

## Tilting transitions in a one-dimensional model lipid monolayer

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys. A: Math. Gen. 25 2889

(<http://iopscience.iop.org/0305-4470/25/10/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.58

The article was downloaded on 01/06/2010 at 16:29

Please note that [terms and conditions apply](#).

## Tilting transitions in a one-dimensional model lipid monolayer

R D Gianotti†, M J Grimson‡ and M Silbert†

† School of Physics, University of East Anglia, Norwich NR4 7TJ, UK

‡ Theory and Computational Science Group, AFRC Institute of Food Research, Colney Lane, Norwich NR4 7UA, UK

Received 4 December 1991, in final form 26 February 1992

**Abstract.** A one-dimensional model is used to study the tilt/no-tilt transition in the liquid condensed phase of a lipid monolayer at the air/water interface. The head groups are modelled by hard rods of length  $b$  and the alkane chains by rigid tails of length  $a$  ( $a \gg b$ ). The interaction between these model lipid molecules is purely repulsive with a soft, short range, repulsion allowed between the tilting tails. The model is aimed at highlighting the excluded volume role in the tilt/no-tilt transition. The model is solved analytically and, in the limit of the temperature  $T \rightarrow 0$ , the equation of state exhibits—at most—three distinct phases; isotropic, ‘tilting’ and ‘non-tilting’. At finite temperatures the transition from one phase to the other is continuous but, at low temperatures, still sharp.

### 1. Introduction

Lipid molecules exhibit surface-active properties due to their amphiphilic character. The molecules possess a polar head group which is hydrophilic and an alkane chain tail that is hydrophobic and—if insoluble in water—usually form a monomolecular film when spread on a water surface, resulting in a quasi-bidimensional behaviour. Henceforth we shall be concerned with lipid monolayer formed at an air/water interface.

Extensive experimental studies of lipid monolayers (Gaines 1966, Gershfeld 1976, Helm *et al* 1987 and Knobler 1989) point to a rich phase behaviour. But broadly speaking the phase diagram shows phases which—with decreasing surface area per chain and increasing lateral pressure—are termed ‘gaseous’, ‘liquid-expanded’ (LE), and ‘liquid-condensed’ (LC) phases. A considerable effort has been devoted to develop a theoretical understanding of the LE–LC transition and related problems (Wiegel and Kox 1980), but there is still controversy in the interpretation and even the existence of this transition (Middleton and Pethica 1981, Middleton *et al* 1984).

In the LC phase the direction of the chains is either perpendicular to the surface or tilted. Albrecht *et al* (1978) have established that, at least for some substances, a phase transition takes place between these two states, the so-called tilt/no-tilt transition.

Safran *et al* (1986), Carlsson and Sethna (1987), and Kreer *et al* (1990) have recently developed theoretical models to study the tilt/no-tilt transition using, in different ways, lattice models. In all cases a one-dimensional lattice is considered, where each of the lattice sites is occupied by the head groups of the lipid molecules, while the alkane chain is treated as a rigid tail with only one orientational degree of freedom. Assuming nearest neighbour interactions between the alkane chains, the phase behaviour is studied as a function of the orientations of the chains. In spite of

its clear limitations, the statistical mechanics of the one-dimensional model exhibits a rich non-trivial phase behaviour that can be tested by computer simulation.

The simulation methods can easily handle two-dimensional case generalizations of this type of model.

In this work we also use a one-dimensional model. However, we take into account the translational degrees of freedom by using an off-lattice model, thus removing the on-lattice restrictions. We specifically propose a one-dimensional model for  $N$  lipid molecules, whose head groups are represented by hard rods of length  $b$ , that lie on the line segment  $[0, L]$ , to which a rigid tail of length  $a$  is attached at the rod centre of mass. We shall assume  $a \gg b$ . This assumption precludes the study of the interplay between the two length scales  $a$  and  $b$  in determining the phase behaviour. The tails have one orientational degree of freedom, quantified by the local tilt angle  $\theta_i$ . This is the angle formed by the  $i$ th rigid tail with the normal to the centre of mass of the  $i$ th hard rod located at  $x_i$ .

A purely repulsive interaction potential between the rigid tails is assumed to act between nearest neighbours which is characterized by an orientational dependence of its strength and range parameters. We further assume that the potential has a soft short-range part that depends on the relative angles of tilt between two adjacent tails. Such a model highlights the crucial role played by the excluded volume in driving the phase transitions.

We shall show that the assumption of small angles of tilt, and a suitable choice for the soft potential between the tails, yields analytic solutions which exhibit—at most—three distinct phases in the limit as the temperature  $T \rightarrow 0$ . At finite temperatures the transitions between the phases is continuous. At low temperatures the different phases are still well defined, but the distinctions become increasingly blurred as the temperature is raised.

We shall be concerned here only with those aspects of the model which can be studied from the analytic results. This limits the scope of this paper to the thermodynamic properties. We are leaving out the study of those properties which require extensive numerical calculations, such as the interplay between the two length scales  $a$  and  $b$  mentioned above, the pair correlation function, and collective excitations.

Similar approaches to this work have been used to address somewhat different problems by Berne and Pechukas (1972) and Chen *et al* (1988).

The outline of the paper is as follows. In section 2 we present the general solution for our model lipid monolayer, and show that it reduces to an eigenvalue problem. In section 3 we introduce the explicit form of the soft repulsion between the tails and work out explicitly the equation of state and composition of each phase. Finally in section 4 we sum up and discuss briefly our results.

## 2. Theory

We consider a system of  $N$  lipid molecules such that the head groups are modelled by hard rods of length  $b$ , which lie on a line segment  $[0, L]$ , while the alkane chains are modelled by hard tails of length  $a$  ( $a \gg b$ ) attached at one end to the centre of mass of the rods as shown in figure 1.

The potential energy of interaction  $V = V(x_1, \dots, x_N; \theta_1, \dots, \theta_N)$  is a function of the position  $x_i$ , and angles  $\theta_i$  ( $i = 1, \dots, N$ ) of the molecules. We shall assume that the angles of tilt are small, with a maximum inclination  $|\theta_m|$ .

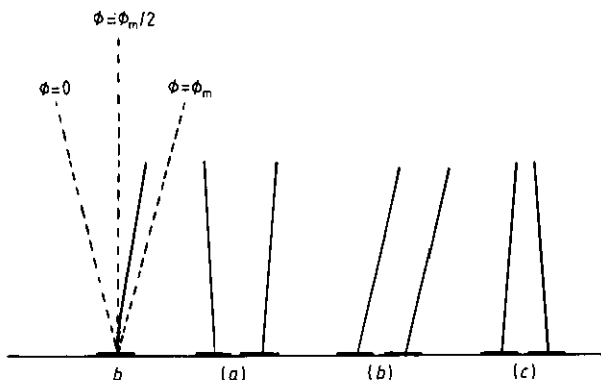


Figure 1. Tilting configurations of the model alkane chains: (a)  $0 < \phi_i < \phi_m/2$  or  $\phi_m/2 < \phi_{i+1} < \phi_m$ ; (b)  $\phi_m/2 < \phi_i$ ;  $\phi_{i+1} < \phi_m$  or  $0 < \phi_i$ ;  $\phi_{i+1} < \phi_m/2$ ; (c)  $\phi_m/2 < \phi_i < \phi_m$  or  $0 < \phi_{i+1} < \phi_m/2$ .

In the canonical ensemble the partition function reads

$$Q_N(L, \beta) = \Lambda^{-N} \int_0^L \dots \int_0^L dx_1 \dots dx_N \int_{-\theta_m}^{\theta_m} \dots \int_{-\theta_m}^{\theta_m} d\theta_1 \dots d\theta_N \exp\{-\beta V\} \tag{2.1}$$

where  $\Lambda = h^3/(2\pi\beta mI)^{1/2}$ ;  $\beta^{-1}$  is the product of the temperature  $T$  and the Boltzmann constant  $k_B$ ,  $m$  is the mass of the molecules, and  $I$  their moment of inertia. The assumption of pairwise additive nearest-neighbour interactions means that the Boltzmann factor may be written as

$$\exp\{-\beta V\} = \prod_{i=1}^{N-1} \exp\{-\beta V(x_i, x_{i+1}; \theta_i, \theta_{i+1})\}. \tag{2.2}$$

We define the direction of positive rotation to be counterclockwise. It is convenient to make the following change of variables for the angles of tilt, from  $\{\theta_i\}$  to  $\{\phi_i\}$ , such that  $\phi_i = 0$  when  $\theta_i = -\theta_m$ ,  $\phi_i = \phi_m/2$  when  $\theta_i = 0$  and  $\phi_i = \phi_m$  when  $\theta_i = \theta_m$ . Moreover, with reference to figure 1, the distance of closest approach between two head groups depends not only on their length  $b$ , but also on the relative angle of tilt between the adjacent tails. These changes in the distance of closest approach will be characterized by a parameter  $\mu$ . In figure 1 we have plotted the possible arrangements of the adjacent tails; these result in the distances of closest approach quantified by equation (2.4) below.

We assume that

$$V(x_i, x_{i+1}; \phi_i, \phi_{i+1}) = \begin{cases} \infty & \text{for } |x_{i+1} - x_i| < b(\phi_i, \phi_{i+1}) \\ U(x_i, x_{i+1}, \phi_i, \phi_{i+1}) & \text{for } |x_{i+1} - x_i| > b(\phi_i, \phi_{i+1}) \end{cases} \tag{2.3}$$

where

$$U(x_i, x_{i+1}; \phi_i, \phi_{i+1}) = U(x_i - x_{i+1} - b(\phi_i, \phi_{i+1}); \phi_i, \phi_{i+1})$$

and

$$b(\phi_i, \phi_{i+1}) = \begin{cases} b & \text{for } 0 < \phi_i < \phi_m/2 \text{ or } \phi_m/2 < \phi_{i+1} < \phi_m \\ b & \text{for } \phi_m/2 < \phi_i; \phi_{i+1} < \phi_m \text{ or } 0 < \phi_i; \phi_{i+1} < \phi_m/2 \\ b(1 + \mu) & \text{for } \phi_m/2 < \phi_i < \phi_m \text{ or } 0 < \phi_{i+1} < \phi_m/2. \end{cases} \tag{2.4}$$

In equation (2.3) the potential energy of interaction between two adjacent lipid molecules  $V(x_i, x_{i+1}; \phi_i, \phi_{i+1})$  is assumed to be infinitely repulsive at contact, while it

is given by the interaction potential between adjacent tails  $U(x_i - x_{i+1} - b(\phi_i, \phi_{i+1}); \phi_i, \phi_{i+1})$  for distances larger than contact. The specific choice of  $U$  used in this work is given by equation (3.1).

We can integrate over most of the translational degrees of freedom—excluding those arising from any two adjacent head groups—by transforming from the canonical to the isothermal-isobaric ensemble. Since these are related by a Laplace transform, and given the assumption of nearest-neighbour interaction, the convolution theorem takes care of the translational variables. The calculations are more conveniently carried out by the following change in the translational variables,

$$x_1 = t_1 \quad x_2 = t_1 + t_2 \quad x_N = \sum_{i=1}^N t_i \quad x_{N+1} = L = \sum_{i=1}^{N+1} t_i. \quad (2.5)$$

Now, transforming from  $Q_N(L, \beta)$  to the isothermal-isobaric partition function  $T(s, \beta)$  via

$$T(L, \beta) = \int_0^\infty dL e^{-sL} Q_N(L, \beta) \quad (2.6)$$

we obtain

$$\Lambda^N T(s, \beta) = \int_0^{\phi_m} \dots \int_0^{\phi_m} d\phi_1 \dots d\phi_N \prod_{i=1}^{N-1} f(s, \phi_i, \phi_{i+1}) \quad (2.7)$$

where  $s = \beta p$ , with  $p$  denoting the one-dimensional lateral pressure, and

$$f(s, \phi_i, \phi_{i+1}) = \exp\{-sb(\phi_i, \phi_{i+1})\} \int_0^\infty dt e^{-st} \exp\{-\beta U(t, \phi_i, \phi_{i+1})\}. \quad (2.8)$$

Using the cyclic boundary conditions ( $\phi_1 \equiv \phi_{N+1}$ ), equation (2.7) can be evaluated on taking the trace of the  $N$ th iterate of the symmetric kernel  $f(s, \phi_i, \phi_{i+1})$ . Then, we rewrite equation (2.7) as

$$\Lambda^N T(s, \beta) = \int_0^{\phi_m} d\phi_1 f^{(N)}(s, \phi_1, \phi_1). \quad (2.9)$$

The thermodynamic properties follow from equation (2.9) by evaluating the excess Gibbs free energy per particle  $g(s, \beta)$ , the characteristic thermodynamic function for this ensemble, by taking the limit of trace as  $N \rightarrow \infty$ , we have

$$-\beta g(s, \beta) = \ln \lambda_{\max} \quad (2.10)$$

where  $\lambda_{\max}$  is the maximal eigenvalue of the Fredholm integral equation

$$\int_0^{\phi_m} d\phi_1 f(s, \phi_1, \phi_2) \Psi_n(\phi_1) = \lambda_n \Psi_n(\phi_2). \quad (2.11)$$

To obtain  $\lambda_{\max}$  we have to specify  $U(t, \phi_i, \phi_{i+1})$ . The particular choice we make has the distinct advantage of yielding an analytic solution.

### 3. Results

We assume  $U(t, \phi_i, \phi_{i+1})$  to be repulsive and short-ranged, and that it is possible to partition the contribution of the position and tilting coordinates as follows

$$U(t, \phi_i, \phi_{i+1}) = \begin{cases} (1 - t/b)u(\phi_i, \phi_{i+1}) & \text{for } t < b \\ 0 & \text{for } t > b \end{cases} \quad (3.1)$$

with

$$u(\phi_i, \phi_{i+1}) = \begin{cases} u_1 & \text{for } 0 < \phi_i < \phi_m/2 \text{ or } \phi_m/2 < \phi_{i+1} < \phi_m \\ u_1 - \Delta_1 & \text{for } \phi_m/2 < \phi_i; \phi_{i+1} < \phi_m \text{ or } 0 < \phi_i; \phi_{i+1} < \phi_m/2 \\ u_1 - \Delta_2 & \text{for } \phi_m/2 < \phi_i < \phi_m \text{ or } 0 < \phi_{i+1} < \phi_m/2. \end{cases} \quad (3.2)$$

The parameters  $u_1$ ,  $\Delta_1$  and  $\Delta_2$  determine the strength of the potential  $U(t, \phi_i, \phi_{i+1})$  as shown in figure 2.

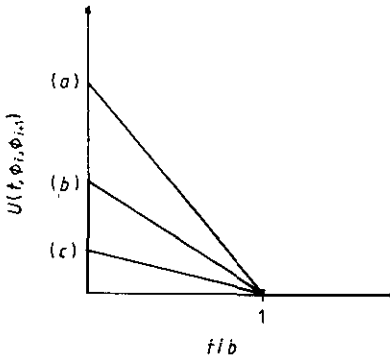


Figure 2. Strength of the soft, short-range, repulsive potential  $U(t, \phi_i, \phi_{i+1})$  for different configurations of two neighbouring tails.  $t$  is the relative distance between the centres of mass of the corresponding adjacent head groups: (a)  $0 < \phi_i < \phi_m/2$  or  $\phi_m/2 < \phi_{i+1} < \phi_m$ ; (b)  $\phi_m/2 < \phi_i; \phi_{i+1} < \phi_m$  or  $0 < \phi_i; \phi_{i+1} < \phi_m/2$ ; (c)  $\phi_m/2 < \phi_i < \phi_m$  or  $0 < \phi_{i+1} < \phi_m/2$ .

In order to evaluate  $\lambda_{\max}$ , it is sufficient to note that now, with  $U(t, \phi_i, \phi_{i+1})$  given by equations (3.1) and (3.2), equation (2.9) reduces to the matrix equation

$$\begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} = \lambda \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} \quad (3.3)$$

with

$$\begin{aligned} F_{11} &= F(\beta, p, u_1) & F_{12} &= F_{21} = F(\beta, p, u_1 - \Delta_1) \\ F_{22} &= F(\beta, p, u_1 - \Delta_2) e^{-\beta p b \mu} \end{aligned} \quad (3.4)$$

and

$$F(\beta, p, u) = \frac{b}{2} \exp\{-2\beta p b\} \left( \frac{\exp\{\beta(p b - u)\}}{\beta(p b - u)} + \frac{1}{\beta p b} \right). \quad (3.5)$$

Hence

$$\lambda_{\max} = (b/2) e^{-2\beta p b} \{ (F_{11}^+ + F_{22}^+) + [(F_{11}^+ - F_{22}^+)^2 + 4F_{12}^+]^{1/2} \} \quad (3.6)$$

with

$$F_{ij}^+ = (e^{2\beta p b} / b) F_{ij}. \quad (3.7)$$

We now introduce reduced variables with lengths scaled to  $b$ , the length of the head groups, and energies scaled to  $u_1$ , which characterizes the strength of the soft repulsive potential between two neighbouring tails. Thus, we define:  $l^* = l/b$ ,  $\lambda^* = \lambda_{\max}/b$ ,  $\beta^* = \beta u_1$ ,  $\Delta_1^* = \Delta_1/u_1$ ,  $\Delta_2^* = \Delta_2/u_1$  and  $p^* = \beta^* p b / u_1$ .

In reduced units, the length per molecule is given by

$$l^* = 2 - (d\lambda^*/dp^*)/\lambda^* \quad (3.8)$$

and in the limit  $\beta \rightarrow \infty (T \rightarrow 0)$   $p^*$ ,  $1 - \Delta_1^*$  and  $1 - \Delta_2^*$  diverge.

Thus, using equation (3.8), we obtain

$$l^* = \begin{cases} 1 & p^* > (\Delta_2^* - \Delta_1^*)/\mu \\ 1 + \mu & (1 - \Delta_2^*)/(1 - \mu) < p^* < (\Delta_2^* - \Delta_1^*)/\mu \\ 2 & 0 < p^* < (1 - \Delta_2^*)/(1 - \mu) \end{cases} \quad (3.9)$$

and the equation of state reads

$$p^* = \begin{cases} 0 & l^* > 2 \\ (1 - \Delta_2^*)/(1 - \mu) & 1 + \mu < l^* < 2 \\ (\Delta_2^* - \Delta_1^*)/\mu & 1 < l^* < 1 + \mu. \end{cases} \quad (3.10)$$

The equation of state given above exhibits three distinct phases provided the inequality

$$(1 - \Delta_2^*)/(1 - \mu) < (\Delta_2^* - \Delta_1^*)/\mu \quad (3.11)$$

is satisfied, otherwise only two distinct phases are present. At  $T = 0$  these phases are separated by first-order phase transitions; there are no critical points in the phase diagram which is to be expected as we have not included attractive forces in the potential of interaction between the lipid molecules.

In going from the lower to higher lateral pressures the following phases are present. At  $p^* = 0$  we have an 'isotropic' phase in which the tails are randomly tilted. At  $p^* = (1 - \Delta_2^*)/(1 - \mu)$  the system changes to a more ordered phase in which the neighbouring tails are tilted relative to one another. Finally, at  $p^* = (\Delta_2^* - \Delta_1^*)/\mu$  the system changes to an even more ordered phase in which neighbouring tails are not tilted relative to one another, but may be tilted relative to the head groups.

At finite, albeit low, temperatures these three phases are still present but the transition from one phase to another is continuous with the coexistence regions—assuming they can be uniquely defined—exhibiting slopes.

These features are shown in figure 3, where we show the phase behaviour of the system for the inverse temperature  $\beta^* = 120$  to which we superpose the  $T = 0$  behaviour.

In order to study the composition of these phases, let us assume that the angles of tilt are restricted to the intervals  $(0, \varepsilon\phi_{\max})$  and  $(\varepsilon\phi_{\max}, \phi_{\max})$ , with  $0 < \varepsilon < \frac{1}{2}$ . Under this assumption  $F_{11}$ ,  $F_{12}$ ,  $F_{22}$ , given by equations (3.4) and (3.5), should be multiplied by the factors  $\varepsilon$ ,  $\varepsilon(1 - \varepsilon)^{1/2}$  and  $(1 - \varepsilon)$  respectively. But, there is no change in the equation of state (3.10).

Let us define  $c$  as the fraction of tails whose angle of tilting lie in the interval  $(0, \varepsilon\phi_{\max})$ , namely

$$c = \lim_{N \rightarrow \infty} \left\langle \sum_{i=1}^N H(\varepsilon\phi_{\max} - \phi_i) \right\rangle / N \quad (3.12)$$

where  $H(x)$  is the Heaviside function. Actually  $c$  is the one-particle correlation function.

Equation (3.12) may be related to the excess free energy, which we write as  $g(\beta, s, h)$  with  $h$  denoting a dummy external parameter. Differentiating  $g(\beta, s, h)$  with respect to  $h$  in the limit  $h \rightarrow 0$ , we obtain

$$c = \{(F_{11} - F_{22} + D)F_{11} + 2F_{12}^2\} / \{(F_{11} + F_{22} + D)D\} \quad (3.13)$$

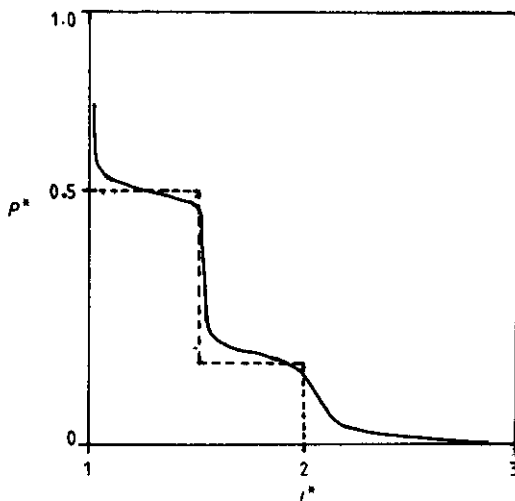


Figure 3. Reduced lateral pressure  $p^*$  against reduced length per molecule  $l^*$  with  $\Delta_1^* = 0.6$ ;  $\Delta_2^* = 0.9$  and  $\mu = 0.5$  at the reduced inverse temperature  $\beta^* = 120$  (full line). The dotted lines show the phase behaviour at  $T = 0$  for the same parametrization.

with

$$D = \{(F_{11} - F_{22})^2 + 4F_{12}\}^{1/2}.$$

In the limit of  $\beta \rightarrow \infty$  ( $T \rightarrow 0$ ) equation (3.13) reads

$$c = \begin{cases} \varepsilon & l^* > 2 \\ \frac{1}{2} & 1 + \mu < l^* < 2 \\ 1 & 1 < l^* < 1 + \mu. \end{cases} \quad (3.14)$$

Equation (3.14) shows the composition of the three phases discussed above.

The isotropic phase composition depends on the actual value given to the parameter  $\varepsilon$ . We recall that  $\varepsilon$  was introduced in order to partition the ranges of the angles of tilt into two intervals in order to facilitate the study leading to equation (3.14). If  $\varepsilon$  takes on a small value, say  $\varepsilon \approx 0$ , then the tails may take on any value of angles of tilt from  $\phi \approx 0$  to  $\phi_{\max}$ , or from  $\theta \approx -\theta_{\max}$  to  $\theta_{\max}$ , and we expect short range correlations between the tails.

In the second phase, which we call the 'tilted phase', half of the tails have an angle of tilt in the interval  $(0, \varepsilon\phi_{\max})$ , or  $(-\varepsilon\phi_{\max}, 0)$ . The other half of the tails have angles of tilt in the interval  $(\varepsilon\phi, \phi_{\max})$  or  $(0, \varepsilon\theta_{\max})$ . It appears that the most likely configuration between two adjacent tails is one when one of the tails has an angle of tilt in the range  $(-\varepsilon\theta_{\max}, 0)$ , while the other has an angle of tilt in the range  $(0, \varepsilon\theta_{\max})$ , and the system exhibits intermediate range order. A full picture will emerge as detailed numerical calculations of pair correlation functions—which are not trivial—are completed.

Finally in the third phase, which we call the 'no tilted phase', all tails are tilted the same way, but not every tail has the same angle of tilt. More precisely, either all tails are tilted in the range  $(-\varepsilon\theta_{\max}, 0)$  or they are all tilted in the range  $(0, \varepsilon\theta_{\max})$ . However, and unlike the on-lattice model where the heads have inbuilt translational symmetry, this arrangement does not result in a translational invariance of the tails. It is likely that within the present model these phase changes are more akin to those found in liquid crystals than to a liquid-solid transition.



However, we are at present unable to predict whether the system, depending on the choice of the parameter  $\mu$ , prefers to have angles of tilt in either of the  $(-\varepsilon\theta_{\max}, 0)$  or  $(0, \varepsilon\theta_{\max})$  ranges or, indeed, the most likely configuration is around  $\theta=0$ , and whether there is a value of  $\mu$  which takes the system from one type of configuration to the other. Again details on the nature of this phase have to await the calculation of the pair correlation functions.

A similar argument may be carried forward to finite temperatures but, due to thermal fluctuations, it is no longer possible to be as precise as in the limiting case discussed above.

#### 4. Discussion

In this work we have used a one-dimensional model to study the tilting transitions in lipid monolayers at the air/water interface. While the one-dimensional character of the model is its greatest weakness, its ability to yield analytic results is its main strength. Moreover, our results exhibit some of the qualitative features found in experiment.

In our model the interaction between the lipid molecules is assumed to be purely repulsive, highlighting the role played by these forces in driving the tilting transition. Furthermore equation of state (3.10) shows that the phases depend on the parameter  $\mu$  which scales the effective length of the head groups by taking into account the angles of tilt of the alkane chains.

#### Acknowledgments

We are grateful to J Mingins for introducing us to this field and for his constant interest in the work, and to G C Barker for many useful discussions and suggestions. The financial support of the AFRC is gratefully acknowledged.

#### References

- Albrecht O, Gruler H and Sackmann E 1978 *J. Physique* **39** 301
- Berne B J and Pechukas P 1972 *J. Chem. Phys.* **56** 4213
- Carlsson J M and Sethna J P 1987 *Phys. Rev. A* **36** 3359
- Chen Z Y, Talbot J, Gelbart W M and Ben Shaul A 1988 *Phys. Rev. Lett.* **61** 1376
- Gaines G L 1966 *Insoluble Monolayers at Liquid-Gas Interfaces* (New York: Wiley-Interscience)
- Gershfeld N L 1976 *Ann. Rev. Phys. Chem.* **27** 349
- Helm C A, Möhwald H, Kjaer K and Als-Nielsen J 1987 *Biophys. J.* **52** 381
- Knobler C M 1989 *Adv. Chem. Phys.* **77** 397
- Kreer M, Kremer K and Binder K 1990 *J. Chem. Phys.* **92** 6195
- Middleton S R and Pethica B A 1981 *Faraday Symp. Chem. Soc.* **16** 109
- Middleton S R, Iwahashi M, Pallas N R and Pethica B A 1984 *Proc. R. Soc. A* **396** 143
- Safran S A, Robbins M O and Garoff S 1986 *Phys. Rev. A* **33** 2186
- Wiegel F W and Kox A J 1980 *Adv. Chem. Phys.* **41** 195