Liquid–Liquid Equilibria for Solutions of Polydisperse Polymers. Continuous Thermodynamics for the Close-Packed Lattice Model

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Received April 16, 1993; Revised Manuscript Received September 17, 1993⊛

ABSTRACT: A continuous thermodynamic framework is presented for phase-equilibrium calculations for solutions of polydisperse polymers. An expression for the Helmholtz function of mixing is based on a mathematically simplified Freed model developed previously. A binary mixture requires a size parameter c_r and an energy parameter ϵ; the former can be temperature dependent, while the latter can depend on temperature and chain length. The functional approach is adopted to define thermodynamic functions and to derive expressions for chemical potentials, spinodals, and critical points. Computation programs are established for cloud-point-curve, shadow-curve, spinodal, and critical-point calculations for polymer solutions where the molecular-mass distribution of the polymer is specified. Examples for phase-equilibrium calculations are shown for cyclohexane–polydisperse polystyrene systems. Satisfactory results indicate the utility of the proposed framework and the computation procedures.

1. Introduction

The phase behavior of binary polymer solutions and blends differs appreciably from that of ordinary liquid mixtures not only because of the large molecular-size difference between different solutes and solvents, but also because the polymer solute is likely to be polydisperse. As indicated in a typical textbook,[1] the phase diagram shown in Figure 1b for a polydisperse solute is qualitatively different from that for a monodisperse sample, shown in Figure 1a. In the latter case, an open circle represents the principal phase and the corresponding filled circle represents the conjugate phase; they are located on the same coexistence (or cloud-point) curve. The maximum of that curve is the critical point. However, in the former case [Figure 1b], the cloud-point curve for principal phases does not coincide with the corresponding plot for conjugate phases. The latter plot is called the shadow curve. The molar-mass (or chain-length) distribution for the principal phase is usually different from that of the conjugate phase, as shown in the upper part of the figure. In some cases, the content of the polymer is higher in the conjugate phase than that in the principal phase with a wider distribution shifted to the higher molar-mass region, while in other cases, the content of the polymer is lower in the conjugate phase than that in the principal phase with a narrower distribution shifted to the lower molar-mass region. Of particular interest is the point of intersection of the cloud-point curve and the shadow curve, where the principal phase and the conjugate phase have the same composition, i.e., the same total polymer content and the same polymer molecular-mass distribution. This is the critical point of the polydisperse polymer solution.

For development, production, and processing of advanced polymer materials, it is necessary to have a satisfactory understanding of the phase behavior of polydisperse polymer solutions and polydisperse polymer blends.

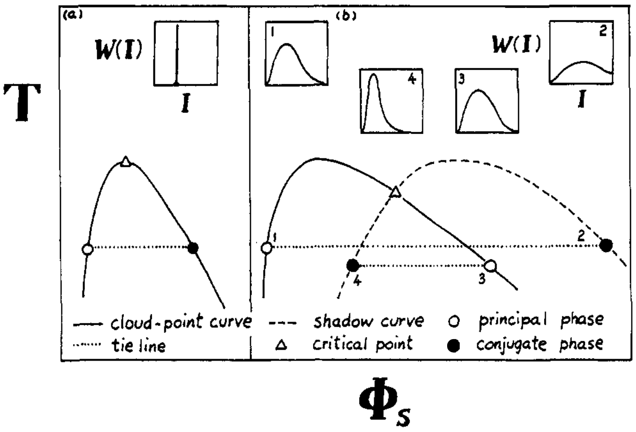

Figure 1. Schematic phase diagram for liquid–liquid equilibria of a polymer solution with (a) a monodisperse polymer sample and (b) a polydisperse polymer sample. Φ_s and T are the volume fraction of polymer and temperature, respectively. The small squares on the upper part are corresponding distribution curves for the polymers. $W(I)$ is the distribution function.

Although basic thermodynamic relations for polymer–solution phase equilibria are well-known, application to polydisperse polymer systems is not trivial because for a solution containing a polydisperse solute, a "binary" solution is, in fact, a multicomponent system with very many components. Instead of using two equations for equating chemical potentials of the solute and the solvent for a binary, we now have to use a huge number of equations corresponding to polymer molecules with different molar masses or chain lengths. Polymer molecules with different molar masses should be considered as different components. Expressions for spinodals and critical points are then determinants of large capacity with a great number of second-order derivatives and third-order derivatives as

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⊛ Abstract published in *Advance ACS Abstracts*, November 1, 1993.

0024-9297/93/2226-6817$04.00/0

their elements. For a true binary, only a simple second-order derivative and a simple third-order derivative are needed,[2] but for a solution containing many components, the mathematical problem becomes prohibitive.

The literature contains several methods for describing the thermodynamics of polydisperse polymer systems. The essential goal is to obtain the partition coefficient K_i for the polymer species i with relative molar mass M_i or chain length r_i; the latter is defined as the number of fundamental segments of a chain molecule, or the number of sites occupied by a molecule if the system is treated as a lattice. K_i is defined as

$$K_i = \Phi_i^{(\alpha)}/\Phi_i^{(\beta)} \qquad (1)$$

where $\Phi_i^{(\alpha)}$ and $\Phi_i^{(\beta)}$ are volume fractions of polymer species i in coexisting phases α and β, respectively. Schultz[3] in 1939 was the first to carry out such calculations by suggesting that partitioning is governed by energy differences only and is independent of concentration. Later, Scott[4] used an improved method to calculate K_i by introducing two assumptions: a negligible concentration of polymer in the dilute phase and omitting the term $1/r_n$ (where r_n is the number-average chain length in the Flory–Huggins equation). Some other authors[5–9] adopted the empirical expressions for K_i,

$$K_i = \exp(\sigma r_i) \qquad (2)$$

where σ is a parameter obtained by fitting experimental data. The most rigorous method was developed by Koningsveld[10] and by Solc[11] based on Tompa's work.[12] Koningsveld adopted a generalized Flory–Huggins model for the Helmholtz function of mixing by introducing a concentration dependent polynomial for the Flory parameter g,

$$g = \sum_k g_k \Phi_s^{\,k} \qquad (3)$$

where coefficients g_k may be functions of temperature and where Φ_s is the total volume fraction of the polymer solute. With this model, Koningsveld was able to express σ as an analytical function of g and Φ_s and to derive closed-form expressions for spinodals and critical points from corresponding determinants. An algorithm for calculations of the cloud-point curve and the shadow curve was also presented. In Koningsveld's work, the importance of the chain-length dependence of the Flory–Huggins parameter g has been noted, and a priliminary deviation for the spinodal criterion was given. However, no further details were presented for a critical-point criterion and phase-equilibrium calculations.

The references cited above are based on discrete multicomponent thermodynamics. During the last 10 years, Rätzsch, Kehlen, and co-workers[13–15] and Cotterman and Prausnitz[16,17] developed a functional approach, where chemical potentials are defined using functionals to incorporate the molar-mass distribution or the chain-length distribution of a polymer solute. The functional form of partial derivatives and higher-order variations of functionals are also defined to derive thermodynamic relations for chemical potentials, spinodals, and critical points. For the original Flory–Huggins model, Rätzsch et al. were able to prove the consistency between the functional approach and the classical discrete-multicomponent approach. In this work, we use the functional approach for a lattice model based on the work of Freed and co-workers.[21–23]

For a solution containing a polydisperse polymer, the composition is usually characterized by a continuous molar-mass (or chain-length) distribution. Phase-equilibrium thermodynamics, where discrete compositions have been replaced by continuous distributions, is often called continuous thermodynamics. The primary merit of the continuous-thermodynamic method is convenience: integration replaces summation over components. For an arbitrary distribution, Ying, Ye, and Hu[18] developed a derivative method based on spline functions, which can be used for phase-equilibrium calculations.

The next section presents a thermodynamic framework for phase-equilibrium calculations for mixtures containing a polydisperse polymer solute. The model used is a generalized expression for the Helmholtz function of mixing presented previously,[19,20] based on the lattice theory of Freed et al.[21–23] Two parameters are used: the size parameter c_r which is temperature dependent, and the energy parameter ϵ/k which can depend on both temperature and chain length. Expressions for chemical potentials, spinodals, and critical points are derived. For illustration, calculated results are given later for polystyrene–cyclohexane systems.

2. Thermodynamic Framework

2.1. Helmholtz Function of Mixing. Polymer solutions are often described by a lattice theory. For a binary, the mathematically simplified Freed model[19,20] can accurately duplicate the phase behavior of an Ising lattice and can obtain almost the same critical coordinates for cases with $r_1 = 1$ and $r_2 = 1$–$10\,000$ as those from the original Freed theory. The mathematically simplified model gives a convenient and brief Helmholtz function of mixing:

$$\frac{\Delta_{\text{mix}}A}{N_r kT} = \frac{\Phi_1}{r_1}\ln\Phi_1 + \frac{\Phi_2}{r_2}\ln\Phi_2 + g\Phi_1\Phi_2 \qquad (4)$$

$$g = \frac{1.2}{9}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 + 2\tilde{\epsilon} + \frac{\tilde{\epsilon}}{r_1}\Phi_2 + \frac{\tilde{\epsilon}}{r_2}\Phi_1 - \frac{3}{2}1.074\,\tilde{\epsilon}^2\Phi_1\Phi_2 \qquad (5)$$

where N_r is the total number of sites in the lattice, r_1 and r_2 are numbers of sites occupied by one molecule of component 1 and one molecule of component 2, respectively, and

$$\tilde{\epsilon} = \epsilon/kT \qquad (6)$$

$$\epsilon = \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12} \qquad (7)$$

Here ϵ_{ij} is the (positive) energy for each i–j pair, ϵ is the interaction energy parameter for the binary, while $\tilde{\epsilon}$ is the corresponding reduced energy parameter. Equation 5 is derived for a cubic lattice. Here, subscripts i and j refer to nonbonded polymer segments or to solvent monomers.

For a binary polymer solution with a polydisperse polymer solute, with a slight change of notation, the Helmholtz function of mixing can be expressed as

$$\frac{\Delta_{\text{mix}}A}{N_r kT} = \frac{\Phi_o}{r_o}\ln\Phi_o + \sum_i \frac{\Phi_i}{r_i}\ln\Phi_i + \Phi_o\sum_i \Phi_i g_i \qquad (8)$$

where subscript o stands for solvent. The corresponding chain length r_o is usually taken to be unity. Subscript i stands for polymer species i; the corresponding chain length r_i can be estimated by

$$r_i = c_r V_{mi}/V_{mo} = c_r v_s M_i/v_o M_o \qquad (9)$$

where V_{mo}, v_o, M_o, and V_{mi}, v_s, M_i are molar volumes, specific volumes, and molar masses for solvent and polymer species i, respectively. Subscript s (solute) stands for polymer; c_r is a binary size parameter. Flory parameter

g_i is given by eq 5, which is now chain-length and composition dependent. The summation is over all polymer species with different molar masses.

Using continuous thermodynamics, eq 8 is rewritten

$$\frac{\Delta_{\mathrm{mix}}A}{N_r kT} = \frac{\Phi_o}{r_o}\ln \Phi_o + \int_0^\infty \frac{\Phi_s W(I)}{r(I)} \ln[\Phi_s W(I)]\, \mathrm{d}I + \Phi_o \int_0^\infty \Phi_s W(I) g(I)\, \mathrm{d}I \quad (10)$$

where $W(I)$ is the distribution function for a polymer which satisfies the normalization constaint

$$\int_0^\infty W(I)\, \mathrm{d}I = 1 \quad (11)$$

Here I is the distribution variable such as relative molar mass or chain length. Solvent o is a discrete component as usual, while the infinite number of polymer species is represented by distribution function $W(I)$. In the functional approach, $\Phi_s W(I)$ is comparable to Φ_i in the discrete approach. In eq 10, $\Delta_{\mathrm{mix}}A$ is a functional. We further assume that $g(I)$ is independent of the distribution as a reasonable approximation. Similar to eq 5, we then have

$$g(I) = \frac{1.2}{9}\left(\frac{1}{r_o} - \frac{1}{r(I)}\right)^2 + 2\tilde{\epsilon}(I) + \frac{\tilde{\epsilon}(I)}{r_o}\Phi_s + \frac{\tilde{\epsilon}(I)}{r(I)}(1 - \Phi_s) - \frac{3}{2}1.074\, \tilde{\epsilon}^2(I)\Phi_s (1 - \Phi_s) \quad (12)$$

where $\tilde{\epsilon}(I)$ depends on chain length. An empirical dependence is given by

$$\tilde{\epsilon}(I) = e_0 + e_r[r(I)]^{-n} \quad (13)$$

where n is a positive number and e_0 and e_r are adjustable parameters. The longer r, i.e., the larger the molar mass, the weaker is the chain-length dependence of $\tilde{\epsilon}$. In principle, parameters c_r, e_0, and e_r can be temperature dependent.

2.2. Expressions for Chemical Potentials. For the discrete solvent component o, the chemical potential can be derived directly. It is

$$(\mu_o - \mu_o^*)kT = \partial(\Delta_{\mathrm{mix}}A/kT)/\partial N_o = \ln(1 - \Phi_s) + \Phi_s(1 - r_o/r_n) + r_o\Phi_s^{\,2}\left[\int_0^\infty g(I)W(I)\, \mathrm{d}I - (1 - \Phi_s) \int_0^\infty g'(I)W(I)\, \mathrm{d}I\right] \quad (14)$$

where $g'(I) = \partial g(I)/\partial \Phi_s$. Superscript * stands for the reference state, which is the close-packed pure component at the system temperature. The number-average chain length is denoted by r_n.

For continuous components, the chemical potential of solute I is defined as

$$\mu(I) = \partial A/\partial[N_r\Phi_s W(I)/r(I)] \quad (15)$$

where the denominator is physically comparable with ∂N_i in the discrete approach. But now it is a variation of a function. When applying eq 15 to eq 10, we meet the problem of taking derivatives for an integral with respect to a functional. In the theory of functionals, for an integral $\Psi = \int f(N_{\mathrm{I}})\, \mathrm{d}I$, the derivative of Ψ with respect to the functional N_{I} is defined by

$$\frac{\partial \Psi}{\partial N_{\mathrm{I}}} = \frac{\partial f(N_{\mathrm{I}})}{\partial N_{\mathrm{I}}} \quad (16)$$

Taking the first integral on the right side of eq 10 as an example, we first set $N_r\Phi_s W(I)/r(I) = N_{\mathrm{I}}$ for abbreviation. The integral (times N_r) is then rearranged as $\int N_{\mathrm{I}}[\ln N_{\mathrm{I}} + \ln r(I) - \ln N_r]\, \mathrm{d}I$. Applying eq 16, we obtain $\ln[\Phi_s W(I)] + 1 - r(I)\int \Phi_s r^{-1}(I^+) W(I^+)\, \mathrm{d}I^+$. Here we have used $\partial N_r/\partial N_{\mathrm{I}} = r(I)$ and $\partial \Phi_s/\partial N_{\mathrm{I}} = -\partial \Phi_o/\partial N_{\mathrm{I}} = r(I)(1 - \Phi_s)/N_r$.

An expression for the chemical potential of a continuous component I can then be derived. It is

$$[\mu(I) - \mu^*(I)]/kT = \partial(\Delta_{\mathrm{mix}}A/kT)/\partial[N_r\Phi_s W(I)/r(I)] = \ln[\Phi_s W(I)] + 1 - r(I)/r_o + r(I)\Phi_s(1 - r_o/r_n)/r_o + (1 - \Phi_s)r(I)g(I) - r(I)\Phi_s(1 - \Phi_s)\left[\int_0^\infty g(I^+)W(I^+)\, \mathrm{d}I^+ - (1 - \Phi_s) \int_0^\infty g'(I^+)W(I^+)\, \mathrm{d}I^+\right] \quad (17)$$

2.3. Spinodal Criterion. From the theory of stability, the boundary between the metastable and unstable regions satisfies the condition that the second-order variation for the Gibbs function of mixing with composition equals zero. For a close-packed lattice, the Gibbs and Helmholtz functions are virtually the same. We define the reduced Gibbs function of mixing per site as

$$\tilde{G}_\upsilon = \frac{\Delta_{\mathrm{mix}}G}{N_r kT} = \frac{\Delta_{\mathrm{mix}}A}{N_r kT} \quad (18)$$

where $\tilde{G}_\upsilon$ is a functional. We now need to derive an expression for $\delta^2\tilde{G}_\upsilon$ as the spinodal criterion.

For deriving a high-order variation for functionals, Kehlen, Rätzsch, Bergmann, and Beerbaum[14,15] suggested

$$\delta^k\tilde{G}_\upsilon = \partial^k\tilde{G}_\upsilon\{\Phi_o + t\delta\Phi_o, \Phi_s W(I) + t\delta[\Phi_s W(I)]\}/\delta t^k|_{t=0} \quad (19)$$

Then they used the Lagrange method of undetermined multipliers to determine the relation between the two dependent variations $\delta\Phi_o$ and $\delta[\Phi_s W(I)]$ in eq 19. Finally, $\delta^k\tilde{G}_\upsilon/(\delta\Phi_o)^k$ can be obtained. Details are given in Appendix 1. For $k = 2$, we obtain

$$\frac{\delta^2\tilde{G}_\upsilon}{(\delta\Phi_o)^2} = \frac{1}{r_o\Phi_o} + \frac{1}{r_w\Phi_s} + \Phi_s\frac{(\langle gr\rangle - \Phi_o\langle g'r\rangle)^2}{r_w} - 2\frac{\langle gr\rangle - \Phi_o\langle g'r\rangle}{r_w} - \Phi_s(\langle g^2r\rangle - 2\Phi_o\langle gg'r\rangle + \Phi_o^{\,2}\langle g'^2r\rangle) - 2\Phi_s(\langle g'\rangle - \Phi_o\langle g''\rangle/2) \quad (20)$$

where r_w is the weight-average chain length.

$$\langle g^l g'^m g''^n r\rangle = \int_0^\infty g^l(I)g'^m(I)g''^n(I)r(I)W(I)\, \mathrm{d}I \quad (21)$$

Here, $g'(I) = \partial g(I)/\partial\Phi_s$, $g''(I) = \partial^2 g(I)/\partial\Phi_s^{\,2}$. We then have the spinodal criterion,

$$F_{\mathrm{sp}} = \frac{\delta^2\tilde{G}_\upsilon}{(\delta\Phi_o)^2} = 0 \quad (22)$$

The same results can be obtained from the discrete approach, as shown in Appendix 3.

2.4. Critical-Point Criterion. For the critical point, it is necessary that the third-order variation of the Gibbs function of mixing equals zero. Using a procedure similar to that used for the derivation for the spinodal, we obtain $\delta^3\tilde{G}_\upsilon/(\delta\Phi_o)^3$. The lengthy expression is given in Appendix 2. We then have the critical-point criterion,

$$F_{\mathrm{cr}} = \frac{\delta^3\tilde{G}_\upsilon}{(\delta\Phi_o)^3} = 0 \quad (23)$$

Again, the same results can be obtained from the discrete approach, as shown in Appendix 3.

3. Phase Equilibria

3.1. Fundamental Equations for Phase-Equilibrium Calculations. When phases α and β are at equilibrium,

$$\mu_0^{(\alpha)} = \mu_0^{(\beta)} \tag{24}$$

$$\mu^{(\alpha)}(I) = \mu^{(\beta)}(I) \tag{25}$$

To solve eqs 24 and 25, we define

$$S_o = \int_0^\infty g(I)W(I)\,\mathrm{d}I - (1-\Phi_s)\int_0^\infty g'(I)W(I)\,\mathrm{d}I \tag{26}$$

$$\sigma_o = \ln(1-\Phi_s) + \Phi_s(1 - r_o/r_n) + r_o\Phi_s^2 S_o \tag{27}$$

Substitution into eqs 14 and 17 yields

$$(\mu_o - \mu_o^*)/kT = \sigma_o \tag{28}$$

$$[\mu(I) - \mu^*(I)]/kT = \ln[\Phi_s W(I)] + 1 - r(I)/r_o + (1-\Phi_s)r(I)g(I) - r(I)\Phi_s S_o + r(I)(\sigma_o - \ln\Phi_o)/r_o \tag{29}$$

Equations 24 and 25 become

$$\sigma_o^{(\alpha)} = \sigma_o^{(\beta)} \tag{30}$$

$$\ln K(I) = \ln\frac{\Phi_s^{(\beta)}W^{(\beta)}(I)}{\Phi_s^{(\alpha)}W^{(\alpha)}(I)} = r(I)\{[(1-\Phi_s)g(I) - r_o^{-1}\ln(1-\Phi_s) - \Phi_s S_o]^{(\alpha)} - [(1-\Phi_s)g(I) - r_o^{-1}\ln(1-\Phi_s) - \Phi_s S_o]^{(\beta)}\} \tag{31}$$

We also define

$$M_0^* = \int_0^\infty K(I)W^{(\alpha)}(I)\,\mathrm{d}I \tag{32}$$

Substituting $K(I) = \Phi_s^{(\beta)}W^{(\beta)}(I)/\Phi_s^{(\alpha)}W^{(\alpha)}(I)$ into eq 32 and accounting for the normalization constaint [eq 11], we have

$$M_o^*\Phi_s^{(\alpha)}/\Phi_s^{(\beta)} = 1 \tag{33}$$

Equations 30 and 33 permit us to establish two fundamental equations for phase-equilibrium calculations for binary polymer solutions with a polydisperse polymer.

$$F_o = 1 - \sigma_o^{(\alpha)}/\sigma_o^{(\beta)} = 0 \tag{34}$$

$$F_s = 1 - M_0^*\Phi_s^{(\alpha)}/\Phi_s^{(\beta)} = 0 \tag{35}$$

The former is for the solvent, while the latter is for the polymer. By solving these two equations, we can obtain cloud-point and shadow curves.

We can obtain spinodals and critical points by solving eqs 22 and 23.

3.2. Derivative Method for Arbitrary Distribution. To use eqs 34 and 35, we encounter several integrations with respect to the molar-mass or chain-length distribution, such as M_o^* of eq 32 and various $\langle g^l g'^m g''^n r\rangle$ in eq 21. Because energy parameter $\tilde{\epsilon}$ in g can be molar-mass or chain-length dependent [see eq 13], in some integrations chain length r may rise to a power different from 1. Therefore, in general, we may need to calculate the following integral,

$$S = \int_0^\infty r^k(I)K(I)W(I)\,\mathrm{d}I \tag{36}$$

where $W(I)$ is the distribution function.

Sometimes we can use a standard distribution such as a γ-distribution or a log-normal distribution. The advantage of using a standard distribution comes from simplified computation. In some fortunate cases, we can obtain analytically the distribution parameters for a conjugate phase from the corresponding parameters for the principal phase.[16]

Table I. Critical Coordinates for the System Cyclohexane–Polystyrene

				T_c/K[a]		Φ_{sc}[b]	
no.	10^3M_n	10^3M_w	10^3M_z	expt	calc	expt	calc
1	1250	1500	1700	303.20	303.87	0.0305	0.0293
2	490	527	593	301.15	301.32	0.0470	0.0464
3	375	394	423	300.70	300.36	0.0510	0.0515
4	200	286	438	298.70	298.90	0.0700	0.0673
5	154	166	181	296.60	296.58	0.0735	0.0731
6	91	93	96	293.65	293.15	0.0875	0.0884
7	55	61.5	70.5	290.45	290.07	0.1070	0.1062
8	49	51	55	287.85	288.57	0.1100	0.1102
9	27	35.4	45.5	284.60	285.04	0.1360	0.1325

[a] RMS(T) = 0.44 K. [b] RMS(Φ) = 0.0016.

However, when the polymer chain length has an arbitrary distribution, or when the energy parameter is molar-mass dependent, this advantage disappears. In that more general case, the previously presented derivative method[18] should be used.

The derivative method represents distribution data by an interpolation polynomial with derivatives, i.e., a Hermite polynomial,

$$y(x) = \left[\frac{3}{h_j^2}(x_{j+1}-x)^2 - \frac{2}{h_j^3} - (x_{j+1}-x)^3\right]y_j + \left[\frac{3}{h_j^2}(x-x_j)^2 - \frac{2}{h_j^3}(x-x_j)^3\right]y_{j+1} + h_j\left[\frac{1}{h_j^2}(x_{j+1}-x)^2 - \frac{1}{h_j^3}(x_{j+1}-x)^3\right]y_j' - h_j\left[\frac{1}{h_j^2}(x-x_j)^2 - \frac{1}{h_j^3}(x-x_j)^3\right]y_{j+1}' \tag{37}$$

where

$$h_j = x_{j+1} - x_j \tag{38}$$

In eq 37, x_j, y_j, and y_j' are respectively the independent variable, the value of the function, and the corresponding first-order derivative with respect to x at data point j. A third-order spline function is always used to obtain those derivatives from the scattered data of x_j and y_j. The integral of eq 37 can be obtained by

$$S = \int_{x_1}^{x_n} y(x)\,\mathrm{d}x = \sum_{j=1}^{n-1}\left[\frac{1}{2}h_j(y_{j+1}+y_j) - \frac{1}{12}h_j^2(y_{j+1}'-y_j')\right] \tag{39}$$

Applying to eq 36, $x \rightarrow r(I)$,

$$y(I) = r^k(I)K(I)W(I) \tag{40}$$

$$y'(I) = y(I)\left[\frac{k}{r(I)} + \frac{K'(I)}{K(I)} + \frac{W'(I)}{W(I)}\right] \tag{41}$$

where $K'(I)$ and $W'(I)$ are corresponding derivatives for $K(I)$ [defined by eq 31] and $W(I)$ with respect to $r(I)$.

3.3. Illustration: Liquid–Liquid Equilibria for Cyclohexane–Polystyrene Systems. Koningsveld, Kleintjens, and Shultz[24] reported high-quality experimental liquid–liquid-equilibrium data for cyclohexane–polydisperse polystyrene systems. Data reported by Koningsveld et al. include critical coordinates for nine samples with different number-average, weight-average, and z-average molar masses, M_n, M_w, and M_z (shown in Table I).

We use two parameters in our lattice model, a temperature-dependent size parameter c_r in eq 9, and in eq 4, an energy parameter ϵ which depends on temperature and chain length by eq 13, where $n = {}^1/_3$. They can be expressed as

$$c_r = c_{r0} + c_{r1}T^{-1} \tag{42}$$

$$\epsilon/k = e_0 + e_1T^{-1} + e_r r^{-1/3} \tag{43}$$

Using eqs 22 and 23 for each pair of critical coordinates T_c and Φ_{sc},

$$F_{sp} = 0 \qquad F_{cr} = 0$$

We can then obtain c_r and ϵ/k for each sample. For altogether nine samples, we then estimate all model parameters. For cyclohexane–polystyrene systems, results are

$$c_{r0} = -1.518\,90 \qquad c_{r1} = 614.300\text{K}$$

$$e_0 = 44.5297\text{K} \qquad e_1 = 10748.8\text{K*K} \qquad e_r = 9.84750$$

Standard deviations of fitting for critical temperatures and critical volume fractions, respectively, are

$$\text{RMS}(T_c) = 0.44\text{K} \qquad \text{RMS}(\Phi_c) = 0.0016$$

For details, see Table I. If both for the principal phase and for the conjugate phase we have polymer concentrations Φ_s and corresponding distribution functions $W(I)$, the latter can be measured by gel-permeation chromatography or calculated by experimentally determined M_n, M_w, and M_z; the above parameters can also be estimated using eqs 34 and 35, i.e., $F_0 = 0$ and $F_s = 0$.

Using these parameters, we can calculate spinodals using eq 22. Figure 2 shows calculated spinodals for samples 1, 3, 5, 7, and 9. Cloud-point curves and shadow curves are obtained by solving eqs 34 and 35. An arbitrary example with M_n = 159 kg/mol, M_w = 343 kg/mol, and M_z = 548 kg/mol is chosen. Rehage et al.[25] have reported experimental cloud-point and shadow curves for a similar sample. Figure 3 shows calculated cloud-point and shadow curves and the spinodal curve for that sample. Figure 4 shows Rehage's experimental results for comparison. In view of the uncertainties in parameter estimation, and the subtle difference between M's of the calculated sample and that of Rehage, general agreement with experiment is satisfactory. Figure 5 shows typical distributions for a principal phase and an equilibrated conjugate phase. These two distributions differ markedly from each other.

The preceding calculations only serve as an example. For that example, a chain-length dependent parameter is not needed. Similar good results can be obtained when the energy parameter ϵ/k is only temperature dependent. Chain-length dependence, however, will play a vital role when the chain-length distribution of the polymer includes short chains.

4. Discussion and Conclusions

Although continuous thermodynamics has been widely accepted for phase-equilibrium calculations for systems with very many components, some computational problems remain, especially for systems containing polymers. One of those problems is how to obtain analytical expressions for spinodals and critical points, which are often more important in phase equilibria for polymer systems than for ordinary systems. These problems are minimal for simple Flory–Huggins theory, but these problems are not trivial when we choose a better model, such as the Freed model, especially when we account for the molar-mass dependence of the parameters.

The functional approach gives us new impetus not only because of its theoretical integrity, and its consistent framework for multicomponent systems, but also because it requires a comparatively simple mathematical procedure in comparison with the tedious determinant derivations in the usual discrete approach when calculating the spinodal and the critical-point criteria. However, the functional approach is still in an early stage. Some

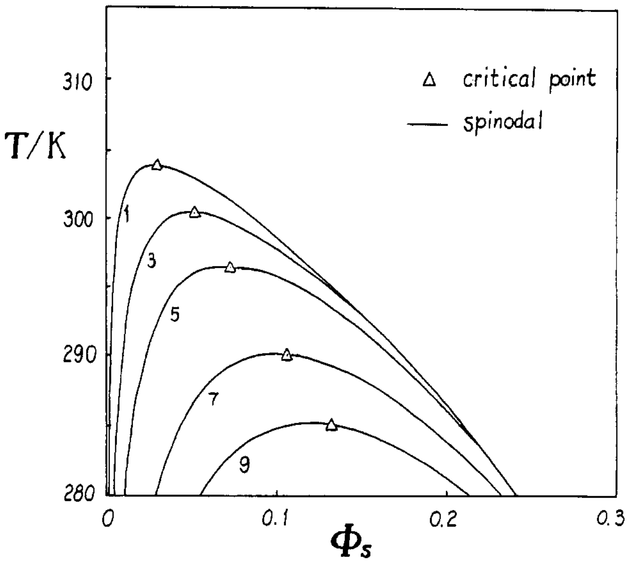

Figure 2. Spinodals calculated for the system cyclohexane–polystyrene, corresponding to sample numbers in Table I.

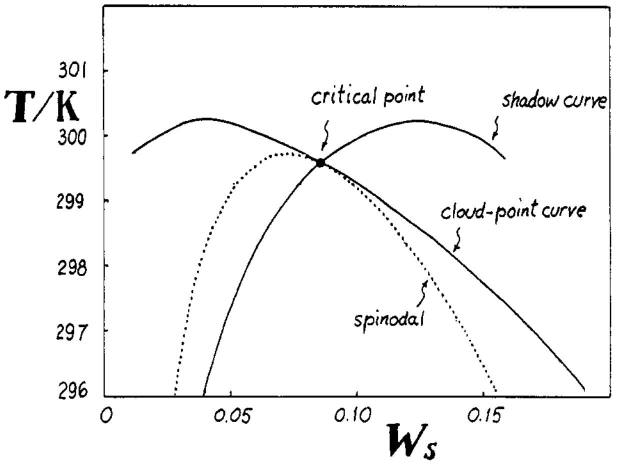

Figure 3. Cloud-point curve, shadow curve, and spinodal curve for system cyclohexane–polystyrene. M_n = 159 kg/mol, M_w = 343 kg/mol, M_z = 548 kg/mol. W_s is the weight fraction of the polymer.

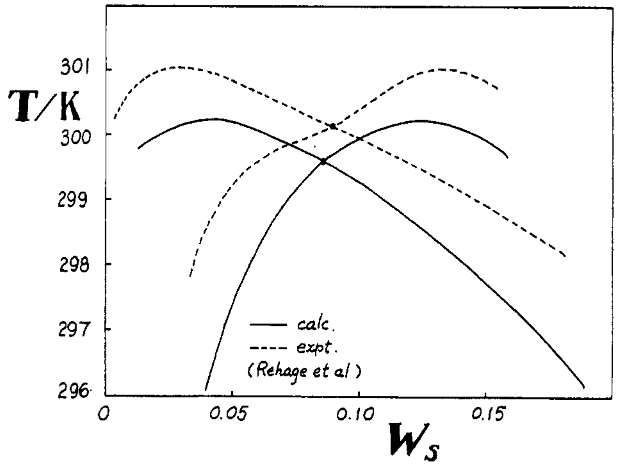

Figure 4. Cloud-point curve and shadow curve for the system cyclohexane–polystyrene showing the comparison with experimental results by Rehage et al. Calc: M_n = 159 kg/mol, M_w = 343 kg/mol, M_z = 548 kg/mol. Expt: M_n = 210 kg/mol, M_w = 346 kg/mol, M_z = 550 kg/mol.

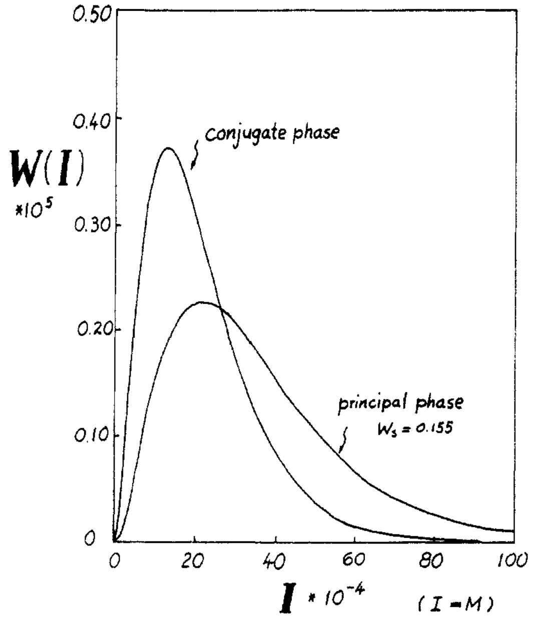

Figure 5. Molar-mass distributions of conjugate phases in liquid–liquid equilibrium for the system cyclohexane–polystyrene.

simplifications have been introduced, such as the suggested method of obtaining variations of functions using Lagrange undetermined multipliers. In the present stage of development, everything obtained by the functional approach must be checked with calculations based on the discrete approach. The latter is rigorous. In this work, we have derived expressions for chemical potentials for the revised Freed model with a molar-mass dependent energy parameter. The reliability of these equations follows because no approximation has been used. We have also derived expressions for spinodals and critical points; their reliability is subject to test. Fortunately, the result of the test is successful. Therefore, we can reach the conclusion that the thermodynamic framework developed here is a general one which can be used for other polymer solution models.

Phase-equilibrium calculations for polydisperse polymer solutions require a molar-mass or chain-length distribution for the polymer. Standard distributions such as the γ-distribution or the log-normal distribution are often used to approximate the characteristics of polymer systems. We can now determine experimentally all the average molar masses, such as M_n, M_w, and M_z. However, M_z predicted by those standard distributions with their parameters obtained by fitting M_n and M_w may differ appreciably from the experimental value. The derivative method used in this work does not have this deficiency. It offers a more accurate description of the distribution of polymer species at a reasonable cost of slightly longer computation time.

In this work, the model is limited to a close-packed lattice where r_o is arbitrarily set at unity. Therefore, it cannot be used for polymer blends. In a future article, the volume effect is taken into account with an equation of state and the restraint $r_o = 1$ is eliminated.

Acknowledgment. This work was supported by the Chinese National Science Foundation and the Marshall Laboratory, E. I. Du Pont de Nemours & Co. Additional support was provided by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF0098.

Appendix 1: Derivation of the Spinodal Criterion

We first express eq 18 or 10 for the reduced Gibbs function of mixing per site as a functional of variations $\delta\Phi_o$, $\delta[\Phi_s W(I)]$, and variable t as follows:

$$\tilde{G}_\upsilon = \frac{\Phi_o + t\delta\Phi_o}{r_o}\ln(\Phi_o + t\delta\Phi_o) + \int_0^\infty \frac{\Phi_s W(I) + t\delta[\Phi_s W(I)]}{r(I)}\ln\{\Phi_s W(I) + t\delta[\Phi_s W(I)]\}\,\mathrm{d}I + (\Phi_o + t\delta\Phi_o)\int_0^\infty \{\Phi_s W(I) + t\delta[\Phi_s W(I)]\}\left[g(I) + t\frac{\partial g(I)}{\partial \Phi_o}\delta\Phi_o + \frac{1}{2}t^2\frac{\partial^2 g(I)}{\partial {\Phi_o}^2}(\delta\Phi_o)^2\right]\mathrm{d}I \quad \text{(A1)}$$

Substitution of this equation into eq 19 for $k = 2$ gives the second-order variation,

$$\delta^2\tilde{G}_\upsilon = \frac{(\delta\Phi_o)^2}{r_o\Phi_o} + \int_0^\infty \frac{\{\delta[\Phi_s W(I)]\}^2}{r(I)\Phi_s W(I)}\,\mathrm{d}I + 2\int_0^\infty \delta\Phi_o\delta[\Phi_s W(I)][g(I) - \Phi_o g'(I)]\,\mathrm{d}I - 2\int_0^\infty (\delta\Phi_o)^2\Phi_s W(I)[g'(I) - \Phi_o g''(I)/2]\,\mathrm{d}I \quad \text{(A2)}$$

where $g''(I) = \partial^2 g(I)/\partial{\Phi_s}^2$. Variations $\delta\Phi_o$ and $\delta[\Phi_s W(I)]$ are not independent. For obtaining their relation, Kehlen et al.[14,15] suggested that $\delta^2\tilde{G}_\upsilon$ should be a minimum when $\delta\Phi_o$ and $\delta[\Phi_s W(I)]$ are correctly related. On the other hand, they are also subjected to the following constraint,

$$\int_0^\infty \delta[\Phi_s W(I)]\,\mathrm{d}I = \delta\Phi_s = -\delta\Phi_o \quad \text{(A3)}$$

Using this equation as a constraint, the relation between two variations can be obtained by seeking the conditional extremum for $\delta^2\tilde{G}_\upsilon$ by applying the Lagrange undetermined-multiplier method.

We first take the derivative for $\delta^2\tilde{G}_\upsilon$ in eq A2 with respect to the variation $\delta[\Phi_s W(I)]$, according to eq 16, keeping $\delta\Phi_o$ unchanged. We obtain

$$\frac{\partial\delta^2\tilde{G}_\upsilon}{\partial\delta[\Phi_s W(I)]} = \frac{2\delta[\Phi_s W(I)]}{r(I)\Phi_s W(I)} + 2\delta\Phi_o[g(I) - \Phi_o g'(I)] \quad \text{(A4)}$$

We then introduce undetermined multiplier -2λ to eq A3. After taking the derivative and adding to eq A4, we set it equal to zero. We obtain

$$\lambda = \frac{\delta[\Phi_s W(I)]}{r(I)\Phi_s W(I)} + \delta\Phi_o[g(I) - \Phi_o g'(I)] \quad \text{(A5)}$$

Substituting this equation into eq A3, we can solve for λ,

$$\lambda = \delta\Phi_o[\Phi_s(\langle gr\rangle - \Phi_o\langle g'r\rangle) - 1]/\Phi_s r_w \quad \text{(A6)}$$

where

$$\langle gr\rangle = \int_0^\infty g(I)r(I)W(I)\,\mathrm{d}I \quad \text{(A7)}$$

$$\langle g'r\rangle = \int_0^\infty g'(I)r(I)W(I)\,\mathrm{d}I \quad \text{(A8)}$$

$$r_w = \langle r\rangle = \int_0^\infty r(I)W(I)\,\mathrm{d}I \quad \text{(A9)}$$

r_w is usually called the weight-average chain length. Combine eqs A6 and A5. We obtain the relation between two variations,

$$\delta[\Phi_s W(I)] = (\delta\Phi_o)\Phi_s r(I)W(I)\left[\frac{\langle gr\rangle - \Phi_o\langle g'r\rangle}{r_w} - \frac{1}{\Phi_s r_w} - g(I) + \phi_o g'(I)\right] \quad \text{(A10)}$$

Substituting this equation into eq A2, we have eq 20.

Appendix 2: Critical-Point Criterion

$$\frac{\delta^3\tilde{G}_\upsilon}{(\delta\Phi_o)^3} = -\frac{1}{r_o\Phi_o^{\ 2}} - \frac{\Phi_s\langle r^2\rangle}{\langle r\rangle^3}((\langle gr\rangle - \Phi_o\langle g'r\rangle))^3 + \frac{\langle r^2\rangle}{\Phi_s^{\ 2}\langle r\rangle^3} + ((\langle g^3r^2\rangle - 3\Phi_o\langle g^2g'r^2\rangle + 3\Phi_o^{\ 2}\langle gg'^2r^2\rangle - \Phi_o^{\ 3}\langle g'^3r^2\rangle)\Phi_s + 3\frac{\langle r^2\rangle}{\langle r\rangle^3}((\langle gr\rangle - \Phi_o\langle g'r\rangle))^2 + 3\Phi_s\frac{\langle gr^2\rangle - \Phi_o\langle g'r^2\rangle}{\langle r\rangle^2}((\langle gr\rangle - \Phi_o\langle g'r\rangle))^2 - 3\frac{\langle r^2\rangle}{\langle r\rangle^3\Phi_s}((\langle gr\rangle - \Phi_o\langle g'r\rangle)) - 3\Phi_s\frac{\langle g^2r^2\rangle - 2\Phi_o\langle gg'r^2\rangle + \Phi_o^{\ 2}\langle g'^2r^2\rangle}{\langle r\rangle}((\langle gr\rangle - \Phi_o\langle g'r\rangle)) + 3\frac{\langle gr^2\rangle - \Phi_o\langle g'r^2\rangle}{\langle r\rangle^2\Phi_s} + 3\frac{\langle g^2r^2\rangle - 2\Phi_o\langle gg'r^2\rangle + \Phi_o^{\ 2}\langle g'^2r^2\rangle}{\langle r\rangle} - 6\frac{\langle gr\rangle - \Phi_o\langle g'r\rangle}{\langle r\rangle^2}((\langle gr^2\rangle - \Phi_o g'r^2\rangle)) - 6\Phi_s\langle g'r\rangle\frac{\langle gr\rangle - \Phi_o\langle g''r\rangle}{\langle r\rangle} + 6\frac{\langle g'r\rangle}{\langle r\rangle} + 3\Phi_s\langle g''\rangle + 6\Phi_s((\langle gg'r\rangle - \Phi_o\langle g'^2r\rangle)) + 3\Phi_o\Phi_s\langle g''r\rangle\frac{\langle gr\rangle - \Phi_o\langle g'r\rangle}{\langle r\rangle} - 3\Phi_o\frac{\langle g''r\rangle}{\langle r\rangle} - 3\Phi_o\Phi_s((\langle gg''r\rangle - \Phi_o\langle g'g''r\rangle)) \quad \text{(B1)}$$

The meaning of terms ⟨...⟩ in this equation is similar to those in eq 20, as defined by eq 21.

Appendix 3: Comparison with the Results Derived by the Discrete Approach

For testing the reliability of derivations for the spinodal and the critical-point criteria, we set relations between some terms and their corresponding terms in the discrete approach as follows:

$$r_o^{\ -1}\Phi_o^{\ -1} - 2\Phi_s\langle g'\rangle + \Phi_o\Phi_s\langle g''\rangle \rightarrow J \quad \text{(C1)}$$

$$-g(I) + \Phi_o g'(I) \rightarrow J_i \quad \text{(C2)}$$

$$1/[r(I)\Phi_s W(I)] \rightarrow \lambda_i \quad \text{(C3)}$$

Then we have

$$\Phi_s r_w = \int_0^\infty \Phi_s r(I)W(I)\,\mathrm{d}I = \sum_i \lambda_i^{-1} \quad \text{(C4)}$$

$$-\Phi_s((\langle gr\rangle - \Phi_o\langle g'r\rangle)) = \sum_i J_i\lambda_i^{-1} \quad \text{(C5)}$$

$$\Phi_s((\langle g^2r\rangle - 2\Phi_o\langle gg'r\rangle + \Phi_o^{\ 2}\langle g'^2r\rangle)) = \sum_i J_i^{\ 2}\lambda_i^{-1} \quad \text{(C6)}$$

Substitution into eq 20 and defining a new F_{sp},

$$F_{sp}\Phi_s^{\ -1}r_w^{\ -1} \rightarrow F_{sp} \quad \text{(C7)}$$

We have the spinodal criterion with a discrete version,

$$F_{sp} = 1 + J\sum_i\frac{1}{\lambda_i} + \left(\sum_i\frac{J_i}{\lambda_i}\right)^2 - \sum_i\frac{1}{\lambda_i}\sum_i\frac{J_iJ_i}{\lambda_i} + 2\sum_i\frac{J_i}{\lambda_i} \quad \text{(C8)}$$

This equation can be derived from the discrete approach.

For the critical point, we set two further relations as follows:

$$r_o^{\ -1}\Phi_o^{\ -2} - 3\Phi_s\langle g''\rangle \rightarrow J' \quad \text{(C9)}$$

$$-2g'(I) + \Phi_o g''(I) \rightarrow J_i' \quad \text{(C10)}$$

Upon substitution of the above equations into eq B1, we have the critical-point criterion in a discrete version

$$F_{cr} = \sum_i J_i^{\ 3}r_i\lambda_i^{-1} + J' - 3\sum_i J_iJ_i'\lambda_i^{-1} - 3\left(\sum_i J_i^{\ 2}r_i\lambda_i^{-1}\right)\frac{1 + \sum_i J_i\lambda_i^{-1}}{\sum_i\lambda_i^{-1}} + 3\sum_i J_ir_i\lambda_i^{-1} \times \left(\frac{1 + \sum_i J_i\lambda_i^{-1}}{\sum_i\lambda_i^{-1}}\right)^2 - \sum_i r_i\lambda_i^{-1}\left(\frac{1 + \sum_i J_i\lambda_i^{-1}}{\sum_i\lambda_i^{-1}}\right)^3 \quad \text{(C11)}$$

This equation can also be derived from the discrete approach.

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