pronouncedly than its Kynar counterparts. One possible reason for this may lie in the greater chain perfection of the Kureha resin which is known[29] to contain a smaller percentage of reversed monomeric units. As was mentioned above, such units may interrupt dehydrofluorination along the chain, a process which has been recorded[23] at intermediate melt temperatures (~200 °C).

The difference in discoloration between Kynar and Kureha polymers is even more impressive in solution: As soon as KF-1100 is added to distilled DMF at room temperature, the solution immediately assumes a yellow or orange color. On the other hand, solutions of the Kynar polymers in DMF show no visible discoloration for days. With increasing temperature, solutions of both resins in DMF discolor much earlier, with the Kureha solution again becoming the darker one. Of course, DMF is a typical aprotic solvent; as such, it acts as a base, promoting attack on alkyl halides, which results in dehydrohalogenation. Such elimination of HF may again proceed more extensively along PVF_2 molecules that have fewer head-to-head and tail-to-tail units, thus increasing discoloration. On the other hand, solvents such as acetone and cyclohexanone, which are much weaker bases than DMF and which promote nucleophilic addition to their carbonyl groups, do not discolor upon dissolution of PVF_2 at any temperature.

Finally, other factors that might be of relevance to the inhomogeneous degradation of PVF_2 may be considered by extension from the much richer literature on the degradation of poly(vinyl chloride).[31] It is of interest to note that the rate of thermal dehydrochlorination in PVC is known to depend upon the tacticity of its chains, with syndiotactic sequences degrading more markedly.[32-34] This enhanced dehydrochlorination has been interpreted as arising from faster propagation of polyene sequences in the all-trans molecules of syndiotactic PVC[32,33] or from a decreased rate of termination in this polymer.[33,34] Clearly, therefore, the role that similar effects might play in the inhomogeneous degradation of PVF_2 is of considerable interest for further research.

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Block Copolymer Theory. 6. Cylindrical Domains

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ABSTRACT: Formulas are presented for the free energy of diblock and triblock copolymer systems which develop cylindrical microdomain structure. These algebraic equations are used to determine the domain sizes and periodicity distances in such systems. Comparisons with experiments are presented.

When a phase separation occurs in block copolymer systems, a spherical, cylindrical, or lamellar pattern of microdomains forms. The geometry and size of these microdomains are such as to minimize the free energy. Thus, the object of an equilibrium theory of microdomain structure in block copolymer systems is the determination of the free energy as a function of domain size and geometry. A general theory of inhomogeneous polymeric systems, developed earlier,[1] has been applied previously to block copolymers in lamellar[2,3] and spherical[4] arrays. The picture is completed in this paper with a study of diblock copolymers, AB, and triblock copolymers, ABA or BAB,

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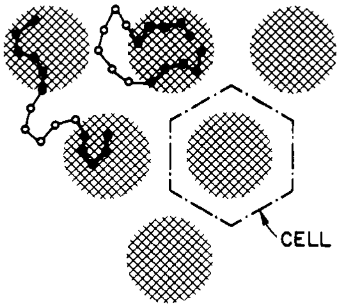

Figure 1. Schematic diagram of the cross section of a block copolymer system which has developed cylindrical domains. The unit cell will be approximated by a circle of the same area as the hexagon.

which form cylindrical domains of A in a matrix of B.

The general theory alluded to may be used either in its complete form[3] or in an approximate version appropriate when the interfacial region between phases is narrow compared with the size of the domains.[2,4] The full theory involves extensive computer calculations for each change of parameters and will not be employed here. Considerable simplification occurs when the narrow interphase approximation is introduced. Then computations of domain size and free energy may be performed by solution of an algebraic equation. Indeed, to further simplify matters we have written a Fortran program[5] which accepts the parameters conveniently, does the algebra, and produces as output the type of information usually sought.

A further dividend of the narrow interphase approximation is that the free energy separates into terms to which physical meaning can be attached. Therefore, after definition of the system's parameters in section I, the physics of the free energy expression is discussed qualitatively in section II. Formulas to be used in calculations are presented in section III. We have applied these formulas to all the systems for which measurements have been made and the parameters are available, with good results, for the most part.

I. Geometry and Parameters

Figure 1 is a cross-sectional view of a regular array of cylinders. The Wigner–Seitz unit cell for this two-dimensional lattice is a hexagon. With d defined as the spacing between axes of the cylinders, the area of the hexagonal cell is $^1/_2 3^{1/2} d^2$. The equations arising in the theory are difficult to solve with boundary conditions defined on a hexagon, so the unit cell will be circularized. This is an approximation which should not be too serious. The cylindrical domain of material A has radius a_A, and the part of the B matrix in the unit cell is taken as occupying an annulus of thickness a_B. In order that the hexagonal and the circularized cell have the same area one must set

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

For the purposes of the theory the polymeric materials may be characterized by a number of parameters. One is the monomer density of pure polymer K, ρ_{0K}. Another is the degree of polymerization of the K block, Z_K. In terms of these the volume fraction of K is for a diblock copolymer, AB

$$\phi_K = \frac{\rho_{0K}/Z_K}{\rho_{0A}/Z_A + \rho_{0B}/Z_B} \tag{I.2}$$

and for a triblock copolymer, CDC

$$\phi_C = \frac{2\rho_{0C}/Z_C}{2\rho_{0C}/Z_C + \rho_{0D}/Z_D} \tag{I.3}$$

$$\phi_D = \frac{\rho_{0D}/Z_D}{2\rho_{0C}/Z_C + \rho_{0D}/Z_D} \tag{I.4}$$

These are good approximations even though some mixing occurs in the interphase because (1) the volume change on mixing is generally small and (2) the fraction of what may be regarded as interphase is small when the narrow interphase approximation is valid.

Another expression for the volume fraction of A is the geometric one

$$\phi_A = a_A^2/(a_A + a_B)^2 \tag{I.5}$$

This equation is easily solved for the ratio

$$\xi \equiv a_A/a_B \tag{I.6}$$

$$= (\phi_A^{-1/2} - 1)^{-1} \tag{I.7}$$

or the individual sizes can be obtained by combining with eq I.1

$$a_A = (3^{1/2}/2\pi)^{1/2} \phi_A^{1/2} d \tag{I.8}$$

$$a_B = (3^{1/2}/2\pi)^{1/2} (1 - \phi_A^{1/2}) d \tag{I.9}$$

All extensive variables which are introduced will refer to a hexagonal cylinder unit cell one unit in length. In particular the number of polymer blocks of A in such a region is

$$N_A = \pi a_A^2 / Z_A \rho_{0A} \tag{I.10}$$

For a diblock copolymer, AB, or triblock BAB, this is also the number, N, of polymer molecules. For a triblock ABA, one has $N = {}^1/_2 N_A$.

In the statistical thermodynamic theory of inhomogeneous polymers an important part of the free energy is the conformational entropy, which, under appropriate conditions, is parameterized by the Kuhn statistical length of a monomeric unit, b_K, defined in such a way that in bulk (or Θ solvent) the root mean square end-to-end distance of a chain of degree of polymerization Z_K is $b_K Z_K^{1/2}$. Another important parameter characterizing mixtures of A and B is the mixing parameter α, defined so that a homogeneous mixture of A and B has a residual free energy of mixing per unit volume of

$$k_B T \alpha \tilde{\rho}_A \tilde{\rho}_B / (\tilde{\rho}_A + \tilde{\rho}_B)$$

where $\tilde{\rho}_K = \rho_K / \rho_{0K}$.

Since, in the limit defined by the narrow-interphase approximation, the distance scale of the domains is so much larger than that of the interphase, it can be shown that the interphase properties are the same as those between bulk A and B. In particular, the free energy expression has a term proportional to the interfacial area and an expression which can be identified as the bulk interfacial tension, γ. Since the interfacial tensions between the polymers of interest have generally not been measured, we will use the theoretical expression of Helfand and Sapse[6]

$$\gamma = k_B T \alpha^{1/2} \left[\frac{\beta_A + \beta_B}{2} + \frac{1}{6} \frac{(\beta_A - \beta_B)^2}{\beta_A + \beta_B} \right] \tag{I.11}$$

$$\beta_K^2 = \rho_{0K} b_K^2 / 6 \tag{I.12}$$

II. Free Energy—Theory

In ref 2–4 we discussed in some detail the theory of lamellar and spherical block copolymer systems. The basic theory is not substantially different for cylindrical domains. The minor changes in the equations are discussed in the Appendix. In any event, a detailed familiarity with these equations is not necessary to understand the physics of the description which emerges from the narrow-interface approximation theory and to use the results. Consider, first, diblock copolymer material, AB. Just as in the earlier papers, it can be shown that the free energy separates into several terms, to each of which a physical meaning may be attached

$$\frac{F_{AB}}{Nk_BT} = \frac{2\pi a_A\gamma}{Nk_BT} + \log\frac{\pi(a_A+a_B)^2}{2\pi a_A a_J} - \log \mathcal{Q}_A - \log \mathcal{Q}_B - \alpha Z_A\phi_B/\rho_{0A} \qquad \text{(II.1)}$$

The first term on the right, proportional to the interfacial area and interfacial tension, represents the interfacial free energy between the A and B domains. Since a_A/N decreases like $1/d$, the reciprocal of the periodicity distance, this term drives the structure toward large phases. The second term opposes this. It represents the loss of entropy involved in localizing the joint in the interphase. It has been shown that the joint of a block copolymer is effectively localized in an interfacial region of constant width a_J given by eq II.42 of ref 4. Thus, the denominator of the logarithm is the effective volume per cell available to the joint, while the numerator is the total volume per cell available if the joint were not localized. Since $(a_A + a_B)^2/a_A$ grows like d, this free energy contribution opposes domain growth like log d.

Another effect opposing domain growth arises from the fact that all the molecules have their block joints in the interphase, which on the scale of distance characterizing the domains may be taken as a wall of the domain. Polymeric blocks would have a nonuniform density if they were regarded as free random walks in the domains, subject to the initial condition of orginating at the wall and the appropriate boundary condition to create a proper interfacial structure. Since the walk starts at the wall, the density is lower near the domain center. Such a nonuniform density is strongly opposed by the forces in a condensed system, so that the system redistributes its conformational probability to favor shapes which fill the domain center, with an accompanying loss of conformational entropy. The extra free energy this represents, $-k_BT$ log $\mathcal{Q}_K$ in domain K, has been calculated by solving the equations referred to in the Appendix. In the A (cylindrical) domain, $\mathcal{Q}_A$ is a function of the single variable X_A

$$X_K = 6^{1/2}a_K/b_KZ_K^{1/2} \qquad \text{(II.2)}$$

Calculated values of $-\log \mathcal{Q}_A(X)$ vs. X are shown in Figure 2a. The points are fitted well by the formula

$$-\log \mathcal{Q}_K(X) = \eta_{K1}(X^2 + \eta_{K2}{}^2)^{\eta_{K3}/2} - \eta_{K1}\eta_{K2}{}^{\eta_{K3}} \qquad \text{(II.3)}$$

$$\eta_{A1} = 0.0274$$
$$\eta_{A2} = 0.202 \qquad \text{(II.4)}$$
$$\eta_{A3} = 2.605$$

which is convenient to use in computer calculations of the block copolymer thermodynamic properties.

While the geometry of the inner region is completely characterized by the radius a_A, the circularized outer region requires specifications of the inner and outer radius or of the thickness a_B and ratio $\xi = a_A/a_B$. Thus, $\mathcal{Q}_B$ is a function of both X_B and ξ, as shown in Figure 2b. The calculated values of $-\log \mathcal{Q}_B(X, \xi)$ are fit again by the functional form of eq II.3 with

$$\eta_{B1} = 0.0792 + 0.0412/\xi$$
$$\eta_{B2} = 0.539 - 0.206/\xi \qquad \text{(II.5)}$$
$$\eta_{B3} = 2.53 - 0.152/\xi$$

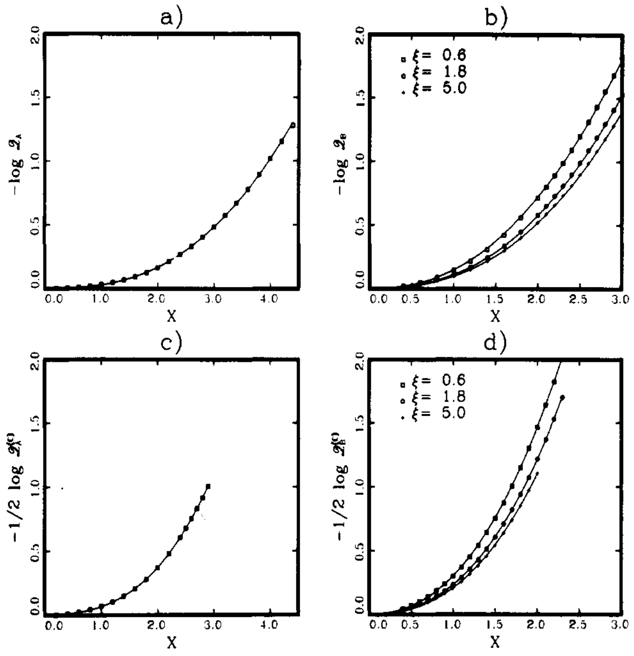

Figure 2. Free energy terms associated with the conformational entropy loss involved in keeping domain densities uniform. The solid lines are the functional fits of eq II.3 or II.8 to the points calculated for specific values of the variable X. (a) A free end block in a cylindrical domain (eq II.4). (b) A free end block in the matrix domain (eq II.5). (c) A central block in a cylindrical domain (eq II.9). (d) A central block in the matrix domain (eq II.11). In b and d not all the ξ for which calculations were performed are shown.

Since X is proportional to d, the terms $-\log \mathcal{Q}_K$ increase with d, limiting the domain size. Physically, as the phases grow larger it becomes more and more difficult for the blocks to reach into the center of the domains to fill them up uniformly.

The final term of eq II.1 is independent of d and serves merely to set the zero of free energy as a homogeneous, single phase. Such a homogeneous phase may be hypothetical in the sense that it is thermodynamically less stable than a microdomain structure, as indicated by F being negative. In ref 4 we discussed (for spherical domains) the use of $F = 0$ as an indicator of a phase transition and found that the predicted transition temperatures are very close to the observed rheological changes in block copolymer systems. There is a danger in this, however, since close to the phase transition the narrow-interface approximation breaks down. This may be a point of rapid structural change (phase interpenetration) without there being an actual transition.

Only minor modifications need be made in the previous formulas to apply them to triblock copolymers. Note, first, that the properties of a triblock copolymer are very similar to those of a system of diblock copolymers achieved by cutting each triblock molecule at the middle of the central block. It is useful to set up the equations in such a way as to explicitly display this fact. Therefore, we write for systems of BAB (A cylinders)

$$\frac{F_{BAB}}{2Nk_BT} = \frac{2\pi a_A\gamma}{2Nk_BT} + \log\frac{\pi(a_A+a_B)a_A}{2\pi a_A a_J} - \tfrac{1}{2}\log \mathcal{Q}_A^{(C)}(X_A^{(C)}) - \log \mathcal{Q}_B(X_B, \xi) - \alpha(\tfrac{1}{2}Z_A)\phi_B/\rho_{0A} \qquad \text{(II.6)}$$

$$X_K^{(C)} = \frac{6^{1/2}a_K}{b_K(\frac{1}{2}Z_K)^{1/2}} \qquad \text{(II.7)}$$

The function $-^1/_2 \log \mathcal{Q}_A^{(C)}$ is fitted well by (Figure 2c)

Table I
Densities and Monomer Lengths

polymer	ρ_{0K}, kmol/m^3	b_K, nm
PS	10.1	0.68
PB	13.6	0.63
PI	16.5	0.63 0.59[a]
PMMA	11.6	0.64

[a] Result of a determination of the Kuhn statistical length for the polyisoprene of the type present in the block copolymers of ref 20 and 22. (T. Hashimoto, private communication).

$$-\tfrac{1}{2}\log Q_K^{(C)}(X) = \eta_{K4}(X^2 + \eta_{K5}{}^2)^{\eta_{K6}/2} - \eta_{K4}\eta_{K5}{}^{\eta_{K6}} \quad \text{(II.8)}$$

$$\begin{aligned} \eta_{A4} &= 0.0166 \\ \eta_{A5} &= 1.051 \\ \eta_{A6} &= 2.86 \end{aligned} \quad \text{(II.9)}$$

For triblock copolymer ABA one has

$$\frac{F_{ABA}}{2Nk_BT} = \frac{2\pi a_A\gamma}{2Nk_BT} + \log\frac{\pi(a_A + a_B)[(a_A + a_B)^2 - a_A{}^2]^{1/2}}{2\pi a_A a_J} - \log Q_A(X_A) - \tfrac{1}{2}\log Q_B^{(C)}(X_B^{(C)}, \xi) - \alpha Z_A\phi_B/\rho_{0A} \quad \text{(II.10)}$$

Table II
Comparison between Experimental and Theoretical Results for the Periodicity Distance (d) and Cylindrical Diameter ($2a_A$) of Cylindrical Block Copolymer Microdomains

			d, nm		$2a_A$, nm		
polymer[a]	cyl	MW, kg/mol	exptl	calcd	exptl	calcd	ref
SB	S	12-22	28.8	29.7	15.7	17.5	8
		13-35		35.1	17.8, 20.3[b]	18.1	
		15-35	33.6	37.1	20.0	20.1	
		20-50	37.0	46.2	20.6, 19.5[b]	22.4	
		25-72	44.0	56.2	25.2	28.1	
		36-121	56.5	75.5	31.6	35.6	
		49-76	63.5	73.8	39.3	46.1	9, 10
		49-124	74.3	84.9	39.3	44.7	
BS	B	24-52	32.8	52.8	19.5	32.9	8
		26-56	33.6	55.6	19.8, 20.9[b]	34.7	
		12.4-49	36.0	39.1	18.2	19.7	9, 10
		21.5-49	44.7	49.5	27.5	30.4	
		22.5-52.5	44.2	51.4	22, 25[b]	31.2	11
		115-306	55[b]	158	33[b]	92.1	12
SBS	S	9-32-9	26.1	24.2	18.7, 16.0	14.5	8
		10-46-10	32.0	28.1	23.0, 22.7	15.3	
		11-52-11	31.3	30.3	16.7, 16.3	16.6	
		9.5-56-9.5	30.0	29.3	15.8	14.6	13
		15.9-61.2-15.9	62.3	36.8	36.2	21.4	14
		14.1-69.8-14.1	32.8	36.4	17.5	19.3	15
		23.8-77.5-23.8	53[c]	46.2	30[b,c]	28.4	16
		11.3-68.4-11.3	34[b]	33.4	14[b]	16.4	17
		13.3-75-13.3	44[b]	36.5	21[b]	18.4	
		13.6-86.3-13.6	38[b]	38.5	16[b]	18.6	
		15.7-99.6-15.7	43[b]	42.5	21[b]	20.5	
	B	47.5-59-47.5		57.6	35.8	39.3	14, 9
		60.5-59-60.5	54.8	60.5	34.8	38.4	
		191-132-191	33[b]	112	18[b]	63.5	12
BSB	S	24-16-24	25.6	26.3	14.1, 13.3[b]	13.0	8
		61-40.8-61	47.6	50.0	23.8	24.7	18, 9
	B	11.2-82.3-11.2	40.8	36.1	21.0	18.6	18, 9
		14.9-82.3-14.9	48.2	40.8	27.6	23.4	
		19-82.3-19	53.5	45.4	33.2	28.3	
		37-212-37	40[b]	76.4	20[b]	43.3	12
SI[d]	S	12.5-35.6	36.0	33.0	18.7	16.8	19
		229-309		185	66	122	20
IS[d]	I	6-12.6	17.5	18.6	10.4	11.6	21, 9
		7-29	27.2, 28.5[b]	25.0	12.8	12.2	
		27.5-93.5		58.5	18.5	30.8	22
		28-116		62.8	23	30.6	
		48-173		86.7	23	44.5	
		66-237		107	29	55.1	
SIS[d]	S	7.5-35-7.5	23.1	21.9	12.6	12.1	23
		12.5-71-12.5	33.7	33.2	17.0	17.0	17
		68.4-458-68.4		108	29	51.5	22
MI	M	21-46	43.6, 43[b]	44.1	27.6	27.9	24, 9

[a] S = polystyrene, B = polybutadiene, I = polyisoprene, M = poly(methyl methacrylate). [b] Determined by measurements on electron micrographs. All other results are by the more accurate X-ray scattering technique. [c] Although Fischer considered his PS domains as spheres, they may well have been cylinders at this composition, and so we have tentatively interpreted them as such here. [d] The value of b_I is taken as 0.63 nm for all calculations except those pertaining to ref 20 and 22. For these polyisoprenes T. Hashimoto (private communications) has measured a b_I of 0.59 nm, which we have used. The differences between results calculated with the two b_I's are only a few percent.

with the functional form of eq II.8 for $Q_B^{(C)}$ (Figure 2d), and

$$\begin{aligned} \eta_{B4} &= 0.0659 + 0.0357/\xi \\ \eta_{B5} &= 0.757 - 0.132/\xi \qquad \text{(II.11)} \\ \eta_{B6} &= 2.59 - 0.147/\xi \end{aligned}$$

In order to use these expressions to calculate the periodicity distance, the free energy must be minimized with respect to d (or, equivalently, a_A) at constant ϕ_A (equivalently ξ). We will not display here the resulting equations for d or the explicit free energy formulas, as we did in ref 4. The required substitutions and differentiation are not difficult to perform, and, in any event, we recommend that those interested in performing calculations avail themselves of our Fortran program[5] to do the required algebra for free energy and domain size evaluation.

III. Comparison with Experiment

The equations of the previous section have been employed in performing calculations on all amorphous systems for which data are available. (Domain sizes have been measured on vinylpyridine and naphthalene block copolymers but the required parameters of these materials are unknown.) The physical constants employed are listed in Table I. For interaction parameter we have used

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

which Rounds and McIntyre[7] measured for the pairs polystyrene (PS)–polybutadiene (PB) and polystyrene–polyisoprene (PI). Since the solubility parameter of poly(methyl methacrylate) (PMMA) is close to that of PS and no other data are available, we have used the same α for the pair PMMA–PI. A temperature of 90 °C was employed as an estimate of the point at which the structure is fixed by the glass transition.

A Fortran program[5] was used in finding the cylindrical domain sizes and spacing reported in Table II. Bear in mind that there are no adjustable parameters, the physical constants are not well-known (especially α), and the closeness of the samples to equilibrium is uncertain. The agreement between experiments and theory is quite good, as it was for lamellar and spherical domain formers. An exception, again, is the PS–PI work of ref 20 and 22. As was discussed earlier,[4] this may be due to the sluggishness of very large molecules in achieving an equilibrium structure. There are a few other measurements which the theory does not match, but these sizes also do not seem to fit into the pattern of other investigators' results.

IV. Outlook

The size and spacing for various geometric forms of the microdomain structure in block copolymers (lamellae,[2] cylinders, and spheres[4]) have been calculated by using the narrow-interface-approximation block copolymer theory. The formulas for the free energy have been reported and these will be employed in subsequent work to determine the phase diagram marking the regions of thermodynamic stability for the various geometric arrangements.

Appendix. Equations for Cylindrical Domains

As one might imagine, the differential equations to be solved to determine $-\log Q_K$ for cylindrical domains are not very different from those describing spherical domains, the major changes being in volume and surface element expressions. Therefore, rather than repeat the full exposition of the equations, we refer the reader to ref 4. The differences between the spherical equations of that paper and the cylindrical equations used in the present calculations are indicated in Table III.

Table III
Difference between Equations Describing Spherical and Cylindrical Domains

eq of ref 4	spherical	cylindrical
II.8	4π	2π
	$d\Omega = \sin\theta \; d\theta \; d\phi$	$d\Omega = d\phi$
II.9	$4\pi r_0^2$	$2\pi r_0$
II.11 and II.15	a_A^{-3}	a_A^{-2}
II.13	a_B^{-3}	a_B^{-2}
II.16	$\frac{1}{y^2}\frac{\partial}{\partial y}y^2\frac{\partial}{\partial y}$	$\frac{1}{y}\frac{\partial}{\partial y}y\frac{\partial}{\partial y}$
II.18	$4\pi y_0^2$	$2\pi y_0$
II.21	$4\pi/3$	π
	$4\pi y_1^2$	$2\pi y_1$
II.22 and II.34	$4\pi y^2$	$2\pi y$
II.23	$\frac{1}{z^2}\frac{\partial}{\partial z}z^2\frac{\partial}{\partial z}$	$\frac{1}{z}\frac{\partial}{\partial z}z\frac{\partial}{\partial z}$
II.25	$4\pi z_0^2$	$2\pi z_0$
II.28	$\frac{4\pi}{3[(\xi+1)^3-\xi^3]}$	$\frac{\pi}{(\xi+1)^2-\xi^2}$
	$4\pi z_1^2$	$2\pi z_1$
II.29 and II.34	$4\pi z^2$	$2\pi z$
II.34	$4\pi y^2$	$2\pi y$
II.36	$4\pi a_A^2$	$2\pi a_A$

References and Notes

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(5) A Fortran program to perform the calculation of domain size and free energy is available by request from the authors. It is a generalization of the program presented in ref 4.
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