

PRELIMINARY COMMUNICATION

Evidence of phase separation in mixtures of Lennard-Jones and Stockmayer fluids

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Molecular dynamics computer simulations have been performed for mixtures of Lennard-Jones (LJ) and Stockmayer molecules of various compositions and dipolar strengths. The free energy of mixing was determined and found to be highly asymmetric with respect to its composition dependence. For values of the dimensionless dipolar strength, $\mu^* = \sqrt{(\mu^2/\epsilon\sigma^3)}$, greater than 2 demixing occurs.

Mixtures of Lennard-Jones and Stockmayer molecules provide a convenient model system which can be used to study the effects of composition and polarity in polar/non-polar mixtures. The structure and phase behaviour of such mixtures are currently topics of great interest [1].

Since the Stockmayer potential, ϕ_S , is obtained from the usual Lennard-Jones potential, ϕ_{LJ} , by the sole addition of a point dipole interaction, the free energy of mixing can be determined in a particularly simple and straightforward manner. Moreover, knowledge of the free energy of the pure components is not required, as can be seen by considering the following two-stage process.

Firstly a fraction of atoms, x , in a pure Lennard-Jones liquid is changed into molecules with a moment of inertia I . One may think of these as Stockmayer molecules with dipole moment $\mu = 0$. The free energy per particle (in units of the LJ well depth ϵ) of this ideal mixture is given by

$$f_1(x) = f_{LJ} + x f_R + T^*[x \ln x + (1-x) \ln(1-x)]. \quad (1)$$

Here f_{LJ} is the free energy of the pure LJ liquid, f_R is the rotational contribution to the free energy, and the last term on the right-hand side of equation (1) is the free energy of ideal mixing. T^* is the reduced temperature defined as $T^* = kT/\epsilon$, where k is Boltzmann's constant.

In the second stage, the Stockmayer molecules are charged to the required value of μ . The free energy change during the charging process can be obtained by thermodynamic integration [2, 3]

$$f(x) = f_1(x) + \int_0^{\mu^2} \left\langle \frac{\partial U}{\partial \mu^2} \right\rangle_{\mu^2} d\mu^2 = f_1(x) + \int_0^{\mu^{*2}} \langle U^{dd} \rangle_{\lambda} \frac{d\lambda}{\lambda}, \quad (2)$$

where U^{dd} is the dipolar energy per particle in reduced units and μ^* is the reduced dipole moment previously defined. The integral in equation (2) represents the work required to charge the dipoles from a dipolar strength of $\lambda = 0$ to their final value of $\lambda = \mu^{*2}$. It is important to recognize that $f(x = 1)$ is the free energy of the pure Stockmayer system, f_s . The free energy of mixing, $\Delta f(x)$, is now readily obtained as

$$\Delta f(x) = f(x) - (1-x)f_{LJ} - xf_s \\ = \int_0^{\mu^{*2}} \{ \langle U^{dd}(x) \rangle_\lambda - x \langle U^{dd}(1) \rangle_\lambda \} \frac{d\lambda}{\lambda} + T^*[(1-x) \ln(1-x) + x \ln x]. \quad (3)$$

Therefore the free energy of mixing can be determined directly from a knowledge of the mean dipolar energy in the mixture and in the pure Stockmayer fluid. These quantities are easily accessible in a molecular dynamics simulation.

We have performed a number of MD computer simulations for mixtures of 108 particles with different compositions, x , and dipolar strengths, μ^* . After equilibration, the equations of motion were integrated over 30 000 time intervals of $\Delta t = 0.002\tau$, where τ is the dimensionless unit time defined as $\tau = \sqrt{(m\sigma^2/\epsilon)}$. The density was fixed at $\rho^* = \rho\sigma^3 = 0.822$ and the temperature at $T^* = 1.15$; the temperature was held constant using a Nosé thermostat [4]. The pure Stockmayer fluid has been studied extensively at this state point previously [5-7].

The results for the mean dipolar energy obtained from the computer simulations are given in the table. In all cases except for $x = 0.167$ the statistical accuracy of our results is 1-2 per cent for the lowest dipole moment and improves to better than 0.1 per cent for the high dipole moment simulations. We have found that $\langle U^{dd} \rangle$ can be well described by

$$\langle U^{dd} \rangle = x^2 \frac{1.697\mu^{*4}}{1 + \alpha(x)\mu^{*2}}. \quad (4)$$

Equation (4) has the correct limiting behaviour [8] as $\mu^{*2} \rightarrow 0$ (in which case one expects $\langle U^{dd} \rangle$ to be proportional to the square of the mole fraction). In the limit of large dipolar strengths equation (4) gives $\langle U^{dd} \rangle \simeq \mu^{*2}$ as estimated by Onsager [9] some 50 years ago. Values of the free parameter α were obtained by fitting equation (4) to the results obtained for $\langle U^{dd} \rangle$ for all mole fractions, x , except again for $x = 0.167$. However, these values are included in the table for completeness. Note

Dipolar energy per particle $-\langle U^{dd}(x) \rangle / (x^2 \mu^{*2})$ for various compositions x and dipolar strengths μ^{*2} ($T^* = 1.15$, $\rho^* = 0.822$).

Dipolar strength μ^{*2}	Fraction of Stockmayer particles, x					
	0.167	0.333	0.500	0.667	0.833	1.000
0.50	0.997	0.749	0.767	0.720	0.676	0.632
1.00	1.195	1.458	1.228	1.125	1.062	0.982
1.50	2.484	2.040	1.644	1.461	1.311	1.199
2.25	3.615	2.816	2.169	1.837	1.607	1.416
3.00	5.946	3.522	2.599	2.107	1.822	1.575
4.00	7.414	4.385	3.086	2.435	2.035	1.766
α	—	0.1433	0.3145	0.4634	0.5959	0.7327

that α varies almost linearly with x according to

$$\alpha(x) = 0.8761x - 0.1341. \quad (5)$$

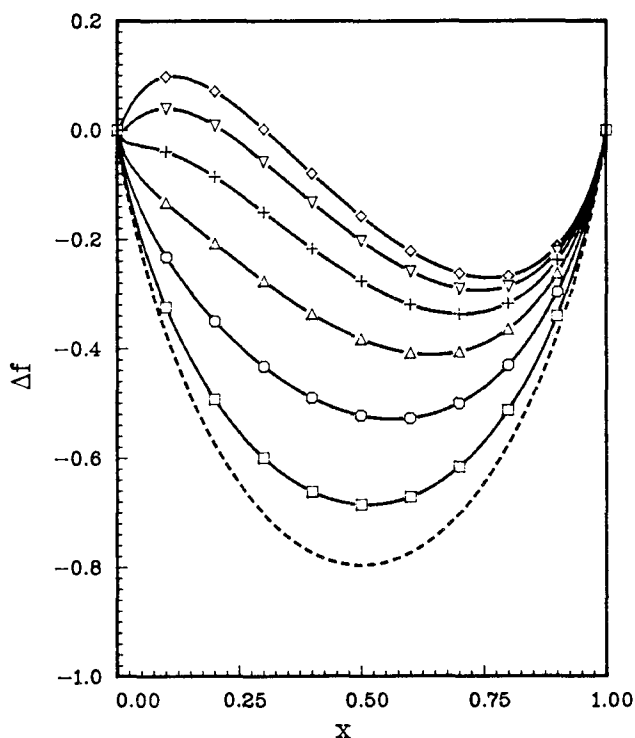
Equation (5) predicts negative values of α for mole fractions $x < 0.153$. At this concentration a plot of $\langle U^{dd} \rangle / \mu^{*2}$ versus μ^{*2} should yield a straight line. Inspection of the data of the table at $x = 0.167$ shows that this is indeed the case. A negative value for α leads to unphysical singularities in the dipolar energy. However, such singularities occur at much higher values of the dipolar strength, μ^* , than those considered here. Moreover, the results for the free energy of mixing appear not to be very sensitive to the precise value of α or indeed to the precise form of equation (4).

The integration in equation (3) can now be performed analytically to yield a rather lengthy expression for the free energy of mixing $\Delta f(x)$. It is then a simple task to construct a plot of $\Delta f(x)$ versus x for various dipolar strengths μ^* . This has been done and the results are shown in the figure.

There are two features worth noting in this figure. Firstly, there is strong asymmetry in the composition dependence of Δf . The excess heat of mixing also shows an

\square $\mu^{*2} = 1.0$	$+$ $\mu^{*2} = 4.0$
\circ $\mu^{*2} = 2.0$	∇ $\mu^{*2} = 5.0$
\triangle $\mu^{*2} = 3.0$	\diamond $\mu^{*2} = 6.0$

IDEAL MIXING



Dimensionless free energy of mixing per particle Δf of mixtures of Lennard-Jones and Stockmayer fluids at $T^* = 1.15$ and $\rho^* = 0.822$ for various values of dipolar strength μ^{*2} . The points are there to label the curves.

asymmetry with respect to composition with a maximum in the region of low concentrations of the polar component. This corresponds with what has been observed experimentally for a number of polar/non-polar liquid mixtures [10], such as methanol/carbon tetrachloride and ethanol/benzene. Secondly, for dipolar strengths $\mu^* > 2$ demixing will occur, giving a Stockmayer rich phase and an almost pure Lennard-Jones phase. The phase separation occurs with mixtures having low concentration of the polar component as would be expected from the maximum in the heat of mixing at these concentrations.

Therefore, we conclude that phase separation can occur in mixtures of Lennard-Jones and Stockmayer liquids with a certain dipolar strength. The full results of our calculations will be published elsewhere [11].

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