

## PRELIMINARY COMMUNICATION

### Vapour-liquid equilibria for Stockmayer fluids

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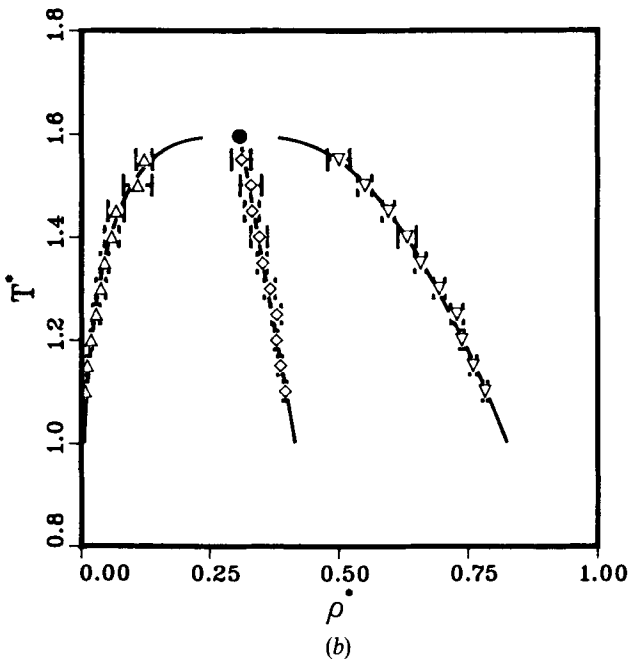
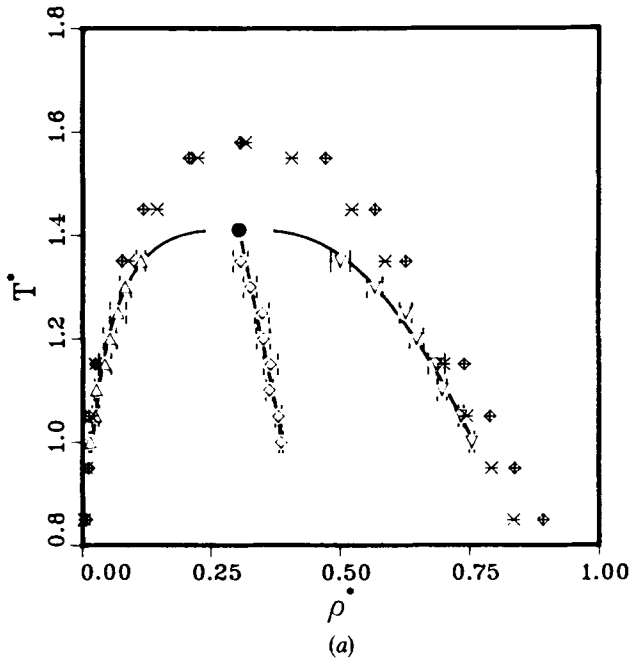
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Results of Monte Carlo simulations in the Gibbs ensemble for the vapour-liquid equilibria of Stockmayer fluids are presented. The vapour-liquid curves, critical temperatures and critical densities are calculated for dipolar strengths of  $\mu^{*2} = \mu^2/\epsilon\sigma^3 = 1.0$  and  $2.0$ . Comparison of these results shows that perturbation theory over-estimates the critical point.

The Stockmayer potential is a convenient model to study the influence of dipolar interaction on the properties of polar fluids. Although the Stockmayer fluid has been frequently studied using computer simulation techniques [1-7], an accurate calculation of the vapour-liquid curves has yet to be published. Because the long-range interactions require substantially more computer time than, for example, the Lennard-Jones fluid, using the conventional techniques [8] the calculation of the phase diagram of a Stockmayer fluid would be an enormous task. However, a new simulation technique proposed by Panagiotopoulos [9-11], which samples the Gibbs ensemble, drastically reduces the amount of computer time to calculate the vapour-liquid curve. Using this elegant technique one can obtain from a single simulation data on the coexisting vapour and liquid phases. In this article we present the results of Gibbs ensemble simulations for the Stockmayer fluid for  $\mu^{*2} = 1.0$  and  $2.0$ . Furthermore, the results of the calculations are compared with the perturbation theory of Stell *et al.* [12, 13].

For most of the simulations we have used 216 particles. Close to the critical temperature and at low temperatures some simulations were performed with 512 particles. The Lennard-Jones potential was truncated at half the box size and the standard long-tail corrections were added. The long-range dipolar interactions were handled with the standard Ewald summation technique using 'tin foil' boundary conditions [14]. The Gibbs ensemble simulations were performed in cycles, each cycle having three steps. In the first step the particles of both boxes were given successively a new position and new orientation in such a way that approximately 50 per cent of the new configurations were accepted. In the second step the volume of the sub-systems was changed (keeping the total volume constant) with an acceptance of 50 per cent. In the final step we have performed  $N_{\text{try}}$  attempts to exchange particles between the two boxes. Before each attempt it was decided at random



Vapour-liquid equilibrium results for the Stockmayer fluid for various dipolar strengths (a)  $\mu^{*2} = 1.0$ , and (b)  $\mu^{*2} = 2.0$ .  $T^*$  ( $=kT/\epsilon$ ) is the reduced temperature and  $\rho^*$  ( $=\rho\sigma^3$ ) is the reduced density. The points are the results obtained by Monte Carlo simulations in the Gibbs ensemble. The lines are fits of scaling laws through the data points. (a)  $\diamond$ , Stell *et al.*  $O(\mu^4)$ ;  $*$ , Stell *et al.*  $O(\text{Padé})$ ;  $\triangle$ , density gas phase;  $\nabla$ , density liquid phase;  $\diamond$ , rectilinear law;  $\bullet$ , estimated critical point. (b)  $\triangle$ , density gas phase;  $\nabla$ , density liquid phase;  $\diamond$ , rectilinear law;  $\bullet$ , estimated critical point.

Results of the Monte Carlo simulations in the Gibbs ensemble for a Stockmayer fluid for various dipolar strengths (a)  $\mu^{*2} = 1.0$  and (b)  $\mu^{*2} = 2.0$ .  $N$  is the total number of particles,  $T^*$  is the reduced temperature,  $N_{\text{cycl}}$  is the number of Monte Carlo cycles,  $\rho^*$  is the reduced density,  $P^*$  ( $= P\sigma^3/\epsilon$ ) is the reduced pressure.  $E^*$  ( $= E/\epsilon$ ) is the reduced energy, and  $c$  is the reduced residual chemical potential (note that we have used a different symbol for the chemical potential in order to avoid confusion with the dipole moment). The number in brackets is the accuracy of the last digit(s), so 0.564 (24) means  $0.564 \pm 0.024$ .

(a)  $\mu^{*2} = 1.0$ .

N	$\mu^{*2} = 1.0$				Gas phase				Liquid phase			
	$T^*$	$N_{\text{cycl}}$	$\rho_g^*$	$P_g^*$	$E_g^*$	$c_g$	$\rho_l^*$	$P_l^*$	$E_l^*$	$c_l$		
512	1.00	3000	0.015 (2)	0.014 (2)	-0.18 (5)	-4.37	0.755 (5)	0.01 (3)	-6.16 (5)	-4.44		
512	1.05	3000	0.052 (7)	0.022 (5)	-0.30 (9)	-4.24	0.734 (5)	0.04 (4)	-5.94 (4)	-4.27		
512	1.10	3000	0.027 (7)	0.025 (3)	-0.32 (7)	-4.32	0.697 (9)	0.01 (2)	-5.60 (7)	-4.28		
216	1.15	3000	0.032 (4)	0.031 (5)	-0.32 (7)	-4.28	0.684 (12)	0.04 (6)	-5.5 (1)	-3.89		
216	1.20	6000	0.055 (8)	0.049 (8)	-0.54 (10)	-4.09	0.646 (9)	0.07 (4)	-5.2 (1)	-4.10		
216	1.25	5000	0.069 (13)	0.065 (14)	-0.66 (17)	-3.99	0.648 (14)	0.09 (4)	-5.0 (1)	-3.85		
216	1.30	3000	0.083 (11)	0.074 (08)	-0.76 (11)	-4.07	0.568 (15)	0.07 (3)	-4.5 (1)	-4.08		
216	1.35	7000	0.122 (20)	0.103 (10)	-1.13 (28)	-4.00	0.514 (15)	0.10 (4)	-4.2 (1)	-4.00		
512	1.35	3000	0.113 (9)	0.093 (5)	-1.07 (10)	-3.99	0.501 (19)	0.09 (1)	-4.0 (1)	-3.97		
216	1.37	4000	0.148 (30)	0.109 (13)	-1.28 (34)	-3.97	0.489 (20)	0.11 (4)	-3.9 (1)	-3.95		

(b)  $\mu^{*2} = 2.0$ .

N	$\mu^{*2} = 2.0$				Gas phase				Liquid phase			
	$T^*$	$N_{\text{cycl}}$	$\rho_g^*$	$P_g^*$	$E_g^*$	$c_g$	$\rho_l^*$	$P_l^*$	$E_l^*$	$c_l$		
512	1.15	3000	0.012 (2)	0.012 (2)	-0.23 (9)	-5.29	0.759 (7)	0.00 (5)	-7.56 (6)	-5.11		
512	1.20	4000	0.019 (2)	0.019 (1)	-0.37 (14)	-5.09	0.737 (4)	0.03 (4)	-7.29 (5)	-5.25		
216	1.20	3000	0.018 (5)	0.018 (5)	-0.31 (14)	-5.13	0.737 (11)	0.01 (7)	-7.31 (11)	-5.58		
216	1.25	3000	0.029 (7)	0.028 (5)	-0.47 (18)	-4.94	0.728 (12)	0.05 (6)	-7.19 (11)	-5.00		
216	1.30	6000	0.038 (10)	0.034 (4)	-0.58 (11)	-4.87	0.694 (14)	0.02 (4)	-6.74 (18)	-5.14		
216	1.35	6000	0.045 (11)	0.046 (8)	-0.69 (18)	-4.89	0.658 (18)	0.06 (3)	-6.47 (11)	-4.86		
216	1.40	3000	0.059 (14)	0.058 (8)	-0.88 (28)	-4.85	0.632 (18)	0.03 (6)	-6.18 (16)	-4.87		
216	1.45	3000	0.067 (12)	0.066 (8)	-0.93 (16)	-4.85	0.596 (12)	0.05 (3)	-5.83 (10)	-4.81		
216	1.50	3000	0.115 (32)	0.096 (15)	-1.46 (43)	-4.66	0.576 (07)	0.12 (3)	-4.42 (10)	-4.81		
512	1.50	3000	0.109 (20)	0.092 (5)	-1.53 (24)	-4.68	0.550 (14)	0.07 (3)	-5.40 (12)	-4.74		
512	1.55	3000	0.122 (20)	0.101 (06)	-1.57 (20)	-4.66	0.500 (22)	0.10 (3)	-4.95 (17)	-4.67		

which box is to accept the particle. The chemical potential was calculated during the exchange step using the particle insertion formula for the Gibbs ensemble [15]. The accuracy of the simulations was estimated by dividing the total simulation into ten sub-runs. Standard deviations were obtained from block averages. A more extensive description of this technique may be found elsewhere [9, 10]. A formal proof of the equivalence of the Gibbs ensemble and the canonical ensemble can be found in [11].

In order to check the consistency of the simulations in the Gibbs ensemble we have performed several conventional  $N$ ,  $V$ ,  $T$  molecular dynamics simulations for 108 particles with  $\mu^{*2} = 1.0$  at  $T = 1.25$  around the liquid coexistence density. In [6, 7] details on these simulations can be found. Comparison of the data from these molecular dynamics simulations with the data from the Gibbs ensemble show that the results of the two methods are consistent.

The results of the Gibbs ensemble calculations are summarized in tables (a) and (b). Comparison of the results for 216 particles with the results for 512 particles shows that the  $N$ -dependence is very weak. Without the Ewald summation the  $N$ -dependence appears to be much stronger [16]. The coexistence curves are shown in figures (a) and (b). The critical temperatures are estimated from fitting the results to the law of rectilinear diameters and to a scaling law for the density [17] with critical exponent  $\beta = 0.32$  [18]. The estimated critical temperature and densities are for  $\mu^{*2} = 1.0$ :  $T_c = 1.41 \pm 0.01$  and  $\rho_c = 0.30 \pm 0.01$  and for  $\mu^{*2} = 2.0$ :  $T_c = 1.60 \pm 0.01$  and  $\rho_c = 0.31 \pm 0.01$ . Our estimates of the critical temperature and density for  $\mu^{*2} = 1.0$  differ slightly from the results by Powles [19], who obtained  $T_c = 1.45$  and  $\rho_c = 0.33$ . However, this estimate of the critical temperature was based on the simulation results of Yao *et al.* [20], in which the long-tail contributions of the dipolar interactions were not taken into account.

It is interesting to compare the results of these simulations with the prediction from thermodynamic perturbation theory of Stell *et al.* [12, 13]. From figure (a) we observe that thermodynamic perturbation theory at  $O(\mu^{*4})$  predicts the vapour density correctly but overestimates the liquid density significantly. Including terms at  $O(\mu^{*6})$  using a Padé approximation gives a significant improvement for the liquid density but the critical temperature is still over-estimated. It is important to note that the thermodynamic perturbation theory results of Stell *et al.* are based on early data for the Lennard-Jones reference fluid. The use of more recent data, which have been incorporated in the equation of state of Nicolas *et al.* [21], may improve these perturbation results.

In this article vapour-liquid curves for the Stockmayer fluid have been calculated using Gibbs ensemble calculations. We demonstrate that the thermodynamic perturbation theory of Stell *et al.* [12, 13] of order  $O(\mu^{*4})$  and  $O(\mu^{*6})$  gives good agreement at low temperature but starts to deviate as the critical point is approached. A more extensive description of the simulations results, which will include the calculation of the dielectric constant in the Gibbs ensemble, and a more extensive comparison with perturbation theories will be published shortly.

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