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Computer simulations of self-assembled monolayers

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Abstract

Self-assembled monolayers of organic molecules on solid substrates build well-defined surfaces, which can be structured efficiently on a nanometre scale. The molecular order of the molecules, in particular their tilt with respect to the surface, is believed to be important for the stability of those patterns. We discuss Monte Carlo simulations of a simple, idealized model for self-assembled monolayers, with particular emphasis on the different types of tilt order and tilting transitions.

1. Introduction

Self-assembled monolayers are formed by organic molecules which spontaneously chemisorb onto solid substrates [1, 2], e.g., alkanethiolates attaching to gold surfaces with their sulphur head groups. The structures may or may not be commensurate with the periodicity of the substrate. In most cases, the long axis of the molecules is tilted towards the surfaces. Different techniques have been employed successfully to pattern such monolayers [3–5], e.g., photolithography or scanning tunnelling microscope (STM) lithography. Since they resist several wet-etching solutions, self-assembled monolayers are of growing technological interest as wet-etching masks on the nanometre scale [6].

The long-time stability of the nanopatterns is rather surprising: even though the lateral diffusion constant of alkanethiolates on gold is roughly $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, nanopatterns on gold subsist over several hours. The reason for their longevity is not yet fully understood. It has been speculated that the tilt of the molecules plays an important role. If, for example, the molecules tilt towards the grooves of the patterns, this may kinetically stabilize the latter. A sound theoretical understanding of the monolayer structure, in particular of the tilting behaviour, seems crucial to comprehending the mechanisms involved in the patterning process.

As a first step in this direction, we have studied an idealized model of chain molecules adsorbed on a flat substrate by means of extensive Monte Carlo simulations. The molecules are modelled as chains of Lennard-Jones beads with interactions

$$V(r) = \begin{cases} \epsilon(V_{LJ}(r) - V_{LJ}(r_c)) & \text{for } r < r_c \\ 0 & \text{for } r > r_c \end{cases} \quad \text{with } V_{LJ}(r) = \left(\frac{\sigma}{r}\right)^{12} - 2\left(\frac{\sigma}{r}\right)^6. \quad (1)$$

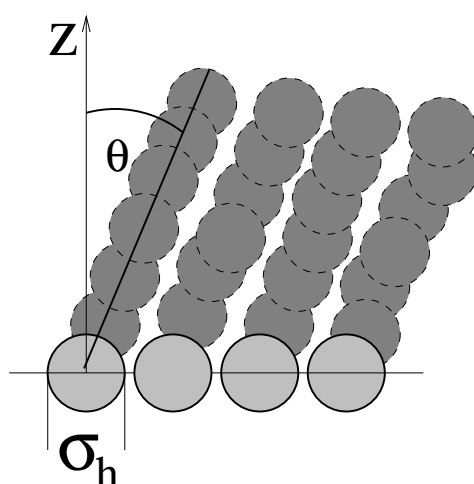


Figure 1. A schematic sketch of our model.

Here, $r_c = 2\sigma$, and the beads are connected by springs of length d , equilibrium length $d_0 = 0.7\sigma$, and spring constant $k_s = 100\epsilon$, which are subject to an additional stiffness potential $V_a = k_a(1 - \cos\theta)$ penalizing nonzero angles θ between subsequent springs. One of the end beads, the head bead, is chosen slightly larger than the others ($\sigma_H > \sigma$) and confined to a two-dimensional plane ($z = 0$), although it is free to move within this plane. Neither head nor tail beads are allowed into the half-space $z < 0$. A schematic sketch of the model is shown in figure 1.

For reasons of computational efficiency, head potentials were chosen as purely repulsive ($r_{c,H} = \sigma_H$). A similar model was originally suggested by Haas *et al* as a model for Langmuir monolayers [7], i.e., monolayers of amphiphiles at the air–water interface. However, at the present level of idealization, it is equally suited to describe self-assembled monolayers on solid substrates.

The simulations were carried out at constant lateral pressure in a simulation box of variable size and shape with periodic boundary conditions in the x - and y -directions. In most cases, systems of 144 chains each consisting of seven beads were studied. A few simulation runs were conducted with 900 molecules.

2. Results

Five different phases were observed [8, 9]. At high temperatures and low surface coverage, the molecules form a two-dimensional disordered liquid. Various condensed phases are encountered at higher surface coverage, which differ from each other mainly with respect to their tilt order: at low temperatures, the chains tilt collectively in a direction determined by a subtle interplay of the two-dimensional head lattice structure and the chain interactions [10, 11]—at high surface coverages, where the area per head is small, the tilt points towards the next-nearest neighbours, and at intermediate surface coverage, towards the nearest neighbours. If the size of the head exceeds a certain value ($\sigma_H > 1.14\sigma$ at chain length 7), we observe an additional modulated striped phase with an average tilt direction between nearest and next-nearest neighbours. Upon increasing the temperature, one finds that the chains gradually lose the common tilt and on average stand upright (even though individual chains may still retain

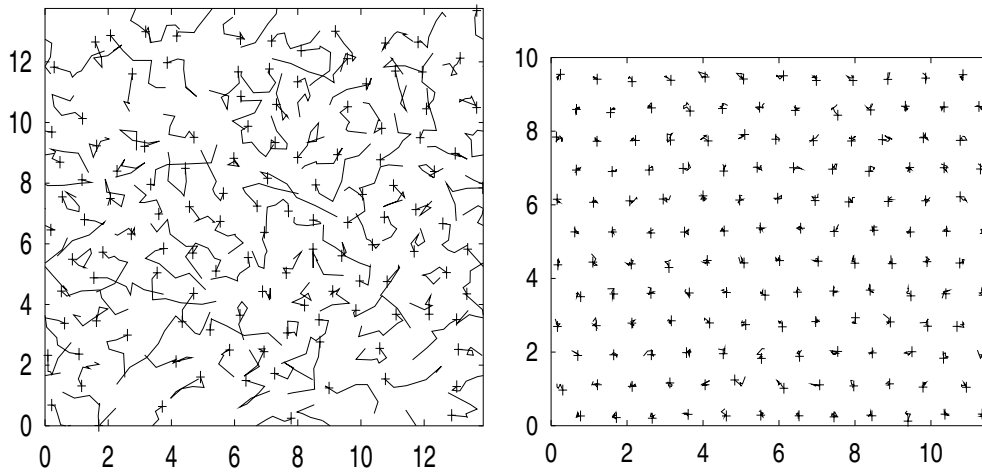


Figure 2. Top views of configuration snapshots in the disordered state (left) and in an ordered untilted state (right). Crosses mark the positions of head beads, and lines the projections of the springs connecting the chain beads to the xy -plane.

some tilt). Figures 2 and 3 show bird's-eye-view images of configurations in the different phases.

Top views of configuration snapshots in the disordered state (left) and in an ordered untilted state (right). Crosses mark the positions of head beads, and lines the projections of the springs connecting the chain beads to the xy -plane.

Top views of configuration snapshots in various tilted states: tilted towards next-nearest neighbours (top left); tilted towards nearest neighbours (top right); modulated striped state (bottom).

Phase diagrams were obtained by inspection of the order parameter

$$\Psi_6 = \left\langle \left| \frac{1}{6n} \sum_{j=1}^n \sum_{k=1}^6 \exp(i 6\phi_{jk}) \right|^2 \right\rangle$$

which measures the orientational order of the vectors \vec{r}_{jk} connecting a head j with its six closest neighbours k —where ϕ_{jk} is the angle between \vec{r}_{jk} and an arbitrary reference axis, and of the tilting parameter

$$R_{xy} = \sqrt{\langle [x]^2 + [y]^2 \rangle}$$

where $[x]$ and $[y]$ denote the x - and y -components of the head-to-end vector averaged over all chains of a configuration. As demonstrated in figure 4, the parameter Ψ_6 jumps to zero at the transition line between the disordered and the condensed region, and the tilt parameter R_{xy} approaches zero continuously at the transition line between tilted and untilted condensed states. This allowed us to locate the phase boundaries and to speculate on the nature of the phase transitions: the order–disorder transition appears to be first order, whereas the tilting transition seems continuous. A more reliable classification would involve a systematic finite-size analysis and require much more computing time than was available to us in this study.

Order parameters R_{xy} and Ψ_6 versus temperature in units of ϵ/k_B at constant pressure $\Pi = 50\epsilon/\sigma^2$. The size of the heads is $\sigma_H = 1.1\sigma$. One observes two successive phase

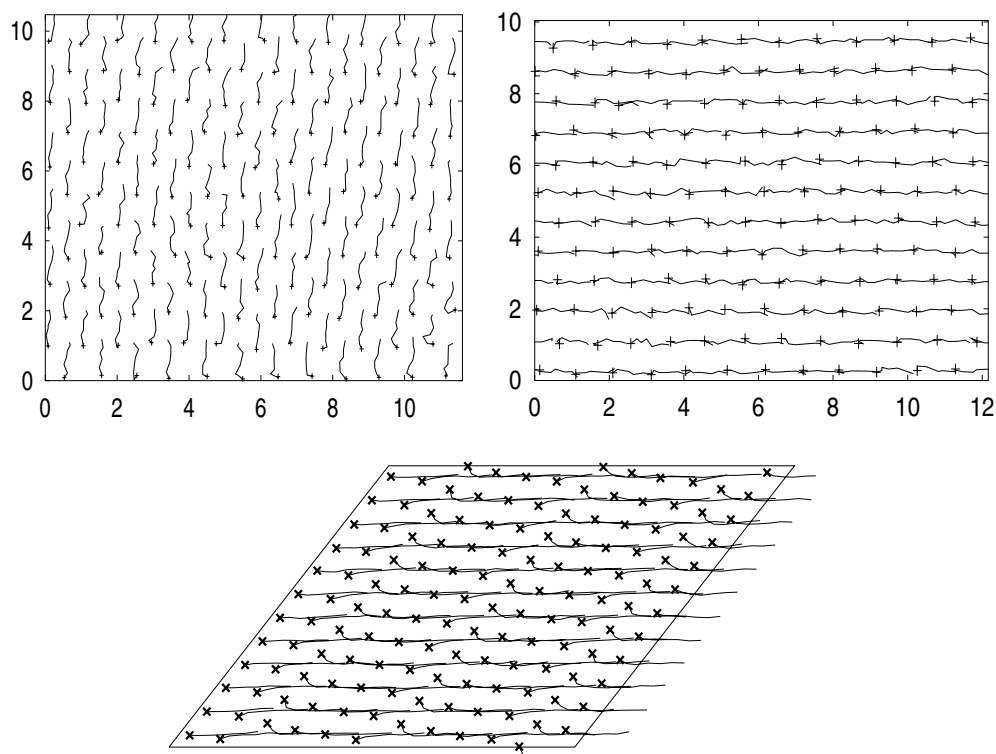


Figure 3. Top views of configuration snapshots in various tilted states: tilted towards next-nearest neighbours (top left); tilted towards nearest neighbours (top right); modulated striped state (bottom).

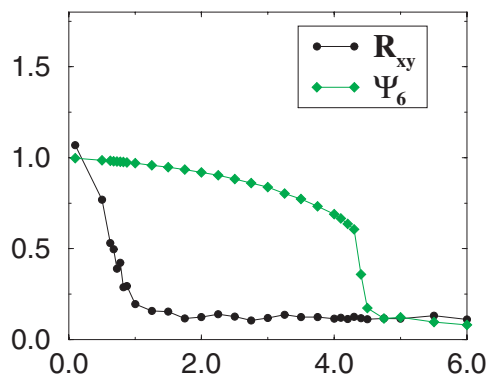


Figure 4. Order parameters R_{xy} and Ψ_6 versus temperature in units of ϵ/k_B at constant pressure $\Pi = 50\epsilon/\sigma^2$. The size of the heads is $\sigma_H = 1.1\sigma$. One observes two successive phase transitions, a tilting transition at low temperature and an order/disorder transition at high temperature.

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The swivelling transitions between different tilted phases are hard to identify at high temperatures, but are clearly discontinuous at lower temperatures, as evidenced by strong

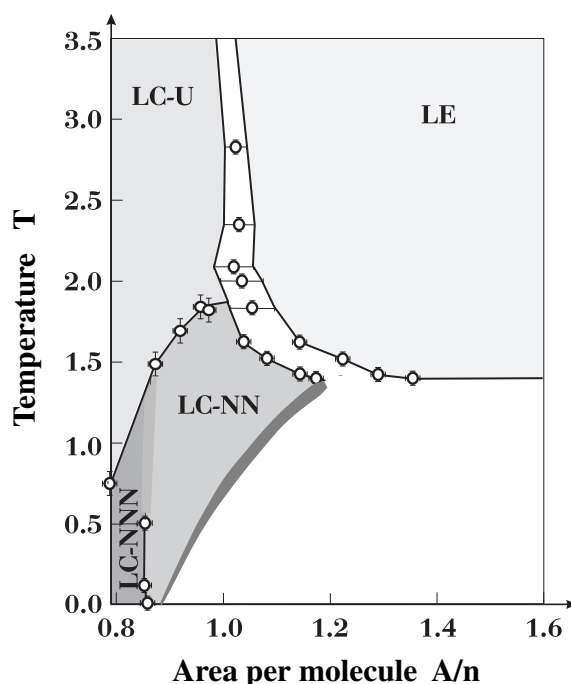


Figure 5. The phase diagram for monolayers of chains of length 7 and head size $\sigma_H = 1.1\sigma$. The temperature is given in units of ϵ/k_B , and the area in units of σ^2 . LE denotes the disordered liquid and LC the different condensed phases: LC-U, untilted, and LC-(N)NN, tilted towards (next-) nearest neighbours.

hysteresis effects. The latter obviously make it difficult to establish the exact location of the transition lines. In order to circumvent this problem, we have supplemented the simulations with a low-temperature phonon expansion, which enabled us to calculate the phase boundaries analytically at temperatures close to zero, and to trace them from there by thermodynamic integration, i.e., applying the Clausius–Clapeyron equation.

The resulting phase diagrams for head sizes $\sigma_H = 1.1\sigma$ and $\sigma_H = 1.2\sigma$ are shown in figure 5 [8] and figure 6 [9]. They share as common features a complex polymorphism of condensed phases at high surface coverage, followed at lower surface coverage by a disordered fluid at high temperatures and a wide two-phase gap at lower temperatures.

The phase diagram for monolayers of chains of length 7 and head size $\sigma_H = 1.1\sigma$. The temperature is given in units of ϵ/k_B , and the area in units of σ^2 . LE denotes the disordered liquid and LC the different condensed phases: LC-U, untilted, and LC-(N) NN, tilted towards (next-) nearest neighbours.

As figure 4, but for head size $\sigma_H = 1.2\sigma$. Additionally the striped modulated phase LC-mod is found.

In order to investigate the effect of the substrate potential on the phase behaviour, we have performed simulations of chains with heads of size $\sigma_H = 1.1\sigma$, which were bound to the surface by a soft harmonic potential rather than a rigid constraint. As one might expect, the transition pressures of the tilting transitions drop considerably as compared to the constrained model. In terms of the molecular area or surface coverage, however, the phase diagram largely resembles the one shown in figure 5 [12, 13].

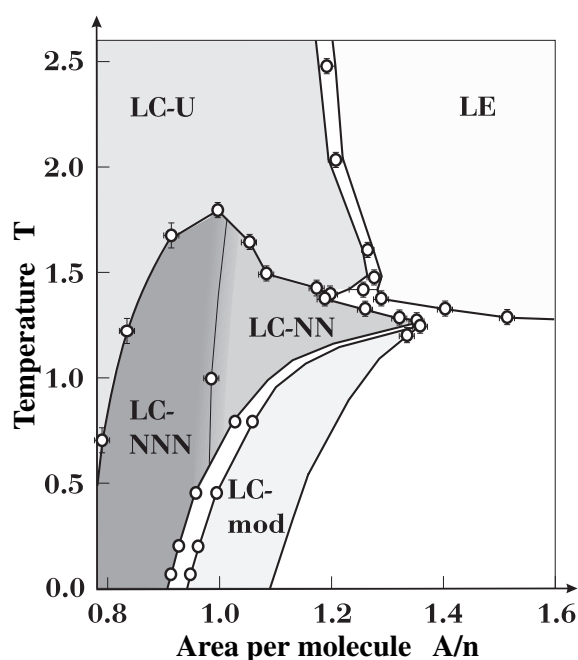


Figure 6. As figure 4, but for head size $\sigma_H = 1.2\sigma$. Additionally the striped modulated phase LC-mod is found.

3. Conclusions and outlook

Our studies have demonstrated that a very simple model for monolayers of chain molecules, which totally disregards the structure of the substrate, already exhibits a remarkably rich phase behaviour and a large number of different tilted phases. The transitions between the tilted phases are driven by an interplay between the head lattice structure and the chain interactions. Note that the flat substrates studied so far do not influence the periodicity of the head lattice. The situation will become even more complex when the corrugation of the substrate is taken into account. Not only will that affect the tilting transitions, but in addition, we also anticipate commensurate–incommensurate transitions, similar to the ones observed experimentally.

In order to address the issue of pattern stability discussed in the introduction, it will be particularly interesting to study laterally inhomogeneous monolayers, i.e., tilted monolayers with topological defects, and boundaries between coexisting condensed and disordered phases. We expect that such studies will provide valuable insights into the microscopic structure of nanopatterns in self-assembled monolayers, possibly even guidelines for optimal pattern design and pattern stabilization.

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