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Theory of Block-Copolymer Interfaces in the Strong Segregation Limit

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ABSTRACT: An extension of the Helfand theory of equilibrium properties of interfaces between different polymers is presented. The corrections to the interface width due to higher-order terms in gradient expansion of the free energy of the system are shown to be negligible in comparison with "end" corrections due to the connectivity of blocks. It is also shown that the latter corrections that are specific for block copolymers are typically much larger than end corrections for a system of immiscible homopolymers. The effect of fluctuations of concentration profiles is also analyzed. It is shown that the effect results in an appreciable increase of the apparent interface width.

1. Introduction

An understanding of the properties of polymer–polymer interfaces is important from both fundamental and practical points of view. Naturally these properties attract considerable interest from polymer scientists.[1–4] One of the first theories of an interface between two immiscible long homopolymers A and B was proposed by Helfand and co-workers.[5,6] The theory adopts Cahn–Hilliard[7] and mean-field approximations and in particular predicts interfacial tension, γ, and interfacial thickness, Δ, in terms of microscopic incompatibility parameter $\chi = \chi_{AB}$:

$$\gamma_0 = \chi^{0.5} a/v; \qquad \Delta_0 = 2a\chi^{-0.5} \tag{1.1}$$

where v is the volume per link and $a = \tilde{a}/6^{0.5}$, $\tilde{a}$ being the statistical length of polymer chains (γ_0 is expressed in kT units). The theory successfully describes the main properties of homopolymer A–homopolymer B and also AB block-copolymer interfaces in the strong segregation limit, SSL ($\chi N \gg 1$, where N is the number of links per chain).

In ref 8 the effect of the finite molecular weight of homopolymers was considered theoretically on the basis of the same mean-field approach. It was shown that the effect results in some increase of the interface thickness and a decrease of the interface tension in qualitative agreement with experiments.[2–4] However, for high molecular weight polymers the experimental deviations from the basic Helfand predictions (eq 1.1) turn out to be much larger than the theoretical corrections (particularly for block-copolymer systems[4]). Also detailed numerical analysis of the mean-field equations for lamellar block copolymers[9] reveals appreciable positive corrections in SSL to the interfacial thickness as given by eq 1.1.[10]

The properties of the interface between block-copolymer domains were also considered by Ohta and Kawasaki.[11] I comment that their general approach is useful in providing a connection between weak and strong segregation limits; however, in mere SSL their results are less accurate than those obtained by Helfand.[6] For example, the appreciable composition dependence of Δ, predicted in ref 11, is incorrect in SSL (in this limit Δ almost does not depend on block-copolymer composition). In the present paper I am going to show that (1) the finite molecular weight corrections to the thicknesses of homopolymer–homopolymer and block-copolymer interfaces are not the same and (2) a quantitative theory for interfacial thickness and other properties for both types of systems must take into account the effect of composition fluctuations. In the next three sections I consider three types of corrections to the thickness Δ: due to corrections to the square-of-gradient form for conformational free energy (i.e., due to nonlocal effects connected with finite-size orientational memory of a polymer backbone); due to connectivity of blocks in a block copolymer; and due to fluctuational effects.

2. Corrections Due to Orientational Effects

The results of the current section are equally applicable to homopolymer–homopolymer and block-copolymer interfaces. Let us assume the homopolymer case for simplicity and consider a system of two long immiscible homopolymers A and B consisting of N_A and N_B links (N_A, $N_B \to \infty$). Let $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ be local volume fractions of A and B links at point $\mathbf{r}$. The free energy of the system (in kT units) in the mean-field approximation could be represented as (see, e.g., ref 8):

$$F = F_{\text{conf}}[\phi_A] + F_{\text{conf}}[\phi_B] + \chi \int \phi_A(\mathbf{r})\, \phi_B(\mathbf{r})\, d^3r/v \tag{2.1}$$

where

$$F_{\text{conf}}[\phi] = (a^2/4v) \int [\nabla\phi(\mathbf{r})]^2 \phi^{-1}\, d^3r \tag{2.2}$$

is the conformational free energy corresponding to a decrease of the conformational entropy of polymer chains for a given distribution $\phi(\mathbf{r})$. Here $a_A = a_B = a$ is the statistical segment of polymer chains divided by $6^{0.5}$ and v is the volume per link (note that the gyration radius of an N chain in the unperturbed state is $R_g = N^{0.5}a$). I also assume incompressibility conditions:

$$\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1 \tag{2.3}$$

The minimum of eq 2.1 under the restriction (2.3) corresponds to

$$\phi_A(z) = 0.5[1 + \tanh(2z/\Delta)]; \qquad \phi_B = 1 - \phi_A \tag{2.4}$$

where $\Delta = \Delta_0$ is defined by eq 1.1 and the z-axis is normal to the A–B interface.

Equation 2.2 could be obtained in the following way:[12] first we consider a system of *ideal* polymer chains (without volume interactions) but under some external field $U(\mathbf{r})$. This field is defined by the condition that the equilibrium distribution of links should be equal to the given one, $\phi(\mathbf{r})$. Then we calculate the total free energy of the system in the field, $F[U]$, and obtain F_{conf} as a difference between $F[U]$ and the direct field contribution:

$$F_{\text{conf}}[\phi] = F[U] - \int U(\mathbf{r})\, \phi(\mathbf{r})\, d^3r \tag{2.5}$$

Strictly speaking eq 2.2 is valid if unperturbed conformations of polymer chains correspond to ideal (truly

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Markovian) random walks. In this case the partition function of an N chain with the end at point $\mathbf{r}$, $\Psi(N,\mathbf{r})$, satisfies the following modified diffusion equation (see ref 12 or ref 13):

$$\partial\Psi/\partial N = a^2\nabla_{\mathbf{r}}^2\Psi - U(\mathbf{r})\,\Psi \qquad (2.6)$$

Equation 2.2 for the conformational free energy could be obtained using eq 2.6 and the general procedure described above in the limit $N \to \infty$.

In the general case we should take into account that macromolecular conformations are not exactly Markovian: the orientations of neighboring links of polymer chains are correlated. The orientational correlations are characterized by the Kuhn segment,

$$l = 6a^2/b \qquad (2.7)$$

where b is the length of one link along the backbone. The external field $U(\mathbf{r})$ could induce some *orientational* order in the polymer system. Thus we should consider the partition function which now depends also on the link orientation $\mathbf{n}$ ($\mathbf{n}$ is the unit vector tangential to the chain backbone). Assuming a *persistent* (wormlike) type of chain flexibility,[14] we get the following generalization of the master equation (2.6) (see, e.g., ref 15):

$$\partial\Psi/\partial N = -b\mathbf{n}\;\partial\Psi/\partial\mathbf{r} + (b/l)\nabla_{\mathbf{n}}^2\Psi - U(\mathbf{r})\,\Psi \qquad (2.8)$$

Assuming weak orientational order (this assumption is valid if the characteristic spatial scale, Δ, is much larger than l), we expand Ψ in spherical functions:

$$\Psi(N,\mathbf{r},\mathbf{n}) = \psi_0(\mathrm{N},\mathbf{r}) + n_\alpha\psi_\alpha(N,\mathbf{r}) + (n_\alpha n_\beta - \delta_{\alpha\beta}/3)\psi_{\alpha\beta}(N,\mathbf{r}) + [n_\alpha n_\beta n_\gamma - (n_\alpha\delta_{\beta\gamma} + n_\beta\delta_{\gamma\alpha} + n_\gamma\delta_{\alpha\beta})/5]\psi_{\alpha\beta\gamma}(N,\mathbf{r}) + \ldots \qquad (2.9)$$

Treating $(l/\Delta)^2$ as a small parameter and using eqs 2.8 and 2.9, one can get eq 2.6 for $\psi_0(N,\mathbf{r})$ in the main (first-order) approximation. In the next (second) order we obtain

$$F_{\mathrm{conf}}[\phi] = (a^2/v)\int K[\phi^{0.5}]\,\mathrm{d}^3r \qquad (2.10)$$

where

$$K[\psi] = (\nabla\psi)^2 - (l^2/12)[(4/15)(\nabla^2\psi)^2 + \nabla^2\psi(\nabla\psi)^2/\psi] \qquad (2.11)$$

The first term on the right-hand side of eq 2.11 corresponds to eq 2.2; the last term represents the correction. Using a "hyperbolic-tangent" density distribution (eq 2.4) as a trial function, we get the "second-order" free energy per unit area of the interface, $\gamma \equiv F/(\text{area})$ (see eqs 2.1 and 2.2 and eqs 2.10 and 2.11):

$$\gamma(\Delta) = (a^2/v\Delta)[1 - 0.1l^2/\Delta^2] + \chi\Delta/(4v) \qquad (2.12)$$

The second term in square brackets is just the correction due to "orientational" memory (which corresponds to the last term on the right-hand side of eq 2.11). In general, we should also take into account a correction due to the nonlocality of interactions (to the last term on the right-hand side of eq 2.12). Note, however, that this correction should be of order $\delta\gamma_{\mathrm{int}} \sim \gamma_0(d/\Delta)^2$ that is appreciably smaller than the orientational correction $\delta\gamma_{\mathrm{ori}} \sim \gamma_0(l/\Delta)^2$ since the characteristic scale of the interactions is on the order of effective chain diameter d, and $(d/l)^2 \lesssim 0.1$ for most polymers.

Equilibrium interface thickness can be easily obtained by minimization of eq 2.12. The result is

$$\Delta \simeq \Delta_0(1 - 0.15l^2/\Delta_0^2) \qquad (2.13)$$

Let us apply this result to the polystyrene (PS)–poly(methyl methacrylate) (PMMA) block-copolymer interface (with nearly equal molecular weights of blocks). These polymers are characterized by[4,16,17]

$$\chi \simeq 0.0372;\quad a = \tilde{a}/\sqrt{6} \simeq 2.8\ \text{Å};\quad b \simeq 3.1\ \text{Å};\quad l \simeq 15\ \text{Å} \qquad (2.14)$$

(the difference between the statistical segments of PS and PMMA is within experimental errors). Using eqs 1.1, 2.13, and 2.14, we get $\Delta_0 \simeq 29$ Å and $\Delta \simeq 28$ Å; these values should be compared with experimental thickness $\Delta_{\mathrm{exp}} \simeq 50$ Å.[4] Thus the correction is small and works in an unfavorable (negative) direction. It could be neglected in comparison with corrections of other types considered below.

3. Correction Due to the Connectivity of Blocks

Let us consider a melt of symmetric AB block copolymers in SSL,

$$\chi N \gg 10 \qquad (3.1)$$

where N is the total number of links per chain. At equilibrium the system should form a lamellar microdomain structure, the period $2D$ of this structure being proportional to $N^{2/3}$. More precisely[18]

$$D \simeq 2(3/\pi^2)^{1/3}aN^{2/3}\chi^{1/6} \qquad (3.2)$$

The properties of an interface between A and B domains in the *main* approximation can be obtained by minimization of the interface free energy functional (eqs 2.1 and 2.2). The result is the same as for homopolymers (see eq 1.1) since $D \gg \Delta_0$.

Let us consider corrections to the interface thickness due to the polymer end effect (which can also be called an effect of finite molecular weight since the averaged concentration of the ends is proportional to $1/N$). We shall see that the main effect of the ends for *block copolymers* stems from the condition that the ends of A and B *blocks* are connected. Let us relax this condition for a moment and consider A and B blocks separately. The partition function of an A block with an end located at point $\mathbf{r}$ is $Z_{\mathrm{A}}(\mathbf{r}) = \text{const} \times \phi_{\mathrm{A}}^{1/2}$ (this is a general result which is valid since the Gaussian polymer size is much larger than the interface thickness, $N^{0.5}a \gg \Delta$; see, e.g., ref 19 for more details). Therefore, the partition function of a block copolymer with a given position of the junction point is

$$Z_{\mathrm{AB}}(\mathbf{r}) = \text{const} \times (\phi_{\mathrm{A}}\phi_{\mathrm{B}})^{1/2} \qquad (3.3)$$

Thus for a given distribution $\rho(\mathbf{r})$ of junction points the free energy of the block-copolymer system can be written as:

$$F = F^{(0)} + \int[\rho\ln(\rho/e) - (\rho/2)\ln(\phi_{\mathrm{A}}\phi_{\mathrm{B}})]\,\mathrm{d}^3r \qquad (3.4)$$

where $F^{(0)}$ is given by eq 2.1. Equation 3.4 was derived in Appendix B of ref 18 using the general approach outlined in ref 20. Assuming the usual form (eq 2.4) for ϕ_{A} and ϕ_{B} and minimizing the free energy (eq 3.4) over $\rho(\mathbf{r})$, we get the interface tension:

$$\gamma = [a^2/(v\Delta) + \chi\Delta/(4v)] - \sigma[\ln(\Delta) + \text{const}] \qquad (3.5)$$

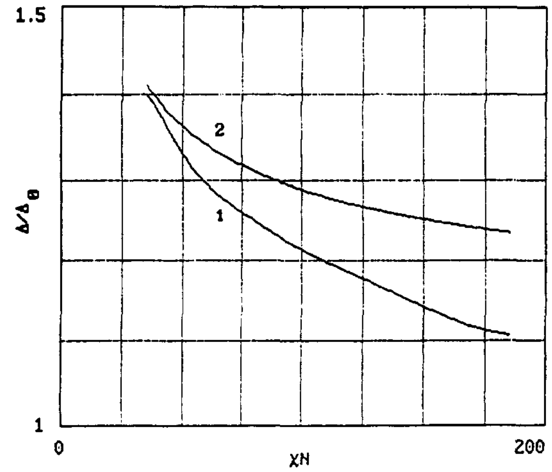

Figure 1. Reduced thickness of the interface for symmetric lamellar morphology as a function of χN. Curve 1: numerical results.[9] Curve 2: eq 3.7.

where

$$\sigma = \int_{-\infty}^{\infty} \rho(z)\, dz = D/(Nv) \tag{3.6}$$

is the number of block-copolymer chains per unit area.

The physical meaning of eq 3.5 is clear: the first two terms in square brackets correspond to the main approximation (eq 2.1); the correction, $-\sigma \ln \Delta$, is the ideal gas free energy of the junction points confined in the layer of thickness Δ. Minimizing $\gamma = \gamma(\Delta)$ (eq 3.5) and using eqs 3.2 and 3.6, we get the equilibrium thickness:

$$\Delta \simeq \Delta_0 + 2D/(N\chi) \simeq \Delta_0[1 + 1.34/(\chi N)^{1/3}] \tag{3.7}$$

with Δ_0 defined in eq 1.1.

So far I have not taken into account that copolymer chains in SSL (see eq 3.1) are elongated in the direction normal to the interfaces (since $D \gg N^{0.5}a$). This elongation could affect the interfacial properties. Let us estimate the effect. Crudely the free energy of elongation per block is $F_{el}(z_1,z_0) \sim (z_1 - z_0)^2/Na^2$, where z_1 is the coordinate of the free end and z_0 of the junction point. For a given z_1 the mean value of F_{el} is

$$\langle F_{el}\rangle = \int \rho(z)\, F_{el}(z_1,z)\, dz \simeq (1/Na^2)[z_1^{\,2} + \text{const} \times \Delta^2]$$

where const ~ 1 and typical $z_1 \sim D$. Thus the *relative* correction to the free energy is of order $\epsilon_{el} \sim (\Delta/D)^2 \sim 1/(\chi N)^{4/3}$, that is much smaller than the correction due to connectivity of order $\epsilon_{co} \sim 1/(\chi N)^{1/3}$ (see eq 3.7). More careful analysis shows that the next order correction to eq 3.7 is proportional to $1/(\chi N)^{2/3}$:

$$\Delta/\Delta_0 = f(1/(\chi N)^{1/3}), \qquad f(\alpha) = 1 + 1.34\alpha + \mathcal{O}(\alpha^2) \tag{3.8}$$

The end correction to the interfacial thickness for a system of two immiscible *homopolymers* was calculated in ref 8. The result is

$$\Delta = \Delta_0[1 + 2\ln(2)/(\chi N)] \tag{3.9}$$

where $N = N_A = N_B$ is the number of links per homopolymer. Thus in SSL an increase of the interfacial thickness due to end effects is much weaker for homopolymers in comparison with block copolymers.

The interfacial thickness for lamellar block copolymers was also calculated by Shull[9] by numerical evaluation of basic mean-field equations (like eq 2.6). The numerical results[9] are compared with eq 3.7 in Figure 1. The two approaches agree within an order of magnitude; eq 3.7 gives a somewhat larger thickness in the region of high χN.[21] Equation 3.7 is also compared with experimental[4] results in Table I (see the Discussion and Conclusions section).

Table I. Comparison of Theoretical Predictions for Interfacial Width Δ (Å) with Experiments for dPS–PMMA Block Copolymers

mol wt, M	expt,[4] Δ_{expt}	eq 1.1 (Helfand), Δ_0	eq 3.7 ("end" corrections), Δ	eqs 4.12 and 3.7 (fluctuation and "end" corrections), Δ^*
30K	50 ± 2	29	47	51
100K	50 ± 3	29	41	48
120K	48 [illegible] 3	29	40	48
300K	50 ± 5	29	37	48
110/107K (blend)	50 ± 5	29	30	49

4. Fluctuation Corrections

So far we have analyzed interfacial properties within the basic mean-field approximation. Now let us go beyond this approximation and take into account thermal fluctuations of concentration profiles. The most important for the interfacial thickness type of fluctuations can be described as follows. Let us consider the surface defined by conditions

$$\phi_A = \phi_B = 0.5 \tag{4.1}$$

In the *mean-field* this is just the plane $z = 0$. However, actually at any given moment condition (4.1) defines some rough surface, $z = \zeta(x,y,t)$; its statistical properties are governed by additional interface free energy (due to an increase of the interface area):

$$F_a \simeq (1/2)\int \gamma_0(\nabla\zeta)^2\, dx\, dy \tag{4.2}$$

In particular eq 4.2 implies that at any given x, y, t the value ζ is distributed with Gaussian density,

$$P(\zeta) = (2\pi s^2)^{-1/2} \exp(-\zeta^2/2s^2) \tag{4.3}$$

where

$$s^2 \equiv \langle\zeta^2\rangle \simeq \int (\gamma_0 q^2)^{-1}\, d^2q/(2\pi)^2 \tag{4.4}$$

and q is the scattering wave vector.

The integral in eq 4.4 should be cut off at both limits. At the upper limit the cutoff is

$$q_{max} \sim 1/\Delta_0 \tag{4.5}$$

since it is meaningless to consider the shape (waviness) of the interface for lateral scales smaller than the interface thickness (careful analysis which is not presented here confirms this point). In order to estimate the lower cutoff, q_{min}, we must take into account an additional contribution to the free energy of wavy interface, δF_{el}, which is due to the elastic energy of the stretching of blocks. This contribution (slightly) depends on the number of lamellar layers in the film. In order to just *estimate* δF_{el}, let us consider a film with the total thickness D equal to the half-period of the lamellar structure of symmetric AB block copolymer. Thus the film consists of two layers, A and B with equal thicknesses, $D_A = D_B = D/2$, and an interface in the middle. The elastic free energy per unit area of one layer (in SSL) is (see, e.g., ref 18)

$$F_A = (\pi^2/48)D_A^{\,3}/(N_A^{\,2}a^2) \tag{4.6}$$

and an analogous equation is valid for the B layer (here $N_A = N_B = N/2$). For a wavy interface the thicknesses are not constant anymore:

$$D_A = D/2 + \zeta(x,y); \qquad D_B = D/2 - \zeta(x,y) \qquad (4.7)$$

so that the blocks are more stretched on the average. Using eqs 4.6 and 4.7, we get

$$F_{el} = \int [F_A + F_B]\,dx\,dy = \text{const} + \delta F_{el}$$

with

$$\delta F_{el} = 0.5K\int \zeta^2\,dx\,dy \qquad (4.8)$$

and

$$K = (\pi^2/2)D/(N^2a^2v)$$

Taking now into account both terms, F_A and δF_{el}, we arrive at the expression for $\langle\zeta^2\rangle$ analogous to eq 4.4 with the integrand $[\gamma_0(q^2 + q_{min}^2)]^{-1}$ instead of $(\gamma_0 q^2)^{-1}$, where

$$q_{min} = (K/\gamma_0)^{0.5} \sim 1/D \qquad (4.9)$$

Hence, we obtain[22]

$$s^2 \simeq (2\pi\gamma_0)^{-1}\ln(q_{max}/q_{min}) \simeq (2\pi\gamma_0)^{-1}\ln(D/\Delta_0) \qquad (4.10)$$

Obviously the concentration profile (along the z-axis) should be smoothed out with the weight (eq 4.3):

$$\phi_A^{(app)}(z) = \int \phi_A(z-\zeta)\,P(\zeta)\,d\zeta \qquad (4.11)$$

where $\phi_A(z)$ is the mean-field result (eq 2.4). It is this apparent profile $\phi^{(app)}$ that is measured by neutron scattering or reflectivity[1–4] (note that the coherent radius in experiments is typically much larger than D). Using eqs 2.4, 4.3, and 4.11, we get $\phi_A^{(app)}(z)$ which is very close to the hyperbolic-tangent form with

$$\Delta^* \simeq [\Delta^2 + 2\pi s^2]^{0.5} = \left[\Delta^2 + \frac{v\Delta_0}{2a^2}\ln(D/\Delta_0)\right]^{0.5} \qquad (4.12)$$

The second term in square brackets represents the fluctuation correction. End effects could be also accounted by eq 4.12 if one takes Δ as defined by eq 3.7.

5. Discussion and Conclusions

Let us compare the results obtained in the previous two sections with neutron reflectivity data[4] for nearly symmetric lamellar dPS–PMMA copolymers. The (averaged) volume per link can be calculated as

$$v = \bar{m}_0/(\bar{\rho}N_{Av}) \simeq 154\ \text{Å}^3 \qquad (5.1)$$

where $\bar{m}_0 = 106$ is the mean molecular weight of a link, $\bar{\rho} = 1.14$ g/cm^3 is the mean density, and N_{Av} is the Avogadro's number. Experimental and theoretical results obtained using eqs 2.13, 2.14, 3.7, 4.12, and 5.1 are collected in Table I. We see that the experimental thickness is much higher than that predicted by the basic Helfand theory. However, a very good agreement is achieved by taking into account both end and fluctuational corrections (which are almost equally important in the molecular weight range of interest). Note that the interfacial thickness is nearly independent of molecular weight, M, since the end correction is a decreasing and the fluctuational one is an increasing function of M.

The values of the interface thickness for a symmetric A/B ≡ PS/PMMA homopolymer blend ($M_A \simeq M_B \simeq 10^5$) are also included in Table I (last line). Note that the end correction here is very small ($\simeq$1 Å). However, the final theoretical estimate for the thickness is not smaller but rather nearly the same as for the block-copolymer case since the fluctuation correction is appreciably larger for the homopolymer system. The reason is the following: Equation 4.9 for the lower cutoff is no more applicable for the homopolymer case since there is no D (no period of the lamellar structure) and more importantly no additional stretching of polymer chains which might be coupled with the waviness. Thus the cutoff, q_{min}, should be determined either by weak (van der Waals) interactions between the interface and the film boundaries or by the coherence length of the neutron reflectivity experiment. The first possibility could be easily ruled out: the van der Waals interactions are too weak for the distances of order 1000 Å (the thickness of the PS layer; the PMMA layer is even thicker[4]). Thus q_{min} should be on the order of the typical projection of the scattering vector onto the interface plane:

$$q_{min} = (2\pi/\lambda)\theta\,\delta\theta_d$$

where θ is typical glancing angle (angle between the neutron beam and the interface), $\delta\theta_d$ is the acceptance angle of the detector, λ is the wavelength of the neutrons. Using the experimental values[4]

$$\theta \sim 0.8°; \qquad \delta\theta_d \sim 0.35°; \qquad \lambda = 2.35\ \text{Å}$$

we get

$$q_{min} \sim 2.2 \times 10^{-4}\ \text{Å}^{-1} \qquad (5.2)$$

Thus we have to rewrite eq 4.12 as

$$\Delta^* \simeq [\Delta^2 + 2\pi s^2]^{0.5} = \left[\Delta^2 - \frac{v\Delta_0}{2a^2}\ln(q_{min}\Delta_0)\right]^{0.5}$$

Using the last equation and eqs 3.9 and 5.2, we get the interface thickness $\Delta^* = 49$ Å which is included in the last line of Table I.

So far we assume that the χ-parameter is constant, i.e., independent of the composition (see eq 2.1). The effective χ-parameter for a real polymer system might be (strictly, should be) composition-dependent. The effect of composition dependence of the χ-parameter on the interfacial thickness was analyzed[23] using the model

$$\chi(\phi) = \chi_0 + \chi_1(\phi - 0.5) + 0.5\chi_2(\phi - 0.5)^2 \qquad (5.3)$$

where $\phi = \phi_A$ is the volume fraction of one of the polymer components. (In fact two cases were considered in ref 23: $\chi_1 = 0$, $\chi_2 \neq 0$; and $\chi_1 \neq 0$, $\chi_2 = 0$.) The final results can be expressed in terms of a ratio of the interface thickness, calculated from "composition-independent" theory (Helfand theory),

$$\Delta_0(\bar{\phi}) = 2a[\chi_{SANS}(\bar{\phi})]^{-0.5}$$

and the prediction of full (composition-dependent) theory, Δ_{cd}. Here $\chi_{SANS}(\bar{\phi})$ is the *apparent* χ-parameter measured in a small-angle neutron scattering (SANS) experiment for a blend with composition $\bar{\phi}$. Note that the value used in the present paper (see eq 2.14) was measured[16] for a symmetric system, $\bar{\phi} = 0.5$. Just for this symmetric composition ($\bar{\phi} = 0.5$) the dependence of Δ_{cd}/Δ_0 on χ_1 turns out to be much weaker than that on χ_2;[23] thus the effect of χ_1 can be neglected. For $\chi_1 = 0$ the result is[23]

$$\Delta_{cd}/\Delta_0 = [1 - \chi_2/(8\chi_0)]^{0.5} \qquad (5.4)$$

In order to estimate the effect of χ_2, one needs to know an estimate on the ratio χ_2/χ_0. Unfortunately, I am not aware of any reliable experimental data on the parameter χ_2/χ_0 for a polymer blend, and, in particular for the PS–PMMA blend studied in ref 4. For a crude estimate of this parameter one can use the results of computer simulations for a model polymer mixture;[24] using the results plotted in Figure 15 of ref 24 for the largest chain lengths (N = 32 steps), I get

$$\chi_2/\chi_0 \simeq 1.5$$

Equation 5.4 with this value of χ_2/χ_0 thus predicts that the correction to the interface thickness due to the composition dependence of the χ-parameter is (1) negative and (2) on the order of 10%. Therefore, this correction should not be of primary importance in view of the much larger positive difference between experimental values, Δ_{expt}, and Δ_0.

Generally the role of fluctuations could be estimated by comparing the second and the first terms in square brackets in eq 4.12. Their ratio is $\epsilon_{\text{fluct}} \ln(D/\Delta_0)$, where

$$\epsilon_{\text{fluct}} = (0.25v\chi^{0.5}/a^3) \tag{5.5}$$

We should expect a relative correction of order ϵ_{fluct} to most of measurable characteristics of a homopolymer or block-copolymer system, in particular to an interface tension or scattering function (normally without a logarithmic factor which is specific to interfacial thickness). Using eqs 2.14, 5.1, and 5.5, we get for a PS–PMMA system $\epsilon_{\text{fluct}} \simeq 0.34$. So the fluctuational corrections are most probably not small and should be taken into account in a quantitative theory.

In conclusion, I have shown that corrections to the interface width due to fourth-order terms in gradient expansion of the free energy are normally negligible. The most important corrections for the case of the block-copolymer interface are due to the chain end effects (for block copolymers these corrections are much more pronounced than for homopolymer systems) and also are due to fluctuations of concentration profiles.

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(21) Note, however, that eq 3.7 was obtained using the assumption of a "hyperbolic-tangent" concentration profile (eq 2.4). If we take into account the deviations from distributions (eq 2.4) (implied by the second term on the right-hand side of eq 3.4) and use the common definition of the thickness,

$$\Delta \equiv [\max|d\phi_A/dz|]^{-1}$$

we will get finally the correction which is smaller by an additional factor $2/\pi$:

$$\Delta/\Delta_0 - 1 \simeq (2/\pi)(1.34)/(\chi N)^{1/3}$$

(22) Note that we omitted numerical prefactors in both estimates (4.5) and (4.9) for the cutoffs; the result (4.10) is valid in a logarithmic approximation.

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