Elasticity drives effective attraction between equal charges in colloidal crystals

Electrostatic-elastic coupling in colloidal crystals
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Colloidal crystals share many common traits with atomic crystals, where colloids substitute for atoms. Due to the micron scale of colloids, their structure and dynamics can be directly studied using standard optical microscopy, making colloidal crystals a popular model system for exploring both electric and elastic properties of crystals. For example, simulations of ionic behavior in colloidal crystals reveal a localized-delocalized transition of ions within the crystal [1]. Additionally, recent experiments have demonstrated that colloidal crystals exhibit work hardening due to increased defect density that was measured directly [2].

Another fascinating finding comes from recent experimental and simulation work, where equally charged tracer particles moving within a two-dimensional colloidal crystal displayed short-range attraction, resembling the phonon-mediated attraction of Cooper pairs in a superconductor [3]. Beyond the evocative analogy, the key insight is how an electrostatic-elastic coupling renormalizes the interaction between equally charged particles in a colloidal crystal. This forms the motivation for the theoretical work by Wu, Ou-Yang, and Podgornik, which is recommended here.

The authors consider an isotropic colloidal crystal embedded in an electrolyte solution of monovalent ions. The goal of the paper is to calculate the equilibrium interaction energy between two equally charged test particles, placed in the interstitial spaces of the crystal. To do so, the authors formulate a continuum mean-field theory as a function of the ionic concentrations and solid displacement vector, $\boldsymbol{u}$. The ionic concentrations are treated within the Debye-Hückel framework (adequate for small electrostatic potentials) and the solids displacement - within linear elasticity (adequate for small deformations).

A subtle but important point is that the colloids themselves carry charge, although this is not explicitly accounted for in the theory. This can be understood as follows: the colloids are dispersed in water (without added salt), where they, along with their counterions, form a crystal that is electroneutral on length scales larger than the lattice spacing. An equal number of cations and anions are then introduced into the system. These are the only ions explicitly included in the theoretical framework. The colloidal crystal adopts an equilibrium state, and any deviation from

this state increases the free energy. These deviations, along with their associated free-energy penalties, are captured through the displacement vector and predefined elastic constants.

While the colloidal charge is not explicitly included in the theory, it plays a crucial role in coupling between electrostatics and elasticity. The crux of the paper is a minimal coupling term in the free energy density δf that couples the local charge density ρ to isotropic deformations $\delta f \sim \rho \nabla \cdot \boldsymbol{u}$. The idea, illustrated in figure 1a and 1b, is that a local charge density repels/attracts the colloids leading to an expansion/contraction. This is the first term in a series of couplings allowed by the symmetry, neglecting higher-order corrections (e.g., ionic corrections to the bare elastic moduli).
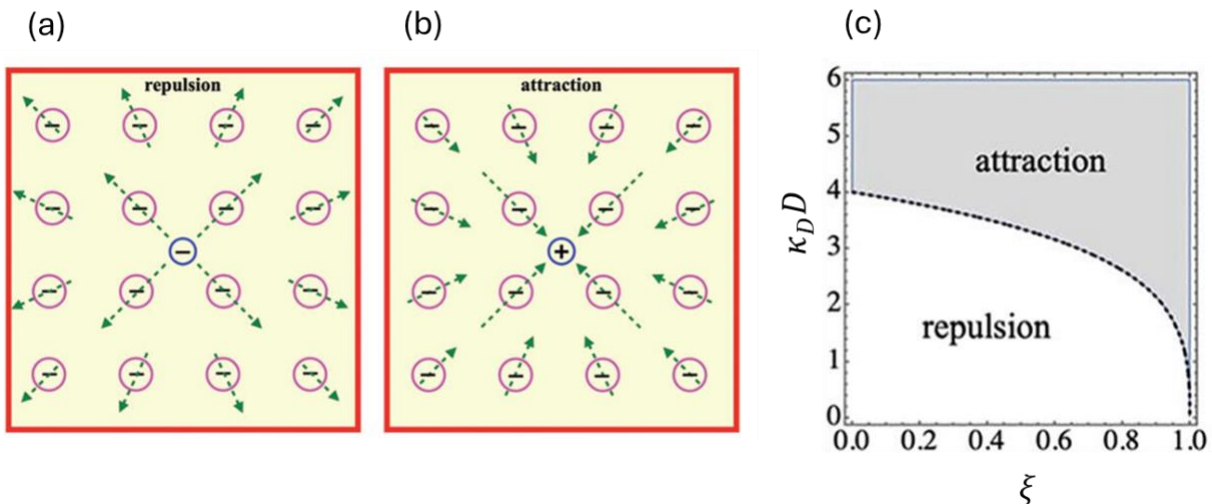
Figure 1 : **Electrostatic-elastic coupling in colloidal crystals**. A crystal of negatively charged colloids locally expands in the presence of a negative test charge (a) and contracts in the presence of a positive test charge (b). The resulting interaction energy between equally charged test particles is either attractive or repulsive (c), depending on the electrostatic-elastic coupling constant ξ and inter-particle separation normalized by the Debye screening length, $\kappa_D D$. Adapted from the recommended paper.

Building upon this coupling, quantified by a coupling constant $0 \leq \xi < 1$, the authors find the interaction energy between two test interstitial charges, separated by a distance D. The consequence of elasticity is two-fold: first, the effective charge is enhanced by a factor $1/(1 - \xi)$. Second, the screening length is shorter by a factor $\sqrt{1 - \xi}$. The interplay between these competing effects determines whether elasticity adds an effective repulsion (charge renormalization wins) or effective attraction (enhanced screening wins). The authors find that attraction prevails at sufficiently large couplings ξ, as illustrated in figure 1c. Stronger couplings are required at smaller separations. For $\kappa_D D > 4$ (where $1/\kappa_D$ is the Debye screening length) attraction prevails even for vanishingly small ξ.

This framework provides a clear criterion for determining the sign of lattice-mediated interactions and highlights how counterions neutralize both the electric and "elastic charge" of test particles, leading to an effective attraction. Note that the overall interaction between the charges vanishes at most and never becomes fully attractive. What makes this work particularly elegant, in my opinion, is how the complex, full electrostatic problem is significantly simplified through the framework of

elasticity. The resulting physical picture is both intuitive and compelling, owing to the analogous distance-dependence of electrostatic and elastic interactions.

It is important to note that the validity of this framework is nuanced. The paper includes a self-consistency check by ensuring that the resulting dimensionless potential remains smaller than unity. Beyond that, the framework of continuum elasticity imposes that the lattice spacing must be the smallest meaningful separation between particles. For measurable electrostatic effects, the Debye screening length must not be smaller than the lattice spacing, limiting the theory to low salt concentrations. Simultaneously, the ionic concentration cannot fall below the concentration of the colloids' original counterions; otherwise, the screening would primarily result from counterions [4], which are not explicitly accounted for in this framework. Together, these constraints limit the theory to sufficiently weakly charged colloids.

The electrostatic-elastic coupling can be further explored in several avenues. For example, the authors suggest exploring a similar continuum framework in the strong-coupling electrostatic regime, as opposed to the weak-coupling Debye-Hückel theory. This is the regime where equally charged surfaces may attract [5] even in the absence of elasticity, but rather via mutual interaction with highly charged counterions. Another compelling direction, in my view, involves examining the role of defects in the colloidal crystal. For example, a test charge close to a defect may induce shear deformation over a finite range, rather than merely causing contraction or expansion.

The supervising author of this paper was Prof. Rudolf (Rudi) Podgornik, who sadly and unexpectedly passed away last month at the age of 69. Rudi was a distinguished physicist, and he has made important contributions to the study of dispersion interactions, ionic fluids, DNA mesophases and physics of viruses. I had the privilege of working with Rudi during my PhD, while he was visiting my advisor, Prof. David Andelman. Rudi was a gentleman of science with captivating curiosity and enthusiasm. He will be deeply missed.

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