

## Colloidal Ordering on a 2D Quasicrystalline Substrate

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By using Monte Carlo simulations, we study the complex phase behavior of charged-stabilized colloidal particles in a two-dimensional substrate potential with quasicrystalline decagonal symmetry. In the regime where the strengths of the substrate and colloidal pair potential are comparable, we identify a novel and unexpected quasicrystalline phase with pure 20-fold bond order and a disordered structure without any apparent rotational symmetry. Furthermore, we demonstrate how phasonic displacements in the substrate potential induce phasonic flips in the colloidal monolayer.

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Quasicrystals are nonperiodic solids that nevertheless exhibit Bragg reflection due to their long-range positional order [1,2]. In particular, they possess rotational point symmetries [3], such as fivefold or tenfold rotational axes, that are not allowed in periodic crystals. A distinctive physical property of quasicrystals are phasons, which correspond to correlated rearrangements of atoms throughout the quasicrystal. Phasons, like phonons, are hydrodynamic modes since they do not cost free energy in the long-wavelength limit [4]. Their different features are still a main topic and intensely discussed in the field [5,6].

In recent years, increasing research activities have been directed towards the question of how atoms order on quasicrystalline surfaces [7–11]. The goal of such studies is to control the growth of quasicrystals and ultimately their exceptional material properties [7], exemplified by low coefficients of friction [12], catalytic qualities [13], and the possibility of producing photonic band gaps [14].

Colloidal suspensions of micron-sized particles are well-known model systems for statistical physics and for mimicking atomic systems [15–17]. In this Letter, we will theoretically study the complex phase behavior of charge-stabilized colloidal suspension in a two-dimensional decagonal potential. While atomic quasicrystalline surfaces are strongly determined by chemical details, our approach offers the opportunity to concentrate on the fundamental aspects of phase ordering on such substrates and thereby identifies possible phases in atomic monolayers. In particular, we will investigate bond-orientational order following the seminal work of Nelson and Halperin for melting on neutral and periodic substrates [18]. Furthermore, we will shortly demonstrate that a phasonic displacement in the model substrate induces colloidal reordering. The dynamics of a single colloidal particle in a decagonal potential was already described in [19].

Although our work is purely theoretical, we note that the decagonal substrate potential for colloids can be realized, e.g., by the intensity pattern of interfering laser beams. This method provides a nontrivial external potential for inducing novel complex colloidal structures commonly referred to as optical matter [20]. On the other hand, light

fields with quasicrystalline symmetry have already been used to create nonlinear photonic quasicrystals [6], to induce quasicrystalline ordering in liquid crystals [21], or to trap atomic clouds [22].

In our case, the external potential would correspond to a decagonal light field created by five interfering laser beams with identical polarization [cf. Fig. 1(a)]. For a vanishing tilt angle  $\theta \rightarrow 0$  between the beams, the potential in the  $xy$  plane is [21]  $V(\mathbf{r}) = -\frac{V_0}{25} \sum_{j=0}^4 \sum_{k=0}^4 \cos[(\mathbf{G}_j - \mathbf{G}_k) \cdot \mathbf{r} + \phi_j - \phi_k]$ , where  $\phi_j$  are the phases of the laser light waves and  $\mathbf{G}_j$  their wave vectors projected onto the  $xy$  plane [cf. Fig. 1(b)]. The prefactor is chosen such that  $-V_0$  gives the minimum value of the potential. We use the phases to specify the phasonic displacement field  $\mathbf{u} = [u_x, u_y]$  and the phasonic field  $\mathbf{w} = [w_x, w_y]$  in the decagonal pattern, following the convention of Ref. [4],  $\phi_j = \mathbf{u} \cdot \mathbf{G}_j + \mathbf{w} \cdot \mathbf{G}_{3j \bmod 5}$ . We have checked that constant phasonic displacements do not influence the phase behavior of the

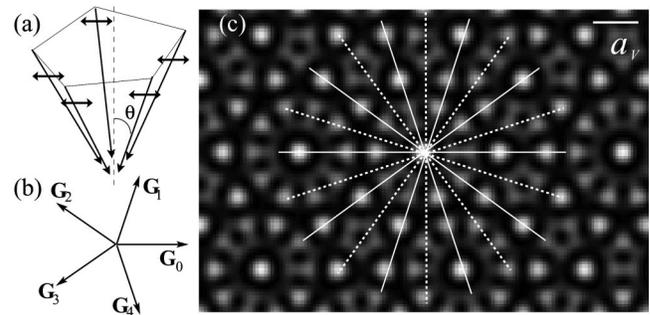


FIG. 1. (a) The colloidal potential corresponds to the interference pattern of five laser beams arranged symmetrically around the vertical. A small tilt angle is assumed so that the polarization vectors can be chosen all the same. (b) The five wave vectors of the beams projected along the vertical onto the  $xy$  plane. (c) Gray-scale representation of the decagonal potential. White indicates a high laser intensity and therefore a potential minimum. The bar in the upper right corner marks the length scale  $a_V = 2\pi/|\mathbf{G}_j|$ . The full and dashed lines indicate, respectively, the 10 bond directions for  $\psi_{10} \neq 0$  and the additional bond directions for  $\psi_{20} \neq 0$ .

colloids and therefore usually chose  $\mathbf{u} = \mathbf{w} = \mathbf{0}$ . At the end of this Letter, however, we will explicitly illustrate the effect of phasonic displacements on this ordering.

The screened Coulomb interaction between the colloids is implemented by the pair potential  $\phi(d) = A \exp(-\kappa d)/d$  of the Derjaguin-Landau-Verwey-Overbeek theory, where  $d$  is the distance between two colloids,  $\kappa$  the inverse Debye screening length, and  $A = [Z^* e \exp(\kappa R)]^2 / [4\pi\epsilon_0\epsilon_r(1 + \kappa R)^2]$  is a prefactor depending on the radius  $R$  of a colloid, its effective surface charge  $Z^*$ , and the dielectric constant of water  $\epsilon_r$ . We quantify the particle density by the spacing  $a_S$  of the particles in an ideal triangular lattice. We use the density with  $a_S \approx 0.7a_V$ , where the colloids occupy exactly all of the minima in the decagonal potential, to distinguish between the low ( $a_S > 0.7a_V$ ) and high ( $a_S < 0.7a_V$ ) density cases. To

study systems with small densities, we employ parameters used by Strepp, Sengupta, and Nielaba in [23]:  $R = 0.535 \mu\text{m}$ ,  $Z^* = 7800$ ,  $\epsilon_r = 78$ , and temperature  $T = 293.15 \text{ K}$ . Furthermore, the length scale of the potential is fixed to  $a_V = 2\pi/|G_j| = 2.53 \mu\text{m}$  and the screening length to  $\kappa^{-1} = 0.506 \mu\text{m} = a_V/5$ . In the simulations with high densities ( $a_S < 0.7a_V$ ), the set of parameters is  $R = 1.2 \mu\text{m}$ ,  $Z^* = 1000$ ,  $\epsilon_r = 78$ ,  $T = 300 \text{ K}$ ,  $a_V = 5.0 \mu\text{m}$ , and  $\kappa^{-1} = 0.25 \mu\text{m} = a_V/20$ . For 400–900 colloids, we performed Monte Carlo simulations using the METROPOLIS algorithm [24] with periodic boundary conditions, where the box size is chosen such that the decagonal potential displays only small discontinuities at the boundaries.

We classify the observed colloidal structures by the bond-orientational order parameter

$$\psi_m = \left\langle \left| \frac{1}{N} \sum_{j=1}^N \frac{1}{n_j} \sum_{k=1}^{n_j} e^{im\theta_{jk}} \right| \right\rangle, \quad (1)$$

where the inner sum is over all  $n_j$  nearest neighbors of colloid  $j$ ,  $N$  is the total number of particles, and  $\theta_{jk}$  is the angle of the bond connecting colloids  $j$  and  $k$  given with respect to some arbitrary reference direction. The ensemble average in Eq. (1) is calculated over 1000 configurations taken every 100 steps after the system has been equilibrated during  $10^6$  Monte Carlo steps. We are particularly interested in bond-orientational order with  $m = 6, 10,$

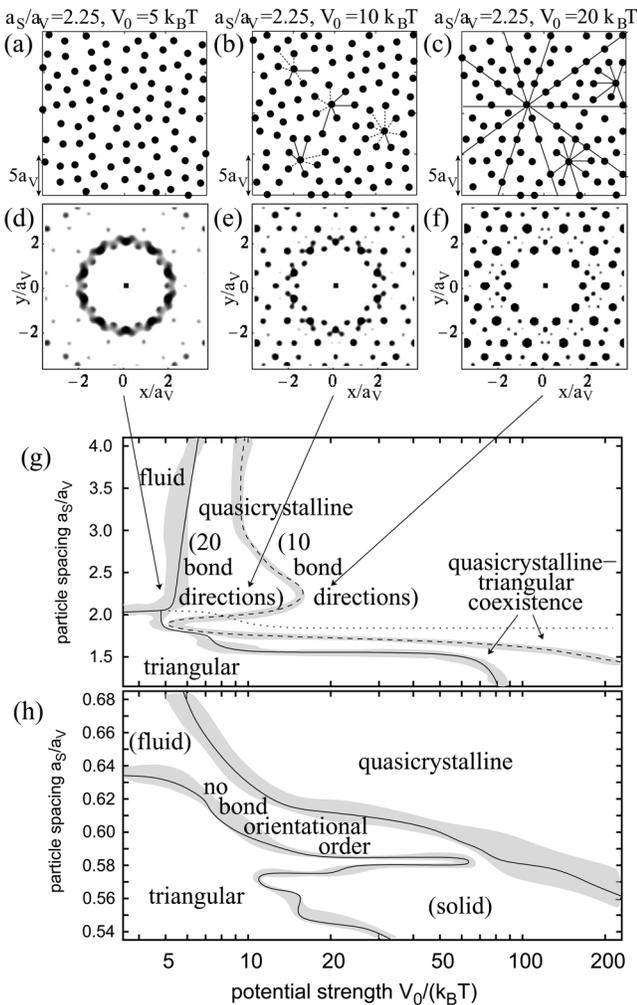


FIG. 2. (a)–(c) Snapshots for particle positions and (d)–(f) direct correlation functions for (a),(d) the fluid, (b),(e) the phase with 20-fold bond order, and (c),(f) with 10-fold bond order. (g),(h) Phase diagrams for low (g) and high (h) colloidal densities depending on the potential strength  $V_0$  (in units of  $k_B T$ ) and the particle spacing  $a_S$  (in units of  $a_V = 2\pi/|G_j|$ ) in an ideal triangular lattice. For a detailed description, see the main text.

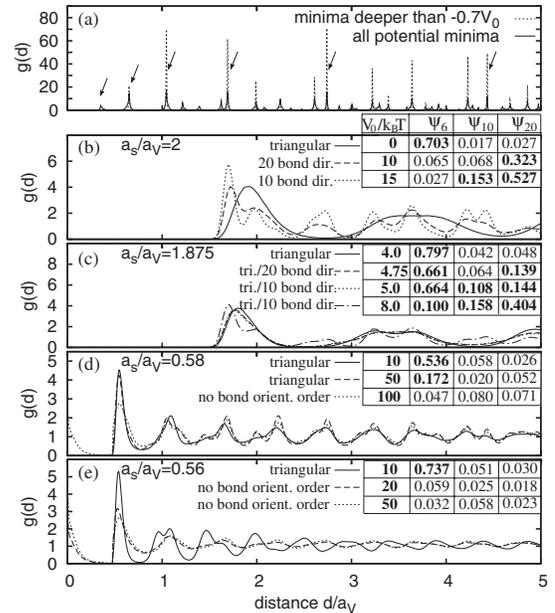


FIG. 3. Pair correlation function  $g(d)$  as a function of the particle distance  $d$ : (a) for colloids placed at the positions of all minima (solid line) or of all minima deeper than  $-0.7V_0$  (dotted line) in the decagonal potential, (b)–(d) determined by Monte Carlo simulations in the low (b),(c) and high (d),(e) density cases. In each graph,  $g(d)$  is drawn for constant  $a_S/a_V$  and several strengths  $V_0$ . The inset tables give the values of  $\psi_m$  for  $m = 6, 10,$  and  $20$ .

or 20. In the phase diagrams of Figs. 2(g) and 2(h), discussed below, a  $m$ -fold bond order was assigned to the phases for  $\psi_m > 0.1$ . Note that a nonvanishing  $\psi_m$  indicates long-range orientational order. In particular, we call phases with  $\psi_6 > 0.1$  triangular including structures where only clusters of triangles occur with the same orientation. The shaded regions in the phase diagrams mark the shift of the phase boundaries if the threshold value 0.1 is varied by  $\pm 0.03$ . A threshold value is necessary to suppress small random fluctuations of  $\psi_m$ , which even for the fluid usually is about 0.02 to 0.05.

Figures 2(g) and 2(h) show the respective phase diagrams for the low and high density cases in the parameter space, particle spacing  $a_S$  versus potential strength  $V_0$ . The colloidal parameters introduced above guarantee that for  $V_0 = 0$  and also for weak potential strengths [ $V_0/(k_B T) < 5$ ] the phase transition from the solid triangular ( $\psi_6 > 0.1$ ) to the fluid ( $\psi_m < 0.1$ ) phase is observed for both cases. At sufficiently large  $V_0$ , a quasicrystalline phase with ten preferred bond directions ( $\psi_{10} > 0.1$ ) is favored by the decagonal potential. Its 2D direct correlation function in Fig. 2(f) clearly displays 10-fold rotational symmetry and the long-range quasiperiodic order enforced by the substrate is also evident in the 1D pair correlation function in Fig. 3(b) to be discussed later. The interesting phases occur for intermediate potential strengths. In the low density case [cf. Fig. 2(g)] a quasicrystalline phase with pure 20-fold bond order is found, i.e., where  $\psi_{20} > 0.1$  but  $\psi_{10} < 0.1$ . It is bounded by the solid and dashed lines. Furthermore, between the dotted and full lines a triangular-quasicrystalline coexistence region exists, where we find that both the triangular and the quasicrystalline order parameters are nonzero. In the high density case [cf. Fig. 2(h)], the intermediate phase does not display any bond-orientational order. We checked that  $\psi_m < 0.1$  for  $m = 6, 10, 12, 15, 20$ , and 30. In addition, preliminary studies on the self-diffusion of the colloids indicate that this disordered phase changes from a fluid to a solid with increasing density.

To understand the occurrence of the intermediate phase with 20-fold bond order in Fig. 2(g), we draw possible bond directions in the representation of the decagonal potential in Fig. 1(c). The full lines indicate 10 directions where predominantly deep minima are found. They are occupied for large potential strengths, and, therefore, the phase with 10-fold bond order is stable. If the potential strength is decreased, the colloidal interactions become more important, and some particles are pushed to more shallow minima situated along the dashed lines in Fig. 1(c) in order to increase the interparticle distance. When the colloids occupy all 20 bond directions uniformly,  $\psi_{10}$  vanishes and  $\psi_{20} > 0.1$  indicates the 20-fold bond-orientational order. Figures 2(b) and 2(c) show snapshots of the two quasicrystalline phases. In Fig. 2(c), where 10-fold bond order exists, one can identify lines of particles oriented along the 10 bond directions. Examples of these directions are given. In Fig. 2(b), additional bond directions for the 20-fold bond order are indicated. However,

clear lines where particles are situated are hard to recognize. The direct correlation function for the phase with ten bond directions [see Fig. 2(f)] possesses ten nearest neighbor peaks that are caused by colloids occupying the deepest minima of the potential. They also exist as narrow peaks for the phase with 20-fold bond order [cf. Fig. 2(e)]. There in addition ten broad peaks, each with two side peaks, occur due to the occupation of more shallow minima. The integrated intensities for each of the ten narrow and the ten broad peaks are about the same. Quantitatively, this is reflected by the fact that  $\psi_{10}$  vanishes for the phase with 20-fold bond order.

The interpretation just discussed is supported by the pair correlation functions  $g(d)$  in Fig. 3. In Fig. 3(a),  $g(d)$  is plotted when the colloids are only allowed to occupy the potential minima: namely, all of them (full line) or just the deepest one (dotted line). Clearly, in the second case a few distances are preferred. The arrows indicate peak positions that follow from their left-hand neighbors by multiplication with the number of the golden mean  $\tau \approx 1.618$  revealing a self-similar property of the decagonal potential. The pair correlation function determined from Monte Carlo simulations [cf. Fig. 3(b)] indicates for small  $V_0$  a clear peak close to  $d = a_S = 2a_V$ , as expected for the ideal triangular phase. For increasing potential strength  $V_0$ , new peaks start to develop in the quasicrystalline region at positions of the deepest minima, but they are still quite broad so that only  $\psi_{20}$  is nonzero (dashed line). Just crossing the phase boundary to the 10-bond-direction phase, the peaks become more pronounced (dotted line), meaning that the colloids settle more and more into the deepest minima. Furthermore, for densities with  $a_S$  around  $1.85a_V$ , the quasicrystalline phase with 20-fold bond order exists only in a very small range of  $V_0$  [cf. Fig. 2(g)]. This is understandable from the pair correlation functions in Fig. 3(c). They show that the main peak in the triangular phase is already close to one pronounced peak of the ideal  $g(d)$  in Fig. 3(a). As a result, the colloids can settle into the deepest minima of the decagonal potential without the need of strong rearrangements, and, therefore, the 20-bond-direction phase hardly occurs.

In the high density case, all of the minima of the decagonal potential are occupied by particles, and an excess of colloids has to fill the space between the minima. This precludes any 20-fold bond-orientational order in the intermediate phase of the phase diagram of Fig. 2(h). From the theory of melting on incommensurate substrates [18], one would at least expect an intermediate phase with 30 bond directions where the six triangular directions lock into the ten preferred directions of the potential. However, from the simulations we find  $\psi_{30} < 0.1$  in all points of the intermediate phase, probably because very small displacements, due to the interactions between the particles and with the substrate, can easily destroy any detectable 30-fold bond order.

In Fig. 3(e), we plot the pair correlation function for  $a_S = 0.56a_V$  for increasing potential strengths  $V_0$ . The

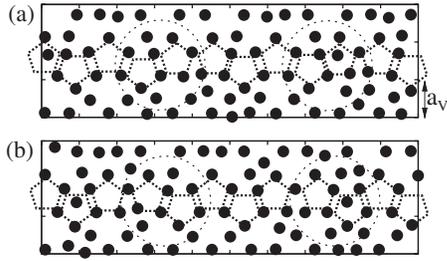


FIG. 4. Colloidal ordering in the quasicrystalline phase for  $a_S/a_V = 0.65$  and  $V_0/(k_B T) = 1000$ , (a) before and (b) after a phasonic displacement with  $w_x = 0.1a_V$ . Note the flips of neighboring pentagons indicated by dotted circles.

most pronounced peak is just determined by the colloidal density. During the transition from the triangular ( $\psi_6 > 0.1$ ) to the disordered ( $\psi_m < 0.1$ ) phase,  $g(d)$  changes so that the other peaks better fit to the ideal pair correlation function in Fig. 3(a). A distinctive feature occurs in the phase diagram of Fig. 2(h) at densities with particle spacing  $a_S$  around  $0.58a_V$ ; the triangular phase reaches deep into the region where bond-orientational order is not expected. A partial explanation for this is given by the pair correlation functions in Fig. 3(d). Already for the triangular phase, the peaks (besides the highest one) fit very well to the ideal  $g(d)$  in Fig. 3(a), and therefore the transition into the disordered phase is delayed to larger  $V_0$  [25].

In the end, we demonstrate how a phasonic displacement of the decagonal potential influences the colloidal ordering. Between the snapshots of the quasicrystalline phase in Figs. 4(a) and 4(b), a phason is introduced with  $w_x = 0.1a_V$ . It leads to local rearrangements of the colloids, commonly called phasonic flips, which we illustrate by the row of pentagons sketched in the figures. Interestingly, it seems that always two neighboring pentagons flip their orientations simultaneously. The row itself does not change its vertical position. This is in agreement with the dark horizontal lines in the intensity pattern of Fig. 1(c), which also do not move when  $w_x$  is changed.

In conclusion, we have demonstrated the rich phase behavior of colloidal suspensions in a two-dimensional quasicrystalline potential. Using a bond-orientational order parameter, we are able to identify a novel and unexpected quasicrystalline phase with 20-fold bond order and a disordered phase in the regime where the strengths of the substrate and colloidal pair potential are comparable. At a certain particle density, a particular stable triangular phase with 6 bond directions is identified. Our results will help to clarify atomic ordering on surfaces of quasicrystals and thus contribute to the vision of controlling the growth of quasicrystalline films and of tailoring their extraordinary material properties. Phasons strongly determine the behavior of quasicrystals as summarized in the discussion paper [5]. It is possible to introduce, e.g., uniform phasonic displacements or strains into the light-induced decagonal substrate potential. Therefore, our colloidal model system offers the possibility to study specific static and dynamic

properties of the still hotly debated phasonic degree of freedom in a controlled manner.

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