AN APPLICATION OF FLORY-HUGGINS LATTICE THEORY THROUGH MOLECULAR SIMULATION

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ABSTRACT

Fundamental parameters in the Flory-Huggins theory of binary mixture, including the heat of mixing associated with pairwise interactions (Δw_{12}) and the coordination number, z, are calculated through 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 from this study.

INTRODUCTION

Study of miscibility behavior involves the calculation of the free energy of mixing as a function of composition at different temperatures. 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 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

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

where z is the coordination number of the model lattice and Δw_{12} is the energy of formation of an unlike pair ($\Delta w_{12} = w_{12} - 1/2(w_{11}+w_{22})$)

When equations 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. With the method discussed here, it is possible to apply Flory-Huggins theory in a new and useful manner.

SIMULATION TECHNIQUE

In the molecular simulation 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 terms. Covalent interactions may be described by terms such as bond, valence angle, torsion, and hybridization terms; terms describing non-bonded interactions include van der Waals, electrostatic, and hydrogen bonding interactions. The specific force field used in our study has been previously defined.[3] The software *POLYGRAF* is from Molecular Simulations, Inc.

A critical step in the calculation of Δw_{12} used in equation 2 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.[4] The procedure 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.

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

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 surface 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 through 6, typically, 50,000 times. 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}.

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 random vector in a 3 dimensional space. Details regarding these two steps were provided elsewhere. [5] Similar routines to perform these two operations can also be found in a molecular simulation text. [6] A discussion concerning steps 5 through 7 follows.

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 1. Initially the two atoms, located near the origin, overlap. The positions of the two atoms are defined by vectors r_i and 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 rn. The geometric relationships between vectors defined in Figure 1(a) yield the following equations

$$r_{ij} = r_j - r_i$$

$$rn + r_{ij} = R$$

$$|rn + r_{ij}|^2 = (R_i + R_j)^2$$

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

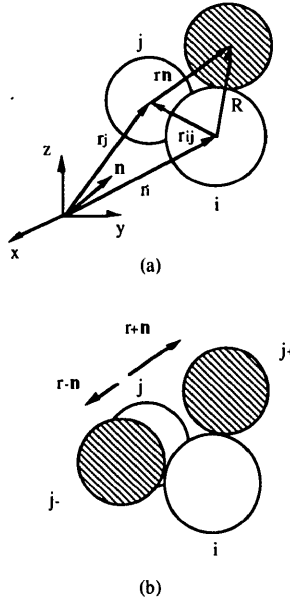where R_i and R_j are the van der Waals's radii of atom i and j respectively.

(a)

(b)

Figure 1.   Calculation of translation vector rn (n is determined in step 4) for a two atoms 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) shows two possible solutions for the translation vector rn, r_+n and r_-n, and two corresponding new positions of atom j, j_+ and j_-.

The minimum displacement r, therefore, is the solution of the following equation:

$$r_\pm = -(r_{ij} \cdot n) \pm \sqrt{(r_{ij} \cdot n)^2 - |r_{ij}|^2 + (R_i + R_j)^2} \ . \qquad (3)$$

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 1(b). 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 equation 3. The maximum and minimum r_{ij} will be the two correct solutions for the translation vector rn. 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.

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 use a Metropolis Monte Carlo sampling method to weigh the appropriateness of the generated configurations. 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 [7]

$$u_{vv'} = \begin{cases} 1, & \Delta E_{vv'} \leq 0 \\ \exp\left(-\dfrac{\Delta E_{vv'}}{RT}\right), & \Delta E_{vv'} \geq 0 \end{cases} \tag{4}$$

where $\Delta E_{vv'} = E_{v'} - E_v$. The configuration is accepted if its energy is less 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 less than the value of the random number.

Calculation of coordination number z

Calculation of z is performed by packing nearest neighbor molecules around the center one. When the position of the first nearest neighbor is determined by steps 2 through 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 need 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 nearest neighbor molecules already added. By repeating this calculation, one obtains an average coordination number for the two molecules considered. The initial packing scheme has proven to be very effective. After a few neighbors are introduced, it becomes difficult to introduce additional molecules about the center molecule. The number of nearest neighbor then increase very slowly with the 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.

RESULTS AND DISCUSSIONS

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. The results for a solvent-polymer system, diisobutyl ketone and polyisobutylene, are presented here. The chemical structure of the solvent and polymer repeat unit are $(CH_3)_3CCOC(CH_3)_3$ and $-C(CH_3)_2CH_2-$ respectively. Details regarding the treatments of size mismatch between solvent molecules and polymer segment as well as the effects of polymer connectivity are provided elsewhere. [5]

The calculated $\Delta w_{12}(T)$ as plotted in Figure 2 can be fitted with the following equation

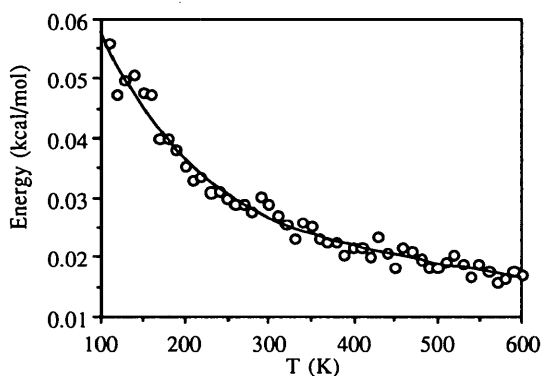$$\Delta w_{12} = 8.20 \times 10^{-3} + 5.45 / T. \tag{5}$$

Figure 2. Δw_{12} of diisobutyl ketone and polyisobutylene segment as a function of temperature.

The phase diagram for three different molecular weights of the polymer is shown in Figure 3. The results compare favorably with experimental data. [1]

The philosophy of this approach is relatively simple: use a simple theoretical model which contains parameters having 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.
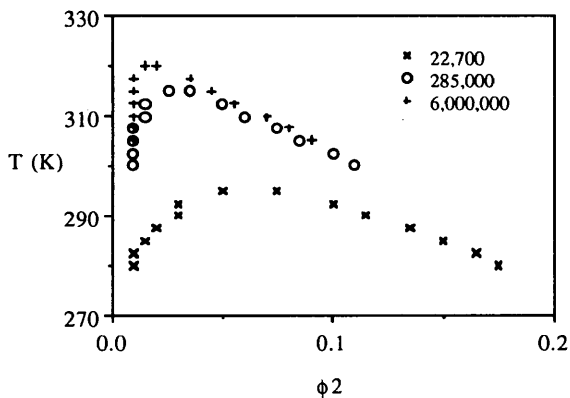
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Figure 3. Phase diagrams (coexistence curve) of diisobutyl ketone and polyisobutylene with three different molecular weight polyisobutylene: (x) 22,700, (o) 285,000, and (+) 6,000,000.

ACKNOWLEDGMENT.

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