Freezing and Melting of a Colloidal Adsorbate on a 1D Quasicrystalline Substrate

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Using Monte Carlo simulations and an extended Landau-Alexander-McTague theory, we demonstrate that colloids in a one-dimensional quasicrystalline potential order in triangular and rhombic-α crystalline phases. Increasing the strength of the potential further, a new type of light-induced melting is discovered that has its origin in the nonperiodicity of the potential. In contrast to reentrant melting in periodic potentials, the quasicrystalline potential melts the crystalline phases even when they already exist at zero potential.

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Colloids are widely used as model systems of statistical mechanics and for investigating nonequilibrium. Their crystallization, ordering, and dynamics in external fields are of particular interest [1]. The seminal work of Ashkin, where he demonstrated that colloidal particles are forced into the direction of highest laser intensity [2], inspired new exciting studies. A charge-stabilized colloidal suspension, confined between two glass plates to form a quasi-two-dimensional system, can be manipulated by applying interfering light fields in order to create complex structures, also referred to as optical matter [3]. With such an experimental setting, Chowdhury, Ackerson, and Clark discovered that a one-dimensional periodic potential can induce a two-dimensional triangular ordering of colloidal particles [4]. The wave number G_0 of the potential was chosen such that it coincides with the position of the first peak in the direct correlation function of the colloidal system in the liquid phase. Chowdhury *et al.* termed this phenomenon light-induced freezing and explained it with the help of an extension of the Landau-Alexander-McTague theory. In its original form, this theory was used to discuss the stability of competing crystal structures and their melting transitions [5]. An alternative theoretical explanation of light-induced freezing employs density functional theory [6]. Experiments [7] and Monte Carlo simulations [8,9] reveal the surprising phenomenon that the laser-induced crystal can melt again when the laser intensities are increased further. After Bechinger *et al.* stressed the importance of thermal fluctuations [7], Radzihovsky, Frey, and Nelson presented a theory based on dislocation unbinding that explains the observed laser-induced freezing and reentrant melting [10], followed by a detailed study in Ref. [11]. The theory also shows that the one-dimensional periodic potential cannot melt the colloidal crystal when it is already stable at zero potential.

In this Letter we study colloidal ordering in a one-dimensional quasicrystalline potential that consists of incommensurate modulations with wave numbers $G_0\tau$ and G_0/τ, where $\tau = (1 + \sqrt{5})/2$ is the golden mean. Using Monte Carlo simulations and a careful implementation of the extended Landau-Alexander-McTague theory, we identify stable triangular and rhombic phases. However, we cannot confirm the result of Das and Krishnamurthy [12], who report a stable quasicrystalline phase with pentagonal symmetry as indicated in Fig. 1(a). Remarkably, we discover that the nonperiodicity of the potential enables a new mechanism for laser-induced melting. It even occurs for crystalline phases that are already stable at zero potential.

We performed Monte Carlo simulations of a charge-stabilized colloidal system using the Metropolis algorithm [13,14] with 1054 particles in a box with periodic boundary conditions. A rational approximation was used for the box size such that a pentagonal crystal can fit into the box with only minor distortions. The colloids interact via the pair potential $\phi(r)$ given by the Derjaguin-Landau-Verwey-Overbeek theory [15,16]:

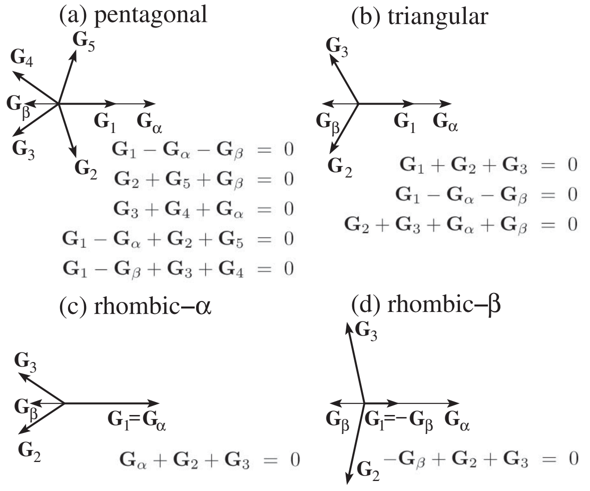

FIG. 1. Reciprocal lattice vectors of four possible phases in a laser potential modulated with the wave vectors $\mathbf{G}_\alpha = \tau G_0 \mathbf{e}_x$ and $\mathbf{G}_\beta = (1/\tau) G_0 \mathbf{e}_x$. In the pentagonal and triangular phase the lengths of the lattice vectors are $G_j = G_0$ ($j = 1, \ldots, 5$ or $1, \ldots, 3$). In the rhombic phases $\mathbf{G}_1$ equals either $\mathbf{G}_\alpha$ or $-\mathbf{G}_\beta$; $\mathbf{G}_2$ and $\mathbf{G}_3$ are chosen such that the colloidal density is the same as in the triangular lattice.

$$\phi(r) = \frac{(Z^* e)^2}{2\pi\epsilon_0\epsilon_r}\left(\frac{e^{\kappa R}}{1+\kappa R}\right)^2 \frac{e^{-\kappa r}}{r}, \tag{1}$$

where r is the distance between two interacting colloids, R the radius of a colloid, Z^* its effective surface charge, ϵ_r the dielectric constant of water, and κ the inverse Debye screening length. We employ the same values for the parameters as used by Strepp, Sengupta, and Nielaba [9]: $R = 0.535\ \mu\text{m}$, $Z^* = 7800$, $\epsilon_r = 78$, and the temperature $T = 293.15$ K. The density is chosen such that the spacing in an ideal triangular lattice would be $a_s = 2.53\ \mu\text{m}$. In the simulations, the colloids are not allowed to overlap and a large distance cutoff of the potential was used at $5a_s$. The laser potential is given by

$$V_{\text{ext}}(\mathbf{r}) = -\frac{V}{2}[\cos(\mathbf{G}_\alpha \cdot \mathbf{r}) + \cos(\mathbf{G}_\beta \cdot \mathbf{r})], \tag{2}$$

with $\mathbf{G}_\alpha = \tau_\alpha G_0 \mathbf{e}_x$, $\mathbf{G}_\beta = (-1/\tau_\beta) G_0 \mathbf{e}_x$, where $\mathbf{e}_x$ is the unit vector in the x direction and $G_0 = \pi/(\sqrt{3}a_s)$. In an infinite system $\tau_\alpha = \tau_\beta = \tau = (1+\sqrt{5})/2$ is the golden mean. To implement the periodic boundary conditions, we use the approximations $\tau_\alpha = 55/34$ and $\tau_\beta = 34/21$, which are ratios of consecutive Fibonacci numbers. The free parameters of the system are the potential strength V and the reduced inverse screening length κa_s.

The results from our simulations are summarized in the phase diagram of Fig. 2, where we plot the order parameters $\rho(\mathbf{G}_2) = \langle \sum'_{i,j} \exp[i\mathbf{G}_2 \cdot (\mathbf{r}_j - \mathbf{r}_i)] \rangle / N$. Here $\mathbf{G}_2$ belongs to either the triangular or the rhombic phases, $\mathbf{r}_i$, $\mathbf{r}_j$ are the particle locations, $\sum'_{i,j}$ means sum over all nearest neighbors, and N is the total number of terms in the sum [17]. We do not find a stable pentagonal phase. For small potential strength V and low κa_s, the colloidal ordering is triangular. For larger laser intensities, we identify a rhombic phase with one of its reciprocal lattice vectors matching the wave vector $\mathbf{G}_\alpha$ of the external potential [see Figs. 1(c) and 3(a)]. We therefore call it the rhombic-α phase. Note that it also occurs in two-dimensional colloids that are liquid for zero potential. So laser-induced freezing is possible in our system.

Interestingly, at very large potential strengths, the crystal phases melt into a modulated liquid phase. Even more surprising, melting also occurs for small inverse screening lengths; i.e., a colloidal crystal, already existing at zero external potential, can be melted by applying a quasiperiodic light field. This is in stark contrast to the well-known laser-induced reentrant melting observed for the periodic laser potential $V_{\text{ext}}(\mathbf{r}) = V\cos(G_0 \mathbf{e}_x \cdot \mathbf{r})$ [7]. These systems are strongly governed by fluctuations, and only crystals produced by light-induced freezing can exhibit reentrant melting [7,10]. On the other hand, colloidal crystals, already stable at zero potential, will never melt for increasing V. In each potential well of a periodic light field, the particle density or the average particle distance is the same so that neighboring lines of particles will always remain locked relative to each other to form a crystal.

To understand the mechanism behind the observed melting scenario in a quasiperiodic potential, we take a closer look at the modulated liquid phase, a snapshot of which is presented in Fig. 3(b). All particles are located in local minima of the quasiperiodic potential which is illustrated in the lower part of the figure. The potential wells have an approximate distance of a_s/τ, and their depths are modulated on the length τa_s. Thus the line density of the particles differ from one well to the other. Some wells are even empty or at least the probability for finding a particle in such wells is very low. This creates a quasiperiodic ordering in the direction perpendicular to the wells. Since the ratios of the line densities of neighboring wells are usually irrational, a global periodic ordering along the direction of the wells is impossible. This explains that a strong one-dimensional quasicrystalline potential destroys all possible periodically ordered phases and thus a new kind of melting into a modulated liquid structure is observed which is not driven by fluctuations.

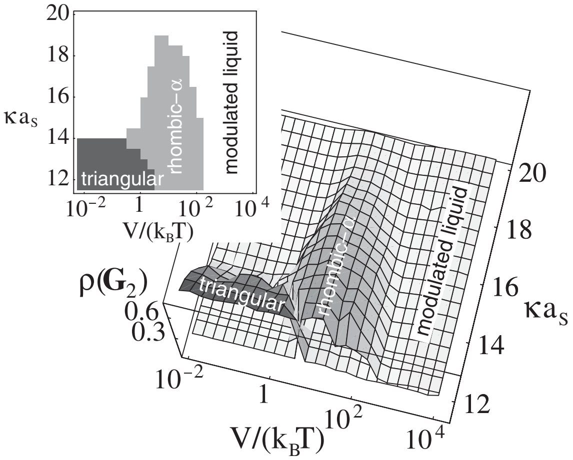

FIG. 2. The order parameters $\rho(\mathbf{G}_2)$ characterizing the crystalline ordering of the colloids as a function of the strength V of the 1D quasicrystalline potential and the reduced inverse Debye length κa_s. Inset: resulting phase diagram.

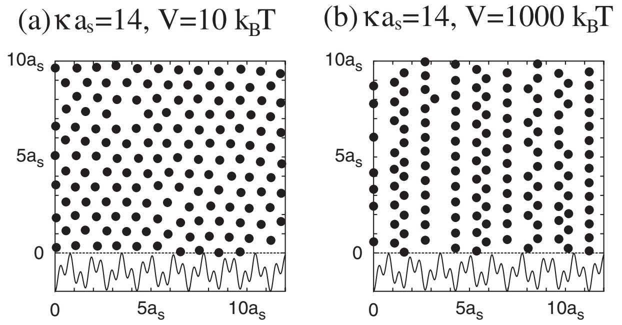
(a) $\kappa a_s = 14$, $V = 10\ k_BT$ (b) $\kappa a_s = 14$, $V = 1000\ k_BT$

FIG. 3. Snapshots of particle positions in a one-dimensional quasicrystalline potential indicated in the lower part of each figure. The inverse screening length $\kappa a_s = 14$ is chosen such that the colloidal system is solid for zero potential. For $V = 10k_BT$ (a) the rhombic-α phase occurs; for $V = 1000k_BT$ (b) the rhombic ordering has melted into a modulated liquid.

The structure and the dynamic properties of the modulated liquid are very interesting especially for large screening lengths where neighboring colloidal lines are strongly coupled to each other. In Brownian dynamic simulations we find that the lines are able to slide past each other on very long time scales; for more distant lines of particles, the sliding is clearer visible. This seems to preclude any two-dimensional solid structure. On the other hand, a possible glassy or even quasicrystalline ordering for very large screening lengths (i.e., very small κa_s) has to be investigated in more detail and will be presented elsewhere [18].

Since laser-induced melting in a quasicrystalline potential is not driven by fluctuations, we apply an extended Landau-Alexander-McTague theory, i.e., a typical mean-field theory, to explain the phase diagram in Fig. 2 analytically. For each of the four possible phases shown in Fig. 1, we need to calculate the free energy. Since their reciprocal lattice vectors have different lengths and in order to be able to distinguish between the two rhombic phases, an elastic term has to be included in the free energy. We therefore start with an expansion of the free energy in terms of mass density variations, $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$, where $\rho(\mathbf{r})$ is the density field in real space and ρ_0 its mean value [19]. In addition to the Alexander-McTague theory, we supplement it by an external-field term:

$$\mathcal{F} = \int dA\Big\{-V_{\text{ext}}(\mathbf{r})\delta\rho(\mathbf{r}) + \frac{b'}{2}[\delta\rho(\mathbf{r})]^2 - \frac{c_1}{2}[\nabla\delta\rho(\mathbf{r})]^2 + \frac{c_2}{2}[\nabla^2\delta\rho(\mathbf{r})]^2 - \frac{d}{6}[\delta\rho(\mathbf{r})]^3 + \frac{e}{24}[\delta\rho(\mathbf{r})]^4\Big\}. \qquad (3)$$

The integration is over the whole plane. The signs are chosen such that for positive constants b', c_1, c_2, d, and e and sufficiently small b', a phase transition to some (quasi)crystalline phase should occur. With the Fourier series for the density modulation, $\delta\rho(\mathbf{r}) = \sum_j \rho_j e^{-i\mathbf{G}_j\cdot\mathbf{r}}$, where $\mathbf{G}_j$ denotes the relevant reciprocal lattice vectors, including $\mathbf{G}_\alpha$ and $\mathbf{G}_\beta$, the free energy (3) is transformed into reciprocal space. The second-order term assumes the following form: $\sum_j(b' - c_1G_j^2 + c_2G_j^4)|\rho_j|^2$. The prefactor of $|\rho_j|^2$ prefers a certain wave number which we choose to be $G_j = G_0$ so that a phase transition to the triangular phase occurs at zero external potential. Introducing new constants b and c, the second-order term is then rewritten as $\sum_j(b - c[G_j^2 - G_0^2]^2)\rho_j^2$. The parameter b controls, as usual, the phase transition from the liquid to the crystalline phases and c is a typical elastic constant that distinguishes soft (small c) from rigid (large c) crystals. Since the lengths of the lattice vectors of the rhombic phases in Fig. 1 deviate from G_0, they are penalized by the elastic free energy relative to the triangular crystal.

To reduce the number of the six free parameters V, b, c, d, e, and G_0, we rescale the free energy $\mathcal{F}$ and the order parameters ρ_j appropriately and measure the wave numbers G_j in units of G_0. Using the external potential (2) in Eq. (3) for $\mathcal{F}$, the free energy density $\mathcal{F}/A$ in reciprocal space assumes the final form

$$\frac{\mathcal{F}}{A} = -V(\rho_\alpha + \rho_\beta) + \sum_j (b + c[G_j^2 - 1]^2)|\rho_j|^2 - \frac{1}{6}\sum_{j,k,l}\rho_j\rho_k\rho_l\delta(\mathbf{G}_j + \mathbf{G}_k + \mathbf{G}_l) + \frac{1}{24}\sum_{j,k,l,m}\rho_j\rho_k\rho_l\rho_m\delta(\mathbf{G}_j + \mathbf{G}_k + \mathbf{G}_l + \mathbf{G}_m), \qquad (4)$$

where $\delta(\cdots)$ denotes the Kronecker symbol. Note that, for convenience, all the reduced quantities and parameters are named the same way as the original ones.

The reduced free energy density only contains three essential parameters. The quantity V determines the strength of the quasiperiodic potential. The parameter b is usually identified with the reduced temperature. However, in experiments [7] and in our simulations (see Fig. 2) of the two-dimensional colloid system, crystallization is controlled by the reduced inverse Debye length κa_s. So it makes sense to identify b with κa_s. For small V our theory predicts crystallization for decreasing b, which corresponds to decreasing the inverse Debye length κa_s as illustrated in Fig. 2. Finally, c is an effective elastic constant as already noted.

For each phase characterized in Fig. 1 by a set of reciprocal lattice vectors, the free energy density (4) can be calculated using the relations between the lattice vectors, indicated in Fig. 1, to construct the third- and fourth-order terms of $\mathcal{F}/A$. Obvious fourth-order terms of the form $|\rho_i|^2|\rho_j|^2$ are not included in Fig. 1. We realized that Das and Krishnamurthy could identify a stable pentagonal phase [12] since they did not take into account the nontrivial fourth-order terms indicated in Fig. 1 as well as the rhombic phases. Symmetry dictates that $\rho_2 = \rho_5$ and $\rho_3 = \rho_4$ in the pentagonal phase; i.e., the free energy depends only on ρ_α, ρ_β, ρ_1, ρ_2, and ρ_3. For all other phases, $\rho_2 = \rho_3$, and the independent order parameters are ρ_α, ρ_β, ρ_1, and ρ_2 for triangular ordering and ρ_α, ρ_β, and ρ_2 in the rhombic phases. For a given point (V, b, c) in parameter space, the free energies of the crystalline phases are minimized with respect to the order parameters. The phase with the lowest free energy is then identified as the stable, solid phase if all its order parameters ρ_j differ from zero. Otherwise, if only the order parameters associated with $\mathbf{G}_\alpha$, $\mathbf{G}_\beta$, and $\mathbf{G}_1$ are nonzero, the system's phase is called modulated liquid. The numerical minimization of the free energies was performed with the help of the algebraic program MATHEMATICA.

The final phase diagram in the three-dimensional parameter space is shown in Fig. 4(a). The dark-gray and light-gray regions indicate, respectively, the stable triangular and stable rhombic-α phases. In the rest of the parameter space, a modulated liquid was found. So neither a pentagonal nor a rhombic-β phase exists. In Figs. 4(b)–

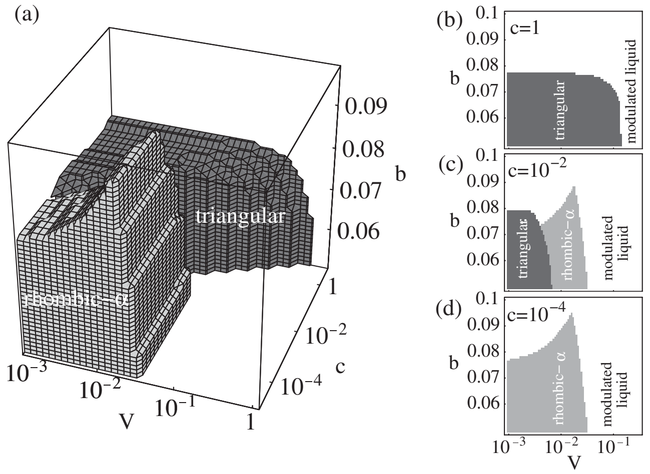

FIG. 4. (a) Phase diagram showing the regions of a stable triangular (dark gray) and rhombic-α (light gray) phase. In all other regions of the parameter space, only the modulated liquid phase is stable. (b)–(d) Phase diagrams for rigid crystals with $c = 1$ (b), intermediate systems with $c = 10^{-2}$ (c), and soft systems with $c = 10^{-4}$ (d).

4(d), phase diagrams for three constant elastic coefficients c are shown. Rigid triangular crystals [see Fig. 4(b)] can only be melted with very high laser intensities. A rhombic-α phase is strongly penalized by a large elastic constant c and therefore does not occur. For systems of intermediate [see Fig. 4(c)] or soft [see Fig. 4(d)] elasticity, a rhombic-α phase does exist. Note that for small c [see Fig. 4(d)], the triangular phase is only stable for $V < 10^{-4}$ and therefore is not visible in the phase diagram. The phenomena of light-induced freezing of the rhombic-α phase and light-induced melting of both stable phases are reproduced by the mean-field theory. The melting of the triangular phase followed by laser-induced freezing into the rhombic-α phase for increasing V [see Fig. 4(c)] could be an artifact since we cannot resolve it in our Monte Carlo simulations. Note that the validity of the mean-field theory for large V or laser intensities is not obvious. For periodic potentials, it was realized that the results at large V differ from the outcome of density functional theory [6]. The reason seems to be the truncation of the Landau expansion. However, the phase diagrams for the quasicrystalline potential calculated with Monte Carlo simulations [see Fig. 2] and the extended Landau-Alexander-McTague theory for sufficiently soft systems [see Fig. 4(c)] are very close. This demonstrates the validity of the mean-field theory and the fact that fluctuations do not determine the behavior of our system.

Using Monte Carlo simulations and an extended Landau-Alexander-McTague theory, we demonstrate that colloids in a one-dimensional quasicrystalline potential order in triangular and rhombic-α crystalline phases. Increasing the strength of the substrate potential further, a new type of light-induced melting is discovered that has its origin in the nonperiodicity of the potential. In contrast to reentrant melting on periodic substrates, the quasicrystalline potential melts the crystalline phases even when they already exist at zero potential. The resulting modulated liquid suggests interesting structural and dynamic properties that need to be fully explored. Our results should be observable in experiments. Given that colloids serve as model systems for statistical mechanics, our work provides guidance for investigating the ordering in appropriately nanostructured systems. On an atomic scale, the 1D quasicrystalline potential may be realized by atomic surfaces of decagonal quasicrystals cut along the tenfold symmetry axis.

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