Formation of a Columnar Liquid Crystal in a Simple One-Component System

A. Metere\textsuperscript{1} T. Oppelstrup\textsuperscript{2} S. Sarman\textsuperscript{1}, and M. Dzugutov\textsuperscript{3}
\textsuperscript{1} Dept. of Materials and Environmental Chemistry, Stockholm University, Arrenius Våg. 16C S-106 91 Stockholm, Sweden
\textsuperscript{2} Lawrence Livermore National Laboratory - 7000 East Avenue, Livermore, California 94551, USA
\textsuperscript{3} Dept. of Mathematics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

(Dated: July 1, 2014)

We report a molecular dynamics simulation demonstrating that a columnar liquid crystal commonly formed by disc-shaped molecules can be formed by a system of identical particles interacting via a spherically symmetric potential. A weak first order transition was observed upon cooling a low-density isotropic liquid. It produced a liquid crystal composed of hexagonally packed parallel particle columns with liquid structure and significant intracolumn diffusion. Further cooling resulted in another transition transforming the liquid crystal into a crystal, as the columns became periodically ordered in three dimensions. This is the first observation of a liquid crystal formation in a simple one-component particle system. It indicates that liquid crystals that have so far only been produced in systems of anisometric molecules, can also be formed by mesoscopic soft-matter and colloidal systems of spherical particles with appropriately tuned force field.

PACS numbers: 61.20.Ja, 61.30.Cz, 64.70.mf

Liquid crystals\textsuperscript{[1,2]} are anisotropic phases with periodicity in less than three dimensions. The spacial extent of 1D periodic order of layer stacking in smectic phases is limited due to Landau-Peierls instability\textsuperscript{[3]} whereas columnar liquid crystals\textsuperscript{[2]}\textsuperscript{[4]} possess stable global 2D periodicity. The latter is formed by close packing parallel columns of axially stacked molecules into regular 2D patterns, with remaining continuous translational symmetry dimension directed along the column axis. The columns are commonly formed by disk-like molecules\textsuperscript{[4]} or wedge-shaped dendrons\textsuperscript{[5]}. The close packing of columns fixes the position of a molecule in the plane perpendicular to the column axis, but the molecules’ stacking along the axis is irregular, and the axial position of a molecule is not defined with respect to its neighbors in adjacent columns, which gives rise to the continuous translational symmetry in the axial dimension.

Particle simulations have proved to be an indispensable tool for understanding the relationship between the phase behaviour and the molecular-level properties of liquid crystals\textsuperscript{[6–8]}. These simulations have so far followed the phenomenological paradigm that dominated the science of liquid crystals for decades, whereby the structural anisotropy of liquid crystals was assumed to be determined by anisometric shape of a molecule. Particle shapes in the models of liquid crystals imitated the shapes of the molecules in the respective mesogens: the smectic phases have been simulated using rod-like particles\textsuperscript{[9–11]}, and models of columnar liquid crystals\textsuperscript{[8,12–15]} commonly used flat discotic particles or oblate ellipsoids. Moreover, simulations using hard anisometric particles\textsuperscript{[10–15]} stressed the entropic aspect of the liquid-crystal formation due to thereby determined geometry of the excluded volume.

A question of conceptual interest for the statistical mechanics of condensed matter is whether the anisometry of the mesogenic molecules is indeed a prerequisite for producing liquid-crystal structures or the entropic effects of the particle geometry on the structure formation can be compensated by an appropriately designed spherically symmetric interaction potential (disregarding orientational particle ordering).

In this Letter, we report a molecular-dynamics simulation addressing that question. It is demonstrated that a thermodynamically stable hexagonal columnar liquid crystal can be formed in a single-component system of particles interacting via a spherically-symmetric potential. The formation of this mesophase was observed as a first-order phase transition when cooling the system at constant density from its equilibrium isotropic liquid state. Liquid structure and considerable diffusion was observed within the columns. Under further cooling, another phase transition took place, transforming the 2D-periodic columnar liquid crystal into a columnar structure with global 3D periodicity. This observation is the first compelling evidence that an anisotropic liquid crystal phase can be produced in a system of identical particles interacting via a spherically symmetric potential. This result opens a possibility of producing columnar liquid-crystal phases in colloidal and soft-matter systems composed of spherically-shape particles.

The simulation we report here utilized the pair potential shown in Fig. 1. The functional form of the potential energy for two particles separated by the distance $r$ is defined as:

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

(1)

where

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

(2)

The values of the parameters are presented in Table
I. The first term of this functional form describes the short-range repulsion part of the potential, and its first minimum, whereas the second term is responsible for the long-range repulsion. All the quantities we report here are expressed in the reduced units used in the definition of the potential. We also note that the short-range repulsion part of the potential, and the position of its first minimum closely approximate those in the Lennard-Jones (LJ) potential [16], which makes it possible to directly compare the reduced number densities, and other thermodynamic parameters of the two systems. An earlier reported relevant simple one-component particle model [17] has to be mentioned that was found to produce the smectic-B crystal.

The described pair potential was exploited in a molecular dynamics model comprised of 16384 identical particles confined to a cubic box with periodic boundary condition. We began the simulation by equilibrating the system in its stable isotropic liquid state at sufficiently high temperature and the number density \( \rho = 0.3 \). Note that this density is very low as compared with the density of the LJ liquid at its triple-point, \( \rho = 0.84 \) [16]. The liquid was then isochorically cooled, in a stepwise manner, comprehensively equilibrating it after each temperature step. A discontinuous reduction of energy was detected when the system was cooled below \( T = 1.1 \), Fig. 2, accompanied by a sharp reduction of the diffusion rate. The first-order nature of this transition was demonstrated by a significant hysteresis observed when reheating the low-temperature phase. We remark that no singularity in the pressure variation have been found within that range of temperature, which indicates a weak nature of this first-order transition [18]; this kind of phase behaviour has been theoretically conjectured for columnar liquid crystals [19].

Further cooling of this phase resulted in another first-order phase transition; in this case, a clear hysteresis in both energy and pressure was observed, see Fig. 2. This transition further reduced the diffusion rate to the value characteristic of a solid phase. Thus produced low-temperature phases will hereinafter be referred to as Phase I and Phase II, according to the order of their occurrence upon cooling. Evidently, the Phase I remains in a thermodynamically stable equilibrium within a finite range of temperature.

The structure characterisation of the two phases has first been performed by analysing the pattern of their density correlations in the the Fourier-space. 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 number density of a system of \( N \) particles:

\[
\rho(Q) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \exp(-iQr_i) \tag{3}
\]

\( r_i \) being the positions of the system’s particles, and \( \langle \rangle \) denote ensemble averaging. \( S(Q) \) represents the diffraction intensity as measured in diffraction experiments.

The structure factor was first calculated on the \( Q \)-space sphere of the radius corresponding to position of the first peak of the spherically averaged \( S(Q) \). A well-defined pattern of \( S(Q) \) maxima was observed, which made it possible to determine the global symmetry and
FIG. 3. The isointensity plots of the structure factor $S(Q)$ for Phase I and Phase II calculated in two orthogonal $Q$-space planes. From top to bottom: Phase I, $Q_z = 0$; Phase I, $Q_y = 0$; Phase II, $Q_z = 0$; Phase I, $Q_y = 0$. $Q_z$ denotes the axial dimension, and $Q_y$ corresponds to one of the translational symmetry vectors orthogonal to the axis.

The axis orientation having been found, $S(Q)$ was calculated, for each phase, in two characteristic $Q$-planes: $Q_z = 0$, $Q_z$ being the axis coordinate, and $Q_y = 0$, $Q_y$ coordinate corresponding to a translational symmetry vector orthogonal to the axis. The results, for both phases, are shown in Fig. 3. These results compel us to make the following conclusions. First, the Phase I exhibits 2D global hexagonal periodicity in the plain perpendicular to the axis; no structure is found in the axial dimension. Thus, Phase I appear to be a 2D-periodic columnar liquid crystal, composed of parallel columns arranged in a hexagonal pattern in the plane perpendicular to the column axis. In the axial dimension, the phase remain structureless. The transformation of Phase I into Phase II under its further cooling breaks the symmetry in the remaining continuous dimension by inducing crystalline order within column in all three dimensions. This ordering within columns apparently occurs in a globally coherent manner, producing a 3D-periodicity. This is indicated by additional sets of diffraction peaks which appear in both $Q$-planes. Thus, Phase II appear to be a true 3D crystal, composed of crystalline columns arranged in the same hexagonal pattern as in Phase I. We note that the intercolumn separation as inferred from the diffraction pattern is consistent with the long-range repulsion range of the pair potential, Fig. 1.

These conclusions are confirmed by the real-space im-

FIG. 4. The real-space images of the two phases configurations. a) and c): view from the axial direction, Phase I and Phase II, respectively. b) and d): a one-column layer of the structure, cut parallel to the layer axis, as viewed perpendicular to the axis. The particle diameter in the plot is assumed to be 1, in reduced units, which corresponds to the particles separation distance at the hard-core contact, see the pair potential in Fig. 1.
ages of the two phases in Fig. [4]. Both phases are columnar structures where parallel columns are arranged in triangular-hexagonal pattern in the plane perpendicular to the column axis. In the Phase I, the particles within columns form an essentially fluid structure which transforms into a crystalline structure with a globally coherent 3D periodicity as a result of the system’s transition into the Phase II. We note that in the latter phase planes of periodically stacked particle layers that can be observed from the view perpendicular to the columns, Fig [4] are tilted with respect to the column axis. A detailed analysis of this crystal structure will be reported elsewhere.

A conceptually significant structural distinction of the Phase I as compared with the discotic columnar liquid crystals has to be pointed out, which also concerns its dynamics and the crystallization mechanism. In the discotic phases, columns of axially stacked disc-like particles are densely packed in a regular pattern in the plane perpendicular to the axis. Under these constraints, only vibrational dynamics is possible, and the continuous translation symmetry of these phases in the axial dimension arises as a result of the lack of coherence between columns in the stacking order. By contrast, there is a significant spacing between columns in the Phase I, and each column is sufficiently wide to accommodate a typical 3D liquid structure, which can be observed in Fig4. Also, a considerable diffusion within the columns has been detected. Thus, a column in the Phase I is a 3D liquid, both structurally and dynamically.

Respectively, crystallization of the Phase I represents transformation of a 3D liquid column structure into a crystal, with periodicity coherent with that of the neighbour columns; this can be seen in Fig. 4. The development of a globally-coherent periodic order within columns in the plane perpendicular to the axis can also be concluded from the additional structure appearing in the respective diffraction pattern in Fig. 3 as a result of the transition.

One possible application of this study to real systems is straightforward. Columnar liquid crystals have so far been produced in colloidal systems of anisometric particles, commonly of disk-like shape. The present result suggests that columnar liquid crystals with the structure similar to that we report here, and possibly other liquid-crystal phases, can be formed by spherical colloidal particles, with appropriate tuning of the effective force field. It has to be mentioned that the main features of the pair potential we exploited in this simulation are consistent with the classical theory for colloidal interactions by Deryagin, Landau, Verwy and Overbeek (DLVO) [20], amended with hard-core repulsion or steric repulsion close to the contact.

In summary, we used a molecular dynamics simulation to demonstrate that a thermodynamically stable hexagonal columnar liquid crystal can be formed in a single-component system of particles with a spherically symmetric interaction. This is the first observation of a liquid crystal phase formation in a simple system of identical particles. The scope of impact of this finding is expected to include columnar liquid crystals produced in colloids and other soft-matter mesoscopic particle systems.

We thank Dr. B. Sadigh for very useful discussions. This study was supported by the Swedish E-Science Research Foundation (SERC). Funding from the Swedish National Research Council (VR) is gratefully acknowledged. This work has been approved for release under Lawrence Livermore Release No...

[1] P. G. De Gennes and J. Prost, *The Physics of Liquid Crystals*, Oxford University Press, Oxford (1995)
[2] S. Chandrasekhar, *Liquid Crystals*, Cambridge University Press, Cambridge (1992).
[3] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1980)
[4] H. Bock, in: *Chirality in Liquid Crystals*, H.-S. Kitzerow and C. Bahr Eds., Springer Verlag, Berlin Heidelberg (2001)
[5] X. Zeng, G. Ungar, Y. Uu, V. Percec, A.E. Dulcey, and J. Hobs, Nature (London), 428, 157 (2004)
[6] C.M.Care and D.J.Cleaver, Rep. Progr. Phys. 68, 2665 (2005)
[7] M.A.Bates and G.R.Luckhurst, in: *Structure and Bonding* 94, Springer Verlag, Berlin Heidelberg (1999)
[8] C. Zannoni, J. Mater. Chem., 11, 2637 (2001)
[9] P. Bolhuis and D. Frenkel, J. Chem. Phys., 106, 666 (1997)
[10] M. P. Allen, G. T. Evans, D. Frenkel and B. M. Mulder, Advances of Chemical Physics, Ed. I. Prigogine and S. A. Rice, 76, 1 (1993)
[11] S. Sarman and A. Laaksonen, Phys. Chem. Chem. Phys. 15 3442 (2013); S. Sarman and A. Laaksonen, J. Comp. Theor. Nanosci. 8, 1081 (2011)
[12] M.A.Bates and G.R.Luckhurst, J. Chem. Phys., 104, 6696 (1996)
[13] B. Martinez-Haya and A. Cuetos, J.Chem. Phys. 131, 074901 (2009)
[14] D. Andrienko, V. Marcon, and K. Kremer J.Chem. Phys. 125, 124903 (2006)
[15] J.A.C. Veerman and D. Frenkel, Phys. Rev. A, 45, 5632 (1992)
[16] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1976)
[17] A. Metere, T. Oppelstrup, S. Sarman, A. Laaksonen, and M.Dzugutov, *Phys. Rev. E*, 88, 062502 (2013)
[18] E.I. Kats, V.V. Lebedev and A.R. Muratov, Phys. Rep., 228, 1 (1993)
[19] G.M. Grason, Phys. Rev. Lett. 101, 105702 (2008)
[20] B. Derjaguin and L. Landau, Acta Physico Chemica URSS 14, 633 (1941); E. J. Verwy and J. Th. G. Overbeek, “Theory of the stability of lyophobic colloids, Amsterdam, Elsevier (1948); J. N. Israelachvili, “*Intermolecular and Surface Forces*”, Academic Press (2011),