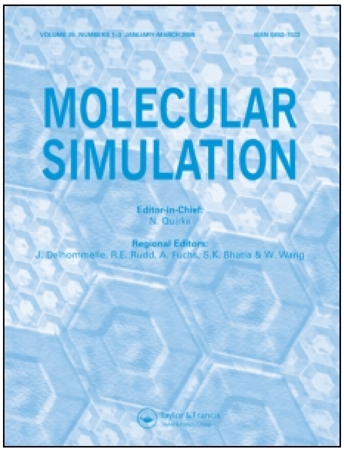

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# Calculation of Vapour-Liquid Equilibria of Lennard-Jones Binary Systems by the Gibbs Ensemble Monte Carlo Simulation

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# CALCULATION OF VAPOUR-LIQUID EQUILIBRIA OF LENNARD-JONES BINARY SYSTEMS BY THE GIBBS ENSEMBLE MONTE CARLO SIMULATION

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The Gibbs ensemble Monte Carlo simulation has been used to calculate vapour-liquid equilibria of a Lennard-Jones (LJ) binary mixture. The mixture studied is the LB-2-1 model which has been used in our previous calculations on PVT relation and density-dependent local composition. The P-x-y relation has been established at two different temperatures and used to determine vapour-liquid coexistence region in the PVTx space.

KEY WORDS: Monte Carlo, vapour-liquid equilibria, Gibbs ensemble, Lennard-Jones mixture.

## INTRODUCTION

Recently we have carried out an extensive molecular simulatin study on the PVT relation for Lennard-Jones (LJ) fluids [1]. Both pure LJ fluid and an LJ fluid mixture have been studied. While vapour-liquid coexistence region below the critical point can be determined by the use of Maxwell equi-area rule for the van der Waals loop in the case of pure fluid isotherms, no rigorous method is available in the case of fluid mixtures. We have to determine coexistence curves from the condition of phase equilibria. In addition to such demand, it is also an urgent task in the study on the dependence of local composition (LC) on fluid density [2].

Indirect methods have been previously used to calculate phase equilibrium relation by molecular simulation. These involve the evaluation of chemical potentials of phases in equilibrium with each other, which is by no means a well-established technique [3]. Recently, Panagiotopoulos proposed a new method of calculating phase equilibria directly [4]. This new method is proved to be useful for the calculation of vapour-liquid equilibria (VLE) of one-component systems [4] and the application of this method to two-component systems seems to be promising [5]. Although some attempts have been made to improve and extend this Gibbs ensemble Monte Carlo (GEMC) method [6–9], the method of calculation for two-component systems has not been firmly established.

In the present study, we have determined, by using GEMC method, the P-x-y relations at two different temperatures of the LB-2-1 fluid mixture, a typical LJ model which has been extensively used by us in PVT relation [1], free energy [10] and local composition [2,10,11] studies. We will discuss in this paper our results on phase equilibria as well as its significance in PVT relation and LC for the LB-2-1 model. Preliminary accounts of the present study have been given elsewhere [12]. It should also be noted here that, in the course of preparing this paper, we were informed the present model being used for the same purpose [13].

## MODEL

The model fluids are those interacting with each other by the Lennard-Jones pair potential

$$\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

where $\sigma$ and $\varepsilon$ are size and energy parameters, respectively. As a fluid mixture, we use the LB-2-1 model [10] where

$$\sigma_{11} = \sigma_{22}, \quad \varepsilon_{11} = 2\varepsilon_{22}$$

We adopt as usual the Lorentz-Berthelot rule for the unlike interaction in this model. Thus,

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2, \quad \varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}$$

## MONTE CARLO CALCULATION

The principle of the GEMC method is already well documented [4–5]. In brief, it is a combination of conventional NVT Monte Carlo calculations with NPT and $\mu$VT ensemble Monte Carlo calculations. In the calculation we assume the values of $T$, $P$ and $\mu$ (chemical potential) to define the systems to be studied. Then we proceed a Monte Carlo run by preparing two system with the same values of these three quantities and making a simultaneous but reverse change in the volume (NPT) and the number of molecule for these two systems under the given transition probabilities. In addition, conventional NVT Monte Carlo procedures have also been carried out for the configurations of each state. Actually, we need not to know the values of $P$ and $\mu$, and this procedure is called 'constant volume method' [4–5]. In the case of two-component systems, Monte Carlo simulation can also be carried out by giving appropriate $P$ value as an external parameter. This is called 'constant pressure method'.

In practice, calculations proceed as in the following: The initial state is a lattice configuration of 512 or 1000 LJ molecules of two kinds (216 or 300 in the case of one-component system), and one MC step consists of 10 ~ 20 {1 intra-phase particle move (NVT) plus 5 ~ 50 inter-phase particle move ($\mu$VT)} plus 1 volume change (NPT). The accept/reject ratios for intra-phase particle move and volume change are adjusted to be about 50 %. Starting from an arbitrarily chosen initial state, two phases gradually move to an equilibrium state and the confirmation of stable state needs some 100,000 MC steps. The MC run is continued further until 50,000 to 400,000 MC steps have been sampled. An example of earlier stage of an MC run is shown in Figure 1.

All the calculations described in this paper have been done with Hitachi S-820 supercomputer and typical CPU time necessary for one MC run is as large as 15 minutes.

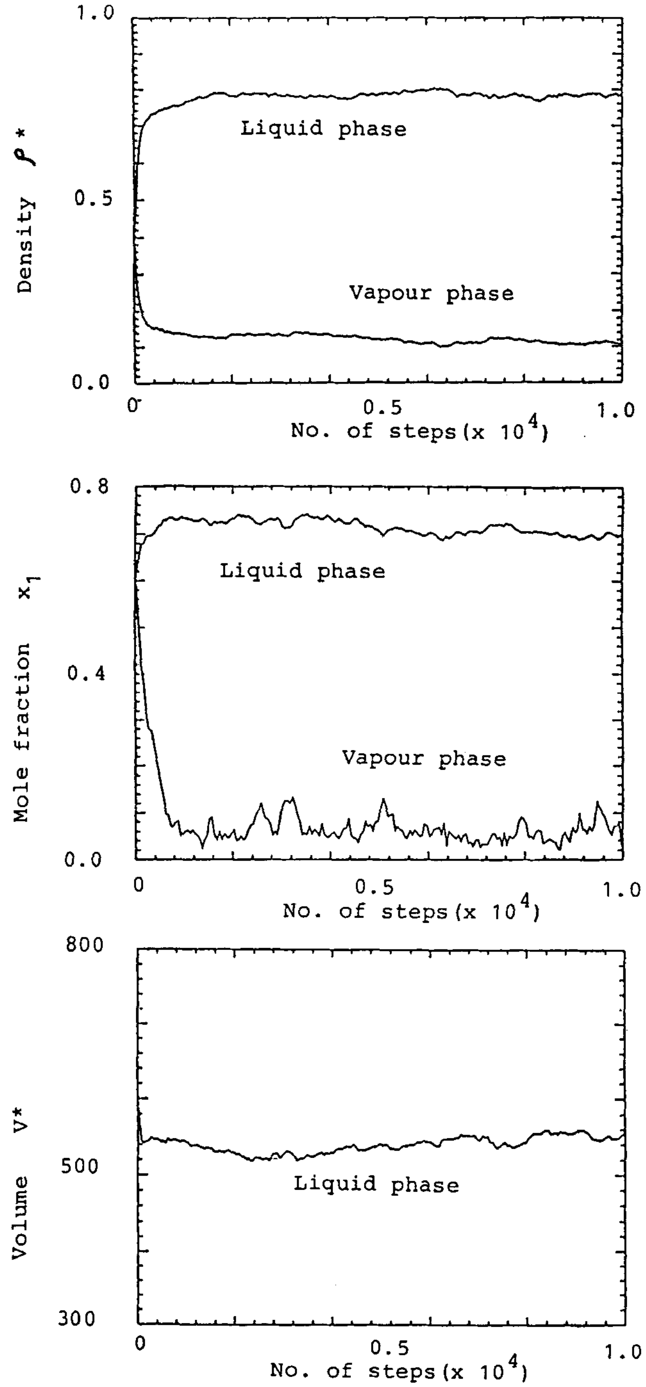

**Figure 1** Formation of vapour and liquid phases which are in equilibrium with each other by GEMC calculation.

## RESULTS AND DISCUSSION

### *One-Component LJ Fluid*

In order to confirm the validity of the present calculation procedure, two vapour-liquid equilibrium data have been determined for LJ fluid. Two temperatures adopted are between the critical temperatures of the two components, more explicitly, $T^* = 0.707$ and 0.900, with reference to the $\varepsilon$ value of higher critical temperature component (denoted as the component 1). These correspond to 120 K and 135 K, respectively, as we assume that the unlike interaction parameters are the same with those for argon, namely, $\varepsilon_{12} = 119.8\,\mathrm{K}$ and $\sigma_{12} = 0.3405\,\mathrm{nm}$.

The MC run reaches an equilibrium within 10,000 steps and further 50,000 steps are used for the analysis of the results. As shown in Table 1, one of the present results can be successfully compared with those obtained by Panagiotopoulos [4]. Hereafter, standard units, MPa, g cm$^{-3}$ and K will be used for P, $\rho$ and $T$, and the reduced unit is used only when comparisons are made with literature values.

### *Two-Component LJ Fluid Mixture*

The GEMC calculations for LJ fluid mixtures have been carried out with the LB-2-1 model. The temperatures adopted are again 120 and 153 K and the number of molecule is either 512 or 1000. The 'constant pressure method' is used almost exclusively with

**Table 1** Vapour-liquid equilibrium data for one-component Lennard-Jones fluid as determined by GEMC calculations

[1] The Present Data

| *Temp. (K)* | *No. of MC step* | *Phase* | *No. of Molecule* | *Pot. Energy (kJ mol$^{-1}$)* | *Pressure (MPa)* | *Density (g cm$^{-3}$)* | *Chem. Pot. (kJ mol$^{-1}$)* |
|---|---|---|---|---|---|---|---|
| 153 | 50,000 | vapour | 14 | −0.22 | 0.81 | 0.029 | −5.44 |
| | | liquid | 202 | −7.47 | 0.9 | 1.261 | −5.35 |
| 120 | 200,000 | vapour | 44 | −0.075 | 0.176 | 0.0074 | −5.83 |
| | | liquid | 256 | −10.17 | ~0 | 1.61 | −5.87 |

[2] Comparison with Literature Values*

| | *This Work* | | *Panagiotopoulos [4]* | |
|---|---|---|---|---|
| | *Vapour Phase* | *Liquid Phase* | *Vapour Phase* | *Liquid Phase* |
| Potential Energy $E^*$ | −0.15<br>(±0.01) | −5.30<br>(±0.03) | −0.145 | −5.36 |
| Pressure $P^*$ | 0.0136<br>(±0.001) | 0.015<br>(±0.006) | 0.0123 | 0.014 |
| Density $\rho^*$ | 0.017<br>(±0.001) | 0.750<br>(±0.004) | 0.0151 | 0.758 |
| Chemical Potential $\mu^*$ | −3.86<br>(±0.06) | −3.80<br>(±0.09) | −3.95 | −3.86 |

*All the values in [2] of this table are in reduced units on the basis of $\varepsilon/k = 119.8\,\mathrm{K}$ and $\sigma = 0.3405\,\mathrm{nm}$ for argon. The numbers in parentheses are the standard deviation for each quantities.

**Table 2** Vapour-liquid equilibrium data for binary Lennard-Jones fluid mixtures LB-2-1 as determined by GEMC calculations with 'pressure constant method', unless stated otherwise

| *Pressure assumed (MPa)* | *No. of MC step* | *Phase* | *No. of Molecule N* | *Mole Fraction $x_1$* | *Pot. Energy ($kJ mol^{-1}$)* | *Pressure (MPa)* | *Density ($g cm^{-3}$)* | *Chem. Pot. ($kJ mol^{-1}$)* | |
|---|---|---|---|---|---|---|---|---|---|
| *Temperature T = 153 K* | | | | | | | | | |
| 5.93 | 200,000 | vapour | 256 | 0.26 | −1.2 | 5.92 | 0.32 | −5.61 | −3.35 |
| | | liquid | 257 | 0.74 | −5.7 | 5.9 | 1.15 | −5.58 | −3.38 |
| 5.33 | 250,000 | vapour | 172 | 0.27 | −1.1 | 5.33 | 0.27 | −5.56 | −3.47 |
| | | liquid | 340 | 0.75 | −5.9 | 5.3 | 1.17 | −5.59 | −3.49 |
| 4.74 | 400,000 | vapour | 187 | 0.26 | −0.83 | 4.74 | 0.211 | −5.57 | −3.62 |
| | | liquid | 325 | 0.79 | −6.1 | 4.7 | 1.18 | −5.59 | −3.61 |
| 4.15 | 150,000 | vapour | 215 | 0.28 | −0.66 | 4.15 | 0.173 | −5.53 | −3.82 |
| | | liquid | 297 | 0.83 | −6.3 | 4.2 | 1.20 | −5.56 | −3.79 |
| 3.56 | 450,000 | vapour | 120 | 0.24 | −0.17 | 3.555 | 0.1205 | −5.60 | −3.92 |
| | | liquid | 393 | 0.84 | −6.4 | 3.5 | 1.2 | −5.61 | −3.90 |
| 2.96 | 150,000 | vapour | 152 | 0.27 | −0.122 | 2.961 | 0.0982 | −5.62 | −4.18 |
| | | liquid | 361 | 0.88 | −6.68 | 3.0 | 1.219 | −5.63 | −4.15 |
| 2.37 | 150,000 | vapour | 204 | 0.36 | −0.12 | 2.370 | 0.0788 | −5.49 | −4.62 |
| | | liquid | 309 | 0.92 | −6.93 | 2.3 | 1.232 | −5.49 | −4.62 |
| 2.07 | 100,000 | vapour | 228 | 0.40 | −0.073 | 2.076 | 0.0675 | −5.46 | −4.84 |
| | | liquid | 285 | 0.94 | −7.03 | 2.1 | 1.238 | −5.47 | −4.84 |
| 1.78 | 450,000 | vapour | 155 | 0.45 | −0.120 | 1.777 | 0.0590 | −5.53 | −5.16 |
| | | liquid | 358 | 0.95 | −7.14 | 1.8 | 1.245 | −5.54 | −5.17 |
| 1.48 | 350,000 | vapour | 216 | 0.57 | −0.13 | 1.482 | 0.0494 | −5.45 | −5.68 |
| | | liquid | 297 | 0.968 | −7.26 | 1.5 | 1.251 | −5.44 | −5.66 |
| 1.19 | 250,000 | vapour | 121 | 0.64 | −0.082 | 1.186 | 0.0388 | −5.52 | −6.21 |
| | | liquid | 392 | 0.978 | −7.33 | 1.3 | 1.255 | −5.53 | −6.19 |
| 1.13 | 200,000 | vapour | 169 | 0.73 | −0.093 | 1.127 | 0.0370 | −5.50 | −6.58 |
| | | liquid | 344 | 0.985 | −7.38 | 1.1 | 1.258 | −5.44 | −6.58 |
| *Temperature T = 119.8 K* | | | | | | | | | |
| 4.15 | 300,000 | vapour | 495 | 0.061 | −1.2 | 4.14 | 0.35 | −6.45 | −2.67 |
| | | liquid | 506 | 0.34 | −4.2 | 4.2 | 1.12 | −6.47 | −2.66 |
| 3.77 | 400,000 | vapour | 743 | 0.068 | −0.91 | 3.77 | 0.26 | −6.17 | −2.75 |
| | | liquid | 257 | 0.58 | −5.8 | 3.7 | 1.27 | −6.08 | −2.73 |
| * | 250,000 | vapour | 209 | 0.060 | −0.723 | 3.4 | 0.21 | −6.17 | −2.81 |
| | | liquid | 303 | 0.64 | −6.14 | 3.4 | 1.29 | −6.18 | −2.81 |
| 2.90 | 100,000 | vapour | 249 | 0.059 | −0.53 | 2.906 | 0.158 | −6.18 | −2.93 |
| | | liquid | 263 | 0.73 | −6.7 | 2.9 | 1.33 | −6.22 | −2.95 |
| 1.78 | 100,000 | vapour | 190 | 0.09 | −0.31 | 1.778 | 0.0849 | −5.96 | −3.36 |
| | | liquid | 323 | 0.85 | −7.6 | 1.9 | 1.373 | −6.12 | −3.40 |
| 1.19 | 100,000 | vapour | 216 | 0.12 | −0.200 | 1.183 | 0.0531 | −5.97 | −3.75 |
| | | liquid | 297 | 0.91 | −7.9 | 1.2 | 1.39 | −5.98 | −3.75 |
| 0.59 | 50,000 | vapour | 257 | 0.198 | −0.1068 | 0.5926 | 0.02527 | −5.97 | −4.49 |
| | | liquid | 255 | 0.956 | −8.30 | 0.6 | 1.406 | −6.11 | −4.44 |

*by 'volume constant method' at 120 K.

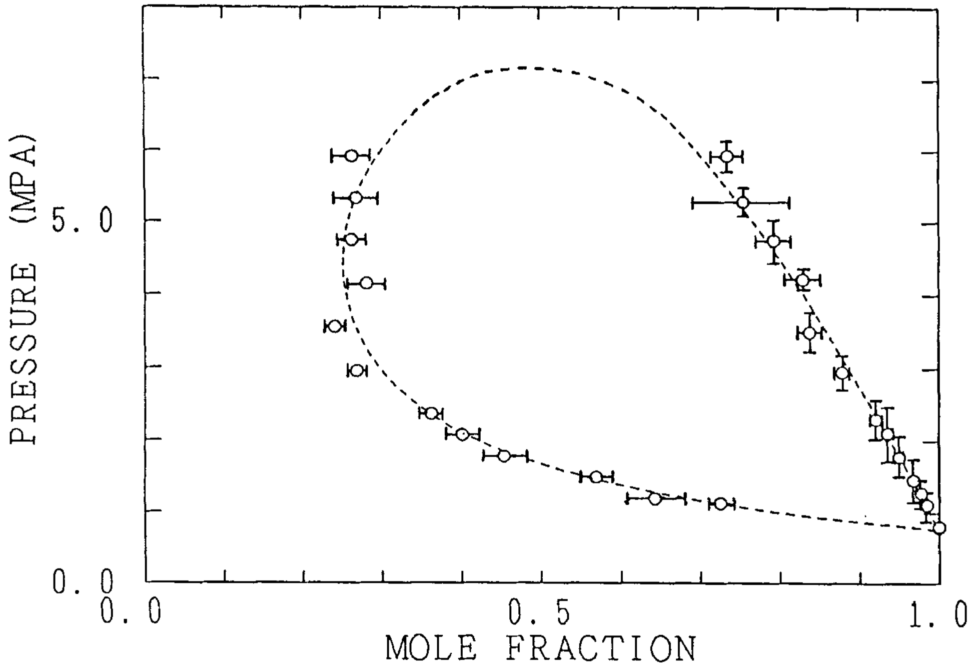

**Figure 2** P-x-y relation for LB-2-1 fluid mixture at 153 K.

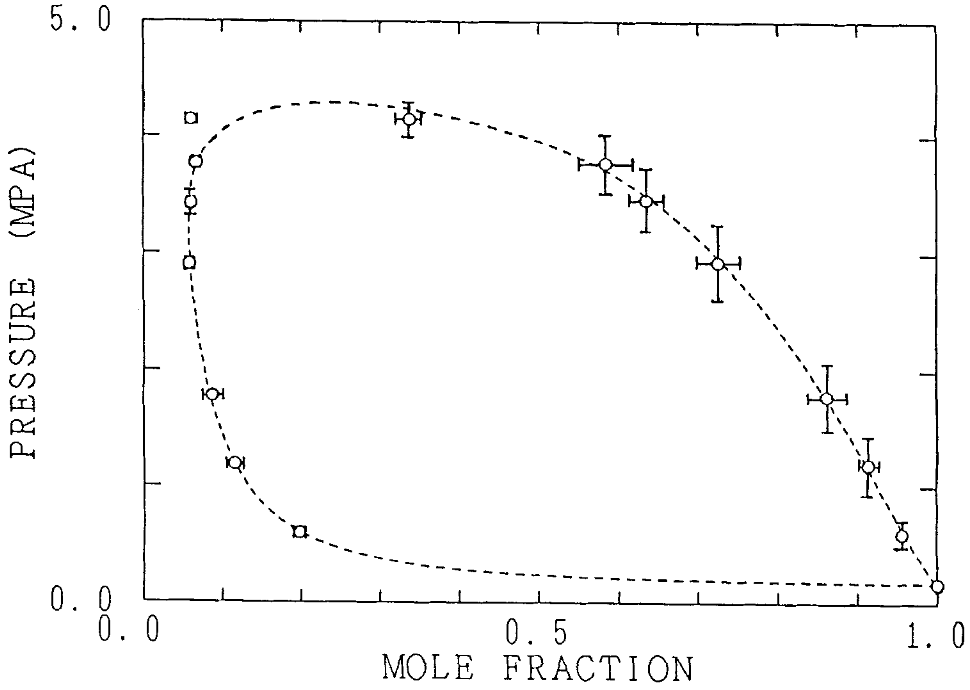

**Figure 3** P-x-y relation for LB-2-1 fluid mixture at 120 K.

**Table 3** Vapour-liquid phase equilbrium points for equimolar mixture of LB-2-1 as determined by NVT or NPT ensemble Monte Carlo calculation*

| *Temperature (K)* | *Ensemble* | *Phase* | *Pressure (MPa)* | | *Pot. Energy ($kJ\,mol^{-1}$)* | *Density ($g\,cm^{-3}$)* | *Chem. Pot.* | *($kJ\,mol^{-1}$)* |
|---|---|---|---|---|---|---|---|---|
| | | | *Assumed* | *Calcd.* | | | $\mu_1$ | $\mu_2$ |
| 153 | NPT | vapour | 1.67 | 1.663 | −0.316 | 0.0603 | −5.54 | −5.33 |
| 153 | NVT | liquid | – | 6 | −4.03 | 0.960 | −6.00 | −3.21 |
| 120 | NPT | vapour | 0.258 | 0.2581 | −0.0647 | 0.01075 | −5.82 | −5.78 |
| 120 | NPT | liquid | 3.96 | 3.9 | −5.23 | 1.217 | −6.72 | −3.13 |

*The total number of molecule is 108 and 1,000,000 configurations are generated for analysis.

one exception. In Table 2 are given numerical results of potential energy, pressure, density, the total number of molecules, and the mole fraction and chemical potential of each component for each MC run with the assumed pressure value.

Figures 2 and 3 show the P-x-y relations for LB-2-1 model at two different temperatures. The curves make loops as the two temperatures are between critical temperatures of the two components. It is clear that, while the vapour side (less dense phase) is established fairly well, the liquid side (denser phase) is somewhat difficult to determine accurately.

### *PVT Relation of LB-2-1 Model*

The results of P-x-y given above can be used to determine vapour-liquid equilibrium curve for LB-2-1 model mixture. For this purpose, further conventional (NPT and NVT ensemble) MC calculations have been made with equimolar mixture of LB-2-1 model. Table 3 shows PVT values thus obtained for two set of coexisting vapour and liquid phases. These values, together with the critical data [1], can give a rough sketch for a complete PVT diagram for the equimolar mixture of the LB-2-1 model. Original PVT data for the LB-2-1 model is found in our previous paper [1].

The PVT data given in Table 3 are also useful for establishing phase equilibrium limits in the local composition vs. fluid density curves given previously (see Figure 4 of ref. [2]), though exact determination of coexistence region is impossible because of the difference in the temperature adopted.

## CONCLUDING REMARK

In this work we attempted to establish a calculation scheme of GEMC for vapour-liquid equilibria in binary LJ mixtures. Although further efforts should be made to improve the accuracy of dense phase determination, the GEMC method is proved to be quite useful in the equation of state calculation for model fluid mixtures.

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