Simulated melting in an organic monolayer

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Abstract: Melting in a dense organic monolayer has been studied using Monte Carlo simulations on the skeletal model for the molecules. We find that melting causes enfolding of the hydrocarbon chains. In the pseudo-atom planes this melting is manifested as formation of a hexatic-like phase leading to an 'isotropic fluid' through creation of 'voids', the process starting from the methyl end. It is also observed that three characteristic phases, namely 2D solid, hexatic like liquid and 2D gas, through which the melting process occurs, get arrested in different pseudoatomic planes.

Key words: ultrathin organic films, 2-dimensional melting.
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Introduction

Langmuir-Blodgett technique to form ultrathin organic films has recently become the subject of intensive research effort both in technological and academic areas. This is mainly because ultrathin organic films have wide range applications in newly developing technological devices [1,2] and also that they show up important features which allow for new physics in quasi 2-dimensional systems [3,4]. These films are deposited on a solid substrate from a monolayer at the air- water interface. Advent of recent techniques, like grazing incident X-ray scattering (GIXS) and Atomic Force Microscopy (AFM) to probe surface with almost atomic resolution, has revealed considerable disorder in both multilayer and monolayer organic films [5,6]. To

understand this disorder and melting in 2-dimensional system, we have per-
formed a Monte Carlo simulation of a model monolayer. Melting in Lang-
muir monolayer, which is a quasi 2-dimensional system, will have distinct
features of its own, which, however, have not been investigated thoroughly.
Surface melting or quasi 2-dimensional melting has certain features distinct
from 3-dimensional melting such as two continuous phase transitions instead
of a single first order phase transition [7].

Model and calculation

The monolayer model considered for our simulation is that of a fatty-acid
with the general formula $CH_3 - (CH_2)_n - COOH$, where we have taken the
actual structure of the hydrocarbon skeleton with a constant $< CCC$ bond
angle of $114°$ and a $C - C$ bond length of $1.5 Å$. Our model treats the CH_2,
CH_3 and $COOH$ groups as pseudoatoms. We have assumed the $C - C$ bond
length and $< CCC$ bond angles to be fixed and allowed free rotations of the
pseudoatoms with respect to the preceeding bond direction. We have not
implemented any bond vibrational motion because energy required for this
type of motion is much higher than torsional motion[8]. We have taken a
close-packed triangular lattice of 95 molecules within rigid walls,each hav-
ing three CH_2 groups, their $COOH$ 'heads' fixed to the basal plane. The
intermolecular interaction is through a 12-6 Lennard-Jones potential, active
between nearest and next-nearest neighbour pseudoatoms present in all di-
rections. All distances are measured in units of $(\sigma/2)$ and all temperatures
T in units of $k_B\tau/u_0$ where τ is the temperature in Kelvin and k_B is the
Boltzmann constant, σ and u_0 being the range and depth of the L-J po-
tential considered. The lattice spacing is assumed to be constant at the
value of two units ($\simeq 5 Å$ as found experimentally [9]). We have started
with the initial configuration at $T = 0$ where the hydrocarbon tails are all
in *trans*-configuration and also parallel to each other.

With the increase in temperature, the position of each pseudoatom was
varied randomly. With each random variation the position of all the pseu-

doatoms (except the lowermost (head) and the next lowermost ones) in each molecule was obtained through the Eulerian transformation. This transformation enabled random variation in both the polar (θ) and azimuthal (ϕ) angles in the rotation of the CH_2 and CH_3 groups (pseudoatoms) about the bonds. The finite temperature equilibrium configuration were generated using the standard Metropolis algorithm [10]. Ten thousand MC steps per molecule took about ninety minutes of CPU time of an HP 9000 Workstation. We have studied the variation of the average equilibrium monolayer width

$$< h >_{eq} = < \frac{1}{N} \sum_{i=1}^{N} h_i >^{eq}, (N = 95) \tag{1}$$

with temperature. Here, h_i denotes the height of ith molecule from the substrate. We have also studied the positional disordering of pseudoatoms at equilibrium both in 2-dimensional planes and in 3-dimensional spaces, with temperature 0.0005, 0.001, 0.005 and 0.01.

.**Results and discussion**

Figure 1 shows a random sampling of some molecules at 0.01 temperature.
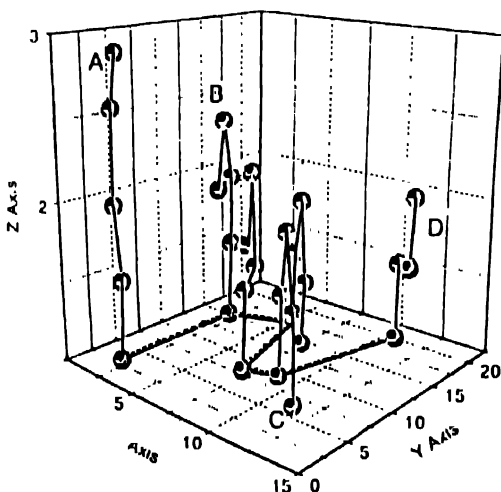

Fig. 1. Equilibrium configurations of some molecules at temperature 0.01, heads of the molecules are joined by double lines. Unit along X, Y or Z axes = 2.5λ. Same for Fig. 2 also.

We find that there is considerable enfolding of the hydrocarbon chains pointing out the importance of variation of both the polar and azimuthal angle. Apart from few molecules (for example A in Fig.1) almost all the chains show some enfolding (B and D of Fig.1) while a few have been totally folded (C of Fig. 1). The bending starts on the average from the CH_3 group at top but other chain segments are also possible starting points. This bending and final folding of the chain leads to a decrease in the average monolayer width which is measurable through GIXS. If we look at the planes containing the pseudoatoms, this rotations of the pseudoatoms about their bonds provides out-of-plane motions. It is quite apparent from Fig.1 that maximum deviation from perfect ordering occurs at the top pseudoatomic plane. This is consistent with the finding of AFM [8] that the topmost plane has the maximum surface disorder at any finite temperature.

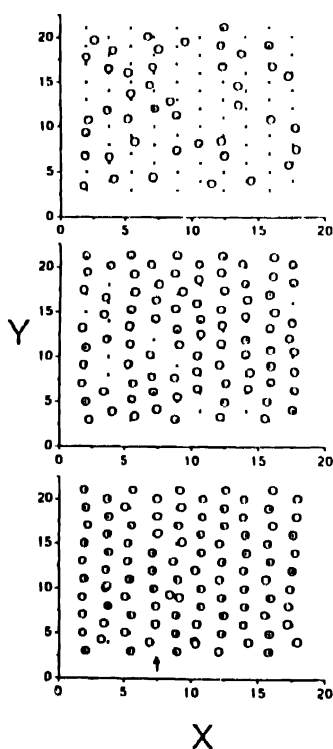To understand the process of melting, we have shown different pseudoatomic planes in Fig.2.

Fig. 2. Pseudoatomic planes in equilibrium. (bottom and middle) views of 3rd and 5th plane respectively at temperature 0.001(top) view of 5th plane at temperature 0.01. Plane thickness = 1.25λ.

Interestingly, different phases of melting get arrested in different pseudoatomic planes of equilibrium configurations at various temperatures. In Fig.2 we have shown three such phases which we believe are characteristic of this melting process and we feel that these are measurable in suitable AFM experiments. In the third plane (bottom of Fig.2) at 0.001 temperature, melting process is just setting in through 'fluctuation'. One column of atoms is marked to illustrate this interesting phenomenon. In the 5th plane (middle of Fig.2) a few random 'voids'are created due to the out-of-plane motion resulting in islands of pseudoatoms with orientational order among themselves but no positional order. Hence a phase with quasi long-range orientational order and short-range positional order analogous to the 'hexatic' phase evolves, as expected in 2-dimensional melting [7]. At temperature 0.01 melting affects all the planes and large number of pseudoatoms of upper plane take 'inter-plane' and lower plane positions through the chain enfolding (molecules B, C and D of Fig.1). The effect of this on the top most plane is shown in the top of Fig.2. This plane behaves like an 'isotropic fluid' or a 'gas', the final stage in 2-dimensional melting. It is interesting to note in Fig.2 that the displayed three planes behave as 2-dimensional 'solid', 2-dimensional 'hexatic' liquid and 2-dimensional 'gas' respectively. Looked at from the pseudoatom planes melting in a fatty acid monolayer has features of 2-dimensional melting. Features such as these have been reported theoretically [11] and experimentally [12,13] in various organic films.

In conclusion, we have investigated melting of Langmuir monolayer using Monte Carlo simulation and the actual molecular structure in the model. We believe that the basic features of this melting process canbe investigated through GIXS and AFM.

Acknowledgement

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