Second-Order Phase Changes in Phospholipid Monolayers at the Oil/Water Interface and Related Phenomena

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Surface pressure against area isotherms for phospholipid monolayers at the oil/water interface display second-order phase transitions which resemble the ones between " condensed " and " expanded " monolayers at air/water interfaces. Behaviour at lower surface densities indicates a strong repulsive interaction between the phospholipid molecules at the oil/water interface. A statistical mechanical model is developed in which the monolayer molecules occupy sites on a two-dimensional lattice and adopt one of two possible orientational states. By appropriate choice of the interaction energies of the molecules in these states and the use of order–disorder statistics the features characteristic of a second-order phase transition are obtained for isotherms at both interfaces. From the point of view of our present theory what is termed the " expanded " state is in fact a fluid phase whose degree of order is lower than that of the " condensed " state. The choice of a large overall attractive interaction energy between nearest-neighbours yields the liquid–vapour phase transition which has been observed in experiments at the air/water interface whereas with an overall repulsive interaction the liquid–vapour transition is absent, as in the oil/water case.

1. INTRODUCTION

In recent years attention has been increasingly directed towards the phase properties of natural membranes to explain their structure and some of their functions.[1-9] Once it was recognised that lipid fractions isolated from membranes display phase properties similar in many aspects to those of the parent membrane, the use of lipid bilayers, multilayers or vesicles as membrane models gained credibility and numerous physico-chemical studies ensued. The major distinction between real and model membranes was seen in the main phase transition, the one for pure lipids being much sharper than that found in membranes or membrane-derived lipids where cooperative effects are upset by the wide distribution of chain lengths, the presence of double bonds or branching in the chains and interactions with non-lipid species.

An important adjunct to this work on bilayer models has been the study of lipid monolayers at the air/water (A/W) interface. Under suitable conditions monolayers of insoluble long-chain amphipathic molecules undergo two-dimensional phase transitions.[10-12] In particular, two-dimensional analogues of the gaseous, liquid and solid states can be recognized, but in addition several intermediate states have been variously described,[10, 11, 13, 14] albeit with different nomenclature. Gaines [12] has reviewed these phase properties and stressed the need to distinguish phase changes from kinetic effects during monolayer compression. Two well-established intermediate states termed " liquid-expanded " and " liquid-condensed " occur over a

range of surface densities which correspond to the head-group densities in the plane of liquid bilayers.   At the present time these intermediate phases are little understood. As in bilayers or the membrane lipid core, changes in parameters such as the length, unsaturation or branching of the hydrocarbon chains, size or charge of the head groups, temperature or even salt concentration in the aqueous phase affect monolayer phase properties to a remarkable degree.   A study of monolayers has the advantage that the number density of lipid molecules is accurately known and is an easily controlled independent variable; this factor coupled with the ease with which lipid mixtures can be studied makes monolayers one of the most accessible systems for investigating phase behaviour.   The comprehensive data of Phillips and Chapman [15] on fully saturated lecithins and cephalins cover the most relevant classes of lipid monolayers for membrane studies.   At intermediate chain lengths (C_{14}—C_{16}) and temperatures near ambient, Phillips and Chapman observed second order phase transitions* which depended on the nature of the monolayer head group; similar distinctions between lecithins and cephalins have been recognised in lipid bilayers. The isotherms bear a strong resemblance to the classic ones found for non-ionised fatty acids of intermediate chain length [10] where an increase of temperature or decrease of chain length moves the monolayer state from liquid-condensed to liquid-expanded.

The temperature, chain length and head-group dependence of the phase transitions in phospholipid monolayers have recently been followed at the non-polar oil/water (O/W) interface using both single and multi-component monolayers.[16-18]   The mixing or partial mixing of the monolayer chains with hydrocarbon solvent extends the range of chain lengths for which the second order phase transition is found, and for the chain lengths studied (up to C_{22}) gives asymptotic surface pressure-area isotherms at low surface pressure out to the limits of measurement with the present apparatus on ultra-dilute monolayers.

In this paper we apply a statistical mechanical approach for critical phenomena to the monolayer phase transitions, and have chosen to interpret the well-defined second order phase changes found with di-C_{16} lecithin at the O/W interface. Modifications to the theory are then made to explain the form of the phase changes for the same molecule at the A/W interface.   The effects of chain length and head-group as well as the implications for lipid bilayers and membrane models will be dealt with in a later paper.

Before developing our model we must briefly consider some previous work on the statistical mechanics of phase transitions in lipid systems.   Nagle [19] [and later in ref. (20), (21)] regards the co-operative rotation of chain-segments as the essential feature in the ordering transitions for lipid monolayers and bilayers.   In his model the segments occupy edges of a triangular lattice and the chains are of infinite length, the low temperature all *trans*-configuration of a molecule being represented as one in which the segments lie in a straight line.   It is shown [19] that this model is mathematically equivalent to a lattice dimer assembly, for which accurate results are obtainable.   The van der Waals, head-group and extended hard-core interactions are approximated by mean–field terms.   In Nagle's monolayer model [20, 21] the transitions involve a discontinuity in the density, a feature not apparently shared by the experimental results.   Nagle attributes the discrepancy to either kinetic or boundary effects in the experimental systems.   It should be remarked however that the second-order or " kink-point " transitions have been observed in a number of systems over many years.   Also, if either the non-attainment of full equilibrium or

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* By a second order phase transition we mean a transition showing a discontinuity in the slope of the isotherm without a discontinuity in density.

the insufficient size of the adsorbed phase prevents the occurrence of a density-discontinuity it is hard to see how they could give rise to a discontinuity in the slope of pressure against density. It may also be noted that infinite chain length, though crucial to Nagle's theory, is unrealistic, and that experimental results, like the temperature and density at which the transition occurs, are dependent on the length of the finite chain. (See section 4, below).

Scott [22] gives approximate solutions for cell models of lipid layers where, as in Nagle's model, the chains lie in a plane but are now of finite length with their ends on a line. He remarks that the presence of a mean–field approximated Van der Waals interaction is necessary for the occurrence of transitions, which are first order in character. This is to be expected, since the model is essentially one-dimensional and transitions can only occur in one-dimensional models with interactions of infinitely long range to which mean-field approximated energies implicitly correspond. Scott compares his theoretical results with the monolayer experiments of Phillips and Chapman.[15] However, it should be noted that in Scott's results the transitions are of the first-order Van der Waals fluid type and thus, like Nagle's, show a density-discontinuity. Rather similar remarks apply to the mean-field theory of Marčelja [23] who again compares theoretical first-order transitions with the data of Phillips and Chapman. In earlier work, Scott [24] considered a model where the molecules have several rotational states and can also be displaced from cell-centres to interstitial sites, and which displays successive first-order transitions. It should be remarked that Nagle, Scott and Marčelja all considered monolayer systems where the carbon chains are in air and there is a fairly long-range attractive force between them whereas a large part of the present paper is concerned with a system where the carbon chains are in an oil phase, an environment chemically similar to the chains.

2. THE MODEL AND FREE ENERGY

In the statistical theory we wish to make the film area $\mathscr{A}$ variable for a fixed number, M, of identical monolayer molecules. We adopt a model in which each head group is localised on one of N available sites in a plane lying parallel to the interface. The area A_0 per site is taken as constant and $N-M$ sites are vacant. To introduce the possibility of orientational ordering each molecule is supposed to be in one of two orientational states, labelled 1 and 2 respectively. Denoting the area per molecule by A, the fraction of occupied sites by ρ, the number of vacant sites or " holes " by N_h and the numbers of molecules in the two orientational states by N_1 and N_2 respectively, we have

$$\rho = M/N = A_0/A$$
$$N_1 + N_2 = M = N\rho, \quad N_h = N - M = N(1 - \rho). \tag{2.1}$$

The sites are regarded as arranged in a regular two-dimensional array of coordination number z so that we are using a " lattice gas " type model for the monolayer. Nearest-neighbour pairs of types 11 and 22 have interaction energy $-\varepsilon - J$ but nearest-neighbour pairs of type 12 have interaction energy $-\varepsilon + J\,(J > 0)$. No interaction is assumed for pairs at greater than nearest-neighbour distance. The parameter J corresponds to a preferential interaction between similarly oriented molecules while ε, which may be positive or negative, represents the orientation-independent part of the intermolecular interaction. We refer to J and ε as " energies " for brevity and correspondence with existing statistical theory. However, the process of bringing chain molecules together and changing their relative configuration may well involve changes of entropy as well as energy. Hence in the interpretation of experimental

results it may be necessary to regard ε and J as temperature-dependent free energies of interaction. This has no effect on the form of the equilibrium conditions at a given temperature.

It is assumed that in a monolayer at given temperature and surface density the orientational species and holes are in thermodynamic equilibrium. The model is thus formally equivalent to that of Bell [25] who considered the effect of the introduction of a neutral component on phase-separation or ordering. Since diluting atoms there took the place of the " holes " of the present model the problem of the variation of pressure with density ρ, which is central to the present paper, did not arise. The present system is also equivalent to the equilibrium form of a diluted Ising model in a zero external field. Bell [26] pointed out the distinction between the equilibrium or " annealed " form of the model and the " frozen " or " quenched " case in which the distribution of the diluting atoms is fixed. In recent years most work on the diluted Ising model has been done on random mixtures which are a particular example of the frozen case, and thus is not relevant to the system considered in the present paper. The diluted Ising model has recently been discussed by Essam,[27] Rapaport,[28] Domb [29] and Bell.[30]

We shall use a first-order statistical approximation for the three species system in a formulation similar to that of Bell [25] with certain improvements due to Wheeler and Widom.[31] Denoting the number of nearest neighbour i-j pairs by N_{ij}, the configurational energy is given by

$$E_{\mathrm{c}} = (N_{12} - N_{11} - N_{22})J - (N_{12} + N_{11} + N_{22})\varepsilon, \tag{2.2}$$

the parameters ε and J having been introduced above. Using the label " h " for vacant sites or " holes " and disregarding boundary effects, the species and pair numbers are connected by the relations

$$N_{11} + \tfrac{1}{2}N_{12} + \tfrac{1}{2}N_{1\mathrm{h}} = \tfrac{1}{2}zN_1,$$
$$N_{22} + \tfrac{1}{2}N_{12} + \tfrac{1}{2}N_{2\mathrm{h}} = \tfrac{1}{2}zN_2, \tag{2.3}$$
$$N_{\mathrm{hh}} + \tfrac{1}{2}N_{1\mathrm{h}} + \tfrac{1}{2}N_{2\mathrm{h}} = \tfrac{1}{2}zN_{\mathrm{h}}.$$

From these relations and (2.1) it can be seen that we cannot regard all the species and pair numbers as independent variables. We choose N_{11}, N_{22}, N_{hh} and N_2 as dependent variables given in terms of the others by (2.1) and (2.3). Eliminating dependent variables the expression for E_{c} becomes

$$E_{\mathrm{c}} = 2N_{12}J + \tfrac{1}{2}(J + \varepsilon)(N_{1\mathrm{h}} + N_{2\mathrm{h}}) - \tfrac{1}{2}zM(J + \varepsilon). \tag{2.4}$$

[The energy parameters w and w' of Bell [25] correspond to $2J$ and $\tfrac{1}{2}(J + \varepsilon)$ here]. The configurational free energy is given by

$$F_{\mathrm{c}} = E_{\mathrm{c}} - kT \ln g, \tag{2.5}$$

where g is the number of the configurations on the lattice corresponding to a given set of species and pair numbers. The first order approximation is introduced by writing

$$g = \left(\frac{N_1! N_2! N_{\mathrm{h}}!}{N!}\right)^{z-1} \frac{(\tfrac{1}{2}zN)!}{N_{11}! N_{22}! N_{\mathrm{hh}}! \{(\tfrac{1}{2}N_{12})!(\tfrac{1}{2}N_{1\mathrm{h}})!(\tfrac{1}{2}N_{2\mathrm{h}})!\}^2}. \tag{2.6}$$

The internal equilibrium relations are obtained by minimising F_{c} with respect to the independent internal variables N_{12}, $N_{1\mathrm{h}}$, $N_{2\mathrm{h}}$ and N_1, for given values of the external or thermodynamic variables M, T and N (equivalent to film area $\mathscr{A} = NA_0$).

After using Stirling's formula for terms in $\ln g$, we have the necessary equilibrium conditions

$$\frac{\partial F_c}{\partial N_{12}} = kT\{\ln\left(\tfrac{1}{2}N_{12}\right)-\tfrac{1}{2}\ln N_{11}-\tfrac{1}{2}\ln N_{22}\}+2J = 0 \tag{2.7}$$

$$\frac{\partial F_c}{\partial N_{1h}} = kT\{\ln\left(\tfrac{1}{2}N_{1h}\right)-\tfrac{1}{2}\ln N_{11}-\tfrac{1}{2}\ln N_{hh}\}+\tfrac{1}{2}(\varepsilon+J) = 0 \tag{2.8}$$

$$\frac{\partial F_c}{\partial N_{2h}} = kT\{\ln\left(\tfrac{1}{2}N_{2h}\right)-\tfrac{1}{2}\ln N_{22}-\tfrac{1}{2}\ln N_{hh}\}+\tfrac{1}{2}(\varepsilon+J) = 0 \tag{2.9}$$

$$\frac{\partial F_c}{\partial N_1} = kT\{\tfrac{1}{2}z \ln (N_{11}/N_{22})-(z-1)\ln (N_1/N_2)\} = 0. \tag{2.10}$$

We may use eqn (2.10) which represents equilibrium with respect to long range orientational ordering, to define a parameter s by

$$s = (N_2/N_1)^{1/z} = (N_{22}/N_{11})^{1/2(z-1)}. \tag{2.11}$$

Long range orientational order exists when $s \neq 1$ but when $s = 1$ the system is disordered. Since the states 1 and 2 are equivalent in their properties there is always a " disordered " solution to the equilibrium equations but at lower temperatures and higher densities " ordered " solutions appear which reduce the free energy relative to the disordered state. It is convenient to introduce a second parameter u by

$$u^2 = N_{hh}/N_{11} \tag{2.12}$$

and Boltzmann factors η and ξ by

$$\eta = \exp(-2J/kT), \quad \xi = \exp(-\tfrac{1}{2}(\varepsilon+J)/kT). \tag{2.13}$$

In conjunction with eqn (2.11) the equilibrium equations can now be expressed in the form

$$N_{12} = 2\eta s^{z-1}N_{11}, \; N_{1h} = 2\xi u N_{11}, \; N_{2h} = 2\xi s^{z-1}u N_{11}. \tag{2.14}$$

We follow different routes to the solution of the equilibrium equations in the ordered and disordered states respectively. In the ordered state we substitute from eqn (2.11) and (2.14) into the relation

$$N_2/N_1 = (N_{22}+\tfrac{1}{2}N_{12}+\tfrac{1}{2}N_{2h})/(N_{11}+\tfrac{1}{2}N_{12}+\tfrac{1}{2}N_{1h}) \tag{2.15}$$

which is derived from eqn (2.3). The resulting relation can be solved for u to give

$$u = \{s^{z-1}-s-(s^{z-1})\eta\}/\{\xi(s-1)\}. \tag{2.16}$$

A relation between the ordering parameter s and the density ρ can be obtained by again using eqn (2.3) and substituting from eqn (2.11) and (2.14) to give

$$\begin{aligned}
\frac{1-\rho}{\rho} &= \frac{N_h}{M} = \frac{N_h}{(1+s^z)N_1} = \frac{N_{hh}+\tfrac{1}{2}N_{1h}+\tfrac{1}{2}N_{2h}}{(1+s^z)(N_{11}+\tfrac{1}{2}N_{12}+\tfrac{1}{2}N_{1h})}\\
&= \frac{u(u+\xi+\xi s^{z-1})}{(1+s^z)(1+\eta s^{z-1}+\xi u)}.
\end{aligned} \tag{2.17}$$

In conjunction with eqn (2.16), eqn (2.17) can be regarded as an implicit equation for the ordering parameter s at given density and temperature. It is, however, much simpler to assume values of s and calculate the corresponding values of the density ρ at given temperature.

In the disordered state, when $s = 1$, eqn (2.16) for u becomes indeterminate. However eqn (2.17) can now be treated as a quadratic giving u in terms of density and temperature. Discarding the negative solution we then have

$$u = \rho^{-1}[(1-2\rho)\xi + \{(1-2\rho)^2\xi^2 + 2\rho(1-\rho)(1+\eta)\}^{\frac{1}{2}}]. \tag{2.18}$$

3. SURFACE PRESSURE, ORDERING AND PHASE SEPARATION

We first obtain an expression for the surface pressure Π of the monolayer of M molecules on a surface of area $\mathscr{A} = NA_0$ where A_0, the area per site, is taken as constant. Thus

$$\Pi = -(\partial F_c/\partial \mathscr{A})_{M,T} = -A_0^{-1}(\partial F_c/\partial N)_{M,T}. \tag{3.1}$$

Taking into account the dependence of N_h and N_{hh} on N through eqn (2.1) and (2.3) respectively, F_c, as given by eqn (2.5) and (2.6) yields

$$\begin{aligned}\Pi A_0/kT &= (z-1)\ln(N_h/N) - \tfrac{1}{2}z\ln\{N_{hh}/(\tfrac{1}{2}zN)\}\\ &= (\tfrac{1}{2}z-1)\ln(N_h/N) - \tfrac{1}{2}z\ln\{N_{hh}/(\tfrac{1}{2}zN)\}.\end{aligned} \tag{3.2}$$

Again using eqn (2.1) and (2.3) and also the equilibrium conditions in the form of eqn (2.14) we finally derive

$$\Pi A_0/kT = \tfrac{1}{2}z\ln\left\{\frac{u+\xi(1+s^{z-1})}{u}\right\} + (\tfrac{1}{2}z-1)\ln(1-\rho). \tag{3.3}$$

We now consider the transition from the orientationally ordered to the disordered state, distinguishing quantities evaluated at the transition point by the index t. By allowing s to tend to the limit 1, eqn (2.16) gives

$$u_t = (z-2-z\eta)/\xi. \tag{3.4}$$

Substitution of $s = 1$ and $u = u_t$ in eqn (2.17) yields, after some manipulation,

$$\frac{A_0}{A_t} = \rho_t = \frac{(z-1)(1-\eta)\xi^2}{\tfrac{1}{2}(z-2-z\eta)^2 + \{(2z-3)-(2z-1)\eta\}\xi^2}. \tag{3.5}$$

Eqn (3.5) gives the critical ordering density ρ_t as a function of temperature. A value $\rho_t < 1$ is found for all $kT < kT_1 = 2J/\{\ln z/(z-2)\}$ and $\rho_t \to 1$ as T tends to T_1 from below. For $\rho > \rho_t$ ($A < A_t$) the free energy is minimised by an "ordered" solution of the equilibrium relations with $s \neq 1$ but for $\rho < \rho_t$ the system is disordered with $s = 1$. The pressure at the transition point is found by substituting $s = 1$ and $u = u_t$ in eqn (3.3), yielding

$$\Pi_t A_0/kT = \tfrac{1}{2}z\ln\left(1 + \frac{2\xi^2}{z-2-2\eta}\right) + (\tfrac{1}{2}z-1)\ln(1-\rho_t). \tag{3.6}$$

A discontinuity in the slope $d\Pi/dA$ (or $d\Pi/d\rho$) is found at the transition point on any isotherm for $T < T_1$ and the value of $-d\Pi/dA$ is larger on the high area (low ρ) side of the transition point than it is on the low area (high ρ) side. This type of discontinuity occurs for both positive and negative values of ε and thus provides a theoretical equivalent for the slope-discontinuity observed in (Π, A) isotherms for both monolayers where the overall intermolecular interaction is attractive and monolayers where it is repulsive. Slope-discontinuities are shown for these two cases in fig. 3 and 2 respectively of section 4 below.

For small ρ, putting $s = 1$ in eqn (3.3) and using eqn (2.18) it is possible to show that

$$\Pi A_0/kT = \rho + \tfrac{1}{2}\rho^2[1 - z\{\exp(\varepsilon/kT)\cosh(J/kT) - 1\}] + \mathcal{O}(\rho^3). \tag{3.7}$$

This result is more general than the first order method. It gives the first two terms in an accurate virial series and can be obtained from the low density terms in a series expansion for the grand partition function. If $\varepsilon = J = 0$, eqn (3.7) reduces to the expansion for a hard-core lattice gas and it can be seen that the pressure is greater than that for such a gas if

$$\exp(-\varepsilon/kT) > \cosh(J/kT) \tag{3.8}$$

while the pressure is reduced relative to such a gas if the inequality eqn (3.8) is reversed. For $\varepsilon > 0$ it follows that the overall intermolecular interaction is attractive at low densities for all temperatures while for $-\varepsilon > J$ the reverse is true. For $0 > \varepsilon > -J$, the inequality (3.8) is satisfied at high temperatures but not at low temperatures.

To discuss phase-separation we need an expression for the configurational chemical potential

$$\mu_c = (\partial F_c/\partial M)_{\mathscr{A},T} = (\partial F_c/\partial M)_{N,T}. \tag{3.9}$$

With similar methods to those used in deriving expressions for Π we obtain

$$\begin{aligned}
\mu_c &= -\tfrac{1}{2}z(J+\varepsilon) + kT\left[(z-1)\ln\frac{N_h}{N_2} - \tfrac{1}{2}z\ln\frac{N_{hh}}{N_{22}}\right] \\
&= kT\left[(z-1)\ln\left(\frac{(1-\rho)(1+s^z)}{\rho}\right) - z\ln(u/\xi)\right].
\end{aligned} \tag{3.10}$$

For large enough positive values of ε, phase-separation occurs in the disordered region. From eqn (2.18), (3.3) and (3.10) it can be verified that the disordered conjugate phases correspond to pairs of densities $(\rho, 1-\rho)$. Hence the conjugate phases can be found by calculating pressure and chemical potential for pairs of values ρ and $1-\rho$ and varying ρ till $\Pi A_0/kT$ and μ_c/kT both take equal values at ρ and $1-\rho$.

At lower temperatures separation between high density ordered phases and low density disordered phases occurs. This type of phase-separation is started either by the merging of the ordered region with the region of disordered phase separation or by the setting in of instability on the order–disorder transition curve. The conjugate phases are now most easily obtained by plotting μ_c/kT against $\Pi A_0/kT$ and finding the intersection of the low density and high density branches of the curve either graphically or numerically. The two middle curves of fig. 3 of section 4 below display disordered phase separation at values of A higher than the value at which the ordering transition with the slope-discontinuity on the (Π, A) curve occurs. The lowest temperature curve shown on the same figure illustrates the situation when the ordering transition has been incorporated in the phase-separation region and the conjugate phases are respectively ordered and disordered.

We have not attempted here to give a detailed account of the mechanism of orientational ordering but have merely assumed the existence of " similarly oriented " and " oppositely oriented " states for a nearest-neighbour pair of molecules. For definiteness we have taken the similarly oriented state as that of lowest energy $(J > 0)$ which gives order of " ferromagnetic " type. However the same formalism can be used when the members of a pair are oppositely oriented in the lowest energy state $(J < 0)$ giving rise to order of " antiferromagnetic " type, such as that postulated in egg lecithin bilayers. The correspondence between ferromagnetism and anti-ferromagnetism is well-known for the Ising model. Bell [25] extended this correspondence to equilibrium diluted systems, considering phase-separation and sub-lattice order–disorder which are respectively equivalent to ferromagnetic

and antiferromagnetic ordering. An essential condition is that the lattice should be " loose-packed " which means that it divides into two equivalent sub-lattices with all the nearest-neighbours of a site in one sub-lattice situated in the other sub-lattice. It is then not difficult to show that if the sign of J is changed from positive to negative while ε remains unchanged the new equilibrium state at any tempera-ture and density can be obtained from the old one simply by reversing the orientations of the molecules on one sub-lattice while leaving the occupation of the other sub-lattice unaltered. The ground state of the assembly for $J > 0$ with all molecules lined up now goes over into a ground-state for $J < 0$ with the molecules on the two sub-lattices oppositely oriented. The form of the pressure–density isotherm is unchanged. The only modification needed in the numerical work below results from the fact that the triangular lattice is not loose-packed so that for anti-ferromagnetic order we would have to use, say, the quadratic lattice and change z from 6 to 4. Results, however, would not be changed in any essential respect.

4. NUMERICAL RESULTS AND DISCUSSION

We first attempt a comparison between experimental results for di-C_{16} lecithin monolayers at the O/W interface at the three temperatures 10, 15 and 20°C and theoretical results derived from the model discussed in previous sections. The experimental (Π, A) isotherms showing the phase transition are given in fig. 1 ; they
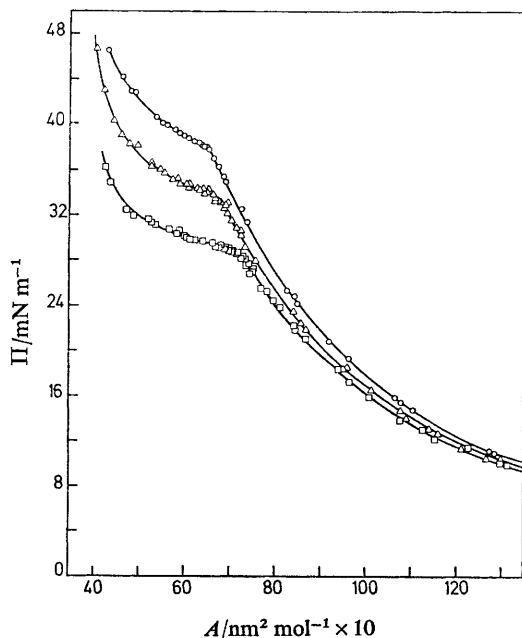
FIG. 1.—Surface pressure against A isotherms for di-C_{16} lecithin monolayers at the n-heptane/ aqueous NaCl interface. Concentration of NaCl—0.01 mol dm^{-3}. Monolayers are spread from n-heptane+ethanol mixtures. □, 10 ; △, 15 ; ⊙, 20°C.

were obtained using a highly purified synthetic sample of di-C_{16} lecithin and the surface chemical techniques described in earlier papers.[32, 33] The oil phase is the saturated hydrocrabon n-heptane and the aqueous phase contains 0.01 mol dm^{-3} sodium chloride at a pH of 5.5, where the lecithin molecule is zwitterionic. The two

available parameters J and ε are used at each temperature to give a theoretical point of slope-discontinuity on the (Π, A) curve which is coincident with the experimental one. We put $z = 6$, corresponding to a two-dimensional triangular lattice in which six nearest-neighbour sites are symmetrically arranged around each site. Then η and ξ are determined at each temperature by inserting the experimental values of Π_t and A_t in eqn (3.5) and (3.6), taking $A_0 = 0.4 \, \text{nm}^2$ molecule^{-1}, roughly the cross-sectional area of the oriented lecithin molecule. Table 1 shows the values of η and ξ thus obtained together with the corresponding values of ε and J in joules $\times 10^{23}$.

TABLE 1.—ENERGY PARAMETERS FOR FITTING SLOPE-DISCONTINUITIES IN (Π, A) ISOTHERMS FOR di-C$_{16}$ LECITHIN MONOLAYERS AT THE n-HEPTANE/AQUEOUS NaCl INTERFACE

$T/^\circ$C	η	ξ	J	ε	ε/J
10	0.3051	1.9640	231.6	-759.5	-3.279
15	0.3615	2.0380	202.3	-768.6	-3.799
20	0.3854	2.1436	192.9	-809.8	-4.199

Both ε and J vary with temperature indicating that they should be regarded as free energies with an entropy term included rather than as simple energy parameters. Since both ε and J decrease with temperature there is entropy loss involved both in bringing two neighbouring molecules into their position of least free energy and in bringing two separated molecules together. The ratio ε/J is large in magnitude and negative in sign at all three temperatures shown in the table, corresponding to the absence of vapour–liquid phase-separation and the much larger than ideal pressure at large A observed experimentally. Although qualitative agreement with experiment is thus obtained the (Π, A) curves calculated from eqn (2.17) and (3.3) using the values
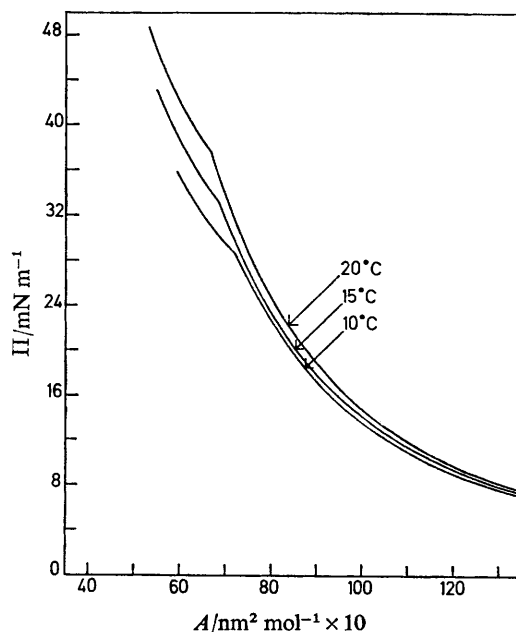

FIG. 2.—Theoretical surface pressure against A isotherms for di-C$_{16}$ lecithin at the n-heptane/water interface. Curves are calculated using the values of η and ξ given in table 1. $A_0 = 0.4 \, \text{nm}^2$ molecule^{-1}.

of ε and J from table 1 do show quantitative differences from experimental isotherms. As seen in fig. 2 theoretical slopes of the (Π, A) isotherms around the phase transitions are much larger in magnitude than the experimental ones. These differences may be due either to the simplification inherent in the model used or to the statistical approximations made or, more probably, to both.
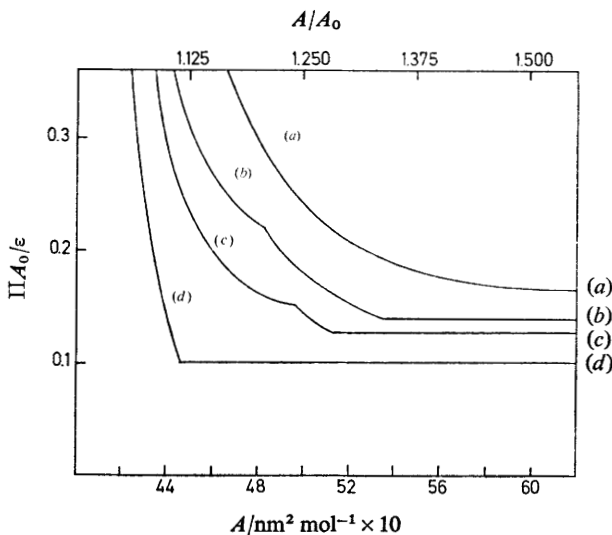

Fig. 3.—Theoretical surface pressure against A isotherms for monolayers at the air/water interface. The surface pressure is plotted in units of ε/A_0 and the upper scale for the abscissa refers to the reduced area A/A_0. Values of parameters used in the theory are $z = 6$, $\varepsilon/J = 3.5$ and $A_0 = 0.4 \text{ nm}^2 \text{ molecule}^{-1}$. The values of reduced temperature, kT/ε, are: (a), 1.2368; (b), 1.1954; (c), 1.1715; (d), 1.1186.

In order to compare with results for monolayers at the A/W interface, fig. 3 shows theoretical (Π, A) isotherms calculated for a large positive value of ε/J, A_0 again being taken as 0.4 nm^2 molecule^{-1}. In fig. 3 the curve for the lowest temperature drops fairly sharply to a liquid–vapour phase separation with no slope-discontinuity present. On each of the two curves for intermediate temperatures there is a slope-discontinuity with the slope-magnitude larger on the high area side and also a liquid–vapour phase separation. The pressure at which the slope-discontinuity occurs increases with temperature while the area decreases. On the curve for the highest temperature shown the pressure at the slope-discontinuity is too large for the latter to appear on the diagram. These theoretical isotherms qualitatively resemble several experimental isotherms at the A/W interface, for example those of Adam and Jessop [34] for myristic acid and those of Nutting and Harkins [35] for other fatty acids. The (Π, A) isotherms published for some monolayers at the A/W interface, for instance those of Phillips and Chapman [15] for phospholipid monolayers, show a slope-discontinuity with the curve afterwards apparently meeting the $\Pi = 0$ axis at a non-zero angle. Since the surface pressure can hardly be identically zero even at high areas it seems likely that this corresponds to a liquid–vapour phase separation at very low surface pressures indeed. See also Harkins [36] and the more recent work of Gershfeld and Pagano [37].

The term " expanded state " has frequently been used for the condition of the monolayer on the high area side of the slope-discontinuity. From the point of view of the present paper the transition to the " expanded state " is one to a disordered

fluid phase from a state with long range orientational order. Quantitatively, both the area and pressure ranges shown on the theoretical diagram for the "expanded state" at the A/W interface are compressed compared with those found experimentally. In particular, the theoretical ratio of phase-separation pressure to slope-discontinuity pressure is larger than the experimental value. However, the present formalism does account, at least qualitatively, for the appearance of apparently similar second-order transitions, both in cases where the overall chain interaction is repulsive and where it is attractive.

Both Scott [22] and Marčelja [23] have attributed th lack of agreement between the first order transitions predicted by their mean-field theories and the second order transitions seen in the experimental A/W results of Phillips and Chapman [15] to the presence of impurities in the monolayer-forming compound. A similar hypothesis could be put forward for the second order phase transitions found here at the O/W interface. Indeed, these O/W results were obtained at the same time as the Phillips and Chapman data using the very same sample. Comparison of the O/W isotherms for di-C_{16} lecithin with those published for two different pure samples of di-C_{18} lecithin [16] shows an increased degeneracy of the phase transition as the chain length decreases; this trend is very marked in some unpublished results [38] on a homologous series of very pure saturated lecithins over the wider range of C_{14} to C_{22}. Phillips and Chapman's isotherms for both lecithins and cephalins again show a clear-cut dependence of the phase properties on the hydrocarbon chain length of the monolayer; this has been a generally recognized feature of monolayer data at the A/W interface.[10-12] Hence, if impurities were the sole reason for the discrepancy between theory and experiment, these results would require that the impurity-levels are higher or their effect is greater in the lower chain length monolayers. We consider that the response of the phase properties to chain length changes at both interfaces means that the second order phase transitions found with some monolayers are real, and that differences between experiment and the theories of Scott [22] and Marčelja are more likely due to deficiencies in their statistical models.

Kirkwood [39] explains the second-order transition at the A/W interface by rotational hindrance between molecules in close proximity. In his theory the orientational states of each molecule are continuous rather than discrete and the statistical approach is equivalent to a zeroth-order (molecular field) approximation rather than the first-order approximation used here. However, a more important difference from our lattice–fluid model is that there are no vacant sites; decrease in density is due to a uniform expansion of the lattice, and the interaction energy parameter is density-dependent. Hence the model does not provide for a first-order "liquid–vapour" transition in addition to the second-order "orientational" transition. Kaye and Burley [40] do discuss a model with two types of transition. They point out the similarity between the phase diagram of a lattice–fluid with first-neighbour "hard-core" exclusion together with attractive interactions up to ninth-neighbour distance and the monolayer phase diagram of Harkins.[36] According to Runnels [41] the second-order "melting" transition in a lattice fluid becomes first-order in character if the hard-core is extended beyond first-neighbour distance. However Kaye and Burley regard the first-neighbour exclusion hard core as constituting molecular "roughness" corresponding to Kirkwood's orientational restriction on close-packed molecules. This is not easy to understand since their model contains no mechanism for the orientation of either adjacent or separated molecules. At least it can be said that Kirkwood and Kaye and Burley agree with us in regarding the second-order transition as one from a partially ordered to a disordered state.

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