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Tilting and Swiveling Transitions in a Molecular Model for Langmuir Monolayers

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Abstract The ground state of a rigid chain molecular model for Langmuir monolayers is investigated. Model molecules are made up of two rigid chains of "atoms" interacting by Lennard–Jones potentials. It is found out that a minimum of the interaction energy occurs when the molecules are in a herringbone configuration with (nearest neighbor) tilted chains. Upon increasing the applied surface pressure the model displays a reorientation of chains towards next nearest neighbors, resembling that observed in some real surfactant monolayers. At higher pressure the model also displays a 2–nd order transition to an untilted state.

Keywords Langmuir Monolayer; Molecular Model; Rigid Chain.

INTRODUCTION

The characteristic of amphiphilic molecules is the presence of a polar head and a hydrophobic tail in the same molecule [1]. When amphiphilic molecules are placed at the air-water interface, they tend to orient with the tails upward in the air and self-assemble into a two-dimensional structure called a Langmuir monolayer [2].

Langmuir monolayers exhibit a rich variety of condensed phases, characterized by different arrangements of the hydrophobic chains, and many features of their pressure-temperature phase diagram are experimentally well-known and quite independent of the particular

substance used [2,3].

A successful Landau theory has been proposed [3] for these systems, and the problem of determining the typical phase diagram of a Langmuir monolayer through the statistical mechanics of a microscopic model has received a lot of interest in recent years but a complete description is far from being reached [4].

Models of various complexity have been proposed [4]: "atomic" models, with variable conformation of hydrocarbon chains, usually investigated by molecular dynamic simulations [5–8] and Monte Carlo methods [9,10], or "molecular" models, with simplified degrees of freedom, in which molecules are represented as rigid objects [11,12]. Further simplifications are usually done on molecular models, assuming that molecules are constrained to a lattice and rotationally invariant (rod models) [13–19]. The latter assumption does not allow to reproduce herringbone ordering, which has been investigated by means of models made up of planar molecules which break the rotational symmetry [20–29].

Here we present a lattice model for the condensed phases which includes, in a simplified way, both tilt and rotation about the molecule axis degrees of freedom, aiming to describe both herringbone ordering and tilt transitions. A molecule is represented by a rigid "ladder" of interaction centers (see Figure 1). The interaction between atoms of different molecules are assumed to be of the Lennard-Jones type. In the present paper we describe the model and report the results of a ground state analysis.

THE MODEL

We model the tail of a molecule as a ladder of interaction centers, which will be called "atoms" from now on (see Figure 1). Although the backbone of a molecule's tail forms actually (in the all-trans conformation) a zig-zag chain instead of a ladder, we believe that the relevant fact is that chain atoms are arranged in a two-dimensional structure rather than in a line. Interactions involving the heads of the molecules are not taken into account and so heads are not explicitly represented in our model. A molecule is therefore characterized by three parameters: the number of atoms, which will be denoted by $2n$, the distance d_u between two atoms along the main axis of the

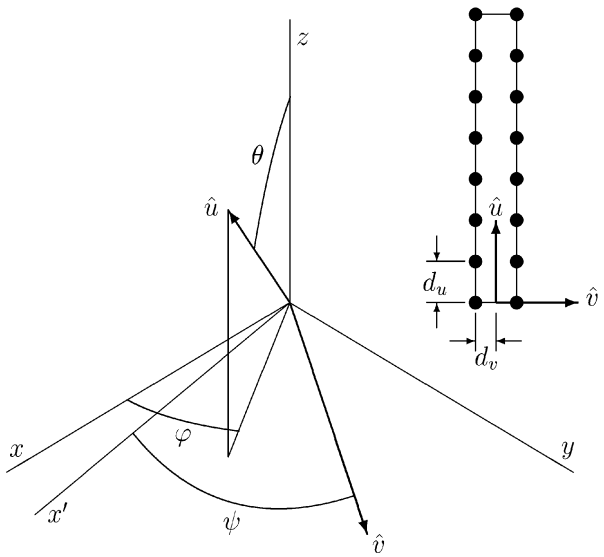

FIGURE 1 Our model molecule and its degrees of freedom. The molecule structure is sketched in the upper right part of the figure: black dots represent interaction centers ("atoms"), whereas $\hat{u}$ and $\hat{v}$ are unit vectors that define the molecule backbone plane. The position of $\hat{u}$ and $\hat{v}$ with respect to the main reference frame xyz is defined by the three angles θ, φ, ψ, as shown in the central part of the figure. More details are given in the text.

molecule, and the distance d_v between each atom and the main axis itself (see Figure 1). Such a molecule has three degrees of freedom, which are best defined in terms of the unit vectors $\hat{u}$ and $\hat{v}$, respectively parallel and orthogonal to the main axis of the molecule, and both in the plane of the ladder. The first degree of freedom is the tilt angle θ, formed by $\hat{u}$ with the z (vertical) axis. Then we have the tilt azimuth φ, the angle which the projection of $\hat{u}$ on the xy (monolayer) plane forms with the x axis. The latter could be any reference direction, we will choose the direction corresponding to the larger lattice constant b (see below). Finally we have the azimuth ψ of the backbone (ladder) plane, defined as the angle formed by $\hat{v}$ with the x' direction, obtained by projecting the x axis onto the

plane orthogonal to the $\hat{u}$ vector which passes through the origin of the molecule's reference frame.

In our model the molecules lie at the sites of a centered rectangular lattice of lattice constants $a < b$. More precisely, the origin of each molecule's reference frame is placed at the lattice site.

Atoms belonging to different molecules are assumed to interact by means of a Lennard-Jones potential

$$V(r) = \left(\frac{1}{r}\right)^{12} - 2\left(\frac{1}{r}\right)^{6}, \tag{1}$$

where r is the distance between interaction centers. Notice that the functional form of the potential is normalized in such a way that both depth and distance of the minimum are equal to 1, thus defining the length and energy units.

GROUND STATE ANALYSIS

In order to determine the ground state properties of the model we have to look for the global minimum of the total energy

$$E = \sum_{(k,l)} \tilde{V}(|\vec{r}_k - \vec{r}_l|), \tag{2}$$

where the sum runs over all pairs of atoms belonging to different molecules. Instead of the exact Lennard-Jones potential we use its simple truncation

$$\tilde{V}(r) = \begin{cases} V(r) - V(r_{\text{cutoff}}), & r < r_{\text{cutoff}} \\ 0, & r \geq r_{\text{cutoff}} \end{cases} \tag{3}$$

and check that our results do not depend significantly on the cutoff radius r_{cutoff}.

The total energy E is, in principle, a function of the lattice constants and of the angles $\{\theta_i, \varphi_i, \psi_i\}$ of all molecules. In the ground state of course we expect that the minimum of the energy is attained for ordered structures. The angles θ and φ can be assumed to be independent of the lattice site, while in order to be able to describe herringbone-like structures we have to split our centered rectangular lattice in two sublattices L_1 and L_2, as shown in Figure 2, with different values of the angle ψ, respectively ψ_1 and ψ_2. Therefore we will

have to consider a function of six variables $E = E(a, b; \theta, \varphi, \psi_1, \psi_2)$. The global minimum of E actually corresponds to the ground state at zero surface pressure, whereas, to take into account the effect of an applied surface pressure Π, we shall search the minimum of the enthalpy $H = E + N\Pi A$ (where N is the number of molecules and $A = ab/2$ is the area per molecule), according to Reference [29]. We

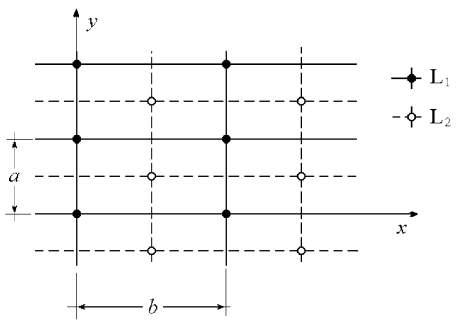

FIGURE 2 The centered rectangular lattice and its sublattices

have investigated the cases $n = 10$ (corresponding to 20 atoms per molecule) and $n = 20$, $d_u = 2d_v$ (ladder made up of squares) and $d_v = 1/4$ (roughly consistent with estimates that can be made on the basis of packing models [30]). Our main results are reported in Figures 3 and 4. At low pressure we find a herringbone structure ($\psi_1 = -\psi_2 \sim 10°$), like the one depicted in Figure 4(a), with a tilt angle $\theta \sim 15°$ towards nearest-neighbors (NN). $\varphi \sim 90°$ corresponds to a tilt in the direction of the smaller lattice constant. Upon increasing the pressure we have a first order transition to a phase tilted in a direction which is intermediate between nearest and next-nearest neighbor (NNN). A typical configuration is reported in Figure 4(b). The tilt rotates towards NNN (φ decreases) and decreases in magnitude as the pressure gets larger, up to a second order transition in which the tilt locks in the NNN direction ($\varphi = 0$, Figure 4(c)). Increasing further the pressure the tilt goes on decreasing in magnitude and eventually vanishes at a second order transition to an untilted phase (Figure 4(d)). While the tilt undergoes all these transforma-

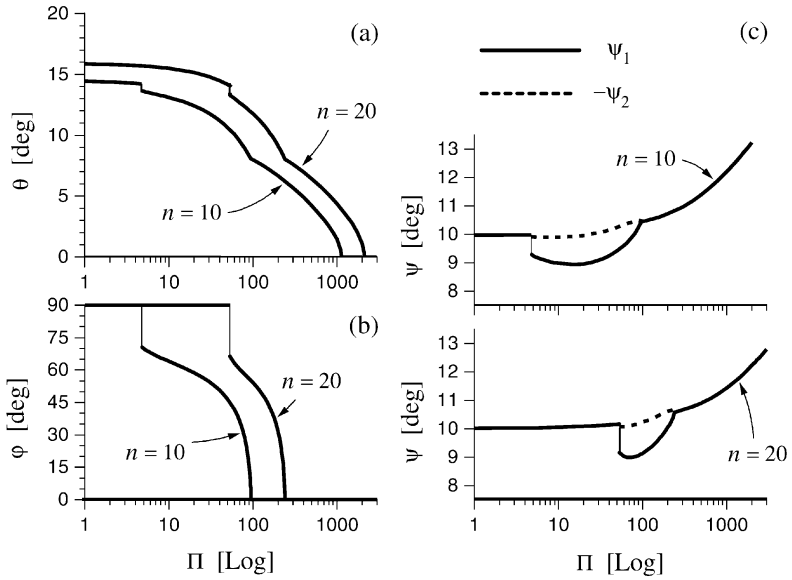

FIGURE 3 (a) Tilt angle θ, (b) tilt azimuth φ and (c) backbone plane azimuths $\psi_{1,2}$ vs. surface pressure for $d_u = 2d_v$ and $d_v = 1/4$.

tion, the azimuth $\psi_{1,2}$ varies only slightly. Interestingly, the antisymmetry $\psi_1 = -\psi_2$ is broken in the intermediate phase. The transition pressure increases with the chain length and the region corresponding to the swiveling transition shrinks.

It is noteworthy that the rotation (swiveling) of the tilt director from NN to NNN for increasing pressure is usually observed for instance in experiments on fatty acids [31], but only in an intermediate temperature range, whereas at lower temperature a direct (second order) transition between a NN tilted and an untilted phase takes place. Nevertheless a recent work about monolayers composed of a chiral amphiphile (hexadecylglycerol [32]) reports the swiveling transition until the lowest temperature investigated (5°C). In particular, only in the case of pure enantiomer, the reorientation turned out to be quite smooth, resembling that predicted by our model. From the theoretical point of view it has been reported that models

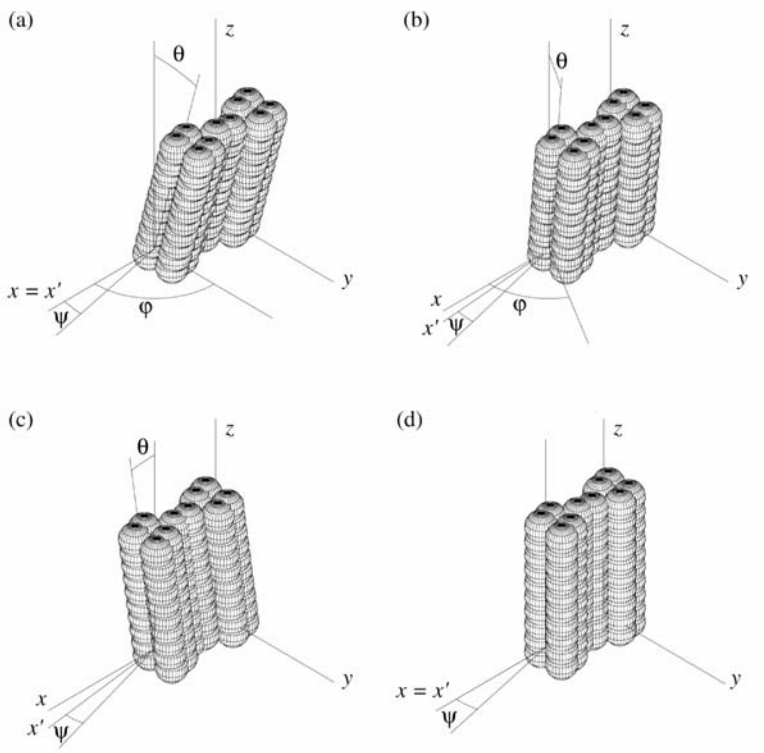

FIGURE 4 Typical configurations in the NN tilted (a), intermediate (b), NNN tilted (c) and untilted (d) phases.

of rigid rods grafted to an undistorted hexagonal lattice always exhibit NNN tilt [12], and this remains true even if lattice distortions are allowed [16]. Some authors propose that the NN tilt could be induced by attractive interactions between the rods and the water surface [14,16] or by head size effects [18]. In this paper we suggest that both NN tilt and the swiveling transition might be due to a coupling between two different degrees of freedom, namely the orientations of molecule main axes (tilt) and of backbone planes.

CONCLUSIONS

We reported on an investigation of the ground state properties of a lattice model of Langmuir monolayers, in which amphiphilic molecules are represented by rigid ladders. At low pressure the molecules arrange themselves in a herringbone structure with nearest-neighbor tilt. Increasing the pressure the tilt rotates towards next-nearest-neighbors and eventually disappears at a second order transition. Our results are consistent with experimental data and further work will be devoted to determine the phase diagram of the model at finite temperature and, if this proves necessary, to include head interactions in the model.

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