Orientational ordering in lipid monolayers: A two-dimensional model of rigid rods grafted onto a lattice

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A simple model for lipid monolayers on water surfaces at high spreading pressure is investigated in this work. In this model, the hydrophilic head group of the lipid molecules form a rigid regular triangular lattice, and the hydrophobic alkane chains (assumed to be in an all-*trans* state) are represented by rigid rods with two angular degrees of freedom (θ, φ). The rods consist of "effective monomers," and between the effective monomers on neighboring rods a Lennard-Jones interaction is assumed. The model is studied by exact ground-state calculations, mean-field theory, and Monte Carlo simulations. Basic parameters are rod length a and lattice constant b. The ground-state phase diagram shows the following phases: for small b, the rods are oriented perpendicularly to the monolayer plane (no-tilt phase, $\langle \theta \rangle = 0$); for somewhat larger b, a sixfold degenerate uniform-tilt state occurs with all rods tilted towards one of their next-nearest neighbors. For still larger b, the rods are tilted nonuniformly and form a "striped" structure. These unexpected phases do not occur if we allow a rectangular distortion of the lattice. For $T > 0$, the simplest mean-field theory predicts a gradual disordering of the uniform-tilt state via a second-order phase transition. For the transition region, the Monte Carlo results disagree with this picture. Instead they show a strong asymmetric first-order phase transition with pronounced hysteresis. The transition temperature increases with increasing rod length a, qualitatively similar to experiment.

I. INTRODUCTION AND DEFINITION OF THE MODEL

Lipid monolayers at the air–water interface are of great interest because they are model systems for more complex biological membranes and because they exhibit various kinds of ordered phases.[1-7] The lipid molecules forming these layers have a hydrophilic head group to which one or two alkane chains $(CH_2)_M CH_3$ with $12 \leqslant M \leqslant 22$ are attached. While there has been enormous activity on the "main transition", i.e., the melting of the layer (see e.g., Ref. 8 for a review on models of this transition), somewhat less attention has been paid towards the understanding of the transitions between various solid phases.[9,10] These transitions occur at high spreading pressure[3,5-7] and exhibit different kinds of orientational order. Because of the complexity of the molecules, it is difficult to develop microscopically realistic analytic theories for such systems, and even atomistic computer simulations can yield only qualitative insight into the phase behavior.[8,11-13]

Following the arguments of Refs. 8–10, we consider here only a simplified "coarse-grained" model, where the alkane chains are described as rigid rods. In order that the model remains tractable, each rod has only two orientational degrees of freedom θ, φ [Fig. 1(a)]. The rods have the length A and are grafted on a rigid triangular lattice with lattice constant B. Within the lattice, there are no further degrees of freedom.

For the interaction between the alkane chains, we assume a Lennard-Jones potential $U_{LJ}(d)$ between effective monomers

$$U_{LJ}(d) = U_0 \{(\sigma/d)^{12} - 2(\sigma/d)^6\}, \tag{1}$$

where U_0 describes the strength, σ the range of this potential, and d is the distance between effective monomers. Assuming that there are ν_0 effective monomers per rod, and measuring all lengths in units of σ, we have the rescaled rod length $a = A/\sigma$ and the rescaled lattice parameter $b = B/\sigma$. The total potential energy between a pair of rods becomes, cf. Fig. 1(b)

$$U_{12}(\theta_1,\varphi_1,\theta_2,\varphi_2) = (a^2/\nu_0^2) \sum_{j,l=1}^{\nu_0} [(d_{1j,2l})^{-12} - (2d_{1j,2l})^{-6}]. \tag{2}$$

Here the units of energy and temperature have been chosen such that the constant U_0 in Eq. (1) is absorbed in these units. $\mathbf{d}_{1j,2l}$ is the distance between monomer j at rod 1 and monomer l at rod 2, where

$$(d_{1j,2l})^2 = (ja/\nu_0)^2 + (la/\nu_0)^2 + (b_{12})^2$$
$$- 2(jla^2/\nu_0^2)\mathbf{S}_1 \cdot \mathbf{S}_2 + 2b_{12}[(ja/\nu_0)\mathbf{S}_1$$
$$+ (la/\nu_0)\mathbf{S}_2], \tag{3}$$

with $\mathbf{S}_i = (\cos \varphi_i \sin \theta_i,\ \sin \varphi_i \sin \theta_i,\ \cos \theta_i)$ denoting an unit vector along rod i, and $\mathbf{b}_{12} = [b \cos (k\pi/3), b \sin (k\pi/3),\ 0]$, with $k = 0,1,\cdots 5$ a vector connecting lattice sites 1 and 2 [Fig. 1(b)]. Finally, the model is fully specified by the restriction to interactions between nearest-neighbor rods.

In previous work on the one-dimensional version of this

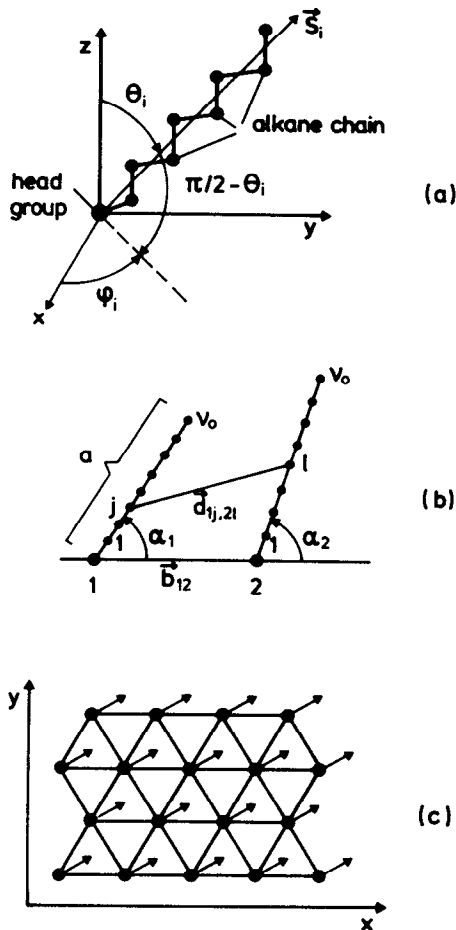[a] Present address: Laboratorium für physikalische Chemie, ETH-Zentrum, 8092 Zürich, Schweiz.

FIG. 1. (a) Schematic modelling of a lipid molecule (labeled by index i): the head group lies in the air–water interface which is oriented in the xy plane, while the alkane chain in its all-*trans* state is characterized by an unit vector S_i or its associate polar angles (θ_i, φ_i). (b) The interaction between two rods 1 and 2 occurs between effective monomers j $(1 \leqslant j \leqslant v_0)$ and l $(1 \leqslant l \leqslant v_0)$. If we choose new polar coordinates such that the polar axis coincides with the vector b_{12} (connecting the two head groups) and that the x-axis lies in the plane formed by the vectors b_{12} and S_1, the distance $d_{1j,2l}$ can be expressed in terms of the two polar angles α_1, α_2, and one azimuthal angle β_2 for rod 2. (c) Top view of the layer with uniform-tilt structure. Head groups form a regular triangular lattice, and the projections of the unit vectors S_i into the xy plane (arrows) point towards their next-nearest neighbors.

model it was found[10] that in the groundstate there are two distinct phases: a (nondegenerate) state where the rods are oriented perpendicularly to the lattice (no-tilt state), and a (twofold degenerate) state where the rods are uniformly tilted (i.e., $\theta_i = \pm \theta_0$ for all i). At nonzero temperature T, fluctuations destroy the long range order of the latter state, and the remaining regions of uniform tilt extend only over a finite correlation length.

In the present two-dimensional case, we expect that in addition to the no-tilt state there should be a (sixfold degenerate) uniform-tilt phase [Fig. 1(c)] which should be stable over a nonzero temperature range. There exists also a third ordered phase where the rods lie in the xy plane. This phase will remain outside of consideration here because it does not correspond to any of the experimentally observed phases.

We study the model in Sec. II by exact ground-state calculations and in Sec. III by the simplest version of a mean field theory. Section IV presents our Monte Carlo method and discusses the numerical results. Because for $v_0 = 15$ the reorientation of a single rod inside its wreath of nearest neighbors requires to evaluate $6v_0^2 = 1350$ Lennard-Jones interactions even the simulation of this very simple model is not at all straightforward. We have found it convenient and feasible to discretize angular space and store the necessary pair energies between neighboring rods in a huge table. In Sec. V we compare our results briefly to corresponding experimental data and discuss possible improvements of the present model.

II. GROUND STATE ANALYSIS

If we assume a structure of uniform-tilt type, the total potential energy U depends only on two angular variables θ_0 and φ_0. It is straightforward to calculate $U(\theta_0, \varphi_0)$ numerically. From its partial first and second derivatives we locate the minimum in order to obtain the ground state structure.[14] As in the one-dimensional case, the no tilt phase is the ground state for small enough b, i.e., $b < b_c(a, v_0)$. At the critical line $b = b_c(a, v_0)$ a second-order transition to the structure with uniformly tilted rods occurs. This structure is characterized by $\theta_0 \sim [b - b_0(a, v_0)]^{1/2}$ and $\varphi_0 = \pi/6$, if, because of the sixfold symmetry of the problem, φ is restricted to the interval $0 \leqslant \varphi_0 \leqslant \pi/3$, The function $b_c(a, v_0)$ is found to be identical to the one-dimensional case.[10]

While for dimensionality $d = 1$ no other phases need to be considered, this is no longer true for $d = 2$. We have discovered this fact from Monte Carlo calculations at low temperatures. These calculations were started from the uniform-tilt configuration, and in a broad regime in the (a,b) plane, they generated configurations with a *lower* energy than the energy of the uniform-tilt configuration.

Visual inspection of these configurations revealed various patterns of structures with nonuniformly tilted rods. This fact suggested to include a two-sublattice striped phase into the ground-state analysis. In this phase the triangular lattice is decomposed into rows, where the vectors S_i are characterized by angles θ_{0a}, φ_{0a} alternating with rows where the vectors S_i are characterized by angles θ_{0b}, φ_{0b}. Using "simplex-downhill" minimization routines,[15] we located the minima of the resulting fourdimensional energy hypersurface for some points of the (a,b) plane. In Table I the energy of this two-sublattice structure is compared to the energy of the uniform-tilt state. It is seen that the two-sublattice structure in this case $(a = 5)$ is lowest in energy from about $b \approx 1.08$ to about $b \approx 1.36$. For other values of b the two-sublattice solution converges also to the uniform-tilt state. However, Monte Carlo simulations for some values of b lead to even lower energies than those of the two-sublattice state (Table II).

The nature of these phases with nonuniformly tilted rods is difficult to identify, since the variation of the energy with the lattice size L is nonuniform. For arbitrary values of L, structures with sublattices will not fit to the lattice, because, due to the periodic boundary conditions, a misfit occurs if L is not an integer multiple of the period of the struc-

TABLE I. Potential energy per lattice site for uniform and double-striped configurations; $a = 5.0$.

b	U_u	U_{2-Str}
0.80	+ 29.526 031	+ 29.526 031
0.90	− 20.037 141	− 20.037 141
1.00	− 22.071 011	− 22.071 011
1.05	− 21.029 010	− 21.029 010
1.07	− 20.577 621	− 20.577 621
1.08	− 20.351 128	− 20.351 130
1.10	− 19.901 882	− 19.919 490
1.15	− 18.833 338	− 18.935 529
1.20	− 17.877 487	− 18.062 125
1.25	− 17.039 778	− 17.242 076
1.30	− 16.307 144	− 16.446 018
1.35	− 15.665 778	− 15.685 392
1.36	− 15.547 412	− 15.551 187
1.37	− 15.432 129	− 15.412 329
1.40	− 15.103 769	− 15.103 769
1.50	− 14.165 706	− 14.165 706

ture. The small energy differences between odd and even L suggest that possibly long period superstructures might occur. We have not investigated the ground-state phase diagram (Fig. 2) further, since this would be a formidable numerical problem. Any results of that kind are probably irrelevant because only no-tilt phases and various uniform-tilt phases have been detected so far in experiments on fatty acids.[7] Experimentally, the triangular lattice has the full hexagonal symmetry only in the no-tilt phase: in the uniform-tilt phase, an orthorhombic distortion occurs so that a centered rectangular lattice results rather than a standard triangular lattice. Allowing such orthorhombic distortions of the lattice [which are measured by a distortion factor f with $(\partial U/\partial f) = 0$], we obtain Table III. In this calculation the elastic energy of the deformation is neglected in comparison with the Lennard-Jones interactions. It shows that the lattice contracts in the direction perpendicular to the tilt, and that the phase with uniformly tilted rods is always stable for $b > b_c(a)$. In this case, the phase diagram for $T = 0$ is again simple (Fig. 3). The angle θ_0 in the uniform-tilt phase depends only very little on whether the lattice is deformable or not (see Table III). This indicates a considerable robustness of our model against changes of details.

III. MEAN-FIELD THEORY

A prerequisite for a mean-field calculation is the identification of the ordering that one wishes to study. Here we restrict attention to the uniform-tilt state only. This yields two self-consistency conditions for the two angular degrees of freedom of the central rod. With the notation $\vartheta_i = (\theta_i, \varphi_i)$ ($i = 1,2$) one obtains as a self-consistency condition

$$\vartheta_2 = \langle \vartheta_1 \rangle = \frac{\Sigma_{\theta_1} \Sigma_{\varphi_1} \vartheta_1 \, \Pi_{k=0}^5 \exp[\, - U_k(\vartheta_1,\vartheta_2)/T\,]}{\Sigma_{\theta_1} \Sigma_{\varphi_1} \Pi_{k=0}^5 \exp[\, - U_k(\vartheta_1,\vartheta_2)/T\,]}. \tag{4}$$

In our notation we have already expressed the fact that for the numerical implementation the integrals over the angles of the central rod (θ_1,φ_1) in the "field" of its six neighbors (which all have orientation ϑ_2) are discretized. The product $\Pi_{k=0}^5$ represents the decomposition of the total energy into six contributions U_k of single nearest-neighbor pairs [Eqs. (2) and (3)]. Note that we have chosen $k_B \equiv 1$.

The numerical solution of Eq. (4) is laborious because of the complexity of the energy surface $\Sigma_{k=0}^5 \, U_k(\vartheta_1,\vartheta_2)$, see Fig. 4 for an illustrative example. One can see that the uniform-tilt minimum disappears for $\theta_2 > 0.8$, indicating the importance of states with nonuniform tilt also on the mean-field level. This must be expected, since such states appeared in the $T = 0$ calculation.

At low temperatures it is clearly permissible to exploit the approximate degeneracy of Eq. (4) in the φ variable. Restricting φ_1,φ_2 as $\varphi_1 = \varphi_2 = \pi/6$ leads to an one-dimensional self-consistency equation $\vartheta_2 = \langle \vartheta_1 \rangle$, which can be solved straightforwardly (Fig. 5). This procedure obviously leads to a second order transition. We shall compare the results of this treatment to the Monte Carlo data in the next section.

IV. MONTE CARLO STUDIES

As has been mentioned in Sec. I, for $\nu_0 = 15$ already $6\nu_0^2 = 1350$ Lennard-Jones interactions must be considered for reorienting a single rod. Consequently, such a Monte Carlo algorithm is very slow: for a small 21×21 lattice, 10^4 Monte Carlo steps (MCS) per rod take already 30 min CPU time on a CRAY-XMP or Siemens–Fujitsu VP100 computer. Therefore, even a study of this very simple model by Monte Carlo methods using continous angles (θ_i,φ_i) would

TABLE II. Simulation results for various system sizes at $T = 0.001$ (potential energy per lattice site).

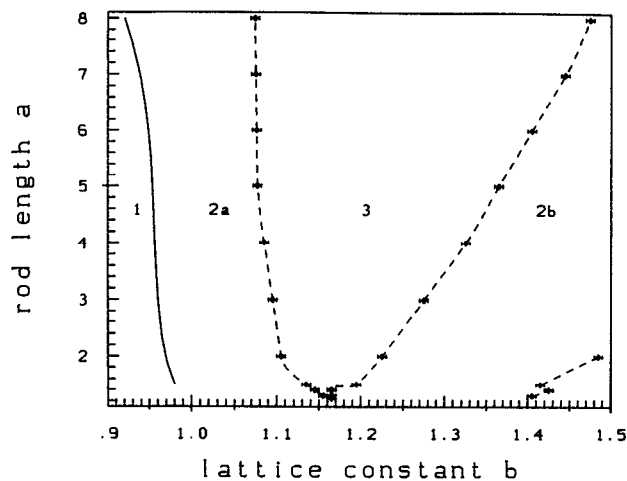| b	$L = 5$	$L = 8$	$L = 11$	$L = 14$	$L = 17$	$L = 20$
1.00	− 22.070	− 22.070	− 22.0701			
1.10	− 19.989	− 19.9705	− 19.915	− 19.988	− 19.982	− 19.981
1.20	− 18.0686	− 18.061	− 18.063	− 18.066	− 18.065	− 18.066
1.25	− 17.199	− 17.241	− 17.223	− 17.212	− 17.198	− 17.205
1.30	− 16.438	− 16.445	− 16.38	− 16.428	− 16.436	− 16.433
1.35	− 15.666	− 15.666	− 15.673	− 15.686	− 15.706	− 15.705
1.40	− 15.1027	− 15.1027	− 15.1027	− 15.1027	− 15.1027	− 15.1028

FIG. 2. Ground-state phase diagram for the model with rigid regular triangular lattice. Lines separate different phases in the plane of variable a (rescaled rod length) and b (rescaled lattice spacing). 1 labels the no-tilt phase, 2 labels the uniform-tilt phase, 3 contains (possibly several) phases with structures of nonuniformly tilted rods. This phase diagram corresponds to the choice $v_0 = 15$ [in the limit $v_0 \to \infty$ the boundary between the no-tilt and uniform-tilt phase would be at $b = b_c(a) \equiv 1$].

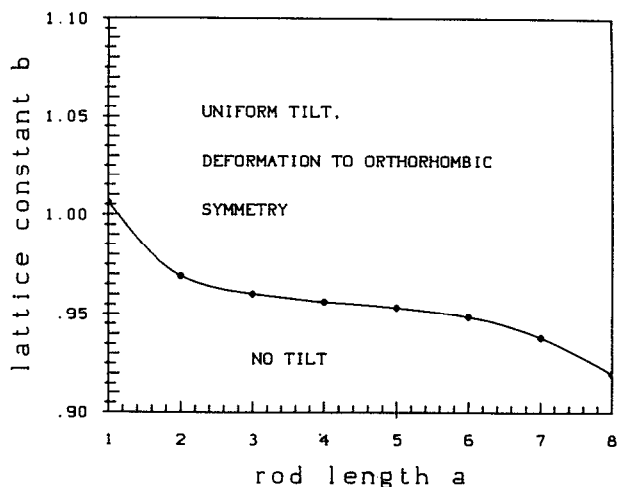
FIG. 3. Ground-state phase diagram for the model with deformable lattice. Nature of the phases is indicated in the figure.

take excessive amounts of computer time. In the one-dimensional case[10] it has been found that discretizing the angles $\{\theta_i\}$ into 500 values, which must be situated in a suitably chosen interval, yields a program speedup by a factor of 25.

Direct extension of this technique to the two-dimensional model is not possible, because each rod has now two degrees of freedom (θ_i, φ_i). In order to discretize the four angles $(\theta_1, \varphi_1, \theta_2, \varphi_2)$ of a pair of neighboring rods and to store the corresponding interaction energies, we first tried to use the largest possible table fitting into the computer memory. But it was found that there were still systematic discrepancies between this discretized program version and the correct calculation using continuous angles. However, as indicated in Fig. 1(b), for each pair of rods it is possible to

TABLE III. Groundstate energy U_0 and tilt angle θ_0 for the orthorhombic lattice; $a = 5.0$. U_0^u and θ_0^u are the corresponding quantities for the uniform tilt state of the undeformed lattice.

b	U_0	θ_0	f	U_0^u	θ_0^u
0.95	−22.649	0	1	−22.649	0
0.96	−22.629	0.1328	0.9904	−22.610	0.1332
0.97	−22.598	0.2102	0.9802	−22.521	0.2116
0.98	−22.562	0.2656	0.9702	−22.244	0.2682
1.00	−22.487	0.3492	0.9508	−22.071	0.3549
1.05	−22.290	0.4906	0.9055	−21.029	0.5064
1.10	−22.082	0.5880	0.8644	−19.902	0.6158
1.15	−21.866	0.6635	0.8268	−18.833	0.7043
1.20	−21.652	0.7252	0.7923	−17.877	0.7800
1.25	−21.440	0.7772	0.7607	−17.040	0.8464
1.30	−21.228	0.8217	0.7314	−16.307	0.9059
1.35	−21.016	0.8606	0.7043	−15.666	0.9604
1.40	−20.807	0.8951	0.6792	−15.104	1.0111
1.45	−20.602	0.9260	0.6557	−14.608	1.0590
1.50	−20.399	0.9538	0.6339	−14.166	1.1045

carry out a coordinate transformation from the angles $(\theta_i, \varphi_i, \theta_2, \varphi_2)$ to a new set $(\alpha_1, \alpha_2, \beta_2)$ involving three angles only. A discretization where α_1, β_2 take 199 values and α_2 takes 398 values has been found to reproduce with sufficient accuracy the results of the Monte Carlo program which uses continuous angles. Although this discretization involves a lookup table of 64 MByte for the pair energy, it is still faster than the continuous program version by a factor of 20.

In both versions of the Monte Carlo program the standard Metropolis algorithm was used,[16] and the triangular lattice was decomposed into three sublattices so that straightforward vectorization (in analogy with the checkerboard algorithm for the square lattice[17]) was possible.

The following quantities were recorded ($N = L \times L$ is the number of rods):

(I) The potential energy per rod $\langle U \rangle$.

(ii) The tilt angle $\langle \theta_i \rangle$ of each rod as well as the average tilt angle

$$\langle \theta \rangle = (1/N) \sum_{i=1}^{N} \langle \theta_i \rangle. \qquad (5)$$

(iii) The polar angle $\langle \varphi_i \rangle$ of each rod as well as the average

$$\langle \varphi \rangle = (1/N) \sum_{i=1}^{N} \langle \varphi_i \rangle. \qquad (6)$$

(iv) The z component of the orientational vector S_i, $\langle S_i^z \rangle$, as well as its average

$$\langle S^z \rangle = (1/N) \sum_{i=1}^{N} \langle S_i^z \rangle. \qquad (7)$$

(v) The root mean square value of the transverse components S_i^x, S_i^y, which can be interpreted as an order parameter for the uniform-tilt–no-tilt transition,

$$\langle R_{xy} \rangle = (\langle S^x \rangle^2 + \langle S^y \rangle^2)^{0.5}, \quad \langle S^x \rangle = (1/N) \sum_{i=1}^{N} \langle S_i^x \rangle,$$

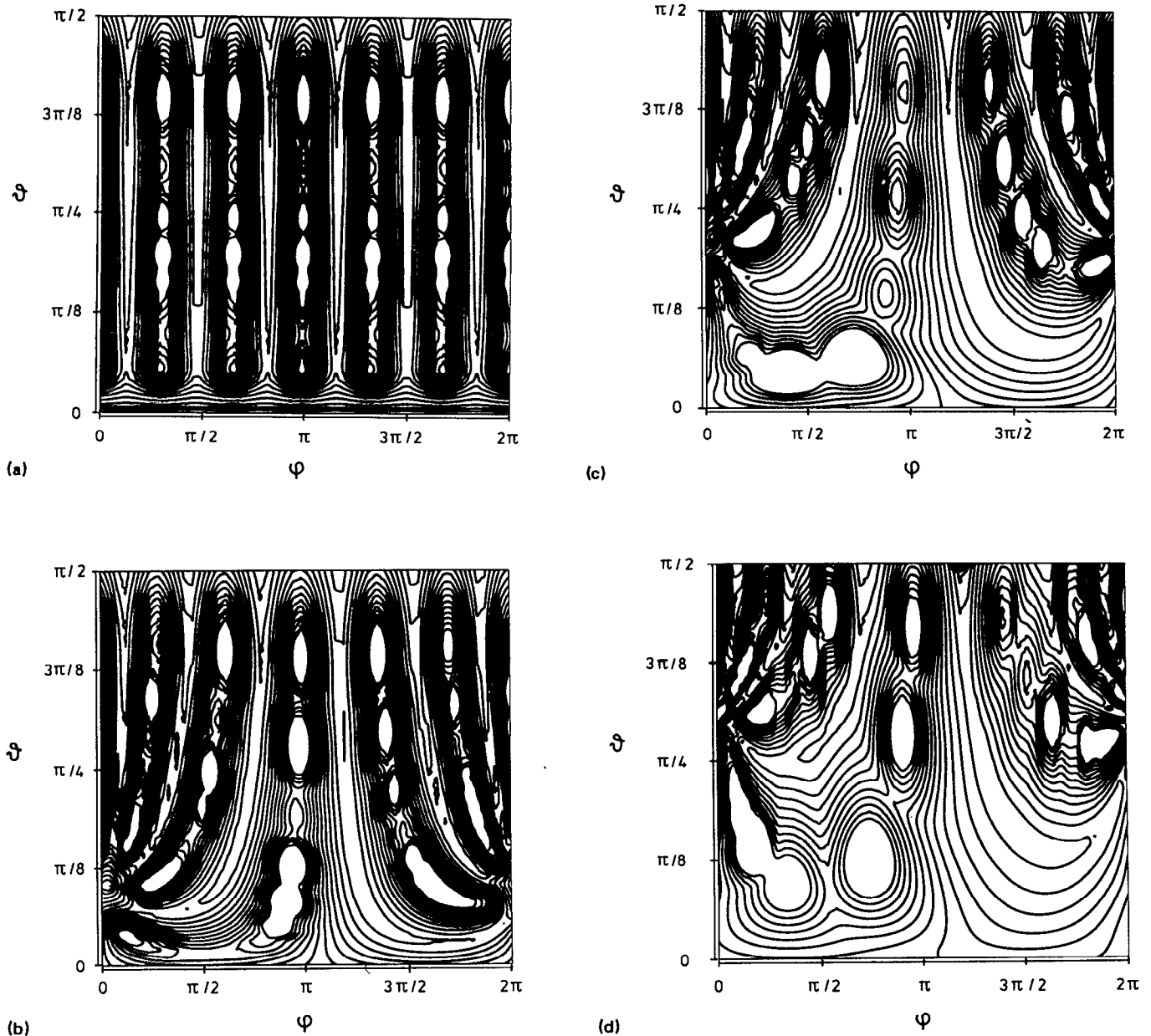$$\langle S^y \rangle = (1/N) \sum_{i=1}^{N} \langle S_i^y \rangle. \qquad (8)$$

FIG. 4. Contour plot of the energy surface $\log_{10}\{\Sigma_{k=0}^{5}U_k(\vartheta_1,\vartheta_2) - U_{\min} + 1\}$ for the choice $\nu_0 = 15$, $a = 5$, $b = 1$, as a function of θ_1 (y axis) and φ_1 (x axis). Case (a) corresponds to $\theta_2 = 0$, $\varphi_2 = 0.2$, case (b) to $\theta_2 = 0.35$, $\varphi_2 = 0.2$, case (c) to $\theta_2 = 0.7$, $\varphi_2 = 0.2$, and case (d) to $\theta_2 = 1.0$, $\varphi_2 = 0.2$. Contours correspond to values $i/2$, $i = 1, \cdots 20$. In case (a) the minima occur at $\varphi = k\pi/6$, $k = 0, \cdots 5$, the global minimum at $\theta = 0$ and further minima at $\pi/2$.

(vi) The heat capacity c_V is calculated from energy fluctuations as usual,

$$c_V = N(\langle U^2\rangle - \langle U\rangle^2)/T^2. \tag{9}$$

(vii) The orientational pair correlation function

$$\langle K_\Delta\rangle \equiv (1/6N) \sum_{i=1}^{N} \sum_{k=0}^{5} (3\langle\cos^2\{\theta(\mathbf{r}_i)$$

$$- \theta(\mathbf{r}_i + \Delta\mathbf{b}_{12}(k))\}\rangle - 1)/2, \tag{10}$$

where $\Delta = 1,2,...L/2$ and $\mathbf{b}_{12}(k)$ is a nearest-neighbor vector as defined in Eq. (3), while $\mathbf{r}_i$ is the lattice vector labeling

the site i, $\theta(\mathbf{r}_i) \equiv \theta_i$. In practice, we have calculated the average of all correlations with the same value of the distance Δ (measured in units of the lattice constant $b = |\mathbf{b}_{12}|$).

For the parameter values $a = 5$, $b = 1$, all simulations were carried out for three lattice sizes 15×15, 21×21, and 36×36. Because the finite size effects were found to be smaller than the statistical errors, simulations for $a = 4$ and $a = 6$ were carried out for one lattice size ($L = 15$) only.

We now briefly describe our numerical results. Figure 6(a) and 6(b) show the average tilt angle $\langle\theta\rangle$ and order parameter $\langle R_{xy}\rangle$ over the full temperature range studied and
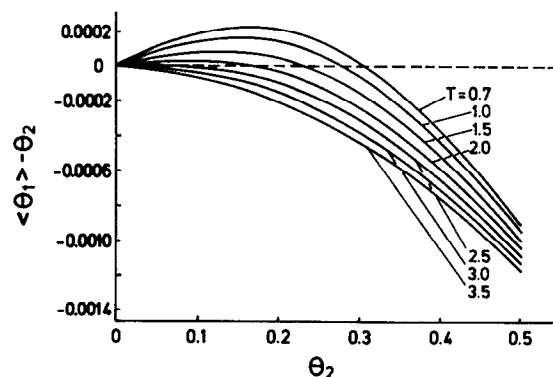
FIG. 5. Plot of the simplified mean field construction $\langle \theta_1 \rangle - \theta_2$ vs θ_2 (zeros in this plot correspond to selfconsistent solutions). Parameters chosen are $v_0 = 15$, $a = 5$, $b = 1$, and the various temperatures as indicated in the figure.

(a)

(b)

FIG. 6. Average tilt-angle $\langle \theta \rangle$ (a) and order parameter $\langle R_{xy} \rangle$ (b) plotted vs temperature for the model with $v_0 = 15$, $b = 1$ and $a = 5$. Points denote Monte Carlo data for $L = 15, 21$, and 36, while the full curves are the result of mean-field theory, which implies a second-order transition at $T \approx 2.6$.

compares these results to the mean field calculation of the previous section. It is seen that for $T \lesssim 2$ Monte Carlo and mean field results are in very good agreement, while for $T > 2$ there is marked disagreement: both order parameter $\langle R_{xy} \rangle$ and the angle $\langle \theta \rangle$ stay roughly constant, until at $T \approx 4$ (i.e., a temperature much *higher* than the mean field transition temperature $T_c^{MF} \approx 2.6$) a pronounced first order transition occurs. This transition leads to a disordered high-temperature phase, and after all, in the temperature range studied, the model shows three different regimes. In Fig. 9 we display equilibrated configurations at $T = 1$, $T = 3$, and $T = 7$, corresponding to these three regimes.

We interpret the surprising discrepancy between mean-field theory and Monte Carlo simulations as an indication that the simple order with uniform tilt and orientation persists only for $T < 2$, while for $T > 2$ a nonuniform type of ordering takes over. This interpretation is confirmed by Figs. 9(a) and 9(b). It is interesting to note that the angular correlation $\langle K \rangle$ stays nearly perfect in the intermediate regime [Fig. 7(a)]. In the disordered high-temperature phase $\langle K \rangle$ decreases steadily with temperature, however. Not unexpectedly, the structure of this high-temperature phase depends critically on the restriction of the model to interactions between nearest-neighbor rods: there are intersections of not neighbouring rods [see Fig. 9(c)].

Both from $\langle K_\Delta \rangle$ and from the potential energy $\langle U \rangle$ [Fig. 7(b)] we notice pronounced hysteresis at the first-order transition to the disordered phase. The first-order character of this transition is also evident from the lack of significant finite size effects in both $\langle U \rangle$ and the heat capacity c_V [Fig. 7(c)]. Only in the order parameter $\langle R_{xy} \rangle$ in the disordered phase there is a systematic size effect, which is trivially understandable since $\langle R_{xy} \rangle$ in Eq. (8) is defined as a nonnegative quantity and the fluctuations measured there are the larger the smaller the system. This first order character becomes somewhat less pronounced for longer rod length a (Fig. 8). The transition temperature increases with the rod length a, qualitatively consistent with experiment.[7]

V. DISCUSSION

In the present paper, we studied a model of orientational ordering in dense lipid monolayers by investigating the ground state by exact analysis and the finite-temperature behavior by Monte Carlo simulations. In the model the alkane chains are treated as perfectly rigid rods interacting with each other by a Lennard-Jones potential; the head groups of the lipid molecules were assumed to form a perfect and rigid triangular lattice. The rods are discretized into effective monomers and the interactions were restricted to nearest-neighboring rods. Of course, this crude model is no longer related to any particular material, but it may still capture some of the essential physics of hard-rod-like molecules grafted on a planar surface at high surface density.

We have found that already in the ground state several phases occur—a phase where the rods are oriented perpendicularly to the surface (no-tilt phase), a sixfold degenerate phase where the rods are uniformly tilted in the direction towards a next-nearest neighbor, and various phases with
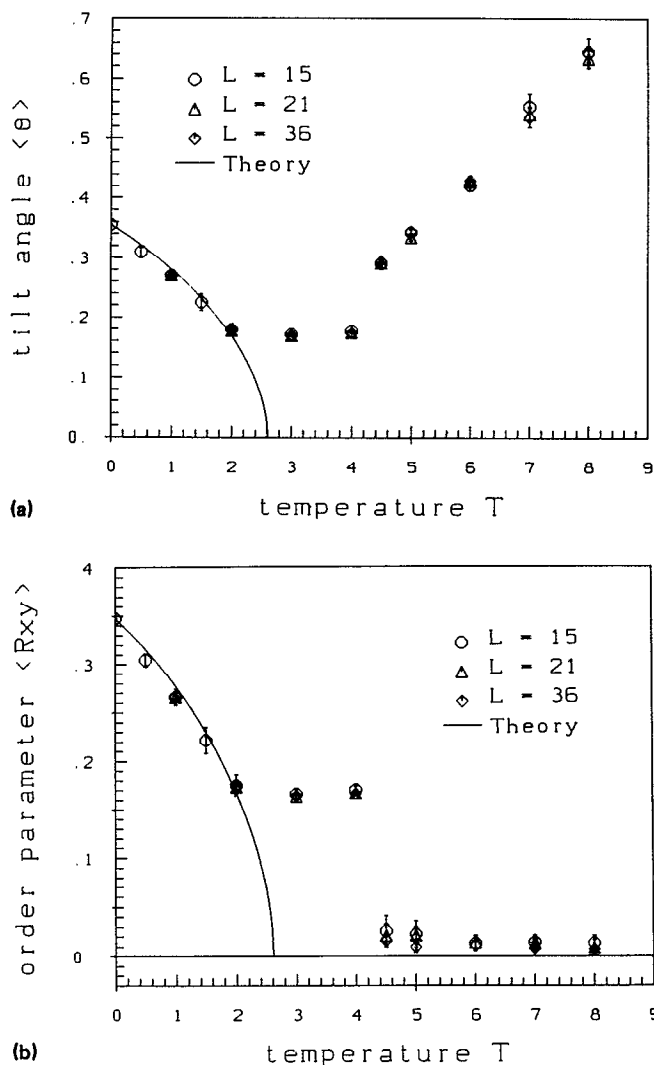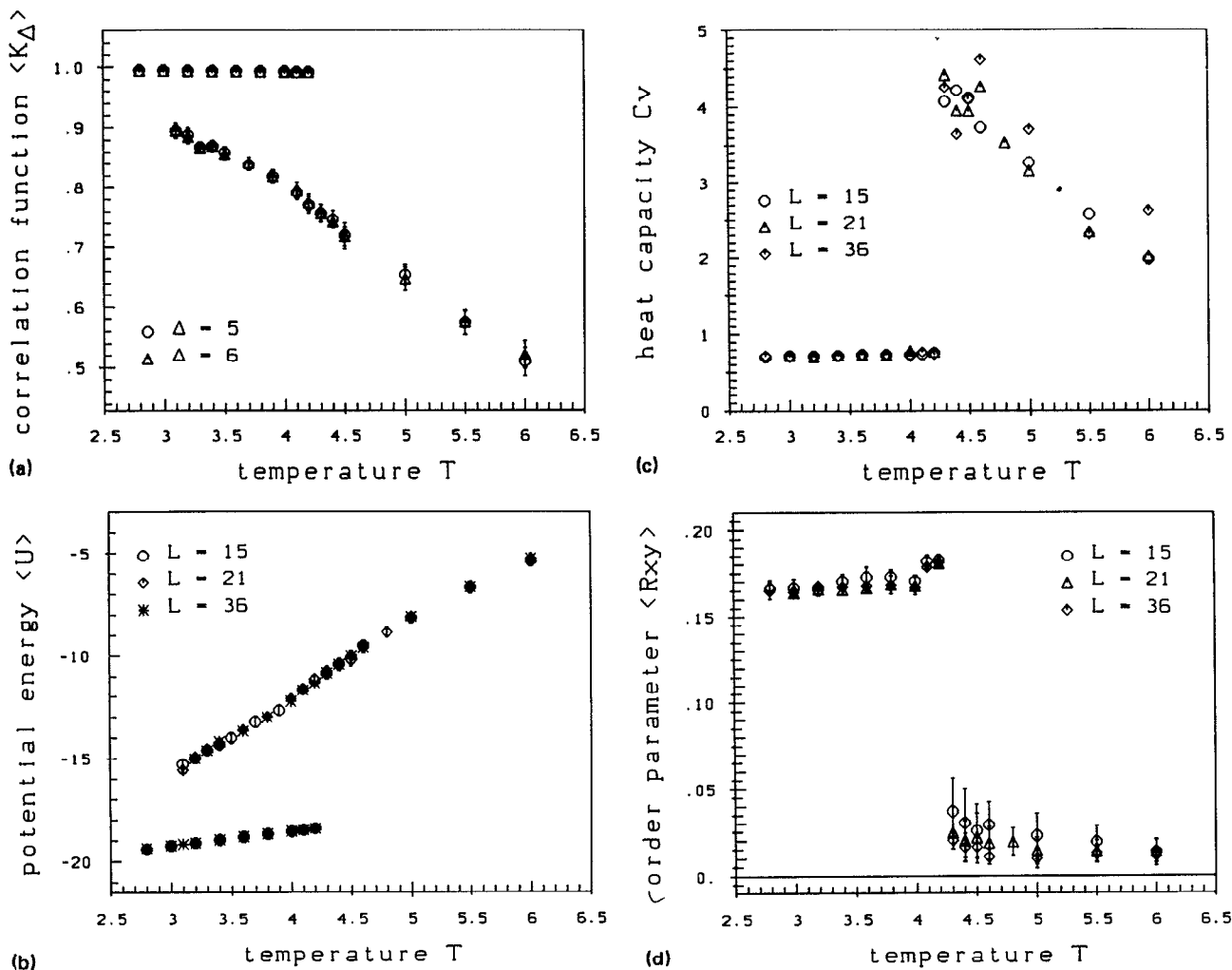
FIG. 7. (a) Angular correlation function $\langle K_\Delta \rangle$ plotted vs temperature, for $\Delta = 5$ and $\Delta = 6$. (b) Potential energy $\langle U \rangle$ plotted vs temperature, for three different lattice sizes L. (c) Specific heat c_V plotted vs temperature, for three values of L. (d) Order parameter $\langle R_{xy} \rangle$ plotted vs temperature, for three values of L.
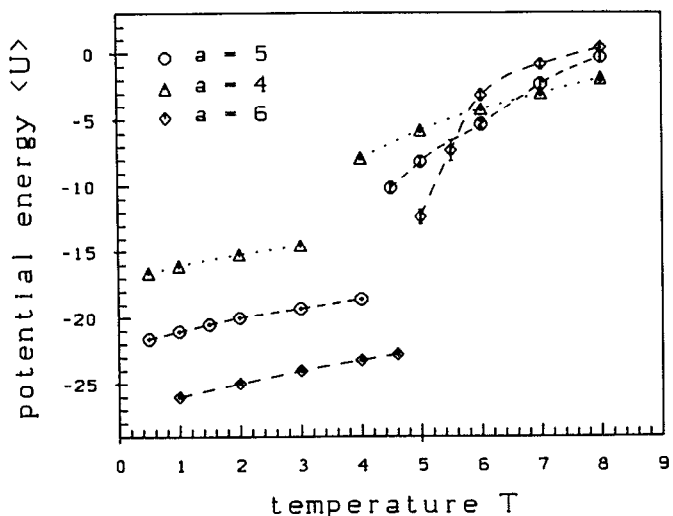

FIG. 8. Potential energy $\langle U \rangle$ plotted vs temperature for $L = 15$ and three choices of rod length a.

nonuniformly tilted rods. Which phase is stable depends on the two parameters of the model, the rod length a and the lattice spacing b (measured in units of the LJ-interaction range). Thus at $T = 0$, the ordering is considerably more complex than in the corresponding one-dimensional version of the model, where only the no-tilt phase and a twofold degenerate uniform-tilt phase occur.

At nonzero temperature, we have focused attention on the disordering of the uniform-tilt phase only. It turns out that three different regimes can be distinguished: in the first regime, the character of the sixfold degenerate ordering is still the same as at $T = 0$, only the tilt angle decreases with increasing temperature. This ordering is well accounted for by a mean-field theory, which is in quantitative agreement with our Monte Carlo results. In the second regime, the symmetry breaking with respect to the azimuthal angle is destroyed, as can be verified by direct inspection of Fig. 9(b), and thus there is considerable disorder with respect to this azimuthal variable, while the polar tilt angle stays nearly
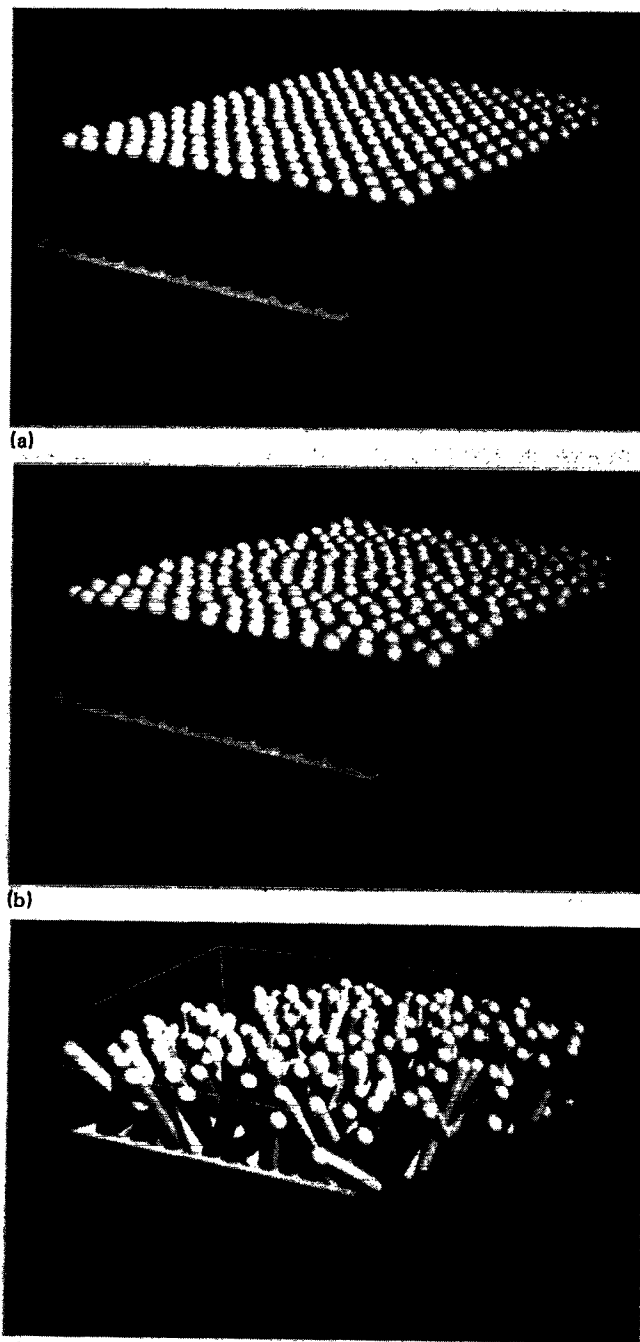
(a)

(b)

(c)

FIG. 9. Equilibrated configurations of a 15×15 lattice for $v_0 = 15$, $b = 1$, and $a = 5$. (a) $T = 1$; (b) $T = 3$; (c) $T = 7$.

independent of temperature. This phase is somewhat reminiscent of the "floating phase" of the well-known six-state clock model. The third regime is characterized by a complete loss of long range order. The transition between regime II and III is strongly of first order, with pronounced hysteresis, while the transition between regime I and II is continuous. In regime III there is a pronounced increase of the average tilt angle with temperature, because some of the rods are strongly tilted and almost reach the xy plane. The fact that such an orientation may be energetically favorable certainly

is an unphysical feature of our model and has probably no counterpart in real systems, where there is repulsive interaction between head groups and the rods.

Changing the rod length, we find that the temperature of the transition to the fully disordered phase increases significantly with rod length. Qualitatively, but not quantitatively, the same trend is observed in recent experiments on fatty acids.

The present work should only be considered as a first step, and further refinement of the model would be desirable to allow for a better comparison with experiments: the lattice of the head groups should not be treated as rigid and strictly triangular, but one should allow for elastic deformations towards centered rectangular structures. The latter are observed experimentally. As mentioned above, forces between the monomers of the rods and the head groups should be accounted for. We have not yet tried to implement and study such improved models, since already the model studied here took an extremely large amount of CPU time. This amount of CPU time could not be further reduced in spite of our working technique of using a discretized instead of a continous angular space. With the latter, our simulations would have taken CPU times larger by a factor of 20. Thus the formulation of tractable coarse-grained models, by which phase transitions in lipid monolayers or other systems containing rods grafted on surfaces can be studied, remains a challenge for every computational treatment.

ACKNOWLEDGMENTS

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