Scattering of Statistical Structure of Polymer/Polymer Interfaces

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ABSTRACT: A theory for scattering of compositional fluctuations near a flat interface between two strongly incompatible polymers is presented. It is shown that scattering of fluctuations gives rise to an appreciable correction to the apparent interfacial thickness. The magnitude of this correction is shown to be crucially dependent on the particular experimental geometry (e.g., oriented interface vs random orientation).

I. Introduction

1. Background. Small-angle X-ray scattering can provide important information on the structure of polymer blends. Macroscopically inhomogeneous systems (e.g., a system of two immiscible homopolymers or microphase-separated block copolymers in the strong segregation limit) reveal two types of scattering: from the *mean* concentration profile and from concentration *fluctuations*. For virtually incompressible two-phase systems (e.g., a system of two immiscible homopolymers or microphase-separated block copolymers in the strong segregation limit) the scattering is mainly due to interfaces between different phases or microdomains. In spite of the apparent importance of scattering from concentration fluctuations near interfaces (statistical structure of interfaces),[1,2] it has not received much theoretical attention. The only theory that I am aware of (ref 1) is based on the phenomenological "finger" model which assumes a particular interface structure and also uses the characteristic width of a finger as a fitting parameter. The aim of the current contribution is to present a new theory for scattering from interfaces employing modern concepts of polymer physics. The results are equally applicable to both homopolymer and block copolymer interfaces.

2. Scattering of a Mean Concentration Profile. Let us consider the simplest example: an incompressible system of two immiscible homopolymers A and B, which are separated into two macrophases, almost pure A and almost pure B with the interface plane at $z = 0$ (thus we assume strong separation, which is valid if the molecular weights of the polymer chains are large enough: $\chi N_A, \chi N_B \gg 1$, where $\chi = \chi_{AB}$ is the Flory parameter of incompatibility of the A and B components). The volume fraction of A-links, $\phi(\mathbf{r}) \equiv \phi_A(\mathbf{r})$, varies smoothly near the interface from 1 to 0. Mean-field theory predicts the following composition profile:[3]

$$\phi(z) = \phi_0(z) = 0.5[1 - \tanh(z/\Delta)] \tag{1}$$

where Δ is the half-width of the interface. The profile for B-links is related to that for A-links by the incompressibility condition:

$$\phi_A(z) + \phi_B(z) = 1 \tag{2}$$

The scattering intensity (for pinhole collimation and apart from a constant prefactor) is given by the square of the Fourier transform of the density distribution of one component:

$$SI_0(\mathbf{q}) = |\int \phi_0(\mathbf{r}) \exp(-i\mathbf{qr})\, d^3r|^2 \equiv |\tilde{\phi}_0(\mathbf{q})|^2 \tag{3}$$

where $\mathbf{q}$ is the scattering wave vector (S is the total interface area). For a 1d profile, eq 1, we get the following intensity per unit area of the interface:

$$I_0(\mathbf{q}) = \frac{(2\pi)^2}{q_z^{\,2}}\delta^{(2)}(q_\parallel)\, H_0(q_z\Delta) \tag{4}$$

where

$$H_0(K) = |\int \phi_0'(z) \exp(-iKz)\, dz|^2 = \left[\frac{\pi K}{2\sinh(\pi K/2)}\right]^2 \tag{5}$$

and $\delta^{(2)}(q_\parallel) = \delta(q_x)\delta(q_y)$. After averaging over all possible orientations of the scattering vector $\mathbf{q}$ (for a given $|\mathbf{q}|$), we get

$$\tilde{I}_0(q) \equiv (4\pi)^{-1}\int I_0(q\mathbf{n})\, d^2n = (2\pi/q^4)H_0(q\Delta) \tag{6}$$

(here $\mathbf{n}$ is a unit vector). Note that in the limit of extremely sharp interface, $\Delta \rightarrow 0$, we recover the well-known Porod law:[4] $\tilde{I} \sim q^{-4}$. Thus deviations of $\tilde{I}$ from Porod's form can give information about the interface width. However, these deviations are affected by concentration fluctuations which are considered in the next section.

II. Fluctuations of Concentration Profile

In the general case the scattering intensity is proportional to the *mean square* of the Fourier transform of the concentration distribution:

$$I(\mathbf{q}) = \langle|\tilde{\phi}(\mathbf{q})|^2\rangle = I_m(\mathbf{q}) + I_{fl}(\mathbf{q}) \tag{7}$$

where

$$I_m(\mathbf{q}) = |\langle\tilde{\phi}(\mathbf{q})\rangle|^2 \tag{8}$$

corresponds to scattering from the mean profile and

$$I_{fl}(\mathbf{q}) = \langle|\delta\tilde{\phi}(\mathbf{q})|^2\rangle \tag{9}$$

corresponds to fluctuations. Here, $\delta\tilde{\phi}(\mathbf{q}) = \tilde{\phi}(\mathbf{q}) - \langle\tilde{\phi}(\mathbf{q})\rangle$ is the Fourier transform of the concentration fluctuation at some particular moment and $\langle ... \rangle$ stands for the time average.

The statistical properties of the interface are determined by the effective Hamiltonian, that is the free energy as a

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functional of the concentration distributions, which can be represented as (see, e.g., ref 5)

$$F[\phi] = F_{\rm conf}[\phi_A] + F_{\rm conf}[\phi_B] + \chi \int \phi_A(\mathbf{r})\, \phi_B(\mathbf{r})\, d^3r \quad (10)$$

where

$$F_{\rm conf}[\phi] = \frac{a^2}{4v}\int [\nabla\phi(\mathbf{r})]^2 \phi^{-1}\, d^3r \quad (11)$$

is the conformational free energy which accounts for a decrease of available conformational space with an inhomogeneous distribution of a polymer component (here and below all energetic quantities are expressed in kT units). The last term in eq 10 corresponds to the (unfavorable) interactions between A- and B-links. Here, $a = a_{st}/6^{1/2}$, a_{st} being the statistical length of a polymer chain, and v is the volume per link (we also assume that polymers are "geometrically" symmetric: $a_A = a_B = a$; $v_A = v_B = v$). Equation 11 is valid provided that the characteristic scale of inhomogeneity, Δ, is much larger than a but much smaller than the coil size, $R_g = N^{0.5}a$:[6]

$$a \ll \Delta \ll N^{0.5}a \quad (12)$$

Minimization of eq 10 under the condition, eq 2, gives the mean-field prediction for the interfacial profile (see eq 1) with

$$\Delta = \Delta_0 \equiv a\chi^{-0.5} \quad (13)$$

Thus the inequalities, eq 12, are satisfied if χ is small and χN is large.

The density distribution, $P[\phi]$, of static (equal-time) fluctuations is governed by the classical relation:

$$P[\phi] = \text{const} \exp(-F[\phi]) \quad (14)$$

In a dense system like a polymer melt or blend, the fluctuations are typically small[7] so that $\delta\phi \ll 1$; therefore we can expand $F[\phi]$ around its minimum value $F_0 = F[\phi_0]$ and omit higher-order terms:

$$F[\phi] \simeq F_0 + 0.5\int K(\mathbf{r},\mathbf{r}')\, \delta\phi(\mathbf{r})\, \delta\phi(\mathbf{r}')\, d^3r\, d^3r' \quad (15)$$

The concentration correlation function can now be easily related to the kernel K:

$$\langle \delta\phi(\mathbf{r})\, \delta\phi(\mathbf{r}')\rangle = [K(\mathbf{r},\mathbf{r}')]^{-1} \quad (16)$$

where $[...]^{-1}$ means the inverse operator.

To obtain $[K]^{-1}$ we make use of the substitution

$$\phi = \sin^2(\xi/2) \quad (17)$$

where $\xi = \xi_0 + \delta\xi$, $\xi_0(z) = \arccos(\tanh(z/\Delta))$, and

$$\delta\phi = \frac{1}{2\cosh(z/\Delta)}\delta\xi \quad (18)$$

and rewrite the effective Hamiltonian in terms of $\delta\xi$:

$$F = F_0 + \frac{a^2}{4}\int (\nabla\delta\xi)^2\, d^3r + \frac{\chi}{4}\int \left[1 - \frac{2}{\cosh^2(z/\Delta)}\right]\delta\xi^2\, d^3r \quad (19)$$

Taking into account that the system is homogeneous (on the average) in x,y plane, we write

$$\delta\xi(r) = \exp(iq_x x + iq_y y)\, \psi(z) \quad (20)$$

Diagonalization of the quadratic form $(F - F_0)$ yields the following equation for $\psi(z)$:

$$(-\psi'' + q_\parallel^2\psi)\Delta^2 + \left[1 - \frac{2}{\cosh^2(z/\Delta)}\right]\psi = E\psi \quad (21)$$

For any given projection of the wave vector onto the interface plane, $q_\parallel = (q_x^2 + q_y^2)^{1/2}$, the spectrum of eq 21 consists of one discrete level, $E = (q_\parallel\Delta)^2$, corresponding to

$$\psi_d(z) = 2^{-0.5}/\cosh(z/\Delta) \quad (22)$$

and a continuous branch, $E = 1 + (q_\parallel\Delta)^2 + \kappa^2$, $\kappa^2 > 0$, with

$$\psi_c(\kappa,z) = (1 + \kappa^2)^{-0.5} \exp(i\kappa z/\Delta)[\tanh(z/\Delta) - i\kappa] \quad (23)$$

We can represent the function of $\delta\xi$ as a combination of eigenfunctions:

$$\delta\xi(\mathbf{r}) = \int \frac{d^2q_\parallel}{(2\pi)^2} \exp[i(q_x x + q_y y)]\, \Xi(\mathbf{q}_\parallel, z) \quad (24)$$

where

$$\Xi(\mathbf{q}_\parallel,z) = D(\mathbf{q}_\parallel)\, \psi_d(z) + \int \frac{d\kappa}{2\pi} C(\kappa,\mathbf{q}_\parallel)\, \psi_c(\kappa,z) \quad (25)$$

Note that first term on the right-hand side of eq 25 corresponds to the discrete spectrum fluctuations of interfacial profile ($\delta\phi_d$), while the second term corresponds to the continuous spectrum ($\delta\phi_c$).

The free energy can now be written as

$$F - F_0 = \frac{\chi\Delta}{4}\int \frac{d^2q_\parallel}{(2\pi)^2}(q_\parallel\Delta)^2|D(\mathbf{q}_\parallel)|^2 + \int \frac{d\kappa}{2\pi}[1 + (q_\parallel\Delta)^2 + \kappa^2]|C(\kappa,\mathbf{q}_\parallel)|^2 \quad (26)$$

Thus (within the Gaussian approximation) the variables $D(\mathbf{q}_\parallel)$, and $C(\kappa,\mathbf{q}_\parallel)$ fluctuate independently. The corresponding correlation functions are

$$\langle D(\mathbf{q})\, D(-\mathbf{q})\rangle = \frac{2}{\chi\Delta}(q\Delta)^{-2} \quad (27)$$

$$\langle C(\kappa,\mathbf{q})\, C(-\kappa,-\mathbf{q})\rangle = \frac{2}{\chi\Delta}[1 + \kappa^2 + (q\Delta)^2]^{-1} \quad (28)$$

Using eqs 9, 18, 24, 27, and 28, we get finally the scattering intensity (per unit area)

$$I_{fl}(\mathbf{q}) = \frac{av}{\chi^{3/2}}[F_l(q_z\Delta,q_\parallel\Delta) + F_s(q_z\Delta,q_\parallel\Delta)] \quad (29)$$

where the functions F_l and F_s correspond to the contributions due to the discrete spectrum and the continuous spectrum of eq 21, respectively:

$$F_l(K,Q) = H_0(K)/Q^2 \quad (30)$$

$$F_s(K,Q) = (\pi/4)K^2\int_{-\infty}^{\infty} d\kappa \left\{(1 + \kappa^2)(1 + Q^2 + \kappa^2) \times \cosh^2\left[\frac{\pi}{2}(K - \kappa)\right]\right\}^{-1} \quad (31)$$

After some transformations eq 31 can be simplified as

$$F_s(K,Q) = \frac{K^2}{Q^2}\left\{K^{-2} - \frac{\pi^2}{4\sinh^2(\pi K/2)} - \frac{1}{2(1+Q^2)^{1/2}} \operatorname{Re} \Psi'\left(\frac{1+(1+Q^2)^{1/2}+iK}{2}\right)\right\} \quad (32)$$

where $\Psi'(z) = d^2 \ln[\Gamma(z)]/dz^2$.

Note that discrete-spectrum fluctuations, $\delta\phi_d$ (see eqs 18, 22, 24, and 25), correspond to a shift of the interface profile as a whole in the z direction:

$$\phi_0(z) \rightarrow \phi(\mathbf{r}) = \phi_0(z) + \delta\phi_d = \phi_0(z - \zeta(x,y))$$

where the equation $z = \zeta(x,y)$ defines the deformed rough (waved) interface. On the other hand, the continuous-spectrum fluctuations, $\delta\phi_c$, correspond to a roughness of the interface *profile* (rather than the roughness of the interface as a 2d object) under the condition

$$\text{for any } x,y\text{:} \quad \int \delta\phi_c(x,y,z)\, dz = 0 \quad (33)$$

Thus, the F_l contribution to the scattering intensity is due to the roughness of the interface, and F_s is due to fluctuations of the interface profile.

For a random orientation of the interface boundary (or alternatively after averaging over orientations of the scattering vector), we get

$$\tilde{F}_l(K) \equiv \int_0^1 F_l(Kt, K(1-t^2)^{1/2})\, dt = \begin{cases} K^{-2}\ln(2K/\epsilon), & K \ll 1 \\ (\pi/3)K^{-3}, & K \gg 1 \end{cases} \quad (34)$$

$$\tilde{F}_s(K) = \int_0^1 F_s(Kt, K(1-t^2)^{1/2})\, dt = \begin{cases} 0.237\, K^2, & K \ll 1 \\ K^{-2}, & K \gg 1 \end{cases} \quad (35)$$

where $K = q\Delta$. Thus the F_l term is dominant for small q (long wavelength, $q^{-1} \gg \Delta$), and the F_s term is dominant for large q (short wavelength). Here, $\epsilon = q_{min}\Delta$, where q_{min} is the cutoff wave vector corresponding to the largest scale in the interface plane, that is to the characteristic lateral size of a lamellar stack.

III. Fluctuational Corrections to the Mean Interface Profile

We have to take into account that the effect of fluctuations for scattering is twofold: first, a direct contribution I_{fl}, and second, a correction to the *mean* composition profile, $\langle\phi\rangle$, which actually does not coincide with the mean field prediction (eq 1) with Δ_0 (eq 13). We are now in a position to consider this second effect which results in a difference between I_0 (eq 4) and I_m (eq 8). The difference between $\langle\phi\rangle$ and ϕ_0 is mainly due to the waviness of the interface (discrete mode), which leads to a larger value of an apparent thickness.[8] Using the simple approach of ref 8, we write

$$\langle\phi(z)\rangle = \langle\phi_0(z+\zeta)\rangle$$

where ζ is a random shift of the interface profile as a whole in the z direction. Thus

$$\langle\tilde{\phi}(\mathbf{q})\rangle = \tilde{\phi}_0(\mathbf{q})\,\langle\exp(iq_z\zeta)\rangle \approx \tilde{\phi}_0(\mathbf{q})(1 - q_z^{\,2}\langle\zeta^2\rangle/2) \quad (36)$$

Here, we take into account that $\langle\zeta\rangle = 0$ and also assume that the amplitude of fluctuations is typically small: $q\zeta \ll 1$. The distribution of ζ can be easily deduced from the results of the previous section. However, we prefer to derive it here again using more simple arguments. The statistics of ζ is governed by the additional free energy of a rough (wavy) interface due to an increase of the interface area:

$$F[\zeta(x,y)] = F_0 + 0.5\int \gamma_0(\nabla\zeta)^2\, dx\, dy \quad (37)$$

where

$$\gamma_0 = a\chi^{0.5}/v \quad (38)$$

is the interface tension.[3] Thus (compare with eqs 14–16)

$$\langle\zeta^2\rangle = \int \frac{d^2q_\parallel}{(2\pi)^2\gamma_0 q_\parallel^{\,2}} \quad (39)$$

Clearly, the integral in eq 39 is log-divergent; thus the cutoffs at the large q and small q limits should be specified: $q_{min} = \epsilon/\Delta$, $q_{max} \sim 1/\Delta$. The upper cutoff is due to the coupling between the discrete and continuous modes of fluctuations which is essential for $q \lesssim 1/\Delta$; a more detailed analysis (similar to that of section 2) shows that this coupling leads to the effective cutoff at

$$q_{max} = 2/\Delta$$

Thus we get

$$\langle\zeta^2\rangle = \frac{v\ln(2/\epsilon)}{(2\pi)a\chi^{0.5}} \quad (40)$$

Using eqs 36 and 8, we get $I_m(\mathbf{q}) = I_0(\mathbf{q})[1 - q_z^2\langle\zeta^2\rangle]$. Note that the contribution to the scattering intensity due to smearing out of the mean profile by fluctuations is negative: a thicker interface always produces less scattering. Finally, using eqs 7 and 29, we obtain

$$I(\mathbf{q}) = I_0(\mathbf{q}) + \frac{av}{\chi^{3/2}}[F_L(q_z\Delta, q_\parallel\Delta) + F_s(q_z\Delta, q_\parallel\Delta)] \quad (41)$$

where

$$F_L(K,Q) = H_0(K)[Q^{-2} - (2\pi)\delta^{(2)}(Q)\ln(2/\epsilon)] \quad (42)$$

Note that the term F_L accounts for two different effects of the interface roughness (see two terms in square brackets on the right-hand side of eq 42): the direct scattering due to discrete-mode fluctuations (F_l; see eqs 29 and 30) and the (negative) contribution due to the fluctuation-induced smearing of the concentration profile. For a random orientation of the interface, we get

$$\tilde{I}(q) = \tilde{I}_0(q) + \frac{av}{\chi^{3/2}}[\tilde{F}_L(q\delta) + \tilde{F}_s(q\delta)] \quad (43)$$

where $\tilde{F}_s(K)$ is defined in eq 35 and

$$\tilde{F}_L(K) = \frac{\ln(K)}{K^2}H_0(K) + K^{-2}\int_0^1 \frac{H_0(Kt) - H_0(K)}{1-t^2}\, dt \quad (44)$$

with the following asymptotic behavior:

$$\tilde{F}_L(K) = \begin{cases} K^{-2}\ln(K), & K \ll 1 \\ (\pi/3)K^{-3}, & K \gg 1 \end{cases} \quad (45)$$

Thus the logarithmic dependence of the orientation-averaged scattering on the cutoff at small wave vectors (i.e., the dependence on the lateral size of lamellar stacks) is finally canceled.

IV. Discussion and Conclusion

To show the role of scattering due to fluctuations of the interface profile (statistical structure of the interface), we rewrite the final result (eq 43) as

$$\tilde{I}(q) = \tilde{I}_0(q)\{1 + A_{fl}[H_0(q\delta)]^{-1}(q\delta)^4[\tilde{F}_L(q\delta) + \tilde{F}_s(q\delta)]\} \quad (46)$$

where

$$A_{fl} = \frac{v\chi^{0.5}}{(2\pi)a^3} \quad (47)$$

is the dimensionless parameter. Normally, the parameter A_{fl} is not large (e.g., for a PS/PMMA blend $A_{fl} \approx 0.2$).[8] For $K = q\Delta \ll 1$ eq 46 can be simplified:

$$\tilde{I}(q) = \tilde{I}_0(q)\{1 + A_{fl}(q\Delta)^2 \ln(q\Delta)\} \quad (48)$$

Thus the total fluctuational contribution to the scattering intensity is *negative* for scattering vectors smaller than the inverse interface thickness. The *relative* effect of the fluctuations is small (for $K \lesssim 1$) provided that A_{fl} is small.

For $K \gg 1$ we get

$$\tilde{I}(q) = \tilde{I}_0(q)[1 + A_{fl}\pi^{-2} \exp(\pi q\Delta)] \quad (49)$$

Thus in the region of large q the scattering of fluctuations (of the statistical structure of the interface) turns out to be more important than the scattering from the regular structure (averaged interface profile). In fact, the contribution from fluctuations dominates over the regular part already for $K \gtrsim 1.5$, that is, for scattering vectors $q \gtrsim 1.5/\Delta$ (here we assume that $A_{fl} \sim 0.2$).

Now let us compare the predicted scattering intensity with the earlier results[1] which in our current definitions can be represented as

$$I(\mathbf{q}) = I_0(\mathbf{q}) + (\pi R_0^2)q_z^{-2} \times \exp[-(R_0 q_{\parallel}/2)^2][1 - H_0(q_z\Delta)] \quad (50)$$

where R_0 is the effective radius of a finger which is assumed to be smaller than the interface thickness. After an averaging over random orientations, we get (from eq 50)

$$\tilde{I}(q) = \tilde{I}_0(q) + \delta\tilde{I}(q) \quad (51)$$

with

$$\delta\tilde{I}(q) = \begin{cases} (\pi^3/12)R_0^2 a^2/\chi, & q \ll 1/\Delta \\ (\pi/2)q^{-4}, & q \gg 1/R_0 \end{cases} \quad (52)$$

On the other hand, eq 43 implies that

$$\delta\tilde{I}(q) = \begin{cases} (av/\chi^{3/2}) \ln(q\Delta)(q\Delta)^{-2}, & K = q\Delta \ll 1 \\ (av/\chi^{3/2})(q\Delta)^{-2}, & K \gg 1 \end{cases} \quad (53)$$

Therefore (1) the asymptotic behaviors (for $q \ll 1/\Delta$ and $q \gg 1/R_0$) of the scattering of the statistical structure of the interface obtained in ref 1 (eq 52) and in the present paper are qualitatively different (in both limits eq 52 underestimates the scattering intensity) and (2) comparing the absolute values of $\delta\tilde{I}$ for $q \sim 1/\Delta$, we get an estimation for the finger width:

$$R_0 \sim (v/a)^{0.5}\chi^{-0.25} \quad (54)$$

Note that R_0 depends not only on the "geometrical" parameters of the links (a, v) but also on the χ parameter.

We close with a final note concerning the apparent interface thickness, Δ^*, which could be defined in the following way: Let us consider the scattering for small wave vectors, $q \ll 1/\Delta$, and let us attribute the fluctuational correction, δI, to the effective change of the thickness, $\Delta \rightarrow \Delta^*$:

$$I(\mathbf{q}) = I_0(\mathbf{q},\Delta) + \delta I(\mathbf{q}) \cong I_0(\mathbf{q},\Delta^*) \quad (55)$$

where I_0 is defined in eq 4. Using this definition for $\mathbf{q}$ strictly normal to the interface, we get (with logarithmic accuracy)

$$\Delta^* \simeq \Delta[1 + (6/\pi^2)A_{fl} \ln(1/\epsilon)] \quad (56)$$

On the other hand, for *random* orientation the result (with the same accuracy) is

$$\Delta^* \simeq \Delta[1 - (6/\pi^2)A_{fl} \ln(q\Delta)] \quad (57)$$

Thus in both cases the apparent thickness is increased due to the waviness of the interface.[8] In the first case the projection of the wave vector onto the interface plane is zero; therefore all modes of waviness with characteristic scales between Δ and Δ/ϵ contribute to the smearing effect. On the other hand, in the second case (of random orientation) the range of the wavelengths is more narrow: between Δ and $1/q$.

In conclusion, the apparent interface thickness might depend on the geometry of the scattering experiment (oriented interface/random orientation) and on the scattering wavevector.

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