Novel Colloidal Crystalline States on Two-Dimensional Periodic Substrates

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(Received 15 January 2002; published 31 May 2002)

We show, using numerical simulations, that a rich variety of novel colloidal crystalline states are realized on square and triangular two-dimensional periodic substrates which can be experimentally created using crossed-laser arrays. When there are more colloids than potential substrate minima, multiple colloids are trapped at each substrate minima and act as a single particle with a rotational degree of freedom, giving rise to a new type of orientational order. We call these states colloidal molecular crystals. A two-step melting can also occur in which individual colloidal molecules initially rotate, destroying the overall orientational order, followed by the onset of interwell colloidal hopping.

DOI: 10.1103/PhysRevLett.88.248301 PACS numbers: 82.70.Dd, 73.50.–h

Colloidal particles are an ideal system for studying 2D ordering and melting as the individual particle positions and dynamics can be directly visualized. Colloidal melting has been extensively studied for systems with smooth substrates, where evidence for defect-mediated melting transitions has been found [1–3]. Colloidal crystallization and melting in the presence of a 1D periodic substrate, typically created with laser arrays [4–9], have also been examined. These studies have revealed a novel laser-induced freezing, as well as a reentrant laser-induced melting as a function of substrate strength [5,7]. A far less studied case is colloidal crystallization on 2D periodic substrates, where commensuration effects can occur when the periodicity of the colloidal and substrate lattices match. In several recent experimental studies, a 2D substrate for colloids was created using optical tweezer arrays [10], templating [8,11], and 2D crossed-laser arrays [12]. Almost nothing is known, however, about what type of colloidal crystalline states and melting can occur in this system. Although colloids interacting with 1D substrates have been investigated theoretically [6,7] and numerically [6], the case of a 2D substrate has not. The study of colloidal crystals with 2D substrates can also lend insight into other condensed matter systems which can be described as elastic particles on 2D substrates, including atoms on atomic surfaces [13] and vortices in superconductors with periodic pinning arrays [14]. It should be possible to realize entirely new states in the 2D colloidal system, since, when there are more colloids than substrate minima, each minima will contain multiple colloids which can have their own internal degrees of freedom. This is very different from the colloidal states seen for periodic 1D arrays. Colloidal crystallization on 2D substrates may also be of practical relevance since methods of quickly making different types of colloidal crystals can be of importance for the construction of certain devices, such as photonic band-gap materials.

In this Letter we examine colloidal ordering and melting on 2D periodic square and triangular substrates using Langevin simulations. We find that a rich variety of novel colloidal crystalline states can be achieved. We focus on the case of filling fractions at which there are an integer number of colloids per substrate minima. When there are more colloids than potential substrate minima, multiple colloids are trapped at each minima. The colloids within each of these minima can act as a single particle with internal degrees of rotational freedom, forming trimer and dimer states that have an additional long-range orientational order with respect to neighboring minima. These states are similar to molecular crystals; hence, we term them colloidal molecular crystals (CMC's). These crystalline states also exhibit a novel multistage melting where, for low T, the colloidal molecules possess both orientational and translational order. At higher T, the orientational order is lost as the colloidal molecules in each minima begin to rotate, but individual colloidal diffusion does not occur and the colloids are still confined in each substrate minima. For large enough temperature, individual colloidal diffusion occurs. We map out the phase diagram for temperature vs substrate strength and find that two-stage melting occurs only for sufficiently strong substrates, and that the transition temperature from the solid to the disordered solid in the presence of a substrate is lower than the same transition temperature for a sample without a substrate. In addition, for fixed temperature and increasing substrate strength, we observe a transition from the ordered solid phase to a partially ordered solid phase, similar to the reentrant melting seen for colloids interacting with 1D periodic substrates.

We simulate a 2D system of N_c colloids with periodic boundary conditions in the x and y directions, using Langevin dynamics as employed in previous colloidal simulations [15]. The overdamped equation of motion for a colloid i is

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{f}_i + \mathbf{f}_s + \mathbf{f}_T . \qquad (1)$$

Here $\mathbf{f}_i = -\sum_{i \neq j}^{N_c} \nabla_i V(r_{ij})$ is the interaction force from the other colloids. The colloid-colloid interaction is a Yukawa or screened Coulomb potential, $V(r_{ij}) = (Q^2/|\mathbf{r}_i - \mathbf{r}_j|) \exp(-\kappa|\mathbf{r}_i - \mathbf{r}_j|)$, where $Q = 1$ is the charge of the particles, $1/\kappa$ is the screening length, and $\mathbf{r}_{i(j)}$ is the position of particle i (j) . The system length is measured in units of the lattice constant a_0 and we take the screening length $1/\kappa = a_0/2$. For the force from the 2D substrate, $\mathbf{f}_S$, we consider both square and triangular substrates with strength A (and relative strength A/Q), period a_0, and N_m minima. For square substrates, $\mathbf{f}_s = A\sin(2\pi x/a_0)\hat{\mathbf{x}} + A\sin(2\pi y/a_0)\hat{\mathbf{y}}$, and for triangular substrates, $\mathbf{f}_s = \sum_{i=1}^{3} A\sin(2\pi p_i/a_0)[\cos(\theta_i)\hat{\mathbf{x}} - \sin(\theta_i)\hat{\mathbf{y}}]$, where $p_i = x\cos(\theta_i) - y\sin(\theta_i) + a_0/2$, $\theta_1 = \pi/6$, $\theta_2 = \pi/2$, and $\theta_3 = 5\pi/6$. The thermal force $\mathbf{f}_T$ is a randomly fluctuating force from random kicks. We start the system at a temperature where all the colloids are diffusing rapidly and gradually cool to $T = 0.0$. We define the melting temperature at zero substrate strength as T_m^0. We do not take into account hydrodynamic effects or possible long-range attractions between colloids. We have conducted a wide variety of simulations for different system sizes, a_0 values, and screening lengths $1/\kappa$, and find that all qualitative features are robust.

In Fig. 1 we show the colloidal positions for a system with a square substrate. In Fig. 1(a) the colloidal periodicity matches the substrate periodicity, $N_c = N_m$, so that each colloid is located at the center of the potential minima and a square colloidal crystal forms. In Fig. 1(b), for twice as many colloids $N_c = 2N_m$, each minima now captures two colloids. Neither colloid is located at the exact minima; instead, they are offset from it due to the colloid-colloid repulsion. The states inside the minima can be regarded as a colloidal dimer with a rotational degree of freedom. Figure 1(b) also shows that there are *two types of ordering* occurring: one arising from the square substrate, and the other due to the specific rotational orientation of the colloidal dimers, with neighboring dimers perpendicular to one another. The orientational ordering of the dimers is due to the colloidal repulsion, and allows the distance between the colloids to be maximized under the constraint of the square substrate. If the colloid interaction range is short, such that one dimer pair does not interact with the neighboring pair, the orientational dimer ordering seen in Fig. 1(b) does not occur. In Fig. 1(c), the configuration for $N_c = 3N_m$ again shows two types of ordering, with each minima capturing three colloids that form a trimer state. The trimers have a specific orientational order in which trimers in adjacent columns of minima are rotated by 60°, due to the repulsion of neighboring trimers. In Fig. 1(d), $N_c = 4N_m$ also has an ordered superlattice structure with orientational ordering. The colloidal quadrimer states are all aligned in the same direction. For increasing colloid densities $N_c = nN_m$, one can expect even more orderings with each potential minima capturing n colloids. Since the colloids in each minima act as a single object with an internal degree of freedom, similar to a molecular dimer or trimer, and since these states are confined in a lattice, we call these states colloidal molecular crystals.

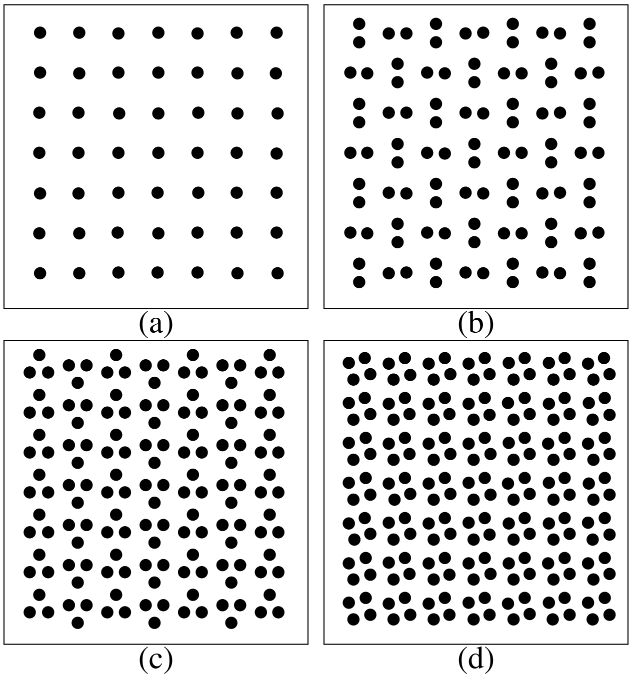
(a) (b) (c) (d)

FIG. 1. The colloid configurations (black dots) at $T = 0.0$ for a square 2D periodic substrate with $A = 2.5$, for different densities of colloids. (a) $N_c = N_m$. The colloids form a square commensurate lattice. (b) $N_c = 2N_m$ forms a colloidal dimer state, with each dimer perpendicular to neighboring dimers. (c) $N_c = 3N_m$ forms a trimer state with orientational ordering. (d) $N_c = 4N_m$ produces an aligned quadrimer state.

In Fig. 2 we illustrate the CMC's on a triangular substrate. For one colloid per minima, $N_c = N_m$, shown in Fig. 2(a), the colloids form a commensurate triangular lattice with each colloid located at the center of the potential minima. For $N_c = 2N_m$, a dimer state occurs in each minima, as seen in Fig. 2(b). As in the square pinning case, an additional orientational ordering of the dimers occurs. The dimers in each row have the same orientation, which is rotated 45° with respect to the adjacent rows. For $N_c = 3N_m$, illustrated in Fig. 2(c), a trimer state forms and an orientational ordering occurs in which, unlike the square case [Fig. 1(c)], all the trimers have the *same* orientation. In Fig. 2(d) a superlattice state also occurs with the colloid molecules forming a diamond substructure with a triangular superstructure.

We find that it is also possible to create partially ordered and disordered states at fractional filling, such as $N_c = 1.5N_m$. In this case, for the square substrates every other minima forms a colloidal dimer state; however, the dimers do not have long-range orientational order. Similarly, for the triangular substrates it is not possible to arrange a state such that minima with only one colloid will be between every other dimer, so again dimer ordering is not observed at fractional filling.

In Fig. 3 we show a representative example of the two-stage melting of the CMC, in the dimer state for the square substrate [Fig. 1(b)]. As illustrated in Fig. 3(a) at low temperatures $T/T_m^0 < 0.25$ (where T_m^0 is the melting temperature at zero substrate strength), both orientational and translational order are present and the system is

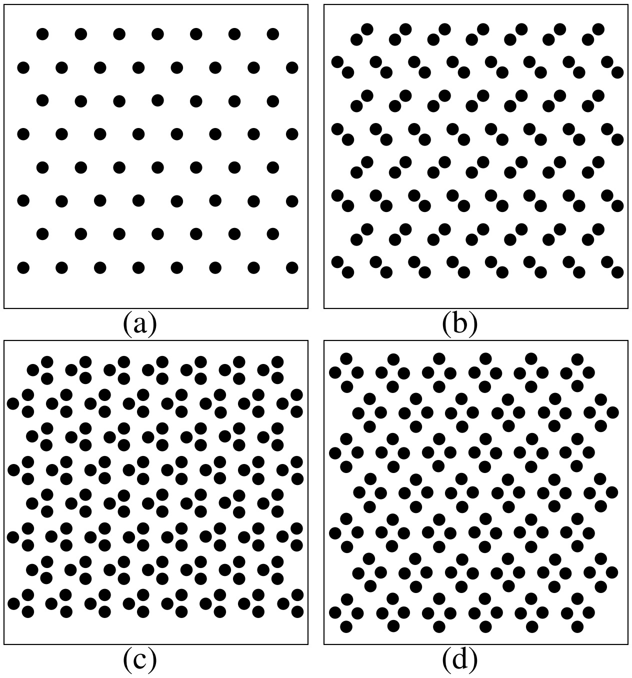
(a) (b) (c) (d)

FIG. 2. The colloid configurations (black dots) at $T = 0.0$ for a triangular 2D periodic substrate with $A = 2.5$, for different densities of colloids. (a) $N_c = N_m$ forms a commensurate triangular lattice. (b) $N_c = 2N_m$ forms an orientationally ordered dimer state, with the same dimer orientation in every other row. (c) $N_c = 3N_m$ forms an orientationally ordered trimer state. (d) $N_c = 4N_m$ forms a pattern of aligned diamonds.

frozen. We label this phase "ordered solid." In Fig. 3(b), at $T/T_m^0 = 1.5$, the dimers begin to rotate within the minima; however, diffusion of individual colloids throughout the sample does not occur so the system is still frozen with the dimer orientational order lost. We label this phase "partially ordered solid." In Fig. 3(b), the dimers generally switch from the north-south to east-west positions. This is likely due to some remaining short-range orientational order seen in Fig. 3(a). For a higher temperature $T/T_m^0 = 4.0$ [Fig. 3(c)], the system enters a modulated liquid phase. Here the colloids began to diffuse throughout the system. We have observed this same type of multistage melting for the other CMC's in Figs. 1 and 2.

We briefly comment that, if the time spent annealing from high temperature is not sufficiently long, then, rather than reaching the configuration in Fig. 3, fairly robust metastable states containing trimers and monomers can appear at low temperatures, since there is still a potential energy barrier to overcome. For increasing substrate strengths, the annealing time must be increased to avoid these effects. This implies that, in experiments, the substrate strength should be increased slowly.

In Fig. 4 we show the phase diagram of the temperature T/T_m^0 vs substrate strength A for a square substrate and $N_c = 2N_m$. The melting line T_m is determined from the onset of diffusion, and the solid to disordered solid transition line is determined from the correlation between the dimers as well as the onset of dimer rotation, measured using the average particle displacements. For $A = 0$, the colloids form a triangular lattice which melts at the clean melting temperature T_m^0. For increasing A, T_m monotonically increases. The ordered solid melts directly to the liquid for $A < 2.0$. For $A > 2.0$ an intermediate rotational melting transition between the ordered solid and partially ordered solid occurs. The rotational melting temperature is always less than T_m^0, since both these melting temperatures are determined by the elastic properties of the colloids, which is maximum for a triangular lattice in the zero substrate limit. The ordered solid is not triangular and hence should have less elasticity. In addition, for increasing A the transition line from the ordered solid to partially ordered solid decreases in temperature. This occurs since, as A is increased, the dimer length decreases, the dimers become effectively farther apart, and the dimer-dimer interaction strength goes down. This implies that at fixed temperature it is possible to observe a transition from the ordered to partially ordered solid by increasing the strength of the substrate. This is similar to the reentrant melting observed for increasing substrate strength for colloids in 1D periodic substrates [5,7]. We find qualitatively similar phase diagrams for square and triangular substrates for both the dimer and the trimer states. For the trimers the onset of

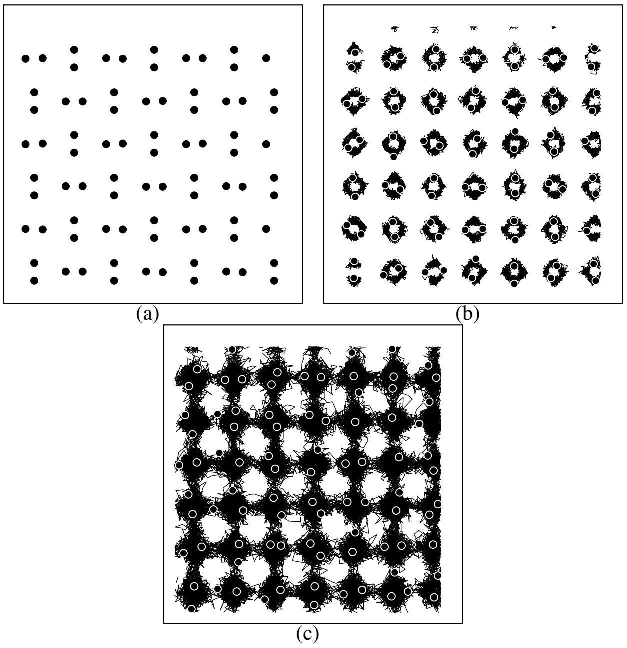
(a) (b) (c)

FIG. 3. The colloid positions (black dots) and trajectories (lines) over fixed time intervals at different temperatures for the dimer state on a square substrate shown in Fig. 1(b). (a) The ordered solid phase at $T/T_m^0 = 0.25$, where T_m^0 is the melting temperature at zero substrate strength. (b) $T/T_m^0 = 1.5$. Orientational order is destroyed as the dimers rotate within the substrate minima, but the colloids remain trapped inside each minima so the system is still in a solid phase. (c) $T/T_m^0 = 4.0$. Individual colloidal diffusion occurs throughout the sample and the system is in the liquid phase.

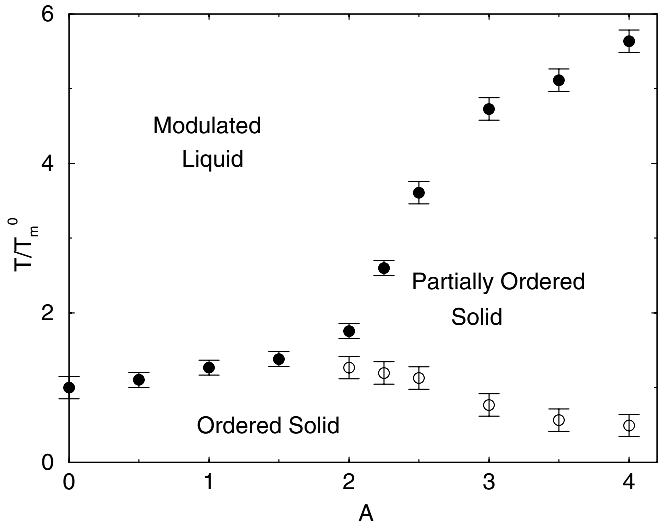

FIG. 4. Phase diagram of temperature T/T_m^0 vs substrate strength, for the square substrate with two colloids per potential minima. T_m^0 is the melting temperature for a sample with no substrate. Black circles: the melting line as determined from the onset of diffusion. Open circles: the transition to the partially ordered or rotating dimer phase as determined from the orientational correlation of the dimers.

rotational melting occurs at weaker substrate strengths than for the dimers, due to the decreased anisotropy of the trimer state compared to the dimers. In addition for stronger screening the transition from the ordered solid to the partially ordered solid occurs for both lower temperature and substrate strength. An interesting issue is the nature of the melting transitions, which is beyond the scope of this paper.

To summarize, we have demonstrated that a rich variety of novel colloidal crystalline states can be achieved with square and triangular two-dimensional substrates. We find that when there are more colloids than substrate potential minima, certain colloidal molecular crystals appear in which each minima captures an equal number of colloids. The colloids in these traps can act as a single particle with a rotational degree of freedom, such as a dimer or trimer. We also show that CMC states exhibit a multistage melting for sufficiently strong substrates, where the orientational order of the colloidal molecule states is lost first, followed by the translational order. We map out the phase diagram and show that the solid-to-disordered-solid transition occurs for temperatures lower than the clean melting temperature. It is also possible to have a transition at fixed temperature for increasing substrate strength from an ordered solid to a partially ordered solid, similar to the reentrant melting observed for colloids on 1D periodic substrates. Since the colloids within a minima can act as a single particle with a rotational degree of freedom, our results also suggest that certain canonical statistical mechanics models, such as Ising, *XY*, Potts, and frustrated models, may be realized with colloids on two-dimensional periodic substrates. The states predicted here should be observable for colloids interacting with crossed-laser arrays or optical tweezer arrays, dusty plasmas in 2D with periodic potentials, and vortices in superconductors with periodic substrates.

We thank C. Bechinger, D. G. Grier, P. Korda, S. Ling, A. Persinidis, and G. Spalding for useful discussions. This work was supported by the U.S. Department of Energy under Contract No. W-7405-ENG-36.

Note added.—Recently we learned that experiments have been performed on the system studied here, in which an orientationally ordered trimer, orientationally disordered, and liquid states are observed, along with multistage melting as a function of substrate strength at constant temperature [16].

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