

Rotational Phase Transition and Melting in a Two-Dimensional Hard-Cyclic-Tetramer System

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(Received 3 December 1982)

Mechanical simulations of a two-dimensional system of N cyclic tetramers, studied in square ($N = 289$) and hexagonal ($N = 331$) boxes, demonstrate the existence of crystalline ($d = V/V_0 \lesssim 1.14$; different structures are observed), rotator ($1.18 \lesssim d \lesssim 1.29$), and fluid ($d \gtrsim 1.31$) phases (V_0 is the area of the box with close-packed structure). Observed phase coexistences suggest first-order transitions.

PACS numbers: 64.70.Kb, 61.20.Ja, 64.70.Dv

Systems of nonspherical molecules can exist in intermediate phases between the liquid and crystalline phases. The simplest classification distinguishes two extreme cases: first, liquid crystals,¹ in which the centers of mass of molecules are disordered² but their orientations display long-range order, and second, plastic crystals,³ in which molecules are arranged on an ordered lattice but their orientations have a certain degree of disorder. There is no doubt that molecular shape plays a crucial role in the existence of these phases.^{4,5} The problem is complicated mathematically and it seems reasonable to study first two-dimensional (2D) systems.

2D systems of molecules for which the plastic phase occurs exist in nature as layers adsorbed on Grafoil⁶ and have been recently studied by computer simulations.⁷ The simplest 2D systems which can show orientational transitions are those with hard-core interactions only. Being still too complicated for theoretical treatment they may be investigated by simulations. In this Letter results of such mechanical simulation experiments⁸ for the system of hard cyclic tetramers (see Fig. 1) are reported.

Each "molecule" consists of four polished steel balls of diameter σ glued together (for simplicity $\sigma = 1$). Positions and orientations of molecules are recorded by a camera (each ball reflects the light which, with the proper choice of the cam-

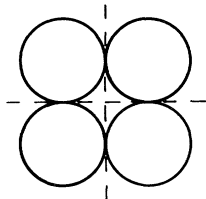


FIG. 1. Geometry of hard cyclic tetramer. Dashed lines indicate molecular axes.

era's diaphragm, is recorded as a point indicating the center of the ball). Molecules are put in motion by the vibration (~ 70 Hz) of a flat horizontal plate. Their vertical jumps are very small in comparison with σ because a glass plate is applied from above. Thus, the system can be treated as a mechanical model of the 2D system of hard cyclic tetramers. Horizontal motions of the molecules are limited to the plane of variable area V (the box size) by hard walls which vibrate together with the bottom and the glass plate to eliminate "cold" collisions, mentioned in Ref. 8. By changing the amplitude of vibration one can control the temperature of the system. Because for any hard-molecule system the configurational partition function is independent of temperature and the phase of the system is fully determined by its density, one can study phase transitions in hard-cyclic-tetramer systems at any temperature. In the present study the temperature was used for which an average rate of collisions per molecule was of the order 10 s^{-1} . It was sufficiently high to obtain many collisions and sufficiently low to not destroy the molecules.

Figure 2 shows typical pictures obtained for a system of $N = 289$ tetramers in a square box at different values of relative area parameter $d = V/V_0$ (V_0 is the area of the box for the close-packed tetramer structure of type α). Details of molecular trajectories that are visible in a short-time exposure ($t = 5$ s) are lost in longer exposures ($t = 10$ min). There were five different structures observed, denoted in Fig. 2 as $\alpha - \epsilon$:

(α) $1.00 \lesssim d \lesssim 1.02$.—Centers of molecules form a square lattice with cell sides $\vec{a}_\alpha = a_0 \vec{\tau} \vec{x}$ and $\vec{b}_\alpha = a_0 \vec{\tau} \vec{y}$ [\vec{x} and \vec{y} are, respectively, unit vectors in the x and y directions, $a_0 = (2 + \sqrt{3})^{1/2}$, and $\tau = \sqrt{d}$]. The molecular axes are not parallel to the lattice lines—the angle between them equals $\pi/12$. The molecules execute small oscillations and librations around their lattice sites and directions. Direct observation enables one to state

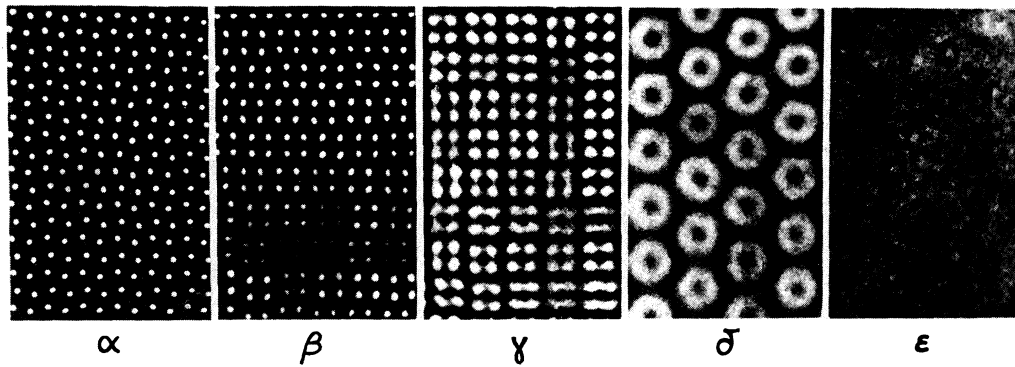


FIG. 2. Long-time exposures for the system of $N=281$ tetramers in a square box for (α) $d=1.01$, (β) $d=1.06$, (γ) $d=1.11$, (δ) $d=1.21$, and (ϵ) $d=1.34$.

that no reorientations by angles comparable to $\pi/2$ occurs.

(β) $1.02 \lesssim d \lesssim 1.07$.—The molecules form a rectangular lattice of cell sides $\vec{a}_\beta = a_0^2 \vec{\gamma}$ and $\vec{b}_\beta = 2\vec{\gamma}$, with a unit cell containing two molecules placed at $\vec{r}_1 = 0$ and $\vec{r}_2 = (\vec{a}_\beta + \vec{\gamma})/2$. The molecular axes are parallel to the lattice lines. Jump reorientations by $\pi/2$ occur; their frequency, starting from zero at $d=1.02$, increases smoothly with d .

It is easy to verify that α and β structures have the same density at close packing. The area per molecule is equal to $v_0 = 2 + \sqrt{3}$ for both structures.

(γ) $1.10 \lesssim d \lesssim 1.14$.—The molecules are arranged on a square lattice, like in case α , but are oriented parallel to the lattice. The frequency of reorientation jumps is about five times higher than in case β , but increases more slowly—by only about 25% in this whole interval. Despite considerable translational and orientational motions localization of elementary disks is visible in the form of spots.

(δ) $1.18 \lesssim d \lesssim 1.29$.—The picture is drastically different from the case γ . The system lost its orientational order, and in place of fourfold symmetry of molecular images, diffusive rings are observed. It follows from direct observations that molecules undergo frequent reorientations by angles different from $\pi/2$ or its multiple. The lattice symmetry also increases to a sixfold one—the molecules oscillate around sites of the perfect hexagonal lattice.

(ϵ) $d > 1.31$. The system is in the fluid phase—translational order is lost.

In the range $1.07 \lesssim d \lesssim 1.10$ the structure of the system evolves from β to γ as \vec{r}_2 approaches $\vec{a}/2$. The frequency of jumps increases rapidly in this

interval.

The ranges $1.14 \lesssim d \lesssim 1.18$ and $1.29 \lesssim d \lesssim 1.31$ cover, respectively, rotational and translational melting. In Fig. 3 short-time exposures for d in these two ranges are shown: Coexistence of the orientationally ordered phase and the rotator phase is clearly visible in Fig. 3(a), and the latter clearly coexists with fluid in Fig. 3(b). This suggests strongly that both the transitions are of the first order.

To determine the influence of the boundary conditions, the system of $N=331$ tetramers in a hexagonal box was also studied. For $d \lesssim 1.14$ different pictures than evident were recorded. Two typical examples for different ranges of d are shown in Fig. 4.

Figure 4(a) is for $d \lesssim 1.10$. A structure with defects composed of differently oriented fragments of a new structure, called η , is observed. The η structure consists of an oblique lattice with cell sides $\vec{a}_\eta = \vec{r}_2$ and $\vec{b}_\eta = b_\beta$ and molecular axes par-

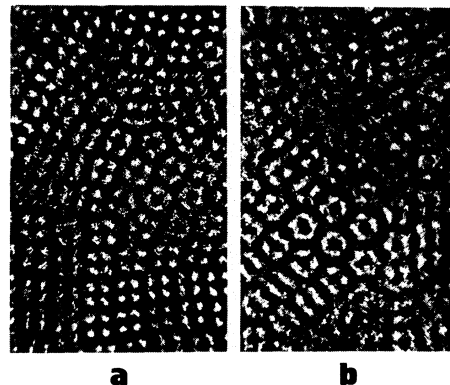


FIG. 3. Short-time exposures for the same system as in Fig. 2. (a) $d=1.17$, (b) $d=1.29$.

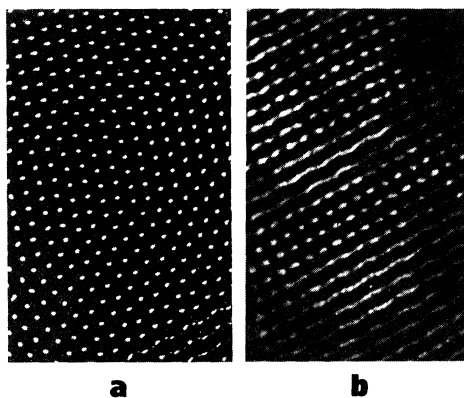


FIG. 4. Long-time exposures for the system of $N=331$ tetramers in a hexagonal box. (a) $d=1.06$, (b) $d=1.13$.

allel (or, because of fourfold symmetry, perpendicular) to \vec{b}_η .

It is noticeable that the only difference between the β and η structures involves the relative positions of sequences of rows parallel to the \vec{b} sides. For the β structure the nearest molecules of the next-nearest-neighboring rows have the same ordinates, whereas in the η -structure ordinates of such molecules differ by 1.

No α structure nor its fragment was found. This suggests that such a structure may be metastable and can exist only in small systems as a result of square boundary conditions. Calculating a "smoothed" free volume per particle, v_f , in the "fixed neighbor" approximation⁹ for α , β , and η structures, one obtains in the limit $\tau \rightarrow 1 = \xi \rightarrow 0$

$$v_f^\alpha = \pi(3 + 5/\sqrt{3})\xi^3 \approx 18.49\xi^3,$$

$$v_f^\beta = v_f^\eta = \pi(2\sqrt{3} + \frac{29}{8})\xi^3 \approx 22.27\xi^3.$$

Since the configurational part of the free energy ($A = -NkT \ln v_f$, with k the Boltzmann factor, and T the temperature) in the α structure is higher than in the β and η structures, this supports the above suggestion.

It remains an open question whether the β or η structure is thermodynamically stable. This may be solved by computer simulations using variable shape boxes¹⁰ or taking larger N .¹¹

In Fig. 4(b) we have $1.10 \lesssim d \lesssim 1.14$. Instead of the γ -structure, correlated sliding of rows is observed. Orientational order is preserved. For $d=1.13$, molecules near the walls of the box start to rotate; the central molecules keep their orientational order.

For $d > 1.15$ properties of both systems (square

and hexagonal) are identical within the accuracy of the experiment ($\Delta d = 0.01$).

The explanation of the differences for $d \approx 1.14$ is the following. For high densities the influence of hard boundaries (used in the experiment for obvious reasons) on the properties of the system is large. Close-packed structures of tetramers are incommensurate with a hexagonal box, so that defect structures must occur at high densities. At lower densities these defects are concentrated mainly near the walls and hence the density is lower there than in the central part of the system. This is the reason for the observation of sliding of rows, and rotational melting occurring first near the walls.

Systems of cyclic molecules of different shape were also studied.¹² Rotator phase was found for multimers higher than tetramers (pentamers and hexamers).

In the present version the mechanical simulation leads to a fast algorithm which can be exploited to investigate the qualitative features of simple model systems in the various ranges of density for further quantitative computer study. Many modifications (pressure and temperature measurements, creation of a periodic substrate, study of particles with magnetic moments, etc.) of the method are possible to extend comparison with real systems.

The idea studied in the present paper has been suggested by Dr. Piotr Pierański. We are grateful to him and Professor J. Małecki for their constant help. One of us (K.W.W.) wishes to thank Dr. M. Parrinello for useful discussions during the former's stay at the International Centre for Theoretical Physics in Trieste. This work was done under Research Project MR-I.9.

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⁹One molecule moves in a cell bounded by its neighbors fixed in their lattice positions and orientations. The area $v_f(\varphi)$ accessible for the molecular center at a given orientation φ of this molecule is approximated by an ellipse. Integrating $v_f(\varphi)$ over φ one obtains v_f . See also J. A. Barker, *Lattice Theories of the Fluid State*, edited by J. S. Rowlinson (Pergamon, Oxford, 1963).

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Observation of Bands of Faces on Incommensurate Rb_2ZnBr_4 Single Crystals

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(Received 29 September 1982)

The macroscopic consequences of displacive modulation on the morphology of incommensurate single crystals are confirmed. Bands of faces in the neighborhood of stable normal crystal faces have been observed on spherically shaped Rb_2ZnBr_4 crystals. An interpretation is given in terms of classical morphological theory extended to include (four-dimensional) superspace group symmetry. This leads to the view that the formation of these bands involves, at least partly, so-called satellite faces and gives a simple explanation of why the set of bands has a lower point-group symmetry than the set of normal faces.

PACS numbers: 61.50.Em, 61.50.Cj

As observed first by de Wolff and collaborators,¹ incommensurate single crystals of Rb_2ZnBr_4 and Rb_2ZnCl_4 grown in an aqueous solution show morphological features due to their modulation in the form of so-called satellite faces. These satellite faces could be interpreted² by extension of the classical geometrical theories of Bravais,³ Friedel,⁴ and Donnay and Harker.⁵

On the basis of the Bravais-Friedel-Donnay-Harker law, a fairly large number of satellite faces is expected to have about the same morphological importance. Their simultaneous appearance is favored by use of spherically shaped single crystals as the initial growth form. Indeed, as reported below, with this technique a number of growth bands could be made visible in addition to the normal faces. A normal face appears as a depression on the growing sphere. Satellite faces appear within a strip of ledged faces forming a kind of staircase, which will here be called a "staircase band" (or simply a "band")

of faces, the faces being called "steps." Bands of this kind have also been observed on a number of inorganic single crystals like ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) and KDP (KH_2PO_4)^{6,7} (see Fig. 1), and on crystalline metals like cadmium and zinc.⁸

For the sphere experiments two large, transparent, single crystals of Rb_2ZnBr_4 were selected and polished into half spheres of about 1 cm diam with poles along the $\langle 101 \rangle$ and $\langle 110 \rangle$ directions, respectively. Because of inversion symmetry half a sphere already contains all relevant information. After growth for about 1 h in a slightly supersaturated solution at about 30 °C, beautiful faces and bands could be observed. Goniometer measurements allowed the faces to be indexed as (100), (001), (201), (111), (110), and (310). These are normally expected crystal faces in crystals of the K_2SO_4 structure type.⁹ As far as the observations allowed us to conclude, all these faces obey the mmm point-group symmetry of the average crystal structure (space group $Pcmm$).

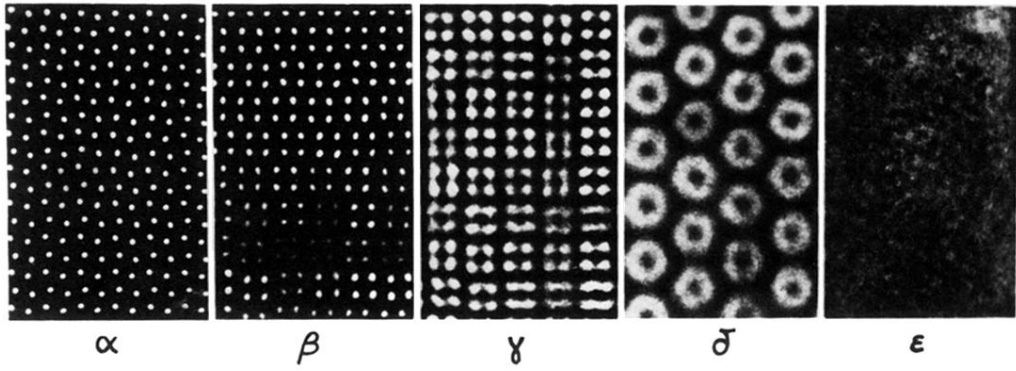


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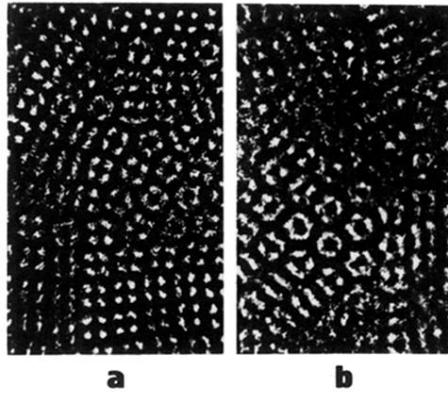


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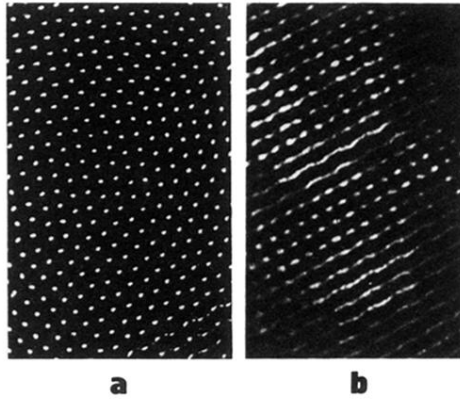


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