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A Test of the Mean Density Approximation for Lennard–Jones Mixtures with Large Size Ratios[1]

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The mean density approximation for mixture radial distribution functions plays a central role in modern corresponding-states theories. This approximation is reasonably accurate for systems that do not differ widely in size and energy ratios and which are nearly equimolar. As the size ratio increases, however, or if one approaches an infinite dilution of one of the components, the approximation becomes progressively worse, especially for the small molecule pair. In an attempt to better understand and improve this approximation, isothermal molecular dynamics simulations have been performed on a series of Lennard–Jones mixtures. Thermodynamic properties, including the mixture radial distribution functions, have been obtained at seven compositions ranging from 5 to 95 mol%. In all cases the size ratio was fixed at two and three energy ratios were investigated, $\varepsilon_{22}/\varepsilon_{11} = 0.5$, 1.0, and 1.5. The results of the simulations are compared with the mean density approximation and a modification to integrals evaluated with the mean density approximation is proposed.

KEY WORDS: computer simulation; Lennard–Jones mixtures; mean density approximation; molecular dynamics.

1. INTRODUCTION

Recently, there has been renewed interest in the development of more accurate corresponding states theories for fluid mixtures. Much of the research in this area has been focused on the development of local composition models which combine an intuitive microscopic picture of fluid structure with a semiempirical equation of state. In this type of model the

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local compositions are obtained theoretically from the particle coordination numbers n_{ij}, which are defined by

$$n_{ij}(R_{ij}) = 4\pi\rho x_i \int_0^{R_{ij}} g_{ij}(r, \Omega; \{\rho_k\}, T; \{\varepsilon_{kl}\}, \{\sigma_{kl}\}, \{\mu_k\},...)\, r^2\, dr$$

g_{ij} is the radial distribution function for the ij pair, which is proportional to the probability of finding a molecule of type i a distance r with relative orientation Ω away from a central molecule of type j in the mixture. Generally, the radial distribution function depends upon the set of component number densities $\{\rho_k\}$, the temperature T, and the complete set of intermolecular potential parameters $\{\varepsilon_{kl}\}$, $\{\sigma_{kl}\}$, $\{\mu_k\}$,..., for all components in the mixture. Even though this type of approach is intuitively pleasing, the ambiguity associated with the value of "cutoff" parameter, R_{ij}, makes its application in predictive models difficult [1, 2].

An alternate approach which avoids this problem was proposed by Leland and co-workers [3–5]. In Leland's approach one directly makes an approximation which relates the radial distribution function of a pair in a mixture to that of a hypothetical pure fluid. This approximate distribution function can then be used to derive mixing rules for use in corresponding-states models.

The most successful of these approximations is the mean density approximation (MDA) proposed by Mansoori and Leland [3], which for spherical molecules, states that

$$g_{ij} = g_0(r/\sigma_{ij}; kT/\varepsilon_{ij}; \rho\bar{\sigma}^3) \tag{1}$$

where the subscript 0 denotes a pure fluid radial distribution function which is to be evaluated at a reduced distance r/σ_{ij}, reduced temperature kT/ε_{ij}, k is Boltzmann's constant, $\rho\bar{\sigma}^3$ is the "mean" reduced density where

$$\bar{\sigma}^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \tag{2}$$

and x_i is the bulk concentration of component i.

Since at a low density g_{ij} approaches $\exp(-\beta u_{ij})$, where u_{ij} is the intermolecular potential, Eq. (1) is exact in that limit. Recently, however, it has become obvious that Eq. (1) has some shortcomings in the limit of infinite dilution [6] and large size and energy ratios [7]. The latter result led Hoheisel and Lucas [7] to propose an empirical modification to perturbation theory integrals which has been evaluated using the MDA. It is also obvious that when the energy parameters for the components are identical, the MDA reduces to the van der Waals one-fluid assumption [8], which is known to be inaccurate for large size differences.

In this communication, the results of molecular dynamics simulations are reported for 21 Lennard–Jones mixtures. This study was undertaken to provide a base of radial distribution functions for mixtures which could be used to test and improve approximations such as the MDA. In the course of this study a new approximation for integrals involving mixture radial distribution functions was developed and is briefly discussed in Section 4.

2. DESCRIPTION OF SIMULATIONS

The systems investigated in this study were chosen to overlap some of the results of previous investigators [7, 9] and to extend the base of calculations to the more dilute regimes. The components of the mixtures interacted with a pairwise additive Lennard–Jones (12–6) potential

$$u_{ij}(r) = 4\varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$$

where i and j denote the components, ε_{ij} denotes the value of the intermolecular potential depth at the minimum $r_m = 2^{1/6}\sigma_{ij}$, and σ_{ij} is the collision diameter, $u_{ij}(\sigma_{ij}) = 0$. In these calculations the smaller molecule was assigned the potential parameters associated with argon, $\sigma_{11} = 3.405 \times 10^{-10}$ m and $\varepsilon_{11}/k = 120$ K. In all of the calculations presented in this report $\sigma_{22}/\sigma_{11} = 2$, with $\varepsilon_{22}/\varepsilon_{11}$ varying from 0.5 to 1.5. The unlike-pair parameters were calculated from the Lorentz–Berthelot rules

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{12})^{\frac{1}{2}}$$

and

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})^{\frac{1}{2}}$$

2.1. Computational Details

The simulations were performed on a Cyber 205 using a system size of 864 particles. Hamilton's equations of motion were solved at a constant temperature by imposing a Gaussian thermostat of the form proposed by Evans and Hoover [10–12]. The algorithm was a fourth-order Gear predictor–corrector with an integration time step of approximately 10 fs. The simulations were initiated from a fcc crystal with random assignments to the lattice sites. The systems were typically equilibrated a minimum of 1000 time steps to remove any memory of the initial configuration. The intermolecular potential was truncated at 2.5 σ_{ij} and neighbor lists were maintained out to a radius of 2.8 σ_{ij}.

Typically 20000 equilibrium time steps were generated for each state point except in the cases where the concentration of one component was less than 10%. In those cases, the simulations were continued to 30000 time steps. The pair correlation functions were determined by randomly sampling the system at an approximate frequency of twice every hundred time steps. The step size of the resulting histograms was chosen to be $0.025\,\sigma_{ij}$. Long-range corrections to the thermodynamic pressure and energy were added to the simulation results by assuming that the distribution functions were unity beyond $2.5\,\sigma_{ij}$.

The overall accuracy of the simulations is a strong function of the system size and concentration. In all cases the total energy of the system with the thermostat off was conserved to within 0.1% per 10,000 time steps. It is estimated that the accuracy of the radial distribution functions is better than 0.5% except for the like–like distribution functions for the cases where the concentrations were less than 10% of that component. In the latter case uncertainties are of the order of 2%.

3. RESULTS AND COMPARISONS

The results of the simulations are summarized in Table I, which gives the compositions and energy ratios studied, in addition to the relevant thermodynamic state data. Figure 1 shows the excess internal energy for the systems studied relative to the pure Lennard–Jones values obtained from the Nicolas equation of state [13]. Three of the systems studied ($\varepsilon_{22}/\varepsilon_{11} = 1$, $x_1 = 0.25$, 0.50, and 0.75) were chosen to be identical to those investigated by Gupta [9]. Differences in the configurational energy and distribution functions obtained in this study and those reported by Gupta are within the combined uncertainty of the simulations.

The primary purpose of this study was to provide a more detailed comparison of the mean density approximation given in Eq. (1) with accurate simulation results. Since this approximation requires a knowledge of the pure fluid distribution function at many state conditions, it was decided to use the parameterization of the dense pure Lennard–Jones fluid radial distribution function developed by Goldman [14]. The stated accuracy of this approximation is an rms deviation of 0.034 in the temperature range of $0.5 \leqslant T^* \leqslant 5.0$ and $0.35 \leqslant \rho^* \leqslant 1.10$. Comparisons of a few simulated pure fluid results and the results of Goldman's equation agreed with this estimate.

Figure 2 compares the simulated and MDA calculated 1–1 distribution functions at three compositions with $\varepsilon_{22}/\varepsilon_{11} = 1$. This figure demonstrates the general result that the MDA underestimates the height of the 1–1 first-neighbor peak and, for compositions less than $x_1 = 0.5$, does not represent the "solvation" first-neighbor peak at $r^* = \sigma_{12}/\sigma_{11}$. Figure 3 shows similar results for the 1–2 distribution function. In this case the

Table I. Summary of Simulation Results for Mixtures of 864 Lennard-Jones Particles[a]

N_1	$\varepsilon_{22}/\varepsilon_{11}$	p^*	ρ^*	T^*	U_c^*
821	0.5	0.447	0.5800	1.000	−4.766
	1.0	0.483	0.5980	1.000	−5.340
	1.5	0.512	0.6130	1.000	−5.841
778	0.5	0.422	0.4660	1.000	−4.374
	1.0	0.512	0.4939	1.000	−5.381
	1.5	0.504	0.5080	1.000	−6.210
648	0.5	0.521	0.3030	1.000	−3.731
	1.0	0.500	0.3190	1.000	−5.416
	1.5	0.660	0.3380	1.000	−7.108
432	0.5	0.520	0.1900	1.000	−3.098
	1.0	0.488	0.2000	1.000	−5.573
	1.5	0.527	0.2100	1.000	−8.108
216	0.5	0.510	0.1386	1.000	−2.728
	1.0	0.507	0.1466	1.000	−5.849
	1.5	0.497	0.1520	1.000	−9.090
86	0.5	0.344	0.1100	1.000	−2.459
	1.0	0.520	0.1265	1.000	−6.040
	1.5	0.440	0.1300	1.000	−9.685
43	0.5	0.518	0.1150	1.000	−2.538
	1.0	0.623	0.1238	1.000	−6.184
	1.5	0.345	0.1280	1.000	−10.523

[a] $p^* = p\sigma_{11}^3/\varepsilon_{11}$, $\rho^* = \rho\sigma_{11}^3$, $T^* = kT/\varepsilon_{11}$, and $U_c^* = U_c/N\varepsilon_{11}$.

height of the first-neighbor peak is well represented at all compositions, although the second-neighbor peak is incorrectly represented at all compositions. Figure 4 shows the 2–2 distribution functions. In this case the first-neighbor peaks are well represented but the solvation peak is incorrectly placed by the MDA for $x_1 \geqslant 0.5$.

In Fig. 5 the effect of the energy ratio on the 2–2 distribution function is shown at a fixed composition of $x_1 = 0.5$. In this case the MDA correctly tracks the height of the first-neighbor peak. Although not shown, the MDA consistently underestimates the first-neighbor peak height for the 1–1 distribution. Finally, Fig. 6 shows the average deviation between the mean density approximation and the simulation results for all 20 state points reported here. Again, the first-neighbor peak in the 1–1 distribution function is consistently underestimated.

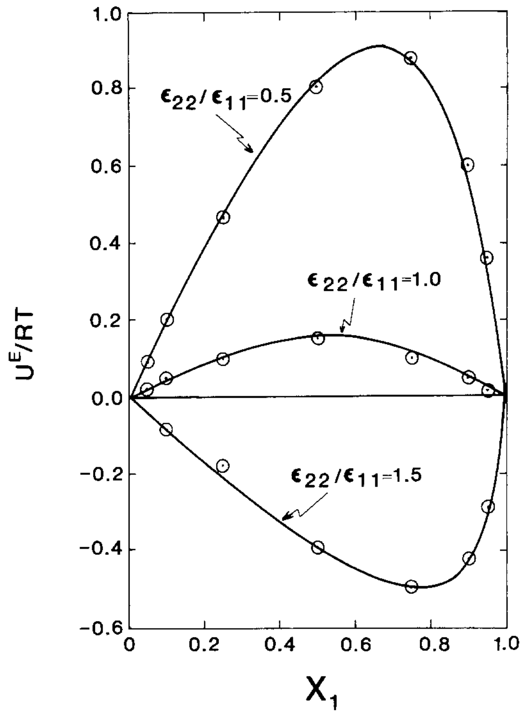

Fig. 1. Dimensionless excess energy for the Lennard–Jones mixtures simulated in this study. The points indicate the simulation results and the lines are included only to help guide the eye.

One can conclude from these results that the MDA provides a reasonable estimate of distribution functions in mixtures. Its two greatest errors are the height of the first-neighbor peak for the small molecule pair and its inability to mimic the packing effects (e.g., the solvation first-neighbor peaks) associated with a system of molecules of different sizes. Since the latter effect is apparent only at relatively large intermolecular separations, the effect on the thermodynamic properties should be small. The first effect, however, can have a substantial impact on the calculation of properties and warrants some correction.

4. MODIFICATION TO THE MEAN DENSITY APPROXIMATION

Hoheisel and Lucas (HL) [7] have pointed out that it is possible to improve the accuracy of the integrals of the form

$$J_{ij}^{(n)} = \int_0^\infty g_{ij} r^{n-2}\, dr$$

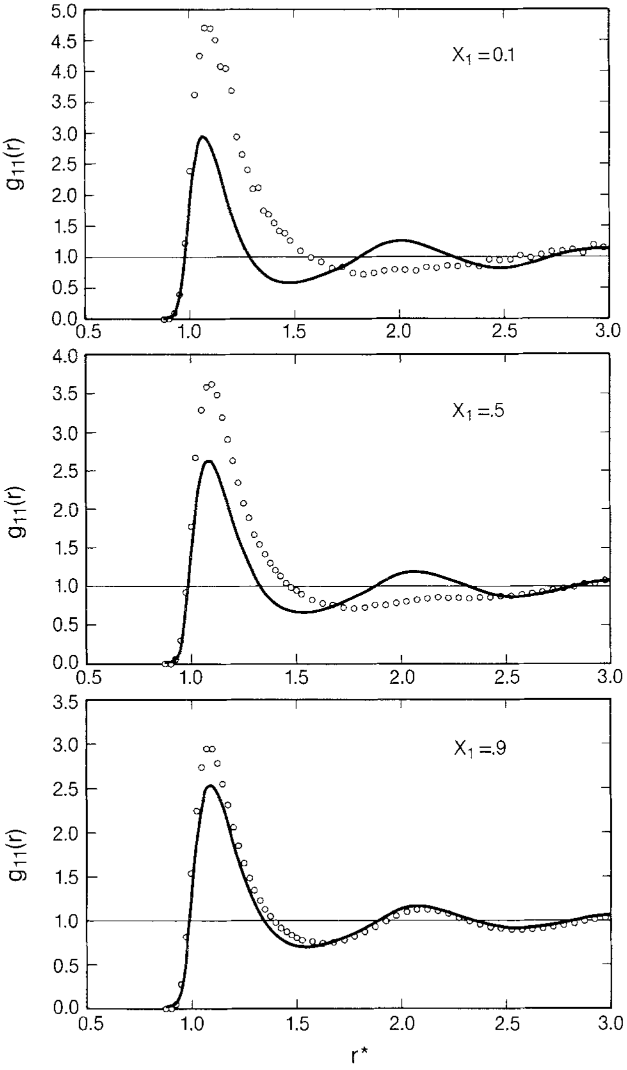

Fig. 2. Comparison of the mean density approximation (solid line) and simulation results for the 1–1 radial distribution function at three compositions. In all cases $\varepsilon_{22}/\varepsilon_{11} = 1$ and $\sigma_{22}/\sigma_{11} = 2$.

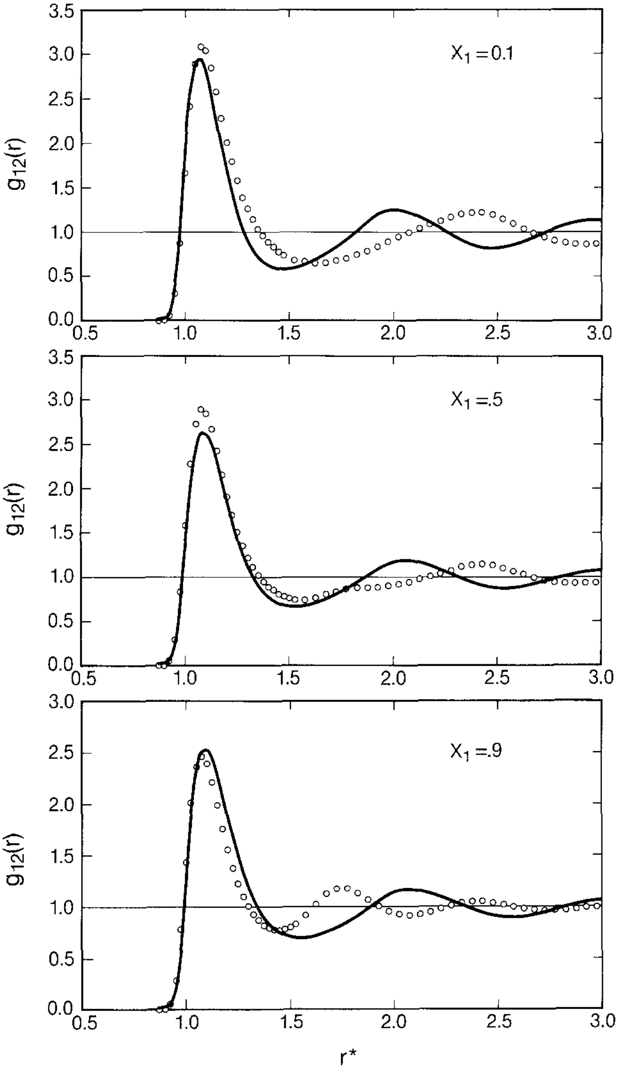

Fig. 3. Comparison of the mean density approximation (solid line) and simulation results for the 1–2 radial distribution function. The compositions and potential parameter ratios are identical to those in Fig. 2.

by multiplying the MDA results by an empirical factor which they correlated from their simulation studies. Examination of their results shows (as the results obtained here) that the $J_{ij}^{(n)}$ obtained from the MDA are low for the small molecule pair and generally slightly high for the large pair.

As an alternative to the HL procedure, we propose here a scaling of the J integrals based on the first-neighbor peak heights for soft-sphere

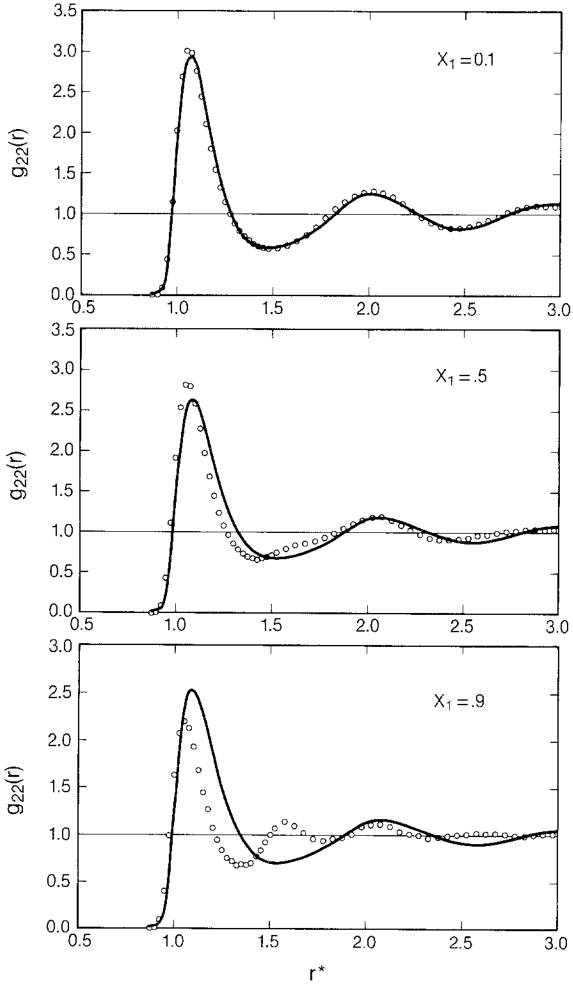

Fig. 4. Comparison of the mean density approximation (solid line) and simulation results for the 2–2 radial distribution functions. Compositions and potential parameters are identical to those in Fig. 2.

mixtures. In particular, we define a modified mean density approximation (MMDA) as

$$g_{ij}(r) = S_{ij}\, g_0(r/\sigma_{ij};\, kT/\varepsilon_{ij},\, \rho\bar{\sigma}^3) \tag{3}$$

where S_{ij} is given by

$$S_{ij} = g_{ij}^{ss}(r_x/d_{ij};\, \{\rho_k\},\, \{d_{kl}\})/g_0^{ss}(r_x/\bar{d};\, \rho\bar{\sigma}^3) \tag{4}$$

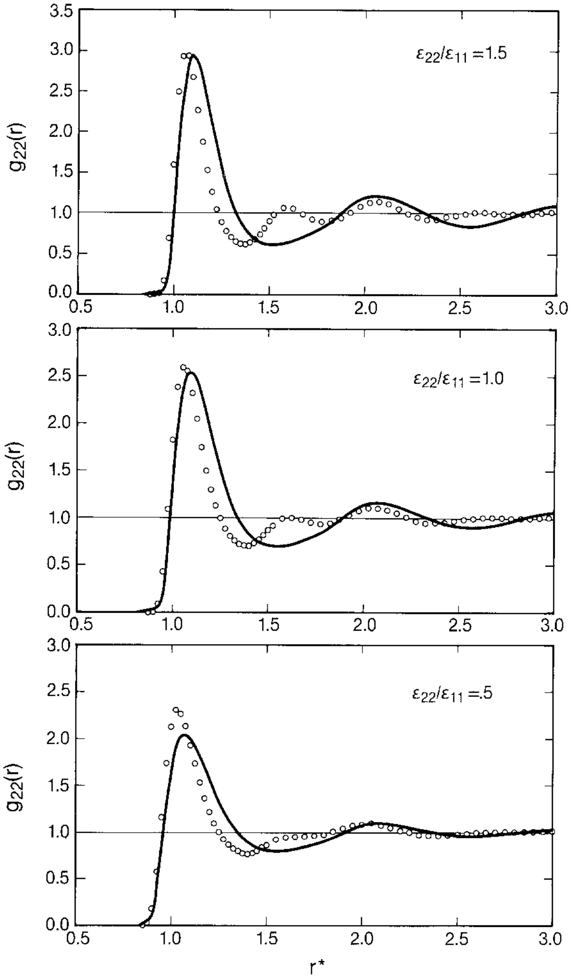

Fig. 5. Comparison of the mean density approximation (solid line) and simulation results for the 2–2 radial distribution function at three energy ratios: 1.5, 1.0, and 0.5. In all cases the composition was $x_1 = 0.5$ and $\sigma_{22}/\sigma_{11} = 2$.

The soft-sphere distribution functions are obtained from the Weeks–Chandler–Anderson [15] soft-sphere potential

$$u_{ij}^{0}(r) = u_{ij}^{\mathrm{LL}}(r) + \varepsilon_{ij} \qquad (r \leqslant r_m)$$

and the approximation that the soft-sphere background correlation functions may be calculated from the relation

$$y_{ij}(r) = \exp(-\beta u_{ij})\, g_{ij}^{\mathrm{HS}}(r; \{d_{kl}\})$$

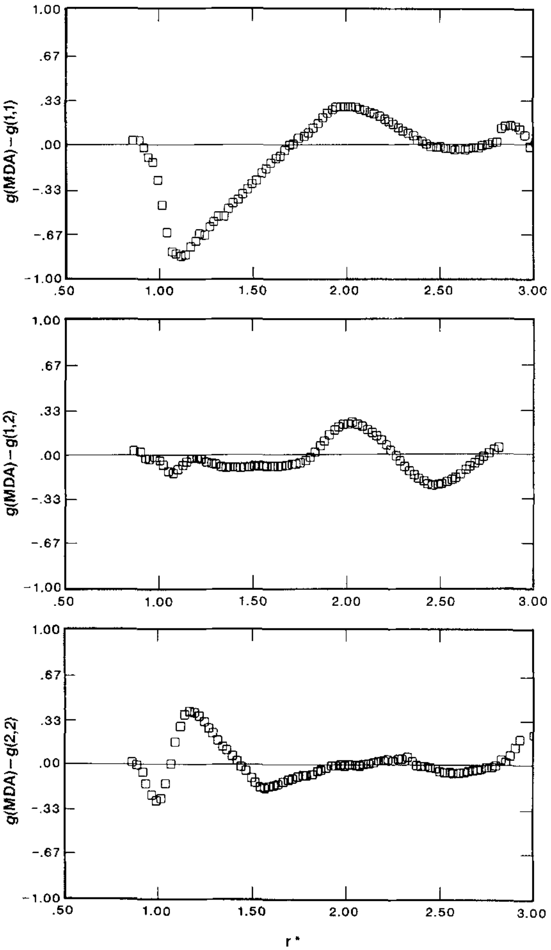

Fig. 6. Average of the differences between the mean density approximation and all 21 simulation results. In the cases studied here, the MDA consistently underestimates the first-neighbor peak high for the 1–1 distribution function.

Table II. Comparison of Predicted and Simulated J Integrals for Lennard-Jones Mixtures with $\varepsilon_{22}/\sigma_{11} = 2^a$

		J^6				J^{12}			
$\varepsilon_{22}/\varepsilon_{11}$	Pair	MD	HL	MMDA	MDA	MD	HL	MMDA	MDA
1.0	11	0.688	0.687	0.701	0.632	0.530	0.542	0.583	0.527
	12	0.666	0.687	0.686	0.632	0.548	0.549	0.569	0.527
	22	0.670	0.673	0.683	0.632	0.613	0.597	0.570	0.527
1.5	11	0.703	0.691	0.714	0.632	0.545	0.548	0.595	0.527
	12	0.662	0.675	0.677	0.619	0.518	0.512	0.533	0.487
	22	0.641	0.648	0.654	0.609	0.524	0.514	0.488	0.454
3.0	11	0.712	0.701	0.739	0.632	0.573	0.565	0.616	0.527
	12	0.661	0.651	0.660	0.594	0.481	0.450	0.472	0.425
	22	0.597	0.602	0.600	0.566	0.401	0.398	0.373	0.351
5.0	11	0.713	0.713	0.752	0.632	0.582	0.584	0.627	0.527
	12	0.659	0.637	0.651	0.581	0.454	0.413	0.436	0.389
	22	0.571	0.578	0.570	0.543	0.338	0.336	0.312	0.297

[a] MD, molecular dynamics simulations [7]; HL, calculated by Hoheisel and Lucas [7]; MMDA, modified mean density approximation presented in this work; MDA, original mean density approximation.

In these equations g_{ij}^{HS} is a hard-sphere distribution function with effective diameters d_{ij}, and r_x denotes the position of the maximum of the soft-sphere distribution function. g_0^{ss} is a radial distribution function for a system of pure soft spheres evaluated at a mean density.

In order to test this approximation, Percus-Yevick hard-sphere mixture distribution functions were evaluated by Perram's method [16] and temperature-dependent effective hard-sphere diameters were obtained from the prescription of Barker and Henderson [17]. Table II compares the results of the calculations with those reported by HL for a size ratio of two. Generally the results are in the right direction but are not as accurate as the correlation presented by HL. This could be improved by making a more sophisticated calculation of the effective hard-sphere diameters in Eq. (4). The advantage of this approximation, however, is that it can be used in the development of conformal solution mixing rules.

5. SUMMARY

We have presented the results of some preliminary molecular dynamics simulations for Lennard-Jones mixtures with a size ratio of two.

The mean density approximation, although realistic, fails to represent the size effects in mixture distribution functions, especially for the small molecule pair. A correction to integrals evaluated with the MDA has been proposed which is an improvement over the uncorrected MDA. Future work will incorporate this approximation in the development of conformal solution mixing rules.

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REFERENCES

1. G. A. Mansoori and J. F. Ely, *Fluid Phase Equil.* (in press) (1985).
2. P. M. Mathias and T. W. Copeman, *ACS Symposium Series* (in press).
3. G. A. Mansoori and T. W. Leland, *J. Chem. Soc. Faraday Trans. II* **6**:320 (1972).
4. T. W. Leland, *Adv. Cryo Eng.* **21**:466 (1976).
5. J. B. Gonsalves and T. W. Leland, *A.I.Ch.E. J.* **24**:279 (1978).
6. K. S. Shing and K. E. Gubbins, *Mol. Phys.* **46**:1109 (1982); **49**:1121 (1983).
7. C. Hoheisel and K. Lucas, *Mol. Phys.* **53**:51 (1984).
8. D. Henderson and P. J. Leonard, in *Physical Chemistry, An Advanced Treatise, Vol. VIIIB*, H. Eyring, D. Henderson, and W. Jost, eds. (Academic Press, New York, 1971), pp. 413–510.
9. S. Gupta, Ph.D. dissertation (Clemson University, Clemson, S.C., 1984).
10. D. J. Evans, W. G. Hoover, B. H. Failor, B. Moran, and A. J. C. Ladd, *Phys. Rev.* **A28**:1016 (1983).
11. D. J. Evans, *J. Chem. Phys.* **78**:3297 (1983).
12. D. J. Evans and G. P. Morriss, *Comp. Phys. Reports* **1**:297 (1984).
13. J. J. Nicolas, K. E. Gubbins, W. B. Street, and D. J. Tildesley, *Mol. Phys.* **37**:1429 (1979).
14. S. Goldman, *J. Phys. Chem.* **83**:3033 (1979).
15. J. D. Weeks, D. Chandler, and H. C. Anderson, *J. Chem. Phys.* **54**:5237 (1971).
16. J. W. Perram, *Mol. Phys.* **30**:1505 (1975).
17. D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976), p. 322.