Theory of Orientational Ordering in Colloidal Molecular Crystals

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Freezing of charged colloids on square or triangular two-dimensional periodic substrates has recently been shown to realize a rich variety of orientational orders. We propose a theoretical framework to analyze the corresponding structures. A fundamental ingredient is that a nonspherical charged object in an electrolyte creates a screened electrostatic potential that is anisotropic at any distance. Our approach is in excellent agreement with the known experimental and numerical results, and explains in simple terms the reentrant orientational melting observed in these so-called colloidal molecular crystals. We also investigate the case of a rectangular periodic substrate and predict an unusual phase transition between orientationally ordered states, as the aspect ratio of the unit cell is changed.

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The theoretical scenario put forward by Kosterlitz, Thouless, Halperin, Nelson, and Young for 2D melting has fostered many experimental investigations [1]. Most of these studies focused on 2D ordering on homogeneous substrates. On the other hand, the situation of a corrugated substrate has received much less attention in spite of its experimental relevance, e.g., to describe an atomic adsorbate on a crystalline surface. Colloidal particles subjected to light lattices created by laser arrays, appear as an ideal system to investigate the latter problem, see Refs. [2–5]. These studies, mostly with 1D periodic substrates, have revealed a novel laser induced freezing and laser induced melting that seems now well understood [6]. It was only very recently that colloidal crystallization on 2D (triangular or square) periodic substrates has been investigated both experimentally [7] and numerically [8]. The compatible results reported there call for a theoretical description that remains hitherto open. A rich variety of novel colloidal states were reported. When there are more colloids (number N_c) than the N substrate minima, the N_c/N colloids trapped in each well may be considered as a single bound entity with only rotational degrees of freedom. These "colloidal molecules" (dimers for $N_c = 2N$, trimers for $N_c = 3N\ldots$) were found experimentally and numerically to display long range orientational order. The corresponding state has been coined "colloidal molecular crystal" in Ref. [8]. Quite an unusual two stage melting process may be observed for such systems. Decreasing the temperature T from an initial standard 2D liquid, individual diffusion is first inhibited. The particles localize in the substrate wells (traps) thereby forming the colloidal molecules. The orientational order in this partially ordered solid is short range. Upon further decreasing T, the colloidal molecules no longer rotate freely and acquire orientational order. Surprisingly, increasing the substrate strength V_0 at fixed T leads to reentrant melting: the colloidal molecular crystal is destabilized into the partially ordered solid, and orientational order is lost.

The aim of the present Letter is to provide a simple theoretical framework for the phase behavior of such a system, that is very different from that on homogeneous or 1D periodic substrate potentials. We adopt here the simplest viewpoint and consider a trapped molecule (n-mer) as a single rigid object with n-fold symmetry and one orientational degree of freedom within a common given plane. Additional degrees of freedom such as radial or angular fluctuations will be discarded. We shall consequently not investigate the liquid phase (at high T and low V_0 where the n-mers are dissolved) and concentrate on the orientational freezing transition. In connection with numerical and experimental outputs, three questions naturally arise: (a) Is it possible to predict the nontrivial ground state observed in the experiments and simulations? (b) What are the characteristics of the above phase transition, in particular, its order? (c) Can we explain the reentrant melting considering rotational degrees of freedom only? In addition, we provide predictions for further experimentally relevant situations.

Before addressing these questions, general considerations concerning screened electrostatic interactions between anisotropic charged molecules (the n-mers) are in order. Because their surface groups dissociate in solution, the colloids under scrutiny here are highly charged. They strongly repel each other and experience a screened Coulomb (Yukawa) potential [9] $\phi(r) \propto \exp(-\kappa r)/r$, where the r dependence only is relevant for the discussion, not the prefactor depending both on particle size and charge [8]. In this expression, r is the center to center distance and κ^{-1} the Debye screening length (smaller than the periodicity of the underlying 2D substrate). Once an n-mer is formed in a trap, how does it interact with a neighboring n-mer? Consider dimers for simplicity. One could naively think that in an electrolyte, the electrostatic potential created by such an object becomes isotropic at large distances, as is the case in vacuum or in a plain dielectric medium. This is, however, incorrect and summing the screened contributions from each particle forming dimers i and j, one obtains the leading order large distance expression (see Fig. 1 for the notations used)

$$\phi_{ij}(r, \theta_{ij}, \theta_{ji}) \propto \cosh[\kappa d \cos(\theta_{ij})] \cosh[\kappa d \cos(\theta_{ji})] \frac{e^{-\kappa r}}{r}. \tag{1}$$

The key point here is that the radial and angular dependence of the interaction potential are factorized. The anisotropy of a dimer is therefore felt at all distances even for $\kappa r \gg 1$, provided the Debye length is small enough to resolve the dimer structure (when $d \ll 1/\kappa$, the isotropic screened Coulomb potential is recovered). It is noteworthy to mention in passing that considering dipoles (two point charges $+q/-q$ at a distance $2d$) instead of a dimer $+q/+q$, the same potential would hold provided the cosh function in Eq. (1) is replaced by a sinh. The angular dependence of such an expression differs much from that of the unscreened dipolar interaction. In addition, the distance dependences of both dimer and dipole potentials are identical $[\exp(-\kappa r)/r$ in the far field region]. The same holds for higher order multipoles, that all contribute to the same order in distance. As a consequence, when considering the interactions between arbitrary charged objects in a electrolyte, a usual truncated multipolarlike expansion [10] is doomed to fail [11]; in the case of dimers, resumming all multipole orders would lead to Eq. (1), to leading order in r. These considerations, that seem to have been overlooked in soft matter literature, appear to account in simple terms for orientational freezing in colloidal molecular crystals.

In Ref. [8], Reichhardt and Olson showed numerically that dimers on a square 2D periodic substrate (hereafter referred to as the underlying lattice of traps) adopt the ground state represented in Fig. 2(a). Such an ordering should follow from minimizing the total electrostatic energy $\mathcal{E}$ where each pair of dimers interact through the potential (1). Given the exponential screening with distance and that κ^{-1} is smaller than lattice spacing, we further restrict to nearest neighbors of dimers and write the relevant angular dependent part of the energy as

$$\mathcal{E} = \sum_{\langle i,j \rangle} \cosh[\kappa d \cos(\theta_{ij})] \cosh[\kappa d \cos(\theta_{ji})], \tag{2}$$

where the angular brackets denote nearest neighbors. A given pair minimizes its repulsion by setting $\theta_{ij} = \theta_{ji} = \pi/2$ (parallel dimers, perpendicular to the center-to-center vector, see Fig. 1). Such a pair configuration is however not space filling, so that no trivial ground state may be identified at this stage. By analogy with spin systems, we may invoke frustration. To proceed further, it is instructive to approximate the cosh function in (2) by a parabola. Introducing next a new set of variables where $\theta_i \in [-\pi/2, \pi/2]$ is defined as the angle between dimer axis and one of the principal lattice directions [12] we get

$$\mathcal{E} = \text{cst} + (\kappa d)^4 \sum_{\langle i,j \rangle} (\cos\theta_i)^2 (\cos\theta_j)^2. \tag{3}$$

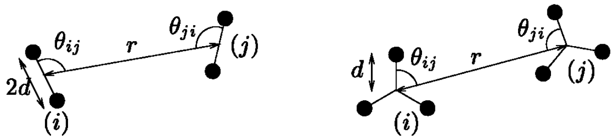

FIG. 1. Definition of the notations adopted to compute dimer (left) and trimer (right) interactions. The black dots show the colloids, and the line between them is a guide to the eye.

Remarkably, this expression takes the form of an antiferromagnetic Ising-like Hamiltonian, once the variables $\sigma_i = \cos 2\theta_i$ have been introduced $(-1 \leq \sigma_i \leq 1)$:

$$\mathcal{E} = \text{cst} + (\kappa d)^4 \sum_{\langle i,j \rangle} \sigma_i \sigma_j. \tag{4}$$

With the "spin" variables, frustration vanishes and the ground state simply consists of $\sigma_i = \pm 1$, with opposite signs on neighboring sites. This corresponds to $\theta_i = 0$ or $\pi/2$, which is in perfect agreement with the results of the numerical simulations of Ref. [8] (see Fig. 2). We have checked that keeping the original expression (2) without the parabolic approximation for the cosh leads to the same results.

Having answered question (a) above in the case of dimers on the square lattice, we now address questions (b) and (c), in particular, the reentrant melting phenomenon. At high temperature, the system has to be

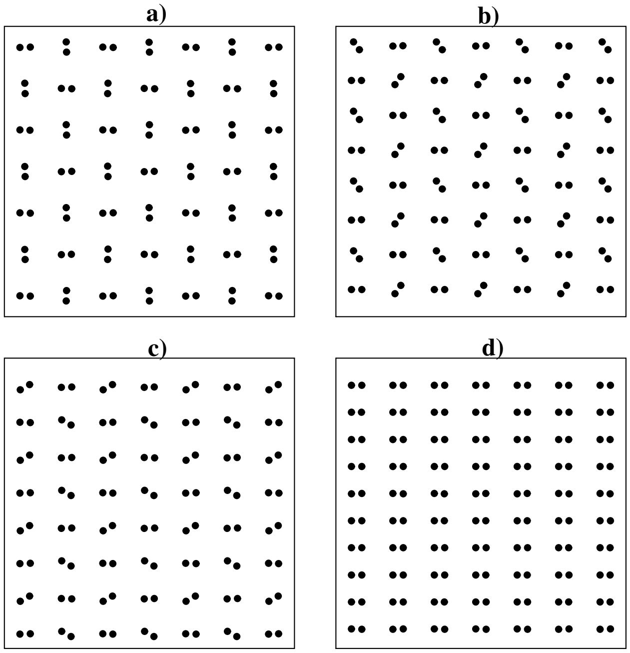

FIG. 2. Configuration of colloids (black dots) at $T = 0$ on a rectangular lattice of traps, when $N_c = 2N$ and $\kappa d = 1.5$. (a) Situation on the square lattice (aspect ratio $\alpha = 1$); (b) rectangular lattice with $\alpha = 0.90$; (c) $\alpha = 0.85$; (d) $\alpha = 0.7$, i.e., smaller than the threshold α^* reported in Fig. 3. Plots (b) and (c) correspond to the transition region $\alpha^* < \alpha < \alpha^{**}$ between FM and AF phases.

in a disordered state, a paramagnetic phase in spin language, and on purely dimensional grounds, Eq. (4) indicates that the critical temperature of the antiferromagnetic/paramagnetic transition scales like $T_c \propto (\kappa d)^4$. At fixed temperature T, increasing the substrate pinning strength V_0, the n-mers constituting a colloidal molecule become of smaller spatial extent: d decreases, so that T_c eventually becomes smaller than T. Orientational order is correspondingly lost. More specifically, we find $T_c \propto V_0^{-4/3}$. As emphasized above, we discard the possible loss of positional order, that occurs at large T. The corresponding fusion temperature T_f has to increase with V_0. For large enough V_0, the transition between the ordered and partially ordered solids is therefore always present, since $T_c < T_f$. At low V_0, this transition is preempted by the positional melting ($T_f < T_c$).

The above arguments may be rationalized by computing the partition function associated to the Hamiltonian (2) [13]. A mean-field analysis, simplified by the introduction of two sublattices to describe the order displayed in Fig. 1, leads to the conclusion that orientational freezing is a second order phase transition [14].

The same procedure may be extended to other substrate geometries, or more complex colloidal molecules. For n-mers, the counterpart of Eq. (1) reads

$$\phi_{ij}(r, \theta_{ij}, \theta_{ji}) = f(\theta_{ij}, \kappa d) f(\theta_{ji}, \kappa d) \frac{e^{-\kappa r}}{r}, \qquad (5)$$

where

$$f(\theta, \kappa d) = \sum_{k=0}^{n-1} \exp\left[\kappa d \cos\left(\theta + \frac{2k\pi}{n}\right)\right], \qquad (6)$$

which reduces to Eq. (1) in the case of dimers ($n = 2$). The variable θ_{ij} is defined as the angle between one arm of the symmetric n-fold colloidal molecule i and the center-to-center direction (ij), see Fig. 1 for the cases $n = 2$ and $n = 3$. For the situation of a triangular substrate with trimers as colloidal molecules (the experimental situation investigated in [7], we may follow similar steps as above, i.e., minimize $\sum f(\theta_{ij}) f(\theta_{ji})$ where the summation is restricted to nearest neighbors. This leads to the ground state where all trimers point in the same direction, with an angle $\theta = \pi/3$ between one arm of the trimers and one of the principal lattice direction [or equivalently, $\theta_{ij} = \pi/3 \pm \pi/3$ depending on the pair $(i$-$j)$]. This is exactly the order observed experimentally [7], and in numerical simulations [8]. For dimers on a triangular substrate (not studied experimentally), we also obtain the same orientational order as in Ref. [8] (herringbone structure with $\theta = \pm\pi/4$, or equivalently $\theta_{ij} = \pi/4 \pm \pi/3$).

Our framework allows us to investigate the situation of noninteger filling. We will focus on the half integer case $N_c/N = 3/2$, as considered numerically in [15]. To minimize electrostatic repulsion on the square lattice, the colloids create a checkerboard order with two sublattices such that the nearest neighbors of monomer are exclusively dimers, and vice versa [15]. In this configuration, nearest neighbors interaction do not depend on the angular coordinates, so that the electrostatic energy to consider should include second nearest neighbor terms. We find that the corresponding ground state is degenerate, with dimer orientations $\theta_i = 0$ or $\theta_i = \pi/2$. Since there are N_c dimers, this ground state is 2^{N_c} degenerate, and no long range order can be observed. This finding supports the numerical results reported in [15]. Changing the geometry of the underlying substrate from square to triangular does not allow one to tile the lattice such that minima with only one colloid will be in between every other dimer [15]. The partitioning of the $3N_c$ colloids in the $2N$ traps is therefore a frustrated problem with no ordering, be it positional or orientational.

We now consider a final geometry of experimental relevance, namely, dimers on a rectangular lattice (with unit cell of lengths αl and l; by definition, $\alpha < 1$, and the direction along the long axis is called "horizontal" for convenience). When the aspect ratio α is one the checkerboard order is that of Fig. 2(a) (antiferromagnetic-like phase, denoted AF). On the other hand, when $\alpha \ll 1$, there are only two nearest neighbors per particle, and from expression (1) the preferred configuration is $\theta_{ij} = \theta_{ji} = \pi/2$: all dimers are parallel to the horizontal direction. This ferromagnetic-like phase is denoted FM. We have studied the transition between the FM and AF phases, minimizing the relevant energy

$$\mathcal{E}_{\text{rect}} = \sum_{\langle i,j \rangle} \beta_{ij} \cosh[\kappa d \cos(\theta_{ij})] \cosh[\kappa d \cos(\theta_{ji})], \quad (7)$$

where $\beta_{ij} = \alpha^{-1} \exp[\kappa l(1 - \alpha)]$ (respectively $\beta_{ij} = 1$) for a vertical (respectively horizontal) bond i-j. As expected, when α is close to 1 (in fact $\alpha > \alpha^{**}$), the order is the AF phase of Fig. 2(a) and when α is small enough ($\alpha < \alpha^*$), the FM phase of Fig. 2(d) is observed. As shown in Fig. 3, the thresholds α^* and α^{**} depend on screening conditions and dimer length through κl and κd. Investigating the behavior in the transition region $\alpha^* < \alpha < \alpha^{**}$ requires the inclusion of next nearest neighbors [14], and leads to the conclusion that the system divides into two sublattices A and B [see Figs. 2(b) and 2(c)]. On A, the dimers remain parallel to the horizontal axis while on B, they have alternating orientations $\pm\theta$ depending on the row (see Fig. 2). The inset of Fig. 3 shows how the orientations evolve from the FM state with $\theta = 0$ to the AF order with $\theta = \pi/2$. The F/AF transition driven by α is therefore second order. We have also studied more complex situations with higher fillings (integer and half integer), that realize a host of nontrivial colloidal crystalline states [14].

Our approach relies on the validity of the pair potential (1) which is an expansion obtained at large distances from

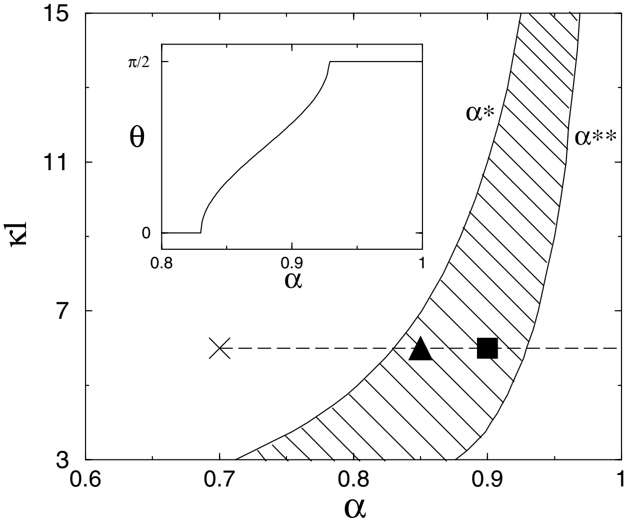

FIG. 3. Phase diagram for dimers on a rectangular substrate as a function of the aspect ratio α. The FM phase is obtained for $\alpha < \alpha^*$, while $\alpha > \alpha^{**}$ corresponds to the AF region. Here κd is fixed to 1.5, which would correspond experimentally to a fixed depth V_0. For a given value $\kappa l = 6$ (horizontal dashed line in the main graph such that $\alpha^* \simeq 0.82$ and $\alpha^{**} \simeq 0.93$), the inset shows how the system evolves from the FM to AF phase as α increases. The cross, triangle, and square correspond, respectively, to the situations of Fig. 2(d) with $\alpha = 0.7$, Fig. 2(c) with $\alpha = 0.85$, and Fig. 2(b) with $\alpha = 0.90$.

the original Yukawa expression. Such an expansion is justified for $d \ll l$ and $(\kappa d)^2 \ll \kappa l$. In addition, we restricted to nearest or second nearest neighbors interactions, which requires $\kappa l \gg 1$. Knowledge of the precise parameter bounds where our predictions apply, in particular, on the triangular lattice, is an important question of experimental relevance, that can only be answered numerically. Equally relevant is the influence of temperature, that may affect the scenarios reported here for the ground state behavior (such as those of Figs. 2 and 3). Work along these lines is in progress, with Monte Carlo simulations.

In conclusion, our theoretical approach explains in simple terms the rich orientational phenomenology of colloidal molecular crystals, both the emergence of long range order and reentrance. Our work establishes a natural connection between the situation of dimers on a square lattice and the canonical Ising model of statistical mechanics. The possibility of such a mapping, however, seems lost for more complex colloidal molecules or with other substrate geometries. The mechanisms at work here discard the radial and angular fluctuations of a trapped colloidal molecule, that appear to be of secondary importance. On the other hand, such fluctuations are prevalent on one-dimensional periodic substrates [6] and could *a priori* have played a role in the present two-dimensional situation [7]. Finally, we hope that our results will stimulate further experimental investigations in this field.

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