Double-Lattice Model for Binary Polymer Solutions

Ying Hu,[†] Stephen M. Lambert, David S. Soane, and John M. Prausnitz*

Department of Chemical Engineering, University of California, Berkeley, and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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ABSTRACT: Freed's lattice-field theory provides a basis for a double-lattice model for the Helmholtz energy of mixing for binary polymer solutions. When Freed's series-expansion terms for the simple Ising lattice and for the Flory–Huggins lattice with $r_1 = 1$ and $r_2 = 100$ are revised slightly, predicted liquid–liquid coexistence curves are in excellent agreement with those calculated from Scesney's Padé-approximant coefficients and from computer simulation results by Madden, Pesci, and Freed; here r_1 and r_2 are the numbers of sites required by molecule 1 and molecule 2, respectively. For real systems, the interchange energy (ϵ/k) and r_2 are adjusted to fit the experimental concentration dependence of the Flory–Huggins parameter χ determined by vapor sorption, osmotic pressure, light scattering, or sedimentation. To account for highly oriented interactions between segments, a secondary lattice is introduced. This secondary lattice requires an additional parameter ($\delta\epsilon/k$) related to the energy of the oriented interaction and one empirical parameter c_{10}. With the double-lattice theory, coexistence curves can be reproduced for systems having an upper critical solution temperature (UCST), a lower critical solution temperature (LCST), or a miscibility loop with both UCST and LCST.

Introduction

The phase behavior of binary polymer/solvent mixtures differs from that for ordinary liquid mixtures because of the large molecular size difference of the components. For example, lower critical solution temperatures (LCST) and "hour-glass" shaped and closed-miscibility loop phase diagrams are commonly encountered for polymer solutions, but they are not common for "ordinary" fluid mixtures.[1] Quantitative understanding of the phase behavior of polymer solutions is important for the development, production, and processing of advanced polymer materials. In this work, we extend our previous theory for small-molecule systems[2] to polymer/solvent mixtures. We are here concerned with polymer mixtures at temperatures well below the solvent's critical temperature. We are therefore not concerned with the free-volume effect that leads to lower critical solution temperatures as described by Patterson.[3]

A variety of polymer-solution theories has been developed during the last half century; most of them are revised forms of the classical work proposed by Flory[4] and Huggins.[5] The classical theory of Flory and Huggins is based on a lattice model for polymer solutions wherein all lattice sites are occupied by segments of molecules. A mean-field approximation was used to obtain the Helmholtz energy of mixing, ΔA. In the mean-field approximation, ΔA is the sum of a combinatorial entropy and a simple term for the energy of mixing

$$\Delta A/N_r kT = (\Phi_1/r_1)\ln\Phi_1 + (\Phi_2/r_2)\ln\Phi_2 + g_{12}\Phi_1\Phi_2 \quad (1)$$

where N_r is the total number of lattice sites, r_i is the number of lattice sites occupied by a molecule of component i, and Φ_i is the volume fraction of component i. The interaction parameter g_{12} reflects nearest-neighbor interaction energies. In practice, g_{12} is adjusted to give quantitative agreements between theory and experiment. Typical experimental results indicate that g_{12} depends on temperature and concentration. To obtain a more accurate fit, Tompa[6] suggested a power-series expansion in concentration with empirical coefficients for g_{12}. Later, Koningsveld and Kleintjens[7] derived a closed-form expression for g_{12} by replacing the volume fraction with the nearest-neighbor site-occupancy probability. Further, an extra entropy correction term was added.

Although these modified models of the original Flory–Huggins theory provide improvements for data fitting, they cannot describe the phase behavior of the systems with LCST or with miscibility loops (both LCST and UCST). Such phase behavior may be due to highly oriented interactions such as hydrogen bonding, as first indicated by Hirschfelder, Stevenson, and Erying.[8] For systems with miscibility loops, an early model was proposed by Barker and Fock;[9] they introduced a special lattice in which each molecule carries several contact points with different interaction energies. When the quasi-chemical method (a version of the mean-field approximation) was used, a qualitative description of the miscibility loop was obtained. Quantitative description cannot, however, be achieved with a mean-field approximation. The first successful non-mean-field method for describing the miscibility loop was developed by Wheeler and Anderson,[10,11] who suggested a decorated lattice that can be mapped on a spin $^1/_2$ Ising lattice. Using Scesney's exact Padé-approximant coefficients for spontaneous magnitization,[12] Wheeler and Anderson could simulate coexistence curves with both LCST and UCST. Although the language of Ising statistics is unfamiliar to most chemists and chemical engineers and the procedure is too complicated for practical purposes, the decorated-lattice results provide useful insights.

The above theories are all based on a close-packed lattice. To account for compressibility and changes in volume upon isothermal mixing, Sanchez and Lacombe[13] and Koningsveld and Kleintjens[14] have derived different forms of a lattice-fluid model based on Flory–Huggins theory. The equation of state as well as the Gibbs (or Helmholtz) energy of mixing has been obtained. Recently, Sanchez and Balazs[15] introduced corrections for oriented interactions between dissimilar components. The resulting lattice-fluid model can describe at least qualitatively the miscibility loop. On the other hand, Flory[16] and Patterson and Delmas[17] developed free-volume theories for polymer solutions. Model parameters can be obtained from experimental thermal-expansion and compressibility coefficients. At about the same time, Heil and Prausnitz[18]

[†] Present address: Thermodynamics Research Laboratory, East China Institute of Chemical Technology, Shanghai 200237, China.

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and later Brandani[19] developed a semiempirical local-composition theory; good agreement was found between theory and experiment for polymer solutions, but these were not able to describe LCST.

Freed and co-workers[20-22] recently developed a complicated lattice-field theory for polymer solutions which is formally an exact mathematical solution of the Flory–Huggins lattice. Good agreement was found between predicted results and the computer simulation data by Dickman and Hall[23] for the chain-insertion probability and for the pressures in a system of athermal chains and voids. Freed's theory does not use a mean-field approximation.

In this paper, we introduce a double-lattice model based on Freed's theory. "Ordinary" polymer solutions are described by the primary lattice, while a secondary lattice is introduced as a perturbation to account for oriented interactions.

Model Development

Our aim here is to establish expressions for the Helmholtz energy of mixing for binary polymer solutions. We begin with a primary lattice for the solvent/polymer mixture and later incorporate a secondary lattice.

1. Partition Function for a Double Lattice. Binary polymer solutions are described by a Flory–Huggins lattice, which we define as the primary lattice. Each molecule of solvent (1) occupies one site and each molecule of flexible polymer (2) occupies r_2 sites, where r_2 is the number of segments in the polymer molecule relative to $r_1 = 1$ for the solvent.

At temperature T, the canonical partition function Q is given by

$$Q = \sum_{\alpha} \exp(-E_\alpha/kT) \tag{2}$$

where k is the Boltzmann constant and the summation is over all possible configurations of the system. E_α is the potential energy of the system at configuration α. For a binary mixture where only nearest-neighbor interactions contribute to the potential energy

$$E_\alpha = -(N_{11}\epsilon_{11} + N_{22}\epsilon_{22} + N_{12}\epsilon_{12})_\alpha \tag{3}$$

where N_{11}, N_{22}, and N_{12} are the numbers of 1–1, 2–2, and 1–2 nearest-neighbor (nonbonded) segment–segment pairs. They are related by the conservation equations

$$2N_{11} + N_{12} = zq_1N_1$$

$$2N_{22} + N_{12} = zq_2N_2 \tag{4}$$

where z is the coordination number, N_1 and N_2 are numbers of molecules of solvent (1) and polymer (2), respectively, and q_1 and q_2 are external surface parameters for molecule 1 and molecule 2, related to r_1 and r_2 by

$$q_1 = (zr_1 - r_1 + 2)/z$$

$$q_2 = (zr_2 - r_2 + 2)/z \tag{5}$$

The positive energy parameters, ϵ_{11}, ϵ_{22}, and ϵ_{12}, are for the corresponding nearest-neighbor segment–segment interactions. For the mixtures of interest here, eq 2 can also be expressed by

$$Q = \sum_{N_{12}} g(N_1,r_1,N_2,r_2,N_{12})(\exp(\epsilon_{11}/kT))^{N_{11}} \times (\exp(\epsilon_{22}/kT))^{N_{22}}(\exp(\epsilon_{12}/kT))^{N_{12}} \tag{6}$$

where $g(N_1,r_1,N_2,r_2,N_{12})$ is the combinatorial factor which depends on the number of 1–2 segment–segment pairs (not to be confused with g_{12} in eq 1). The summation is over all possible N_{12}. The Helmholtz energy of mixing can then be calculated by

$$\Delta A/kT = -N_r \ln Q + N_{r_1} \ln Q_1 + N_{r_2} \ln Q_2 \tag{7}$$

where Q_1 and Q_2 are partition functions for the pure components; N_r, N_{r_1}, and N_{r_2} are the numbers of lattice sites for the mixture and the pure components, respectively.

Next, we consider polymer solutions where segment–segment interactions between i and j include oriented interactions originating from hydrogen-bonding, donor–acceptor electron transfer or strong dipole–dipole interactions. The surface fraction of a segment permitting oriented interactions is designated by η. In general, η is different for different components; for simplicity, we treat η as a constant. Later we show that the calculated results are insensitive to the numerical value of η. The total number of i–j segment–segment interactions, N_{ij}, is determined from the primary lattice, including both nonspecific and oriented interactions. We visualize three types of interactions. The first (hh) occurs when both i and j interact using their oriented surfaces. The second (nn) occurs when both i and j interact between their nonoriented surfaces. The third (nh) occurs when i and j interact such that one entails an oriented and the other a nonoriented surface for interaction. Only the first type is responsible for oriented interactions. In the limit of complete randomness, the respective numbers of interactions for these three types are $N_{ij}\eta^2$, $N_{ij}(1 - \eta)^2$, and $N_{ij}2\eta(1 - \eta)$, giving

$$N_{ij} = N_{\rm hh} + N_{\rm nn} + N_{\rm nh} = N_{ij}[\eta^2 + (1 - \eta)^2 + 2\eta(1 - \eta)] \tag{8}$$

where $N_{\rm hh}$, $N_{\rm nn}$, and $N_{\rm nh}$ are numbers of h–h, n–n, and n–h pairs, respectively. However, we do not use eq 8; we present it here only for conceptual purposes. For more realistic systems, the number of oriented i–j interactions $N_{\rm hh}$ differs appreciably from $N_{ij}\eta^2$; it depends on the competition between energetic and entropic effects. Generally, the specific oriented interaction is energetically favored because the energy is lowered upon pair formation. However, it is entropically unfavored because the number of configurations characteristic of the nonspecific interaction outweighs the number of configurations characteristic of the specific oriented interaction.

To account for the additional Helmholtz energy associated with oriented i–j interactions, we construct a simple Ising model, which we describe by a secondary lattice. In this secondary lattice, the total number of lattice sites, N_l, is related to the number of i–j pairs N_{ij} by the conservation equation

$$N_lz/2 = N_{ij} \tag{9}$$

The number of sites available for oriented interaction in this lattice is $N_l\eta$, while the remaining $N(1 - \eta)$ sites cannot participate in oriented interactions. The numbers of oriented i–j interactions and nonoriented i–j interactions are consistent with those mentioned in eq 8 in the limit of complete randomness.

The partition function of this secondary lattice can be expressed as

$$Q_{{\rm sec},ij} = \sum_{N_{\rm hh}} g(N_{ij},\eta,N_{\rm hh})(\exp \delta\tilde{\epsilon}_{ij})^{N_{\rm hh}} \tag{10}$$

where $\delta\tilde{\epsilon} = \delta\epsilon/kT$ and $\delta\epsilon$ is the additional (positive) energy responsible for the oriented interaction for each i–j

segment–segment pair. The corresponding additional Helmholtz energy is

$$\Delta A_{\mathrm{sec},ij} = -kT \ln Q_{\mathrm{sec},ij} \tag{11}$$

For one i–j segment–segment pair, the additional Helmholtz energy is

$$\Delta A_{\mathrm{sec},ij}/N_{ij} = 2\Delta A_{\mathrm{sec},ij}/zN_1 = -(2kT/zN_1) \ln Q_{\mathrm{sec},ij} \tag{12}$$

To make progress, we use a reasonable approximation: the secondary lattice is independent of the primary lattice. In other words, we consider the secondary lattice as a perturbation about the primary lattice, which serves as the reference system. With the oriented interaction taken into account, the total partition function of the primary lattice for a binary mixture is given by

$$Q = \sum_{N_{12}} g(N_1,r_1,N_2,r_2,N_{12})\left(\exp\left(\frac{\epsilon_{11} - \Delta A_{\mathrm{sec},11}/N_{11}}{kT}\right)\right)^{N_{11}} \times \left(\exp\left(\frac{\epsilon_{22} - \Delta A_{\mathrm{sec},22}/N_{22}}{kT}\right)\right)^{N_{22}} \times \left(\exp\left(\frac{\epsilon_{12} - \Delta A_{\mathrm{sec},12}/N_{12}}{kT}\right)\right)^{N_{12}} \tag{13}$$

where $\Delta A_{\mathrm{sec},11}$, $\Delta A_{\mathrm{sec},22}$, and $\Delta A_{\mathrm{sec},12}$ are given by eq 11 or eq 12.

Because $\Delta A_{\mathrm{sec},ij}$ is temperature dependent, the essential feature of the secondary lattice is to introduce a temperature dependence for the "effective" energy parameter ϵ_{ij}. For calculations under isothermal conditions, the secondary lattice provides no functional advantage.

The summations in eqs 6 and 10 are over all possible values for N_{12} and N_{hh}. However, no closed-form analytical solution is available for either eq 6 or eq 10. The mean-field approximation gives a comparatively simple expression for the partition function and for the Helmholtz energy of mixing by taking the most probable value of N_{11}, N_{22}, and N_{12} through minimization of the Helmholtz energy. However, this procedure gives incorrect results near the critical point. On the other hand, Freed's theory seems to be promising because of its non-mean-field nature. Therefore, our model is based on the Helmholtz energy of mixing from Freed's theory.

2. $\Delta A_{\mathrm{sec},ij}$ for the Secondary Lattice. The secondary lattice is a simple Ising lattice where each component has only one segment and occupies one site. Then $r_1 = 1$ and $r_2 = 1$. To obtain an analytical expression for the Helmholtz energy of mixing for the Ising lattice, we use Freed's theory developed for a Flory–Huggins lattice. We set the numbers of segments of both components equal to unity and expand the Helmholtz energy of mixing to second order in reduced energy; we then obtain an approximate solution for the Ising model

$$\Delta A/N_r kT = x_1 \ln x_1 + x_2 \ln x_2 + z\tilde{\epsilon}x_1x_2/2 - z\tilde{\epsilon}^2 x_1^2 x_2^2/4 \tag{14}$$

where $\tilde{\epsilon}$ is a reduced interaction parameter defined by

$$\tilde{\epsilon} = \epsilon/kT = (\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/kT \tag{15}$$

To test eq 14, we calculate the coexistence curve using traditional phase-equilibrium thermodynamics. By adoption of a series-expansion method, accurate numerical results of coexistence curves have been obtained for the Ising model by Scesney[12] in the form of Padé-approximant coefficients for spontaneous magnetisation. We then compare the result calculated from eq 14 with that calculated from the Padé-approximant coefficients. In these calculations, $\tilde{\epsilon}_c$ for the critical temperature is evaluated by solving the equation

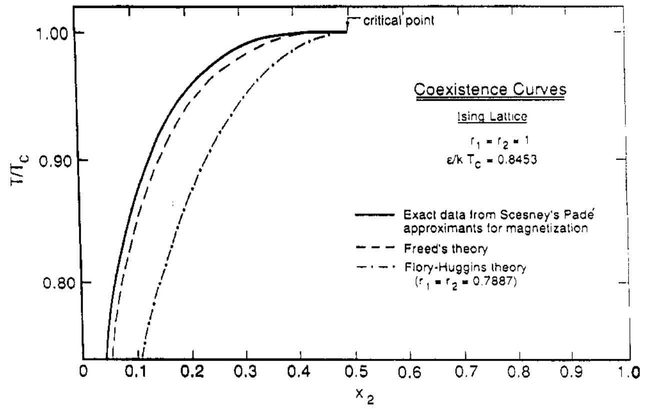

Figure 1. Comparison of coexistence curves calculated from various models with Scesney's accurate results.

$$(\partial^2 \Delta A/\partial x_1^2)_{x_1=0.5} = 0 \tag{16}$$

Figure 1 compares Scesney's accurate numerical solutions to predictions of the truncated Freed theory. Only half of the coexistence curve is shown because it is symmetrical about $x_1 = 0.5$. Figure 1 also shows results of the Flory–Huggins theory (given by eq 1 and $r_1 = r_2 = 0.7887$); here the value of r was chosen to obtain the same critical point as that calculated from Freed's theory. The results of Freed's theory (eq 14) are much better than those from Flory–Huggins theory. For the range from $T/T_c = 1$ to $T/T_c = 0.75$, the standard deviation of compositions of the conjugated phases of the coexistence curve (calculated in comparison with Scesney's accurate results), RMSx, is 0.0193.

However, agreement between phase boundaries calculated by Freed's theory and the results from Scesney is not complete, probably because eq 14 does not include higher terms. There are several ways to revise eq 14 to improve the coexistence curves. Two of them are investigated here. One way is to introduce an empirical coefficient c_2 to the $z\tilde{\epsilon}^2x_1^2x_2^2/4$ term. The best choice is $c_2 = 1.074$. The other way is to add to eq 14 an additional high-order term, $c_{10}z\tilde{\epsilon}^{10}x_1^{10}x_2^{10}$, arbitrarily taken to be of order 10. The best choice of the numerical coefficient is $c_{10} = 380.0$. The results of these two revisions are well-matched. If $c_2 = 1.074$ and $c_{10} = 0$, RMSx = 0.0015; if $c_2 = 1$ and $c_{10} = 380.0$, RMSx = 0.0066. Any linear interpolation between these two limits gives nearly equally good results. Therefore, we can write a general expression for the Helmholtz energy of mixing for the Ising model. For this special case where $r_1 = r_2 = 1$

$$\Delta A/N_r kT = x_1 \ln x_1 + x_2 \ln x_2 + z\tilde{\epsilon}x_1x_2/2 - c_2 z\tilde{\epsilon}^2 x_1^2 x_2^2/4 - c_{10} z\tilde{\epsilon}^{10} x_1^{10} x_2^{10} \tag{17}$$

where c_2 and c_{10} are related by

$$c_{10} = 5515.1 - 5135.1c_2 \tag{18}$$

The coefficients of eq 18 are obtained from the two limits mentioned above.

The calculated coexistence curve using eq 17 is nearly perfect when compared to Scesney's accurate results. For some binary systems, we use $c_2 = 1.074$ and $c_{10} = 0$. However, as shown later, for some binary mixtures, it is better to retain the high-order term while restricting constants c_2 and c_{10} according to eq 18.

For the secondary lattice, component 1 represents those sites available for oriented interactions while component 2 represents those sites not participating in oriented interactions. The contribution to the Helmholtz energy of mixing ($\Delta A_{\mathrm{sec},ij}$) is obtained directly from eq 17 with three changes. First, x is replaced by η; second, $\tilde{\epsilon}$ is replaced by $\delta\tilde{\epsilon}$; and third, we add the additional energy of the reference state

$$\Delta A_{\mathrm{sec},ij} = N_1kT[\eta \ln \eta + (1-\eta) \ln (1-\eta) + z\delta\tilde{\epsilon}_{ij}\eta(1-\eta)/2 - c_2 z(\delta\tilde{\epsilon}_{ij})^2\eta^2(1-\eta)^2/4 - c_{10}z(\delta\tilde{\epsilon}_{ij})^{10}\eta^{10}(1-\eta)^{10} - z\eta\delta\tilde{\epsilon}_{ij}/2] = N_1kT[\eta \ln \eta + (1-\eta) \ln (1-\eta) - z\delta\tilde{\epsilon}_{ij}\eta^2/2 - c_2 z(\delta\tilde{\epsilon}_{ij})^2\eta^2(1-\eta)^2/4 - c_{10}z(\delta\tilde{\epsilon}_{ij})^{10}\eta^{10}(1-\eta)^{10}] \quad (19)$$

The first two terms on the right-hand side account for the Flory–Huggins entropy that arises from mixing $N_1\eta$ sites with $N_1(1-\eta)$ sites. The term $-z\eta\delta\tilde{\epsilon}_{ij}/2$ accounts for the energy of the reference state where all the sites in the lattice are responsible for oriented interactions. The contribution of the other reference state (where all the sites in the lattice cannot participate in oriented interactions) is zero. Constants c_2 and c_{10} satisfy eq 18.

For one i–j segment–segment pair, the additional Helmholtz energy is

$$\Delta A_{\mathrm{sec},ij}/N_{ij} = 2\Delta A_{\mathrm{sec},ij}/zN_1 = (2kT/z)[\eta \ln \eta + (1-\eta) \ln (1-\eta) - z\delta\tilde{\epsilon}_{ij}\eta^2/2 - c_2 z(\delta\tilde{\epsilon}_{ij})^2\eta^2(1-\eta)^2/4 - c_{10}z(\delta\tilde{\epsilon}_{ij})^{10}\eta^{10}(1-\eta)^{10}] \quad (20)$$

Calculated results are insensitive to η because it is coupled with the additional energy $\delta\epsilon_{ij}$.

3. ΔA for the Primary Lattice. In this work, the primary lattice for fluid mixtures is a Flory–Huggins lattice. In Freed's theory, there are three contributions to the Helmholtz energy of mixing for a Flory–Huggins lattice: the mean-field contribution plus two corrections for deviations from mean-field behavior, one energetic and one entropic. After rearrangement, the Helmholtz energy of mixing can be expressed as

$$\Delta A/N_r kT = (\Phi_1/r_1) \ln \Phi_1 + (\Phi_2/r_2) \ln \Phi_2 + \sum_m \sum_n a_{mn}\Phi_1{}^m\Phi_2{}^n \quad (21)$$

where coefficients a_{mn} are functions of z, r_1, r_2, and $\tilde{\epsilon}$. Upon expansion of the Helmholtz energy of mixing to order $\tilde{\epsilon}^2$ and z^{-2} for a cubic lattice ($z = 6$), the coefficients are

$$a_{11} = (4/9)(1/r_1 - 1/r_2)^2 + 2\tilde{\epsilon}$$

$$a_{21} = -(1/2 - 11/54r_2 - 11/27r_1 + 1/9r_1r_2)(1/r_1 - 1/r_2)^2 + \tilde{\epsilon}/r_2$$

$$a_{12} = -(1/2 - 11/54r_1 - 11/27r_2 + 1/9r_1r_2)(1/r_1 - 1/r_2)^2 + \tilde{\epsilon}/r_1$$

$$a_{31} = (1/3 - 2/9r_2 - 4/9r_1 + 1/18r_2{}^2 + 1/6r_1{}^2 + 1/9r_1r_2)(1/r_1 - 1/r_2)^2$$

$$a_{13} = (1/3 - 2/9r_1 - 4/9r_2 + 1/18r_1{}^2 + 1/6r_2{}^2 + 1/9r_1r_2)(1/r_1 - 1/r_2)^2$$

$$a_{22} = (2/3 - 2/3r_1 - 2/3r_2 + 1/6r_1{}^2 + 1/6r_2{}^2 + 1/3r_1r_2)(1/r_1 - 1/r_2)^2 - 3c_2\tilde{\epsilon}^2/2 \quad (22)$$

where $c_2 = 1$ in Freed's work. Here, however, we use $c_2 = 1.074$. All other coefficients a_{ij} not mentioned in eq 22 are zero.

To test the theory, we first calculate the coexistence curve for a polymer solution with $r_1 = 1$ and $r_2 = 100$; we then compare the results with the computer simulation data recently presented by Madden, Pesci, and Freed.[24] For these calculations, we need chemical potentials for solvent 1 and polymer 2. They are found from

$$\mu_1 - \mu_1{}^\circ = \partial\Delta A/\partial N_1$$

$$\mu_1 - \mu_1{}^\circ = kT[\ln \Phi_1 + \Phi_2(1 - r_1/r_2) + r_1\sum_m \sum_n a_{mn}(m\Phi_1{}^{m-1}\Phi_2{}^{n+1} + (1-n)\Phi_1{}^m\Phi_2{}^n)] \quad (23)$$

$$\mu_2 - \mu_2{}^\circ = \partial\Delta A/\partial N_2$$

$$\mu_2 - \mu_2{}^\circ = kT[\ln \Phi_2 + \Phi_1(1 - r_2/r_1) + r_2\sum_m \sum_n a_{mn}(n\Phi_1{}^{m+1}\Phi_2{}^{n-1} + (1-m)\Phi_1{}^m\Phi_2{}^n)] \quad (24)$$

Superscript degree refers to the standard state (pure close-packed liquid at system temperature T). The comparison is shown in Figure 2 which also gives results from the Flory–Huggins theory. It is surprising that Freed's theory cannot predict the correct coexistence curve, even qualitatively. The prediction is even worse than that of the Flory–Huggins theory. The poor results may be due to neglect of higher terms in the expansion of the partition function or Helmholtz energy of mixing. We find that the entropic correction is the weakest term. Once we omit it, the prediction will be much better, although improvement is still needed. We therefore revise the entropic correction term by dropping all the higher order terms and retaining only the first-order term but multiplied by an empirical coefficient c_s. The a_{mn} in eq 20 are then revised as

$$a_{11} = (4/9)c_s(1/r_1 - 1/r_2)^2 + 2\tilde{\epsilon}$$

$$a_{21} = \tilde{\epsilon}/r_2, \quad a_{12} = \tilde{\epsilon}/r_1$$

$$a_{22} = -3c_2\tilde{\epsilon}^2/2 \quad (25)$$

where $c_2 = 1.074$. All other coefficients a_{mn} not mentioned in eq 25 are zero. As shown in Figure 2, with $c_s = 0.3$, we obtain a very good prediction of the coexistence curve when compared with the computer simulation results by Madden et al.

To account for the oriented interactions, we need a secondary lattice. The secondary-lattice contribution is a perturbation to a fixed reference system (i.e., the primary lattice) whose Helmholtz energy of mixing is given by eq 21. Equation 13 gives the total partition function, which includes both reference and perturbation contributions. The general equation for the Helmholtz energy of mixing, eq 21, follows from eq 6. Equation 13 also follows from eq 6. To account for oriented interactions, we use eq 6 but we must replace ϵ_{ij} by $\epsilon_{ij} - \Delta A_{\mathrm{sec},ij}/N_{ij}$. Following the definition of $\tilde{\epsilon}$ in eq 15, if oriented interactions occur in 1–2 segment–segment pairs, we replace $\tilde{\epsilon}$ by $\tilde{\epsilon} + 2\Delta A_{\mathrm{sec},12}/N_{12}kT$ in eqs 21 and 23–25. If oriented interactions occur in 1–1 segment–segment pairs, $\tilde{\epsilon}$ is replaced by $\tilde{\epsilon} - \Delta A_{\mathrm{sec},11}/N_{11}kT$ in these equations. If oriented interactions occur in 2–2 segment–segment pairs, $\tilde{\epsilon}$ is replaced by $\tilde{\epsilon} - \Delta A_{\mathrm{sec},22}/N_{22}kT$.

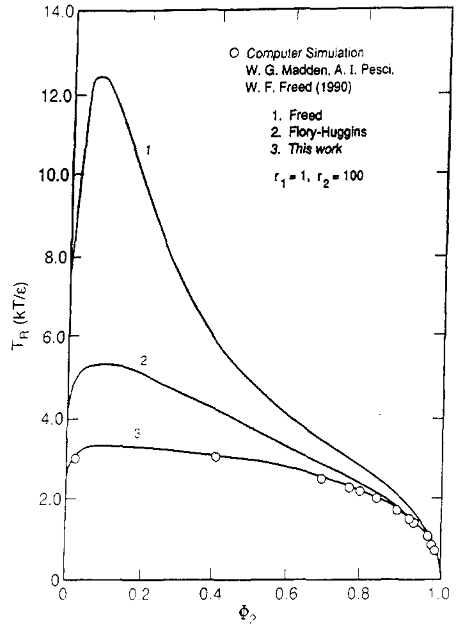

Figure 2. Comparison of coexistence curves calculated from various models with computer simulation results.

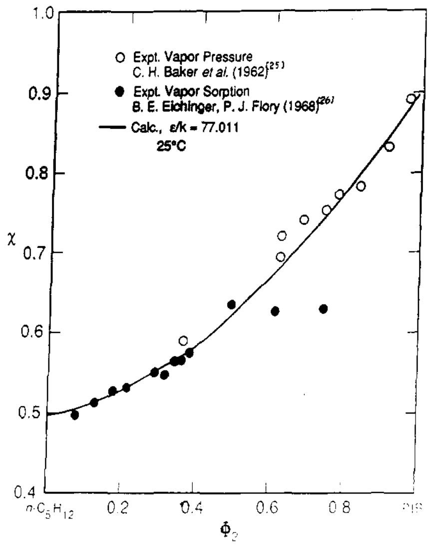

Figure 3. Composition dependence of χ for n-pentane/PIB.

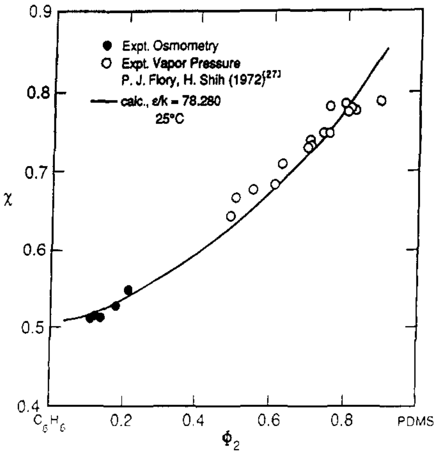

Figure 4. Composition dependence of χ for benzene/PDMS.

Phase-Equilibrium Calculations

1. Results for Flory–Huggins Parameter χ. The Flory–Huggins parameter χ is often used to characterize the relative solvent–polymer interaction. It is defined by the chemical potential of the solvent

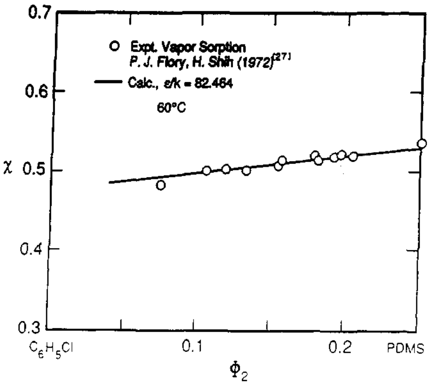

Figure 5. Composition dependence of χ for chlorobenzene/PDMS.

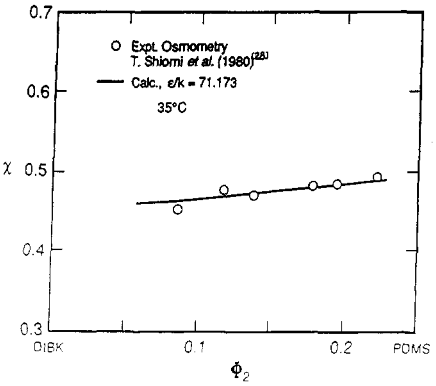

Figure 6. Composition dependence of χ for DIBK/PDMS.

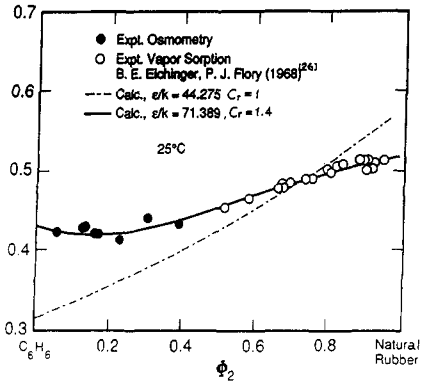

Figure 7. Composition dependence of χ for benzene/nature rubber.

$$\mu_1 - \mu_1^\circ = kT[\ln \Phi_1 + \Phi_2(1 - r_1/r_2) + \chi\Phi_2^{\,2}] \qquad (26)$$

where r_1 is usually set equal to unity; r_2 is then calculated using specific volumes ν_1 and ν_2 for solvent and polymer

$$r_2 = M_2\nu_2/M_1\nu_1 \qquad (27)$$

where M_1 and M_2 are molecular masses for solvent and polymer, respectively. If the interaction parameter g_{12} in eq 1 does not depend on the concentration, $\chi = g_{12}$.

The relative chemical potential for solvent $\mu_1 - \mu_1^\circ$ can be determined experimentally by various methods such as vapor sorption, osmotic pressure, light scattering, and sedimentation. When carried out with care, results from different experimental methods show good consistency with respect to each other.

To test our model, we substitute the relative chemical potential of solvent from eq 23 into eq 26; we then calculate parameter χ. It is important to note that we calculate

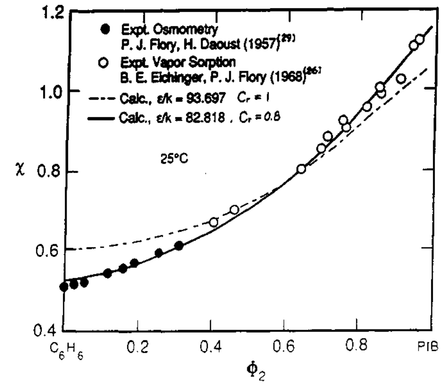

Figure 8. Composition dependence of χ for benzene/PIB.

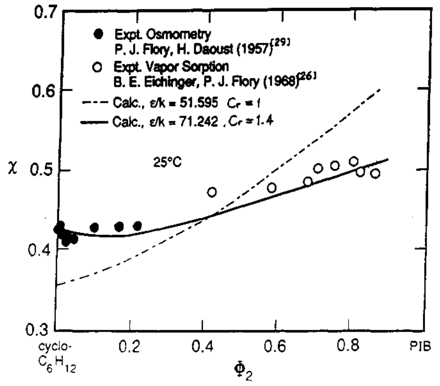

Figure 9. Composition dependence of χ for cyclohexane/PIB.

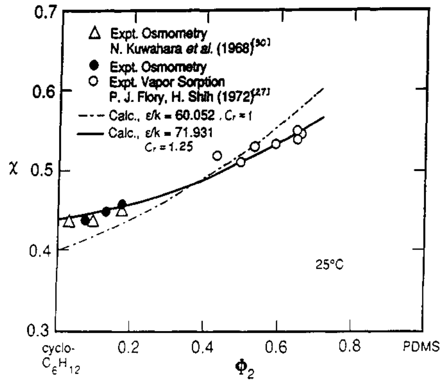

Figure 10. Composition dependence of χ for cyclohexane/PDMS.

volume fractions Φ in eq 23 using model parameter r_2, which sometimes should be adjusted; however, in eq 26, r_2 is calculated by eq 27.

To calculate parameter χ, the secondary lattice is not used because the data we examined are isothermal. Usually, two parameters are needed, the energy parameter ϵ/k and size parameter c_r. The latter is defined as

$$c_r = r_2(\text{optimal fit})/r_2(\text{from eq 26})$$

Figures 3–6 show results for *n*-pentane/PIB (polyisobutene) at 25 °C, benzene/PDMS [poly(dimethylsiloxane)] at 25 °C, chlorobenzene/PDMS at 60 °C, and DIBK (diisobutyl ketone)/PDMS at 35 °C. In these cases, r_2 does not require adjustment; i.e., $c_r = 1$. One parameter ϵ/k gives a good fit. The concentration dependence of χ, which cannot be described by the original Flory–Huggins theory, can be reproduced satisfactorily. However, sometimes two parameters are needed. Figures 7–11 show results for benzene/natural rubber at 25 °C, benzene/PIB at 25 °C, cyclohexane/PIB at 25 °C, cyclohexane/PDMS at 25 °C, and MEK (methyl ethyl ketone)/PDMS at 20 and 50 °C. One parameter is not enough for a good fit. Two parameters, ϵ/k and c_r, are needed. Note that the minima in χ–Φ curves for benzene/nature rubber and cyclohexane/PIB systems can be reproduced quite well. Figure 11 showing MEK/PDMS at two temperatures suggests that a temperature-dependent ϵ/k is needed. Because of the scarcity of data at different temperatures, we did not try to introduce the secondary lattice, which provides a temperature coefficient for χ.

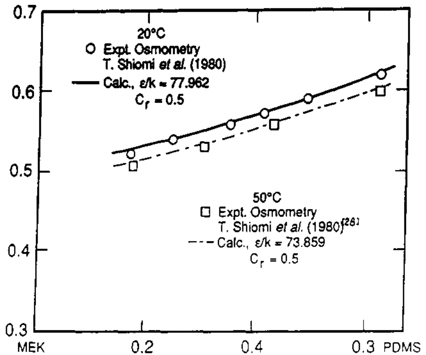

Figure 11. Composition dependence of χ for MEK/PDMS.

2. Results for Liquid–Liquid Equilibria. For liquid–liquid equilibrium calculations, we require the experimental coordinates of the critical point. We find these coordinates using

$$\frac{\partial^2(\Delta A/N_r kT)}{\partial {\Phi_2}^2} = 0$$

$$\frac{\partial^2(\Delta A/N_r kT)}{\partial {\Phi_2}^2} = \frac{1}{r_1\Phi_1} + \frac{1}{r_2\Phi_2} + \sum_m \sum_n a_{mn}[[m(m - 1){\Phi_1}^{m-2}{\Phi_2}^{n} - 2mn{\Phi_1}^{m-1}{\Phi_2}^{n-1} + n(n-1){\Phi_1}^{m}{\Phi_2}^{n-2}] \quad (28)$$

and

$$\frac{\partial^3(\Delta A/N_r kT)}{\partial {\Phi_2}^3} = 0$$

$$\frac{\partial^3(\Delta A/N_r kT)}{\partial {\Phi_2}^3} = \frac{1}{r_1{\Phi_1}^2} - \frac{1}{r_2{\Phi_2}^2} + \sum_m \sum_n a_{mn}[[-m(m-1) \times (m-2){\Phi_1}^{m-3}{\Phi_2}^{n} + 3mn(m-1){\Phi_1}^{m-2}{\Phi_2}^{n-1} - 3mn(n - 1){\Phi_1}^{m-1}{\Phi_2}^{n-2} + n(n-1)(n-2){\Phi_1}^{m}{\Phi_2}^{n-3} \quad (29)$$

Using the experimental upper (or lower) critical coordinates, eqs 28 and 29 are solved to yield energy and size parameters ϵ/k and r_2 ($r_1 = 1$).

For hydrogen-bonding systems or for systems whose components differ appreciably in molecular size, the primary lattice alone always yields a narrower coexistence curve. Therefore, we have to introduce the secondary lattice to obtain a satisfactory fit.

For systems having only a UCST, we set $c_2 = 1.074$ and $c_{10} = 0$. The results are not sensitive to η. It can be arbitrarily set within a reasonable range from 0.3 to 0.5. The only additional adjustable parameter is $\delta\epsilon/k$, the extra energy contributed by an oriented interaction. This parameter is obtained from fitting data for one tie line. Figures 12 and 13 show results for DIBK/PIB22700 (polyisobutene, M_w = 22 700) and DIBK/PIB285000 (polyisobutene, M_w = 285 000). A single lattice exhibits only

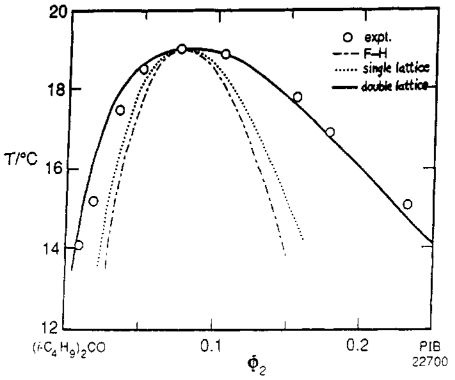

Figure 12. Coexistence curves for DIBK (1)/PIB22700 (2). FH: $r_1 = 1$, $r_2 = 142.6$, $\epsilon/k = 57.187$ K. Single lattice: $r_1 = 1$, $r_2 = 160.7$, $\epsilon/k = 86.705$ K. Double lattice: $r_1 = 1$, $r_2 = 160.7$, $\epsilon/k = -346.029$ K. $\delta\epsilon_{11}/k = 1658.57$ K, $\eta = 0.3$. Exptl: Shultz and Flory.[31]

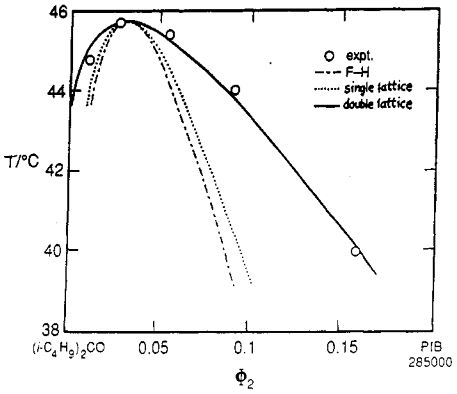

Figure 13. Coexistence curves for DIBK (1)/PIB285000 (2). FH: $r_1 = 1$, $r_2 = 1540$, $\epsilon/k = 55.884$ K. Single lattice: $r_1 = 1$, $r_2 = 1712$, $\epsilon/k = 86.162$ K. Double lattice: $r_1 = 1$, $r_2 = 1712$, $\epsilon/k = -332.347$ K. $\delta\epsilon_{11}/k = 1658.57$ K, $\eta = 0.3$. Exptl: Shultz and Flory.[31]

a small improvement over those calculated from original Flory–Huggins theory. Using a double lattice, we obtain a very good fit.

For systems having an LCST or having closed-miscibility loops (both UCST and LCST), c_{10} cannot be set to zero; c_{10} or c_2 must be adjusted to obtain a good fit with the restraint shown by eq 18. In these cases, altogether four parameters are needed. Besides ϵ/k and r_2 obtained from one critical point, we have to use another two, viz., $\delta\epsilon/k$ for special interactions and c_{10}. They can be obtained by fitting another set of experimental (upper or lower) critical coordinates and one tie line, giving the equilibrium compositions for a pair of conjugated phases. If the critical compositions for upper and lower critical points differ appreciably, then r_2 obtained from LCST will differ from that obtained from UCST. In this case, we use a linear relation to calculate r_2 for temperatures between UCST and LCST. For polymer solutions, because of experimental difficulties at higher temperatures, usually we only have an experimental LCST. In this case, we postulate a reasonable pseudo-UCST and then follow the preceding procedure. Figures 14 and 15 show results for water/PEG5000 [poly(ethylene glycol), $M_w = 5000$] and water/PPG400 [poly(propylene glycol), $M_w = 400$]; they are systems with an experimental LCST. Excellent fits are obtained. Figure 16 shows results for water/PEG3000 [poly(ethylene glycol), $M_w = 3000$] with a miscibility loop. In this case we get a fair fit with $c_{10} = 328.65$. The standard deviation of compositions in weight percent for the coexistence curve RMSw = 0.035. The dotted line in this figure is calculated with $c_{10} = 0$. The corresponding RMSw = 0.080. An essentially perfect fit can be obtained by using an empirical value for c_{10} and eq 18, but, in that case, c_2 is negative. We do not assign any significance to that result because, first, we have no information con-

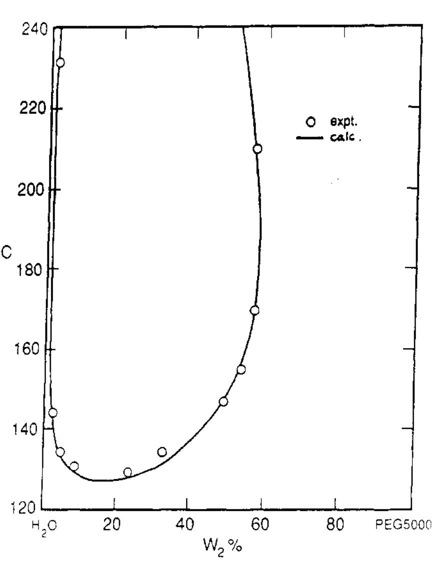

Figure 14. Coexistence curves for water (1)/PEG5000 (2). Double lattice: $r_1 = 1$, $r_2 = 1069.2$, $\epsilon/k = 949.143$ K. $\delta\epsilon_{12}/k = 1346.971$ K, $\eta = 0.3$, $c_{10} = 2.3325$. Exptl: Malcolm and Rowlinson.[32]

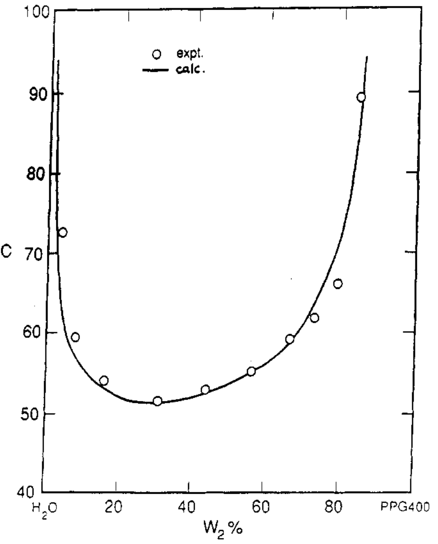

Figure 15. Coexistence curves for water (1)/PPG400 (2). Double lattice: $r_1 = 1$, $r_2 = 49.143$, $\epsilon/k = 1126.365$ K. $\delta\epsilon_{12}/k = 1581.108$ K, $\eta = 0.3$, $c_{10} = 0.084\,473$. Exptl: Malcolm and Rowlinson.[32]

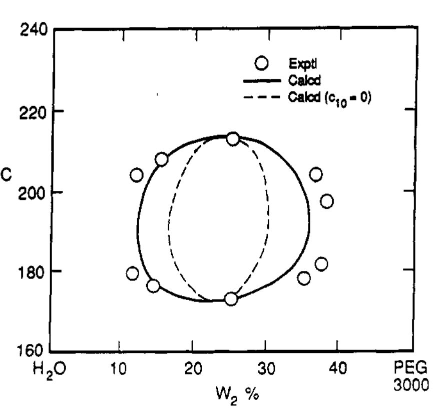

Figure 16. Coexistence curves for water (1)/PEG3000 (2). Double lattice: $r_1 = 1$, r_2(UCST) = 470.91, r_2(LCST) = 489.24, $\epsilon/k = 737.339$ K. $\delta\epsilon_{12}/k = 858.503$ K, $\eta = 0.3$, $c_{10} = 328.65$. Exptl: Malcolm and Rowlinson.[32]

cerning the accuracy of the experimental data (these data are not shown in tabulated form but only by a small graph), and, second, near the upper critical solution temperature (214 °C), it is likely that free-volume corrections (neglected here) are required.

Discussion and Conclusions

The model presented here assigns a significant composition dependence to the Flory parameter g_{12} (eq 1) even when there is no specific solute–solvent interaction such as hydrogen bonding. A significant part of this composition dependence is given by Freed et al.,[22] and, as shown by them, it is essentially equivalent to replacing volume fractions in the last term of eq 1 by surface fractions, as suggested many years ago by Orofino and Flory[33] and in somewhat different form by Koningsveld and Kleintjens.[7] However, Freed et al.'s corrections to the original Flory–Huggins theory go further; they show that additional terms are required because their theory, unlike those of most earlier authors, does not make the usual mean-field assumptions. In eq 25, the second term for a_{11} is the original Flory–Huggins term; the first term for a_{11} corrects the entropy for deviations from mean-field behavior. Coefficients a_{12} and a_{21} are (essentially) equivalent to the effect that concerned Orofino and Flory[33] and Koningsveld and Kleintjens.[7] Coefficient a_{22} corrects for the Flory–Huggins mean-field energy.

When the system temperature is well below the gas–liquid critical temperature of the solvent, polymer solutions can be properly described by using a lattice model. However, the mean-field approximation widely adopted in derivations of the Helmholtz energy of mixing has seriously limited the applicability of lattice models. Besides its well-known poor performance in the vicinity of the critical consolution point, the dependence of Flory–Huggins parameter χ on composition exposes another weakness of the mean-field approximation. Many attempts have been made to overcome these difficulties. However, empirical terms or empirical coefficents have to be introduced. Freed's lattice field theory provides a new impetus because of its non-mean-field nature. The present work shows that, with small empirical revisions, Freed's results are useful for describing the phase behavior of strongly nonideal fluid mixtures including polymer solutions. The successful description of the concentration dependence of Flory–Huggins parameter χ and the coexistence curves, especially near the critical consolute points, leads us to the conclusion that, in modified form, the Ising lattice as well as the Flory–Huggins lattice can provide good representations of phase equilibria for polymer solutions. The deficiency of Flory–Huggins theory does not lie in the lattice model but in the approximations used to obtain an expression for the Helmholtz energy of mixing. When the Helmholtz energy of mixing is modified to agree with accurate results of spontaneous magnetization of the Ising model, and the computer simulation coexistence curve for a lattice polymer mixture with $r_1 = 1$ and $r_2 = 100$, the phase behavior of polymer solutions can be reproduced well.

In our model, we have two adjustable parameters: the energy parameter ϵ/k and the size parameter c_r. For liquid–liquid equilibria showing a LCST or a miscibility loop, we need two additional parameters, the additional energy for an oriented interaction $\delta\epsilon/k$ and c_{10}. The need for c_r arises because the lattice model provides only an approximation for polymer solutions; a solvent molecule can hardly be considered a spherical monomer. A polymer molecule is not an ideal flexible chain as we have assumed in the theory. Upon introducing c_r we can fit the χ–Φ curves for several polymer/solvent mixtures. For mixtures with oriented interactions, a double-lattice model is useful. Incorporating c_2 and c_{10} makes the model more flexible.

The model presented here is for polymer solutions at high densities, i.e., near close packing. It can serve as a basis for constructing models for polymer solutions that are compressible; for such mixtures, it will be necessary to add free-volume corrections.[3]

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