Application of Molecular Simulation To Derive Phase Diagrams of Binary Mixtures

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Received January 24, 1992; Revised Manuscript Received April 2, 1992

ABSTRACT: The miscibility behavior of three binary mixtures, solvent with solvent, polymer with solvent, and polymer with polymer, was studied by use of a combination of the Flory–Huggins theory and molecular simulation techniques. Fundamental parameters in the Flory–Huggins theory, including the heat of mixing associated with pairwise interactions (Δw_{12}) and the number of possible interaction partners, i.e., coordination number, z, are calculated from molecular simulations. The pair energies (w_{11}, w_{22}, w_{12}) are obtained by averaging a large number of configurations generated by a Monte Carlo approach which includes the constraints associated with excluded volume. The temperature dependence of the interaction parameter χ is obtained with the formalism developed in this study. In all cases, the calculated upper critical solution temperatures compare favorably with experimental values. This approach provides an opportunity to test the Flory–Huggins theory for a number of model binary systems and to characterize their miscibility behavior. This combined approach also facilitates study of the thermodynamic behavior of a binary mixture without possessing specific knowledge or experimental data of the system under investigation.

Introduction

The miscibility behavior of binary mixtures, both small molecular systems and macromolecular systems, has proven to be of interest from theoretical and practical points of view. Some important applications directly related to this subject include selection of solvent for a particular solute, definition of solvent mixing behavior, inclusion of plasticizers in polymers, definition of polymer dissolution and swelling processes, and derivation of phase diagrams for molecular and polymeric alloys. Although the solution thermodynamics and phase equilibrium theory have been well established to perform such calculations for binary systems, difficulties are often encountered during actual implementation due to the absence of detailed information regarding each component. Many parameters characteristic of a binary mixture are thus obtained by fitting a theoretical model with some experimental data. Prediction of the thermodynamic behavior for a system which is not well-known remains a difficult task.

This situation has recently been improved by advances in the area of atomistic and molecular simulation techniques using powerful workstations. Accurate force fields can usually be established by defining parameters in interatomic potentials using structural and spectral data. Molecular simulations can then be accomplished for a variety of systems, including well-characterized ones in order to gain a better fundamental understanding of atomic level interactions and statistics and ill-characterized systems in order to predict useful physical properties. Many factors govern mixing processes, including the chemical nature of individual components as well as temperature. For polymers, additional factors may include chain packing, the degree of crystallinity, molecular weight, and chain flexibility. Although all these factors cannot be addressed by the molecular simulation technique, it is possible in selected cases to obtain structural data for individual components in the mixture as well as the interaction energy terms required for the thermodynamic expressions.

Miscibility behavior can best be illustrated by calculating the free energy of mixing as a function of composition at different temperatures. A schematic drawing of such a calculation for a system exhibiting the upper critical solution temperature (UCST) is shown in Figure 1 as an example. At temperatures above the critical temperature T_{cr}, the ΔG (Gibbs free energy of mixing) versus ϕ_2 (volume fraction of second component) has only one minimum. Two components are miscible for any composition. For temperatures below T_{cr}, the two points in contact with the straight line define two binodal points, A and D (for a symmetric case there are two minima with $\partial\Delta G/\partial\phi = 0$). Two inflection points with $\partial^2\Delta G/\partial\phi^2 = 0$ define spinodal points B and C. In the region of $\phi_2 < \phi_A$ and $\phi_2 > \phi_D$ two components are miscible. In the region between ϕ_B and ϕ_C, the system is unstable, separating into two phases with compositions equal to ϕ_A and ϕ_D. When ϕ_2 is between ϕ_A and ϕ_B or ϕ_C and ϕ_D, the system is metastable; i.e., the system is stable for small fluctuations in composition and becomes unstable for larger fluctuations, phase separating by the spinodal mechanism into two phases with compositions ϕ_A and ϕ_D. At the critical temperature, T_{cr}, A–D merge into a single point defined by $\partial^2\Delta G/\partial\phi^2 = \partial^3\Delta G/\partial\phi^3 = 0$. By connecting the binodal points at different temperatures, the coexistence curve designated by the dotted line shown in Figure 1 can be obtained. This curve, also known as the phase diagram, describes the phase change as a function of temperature and composition.

The actual calculation of the ΔG of mixing depends on the specific theory or model used. The Flory–Huggins lattice theory is probably the simplest and most widely used theory to calculate the free energy of mixing, ΔG, and to construct the phase diagram of a binary system.[1] A general expression for the ΔG of a binary system, be it solvent–solvent, solvent–polymer, or polymer–polymer,

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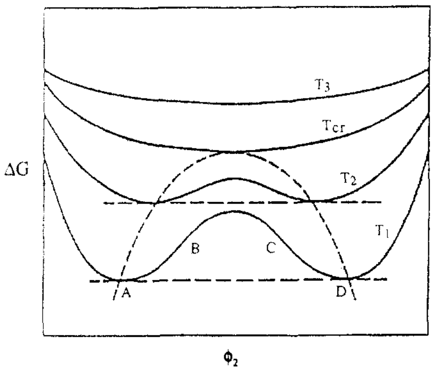


Figure 1. Schematic diagram illustrating the free energy of mixing change as a function of composition at different temperatures. The dashed line is the coexistence curve (phase diagram) constructed from the free energy plot.

can be expressed as[2]

$$\frac{\Delta G}{RT} = \frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2 + \chi\phi_1\phi_2 \qquad (1)$$

where ΔG is the free energy of mixing per mole of lattice site, ϕ is the volume fraction, and x is the chain length with each repeating unit defined as occupying a lattice site. The χ parameter is defined as

$$\chi = z\Delta w_{12}/RT \qquad (2)$$

where z is the coordination number of the model lattice and Δw_{12} is the energy of formation of an unlike pair from the stoichiometric equation

$$\frac{1}{2}[1,1] + \frac{1}{2}[2,2] = [1,2] \qquad (3)$$

and is defined as

$$\Delta w_{12} = w_{12} - \frac{1}{2}(w_{11} + w_{22}) \qquad (4)$$

where w_{ij} is the energy of a particular ij pair.

When eqs 1 and 2 are used to calculate the free energy of mixing, it is necessary to compute z and Δw_{12}. In this study, the procedure to calculate these parameters using a molecular simulation technique will be discussed. In addition, the phase behavior associated with three classic *textbook* examples, a solvent–solvent mixture, a polymer–solvent solution, and a polymer–polymer mixture, will be analyzed. Polymer solutions or blends represent extremely exciting areas of research. Sophisticated theories such as the reference interaction site model (RISM) and lattice cluster theory (LCT) have been recently developed to treat the problems beyond Flory–Huggins original approximations.[3,4] In a recent series of papers, Dudowicz et al. provided a very detailed discussion concerning deficiencies in the original Flory–Huggins theory.[5] From those and other studies using Monte Carlo methods[6] it is evident that the Flory–Huggins theory is somewhat inadequate in many aspects. It is not our intention, however, to analyze the validity of the Flory–Huggins theory itself but only to provide a methodology for use of the theory incorporating molecular simulation techniques to study mixing in binary systems. Due to its clarity in concept and simplicity in application, Flory–Huggins theory will always remain a good reference regardless of other developments in this area. With the methodology developed in this study, it is possible to apply Flory–Huggins theory in a new and useful manner.

Simulation Technique

The classical force-field characteristic of interatomic interactions, whether intramolecular or intermolecular, is the single most important and essential parameter governing the accuracy of many simulation techniques. These include energy minimization using molecular mechanics, molecular dynamics, and Monte Carlo approaches.[7] The energy of a system, which can be a single molecule, a pair of molecules, or even a condensed state assembled with a large number of molecules, is defined by different energy terms. Covalent interactions may be described by terms such as bond, valence angle, torsion, and hybridization terms; terms describing nonbonded interactions include van der Waals, electrostatic, and hydrogen-bonding interactions. The specific force field used in our study has been previously defined.[8] The software POLYGRAF is from Molecular Simulations, Inc. The necessity for incorporating partial charges depends on the specific force fields used. Earlier studies have shown that incorporation of charges appeared unnecessary.[9-11] Some contributions from charges have been incorporated in the force field. In this study, we found that, for some systems, ignoring electrostatic effects will lead to unfavorable results when compared to experimental data. In these cases, partial charges can be calculated utilizing the charge equilibrium method.[12] We have generally used experimental data as a reference.

Δw_{12} used in eq 2 can be obtained in a straightforward fashion simply by calculating the energies of three different pairs as defined by eq 4. A question arises as to whether the calculated Δw_{12} from simple pairwise interactions is sufficiently accurate to represent interactions in the actual condensed state. To improve the reliability of the calculation of Δw_{12}, we chose to take into account and properly weigh a large number of relative orientations of the two molecules (like or unlike). Simple energy minimization using several selected configurations is not representative of the interaction energy for binary mixtures exhibiting normal Boltzmann distributions. Molecular dynamics represents an improved sampling technique. At low temperatures, relative movement of the two molecules forming a pair is quite small. Molecular dynamics samples only localized configurational space which can lead to incorrect sampling using reasonable amounts of computer time. At high temperatures, two molecules may have sufficient kinetic energy to drift apart, an event which cannot occur in the actual condensed state. A manifestation of these problems using straightforward molecular dynamics simulations is that the Δw_{12} is strongly dependent on the initial configurations chosen.

A critical step in the reliable calculation of Δw_{12} is to establish an efficient algorithm for sampling relative orientations of a pair of molecules. In this study, an approach employing the Monte Carlo method which includes constraints arising from excluded volume is developed.[13] The excluded-volume constraint method can be applied in a variety of situations to sample energetics of molecules embedded in simple or complex topological environments, i.e., molecular packing or solvation.[13] The procedure used in this study, as illustrated in Figure 2, includes the following steps:

1. Construct proper structures for the molecules of interest, either the whole molecule in the case of solvent or the monomer repeat unit in the case of polymer. The structures are optimized using molecular mechanics. The overall shape of each molecule is represented by its van der Waals surface.

2. Position the geometric centers of both molecules (1 and 2) being considered near the origin of the Cartesian coordinate frame.

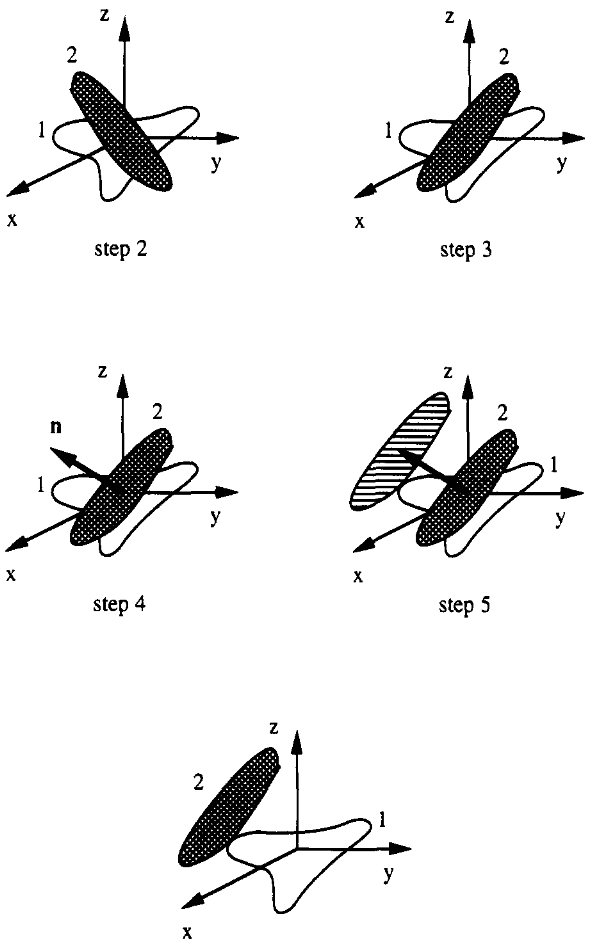


Figure 2. Consecutive steps to perform a calculation of the pair energy of a single configuration. The shape of the molecules is represented by their van der Waals surfaces. In step 1 (not shown here) the optimum structures of the two molecules are generated. Step 2 positions two molecules near the origin; the coordinates of molecule 1 (unshaded) will be unchanged throughout the calculations. Step 3 randomly rotates molecule 2. Step 4 chooses a random direction **n** in the space. Step 5 translate molecule 2 along **n** with a minimum distance to void overlap between two molecules. Step 6 shows the final position of two molecules for which the energy of the configuration is calculated.

3. Choose a particular orientation of molecule 2 by randomly choosing the three Euler angles.
4. Randomly choose a vector pointing from the origin to the surface of a unit sphere.
5. Translate molecule 2, the orientation of which is determined by step 3, along the vector determined by step 4, until the van der Waals surfaces of each molecule just touch each other.
6. Calculate the pairwise interaction energy of this specific configuration and use the Metropolis transition matrix to determine whether to accept this configuration.
7. Repeat steps 3–6. Calculate w_{ij} by averaging all the accepted configurations. Monitor the convergence of w_{ij} as a function of the number of Monte Carlo trials. The resultant w_{ij} can then be used to calculate Δw_{12} using eq 4.

The first two steps are quite simple and straightforward. Steps 3 and 4 involve using a procedure to randomly rotate a molecule and generate a vector in a three-dimensional space. Similar routines to perform these two operations can be found in molecular simulation texts.[14] A detailed discussion concerning steps 3–6 follows.

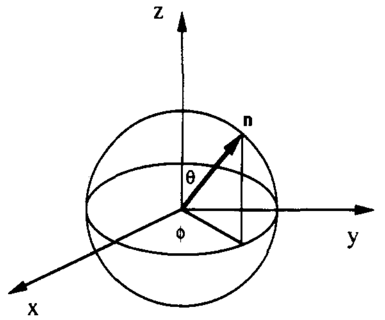


Figure 3. Schematic drawing of a random direction **n** pointing to the surface of a unit sphere.

Relative Orientation of the Two Molecules. If the position of molecule 1 is fixed near the origin, the relative orientation of molecule 2 with respect to molecule 1 can be specified with five angular variables. The first three variables are the Euler angles (α, β, γ) which specify the orientation of molecule 2 in the defined coordinate system. The function of step 3 is to randomly choose three Euler angles to generate a particular orientation of molecule 2. To ensure uniform sampling in the configurational space, the three Euler angles are determined by

$$\alpha = 2\pi(\mathrm{rand}_1)$$

$$\cos\beta = 1-2(\mathrm{rand}_2)$$

$$\gamma = 2\pi(\mathrm{rand}_3) \tag{5}$$

where rand_1, rand_2, and rand_3 are random numbers ranging between 0 and 1. The random numbers used in the three equations are generated independently. The new coordinates of the atom j in molecule 2, $r_j(x,y,z)$, after application of step 3 are

$$r_j(x,y,z) = \mathbf{A}r_j^0(x,y,z) \tag{6}$$

where $r_j^0(x,y,z)$ is the initial coordinate of atom j in molecule 2 before rotation and **A** is the transformation matrix defined by[15] eq 7.

$$\mathbf{A} = \begin{pmatrix} \cos\gamma\cos\beta\cos\alpha - \sin\gamma\sin\alpha & \cos\gamma\cos\beta\sin\alpha + \sin\gamma\cos\alpha & -\cos\gamma\sin\beta \\ -\sin\gamma\cos\beta\cos\alpha - \cos\gamma\sin\alpha & -\sin\gamma\cos\beta\sin\alpha + \cos\gamma\cos\alpha & \sin\gamma\sin\beta \\ \sin\beta\cos\alpha & \sin\beta\sin\alpha & \cos\beta \end{pmatrix} \tag{7}$$

The last two angular variables are the polar angles ϕ and θ as shown in Figure 3. The unit vector **n** defined by these two angles is

$$\mathbf{n} = (\sin\theta\cos\phi \quad \sin\theta\sin\phi \quad \cos\theta) \tag{8}$$

which will determine the relative position of molecule 2 to molecule 1 when molecule 2 is translated along this direction in step 5. This step is necessary to ensure that all specific interactions are considered. A uniform sampling scheme for ϕ and θ can be achieved using[16]

$$\phi = 2\pi(\mathrm{rand}_4)$$

$$\cos\theta = 1-2(\mathrm{rand}_5) \tag{9}$$

where rand_4 and rand_5 are random numbers ranging between 0 and 1. Figure 4 shows the projections of the end of the vectors generated through eq 9 onto three mutually perpendicular planes. It demonstrates the

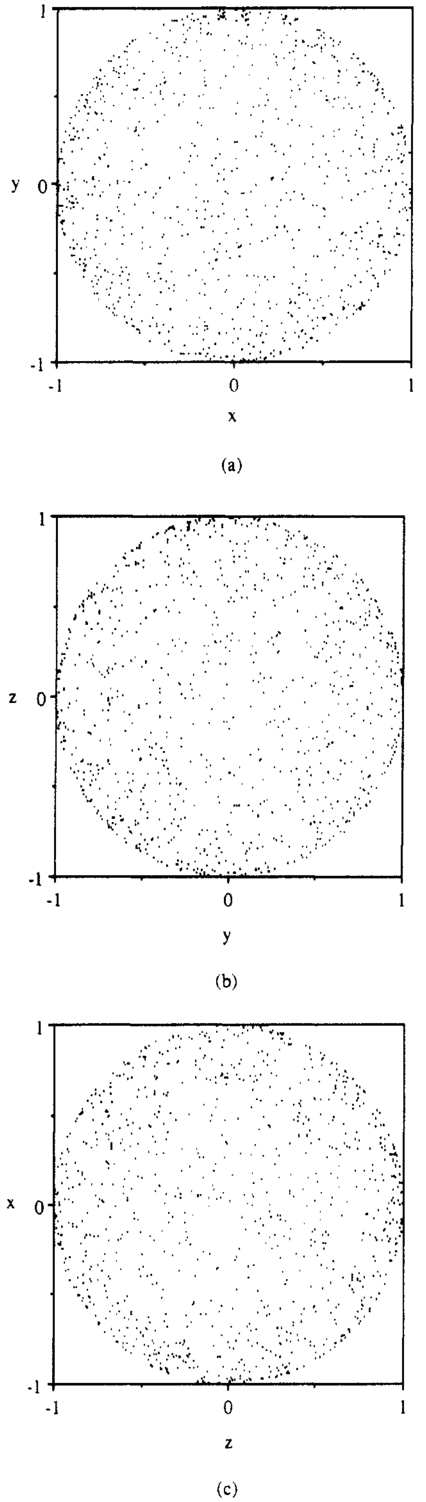


Figure 4. Projections of the end position of a random vector **n** pointing to the surface of a unit sphere after 1000 sampling: (a) on the x–y plane; (b) on the y–z plane; (c) on the z–x plane.

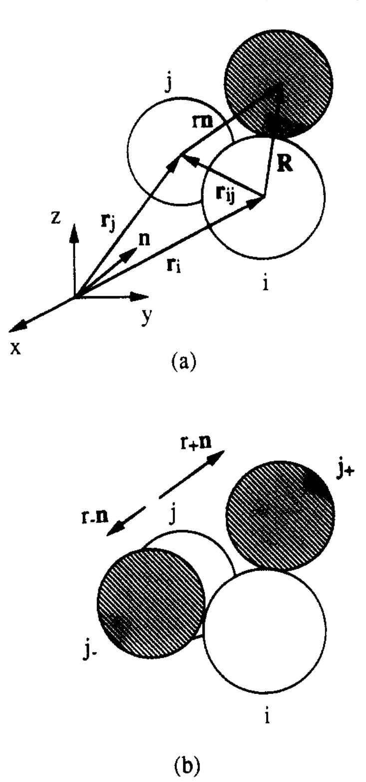


Figure 5. Calculation of translation vector $r\mathbf{n}$ ($\mathbf{n}$ is determined in step 4) for a two-atom system: (a) Geometric relationship between different positions before and after the translation. The large sphere (i) represents the fixed atom and the small sphere (j) represents the movable atom. The shaded sphere is the position of j after the translation. (b) Two possible solutions for the translation vector $r\mathbf{n}$, $r_+\mathbf{n}$ and $r_-\mathbf{n}$, and two corresponding new positions of atom j, j_+ and j_-.

uniformity of the distribution of these vectors in all directions (the density becomes higher outward due to the direction of projection). This uniform sampling make it possible for molecule 2 to access any position on the van der Waals surface of molecule 1 if topologically permissible. These data are obtained for a sampling number of 1000.

Translation of Molecule 2 to the van der Waals Surface of Molecule 1. The purpose of step 5 is to perform the minimum translation in the direction **n**, determined at step 4, necessary for molecule 2 to avoid an overlap of van der Waals volume with molecule 1. To demonstrate this method, we use a simplified case containing only two atoms as shown in Figure 5. Initially the two atoms, located near the origin, overlap. The positions of the two atoms are defined by vectors $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively. Suppose atom j is moved in the **n** direction (chosen in step 4) to avoid any overlap between the two; the new position of atom j, represented by the shaded sphere, is at the distance determined by vector $r\mathbf{n}$. The geometric relationships between vectors defined in Figure 5a yield the equations

$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$$

$$r\mathbf{n} + \mathbf{r}_{ij} = \mathbf{R}$$

$$|r\mathbf{n} + \mathbf{r}_{ij}|^2 = (R_i + R_j)^2$$

$$r^2 + 2(\mathbf{r}_{ij}\cdot\mathbf{n})r + |\mathbf{r}_{ij}|^2 - (R_i + R_j)^2 = 0$$

where R_i and R_j are the van der Waals radii of atoms i and j, respectively. The minimum displacement r, therefore, is the solution of the following equation:

$$r_\pm = -(\mathbf{r}_{ij}\cdot\mathbf{n}) \pm [(\mathbf{r}_{ij}\cdot\mathbf{n})^2 - |\mathbf{r}_{ij}|^2 + (R_i + R_j)^2]^{1/2} \quad (10)$$

The two roots indicate that atom j can be translated in two ways. In this specific case, r_+ represents an atom being moved in the positive direction. r_- is associated with the atom being moved in the negative direction as shown in Figure 5b. If the number of atoms in molecules 1 and 2 are m_1 and m_2, respectively, it is then necessary to calculate all the r_{ij}'s ($m_1 \times m_2$) between atoms of these two molecules using eq 10. The maximum and minimum r_{ij} will be the two correct solutions for the translation vector $r\mathbf{n}$. All the other r_{ij}'s will cause some overlap. In this study, the maximum r_{ij} is chosen to determine the displacement of molecule 2.

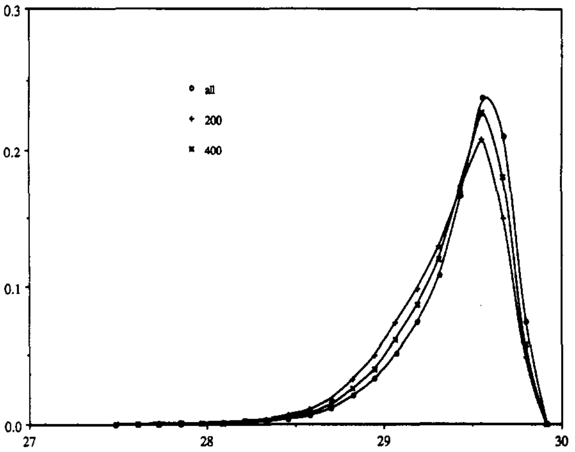


Figure 6. Pair energy distributions of polyisoprene and polystyrene segments: (○) the original data of all the configurations generated; (+) after the original data were sampled using the Metropolis algorithm at 200 K and (×) at 400 K.

Calculation of the Pair Energy. Generation of relative orientations using the above procedure leads to configurations of varying energetics. The configuration of the two molecules often gives very favorable energies. Many actually locate a local minimum on the potential energy surface. We considered three sampling methods to weigh the appropriateness of the generated configurations: (1) The energy of each configuration can be lowered by molecular mechanics, and all are accepted. This approach excludes temperature effects and does not lead to a Boltzmann distrubition. (2) Accept all the configurations generated but weigh each with the Boltzmann factor, $e^{-E/kt}$. (3) Use a Metropolis Monte Carlo sampling algorithm. If we define $u_{vv'}$ as the probability that if the system is in state v making a transition to state v′, then $u_{vv'}$ is given as[17]

$$u_{vv'} = \begin{cases} 1, & \Delta E_{vv'} \leq 0 \\ \exp\left(-\dfrac{\Delta E_{vv'}}{RT}\right), & \Delta E_{vv'} \geq 0 \end{cases} \tag{11}$$

where $\Delta E_{vv'} = E_{v'} - E_v$. The configuration is accepted if its energy is less than or equal to the energy of the previous configuration. If the energy is higher, a random number between 0 and 1 is generated. The configuration is accepted only if $\exp(-\Delta E_{vv'}/RT)$ is larger than or equal to the value of the random number. The third method is the more rigorous sampling technique and is used throughout this study.

In practice, the energies of all generated configurations are stored and the Metropolis algorithm is then used to process the stored data at different temperatures. Figure 6 shows the pair energy distribution of polyisoprene and polystyrene segments of the original data for 50 000 configurations as well as the distributions at two different temperatures, 200 and 400 K, obtained by Metropolis sampling. The average pair energy for all the configurations is 29.501 kcal/mol and for temperatures at 400 and 200 K is 29.464 and 29.419 kcal/mol, respectively. Each distribution is somewhat asymmetrical. There is a long, low-energy tail. The number of configurations with energy higher than the peak value decreases dramatically. This phenomenon clearly indicates the merit of this sampling technique; i.e., very few configurations with high energy or bad van der Waals contacts are generated.

If N configurations are generated, the average energy $\langle E\rangle_N$ is calculated. Only when N goes to infinity will a truly average pair energy $\langle E\rangle$ be obtained. Limited sampling statistics, i.e., finite N, will cause $\langle E\rangle_N$ to oscillate about $\langle E\rangle$. The uncertainty can be analyzed by dividing the N configurations into M subdivisions, with each division containing L ($L = N/M$) configurations. The average energy of each subdivision is $\langle E\rangle_L{}^I$ ($I = 1, M$). The statistical error due to a finite number, N, is given by[17]

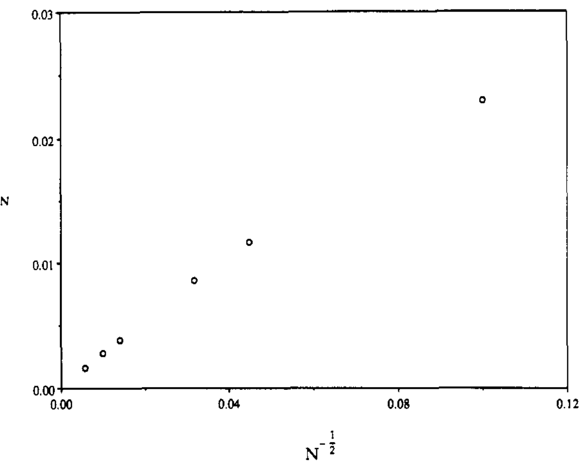


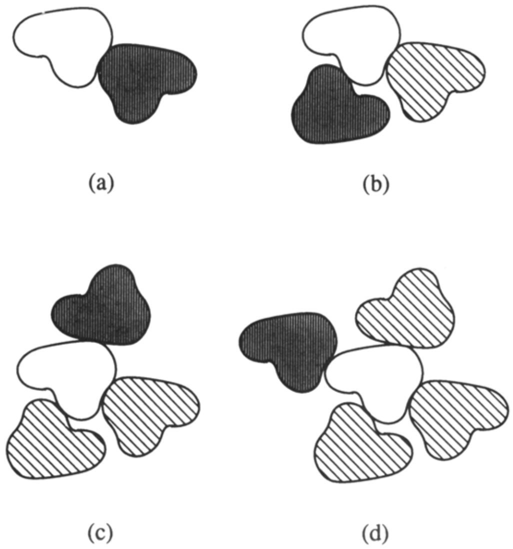
Figure 7. Statistical error due to finite sampling as a function of sampling time N.

$$\Delta\langle E\rangle_N = \left[\left(\frac{L}{N}\right)^2 \sum_{i=1}^{M} (\langle E\rangle_M{}^i - \langle E\rangle_N)^2\right]^{1/2} \tag{12}$$

The error monotonically decreases as N increases. Different values of $\langle E\rangle_N$ for different L (L = 1, 10, 100, 1000) have been calculated. For example, if N is 30 000, the statistical uncertainty for $\Delta\langle E\rangle_N$ for different L converges to 0.0016. Considering the smallest Δw_{12} to be ~0.01 (polyisoprene/polystyrene system) for the systems study here, sampling 100 000 configurations (about 7% error) should provide reasonable accuracy. The statistical errors for the other two systems studied here are much smaller due to larger Δw_{12}s. As expected, there is a linear relationship between $\Delta\langle E\rangle_N$ and $N^{-1/2}$ as shown in Figure 7 (L = 1). The statistical error at different N, therefore, can be estimated from this plot. Generating 100 000 pair configurations with the total atom number of a pair being ~50 and calculating their energies required ~3 h on a SGI 4D35 workstation. The computation time has not proven to be a major limitation in this study.

Calculation of Coordination Number z. In the Flory–Huggins scheme, χ, defined in eq 2, is perhaps the single most important parameter required to describe the miscibility behavior of a binary system. None of the free energy expressions contains explicit dependence on the coordination number, i.e., how many neighbors of interaction need be considered. In this study, however, the coordination number of a system has to be computed directly. A single coordination number, as in eq 2, has a definite physical significance only when the two components, either molecules or polymer segments, have a similar volume or surface area. The difficulty in defining a coordination number for a system in which two components are not compatible in size clearly limits the applicability of the approach developed here, and an independent study is necessary.

An algorithm to approximate the possible number of the nearest neighbors in contact with the center molecule can be provided. For a binary system, at least four different combinations are possible; i.e., the center molecule, as well as the surrounding molecule, can be either species 1 or 2. This leads to four coordination numbers. A more complex


(a) (b)

(c) (d)

Figure 8. Calculation of coordination number z by packing nearest neighbors around the center molecule (unshaded). The darkly shaded molecule represents the one being packed, and the lightly shaded molecules represent existing nearest neighbors. The shape of the molecules represents their van der Waals surface: (a) with no existing neighbor; (b) with one existing neighbor; (c) with two existing neighbors; (d) with three existing neighbors. After d no more space around the center molecule is available to pack one more nearest neighbor. The coordination number obtained in this particular search is 4.

situation is that the surrounding molecule can be a mixture of 1 and 2. We find that the four types of coordination numbers are quite similar when the molecular sizes of the 2 species are similar. As shown in Figure 8, when the position of the first nearest neighbor is determined by steps 2–5, placement of the second nearest neighbor needs to avoid overlap with both the center molecule and the first nearest-neighbor molecule. In addition, it also needs be in contact with the center molecule to qualify as a nearest neighbor. Additional constraints need therefore be introduced to pack molecules around the center molecule. These constraints dictate that the maximum displacement r_+ has to be determined by the atoms of the reference molecule and the atoms of the molecules being added. By repeating this calculation, one obtains an average coordination number for the two molecules considered. The coordination number obtained in this fashion depends on the number of sampling or packing undertaken. The initial packing scheme has proven to be very effective. After a certain number of sampling, little space remains available for additional nearest neighbors. After a few neighbors are introduced, it becomes difficult to introduce additional molecules about the center molecule. The number of nearest neighbors then increase very slowly with an increase of the packing number. In these calculations, we have taken the value at the onset of a plateau of the plot of nearest neighbor against packing number. The coordination number obtained is about 7. The critical temperature is usually strongly dependent on the coordination number.

It is clear that a method can be developed to apply the molecular simulation technique in conjunction with the Flory–Huggins theory for analyzing binary mixtures. In this study, three systems have been chosen to validate the methodology outlined above. The examples are relatively simple, and relevant experimental data are available for comparison with calculation. The first is the n-hexane and nitrobenzene solvent–solvent system. The phase diagram of this mixture appears in most physical chemistry textbooks.[18] The solvent–polymer system chosen is diisobutyl ketone and polyisobutylene. The phase diagram with different molecular weights of polymer has been presented earlier.[1] The polymer–polymer system studied is oligomer mixtures of polyisoprene and polystyrene, one of the few systems with a clearly defined UCST and an availability of the entire phase diagram.

Results and Discussion

Solvent–Solvent System. For simplicity, a well-known solvent–solvent system is chosen. This study also serves as a useful reference for comparison to polymer results. The phase diagram of n-hexane ($CH_3(CH_2)_4CH_3$) as component 1 and nitrobenzene ($PhNO_2$) as component 2 is used as a typical example of partially miscible binary mixtures in many physical chemistry textbooks.[18] The application of the approach discussed above to a solvent–solvent system is straightforward. The structures of both molecules are optimized with the Dreiding force field.[8] Two routes are available to calculate the energy of an unlike pair, w_{12}. It is possible to fix molecule 1 (n-hexane) and sample different configurations of molecule 2 (nitrobenzene) or its converse. These two methods provide exactly the same distribution of w_{12}, an indication of the self-consistency of the methods. The calculated Δw_{12} as a function of temperature is shown in Figure 9. For the convenience of calculation of the critical temperature we have fitted Δw_{12} versus T of this system with the following functional form:

$$\Delta w_{12} = -7.66 \times 10^{-3} + 1.05 \times 10^4/T^2 \qquad (13)$$

The original Flory–Huggins theory considers only the lattice configuration entropy. By using the expression of the Δw_{12} or χ as a function of temperature, it is possible to account for other entropic contributions due to specific interactions between the two components and their relative orientations. The molecular origin of the temperature dependence of χ is that the different configurations of pairs have different energies and their contribution to the Δw_{12} is temperature dependent. With the availability of $\chi(T)$, the entropy and heat of mixing can be calculated by the following equations:[1]

$$\Delta S_{\mathrm{M}} = -k\left[\frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2 + \frac{\partial\chi(T)}{\partial T}\phi_1\phi_2\right] \qquad (14)$$

$$\Delta H_{\mathrm{M}} = -kT^2\frac{\partial\chi}{\partial T}\phi_1\phi_2 \qquad (15)$$

The calculated coordination number for this system is 7.8. The phase diagram of n-hexane and nitrobenzene is shown in Figure 10. The calculated critical temperature is 268 K while the value in the literature is 293 K.[18] It is clear from eq 2 that the χ and, therefore, T_{cr} depend strongly on the coordination number z. Figure 11 shows the critical temperature as a function of assumed different z values. The calculated critical temperature would be matched with the experimental value 293 K if an assumed z of 11.5 were used. This z of 11.5 actually occurs in this simulation after an average of 10 000 tries of consecutive packing. When the coordination number is not well defined or easily calculated, it might be possible to fit the calculated critical temperature with the experimental one to obtain z and acquire certain information concerning microstructure or packing.

Solvent–Polymer System. A diisobutyl ketone (component 1) and polyisobutylene (component 2) mixture is one of interesting examples of a solvent–polymer system. The polymer's molecular weight dependence of the critical

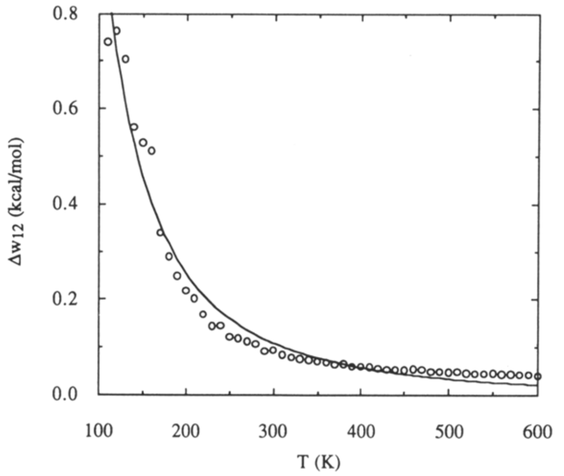


Figure 9. Δw_{12} of *n*-hexane and nitrobenzene as a function of temperature.

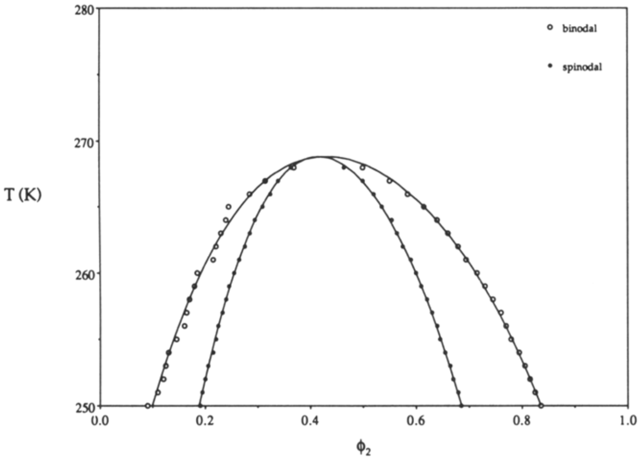


Figure 10. Calculated coexistence (○) and spinodal (●) curves of *n*-hexane and nitrobenzene binary mixtures.

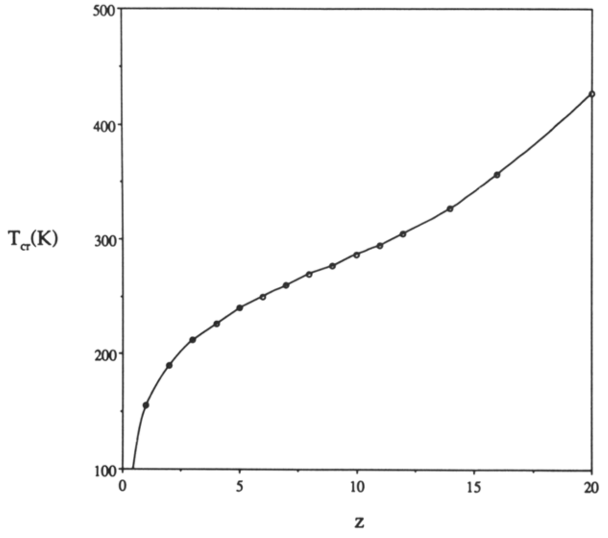


Figure 11. Upper critical solution temperature of the *n*-hexane and nitrobenzene system as a function of coordination number *z*.

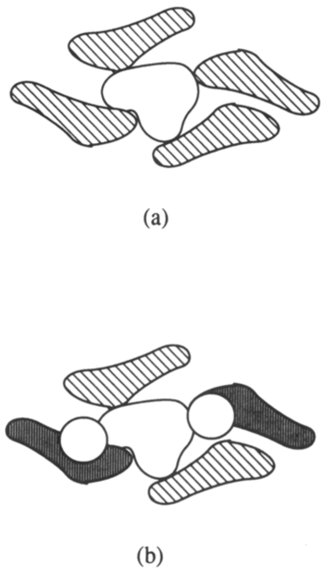


Figure 12. Constraints in the calculation of the pair energy for a system containing polymer. (a) A solvent–solvent system. There are no constraints. All four configurations of molecule 2 (shaded) are possible. (b) A solvent–polymer system. The unshaded spheres represent two dummy atoms introduced at the head and tail positions of the polymer segment. Because of chain connectivity these two positions are inaccessible to the solvent molecules. The configurations of molecule 2 (darkly shaded) in contact with the dummy atoms will be rejected in the calculation of the pair energy. The radii of the dummy atoms are their van der Waals radii.

temperature and the phase diagram of this binary mixture has been presented in Flory's classical book.[1] This system contains typical questions in need of consideration when applying the methodology developed here to a polymer system. The chemical structure of the solvent and polymer repeat unit are $(CH_3)_3CCOC(CH_3)_3$ and $-C(CH_3)_2CH_2-$, respectively. The first question to be addressed is the definition of the lattice size because the solvent size is significantly larger than the polymer monomer repeat unit. The most convenient way to define the size of a lattice site is for it to be sufficiently large to hold one solvent molecule or one polymer segment containing *two* monomer repeat units. A polymer segment then becomes $-C(CH_3)_2CH_2C(CH_3)_2CH_2-$. With this definition, the relative sizes of the solvent molecule and the polymer segment are almost identical, within 5% in either the area of the molecule's van der Waals surface or the volume encompassed by this surface. The molecular surface area and volume are calculated using the van der Waals radii of the atoms in the molecule. Such an approach to define the size of a lattice site may, however, not be generally applicable.

Effects of polymer connectivity also require consideration. Any configuration generated in the two-solvent mixture is physically acceptable. For a long-chain polymer, the situation is quite different. The ends of a polymer segment are normally connected to other segments, making some positions of the polymer segment inaccessible to solvent molecules as shown in Figure 12. Chain connectivity must be considered in the solvent–polymer system, and configurations violating this constraint should be rejected. It is possible to introduce two dummy atoms at the head and tail positions of the polymer segment as the two unshaded spheres drawn schematically in Figure 12b. The polymer segment now becomes $C'C(CH_3)_2CH_2C(CH_3)_2CH_2C'$. The two C' atoms at the ends of the polymer segment are dummy atoms. To obtain the optimum structure of the redefined polymer segment, these two dummy atoms C's represent $-CH_3$ in the united atom approximation. The structure of the segment is then optimized.

Upon generation of a configuration, contacts between atoms in the solvent molecule and these C' atoms are examined. Any configuration containing such contacts is rejected as shown in Figure 12b. In the calculation of pair energy w_{12}, the energy terms (bond, angle, torsion, and

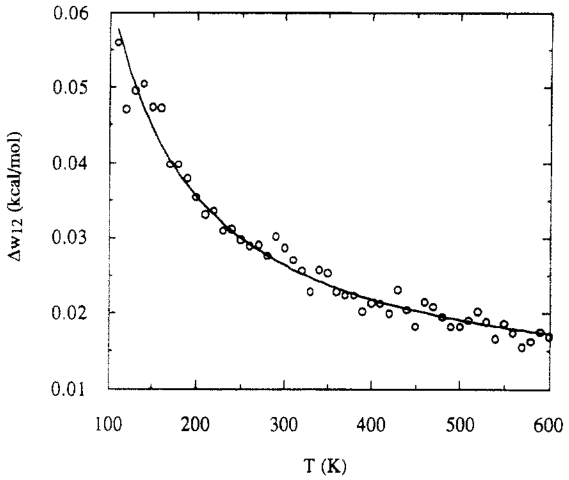


Figure 13. Δw_{12} of the diisobutyl ketone and polyisobutylene segment as a function of temperature.

van der Waals energy) associated with the two C′ atoms are not included. The sole function of these C′ atoms in the calculation of w_{12} is the use of their van der Waals radii to reject improper configurations which violate chain connectivity. The same approach is used to calculate w_{22}, the pair energy between polymer segments. One may argue, using this criteria, that certain generated polymeric configurations, e.g., when a segment is connected to another segment, are excluded. These configurations do not affect the mixing process, since they should have no contribution to the heat of mixing. The competition between like and unlike species only occurs for those configurations accessible to both the solvent molecule and other polymer segments. Therefore, a similar constraint for calculating w_{22} is justifiable.

The calculated $\Delta w_{12}(T)$, plotted in Figure 13, can be fitted with following equation:

$$\Delta w_{12} = 8.20 \times 10^{-3} + 5.45/T \qquad (16)$$

The argument for taking chain connectivity into account in the calculation of w_{12} and w_{22} also holds in the calculation of z. We define z_0 as the maximum coordination number of the system and z as the coordination number calculated with the constraint associated with chain connectivity. The precise number of neighboring lattice sites used in eq 2 for a polymer segment should be $z_0 - 2$.[1] When the constraint discussed above is applied to a solvent–polymer system, the calculated result should be z_0 for pair [1,1], $z_0 - 2$ for pair [2,2], and $z_0 - 1$ for the average of the pairs [1,2] and [2,1]. Thus, when the constraint is imposed, the number of possible nearest neighbors for a particular pair is automatically obtained and the approximation cited in the original derivation eliminated. A single z can be obtained by averaging different pairs which is about 6.5 for the system discussed here.

The phase diagram for three different molecular weights of the polymer is shown in Figure 14. The numbers of repeat units, x_2 used in eq 1, of three polymers are 203, 2544, and 53 571. These numbers are only half of the real degrees of polymerization because the polymer segment is defined as twice as large as the real monomer repeat unit. Table I presents a comparison of experimental data with the calculated results for several different z's. The agreement between the calculated results of $z = 6.5$ and the experimental data is excellent. The critical temperatures calculated for three different molecular weight polymer–solvent systems are all within a few degrees of the experimental data.

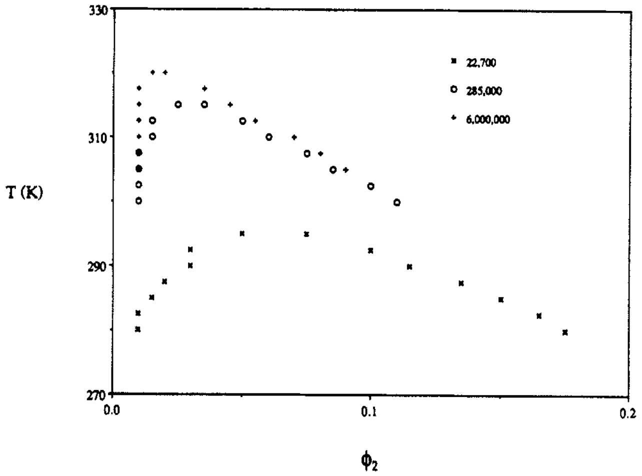


Figure 14. Phase diagrams (coexistence curve) of diisobutyl ketone and polyisobutylene with three different molecular weight polyisobutylene: (×) 22 700, (○) 285 000, and (+) 6 000 000.

Table I
Critical Temperatures of Diisobutyl Ketone and Polyisobutylene

	T_{cr} (K)			
MW	exptl	calc (z = 5)	calc (z = 6.5)	calc (z = 8)
22 700	292	225	295	360
285 000	319	240	315	390
6 000 000	329	245	320	395

Polymer–Polymer System. Most polymer pairs are immiscible, as easily understood from eq 1. With high molecular weight polymers (large x in the equation), a slightly positive value of Δw_{12} will lead to phase separation. An oligomeric polyisoprene (component 1) and polystyrene (component 2) mixture is perhaps one of the best studied binary blends exhibiting an upper critical solution temperature.[19–21] The monomer repeat units of polyisoprene and polystyrene are $-H_2C(CH_3)C{=}CHCH_2-$ and $-PhCHCH_2-$, respectively. The double bond in polyisoprene has a cis configuration. The isoprene segment can have different conformations, with the optimum structure obtained after several cycles of energy minimization and molecular dynamics. The calculated results were not found to be very sensitive to the initial conformation of the polymer segment, mainly because the sampling method assures that nearly every part of the molecule is *touched* by another segment. A problem with the polystyrene segment defined above is that the tacticity has not been taken into account. A more complicated segment needs be defined if this factor is to be considered. The choice made in this study is applicable to an atactic polymer. Very high molecular weight (MW > 20 000) polyisoprene and polystyrene are known to be immiscible. Accurate experimental data exist for systems with molecular weights ranging from 1000 to 3000.

The discussion in the previous sections regarding the effects of chain connectivity should also be applicable to the mixture involving two polymers. The calculated Δw_{12} as a function of temperature is shown in Figure 15. The data, after fitting, yield the following equation:

$$\Delta w_{12} = 6.49 \times 10^{-3} + 1.66/T \qquad (17)$$

The calculated coordination number is about 5. As discussed previously, the coordination number should be $z_0 - 2$. We find that z_0, the coordination number without the constraint of the chain effect, is quite consistent for all three systems, i.e., ~7. This consistency indicates that using a single dummy atom at both ends of the polymer

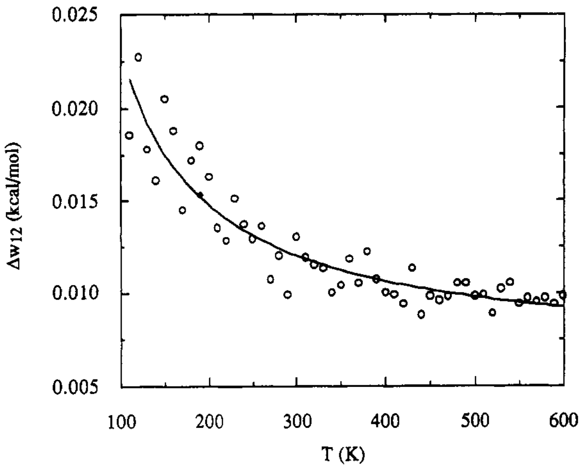


Figure 15. Δw_{12} of polyisoprene and polystyrene segments as a function of temperature.

Table II
Critical Temperature of Polyisoprene (pip) and Polystyrene (ps)

MW		T_{cr} (K)		
pip	ps	exptl	calc (z = 4)	calc (z = 5)
1000	1000	243	230	267
2000	2700	329	397	473
2700	2100	408	410	495
2700	2700	448	450	550

segment in this approach is justifiable. Instead, if one introduces a monomer unit at the ends of the polymer segment, the excluded-volume effect of this bulky dummy group will reject most of the configurations in the calculation of both Δw_{12} and z. The z will be too small compared to z_0 to be reasonable. This characteristic of our approach has its root in the step of determining the translation vector.

Experimental results for polyisoprene and polystyrene have been obtained from two sources.[19-21] The data are listed in Table II, together with calculated results. If a coordination number of 5 is used, calculated results differ significantly from the experimental values. Except for the case of relatively low molecular weight (MW ~ 1000), the discrepancy between the experimental values and the calculated results can be very large, near or over 100 K. However, if the coordinate number is reduced to a value of 4, the calculated results become quite consistent with the experimental values.

It is very difficult to accurately predict critical temperatures of a polymer mixture by use of the Flory–Huggins theory. The heat of formation for an unlike pair, Δw_{12}, is usually small. The Δw_{12} of the polyisoprene and polystyrene system treated here is only about 0.01 (kcal/mol of polymer segment) near room temperature. The degree of polymerization has to be less than 30 for the system to exhibit an upper critical solution temperature near room temperature. By increasing the x to about 100, the system becomes immiscible even at reasonably high temperatures. The small value of Δw_{12} and large x, the degree of polymerization, sensitize the critical temperature to both Δw_{12} and z. Thus both Δw_{12} and z need be accurately calculated, a condition that cannot be easily satisfied in real calculations. The calculations carried out in this study provide the means to describe the miscibility behavior of a binary system, with small scaling of the z taken into account.

The methodology outlined in this study can be used for any system as long as a proper force field exists to describe all the interatomic interactions. The major obstacle for this type of calculation is related to the size of a lattice site. No two molecules or polymer segments or a combination of the two have exactly the same van der Waals volume or surface area. If the size difference of the two components is small, one can use x, the chain length, to adjust the lattice size, even for a small-molecule system. For example, the van der Waals volumes of n-hexane and nitrobenzene are 180 and 147 Å^3, respectively. If we define the size of the lattice as the volume of nitrobenzene, then x_1 in eq 1 is 1.22 while x_2 is 1. However, the physical meaning of pair energies then becomes ill-defined. For example, w_{11} is the pair energy of two 1.22 [1]. w_{12} is one 1.22 [1] and one [2]. The w_{22} remains the pair energy of two [2]. A scale down of the w_{11} and w_{12} values of this system according to the volume ratio (1.22) was unsuccessful. The calculated critical temperature changed drastically with the volume ratio. No easily definable procedure exists to reasonably correct for both x and w. This factor was thus ignored in this study. When the size difference of two molecules is large, this approximation will introduce serious problems. Another problem caused by the size mismatch, as mentioned previously, is that the coordination number z becomes ill-defined. One needs to exercise judgement about the approximations applicable for each system. Nevertheless, this approach can be applied to many different systems especially when only qualitative results or relative comparisons are required.

The validity of using the molecular simulation technique to predict polymer miscibility depends on the theoretical model it is based upon and the simulation technique applied. The Flory–Huggins theory has certain deficiencies. It cannot predict the existence of the lower critical solution temperature; it fails for the composition dependence of χ, and it fails to recognize additional entropic contributions other than a purely mixing component. The approach used in this study also possesses some of the deficiencies of this theory. Advancement is achieved, however, by providing the molecular basis of the temperature dependence of χ as well as the capability to calculate this dependence. Some studies suggest that the Flory–Huggins theory strongly overestimates values of the critical temperature,[22] and this tendency is also evident in our polymer calculations. We should, however, be cautious about this conclusion, since the accuracy of the force field for different systems may vary.

The philosophy of this approach is relatively simple: use a simple theoretical model which contains parameters having a definite physical meaning or molecular origin (z and Δw_{12} in this case) and then calculate these parameters with computer simulation. The theory need not be as elementary as the Flory–Huggins theory. However, the molecular origin of the parameters is required as well as the capability for calculation in order to avoid arbitrary fitting. In principle, specific knowledge about the system is unnecessary as information which is unavailable by either purely theoretical or experimental means may be generated.

Conclusions

A systematical approach to calculate the temperature dependence of the χ parameter in the Flory–Huggins theory of a binary mixture is developed in this study. The method consists of a Monte Carlo sampling and a consideration of excluded-volume contraint in the calculation of pairwise interactions (Δw_{12}) and coordination number z. Calculated results for a solvent–solvent and a solvent–polymer system compare favorably with the experimental data, even with a generic force field. In the calculation of a polymer–polymer binary mixture a small scaling on the coordination number *z* is necessary in order to match the experimental data. The accuracy of this type of calculation depends on the theoretical model, the force field, and the limitation of the method itself. Further improvements in all three aspects are required for a more definite prediction of the behavior of binary mixtures. Nevertheless, the calculations in this study clearly demonstrate the applicability of molecular simulations in this exciting area.

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