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CHEMICAL SCIENCES DIVISION

To be presented at the Sixth International Conference on Fluid Properties and Phase Equilibria for Chemical Process Design, Cortina d'Ampezzo, Italy, July 19-24, 1992, and to be published in the Proceedings

Liquid-Liquid Equilibria in Binary Systems: Monte-Carlo Simulations for Calculating the Effect of Nonrandom Mixing

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April 1992

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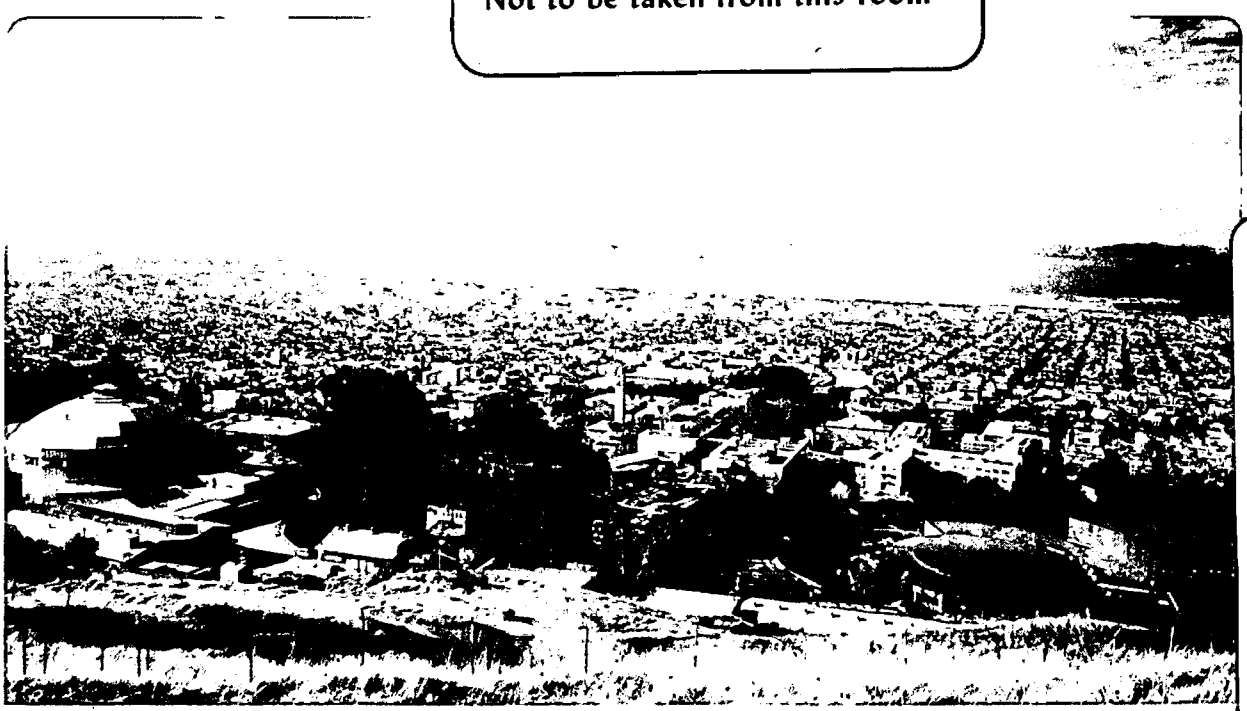

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098. Additional support was provided by E. I. du Pont de Nemours & Co., Montedipe s.r.l., Atochem, and Koninklijke/Shell.

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LIQUID-LIQUID EQUILIBRIA IN BINARY SYSTEMS: MONTE-CARLO SIMULATIONS FOR CALCULATING THE EFFECT OF NONRANDOM MIXING

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ABSTRACT

Monte-Carlo simulations of a lattice model for incompressible monomer/r-mer mixtures are used to obtain accurate results for the configurational energy of mixing. Based on simulation results, the energy of mixing is correlated as a function of temperature and composition using an empirical expression. The configurational Helmholtz energy is obtained upon using the Gibbs-Helmholtz equation with Guggenheim's athermal entropy of mixing as boundary condition. Since Monte-Carlo simulations give essentially exact results for the lattice model, the effects of nonrandom mixing on the configurational thermodynamic properties of a binary mixture can be determined. The expression generated here produces coexistence curves that are more accurate than those from other models, especially near the critical region.

INTRODUCTION

Lattice models provide a convenient starting point for a theoretical description of the thermodynamic properties of concentrated solutions. Historically, they have proven useful in the correlation of single-phase mixture properties such as activity coefficients and heats of mixing, but they frequently give inadequate results when applied to liquid-liquid phase equilibria. Common models, such as the Flory-Huggins (FH) model (Flory, 1953) or the Quasi-Chemical (QC) model (Guggenheim, 1952), produce liquid-liquid coexistence curves which are too narrow or parabolic near the critical region when compared to experimental data.

Previously reported failures of the lattice model for liquid-liquid coexistence curves is due, at least in part, to *mathematical* approximations for taking into account effects of nonrandom mixing to obtain an analytical solution to the lattice model. These failures are not primarily due to the use of a lattice to visualize the effects of nonrandom mixing on local composition. Some models, such as the FH model, do not take nonrandom mixing into account at all; the FH model is only the Bragg-Williams Random Mixing (RM) model (Hill, 1956) extended to chain systems. The QC model attempts take nonrandom mixing into account, but it is only accurate for small deviations from random mixing. More recent is the Lattice Cluster (LC) model (Madden,

Pesci, & Freed, 1990; Dudowicz, Freed & Madden, 1990) which is a formal method for the exact solution of the lattice model. However, in practice (to date) the LC model remains deficient for the correlation of liquid-liquid equilibria.

The goal of this work is to evaluate the effects of nonrandom mixing on liquid-liquid equilibria using Monte-Carlo simulations of the same lattice used in earlier models. Results of the Monte-Carlo simulations are used to formulate a more accurate expression for the energy of mixing of monomer/r-mer mixtures; this expression is used to obtain an expression for the Helmholtz energy of mixing. The coexistence curves predicted using this expression are compared to those from other models and to Monte-Carlo simulations for finding the binodal. Finally, some comments are presented concerning the ability of the lattice model to correlate experimental liquid-liquid equilibria.

DESCRIPTION OF MODEL

The description of the lattice model starts with a simple cubic lattice (coordination number, $z = 6$) containing N_r sites. The lattice is filled completely by N_1 molecules of type 1 and N_2 molecules of type 2. Molecules of type 1 occupy only one lattice site ($r_1 = 1$), whereas molecules of type 2 are flexible chain molecules (r-mers) which occupy r_2 nearest-neighbor lattice sites. Consideration is restricted to nearest-neighbor interactions. The configurational partition function on mixing, $Q(N_r,N_1,T)$, is

$$Q(N_r,N_1,T) = \sum_{N_{12}} g(N_{12}) \exp\left[-\frac{N_{12}\,\varepsilon}{2kT}\right] \tag{1}$$

where the sum is over all possible numbers of 1-2 nearest-neighbor pairs, N_{12}. The combinatorial factor, $g(N_{12})$, is the degeneracy of configurational states which have N_{12} nearest-neighbor 1-2 pairs. Since the lattice is incompressible, the only relevant interaction energy is the interchange energy, $\varepsilon = 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}$, where ε_{ij} is the (non-bonded) i-j nearest-neighbor interaction energy. A dimensionless temperature is defined by $\tilde{T} = kT/\varepsilon$, where T is absolute temperature and k is Boltzmann's constant. The sum in equation (1) is replaced by its maximum term. As a result, concentration fluctuations, or fluctuations in N_{12}, are not considered. The relationship between N_{12} and $g(N_{12})$ to the configurational Helmholtz energy, $\Delta_{mix}A$, is given by:

$$\frac{\Delta_{mix}A}{N_r\,kT} = -\frac{\ln g(N_{12})}{N_r\,k} + \frac{N_{12}\,\varepsilon}{2\,N_r\,kT} = -\frac{\Delta_{mix}S}{N_r\,k} + \frac{\Delta_{mix}U}{N_r\,kT}\,. \tag{2}$$

The logarithm of the combinatorial factor is proportional to the entropy of mixing, $\Delta_{mix}S$, and N_{12} is proportional to the energy of mixing, $\Delta_{mix}U$. Most models begin by proposing a form of $g(N_{12})$ and then derive the average value of N_{12} by finding the maximum term in equation (1) using a variational technique (Kemeny, et al., 1990). It is in the choice of $g(N_{12})$ where most of the severe mathematical simplifications are made to obtain an analytical solution for $\Delta_{mix}A$.

Because no statistical mechanical method is available for determining $g(N_{12})$ exactly, an alternative method is used here for determining the Helmholtz energy of mixing. This method focuses on knowledge of N_{12} as obtained from Monte-Carlo simulation. The energy of mixing is related to the number of nearest-neighbor pairs by

$$\frac{\Delta_{mix}U}{N_r\,\varepsilon} = \frac{1}{2}\frac{N_{12}}{N_r}\,. \tag{3}$$

If N_{12} is known as a function of composition and (dimensionless) temperature, then the contribution to the Helmholtz energy due to nonrandom mixing can be calculated by integrating the Gibbs-Helmholtz equation:

$$\frac{\Delta_{mix}A}{N_r\,kT} - \left(-\frac{\Delta_{mix}S^*}{N_r\,k}\right) = \int_0^{\frac{1}{\tilde{T}}} \frac{\Delta_{mix}U}{N_r\,\varepsilon}\, d\left(\frac{1}{\tilde{T}}\right)\,. \tag{4}$$

The lower limit of integration is the athermal reference state designated by *. Therefore, we must know the *athermal* entropy of mixing [or equivalently $g(N_{12}^*)$, where N_{12}^* is the number of nearest-neighbor 1-2 pairs in a random or athermal mixture]. There are several choices: Flory's (1953) expression, Guggenheim's (1952) expression, or the LC expression. Guggenheim's athermal entropy of mixing is chosen here because it includes chain connectivity, which Flory's expression does not. For athermal systems, Guggenheim's expression produces results essentially identical to those of the LC model. Guggenheim's athermal entropy of mixing is

$$-\frac{\Delta_{mix}S^*}{N_r\,k} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \frac{z}{2}\left[\phi_1\frac{q_1}{r_1}\ln\frac{\theta_1}{\phi_1} + \phi_2\frac{q_2}{r_2}\ln\frac{\theta_2}{\phi_2}\right] \tag{5}$$

where ϕ_i is the volume fraction of component i, $\theta_i = N_1q_1/(N_1q_1 + N_2q_2)$ is the surface fraction of component i, and q_i is the surface area parameter; $zq_i = r_i(z-2) + 2$.

MONTE-CARLO SIMULATIONS

Monte-Carlo simulations were performed using a simple cubic lattice with L sites on each box edge and with periodic boundary conditions. The lattice is completely filled with a fixed composition of monomer and r-mer. Standard Metropolis Monte-Carlo sampling (Allen & Tildesley, 1987; Chandler, 1987) was used to accept or reject generated configurations. For the case where $r_1 = r_2 = 1$ (Ising Lattice), new configurations were sampled by randomly picking two different types of molecules and switching their identities.

For cases where $r_1 = 1$ and $r_2 > 1$, r-mer conformations are sampled by reptation (Wall & Mandel, 1975). A brief description of the reptation algorithm is as follows: 1) A chain is picked at random. 2) A segment at one end of the picked chain is chosen also at random. 3) A nearest-neighbor site of the segment at the other end is chosen. 4) If this site is occupied by another r-mer segment then the move is rejected. If occupied by a monomer, then the end segment is switched with the monomer and made the head of the chain generating a new configuration.

Only the linear combination of interaction energies, ε, is important. Therefore, the simulation is simplified by setting ε_{11} and ε_{22} to zero and only setting ε_{12}. The dimensionless temperature of the simulation is fixed by specifying $kT/2\varepsilon_{12}$. The energy of the system (in units of kT) is given by $N_{12}^{(v)}/2\tilde{T}$, where $N_{12}^{(v)}$ is the number of nearest-neighbor 1-2 pairs of configuration v. Consequently, determination of the number of nearest-neighbor 1-2 pairs appears naturally in the simulation. Simulations were only performed at temperatures in the single-phase region.

The lattice size varied with the length of the polymer chains simulated. As a rule of thumb, lattice sizes $L > 2\sqrt{r_2} + 5$ were used (Rodriguez & Freire, 1991). Table 1 lists the box size and number of (equilibrated) attempted moves averaged for each chain length simulated. For a specific chain length, no change in the

results was observed when the box size was increased to a value larger than that listed in Table 1. Figure 1 shows typical results for the energy of mixing for monomer/20-mer mixtures as a function of r-mer volume fraction for different dimensionless temperatures. Since the reptation algorithm is not efficient for long polymer chains at high polymer volume fractions, results could not be obtained at volume fractions of r-mer > 0.8 for $r_2 > 50$.

CORRELATION OF SIMULATION DATA

The algebraic form to correlate energy of mixing data from Monte-Carlo simulations is a Redlich-Kister expansion truncated after the third term:

$$\frac{2\,\Delta_{mix}U}{N_r\,\varepsilon} = \phi_1\,\phi_2\left[A' + B'(\phi_2-\phi_1) + C'(\phi_2-\phi_1)^2\right] \tag{6}$$

where ϕ_1 and ϕ_2 are monomer and r-mer volume fractions, respectively. Parameters A′ and C′ depend on dimensionless temperature and r-mer chain length only. To a good approximation, B′ is independent of dimensionless temperature and depends only on r-mer chain length. The temperature dependence of A′ and C′ is correlated by

$$A' = a_0 + a_1\left[\exp\left(1/\tilde{T}\right) - 1\right] \quad ; \quad C' = c_0 + c_1\left[\exp\left(1/\tilde{T}\right) - 1\right] \tag{7}$$

Parameters a_0, a_1, B′, c_0, and c_1 depend only on r-mer chain length. The function of temperature, $\exp(1/\tilde{T}) - 1$, arises in Guggenheim's Quasi-Chemical model. It was found that the temperature dependence of A′ and C′ behaved linearly (to within the relative error of the fit) with this temperature function.

Figure 2 shows the chain-length dependence of a_0, a_1, and B′. The parameters appear to reach asymptotic values as r_2 increases. Parameters c_0 and c_1 do not behave as smoothly as a function of r_2 as a_0, a_1, and B′. Fortunately, these two parameters provide only very small contributions to the energy of mixing. Fixing $c_0 = 0$ and $c_1 = 1.20$ does not affect the quality of the fits of the simulation data nor the resulting coexistence curves. The following equations represent the r-mer dependence of a_0, a_1, and B′:

$$a_0(r_2) = 6 - \frac{0.9864\,(r_2-1)}{1 + 0.8272\,(r_2-1)} \tag{8}$$

$$a_1(r_2) = -1.2374 - \frac{0.09616\,(r_2-1)}{1 + 0.1458\,(r_2-1)} \tag{9}$$

$$B'(r_2) = \frac{0.8186\,(r_2-1)}{1 + 0.76494\,(r_2-1)} \tag{10}$$

These equations allow smooth extrapolation to larger values of r_2 not simulated.

Substitution of equation (6) into equation (4) yields

$$\frac{\Delta_{mix}A}{N_r\,kT} = -\frac{\Delta_{mix}S^*}{N_r\,k} + \frac{1}{2}\phi_1\,\phi_2\left[A + B(\phi_2-\phi_1) + C(\phi_2-\phi_1)^2\right] \tag{11}$$

where A, B, and C are the integrated forms of A′, B′, and C′:

$$A = a_0/\tilde{T} + a_1\left[\exp\left(1/\tilde{T}\right) - 1\right] \quad ; \quad B = B'/\tilde{T} \quad ; \quad C = c_0/\tilde{T} + c_1\left[\exp\left(1/\tilde{T}\right) - 1 - 1/\tilde{T}\right] \quad . \tag{12}$$

Equations (11) and (12), together with Guggenheim's athermal entropy of mixing [equation (5)], give an expression for the Helmholtz energy of mixing of a monomer(1)/r-mer(2) mixture. Equation (11) provides a

simple and accurate lattice model expression for predicting liquid-liquid equilibria. It must emphasized that parameters a_0, a_1, B', c_0 and c_1 are *not* adjustable parameters. They are known functions of r_2 as determined from Monte-Carlo simulation results. The equation for $\Delta_{mix}A$ derived here has the same two inputs as those for all previous lattice models: r-mer chain length, r_2, and interchange energy ε/k.

RESULTS AND DISCUSSION

Comparison with MC calculation of binodal and other models

Figure 3 presents a comparison of coexistence curves for a monomer/monomer (Ising lattice) mixture. The points in Figure 3 are results of a lattice Gibbs-ensemble Monte-Carlo simulation (Panagiotopolous, et al, 1988) used explicitly to find the binodal. Agreement between the Monte-Carlo points and the result calculated using equation (11) is excellent. Note the deficiency of the LC model for this mixture, which gives results poorer than those from both this model and the QC model. As expected, the RM model gives the poorest agreement. Figure 3 is analogous to the result when models, such as the RM or QC models, are used to correlate experimental liquid-liquid equilibria. If a tie line is used to determine model parameters, the calculated coexistence curves overshoot the critical point. If the critical point is fit, the models produce coexistence curves which are much too narrow relative to experiment. The dimensionless critical temperature, $\tilde{T}_c = 1.129$, for the model presented here, comes close to the most accurate theoretical value $\tilde{T}_c = 1.128$ (Fisher, 1967).

Figure 4 compares coexistence curves for a highly asymmetric monomer/100-mer mixture. Monte-Carlo simulation points are from Madden, et al. (1990). Here equation (11) slightly under-predicts the simulation results. Here the LC model appears to do a better job, but this result is deceiving. If the LC coexistence curve near the critical point is examined closely, an anomalous curvature can be seen which is not realistic. If coexistence curves for higher values of r_2 are calculated, the anomalous curvature persists at low r-mer concentrations. Also, as demonstrated in Figure 3, the LC model produces inaccurate coexistence curves for mixtures where r_2 is small, i.e. $1 \leq r_2 \leq 20$.

Figure 5 compares the scaling behavior of the critical point with r-mer chain length for this model to those of other models. Note the difference in critical dimensionless temperature between this model and the FH and QC models. A difference also exists between the calculated values of the critical r-mer volume fraction. At larger values of r_2, the critical r-mer volume fraction is about twice that calculated by the FH model. This is consistent with comparisons to experiment (Shultz & Flory, 1952). Note, however, that at larger r_2 values, both this model and the FH model give the same slope of –1. The strange curvature exhibited by the LC model is indicative of the anomalous shapes of the coexistence curves indicated above.

Comparison with experiment

To correlate experimental liquid-liquid equilibria, it is necessary to fix lattice-model parameters, r_2 and ε/k. The simplest choice for the determination of ε/k is to use the experimental upper-consolute critical temperature. For r_2, there are two simple choices. One is make the ratio r_2/r_1 equal to a ratio of characteristic volumes, such as the molar volumes at a specified temperature. A second choice is to adjust r_2 to give agreement with the experimental critical composition. The energy parameter, ε/k, has no effect on the shape of the coexistence curve for a specified value of r_2. Therefore, r_2 is the most important parameter to determine the shape of calculated coexistence curves. Unless otherwise noted, the first method for the estimation of r_2 was

used. The four examples used are binary systems consisting of nearly non-polar molecules, consistent with the assumptions of the lattice model. Two of the systems contain large molecules (polymers) in a solvent. The other systems contain smaller molecules of roughly equal size.

Figure 6 compares calculated and experimental coexistence curves for poly(isobutylene)/diisobutyl ketone mixtures (Shultz & Flory, 1952). For the two larger molecular weights of polymer, r_2 was determined by the ratios of molar volumes. For the lowest molecular weight, r_2 was adjusted to agree with the experimental critical volume fraction. Agreement between the model and experiment is good. The calculated values of ε/k depend weakly on molecular weight; they are (from highest to lowest molecular weight) 97.4 , 97.0 , and 93.0 K. Figure 6 also shows results obtained from the FH model.

Figure 7 compares calculated and experimental coexistence curves for poly(styrene)/cyclohexane mixtures (Bae, et al., 1991). The nearly equal energy parameters are (from highest to lowest molecular weight) 90.5 , 90.6 , and 90.9 K. For this case the agreement between experiment and the model is not good. While the model does a reasonable job in predicting the critical volume fractions, the shapes of the coexistence curves are not accurately represented.

Figure 8 compares calculated and experimental coexistence curves for carbon tetrachloride(1) and perfluoromethylcyclohexane(2) (Hildebrand & Cochran, 1949). At 20°C the ratio of molar volume for these component is 2.00. The calculated energy parameter is 197.8 K. Again the coexistence curve calculated using the model developed here does not accurately represent the experimental coexistence curve. It is also slightly off in the prediction of the critical composition. The model does, however, produce a coexistence curve wider than those from the RM model or the QC model.

Figure 9 compares calculated and experimental coexistence curves for methane(1) and perfluoromethane(2). Here the value $r_2 = 1.20$ was adjusted to give good agreement with experiment. The calculated coexistence curve does not quite match experiment, but it significantly better than that obtained from the RM model and the QC model.

Comparison with experiment shows that the much-improved lattice model derived here is not, in general, reliable for representing binary liquid-liquid equilibria with an upper consolute temperature. While representation with the improved model is much better than with the Random-Mixing or Quasi-Chemical models, some deficiency remains. Possible sources for this deficiency are:

1) Density (equation-of-state) effects which relax the assumption of close packing. Much previous work (Sanchez & Lacombe, 1978; Patterson, 1969) has shown that density effects are essential for explaining lower critical solution temperatures that lie above the upper critical solution temperature. The work presented here has considered only liquid-liquid equilibria with an upper critical solution temperature where neither component is appreciably expanded. Nevertheless, even small density effects may have a nontrivial effect on liquid-liquid equilibria below the upper critical solution temperature.

2) Fluctuations in N_{12} near the critical point. The derivation presented here neglects contributions of such fluctuations to the Helmholtz energy because the summation in the partition function is replaced by its maximum term. These fluctuations are important only very close (less than 0.1 °C) to the critical point and it is therefore not likely that they have a significant influence on the liquid-liquid coexistence curves of

temperatures more than say, 1 °C below the critical temperature. Nevertheless, it may be useful to study the effect of fluctuations using modern theory of critical phenomena (McMahon & Glandt, 1988).

3) Oriented intermolecular forces. For the systems shown in Figures 6-9, it is unlikely that oriented forces play a significant role. Nevertheless, it is likely that a better fit of the data can be obtained by using a secondary lattice (Hu, et al., 1991). This likely better fit, however, requires at least one more binary parameter.

4) In the model used here, no allowance is made for variable flexibility of the chain molecules. The model implicitly assumes that poly(isobutylene) (Figure 6) has the same flexibility as polystyrene (Figure 7). Further, the solvent molecule (diisobutyl ketone in Figure 6 and cyclohexane in Figure 7) is considered to be a monomer where the concept of flexibility does not apply. It is likely that this deficiency is primarily responsible for lack of consistent agreement between lattice-model and experimental results.

CONCLUSION

Because statistical mechanics cannot provide a reliable expression for the combinatorial factor of a binary mixture represented by a Flory-Huggins lattice, Monte-Carlo simulations have been obtained for the number of monomer/r-mer nearest neighbors for a large number of representative binary systems. The Monte-Carlo results were fit empirically to yield an expression for the Helmholtz energy of mixing. This expression permits calculation of liquid-liquid equilibria without using restrictive approximations for the effect of nonrandom mixing present in other models.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Dept. of Energy under Contract DE-AC03-76SF00098. This work was also supported by E.I. du Pont de Nemours & Co., Montedipe s.r.l, Atochem, and Koninklijke/Shell. The authors also thank Juan de Pablo and Alex Sassi for advice and assistance with the Monte-Carlo simulations.

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TABLE 1.
Monte-Carlo simulation parameters.

r-mer chain length, r_2	Box edge length, L	Dimensionless temperatures simulated, kT/ε	Number of (equilibrated) moves attempted at each T ($\times 10^{-6}$)
1	20	∞, 50, 20, 10, 8, 6, 4, 3, 2, 1.5	24
2	20	∞, 10, 8, 6, 4, 3, 2	24
3	20	∞, 10, 8, 6, 4, 3, 2	81
4	20	∞, 10, 8, 6, 4, 3, 2	24
5	20	∞, 10, 8, 6, 4, 3	24
10	20	∞, 10, 8, 6, 4, 3	24
20	30	∞, 10, 8, 6, 4, 3	24
50	30	∞, 10, 8, 6, 4, 3	81
100	40	∞, 10, 8, 6, 4	96

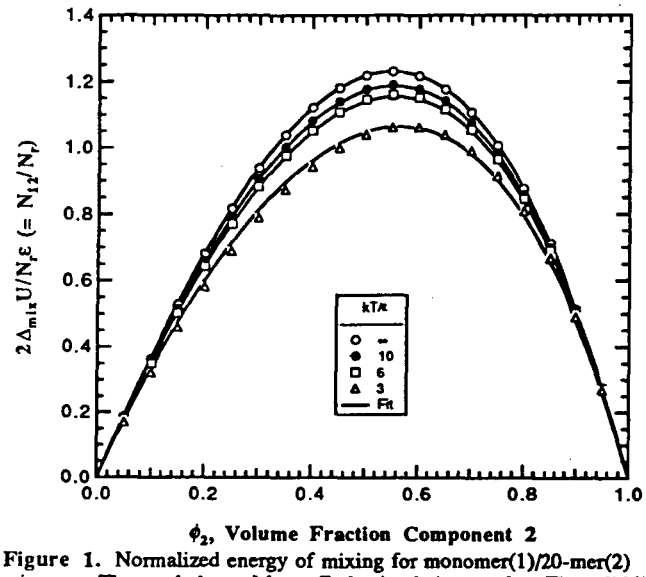

Figure 1. Normalized energy of mixing for monomer(1)/20-mer(2) mixtures. The symbols are Monte Carlo simulation results. The solid lines are the fit given by Equation (6).

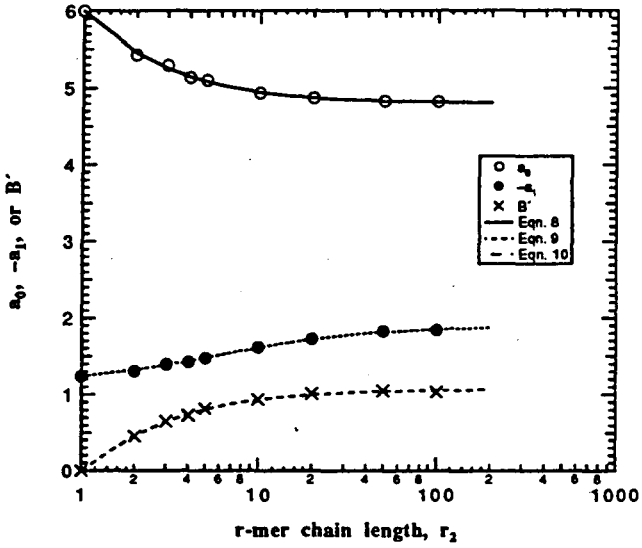

Figure 2. Dependence of parameters a_0, a_1, and B′ on r-mer chain length. (Note log scale on horizontal axis.)

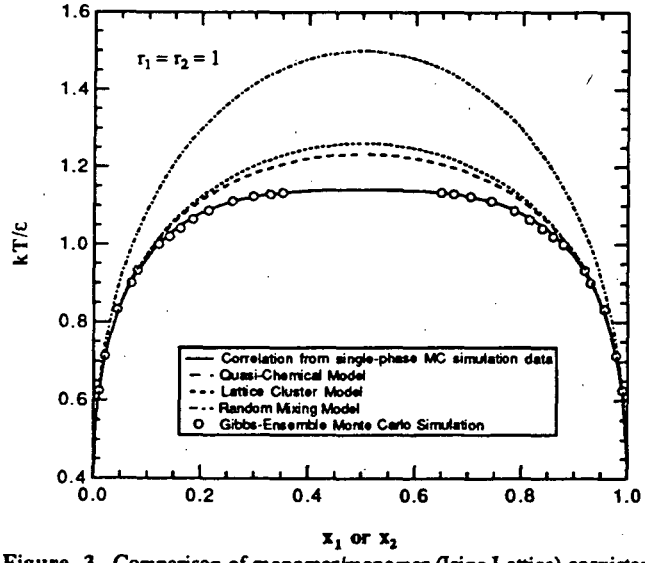

Figure 3. Comparison of monomer/monomer (Ising Lattice) coexistence curves calculated by various models and by Gibbs-Ensemble Monte-Carlo simulation.

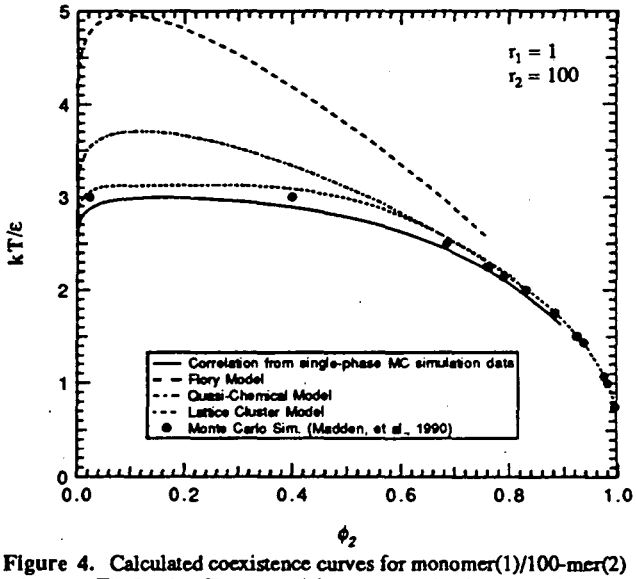

Figure 4. Calculated coexistence curves for monomer(1)/100-mer(2) mixtures. The Lattice Cluster model appears to give better results; however, that model gives (erroneous) points of inflection on the coexistence curve near the critical point.

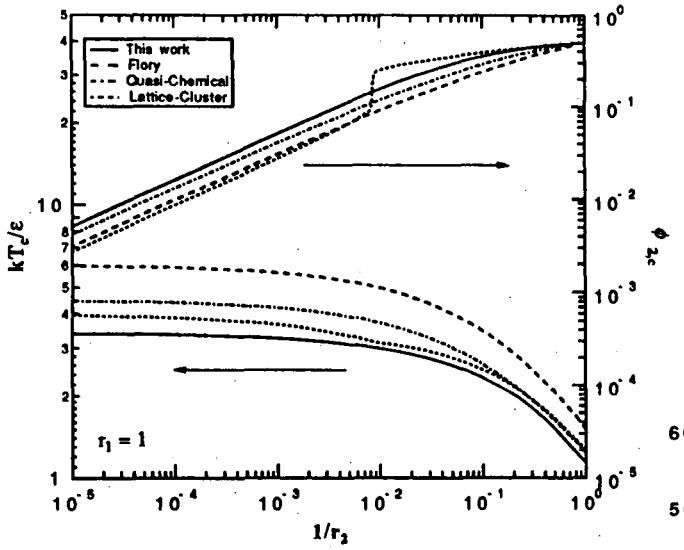

Figure 5. Critical dimensionless temperatures and critical r-mer volume fractions as a function of reciprocal r-mer chain length.

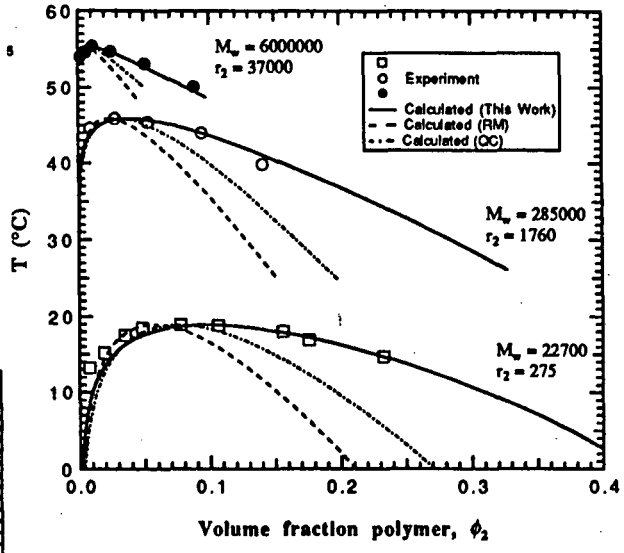

Figure 6. Coexistence curves for poly(isobutylene)/diisobutyl ketone mixtures.

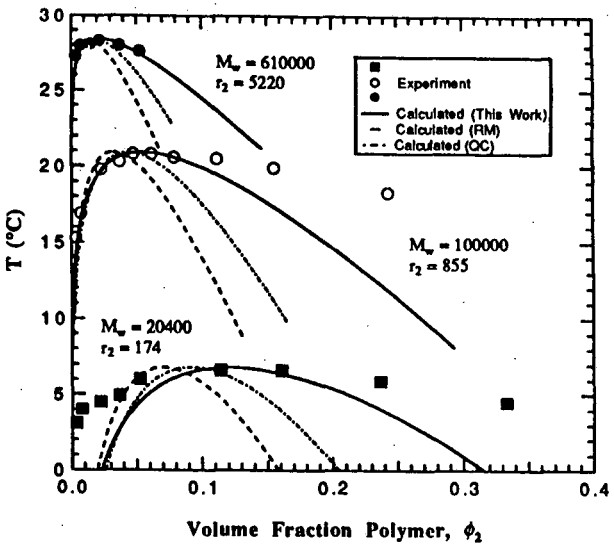

Figure 7. Coexistence curves for poly(styrene)/cyclohexane mixtures.

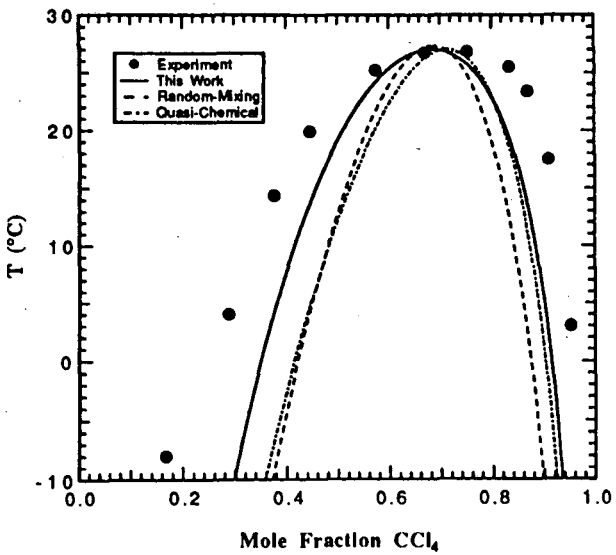

Figure 8. Coexistence curve for $CCl_4(1)/c\text{-}C_6F_{11}CF_3(2)$ mixtures.

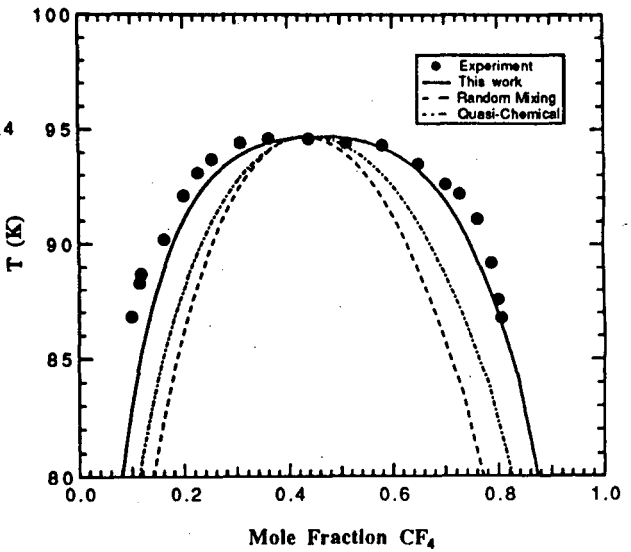

Figure 9. Coexistence curves for $CH_4(1)/CF_4(2)$ mixtures.

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