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Nonionic Diblock Copolymers as Surfactants between Immiscible Solvents

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ABSTRACT: A theoretical study is done to investigate nonionic diblock copolymers used as amphiphilic surfactants for a pair of otherwise immiscible solvents. It is assumed that the block junction points rest on the interfaces, with no chain adsorption, each chain staying in its preferred solvent. First the properties of a single flat interface saturated with polymer chains are obtained; then its curvature properties are calculated. We examine also the properties of a multilamellar arrangement, both in equilibrium with excess solvent and in the absence of either or both bulk solvent phases. The calculations are all done in mean field approximation for chains in at least moderately good solvent in semidilute solution. A phase diagram is obtained, under the constraint of multilamellar geometry.

I. Introduction

There exist a wide variety of amphiphilic surfactants (and combinations of surfactants) used to lower the effective surface tension at the interface between otherwise immiscible solvents.[1] There has been much recent interest in using nonionic diblock copolymers as surfactants, particularly for oil/water systems, where the two blocks strongly prefer different solvents.[2] In principle, these can lead to a variety of geometrical arrangements, depending on the properties of the three components.[3,4] In the current study, we will attempt to analyze such systems for a few simple cases; that is, we restrict ourselves to a simple lamellar geometry to obtain the characteristic equilibrium properties of the system, except to consider local slight curvature to determine the elasticity and curvature properties of the interface.

We consider first a single interface saturated by the chains. By "saturated" is meant the state for which the concentration of chains at the interface is such as to force the chains to stretch perpendicular to the interface and thus to generate a lateral pressure equal and opposite to the "bare" surface tension, γ_0, such that the effective surface tension, $\gamma = \gamma_0 - \pi$, vanishes. This is done by assuming first a flat interface; this restriction is then relaxed somewhat to allow slight, spherically symmetric curvature in order to obtain the equilibrium radius of curvature and the coefficient of elasticity.

In the next part, we consider a concentration of chains many times that needed to saturate one interface. We consider the formation of a multilamellar "middle-phase"[2,5] geometry; that is, between the two bulk solvent phases is formed a phase consisting of many alternating layers of the two solvents stabilized at their interfaces by the chains. The conditions for which this geometry is most likely are calculated by analyzing the spontaneous radius of curvature obtained earlier. It will be shown that to good approximation, these layers will have the same properties as the single saturated layer described in the first part; they will neither compress nor swell, assuming that there remains enough of each solvent to form a three-phase system. We will then consider the case for which one or both of the bulk solvent phases is exhausted, determining the equilibrium properties of the resulting two-phase and one-phase systems. Finally, these results will be summarized in a phase diagram for the three-component system.

II. Single Saturated Interface

1. Flat Interface. We consider a system consisting of uncharged homogeneous diblock copolymers A/B of arbitrary but uniform number of monomers n_A and n_B, and two immiscible solvents labeled a and b. We assume that the two solvents are sufficiently incompatible so that the density profile going from one bulk solvent to the other can be replaced to good approximation by a sharp dividing plane. It is assumed that a is a good, although not necessarily athermal, solvent for block A monomers, and likewise for B in b, and that a is a poor solvent for monomers B, and likewise for A in b. That is, we assume that both χ_{Aa} and $\chi_{Bb} < {}^1/_2$, but not necessarily zero (χ_{Ik} is the Flory interaction parameter[6] for block I in solvent k), and χ_{Ab} and $\chi_{Ba} > {}^1/_2$; there is no adsorption of chains at the interface.

We consider the case where to good approximation we can assume that the A chains rest entirely on the a side and likewise for B in b, and thus where the distribution of block junction points is sufficiently narrowly peaked at

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the solvent dividing plane such that we can constrain the junction points to lie on that plane to simplify the calculation. It will be shown at the end of this section that this limitation can be expressed roughly as a restrictive relation among Flory parameters. We restrict discussion to the semidilute regime,[7] for which the monomer concentration is sufficiently low so that the bare surface tension, γ_0, can be regarded as independent of Σ, the interfacial area per chain. That is, for $\phi \ll 1$, the van der Waals force between the two solvent phases is not affected by the presence of the chains. In this regime, the chains overlap, although the monomer concentration remains low. Since, for each block, one end is constrained to rest on the interfacial plane, the chains will stretch somewhat, perpendicular to the interface, to decrease the chain energy, resulting in a lateral pressure π which opposes γ_0.

We calculate the equilibrium properties in mean field theory for semidilute solutions, assuming long chains, in the spirit of Flory.[6,7] In the context of that theory, we have for the energy of block I in solvent i

$$\frac{F_{\mathrm{I,i}}}{T} = \frac{3}{2}\frac{L_\mathrm{I}^2}{n_\mathrm{I} l_\mathrm{I}^2} - N_{\mathrm{Ii}}(1 - \chi_{\mathrm{Ii}}) + \frac{1}{2}N_{\mathrm{Ii}}\phi_\mathrm{I} v_\mathrm{I} \qquad (1)$$

where $v_\mathrm{I} = 1 - 2\chi_\mathrm{I}$, L_I is the end-to-end distance of the I = A or B block and thus the width of that side of the interface, l_I^3 is the volume of an I monomer, and N_{Ii} is the ratio of the volumes of the I block and the i solvent. N_{Ii} and the polymer index n_I are thus related by $N_{\mathrm{Ii}} a_\mathrm{i}^3 = n_\mathrm{I} l_\mathrm{I}^3$, where a_i^3 is the volume of a molecule of solvent i. $\phi_\mathrm{I} = n_\mathrm{I} l_\mathrm{I}^3 (\Sigma L_\mathrm{I})^{-1}$ is the volume fraction of I monomers, where Σ is the surface area per chain at the interface. We assume that ϕ_A is constant up to a distance L_A from the interface beyond which $\phi_\mathrm{A} = 0$ and similarly for ϕ_B and L_B. For the purpose of calculating equilibrium properties, this seems to be a good approximation for long chains.[8] The temperature is in units of the Boltzmann constant, k_B.

The first term is due to the entropy loss resulting from chain stretching, assuming weak stretching, $L_\mathrm{I} \ll n_\mathrm{I} l_\mathrm{I}$.[15] The last two terms are the first two terms of an expansion for small ϕ_I of the entropy of mixing of polymer and solvent. Thus, summing over the two blocks, we have for the chain energy, F_c

$$F_\mathrm{c} = F_{\mathrm{A,a}} + F_{\mathrm{B,b}} \qquad (2)$$

Using the definitions given above, we obtain

$$\frac{F_{\mathrm{I,i}}}{T} = n f_\mathrm{I}\left[\frac{3}{2}\left(\frac{L_\mathrm{I}}{n_\mathrm{I} l_\mathrm{I}}\right)^2 - \left(\frac{l_\mathrm{I}}{a_\mathrm{i}}\right)^3 (1 - \chi_{\mathrm{Ii}}) + \frac{\eta_\mathrm{I}}{2}\frac{n_\mathrm{I} l_\mathrm{I}}{\Sigma L_\mathrm{I}}\right] \qquad (3)$$

where $n \equiv n_\mathrm{A} + n_\mathrm{B}$ is the polymer index of the entire chain, $f_\mathrm{I} \equiv n_\mathrm{I}/n$, and we define $\eta_\mathrm{I} \equiv v_\mathrm{I} l_\mathrm{I}^5 / a_\mathrm{i}^3$.

For a given Σ, which determines π (the lateral pressure), we can minimize the energy with respect to both L_A and L_B. Thus, setting $\partial F_\mathrm{c}/\partial L_\mathrm{A} = \partial F_\mathrm{c}/\partial L_\mathrm{B} = 0$, we obtain, for arbitrary Σ

$$F_\mathrm{c}(\Sigma)/nT = -C + (3/4)6^{1/3} Q_1 \Sigma^{-2/3} \qquad (4)$$

$$L_\mathrm{I}(\Sigma) = n_\mathrm{I} l_\mathrm{I}(\eta_\mathrm{I}/6)^{1/3}\Sigma^{-1/3} \qquad \phi_\mathrm{I}(\Sigma) = l_\mathrm{I}^2(\eta_\mathrm{I}/6)^{-1/3}\Sigma^{-2/3} \qquad \mathrm{I = A, B} \qquad (5)$$

with

$$C \equiv f_\mathrm{A}(l_\mathrm{A}/a_\mathrm{a})^3(1 - \chi_{\mathrm{Aa}}) + f_\mathrm{B}(l_\mathrm{B}/a_\mathrm{b})^3(1 - \chi_{\mathrm{Bb}})$$

$$Q_1 \equiv \sum_{\mathrm{I=A,B}} (f_\mathrm{I}\eta_\mathrm{I}^{2/3})$$

The lateral pressure generated by the chains, opposing the bare surface tension is $\pi = -(\partial F_\mathrm{c}/\partial \Sigma)$. To determine the saturation conditions, i.e., the surface area per chain at which $\gamma_0 = \pi$, we set $\gamma_0 = -(\partial F_\mathrm{c}/\partial\Sigma)$ to obtain

$$\Sigma_\mathrm{s} = (3/4)^{1/5}(Q_1 nT/\gamma_0)^{3/5} \qquad (6)$$

Thus, at saturation

$$L_\mathrm{I} = \frac{n_\mathrm{I} l_\mathrm{I}}{2}\left(\frac{3}{4}\right)^{-2/5}\eta_\mathrm{I}^{1/3}\left(\frac{Q_1 nT}{\gamma_0}\right)^{-1/5} \qquad \mathrm{I = A, B} \qquad (7)$$

$$\phi_\mathrm{I} = 2\left(\frac{3}{4}\right)^{1/5}\eta_\mathrm{I}^{-1/3} l_\mathrm{I}^2\left(\frac{Q_1 nT}{\gamma_0}\right)^{-2/5} \qquad \mathrm{I = A, B} \qquad (8)$$

For monomers and solvent molecules all of the same volume $\equiv a^3$ and for $v_\mathrm{A} = v_\mathrm{B} \equiv v$, we get the simpler expressions

$$\frac{\Sigma_\mathrm{s}}{a^2} = \left(\frac{3}{4}\right)^{1/5}\left(\frac{\gamma_0 a^2}{nT}\right)^{-3/5} v^{2/5}$$

$$\frac{L_\mathrm{A}}{n_\mathrm{A} a} = \frac{L_\mathrm{B}}{n_\mathrm{B} a} = \frac{1}{2}\left(\frac{3}{4}\right)^{-2/5}\left(\frac{\gamma_0 a^2}{nT}\right)^{1/5} v^{1/5} \qquad (9)$$

$$\phi_\mathrm{A} = \phi_\mathrm{B} = \left(\frac{6}{v}\right)^{1/3}\left(\frac{\Sigma}{a^2}\right)^{-2/3} = 2\left(\frac{3}{4}\right)^{1/5}\left(\frac{\gamma_0 a^2}{nT}\right)^{2/5} v^{-3/5}$$

Equations 6–8 represent the equilibrium properties of a saturated single interface. These results will be used later to determine the properties of a multilamellar phase, since the properties of the interfaces in such a system will be shown to be very nearly the same as for a single interface, when in equilibrium with excess solvent.

We can also calculate the effective surface tension which results when the surface chain density is less than that necessary to saturate the interface. Using eq 4, we obtain $\pi(\Sigma) = -(F_\mathrm{c}(\Sigma)/\partial\Sigma)$, and thus $\gamma(\Sigma) = \gamma_0 - \pi(\Sigma)$, in terms of Σ_s, the surface area per chain at saturation (eq 6)

$$\gamma(\Sigma)/\gamma_0 = 1 - (\Sigma/\Sigma_\mathrm{s})^{-5/3} \qquad (10)$$

This is valid for $\Sigma^* > \Sigma > \Sigma_\mathrm{s}$, where Σ^* is the surface area above which the chains are in the dilute regime, for which $\gamma = \gamma_0$; $\Sigma^* \simeq N^{6/5}a^2$.

At this point, it is important to discuss both the accuracy and domain of validity of the above calculation. First of all, it should be explained why mean field theory was chosen over a scaling law approach.[7] Alexander[12] has obtained scaling relationships (without numerical coefficients) for chains attached to a wall in athermal solvent, obtaining

$$L \sim (nT/\gamma_0)^{9/11} \qquad \phi \sim (nT/\gamma_0)^{-4/11}$$
$$\Sigma \sim (nT/\gamma_0)^{6/11}$$

Comparing these results to eq 6–8, we see that the relative errors in the saturation characteristics, ignoring numerical coefficients, are

$$\delta L \sim (nT/\gamma_0)^{-1/55} \qquad \delta\phi \sim (nT/\gamma_0)^{-2/55}$$
$$\delta\Sigma \sim (nT/\gamma_0)^{3/55}$$

where $\delta L = [L(\text{mean field}) - L(\text{scaling})]/L(\text{scaling})$ etc. Since these are fairly small corrections, and since obtaining numerical coefficients for systems with nonvanishing Flory parameters would be far more difficult with a scaling approach, it was decided to use the mean field approximation.

Both the mixing and stretching contribution to the free energy in eq 1 are approximations to the full mean field expressions,[6,15] being expansions for low ϕ_I and $L_\mathrm{I}/n_\mathrm{I} l_\mathrm{I}$, respectively. We can get an idea of the high-concentration limit on these approximations by considering a few specific cases. For example, for $\phi = {}^1/_2$, the entropy of mixing is underestimated by about 8%; for $\phi = {}^1/_4$, this error is about 1%. For the simple case described by eq 9, for $\phi = {}^1/_2$, $L/na = (v/6)^{1/2}$. For $\chi = 1$ (the worst case), this gives $L/na \simeq 0.3$, for which the stretching energy is underestimated by $\simeq$5%. For $\phi = {}^1/_4$, this error is of the order of 2%. Thus the simplification of the free energy expression is a very small source of error even for quite concentrated solutions.

We assumed γ_0, and thus the van der Waals force, to be independent of ϕ_A and ϕ_B; this becomes a poorer approximation as the solution concentration increases, particularly the larger the values of χ_{Aa} and χ_{Bb}, since they reflect differences in the dielectric constants of monomer and solvent. In principle, given the general form of $\gamma(\phi_A,\phi_B)$ and thus of $\gamma(L_A,L_B,\Sigma)$ we would have to redo the calculation to minimize the free energy, using the more general equations

$$\partial F/\partial L_A = \partial F/\partial L_B = \partial F/\partial \Sigma = 0 \qquad (11)$$

with $dF = dF_c + \gamma(L_A,L_B,\Sigma)\,d\Sigma$.

There is an additional surface effect which renders γ dependent on Σ. Due to the chemical bonds across the interface at the junction points of the blocks, the surface tension is reduced, possibly in a complicated way, as Σ decreases. If, however, this reduction were proportional to good approximation to the fraction of bonded sites at the interface, which would seem a reasonable first guess, then we would expect $\gamma' = \gamma[1 - (a^2/\Sigma)]$. For the simple case described by eq 9, for $\phi = {}^1/_2$ and $\chi = 1$, this is an error of $\simeq$15% in the surface tension; for $\phi = {}^1/_4$ it is about 5%.

We have also used the approximation that the A blocks stay completely on the a side, and similarly for B in b. To obtain a rough estimate of the number of monomers which cross the interface in either direction, using eq 1 and 2, we calculate the free energy increase of a chain due to a shift of the first e_A monomers of its A block into the b solvent and obtain

$$\Delta F(e_A)/T \simeq e_A(\chi_{Ab} - \chi_{Aa}) \qquad (12)$$

and for the symmetric case of e_B monomers into a

$$\Delta F(e_B)/T \simeq e_B(\chi_{Ba} - \chi_{Bb}) \qquad (13)$$

Thus, in order for the above assumption to be reasonable, roughly speaking, we must have $e_A \ll n_A$ and $e_B \ll n_B$ for thermal fluctuations $\Delta F \simeq T$; i.e., we have the restrictive conditions

$$n_A \gg (\chi_{Ab} - \chi_{Aa})^{-1} \quad \text{and} \quad n_B \gg (\chi_{Ba} - \chi_{Bb})^{-1} \qquad (14)$$

which are easily met.

Finally, to get an idea of the predicted values of ϕ, L, and Σ, we take the simple case described by eq 9. For pairs of immiscible liquids, $\gamma_0 a^2/k_BT$ is typically of order unity; for $n = 1000$ and $v = 0.6$ we have $L/na \simeq {}^1/_8$, $\phi \simeq {}^1/_6$, and $\Sigma/a^2 \simeq 50$.

2. Elasticity Properties of the Interface. Up to this point we have assumed a strictly planar interface; we would like to examine its elasticity properties as well. More specifically, we investigate its spontaneous radius of curvature and the coefficient of elasticity. We do so in the following manner: we use the same type of calculational method as for the flat interface above, except insofar as to allow the possibility of slight curvature of the interface. We assume for simplicity that the curvature is spherically symmetric, i.e., describable by one radius of curvature, R. This is sketched in Figure 1. By slight curvature we mean that the area per chain only varies slightly through the layer; equivalently, $R \gg L_A$ or L_B. Thus, we continue to assume that ϕ_A and ϕ_B remain uniform throughout each side of the interface. We assign, arbitrarily, A to the convex side and B to the concave side. The curvature properties, i.e., the spontaneous radius of curvature and the elasticity, are calculated in the manner of Helfrich for the case of lipid bilayers.[9]

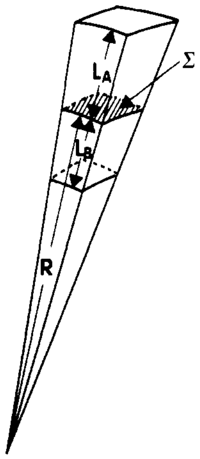

Figure 1. A spherically curved single interface of area equal to the average chain surface area at the interface.

Assuming constant density on each side, we obtain

$$\phi_A = \frac{n_A l_A}{\Sigma L_A}\left[1 + \frac{L_A}{R} + \frac{1}{3}\left(\frac{L_A}{R}\right)^2\right]^{-1}$$
$$\phi_B = \frac{n_B l_B}{\Sigma L_B}\left[1 - \frac{L_B}{R} + \frac{1}{3}\left(\frac{L_B}{R}\right)^2\right]^{-1} \qquad (15)$$

Substituting these values into eq 1 and 2, we continue as for a flat interface: we minimize F_c with respect to L_A and L_B and then set $\pi = \gamma_0$, always keeping terms up to second order in R^{-1}. From this we obtain the free energy per cm^2 of interface, F/cm^2, in the form of an expansion to second order in R^{-1}, which can be written in terms of the spontaneous curvature R_0^{-1} which minimizes F/cm^2, and the elastic constant K_{el} as

$$F/\text{cm}^2 \simeq F_0 + (K_{el}/2)(R^{-1} - R_0^{-1})^2 \qquad (16)$$

with

$$R_0 = \frac{1}{3}\left(\frac{3}{4}\right)^{-2/5} n \frac{Q_3}{Q_1^{1/5}Q_2}\left(\frac{\gamma_0}{nT}\right)^{1/5} \qquad (17)$$

$$\frac{K_{el}}{T} = \frac{4}{45}\left(\frac{3}{4}\right)^{1/5}\frac{Q_3}{Q_1^{7/5}}n^{8/5}\left(\frac{\gamma_0}{T}\right)^{7/5} \qquad (18)$$

and the layer widths

$$L_I = \frac{1}{2}\left(\frac{3}{4}\right)^{-2/5}\frac{v_I l_I^{8/3}}{a_i}Q_1^{-1/5}n_I\left(\frac{\gamma_0}{nT}\right)^{1/5} \qquad I = A, B \quad (19)$$

where

$$Q_k \equiv f_A^{\,k} v_A^{(k+1)/3} l_A^{2(4k+1)/3} a_a^{-k-1} + (-1)^{k+1} f_B^{\,k} v_B^{(k+1)/3} l_B^{2(4k+1)/3} a_b^{-k-1}$$

We can calculate the conditions for which the spontaneous curvature (eq 17) is zero: setting $R_0^{-1} = 0$, this gives $Q_2 = 0$, and thus

$$f_A/f_B = (v_B/v_A)^{1/2}(l_B/l_A)^3(a_a/a_b)^{3/2} \qquad (R_0^{-1} = 0) \quad (20)$$

The A monomer fraction for which the system will have zero spontaneous curvature is therefore

$$f_A = [1 + (v_A/v_B)^{1/2}(l_A/l_B)^3(a_b/a_a)^{3/2}]^{-1} \qquad (21)$$

To get a better sense of the size of R_0 for other values of f_A, we first express R_0 in terms of L_B, the size of the inner layer:

$$\frac{R_0}{L_B} = \frac{2}{3}\frac{Q_3}{Q_2}f_B^{-1}\frac{a_b}{v_B^{1/3}l_B^{8/3}} \tag{22}$$

We consider the simple case when $v_A = v_B$ and the solvents and monomers have all the same size; then

$$\frac{R_0}{L_B} = \frac{2}{3}\frac{f_A^3 + f_B^3}{(f_A - f_B)f_B} \tag{23}$$

which tends to infinity for $f_A = {}^1/_2$ and has a minimum of $R_0/L_B = 2$ when $f_A = {}^2/_3$, i.e., when $n_A = 2n_B$. In doing the calculation, we assumed $L_B \ll R_0$, which is no longer the case for chains as dissymmetric as those with $f_A = {}^2/_3$. Thus, for this simple case, we expect the derived value of R_0/L_B to have at best qualitative significance near $f_A = {}^2/_3$ (where R_0 is certainly underestimated). However, as f_A approaches ${}^1/_2$, R_0/L_B tends to infinity, and thus, for more symmetric chains, its derived value can be expected to have quantitative significance.

To get an idea of the size of K_{el}, we consider the same simple case as before, where $v_A = v_B \boxminus v$ and $l_A = l_B = a_a = a_b \equiv a$. Then

$$K_{el}/T = (1/45)(3/4)^{1/5}4(f_A^3 + f_B^3)v^{2/5}n^{8/5}(\gamma_0 a^2/T)^{7/5} \tag{24}$$

We substitute the following typical values: $a = 5 \times 10^{-8}$ cm, $\gamma_0 = 30$ ergs/cm^2, $T = 300$ K (in units of the Boltzmann constant), $\chi = 0.3$ ($v = 0.4$), and $f_A = f_B = {}^1/_2$. Then

$$K_{el}/T \simeq n^{8/5}/30$$

For $n = 1000$, $K_{el}/T \simeq 2000$.

de Gennes[15] has obtained a scaling relation for K_{el}, ignoring all prefactors, of the form

$$K_{el}/T \simeq n^{18/11}(\gamma_0 a^2/T)^{15/11}$$

Thus, the relative error in using mean field theory, ignoring coefficients, is $\delta K_{el} \simeq (\gamma_0 a/nT)^{2/55}$, a fairly small error.

III. Multiple Saturated Interfaces. A Multilamellar Middle Phase

We have worked out the properties of a single saturated interface; we now ask what happens if the relative concentration of copolymer chains is many times that needed to saturate one interface. We consider here the situation which obtains when the spontaneous curvature is zero or very low (eq 21). We can conceive of the system forming many alternating flat slices of the solvents between the two bulk solvent phases, the layers being stabilized by the copolymer chains[2] (Figure 2a). Assume for the moment that the copolymer concentration is sufficient to generate many layers, but not so high as to exhaust either or both of the bulk solvent reservoirs. A question then arises: What are the equilibrium widths of the alternating layers? More specifically: How is the excess solvent distributed? We can conceive of inserting slices of pure solvent between the opposing chain ends in either or both of the layer types a or b (Figure 2b). Its effect would be to vary the bare surface tension, since γ_0 is due to the van der Waals forces among the layers, which is a function of the layer widths D_a and D_b. In the Appendix we sketch an approximate calculation of $\gamma_0(D_a,D_b)$ similar to that of Huh,[2] the result of which (eq A17 and A18) can be expressed generally as

$$\gamma_0 = \gamma_\infty[1 - c(a^2/D^2)] \tag{25}$$

We define γ_∞ as the bare surface tension for infinitely wide layers; c is a constant of order unity depending on system parameters, independent of $D = D_a + D_b$. Thus, for swollen layers, i.e., for $D_a > 2L_A$ and $D_b > 2L_B$, the energy of the system is proportional to the chain energy obtained for a single saturated interface (which is a function of γ_0) to very good approximation, since the number of chains is constant. From eq 4 and 6 we see that $F_c \propto \gamma_0^{2/5}$ + const, and thus $F - F_\infty \simeq -(a^2/D^2)$ (leaving out the coefficient) since $a \ll D$. Thus, for $D_a \geq 2L_A$ and $D_b \geq 2L_B$, the free energy is minimized by minimizing D, i.e., by setting $D_a = 2L_A$ and $D_b = 2L_B$. In other words, the system prefers to have no pure solvent slices in the multilamellar phase.

We now know that the system will not swell; we must also consider the possibility of compression of the layers. This can be done by reworking the single-interface calculation (eq 1–8), but allowing for the width dependence of $\gamma_0(L_A,L_B)$. To very good approximation, the effect of that (more complicated) calculation is to substitute $\gamma_0(L_A,L_B)$ for γ_0 in the final results (eq 6–8), which is a negligible correction for the purposes of calculating the equilibrium values of L_A, L_B, ϕ_A, and ϕ_B. Hence, to very good approximation, we can assume that the layers are neither compressed nor swollen and thus that the equilibrium state of the multilayer phase corresponds to alternating layers of widths $D_a = 2L_A$ and $D_b = 2L_B$, where L_A, L_B, ϕ_A, and ϕ_B have the form given for a single interface (eq 6–8), given that there are sufficient quantities of both solvents to generate a three-phase system. Thus we can now calculate the volume fractions of the two bulk solvent phases and the multilayer phase, which indicates the solubilizing power of the copolymer chains, given the relative amounts of the three components in the system. We shall not examine the variation of the system equilibrium properties with temperature since, in addition to the explicit dependence on T in the results obtained so far, we must consider the temperature dependence of the parameters (γ_0, χ_{Aa}, χ_{Bb}, a_a, a_b, l_A, and l_B) as well. This may be quite

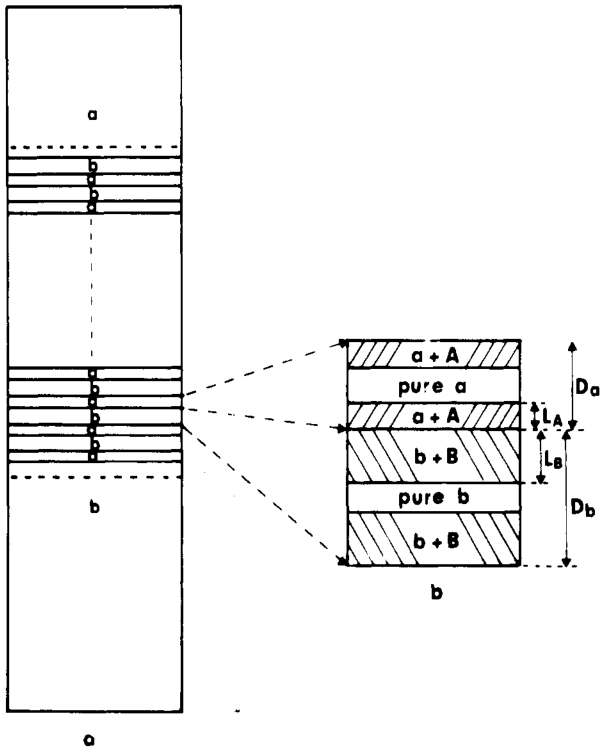

Figure 2. (a) An overview of the three-phase system (the middle phase lamellae are not drawn to scale). (b) View of the structure of two adjacent layers allowing the possibility of sandwiched slices of pure solvent.

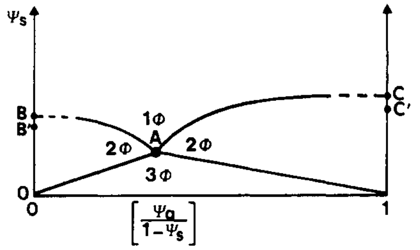

Figure 3. Phase diagram assuming lamellar middle-phase geometry. The points A, B′, and C′ have the compositions given by eq 29–31, 48 and 49, and 50 and 51 in the text, respectively. The positions of B′ and C′ depend on γ_A and γ_B; their positions on this diagram have no quantitative significance. It is assumed that $\psi_s \ll 1$ everywhere on this diagram. The dashed lines signify that we leave the semidilute regime, and thus the line can have at best qualitative significance there.

complicated and thus not possible to write in a general form valid for a wide range of components.

1. Three-Phase System. Let ψ_i be the total volume fraction of component i (i = a, b, s: solvent a, solvent b, and copolymer surfactant, respectively). Let ψ_i^M be the volume fraction of component i in the middle phase. Then

$$\psi_a^M = \frac{L_A(1-\phi_A)}{L_A+L_B} = \frac{f_A(1-\phi_A)}{f_A + f_B(l_B/l_A)^3(\phi_A/\phi_B)} \qquad (26)$$

$$\psi_b^M = \frac{L_B(1-\phi_B)}{L_A+L_B} = \frac{f_B(1-\phi_B)}{f_A(l_A/l_B)^3(\phi_B/\phi_A) + f_B} \qquad (27)$$

$$\psi_s^M = \frac{L_A\phi_A + L_B\phi_B}{L_A+L_B} = \frac{l_A^3 f_A + l_B^3 f_B}{f_A l_A^3 \phi_A^{-1} + f_B l_B^3 \phi_B^{-1}} \qquad (28)$$

Using the values obtained in eq 8 for ϕ_A and ϕ_B, we obtain

$$\psi_s^M = 2\left(\frac{3}{4}\right)^{1/5}\left(\frac{\gamma_0}{Q_1 nT}\right)^{2/5} \frac{\sum\limits_I (f_I l_I)^3}{\sum\limits_I (f_I l_I \eta_I^{1/3})} \qquad (29)$$

$$\psi_a^M = (1-\phi_A)\frac{f_A l_A \eta_A^{1/3}}{\sum\limits_I (f_I l_I \eta_I^{1/3})} \qquad (30)$$

$$\psi_b^M = (1-\phi_B)\frac{f_B l_B \eta_B^{1/3}}{\sum\limits_I (f_I l_I \eta_I^{1/3})} \qquad (31)$$

Clearly, for a given value of $\psi_s < \psi_s^M$, we can have a three-phase region only when both

$$\psi_a > \psi_a^M(\psi_s/\psi_s^M) \qquad \psi_b > \psi_b^M(\psi_s/\psi_s^M)$$

To good approximation $\psi_b = 1 - \psi_a$. Thus, we have three phases for

$$1 - \frac{\psi_s}{\psi_s^M}\psi_b^M > \psi_a > \frac{\psi_s}{\psi_s^M}\psi_a^M \quad \text{with} \quad \frac{\psi_s}{\psi_s^M} < 1 \qquad (32)$$

We obtain the conditions for which both bulk solvent phases are exhausted when the above conditions coincide, i.e., at the point

$$\psi_s = \psi_s^M \qquad \psi_a = \psi_a^M \qquad \psi_b = \psi_b^M \qquad (33)$$

This is summarized in the bottom of the phase diagram given in Figure 3.

2. Two- and One-Phase Systems. The question then arises: If we are at that boundary, having exhausted one (or both) of the bulk solvent phases, what happens if we increase the amount of copolymer? Assume for the moment that we have exhausted the a bulk solvent phase, but that there remains some bulk b solvent (i.e., along the OA line of Figure 3.) In adding chains, the b layers in the multilayer phase can still adjust L_B so as to minimize the energy; equivalently, ϕ_B is still variable. However, ϕ_A, and thus L_A, clearly can no longer be varied independently of Σ. Thus the single-interface calculation of section II.1 can no longer be applied; it must be done differently to take this into account, for the two cases depending on which solvent remains in bulk phase. In addition, we have to determine what happens when only the multilayer phase remains, in which case neither ϕ_A nor ϕ_B, and thus neither L_A nor L_B, is independently variable. We do this assuming that although we continue to increase the copolymer concentration in the layers, it can still be described as semidilute.

i. Properties of Middle-Phase Layers in Equilibrium with Only One Bulk Solvent Phase. Assume first that the bulk a phase has been exhausted. In this case, ϕ_A is determined completely from ψ_s and ψ_a and can thus be treated as a constant. Since $L_A = n_A l_A^3/(\phi_A \Sigma)$, L_A and Σ are no longer independent. However, L_B remains variable. Thus we minimize the interfacial free energy, eq 1 and 2, with respect to L_B as before, substitute $L_A(\Sigma)$, and set $\pi = \gamma_0$. This gives the saturation condition, i.e., an equation for Σ_s which can be solved reiteratively:

$$\Sigma_s = (3/4)^{1/5}[\sum_I (f_I \eta_I^{2/3} \xi_I^2)]^{3/5} (\gamma_0/nT)^{-3/5} \qquad (34)$$

where we define

$$\xi_I \equiv 6^{1/3} \eta_I^{-1/3} l_I^2 \phi_I^{-1} \Sigma_s^{-2/3}$$

Clearly, at the three-phase/two-phase boundary, $\xi_A = 1$ (eq 5); as copolymer is added, ξ_A decreases. $\xi_B \equiv 1$ for this case of excess bulk b solvent. The parameters ϕ_B and L_B have the same form as in eq 5, substituting the expression for Σ_s from eq 34. Also, we can write

$$\phi_B/\phi_A = (\xi_A/\xi_B)(\eta_B/\eta_A)^{-1/3}(l_B/l_A)^2 \qquad (35)$$

For the other case, when the bulk b phase is exhausted, we obtain the same formula for Σ_s (eq 34), using the definitions of ξ_I given above. However, here $\xi_A \equiv 1$; $\xi_B = 1$ only at the two-phase/three-phase boundary (eq 5), and it decreases as copolymer is added. Equation 35 holds in this case as well, where now ϕ_A (and L_A) have the same form as in eq 5, again using eq 34 for Σ_s.

ii. Properties of Middle-Phase Layers When Both Bulk Phases Exhausted. In this case, both ϕ_A and ϕ_B are determined, and thus neither L_A nor L_B is variable. Again, substituting into eq 1 and 2 and setting $\pi = \gamma_0$, we obtain the saturation condition

$$\Sigma_s = 3^{1/3}(\gamma_0/nT)^{-1/3}[\sum_I (f_I l_I^4/\phi_I^2)]^{1/3} \qquad (36)$$

$$L_I = (n_I l_I^3/\phi_I)\Sigma_s \qquad (37)$$

Thus, once within the one-phase region, the qualities of the solvents no longer have any effect, although the positions of the one-phase/two-phase dividing lines do depend on them.

iii. Two-Phase Regions of the Phase Diagram. With the two-phase interfacial information obtained in section i above, we can determine the boundaries and characteristics of the semidilute two-phase regions. To obtain the characteristics of the multilayer phase, we substitute the results of section III.2.i into eq 26–28. This gives

$$\psi_s^M = 2\left(\frac{3}{4}\right)^{1/5}\left(\frac{\gamma_0}{nT}\right)^{2/5} \sum_I (f_I \eta_I^{2/3} \xi_I^2)^{-2/5} \frac{\sum\limits_I (f_I l_I^3)}{\sum\limits_I (f_I l_I \eta_I^{1/3} \xi_I)} \qquad (38)$$

$$\psi_j^M = (1 - \phi_J)\frac{f_J l_J \eta_J^{1/3} \xi_J}{\sum_I (f_I l_I \eta_I^{1/3} \xi_I)} \qquad (39)$$

$$(j, J) = (a, A) \text{ or } (b, B)$$

where for the case of excess a solvent, $\xi_A = 1$ and $\xi_B \leq 1$; for the case of excess b solvent, $\xi_B = 1$ and $\xi_A \leq 1$. For the limiting case of $\xi_B = 1$ and $\xi_A \ll 1$ (middle phase plus bulk b), still assuming that the layers remain semidilute, we have

$$\psi_s^M(\xi_A \ll 1) \simeq 2\left(\frac{3}{4}\right)^{1/5}\left(\frac{\gamma_0}{nT}\right)^{2/5} f_B^{-7/5}\eta_B^{-3/5} l_B^{-1}\sum_I (f_I l_I^3) \qquad (40)$$

For the opposite case of $\xi_A = 1$, $\xi_B \ll 1$ (middle phase plus bulk a), we have

$$\psi_s^M(\xi_B \ll 1) \simeq 2\left(\frac{3}{4}\right)^{1/5}\left(\frac{\gamma_0}{nT}\right)^{2/5} f_A^{-7/5}\eta_A^{-3/5} l_A^{-1}\sum_I (f_I l_I^3) \qquad (41)$$

We obtain the condition for the disappearance of the second (pure) phase by setting $\psi_i = \psi_i^M$, i = a, b, s, using the expressions given in eq 38 and 39. For the case of excess bulk a, the line separating the two-phase and one-phase regions is then generated by allowing ξ_B to vary with $\xi_B \leq 1$ and $\xi_A = 1$; for the case of excess b, ξ_A is varied with $\xi_A \leq 1$ and $\xi_B = 1$, as long as the layers remain semidilute.

In the above calculations of the two-phase/one-phase dividing lines, we have assumed that the polymer solution layers remain semidilute. Thus we cannot extend these lines to the edges of the phase diagram (toward points B and C in Figure 3) since near the edges one of the layer types becomes concentrated in polymer. (This corresponds to letting ξ_A or $\xi_B \to 0$ in eq 40 and 41.) However, we can calculate the *end points* of those two lines (at the edge of the phase diagram), at which the concentration of one of the solvents is zero. In order to do this, we must calculate first the characteristics of an interface consisting of a semidilute solution of one block of the copolymer on one side and a melt of the other block on the other side.

iv. Melt/Semidilute Interface Properties. Let the I side be the melt, i.e., $\phi_A = 1$; there is no i solvent. The J side is in semidilute solution, where (I, J) = (A, B) or (B, A). Now, for the melt, the chains act as if they were ideal;[7] the only contribution to their energy is from the stretching term. Thus, we have for the chain energy

$$\frac{F_c}{T} = \frac{3}{2}\frac{L_I^2}{n_I l_I^2} + n_J\left[\frac{3}{2}\left(\frac{L_J}{n_J l_J}\right)^2 - \left(\frac{l_J}{a_j}\right)^3 (1 - \chi_{Jj}) + \frac{\eta_J}{2}\frac{n_J l_J}{\Sigma L_J}\right] \qquad (42)$$

Assume for the moment a two-phase system, i.e., that there is enough j solvent available so that L_J is independent of Σ, and thus L_J can be varied so as to minimize the free energy. Doing so, we obtain

$$\frac{F_c}{nT} = \frac{3}{2}\frac{f_I l_I^4}{\Sigma^2} - f_J\left(\frac{L_J}{a_j}\right)^3 (1 - \chi_{Jj}) + \frac{3}{4}6^{1/3} f_J \eta_J^{2/3}\Sigma^{-2/3} \qquad (43)$$

We will drop the first term, since it is of order $(\Sigma/a^2)^{4/3}$, smaller than the last term. Thus we see that the polymer block in the melt contributes only negligibly to the chain energy. In the previous calculations we assumed that the effect of very low concentrations of polymer on the bare surface tension was very small; $\gamma(\phi_A,\phi_B)$ was approximated by its value for pure solvents a and b. In this case, however, with $\phi = 1$ on one side of the interface, we can no longer make that assumption, and thus we denote the (possibly different) bare surface tension by γ_I. Setting $\pi = \gamma_I$, we obtain

$$\Sigma_s = \left(\frac{3}{4}\right)^{1/5} f_J^{3/5} l_J^2 \left(\frac{v_j}{a_j^3}\right)^{2/5}\left(\frac{\gamma_I}{nT}\right)^{-3/5} \qquad (44)$$

$$\frac{L_I}{n_I l_I} = \left(\frac{3}{4}\right)^{-1/5} f_J^{3/5}\left(\frac{l_I}{l_J}\right)^2\left(\frac{v_J}{a_j^3}\right)^{-2/5}\left(\frac{\gamma_I}{nT}\right)^{3/5} \qquad (45)$$

$$\frac{L_J}{n_J l_J} = \frac{1}{2}\left(\frac{3}{4}\right)^{-2/5} f_J^{-1/5} l_J \left(\frac{v_J}{a_j^3}\right)^{1/5}\left(\frac{\gamma_I}{nT}\right)^{1/5} \qquad (46)$$

$$\phi_J = 2\left(\frac{3}{4}\right)^{1/5} f_J^{-2/5} l_J^{-1}\left(\frac{v_J}{a_j^3}\right)^{-3/5}\left(\frac{\gamma_I}{nT}\right)^{2/5} \qquad (47)$$

For the case of a melt of A blocks, we set (I, J) = (A, B) and substitute this expression for $\phi_J = \phi_B$ and $\phi_A = 1$ into eq 27 and 28 to obtain

$$\psi_s^M = 1 - \psi_b^M \simeq 2\left(\frac{3}{4}\right)^{1/5}\frac{f_A l_A^3 + f_B l_B^3}{f_B^{7/5} l_B^4}\left(\frac{v_B}{a_b^3}\right)^{-3/5}\left(\frac{\gamma_A}{nT}\right)^{2/5} \qquad (48)$$

At the end of the two-phase (excess b solvent)/one-phase dividing line

$$\psi_s = 1 - \psi_b = \psi_s^M \qquad (49)$$

using the expression for ψ_s^M in eq 48.

For the case of a melt of B blocks we now set (I, J) = (B, A) and substitute eq 47 and $\phi_B = 1$ into eq 26 and 28 to obtain

$$\psi_s^M = 1 - \psi_a^M \simeq 2\left(\frac{3}{4}\right)^{1/5}\frac{f_A l_A^3 + f_B l_B^3}{f_A^{7/5} l_A^4}\left(\frac{v_A}{a_a^3}\right)^{-3/5}\left(\frac{\gamma_B}{nT}\right)^{2/5} \qquad (50)$$

Similarly, at the end of the two-phase (excess a solvent)/one-phase line

$$\psi_s = 1 - \psi_a = \psi_s^M \qquad (51)$$

using the expression for ψ_s^M in eq 50.

The results of the two- and one-phase system calculations are summarized in the phase diagram (Figure 3.)

For the sake of completeness, we consider one last case, when both blocks are in the melt, i.e., when there is no solvent of either type. Then, since $\phi_A = \phi_B = 1$, we have

$$F_c/nT = (3/2)(f_A l_A^4 + f_B l_B^4)\Sigma^{-2} \qquad (52)$$

Setting $\pi = \gamma$, we obtain

$$\Sigma = 3^{1/3}[\sum_I (f_I l_I^4)]^{1/3}(\gamma/nT)^{-1/3} \qquad (53)$$

$$L_I = 3^{-1/3} l_I^3 [\sum_I (f_I l_I^4)]^{-1/3}(\gamma/T)^{1/3} n_I^{2/3} \qquad (54)$$

This $n^{2/3}$ dependence is very close to that of Helfand,[16] obtained by a considerably more sophisticated approach. He obtains $L \simeq n^{9/14}$ for large n; this gives a relative error of $\delta L \simeq n^{1/42}$.

IV. Discussion

It should be stressed that the results obtained from this calculation are valid only subject to the geometrical constraint of planar interfaces. Thus, "equilibrium properties" of the system are obtained always under the assumption that there exists no other geometrical arrangement of chains for which the chains would have a lower chemical potential. Now, a lamellar arrangement is not uncommon in nature, but it is certainly not the only possibility; there are many other possible geometries involving a variety of interfacial curvature characteristics. It would seem reasonable to assume that the conditions for which a simple interface has a very large spontaneous radius of curvature (eq 21) would be the conditions for which a multilamellar phase is most likely to result and thus to which the results of this study would be most likely to apply. However, it is clear that calculations should be attempted for other experimentally common geometries. If, eventually, we wish to compare the chain *energies*, we must be more careful. Since, in general, the discrepancy between mean field and scaling law results is much greater in determining chemical potentials than equilibrium distances, it will be necessary to use a more sophisticated approach.

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Appendix. van der Waals Forces and Resulting Bare Surface Tension of the Multilayer Phase

The system consists of a fixed, very large number of alternating layers of solvents a and b, of widths D_a and D_b, respectively, stabilized by the block copolymers at the interfaces (see Figure 2). We calculate the van der Waals energy of the multilayer system as a function of D_a and D_b, relative to the state which results from the two-step process of taking each layer to infinite separation and then reassembling the layers of each of the two types separately to form a homogeneous block of each of the two solvents. This state clearly does not depend on D_a or D_b and thus can be used as a reference.

We will assume that the interfaces are sharp (the solvents are strictly incompatible) and planar and that the copolymer is present in sufficiently low concentration so as not to affect appreciably the van der Waals forces among layers. We perform the calculation in the following approximation.[11] The general form for the energy between pairs of layers is obtained (relative to infinite separation), and the total energy is approximated by the sum of all those pair energies. From this energy is subtracted the energy of forming one homogeneous block of each type from the layers at infinite separation, using the same approximation of pairwise summation.

Let m be the number of layers a = number of layers b; we assume a very large number. We define $D = D_a + D_b$. Also, we set

$$g_a \equiv D_a/D \qquad g_b \equiv D_b/D$$

The form for the energy between two layers i and j (i = a or b, j = a or b) separated by a distance d (relative to infinite separation), ignoring retardation effects, is[13]

$$E(\mathrm{i,j}) = \frac{-A_{\mathrm{ij}}}{12\pi}\left(\frac{1}{d^2} + \frac{1}{(d + D_{\mathrm{i}} + D_{\mathrm{j}})^2} - \frac{1}{(d + D_{\mathrm{i}})^2} - \frac{1}{(d + D_{\mathrm{j}})^2}\right) \tag{A1}$$

This is valid assuming $d \gg a$, the molecular size, i.e., for all layer pairs except nearest neighbors. A_{ij} is the Hamaker constant between materials of which layers i and j are composed. This constant is affected by the intervening medium; however, we will assume for the purposes of calculation that it is only a function of i and j; i.e., we approximate that a change in the number of intervening layers affects it only slightly. We obtain, for the interaction of a given i layer with all other layers of the same type i (i, j = a, b or b, a)

$$E_{\mathrm{ii}} = \frac{-2A_{\mathrm{ii}}}{12\pi}\sum_{k=0}^{\infty}\left[\frac{1}{(D_{\mathrm{j}} + kD)^2} + \frac{1}{[D_{\mathrm{i}} + (k+1)D]^2} - \frac{2}{[(k+1)D]^2}\right] \tag{A2}$$

where, to very good approximation for large m, we have let the sum go to infinity. For the sum of the interactions of a layer of type i with all those of type j, i ≠ j, excluding nearest-neighbor interactions, we obtain

$$E_{\mathrm{ab}} = E_{\mathrm{ba}} = \frac{-2A_{\mathrm{ab}}}{12\pi}\sum_{k=1}^{\infty}\left[\frac{1}{(kD)^2} + \frac{1}{[(k+1)D]^2} - \frac{1}{(D_a + kD)^2} - \frac{1}{(D_b + kD)^2}\right] \tag{A3}$$

We call E_N the nearest-neighbor interaction energy (to be calculated later) between a layer a and an adjoining layer b. Now, since there are m layers of each type, we have for the total energy relative to infinite separation

$$E = (m/2)(E_{\mathrm{aa}} + E_{\mathrm{bb}} + E_{\mathrm{ab}} + E_{\mathrm{ba}}) + 2mE_{\mathrm{N}} \tag{A4}$$

We ignore the energy of interaction of the end bulk solvent layers with the multilayer phase, since it has the same order of magnitude as E_{ij} but lacks the coefficient m. The factor $^1/_2$ in the first term corrects for double counting of pair interactions.

To calculate $E' \equiv E_{\mathrm{aa}} + E_{\mathrm{bb}} + E_{\mathrm{ab}} + E_{\mathrm{ba}}$, we use eq A2 and A3 to obtain, after some algebra

$$E' = -\frac{1}{6\pi D^2}\left(-\alpha\tilde{A} + \frac{A_{\mathrm{aa}}}{g_b{}^2} + \frac{A_{\mathrm{bb}}}{g_a{}^2} - 2A_{\mathrm{ab}}\right) \tag{A5}$$

with

$$\alpha \equiv -\pi^2[\csc^2(\pi g_a) - \tfrac{1}{3}] + 1/g_a{}^2 + 1/g_b{}^2$$

$$A \equiv A_{\mathrm{aa}} + A_{\mathrm{bb}} - 2A_{\mathrm{ab}}$$

We used a sum formula for Riemann ζ functions[14]

$$\pi^2\csc^2(\pi q) = \sum_{k=-\infty}^{\infty}(q-k)^{-2} = \zeta(2,q) + \zeta(2, 1-q) \qquad 0 < q < 1 \tag{A6}$$

with $\zeta(z,q) = \sum_{k=0}^{\infty}(q+k)^{-z}$. α has even symmetry around $g_a = g_b = {}^1/_2$ and is a slowly varying function with a maximum of $\alpha \sim 1.3$ at $g_a = {}^1/_2$ and approaches a minimum of $\alpha = 1$ as $g_a \to 0$ or $g_a \to 1$.

To calculate E_N, we sketch here a calculation similar to that of Mahanty and Ninham,[12] to which the reader is referred, who calculate the energy of two juxtaposed semiinfinite slabs, using an integral approximation to pairwise summation between molecules. We obtain for the energy per unit area (changing the integration limits in their calculation)

$$E_{\mathrm{N}} = (-A_{\mathrm{ab}}/\pi^2)\int_0^{D_a}\mathrm{d}z\int_0^{D_b}\mathrm{d}z'\int_0^{\infty}2\pi\rho\;\mathrm{d}\rho\;F_{12}(R)/R^6 \tag{A7}$$

with

$$R = [\rho^2 + (z + z')^2]^{1/2}$$

and

$$F_{12}(R) = (1/3)\prod_{j=1}^{2}[\mathrm{erf}\,(R/a_j) - (2R/\pi^{1/2}a_j)\exp(-R^2/a_j^2)](2/3) \times \prod_{j=1}^{2}[\mathrm{erf}\,(R/a_j) - (2/\pi^{1/2})(R/a_j + R^3/a_j^3)\exp(-R^2/a_j^2)] \tag{A8}$$

where a_1 and a_2 are the sizes of the molecules on the two sides a and b, respectively. For $R \gg a_1,a_2$, $F_{12}(R) \rightarrow 1$; as $R \rightarrow 0$, $F_{12}(R) \rightarrow (8/9\pi)(R^2/a_1a_2)^3$. We can rewrite the energy as

$$E_N = -\frac{A_{ab}}{\pi^2}\left[\int_0^\infty dz \int_0^\infty dz' \int_0^\infty 2\pi\rho\, d\rho\, \frac{F_{12}(R)}{R^6} - \int_{D_a}^\infty dz \int_{D_b}^\infty dz' \int_0^\infty 2\pi\rho\, d\rho\, R^{-6}\right] \tag{A9}$$

where we have replaced $F(R)$ by unity in the second term. The first term is the energy of two juxtaposed semiinfinite slabs. After some work, this gives

$$E_N = \frac{-A_{ab}}{\pi}\left[\int_0^\infty dz\, \frac{F_{12}(z)}{z^3}\right] + \frac{A_{ab}}{12\pi}D^{-2} \tag{A10}$$

The integral can be expressed as

$$\int_0^\infty dz\, \frac{F_{12}(z)}{z^3} = k\frac{(\pi - 1)}{3\pi}\,\frac{1}{a^2} \tag{A11}$$

where a is the smaller of a_1 and a_2, and $1 < k < \pi/(\pi - 1)$, depending on a_1 and a_2: $k = 1$ for $a_1 = a_2$ and $k = \pi/(\pi - 1)$ for $a_1 \ll a_2$ or $a_2 \ll a_1$. Thus

$$E_N = [-k(\pi - 1)/3\pi^2a^2 + 1/12\pi D^2]A_{ab} \tag{A12}$$

Substituting eq A5 and A12 in eq A4, we obtain the energy relative to infinite separation of the layers

$$E = (m/2)E' + 2mE_N = m\left[\frac{-1}{12\pi D^2}\left(-\alpha\tilde{A} + \frac{A_{aa}}{g_b^2} + \frac{A_{bb}}{g_a^2}\right) - \frac{A_{ab}}{a^2}\,\frac{2k(\pi - 1)}{3\pi^2}\right] \tag{A13}$$

We need now calculate the energy of formation of homogeneous blocks of each of the two components, as described earlier; call them E_a and E_b. For component a, if $E_N(x,x')$ is the energy with respect to infinite separation between adjoining layers of widths x and x', then to good approximation

$$E_a = \sum_{k=1}^{m} E_N(D_a,kD_a) = m\left[\left(\frac{-A_{aa}}{\pi}\int_0^\infty dz\, \frac{F_{11}(z)}{z^3}\right) + \frac{1}{m}\,\frac{A_{aa}}{12\pi}\sum_{k=1}^{m}\frac{1}{(D_a + kD_a)^2}\right] \tag{A14}$$

where we have used eq A10, replacing A_{ab} and F_{12} with A_{aa} and F_{11}, since these layers are made of the same material. With eq A11 we obtain

$$E_a = m(-A_{aa}/a_1^2)[(\pi - 1)/3\pi^2] \tag{A15}$$

neglecting the $1/m$ term. In the same way, we obtain for the b layers

$$E_b = m(-A_{bb}/a_2^2)[(\pi - 1)/3\pi^2] \tag{A16}$$

Thus we obtain for the total surface energy of the multilayer system, combining eq A13, A15, and A16

$$E_s = [(m/2)E' + 2mE_N - E_a - E_b] = m\left\{(A_{aa} + A_{bb}\eta^{-2} - 2k'A_{ab})\left(\frac{\pi - 1}{3\pi^2a^2}\right) - \left(-\alpha A + \frac{A_{aa}}{g_b^2} + \frac{A_{bb}}{g_a^2}\right)\frac{1}{12\pi D^2}\right\} \tag{A17}$$

where $\eta \equiv a_2/a_1$, $a \equiv a_1$, $k' = k$ for $\eta > 1$, and $k' = k/\eta^2$ for $\eta < 1$ (see eq A12). Now, E_s/m is the surface energy per layer per unit area, which is γ_0, the bare surface tension. Calling γ_∞ the surface tension for infinitely wide blocks, we obtain

$$\gamma_0 = \gamma_\infty - \frac{1}{12\pi}\left(\frac{A_{aa}}{D_b^2} + \frac{A_{bb}}{D_a^2} - \alpha\frac{\tilde{A}}{D^2}\right) \tag{A18}$$

Now, for most pairs of liquids, $\tilde{A} = A_{aa} + A_{bb} - 2A_{ab} \ll A_{aa}$ or A_{bb}. Thus $\alpha(\tilde{A}/D^2) \ll A_{aa}/D_b^2 + A_{bb}/D_a^2$, and therefore γ_0 decreases with decreasing D_a or D_b. Thus, the energy due solely to van der Waals forces has no minimum and diminishes with diminishing width of either layer type.

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