THE EFFECT OF LONG AND SHORT RANGE FORCES IN AMPHIPHILIC MONOLAYERS AT THE LE-LC TRANSITION

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In order to describe the liquid expanded - liquid condensed phase transition, a model with broken symmetry and cooperative packing of hydrocarbon chain defects is used. Various treatments of this model (mean-field approximation, position space renormalisation group and mean-field simulation in the Migdal-Kadanoff procedure) lead to different results which allow us to interpret some experimental data in terms of long and short range forces in the monolayer. The compressibility jump, which is associated with the LE-LC transition, appears to be linked to the existence and the orientation of dipoles at the interface.

INTRODUCTION

Monolayers of some amphiphilic molecules (e.g. fatty acids) at the air-water interface exhibit a variety of phase transitions. A phase diagram can be obtained from isotherms in the surface pressure (π)-molecular area (σ) plane. The so-called liquid expanded (LE) - liquid condensed (LC) phase transition occurs at relatively high surface density. In contrast with the gas-liquid transition in monolayers, the nature of the LE-LC transition is not yet completely clear and the structures of these two phases are not well identified. Experimental data from fluorescence or electronic microscopy are not reliable because artifacts are too important. In the absence of other results, it would be very tempting to suppose the mechanism of the LE-LC transition similar to a cooperative melting of the hydrocarbon chains, as for the main transition of the lipid bilayers. This mechanism would give a first order phase transition. In fact, the LE-LC transition is revealed by a compressibility jump. A perfectly horizontal plateau, which would be the unmistakable signature of a first order transition has never been observed despite very careful experimentation. Moreover recent experiments show the existence of a critical slowing down at the transition: starting from the LE phase and decreasing the area, one observes that the relaxation time for the pressure remains short and constant in the expanded phase, approaches infinity at the transition and decreases slowly in the condensed phase. Thus the isotherms appear to pass through a line of critical points and the transition appears to be of second order. In this view a broken symmetry must occur for the system. However, chain melting is to be taken into account because molecules with rigid chains (such as cholesterol) do not give the compressibility jump associated...
with the LE-LC transition. Now, from a thermodynamical point of view, hydrocarbon chain defects, obtained by permuting gauche + and gauche - bonds, present a perfect symmetry. Moreover nearest neighbor complementary defects may give rise to cooperative packing. The model, which will be used here, is based on these two facts and is detailed in Section II. In Section III, the model is treated by means of different statistical procedures, which involve either long range interactions or short range interactions. The existence of the compressibility jump at the transition depends on the treatment that one uses. In Section IV, we show how some experimental data allow us to interpret our results in terms of interactions due to the hydrophilic groups in the aqueous substrate.

THE MODEL

Description

The model is a three-state lattice-gas model. A triangular lattice, which corresponds to the organisation of the most condensed phase has been chosen.

The state (O) corresponds to a vacancy. This state allows us to describe the dilute phases and allows the number of effective nearest neighbors to vary in the condensed phase.

The studies of Bothorel et al. show that the kink configuration is the most probable one for chain defects near the LE-LC transition. Thus, the two remaining states are defined as follows: the state (+) corresponds to a molecule whose hydrocarbon chain has a sequence (gauche+, trans, gauche-), the state (-) corresponds to a molecule whose hydrocarbon chain has a sequence (gauche-, trans, gauche+).

These states are shown in Fig. 1, but when visualized in two dimensions, the representation is misleading. We must note that a molecule cannot change from the (+) to the (-) state by a simple rotation of 180°. The conversion of one molecular state to another can only be obtained by crossing an energy gap. Our choice of molecular states can give rise to a decrease in molecular area by the creation of (+,+) or (-,-) pairs of nearest neighbors.

Taking 2σ for the excluded area of a molecule, we have chosen 3σ for a pair (+,+) or (-,-). So, the total area can be written as :

\[ A = \sigma_0 \left( 2(N_+ + N_-) + \nu N_0 - (N_+ + N_-) \right) \]

where \( N_0 \) is the number of vacancies. (i) and (j) mark the directions where the packing occurs. We take also into account an entropy loss for kinks in a pair, because they are less free to move along the chains.

If \( \Delta S \) is the internal entropy for (+) and (-) states, whose kink is free to move along the chain, and \( \alpha \) a positive coefficient which phenomenologically describes the entropy loss for complementary kinks in a pair, we have for the sum of internal entropies :

\[ \Delta S = \Delta S \left( N_+ + N_- - \alpha (N_+ + N_-) \right) \]

If \( /\omega/ \) is the attractive interaction energy for nearest neighbor molecules, and \( /\Delta \omega/ \) an extra attractive interaction for (+,+) and (-,-) pairs, the interactions can be written as :

\[ K_{++} = K_{--} = - /\omega/ - /\Delta \omega/ \]
\[ K_{+-} = K_{-+} = - /\omega/ \]