LOCAL COMPOSITIONS AND THERMODYNAMICS OF POLAR/NON-POLAR MIXTURES

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ABSTRACT

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Results of computer simulations are presented for the thermodynamic properties of mixing and the local compositions for mixtures of Stockmayer and Lennard-Jones fluids with varying concentrations and dipole strengths The results show a strong asymmetry with respect to the concentration which is attributed to the influence of the orientation dependence of the dipole-dipole interaction and explained in terms of a "frustration" effect

1. INTRODUCTION

The concept of local compositions, which describes the deviations of concentrations within a region around a specific particle from the overall bulk concentrations, and the importance of such deviations for liquid models, can be traced back as far as the work of Rushbrooke (1938) and Guggenheim (1944) Recently there has been renewed interest in these ideas primarily motivated by efforts to extend the applicability of equations of state to include the liquid-phase description of non-ideal mixtures through the use of fundamental mixing rules Methods have been proposed (Mollerup, 1981, Whiting and Prausnitz, 1982, Li et al , 1986) by which the local composition mixing rules may be combined with an equation of state

By using computer simulations it has become possible to determine the local composition of well defined model systems and to use these data for further improvement of the local composition models Previously, computer simulations have been concerned mainly with the local composition of particles with isotropic potentials The results of these earlier studies suggested that the local compositions and phase behaviour were highly symmetric with respect to the bulk concentration This is in direct contrast with experimental observations for polar/non-polar mixtures

Mixtures of Lennard-Jones and Stockmayer particles provide a convenient model system which can be used to study the microscopic behaviour of polar/non-polar mixtures with computer simulation techniques Furthermore the simulations also allow the calculation of the thermodynamic properties of mixing for these theoretical fluid mixtures

2. COMPUTATIONAL DETAILS

The energy of interaction between two Stockmayer molecules with dipole moments $\vec{\mu}_1$ and $\vec{\mu}_2$ separated by a distance r_{12} is given by

$$\phi_S(\vec{\mu}_1, \vec{\mu}_2, \vec{r}_{12}) = -\frac{\vec{\mu}^2}{r_{12}^3} D(1,2) + \phi_{LJ}(\vec{r}_{12}) \tag{1a}$$

where

$$D(1,2) = 3(\hat{\mu}_1 \cdot \hat{r}_{12})(\hat{\mu}_2 \cdot \hat{r}_{12}) - \hat{\mu}_1 \cdot \hat{\mu}_2 \tag{1b}$$

where $\wedge$ denotes the unit vector $D(1,2)$ is the angular dependence of the dipolar interaction and ϕ_{iJ} is the usual Lennard-Jones interaction

$$\phi_{LJ}(r) = 4\varepsilon\left\{\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^6\right\} \tag{2}$$

In the work reported here we have studied fluid mixtures of Stockmayer and Lennard-Jones molecules in which the size parameter, σ, and the energy parameter, ε, of the Stockmayer molecules are identical to those of the Lennard-Jones molecules Deviations from ideal mixing in these systems are therefore due entirely to the polarity of the Stockmayer molecules and allows us to study the effect of polarity and composition on the microscopic structure and the thermodynamic properties of these mixtures

Isothermal-isochoric molecular dynamics (MD) calculations have been performed for mixtures with various mole fractions, x_s, of Stockmayer molecules The temperature was held constant with a Nose thermostat (Nose, 1984) using a Nose mass of 100 in reduced units

The simulations were performed at a reduced temperature of $T^* = kT/\varepsilon = 1\ 15$ and a reduced density of $\rho^* = \rho\sigma^3 = 0\ 822$. Both the pure Lennard-Jones and the pure Stockmayer fluids have been studied extensively at this state point previously (Adams and Adams, 1981, Neumann et al 1984, Petersen et al, 1988) The reduced dipole moment, $\mu^* = \mu/\sqrt{\varepsilon\sigma^3}$ was varied between 0 0 and 2 0, covering a range of physically realistic values The long-range dipolar interactions were handled with standard Ewald summation techniques using 'tinfoil' boundary conditions (de Leeuw et al, 1986) A total of 309 reciprocal lattice vectors were used for the evaluation of the Fourier part of the Ewald summation The value of α, the parameter which governs the convergence of the two series in the Ewald sum, was set to 6 58

The simulations were carried out for a total of $N = 108$ particles A few runs were performed with a larger number of particles to study the N-dependence of the results The total energy was found to be almost independent of the number of particles and for the pressure a slight dependence (a few percent) was observed

In the simulations, the system was equilibrated for at least 5000 time-steps and followed by a production run of at least 15,000 time-steps A time-step of $0\ 0025\tau$ was used, where τ is the reduced unit of time defined as $\tau = \sqrt{m\sigma^2/\varepsilon}$

3. RESULTS

3.1 Thermodynamic Properties

In table I we have collected the values of the potential energy obtained from our simulations for various compositions and dipolar strengths The contributions due to the Lennard-Jones interactions, including the long-tail correction, have also been included These contributions are seen to increase with dipolar strength and mole fraction x_s of the Stockmayer molecules This is of course expected due to the tendency of the dipolar interactions to decrease the distance of closest approach which in turn increases the contribution of the repulsive energy in the Lennard-Jones potential

μ^{*2}	Fraction of Stockmayer particles, x_s						
	0 000	0 167	0 333	0 500	0.667	0 833	1 000
0 50	5 526	5 518	5 589	5 599	5 658	5 749	5 825
		5 503	5 548	5 503	5 498	5 515	5 510
1 00	5 526	5 585	5 679	5 831	6 026	6 219	6 451
		5 551	5 517	5 523	5 526	5 481	5 469
1.50	5 526	5 630	6 845	6 125	6 453	6 822	7 223
		5 526	5 514	5 501	5 478	5 456	5 426
2 25	5 526	5 756	6 188	6 683	7 259	7 866	8 517
		5 528	5 484	5 463	5 413	5 355	5 331
3 00	5 526	5 986	6 606	7 331	8 136	9 049	9 920
		5 490	5 432	5 383	5 326	5 253	5 194
4.00	5 526	6 274	7 302	8.364	9.510	10 724	12 039
		5 450	5 353	5 278	5 181	5 070	4 975

TABLE I Potential energy $- U/(N\varepsilon)$ for mixtures of Lennard-Jones and Stockmayer fluids for various compositions x_s and reduced dipolar strengths μ^{*2} (The lower number is the contribution of L-J interactions)

The excess energy of mixing U_{ex} can be readily obtained from the data in table I In figure 1 the variation of U_{ex} with composition is shown for three different values of the reduced dipolar strength μ^{*2} As expected U_{ex} increases with increasing reduced dipolar strength, however the most interesting feature of the figure is the asymmetric behaviour of U_{ex} with respect to the composition The energy of mixing has a maximum at mole fractions x_s slighly less than 0.5, i e at compositions rich in the non-polar component This corresponds with what has been observed experimentally in a number of polar/non-polar mixtures such as CH_3OH/C_6H_8 and C_2H_5OH/C_6H_{14} (King, 1969, pp 27-35)

The asymmetric behaviour has also been observed in the variation of the excess free energy of mixing f_{ex}, as shown elsewhere (de Leeuw et al , 1988) For values of $\mu^{*2} > 4$ it was shown that this leads to a phase separation into an almost pure Lennard-Jones fluid and a Stockmayer-rich phase This agrees with the results of Morriss and Isbister (1986) who solved the site-site Ornstein-Zernicke equation, using the mean spherical approximation closure, for mixtures of polar and non-polar hard-dumbbells

It is instructive to compare our results with those of Wong and Johnston (1984) who performed Monte Carlo simulations of strongly non-ideal liquid mixtures. The dipolar interactions were included in the form of an angle-averaged expression and the behaviour of the excess properties with respect to the composition was found to be highly symmetric. This comparison demonstrates that it is indeed the orientation dependence of the dipolar interactions that is responsible for the asymmetry in the composition dependence of U_{ex} and f_{ex}. A similar asymmetric behaviour is observed for the local composition as a function of the mole fraction of Stockmayer molecules which is discussed in the following section.
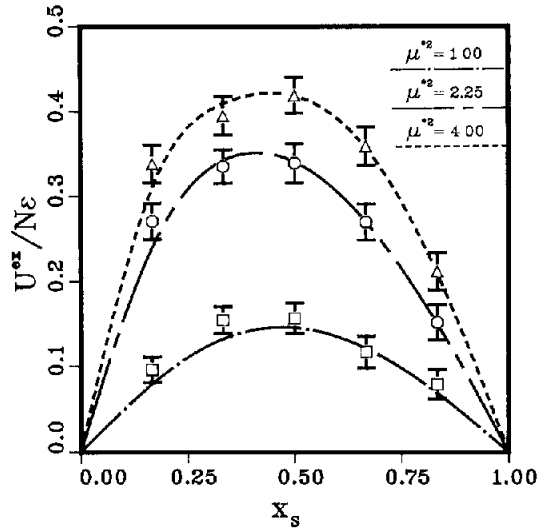

Fig 1 Excess energy of mixing $U_{ex}/N\varepsilon$ versus concentration x_S

In table II values for the compressibility factor $(Z = PV/NkT)$ are given for the various compositions and reduced dipole moments. Again we observe deviations from ideality which behave asymmetrically with respect to the composition.

3.2 Local Composition

The local composition in mixtures of square-well fluids has been thoroughly examined in a series of papers by Lee and Sandler and their co-workers (1984, 1986a, 1986b, 1987). The use of square-well fluids is advantageous in that the cut-off distance in the integrations for the calculation of the local mole fraction is unambiguously defined. Furthermore the properties of such fluid mixtures are claimed to resemble mixtures of Lennard-Jones molecules.

The local composition of equimolar, equal-sized Lennard-Jones mixtures have themselves been studied previouly (Nakanishi and Toukubo, 1979, Nakanishi and Tanaka. 1983, Nakanishi et al 1983) using molecular dynamics and by Wong and Johnston (1984) using Monte Carlo simulations. In both studies a variety of combining rules were used for the energy parameter

μ^{*2}	Fraction of Stockmayer particles, x_S						
	0 000	0 167	0 333	0 500	0 667	0 833	1 000
0 50	2 2	2 4	2 1	2 3	2 2	2 1	2 1
1 00	2 2	2 1	2 2	2 0	1 8	1 9	1 7
1 50	2 2	2 2	2 0	1 8	1 7	1 4	1 2
2 25	2 2	2 1	1 9	1 5	1 3	1 0	0 5
3 00	2 2	2 0	1 7	1 3	0 9	0 4	-0 1
4 00	2 2	1 9	1 5	0 9	0 3	-0 3	-1 0

TABLE II Compressibility factor PV/NkT for mixtures of Lennard-Jones and Stockmayer fluids for various compositions x_S and reduced dipolar strengths μ^{*2}

ε_{ij}, representative of association and solvation forces, in addition to the usual Lorentz-Berthelot (L-B) geometric mean typical of dispersive-only forces

The local composition of Lennard-Jones mixtures with differing component sizes, obeying the L-B mixing rules, has been studied using molecular dynamics (Gierycz and Nakanishi, 1984, Gierycz et al , 1984) Hoheisel and Kohler (1984) investigated the local composition in L-B mixtures of Lennard-Jones fluids with both equal and differently sized particles Lee et al (1986) studied the effects of size and energy differences in both Lennard-Jones and Kihara mixtures These studies concluded that packing effects, and not the attractive forces, are the dominant cause of non-randomness in liquid mixtures obeying the L-B combining rules

The number of i-particles around a central j-particle, within a given distance L, is rigorously defined in terms of the distribution function $g_{ij}(r)$ (Lee et al , 1983) and is given by

$$N_{ij}(L) = x_i\rho \int_0^L dr\, g_{ij}(r) \tag{3a}$$

and similarly for j-particles around a central j-particle

$$N_{jj}(L) = x_j\rho \int_0^L dr\, g_{jj}(r) \tag{3b}$$

For a binary mixture the local mole fractions may then be defined according to the following

$$X_{ij}(L) = \frac{N_{ij}(L)}{(N_{ij}(L) + N_{jj}(L))} \tag{4}$$

with the condition that

$$X_{ij}(L) + X_{jj}(L) = 1\,0 \tag{5}$$

Obviously for continuous interaction potentials the actual value of $X_{ij}(L)$ depends on the choice of L, the cut-off point for the integrations. This is typically chosen to correspond with the end of the first-coordination shell and, as pointed out by Hoheisel and Kohler (1984), should be independent of the type of contact so as to fulfill the requirement that, as L becomes large

$$X_{21} \rightarrow x_2 \tag{6a}$$

$$X_{12} \rightarrow x_1 \tag{6b}$$

In this paper we are more concerned with the trends in the local mole fractions rather than the specific values, however for comparison we have chosen $L/\sigma = 1.35$ in keeping with previous work (Hoheisel and Kohler, 1984)

The local mole fractions X_{ij}, defined by equations (3-5), have been determined for the simulations discussed earlier. The results for X_{SS} and X_{LL} for two of the Stockmayer/Lennard-Jones fluid mixtures studied are shown in figure 2(a,b), for the same three values of the reduced dipole moment shown in figure 1. The values of $X_{SL} (L/\sigma = 1.35)$ and $X_{LS} (L/\sigma = 1.35)$ for all mixtures and dipole moments are given in table III

	Fraction of Stockmayer Particles, x_S				
μ^{*2}	0.167	0.333	0.500	0.667	0.833
0.50	0.1673	0.3315	0.5046	0.6773	0.8312
	0.8419	0.6632	0.5041	0.3393	0.1661
1.00	0.1664	0.3205	0.4980	0.6606	0.8285
	0.8365	0.6418	0.4994	0.3311	0.1654
1.50	0.1614	0.3151	0.4917	0.6611	0.8221
	0.8056	0.6274	0.4917	0.3315	0.1652
2.25	0.1629	0.3055	0.4716	0.6269	0.8294
	0.8103	0.6113	0.4707	0.3132	0.1670
3.00	0.1392	0.2910	0.4692	0.6550	0.7728
	0.6893	0.5860	0.4717	0.3319	0.1550
4.00	0.1424	0.2875	0.4476	0.6171	0.8038
	0.7155	0.5798	0.4541	0.3134	0.1626

TABLE III Local mole fractions X_{SL}(upper) and X_{LS}(lower) at $L/\sigma = 1.35$ for each composition x_S and reduced dipole moment μ^{*2}

The results are also presented in the form used by Lee and Sandler (Lee and Sandler, 1987), who suggested using the ratio
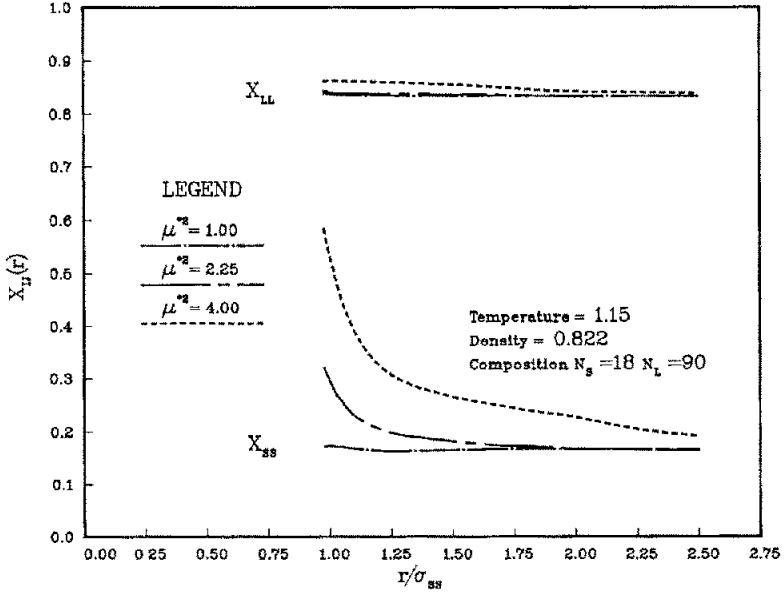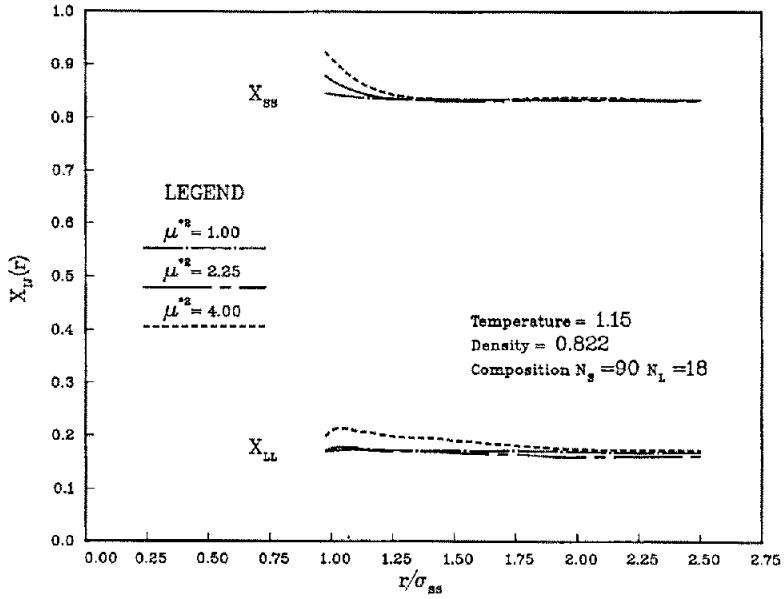
LOCAL MOLE FRACTIONS

FIG 2 a,b Local mole fractions X_{SS} and X_{LL} for two compositions x_S (0 167 and 0 833) and three reduced dipole moments μ^{*2} (1.00, 2 25, 4 00)

$$\frac{N_{ij}x_j}{N_{jj}x_i} \tag{7}$$

which, if equal to unity would indicate a completely random solution These results are shown in figure 3(a,b) and given in table IV (again at $L/\sigma = 1\,35$) for all mixtures considered

The most notable feature of these results is the asymmetry with respect to the composition, as seen previously, with the greatest deviation from a random solution being found for mixtures with low concentrations of Stockmayer particles As discussed above, this is in agreement with our earlier work (de Leeuw et al , 1988)

μ^{*2}	Fraction of Stockmayer Particles, x_s				
	0 167	0 333	0 500	0 667	0 833
0 50	1 0046	0 9916	1 0185	1 0496	0 9847
	1 0653	0 9847	1 0164	1 0270	0 9961
1 00	0 9984	0 9433	0 9920	0 9732	0 9662
	1 0230	0 8958	0 9975	0 9900	0 9911
1 50	0 9623	0 9199	0 9674	0 9754	0 9243
	0 8286	0 8418	0 9674	0 9918	0 9895
2 25	0 9727	0 8799	0 8923	0 8401	0 9724
	0 8543	0 7863	0 6893	0 9119	1 0023
3 00	0 8085	0 8208	0 8839	0 9491	0 6801
	0 4437	0 7077	0 8927	0 9934	0 9171
4 00	0 8300	0 8071	0 8104	0 8057	0 8195
	0 5030	0 6898	0 8317	0 9130	0 9707

TABLE IV Local composition ratios $N_{SL}x_L/N_{LL}x_S$(upper) and $N_{LS}x_S/N_{SS}x_L$(lower) at $L/\sigma = 1.35$ for each composition x_S and reduced dipole moment μ^{*2}

Wong and Johnston (1984) also reported values for the local mole fractions for nonpolar/"polar-like" mixtures Similar to their observations concerning the thermodynamic properties of mixing discussed previously, they found that the local compositions of the systems were symmetric with respect to the bulk concentration This again reinforces our suggestion that the orientation-dependence of the dipole-dipole interaction plays an important role in determining the behaviour of this type of system

4. DISCUSSION

It is interesting to speculate about the origin of the asymmetric behaviour shown in the results given above If one considers two Stockmayer particles within close proximity of each other, in a background of Lennard-Jones particles, then the two polar particles are free to orientate themselves in the most energetically favourable orientation For dipolar particles this occurs when the two are aligned "nose-to-tail" However, increasing the overall concentration of Stockmayer particles increases the probability of a third polar particle also being in the vicinity One can then imagine that the particles are frustrated in their attempts to achieve this optimal orientation for each pair-interaction Therefore some compromise must be achieved
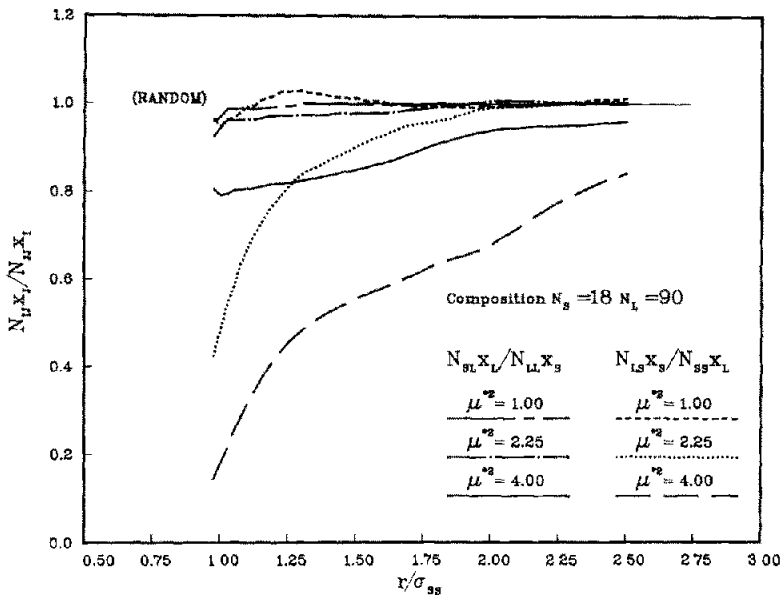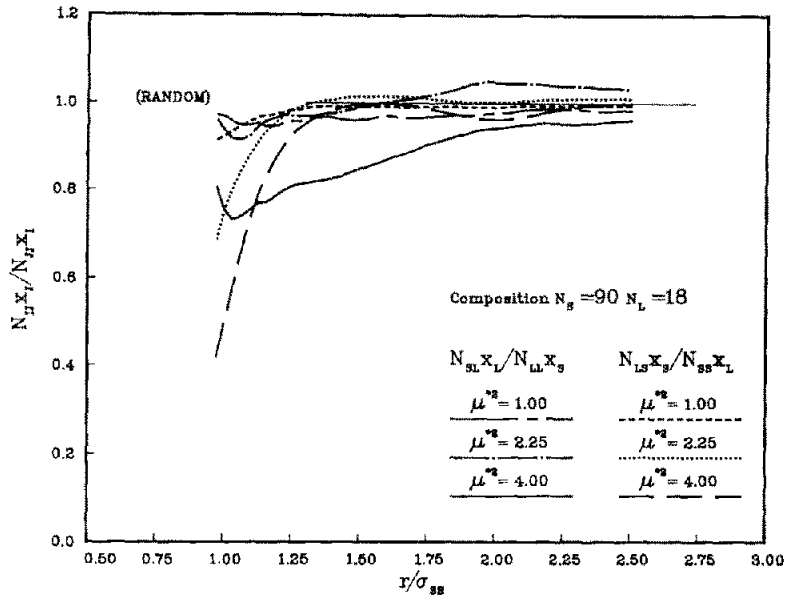
LOCAL COMPOSITION RATIOS

FIG 3 a,b Local composition ratios $N_{Si}x_L/N_{LL}x_S$ and $N_{LS}/N_{SS}x_L$ for two compositions x_S (0 167 and 0 833) and three reduced dipole moments μ^{*2} (1 00, 2 25 and 4 00)

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which will then result in a decrease in the interaction between each pair This arguement is then the basis for our explanation of the observed asymmetry of the results, with respect to the concentration, in terms of our so-called "frustration effect" This suggestion is further re-inforced by the orientation correlation functions for these mixtures which will appear else-where shortly

Acknowledgements

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