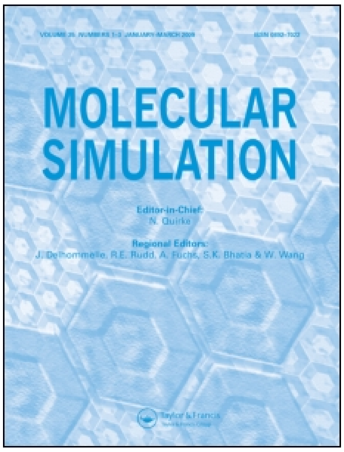

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Determination of Thermodynamic Excess Properties of Mixtures from Computer Simulation

Anping Liu[a]; Rakesh Govind[a]
[a] Department of Chemical Engineering, University of Cincinnati, Ohio, USA

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DETERMINATION OF THERMODYNAMIC EXCESS PROPERTIES OF MIXTURES FROM COMPUTER SIMULATION

ANPING LIU and RAKESH GOVIND

Department of Chemical Engineering University of Cincinnati, Ohio 45221, USA

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This paper reports excess Gibbs free energy, excess enthalpy, and excess volume from isothermal-isobaric molecular dynamics simulations of binary Lennard-Jones mixtures at $\kappa T/\varepsilon = 2, p\sigma^3/\varepsilon = 2.5$, for three parameter ratios, $\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$, $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1$, $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1.5$, and at different concentrations, $x_A = 0.02, 0.05, 0.1, 0.25, 0.5, 0.75, 0.9, 0.95$, and 0.98. The density range is between $0.25 < \rho^* < 0.75$. The excess Gibbs free energies were determined by fitting the differences in residual chemical potentials, which were evaluated by using the '$f_A - f_B$ sampling' method. The results showed very good agreement with literature data.

KEY WORDS: Simulation, excess properties, LJ mixtures

1 INTRODUCTION

Among thermodynamic excess properties, excess Gibbs free energy or chemical potential are most difficult and time consuming when obtained from computer simulations, whereas excess enthalpy and excess volume can be easily calculated directly. There are two methods for calculation of chemical potential. One is the test particle method, in which a test or "ghost" particle is generated at random to measure the interaction [1]. The chemical potential is related to the interaction of the test particle with all of the surrounding particles in the fluid. This method can be easily incorporated in conventional MD or MC programs and is accurate at or up to medium density, but fails at high density due to difficulty in the insertion of the test particle [2]. The other method for calculation of chemical potential is the thermodynamic integration method [3,4]. Chemical potential can be obtained by integration of internal energy or pressure along a suitable thermodynamic path. Because internal energy and pressure are easily measurable in simulations and statistically well-behaved, this method works well at low and high densities. The disadvantages of this method is that it is computationally intensive, since several simulations must be carried out to obtain the integrands for a single state condition.

To improve the efficiency of computer simulation for calculation of excess Gibbs free energy, many efforts have been made to develop modified approaches [5–12]. Recently, we have developed a new sampling method in MD simulation to calculate the difference in chemical potentials of a mixture [13]. The method is based on distribution functions of fictively inflating and shrinking real particles in the system, a combination of the '*f*-*g*' method [5, 6] and the difference method [11, 12]. Since the virtual transformation is only the difference between the two different particles, there is no serious problem of insertion as in the test particle method. The overlap of the two distribution functions is large, and can extend into high density. Thus, this method can be applied to evaluation of the difference in chemical potentials at high density.

If we assume an equation that is appropriate for the excess Gibbs free energy and have the differences in chemical potentials at different concentrations, we can determine the coefficients of the equation by fitting these data. The advantages of this procedure are that the method is time-saving and does not require the knowledge of the chemical potential of pure component. In this paper we report some results of thermodynamic properties from isothermal-isobaric molecular dynamics simulations of binary mixtures of Lennard-Jones fluids at different size-parameter and energy-parameter ratios using such a procedure.

2 THE FORMULAE

We can directly evaluate thermodynamic excess properties v^E and h^E from the definitions

$$v^E = v_{\text{mix}} - x_A v_A^o - x_B v_B^o \tag{1}$$

$$h^E = P v^E + u_{\text{mix}}^c - x_A u_A^{\circ} - x_B u_B^{\circ} \tag{2}$$

where $^{\circ}$ indicates the pure component and the superscript c the configurational internal energy. The mixture and each pure component are at the same temperature and pressure. We chose the Redlich-Kister equation to represent excess Gibbs free energy for the LJ mixtures

$$\frac{g^E}{\text{RT}} = x_A x_B [A + B(x_A - x_B) + C(x_A - x_B)^2] \tag{3}$$

From (3) we obtain [14]

$$\ln\left(\frac{\gamma_B}{\gamma_A}\right) = A(x_A - x_B) + B(1 - 6x_A x_B) + C(x_B - x_A)(8x_A x_B - 1) \tag{4}$$

The coefficients A, B, and C are determined by fitting the data of the difference in residual chemical potentials from simulations. Since the method for evaluation of the residual chemical potential difference has been described in detail elsewhere [16], only a brief summary of the approach is given here.

A mixture consists of particles N_A and N_B at constant T and V or at constant T and P [12]. The difference in residual chemical potentials between the particle A and B can be expressed as

$$\exp(-\beta \Delta \mu_{AB,r}) = \langle \exp(-\beta \Delta U_{t,AB}) \rangle_{N_A - 1, N_B} \tag{5}$$

where the subscript r means that the reference is the difference of the ideal gas values of components A and B at the same temperature, density, and composition as the real fluid. Since we used the same atomic mass for all atoms, regardless of species, the ideal gas values of the two components are the same. $\beta = 1/kT$, $\Delta U_{t,AB}$ is the difference of the configurational internal energy of a test particle A before and after the switching, $\langle \ldots \rangle_{N_A-1,N_B}$ is an ensemble average over the system of the $N-1$ unchanged real particles. Analogously we have

$$\exp(-\beta\Delta\mu_{BA,r}) = \langle \exp(-\beta\Delta U_{t,BA})\rangle_{N_A,N_B-1} \tag{6}$$

for fictively switching a particle B to a particle A. These two equations can be related through their distribution functions of the energy difference as follows

$$f_B(-\Delta U_{t,BA}) = \exp(\beta\Delta\mu_{AB,r}) f_A(\Delta U_{t,AB}) \exp(-\beta\Delta U_{t,AB}) \tag{7}$$

where f_A and f_B are the distribution functions of the energy difference from the particle A to B and B to A, respectively. In (7) $\exp(\beta\Delta\mu_{AB,r})$ is a constant, independent of ΔU_t. The residual chemical potential difference can be calculated from (7) if both f_A and f_B re known for the same value of ΔU_t. If particle B is smaller than particle A, the switching of B to A explores more of the repulsive configurations, whereas A to B explores more of the attractive configurations. In this case the energy contribution function f_B corresponds to the g-function and the f_A the f-function in the 'f-g sampling' method [5, 6]. We call this method the '$f_A - f_B$ sampling', in which all test particles are real particles.

The right side of (4) is related to $\beta\Delta\mu_{BA,r} = -\beta\Delta\mu_{AB,r}$ as follows:

$$A(x_A - x_B) + B(1 - 6x_Ax_B) + C(x_B - x_A)(8x_Ax_B - 1) + \beta(\mu_B^o - \mu_A^o)^{\text{res}} = \beta\Delta\mu_{BA,r} \tag{8}$$

In (8) there are four unknown parameters, A, B, C, and the difference of the pure residual chemical potentials $\beta(\mu_B{}^o - \mu_A{}^o)^{\text{res}}$. If we have sufficient data of $\beta\Delta\mu_{BA,r}$ the four unknown parameters can be determined through mean square regression.

3 THE SIMULATION

Molecular dynamics simulations were performed for LJ mixtures in the NPT-ensemble. For the solution of the translational equations of motion a fifth order Gear predictor-corrector algorithm was used. Periodic boundary conditions and a neighborhood list were applied, which was updated at every 10 time steps. In the program the temperature was kept constant by momentum scaling. The pressure was controlled by using the Andersen's method [15], with the value of the volume inertial parameter $M = 10^{-4}$. A number of 256 particles were used with a cut-off radius $r_{cr} = 2.5\sigma_{AA}$ for the real particles. The starting configuration was the standard fcc lattice sites if there was no previous configuration available. After the start the system was allowed to equilibrate for a period of 2000 time steps. Production runs were 8,000–15,000 time steps. The time step was $\Delta t^* = 0.005$. All units were reduced with respect to the parameters of component A. We have added subroutines to determine the difference of the residual chemical potentials. At every ten time steps each particle was fictively switched to the other type of particle by turns. The change of the interaction energy before and after the switching was obtained. The quantity $\exp(-\beta\Delta U_t)$ was evaluated and averaged cumulatively for (7). We stored a histogram of the number of realizations of ΔU_t in bins of width 0.2 in the range $-20 < \Delta U_t < 20$. For ΔU_t out of the range we simply kept a record of the number of events for use in normalization of the distribution functions. The simulations reported here were performed on a Cray Y-MP at $k\ T/\varepsilon = 2, P\sigma^3/\varepsilon = 2.5$. For the cross interaction the Lorentz-Berthelot combination rule was applied.

Table 1 provides the simulation results for LJ mixtures at $\kappa\,T/\varepsilon = 2, P\sigma^3/\varepsilon = 2.5$, $\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$, $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1$, $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1.5$, with $\varepsilon/k = \varepsilon_{AA}/\mathrm{k} = 119.8$ K, and $\sigma = \sigma_{AA} = 3.405$ Å. The pure and equimolar densities and internal energies of these three series mixtures were compared with other simulation values [16] and values from perturbation theory [17, 18]. The absolute deviations were less than 0.3 percent in density and 0.4 percent in the energy. The pure fluid simulations were performed by using the mixture program at $x_A = 0$ or $x_A = 1$. Table 2 contains the parameters of (8) determined by fitting the differences in

Table 1 NPT-MD Simulation results for density, internal energy, and difference in chemical potentials of LJ mixtures at $k\ T/\varepsilon = 2$, $P\sigma^3/\varepsilon = 2.5$, with $\varepsilon/k = \varepsilon_{AA}/k = 119.8$ K, $\sigma = \sigma_{AA} = 3.405$ Å.

x_A	ρ^*	U^*	$\beta\Delta\mu_{BA,r}$	*steps*
		$\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$		
0.00	0.2617 ± 0.0003	−4.959 ± 0.012		14900
0.02	0.2648 ± 0.0004	−4.949 ± 0.014	2.90	14000
0.05	0.2699 ± 0.0002	−4.926 ± 0.004	2.80	13800
0.10	0.2787 ± 0.0002	−4.902 ± 0.007	2.81	10600
0.25	0.3086 ± 0.0002	−4.830 ± 0.004	2.80	11500
0.50	0.3760 ± 0.0003	−4.672 ± 0.008	2.66	10800
0.75	0.4810 ± 0.0004	−4.458 ± 0.005	2.30	10000
0.90	0.5758 ± 0.0007	−4.278 ± 0.007	2.08	8500
0.95	0.6170 ± 0.0008	−4.196 ± 0.005	1.74	14300
0.98	0.6458 ± 0.0008	−4.148 ± 0.007	1.73	10400
1.00	0.6634 ± 0.0008	−4.105 ± 0.007		14300
		$\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1$		
0.0	0.7483 ± 0.0008	−7.457 ± 0.008		9300
0.02	0.7470 ± 0.0006	−7.383 ± 0.007	−1.34	11600
0.05	0.7439 ± 0.0016	−7.257 ± 0.022	−1.33	11700
0.10	0.7390 ± 0.0010	−7.050 ± 0.013	−1.28	11700
0.25	0.7274 ± 0.0018	−6.506 ± 0.023	−1.25	10600
0.50	0.7067 ± 0.0013	−5.638 ± 0.011	−1.17	11000
0.75	0.6852 ± 0.0023	−4.834 ± 0.021	−1.04	11200
0.90	0.6732 ± 0.0007	−4.399 ± 0.007	−1.02	11500
0.95	0.6672 ± 0.0010	−4.242 ± 0.007	−0.94	11500
0.98	0.6664 ± 0.0008	−4.170 ± 0.004	−0.94	15800
1.00	0.6634 ± 0.0008	−4.105 ± 0.007		14300
		$\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1.5$		
0.00	0.2676 ± 0.0004	−8.482 ± 0.016		14700
0.02	0.2711 ± 0.0003	−8.422 ± 0.016	1.70	12600
0.05	0.2762 ± 0.0005	−8.302 ± 0.024	1.65	11200
0.10	0.2851 ± 0.0002	−8.114 ± 0.008	1.77	11000
0.25	0.3167 ± 0.0003	−7.618 ± 0.009	1.60	10200
0.50	0.3861 ± 0.0002	−6.654 ± 0.009	1.32	8700
0.75	0.4917 ± 0.0004	−5.539 ± 0.007	0.87	8500
0.90	0.5841 ± 0.0006	−4.748 ± 0.005	0.49	8300
0.95	0.6218 ± 0.0006	−4.441 ± 0.007	0.16	8900
0.98	0.6453 ± 0.0006	−4.218 ± 0.005	0.05	8700
1.00	0.6634 ± 0.0008	−4.105 ± 0.007		14300

Table 2 Parameters of (3) and difference of pure residual chemical potentials determined by curve smoothing for the LJ mixtures in Table 1.

	$\varepsilon_{BB}/\varepsilon_{AA} = 1$ $\sigma_{BB}/\sigma_{AA} = 1.5$	$\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ $\sigma_{BB}/\sigma_{AA} = 1$	$\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ $\sigma_{BB}/\sigma_{AA} = 1.5$
A	−0.496543	0.193984	−0.776469
B	−0.268873	0.012513	−0.335487
C	−0.114885	0.013746	−0.090761
$\beta(\mu_B{}^o - \mu_A{}^o)^{res}$	2.523	−1.149	1.192

potentials. A, B, and C are the coefficients of the Redlich-Kister eqution (3). Determination of $\beta(\mu_B{}^o - \mu_A{}^o)^{res}$ enables the simulation data automatically to satisfy the area test of phase-equilibrium data. A plot of (8) and $\beta(\mu_B{}^o - \mu_A{}^o)^{res}$ versus x_A shows that the areas under the curve and above the line are equal to that below the line; thus, the requirement of thermodynamic consistency is met. The value of $\beta(\mu_B{}^o - \mu_A{}^o)^{res}$ can be regarded as an additional examination of the procedure. Figure 1 shows the plots of (8) versus x_A for the mixtures in Table 1. In Table 3 a comparison of some quantities from fitting the curves with literature data are provided. It can be seen that all quantities are in agreement with the literature data, within the simulation uncertainties. We used the method [19] to estimate the simulation uncertainties. In evaluation of the difference in residual chemical potentials we used the mid-part of the histogram for the average. At both sides of the histogram the fluctuation is larger. If we considered the values at both sides in the average, the difference between the two averages were in general less than 0.1.

Figure 2 shows a typical histogram of the energy distribution from the '$f_A - f_B$ sampling'. We can see that the region of the histogram is broad and covers negative as well as positive regions. With increasing density, the overlap of the energy distribution functions f_A and f_B becomes less; therefore, the histogram becomes narrower. Since the switching in the '$f_A - f_B$ sampling' method is just the difference of the two different particles, the overlap of the two distribution functions may extend into very high

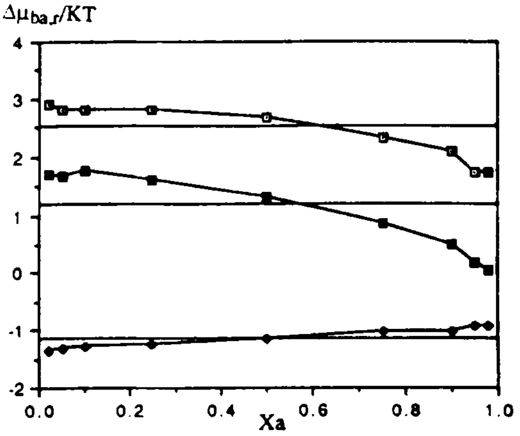

Figure 1 Plots of (8) versus x_A for mixtures in Table 1. —☐ $\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$—◆ $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1$ —■ $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1.5$.

Table 3 Comparison of some quantities from this work with literature data at $k\,T/\varepsilon = 2$, $P\sigma^3/\varepsilon = 2.5$, with $\varepsilon/k = \varepsilon_{AA}/k = 119.8$ K, $\sigma = \sigma_{AA} = 3.405$ Å.

	$\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ *and* $\sigma_{BB}/\sigma_{AA} = 1$ *(this work)*			
$(\mu_B{}^o - \mu_A{}^o)^{res}/\varepsilon_A$	−2.298	−2.279[18]	−2.265[18][a]	−2.287[18][b]
γ_A^∞	1.216	1.257 – 1.20[18]	1.228[18][a]	
γ_B^∞	1.246	1.229 – 1.21[18]	1.218[18][a]	
$g_{0.5}^E$(J/mol)	97	99[16]		
$h_{0.5}^E$(J/mol)	126	112[16]		
$v_{0.5}^E$(cm^3/mol)	−0.16	−0.21[16]		
	$\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$			
$g_{0.5}^E$(J/mol)	−247	−235[16]		
$h_{0.5}^E$(J/mol)	−151	−156[16]		
$v_{0.5}^E$(cm^3/mol)	−0.11	−0.16[16]		
	$\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1.5$			
$g_{0.5}^E$(J/mol)	−387	−392[16]		
$h_{0.5}^E$(J/mol)	−439	−428[16]		
$v_{0.5}^E$(cm^3/mol)	−0.76	−0.75[16]		

[a] Fischer-Lago-Bohn perturbation theory, quoted from [18]. [b] Nicolas *et al.* equation of state, quoted from [18].

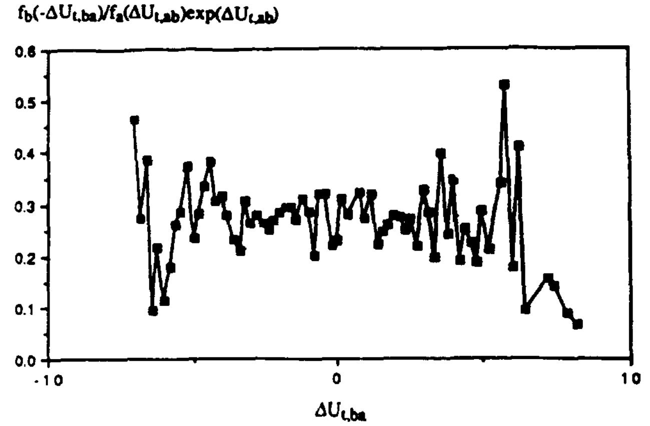

Figure 2 The histogram of the energy distribution from the 'f_A – f_B sampling' for the mixture $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1.5$ at $KT/\varepsilon = 2$, $P\sigma^3/\varepsilon = 2.5$, and $x_A = 0.5$, with $\varepsilon/K = \varepsilon_{AA}/K = 119.8$ K, $\sigma = \sigma_{AA} = 3.045$ Å.

densities. Figure 3–5 represent the composition dependence of the excess properties g^E, h^E, and v^E of the mixtures in Table 1. For mixtures with equal atom size ($\sigma_{AA} = \sigma_{BB}$), g^E and h^E are positive and relatively symmetric. For mixtures with equal atom energy ($\varepsilon_{AA}/k = \varepsilon_{BB}/k$), g^E and h^E are negative and unsymmetric, skewed toward mixtures rich in the smaller component. g^E and h^E becomes more negative with increasing energy-ratio at size-ratio larger than 1. The unsymmetry of such mixtures is mainly due to the effect of size difference. In all mixtures studied here, v^E is negative as energy-ratio increases at size-ratio larger than 1. All states studied here are supercritical. The density range is between $0.26 < \rho^* < 0.75$, in which other methods for calcualtion of Gibbs free

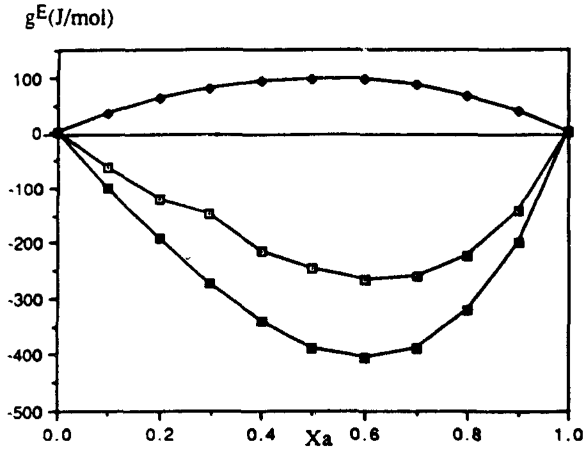

Figure 3 excess Gibbs free energy versus x_A for mixtures in Table 1. □ $\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$ ◆ $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1$ ■ $\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$.

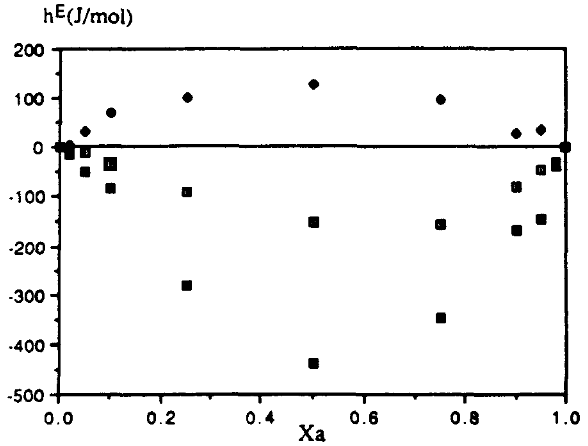

Figure 4 excess enthalpy versus x_A for mixtures in Table 1. □ $\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$ ◆ $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1$ ■ $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1.5$.

energy can work well. The advantage of the new method at high density is shown in [13]. We are going to apply the new method to nonspherical mixtures at high density and investigate the capability of the method more thoroughly.

4 CONCLUSIONS

We have proposed a new procedure for evaluation of excess Gibbs free energy by fitting data of the difference in residual chemical potentials, which were determined by using the '$f_A - f_B$ sampling' method. The results are in excellent agreement with data from

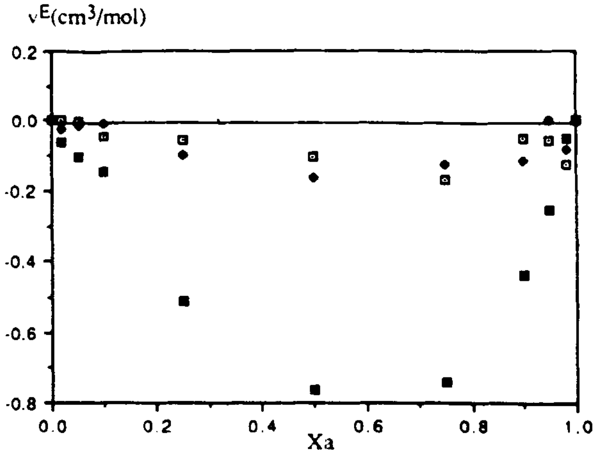

Figure 5 excess volume versus x_A for mixtures in Table 1. □$\varepsilon_{BB}/\varepsilon_{AA} = 1$ and $\sigma_{BB}/\sigma_{AA} = 1.5$ ◆$\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1$ ■ $\varepsilon_{BB}/\varepsilon_{AA} = 1.5$ and $\sigma_{BB}/\sigma_{AA} = 1.5$

theoretical calculations and the thermodynamic integration method that is regarded as the most reliable computer simulation method for calculation of excess Gibbs free energy. The proposed procedure has several advantages. It is simple and can be easily incorporated in conventional MD or MC programs. Because the switching of particles is at every 10 time steps in our simulations, the extra time for evaluation of the difference in residual chemical potentials is less than 10% of the total time of production runs. In this procedure all excess properties such as g^E, h^E, and v^E can be determined over the entire concentration region with a few runs. Another advantage is that it does not require the knowledge of the chemical potentials of pure components to obtain excess Gibbs free energy. Comparison with literature data shows that this procedure is relatively accurate and reliable. We are now in the process of applying this method for various larger size- and energy-parameter ratios at high densities for model mixtures and real mixtures.

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