynamic properties of the system in the vicinity of the critical point. By consistency we mean that the critical point of the liquid–gas coexistence curve, obtained from the Maxwell construction (equation (2)), should coincide with the critical point of the spinodal line defined by the condition

$$
\frac{1}{k_B T} \left( \frac{\partial P}{\partial \rho} \right)_{T} = 1 - \rho_c^* (k = 0) = 0,
$$

(3)
where $\hat{c}(k)$ is the Fourier transform of the direct correlation function. To avoid this inadequacy of the PY approximation one can use, for example, the compressibility route to the pressure and chemical potential. However, this has not been done so far due to the difficulties in performing the mixed path thermodynamic integration (along isotherms and isochores).

As can be seen from figure 2, the MSA is free from the first of the drawbacks mentioned here. Although the MSA shares with the PY approximation the property of being thermodynamically consistent, this inadequacy can be eliminated by using the concept of the generalized MSA (GMSA) [12, 8]. This was demonstrated in [13], where GMSA results for an infinitely dilute binary solution of HCY fluids was utilized to study the effects of gas solubility under near-critical conditions. In addition, the MSA and GMSA are free from the artificial asymmetry between liquid and vapour phases present in the PY [15] and, unlike the HNC approximation [16], give true spinodal lines on the both sides of the critical density. One might also expect to achieve higher accuracy with the MSA by using a more accurate method for calculating the hard-core diameter [14] and including more Yukawa terms to obtain a better fit to the long range part of the LJ potential. Finally, an important advantage of the MSA is the availability of its analytical solution, which makes it much less time consuming to apply than either the PY or especially the RHNC theories.

This short discussion leads us to conclude that, in many circumstances, the MSA is a quite reasonable candidate as an integral equation method in the molecular-based study of the properties of near-critical and supercritical fluids.

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References