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Theory of Phase Equilibria in Mixtures of Copolymers and Homopolymers. 2. Interfaces near the Consolute Point

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ABSTRACT: A simple mean field formalism is developed to study the interfacial properties of nearly compatible mixtures of two homopolymers A and B and a copolymer A–B. The interfacial composition profile and interfacial tension are calculated analytically, and the interfacial activity of copolymer additives is discussed. The mechanism involved is quite different from that evoked for highly immiscible species: the dominant effect is the presence of copolymer chains in both A-monomer-rich and B-monomer-rich phases. The effect of preferential location of copolymer chains at the interface plays only a role for high copolymer contents. The reduction of interfacial tension is shown to be stronger in the case of diblock rather than multiblock copolymer chains.

I. Introduction

Copolymer molecules may show an important interfacial activity when added into a multiphase system. For example, in the case of two immiscible low-molecular-weight liquids, copolymer chains act in a way analogous to that of classical nonionic or soap surfactants and may even lead to a microemulsion formation.[1–5] Another particular case of practical importance is a blend containing highly incompatible homopolymers.[6–13] It has been recognized that copolymer additives lower the interfacial tension[9,13] and, therefore, may facilitate phase dispersion and improve mechanical properties of blends.[14,15] The interfacial activity of copolymers has been attributed to their preferential location at the interface.[16] This interpretation has been confirmed recently by Noolandi and Hong, who have developed a detailed theory of interaces in a quaternary system, a solution in a good solvent of two highly incompatible homopolymers, and a diblock copolymer.[17] Actually, the calculation of interfacial density profiles has shown that the block copolymers locate at the interface and exclude the homopolymers from the interphase region.[17] However, the important question remained (cf. ref 10 and 18) whether the same effect will occur for a system in which the two homopolymers are relatively compatible. The present theory indicates that for nearly miscible species the copolymer chains still play an important emulsifying role although the mechanism involved is very different.

We will deal with a ternary amorphous blend containing two homopolymers A and B and a copolymer A–B. In a previous paper[19] the phase diagram of such a system has been discussed for different degrees of incompatibility of the chains. In particular, it has been concluded that in the case of nearly miscible species, on which we focus in the present paper, copolymer additives play an interesting compatibilizing role. First, the addition of copolymers displaces the critical point of demixing and may even cause a two-phase blend to become one phase. Second, the copolymer chains are present in both phases of the two-phase blend and favor a closer mixing of the chemical species A and B. Our aim here is to calculate both the interfacial concentration profile and the interfacial tension in order to extend the analysis of emulsifying properties of copolymer additives. We will compare the effectiveness of diblock and multiblock copolymers.

The essential problem encountered by microscopic theories of interfacial properties is to find the free energy of the nonhomogeneous system, i.e., to include the spatial density fluctuations. For a macromolecular system two equivalent mean field approaches have been hitherto applied. The first one uses the functional integral representation of the partition function, as introduced by Edwards.[25] When copolymers are present in the system, this method is not particularly convenient as it leads to a complex set of integrodifferential equations which requires complicated numerical methods to be solved.[17,23,24,26] The second method expresses the free energy in terms of monomer concentration correlation functions. The correlation functions are calculated in a self-consistent way within the random phase approximation introduced by de Gennes.[27,28] This method particularly adapted to study concentration profiles of diffuse interfaces[29,30] will be used in this work.

In section II we study monomer concentration fluctuations and find the free energy density of a nonhomogeneous system. Then in section III we calculate the composition profile and interfacial tension, focusing on the systems close to the critical point of demixing. Physical mechanisms underlying the emulsifying activity of copolymer chains are discussed in section IV.

II. Correlation Functions and Free Energy of a Nonuniform System

We study a liquid mixture composed of two flexible homopolymers A and B and a copolymer A–B. For the sake of simplicity we will deal with the symmetric case, assuming that all chains have the same polymerization index N and that each copolymer chain contains $N/2$ monomers A (B). Various types of copolymer structures (diblock, multiblock) will be considered but it will be supposed that the copolymer molecule is symmetric with

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respect to the interchange of monomers A and B (e.g., a periodic multiblock copolymer A–B–A–B–...–A–B with blocks containing the same number of monomers).

In a Flory–Huggins picture[31] the free energy density (per monomer) F_0 of a homogeneous phase may be approximated by[19,32]

$$F_0/k_{\rm B}T = \frac{1}{N}\sum_{i=1}^{3}\phi_i \ln \phi_i - \frac{1}{4}\chi(\phi_1 - \phi_2)^2 \qquad (1)$$

where $k_{\rm B}$ is the Boltzmann constant, T is the absolute temperature, and ϕ_1, ϕ_2, and ϕ_3 denote, respectively, the volume fraction of monomers of the homopolymer A, homopolymer B, and copolymer A–B. The effective interaction between two monomers A and B is equal to $k_{\rm B}T\chi$. In most cases χ is positive so that unlike species repel each other. In writing (1), we have neglected the compressibility of the melt; i.e., it has been assumed that $\phi_1 + \phi_2 + \phi_3 = 1$ at any point.

The phase diagram of the system strongly depends on the degree of incompatibility of the species characterized by the product χN.[19] We shall be concerned here with the nearly miscible case of $2 < \chi N < 6$. In this case a standard analysis of (1) predicts the existence of the critical point of demixing for

$$\phi_1^{(c)} = \phi_2^{(c)} = 1/(\chi N)$$
$$\phi_3^{(c)} = 1 - 2/(\chi N) \qquad (2)$$

For $\phi_3 > \phi_3^{(c)}$ homopolymers are miscible in all proportions. For smaller copolymer content ($\phi_3 < \phi_3^{(c)}$) a demixing into two phases, A-monomer rich and B-monomer rich, may occur. The concentrations of the components may be easily calculated by equating the chemical potentials in the two phases.[19]

In order to bring out the specific features of emulsifying activity of copolymers in the critical region we focus our considerations on systems with the average copolymer content ϕ close to the critical concentration $\phi_3^{(c)}$ ($\phi < \phi_3^{(c)}$). Then it is convenient to express the free energy density F_0 in terms of two independent variables ϵ and η:

$$\eta = \phi_1 - \phi_2$$
$$\epsilon = \phi_1 + \phi_2 + \phi - 1 \qquad (3)$$

In fact, because of the incompressibility assumption, two concentrations are sufficient to describe the local composition of the ternary blend. The quantity $-\epsilon = \phi_3 - \phi$ gives the difference between the copolymer concentrtion ϕ_3 in the considered phase and ϕ, the average copolymer content in the two-phase system, whereas $^1/_2\eta$ may be regarded as the deviation of $\phi_{\rm A} = \phi_1 + {}^1/_2\phi_3$, the overall monomer A concentration, from $\phi_{\rm A} = {}^1/_2$. When $|\epsilon|$ and $|\eta|$ are small, i.e., when

$$|\epsilon| \ll 3\phi$$
$$\eta^2 \ll 10(1-\phi)^2 \qquad (4)$$

F_0 may be expanded in powers of ϵ and η:

$$F_0/k_{\rm B}T \simeq \frac{1}{2}\Gamma_1\epsilon^2 + \frac{1}{2}\Gamma_2\eta^2 + \frac{1}{4}\Gamma_3\eta^4 - \frac{1}{2}\Gamma_4\eta^2\epsilon \qquad (5)$$

where

$$\Gamma_1 = 1/\{N\phi(1-\phi)\}$$
$$\Gamma_2 = \{1/(1-\phi) - \chi N/2\}/N$$
$$\Gamma_3 = 1/\{3N(1-\phi)^3\}$$
$$\Gamma_4 = 1/\{N(1-\phi)^2\} \qquad (6)$$

In expression 5 we have dropped out terms of order η^6, η^8, and higher, which are small compared with the term of order η^4. We also neglect terms of order ϵ^3, ϵ^4, and higher, which are small compared with that of order ϵ^2. Also the terms of order $\epsilon^2\eta^2$ may be neglected in comparison with the term $\Gamma_4\eta^2\epsilon$.

Expression 5 is a very good approximation of (1) in the critical region. In fact, the concentration ϵ_α, η_α and ϵ_β, η_β in two coexisting phases (A-monomer rich and B-monomer rich, respectively) are determined by the conditions

$$\mu_\epsilon(\epsilon_\alpha,\eta_\alpha) = \mu_\epsilon(\epsilon_\beta,\eta_\beta) = \mu_\epsilon({\rm e})$$
$$\mu_\eta(\epsilon_\alpha,\eta_\alpha) = \mu_\eta(\epsilon_\beta,\eta_\beta) = \mu_\eta({\rm e})$$
$$\pi(\epsilon_\alpha,\eta_\alpha) = \pi(\epsilon_\beta,\eta_\beta) \qquad (7)$$

where $\mu_\epsilon = \partial F_0/\partial\epsilon$, $\mu_\eta = \partial F_0/\partial\eta$, and $\pi = F_0 - \epsilon\mu_\epsilon - \eta\mu_\eta$. These conditions, equivalent to the equalities of chemical potentials of components in two phases, give

$$\epsilon_\alpha = \epsilon_\beta = 0$$
$$\eta_\alpha = -\eta_\beta = (|\Gamma_2|/\Gamma_3)^{1/2} = \sigma \qquad (8)$$

The important result is that both coexisting phases contain the same fraction $\phi_3 = \phi$ of copolymer monomers.[19] In the vicinity of the critical point, when

$$\phi_3^{(c)} - \phi \ll 20/(3\chi N) \qquad (9)$$

condition 4 is fulfilled.

In the interfacial region the composition varies smoothly in space. For example, even though very far from the interface the copolymer content is equal to ϕ in both phases, the quantity $\epsilon(\vec{r}) = \phi - \phi_3(\vec{r})$ may not vanish at the interace. The free energy density in a region of nonuniform composition depends on both the local concentrations and the composition of the immediate environment. The nonlocal contribution is due to the correlation effects. In order to find the total free energy of the nonuniform system we take into account the spatial monomer concentration fluctuation and generalize expression 5. The dominant term in the expansion of the free energy density is (cf. ref 29 and 30)

$$F/k_{\rm B}T \simeq {}^1\!/\!_2\sum_{\vec{q}}\{\Gamma_{11}(\vec{q})\epsilon(\vec{q})\epsilon(-\vec{q}) + 2\Gamma_{12}(\vec{q})\epsilon(\vec{q})\eta(-\vec{q}) + \Gamma_{22}(\vec{q})\eta(\vec{q})\eta(-\vec{q})\} \qquad (10)$$

where $\epsilon(\vec{q})$ and $\eta(\vec{q})$ denote the Fourier transform of the local concentrations $\epsilon(\vec{r})$ and $\eta(\vec{r})$ and

$$\Gamma_{ij}(\vec{q}) = G_{ij}^{-1}(\vec{q}) \qquad (i, j = 1, 2)$$

The matrix $||G^{-1}(\vec{q})||$ denotes the inverse matrix of $||G(\vec{q})||$, the elements of which, $G_{kh}(\vec{q})$ (k, h = 1, 2), are equal to the Fourier transform of the correlation functions of a homogeneous phase with the average composition $\phi_3 = \phi$ and $\phi_1 = \phi_2 = (1-\phi)/2$

$$G_{11}(\vec{r}) = \langle\epsilon(0)\epsilon(\vec{r})\rangle$$
$$G_{12}(\vec{r}) = \langle\epsilon(0)\eta(\vec{r})\rangle = G_{21}(\vec{r})$$
$$G_{22}(\vec{r}) = \langle\eta(0)\eta(\vec{r})\rangle \qquad (11)$$

It is useful to express the correlation functions G_{ij} in terms of the homopolymer monomers' correlation functions

$$\tilde{S}_{ij}(\vec{r}) = \langle\delta\phi_i(0)\delta\phi_j(\vec{r})\rangle \qquad (12)$$

where $\delta\phi_i(\vec{r}) = \phi_i(\vec{r}) - (1-\phi)/2$ (i = 1, 2) denote the local variations of the concentration of monomers of homopolymers A and B, respectively. From the definitions (3) of η and ϵ one gets

$$G_{11} = \tilde{S}_{11} + \tilde{S}_{22} + 2\tilde{S}_{12}$$
$$G_{12} = \tilde{S}_{11} - \tilde{S}_{22}$$
$$G_{22} = \tilde{S}_{11} + \tilde{S}_{22} - 2\tilde{S}_{12} \qquad (13)$$

It should be remarked that because of the incompressibility assumption, only three correlation functions (e.g., $\tilde{S}_{11}$, $\tilde{S}_{12}$, and $\tilde{S}_{22}$) are independent. A further simplicication is due to the particular symmetry of the system: $\tilde{S}_{11} = \tilde{S}_{22}$ and consequently $G_{12} = 0$. Hence, to calculate the free energy density (10), it is sufficient to determine the correlation functions $\tilde{S}_{11}$ and $\tilde{S}_{12}$, since the coefficients Γ_{ij} are related to the homopolymer correlation functions in a particularly simple way:

$$\Gamma_{11} = 1/\{2(\tilde{S}_{11} + \tilde{S}_{12})\}$$

$$\Gamma_{22} = 1/\{2(\tilde{S}_{11} - \tilde{S}_{12})\}$$

$$\Gamma_{12} = 0 \tag{14}$$

(a) Correlation Functions. We calculate the chain correlation functions $\tilde{S}_{ij}$ with the help of the random phase approximation (RPA) method.[27,28] We suppose formally that, modulated in space, external weak potentials k_BTU_i ($i = 1, 2, 3$) act on monomers of chains of type i. The associated interaction energy equals

$$k_BT \sum_{j=1}^{3} \int \mathrm{d}^3r\ U_i(\vec{r})\delta\phi_i(\vec{r})$$

The average change of the monomer densities $\Delta\phi_i$ at the point $\vec{r}$ due to the action of this perturbation may be given in terms of the response functions directly related to the correlation functions:

$$\Delta\phi_i(\vec{r}) = -\sum_{j=1}^{3} \int \mathrm{d}^3r'\ \tilde{S}_{ij}(\vec{r} - \vec{r}\,')U_j(\vec{r}\,') \qquad (i = 1, 2, 3) \tag{15}$$

or for Fourier transforms:

$$\Delta\phi_i(\vec{q}) = -\sum_{j=1}^{3} \tilde{S}_{ij}(\vec{q})U_j(\vec{q}) \qquad (i = 1, 2, 3) \tag{16}$$

From the incompressibility condition

$$\sum_{i=1}^{3} \Delta\phi_i = 0 \tag{17}$$

and

$$\tilde{S}_{13} = -\tilde{S}_{11} - \tilde{S}_{12}$$

$$\tilde{S}_{23} = -\tilde{S}_{12} - \tilde{S}_{22}$$

$$\tilde{S}_{33} = \tilde{S}_{11} + \tilde{S}_{22} + 2\tilde{S}_{12}$$

In the random phase approximation the response of the system to the external potential U_i is calculated as if the chains were independent(uncorrelated) but the potentials acting on the monomers were corrected to take into account monomer interactions. These corrections are due to two different correlation effects. First of all, a self-consistent potential k_BTU acting on all monomers is present to ensure the constant overall monomer density (incompressibility). Second, the potential $-2k_BT\chi\Delta\phi_B$ acting only on monomers B is introduced to express the fact that external potentials U_i change the average monomer A and monomer B concentrations and, consequently, change also the effective monomer interaction by the quantity $-k_BT\chi\Delta\phi_B^2$. Thus

$$\Delta\phi_1 = -S_A(U_1 + U)$$

$$\Delta\phi_2 = -S_B(U_2 + U - 2\chi\Delta\phi_B)$$

$$\Delta\phi_3^A = -S_{AA}(U_3 + U) - S_{AB}(U_3 + U - 2\chi\Delta\phi_B)$$

$$\Delta\phi_3^B = -S_{BA}(U_3 + U) - S_{BB}(U_3 + U - 2\chi\Delta\phi_B)$$

$$\Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3^A + \Delta\phi_3^B = \Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3 = 0 \tag{18}$$

where $\Delta\phi_B = \Delta\phi_2 + \Delta\phi_3^B$. $S_A(\vec{q})$ and $S_B(\vec{q})$ denote, respectively, the monomer concentration correlation functions of *independent* (noninteracting) homopolymer A and homopolymer B chains. In polymer melts, excluded volume effects are screened out and chains may be supposed to be nearly ideal (Gaussian) on the scale of a coil.[28,33] Therefore

$$S_A(\vec{q}) = \frac{1 - \phi}{2} Ng(1,\vec{q}^2R^2) \tag{19}$$

where R is equal to the radius of gyration of the chains and $g(1,x)$ denotes the Debye scattering function:

$$g(f,x) = 2\{fx + \exp(-fx) - 1\}/x^2 \tag{20}$$

In the symmetric case, $S_A(\vec{q}) = S_B(\vec{q})$. $S_{AA}(\vec{q})$, $S_{BB}(\vec{q})$, and $S_{AB}(\vec{q})$ denote, respectively, monomers A–A, B–B, and A–B correlation functions of independent copolymer chains.[30] Obviously, these functions depend on the architecture of the copolymer chains. In the Appendix we derive the formulas for multiblock linear copolymers. It should be pointed out that S_{AA}, S_{BB}, and S_{AB} may be expressed in terms of Debye functions of the form (20). For example, for diblock chains with the composition f (f is the fraction of monomers A in the chain)[30]

$$S_{AA}(\vec{q}) = \phi Ng(f,\vec{q}^2R^2)$$

$$S_{BB}(\vec{q}) = \phi Ng(1 - f, \vec{q}^2R^2)$$

$$S_{AB} = \tfrac{1}{2}\{\phi Ng(1,\vec{q}^2R^2) - S_{AA}(\vec{q}) - S_{BB}(\vec{q})\} \tag{21}$$

Of course, in the symmetric case $S_{AA}(\vec{q}) = S_{BB}(\vec{q})$.

By comparing the set of eq 18 with eq 14, we may easily obtain the formulas expressing the correlation functions $\tilde{S}_{ij}$ ($i, j = 1, 2$) in terms of S_A, S_B, S_{AA}, S_{BB}, and S_{AB}. For the symmetric case one gets

$$\tilde{S}_{11} = \tilde{S}_{22} = S_A\{S_A + S_C - 2\chi(S_{AA}^2 - S_{AB}^2 + S_AS_{AA})\}/D$$

$$\tilde{S}_{12} = \tilde{S}_{21} = -S_A^2(1 + 2\chi S_{AB})/D \tag{22}$$

where

$$D = 2S_A + S_c - 2\chi\{(S_A + S_{AA})^2 - S_{AB}^2\} \tag{23}$$

and

$$S_c = S_{AA} + S_{BB} + 2S_{AB}$$

It is interesting to note that in the limiting case of no copolymers in the blend ($\phi = 0$), (22) yields

$$1/\tilde{S}_{12}(\vec{q}) = 2/S_A(\vec{q}) - 2\chi$$

the well-known scattering function of a mixture of two homopolymers.[28]

The correlation functions $\tilde{S}_{ij}(\vec{q})$ may be measured by radiation scattering experiments. Particularly suitable would be the small-angle neutron scattering technique, which enables one to separate $\tilde{S}_{11}$ and $\tilde{S}_{12}$ with the help of the selective deuteration of chains.

(b) Free Energy of a Nonuniform Phase. The leading term in the expansion of the free energy density is given by eq 10. From the formulas on the correlation functions and eq 14 we get

$$\Gamma_{11}(\vec{q}) = 1/S_c(\vec{q}) + 1/\{2S_A(\vec{q})\} \tag{24}$$

$$\Gamma_{22}(\vec{q}) = \tfrac{1}{2}[1/S_A(\vec{q}) - \chi/\{1 - \chi(S_{AA} - S_{AB})\}] \tag{25}$$

and as pointed out before $\Gamma_{12} = 0$. In the critical region the interface is particularly thick, so it is reasonable to assume that the essential contribution to the free energy is due to the fluctuations $\epsilon(\vec{q})$ and $\eta(\vec{q})$ with $|\vec{q}| \ll 1/R$.

Therefore, the coefficients $\Gamma_{11}(\vec{q})$ and $\Gamma_{22}(\vec{q})$ may be expanded in powers of $\vec{q}$. From the Guinier theorem

$$S_c(\vec{q}) \simeq \phi N(1 - {}^1\!/_3\vec{q}^2R^2)$$

$$S_A(\vec{q}) = \frac{1-\phi}{2}(1 - {}^1\!/_3\vec{q}^2R^2) \qquad (26)$$

and so quite generally

$$\Gamma_{11}(\vec{q}) = \Gamma_1(1 + {}^1\!/_3\vec{q}^2R^2) \qquad (27)$$

where Γ_1 is defined by eq 6. For small $\vec{q}$ vectors the coefficient $\Gamma_{22}(\vec{q})$ may be approximated by

$$\Gamma_{22}(\vec{q}) \simeq \Gamma_2 + |\Gamma_2|\xi^2\vec{q}^2 \qquad (28)$$

where ξ is the correlation length, which depends on the structure of the copolymer chains. For example, for diblock copolymers, from eq 19–23 and 25

$$\xi^2 = 2R^2\{1 - \chi^2N^2\phi(1-\phi)/8\}/\{3|\chi N(1-\phi) - 2|\} \qquad (29)$$

for periodic multiblock chains (cf. Appendix, eq A-7)

$$\xi^2 = 2R^2\{1 - \chi^2N^2\phi(1-\phi)/8k^2\}/\{3|\chi N(1-\phi) - 2|\} \qquad (30)$$

where k denotes the number of A blocks (B blocks) of the copolymer chains of the type A–B–A–B...–A–B. It should be pointed out that in writing (28), we have neglected the terms of higher order in $\vec{q}$. Such an approximation is valid only for small interaction parameters χN. Actually, eq 29 shows that for diblock chains the second-order term $|\Gamma_2|\vec{q}^2\xi^2$ may vanish for $\chi N > 4(2^{1/2})$. In that case it is necessary to take into account the terms of higher order in $\vec{q}$. In the following, we limit our considerations to $\chi N < 4(2^{1/2})$ and then approximate the coefficient $\Gamma_2(\vec{q})$ by (28).

When ϕ tends to the critical concentration $\phi_3^{(c)}$, the correlation length ξ diverges. However, the term $|\Gamma_2|\xi^2$ is always finite. If one fixes the copolymer concentration ϕ ($\phi > \phi_3^{(c)}$) and changes the interaction parameter χ, the singularity of ξ when $\chi \to \chi_c = 2/(1-\phi)$ is characterized by the mean field exponent $\nu = {}^1\!/_2$. It may be shown with the help of a Ginzburg criterion that a mean field theory is an adequate approximation to describe the critical properties of the demixing transition (cf. ref 34).

Hence, coming back to the $\vec{r}$-space representation, we may approximate the free energy density (per monomer) by

$$F/k_BT \simeq F_0 + \frac{1}{2}\Gamma_1R^2|\nabla\epsilon|^2 + \frac{1}{2}|\Gamma_2|\xi^2|\nabla\eta|^2 \qquad (31)$$

where F_0 is given by eq 5. The total free energy is then equal to $F_{tot} = (1/a^3)\int d^3r\, F(\epsilon,\eta)$ (a^3 denotes the volume per monomer). In the absence of copolymer chains ($\phi = 0$), expression 31 reduces to

$$F/k_BT \simeq \frac{1}{2}\Gamma_2\eta^2 + \frac{1}{4}\Gamma_3\eta^4 + \frac{1}{2}|\Gamma_2|\xi^2|\nabla\eta|^2 \qquad (32)$$

equivalent to the standard one for the free energy of a mixture of two homopolymers A and B (η should be replaced by $2\delta\phi_A$).[29] It is interesting to note that expression 31 may be treated as a generalization of the classical Cahn–Hilliard gradient expansion theory for low-molecular-weight liquid mixtures.[35]

Equation 31 is the central one of the treatment. First, it shows that the free energy may be approximated by the sum of two contributions: one is the free energy F_0 that would have a homogeneous mixture and the other is due to the gradient of composition. Second, two characteristic lengths appear in the problem, the radius of gyration R and the correlation length ξ, which determine the thickness of the interfacial region.

III. Interfacial Properties

We consider a flat interface between A-monomer-rich ($\epsilon_\alpha = 0$, $\eta_\alpha = \sigma$) and B-monomer-rich ($\epsilon_\beta = 0$, $\eta_\beta = -\sigma$) phases. We suppose that the composition characterized by $\bar\epsilon(x)$ and $\bar\eta(x)$ varies smoothly along the x axis, and

$$\bar\epsilon(x) \to 0; \qquad \bar\eta(x) \to \sigma \qquad \text{when } x \to \infty \qquad (33)$$

$$\bar\epsilon(x) \to 0; \qquad \bar\eta(x) \to -\sigma \qquad \text{when } x \to -\infty \qquad (34)$$

The interfacial tension γ is defined as the difference per unit area of the interface between the actual total free energy of the system and that which it would have if there was no interface:

$$\gamma = \int_{-\infty}^{\infty} dx\, \{F(\bar\eta,\bar\epsilon) - N\sum_{i=1}^{3}\bar\phi_i(x)\tilde\mu_i(e)\}/a^3 \qquad (35)$$

where $F(\bar\eta,\bar\epsilon)$, given by eq 31, is the free energy density per monomer at point x, $N\bar\phi_i(x)$ ($i = 1, 2, 3$) give the chain volume fraction profiles, and $\tilde\mu_i(e)$ is equal to the chemical potential of the ith type of chains in two coexisting phases. The chain chemical potentials $\tilde\mu_i = \partial F_0^{tot}/\partial N_i$ (F_0^{tot} is the total free energy of a uniform phase and N_i is the number of chains of the ith type) may be easily expressed in terms of the exchange potentials μ_ϵ and μ_η used in section II:

$$\tilde\mu_1 = N\{F_0 + (\phi - \epsilon)\mu_\epsilon + (1-\eta)\mu_\eta\}$$

$$\tilde\mu_2 = N\{F_0 + (\phi - \epsilon)\mu_\epsilon - (1+\eta)\mu_\eta\}$$

$$\tilde\mu_3 = N\{F_0 - (1 - \phi + \epsilon)\mu_\epsilon - \eta\mu_\eta\} \qquad (36)$$

For the phases in equilibrium, $\mu_\eta(e) = 0$ (from the symmetry) and $\epsilon = 0$, and eq 3, 35, and 36 yield

$$\gamma = \int_{-\infty}^{\infty} dx\, \{F(\bar\eta(x),\bar\epsilon(x)) - F_0(e) - \bar\epsilon(x)\mu_\epsilon(e)\}/a^3 \qquad (37)$$

In order to determine the composition profile $\bar\epsilon(x)$ and $\bar\eta(x)$, the functional

$$\gamma(\epsilon,\eta) = \int_{-\infty}^{\infty} dx\, \{F(\eta,\epsilon) - \epsilon(x)\mu_\epsilon(e) - F_0\}/a^3 \qquad (38)$$

should be minimized. This minimization procedure may be just interpreted as the minimization of the total free energy of the interfacial region. In fact, $F(\eta,\epsilon) - \epsilon\mu_\epsilon(e)$ may be regarded as the free energy density of the system with the constraint of ϵ and η equal to their equilibrium values ($\epsilon = 0$, $\eta = \pm\sigma$) when there is no spatial variation of the composition ($\nabla\epsilon = \nabla\eta = 0$). $\mu_\epsilon(e)$ and $\mu_\eta(e) = 0$ play then the role of the Lagrange multipliers.

(a) Composition Profile. The substitution of the free energy density $F(\eta,\epsilon)$ given by eq 31 into the functional (38) leads to the following Euler–Lagrange equations for the interfacial concentration profiles:

$$|\Gamma_2|\xi^2\ddot{\bar\eta} = -|\Gamma_2|\bar\eta + \Gamma_3\bar\eta^3 - \Gamma_4\bar\eta\bar\epsilon \qquad (39)$$

$${}^1\!/_3\Gamma_1R^2\ddot{\bar\epsilon} = \Gamma_1\bar\epsilon + {}^1\!/_2\Gamma_4(\sigma^2 - \bar\eta^2) \qquad (40)$$

where $\dot{y}$ denotes the derivative $dy(x)/dx$ and we have put $\mu_\epsilon(e) = -\Gamma_4\sigma^2/2$.

Inspection of eq 39 and 40 together with the boundary conditions (33) and (34) indicates that the overall A-monomer concentration profile $\delta\phi_A(x) = \phi_A(x) - {}^1\!/_2 = \eta(x)/2$ is sigmoid in shape: $\bar\eta(-\infty) = -\sigma$ and $\dot{\bar\eta}(-\infty) = \ddot{\bar\eta}(-\infty) = 0$, then $\bar\eta(x)$ increases monotonously, passes through ($\dot{\bar\eta}(\infty) = 0$) at $x = 0$, and still increases up to $+\sigma$ when $x \to \infty$ ($\dot{\bar\eta}(\infty) = 0$). The function $\bar\epsilon(x)$ has a minimum at $x = 0$ ($\bar\epsilon(0) < 0$) and tends to zero when $x \to \pm\infty$. Hence, copolymer chains locate preferentially at the interface. Making use of eq 40, one may write (30) in the following form:

$${}^1\!/_2|\Gamma_2|D^2\ddot{\bar\eta} = -|\Gamma_2|\bar\eta + \Gamma_3\bar\eta^3 - \Gamma_4(1 - 3\phi/2)^{-1}L^2\bar\eta\ddot{\bar\epsilon} \qquad (41)$$

where

$$D^2 = 2\xi^2(1 - 3\phi/2)^{-1}$$

$$L^2 = R^2/3 \tag{42}$$

In the critical region on which we focus, within a very good approximation, the last term on the right-hand side or eq 41 may be neglected in comparison with the first two terms. The validity of this Ansatz will be checked below (cf. eq 52). Then one obtaines

$$\bar{\eta}(x) \simeq \sigma \tanh (x/D) \tag{43}$$

a classical mean field profile.[35] The distance D that characterizes the thickness of the interface is of the order of the correlation length ξ as might be expected. Substituting the solution (43) into eq 40 yields

$$L^2\ddot{\bar{\epsilon}} = \bar{\epsilon} + B \,\mathrm{ch}^{-2}\,(x/D) \tag{44}$$

where

$$B = \Gamma_4\sigma^2/2\Gamma_1 = (3/4)\phi(1 - \phi)\xi\{\chi N(1 - \phi) - 2\} \tag{45}$$

The analytical solution of (44) is straightforward:

$$\bar{\epsilon}(x) = -\alpha B\{h(2x/D) + h(-2x/D) - 1\} \tag{46}$$

with the function $h(z)$ defined as

$$h(z) = \{1 + \exp(-z)\}^{-1}F(1,1;\, 1 + \alpha/2;\, \{1 + \exp(z)\}^{-1}) \tag{47}$$

where $\alpha = D/L$ and $F(a,b;c,z)$ denotes the Gauss hypergeometric series. It may be verified that the solution (46) fulfills the boundary conditions $\bar{\epsilon} \rightarrow 0$ when $x \rightarrow \pm\infty$. It is interesting to note that for copolymer content ϕ for which α is an integer, $\bar{\epsilon}(x)$ may be expressed solely in terms of elementary functions. For example, for $\alpha = D/L = 3$

$$\bar{\epsilon} = -3B\{[3 \,\mathrm{arctg}\, (\mathrm{sh}\, u) - 4 \,\mathrm{sh}\, u] \,\mathrm{sh}\, (3u) + (4 \,\mathrm{ch}\, u + \mathrm{ch}^{-1}\, u - 3\pi/2) \,\mathrm{ch}\, (3u)\} \tag{48}$$

for $\alpha = 4$

$$\bar{\epsilon} = -4B\{2 \,\mathrm{ch}\, (2u) + (4u) \,\mathrm{sh}\, (4u) - (4 \ln 2 - 1) \times \mathrm{ch}\, (4u) - 4[\ln (\mathrm{ch}\, u)] \,\mathrm{ch}\, (4u) - \mathrm{th}\, u \,\mathrm{sh}\, (4u)\} \tag{49}$$

where $u = x/D = x/(\alpha L)$.

In Figure 1 we have shown a typical example of the interfacial profile in the case of rather high content ϕ of copolymer chains in the system calculated with the help of eq 43 and 49. As we have already pointed out, the copolymer chains locate at the interface.

The excess concentration of copolymers at the interface is characterized by

$$|\bar{\epsilon}(0)| = \int_{-\infty}^{\infty} \mathrm{d}t \exp(-\alpha t) \,\mathrm{ch}^{-2}\, t = B\alpha[\alpha\beta(\alpha/2) - 1] \tag{50}$$

where the β function is given by $\beta(x) = \{\psi((x + 1)/2) - \psi(x/2)\}/2$, with $\psi = \mathrm{d}\{\ln \Gamma(x)\}/\mathrm{d}x$, $\Gamma(x)$ being the standard gamma function (Euler's integral of the second kind).[36] In the vicinity of the critical point ($\alpha \gg 1$)

$$|\bar{\epsilon}(0)| \simeq B(1 - 2/\alpha^2) \tag{51}$$

and the condition (4) ($|\bar{\epsilon}| \ll 3\phi$) required for the validity of the free energy expression (31) holds. It should be also stressed that in the critical region the peak of the copolymer fraction profile is broad: it spreads over the distance of about $D = \alpha L$. This explains why, in the first approximation, we could drop out the term $-\Gamma_4(1 - 3\phi/2)^{-1}L^2\bar{\eta}\ddot{\bar{\epsilon}}$ in eq 41. Actually, eq 44 and 51 indicate that

$$L^2\ddot{\bar{\epsilon}} \lesssim 2B/\alpha^2 = \Gamma_4|\Gamma_2|/\alpha^2\Gamma_1 \tag{52}$$

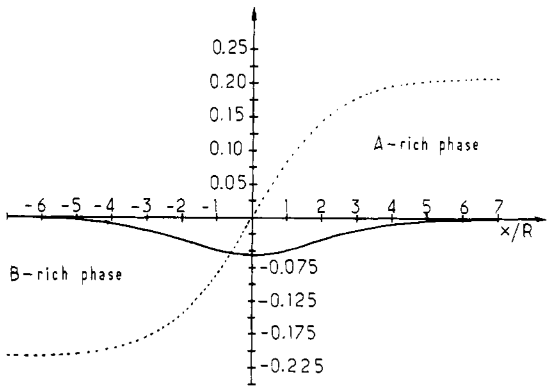

Figure 1. Interfacial composition profiles of homopolymer A–homopolymer B diblock copolymer A–B two-phase blend. The interaction parameter $\chi N = 4$ and the copolymer content in the bulk phase is $\phi = 0.415$. The solid line represents the function $\bar{\epsilon}(x) = \phi - \bar{\phi}_3(x)$, characterizing the variation of copolymer monomer volume fraction through the interface. The dotted line corresponds to the change of the total volume fraction of monomers A, $\delta\phi_A(x) = \phi_A(x) - 0.5$. The length through the interface is measured in units of radius of gyration $R = Na^2$.

is small compared with $|\Gamma_2|(1 - 3\phi/2)/\Gamma_4$ in the critical region. Very close to the critical point $\ddot{\bar{\epsilon}}L^2$ is extremely small and the copolymer concentration profile may be roughly approximated by (cf. (44))

$$\bar{\epsilon}(x) = -B \,\mathrm{ch}^{-2}\,(x/D) \tag{53}$$

(b) Interfacial Tension. The interfacial tension γ may be now calculated with the help of eq 37 and already-calculated profiles $\bar{\eta}(x)$ and $\bar{\epsilon}(x)$.

Before, however, it is convenient to make use of the Euler–Lagrange equations and to transform the expression on γ. Taking into account the boundary conditions, one obtains

$$\int_{-\infty}^{\infty} \mathrm{d}x \,\dot{\bar{\eta}}^2 = -\int_{-\infty}^{\infty} \mathrm{d}x \,\bar{\eta}\ddot{\bar{\eta}}$$

and a similar expression for the term with $\bar{\epsilon}^2$. Then by putting eq 39 and 40 into (37), it is found that γ may be split into two parts:

$$\gamma = \gamma_0 - \gamma_1 \tag{54}$$

with

$$\gamma_0 = \frac{1}{4}\frac{k_BT}{a^3}\Gamma_3\int_{-\infty}^{\infty} \mathrm{d}x \,(\sigma_4 - \bar{\eta}^4) \tag{55}$$

and

$$\gamma_1 = \frac{1}{2}\frac{k_BT}{a^3}\Gamma_4 \int_{-\infty}^{\infty} \mathrm{d}x \,|\bar{\epsilon}|(\bar{\eta}^2 + \sigma^2) \tag{56}$$

An interesting physical interpretation may be attributed to these two terms. The first term, γ_0, represents the interfacial energy due to the nonhomogeneity of the overall A-monomer concentration. Formally the same expression would be obtained if there were no copolymer chains in the system. The second contribution, γ_1, expresses a decrease of the interfacial tension due to the effect of the preferential location of copolymers at the interface.

Putting of eq 43 into (55) gives

$$\gamma_0 = (k_BT/a^2)(2D\Gamma_2^2/3\Gamma_3) \tag{57}$$

or more explicitly

$$\gamma_0 = \gamma_0(0)\mathcal{R}(\phi) \tag{58}$$

where

$$\gamma_0(0) = 2^{1/2}k_BTN^{-1/2}(\chi N - 2)^{3/2}/6a^2 \qquad (59)$$

is equal to the interfacial tension in the absence of copolymer additives. This case ($\phi = 0$) has been discussed in detail in ref 29. The function $\mathcal{R}(\phi)$ depends on the structure of copolymer chains. For diblock chains

$$\mathcal{R}(\phi) = (1 - \phi) \times \{\chi N(1 - \phi) - 2\}^{3/2}(\chi N - 2)^{-3/2}\{1 - \chi^2N^2\phi(1 - \phi)/8\}^{1/2} \qquad (60)$$

or for periodic multiblock chains

$$\mathcal{R}(\phi) = (1 - \phi) \times \{\chi N(1 - \phi) - 2\}^{3/2}(\chi N - 2)^{-3/2}\{1 - \chi^2N^2\phi(1 - \phi)/8k^2\}^{1/2} \qquad (60a)$$

It should be stressed that $\gamma_0(\phi)$ monotonously decreases with the increase of copolymer content ϕ. For $\phi = \phi_3^{(c)}$, at the critical point, $\gamma_0 = 0$.

Equations 47 and 56 yield

$$\gamma_1 = (3\Gamma_4^2/4\Gamma_1\Gamma_3)\gamma_0\{1 - C(\alpha)\} = (9/4)\phi\gamma_0\{1 - C(\alpha)\} \qquad (61)$$

where

$$C(\alpha) = \alpha \sum_{k=1}^{\infty} \frac{\Gamma(1 + \alpha/2)k!}{\Gamma(k + 1 + \alpha/2)(k + 1)(k + 2)} \qquad (62)$$

The coefficient $C(\alpha)$ depends on ϕ through $\alpha = D/L$. It is a monotonously increasing function of α and tends to $^2/_3$ when $\alpha \rightarrow \infty$. In the critical region when $\alpha \gg 1$, $C(\alpha)$ may be well approximated by its limiting value and its dependence on ϕ neglected (e.g., $C(2) = 2\pi^2/3 - 6 \simeq 0.58$, $C(4) = 16\pi^2/3 - 52 \simeq 0.64$, $C(6) = 18\pi^2 - 177 \simeq 0.652$). Hence

$$\gamma_1 \simeq {}^3\!/_2\phi\gamma_0 \qquad (63)$$

It should be noted that (63) may be obtained simply from the approximative equation for the interfacial profile $\bar{\epsilon}$, eq 53. As already mentioned, γ_1 is entirely due to the presence of copolymer chains in the system and obviously it vanishes when $\phi = 0$. It also vanishes at the critical point for $\phi = \phi_3^{(c)}$.

IV. Discussion and Conclusions

When copolymer chains are added, the two-phase polymer blend is closer to its consolute point. A particular manifestation of this property is the change of the interfacial composition profile and a decrease of the interfacial energy. We have shown (eq 54–63) that the interfacial tension γ may be represented as a difference of two contributions: $\gamma = \gamma_0 - \gamma_1$.

The first part, γ_0, may be interpreted as an interfacial energy due to the variation of the overall A-monomer concentration through the interface. In the vicinity of the critical point of demixing this profile is given by the classical expression (eq 43)

$$\phi_A(x) = {}^1\!/_2\{1 + \sigma \tanh (x/D)\} \qquad (64)$$

Figure 2 shows the variation of the overall monomer A volume fraction through the interface for various copolymer contents ϕ. The main effect is that copolymer chains are present in both phases, and in consequence when ϕ increases, the difference between the total volume fraction of monomers A in A-monomer-rich and B-monomer-rich phases (σ) decreases. This affects γ_0 in a substantial way: as shown in Figure 3 the contribution γ_0 to the interfacial energy decreases monotonously with the copolymer content ϕ and vanishes at the critical point for $\phi = \phi_3^{(c)} = 1 - 2/(\chi N)$. For small copolymer contents and for nearly compatible species ($\chi N \simeq 2$), the decrease of γ_0 may be quite important (eq 57–60):

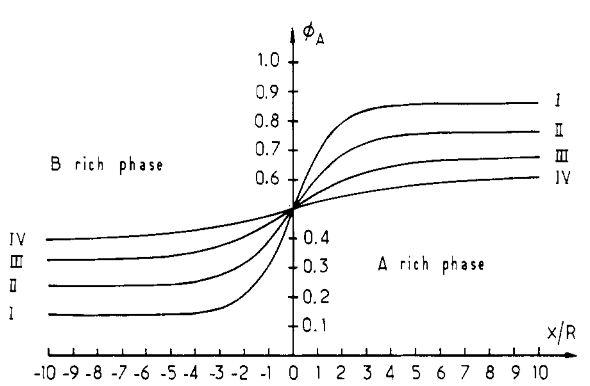

Figure 2. Inteffacial composition profiles of the overall volume fraction of monomers A for different copolymer contents ϕ: (I) $\phi = {}^1/_6 \simeq 0.1667$; (II) $\phi = 0.23$; (III) $\phi = 0.28$; (IV) $\phi = 0.31$. Monomer interactions are characterized by $\chi N = 3$, and critical composition $\phi_3^{(c)} = {}^1/_3$.

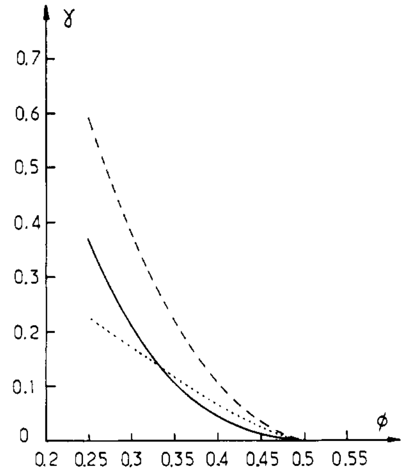

Figure 3. Variation of interfacial tension γ (solid line) as a function of diblock copolymer fraction ϕ for the interaction parameter $\chi N = 4$. The interfacial tension γ is equal to the difference of two contributions γ_0 (dashed line) and γ_1 (dotted line). The interfacial tension is measured in units of $2^{1/2}k_BT/6N^{1/2}a^2$.

$$\gamma_0(\phi) \simeq \gamma_0(0)\{1 - \phi[1 + \chi^2N^2/8 + 3\chi N/2(\chi N - 2)]\} \qquad (65)$$

(for the case of diblock chains)

The second source of activity of copolymers is their preferential location at the interface. Actually, the copolymer concentration profile

$$\phi_3(x) = \phi - \bar{\epsilon}(x) \qquad (66)$$

has a maximum at the interface at $x = 0$ (Figure 4). For nearly compatible species the peak is broad and spreads over the distance D, which diverges when ϕ approaches the critical value $\phi_3^{(c)}$. Moreover, the maximum is not very pronounced ($|\bar{\epsilon}(0)| = 0$ at $\phi = 0$), increases with ϕ, and then falls ($|\bar{\epsilon}(0)| = 0$ for $\phi = \phi_3^{(c)}$). In the critical region, the term γ_1 due to the preferential location of copolymers at the interface is approximately equal to $\gamma_1 \simeq 1.5\phi\gamma_0$ (eq 63). Therefore, the main contribution to the interfacial tension γ comes from the term γ_0. Figure 5 shows the dependence of the interfacial tension γ and of the term γ_1 on the copolymer content for $\chi N = 2.5$. In this case of nearly miscible species the surfactant effect due to the location of copolymer chains at the interface is very small. For higher incompatibility degree, in the critical region ϕ is relatively high and the term γ_1 may be comparable with

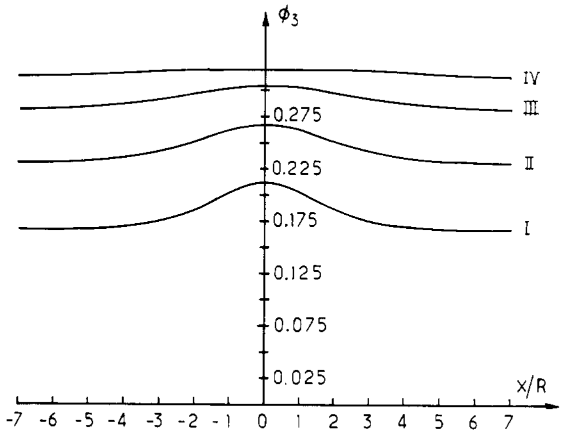

Figure 4. Interfacial composition profile of the copolymer monomer volume fraction $\phi_3(x)$ for different copolymer contents ϕ in the bulk phase: (I) $\phi = {}^1/_6 \simeq 0.167$; (II) $\phi = 0.23$; (III) $\phi = 0.28$; (IV) $\phi = 0.31$. The interaction parameter $\chi N = 3$ (cf. Figure 2). The parameter $\alpha = D/L$ equals, respectively, 3, 4, 6, and 9 for curves I, II, III, and IV ($L = R/3^{1/2}$). The length is measured in units of radius of gyration R.

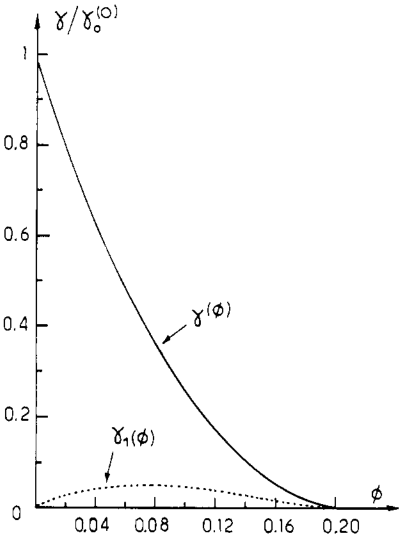

Figure 5. Variation of the interfacial tension γ (solid line) as a function of diblock copolymer fraction ϕ for the interaction parameter $\chi N = 2.5$. The dotted line shows the contribution γ_1, the decrease of the interfacial tension due to the preferential location of the copolymer chains at the interface. The interfacial tension is measured in units of $\gamma_0(0) = 2^{1/2}k_BT(\chi N - 2)^{3/2}/6N^{1/2}\alpha^2$, the interfacial tension of a two-phase homopolymer blend without copolymer additives.

γ_0 as illustrated in Figure 3 for $\chi N = 4$.

To sum up, we may say that for nearly compatible species ($2 < \chi N < 4(2^{1/2})$) two mechanisms of the interfacial activity of copolymer chains are to be distinguished: the species A and B are more closely mixed as copolymer chains are present in both phases and copolymers have a certain tendency to locate at the interface. In the case of nearly miscible species (near the consolute point), the first mechanism dominates whereas for the highly incompatible case, the second factor is dominant.

The thickness of the interface D is essentially of the order of the magnitude of the correlation length ξ. therefore, the interface becomes thicker when ϕ increases and approaches the critical concentration $\phi_3^{(c)}$. The interface thickness depends on the architecture of the copolymer chains as correlation effects do (cf. eq 29 and 30). In consequence, the interfacial tension is slightly smaller when diblock copolymer chains rather than multiblock copolymers are added (cf. eqs 60 and 60a).

It is important to stress some limitations of the applicability of the present treatment. A basic assumption is that the system separates into two homogeneous phases. This is expected to be the case for nearly miscible species ($\chi N < 4(2^{1/2})$) and relatively small copolymer contents. For high incompatibility degree and small copolymer fractions our treatment requires some modifications as short-range fluctuations become important: the interfacial region is narrow (cf. ref 17). Moreover, in this case the microdomain structure formation is likely to occur especially for higher copolymer contents and the phase diagram becomes particularly complex. Our project is to generalize the present treatment in order to deal with these more complex situations. From an experimental point of view, the use of multiblock or statistical copolymers is more convenient to verify the predictions of the present theory as in such systems the microphase separation requires a higher degree of incompatibility as compared to the case for diblock copolymers.

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Appendix. Correlation Functions of Multiblock Copolymer Chains

We consider the case of $2k$-block symmetric copolymer chains of type A–B–A–B–...–A–B; each block is supposed to contain the same number of monomers, $N/2k$. If the chains are independent, the correlation functions are given by[30]

$$S_{AA}(\vec{q}) = (\phi/N)\sum_{i=1}^{N}\sum_{j=1}^{N} v_i v_j P_{ij}(\vec{q}) \qquad \text{(A-1)}$$

$$S_{AB}(\vec{q}) = (\phi/N)\sum_{i=1}^{N}\sum_{j=1}^{N}(1 - v_i)v_j P_{ij}(\vec{q}) \qquad \text{(A-2)}$$

where ϕ is the concentration of copolymer monomers, $v_i = 1$ when the ith monomer of the chain is an A monomer and $v_i = 0$ otherwise. For Gaussian chains

$$P_{ij}(\vec{q}) = \exp(-|i - j|\vec{q}^2a^2/6) \qquad \text{(A-3)}$$

Obviously, for symmetric molecules $S_{AA}(\vec{q}) = S_{BB}(\vec{q})$ and

$$S_{AB}(\vec{q}) = \phi N g(1,x)/2 - S_{AA} \qquad \text{(A-4)}$$

where $g(1,x) = \sum P_{ij}$ is the Debye scattering function defined by eq 20 with $x = \vec{q}^2R^2 = \vec{q}^2Na^2$.

In the case of multiblock chains considered here, (A-1) yields

$$S_{AA} = \phi N[kg(c) + \sum_{i=1}^{k-1}\{(k - i)g((2i - 1)c) - 2g(2ic) + g((2i + 1)c)\}] \qquad \text{(A-5)}$$

with $g(f) = g(f,x)$ and $c = 1/(2k)$. A more explicit formula reads

$$S_{AA}/\phi N = kg(c) + \frac{4(\mathrm{ch}\,(cx) - 1)[(k - 1)\exp(2cx) - k + \exp\{-(1 - 2c)x\}]}{x^2\{\exp(2cx) - 1\}^2} \qquad \text{(A-5a)}$$

In the limit of small $\vec{q}$ vectors ($qR \ll 1$), eq A5 may be simplified:

$$S_{AA} \simeq \phi N\{1 - c(2 - 1/k^2)/6\}/4 \qquad \text{for } qR \ll 1 \quad \text{(A-6)}$$

By substituting (A-5) into (A-4) and (22), one gets the correlation functions in the homogeneous melt $\tilde{S}_{11} = \tilde{S}_{22}$ and $\tilde{S}_{12}$. Similarly, the coefficient $\Gamma_{22}(\vec{q})$, eq 25, in the expansion of the free energy may be calculated, and one gets

$$\xi^2 = 2R^2\{1 - \chi^2 N^2 \phi(1 - \phi)/8k^2\}/3|\chi N(1 - \phi) - 2| \quad \text{(A-7)}$$

In the case of diblock chains, $k = 1$, this formula reduces to (29).

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Estimates of the Bound Fraction of an Adsorbed Polymer at the Solid–Liquid Interface. Exact Enumeration Study of a Self-Avoiding Walk Model

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ABSTRACT: Exact enumeration results of terminally attached self-avoiding walks on the tetrahedral lattice have been used to calculate $\langle p \rangle$, the fraction of polymer segments of an adsorbed polymer lying in an interface, as a function of the adsorption energy (ϵ). Neville table estimates have been used to extrapolate the $\langle p \rangle$ results to infinite chain lengths as a function of ϵ. Below a critical value of ϵ, $\langle p \rangle$ is found to vary inversely with the degree of polymerization. Comparisons of $\langle p \rangle$ estimates on various lattices are also made.

1. Introduction

The adsorption of polymers at solid surfaces from solution is unique in the sense that only a few segments need be in contact with the surface for the polymer to be essentially irreversibly adsorbed. Although considerable experimental data exist on adsorbed polymer systems,[1] basically only two experimental parameters have been used to describe the microscopic structure of the adsorbed layer. One of these, the adsorbed layer thickness, has been measured by several techniques, including ellipsometry,[2] photon correlation spectroscopy,[3] and viscous flow.[4] The difficulty with these techniques, however, is that there is at present no unambigous way to relate the experimental measurement to a theoretically calculable quantity such as the segment density distribution of the adsorbed polymer. Recently, the segment density distribution[5,25,26] has been measured explicitly by small-angle neutron scattering and this should prove a useful test of theories of polymer adsorption.

The other experimentally accessible quantity is $\langle p \rangle$, the mean fraction of monomers in direct contact with the surface. This can be measured by a variety of techniques, including infrared spectroscopy,[6] electron spin resonance,[7] nuclear magnetic resonance,[5,22] and microcalorimetry.[6] The dependence of $\langle p \rangle$ on the degree of polymerization and temperature has been predicted by a variety of theories of polymer adsorption.[8-14] Theories of the high surface coverage regime use a Flory–Huggins mean field approach.[12,14] At low surface coverage, however, the polymer molecules do not interact appreciably with one another and a model based on an isolated chain is more appropriate. Although random walk models of an isolated chain can be treated exactly,[1,8,9] the incorporation of the excluded volume effect makes a detailed analytical treatment very

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