A hexatic smectic phase with algebraically decaying bond-orientational order

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The hexatic phase predicted by the theories of two-dimensional melting is characterised by the power law decay of the orientational correlations whereas the in-layer bond orientational order in all the hexatic smectic phases observed so far was found to be long-range. We report a hexatic smectic phase where the in-layer bond orientational correlations decay as $\propto r^{-1/4}$, in quantitative agreement with the hexatic ordering predicted by the theory for two dimensions. The phase was formed in a molecular dynamics simulation of a one-component system of particles interacting via a spherically symmetric potential. This is the first observation of the theoretically predicted two-dimensional hexatic order in a three-dimensional system.

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The theory of two-dimensional (2D) melting by Kosterlitz, Thouless, Halperin, Nelson and Young (KTHNY)\cite{Kosterlitz1973} predicts the existence of a distinct new phase intervening between a solid and a liquid. This phase, called hexatic, is a 2D fluid characterised by a quasi-long range bond orientational order (BOO) (decaying as power law) and short-range (exponentially decaying) positional correlations. The hexatic phase predicted by the KTHNY theory has been observed in a number of real 2D systems\cite{Spanton2003}, but the attempts to find it in three-dimensional (3D) systems have so far been unsuccessful. Nevertheless, its terminology has been carried over to 3D liquid crystals\cite{Leibler1980} to describe the bond-ordered liquid states found in the axially stacked layers of some smectic liquid crystals\cite{Sanchez1995a,Sanchez1995b,Mishra2013}. These smectic phases, calles hexatic smectics, were thus suggested to be the 3D analog of the 2D hexatic phase conjectured by the KTHNY scenario\cite{Sanchez1995a}. It has to be stressed, however, that this analogy is purely heuristic. The principal difference between the two phases is that the hexatic smectics exhibit true long-range in-layer BOO in contrast to its power law decay in the 2D hexatic phases. This difference was tentatively attributed to the interaction between the smectic layers and the effect of anisotropic forces\cite{Sanchez1995a}, but the nature, and the origin of the long-range BOO in the hexatic smectic phases still elude comprehensive understanding.

Particle simulations have been actively used to understand the formation mechanism of the smectic liquid crystals in terms of the molecular-level properties\cite{Sanchez1990}. Following the seminal work of Onsager\cite{Onsager1949}, it was commonly believed that formation of smectic phases is driven by the packing entropy of anisometric (rod-like) mesogenic molecules\cite{Barnes1994}. Accordingly, a rod-like particle shape was assumed in the computer models of smectic phases\cite{Bakr2013a,Bakr2013b}. However, no unconstrained simulation of a hexatic smectic phase has so far been reported\cite{Bakr2013a}.

Two questions of general conceptual interest arise in this context. (i) Is the anisometry of the mesogenic molecules a prerequisite for producing a smectic mesophase and, in particular, a hexatic smectic phase? (ii) Can the true long-range BOO observed in the hexatic smectic phases be related to the specific shape of their constituent molecules and the anisotropy of the intermolecular forces?

In this Letter, we report a molecular-dynamics simulation addressing these questions. It is demonstrated that a single-component system of particles interacting via a spherically-symmetric potential forms an equilibrium hexatic smectic mesophase where the in-layer BOO decays as a power law, in quantitative agreement with the KTHNY theory prediction.

We investigated a molecular-dynamics model of 50000 identical particles confined to a cubic box with periodic boundary conditions interacting via the pair potential shown in Fig. 1. The functional form of the potential energy for two particles separated by the distance $r$ is:

$$V(r) = a_1(r^{-m} - d)H(r, b_1, c_1) + a_2H(r, b_2, c_2)$$

where

$$H(r, b, c) = \begin{cases} \exp \left( \frac{b}{r-c} \right) & r < c \\ 0 & r \geq c \end{cases}$$

The values of the parameters are presented in Table I.

$$ V(r) = a_1(r^{-m} - d)H(r, b_1, c_1) + a_2H(r, b_2, c_2) $$

$$ H(r, b, c) = \begin{cases} \exp \left( \frac{b}{r-c} \right) & r < c \\ 0 & r \geq c \end{cases} $$
TABLE I: Values of the parameters for the pair potential used in this simulation (Eq 1, Fig.1).

| m | a_1 | b_1 | c_1 | a_2 | b_2 | c_2 | d |
|---|-----|-----|-----|-----|-----|-----|---|
| 12 | 113 | 2.8 | 1.75 | 2.57 | 0.3 | 3.1 | 1.4 |

The simulation reduced units are those used in the definition of the potential. This pair potential represents a modification of an earlier reported one [14] that was found to produce a smectic-B crystal. The main difference between the two potentials is that in the present one the long-range repulsion is extended to a significantly larger distance. In that earlier simulation the latter parameter was found to determine the interlayer spacing.

The system’s phase behaviour was investigated at a constant number density $\rho = 0.41$. The temperature was changed in a stepwise manner, performing a comprehensive equilibration after each step which typically amounted to $10^7$ timesteps. The simulation started by equilibrating an isotropic liquid state at sufficiently high temperature. Fig. 2 shows system’s energy and pressure as functions of temperature. Upon cooling, both quantities exhibited a discontinuity at $T = 1.15$, followed by another one at $T = 0.95$. The latter was accompanied by a sharp drop in the diffusion rate, Fig. 2 indicating the formation a solid state; this was identified as a smectic B crystal [15]. Upon re-heating the described temperature variations of the pressure and energy were reproduced. Each observed singularity was found to be accompanied by a hysteresis, a signature of the first-order nature of the respective transition.

The observed phase behaviour thus demonstrates the existence of a distinct equilibrium fluid phase interposed between the isotropic liquid and the Smectic B crystal, separated from each of the latter two phases by a first-order transition. The general view of its instantaneous configuration presented in Fig. 3 suggests that this is a smectic liquid crystal composed of uniaxially stacked layers with a liquid-like in-layer diffusion, Fig. 2. We note that its estimated interlayer spacing [15] is consistent with the long-range repulsion distance of the pair potential, Fig.1.

In order to understand the exact nature of thus produced smectic mesophase we performed a detailed analysis of its in-layer structure. As a first step in the structure characterisation we calculated the structure factor $S(Q)$ [15] representing the scattered intensity in the diffraction experiments. Having established the global uniaxial symmetry of the configuration and the axis orientation [15], we then calculated $S(Q)$ in the layer plane $Q_z = 0$, $Q_z$ being the axis coordinate. Fig.4 shows $S(Q)$ for a single layer averaged over $10^4$ timesteps. It exhibits a pronounced azimuthal modulation in the form of six diffuse
FIG. 4: (a) $S(Q)$ of a single layer calculated in the layer plane.
(b) Bond angle distribution. Solid line and dash-dotted line, respectively: one layer at $T = 1.0$ and at $T = 1.1$. Dashed line: entire system, $T = 1.0$.

arcs characteristic of the diffraction patterns of hexatic smectic phases. Their radial position can be identified as $Q = 4\pi/(a\sqrt{3})$ where $a$ is the in-layer nearest neighbour distance. We notice that this distance is in good agreement with the position of the first potential minimum, Fig. 4a. In this way, the short repulsion and the long repulsion parts of the pair potential act, respectively, as the length and the diameter of the mesogenic molecules forming the real smectic phases: the former define the interlayer particle packing whereas the latter define the interlayer spacing.

The sixfold angular symmetry of the diffraction pattern is a necessary but not sufficient condition for identifying the simulated phase as a hexatic smectic. To get further evidence for the hexatic nature of its in-layer structure we calculated the bond-orientation distribution which is shown in Fig. 4b. The bonds were defined as the pairs of particles within a layer separated by the nearest-neighbour distance $a$ as indicated above. The angles presented in the statistics were measured between the bonds and an axis chosen in the layer plane. The statistics was calculated for an ensemble of configurations produced within a simulation run of $10^4$ time steps. The bond angle distribution for a single layer at $T = 1.0$ demonstrates a pronounced six-fold modulation with the amplitude consistent to that observed in the azimuthal variation of $S(Q)$, Fig. 4a. The amplitude of the distribution modulation for the same layer at $T = 1.1$ is significantly smaller, as well as the one calculated for the entire system.

Next, we analyse the pattern of the local six-fold BOO in a layer configuration. For each particle position $r_j$ we calculated a vector $\Psi(r_j) = \frac{1}{N_k} \sum_{k=1}^{N_k} e^{i\theta_{jk}}$ where $\theta_{jk}$ is the angle formed by the bond linking particle $j$ with its nearest neighbour $k$ relative to an arbitrary axis, and $N_k$ is the number of the nearest neighbours. Fig 5a shows the distribution of these vectors in a layer at $T = 1.0$. Each vector $\Psi(r_j)$ is represented by a dot; the dot’s size

FIG. 5: (a) The local BOO distribution in a layer at $T = 1$. Each dot represents a particle; the size of the dot representing particle $j$ is proportional to $|\Psi(r_j)|$, its color indicates $Re(\Psi(r_j))$ according to the scale. (b) Solid line: BOO correlation function $g_6(r)$; dashed line: $g(r) - 1$, both at $T = 1$.; dash-dotted line: $\propto r^{-1/4}$. 

is proportional to $|\Psi(r_j)|$ and the vector orientation is indicated by the dot’s colour, according to the scale. The distribution exhibits an apparent domain structure. A cluster of coherent hexagonal order percolates through the entire layer, which can account for the six-fold symmetry breaking in both in the diffraction pattern and in the bond-angle distribution. Besides, there are twinning domains of hexagonal order rotated by 30° and 15° with respect to the main domain. These domains can be discerned in the pattern of bonds produced for the same particle configuration [15].

The identifying feature of the hexatic phase according to the KTHNY theory is the algebraic decay of its BOO. The latter can be quantified as follows:

$$g_6(r) = \frac{\langle \sum_{k \neq j} \Psi(r_j)\Psi(r_k)\delta(r - |r_j - r_k|) \rangle}{\langle \sum_{k \neq j} \delta(r - |r_j - r_k|) \rangle}$$

(3)

where $N$ is the number of particles, and $\langle \rangle$ denote ensemble averaging. Fig. 5b shows $g_6(r)$ calculated for an ensemble of configurations of a single layer produced in a simulation run of $10^4$ time steps. It is compared with the radial distribution function $g(r)$ [16] expressing the decay of the positional correlation. We find that the calculated $g_6(r)$ asymptotically decays as $r^{-\eta}$ with $\eta = -1/4$ which is in quantitative agreement with the prediction of the KTHNY theory for the 2D hexatic [1], whereas $g(r)$ decays exponentially. These results explicitly prove that the layers of the simulated smectic represent 2D hexatic phases as defined by the theory.

Three conceptually new aspects of this study deserve to be remarked.

First, the finding that a system of identical particles interacting via a spherically-symmetric potential can form a hexatic smectic phase changes the basic model of smectic phases, thereby advancing our understanding of the causes underlying the occurrence of particular structures in the phase transformations of liquid crystals.

Second, the observed algebraic power-law decay of the in-layer BOO in a hexatic smectic phase formed by a system of particles with spherically-symmetric interaction suggests that the true long-range BOO that has so far been found in the hexatic smectics can be attributed to the rod-like shape of their constituent molecules and the anisotropy of the intermolecular forces.

Third, the hexatic phase predicted by the KHTNY theory of 2D melting has so far never been found in a 3D system. The smectic phase we report here demonstrates the in-layer hexatic order that quantitatively agrees with the theory’s prediction. This is the first indication that the theory’s application scope can include 3D systems.

We note that the pair potential we report is similar to that predicted for colloidal systems [17] (amended with steric repulsion) suggesting that a hexatic smectic phase can be formed by spherical colloidal particles with an appropriately tailored interaction, as microgels or through a cosolute [18].

In summary, we report a hexatic smectic phase formed in a molecular dynamics simulation of a one-component system of particles interacting via a spherically symmetric potential. In contrast to the hexatic smectics observed so far, its BOO decays algebraically in quantitative agreement with the KTHNY theory prediction for the 2D hexatic phase. This is the first hexatic smectic phase produced in a particle simulation, and the first observation of the 2D hexatic phase in a 3D system.

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