Constrained deformation of a confined solid: a strain induced crystal-smectic transition

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(Dated: January 1, 2022)

We report results of computer simulations of two-dimensional hard disks confined within a quasi one-dimensional “hard-wall” channel, a few atomic radii wide. Starting from a commensurate triangular solid a reshaping of the system size parallel to the channel length introduces a rectangular distortion of the solid which, beyond a critical limit, phase separates into alternating bands of solid and smectic phases. The resulting solid-smectic interfaces are broad and incorporate misfit dislocations. The stress-strain curve shows large plastic deformation accompanying the crystal-smectic transition which is reversible. The smectic phase eventually melts into a modulated liquid with a divergent Lindemann parameter.

Studies of small assemblages of molecules with one or more dimensions comparable to a few atomic spacings are significant in the context of nano-technology. Designing nano-sized machines requires a knowledge of the mechanical behavior of systems up to atomic scales, where, a priori, there is no reason for continuum elasticity theory to be valid. In most cases, however, the effects of finite size are relatively mild, showing up mainly as a variation of the numerical value of the elastic constants as a function of length scale. In this Letter, we show, on the other hand, that small size and hard constraints can produce essentially new phenomena without a counterpart in the bulk system. We perform computer simulations of the simplest possible, nontrivial, molecular system, namely, two-dimensional hard disk “atoms” confined within a quasi one-dimensional channel; the physics of which is entirely governed by geometry. Bulk hard disks in two dimensions are known to melt from a high density triangular lattice to an isotropic liquid with a narrow intervening hexatic phase. In contrast, for channel widths of a few atomic spacings, we find evidence for a smectic phase which nucleates as prominent bands within the solid. The smectic phase arises when the size of the system in the direction parallel to the fixed walls is increased. A crystal to smectic transition, though predicted for anisotropic molecules, is unusual for hard disks – the anisotropy in this case arising purely from the external confining potential. In this respect, our results resemble the phenomenon of laser induced freezing where an external modulated electric field produced by crossed laser beams induces a series of phase transitions involving triangular solid, modulated liquid as well as smectic phases. The analog of the modulating potential in our case is, of course, provided by the walls which induce a periodic potential of mean force decaying with distance from the walls. The nature of the crystal-smectic transition in our system, as we show below, are, however, different. Our results may be directly verified in experiments on sterically stabilized “hard sphere” colloids confined in glass channels and may also be relevant for similarly confined atomic systems interacting with more complex potentials.

The bulk system of hard disks where particles $i$ and $j$, in two dimensions, interact with the potential $V_{ij} = 0$ for $|r_{ij}| > d$ and $V_{ij} = \infty$ for $|r_{ij}| \leq d$, where $d$ is the hard disk diameter and $r_{ij} = r_j - r_i$ the relative posi-
FIG. 2: A plot of the normal stress $\sigma_d$ versus the conjugate strain $\varepsilon_d = (\eta_0 - \eta)/\eta_0$ ($\eta_0 = 0.85$) obtained from our Monte Carlo simulations of $65 \times 10$ hard disks showing a typical Van der Waals loop in the constant strain ensemble. Data for the plot is obtained by equilibrating at each strain value for $2 \times 10^5$ MCS and averaging the data for a further $3 \times 10^4$ MCS. The stress for the hard disk system has been calculated by the standard method$^{[14]}$ by averaging the collision probability. It is minimum at $\eta = \eta_c \approx .74$. The entire cycle consisting of increasing $\varepsilon_d(\phi)$ and again decreasing to zero (+) using typical parameters appropriate for an atomic system, corresponds to a real frequency of $\approx 100$KHz. The lines in the figure are a guide to eye. The solid ($\eta > \eta_c$), two phase ($\eta_c < \eta < \eta_s$) and smectic (Sm) ($\eta < \eta_s$) regions are indicated in the figure. We have repeated this calculation with a cycle frequency $10^5$ KHz $- 1$M Hz with no essential change in the results.

Consider a narrow channel in two dimensions of width $L_y$ defined by hard walls at $y = 0$ and $L_y$ ($V_{\text{wall}}(r) = 0$ for $0 < r < L_y$ and $= \infty$ otherwise) and length $L_x$ with $L_x \gg L_y$. Periodic boundary conditions are assumed in the direction $x$ implying $x + L_x = x$. In order that the channel may accommodate $n_l$ layers of a homogeneous, triangular lattice with lattice parameter $a_0$ of hard disks of diameter $d$, (Fig. 1) one needs,

$$L_y = \frac{\sqrt{3}}{2}(n_l - 1)a_0 + d$$

(1)

Defining $\chi = 1 + 2(L_y - d)/\sqrt{3}a_0$, the above condition reads $\chi = \text{integer} = n_l$ and violation of Eqn. (1) implies a rectangular strain away from the reference triangular lattice of $n_l$ layers. The lattice parameters of a centered rectangular (CR) unit cell are $a_x$ and $a_y$ (Fig. 1 inset). In general, for a CR lattice with given $L_y$ we have, $a_y = 2(L_y - d)/(n_l - 1)$ and, ignoring vacancies, $a_x = 2/\rho a_y$.

The normal strain $\varepsilon_d = \varepsilon_{xx} - \varepsilon_{yy}$ is then,

$$\varepsilon_d = \frac{n_l - 1}{\chi - 1} \frac{\chi - 1}{n_l - 1},$$

(2)

where the number of layers $n_l$ is the nearest integer to $\chi$ so that $\varepsilon_d$ has a discontinuity at half-integral values of $\chi$.

For large $L_y$ this discontinuity and $\varepsilon_d$ itself vanishes as $1/L_y$ for all $\eta$.

We study the effects of this strain $\varepsilon_d$ on the hard disk triangular solid at fixed $L_y$ large enough to accommodate a small number of layers $n_l \sim 9 - 25$. The strain $\varepsilon_d$ is imposed by expanding the dimension of the system $L_x$ parallel to the walls keeping $L_y$ fixed so that $\varepsilon_d = (\eta_0 - \eta)/\eta_0$, where $\eta_0$ is the packing fraction corresponding to an unstrained triangular solid. We monitor the Lindemann parameter $l = \langle (u_{xi} - u_{yj})^2 \rangle/\langle a^2 \rangle + \langle (u_{yi} - u_{yj})^2 \rangle/\langle a^2 \rangle$ where the angular brackets denote averages over configurations, $i$ and $j$ are nearest neighbors and $u_{yi}$ is the $\alpha$-th component of the displacement of particle $i$ from its mean position. The parameter $l$ diverges at the melting transition $^{[12]}$. We also measure the structure factor $\rho G = \left\langle \frac{1}{\sqrt{2}} \sum_{i,j=1}^{N} \exp(-iG\cdot r_{ij}) \right\rangle$, for $G = \pm G_1(\eta)$, the reciprocal lattice vector (RLV) corresponding to the set of close-packed lattice planes of the CR lattice perpendicular to the wall, and $\pm G_2(\eta)$ the four equivalent RLVs for close-packed planes at an angle $( = \pi/3$ and $2\pi/3$ in the triangular lattice) to the wall (see Fig. 1 inset).

We find, throughout, $\rho G_3(\eta) < \rho G_1(\eta) \neq 0$, a consequence of the hard wall constraint$^{[12]}$ which manifests as an oblate anisotropy of the local density peaks in the solid. As $\eta$ is decreased (see Fig. 1 for details) both $\rho G_1$ and $\rho G_2$ show a jump at $\eta = \eta_c$ close to $\chi \approx n_l - 1/2$. For $\eta < \eta_c$ we get $\rho G_2 = 0$ with $\rho G_1 \neq 0$ signifying a transition from crystalline to smectic like order. The Lindemann parameter $l$ remains zero and shows a divergence only below $\eta = \eta_3(\approx \eta_{\text{nm}})$ indicating a finite-size- broadened melting of the smectic to a modulated liquid phase. We have also calculated the normal stress $\sigma_d = \sigma_{xx} - \sigma_{yy}$ (see Fig. 2). For $\eta = \eta_0$ the stress is purely hydrostatic
with $\sigma_{xx} = \sigma_{yy}$ as expected. As $\eta$ decreases, the stress increases linearly in the elastic limit, flattening out at the onset of non-linear behavior at $\eta \approx \eta_c$. At $\eta_c$, $\sigma_d$ decreases and eventually becomes negative. On further decrease in $\eta$ below $\eta_{c2}$ (Fig. 4), $\sigma_d$ approaches 0 from below thus forming a Van der Waals loop typical of the constant strain ensemble. If the strain is reversed by increasing $\eta$ back to $\eta_0$ the entire stress-strain curve is traced back with no remnant stress at $\eta = \eta_0$ showing that the plastic region is reversible. As $L_y$ is increased, $\eta_{c1}$ merges with $\eta_{c3}$ for $\chi \approx 25$. If instead, $L_x$ and $L_y$ are both rescaled to keep $\chi$ fixed or periodic boundary conditions are imposed in both $x$ and $y$ directions, the transitions in the various quantities occur approximately simultaneously as expected in the bulk system. Varying $\eta_x$ in the range $10 - 1000$ produces no essential change in results.

For $\eta_{c3} < \eta < \eta_{c1}$ we observe that the smectic order appears within narrow bands (Fig. 4) which nucleate at $\eta_{c1}$. Inside these bands the number of layers is less by one and the system in this range of $\eta$ is in a mixed phase. A plot (Fig. 4(a)) of $\chi(x)$, obtained by averaging the instantaneous $a_y$ from particle configurations over a strip spanning $L_y$, shows bands in which $\chi$ is less by one compared to the crystalline regions. Once nucleated narrow bands coalesce to form wider bands, the dynamics of which is, however, extremely slow. The bands grow as $\eta$ is decreased. Calculated diffraction patterns (Fig. 4(b)) show that, locally, within a smectic band $\rho_{G_2} \gg \rho_{G_1}$ in contrast to the solid region where $\rho_{G_1} \approx \rho_{G_2} \neq 0$.

Strong finite size corrections make a complete theoretical treatment of this problem difficult. However, significant progress may be made using qualitative arguments as we show below. The total free energy of the system $\mathcal{F}_T$ may be decomposed as,

$$\mathcal{F}_T (\eta, \chi) = K^\Delta (\eta)\epsilon_d^2 (\chi) + \mathcal{F}_0 (\eta)$$

where $K^\Delta (\eta)$ is an elastic constant and $\mathcal{F}_0 (\eta)$ the free energy of the perfect triangular lattice in contact with a hard wall at packing fraction $\eta$. It is clear that $\mathcal{F}_T$ has minima for all $\chi = n_l$. For half integral values of $\chi$ the crystalline structure is metastable with respect to an intervening smectic when adjacent local density peaks of the solid overlap in the $x$ direction. This overlap is facilitated by the (oblate) anisotropy of the solid density peaks. For large $L_y$ the minima in $\mathcal{F}_T$ merge to produce a smooth free energy surface independent of $\chi$. For small $L_y$ all regions of the parameter space corresponding to non-integer $\chi$ are also globally unstable as belied by the loop in the stress-strain curve (Fig. 2). The system should therefore break up into regions with various $n_l$. Such fluctuations are, however, suppressed due to the structure of interfaces between regions of differing $n_l$. A superposition of many particle positions near such an interface (see Fig. 3(b)) shows that: (1) the width of the interface is large, spanning about $10 - 15$ atomic spacings and (2) the interface between $n_l$ layered crystal and $n_l - 1$ layered smectic contains a dislocation with Burger’s vector in the $y$ direction which makes up for the difference in the number of layers. Note that the presence of these dislocations breaks inversion symmetry as observed in the local diffraction patterns. The core region of this dislocation extends over many layers with some of the disks within the interface alternating between positions corresponding to either a smectic or a solid. Each band of width $s$ is therefore held in place by a dislocation-anti-dislocation pair (Fig. 4). In analogy with classical nucleation theory the free energy $F_b$ of a single band can be written as

$$F_b = -\Delta F s + E_c + \frac{1}{4\pi}b^2 K^\Delta \log \frac{s}{a_0}$$

where $b = a_y/2$ is the Burger’s vector, $\Delta F$ the free energy difference between the crystal and the smectic per unit length and $E_c$ the core energy for a dislocation pair. Bands nucleate when dislocation pairs separated by $s > \frac{1}{4\pi}b^2 K^\Delta / \Delta F$ arise due to random fluctuations. Band coalescence occurs by diffusion aided dislocation “climb” which is extremely improbable in a high density phase leading to slow kinetics. The growing smectic
bands are in a state of tension in the $y$ direction implying $\sigma_{yy} > \sigma_{xx}$ which is countered by the compressive stress in the crystalline region. Growth of smectic bands therefore reduces $\sigma_d$ which attains a minimum at $\eta = \eta_{c2}$ when a single band spans the entire length. Subsequently $\sigma_d \to 0$, the value in the liquid phase. Since orientation relationships between the crystal and smectic are preserved, the stress-strain relationship is completely determined by the amount of the co-existing phases which explains the reversibility \cite{19}. For large values of $L_y$ the smectic phase vanishes since the strains involved themselves go to zero. Nevertheless, transition between $n_l$ and $n_l \pm 1$ layered crystals have been observed by us. We must mention here that the choice of the ensemble, viz. constant strain, is crucial since, in the constant stress ensemble, the hard disk system fails at $\eta_{c1}$, and the strain diverges producing a homogeneous low density gas with no interface. Finally, our smectic bands are reminiscent of “slip” or “deformation” bands which arise during plastic flow of macroscopic ductile materials \cite{20}.

Apart from constrained hard sphere colloids \cite{13} where our results are directly testable, strain induced crystal-smectic transition may be observable in experiments on the deformation of mono-layer atomic nano-beams or strips of real materials confined to lie within a channel \cite{1}. This is because the constraints we choose to study are geometrical and would exist in any system. The occurrence of a smectic phase may be important for the tribological \cite{21} properties of nano-scale machine parts where atomic friction plays an important role in their function. In the future we would like to study the kinetics of the crystal-smectic transition in detail as well as the effect of substrate disorder on the nature of this transition.

The authors thank M. Rao, V. B. Shenoy and A. Datta for useful discussions; D. C. thanks C.S.I.R., India, for a fellowship. Financial support by Department of Science and Technology, India, is gratefully acknowledged.

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