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Free Energy of Mixing for Polymer Solutions

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ABSTRACT: The validity of the correction for the interaction parameter g of the Flory−Huggins free energy (*Langmuir* **2003**, *19*, 5240) was examined by taking the contributions of spatial variation in the volume fraction into account. Developing the statistical-mechanical view of the invariance conjecture and the Landau expansion with the nonanalytic coefficients for the polymer solutions, we showed that the chain-length dependent correction term H in the interaction parameter g was reasonably introduced. We derived the explicit function form of H as a function of chain-length and temperature to be consistent with the critical power laws for both the concentration difference and the diameter in coexisting phases. It was successfully applied to the systems polystyrene in methylcyclohexane and poly(methyl methacrylate) in 3-octanone.

I. Introduction

Determination of the free energy of mixing for polymer solutions and precise prediction of their thermodynamic behavior have been of great interest from both academic and practical aspects[1] and are still challenging both theoretically and experimentally.[2,3] Mean-field theories, such as the Flory−Huggins(FH) theory, have made a considerable contribution to this subject, since these theories enabled us to predict some basic thermodynamic behaviors of the polymer systems, especially the chain length dependence.

The free energy of mixing per site based on the FH theory is expressed as[4]

$$f_{\mathrm{FH}} = (1 - \phi)\ln(1 - \phi) + \frac{\phi}{P}\ln \phi + g_0(1 - \phi)\phi \quad (1)$$

where the unit of energy is k_BT (k_B and T are, respectively, the Boltzmann constant and the absolute temperature). ϕ and P are the volume fraction and the chain length of the polymer, respectively. The presence of the system specific parameter g_0 in eq 1 makes the FH-based theory a powerful tool to analyze the polymer solution systems. Koningsveld and Kleintjens have proposed the following expression[5]

$$g_0 = a + \frac{b(T)}{1 - c\phi} \quad (2)$$

where a and c are the parameters independent of T and P, and b has a dependence on T. In terms of the system specific parameters b_i (i = 0, 1, 2), the temperature dependence of $b(T)$ is expressed as[6]

$$b(T) = b_0 + b_1/T + b_2T \quad (3)$$

For polystyrene solutions, all the system specific parameters were determined and the polymer length dependence of the critical point $T_c = t(P)$ and $\phi_c = u(P)$ was correctly derived.[5,6] Therefore, we can predict the critical point from the FH-based theory.

However, the FH theory fails to express the critical behavior, since large fluctuations appearing in the critical region are neglected in the mean-field theories inclusive of the FH theory. In the language of statistical mechanics, the FH theory neglects the contributions of spatial variations in the polymer volume fraction to the partition function by selecting out of all possible configurations only the one that gives the largest term in the partition sum. Hence, in the FH theory, only the most probable configuration is taken into account and all the fluctuations from the most probable configuration are neglected. As is well-known,[7,8] to analyze the critical behavior correctly, we should consider the fluctuations carefully.

Near the critical point a variety of systems exhibit a universal behavior, since the range of the fluctuations of the order parameter becomes much larger than the microscopic scale of any molecular interactions in the critical region. This principle of critical universality has been applied to develop the equations of state and the free energy of fluids and fluid mixtures.[7,8] Therefore, to bridge the gap between the universal asymptotic regime near the critical point and the mean-field limit is very important.[9] It is, however, difficult in principle, because the scales of time and space, which need to be taken into account, are considerably different between the two regimes. To start with challenging this subject, it is worth noticing the experimental fact that the power laws around the critical point have been successfully applied in a wide range of concentration and temperature. Sengers, Anisimov, et al. proposed a scaling description of phase separation of polymer solutions, and discussed the crossovers both from the mean field behavior far apart the critical point to the critical behavior near the critical point and the critical behavior at finite chain length to the tricritical behavior at infinite chain length.[3] They derived a modified free energy based on the Flory−Huggins type and the virial expansion using system-dependent crossover parameters. The observed coexistence curves were well expressed by their theory except for the region far apart from the critical point because of the higher-order term.

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Their approach is physically smart, but it is rather complicated in application to each polymer solution. It is also an important aspect to derive simple expressions of free energy with examined validity.

In a previous paper,[10] we introduced a chain length dependence $H(P,T)$ of the interaction parameter g in the free energy of mixing f_{mix} for polymer solutions based on the FH equation by taking account of the universal behavior of the concentration difference of the coexisting phases near the critical point:

$$\begin{bmatrix} f_{\mathrm{mix}}(\phi;T,H) = (1-\phi)\ln(1-\phi) + \dfrac{\phi}{P}\ln\phi + g(1 - \phi)\phi \\ g = g_0 + H(P,T) = a + \dfrac{b(T)}{1-c\phi} + H(P,T) \end{bmatrix} \tag{4}$$

The newly introduced term $H(P,T)$ may have a nonanalytic dependence on the temperature and the chain length. In the phase coexistence region, it behaves as

$$H \propto P^{-0.46}|\tau|^{0.664} \tag{5}$$

where $\tau = (T - T_{\mathrm{c}})/T_{\mathrm{c}}$ is the reduced temperature. The coexistence curve calculated from the resultant free energy for the system of polystyrene in methylcyclohexane agreed with the observed one semiquantitatively.

The essential ideas introduced in the previous paper are as follows.

Idea 1: Introduction of *the Landau expansion with nonanalytic coefficients*.

Idea 2: Introduction of *the invariance conjecture* for the form of the free energy of mixing.

The Landau expansion in the idea (idea 1) is the expansion of the free energy of mixing in powers of $\Delta\phi = \phi - \phi_{\mathrm{c}}$ as

$$\begin{bmatrix} f_{\mathrm{mix}} = J_{\phi_{\mathrm{c}}}|_{T=T_{\mathrm{c}}}\,\Delta\phi + \Delta f_{\mathrm{mix}} \\ \Delta f_{\mathrm{mix}} = f_{\mathrm{mix}}|_{T=T_{\mathrm{c}},\phi=\phi_{\mathrm{c}}} + \dfrac{1}{2}B_{\mathrm{R}}\Delta\phi^2 + \dfrac{1}{4!}D\Delta\phi^4 \end{bmatrix} \tag{6}$$

where $J_\phi = \partial f_{\mathrm{mix}}/\partial\phi$. The coefficient D is given by

$$D = \frac{2}{(1-\phi_{\mathrm{c}})^3} + \frac{1}{P}\frac{2}{\phi_{\mathrm{c}}^{\,3}} + 24\frac{c^2 b(T_{\mathrm{c}})(c-1)}{(1-c\phi_{\mathrm{c}})^5} \tag{7}$$

By searching the value $\Delta\phi_{\mathrm{eq}}$ of $\Delta\phi$ minimizing the "Landau free energy" Δf_{mix}, we have the coexistence curve $\phi = \phi_{\mathrm{c}} + \Delta\phi_{\mathrm{eq}}$. In the conventional Landau expansion, the coefficient B_{R} is analytically expressed as $B_{\mathrm{R}} \propto \tau$. This leads to the classical behavior of the coexistence curve; $\Delta\phi_{\mathrm{eq}} \propto \sqrt{|\tau|}$. Of course, the classical behavior does not agree with the experimental results. The experimental results require the behavior $\Delta\phi_{\mathrm{eq}} \propto P^{-0.23}|\tau|^{0.332}$. The observed critical behavior can be obtained from the free energy (6) with assuming that $B_{\mathrm{R}} = kP^{-0.46}|\tau|^{0.664}$. Let us call the Landau expansion with nonanalytic coefficients, "*nonanalytic Landau expansion*", in the present article. The constant k depends on the solvent and the monomer constituting the polymer chains but does not depend on the polymer chain length. Therefore, once the value of k is obtained from the coexistence curve of the solution of a certain-length polymer, the behavior of the coexistence curves near the critical point of the solution of arbitrary-length polymers is precisely predicted by means of the free energy. In this sense, the nonanalytic Landau expansion is practically very useful. However, the statistical-mechanical base beyond the semiempirical theory is not clear.

The idea (idea 2) is that the spatial variation in the volume fraction may change the parameter properties such as the value and the analyticity but could not change the form as a function of the volume fraction; all the contributions of the spatial variation could be renormalized into the parameters. It is natural to choose this conjecture as a guiding principle to bridge the gap between the universal asymptotic regime near the critical point and the mean-field limit since the conjecture guarantees the derivation of the correct critical point. The temperature T and the chain length P are not renormalized, since they are regarded as the external control parameters (the external fields). Therefore, the spatial variation effect is renormalized into the parameters in the term g_0 expressing the strength of the interaction between the polymer and the solvent, and the values of the parameters in g_0 give the correct critical temperatures and critical volume fractions. A new parameter H also should be introduced into g_0 as shown in eq 4, since this type of the correction does not change the form of the free energy. Hence, the "renormalized" FH free energy (4) is reasonably obtained.

The invariance conjecture is a powerful tool to analyze the systems that are expressed by the coarse-grained Hamiltonian and have no characteristic scale lengths longer than the coarse-grained length. The biomembrane system is one of such systems. Suzuki and Izuyama studied the elastic properties of biomembranes by means of a statistical-mechanical method based on the invariance conjecture.[11] They have derived the renormalization group equation and have succeeded in explaining the existence of stable vesicles on the basis of the equation. This is an excellent example showing the validity of the invariance conjecture. As discussed in the next section, the polymer solution systems are also expected to be analyzed validly by the invariance conjecture.

The present article has three aims. The first aim is to clarify the meaning of the invariance conjecture (idea 2) introduced in the previous article by discussing the relation between the microscopic picture and the coarse-grained picture of the polymer systems, and the relation between the coarse-grained picture and the free energy of mixing statistical-mechanically. In the statistical-mechanical approach, we do not pay attention to the calculation method but to the "structure" of the statistical-mechanical approach. In the statistical-mechanical approach, the FH type free energy is regarded as a local free energy in the coarse-grained picture. All the parameters in the FH type free energy as the local free energy are "bare". To obtain the final form of the free energy of mixing, the spatial variations in the volume fraction should be renormalized into the local free energy. To perform this renormalization, we introduce a renormalization hypothesis for the critical line. On the basis of the scale invariance of the local free energy, the form of the free energy of mixing obtained finally is expected to be similar to that of the FH free energy. Then, it is required that the final form of the free energy of mixing should be obtained by minimal modification of the FH free energy. In the present article, this requirement is called the invariance conjecture. We choose this invariance conjecture and the renormalization hypothesis as the guiding principles to evaluate the free energy of mixing. This type of nonperturbative method is a practically powerful technique.

The second aim is to show a statistical-mechanical basis of the nonanalytic Landau expansion (idea 1). The statistical-mechanical analysis not only verifies the nonanalytic Landau expansion but also predicts the polymer chain length dependence of the critical phenomena both below and above the critical temperature.

The last aim is to derive the form of $H(P,T)$ correctly expressing the coexistence curve in a wider-temperature region according to idea 2. As lowering the temperature, the calculated coexistence curve using eq 5 deviates from the observed one to the dilute side. This deviation results from a significant contribution of the deviation of the diameter from the rectilinear law.[12] To improve eq 5, we take notice of the universal behavior of the diameter. The invariance conjecture makes it possible to express the term $H(P,T)$ by the "form" of the FH free energy, the concentration difference and the diameter explicitly. Using the universal power law behaviors of the concentration difference and the diameter, we derive the explicit function form of $H(P,T)$. It is applied to the systems of polystyrene in methylcyclohexane (PS/MCH) and poly(methyl methacrylate) in 3-octanone (PMMA/3-OCT), for which precise coexistence curves were reported.[6,13]

II. Statistical-Mechanical Approach: Introduction of Two Guiding Principles.

Why Does the FH Type Approach Predict the Critical Point Correctly? In principle, the free energy of mixing should be derived from the microscopic Hamiltonian for polymer solutions by means of the statistical mechanical method. However, to perform this procedure is evidently quite difficult. To abort the difficulty, we could introduce various types of approximations. Although the approximation methods always allow us to analyze only restrictive properties, it is still important to obtain an overall picture and a concrete plan.

The FH theory is, in a sense, an approximation method to derive the thermodynamic properties from a microscopic polymer-solution model. Concerning the phase diagram, we can predict only the critical point by the FH theory; the critical point is a restriction property correctly analyzed by the FH theory and the shape of the coexistence curve, i.e. the critical behavior of the coexistence curve, is not. By the FH type approach, it might be impossible to obtain the correct critical behavior as well as the critical point. However, we should pay attention to the "critical point" predicted by the FH theory with the Koningsveld–Kleintjens (KK) parameters again before abandoning the FH type approach. We derive the "function forms" of the critical temperature $T_c = t(P)$ and the critical volume fraction $\phi_c = u(P)$ with respect to the chain length P although the number of the KK parameters is finite. Precisely speaking, we can determine the KK parameters by means of the experimentally observed critical temperature and the critical volume fraction. For the experimental data whose number is larger than the number of the KK parameters, the KK parameters are consistently obtained. This ability of the FH type approach is quite attractive.

The ability is not due to the mean-field approximation method itself but due to the "form" of the free energy since the KK parameters are determined by "fitting". Hence, in the language of the field theory, it means that the FH free energy with the KK parameters is suitably "renormalized" by means of the experimental data for the critical point. To clarify the meaning of the "renormalization", let the statistical-mechanical view of the renormalization be shown. From now on, let us call the FH free energy with the suitable KK parameters the FH free energy simply.

Coarse Grained Picture. The statistical mechanics of polymer solutions has been discussed on the basis of the lattice model. Usually the simple cubic lattice is chosen. The lattice size and the lattice constant are respectively taken to be $L \times L \times L$ and a_0. Let us consider an n_{poly}-polymer system composed of n_{seg} segments sitting on the lattice. Position of the jth segment in the ith polymer is denoted by $\mathbf{R}_{ij}$. In terms of $\mathbf{R}_{ij}$, the Hamiltonian of the polymer solution is denoted as $H_{\mathrm{micro}}(\{\mathbf{R}_{ij}\})$. The volume fraction ϕ of the polymer chains is defined by the occupation of the lattice site and is given by $\phi = n_{\mathrm{poly}}n_{\mathrm{seg}}/L^3$. On the basis of the microscopic model, the partition function of the system is given by

$$Z(\phi) = \sum_{\mathbf{R}_{ij}} \exp\left(-\frac{H_{\mathrm{micro}}(\{\mathbf{R}_{ij}\})}{k_B T}\right) \qquad (8)$$

Regarding n_0 neighboring-lattice-sites as a cell whose position $\mathbf{r}$ is defined by the center of the cell and introducing the number of the sites occupied by the polymer chains in the cell $\bar{n}(\mathbf{r})$, we can define the local volume fraction field $\varphi(\mathbf{r}) = \bar{n}(\mathbf{r})/v_0$, where $v_0 = n_0 a_0^3$ is the volume of the cell. Note that $0 \le \varphi(\mathbf{r}) \le 1/a_0^3$. We use the local volume fraction instead of the configuration of the segments $\mathbf{R}_{ij}$ as the statistical mechanical variable. In the coarse-grained limit $v_0 \to 0$, the cell point $\mathbf{r}$ is regarded as a point in the space with volume $V = L^3 a_0^3$. The coarse-grained Hamiltonian in units of $k_B T$ may be generally given by

$$\Phi = \int \mathrm{d}^3\mathbf{r} \left[\frac{1}{2}\hat{\kappa}\left|\nabla\varphi\right|^2 + \frac{U(a_0^{\,3}\varphi)}{a_0^{\,3}}\right] \qquad (9)$$

where the term $^1/_2\hat{\kappa}|\nabla\varphi|^2$ with a positive coefficient $\hat{\kappa}$ expresses the cell–cell interaction in the view of the lattice picture and the effect of the spatial variation in the view of the local volume fraction picture. The term U represents the free energy per site of the polymer system in a cell. The partition function for the system with the mean volume fraction ϕ is given by

$$Z(\phi) = \int_D D\varphi\, \delta\left(\phi - \frac{1}{N}\int \mathrm{d}^3\mathbf{r}\, \varphi(\mathbf{r})\right) \exp[-\Phi] \qquad (10)$$

where $N = L^3$ is the total number of the lattice sites and the symbol for "the functional integral" stands for

$$\int_D D\varphi = \prod_{\mathbf{r}} \int_0^{1/a_0^3} \mathrm{d}\varphi\,(\mathbf{r}) \qquad (11)$$

The partition functions (8) and (10) should be the same. Thus, the coarse-grained Hamiltonian Φ is expressed in terms of the parameters in the microscopic Hamiltonian $H_{\mathrm{micro}}(\{\mathbf{R}_{ij}\})$.

The free energy of mixing per site in units of k_BT is given by

$$f_{\rm mix} = \frac{1}{N}\{-\ln Z(\phi) - [-\phi \ln Z(1) - (1-\phi)\ln Z(0)]\} \equiv -\frac{1}{N}\ln Z_{\rm m}(\phi) \quad (12)$$

where $Z_{\rm m}(\phi)$ is the partition function of mixing given by

$$Z_{\rm m}(\phi) = \int_D D\varphi\,\delta\left(\phi - \frac{1}{N}\int {\rm d}^3\mathbf{r}\,\varphi(\mathbf{r})\right)\exp\left[-\Phi - \phi\ln\frac{Z(1)}{Z(0)} - \ln Z(0)\right] \quad (13)$$

By using the Legendre transformation, the delta function in the functional integral (13) can be removed

$$f_{\rm mix} = \tilde{f}_{\rm mix}(J_\phi) + J_\phi\phi \quad (14)$$

where

$$\tilde{f}_{\rm mix}(J) = -\frac{1}{N}\ln\tilde{Z}(J) \quad (15)$$

with

$$\tilde{Z}(J) = \int_D D\varphi\,\exp[-\tilde{\Phi}] \quad (16)$$

$$\tilde{\Phi} = \int {\rm d}^3\mathbf{r}\left[\frac{1}{2}\hat{\kappa}\left|\nabla\varphi\right|^2 + \frac{\tilde{U}(a_0{}^3\varphi)}{a_0{}^3} - J\varphi\right] \quad (17)$$

and

$$\tilde{U}(a_0{}^3\varphi) = U(a_0{}^3\varphi) + a_0{}^3\varphi\frac{1}{N}\ln\frac{Z(1)}{Z(0)} + \frac{1}{N}\ln Z(0) \quad (18)$$

The external field J_ϕ corresponding to the chemical potential difference of the polymer and the solvent is defined by the solution of the equation;

$$\frac{\partial\tilde{f}_{\rm mix}(J_\phi)}{\partial J_\phi} = -\phi \quad (19)$$

The mean field calculation for the microscopic lattice model (8) corresponds to the saddle point evaluation of the path integral (16). Therefore, we can expect to obtain the FH type free energy form by the saddle point evaluation. Then, the cell free energy of mixing $\tilde{U}$ should have the following form (see Appendix)

$$\tilde{U}(\phi) = (1-\phi)\ln(1-\phi) + \frac{\phi}{P}\ln\phi + \hat{g}_0(1-\phi)\phi \quad (20)$$

$$\hat{g}_0 = \hat{a} + \frac{\hat{b}(T)}{1-\hat{c}\phi} \quad (21)$$

$$\hat{b}(T) = \hat{b}_0 + \hat{b}_1/T + \hat{b}_2T \quad (22)$$

where the KK parameters with the hat symbol are the "bare" parameters and they are independent of temperature and chain length.

Renormalization Hypothesis. As mentioned before, the bare parameters can be related to the microscopic parameters in $H_{\rm micro}(\{\mathbf{R}_{ij}\})$. However, the relationship is not worthy to be considered because the microscopic parameters are unknown and are usually estimated from macroscopically observed data. The similar (but not the same) situation appears in the quantum electrodynamics. In the quantum electrodynamics, since the electron is decorated by the electromagnetic field, the observed charge and mass are always influenced by the electromagnetic field and the calculated quantities are expressed in terms of the observed variables through expressing the bare variables by the observed ones (the renormalization method).

The critical line is obtained by the simultaneous equations

$$\left.\begin{array}{l}\dfrac{\partial^2 f_{\rm mix}}{\partial\phi^2} = 0\\[2ex] \dfrac{\partial^3 f_{\rm mix}}{\partial\phi^3} = 0\end{array}\right] \quad (23)$$

From the above equations, the chain length dependence of the critical temperature and the critical volume fraction, $T_{\rm c} = t({\rm P})$ and $\phi_{\rm c} = u(P)$, are obtained. It has been shown that the polymer chain length dependence of the critical point derived from the FH free energy with adequately chosen values of the KK parameters agrees with the experimental results very well.[5,6] Therefore, let us adopt the following renormalization hypothesis. All the bare parameters are determined so that the critical-line equations (eq 23) are equivalent to those in terms of the FH free energy

$$\left.\begin{array}{l}\dfrac{\partial^2 f_{\rm FH}}{\partial\phi^2} = 0\\[2ex] \dfrac{\partial^3 f_{\rm FH}}{\partial\phi^3} = 0\end{array}\right] \quad (24)$$

Comparing eq 23 expressed in terms of the bare parameters with eq 24, we can write the bare parameters in terms of the observed parameters, a, $\{b_i\}_{i=0,1,2}$ and c

$$\left[\begin{array}{l}\hat{\kappa} = \hat{\kappa}(a,\{b_i\}_{i=0,1,2},c)\\ \hat{a} = \hat{a}(a,\{b_i\}_{i=0,1,2},c)\\ \hat{b}_j = \hat{b}_j(a,\{b_i\}_{i=0,1,2},c)\ \ (j = 0,1,2)\\ \hat{c} = \hat{c}(a,\{b_{\rm i}\}_{i=0,1,2},c)\end{array}\right]$$

When we evaluate the free energy of mixing by means of the saddle point method, we have only the simple relations; $\hat{a} = a$, $\hat{b}_i = b_i$, $\hat{c} = c$. Since $\hat{\kappa}$ does not influence the free energy in this approximation, the value of $\hat{\kappa}$ is not determined.

Invariance Conjecture. The free energy form derived by the FH type approach is the simplest form satisfying the above renormalization hypothesis; the FH type approach predicts the critical point correctly. To obtain the correct critical behaviors in addition to the critical point, the spatial variation term $^1/_2\hat{\kappa}|\nabla\varphi|^2$ should be taken into account. Thus, the approach beyond the FH type approach is required. As the method beyond the saddle point analysis, the loop expansion method has been known well. Since the loop expansion alone gives only the mean-filed type critical phenomena and the renormalization equation such as the Callan–Symanzik[14] required additionally to obtain the correct critical phenomena cannot derive the free energy, this type of approach is not suitable for our aim.

To construct a new method, we pay attention to the cell volume v_0, the coarse-grained size in the coarse-grained picture. The cell size v_0 is determined so that we obtain the cell free energy of mixing with the same form as the FH free energy. We obtain the cell free energy in the coarse-grained scale v larger than v_0 by performing the functional integral with respect to the variables with the wavelength between the scale v_0 and v. The form of the new-scale cell free energy may be different from the FH free energy. However, it is naturally expected that the cell free energy in the scale v' larger than the scale v have the same form as the cell free energy in the scale v since there are no characteristic scale length in the scale larger than v_0. From the relation between the cell free energies in the scale v and in the scale v', it is also expected that we can express the cell free energies in the scale v_0 and in the scale v in the same form by adding some parameters (they will be denoted by r_0, r_1, Δj, and H later) into the cell free energy in the scale v_0. Hence, in the scale larger than v_0, the form of the cell free energy is invariant with respect to the scale change. When the scale v becomes the volume of the system V, the cell free energy becomes the free energy of mixing f_{mix}. This leads to the result that the forms of the invariant cell free energy and of the free energy of mixing are the same. Hence, we assume that the form of the free energy f_{mix} be similar to the form of the FH free energy; the free energy could be obtained by minimal modification of the FH free energy.

However, by just using the the invariance conjecture, we cannot obtain the form of the free energy of mixing. Then, we note the renormalization hypothesis again. Let the renormalization hypothesis, the equivalence between (23) and (24), be regarded as the condition that the correct free energy f_{mix} should be satisfied as well as the condition to evaluate the bare parameters. This idea is also a powerful tool to derive the free energy of mixing. In the present article, we evaluate the form of the free energy of mixing f_{mix} on the basis of the two guiding principles, the invariance conjecture and the renormalization hypothesis.

III. Critical Point and Invariant Form of the Free Energy of Mixing

At first, let us express the phase separation phenomena in terms of the field theory to introduce some notations used later. Using eqs 14 and 19, we have the equation of state

$$f^{(1)}_{\text{mix}}(\phi) = J \tag{25}$$

where $f^{(1)}_{\text{mix}}(x) = \partial f_{\text{mix}}(x)/\partial x$. From (25), we have the volume fraction as a function of the chemical potential J; $\phi = \phi(J)$. However, the solution of the equation $\phi(J)$ is not always obtained uniquely. The presence of multiple solutions shows a possibility that the uniform phase is thermodynamically unstable and the phase coexistence appears. When at a line $J = j(T)$ in the $J-T$ plane the two limits $\lim_{J\to j(T)-0} \langle a_0{}^3\varphi(\mathbf{r})\rangle_{\mathbf{J}} = \phi_+$ and $\lim_{J\to j(T)+0} \langle a_0{}^3\varphi(\mathbf{r})\rangle_{\mathbf{J}} = \phi_-$ are different, the two phases with the volume fractions ϕ_+ and ϕ_- coexist ($\phi_+ > \phi_-$), where $\langle O_J\rangle$ stands for the average of the quantity O with respect to the action $\tilde{\Phi}$. The quantity $j(T)$ stands for the value of the chemical potential when the two phases coexist. The coexistence chemical potential line $J = j(T)$ and the volume fractions ϕ_+ and ϕ_- are obtained from the simultaneous equations:

$$\left.\begin{array}{l} f^{(1)}_{\text{mix}}(\phi_+) = j(T) \\ f^{(1)}_{\text{mix}}(\phi_-) = j(T) \\ f_{\text{mix}}(\phi_+) - j(T)\phi_+ = f_{\text{mix}}(\phi_-) - j(T)\phi_- \end{array}\right] \tag{26}$$

Above the critical temperature T_c, only one solution exists; the point $(J_c(= j(T_c)),T_c)$(the critical point) is an end point of the coexistence chemical potential line $J = j(T)$. Next, let us search the function form of $f_{\text{mix}}(\phi)$ whose critical line of eqs 23 are equivalent to eqs 24. We have found a simple form of $f_{\text{mix}}(\phi)$

$$f_{\text{mix}}(\phi) = r_0(P,T)f_{\text{FH}} + \Delta j(P,T)\phi + K(P,T;\phi) \tag{27}$$

where the prefactor r_0 and the factor Δj are independent of the volume fraction ϕ, and the correction term $K(P,T;\phi)$ is a function whose first, second and third derivatives with respect to ϕ vanish at the critical point simultaneously. The factor $\Delta j(P,T)$ stands for the additional correction to the chemical potential; the "renormalized" chemical potential is given by

$$J_\phi = \frac{\partial f_{\text{mix}}(\phi)}{\partial \phi} = r_0\left(\frac{\partial f_{\text{FH}}(\phi)}{\partial \phi}\right) + \Delta j = r_0 J_\phi^{\text{FH}} + \Delta j \tag{28}$$

where J_ϕ^{FH} is the chemical potential for the FH free energy. The correction Δj and the prefactor r_0 do not change the coexistence curve $\phi = \phi_+\,(T)$ and $\phi = \phi_-\,(T)$, since $(f_{\text{mix}} - \Delta j\phi)/r_0$ satisfies eq 26 when f_{mix} does. Thus, the coexistence curve does not depend on the correction Δj and the prefactor r_0. However, r_0 is required to obtain the correct critical behaviors for the specific heat and the "susceptibility" $\chi_\phi \equiv (\partial^2 f_{\text{mix}}/\partial\phi^2)^{-1}$. Note that the prefactor r_0 also modifies the chemical potential as shown in eq 28.

Let the rest of the present section be devoted to discussing the invariant form of the free energy of mixing. In the previous paper,[10] the form of the FH free energy itself was chosen as the invariant form. To take account of the prefactor r_0 and the chemical potential correction Δj, however, more generalized form as the invariant form is required. According to the guiding principle that the invariant form should be constructed by minimal modification of the FH free energy, we have the following generalized form consistent with eq 27

$$f_{\text{mix}}(\phi) = r_0(P,T)\left[(1-\phi)\ln(1-\phi) + \frac{\phi}{P}\ln\phi + g(1-\phi)\phi\right] + \Delta j(P,T)\phi + r_1(P,T) \tag{29}$$

$$g = a + \frac{b(T)}{1 - c\phi} + H(P,T) \tag{30}$$

where the term r_1 is generated by the spatial variation in the volume fraction. If no spatial variation is renormalized, the prefactor r_0 becomes unity and the term r_1 vanishes; the "bare" values of them are, respectively, $\hat{r}_0 = 1$ and $\hat{r}_1 = 0$. Comparing eq 27 with eq 29, we have the correction term $K(P,T;\phi)$ as

$$K(P,T;\phi) = r_0 H(P,T)(1-\phi)\phi + r_1 \tag{31}$$

In order that the first and the second derivatives of K

with respect to ϕ vanish at the critical point, $H(P,T)$ is expected to vanish at $T = T_c$.

IV. Nonanalytic Landau Expansion

Near the critical point, the polymer system can be analyzed by means of the ϕ^4-theory for the order parameter field $\delta\varphi(\mathbf{r}) \equiv \varphi(\mathbf{r}) - \phi_c/a_0{}^3$. The effective potential for the system described by the ϕ^4-theory based on the action $\tilde{\Phi}$ is given by[14]

$$f_{\mathrm{eff}}(\phi) = f_{\mathrm{mix}}(\phi) - J_c\phi \tag{32}$$

Equilibrium thermodynamic state is realized at the minimum point of the effective potential. Calculating the effective potential by the saddle point approximation (the tree approximation), we have the conventional Landau free energy.

As shown in the Appendix, combining the field theoretical analysis with the scaling analysis for the free energy,[14−18] we can obtain a novel expansion form of the effective potential with respect to $\Delta\phi = \phi - \phi_c$

$$f_{\mathrm{eff}} = \Gamma_0(\tau) + q(\tau,\Delta\phi) + |\tau|^{\theta}\left(\frac{1}{2}\eta_1\tau\left|\tau\right|^{2\beta-1}\Delta\phi^2 + \frac{1}{4}\eta_2\Delta\phi^4\right) \tag{33}$$

with

$$\theta = \beta(\delta - 3) \tag{34}$$

where $\Gamma_0(\tau)$ is the value of the effective potential for $\phi = \phi_c$, η_n (n = 1,2) is a constant, and β and δ are the critical exponents for the three-dimensional binary fluid. The term $q(\tau,\Delta\phi)$ defined by eqs A13−A15 is finite near and at $\tau = 0$, and gives only higher order correction with respect to the last term in the rhs of (33).

The validity of the expression is guaranteed only in the uniform phase region since the scaling function f_1 defined by (A15) (or the function q) can be safely introduced only in the uniform phase region. To discuss the coexistence curve, however, the extension of the above expansion to the phase coexistence region is required. This difficulty is avoidable by the following concept. Let us neglect the term $q(\tau,\Delta\phi)$ for the reason that the term is of higher order when the term is expanded in powers of $\Delta\phi$ in the uniform region. The remaining terms

$$\Delta f_{\mathrm{mix}} = \Gamma_0(\tau) + |\tau|^{\theta} f'_{\mathrm{m}} \tag{35}$$

with

$$f'_{\mathrm{m}} = \frac{1}{2}\eta_1\tau|\tau|^{2\beta-1}\Delta\phi^2 + \frac{1}{4}\eta_2\Delta\phi^4 \tag{36}$$

are well-defined in the phase coexistence region. Therefore, Δf_{mix} is regarded as the “extended” effective potential expressing the thermodynamic properties in both the uniform region and the coexistence region near the coexistence curve. The coexistence curve $\Delta\phi = \Delta\phi_{\mathrm{eq}}$ is obtained by minimizing the function f'_{m}. For $\tau \geq 0$, f'_{m} is minimized at $\Delta\phi = 0$ and for $\tau < 0$, a finite value of $\Delta\phi_{\mathrm{eq}}$ is obtained

$$\Delta\phi_{\mathrm{eq}} = \pm\sqrt{\frac{\eta_1}{\eta_2}}|\tau|^{\beta} \tag{37}$$

The above shows the correct critical phenomena for the coexistence curve. Equation 35 or 36 is regarded as the Landau free energy having a nonanalytic coefficient.

Let us summarize the derivation procedure of the nonanalytic Landau free energy from the precise free energy f_{mix} given by eqs 12 and 13. (i) Expand f_{mix} in powers of $\Delta\phi$. (ii) Eliminate the term proportional to $\Delta\phi$ and the higher order terms than $\Delta\phi$.[4] (iii) Regard the rest term as the Landau free energy. Presence of the above procedure, points i−iii, gives the statistical mechanical basis on the nonanalytic Landau free energy and verifies the semiempirical introduction of that in the previous paper.

V. Behavior of *H*(*P*,*T*) near Critical Temperature

Correction Term *K*(*P*,*T*;ϕ). The Landau expansion of the FH free energy is given by

$$\begin{bmatrix} f_{\mathrm{FH}} = J_c\Delta\phi + \Delta f_{\mathrm{FH}} \\ \Delta f_{\mathrm{FH}} = f^{\,c}_{\mathrm{FH}} + \dfrac{1}{2}\tilde{B}\tau\Delta\phi^2 + \dfrac{1}{4!}D\Delta\phi^4 \end{bmatrix} \tag{38}$$

where $f^{\,c}_{\mathrm{FH}}$ is the FH free energy at the critical point and $\tilde{B}$ is given by

$$\tilde{B} = \frac{2b'(T_c)(c-1)}{(1-c\phi_c)^3}T_c \tag{39}$$

In eqs 38 and 39, all the coefficients are analytic with respect to temperature. Therefore, the nonanalyticity shown in (A12) should appear in the correction term $K(P,T;\phi)$ in eq 27. On the basis of the nonanalytic Landau expansion, the effective potential near the critical point is given by $f_{\mathrm{eff}} \cong \Delta f_{\mathrm{mix}} = \Gamma_0(\tau) + |\tau|^{\theta} f'_{\mathrm{m}}$. Therefore, the correction term is expressed as

$$\begin{aligned} K(P,T;\phi) &= f_{\mathrm{eff}}(\phi) - r_0 f_{\mathrm{FH}} + (J_c - \Delta j)\phi \cong |\tau|^{\theta} \times \\ &\left(\frac{1}{2}\eta_1\tau\left|\tau\right|^{2\beta-1}\Delta\phi^2 + \frac{1}{4}\eta_2\Delta\phi^4\right) - r_0\left(\frac{1}{2}\tilde{B}\tau\Delta\phi^2 + \frac{1}{4!}D\Delta\phi^4\right) + \\ &(J_c - r_0J_c - \Delta j)\Delta\phi + \Gamma_0 - r_0 f^{\,c}_{\mathrm{FH}} + (J_c - r_0J_c - \\ &\Delta j)\phi_c = r_0\left(\frac{1}{2}\eta_1\tau\left|\tau\right|^{2\beta-1}\frac{|\tau|^{\theta}}{r_0} - \frac{1}{2}\tilde{B}\tau\right)\Delta\phi^2 + |\tau|^{\theta}\left(\frac{1}{4}\eta_2 - \right. \\ &\left. r_0\tau^{-\theta}\frac{1}{4!}D\right)\Delta\phi^4 + (J_c - r_0J_c - \Delta j)\Delta\phi + K(T,P;\phi_c) \end{aligned} \tag{40}$$

where $K(P,T;\phi_c) = \Gamma_0 - r_0 f^{\,c}_{\mathrm{FH}} + (J_c - r_0J_c - \Delta j)\phi_c$. Since the expression (31) shows that $K(P,T;\phi)$ should be a quadratic polynomial of $\Delta\phi$, the following relation should be satisfied.

$$\frac{1}{4}\eta_2 - r_0\tau^{-\theta}\frac{1}{4!}D = 0 \tag{41}$$

Thus, near T_c, r_0 should behave as

$$r_0 \approx 6|\tau|^{\theta}\frac{\eta_2}{D} \tag{42}$$

Then, we have

$$K(P,T;\phi) = r_0\left(\frac{1}{12}\frac{\eta_1}{\eta_2}D\tau\left|\tau\right|^{2\beta-1} - \frac{1}{2}\tilde{B}\tau\right)\Delta\phi^2 + (J_c - r_0J_c - \Delta j)\Delta\phi + K(P,T;\phi_c) \tag{43}$$

Expression of $H(P,T)$. Using eq 31, $K(P,T;\phi)$ is expressed in terms of $H(P,T)$

$$K(P,T;\phi) = -r_0H(P,T)\Delta\phi^2 + r_0H(P;T)(1-2\phi_c)\Delta\phi + r_0\phi_c(1-\phi_c) + r_1 \quad (44)$$

Comparing (43) with (44), we have

$$H(P,T) = -\frac{1}{12}\frac{\eta_1}{\eta_2}D\tau|\tau|^{2\beta-1} + \frac{1}{2}\tilde{\mathrm{B}}\tau \quad (45)$$

$$\Delta j = J_c - r_0J_c - r_0H(P,T) \cong J_c \quad (46)$$

The chain length dependence of the critical amplitude $\Delta\phi_0$ of the coexistence curve $\Delta\phi_{eq} = \pm\Delta\phi_0|\tau|^\beta$ is expressed as

$$\Delta\phi_0 = \Delta\phi_{00}P^\sigma \quad (47)$$

where $\Delta\phi_{00}$ is a positive constant depending only on the species of the monomer and the solvent. The value of the exponent σ has been obtained experimentally and does not depend on system specifics; $\sigma \approx -0.23$.[6] By this result and eq 37, the ratio η_1/η_2 is given by

$$\frac{\eta_1}{\eta_2} = (\Delta\phi_{00})^2P^{2\sigma} \quad (48)$$

Thus, we have

$$H(P,T) = -\frac{1}{12}D(\Delta\phi_{00})^2P^{2\sigma}\tau|\tau|^{2\beta-1} + \frac{1}{2}\tilde{\mathrm{B}}\tau \quad (49)$$

Note that the above expression is valid both above and below T_c. Hence, the behavior of $H(P,T)$ above T_c can be expressed in terms of the factor $(\Delta\phi_{00})^2$ derived in the previous paper for $T \le T_c$.

Higher Dimension Limit. In the ϕ^4 theory with the space dimension larger than four, the values of the critical exponents are equal to those derived by the mean field approximation. In this higher dimension limit, the exponents β and δ respectively become $\beta_{MF} = {}^1/_2$ and $\delta_{MF} = 3$. Therefore, the exponent θ becomes $\theta_{MF} = 0$. The coefficients η_1 and η_2 become $\tilde{B}$ and $6D$, respectively. Then, we have the values of the correction factors as expected; $r_0 = 1$, $H(P,T) = 0$ and $\Delta j = 0$. This analysis shows that the FH free energy of mixing is exact for polymer solutions in the space whose dimension is larger than four.

VI. Effective Part of the Free Energy of Mixing

Determination of Function Form of $H(P,T)$ in Wide Range of Temperature. As shown in the previous paper and in the previous section, the universal polymer length dependence of the critical amplitude for the coexistence curve gives us the method by which the coexistence curve and the spinodal line for various chain-length polymer solutions are derived. This is based on the fact that only the parameter $(\Delta\phi_{00})^2$ is the parameter determined experimentally. Once the parameter is obtained, the coexistence curve and the spinodal line for the solution of polymer with arbitrary chain lengths can be derived. However, the coexistence curve and the spinodal line are correct only near the critical temperature, because the function form (49) of $H(P,T)$ determined only with the parameter $(\Delta\phi_{00})^2$ is valid near the critical temperature. In the present section, we derive the function form of $H(P,T)$ valid in a wider temperature range on the basis of the universality of the diameter.

Under constant pressure, the coexistence curve is given by[19]

$$f_{mix}(\phi_+) + (1-\phi_+)f^{(1)}_{mix}(\phi_+) = f_{mix}(\phi_-) + (1-\phi_-)f^{(1)}_{mix}(\phi_-) \quad (50)$$

By using (29), the above is rewritten as

$$f_R(\phi_+) + (1-\phi_+)f^{(1)}_R(\phi_+) = f_R(\phi_-) + (1-\phi_-)f^{(1)}_R(\phi_-) \quad (51)$$

where $f_R(\phi)$ is the effective part of the free energy of mixing (let it be simply called the effective free energy) and is given by

$$f_R(\phi) = (1-\phi)\ln(1-\phi) + \frac{\phi}{P}\ln\phi + \left(a + \frac{b(T)}{1-c\phi} + H(P,T)\right)(1-\phi)\phi \quad (52)$$

and $f^{(1)}_R(\phi) = \partial f_R(\phi)/\partial\phi$. The spinodal line is given by the solution $T = T_{sp}(\phi)$ of the equation

$$\frac{\partial^2 f_{mix}(\phi)}{\partial\phi^2} = 0 \quad (53)$$

In terms of $f_R(\phi)$, this equation is also rewritten as

$$\frac{\partial^2 f_R(\phi)}{\partial\phi^2} = 0 \quad (54)$$

Thus, only H in all the correction factors is necessary to discuss both the coexistence curve and the spinodal line. Since the chain-length dependence of the critical point is derived from the rest part of the effective free energy, all the properties relating to the phase separations are derived from the effective free energy.

In terms of the FH free energy (1), the effective free energy is expressed as

$$f_R(\phi) = f_{FH}(\phi) + H(P,T)(1-\phi)\phi \quad (55)$$

The form of the free energy is equivalent to that discussed in the previous paper.[10]

Using the above and eq 51, we have the expression of H in terms of ϕ_+ and ϕ_-;[10]

$$H = \frac{f_{FH}(\phi_+) + (1-\phi_+)f^{(1)}_{FH}(\phi_+) - f_{FH}(\phi_-) - (1-\phi_-)f^{(1)}_{FH}(\phi_-)}{(1-\phi_-)^2 - (1-\phi_+)^2} \quad (56)$$

where $f^{(1)}_{FH}(\phi) = \partial f_{FH}(\phi)/\partial\phi$. The independent concentration variables ϕ_+ and ϕ_- are replaced by $x = \phi_+ - \phi_-$ and $y = (\phi_+ + \phi_-)/2 - \phi_c$, each standing for the concentra-tion difference and the diameter, respectively. Then theoriginal variables of ϕ_+ and ϕ_- are expressed using new variables x and y by a set of equations

$$\phi_{+} = y + \frac{1}{2}x + \phi_{\mathrm{c}} \tag{57}$$

$$\phi_{-} = \phi_{+} - x = y - \frac{1}{2}x + \phi_{\mathrm{c}} \tag{58}$$

Therefore, H is expressed as

$$H = \Big[f_{\mathrm{FH}}\Big(y + \frac{x}{2} + \phi_{\mathrm{c}}\Big) + \Big(1 - y + \frac{x}{2} + \phi_{\mathrm{c}}\Big)f^{(1)}_{\mathrm{FH}}\Big(y + \frac{x}{2} + \phi_{\mathrm{c}}\Big) - f_{\mathrm{FH}}\Big(y - \frac{x}{2} + \phi_{\mathrm{c}}\Big) - \Big(1 - y - \frac{x}{2} + \phi_{\mathrm{c}}\Big) \times f^{(1)}_{\mathrm{FH}}\Big(y - \frac{x}{2} + \phi_{\mathrm{c}}\Big)\Big]\Big/\Big[2x(1 - y - \phi_{\mathrm{c}})\Big] \tag{59}$$

The above equation shows that the correction term $H(P,T)$ can be expressed in terms of the form of the FH free energy, the concentration difference and the diameter.

To clarify the correction by the diameter to the expression $H(P,T) \cong {}^{1}/_{2}\tilde{B}\tau + 1/48\ Dx^{2}$ obtained in the previous paper, we expand the rhs of eq 59 in a Taylor's series with respect to x and y

$$H(P,T) \cong \frac{1}{2}\tilde{B}\tau + \left[\frac{1}{48}D + \left(\frac{1}{48}D_{5} - \frac{1}{24}\frac{D}{1 - \phi_{\mathrm{c}}}\right)y\right]x^{2} + \tilde{B}_{3}\tau y + \frac{1}{2}Dy^{2} + O(x^{4}) + O(y^{2}x^{2}) + O(y^{3}) \tag{60}$$

where

$$\tilde{B}_{3} = \frac{6cb'(T_{\mathrm{c}})(c - 1)}{(1 - c\phi_{\mathrm{c}})^{4}}T_{\mathrm{c}} \tag{61}$$

and

$$D_{5} = \frac{6}{(1 - \phi_{\mathrm{c}})^{4}} - \frac{1}{P}\frac{6}{\phi_{\mathrm{c}}^{\ 4}} + \frac{120c^{3}b(T_{\mathrm{c}})(c - 1)}{(1 - c\phi_{\mathrm{c}})^{6}} \tag{62}$$

In the above, the coefficient of each term is expanded with respect to τ and only the term with the smallest power of τ is shown. Note that the terms with odd power of x do not appear but of y appear in the expansion.

Both the theoretical predictions[20−24] and the experimental fact[6,13,25,26] suggest a set of function forms of x and y as

$$x = \Delta\phi_{00}P^{\sigma}|\tau|^{0.327} \tag{63}$$

$$y = d_{00}P^{\rho}|\tau|^{0.89} \tag{64}$$

The exponents σ and ρ are expected to be system-independent when the chain length is large. For the exponent σ, it was confirmed that the common value of $\sigma \cong -0.23$ was obtained for carefully observed systems of PS/MCH and PMMA/3-OCT in the experimental range of chain length between 70 and 5200.[6,13]

Tricritical Limit. Let us consider the free energy behavior in the long chain-length limit $P \rightarrow \infty$. In this limit, the critical volume fraction behaves as $\phi_{\mathrm{c}} \propto 1/\sqrt{P} \rightarrow 0$. Then, the volume fraction in the dilute phase should be zero. This requires that

$$x = 2y = \phi_{+} \tag{65}$$

in this limit. The expressions 63 and 64 apparently conflict with this result. This does not mean that the expressions are incorrect but means that the variables noticed are different. In the discussion for (63) and (64), the leading terms for *the small reduced-temperature* $|\tau| \rightarrow 0$ in $x = x(P,\tau)$ and in $y = y(P,\tau)$ are required, but for the long chain-length limit the leading terms for *the long chain-length* $P \rightarrow \infty$ are required. The P dependencies in (63) and (64) show only the leading part for the long-chain limit *in the leading term for the small reduced-temperature*.

Requiring that ϕ_{+} should be finite in the long chain-length limit, we have the result that the P dependence of ϕ_{+} should vanish; the leading terms for the long chain length in x and y are independent of P. In terms of ϕ_{+} in (65), H in the long chain-length limit is obtained

$$H = \frac{2g_{0} - 1}{2\phi_{+}} - g_{0} \tag{66}$$

From this expression and eq 51 with $\phi_{-} \rightarrow 0$ and $P \rightarrow \infty$, we have the equation determining ϕ_{+}

$$(1 - \phi_{+})[2(g_{0} + H) - 1 - 2(g_{0} + H)\phi_{+}] = 0 \tag{67}$$

Then, we have the volume fraction in the concentrated phase:

$$\phi_{+} = \frac{2g_{0} - 1}{2g_{0}} \tag{68}$$

From this and eq 66, it is found that $H = 0$ in the long chain-length limit. Hence, the spatial variation in the volume fraction does not correct the phase behavior for the long chain-length limit. Near the tricritical point, we have the linear behavior:

$$\phi_{+} \cong \frac{g'_{0\mathrm{c}}T_{\mathrm{c}}(\infty)}{g_{0c}}\tau \tag{69}$$

where

$$g_{0\mathrm{c}} = g_{0}|_{T=T_{\mathrm{c}}(\infty)},\ g'_{0\mathrm{c}} = \frac{\mathrm{d}g_{0}}{\mathrm{d}T}\Big|_{T=T_{\mathrm{c}}(\infty)}$$

and the critical temperature $T_{\mathrm{c}}(\infty)$ (the Θ temperature) is obtained from the equation, $2g_{0} - 1 = 0$.

Region Far Away from the Critical Point. For the region far away from the critical point, the expressions given by eqs 63 and 64 are not suitable and the higher order terms as discussed by Wegner[27] are required. Theoretical derivation of the higher order terms is quite difficult since many system-specific parameters appear in the higher order terms. However, the effective free energy in (55) with (56) gives a solution for the difficulty. The term H can be numerically obtained from the data of the coexistence curve observed experimentally. It is tautological to derive the coexistence curve from the

Table 1. Parameters in the Effective Free Energy of Mixing of (52) and (59)

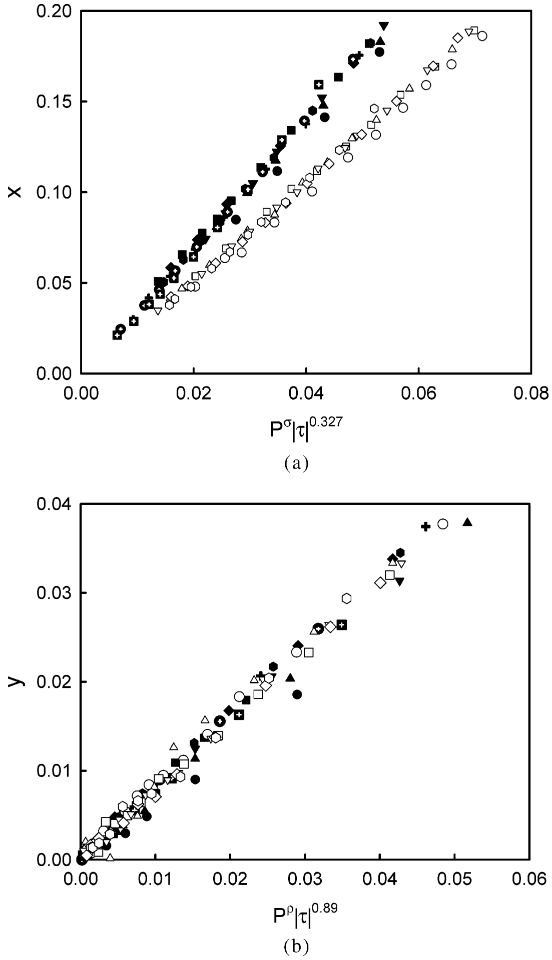
system	a	$b(T)$	c	x	y
PS/MCH	−0.1091	$-0.5832 + 278.6/T$ $+ 1.695 \times 10^{-3}T$	0.2481	$3.54P^{-0.212}\|\tau\|^{0.327}$	$0.79P^{0.090}\|\tau\|^{0.89}$
PMMA/3-OCT	−0.2145	$-0.7950 + 66.48/T$ $-2.264 \times 10^{-4}T$	0.2166	$2.67P^{-0.184}\|\tau\|^{0.327}$	$0.80P^{0.083}\|\tau\|^{0.89}$

effective free energy obtained by the above experiment-aided method, but it is worthwhile to derive the entire phase diagram including the spinodal line. Hence, even in the region, the effective free energy is useful as a practical tool to derive the spinodal line from the coexistence curve.

VII. Application to Polymer Solutions

Carefully observed coexistence curves of nine data sets for the system PS/MCH[6] and six data sets for the system PMMA/3-OCT[13] were used for determining the function $H(P,T)$. For PS/MCH, the parameters in g_0, a, $b(T)$, and c were determined in a previous paper as $a = -0.1091$, $b(T) = -0.5832 + 278.6/T + 1.695 \times 10^{-3} \times T$, and $c = 0.2481$.[25] We determined the parameters in g_0 for PMMA/3-OCT, according to the procedure by Koningsveld and Kleintjens,[5] as $a = -0.2145$, $b(T) = -0.7950 + 66.48/T - 2.264 \times 10^{-4} \times T$, and $c = 0.2166$, using the critical point data T_c and ϕ_c at various chain lengths.[13] The polymer chain lengths of PMMA were estimated from the densities of PMMA, 1.188 g/cm^2,[28] and 3-OCT, 0.822 g/cm^2, and the molecular weights reported in ref 13. The concentration difference of coexisting phases x and the diameter y were expressed as $x = 3.54P^{-0.212}|\tau|^{0.327}$ and $y = 0.79P^{0.090}|\tau|^{0.89}$ for PS/MCH, and $x = 2.67P^{-0.184}|\tau|^{0.327}$ and $y = 0.80P^{0.083}|\tau|^{0.89}$ for PMMA/3-OCT in the experimental chain-length range between 70 and 5200, as shown in Figure 1. The exponents for the chain length σ and ρ are slightly different between the systems PS/MCH and PMMA/3-OCT. These differences might be a result of finite chain length of polymers used in the experiments.[10] Successful fittings and resultant master curves shown in Figure 1 for much different polymer solutions support the methodology presented in this paper. All the system-specific parameters for the systems PS/MCH and PMMA/3-OCT are summarized in Table 1.

For a demonstration the coexistence curves were calculated using the effective free energy f_R. Equations 51, 52, 59, 63, and 64 with the above numerical values, as shown in Figure 2, agree with the observed ones fairly well. The slight difference of the critical temperature observed and calculated for systems b and c in Figure 2a and b′−f′ in Figure 2b should be attributed to the experimental error in determining the molecular weights and/or small molecular weight distributions. The deviation of the calculated one from the observed one for systems i and g results from the higher order terms in the Wegner expansion,[27] a correction for simple scaling near the critical point. Thus, it is meaningless to require further agreement at this stage. For system g, the numerical calculation based on the expression in the previous paper, $H \cong 1/48\ Dx^2$, is also shown by the dash line in Figure 2a. The calculation in the present paper agrees with the experimental result in the temperature region $|T - T_c| \leq 5$ K whereas that based on the previous result only in the region $|T - T_c| \leq 2$ K. The fair agreement of observed and calculated from the effective free energy permits us to predict precise phase equilibrium behavior in practical application.



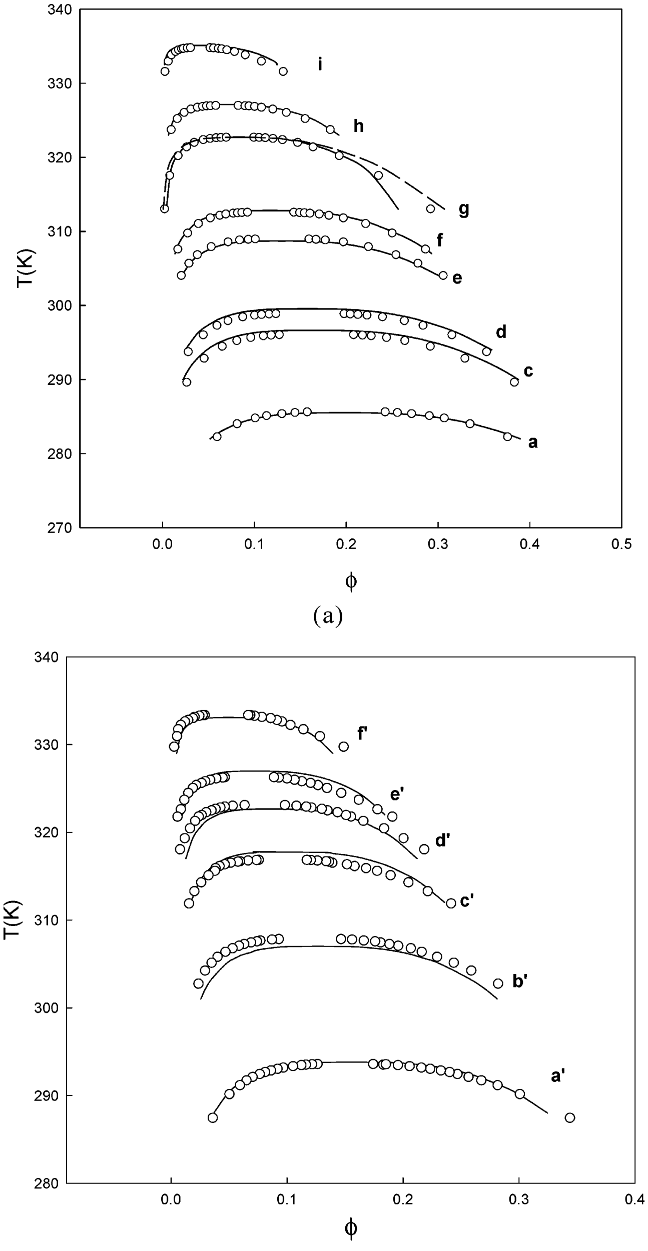
(a)

(b)

Figure 1. Concentration difference of coexisting phases x (a) and diameter y (b) as a function of a combination of reduced temperature and chain length for PS/MCH and PMMA/3-OCT. The values of the exponent σ and ρ for each system are given in the text. The symbols denote the systems a (M = 10 200) (solid circle), b (M = 16 100) (solid square), c (M = 17 300) (solid triangle up), d (M = 20 200) (solid triangle down), e (M = 34 900) (solid diamond), f (M = 46 400) (solid hexagon), g (M = 109 000) (crosshair), h (M = 181 000) (circle x-hair), and i (M = 719 000) (square x-hair) in ref 5 and a′ (M = 26 900) (open circle), b′ (M = 48 600) (open square), c′ (M = 95 000) (open triangle up), d′ (M = 143 000) (open triangle down), e′ (M = 227 000) (open diamond), f′ (M = 596 000) (open hexagon) in ref 13.

VIII. Summary

Theoretically, phase coexistence curves of polymer solution systems are derived based on the free energy of mixing. To obtain correct coexistence curves, it is necessary to give full consideration to the critical phenomena since the critical phenomena govern the behavior of the coexistence curve. The mean-field theories inclusive of the Flory−Huggins (FH) theory fail to express the critical phenomena because they neglect the fluctuations caused by the spatial variation of the volume fraction of the polymer. In the previous article,[10] we have semiempirically introduced a chain-length-dependent interaction parameter to improve the FH



(a)

(b)

Figure 2. Coexistence curve observed (open circles) and calculated from the effective free energy given by eqs 52 and 59 (solid lines) for PS/MCH (a) and PMMA/3-OCT (b). The plot for the system b in ref 6 is not shown since the plot is quite close to that for system c in ref 6. The dashed line for system g is the coexistence curve calculated by the previous theory in ref 10.

theory so as to express the coexistence curve correctly.

The theory in the previous paper is based on the invariance conjecture and the nonanalytic Landau expansion in a naïve sense. In the present article, we have developed the statistical-mechanical view of the two ideas. The meaning of the invariance conjecture for the polymer solution systems is clarified by introducing the coarse-grained picture and the renormalization hypothesis for the parameters in those systems. We have improved the naïve invariance conjecture and have obtained the result that the form of the invariant local free energy with respect to the scale change is not the same form as the FH free energy. A generalization by introducing some renormalization parameters is required. The free energy of mixing renormalized by the spatial variation is obtained by increasing the coarse-grained scale to the system size. Then, the generalized version of the "renormalized" free energy in previous paper has been obtained. Also in the generalized version, the chain-length dependent correction term H in the interaction parameter g appears.

We have shown a basis of the nonanalytic Landau expansion by combining the field theoretical analysis and the scaling analysis for the free energy. Analyzing the renormalized free energy by the nonanalytic Landau expansion, the chain-length dependence of the correction term H in the uniform phase has been newly derived.

Considering the coexistence curve by the renormalized free energy, we have derived the expression of H and determined the "effective" part of the renormalized free energy giving us the phase diagram. Using the universal power law behaviors of the concentration difference and the diameter, the explicit function form of H was derived to obtain the correct coexistence curve in a wider temperature range. The function form was successfully applied to the systems of polystyrene in methylcyclohexane and poly(methyl methacrylate) in 3-octanone.

Appendix

Cell Free Energy of Mixing. Let us evaluate the functional integral $\tilde{Z}(J)$ by the saddle point method.[14] The saddle point $\varphi_{\mathrm{MF}}(\mathbf{r})$ is given by the solution of the equation $\delta\tilde{\Phi}/\delta\varphi(\mathbf{r}) = 0$. Hence,

$$-\kappa\nabla^2\varphi_{\mathrm{MF}}(\mathbf{r}) + \frac{1}{{a_0}^3}\frac{\partial\tilde{U}({a_0}^3\varphi_{\mathrm{MF}}(\mathbf{r}))}{\partial\varphi_{\mathrm{MF}}(\mathbf{r})} - J = 0 \qquad \text{(A1)}$$

Since $\varphi_{\mathrm{MF}}(\mathbf{r})$ is not expected to have the position dependence, the above equation is rewritten as

$$\frac{\partial\tilde{U}({a_0}^3\bar{\varphi}_{\mathrm{MF}})}{\partial {a_0}^3\bar{\varphi}_{\mathrm{MF}}} - J = 0 \qquad \text{(A2)}$$

In terms of $\bar{\varphi}_{\mathrm{MF}} = \bar{\varphi}_{\mathrm{MF}}(J)$, we have

$$\tilde{f}_{\mathrm{mix}}(J) = \tilde{U}({a_0}^3\bar{\varphi}_{\mathrm{MF}}) - J{a_0}^3\bar{\varphi}_{\mathrm{MF}} \qquad \text{(A3)}$$

Then, eq 19 is rewritten as

$$\left(\frac{\partial\tilde{U}({a_0}^3\bar{\varphi}_{\mathrm{MF}})}{\partial\bar{\varphi}_{\mathrm{MF}}} - {a_0}^3 J_\phi\right)\frac{\partial\bar{\varphi}_{\mathrm{MF}}}{\partial J_\phi} = {a_0}^3\bar{\varphi}_{\mathrm{MF}} - \phi \qquad \text{(A4)}$$

Since eq A2 is satisfied for $J = J_\phi$, eq A4 shows $\phi = a_0{}^3\bar{\varphi}_{\mathrm{MF}}$. Hence, from eqs 14, A2, and A3, we have

$$f_{\mathrm{mix}}(\phi) = \tilde{U}(\phi) \qquad \text{(A5)}$$

Thus, the cell free energy of mixing $\tilde{U}(\phi)$ is equivalent to that evaluated by the saddle point approximation.

Let the FH free energy f_{FH} be derived by the saddle point approximation of the more precise theory expressed by eqs 14–18. Then, the cell free energy of mixing in the precise theory and the FH free energy should be expressed in the same form. This means that the cell free energy of mixing is expressed in terms of the Koningsveld–Kleintjens (KK) type parameters, $\hat{a}$, $\{\hat{b}_j\}_{j=0,1,2}$, $\hat{c}$ independent of the temperature and the chain length *in the coarse-grained picture*. It should be noted, however, that the KK parameters in the cell free energy are "bare" and those in the FH theory are "renormalized". The temperature T is *not* renormalized since it, as well as the volume fraction ϕ, is the thermodynamic macroscopic parameter; the temperature in the coarse-grained model is equivalent to that in the microscopic model. As discussed in section II, the renormalization of the KK parameters is performed on the basis of the chain length dependence of the critical point, $T_c = t(P)$ and $\phi_c = u(P)$. Then, the chain length P should be free from the renormalization; the chain length in the coarse-grained model is equivalent to that in the microscopic model. Hence, in terms of the temperature T and the chain length P introduced in the microscopic model as the thermodynamic parameters, and the bare KK parameters independent of T and P, the cell free energy of mixing is expressed as eqs 20–22.

Derivation of Novel Expansion Form of Effective Potential. On the basis of the ϕ^4-theory, the expansion form for the effective potential (32) in the uniform phase region is obtained as

$$f_{\mathrm{eff}} = \Gamma_0(\tau) + \sum_{N=1}^{\infty} \frac{1}{(2N)!} \Gamma^{(2N)}(\tau) \Delta\phi^{2N} \tag{A6}$$

where $\Gamma_0(\tau)$ is the value of the effective potential at $\phi = \phi_c$, $\Gamma^{(2N)}(\tau)$ is the vertex function with zero momentum and $\Delta\phi = \phi - \phi_c$.[14] From this we have

$$\frac{\partial f_{\mathrm{eff}}}{\partial \phi} \equiv f^{(1)}_{\mathrm{eff}} = \sum_{N=1}^{\infty} \frac{1}{(2N-1)!} \Gamma^{(2N)}(\tau) \Delta\phi^{2N-1} \tag{A7}$$

Widom has proposed a scaling form[15]

$$f^{(1)}_{\mathrm{eff}} = \Delta\phi^{\delta} f_1(\tau/\Delta\phi^{1/\beta}) \tag{A8}$$

where the function $f_1(x)$ is analytic in the homogeneous region. Griffiths has derived an expansion form of the function $f_1(x)$ for large x on the basis of the analyticity[16]

$$f_1(x) = \sum_{n=1}^{\infty} \eta_n x^{\beta(\delta+1-2n)} \tag{A9}$$

By the ϵ-expansion method, Brezin et al. have verified the expansion.[17] Substituting (A9) into (A8), we have

$$f^{(1)}_{\mathrm{eff}} = \sum_{n=1}^{\infty} \eta_n \tau^{\beta(\delta+1-2n)} \Delta\phi^{2n-1} \tag{A10}$$

Comparing the above with eq A7, we derive the "formal" expression of the vertex function:[18]

$$\Gamma_N(\tau) = (2N-1)! \eta_N \tau^{\beta(\delta+1-2N)} \tag{A11}$$

From (A6) and (A11), we have the expansion form of f_{eff} near the critical point:

$$f_{\mathrm{eff}} = \Gamma_0(\tau) + \sum_{N=1}^{\infty} \frac{1}{2N} \eta_N \tau^{\beta(\delta+1-2N)} \Delta\phi^{2N} \tag{A12}$$

For a fixed $\Delta\phi$, the terms with $N > 3$ in the summation diverge when τ approaches zero. Of course, this divergence does not show the divergence of f_{eff} but show the invalidity of the expansion in the limit. Let us introduce a function which is finite near and at $\tau = 0$

$$q(\tau,\Delta\phi) = \Delta\phi^{\delta+1} f_2(\tau/\Delta\phi^{1/\beta}) \tag{A13}$$

with[16]

$$f_2(x) = \beta\left\{\frac{h_0}{\beta(\delta+1)} + \frac{h_1 x}{\beta(\delta+1)-1} - x\left|x\right|^{\beta(\delta+1)-1} \int_0^x \frac{f_1(y) - h_0 - h_1 y}{|y|^{\beta(\delta+1)+1}} \mathrm{d}y\right\} - \frac{1}{2}\eta_1 x|x|^{\beta(\delta-1)-1} - \frac{1}{4}\eta_2 |x|^{\beta(\delta-3)} \tag{A14}$$

where h_j ($j = 0, 1$) is the coefficient of the following series expansion convergent near $x = 0$:

$$f_1(x) = \sum_{j=0}^{\infty} h_j\, x^{j} \tag{A15}$$

Using $q(\tau,\Delta\phi)$, we have the expansion form of the effective potential eq 33.

References and Notes

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