

## PRELIMINARY COMMUNICATION

### Free-energy computations for mixtures of Stockmayer and polarizable Lennard-Jones fluids

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Molecular-dynamics calculations are presented for mixtures of polarizable Lennard-Jones and Stockmayer particles. The free energy of mixing is determined as a function of the polarizability. These calculations show that an immiscible mixture of (non-polarizable) Lennard-Jones and Stockmayer molecules can become miscible by adding a sufficiently high polarizability to the Lennard-Jones molecules.

Mixtures of polar/nonpolar constituents are not only important technologically [1], but are also of interest from a theoretical point of view [2-5]. A convenient model for these mixtures is a system of Stockmayer and Lennard-Jones molecules, for which the free energy of mixing has recently been calculated [4]. However, in most studies the effect of polarization of the non-polar molecule is not taken into account. In this paper we show that adding a polarization  $\alpha$  to the (non-polar) Lennard-Jones molecules changes the phase behaviour significantly.

For a mixture of Stockmayer and polarizable Lennard-Jones molecules the energy  $U$  is given by

$$U = \frac{1}{2} \sum_{i,j=1,j \neq i}^N \phi_{LJ}(r_{ij}) - \frac{1}{2} \sum_{i,j=1,j \neq i}^N \boldsymbol{\mu}_i \cdot \mathbf{T}_{ij} \cdot \boldsymbol{\mu}_j + \frac{1}{2} \sum_{i=1}^N \frac{\mu_{\text{induced}}^2}{\alpha}, \quad (1)$$

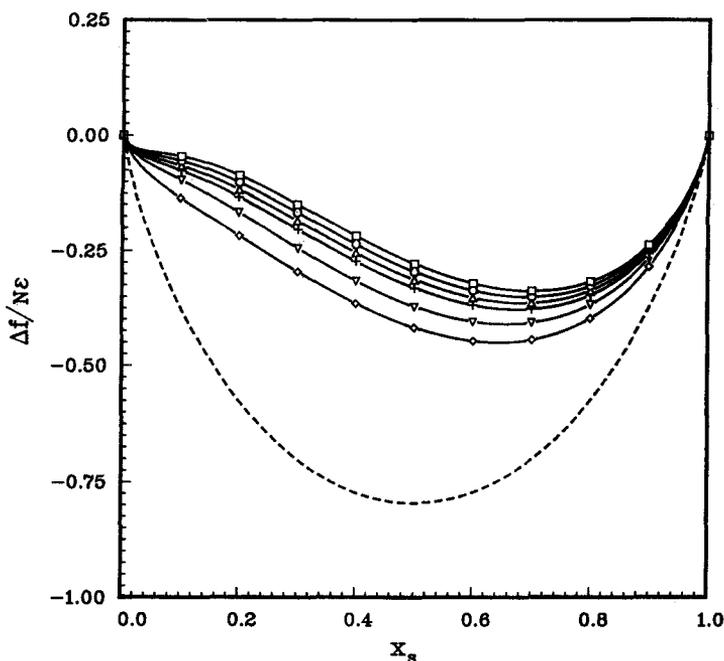
where  $\phi_{LJ}$  is the Lennard-Jones potential and the dipolar interactions are given by

$$\boldsymbol{\mu}_i \cdot \mathbf{T}_{ij} \cdot \boldsymbol{\mu}_j = 3 \frac{(\boldsymbol{\mu}_i \cdot \mathbf{r})(\boldsymbol{\mu}_j \cdot \mathbf{r})}{r^5} - \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r^3}, \quad (2)$$

where for the Stockmayer molecules

$$\boldsymbol{\mu}_i = \boldsymbol{\mu}_{\text{permanent}} \quad (3)$$

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Dimensionless free energy of mixing per particle,  $\Delta f$ , of mixtures of polarizable Lennard-Jones and Stockmayer particles for various polarizabilities  $\alpha^*$ :  $\square$ ,  $\alpha^* = 0$ ;  $\circ$ , 0.01;  $\Delta$ , 0.02;  $+$ , 0.03;  $\nabla$ , 0.05;  $\diamond$ , 0.075; ---, ideal mixing.

and for the Lennard-Jones molecules

$$\mu_i = \mu_{\text{induced}} = \alpha E_{i,\text{local}} = \alpha \sum_{j=1, j \neq i}^N T_{ij} \mu_j, \quad (4)$$

in which  $E_{i,\text{local}}$  is the local field on the  $i$ th molecule.

The effect caused by this polarizability on the free energy of mixing can be calculated by thermodynamic integration:

$$\mathcal{F}(\alpha, \mu) = \mathcal{F}(\alpha = 0, \mu) + \int_0^\alpha d\alpha' \left\langle \frac{\partial U}{\partial \alpha'} \right\rangle_{\alpha'}, \quad (5)$$

where  $\mathcal{F}(\alpha, \mu)$  is the free energy of the mixture and  $\mathcal{F}(\alpha = 0, \mu)$  is the free energy of

The results for  $\langle \partial U / \partial \alpha \rangle$  as a function of the concentration of Stockmayer molecules  $x_s$  and polarization  $\alpha^*$  for  $\mu^{*2} = 4$ ,  $T^* = 1.15$  and  $\rho^* = 0.822$

$\alpha^*$	Fraction of Stockmayer particles, $x_s$				
	0.167	0.333	0.500	0.667	0.833
0.000	1.43	1.86	1.77	1.40	0.81
0.010	1.36	1.80	1.74	1.44	0.84
0.020	1.43	1.81	1.73	1.45	0.86
0.030	1.53	1.80	1.81	1.47	0.88
0.040	1.42	1.91	1.92	1.60	0.91
0.050	1.60	2.00	1.95	1.63	0.93
0.075	1.63	2.16	2.22	1.78	1.03

a mixture of polar/(non-polarizable) non-polar components. The latter has been computed in [4]. It can be shown that for  $\langle \partial U / \partial \alpha \rangle$  [6],

$$\left\langle \frac{\partial U}{\partial \alpha} \right\rangle = \left\langle -\frac{1}{2} \sum_i' \mathbf{E}_{i,\text{local}}^2 \right\rangle, \quad (6)$$

where the prime denotes that the summation is carried out only over the polarizable molecules.

We have performed MD computer simulation for mixtures of 108 particles with density 0.822 and different fractions of Stockmayer molecules  $x_s$  and polarizabilities. The chosen polarizabilities cover the range of values typical of noble-gas atoms [7]. The temperature was kept constant at  $T^* = 1.15$  using a Nosé thermostat [8]. After 10 000 equilibration steps the equations of motion were integrated over at least 30 000 time intervals  $\Delta t = 0.002\tau^*$  ( $\tau^* = (m\sigma^2/\epsilon)^{1/2}$ ). The long-range dipole interactions were handled with the Ewald summation technique using 'tinfoil' boundary conditions [5]. The induced dipole moments were computed by solving (3) iteratively, using one second-order predictor step [9] followed by about three iteration steps.

In this study we used  $\mu^* = 2(\mu^* = \mu/(\epsilon\sigma^3)^{1/2})$ , since previous results have indicated that at this dipolar strength, for  $\alpha = 0$ , phase separation may occur into a phase rich in polar component and an almost pure Lennard-Jones phase.

The results for  $\langle \partial U / \partial \alpha \rangle$  for various  $\alpha^*$  ( $= \alpha/\sigma^3$ ) and  $x_s$  are given in the table. These data were fitted to a second-order polynomial for each composition. Using this polynomial, the integration of (1) was performed analytically. The resulting free energy appears not to be very sensitive to the details of the fit. The final values were fitted to a NRTL equation of state [10]. The results are shown in the figure. From this figure we conclude that, as the polarizability increases, the excess free energy of the mixture becomes more symmetric with respect to the composition. Furthermore, if we assume that the excess volume can be disregarded, the figure suggests that for  $\alpha^* \lesssim 0.075$  the polar/polarizable non-polar mixture becomes miscible.

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