REPULSION OF INTERFACES DUE TO BOUNDARY WATER

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The exponential repulsion of bilayers in lecithin–water dispersions is explained as arising from modification of water structure near the lecithin–water interface.

A recent measurement by LeNeveu et al. [1] provided the first accurate data on strong repulsive forces between lecithin bilayers. The strength of the interaction immediately rules out previous explanations [2,3] in terms of forces between zwitterion dipoles.

Both differential scanning calorimetry [4] and NMR [5–8] experiments indicate a change in water structure near the lecithin–water interface. Such water is commonly referred to as "bound" or "frozen". More detailed experiments [7] reveal several different types of "bound" water. Up to 21 water molecules per lecithin molecule are oriented to some extent. It is therefore natural to examine the bilayer interaction arising from the modification of water structure near the interface with lecithin. We show here that the data of ref. [1] are explained on such a basis with only very general assumptions. While the discussion here is applied to lecithin bilayers, the result is a general feature of the interaction between polar interfaces in aqueous solutions.

Near the interface with lecithin, water molecules have preferred orientation, while at the same time the rate of molecular motion is severely restricted [5–8]. To find the ordering of water between bilayers we assume that the interfaces are positioned at $x = d/2$ and $x = -d/2$. If the order imposed by the interfaces is described by the order parameter $\eta(x)$, the Landau expansion of the free energy density is

$$g = g_0 + a\eta^2(x) + b\eta^3(x) + \ldots + c[\partial\eta(x)/\partial x]^2 + \ldots . \quad (1)$$

The free energy has to be minimized subject to boundary conditions determining the values of $\eta(d/2)$ and $\eta(-d/2)$. Since the mean orientation at the two interfaces is in opposite directions, the boundary conditions are $\eta(d/2) = -\eta(-d/2) = \eta_0$. Bulk water is not ordered, and it is therefore enough to keep only quadratic terms in eq. (1). With these assumptions, the minimization problem leads to the differential equation

$$\mathrm{d}^2\eta(x)/\mathrm{d}x^2 - (a/c)\,\eta(x) = 0 . \quad (2)$$

The solution satisfying the boundary conditions is

$$\eta(x) = \eta_0 \sinh[(a/c)^{1/2}x]/\sinh[(a/c)^{1/2}d/2] . \quad (3)$$

The excess free energy per unit area is

$$\Delta G = \int_{-d/2}^{d/2} (g - g_0)\,\mathrm{d}x = 2(ac)^{1/2}\eta_0^2 \coth[(a/c)^{1/2}d/2]. \quad (4)$$

The pressure on the interfaces is given by the derivative

$$P = \partial\Delta G/\partial d = -\epsilon_0/\sinh^2(\xi_0 d/2) , \quad (5)$$

where we have introduced the notation

$$\xi_0 = (c/a)^{1/2}, \qquad \epsilon_0 = a\eta_0^2 . \quad (6)$$

For $d > \xi_0$, the repulsion follows an exponential law

$$P = -4\epsilon_0 \, e^{-d/\xi_0} . \qquad (7)$$

Before this result is compared with experiment, we should ask what are the expected values for ξ_0 and ϵ_0. In Landau theory, ξ_0 is the order parameter correlation length. Analogy with orientational ordering in other systems, e.g. ferromagnets or liquid crystals, suggests that the correlation length ξ_0 is of the order of the intermolecular separation.

With only quadratic terms retained in eq. (1), ϵ_0 is the free energy change associated with ordering the system to the state $\eta(x) = \eta_0$. Since the structure of the boundary water is not known, a priori we can only know the order of magnitude for ϵ_0. The relevant energy scale is established by the energy of the hydrogen bond in ice (6.7 kcal mole^{-1}) and the latent heat of fusion of water (1.4 kcal mole^{-1}).

LeNeveu et al. [1] have found that their data covering the region $17.5 < d < 26.6$ Å are well described by an exponential function with the resulting values of $\xi_0 = 1.93$ Å and $4\epsilon_0 = 1.0 \times 10^{11}$ dyne cm^{-2}. To compare this with the discussion in the previous paragraph we note that at 10°C the first peak in the oxygen–oxygen correlation function for water is at 2.8 Å, while the first peak in the oxygen–hydrogen correlation function is at 1.9 Å [9]. The experimental value for ϵ_0 amounts to the ordering free energy of 9.6 kcal mole^{-1}. It should be noted [1] that the definition of d using lecithin volume fractions [1] does not take into account the intercalation of water and lecithin polar heads. The value of ϵ_0 depends sensitively upon the values of d. For example, if the effective thickness of the water region is 4 Å units smaller (due to water–lecithin mixing) the corresponding experimental value of ϵ_0 is reduced by almost one order of magnitude.

In conclusion, we have found that the modification of water structure near the lecithin–water interface accounts for the strong repulsion between the interfaces observed by LeNeveu et al. We expect a similar situation to arise near other strongly polar interfaces in an aqueous environment. An analogous effect, where membrane integral proteins modify the lipid chain order leading to an effective protein–protein attraction within a membrane, has been considered in a separate report [10]. A formulation of the present theory where water order is calculated for a discrete number of layers has also been constructed. While the results are algebraically more complicated, the conclusions remain unchanged. However, in a discrete theory it is easier to follow the molecular mechanism of water ordering and the work on this point is in progress.

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