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Classification

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Equilibrium emulsification of polymer blends by diblock copolymers

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Résumé. — On a étudié l'apparition et la morphologie de diverses phases à l'équilibre, du type émulsion, formées par le mélange d'homopolymères A et B avec des copolymères diblocs A-B jouant le rôle d'agents de compatibilité. On s'intéresse, en particulier, au rapport entre les longueurs relatives des blocs et les propriétés élastiques de la couche interfaciale qui détermine le comportement de la phase. On évalue les modules élastiques de courbure K et \bar{K} , ainsi que le rayon de courbure spontané R_0 . La situation abordée diffère de celle traitée par l'approche habituelle des interfaces de micro-émulsions contenant des surfactants de chaînes courtes pour deux raisons : (1) la surface par copolymère Σ à l'interface n'est pas fixée, mais déterminée à partir de l'équilibre entre l'énergie élastique de la chaîne et la tension interfaciale ; ainsi Σ dépend aussi des courbures. (2) En conséquence de (1), les coefficients élastiques K , \bar{K} et R_0 sont interdépendants et, au contraire de ce qui se passe avec les systèmes à chaîne courte, le module \bar{K} est toujours négatif (voir le texte pour la convention sur les signes). Le diagramme de phase, en fonction de ces paramètres, est donc différent de celui obtenu à partir des descriptions conventionnelles d'interfaces avec des surfactants à chaînes courtes.

Abstract. — The onset and morphology of various equilibrium emulsion phases for an A and B homopolymer mixture with diblock A-B copolymers as the compatibilizer, is investigated. Attention is focused on the relation between the relative lengths of the blocks and the elastic properties of the interfacial layer which determines the phase behavior. The curvature elastic moduli K and \bar{K} , as well as the spontaneous radius of curvature, R_0 , are obtained. The situation studied here differs from the conventional interfacial approach to microemulsions with short-chain surfactants, in that (1) the area per copolymer Σ on the interface is not fixed, but is determined by a balance between the elastic energy of the chain and the interfacial tension ; thus Σ also depends on the curvatures ; (2) as a result of (1), the elastic coefficients K , \bar{K} and R_0 are interdependent, and in contrast to the short chain systems, the saddle-splay modulus \bar{K} is always negative (see text for the sign convention). The phase diagram as a function of these parameters is therefore different from that obtained by conventional interfacial descriptions for short surfactants.

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1. Introduction.

Blends of two homopolymers of different chemical constituents often phase separate, due to the very low entropy of mixing of these macromolecules. They can be compatibilized by adding some diblock copolymers composed of the two homopolymers [1] : these copolymers are analogous to surfactants in systems of small molecules. Like oil-water-surfactant systems, the morphology of systems of A and B homopolymer compatibilized with A-B block copolymer changes as a function of the volume fractions of the various components [2]. On a phenomenological level, the phase behavior of such systems can be obtained from an interface description which focuses on the role of the curvature energy [3-7]. The curvature energy is described by a few parameters, such as the bending moduli K and \bar{K} and the spontaneous radius of curvature R_0 [8], which depend, in general, on the microscopic details of the systems in consideration. For the polymer systems, the dependence of these parameters on the polymer properties (such as molecular weight) can be obtained fairly accurately. This is because the dominant contribution to the polymer free energy comes from the chain connectivity, a feature that is largely independent of many microscopic details. Such a study then provides the basis for achieving the desired properties and phase behavior by tailoring the polymers to be used.

In this paper, we establish the relationship between the relative lengths of the two blocks in the copolymer and the morphologies of the emulsified phases. Such a study offers a comparison between the results obtained here on a more fundamental level and those obtained by phenomenological approaches.

The physical origin of the emulsifying power of the diblock copolymers comes from the exceedingly low solubility of the diblocks in either solvent due to the positive Flory-Huggins parameter and the large molecular weight of the chains. By migrating to the A-B interface, this energy cost is partially relieved, at the cost of both a loss of translational entropy (due to the localization at the interface) and an increase in the stretching free energy. When this competition is balanced — this is achieved when the volume fraction is above some critical value — a macroscopic number of domains of A and B homopolymer separated by a single interfacial layer of diblock copolymer spontaneously form. In what follows, we calculate the interfacial energy of the surfactant (diblock copolymer) layer and use statistical thermodynamics to obtain the sequence of morphologies and phase equilibria.

The relation of the elastic constants to the molecular properties in short-chain surfactants is discussed in references [9-11]. The curvature energy of grafted homopolymer chains have recently been calculated in reference [12]. Cantor [13] has also studied the interfacial properties for diblock copolymers adsorbed at the interface of two incompatible small-molecule liquids. His work was concerned with the scaling properties of polymers in good solvents, as opposed to our present study of polymer melts. In a recent paper, Leibler [14] has treated the problem of the instability of the random mixing of A and B homopolymer by a small amount of A-B block copolymer. However, that work did not apply to the case where a macroscopic number of interfaces (globules, domains) exist and does not predict the dependence of the morphologies on the properties of the diblock copolymer.

A simplifying feature in the problem we treat, as opposed to systems of diblock copolymer with small-molecule solvents, is that the penetration of the homopolymers to the interfacial copolymer layer is rather small. This is because the copolymers at the interfacial layer are strongly stretched (see Refs. [15, 16] and discussions below) ; hence the internal pressure of the layer, which is sufficient to extend the chains far beyond their ideal radius, excludes unattached chains from the layer [17]. (The work required to insert an additional chain into the layer is much larger than kT). Thus, for long homopolymers, to a first approximation, the

interfacial properties can be regarded as those of the pure diblock layer only. This allows us to make use of some of the known results obtained for the latter to the present problem.

The interfacial layer is depicted schematically in figure 1. It consists predominantly of the diblock copolymers in their melt condition, with very little homopolymer penetration. This melt state implies space filling. For short surfactants, such a condition implies a more or less fixed surface coverage ; but for polymers, space filling imposes no restriction on the area per copolymer molecule, Σ . In fact, Σ is determined by balancing the stretching energy which favors large values of Σ , with the surface tension energy which favors small values of Σ . For the flat layer, this balance leads to the well-known $2/3$ power scaling $D \sim N^{2/3}$ [18-20] for the equilibrium layer thickness, D , as a function of the molecular weight, N . In the case of a curved interface, the area per chain, Σ , depends on the curvature. This curvature dependence of Σ makes a contribution to the elastic moduli K and \bar{K} that is proportional to the square of the spontaneous curvature, as discussed below.

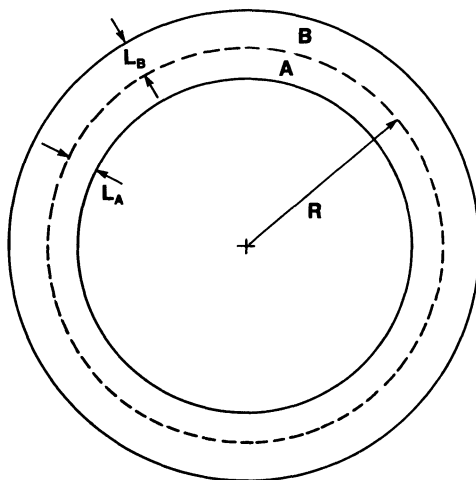


Fig. 1. — A schematic cross section illustration of a spherical (cylindrical) block copolymer shell for the calculation of the bending free energy. The dashed curve represents the location of the junction points between the two blocks. No-penetration of homopolymers, strong segregation of the A and B domains, and incompressibility relate the layer thickness of each block to the radius R and the area per copolymer Σ via : $N_A = d^{-1} \Sigma R [1 - (1 - L_A/R)^d]$, and $N_B = d^{-1} \Sigma R [(1 + L_B/R)^d - 1]$ ($d = 2$ for a cylinder and $d = 3$ for a sphere).

The organization of the paper is as follows : in section 2, the elastic properties of the diblock layer are derived from the stretching free energy of the system. The bending elastic moduli, K and \bar{K} and the spontaneous radius curvature, R_0 , are obtained. In section 3, the thermodynamics of the system is analyzed and the phase diagram of the system indicating the morphology (spheres, cylinders, lamellae) is obtained as a function of the volume fractions and the relative lengths of the A-B regions in the diblock copolymer. The paper concludes with a discussion in section 4.

2. Elastic properties of a diblock copolymer layer.

In the classical theory of curvature elasticity, the properties of a sheet (layer) are characterized by three phenomenological parameters [8] : the splay modulus K , the saddle

splay modulus \bar{K} , and the spontaneous radius of curvature R_0 . Thus, the local free energy per unit area f for a deformation of curvature radii R_1 and R_2 is written as

$$f = f_0 + (1/2) K(1/R_1 + 1/R_2 - 2/R_0)^2 + \bar{K}(1/R_1)(1/R_2). \quad (1)$$

For a layer of diblock copolymer, where the area per molecule is not fixed, it is more meaningful to consider the free energy per copolymer molecule, h . However, we still assume that the elastic description takes the form of equation (1), although the dimension of K and \bar{K} in h will differ from those appearing in equation (1). In addition, we take all energies in units of kT .

The free energy per chain for polymer chains grafted on a slightly curved surface (polymer brush), can be obtained by using the Alexander-de Gennes argument [21, 22] for the stretching energy together with the assumption of incompressibility of the melt. Recently, Milner and Witten [12] have gone beyond the simplified description of references [21, 22] and have calculated the curvature elastic properties of the stretched polymer brush. The stretching energy for a copolymer layer involves a straightforward generalization of these results ; one adds the stretching energies of the two diblock sections.

We denote the total length of the copolymer chain as N , with N_A and N_B the lengths of the A and B blocks, respectively. Defining an asymmetry parameter, ε , as $\varepsilon = 1/2 - N_A/N$, the stretching energy per chain for a uniform (spherical or cylindrical) deformation of radius R at fixed area per molecule Σ , can be shown to be

$$g = (\pi^2/24)[Nv^2/(a^2 \Sigma^2)][1 - 3(d-1)\varepsilon c + (1/20)(d-1)(11d-7)(1+12\varepsilon^2)c^2] \quad (2)$$

where $d = 2$ applies to a cylinder and $d = 3$ applies to a sphere. The dimensionless curvature, c , is defined as $c = (1/2)Nv/(\Sigma R)$, and a and v are, respectively, the length and volume of a monomer.

In equation (2), we have assumed that the two blocks of the copolymer have identical microscopic features, a and v ; these parameters are set to unity in subsequent discussions for simplicity. The asymmetry in the microscopic structures of the diblock sections can be easily incorporated when comparing with experimental data, with only a slight modification [23].

For a more general deformation, assuming the local form of free energy is still valid, equation (2) is replaced by

$$g = (\pi^2/24)(N/\Sigma^2)[1 - 3\varepsilon(c_1 + c_2) + (3/4)(1+12\varepsilon^2)(c_1 + c_2)^2 - (2/5)(1+12\varepsilon^2)c_1 c_2] \quad (3)$$

where c_1 and c_2 are the local (dimensionless) curvatures.

The total free energy of the layer consists of the stretching energy and the interfacial tension, the latter being linearly proportional to the area of contact between A and B segments which must occur at the surface dividing the diblock. In the strong segregation limit, we have

$$h = g + \gamma \Sigma \quad (4)$$

where γ is the interfacial tension between A and B, and is related to the Flory-Huggins parameter by $\gamma \sim \chi^{1/2}av^{-1}$ [24].

Equation (4) contains two competing terms : the interfacial tension term which tends to decrease Σ , and the stretching term, g , which tends to increase Σ . For a flat layer, the optimal value of $\Sigma = \Sigma^*$ is obtained by minimizing the total free energy h with respect to Σ , yielding

$$\Sigma^* = (\pi^2/12)^{1/3} N^{1/3} \gamma^{-1/3}. \quad (5)$$

The value of the free energy for $\Sigma = \Sigma^*$ is h^* , given by

$$h^* = (3/2) \gamma \Sigma^* = (3/2)(\pi^2/12)^{1/3} N^{1/3} \gamma^{2/3}. \quad (6)$$

To obtain the correct dimensions for Σ^* and h^* , we merely replace N with Nv^2/a^2 and use the dimensional γ ($\gamma \sim \chi^{1/2} av^{-1}$).

For a slightly curved layer, we seek an expansion of Σ up to second order in the curvatures c_1 and c_2 . After collecting terms, we obtain the following expansion of the free energy per chain,

$$h = h^*[1 - \varepsilon(\bar{c}_1 + \bar{c}_2) + (1/4)(1 + 3\varepsilon^2)(\bar{c}_1 + \bar{c}_2)^2 - (2/15)(1 + 12\varepsilon^2)\bar{c}_1\bar{c}_2] \quad (7)$$

where the \bar{c}_i 's are defined as $\bar{c}_i = (1/2)N/(\Sigma^* R_i)$, $i = 1, 2$, and where Σ^* and h^* are the values derived for the flat layer in equations (5) and (6).

Comparing equation (7) with equation (1), we identify the splay and saddle splay moduli as

$$\begin{aligned} K &= (1/2)(1 + 3\varepsilon^2)h^*(N/2\Sigma^*)^2 \\ &= (3/16)(1 + 3\varepsilon^2)(12/\pi^2)^{1/3}N^{5/3}\gamma^{4/3} \end{aligned} \quad (8a)$$

and

$$\begin{aligned} \bar{K} &= - (2/15)(1 + 12\varepsilon^2)h^*(N/2\Sigma^*)^2 \\ &= - (1/20)(1 + 12\varepsilon^2)(12/\pi^2)^{1/3}N^{5/3}\gamma^{4/3}. \end{aligned} \quad (8b)$$

The spontaneous radius of curvature is

$$R_0 = (1/2)\varepsilon^{-1}(1 + 3\varepsilon^2)(12/\pi^2)^{1/3}N^{2/3}\gamma^{1/3}. \quad (8c)$$

Another commonly used definition of the bending moduli results from writing the free energy in the form [7, 11]

$$h = h_0 + (1/2)k(1/R_1 + 1/R_2 - 2/\tilde{R}_0)^2 + (1/2)\bar{k}(1/R_1 - 1/R_2)^2. \quad (9)$$

This definition has the advantage that the spontaneous radius is that of a sphere which minimizes the free energy for any $\bar{k} > 0$. The conversion from K , \bar{K} , and R_0 to k , \bar{k} , and \tilde{R}_0 is straightforward, and we find,

$$k = K + \bar{K}/2 = (1/80)(13 + 21\varepsilon^2)(12/\pi^2)^{1/3}N^{5/3}\gamma^{4/3} \quad (10a)$$

$$\bar{k} = -\bar{K}/2 = (1/40)(1 + 12\varepsilon^2)(12/\pi^2)^{1/3}N^{5/3}\gamma^{4/3} \quad (10b)$$

and

$$\tilde{R}_0 = (1/30)\varepsilon^{-1}(13 + 21\varepsilon^2)(12/\pi^2)^{1/3}N^{2/3}\gamma^{1/3}. \quad (10c)$$

Throughout the entire range of ε , the saddle splay modulus $\bar{K}(\bar{k})$ is always negative (positive); thus a saddle shaped deformation is disfavored energetically [25]. It is often of interest to consider the ratio κ , of the saddle splay to the splay modulus. This ratio, for k and \bar{k} is, from equations (10a) and (10b),

$$\kappa = \bar{k}/k = 2(1 + 12\varepsilon^2)/(13 + 21\varepsilon^2) \quad (11)$$

and is seen to have a limited range of variation during the range of ε between 0 and 1/2. The latter has its consequence in the phase diagram in these parameters.

We note that the bending modulus K for the lamellar phase of strongly segregated diblock copolymers has also been calculated by Kawasaki and Ohta [26]. Their result, obtained by using a density functional theory [27, 28], however, has a rather sensitive dependence on the fractional length of a block f ($f = 1/2 + \varepsilon$ in our presentation). In fact, even the equilibrium layer spacing calculated by the same authors [28], has a strong dependence on f , whereas on physical ground it is expected to depend only on the total length of the chain in the strongly segregated regime.

3. Thermodynamics and phase behavior.

In this section, we discuss the stability of various equilibrium, emulsion phases, where domains of A and B homopolymer are separated by internal interfaces consisting of A-B diblocks. This can be achieved by using the results of the previous section for K , \bar{K} and R_0 . However, for the uniform shapes (lamellae, cylinders, and spheres) considered in this paper, we prefer to use the interfacial energy in the form of equation (4), with the stretching energy g given by equation (2). In 3.1, the emergence of the emulsion phase, with a macroscopic number of internal interfaces, is discussed and the critical diblock volume fraction is derived. In 3.2, the sequence of microstructures obtained by varying the volume fractions is analyzed and the phase diagram of the system is presented. The essential physics are described in the discussion preceding equation (14), and the phase diagram is described at the end of section 3.2; the intervening material represents the mathematical details which may be omitted by the general reader.

3.1 EMERGENCE OF THE EMULSION PHASE. — When two incompatible fluids are brought together they phase separate, with a minimal interfacial area, usually a flat, macroscopic meniscus. Surfactant-like molecules, randomly dissolved in the two incompatible fluids, are attracted to the interface. In this section, we study the transition from dilute solutions of diblock copolymers in A and B to the spontaneous formation of a macroscopic number of internal interfaces. We assume that the two homopolymers A and B are completely immiscible, but that either of them can dissolve a limited amount of the copolymer C molecules.

We first study the transition from the completely phase-separated to the lamellar phase as this is the simplest. The reference state is taken to be that of pure A, B, and C, the latter assumed to be in its lowest free energy state, which we take to be a lamellar mesophase (see discussion Sect.). The free energy of mixing per unit volume, with volume fractions ϕ_A , ϕ_B and ϕ_C , respectively, is

$$\Delta f = (\phi_A/N) F(\phi_C^A, \varepsilon) + (\phi_B/N) F(\phi_C^B, -\varepsilon) + [(S/\Sigma V) h(\Sigma) - (\phi_C/N) h^*] \quad (12)$$

where

$$F(\phi_C^i, \varepsilon) = [\phi_C^i(1 - \phi_C^i)^{-1} \ln(\phi_C^i/N) + \ln(1 - \phi_C^i) + (1/2 + \varepsilon) \phi_C^i(1 - \phi_C^i)^{-1} \chi N]$$

($i = A, B$) with ϕ_C^A and ϕ_C^B being the concentration (volume fraction) of the copolymers in A homopolymers and B homopolymers, respectively, S is the total interfacial area, and V is the total volume. The terms in F represent the free energy of mixing [29] of C and A (B), while the two terms in the brackets in equation (12) are the interfacial free energy of the copolymer layer, relative to its equilibrium value for a flat sheet. The system is assumed to be

incompressible, namely, $\phi_A + \phi_B + \phi_C = 1$. For simplicity, we also assume that both A and B have the same molecular weight N as the copolymer. Defining $\phi_C^S = SN/(\Sigma V)$ which is the total volume fraction of copolymers in the interfacial layer, the conservation law for the copolymers can be written as,

$$G = \phi_A \phi_C^A / (1 - \phi_C^A) + \phi_B \phi_C^B / (1 - \phi_C^B) + \phi_C^S - \phi_C = 0. \quad (13)$$

This conservation law, together with the free energy equation (12) completely determine the thermodynamic states of the system.

In writing down the free energy equation (12), we have neglected the contribution coming from the entropy of mixing of the surfaces. Such a contribution is vanishingly small for the lamellae and cylinders, since they are one and two dimensional respectively. The entropy of mixing is also unimportant for the spheres, except when the spheres are small and their concentration is low. Another defect of equation (12) is the neglect of the fluctuations of the surfaces and the interactions among them [30]. These factors may quantitatively modify the phase diagrams, but are beyond the scope of the present treatment. They are not expected to have major qualitative effects on the aspects we are concerned with in this paper. Under these approximations and assuming no homopolymer penetration of the diblock layer, the interfacial layer should then behave the same as an isolated one, as will be seen below.

The minimum of the free energy subject to the constraint, equation (13), can be obtained by using the method of Lagrange multiplier, i.e. by letting $\partial F / \partial s_i - \lambda \partial G / \partial s_i = 0$, where $s_i = \phi_C^A, \phi_C^B, \phi_C^S$ and σ ($\sigma = \Sigma / \Sigma^*$), λ is the Lagrange multiplier, and $F = N \Delta f$. Taking derivatives in the above order, we find

$$\phi_A \{ \ln [\phi_C^A / N] + (1/2 + \varepsilon) \chi N \} - \lambda \phi_A = 0 \quad (14a)$$

$$\phi_B \{ \ln [\phi_C^B / N] + (1/2 - \varepsilon) \chi N \} - \lambda \phi_B = 0 \quad (14b)$$

$$\partial h / \partial \sigma = 0 \quad (14c)$$

$$h - \lambda = 0. \quad (14d)$$

The last two equations lead directly to $\sigma = 1$ and $\lambda = h = h^*$. These results imply that the chemical potential (the Lagrange multiplier) λ is equal to the minimized surface free energy when the amount of surface is free to vary. The concentrations ϕ_C^A and ϕ_C^B can be obtained by substituting λ back into equations (14a) and (14b), and we find,

$$\phi_C^A = N \exp [h^* - (1/2 + \varepsilon) \chi N] \quad (15a)$$

$$\phi_C^B = N \exp [h^* - (1/2 - \varepsilon) \chi N] \quad (15b)$$

where h^* is a function of the surface tension γ and the polymerization index N (Eq. (6)).

The critical concentration ϕ_C^* for the onset of spontaneous formation of surfaces, i.e. when $\phi_C^S = 0$, is, from equation (13),

$$\phi_C^* = \phi_A \phi_C^A / (1 - \phi_C^A) + \phi_B \phi_C^B / (1 - \phi_C^B) \quad (16)$$

with ϕ_C^A, ϕ_C^B given by equations (15a) and (15b), respectively. These equations have also been given by Leibler [14]. For $\phi_C > \phi_C^*$, a finite fraction of the copolymer molecules will be in the interfacial layers. If an experiment is performed by adding C at fixed amount of A and B, then the volume fraction of the copolymer molecules in the interfaces is

$$\phi_C^S = (\phi_C - \phi_C^*) / (1 - \phi_C^*). \quad (17)$$

For $\varepsilon \neq 0$, we expect drops of a particular curvature to form instead of flat sheets. In this paper we use the convention that A is always the interior phase so that $\varepsilon > 0$. We start from the situation depicted in figure 2, where we have drops of A suspended in B in coexistence with a phase of excessive A homopolymers. Because there is a definite relation between the volume and the area of the spheres, the total amount of C in the surface layers is related to the radius of the spheres and the number of spheres. If the volume fraction of A in the interior of the spheres is $\bar{\phi}_A$, then the volume fraction of copolymers on the surfaces is

$$\phi_C^S = \bar{\phi}_A W_d / (1 - \phi_C^A) \quad (18)$$

where the function W_d arises from the (dimensionless) surface to volume ratio and is related to the (dimensionless) curvature c by

$$W_d = 2 dc / [1 - dc(1 - 2\varepsilon)] . \quad (19)$$

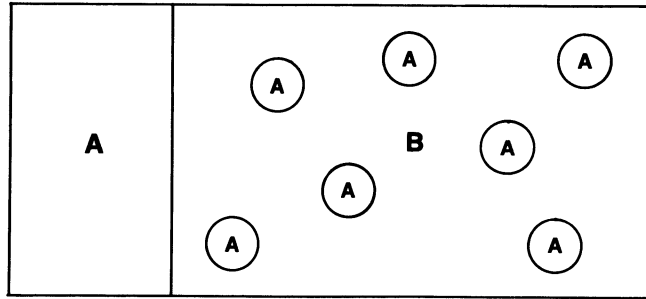


Fig. 2. — A schematic illustration of the phase equilibrium considered in section 3. A, where emulsified droplets of A homopolymers coexist with excessive A homopolymers.

In equation (19), the second term in the denominator results from the finite thickness of the layer. We have used W_d to allow for simultaneous treatment of spheres and cylinders : $d = 2$ for cylinders and $d = 3$ for spheres. In what follows we sometimes drop the subscript d for notational simplicity. It should be kept in mind, however, that the relation between W and c is different for cylinders than for spheres (see Eqs. (19) and (24)). If the solubility of the copolymer is very low in either homopolymers, W is approximately the ratio of the volume fraction of the copolymer layer over the volume fraction of the interior A homopolymers (cf. Eq. (18)).

The conservation law for the surfactants now becomes

$$G = \phi_A \phi_C^A / (1 - \phi_C^A) + \phi_B \phi_C^B / (1 - \phi_C^B) + \bar{\phi}_A W / (1 - \phi_C^A) - \phi_C = 0 \quad (20)$$

and the free energy of the (multiphase) system is

$$F = \phi_A F(\phi_C^A, \varepsilon) + \phi_B F(\phi_C^B, -\varepsilon) + \bar{\phi}_A W (1 - \phi_C^A)^{-1} h_d(\sigma, c) - \phi_C h^* \quad (21)$$

where the function $F(\phi_C^i, \varepsilon)$ is the same as is given below equation (12). The surface free energy $h_d(\sigma, c)$ applies to spheres ($d = 3$) or cylinders ($d = 2$) at fixed radius R and fixed (reduced) surface area per copolymer, $\sigma = \Sigma / \Sigma^*$,

$$h_d = (1/3) h^* [S_d(c) / \sigma^2 + 2\sigma] \quad (22)$$

where $S_d(c)$ is

$$S_d(c) = 1 - 3(d-1)\varepsilon c + (1/20)(d-1)(11d-7)(1+12\varepsilon^2)c^2 \quad (23)$$

with $c = (1/2)N/(\Sigma R)$.

In terms of W ,

$$c = d^{-1}W/[2 + W(1 - 2\varepsilon)] \quad (24)$$

and $S_d(c)$ becomes,

$$S_d(W) = 1 - 3(1 - d^{-1})\varepsilon W/[2 + W(1 - 2\varepsilon)] + \\ + (1/20)(1 - d^{-1})(11 - 7d^{-1})(1 + 12\varepsilon^2)W^2/[2 + W(1 - 2\varepsilon)]^2. \quad (25)$$

It should be noted that equation (23) was obtained as an expansion for small curvatures, keeping terms to only second order in the curvature; therefore, $S_d(W)$ should also be expanded to the same order. However, since we will be interested in the full range of W , and since equation (24) implies that the curvature, c , cannot be large even for large W (except when ε is very close to $1/2$), we keep the form of equation (25) and will assume it is valid for all W . For large W , $S_d(W)$ is still expected to be qualitatively correct; for small W , the difference between an expansion and equation (25) is not important anyway.

Equilibrium is obtained when the free energy is minimized with respect to all five variables ϕ_C^A , ϕ_C^B , σ , W and $\bar{\phi}_A$, subject to the conservation condition equation (20). Again, we introduce the Lagrange multiplier λ . Taking the partial derivatives in the order indicated above, we obtain,

$$\phi_A[\ln(\phi_C^A/N) + (1/2 + \varepsilon)\chi N] + \bar{\phi}_A Wh(\sigma, W) - \lambda(\phi_A + \bar{\phi}_A W) = 0 \quad (26a)$$

$$\phi_B[\ln(\phi_C^B/N) + (1/2 - \varepsilon)\chi N] - \lambda\phi_B = 0 \quad (26b)$$

$$\partial h(\sigma, W)/\partial \sigma = 0 \quad (26c)$$

$$\bar{\phi}_A[h(\sigma, W) + W\partial h(\sigma, W)/\partial W] - \lambda\bar{\phi}_A = 0 \quad (26d)$$

$$Wh(\sigma, W) - \lambda W = 0. \quad (26e)$$

The last equation yields $\lambda = h(\sigma, W)$, whereas equations (26c) and (26d) are none other than conditions for a minimum of $h(\sigma, W)$. The σ and W values that minimize $h(\sigma, W)$ are,

$$\sigma = S_d^{1/3}(W) \quad (27)$$

and

$$W_3^* = 90\varepsilon/(13 - 45\varepsilon + 246\varepsilon^2) \quad (28)$$

$$W_2^* = 8\varepsilon/(1 - 4\varepsilon + 20\varepsilon^2). \quad (29)$$

It can be shown that for $\varepsilon \neq 0$ ($\varepsilon > 0$ by our convention), $W_3^* < W_2^*$, and $h_3^* < h_2^* < h^*$. Thus, the first emulsion phase to appear as the surfactant to interior ratio W increases is that of spheres. The onset of the formation of spheres is obtained by setting $\bar{\phi}_A = 0$, i.e. when a macroscopic amount of droplets with A interior first begin to form, from which we find,

$$\phi_C^* = \phi_A \phi_C^A/(1 - \phi_C^A) + \phi_B \phi_C^B/(1 - \phi_C^B) \quad (30)$$

where

$$\phi_C^A = N \exp[h_3^* - (1/2 + \varepsilon) \chi N] \quad (31a)$$

$$\phi_C^B = N \exp[h_3^* - (1/2 - \varepsilon) \chi N] . \quad (31b)$$

Again, if an experiment is performed by adding C while keeping the amount of A and B fixed, the volume fraction of C in the interfacial layers for $\phi_C > \phi_C^*$ will be

$$\phi_C^S = (\phi_C - \phi_C^*) / (1 - \phi_C^*) \quad (32)$$

and the amount of A in the interior of the droplets is (from Eq. (19))

$$\bar{\phi}_A = \phi_C^S (1 - \phi_C^A) / W_3^* . \quad (33)$$

In the phase-coexistence region, the chemical potential λ is fixed at the value of h_3^* ; hence the concentrations of C in A and B remain unchanged; only the amount of each phase changes, as given by equations (32) and (33). Such a coexistence terminates when all the A homopolymers are in the interior of spheres, i.e., when $\bar{\phi}_A = \phi_A$. If an experiment is conducted starting from a blend of A and B by adding copolymers C, then $\phi_A = \phi_A^0 (1 - \phi_C)$, where ϕ_A^0 is the volume fraction of A before adding any copolymers.

From equations (32) and (33), we easily find the volume fraction of the copolymer surfactants above which all A homopolymers are in the droplets, to be

$$\phi_C^e = \phi_C^* + (1 - \phi_C^*) \phi_A W_3^* / (1 - \phi_C^A) \quad (34)$$

or in terms of ϕ_A^0

$$\phi_C^e = [\phi_C^* + (1 - \phi_C^*) \phi_A^0 W_3^* / (1 - \phi_C^A)] / [1 + (1 - \phi_C^*) \phi_A^0 W_3^* / (1 - \phi_C^A)] . \quad (35)$$

For $\phi_C < \phi_C^e$, there are not enough copolymers to emulsify the blends. This value of ϕ_C^e is called the emulsification failure in references [7, 11]. In the emulsification failure regime, the microemulsion coexists with a phase of excessive A homopolymers. Above the emulsification failure $\bar{\phi}_A = \phi_A$, so that it is no longer a quantity free to vary. Then equation (26e) no longer applies. The chemical potential now becomes

$$\lambda = h(\sigma, W) + W \partial h(\sigma, W) / \partial W \quad (36)$$

where σ is still given by $\sigma = S_d^{1/3}(W)$. The concentrations ϕ_C^A and ϕ_C^B are then

$$\phi_C^A = N \exp[\lambda + W^2 \partial h(\sigma, W) / \partial W - (1/2 + \varepsilon) \chi N] \quad (37a)$$

$$\phi_C^B = N \exp[\lambda - (1/2 - \varepsilon) \chi N] . \quad (37b)$$

Notice that the concentration in the interior phase is no longer determined by the chemical potential alone, but has an additional piece $W^2 \partial h(\sigma, W)$, which does not vanish in general.

3.2 EQUILIBRIUM EMULSION PHASES. — We now consider the case of very incompatible A and B homopolymers, where $\chi N \gg 1$, so that the concentration of the copolymer in either homopolymer solvent is exceedingly low; essentially all the copolymers are found at the A-B interfaces. In this case, it is a rather accurate approximation to neglect the free energy contributions coming from these dilute solutions of copolymers in A and B regions, and to

consider only the interfacial layers. The conservation law in the case of only one emulsion phase reduces simply to $\phi_C = \phi_A W$, so that the volume fraction ratio of copolymers to A homopolymers is $W = \phi_C / \phi_A$. In what follows, we will use the variable W to study the various phase transitions. For a given value of W , the free energy per copolymer on the surface is obtained after minimizing $h(\sigma, W)$ with respect to σ . This process yields $\sigma = S_d^{1/3}(W)$ (Eq. (27)) and

$$h_d(W) = S_d^{1/3}(W). \quad (38)$$

This free energy for $\varepsilon = 0.1$ for the three different morphologies considered, i.e. spheres, cylinders and lamellae, is shown in figure 3. As the volume fraction ratio W increases, first the spheres have the lowest free energy, but when

$$W = 720 \varepsilon / [73 - 360 \varepsilon + 1596 \varepsilon^2] \quad (39)$$

spheres and cylinders have the same free energy. For W larger than the value given by equation (39), cylinders become the favored morphology in terms of the free energy, until they are overtaken by the lamellae at

$$W = 180 \varepsilon / [13 - 90 \varepsilon + 336 \varepsilon^2]. \quad (40)$$

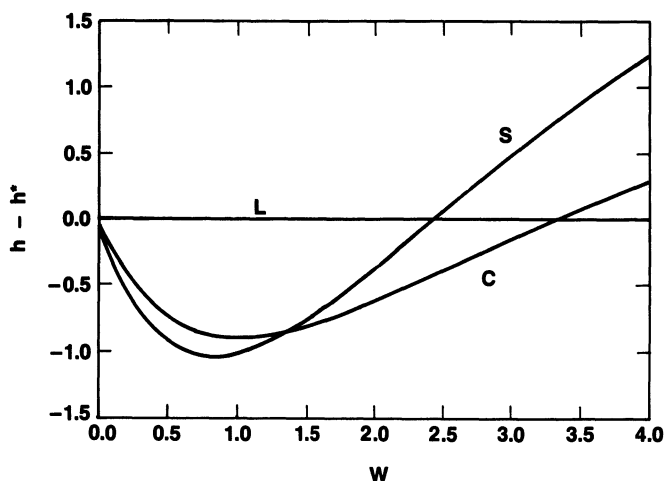


Fig. 3. — The three branches of layer free energy (unit arbitrary) as a function of the volume fraction ratio the copolymer to the (interior) A homopolymer W (see Eq. (18) for the definition of W). The letters L, C and S stands for lamellar, cylinder and sphere, respectively.

Of course, when considering first-order phase transitions, the correct construction is the common tangent construction [31]. This construction is equivalent to the equality of the chemical potentials and the equality of pressure-like variables, as we now discuss.

The free energy per copolymer, in the case of two coexisting phases, can be written, neglecting contributions from the solution, as

$$f = \xi h_2(\sigma_2, W_2) + (1 - \xi) h_3(\sigma_3, W_3) \quad (41)$$

where for concreteness, we consider the coexistence between the cylinder (2) and sphere (3)

phases. The variable ξ is the fraction of copolymers in the cylinder phase. The conservation condition is then given by

$$1/W = \xi/W_2 + (1 - \xi)/W_3 . \quad (42)$$

Minimizing f with respect to σ_i , W_i , and ξ , we find

$$\partial h_i(\sigma_i, W_i)/\partial \sigma_i = 0 , \quad i = 2, 3 \quad (43a)$$

$$\partial h_i(\sigma_i, W_i)/\partial W_i - \lambda \partial (1/W_i)/\partial W_i = 0 , \quad i = 2, 3 \quad (43b)$$

$$h_2(\sigma_2, W_2) - h_3(\sigma_3, W_3) - \lambda (1/W_2 - 1/W_3) = 0 . \quad (43c)$$

Equation (43a) yields the relation, $\sigma_i = S_d^{1/3}(W_i)$, whereas equation (43b) gives

$$\lambda = -W_2^2 \partial h(\sigma_2, W_2)/\partial W_2 = -W_3^2 \partial h(\sigma_3, W_3)/\partial W_3 . \quad (44)$$

Combining this with equation (43c) yields

$$h_2(\sigma_2, W_2) + W_2 \partial h_2(\sigma_2, W_2) = h_3(\sigma_3, W_3) + W_3 \partial h_3(\sigma_3, W_3) . \quad (45)$$

If we define a Legendre transform by

$$Q_i = -\partial h(\sigma_i, W_i)/\partial (1/W_i) \quad (46)$$

then equations (44) and (45) become

$$Q_2 = Q_3 \quad (47)$$

$$\mu_2 = \mu_3 \quad (48)$$

where the chemical potential μ_i is defined as

$$\mu_i = h_i(\sigma_i, W_i) + Q_i/W_i . \quad (49)$$

Recalling the standard thermodynamic relations [32], we see that Q is a pressure-like variable conjugate to the density-like variable W , and that h plays the role of the Helmholtz free energy, whereas μ plays the role of the Gibbs free energy (the chemical potential). It should be noted that the derivative $\partial h/\partial W$ is a partial derivative at fixed σ .

From equations (47), (48) with equations (46) and (49), the values of W_i can be obtained, and using the relation equation (42), ξ can be obtained. The case involving coexistence with the lamellar phase is a bit trickier. However, it can be shown that the condition for coexistence with the lamellar phase with chemical potential μ_1 and surface free energy h_1 , respectively, is

$$\mu_1 = h_1 = h^* = \mu_i \quad (50)$$

where μ_i is the chemical potential of the other phase (cylinder or sphere) defined through equation (49). The value of W_1 is obtained by using the thermodynamic relation,

$$\partial \mu / \partial Q = 1/W . \quad (51)$$

Since $h_1(\mu_1)$ is constant, it is independent of the « pressure » ; therefore,

$$\partial \mu_1 / \partial Q = 0 \quad (52)$$

i.e. $1/W_1 = 0$ or $W_1 = \infty$. This suggests that the coexisting lamellar phase is the pure state consisting only of block copolymer sheets.

This result should not be surprising because, in our model, the pure lamellar mesophase and the emulsion lamellar phase are energetically equivalent since interactions between the sheets are neglected. This artifact can be corrected by incorporating, for example, the Helfrich entropic repulsive interactions [30] between the sheets. The implementation of this calculation is beyond the scope of the present work.

The preceding results are summarized in figure 4 which shows the complete (mean-field) phase diagram in the ε - W plane, where $\varepsilon = 1/2 - N_A/N$ and $W = \phi_C/\phi_A$. (The exact relation is Eq. (18)).

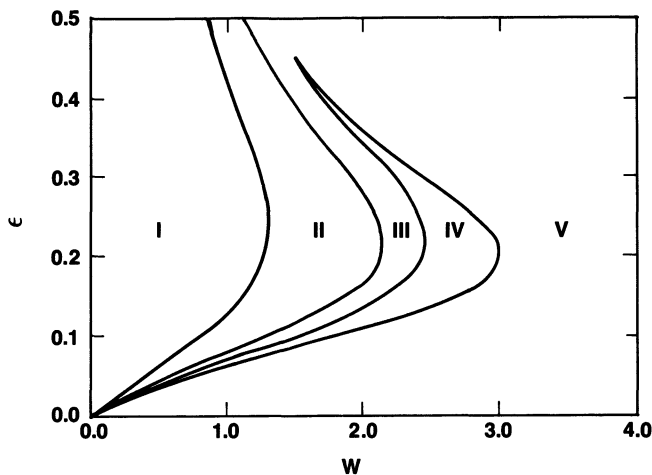


Fig. 4. — Phase diagram in the ε - W plane where $\varepsilon = 1/2 - N_A/N$, which defines the asymmetry in the lengths of the two blocks of the copolymer, and where $W \approx \phi_C/\phi_A$, which is the volume fraction ratio of the copolymer to the (interior) A homopolymer. Regions I, II, III, IV and V correspond, respectively, to spheres + excessive A, spheres, spheres + cylinders, cylinders, and cylinders + lamellae.

The sequence of the appearance of various phases is as described above : When $\phi_C > \phi_C^*$, first there is a two phase region of excessive A homopolymers in coexistence with spherical droplets of A suspended in B. As W , the volume fraction ratio, increases past W_3^* , all the A homopolymers will be in the interior of the spherical drops. This one-phase region continues until the first appearance of the cylinder phase whence we have a two-phase coexistence of spheres and cylinders. As W increases further, the spheres disappear, leaving a single phase of cylinders. For sufficiently large W , the lamellar phase appears as in coexistence with the cylinder phase. Because the coexisting lamellar phase has $W = \infty$ in our calculation, a single phase of lamellae is not predicted ; on physical grounds, however, we expect a single phase of lamellae at small values of ε .

To compare our results with the predicted morphologies of short-chain surfactant microemulsions, where the area per molecule is held fixed, it is of interest to re-plot the phase diagram using the variables r and κ , where $r = W_3^*/W$, and $\kappa = \bar{k}/k$; this is shown in figure 5. This phase diagram appears rather different from the one in reference [11] for short surfactant systems in both the curvatures of the phase boundary and the topology of the

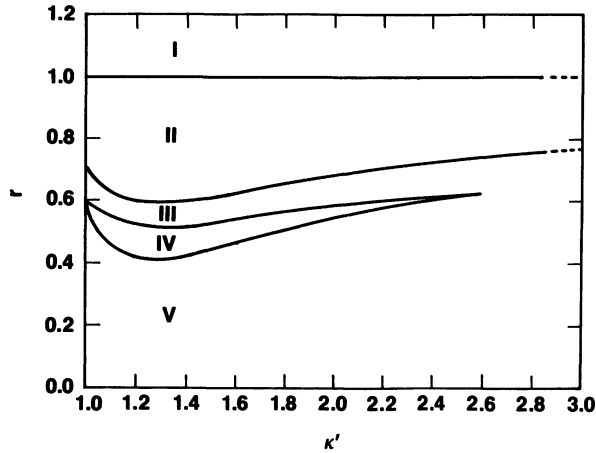


Fig. 5. — Phase diagram in the r - κ' plane. $r = W_3^*/W$ and $\kappa' = (13/2)\kappa$ where W is the volume fraction ratio of the copolymer to the (interior) A homopolymer, W_3^* is the value of W which minimizes the free energy of the sphere, corresponding to the spontaneous radius (cf. Eq. (28)), and κ is the ratio between the two bending moduli \bar{k} and k given by equation (12). Regions I, II, III, IV and V correspond, respectively, to spheres + excessive A, spheres, spheres + cylinders, cylinders, and cylinders + lamellae. The region $\kappa' > 280/73$ (the limiting value for κ' at $\varepsilon = 1/2$) is physically inaccessible.

regions. (It should be noted, however, that the « phase diagram » in reference [11] is not a rigorous one in that it is obtained by comparing the free energies of different branches instead of by the correct common tangent construction. Nevertheless, the difference in the interdependence among k , \bar{k} and \bar{R}_0 , in the two cases, has a major effect in the difference between these two phase diagrams.)

Notice that in figure 4, for $\varepsilon > 0.45$, the cylinder phase disappears. This disappearance of the cylinder region is known also for short surfactant systems for large, positive values of the saddle splay, \bar{k} and hence, κ values, and is a result of our free energy in the form of equation (23). However, our predictions for values of ε close to $1/2$ are only qualitative because of possible complications of the phase diagram by, e.g., the formation of micelles, a possibility which we have neglected so far but is discussed in the next section.

4. Discussion.

We have presented results of a mean-field calculation of the thermodynamics of different morphologies in systems consisting of two incompatible homopolymer mixtures and diblock copolymers made of these homopolymers. The phase equilibria of isolated spheres, cylinders and lamellar sheets have been analyzed. The interfacial free energy is modeled rather accurately by adapting the recent results of Milner and Witten for polymer layers of high molecular weight.

Elastic properties, such as the two bending moduli K and \bar{K} , and the spontaneous curvature radius R_0 , are calculated explicitly as functions of the molecular weight of each block. The ratio \bar{K}/K changes only weakly as the asymmetry parameter ε is varied between 0 and $1/2$, and remains negative even when the sign of the spontaneous curvature is reversed. In addition, the saddle splay modulus, \bar{K} , is seen to have a contribution which is quadratic in the

spontaneous curvature. These features are in marked contrast to the phenomenological theories where K , \bar{K} , and R_0 are treated as independent parameters and to other « microscopic calculations » [9-11, 33] of these parameters. A more complete analysis of molecular origin of these phenomenological coefficients and their interrelationship will be presented in a future publication [34].

The phase diagram calculated using the free energy forms equations (22) and (23), predicts the morphological change in the emulsion phases as functions of ε and the volume fraction ratio, $W = \phi_C/\phi_A$, where ε is the asymmetry of the two block lengths and ϕ_C and ϕ_A are the volume fractions of the block copolymer and the A type homopolymer respectively. For $\varepsilon \neq 0$, the sphere is always the first emulsion phase to appear as W increases. Below W_3^* (cf. Eq. (28)), the radius is unchanged by adding more copolymer, if the entropy of mixing is neglected. This radius is determined by the surface tension between A and B, and the molecular weight of each block, which suggests a possible means for measuring the interfacial tension by using equation (10c).

In our calculation, we have completely neglected the possibility of micellization, since we always assume that the system forms domains of A and B homopolymer with a monolayer of copolymer at the interface. This monolayer can coexist with (a very small number of) isolated copolymer chains solubilized in the A and B domains, but we have neglected any additional equilibria with copolymer micelles within these domains. It is expected that when the diblock copolymer is very asymmetric, or if the volume fraction of one of the homopolymers is very low, such micelle formation will be important, and indeed could possibly preclude the emulsion phases [14]. Thus, our calculation is most appropriate when the molecular weights of the two blocks and the volume fractions of the two homopolymers, are comparable. That in these cases the formation of micelles can be neglected can be argued as follows: In the strongly segregated limit, the lowest free energy state for the pure diblock copolymers, is the lamellae phase up until $\varepsilon = 0.28$, according to a recent calculation by Semenov [15]. Below this value, the spherical and cylindrical mesophases both have higher free energy than the lamellar phase. Furthermore, Semenov shows that the spherical and cylindrical mesophases both have lower free energy than their respective single micelles. It follows then that these micellar phases must be a higher free energy state than the pure lamellar phase. Thus, for $\varepsilon < 0.28$, these higher free energy states can be safely neglected, since the lamellae phase is the last one to appear in our calculation. For $\varepsilon > 0.28$, the phase diagram predicted in this paper becomes doubtful, as micellization can no longer be ignored. Formation of micelles has also been discussed by Leibler [14], who obtained a different numerical value for ε by using an Alexander-de Gennes type argument for the stretching energy.

The present calculation has also neglected the effects of thermal fluctuations of the interfacial copolymer film as well as interactions between the droplets. These effects can modify the simple picture presented in this paper. The effects of film fluctuations and globular interactions have been treated in the context of microemulsions of short-chain surfactants [35]. A similar analysis can be used in the present case. The focus of this paper has been to derive the curvature elasticity description of the copolymer layer from a more fundamental description of the free energy of the film and to point out some important differences between the polymer system and the short surfactant systems. The model and calculations presented in this paper suffice to serve this end, and the important features that are primarily associated with the polymeric nature of the systems in study should persist, even if more rigorous approaches are used.

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