

Gibbs ensemble simulation of phase equilibrium in the hard core two-Yukawa fluid model for the Lennard-Jones fluid

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We report Gibbs ensemble simulations of the coexistence region of the hard core two-Yukawa fluid with Yukawa parameters chosen to mimic the Lennard-Jones fluid. The phase envelope of the Lennard-Jones fluid is found to be well approximated by that of the Yukawa fluid. The results suggest that theoretical approaches to the hard core two-Yukawa fluid (such as integral equations and perturbation theory) could provide an analytic basis for predicting the physical properties of the Lennard-Jones fluid.

1. Introduction

The prediction of fluid phase equilibrium from a molecular basis is a much studied and important problem [1]. The goal of research in this area is to develop a fundamentally sound methodology for the calculation of the physical properties at equilibrium of coexisting phases. The grand canonical ensemble (or μVT ensemble, where μ is the chemical potential, V is volume and T is temperature) Monte Carlo technique has been used to compute vapour-liquid coexistence for the Lennard-Jones fluids [2, 3]. This method requires specification of the chemical potential and separate simulations of the liquid and gas phases. A more direct route to the phase equilibrium properties is the Gibbs ensemble Monte Carlo (GEMC) simulation method introduced by Panagiotopoulos [4, 5], described in greater detail in §2 below. It permits the calculation of coexistence properties of both phases in a single simulation without specifying the chemical potential.

There have been a number of studies which report phase equilibrium calculations for the hard core Yukawa fluid (HCYF) [6, 7]. These studies have been based on the analytic solution of the mean spherical integral equation approximation for the HCYF, the molecules of which interact via the pair potential

$$u_{\text{HCYF}}(r) = \begin{cases} \infty, & r < \sigma \\ -J \exp[-z(r - \sigma)]/r, & r > \sigma, \end{cases} \quad (1)$$

where J is the depth of the pair potential, z is the inverse range of the potential, r is the intermolecular distance and σ is the hard sphere diameter of the HCYF molecules. Much of the interest in the HCYF [8] arises because the HCYF is a non-trivial model for simple fluid with attractive interactions; on the other hand, the exponential form in the attractive term renders the mean spherical approximation (MSA) analytically solvable [6, 7]. Thus, it is intrinsically interesting as a simple system to test theoretical approaches to simple fluids, and it has been used as the

reference system in perturbation theory for the Lennard-Jones (LJ) [9] fluid which interacts via the potential

$$u_{LJ}(r) = 4\epsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r} \right)^{12} - \left(\frac{\sigma_{LJ}}{r} \right)^6 \right]. \tag{2}$$

In this equation, ϵ_{LJ} is the depth of the attractive potential well and σ_{LJ} , the point at which potential is zero, is a measure of molecule diameter. The LJ fluid, while it is a more realistic model for simple fluids than the HYCF, has the disadvantage of not being analytically solvable in any integral equation approximation valid in the dense fluid and liquid region.

A model for simple fluids that closely mimics the LJ fluid but which remains analytically solvable in the MSA is the hard core two-Yukawa fluid (HC2YF) with interaction potential

$$u_{HC2YF}(r) = \begin{cases} \infty, & r < \sigma, \\ -J_1 \exp [-z_1(r - \sigma)]/r + J_2 \exp [-z_2(r - \sigma)]/r, & r > \sigma. \end{cases} \tag{3}$$

The LJ potential can be well approximated by the HC2YF potential when the parameters J_1, J_2, z_1, z_2 and σ are regarded as adjustable and used to least squares fit of the second virial coefficient of the HC2YF potential to that of the LJ potential. This is illustrated in figure 1. The HC2YF parameters determined by Jedrzejek and

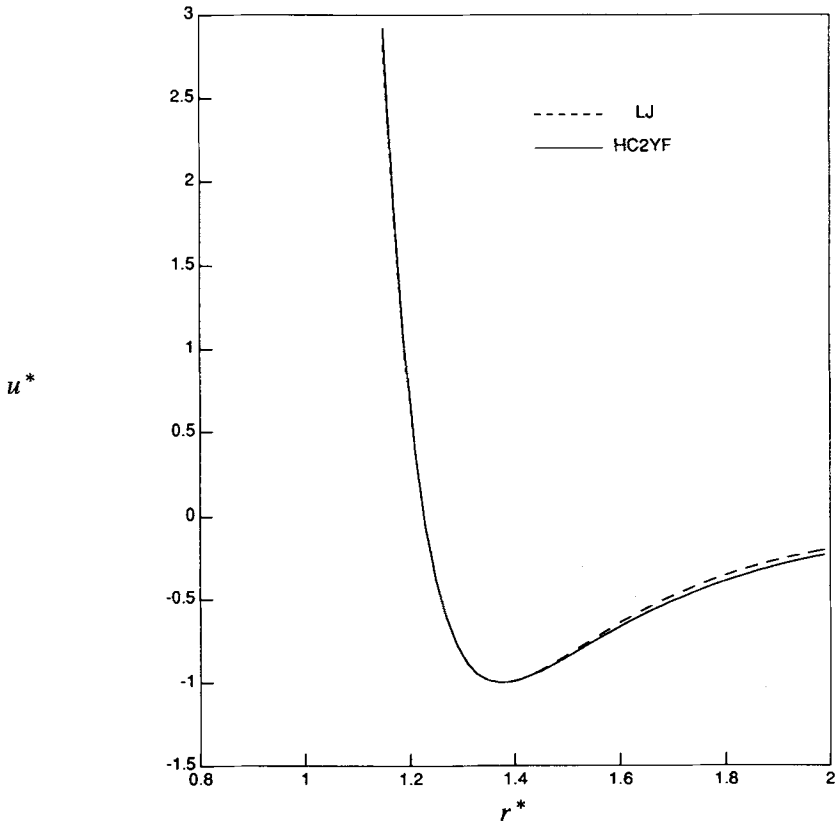


Figure 1. Comparison between LJ potential and HC2YF potential with HC2YF parameters determined by Jedrzejek and Mansoori [10] and given in the text.

Mansoori [10] that best fit the LJ fluid are: $J_1/\epsilon_{LJ} = 3.913$, $J_2/\epsilon_{LJ} = 34.144$, $\sigma/\sigma_{LJ} = 0.8220$, $z_1\sigma = 2.1786$ and $z_2\sigma = 12.1720$. Jedrzejek and Mansoori report good agreement between the thermodynamic properties of the HC2YF and the LJ fluid.

In this paper, we describe GEMC simulations of the HC2YF and compare the results to similar calculations for the LJ fluid by Panagiotopoulos [4]. The aim of these simulations is to determine the degree to which the phase equilibria properties of the HC2YF agree with those of the LJ fluid. As described in §3, we find that the HC2YF with parameters given above has essentially the same vapour–liquid $T - \rho$ envelope (where T is temperature and ρ is number density) as the LJ fluid. This suggests that the HC2YF can be used as an analytically more tractable version of the LJ fluid, in both single phase and multiple phase situations.

2. Gibbs ensemble simulations of the HC2YF

The GEMC simulation technique is the most direct way of computing phase equilibria, and therefore of comparing the vapour–liquid equilibrium properties of the LJ fluid and the HC2YF. Panagiotopoulos [4] calculated the vapour–liquid coexistence curve of the LJ fluid. The corresponding results for the HC2YF presented in this paper are calculated in an analogous manner and compared with the results of Panagiotopoulos.

The GEMC method is a simulation technique in which two phases are simulated simultaneously. The algorithm consists of three basic moves: the displacement step, the volume exchange step and the molecule exchange step. The details of the theoretical basis of the Gibbs ensemble Monte Carlo algorithm are described by Panagiotopoulos [4]. We mention some details to clarify our implementation of GEMC.

Displacement step: This step is essentially the same as that for NVT ensemble MC simulations. The length of the displacement step (equal to the number of attempted configurations) is a variable in the simulation. For the HC2YF simulations, simultaneous moves in the two phases were attempted and the probability of acceptance (approximately 50 per cent was based on the change in the sum of the energy of the two phases. The displacement step consisted of a sequence of $N/2$ such attempts, where N is the total number of molecules in the GEMC simulation.

Volume exchange step: The intention of this step is to maintain pressure (P) equilibrium between the two phases in a manner similar to that of NPT ensemble simulations. One volume exchange was attempted at the end of each displacement step with the size of the attempted change determined by a constant multiplied by the smallest volume of the two phases. The constant was chosen in order to yield a 50 per cent acceptance rate.

Molecule exchange step: The purpose of this step is to maintain equality of chemical potential μ between the two phases similar to the way in which chemical potential is held fixed in μVT ensemble simulations. The number of attempted exchanges of molecules between the two phases is a variable. The number should be large enough to maintain equilibrium, but if it is too large phase instabilities are observed. Panagiotopoulos [4] recommends a number such that 1 to 3 per cent of the molecules are exchanged, on average, at the end of each displacement step. For the HC2YF simulations, it was likewise found that 0.5 to 3 per cent was sufficient.

The values of the parameters J_1 , J_2 , z_1 , z_2 , σ , optimized for agreement with the LJ potential and used in the present study, were given in the previous section. Due

to differences in σ and the corresponding LJ parameter σ_{LJ} , the reduced density ρ^* of the LJ fluid is related to that of the HC2YF fluids by

$$\rho^* = \rho\sigma_{LJ}^3 = 1.798\rho\sigma^3, \quad (4)$$

where ρ is the number density.

3. Results and conclusions

The table reports the results of the GEMC simulation of the HC2YF and compares the results to the GEMC results of Panagiotopoulos [4] and the μVT ensemble simulations results of Adams [2, 3] for the LJ fluid. The reduced densities (ρ_v^* and ρ_l^*) and the configurational energies (E_v and E_l) of the vapour and liquid phases respectively are reported for reduced temperatures $T^* = k_B T/\epsilon_{LJ}$ varying from 0.75 to 1.30. In this table, N is the total number of molecules in the simulation. For all temperatures, the starting conditions (i.e. initial densities of the phases) of the HC2YF and LJ GEMC simulations were the same for both potentials. The HC2YF simulations for temperatures between 0.75 and 1.15 were calculated with 216 total molecules—108 initially in each phase. This as compares to 300 and 500 total molecules for the LJ simulations. The results indicate that 216 molecules are adequate to provide reasonable average phase properties, although for most states

Densities and configurational energies of vapour and liquid phases for HC2YF. Corresponding results for LJ fluid obtained by Panagiotopoulos [5] and Adams [2, 3] are also shown.

Reference	T^*	N	ρ_v^*	$E_v/N\epsilon_{LJ}$	ρ_l^*	$E_l/N\epsilon_{LJ}$
HC2YF	1.30	512	0.275 (5)	-1.95 (7)	0.458 (20)	-4.77 (14)
[5]	1.30	500	0.24 (2)	-1.74 (13)	0.45 (3)	-3.10 (12)
[5]	1.30	300	0.17 (1)	-1.30 (8)	0.47 (3)	-3.22 (19)
[2, 3]	1.30		0.22 (2)		0.43 (2)	
HC2YF	1.25	512	0.161 (16)	-1.29 (9)	0.515 (37)	-3.58 (19)
[5]	1.25	500	0.123 (14)	-0.95 (14)	0.505 (23)	-3.47 (15)
[5]	1.25	300	0.110 (17)	-0.88 (4)	0.533 (40)	-3.66 (24)
[2, 3]	1.25		0.19	-1.54	0.544	-3.73
HC2YF	1.15	216	0.086 (11)	-0.807 (97)	0.597 (27)	-4.10 (16)
[5]	1.15	500	0.076 (7)	-0.657 (12)	0.606 (12)	-4.17 (8)
[5]	1.15	300	0.082 (5)	-0.706 (4)	0.610 (2)	-4.20 (10)
[2, 3]	1.15		0.077	-0.673	0.609	-4.20
HC2YF	1.00	216	0.0321 (38)	-0.327 (23)	0.689 (16)	-4.77 (14)
[5]	1.00	500	0.0281 (32)	-0.255 (31)	0.698 (3)	-4.87 (3)
[5]	1.00	300	0.0271 (37)	-0.249 (33)	0.695 (5)	-4.86 (5)
[2, 3]	1.00		0.0262	-0.237	0.703	-4.91
HC2YF	0.90	216	0.0136 (21)	-0.142 (28)	0.738 (7)	-5.23 (14)
[5]	0.90	300	0.0115 (14)	-0.113 (14)	0.753 (7)	-5.32 (3)
[2, 3]	0.90		0.0131	-0.126	0.756	-4.91
HC2YF	0.75	216	0.0037 (2)	-0.051 (10)	0.805 (6)	-5.77 (13)
[5]	0.75	500	0.0028 (2)	-0.030 (2)	0.820 (6)	-5.90 (5)
[5]	0.75	300	0.0027 (4)	-0.030 (4)	0.820 (5)	-5.90 (5)
[2, 3]	0.75		0.0033	-0.038	0.826	-5.96

the standard deviations for the HC2YF properties are larger than for those for the LJ simulations (300 or 500 molecules). In addition to the obvious advantage of shorter execution time, using fewer molecules implies that at low temperatures the number of attempted molecule exchanges is significantly reduced. At a reduced temperature of 0.75, the LJ simulation required 2000 attempted exchanges for both the 300 and 500 molecule cases, whereas for the HC2YF simulation with 216 molecules 500 attempted exchanges was sufficient to reach equilibrium. This difference is probably more related to the size of the ensembles rather to differences in pair potential. The HC2YF results were based on the averaging of blocks of 90 000 configurations. Several blocks were eliminated at the beginning of each run to allow for equilibration and eliminate biasing based on the starting conditions.

In figure 2, the coexistence curve for the two potentials are compared. The results show good agreement at the low and intermediate temperatures. As the critical temperature is approached, the results for the two potentials begin to differ. The difference is not necessarily related only to the difference in the potentials. The simulation method becomes increasingly sensitive to the values of the simulation parameters as the critical temperature was approached. It is not possible to achieve

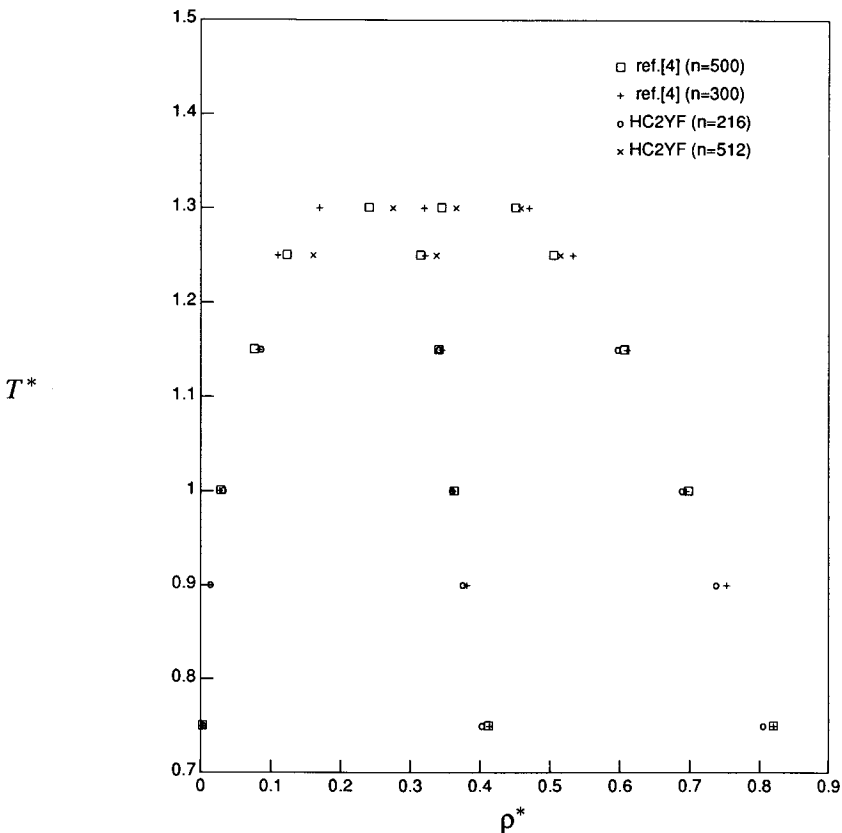


Figure 2. Comparison between the coexistence curve of LJ and HC2YF fluids computed using the GEMC simulation method. The circles and the crosses are the HC2YF, the squares and the plus symbols are the LJ fluid [4]. The symbols in the center of the diagram represent the line of rectilinear diameters.

stable phase separation at temperatures of 1.25 or 1.30 with 216 molecules. The LJ results also show increasing differences between the 300 and 500 molecules cases as the temperature increases. The HC2YF results, for 500 molecules, at $T = 1.30$ were found to be unstable at large numbers of configurations, but the phases remained separated for a sufficient number of configurations to allow the computation of meaningful average properties. The long term instability suggests that the HC2YF may be closer to its critical point than the LJ fluid is at temperature $T^* = 1.30$. At the low and intermediate temperatures the LJ fluid results for the two different size ensembles are in better agreement with each other than they are with the HC2YF properties. However, as the critical temperature is approached the HC2YF properties and the LJ properties corresponding to 500 molecules are in better agreement than the 300 and 500 molecule LJ simulations. This emphasizes the already noted increasing sensitivity in the simulation as the critical temperature is approached. It should also be noted that there is a discernible, though small difference between the HC2YF liquid densities and the corresponding LJ results near the triple point. This is reasonable since the HC2YF parameters were obtained by optimizing agreement between the low density properties (second virial coefficient). It is conceivable that this agreement might be improved upon by adjusting the parameters in the HC2YF. For example, a slight reduction in σ would, from equation (4), lead to slightly higher LJ densities for both liquid and vapour phases since the ratio σ_{LJ}/σ would increase. This leads to better liquid densities but, in general, worse vapour densities. We regard the present agreement as sufficiently good for most practical problems.

The results of this investigation indicate that the HC2YF, with potential parameters adjusted to approximate the LJ potential, exhibits coexistence properties very similar to those of the LJ fluid. This result should encourage the effort to develop an analytic theory of the HC2YF since LJ-like fluid coexistence properties could then be determined analytically. For example, Jedrzejek and Mansoori [10] developed a variational perturbation theory of the HC2YF that is analytic since for the HC2YF the terms required for evaluation in the perturbation theory are simply Laplace transforms of hard sphere correlation functions, for which analytic expressions exist. Other authors have considered the analytic solution of the MSA for the HC2YF [11, 12, 13] as the starting point for analytic theories of either the HCYF or the HC2YF. Konior and Jedrzejek [14] have solved the MSA for the hard core three-Yukawa fluid in order to obtain the generalized mean spherical approximation for the HC2YF. These analytic theories of the HC2YF have been developed to varying degrees of explicitness. The HC2YF could then be used as a computationally convenient reference system for perturbation theories, in much the same way that Cummings and Wright [9] used the HCYF.

We conclude with an interesting observation on the GEMC method. This study of phase equilibria in the HC2YF began with the goal of using the GEMC method to compute the phase equilibria of the HCYF. However, this was not successful since HCYF molecules tend to 'stick' together with intermolecular separations at or very near contact. (This is because the minimum energy of the HCYF is at contact of the hard cores of the molecules.) This phenomenon makes it extremely difficult to decrease the volume of the two systems in the GEMC method since in almost all cases volume reduction leads to at least one pair of molecules overlapping. This results in a hard core overlap and rejection of nearly all volume exchange steps. Therefore, the volume exchange step, necessary for establishing pressure equilibrium between the two systems, could not be carried out effectively. This suggests that

straightforward GEMC method cannot be used with the HCYF, nor for any system in which the molecules have hard cores and minimum of energy at contact (such as charged hard spheres, since the attraction between unlike species has this difficulty). One possible remedy would be to bias the moves in the displacement step away from generating molecule pairs at contact.

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