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Block Copolymer Theory. 4. Narrow Interphase Approximation

Eugene Helfand* and Z. R. Wasserman

Bell Laboratories, Murray Hill, New Jersey 07974. *Received April 23, 1976*

ABSTRACT: A theory of microdomain structure in block copolymers, developed earlier, is simplified by approximations appropriate to the case where the interphase width is narrow compared to the domain size. In this case one identifies contributions to the free energy from: interfacial tension; localization of block joints in the interface; and entropy loss arising from preferential selection of conformations which keep the density uniform. The free energy for lamellar microphases is written as an algebraic function of domain size and minimized to obtain predictions of domain periodicity distance. These are compared with experiments.

Block copolymers are receiving widespread attention because they offer great opportunity to the chemist to create polymeric blends with desirable physical features. It is fundamental that if the A and B chains which are joined in the block copolymer have a positive heat of mixing there is a tendency toward phase separation. However, the bond between A and B chains puts limits on the degree to which spatial separation can occur. The result is a microdomain morphology, the key to many of the valuable mechanical properties of these systems. In this paper we will develop a practical means of calculating the equilibrium size of these domains for amorphous block copolymers and apply the technique to lamellar systems.

In earlier works[1–5] we have presented a general theory[2,3] of inhomogeneous polymeric systems which will be reviewed in section I. An application was made to the interface between two immiscible homopolymers.[3,4] Since the results are of importance in the present theory, they will be summarized in section II. The theory was also applied to the block copolymer problem,[5] but its use requires a moderately difficult numerical computation. In the present paper we develop a more approximate theory of block copolymers in which we assume that the interphase between the domains is narrow compared with the size of the domains. This enables us to fuse the closed-form solutions of the equations for homopolymer interfaces to a solution appropriate to pure microdomains in which the blocks all originate at the interface. While the solution for the blocks in the domains must be obtained numerically this is done once and the result applied to all cases of a given geometry.

The physical picture of a block copolymer system which emerges from this work is the following. As in an ordinary phase separation the tendency is for the domains to grow in order to reduce the interfacial free energy per unit volume. If d is a measure of domain size, e.g., the periodicity distance which is the sum of the A and B lamellar widths (see Figure 1), then the interfacial free energy per unit volume falls off as $1/d$, within the context of the approximations of this paper. To understand the free energy terms which oppose domain growth, the consequences of the existence of the A–B joints along the macromolecule must be pursued. These bonds are most likely to be found in the interphase. In the present approximation the width of the interphase is independent of domain size. Hence the localization of the joint's degree of freedom leads to a loss of entropy which grows as log d.

There is another severe consequence of the joint being localized in the narrow interfacial region. Focus on the A chains in an A-rich domain. Each chain has one end, the one that is linked to B, near the outer border of the domain. This produces a tendency for the density to be higher near the boundaries than in the domain center. Any such inhomogeneous density pattern has too high a free energy to be commonly observed. What occurs is that the system statistically suppresses the large number of conformations which lead to inhomogeneity and favors the rarer conformations which reach into, and fill, the lamellae's centers. Associated with this unequal weighting of conformations is a loss of conformational entropy, which increases as the microdomains grow. Solution of the equations presented in this paper indicates that this entropy loss term is well fitted by a $d^{2.5}$ power law.

Combination of these terms produces a free energy density, eq 5.2, which has a minimum as a function of d. The minimum is the predicted domain size. Comparison with a number of experimental determinations of block copolymer lamellar spacings is made in section VII and the results are good.

The theory is developed for both diblock, A–B, and triblock, A–B–A, copolymers. We predict that the domain sizes for these two types of molecules will differ by only a few percent if the A blocks are the same size and the B block of A–B–A is twice the size of the B block of A–B (the weight percents of A and B are the same in the two materials).

In the Appendix details of the calculational procedure for block copolymer problems will be presented.

I. General Theory of Inhomogeneous Polymer Blends

In many problems which arise in the study of inhomogeneous polymer blends we are called upon to study the statistics of polymer molecule conformations in an inhomo-

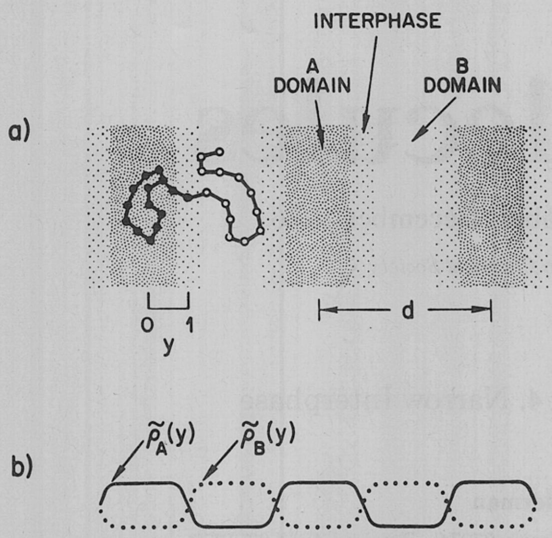

Figure 1. (a) Schematic diagram of a lamellar microdomain structure in a block copolymer system. The periodicity distance is d. The basic cell in which eq III.18 to III.27 are to be solved goes from the center of one domain to the interface and is measured on a scale y which goes from 0 to 1. (b) The density profiles through the interface.

geneous medium, perhaps a mixture of A and B with density patterns $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$. There are a number of parameters which characterize this system:

1. The density of the polymer of type K when pure is ρ_{0K}, the number of segments (which we will take as corresponding to the monomers) per unit volume. We will frequently express the density of K in the blend in reduced units:

$$\tilde\rho_K(\mathbf{r}) = \rho_K(\mathbf{r})/\rho_{0K} \tag{I.1}$$

2. The degree of polymerization of a molecule or block of K is Z_K.

3. The Kuhn statistical length of a segment of K is b_K. The quantities ρ_{0K}, Z_K, and b_K all depend on the arbitrary specification of what a segment is. The combinations of variables $Z_K b_K^2$, $\tilde\rho_K$, and

$$\beta_K^2 \equiv \rho_{0K} b_K^2/6 \tag{I.2}$$

which are independent of this choice of segment, are all that appear in the final formulas.[4]

4. The degree of repulsion between A and B relative to AA and BB interactions is measured by a parameter α such that the heat of mixing (more generally, the contact free energy of mixing) per unit volume of a uniform mixture of density ρ_A and ρ_B is

$$k_B T \alpha \tilde\rho_A \tilde\rho_B/(\tilde\rho_A + \tilde\rho_B) \tag{I.3}$$

where k_B is Boltzmann's constant and T is temperature.

5. For simplicity we will assume that there is zero volume of mixing; i.e., for all uniform mixtures at the reference pressure

$$\tilde\rho_A + \tilde\rho_B = 1 \tag{I.4}$$

If the pressure is changed, or if the system is nonuniform, eq I.4 need not hold. In that case there will be an additional contribution to the free energy density of

$$\tfrac{1}{2}(1/\kappa)(\tilde\rho_A + \tilde\rho_B - 1)^2 + 0(\tilde\rho_A + \tilde\rho_B - 1)^3 \tag{I.5}$$

The compressibility, κ, will be assumed to be independent of composition. The removal of that assumption produces no change in results when κ is small. Other assumptions, such as the concentration independence of α or the zero volume change of mixing, can be removed with only slight increase in the complexity of calculations.[4]

In the development of a quantitative theory of polymer conformational statistics, attention focuses on a function $Q_K(\mathbf{r},t;\mathbf{r}_0)$, which is proportional to the probability density that a chain of type K with number of segments (degree of polymerization) t has one end at $\mathbf{r}_0$ and the other at $\mathbf{r}$.[2,3] The constants of proportionality which multiply formulas involving Q_K are determined by appropriate normalization conditions. For the Gaussian random walk model in a uniform system of type K, Q_K is the familiar Gaussian; or, equivalently stated, Q_K satisfies a diffusion equation. Employing mean field theory one shows that in an inhomogeneous system Q_K satisfies a modified diffusion equation (ref 2, eq 3.9 and 5.9)

$$\frac{\partial Q_K}{\partial t} = \frac{b_K^2}{6}\nabla^2 Q_K - \frac{1}{\rho_{0K}}\left\{\alpha\left[\frac{\tilde\rho_{K'}(\mathbf{r})}{\tilde\rho_A(\mathbf{r}) + \tilde\rho_B(\mathbf{r})}\right]^2 + \frac{1}{\kappa k_B T}[\tilde\rho_A(\mathbf{r}) + \tilde\rho_B(\mathbf{r}) - 1]\right\} Q_K \tag{I.6}$$

where K′ is B if K is A, and vice versa. The term in braces represents $(1/k_B T)$ times the chemical potential change of bringing a segment of K from pure K into the mixture of densities $\tilde\rho_A(\mathbf{r})$ and $\tilde\rho_B(\mathbf{r})$. (In an earlier paper[3] a rational was presented for using the first power of $[\tilde\rho_{K'}/(\tilde\rho_A + \tilde\rho_B)]$ in eq I.6 instead of the square. It can be shown that all final results are the same when there is zero volume of mixing and $\kappa \to 0$. Difference are absorbed into the function w_κ introduced below. The essential point is that the relations between w_κ and a function w_κ' which might have been introduced would be

$$\alpha\tilde\rho_B^2 + w_\kappa = \alpha\tilde\rho_B + w_\kappa'$$

$$\alpha\tilde\rho_A^2 + w_\kappa = \alpha\tilde\rho_A + w_\kappa'$$

These two equations are compatible if $\tilde\rho_A + \tilde\rho_B = 1$. We have employed the quadratic density formula in recent works[1,4,5] because it is more directly related to the Flory–Huggins formula for chemical potential. Thus it is probably better for nonzero κ, though it has been shown that the formulas are equivalent for $\kappa \to 0$.[2] The quadratic density form is also superior because for a homogeneous system w_κ is zero but w_κ' would not be.) Q_K satisfies the initial condition

$$Q_K(\mathbf{r},0;\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0) \tag{I.7}$$

Boundary conditions will be discussed later.

For diblock copolymers, the densities involved in eq I.6 are related to the Q_K's by the formula[2,5]

$$\rho_A(\mathbf{r}) = \frac{N}{\mathcal{Q}V}\int_0^{Z_A} dt' \int^V d\mathbf{r}_A\, d\mathbf{r}_J\, d\mathbf{r}_B \times Q_A(\mathbf{r}_A, Z_A - t'; \mathbf{r}) Q_A(\mathbf{r}, t'; \mathbf{r}_J) Q_B(\mathbf{r}_J, Z_B; \mathbf{r}_B) \tag{I.8}$$

$$\mathcal{Q} = \frac{1}{V}\int^V d\mathbf{r}_A\, d\mathbf{r}_J\, d\mathbf{r}_B\, Q_A(\mathbf{r}_A, Z_A; \mathbf{r}_J) Q_B(\mathbf{r}_J, Z_B; \mathbf{r}_B) \tag{I.9}$$

with a similar equation for ρ_B. N is the number of diblock copolymer molecules which have their joints in the region V.

II. Interface between Homopolymers

We shall review the theory of the interface between immiscible homopolymers A and B.[3,4] Define a function $q_K(\mathbf{r},t)$

$$q_K(\mathbf{r},t) = \int d\mathbf{r}_0\, Q_K(\mathbf{r},t;\mathbf{r}_0) \tag{II.1}$$

which satisfies eq I.6, too. For very high degrees of polymerization, t, the unit at $\mathbf{r}$ is unaware of the condition of the ends of the macromolecule. This manifests itself in $q_K(\mathbf{r},t)$ being independent of t. Thus $q_K^I(x)$, the interfacial solution, satisfies the equation

$$0 = \beta_K^2 \frac{\partial^2 q_K^I(x)}{\partial x^2} - \left\{\alpha\left[\frac{\tilde\rho_{K'}(x)}{\tilde\rho_A(x) + \tilde\rho_B(x)}\right]^2 + \frac{1}{\kappa k_B T}[\tilde\rho_A(x) + \tilde\rho_B(x) - 1]\right\} q_K^I(x) \tag{II.2}$$

where all inhomogeneity is in the direction x normal to the interface. In this case the density is given by

$$\tilde\rho_K(x) = [q_K^I(x)]^2 \tag{II.3}$$

The solution of eq II.2 and II.3 in the limit of vanishing compressibility is given by a rather lengthy algebraic expression, eq 4.3 of ref 4. The general formula need not be reproduced here, but note that it simplifies greatly to[3]

$$\tilde\rho_A(x) = [1 + \exp(2\alpha^{1/2}x/\beta)]^{-1} \tag{II.4}$$

$$\tilde\rho_B(x) = \tilde\rho_A(-x) \tag{II.5}$$

for the symmetric case $\beta_A = \beta_B \equiv \beta$.

A measure of the width of the interface is

$$a_I \equiv (\mathrm{d}x/\mathrm{d}\tilde\rho_A)_{\tilde\rho_A=1/2} \tag{II.6}$$

$$a_I = 2\left(\frac{\beta_A^2 + \beta_B^2}{2\alpha}\right)^{1/2} \tag{II.7}$$

The interfacial tension is found to be

$$\gamma = k_B T \alpha^{1/2}\left[\frac{\beta_A + \beta_B}{2} + \frac{1}{6}\frac{(\beta_A - \beta_B)^2}{\beta_A + \beta_B}\right] \tag{II.8}$$

In these explicit formulas the effects of nonlocality of the interactions (a molecule at $\mathbf{r}$ interacts with molecules at $\mathbf{r}' \neq \mathbf{r}$) are not included, though the nonlocal case is treated in ref 4 and by a lattice model in ref 6.

III. Approximate Block Copolymer Theory

In an earlier paper[5] numerical solutions were obtained to the eq I.6 to I.9 for Q_K for a symmetric case where $\beta_A = \beta_B$, $b_A^2 Z_A = b_B^2 Z_B$, and lamellar microdomains. In this paper we will approximate solutions for the case of an interface much narrower than the domains. First the approximation is formulated in a mathematical way, and then the same result is achieved by more physical arguments. The above symmetry will not be assumed.

We treat initially the case of a diblock copolymer in a lamellar microdomain morphology, as illustrated in Figure 1. (Work is now in progress on the cylindrical and spherical systems.) The periodicity distance, d, is related to the domain widths d_K by

$$d = d_A + d_B \tag{III.1}$$

The dividing plane between A and B may be taken, just for reference, as the Gibbs dividing surface, which is the same for A and B when there is zero volume change of mixing. The thicknesses d_A and d_B must be related by

$$\frac{d_A \rho_{0A}}{Z_A} = \frac{d_B \rho_{0B}}{Z_B} = \frac{d}{(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})} \tag{III.2}$$

It suffices to solve the equations in a region of width ½d which goes from the center of an A domain to the center of a B domain.

To exploit the fact that the central plane of every domain is a plane of symmetry, consider, as an alternative to section II, functions $Q_K(x,t;x_0)$ with x measured from the center of a K domain. Let these Q_K satisfy the boundary condition

$$\left.\frac{\partial Q_K(x,t;x_0)}{\partial x}\right|_{x=(1/2)nd} = 0 \tag{III.3}$$

$$n = -\infty \text{ to } +\infty$$

i.e., the derivative of Q_K vanishes at the center of every domain. Then $Q_K(x,t;x_0)$ is proportional to the probability of a K chain of degree of polymerization t having one end on plane x when the other end is at x_0 or at the mirror images of x_0 in every domain center plane (viz., the points $nd \pm x_0$). Note that one of the points $nd \pm x_0$ lies in each of the fundamental cells, so that an integration of Q_K with respect to x_0 over the region 0 to ½d is equivalent to integrating the Q_K of section II over the whole volume. Thus in eq I.8 and I.9 we may take

$$V = \tfrac{1}{2}d \tag{III.4}$$

$$N = \tfrac{1}{2}d[(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})]^{-1} \tag{III.5}$$

V and N being on a per-unit-cross-sectional-area basis. With this definition Q_K has the symmetry of the system:

$$Q_K(nd \pm x,t;x_0) = Q_K(x,t;x_0) \tag{III.6}$$

and we need only solve for Q_K in the domain $x = 0$ to ½d.

Q_K satisfies eq I.6. In the limit of small compressibility the condition of zero volume of mixing holds to within order κ, i.e.,

$$\tilde\rho_A(x) + \tilde\rho_B(x) = 1 + 0(\kappa) \tag{III.7}$$

and the last term of eq I.6 becomes an indeterminant form

$$\lim_{\kappa\to 0}\frac{1}{\kappa k_B T}[\tilde\rho_A(x) + \tilde\rho_B(x) - 1] \equiv w_\kappa(x) \tag{III.8}$$

The equations for Q_K become

$$\frac{\partial Q_K}{\partial t} = \frac{b_K^2}{6}\frac{\partial^2 Q_K}{\partial x^2} - \frac{1}{\rho_{0K}}\{\alpha[\tilde\rho_{K'}(x)]^2 + w_\kappa(x)\}Q_K \tag{III.9}$$

$$\rho_K(x) = \frac{2N}{Qd}\int_0^{Z_K}\mathrm{d}t'\int_0^{(1/2)d}\mathrm{d}x_K\,\mathrm{d}x_J\,\mathrm{d}x_{K'}\,Q_K \times (x_K, Z_K - t';x)Q_K(x,t';x_J)Q_{K'}(x_J,Z_{K'};x_{K'}) \tag{III.10}$$

$$Q = \frac{2}{d}\int_0^{(1/2)d}\mathrm{d}x_A\,\mathrm{d}x_J\,\mathrm{d}x_B\,Q_A(x_A,Z_A;x_J)Q_B(x_J,Z_B;x_B) \tag{III.11}$$

The function $w_\kappa(x)$ is then to be adjusted so that the equation

$$\tilde\rho_A(x) + \tilde\rho_B(x) = 1 \tag{III.12}$$

is satisfied for all x.

We seek an approximate solution of the equations which will be appropriate in the case that the interface is much narrower than the domain size. In this case we may consider that there is a narrow interfacial region, with width of $0[(\beta_A^2 + \beta_B^2)/\alpha]^{1/2}$ according to eq II.7, dividing two domains that are essentially pure A or B at densities ρ_{0A} or ρ_{0B}. In this limit we shall find that it is consistent to assume that the density profiles through the interface are identical with those found between semiinfinite homopolymer phases. From eq III.10 we see that we will be concerned with $Q_K(x,t;x_0)$ for $t = 0(Z_K)$, for x and x_0 in the K domain or the interface. For these cases write Q_A in the form

$$Q_A(x,t;x_0) = \frac{2}{d_A}Q(y,t;y_0)q_A^I(x - x_G)q_A^I(x_0 - x_G) \tag{III.13}$$

where $q_A^I(x)$ is the homopolymer interfacial solution; reduced distance units are defined by

$$y = 2x/d_A \tag{III.14}$$

and x_G is the Gibbs dividing surface. In particular, for x_0 in the interphase write

$$Q_A(x,t;x_0) = \frac{2}{d_A} Q(y,t;1) q_A^I(x - x_G) q_A^I(x_0 - x_G) \tag{III.15}$$

because on the scale of y the entire interphase lies very close to $y = 1$. When x is far from the interface in the A domain $q_A^I(x - x_G)$ will be close to unity. When both x and x_0 are far from the interface

$$Q_A(x,t;x_0) \approx \frac{2}{d_A} Q(y,t;y_0) \tag{III.16}$$

If we substitute eq III.13 in eq III.9 for Q_A we find that $Q(y,t;y_0)$ satisfies

$$\frac{\partial Q}{\partial t} = \frac{4}{6}\frac{b_A^2}{d_A^2}\frac{\partial^2 Q}{\partial y^2} + \frac{b_A^2}{3d_A}\frac{\partial \log q_A^I(x - x_G)}{\partial x}\frac{\partial Q}{\partial y} - \frac{\alpha}{\rho_{0A}}\{[\tilde{\rho}_B(x)]^2 - [\tilde{\rho}_B^I(x)]^2\}Q - \frac{1}{\rho_{0A}}[w_\kappa(x) - w_\kappa^I(x)]Q \tag{III.17}$$

where $\rho_B^I(x)$ and $w_\kappa^I(x)$ are the values of these functions for a homopolymer interphase. A solution can be found which produces nearly the same density distribution through the interphase of block copolymer domains as between homopolymers A and B. In this case the third term on the right will be small. The second term vanishes by employing the boundary condition $\partial Q/\partial y = 0$ at $y = 1$, while for values of y significantly smaller than unity $\partial q_A^I/\partial x$ vanishes.

In summary, the equations which determine the properties of the system in the A domain and into the interphase are

$$R_A^2 \frac{\partial Q}{\partial t} = -\mathcal{L} Q \tag{III.18}$$

$$\mathcal{L} = -\frac{\partial^2}{\partial y^2} + u(y) \tag{III.19}$$

$$R_A = 6^{1/2} d_A / 2b_A \tag{III.20}$$

$$\tilde{\rho}_A(x) = \tilde{\rho}(y)\tilde{\rho}_A^I(x - x_G) \tag{III.21}$$

$$\tilde{\rho}(y) = \frac{1}{\mathcal{Q}_A Z_A}\int_0^{Z_A} \mathrm{d}t \int_0^1 \mathrm{d}y_A\, Q(y_A, Z_A - t; y) Q(y,t;1) \tag{III.22}$$

$$\mathcal{Q}_A = \int \mathrm{d}y_A\, Q(y_A, Z_A; 1) \tag{III.23}$$

with boundary conditions

$$\left.\frac{\partial Q}{\partial y}\right|_{y=0} = \left.\frac{\partial Q}{\partial y}\right|_{y=1} = 0 \tag{III.24}$$

and initial condition

$$Q(y, t = 0; y_0) = \delta(y - y_0) \tag{III.25}$$

(which is correct on the scale of domain size and $t \to 0$ on a scale of Z_A). The function $u(y)$ is to be selected so as to maintain uniform density in the domain:

$$\tilde{\rho}(y) = 1 \qquad 0 \le y \le 1 \tag{III.26}$$

Actually this defines $u(y)$ only to within an additive constant, and all physical features are independent of that constant. It is convenient to fix the constant with the auxiliary condition

$$\int_0^1 \mathrm{d}y\, u(y) = 0 \tag{III.27}$$

The description of A domains by eq III.18 to III.27 is equally applicable to B domains.

In deriving these equations use has been made of the fact that the $\mathcal{Q}$ of eq I.9 factors into

$$\mathcal{Q} = \mathcal{Q}_A \mathcal{Q}_B a_J / \tfrac{1}{2} d \tag{III.28}$$

$$a_J = \int_{d_A}^{d_B} \mathrm{d}x\, q_A^I(x) q_B^I(x) \tag{III.29}$$

By extending the limits of integration to ±∞ (as is appropriate for a narrow interface), changing the variable of integration to $\rho_A^I(x)$, and using eq 4.3 of ref 4, one finds

$$a_J = \frac{\pi}{2}\left(\frac{\beta_A\beta_B}{\alpha}\right)^{1/2} P_{1/2}\left(\frac{\beta_A^2 + \beta_B^2}{2\beta_A\beta_B}\right) \tag{III.30}$$

where $P_{1/2}$ is a Legendre function. This explicit form of a_J will not be needed, though, in the determination of microdomain size.

There is an alternative, and somewhat more physical, argument which leads to the same set of equations describing the conformational statistics in the block copolymer domains. For a narrow interphase we hypothesize that the structure in the interphase is the same as that in a homopolymer interphase. In particular, in this region, $q_A(x,t)$, as defined by eq II.1, is just

$$q_A(x,t) \propto q_A^I(x - x_G) \tag{III.31}$$

As we go into the A domain to a plane x', a distance large on the scale of interphase width ($x' - x_G \to \infty$) but small on the scale of A domain size ($y' \approx 1$ still), the interfacial transition from pure B to pure A can be regarded as essentially complete. From this point in toward the center $\rho_B(x)$ and $w_\kappa^I(x)$ are nearly zero so eq III.18 for $Q(y,t;y_0)$ is obtained. It remains only to specify how to join the domain solution to the interphase solution at the plane x'. Since the transition to A is essentially complete at x', we will say that, for every molecule which crosses x' from the domain, statistically an equivalent one crosses the plane from the interphase. Thus the plane x' acts as a reflecting surface as far as the statistical function Q_A is concerned; as an equation,

$$0 \approx \left.\frac{\partial Q_A}{\partial x}\right|_{x=x'} \approx \frac{2}{d_A}\left.\frac{\partial Q}{\partial y}\right|_{y=1} \tag{III.32}$$

as before.

IV. Free Energy

In ref 2 the formula for the free energy,

$$\frac{F}{Nk_BT} = \frac{1}{Nk_BT}\int \mathrm{d}\mathbf{r}\left\{\Delta f^*[\rho_A(\mathbf{r}),\rho_B(\mathbf{r})] - \rho_A(\mathbf{r})\frac{\partial \Delta f^*}{\partial \rho_A(\mathbf{r})} - \rho_B(\mathbf{r})\frac{\partial \Delta f^*}{\partial \rho_B(\mathbf{r})}\right\} - \log \mathcal{Q} - \frac{\alpha(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})} \tag{IV.1}$$

was derived, where Δf^* is the free energy density of mixing. The final term sets the zero of free energy as a homogeneous phase of the block copolymer. With Δf^* given by the Flory–Huggins form, eq I.3, plus the term eq I.5 to account for volume change, we find

$$\frac{F}{Nk_BT} = -\frac{1}{N}\int \mathrm{d}\mathbf{r}\, w_\kappa(\mathbf{r}) - \log \mathcal{Q} - \frac{\alpha(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})} \tag{IV.2}$$

It is convenient to take out of thisequation a term which represents the surface free energy,

$$\frac{\gamma}{Nk_BT} = -\frac{1}{N}\int \mathrm{d}\mathbf{r}\, w_\kappa^I(\mathbf{r}) \tag{IV.3}$$

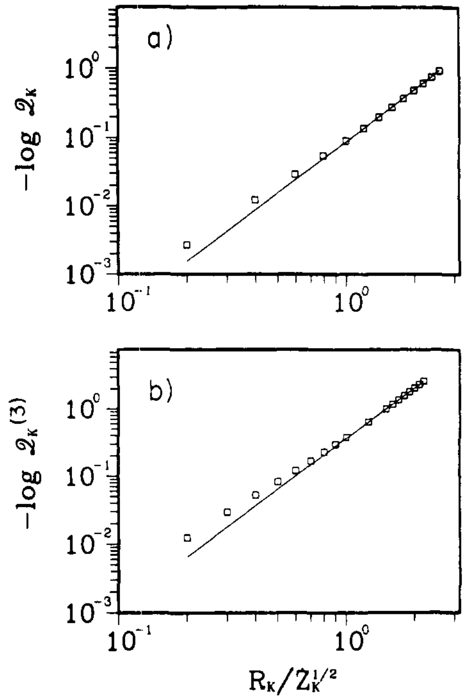

Figure 2. (a) Plot of $-\log Q_K$ vs. $R_K/Z_K{}^{1/2}$ on a log–log scale. The solid line represents $-\log Q_K = 0.085(R_K/Z_K{}^{1/2})^{2.5}$. (b) Plot of $-\log Q_K{}^{(3)}$ vs. $R_K/Z_K{}^{1/2}$. The data are fitted by $-\log Q_K{}^{(3)} = 0.36_5(R_K/Z_K{}^{1/2})^{2.5}$.

given by eq II.8. Next set the level of the remainder, $w_\kappa - w_\kappa{}^{\mathrm{I}}$, so the integral is zero, eq III.27. Use the factored form, eq III.28, for Q, and introduce eq III.5 for N. The result is

$$\frac{F}{Nk_BT} = \frac{2\gamma}{k_BT}\left(\frac{Z_A}{\rho_{0A}} + \frac{Z_A}{\rho_{0B}}\right)\frac{1}{d} + \log\left(\frac{d}{2a_J}\right) - \log Q_A - \log Q_B - \frac{\alpha(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})} \quad \text{(IV.4)}$$

V. Calculations

The eq III.18 to III.27, describing block copolymer statistical properties in the domain morphology, must be solved by numerical techniques. These will be discussed in some detail in the Appendix, but basically use is made of a spectral representation of the function Q in terms of the eigenfunctions and eigenvalues of the operator $\mathcal{L}$. A multidimensional Newton's method is employed to solve for the $u(x)$ which is implicity given by eq III.26.

For determination of the free energy we calculate $-\log Q_K$ by eq III.23. It is a function only of the variable $R_K/Z_K{}^{1/2} \equiv 6^{1/2}d_K/2b_KZ_K{}^{1/2}$. Figure 2 shows a plot of $-\log Q_K$ on a log–log scale. For $R_K/Z_K{}^{1/2}$ less than unity the free energy term is approximately proportional to the square of this variable. We shall be more interested in values of this variable greater than unity, where a 2.5 power relation seems quite appropriate. (Actually, a least-squares fit to the log–log plot gives a 2.48 power law, but we cannot regard the difference from 2.50 as significant.) Shown is the fit of the data to

$$-\log Q_K = 0.085(R_K/Z_K{}^{1/2})^{2.5} \quad \text{(V.1)}$$

which is the formula to be adopted for calculational purposes. Bear in mind that in Figure 2 the log–log scale unduly exaggerates $R_K/Z_K{}^{1/2} \lesssim 1$.

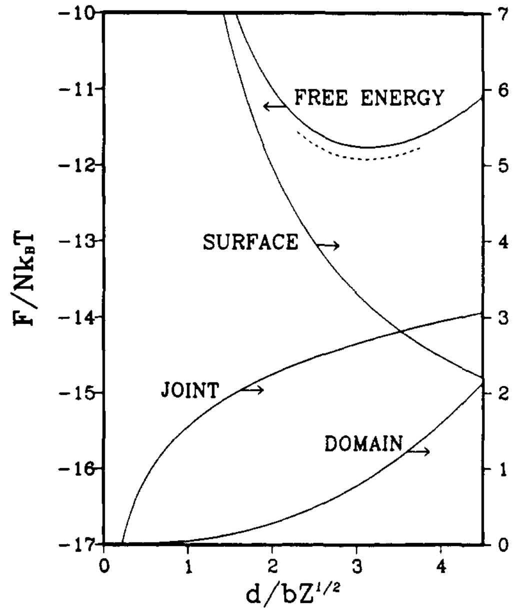

Figure 3. Free energy per molecule as a function of periodicity distance d for $\chi Z = 37$. The components of the free energy labeled surface, joint, and domain are respectively the first three terms on the right-hand side of eq V.2. The dotted curve is the more exact result calculated in ref 5 by the full theory of eq III.9 to III.12.

The free energy formula for a diblock copolymer in a domain geometry with repeat distance d is thus given by

$$\frac{F}{Nk_BT} = \frac{2\gamma}{k_BT}\left(\frac{Z_A}{\rho_{0A}} + \frac{Z_B}{\rho_{0B}}\right)\frac{1}{d} + \log\left(\frac{d}{2a_J}\right) + 0.141\,\frac{(Z_A{}^{1/2}/b_A\rho_{0A})^{2.5} + (Z_B{}^{1/2}/b_B\rho_{0B})^{2.5}}{[(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})]^{2.5}}\,d^{2.5} - \frac{\alpha(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})} \quad \text{(V.2)}$$

with γ given by eq II.8 (or γ could be taken from experiment if available). This is the free energy expression qualitatively described in the introductory section. Figure 3 is a plot of the free energy per molecule vs. d for a diblock copolymer system with lamellar domains. We have taken a symmetric case: $b_A = b_B = b$, $\rho_{0A} = \rho_{0B} = \rho_0$, and $Z_A = Z_B = 2$. It is convenient to define a mixing parameter $\chi = \alpha/\rho_0$. In Figure 3 we set $\chi Z = 37$. The illustration shows that, as the domain size increases, the surface free energy per molecule falls off as $1/d$, the free energy coming from localization of the joint rises as $\log d$, and the free energy associated with loss of conformational entropy rises as $d^{2.5}$. The total free energy has a minimum at $d/bZ^{1/2} = 3.1$, which is the predicted domain periodicity. In general the value of d is given by the condition for a minimum of F/N:

$$0 = -\frac{2\gamma}{k_BT}\left(\frac{Z_A}{\rho_{0A}} + \frac{Z_B}{\rho_{0B}}\right) + d + 0.35_3\,\frac{(Z_A{}^{1/2}/b_A\rho_{0A})^{2.5} + (Z_B{}^{1/2}/b_B\rho_{0B})^{2.5}}{[(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})]^{2.5}}\,d^{3.5} \quad \text{(V.3)}$$

In ref 5 eq III.9 to III.12 were solved numerically without assuming that it was proper to divide the system into pure domains separated by a narrow interphase. The free energy calculated by this more exact theory is shown by the dotted curve in Figure 3. The agreement is excellent both as to the location of the minimum (both at $d/bZ^{1/2} = 3.1$) and the magnitude of the free energy ($F/Nk_BT = -11.8$ for the narrow interphase model vs. -11.9 for the full theory). The density profile predicted by the approximate eq iii.18 to III.27 is

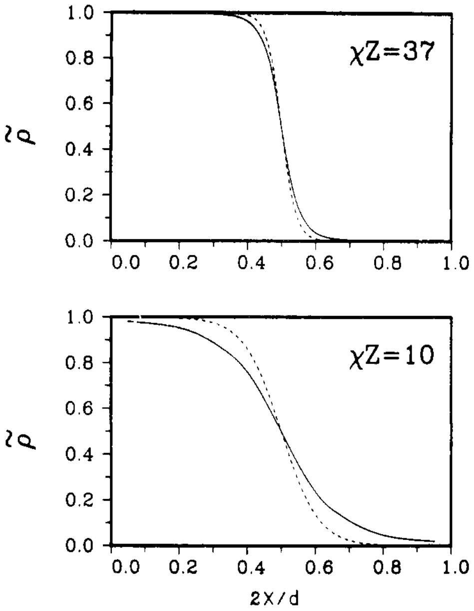

Figure 4. The density profile as a function of distance, for $\chi Z = 37$ and 10. The dashed curves are the density profiles according to the narrow interphase assumptions, eq III.21. The solid line is calculated without approximation in ref 5. For $\chi Z = 37$ the approximation appears to be good. For $\chi Z = 10$ significant interpenetration is occurring, but the approximation still seems qualitatively reasonable.

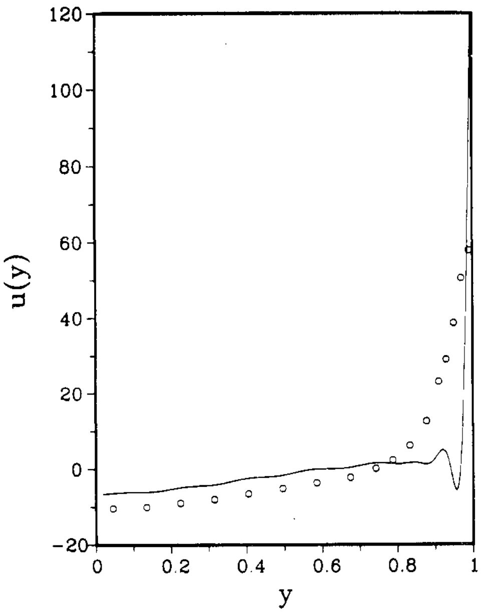

Figure 5. The function $u(y)$, which forces $\tilde{\rho}(y)$ to equal unity in an incompressible material, is shown solid. It is an approximation to $(R_A^2/\rho_{0A})[w_\kappa(\tfrac{1}{2}d_A y) - w_\kappa^I(x - x_G)]$ in the limit of $\chi Z \to \infty$. The latter function for $\chi Z = 37$, using results of ref 5, is shown by the circles.

contrasted with the exact results in Figure 4. For $\chi Z = 37$ the agreement is good. For $\chi Z = 10$ the interphase is clearly not narrow compared with the domain width. Still eq III.21 seems to give a reasonable density profile. So, too, the free energy function for $\chi Z = 10$ is not bad even for this extreme case. The approximate eq V.2 has a minimum of $F/Nk_BT = -0.63$ at $d/bZ^{1/2} = 2.4$, whereas the exact results are -1.02 and 2.3, respectively.

It is not surprising that the exact results show deeper penetration of B into the A phase and vice versa. There is more freedom in placement of the joint, and it is easier to fill the domain centers, when the interphase is broader.

In achieving the numerical solutions we have assumed for $u(y)$ a piecewise constant function. The results for $u(y)$ at $R_K/Z_K^{1/2} = 1.9$ are shown in Figure 5. Near $y = 0$, the center of a domain, the function u shows a dip which has the effect of bringing the chains into this region. Conversely, the rise in the u function near $y = 1$ opposes the tendency for material to accumulate near the interface, as is exhibited when $u = 0$. We cannot say that the exact form of u near the wall is as shown since this tends to vary from calculation to calculation without significantly changing Q_K. Also the ripples are not significant. In Figure 5 we plot, too, the value of $(R_A^2/\rho_{0A})[w_\kappa(1/2d_A y) - w_\kappa^I(x - x_G)]$ from the full theory. According to eq III.17 it is this combination which is approximated by $u(y)$. Most noteworthy is the narrow, sharp peak of $u(y)$ near the interface. This feature is definitely necessary to keep $\tilde{\rho}(y)$ uniform, but it is difficult to interpret physically its magnitude.

VI. Triblock Copolymers

Triblock copolymers, A–B–A, can be treated by only a minor extension of the previous formulas. The density of component B can be written

$$\rho_B(x) = \frac{2N}{Q^{(3)}d}\int_0^{Z_K} \mathrm{d}t \int_0^{(1/2)d} \mathrm{d}x_{A1}\,\mathrm{d}x_{J1}\,\mathrm{d}x_{J2}\,\mathrm{d}x_{A2} \times Q_A(x_{A1},Z_A;x_{J1})Q_B(x_{J1},Z_B - t;x) \times Q_B(x,t;x_{J2})Q_A(x_{J2},Z_A;x_{A2}) \quad \text{(VI.1)}$$

$$Q^{(3)} = \frac{2}{d}\int_0^{(1/2)d} \mathrm{d}x_{A1}\,\mathrm{d}x_{J1}\,\mathrm{d}x_{J2}\,\mathrm{d}x_{A2} \times Q_A(x_{A1},Z_A;x_{J1})Q_B(x_{J1},Z_B;x_{J2})Q_A(x_{J2},Z_A;x_{A2}) \quad \text{(VI.2)}$$

With the interfacial part of the Q function factored out as in eq III.13 this simplifies to

$$\tilde{\rho}(y) = \frac{1}{Q_B^{(3)}Z_B}\int_0^{Z_B} \mathrm{d}t\; Q(1,Z_B - t;y)Q(y,t;1) \quad \text{(VI.3)}$$

$$Q_B^{(3)} = Q(1,Z_A;1) \quad \text{(VI.4)}$$

for the density of the center block in its domain. Solution of eq III.18 for Q, with $u(y)$ now adjusted so that the new $\tilde{\rho}(y)$ is unity throughout, produces a result for $-\log Q_B^{(3)}$ which is again fitted by a 2.5 power law:

$$\begin{aligned} -\log Q_B^{(3)} &= 0.36_5(R_B/Z_B^{1/2})^{2.5} \\ &= 2(0.077)[R_B/(1/2Z_B)^{1/2}]^{2.5} \end{aligned} \quad \text{(VI.5)}$$

The coefficient 0.077 being close to the coefficient 0.085 of eq V.1 indicates that the free energy of a triblock copolymer, hence the domain size, does not differ greatly from that of a diblock copolymer obtained by cutting the middle block at the center.

Without going through all the details, we present the working formula for the free energy per molecule of a system of A–B–A triblock copolymers with degrees of polymerization Z_A, Z_B, and Z_A in the respective blocks:

$$\frac{F^{(3)}}{Nk_BT} = 2\left\{\frac{2\gamma}{k_BT}\left(\frac{Z_A}{\rho_{0A}} + \frac{\tfrac{1}{2}Z_B}{\rho_{0B}}\right)\frac{1}{d} + \log\frac{d}{2a_J} + 0.141\,\frac{(Z_A^{1/2}/b_A\rho_{0A})^{2.5} + 0.90[(\tfrac{1}{2}Z_B)^{1/2}/b_B\rho_{0B}]^{2.5}}{[(Z_A/\rho_{0A}) + (\tfrac{1}{2}Z_B/\rho_{0B})]^{2.5}}\,d^{2.5} - \frac{\alpha(Z_A/\rho_{0A})(\tfrac{1}{2}Z_B/\rho_{0B})}{(Z_A/\rho_{0A}) + (\tfrac{1}{2}Z_B/\rho_{0B})}\right\} \quad \text{(VI.6)}$$

This is to be minimized with respect to d (cf. eq V.3).

VII. Comparison with Experiment

In the following discussion the notation PS or S = poly-

Table I
Comparison of Measured and Predicted Periodicity, *d*, of Lamellar Block Copolymer Microdomains

Polymer	Mol wt, kg/mol	d_{exptl}, nm	d_{calcd}, nm	Σ, nm^2	Ref
S-I	70–70	59	68	6.9	7, 8
S-I	23–8	22	23	4.3	9, 10
S-I	23–17.5	29	29	4.7	9, 10
S-I	23–21	31	31	4.8	9, 10
S-I	23–28	36	35	5.0	9, 10
S-I	30–17.5	34	32	4.9	9, 10
S-I	46.9–17	45	38	5.4	9, 10
S-I	29–34	50	40	5.4	9
S-I	22.9–30.9	95	36	5.1	11
S-I	62–43	66–67	55	6.4	12
S-I-S	28.5–20–28.5	37	27	4.6	9
S-B	32–48	44.5	51	5.5	13
S-B	35.5–54.5	49	55	5.7	13, 14
S-B	71–46	74	63	6.3	10
S-B	48.9–32.4	46	49	5.6	15
B-S-B	19.4–72–19.4	40	38	4.9	16
B-S-B	24–72–24	44	41	5.0	16
B-S-B	37.5–72–37.5	48	48	5.3	16
B-S-B	73–72–73	66	64	6.0	16
S-B-S	14.1–27.9–14.1	27–30	24	4.0	17
S-B-S	17–68–17	30	38	4.7	18

Table II
Densities and Monomer Lengths

Polymer	Density, $\rho_{0\mathrm{K}}$, mol/m^3 × 10^{-3}	Length, b_{K}, nm
PS	10.1	0.68
PI	13.6	0.63
PB	16.5	0.63

styrene, PI or I = polyisoprene, and PB or B = polybutadiene is used.

We have calculated the periodicity distance, *d*, for a number of block copolymers using eq V.3 or the minimization of eq VI.6. These are compared with experiments in Table I. (Also included is the cross-sectional area per A–B joint, Σ, which equals $1/N$ for diblock copolymers and $2/N$ for triblocks.) The agreement is good considering that the present theory has no adjustable parameters and that the values of the physical variables are not known with high accuracy. A wide variety of values are reported for b_{K} in the Polymer Handbook.[19] Neutron scattering experiments should soon reduce the uncertainty, and indeed it is this source that we use for PS.[20] The values used for b_{K} and $\rho_{0\mathrm{K}}$ are listed in Table II. In view of the other uncertainties no effort was made to correct for temperature.

For α we have adopted the expression given by Rounds and McIntyre:[21]

$$\alpha = -900 + (7.5 \times 10^5/T)(\mathrm{mol/m^3}) \qquad \text{(VII.1)}$$

They assume a common value for PS/PI and PS/PB. This α is based on the miscibility of oligomers. The 95% confidence limits are reported as ±90% on the first term and ±35% on the second.

A further uncertainty is what temperature to use. Because most of the experimental determinations of microdomain sizes are performed at temperatures below the glass transition temperature of PS, the literature values of the periodicity distance are not equilibrium values. A number of researchers have prepared or annealed their samples at temperatures of 100 °C or greater. We suppose that the size and structure of the domains are fixed as the system passes through the glass transition temperature on cooling, except for thermal contraction. The domain structure is known to become more ordered when solvent cast samples are annealed, but the ordering is slow below the 90–100 °C range.[13] Kawai et al.[11] report a change of *d* from 59 to 66 nm upon annealing their S–I samples. Terrisse and Skoulios[7,8] have done systematic studies on the effect of temperature on the structure parameter, *d*, of a previously annealed S–I material. Their values of *d* varied from 56 nm at 0 °C to a maximum of 59 nm at 105 °C (probably not an equilibrium phenomenon) and then fell. Other investigators[9,10,15,16] have gathered data in a variety of solvents and extrapolated to zero solvent concentration. The results are reported not to differ significantly from those obtained on annealed samples. In view of this picture we have selected a value of $\alpha = 1.1_4 \times 10^3$ (mol/m^3), which corresponds to 90 °C, and used it for all the calculations.

A number of other block copolymers, such as polystyrene–poly-2-vinylpyridine,[10] have been studied but not included in Table I because we have no estimate for α. Note that α enters only in the determination of the interfacial tension, so a more direct approach to acquiring the data needed for prediction of domain size would be direct measurement of interfacial tension.[22,23] We are surprised that, to our knowledge, the interfacial tension between polystyrene and the polydienes has not even been measured, although all manners of blends of these materials are so common!

When the molecular weight of the blocks is very high the entropy loss associated with maintaining uniform density outweighs that associated with joint localization, so that asymptotically

$$d \propto M^{0.643}$$

where $9/14 \approx 0.643$. Hoffman et al.[14] have attempted to fit their data with a power relationship. For spheres and cylinders they find a 0.58 power law, using less than a decade of *M* values. They do not report an uncertainty of this exponent, but 0.643 does not yield an unreasonable fit either.

VIII. Appendix. Computational Methods

Central to the theory presented above is the solution of a modified diffusion equation for a function *Q* which describes the conformational statistics of the macromolecules. An unusual feature of that equation is that it contains an unknown field, $u(y)$, something like a Lagrange multiplier, which must be adjusted to maintain overall uniform density. The numerical procedures employed for solution of the problem are out of the ordinary, and it is for this reason that we are providing some detail of the computational methods.

Basically, to solve eq III.18 to III.27 a function $u(y)$ is selected as a first approximation. Q, $\tilde{\rho}$, and Q_{A} are then written in terms of the spectrum of $\mathcal{L}$. If $\tilde{\rho}(y)$ is not everywhere equal to unity, then $u(y)$ is readjusted by a Newton's iteration technique. The functional derivative $\delta u(y)/\delta\rho(y')$ required is also derived from a spectral representation. To prevent uncontrolled oscillations from developing in $u(y)$ upon iteration the Tikhonov[24] regularization procedure is employed.

As a practical matter it is necessary to use a function $u(y)$ which is piecewise constant over regions. The special features of the calculation resulting from this discretization are discussed in section B.

In ref 5 equations of greater generality are presented for the description of lamellar domains; i.e., the narrow interphase approximation is not made. The equations are somewhat more involved, but the numerical iteration seems better behaved. We have solved only the simplified case where the A and B blocks are symmetric in the sense that they have the same density when pure, same monomer length, and same block size. The procedure is an extension of that employed for a single domain except that some extra self-consistency must be achieved.

A. General Solution in a Single Domain. When the narrow interphase approximation is made for diblock copolymers one need only treat equations which describe a polymer block with one end at the outer border of a single, pure domain. Solution to the set of eq III.18 to III.27 will be achieved in terms of the spectrum of $\mathcal{L}$ (eq III.19). A guess is made about $u(y)$ [on the basis of previous results for closely related parameters, by intuition, or even $u(y) = 0$]. The eigenvalues and eigenfunctions of $\mathcal{L}$ we call ϵ_p and $\varphi_p(y)$. The Q is given by

$$Q(y,t;y_0) = \sum_p \varphi_p(y)\varphi_p(y_0)\exp(-\epsilon_p t/R_A{}^2) \qquad (A.1)$$

When this is inserted into eq III.23 for $\mathcal{Q}_A$ one finds

$$\mathcal{Q}_A = \sum_p c_p{}^\dagger c_p \exp(-\epsilon_p Z_A/R_A{}^2) \qquad (A.2)$$

$$c_p{}^\dagger = \varphi_p(1) \qquad (A.3)$$

$$c_p = \int_0^1 \varphi_p(y)\,dy \qquad (A.4)$$

The formula for the density is

$$\tilde{\rho}(y) = \frac{R_A{}^2}{Z_A\mathcal{Q}_A}\sum_{p,q} c_p{}^\dagger c_q \varphi_p(y)\varphi_q(y) \times \frac{\exp(-\epsilon_q Z_A/R_A{}^2) - \exp(-\epsilon_p Z_A/R_A{}^2)}{\epsilon_p - \epsilon_q} \qquad (A.5)$$

where

$$\lim_{r\to s}\frac{e^{-s} - e^{-r}}{r - s} = e^{-s} \qquad (A.6)$$

For the correct choice of $u(y)$ the density $\tilde{\rho}(y)$ will equal unity for all y, and the solution is complete. In general the correct u will not have been used, so a better one must be selected. A multivariable Newton's iteration scheme will be employed, i.e., linear extrapolation. Explicitly, we can write

$$\Delta u(y) \equiv u_{\text{new}}(y) - u_{\text{old}}(y) = -\int_0^1 [\delta u(y)/\delta\tilde{\rho}(y')][\tilde{\rho}(y') - 1]dy' \qquad (A.7)$$

where $1 - \tilde{\rho}(y')$ is the change in $\tilde{\rho}$ which we are attempting to induce with the change $\Delta u(y)$ in u. The functional derivative $\delta u(y)/\delta\rho(y')$ gives the rate of change of the function u with change in the function $\tilde{\rho}$.

Actually it is easier to calculate the inverse functional derivative

$$K(y,y') \equiv -\delta\tilde{\rho}(y)/\delta u(y') \qquad (A.8)$$

and we will discuss the "inversion" of K in the next section. According to eq III.22 for $\tilde{\rho}$, K can be expressed totally in terms of the functional derivative $\delta Q(y,t;y_0)/\delta u(y')$. An equation for the latter is obtained by functionally differentiating eq III.18:

$$\left[R_A{}^2\frac{d}{dt} - \mathcal{L}\right]\frac{\delta Q(y,t;y_0)}{\delta u(y')} = \delta(y - y')Q(y,t;y_0) \qquad (A.9)$$

which has as a solution

$$\frac{\delta Q(y,t;y_0)}{\delta u(y')} = -\frac{1}{R_A{}^2}\int_0^t dt'\,Q(y,t - t';y')Q(y',t';y_0) \qquad (A.10)$$

It is straightforward to show that in spectral representation

$$K(y,y') = \frac{R_A{}^2}{Z_A\mathcal{Q}_A}\sum_{pqs}(c_p{}^\dagger c_q + c_q{}^\dagger c_p)\varphi_p(y)\varphi_q(y)\varphi_q(y')\varphi_s(y') \times \left[\frac{\exp(-\epsilon_p Z_A/R_A{}^2)}{(\epsilon_p - \epsilon_q)(\epsilon_p - \epsilon_s)} + \frac{\exp(-\epsilon_q Z_A/R_A{}^2)}{(\epsilon_q - \epsilon_s)(\epsilon_q - \epsilon_p)} + \frac{\exp(-\epsilon_s Z_A/R_A{}^2)}{(\epsilon_s - \epsilon_p)(\epsilon_s - \epsilon_q)}\right] - \frac{Z_A}{R_A{}^2}\tilde{\rho}(y)\tilde{\rho}(y') \qquad (A.11)$$

L'Hopital's rule must be used when two or three of the indices p, q, s are equal.

A problem develops in efforts to make straightforward use of the multidimensinal Newton's iteration, eq A.7. The density is fairly insensitive to rapid oscillations in the function u. Thus there is a tendency for such oscillations to develop in $\Delta u(y)$ in an uncontrolled manner in response to small oscillations in $\tilde{\rho}(y)$. This is like the so-called ill-posed problems (a prime example being inversion of Laplace transforms). To prevent these oscillations we will use a method due to Tikhonov.[24] Formulate eq I.9 as a variational problem of the form

$$\int_0^1\left[1 - \rho(y'') + \int_0^1 K(y'',y')\Delta u(y')\,dy'\right]^2 dy'' = \text{min.} \qquad (A.12)$$

The statement that as we iterate we do not expect wide oscillations in $\Delta u(y)$ can be put

$$\int_0^1 \alpha(y'')\left[\frac{\partial\Delta u(y'')}{\partial y''}\right]^2 dy'' = \text{small} \qquad (A.13)$$

where $\alpha(y)$ is some function we will later specify in a reasonable way. Minimizing the sum of eq A.12 and A.13 yields

$$\int_0^1 K(y,y'')\left[1 - \rho(y'') + \int_0^1 K(y'',y')\Delta u(y')\,dy'\right]dy'' - \frac{\partial}{\partial y}\left[\alpha(y)\frac{\partial}{\partial y}\Delta u(y)\right] = 0 \qquad (A.14)$$

This equation is not equivalent to eq A.7 unless $\alpha(y) = 0$. The strategy is to use a finite α when fairly far from a solution, i.e., an α just large enough to suppress oscillations. As the solution is approached α can be reduced.

We have done some calculating with $\alpha(y) = \alpha$, a constant. However, we expect that $\partial\Delta u/\partial y$ will be larger in regions where $|\partial u/\partial y|$ is large. Therefore we have also used

$$\alpha(y) = \alpha/\{\text{maximum}[|du/dy|, 10]\}^2 \qquad (A.15)$$

with better results.

To handle the middle block of a triblock copolymer, $c_p{}^\dagger$ replaces c_p in all formulas of this section.

B. Practical Numerical Procedures. As a practical matter we will seek a solution for $u(y)$ which is piecewise constant over short intervals. Divide the y range, which runs from 0 to 1, at the points $y_0 = 0, y_1, y_2, \ldots, y_{n-1}, y_n = 1$. The pieces have sizes

$$h_k \equiv y_k - y_{k-1} \qquad (A.16)$$

Let the value of $u(y)$ between y_{k-1} and y_k be u_k. Since u is piecewise constant the eigenfunctions of $\mathcal{L}$ are linear combinations of trigonometric or hyperbolic functions. For $y_{k-1} < y < y_k$:

$$\varphi_p(y) = A_{pk}\hat{c}[\kappa_{pk}(y - y_{k-1})] + B_{pk}\hat{s}[\kappa_{pk}(y - y_{k-1})] \qquad (A.17)$$

where the functions ĉ and ŝ are

$$\hat{c} = \cos \quad \text{and} \quad \hat{s} = \sin \quad \text{if} \quad \epsilon_p \geq u_k$$

$$\hat{c} = \cosh \quad \text{and} \quad \hat{s} = \sinh \quad \text{if} \quad \epsilon_p < u_k \qquad (A.18)$$

and

$$\kappa_{pk} \equiv |\epsilon_p - u_k|^{1/2} \qquad (A.19)$$

A relationship among the A's and B's of successive regions follows from the required continuity of φ_p and its derivative:

$$\mathbf{U}_k = \left[\prod_{m=1}^{k-1}\mathbf{S}_m\right]\mathbf{U}_1 \qquad (A.20)$$

$$\mathbf{U}_k \equiv \begin{pmatrix} A_k \\ B_k \end{pmatrix} \qquad (A.21)$$

$$\mathbf{S}_k = \begin{pmatrix} \hat{c}(\kappa_k h_k) & \hat{s}(\kappa_k h_k) \\ -(\kappa_k/\kappa_{k+1})\theta_k\hat{s}(\kappa_k h_k) & (\kappa_k/\kappa_{k+1})\hat{c}(\kappa_k h_k) \end{pmatrix} \qquad (A.22)$$

where the subscript p has been left implicit, and

$$\theta_k = \text{sgn}\,(\epsilon_p - u_k) \qquad (A.23)$$

The boundary conditions of zero derivatives at $y = 0$ and 1 require

$$B_1 = B_{n+1} = 0 \qquad (A.24)$$

or equivalently the vanishing of the 2,1 element of the matrix product $\mathbf{S}_n\mathbf{S}_{n-1}\ldots\mathbf{S}_2\mathbf{S}_1$:

$$(\mathbf{S}_n\mathbf{S}_{n-1}\ldots\mathbf{S}_2\mathbf{S}_1)_{21} = 0 \qquad (A.25)$$

The latter equation may be used to determine ϵ_p. Finally A_1 can be set by normalization.

The function $u(y)$ has been specified by n numbers, of which only $n - 1$ are independent due to the vanishing of the integral, eq III.27, which may be written in the form

$$\sum_{k=1}^n u_k h_k = 0 \qquad (A.26)$$

This means that we cannot force $\tilde{\rho}(y)$ to equal unity at all y. Rather, let us define

$$\tilde{\rho}_k = \frac{1}{h_k}\int_{y_{k-1}}^{y_k}\tilde{\rho}(y)\,dy, \qquad k = 1, \ldots, n \qquad (A.27)$$

of which only $n - 1$ are independent since, by the definition of eq III.22:

$$\sum_{k=1}^n \tilde{\rho}_k h_k = 1 \qquad (A.28)$$

We will choose the u_k so that all the $\tilde{\rho}_k = 1$.

To improve upon a set of values u_k which is not a solution we need a discrete version of eq A.14. Define the matrix

$$K_{lm} = \frac{1}{h_l h_m} \int_{y_{l-1}}^{y_l} \int_{y_{m-1}}^{y_m} K(y,y')\,\mathrm{d}y\,\mathrm{d}y' \tag{A.29}$$

(in practice we actually evaluate this integral and eq A.27 by a traperiod integration rule rather than explicitly integrating eq A.11 and A.5). By its definition the matrix **K** is singular since, as is easily proved from eq A.28 and A.8,

$$\mathbf{Kh} = 0 \tag{A.30}$$

The discretized form of eq A.14 which tells us how to improve u, is

$$(\mathbf{KHK} - \boldsymbol{\Gamma})\mathbf{H}\Delta\mathbf{u} = -\mathbf{KH}\Delta\tilde{\boldsymbol{\rho}} \tag{A.31}$$

where the vector $\Delta\hat{\boldsymbol{\rho}}$ is defined by

$$(\Delta\hat{\boldsymbol{\rho}})_k = 1 - \tilde{\rho}_k \tag{A.32}$$

$\Delta\mathbf{u}$ is the vector of changes $u_{k,\mathrm{new}} - u_{k,\mathrm{old}}$, **H** is a diagonal matrix with

$$H_{kl} = h_k \delta_{kl} \tag{A.33}$$

and the matrix $\boldsymbol{\Gamma}$ has nonvanishing elements

$$\Gamma_{l,l-1} = -\frac{\alpha_{l-l}}{\tfrac{1}{2}h_l(h_l + h_{l-1})h_{l-1}}$$

$$\Gamma_{l,l+1} = -\frac{\alpha_l}{\tfrac{1}{2}h_l(h_{l+1} + h_l)h_{l+1}}$$

$$\Gamma_{l,l} = -(1/h_l)(\Gamma_{l,l-1}h_{l-1} + \Gamma_{l,l+1}h_{l+1}), l = 2,n-1$$

$$\Gamma_{11} = -\Gamma_{12}h_2/h_1$$

$$\Gamma_{nn} = -\Gamma_{n,n-1}h_{n-1}/h_n \tag{A.34}$$

The matrix $\mathbf{KHK} - \Gamma$ is singular, having as an eigenvector **h** with eigenvalue zero. The right side of the equation is orthogonal to **h**, so the equation can still be solved. Put another way, the n simultaneous linear equations represented by eq A.31 are not linearly independent. Therefore, a way to solve the set is to replace one of the equations, let us say the nth, with eq A.26, $\mathbf{h}\cdot\Delta\mathbf{u} = 0$.

We have found that a practical choice for the division of y is 17 regions of sizes: 8 regions with $h = 0.09$ filling $y = 0$ to 0.72, 4 with $h = 0.045$, and 5 with $h = 0.02$. A few calculations were done with a finer grid, but differences were not significant. We use the 20 lowest eigenvalues of $\mathcal{L}$ and their eigenfunctions in the spectral expansions, though for $R_\mathrm{A}/Z^{1/2} \approx 1$ twelve terms is quite sufficient. A calculaion generally takes 10 to 30 s on a Honeywell 6700. This involves 5 to 10 iterations for the proper $u(y)$ to be found.

C. Solution to More General Equations. In ref 5 (referred to as III) diblock copolymer systems are analyzed without making the narrow interphase assumptions. We will only consider explicitly the case where $\rho_{0\mathrm{A}} = \rho_{0\mathrm{B}} = \rho_0$, $b_\mathrm{A} = b_\mathrm{B} = b$, $Z_\mathrm{A} = Z_\mathrm{B} = Z$, and $\alpha \equiv \chi\rho_0$. The basic equation for $Q(y,t;y_0)$ is

$$R^2\frac{\partial Q}{\partial t} = -\left\{-\frac{\partial^2}{\partial y^2} + \chi R^2[\tilde{\rho}(1-y)]^2 + u(y)\right\}Q \tag{A.35}$$

where $y = 2x/d$ goes from zero to unity as x goes from the center of an A domain to the center of a B domain, and

$$R \equiv 6^{1/2}d/2b \tag{A.36}$$

The densities of A and B are related to Q by

$$\tilde{\rho}_\mathrm{A}(\tfrac{1}{2}dy) = \tilde{\rho}_\mathrm{B}(\tfrac{1}{2}d - \tfrac{1}{2}dy) \tag{A.37}$$

$$\equiv \tilde{\rho}(y) = \frac{1}{2Z\mathcal{Q}}\int_0^Z \mathrm{d}t \int_0^1 \mathrm{d}y_\mathrm{A}\,\mathrm{d}y_\mathrm{J}\,\mathrm{d}y_\mathrm{B}$$

$$Q(y_\mathrm{A},Z-t;y)Q(y,t;y_\mathrm{J})Q(1-y_\mathrm{J},Z;y_\mathrm{B}) \tag{A.38}$$

$$\mathcal{Q} = \int_0^1 \mathrm{d}y_\mathrm{A}\,\mathrm{d}y_\mathrm{J}\,\mathrm{d}y_\mathrm{B}\,Q(y_\mathrm{A},Z;y_\mathrm{J})Q(y_\mathrm{J},Z;y_\mathrm{B}) \tag{A.39}$$

In eq A.35 the term $\chi R^2[\tilde{\rho}(1-y)]^2$ arises from the repulsion between species. It forces the separation into domains and helps shape the interphase. The function $u(y)$ is to be adjusted so that $\tilde{\rho}_\mathrm{A}(x) + \tilde{\rho}_\mathrm{B}(x) = 1$, or

$$\tilde{\rho}(y)\ .\ \tilde{\rho}(1-y) = 1 \tag{A.40}$$

The cycle of iteration that we use is as follows. An initial guess is made about $\tilde{\rho}(y)$ and $u(y)$. One can then write spectral representations of Q, $\tilde{\rho}$, and $\mathcal{Q}$ which are identical with eq A.1, A.2, and A.5 except that now R replaces R_A, and

$$c_p{}^\dagger = \sum_q c_q \exp(-\epsilon_q Z/R^2)\int_0^1 \mathrm{d}y\,\varphi_q(1-y)\varphi_p(y) \tag{A.41}$$

The $\tilde{\rho}$ which comes out of the calculation by eq A.38, call it $\tilde{\rho}_\mathrm{out}(y)$, is not the same as the initial guess, $\tilde{\rho}_\mathrm{in}(y)$. The first step is to find the density $\tilde{\rho}_u(y)$ which is self-consistent for a given u. To do so, define

$$w(y) \equiv \chi R^2[\tilde{\rho}(1-y)]^2 + u(y) \tag{A.42}$$

We need the functional derivative

$$M(y,y') = -\frac{\delta\tilde{\rho}(y)}{\delta w(y')} \tag{A.43}$$

This is just a bit more complicated than the calculation of K in section B but it is a straightforward use of eq A.38 and A.10 ($u \rightarrow w$ and $R_\mathrm{A} \rightarrow R$). We will not present the explicit spectral formula. A linear extrapolation gives

$$\tilde{\rho}_u(y) = \tilde{\rho}_\mathrm{out}(y) - \int \mathrm{d}y'\,M(y,y')[w_\mathrm{new}(y') - w_\mathrm{old}(y')] \tag{A.44}$$

The $w_\mathrm{old}(y)$ is eq A.42 with $\tilde{\rho} = \tilde{\rho}_\mathrm{old}$. The $w_\mathrm{new}(y)$ should be the self-consistent one; i.e., it should have $\tilde{\rho} = \tilde{\rho}_u$. Linearizing in $\tilde{\rho}_u - \tilde{\rho}_\mathrm{old}$, we find

$$\tilde{\rho}_u(y) = \tilde{\rho}_\mathrm{out}(y) - 2\chi R^2\int \mathrm{d}y'\,M(y,1-y')\tilde{\rho}_\mathrm{in}(y')[\tilde{\rho}_\mathrm{u}(y') - \tilde{\rho}_\mathrm{in}(y')] \tag{A.45}$$

which is a linear equation for $\tilde{\rho}_u$. This $\tilde{\rho}_u$ is used as the next $\tilde{\rho}_\mathrm{in}$ until self-consistency of in and out is achieved.

The next question is how to modify $u(y)$ so as to produce a $\tilde{\rho}$ which satisfies eq A.40. First let us consider what the functional derivative

$$K(y,y') \equiv -\partial\tilde{\rho}(y)/\partial u(y') \tag{A.46}$$

is. By a chain rule we find the linear equation

$$K(y,y') = -\int [\delta\rho(y)/\delta w(y'')][\delta w(y'')/\delta u(y')]\,\mathrm{d}y'' \tag{A.47}$$

$$= \int \mathrm{d}y''\,M(y,y'')[\delta(y''-y') - 2\chi R^2\tilde{\rho}(1-y'')K(1-y'',y')] \tag{A.48}$$

This K can be used to update u much as in section A.

Note that eq A.40 is an independent condition on $\tilde{\rho}$ only over the range $0 \leq y \leq \tfrac{1}{2}$. Balancing this is the symmetry requirement that

$$u(1-y) = u(y) \tag{A.49}$$

Thus the equation to update u is

$$\tilde{\rho}_u(y) + \tilde{\rho}_u(1-y) - 1 = \int_0^{1/2} K^\mathrm{SS}(y,y')\Delta u(y'), 0 \leq y \leq \tfrac{1}{2} \tag{A.50}$$

$$K^\mathrm{SS}(y,y') = K(y,y') + K(y,1-y') + K(1-y,y') + K(1-y,1-y') \tag{A.51}$$

In solving, the Tikhonov regularization procedure must be employed, and account must be taken of the singular nature of K^SS, just as in sections A and B. We need not repeat the special considerations involved in using a $u(y)$ which is piecewise constant.

In practice we have divided the zero to unity range of y into 34 pieces with $h_k = 0.045$ in the first and last 8 regions, $h_k = 0.0225$ in regions 9 to 12 and 23 to 26, and $h_k = 0.01$ in regions 13 to 22. The calculations take a bit longer because of the extra self-consistency iterations, but less iterations on u are needed because there is no spike in u, as on the right side of Figure 5.

References and Notes

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Monte Carlo Studies of Conformational Characteristics of Block Copolymer Chains in Solution

T. M. Birshtein,* A. M. Skvortsov, and A. A. Sariban

Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad 199004, USSR. *Received October 22, 1975*

ABSTRACT: The behavior of two-block copolymer chains in solution is studied by computer simulation. The effect of heterointeractions on the chain dimensions is examined and the mean numbers of hetero- and homocontacts are determined. It is found that in the case of incompatibility of the chain components each block is in a "segregated state" which is similar to that of the portion of homopolymer chain in good solvent. In regions where the heterocontacts are favorable the mixing of blocks occurs, accompanied by a sharp decrease of the dimensions of the chain and a small decrease of the dimensions of separate blocks. The behavior of a block copolymer chain under temperature changes is analyzed and a nonmonotonic change of the chain dimensions is found to occur. The results are compared with experimental data on the temperature dependence of specific viscosity of block copolymers.

The properties of copolymers composed of different chemical units depend both on the composition and the chemical sequence distribution, i.e., on the primary macromolecule structure. Block copolymers composed of different chemical blocks of some length are of special interest for their structural characteristics and a whole complex of their properties as well.

This paper presents the results of Monte Carlo studies of the block copolymer chain composed of two blocks of equal length in solution. Such a system has been studied by experimental[1-6] and theoretical methods[7,8] in the Gaussian subchain approximation.

The Model

The structure of a copolymer chain in dilute solution (in particular a block copolymer chain) is essentially influenced by the long-range interactions, i.e., by the interactions of segments which are remote in the chain sequence but randomly approach each other in the process of the fluctuating coiling of the chain. In homopolymers these interactions are eliminated (at least on the average) in the theta solvent. As to copolymers, the theta conditions for each component are different, and therefore the volume interactions will not be compensated.

To study these interactions nonintersecting chains were generated on the five choice simple cubic lattice (see for details ref. 9). Chains of 10 to 128 bonds were composed of two blocks of equal length and flexibility and were simulated by random walks on the lattice. Thus it is the flexible chains which are considered, the average length of a segment being approximately equal to its thickness.

To take into account the excluded volume effects, chain self-intersection was not allowed and the interaction energy was attributed to any pair of nonbonded segments separated by one lattice spacing. As distinct from homopolymers where there is only one energy parameter for all pairs in contact, the two-component copolymers require consideration of three different energy parameters: those for two kinds of homocontacts ϵ_{AA} and ϵ_{BB}, and ϵ_{AB} for heterocontacts. In the two-block copolymers ϵ_{XX} (X = A or B) and ϵ_{AB} characterize the intrablock and interblock contacts, respectively. The parameters ϵ_{XY} (X, Y = A, B), which for simplicity will be referred to as contact energies, measured in units of kT, are the free-energy differences for segment–segment (F_{XY}) and segment–solvent (F_{XS}) interactions

$$\epsilon_{XY} = \frac{F_{XY} + F_{SS}}{kT} - \frac{F_{XS} + F_{YS}}{kT} \qquad (1)$$

(F_{SS} is the solvent–solvent interaction free energy.) They characterize the intramolecular contacts with respect to the case where there are no contacts and segments are immersed in solvent (see Figure 1), i.e., they are measures of the quality of solvent. At $\epsilon_{XX} > 0$ the polymer–solvent contacts are more preferred than the intrachain ones and this corresponds to a good solvent. When ϵ_{XX} decreases the solvent becomes poorer for each block and at $\epsilon_{XX} < \epsilon_{\Theta} < 0$ the structure of a given block becomes more compact than at the theta point. The three parameters ϵ_{XY} are similar to χ_A, χ_B, and χ_{AB} in thermodynamic theories of Flory and others.

On the other hand the quantity

$$\Delta\epsilon_{AB} = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) = \frac{F_{AB}}{kT} - \frac{F_{AA} + F_{BB}}{2kT} \qquad (2)$$

characterizes the degree of polymer component compatibility. At $\Delta\epsilon_{AB} > 0$ the heterocontacts are energetically less favorable than homocontacts and this corresponds to increase of the component incompatibility with increasing $\Delta\epsilon_{AB}$. At $\Delta\epsilon_{AB} < 0$ heterocontacts are more favorable than homocontacts; this is usually connected with specific intercomponent interactions (e.g., hydrogen bonding).

It is obvious that for the individual macromolecules in solution the intramolecular contacts compete mainly with the