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of the depinning transition
in a 2D colloidal layer

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I.D. n° 864967
Academic Year 2016/2017
PACS code: 46.55.+d
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3 October 2017

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1

Introduction

Our work makes a step in the direction of answering the following question: what happens to the dry contact between two crystals when it changes from extremely slippery (“superlubric”) to strongly pinned (i.e. characterized by a large static friction) as the atomic corrugation is increased, e.g. by application of an increasing load? We address this question regarding atomic-scale contact mechanics in an analog system, namely an elastic layer of mutually interacting colloidal particles in aqueous solution in contact with a rigid externally imposed corrugation potential realized by means of a laser-light pattern. We investigate the frictional proprieties of this 2D interface by means of computer simulations.

Motivated by recent experiments [1, 2, 3] and theory [4, 5], we simulate a monolayer of mutually repulsive colloidal particles interacting with an egg-carton optical external potential. Friction is probed by means of the application of a uniform external force pushing the colloids sideways. When the equi-
librium spacing of the mutually interacting colloids is incommensurate to the periodicity of the egg-carton potential, the system undergoes an Aubry-type transition between a superlubric state, where sliding can be activated by an arbitrarily small force, and a statically pinned state as the corrugation-potential amplitude is increased. In the present thesis we characterize this transition by means of molecular-dynamics simulations. Our main contributions in the direction of answering the above question are: a detailed energetic analysis of the system as a function of the misalignment angle between the corrugation lattice and the colloidal monolayer, the computation of the structural phase diagram of the Aubry transition and of the dynamical response of the system, and the characterization of the coexistence region of the first-order transition which the system undergoes from the superlubric to the pinned state.

In the standard approximate Coulomb model \cite{6,7}, friction is defined as the force opposing the relative motion of two objects. This is not a fundamental force and it is introduced by hand in the equation of motion with suitable empirical coefficients. The Coulomb model defines two different kinds of frictional forces: the static friction $F_s$ and the dynamic friction $F_d$. The former one describes the force barrier that a body in contact with another must overcome to start moving. Practically, a static configuration remains stable under the application of a lateral force $F$ which can take all values up to a maximum, which, thus, sets a threshold above which sliding is possible. The threshold depends linearly on the applied load $F_s = \mu_s F_n$, where $\mu_s$ is the static friction coefficient of the system, which depends on the materials in contact, on the temperature, on the possible pressure and type of lubrication. A similar relation holds for the dynamic friction: $F_d = \mu_d F_n$, which kicks in when the two bodies are already sliding; $\mu_d$ is the dynamic friction coefficient, usually smaller than the static one.

In the present work we go beyond the simple Coulomb model, which is actually an emerging property resulting from the multi-contact fractal nature of real solid-solid interfaces and from the elasticity of solids \cite{8}. We rather focus on a single contact and deal with non-linear friction, describing the behavior of systems at the “atomic” scale showing a highly nontrivial dynamical response. The first step in addressing this problem is the introduction of the simple,
yet fascinating, Frenkel-Kontorova (FK) model which provides an excellent starting point to understand the key features of this physics.

### 1.1 1D: the Frenkel-Kontorova model

In its standard formulation, the Frenkel-Kontorova model \([9]\) consists of a 1D chain of \(N\) classical particles (or atoms), interacting with their first neighbors via an harmonic potential and with a sinusoidal external potential, as depicted in fig. 1.1. The Hamiltonian of the system is

\[
H = \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} + \frac{K}{2} (x_{i+1} - x_i - a_c)^2 + \frac{U_0}{2} \left( 1 - \cos \left( \frac{2\pi}{a_l} x_i \right) \right) \right],
\]

where \(\frac{p_i^2}{2m} = \frac{m}{2} \frac{d^2x_i}{dt^2}\) is the kinetic energy of the \(i\)th atom, the next term is the harmonic interaction energy between neighboring atoms with elastic constant \(K\) and rest distance \(a_c\) and the last term is the substrate potential of amplitude \(U_0\) and spacing \(a_l\).

The system is characterized by the amplitude of the substrate potential \(U_0\) and the spring elastic constant \(K\) and their length scales, \(a_l\) and \(a_c\), respectively. While the springs stiffness favors a uniform separation \(a_c\), the substrate
potential tends to pin the atoms to the bottom of the wells spaced at $a_1$. We can define the mismatch ratio as the ratio between the two spacings $\rho = a_1/a_c$, i.e. the number of atoms divided by the number of potential wells.

For $\rho = 1$ we have a commensurate system with a trivial ground state in which each atom sits at the bottom of one potential well. The excitation dynamics is characterized by elementary, nonlinear excitations known as kinks and antikinks in addition to the usual linear excitations, phonons. The FK model has drawn a lot of interest because it can be solved exactly in the continuum approximation, the sine-Gordon equation, and provides a good model for soliton excitations [10].

An easy way to picture this elementary topological excitations is by changing the number of atoms in the system: by adding an atom to the chain, the resulting configuration has a kink in it, that is two particles forced to share the same potential well, which pushes the surrounding ones out of their minimum; on the other hand, the subtraction of an atom leaves a well empty and the equilibrium configuration is characterized by a local expansion of the chain, called antikink. In the commensurate case, where the number of atoms matches the number minima, kinks and antikinks sprout as excited states under the action of a driving force. Intuitively, under a driving force $F$, kinks and antikinks slide more easily than regular atoms at register over the potential because their are composed of particles farther from the potential minima. Figure 1.2 shows the idea of the motion of kinks and antikinks under a driving force: the kink advances when the right particle in the over-crowded well hops to the
next minimum. The antikinks is an empty space which moves in the direction opposite to the force. The motion of these solitons is the main effective mechanism of mass transport along the chain and accounts for diffusivity and mobility in the model immediately above the depinning threshold force, if any \[11\].

From eq. (1.1), we can obtain the dimensionless equation of motion

\[
\frac{d^2 x}{dt^2} + \sin(x_i) - g(x_{i+1} + x_{i-1} - 2x_i) = 0,
\]  
(1.2)

where distances are measured in units of \(a_\ell/2\pi\) and time in \(a_\ell/(2\pi\sqrt{2m/U_0})\). The resulting dimensionless coupling constant \(g = K(a_\ell/2\pi)^2/(U_0/2)\) expresses the fact that the FK physics is determined by a dimensionless ratio between the spring energy \(Ka_\ell^2\) and the corrugation energy \(U_0\). On the other hand, from the continuum limit with \(x_i - i\alpha \to u(x,t)\), we obtain the sin-Gordon equation:

\[
\frac{d^2 u}{dt^2} + \sin(u) - \frac{d^2 u}{dx^2} = 0,
\]  
(1.3)

where the spacial scale has been rescaled \(x \to x/(a_\ell\sqrt{g})\). A soliton solution of the eq. (1.3) has the form

\[
u_\sigma(x,t) = \tan^{-1}\left(e^{-\sigma \gamma(v)}(x-vt)\right),
\]  
(1.4)

where the width of the soliton \(\gamma(v)\) is a function of the its velocity and \(\sigma\) is the topological charge of the excitation: \(\sigma = +1\) for kinks and \(\sigma = -1\) for antikinks.

The sine-Gordon equation provides a good qualitative description of the excitation but cannot account for effects due to the discreetness of the model. A specific property arising from the discrete lattice is the Pierre-Nabarro (PN) potential \(V_{PN}(X)\), which describes the effective potential felt by a kink at position \(X\). Considering the atomic coordinates \(x_i = k(i\alpha - X)\), where \(k\) is a function describing the shape of the soliton, the kink center position \(X\) is

\[1\]This actually is the result in the continuum limit \(u_\sigma(x,t)\) eq. (1.4) with the addition of
defined by the self-consistent equation

\[ X = -\frac{1}{a_l} \int dx k'(x - X). \]  

(1.5)

The PN potential defines the energy barrier against the kink sliding \( E_{\text{PN}} \). Intuitively, it is the energy difference between the stable configuration of the kink (solution of eq. (1.5)) and the unstable one where its center is at a saddle point, as sketched in fig. 1.3.

For suitable spacings \( a_l \) and \( a_c \) and in the limit of an infinite chain, \( \rho \) can become an irrational number and the system is said to be incommensurate. This case is particular interesting: the competition between the two interactions terms (called length scale competition \[ 12 \] or sometimes frustration) gives rise to non-periodic spatially modulated structures and results in a rich phenomenology both in static and dynamical proprieties. The ground state of the system is composed by a sequence of local compressions or expansions of the chain (kinks or antikinks, respectively) by means of which the chain tries to locally match the periodic potential. The kink structures with the same

---

\( a \) correcting term due to the discrete lattice called adiabatic dressing of the kink.
topological charge tend to repel each other: as a result for weak corrugation (large $g$) a kink (or antikink) picked at random would be placed with essentially equal probability in any position relative to the local minimum of the PN potential.

1.1.1 The Aubry transition

In the incommensurate case, the FK model shows an interesting transition as a function of $g$, namely of the ratio between the spring stiffness $K$ and the substrate amplitude $U_0$: above a well defined value $g_c$ the chain can slide freely over the substrate under the driving of an arbitrarily small force, i.e. the static friction $F_s$ disappears, while below this critical $g_c$, the system shows a finite $F_s$ which must be overcome to start the sliding. This transition, defined as transition by breaking of analyticity was studied in great detail by Serge Aubry \[13, 14\], and it is therefore widely known as the Aubry transition.

Even though this transition is characterized by a change in dynamical response to an external force, it is actually a structural transition for the ground state (GS) of this model system. The configuration at rest $\{x_i\}$ that minimizes the energy

$$\frac{\partial H(\{x_i\})}{\partial x_i} = 0$$

(1.6)
as a function of all the $x_i$ has obviously the property that

$$U_0 \frac{\pi}{a_1} \sin \left( \frac{2\pi}{a_1} x_i \right) - K(x_{i+1} + x_{i-1} + 2x_i) = 0.$$  

(1.7)

It can be shown that the GS configuration solution to this equation is described by a hull function $f_\rho(x)$ which is strictly increasing and step periodic, i.e. $f_\rho(x + 1) = 1 + f_\rho(x)$. If this function is continuos as in fig. 1.4(a), for any value $\alpha \in \mathbb{R}$ the ground state configuration $\{x_i\}$ is defined as

$$x_i = f_\rho(i\rho + \alpha),$$

(1.8)

and the vice versa is true as well, i.e. any GS configuration is of the form
A simple explanation of this free-sliding state is that for every atom going up the substrate landscape, there is always another atom somewhere in the infinite chain going down, resulting in an exact energy balance \[11\]. The same can be said for the PN barriers of individual kink/antikinks. Below a critical value, which depends on the mismatch ratio, \( g_c(\rho) \), the function \( f_\rho(x) \) is no longer analytic, but it becomes a step-like function, as in fig. 1.4(b); this is why this transition is called transition by breaking of analyticity. In this non-analytic phase, the presence of forbidden configurations, inaccessible to the system by means of a continuous displacement of the particles, is what actually gives rise to a finite static friction.
The physical meaning of this transition is better understood with the introduction of a “disorder parameter" $\Psi$ \[15\]. For the chain to slide continuously between configurations, the atoms must occupy all the possible position of the substrate, including occasionally the maxima: the probability of finding particles at or near the maxima vanishes at the transition. The disorder parameter $\Psi$ is defined as the smallest distance of atoms from the nearest maximum of the substrate: $\Psi = 0$ in the superlubric state $g > g_c$ and has a finite value in the pinned state $g < g_c$. Near the transition, it vanishes continuously with a power law behavior $\Psi \propto (g_c - g)^\chi$, characteristic of a second order transition \[12\].

Another critical quantity characterizing the transition is the Pierre-Navarro barrier: it is null for the analytic system $g > g_c$ and becomes finite below the transition following a power law: $E_{PN} \sim (g - g_c)^{\chi_{PN}}$.

### 1.2 2D: the Novaco angle

After illustrating the 1D FK model, we want to move to its 2D extension, which has not been studied analytically but can be characterized in detail by means of numerical methods. The first difference we can highlight from the 1D model is the presence of a new global degree of freedom: the substrate and atom lattices can be mutually rotated around the vertical axis. The problem of the misalignment of 2D lattices has been known for a long time in the field of epitaxy, namely the deposition of atomic or molecular layers on a crystalline substrate, and investigated both experimentally \[16\] and by theory \[17, 18\].

In the case of incommensurability between the adsorbate-monolayer spacing and that of the substrate, the competition between adsorbate-substrate interaction and the adsorbate-adsorbate one results in a frustrated system: the spacing of the adsorbate lattice is perturbed by the interaction with the substrate, resulting in an incommensurate stressed structure. The ground state is characterized by a static distortion wave (SDW) \[17\], a distortion of the atoms positions from the ideal lattice spread across the whole sample. This SDW converts some of the compression stress generated by the local commensuration of the lattices to shear displacement, which visually results in a misalignment.
Figure 1.5: The geometry of a triangular lattice in the reciprocal space for the rigid substrate (solid blue circles) with spacing \( \frac{4\pi}{\sqrt{3}a} \) and for the rotated adsorbate layer (hollow pink circles) spaced of \( \frac{4\pi}{\sqrt{3}a_c} \). The figure highlights the lattice vectors \( \mathbf{G} \) and \( \tau \) relative to the substrate and the adsorbate, respectively. Their difference \( q \) determines the phonon dynamics of the system and its length is an increasing function of \( \theta \), which is depicted in the figure as well. The dotted hexagons are a visual aid to help appreciate the rotation.

angle \( \theta \) between the lattices.

We should briefly give an idea of the key mechanism behind this phenomenon in the case of an infinite rigid substrate at \( T = 0 \) treated in the harmonic approximation, valid for small values of the displacements caused by the SDW. Figure 1.5 shows the geometry of the system. The energy shift per atom from the ideal unrotated case is [17]:

\[
E = -\frac{n}{2} \sum_i u_i^2 \frac{(\mathbf{G} \cdot \epsilon_i(\mathbf{q}))^2}{m\omega_i^2(\mathbf{q})},
\]

where the sum is carried on the polarizations, namely transverse (T) and longitudinal (L), \( n \) is the number of rotationally equivalent \( \mathbf{G} \) and \( \mathbf{q} \) vectors,
\( \epsilon_l(q) \) are the polarization vectors, \( u_G^2 \) the mode amplitude and \( \omega^2_l(q) \) the mode frequencies. The \( \omega^2_l(q) \) term tends to minimize the misalignment and, thus, set \( \theta \) at 0; this favors long-wavelength distortions related to low-frequency phonons. However, different phonon modes have a different weight \( \mathbf{G} \cdot \epsilon_l(q) \), which depends on the misalignment angle \( \theta \); the transverse frequency branch has lower frequencies than the longitudinal one but it cannot contribute for \( \theta = 0 \). Since \( \partial_\theta |q| = 0 \), a little misalignment allows the transition mode to lower the energy without a relevant increase in \( |q| \) and, thus, in the \( \omega^2_L \) term. As a result, there will then be a nonzero angle, leading to symmetry breaking, at which the total energy is minimum. The energy can be written as:

\[
E = -\frac{n u_G^2}{2m} \left[ \frac{a_c^2}{c_T^2 q^2} + \frac{a_c^2 a_l^2}{q^4} \sin^2 \theta \left( \frac{1}{c_T^2} - \frac{1}{c_L^2} \right) \right],
\] (1.10)

where \( c_T \) and \( c_L \) are the transverse and longitudinal sound velocities, respectively, and the \( \theta \) dependency is contained also in \( q^n \) terms. Minimization over \( \theta \) leads to:

\[
\cos \theta = \frac{1 + \rho^2 (1 + 2 \delta)}{\rho [2 + \delta (1 + \rho^2)]},
\] (1.11)

being \( \rho = a_l/a_c \) the mismatch ratio and \( \delta = (c_L/c_T)^2 - 1 \). The optimal angle satisfying eq. (1.11) is called Novaco-McTague angle \( \theta_{NM}^{(teo)} \). This result holds until the transverse velocity is significantly smaller than the longitudinal one, specifically for \( \delta < \rho^{-1} \) [17, 19]. This misalignment combined with a static distortion leads to a better interdigitation of the two lattices and the elastic energy cost of moving the atoms closer is overcompensated by a gain in the substrate interaction [19].

Even though the misalignment angle \( \theta \) is usually small, its effect is greatly amplified by the rotation of the moiré pattern. It can be shown [19, 20] that for two lattices rotated by \( \theta_{NM}^{(teo)} \) the domain pattern is rotated by an angle \( \phi \) satisfying the geometric relation

\[
\cos \theta_{NM}^{(teo)} = \frac{\sin^2 \phi}{\rho} + \cos \phi \sqrt{1 - \frac{\sin^2 \phi}{\rho^2}}.
\] (1.12)
Figure 1.6: Equilibrium configurations at different global angle of a system with mismatch $\rho \approx 0.83$ and in the presence of a relatively strong substrate potential (a) Unrotated $\theta = 0^\circ$ and (b) optimally rotated $\theta = \theta_{\text{NM}}^{(\text{opt})}$. The colloids are colored according to their position in the corrugation: dark (light) colloids enjoy the best (worse) substrate potential $W_3(x, y)$. (c) Experimental geometry for the same $\rho$, adapted from Ref. [21], where the moiré angles are best described by (b) rather than (a). Adapted from Ref. [19].

This effect is illustrated in fig. 1.6. We will see that the local misalignment angle describes the superlubric phase above the Aubry transition in 2D, while below the transition in the pinned state, when the coupling with the substrate potential increases, the colloids locally align with substrate potential, as depicted in fig. 1.6. This alignment is only local: even above the transition, the energetically favorable configuration is the one keeping a global misalignment between the lattices.

1.3 Experiments with colloids

In recent years, many experiments have explored 2D extensions of the FK model and incommensurate systems with a ground state described by the Novaco-McTague theory [22] [23]. We will focus on a recent experiment with a pioneer technique developed at the Stuttgart University by C. Bechinger’s group [11] [2] [3].

In this experimental setup [3], the atoms of the FK model are replaced by negatively charged polystyrene spheres with radius $R = 1.95 \mu m$ suspended in an aqueous solvent within a sample holder. The interplay of gravitational
forces and a vertically incident laser beam, which exerts an additional light pressure, ensures that the system really is two-dimensional. The interference pattern of 3 splitted and recombined laser beams produces an almost defect-free substrate potential which interacts with the charged spheres by means of optical gradient forces, see fig. 1.7(a,b). The tuning of the incident light intensity allows one to change the amplitude $U_0$ of the substrate. The angle of incidence of the interfering laser beams is used to control the substrate lattice spacing $a_l$, thus setting the precise incommensurate conditions, namely the $\rho$ value. To probe the dynamics of the system, the entire sample holder is shifted along a symmetry axis of the substrate potential by a piezoelectric motor with given velocity $v$ and, as a result, each colloid feels a Stokes force $F = m \gamma_{\text{eff}} v$, 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{setup.png}
\caption{The experimental setup: (a) schematic representation of the colloidal lattice and the laser-generated substrate and (b) an actual snapshot of the setup (courtesy of T. Brazda). (c) The trajectories of the diffusion of sparse colloids with no substrate potential and driving forces. Green and red dots mark the starting and ending points of each diffusion trajectory.}
\end{figure}
proportional to the sample velocity through an effective viscosity $m_\gamma_{\text{eff}}$.

The key innovative feature of this experimental setup is that by means of a microscopy and a CCD camera it is possible to actually see the colloids inside a central region of the sample and follow the trajectory of each one of them in time, as shown in fig. 1.7(c). This allows the experimentalist to achieve a single-particle resolution of the precise mechanisms governing the dynamics of the system, a possibility which is usually reserved to computer simulations.

This remarkable technique allowed the Stuttgart group to observe the formation of kinks and antikinks in the system and observe their motion in real-time, as depicted in fig. 1.8. Aubry-type signatures have been recently observed experimentally in a mono-dimensional finite chain of cold ions trapped in an optical lattice [24]. The goal of the Stuttgart group is to observe for the first time the Aubry transition in a system which is fully 2-dimensional and close to the thermodynamic limit.

We have worked closely with this experimental group providing estimations of physical quantities not directly accessible to the experimental setup and validating their results with simulation parameters chosen as close as possible to those of the real system. The present thesis reports the results of these simulations.

---

2Each experiment is composed of thousands of colloids and the ones within the field of view of the camera are between 2000 and 4000.
Figure 1.8: Propagation of a kink on a substrate commensurate to the colloid lattice, adapted from the Stuttgart experiment [1]. The dark-green zones mark a compression zone, with higher density: the soliton excitation spreads over multiple colloids. A force \( F = 40 \text{fN} \) along the \( x \) axis is applied to each colloid; the time interval between the snapshots is 13 s.
We describe each colloid as a point-like object immersed in a liquid. This solvent is treated implicitly with the Langevin approach. Accordingly, our model describes only the translational degrees of freedom of the center of mass of each colloid. The equation of motion of the $j^{\text{th}}$ colloid is:

$$m \ddot{r}_j(t) = -m \gamma \dot{r}_j(t) + \eta_T(t) - \nabla_{r_j}(U_{\text{pp}} + U_{\text{ext}}) + F \hat{x}. \quad (2.1)$$

In addition to regular conservative terms, which we discuss below, this equation includes two terms extraneous to the standard Newton equation for the motion of particles in vacuum. The term $-m \gamma \dot{r}_j(t)$ is the damping term accounting for the viscous dissipation of energy into the solvent. This damping prevents the system from gaining unlimited kinetic energy under a driving force. The term $\eta_T(t)$ is a random variable with a Gaussian distribution which represents the random scattering of the colloid with the implicit solvent particles. Under
the assumptions that this scattering occurs on timescales much shorter than
the ones we want to study, that the random kicks are uncorrelated, and that
they generate a canonical thermal bath at temperature $T$, this random force
satisfies:

$$
\langle \eta_T(t) \rangle = 0
$$
$$
\langle \eta_T(t) \cdot \eta_T(t') \rangle = 2\gamma T \delta(t - t')
$$

Let us now come to conservative terms. The term $F\hat{x}$ describes the con-
stant external force of magnitude $F$ directed along the $x$ axis, which both in
experiments and simulations, is introduced to probe the frictional response of
the system of colloids.

Considering a system of $N_p$ colloids, the term $U_{pp} = \frac{1}{2} \sum_{i,j}^{N_p} V(|r_i - r_j|)$
is the 2-body potential describing the interaction between the colloids. The $V$
function describes the screened Coulomb interaction energy between 2 colloids
as a Yukawa potential:

$$
V(r) = \frac{Qre^{-r/\lambda}}{r}.
$$

(2.2)

The Yukawa potential for a few values of the screening length $\lambda$ is reported in
fig. 2.1. In the experiments, typical distances between colloids are of the order
of $a_c \simeq 5.5 \div 7 \mu m$, while the screening length $\lambda \simeq 0.18 \div 0.30 \mu m$ is much
shorter. Because of the screening length being so small and the potential
so asymmetric, we can ignore the contact interactions: being the radius of
experimental colloids $R = 1.95 \mu m$, the energy cost needed for two colloids to
touch ($r \leq R$) is inaccessible to the system. As an example, fixing realistic
equilibrium distance $a_c = 6 \mu m$, $\lambda = 0.20 \mu m$ and $Q = 1 \times 10^{16} \mu m$, we
have that the repulsive energy of two colloids at the equilibrium separation is
$V(a_c) = 3.5 zJ$ while the energy at the contact point is $V(2R) = 6 \times 10^6 zJ$,
over 6 orders of magnitude higher. Moreover, the Yukawa potential decays so
rapidly that we can neglect its effect beyond a certain distance. We fix this
cutoff distanced to $r_{cut} = C\lambda$ with $C = 100$, as was done in Ref. [25] and fully
tested in Ref. [26]. As an example, in the same system defined above, the
Figure 2.1: The repulsive interaction potential of the colloids as function of the inverse of the screening length $k = 1/\lambda$, with fixed $Q = 1$. The solid purple line relative to $k = 0$, represents the long-range pure Coulomb interaction which is the unscreened limit $\lambda \to \infty$; the other curves are Yukawa potentials for increasing $k$.

Energy at $r_{cut} = 20 \mu m$ is $V(r_{cut}) = 7 \times 10^{-35} zJ$, entirely negligible.

The radius of the colloids fixes also the mass in eq. (2.1): we assume that the colloids density is close the the one of water $d_{water} = 1000 \text{ kg/m}^3$, and, thus, we obtain $m = 4/3 \pi R^3 d_{water} = 3.105 \times 10^{-14} \text{ kg} = 31.06 \text{ fkg}$.

The term $U_{ext} = U_0 \sum_i^N W_n(r_i)$ is the 1-body external potential representing the substrate corrugation. Since the experimental corrugation is created by the interference of $n$ laser beams, we define our potential as:

$$W_n(r) = \frac{1}{n^2} \sum_{l=0}^{n-1} e^{i\mathbf{k} \cdot \mathbf{r}}$$

where $n$ is the order of symmetry and can generate periodic structures ($n = 2, 3, 4, 6$) or quasi-periodic ones ($n = 5, 7$) [4, 1, 2]. The 2D wave vectors needed...
Figure 2.2: The potential $W_3$ described in eq. (2.5). The black lines are isolines: the one at $W_3 = -1/90$ surrounds the maxima, the one $W_3 = -1/9$ goes through the saddle points and separates the hexagonal regions of positive curvature surrounding the minima from the triangular regions with negative curvature surrounding the maxima.

to create the proper ordered structure are:

$$k_l = \frac{c_n \pi}{a_1} \begin{pmatrix} \cos \left( \frac{2\pi l}{n} + \alpha_n \right) \\ \sin \left( \frac{2\pi l}{n} + \alpha_n \right) \end{pmatrix}.$$ \hspace{1cm} (2.4)

The constants $c_n$ are used to ensure that the corrugation periodicity is $a_1$ and $\alpha_n$ to align the pattern to the $x$ axis.

In our system we use a $n = 3$-fold symmetry to obtain a triangular lattice,
Figure 2.3: One-dimensional paths in the 2D potential-energy landscape. The solid purple line is the path along the $x$ axis at $y = 0$ which goes through the lowest possible barrier (where the triangles meet in fig. 2.2). The dashed green line is an orthogonal path along the $y$ axis with $x = 0$ which goes through a minimum and maximum, a saddle point, a second maximum and reaches another minima after total displacement $\Delta y = \sqrt{3}a_l$. The dotted blue line is the saddle point energy $W_3(a_l/2, 0) = -1/9$. The arrows mark the points of maximum slope along the $x$-directed path, those points defining $F_{1n}$, eq. (2.7).

so $c_n = c_3 = 4/3$ and $\alpha_n = \alpha_3 = 0$. Substituting eq. (2.4) in eq. (2.3) with the proper numerical constants and carrying out the simplifications, we find:

$$W_3(r) = -\frac{1}{9} \left[ 3 + 4 \cos \left( \frac{2\pi}{\sqrt{3}a_l} r_y \right) \cos \left( \frac{2\pi}{a_l} r_x \right) + 2 \cos \left( \frac{4\pi}{\sqrt{3}a_l} r_y \right) \right]. \quad (2.5)$$

Figure 2.2 reports a landscape of this potential. From this plot it is clear that there are paths along precise directions, under driving, which are energetically more convenient for the colloids to follow, because they avoid the maxima and go through the saddle points, which correspond to the lowest possible barrier hindering jumps from a well to the next one. If we fix $r_y = 0$ and move along the $x$ direction, we follow one of these paths. In this case the potential is the solid red line plotted in fig. 2.3 namely:

$$W_3(x, 0) = -\frac{1}{9} \left[ 5 + 4 \cos \left( \frac{2\pi}{a_l} r_x \right) \right]. \quad (2.6)$$
Thus, the barrier, i.e. is the difference in energy of the saddle point from the bottom of the well, along this path is \( \frac{8}{9}U_0 \). At \( T = 0 \) we can define the static friction of a single colloid trapped in this potential as the minimum lateral force necessary to overcome the lowest barrier, which lies on the path along \( \hat{x} \). To find this force we simply look for a maximum in the steepness of the potential, namely, its derivative:

\[
F_{1s} = U_0 \max_x [\partial_x W_3(x, 0)] = \frac{8\pi}{9a_1} U_0 \sin \left( \frac{2\pi x}{a_1} \right) \bigg|_{x = a_1/4} = \frac{8\pi U_0}{9a_1}.
\]

We will use this elementary barrier as a reference force for comparison when we study the depinning of entire monolayers in different conditions.

It is worth noting that, at least at \( T = 0 \) and like in the 1D FK model, the Aubry transition we want to investigate is a function of the ratio between the typical pair potential energy and the substrate potential energy. As a result, we can fix one of these quantities and vary the other one to explore the transition. In this work we keep the 2-body potential energy, namely the Yukawa potential parameters \( Q \) and \( \lambda \), fixed, and vary the substrate potential amplitude \( U_0 \). We checked that rescaling the repulsive potential between the colloids has the only effect to modify multiplicatively the entire dependence of the dynamical properties on the corrugation amplitude \( U_0 \).

Practically, in our code, which is written in Fortran90, the coupled set of \( 3N \) second-order differential equations is solved by means of an adaptive fourth-order Runge-Kutta-Fehlberg method if \( T = 0 \). When the temperature is finite, so that random fluctuating terms \( \eta_T \) are present, a fixed-time-step-6-order Runge-Kutta algorithm is used.

To favor clear quantitative comparisons with experiment, we adopt a system of units based on the SI but close to the typical experimental scales. Table 2.1 reports the adopted units.
### Table 2.1: The units used in this work. Length, mass and energy are fixed as fundamental quantities, the derived quantities are measured in suitably derived units.

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>µm=10(^{-6}) m</td>
</tr>
<tr>
<td>mass</td>
<td>fkg=10(^{-15}) kg</td>
</tr>
<tr>
<td>energy</td>
<td>zJ=10(^{-21}) J</td>
</tr>
<tr>
<td>time</td>
<td>ms=10(^{-3}) s</td>
</tr>
<tr>
<td>force</td>
<td>fN</td>
</tr>
<tr>
<td>velocity</td>
<td>mm/s</td>
</tr>
<tr>
<td>mobility</td>
<td>s/mg</td>
</tr>
<tr>
<td>damping rate</td>
<td>ms(^{-1})</td>
</tr>
</tbody>
</table>

2.1 Langevin over-damped dynamics

In certain cases the Langevin equations eq. (2.1) can be simplified, namely when the system is in a strongly overdamped regime. To illustrate this point, consider a free particle moving inside a hypothetical solvent at \(T=0\) and with no force applied:

\[
m\dot{v} = -\gamma mv. \tag{2.8}
\]

The simple solution to this equation is:

\[
v(t) = v_0 e^{-\gamma t}. \tag{2.9}
\]

It means that after a time \(t = \gamma^{-1}\) the system begins to lose a large fraction of the information contained in its initial condition, and its kinetic energy has been largely dissipated into the solvent bath. In situations where the \(\gamma\) term dominates by far over the inertial term, and to the extent that one is not interested in phenomena occurring at a short time scale \(\tau \lesssim \gamma^{-1}\), one could drop the inertial term in the equation of motion. In these conditions one is reduced to Aristotelian motion, where the velocity is ultimately proportional to the applied force, with a proportionality factor \((m\gamma)^{-1}\).

In less ideal conditions than eq. (2.8), the forces generated by potentials
Figure 2.4: The trajectory for a few values of $\gamma$ of a single colloid with initial velocity $v_x = 0.01 \text{ mm/s}$ at the bottom of a well of the 1D potential defined in eq. (2.6) of amplitude $U_0 = 30 \text{ zJ}$ and spacing $a_1 = 5 \mu\text{m}$. For $\gamma = 0$ (purple solid line) the system conserves energy and keeps swinging inside the well. As $\gamma$ increases the motion evolves from an underdamped regime (e.g. $\gamma = 0.5 \text{ ms}^{-1}$, green dashed line) to an over-damped regime, with $\gamma = 3 \text{ ms}^{-1}$, orange dot-dashed line.

introduce their own characteristic time scales $\omega^{-1}$. If $\gamma^{-1} \ll \omega^{-1}$, and we are uninterested in resolving dynamical phenomena at the shortest relaxation scale $\gamma^{-1}$, then we may wish to go for an intermediate time step $\gamma^{-1} < \Delta t \lesssim \omega^{-1}$. Then between successive iterations of the integrating algorithm, the kinetic energy is dissipated and the inertial term in eq. (2.1) plays a negligible role. In this case one can reduce the problem eq. (2.8) to a first order equation, saving 50% of memory storage and adopting a substantially larger time step. What we do in practice, is rather to stick to the regular second-order equation, with a large enough damping rate $\gamma$ that it makes all the oscillatory modes of the colloidal system overdamped, as in the $\gamma = 3$ curve in fig. 2.4. If we went for the first-order approach, there would have been no limit on how large $\gamma$ is. However as we wish to stick to the 2$\text{nd}$ order equation, a very large $\gamma$ would require an extra-small time step $\Delta t \approx \gamma^{-1}$.

The realistic damping rate for colloids moving at velocity $v$ is given by the Stokes formula $F_d = 6\pi m\gamma R v$ and thus $\gamma = F_d / (6\pi m R) = 5.14 \times 10^3 \text{ ms}^{-1}$. 
Due to the vicinity of a static boundary, i.e. the bottom of the sample holder, this value must be corrected by a factor $\zeta = \frac{4}{3}$ \cite{27}, leading to $\gamma = 6.85 \times 10^3 \text{ms}^{-1}$. This value is far too large for an effective integration of the eq. (2.8) for any significant time scale. To overcome this difficulty, we have chosen a $\gamma = 3.43 \text{ms}^{-1}$, namely 2000 times smaller than the actual damping rate relevant to the experiments. As consequence of this much less viscous fluid, fluctuations are much faster in simulation. In the end, we adopt a timestep $\Delta t = 0.034 \gamma^{-1} = 0.01 \text{ms}$.

From the point of view of local fluctuations and transportation, effectively, time flows 2000 times faster in our model than in experiments. This means that when comparing simulated results and experimental ones, all the quantities involving time, e.g. mobilities, must be rescaled accordingly. On the other hand, one should be careful to jump to the conclusion that time is purely accelerated by a factor 2000, since global slow transition phenomena may actually take a simulation time more similar to the real one, due to effects like strong correlations and steric hinderance.
Chapter 2 The Model
In this chapter we will go through a number of technical details regarding the simulations and we will introduce several definitions that are necessary to understand the results presented afterwards.

3.1 Periodic boundary conditions

The number of colloids of a real system is much larger than what can be treated with molecular-dynamics simulations. However, simulating a small, finite-size sample, could introduce unexpected and unwanted effects due to the boundaries. To mitigate this problem, we use periodic boundary conditions (PBCs): the simulated system is enclosed in an appropriate supercell, which is repeated infinite times periodically throughout space. This means that each colloid inside the original cell, actually represents an infinite set of colloids:
for each element at position \( \mathbf{r} \), there are images of it, shifted rigidly at positions
\[
\mathbf{r}' = \mathbf{r} + \sum_{i=1}^{D} \sum_{n_i \in \mathbb{Z}} \mathbf{C}_i n_i,
\]
where \( D \) is the dimensionality of the system and \( \mathbf{C}_i \) is the set of primitive vectors of the supercell. Each colloid in the box is interacting with every other colloid in the box and with their images across the boundary condition. This interactions between the colloids and the replicas are calculated by means of the minimum image algorithm. To avoid to compute useless and unphysical self-interactions between a colloid and its infinite images, it is necessary to use a supercell large enough to ensure that these self interactions are negligible, i.e. they are outside the cutoff radius \( r_{\text{cut}} \) defined in chapter 2. Applying PBC to the system implies that the number of colloids is infinite but its density is fixed by the ratio \( d = N_p/A_{sc} \), where \( N_p \) is the number of simulated particles, and \( A_{sc} \) the area of the supercell.

### 3.1.1 Rotated supercells

In the simple case, the supercell is defined by the colloidal lattice symmetry and spacing. For a 2D triangular lattice, the length of the cell side can be taken as an integer multiple \( L \) of the lattice spacing \( a_c \):

\[
\mathbf{C}_1 = L a_c \begin{pmatrix} 1 \\ 0 \end{pmatrix},
\]

\[
\mathbf{C}_2 = L a_c \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix}.
\]

It is nontrivial but possible to define supercells suitable for systems composed by different lattices, in our case the one of the colloids and the one of the substrate potential [28, 19]. This means that the PBC must be compatible with both lattice spacings, possibly in the presence of a misalignment angle. In Appendix A we find the solution for this problem in a slightly more general case \(^1\) but here we are interested in the case of two triangular lattices, which

---

\(^1\)One can imagine an even more general case where there are more than 2 lattices with different symmetries but this goes beyond the needs of this work.
is invariant under rotation of $\Omega = \pi/3$ described by the matrix

$$
R_{\pi/3} = \begin{pmatrix}
\frac{1}{2} & -\frac{\sqrt{3}}{2} \\
\frac{\sqrt{3}}{2} & \frac{1}{2}
\end{pmatrix}.
$$

(3.3)

Let the colloid and corrugation lattices be spaced by $a_c$ and $a_l$ and described by the versors $\hat{a}_i$ and $\hat{b}_i$, respectively. Being the mismatch ratio $\rho = a_l/a_c$ and $\theta$ the misalignment angle between the substrate corrugation and the colloid lattices, we have can relate them to four integer numbers:

$$
N_p = m_1^2 + m_2^2 + m_1m_2
$$

(3.4)

$$
\hat{b}_1 = R_{\theta} \cdot \hat{a}_1 = \begin{pmatrix}
\cos \theta \\
\sin \theta
\end{pmatrix} = \frac{\rho}{2N_p} \begin{pmatrix}
2m_1n_1 + 2m_2n_2 + m_1n_2 + m_2n_1 \\
\sqrt{3}(m_1n_2 - m_2n_1)
\end{pmatrix}
$$

(3.5)

$$
= \frac{\rho}{2N_p} \begin{pmatrix}
S \\
\sqrt{3}B
\end{pmatrix},
$$

being $S$ and $B$ shorthands for the long expressions appearing in the versor of eq. (3.5). From the condition $\|\hat{b}_1\| = 1$ we find:

$$
\rho = \frac{N_p}{\sqrt{S^2 + 3B^2}}
$$

(3.6)

$$
\theta = \arccos \frac{s}{\sqrt{S^2 + 3B^2}}
$$

(3.7)

$$
C_1 = a_l(n_1\hat{a}_1 + n_2\hat{a}_2)
$$

(3.8)

$$
C_2 = -a_l n_1 \hat{a}_1 + a_l(n_1 + n_2)\hat{a}_2.
$$

(3.9)

In order to obtain a system with the desired $\rho$ and $\theta$, we swipe through all possible integers $n_i$ and $m_i$ (within a reasonable range) and select the supercells which happen to have mismatch $\rho$ and misalignment angle $\theta$ close enough to the desired values. Figure 3.1 shows an example of this supercell compatible with two lattices: the lattice of the colloids and that of potential minima are represented as points of different colors.
Figure 3.1: Example of a supercell compatible with mutually tilted perfect lattices of colloids (dark-blue) and of potential minima (gray). The lattice spacing of the colloids is $a_c = 1.7$; the one of substrate potential is $a_1 = 1.792$; this leads to a mismatch ratio $\rho = 1.05$, namely an overdense case. The two lattices are mutually rotated by an angle $\theta = 1.8^\circ$. The four integers describing the supercell are $n_1 = 29$, $n_2 = 26$, $m_1 = 29$ and $m_2 = 29$ They are associated to the substrate lattice and to the colloid one, respectively. The supercell vectors are $C_1 \simeq (75.3, 40.3)$  $C_2 \simeq (2.7, 85.3)$.

### 3.1.2 Supercells for the experimental data

Defects play a crucial role in defining both static and dynamical proprieties of the system. Even when their energy cost is modest, it can be extremely difficult to create or destroy any of them in reasonable simulation times starting from a perfect lattice at room temperature, due to high energy barriers. To ensure
that our simulations at room temperature have a defect level close to what is observed in the experiments and make quantitative comparisons feasible, we will also use experimental snapshots as a starting point.

Even if we work in PBC while the experiment is an open system, the small fluctuation in density allow us to adopt the experimental configuration in our fixed-density simulation and obtain similar results. Since the experimental snapshot is just the image of a small part of a bigger, open system, which is not compatible with any periodic boundary condition, we need to define a protocol to adapt this starting configuration to our simulation technique. The starting configuration we want to obtain must be compatible with the corrugation potential $W_3$ defined in eq. (2.5), which has the symmetry of a perfect triangular lattice of spacing $a_l$ both along $x$ and $y$; the supercell must be exactly compatible with this periodicity. Moreover, the defect-rich colloid lattice of the experiment must conserve its original density, as closely as possible.

Since the field of view of the experimental set is rectangular, we use a supercell which has this symmetry, in order to preserve as many experimental
colloids as possible. As can be seen in fig. 3.2 a rectangular supercell for a
triangular lattice has a periodicity on the vertical axis which is 2 times the $y$
component of the second primitive vector, namely:

$$C_1 = L_x a_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad C_2 = L_y a_1 \begin{pmatrix} 0 \\ \sqrt{3} \end{pmatrix},$$

(3.10)

where $L_x$ and $L_y$ are suitable primitive integers.

We then adopt a rectangular supercell suitable for the imposed corruga-
tion potential and, at the same time, compatible with the experimental frame:
knowing the maximum and minimum position of the colloids, the supercell
must be close to these values, but should leave a little space between the
colloids across the periodic boundaries. Imposing PBC on the experimental
frame, leaves many particles very close to each-other’s images in the neighbor-
ing cells: this is an artifact of the procedure and creates non-physical stress
across this boundaries. To overcome this problem, we start by calculating
the distances between all the atoms across the PBC and, selected those pairs
at a distance under the set threshold $r_{del} = 0.25 \bar{a}_c$ (being $\bar{a}_c$ the mean dis-
tance of the colloids), we delete one of them. This also helps to obtain a
density $d = N_p / A_{sc}$ which is close to experimental one. The adopted supercell
is defined by the vectors $C_1 = (392 \mu m, 0)$ and $C_2 = (0, 290.9845 \mu m)$
obtained with $L_x = 70$ and $L_y = 30$. It contains 2977 colloids, while the origi-
nal cell containing all 3029 experimental colloids was captured in a rectangular
visual window identified by $C_1 = (392 \mu m, 0)$ and $C_2 = (0, 294.4 \mu m)$.
Considering that the density is the inverse of the area occupied per colloid
and that each rectangular non-primitive cell of side $(a_c, 0, 0, \sqrt{3}a_c)$
contains 2 colloids, we obtain:

$$A_{rc} = \sqrt{3}a_c^2 = 2A_{coll},$$

(3.11)

$$d = \frac{N_p}{A_{sc}} = \frac{N_p}{N_p A_{coll}} = \frac{1}{\sqrt{3}a_c^2},$$

(3.12)

$$a_c = \sqrt{\frac{2}{\sqrt{3}d}},$$

(3.13)
Figure 3.3: Displacement of the colloids (red arrows) between the original unrelaxed experimental snapshot (black points) and the relaxed, PBC-compatible final configuration (blue points).

where $A_{rc}$ in eq. (3.11) is the area of the rectangular, non primitive cell. As a result, if the colloids of the original experimental cell were arranged in a perfect lattice, the spacing would have been $a_{c}^{(exp)} = 6.6328 \mu m$, while in our simulation supercell is $a_{c}^{(simul)} = 6.6515 \mu m$, that corresponds to a relative difference of less than 0.3%.

We then proceed to let the system relax and dissipate the residual stress into the Langevin thermal bath of the simulation, tuning the substrate potential amplitude as we need. In order to prevent the colloids near the boundaries with high repulsive potential energy from destroying the crystal, we let the system relax through multiple MD runs of short duration, resetting the kinetic energy to 0 between each of them. The time step is set to be at least 3 orders of magnitudes smaller than the total time of the simulation, in order to avoid failures in the Runge-Kutta integration algorithm.

We have found that $N \approx 100$ runs of total time ranging from $1 \times 10^{-4}$ ms to 0.1 ms followed by a thermal run of 100 ms effectively dissipate the stress
while preserving the crystal structure and defects of the system. The precious defects are almost unchanged in the bulk far away from the PBC while minor rearrangements can be found at the boundaries (where of course novel defects arise), as shown in fig. 3.3. The energetics during the relaxation of an experimental snapshot is reported in fig. 3.4: the average pair interaction potential energy per colloid decreases from a value of approximately 100 zJ to the order of unity, which is compatible with the average interaction energy of a perfect lattice for the potential parameters we are using; the temperature, proportional to the kinetic energy via the equipartition theorem, tends to rise rapidly during the first simulations, but is reset to zero at the end of each, while during the last simulation, it correctly reaches the value of \(4.15 \text{ zJ} = 300 \text{ K}\).
3.2 Optimization of the pair potential parameters

A fundamental task is to define suitable parameters for the pair interaction potential of the model; since we want to carry out quantitative comparisons with the experimental data, the interaction potential should be as close as possible to the real one. However, from the experimental condition we just know that the charged colloids interact with a screened Coulomb potential (Yukawa potential) defined in Chapter 2, but the values of the potential strength $Q$ and of the screening length $\lambda$ are not directly measurable. In order to estimate their values, we define a protocol based on the pair correlation function of the system. Before explaining this protocol, we should introduce its ingredients: the $g(r_1, r_2)$ function, the concept of the simplex and the definition of the rigidity of the system, which will be used in the following.

The pair correlation function, or radial distribution function, $g(r_1, r_2)$ of a system of $N_p$ particles in a volume $V$ (in our case an area $A$) is defined as follows:

$$g(r_1, r_2) = \frac{p^{(2)}(r_1, r_2)}{p^{(1)}(r_1) \cdot p^{(1)}(r_2)}.$$  \hspace{1cm} (3.14)

That is, the 2-particle joint probability density of finding a particle at $r_1$ and another at $r_2$ normalized by the single-particle probability densities evaluated at the same positions. For a translationally invariant situation $g(r_1, r_2) = g(r_1 - r_2)$. If the system is also invariant for rotations, like a fluid, $g(r_1 - r_2) = g(|r_1 - r_2|) = g(r)$. In the case of the ideal gas, the joint probability factorizes into the single particles ones and so $g(r) = 1 \forall r$.

Figure 3.5 illustrates a simple example of a $g(r)$: the first peak represents the increase in probability in correspondence of the distance between nearest neighbors, the second peak accounts from the second neighbors, and so on. The width of these peaks is related to the rigidity of the system, temperature and disorder. If we considered a perfect crystal at $T = 0$, each peak would become a Dirac $\delta$, because the particles would not move under thermal fluctuations and all particle pairs would give the same contribution at the same geometrically
equivalent distances. In our system, because of the repulsive potential, the
ground state of a free system would be the one with the particles as far as
possible, i.e. an infinite diluted gas. Confinement in a finite space forces the
colloids to arrange themselves in a periodic structure with nearest neighbors
at relatively constant distance of the order of $a_c$.

To characterize the interparticle potential we can define the rigidity of the
system as follows. In the linear approximation for the elastic response of the
system, each particle feels a recalling force proportional to its displacement
and to the constant $\kappa = \frac{\partial^2 V(r)}{\partial r^2}$. For our Yukawa potential defined in eq. (2.2) we find:

$$\kappa = \left. \frac{\partial^2 V(r)}{\partial r^2} \right|_{r_{eq}} = \frac{Q e^{-r}}{2 a_c^3} \left( 2 + \frac{2}{r^2 \lambda} + \frac{1}{r \lambda} \right)_{r_{eq}}.$$ (3.15)

At equilibrium, potential and thermal energy are equal: $\frac{1}{2} k_b \langle x^2 \rangle = \frac{1}{2} k_b T$; the
broadening of the peaks is given by the maximum displacement due to thermal
excitations a colloid can undergo before the recalling force $-kx$ resulting from

---

\[2\]In our case, in the periodic simulation supercell.
the Yukawa potential pushes it back at its equilibrium position. As a result, while the density of the system defines the position of the peaks, the width is determined by the interplay of $Q$ and $\lambda$ which both affect the rigidity $\kappa$.

To adopt the parameter $Q$ and $\lambda$ we need to go through a minimization. For this, we adopt the Nelder-Mead method \cite{29}, which is an heuristic minimum search method that does not rely on gradients. We use this method to explore the parameters space in search of the optimum values, instead of manually tune $Q$ and $\lambda$. This method is based on the concept of the simplex, which is a generalization of the triangle to $D$ dimensions. The idea is that given the $D+1$ points which form the starting simplex and a function $f(x)$ to minimize, the algorithm calculates the function at these points $\{f(x_1), f(x_2) \cdots f(x_{D+1})\}$ and then replaces the worst (highest) one by means of a reflection, an expansion or a contraction of the simplex along the direction of the best vertex, or the shrinking of the simplex around the minimum point. Figure 3.6 sketches how the Nelder-Mead simplex algorithm works. The Nelder-Mead method is implemented in the SciPy python module \cite{30}.

The final ingredient for our task is an appropriate error function to minimize, i.e. one which can tell a good set of parameters apart from a bad
one. The function we adopt for this purpose is the squared distance between experimental and simulated $g(r)$:

$$\chi^2 = \frac{1}{W} \int_0^\infty |g_{exp}(r) - g_{simul}(r)|^2 w(r) \, dr$$  \hspace{1cm} (3.16)

$$= \frac{1}{W} \sum_{r_i=0}^{r_{max}} |g_{exp}(r_i) - g_{simul}(r_i)|^2 w(r_i) \delta r_i,$$  \hspace{1cm} (3.17)

where $w(r) = \frac{1}{r^2}$ is used to increase the weight of the first peaks, both because the potential is short-ranged and both experiment and simulation system do not provide data to evaluate $g(r)$ reliably at long distances, and $W = \sum_{r_i=0}^{r_{max}} w(r_i)$ is the normalization constant. In this work we adopt a discretization $\delta r = 0.05 \mu m$ and $r_{max} = 147 \mu m$, which define the set of $r_i$. Since a small variation of $\lambda$ results in a great variation in energy whereas the energy scales linearly with $Q$, we prefer to carry out the minimization of $\chi^2$ as a function of $\log Q$ and $\lambda$.

To obtain the optimal potential amplitude and range we use the following protocol. We evaluate a smooth $g(r)$ for the experimental system by averaging the function over all the successive $n_{exp} = 600$ configurations recorded in a static experiment without substrate potential. The available data are therefore a discrete set of pairwise distances between colloids: we evaluate the $g(r)$ simply as an histogram of the particle-particle distances $r_{ij}$. The experimental system is contained in a finite box: to avoid systematic errors in evaluating the histogram we have to define a smaller box when calculating the pair correlation function. We select a smaller square box whose side is $\frac{1}{4}$ of the smallest side of the cell: the particles inside this box are taken as those cycled by $i$, and all, including the ones outside the smaller box, are cycled as particles $j$ to evaluate the distances $r_{ij}$ and obtain the distribution. This reference function $g_{exp}(r_i)$ is computed once for all at the beginning. Basically the rest of the calculation is a fit of $g_{exp}(r)$, where the parameters $\lambda$ and $\log Q$ defining the simulated system are tuned repeatedly.

We have repeated this fitting procedure for 3 different experimental datasets whose $g_{exp}(r)$’s as reported in fig. 3.7. In order to choose a sensible initial set
Figure 3.7: The 3 curves report the first peaks of $g(r)$ in the 3 datasets analyzed. The first peak is the most important part of the function because it is the one most strongly affected by the short-range colloid-colloid potential. Apart from the different position of the peaks, signaling a slightly different density in each system, it is important to note that the shape of the peaks is also different: the dot-dashed purple curve relative to $a_c = 6.59 \mu m$ is broader than the solid green one, for $a_c = 6.66 \mu m$; this will lead to some amount of discrepancy in the resulting rigidity of the two systems.

of potential parameters $Q_0$ and $\lambda_0$ to start the minimization with, we carry out some preliminary mono-dimensional minimization over $Q$ at fixed $\lambda$ and pick up the pair $(Q_{\text{best}}(\lambda), \lambda)$. Each iteration of the algorithm calls, on every newfound vertex, the function we want to minimize, which is composed of the following steps:

- run a long simulation with the current parameter values in order to first relax the system and then generate a good sampling of the successive equilibrium configurations;\footnote{The simulations are carried out without substrate potential $U_0 = 0$ in the supercell defined by $C_1 = (392, 0)$ and $C_2 = (0, 294.4)$. The starting configuration is created from an experimental snapshot with the protocol defined in section 3.1.2.}

- compute $g_{\text{simul}}(r)$ for these resulting configurations;

- compare this pair correlation function with the reference $g_{\text{exp}}(r)$ and
Table 3.1: The optimized values of $Q$ and $\lambda$ for the 3 experimental datasets analyzed. $N_p$ is the mean number of particles in experiments. $\kappa$ is the rigidity of the system obtained from $Q$ and $\lambda$ according to eq. (3.15). $E_{\text{int}}^{\text{(ideal)}}$ is the potential energy for an ideal lattice considering only the nearest neighbors:

$$E_{\text{pp}} = \frac{1}{2} \sum_{i \neq j} V_{ij}(|r_i - r_j|) \approx \frac{N_p}{2} 6V(a_c) = N_p E_{\text{int}}^{\text{(ideal)}}.$$ 

It is then clear that each function evaluation involves a MD simulation, which can take several hours, plus a calculation of the $g(r)$ of the system, which scales as $N^2$ within each frame saved from the simulation and can need significant time to compute as well. For this reason, there is a tradeoff between the length of the simulation (i.e. the number of saved frames, which increases the accuracy of the sampled $g_{\text{simul}}(r)$) and the time one can wait for the optimization to converge. In practice, the total simulation time 100 ms (i.e. 2000 s of real time), of which the initial equilibration time lasts 30 ms, and over remaining time, we save 30 equally spaced snapshots to be used for the computation of $g_{\text{simul}}(r)$.

We have carried out this minimization over 3 different experimental sets:
Figure 3.9: The error function $\chi^2$, eq. (3.17), as function of log $Q$ and $\lambda$, for the dataset characterized by $a_c = 7.17 \, \mu m$ (first row of table 3.1). A narrow region (deep blue) of small $\chi^2$ value is visible near the center of the region. Outside this valley, the function grows rapidly, as suggested by the colors, and soon reaches values orders of magnitude higher than the one in the valley (top-right and bottom-left corners).

Both the characteristics of the systems and the results of the optimization are collected in table 3.1. Figure 3.8 compares $g_{\text{simul}}(r)$ and $g_{\text{exp}}(r)$ at the initial step of the optimization and for the final best fit parameters.

As is apparent from eq. (3.15) for given rigidity $\kappa$, the parameters $Q$ and $\lambda$ are not independent: a small decrease of $\lambda$ can be compensated by an increase in log $Q$. This means that in the (log $Q$, $\lambda$) there is a valley of similarly good parameters. This is illustrated in fig. 3.9 obtained by evaluating the $\chi^2$ function over a region in the parameter space. This results indicate that there is no optimal parameter set for the interparticle potential, but rather long curved “valley” of (log $Q$, $\lambda$) pairs that yield a similar $\chi^2$ and essentially the same rigidity and particle-particle average potential energy as illustrated by the two rightmost columns of table 3.1. Eventually in the remainder of the simulations reported in this work, we will adopt the parameters reported in the third row of table 3.1 since they are the close to most of the experimental
3.3 Definition of the sliding steady state

Friction is an out-of-equilibrium phenomenon and thus, when the lateral force $F$ is turned on there is no equilibrium state of the system by definition. However, after an initial transient the system can reach a steady state. In practice this state can be difficult to identify because it is impossible to be sure that the dynamical trajectory over the entire simulation time would not change completely if one could extend the calculation to longer simulated timescales. In our simulation protocol, we study the tribological proprieties of the system dynamics by applying a constant driving force to each colloid and change it in small steps. As a result, after each force change there will be some transient response which we need to discard. Complex systems at finite temperature often represent a challenge both in determining this transient and also in defining precisely the properties of the sliding state. For a start, from a solely theoretical point of view, static friction does not exists at finite temperature, because thermal fluctuations will promote some slow creep motion even under the smallest applied force: albeit slowly the system is found in motion if one can afford to observe it for a very long time. Additionally, solitons, which arise in an incommensurate system, and other kinds of crystal defects usually enhance the mobility of the system at small forces. As a result, in practice it can be a tricky task to tell apart a slow steady sliding of the whole system from a slow transient rearrangement of the contact’s weak point, i.e. the defects.

In the present work we decide to define a monolayer to be in the sliding state if the mobility of its center of mass is $10\%$ of the mobility under the same force without any substrate potential, $U_0 = 0$. In these free-sliding conditions, the system is translationally invariant and only the viscous force opposes free acceleration. As a result the system center of mass would soon reach a speed $F/(m\gamma)$, corresponding to a mobility $(m\gamma)^{-1} = 9.4 \times 10^{-3} \text{s/mg}$. We set the arbitrary threshold at $10\%$ of this value, i.e. $\mu_{th} = 0.94 \times 10^{-3} \text{s/mg}$. Note that free mobility and, correspondingly, the actual mobilities observed in simulations are quite different from the experimental ones, where the damping
Definition of the sliding steady state

rate $\gamma$ is 2000 times larger, see chapter 2. However, the adopted definition of depinning, based not on an absolute mobility threshold, but rather on a fraction of the free mobility, can be applied as is both to experimental and to simulation data. For ease of comparison with experiments, in the plots, we will rescale computed mobilities to match experimental ones. Moreover, since we probe the system with a discrete set of force values and the mobility can change dramatically in a small range around the depinning transition, the force $F_s$ at which the depinning occurs, i.e. the static friction of the system, is estimated via a linear interpolation between the last pinned configuration $(F_{\text{pin}}, \mu_{\text{pin}})$ immediately before the first time $\mu_{\text{th}}$ is crossed and the first sliding configuration $(F_{\text{slid}}, \mu_{\text{slid}})$, the one immediately after the last time the mobility curve has fallen below $\mu_{\text{th}}$, namely:

$$F_s = \frac{\mu_{\text{th}} - \mu_{\text{pin}}}{\mu_{\text{slid}} - \mu_{\text{pin}}} F_{\text{slid}} + \frac{\mu_{\text{slid}} - \mu_{\text{th}}}{\mu_{\text{slid}} - \mu_{\text{pin}}} F_{\text{pin}}.$$  

(3.18)

Figure 3.10 reports the depinning of two systems; our definition correctly identifies the depinning force in the simplest case, i.e. a single colloid in periodic potential, where the depinning force is $F_{1s}$, eq. (2.7), and gives reasonable results with an incommensurate monolayer, where the interaction between particles lowers the depinning force from the single-colloid case.

In order to explore systematically the dynamical proprieties, we need to define a suitable protocol. The key aspect is that effects at small forces happen at a slower pace than those at large ones. As a result, we fix the product $\Xi_0 = F_{\text{min}} \cdot t_{\text{max}}$, and, accordingly, give a simulation at driving force $F$ a total time of $\tau = \Xi_0/F$. This procedure allows the system more time to evolve and reach a steady state for small forces, while for large force it will reduce the simulation time to save computation time. However, we will keep $\tau$ always larger than a minimum amount $\approx 100\gamma^{-1}$ in order to allow the system to relax transients induced by the force increase. Moreover in our protocol, each new simulation begins with the end point of the previous one. As a result of the “adiabatic” increase of $F$ in small step, it will take less time for the system to

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$^4$This definition provides a meaningful estimation of $F_s$ and the error on it even in those cases where the mobility is not a monotonous function of $F$. 

Figure 3.10: Depinning two colloidal systems at $U_0 = 145 \text{ zJ}$. The black dashed horizontal line is the free-sliding mobility. The red dotted horizontal line is the depinning threshold $\mu_\text{th} = 10\% (m\gamma)^{-1}$. This threshold correctly locates the depinning force of the $T = 0$ commensurate layer (blue arrow) extremely close to the correct $F_s = F_{1s}$. For the incommensurate monolayer ($\rho = 0.8615$) the static friction (black arrow) is estimated very near to the first point which has a mobility significantly different from 0. The small but nonzero mobility of the previous force point at $F/F_{1s} = 0.27$ seems due to thermal-induced local defect diffusion rather than an actual global sliding of the lattice, but it is obviously very hard to tell.

reach its steady state after each increase, since the previous simulation already had partially “digested” the effect of a very similar applied force.

3.4 Calibration of the static structure factor

A good tool to highlight ordered structures and long-range correlation in a system is the static structure factor $S(q)$. Although the structure factor is usually related to the interpretation of scattering patterns obtained with diffraction experiments, it can also be read as the spatial Fourier transform of a system. As a result, the function $S(q)$ contains informations about the periodicity of the sample and it is very sensible to ordered structures both on long and short
Calibration of the static structure factor

In a system of \( N_p \) identical point-like scatterers (colloids or atoms) at positions \( r_i \) the structure factor is

\[
S(q) = \frac{1}{N_p} \sum_{i=1}^{N_p} \sum_{j=1}^{N_p} e^{i q (r_i - r_j)}. \tag{3.19}
\]

In the present work, we use this tool to seek the fingerprint of the long-range-ordered structures arising in the colloidal system above the Aubry transition presented in section 1.1.1 and which should not be found neither in the perfect lattice nor in the superlubric state. Furthermore, \( S(q) \) can be a useful tool to investigate the effects described by the McTague-Novaco theory outlined in section 1.2: if the lattice is rotated, there will a clear trace of this in the diffraction pattern, that rotates accordingly. The function \( S(q) \) is very sensitive to small changes in its argument, which makes it quite expensive to compute. Because of this and the fact that we are dealing with complex, inhomogeneous systems at finite temperature, it is desirable to analyze simple versions of our system and set the parameters correctly for these systems at first.

Figure 3.11a reports \( S(q) \) for a perfect triangular lattice with spacing \( a_c = 6.5 \mu m \). This lattice generates a pattern in the \( q \)-space which is rotated by \( 30^\circ \), and spaced by \( b = 4\pi/(\sqrt{3}a_c) \). In other words, the pattern in fig. 3.11(a) generated by the lattice in fig. 3.11(b) is itself a triangular lattice with primitive vectors

\[
b_1 = \frac{4\pi}{\sqrt{3}a_c} \begin{pmatrix} \sqrt{3}/2 \\ -1/2 \end{pmatrix}, \quad b_2 = \frac{4\pi}{\sqrt{3}a_c} \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{3.20}
\]

For example, the intensity peak at \( b_2 \) in fig. 3.11(a) is at \( q_x = 0 \) and \( q_y = \frac{4\pi}{\sqrt{3}a_c} \approx 1.12 \mu m^{-1} \). This is the smallest periodicity in real space and, thus, the largest one in the \( q \) space. The smallest real-space lattice spacing we work with is \( a_l = 5.6 \mu m \), corresponding to \( b = 1.3 \mu m^{-1} \). For this reason, we compute \( S(q) \) up to \( q = 1.5 \mu m^{-1} \). A sample rotated by \( \theta \) leads to Bragg peaks in \( S(q) \) rotated by the same angle (fig. 3.11c,d).

The structure factor is also sensitive to the shape of the entire sample, as it convolutes with the actual signal during the Fourier transform. As can be
seen in fig. 3.11a,c, a square box produces a sort of cross “start” around the peaks along the $q_x$ and $q_y$ directions. In contrast, as fig. 3.11e shows, a circular sample, representing a circular “aperture”, disperses the peak intensity more symmetrically around it. This dispersion is better localized and perturbs the actual diffraction pattern less. For this reason, we will adopt circular aperture for our data analysis throughout this work.
Figure 3.11: The $S(q)$ function (a,c,e) for a finite portion of a perfect hexagonal lattice with spacing $a_c = 6.5 \mu m$ (b,d,f). (a): for a square portion ($N_p = 1067$) of an aligned crystal; (b): for a crystal tilted by $\theta = 5.4^\circ$ ($N_p = 1095$); (e) for a circular region of the same tilted lattice ($N_p = 1099$). The structure factor is computed from $q = -1.5 \mu m^{-1}$ to $q = 1.5 \mu m^{-1}$ both along $q_x$ and $q_y$ with a step $\delta q = 0.005 \mu m^{-1}$. Intensity is given in logarithmic scale. The vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ generating the reciprocal lattice are indicated in panel (a).
The objective of this chapter is to investigate the equilibrium properties of the colloids layer across the superlubric-pinned transition. This means that we will investigate the structural properties of the lattice mismatched monolayers in different equilibrium or quasi-equilibrium situations, without any external force ($F = 0$). We will mainly characterize the Aubry transition between the superlubric and the pinned state by means of equilibrium observables, such as the local angle of the colloid-colloid bonds lattice with respect of the crystalline directions of the substrate potential and a disorder parameter representing the fraction of colloids sitting at locally energetically unfavorable regions of the corrugation potential profile. We will carry out this analysis both at $T = 0$, where the results are clearer and usually faster to obtain in terms of computational effort, and at $T = T_{\text{room}}$, to verify what results survive in the presence of thermal fluctuations and to allow direct comparison with experiment.
Chapter 4 Structural Properties

The main additional degree of freedom that 2D provides compared to the standard 1D FK model consists in the angular misalignment of the two lattices. One can study the structure and the energetics of the system for given mismatch as a function of the misalignment angle by means of the construction of suitable PBC supercells. We start off investigating to which extent the favorable state is the one tilted at the angle predicted by the Novaco theory \[18, 17\]. Subsequently, we study the phase diagram of the system, as a function of the corrugation amplitude \( U_0 \), and for both temperatures.

In order to probe the behavior of the system as a function of the \( U_0 \) parameter, we use the following protocol: defined a starting configuration containing the positions and the velocities of the colloids, i.e., a snapshot of the phase space of the system, we run successive simulations at different \( U_0 \) values and let the system equilibrate; the starting point of each molecular-dynamics simulation is the final configuration of the previous run. In order to characterize structurally this transition, we focus on two observables: the local angle \( \theta \) and the disorder parameter \( \Psi \).

The local angle \( \theta_i \) of a colloid is defined as the arithmetic mean of the angles of bonds joining the considered colloid with its nearest neighbors. Specifically, given a colloid \( i \) and one of its nearest neighbors \( j \), the bond angle between them is defined as

\[
\theta_{ij} = \tan^{-1}\left(\frac{y_j - y_i}{x_j - x_i}\right) \mod \frac{\pi}{3} \quad (4.1)
\]

and thus \( \theta_{ij} \) belongs to the interval \((-\pi/6, +\pi/6]\). As a result, the local angle \( \theta_i \) of each colloid \( i \) is:

\[
\theta_i = \frac{1}{N_i^{(nn)}} \sum_{j=1}^{N_i^{(nn)}} \theta_{ij}, \quad (4.2)
\]

being \( N_i^{(nn)} \) the number of neighbors of the \( i^{th} \) colloid. In a perfect triangular lattice of spacing \( a_c \), the \( N_i^{(nn)} = 6 \) nearest neighbors of each colloid are placed at distance \( a_c \), while the 6 second neighbors are at \( d_2 = \sqrt{3}a_c \) from colloid \( i \). We need to be able to apply this definition even for a layer affected by thermal
fluctuations or defects of any sort: we need to introduce a suitable cutoff used to distinguish between the first shell of neighbors and the second. To do this we decide that a colloid \( j \) is a neighbor of a given colloid \( i \), if

\[
d_{ij} < d_{\text{cut}} = f \min_{\forall j} d_{ij},
\]

where \( f \) is an appropriate cutoff factor for the lattice considered: in the case of the triangular lattice, it must be \( f \lesssim \sqrt{3} \). In practice we take \( f = 1.35 \), which allows some tolerance beyond the perfect lattice spacing, but it is significantly less than the second-neighbor distance. With this choice we can label uniquely those colloids which are surrounded by a shell of 6 neighbors. In those cases a very robust determination of the average angle \( \langle \theta_{ij} \rangle \) is obtained, except in the quite unlikely case where it comes close to \( \pi/6 \).

We define a global parameter \( f_{\text{tilt}} \) as

\[
f_{\text{tilt}} = \frac{N(|\theta| > 2.5^\circ)}{N_p}.
\]

In order to explain how the transition is characterized operatively by means of the local angle and this global parameter \( f_{\text{tilt}} \), we need to anticipate some results; this is because we need a basic knowledge of where the transition is in order to choose a suitable threshold. Figure 4.1 reports the local angle distribution and the actual position of the colloids in the central portion of the system for a few values of \( U_0 \). We need to define a cutoff value on the local angle \( \theta \) in order to label colloids as tilted (hence, belonging to the superlubric phase), or as aligned with the substrate (and therefore in the pinned phase). From the histograms in fig. 4.1a-c, we set this cutoff value to \( \theta_{\text{cut}} = 2.5^\circ \) because this value is mid way between the distributions of the superlubric phase and the pinned phase, and gives reasonable results for the coexistence region.

A second useful global indicator for the characterization of the configurations is the disorder parameter \( \Psi \), inspired by the work of Ref. [15]. The disorder parameter \[15\] \( \Psi \) is defined as the fraction of colloids above the saddle point of the underlying external potential \( W_3(r) \), defined in eq. (2.5); in other
Figure 4.1: Distribution of the local colloid-colloid “bond” angle and snapshots of the system below the transition ($U_0 = 7\, zJ$, a,d), in the coexistence region ($U_0 = 15\, zJ$, b,e) and above the transition ($U_0 = 35\, zJ$, c,f). The plots (a-c) report all three distributions but the one relative to the given amplitude is filled. The bins in the histograms (a-c) are $\Delta \theta = 0.25^\circ$-wide and the counts are normalized; the distributions include only colloids with 6 neighbors, since the angle estimate is reliable only for these ones. In the snapshots (e-f) red colloids have $\theta > 2.5^\circ$, the gray ones have $|\theta| \leq 2.5^\circ$; the green ones are those with a number of neighbors different from 6.

words, $\Psi$ is the number of colloids at coordinates $\mathbf{r}$ at which $W_3(\mathbf{r}) \geq -U_0/9$:

$$\Psi = N_{\text{saddle}}/N_p.$$  \hfill (4.5)

Because of the geometry of the potential illustrated in figs. 2.2 and 4.2, the region above the saddle point is 1/4 of the total area of the unit cell. As a result, the maximum value of $\Psi$ is 0.25, and this value is obtained equally for a gaseous uniform phase, or an infinitely rigid lattice-mismatched crystal. While the average twist angle is a local indicator, $\Psi$ is rather a global parameter characterizing the layer.
Figure 4.2: Contour plot of $W_3(x, y)$. The area of the two blue triangles highlights the region above the saddle point: $W_3(x, y) \geq -U_0/9$. The rhombic region inside the red thick dashed line is a unit cell: this construction shows that the blue region is 25% of the total area of the unit cell (thinner dotted line are a visual aid helping identify the 8 triangles of equal size forming the unit cell). The Wigner-Seitz cell of the lattice is highlighted by the green dashed hexagon at the right; the solid green triangles are an equivalent representation of the blue region of above-the-saddle potential in the other cell. Orange dots mark the saddle points of the potential.
4.1 Novaco analysis

As was done in Ref. [19], we verify if the configuration tilted at the angle predicted by the McTague-Novaco [18, 17, 20] weak-coupling theory is indeed the energetically favored state of the colloid system. We work with a mismatch ratio $\rho = 0.8615$ which is close to what is obtained in experiments $\rho_{\text{exp}} \simeq 0.86$; for this value of the mismatch, the coupling to the corrugation is expected to be effectively weak up to a significantly large substrate potential amplitude $U_0$: because of the asymmetry of the pair-interaction potential, to reach a regime of “infinitely deep” corrugation wells, where the colloid-colloid interaction energy would be negligible compared to the external corrugation (i.e. $U_{\text{ext}} \gg U_{\text{pp}}$), requires huge value of $U_0$. Recall that at the repulsive energy at the equilibrium spacing $a_c = 6.5 \, \mu m$ is $E_{\text{int}}^{(\text{ideal})} = 2.51 \, zJ$, but if the colloids were compressed into the potential wells spaced of $a_1 = 5.6 \, \mu m$, it would grow to $E_{\text{int}}^{(\text{ideal})} = 404 \, zJ$. This means that to consider $U_{\text{pp}}$ negligible we must take $U_0 \gtrsim 4000 \, zJ$, which is a value well beyond experimental feasibility, although it may be interesting to simulate.

In the angular analysis, we keep the mismatch $\rho$ as close as possible to the reference value and impose different angles to the colloids by means of the supercells constructed as described in section 3.1. The specifically considered cells are reported in Appendix A, table A.1. We work at $T = 0$ where the results are clearer and we do not have to deal with entropy and thermal fluctuation. Each cell, i.e. each global tilt angle $\theta$, is let fully relax with corrugation $U_0$ of increasing magnitude, starting from the final configuration of the previous amplitude.

Figure 4.3 exemplifies the patterns resulting at the end of this relaxation, at three sample twist angles. Figure 4.4 shows the energetics as function of global $\theta$ at two different substrate corrugation amplitudes: $U_0 = 12 \, zJ$, a weak coupling value, and $U_0 = 200 \, zJ$, a intermediate-strong coupling one. Of the pair potential energy we report the excess relative the value for a perfect lattice without substrate potential. The interaction of the substrate potential is measured relative to the average of the substrate potential over space, $\langle W_3(r) \rangle = 1/3$, being $W_3(r)$ defined in the interval $[-1, 0]$, see chapter 2.
Figure 4.3: Snapshots of the colloids relaxed configuration at an intermediate-large corrugation $U_0 = 200 \text{zJ}$ at different angles: (a) $\theta = 0.29^\circ$, (b) $\theta = 5.44^\circ = \theta_{\text{NM}}$, and (c) $\theta = 7.45^\circ$. The colloids are colored according to their position in the substrate potential; the saddle point value is marked by a tic in the color scale.

For both values of $U_0$, and for all the other amplitudes that we explored, the minimum of the total energy per colloid is at $\theta_{\text{NM}} = 5.45$, close to the angle predicted by the Novaco-McTague theory $\theta^{(\text{teo})}_{\text{NM}} = 5.48$. Since the energy cannot depend on the sign of the tilting angle, one would expect $\theta = 0$ to be an extremal point and, indeed, in fig. 4.4, energy approaches $\theta = 0$ with a flat curve, signaling a vanishing derivate. The optimal nature of $\theta_{\text{NM}}$ can be understood going back to fig. 4.3, the configuration at the Novaco angle determines sharp, well organized soliton lines, while in the other configurations the soliton network is distorted and more colloids end up occupying spots at higher external potential energy.

It is important to notice a qualitative difference between the two substrate amplitude values. Even though the minimum of the total energy is always at the Novaco angle, for a weak substrate the repulsive energy between the colloids $U_{pp}$ reaches its maximum at $\theta = \theta_{\text{NM}}$. In the case of a strong substrate, instead, the repulsive energy decreases from $\theta = 0$ to $\theta = \theta_{\text{NM}}$ and then flattens out. This means that the response of the system is qualitatively different: when the
Figure 4.4: (a-b) Total energy per colloid, difference between relaxed pair potential interaction energy $U_{pp}$ and the one from an ideal unrelaxed lattice $U_{pp}^{(0)}$ and difference between interaction energy with the substrate $U_{ext} = U_0 \sum_i^N W_3(r_i)$ and average of the substrate corrugation $U_0 \langle W_3(r) \rangle = U_0 / 3$ of a colloidal lattice tilted at different angles relaxed at $T = 0$ over a corrugation: (a) $U_0 = 12 \text{ zJ}$ and (b) $U_0 = 200 \text{ zJ}$. Note the qualitatively different behavior of the interaction energy and the change of sign of the substrate interaction energy.

wells of the corrugation become deeper and the colloids are compressed in the islands, the network of soliton lines created at the Novaco configuration lowers the interactions between the particles more efficiently than the one created at lower angles.

The different relaxed structures obtained at global angle $\theta = 0$ and at $\theta = \theta_{NM}$ leave a clear trace in the structure factors $S(q)$, as fig. 4.5 shows. At $\theta = 0$ the compressed islands, and the soliton lines produce a pattern which has the same orientations as the colloid lattice in real space, while at $\theta = \theta_{NM}$ the situation is radically different: the pattern produced by the islands is rotated
of $\theta_{\text{isl}} = 30^\circ$ and, while the locally unrotated colloids inside the islands give rise to the same pattern as for $\theta = 0$, the soliton lines bear the memory of the angle $\theta_{\text{NM}}$ originally imposed to the entire sample and are still tilted that way. The spacing of the islands pattern\(^1\) shows a nontrivial dependence on the mismatch ratio $\rho$ and the misalignment angle $\theta$ [19, 20] which is given by

$$a_{\text{isl}} = \frac{a_c}{\sqrt{1 + \rho^{-2} - 2\rho^{-2}\cos\theta}}.$$  \hspace{1cm} (4.6)

For our system with $a_c = 6.5 \mu m$ and $\rho = 0.8615$ tilted at $\theta_{\text{NM}}$ we obtain $a_{\text{isl}} = 34.1 \mu m$, i.e. the centers of the islands are approximately 6 colloids apart. This periodicity generates peaks at $|q_{\text{isl}}| = 0.213 \mu m^{-1}$ forming the purple-highlighted hexagon in fig. 4.5(b).

### 4.1.1 Extremely large corrugation limit

When $U_0$ becomes large enough to become the dominant energy scale, the Novaco-McTague theory has no reason to retain its validity and we reach a strong-coupling regime. The colloids fall to the bottom of the corrugation wells and the effect of the pair potential interaction is to favor the configuration in which colloids are surrounded by the least number of nearest neighbors. Given that the number $N_p$ of colloids and of potential minima $M$, with $\rho^2 = \frac{N_p}{M}$, is fixed, we can look for the ground state of this system by solving the problem of distributing $N_p$ balls in $M$ boxes, organized in a triangular lattice, trying to avoid putting 2 balls in adjacent spots. The solution clearly depends on $N_p$ and $M$, i.e. on the mismatch.

Starting from $\rho^2 = 1$, where each colloid occupies a potential well and has 6 nearest neighbors, reducing $\rho^2$ can be viewed as taking a colloids away from the system, leaving some minima unoccupied and, thus, reducing the number of nearest neighbors of the system. As we keep taking colloids away, at $\rho^2 = 2/3$ the best way to reduce the number of first neighbors is to arrange the colloid in a honeycomb lattice, as illustrated in fig. 4.6. In this configuration each colloid

\(^1\)Equivalently one can consider the spacing of the soliton lines marked by the green colloids in fig. 4.5(d)
Figure 4.5: Snapshots of the relaxed colloidal configuration for $U_0 = 200 \, \text{zJ}$ “circular aperture” ($r = 400 \, \mu\text{m}$) (c,d) and the corresponding function $S(q)$ (a,b). The calculation is done for global angle $\theta = 0$ (a, c) and for $\theta = \theta_{\text{NM}}$ (b,d). The hexagons are a color-wise visual help: the gray ones highlight the pattern coming from the gray colloids inside the islands in real space, the green ones are related to the soliton lines and the purple hexagons highlights the small-q traces of the long-range island superstructure.

has 3 nearest neighbors rather than 6. Further decreasing the mismatch until $\rho^2 = 1/2$, the colloids arrange themselves in hexagons surrounded by another hexagon of empty wells. In such way, the neighbors of a single colloid are only 2, like fig. 4.7. The same number of neighbors and therefore the same energy is obtained with other configurations, e.g. with alternating zig-zagging stripes.

At $\rho^2 = 1/3$, it becomes possible to put a colloid at the center of each hexagon leaving it surrounded by empty minima, i.e. in fig. 4.6 the red dots are now the empty minima and the white spots are those where colloids sit. It is equivalent to the triangular lattice of $\rho^2 = 1$, only with a spacing of
Figure 4.6: Honeycomb lattice, an optimal configuration for filling $\rho^2 = 2/3$. Red dots indicate the wells filled with colloids, while white spots are the empty ones. The dashed gray line highlights the unit cell of this periodic structure with a 2-atom basis.

$\sqrt{3}a_c$. With this configuration, the colloids have no neighbors at distance $a_c$. If $\rho^2$ is further decreased, the most convenient configuration is decided by the energy contribution due to the former second (now nearest) neighbors and the problem is the same we just discussed, only on a larger length scale. This problem is scale-invariant: when $\rho^2 \leq 1/9$, colloids have no second neighbors, the third ones will be the only contribution to the energy and so on and so forth. Since the Yukawa potential decays so rapidly that the potential at the second neighbors distance $\sqrt{3}a_c$ is orders of magnitudes smaller than it is at $a_c$, further investigation of this problem has little physical meaning for our physical problem.

For intermediate nontrivial values of $\rho^2$, the determination of actual ground-state configurations could become nontrivial. To compute the energetics of the system molecular dynamics simulation are not the best tool in this case: the energy cost of moving a colloid from a well to the other is unavailable to the system at $T = 0$ and it is extremely rare at $T = T_{\text{room}}$, and thus it would take infinite time to the system to reorganize itself and find the minimum-energy configuration. A way to solve this problem is to use Monte Carlo methods:
Figure 4.7: The “encapsulated honeycomb” lattice at $\rho^2 = 1/2$. Hollow red dashed circles indicates the colloids removed from the honeycomb lattice of $\rho^2 = 2/3$ in fig. 4.6. The dashed gray line highlights the unit cell and the dotted lines show the 4 honeycomb cell composing it. Hexagons with colloids at all 6 vertexes are shaded with a darker tint. The same energy and density could be obtained with alternating zig-zagging stripes.

defining tho hopping of a colloid as a move of the simulation, it would be possible to study the energetics of the the system with greater efficiency. A warning to this approach, though: a long Monte Carlo simulation could drive the system away from the local minimum defined by the initial angle imposed to the system and end up in the absolute minimum independently of $\theta$. Since this process is long even in the real word, one is usually interested also in the metastable states generate by the initially imposed global tilt angles.
4.2 The Phase Diagram

Here we characterize structurally the Aubry transition introduced in section [1.1.1]. Since we fixed the $U_{pp}$ energy as discussed in chapter 2, we will explore the transition as a function of the substrate potential, at two temperatures: $T = 0$, and $T = T_{room} = 300$ K at which the experiments are performed. The results of section [1.1] tell us that it is sufficient to focus on configurations tilted at $\theta = \theta_{NM}$. Because the transition is of first order and even $T = 300$ K is far below the critical point [5], we expect the system to show a coexistence region, namely a range of substrate potential values at which both phases of the system, the superlubric tilted one and the pinned straightened one, are thermodynamically allowed and manifest locally themselves in simulations. This means that the Aubry transition does not occur at any single value of corrugation, but is diluted over this coexistence region.

This thermodynamical coexistence is rather difficult to probe numerically, because at finite temperature due to local fluctuations there may always emerge for a short time a pinned region, even deep in the superlubric region before the Aubry transition takes place. Likewise, even when the corrugation is large, simulations do show occasional fluctuating tilted regions. One may attempt a measurement of the areas of the 2 phases in a true equilibrium coexistence using long simulations (after any hysteric memory of the initial condition is safely lost). As a function of $U_0$, neither one of the two areas would ever be exactly 0, but there would be a $U_0$ region where the pinned fraction is quite small, an intermediate region with a crossover with both fractions significantly nonzero, and a large $U_0$ region where the sample is almost completely in the pinned phase. Nevertheless this procedure is extremely costly numerically as it requires significant sampling of the slowly fluctuating boundaries between phases. For this reason in the present work we use a different methodology. In order to investigate the phase coexistence, we prefer to probe the behavior of the system following different paths in the phase diagram: the upward pathway starts without corrugation, $U_0 = 0$, and a fully tilted $\theta = \theta_{NM}$ ideal configuration and reaches a fully pinned configuration characterized by commensurate islands and large substrate potential. The downward pathway starts with the
final configuration and corrugation of the upward pathway and goes back down to $U_0 = 0$. Due to the finite and rather short duration of the simulations, we observe hysteresis: within the coexistence region the initial phase of the system (tilted for the upward branch and pinned for the downward one) lasts longer within the coexistence before turning into the other phase, which is becoming more and more favorable as $U_0$ is changed.

4.2.1 Zero-Temperature Results

The system analyzed is composed by 18634 colloids arranged in a perfect lattice of spacing $a_c = 6.5 \mu m$ and the substrate corrugation potential described in chapter 2, with lattice spacing $a_l = 5.599992 \mu m$; this corresponds to a mismatch $\rho = 0.861537$ close to the reference value of the experiments $\rho \simeq 0.86$. The supercell compatible with these two lattices is generated with $n_1 = 91$, $n_2 = 92$, $m_1 = 91$, $m_2 = 66$ with the notation of section 3.1. The relative line in table A.1 is highlighted in bold. The primitive versors are

$$C_1 = \begin{pmatrix} 767.2 \\ 446.2 \end{pmatrix} \quad C_2 = \begin{pmatrix} -2.8 \\ 887.5 \end{pmatrix}.$$  (4.7)

Figure 4.8 shows the evolution in the fraction of colloids belonging to different phases during the upward pathway. The starting configuration is a perfect crystal lattice oriented at the Novaco angle without substrate potential with all colloids belonging the superlubric phase ($f_{\text{tilt}} = 100\%$). As the substrate potential amplitude increases, the fraction of tilted colloids starts to decrease while pinned regions begin to appear, eventually taking up the whole sample for large corrugation. From the last fully-pinned configuration of the upward path ($U_0 = 44 \text{zJ}$), we move downward in $U_0$, back to $U_0 = 0$.

Figure 4.9 reports the fraction of tilted colloids $f_{\text{tilt}}$ during the upward (dotted-dashed line of fig. 4.8) and the downward path. The hysteresis in the local angle $\theta$ is clear and it provides a definition of the coexistence region. In the same figure, we also report the disorder parameter $\Psi$, which also completes a similar hysteresis cycle. In the interval between $U_{c1} = 13 \text{zJ}$ and $U_{c2} = 17 \text{zJ}$
Figure 4.8: The fraction $f_{\text{tilt}}$ of superlubric colloid at local angle $|\theta| > 2.5$ (dashed blue line) and $f_{\text{pin}}$ of pinned ones at $|\theta| \leq 2.5$ (dash-dot red line) as function of the substrate potential following the upward path, i.e. from a totally tilted sample to a completely pinned one.

the two curves follow different paths, meaning that the system explores in a different ground states depending on to the initial condition. The two different equilibrium states are characterized by different values of $f_{\text{tilt}}$ and $\Psi$.

At $T = 0$ the transition can be characterized also by means of the energy of the system. Figure 4.10 reports the total energy of the system, and its two contributions, as functions of the substrate potential amplitude $U_0$ within the coexistence region, for both pathways. The two branches of the total energy $E_{\text{tot}}$, as sums of the contributions from the repulsive pair interaction $U_{pp} > 0$ and interaction with the substrate potential $U_{\text{ext}} < 0$, cross within the coexistence region (arrow in fig. 4.10a), signaling where a phase becomes more favorable than the other. Figure 4.10 indicates that at fixed $U_0$, the energy gap between the two phases is generally much larger for the individual contributions than for the total energy, due to substantial cancellation.

4.2.2 Room-Temperature Results

We now proceed to analyze the transition at finite temperature, both for an ideal, defect-free system and a more realistic one. At room temperature, we expect the transition to shift to higher values of the corrugation as found in
Figure 4.9: Hysteresis cycle of Ψ and $f_{\text{tilt}}$, i.e. the fraction of superlubric colloids (characterized by $|\theta| > 2.5^\circ$), for a perfect lattice at $T = 0$. The disorder parameter Ψ is multiplied by a factor 4 in order to span the same range as θ. For both observables, the upper curve is relative to the upward path, another lower curve to the downward one. The coexistence, characterized by hysteresis in $f_{\text{tilt}}$ and Ψ region is highlighted by dotted lines. The two considered observables identify the same coexistence region.

previous theoretical work by Mandelli et al. [5]. Thermal fluctuations enhance the colloids ability to move, escape from the potential wells and occupy higher-energy positions and, thus, help to preserve superlubricity. It is worth recalling that now the equilibrium state of the system is not the one at minimum energy, but the one that minimizes the free energy of the system $F = U_{\text{pp}} + U_{\text{ext}} - TS$, where $U_{\text{pp}}$ and $U_{\text{ext}}$ are the thermodynamic averages of the potential energy contributions defined in chapter 2. $T$ is temperature and $S$ is the entropy of the system. As found in Ref.[5], entropy favors the superlubric state over the pinned one where colloids are localized at the potential minima, and this also contributes to explain why the transition shifts toward higher substrate corrugations. The perfect-lattice configuration is generated with the same parameter as for $T = 0$, as described in the previous section. The realistic configuration is generated according to the protocol discussed in section 3.1: an experimental snapshot is inserted inside a proper periodic supercell, let relax and taken as starting configuration.
Figure 4.10: Energetics of the $T = 0$ transition. (a) The total energy of the system, (b) the pair interaction $U_{pp}$ term and (c) the interaction with the substrate term $U_{ext}$ as $U_0$ is cycled upward (x) and then downward (+). All energy is normalized to the number of particles $N_p$. $U_{pp}$ and $U_{ext}$ are expressed in units of the corrugation amplitude $U_0$. An arbitrary linear term was added to the total energy to reduce its range of variation and makes the coexistence region more clearly visible.
We shall first compare the results for the perfect lattice with the $T = 0$ behavior. The system preserves all the qualitative characteristics found at zero temperature, but the variation of $\Psi$ and $f_{\text{tilt}}$ with $U_0$ is smoother, as one could expect: without thermal energy the colloids manage to change phase only when a downhill pathway leading to an energy gain allows them, while now regions of a different phase can sprout up and coexist thanks to thermal fluctuations. This smoother evolution in the quantities also results in a broader coexistence region than for $T = 0$, namely $U_{c1} = 25\,\text{zJ}$ and $U_{c2} = 32\,\text{zJ}$, highlighted in fig. 4.11(a).

The case of the system generated from an experimental configuration and therefore rich of defect is even more complex. The presence of defect enlarges the coexistence region further, which is estimated from $U_{c1} = 19\,\text{zJ}$ to $U_{c2} = 35\,\text{zJ}$, as shown in fig. 4.11(b). Moreover, defects can and do affect the coexistence dynamics, hindering the flow of domains of different local orientation. As a result the hysteresis is not as clear and sharp as for the perfect crystal. The upward and downward curve of the disorder parameter do not close exactly at the left side of the transition, while the ones of the fraction of tilted colloids remain apart at the right end of the transition when the curves of $\Psi$ have already rejoined. This means that in this defected case it is more arbitrary than for the perfect lattice to define where the limits $U_{c1}$ and $U_{c2}$ of the coexistence regions are. We define $U_{c1}$ as the middle point between the last value of $U_0$ in which the $f_{\text{tilt}}$ curves are degenerate within the error bars and the first one at which this is not true. The same procedure is used to define the right boundary $U_{c2}$ but with the $\Psi$ curves.

From these results, we conclude that the two adopted observables are quite useful to characterize nicely the Aubry transition and allow us to estimate coherently the boundary of the coexistence region, especially in the ideal cases.
4.3 Structural characterization

The Aubry transition should leave a trace in the structure factor $S(q)$ of the system. Figure 4.12 shows the change of $S(q)$ as a function of $U_0$ for the perfect crystal at $T = 0$. The data are presented along with the corresponding snapshot of the actual colloids position. As the system undergoes the Aubry transition, the structure factor evolves from the simple hexagonal pattern generated by the superlubric phase to the more complex one of the pinned phase.

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2Even though the lattice looks perfect in fig. 4.12, the small but nonzero corrugation induces tiny local compressions and expansions which are not detected by $S(q)$.
In the latter we can see the signal at $|q| \simeq 1.3 \mu m^{-1}$ coming from the colloids in the islands and the peaks at $|q_{isl}| \simeq 0.213 \mu m^{-1}$ one from the global pattern of islands superstructures, as discussed in section 4.1. The structure factor in the coexistence region corrugation $U_0 = 16 zJ$ (taken along the downward pathway) is a mixture of that of the two phases: the peaks relative to the islands long range periodicity are starting to form but the peaks generate by the regions tilted at $\theta = \theta_{NM}$ are still dominant.

Figure 4.13 shows the structure factor from the perfect crystal at $T = T_{room}$. The results are essentially the same as the $T = 0$ case but thermal fluctuations and diffusion lead to broader peaks.

Figure 4.14 shows the structure factor from the defected crystal at $T = T_{room}$. Here defects, thermal fluctuations and diffusion result in a substantial broadening of the peaks. Nevertheless, the fingerprint of the transition is still clearly visible: at low corrugation amplitude the two equivalent superlubric phases at $+\theta_{NM}$ and $-\theta_{NM}$ generate the bulk of the $S(q)$ function (fig. 4.14a). As $U_0$ is increased, the signal from the islands and the soliton lines grow in strength and at very large $U_0 = 150.8 zJ$ the small-$|q| \pi/6$-rotated hexagon is clearly visible along with its harmonics and combinations at the $G$ points (fig. 4.14e).
Figure 4.12: The structure factor $S(q)$ for the perfect lattice at $T = 0$ described in section 4.2.1 along with corresponding snapshots of a portion of the system for the following values of the substrate corrugation $U_0$: (a,b) $U_0 = 6\ zJ$; (c,d) $U_0 = 14\ zJ$; (e,f) $U_0 = 44\ zJ$. The structure factor is computed as described in section 4.1. The colloids are colored according to the local bond angle introduced in chapter 4. The coloring coding is the same as in fig. 4.1.
Figure 4.13: The structure factor $S(q)$ for the perfect lattice at $T = T_{room}$ described in section 4.2.2 along with corresponding snapshots of a portion of the system for the following values of the substrate corrugation $U_0$: (a,b) $U_0 = 6 \, \text{zJ}$; (c,d) $U_0 = 26 \, \text{zJ}$; (e,f) $U_0 = 90 \, \text{zJ}$. The structure factor is computed as described in section 4.1. The colloids are colored according to the local bond angle introduced in chapter 4: coloring coding is the same as in fig. 4.1.
Structural characterization

Figure 4.14: The structure factor $S(q)$ for the defected lattice at $T = T_{\text{room}}$ described in section 4.2.2 along with corresponding snapshots of a portion of the system for the following values of the substrate corrugation $U_0$: (a,b) $U_0 = 16.6 \text{ zJ}$; (c,d) $U_0 = 21.5 \text{ zJ}$; (e,f) $U_0 = 150.8 \text{ zJ}$. The structure factor of each configuration is computed with the same parameters as in section 4.1 and averaged over 17 snapshots to take thermal fluctuations into account. The color scheme is the same as fig. 4.12 with blue colloids tilted near $-\theta_{\text{NM}}$. 
We probe the system dynamics by dragging it driven with the application of a constant driving force $F$ to each colloid. Being out of equilibrium, the system is not characterized by an equilibrium state, but it can eventually reach a steady state. The initial transient time must be identified after any change in the value of $F$ and ignored when computing steady-state properties. In this dynamical situation, the dissipative term $-m\gamma\dot{r}$ in the equation of motion prevents the system from gaining unlimited kinetic energy from this constant force. Globally, the Langevin thermostat attempts to keep the colloids close to the thermal equilibrium at the desired temperature, either $T = 0$ or $T = T_{\text{room}}$ in our simulation. The thermostat time scale implies that after any change of the applied force the initial transient duration is surely at least $\gamma^{-1}$, although according to our own experience it can easily be much longer. Systems characterized by different substrate potential $U_0$ amplitudes have different typical
Chapter 5 Dynamical Properties

scales for forces and for steady-state velocities of the monolayer. As a result, it is convenient to normalize these quantities in order to compare different system. The forces are naturally measured in units of the elementary barrier $F_{1s}$ defined in eq. (2.7), proportional to $U_0$. In order to understand if the whole monolayer of colloid is sliding, we compute the velocity of the center of mass of the system. However, forces of different magnitude will drive the system to different velocities: in the simplest case of a single free-sliding colloid the steady-state velocity is proportional to the applied force:

$$v_{fs} = \frac{F}{m\gamma}. \tag{5.1}$$

Since we are not interested in the absolute magnitude of the sliding velocities itself, but rather in whether the system is sliding or not, it is natural to compare the CM speed of the colloids to that of the free colloid and, thus, we could monitor $v_{CM}/v_{fs}$. However, following the tradition of the field will use a different but equivalent quantity. The average mobility is defined as the ratio

$$\mu = \frac{\langle v_{CM} \rangle}{F}. \tag{5.2}$$

The mobility is therefore simply a factor $(m\gamma)^{-1}$ larger than the dimensionless ratio $v_{CM}/v_{fs}$. In practice the highest possible mobility, that of free colloids sliding over a flat substrate is $\mu_0 = (m\gamma)^{-1}$. As reported in table 2.1 the units of $\mu$ are that of time over mass and in our model we measure it in $s/mg$. For the experimental system the free mobility is $\mu_0 = 18.8 s/mg$, while in our model we have $\mu_0 = 0.0094 s/mg$, namely 2000 times smaller due to the reduced $\gamma$ discussed in section 2.1; nevertheless, will always rescale the computed mobility to be comparable with experiment.

We will also compute the static friction threshold $F_s$ (if any) as defined in section 3.3. We expect two well-defined regimes: one superlubric, before the Aubry transition, and one pinned, after the transition. For corrugation values $U_0$ below the transition, we expect the relative mobility curves to follow a superlubric behavior, with a mobility greater than 0 even in the limit of vanishing forces. For such situations we will set $F_s = 0$. At $U_0$ values above
the transition, we should find a pinned regime: below the threshold $F_s$, the mobility is compatible with 0 and the monolayer is stuck because most of the colloids are trapped near the bottom of the potential wells; above $F_s$, the system begins to slide over the substrate and the mobility grows. Between these two distinct phases, namely within the coexistence region, it is not clear how the system will behave.

5.1 Depinning transition

We analyze the mobility of the system under driving in the same three cases investigated for the static proprieties in chapter 4: a perfect lattice at $T = 0$ and at $T = T_{\text{room}}$, and a defective sample closer to the real experimental system at $T = T_{\text{room}}$.

Figure 5.1 compares the $T = 0$ mobility of lattice-matched system, depinning at the full barrier force $F_{1s}$, to that of a mismatched ($\rho = 0.8615$) system.

![Figure 5.1](image)

**Figure 5.1:** The perfect-crystal mobility at $T = 0$ as function of the driving force for characteristic substrate potential amplitudes $U_0$. Three curves illustrate the typical mobility behavior of a lattice-mismatched system ($\rho = 0.8615$), one for each region (superlubric - $U_0 = 10\text{ zJ}$, coexistence - $U_0 = 14\text{ zJ}$, pinned - $U_0 = 30\text{ zJ}$). For comparison, we report the mobility of a lattice-matched system (or equivalently of a single colloid), which, of course, depins at $F = F_{1s}$, far later than the mismatched system.
The depinning curve for the lattice-matched case \((\rho = 1)\) is the same regardless of the corrugation amplitude \(U_0\). As function of \(U_0\), the mismatched lattice exhibits a richer behavior than the commensurate case, ranging from a superlubric regime with depinning occurring right from the lowest probed force, to a pinned one, characterized by a non-zero static friction force \(F_s < F_{1s}\). Between these two, there is the coexistence region identified in chapter 4. Albeit showing a finite static friction, the system at substrate amplitude \(U_0 = 14 \, \text{zJ}\), reported in fig. 5.1, behaves quite differently from a truly pinned configuration: the static friction is found at smaller fraction of \(F_{1s}\) and the growth of the mobility toward the free value \(\mu_0\) is faster.

Figure 5.2 reports the mobility of the perfect crystal with mismatch \(\rho = 0.8615\) at \(T = T_{\text{room}}\) at different substrate potentials for a range of forces; fig. 5.3 illustrates the same quantity for the defective crystal, also at \(T = T_{\text{room}}\). The superlubric and pinned regimes remain clearly distinct even at finite \(T\). As it was at \(T = 0\), also at finite temperature the curves in the coexistence region are characterized by a depinning force if any lower than that of the truly pinned configurations obtained for \(U_0\) above the Aubry transition. The mobility approaches the free mobility \(\mu_0\) faster than for the pinned case.
Depinning transition

Figure 5.3: Mobility as function of the driving force for multiple substrate potential amplitudes for the defected mismatched lattice in close-to-real conditions ($T = T_{\text{room}}$). The curves relative to superlubric samples ($U_0 \leq 16.6 \text{ zJ}$) are easily spotted as their mobility remains finite down to $F = 0$. The curves relative to substrate potential values within the coexistence ($16.6 \text{ zJ} < U_0 < 61.3 \text{ zJ}$) region are the fast-growing ones at the middle of the plot. The curves for $U_0 \geq 61.3 \text{ zJ}$ are characteristic of the pinned regime: the mobility is 0 until the depinning force $F_s$ is reached.

Anticipating the discussion of the next chapter, this is due to a force-induced reverse transition: under small forces, the superlubric phase “eats up” the pinned region, resulting in a rapid gain in mobility.

Regardless of the substrate potential and the incommensurability, all the mobility curves must reach asymptotically the free sliding value $\mu_0$ in the limit of infinite driving force $F$. Figure 5.4 shows that this indeed happens when $F \simeq 5 \div 10 \times F_{1s}$. With forces well above the elementary barrier, the substrate potential cannot possibly hold back the colloids which slide almost freely above it, effectively averaging out the corrugation potential.
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Figure 5.4: The $T=0$ mobility of the perfect crystal under large driving forces. The corrugation potential parameters are $U_0 = 70 \, zJ$ and $a_1 = 5.6 \, \mu m$. For a force $F \gg F_{1s}$ both a single colloid and a monolayer with $a_c = 6.5 \, \mu m$, i.e. a mismatch ratio $\rho = 0.8615$, reach very close the mobility of a free colloid $\mu_0 = (m \gamma)^{-1}$ (dashed line).

5.2 Static friction

Starting from the mobility data, we evaluate the static friction as outlined in section 3.3. In chapter 4 we have seen that the first-order Aubry transition is diluted within the inhomogeneous coexistence region $U_{c1} < U_0 < U_{c2}$. At substrate amplitudes outside this region, superlubric ($F_s = 0$) and pinned ($F_s \neq 0$) regimes should be clearly visible. The coexistence region is characterized by the simultaneous presence of tilted regions, which should be able to slide under arbitrarily small driving forces $F$, and of pinned ones, with a threshold force $F_s$ that must be overcome to start the sliding. We will see in this section and in the next chapter how the interplay of this two phases determines the behavior of the system.

Figure 5.5 shows the behavior of the static friction for an incommensurate perfect crystal at $T = 0$. The superlubric curves at $U_0 \leq 14 \, zJ$ (like the green dashed one in fig. 5.1) are characterized by $F_s = 0$, showing finite mobility over the threshold $\mu_{th}$ for vanishing forces. In the pinned regime the static friction $F_s$ is finite but consistently smaller than $F_{1s}$. Note that the left bound of the
coexistence region $U_{c1} = 13 \, zJ$ does not mark exactly the end of the superlubric regime. This is because, until the tilted fraction $f_{\text{tilt}}$ is large enough, the pinned regions cannot lock the whole sample. Moreover, the application of a small force promotes the growth of the tilted fraction, increasing the mobility, as discussed later in chapter 6. As $U_0$ increases within the coexistence region, the pinned fraction of the system manages to lock the system up to a finite $F_s$ and the growth of the tilted fraction is observed only for forces above this threshold.

Figure 5.5 reports the static friction $F_s$ obtained taking as a starting configuration both the one generated in the upward and in the downward paths in $U_0$, section 4.2.1. Because of hysteresis and, thus, of different values of $f_{\text{tilt}}$ at the same substrate amplitude $U_0$, depinning is different in the two paths: the last superlubric configuration along the upward pathway is found at $U_0 = 15 \, zJ$, where $f_{\text{tilt}} = 1$ (see fig. 4.8), while along the downward pathway, at the same substrate amplitude $f_{\text{tilt}} = 0.3$. The superlubric regime is restored only at $U_0 = 14 \, zJ$, characterized by $f_{\text{tilt}} = 0.8$ (see fig. 4.9). This effect is probably due to our simulation protocol based on hysteresis: true equilibrium, and,
hence, extremely long simulations, in which memory of the initial configuration has been lost, should yield a single value for $F_s$.

Figure 5.6 show the results for the perfect mismatched crystal at $T = T_{\text{room}}$ for the downward pathway. The superlubric and pinned regimes are still clearly visible. Also at finite temperature, the superlubric regime ends within the coexistence region like as at $T = 0$. Moreover, the order of magnitude of $F_s$ in the pinned regime is comparable with the $T = 0$ case.

Figure 5.7 shows the results for the defective mismatched systems at $T = T_{\text{room}}$. The behavior of the static friction is of course similar to that of the perfect sampled analyzed. However, here the superlubric regime ends at a significantly smaller $U_0$. The defects, even though mobile themselves, may hinder the reverse transition toward the tilted phase, effectively locking the sample sooner than in the perfect crystal. Similar results were found by Guerra et al. in the 1D FK model[31]: quenched disorder in the substrate helps commensurate patches to nucleate and destroys the superlubric regime. Moreover, the presence of these defects makes is difficult to estimate the static friction reliably and leads to a non-strictly-monotone trend to the static friction curve.

Eventually, in the limit of infinite substrate potential, the static barrier should be affected only marginally by the colloid-colloid repulsion and thermal
fluctuations, and should therefore approach the elementary barrier, namely

\[ \lim_{U_0 \to \infty} F_s = F_{1s}. \]  

(5.3)

**Figure 5.7:** The static friction along the downward path as a function of the substrate potential at \( T = T_{\text{room}} \) for the defected colloid lattice with \( a_l = 6.5 \, \mu m \) and substrate with \( a_c = 5.6 \, \mu m \) in close-to-real conditions.

**Figure 5.8:** The static friction as function of the substrate potential at \( T = 0 \) for extremely large \( U_0 \). The dashed black line marks the elementary barrier \( F_{1s} \). The \( x \) axis reporting the substrate amplitude is in logarithmic scale.
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We verified that this indeed happens for extremely large (experimentally impossible to achieve) corrugation amplitude, as shown in fig. 5.8.
6

Force-induced reverse transition

The two-phase coexistence is a static phenomenon, namely a region of the equilibrium phase diagram where, at constant volume, two phases coexist. The presence of two phases in the system is not an artifact of peculiar initial condition or an issue of the simulation technique, but it is a real physical phenomenon. On the other hand, our simulation protocol based on hysteresis heavily enhances the dependance on the initial condition of the system and only produces metastable states in the phase coexistence region, due to relative short simulation time that artificially prevents full ergodic exploration of the configuration space. This would not be the case for a large and long enough equilibrium simulation or experiment within the coexistence region, where the simultaneous presence of the two phases would be fully probed regardless of the initial condition.

In this chapter we take the system in the coexistence region out of equilib-
Figure 6.1: (a) The time evolution of the fraction of tilted colloids $f_{\text{tilt}}$ (solid purple line) and of the instantaneous mobility $\mu$ divided by $\mu_0$ (dashed green line) from the start of the application of a force $F = 1.07F_s$. The shaded blue rectangles in (a) highlight the time windows of amplitude $\Delta t = 100\text{ ms}$ from which the mobility maps (b) and (c) come from. The snapshots (b) and (c) show a small, yet representative, portion of a large initially rotated crystal described in section 4.2. The colloids are plotted with the color convention introduced in chapter 4. Arrows show the displacement $\mathbf{r}(t_2) - \mathbf{r}(t_1)$ magnified by a factor 2.45. The simulation times are (b) $t_1 = 100\text{ ms}$, (c) $t_1 = 2900\text{ ms}$, corresponding to $200\text{ s}$ and $5800\text{ s}$, respectively.

We focus on a perfect crystal (defined by the parameters in section 4.2.1) at $T = T_{\text{room}}$ (the relative static results can be found in section 4.2.2 and the dynamical ones in chapter 5) with a substrate amplitude $U_0 = 36\text{ zJ}$, just above the estimated right boundary of the transition $U_{c2} = 32\text{ zJ}$. We increase $F$ in relatively small steps $\delta F = 0.05F_{1s} = 0.9\text{ fN}$ until $F = 1.8\text{ fN} = 0.83F_s$, then suddenly raise the driving force to $F = 2.7\text{ fN}$, corresponding to $F = 1.09F_s$ =
0.13F_{1s}, just above the depinning force $F_s$ and far below the elementary barrier of the system $F_{1s} = 17.95 \text{fN}$. What we observe is a dramatic change in the system structure: as time goes by, the tilted phase “eats away” the pinned phase formed by compressed islands separated by dislocation lines. The tilted fraction rises from 20% to 70% of the whole system and in correspondence with this structural change, the mobility rises from 10% to 40% of the free-colloid mobility value $\mu_0$. This process is quite slow: it takes the system approximately 3s of simulation time to reach the steady state, corresponding to 6000s with the realistic damping rate. Since this structural change toward the tilted phase from a system mostly pinned at equilibrium is promoted by the application of a driving force $F$ at fixed substrate corrugation amplitude $U_0$, we can call this phenomenon force-induced reverse transition.

In order to visualize this growing flow of colloids eroding the pinned islands, fig. 6.1b-c reports two snapshots, one before the transition takes place and one after, as steady state is reached. The figures also report the displacement $\Delta r_{t_1,t_2} = r(t_2) - r(t_1)$ of each colloid in the given time window $\Delta t = t_2 - t_1$. Figures 6.2 and 6.3 are a zoomed-out version of the same snapshots of fig. 6.1b-c) which give a more global picture of the large scale of this structural change.

Since the simulation considered is carried out at $T = T_{\text{room}}$, no colloid is ever actually fully pinned but they all fluctuate and diffuse. To filter out the thermal fluctuation and highlight the motions induced by the external force, we set a threshold on the displacement that the arrows actually report. From the distribution of $||\Delta r_{t_1,t_2}||$ within the analyzed time ranges of fig. 6.1, reported in fig. 6.4, we set the threshold $\Delta r_{\text{th}} = 1 \mu\text{m}$: only above it in figs. 6.1 to 6.3 we draw an arrow going from $r(t_1)$ to $r(t_2)$, amplified by the 2.45 factor to make it visible.

The snapshots of fig. 6.5 illustrate the mechanism by which this structural change takes place locally. During sliding, we observe initially pinned islands rotate, turning themselves spontaneously into tilted regions, and start to slide. This rotation is the opposite to what happens to a perfect crystal tilted at $\theta_{\text{NM}}$ relaxing over a strong enough substrate: in the that case the initially tilted domains locally rotate to align to the substrate lattice. As noted in
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Ref. [19], this is not the case for a colloidal lattice globally aligned with the corrugation. In that case the commensuration to the substrate can occur only by means of local isotropic compressions. Also in the driven system at hand, the opposite phenomenon of tilted region becoming pinned islands occurs, but at a lower rate than rotations to tilted phase, until a steady state is reached. In this steady state, islands and tilted regions keep on sprouting, advancing (the tilted ones only) and rotate back again. They do not involve specific colloids but, rather, remain delocalized with diffusive boundaries.

Another interesting feature of an applied force large enough to support sliding is that it helps erase the system memory. The starting configuration for the static analysis was a perfect crystal in the pure $+\theta_{NM}$ phase: this “red.colored” phase was the only tilted phase observed in equilibrium simulations.\(^1\) Instead, during this out-of-equilibrium process, large blue $-\theta_{NM}$ regions form, as shown in fig. 6.3. This indicates that the application of a driving force is a quite effective tool helping the system explore the available phases. The application

\(^1\)Essentially no blue clusters of colloids at $-\theta_{NM}$ are visible at equilibrium. The very few small ones are due to local thermal fluctuations.
Figure 6.3: A larger part of the system of fig. 6.1c). Note the blue patches ($\theta < -2.5^\circ$) relative to the $-\theta_{\text{NM}}$ phase, which were not present in the original starting configuration and in the quasi-equilibrium results but have sprouted spontaneously under driving.

of a force was used in experiments and could be used in future simulations to retrieve ergodicity.

In a structural characterization of the transition by means of the the structure factor $S(q)$ (like in section 4.3), we should verify that this reverse transition modifies the $S(q)$ function as well. This is indeed the case, as figs. 6.6 and 6.7 show: in the initial part of the trajectory (100 ms to 200 ms), the trace of the islands pattern described in section 4.3 is similar to the one in fig. 4.14c, while the structure factor of fig. 6.7 (2900 ms to 3000 ms), at the end of the reverse transition, is comparable to the superlubric one of fig. 4.14a.
Chapter 6 Force-induced reverse transition

**Figure 6.4:** Distribution of the displacement amplitude $\|\Delta r_{t_1,t_2}\|$ for $t_1 = 100$ ms and $t_2 = 200$ ms (solid purple curve) and for $t_1 = 2900$ ms and $t_2 = 3000$ ms (dashed green curve). The histogram bins are 0.10 $\mu$m-wide. The dotted line at 1 $\mu$m is the threshold we set for the drawing of the arrows in figs. 6.1 to 6.3.

**Figure 6.5:** The elementary mechanism of phase changing at subsequent time steps $\Delta t_a = 200-100$ ms (a) and $\Delta t_b = 300-200$ ms (b); all the snapshots report the same area of the sample. In snapshot (a) three islands are rotating counter-clockwise, as illustrated by the arrows, and become bona-fide tilted, superlubric regions in panel (b).
**Figure 6.6:** The function $S(q)$ of the system in the time window $100 - 100 \text{ ms}$ shown in fig. 6.2. The structure factor is computed as described in section 4.3 and averaged over 10 configurations.

**Figure 6.7:** The function $S(q)$ of the system in the time window $2900 - 3000 \text{ ms}$ shown in fig. 6.3. The structure factor is computed as described in section 4.3 and averaged over 10 configurations.
Chapter 6 *Force-induced reverse transition*
Conclusions

This work has touched several arguments and analyzed many facets of the behavior of a mismatched layer of colloids in a periodic potential. Thus, it is necessary now to draw conclusions about the achievements and the next possible steps.

On the structural side, we verified that the Novaco-McTague theory applies to our system and we observed an undocumented behavior of the pair-potential energy $U_{pp}$ at large substrate amplitude $U_0$. We proposed a simple argument to determine the ground state of the system at very large corrugation $U_0$, beyond the validity of the Novaco-McTague theory, which could be verified in the future.

We explored the phase diagram of the system, verifying that the Aubry transition is indeed first order in 2D. We estimate the coexistence region by means of the standard disorder parameter $\Psi$, plus the tilted fraction $f_{\text{tilt}}$ based
on the local angle of the colloids. We have compared the structural phase
diagram, also characterized by means of the structure factor $S(q)$ for an ideal
crystal at $T = 0$ and a more realistic situation at finite temperature. We found
that the coexistence region is strongly affected by crystal defects.

We analyzed the behavior of the system out of the thermodynamic equi-
librium, under a driving force and its dynamical response: as function of the
substrate amplitude $U_0$, we found a superlubric region, characterized by the
absence of static friction $F_s = 0$, and a pinned one with finite friction, as we
expected from the literature. Within the coexistence region we identified a sort
of “running in” behavior that we named force-induced reverse transition that
consists in a structural rearrangement of the system promoted by the driving
force which lead to a friction reduction and a corresponding slow increase of
the average velocity of the monolayer. This phenomenon could explain why
the mobility grows faster with force within the coexistence region than in the
pinned one.

All this work has been carried out in contact with ongoing experiments in
Stuttgart, with which we were able to carry out quantitative comparisons. For
both theory and experiment, a clear step forward could be a “fully ergodic”
investigation of the coexistence region in a detailed exploration of the equilib-
rium configurations, by following the evolution of the superlubric and pinned
regions as a function of $U_0$ in the absence of any hysteresis.

Regarding the first-order nature of the Aubry transition in two dimensions,
we consider it an interesting challenge to observe the system at the critical
point at the end of the first-order transition line, where this transition should
leave room for a continuos crossover.

Due to the asymmetry of the pair interaction potential, the phase transition
and the dynamical response of the system may show different features in the
overdense case $\rho > 1$.

Another question related to ergodicity which remains open is how the col-
loidal system stores information about its past within the network of disloca-
tion lines.

Related future work could focus on the possible Aubry transition and dy-
amics of the colloidal systems over a quasi-crystalline substrate.
Appendices
Supercell construction and data

Let $a_c$ and $a_l$ be the lattice spacing of the colloids and the corrugation, respectively, and $\hat{a}_1 = (1, 0)$ be one of the primitive versor of the corrugation lattice; the lattice with the desired periodicity is generated by a primitive vectors $a_i = a_i \hat{a}_i$. The matrix representing the discrete rotational symmetry of the lattice by an angle $\Omega$ is:

$$R_\Omega = \begin{pmatrix}
    \cos \Omega & -\sin \Omega \\
    \sin \Omega & \cos \Omega
\end{pmatrix} = \begin{pmatrix}
    u & -\nu \\
    \nu & u
\end{pmatrix}.$$  

(A.1)

Thus, the second versor defining the lattice is $\hat{a}_2 = R_\Omega \hat{a}_1$. Since we assume that the two lattices have the same symmetry, we can define a matrix describing the misalignment $R_\theta = \begin{pmatrix}
    \cos \theta & -\sin \theta \\
    \sin \theta & \cos \theta
\end{pmatrix}$. This way, the versors defining the second
The supercell lattice are

\begin{align*}
\hat{b}_1 &= \frac{R_\Omega}{R_\Omega} \cdot \hat{a}_1 \\
\hat{b}_2 &= \frac{R_\Omega}{R_\Omega} \cdot \hat{b}_1 = \frac{R_\Omega}{R_\Omega} \cdot R_\theta \cdot \hat{a}_1.
\end{align*}

(A.2) 

(A.3)

The supercell will be compatible with both lattices if their cells match exactly, namely, the following matching condition is satisfied:

\begin{equation}
\frac{a_l}{a_c} (n_1 \hat{a}_1 + n_2 \hat{a}_2) = a_c (m_1 \hat{b}_1 + m_2 \hat{b}_2).
\end{equation}

(A.4)

The condition in eq. (A.4) can be rewritten with a matrix formalism:

\begin{equation}
\frac{a_l}{a_c} (n_1 \hat{a}_1 + n_2 \frac{R_\Omega}{R_\Omega} \cdot \hat{a}_1) = m_1 \frac{R_\Omega}{R_\Omega} \cdot \hat{a}_1 + m_2 \frac{R_\Omega}{R_\Omega} \cdot R_\theta \\
\rho \left( \begin{array}{c}
I \\
\frac{R_\Omega}{R_\Omega}
\end{array} \right) \cdot \left( \begin{array}{c}
n_1 \\
n_2
\end{array} \right) = \left( \begin{array}{c}
I \\
\frac{R_\Omega}{R_\Omega}
\end{array} \right) \cdot \left( \begin{array}{c}
m_1 \\
m_2
\end{array} \right) \cdot R_\theta
\end{equation}

(A.5)

where we used the definition of the lattice vectors in eqs. (A.2) and (A.3), introduced the mismatch ratio \( \rho = a_l/a_c \), grouped the matrices and the indexes in vectors and simplified \( \hat{a}_1 \) from both sides. Given the four indexes \( \{m_i, n_i\}_{i=1,2} \), we can invert the system and find the mismatch ratio \( \rho \) and the misalignment angle \( \theta \) that match the two lattices defined by the four indexes and thus find a suitable supercell for both of them. In order to do so, we solve equation (A.5) for the matrix \( \frac{R_\Omega}{R_\Omega} \) and for \( \rho \) together with the request that \( \frac{R_\Omega}{R_\Omega} \) is a rotation matrix, namely:

\begin{equation}
\frac{R_\Omega}{R_\theta} = \rho \left( m_1 I + m_2 \frac{R_\Omega}{R_\Omega} \right)^{-1} \left( \begin{array}{c}
I \\
\frac{R_\Omega}{R_\Omega}
\end{array} \right) \cdot \left( \begin{array}{c}
n_1 \\
n_2
\end{array} \right)
\end{equation}

(A.6)

\begin{equation}
\det \frac{R_\Omega}{R_\theta} = 1.
\end{equation}

(A.7)
We can easily calculate the inverse of the matrix in (A.6):

\[
\left( m_1I + m_2R_\Omega \right)^{-1} = \frac{1}{m_1^2 + m_2^2(u^2 + \nu^2) + 2m_1m_2u} \begin{pmatrix} m_1 + um_2 & \nu m_2 \\ -\nu m_2 & m_1 + um_2 \end{pmatrix}
\]

\[
= \frac{1}{N_p} \left( m_1I + m_2R_\Omega^T \right),
\]

(A.8)

where we have defined \( N_p = \det \left( m_1I + m_2R_\Omega \right) = m_1^2 + m_2^2(u^2 + \nu^2) + 2m_1m_2u \) because it actually is the number of particles of spacing \( a_c \) within the supercell.

We can now solve equation (A.6):

\[
R_\theta = \frac{\rho}{N_p} \left( m_1I + m_2R_\Omega^T \right) \cdot \left( m_1I + m_2R_\Omega \right)
\]

\[
= \frac{\rho}{N_p} \begin{pmatrix} m_1n_1 + m_2n_2 + u(m_2n_2 + m_2n_1) & -\nu(m_1n_2 - m_2n_1) \\ \nu(m_1n_2 - m_2n_1) & m_1n_1 + m_2n_2 + u(m_2n_2 + m_2n_1) \end{pmatrix}
\]

\[
= \frac{\rho}{N_p} \left( \mathbb{I}(m_1n_2 + m_2n_2) + \frac{R_{\Omega}m_1n_2 + R_{\Omega}^Tm_2n_1}{\sqrt{\det A}} \right) = \frac{\rho}{N_p} A
\]

(A.9)

where the matrix \( A \) is defined implicitly in the last step of the equation. We can now use eq. (A.7) to find \( \rho \) and put it back in eq. (A.9) to get an expression for \( R_\theta \) and, thus, for \( \theta \):

\[
1 = \det R_\theta = \frac{\rho^2}{N_p^2} \det A
\]

(A.10)

\[
\rho = \frac{N_p}{\sqrt{\det A}}
\]

(A.11)

\[
R_\theta = \frac{A}{\sqrt{\det A}}
\]

(A.12)

\[
\theta = \arccos \left( \frac{1}{\sqrt{\det A}} A_{11} \right)
\]

\[
= \arccos \left( \frac{1}{\sqrt{\det A}} \left[ m_1n_1 + m_2n_2 + u(m_2n_2 + m_2n_1) \right] \right).
\]

(A.13)
Chapter A *Supercell construction and data*

The first primitive vector of the obtained supercell is $\mathbf{C}_1 = a_1(n_1\hat{a}_1 + n_2\hat{a}_2)$ and the second one is obtained by a rotation of $\Omega$:

\[
\mathbf{C}_2 = R_{\Omega} \cdot \mathbf{C}_1 = a_1(n_1R_{\Omega}\hat{a}_1 + n_2R_{\Omega}\hat{a}_2) = a_1n_1 \left( \begin{array}{c} u \\ \nu \end{array} \right) + a_1n_2 \left( \begin{array}{c} u^2 - \nu^2 \\ 2uv \end{array} \right).
\] (A.14)

Relations eq. (A.13) and eq. (A.14) for the triangular case ($\Omega = \pi/3$) are reported in section 3.1. We can use them to generate many cells for $0^\circ \leq \theta \leq 30^\circ$ and for ratios $\rho$ as close as possible to the experimental value $\rho_{\text{exp}} \simeq 0.86$. These informations are listed in table A.1.

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Table A.1: The parameter of the supercells used in section 4.1 to investigate the angular dependence of energy. The bold line at $\theta = 54.3623^\circ$ highlights the supercell used in the static and dynamical analysis.
Chapter A *Supercell construction and data*
Bibliography


BIBLIOGRAPHY
Breathe, keep breathing. Don't loose your nerve.
Breathe, keep breathing. I can't do this alone.
Radiohead. “Exit Music (For a Film)”.

Acknowledgments

Innanzitutto vorrei ringraziare Nicola Manini per avermi guidato attraverso questa tesi con infinita pazienza e per le inestimabili lezioni durante tutti questi mesi. Ringrazio inoltre Andrea Vanossi, Roberto Guerra, Erro Tosatti, Clemens Bechinger e Thorsten Brazda per le numerosi discussioni e i consigli che hanno forgiato questa tesi e, in parte, il sottoscritto.

Un ringraziamento senza confini alla mia famiglia, per non aver mai dubitato di me, per avermi sostenuto in tutti questi anni ed essere sempre stati presenti.

Grazie ai colleghi e agli amici: Poli, Stefania, Panzeri, Admin, Mirigliano, Sara, Chantal, Mike, Stella, Mario, Fabrizio e Giulia per aver reso Milano una città stupenda in cui vivere (e il dipartimento di Fisica un posto più gioioso). Grazie a Marco, per cos’è tanto che non provo neppure a scrivere lo qui. Grazie a Piero, che anche se fa il valligiano burbero, gli fa piacere sopportarmi. Grazie a Luca, per le discussioni intrise di cattiveria sulla fisica e sulla vita che mi hanno accompagnato in questi anni e durante questo lavoro. Grazie a Campa e a Toni per avermi sorretto (anche letteralmente a volte…) nell’ultimo anno e per essere le persone incredibili che sono. Grazie a LCM e ai suoi abitanti per creare l’ambiente di lavoro migliore in cui si possa sperare e, soprattutto, per i frag.

Grazie agli amici con cui ho ormai condiviso lustri e collezionato una miriade di ricordi stupendi tra Como, Cantù e Chiavari: Vale, Simo, Chiara, Moma, GrandeC, Santra, Bare, Dona, Leila, Omar, Pietro, Silvia, Prugna, Jüsh, Mik, Mosca, Sgu, Matteo, Marco e Andrea.