Swelling and Surface Thermodynamics of Lamellar Lecithin-Water Liquid Crystals

Jan Christer Eriksson and Stig Ljunggren

Department of Physical Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

Eriksson, Jan Christer and Ljunggren, Stig, 1986. Swelling and Surface Thermodynamics of Lamellar Lecithin-Water Liquid Crystals. – Acta Chem. Scand. A 40: 261-270.

A thermodynamic analysis is presented of the swelling of lamellar lecithin-water liquid crystals, the ultimate purpose being to trace out the correspondence of water vapour pressure measurements with direct surface force experiments. It is concluded that the overall swelling/disjoining pressure, π, in water and the associated lateral tension of a repeat unit, γ, can be computed from water pressure data (p_1) by means of the formulae

$$\pi = (kT/v_1)\left[1 + \frac{d\ln a}{d\ln h}\right]\ln(p_1^\circ/p_1), \quad \tfrac{1}{2}\gamma a = kT \int_{y_1}^{y_1^*} [\ln(p_1^\circ/p_1)]dy_1,$$

where v_1 is the molecular volume of water, a the surface area per lecithin molecule, h the repeat distance perpendicular to the lamellae and y_1 the mole fraction ratio water/lecithin. Superscript * refers to the swelling limit. According to the available X-ray diffraction results, the term $d\ln a/d\ln h$ is of the order of 1. Furthermore, we argue that π and γ are composed of three major components associated with changes of (i) the hydrocarbon/water contact area, (ii) the hydrocarbon chain conformational state and (iii) the head group/water and head group/image charge interactions. The large contributions (i) and (ii) are related primarily to the variation of the lateral packing of the lecithin molecules in the bilayers. This variation can be rationalized as a consequence of the mechanical equilibrium conditions and calls for sizeable corrections after which, however, fair agreement with direct surface force measurements is demonstrated.

In their well-known papers from 1976, 1977 and 1979 LeNeveu et al.[1,2] and Parsegian et al.[3] have established that useful information can be derived about the (interlamellar) forces operating in lecithin/water lamellar liquid crystals from combined measurements of the water chemical potential, μ_1, the bilayer repeat distance, h, and the bilayer separation, h_w. The X-ray data reported thus far indicate, however, that the surface area per lecithin head group, a, increases significantly as more water is added, at a typical rate, da/dh_w, of about 1 Å²/Å. This observation raises the question to what extent free energy changes which are related primarily to the variable head group surface area, actually contribute to the value of the water chemical potential μ_1 and to the swelling pressure, π.[3-5] In order to treat this problem in a sufficiently general and systematic

fashion, we performed an analysis of the water swelling of a lamellar liquid crystal employing a surface/swelling-thermodynamic approach. The numerical results presented indicate that the hydrocarbon/water contact and hydrocarbon chain conformational free energy changes which occur when h is varied are in fact sizeable in comparison with the resulting net change in free energy.

Thermodynamics of a lamellar repeat unit

The (electroneutral) system considered here is part of a lamellar liquid crystal and is depicted in Fig. 1. It is a macroscopic extension in the lateral X-, Y-directions and includes one water lamella containing N_1 water molecules and two adjacent lecithin monolayers made up of, in all, N_2 lecithin molecules. However, we may even occasionally imagine that these two lecithin monolayers are attached to hydrophobised mica surfaces as

---

Dedicated to Professor Per Ekwall on his 90th birthday.

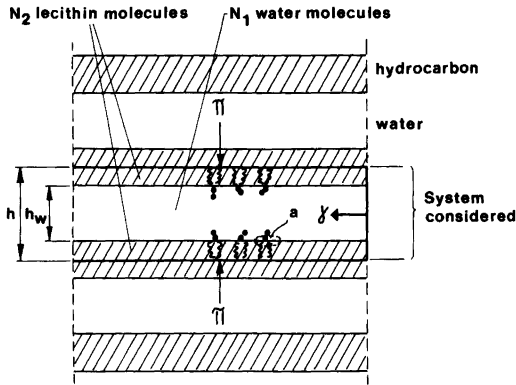N₂ lecithin molecules ⌐N₁ water molecules

Fig. 1. Sketch of the system considered which includes a planar water lamella and its adjacent lipid monolayers in a lamellar lecithin/water liquid crystal.

would be the situation in a surface force experiment using Israelachvili's apparatus.[6] Since we need to have a general enough framework within which swelling pressures can be treated, we shall assume that an extra (disjoining or swelling pressure) force, πA, operates in the Z-direction perpendicular to the planes of the lamellae and, moreover, that the repeat unit can also be subject to a resulting tension, γ, in lateral directions. Referring to the pressure tensor and the conventional Bakker integral, this tension may be defined mechanically by the relation

$$\gamma = \int_{-h/2}^{+h/2} [p_e - p_T(Z)]dZ , \qquad (1)$$

where p_e is the external pressure and $p_T = p_{XX} = p_{YY}$. It is straightforward to demonstrate that this integral is invariant with respect to the convention used to evaluate the p_T component of the pressure tensor. Accordingly, we may consider a repeat unit of a lamellar liquid crystal to be enclosed by walls which are perpendicular to the X-, Y- and Z-directions and on which the forces πA, γL_X and γL_Y are acting, L denoting the perimeter length.

For the differential of the Gibbs free energy of this system, defined as $G = F + p_e V$, we can write in a corresponding manner as for a soap film (cf. Ref.7):

$$dG = -SdT + Vdp_e + \gamma dA - \pi Adh + \mu_1 dN_1 + \mu_2 dN_2 , \qquad (2)$$

where conventional notation is being employed and where we anticipate that a lamellar repeat unit might be subject to net forces in lateral as well as normal directions. For a "free" lamellar liquid crystal, the molecular surface area, a, and the repeat distance, h, depend only upon T, p_e and the composition variable $y_1 = N_1/N_2$ and, in this case, eq. (2) must reduce to the ordinary bulk phase expression

$$dG = -SdT + Vdp_e + \mu_1 dN_1 + \mu_2 dN_2 , \qquad (3)$$

since mechanical equilibrium then requires that the tension γ and the pressure π are each *separately* equal to zero. This point is perhaps most readily seen by referring to the following differential of the Legendre transformation $F + p_e V - \mu_1 N_1 - \mu_2 N_2 = \Omega + p_e V$ which results from eq. (2)

$$d(\Omega + p_e V) = -SdT + Vdp_e + \gamma dA - \pi Adh - N_1 d\mu_1 - N_2 d\mu_2 . \qquad (4)$$

For $\Omega + p_e V$ to have a minimum at constant T, p_e, μ_1, μ_2 and A, it is evident that π must vanish. In addition, for a planar or nearly planar system without any meniscus where mechanical contact to matter in a different state is arranged (as, for instance, a bilayer in a liposome structure), it is equally clear that γ must likewise vanish at equilibrium. For further details, see the Appendix.

In what follows, it turns out to be helpful to clearly distinguish between the two cases of (i) a stressed state (superscript ˢ) in physico-chemical equilibrium with liquid water saturated with molecularly dispersed lecithin, that is, with water containing immersed liquid crystals of lecithin at the swelling limit and (ii) an unstressed, free liquid crystal (superscript ᵘ) in contact with water vapour below the saturation vapour pressure p_1^0. The chemical potentials at the swelling limit are denoted by μ_1^* for water and μ_2^* for lecithin whereas the corresponding chemical potentials for free liquid crystals in contact with water vapour at $p_1 < p_1^0$ are μ_1 and μ_2, respectively.

Accordingly, in place of eqs. (2) and (3) we now write

$$dG^s = -S^s dT + V^s dp_e + \gamma dA^s - \pi A^s dh^s + \mu_1^* dN_1^s + \mu_2^* dN_2^s , \qquad (5)$$

$$dG^u = -S^u dT + V^u dp_e + \mu_1 dN_1^u + \mu_2 dN_2^u . \qquad (6)$$

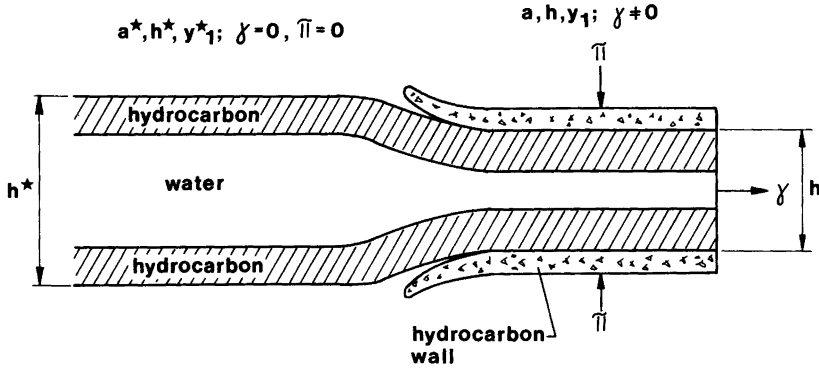By applying eqs. (5) and (6) to systems containing a *fixed* number of lecithin molecules and in-

262

Fig. 2. Hypothetical stretching experiment performed at constant T, p_e, μ_1^*, μ_2^* by which a bilayer repeat unit of some specified constitution (a, h, y_1) is formed out of a fully swollen lecithin/water liquid crystal (a^*, h^*, y_1^*). The contacting walls are imagined to have hydrocarbon-covered surfaces. Note that no work is expended that is due to the π forces.

troducing the (integral) molecular free energy per lecithin molecules, $\hat{\mu}_2$, by the relation

$$\hat{\mu}_2 = G/N_2 , \qquad (7)$$

we can rewrite these equations on alternative forms (constant T, p_e):

$$d\hat{\mu}_2^s = \tfrac{1}{2}\gamma da^s - \tfrac{1}{2}\pi a^s dh^s + \mu_1 dy_1^s , \qquad (8)$$

$$d\hat{\mu}_2^u = \mu_1 dy_1^u , \qquad (9)$$

where $a \equiv 2A/N_2$.

According to eq. (8), the tension γ and the pressure π are defined formally by the relations $\gamma = 2(\partial\hat{\mu}_2^s/\partial a^s)_{T,p,h^s,y_1^s}$ and $\pi = -(2/a^s) (\partial\hat{\mu}_2^s/\partial h^s)_{T,p,a^s,y_1^s}$. These relations are inconvenient, however, when it comes to evaluating γ and π from exprimental data since $\hat{\mu}_2^s$ is not in general known as a function of the (independent) variables a^s, h^s and y_1^s.

In order to proceed, suppose now that a liquid crystal characterized by some particular values of a, h and y_1 is formed reversibly by "stretching" in the X- and Y-directions at constant T and p_e from water and lecithin kept at the swelling limit of the liquid crystal where the chemical potentials are $\mu_1^* \sim \mu_1^o$ (superscript ^{o} denotes pure water) and μ_2^* (cf. Fig. 2). Integration of eq. (5) under these conditions yields

$$G^s = \hat{\mu}_2^s N_2^s = \gamma A^s + \mu_1^* N_1^s + \mu_2^* N_2^s . \qquad (10)$$

For the corresponding free liquid crystal we get

$$G^u = \hat{\mu}_2^u N_2^u = \mu_2 N_1^u + \mu_2 N_2^u . \qquad (11)$$

Dividing these two equations by N_2^s and N_2^u, respectively, and noting that $a \equiv 2A/N_2$, we obtain

$$\hat{\mu}_2^s = \tfrac{1}{2}\gamma a^s + \mu_1^* y_1^s + \mu_2^* , \qquad (12)$$

$$\hat{\mu}_2^u = \mu_1 y_1^u + \mu_2 . \qquad (13)$$

As the next step, let us compare a stressed ^{s}-state with the same a, h, y_1 values as for an unstressed ^{u}-state, i.e., let us assume that

$$a = a^u \simeq a^s, \quad h = h^u \simeq h^s, \quad y_1 = y_1^u \simeq y_1^s, \qquad (14)$$

implying that the molecular constitution of the two mechanically different states is approximately the same (Fig. 3). This is not unreasonable since only very minor adjustments are needed of the density profiles in order to pass from an unstressed to a mechanically stressed state in view of the fact that liquids are normally almost incompressible. Thus, by proper adjustment of $p_T(Z)$ and p_N, physico-chemical equilibrium with the surrounding bath at T, p_e, μ_1^* and μ_2^* can be realized without any sensible changes of the parameters a, h, y_1. Furthermore, we can also claim that the relation

$$\hat{\mu}_2 = \hat{\mu}_2^u \simeq \hat{\mu}_2^s \qquad (15)$$

should constitute a rather good approximation insofar as the equations (14) are fulfilled. This is
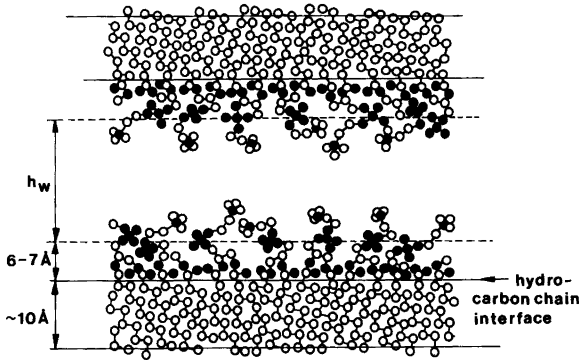
263

Fig. 3. Molecular constitution of a DLPC bilayer system.[6]

so because $\hat{\mu}_2$ is essentially a molecular Helmholtz free energy and it is well-known that the Helmholtz free energy of an approximately incompressible fluid is practically independent of pressure.[8]

By combining eqs. (12)–(15), we get

$$\hat{\mu}_2 - (\mu_1^* y_1 + \mu_2^*) = (\mu_1 - \mu_1^*)y_1 + (\mu_2 - \mu_2^*) = \tfrac{1}{2}\gamma a. \tag{16}$$

From this equation it appears that $\tfrac{1}{2}\gamma a$ corresponds to the excess free energy per lecithin molecule relative to the starred reference state at the swelling limit. The situation here is in fact completely analogous to an ordinary fluid interface where the bulk phase chemical potentials play the same rôles as μ_1^* and μ_2^* in the present context. Now, from eqs. (5) and (10), the following Gibbs-Duhem condition results (T, p_e are held constant):

$$-d\gamma = \pi dh + (N_1/A)d\mu_1^* + (N_2/A)d\mu_2^*, \tag{17}$$

which is a generalized Gibbs surface tension equation previously well-known from the thermodynamics of thin soap films (cf. Ref. 7). Accordingly, the swelling pressure π can be computed as the partial derivative

$$-\left(\frac{\partial \gamma}{\partial h}\right)_{T,p_e,\mu_1^*,\mu_2^*} = \pi, \tag{18}$$

where the reference state chemical potentials are fixed. In broad terms, this swelling pressure corresponds to the interaction force per unit surface area which might be measured by means of Israelachvili's surface force apparatus as a function of the separation between (hydrophobic) surfaces covered with lecithin molecules immersed in a μ_1^*-, μ_2^*-lecithin/water solution. However, when such an experiment is actually carried out in practice, as has been done recently by Marra and Israelachvili,[6] there should be a tendency to alter the packing densities of lecithin on the two interacting, cylindrically shaped, surfaces so as to amplify the attraction at comparatively large separations and attenuate the repulsion at short separations. Still, insofar as these interactive forces are of a moderate strength one might claim that a is kept approximately constant during such an experiment. Conversely, for the case under discussion of a free lamellar liquid crystal of variable water content, γ and π are equal to zero for mechanical reasons and the molecular surface area a and the repeat distance h vary in manners which are fixed by these mechanical conditions. Hence, as will be further elaborated below, when using eqs. (16) and (18) to evaluate the swelling pressure π, from vapour pressure data for free liquid crystals, we have to take into account that we are then presumably dealing with interacting bilayer surfaces of a packing density that varies with the bilayer separation h.

Now, using eq. (16) and the ordinary Gibbs-Duhem condition for bulk phases, viz.,

$$d\mu_2 + y_1 d\mu_1 = 0, \tag{19}$$

which must hold for the ordinary, free liquid crystal (γ, $\pi = 0$), it is easy to demonstrate that

$$\tfrac{1}{2}\gamma a = \int_{y_1}^{y_1^*} (\mu_1^* - \mu_1)\, dy_1 = kT \int_{y_1}^{y_1^*} [\ln(p_1^0/p_1)]dy_1, \tag{20}$$

implying that $\tfrac{1}{2}\gamma a$ can be obtained, rather simply, as a function of y_1 by means of integrating water vapour pressure data.

Eq. (20) can also be derived, if we so would prefer, without making any reference to surface thermodynamics. From (9), we obtain after adding $-\mu_1^* dy_1$ to both sides and removing the superscripts " which are now redundant,

$$d(\hat{\mu}_2 - \mu_1^* y_1) = (\mu_1 - \mu_1^*)dy_1. \tag{21}$$

Straightforward integration yields

$$(\hat{\mu}_2 - \mu_1^* y_1) - (\hat{\mu}_2^* - \mu_1^* y_1^*) =$$

$$(\mu_1 - \mu_1^*) y_1 + (\mu_2 - \mu_2^*) = \int_{y_1}^{y_1^*} (\mu_1^* - \mu_1) \mathrm{d}y_1 , \qquad (22)$$

which is the same as eq. (20). Eq. (16) says in addition, however, that the excess free energy quantity involved in eq. (22), $(\mu_1 - \mu_1^*) y_1 + (\mu_2 - \mu_2^*)$, is physically closely related to the lateral tension γ. This tension would arise if an initially unstressed liquid crystal characterized by h, a, y_1 and supposed to be enclosed by rigid but permeable walls, were placed in contact with a water solution of molecularly dispersed lecithin in equilibrium with liquid-crystalline lecithin at the swelling limit. Simultaneously, a swelling pressure π would develop.

By combining eqs. (18) and (20) we get

$$\pi = (2/a)(\mu_1^* - \mu_1) \frac{\mathrm{d}y_1}{\mathrm{d}h} + \gamma \frac{\mathrm{d}\ln a}{\mathrm{d}h} , \qquad (23)$$

where only the composition of the liquid crystal is supposed to vary but not its T, p_e, μ_1^*, μ_2^*-environment. For the lecithin/water system considered it turns out that the last term of eq. (23) is always small enough to be neglected compared with the first term on the right side of the equation. Thus, there is, indeed, a simple relation between the swelling pressure π and the water activity, at least in the case under discussion:

$$\pi = (2kT/a) \frac{\mathrm{d}y_1}{\mathrm{d}h} \ln(p_1^o/p_1). \qquad (24)$$

Note that the omission of the last term in eq. (23) also implies that the following approximate relations are valid

$$\pi a = 2(\mu_1^* - \mu_1) \frac{\mathrm{d}y_1}{\mathrm{d}h} = - \frac{\mathrm{d}(\gamma a)}{\mathrm{d}h} =$$

$$-2 \frac{\mathrm{d}(\hat{\mu}_2 - \mu_1^* y_1)}{\mathrm{d}h} \quad (T, p_e, \mu_1^*, \mu_2^* \text{ constant}), \qquad (25)$$

which are all, in fact, independent of our surface-thermodynamic point of departure and which

are, in addition, readily understood in physical terms.

A further reduction of eq. (24) becomes possible when we can account for the total volume per lecithin molecule by assuming the relation

$$v_1 y_1 + v_2 = \tfrac{1}{2} ah \qquad (26)$$

to hold where v_1 and v_2 are the (constant) molecular volumes of water and lecithin, respectively. This yields

$$\pi = \left(\frac{kT}{v_1} \right) \left[1 + \frac{\mathrm{d}\ln a}{\mathrm{d}\ln h} \right] \ln(p_1^o/p_1). \qquad (27)$$

Thus, the simplified and often used "osmotic pressure" equation

$$\pi = kT/v_1 \ln(p_1^o/p_1) \qquad (28)$$

holds only when the molecular surface area, a, is approximately independent of the repeat distance, h. This does not seem to be the case, however, for lecithin/water systems where it has been found experimentally that $\mathrm{d}\ln a/\mathrm{d}\ln h$ is of the order of 1.[3,4] To apply eq. (28) under these circumstances amounts primarily to making a mathematical transformation of the vapour pressure data that is devoid of any physical significance.

To summarize, we have derived a series of equations, eqs. (23), (24), (27) and (28), for computing the swelling pressure π. The approximations leading to eqs. (24) and (27) should be rather satisfactory whereas eq. (28) actually underestimates the swelling pressure to a substantial extent.

It is worth pointing out here that the factor $(1 + \mathrm{d}\ln a/\mathrm{d}\ln h)$ in our eq. (27) which links the swelling pressure π to vapour pressure data, is basically unrelated to a somewhat resembling factor introduced by Parsegian et al.[3] to account for the ratio of the work of separation of the bilayers to the work of straining the bilayers (cf. the Appendix). As a matter of fact, the papers by LeNeveu et al.,[1,2] Parsegian et al.[3] and Lis et al.[4] on repulsive hydration forces in lamellar liquid crystals are based entirely on eq. (28) or some thermodynamically equivalent equation.

About the molecular factors which determine $\frac{1}{2}\gamma a$, π and μ_1

Referring to eq. (25), we have the obvious expression

$$\mu_1^* - \mu_1 = -\frac{d(\frac{1}{2}\gamma a)}{dy_1} \qquad (29)$$

which provides a convenient starting point when considering those factors which actually determine the water chemical potential difference $\mu_1^* - \mu_1$. Hence, it appears that the excess free energy quantity $\frac{1}{2}\gamma a$ is of a fundamental importance in the present context. By differentiating $\frac{1}{2}\gamma a$ we can readily obtain π as well as $\mu_1^* - \mu_1$. Tentatively, we must distinguish among the following three major contributions to the change of the molecular excess free energy $\frac{1}{2}\gamma a$ relative to the fully swollen bilayer state.

(i) $\Delta(\frac{1}{2}\gamma a)_{conf} = (\hat{\mu}_2 - \hat{\mu}_2^*)_{conf}$. This term accounts for the change in hydrocarbon chain conformational free energy associated with a variable hydrocarbon chain packing density and can be estimated on basis of the statistical mechanical calculation results of Gruen.[9]

(ii) $\Delta(\frac{1}{2}\gamma a)_{hc,w} = (\hat{\mu}_2 - \hat{\mu}_2^*)_{hc,w}$. This term yields the free energy excess associated with the hydrocarbon/water contact. Typically, we can anticipate this contribution to be ~35 $(a - a^*)$ mJ per lecithin molecule, i.e., corresponding to somewhat less than 50 mJm^{-2} which is the surface free energy of a planar macroscopic hydrocarbon/water interface (cf. Ref. 10).

(iii) $\Delta(\frac{1}{2}\gamma a)_{pg,w} = [(\hat{\mu}_2 - \mu_1^* y_1) - (\hat{\mu}_2^* - \mu_1^* y_1^*)]_{pg,w}$. This term would account for the difference in excess free energy between the state considered and the reference state, due to the (favourable) interactions between the water and the polar cholin head groups (pg) and also to (unfavourable) interactions between the zwitterionic head groups and their image charges.[11]

The first contribution, $\Delta(\frac{1}{2}\gamma a)_{conf}$, should evidently be associated with a negative tension, or rather, a tangential *surface pressure,* inside the hydrocarbon core whereas the contribution (ii) which is localized largely in the contact zone between the water and hydrocarbon lamellae,
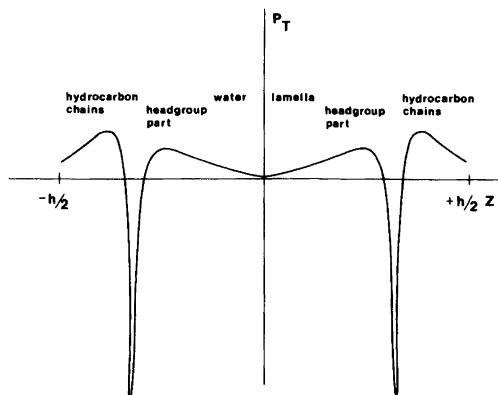

Fig. 4. Tentative tangential pressure (p_T) profile of a bilayer system.

should, of course, generate a *tension.* The last contribution (iii) is similarly expected to give rise to an extra tangential *pressure* within most of the water lamellar (cf. Fig. 4).

Using data for dilauroyllecithin (DLPC) presented in Ref. 4, kindly provided in full detail by A. Parsegian, and estimating $\Delta(\frac{1}{2}\gamma a)_{conf}$ and $\Delta(\frac{1}{2}\gamma a)_{hc,w}$ as described above, we have generated the plots in Fig. 5 where the lecithin head group area is on the x axis. The $\frac{1}{2}\gamma a$ function in Fig. 5 was actually calculated from Parsegian's water activity and X-ray diffraction data by means of the equation

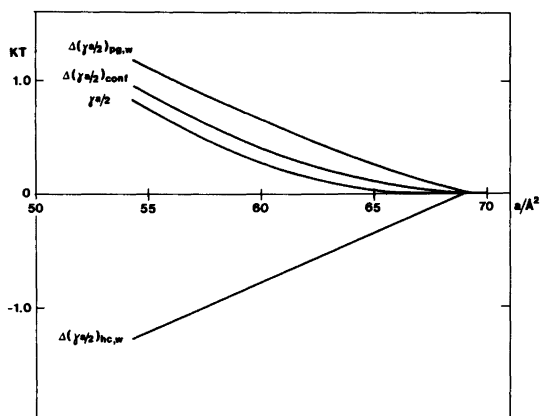$$\gamma a = (kT/v_1) \int_{ah_w}^{(ah_w)^*} [\ln(p_1^0/p_1)]d(ah_w), \qquad (30)$$

Fig. 5. The molecular free energy excess $\frac{1}{2}\gamma a$ and its different components plotted against the head group area, a.
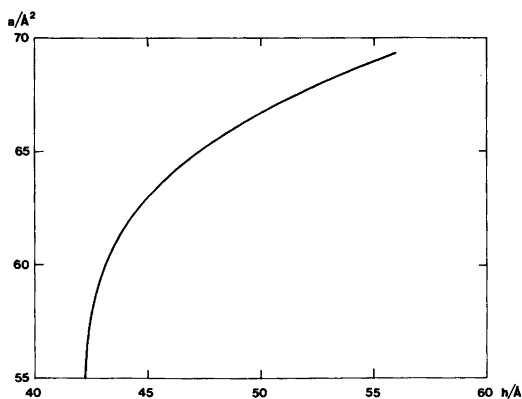
Fig. 6. The experimental a versus h_w function obtained for DLPC at 25 °C by Lis et al.[4]

which is eq. (20) in a slightly different disguise. v_1 was set equal to 29.9 Å^3 per H_2O molecule and v_2 = 2×326.4 + 324.5 = 977.3 Å^3 per lecithin molecule. $\Delta(\frac{1}{2}\gamma a)_{\text{pg.w}}$ was obtained as the difference

$$\Delta(\tfrac{1}{2}\gamma a)_{\text{pg.w}} = \tfrac{1}{2}\gamma a - \Delta(\tfrac{1}{2}\gamma a)_{\text{conf}} - \Delta(\tfrac{1}{2}\gamma a)_{\text{hc.w}}. \quad (31)$$

It appears from Fig. 5 that all three contributions to $\Delta(\frac{1}{2}\gamma a)$ listed above are sizeable. The conformational free energy change runs rather close and roughly parallel to the $\frac{1}{2}\gamma a$ function. Hence the unfavourable hydrocarbon-water contact contribution is nearly counterbalanced by the favourable hydration interaction with the cholin head groups.

It is evident from Fig. 5 that $\frac{1}{2}\gamma a$ has a minimum at $a^* \sim 69.5$ Å^2 where, by definition, this quantity must be equal to zero. This minimum arises because of the opposing effects of a "hydrocarbon" contribution, $\Delta(\frac{1}{2}\gamma a)_{\text{conf}}$, that wins for small a values and a "water" contribution, $\Delta(\frac{1}{2}\gamma a)_{\text{hc.w}} + \Delta(\frac{1}{2}\gamma a)_{\text{pg.w}}$, that tends to become increasingly unfavourable at large a values, in line with our previous results for micelles.[10,12] The latter contribution may also be described, at least to some extent, as a van der Waals attraction between the two lipid monolayers (cf. Ref. 4).

In the past it has often been assumed that such contributions as $\Delta(\frac{1}{2}\gamma a)_{\text{conf}}$ and $\Delta(\frac{1}{2}\gamma a)_{\text{hc.w}}$ can be neglected in comparison with the excess free energy of the water lamella, $\Delta(\frac{1}{2}\gamma a)_{\text{pg.w}}$. Such a proposition, however, is definitely not in accord with the results shown in Fig. 5 which indicate that all of the terms noted there have to be con-

sidered before valid comparisons can be made between experiments and theory as regards the magnitude and range of hydration forces.

The mechanism causing the head group area, *a*, to diminish simultaneously with *h*

In Fig. 6, we have plotted how a varies with h for dilauroyllecithin according to the data available. This kind of behaviour is typical for a large number of lecithin/water systems.[3,4] It is seen that a substantial bilayer expansion in the lateral direction takes place when increasing the water content. This expansion is accompanied by a diminishing hydrocarbon core thickness of each bilayer (cf. eq. (26)). In order to account for this observation, let us consider a free lamellar liquid crystal of lecithin/water in mechanical and physico-chemical equilibrium at the swelling limit where $h_w^* \sim 27.5$ Å and the chemical potentials are μ_1^* and μ_2^*. Suppose now that this liquid crystal is enclosed by four non-interacting walls, permeable to water only and perpendicular to the X- and Y-directions, and then transferred to the saturated water vapour phase where $p_1^* = p_1^\circ$. We next start to reduce the water content (i.e. h_w) of the liquid crystal by lowering the vapour pressure to below p_1°. Let us first assume that the lamellar area, A, and hence the head group area, a, is kept fixed while letting h_w (and thus also h) decrease. As a result of the process of gradually diminishing h_w it is likely that the (negative) excess free energy $(\frac{1}{2}\gamma a)_{\text{pg.w}}$ is also being reduced in magnitude, chiefly since this process would involve a removal of rather well-bound water molecules. Consequently, we may expect the surface pressure $-\gamma_{\text{pg.w}}$ to be reduced as well. This, however, would imply an *increase* of the overall lateral tension γ since γ_{conf} and $\gamma_{\text{hc.w}} \sim 70$ mNm^{-1} should remain approximately unaffected by the variation of h_w at constant a. In order to reestablish that γ = 0 at a water vapour pressure, $p_1 < p_1^\circ$, it would thus be needed to move the enclosing walls so as to diminish the head group surface area, a, in this way raising $-\gamma_{\text{pg.w}}$ and, above all, $-\gamma_{\text{conf}}$. By this lateral contraction, the free energy of the liquid crystal is, of course, also lowered. The mechanism proposed here to account for the decrease of the head group surface area, a, which is experimentally observed upon reducing the water chemical potential μ_1, thus implies that the observed response of the system is expected be-

cause of the requirements for the mechanical equilibrium of a free liquid crystal, γ, $\pi = 0$.

Comparison with direct surface force measurements

In Fig. 7, we compare graphically the γ versus h_w function generated by applying eq. (20) to the data of Lis et al.[4] with the corresponding function, $\Delta\gamma(SF)$, as obtained from direct measurements carried out by Marra and Israelachvili[6] of the surface forces operating between lecithin monolayers ($a \simeq 70$ Å^2) attached to hydrophobised mica surfaces. Furthermore, we have included the $\Delta\gamma_{pg,w}$ data of Fig. 5. Taking into account that the head group area is generally smaller ($a = 55–69.2$ Å^2) for the first set of (liquid crystal) data referred to here, it is evident that a reasonable agreement is within reach between the $\Delta\gamma_{pg,w}$ and $\Delta\gamma(SF)$ data. As regards the computed γ versus h_w function, however, we note an obvious disagreement with $\Delta\gamma(SF)$. This is in support of our conclusion that the γ function obtained from measurements on free liquid crystals has to be corrected for the free energy effects associated with the variable head group area before valid comparisons can be made with direct surface force measurements. In fact, it appears that generally there would be a rather close balance
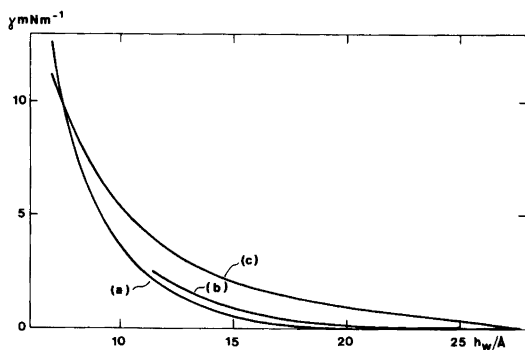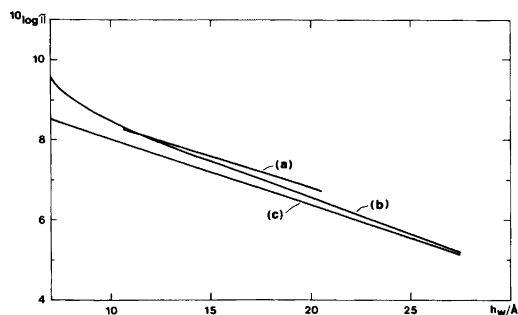

Fig. 8. Swelling/disjoining pressures π (in dynes/cm^2) plotted versus the bilayer separation h_w: (a) computed by differentiation of the $\Delta\gamma$ (SF) function (b) in Fig. 7; (b) computed from free liquid crystal data using eq. (27); (c) computed from the same data as in (b) but using eq. (28).

between favourable and unfavourable free energy effects on the water lamella and that the course of the γ function is effectively determined by $\hat{\mu}_{conf}$.

The emerging picture is basically much the same, of course, when comparing swelling pressures rather than lateral tensions. This is evident from Fig. 8 where the π versus h_w function based on liquid crystal data and Eq. (27) is largely below the swelling pressures derived from direct surface force measurements in spite of the fact that the head group packing is always denser in the former case. In addition, it is worth noting that the rather crude eq. (28) yields swelling pressures on the low side, particularly so for small bilayer separations.

Concluding remarks

Contrary to what has often been claimed during recent years, this thermodynamic study of lecithin/water lamellar liquid crystals indicates that there are major energetic effects accompanying the lateral bilayer expansion which occurs simultaneously with increasing the bilayer separation, h_w. These effects are chiefly due to changing the conformational state of the hydrocarbon chains and the extension of the hydrocarbon/water contact area. In order to make valid comparisons with direct surface force experiments as regards repulsive hydration forces, it is thus necessary to estimate these other contributions with a high degree of accuracy by using appropriate theoretical calculation schemes. Moreover, when consider-

Fig. 7. The lateral tension γ derived from liquid crystal data using eq. (20) (a) and the corresponding $\Delta\gamma(SF)$-function obtained by Marra and Israelachvili[6] for lecithin monolayers with $a \sim 70$ Å^2 (b). Also shown is the calculated $\Delta\gamma_{pg,w}$ function which refers to a-values ranging from 55 Å^2 at short separations to 69.2 Å^2 at the swelling limit (c).

ing the component of the swelling pressure π that is due to the interactions between water and the head groups and between the head groups and their image charges, corrections are also needed because of the variable surface density of polar groups. Still, this study indicates an approximate agreement between (vapour pressure and X-ray diffraction) data for free liquid crystals of lecithin and the corresponding direct surface force measurements.

Appendix: comments on the analysis of bilayer energetics given by Parsegian et al.

Parsegian et al.[3] have presented a short thermodynamic treatment of the energetic effects associated with the lateral bilayer expansion which occurs when increasing the bilayer separation h_w. Using our approach and notation, these authors argue as follows. In effect, eq. (8), q.v., is used as the starting point.

$$d\hat{\mu}_2 = \tfrac{1}{2}\gamma da - \tfrac{1}{2}\pi a dh + \mu_1 dy_1 \qquad (A1)$$

The volume condition (26), written in the form

$$h = 2v_2/a + h_w, \qquad (A2)$$

is introduced by means of which one can easily select a and h_w as the independent variables in place of a and h. Hence at constant T and p_e, we get the following alternative expression for the differential of $\hat{\mu}_2$:

$$d\hat{\mu}_2 = (\tfrac{1}{2}\gamma + \pi v_2/a)da - \tfrac{1}{2}\pi a dh_w + \mu_1 dy_1, \quad (A3)$$

from which it is evident that

$$\left(\frac{\partial \hat{\mu}_2}{\partial a}\right)_{T,p_e,h_w,y_1} = \tfrac{1}{2}\gamma + \pi v_2/a, \qquad (A4)$$

$$\left(\frac{\partial \hat{\mu}_2}{\partial h_w}\right)_{T,p_e,a,y_1} = -\tfrac{1}{2}\pi a, \qquad (A5)$$

The above partial derivatives were discussed at some length in Ref. 3 without, however, invoking their mechanical significance. There is also the obvious volume condition

$$ah_w = 2y_1v_1. \qquad (A6)$$

By assuming v_1 to remain constant, employing eq. (A6) and minimizing $\hat{\mu}_2$ at constant y_1, we can readily establish that the relation

$$\gamma + \pi h = 0 \qquad (A7)$$

must be fulfilled in order for $\hat{\mu}_2$ to have a minimum under the constraints imposed. However, for mechanical reasons, it is evident that $\pi = 0$ is the only acceptable solution when we are referring to a free liquid crystal system which can respond without any restrictions to forces operating in the Z-direction. Hence eq. (A7) implies that γ also equals zero for such a system. Contrary to this result, it is assumed implicitly in Ref. 3 that γ and π are both different from zero though satisfying (A7).

To minimize $\hat{\mu}_2$ at constant T,p_e and y_1 is equivalent, of course, to minimizing $G = F + p_eV$ at constant T,p_e and N_1,N_2. The partial solution (A7) results from limiting the geometrical variations by the *approximate* volume condition (A6). Allowing for density fluctuations, this coupling between the a- and h_w-variations might be removed and the complete solution $\gamma,\pi = 0$ obtained. However, the system considered is actually an entirely open system, immersed in a T,p_e,μ_1,μ_2 bath. For a system of this kind to be in mechanical equilibrium, the differential of the potential $\Omega + p_eV$ must vanish at all concievable geometrical variations at fixed values of the environmental variables T,p_e,μ_1,μ_2 (cf. eq. (4)). In a perhaps more straightforward way, this latter deductive procedure yields the two mechanical equilibrium conditions $\gamma = 0$, $\pi = 0$.

A further consequence of the circumstance that γ and π are necessarily zero for a free liquid crystal is that no work needs to be expended at a (first-order) differential change of a or h_w. Consequently, there is no sense in forming the ratio

$$X \equiv (\partial\hat{\mu}_2/\partial h_w)_{T,p_e,a,y_1}\, dh_w/(\partial\hat{\mu}_2/\partial a)_{T,p_e,h_w,y_1}\, da$$
$$(= d\ln h_w/d\ln a) \qquad (A8)$$

as was done by Parsegian et al.[3] since both the

numerator and the denominator are equal to zero as follows from eqs. (A4) and (A5) after inserting $\gamma, \pi = 0$. The equality within paranthesis in eq. (A8) results from making use of eqs. (A4), (A5), (A7) and erroneously assuming that $\gamma, \pi \neq 0$. In order to estimate the ratio of the free energy changes associated with bilayer separation and bilayer deformation, respectively, it is necessary to consider in detail the molecular mechanisms involved, similarly to how we have attempted to do it in this paper.

References

1. LeNeveu, D. M., Rand, R. P. and Parsegian, V. A. *Nature 259* (1976) 601.
2. LeNeveu, D. M., Rand, R. P., Parsegian, V. A. and Gingell, D. *Biophys. J. 18* (1977) 209.
3. Parsegian, V. A., Fuller, N. and Rand, R. P. *Proc. Natl. Acad. Sci. USA 76* (1979) 2750.
4. Lis, L. J., McAlister, M., Fuller, N., Rand, R. P. and Parsegian, V. A. *Biophys. J. 37* (1982) 657.
5. Guldbrand, L., Jönsson, B. and Wennerström, H. *J. Colloid Interface Sci. 89* (1982) 532.
6. Marra, J. and Israelachvili, J. *Biochemistry.* Submitted for publication.
7. Eriksson, J. C. and Toshev, B. *Colloids and Surfaces 5* (1982) 24.
8. Guggenheim, E. A. *Thermodynamics,* 4th edition. North-Holland Publ. Co., Amsterdam 1959. 134.
9. Gruen, D. W. R. *J. Phys. Chem. 89* (1985) 153.
10. Eriksson, J. C., Ljunggren, S. and Henriksson, U. *J. Chem. Soc., Faraday Trans. 2, 81* (1985) 833.
11. Jönsson, B. and Wennerström, H. *J. Chem. Soc., Faraday Trans. 2, 79* (1983) 19.
12. Eriksson, J. C. and Ljunggren, S. *J. Chem. Soc., Faraday Trans. 2, 81* (1985) 1209.