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Monte Carlo Simulations of Binary Lennard–Jones Mixtures: A Test of the van der Waals One-Fluid Model[1]

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Monte Carlo simulations in the canonical ensemble have been performed in the liquid and supercritical regions of a binary Lennard–Jones mixture with differences in size parameters of 6.4% and energy parameters of 37%. The results are compared with a recent fundamental equation of state employing the van der Waals one-fluid model and new simulation data at the corresponding state conditions of the pure Lennard–Jones fluid. The van der Waals one-fluid model describes the mixture properties well at high densities, while at low densities the predicted internal energies and isochoric heat capacities are too low.

KEY WORDS: heat capacity; internal energy; Lennard–Jones mixture; Monte Carlo simulation; van der Waals one-fluid model.

1. INTRODUCTION

Hypothetical mixtures of particles interacting by pairwise additive Lennard–Jones potentials can serve as a prototype for models of real fluid mixtures. When the parameters of the Lennard–Jones potential for the like and unlike interactions are varied, a wide variety of phase behavior and mixing effects can be observed. Binary Lennard–Jones mixtures have been studied for over 30 years by computer simulation, liquid state theory, and equation of state (EOS) modeling, with the main goal to develop mixing rules which can be employed in mixture EOS or corresponding-states models. When

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testing mixing rules for Lennard–Jones mixtures, EOS predictions have to be compared with macroscopic thermodynamic properties of the model mixture which are obtained in Monte Carlo or molecular dynamics computer simulations. Although many data sets of single-phase properties for binary Lennard–Jones systems are available in the literature, most of the older computer simulations were carried out with small particle numbers and simulation runs were often very short. Thus, the data obtained in early simulations were associated with large uncertainties and comparisons with EOS predictions sometimes did not yield a clear evaluation of the employed mixing rules. With the appearance of the Gibbs ensemble technique in the late 1980s, the attention concentrated mainly on phase equilibrium studies. Only a few accurate data sets have been published for single-phase properties in recent years.

In this study computer simulation data for a binary Lennard–Jones system with small differences in the size parameters are reported. *NVT* Monte Carlo simulations have been performed in the liquid and supercritical regions of the mixture, providing internal energies, pressures, and isochoric heat capacities at each state-point. The results are compared with the fundamental EOS published by Mecke et al. [1] for the pure Lennard–Jones fluid employing the van der Waals one-fluid mixing rule and also with new simulation data at the corresponding state-points of the pure Lennard–Jones fluid.

2. THEORETICAL BACKGROUND

The van der Waals one-fluid model is a special case of a conformal solution model. Conformal solutions are defined as mixtures in which all intermolecular interactions obey the same functional form:

$$u_{ij}(r) = \varepsilon_{ij} f(r/\sigma_{ij}) \tag{1}$$

where u_{ij} is the interaction energy between a pair of particles, ε_{ij} an energy parameter, σ_{ij} a size parameter, and f a universal function of the reduced distance r/σ_{ij} [2]. The Lennard–Jones potential is of this type. In conformal solution models residual mixture properties are expressed by a reference fluid, whose interactions also obey Eq. (1). For Lennard–Jones mixtures the pure Lennard–Jones fluid is used as reference fluid.

According to a one-fluid model the residual part of the fundamental EOS in terms of the Helmholtz free energy of the mixture $A_x^{\mathrm{r}} = A^{\mathrm{r}}/\varepsilon_x$ is expressed by the residual Helmholtz free energy of the reference fluid $A_0^{\mathrm{r}} = A^{\mathrm{r}}/\varepsilon_0$ as

$$A_x^{\mathrm{r}}(\rho_x, T_x) = \frac{\varepsilon_0}{\varepsilon_x} A_0^{\mathrm{r}}\left(\rho_x \frac{\sigma_x^3}{\sigma_0^3}, T_x \frac{\varepsilon_0}{\varepsilon_x}\right) \tag{2}$$

where ρ is the density and T the thermodynamic temperature. The properties of the reference fluid and mixture are denoted by the indices 0 and x. The parameters σ_x and ε_x are functions of the composition according to

$$\varepsilon_x \sigma_x^3 = (1-x)^2\, \varepsilon_{11} \sigma_{11}^3 + 2x(1-x)\, \varepsilon_{12} \sigma_{12}^3 + x^2 \sigma_{22} \sigma_{22}^3 \tag{3}$$

$$\sigma_x^3 = (1-x)^2\, \sigma_{11}^3 + 2x(1-x)\, \sigma_{12}^3 + x^2 \sigma_{22}^3 \tag{4}$$

where x is the mole fraction of component 2. The underlying assumption of the van der Waals one-fluid model is that all radial distribution functions of the reference fluid and the mixture become equal if the radial coordinate is scaled with its corresponding average "size" parameter σ_x. This assumption should be reasonably good, if the difference in size parameters is small and packing effects are absent. A more detailed discussion including other conformal solution models is, for example, given by Mansoori [3].

The application of a one-fluid model can be understood as a mapping of a reference fluid isotherm T_0 on an isotherm T_x of the mixture at constant composition being also stretched with respect to density, so that there is one corresponding state-point (T_x, ρ_x) for each state-point (T_0, ρ_0) of the reference fluid. From this interpretation, a mixing rule can be tested using computer simulation data for given T_x along various isoplethes at various densities. By mapping these mixture data on the respective reference fluid isotherms, they can be compared to computer simulation data at the corresponding state-points of the pure Lennard-Jones fluid.

3. MONTE CARLO SIMULATION RESULTS

The mixture studied in this work was previously used by Panagiotopoulos [4] to model the phase behavior of the binary system argon/krypton at $T_x = 1.2183$, 1.5096, and 1.6438. The Lennard-Jones parameters are $\sigma_{11} = 1$,

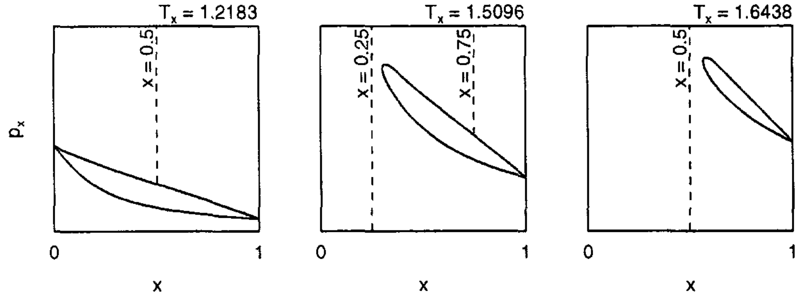

Fig. 1. Compositions at which simulations were carried out in relation to the phase boundaries of the mixture.

$\sigma_{12} = 1.0339$, $\sigma_{22} = 1.0640$ and $\varepsilon_{11} = 1$, $\varepsilon_{12} = 1.1523$, $\varepsilon_{22} = 1.3702$. The size parameters differ by only 6.4%, so that a good performance of the van der Waals one-fluid model should be expected. In the present work, *NVT* Monte Carlo simulations were performed at the same three temperatures as chosen by Panagiotopoulos and, additionally, on the supercritical isotherm at $T_x = 2.1191$. The compositions of our simulations are shown in relation

Table I. Monte Carlo Simulation Results for the Mixture. Number of Particles: $N = 1372$[a]

T_x	x	$\rho_x = \rho\sigma_{11}^3$	$U_x^r = \dfrac{U^r}{\varepsilon_{11} N}$	$p_x = \dfrac{p\sigma_{11}^3}{\varepsilon_1}$	$C_{V,x}^r = \dfrac{C_V^r}{Nk}$
1.2183	0.5	0.8	−6.9919(12)	3.201(6)	1.093809
		0.7	−6.2839(9)	0.8574(47)	0.790271
		0.65	−5.8675(6)	0.2685(34)	0.680394
1.5096	0.25	0.8	−5.8732(6)	3.9408(31)	0.880653
		0.7	−5.28304(46)	1.7552(25)	0.661137
		0.6	−4.5791(5)	0.7281(18)	0.507062
		0.5	−3.8460(10)	0.3263(8)	0.449448
		0.4	−3.1456(25)	0.2074(13)	0.595457
		0.3	−2.4461(33)	0.1763(5)	0.773326
		0.2	−1.7183(30)	0.15592(14)	0.673554
		0.1	−0.8834(10)	0.10918(5)	0.309038
	0.75	0.8	−7.5288(13)	5.926(6)	1.140347
		0.7	−6.8900(8)	2.2678(36)	0.869371
		0.6	−6.00581(45)	0.6247(23)	0.622858
		0.55	−5.5261(6)	0.2628(20)	0.545490
1.6438	0.5	0.8	−6.5440(10)	5.4895(48)	0.964490
		0.7	−5.9565(7)	2.4530(33)	0.726392
		0.6	−5.1883(6)	0.9934(18)	0.536935
		0.5	−4.3585(9)	0.4104(19)	0.451576
		0.4	−3.5490(19)	0.2328(10)	0.513774
		0.3	−2.7683(27)	0.1892(5)	0.680048
		0.2	−1.9369(31)	0.16643(16)	0.660221
		0.1	−1.0041(11)	0.11721(6)	0.330934
2.1191	0.5	0.9	−6.2155(11)	14.237(5)	1.152770
		0.8	−6.0906(13)	7.804(6)	0.892329
		0.7	−5.6218(12)	4.0826(49)	0.669948
		0.6	−4.9438(5)	2.0923(25)	0.491177
		0.5	−4.1656(7)	1.1229(11)	0.377745
		0.4	−3.3616(9)	0.6711(9)	0.313865
		0.3	−2.5613(14)	0.4518(7)	0.299916
		0.2	−1.7503(17)	0.31275(20)	0.254442
		0.1	−0.90154(45)	0.177826(45)	0.147630

[a] The number in parentheses denotes the estimated uncertainty of the calculated properties. No error estimation was made for the heat capacity data.

to the phase boundaries in Fig. 1 for the three lowest temperatures. At $T_x = 2.1191$ the equimolar mixture was chosen.

The programs used in this study were developed from the recipe listings published by Allen and Tildesley [5]. The simulations were performed with 864 and 1372 particles, except at $T_x = 2.1191$, where they were carried out with 1372 particles only. The cutoff radius was set to $r_C = 4 \cdot \sigma_{11}$, and the

Table II. Monte Carlo Simulation Results for the Pure Lennard-Jones Fluid[a]

T_0	N	$\rho_0 = \rho\sigma_0^3$	$U_0^r = \frac{U^r}{\varepsilon_0 N}$	$p_0 = \frac{p\sigma_0^3}{\varepsilon_0}$	$C_{V,0}^r = \frac{C_V^r}{Nk}$
1.034866	1372	0.882985	−5.9426(13)	2.989(6)	1.113102
		0.772612	−5.3390(5)	0.7960(27)	0.765962
		0.717425	−4.98341(37)	0.2475(22)	0.696112
	2048	0.882985	−5.9435(8)	2.9858(44)	1.085886
		0.772612	−5.3384(5)	0.7965(31)	0.790079
		0.717425	−4.98236(31)	0.2524(21)	0.665958
1.3963	1372	0.882985	−5.5621(8)	5.1378(45)	1.006091
		0.772612	−5.0621(1)	2.286(5)	0.734039
		0.662238	−4.40633(48)	0.9270(20)	0.545551
		0.551865	−3.6981(7)	0.3830(12)	0.442500
		0.441492	−3.0042(15)	0.2175(10)	0.499410
		0.331119	−2.3373(30)	0.1774(5)	0.768881
		0.220746	−1.6324(21)	0.15630(18)	0.617242
		0.110373	−0.84414(49)	0.11009(7)	0.312921
1.3963	2048	0.882985	−5.5612(6)	5.1412(30)	0.940556
		0.772612	−5.05957(28)	2.3007(18)	0.727605
		0.662238	−4.40555(30)	0.9321(7)	0.543129
		0.551865	−3.6983(6)	0.3845(10)	0.443708
		0.441492	−3.0080(13)	0.2177(8)	0.506133
		0.331119	−2.3394(26)	0.17691(34)	0.685932
		0.220746	−1.6329(37)	0.15731(11)	0.778203
		0.110373	−0.8460(5)	0.11001(6)	0.293400
1.8	1372	0.993358	−5.2845(23)	13.332(12)	1.186388
		0.882985	−5.1764(8)	7.3044(38)	0.904479
		0.772612	−4.7775(6)	3.8182(31)	0.610535
		0.662238	−4.19827(45)	1.9673(21)	0.480758
		0.551865	−3.53588(37)	1.0542(12)	0.367704
		0.441492	−2.8516(8)	0.6281(9)	0.317833
		0.331119	−2.1706(9)	0.42298(40)	0.285927
		0.220746	−1.4806(9)	0.29394(17)	0.233093
		0.110373	−0.76224(35)	0.16684(6)	0.143928

[a] The number in parentheses denotes the estimated uncertainty of the calculated properties. No error estimation was made for the heat capacity data.

usual long-range corrections were applied. The initial configuration was either a cubic-face-centered lattice or the final configuration of a previous simulation at a higher density. Each simulation covered 5×10^4 cycles and was preceded by an equilibration of 10^4 cycles. One cycle consisted of one attempted displacement of every particle where the acceptance ratio was 0.5 or 0.65 at low densities. The results for the mixture simulations with 1372 particles are reported in Table I.

Additional simulations for the pure Lennard–Jones fluid were carried out as described above, with 864, 1372, and 2048 particles at $T_0 = 1.034866$, 1.3963, and 1.8 corresponding to the equimolar mixtures at $T_x = 1.2183$, 1.6438, and 2.1191. The densities along these isotherms were chosen so that the pure Lennard–Jones fluid densities correspond to the mixture densities, thus allowing a direct assessment of the validity of the chosen mixing rule. The results for 1372 and 2048 particles are given in Table II.

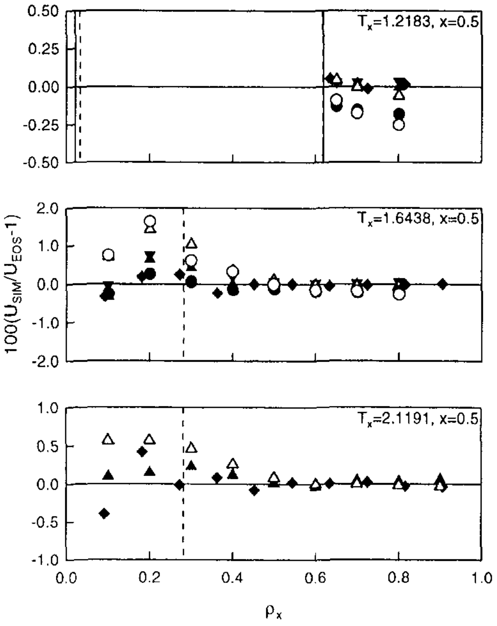

Fig. 2. Deviations of the residual internal energy data from the EOS. Mixture: (○) $N = 864$; (△) $N = 1372$. Pure Lennard–Jones fluid: (●) $N = 864$; (▲) $N = 1372$; (▼) $N = 2048$; (◆) Johnson et al. [6]. (——) Saturated liquid and vapor densities of the mixture; (----) saturated liquid and vapor densities (subcritical) or critical density (supercritical) of the pure Lennard–Jones fluid.

4. DISCUSSION

The simulation results are compared with the fundamental EOS published recently by Mecke et al. [1] in Figs. 2–4. This EOS can be applied to mixtures when using the van der Waals one-fluid mixing rules according to Eqs. (3) and (4). Beside the mixture data, the results for the pure Lennard-Jones fluid (Table II), as well as the pure-fluid *NVT* molecular dynamics data of Johnson et al. [6], are included.

The mixture internal energy data agree with the mixture EOS within 0.6%, except in the critical region, where larger deviations, up to 1.8%, are found. At high densities the 1372-particle data agree with the EOS within 0.1%, whereas the 864-particle data are systematically lower. The new pure-fluid data show a similar deviation pattern. Nevertheless, mixture and corresponding pure-fluid data for the same number of particles agree well at high densities, while on supercritical isotherms at low densities the pure-fluid data are systematically lower than the mixture data. Also, the agreement between the molecular dynamics data of Johnson et al. [6] with 864 particles and the Monte Carlo simulation data with 1372 particles for the pure fluid of this work is excellent.

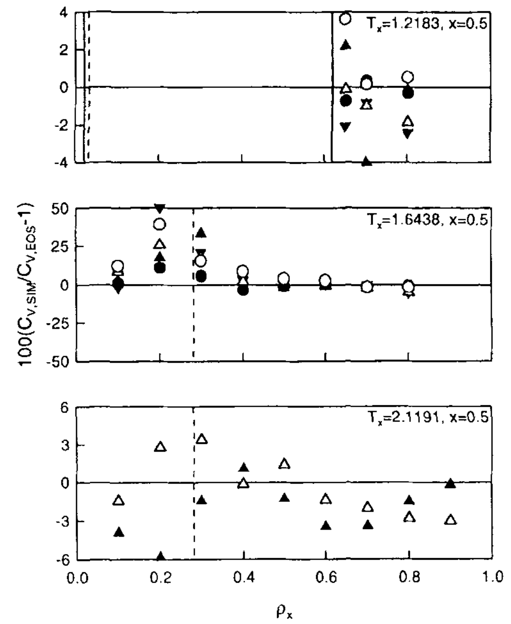

Fig. 3. Deviations of the residual isochoric heat capacity data from the EOS. Symbols as in the legend to Fig. 2.

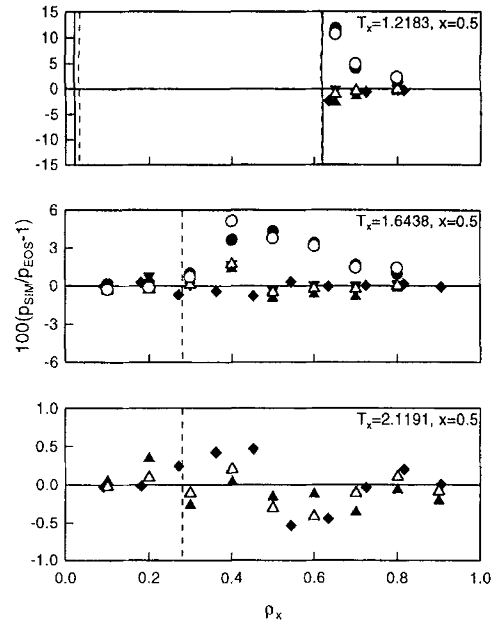

Fig. 4. Deviations of the pressure data from the EOS. Symbols as in the legend to Fig. 2.

The results for the isochoric heat capacities are similar to those of the internal energies, resembling the close relation between the isochoric heat capacity and fluctuations of the internal energy. Mixture and pure-fluid data agree with the EOS generally within 6%, except in the critical region, where deviations up to 50% are found. On supercritical isotherms the pure-fluid data at low densities are systematically lower than the mixture data as already observed for the internal energy. The heat capacities scatter much more than the internal energies, so that it is not possible to draw further conclusions about systematic trends.

The results for the pressure show a different behavior. The deviations of the 864-particle data are moderate at high densities but increase to almost 15% near the phase boundary, while the 1372-particle data agree much better with the EOS. Similar, but less expressed behavior is found at high densities in the supercritical region. Again, the agreement between the data set of Johnson et al. [6] and the 1372-particle data of this work is excellent. On the supercritical isotherm at $T_x = 1.6438$ the low density data agree well with the EOS for both the pure fluid and the mixture, while higher deviations are found above the critical density. At $T_x = 2.1191$ the deviations are within 0.5%.

Overall, the van der Waals one-fluid model predicts the mixture properties quite well, as could be expected from the small differences in the size parameters. This can be derived especially from the direct comparison of the mixture data with their corresponding pure fluid data. On supercritical isotherms internal energy and heat capacity data indicate a failure of the van der Waals one-fluid model at low densities. However, due to higher uncertainties, this observation cannot be confirmed with the pressure data. The simulation data with different particle numbers reveal significant finite-size effects, which are especially pronounced for the pressure near the phase boundary. The pure Lennard-Jones fluid data obtained with 864, 1372, and 2048 particles show that the finite-size effect is negligible for systems having more than 1372 particles at the accuracy level of the data presented here.

5. CONCLUSIONS

The performance of the van der Waals one-fluid mixing rule was examined for a binary Lennard-Jones system with small differences in size parameters. It was found that the van der Waals one-fluid model describes the mixture properties at high densities well, whereas on supercritical isotherms the predicted internal energies and heat capacities at low densities are too low. For a more definitive assessment of the mixing rule, a more accurate EOS for the Lennard-Jones fluid would be desirable. This must be based on new and more accurate simulation data similar to those presented in this work.

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