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Quantitative Theory of the Globule-to-Coil Transition. 3. Globule–Globule Interaction and Polymer Solution Binodal and Spinodal Curves in the Globular Range

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ABSTRACT: In this series of papers new results and a brief review of the current state of mean-field theories of the condensed globular state and of the globule-to-coil transition in the Θ-region for a linear, homogeneous, noncharged macromolecule are presented. As a basis of our consideration, we use both Lifshitz's theory and interpolation Flory-type theory. Complete quantitative theoretical results are obtained and compared with experimental data. In this paper (the third in this series) we analyze quantitatively interactions between chains in a poor solvent. At first we calculate density distributions and the interaction free energy for two globules equilibrated at an arbitrary distance ζ from each other; a special method has been used for this calculation based on the introduction of two auxiliary uniform fields which do not perturb the globules' inner structures but fix the value of ζ. Then we calculate the corresponding pair virial coefficient and the coexistence binodal curve on the T–c plane in the second virial approximation. We estimate also the spinodal T–c curve.

1. Introduction

In accordance with the outline of the series of papers,[1] here we discuss the problems connected with chain–chain interaction in a poor solvent. Different aspects of the problem were discussed theoretically in refs 2–8. There exists also a number of experimental works dealing with polymer precipitation in a poor solvent (see, for example, refs 9–13). The detailed quantitative theory, presented below, will be compared with experiments in the fourth paper of this series.

The key point of our approach in this paper is the evaluation of the pair virial coefficient of chain–chain interaction. The value of this coefficient can be expressed[2] as

$$A_2 = \frac{1}{2}\int\left\{1 - \exp\left[\frac{2F_{\mathrm{single}} - F_{\mathrm{pair}}(\zeta)}{T}\right]\right\}d^3\zeta \qquad (1)$$

Here F_{single} and $F_{\mathrm{pair}}(\zeta)$ mean the values of free energy respectively of a single chain equilibrated in the solvent under some given conditions and of two chains placed at a distance ζ from each other in the same solvent and under the same conditions; T stands for the temperature. (The usual chemical definition of A_2 differs from this one as $A_2^{(\mathrm{usual})} = (N_{\mathrm{A}}/M^2)A_2$, where M is the molecular weight and N_{A} is Avogadro's number.) The difference

$$u_{\mathrm{eff}}(\zeta) \equiv F_{\mathrm{pair}}(\zeta) - 2F_{\mathrm{single}}$$

can be interpreted as the effective potential energy of chain–chain interaction through the solvent medium.

This paper is organized as follows. In section 2, in order to calculate the pair free energy $F_{\mathrm{pair}}(\zeta)$, we analyze the state and the density spatial distribution of two chains placed at a fixed distance ζ from each other. Using these results, we calculate and analyze in section 3 the second virial coefficient (eq 1) of globule–globule interaction. At last, section 4 is devoted to the binodal (coexistence) and spinodal curves of a polymer solution.

2. Effective Potential of Chain–Chain Interactions in a Poor Solvent

Let us consider the system of two polymer chains of the same chemical nature in a sufficiently poor solvent, where each chain itself should collapse to the globular state. In the most interesting and nontrivial case the distance ζ between globule mass centers is comparable with their own size R. Due to the attraction of monomers in this case both globules should draw out to each other.

Such a drawn-out structure cannot be described in terms of a single scalar order parameter like the expansion factor α. For example, this is why some noncontrolled and nonobvious suppositions were inevitable in ref 4, where attempts were made to describe intermolecular interactions in the framework of Flory-type theory.

Our plan is to use Lifshitz-type theory. The spatial density distribution, which is the order parameter in this theory, can be used, of course, for the structure description of a stressed nonspherical globule, but the following problem exists. Lifshitz-type theory is of the self-consistent type, and, therefore, it is based on a free energy minimization procedure. The two-chain free energy $F_{\mathrm{pair}}(\zeta)$, however, has no minima at any nonzero distance ζ. The free energy minima correspond only to the globules merging with each other, i.e., to $\zeta = 0$.

Our solution of this problem can be explained in two ways: physically and mathematically. From the physical point of view, the idea is to introduce two fictitious uniform fields; the first field acts on a first chain, and the second field acts on another chain. These two fields pull the globules in opposite directions. Being uniform, these fields do not perturb the globules' inner structures. In the meantime, the values of these fields can be chosen in such a way that they cause the given value of the distance between globules.

Let us consider our approach in more detail. As usual, the free energy of our system in the framework of mean-field theory should be written as

$$F_{\mathrm{pair}} = F_{\mathrm{pair}}^{(\mathrm{int})} + F_{\mathrm{pair}}^{(\mathrm{el})} \qquad (2)$$

where $F_{\mathrm{pair}}^{(\mathrm{int})}$ describes volume interactions between monomers and $F_{\mathrm{pair}}^{(\mathrm{el})} = -TS_{\mathrm{pair}}$ corresponds to the conformational entropy of chains.

The interaction energy $F^{(\mathrm{int})}$ depends on the total density of the monomers only, since all the monomers of both chains are identical. If we denote the spatial density distribution of the monomers of the chain number i (i =

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1 and 2) as $n_i(\mathbf{X})$, then the total density will be

$$n(\mathbf{X}) = n_1(\mathbf{X}) + n_2(\mathbf{X})$$

and, therefore, the interaction energy can be written in the form

$$F^{(\mathrm{int})} = \int f^*(n(\mathbf{X}))\, \mathrm{d}^3x \qquad (3)$$

Here, as in the previous paper of this series,[1] $f^*(n(\mathbf{X})) \cong TBn^2 + TCn^3 + ...$ is the interaction energy of the link system, and B and C are the interaction constants of quasi-monomers.

The elastic energy (i.e., polymer conformational entropy), contrary to the interaction energy, depends for each chain on its own density only:

$$S_{\mathrm{pair}} = S_{\mathrm{single}}\{n_1(\mathbf{X})\} + S_{\mathrm{single}}\{n_2(\mathbf{X})\} \qquad (4)$$

where the standard Lifshitz expression[14] is valid for single-chain entropies:

$$S_{\mathrm{single}}\{n_i(\mathbf{X})\} = \int n_i(\mathbf{X}) \ln (\hat{g}\psi_i/\psi_i) \mathrm{d}^3x \cong a^2 \int \psi_i(\mathbf{X})\, \Delta\psi_i(\mathbf{X})\, \mathrm{d}^3x \qquad (4a)$$

$$n_i(\mathbf{X}) \cong \psi_i^{\,2}(\mathbf{X})$$

$\hat{g} \cong 1 + a^2\Delta$ stands for the linear memory operator, and a is the link size for the standard Gaussian model of the chain.

Three conditions should be taken into account for the free energy minimization: in addition to the ordinary requirement of conservation of the total number of monomers for each chain

$$\int n_i(\mathbf{X})\, \mathrm{d}^3x = N_i \quad (i = 1 \text{ and } 2)$$

the distance between the mass centers of the two chains must be fixed:

$$\vec{\zeta} = \frac{\int \mathbf{X} n_1(\mathbf{X})\, \mathrm{d}^3x}{N_1} - \frac{\int \mathbf{X} n_2(\mathbf{X})\, \mathrm{d}^3x}{N_2}$$

Therefore, three Lagrange multipliers (λ_1, λ_2, and $\mathbf{E}$) should be introduced, and the following effective potential should be minimized:

$$G = F^{(\mathrm{int})} - TS_1 - TS_2 - \lambda_1\left[\int n_1(\mathbf{X})\, \mathrm{d}^3x - N_1\right] - \lambda_2\left[\int n_2(\mathbf{X})\, \mathrm{d}^3x - N_2\right] - \mathbf{E}\left[\frac{\int \mathbf{X} n_1(\mathbf{X})\, \mathrm{d}^3x}{N_1} - \frac{\int \mathbf{X} n_2(\mathbf{X})\, \mathrm{d}^3x}{N_2} - \vec{\zeta}\right] \qquad (5)$$

The last term plays the role of the energy of chains in the external uniform field $\pm\mathbf{E}$, and this is the mathematical nature of our approach.

Further calculations can be done automatically (see the appendix for details): (I) potential (eq 5) minimization leads to the corresponding Euler equations (eq A1) for the equilibrium density distribution of both chains; (II) these equations can be simplified by the virial expansion and by neglect of more than three-particle terms; (III) the use of dimensionless variables gives some additional simplifications; (IV) the resulting equations of the nonlinear Schroedinger type (eq A3) are simple enough for numerical solution; (V) substitution of the calculated densities $n_i(\mathbf{X})$ into the free energy $F_{\mathrm{pair}}\{n_i\}$ expression allows us to obtain the results of interest on $F_{\mathrm{pair}}(\zeta)$ or $u_{\mathrm{eff}}(\zeta)$.

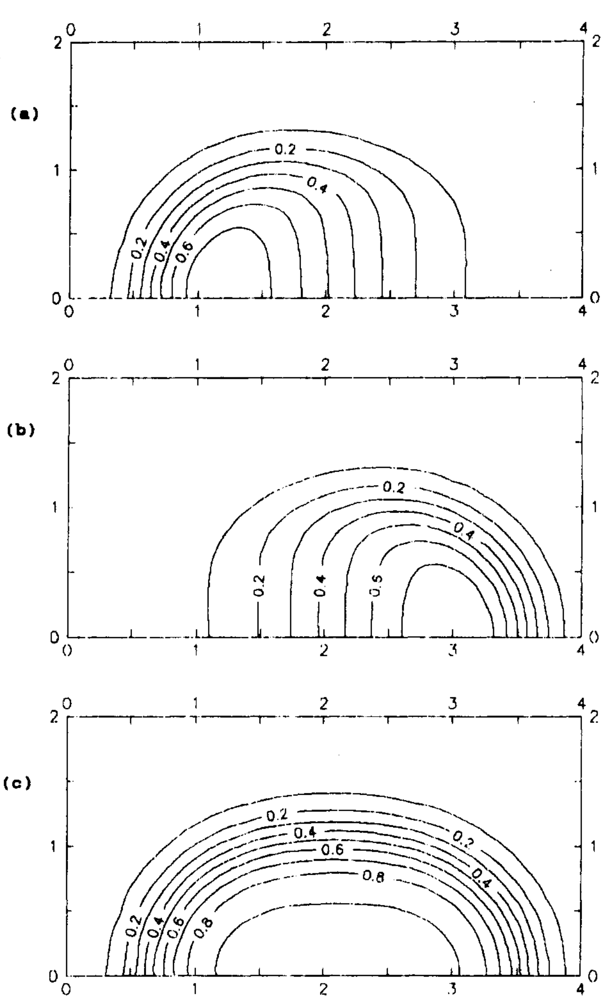

Figure 1. Density distributions (presented as level curves on a half-plane) of two polymer globules placed at a fixed nonzero distance from each other for the reduced temperature $t \simeq -30$: (a) the first chain, (b) the second chain, (c) their summary density.

We restrict ourselves to the case of two chains of the same length $N_1 = N_2 = N$. The results for this case are as follows:

A. The theory, for the single-chain case, remains to be a three-parameter one. It involves a one-dimensional parameter and two dimensionless ones, namely, the values of (1) the Gaussian-coil state size of the chain $aN^{1/2}$, (2) the reduced temperature

$$t = \frac{BN^{1/2}}{C^{1/4}(a^2/6)^{3/4}} \sim \frac{T-\Theta}{\Theta}N^{1/2} \qquad (6)$$

and (3) the chain stiffness parameter $\sqrt{C}/a^3$ (it is proportional to $(d/l)^{3/2}$, where d and l are the diameter and the effective segment of the chain).

B. The calculated density distributions for two similar interacting globules are shown in Figure 1 for a certain nonzero distance ζ and the reduced temperature $t \simeq -30$.

C. The two-chain free energy $F_{\mathrm{pair}}(\zeta)$, just like the single-chain one F_{single}, scales as $a^3/\sqrt{C}$ with chain stiffness and can be written in the form

$$F_{\mathrm{pair}}(\zeta) = T(a^3/\sqrt{C})\tilde{F}_{\mathrm{pair}}(t,\delta) \qquad (7)$$

Here $\tilde{F}$ is a dimensionless function, which depends on the dimensionless values of t (eq 6) and distance $\delta \sim \zeta$. We remind everyone that[1]

$$F_{\mathrm{single}} = T(a^3/\sqrt{C})\tilde{F}_{\mathrm{single}}(t)$$

D. Calculated profiles of the effective chain–chain interaction potential are shown in Figure 2 for two values

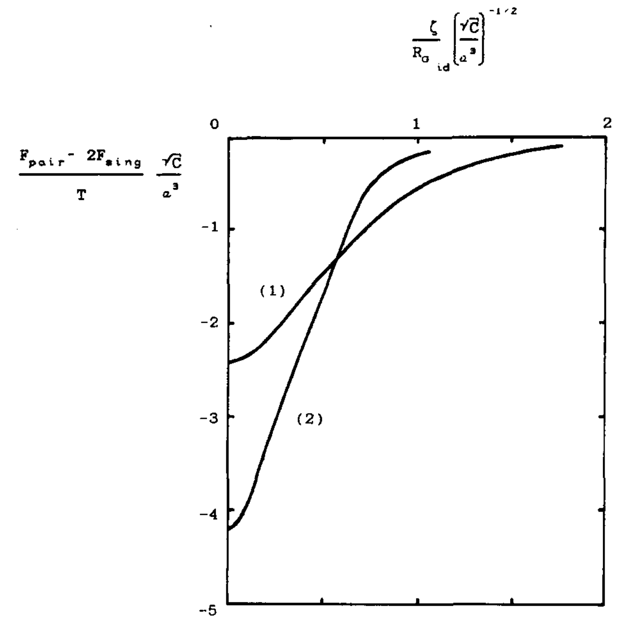

Figure 2. Effective potential of chain–chain interactions $u_{\rm eff}(\zeta) \equiv F_{\rm pair}(\zeta) - 2F_{\rm single}$ vs distance ζ using dimensionless variables for two values of the reduced temperature t = −24 (1) and −34 (2) in the globular range.

of reduced temperature, t = −24 and −34. Both these temperatures lie in the globular range, since the coil–globule transition point corresponds[1] to $t = t_{\rm tr} \cong -10.2$.

3. Pair Virial Coefficient of Chain–Chain Interaction

In the framework of three-parametric theory, the expression in eq 1 for the chain coupling constant A_2 can be rewritten as

$$A_2 = N^2Bh(t,\sqrt{C}/a^3) = t(\sqrt{C}/a^3)^{1/2}(6^{3/4})R_{G_{\rm id}}{}^3h(t,\sqrt{C}/a^3) \quad (8)$$

where $R_{G_{\rm id}}$ is the root-mean-square radius of gyration.

In the neighborhood of the Θ-point, the value of dimensionless coefficient h was earlier calculated using the perturbation theory:[2]

$$h = 1 - 0.4931t(\sqrt{C}/a^3)^{1/2}$$

For the globular range we calculate this value in this paper using the above-discussed results dealing with $F_{\rm pair}(\zeta)$ determination. Our results are shown in Figure 3 on a semilogarithmic scale log $(-A_2/R_{G_{\rm id}}{}^3)$ versus t for a few realistic values of chain stiffness.

4. Binodal and Spinodal Curves of a Polymer Solution

The above-obtained results allow us to analyze quantitatively the mean-field thermodynamic theory of the precipitation of a monodisperse polymer solution in a poor solvent. Of course, the mean-field approach can be valid far enough from the critical point only.

The opposite limiting case of the critical point neighborhood, where the scaling approach is valid, has been considered by Sanchez[6] and by Chu and Wang[7] (see also refs 3 and 8). They generalized the ordinary scaling theory of the liquid–gas critical point for the case when molecules are long chains with $N \gg 1$. The results of these papers were formulated in terms of the scaling combination of parameters of the type ϵN^b, where $b = 0.313 \pm 0.004$, while ϵ is the dimensionless deviation from the critical point $T_{\rm cr}$ but not from the Θ- point; i.e.

$$\epsilon = (T_{\rm cr} - T)/T_{\rm cr} = (\tau_{\rm cr} - \tau)/(\tau_{\rm cr} + 1), \quad \tau = (T - \Theta)/\Theta$$

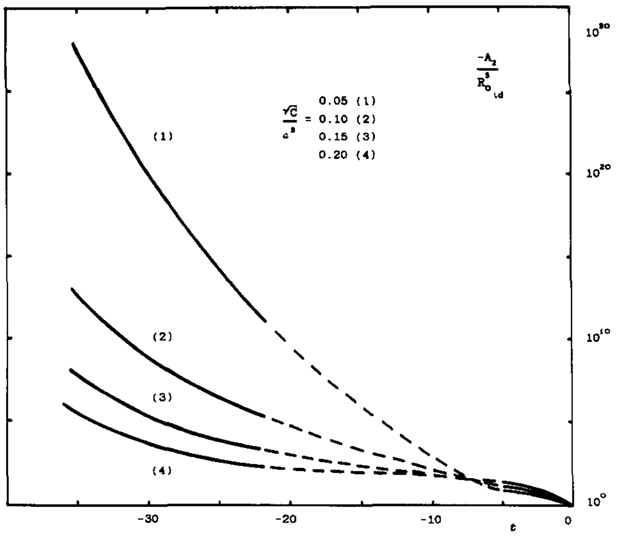

Figure 3. Pair virial coefficient A_2 of chain–chain interactions, normalized to the ideal Gaussian-coil volume, vs the reduced temperature t for the following realistic values of the chain stiffness parameter: $\sqrt{C}/a^3$ = 0.05 (1), 0.10 (2), 0.15 (3), and 0.20 (4). Dashed parts of the curves are simple interpolations between the coil region, where we have used the perturbation theory results,[2] and the globular region, where we have shown the results of this paper.

The form of the coexistence curve in ref 6 is valid for $\epsilon < 0.075/N^{0.3}$. This strong restriction was weakened in ref 7 up to $\epsilon < 0.3/N^{0.3}$. Nevertheless, these values of ϵ are essentially insufficient for the globule range description, which is of interest to us here.

Thus, now we consider the mean-field theory of polymer solution precipitation, and we focus on the case when the dilute phase consists of the suspended globules. Our theory differs from the classical Flory–Huggins one with respect to the single-chain free energy in the dilute phase only. Really, the standard conditions of phase equilibrium require the coincidence of polymer osmotic pressures ($\pi_{\rm pol}$) and chemical potentials ($\mu_{\rm pol}$) in both coexisting phases:

$$\pi_{\rm pol} = \left(\frac{c}{N}\mu_{\rm pol} - f_{\rm pol}\right)_{c=c_{\rm dil}} = \left(\frac{c}{N}\mu_{\rm pol} - f_{\rm pol}\right)_{c=c_{\rm conc}} \quad (9)$$

$$\mu_{\rm pol} = N\frac{\partial f_{\rm pol}}{\partial c}\Big|_{c=c_{\rm dil}} = N\frac{\partial f_{\rm pol}}{\partial c}\Big|_{c=c_{\rm conc}} \quad (10)$$

Here, we refer to the polymer solvent free energy per unit volume as $f_{\rm pol}$, and c is the average number of polymer links per unit volume in dilute ($c_{\rm dil}$) and concentrated ($c_{\rm conc}$) phases. (Accordingly, c/N is the number of polymers per unit volume.)

The concentrated phase, in the context of this paper, can be considered as a "very large globule", so that

$$f_{\rm pol}(c)|_{c=c_{\rm conc}} \cong T\frac{c_{\rm conc}}{N}\ln\frac{c_{\rm conc}}{Ne} + \frac{c_{\rm conc}}{N}F_{\rm single}^{\rm (vol\ appr)}(c_{\rm conc}) \quad (11)$$

where

$$F_{\rm single}^{\rm (vol\ appr)}(c) = (N/c)f^*(c) \cong T(N/c)(Bc^2 + Cc^3)$$

is the single globule free energy in the so-called volume approximation,[1,14] neglecting globule surface energy, which is caused by chain finiteness. This approximation is just valid for a macroscopic precipitate. Naturally, the ex-

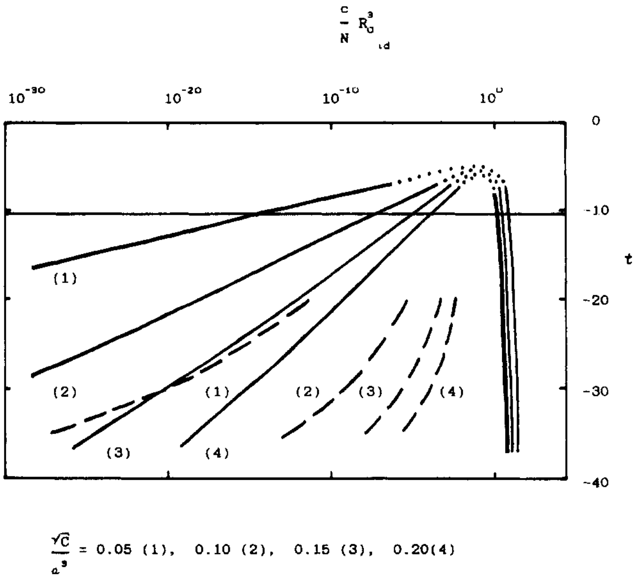

Figure 4. Phase diagram of a polymer solution for the following typical values of the chain stiffness parameter: $\sqrt{C}/a^3 = 0.05$ (1), 0.10 (2), 0.15 (3), and 0.20 (4). The solid curves are binodals, and the dashed ones are spinodals. The dotted parts of the binodal curves show schematically the critical point neighborhood, where use of the mean-field theory is not valid.

pression in eq 11 is practically equivalent to the well-known Flory–Huggins formula.[3]

However, a novelty of our approach concerns the dilute phase which is nearly an ideal "gas" but consists of globules instead of coils; therefore

$$f_{\text{pol}}(c)|_{c=c_{\text{dil}}} = T\frac{c_{\text{dil}}}{N}\ln\frac{c_{\text{dil}}}{Ne} + TA_2\left(\frac{c_{\text{dil}}}{N}\right)^2 + \frac{c_{\text{dil}}}{N}F_{\text{single}}(t) \quad (12)$$

Now we can use the results of the quantitative globule theory for single-chain free energy F_{single}, as well as for pair virial coefficient A_2.

Some technical details, concerning the solution of eqs 9 and 10, can be found in the appendix. The results, representing the coexisting curve, i.e., binodal, on the phase diagram in the globular range can be expressed as

$$c_{\text{conc}} \cong -B/2C, \quad c_{\text{dil}} \cong c_{\text{conc}} \times \exp\left[\frac{1}{T}(F_{\text{single}}^{\text{(vol appr)}}(t) - F_{\text{single}}(t))\right] - \frac{2A_2}{N}c_{\text{conc}}^{\ 2}\exp\left[\frac{2}{T}(F_{\text{single}}^{\text{(vol appr)}}(t) - F_{\text{single}}(t))\right] \quad (13)$$

where

$$F_{\text{single}}^{\text{(vol appr)}}(t) = F_{\text{single}}^{\text{(vol appr)}}(c_{\text{conc}}(t)) \cong -T\frac{a^3}{\sqrt{C}}\frac{t^2}{(4)(6^{3/2})}$$

The function $F_{\text{single}}(t)$ was calculated in our previous work;[1] A_2 is described above.

As a rule, however, it is difficult to establish from an experiment whether equilibrium or not quite equilibrium phases are observed in one or another cases. This is why the spinodal curve limit, as well as the binodal one, of uniform phase stability is of interest. The general spinodal equation, as is well-known, is of the type

$$\partial^2 f_{\text{pol}}(c)/\partial c^2 = 0 \quad (14)$$

Of course, the second virial approximation (eq 12) for $f_{\text{pol}}(c)$ is not sufficient for spinodal curve quantitative analyses. Nevertheless, it can be used for the simplest estimation, and this estimation is the only one available now. Substitution of the f_{pol} expression (eq 12) into spinodal eq 14 gives

$$c_{\text{dil}}^{\text{(spin.)}} = -N/2A_2 \quad (15)$$

but it is really an overestimation so that

$$c_{\text{dil}}^{\text{(spin.)}} \lesssim -N/2A_2 \quad (15a)$$

The phase diagram of a polymer solution is shown in Figure 4 on a semilogarithmic scale for a few typical values of the chain stiffness parameter $\sqrt{C}/a^3$. Solid and dashed lines correspond to binodal curves (eq 13) and to spinodal curves (eq 15), respectively.

In the fourth paper of this series we compare the phase diagram of Figure 4 with some experimental results.

Appendix: Calculation of the Density Distribution for Two Interacting Globules

Minimization of the effective potential (eq 5) with respect to the density distributions $n_i(\mathbf{X})$ (i = 1 and 2) with the above-discussed additional conditions leads to the following equations:

$$(a^2/6)\Delta\psi_i(\mathbf{X}) = [\exp((\mu_i^{**} - \lambda_i)/T) - 1]\psi_i(\mathbf{X})$$

$$n_i(\mathbf{X}) = \psi_i^{\ 2}(\mathbf{X})\exp(\mu_i^{**}/T)$$

$$N_i = \int n_i(\mathbf{X})\mathrm{d}^3x$$

$$\zeta = |N_1^{\ -1}\int n_1(\mathbf{X})\,\mathbf{X}\,\mathrm{d}^3x - N_2^{\ -1}\int n_2(\mathbf{X})\,\mathbf{X}\,\mathrm{d}^3x| \quad (\text{A1})$$

Here $\psi_i(\mathbf{X})$ can be considered as eigenfunctions, Δ stands for Laplacian operator, and

$$\mu_i^{**} = \mu^*(n_1+n_2) - (\mathbf{E}_i\mathbf{X}) \quad (\text{A2})$$

$\mu^*(n)$ depends on the total monomer density and is the self-consistent field; it is determined by volume interactions between monomers. The second term in eq A2 corresponds to the external uniform fields, which fix the distance ζ between the mass centers of the two chains.

For $\zeta \to \infty$, i.e., $\mathbf{E}_i \equiv 0$ and $\mu_i^{**} = \mu^*(n_i)$, the equations in eq A1 are the same ones as those for a single globule.[14] This fact allows us to use the same virial expansion (neglect of more than three-particle terms) and the same dimensionless variables as in ref 1. Therefore, eqs A1 and A2 take the following form:

$$\Delta\chi_i = \chi_i[\varkappa_i(2 - 3\varkappa_i) - 2\varkappa_i(\chi_1^{\ 2} + \chi_2^{\ 2}) + 3\varkappa_i^{\ 2}(\chi_1^{\ 2} + \chi_2^{\ 2})^2 - (\vec{e}\mathbf{r})]$$

$$\varkappa_i t_i^{\ -2}\int \chi_i^{\ 2}(\mathbf{r})\,\mathrm{d}^3r = 1$$

$$\delta = |\varkappa_1 t_1^{\ -2}\int \mathbf{r}\chi_1^{\ 2}(\mathbf{r})\,\mathrm{d}^3r - \varkappa_2 t_2^{\ -2}\int \mathbf{r}\chi_2^{\ 2}(\mathbf{r})\,\mathrm{d}^3\mathbf{r}|$$

$$t_1/t_2 = (N_1/N_2)^{1/2} \quad (i = 1 \text{ and } 2) \quad (\text{A3})$$

Here we have used the following dimensionless variables: (i) position vector $\mathbf{r} = \mathbf{X}|B|/C^{1/2}(a^2/6)^{1/2}$ and the distance between mass centers $\delta = \zeta|B|/C^{1/2}(a^2/6)^{1/2}$; (ii) parameter $\varkappa_i$ defined so that $\lambda_i \equiv \mu^*(\tilde{n}_i) \simeq 2\tilde{n}_iTB + 3\tilde{n}_i^2TC$, where $\tilde{n}_i = -\varkappa_iB/C$, and $\vec{e} = (\vec{E}/T)[C^{3/2}/(-B)^3](a/6^{1/2})$; (iii) densities $\chi_i^2(\mathbf{r}) \equiv n_i(\mathbf{X})/\tilde{n}_i$.

Now we consider two polymers that are the same not only in chemical structure but also in $N_1 = N_2$. This means that $t_1 = t_2$, $\varkappa_1 = \varkappa_2$, and the spatial density distributions

($\chi_1(\mathbf{r})$ and $\chi_2(\mathbf{r})$) are under mirror symmetry to each other with respect to a plane, which is perpendicular to the line connecting the mass centers of the two chains. This fact allows us to decouple the equations in eq A3 (for two macromolecules) into independent ones for every macromolecule.

It is natural for the following calculations to use the cylindrical coordinate system. Let us remind everyone that for a single polymer chain the problem was of the one-dimensional type because we have used the spherical coordinate system. If z is the coordinate axis along the line connecting the centers of our two chains and r is the distance from a point to this z-axis, then

$$\chi_1(\mathbf{r}) \equiv \chi_1(r,z), \quad \chi_2(\mathbf{r}) = \chi_1(r,2z_0-z) \tag{A4}$$

where z_0 is the symmetry plane coordinate, which depends on the zero-point choice only. Equation A3 can now be rewritten as

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}\right)\chi(r,z) = \chi(r,z)\,\{\varkappa(2-3\varkappa) - 2\varkappa[\chi^2(r,z) + \chi^2(r,2z_0-z)] + 3\varkappa^2[\chi^2(r,z) + \chi^2(r,2z_0-z)]^2 - ez\}$$

$$2\pi\varkappa t^{-2}\int_0^\infty \int_{-\infty}^{\infty}\chi^2(r,z)\, r\, \mathrm{d}r\, \mathrm{d}z = 1 \tag{A5}$$

$$2\pi\varkappa t^{-2}\int_0^\infty \int_{-\infty}^{\infty}\chi^2(r,z)\, r\, z\, \mathrm{d}r\, \mathrm{d}z = z_0 - \delta/2$$

with the following additional conditions: (1) $\partial\chi/\phi r|_{r=0} = 0$; (2) $\chi(r,z)$ decreases exponentially at $r \to \infty$ or $(z - z_0) \to \pm\infty$, where z_c is the mass center coordinate.

Equations A4 and A5 describe the density distribution for every one of the two contacting polymer globules as a function of the reduced temperature t and the dimensionless distance δ in the inexplicit form, which, however, is convenient for standard numerical computations.

Taking into account eqs 3, 4, and A1, the free energy (eq 2) of the two macromolecules can be written as

$$F_{\text{pair}} = 2N\lambda - \int p^*(n_1+n_2)\, \mathrm{d}^3x \tag{A6}$$

where $p^*(n) = n\mu^*(n) - f^*(n) \cong TBn^2 + 2TCn^3$ is the pressure of the equivalent system of separate polymer links without the ideal gas term. Of course, at the distance between polymers $\zeta \to \infty$ eq A6 corresponds to double the free energy of a single macromolecule. Using the above-introduced dimensionless variables, eq A6 takes the form of eq 7 with

$$\tilde{F}_{\text{pair}}(t,\delta) = -6^{-3/2}\varkappa\{2(2-3\varkappa)t^2 - \varkappa\int[(\chi_1^{\;2} + \chi_2^{\;2})^2 - 2\varkappa(\chi_1^{\;2} + \chi_2^{\;2})^3]\, \mathrm{d}^3r\} \tag{A7}$$

where eqs A4 and A5 are valid for the χ_1 and χ_2 functions.

The pair virial coefficient A_2 of chain–chain interaction is described by eqs 1 and 8. For the globular range in our dimensionless quantities the function $h(t,\sqrt{C}/a^3)$ (in eq 8) is

$$h = -6^{3/2}t^{-4}\frac{\sqrt{C}}{a^3}\frac{1}{2}\int\left\{1 - \exp\left[\frac{a^3}{\sqrt{C}}(2\tilde{F}_{\text{single}}(t) - \tilde{F}_{\text{pair}}(t,\delta))\right]\right\}\mathrm{d}^3\delta \tag{A8}$$

For the coexistence curves of a polymer solution it is convenient to use the dimensionless density

$$Y \equiv (c/N)R_{G_{\text{id}}}^{\;\;3}$$

and the parameter $w \equiv 6^{3/2}(\sqrt{C}/a^3)$. Then from eq 10 we obtain

$$Y_{\text{dil}} \cong Y_{\text{conc}} + tw^{1/2}Y_{\text{conc}}^{\;\;2} + 2w^2Y_{\text{conc}}^{\;\;3}$$

Hence, for the concentrated region of the coexistence curve, we have

$$Y_{\text{conc}} \cong -\frac{t}{4w^{3/2}}\left\{1 + \left[1 - \frac{8w}{t^2}(1-\epsilon)\right]^{1/2}\right\} \tag{A9}$$

where $\epsilon \equiv Y_{\text{dil}}/Y_{\text{conc}} \ll 1$ is a negligible parameter in the globular and transition ranges that are under consideration. It is natural that

$$Y_{\text{conc}}|_{t\to-\infty} \cong -t/2w^{3/2} \sim -\tau N^{1/2}$$

For the dilute region from eq 9 or eq 13 we can obtain the following expression:

$$Y_{\text{dil}} \cong Y_{\text{conc}}\exp\left[\frac{1}{T}(F_{\text{single}}^{(\text{vol appr})}(t) - F_{\text{single}}(t))\right] - (2)(6^{3/4})th(t,\sqrt{C}/a^3)\left[\frac{\sqrt{C}}{a^3}\right]^{1/2}Y_{\text{conc}}^{\;\;2} \times \exp\left[\frac{2}{T}(F_{\text{single}}^{(\text{vol appr})}(t) - F_{\text{single}}(t))\right] \tag{A10}$$

The spinodal curve in eq 15 (in dimensionless values of this paper) takes the form

$$Y_{\text{dil}}^{(\text{spin.})} = [(6^{3/4})(2)(\sqrt{C}/a^3)^{1/2}(-t)h(t,\sqrt{C}/a^3)]^{-1} \tag{A11}$$

References and Notes

(1) Parts 1 and 2: Grosberg, A. Yu.; Kuznetsov, D. V. *Macromolecules*, previous papers in this issue.

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