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The effect of adsorbed polymer on the elastic moduli of surfactant bilayers

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Abstract. — We study theoretically the effect of adsorbed homopolymer on surfactant bilayers, restricting ourselves to homogeneous equilibrium adsorption of polymer on both sides of the bilayer, with no penetration. We formulate the energy of adsorption per unit area as a Taylor series in curvature for both spherical and cylindrical surfaces. In the limit of weak adsorption analytic expressions for the polymeric contribution to the mean and Gaussian elastic moduli of the bilayer are derived, using both a mean-field and a scaling functional approach. For stronger adsorption numerical calculations have been made, and in the limit of very strong adsorption, asymptotic functional forms for the elastic moduli found. In all cases the presence of the polymer leads to a decrease in the mean curvature rigidity K and an increase in the Gaussian rigidity \bar{K} . At the mean-field level these contributions are always small compared to the thermal energy $k_B T$. However the scaling theory predicts qualitatively similar, but quantitatively larger effects, thus the presence of adsorbed polymer can strongly influence the elasticity of surfactant bilayers.

1. Introduction.

The physics of fluid membranes formed by reversible self-assembly of surfactant molecules is of interest both in the biological realm (cell membranes, vesicles) and in the study of surfactant systems. The latter often form dilute smectic phases in which the local structural unit is a bilayer or monolayer (depending on whether one or two solvents are present). In both cases it is interesting to ask what happens when long flexible polymers are added to the system. Clearly there are many possibilities, and fundamental theoretical and experimental studies remain at an early stage of development. Industrially, mixed systems of this kind are used in many products (paints, lubricants, drug delivery, etc.) often exploiting the special rheological properties of these complex fluids.

Arguably the most basic and important parameters of a bilayer are the mean and Gaussian elastic moduli (In the case of a monolayer, a third parameter, the spontaneous curvature is needed as well.) Indeed, there has been much progress made in studying the phase behaviour and other properties in surfactant systems using the continuum elastic description of fluid

films [1-12]. In this approach, the free energy of a bilayer is written as an harmonic expansion in local curvatures, which should be valid when the principle radii of curvature are much larger than the bilayer thickness or, if longer range forces are present, an effective interaction range (such as the Debye length in charged systems). In this paper we consider the effect on the elastic moduli of a surfactant bilayer upon addition of soluble, adsorbing polymer to the external solvent, preliminary results were given in [13]. We anticipate that the harmonic curvature expansion still applies for radii of curvature large enough compared to the (larger of the) adsorbed layer thickness and the correlation length of the bulk polymer solution. (The latter is the usual screening-length for polymer-mediated interactions). At shorter length-scales one must instead consider directly the nonlocal effective interaction between pieces of bilayer; for simplicity we avoid this regime in the present study.

Our investigation of the polymeric effect on the elastic moduli is motivated by the previous work of Hone and Hong Ji [14] and de Gennes [15]. Hone *et al.* considered reversible polymer adsorption on curved surfaces, calculating the energy of adsorption as an expansion in curvature to first order; their results are thus applicable to a surfactant monolayer (a dividing surface between oil and water), and describe the effect on the spontaneous curvature due to adsorbed polymer in one phase. More recently de Gennes [15] considered the shift in the elastic moduli of a surfactant bilayer upon addition of strongly adsorbing polymer to the external phase. His approach correctly determines the functional form for the polymeric contributions to the elastic moduli, but gives no reliable indication as to their signs. Our aim is to consider fully the polymeric effect upon the elastic moduli of a bilayer. It is possible to envisage many scenarios for the adsorbing polymer and surfactant system, but we restrict our attention to cases where the polymer homogeneously and reversibly adsorbs onto the surfactant bilayer without penetrating it; see figure 1. Our results indicate that the adsorption of polymer always leads to a *decrease* in the mean curvature rigidity K and an *increase* in the Gaussian rigidity \bar{K} . Although the assumption of reversible adsorption is not appropriate in all experimental situations (e.g. adsorption onto solid surfaces), it seems a reasonable starting point for the discussion of polymer-surfactant systems. In these, the amount of adsorbed

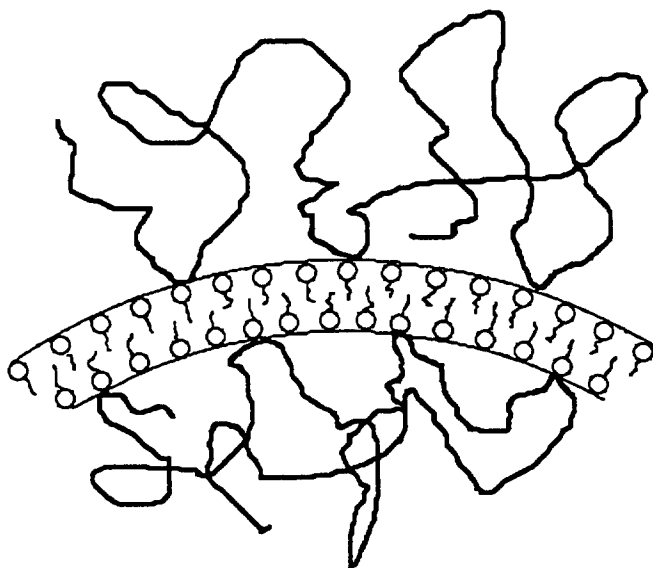


Fig 1 — Polymer adsorption on a bilayer

polymer per unit area of bilayer can change not only by adsorption/desorption (a slow process) but by varying the number of surfactant molecules in the film so as to change its area at fixed adsorbed amount. It is plausible, therefore, that full equilibrium is maintained in systems where surfactant exchange is rapid, although this is less likely in (say) phospholipid vesicles where such processes may be very slow.

The outline of the paper is as follows. In section 2 we discuss the formulation of the adsorption in mean-field, and go on to use this approach in section 3 to calculate the renormalization of the elastic moduli in various adsorption regimes. In section 4 we discuss the results obtained. In sections 5, 6 and 7 we repeat the procedure using the de Gennes adsorption functional in place of the true mean-field functional (the mean-field exponents are replaced with exponents corresponding to the observed scaling behaviour in good polymer solvent). We find this leads to much larger shifts in the elastic moduli than found from the mean-field approach. We give our conclusions in section 8.

2. Formulation of adsorption in mean-field.

2.1 RELATION BETWEEN INTERFACIAL ENERGY AND ELASTIC CONSTANTS — Formally the energy per unit area of a surfactant bilayer/monolayer can be written as [16, 17]

$$H = H_0 + \frac{1}{2} K (c_1 + c_2 - 2c_0)^2 + \bar{K} c_1 c_2 \quad (1)$$

where K and \bar{K} are the mean and Gaussian rigidity moduli respectively, $c_1, c_2 = 1/R_1, 1/R_2$ are the local curvatures (inverses radii of curvature), and c_0 is the «spontaneous» curvature (which vanishes for a bilayer).

If it is possible to calculate the energy associated with the polymer adsorption for both a spherical and cylindrical surface then we can extract the polymeric contribution to $K, \bar{K},$ and c_0 by use of equation (1). It should be noted that the application of equation (1) requires the energy per unit area of adsorption to be a power series in curvature to second order, and thus we must consider spherical (cylindrical) surfaces with very large radii (large with respect to the fundamental length in the problem, which is normally the bulk correlation length of the polymer solution). In this paper we restrict ourselves to the case of adsorption on bilayers where, by symmetry, the spontaneous curvature c_0 remains zero even under the addition of polymer. (For a monolayer the shift in c_0 was calculated by Hone and Ji [14] using methods similar to those adopted below.) The surfactant and polymer contributions are then independent and purely additive. In contrast for a system with a finite c_0 , such as a monolayer, addition of the polymer could cause c_0 to be shifted enough that the surfactant contributions to the elastic moduli would themselves be affected in a non-trivial way. We assume here that the surface-monomer potential can be modelled as a contact potential, so that the adsorbing boundary condition at the surface is independent of curvature when that is weak. This choice is made for simplicity, although it has been shown [18] that the use of more realistic continuum potentials can lead to a curvature dependent boundary condition. Likewise we assume that the thickness of the bilayer is negligible so that the area of each adsorbing surface is independent of curvature. In principle it is straightforward to incorporate these effects within the general framework laid out below.

We write $\gamma_s(R), \gamma_c(R)$ as the energy of adsorption per unit area on a large sphere and cylinder (throughout we will use the subscripts s and c to refer to spherical and cylindrical properties respectively), R is the radius of the sphere (cylinder) and is taken as positive if the adsorption is on the outside of the sphere (cylinder). The adsorption energy associated with a

curved bilayer, by symmetry, is then just $\gamma(R) + \gamma(-R)$, and use of equation (1) then implies for the polymeric contributions ΔK , $\Delta \bar{K}$ to the elastic constants

$$\begin{aligned} \Delta K &= 2 R^2 [\gamma_c(R) + \gamma_c(-R) - 2 \gamma_p] \\ 2 \Delta K + \Delta \bar{K} &= R^2 [\gamma_s(R) + \gamma_s(-R) - 2 \gamma_p] \end{aligned} \quad (2)$$

where γ_p is the adsorption energy per unit area of a corresponding flat surface. Since we are assuming homogeneous adsorption of the polymer with no penetration into the surfactant layer, we can calculate $\gamma_s(R)$ and $\gamma_c(R)$ within the standard Cahn-de Gennes framework [19, 20] which describes adsorption on impenetrable surfaces, and has been successful in describing many adsorption problems [21-24]. We next briefly outline this description of adsorption; for a clear explanation see the introduction of reference [14]

2.2 THE INTERFACIAL FREE ENERGY FUNCTIONAL. — Generally the surface energy associated with the adsorption of a solute from a dilute solution can be written in an obvious notation as

$$U - U_0 = - \gamma_1 \int \phi \, dS + \int [L(\phi)(\nabla\phi)^2 + G(\phi)] \, dV \quad (3)$$

where the first integral represents the contact energy between the solute and surface; the second integral represents the contribution from distortions of the concentration profile decaying into the bulk. U_0 is the surface energy of the pure solvent, ϕ is the solute volume fraction, γ_1 is the solute sticking energy per unit area ($\gamma_1 > 0$ for adsorption), $G(\phi)$ is an osmotic free energy density, and $L(\phi)$ describes the « stiffness » of the solution to spatial deformations in concentration

We assume the case of reversible adsorption of a homopolymer, which is in diffusive equilibrium with a bulk reservoir. The corresponding Cahn-de Gennes energy, in units where k_B is unity, is given by [25]

$$U - U_0 = - \gamma_1 \int \phi \, dS + \frac{T}{a^3} \int \left[\frac{a^2}{24 \phi} (\nabla\phi)^2 + \frac{1}{2} v (\phi - \phi_b)^2 \right] \, dV \quad (4)$$

where T is the temperature, a is the monomer size, ϕ_b is the volume fraction in the bulk, and v is a dimensionless excluded volume parameter ($v = 1 - 2 \chi$ where χ is the Flory interaction parameter). As usual, the functional can be simplified by using the order parameter ψ defined by $\psi^2 = \phi$; Equation (4) then becomes

$$U - U_0 = - \gamma_1 \int \psi^2 \, dS + \frac{T}{a^3} \int \left[\frac{a^2}{6} (\nabla\psi)^2 + \frac{1}{2} v (\psi^2 - \psi_b^2)^2 \right] \, dV \quad (5)$$

The equations governing the concentration profile are determined by minimising equation (5) resulting in the standard Euler-Lagrange equation and a logarithmic boundary condition at the surface:

$$\frac{a^2}{6} \nabla^2 \psi - v \psi^3 + v \psi_b^2 \psi = 0 \quad (6)$$

$$\left[\frac{1}{\psi} \frac{\partial \psi}{\partial n} \right]_{\text{surf}} = -k \quad (7)$$

where n indicates the normal to the surface, and $k = 6 \gamma_1 a/T$. The boundary condition of equation (7) defines an extrapolation length D , which we define by $2D = k^{-1}$. The length D

characterizes the strength of the surface attraction to monomers. For $D > \xi_E = a/(3 v \phi_b)^{1/2}$, where ξ_E is the Edwards correlation length of the bulk solution, the monomer-monomer interaction dominates the attraction to the surface, and this leads to weak adsorption, whereas $D < \xi_E$ corresponds to strong adsorption. For a qualitative picture of the adsorption profile on a planar surface see figure 2.

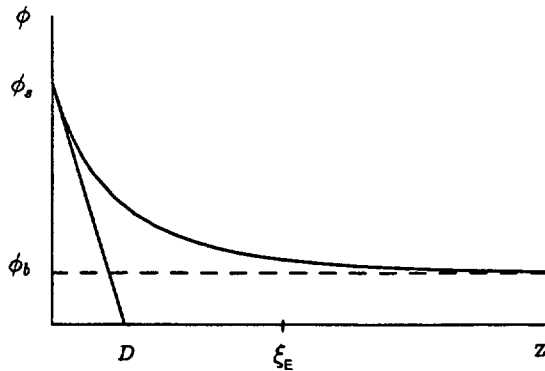


Fig 2 — Qualitative plot of the polymer concentration with distance from a planar surface. It should be noted that $D < \xi_E$ and thus the plot is in the regime of strong adsorption. Horizontal axis: distance from the surface (z), vertical axis: polymer volume fraction (ϕ)

The profile equations (6) and (7) can be re-written as

$$\tilde{\nabla}^2 \theta = 2 \theta (\theta^2 - 1) \tag{8}$$

$$\left[\frac{1}{\theta} \frac{\partial \theta}{\partial \vec{n}} \right]_{\text{surf}} = -\tilde{k} \tag{9}$$

where θ is the reduced mean-field order parameter defined by $\theta^2 = \phi/\phi_b$. These two equations have been written in dimensionless form, all lengths being measured in units of the Edwards correlation length, $\xi_E = a/(3 v \phi_b)^{1/2}$ (e.g. $\tilde{\nabla}^2 = \xi_E^2 \nabla^2$). In terms of these parameters the adsorption energy is given by

$$U - U_0 = \frac{T \phi_b \xi_E}{6 a} \left\{ -\tilde{k} \int \theta^2 d\tilde{S} + \int [(\tilde{\nabla} \theta)^2 + (\theta^2 - 1)^2] d\tilde{V} \right\} \tag{10}$$

all variables inside the brackets $\{ \}$ now being dimensionless.

Finally, from equation (10), $\gamma_s(\tilde{R})$ and $\gamma_c(\tilde{R})$ can be simply written down as

$$\gamma_s(\tilde{R}) - \gamma_0 = \frac{T \phi_b}{6 a \xi_E} \left[-\tilde{k} \theta_s^2(\tilde{R}) + \int_{\tilde{R}}^{\infty} [(\tilde{\nabla} \theta_s)^2 + (\theta_s^2 - 1)^2] \left(\frac{\tilde{r}}{\tilde{R}} \right)^2 d\tilde{r} \right] \tag{11}$$

$$\gamma_c(\tilde{R}) - \gamma_0 = \frac{T \phi_b}{6 a \xi_E} \left[-\tilde{k} \theta_c^2(\tilde{R}) + \int_{\tilde{R}}^{\infty} [(\tilde{\nabla} \theta_c)^2 + (\theta_c^2 - 1)^2] \left(\frac{\tilde{r}}{\tilde{R}} \right) d\tilde{r} \right] \tag{12}$$

where the concentration profiles $\theta_s(\tilde{r})$ and $\theta_c(\tilde{r})$ by symmetry just depend upon the radial distance \tilde{r} from the centre of the sphere or cylinder, and are solutions of equations (8) and (9) in spherical and cylindrical co-ordinates respectively

3. Calculation in the mean-field approach.

3.1 PERTURBATION CALCULATION — It is not possible in general to solve analytically the profile equations, equations (8) and (9), in spherical (cylindrical) co-ordinates, and thus it is necessary to turn to numerical methods. However, in the limit of weak adsorption, $\tilde{k} = \xi_E/2D \ll 1$, the attraction of the surface is much weaker than the monomer-monomer interaction allowing a perturbative solution to be found [14]. Using \tilde{k} as a perturbation parameter we can write to first order

$$\theta(\tilde{r}) \approx 1 + \tilde{k}\theta_1(\tilde{r}) \quad (\tilde{r} \geq \tilde{R}) \quad (13)$$

Again all lengths are measured in units of the Edwards correlation length ξ_E . Since we are always considering large bends (i.e. adsorption on large spherical and cylindrical surfaces of radius R) it is possible to expand $\theta_1(\tilde{r})$ as a power series in \tilde{c} ($\tilde{c} = 1/\tilde{R}$) giving

$$\theta(\tilde{r}) \approx 1 + \tilde{k}[\theta_{10}(\tilde{r}) + \theta_{11}(\tilde{r})\tilde{c} + \theta_{12}(\tilde{r})\tilde{c}^2] \quad (\tilde{r} \geq \tilde{R}). \quad (14)$$

Substitution of equation (14) into the profile equations (8) and (9) now gives a set of coupled linear differential equations which govern the θ 's. Solution of these gives the following results for the concentration profiles

$$\theta_s \approx 1 + \frac{\tilde{k}}{2}e^{-2\rho} \left[1 - \left(\frac{1}{2} + \rho \right) \tilde{c} + \left(\frac{1}{4} + \frac{\rho}{2} + \rho^2 \right) \tilde{c}^2 \right] \quad (15)$$

$$\theta_c \approx 1 + \frac{\tilde{k}}{2}e^{-2\rho} \left[1 - \left(\frac{1}{4} + \frac{\rho}{2} \right) \tilde{c} + \left(\frac{3}{32} + \frac{3\rho}{16} + \frac{3\rho^2}{8} \right) \tilde{c}^2 \right] \quad (16)$$

where $\rho = \tilde{r} - \tilde{R}$. Comparing with the flat case ($\tilde{c} = 0$) we see that to first order in curvature the effect of bending is to decrease the monomer concentration in the region of the surface. To calculate the corresponding energies of adsorption we substitute equations (15) and (16) into equations (11) and (12) respectively to find

$$\gamma_s(\tilde{c}) - \gamma_0 \approx \frac{T\phi_b}{6a\xi_E} \left[\left(-\tilde{k} - \frac{\tilde{k}^2}{2} \right) + \frac{\tilde{k}^2}{4}\tilde{c} - \frac{\tilde{k}^2}{8}\tilde{c}^2 \right] \quad (17)$$

$$\gamma_c(\tilde{c}) - \gamma_0 \approx \frac{T\phi_b}{6a\xi_E} \left[\left(-\tilde{k} - \frac{\tilde{k}^2}{2} \right) + \frac{\tilde{k}^2}{8}\tilde{c} - \frac{3\tilde{k}^2}{64}\tilde{c}^2 \right]. \quad (18)$$

To first order in curvature the effect on the energy of adsorption is a decrease if the surface is bent towards the solution, whilst bending the surface away causes an increase. It should be noted that in the spherical case the first order curvature term is always twice that of the cylinder, this is a geometrical result of the fact that for a given radius the mean curvature of the sphere is twice that of the cylinder.

As previously stated our formulation is really intended for bilayers, but in this limit of weak adsorption, where the presence of the polymer is only a small perturbation, we can consider the effect on the spontaneous curvature of a surfactant monolayer (a dividing surface between oil and water). Assuming the monolayer has an initial $c_0 = 0$, addition of the polymer would cause a finite spontaneous curvature which can be calculated from equation (18) by use of equation (1), giving

$$c_0 \approx -\frac{1}{64K_{\text{bare}}} \frac{T\phi_b}{6a} \left(\frac{\xi_E}{D} \right)^2 \quad (19)$$

where K_{bare} is the bare surfactant mean modulus and the negative sign indicates that the preferred bend is towards the adsorbed polymer

Returning to the elastic moduli of a bilayer, we may use equations (17) and (18) in equation (2) to find the following polymer-induced shifts in the elastic constants for the perturbative regime

$$\Delta K \approx -\frac{3}{64} \frac{T\phi_b \xi_E}{6a} \left(\frac{\xi_E}{D} \right)^2, \quad \Delta \bar{K} \approx +\frac{1}{32} \frac{T\phi_b \xi_E}{6a} \left(\frac{\xi_E}{D} \right)^2 \quad (20)$$

We see that the polymer causes a decrease in the mean curvature rigidity of the bilayer, accompanied by an increase in the Gaussian rigidity. It should be emphasized that the perturbation results are strictly valid for the limit $D \gg \xi_E$ and thus the effect upon K and \bar{K} is very small in the regime where equation (20) applies. In terms of the sticking energy γ_1 and the bulk polymer volume fraction ϕ_b , these polymeric contributions to the elastic moduli scale as $\gamma_1^2 \phi_b^{-1/2}$.

3.2 NUMERICAL MEAN-FIELD CALCULATIONS — To investigate the effects of stronger adsorption we have made numerical calculations of $\gamma_s(\tilde{c})$ and $\gamma_c(\tilde{c})$ as derived within the mean-field theory in section 2.2. The method adopted is outlined as follows

- (a) A strength of adsorption, namely \tilde{k} , is chosen
- (b) The profile equations, equations (7) and (8), are solved using a standard relaxation method [26] for a large sphere and cylinder ($\tilde{c} \sim 0.001$).
- (c) From the numerically calculated profile the energies $\gamma_s(\tilde{c})$ and $\gamma_c(\tilde{c})$, at fixed \tilde{c} , are calculated *via* equations (11) and (12)
- (d) Steps b) and c) are repeated for several different sphere and cylinder radii \tilde{R} , allowing a data set at fixed \tilde{k} to be obtained.
- (e) The data is fitted to a quadratic in curvature, \tilde{c} , to obtain an expansion of the form

$$\gamma_i(\tilde{c}) - \gamma_0 \approx \frac{T\phi_b}{6a\xi_E} [A_i(\tilde{k}) + B_i(\tilde{k})\tilde{c} + C_i(\tilde{k})\tilde{c}^2] \quad (21)$$

where the subscript $i = s$ (sphere), c (cylinder)

Using this procedure the expansion in curvature of $\gamma_s(\tilde{c})$ and $\gamma_c(\tilde{c})$ was calculated for various adsorption strengths, from weak adsorption ($\tilde{k} = 0.001$), to strong ($\tilde{k} = 100$). The resulting data are shown in figures 3a, 3b and 3c

The relaxation technique adopted used a fixed step-length, chosen for ease in applying standard numerical integration formulae. For weak adsorption the numerical results are in exact agreement with the analytic results. For stronger adsorption it is possible to check the accuracy of the numerical results by looking at the zeroth order term in the curvature expansion. This term is known analytically and comparison with the numerical value gives an estimate of the maximum numerical error as 0.06 %

Figure 3a shows the variation of B_s with \tilde{k} , and indicates that throughout the range of adsorption this contribution is positive (we have omitted a plot of the cylindrical B_c since this is just a half of B_s). However, for bilayers with equal adsorption on both sides this spontaneous curvature contribution cancels out. Figures 3b and 3c show the variation of ΔK and $\Delta \bar{K}$ respectively, with \tilde{k} . The data shows that the polymeric contribution to the mean curvature rigidity ΔK is always negative, whereas the increment of Gaussian rigidity $\Delta \bar{K}$ is always positive

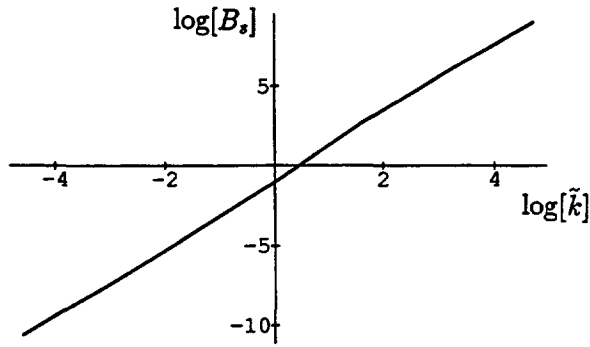


Fig. 3a — The spherical linear curvature coefficient B_s , calculated using mean-field theory. Horizontal scale $\log[\tilde{k}]$; vertical scale $\log[B_s]$.

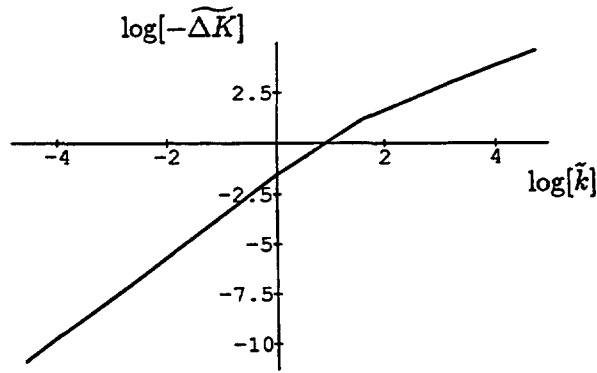


Fig. 3b — The mean curvature rigidity ΔK , calculated using mean-field theory. Horizontal scale $\log[\tilde{k}]$, vertical scale $\log[-\widetilde{\Delta K}] \equiv \log\left[-\Delta K / \left(\frac{T\phi_b \xi_E}{6a}\right)\right]$

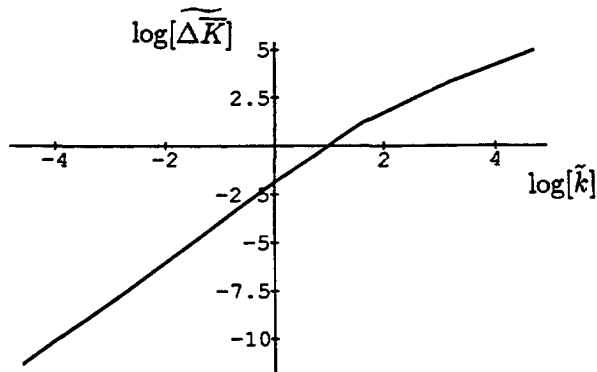


Fig. 3c. — The Gaussian rigidity $\Delta \bar{K}$, calculated using mean-field theory. Horizontal scale : $\log[\tilde{k}]$ vertical scale $\log[\widetilde{\Delta \bar{K}}] \equiv \log\left[\Delta \bar{K} / \left(\frac{T\phi_b \xi_E}{6a}\right)\right]$

3.3 ASYMPTOTIC LIMIT OF VERY STRONG ADSORPTION — In the limit of very strong adsorption on a flat surface it is well known that the effect of the bulk concentration upon the profile (and hence the adsorption energy) becomes negligible [20, 25]. The adsorption energy is then independent of the Edwards correlation length, the fundamental length in the problem is instead the extrapolation length D . We assume that this remains true for bent surfaces in the limit $D \ll \xi_E$, and use this to predict the asymptotic scaling behaviour for $\gamma_i(\bar{c})$. In our formulation the adsorption energy has the form given in equation (21), where A_i , B_i , and C_i are always dimensionless functions of the adsorption parameter \tilde{k} . Writing ϕ_b in terms of ξ_E reduces equation (21) to the form

$$\gamma_i(\bar{c}) - \gamma_0 = \frac{Ta}{18 v \xi_E^3} [A_i(\tilde{k}) + B_i(\tilde{k})(\xi_E c) + C_i(\tilde{k})(\xi_E c)^2]. \tag{22}$$

We now assume that asymptotically A_i , B_i and C_i approach simple powers laws of \tilde{k} . To determine the corresponding exponents for A_i , B_i and C_i we demand that the adsorption energy is independent of ξ_E at high adsorption. This gives the following results

$$A_i \sim \tilde{k}^3, \quad B_i \sim \tilde{k}^2, \quad C_i \sim \tilde{k} \tag{23}$$

These \tilde{k} dependences were tested by fitting to numerical data obtained for strong adsorption ($\tilde{k} \sim 100$). The fits obtained using the predicted power laws are good, and give the following numerical results:

$$\gamma_s(\bar{c}) - \gamma_0 = \frac{T\phi_b}{6 a \xi_E} [-0.33 \tilde{k}^3 + 0.67 \tilde{k}^2 \bar{c} - 0.24 \tilde{k} \bar{c}^2] \tag{24}$$

$$\gamma_c(\bar{c}) - \gamma_0 = \frac{T\phi_b}{6 a \xi_E} [-0.33 \tilde{k}^3 + 0.33 \tilde{k}^2 \bar{c} - 0.22 \tilde{k} \bar{c}^2] \tag{25}$$

It should be noted that the first term, that corresponding to the flat plane, is known analytically, the exact numerical coefficient being $-1/3$. Use of equations (24) and (25) in equation (2) then gives

$$\Delta K \approx -0.024 \frac{Ta}{vD}, \quad \Delta \bar{K} \approx 0.036 \frac{Ta}{vD} \tag{26}$$

In the limit of maximum adsorption, $D \sim a$, and assuming good solvent conditions, $v = 1$, we can write

$$\Delta K \sim -0.02 T, \quad \Delta \bar{K} \sim +0.036 T. \tag{27}$$

These results are quite small in comparison with surfactant elastic moduli which are of the order T , although in view of the v dependence in equation (26) larger shifts can be expected in the case of a poor solvent. [Note however that as v becomes small three-body and higher many-body terms become more dominant and the validity of equation (26) fails.] These relatively small shifts in the elastic moduli at strong adsorption contrast with those found by a scaling approach in section 6 below.

4. Discussion of the mean-field results.

To re-iterate, it was found above for both the sphere and the cylinder that the linear coefficient B_i in equation (21) is always positive, whilst the quadratic coefficient C_i is always negative. At first glance the positive B_i seems rather surprising, but the situation can be clarified by considering the three separate contributions to the adsorption energy that arise

within the Cahn-de Gennes description. These are (i) the surface contact term, (ii) the $(\nabla\phi)^2$ term which represents the local stretching of the chains, and (iii) the osmotic term arising from the monomer-monomer interaction. It is possible to calculate these contributions *individually*, for both the cylinder and the sphere, using the numerical and perturbative methods described in section 3. We find that the osmotic contribution is negative, the surface term is almost exactly twice the osmotic term and is positive, whilst the stretching term is negligible throughout the range of adsorption strengths. The negative sign of the osmotic contribution can be understood by realizing that bending the surface away from the solution (i.e. \tilde{R} positive) « frees » excluded volume. Simultaneously a decrease in the surface concentration gives a positive shift in the surface contribution which, it turns out, outweighs the osmotic term

Performing a similar analysis of the three contributions to C_1 , for both the cylinder and the sphere, indicates that in the limit of weak adsorption the surface term is dominant, whilst in the strong adsorption limit all three terms are comparable in magnitude, the surface and stretching terms are negative, whilst the osmotic term is positive. Since they correspond to *second order* coefficients in the curvature expansion it is difficult to find a simple physical explanation for the signs and magnitudes of the contributions to the elastic constants calculated in mean-field theory. Nonetheless we have found that the increments ΔK and $\Delta\bar{K}$ are respectively negative and positive, but rather small in most cases of interest (with the possible exception of strong adsorption from poor solvent, small v in equation (26)).

All our calculations have been made with the constraint of diffusive equilibrium, and it is also interesting to consider the effect upon the energy expansion by applying the constraint of fixed surface coverage [23]. This can be achieved experimentally by allowing the adsorption profile to build up, and then washing out the solution with pure solvent. Bending the surface with this « constrained » equilibrium must result in an adsorption energy which is larger than the diffusive case (this can be seen from simple thermodynamics)

Since for a surface bent in either a positive or a negative sense the constraint must give an increase in the energy, its lowest order effect must be an increase in the quadratic coefficient C_1 . Analytic calculations in the weak adsorption limit indicate that the sign of C_1 remains negative, but at higher adsorption it is possible that constrained equilibrium could lead to a positive polymer contribution ΔK .

5. Formulation of adsorption in scaling theory.

The mean-field theory of homopolymer adsorption often gives good qualitative results, but it does not take into account correctly the concentration correlations induced by the excluded volume. For example, in mean-field the adsorption energy per unit area has units of aT/ξ^3 which scales incorrectly with the correlation length ξ , since the adsorption is essentially a 2-dimensional problem the correct scaling is T/ξ^2 [25]. It was shown by de Gennes [20] that an amended adsorption functional could be made to give the correct scaling results, where it is assumed that the polymer concentration profile is regular in the proximal region. The existence of a proximal singularity [27] has been shown to have little effect in the regime of strong adsorption, which is of most interest, and thus we use the usual de Gennes functional which (in units where k_B is unity) takes the form [28]

$$U - U_0 = -\gamma_1 \int \phi \, dS + \frac{T}{a^3} \times \int \left[\frac{\alpha a^2}{6 \phi^{4/5} (\phi + \phi_b)^{9/20}} (\nabla\phi)^2 + \beta \phi^{9/4} - \frac{9}{4} \beta \phi_b^{5/4} \phi + \frac{5}{4} \beta \phi_b^{9/4} \right] dV \quad (28)$$

where the variables are the same as defined previously in section 2, and α and β are two unknown numerical constants. As in the mean-field case this can be minimised to obtain the profile equations which can be written in dimensionless form using $\phi = \Phi \phi_b$

$$2 \bar{\nabla}^2 \Phi - |\bar{\nabla} \Phi|^2 \left(\frac{4}{5} \Phi^{-1} + \frac{9}{20} (1 + \Phi)^{-1} \right) = \frac{9}{4} (\Phi^{5/4} - 1) \Phi^{4/5} (1 + \Phi)^{9/20} \quad (29)$$

$$\left[\Phi^{-4/5} (1 + \Phi)^{-9/20} \frac{\partial \Phi}{\partial \tilde{n}} \right]_{\text{surf}} = - \tilde{\delta} \quad (30)$$

where $\tilde{\delta} = \frac{3 \alpha \gamma_1}{\alpha T} \xi_b \phi_b^{1/4}$, and all lengths are measured in units of the bulk correlation length $\xi_b = a \sqrt{\frac{\alpha}{6 \beta}} \phi_b^{-3/4}$. The variable $\tilde{\delta}$ characterizes the strength of the adsorption, but δ^{-1} is now not the extrapolation length D as was the case in mean-field. However, a suitable extrapolation length can still be defined for the planar case by $\left(\frac{1}{\phi} \frac{\partial \phi}{\partial n} \right)_{\text{surf}} = - \frac{1}{D}$, giving

$$\tilde{D}^{-1} = \tilde{\delta} [\Phi_p^{-1/5} (1 + \Phi_p)^{9/20}]_{\text{surf}} \quad (31)$$

In general this now depends upon the surface concentration, and in principal there is a corresponding variation of the extrapolation length with curvature, but this effect is always small. For convenience we choose to write $\tilde{k} = \tilde{D}^{-1}$ (note that this differs from the mean-field definition by a factor of 1/2).

The adsorption energy per unit area on a sphere and a cylinder is now given, in terms of the radial density profile $\Phi(\tilde{r})$, by

$$\gamma_s(\tilde{R}) - \gamma_0 = \frac{\alpha T \phi_b^{3/4}}{6 a \xi_b} \left[- 2 \tilde{\delta} \Phi_s(\tilde{R}) + \int_{\tilde{R}}^{\infty} \left(\Phi_s^{-4/5} (1 + \Phi_s)^{-9/20} (\bar{\nabla} \Phi_s)^2 + \Phi_s^{9/4} - \frac{9}{4} \Phi_s + \frac{5}{4} \right) \left(\frac{\tilde{r}}{\tilde{R}} \right)^2 d\tilde{r} \right] \quad (32)$$

$$\gamma_c(\tilde{R}) - \gamma_0 = \frac{\alpha T \phi_b^{3/4}}{6 a \xi_b} \left[- 2 \tilde{\delta} \Phi_c(\tilde{R}) + \int_{\tilde{R}}^{\infty} \left(\Phi_c^{-4/5} (1 + \Phi_c)^{-9/20} (\bar{\nabla} \Phi_c)^2 + \Phi_c^{9/4} - \frac{9}{4} \Phi_c + \frac{5}{4} \right) \left(\frac{\tilde{r}}{\tilde{R}} \right) d\tilde{r} \right] \quad (33)$$

6. Calculation in the scaling approach.

6.1 PERTURBATION CALCULATION IN SCALING. — In the limit of weak adsorption, $\tilde{\delta} = \delta \xi_b \ll 1$, the profile equations, equations (29) and (30), can be solved using the same method as was done previously in mean-field. The resulting concentration profiles and adsorption energies are qualitatively the same as in the mean-field case⁽¹⁾. The resulting

⁽¹⁾ The adsorption energies calculated within the perturbative regime using the scaling functional are

$$\gamma_s(\tilde{c}) - \gamma_0 = \frac{2^{-9/10} \alpha T \phi_b^{3/4}}{6 a \xi_b} \left[- 2^{29/20} \left(\frac{\xi_b}{D} \right) + \left(\frac{\xi_b}{D} \right)^2 \left\{ - 2^{9/40} \left(\frac{32}{45} \right)^{1/2} + \frac{32}{45} \tilde{c} - 2^{-9/40} \left(\frac{32}{45} \right)^{3/2} \tilde{c}^2 \right\} \right]$$

$$\gamma_c(\tilde{c}) - \gamma_0 = \frac{2^{-9/10} \alpha T \phi_b^{3/4}}{6 a \xi_b} \left[- 2^{29/20} \left(\frac{\xi_b}{D} \right) + \left(\frac{\xi_b}{D} \right)^2 \left\{ - 2^{9/40} \left(\frac{32}{45} \right)^{1/2} + \frac{16}{45} \tilde{c} - \frac{3}{8} 2^{-9/40} \left(\frac{32}{45} \right)^{3/2} \tilde{c}^2 \right\} \right]$$

effect upon the elastic moduli of a bilayer is found as before. We obtain within the perturbative regime :

$$\Delta K \approx -\frac{3}{2} \left[\frac{\bar{\alpha} T \phi_b^{3/4} \xi_b}{6a} \right] \left(\frac{\xi_b}{D} \right)^2, \quad \Delta \bar{K} \approx \left[\frac{\bar{\alpha} T \phi_b^{3/4} \xi_b}{6a} \right] \left(\frac{\xi_b}{D} \right)^2 \quad (34)$$

where $\bar{\alpha} = \left(\frac{32}{45} \right)^{3/2} 2^{-9/8} \alpha$. In terms of the sticking energy γ_1 and the bulk polymer volume fraction ϕ_b these polymeric contributions to the elastic moduli scale as $\gamma_1^2 \phi_b^{-1}$.

6.2 NUMERICAL CALCULATIONS IN SCALING — Numerical calculations were performed, the method adopted being that described in section 3.2, with the data being acquired at fixed $\tilde{\delta}$. From $\tilde{\delta}$ a value of the extrapolation length \tilde{D} is calculated as described in section 5 allowing the data to be expressed in a similar form to the mean-field case. The expansion of the adsorption energy in curvature now has the form :

$$\gamma_i(\tilde{c}) - \gamma_0 \approx \frac{\alpha T \phi_b^{3/4}}{6 a \xi_b} [A_i(\tilde{k}) + B_i(\tilde{k}) \tilde{c} + C_i(\tilde{k}) \tilde{c}^2] \quad (35)$$

where $i = s$ or c . The data is shown in figures 4a, 4b and 4c. Figure 4a shows the variation of the linear coefficient B_s with \tilde{k} and indicates that throughout the range of adsorption the contribution is always positive (qualitatively the same as the mean-field result). Figures 4b and 4c show the variation of ΔK and $\Delta \bar{K}$ respectively with \tilde{k} . Again the data is qualitatively the same as mean-field, ΔK is always negative and $\Delta \bar{K}$ is always positive.

6.3 ASYMPTOTIC LIMIT OF STRONG ADSORPTION IN SCALING. — In the limit of strong adsorption the adsorption energy in a flat geometry is independent of the correlation length, as in the mean-field case [20]. Assuming that this still holds for curved surfaces in the limit $D \ll \xi_b$ we can consider the scaling behaviour for $\gamma_i(\tilde{c})$. Re-writing ϕ_b in terms of the correlation length, enables equation (35) to be expressed as

$$\gamma_i(\tilde{c}) - \gamma_0 \approx \frac{\alpha T}{6 \xi_b^2} \sqrt{\frac{\alpha}{6 \beta}} [A_i(\tilde{k}) + B_i(\tilde{k})(\xi_b c) + C_i(\tilde{k})(\xi_b c)^2] \quad (36)$$

A_i and B_i are now assumed to be simple power laws of the parameter \tilde{k} , and the exponents fixed by demanding that the adsorption energy is independent of ξ_b . C_i can no longer be a simple power law (formally the exponent is zero), but must be a dimensionless function of \tilde{k} . The functional form of C_i is suggested to be logarithmic by de Gennes [15] (See Sect. 7). The expected coefficients can thus be written as

$$A \sim \tilde{k}^2, \quad B \sim \tilde{k}, \quad C \sim \log [\eta \tilde{k}] \quad (37)$$

where η is an unknown numerical prefactor.

These predictions were tested by fitting to numerical data obtained for the strong adsorption case ($\tilde{k} \sim 35$). The fits obtained using the predicted functional forms are good, and give the following numerical results :

$$\gamma_s(\tilde{c}) - \gamma_0 \approx \frac{\alpha T \phi_b^{3/4}}{6 a \xi_b} [-0.67 \tilde{k}^2 + 3.11 \tilde{k} \tilde{c} + 1.64 \log [0.02 \tilde{k}] \tilde{c}^2] \quad (38)$$

$$\gamma_c(\tilde{c}) - \gamma_0 \approx \frac{\alpha T \phi_b^{3/4}}{6 a \xi_b} [-0.67 \tilde{k}^2 + 1.56 \tilde{k} \tilde{c} - 0.65 \log [0.86 \tilde{k}] \tilde{c}^2]. \quad (39)$$

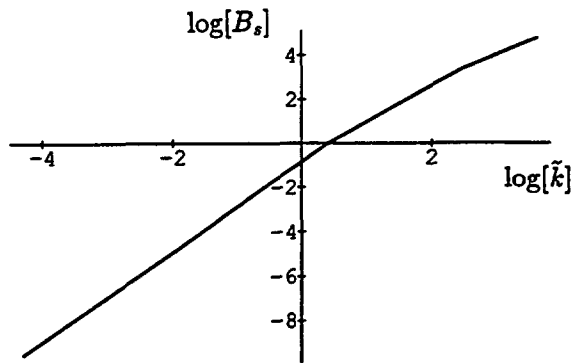


Fig 4a. — The spherical linear curvature coefficient B_s , calculated using scaling theory Horizontal scale $\log [\tilde{k}]$; vertical scale : $\log [B_s]$.

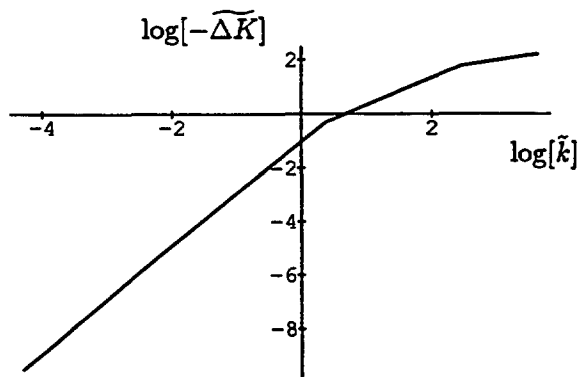


Fig. 4b — The mean curvature rigidity ΔK , calculated using scaling theory Horizontal scale $\log [\tilde{k}]$, vertical scale $\log [-\widetilde{\Delta K}] \equiv \log \left[-\Delta K / \left(\frac{\alpha T \phi_b^{3/4} \xi_b}{6 a} \right) \right]$

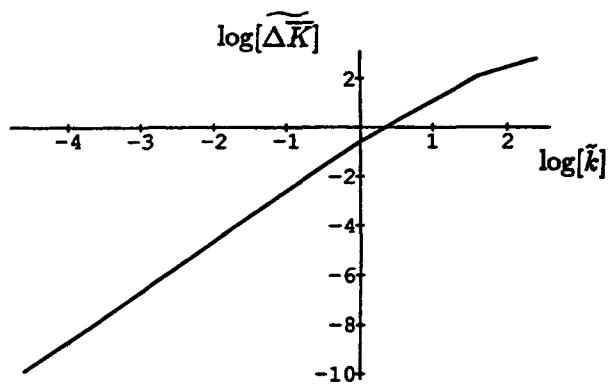


Fig 4c — The Gaussian rigidity $\Delta \bar{K}$, calculated using scaling theory Horizontal scale . $\log [\tilde{k}]$, vertical scale . $\log [\widetilde{\Delta \bar{K}}] \equiv \log \left[\Delta \bar{K} / \left(\frac{\alpha T \phi_b^{3/4} \xi_b}{6 a} \right) \right]$

The above result for the cylinder is qualitatively the same as the mean-field result, the coefficient B_c increases with increasing \tilde{k} (strength of adsorption), whilst C_c decreases (always remaining negative). The sphere is qualitatively the same as the mean-field case for the B_s coefficient only. The numerical calculations reveal that as \tilde{k} increases C_s follows the expected trend and decreases, but in the region of $\tilde{k} \sim 8$, C_s reaches a local minimum. As \tilde{k} increases further C_s begins to increase and tend towards the logarithmic asymptote. Figures 5a and 5b show the variation of C_i with \tilde{k} for the cylinder and sphere respectively.

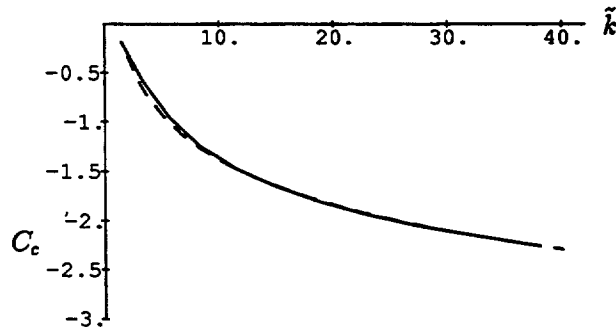


Fig 5a. — The cylindrical quadratic curvature coefficient C_c , calculated using scaling theory, in the regime of strong adsorption (solid curve) Dashed curve logarithmic asymptote Horizontal scale : \tilde{k} , vertical scale C_c

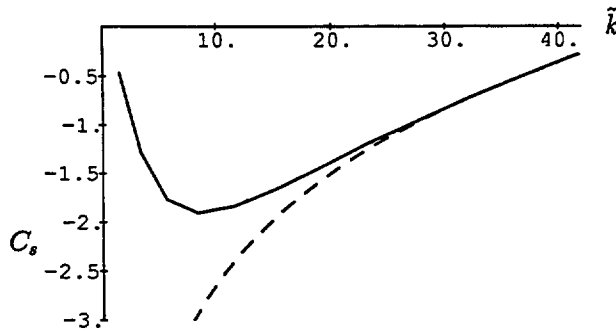


Fig 5b — The spherical quadratic curvature coefficient C_s , calculated using scaling theory, in the regime of strong adsorption (solid curve) Dashed curve logarithmic asymptote. Horizontal scale \tilde{k} ; vertical scale : C_s

The use of equation (38) and (39) in equation (2) gives for the strong adsorption limit in scaling, the following polymeric contribution to the elastic moduli of a bilayer

$$\Delta K \approx -0.43 \alpha T \sqrt{\frac{\alpha}{6\beta}} \log \left(\frac{0.86 \xi_b}{D} \right), \quad \Delta \bar{K} \approx 1.41 \alpha T \sqrt{\frac{\alpha}{6\beta}} \log \left(\frac{0.20 \xi_b}{D} \right). \quad (40)$$

In the above analysis the ratio ξ_b/D can be infinite, so that there is in principle no limit to the magnitude of ΔK and $\Delta \bar{K}$ at strong adsorption. This result of the scaling theory contrasts

strongly with the mean-field predictions of section 3, in which ΔK and $\Delta \bar{K}$ always remain small. Physically, however, the finite length of the polymer chains provides a limit to the magnitudes of the logarithmic factors in equation (40). We now assume chains of finite length and consider the largest possible value of the ratio ξ_b/D , and hence ΔK and $\Delta \bar{K}$. The correlation length must reach its maximum value at R_F , the Flory radius of a chain, and D can be no smaller than the monomer dimension leading to a maximum value of $\xi_b/D = (\lambda N)^{3/5}$ where N is the degree of polymerization and λ is of order unity. Substitution into equation (40) gives ΔK and $\Delta \bar{K}$ at maximum adsorption as

$$\Delta K \sim -0.26 \alpha T \sqrt{\frac{\alpha}{6\beta}} \log(0.8 \lambda N), \quad \Delta \bar{K} \sim +0.85 \alpha T \sqrt{\frac{\alpha}{6\beta}} \log(0.07 \lambda N). \quad (41)$$

The coefficients α and β are unknown, but it seems likely that the logarithmic dependence upon the degree of polymerization can result in ΔK and $\Delta \bar{K}$ being reasonably large compared to T , in contrast to the rather small values predicted by mean-field theory (Sect. 3).

7. Discussion of the scaling results.

In the limit of weak adsorption the scaling results are qualitatively the same as the mean-field results for both the sphere and the cylinder, and hence the same functional form for the perturbation expressions of ΔK and $\Delta \bar{K}$, i.e. $\Delta K \sim -T(\xi/D)^2$ and $\Delta \bar{K} \sim T(\xi/D)^2$ where the prefactors obviously differ in mean-field and in scaling. However, in the strong adsorption limit the scaling results are quite different from the mean-field results, and we thus focus our discussion on this region.

An analysis of the three contributions to the adsorption energy (surface term, osmotic term, and stretching term) can be carried out as described in section 4. For the linear coefficient B , this reveals, for both the sphere and cylinder, that the scaling case is qualitatively the same as mean-field, the osmotic term is negative, the surface term is almost twice the osmotic term and is positive, whilst the stretching term is negligible. The quadratic coefficient C , in mean-field was similar for both the sphere and the cylinder, but in scaling the sphere and cylinder produce very different results. Qualitative plots of the scaling results for the three individual contributions to the quadratic coefficients C_c and C_s are shown in figures 6a and 6b respectively, and demonstrate in the scaling approach an unexpected difference between spherical and cylindrical bends in the limit of strong adsorption.

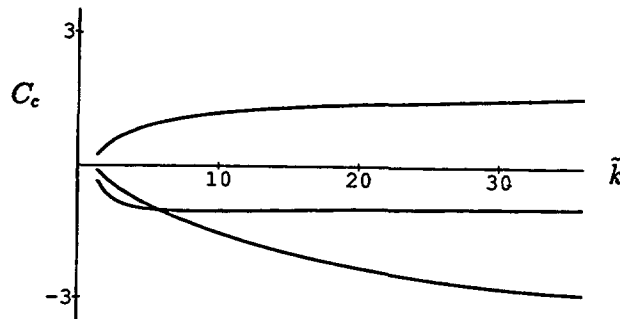


Fig 6a — Qualitative plot of the three individual contributions to the cylindrical quadratic curvature coefficient C_c , calculated using scaling theory. The curves represent the stretching, surface, and osmotic contributions, these are respectively the lower, middle, and upper curves at the right-hand edge of the plot. Horizontal scale \tilde{k} ; vertical scale C_c .

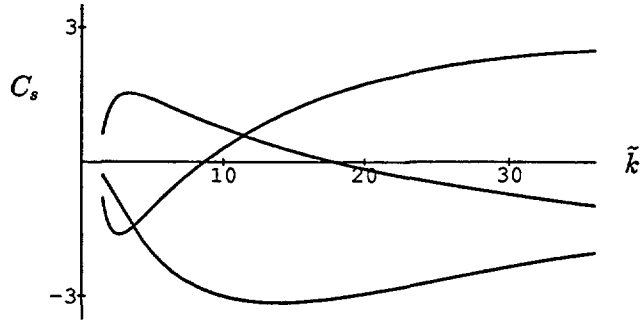


Fig. 6b — Qualitative plot of the three individual contributions to the spherical quadratic curvature coefficient C_s , calculated using scaling theory. The curves represent the stretching, surface, and osmotic contributions, these are respectively the lower, upper, and middle curves at the right-hand edge of the plot. Horizontal scale: \tilde{k} ; vertical scale: C_s .

For the elastic moduli results we found, as in mean-field, that ΔK is always negative and $\Delta \bar{K}$ is always positive, our results in the strong adsorption limit approaching a logarithmic asymptote. The marked difference in the functional forms for ΔK and $\Delta \bar{K}$ between the mean-field and scaling result is a direct result of the importance in the scaling description of the polymer far from the surface, the « adsorption cloud », and we now outline an argument for the origin of the logarithmic form of the elastic moduli.

In our approach we calculate the interfacial energy associated with the polymer on a curved surface directly. Since we are only really interested in changes in the adsorption energy with respect to surface curvature, we could have equally well evaluated the work required to bend a flat surface into a curved surface. This approach would be extremely complex in our system and would involve non-trivial stress tensors, but for a system where only the osmotic term is dominant (e.g. a grafted polymer brush) it has been shown by Helfrich [29], and Milner and Witten [30] that the elastic moduli can be expressed in terms of simple integrals over moments of the osmotic pressure

$$\Delta K_{\text{osmotic}} = - \int z \left. \frac{\partial \Pi_c(z, c)}{\partial c} \right|_{c=0} dz, \quad \Delta \bar{K}_{\text{osmotic}} = - \int z^2 \Pi(z) dz \quad (42)$$

where $\Pi(z)$ is the osmotic pressure, z is the distance from the surface, and c is the curvature. The osmotic contribution to the elastic moduli in the adsorbing homopolymer system has been calculated by de Gennes using the above approach [15]. In strong adsorption the polymer concentration profile near the surface is self similar [20], and the local osmotic pressure scales like T/z^3 . Since the osmotic pressure is a power law it can be shown that $\left. \frac{\partial \Pi_c(z, c)}{\partial c} \right|_{c=0} \sim T/z^2$. Substitution of these quantities into equation (42) with suitable limits now gives

$$\Delta K_{\text{osmotic}} \sim T \log(\mu \xi_b/D), \quad \Delta \bar{K}_{\text{osmotic}} \sim -T \log(\nu \xi_b/D) \quad (43)$$

where μ and ν are unknown prefactors. Since all three terms, stretching, surface, and osmotic are in balance we may expect each to have the same functional form, since a sum of logarithms is itself a logarithm, thus explains the asymptotic formula (41) for ΔK and $\Delta \bar{K}$ in the strong adsorption limit. This type of analysis obviously gives no indication as to the

signs of the final results, and for this there is no alternative to calculations such as those presented here

8. Conclusions.

The simple adsorption approach has provided some very interesting, and somewhat unexpected results for the effects of homopolymer adsorption upon bilayers. Analytic and numerical calculations reveal that adsorption of the polymer leads to a reduction in K and increase in \bar{K} . The polymer has greatest effect in the limit of strong adsorption, in which numerical results and a dimensional argument enabled us to determine the sign and functional form for the polymeric contribution to the elastic moduli. In this limit the scaling and mean-field approaches give significantly different results: the latter predicts (for a good solvent) maximum shifts in the elastic constants that are small fractions of $k_B T$, whereas the scaling approach gives contributions that can be (in principle) arbitrarily large and (in practice) at least comparable to the thermal energy.

It must be emphasized that all our results were obtained within the Cahn-de Gennes description of adsorption where the polymer is flexible, is in diffusive equilibrium with the bulk solution, and homogeneously adsorbs onto the surface. This leads to the three individual contributions to the adsorption energy, surface, osmotic, and stretching. The reduction in K and increase in \bar{K} depend delicately upon the interplay of all three individual contributions; we have found no simple argument to explain the signs of these effects.

Of some experimental interest, for example in the study of polymer/vesicle interactions [15], is the effect of non-equilibrium adsorption, it was argued (Sect. 4) that the constraint of fixed surface coverage must lead to the polymeric contributions ΔK being less negative and $\Delta \bar{K}$ being less positive than the calculated equilibrium values. This resulted from simple thermodynamics, the same argument being equally true when any property of the surface is constrained to remain fixed as a bend imposed. Quantitatively the effect of a constraint could be considered by inclusion of the appropriate Lagrange multiplier in the Cahn-de Gennes free energy functional, and then adopting a method similar to that used in the equilibrium case to calculate the resulting adsorption energy [21].

In our formulation we described the surface-monomer potential as a contact potential, resulting in the boundary condition at the surface being independent of curvature. Ball *et al.* [18] showed that the use of continuum surface-monomer potentials results in a curvature dependent value of \tilde{k} (strength of adsorption). In principle the effect of curvature dependence in the boundary condition could be constructed from our numerical results by following suitable contours in $\tilde{k}(\bar{c})$ space. A similar remark applies if one is interested in the effects of variation in surface area under bending that result from a finite thickness to the bilayer.

As mentioned in the introduction, we expect equilibrium adsorption conditions to be relevant in determining phase equilibria of polymer-surfactant systems, for example in a lamellar stack. A discussion of this involves not only the renormalisation of the elastic moduli, but also direct polymer-induced surface forces between bilayers. The latter should be relatively unimportant if the mean spacing between adjacent bilayers d is much greater than the correlation length of the bulk polymer solution ξ_b . Limiting ourselves to $d \gg \xi_b$, we expect the reduction in K , due to the adsorption of polymer, to increase the flexibility of the bilayers, leading to an increase in the relative stability of the sponge (L_3) phase with respect to the lamellar phase [3]. Turning to the Gaussian rigidity \bar{K} , it is well known that this couples to the topology of the surface; $\bar{K} > 0$ favours more handles and fewer components, whilst $\bar{K} < 0$ favours more components and fewer handles. The increase in \bar{K} , due to the adsorption of polymer, would favour the formation of more handles, increasing the stability not only of

the L_3 phase but also periodic minimal surface phases (cubic phases) with respect to the lamellar state

Our conclusions concerning the incremental elastic moduli may be altered if the polymer is, in practice, in constrained equilibrium. We hope to return to this issue of non-equilibrium adsorption, and detailed consideration of polymer-induced surface forces, in future work.

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