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Dimeric and dipolar ground state orders in colloidal molecular crystals

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ABSTRACT

A two dimensional colloidal suspension subject to a periodic substrate evolves into a colloidal molecular crystal und situations of strong confinement. We focus on the long range orientational order thereby emerging, in the ground sta We study by simulations the situations where in each trap lies a pair of identical colloids, or alternatively a pair oppositely charged macroions. We consider square or triangular geometries for the periodic confinement, together wi less symmetric distorted lattices.

Key words: colloidal molecular crystals, confined colloidal suspensions, orientational ordering, screened Coulor interactions, simulated annealing.

INTRODUCTION AND BACKGROUND

Whereas Coulombic interactions are recognized as essential to the understanding of the phase and structural properties of colloidal suspensions in the broad sense, there has been comparatively little work devoted to the behaviour of charged composite objects in a solution. The spherical shape is, however, more the exception than the rule in the colloidal realm, and to illustrate the non-intuitive features of the coupling between anisotropy of a macroion charge distribution (a colloid), and screening by an atmosphere of microions, we consider the simple dumbbell problem of two identical spherical colloids of charge q in an electrolyte of Debye length κ^{-1} (the solvent is hereafter considered as a structure-less medium of constant dielectric permittivity). One may naively think that, at a large distance from the above dimer, one recovers an isotropic (screened) electrostatic potential ϕ, as is the case in vacuum where only the monopolar contribution matters. To appreciate why such pectation is incorrect, we resort to Debye-Hückel (see e.g. Levin 2002, Levin et al. 2003) where q $\nabla^2\phi = \kappa^2\phi$. Denoting $2d$ the distance between t colloids and ψ the angle between the colloids' to-center line and the vector (with modulus r) the dimer middle to an arbitrary point where t tential ϕ is computed (see Fig. 1), we can wri the superposition of two screened Coulomb pot which admits the large r form

$$\phi(r,\psi) \sim q\,\frac{e^{-\kappa r}}{r}\cosh(\kappa d\cos\psi).$$

Remarkably, the angular and radial dependencies ize, so that the anisotropy of the source of the po is relevant at all scales, at variance with vacuum dielectric phenomenology. Another interesting teristics emerges when one considers a dipole doublet $+q/-q$, with again inter-center distan see Fig. 5): ϕ may again be written as the sum screened Coulomb contributions, which now diffe

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This expression is of the same order in r as Eq. (1), and more generally, all multipoles contribute to the leading term in the large distance decay of the electric potential for an arbitrary charge distribution (Trizac et al. 2002, Agra et al. 2004a, Ramirez and Kjellander 2006).

Surprisingly, these considerations are essential to understand the phase behaviour of the recently obtained colloidal molecular crystals, where a light lattice of traps produced by interfering laser beams induces the crystallization of an otherwise two dimensional suspension of spherical colloids. Such systems exhibit a complex phase diagram that has been studied experimentally (Brunner and Bechinger 2002), numerically and theoretically (Reichhardt and Olson 2002, Agra et al. 2004b, Reichhardt and Olson-Reichhardt 2005, Sarlah et al. 2005, 2007, El Shawish et al. 2008). For illustrative purposes, we consider the case of a rectangular lattice of confining traps in a strong pinning regime where there are exactly two colloids *per* trap, thereby forming a dimer. Restricting for simplicity the analysis to nearest neighbor interactions, and assuming that the large distance form (1) holds, we see that the potential created by a single dimer is minimum in the $\psi = \pi/2$ direction, so that a pair of interacting dimers minimizes its repulsion in the parallel configuration, when both are perpendicular to the line joining their centers (shown with the double arrow of length l in Fig. 1). Such a pair configuration does not allow to construct a trivial ground state on the square lattice, and leads to a frustrated situation. We have, therefore, resorted to numerical simulations to analyse the corresponding order that arises. On the other hand, the situation appears simpler when dipoles are considered on the square lattice: from Eq. (2) a given pair of dipoles maximizes its attraction when both are aligned to their center-to-center separation. A plausible ground state then naturally emerges, with stripes of aligned dipoles with alternating orientation (up and down) from stripe to stripe. In such a configuration, not all pairs of dipoles are in the optimal configuration though, due to the lattice geometry. In this case, and to analyse other lattice geometries, numerical simulations are necessary to clarify the orientational multaneously rotating all dimers or dipoles orientations, at variance with Heisenberg spins.

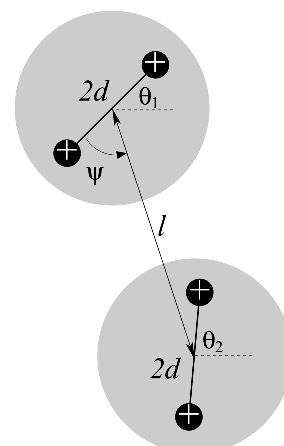

Fig. 1 – Schematic view of charged dimers in two different traps (shaded circles). l is the distance between the neighboring traps, $2d$ is the size of the "colloidal molecule" and $\theta_{1,2}$ are the characteristic angles. The large distance potential created by the upper dimer in the direction of the second one is given by Eq. (1), where the angle ψ is shown on the figure.

In the following, we will concentrate on the ground state of the system, with the idea that the orderings observed experimentally at strong pinning amplitudes correspond to a regime where thermal agitation effects become irrelevant. We shall address both dimer and dipole cases, on rectangular and triangular lattices of light traps. We assume that the (2D) traps are isotropic, with no preferred direction. Such a point of view differs from that adopted in (Sarlah et al. 2005, 2007), and corresponds to a different pinning regime, see (El Shawish et al. 2008) for a discussion. In section 2 where we consider dimers, we will discuss ground state phase diagrams and be in particular concerned with the relevance of envisioning a dimer in a trap as a rigid object. In the case of dipoles (section 3), such an assumption is more natural due to the strong attraction between two oppositely charged colloids confined in the same trap, and we will, therefore, consider the dipole as a bound entity, which allows for a reduction of the complexity of

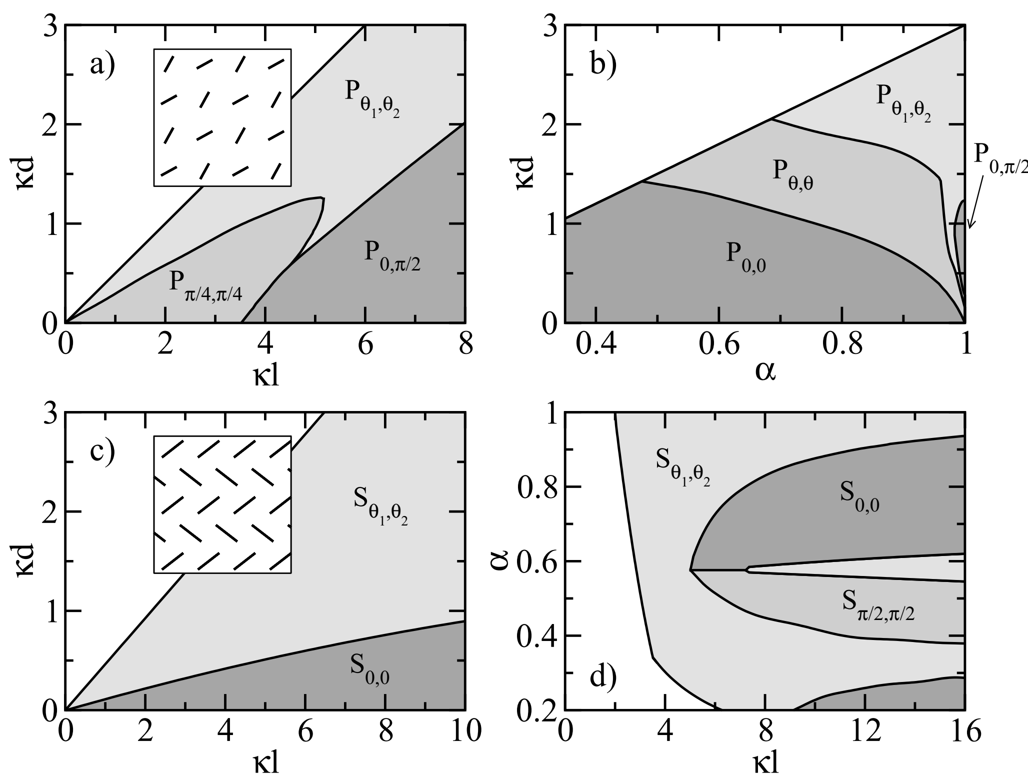

Fig. 2 – Summary of phase diagrams for rigid dimers on a rectangular lattice (upper row) for a) $\alpha = 1$ and b) $\kappa l = 6$, and on a t lattice (lower row) for c) $\alpha = 0.9$ and d) $\kappa d = 1$. Colours denote the different phases with particular values of the bipartite angles θ Note that the void (white) regions correspond to unphysical parameter ranges such as $d \leq \alpha l/2$ (a given trap cannot extend further the inter trap distance).

REPULSIVE IN-TRAP INTERACTIONS

Here we consider the dimeric case with two colloids of the same charge *per* trap. We distinguish between a simplified model of trapping where a fixed dimer size is assumed (rigid dimer model), and the "full" problem where the dimer is allowed to adjust its size to the confining potential imposed. This leads in some cases to a spontaneous symmetry breaking where all dimers do not have exactly the same size in neighboring wells.

In the rigid approach, the intra-trap colloidal distance is fixed to a value $2d$ (see Fig. 1) and we consider that the rigid dimers only have a rotational degree of freedom (θ_i in Fig. 1). The ground state is then determined by minimizing the screened Coulombic energy:

where K is here immaterial since the focus in on state properties, κ measures the range of the scree teraction, and r_{ij} denotes the distance between c i and j (the sum above runs over all possible p colloids). The trapping potential is not account but implicitly taken into account through the d stronger confinement leads to a decrease of this di Within such an approach, the relevant dimensionl rameters are κd and κl (see Fig. 1). In additi introduced the aspect ratio α (rescaling all dista one principal direction of the lattice by a factor α instance, if $\alpha = 1$ corresponds to a square geo $\alpha \neq 1$ is then for a rectangular unit cell.

Minimizing the Coulombic energy with a sin

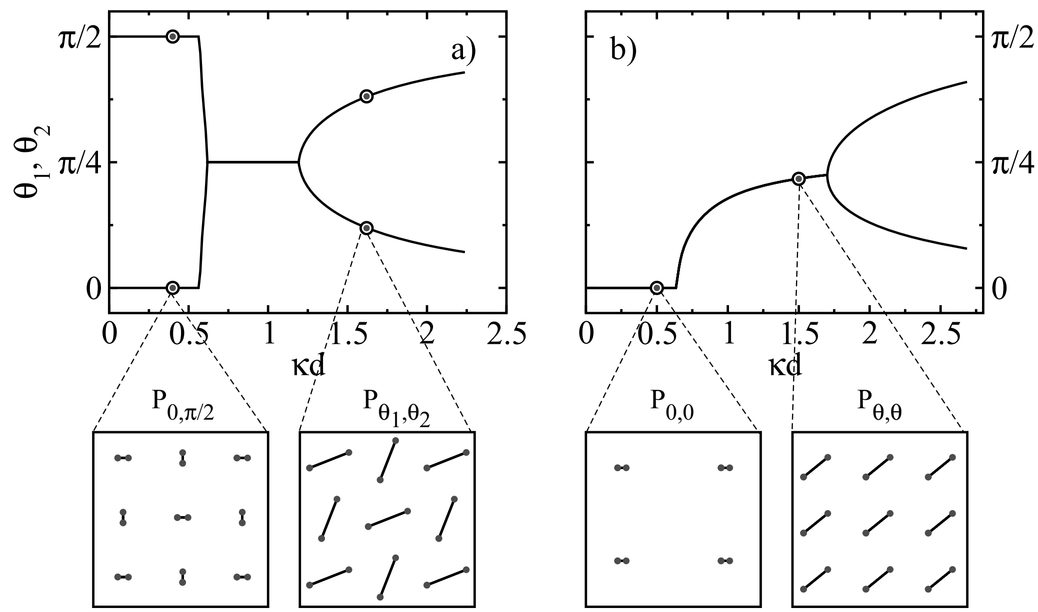

Fig. 3 – Comparison between the ground states for dimers on a square substrate, obtained considering the full "flexible" model including explicitly the trapping potential (results shown with circles), against the restricted approach where the dimers are considered as rigid objects (results shown by the continuous curves). (a) $\kappa l = 4.5$, $\alpha = 1$ and (b) $\kappa l = 6$, $\alpha = 0.9$. The insets display the typical configurations in both rigid and flexible models.

the square lattice (see the inset in the upper row), and in the form of parallel stripes on the triangular lattice. We name these orders P_{θ_1,θ_2} and S_{θ_1,θ_2} respectively. In particular, the $P_{0,\pi/2}$ phase corresponds to an order reminiscent of an antiferromagnetic phase (with alternating "vertical" and "horizontal" dimers on neighboring traps). It should be emphasized that a phase indexed by an unspecified angle θ or a pair of angles θ_1, θ_2 exhibits an order that can be tuned upon changing the parameters $(\alpha, \kappa d, \kappa l)$. An example showing how characteristic angles change is provided in Figure 3. On the other hand, there exists other phases where the angles are constant throughout the whole domain of existence, see e.g. phases $P_{\pi/4,\pi/4}$ in Figure 2-a) or $S_{0,0}$ and $S_{\pi/2,\pi/2}$ in Figure 2-d). We note that, on the equilateral triangular lattice, phases $S_{0,0}$ and $S_{\pi/2,\pi/2}$ coincide, but this is no longer the case in the distorted situation where $\alpha \neq 1$.

than those reported above. To explore the corresponding possible shortcomings, we have relaxed the assumption of a fixed distance d between the colloids, taking thereby due account of the confining potential. We considered that the two colloids in a given trap suffer a harmonic potential with a minimum at the trap center. Modifying the relative importance of harmonic confinement *versus* Coulomb repulsion, the mean intra-trap colloid distance can be tuned. For a meaningful comparison of the rigid and flexible scenarios, the mean colloid distance $2d$ is measured in the full "flexible" approach, and then used in a rigid model simulation. Figure 3 shows that on the square lattice, both routes lead to the same results. However, on the triangular lattice, we have observed that a tetrapartite ordering may emerge at large enough κd, see Figure 4-a). For moderate values of κd, we observed a good agreement rigid / flexible, see e.g. Figure 4-b) which corresponds to a vertical cut in Figure 2-

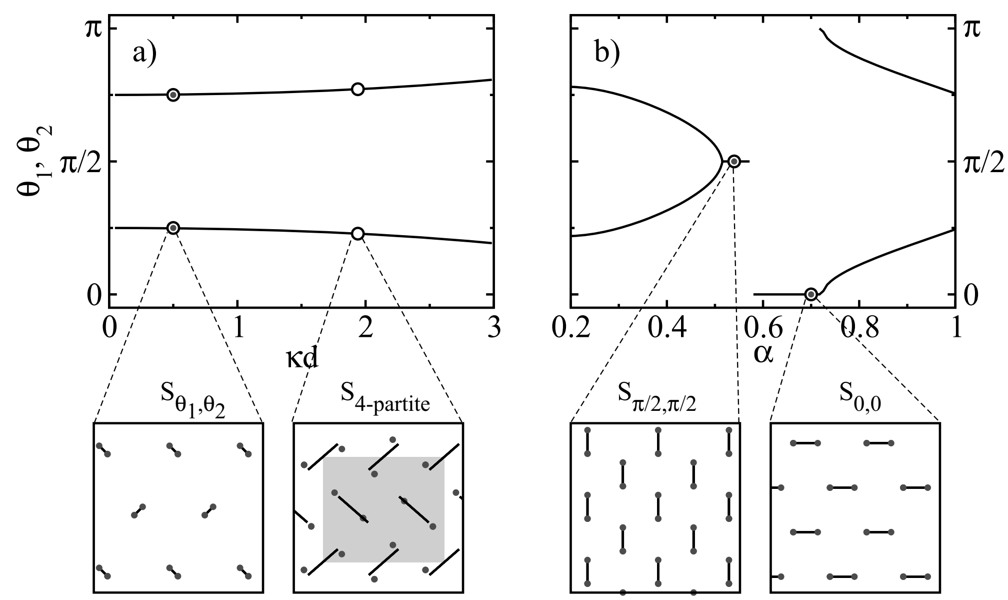

Fig. 4 – Same as Figure 3 but on a triangular lattice with (a) $\kappa l = 6$, $\alpha = 1$ and (b) $\kappa l = 6$, $\kappa d = 1$. In the equilateral configuration ($\alpha = 1$), tetrapartite ground state configurations appear for flexible dimers with large κd (shaded region in a)). A typical tetrapartite configuration (disks) with enlarged unit cell is shown in the inset along with the “rigid” bipartite configuration (lines) for comparison.

ruptly to an $S_{0,0}$ and is finally back to the S_{θ_1,θ_2}, with, however, more separated characteristic angles (larger value of $|\theta_1 - \theta_2|$), than in the low α regime.

ATTRACTIVE IN-TRAP INTERACTIONS

Our interest now goes to the dipolar case, with two oppositely charged colloids *per* trap (see Fig. 5). As alluded to earlier, it becomes irrelevant to distinguish between the rigid and flexible cases: due to the strong colloidal attraction, the dipole behaves as a rigid object. As might have been anticipated, the ground state on the rectangular lattice is of $P_{-\pi/2,\pi/2}$ fashion, see Figure 6. The numerical results have again been obtained with simulated annealing. However, when the relevant structures have been identified, with the correct sublattices, the problem at hand depends on a small number of parameters, and lends itself to a straightforward direct energy minimization. We have compared both approaches (annealing and direct minimization), that give very sim-

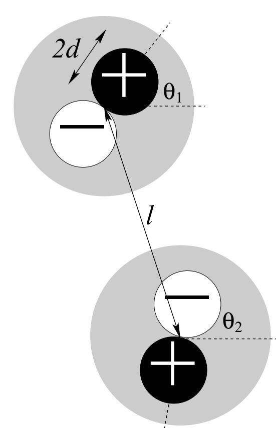

Fig. 5 – Schematic representation of two electric dipoles, i.e composed of positively and negatively charged colloids, in (shaded circles). Here $2d$ is the size of a colloid whereas parameters have the same meaning as in Figure 1.

magnetic $S_{\theta,\pi+\theta}$ and ferromagnetic $S_{\theta,\theta}$ stripe as shown in Figure 7. It can be seen again tha

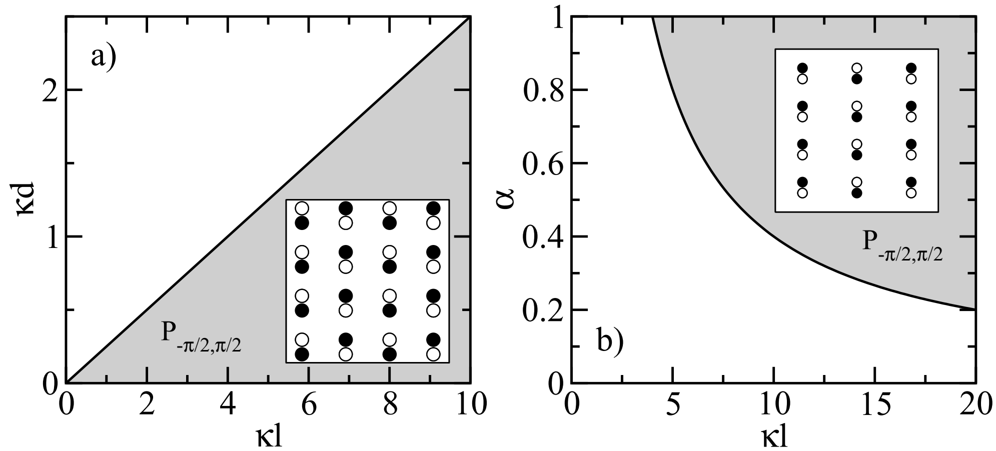

Fig. 6 – Ground state phase diagram of oppositely charged dimers on a rectangular lattice for (a) $\alpha = 1$ and (b) $\kappa d = 1$. The $P_{-\pi/2,\pi/2}$ phase sketched in the insets is the ground state for all values of α, κl and κd.

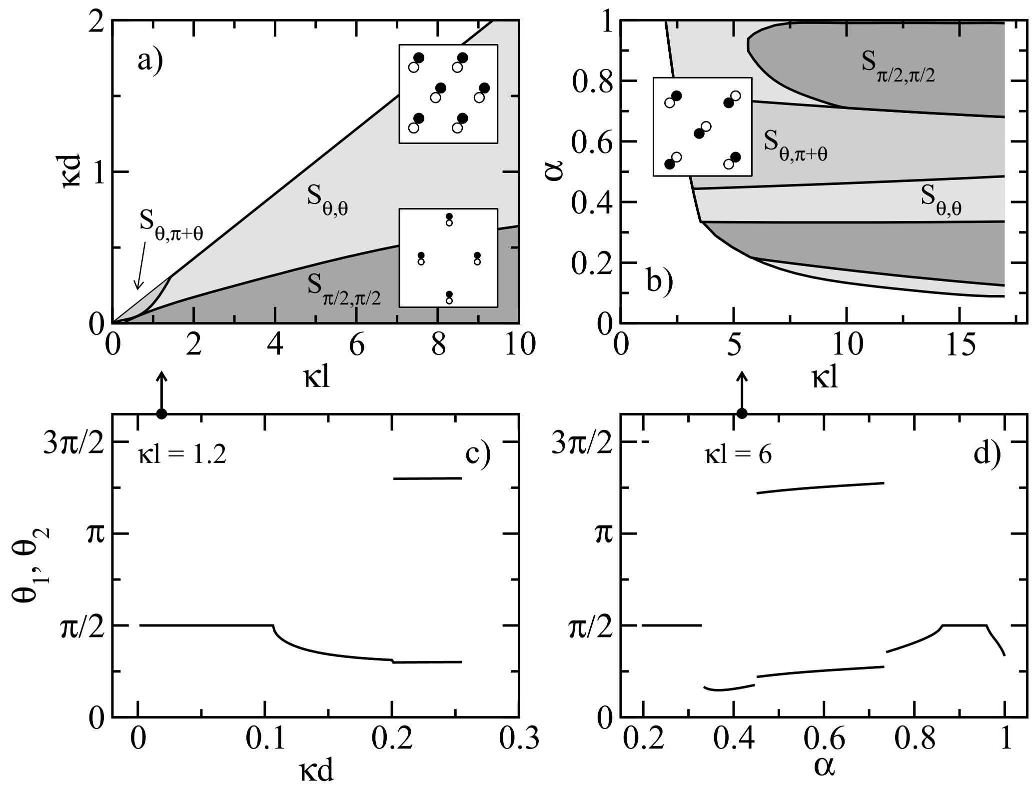

Fig. 7 – Phase diagram for opposite charged dimers on a triangular lattice for (a) $\alpha = 0.8$ and (b) $\kappa d = 0.5$.

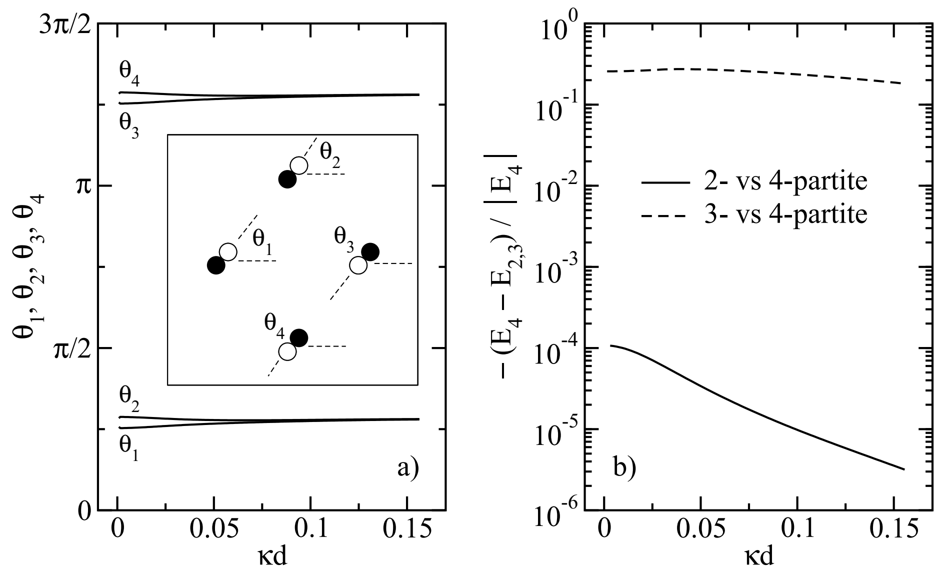

Fig. 8 – Emergence of tetrapartite ground state configurations for opposite charged dimers on a triangular lattice with $\alpha = 0.7$ and $\kappa l = 0.8$: (a) the parameter dependence of tetrapartite angles and (b) a comparison of ground state energies E_i calculated for bipartite (E_2), tripartite (E_3) and tetrapartite (E_4) lattices. In the inset of (a) we show the tetrapartite unit cell configuration for $\kappa d = 0.05$.

the inset, is reminiscent of the ground state $P_{-\pi/2,\pi/2}$ found on the square lattice, which is itself a stripe phase. The reason for this similarity is clear: with the particular scaling factor $\alpha = 1/\sqrt{3} \simeq 0.57$, the triangular lattice is mapped onto a square one (with principal axis rotated by an angle of $\pi/4$ with respect to the horizontal direction corresponding to a principal axis of the unscaled original triangular lattice). For $\alpha \simeq 0.57$ we therefore expect a $S_{\pi/4,5\pi/4}$ phase on the triangular lattice. This is precisely what is observed in Figure 7-d) where one can see that the couple (θ_1, θ_2) hits the value $(\pi/4, 5\pi/4)$ at $\alpha = 1/\sqrt{3}$ (see also the inset of Fig. 7-b) for a visual confirmation). Finally, in the low screening regime and for $\alpha < 1$, we have observed a tendency towards tetrapartite ordering, as shown in Figure 8. This tendency is, however, weak: the resulting angles only slightly differ from those in the bipartite structure (it can be seen in graph 8-a) that $|\theta_2 - \theta_1| \ll \theta_1$) and, furthermore, the energy differences involved are faint (Fig. 8-b)).

called colloidal molecular crystals, that are obtai perimentally when a two dimensional colloidal li highly charged colloids is subject to a modulate lattice. The forces arising from light pressure an the dielectric mismatch between the solvent and c tend to confine the colloids in the regions of large intensity. We investigated the cases of a square angular symmetry for the resulting periodic co potential, together with distorted geometries obta applying a scaling factor α to say the y coordinat ing the x coordinate unaffected. We have address different situations, where either two like-charge c are present in every trap (dimeric case) or where colloids are oppositely charged. In the latter ca restricted ourselves to cases where the resulting object is of vanishing charge (referred to as th lar case). The orientational orderings obtained a and display a variety of phases. Most of them ar ciated to a bipartite lattice, with stripe or checke arrangements. A weak tendency to tetrapartite o

While the dimeric case has been realised experimentally, we are not aware of any experimental studies with oppositely charged colloids. A first difficulty to overcome lies in the fact that, starting from a weakly modulated situation and gradually increasing confinement amplitude, the system may not organize spontaneously with exactly one dipole per trap. On the other hand, with dimers, the strong colloid-colloid repulsion ensures that there are no defects in the corresponding crystal, i.e. exactly one dimer *per* trap.

Finally, we emphasize that the Coulombic energy considered here [Eq. (3)] considers all pairs of dimers/dipoles in the system, and does not assume that only interactions between nearest neighbor traps are relevant. The nearest neighbor assumption might seem natural at first glance, given the exponential dependence with respect to distance of the screened Coulomb potential. It may, however, prove incorrect, as has been uncovered in (El Shawish et al. 2008).

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RESUMO

Uma suspensão bidimensional coloidal sujeita a um substrato periódico evolui para um cristal coloidal molecular em situações de forte confinamento. Nós focamos na ordem de orientação emergindo a partir do estado fundamental. Fazendo uso de simulações, estudamos as situações onde em cada armadilha reside um par de colóides idênticos ou, alternativamente, um par de macro-íons de cargas opostas. Consideramos geometrias quadradas ou triangulares para o confinamento periódico com arranjos simétricos com menor distorção.

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