Formation of the Smectic-B Crystal from a Simple Monatomic Liquid

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We report a molecular dynamics simulation demonstrating that the Smectic B crystalline phase (Cr-B), commonly observed in mesogenic systems of anisotropic molecules, can be formed by a system of identical particles interacting via a spherically symmetric potential. The Cr-B phase forms as a result of a first order transition from an isotropic liquid phase upon isochoric cooling at appropriate number density. Its structure, determined by the design of the pair potential corresponds to Cr-B structure formed by elongated particles with the aspect ratio 1.8. The diffraction pattern, and the real-space structure inspection demonstrate dominance of the ABC-type of axial layer stacking. This result opens a general possibility of producing smectic phases using isotropic interparticle interaction both in simulations and in colloidal systems.

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Computer simulations using particles are now well-established tools for investigating different aspects of liquid crystals\(^2\)[1][2]. The most interesting of these are smectic phases where the molecules, besides uniaxial directional order, form layered structures\(^[3][4]\). In smectic-A phase positional order within layers is entirely absent, whereas hexatic smectic-B phase is characterised by a short-range hexagonal intralayer order\(^5\). This excludes any long-range periodicity and keeps the system fluid due to Landau-Peierls instability\(^6\). Another modification of smectic-B phase is a true 3D crystal (Cr-B). The nature of this phase was a controversial issue for some time, until its global 3D positional order was established in 1979\(^7\).

The simulation studies of models forming liquid-crystal phases provide a unique way to establish a relation between the molecular-level properties and macroscopic behaviour. These simulations demonstrated that the remarkable polymorphism of the mesogens forming liquid crystals phases can be reproduced using quite simple particle models. Systems of elongated molecules interacting via Gay-Berne (GB) potential\(^8\)[11] have been found successful in reproducing the liquid-crystal phase behaviour in a variety of simulation experiments. These models were also exploited for calculating transport properties of the liquid crystals\(^12\). Moreover, it was proved possible to reduce the models of anisotropically interacting GB particles to hard spherocylinders\(^13\)[14], which appears to indicate the entropic origin of the LC phases due to geometry of excluded volume.

This experience poses a question of conceptual interest for the statistical mechanics of condensed matter: how far further can the particle models successfully reproducing the basic features of smectic phases be simplified? In particular, is the anisotropy of the constituent molecules a prerequisite to producing anisotropic structures like those of smectic phases, and could the entropic effects of the particle geometry be compensated by an appropriately designed pair interaction?

This question is addressed in a molecular-dynamics simulation that we report in this Letter. We demonstrate that the Cr-B phase, a characteristic freezing form of mesogenic systems of anisotropic molecules, can be formed in a system composed of a single sort of particles interacting via a spherically-symmetric potential. The crystal occurs upon cooling as a result of a first-order phase transition from isotropic liquid. It represents a uniaxial structure composed of stacked layers with hexagonal close-packed intralayer structure. The structure is consistent with the experimentally observed Cr-B structures\(^7\)[15], demonstrating predominantly ABCA sequence in layers stacking. This result opens a perspective of producing other (non-crystalline) types of smectic phases, like Smectic-A and hexatic phase. It also suggests that this class of layered mesomorphs can possibly be produced in systems of spherically-shaped colloidal particles.

The results we report here have been produced in a molecular-dynamics simulation of a single-component system comprising 16384 particles. The interparticle interaction was assumed to be spherically symmetric, described by the pair potential presented in Figure 1. The functional form of the potential energy for two particles separated by the distance \(r\) is:

\[
V(r) = a_0 \left( r^{-m} - a_1 \right) H(r, b_1, c_1) + H(r, b_2, c_2),
\]

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. The first term describes the short-range repulsion branch
of the potential, and its minimum, whereas the second term expresses the long-range repulsion. All the thermodynamic quantities we report are expressed in terms of the reduced units that were used in the definition of the potential. Note that the steepness of the short-range repulsion, and the position of the minimum, are consistent with those in the Lennard-Jones (LJ) potential [16], which makes it possible to compare the reduced number densities of the two systems.

At the beginning, the system was equilibrated in its stable isotropic liquid state at sufficiently high temperature at the density $\rho = 0.55$. Note that this density is much below of the triple-point density for the LJ system [16]. We then isochorically cooled the system, in a stepwise manner, comprehensively equilibrating it after each temperature step. A discontinuous change in the parameters was detected below $T = 0.65$, see Fig. 2, accompanied by a sharp drop in the diffusivity, an apparent signature of a first-order phase transition to a solid phase. Accordingly, its heating produced a significant hysteresis. A non-trivial character of the low-temperature phase was indicated by an anomalously long time required for its equilibration which amounted to several billions of time-steps.

The structure analysis of the low-temperature solid phase has been performed by inspecting the Fourier-space pattern of its density distribution. For that purpose, we calculated the structure factor $S(Q) = \langle \rho(Q)\rho(-Q) \rangle$, where $\rho(Q)$ is a Fourier-component of the system’s number density:

$$\rho(Q) = \frac{1}{N} \sum_{i=1}^{N} \exp(Qr_i)$$

$r_i$ being the positions of the system’s particles. $S(Q)$ represents the diffraction intensity as measured in diffraction experiments.

As a first step, we calculated the diffraction intensity on the $Q$-space sphere corresponding to the first peak of the spherically averaged $S(Q)$. We observed well-defined diffraction maxima forming a regular pattern. This made it possible to determine the global symmetry of the configuration: a single hexagonal axis was detected. The axis orientation having been found, we calculated $S(Q)$ within two characteristic $Q$-space planes: $Q_z = 0$ and $Q_y = 0$, $Q_z$ being the axis coordinate, and $Q_y$ coordinate corresponding to a translational symmetry vector orthogonal to the axis. The two diffraction patterns are shown in Fig. 3.

These results compel us to make the following conclusions. First, the observable sharpness of the diffraction maxima indicates that the low-temperature phase produced by the phase transition is a true 3D crystal. Moreover, the two diffraction patterns exhibit structural features characteristic of the experimentally produced Cr-$B$ phase [4,15]; the configuration is a uniaxial crystal comprised of stacked layers with dense hexagonal packing of particles in each layer. Based on the diffraction results shown in Fig. 3, we can also estimate the ratio of the interlayer distance to the nearest-neighbour separation within a layer as 1.8.

\begin{table}[h]
\centering
\begin{tabular}{ccccccc}
\hline
m & $a_0$ & $a_1$ & $b_1$ & $c_1$ & $a_2$ & $b_2$ & $c_2$ \\
\hline
12 & 265.85 & 0.8 & 1.5 & 1.45 & 2.5 & 0.19 & 1.89 \\
\hline
\end{tabular}
\caption{Values of the parameters for the pair potential.}
\end{table}
FIG. 3. The isointensity plots of the structure factor $S(Q)$, in two orthogonal $Q$-space planes. a: $Q_z = 0$; b: $Q_y = 0$. $Q_z$ denotes the axial dimension, and $Q_y$ corresponds to a translational symmetry vector, orthogonal to the axis.

The diffraction data presented in Fig. 3 also provide comprehensive information concerning the interlayer correlations in the crystal. The hexagonal arrangement of sharp diffraction peaks in the $Q_z = 0$ plane implies the existence of global positional interlayer correlations. The information about the type of positional correlations of the particles of adjacent layers can be obtained by inspecting the pattern of diffraction intensity in the axial plane, Fig. 3. The hexagonal close-packed layers may be stacked with two possible ordered arrangements: AAA..., ABA... or ABCA... where A, B, and C denote the relative position of the layers. A random array of ABC-type planes is also possible. These types of layer packing, or their mixtures have been experimentally observed [7].

FIG. 4. A fragment of the simulated Cr-B configuration comprising three adjacent layers stacked in ABC-type sequence. Left: axial view; right: orthogonal view along an in-layer translational symmetry direction. The layers are distinguished by colors.

A subtle problem in simulation studies of the Cr-B crystallisation has always been to discriminate between the Cr-B phase, possessing true 3D long-range positional order, and the non-crystalline hexatic phase where the hexagonal order and interlayer correlations exist only in a limited range [9,10]. The difficulty is mainly caused by limitations in the system size and the simulation’s time-scale which can be comparable with the space and time-scales of the positional order in the hexatic phase. Besides, only spherically-averaged interparticle correlations are usually considered [11-17]. In the present simulation, we were able to identify without any ambiguity all the distinctive structural features of the Cr-B phase, including the stacking order, both in the real-space picture and in terms of the diffraction intensity patterns. To the best of our knowledge, this is the first reported simulation of Cr-B phase providing complete information about all the details of its structure.

These results demonstrate that a uniaxial anisotropic structure can be produced in a single-component system by a spherically symmetric interparticle potential. This seemingly paradoxical result can be rationalised by considering the structural effects of the potential’s design. This potential can be regarded as a modification of an earlier reported pair potential [18], judiciously designed to induce predominantly icosahedral ordering of the first coordination shell. It was found to produce a dodecahedral quasicrystal [19], and a number of other tetrahedrally ordered structures [20]. The present potential, while retaining the same short-range repulsive part, and the minimum position, has two major distinctions from the earlier one. First, its minimum is much more narrow due to a more steep attraction part. This inhibits formation of the icosahedral ordering of the first neighbours due to its characteristic frustration, as well as any other conceivable densely packed structure with full first coordination shell and energetically favours a low-density structure with a reduced number of first neighbours. Moreover, the extended width of the following maximum in the present potential shifts its second repulsive part, and thereby the
second neighbours to a significantly longer distance. As a result of this potential design, a local structure is favoured, at appropriate density, with only six equidistant first neighbours arranged in a hexagon. These hexagons are organised in flat densely packed layers which are uniaxially stacked with the interlayer distance determined by the potential’s long-range repulsion.

The anisotropy of smectic phases is measured by the ratio of the nearest-neighbour distance to the interlayer spacing. In systems of elongated molecules, this corresponds to the degree of anisotropy (aspect ratio) of the constituent molecules. In our system, the same effect is induced by the potential design: the interlayer separation is controlled by the long-range repulsion, whereas the in-layer nearest-neighbour distance is determined by the short-range repulsion. This implies that the apparent aspect ratio of a Cr-B phase produced in a manner we report here can be manipulated by choosing the separation of the two repulsive branches of the potential.

At sufficiently high density, where the short-range repulsion dominates the energy, a close-packed structure will be formed, presumably hcp. At low densities and low temperatures, where the structure will be determined by the long-range repulsion, the same kind of lattice is expected to be energetically favourable. A similar kind of isostructural polymorphism has been reported for a stepwise pair potential [21].

We conclude with the following remarks.

1. So far, colloidal smectic phases have only been found to appear in systems of rod-like colloidal particles [22]. The spherically-symmetric nature of the interparticle interaction in the present model, and the similarity of its main features to classical DLVO theory for colloidal interaction [23-25] (amended with hard core repulsion or steric repulsion at close to contact), suggests a possibility that smectic-like layered structures can be produced in colloidal systems of spherically shaped particles, with appropriate tuning of the effective force field.

2. The local structural isomorphism of the Cr-B and fluid hexatic phase suggests that the latter too can possibly be produced using the general approach to the potential design we exploited here, as well as the smectic A phase.

3. An intriguing anomaly of the Cr-B dynamics is the presence of soft shear modes tentatively concluded from spectroscopic measurements [26]. The ultimate simplicity of the present model can facilitate investigation of the underlying mechanism of this dynamical singularity.

In summary, we used a molecular-dynamics simulation to demonstrate that the Cr-B phase that has so far only been observed in mesogenic systems composed of anisotropic molecules can be formed in a system of identical particles interacting via a spherically-symmetric potential. This finding remarkably simplifies 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.

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