Continuum Monte Carlo Simulation of Phase Transitions in Rod-like Molecules at Surfaces (*).

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Summary. — Stiff rod-like chain molecules with harmonic bond length potentials and trigonometric bond angle potentials are used to model Langmuir monolayers at high densities. One end of the rod-like molecules is strongly bound to a flat two-dimensional substrate which represents the air-water interface. A ground-state analysis is performed which suggests phase transitions between phases with and without collective uniform tilt. Large-scale off-lattice Monte Carlo simulations over a wide temperature range show in addition to the tilting transition the presence of a strongly constrained melting transition at high temperatures. The latter transition appears to be related to two-dimensional melting of the head group lattice. These findings show that the model contains both, two- and three-dimensional ergodicity breaking solidification transitions. We discuss our findings with respect to experiment.

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1. – Definition of the model and ground-state analysis.

Amphiphilic rod-like molecules at surfaces or interfaces play an important role in questions as diverse as understanding complex biological membranes and their functionality or the technology of coatings for chemical sensors. The objective of the present paper is to present and investigate a simple model for phase transitions in such systems. The model consists of short chain molecules attached to a flat substrate. Due to space limitations we present here only an overview over selected results, and refer the reader to a forthcoming simulation study [1] for more detail.

Monomolecular layers of water-insoluble surfactant molecules at air-water interfaces, so called Langmuir monolayers, have found renewed experimental interest due to the recent availability of X-ray diffraction methods which complement more traditional thermodynamic measurements [2,3]. A large variety of phases and phase transitions has been observed in these systems [4].

Despite differences in detail many fatty acids, phospholipids, alcohols and esters exhibit a similar phase diagram. This is attributed to the similarities of these amphiphilic molecules which consist typically of a hydrophilic head group to which one or several hydrophobic alkane chains are attached. Often phase boundaries depend only on very coarse properties such as the length of the hydrophobic tails, but not on their detailed chemical nature. As an example, a rule of thumb says that adding a CH_2 group to a fatty acid increases the transition temperatures by roughly 8–10 degrees Celsius. These observations as well as density functional calculations [5] motivate and justify the use of highly idealized coarse-grained models when studying phase transitions in such systems by computer simulation. Further justification derives from the law of universality in phase transitions [6,7].

Given the usefulness of coarse-grained models for monolayers we represent each molecule through seven effective monomers labeled $i = 0, ..., 6$. For a typical fatty acid with chain lengths from 12 to 30 carbons each effective monomer would then represent roughly between two and five methyl groups. The Cartesian coordinate system in three-dimensional space is chosen such that the head group $i = 0$ is restricted to move in the $z = 0$ plane representing the two-dimensional substrate. A schematic cross-section for a single molecule consisting of only 4 effective monomers is shown in fig. 1. All the effective monomers are connected through a cut-off harmonic bond length potential $V_{bl}(d) = c_{bl}(d - d_0)^2$ for $|d - d_0| \leq d_{bl}$ and $V_{bl}(d) = \infty$ elsewhere, where $c_{bl} > 0$ is the spring constant. The stiffness of the rod-like molecules is simulated by a bond angle potential $V_{ba}(\theta_i) = c_{ba}(1 + \cos(\theta_i))$ where c_{ba}
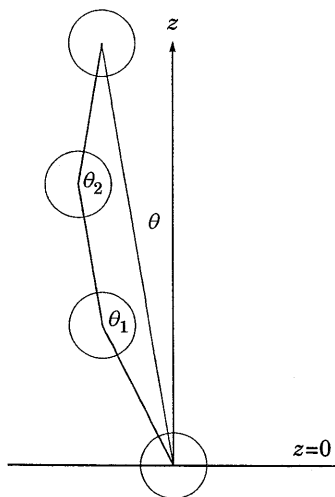

Fig. 1. – Schematic representation of a single chain-like molecule (here depicted with only four effective monomers). The bond angles θ_i are formed by consecutive bonds along the chain. The tilt angle θ is defined as the angle between the surface normal and the end-end vector of the chain.

is the force constant and θ_i is the angle formed by the three monomers $i-1$, i, $i+1$ as depicted in fig. 1 for $i = 1, 2$. All monomers except nearest neighbours within the same chain interact through a Lennard-Jones potential. The Lennard-Jones potential is truncated and shifted such that it vanishes at the truncation point. If ε and σ are used to denote the interaction strength and range, then $V_{\mathrm{LJ}}(d) = \varepsilon((\sigma/d)^{12} - 2(\sigma/d)^6 - (1/d_{\mathrm{LJ}})^{12} + 2(1/d_{\mathrm{LJ}})^6)$ for $d \leq d_{\mathrm{LJ}}\sigma$ where $d = d_{\mathrm{LJ}}\sigma$ is the truncation point, and $V_{\mathrm{LJ}}(d) = 0$ elsewhere.

Lengths and energies in our simulations will be measured in dimensionless units defined by setting $\sigma = 1$ and $\varepsilon = 1$. In these units the other parameters for the simulations are chosen as $d_0 = 0.7$, $d_{\mathrm{bl}} = 0.2$, $d_{\mathrm{LJ}} = 2.0$ and $c_{\mathrm{bl}} = 100$, $c_{\mathrm{ba}} = 10$. The choice c_{bl}, $c_{\mathrm{ba}} \gg \varepsilon$ models stiff rod-like chains. The molecules are enclosed inside a simulation box with side lengths L_x, L_y, L_z. In the simulations below we investigate two system sizes with 64 and 144 chains, respectively. The box dimensions for these two cases are chosen commensurate with the hexagonally ordered low-temperature phase as $L_x = 8$, $L_y = 4\sqrt{3}$ and $L_x = 12$, $L_y = 6\sqrt{3}$, respectively. The height L_z of the simulation box is always chosen much larger than the length of a fully stretched chain. Periodic boundary conditions are applied in the (x, y)-directions.

The model above extends and generalizes our earlier study of a system consisting of perfectly rigid rods grafted to a hexagonal lattice and interacting with Lennard-Jones interactions [8,9]. Most importantly the present model does not restrict the head groups to form a regular crystalline array at all times. This allows for restructuring or even melting of the head group lattice. We emphasize that the singular character of the interactions between substrate and head groups still represents an important idealization whose validity remains open to question. While the model is more realistic than fully discrete lattice models [10] it contains less chemical detail than united atom models which have been investigated using molecular-dynamics simulations [11-13]. We thus feel that our model represents a good compromise between computational efficiency and chemical realism.

Before discussing the simulations we analyse the ground state in order to be able to choose the model parameters in a physically interesting regime. We stress the need for such an analysis also for chemically more realistic models with correspondingly larger parameter spaces. Already the present simple model has too many parameters to fully elucidate its ground-state phase diagram. At very high densities one expects the head groups to form a hexagonal lattice and all the tails to have the same director. The director is defined as the vector from the head group $i = 0$ to the tail group $i = 6$ of the molecule. This expectation depends crucially on the form of the substrate-head group interaction and the rod-like character (c_{bl}, $c_{\mathrm{ba}} \gg \varepsilon$) of the molecules. The question becomes how the expected ordering changes as the model parameters are varied. Because we are interested in rodlike molecules with c_{bl}, $c_{\mathrm{ba}} \gg \varepsilon$ we idealize the bond length and bond angle potentials as infinitely rigid for the purposes of the ground-state analysis. This eliminates the corresponding parameters, and simplifies the analysis. Furthermore we are looking only for states with uniform tilt and a hexagonal head group lattice of lattice constant a. This reduces the problem to finding the tilt angle and direction which minimizes the Lennard-Jones interactions. The minimization is carried out numerically. The results [1] agree qualitatively with the behaviour obtained from a simple geometrical argument. In this argument even the Lennard-Jones parameters are eliminated by replacing the monomers with hard spheres, and then considering the system as a stack of planes. A brief reflection shows that in this case the tilt direction must

always be towards next-nearest neighbours, and that the collective tilt angle θ is related to the lattice constant a and the bond length d_0 through $\sin(\theta) = \{a^2 + d_0^2 - 1\}/\{\sqrt{3}\,a d_0\}$. We expect that in other regions of the parameter space states with non-uniform tilt could appear as ground states. This is indicated by the appearance of discontinuities in the function $\theta(a, d_0)$ obtained from energy minimization[1] as well as from the ground-state analysis of the rigid-rod model[8].

2. – Results and discussion.

The continuum model specified above is simulated in a canonical ensemble at constant temperature, volume and particle number. The simulation is carried out using a Metropolis Monte Carlo procedure in which individual monomer positions are updated in continuous space. The continuous position space requires to use methods adapted from molecular-dynamics simulations for evaluating the interaction energies. We have developed an adaptation of the link-cell algorithm using specially designed linked pointer lists. In fig. 2 we show a snapshot of an equilibrated configuration of 144 chains at temperature $T = 1.0$. Each sphere of radius $\sigma/2$ represents an effective monomer.

Temperature scans over two decades were performed for different box geometries to check for the influence of commensurability effects. Only the hexagonal box geometry described above was found to be free of hysteresis effects and was therefore adopted in further simulations. For each temperature point the system was first equilibrated for 20 000 Monte Carlo steps (updates per monomer). Subsequently averages were recorded every 500th MCS over a period of 50 000 MCS. These calculations consumed several 100 hours of CPU time on IBM RS6000 370 equipment.

Figure 3 shows the results of an extensive temperature scan for the average tilt angle $\langle|\theta|\rangle$ (see fig. 1) for two different system sizes. The results suggest the presence of two phase transitions, one tilting transition between $T = 1$ and $T = 2$ in which the tilt angle vanishes, and a melting transition around $T = 8$ in which the fluctuations of the average tilt angle increase. Note that the average tilt angle is never zero due to thermal fluctuations. This picture is confirmed by the probability density for the projection of the director into the (x, y)-plane as well as other orientational correlation functions[1]. The low-temperature transition from a tilted to an untilted state is well anticipated by theoretical and experimental evidence.
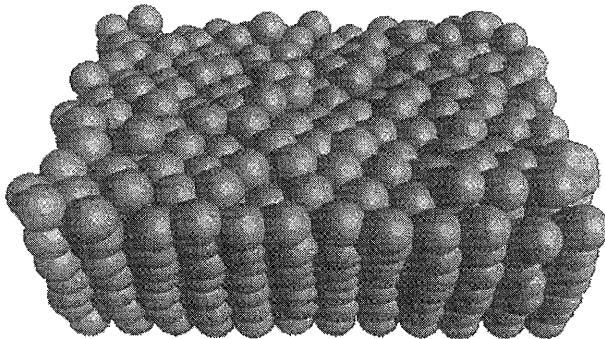

Fig. 2. – Snapshot of an equilibrated configuration with 144 chains at temperature $T = 1$. Each monomer is represented as a sphere of radius $\sigma/2$.
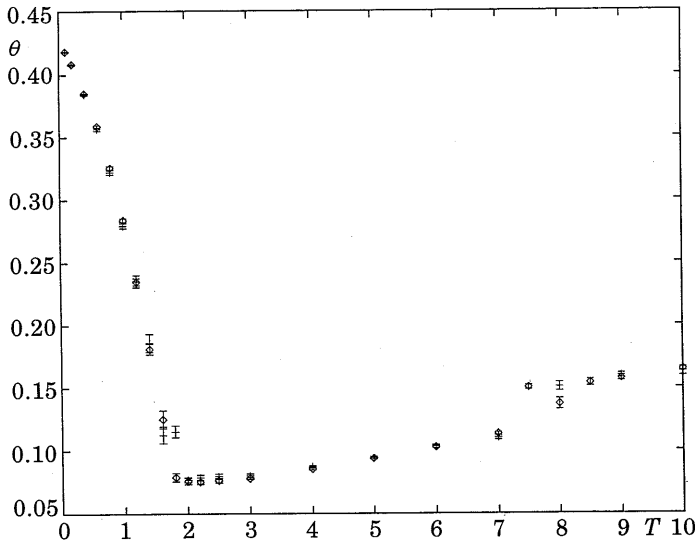
Fig. 3. – Average tilt angle as a function of temperature. Different symbols ($\ddagger$ and Φ, respectively) denote system sizes 64 and 144.

It corresponds to a restoration of ergodicity for the tails which are frozen into their crystalline positions at low temperatures but move freely in a much larger configuration space at high temperatures. The phase transition at high temperatures, however, has to our knowledge not been observed or predicted in models for Langmuir monolayers. It corresponds to a restoration of ergodicity in the strictly
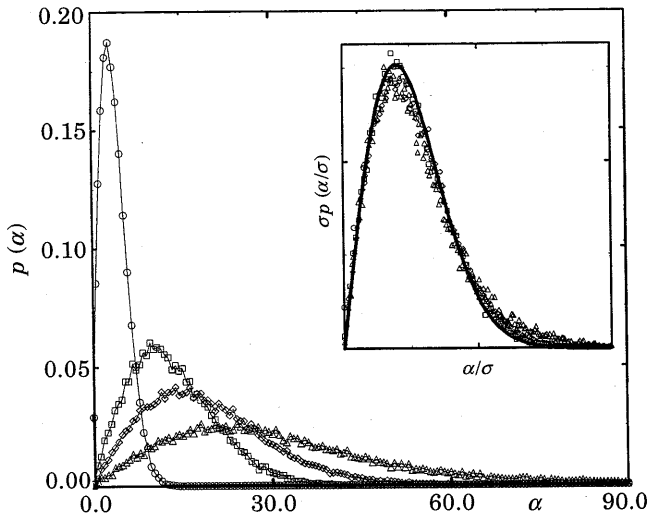

Fig. 4. – Probability density functions for the bond angles $\alpha_i = |\pi - \theta_i|$ at temperatures $T = 0.1$ ($\bigcirc$), 1.0 ($\square$), 2.0 ($\diamondsuit$) and $T = 8.0$ ($\triangle$). The inlay shows the same data scaled with the variance σ of the bond angle distribution. The solid line is the curve $\sigma p(\alpha/\sigma) = (\alpha/\sigma)$ $\exp[-(\alpha/\sigma)^2/2]$ expected for small Gaussian deviations from linearity.

two-dimensional layer of head groups. In fact the intermediate dimensionality of our system allows to view it as a highly constrained three-dimensional film or as a strictly two-dimensional system of head groups with internal degrees of freedom representing the influence of the tails. The high transition temperature of the two-dimensional melting transition appears to be somewhat at variance with the small temperature range for phase transitions in Langmuir layers, and suggests that this transition might be more likely observed on solid substrates.

In fig. 4 we display the distribution of the bond angles $\alpha_i = |\pi - \theta_i|$, where θ_i was defined above (see fig. 1). This distribution appears to be of experimental interest (Ch. Wöll, private communication). Not unexpectedly the bond angle distribution is always peaked at non-zero values, and broadens with temperature. In fact, if the deviations from strict linearity ($\alpha_i = 0$ for all i) are small and Gaussian, we expect all distributions to collapse onto a master curve $p(\alpha) \propto \alpha \exp[-\alpha^2/2]$ after rescaling with the variance. As shown in the inlay to fig. 4 this expectation is indeed borne out. The agreement between the master curve and the scaled data indicates that the bond angle distribution reflects mainly thermal fluctuations, but does not correlate strongly with the microscopic structure of different phases.

More insight is gained from plotting the total monomer density profiles as a function of the distance z from the flat substrate. Figure 5 shows the corresponding plots for temperatures $T = 0.1, 1.0, 2.0, 8.0$. At low $T = 0.1, 1.0$ the structure of the monolayer is crystalline, and the fluctuations within a layer are small. As the temperature is raised the layer starts to melt from the free surface inwards. At $T = 2$ the peak of the layer of tail groups ($i = 6$) has completely vanished indicating that the fluctuations in the z-coordinates of the tail groups are of the same order as the
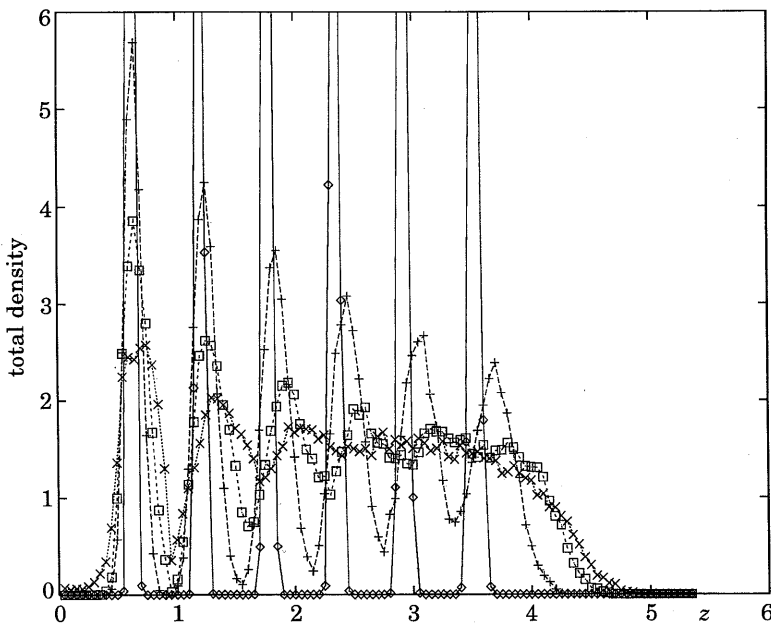

Fig. 5. – Total monomer density profiles as a function of the distance z from the substrate. The densities are normalized to 6. The head group monomer ($i = 0$) at $z = 0$ is not included in the plot. $T = 0.1$ (–◇–), $T = 1.0$ (–+–), $T = 2.0$ (-⊟-), $T = 8.0$ (··×··).

distance to the layer below. At high T the layer of tail groups and the next three monomer layers have merged into a fluid film. This restoration of ergodicity propagates even to the head group lattice. Appropriately measured head group structure factors indicate a melting of the head group lattice at the highest temperatures[1]. The transition between ergodic and non-ergodic behaviour in the present case is particularly interesting in view of the strong internal constraints introduced by the large spring constant $c_{bl} = 100$ and the hard cut-off in the harmonic bond length potential. It is only thanks to these strong internal constraints that the layer can still be identified and studied in the high-temperature ergodic phase, a feature which is otherwise absent.

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