Role of Adsorbed Polymer in Bilayer Elasticity

Role of Adsorbed Polymer in Bilayer Elasticity.

J. T. BROOKS(*), C. M. MARQUES(**) and M. E. CATES(*)

(*) *Theory of Condensed Matter, Cavendish Laboratory*
Madingley Road, Cambridge CB3 0HE
(**) *Institut Charles Sadron, C.N.R.S.*
6 rue Boussingault, 67083 Strasbourg Cedex, France

Abstract. – We study theoretically the effect of adsorbed homopolymer on surfactant bilayers. We formulate the energy of adsorption per unit area as a Taylor series in curvature for both spherical and cylindrical surfaces. In the limits of weak adsorption analytic expressions are derived for the polymeric contribution to the elastic moduli of the bilayer, using a scaling functional approach. For stronger adsorption numerical and asymptotic calculations have been made. 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 $\bar{K}$. For strong adsorption these contributions are comparable to $k_B T$; thus the presence of adsorbed polymer can strongly influence the elasticity of surfactant bilayers.

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. 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.

Arguably the most basic and important parameters of a bilayer are the mean and Gaussian elastic moduli. 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 [1-9]. In this approach, the free energy of a bilayer is written as a 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 letter we consider the effect on the elastic moduli of a surfactant bilayer upon addition of soluble, adsorbing polymer to the external solvent. We anticipate that the harmonic curvature expansion still applies for radii of curvature large enough compared to the adsorbed layer thickness, or the correlation length of the bulk polymer solution (whichever is larger). 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.

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 adsorbs onto the surfactant bilayer without penetrating it. Our investigation builds on the previous work of Hone and Hong Ji [10] and de Gennes [11]. Hone *et al.* considered 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 [11] 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 contribution to the elastic moduli, but gives no reliable indication as to their signs. Below we consider more fully the polymeric effect upon the elastic moduli of a bilayer. Our results indicate that the adsorption of polymer, as described by scaling theory, always leads to a *decrease* in the mean curvature rigidity K and an *increase* in the Gaussian rigidity $\bar{K}$.

Formally the energy per unit area of a surfactant bilayer/monolayer can be written as [12]

$$H = H_0 + \frac{1}{2} K (c_1 + c_2)^2 + \bar{K} c_1 c_2 , \tag{1}$$

where K and $\bar{K}$ are the mean and Gaussian rigidity moduli, respectively, and c_1, $c_2 = 1/R_1$, $1/R_2$ are the local principal curvature (inverse radii of curvature).

If it is possible to calculate the energy associated with the polymer adsorption for both a spherical and a cylindrical surface, then we can extract the polymeric contribution to K and $\bar{K}$ by use of eq. (1). In this letter we restrict ourselves to the case of adsorption onto both sides of a bilayer where, by symmetry, there is no spontaneous curvature even under the addition of polymer. The «bare» (surfactant) and polymer contributions to the elastic constants K and $\bar{K}$ are then independent and purely additive. We assume further 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 [13] 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 relax these assumptions 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 eq. (1) then leads to the following polymeric contributions ΔK, $\Delta \bar{K}$ to the elastic constants:

$$\Delta K = 2R^2 [\gamma_c(R) + \gamma_c(-R) - 2\gamma_p] , \quad 2\Delta K + \Delta \bar{K} = R^2 [\gamma_s(R) + \gamma_s(-R) - 2\gamma_p] , \tag{2}$$

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 [14, 15]. We now give a brief description of our calculations; a more complete account of

this work, along with the corresponding predictions from a somewhat simpler mean-field theory, will be given elsewhere [16].

The scaling theory of polymer adsorption from a good solvent is based on the phenomenological Cahn-de Gennes free-energy functional, which assumes that the polymer concentration profile is regular in the proximal region; the existence of a proximal singularity [17] has been shown to have little effect in the regime of strong adsorption, which is of most interest. We assume the case of reversible adsorption of homopolymer, which is in diffusive equilibrium with a bulk reservoir, and use the usual de Gennes functional which (in units where k_B is unity) takes the form [15]

$$U - U_0 = -\gamma_1 \int \phi \, \mathrm{d}S + \frac{T}{a^3} \int \left[\frac{\alpha a^2}{6\phi^{4/5}(\phi + \phi_b)^{9/20}} (\nabla\phi)^2 + \beta\phi^{9/4} - \frac{9}{4}\beta\phi_b^{5/4}\phi + \frac{5}{4}\beta\phi_b^{9/4} \right] \mathrm{d}V, \qquad (3)$$

where U_0 is the surface energy of pure solvent, γ_1 is the monomer-surface sticking energy, T is the temperature, a is the monomer size, ϕ is the polymer volume fraction (ϕ_b is the bulk value), and α and β are unknown numerical constants. The equations governing the concentration profile are determined by minimizing eq. (3), resulting in a Euler-Lagrange equation and a boundary condition defined at the surface, which can be written in terms of the reduced order parameter $\Phi = \phi/\phi_b$ as

$$2\widetilde{\nabla}^2 \Phi - |\widetilde{\nabla}\Phi|^2 \left(\frac{4}{5}\Phi^{-1} + \frac{9}{20}(1 + \Phi)^{-1} \right) = \frac{9}{4}(\Phi^{5/4} - 1)\Phi^{4/5}(1 + \Phi)^{9/20}, \qquad (4)$$

$$\left[\Phi^{-4/5}(1 + \Phi)^{-9/20} \frac{\partial \Phi}{\partial \widetilde{n}} \right]_{\mathrm{surf}} = -\widetilde{\delta}, \qquad (5)$$

where $\widetilde{\delta} = (3a\gamma_1/\alpha T)\xi_b\phi_b^{1/4}$ and the subscript surf denotes evaluation at the surface. These two equations have been written in dimensionless form, all quantities with tildes (˜), here and below, being measured in units of the bulk correlation length, $\xi_b = a\sqrt{\alpha/6\beta}\,\phi_b^{-3/4}$ (*e.g.* $\widetilde{\nabla}^2 = \xi_b^2 \nabla^2$). The variable $\widetilde{\delta}$ characterizes the strength of the adsorption.

As usual, an extrapolation length D can be defined for a planar surface by $((1/\phi)(\partial\phi/\partial n))_{\mathrm{surf}} = -1/D$, giving

$$\widetilde{D}^{-1} = \widetilde{\delta}[\Phi_b^{-1/5}(1 + \Phi_b)^{9/20}]_{\mathrm{surf}}. \qquad (6)$$

The length D characterizes the strength of the surface attraction to monomers. For $D > \xi_b$ the monomer-monomer interaction dominates the attraction to the surface, and this leads to weak adsorption, wheres $D < \xi_b$ corresponds to strong adsorption. In general, eq. (6) now depends upon the surface concentration, and in principle there is a corresponding variation of the extrapolation length with curvature, which is small and we do not discuss it further. For convenience we choose to write $\widetilde{k} = \widetilde{D}^{-1}$. The adsorption energies per unit area on a sphere and on a cylinder are now written in terms of the radial density profile $\Phi(\widetilde{r})$, as

$$\gamma_s(\widetilde{R}) - \gamma_0 = \frac{\alpha T \phi_b^{3/4}}{6a\xi_b} \left[-2\widetilde{\delta}\Phi_s(\widetilde{R}) + \int_{\widetilde{R}}^{\infty} \left(\Phi_s^{-4/5}(1 + \Phi_s)^{-9/20}(\widetilde{\nabla}\Phi_s)^2 + \Phi_s^{9/4} - \frac{9}{4}\Phi_s + \frac{5}{4} \right) \left(\frac{\widetilde{r}}{\widetilde{R}} \right)^2 \mathrm{d}\widetilde{r} \right], \qquad (7)$$

$$\gamma_c(\widetilde{R}) - \gamma_0 = \frac{\alpha T \phi_b^{3/4}}{6a\xi_b} \left[-2\widetilde{\delta}\Phi_c(\widetilde{R}) + \int_{\widetilde{R}}^{\infty} \left(\Phi_c^{-4/5}(1 + \Phi_c)^{-9/20}(\widetilde{\nabla}\Phi_c)^2 + \Phi_c^{9/4} - \frac{9}{4}\Phi_c + \frac{5}{4} \right) \left(\frac{\widetilde{r}}{\widetilde{R}} \right)^2 \mathrm{d}\widetilde{r} \right]. \qquad (8)$$

It is not possible in general to solve analytically the profile equations, eqs. (4) and (5), and thus it is necessary to turn to numerical methods. However, in the limit of weak adsorption $\tilde{k} = \xi_b/D \ll 1$, the attraction of the surface is much weaker than the monomer-monomer interaction allowing perturbative results for $\gamma_s(\tilde{c})$ and $\gamma_c(\tilde{c})$ to be found (where we have defined $\tilde{c} = 1/\tilde{R}$). From these perturbative solutions the effect upon the elastic moduli can be calculated via eq. (2) resulting in

$$\Delta K \simeq -\frac{3}{2}\left[\frac{\bar{\alpha}T\phi_b^{3/4}\xi_b}{6a}\right]\left(\frac{\xi_b}{D}\right)^2, \qquad \Delta\overline{K} \simeq \left[\frac{\bar{\alpha}T\phi_b^{3/4}\xi_b}{6a}\right]\left(\frac{\xi_b}{D}\right)^2, \tag{9}$$

where $\bar{\alpha} = (32/45)^{3/2}2^{-9/8}\alpha$. The perturbation results are strictly valid for the limit $D \gg \xi_b$ and thus the effect upon K and $\overline{K}$ is very small in the regime where eq. (9) 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 $\gamma_1^2\phi_b^{-1}$.

To investigate the effects of stronger adsorption, we have made numerical calculations of $\gamma_s(\tilde{c})$ and $\gamma_c(\tilde{c})$ for various adsorption strengths $\tilde{k}$. We write the expansion of the adsorption energy in power of the curvature $\tilde{c} = 1/\tilde{R}$ in the form

$$\gamma_i(\tilde{c}) - \gamma_0 \simeq \frac{\alpha T\phi_b^{3/4}}{6a\xi_b}[A_i(\tilde{k}) + B_i(\tilde{k})\,\tilde{c} + C_i(\tilde{k})\,\tilde{c}^2], \tag{10}$$

where the subscript $i = \text{s}$ (sphere), or c (cylinder). The elastic constants ΔK, $\Delta\overline{K}$ are linear combinations of C_s and C_c. Figures 1 and 2 show the dependence of the numerically calculated C_i on $\tilde{k}$ for the cylinder and sphere, respectively. Also shown in fig. 1 and 2 are the three separate contributions to the adsorption energy that arises 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. Since they contribute to *second-order* coefficients in the curvature expansion, it is difficult to find a simple physical explanation for the signs and relative magnitudes of these various contributions to the elastic constants. Nonetheless, we find that the total
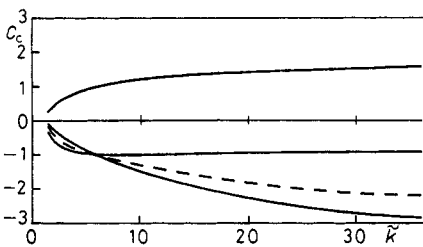

Fig. 1.   Fig. 2.

Fig. 1. – Plot of the three individual contributions, and their sum, to the cylindrical quadratic curvature coefficient C_c. The solid 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. Dashed curve: sum of these contributions. Horizontal scale: $\tilde{k}$; vertical scale: C_c.
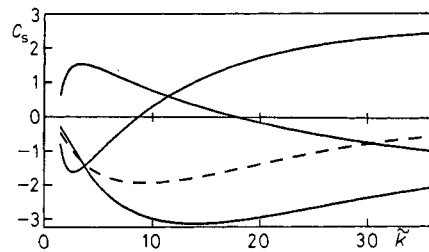
Fig. 2. – Plot of the three individual contributions, and their sum, to the spherical quadratic curvature coefficient C_s. The solid curves represent the stretching, surface and osmotic contributions; these are, respectively, the lower, upper and middle curves at the right-hand edge of the plot. Dashed curve: sum of these contributions. Horizontal scale: $\tilde{k}$; verticale scale: C_s.

increments ΔK and $\Delta \bar{K}$ are, respectively, negative and positive throughout the range of adsorption strengths, consistent with the results (9) for weak adsorption.

We now consider the limit of very strong adsorption, where 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 [15, 18]. The adsorption energy is then independent of the bulk 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 $D \ll \xi_b$ and use this to predict the asymptotic scaling behaviour for $\gamma_i(\tilde{c})$. A_i and B_i are 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 cannot 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 [11].

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. The use of eq. (2) now gives for the strong adsorption limit the following polymeric contributions to the elastic moduli of a bilayer, in which we retain α and β as parameters (of order unity) and determine other prefactors by fitting to our numerical data:

$$\Delta K \simeq -0.43\alpha T \sqrt{\frac{\alpha}{6\beta}} \log\left(\frac{0.86\xi_b}{D}\right), \quad \Delta \bar{K} \simeq 1.41\alpha T \sqrt{\frac{\alpha}{6\beta}} \log\left(\frac{0.20\xi_b}{D}\right). \tag{11}$$

The signs remain the same as for weak adsorption. For ΔK the negative sign of the polymeric contribution is opposite to that suggested by de Gennes [11]. Because of the competition between osmotic, stretching and surface contributions described above, the sign can only be found by a full calculation, although the logarithmic dependence can be predicted by considering, *e.g.*, only the osmotic contribution [11].

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. In practice, however, the finite length of the polymer chains prevents any divergence of the logarithmic factors in eq. (11). For finite polymers the effective correlation cannot exceed R_F, the Flory radius of a chain, and D can be no smaller than the monomer dimension a; this leads to a maximum value of $\xi_b/D \sim (\lambda N)^{3/5}$, where N is the degree of polymerization and λ is of order unity. Substitution into eq. (11) gives ΔK and $\Delta \bar{K}$ at maximum adsorption as

$$\Delta K \sim -0.26\alpha T \sqrt{\frac{\alpha}{6\beta}} \log(0.8\lambda N), \quad \Delta \bar{K} \sim +0.85\alpha T \sqrt{\frac{\alpha}{6\beta}} \log(0.07\lambda N). \tag{12}$$

The coefficients α and β are of order unity, but in view of the logarithmic dependence upon N, we can certainly expect values of ΔK and $\Delta \bar{K}$ that are of the order of or larger than $k_B T$ for strong adsorption of high–molecular-weight polymer. These contributions would then be similar in magnitude to the bare values of the elastic moduli for surfactant bilayers (although perhaps quite small compared to those of lipid systems [1]). It must be emphasized that our results were obtained within an equilibrium approach. Although not considered directly, the effect of nonequilibrium adsorption can be inferred by a simple thermodynamic argument [16] which indicates that the polymeric contributions ΔK would be less negative and $\Delta \bar{K}$ would be less positive than the calculated equilibrium values.

In summary, we have found at both weak and strong adsorption interesting and somewhat unexpected results for the effects of homopolymer adsorption upon bilayer. The *reduction* in K and *increase* in $\bar{K}$, on addition of polymer, could be large enough in the strong adsorption regime to strongly alter the phase behaviour in mixed polymer/surfactant

systems. To discuss fully the possible effects on phase equilibria we must also include the effects of polymer-induced surface forces between bilayers, and we hope to return to this issue in future work.

<center>* * *</center>

REFERENCES

[1] LANGEVIN D. and MEUNIER J. (Editors), *Physics of Amphiphilic Layers* (Springer, Berlin) 1987.
[2] DE GENNES P.-G. and TAUPIN C., *J. Phys. Chem.*, **86** (1986) 2294.
[3] ANDELMAN D., CATES M. E., ROUX D. and SAFRAN S. A., *J. Chem. Phys.*, **87** (1987) 7229.
[4] CATES M. E., ROUX D., ANDELMAN D. and MILNER S. T., *Europhys. Lett.*, **5** (1988) 733.
[5] HELFRICH W., *Z. Naturforsch. A*, **33** (1978) 305.
[6] HUSE D. A. and LEIBLER S., *J. Phys. (Paris)*, **49** (1988) 605.
[7] ROUX D. and SAFINYA C. R., *J. Phys. (Paris)*, **49** (1988) 307.
[8] PORTE G., APPELL J., BASSEREAU P. and MARIGNAN J., *J. Phys. (Paris)*, **50** (1989) 1335.
[9] LEIBLER S., *Statistical Mechanics of Membranes of Surfaces*, edited by D. NELSON, T. PIRAN and S. WEINBERG (World Scientific, Singapore) 1989, and references therein.
[10] JI H. and HONE D., *Macromolecules*, **21** (1988) 2600.
[11] DE GENNES P.-G., *J. Phys. Chem.*, **94** (1990) 8407.
[12] HELFRICH W., *Z. Naturforsch.*, **28c** (1973) 693.
[13] BALL R., BLUNT M. and BARFORD W., *J. Phys. A*, **22** (1989) 2587.
[14] CAHN J. W. and HILLIARD J. E., *J. Chem. Phys.*, **28** (1957) 1958.
[15] DE GENNES P.-G., *Macromolecules*, **14** (1981) 1637.
[16] BROOKS J. T., MARQUES C. M. and CATES M. E., in preparation.
[17] DE GENNES P.-G. and PINCUS P. A., *J. Phys. (Paris)*, **44** (1982) L241.
[18] DE GENNES P.-G., *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, N.Y.) 1979.