Block Copolymer Theory. 5. Spherical Domains

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ABSTRACT: A theory is developed to predict the free energy and domain size of block copolymer systems which develop a spherical microdomain structure. The final equations are put into algebraic form and a Fortran program for their solution presented. Comparison is made with experiments.

In a series of papers a theory of microdomain structure in block copolymer systems has been developed. Here we report on the results of the application of that theory to block copolymers which separate into spherical domains. Because the theory has been described in qualitative terms recently[1,2] (familiarity with at least one of these reviews is probably necessary for an understanding of this paper) we will not provide much in the way of general commentary in this paper; rather we emphasize new results and technique. In section II the general equations[3] for diblock copolymers are specialized to a spherical geometry. Then, under the assumption that the interphase between domains is narrow compared with domain size, the equations are simplified. This parallels the procedure previously employed for lamellar geometry.[3,4] To facilitate calculations the numerical results for the free energy required to keep the density uniform in the domains is curve fitted to an algebraic form. A fairly simple total free energy function can then be exhibited, with domain size as a variable. Minimization provides an equation for this size. Analogous results for triblock copolymers are presented. A comparison is made between the theoretical predictions and experiments. The results are generally good. Questions of domain stability are discussed. In an Appendix (Figure 3) a Fortran program is provided to facilitate use of this theory.

I. Geometry

In Figure 1 we have schematized the block copolymer molecules in a spherical microdomain structure, assumed to be in a close-packed array. The Wigner–Seitz[5] polyhedron surrounding each domain is a dodecahedron, with each face being a plane of symmetry. Because it is difficult to solve equations in such a geometry we will approximate the dodecahedron by a sphere of equivalent volume, as is frequently done in solid state physics, thus obtaining a cell in which the appropriate differential equations are separable. If the distance between domain centers is d then the volume of the dodecahedron is $2^{-1/2}d^3$. Let us call the radius of the inner spherical domain a_A and the thickness of the outer shell of the sphericalized cell a_B. These are to be chosen so that

$$(4\pi/3)(a_A + a_B)^3 = 2^{-1/2}d^3 \tag{I.1}$$

The inner (spherical domain) material, A, will be assumed to have density ρ_{0A} monomer units/unit volume and degree of polymerization Z_A. The corresponding quantities for the outer domain (matrix) material, B, are ρ_{0B} and Z_B. If there are N diblock molecules per cell, V, then

$$2^{-1/2}d^3 = N(Z_A/\rho_{0A} + Z_B/\rho_{0B}) \tag{I.2}$$

$$(4\pi/3)a_A{}^3 = NZ_A/\rho_{0A} \tag{I.3}$$

$$(4\pi/3)[(a_A + a_B)^3 - a_A{}^3] = NZ_B/\rho_{0B} \tag{I.4}$$

Equations I.2–I.4 relate a_A, a_B, N, and d, so that any one may be regarded as the independent variable; we have selected a_A. Extensive use will also be made of the ratio

$$\xi \equiv a_A/a_B \tag{I.5}$$

$$\xi = \{[(\rho_{0A}Z_B/\rho_{0B}Z_A) + 1]^{1/3} - 1\}^{-1} \tag{I.6}$$

The analogous equations for triblock systems are obtained by replacing N by $2N$ and Z_K for the center block by $^1/_2Z_K$. This is clear since, as far as packing is concerned, the molecules could be cut at the center of the middle blocks producing $2N$ equivalent diblock molecules. We find that the free energies of the triblock and diblock copolymer molecules derived by bisection are fairly close, too.

II. Equations for Spherical Domains

(The reader interested primarily in numerical results can look at the definition of b_K and α in this paragraph and then read section IV before sections II and III.) The equations which describe block copolymer molecules in a spherical domain pattern are very similar to those used for lamellar domains. Let $Q_K(\mathbf{r},t;\mathbf{r}_0)$ be proportional to the probability that a type K (with K = A or B) chain of t units will have one end at $\mathbf{r}$ in a cell V, given that its other end is at $\mathbf{r}_0$ in that cell or at any image of the point $\mathbf{r}_0$ in the periodically displaced cells. In mean field theory Q_K satisfies the differential equation

$$\frac{\partial Q_K}{\partial t} = \frac{b_K{}^2}{6}\nabla^2 Q_K - \frac{1}{\rho_{0K}}\{\alpha[\tilde{\rho}_{K'}(\mathbf{r})]^2 + w(\mathbf{r})\}Q_K \tag{II.1}$$

where b_K is the Kuhn statistical length, the reduced density is $\tilde{\rho}_K = \rho_K/\rho_{0K}$, and K′ is B when K is A (and vice versa). The mixing parameter α is a measure of relative repulsion between A and B, such that

$$k_BT\alpha\tilde{\rho}_A\tilde{\rho}_B/(\tilde{\rho}_A + \tilde{\rho}_B) \tag{II.2}$$

is the residual free energy of mixing per unit volume. Q_K satisfies the initial condition

$$Q_K(\mathbf{r},0;\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0) \tag{II.3}$$

and the boundary condition that the normal derivative of Q_K vanishes on the boundaries of the Wigner–Seitz cell, as it must on any plane of symmetry. The density pattern which appears in eq II.1 is given in terms of the Q_K by

$$\rho_K(\mathbf{r}) = \frac{N}{\boldsymbol{Q}V}\int_0^{Z_K} dt \int^V \mathrm{d}\mathbf{r}_K\,\mathrm{d}\mathbf{r}_J\,\mathrm{d}\mathbf{r}_{K'}\,Q_K(\mathbf{r}_K,Z_K-t;\mathbf{r}) \times Q_K(\mathbf{r},t;\mathbf{r}_J)Q_{K'}(\mathbf{r}_J,Z_{K'};\mathbf{r}_{K'}) \tag{II.4}$$

$$\boldsymbol{Q} = \frac{1}{V}\int^V \mathrm{d}\mathbf{r}_A\,\mathrm{d}\mathbf{r}_J\,\mathrm{d}\mathbf{r}_B\,Q_A(\mathbf{r}_A,Z_A;\mathbf{r}_J)Q_B(\mathbf{r}_J,Z_B;\mathbf{r}_B) \tag{II.5}$$

It will be assumed that there is zero volume change on mixing A and B, in which case the function $w(\mathbf{r})$ in eq II.1 is to be chosen in such a way that the condition

$$\tilde{\rho}_A(\mathbf{r}) + \tilde{\rho}_B(\mathbf{r}) = 1 \tag{II.6}$$

is satisfied. The free energy per molecule of the system, F/N, relative to a homogeneous system, is given by

$$\frac{F}{Nk_BT} = -\frac{1}{N}\int^V \mathrm{d}\mathbf{r}\,w(\mathbf{r}) - \log \boldsymbol{Q} - \frac{\alpha(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})} \tag{II.7}$$

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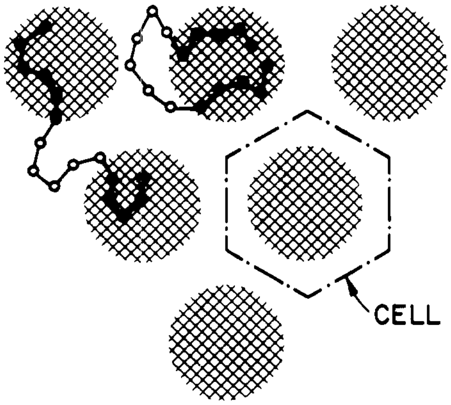

Figure 1. A schematic diagram of a block copolymer system which has developed spherical microdomains (cross section). A Wigner–Seitz cell is indicated. Within it the basic differential equations for the molecules' conformational statistics may be solved, with reflection boundary conditions rigorously applicable on the cell surface.

Note that one may write eq II.4–II.5 in terms of a spherically symmetric function

$$\bar{Q}_K(r,t;r_0) = \frac{1}{4\pi}\int d\Omega_0\, Q_K(\mathbf{r},t;\mathbf{r}_0) = \frac{1}{4\pi}\int d\Omega\, Q_K(\mathbf{r},t;\mathbf{r}_0) \qquad \text{(II.8)}$$

where $d\Omega = \sin\theta\, d\theta\, d\phi$, and that $\bar{Q}_K$ satisfies eq II.1 with ∇^2 replaced by $(d^2/dr^2) + (2/r)(d/dr)$. The initial condition becomes

$$\bar{Q}_K(r,0;r_0) = (1/4\pi r_0^{\,2})\delta(r - r_0) \qquad \text{(II.9)}$$

and the boundary condition is

$$\partial\bar{Q}_K/\partial r|_{r=a_A+a_B} = 0 \qquad \text{(II.10)}$$

So far the assumptions and approximations made (as explained in earlier papers) have been: (1) mean field theory; (2) the form of the residual free energy of mixing; (3) zero volume change of mixing; and (4) sphericalization of the Wigner–Seitz cell. The equations derived to this point could be solved, as we have solved the analogous lamellar equations.[3] However, there is one further assumption which leads to considerable simplification, which is valid under many important circumstances, and which seems to work well for lamellar problems.[4] This approximation is that the interphase between the domains is narrow compared with the characteristic distances in the domains. (We use the term "domain" for both the spherical domains of A and the matrix of B.) In that case we can write

$$\bar{Q}_A(r,t;r_0) \approx a_A^{-3}Q(y,t;y_0)q_A^{\,I}(r - a_A)q_A^{\,I}(r_0 - a_A) \qquad \text{(II.11)}$$

$$y = r/a_A \qquad \text{(II.12)}$$

$$\bar{Q}_B(r,t;r_0) \approx a_B^{-3}Q'(z,t;z_0)q_B^{\,I}(r - a_A)q_B^{\,I}(r_0 - a_A) \qquad \text{(II.13)}$$

$$z = r/a_B \qquad \text{(II.14)}$$

where $q_K^{\,I}$ is the interfacial function solved for in earlier papers in which the theory is applied to the interface between homopolymers A and B. (Although the explicit form of $q_K^{\,I}$ will not be needed in this paper, it can be obtained for the unsymmetric polymer pair from eq 2.11, 4.1, and 4.4 of ref 6. For polymers A and B with symmetric properties the simpler eq 3.2–3.6 of ref 7 are valid.) The $q_K^{\,I}$ determined for a flat interface can be used since the curvature corrections are negligible for a narrow interface.

For the applications to which eq II.11 are put, generally one of the variables, say y_0, is confined to the interphase while the other is in the domain. For narrow interphases we can then write, since $q_K^{\,I}$ goes to 1 in the K phase,

$$\bar{Q}_A(r,t;r_0) = a_A^{-3}Q(y,t;1)q_A^{\,I}(r_0 - a_A) \qquad \text{(II.15)}$$

and similarly for B. When this is substituted in the general equations derived earlier the following simplified set results (the reader attempting to duplicate these equations would do well to study first the analogous formulas in ref 4):

Inner region, $0 \le y \le 1$:

$$R_A^{\,2}\frac{\partial Q}{\partial t} = \frac{1}{y^2}\frac{\partial}{\partial y}y^2\frac{\partial Q}{\partial y} - u(y)Q \qquad \text{(II.16)}$$

$$R_A = 6^{1/2}a_A/b_A \qquad \text{(II.17)}$$

$$Q(y,0;y_0) = (1/4\pi y_0^{\,2})\delta(y - y_0) \qquad \text{(II.18)}$$

$$\partial Q/\partial y|_{y=1} = 0 \qquad \text{(II.19)}$$

$$Q(0,t;y_0) = \text{finite} \qquad \text{(II.20)}$$

$$\tilde{\rho}(y) = \frac{4\pi}{3Z_A\boldsymbol{Q}_A}\int_0^{Z_A} dt \int_0^1 4\pi y_1^{\,2}\, dy_1\, Q(y_1,Z_A\text{-}t;y)Q(y,t;1) \qquad \text{(II.21)}$$

$$\boldsymbol{Q}_A = \int_0^1 4\pi y^2\, dy\, Q(y,Z_A;1) \qquad \text{(II.22)}$$

Outer region, $\xi \le z \le \xi + 1$:

$$R_B^{\,2}\frac{\partial Q'}{\partial t} = \frac{1}{z^2}\frac{\partial}{\partial z}z^2\frac{\partial Q'}{\partial z} - u'(z)Q' \qquad \text{(II.23)}$$

$$R_B = 6^{1/2}a_B/b_B \qquad \text{(II.24)}$$

$$Q'(z,0;z_0) = (1/4\pi z_0^{\,2})\delta(z - z_0) \qquad \text{(II.25)}$$

$$\partial Q'/\partial z|_{z=\xi} = 0 \qquad \text{(II.26)}$$

$$\partial Q'/\partial z|_{z=\xi+1} = 0 \qquad \text{(II.27)}$$

$$\tilde{\rho}'(z) = \frac{4\pi}{3[(\xi + 1)^3 - \xi^3]Z_B\boldsymbol{Q}_B} \times \int_0^{Z_B} dt \int_\xi^{\xi+1} 4\pi z_1\, dz_1\, Q'(z_1,Z_B-t;z)Q'(z,t;\xi) \qquad \text{(II.28)}$$

$$\boldsymbol{Q}_B = \int_0^1 4\pi z^2\, dz\, Q'(z,Z_B;\xi) \qquad \text{(II.29)}$$

The functions $u(y)$ and $u'(z)$ are related to $w(r)$ by

$$w(r) = w^I(r) + (\rho_{0A}/R_A^{\,2})u(r/a_A) \qquad \text{(II.30)}$$

$$w(r) = w^I(r) + (\rho_{0B}/R_B^{\,2})u'(r/a_B) \qquad \text{(II.31)}$$

where $w^I(r)$ is the w function appropriate to a homopolymer interface. The functions u and u' are to be selected so as to maintain

$$\tilde{\rho}(y) = 1 \qquad 0 \le y \le 1 \qquad \text{(II.32)}$$

$$\tilde{\rho}'(z) = 1 \qquad \xi \le z \le \xi + 1 \qquad \text{(II.33)}$$

This only specifies u and u' to within an additive constant, which may be conveniently selected so that

$$\int_0^1 4\pi y^2\, dy\, u(y) = \int_\xi^{\xi+1} 4\pi z^2\, dz\, u'(z) = 0 \qquad \text{(II.34)}$$

The "partition function", $\boldsymbol{Q}$, factors into

$$\boldsymbol{Q} = \boldsymbol{Q}_A\boldsymbol{Q}_B\boldsymbol{Q}_I \qquad \text{(II.35)}$$

$$\boldsymbol{Q}_I = 4\pi a_A^{\,2}a_J/V \qquad \text{(II.36)}$$

$$a_J = \int_{-\infty}^{\infty} dx\, q_A^{\,I}(x)q_B^{\,I}(x) \qquad \text{(II.37)}$$

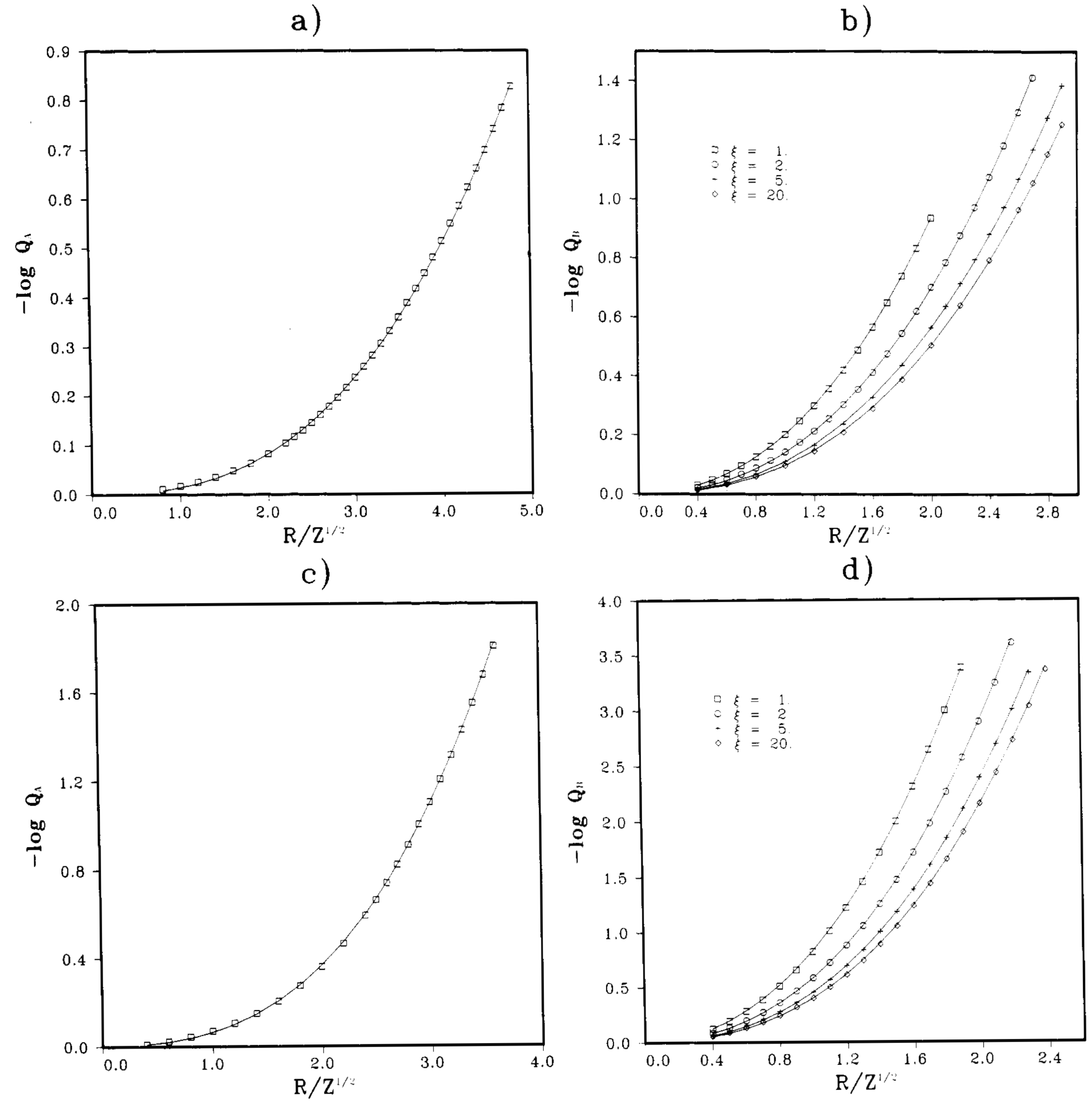

Figure 2. Free energy terms which describe the free energy (loss of entropy) associated with keeping the density uniform in the domain when all joints must be at the interface. The solid lines are functional fits while the points are calculations for specific values of the variables. (a) An end block in the spherical domain (cf. eq II.47). (b) An end block in the matrix domain (cf. eq II.48). (c) A central block in the spherical domain (cf. eq III.3). (d) A central block in the matrix domain (cf. eq III.5). In (b) and (d) not all the ξ for which calculations were performed are shown.

Table I
Densities and Monomer Lengths

polymer	density, ρ_{0K}, mol/m^3 × 10^{-3}	length, b_K, nm
PS	10.1	0.68
PI	13.6	0.63
PB	16.5	0.63

when the narrow interphase approximation is invoked.

The free energy can now be written

$$\frac{F_{AB}}{Nk_BT} = 4\pi a_A{}^2\frac{\gamma}{Nk_BT} + \log\frac{V}{4\pi a_A{}^2 a_J} - \log \boldsymbol{Q}_A - \log \boldsymbol{Q}_B - \alpha\frac{(Z_A/\rho_{0A})(Z_B/\rho_{0B})}{(Z_A/\rho_{0A}) + (Z_B/\rho_{0B})} \qquad \text{(II.38)}$$

The interfacial tension, γ, entered via the formula

$$\gamma = -k_BT\int_{-\infty}^{\infty} dx\, w^I(x) \qquad \text{(II.39)}$$

derived for homopolymer interfaces.[4] One should be able to use measured interfacial tension when available. Otherwise one may use the theoretical formula[6]

$$\gamma = k_BT\alpha^{1/2}\left[\frac{\beta_A + \beta_B}{2} + \frac{1}{6}\,\frac{(\beta_A - \beta_B)^2}{\beta_A + \beta_B}\right] \qquad \text{(II.40)}$$

$$\beta_K{}^2 = \rho_{0K}b_K{}^2/6 \qquad \text{(II.41)}$$

From this theory one also determines that

$$a_J = \beta_G\alpha^{-1/2}E(\beta_G/\beta_S) \qquad \text{(II.42)}$$

where β_G is the greater of β_A and β_B, β_S is the smaller, while E is the elliptic integral of the second kind.

The calculation of Q (this paragraph is developed for the inner domain, but the remarks apply as well to the outer domain) and thereby $\boldsymbol{Q}_A$ can be performed by making a spectral representation of Q in terms of the eigenvalues and eigenfunctions of the operator

$$\mathcal{L} = -(1/y^2)\,(\partial/\partial y)\,y^2\,(\partial/\partial y) + u(y) \qquad \text{(II.43)}$$

where an initial guess is made of u. The density $\bar{\rho}(y)$ can

Table II
Comparison of Measured and Predicted Domain Dimensions for Spherical Domain Block Copolymers

polymer	spheres	mol wt ratio, kg/mol	a_A(exptl), nm	a_A(calcd), nm	d(calcd), nm	N(calcd)	ref
S-B	S	7.2-33	8.6	8.4	28	220	9
		8-40	10.7	9.0	31	240	
		11-47	10.8	11.3	37	350	
		12-147	11.2	11.6	52	340	
		12-163	10.9	11.5	54	340	
		13-59	12.8	12.6	42	410	
		15-32	11.2	14.3	39	520	
		15-83	12.2	13.8	49	470	
S-B-S	S	13-75-13	13.5	12.9	38	220	10
		10-71-10	10	10.7	34	160	
		7-35-7	9.3	8.5	24	110	11
		14-63-14	11.6	13.7	38	240	
		21-98-21	17.0	18.0	50	370	
		120-660-120	21	57	167	2100	
S-I	S	15-75	13	13.4	46	420	12
		51-227	10	31	101	1500	
S-I	I	47-17	16.3	16.8	46	650	13
		62-12	6.8	12.8	41	410	14
		125-20	8.5	18.0	61	680	
		176-20	9.6	17.7	66	640	
		185-34	13.0	26	84	1190	
		251-71	17	43	125	2700	
		513-144	32	69	200	5300	
		158-27	15	22	73	930	15
		116-28	12.5	23	70	1020	

also be expressed in spectral form. According to the deviations of $\tilde{p}(y)$ from unity a new choice of $u(y)$ can be made by a Newton–Raphson technique (plus regularization). In all of this, advantage is taken of the fact that if $\phi_p(y)$, an eigenfunction of $\mathcal{L}$, is written as

$$\phi_p(y) = f_p(y)/[(4\pi)^{1/2}y] \qquad \text{(II.44)}$$

then $f_p(y)$ is an eigenfunction of

$$d^2/dy^2 - u(y) \qquad \text{(II.45)}$$

which bears a strong resemblance to the lamellar problem. Therefore many of the techniques and tricks previously employed could be invoked again. A detailed exposition will not be presented since it would be quite lengthy and would not add greatly to the discussion provided for the lamellar problem.[4]

One can convince oneself by dimensional analysis that $\boldsymbol{Q}_A$ is a function only of $R_A/Z_A^{1/2}$, and that $\boldsymbol{Q}_B$ is a function of $R_B/Z_B^{1/2}$ and ξ. In Figure 2 these functions, as numerically determined, are plotted. One could use these plots to obtain a minimum free energy graphically, but it is far simpler to employ an algebraic fit to the functions. Recall that for lamellar domains we used

$$-\log \boldsymbol{Q}_K = 0.085X^{2.5} \qquad \text{(II.46)}$$

where $X = R_K/Z_K^{1/2}$. While other functional forms than power laws are more convenient to use, we were not able to get a satisfactory fit of the full range with anything simpler than a power law form. The form of the fitting function is really immaterial as long as the fit is good. For the spherical problem we have found a satisfactory match with

$$-\ln \boldsymbol{Q}_A(X) = 0.0123(X^2 + 0.147)^{2.68/2} - 0.000942 \qquad \text{(II.47)}$$

$$-\ln \boldsymbol{Q}_B(X,\xi) = \eta_1(X^2 + \eta_2^{\,2})^{\eta_3/2} - \eta_1\eta_2^{\,\eta_3} \qquad \text{(II.48)}$$

$$\eta_1 = 0.0852 + 0.0744/\xi$$

$$\eta_2 = 0.348 + 0.220/\xi$$

$$\eta_3 = 2.48 - 0.123/\xi \qquad \text{(II.49)}$$

Note that as $\xi \to \infty$ the outer domain becomes a shell with thickness small compared with the radius of curvature. Thus $\boldsymbol{Q}_B(X,\infty)$ should be the function appropriate to lamellar geometry, and the new fitting function does come fairly close to eq II.46. The deviations arise from the compromises required to fit over the full range of ξ, the slight change in functional form, and the number of figures retained (perhaps not all really significant).

III. Triblock Copolymers

Only minor modifications need be made in the formulas to apply them to triblock systems. The reader, after studying the details as applied to lamellar domains,[4] can develop the spherical formulas easily by analogy. For a center block in the inner domain, as in BAB, the partition function is given by

$$\boldsymbol{Q}_A^{(C)} = (4\pi/3)Q(1,Z_A;1) \qquad \text{(III.1)}$$

Of course, in the free energy formula some adjustments must be made for the number of blocks. It is convenient for the sake of comparison with diblock formulas to use $2N$ and $Z_A/2$ as the basic variables. The result is

$$\frac{F_{BAB}}{2Nk_BT} = \frac{4\pi a_A^{\,2}}{2N}\,\frac{\gamma}{k_BT} + \log\frac{(VV_A)^{1/2}}{4\pi a_A^{\,2}a_J} - \tfrac{1}{2}\log \boldsymbol{Q}_A^{(C)}[R_A/(\tfrac{1}{2}Z_A)^{1/2}] - \log \boldsymbol{Q}_B(R_B^{1/2}/Z_B,\xi) - \frac{(\tfrac{1}{2}Z_A/\rho_{0A})(Z_B/\rho_{0B})}{(\tfrac{1}{2}Z_A/\rho_{0A}) + (Z_B/\rho_{0B})} \qquad \text{(III.2)}$$

In eq III.2 V_A is the volume of the inner domain. Our calculations produce a $\boldsymbol{Q}_A^{(C)}$ which is well fit by

$$-\tfrac{1}{2}\log \boldsymbol{Q}_A^{(C)}(X) = 0.810(X^2 + 1.13)^{2.87/2} - 0.965 \qquad \text{(III.3)}$$

For the central block in the outer domain, as in ABA, the analogous formulas are

$$\frac{F_{ABA}}{2Nk_BT} = \frac{4\pi a_A^{\,2}}{2N}\,\frac{\gamma}{k_BT} + \log\frac{(VV_B)^{1/2}}{4\pi a_A^{\,2}a_J} - \log \boldsymbol{Q}_A(R_A/Z_A^{1/2}) - \tfrac{1}{2}\log \boldsymbol{Q}_B^{(C)}\left[\frac{R_B}{(\tfrac{1}{2}Z_B)^{1/2}},\xi\right] - \frac{(Z_A/\rho_{0A})(\tfrac{1}{2}Z_B/\rho_{0B})}{(Z_A/\rho_{0A}) + (\tfrac{1}{2}Z_B/\rho_{0B})} \qquad \text{(III.4)}$$

$$-\tfrac{1}{2} \log Q_{\mathrm{B}}^{(\mathrm{C})}(X,\xi) = \eta_4(X^2 + \eta_5^2)^{\eta_6/2} - \eta_4\eta_5^{\eta_6} \qquad \text{(III.5)}$$

$$\eta_4 = 0.0705 + 0.0578/\xi \qquad \eta_5 = 0.596 + 0.599/\xi \qquad \eta_6 = 2.55 - 0.132/\xi \qquad \text{(III.6)}$$

IV. Free Energy and Domain Size Calculation

In this section we will put together the formulas presented so far for the free energy in a fashion which will make them particularly useful for calculations. These free energies can then be minimized to produce algebraic formulas for the determination of domain sizes.

Consider first a diblock copolymer, AB, with A spheres. The free energy is given by

$$\frac{F_{\mathrm{AB}}}{Nk_{\mathrm{B}}T} = 3\left(\frac{Z_{\mathrm{A}}}{\rho_{0\mathrm{A}}}\right)\left(\frac{\gamma}{k_{\mathrm{B}}T}\right)\frac{1}{a_{\mathrm{A}}} + \log\frac{a_{\mathrm{A}}(1 + 1/\xi)^3}{3a_{\mathrm{J}}} + 0.0123\left(\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{A}}b_{\mathrm{A}}^2} + 0.147\right)^{2.68/2} - 0.000942 + \eta_1\left[\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{B}}b_{\mathrm{B}}^2\xi^2} + \eta_2^2\right]^{\eta_3/2} - \eta_1\eta_2^{\eta_3} - \alpha\frac{(Z_{\mathrm{A}}/\rho_{0\mathrm{A}})(Z_{\mathrm{B}}/\rho_{0\mathrm{B}})}{(Z_{\mathrm{A}}/\rho_{0\mathrm{A}}) + (Z_{\mathrm{B}}/\rho_{0\mathrm{B}})} \qquad \text{(IV.1)}$$

$$\frac{1}{\xi} = \left(\frac{Z_{\mathrm{A}}/\rho_{0\mathrm{A}}}{Z_{\mathrm{B}}/\rho_{0\mathrm{B}}} + 1\right)^{1/3} - 1 \qquad \text{(IV.2)}$$

where η_1, η_2, η_3 are given by eq II.49, $\gamma/k_{\mathrm{B}}T$ by eq II.40, and a_{J} by eq II.42. The equation that determines a_{A} is

$$0 = a_{\mathrm{A}}^2\frac{\mathrm{d}(F/Nk_{\mathrm{B}}T)}{\mathrm{d}a_{\mathrm{A}}} = -3\left(\frac{Z_{\mathrm{A}}}{\rho_{0\mathrm{A}}}\right)\left(\frac{\gamma}{k_{\mathrm{B}}T}\right) + a_{\mathrm{A}} + \frac{0.198}{b_{\mathrm{A}}^2Z_{\mathrm{A}}}a_{\mathrm{A}}^3\left(\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{B}}b_{\mathrm{A}}^2} + 0.147\right)^{0.34} + \frac{6\eta_1\eta_3}{\xi^2b_{\mathrm{B}}^2Z_{\mathrm{B}}}a_{\mathrm{A}}^3\left(\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{B}}b_{\mathrm{B}}^2\xi^2} + \eta_2^2\right)^{(\eta_3/2)-1} \qquad \text{(IV.3)}$$

The analogous equations for triblock copolymer BAB with central A block in the spherical domain are

$$\frac{F_{\mathrm{BAB}}}{2Nk_{\mathrm{B}}T} = 3\left(\frac{\tfrac{1}{2}Z_{\mathrm{A}}}{\rho_{0\mathrm{A}}}\right)\left(\frac{\gamma}{k_{\mathrm{B}}T}\right)\frac{1}{a_{\mathrm{A}}} + \log\frac{a_{\mathrm{A}}(1 + 1/\xi)^{3/2}}{3a_{\mathrm{J}}} + 0.00810\left(\frac{6a_{\mathrm{A}}^2}{\tfrac{1}{2}Z_{\mathrm{A}}b_{\mathrm{A}}^2} + 1.13\right)^{2.87/2} - 0.965 + \eta_1\left(\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{B}}b_{\mathrm{B}}^2\xi^2} + \eta_2^2\right)^{\eta_3/2} - \eta_1\eta_2^{\eta_3} - \alpha\frac{(\tfrac{1}{2}Z_{\mathrm{A}}/\rho_{0\mathrm{A}})(Z_{\mathrm{B}}/\rho_{0\mathrm{B}})}{(\tfrac{1}{2}Z_{\mathrm{A}}/\rho_{0\mathrm{A}}) + (Z_{\mathrm{B}}/\rho_{0\mathrm{B}})} \qquad \text{(IV.4)}$$

$$\frac{1}{\xi} = \left(\frac{\tfrac{1}{2}Z_{\mathrm{A}}/\rho_{0\mathrm{A}}}{Z_{\mathrm{B}}/\rho_{0\mathrm{B}}} + 1\right)^{1/3} - 1 \qquad \text{(IV.5)}$$

so that a_{A} is a solution of

$$0 = -3\left(\frac{\tfrac{1}{2}Z_{\mathrm{A}}}{\rho_{0\mathrm{A}}}\right)\left(\frac{\gamma}{k_{\mathrm{B}}T}\right) + a_{\mathrm{A}} + \frac{0.139}{\tfrac{1}{2}Z_{\mathrm{A}}b_{\mathrm{A}}^2}a_{\mathrm{A}}^3\left(\frac{6a_{\mathrm{A}}^2}{\tfrac{1}{2}Z_{\mathrm{A}}b_{\mathrm{A}}^2} + 1.13\right)^{0.44} + \frac{6\eta_1\eta_3}{Z_{\mathrm{B}}b_{\mathrm{B}}^2\xi^2}a_{\mathrm{A}}^3\left(\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{B}}b_{\mathrm{B}}^2\xi^2} + \eta_2^2\right)^{(\eta_3/2)-1} \qquad \text{(IV.6)}$$

For triblock copolymer ABA with the central B block in the matrix and the end A blocks in the spherical domains one has

$$\frac{F_{\mathrm{ABA}}}{2Nk_{\mathrm{B}}T} = 3\left(\frac{Z_{\mathrm{A}}}{\rho_{0\mathrm{A}}}\right)\left(\frac{\gamma}{k_{\mathrm{B}}T}\right)\frac{1}{a_{\mathrm{A}}} + \log\frac{a_{\mathrm{A}}(1 + 1/\xi)^{3/2}[(1 + 1/\xi)^3 - 1]^{1/2}}{3a_{\mathrm{J}}} + 0.0123\left(\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{A}}b_{\mathrm{A}}^2} + 0.147\right)^{2.68/2} - 0.000942 + \eta_4\left(\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{B}}b_{\mathrm{B}}^2\xi^2} + \eta_5^2\right)^{\eta_6/2} - \eta_4\eta_5^{\eta_6} - \alpha\frac{(Z_{\mathrm{A}}/\rho_{0\mathrm{A}})(\tfrac{1}{2}Z_{\mathrm{B}}/\rho_{0\mathrm{B}})}{(Z_{\mathrm{A}}/\rho_{0\mathrm{A}}) + (\tfrac{1}{2}Z_{\mathrm{B}}/\rho_{0\mathrm{B}})} \qquad \text{(IV.7)}$$

$$\frac{1}{\xi} = \left(\frac{Z_{\mathrm{A}}/\rho_{0\mathrm{A}}}{\tfrac{1}{2}Z_{\mathrm{B}}/\rho_{0\mathrm{B}}} + 1\right)^{1/3} - 1 \qquad \text{(IV.8)}$$

where η_4, η_5, and η_6 are given by eq II.49, so that a_{A} satisfies

$$0 = -3\left(\frac{Z_{\mathrm{A}}}{\rho_{0\mathrm{A}}}\right)\left(\frac{\gamma}{k_{\mathrm{B}}T}\right) + a_{\mathrm{A}} + \frac{0.198}{Z_{\mathrm{A}}b_{\mathrm{A}}^2}a_{\mathrm{A}}^3\left(\frac{6a_{\mathrm{A}}^2}{Z_{\mathrm{A}}b_{\mathrm{A}}^2} + 0.147\right)^{0.34} + \frac{6\eta_4\eta_6}{\tfrac{1}{2}Z_{\mathrm{B}}b_{\mathrm{B}}^2}a_{\mathrm{A}}^3\left(\frac{6a_{\mathrm{A}}^2}{\tfrac{1}{2}Z_{\mathrm{B}}b_{\mathrm{B}}^2} + \eta_5^2\right)^{\eta_6/2-1} \qquad \text{(IV.9)}$$

Employing these equations, calculations have been made of the domain sizes of a number of block copolymer systems using the Fortran program of the Appendix, (Figure 3), the parameters of Table I, and

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

reported by Rounds and McIntyre.[8] As discussed previously[4] a temperature of 90 °C is assumed, which is an estimate of when the structures are fixed by transition of polystyrene to the glass. The domain size predictions are compared with experiment in Table II. Agreement is moderately good (except for comparison with results from the Kyoto University group[14,15]). The predictions are for an equilibrium state, but one imagines that the attainment of equilibrium in a system of spherical domains is more difficult than for lamellar or cylindrical domains. The latter two can change domain size by shrinkage in one or two dimensions, but for spheres to change size the material of the spheres must be transported through the matrix of the other material.

Within the context of the narrow interphase approximation of this paper it may be said that a first-order phase transition from a domain structure to a homogeneous mixture occurs at the temperature for which the free energy is zero. The major temperature dependence (and the only one we consider) is in α as given by eq IV.10. This indirectly affects $\gamma/k_{\mathrm{B}}T$ and a_{J}. Solving eq IV.7 and IV.9 simultaneously we find that for an SBS polymer with molecular weights of 7–43–7 a transition is predicted at 141 °C. Gouinlock and Porter[16] have detected marked changes in the viscoelastic properties of such a system between the temperatures of 138 and 146 °C. They also see changes in the activation energy of a shift factor that indicates increased interpenetration at even lower tem-

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C                           APPENDIX
C    SBCC      PROGRAM TO DETERMINE SIZE OF SPHERICAL DOMAINS
C              IN A BLOCK COPOLYMER SYSTEM
C    SI UNITS
C                   DIBLOC          TRIBLOC BAB     TRIBLOCK ABA
C    J               1              2               3
C    Z1              ZA             ZA/2            ZA
C    Z2              ZB             ZB              ZB/2
     INTEGER POLYMR(3),BLANK,PA,PB
     REAL RHO(3),BETA(3),XM(3),B(3)
     DATA AVOGAD/6.02252E23/
     DATA BLANK/2H  /
     DATA RHO(1),RHO(2),RHO(3)/10100.,13600.,16500./,
   1     BETA(1),BETA(2),BETA(3)/2.79E-8,3.00E-8,3.30E-8/,
   1     XM(1),XM(2),XM(3)/.10414,.06811,.05409/,
   1     B(1),B(2),B(3)/.68E-9,.63E-9,.63E-9/,
   1     POLYMR(1),POLYMR(2),POLYMR(3)/2HPS,2HPI,2HPB/
     FUN(X)=-C1+X+X**3*(C3*(C2*X**2+C4)**C5+C7*(C6*X**2+C8)**C9)
10   WRITE(6,999)
999  FORMAT(35H0PA,PB,J,MOL. WT. A,MOL. WT. B,TEMP)
     READ (6,998) PA,PB,J,XMWA,XMWB,T
998  FORMAT(2(A2,1X),I2,2F6.2,F10.4)
C    PA AND PB ARE THE NAMES OF THE POLYMER COMPONENTS
C    (A REFERS TO THE ONE WITH SPHERICAL DOMAINS)
C    J INDICATES THE TYPE OF BLOCK COPOLYMER
C    1 = DIBLOCK COPOLYMER, A SPHERES
C    2 = TRIBLOCK COPOLYMER BAB
C    3 = TRIBLOCK COPOLYMER ABA
C
C    BLANK LINE AS INPUT TERMINATES THE RUN
     IF(PA.EQ.BLANK) STOP
     IF (J.GE.1 .AND. J .LE. 3) GO TO 20
     WRITE(6,997)
997  FORMAT(19H J MUST = 1, 2 OR 3/)
     GO TO 10
20   IF (T.EQ.0.) T=363.18
     IA=0
     IB=0
     DO 30 I=1,3
     IF(PA.EQ.POLYMR(I)) IA=I
     IF(PB.EQ.POLYMR(I)) IB=I
30   CONTINUE
     IF(IA.NE.0.AND.IB.NE.0) GO TO 40
     WRITE(6,996) (POLYMR(I),I=1,3)
996  FORMAT(46H0ILLEGAL POLYMER NAME  -  THE LEGAL NAMES ARE ,A2,2H, ,
   1  A2,5H AND ,A2)
     GO TO 10
40   ALPHA=-900.+750000./T
     ZA=XMWA/XM(IA)
     Z1=ZA
     IF (J .EQ. 2) Z1=Z1*.5
     ZB=XMWB/XM(IB)
     Z2=ZB
     IF (J .EQ. 3) Z2=Z2*.5
     BETAAV=.5*(BETA(IA)+BETA(IB))
     GAMOKT=SQRT(ALPHA)*(BETAAV+(BETA(IA)-BETA(IB))**2/(12.*BETAAV))
     ZORA=Z1/RHO(IA)
     ZORB=Z2/RHO(IB)
     ZORS=ZORA+ZORB
     RXI=((ZORB/ZORA)+1.)**(1./3.)-1.
     XI=1./RXI
     BTG=AMAX1(BETA(IA),BETA(IB))
     Y=(AMIN1(BETA(IA),BETA(IB))/BTG)**2
     AJ=(BTG/SQRT(ALPHA))*(1.+.4630151*Y+.1077812*Y**2
   1     -(.2452727*Y+.0412496*Y**2)*ALOG(Y))
     IF(J .NE. 2) GO TO 50
     ETAA1=.00810
     ETAA2=1.07
     ETAA3=2.87
     GO TO 60
50   ETAA1=.0123
     ETAA2=.384
     ETAA3=2.68
60    IF(J.NE.3) GO TO 70
     ETAB1=.0705+.0578*RXI
     ETAB2=.596+.599*RXI
     ETAB3=2.55-.132*RXI
     GO TO 80
70   ETAB1=.0852+.0744*RXI
     ETAB2=.348+.220*RXI
     ETAB3=2.48-.123*RXI
80   C1=3.*ZORA*GAMOKT
     C2=6./(B(IA)**2*Z1)
     C3=ETAA1*ETAA3*C2
     C4=ETAA2**2
     C5=ETAA3*.5-1.
     C6=(6./Z2)*(RXI/B(IB))**2
     C7=ETAB1*ETAB3*C6
     C8=ETAB2**2
     C9=ETAB3*.5-1.
     EPS=1.E-15
90   A=C1
     AS=.99*A
     FS=FUN(AS)
     F=FUN(A)
100  ANEW=A-F*(A-AS)/(F-FS)
     AS=A
     A=ANEW
     IF(A.EQ.AS) GO TO 110
     FS=F
     F=FUN(A)
     IF(ABS(F).GE.EPS) GO TO 100
     IF(ABS(F).LT.ABS(FS)) GO TO 120
     WRITE(6,995) A
995  FORMAT(13H0SOLUTION OF ,1PE14.4,5X,22H BUT THIS IS A MAXIMUM)
     GO TO 10
110  WRITE(6,994)
994  FORMAT(19H0ACCURACY DECREASED)
     EPS=EPS*10.
     IF(EPS.LE.1.E-8) GO TO 90
     WRITE(6,993)
993  FORMAT(12H NO SOLUTION)
     GO TO 10
120  XN=4.188790*A**3*AVOGAD*RHO(IA)/ZA
     SIGMA=3.*ZORA/(A*AVOGAD)
     T1=(1.+RXI)**3
     IF(J.EQ.2) T1=SQRT(T1)
     IF(J.EQ.3) T1=SQRT(T1*(T1-1.))
     F=C1/A+ALOG(A*T1/(3.*AJ))
   1   +ETAA1*(C2*A**2+C4)**(.5*ETAA3)-ETAA1*ETAA2**ETAA3
   1   +ETAB1*(C6*A**2+C8)**(.5*ETAB3)-ETAB1*ETAB2**ETAB3
   1   -ALPHA*ZORA*ZORB/ZORS
     D=1.809400*(ZORS/ZORA)**(1./3.)*A
     IF(J.NE.1) GO TO 130
     WRITE (6,992) POLYMR(IA),POLYMR(IB),POLYMR(IA)
992  FORMAT(//19H DIBLOCK COPOLYMER ,A2,1H-,A2,27H WITH SPHERICAL DOMAI
   1 NS OF ,A2)
     GO TO 160
130  IF(J.NE.2) GO TO 140
     IOUT=IB
     IIN=IA
     GO TO 150
140  IOUT=IA
     IIN=IB
150  WRITE(6,991) POLYMR(IOUT),POLYMR(IIN),POLYMR(IOUT),POLYMR(IA)
991  FORMAT(20H0TRIBLOCK COPOLYMER ,A2,1H-,A2,1H-,A2,27H WITH SPHERICAL
   1  DOMAINS OF ,A2)
     F=2.*F
     XN=.5*XN
160  WRITE(6,990)XMWA,XMWB,ZA,ZB,T,XI,A,D,SIGMA,XN,F
990  FORMAT(5H MWA=,F8.3,7X,4HMWB=,F8.3,5X,3HZA=,F7.2,7X,3HZB=,F7.2/
   1  3H T=,F10.1,7X,3HXI=,F9.3,5X,2HA=,1PE11.4,4X,2HD=,E11.4/7H SIGMA=
   1 ,E11.4,2X,2HN=,0PF7.2,8X,6HF/NKT=,1PE11.4)
     GO TO 10
     END
```

Figure 3.

perature. Neither these experiments nor the more detailed theory (of lamellar domains), where the narrow interphase approximation is not made, clearly resolve the question of whether a true phase transition occurs or whether domain interpenetration merely becomes so marked as to free the entanglement structure.

A predicted transition at 167 °C for an 8–38–8 SBS is reasonably compatible with Naylor and Rollman's[17] observations of Newtonian behavior in this system at 160 °C but not 130 °C. But our prediction of a transition in

18–15–18 BSB at 200 °C is not in accord with their observation of Newtonian behavior at 130 °C. Arnold and Meier[18] find that a 10–50–10 SBS is non-Newtonian at 200 °C, which concurs with our prediction of a transition at 213 °C. One would like to see more studies as detailed as Gouinlock and Porter's.

Finally, a few words should be said about the validity of the narrow interphase approximation. We see in Table II that the radii of typical spherical domains range upward from 8 nm. One calculates[6] using the same parameters an interfacial thickness of 1.7 nm between PS and PB, and 1.8 nm between PS and PI (at 20 °C, if equilibrium is achieved, this would be 1.4 and 1.5 nm, respectively). For comparison with spherical domain radii these thicknesses should be halved, i.e., divided between the two domains. An interphase of 2.0 nm has been reported for PS–PI by Hashimoto et al.[19] for lamellar domains. A slightly larger value, reported for spherical domains,[14] may be due to the fact that the X-ray technique does not distinguish between interfacial density distribution and domain size fluctuation. In all, it would seem that the narrow interphase approximation is quite useful, especially in view of the magnitude of other uncertainties. In ref 3 we have presented a comparison of the density profiles and free energies calculated with and without the narrow interphase approximation. Again one concludes that even at this level of detail the approximation is generally good. Near the instability discussed in the paragraphs above the approximation is beginning to break down. The full solution shows fairly large domain interpenetration and does not clearly manifest the first-order transition. Thus the stability limits calculated above must be regarded as surrounded with some ambiguity, as mentioned.

Our next project is an application of the theory to cylindrical geometry, so that the boundaries of stability of the various geometric forms can be mapped as a function of block size.

References and Notes

(1) E. Helfand, *Acc. Chem. Res.*, **8**, 295 (1975).

(2) E. Helfand and Z. R. Wasserman, *Polym. Eng. Sci.*, **17**, 535 (1977).

(3) E. Helfand, *Macromolecules*, **8**, 552 (1975).

(4) E. Helfand and Z. R. Wasserman, *Macromolecules*, **9**, 879 (1976).

(5) F. Seitz, "Modern Theory of Solids", McGraw-Hill, New York, N.Y., 1940, p 331.

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

(7) E. Helfand and Y. Tagami, *J. Chem. Phys.*, **56**, 3592 (1971).

(8) N. A. Rounds, Doctoral Dissertation, 1971, University of Akron. N. A. Rounds and D. McIntyre, private communication.

(9) M. Hoffman, G. Kampf, H. Kromer, and G. Pampus, *Adv. Chem. Ser.*, **No. 99**, 351 (1971).

(10) P. R. Lewis and C. Price, *Polymer*, **12**, 258 (1972).

(11) E. Campos-Lopez, D. McIntyre, and L. J. Fetters, *Macromolecules*, **6**, 415 (1973).

(12) D. J. Meier, *J. Polym. Sci., Part C*, **26**, 81 (1969).

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

(14) A. Todo, H. Uno, K. Miyoshi, T. Hashimoto, and H. Kawai, *Polym. Eng. Sci.*, **17**, 587 (1977).

(15) T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *J. Polym. Sci., Part A-2*, **7**, 1283 (1969).

(16) E. V. Gouinlock and R. S. Porter, *Polym. Eng. Sci.*, **17**, 535 (1977).

(17) G. Kraus, F. E. Naylor, and K. W. Rollman, *J. Polym. Sci., Part A-2*, **9**, 1839 (1971).

(18) K. R. Arnold and D. J. Meier, *J. Appl. Polym. Sci.*, **14**, 427 (1970).

(19) T. Hashimoto, A. Todo, H. Itoi, and H. Kawai, *Macromolecules*, **10**, 377 (1977).

Wormlike Chains Near the Rod Limit: Moments and Particle Scattering Function

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ABSTRACT: Nagai's modification of the Hermans–Ullman recurrence formula was applied to calculate moments $\langle \mathbf{R}^{2m}(\mathbf{R}\cdot\mathbf{u}_0)^n \rangle$ (m, n = 0, 1, 2, ...), $\langle 1/R \rangle$, and the distribution function $G(\mathbf{R};t)$ of the Kratky–Porod wormlike chain up to the fifth-order corrections to the rod limit. Here $\mathbf{R}$ is the end-to-end vector, t is the contour length, and $\mathbf{u}_0$ is the unit tangent vector at one end of the chain. An analytical expression for the particle scattering function $P(\theta)$ of the chain was derived by use of the Fourier transform of the $G(\mathbf{R};t)$. The $P(\theta)$ obtained is useful for analysis of scattered intensities from rodlike macromolecules with a contour length shorter than or comparable to the Kuhn statistical segment length.

The Kratky–Porod (K–P) wormlike chain[1] has long been appreciated as a relevant model for stiff or semiflexible macromolecules. Although much work[2-4] has been on its statistical properties, there still remain quite a few problems to be solved. The present paper is concerned with a theoretical calculation of some properties of the K–P chain near the rod limit.

Daniels[5] was the first to calculate the deviation of the distribution function $G(\mathbf{R},\mathbf{u}_0;t)$ of the K–P chain from the Gaussian distribution correct to the first power in t^{-1}. Here $\mathbf{R}$ is the end-to-end vector of the chain, $\mathbf{u}_0$ is the unit tangent vector at its one end, and t is its reduced contour length. Later, Gobush et al.[6] derived the deviation of the conditional distribution function $G(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)$ from the Gauss limit to the second power in t^{-1}, where $\mathbf{u}$ is the unit tangent vector at the other end of the chain. At about the same time Nagai[7] obtained the distribution function $G(\mathbf{R};t)$ in the same approximation. All these calculations took the Gaussian chain as the zeroth approximation and introduced successively the stiffness characteristic of the K–P chain into it. However, we may start with a completely rigid rod as the zeroth approximation and correct it for chain flexibility in order to explore the behavior of the K–P chain. In fact, this type of approach was first taken by Yamakawa and Fujii,[8] who, using the WKB method, calculated the deviation of $G(\mathbf{R},\mathbf{u}|\mathbf{u}_0;t)$ from the rod limit up to the first order of t. However, they remarked that the distribution function obtained cannot be integrated analytically with respect to $\mathbf{u}$ and $\mathbf{u}_0$. Thus the Yamakawa–Fujii approach does not seem inviting for the

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