Angular analysis of a model colloidal monolayer on a quasicrystalline substrate

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Abstract

We study the energetics of a crystalline colloidal monolayer interacting with a quasiperiodic-substrate potential. By comparison with the known periodic-substrate case, investigated by Novaco and McTague, we perform structural relaxations to investigate the angular dependence of the monolayer’s total energy, by means of FIRE minimizations. In the quasiperiodic case, like in the periodic one, the total energy depends on the mutual misalignment angle. The optimum angle depends on the lattice spacings mismatch ratio and on monolayer’s elastic properties. We find that the adopted method works fairly well in a regime where the monolayer-substrate interaction is relatively, but not extremely, small.

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1 Introduction

In this work we investigate a periodic or quasiperiodic corrugated surface, represented by a two-dimensional potential, which in experiments is generated by the interference of laser beams, interacting with a colloidal crystalline monolayer. As in experiment [1] we construct the substrate potential energy as the interference pattern of $N_s$ laser beams. We take $N_s = 3$ for the periodic triangular lattice case and $N_s = 5$ laser beams to reproduce the quasiperiodic potential represented in fig. [1]. A structure is quasiperiodic when it does show long range order, while not being periodic. In particular, a quasiperiodic structure shows - like periodic ones but unlike disordered amorphous solids - X-ray or neutron diffraction patterns with discrete Bragg peaks [2]. The colloidal lattice is formed by micrometer-sized charged objects forming an hexagonal two-dimensional lattice, due to their mutual repulsion. It is a very good approximation to assume that the substrate is perfectly stiff, while the colloidal lattice can be deformed. The $N_s = 3$ case has already been investigated in the literature, being the subject of Novaco-McTague classic papers [3], [4]. The target of these studies was the determination of the optimal geometric configuration of the system. We notice that the colloidal problem is similar to that of an atomic crystalline monolayer interacting with a solid corrugated surface. In particular, the Novaco-McTague studies [3], [4] focus on the case of substrate corrugation having the same $N_s = 3$ symmetry of the adsorbate, and demonstrated a non trivial angular dependence of the total energy of the system, unless the adsorbate lattice spacing matches exactly the substrate spacing: the system takes advantage of a small distortion that changes as a function of the relative orientation; eventually, the ground state is characterized by a non zero mutual misalignment. It is important to keep in mind that Novaco-McTague results only apply if a weak-coupling interaction is considered, where by weak-coupling we mean that the adsorbate-adsorbate interaction is the dominant one, while the adsorbate-substrate interaction is comparably smaller. While the periodic case is well understood, the behavior of such kind of system when the substrate is a quasiperiodic surface is still an open problem.

The main purpose of this work is to investigate the opportunity of extracting any amount of interesting information about the quasicrystalline case by means of a simulated minimization implemented with the FIRE algorithm. To achieve this task we start investigating the crystalline case, performing simulations to check the coherence of the protocol with the Novaco-McTague theory. If we call, respectively, $a_{pot}$ and $a_{col}$ the substrate and adsorbate lattice spacings and we define $\rho = \frac{a_{pot}}{a_{col}}$, we will call "underdense" a situation with $\rho < 1$ and "overdense" when $\rho > 1$, even though these definitions have a precise meaning in the crystalline
The significant interactions of the considered system are the colloid-colloid repulsion and the absorbate-substrate interaction. The repulsive interaction between \( N \) colloids is assumed to be a sum of two-body terms

\[
U_{cc} = \frac{1}{2} \sum_{j \neq l}^{N} U_{2B}(r_{j,l}),
\]

where \( r_{j,l} = |r_j - r_l| \) is the inter-colloid distance. The two-body interaction is described by the Yukawa potential, of the form

\[
U_{2B}(r_{j,l}) = \frac{Q}{r_{j,l}} e^{-r_{j,l}/\lambda}.
\]

We take for our simulations \( Q = 10^{11} \, \mu m \, zJ \) and \( \lambda = 0.2 \, \mu m \). The quasiperiodic substrate corrugation is treated as an on-site potential

\[
U_{ext} = \sum_{j}^{N} V(r_{j}).
\]
Here $r_j$ is a two-dimensional vector defining the position of the $j$th colloidal particle in the adsorbate plane.

The local terms are of the general form

$$V(r) = -V_0 \left| \sum_{m=1}^{N_s} e^{i k_m \cdot r} \right|^2 = -V_0 \sum_G e^{-iG \cdot r},$$

with

$$k_m = K \left( \cos \frac{2\pi (m-1)}{N_s}, \sin \frac{2\pi (m-1)}{N_s}, 0 \right).$$

Here $V_0$ is the corrugation amplitude of the substrate potential and the integer $N_s$ denotes the $N_s$-fold symmetry of the potential, and it accounts for both the periodic and quasiperiodic case, simply taking $N_s = 3$ (crystalline hexagonal lattice) or $N_s = 5$ (quasicrystalline 5-fold symmetry). $K = c_{N_s} a_{pot}$ is the reciprocal spacing of the potential, where $c_{N_s}$ depends on the symmetry type. In our cases we have $c_3 = \frac{4}{\sqrt{3}}$ and $c_5 = 2$. For the quasicrystalline case we have two sets of $G$s in pair of opposites with two lengths, shown in Fig. 2. The set of $G$s also includes the origin (unimportant, as it gives an overall constant to the energy) and the $N_s(N_s - 1)$ vectors (hence 20 vectors for $N_s = 5$, and 6 for $N_s = 3$) obtained from:

$$G = k_m - k_{m'} \quad \text{for } m \neq m'.$$

The total Hamiltonian is then given by

$$\hat{H}_{tot} = \hat{H}_0 + \hat{H}_1 = \sum_j \frac{\hat{p}_j^2}{2M} + U_{cc} + U_{ext}.$$

In the simulations we neglect the kinetic energy $\sum_j \frac{\hat{p}_j^2}{2M}$, as we consider the static problem of evaluating the optimum potential energy $E = \min_r (U_{cc} + U_{ext})$. In particular, we set several initial angles between the adsorbate and the substrate, let the colloidal particles relax and compute the optimal static energy $U_{cc} + U_{ext}$ after the relaxation.

The Novaco-McTague theory predicts analytically, for the periodic substrate case, the mutual misalignment angle corresponding to the minimizing configuration, as we will see later on. The total static energy exhibits a dependence from the misalignment angle $\theta$ between adsorbate and substrate, both in the crystalline and quasicrystalline case. This dependence shows a periodicity generated by the geometric properties of the considered systems. More precisely, for the crystalline potential, the hexagonal pattern of the substrate leads to a $60^\circ$ periodicity. The range that requires examination can be further reduced to the interval from $0^\circ$...
Figure 2: (a): construction of the $G$ vectors in terms of the $k_m$ vectors. (b): the 20 $G$ vectors of a 5-fold quasicrystalline potential generate a decagonal symmetry characterized by two different length scales $\frac{2\pi}{|G_1|} \simeq 0.85065 a_{pot}$ and $\frac{2\pi}{|G_2|} \simeq 0.52573 a_{pot}$.

to 30° due to the $\theta \to -\theta$ symmetry. The quasicrystalline potential generates in the reciprocal space a decagonal symmetry given by the 20 $G$ vectors, which come in pairs of opposites. The coupling between this 10-fold symmetry and the hexagonal pattern of the colloidal overlayer creates a 12° periodicity for the total energy. Both these symmetries are shown in Fig. 3. Also this periodicity can be reconducted to the study of a 6° range, due to the same $\theta \to -\theta$ symmetry.

We take for our calculations $a_{col} = 5.8 \mu m$, the typical inter-colloid distance in previous studies [1]. At the mentioned distance, the typical inter-colloid repulsion for the nearest neighbours is $\simeq 0.0044 zJ$, corresponding to a repulsive force $\simeq 0.0227 fN$.

2.1 The Harmonic approximation

If we assume that each colloid is denoted by a position $r_j$ and it moves in a neighbourhood of a crystalline equilibrium position $R_j$, calling $\alpha$ and $\beta$ the $x$ and $y$ components we can introduce the displacements $u_j = r_j - R_j$. When the displacements are small, it is a good approximation to Taylor-expand $U_{cc}$ at the
second order around the equilibrium configuration as follows:

\[ U_{cc}(\{r_j\}) \simeq U_{cc}(\{R_j\}) + \sum_{j,\alpha} \frac{\partial U_{cc}(\{R_j\})}{\partial u_{j,\alpha}} u_{j,\alpha} + \frac{1}{2} \sum_{j,\alpha,l,\beta} \frac{\partial^2 U_{cc}(\{R_j\})}{\partial u_{j,\alpha} \partial u_{l,\beta}} u_{j,\alpha} u_{l,\beta} \]  

(8)

The first-order term drops out because it represents the total force acting on the colloid at the equilibrium position. If we denote

\[ \phi_{j,\alpha,l,\beta} = \frac{\partial^2 U_{cc}(\{R_j\})}{\partial u_{j,\alpha} \partial u_{l,\beta}}, \]  

(9)

we end up writing

\[ U_{cc}(\{r_j\}) \simeq U_{cc}(\{r_j\}) + \frac{1}{2} \sum_{j,\alpha,l,\beta} \phi_{j,\alpha,l,\beta} u_{j,\alpha} u_{l,\beta}. \]  

(10)

If \( D \) is the dynamical matrix, given by

\[ D_{j,\alpha,l,\beta} = \frac{1}{M} \phi_{j,\alpha,l,\beta}, \]  

(11)

and we suppose a periodic motion of colloids around the lattice equilibrium position, in the form \( u_j^{\alpha} = \bar{u}_j^{\alpha} e^{i\omega t} \), then we can write the equation of motion for each coordinate of the \( j \)-th colloid as

\[ \omega^2 \bar{u}_j^{\alpha} = \sum_{l,\beta} D_{j,\alpha,l,\beta} \bar{u}_l^{\beta}. \]  

(12)
Using the Fourier notation for the displacement \( \hat{u}_j^\alpha = \epsilon_{\alpha}(k)e^{ikR_j} \) and defining the Fourier transform of the dynamical matrix \( D_{\alpha\beta}(q) = \sum_j D_{j,\alpha\beta}e^{iq(R_j-R_i)} \) we can reëxpress the problem to the diagonalization of a 2 \( \times \) 2 matrix (instead of \( 2N \times 2N \)) given by the equation

\[
\sum_\beta (D_{\alpha\beta}(q) - \omega^2 \delta_{\alpha\beta})\epsilon_{\beta}(q) = 0. \tag{13}
\]

From the diagonalization of this 2 \( \times \) 2 matrix we obtain 2 frequencies, labeled by \( s = 1 \) and \( s = 2 \), for each \( q \) in the first Brillouin zone. For small \( |q| \) the frequencies assume an acoustic behaviour \( \omega_{q,s} \approx v_s|q| \). The corresponding eigenvectors are the phonon polarization vectors \( \epsilon \) and they form, as usual, an orthonormal set:

\[
\epsilon_{q,s} \cdot \epsilon_{q,s'} = \delta_{s,s'} \quad \text{with} \quad \epsilon_{-q,s} = \epsilon^*_q \tag{14}
\]

In terms of these quantities, defining the displacements as:

\[
\hat{u}_j = \frac{1}{\sqrt{N}} \sum_{q} \sum_{s} \sqrt{\frac{\hbar}{2M\omega_{q,s}}} e^{iqR_j} \epsilon_{q,s} \left( \hat{a}^\dagger_{-q,s} + \hat{a}_{q,s} \right), \tag{15}
\]

together with the corresponding momentum, \( \hat{H}_0 \) is diagonalized in the usual way:

\[
\hat{H}_0 = \sum_{q} \sum_{s} \hbar \omega_{q,s} \left( \hat{a}_{q,s}^\dagger \hat{a}_{q,s} + \frac{1}{2} \right), \tag{16}
\]

while the interaction part reads:

\[
\hat{H}_1 = V_0 \sum_j \sum_G e^{-iG \cdot R_j} e^{-iG \cdot \hat{u}_j}. \tag{17}
\]

We now take a variational viewpoint. We assume that the phonon state is a coherent state of the form:

\[
|\Psi \rangle = e^{\sum_q (z_{q,s}^* \hat{a}_{q,s}^\dagger - z_{q,s} \hat{a}_{q,s})} |0 \rangle = e^{-\frac{1}{2} \sum_q |z_{q,s}|^2} e^{\sum_q z_{q,s}^* \hat{a}_{q,s}^\dagger} |0 \rangle, \tag{18}
\]

where the \( z_{q,s} \) are variational parameters, with \( z_{-q,s} = z_{q,s}^* \), and take the average energy on that state. Dropping the irrelevant zero-point-energy term we end-up writing:

\[
E_{\text{harm}} = \langle \Psi | \hat{H}_0 + \hat{H}_1 | \Psi \rangle = \sum_{q} \sum_{s} \hbar \omega_{q,s} \langle \Psi | \hat{a}_{q,s}^\dagger \hat{a}_{q,s} | \Psi \rangle + V_0 \sum_j \sum_G e^{-iG \cdot \hat{u}_j} \langle \Psi | e^{-iG \cdot \hat{u}_j} | \Psi \rangle. \tag{19}
\]
Notice that the total energy $E_{\text{harm}}$ is a function of the variational parameters $z_{q,s}$, as well as of the relative displacement of the $R_j$-lattice relative to the underlying (fixed) substrate, which we can in principle parameterise through the origin $R_0$ of the adatom lattice and, most importantly, of the global orientation of the $R_j$-lattice — and its reciprocal lattice, denoted by $\tau$ — relative to the substrate potential. The average of the different terms are rather simple to calculate on the coherent state, by using the fact that $|\Psi\rangle$ is an eigenstate of the phonon destruction operator, $\hat{a}_{q,s}|\Psi\rangle = z_{q,s}|\Psi\rangle$, hence

$$\langle \Psi | F_1(\hat{a}_{q',s'}^\dagger)F_2(\hat{a}_{q,s})|\Psi\rangle = F_1(z_{q',s'}^*)F_2(z_{q,s})$$

(20)

with arbitrary $F_1$ and $F_2$, provided the operators appear in the (normal) order shown above. For instance:

$$\langle \Psi | \hat{a}_{q,s}^\dagger \hat{a}_{q,s} |\Psi\rangle = |z_{q,s}|^2.$$  

(21)

We will use this device (after appropriate normal ordering) to calculate also the exponential term, $\langle \Psi | e^{-iG \cdot \hat{u}_j} |\Psi\rangle$.

### 2.2 The one-phonon approximation

We follow the Novaco-McTague theory [3] by taking a one-phonon approximation, appropriate for small $|q|$, which consists in expanding the exponential $e^{-iG \cdot \hat{u}_j} \approx 1 - iG \cdot \hat{u}_j$. The term with 1 drops out because $\sum_j e^{-iG \cdot R_j} = 0$ unless $G$ accidentally coincides with one of the reciprocal lattice vectors $\tau$ of the $R_j$-lattice. The variational one-phonon energy can then be written as:

$$E_{1-\text{ph}} = \sum_{q} \sum_{s} \hbar \omega_{q,s} |z_{q,s}|^2 - iV_0 \sum_{j} \sum_{G} e^{-iG \cdot R_j} \langle \Psi | G \cdot \hat{u}_j |\Psi\rangle.$$  

(22)

Starting from the latter term and for now considering only one $G$ term in the sum we can write:

$$\sum_{j} e^{-iG \cdot R_j} \langle \Psi | G \cdot \hat{u}_j |\Psi\rangle = \sum_{j} \frac{1}{\sqrt{N}} \sum_{q} \sum_{s} \sqrt{\frac{\hbar}{2M \omega_{q,s}}} e^{i(q-G) \cdot R_j} G \cdot \epsilon_{q,s} (z_{q,s}^* + z_{q,s}).$$

(23)

Now we use the reciprocal lattice Kronecker-delta relationship:

$$\sum_{j} e^{i(q-G) \cdot R_j} = N e^{i(q-G) \cdot R_0} \sum_{\tau} \delta_{q G - \tau} = N \sum_{\tau} e^{-i\tau \cdot R_0} \delta_{q G - \tau},$$

(24)

where we single-out the position of the first translation point $R_0$ which could in principle move away from the origin, to minimise the energy. Reinstalling now the
sum over $G_s$, let us define the following short-hand (see Eq. (7a) in the original PRB):

$$g_{q,s} = V_0 \sqrt{\frac{\hbar}{2M\omega_{q,s}}} \sum_G \sum_\tau G \cdot \epsilon_{q,s} e^{-i\mathbf{R}_0 \cdot \delta_{q,G - \tau}} \equiv V_0 \sqrt{\frac{\hbar}{2M\omega_{q,s}}} f_{q,s}. \quad (25)$$

Notice that $g_{-q,s} = g_{q,s}^*$, and similarly for $f_{q,s}$, because of the property Eq. (14) under $q \rightarrow -q$ of the polarization vectors, and the fact that both $G$ and $\tau$ are inversion symmetric (for every vector in the sum, there is always the opposite one). In terms of such a quantity we can finally write:

$$E_{1-\text{ph}} = \sum_{q} \sum_s \hbar \omega_{q,s} |z_{q,s}|^2 - iN \sum_q \sum_s g_{q,s} (z_{q,s} + z_{-q,s}^*). \quad (26)$$

This expression suggest the rescaling $z_{q,s} = \sqrt{N} \xi_{q,s}$ which gives the correct behavior for the total energy $E_{1-\text{ph}}$. In terms of such rescaled variational parameters, we get:

$$\frac{E_{1-\text{ph}}}{N} = \sum_{q} \sum_s \left( \hbar \omega_{q,s} |\xi_{q,s}|^2 - i (g_{q,s}^* \xi_{q,s}^* - g_{q,s} \xi_{q,s}) \right), \quad (27)$$

where we have manipulated the sum, using the properties under $q \rightarrow -q$, in such a way that the quantity written is real for each value of $q, s$. Now we minimise this expression with respect to the variational parameters $\xi_{q,s}$, with the usual trick of taking the derivative with respect to $\xi_{q,s}$, assuming $\xi_{q,s}$ to be independent, and imposing this derivative to be zero. This gives the condition (see Eq. (9a) in [4]):

$$\xi_{q,s} = i \frac{g_{q,s}^*}{\hbar \omega_{q,s}} \quad \Rightarrow \quad \xi_{q,s}^* = -i \frac{g_{q,s}}{\hbar \omega_{q,s}}. \quad (28)$$

Substituting back in the expression for $E_{1-\text{ph}}$ we get a cancellation of the $\hbar$ factors:

$$\epsilon_{1-\text{ph}} = \frac{E_{1-\text{ph}}}{N} = -\sum_q \sum_s \frac{|g_{q,s}|^2}{\hbar \omega_{q,s}} = -\frac{V_0^2}{2M} \sum_{q} \sum_s \frac{|f_{q,s}|^2}{\omega_{q,s}^2}. \quad (29)$$

Summarizing, we have now $\epsilon_{1-\text{ph}}$ (energy per colloid) which is still a function of $\mathbf{R}_0$ and of the orientation $\theta$ of the $\tau$-reciprocal lattice relative to the $G$-Fourier (quasi)-crystalline points, and needs to be further minimised:

$$\left\{ \begin{align*}
\epsilon_{1-\text{ph}} &= -\frac{V_0^2}{2M} \sum_{q} \sum_{s=1,2,3} \frac{|f_{q,s}|^2}{\omega_{q,s}^2} \\
 f_{q,s} &= \sum_G \sum_\tau G \cdot \epsilon_{q,s} e^{-i\mathbf{R}_0 \cdot \delta_{q,G - \tau}}.
\end{align*} \right. \quad (30)$$
Figure 4: The relations among the $\mathbf{G}$, $\mathbf{q}$ and $\mathbf{\tau}$ vectors and the angles $\theta$ and $\phi$.

The energy denominator tends to favour small-$\mathbf{q}$ transverse modes (which have lower sound velocity and, thus, smaller frequency); these, in turn, tend to rotate the overlayer so as to make the factor $\mathbf{G} \cdot \mathbf{\epsilon}_{q,s}$ larger. Notice that the sum over $\mathbf{q}$ is really restricted to a finite number of points through the Kronecker-delta present in $f_{q,s}$: generally as many $\mathbf{q}$ points as the $\mathbf{G}$ vectors given by Eq. (6).

For the crystalline case, in the first Brillouin zone at each $\mathbf{\tau}$ is associated a $\mathbf{G}$, and therefore a $\mathbf{q}$. Every $(\mathbf{q}, \mathbf{G})$ set is characterized by the same rotational symmetry, so if $N_s(N_s - 1)$ is the number of $(\mathbf{q}, \mathbf{G})$ pairs we can write

$$\epsilon_{1-\text{ph}} = -\frac{nV_0^2}{2M} \sum_{s=L,T} \frac{(\mathbf{G} \cdot \mathbf{\epsilon}_s)^2}{\omega_s^2}.$$  

(31)

The geometry of these vectors is shown in Fig. 4. Expliciting the dot products $\mathbf{G} \cdot \mathbf{\epsilon}_L = -|\mathbf{G}| \cos(\phi)$ and $\mathbf{G} \cdot \mathbf{\epsilon}_T = |\mathbf{G}| \sin(\phi)$. In the small-$|\mathbf{q}|$ limit $\omega_{L,T} \simeq c_{L,T}|\mathbf{q}|$ and noting that $\sin(\phi) = |\mathbf{\tau}| |\mathbf{q}| \sin(\theta)$ we get

$$\epsilon_{1-\text{ph}} = -\frac{nV_0^2}{2M} \left[ \frac{|\mathbf{G}|^2}{c_L^2 |\mathbf{q}|^2} + \frac{|\mathbf{G}|^2 |\mathbf{\tau}|^2 \sin(\theta)^2}{|\mathbf{q}|^4} \left( \frac{1}{c_L^2} - \frac{1}{c_T^2} \right) \right].$$  

(32)

From the minimization of this energy with respect to $\theta$ in the crystalline case we find the Novaco-McTague formula for the optimal angle

$$\cos(\theta_{NM}) = \frac{1 + \rho^2(1 + 2\delta)}{\rho(2 + \delta(1 + \rho^2))}.$$  

(33)

In this equation we called $\delta = (\frac{c_L}{c_T})^2 - 1$ and $\rho = \frac{|\mathbf{\tau}|}{|\mathbf{G}|} = \frac{a_{\text{pot}}}{a_{\text{col}}}$ is the mismatch ratio. We notice that, since $|\cos(\theta)| \leq 1$, it has to be $\delta > \frac{1}{\rho}$ which gives $c_T \leq c_L \sqrt{\frac{\rho}{\rho+1}}$.

Specifically, following the procedure of Ref. [6] we find for our colloidal system $c_L = 0.3762$ mm/s and $c_T = 0.2072$ mm/s, so that $\delta = 2.296538$ which satisfies the condition $\delta > \frac{1}{\rho}$ for $\rho > 0.43544$. 

11
3 Technical implementation

3.1 Confining and boundary conditions

To maintain a well-defined average inter-colloid distance, we need to oppose their natural repulsion. Starting from a square supercell with a 1000 µm side, that could contain 34326 colloids, we cut out a circular portion. To prevent the island to expand under the \( U_{cc} \) repulsion we add a suitable confining parabolic potential, even at the cost of introduce border effects. We opt for this solution because imposing any periodic boundary conditions would certainly be incompatible with the quasiperiodic potential. The colloids are initially placed on a rotated hexagonal lattice with spacing \( a_{col} \), and a disk of radius \( r_c \) is cut out from it. The confining potential is given by

\[
V_{conf}(\mid r \mid) = \begin{cases} 
0 & \text{for } \mid r \mid < r'_c \\
\frac{A}{2}(\mid r \mid - r'_c)^2 & \text{for } \mid r \mid \geq r'_c.
\end{cases}
\] (34)

The value of A is set to \( A = 0.02 \) fN/µm. The radius \( r'_c \) is tuned in such a way that in a full relaxation in the absence of substrate corrugation (\( V_0 = 0 \)) the mutual distances between colloid placed at more than five lattice spacings from the outer boundary vary by less than 0.01%. In order to demonstrate the size-independence of the model we repeated every calculation using two different confining potentials, one including \( N = 9757 \) colloids and the other including \( N = 8185 \) colloids, with confinement parameters reported in Table. A third one is also reported for completeness. Figure 5 represents the initial condition for the smallest disk at \( \theta = 0 \).

3.2 The FIRE minimization

FIRE stands for Fast Inertial Relaxation Engine [7]. It is a computational relaxation method to find mechanically stable equilibrium configurations of atomistic systems minimizing the potential energy under given initial conditions. Specifically it is an optimized Molecular Dynamics (MD) method: while MD is based

<table>
<thead>
<tr>
<th>( N )</th>
<th>( r_c (\mu m) )</th>
<th>( r'_c (\mu m) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8185</td>
<td>279.2</td>
<td>271.3</td>
</tr>
<tr>
<td>9757</td>
<td>301.6</td>
<td>296.3</td>
</tr>
<tr>
<td>10981</td>
<td>321.94</td>
<td>314.66</td>
</tr>
</tbody>
</table>

Table 1: Parameters characterizing the confining potential.
Figure 5: Initial configuration of the $N = 8185$ colloids sample, at $\theta = 0$. The particles are size and color coded, with big red particles sitting near the $U_{\text{ext}}$ minima and smaller blue ones climbing to the top values of the corrugation.

on integration of the equations of motion, usually with a fixed time step $\delta t$, FIRE is able to tune $\delta t$ to optimize the minimization process. To illustrate the method, consider a blind skier looking for the fastest way to the bottom of a valley in an unknown mountain landscape described by the potential energy $E(x)$, with $x = (x_1, x_2)$. Assuming that the skier is capable, when necessary, to slow down and steer, his motion would be described by

$$\dot{v}(t) = \frac{F}{M} - \gamma(t)|v(t)|(\dot{v}(t) - \dot{F}(t)), \quad (35)$$

where $F = -\nabla E(x)$. The role of the function $\gamma(t)$ is to suitably tune the skier’s acceleration, following directions that are steeper than the current direction of motion, if the dissipated power $P(t) = F(t) \cdot v(t)$ is positive. Conversely, in order to avoid uphill motion, he has to stop as soon as the power $P(t)$ becomes negative. In this way the skier is able to exploit inertia to reach in a quicker way the bottom of the valley.

The FIRE algorithm is a discrete version of Eq. (35), using an adaptive time step $\delta t$ and based on a standard MD integration as follows. The integration trajectory is continuously tuned relying on two velocity modification rules: the
just mentioned stop to avoid uphill motions and an inertial correction \( \mathbf{v} \rightarrow (1 - \alpha)\mathbf{v} + \alpha|\mathbf{v}|\hat{\mathbf{F}} \) based on the parameter \( \alpha = \gamma \delta t \). Initially, increasing and decreasing dimensionless parameters \( f_{\text{inc}}>1 \) and \( f_{\text{dec}}<1 \) are set and initial conditions \( \mathbf{x} = 0, \mathbf{v} = 0, \alpha_{\text{start}} \) and \( \delta t \) are given. At this point, an integration step is carried out. Then, the algorithm evaluates \( P \), sets \( \mathbf{v} = (1 - \alpha)\mathbf{v} + \alpha|\mathbf{v}|\hat{\mathbf{F}} \) and re-evaluates \( P \): if \( P \) has been positive for more than a given \( N_{\text{min}} \) number of steps it increases \( \delta t \rightarrow \min(\delta t f_{\text{inc}}, \delta t_{\text{max}}) \). If the power is negative, instead, FIRE decreases the time step \( \delta t \rightarrow \delta t f_{\text{dec}} \), freezes the system setting \( \mathbf{v} = 0 \) and sets \( \alpha \) back to \( \alpha_{\text{start}} \). Then, it performs the integration and restarts. It is been observed that for most systems the following parameter values are suitable: \( N_{\text{min}} = 5, f_{\text{inc}} = 1.1, f_{\text{dec}} = 0.5 \). The only tunable parameter is \( \delta t_{\text{max}} \): for atomistic systems that need a typical MD integration timescale \( \approx 10^{-15} \) s one can estimate \( \delta t_{\text{max}} \approx 10 \delta t_{\text{MD}} \). We follow the same approach, using our \( \delta t = 0.5 \) ms, because the objects we deal with are colloids, that are micrometer-sized particles far bigger than atoms. In our case we set the algorithm to stop when either the total force acting on the colloids or their kinetic energy becomes smaller than a suitable fixed thresholds, namely \( 10^{-10} \) fN for the force and \( 10^{-15} \) zJ for the energy. We observe that in most cases minimization ends because of crossing the energy threshold.

### 3.3 Simulations

In our computations we take the fixed value of 5.8 \( \mu \)m for the colloidal lattice spacing \( a_{\text{col}} \), and we vary \( a_{\text{pot}} \) to explore a range of values of \( \rho \). Given proper conditions, namely the starting angular configuration and potential spacing, the FIRE routine simulates a rapid relaxation of the monolayer. If enough FIRE relaxation steps are allowed the algorithm reaches a - at least local - minimum finding a compromise between the tendency of the substrate potential to attract as many particles as possible in the potential wells and the colloid-colloid repulsion, trying to maintain the particles in a regular lattice configuration. Our approach consists in performing sequences of simulations, each with fixed corrugation amplitude and potential spacing, looping over the initial angular displacement.

Figure 6 reports the system’s total energy before the relaxation for both crystalline and quasicrystalline case. As there is no relaxation, one expects a perfectly flat energy profile, in the infinite-size limit. The observed oscillations are therefore entirely due to the finite size of the disks. We see that the energy oscillation is of the order \( \approx 0.8\% \) for the crystalline case and \( \approx 0.15\% \) for the quasicrystalline case. They are therefore quite small, even compared to the fraction \( \sqrt{\frac{2\sqrt{3}}{N}} \) of particles at the border, which gives \( \approx 3.6\% \) and \( \approx 3.3\% \) with the two confinements. Oscillations are less relevant with the quasiperiodic potential,
Figure 6: Total energy per particle before the relaxation for the initial condition of perfect hexagonal lattice with two different confinements for crystalline (a) and quasicrystalline (b) substrate. Both figures are for $a_{pot} = 5.2 \, \mu m$ and $V_0 = 1 \, \text{zJ}$.

probably for the weaker total energy of the system.

4 Results

Using FIRE we have to keep in mind that the algorithm performs a blind relaxation seeking for a minimum. In principle, it is not impossible that this relaxation involves an overall rotation of the adsorbate, giving a minimum not reflecting the
investigated angle. This is more likely to happen in a weak-coupling regime, because the adsorbate-substrate interaction is not able to pin down the colloidal lattice, thus allowing an almost rigid rotation that causes the loss of information about the initial angle. This occurrence is illustrated in Fig. 7, showing that colloids after relaxations with quite different angles \( \theta = 2.8^\circ \) and \( \theta = 4.4^\circ \) end up in the same disposition. Following this observation, we compute for every colloid with six nearest neighbours (to mitigate border effects) the average angle \( \theta_{ave} \) that the six bonds form with a given direction, namely the \( x \) axis. The average bond angle that the bonds of the \( j \)-th colloid with its nearest neighbours form with the \( x \) axis neighbour are calculated as

\[
\theta_{j,ave} = \frac{1}{6} \sum_{k=1}^{6} \text{mod(\text{arctan}(\frac{\Delta y_k}{\Delta x_k}), 60)},
\]

where \( \Delta x \) and \( \Delta y \) are represented in Fig. 8. We then calculate the total average angle as

\[
\theta_{ave} = \frac{1}{N_6} \sum_j^{N_6} \theta_{j,ave},
\]

where \( N_6 \) is the number of colloids surrounded by 6
Figure 8: An example of colloid surrounded by its 6 nearest neighbours. For the calculation of its average angle, for each neighbor, the $x$ and $y$ projections of the bond vector are inserted in Eq. (36), so that an average is obtained.

nearest neighbours. We notice that the spontaneous realignment described above occurs for corrugation amplitude $V_0 \simeq 0.01$ zJ and thus consider this magnitude the typical weak-coupling regime for the system. Figure 9 illustrates this situation for both crystalline and quasicrystalline substrate, showing a good correlation between the steps in energetics and those in the final average angle. This is due to the fact that the same final configuration leads to the same energetics. We understand from this preliminary discussion that, even the Novaco-McTague theory applies in a weak coupling regime, the size of the model disk adopted for our simulations introduces a lower limit of corrugation amplitude, of the order of $V_0 \simeq 0.01/0.02$ zJ, below which the method fails to identify a proper angular dependence.

In view of this observation we find that the ideal regime for our method to generate reliable results is around $V_0 \simeq 0.1$ zJ. Indeed, for this corrugation strength the overlayer should remain pinned near to the imposed starting misalignment, but still in a configuration reminescent of the original hexagonal lattice, as shown in Fig. 10. Compared to Fig. 7, note that the moiré pattern is now more pronounced, with a larger portion of colloids sitting at, or very near to, the corrugation minima. Note also how quickly this corrugation pattern rotates with $\theta$. 
4.1 Crystalline substrate

We exemplify the possible mismatching conditions adopting four mismatch values of $\rho$, two underdense and two overdense, exploring a range spreading ±15% around the matched $\rho = 1$ value. During the relaxation, FIRE identifies a compromise between the inter-colloid repulsion, trying to maintain colloids at fixed average mutual positions, and the substrate-adsorbate interaction, trying to rotate and stretch the crystal. Figures 11 and 12 show the angular dependence of the total energy and average bond angle, for $V_0 = 0.1 \ zJ$ and different mismatch conditions.
values. Observe that for $a_{pot} = 5.2 \, \mu m$ and $a_{pot} = 6.6 \, \mu m$ the average angle $\theta_{ave}$ tracks fairly closely the initial angle $\theta$. As a result, the energy profiles express meaningful angular dependencies, as long as $\rho = \frac{a_{pot}}{a_{col}}$ is far from matching. The situation becomes far less clear as $\rho$ approaches unity, for $a_{pot} = 5.6 \, \mu m$ and $a_{pot} = 6.0 \, \mu m$: as we approach a matching value of $a_{pot}$ colloids interact more strongly with the substrate, being closer to an optimum configuration. Furthermore, in underdense systems adsorbate and substrate interact more strongly, due to the major availability of deep wells for each particle. For this reason simulations with $a_{pot}$ values quite far from the matching conserve memory about initial angle, while near matching the minima tend to ”suck in” extended patches of particles, resulting in a relatively small ratio $\frac{N_a}{N}$, and thus have a $\theta_{ave}$ value of little significance. Indeed, near matching we find unrealistically flat average angle curves. Conversely, the energy curve tends to straighten out when moving away from the matching configuration. Interestingly, in the underdense case far from the matching ($a_{pot} = 5.2 \mu m$) illustrated in Fig. [11] (a) and (b), $\theta_{ave}$ follows $\theta$ quite closely, except in a tiny neighbourhood of $\theta_{NM}$, the only range in which FIRE managed to fully rotate the adsorbate. In the overdense condition we have $\theta_{ave} \simeq \theta$ with no special behavior near $\theta_{NM}$. The reason is clear: for the underdense case it is easier for the particles to reach a deep minimum without a large displacement away from the initial perfect hexagonal arrangement, so that even for a weak corrugation the stronger interaction due to the Novaco-McTague
Figure 11: (b,d) Total energy and final average angular orientation (a,c) as a function of the initial angle for a crystalline substrate with $V_0 = 0.1$ zJ, for two underdense mismatch ratios: (a,b) $\rho = 5.2 \approx 0.8966$ and (c,d) $\rho = 5.6 \approx 0.9655$.

angle becomes dominant. Figure 13 shows this effect: near $\theta_{NM}$ the particles can rearrange the layer to profit of the $U_{ext}$ interaction, forming optimally-sized patches of matching colloids.

We also notice a systematic difference between overdense and underdense case. Namely, in the underdense case the algorithm is able to recover almost exactly the theoretical optimum configuration, while it seems to fail in the overdense case. The reason of this behavior is to be researched in the particles dis-
placements: in the underdense case $V(r)$ has more potential wells available than colloids to place, and it takes in average smaller displacements to arrange colloids in the wells. Conversely, in the overdense case, particles need to move more to reach the nearest well available: larger displacement trigger the strongly non-linear short-distance repulsion $U_{2B}$. As a confirmation, Figure 14 reports the contribution of the interaction energy $U_{ext}$ for overdense and underdense cases: it turns out that the underdense case interaction with the substrate is strongly negative, especially in the vicinity of the Novaco angle, indicating that the corrugation effect is by far the dominant one. Conversely, in the overdense case the
adsorbate interacts less strongly with the substrate, leading to the colloid-colloid interaction to dominate. Figure 14 also shows that $U_{\text{ext}}$ is especially dominant close to the matching.

In general, all angular plots are essentially non-smooth, because every single relaxation is independent from the others. As a result, the algorithm finds every time a different minimum uncorrelated with the previous and next ones. However, the general trends are fairly clear.

### 4.2 Quasicrystalline substrate

We come now to the main subject of this thesis. We first investigate matching configurations, to check if an optimal angle $\theta_{NM} = 0^\circ$ like in the crystalline case. In order to find a matching configuration for the quasicrystalline case, the condition to verify is $|\tau| = |G|$: as there are two sets of $G$s characterized by two different lengths, to match $\tau$ vectors two values of $a_{pot}$ are suitable, namely $a_{pot} \simeq 5.905 \, \mu m$ for the short $G$s and $a_{pot} \simeq 9.554 \, \mu m$ for the long $G$s - see Fig. 2. Like for the crystalline case, we focus on a corrugation amplitude $V_0 = 0.1 \, zJ$, leaving stronger couplings for a brief discussion in Sect. 4.3. Figure 15 shows energetics and average angle as a function of the initial angle for the two matched quasicrystalline substrate cases. In both cases we observe the expected minimum at $\theta = 0$, but it turns out that the minimization is not sensitive to small adjustments of the initial angle: in a $\simeq 0.5^\circ$ range around the origin we find the same optimum configuration in a neighborhood of the expected minimum. We also notice that the matched case with smaller $a_{pot}$ exhibits a better correlation between $\theta$ and $\theta_{ave}$. The reason is similar to what happens in the crystalline case: a larger $a_{pot}$ is associated with less wells available for the colloids which are obliged to compete for the wells, causing an overall adsorbate rotation.

Figure 16 shows the angular dependence of the energy and the average angle for two mismatched ratios. We notice that moving away from matching the energetics became rapidly very flat, even though exhibiting some shallow local minima, in analogy to the crystalline case. The resulting optimal configurations are reported in Figure 17 for a few angles $\theta$. Another similarity with the crystalline case is the tendency of the average-angle curve to become flatter approaching one of the matched ratios, because the algorithm is able to find a optimum configuration starting from several different misalignment angles. In contrast, far from matching we have a good $\theta_{ave} \simeq \theta$ correlation for the overdense case.

Figure 18 shows the contribution of the adsorbate-substrate interaction to the total energy for several length ratios. We notice that away from either matching values of $a_{pot}$, and especially for large $a_{pot}$, the interaction with the substrate
becomes effectively quite weak (less negative). The strongest interaction occurs for the smaller matched spacing $a_{pot} = 5.905 \mu m$. Comparing Fig. 14 and 18 we see that, for the same $V_0$, the quasicrystalline substrate interacts significantly less than the crystalline substrate system, having roughly three times less $U_{ext}$ values.

Comparing panels a, c of Figs. 15 and 16 we conclude that, like in the crystalline case, when we move away from the matching values of $a_{pot}$ the minimization preserves the initial angle, so that $\theta_{ave} \simeq \theta$. At the same time the energetics (reported in panels b, d of Figs. 13 and 16) indicate that its angular dependence is far flatter than the crystalline case for the same $V_0$.

4.3 Strong coupling

We come to consider the strong-coupling regime, where the corrugation amplitude is of order of one or several $zJ$. We carry out relaxations with $V_0 = 1 \ zJ$, which is already a quite strong interaction, and $V_0 = 5 \ zJ$, a rather extreme situation.

For the crystalline case, where we knew $\theta_{NM}$ analytically, the aim is to check the validity limits of the theory. For those values of $V_0$ we expect to lose information about the angle, $a_{col}$ and perhaps even the adsorbate crystalline structure - because of the dominant corrugation effects. The simulations usually show a local minimum in a neighbourhood of $\theta_{NM}$, but for $\theta > 10^\circ$ the overlayer finds several different optimal configurations, corresponding to other minima, sometimes even deeper than the theoretical one. The expected loss of information about the starting configuration occurs differently dependingly on $\rho$. In general, memory of initial angle is lost more rapidly in underdense situations than in overdense ones, for the same reason as discussed in Section 4.1. For a 5 $zJ$ corrugation amplitude the adsorbate structure is completely lost, and the colloids are arranged almost exactly at the corrugation wells, as show in Fig. 20.

As for the quasicrystalline potential we observe a fair $\theta_{ave} \simeq \theta$ correlation for small $a_{pot}$, especially in the mismatched condition $a_{pot} = 5.2 \ \mu m$ (Figures 21a and 22a). A larger $a_{pot}$ determines large deviations, similar to Fig 12a. For a large $a_{pot}$ value (overdense condition), the scarcity of deep potential wells lead the colloids to being pushed violently against each other, losing completely the crystalline structure: this is confirmed by the distribution around 0 of the average angle reported in Fig. 21c and 22c. Also the fraction $N_6/N$ is of the order of $\simeq 40\%$, indicating that few colloids are surrounded by 6 nearest neighours and the crystalline structure is lost. In these conditions the significance of $\theta_{ave}$ is scarce, because the mean is computed on a small fraction of the total number of colloids. The asymmetry between overdense and underdense is more evident.
than in the crystalline case. As for the energetics (Figures 21b, d and 22b, d), its angular dependence is quite erratic for all four considered length ratios.

4.4 Exploring the mismatch dependence

The same method can also be applied to explore the dependence of the total energy on the corrugation length scale. For this purpose, we fix the initial angle to $\theta = 3^\circ$ and perform a sequence of simulations changing $a_{pot}$, with a corrugation amplitude $V_0 = 0.1 \text{ zJ}$, both for the crystalline and the quasicrystalline substrate. Figure 23 shows the resulting dependence. The crystalline case, Fig. 23a, exhibits very sharp minima at lattice matching ($a_{pot} = a_{col}$) and its submultiples ($a_{pot} = a_{col}/n$, for integer $n$), with all or most particles ending up in the corrugation wells. Indeed, the total energy per particle is very close to $-V_0$ at these minima. The quasicrystalline case, Fig. 23b, has much shallower minima around the matching values $a_{pot} \approx 1.018 a_{col}$ and $a_{pot} \approx 1.647 a_{col}$, plus other minima at the underdense side.

5 Conclusion

In the present work we simulate structural relaxations with the FIRE algorithm for a system composed by a colloidal lattice adsorbate interaction with a quasicrystalline potential, to investigate if any information can be extracted with this approach. In particular we are interested in finding parameter ranges defining a regime in which this method provides reliable results. By analogy with a crystalline potential system, we investigate the existence of an angular energy dependence in the quasicrystalline case. We find that for a corrugation of magnitude $\approx 0.01 \text{ zJ}$, even though the known theory applies in this regime, the coupling is too weak to distinguish between different initial configurations, at least with a sample of $\approx 10^4$ particles. This causes the impossibility to establish a well-defined minimum. Most likely, a much larger circular sample could improve the situation. We obtain far better results in an intermediate coupling regime, $V_0 = 0.1 \text{ zJ}$, especially in an underdense regime. Specifically, underdense systems are more likely to recover the theoretical minimum in the crystalline case and to maintain their initial orientation in the quasicrystalline one.

Furthermore, near matching conditions are particularly critical. The quasicrystalline geometry has two matching $a_{pot}$ values, compared to only one in the crystalline case. At or near matching the deep ”commensurate” minimum sucks in the overlayer with the result of making a satisfactory control of the angle impossible or at least very difficult. In alternative to simulating huge samples, a
constraint on the overall angular rotation may provide some mitigations to these
difficulties.
Figure 13: Relaxed particles positions with crystalline substrate, for $a_{pot} = 5.2 \, \mu m$ and $V_0 = 0.1 \, zJ$. Comparison between different initial angles: (a) $\theta = 0^\circ$, (b) $\theta = 2^\circ$, (c) $\theta = 3.6^\circ \simeq \theta_{NM}$, (d) $\theta = 5^\circ$, (e) $\theta = 8^\circ$, (f) $\theta = 10^\circ$. 

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Figure 14: Interaction $U_{ext}$ energy per particle comparison for underdense and overdense cases. The calculations are carried out for the $N = 9757$ sample.
Figure 15: Same as Fig. 12 for the two quasicrystalline matched cases, with a corrugation $V_0 = 0.1$ zJ.
Figure 16: The average angle (a and c) and the angular dependence of total energy (b and d) for a two mismatched quasicrystalline substrate.
Figure 17: Same as Fig. 13 but for a quasicrystalline corrugation of amplitude $V_0 = 0.1$ and spacing $a_{pot} = 5.2 \, \mu m$ considering a starting misalignment angle of: (a) 0°, (b) 0.8°, (c) 1.5°, (d) 3°, (e) 4.5°, (f) 6°.
Figure 18: Same as Fig. 14 for the quasicrystalline potential.

Figure 19: Final configurations of the colloids in the quasicrystalline case (including 1345 particles) for $a_{pot} = 9.554 \, \mu m$ and $V_0 = 0.1 \, zJ$. For two different initial angles $\theta = 0^\circ$ (a) and $\theta = 0.6^\circ$ (b) we have the same final configuration: for initial angle from $0^\circ$ to $0.6^\circ$ we obtain the same moirè pattern.
Figure 20:  a: For a corrugation crystalline substrate with strong corrugation amplitude $V_0 = 5 \text{ zJ}$ and $a_{pot} = 5.2 \text{ µm}$, all colloids end up near the bottom of the potential wells, depicted in red.  b: The colloids are placed almost exactly at the crystalline potential spacing.
Figure 21: Same as Fig. [11] but for the quasicrystalline potential with large amplitude $V_0 = 1 \ zJ$: (a,b): a mismatched underdense condition (c,d): a mismatched overdense condition.
Figure 22: Same as Fig. 21 for the two matched conditions.
Figure 23: Mismatch dependence of total energy for crystalline (a) and quasicrystalline (b) substrate, starting from an angle \( \theta = 3^\circ \).
References


