Block Copolymer Theory. III. Statistical Mechanics of the Microdomain Structure

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ABSTRACT: A theory of the microdomain structure in systems of block copolymers is presented. The free energy and concentration distribution are calculated using modified diffusion equations which describe the statistics of the macromolecular conformations. Numerical results, presented for a special type of copolymer, are in fairly close agreement with comparable experiments on domain size. Qualitative conclusions about the factors which govern microdomain structure can be drawn.

The past few years have seen a growth of interest in block copolymers, especially with regard to their use as materials in which a chemical topology induces a microarchitecture with valuable physical properties. The chemical topology is the arrangement of the monomers in long sequences of one component, A, followed by long sequences of B. Common materials are the diblock and triblock copolymers. If the A and B units have a positive heat of mixing, then there is a tendency toward phase separation, but such a separation cannot be complete because of the connecting bonds between A and B. Thus, domain structures result, and this is the microarchitecture referred to above.

Objectives of a statistical thermodynamic theory include predictions of the geometry, size, and stability of the domains. These are matters which can be analyzed by examination of the free energy. In this paper we shall develop a technique for the calculation of the free energy and other structural features of the domains. A numerical illustration of the application of the theory will be presented. This will be for a special type of diblock copolymer molecule, viz., one which is symmetric with respect to the interchange of species A and B. The model calculation will reveal, free of extraneous detail, many of the important characteristics of block copolymer systems. It will also serve as a benchmark against which to appraise a simplified, but less exact, theory which we are now developing, and to gauge theories previously proposed by others.[1,2]

In section I we examine qualitatively the effects which contribute to the free energy of the system.[2,3] Then the problem is set up quantitatively on the basis of Gaussian-random-walk statistics for the polymer molecules. Details of the derivation of such equations have been given in earlier papers.[4,5] This is a self-consistent-field theory, where an assumed polymer density pattern determines the probability distribution of the macromolecules' conformations, and these probabilities predict the assumed densities. In section III a numerical solution of the equations for one set of typical parameters will be discussed.

I. Qualitative Discussion of Theory

Imagine that, due to the relatively repulsive potential between repeat units of A and B of a block copolymer, a phase separation has occurred. The fact that A and B are part of the same chain imposes limitations on this phase formation, viz., that in close proximity to the A phase there must be some B phase. The result is a domain structure: spheres or cylinders of one component in a continuous matrix of the other, or alternating lamellae.

Such domain patterns are characterized by a large amount of interphase with an associated free energy akin to interfacial tension. Interfacial tension is a result of the excess energy of AB contacts, and the loss of conformational entropy involved in avoiding such contacts while maintaining uniform overall density.[5]

However, in block copolymers additional free energy terms enter. If one examines the probability distribution for the AB joint,[5] one finds that it is greatest in the interfacial region. Clearly, an excursion of this joint into the A domain, let us say, involves pulling B material into this A-rich region, and is thus disfavored. The effective confinement of the degree of freedom represented by the joint to a limited region results in a loss of entropy. Furthermore, since each chain of A or B has one end, the joint, in the boundary region of the domain, there is a tendency to have greater density in these outer regions.[1] In condensed media, where the compressibility, κ, is low, such inhomogeneous overall density patterns are strongly opposed. If the densities of pure A and B are ρ_{0A} and ρ_{0B}, respectively, and the volume change on mixing is zero, the system will keep the densities at every point such that

$$(\rho_A/\rho_{0A}) + (\rho_B/\rho_{0B}) = 1 \qquad (I.1)$$

to within small terms of $0(\kappa)$. In the present case this is accomplished by rejecting those conformations which leave a density dip in the center of the domain. The result is a further loss of conformational entropy.

These are the descriptive features of the theory of inhomogeneous polymers[2-5] as applied to block copolymers. After that theory is presented in the form of equations in the next section an attempt will be made to further illuminate this picture. While the effects of interfacial tension, joint confinement, and uniform filling of the domain centers cannot be precisely separated, they are separate enough to be conceptually useful.

II. Quantitative Formulation

In referring to either material A or B we will henceforth use the symbol K. Consider a diblock copolymer system in which the block of type K has degree of polymerization Z_K. The segments of K have a Kuhn statistical segment length, b_K, such that the bulk mean-square end-to-end distance is $Z_K b_K^2$. When pure, the density of K at the given pressure is ρ_{0K}. We will later assume that the materials are incompressible, but for the moment let there be a finite compressibility, κ, independent of composition of an A–B mixture. We also restrict ourselves in this paper to materials which have zero volume change of mixing at the given pressure, so

$$\tilde{\rho}_A + \tilde{\rho}_B = 1 \qquad (II.1)$$

$$\tilde{\rho}_K \equiv \rho_K/\rho_{0K} \qquad (II.2)$$

in a homogeneous bulk mixture. Deviation from eq II.1 is possible, but it raises the free energy significantly. For a free energy density of mixing excluding combinatorial terms we take

$$\frac{\Delta f^*(\rho_A,\rho_B)}{k_BT} = \alpha\,\frac{\tilde\rho_A\tilde\rho_B}{\tilde\rho_A+\tilde\rho_B} + \frac{1}{2\kappa k_BT}(\tilde\rho_A+\tilde\rho_B-1)^2 \quad \text{(II.3)}$$

where k_B is Boltzmann's constant and T is temperature. (The reader is referred to ref 4 for a more detailed definition of Δf^*.) The first term is the usual random mixing enthalpy proportional to the density of A, the fraction of B, and a constant α. (If the pure densities of A and B are equal then we can define a parameter $\chi = \alpha/\rho_0$ as in section III. In general it is best not to introduce a χ. The matter has been carefully discussed in Helfand and Sapse.[6]) The second term of the free energy density accounts for density deviations. These may be brought about in the homogeneous system by increased pressure, or they may be a consequence of the inhomogeneity.

In the development of a statistical mechanical theory of inhomogeneous polymers[4] attention focuses on a function $Q_K(\mathbf{r},t;\mathbf{r}_0)$ which is proportional to the probability density that a type-K chain of t repeat units has one end at $\mathbf{r}_0$ and the other at $\mathbf{r}$. The proportionality constant will be specified below, but, in any event, special care will be taken to explicitly evaluate multiplicative constants on all formulas relating physical parameters to the Q_K's. In a Θ solvent, and in particular in bulk K, Q_K is the well-known Gaussian

$$Q_K(\mathbf{r},t;\mathbf{r}_0) = \left(\frac{3}{2\pi b_K{}^2t}\right)^{3/2}\exp\left(-\frac{3}{2b_K{}^2t}|\mathbf{r}-\mathbf{r}_0|^2\right) \quad \text{(II.4)}$$

i.e., Q_K is a solution of the diffusion equation. In an inhomogeneous system this diffusion equation must be modified with a term representing the work needed to get a monomer unit to the point $\mathbf{r}$ from bulk K. This work, in mean-field approximation, we have shown[4,5] to be a chemical-potential-like quantity

$$\Delta\mu_K{}^* = \frac{\partial\Delta f^*}{\partial\rho_K} \quad \text{(II.5)}$$

The appropriately modified diffusion equation is

$$\frac{\partial Q_K}{\partial t} = \frac{b_K{}^2}{6}\nabla^2Q_K - \frac{\Delta\mu_K{}^*}{k_BT}Q_K \quad \text{(II.6)}$$

or, with the approximation to Δf^* represented by eq II.3,

$$\frac{\partial Q_A(\mathbf{r},t;\mathbf{r}_0)}{\partial t} = \frac{b_A{}^2}{6}\nabla^2Q_A - \left\{\frac{\alpha}{\rho_{0A}}\left[\frac{\tilde\rho_B(\mathbf{r})}{\tilde\rho_A(\mathbf{r})+\tilde\rho_B(\mathbf{r})}\right]^2 + \frac{1}{\kappa k_BT\rho_{0A}}[\tilde\rho_A(\mathbf{r})+\tilde\rho_B(\mathbf{r})-1]\right\}Q_A \quad \text{(II.7)}$$

with a similar equation for B. Here we explicitly see that Q_A is reduced in regions where $\rho_B(\mathbf{r})$ is large or there is a positive density deviation, $\tilde\rho_A + \tilde\rho_B - 1 > 0$. On the other hand, chains are effectively drawn into the regions where $\tilde\rho_A + \tilde\rho_B - 1$ is negative, as expected.

Q_K is subject to the initial condition

$$Q_K(\mathbf{r},0;\mathbf{r}_0) = \delta(\mathbf{r}-\mathbf{r}_0) \quad \text{(II.8)}$$

which, being the only inhomogeneous equation, determines the normalization of Q_K. We will consider only a single symmetry cell, replacing each chain that leaves that cell through a reflection symmetry plane with a statistically equivalent chain which enters from the other side. Then, one has also the boundary condition that

$$\mathbf{n}\cdot\nabla Q_K(\mathbf{r},t;\mathbf{r}_0) = 0 \quad \text{(II.9)}$$

on every reflection symmetry plane of the system ($\mathbf{n}$ is a normal to that plane). These planes form the boundaries of cells in a periodic microdomain structure.

Equation II.7 is incomplete in that it contains the unknown density pattern. However, given the statistics of the polymer conformations, as embodied in Q_K, these density distributions can be calculated with the formula[4]

$$\rho_A(\mathbf{r}) = \frac{N}{\mathcal{Q}V}\int_0^{Z_A}\mathrm{d}t\int^V \mathrm{d}\mathbf{r}_A\mathrm{d}\mathbf{r}_J\mathrm{d}\mathbf{r}_B \times Q_A(\mathbf{r}_A,Z_A-t;\mathbf{r})Q_A(\mathbf{r},t;\mathbf{r}_J)Q_B(\mathbf{r}_J,Z_B;\mathbf{r}_B) \quad \text{(II.10)}$$

$$\mathcal{Q} = \frac{1}{V}\int^V \mathrm{d}\mathbf{r}_A\mathrm{d}\mathbf{r}_J\mathrm{d}\mathbf{r}_B Q_A(\mathbf{r}_A,Z_A;\mathbf{r}_J)Q_B(\mathbf{r}_J,Z_B;\mathbf{r}_B) \quad \text{(II.11)}$$

with a similar equation for ρ_B. The volume V is conveniently taken as the simplest cell from which the whole system can be made up by repetition. N is the number of diblock copolymer molecules in V. Equation II.10 is easily understood. The integrand is proportional to the probability that a monomer of A which is t units from the joint is at $\mathbf{r}$, while the A end is at $\mathbf{r}_A$, the AB joint at $\mathbf{r}_J$, and the B end at $\mathbf{r}_B$. The total A density is obtained by integrating over all units of the A chain, and over nonfixed locations $\mathbf{r}_A$, $\mathbf{r}_B$, and $\mathbf{r}_J$. The normalization constant is selected so that

$$\int^V \mathrm{d}\mathbf{r}\rho_A(\mathbf{r}) = NZ_A \quad \text{(II.12)}$$

Thus, the coupled set of eq II.7 to II.11 is to be solved, which for the block copolymer problem is a numerical task.

Some simplification may be achieved by considering the limit of zero compressibility. An analysis of the differential equation reveals that this limit is appropriate when $\alpha\kappa k_BT$ and $\kappa\rho_{0K}k_BT/Z_K$ are small compared to unity. Generally these combinations of parameters are 10^{-2} or less. When $\kappa \to 0$, and when an 0(1) force is applied, the deviation of $\tilde\rho_A + \tilde\rho_B - 1$ from zero is $0(\kappa)$. Thus the product

$$(1/\kappa k_BT)\,[\tilde\rho_A(\mathbf{r}) + \tilde\rho_B(\mathbf{r}) - 1] \equiv w_\xi(\mathbf{r}) \quad \text{(II.13)}$$

is an indeterminant form which we name $w_\xi(\mathbf{r})$. The additional unknown function $w_\xi(\mathbf{r})$ entering eq II.7 may be solved for using the additional relation

$$\tilde\rho_A(\mathbf{r}) + \tilde\rho_B(\mathbf{r}) = 1 \quad \text{(II.1)}$$

It can be shown that $\rho_K(\mathbf{r})$ is invariant to an additive constant on $w_\xi(\mathbf{r})$, which gives us the freedom to impose the condition

$$\int \mathrm{d}\mathbf{r}w_\xi(\mathbf{r}) = 0 \quad \text{(II.14)}$$

(For other problems, such as the polymer–polymer interfaces,[5,6] other means of fixing the additive constant may be more appropriate.)

Once the conformational characteristics of the block copolymer molecules are known the free energy can be determined from the formula (discussed in the Appendix)

$$\frac{F}{Vk_BT} = -\frac{N}{V}\log\mathcal{Q} - \frac{\alpha(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{[(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})]^2} \quad \text{(II.15)}$$

where the zero of free energy is taken as a hypothetical homogeneous block copolymer phase.

III. Calculations for a Symmetric Block Copolymer

The workings of these formulas and the type of results which emerge are illustrated most simply with the case of a symmetric diblock copolymer. By this we mean that the physical parameters of A and B are identical. We drop the subscript K and write for both materials ρ_0, b, and Z for the density of polymer units when pure, the segment length, and the degree of polymerization, respectively. We also introduce the Flory–Huggins parameter

$$\chi = \alpha/\rho_0 \quad \text{(III.1)}$$

It is expected that the system will phase separate into the most symmetric structure, alternating lamellae of A-

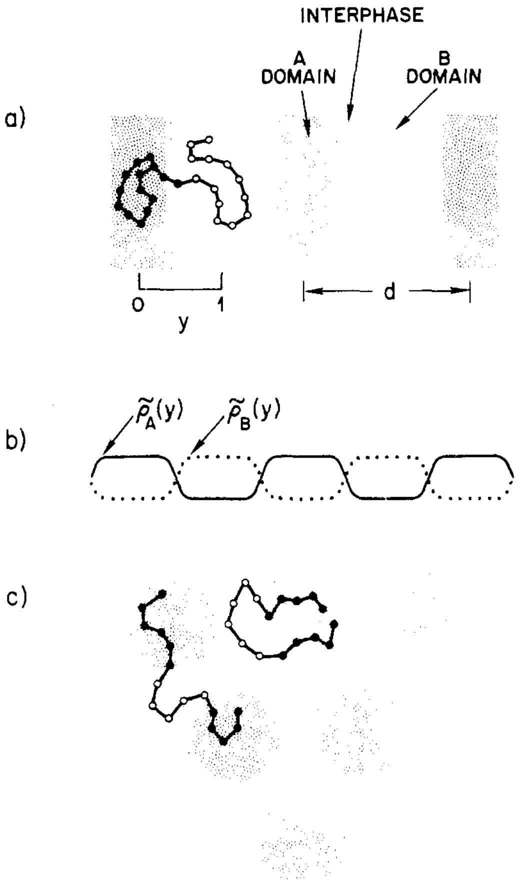

Figure 1. (a) Schematic diagram of a lamellar microdomain structure in a block copolymer system. The periodicity distance is d. The basic cell in which eq 3.6 to 3.11 are to be solved goes from the center of one domain to the next, and is measured on a scale of y going from 0 to 1. (b) The density profiles through the lamellae. (c) A cylindrical domain structure.

rich and B-rich domains, as illustrated in Figure 1. The repeat distance in the x direction is d; this is the sum of the thickness of one A and one B domain. It is convenient to select for the volume V a region of half this size which runs from the center of one domain to the center of the next. These center planes are reflection symmetry planes for the periodic structure. Introduce a dimensionless distance variable

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

which is zero at the center of an A domain and unity at the center of the B domain on the right (see Figure 1). Another convenient variable is a dimensionless repeat distance

$$R = (6^{1/2}/2)(d/b) \tag{III.3}$$

Because of the A–B symmetry the center of the interface is a symmetry plane when all labels A and B are interchanged. Thus

$$\tilde{\rho}_A(\tfrac{1}{2}dy) = \tilde{\rho}_B(\tfrac{1}{2}d - \tfrac{1}{2}dy) \equiv \tilde{\rho}(y) \tag{III.4}$$

$$Q_A(\tfrac{1}{2}dy,t;\tfrac{1}{2}dy_0) = Q_B(\tfrac{1}{2}d - \tfrac{1}{2}dy,t;\tfrac{1}{2}d - \tfrac{1}{2}dy_0) \equiv \frac{2}{d}\tilde{Q}(y,t;y_0) \tag{III.5}$$

The equations to be solved are

$$R^2 \frac{\partial \tilde{Q}(y,t;y_0)}{\partial t} = \frac{\partial^2 \tilde{Q}}{\partial y^2} - \chi R^2[\tilde{\rho}(1-y)]^2\tilde{Q} - u(y)\tilde{Q} \tag{III.6}$$

$$\tilde{Q}(y,0;y_0) = \delta(y - y_0) \tag{III.7}$$

$$\left.\frac{\partial \tilde{Q}(y,t;y_0)}{\partial y}\right|_{y=0} = \left.\frac{\partial \tilde{Q}(y,t;y_0)}{\partial y}\right|_{y=1} = 0 \tag{III.8}$$

$$\tilde{\rho}(y) = \frac{1}{2Z\mathcal{Q}}\int_0^Z \mathrm{d}t \int_0^1 \mathrm{d}y_A \mathrm{d}y_J \mathrm{d}y_B \times \tilde{Q}(y_A, Z-t;y)\tilde{Q}(y,t;y_J)\tilde{Q}(1-y_J,Z;y_B) \tag{III.9}$$

$$\mathcal{Q} = \int_0^1 \mathrm{d}y_A \mathrm{d}y_J \mathrm{d}y_B \tilde{Q}(y_A,Z;y_J)\tilde{Q}(1-y_J,Z;y_B) \tag{III.10}$$

$$\tilde{\rho}(y) + \tilde{\rho}(1-y) = 1 \tag{III.11}$$

Note that

$$u(y) = R^2 w_\xi(\tfrac{1}{2}dy)/\rho_0 \tag{III.12}$$

These equations are to be solved for a given d (or R). Then d is to be selected to minimize the free energy density or the free energy per molecule, given by

$$\frac{F}{NkT} = -\log \mathcal{Q} - \tfrac{1}{2}\chi Z \tag{III.13}$$

The method of solution will be discussed in some detail in a later publication by Wasserman and the author. It was necessary to invoke several unusual procedures. Basically a spectral representation of all functions was used, where the basis was the eigenfunctions of the operator on the right of eq III.6.

The free energy as a function of $R/Z^{1/2}$ is plotted in Figure 2 for $\chi Z = 37$. A minimum occurs at $R/Z^{1/2} = 3.8$. Thus the predicted periodicity distance is $d = 3.1bZ^{1/2}$ (this does not imply that $d \propto Z^{1/2}$ since the location of the minimum depends on χZ). To convert this to material terms let us consider parameters appropriate to a polystyrene–polyisoprene (SI) block copolymer. We will use: $\rho_0 = 0.0117$ (geometric mean); $b = 6.6$ Å (for reasons made clear in ref 6 we take $\rho_0 b^2 = \tfrac{1}{2}\rho_{0S}b_{0S}^2 + \tfrac{1}{2}\rho_{0I}b_{0I}^2$); $\chi = 0.142$ (taken as $\chi = \alpha/\rho_0$, with the value of α from ref 7); and $Z = 261$ (so $\chi Z = 37$). The repeat distance would then be $d = 330$ Å. One may wish to compare this with the measurement of Douy, Mayer, Rossi, and Gallot[9] on a block SI of block molecular weights 23,000 and 21,000. This corresponds to $Z_S = 221$ and $Z_I = 308$. If we define $\chi Z = \tfrac{1}{2}\alpha[(Z_S/\rho_{0S}) + (Z_I/\rho_{0I})]$ then $\chi Z = 37$. Douy et al. find a d of 314 Å. More critical comparisons will be left for a later work, where we will not have to assume symmetry between A and B.

To gain some appreciation of the microdomain structure we have plotted in Figure 3 the concentration profiles $\tilde{\rho}(y)$ for $\chi Z = 37$ and 10. We see that the interpenetration of A and B is quite extensive for small χZ. Previously we have developed a theory of the interface between two infinite molecular weight homopolymer phases. The characteristic interfacial width was found to be $2b/(6\chi)^{1/2}$, or, put on the y scale by dividing by $0.5d$, $2/[(\chi Z)^{1/2}(R/Z^{1/2})]$. In Figure 3 we also graphically contrast the density profile through a block copolymer domain interface with that between homopolymers. For large χZ the interfaces are very similar, but as χZ decreases the excess interpenetration significantly increases.

To further grasp the controlling influences in a block copolymer system we have plotted in Figure 4 the terms $\chi R^2[\tilde{\rho}(1-y)]^2$, $u(y)$, and their sum, which enters the fundamental eq III.6 for $\tilde{Q}$. Note the downward dips of $u(y)$, i.e., of $(\tilde{\rho}_A + \tilde{\rho}_B - 1)/\kappa$, at the centers of the domains and at the interface. The dips at the domain centers have the following origin. Each chain has one point, the joint, which is preferentially located in the interfacial region. Hence, in the absence of the $u(y)$ internal fields, except in the inter-

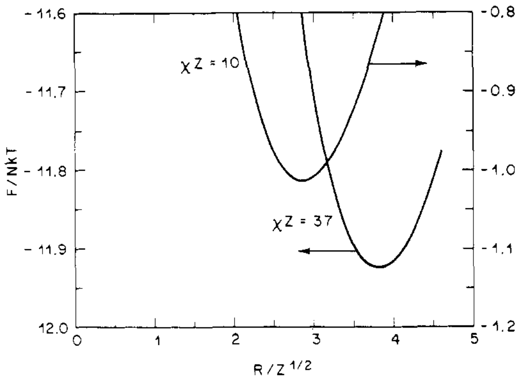

Figure 2. Free energy (on a per molecule basis) as a function of the periodicity distance d [in the form of the dimensionless variable $R/Z^{1/2} \equiv (6^{1/2}/2)(d/bZ^{1/2})$]. For χZ = 37 there is a minimum near $R/Z^{1/2}$ = 3.8; for χZ = 10 the minimum is near $R/Z^{1/2}$ = 2.9. Because d = 0 corresponds to a uniform system, $F(0)$ = 0.

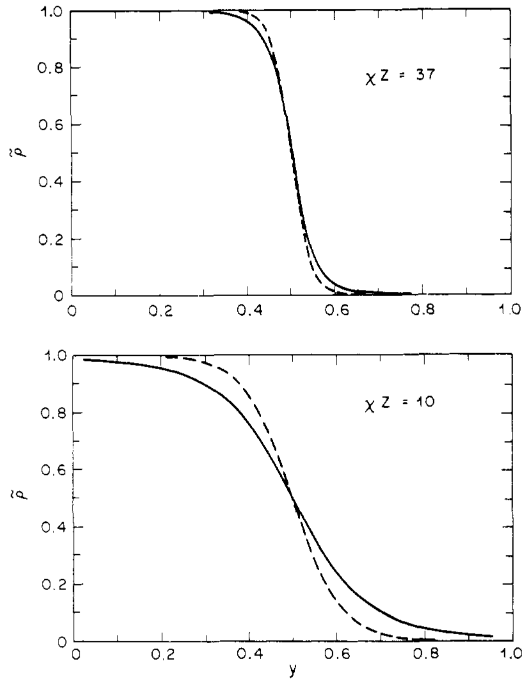

Figure 3. The concentration profile $\tilde{\rho}(y) \equiv \rho_A(\frac{1}{2}dy)/\rho_{0A}$. Shown as solid curves are the results for χZ = 37 and 10. The dashed curves are the theoretical density profiles between homopolymer phases.[5] For χZ = 37 the homopolymer and block copolymer interphases are very similar, but for χZ = 10 significant excess interpenetration is beginning to occur for the block copolymer.

facial region, there is a bias for the rest of the molecule to be preferentially located near the interface, as has been shown by Meier.[1] (This is analogous to the fact that if one end of a free Gaussian chain is fixed then the polymer density has a maximum at that point, or to the fact that if a slab is suddenly heated at the walls the temperature stays lowest in the center.) Such a density dip in a domain's central region would give rise to a large negative u field, which has the effect of favoring the presence of material in the center. The self-consistent solution of eq III.6 corresponds to a balance between the unperturbed walk and u field effects. In this balance a density deviation $\tilde{\rho}_A(y) + \tilde{\rho}_B(y) - 1$ of $0(\kappa)$ is sufficient to create an 0(1) force, embodied in $u(y)$, which induces 0(1) changes in the density. Similarly, we can explain the root of the negative $u(y)$ in the interphase. In the absence of the u field the repulsion between A and B units would push the phases apart, i.e., induce a

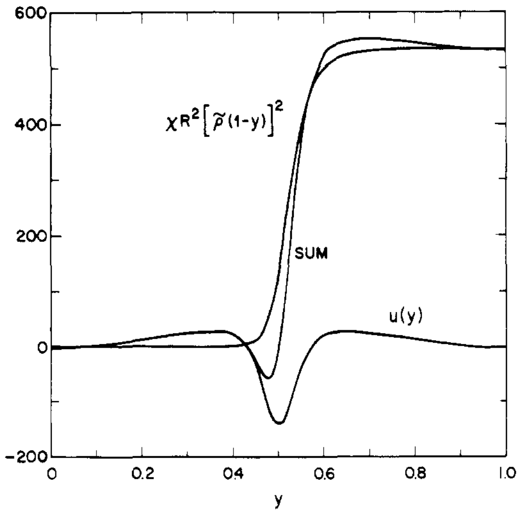

Figure 4. Plots of the terms $\chi R^2[\tilde{\rho}(1-y)]^2$, $u(y)$, and their sum. These terms account for A–B repulsion and the forces maintaining uniform overall density in eq III.6. For these plots χZ = 37 and $R/Z^{1/2}$ = 3.8.

negative density region. Again a negative u field of 0(1) brings the density back to $\tilde{\rho}_A(y) + \tilde{\rho}_B(y)$ being within $0(\kappa)$ of unity.

IV. Connection between Quantitative Theory and Qualitative Description

We shall attempt to make contact between the quantitative theory of sections II and III and the qualitative picture of section I. As we have seen, the density distribution in an interfacial region between A and B domains is not very different from that between semiinfinite phases (except for low χZ). Thus the free energy involved in making an A–B interface is not strongly dependent on the domain size, which is why we compared it with interfacial tension.

We also spoke of a loss of entropy associated with a relative confinement of the joint to an interphase region. This enters via the integral over x_J in eq II.11, which defines $\mathcal{Q}$. Imagine that we had a symmetric block copolymer molecule located not in the interface between two block copolymer domains, but in the similar interface between homopolymers A and B. The integral $\mathcal{Q}$ for that molecule can be written in the form

$$\mathcal{Q} = \frac{2}{d}\int_{-d/4}^{d/4} dx_J q_A(x_J,Z_A) q_B(x_J,Z_B) \qquad \text{(IV.1)}$$

$$q_K(x,Z) = \int dx_0 Q_K(x,Z;x_0) \qquad \text{(IV.2)}$$

where the zero of x is the center of the interphase. We use the functions q_K determined in ref 5,

$$q_A(x) = q_B(-x) = \{1 + \exp[2(6\chi)^{1/2}x/b]\}^{-1/2} \qquad \text{(IV.3)}$$

and, with negligible error, extend the integral to limits $-\infty$ and $+\infty$, to find

$$\mathcal{Q} \approx \frac{\pi}{2}\frac{1}{(6\chi)^{1/2}}\frac{b}{d} \qquad \text{(IV.4)}$$

as a measure of the fractional loss of the joint's freedom of placement. Equation IV.3 represents a slightly different normalization of q_K than that used in section II, namely one based on $u \to 0$ as $x \to \pm\infty$, rather than eq II.14. However, this is appropriate for the present purpose, since it makes $q_A \to 1$ as $x \to -\infty$.

For the block copolymer system $q_K(x)$ turns out to be lower in magnitude than the value given in eq IV.3, although the shape is about right. This is a result of the part of the u field which pulls polymer into the domains' centers, and pushes polymer out of the boundary regions. This lowering of the magnitude of q_K, hence $\mathcal{Q}$, leads to the free energy increase associated with maintaining uniform overall density in the domains.

We will again address the question of the relation between the qualitative and quantitative descriptions of block copolymer systems in a later paper. This will be in the context of a simpler, approximate theory in which a sharp division between domains and interphases is made. We believe that that theory will help make the interpretation of the formulas clearer, as well as provide a theoretical framework which is easier to apply.

Acknowledgment. We are grateful to Mrs. Zelda Wasserman for her extensive programming assistance.

Appendix

Derivation of the Free Energy Formula. In this appendix we shall derive eq II.15 for the free energy. Equation 5.8 of ref 4 is easily adapted to the block copolymer problem, using ideas developed in section IV of that paper. The result is

$$\frac{F}{Vk_BT} = \frac{1}{Vk_BT}\int \mathrm{d}\mathbf{r}\left\{\Delta f^*[\rho_A(\mathbf{r}),\rho_B(\mathbf{r})] - \rho_A(\mathbf{r})\frac{\partial \Delta f^*}{\partial \rho_A(\mathbf{r})} - \rho_B(\mathbf{r})\frac{\partial \Delta f^*}{\partial \rho_B(\mathbf{r})}\right\} - \frac{N}{V}\log \mathcal{Q} - \frac{\alpha(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{[(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})]^2} \quad (A.1)$$

The final term is included so as to make the zero of free energy a single-phase, homogeneous block copolymer system, although this may only be a hypothetical state. Using eq II.3 for Δf^*, and eq II.1 and II.13 we find

$$\frac{F}{Vk_BT} = -\frac{1}{V}\int \mathrm{d}\mathbf{r}\, w_\xi(\mathbf{r}) - \frac{N}{V}\log \mathcal{Q} - \frac{\alpha(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{[(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})]^2} \quad (A.2)$$

If we assume the integral of w_ξ vanishes, then eq II.15 for F results. But let us imagine that a constant $\bar{w}$ is added to this w_ξ. The $Q_K(\mathbf{r},t;\mathbf{r}_0)$ would acquire an additional factor $\exp(-\bar{w}t/\rho_{0K})$ according to eq II.6. This means that $\mathcal{Q}$ has the new factor

$$\exp\left[-\bar{w}\left(\frac{Z_A}{\rho_{0A}} + \frac{Z_B}{\rho_{0B}}\right)\right]$$

When account is taken of the fact that

$$\frac{N}{V}\left(\frac{Z_A}{\rho_{0A}} + \frac{Z_B}{\rho_{0B}}\right) = 1$$

as a special case of eq II.1, we see that F is invariant to $\bar{w}$.

References and Notes

(1) The first important theory of block copolymer microdomain structure was presented by D. J. Meier, *J. Polym. Sci., Part C*, **26**, 81 (1969); this has been extended in D. J. Meier, "The Solid State of Polymers", P. H. Geil, E. Baer, and H. Wada, Ed., Marcel Dekker, New York, N.Y., 1974.

(2) Other theories have been referenced and discussed in E. Helfand, "Recent Advances in Blends, Grafts, and Blocks", L. H. Sperling, Ed., Plenum Press, New York, N.Y., 1974.

(3) E. Helfand, *Acc. Chem. Res.*, to be published.

(4) E. Helfand, *J. Chem. Phys.*, **62**, 999 (1975).

(5) E. Helfand and Y. Tagami, *J. Polym. Sci., Part B*, **9**, 741 (1971); *J. Chem. Phys.*, **56**, 3592 (1971).

(6) E. Helfand and A. M. Sapse, *J. Chem. Phys.*, **62**, 1327 (1975).

(7) D. McIntyre and N. A. Rounds, private communication; N. A. Rounds, Doctoral Dissertation, University of Akron, 1970. The value of α reported (which they assume to be common for polystyrene–polyisoprene and polystyrene–polybutadiene) is $\alpha = [-0.0009 + (0.75/T)]$ cm^{-3}. We have used $T = 298$°K.

(8) The calculations presented in our earlier paper[2] were based on an incorrect value for α, so the preliminary numerical results reported there must be disregarded.

(9) A. Douy, R. Mayer, J. Rossi, and B. Gallot, *Mol. Cryst. Liq. Cryst.*, **7**, 103 (1969).