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Lack of long-range order in confined two-dimensional model colloidal crystals

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We investigate the nature of the ordered phase for a model of colloidal particles confined within a quasi-one-dimensional (Q1D) strip between two parallel boundaries, or walls, separated a distance D in two dimensions (2D). Using Monte Carlo simulations we find that at densities typical of the bulk 2D triangular solid the order in the D1D strip is determined by the nature of the boundaries. While the order is enhanced for a suitably corrugated boundary potential, for a uniformly repulsive smooth boundary potential ordering normal to the walls is enhanced ("layering"), but destroyed parallel to the wall.

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Colloidal particles have been used as readily available physical models for studying collective phenomena in condensed matter [1–4]. This is mainly because colloidal dispersions can be prepared and characterized in a well-controlled way, effective interactions between colloidal particles being tailored by various means. The large size of the particles also allows observation techniques that are not applicable for order-disorder phenomena in atomic systems. Particularly interesting is the possibility of confining colloidal particles in two-dimensional (2D) [5–10] or even 1D [11,12] geometries to test fascinating concepts on the statistical mechanics of low-dimensional systems [13–17].

In the present work, we shall consider systems in between these dimensionalities, i.e., colloids confined in 1D strips of width D [18]. Ordering in strips and half planes has been studied [13–19] in the past for spin systems primarily in the context of surface critical phenomena where both suppression and enhancement of order near free boundaries have been observed.

Studies of the nature of ordering for quasi-1D strips have been done for Wigner crystals [20] and repulsive magnetorheological (MR) colloids [21,22], for instance. The former system is relevant, e.g., for electrons on the surface of liquid helium that is confined in a quasi-1D channel, where unusual ordering phenomena were found [23], and for confined dusty plasmas [24]. MR colloids under confinement are of interest for microfluidic applications; see [21,22] for references and discussions of further related systems. Unusual mechanical behavior of a related system has also been reported [25], and in Ref. [21] it was noted that the properties of the confined system approach those of the unbounded system surprisingly slowly as the channel width is increased. Early experiments on a model hard disk system [26] also showed unconventional behavior. Clearly, the understanding of confined 2D crystals is far from being complete, and it is the purpose of the present work to contribute to a resolution of these puzzles by combining simulations of a generic model with a suitable theoretical analysis.

This problem is similar, but not identical, to the confinement of 2D colloids by periodic laser fields [27–31], where an interesting reentrance of the transition from the crystal to the periodically modulated fluid phase as function of the laser field strength is predicted [30] and observed [27].

For finite D, the system is quasi-one-dimensional, and hence one might argue that long-range order (LRO) is destroyed, for systems with short-range forces [13]. Indeed, a 1D harmonic crystal displays a fluidlike structure factor [32], and this accounts well for real quasi-1D chain compounds such as $Hg_{3-\delta}AsF_6$ (where $\delta \ll 1$) [33]. However, for confined colloidal crystals the situation should be more subtle, since the confinement between hard repulsive boundaries reduces fluctuations in the direction normal to the boundaries, causing a pronounced "layering effect." Ordering is also strongly influenced by the boundaries, for example, it is known that a boundary corrugation potential [13,34] enhances the order parallel to the boundaries.

The interaction among colloidal particles may be conveniently parametrized by $V(r)=\varepsilon(\sigma/r)^n$ where the exponent may vary from $n=\infty$ in the case of hard sphere colloids [1–4] to $n=3$ for superparamagnetic [5,6] dipolar colloids. We have chosen a potential with $n=12$ and with a cutoff at $r_c=5\sigma$, at a temperature $k_BT/\varepsilon=1$ (k_B is the Boltzmann constant) and density (choosing units such that $\sigma=1$) $\varrho=1.05$. This choice retains the advantage of a smooth potential which is also sufficiently short ranged for computational convenience. Further, we believe that the phenomena reported here are independent of the detailed nature of the potential. At the chosen density, melting in the bulk occurs for $k_BT/\varepsilon \approx 1.35$ in this model [35]. We choose two types of wall potentials, with walls oriented parallel to lattice axes of the triangular lattice. (i) (Planar walls) The potential is $V_{wall}(\mathbf{r})=\varepsilon_{wall}(\sigma/|x-x_{wall}|)^{10}$ for a particle at position $\mathbf{r}$, where the x direction is chosen perpendicular to the boundaries, and the positions x_{wall} of the two walls are a distance D apart that is an integer multiple of the distance $a\sqrt{3}/2$, a being the lattice spacing of an ideal triangular lattice compatible with the chosen density. The strength of this potential is typically $\varepsilon_{wall}=0.0005k_BT$ (also much stronger wall potentials were tested). (ii) Structured walls causing a periodic corrugation of the potential were created by choosing two rows of particles fixed in the positions of this ideal triangular lattice, and these particles interact with the mobile particles with the same potential $V(\mathbf{r})$ as specified above. Summing up these potentials due to the fixed particles defines the corrugation potential $V_{struc}(\mathbf{r})$ (structured walls) of such structured boundaries.

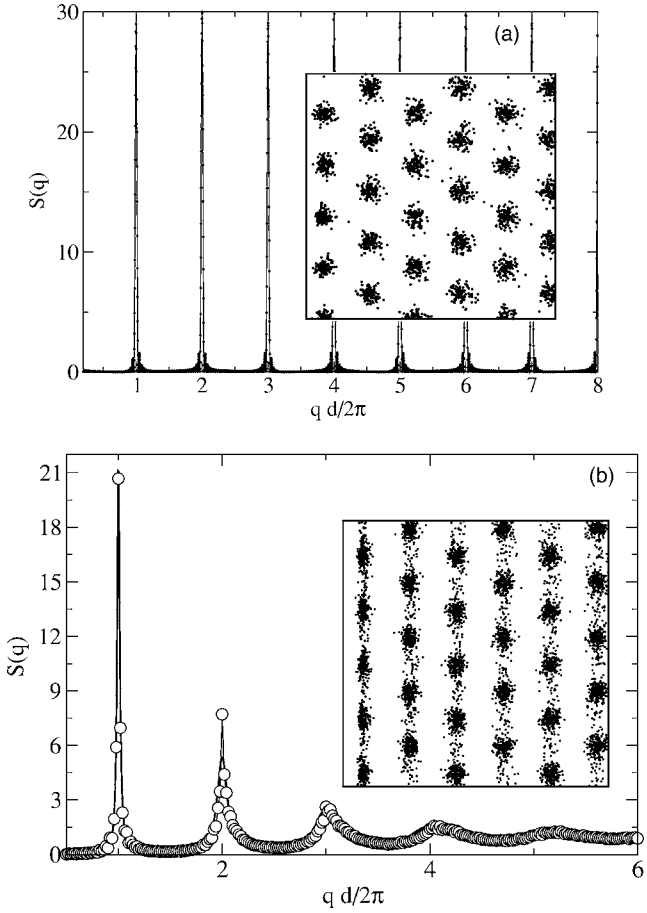

FIG. 1. Static structure factor $S(q)$ plotted vs $qd/2\pi$ (d being the distance between lattice axes in the y direction parallel to the boundaries), for structured (a) and planar (b) walls. All data are for systems of 900 particles. In (b) a fit to the $S(q)$ for a harmonic chain [32] is included. The wave vector **q** is oriented along the y direction. The insets in (a) and (b) show the corresponding particle configurations for eight layers adjacent to the wall on the left; 1000 configurations out of a run lasting 10^6 MCS are superimposed after putting the center of mass into the origin of the coordinate system each time. Note the prominent anisotropy of the density peaks in the inset of (b).

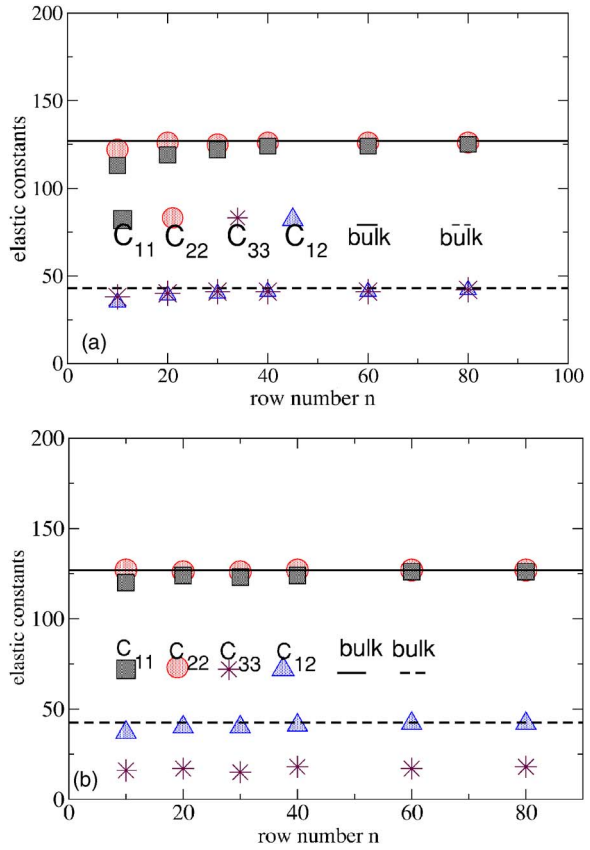

FIG. 2. (Color online) Elastic constants in units of k_BT/σ^2 for structured (a) and planar (b) walls plotted vs the number of rows n between the walls. The Voigt notation for the elastic constants is used. Horizontal straight lines show the bulk values of the corresponding triangular crystal, for which the symmetries $C_{11}=C_{22}$ and $C_{12}=C_{33}$ hold.

We use standard Monte Carlo methods [36], where single particles are selected at random to attempt a small random displacement in a square of linear dimension $\kappa=0.206$ centered at the old position of the particle. Typical runs were performed for systems containing between $D\times L=20\times 20$ and 60×60 particles, carrying out 10^6 Monte Carlo steps (MCS) per particle in each run. In the direction parallel to the walls, periodic boundary conditions are used. For the sake of comparison, also runs for "bulk" systems (with no walls and periodic boundary conditions in both directions) were done. Some runs were also made for a strongly elongated geometry ($D\times L=20\times 500$) to probe the behaviour of displacement correlations at large length scales.

Both types of boundaries enhance the order in the x direction near the walls. This enhancement of order in the direction normal to the walls is even more pronounced (and of larger range) when we approach the transition to the fluid phase [37]. While in the bulk the well-defined orientational LRO and nonzero shear modulus of the 2D crystal have both disappeared in the fluid, some wall-induced orientational LRO persists in the thin strip [37].

In contrast, in the direction parallel to the boundaries the behavior in the two cases differs dramatically. For the structured boundary, the structure factor $S(q)$ exhibits the sharp Bragg peaks expected for a crystal [39] [Fig. 1(a)]. For the structureless repulsive boundary, a typical fluidlike structure factor results, which is almost in quantitative agreement with a fit to the $S(q)$ for 1D harmonic chains [32] [Fig. 1(b)], although we deal here with a system of 30 rows confined between two boundaries, rather than a true 1D system. This reduction of order in the y direction along the boundaries is also seen directly when one superimposes the positions from 1000 configurations of the particles (Fig. 1 inset). This lack of order concerns the positional LRO only, however: the orientational LRO due to the strong confinement in layers parallel to the walls is rather well developed, and even better for the planar walls rather than the structured walls [37]. The analogy to 1D harmonic chains suggests that for $T\to 0$ the range of positional LRO gets gradually very large, but true LRO only occurs for $T=0$. [Note that also Ising model strips of finite width have a transition only at $T=0$ for any finite

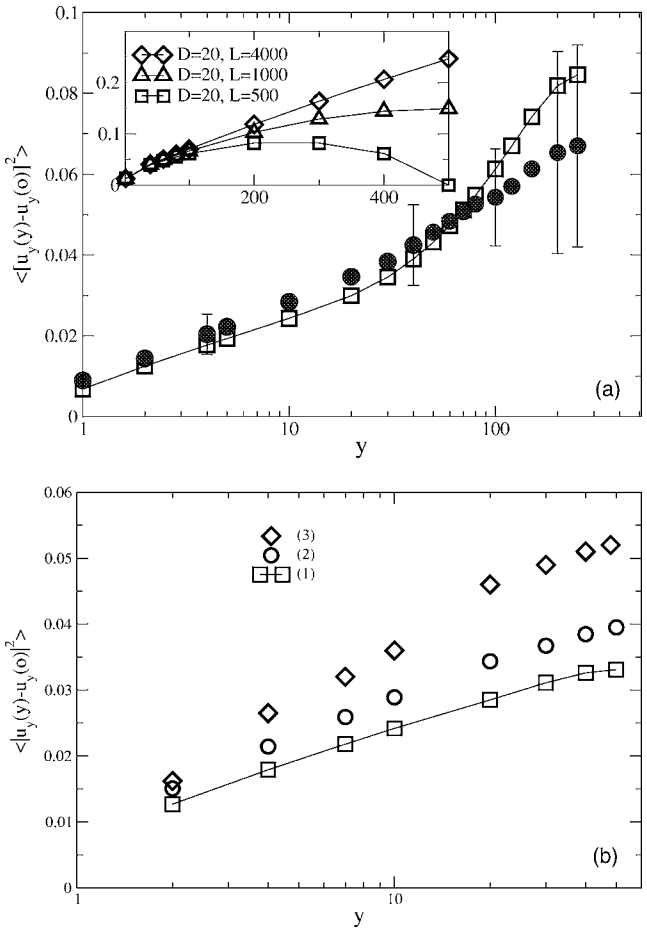

FIG. 3. (a) Comparison of $\langle[u_y(y)-u_y(o)]^2\rangle$ vs y (in logarithmic scale), for the soft disk solid at $\rho\sigma^2=1.05$ and $k_BT/\epsilon=1$ (filled circles) with the results of the harmonic theory (□) for a system with $D=20$ and $L=500$. The input Lamé coefficients $\lambda=42$ and $\mu=41$ in units of k_BT/σ^2 are those of the bulk soft disks at the same ρ and T, and the pressure $P=17.4$ in units of ρk_BT. Inset shows the crossover of $\langle[u_y(y)-u_y(o)]^2\rangle$ in the harmonic approximation from an initial logarithmic to a linear growth for various D and L signifying destruction of positional LRO. Note that for small systems the linear part is cut off due to finite size. (b) Comparison of $\langle[u_y(y)-u_y(o)]^2\rangle$ vs y, for the harmonic solid (1) (the line is a guide to the eye), soft disk solid with periodic boundary conditions (2), and soft disk solid with planar walls (3) at $\rho\sigma^2=1.05$ and $k_BT/\epsilon=1$. All the three systems have 2000 particles ($D=20$ and $L=100$). The displacement correlations are calculated only for the layer closest to the wall for (3). Note the enhancement of fluctuations for the system with planar walls.

value of D, but there the correlation length below the critical temperature T_c of the 2D model is much larger, of order $D\exp(\text{const}\times D)$.]

The fact that confinement by planar structureless boundaries turns a colloidal 2D crystal into a kind of smectic phase [38] (or strongly modulated fluid) also shows up when one examines "bulk" properties of the strip like the elastic constants (Fig. 2). While for structured walls one reaches the behavior of the bulk rapidly, for planar walls one rather has $C_{33}(\text{bulk})\sim 2C_{33}(n)$, which implies a vanishing shear modulus. The elastic constants could be determined directly from an analysis of the configurations of the particles applying the method of Sengupta *et al.* [40,41]. Particularly remarkably the increase of strip thickness (or number n of rows in the strip) does not cause any visible approach to bulk behavior. The question of how for the elastic constants the thermodynamic limit is approached is intriguing. The planar boundary provides an elastic distortion of long range [42] to the crystal, and our results imply that in $d=2$ this distortion disturbs the positional LRO.

This lack of positional LRO may be understood from a calculation of the displacement correlation function $B(y)=\langle[u_y(y)-u_y(o)]^2\rangle$, where u_y is the displacement away from a reference lattice in the direction parallel to the walls and the angular brackets signify ensemble averaging. Using a harmonic elastic Hamiltonian for the strip geometry, this may be written as

$$B(y)=2\sum_{q_x=2\pi n_x/D}\ \sum_{q_y=2\pi n_y/L}\langle|u_{\mathbf{q}}^2|\rangle[1-\cos(q_y y)],$$

$$\langle|u_{\mathbf{q}}^2|\rangle=\frac{k_BT}{(\lambda+2\mu-P)q^2}\hat{q}_y{}^2+\frac{k_BT}{(\mu-P)q^2}(1-\hat{q}_y{}^2). \quad (1)$$

Here, n_x and n_y are integers, $\hat{q}_y=q_y/q$, and the Lamé coefficients λ and μ are those of a bulk soft disk solid at the same density, while P is the overall (nonzero) hydrostatic pressure [40,41]. The result of this calculation is shown in Figs. 3(a) and 3(b). We observe a crossover from the logarithmic increase of mean-square displacements $B(y)\propto\ln y$ with distance y (characteristic for 2D solids) to a linear increase (1D systems [32]) at a distance of order $D\ln(D/a)$ [37] which is cut off by the periodic boundary conditions for small systems. The direct evaluation of $B(y)$ for the soft disk system with periodic boundary conditions is also shown in Fig. 3(a) and agrees well with the harmonic calculation within the error bars of the former. The corresponding calculation with planar walls shows an enhancement of the displacement fluctuations parallel to the walls for the lattice layer closest to the wall Fig. 3(b). This behavior is quite similar to that seen in the XY model [19] with free boundary conditions. Fluctuations of the displacement perpendicular to the walls are, of course, suppressed.

In summary, we have demonstrated that confinement of 2D colloidal crystals by external boundaries has subtle effects on their structure. The least disturbance is caused by "structured boundaries" (rows frozen in the perfect crystalline order). For planar boundaries, however, the positional LRO is destroyed, even for very thick strips. This phenomenon is *not* a standard surface-induced melting, however, since a very strongly layered structure (reminiscent of a smectic) is maintained. Just as the 2D XY model below T_c is in a critical state (power-law decay of correlations implies infinite correlation length), the 2D crystal is in a similar critical state too, and therefore sensitive to boundary conditions

over very large distances. We believe that these effects should be easily observable in experiments involving confined colloids.

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