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Entropy and Energy of Mixing in Polymer Solutions: Simple Expressions That Approximate Lattice Cluster Theory

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ABSTRACT: The phase behavior of polymer solutions, melts, and blends depends on competition between the energy and entropy of mixing. Accurate representation of both the temperature and composition dependence is particularly difficult near mixture critical points. Although a number of theories have been proposed, assessing their accuracy and limitations was difficult until molecular simulations of polymer solutions were made. In this work, a new expression for free energy of mixing is proposed. The repulsive part is Guggenheim's random-mixing theory; the attractive part is a Boltzmann-weighted, surface-fraction-averaged energy. We compare this equation with expressions from Flory, Guggenheim, Born–Green–Yvon, and Freed as well as with Monte Carlo simulations. Comparisons also are made with experimental data for real systems.

Introduction

Lattice models have been used to describe the properties of polymer solutions, melts, and blends since the work of Flory,[1] Huggins,[2] and Guggenheim[3-5] in the 1940s. Generally it is assumed that the partition function of the molecules can be separated into an athermal term and a thermal term. From the macroscopic point of view, the athermal (or repulsive) term corresponds to the combinatorial entropy and the thermal (or attractive) term corresponds to the energy plus the noncombinatorial entropy. Flory derived his entropy of mixing expression by assuming that the polymer concentration is uniform throughout the solution. However, this is a poor assumption at low concentrations. Because the segments of the polymer must be connected, there are regions of the solution that contain more polymer than Flory assumed and there are large domains that are polymer free. While this has little effect on solvent activity, it does lead to incorrect estimates of the polymer activity because the concentration of polymer in those domains that contain polymer is much higher than the overall concentration.

For systems having a nonzero interchange energy, Flory used a volume-fraction-weighted, mean-field term for the energy of mixing. The Helmholtz free energy of mixing is then obtained by combining the entropy and energy of mixing terms. The Flory equation, though simple, gives large deviations from experimental data for most real systems unless a temperature-, size-, and/or composition-dependent energy parameter is used. As shown in Figure 1, Flory theory predicts a higher asymmetry in the phase diagram than is seen in experiments and, at medium and high polymer concentrations, the predicted phase boundary is far from experimental data.

Guggenheim extended Chang's[6,7] technique of deriving the grand canonical partition function for a mixture of dimers and monomers to a mixture of polymers and monomers. By evaluating the insertion probability of arranging polymer and monomer on a group of sites, an expression for the athermal free energy of mixing was obtained. Guggenheim's random-mixing (GRM) theory assumes a completely random arrangement of molecules in a regular mixture. An obvious consequence of the random-mixing assumption is that the mixture's entropy of mixing is independent of its energy of mixing. The energy of mixing is proportional to the interchange energy. By averaging the pair interaction energy over the probability of the corresponding configurations, the energy of mixing is obtained. The energy of mixing is then combined with the entropy of mixing for an athermal mixture to yield the total Helmholtz free energy of mixing.

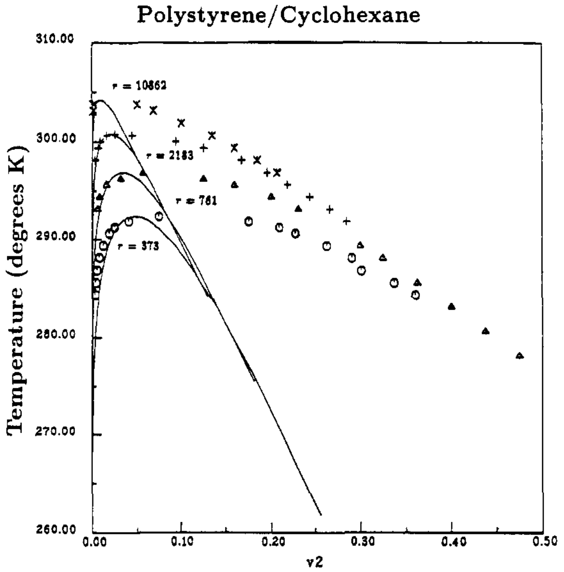

Figure 1. Coexistence curve for polystyrene in cyclohexane plotted against polymer volume fractions ϕ_2. The lines are calculated using the Flory equation, with the χ parameter determined by fitting the critical temperature for each molecular weight. Data points are from Shultz and Flory[21] (figure is extracted from ref 20).

Guggenheim abandoned the assumption of randomness in his quasi-chemical theory (GQC), introducing a variable to characterize the degree of nonrandomness. The degree of nonrandomness is solved from the equilibrium condition assuming that at equilibrium the configurational partition function is maximized.

More recently, Lipson[8] has developed a model for simple fluids using the theory of Born, Green, and Yvon (BGY).[9,10] Lipson's formalism is an expansion of the original BGY theory for the free energy of mixing. The original BGY theory evaluates the N and (N–1) particle distribution functions through a set of linked integral differential functions. Lipson applied the Kirkwood superposition approximation to express the triplet distribution as a product of pair distributions and then applied the independence approximation to the pair distributions. Lip-

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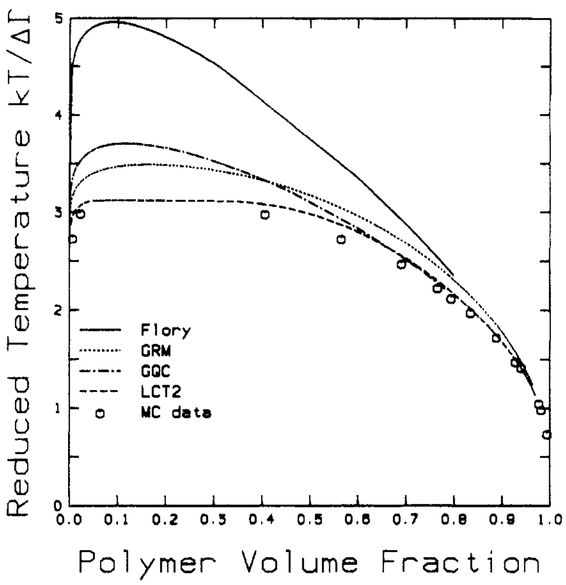

Figure 2. Coexistence curves calculated from Flory's equation, second-order lattice cluster theory (LCT2), and Guggenheim's random-mixing model for a mixture of linear-chain polymers (molecular weight $r = 100$) in a single-bead solvent with coordination number $z = 6$. Also shown are results of molecular dynamics simulations by Madden.[14]

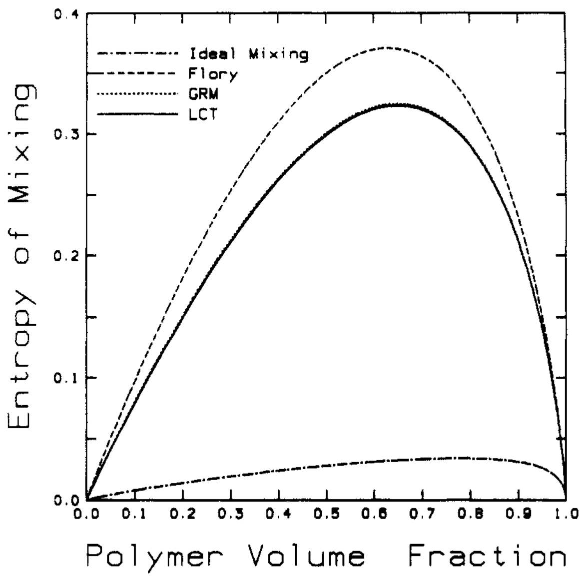

Figure 3. Comparison of the entropy of mixing calculated from the ideal entropy of mixing, Flory's entropy of mixing, Guggenheim's random-mixing theory, and Freed's lattice cluster theory. Calculations are performed for a mixture of linear-chain polymers with $r = 100$ in a single-bead solvent with $z = 6$ and a fixed number of lattice sites.

son's expression for the total free energy of mixing consists of Guggenheim's entropy of mixing term and an energy term (which contains both energetic and noncombinatorial entropic contributions) that is a series expansion of the interchange energy and concentration.

Freed and co-workers[11-13] proposed another way to solve the lattice model for polymer solutions, basing their calculations on "field theory". Freed and co-workers formulated tables of corrections to Flory theory, accounting for the details of polymer and solvent structure. In their model, thermodynamic properties depend not only on molecular size but also on molecular architecture. While their lattice cluster theory (LCT) used the same assumptions as previous lattice theories, such as pairwise additivity and single occupancy of lattice sites, its corrections to Flory theory for the entropy of mixing and energy of mixing are expressed as double expansions in coordination number and interaction energy. To obtain the grand canonical partition function for binary mixtures of polymer and solvent using lattice cluster theory, one must evaluate chain correlations in the athermal limit and interaction diagrams for different species in the nonathermal solution. Results from lattice cluster theory agree closely with Monte Carlo simulation data. Figure 2 shows the coexistence curves for a linear-chain polymer dissolved in a single-bead solvent. The simulation data were calculated by Madden et al.[14] Lattice cluster theory provides the best agreement with the simulation results.

Following Guggenheim rather than Freed, we write the concentration, interchange energy, and coordination number dependences of the entropy and energy of mixing in terms of the surface areas rather than volumes. We have investigated the size, composition, and temperature dependence of these theories and have found that the accuracy of Freed's lattice cluster theory can be obtained with relatively simple expressions suitable for engineering calculations.

Nonrandom Behavior

The complexity of lattice cluster theory limits its utility for practical calculations. Furthermore, applying lattice cluster theory to real systems is difficult if the chain structure differs from those studied by Freed. Our goal is to find simple yet accurate expressions for the entropy and energy of mixing which can be used to describe the phase behavior of polymer solutions.

Entropy of Mixing. Unlike mixtures involving molecules of similar size, the entropy of mixing in polymer solution is an important cause of phase separation. Figure 3 compares the entropy of mixing in a binary mixture for several different theories. Ideal entropy mixing gives the lower bound for entropy of mixing and Flory theory an upper bound. The true entropy of mixing lies within the region enclosed by ideal mixing and Flory theory. It can be seen that Guggenheim's random-mixing model gives an entropy of mixing that is nearly identical to LCT but is much simpler to use. Therefore, we use GRM's entropy of mixing as the repulsive term in our equation.

Energy of Mixing. Two important effects must be considered in developing an energy of mixing equation. First, site–site interactions should be calculated using surface fractions rather than volume fractions, since interactions among the constituent segments depend on the "interaction volume" of the molecules. In a large chain molecule, the volume available for interaction is smaller than the actual volume of the constituent segments because neighboring segments partially overlap. The interaction volume depends on the molecular structure, is characteristic of the molecule under consideration, and is proportional to the surface area of the segment.[15] Figure 4 depicts our view of segment–segment interactions. In this figure the black circles are meant to depict the molecular volumes and the shaded gray areas are meant to represent the attractive well that surrounds the repulsive core of each molecule. Since this gray area, the interaction volume, is proportional to the surface area of the molecule (but not its hard-core volume), it is more appropriate to use surface fractions, rather than volume fractions, in calculating the energy of the system.

The second issue that must be considered is that nonrandomness is important at low temperatures and at low concentrations. Guggenheim's quasi-chemical theory suggests that the nonrandomness correction takes the form of a Boltzmann factor in energy. The question arises with

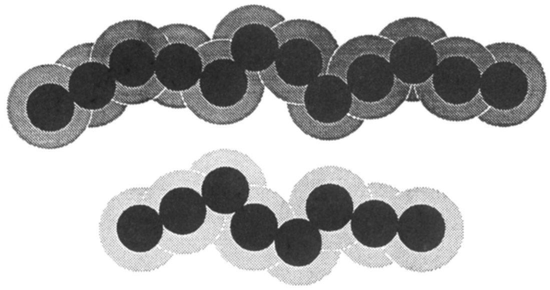

Figure 4. "Interaction volume" proportional to the surface area of a molecule in mixtures with large molecules.

how and where to place the Boltzmann factor. Guggenheim's quasi-chemical theory uses a positively weighted factor in the denominator to describe the nonrandomness in a polymer solution. Here we assume that the energy of a mixture is given as the double summation of the product of surface fractions times pair interaction energies weighted by their Boltzmann factors. To normalize for these Boltzmann factors, this must be divided by a double summation of the weighting factors. Therefore

$$\frac{U_{\mathrm{mix}}}{N_{\mathrm{A}}} = \frac{z}{2}(q_1n_1 + q_2n_2)\frac{\sum\sum\theta_i\theta_j\Gamma_{ij}P_{ij}}{\sum\sum\theta_i\theta_jP_{ij}} \tag{1a}$$

where

$$q_iz = r_i(z-2) + 2 \tag{1b}$$

$$\theta_i = \frac{q_in_i}{\sum_{j=1,2} q_jn_j} \tag{1c}$$

$$P_{ij} = e^{-\Gamma_{ij}/kT} \tag{1d}$$

In these expressions, r_i is the segment number, q_i is the surface number, θ_i and θ_j are surface fractions, Γ_{ij} is the energy of interaction of an i–j pair, and z is the coordination number. If we subtract the pure component values from eq 1a, assuming the $\Gamma_{11} = \Gamma_{22}$, we obtain the internal energy change on mixing (after some manipulation):

$$\frac{\Delta U_{\mathrm{mix}}}{N_{\mathrm{A}}} = \frac{z}{2}(q_1n_1 + q_2n_2)\frac{\theta_1\theta_2\Delta\Gamma e^{-\Delta\Gamma/2kT}}{1 + 2\theta_1\theta_2(e^{-\Delta\Gamma/2kT} - 1)} \tag{2a}$$

$$\Delta\Gamma = 2\Gamma_{12} - \Gamma_{11} - \Gamma_{22} \tag{2b}$$

This equation can be integrated with respect to temperature to obtain the Helmholtz free energy of mixing:

$$\frac{\Delta F_{\mathrm{mix}}}{RT} = n_1 \ln \phi_1 + \frac{z}{2}q_1n_1 \ln \frac{\theta_1}{\phi_1} + n_2 \ln \phi_2 + \frac{z}{2}q_2n_2 \ln \frac{\theta_2}{\phi_2} - \frac{z}{2}(q_1n_1 + q_2n_2) \ln (1 + 2\theta_1\theta_2(e^{-\Delta\Gamma/2kT} - 1)) \tag{3}$$

We refer to this equation as the nonrandom, surface-fraction model (NRSF). [It should be noted that different authors use different notation for the variables in eqs 1 and 2. The quantity $\Delta\Gamma$ is often referred to as the interchange energy and often is denoted by the symbols $(z/2)\omega$ or w. In the papers by Freed and co-workers, the symbol ϵ is used to describe $\Delta\Gamma$. In the paper by Lipson, the symbol ϵ is used to represent $\Delta\Gamma$. The quantity $\Delta\Gamma$ also can be related to the Flory χ parameter by the equation $\chi = (z/2)\Delta\Gamma$.]

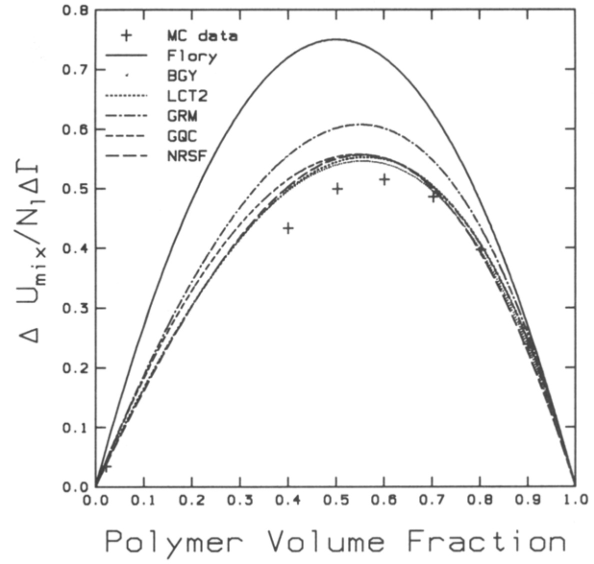

Figure 5. Comparison of energies of mixing calculated from Flory, GRM, GQC, BGY, LCT, and NRSF. Calculations are performed at $\Delta\Gamma/kT = 0.33$ with $r = 100$ and $z = 6$. Simulation data are from Madden.[14]

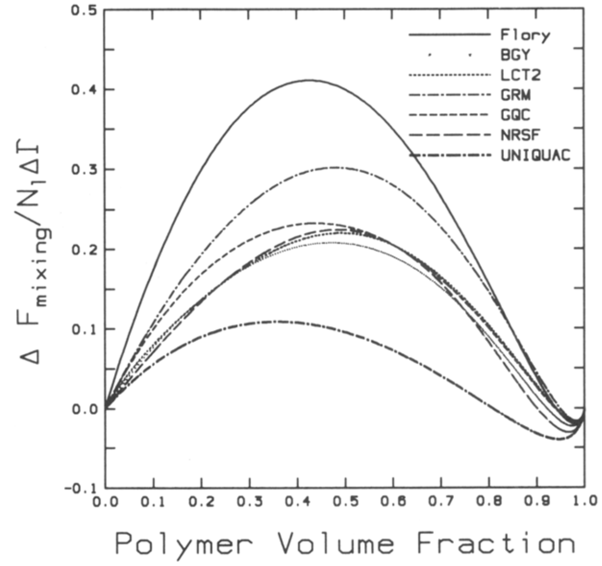

Figure 6. Comparison of the Helmholtz free energy of mixing between lattice theories and UNIQUAC. For a system of linear-chain polymers in a single-bead solvent with $r_2 = 100$, $z = 6$, $\Delta\Gamma/kT = 1.0$.

Comparisons of NRSF with Several Lattice Fluid Theories

Comparisons of the NRSF model with several lattice fluid theories and simulations are made in Figures 5–10 for mixtures of a linear-chain polymer in a single-bead solvent. Simulation data also are available for this system.

Energy of Mixing. Figure 5 shows the internal energy of mixing for a linear chain with $r_2 = 100$ in a single-bead solvent ($r_1 = 1$). The calculations were made with a fixed number of total lattice sites, comparing Flory–Huggins, GRM, GQC, BGY, LCT, and eq 2a. At low polymer concentrations, BGY and NRSF agree closely with LCT. At high concentrations, GQC approaches LCT more closely. In a polymer–solvent mixture, the critical region occurs at low polymer volume fractions because of the size difference of solute and solvent. The greater the size difference between solute and solvent, the lower the critical concentration. A small difference in ΔU_{mix} in the critical region is dramatically exaggerated in the coexistence curve,

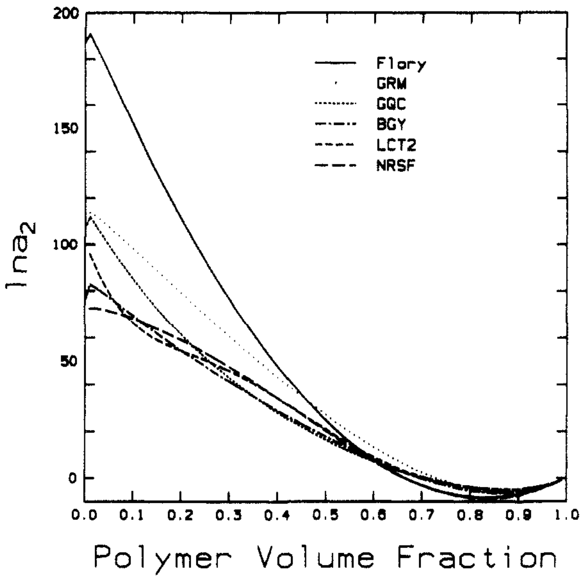

Figure 7. Comparison of activities of calculated from Flory, GRM, GQC, BGY, LCT, and NRSF. Activities of solute with $\Delta\Gamma/kT = 1.0$ and $z = 6$ in a mixture of linear-chain polymers with $r = 100$ in a single-bead solvent.

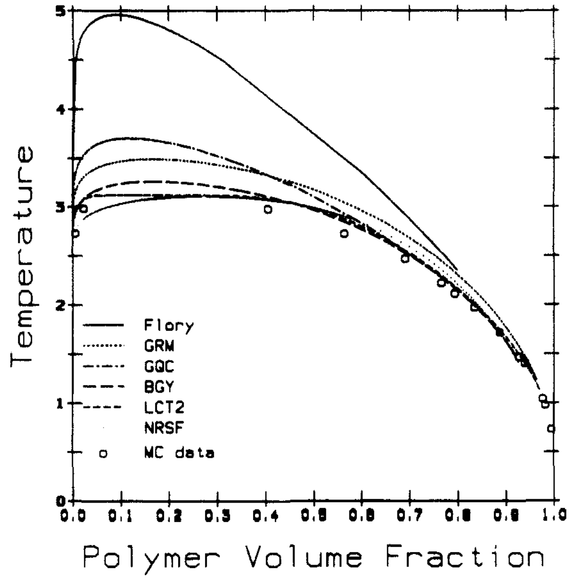

Figure 8. Comparison of coexistence curves calculated from Flory, GRM, GQC, BGY, LCT, and NRSF. For a mixture of linear-chain polymers in a single-bead solvent with $r = 100$ and $z = 6$. Temperatures are expressed as $kT/\Delta\Gamma$.

but differences at high concentrations affect the phase boundary negligibly.

Figure 6 shows the total Helmholtz energy of mixing for the same system. The results are similar to internal energy of mixing. In this figure, calculations for the UNIQUAC model[16,17] also are shown.

Activities. At phase equilibrium, the chemical potentials of each component in each phase must be equal. Phase equilibrium calculations are a stringent test of any theory, since they involve the derivative of the free energy of mixing. Under this condition, not only do the entropy and energy of mixing have to be correct but also the slope of the free energy of mixing curve has to be correct.

For the theories compared, differences in solvent (monomer) activities are small and are not presented here. However, predictions of polymer activities vary greatly among theories and it is the differences in polymer activities that lead to differences in phase behavior. Figure 7 shows the logarithm of solute activities. Generally, NRSF gives the best agreement with LCT. It should be noted that the curvature in LCT comes from the truncation of higher order terms and may not be correct.

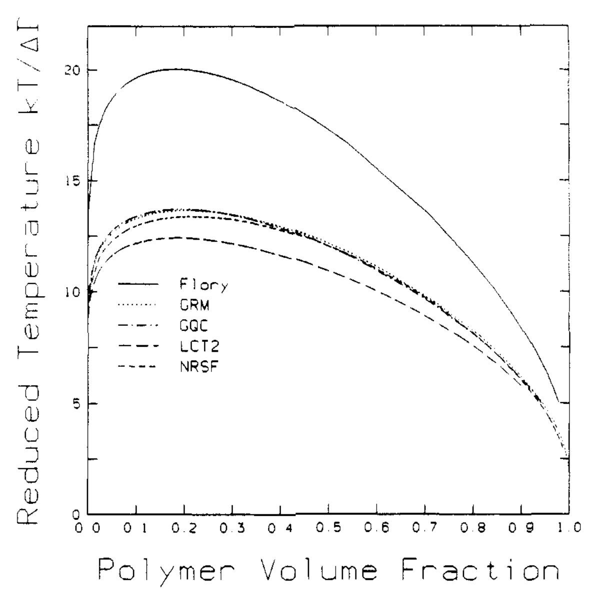

Figure 9. Comparison of coexistence curves calculated from Flory, GRM, GQC, LCT, and NRSF. Effect of increasing solvent size for a mixture of linear-chain polymers in solvent with $r_1 = 5$, $r_2 = 100$, and $z = 6$. Temperatures are expressed as $kT/\Delta\Gamma$.

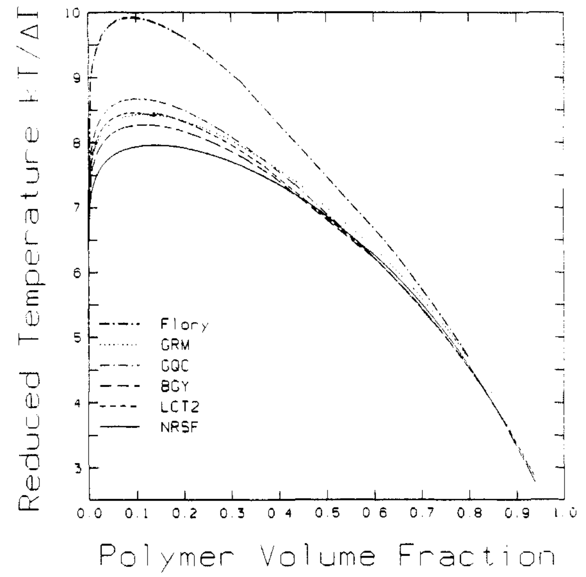

Figure 10. Comparison of coexistence curves calculated from Flory, GRM, GQC, BGY, LCT, and NRSF. Effect of increasing coordination number for a mixture of linear-chain polymers in solvent with $r_1 = 1$, $r_2 = 100$, and $z = 12$. Temperatures are expressed as $kT/\Delta\Gamma$.

Coexistence Curves. Phase diagrams are shown in Figures 8–10. Figure 8 shows the phase diagram for a linear-chain polymer in a single-bead solvent with $z = 6$. The y-coordinate is $kT/\Delta\Gamma$, the reduced temperature. Flory predicts the highest critical temperature. GRM is able to give the overall shape of the phase envelope, though it is not good. GQC agrees with LCT well at high volume fractions of polymer, but in the critical region its predictions are sharp and narrow. LCT predicts an extremely flat critical region. That flatness agrees with the simulation data. The flatness shown here is a consequence of the exact balancing between the repulsive and attractive contributions to the chemical potential. Equation 3 predicts a flat critical region as well. Figure 9 shows the phase diagram for an increased solvent size $r_2 = 5$. Figure

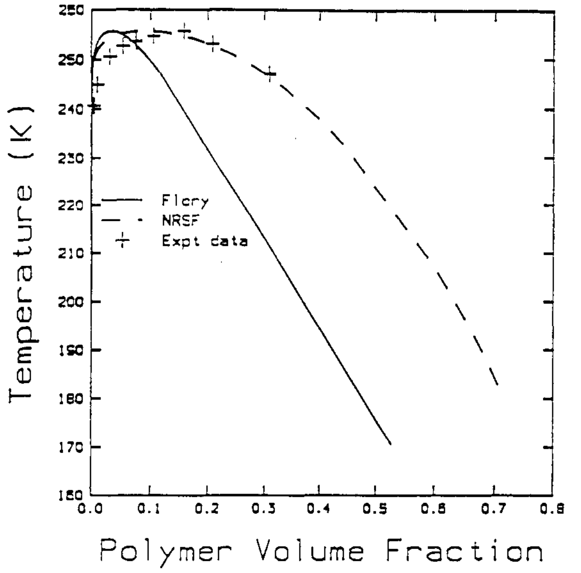

Figure 11. Comparison of coexistence curves predicted by Flory and NRSF with experimental data for the system of polystyrene/*tert*-butyl acetate, MW = 10 000 $M_w/M_n = 1.06$, with $z = 4$, $r_2 = 2706$, and $r_1 = 3$. Experimental data are from Bae and Prausnitz.[19]

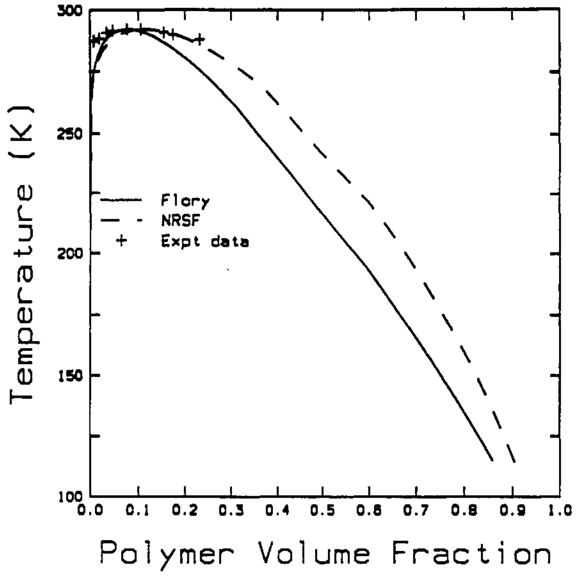

Figure 12. Comparison of coexistence curves predicted by Flory and NRSF with experimental data for the system of polyisobutylene/diisobutyl ketone, MW = 22 700, $M_w/M_n = 1$, with $z = 4$, $r_2 = 560$, and $r_1 = 4$. Experimental data are from Bae and Prausnitz.[19]

10 shows the effect of increasing the coordination number on the phase diagram. Here, z is 12. The NRSF results for the critical region are located furthest below Flory's. LCT and GRM are close together between GQC and BGY. Currently there are no simulation data with which we can compare these predictions. At most, we can say that NRSF predicts the lowest and flattest critical region when the coordination number is increased.

Comparisons of NRSF with Experimental Data

In deriving NRSF, we assumed that the segmental energies are the same for polymer and solvent. This is a widely used assumption in lattice models which greatly simplifies the derivation and final functional form of thermodynamic expressions. While solvent and polymer energies can differ greatly for real polymer solutions, this is an assumption which one is obliged to make if working with an incompressible lattice.[18] Also, no specific interactions are accounted for in this model, so our choice of experimental data carefully avoids systems with hydrogen bonding or other kinds of strong physical or chemical interactions.

Figures 11 and 12 present comparisons with experimental data for polystyrene in *tert*-butyl acetate and polyisobutylene in diisobutyl ketone. In each case, $kT/\Delta\Gamma$ has been fitted to the mixture critical temperature. Data are from Bae et al.[19] We calculate molecular size by a group contribution method. Choices of coordination number and solvent segment number are varied as noted in the figure captions.

One sees that NRSF does open up the phase envelope, allowing it to agree with experimental data over a larger concentration range than Flory's equation. One should note that there are deviations by NRSF from the experimental data at low polymer volume fractions. There are two reasons for these deviations. The first is that polydispersity in the polymer can have a large effect on the measured phase diagram at low polymer concentrations; our calculations did not take this into account. The second is that branching in the polymer structure also affects the behavior of phase equilibrium at low polymer concentrations;[13] the systems considered here all have slight branching along the chain, but the predictions were made with a linear-chain model. In future work, we hope to make predictions more precise in this region.

Conclusions

In this work, a new equation for the free energy of mixing is presented. This equation contains a repulsive part (entropy term) and an attractive part (internal energy term). The entropy of mixing is Guggenheim's random-mixing term. The energy of mixing is a simple, exponentially-weighted, surface-fraction-averaged energy. It is shown that the attractive term is simple, yet accurate. Comparisons are made with Flory theory, Guggenheim's random-mixing approximation, Guggenheim's quasichemical theory, lattice cluster theory, Born–Green–Yvon formalism, and experimental data for real systems. This equation provides good results for phase equilibrium calculations, energies of mixing, and activities.

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