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The Flory χ Parameter and Phase Separation in Semidilute Polymer Mixtures: A Renormalization Group Study

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ABSTRACT: The universal part of the free energy of mixing of semidilute solutions of two polymers in marginal to good solvents is evaluated by using an Edwards' continuum model. Excluded-volume interactions between chains are modeled by the usual δ function pseudopotentials, while polymer–solvent interactions are introduced via the Flory–Huggins lattice theory by requiring that the lattice and continuum theory free energies of mixing coincide at the Θ point. The free energy is calculated perturbatively near four dimensions ($d = 4$) as an expansion to first order in $4 - d$. A renormalized free energy is defined through the introduction of phenomenological osmotic second virial coefficients that absorb divergences in the perturbation expansion. By deriving expressions for the chemical potentials of the various components of the ternary mixture, the Flory χ parameters are obtained as functions of concentration, molecular weight, and temperature. They cannot be represented as pairwise additive polymer–solvent and polymer–polymer contributions because of the screening of excluded-volume interactions in semidilute solutions. Equations for the coexistence curves for phase separation are determined for two special limits, and the predictions are compared with the Flory–Huggins theory. A general theorem is proven that phenomenologically defined Flory χ parameters of ternary mixtures must diverge in the limit that the volume fraction of one of the components vanishes, provided certain regularity constraints are obeyed by the chemical potentials in this limit.

1. Introduction

The study of solutions or blends of different polymers is important in a number of areas of polymer processing, including the development of composites, biological fractionation, and colloid chemistry.[1-3] As a result, these systems have been the subject of numerous experimental[4] and theoretical[5] investigations.

Our present understanding of the salient entropic and enthalpic changes accompanying the formation of polymer mixtures relies heavily on the early lattice theory of mixing of Flory, Huggins, and others[6] for polymer blends. Blends are especially amenable to mean-field treatments of the Flory–Huggins kind as the composition fluctuations in these systems are small over a wide range of temperatures. However, Flory–Huggins-type approaches do not adequately describe the behavior of polymers in semidilute solutions, where long-range correlations lead to the emergence of altered power law dependences of effective interaction energies, osmotic pressures, etc., on concentration. Here we study the free energy of mixing of moderate to good solvent semidilute binary polymer mixtures using renormalization group methods to investigate the concentration dependence of the Flory χ parameter and to explore the ramifications of the abovementioned altered power-law dependences on the coexistence curve for phase separation.

The systematic description of polymers in semidilute solutions has recently been made possible by the methods of the renormalization group[7] (for a detailed discussion, see, for example, ref 8). But the application of these methods to the study of mixtures has so far been somewhat limited.[5d,e] For instance, there is presently no renormalization group treatment of demixing in the simplest system of a mixture of a polymer and a solvent. The difficulties of such a treatment are associated with the necessity of at least including both two- and three-body excluded-volume interactions in the theory.[9] No satisfactory way to do this is yet known for arbitrary values of the two interactions, i.e., away from the theta region. (But see ref 10 for a mean-field treatment.)

Renormalization group approaches are more readily applied to mixtures in which the effects of three-body interactions are unimportant. For example, Schäfer and Kappeler[5d] determine the renormalized spinodal for a ternary solution of two polymers in a solvent that is marginal to good for both polymers. Their calcualtion uses the "tree approxiamtion", however, and thereby neglects excluded-volume screening, which first appears only in the next order in excluded volume and which describes important effects of long-range correlations in semidilute polymer solutions. Although even the mean-field calculations of Schäfer and Kappeler produce qualitative departures from the standard Flory–Huggins theory, Schäfer and Kappeler note that a complete description of critical

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demixing must include screening contributions in the region of strong chain overlap. Schäfer and Kappeler also discuss the phase diagram of the ternary system only in terms of the abstract "flows" of the different excluded-volume interaction parameters as the solvent quality is varied. The "phase diagrams" so obtained are not easily related to the experimentally constructed phase diagrams, which usually present the polymer volume fraction ϕ as a function of the temperature T, and further work is necessary to extend such treatments of the semidilute region to study demixing and the Flory χ parameter as a function of experimental variables.

The qualitative importance of screening in semidilute solutions is well-known[7,11-13] to alter the concentration (c) dependence of the polymer–polymer interaction free energy from the Flory–Huggins c^2 form to the good solvent form of roughly $c^{9/4}$. A simple model of the polymer–polymer interactions in good solvent semidilute binary polymer solutions might use a model of pairwise additive contributions with a $c_i^{9/4}$ type term for polymer i (i = A or B) along with an A–B interaction term. However, the screening of, say, A–A excluded-volume interactions is mediated by both A and B polymers, so the effective polymer A–polymer A interaction free energy becomes dependent of the volume fraction on B and the A–B excluded volume. One of the main purposes of this paper is to investigate the form of this highly correlated interactional free energy and to determine its influence on the effective Flory χ parameters and on the phase separation in binary polymer solutions.

We use renormalization group methods to derive the free energy of mixing of semidilute solutions of two polymers A and B as a function of the molecular weights, concentrations, and experimentally measurable self- and mixed-virial coefficients A_{AA}, A_{BB}, and A_{AB}, applying the Edwards random field formulation[11] of the many-chain system to explicitly incorpoate the effects of screening into the theory. The free energy in turn is used to calculate the chemical potentials of solvent and polymers A and B, which, on the basis of Flory's definition, are further used to obtain expressions for *effective* polymer–polymer and polymer–solvent interaction parameters. In so defining these χ parameters, they are explicit functions not only of temperature and molecular weight (as in the original Flory formulation) but also of composition. They are, however, fully consistent with the Gibbs–Duhen equation and other thermodynamic relations, having been evaluated directly from a single well-defined free energy of mixing. At the same time, they do show decidedly non-Flory–Huggins behavior in the limit of vanishing volume fraction of one of the components, where the effective interaction parameters diverge. This singular behavior originates in the composition dependence introduced through the Flory definition; the renormalization group free energy expression is nondivergent in the two-component limit.

Coexistence curves for phase separation in the ternary mixture are determined from the free energy computed above. For simplicity, the numerical examples of coexistence curves consider chains of equal length and equal molecular weight so as to reduce the number of independent paramters, but the full expressions (with 10 experimental parameters) may be used in the general case. Calculations of phase separation are provided in the special limits where (a) the traditional Fixman excluded-volume parameters z_{AA} and z_{BB} between like chains vanish, while the mixed interaction parameter z_{AB} between different chains is variable and is repulsive, and where (b) the chains are in a marginal to good solvent with $z_{AA} = z_{BB} = \mathcal{O}(1)$ and the mutual repulsion z_{AB} is of the same order.

Section 2 discusses the derivation of a renormalized free energy of mixing for two polymers A and B in the Edwards continuum representation,[11] in which the method of random fields is generalized to a two-component mixture and is used to incorporate the screening of excluded-volume interactions at nonzero concentrations of both polymers. Section 3 provides expressions for the chemical potentials of the components of the ternary mixture, which are then used to determine the experimentally important variations of the Flory χ parameter with experimental variables. Those readers uninterested in the mathematical details provided in sections 2 and 3 may proceed directly to section 3B. Numerical computations of the χ parameter are presented in section 4 along with the computational scheme employed in calculating coexistence curves for the two special limits mentioned above. A general derivation is provided in the Appendix to show that the traditional phenomenological definition of χ_{AB} (through the chemical potential) implies that it must diverge as an inverse volume fraction ϕ_i when ϕ_i tends toward zero, provided the chemical potentials are nonvanishing in this $\phi_i \rightarrow 0$ limit. The derivation is valid for arbitrary ternary systems and may be applied to blends in which the third component is taken to represent free volume.

2. Free Energy of A–B Mixture

A. Two-Parameter Model. The configurational "Hamiltonian" for a given configuration of a mixture of two chemically different polymers A and B at nonzero concentration is a simple generalization of that for a single polymeric species in solution.[7,8,13] The individual polymers are represented by continuous curves in d dimensions whose chain elements at distances τ_A and τ_B along the chain contour are at the spatial points $\mathbf{r}_A(\tau_A)$ and $\mathbf{r}_B(\tau_B)$, respectively.[14] The configuration Hamiltonian is given by

$$\frac{H}{k_BT} = \frac{1}{2}\sum_{j=A,B}\sum_{\alpha=1}^{n_j}\int_0^{N_{0,j}}\mathrm{d}\tau_\alpha\,|\dot{\mathbf{r}}_\alpha^{(j)}(\tau_\alpha)|^2 + \frac{1}{2}\sum_{i,j=A,B}\sum_{\alpha,\beta=1}^{n_i,n_j}\int_0^{N_{0,i}}\mathrm{d}\tau_\alpha\int_0^{N_{0,j}}\mathrm{d}\tau_\beta\,\upsilon_{ij}^0\delta[\mathbf{r}_\alpha^{(i)}(\tau_\alpha) - \mathbf{r}_\beta^{(j)}(\tau_\beta)] \equiv \frac{H_0}{k_BT} + \frac{H_1}{k_BT} \quad (2.1)$$

where n_i for i = A, B sequentially numbers the A or B chains in a volume Ω, $N_{0,A}$ and $N_{0,B}$ are, respectively, the "bare" chain lengths of the two kinds of polymers, υ_{AA}^0, υ_{BB}^0, and $\upsilon_{BA}^0 = \upsilon_{AB}^0$ are the bare excluded-volume interactions between like and unlike polymer species, and $\dot{\mathbf{r}}_\alpha^{(i)}(\tau_\alpha) \equiv \mathrm{d}\mathbf{r}_\alpha^{(i)}(\tau_\alpha)/\mathrm{d}\tau_\alpha$, i = A, B.

The bare partition function Q_B for the A–B system is the weighted sum of all possible configurations,

$$Q_B = \left\{\prod_{i=A,B}\int D[\mathbf{r}_i(\tau_i)]\right\}\exp[-(H_0 + H_1)/k_BT] \quad (2.2)$$

where H_1 is the portion of (2.1) containing the υ_{ij}^0. This term may be written in matrix form as

$$H_1/k_BT = (1/2)\int \mathrm{d}^dr \int \mathrm{d}^dr'\,\rho^T(\mathbf{r})\mathbf{V}\rho(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}') \quad (2.3)$$

where the superscript T denotes transpose, the vector $\rho^T(\mathbf{r})$ is given by

$$\rho^T(\mathbf{r}) = (\rho_A(\mathbf{r}), \rho_B(\mathbf{r})) \quad (2.4)$$

the elements $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ have the representations

$$\rho_\alpha(\mathbf{r}) = \sum_{i=1}^{n_\alpha}\int_0^{N_{0,\alpha}}\mathrm{d}\tau_i\,\delta[\mathbf{r} - \mathbf{r}_i^{(\alpha)}(\tau_i)], \qquad \alpha = A, B \quad (2.5)$$

and the matrix $\mathbf{V}$ is given by

$$\mathbf{V} = \begin{bmatrix} v_{AA}{}^0 & v_{AB}{}^0 \\ v_{BA}{}^0 & v_{BB}{}^0 \end{bmatrix} \tag{2.6}$$

Screening of excluded-volume interactions may be treated by use of methods similar to those pioneered by Edwards.[11] The Edwards random field decoupling scheme may be generalized for two components as

$$\exp(-H_1/k_BT) = N^{-1}\left\{\prod_{\alpha=A,B}\int\delta\phi_\alpha\right\} \times \exp\left\{i\int d^dr\, \rho^T(\mathbf{r})\vec{\phi}(\mathbf{r}) - \tfrac{1}{2}\int d^dr\, \vec{\phi}^T(\mathbf{r})\mathbf{V}^{-1}\vec{\phi}(\mathbf{r})\right\} \tag{2.7}$$

where the vector $\vec{\phi}(\mathbf{r})$ contains the random fields $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ and is given by

$$\vec{\phi}^T(\mathbf{r}) = (\phi_A(\mathbf{r}), \phi_B(\mathbf{r})) \tag{2.8}$$

The symbol $\delta\phi_\alpha$ denotes the measure on the field configuration of ϕ_A and ϕ_B, the normalization factor N in (2.7) is

$$N = \left\{\prod_{\alpha=A,B}\int\delta\phi_\alpha\right\} \times \exp\left\{-\tfrac{1}{2}\int d^dr\int d^dr'\, \vec{\phi}^T(\mathbf{r})\mathbf{V}^{-1}\vec{\phi}(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}')\right\} \tag{2.9}$$

and the matrix inverse of (2.6) is easily calculated to be

$$\mathbf{V}^{-1} = [v_{AA}{}^0 v_{BB}{}^0 - (v_{AB}{}^0)^2]^{-1}\begin{bmatrix} v_{BB}{}^0 & -v_{AB}{}^0 \\ -v_{AB}{}^0 & v_{AA}{}^0 \end{bmatrix} \tag{2.10}$$

From the procedure described in detail in ref 8 and 15 the bare partition function Q_B and the free energy F_B are calculated by expanding the exponential part of (2.2) with (2.6) to second order in ϕ_A and ϕ_B around the unperturbed Gaussian state and by then evaluating the integrals over ϕ_A and ϕ_B. In this way, the bare free energy to first order in the excluded volume is found to be[16]

$$-F_B/k_BT = n_A \ln\Omega + n_B \ln\Omega - (2\Omega)^{-1}(n_A{}^2 v_{AA}{}^0 N_{0A}{}^2 + n_B{}^2 v_{BB}{}^0 N_{0B}{}^2 + 2n_A n_B v_{AB}{}^0 N_{0A}N_{0B}) - \Omega[2(2\pi)^d]^{-1}\int d^dq \ln\{1 + 2n_A\Omega^{-1}v_{AA}{}^0 S_A + 2n_B\Omega^{-1}v_{BB}{}^0 S_B + 4n_A n_B\Omega^{-2}S_A S_B[v_{AA}{}^0 v_{BB}{}^0 - (v_{AB}{}^0)^2]\} + \mathcal{O}(v^2) \tag{2.11}$$

where S_A and S_B are the unperturbed A and B chain Debye scattering functions

$$S_\alpha \equiv 2N_{0\alpha}q^{-2} + 4q^{-4}[\exp(-q^2N_{0\alpha}/2) - 1], \quad \alpha = A, B \tag{2.11a}$$

B. Renormalization of Free Energy. The integral over q in eq 2.11 diverges in the limit $q \to \infty$ for $d \leq 4$. Since it is only near $d = 4$ that a well-controlled perturbation expansion in the excluded-volume exists, the occurrence of singularities in (2.11) necessitates its regularization and renormalization.[7] This is done by adding and subtracting terms containing the divergent portions of (2.11) in the integrand of (2.11) in the manner described in ref 8 and 15. The regularized integral obtained after subtraction is well-defined in $d = 4$ and is evaluated there, while the added portions are chosen such that they may be renormalized by combining them into the definition of the osmotic second virial coefficients. The final results are thus represented in terms of experimental measurables.

Introducing the change in variables $q^2 = 2y^2/(N_{0A} + N_{0B})$ and following the steps of ref 8 and 15, we evaluate the free energy as

$$-\Delta\hat{F} \equiv -F_B/k_BT + [2^{1-d/2}/(2\pi)^{d/2}\Gamma(d/2)] \times \left\{n_A v_{AA}{}^0\int_0^\infty dq\, q^{d-1}S_A + n_B v_{BB}{}^0\int_0^\infty dq\, q^{d-1}S_B\right\} = n_A\ln\Omega + n_B\ln\Omega - \hat{N}_A\Omega(c_A{}^2A_{AA} + c_B{}^2A_{BB} + 2c_Ac_BA_{AB}) - [\Omega/8\pi^2(N_A+N_B)^2]\int_0^\infty dy\, y\{\ln[1 + 4c_AM_AA_{AA}g_A(y) + 4c_BM_BA_{BB}g_B(y) + 16c_Ac_BM_AM_Bg_A(y)g_B(y)\,(A_{AA}A_{BB} - A_{AB}{}^2)] - 4c_AM_AA_{AA}g_A(y) - 4c_BM_BA_{BB}g_B(y) + \tfrac{1}{2}[4c_AM_AA_{AA}g_A(y)]^2 + \tfrac{1}{2}[4c_BM_BA_{BB}g_B(y)]^2 + 16c_Ac_BA_{AB}{}^2g_A(y)g_B(y)\} + \mathcal{O}(v^2) \tag{2.12}$$

where $\Gamma(x)$ is the Γ function, $\hat{N}_A$ is Avogadro's number, c_i (i = A, B) is the weight concentration of i, A_{AA}, A_{BB}, and A_{AB} are the osmotic second virial coefficients for A–A, B–B, and A–B type contacts, M_i (i = A, B) is the molecular weight of i, and $g_i(y) \equiv (y\lambda_i)^{-1} + (y\lambda_i)^{-2}[\exp(-y\lambda_i) - 1]$ (i = A, B), with $\lambda_i \equiv N_i/(N_A + N_B)$. (Reference 8 uses the notation $g(y^2)$ for this function.) In arriving at (2.12) we have used the relations $2n_i\Omega^{-1}v_{ii}{}^0S_i \equiv 4c_iM_iA_{ii}g_i(y) + \mathcal{O}(v^2)$, i = A, B, and $4n_An_B\Omega^{-2}S_AS_B(v_{AB}{}^0)^2 \equiv 16c_Ac_BM_AM_B \times g_A(y)g_B(y)A_{AB}{}^2$, where the A_{ij} are renormalized quantities that can be taken from theory or experiment. The elimination of the divergences in the perturbative expansion of the free energy in (2.12) through the introduction of the renormalized virial coefficients A_{ij} implies that the bare lengths N_{0A} and N_{0B} are to be replaced by their renormalized counterparts, which are denoted by the variables N_A and N_B.

C. Inclusion of the Entropy of Mixing. Equation 2.12 does not explicitly include the entropy of mixing of the polymers and solvent, an important quantity that, because of the point (δ function) effective polymer interactions, lies outside the scope of the model (2.1). The simplest approximation for the free energy of mixing of two polymers and solvent is given by Flory–Huggins theory[6] in units of k_BT as

$$\Delta F_{FH} = n_0\ln\phi_0 + n_A\ln\phi_A + n_B\ln\phi_B + \chi_{0A}n_0\phi_A + \chi_{0B}n_0\phi_B + \chi_{AB}n_A\phi_B \tag{2.13}$$

where ϕ_0, ϕ_A, and ϕ_B and n_0, n_A, and n_B are respectively the volume fractions and numbers of molecules of the solvent and polymers A and B. Henceforth, the symbols ϕ_A and ϕ_B refer to volume fractions and not the random fields of section 2A. The χ_{0A}, χ_{0B}, and χ_{AB} are the Flory interaction parameters for solvent–polymer and polymer–polymer contacts that are defined by Flory as[6]

$$\chi_{ij} = z\Delta w_{ij}x_i/kT \tag{2.13a}$$

where z is the lattice coordination number, Δw_{ij} is the energy associated with a pair of neighboring segments, x_i is the number of segments per molecule in species i and kT is the thermal energy. (More accurate treatments[17] of ΔF are now available for the lattice model used by Flory and others and may be used instead of (2.13). However, in order to simplify the algebra, we retain the form (2.13)).

Under idealized "Θ" conditions $\chi_{0A} = \chi_{0B} = \chi_{AB} = {}^1/_2$, and ΔF_{FH} reduces to

$$\Delta\tilde{F}_{FH} = n_0\ln\phi_0 + n_0\ln\phi_A + n_B\ln\phi_B + \tfrac{1}{2}(n_0\phi_A + n_0\phi_B + n_A\phi_B) \tag{2.13b}$$

On the other hand, these conditions for (2.12) are defined by $v_{AA}{}^0 = v_{BB}{}^0 = v_{AB}{}^0 = 0$, making (2.12) vanish identically apart from $\ln\Omega$ terms. The perturbed free energy is then taken as the sum of (2.12) and (2.13b)

$$\Delta F = \Delta\hat{F} + \Delta\tilde{F}_{FH} \tag{2.14}$$

which expresses the condition that the corrected ΔF equals

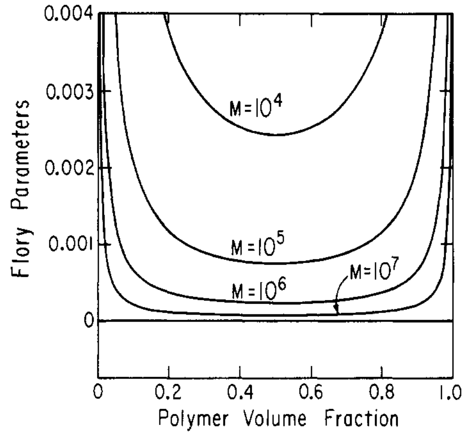

Figure 1. Effective Flory parameters $\tilde{\chi}_{0A}/M_A$, $\tilde{\chi}_{0B}/M_B$, and $\tilde{\chi}_{AB}/(M_AM_B)^{1/2}$ as a function of polymer volume fraction $\phi'_A \equiv \phi_A/(\phi_A + \phi_B)$ for molecular weights in the range $M = 10^4$–10^7 g mol^{-1} as calculated from the renormalization group expressions for the chemical potential. The calculations employ virial coefficients $A_{AA} = A_{BB} \leq A_{AB}$ determined from eq 4.6 –4.7d with the Fixman parameters $z_{AA} = z_{BB} = 1$. The remaining parameters V_0, V_A, V_B, etc. are specified as described in the text. The top four curves refer to $\tilde{\chi}_{AB}/(M_AM_B)^{1/2}$, while the lowest curve refers to $\tilde{\chi}_{0A}/M_A$ and $\tilde{\chi}_{0B}/M_B$, which coincide and which show no molecular weight dependence.

ΔF_{FH} at the Θ point. Thus, after reexponentiation of order ϵ terms (see below) the free energy becomes the lengthy expression

$$\begin{aligned}\Delta F/\Omega\hat{N}_A = {} & (\phi_0/V_0)\ln\phi_0 + (\phi_A/V_A)\ln\phi_A + (\phi_B/V_B)\ln\phi_B + \phi_0\phi_A/2V_0 + \phi_0\phi_B/2V_0 + \phi_A\phi_B/2V_A \\ & + (\phi_A^2M_A^2A_{AA}/V_A^2 + \phi_B^2M_B^2A_{BB}/V_B^2 + 2\phi_A\phi_BM_AM_BA_{AB}/V_AV_B)\exp\{(\phi_A^2M_A^2A_{AA}/V_A^2 + \phi_B^2M_B^2A_{BB}/V_B^2 + \\ & 2\phi_A\phi_BM_AM_BA_{AB}/V_AV_B)^{-1}/8\pi^2\hat{N}_A(N_A + N_B)^2\}\int_0^\infty \mathrm{d}y\, y\{\ln[1 + 4\phi_AM_A^2A_{AA}g_A(y)/V_A + 4\phi_BM_B^2A_{BB}g_B(y)/V_B + \\ & 16\phi_A\phi_BM_A^2M_B^2g_A(y)g_B(y)(A_{AA}A_{BB} - A_{AB}^2)/V_AV_B] - 4\phi_AM_A^2A_{AA}g_A(y)/V_A - 4\phi_BM_B^2A_{BB}g_B(y)/V_B + \\ & 8\phi_A^2M_A^4A_{AA}^2g_A^2(y)/V_A^2 + 8\phi_B^2M_B^4A_{BB}^2g_B^2(y)/V_B^2 + 16\phi_A\phi_BM_A^2M_B^2A_{AB}^2g_A(y)g_B(y)/V_AV_B\} + \mathcal{O}(v^2)\end{aligned} \tag{2.15}$$

where all weight concentrations have been converted to volume fractions through

$$n_i = \phi_i\Omega\hat{N}_A/V_i, \qquad i = \mathrm{A, B} \tag{2.16}$$

with $\hat{N}_A$ Avogadro's number and V_i the molar volume of the ith species. In deriving (2.15) factors of ln Ω may be absorbed into the definition of the zero of free energy and thus removed, because the remainder of the kinetic contribution is not included. Notice that the interaction term of (2.15) (i.e., the term containing the y integral) cannot be decomposed into pairwise additive contributions, as explained heuristically in the Introduction. An important feature of (2.15) is its representation solely in terms of measurable quantities rather than abstract renormalization group variables. The interactions in (2.15) are represented in terms of a monodisperse distribution, but polydispersity averages can readily be introduced. These averages are omitted because of the complexity of (2.15).

D. Approximate Analytic Evaluation of Equation 2.15. The integral over y asympotically yields logarithms,[7,15] so reexponentiation of this term is required to produce the expected power law form[18] for the free energy as a function of concentration in the semidilute region. This process is made explicit by introducing the Ohta–Oono approximation[7] to evaluate the integrals in (2.15) analytically. Here the function $g_i(y)$ of (2.15) is replaced by $(y\lambda_i + 2)^{-1}$, an approximation that correctly reproduces the $y \to 0$ and $y \to \infty$ limits of the exact expression. Between these limits $(y\lambda_i + 2)^{-1}$ has been shown[7] to lie within 3% of the true values. The quantity λ_i is used to model the chain polydispersity. The evaluation of the y integrals in (2.15) using the Ohta–Oono scheme yields the free energy F_S as

$$\begin{aligned}F_S/\Omega RT = {} & (\phi_0/V_0)\ln\phi_0 + (\phi_A/V_A)\ln\phi_A + (\phi_B/V_B)\ln\phi_B + \phi_0\phi_A/2V_0 + \phi_0\phi_B/2V_0 + \\ & \phi_A\phi_B/2V_A + (\bar{\phi}_A^2/A_{AA}M_A^2 + \bar{\phi}_B^2/A_{BB}M_B^2 + 2\bar{\phi}_{AB}^2/A_{AB}M_AM_B)[1 + (\bar{\phi}_A^2/A_{AA}M_B^2 + \bar{\phi}_B^2/A_{BB}M_A^2 + \\ & 2\bar{\phi}_{AB}^2/A_{AB}M_AM_B)^{-1}/8\pi^2\hat{N}_A(N_A + N_B)^2\{(1/\lambda_A^2 + 1/\lambda_B^2 + 4\bar{\phi}_A^2/\lambda_A^2 + 4\bar{\phi}_B^2/\lambda_B^2 + 4\bar{\phi}_A/\lambda_A^2 + 4\bar{\phi}_B/\lambda_B^2 + \\ & 8\bar{\phi}_{AB}^2/\lambda_A\lambda_B)\ln|(4 + 8\bar{\phi}_A + 8\bar{\phi}_B + 16(\bar{\phi}_A\bar{\phi}_B - \bar{\phi}_{AB}^2)/\lambda_A\lambda_B| + \\ & (2\lambda_A + 2\lambda_B + 4\bar{\phi}_A\lambda_B + 4\bar{\phi}_B\lambda_A)(\hat{H}^{1/2}/4\lambda_A^2\lambda_B^2)\ln|(2\lambda_A + 2\lambda_B + 4\bar{\phi}_A\lambda_B + 4\bar{\phi}_B\lambda_A + \hat{H}^{1/2})/(2\lambda_A + 2\lambda_B + 4\bar{\phi}_A\lambda_B + \\ & 4\bar{\phi}_B\lambda_A - \hat{H}^{1/2})| + (2/\lambda_A^2 + 8\bar{\phi}_A/\lambda_A^2 + 8\bar{\phi}_A^2/\lambda_A^2 - 16\bar{\phi}_{AB}^2/\lambda_A(\lambda_A - \lambda_B))\ln\lambda_A + (2/\lambda_B^2 + \\ & 8\bar{\phi}_B/\lambda_B^2 + 8\bar{\phi}_B^2/\lambda_B^2 + 16\bar{\phi}_{AB}^2/\lambda_B(\lambda_A - \lambda_B))\ln\lambda_B - (2/\lambda_A^2 + 2/\lambda_B^2 + 8\bar{\phi}_A/\lambda_A^2 + 8\bar{\phi}_B/\lambda_B^2 + 8\bar{\phi}_A^2/\lambda_A^2 + \\ & 8\bar{\phi}_B^2/\lambda_B^2 - 16\bar{\phi}_{AB}^2/\lambda_A(\lambda_A - \lambda_B) + 16\bar{\phi}_{AB}^2/\lambda_B(\lambda_A - \lambda_B))\ln 2 - 12\bar{\phi}_A^2/\lambda_A^2 - 12\bar{\phi}_B^2/\lambda_B^2 - \\ & 4\bar{\phi}_A/\lambda_A^2 - 4\bar{\phi}_B/\lambda_B^2 - 8\bar{\phi}_{AB}^2/\lambda_A\lambda_B\}]\end{aligned} \tag{2.17}$$

where in analogy with the work of ref 8 and 15 we define the reduced volume fractions $\bar{\phi}_A$, $\bar{\phi}_B$, and $\bar{\phi}_{AB}$ as

$$\bar{\phi}_A = \phi_AA_{AA}M_A^2/V_A \tag{2.18a}$$

$$\bar{\phi}_B = \phi_BA_{BB}M_B^2/V_B \tag{2.18b}$$

$$\bar{\phi}_{AB} = (\phi_A\phi_B)^{1/2}A_{AB}M_AM_B/(V_AV_B)^{1/2} \tag{2.18c}$$

and the quantity $\hat{H}$ is given by

$$\begin{aligned}\hat{H} = {} & 16\bar{\phi}_A^2\lambda_B^2 + 16\bar{\phi}_B^2\lambda_A^2 + 16\bar{\phi}_A(\lambda_B^2 - \lambda_A\lambda_B) + 16\bar{\phi}_B(\lambda_A^2 - \lambda_A\lambda_B) - 32\bar{\phi}_A\bar{\phi}_B\lambda_A\lambda_B + 64\bar{\phi}_{AB}^2\lambda_A\lambda_B - \\ & 8\lambda_A\lambda_B + 4\lambda_A^2 + 4\lambda_B^2\end{aligned} \tag{2.18d}$$

The known scaling limit behavior[7] of F_S is recovered from (2.17) by exponentiating terms involving the logarithms of $\bar{\phi}_A$, $\bar{\phi}_B$, and $\bar{\phi}_{AB}$

$$F_S/\Omega RT = FH + F_1\tilde{F}_2^{\tilde{a}_1/8\pi^2F_1\tilde{Q}}\tilde{F}_3^{\tilde{a}_2/8\pi^2F_1\tilde{Q}} \times \left[1 + \frac{1}{8\pi^2F_1\tilde{Q}}(\tilde{a}_3\ln\lambda_A + \tilde{a}_4\ln\lambda_B - \tilde{a}_5\ln 2 - \tilde{F}_4)\right] + \mathcal{O}(\epsilon^2) \tag{2.19}$$

where we define the quantities

$$FH \equiv (\phi_0/V_0)\ln\phi_0 + (\phi_A/V_A)\ln\phi_A + (\phi_B/V_B)\ln\phi_B + \phi_0\varphi_A/2V_0 + \phi_0\phi_B/2V_0 + \phi_A\phi_B/2V_A \tag{2.19a}$$

$$F_1 \equiv \bar{\phi}_A^2/A_{AA}M_A^2 + \bar{\phi}_B^2/A_{BB}M_B^2 + 2\bar{\phi}_{AB}^2/A_{AB}M_AM_B \tag{2.19b}$$

$$\tilde{F}_2 \equiv |(4 + 8\bar{\phi}_A + 8\bar{\phi}_B + 16(\bar{\phi}_A\bar{\phi}_B - \bar{\phi}_{AB}^2))/\lambda_A\lambda_B| \tag{2.19c}$$

$$\tilde{a}_1 \equiv (1/\lambda_A^2 + 1/\lambda_B^2 + 4\bar{\phi}_A^2/\lambda_A^2 + 4\bar{\phi}_B^2/\lambda_B^2 + 4\bar{\phi}_A/\lambda_A^2 + 4\bar{\phi}_B/\lambda_B^2 + 8\bar{\phi}_{AB}^2/\lambda_A\lambda_B) \tag{2.19d}$$

$$\tilde{Q} \equiv \hat{N}_{\mathrm{A}}(N_{\mathrm{A}} + N_{\mathrm{B}})^2 \tag{2.19e}$$

$$\tilde{F}_3 = |(2\lambda_{\mathrm{A}} + 2\lambda_{\mathrm{B}} + 4\bar{\phi}_{\mathrm{A}}\lambda_{\mathrm{B}} + 4\bar{\phi}_{\mathrm{B}}\lambda_{\mathrm{A}} + \hat{H}^{1/2})/(2\lambda_{\mathrm{A}} + 2\lambda_{\mathrm{B}} + 4\bar{\phi}_{\mathrm{A}}\lambda_{\mathrm{B}} + 4\bar{\phi}_{\mathrm{B}}\lambda_{\mathrm{A}} - \hat{H}^{1/2})| \tag{2.19f}$$

$$\tilde{a}_2 \equiv (2\lambda_{\mathrm{A}} + 2\lambda_{\mathrm{B}} + 4\bar{\phi}_{\mathrm{A}}\lambda_{\mathrm{B}} + 4\bar{\phi}_{\mathrm{B}}\lambda_{\mathrm{A}})\hat{H}^{1/2}/4\lambda_{\mathrm{A}}^2\lambda_{\mathrm{B}}^2 \tag{2.19g}$$

$$\tilde{a}_3 \equiv 2/\lambda_{\mathrm{A}}^2 + 8\bar{\phi}_{\mathrm{A}}/\lambda_{\mathrm{A}}^2 + 8\bar{\phi}_{\mathrm{A}}^2/\lambda_{\mathrm{A}}^2 - 16\bar{\phi}_{\mathrm{AB}}^2/\lambda_{\mathrm{A}}(\lambda_{\mathrm{A}} - \lambda_{\mathrm{B}}) \tag{2.19h}$$

$$\tilde{a}_4 \equiv 2/\lambda_{\mathrm{B}}^2 + 8\bar{\phi}_{\mathrm{B}}/\lambda_{\mathrm{B}}^2 + 8\bar{\phi}_{\mathrm{B}}^2/\lambda_{\mathrm{B}}^2 + 16\bar{\phi}_{\mathrm{AB}}^2/\lambda_{\mathrm{B}}(\lambda_{\mathrm{A}} - \lambda_{\mathrm{B}}) \tag{2.19i}$$

$$\tilde{a}_5 \equiv 2/\lambda_{\mathrm{A}}^2 + 2/\lambda_{\mathrm{B}}^2 + 8\bar{\phi}_{\mathrm{A}}/\lambda_{\mathrm{A}}^2 + 8\bar{\phi}_{\mathrm{B}}/\lambda_{\mathrm{B}}^2 + 8\bar{\phi}_{\mathrm{A}}^2/\lambda_{\mathrm{A}}^2 + 8\bar{\phi}_{\mathrm{B}}^2/\lambda_{\mathrm{B}}^2 - 16\bar{\phi}_{\mathrm{AB}}^2/\lambda_{\mathrm{A}}(\lambda_{\mathrm{A}} - \lambda_{\mathrm{B}}) + 16\bar{\phi}_{\mathrm{AB}}^2/\lambda_{\mathrm{B}}(\lambda_{\mathrm{A}} - \lambda_{\mathrm{B}}) \tag{2.19j}$$

$$\tilde{F}_4 \equiv 12\bar{\phi}_{\mathrm{A}}^2/\lambda_{\mathrm{A}}^2 + 12\bar{\phi}_{\mathrm{B}}^2/\lambda_{\mathrm{B}}^2 + 4\bar{\phi}_{\mathrm{A}}/\lambda_{\mathrm{A}}^2 + 4\bar{\phi}_{\mathrm{B}}/\lambda_{\mathrm{B}}^2 + 8\bar{\phi}_{\mathrm{AB}}^2/\lambda_{\mathrm{A}}\lambda_{\mathrm{B}} \tag{2.19k}$$

Equation 2.17 clearly exhibits a nonseparability into pairwise additive contributions, but it is still too unwieldly to use, so simplifying limits are now investigated.

E. Scaling Limits. Some further simplification is made by considering only symmetric monodisperse semidilute solutions, i.e., those for which $M_{\mathrm{A}} = M_{\mathrm{B}} \equiv M$, $V_{\mathrm{A}} = V_{\mathrm{B}} \equiv V$, $N_{\mathrm{A}} = N_{\mathrm{B}} \equiv N$ (and hence $\lambda_{\mathrm{A}} = \lambda_{\mathrm{B}} = {}^1/_2$), and $A_{\mathrm{AA}} = A_{\mathrm{BB}} \equiv A_2$ and for which $\bar{\phi}_{\mathrm{A}}, \bar{\phi}_{\mathrm{B}}, \bar{\phi}_{\mathrm{AB}} \gg 1$. This reduces the free energy to the form

$$F_{\mathrm{S}}/\Omega RT = FH + F_1 F_2^{a_1/32\pi^2 F_1 Q} F_3^{a_2/32\pi^2 F_1 Q}\left[1 - \frac{1}{32\pi^2 F_1 Q}(a_3 \ln 2 + F_4)\right] \tag{2.20}$$

where

$$F_2 = |16[1 + 2A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})/V + 4\phi_{\mathrm{A}}\phi_{\mathrm{B}}M^4(A_2^2 - A_{\mathrm{AB}}^2)/V^2]| \simeq 32M^2[A_2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}}) + 2\phi_{\mathrm{A}}\phi_{\mathrm{B}}M^2(A_2^2 - A_{\mathrm{AB}}^2)/V]/V \tag{2.20a}$$

$$a_1 = 8[1 + 2A_2^2M^4(\phi_{\mathrm{A}}^2 + \phi_{\mathrm{B}}^2)/V^2 + 2A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})/V + 4\phi_{\mathrm{A}}\phi_{\mathrm{B}}A_{\mathrm{AB}}^2M^4/V^2] \simeq 16M^4[A_2^2(\phi_{\mathrm{A}}^2 + \phi_{\mathrm{B}}^2) + 2\phi_{\mathrm{A}}\phi_{\mathrm{B}}A_{\mathrm{AB}}^2]/V^2 \tag{2.20b}$$

$$Q = \hat{N}_{\mathrm{A}}N^2 = \hat{N}_{\mathrm{A}}n_{\mathrm{m}}^2 l^2 \tag{2.20c}$$

$$\hat{H} = 4M^4[A_2^2(\phi_{\mathrm{A}} - \phi_{\mathrm{B}})^2 + 4\phi_{\mathrm{A}}\phi_{\mathrm{B}}A_{\mathrm{AB}}^2]/V^2 \tag{2.20d}$$

$$F_3 = |[1 + A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})/V + \hat{H}^{1/2}/2]/[1 + A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})/V - \hat{H}^{1/2}/2]| \tag{2.20e}$$

$$a_2 = 8[1 + A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})/V]\hat{H}^{1/2} \simeq 8A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})\hat{H}^{1/2}/V \tag{2.20f}$$

$$a_3 = 32[1 + 2A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})/V + 2A_2^2M^4(\phi_{\mathrm{A}}^2 + \phi_{\mathrm{B}}^2)/V^2] \simeq 64A_2^2M^4(\phi_{\mathrm{A}}^2 + \phi_{\mathrm{B}}^2)/V^2 \tag{2.20g}$$

$$F_4 = 16[A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})/V + 3A_2^2M^4(\phi_{\mathrm{A}}^2 + \phi_{\mathrm{B}}^2)/V^2 + 2\phi_{\mathrm{A}}\phi_{\mathrm{B}}A_{\mathrm{AB}}^2M^4/V^2] \simeq 16M^4[3A_2^2(\phi_{\mathrm{A}}^2 + \phi_{\mathrm{B}}^2) + 2\phi_{\mathrm{A}}\phi_{\mathrm{B}}A_{\mathrm{AB}}^2]/V^2 \tag{2.20h}$$

In the second equality of (2.20c), the quantities n_m and l refer respectively to the number of effective Gaussian links in the chain and the length of each link. The chain length N is related to n_m and l through $N = m_m l$. An additional factor of $l/3$ (actually l/d, with d the dimension of space) is required to multiply the right-hand side of (2.20c) in order to transform back to our standard units. (Recall that the Hamiltonian of (2.1) uses units in which $\mathbf{r}_i(\tau_i)$ has the dimensions $(\text{length})^{1/2}$.)

The emergence of nonclassical scaling behavior for the free energy of (2.19) or (2.20) is somewhat obscured by the complicated structure of the quantities defined by (2.19a)–(2.19k) and (2.20a)–(2.20h). However, the power law form of F_{S} is readily demonstrated to emerge in the limit that only a single polymer component is present in solution. Here, without loss of generality, we may take $\phi_{\mathrm{A}} = \phi_{\mathrm{B}} \rightarrow \phi/2$, together with $A_{\mathrm{AA}} = A_{\mathrm{BB}} = A_{\mathrm{AB}} \rightarrow A_2$ and $M_{\mathrm{A}} = M_{\mathrm{B}} \rightarrow M$. Then the ratios $a_1/32\pi^2F_1Q$ and $a_2/32\pi^2F_1Q$ that appear as the exponents respectively of F_2 and F_3 in eq 2.20 both become equal to $A_2M^2/2\pi^2\hat{N}_{\mathrm{A}}N^2$. As shown earlier,[19] to first order in ϵ ($\epsilon = 4 - d$) the combination A_2M^2/N_{A} is given by $uN^2/2$, where u is the dimensionless strength of the excluded-volume interaction. In good solvents, i.e., in the limit of fully developed excluded volume, u approaches its fixed point value u^* of[19] $u^* = \epsilon\pi^2/2 + \mathcal{O}(\epsilon^2)$. When these expressions are introduced into (2.20) and passage to the semidilute limit $\bar{\phi} \gg 1$ is taken, F_{S} is easily shown to behave in the scaling form[7,15]

$$F_{\mathrm{S}} \sim \bar{\phi}^{2+\epsilon/4} \tag{2.21}$$

For three dimensions, we have $\epsilon = 1$, and (2.21) yields the well-known 9/4 scaling behavior of de Gennes.[18] This is also the scaling behavior derived by Ohta and Oono[7] for the osmotic pressure in the semidilute region. For the present system of two polymers dissolved in a common solvent, a 9/4 "law" in $\alpha_{\mathrm{A}}\bar{\phi}_{\mathrm{A}} + \alpha_{\mathrm{B}}\bar{\phi}_{\mathrm{B}}$ is also anticipated from an order ϵ computation. While there is no simple analytic derivation of this result, numerical calculations of the concentration dependence of the Flory parameters (discussed below) confirm these expectations.

3. Concentration Dependence of Flory χ Parameters

Several different definitions of χ parameters are presented in the literature, and all can be determined from the free energy. Here we explictly consider the original Flory definition, as the others follow similarly and may be obtained from (2.15) or (2.17). Because the Flory χ parameters derived from (2.17) are clearly composition dependent, the Gibbs–Duhem relation imposes an interrelation between first derivatives of these χ parameters with respect to composition. However, the three χ parameters are still linearly independent and represent a traditional rewriting of the free energy (2.17). Our basic intent here is to illustrate the decidedly nonclassical structure of these χ parameters, a feature present for the common alternative definitions.

A. Definition of an Effective χ. Equations 2.13 and 2.15 may be used to calculate the chemical potentials μ_i of the various components in the A–B–solvent system. Because empirical χ parameters are often defined in terms of the Flory–Huggins expression for the μ_i, we evaluate effective χ parameters designated as $\tilde{\chi}$ by equating our renormalization group expression for μ_i with that obtained from the Flory–Huggins expression (2.13) when the latter is rewritten in terms of $\tilde{\chi}$. This procedure enables us to determine the explicit dependence of the effective $\tilde{\chi}_{ij}$ on the composition of the polymer mixture in the homogeneous one-phase region. In general, the chemical potential is determined from the free energy as

$$\mu_i = (\partial F/\partial n_i)_{T,P,n_k} \tag{3.1}$$

where n_k is the number of moles of the kth species in the mixture. The application of (3.1) to the Flory–Huggins free energy of (2.13) is readily shown[6c] to lead to the following expressions for the chemical potentials of solvent, polymer A, and polymer B, referred to the corresponding pure liquid states:

$$\mu_0 - \mu_0{}^0 = RT[\ln \phi_0 + 1 - \phi_0 - \phi_A(V_0/V_A) - \phi_B(V_0/V_B) + (\chi_{0A}\phi_A + \chi_{0B}\phi_B)(\phi_A + \phi_B) - \chi_{AB}(V_0/V_A)\phi_A\phi_B] \quad (3.2a)$$

$$\mu_A - \mu_A{}^0 = RT[\ln \phi_A + 1 - \phi_A - \phi_0(V_A/V_0) - \phi_B(V_A/V_B) + (\chi_{A0}\phi_0 + \chi_{AB}\phi_B)(\phi_0 + \phi_B) - \chi_{0B}(V_A/V_0)\phi_0\phi_B] \quad (3.2b)$$

$$\mu_B - \mu_B{}^0 = RT[\ln \phi_B + 1 - \phi_B - \phi_0(V_B/V_0) - \phi_A(V_B/V_A) + (\chi_{B0}\phi_0 + \chi_{BA}\phi_A)(\phi_0 + \phi_A) - \chi_{0A}(V_B/V_0)\phi_0\phi_A] \quad (3.2c)$$

As discussed in ref 6c the six χ_{ij}'s for a three-component system are reduced to three independent parameters through the relations

$$\chi_{ji} = \chi_{ij}(V_j/V_i) \quad (3.3)$$

To derive expressions for the chemical potentials from the renormalization group free energy of (2.20), it is convenient to define the quantities $f_1 \equiv F_1$, $f_2 \equiv F_2{}^{a_1/32\pi^2F_1Q}$, $f_3 \equiv F_3{}^{a_2/32\pi^2F_1Q}$, and $f_4 \equiv 1 - (a_3 \ln 2 + F_4)/32\pi^2F_1Q$ so as to rewrite (2.20) in the compact form

$$F_S/\Omega RT = FH + f_1f_2f_3f_4 \quad (3.4)$$

When (3.4) is differentiated with respect to mole number, we find

$$\mu_i - \mu_i{}^0 = (FH)'_i + f'_{1,i}f_2f_3f_4 + f_1f'_{2,i}f_3f_4 + f_1f_2f'_{3,i}f_4 + f_1f_2f_3f'_{4,i}, \qquad i = 0, A, B \quad (3.5)$$

in terms of the derivatives $X'_i \equiv (\partial X/\partial n_i)$. The derivatives $(FH)'_i$ are evaluated as

$$FH'_0 = \ln \phi_0 + 1 - \phi_0 - \phi_A(V_0/V_A) - \phi_B(V_0/V_B) + (\phi_A + \phi_B)^2/2 - (V_0/2V_A)\phi_A\phi_B \quad (3.5a)$$

$$FH'_A = \ln \phi_A + 1 - \phi_A - \phi_0(V_A/V_0) - \phi_B(V_A/V_B) + (1/2)[\phi_0(V_A/V_0) + \phi_B](\phi_0 + \phi_B) - (V_A/2V_0)\phi_0\phi_B \quad (3.5b)$$

$$FH'_B = \ln \phi_B + 1 - \phi_B - \phi_0(V_B/V_0) - \phi_A(V_B/V_A) + (1/2)[\phi_0(V_B/V_0) + \phi_A(V_B/V_A)](\phi_0 + \phi_A) - (V_B/2V_0)\phi_0\phi_A \quad (3.5c)$$

with the reduced volume fractions $\bar{\phi}_A$, $\bar{\phi}_B$, and $\bar{\phi}_{AB}$ reexpressed in terms of ϕ_A and ϕ_B for compactness. The remaining derivatives $f'_{i,j}$ follow similarly, but being lengthy, they are omitted.

Effective Flory parameters are defined by equating the chemical potentials $\mu_i = \mu_i{}^0$, $i = 0$, A, B, of the Flory theory (eq 3.2a–3.2c) with the corresponding chemical potentials $\mu_i - \mu_i{}^0$, $i = 0$, A, B, of the renormalization group theory (eq 3.5–3.5c), where the original parameters χ_{0A}, χ_{0B}, and χ_{AB} in (3.2) are replaced by the effective parameters $\tilde{\chi}_{0A}$, $\tilde{\chi}_{0B}$, and $\tilde{\chi}_{AB}$ in establishing the above equalities. Carrying out these operations, $\tilde{\chi}_{0A}$, $\tilde{\chi}_{0B}$, and $\tilde{\chi}_{AB}$ are obtained as

$$(\tilde{\chi}_{0A}\phi_A + \tilde{\chi}_{0B}\phi_B)(\phi_A + \phi_B) - \tilde{\chi}_{AB}(V_0/V_A)\phi_A\phi_B = (\phi_A + \phi_B)^2/2 - (V_0/2V_A)\phi_A\phi_B + f'_{1,0}f_2f_3f_4 + f_1f'_{2,0}f_3f_4 + f_1f_2f'_{3,0}f_4 + f_1f_2f_3f'_{4,0} \quad (3.6)$$

Two additional equations in the three unknowns, $\tilde{\chi}_{0A}$, $\tilde{\chi}_{0B}$, and $\tilde{\chi}_{AB}$, follow from the two pairs of equations (3.2b), (3.5b) and (3.2c), (3.5c). The $\tilde{\chi}$'s may be obtained as the solutions to matrix equations of the form

$$\mathbf{A}\tilde{\chi} = \mathbf{B} \quad (3.7)$$

by using Cramer's rule

$$x_j = (A^{1j}b_1 + A^{2j}b_2 + A^{3j}b_3)/|A| \quad (3.8)$$

where x_j may be $\tilde{\chi}_{0A}$, $\tilde{\chi}_{0B}$, or $\tilde{\chi}_{AB}$, A^{ij} and $|A|$ are respectively the cofactor and determinant of **A**, and the b_is are the elements of **B**. The phenomenologically defined $\tilde{\chi}$'s so obtained define a set of effective or renormalized parameters such that the full chemical potentials are the Flory–Huggins expression written in terms of the $\tilde{\chi}$. These effective $\tilde{\chi}$ differ from the original Flory parameters in displaying an explicit dependence on the volume fraction, molecular weight, and virial coefficient of the component polymers. Experimentally, such additional dependences have been observed,[20] and numerous other improvements of the Flory model[21] have been put forward that similarly attempt to express an effective χ as a function of various previously neglected experimentally relevant variables. These extended Flory models may also be cast into the form (3.7), with **A** remaining the same and only **B** differing from model to model.

B. $\tilde{\chi}$ in the Limit of Zero Concentration of One Component. Of particular significance in this connection is the fact that det (**A**), which appears in the denominator of (3.7), is given by

$$\det(\mathbf{A}) = -(V_B/V_0)\phi_0\phi_A\phi_B \quad (3.9)$$

Clearly, det (**A**) vanishes when either ϕ_0, ϕ_A, or ϕ_B approaches zero. And unless all terms in the numerator of (3.7) vanish at least as fast, this means that $\tilde{\chi}$ diverges when passing to the limit of a binary polymer–solvent solution or to the limit of a binary blend. Experimental observations of interaction parameters that show unphysical divergences in the limit of vanishing amounts of one component may therefore be a result solely of the manner in which the $\tilde{\chi}$ parametes are defined. Indeed, in the limit of vanishing volume fraction of one component, we have a two-component system where three interaction parameters cannot be independent. As our derivation in Appendix A demonstrates, such behavior arises solely from the conventional definition of $\tilde{\chi}$ as the phenomenological quantity generated by equating the right-hand side of (3.2) to the experimental or theoretical chemical potentials; the original free energy is nondivergent. As described further below, explicit evaluation shows that, for example, $\phi_A\phi_B\tilde{\chi}_{AB}$ approaches a constant for ϕ_A (ϕ_B) → 0 and displays the expected linear dependence on ϕ_A (ϕ_B) in this limit.

C. General Concentration Dependence. The expressions (3.6) and (3.7) for the $\{\tilde{\chi}\}$'s of the tenary system require as input parameters two molecular weights, two concentrations, and three Fixman z-parameters (described below). The z-parameters themselves involve two empirical constants each, which enter through the relations $z_{ij} = \Lambda_{ij}(1 - \Theta_{ij}/T)$, with Θ_{ij} the Θ temperature for the i–j excluded-volume interactions. Thus, 10 independent (but readily determinable) experimental parameters are needed to specify the $\tilde{\chi}$'s for a given state of the tenary system. To simplify matters, we consider only certain special limits in our calculations; these reduce the number of required input variables and at the same time focus attention primarily on the variation of the parameter $\tilde{\chi}_{AB}$.

One simplifying limit of this kind involves mixtures that are symmetric in the two polymer components, i.e., $M_A = M_B \equiv M$, $V_A = V_B \equiv V$, and $A_{AA} = A_{BB} \equiv A_2$. Calculations of the behavior of the $\tilde{\chi}$'s for a symmetric ternary system are illustrated in Figure 1, where the three effective Flory parameters $\tilde{\chi}_{0A}/M_A$, $\tilde{\chi}_{0B}/M_B$, and $\tilde{\chi}_{AB}/(M_AM_B)^{1/2}$ are presented as a function of the relative polymer volume fraction $\phi'_A \equiv \phi_A/(\phi_A + \phi_B)$ for a fixed total polymer volume fraction of 0.2 and for selected values of the virial coefficients, molecular weights, and molar volumes of the

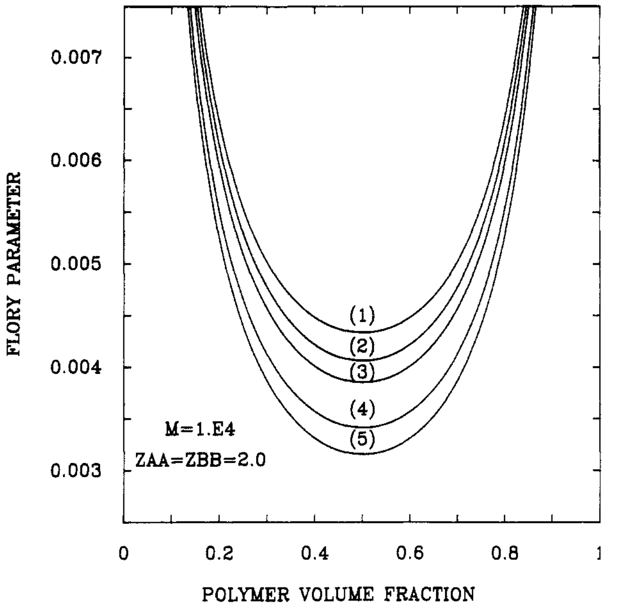

Figure 2. Effective Flory parameter $\tilde{\chi}_{AB}/(M_AM_B)^{1/2}$ as a function of ϕ'_A at fixed $M_A = M_B = 10^4$ and $z_{AA} = z_{BB} = 2.0$ (corresponding to $A_{AA} = A_{BB} = 2.3 \times 10^{-3}$ for the following values of A_{AB}: 2.7×10^{-3} (1); 2.5×10^{-3} (2); 2.3×10^{-3} (3); 1.8×10^{-3} (4); 1.5×10^{-3} (5).

component polymers. Figure 1 is derived from the more general free energy expressions of (2.17), which does not pass to the semidilute limit and which may therefore be used to consider the limit of small polymer volume fractions. The values of the virial coefficients (with $A_{AA} = A_{BB} \leq A_{AB}$) are so chosen so to place the system in the homogeneous good solvent regime.

The choice of parameters in Figure 1 is guided by the representation of the virial coefficient A_2 as a function of the excluded-volume interaction $z_{AA} = z_{BB} \equiv z \equiv (2\pi)^{-3/2}v_2N^{1/2}$ of the two-parameter model in the form[22]

$$A_2(z) = (4\pi R_{G,0}^2)^{3/2}\hat{N}_A\alpha_{R_G}^{2}{}^2(z)\Psi(z)/2M^2 \qquad (3.10)$$

where $R_{G,0}$ is the unperturbed radius of gyration of the chain and the expansion factor $\alpha_{R_G}{}^{2}{}^3$ and the penetration function Ψ are given by[8,22]

$$\alpha_{R_G}{}^{2}{}^3 = (1 + 32z/3)^{3/8}[1 - 0.130(32z/3)/(1 + 32z)]^{3/2}, \quad z \leq 0.15 \qquad (3.10a)$$

$$\alpha_{R_G}{}^{2}{}^3 = 2.26z^{0.5508}, \quad z \geq 0.75 \qquad (3.10b)$$

$$\Psi(z) = (0.207)6.441z/(1 + 6.441z) \qquad (3.10c)$$

and where (3.10a) applies for poor solvents and (3.10b) for marginal to good solvents. In addition, an examination of the polymer free energy (2.17) as a function of z and A_{AB} is used to determine the range of these parameters that ensure complete miscibility of the mixture. The z-parameter in Figure 1 has the fixed value 1.0 for all molecular weights, while A_{AB} is set to that value of A_2, computed from (3.10), at which $z = 1.0$. The unperturbed radius of gyration is chosen to obey the empirical relation[20b] for polystyrene

$$R_{G,0} = 0.3M^{1/2}\ \text{Å} \qquad (3.10d)$$

The predicted divergent behavior of the $\{\tilde{\chi}\}$'s is well shown by $\tilde{\chi}_{AB}$ (top four curves) when $\phi'_A \to 0$ or $\phi'_A \to 1$. The presence of the divergence in this limits induces a substantial composition dependence over a range of values for ϕ'_A. The molecular weight independent polymer–solvent interactions (lowest curve) likewise diverge in these limits, although the scale of the graph prevents the limiting behavior from being distinguished. Figure 2 presents the variation of $\tilde{\chi}_{AB}/(M_AM_B)^{1/2}$ with relative polymer volume fraction ϕ'_A at fixed values $M_A = M_B = 10^4$ and $z_{AA} = z_{BB} = 2.0$ (corresponding to $A_{AA} = A_{BB} = 2.3 \times 10^{-3}$) for a range of values (1.5×10^{-3}–2.7×10^{-3}) for the virial coefficient A_{AB}. Again, when $\phi'_A \to 0$ or 1, the $\tilde{\chi}_{AB}$ parameter increases very steeply. The shapes of the curves 1–5 are largely unchanged at higher molecular weights, although the magnitude of $\tilde{\chi}_{AB}/(M_AM_B)^{1/2}$ at a given ϕ'_A decreases as M increases.

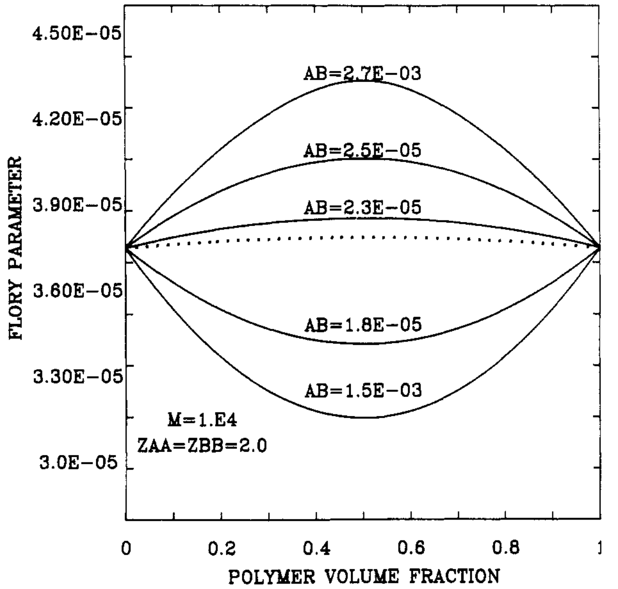

Figure 3. Parameter $\bar{\chi}_{AB} \equiv \tilde{\chi}_{AB}\phi_A\phi_B/(M_AM_B)^{1/2}$ as a function of ϕ'_A at fixed $M_A = M_B = 10^4$ and $z_{AA} = z_{BB} = 2.0$ for the values of A_{AB} (denoted AB) shown on the graph. The dotted lines represent the function 3.75×10^{-5} $(1 + \phi_A\phi_B)$, which is included here for reference.

The $\tilde{\chi}_{0A}/M_A$ and $\tilde{\chi}_{0B}/M_B$ parameters (which are now shown in Figure 2) are largely independent of composition, molecular weight, and the value of A_{AB}, partly because of our choice of a symmetric two-polymer system. The values of $\tilde{\chi}_{0A}/M_A$ and $\tilde{\chi}_{0B}/M_B$ remain very small everywhere except in the immediate vicinity of $\phi_A = 0$ (or $\phi_B = 0$), where they become negative and diverge. The lack of composition dependence of $\tilde{\chi}_{0A}/M_A$ and $\tilde{\chi}_{0B}/M_B$ in the symmetric case is expected, as the screening of A–A excluded-volume interactions by B chains and vice versa is practically identical with self-screening, except for the difference between A_{AB} and $A_{AA} = A_{BB}$. However, in unsymmetrical mixtures the screening of A–A interactions by B chains may differ significantly from the screening by A chains.

Figure 2 represents a simplified description of the actual temperature dependence of the various $\tilde{\chi}$'s. This dependence is contained in the relations $z_{ij} = \Lambda_{ij}(1 - \theta_{ij}/T)$, but the Θ temperatures Θ_i for A–A, B–B, and A–B interactions need not all be the same. Only by specifying these temperatures and the three proportionality factors that relate them to the z-parameters is it possible to more fully characterize the variation of $\{\tilde{\chi}\}$ with T. This information may be obtained for selected systems, but here we only exhibit some general trends by presenting results for symmetric mixtures.

Since the divergence of the $\tilde{\chi}$-parameters of Figures 1 and 2 is due to the use of the limits $\phi'_A \to 0$ or $\phi'_A \to 1$, it is convenient to consider the quantities $\bar{\chi}_{ij} \equiv \tilde{\chi}_{ij}\phi_i\phi_j$ that are finite when ϕ_i or $\phi_j \to 0$. (It is to be noted that $\bar{\chi}_{ij}$ so defined does not enter into the expressions for the free energy; its use here is entirely a matter of illustrative convenience.) Figure 3 displays the variation of $\bar{\chi}_{AB}$ with ϕ'_A for the same parameter values as are used in Figure

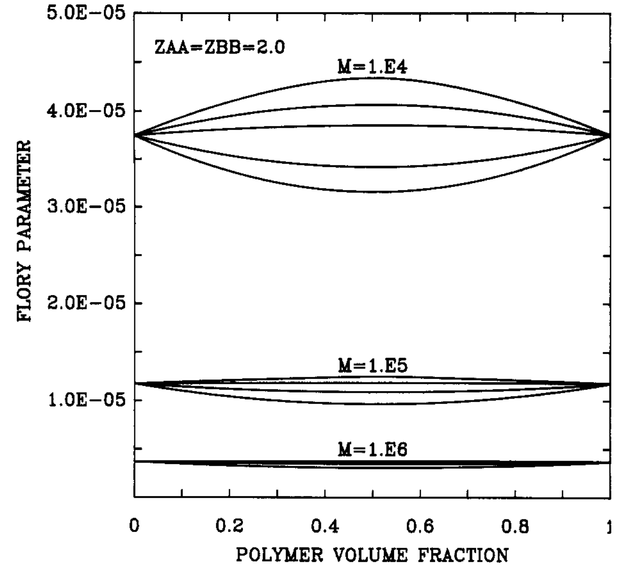

Figure 4. Parameter $\hat{\chi}_{AB}$ as a function of ϕ'_A at fixed $z_{AA} = z_{BB} = 2.0$ for different values of the molecular weight (M) and virial coefficient A_{AB}. The highest set of curves, corresponding to a fixed molecular weight of $M = 10^4$, have the following values of A_{AB} (reading from top to bottom): 2.7×10^{-3}; 2.5×10^{-3}; 2.3×10^{-3}; 1.8×10^{-3}; 1.5×10^{-3}. The middle set of curves, corresponding to a fixed molecular weight of $M = 10^5$, have the A_{AB} values: 7.75×10^{-4}; 7.3×10^{-5}; 6.1×10^{-4}; 4.6×10^{-4}. The lowest set of curves, corresponding to $M = 10^6$, have the A_{AB} values: 2.35×10^{-4}; 2.0×10^{-4}; 1.5×10^{-4}.

2. The dotted line is the function $3.75 \times 10^{-5}(1 + \phi_A\phi_B)$, which is included for reference. The parameters $\hat{\chi}_{AA}$ and $\hat{\chi}_{BB}$, which are not shown, are of the order of less than 10^{-6} and are fairly independent of ϕ'_A and the other variable parameters. The parameter $\hat{\chi}_{AB}$ is indeed finite for all ϕ'_{AB}, and the form of its composiiton dependence is a function of the virial coefficient A_{AB}. This dependence is minimal for $A_{AB} = 2.3 \times 10^{-3}$ ($=A_{AA} = A_{BB}$), because this choice of virial coefficients corresponds to a solution of homopolymers.

Figure 4 depicts the molecular weight dependence of $\hat{\chi}_{AB}$ versus ϕ'_A at fixed $z_{AA} = z_{BB} = 2.0$ and various values of A_{AB}. The top five curves of Figure 4 are simply the curves of Figure 3 drawn on a larger scale. The next four curves correspond to $M_A = M_B = 10^5$ and A_{AB} values of respectively 7.75×10^{-4}, 7.3×10^{-4}, 6.1×10^{-4}, and 4.6×10^{-4} from top to bottom. Here the choice of $z_{AA} = z_{BB} = 2.0$ in (3.10) gives $A_{AA} = A_{BB} = 7.3 \times 10^{-4}$. Again, it is when $A_{AB} = A_{AA}$, corresponding to the homopolymer limit, that the composition dependence of $\hat{\chi}_{AB}$ is very small. The bottom three curves are constructed for $M = 10^6$ and the A_{AB} values of 2.3×10^{-4} ($=A_{AA} = A_{BB}$), 2.0×10^{-4}, and 1.5×10^{-4} from top to bottom.

Figure 5 shows the variation of the parameter $\hat{\chi}_{AB}/(M_AM_B)^{1/2}$ with ϕ'_A as a function of the solvent volume fraction ϕ_0 at fixed $M = 10^4$, $A_{AB} = 2.7 \times 10^{-3}$, and $z_{AA} = z_{BB} = 2.0$. The topmost curve in the figure refers to a solution of highest total polymer concentration (the same as curve 1 in Figure 2), while the lower curves refer to solutions of progressively lower total polymer concentration. The magnitude of $\hat{\chi}_{AB}/(M_AM_B)^{1/2}$ is seen to decrease with decreasing total polymer concentration. This implies that although excluded-volume interactions are less screened in more dilute polymer solutions, there are altogether fewer such interactions at these concentrations. In other words, $\hat{\chi}_{AB}/(M_AM_B)^{1/2}$ is determined, among other things, by two competing factors: on the one hand, screening tends to decrease $\hat{\chi}_{AB}$ as polymer concentration c increases, but on the other, long-range correlations between chain segments tend to make the $\hat{\chi}$ parameters vary as $c^{9/4}$ in the scaling limit, thereby causing the $\hat{\chi}$ parameters to grow as $c^{1/4}$ in this limit. While the parameters used in Figure 5 are not those appropriate to the scaling limit, they illustrate the operation of these competing influences. Figure 5 presents only a single value of A_{AB} to avoid clutter. As the total polymer concentration diminishes, the spread in the curves for the $\hat{\chi}$ parameter, corresponding to different values of A_{AB}, diminishes from that in Figure 2 for $\phi_0 = 0.8$.

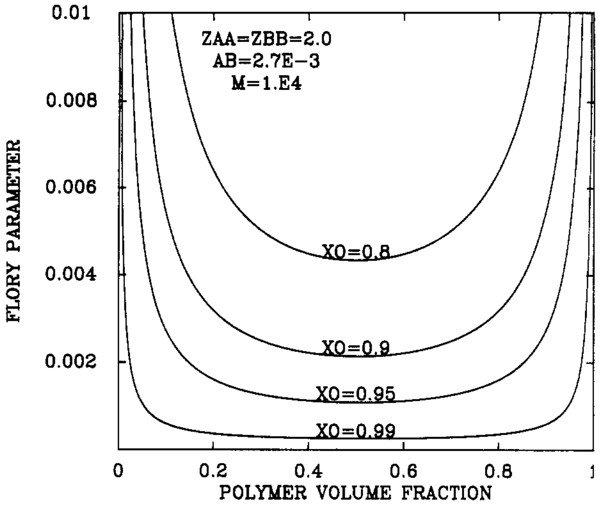

Figure 5. Effective Flory parameter $\hat{\chi}_{AB}/(M_AM_B)^{1/2}$ versus ϕ'_A for fixed values of the molecular weight $M = 10^4$, virial coefficient $A_{AB} = 2.7 \times 10^{-3}$, and Fixman parameters $z_{AA} = z_{BB} = 2.0$ at different solvent fractions ϕ_0 (denoted X0 in the figure).

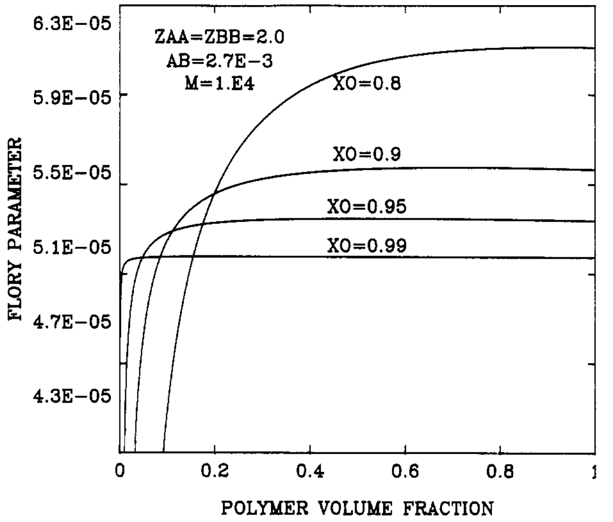

Figure 6. Effective Flory parameter $\hat{\chi}_{0A}/M_A$ versus ϕ'_A at the parameter values of Figure 5 and for the indicated solvent volume fractions.

Figure 6 illustrates the dependence of the parameter $\hat{\chi}_{0A}/M_A$ on the total polymer concentration for the same parameter values are are used in Figure 5. Above a threshold value of ϕ'_A, $\hat{\chi}_{0A}/M_A$ is fairly independent of ϕ'_A and varies with concentration in the manner anticipated from the discussion in the preceding paragraph, viz., $\hat{\chi}_{0A}/M_A$ grows with polymer concentration as a result of the long-range correlations introduced by the excluded volume interactions.

D. $\hat{\chi}$ in the Limit of Strong Chain Overlap. The semidilute limit is characterized by the limit $\bar{\phi}_A, \bar{\phi}_B \gg 1$, where, as discussed earlier, the free energy (and hence the chemical potential) is expected to become a power law function of the overlap concentration alone, independent of the molecular weight. Such a functional form emerges from eq 2.17 when a binary polymer–solvent mixture is considered. The more general ternary mixture can only be studied numerically. A calculation of this kind is carried out to determine the variation of the effective $\tilde{\chi}$ with the total polymer volume fraction $\phi_T \equiv \phi_A + \phi_B$ at values of A_{AA}, A_{BB}, A_{AB}, M_A, M_B, N, V_0, V_A, and V_B that are expected to reflect typical experimental values. The virial coefficients A_{AA}, A_{BB}, and A_{AB}, are all positive and are chosen so as to guarantee that the mixture is in the one-phase region. As mentioned earlier, the chain length N is given by $N = n_m l$, with n_m the number of monomers and l the Kuhn length. n_m is M_i/m_i, where m_i is the monomer molecular weight and is set here to 100 g mol^{-1}. The Kuhn length is taken to be 10 Å. The molecular weights range from 10^4 to 10^7 g mol^{-1}, and the molar volumes are specified as follows: $V_0 = 100$ cm^3 mol^{-1} and $V_i = M_i/\rho$, where the density ρ in g cm^{-3} is set to unity for both A and B. In this system of units, the virial coefficients have the dimensions mol cm^3 g^{-2} are are chosen to satisfy $A_{AA} = A_{BB} \sim A_{AB}$ such that z_{AA} and $z_{BB} \sim \mathcal{O}(1)$.

For molecular weights $\simeq 10^6$, $\tilde{\chi}_{AB}/(M_A M_B)^{1/2}$ is found to vary as a power law in $(\phi_A + \phi_B)$ with an exponent $\simeq 0.98$. The exponent varies slowly as a function of A_{AB} at fixed $A_{AA} = A_{BB}$, increasing to about 1.0 at $M = 10^7$ (the largest molecular weight considered) and decreasing to about 0.86 at $M = 10^4$ (the smallest molecular weight considered). The same trend is observed for smaller and large values of $A_{AA} = A_{BB}$ at fixed A_{AB}. The expected order ϵ power law of 9/4 is anticipated to emerge only for higher molecular weights. The parameters $\tilde{\chi}_{0A}/M_A$ and $\tilde{\chi}_{0B}/M_B$ are found to be essentially independent of volume fraction within the parameter range studied.

Fukuda et al.[20c,d] have recently investigated a symmetric A–B–solvent sytstem that roughly corresponds to the conditions specified in our numerical calculations. Their light-scattering study of the interactions between polystyrene and poly(methyl methacrylate) mixtures in the good solvent bromobenzene exploits the equal but opposite sign of the refractive index increments of the two polymers in bromobenzene to mask the solvent–polymer interactions and to selectively observe the polymer–polymer interactions. The latter are derived from the free energy model of Koningsveld et al.[21b] in the form

$$\Delta F/NRT = \phi_0 \ln \phi_0 + (\phi_A/m_A) \ln \phi_A + (\phi_B/m_B) \ln \phi_B + \phi_0 \phi_A g_{0A}(\phi) + \phi_0 \phi_B g_{0B}(\phi) + \phi_A \phi_B g_{AB}(\phi_A,\phi_B) \quad (3.11)$$

where N is the total number of lattice sites, m_i is the degree of polymerization, and g_{0i} and g_{AB} are the polymer–solvent and polymer–polymer interactions, respectively, with g_{0i} a function of the total polymer concentration $\phi = \phi_A + \phi_B$ and g_{AB} a function of both ϕ_A and ϕ_B. A different set of effective χ parameters $\{\chi^\dagger\}$ is often defined through the second derivative of the free energy with respect to volume fraction of one or other of the components, this quantity being related to the experimentally measurable zero wave vector of the reciprocal scattering function. These $\chi^\dagger$ also differ from the parameters $\tilde{\chi}_{0A}$, $\tilde{\chi}_{0B}$, and $\tilde{\chi}_{AB}$ defined earlier through the chemical potential. Only in the limit of dilute solutions, when g_{AB} becomes independent of the ratio $\phi_i/(\phi_A + \phi_B)$, i = A, B, does $\chi^\dagger_{AB}$ coincide with χ_{AB} of the original Flory–Huggins free energy.

The experiments of Fukuda et al. are performed at a constant 1:1 ratio of the two polymers over a wide range of molecular weight and total polymer concentration up to the spinodal. A scaling region in the variables $\chi^\dagger_{12}$ and $\phi_{PS} + \phi_{PMMA}$ is observed beyond a certain critical volume fraction (which the authors identify as the overlap concentration), where there is no dependence of $\chi^\dagger_{12}$ on the molecular weight of the polymer components. The scaling exponent in the semidilute regime is not found to be a constant but varies between 0.6–0.9 over the entire range of concentrations studied in this domain.

These results are reasonably consistent with the general trends predicted by renormalization group scaling arguments. The scaling limit exponent of 1.25 predicted by the present theory is as much as twice that obtained by experiment in some parts of the scaling regime. One reason for the discrepancy may be the use of different definitions of χ parameters. The free energy model of (3.11) uses a separability approximation in which the polymer–solvent interactions of the ternary system are described by the polymer–solvent interactions of the corresponding binary system. Although this model and others like it (a recent work is that of Einaga et al.[23]) provide practical guidelines for the experimental measurement of various solution-phase χ parameters, it is clear from eq 2.17 and 2.20 that the excluded-volume interactions of multicomponent mixtures are in fact nonseparable. As explained in the introduction, this is because both A and B type chains are involved in the screening of excluded-volume interactions, implying, for instance that the effective A–A interaction is a function of the concentration of B and the strength of A–B interactions.

At the same time, as suggested by our numerical studies, it is likely that the experimental conditions used by Fukuda et al. do not correspond to the asymptotic scaling regime for the A–B polymer interactions. The experimental molecular weights M_e ($\sim 10^4$–10^6 g mol^{-1}) and virial coefficients $A_{AB,e}$ [$\sim$(1.5–3.5) × 10^{-4} mol cm^3/g^{-2}] of some of their samples are not sufficiently high that the z-parameters exceed $\sim$0.75, a figure that previous renormalization group studies[22] suggest marks the onset of marginal power law solvent conditions. Furthermore, in a recent study on finite size corrections in confined polymer mixtures,[24] we have shown that the crossover of the variable z_{AB} from marginal to good solvent values occurs quite slowly, requiring higher molecular weights for the asymptotic scaling region to set in. When the above experimental values are used in our numerical calculations along with the approximation $0 \leq A_{AA} = A_{BB} \leq A_{AB,e}$, power law exponents are found in the range $\sim$0.9–1.0. These values are somewhat larger than those determined experimentally, but they appear to reproduce the general trends in the data. Thus, allowing for discrepancies originating in our different definitions of the χ parameter, it seems quite reasonable that larger molecular weights, higher temperatures, or solvents of better quality could push the scaling exponents to the larger asymptotic values predicted by theory.

4. Calculation of Coexistence Curves

Equation 2.15 is also the starting point for the discussion of the phase behavior of the A–B mixture in the semidilute regime. In principle, the thermodynamic criteria of phase stability[25] may be used with (2.15) to determine the critical points of the ternary ssystem as well as the equations for the spinodal and binodal curves. However, such calculations are very difficult to solve analytically even for the relatively simple Flory–Huggins free energy of eq 2.13, and they are completely intractable for the ΔF of (2.15).

To circumvent some of the difficulties involved in constructing a phase diagram from eq 2.15, we use the approximate relation (2.19) instead. Furthermore, we only consider solutions that are symmetric in A and B; i.e., we set $N_A = N_B \equiv N$, $M_A = M_B \equiv M$, $V_A = V_B \equiv V$, $A_{AA} = A_{BB} \equiv A_2$, and $\lambda_A = \lambda_B = {}^1/_2$, the latter corresponding to

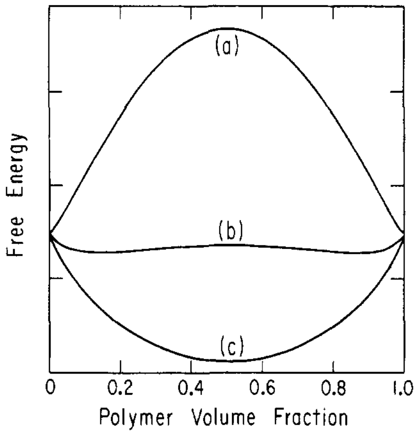

Figure 7. Schematic plot of the free energy of eq 2.20 as a function of polymer volume fraction $\phi'_{\mathrm{A}} \equiv \phi_{\mathrm{A}}/(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})$: (a) and (b) partial miscibility; (c) complete miscibility.

monodisperse solutions.[7] In general, even this simplification necessitates the use of numerical methods, although the added approximation of setting A_{AB} equal to A_2 yields an analytically tractable expression for the free energy which is discussed further below. Our discussion of phase behavior, therefore, focuses on three convenient illustrative cases: (i) $A_{\mathrm{AA}} = A_{\mathrm{BB}} = A_{\mathrm{AB}}$; (ii) $A_{\mathrm{AA}} = A_{\mathrm{BB}} = 0$, $A_{\mathrm{BB}} > 0$, and (iii) $0 < A_{\mathrm{AA}} = A_{\mathrm{BB}} < A_{\mathrm{AB}}$. Cases i and iii correspond to a mixture of mutually repelling, self-avoiding chains and do have experimental analogues in, for instance, the work of Fukuda et al.,[20c,d] which is discussed in section 3. Case ii corresponds to a mixture of two mutually repelling chains A and B at their Θ points, a system which at present is likely to be of more theoretical than practical interest. As far as we are aware, there have been no experimental realizations of case ii polymer mixtures, although Monte-Carlo simulations are possible.

Case i is treated analytically, while cases ii and iii are analyzed numerically as follows: For fixed values of both the solvent volume fraction ϕ_0 and the virial coefficients $A_{\mathrm{AA}} = A_{\mathrm{BB}} \geq 0$ and for suitable choices of chain length, molecular weight, and molar volume, the free energy ΔF is plotted against the relative polymer volume fraction $\phi'_{\mathrm{A}} \equiv \phi_{\mathrm{A}}/(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})$ for a range of values of A_{AB}. Here the choice of parameters ϕ_0, N, M, etc. follows the general guidelines discussed in the previous section. Thus, for instance, we fix ϕ_0 at 80–90%, a concentratioon that from our earlier studies[15] represents passage to the semidilute limit without invalidating the renormalization group approach. (At higher polymer concentrations, the nonzero volume occupied by chain segments must also be included in the Hamiltonian of (2.1).) Similarly, molecular weights M are chosen in the range 10^4–10^7.

The free energy curves so obtained fall typically into three well-known classes, presented schematically as (a), (b), and (c) in Figure 7. Curves a and b correspond to conditions of limited miscibility, while curve c corresponds to conditions of complete miscibility. The initial slopes of all three curves in the limit $\phi'_{\mathrm{A}} \rightarrow 0$ or 1 are linear, indicating adherence to Raoult's law. The double minima in curve c locate the coexistent volume fractions $\phi_{\mathrm{e}}^{\pm}$ of the two segregated phases which eventually coalesce into a single phase at criticality. The locus of $\phi_{\mathrm{e}}^{\pm}$ as a function of A_{AB} defines the coexistence curve. Since the mixture is symmetric in A and B, the critical volume fraction $\phi'_{\mathrm{A,c}}$ is 0.5. A critical value of A_{AB} is determined at $\phi'_{\mathrm{A,c}} = 0.5$ by interpolating between the $\phi_{\mathrm{e}}^{\pm}$ in the vicinity of the critical point. The coexistence curve can then be reexpressed in terms of the reduced variables $(\phi - \phi_{\mathrm{c}})/\phi_{\mathrm{c}}$ and $(T_{\mathrm{c}} - T)/T_{\mathrm{c}}$ mentioned in the Introduction.

Case i. $A_{\mathrm{AA}} = A_{\mathrm{BB}} = A_{\mathrm{AB}} = A_2$. The free energy (2.17) in this limit becomes

$$F_{\mathrm{s}}/\Omega RT = FH + FR \tag{4.1}$$

where

$$FH = (\phi_0/V_0)\ln\phi_0 + (\phi_{\mathrm{A}}/V)\ln\phi_{\mathrm{A}} + (\phi_{\mathrm{B}}/V)\ln\phi_{\mathrm{B}} + \phi_0\phi_{\mathrm{A}}/2V_0 + \phi_0\phi_{\mathrm{B}}/2V_0 + \phi_{\mathrm{A}}\phi_{\mathrm{B}}/2V \tag{4.1a}$$

$$FR = (1/V)2^{3\delta}(A_2M^2/V)^{1+\delta}(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})^{2+\delta} \times \left[1 - \frac{3\delta}{2}\left\{1 + \frac{4}{3}\ln 2 - \frac{4}{3}\frac{\phi_{\mathrm{A}}\phi_{\mathrm{B}}}{(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})^2}(1 + 2\ln 2)\right\}\right] \tag{4.1b}$$

with

$$\delta = A_2M^2/\pi^2\hat{N}_{\mathrm{A}}N^2 \tag{4.1c}$$

The derivation of (4.1) neglects terms of order $V/A_2M^2(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})$ which are assumed to be small by definition of the semidilute limit of strong chain overlap. The relation $\mu_i = (\partial F/\partial n_i)_{T,P,n_j}$, defining the chemical potential of component i, may be used with eq 4.1 to determine the equation of the coexistence curve, which is the locus of points along which $\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{II}}$ with I and II denoting the coexisting phases of the two-phase region. The symmetric mixture of this example has the additional simplifying relations $\phi_0^{\mathrm{I}} = \phi_0^{\mathrm{I}}$, $\phi_{\mathrm{A}}^{\mathrm{I}} = \phi_{\mathrm{B}}^{\mathrm{II}}$, and $\phi_{\mathrm{B}}^{\mathrm{I}} = \phi_{\mathrm{A}}^{\mathrm{II}}$ at coexistence, which enable the chemical potential of, for instance, A to be expressed as

$$\ln x_{\mathrm{A}}^{\mathrm{I}} + (x_{\mathrm{B}}^{\mathrm{I}})^2(1 - \phi_0)\chi_{\mathrm{G}}^{\mathrm{I}} = \ln x_{\mathrm{A}}^{\mathrm{II}} + (x_{\mathrm{B}}^{\mathrm{II}})^2(1 - \phi_0)\chi_{\mathrm{G}}^{\mathrm{II}} \tag{4.2}$$

where

$$x_i^{\mathrm{I}} = \phi_i^{\mathrm{I}}/(\phi_{\mathrm{A}}^{\mathrm{I}} + \phi_{\mathrm{B}}^{\mathrm{I}}), \qquad i = \mathrm{A, B} \tag{4.2a}$$

$$x_i^{\mathrm{II}} = \phi_i^{\mathrm{II}}/(\phi_{\mathrm{A}}^{\mathrm{II}} + \phi_{\mathrm{B}}^{\mathrm{II}}) = \phi_j^{\mathrm{I}}/(\phi_{\mathrm{A}}^{\mathrm{I}} + \phi_{\mathrm{B}}^{\mathrm{I}}) = 1 - \phi_i^{\mathrm{I}}, \quad i \neq j = \mathrm{A, B} \tag{4.2b}$$

$$\chi_{\mathrm{G}}^{\mathrm{I}} = 0.5[1 + 2^{2+3\delta}\delta(1 + 2\ln 2)(A_2M^2/V)^{2+\delta}(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})^{1+\delta}/\phi_{\mathrm{B}}] \simeq 2^{1+3\delta}\delta(1 + 2\ln 2)(A_2M^2/V)^{1+\delta}(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})^{1+\delta}/\phi_{\mathrm{B}} \tag{4.2c}$$

Equation 4.2 is of the same form as the chemical potential for a two-component polymer mixture, the modified volume fraction x_i replacing ϕ_i and the effective concentration-dependent parameter χ_{G} replacing the concentration-independent parameter χ. Consequently, a number of analytical results describing the critical state may be obtained at once by analogy with treatments of binary mixtures. We have omitted this analysis because it has recently been presented (after completion of our work) by Broseta et al.[26] in a theoretical analysis based upon a combination of renormalization group results for the virial coefficients with a scaling ansatz for the free energy of the ternary mixture. Broseta et al. show that there are qualitative departures from the predictions of the Flory–Huggins theory, and additional qualitative differences follow from our renormalization group free energy (4.1).

We presently restrict ourselves to a consideration of how eq 4.1 modifies the analysis of Broseta et al.[26] Their expression for the site free energy in the symmetric limit takes the form

$$\left.\frac{F}{k_{\mathrm{B}}T}\right|_{\mathrm{site}} = \frac{x}{P_{\mathrm{A}}}\ln x + \frac{1 - x}{P_{\mathrm{B}}}\ln(1 - x) + ux(1 - x) \tag{4.3a}$$

where $x \equiv \phi_{\mathrm{A}}/(\phi_{\mathrm{A}} + \phi_{\mathrm{B}})$ is the fraction of A monomers, $P_i \equiv M_i/M_{\mathrm{b}}$, $i = \mathrm{A, B}$, represents the number of blobs per chain of type i with M_i the molecular weight of i and M_{b}

a blob size related to the total polymer concentration c and correlation length ξ through $M_b = c\xi^3$. The important parameter u is an effective interaction between unlike blobs that follows from a renormalization group analysis as having the form

$$u = K_i K c^{\eta} \tag{4.3b}$$

where K_i is roughly proportional to the effective interactions between unlike monomers, and K and η are assumed to be universal constants with values of about 0.02 and 0.28, respectively.[26]

For purposes of comparison with eq 4.4e of Broseta et al.,[26] our eq 4.1 may be rewritten in terms of the relative polymer volume fraction x as

$$F_S/\Omega\phi_T RT = (\phi_0/\phi_T V_0)\ln\phi_0 + \frac{1}{V}\ln\phi_T + \phi_0/2V_0 + \frac{x}{V}\ln x + \frac{(1-x)}{V}\ln(1-x) + u'x(1-x) \tag{4.3c}$$

where $\phi_T = \phi_A + \phi_B$ and u' is the effective interaction for which we have the explicit form

$$u' = \phi_T[1 + (2V/\phi_T^2 x(1-x))(FR)]/2V \tag{4.3d}$$

$$u' \simeq \frac{2^{3\delta}}{x(1-x)V}\left(\frac{A_2M^2}{V}\right)^{1+\delta}(\phi_A + \phi_B)^{1+\delta} \times \left[1 - \frac{3\delta}{2}\left\{1 + \frac{4}{3}\ln 2 - \frac{4}{3}x(1-x)(1 + 2\ln 2)\right\}\right] \tag{4.3e}$$

At fixed total polymer concentration ϕ_T (and therefore at fixed volume fraction ϕ_0 of solvent) the first three terms on the right-hand side of (4.3c) are constants. They may therefore be absorbed into the definition of the zero of free energy, and the resulting expression is of the general form of eq 4.3a with the new effective interaction u'. Here, the exponent of the total polymer concentration [analogous to η of (4.3b)] is $3 + \delta$ [recall that $x = \phi_A/(\phi_A + \phi_B)$], and $\delta = 0.25 + \mathcal{O}(\epsilon^2)$ in the good solvent limit. The function K_i of the blob model is undetermined and can only be postulated to vary as the strength of the interaction between different monomers. Our renormalization group calculation, in contrast, provides the explicit functional form of this quantity and shows its nontrivial dependence on the monomer–monomer interaction and the polymer concentration. Since our more general quantity u' may be easily substituted into the various exact equations derived by Broseta et al. to determine the resultant additional nontrivial composition dependence, we do not pursue this analysis any further.

It should be emphasized that our renormalization group result leading to (4.3) applies only to the special limit $A_{AB} = A_2$, and the more general symmetric case $A_{AB} \neq A_2$ considered by Broseta et al. (and discussed further below) would require the use of the analytically more complicated eq 2.20 from our renormalization group derivation. In other words, the function K_i, necessary to make the scaling model agree with our renormalization group calculations, has a considerably more complicated dependence on concentration and strength of interaction than has been postulated by Broseta et al. from simple scaling arguments.

Case ii. Strongly Interacting Θ Chains. Denoting the critical value of the virial coefficient by $A_{AB}^{(c)}$, we define the immediate vicinity of the critical point by the reduced "temperature" $(A_{AB} - A_{AB}^{(c)})/A_{AB}^{(c)}$ that is less than or equal to about 5×10^{-3}. There is some evidence[27] that the asymptotic region of nonclassical behavior in binary liquids, including polymer–solvent solutions, occurs for reduced temperatures of about 10^{-4}, so we consider about the same range for our ternary mixture. In this region the coexistence curve is calculated from (2.17) to be well represented by the equation

$$(\phi - \phi_c)/\phi_c = \alpha_1[(A_{AB} - A_{AB}^{(c)})/A_{AB}^{(c)}]^{\beta_1} \tag{4.4}$$

for all molecular weights in the range considered, where

$$\alpha_1 = 1.7 \tag{4.4a}$$

and

$$\beta_1 = 0.50 \tag{4.4b}$$

The exponent of β_1 in (4.4b) coincides with the classical prediction for the exponent β characterizing phase separation in binary liquids or alloys.[28] Experimentally, such systems are actually described by β's that are of the order of 0.33, very close to the critical point. A mean-field value of β_1 is expected in our calculations, since the expansion (2.11) for the free energy neglects fluctuations that are important in the immediate vicinity of the critical point.[29]

Away from the asymptotic critical region (defined here as $(A_{AB} - A_{AB}^{(c)})/A_{AB}^{(c)} > 5 \times 10^{-3}$ and up to $\sim$0.1), the coexistence curve is characterized by eq 4.4 with the exponents $\alpha_1 \simeq 0.20$ and $\beta_1 \simeq 0.39$ for molecular weights in the range studied.

Following the procedure used to derive eq 4.4, an equation for the coexistence curve may be similarly calculated from the Flory free energy (2.13), the critical point being exactly determined as

$$\chi_{AB}^{(c)} = 1/\phi_A^{(c)} \tag{4.5}$$

where $\phi_A^{(c)}$ ($=\phi_B^{(c)}$) is the critical volume fraction of A and the critical value of $\phi'_A \equiv \phi_A/(\phi_A + \phi_B)$ is 0.5 by construction. (Equation 4.5 no longer applies if $\tilde{\chi}_{AB}$ is used instead of χ_{AB}, as there is now an added concentration dependence of the interaction parameter; the critical point in this instance, therefore, differs from the Flory result (4.5). The Flory coexistence curve is also given by eq 4.4 for the range of molecular weights studied, with the same exponents α_1 and β_1 as for the renormalization group calculation both near and away from the critical region. However, the Flory theory for phase separation in a ternary system only involves the difference $\chi_{0A} - \chi_{0B}$. Because case i is symmetric, it has $\chi_{0A} = \chi_{0B}$, and the Flory theory becomes independent of the value of the polymer–solvent interaction. In other words, so long as the two polymers are separately miscible in the solvent, "the magnitude of the solvent polymer interaction is of no importance".[6c] In the renormalization group theory the polymer–solvent dependence is much more complicated, and provided A_{AA} and A_{BB} are not zero, the shape of the coexistence curve may be modified, even in the symmetric case. This is discussed further below for case iii. In addition, the form of eq 4.4 contains the empirical virial coefficients, which have nonclassical power law dependences on the molecular weight and reduced temperature in the semidilute region. These variations are absent in the simple Flory theory, and a greater departure between Flory and RG theories would emerge by using the variable $(T - T_c)/T_c$ on the right-hand side of (4.4).

Case iii. Strongly Interacting Self-Avoiding Polymers with $A_{AA} = A_{BB} \neq 0$, $A_{AB} > 0$. The parameters used in constructing the free energy curve of (2.20) are specified in much the same way as before. However, the self-virial coefficients $A_{AA} = A_{BB}$ are required to correspond to good solvent conditions for the two polymers, and the appropriate values are chosen on the basis of eq 3.10. We use the value $z = 1.0$ in our numerical calculations.

A possible molecular weight dependence of the coexistence curve is investigated as before by repeating the calculations for a range of molecular weights. In this way, near criticality the equation of the coexistence curve is obtained as

$$(\phi - \phi_c)/\phi_c = \alpha_2 M^{\delta}[(A_{AB} - A_{AB}^{(c)})/A_{AB}^{(c)}]^{\beta_2} \quad (4.6)$$

where

$$\alpha_2 = 0.47 \quad (4.6a)$$

$$\delta = 0.19 \quad (4.6b)$$

$$\beta_2 = 0.50 \quad (4.6c)$$

Phase separation in symmetric ternary mixtures of two polymers in a solvent, therefore, is found here to depend on polymer–solvent interactions as well as on polymer–polymer interactions, in contrast to the predictions of the simple Flory theory. As these interactions are turned on, the coexistence curve acquires an additional molecular weight dependence [characterized by the exponent $\delta = {}^1/_5$ of (4.6)] that is absent when A_{AA} and A_{BB} are zero in case ii. The exponent $\beta_2 = 0.50$ is again a mean-field-type exponent that originates from the neglect of higher order density–density fluctuations near the critical point.

Away from the critical domain, the exponents δ and β_2 are approximately obtained as 0.13 and 0.39, respectively. The prefactor α_2 remains essentially unchanged, its value now given by 0.50. It is interesting that in this region, case ii, case iii, and Flory theory lead to the same "temperature" exponent [of course, only when the dependent variable in (4.4) is taken as the empirical virial coefficient]. While we are not presently aware of any experimental data with which to compare these results, experimental verification should be possible.

Discussion

This paper shows how the empirical definitions of the Flory χ parameter in terms of chemical potentials may be used in conjunction with renormalization group calculations of semidilute ternary mixtures of two polymers in marginal to good solvents to derive the variation of these effective $\tilde{\chi}$ parameters with polymer concentration ϕ and molecular weight M. The functional dependence of $\tilde{\chi}$ on ϕ and M for a range of molecular weights and virial coefficients is shown by analytic and numerical methods to be characteristically hyperbolic and to diverge in the limit of vanishing amounts of one or other of the component species. The divergences in these limits are shown to stem solely from the defining equations for the $\tilde{\chi}$, which are of considerable generality. In addition, the parameter $\tilde{\chi}_{AB}$ of the good solvent semidilute ternary mixture is found to scale with total polymer concentration in accord with general scaling arguments and the recent experimental data of Fukuda et al. on "optical Θ" ternary solutions.

The renormalization group expression for the free energy of these semidilute ternary mixture is also used to study phase separation in symmetric solutions of "Θ" and "self-avoiding" polymers. In particular, exponents describing the asymptotic region of the coexistence curve are calculated for both these situations. The results for the Θ mixture are found to be equivalent to the corresponding Flory description when empirical virial coefficients are employed to mask serious deficiencies of the Flory theory in describing the molecular weight and temperature dependence of the interaction virial coefficient. On the other hand, the self-avoiding case reveals an added molecular weight dependence that the Flory theory fails to predict even when the equations are expressed in terms of experimental second virial coefficients in order to absorb the dominant nonclassical effects that are absent in Flory theory.

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Appendix A. Variation of χ with Composition: Solution to Equation 3.11

The matrix **A** in (3.7) remains the same regardless of the model used to derive the chemical potentials of the ternary system and is given by

$$\mathbf{A} = \begin{bmatrix} \phi_A(\phi_A + \phi_B) & \phi_B(\phi_A + \phi_B) & -(V_0/V_A)\phi_A\phi_B \\ (V_A/V_0)\phi_0(\phi_0 + \phi_B) & -(V_A/V_0)\phi_0\phi_B & \phi_B(\phi_0 + \phi_B) \\ -(V_B/V_0)\phi_0\phi_A & (V_B/V_0)\phi_0(\phi_0 + \phi_A) & (V_B/V_A)\phi_A(\phi_0 + \phi_A) \end{bmatrix}$$

Using the identity $\phi_0 + \phi_A + \phi_B = 1$ as needed, the determinant and cofactors of **A** are evaluated as

$$\det(\mathbf{A}) = -(V_B/V_0)\phi_0\phi_A\phi_B \quad (A.1)$$

$$A_{11} = -(V_B/V_0)\phi_0\phi_B(\phi_0 + \phi_A) \quad (A.2)$$

$$A_{12} = -(V_B/V_0)\phi_0\phi_A(\phi_0 + \phi_B) \quad (A.3)$$

$$A_{13} = (V_B V_A/V_0^2)\phi_0^3 \quad (A.4)$$

$$A_{21} = -(V_B/V_A)\phi_A\phi_B(\phi_0 + \phi_A) \quad (A.5)$$

$$A_{22} = (V_B/V_A)\phi_A^3 \quad (A.6)$$

$$A_{23} = -(V_B/V_0)\phi_0\phi_A(\phi_A + \phi_B) \quad (A.7)$$

$$A_{31} = \phi_B^3 \quad (A.8)$$

$$A_{32} = -\phi_A\phi_B(\phi_0 + \phi_B) \quad (A.9)$$

$$A_{33} = -(V_A/V_0)\phi_0\phi_B(\phi_A + \phi_B) \quad (A.10)$$

The components of **B** are obtained from the right-hand side of (3.5) by using the definitions (2.20a)–(2.20h) (for general polymer concentration, i.e., the limit of strong chain overlap is not taken), along with (3.5a)–(3.5c) and (2.16). The calculations are routine but lengthy and are not reproduced here. It is only **B** that varies from model to model (it may equally well be obtained from experiment), so the results obtained here are of considerable generality.

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Multiple-Temperature Steps: A Further Test of an Aging Theory for Polymer Glasses

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ABSTRACT: A recent theory for the aging kinetics of polymer glasses has been further tested by comparing its predictions of volume recovery with the experimental results of Kovacs on poly(vinyl acetate) when subjected to two sequential temperature steps. Kovac's results present an important test because the recovering volume goes through a maximum before approaching equilibrium. With the same parameters used previously, the computed curves properly describe the essence of the experimental data: the general height, location, and ranking of the various maxima. A more quantitative fit to the data is obtained, however, by augmenting the free volume theory with an additional activation energy to account more accurately for the purely thermal effects.

Introduction

Liquids near the glass transition can exhibit unusual behavior when subjected to a sequence of steps in temperature or pressure. Properties like volume and enthalpy may pass at constant temperature and pressure through extrema. If, for example, the temperature of a liquid at equilibrium at the temperature T_0 is suddenly stepped to T_1 and held there for a relatively short time and then stepped to a third temperature T_2 somewhere between T_0 and T_1 and held at this temperature, the observed volume is likely to pass through either a minimum or a maximum before evolving toward a final, equilibrium value. A

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