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Vapour–liquid equilibria for quadrupolar Lennard-Jones fluids

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Abstract. Monte Carlo calculations in the Gibbs ensemble are reported for pure quadrupolar Lennard-Jones fluids. The vapour–liquid equilibrium curves, critical temperatures, and critical densities are calculated for various quadrupolar strengths ($Q^{*2} = Q^2/\epsilon\sigma^5 = 1.0, 1.5, 2.0$ and 2.5). It is shown that as the quadrupolar strength increases both the critical temperature and the critical density increase. Comparison of the results for $Q^{*2} = 2.0$ with data from the available literature shows good agreement.

1. Introduction

Until recently it was an enormous and costly task to obtain a vapour–liquid coexistence curve for a model fluid using computer simulation techniques. The conventional method is to perform a number of simulations on various isotherms. For each state point the pressure is calculated and the chemical potential obtained by thermodynamic integration or by test particle methods [1, 2]. The densities of the coexisting liquid and vapour phases at a given temperature are obtained indirectly by equating the pressure and the chemical potential. Along these lines the vapour–liquid curves of, for example, the Lennard-Jones fluid [3], quadrupolar Lennard-Jones fluid [4], and a two-centred Lennard-Jones fluid [5] have been calculated.

Unfortunately, these indirect methods for calculating phase boundaries require many simulations. Therefore, data on vapour–liquid equilibria of model fluids are rather scarce, despite their importance for testing various liquid theories [6, 7].

The reason why this cumbersome route is chosen is preference to a simulation of a system which contains a liquid in coexistence with a vapour is the relatively small number of particles which can be used in a simulation. For such a small number of particles the interface between the gas and liquid phase would dominate the properties of the system and therefore influence the bulk properties.

A new simulation technique proposed by Panagiotopoulos [8], which samples the Gibbs ensemble, allows the vapour–liquid coexistence curve to be simulated without the presence of an interface. Therefore data on vapour–liquid equilibria can be obtained from a relatively small number of particles and, equally important, from one single simulation. This method has already been used successfully to study the phase behaviour of the pure Lennard-Jones fluid [8–9] and mixtures of Lennard-Jones fluids [9].

This article describes the application of Panagiotopoulos's method to calculate the vapour-liquid phase behaviour of pure quadrupolar Lennard-Jones fluids. The majority of existing computer simulation data for quadrupolar fluids have been performed in connection with the development of perturbation theories applicable to such fluids [4, 10–13]. Gupta and co-workers have recently demonstrated the importance of quadrupolar interactions for the modelling of benzene [14] and naphthalene [15]. In addition the influence of quadrupolar interactions on the properties of carbon dioxide has long been recognised. For a quadrupolar Lennard-Jones fluid the vapour-liquid curve has been determined previously by Shing and Gubbins [4] for $Q^{*2} (= Q^2/\epsilon\sigma^5) = 2.0$ using 'test particle' methods for calculating the chemical potential and therefore provides an additional test of this new elegant technique. Furthermore, we have calculated the coexistence curves for other values of the quadrupolar strength Q^* in order to obtain a more complete picture of the phase behaviour of these fluids.

We continue with a short description of the Gibbs ensemble, followed by some computational details; finally, we present our results for the quadrupolar Lennard-Jones fluids studied.

2. The Gibbs ensemble

In his original articles Panagiotopoulos [8, 9] introduced the Gibbs ensemble using fluctuation theory. Here we derive the acceptance rules using the partition function for this ensemble [16, 17]. Formal proof of the equivalence of the Gibbs ensemble and the canonical ensemble in the thermodynamic limit can be found in reference [18].

Consider a system at a constant volume (V), temperature (T), and number of particles (N), which is divided into two (separate) sub-systems labelled 1 and 2. The volumes of the two sub-systems are V_1 and $V - V_1$, and the numbers of particles in the respective sub-systems are N_1 and $N - N_1$. In the partition function for the Gibbs ensemble one must take into account the number of possible distributions of N particles over the two sub-systems and allow for variations of the volumes in the sub-systems. This gives, for the partition function:

$$Q_{N,V,T} \equiv \frac{1}{\Lambda^{3N} N!} \sum_{n_1=0}^N \binom{N}{n_1} \int_0^V dV_1 V_1^{n_1} (V - V_1)^{N-n_1} \int d\xi_1^{n_1} e^{-\beta U_1(n_1)} \times \int d\xi_2^{N-n_1} e^{-\beta U_2(N-n_1)} \quad (1)$$

where Λ is the thermal de Broglie wavelength, $\beta = 1/k_B T$, ξ_1 and ξ_2 are the scaled coordinates of the particles, and $U(n_i)$ is the intermolecular potential.

The ensemble average of a function $f(\xi^N)$ in this ensemble can be obtained from the partition function (1):

$$\langle f(\xi^N) \rangle = \left[\sum_{n_1=0}^N \binom{N}{n_1} \int_0^V dV_1 V_1^{n_1} (V - V_1)^{N-n_1} \int d\xi_1^{n_1} e^{-\beta U_1(n_1)} \times \int d\xi_2^{N-n_1} e^{-\beta U_2(N-n_1)} f(\xi^N) \right] \times \left[\sum_{n_1=0}^N \binom{N}{n_1} \int_0^V dV_1 V_1^{n_1} (V - V_1)^{N-n_1} \right]^{-1}$$

$$\times \int d\xi_1^{n_1} e^{-\beta U_1(n_1)} \int d\xi_2^{N-n_1} e^{-\beta U_2(N-n_1)} \Big]^{-1}. \quad (2)$$

This equation represents an ensemble average with a probability distribution proportional to a pseudo-Boltzmann weight factor given by

$$\exp(-\beta W(\xi_1^{n_1}, \xi_2^{N-n_1}, n_1, V_1)) \equiv \exp[\ln\{N!/[n_1!(N-n_1)!\} + n_1 \ln V_1 + (N-n_1) \ln(V-V_1) - \beta U_1(n_1) - \beta U_2(N-n_1)]. \quad (3)$$

From this pseudo-Boltzmann factor the acceptance rules can be derived [16, 17]. A trial configuration can be generated by displacing a particle, changing a sub-volume in such a way that the total volume remains constant, or changing the number of particles in a sub-volume while keeping the total number of particles constant. From the pseudo-Boltzmann weight factor (3) we obtain

$$\Delta W = W(\xi_1^{\prime\prime n_1}, \xi_2^{\prime\prime N-n_1}, n_1^{\prime\prime}, V_1^{\prime\prime}) - W(\xi_1^{\prime n_1}, \xi_2^{\prime N-n_1}, n_1^{\prime}, V_1^{\prime}) \quad (4)$$

where " denotes the configuration of the trial configurations and ' denotes the old configuration. The new configuration is accepted with a probability P given by

$$P = \begin{cases} 1 & \text{if } \Delta W \leq 0 \\ \exp(-\beta \Delta W) & \text{if } \Delta W > 0. \end{cases} \quad (5)$$

Fundamental thermodynamics states that, for a pure fluid, as the numbers of particles, temperature and volume are specified, there are no additional degrees of freedom and the pressure and chemical potential have a given (but generally unknown) value. Dividing the system is superfluous unless at the given conditions the system would separate into two phases. In such a case the formation of an (unfavourable) interface can be avoided in the Gibbs ensemble if the two coexisting phases are located in the two (separated) sub-systems. Calculating the densities in the two sub-systems yields the corresponding phase boundaries of the vapour–liquid coexistence curve at a given temperature, in one single simulation.

3. Computational details

We have performed the simulations in cycles, each cycle having three steps: a displacement step, a change in the volume and attempts to change the number of particles. In the displacement step every particle in box 1 is successively given a random displacement. The maximum displacement was chosen in such a way that the acceptance ratio was approximately 50%. The same procedure is repeated for box 2.

The next step is an attempt to change the volume of box 1 by an amount ΔV , which results in the volume of box 2 changing by $-\Delta V$. The maximum volume change is adjusted to give an acceptance ratio of approximately 50%. We calculated the energy change associated with this volume change utilising the scaling properties of the Lennard-Jones potential [19] and the quadrupolar potential.

The final step of the cycle is a number, N_{tr} , of attempts to insert a particle (we have used $N_{tr} = 0.5N$). Before each attempt it is decided at random which box will receive a particle.

The Lennard-Jones potential was truncated at half the box size and the usual long tail corrections were applied. For each simulation we performed at least 2000 equilibration

Table 1. Summary of the results of the Monte Carlo simulations in the Gibbs ensemble for a quadrupolar Lennard-Jones fluid for various quadrupolar strengths, (a) $Q^{*2} = 0$ (pure Lennard-Jones fluid), (b) $Q^{*2} = 1.0$, (c) $Q^{*2} = 1.5$, (d) $Q^{*2} = 2.0$, and (e) $Q^{*2} = 2.5$. N is the total number of particles, T^* is the reduced temperature, N_{cyc} is the number of Monte Carlo cycles, ρ^* is the reduced density, P^* ($= P\sigma^3/\epsilon$) is the reduced pressure, E^* ($= E/\epsilon$) is the reduced energy, and μ^* ($= \mu/\epsilon$) is the reduced residual chemical potential. The number in parentheses is the accuracy of the last decimal(s), so 0.564(24) means 0.564 ± 0.024 .

N	T^*	N_{cyc}	Gas phase					Liquid phase				
			ρ_g^*	P_g^*	$-E_g^*$	$-\mu_g^*$	ρ_l^*	P_l^*	$-E_l^*$	$-\mu_l^*$		
(a)	1.15	300000	0.075(3)	0.062(3)	0.67(5)	3.71(1)	0.607(8)	0.07(2)	4.18(7)	3.69(2)		
	1.15	100000	0.065(5)	0.056(3)	0.56(5)	3.72(2)	0.594(14)	0.04(2)	4.09(9)	3.70(2)		
	1.20	200000	0.11(3)	0.079(7)	0.95(3)	3.66(1)	0.564(24)	0.08(3)	3.87(10)	3.66(2)		
	1.20	100000	0.098(9)	0.076(4)	0.81(9)	3.62(2)	0.564(16)	0.08(2)	3.87(10)	3.63(3)		
	1.30	100000	0.20(5)	0.121(8)	1.9(7)	3.57(2)	0.42(7)	0.118(7)	2.59(45)	3.56(2)		
(b)	1.10	2000	0.008(2)	0.008(2)	0.11(5)	5.45(5)	0.858(8)	0.00(5)	8.7(1)	4.20(60)		
	1.20	5000	0.019(4)	0.021(4)	0.27(8)	5.00(20)	0.802(8)	0.01(4)	7.9(1)	5.10(60)		
	1.30	8000	0.035(5)	0.038(5)	0.46(8)	4.79(20)	0.751(10)	0.04(3)	7.2(1)	4.81(40)		
	1.40	8000	0.060(6)	0.064(5)	0.77(8)	4.60(20)	0.687(12)	0.05(3)	6.5(1)	4.60(20)		
	1.50	10000	0.111(24)	0.11(1)	1.3(3)	4.39(15)	0.614(23)	0.11(4)	5.7(2)	4.41(20)		
(c)	1.50	2000	0.113(5)	0.10(1)	1.1(1)	4.42(10)	0.617(8)	0.09(4)	5.7(1)	4.42(10)		
	1.55	2000	0.159(10)	0.13(1)	1.9(1)	4.31(10)	0.563(12)	0.10(5)	5.1(2)	4.50(10)		
	1.30	1000	0.009(2)	0.011(2)	0.06(8)	6.25(20)	0.910(8)	0.03(9)	11.4(1)	5.96(50)		
	1.40	2000	0.026(8)	0.030(8)	0.6(1)	5.58(20)	0.871(8)	0.06(5)	10.7(1)	5.37(50)		
	1.50	2000	0.037(14)	0.043(15)	0.7(2)	5.61(10)	0.814(25)	0.05(7)	9.7(3)	5.56(40)		
(d)	1.60	6000	0.049(12)	0.061(13)	0.8(2)	5.51(10)	0.764(14)	0.06(5)	9.0(2)	5.42(40)		
	1.70	8000	0.089(18)	0.10(1)	1.4(2)	5.26(10)	0.714(7)	0.13(4)	8.2(1)	4.81(40)		
	1.80	8000	0.116(15)	0.139(8)	1.6(2)	5.16(10)	0.631(9)	0.13(3)	7.0(2)	5.19(20)		
	1.85	3000	0.184(30)	0.164(12)	2.5(4)	5.03(10)	0.563(29)	0.15(4)	6.4(3)	5.06(10)		

(d)	512	1.60	2000	0.010(2)	0.014(3)	0.3(2)	7.53(30)	0.918(05)	0.00(5)	13.7(1)	7.82(60)
	512	1.70	2000	0.018(4)	0.029(8)	0.5(2)	7.14(30)	0.891(07)	0.07(9)	13.1(1)	6.21(60)
	216	1.80	6000	0.031(7)	0.047(9)	0.8(2)	6.83(20)	0.851(18)	0.05(7)	12.3(3)	6.42(50)
	512	1.80	2000	0.034(6)	0.052(8)	1.0(1)	6.69(20)	0.851(12)	0.06(5)	12.3(2)	6.03(50)
	216	1.90	7000	0.043(5)	0.065(8)	0.9(1)	6.88(20)	0.798(15)	0.08(1)	11.3(1)	6.59(30)
	216	2.00	10000	0.074(9)	0.11(1)	1.5(4)	6.33(10)	0.748(18)	0.12(6)	10.5(1)	6.65(30)
	216	2.10	10000	0.104(20)	0.15(2)	2.1(4)	6.16(10)	0.682(19)	0.17(5)	9.4(2)	6.36(20)
	512	2.20	4000	0.209(15)	0.21(1)	3.4(5)	5.88(10)	0.554(10)	0.22(5)	7.8(5)	5.80(10)
(e)	512	2.10	2000	0.030(2)	0.067(9)	1.1(2)	7.82(20)	0.880(13)	0.1(1)	15.1(3)	6.40(90)
	216	2.20	6000	0.039(1)	0.07(1)	1.1(3)	7.95(20)	0.846(11)	0.04(7)	14.3(2)	6.51(90)
	216	2.30	8000	0.056(8)	0.098(1)	1.5(2)	7.70(20)	0.794(14)	0.09(6)	13.3(2)	7.04(60)
	216	2.40	8000	0.085(9)	0.14(3)	2.1(5)	7.45(20)	0.735(33)	0.12(8)	12.2(5)	7.34(50)
	512	2.40	2000	0.076(16)	0.13(2)	1.9(5)	7.57(10)	0.724(30)	0.14(5)	11.9(4)	7.84(50)
	216	2.50	8000	0.16(3)	0.20(1)	3.5(8)	7.06(10)	0.65(5)	0.19(5)	10.7(7)	7.24(20)
	512	2.55	2000	0.211(16)	0.25(2)	4.3(4)	6.78(10)	0.648(30)	0.3(1)	10.5(4)	7.23(20)

cycles for $N = 216$ and 1000 cycles for $N = 512$. The number of production cycles are given in table 1. Most simulations were performed using 216 particles. The N -dependence was studied by performing a few simulations with 512 particles close to the critical point and at lower temperatures, but almost no N -dependence could be observed. The listed standard deviations were obtained by dividing each simulation into 10 sub-runs and calculating the block averages.

In his original article Panagiotopoulos [8] suggested that from the interaction energies, calculated during the exchange step the chemical potential can be obtained using the Widom expression. The Widom expression [20], however, is strictly valid only in the N, V, T ensemble. Smit and Frenkel [17] have derived an expression for the chemical potential applicable to the Gibbs ensemble:

$$\mu_i^r = \mu_i + 3k_B T \ln \Lambda = -k_B T \ln \langle [V_i / (n_i + 1)] e^{-\beta \Delta U_i^\dagger} \rangle \quad (6)$$

where subscript i indicates box 1 or 2 and ΔU_i^\dagger is the test particle energy. Note that this expression becomes identical to the Widom expression when the number of particles is large and the fluctuations in the density can be neglected [17]. We have used this equation for the calculation of the chemical potential.

4. Results and discussion

In table 1, a summary of the results for the simulations performed is presented for various quadrupolar Lennard-Jones fluids. The results for the pure Lennard-Jones fluid ($Q^{*2} = 0$) are in close agreement with the results obtained by Panagiotopoulos [8]. In figure 1 we have plotted the vapour–liquid coexistence curves for various quadrupolar strengths. In figure 1(c) the results of Shing and Gubbins [4] are compared with our results for ($Q^{*2} = 2$). This comparison shows that at low temperatures the results from the Gibbs ensemble are in very good agreement with the results from Shing and Gubbins, which were obtained from calculations of the chemical potentials using test particle methods. At temperatures close to the critical point our results differ from the results by Shing and Gubbins.

We have used these vapour–liquid equilibrium data to estimate the critical temperatures and densities of the fluids. For this purpose we have fitted our results to the law of rectilinear diameters [21]

$$(\rho_l^* + \rho_g^*)/2 = \rho_c^* + A(T^* - T_c^*) \quad (7)$$

where ρ^* ($= \rho \sigma^3$) is the reduced density, T^* ($= k_B T / \epsilon$) is the reduced temperature and ρ_c^* and T_c^* are respectively the reduced critical density and temperature. In [18] it is shown that, due to finite size effects which are specific to the Gibbs ensemble, the coexistence of the vapour–liquid cannot be observed *below* the critical temperature. Therefore, the highest temperature at which the coexistence can be observed in the Gibbs ensemble is not a proper estimate of the critical temperature of the system. In order to estimate the critical temperature we have also fitted our results to the scaling law for the density [21]

$$\rho_l^* - \rho_g^* = B(T^* - T_c^*)^\beta \quad (8)$$

where β is the critical exponent ($\beta = 0.32$). Note that this scaling law is strictly valid only close to the critical temperature and should be corrected at lower temperatures. However, due to the inaccuracy of our data and due to the relatively small number of

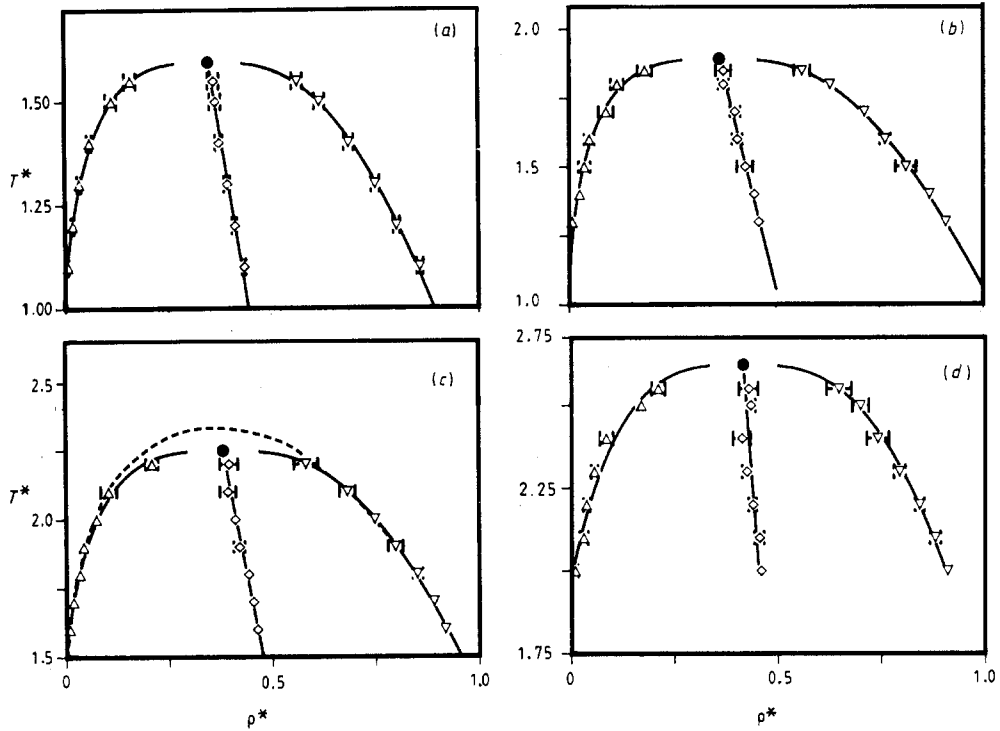


Figure 1. Vapour-liquid equilibrium results for various quadrupolar strengths (a) $Q^{*2} = 1.0$, (b) $Q^{*2} = 1.5$, (c) $Q^{*2} = 2.0$, and (d) $Q^{*2} = 2.5$. T^* ($= k_B T/\epsilon$) is the reduced temperature and ρ^* ($= \rho\sigma^3$) is the reduced density. The points are the results obtained by Monte Carlo simulations in the Gibbs ensemble. The lines are fits of equation (7) through the 'rectilinear' points and of (8) through the vapour-liquid points. Note that in (c) the broken curve gives the results of the Monte Carlo simulations of Shing and Gubbins for $N = 108$ [4]. Δ : density gas phase; ∇ : density liquid phase; \diamond : rectilinear law; \bullet : estimated critical point.

Table 2. Estimates of the critical temperature T_c^* and critical density ρ_c^* for various quadrupolar strengths Q^{*2} . The number in parentheses indicates the accuracy as in table 1.

Q^{*2}	T_c^*	ρ_c^*
0.0	1.31	0.31 [18]
1.0	1.60(2)	0.34(2)
1.5	1.89(2)	0.36(2)
2.0	2.25(2)	0.38(2)
2.5	2.62(3)	0.41(3)

data, including these higher order terms produces no significant improvement of the fit. Furthermore, the results for the critical density and critical temperature appear to be insensitive. The results of these fits are shown in figure 1. The results for the critical temperature and density are listed in table 2.

Shing and Gubbins [4] obtained for $Q^{*2} = 2.0$ as estimates for the critical points $T_c^* = 2.38$, $\rho_c^* = 0.40$ for $N = 32$ and $T_c^* = 2.33$, $\rho_c^* = 0.39$ for $N = 108$. As we have

used more particles ($N = 216$ and close to the critical point $N = 512$) we obtained a lower critical temperature due to the reduced finite size effects.

Summarising, in this article we have demonstrated that Monte Carlo simulations in the Gibbs ensemble can be applied successfully to study the vapour–liquid equilibria of a quadrupolar Lennard-Jones fluid. The results for the pure Lennard-Jones fluid and for the quadrupolar Lennard-Jones fluid (for $Q^{*2} = 2.0$) are in good agreement with data in the available literature.

Note added in proof. After the completion of this work, reference [22] came to our attention, in which the phase behaviour of quadrupolar Lennard-Jones fluids is studied using perturbation theory and Monte Carlo–Gibbs ensemble calculations. The results of Stapleton *et al* [22] are in excellent agreement with the results presented here for $Q^{*2} = 1.0$ and 2.0 . The fact that two completely independent studies show such an excellent agreement is an important demonstration of the reliability of this new simulation technique.

Our results differ in a few aspects from those of Stapleton *et al*. Although we obtained for $Q^{*2} = 2.0$ the same critical temperatures, we have calculated a slightly higher critical density. Furthermore, we observed that the critical density increases systematically as the quadrupolar strength increases. Another aspect is that we have used a different expression for the chemical potential. In reference [17] it is shown that for a pure Lennard-Jones fluid for a small number of particles ($N < 100$) the results for chemical potentials as obtained by these two formulae show systematic differences, for a larger number of particles this difference turned out to be negligible. Comparison of our results for the chemical potential with the results of Stapleton *et al* also show no significant differences, as can be expected because in both studies the number of particles is greater than 100.

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