Frustration and melting of colloidal molecular crystals

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Abstract
Using numerical simulations we show that a variety of novel colloidal crystalline states and multi-step melting phenomena occur on square and triangular two-dimensional periodic substrates. At half-integer fillings different kinds of frustration effects can be realized. A two-step melting transition can occur in which individual colloidal molecules initially rotate, destroying the overall orientational order, followed by the onset of interwell colloidal hopping, in good agreement with recent experiments.

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Colloidal particles are an ideal system for studying 2D ordering and melting for different kinds of substrates as the individual particle positions and dynamics can be directly visualized. Crystallization and melting on 2D periodic substrates is also relevant to vortices in superconductors with periodic pinning arrays [1–3] and the ordering of molecular monolayers on atomic substrates [4–8]. Colloidal crystallization on 2D periodic substrates has been the subject of considerable recent interest. In several recent experimental studies, 2D substrates for colloids have been created. Optical tweezers attract colloidal particles due to the refraction of the light by the colloid. Arrays of optical tweezers [9] and 2D crossed laser arrays [12] have thus been used to generate ordered substrates. Additionally, substrates with arbitrary ordering have been created by templating a pattern into the confining wall [10, 11]. Colloidal ordering and melting on 2D periodic square and triangular substrates have been studied through simulation [13] and experiment [14]. It was shown that a rich variety of novel colloidal crystalline states, referred to as colloidal molecular crystals (CMCs), form at integer filling of the periodic substrates.

In [13], integer matching states up through a filling of four colloids per minima were illustrated for both square and triangular arrays, and the two-stage melting behaviour of the dimer state at a filling of two colloids per minima was demonstrated for the square substrate. Here, we present the structures observed at half-integer filling for the square and triangular substrates, showing that the perfect regularity of the integer filling state is destroyed away from integer filling. We also demonstrate a two-stage melting transition for the trimer state at a filling of three colloids per minima for the square substrate.
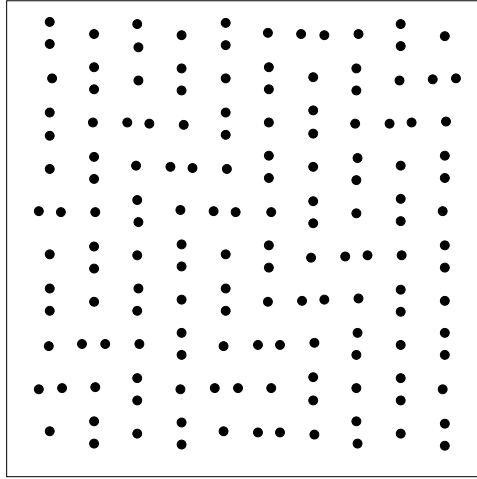
Figure 1. The colloid configurations (black dots) at $T = 0.0$ for a square 2D periodic substrate with $A = 2.5$, for a half-integer colloidal density, $N_c = 1.5N_m$. Every other minima captures a single colloid, while the remaining minima capture two colloids in a dimer state. There is no long-range rotational order of the dimers.

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

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

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, we consider both square and triangular substrates with strength A, period a_0 and N_m minima. For square substrates, $\mathbf{f}_s = A \sin(2\pi x/a_0)\hat{x} + A \sin(2\pi y/a_0)\hat{y}$, and for triangular substrates, $\mathbf{f}_s = \sum_{i=1}^{3} A \sin(2\pi p_i/a_0)[\cos(\theta_i)\hat{x} - \sin(\theta_i)\hat{y}]$, 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 do not take into account hydrodynamic effects or possible long-range attractions between colloids.

The colloidal positions for a system with a square substrate at integer matching between the colloidal periodicity and the substrate periodicity, $N_c = nN_m$, are illustrated in figure 1 of [13] for $n = 1$ to 4. In particular, at $N_c = N_m$, each colloid is located at the centre of the potential minima and a square colloidal crystal forms, while at $N_c = 2N_m$, each minima captures two colloids which can be regarded as a colloidal dimer with a rotational degree of freedom. Over a range of substrate strengths, the colloidal dimers form a rotationally ordered state, with neighbouring 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. In figure 1, we show the colloidal positions for the square substrate system at a half-integer filling, $N_c = 1.5N_m$. Here we find a combination of the single colloids and dimer colloids. The single colloids are located at every
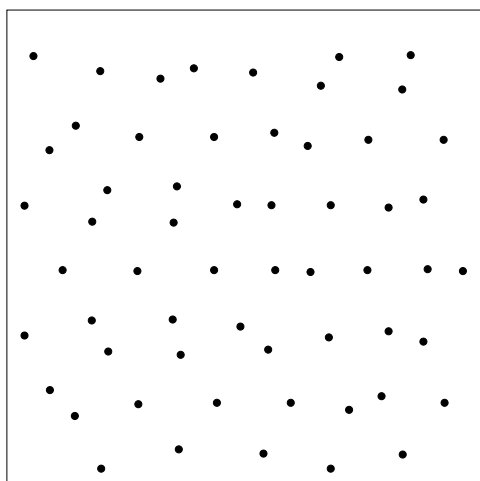
Figure 2. The colloid configurations (black dots) at $T = 0.0$ for a triangular 2D periodic substrate with $A = 2.5$, for a half-integer colloidal density, $N_c = 1.5N_m$. It is not possible to arrange a state such that minima with only one colloid will be between every other dimer. Therefore, there is no dimer ordering.

other site with intervening dimers, creating a checkerboard ordering. The strong orientational ordering of the dimers observed at $N_c = 2N_m$ is lost in this state. The dimers alternate their orientation between vertical and horizontal in a disordered fashion, forming a pattern of grain boundaries.

The ordered colloidal crystalline states that form on a triangular substrate at integer matching from $n = 1$ to 4 are illustrated in figure 2 of [13]. As in the case of the square substrate, at $N_c = N_m$ each minima captures a single colloid, while at $N_c = 2N_m$ each minima captures two colloids which form a dimer state. The dimers again have an additional orientational ordering in which the dimers in each row have the same orientation, which is rotated by 45° with respect to the adjacent rows. This herringbone ordering resembles patterns observed experimentally for N_2 monolayers adsorbed on graphite [16], or H_2 molecules on a triangular lattice [17]. In figure 2 we illustrate the colloidal positions for the triangular substrate at half-integer filling, $N_c = 1.5N_m$. Unlike the square substrate, where dimers could tile the lattice in an orderly way, filling every other minima, for the triangular substrate the positioning of the dimers is frustrated. It is not possible to arrange a state such that minima with only one colloid will be between every other dimer. As a result, the colloids form a very disordered state in which the dimers show a wide range of orientations, and not merely two as in the case of the square substrate at $N_c = 1.5N_m$, or the triangular substrate at $N_c = 2N_m$.

In figure 3 we show the two-stage melting of the CMC at $N_c = 3N_m$ on the square lattice. As illustrated in figure 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 orders of the trimers are present and the system is frozen. This is the 'ordered solid' phase. In figure 3(b), at $T/T_m^0 = 1.5$, the trimers begin to rotate within the minima; however, diffusion of individual colloids throughout the sample does not occur. The system is still frozen but the trimer orientational order is lost. This is the 'partially ordered solid' phase. In figure 3(c), for a higher temperature T/T_m^0, the system enters a modulated liquid phase. Here the colloids begin to diffuse throughout the system. We note that in the recent experiments of Brunner
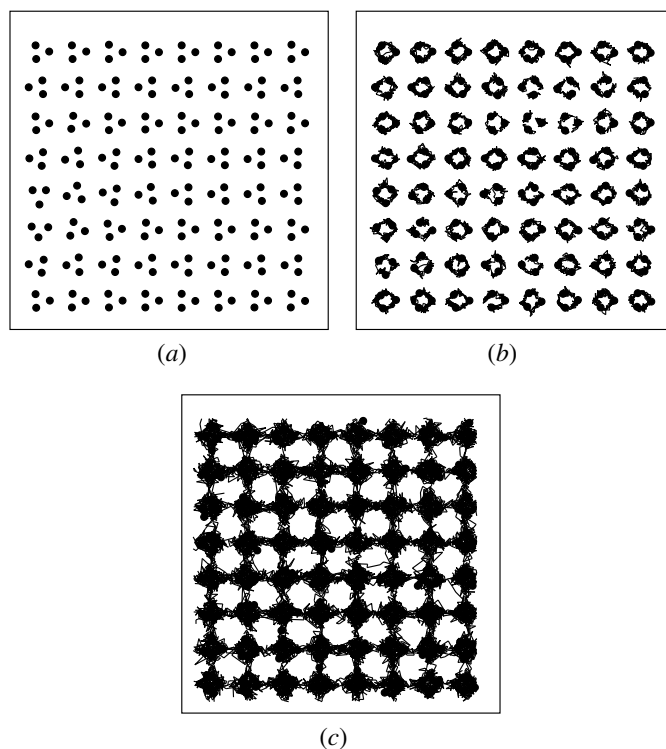
Figure 3. The colloid positions (black dots) and trajectories (lines) over fixed time intervals at different temperatures for the trimer state on a square substrate shown in figure 1(c) of [13]. (a) The ordered solid phase at $T/T_m^0 = 0.25$, where T_m^0 is the melting temperature at zero substrate strength. (b) $T/T_m^0 = 1.5$. Orientational order is destroyed as the trimers 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.

and Bechinger [14], the same melting phenomena was also found for trimers on a triangular substrate. Modulated liquids have also been observed in simulations of N_2 adsorbed on graphite [5].

To summarize, we have shown the rich variety of novel colloidal crystalline and disordered states that can be achieved with square and triangular two-dimensional substrates. The colloidal molecular crystal states that appear at integer filling of the substrate minima persist at half-integer filling, appearing as a mixture of the two neighbouring integer filling states. For the case of $N_c = 1.5N_m$, the single and dimer states coexist. An ordered filling of dimers can be arranged on the square substrate at $N_c = 1.5N_m$, but the dimer arrangement is frustrated on the triangular substrate and a strongly disordered state results. The triangular lattice at $N_c = 1.5N_m$ is thus a realization of a frustrated system which would provide an interesting topic for further study. For integer filling of $N_c = 3N_m$ on a square substrate, we demonstrate the multistage melting of the CMC, where the orientational order of the colloidal molecule states is lost first, followed by the translational order. 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, molecules adsorbed on substrates and vortices in superconductors with periodic substrates.

Acknowledgments

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