

Colloidal Molecular Crystals

Colloids are small particles in solution that exhibit a remarkable variety of equilibrium and nonequilibrium behaviors. At about a micron in size, colloids are large enough that the microscopic dynamics and particle positions can be directly accessed with experimental techniques such as video-microscopy. This makes colloidal assemblies ideal for study as model systems in which to understand collective phenomena that appear in other condensed matter systems where it is difficult to measure experimentally the dynamics on the individual particle level, such as atomic ordering on surfaces, vortex physics in superconductors, and relaxation in molecular glasses.

Repulsively interacting colloids in two dimensions form a triangular lattice for high enough colloidal density or low enough temperature. A considerable amount of work has been done for colloids interacting with smooth two-dimensional substrates, but recent efforts have focused on the fact that it is now possible to create some form of periodic substrate for the colloids. The physics of an elastic lattice of particles interacting with a periodic substrate is relevant for atoms and molecules adsorbed on surfaces, vortices in superconductors interacting with artificial nanostructured pinning arrays, as well as charge density waves. Further, the use of periodic substrates to stabilize a variety of new colloidal crystalline structures may prove highly valuable for creating new types of optical devices. For colloids interacting with periodic substrates, a number of possible structures can occur due to the competition between the periodicity of the colloidal lattice and the periodicity imposed by the substrate. The questions that arise include what types of ordered or disordered colloidal crystals form when the number of colloids is commensurate with the underlying substrate, how these commensurate and incommensurate colloidal crystals would melt, and what happens to the colloidal crystals as the substrate strength is reduced.

To investigate this problem we have performed a series of large scale Langevin simulations for colloids in two dimensions interacting via a screened Coulomb potential. We impose a square or triangular periodic substrate of variable strength [1, 2], corresponding to substrates produced with varying laser power in experiments. We first consider the commensurate cases where the number of colloids N_c is an integer multiple of the number of potential minima N_s . In Fig. 1 we illustrate the colloidal crystal configurations for $N_c/N_s = 1, 2, 3,$ and 4 for a square substrate. For $N_c/N_s = 2$, shown in Fig. 1(b), the colloids form a dimerized state with each substrate minimum capturing two colloids. The dimers have an additional orientational ordering in which every other dimer is perpendicular. For $N_c/N_s = 3$, shown in Fig. 1(c),

the colloids form trimer states with the trimers also having orientational order along every other column. For $N_c/N_s = 4$ the colloids form an orientationally ordered quadrimer state, as illustrated in Fig. 1(d).

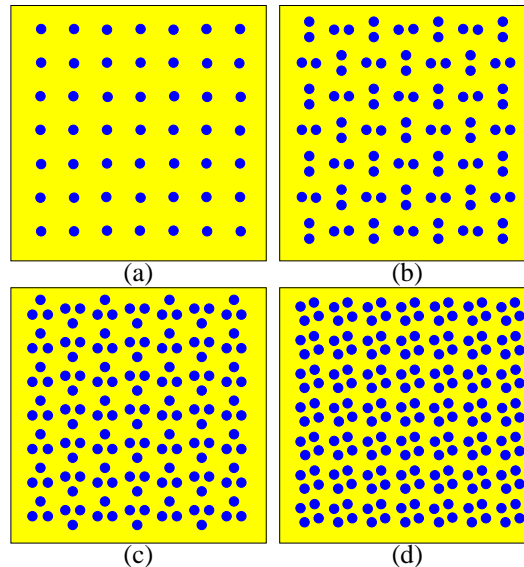


Figure 1: Colloids (blue dots) interacting with a square underlying substrate for ratios of colloids N_c to potential substrate minima N_s of $N_c/N_s =$ (a) 1, (b) 2, (c) 3, and (d) 4.

We name the ordered colloid states colloidal molecular crystals (CMCs) in analogy with molecular crystals where the molecules form a crystal in which the orientation of the molecules is also aligned. Similar CMCs appear for triangular substrates.

We next explore how colloidal molecular crystals melt. In general, the commensurate fillings have three melting phases. Phase I is the orientationally ordered CMC. In phase II, the n -mers lose their orientational ordering but remain confined in the traps. The n -mers dissolve in phase III and the colloids begin to diffuse throughout the entire sample. We illustrate the three phases in Fig. 2 by plotting the colloidal trajectories over a fixed period of time for the case of two colloids per minimum on a square substrate. All of the CMC states pass through these three phases when the substrate strength is sufficiently strong. When the substrate strength is lowered, there is a transition to a floating solid phase where portions of the colloidal lattice regain the triangular ordering that would occur in the absence of a substrate. Recent analytical work has proved that the transition between phases I and II can be mapped onto a square antiferromagnetic Ising model which exhibits a second order phase transition [3]. In this case the dimers act like spins which align perpendicular to one another. This opens the exciting possibility

that colloids interacting with periodic substrates can be used as model systems in which to experimentally realize several canonical statistical mechanics models such as Ising, Heisenberg, or clock models as well as spin glasses. We have also found that at certain incommensurate fillings such as $N_c/N_s = 1.5$ on a triangular lattice, the dimers are frustrated in a manner similar to an antiferromagnetic Ising model on a triangular lattice [2].

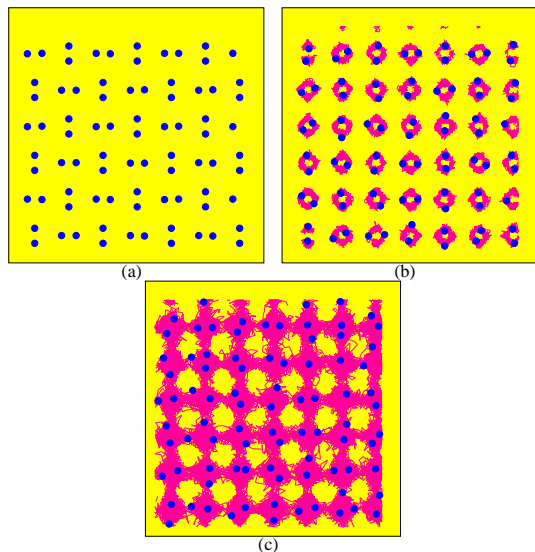


Figure 2: Colloid particles (blue dots) and trajectories (red lines) over a fixed period of time at different temperatures for a system with $N_c/N_s = 2$ on a square substrate. (a) At low temperatures an ordered colloidal molecular crystal is stable. (b) For higher temperature, the system enters phase II, a disordered colloidal molecular crystal. (c) At still higher temperatures, confinement by the wells is lost and the system enters phase III, a modulated liquid.

Our simulations show that the temperature T_c of the transition between phases I-II decreases with increasing substrate strength. This occurs since the effective interaction between any two dimers is dominated by the quadrupole moment. As the substrate strength increases, the quadrupole moment decreases because the distance between the two colloids comprising the dimer decreases with increasing substrate strength. Recent experiments have confirmed the existence of the colloidal molecular crystal structures, the multi-step melting, and the reentrant disordering as the substrate strength is increased [4].

When the colloidal lattice is incommensurate with the substrate, it is possible to create new types of ordering as well as disordered states. In Fig. 3(a) we show the system for a filling of $N_c/N_s = 1.5$ on a triangular substrate. Here the dimers are disordered. In contrast, at a filling of $N_c/N_s = 1.75$, illustrated in Fig. 3(b), an ordered state can be realized in which hedgehog type structures form with the dimers pointed at the monomers. At other fillings, further types of ordering can occur, including ordered and

disordered pinwheel states [5].

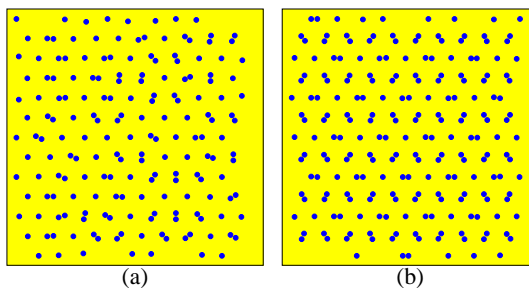


Figure 3: Colloidal particles (blue dots) interacting with a triangular substrate for $N_c/N_s =$ (a) 1.5 and (b) 1.75.

References

- [1] C. Reichhardt and C.J. Olson, *Novel Colloidal Crystalline States on Two-Dimensional Periodic Substrates*, Phys. Rev. Lett **88**, 248301 (2002).
- [2] C.J. Olson Reichhardt and C. Reichhardt, *Frustration and Melting of Colloidal Molecular Crystals*, J. Phys. A: Math. Gen. **36**, 5841 (2003).
- [3] R. Agra, F. van Wijland, and E. Trizac, *Theory of Orientational Ordering in Colloidal Molecular Crystals*, Phys. Rev. Lett. **93**, 018304 (2004).
- [4] M. Brunner and C. Bechinger, *Phase Behavior of Colloidal Molecular Crystals on Triangular Light Lattices*, Phys. Rev. Lett. **88**, 248302 (2002).
- [5] C. Reichhardt and C.J. Olson Reichhardt, *Ordering and Melting in Colloidal Crystal Mixtures*, cond-mat/0412104.

Contact Information: Charles Reichhardt – Center for Nonlinear Studies and Complex Systems Group, Theoretical Division, Los Alamos National Laboratory, T-CNLS MS B258, Los Alamos, NM, 87545, Phone: (505) 665-0059, email: charlesr@cnls.lanl.gov.