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*Dedicated to Labrini and Ali, the two shining stars of my life,
and to my parents Mehru and Asif.*

Zusammenfassung

Diese Dissertation beinhaltet eine Reihe von theoretischen Untersuchungen von kolloidalen Teilchen, die mit Laserlicht wechselwirken. Je nach chemischer Zusammensetzung werden die Teilchen entweder von Regionen mit hoher Lichtintensität angezogen oder sie werden zu aktiven Schwimmern, falls sie beleuchtet werden. Systeme solcher Teilchen sind Beispiele für “Optische Materiallien”, und bilden eine Untergruppe der weichen Materie. Das Ziel dieser Dissertation ist es, die entstehenden Strukturen und das dynamische Verhalten zwei-dimensionaler Anordnungen solcher Teilchen zu untersuchen, wenn sie von Lichtmustern unterschiedlicher Geometrie und Intensität beleuchtet werden. Kapitel 1 ist eine Übersicht dieser Dissertation und besteht aus einer kurzen Einführung in das Gebiet der weichen Materie, einer Aufzählung der typischen Herausforderungen, die sich in der Simulation ergeben, einer Erläuterung der Forschungsstrategie und einer Zusammenfassung der darauf folgenden Kapitel.

In Kapitel 2 wird eine Untersuchung der dynamischen Phasen einer Monolage kolloidaler Teilchen, die mittels einer konstanten Kraft über eine externe Potentiallandschaft getrieben werden, unternommen. Die Bewegung der Teilchen lässt sich in guter Näherung mit einer überdämpften Langevin Gleichung beschreiben. Die auftretenden dynamischen Phasen lassen sich abhängig von der Stärke der Teilchen-Teilchen Wechselwirkung in drei Regime gliedern. Für schwache Wechselwirkungen bewegt sich die Monolage durch die Entstehung vieler unabhängiger Defekte. Wenn man die Wechselwirkungsstärke erhöht bewegt sich der Kristall durch Bildung ausgedehnter Kompressions- und Dekompressionszonen. Für große Teilchen-Teilchen Abstoßung beobachtet man eine “stick-slip” Bewegung, in der die Monolage als Ganzes über das Lichtmuster gleitet. Die Vorhersagen dieses Kapitels können mittels kolloidaler Teilchen, die mit periodischen Lichtfeldern bestrahlt werden, experimentell überprüft werden. Die Analyse der Simulationsergebnisse zeigt, dass die Teilchen-Teilchen Wechselwirkung Korrelationen erzeugt, welche den Gleitmechanismus der Monolage bestimmen.

In Kapitel 3 wird eine analytische Theorie präsentiert, die den Gleitmechanismus einer harten Monolage, die über eine kommensurable Potentiallandschaft getrieben wird, quantitativ beschreibt. Mittels einer harmonischen Approximation und elementarer statistischer Mechanik wird die Bewegungsgleichung der Monolage auf eine einfache Differentialgleichung abgebildet. Die analytischen Ausdrücke, die mit diesem Verfahren erlangt werden, sagen einen Übergang zwischen einer Serie von thermisch aktivierten Sprüngen über Energiebarrieren zu “thermischem Gleiten” voraus. Unter starken äußeren Kräften verschwindet die effektive Barriere aufgrund thermischer Fluktuationen, was zur Folge hat, dass die Monolage kontinuierlich über das Substrat gleitet. Weiters wurde

festgestellt, dass die mittlere Geschwindigkeit für große Antriebskräfte ein einfaches Skalierungsverhalten aufweist, das konsistent mit der Existenz einer statischen Reibungskraft ist. Für kleine Antriebskräfte hingegen existiert ein Nukleationsmechanismus, der für eine kleine, aber von Null verschiedene Mobilität sorgt. Die Theorie wurde mit Hilfe extensiver Simulationsdaten validiert und eine quantitative Übereinstimmung von Theorie und Simulation wurde gefunden. Die Theorie ist auf Systeme anwendbar, in denen die Wechselwirkung zwischen Teilchen sehr groß ist und liefert präzise Aussagen, die experimentell überprüft werden können.

In den vorherigen Kapiteln wurde eine Theorie entwickelt, die auf kurzreichweitige, rein abstoßenden Potentiale zutrifft. In Kapitel 4 werden die dynamischen Phasen einer Monolage von Teilchen untersucht, die mit einem Lennard-Jones-Potential wechselwirken. Das Lennard-Jones-Potential besitzt einen abstoßenden und einen anziehenden Anteil, wodurch die Wechselwirkung eine charakteristische Länge aufweist, die mit dem Abstand der Substratpotentialminima in Konkurrenz steht. Die resultierenden Veränderungen im Systemverhalten wurden untersucht, in dem die Wechselwirkungsreichweite des Lennard-Jones-Potentials größer, gleich, und kleiner als die Gitterkonstante des Substratpotentials gesetzt wurde. Wie erwartet, gab es qualitative Ähnlichkeiten zur vorherigen Arbeit solange die Teilchen im System sich typischerweise abstoßen, während die dynamischen Phasen im attraktiven Bereich durch Bildung von Rissen in der Monolage gekennzeichnet sind.

Motiviert durch Experimente, in denen kolloidale Teilchen mittels Laserlicht zu aktiven Schwimmern gemacht werden, wird in Kapitel 5 das Verhalten solcher Teilchen untersucht, wenn sie von einem Lichtmuster bestrahlt werden. Das Lichtmuster bewirkt, dass nur die Teilchen, die sich in einem stark beleuchteten Teil des Raums befinden, zu aktiven Schwimmen werden ("Active Patches"). Simulationen dieser Active-Patch-Systeme und Analyse der Struktur und Dynamik des entstehenden stationären Zustands wurden durchgeführt. Für symmetrische aktivitätsinduzierende Zonen gibt es eine qualitative Ähnlichkeit zu einem rein Brownchen System, das einem Temperaturgradient unterliegt. Für asymmetrische Active Patches hingegen bricht diese Analogie zusammen, da ein Teilchenfluss auftritt. Die Ergebnisse dieser Studie sind experimentell zugänglich und könnten zu einem tieferen Verständnis von Chemotaxis beitragen.

Abstract

This thesis is a compilation of a series of projects in which simulations and analytical calculations of colloidal particles that interact with laser light were performed. Depending upon their chemical composition, these colloidal particles are either attracted to regions of high laser light intensity or can be made into active swimmers if illuminated. Systems of these particles therefore belong to a class of new materials called “optical matter”, which is a subset of the broader field of soft matter. The aim of this thesis is to study the typical dynamics and structures that arise when a two-dimensional arrangement of these colloids are subject to light patterns of varying intensity and geometry. The first chapter of this thesis consists of an introduction to the field of soft matter, a survey of the typical difficulties encountered by computational physicists, an explanation of the research philosophy that was employed, and an outline of the ensuing chapters.

In Chapter 2, an examination is made of the dynamical phases of a monolayer of charge-stabilized colloids driven over a substrate potential by an external dc force acting along a symmetry axis of the monolayer. Using overdamped Langevin dynamics, the sliding transition for various inter-particle interaction strengths as a function of the driving force was studied. For weak interactions, the diffusion of individual defects is responsible for the motion of the monolayer. As the interaction strength is increased, sliding is induced by distinct density compression and decompression zones. For very strong interactions, a type of stick-slip mechanism emerges, in which the sliding of the monolayer is mediated by the propagation of collective distortion waves. The predictions made in this chapter can be tested experimentally with two-dimensional arrangements of colloidal particles exposed to periodic light fields and it is shown that the inter-particle interaction strength tunes the degree of correlation in the sliding mechanism adopted by a monolayer driven over a commensurate substrate.

In Chapter 3, an analytical theory and computer simulations to study the effect of thermal fluctuations on the stick-slip mechanism characteristic for the frictional response of a stiff colloidal monolayer on a commensurate substrate is presented. By performing a harmonic expansion of the energy and employing elementary statistical mechanics, the motion of the monolayer can be mapped onto a simple differential equation. Analytical expressions derived from this approach predict a transition from nucleation dynamics, where the monolayer moves in a sequence of activated hops over energy barriers, to “thermal sliding”, in which the effective substrate barrier opposing the motion of the monolayer disappears due to thermal fluctuations, leading to continuous, uninterrupted sliding motion. Furthermore, it is found that the average velocity of the monolayer for large driving forces obeys a simple scaling behavior that is consistent with the existence of

a static friction. For small driving forces, however, nucleation provides a mode of motion that leads to a small but non-vanishing mobility of the monolayer. Data obtained from simulations confirm this picture and agree quantitatively with our analytical formulae. The theory developed here holds under general conditions for sufficiently strong inter-particle repulsions and yields specific predictions that can be tested in experiments.

In the previous chapters, a theory was developed that applies to short-ranged, repulsive, potentials. In Chapter 4 an examination of the dynamical phases of a monolayer of particles that interact via a Lennard-Jones interactions is undertaken. The Lennard-Jones interaction is special because it consists of both a repulsive and an attractive part, which results in a characteristic length scale of the interaction that is in competition with the length scale of the external substrate potential. The resulting change in the dynamical phases was probed by simulating systems in which the range of the interaction was set to larger, equal, and less than the lattice constant of the substrate potential. As expected, there was a qualitative correspondence to the previous studies if particles typically repelled each other, whereas the dynamical phases in the attractive regime were mediated through the formation of cracks in the monolayer.

Motivated by recent experiments in which colloidal particles can be made into active swimmers through the use of laser light, Chapter 5 is dedicated to studying the effects of applying a light pattern on the sample, thereby creating activity inducing zones, or active patches. A system of interacting Brownian diffusers that become active swimmers if they enter an active patch was simulated and an analysis of the structure and dynamics of the ensuing stationary state was performed. For symmetric activity zones, the system reacts qualitatively similar to a system with a temperature differential. For asymmetric active patches, this analogy breaks down because we observe a net flow in the system. The predictions herein can be tested experimentally and may form the basis for a deeper understanding of chemotaxis.

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Chapter 1

Introduction

1.1 An overview of soft matter

Although the objects studied in soft matter are of varied composition and shape, they invariably consist of building blocks that range from several hundred nanometers to micrometers in size. Examples of such building blocks include polystyrene spheres, polymers, and bubbles formed from a multitude of materials. The aggregates formed by these objects are typically called colloidal suspensions, gels, and foams, respectively. In this section, it will be argued that the complexity of soft matter systems arises due to the simultaneous interplay of thermal, hydrodynamic, chemical, geometrical, and in this thesis, electromagnetic effects.

The three related fields that pre-occupy themselves with the influence of temperature on a system are the study of stochastic processes, thermodynamics, and statistical physics and each of them plays a significant role in soft matter. A solitary colloidal particle, for instance, performs Brownian diffusion because it is so small that the thermal fluctuations in the fluid it is suspended in are large enough to exert a relevant stochastic force on the particle, causing it to perform a random walk in space. Furthermore, since one usually finds large numbers of soft matter objects suspended in a medium, a thorough investigation requires a knowledge of thermodynamics and statistical physics, with their predictions of order-disorder transitions. The influence of temperature has a significant and dramatic effect on both their individual and collective behavior [1].

In addition to inducing the stochastic motion mentioned in the previous paragraph, the suspending fluid of a soft matter object can also be the origin of steric and hydrodynamic interactions. An example of steric interactions between soft matter objects are depletion interactions that usually arise from the interaction between large soft matter objects in a bath of smaller particles. To illustrate this, micrometer sized beads suspended in a polymer mixture form a zone around them that is inaccessible to the polymers. If two such beads are brought close together, then the overlap of these exclusion zones

results in an osmotic pressure that makes them effectively attractive [2]. Hydrodynamic interactions between particles are due to the fact that the motion of a particle in a fluid creates a flow field that propagates through space and influences the motion of neighboring particles. Both of these effects are due to the fact that the motion of soft matter objects can be strongly affected by the pressures and flows that they induce in the fluid they are suspended in [3].

The study of biochemistry also has many important implications for the field of soft matter. Many processes in biological systems, such as the function of cells and proteins, occur at a similar length scale of soft matter systems and many advances in biochemistry can be used to create new soft matter systems. One of the aspirations of the soft matter community is to build “smart materials” such as the often cited drug delivery system in which specialized proteins are grafted onto a colloid so that it only bonds to damaged cells before depositing its payload of medicine [4]. The fact that a deeper understanding and control of biological systems on a chemical level can be transferred to soft matter systems is part of the reason why this field is growing so rapidly today [1].

There is a great deal of physics and mathematics that can be observed even when the particles under consideration are only hard bodies. In this case, the behavior of ensembles of such particles is entirely determined by the shape of the particles under consideration. In its simplest incarnation, the study of liquid crystals, which constitutes a large area in soft matter, preoccupies itself with systems consisting of rod, flat, or bowl-like objects. At sufficiently high densities, a collection of rods form phases with orientational order. These structures are called smectic and nematic phases and considerable topological analysis are necessary to predict and explain the veritable zoo of structures that have been observed [5].

The final overlap that will be mentioned is the marriage between electromagnetism and soft matter. By using materials that respond to electric or magnetic fields, one is able to create systems such as liquid crystals and ferro-fluids that comprise a new generation of materials that can be manipulated on a per-building block level with reasonably small field strengths, such as the light emitted from a laser. Here, again, the size of the objects under considerations is taken advantage of, since the electric and magnetic fields required to move a bead that is micrometers in size is so small, that laser tweezing is a common tool of the trade.

In summary, soft matter can be considered a quintessential example of classical physics since it is a field in which electromagnetism, Newtonian mechanics, hydrodynamics, statistical physics, and thermodynamics meet.

1.2 A heuristic description of soft matter

In the previous section, an introduction was made of the specific behaviors typically encountered in the field of soft matter. In this section, a heuristic derivation of the name soft matter will be attempted, so that its relation to the other fields of physics can be made clear.

So far, the working definition of soft matter has been the length scale under consideration. Therefore, one might be tempted to call this field *mesoscopic* matter instead of *soft* matter, since the latter has absolutely no relation to a length scale. In his inaugural lecture at the University of Vienna, Professor Christos Likos gave an elegant rationale as to why the term *soft* matter is appropriate. The qualification *soft* refers to the *hardness* of a material. To relate a *hardness* to a length scale, consider the following dimensional analysis of the yield stress, ϵ , which is a typical measure of the rigidity of an object. The yield stress is defined as the pressure above which a material begins to deform plastically (irreversibly) and is therefore a measure of how difficult it is to dent an object. The yield stress is measured in Megapascals for materials such as iron or wood and can be rewritten as a force per unit area $\epsilon = \tilde{F}/\tilde{L}^2$, which in turn can be recast as $\tilde{E}/\tilde{L}^3$, where $\tilde{L}$ is the typical length scale of the material and $\tilde{E}$ is the typical energy required to deform it. Imagine a crystal with a typical length scale $\tilde{L}$ composed of objects that interact with an energy $\tilde{E}$, where both quantities are given in Joules and meters, respectively,

$$\begin{aligned}\epsilon &\approx \frac{\tilde{E}}{\tilde{L}^3} \left[\frac{J}{m^3} \right] \\ &= \frac{4.11 \times 10^{-21}}{10^{-18}} \frac{E}{L^3} \left[\frac{k_B T}{\mu m^3} \right] \\ &= \frac{1.025}{250} \frac{E}{L^3} \left[\frac{k_B T}{\mu m^3} \right].\end{aligned}\tag{1.1}$$

By rewriting the yield stress in terms of micrometers, μm , which is the typical length scale encountered in soft matter, and $k_B T$ which is the energy of a thermal fluctuation, one obtains the prefactor $1/250$. For soft matter systems, the typical values of E and L are close to unity in these units, and so the resulting yield stress is of the order $\epsilon = 10^{-3} k_B T / \mu m^3$. Typical values of ϵ for steel, brass, and aluminum are $\epsilon \approx 10^{11} k_B T / \mu m^3$ (several hundred mega Pascals). This dimensional analysis shows, that the interaction energy between the elements of a soft matter crystal must be several orders of magnitude larger than $k_B T$ to obtain a large yield stress. Thus, at this length scale, unless the constituent particles of an aggregate strongly interact with each other, they tend to be soft.

By decreasing the size of the building blocks to the Angstrom world of atoms and electrons, $L = 10^{-4} \mu m$, not only does one find that the yield stress automatically grows due to the shift in length scale, but the binding energy between the constituents also

increases; the typical binding energy between atomic particles is measured in electron volts, where $1\text{eV} \approx 40k_{\text{B}}T$. Molecular bond energies, for example range from $1 - 10\text{eV}$, corresponding to $E = 40 - 400k_{\text{B}}T$, almost two orders of magnitude larger than soft matter systems. This rough analysis places the yield stress of a crystal formed by atoms in the range of $\epsilon \approx 10^{11}k_{\text{B}}T/\mu\text{m}^3$ which is consistent with the aforementioned experimental findings.

This dimensional analysis remains unchanged when performed on the bulk modulus, which represents the resistance of a material to a uniform compression, and on the Young's modulus, which relates the elastic extension of a sample due to a force, because these two quantities are also measured in units of pressure.

Systems made of building blocks in the micron range and larger, usually belong to the field of granular matter. Examples of granular material include sand, snowflakes, and billiard balls. Aggregates of such objects are called piles or stacks, and do not have a meaningful yield stress since it is either impossible to compress an such assortment of objects, or one creates flows, avalanches, or cascades. The fundamental difference between soft matter and granular matter is that the interactions between individual grains vanishes unless they touch and therefore there is no restoring force to keep its aggregates intact. As a result, one way of thinking of the field of soft matter is, “the largest objects that are still capable of forming stable phases” [8], and by virtue of their characteristic energy and length scales, theses phases are typically soft.

1.3 Insight by analogy

In addition to being interesting in and of themselves, soft matter systems also offer an “insight by analogy”. This is due to the eminent customizability of soft matter systems that allows one to make experimental realizations of Ising models, toy models for DNA, and observe the melting transition in two dimensions. In fact, the entirety of this thesis is dedicated to the analysis of experiments and mathematical models whose behaviors are intended to mimic completely different systems. In Chapters 2-4, simulations of colloidal particles in an external field are discussed, and although they describe the behavior of a mesoscopic system, the main goal is to draw an analogy between the collective motion of an ensemble of colloidal particles to the collective motion of an ensemble of atoms. The fact that atoms interact with a much more sophisticated potential or the fact that quantum effects may influence their motion is not a drawback of the approach but instead provides us with an insight as to which effects can and cannot be ignored. By making predictions of simpler models and carefully tracking their “failure” to describe the real thing, one hopes to discover the missing concept necessary for a complete understanding. Similarly, the simulations in Chapter 5, were motivated by experiments on colloidal particles that were modified so that their equations of motion

resemble those of swimming bacteria, and again, although the system is inspired by experiments of “dead” soft matter, the aim of this study is to explore the physics of a biological, non-equilibrium system. As Richard Feynman famously stated, “the same equations have the same solutions”.

1.4 Salute to experimental prowess and methodology of the thesis

Since most of the physics in soft matter occurs at the mesoscopic scale, experiments in this field usually yield very precise measurements with a high level of detail. There are remarkable experiments of liquid crystals, colloidal particles, and nano-scale materials that are being conducted, in which one can see an actual image of the physical process as it unfolds in experiment, oftentimes with a per-particle resolution. As a result, for a computational physicist, providing new insights can be a challenge. The problem lies in the fact that, broadly put, most simulations use some sort of physically motivated algorithm to produce a series of representative configurations (or density fields in the case of a continuum theory), from which physical quantities such as free energies, specific heat capacities, or average densities are to be extracted. However, if on the experimental level, techniques such as video microscopy are used to obtain precisely those configurations one hopes to obtain from simulations, then it is an open question as to what “added value” is offered by simulation. The justification that, “our simulation results predict that the experiment exists” is unlikely to garner gasps of insight.

Given that both simulation and experiment are producing a similar data (*i.e.* a sequence of configurations that are representative of the system), there are two philosophies that have proven helpful in creating this thesis. As discussed in the first section of this introduction, soft matter phenomena are usually the simultaneous interplay of multiple effects. One avenue available to computer simulation is that each “layer” of physics can be successively added onto the simulation. Much as the theoretician can set various coefficients to zero or infinity in an equation, the influence of various effects in a simulation model can be switched on or off at will. For example, one can compare a system of hard spheres both in the presence and in the absence of gravity by changing a single line of code. This ease of manipulation allows one to quantitatively isolate the role of a boundary, defect, or of temperature usually unavailable to other methods of inquiry. The second facility is related to the first; in any simulation algorithm, there are a series of parameters that represent the physical details of the system. Once the architecture of the code is complete, varying these parameter values comes at the cost of electricity only, and as such, one can not only find the limits of validity of a known effect, but, ideally, offer interesting regimes in parameter space around which real experiments can

be designed. A common line of inquiry in our field lies in calculating the phase diagrams of various models; this family of experiments relies on formulating a sensible interaction between particles in a simulation cell, and documenting the structures that arise for all possible temperatures, pressures, and densities.

For each topic that was treated in this thesis, inspiration was drawn from seminal experiments for which the simulation algorithms are well known, simple and precise. The “added value” that is offered in Chapters 2-4, came from the ability to manipulate the simulation parameters in such a way as to suppress the influence of temperature on the system and then to make it the dominant effect. By interpolating between these two extremes one can then qualitatively and sometimes quantitatively “understand” its influence. In Chapter 5, this approach is repeated by comparing all of the simulation results of a system active swimmers with a more conventional diffusive system.

Try as we might, physical phenomena do not always occur in a vacuum, especially in soft matter. In fact, it is precisely this interplay of temperature, geometry, energy, and shape that actually gives rise to many exciting and fundamental processes worth exploring. It is therefore essential that theoretical, virtual, and tangible experiments are designed in such a way as to be able to compare the role that each of these effects has.

1.5 Summary of this thesis

A great deal of effort was placed into writing clear and precise reports of the research that was done for this thesis. As a result, the author hopes that the brevity of this section is not taken amiss, and assures the reader that each chapter is a self contained work. Chapters 2-4 are reports that have already been published [9–11], whereas Chapter 5 is a work in progress that is intended to be published at a later date.

Chapters 2-4 of this thesis are dedicated to an exploration of the two-dimensional Frenkel–Kontorova (FK) model [12]. The original formulation of this model was proposed in the early 20th century, and its aim was to describe friction on an atomic level. The friction between two surfaces that are in contact with one another, also known as dry friction, consists of the motion of the atoms of one body as it is pressed against another and then sheared or driven. The insight of Frenkel and Kontorova was in imagining that one surface can be modeled as a chain of harmonically coupled particles and the other surface is so rigid that it acts as an external potential. They were then able, through the use of advanced mathematical methods, to solve this system, and found that when a force driving force is applied onto the chain of particles, the system evolves so-called kinks and anti-kinks, which are solitonic solutions of the FK model [12]. Although this success is profound, the model cannot be easily solved in two dimensions. In 2012 Clemens Bechinger and colleagues were able to create an experimental realization of the FK model through the use of charge stabilized colloids that can be optically trapped

by laser light [6]. By applying a hexagonal diffraction pattern onto a two-dimensional monolayer of these colloids, they created external, sinusoidal, potential that pinned the monolayer of particles in place. The advantage of the soft matter realization of this model is that, unlike the experiments that probe the friction of a material on an atomic scale and *in situ* (examples include atomic force microscopy and Quartz microbalance studies), the soft matter version provided an opportunity to observe the kink/anti-kink excitations in the monolayer in real time.

As discussed in the previous section, it was unclear what interesting questions could be answered by simulation considering that the data obtained from experiment were configurations of real particles. At best, it could be expected that the simulations would produce the same behavior already observed in experiment, and, at worst, deviations would be attributed to the limits of simulation. In order to arrive at results that complement and extend what was already known, the simulations performed in Chapter 2 were designed to probe the range of behaviors that the system exhibits for all possible interparticle interaction strengths. At first, this approach might be considered arbitrary, however, consider that in the complete absence of interparticle interactions, the system formally becomes an ideal gas of particles traveling in a sinusoidal potential, the behavior of which is entirely determined by thermal effects. Furthermore, the analytical solution of this system is literally a textbook example. As the interaction energies between particles are gradually increased, the motion of the crystal becomes less dependent on thermal energy and is more strongly influenced by the potential energy. For infinitely large interaction strengths, the colloidal monolayer becomes a rigid lattice and thermal vibrations are completely suppressed. For this extreme, an analytical solution was also easily obtained. Since these extremal regimes can be well understood, the sliding dynamics at intermediate interparticle interaction energies can be understood as varying degrees of mechanical and thermally activated sliding. The lesson learned in Chapter 2 is that there are three different types of sliding mechanism that a monolayer of repulsive particles adopts, each of which can be attributed to the relative importance of thermal to mechanical effects.

Inspired by the analogy to the rigid lattice, a closer look was taken at the motion of a “stiff” monolayer, *i.e.* for large, but finite interaction strengths between colloidal particles. In Chapter 3, it is shown that it is possible to obtain an analytical solution for a crystal in which the thermal motion is small compared to the typical interaction energy. By performing a quasi-static harmonic expansion of the two-dimensional FK model and comparing the predictions to simulations of strongly interacting particles, it was found that there is both a qualitative and a quantitative correspondence with the approximation without the need for any fit parameters. It was satisfying to find that there is a regime of the FK model, in which repulsive particles slide along the substrate

in a manner that can be accurately treated using the tenants of nucleation theory and harmonic crystals.

As mentioned before, the analytical solution that was obtained applies only to repulsive particles. Having obtained an intuitive understanding of the motion of repulsive particles, a natural direction for the research was to examine the sliding dynamics of more complex potentials. In Chapter 4, an analysis is performed on particles that interact via the Lennard-Jones potential. This potential has both a short range repulsive part, that is essential to ensure that particles do not overlap, and a long range attractive part. This property introduces two competing length scales to the problem; the first length scale is the point at which the interaction potential switches from being repulsive to being attractive and the second length scale is the distance between two adjacent external potential minima. It can be shown, for a purely repulsive potential, that the density does not change the qualitative behavior of the FK model, since rescaling all lengths just affects the coupling strength of the interaction. For potentials that are attractive and repulsive, the density of the particles does play a significant role because it determines whether particles typically attract or repel each other. The first step in such an examination is to parametrize the Lennard-Jones potential so that particles tend to repel each other. In this case, it can be expected, at least qualitatively, that the system is similar to the monolayers considered in the previous chapters. There should even exist a range of interaction strengths in which the harmonic approximation is valid. However, if the monolayer is stretched, *i.e.* the particles typically attract each other if they all sit in their respective external potential minima, then one can safely predict that a qualitative change in the dynamics is to occur.

Although the results obtained in these works offer a consistent picture of the motion of monolayers in two dimensions, it is still adventurous to suggest that much is known about dry friction. First of all, the overwhelming majority of frictional processes consist of two objects with a contact surface and a bulk perpendicular to it. If one shears the two objects, the motion of the solids with respect to each other is governed by a complex deformation of the contact surface which is responsible for the flow of atoms. It must be expected that this deformation not only propagates into the bulk, but the capability of the bulk of the material to accommodate a sliding phase plays a significant role in the frictional response of a material. At the same time, the work in Chapters 2-4 does not consider mismatches in the geometry or the driving angle between the two surfaces. Even a cursory examination of the equation of motion of the system shows that this plays a very important role in the frictional response of the monolayer. What is offered instead, is a methodology: in the absence of interparticle interactions, one ought to be able to obtain a quantitative theory describing the simulations results and the same is true for a completely rigid pair of lattices. These two limits can perhaps

form a basis with which one can compare results obtain for more detailed simulations and experiments.

Chapter 5 in this thesis is dedicated to a side project, that is also a work in progress. Motivated by the experiments of Palacci and Bechinger, the code used for the charge stabilized colloids was adapted to simulate the motion of active particles. This type of system is part of a rapidly growing study of mesoscopic particles that swim stochastically in a preferential direction while performing Brownian diffusion. In addition to mimicking the behavior of bacteria and actin molecules along proteins, the study of active matter preoccupies itself with concepts such as swarming and with minimal models of collective motion by agents propel themselves through space. The experiments of Palacci and Bechinger in particular, were inspiring in the manner in which activity was achieved; in both cases, colloidal particles were specially prepared so that the application of laser light induced them to travel along a particular orientation vector that performed an independent random walk of its own. Having worked on simulations of particles exposed to light patterns before, natural question was to ask how this system responds when only part of the sample is illuminated, thereby creating an activity inducing zone that is connected to a passive region. As before, the comparison with a more “intuitive” system was made. In this case, the behavior of interacting particles with position dependent activity was compared to the behavior of a system in with a diffusivity gradient. Furthermore, to isolate the role of the interparticle interactions, an analysis of the ideal gas version of this system was also conducted. All of these systems are examples of non-equilibrium dynamics but each of the gradients are of different origin. The results of this study can be split into two categories. The phenomenological predictions of the simulation are that if one embeds a passive, diffusive, zone in an active fluid then, given an easily realizable activity, one can induce crystallization in the passive region. The shape of the crystallized domain is entirely determined by the shape of the passive zone. Although this can, in principle be achieved with a temperature induced diffusivity gradient, the former mechanism is much easier to realize than the latter. Also, it is to be expected that sufficiently small arbitrarily shaped, passive particles in an active fluid will naturally be trapped in the passive zone as well. Finally, unlike the purely diffusive systems, any asymmetry in the passive zone leads to a net flow in active particles. On a theoretical level, the treatment of diffusivity and activity gradients is given by the Fokker–Planck equation (FPE), which relates the evolution of the probability distribution function of an ensemble of particles to the degree of diffusivity and the classical forces acting on the particles. One can describe the behavior of a system with a diffusion gradient fairly well, but the Smolukowski equation (FPE for overdamped particles) for active particles is far more difficult to solve and ought to be the subject of future study.

It is the sincere hope of the author that the ensuing chapters give the reader, not so much a series facts to memorize, but instead a sense with which to approach the models

under consideration.

Chapter 2

Dynamic phases of colloidal monolayers sliding on commensurate substrates

We report on numerical simulations of a monolayer of charge-stabilized colloids driven over a substrate potential by an external dc force acting along a symmetry axis of the monolayer. Using overdamped Langevin dynamics, we studied the sliding transition for various inter-particle interaction strengths as a function of the driving force. For weak interactions, the diffusion of individual defects is responsible for the motion of the monolayer. As the interaction strength is increased, sliding is induced by distinct density compression and decompression zones. For very strong interactions, a type of stick-slip mechanism emerges, in which the sliding of the monolayer is mediated by the propagation of collective distortion waves. Our predictions can be tested experimentally with two-dimensional arrangements of colloidal particles exposed to periodic light fields and our work shows that the inter-particle interaction strength tunes the degree of correlation in the sliding mechanism adopted by a monolayer driven over a commensurate substrate.

2.1 Introduction

The dynamics of two surfaces that are in contact with each other has been studied for centuries and empirical approaches based on the Amontons-Coulomb law [13] have enjoyed great success in predicting the frictional response of macroscopic objects. However, a truly atomistic understanding of friction remains elusive. At the beginning of the last century, simplified atomistically resolved descriptions of friction such as the Frenkel-Kontorova (FK) [12, 14] and Tomlinson-Prandtl [15, 16] models were developed and have since been the subject of much attention on a theoretical level [17–25]. The

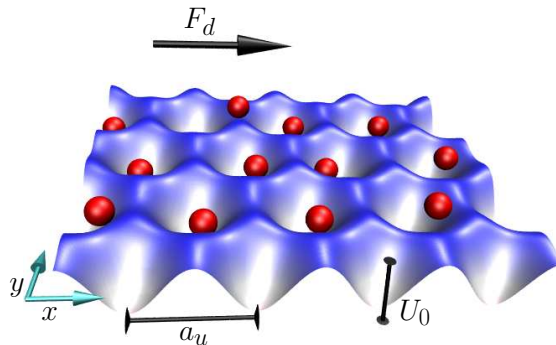


Figure 2.1 Sketch of the model; the colloids are subject to a substrate potential with lattice constant a_u and well depth U_0 . In addition to the forces exerted by the substrate, colloidal particles also experience inter-particle Yukawa forces, random buffeting forces due to the solvent, and a constant driving force, F_d .

recent advances in experimental realizations of the FK model through the use of quartz-crystal microbalance setups [26–28] and atomic force microscopy [29] inspired a number of simulation studies that extend beyond the classical FK model [30–35].

Furthermore, soft matter systems, and in particular colloidal suspensions of particles with tunable interactions, provide a way to study condensed phase phenomena with single-particle resolution usually unavailable to atomistic systems [36, 37]. Recently, Bechinger and collaborators [6] devised an experiment that is a two-dimensional (2d) extension of the FK model and Vanossi *et al.* [38] performed simulations which reproduce and elucidate the key features of this experiment in which the motion of a monolayer subjected to a substrate potential is initiated through the formation of kink-antikink pairs, as predicted by the FK model.

In an attempt to build upon the aforementioned work, we performed computer simulations of overdamped Yukawa particles driven over a commensurate substrate (*i. e.* the number of the minima of the external potential is the same as the number of particles in the monolayer) in order to understand the role that the inter-particle interaction plays on the dynamical steady state adopted by the monolayer. We have been able to draw a consistent picture for all possible inter-particle interaction strengths for the particular substrate we considered, and find that the degree of clustering of the kinks and antikinks that are formed in the monolayer increases as the inter-particle interaction strength is increased or the density of colloidal particles is decreased.

2.2 Simulation details

We studied the dynamics of colloidal monolayers driven by a constant force while being subjected to a commensurate substrate potential, as shown schematically in Fig. 2.1. The motion of a colloidal particle is governed by the overdamped Langevin equation

[39, 40],

$$\gamma \dot{\mathbf{r}}_i = \mathbf{F}_i^{\text{Yukawa}} + \mathbf{F}_i^{\text{sub}} + \mathbf{F}_d + \tilde{\mathbf{f}}_i. \quad (2.1)$$

Here, $\dot{\mathbf{r}}_i$ is the velocity of particle i and γ is the friction constant related to the diffusion coefficient D of a single particle in the fluid by the Einstein relation $\gamma = k_B T / D$, where k_B is the Boltzmann constant and T is the temperature. In all of our simulations, we set $k_B T$ and γ to unity, but in the following we keep the notation for clarity. We have neglected hydrodynamic interactions, but obtain good qualitative agreement with experiment. The particle-particle interactions of charge stabilized colloids are described by the screened Yukawa potential [41],

$$U_{\text{Yukawa}}(r) = [\Gamma a e^{\kappa a}] \frac{e^{-\kappa r}}{r}, \quad (2.2)$$

where r is the inter-particle distance, a is the lattice constant of the ideal monolayer, and κ is the inverse screening length of the solvent. We set $a = 6 \mu m$ and $\kappa a = 37.5$, similar to the values realized in experiments [6]. The prefactor in square brackets is the coupling strength of the interaction and Γ is the potential energy of two particles that are separated by one lattice constant.

The substrate is a hexagonal arrangement of potential wells defined as

$$U_{\text{sub}}(\mathbf{r}) = -\frac{U_0}{9} \sum_{i,j=1}^3 \cos[(\mathbf{k}_i - \mathbf{k}_j) \cdot \mathbf{r}], \quad (2.3)$$

where $\mathbf{r}$ denotes the position of a colloidal particle. The depth of the potential wells was set to $U_0 = 27 k_B T$, which was chosen because of the good qualitative correspondence to experiment. The wave vectors, $\mathbf{k}_i / \|\mathbf{k}\| \in \{(0, 1), (\sqrt{3}/2, -1/2), (-\sqrt{3}/2, -1/2)\}$, were chosen so that the ensuing hexagonal substrate potential has the same orientation as a colloidal crystal with lattice vectors $\mathbf{g}_i \in \{(a, 0), (a/2, a\sqrt{3}/2)\}$. The lattice constant of the substrate potential is $a_u = 4\pi/3 \|\mathbf{k}\|$, where $\|\mathbf{k}\|$ is the norm of the wave vectors, and, since we consider only the commensurate case, is set so that $a_u = a$ for all simulation runs. This definition of U_{sub} corresponds to the interference pattern produced by 3 coherent laser beams in experiments [6]. The driving force, $\mathbf{F}_d = (F_d, 0)$, is constant in time. The components of the random buffeting forces, $\tilde{\mathbf{f}}$, that the fluid exerts on the particle are uncorrelated in time and follow a Gaussian distribution with zero mean and variance $\langle \tilde{f}(t) \tilde{f}(0) \rangle = 2k_B T \gamma \delta(t)$, where $\delta(t)$ is the Dirac delta function and t is time.

We examined monolayers with interaction strengths ranging from $\Gamma = 0$ to $10k_B T$ subject to various driving forces, F_d . Each monolayer consisted of 5476 particles and periodic boundary conditions were imposed. For each set of parameters, 5 simulation runs of 10^6 time steps of length $\delta t = 10^{-4} \gamma^{-1}$ were conducted and before any measurements were made, the systems were equilibrated for 2×10^5 time steps.

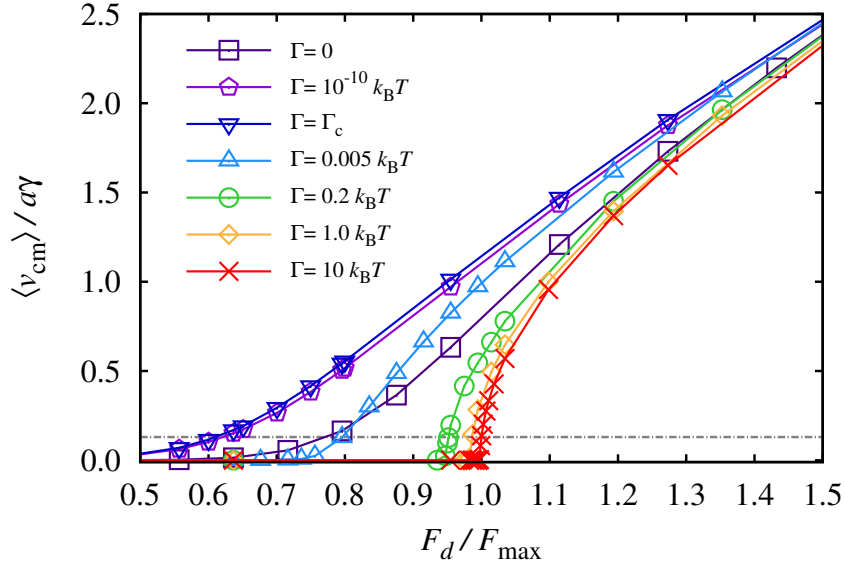


Figure 2.2 Average drift velocity of the colloidal crystal, $\langle v_{\text{cm}} \rangle / a\gamma$, as a function of the applied driving force, F_d / F_{max} . The lines are guides to the eye and the differences of the mean velocities between simulation runs are of the order of the symbol size. The points in the curves for $\Gamma = 0.005, 0.2$, and $1.0 k_B T$ that are closest to the horizontal line $\langle v_{\text{cm}} \rangle / a\gamma = 0.13$ (dot-dashed) are the subject of a detailed discussion.

2.3 Results and discussion

2.3.1 Drift velocity of the monolayer

We begin with the analysis of the average drift velocity $\langle v_{\text{cm}} \rangle$ of the colloidal particles in the driving direction, which is presented in Fig. 2.2 as a function of the driving force F_d . We express F_d in units of $F_{\text{max}} = 8\pi U_0 / 9a$, the maximum force that the substrate potential can exert on a colloid in the driving direction. In all simulation runs, the diffusion perpendicular to the direction of driving was indistinguishable to the undriven case. Before we discuss the sliding mechanisms adopted by the monolayer, we will present considerations on the particle mobility in the limiting cases of very large and small inter-particle interaction strengths as well as in the intermediate regime.

2.3.1.1 Infinitely stiff crystal.

The lower bound of all drift velocity profiles is given by the limit of $\Gamma = \infty$. For very large interaction strengths, thermally induced fluctuations of the particles in a crystal are completely suppressed and inter-particle distances always correspond to those of a perfect lattice. Hence, the entire monolayer moves as a completely rigid crystal with a dynamics governed only by the force due to the substrate, F^{sub} , and the driving force, F_d . Since the driving force acts only in the x -direction, the equation of motion of the

colloidal monolayer is reduced to an one-dimensional differential equation,

$$\gamma \dot{x} = F^{\text{sub}}(x) + F_d, \quad (2.4)$$

which can easily be solved. The differential equation (2.4) is periodic, so we can restrict our analysis to the interval $x \in [0, a]$. The integration of the equation of motion (2.4) yields the time T that particles need to travel from one potential minimum to the next:

$$T = \begin{cases} \frac{\gamma a}{\sqrt{F_d^2 - F_{\text{max}}^2}} & \text{if } F_d > F_{\text{max}}, \\ \infty & \text{else.} \end{cases} \quad (2.5)$$

The average velocity is therefore given by

$$\langle v_{\text{cm}} \rangle_{\Gamma=\infty} = \frac{a}{T} = \begin{cases} \gamma^{-1} \sqrt{F_d^2 - F_{\text{max}}^2} & \text{if } F_d > F_{\text{max}}, \\ 0 & \text{else.} \end{cases} \quad (2.6)$$

The prediction of this equation is shown in Fig. 2.3 as the red dotted line. The limit is approached already at $\Gamma = 10k_B T$, as can be seen in Fig. 2.3. This velocity profile constitutes a lower bound for all of the velocity profiles in Fig. 2.2. For driving forces smaller than F_{max} , such a monolayer is completely pinned to the substrate and no drift occurs. However, as soon as the driving force F_d exceeds F_{max} , the monolayer gains a non-vanishing average velocity. At non-zero temperatures and finite Γ , this sharp transition from pinned to drifting monolayer, known as the depinning transition, is a smooth function in terms of $\langle v_{\text{cm}} \rangle$.

2.3.1.2 Ideal gas, $\Gamma = 0$.

In the limit of vanishing interaction strength, the motion of the colloidal monolayer can also be understood in a single particle picture. In this case, the particles move independently of each other and their average drift velocity can be computed analytically by solving the Fokker-Planck equation of a driven Brownian diffuser in a sinusoidal potential. In the following, we sketch the derivation of the average velocity presented by Risken [42]. Again, we restrict the analysis to one dimension. For a system of non-interacting particles driven over a periodic potential at a given temperature, the Fokker-Planck equation can be written as

$$\frac{\partial W}{\partial t} = \gamma^{-1} \frac{\partial}{\partial x} \left(U'_{\text{sub}} - F_d + k_B T \frac{\partial}{\partial x} \right) W = -\frac{\partial S}{\partial x}, \quad (2.7)$$

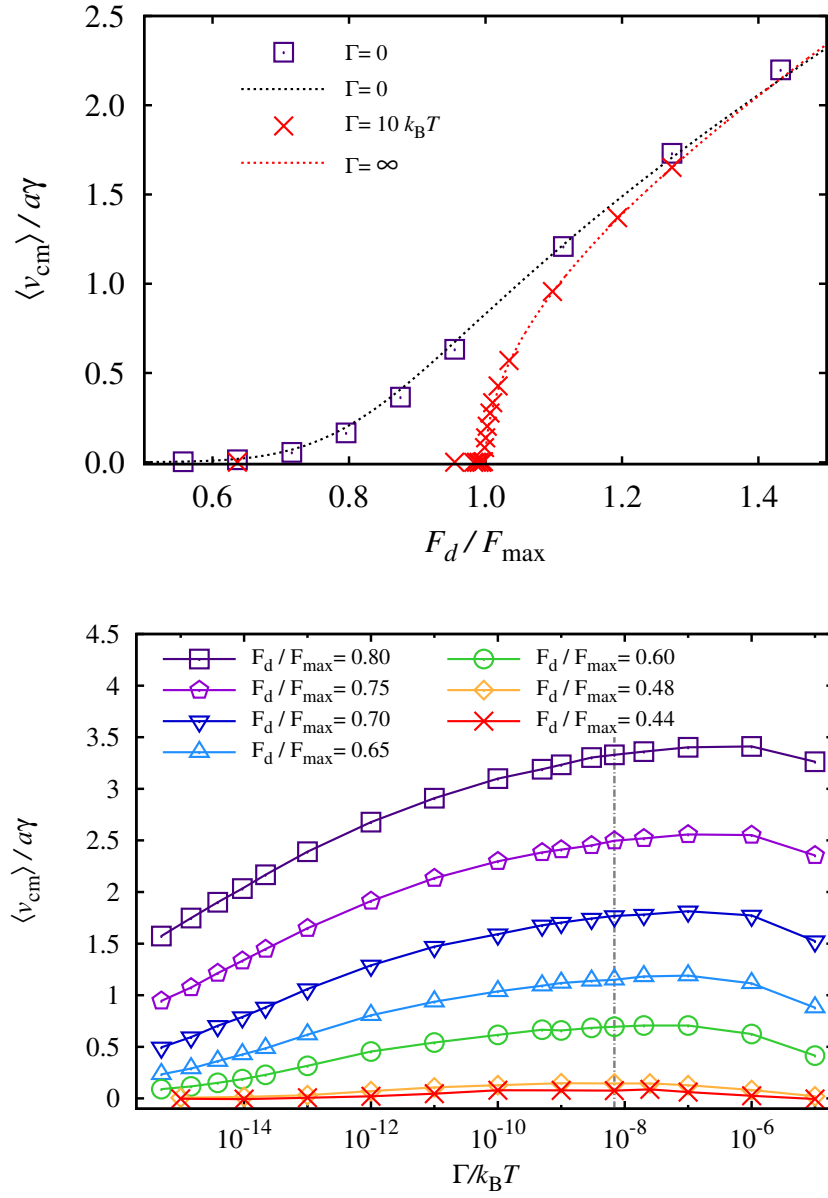


Figure 2.3 Comparison of simulation data to theoretical predictions. Top: The lines are the theoretical predictions of Eq. (2.6) corresponding to $\Gamma = \infty$ (red dotted line) and Eq. (2.10) corresponding to $\Gamma = 0$ (black dotted line). The symbols are data sets obtained from simulation for $\Gamma = 0$ and $\Gamma = 10$. Bottom: Mean velocities of monolayers as a function of Γ for different driving forces F_d . Our estimation of Γ_c is indicated by the vertical dashed line. The error bars are smaller than the symbol size.

where $W(x, t)$ is the probability density distribution of the particle positions and $S(x, t)$ is the probability current. Since we are only interested in the stationary distribution of the system, the probability current is a constant given by

$$\gamma S = (F_d - U'_{\text{sub}}) W(x) - k_B T \frac{\partial W(x)}{\partial x}. \quad (2.8)$$

We note that these relations hold for any kind of external potential. One can then proceed to obtain $W(x)$,

$$W(x) = e^{-V(x)/k_B T} \left(N - \gamma S / k_B T \int_0^x e^{V(\tilde{x})/k_B T} d\tilde{x} \right), \quad (2.9)$$

where $V(x) = U_{\text{sub}}(x) - F_d x$. If one applies the condition that U_{sub} is periodic, then the integration constants S and N follow from the requirements that $W(x)$ is also periodic and normalized. Risken [42] applied the method of continued fractions expansion proposed by Ivanchenko and Zil'berman [43] to obtain $W(x)$ by solving Eq. (2.9) numerically for an external potential described by a cosine function. The average velocity is then given by

$$\langle v_{\text{cm}} \rangle_{\Gamma=0} = \gamma^{-1} \int_0^a (F_d - U'_{\text{sub}}) W(x) dx. \quad (2.10)$$

The solution obtained numerically for $\Gamma = 0$ is shown in Fig. 2.3 as black dotted line together with our simulation results. Evidently, we recover the analytical solution for the case of non-interacting particles.

2.3.1.3 Estimation of Γ_c .

We find that, for the inter-particle interaction strengths that lie between the two limiting cases discussed above, the frictional response is not monotonic in Γ , as demonstrated in Fig. 2.2. For large values of Γ , a reduction of the interaction strength *increases* the mobility of the monolayer. This is easily explained by noting that particles are hindered from hopping between substrate minima by the interactions with their neighbors, and a reduction of Γ eases this restoring force. However, below a certain threshold value Γ_c , further reductions of the interaction strength *decrease* the mobility of the monolayer. This is due to the fact that, for minuscule values of Γ , it is much more likely that two or more particles can be trapped in the same substrate potential well, thereby slowing the sequence of particle hops that are the origin of sliding.

To make a rough estimate of Γ_c , we derive the highest value of Γ for which a configuration of two particles sharing the same substrate potential minimum is mechanically stable. For all interaction strengths above this value, if a colloid hops from one substrate minimum to the next (occupied by another colloid), it will necessarily initiate a sequence of particle hops by forcing the particle previously residing in this minimum to move out of it. In the following, we neglect the effects of temperature, driving force, and the interactions with the surrounding particles and restrict the analysis to one dimension. We start with the Hamiltonian given by

$$H = U_{\text{Yukawa}}(|x_1 - x_2|) + U_{\text{sub}}(x_1) + U_{\text{sub}}(x_2), \quad (2.11)$$

where x_1 and x_2 are the positions of the particles. The equilibrium positions are given by $\nabla H = 0$, while an evaluation of the Hessian determines whether these configurations are stable. We find that two particles are bound in a potential minimum if $|x_1 - x_2| < \frac{a}{2}$. Hence, we estimate that

$$\Gamma_c = \frac{2\pi}{9} U_0 \frac{e^{-\kappa a/2}}{1 + \kappa a/2} = 6.866 \times 10^{-9} k_B T, \quad (2.12)$$

which is the largest value of Γ for which two particles can be trapped in the same substrate well. For larger inter-particle interaction strengths, small perturbations, *e. g.*, due to thermal fluctuations or the driving force, will knock one of the particles out of the potential well. For smaller inter-particle interaction strengths, the system will tend to restore the initial configuration, thus, suppress a particle hop. Therefore, all monolayers with $\Gamma < \Gamma_c$ will move slower than the monolayer with $\Gamma = \Gamma_c$. To account for the eventual slowing down of the monolayers at larger interaction strengths, we would have to consider the influence of the neighboring particles, which increases the complexity of the calculation significantly.

In the bottom frame of Fig. 2.3, we plotted the mean velocity of the monolayer $\langle v_{\text{cm}} \rangle$ as a function of Γ for different driving forces F_d . All monolayers with $\Gamma < \Gamma_c$ are indeed less mobile than those with $\Gamma = \Gamma_c$ for all driving forces considered. In addition, Fig. 2.3 demonstrates that the effects due to the neighboring particles become perceivable at interaction strengths a few orders of magnitude above Γ_c , where the velocity of monolayers starts to decrease. It is to be expected that this crossover behavior is particularly pronounced for potentials that change drastically as particles approach each other, as in the case of the Yukawa potential.

2.3.2 Sliding mechanisms

An inspection of the trajectories of the monolayers revealed that, for different values of Γ , characteristic mechanisms (that persist for all driving forces) are responsible for the sliding motion. In order to investigate these mechanisms, we present a more detailed description of the motion of the monolayers for $\Gamma = 1.0, 0.2$, and $0.005 k_B T$ that are driven by the forces $F_d/F_{\text{max}} = 0.987, 0.948$, and 0.717 , respectively. These values of Γ span the range of mechanisms available to the system, and the driving forces were selected so that they lead to the same average drift velocity for each monolayer (as indicated by the horizontal line in Fig. 2.2). In the top panel of Fig. 2.4, we show examples of the average displacement of the selected monolayers in the direction of the driving force as a function of time for these three cases. The curve for the largest interaction strength, $\Gamma = 1.0 k_B T$, consists of distinct steps, indicating that the monolayer alternates between periods of rest and rapid spurts of motion. The difference in the height of two successive steps is one lattice constant, and the width of the plateaus is irregular, although there

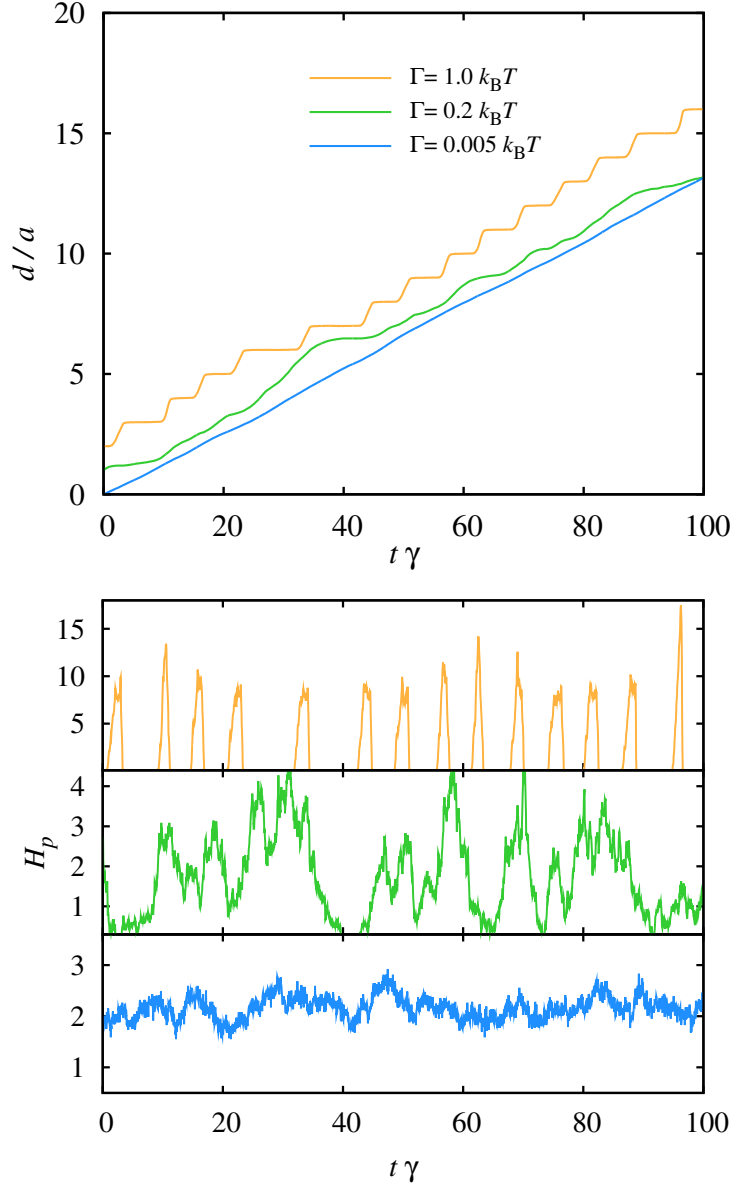


Figure 2.4 Top: Displacement of the center of mass of the colloidal crystal, d/a , as a function of time, $t\gamma$, for three representative cases at interaction strengths and driving forces $\{\Gamma/k_B T, F_d/F_{\max}\} = \{0.005, 0.717\}$, $\{\Gamma/k_B T, F_d/F_{\max}\} = \{0.2, 0.948\}$, and $\{\Gamma/k_B T, F_d/F_{\max}\} = \{1.0, 0.987\}$. Curves are shifted vertically for the sake of clarity. Bottom: Percentage H_p of the particles undergoing a hop for each of the curves shown in the top panel.

is a characteristic time between steps [31]. The $\Gamma = 0.2 k_B T$ monolayer is perpetually in motion but there are large fluctuations in its drift velocity, whereas the $\Gamma = 0.005 k_B T$ curve appears as a smooth line at this resolution but is in fact the result of a stochastic process with very small variance.

To obtain additional insights into the sliding mechanisms, we computed the fraction of particles undergoing a hop at a particular instant (in percent of the system size), H_p , as a function of time, for the same trajectories as in the top frame of Fig. 2.4. Particles are classified as undergoing a hop if the potential energy due to the substrate exceeds

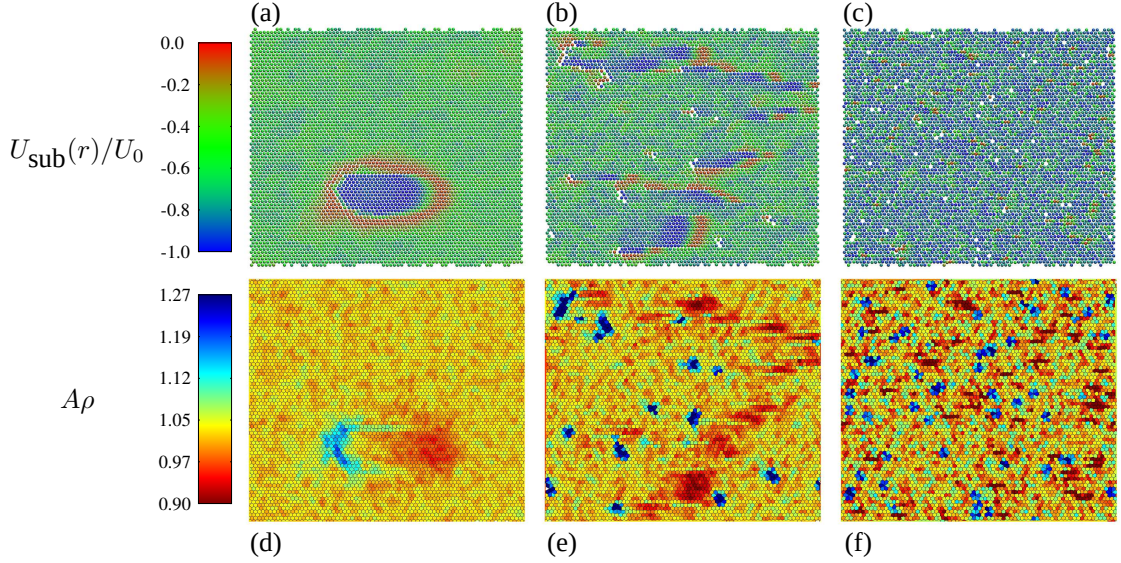


Figure 2.5 Snapshots (top) and corresponding Voronoi tessellations (bottom) of typical configurations obtained for monolayers with (a, d) $\{\Gamma/k_B T, F_d/F_{\max}\} = \{1.0, 0.987\}$, (b, e) $\{\Gamma/k_B T, F_d/F_{\max}\} = \{0.2, 0.948\}$, and (c, f) $\{\Gamma/k_B T, F_d/F_{\max}\} = \{0.005, 0.717\}$, as they are driven by a force that acts from left to right. The top color scale corresponds to the substrate potential values of the colloidal particles shown in (a-c), in units of the well depth, U_0 . The bottom color scale corresponds to the area A of the Voronoi cells depicted in (d-f), in units of the mean area per particle, $\rho^{-1} = (\sqrt{3}/2)a^2$. See Supplemental Material [URL] for videos of the trajectories from which these snapshots were taken.

$-7k_B T$ because we observed in our simulations that colloids entering this energy range almost invariably go from one substrate well to the next. While the average number of hopping particles, presented in the bottom frame of Fig. 2.4, is very similar for the three monolayers (all lie within the range of 1.7% to 2%), the signal continuously loses its structure as Γ is reduced. For large values of Γ , distinct peaks in the number of hopping particles separated by periods of rest indicate that many particles move at the same time in a correlated way. As Γ is decreased, the correlation of particle hops becomes smaller and the sliding motion becomes the result of independent hopping events leading to an almost time-independent fraction of hopping particles.

This general picture of a sliding mechanism increasingly dominated by correlations for growing interaction strength Γ is confirmed by an examination of the configurations computed over the course of a simulation run. Figure 2.5 shows typical configurations chosen from trajectories of the discussed monolayers. The upper panels are depictions of configurations in which the colloids are colored according to their substrate potential values. The panels at the bottom show the local density compressions and decompressions corresponding to the kinks and anti-kinks of the FK model through the use of the configurations' Voronoi tessellations. In order to view movies of the trajectories from which these configurations were taken, we refer to the Supplemental Material [URL].

For a monolayer with $\Gamma = 1.0 k_B T$ and a driving force of $F_d/F_{\max} = 0.987$, there are long

stretches of time in which each particle oscillates about the point where the substrate force counteracts the driving force. These particles appear green in the substrate potential representation of Fig. 2.5a. The hopping mechanism begins when a small cluster of particles reach the top of their respective substrate potential barriers. This small nucleus of particles initiates a circular sequence of particle hops that encompasses the entire system. In Fig. 2.5a, the particles that appear red are in the process of hopping from one substrate minimum to the next and this ring of hopping particles will subsequently continue to grow until each particle has hopped once. After the hopping wave has run its course, the system remains at rest until a new hopping nucleus spontaneously appears. The blue particles that form a core in the middle of the wave have recently hopped and are in the process of diffusing from the bottom of their respective substrate wells to their new equilibrium positions. The corresponding Voronoi representation, shown in Fig. 2.5(d), illustrates that the front of the wave is a zone of local compressions (kinks) whereas the rear of the hopping wave is a decompression (anti-kink) region. As the ring of hopping particles expands, the compression region propagates in the direction of the driving force while the decompression zone travels in the opposite direction. Due to periodic boundary conditions used in our simulations, these two zones eventually collide and annihilate each other. The top and bottom of the hopping wave are not detected by this representation because the Voronoi cells of those particles are sheared, not compressed. For large driving forces, the likelihood of forming a hopping wave increases to such an extent that multiple waves appear simultaneously. This mechanism has been observed and analyzed in simulations of the 2d FK model[31] aimed at reproducing quartz-crystal microbalance experiments, in which the activation energy of the slip motion is derived by means of classical nucleation theory.

For $\Gamma = 0.2k_B T$ and $F_d/F_{\max} = 0.948$, the average drift velocity of the colloidal crystal is almost identical to the previous case, but the motion of the monolayer follows an entirely different dynamical pattern. Typical configurations, such as the one shown in Fig. 2.5b, feature a number of clusters of vacancies. For each vacancy cluster, there is a corresponding island of (red) interstitial particles that are traveling through the system via inter-well hops, leaving low energy particles (blue) in their wake. As in the previous case, the blue particles then turn green when they reach their equilibrium position where the substrate force and the driving force cancel. In the Voronoi representation shown in Fig. 2.5e, one can clearly see that the traveling interstitials form compression zones or kinks (red) while the vacancies in the colloidal crystal are decompression zones (blue). In the course of a simulation run, many clusters of interstitials travel through the system, whereas the vacancy regions remain virtually stationary.

For $\Gamma = 0.005k_B T$ and a driving force of $F_d/F_{\max} = 0.717$, the arrangement of the defects loses all structure (Fig. 2.5c). Here, vacancies are locked in place while single

interstitial particles diffuse through the monolayer. As in the previous case, compression zones (kinks) are mobile whereas decompression zones (anti-kinks) are immobile.

Videos of trajectories from simulations of larger systems (see Supplemental Material [URL]) reveal conclusively that the hopping waves encountered in the $\Gamma = 1.0k_B T$ case also display a kink-antikink asymmetry because the kink region (front) of the wave travels more quickly than the anti-kink region (rear) by about a factor 3. This finding is corroborated by simulations of similar non-driven systems [44], where it was found that interstitials are more mobile than vacancies. Furthermore, simulation and experimental measurements of kink and anti-kink velocities demonstrate that, in charge-stabilized colloidal systems, anti-kinks are consistently slower than kinks [6, 38]. We ascribe the differences in the kink-antikink mobility to the purely repulsive nature of the Yukawa potential for which the motion of vacancies incurs larger energy penalties than interstitials. In the FK model, on the other hand, particles in the 1d chain interact via an harmonic potential, which is perfectly symmetric and we expect this to be the reason why kinks and anti-kinks are equally mobile in that case.

2.4 Conclusions

In conclusion, we analyzed the mechanisms of thermally induced depinning of colloidal monolayers driven by an external force over a substrate potential and showed that the occurrence of different sliding mechanisms is determined by the strength of the inter-particles interactions. We have also been able to find upper and lower bounds to the frictional response of the monolayer in terms of the interaction strength and preliminary results suggest that the approximations remain valid even for significantly weaker field strengths.

The origins of the various depinning mechanisms involving different degrees of correlation can be explained in terms of the energetics associated with vacancy-interstitial pairs. For strong inter-particle interactions, the creation of a vacancy-interstitial pair is energetically so disadvantageous that motion can only be achieved through correlated hopping waves that involve many particles and only weakly distort the hexagonal structure of the monolayer. As the interaction strength is reduced, smaller clusters of particles can escape from the local substrate potential minima and diffuse through the lattice. Finally, for weak interactions, the energetic costs of a defect is so low that correlations are lost and individual particles can travel along one-dimensional channels in the direction of the driving force.

Further research into the dynamical asymmetry of kinks-antikinks is warranted as well as a quantitative treatment of the vacancy-interstitial energetics that give rise to the different sliding phases that have been observed. The role of incommensurabilities,

variation of direction and frequency of the driving force, as well as the role of the shape of the substrate are also worth examining.

Acknowledgements

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Chapter 3

Frictional dynamics of stiff monolayers: from nucleation dynamics to thermal sliding

The inherently nonlinear dynamics of two surfaces as they are driven past each other, a phenomenon known as dry friction, has yet to be fully understood on an atomistic level. New experiments on colloidal monolayers forced over laser-generated substrates now offer the opportunity to investigate friction with single-particle resolution. Here, we use analytical theory and computer simulations to study the effect of thermal fluctuations on the stick-slip mechanism characteristic for the frictional response of a stiff colloidal monolayer on a commensurate substrate. By performing a harmonic expansion of the energy and employing elementary statistical mechanics, we map the motion of the monolayer onto a simple differential equation. Analytical expressions derived from our approach predict a transition from nucleation dynamics, where the monolayer moves in a sequence of activated hops over energy barriers, to “thermal sliding”, in which the effective substrate barrier opposing the motion of the monolayer disappears due to thermal fluctuations, leading to continuous, uninterrupted sliding motion. Furthermore, we find that the average velocity of the monolayer for large driving forces obeys a simple scaling behavior that is consistent with the existence of a static friction. For small forces, however, nucleation provides a mode of motion that leads to a small but non-vanishing mobility of the monolayer. Data obtained from simulations confirm this picture and agree quantitatively with our analytical formulae. The theory developed here holds under general conditions for sufficiently strong inter-particle repulsions and it yields specific predictions that can be tested in experiments.

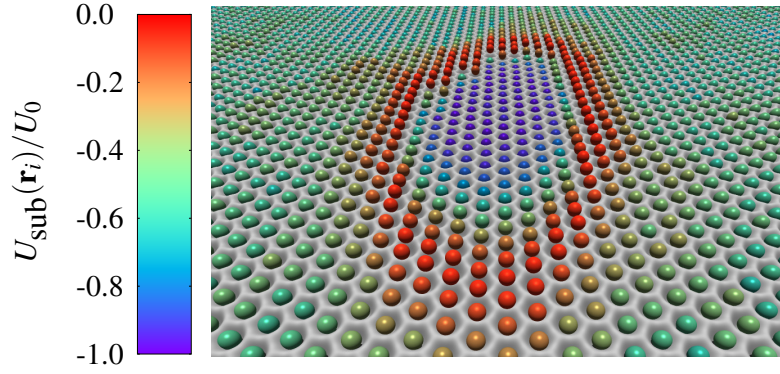


Figure 3.1 Snapshot of a stiff monolayer driven by a constant force, F_d , that acts from top to bottom. Each of the particles is colored according to its substrate potential value. Red particles are at the top of their substrate potential barriers, purple particles are at the bottom of the wells, and green particles are somewhere along the walls.

3.1 Introduction

Although macroscopic laws of friction are centuries old and sufficiently accurate for a multitude of applications [13], and mesoscopic treatments have yielded great insights into this phenomenon [45, 46], advances in nanotechnology require an understanding of friction on length and time scales in which atomistic details become important [30, 33]. Experimentally, several recent approaches, including atomic force microscopy setups [47–50], quartz-microbalance setups [26–28, 51], and monolayers of charge-stabilized colloidal particles exposed to light-induced interference patterns [6], have made it possible to study friction on an atomistic level. In all of these cases, insights are gleaned from the dynamical response of small samples of particles that are driven across an external potential landscape. In particular, the remarkable accuracy and level of control achieved in experiments using two-dimensional crystals in laser fields [6] have shed new light on the dynamics of collective excitations lying at the origin of friction. These experiments have been complemented by simulations and analytical studies of the Frenkel-Kontorova (FK) model [12, 15, 17, 21, 23, 24, 31, 38, 52]. Despite its simplicity, this model captures the rich dynamical behavior and, more specifically, the soliton and anti-soliton structures largely determining the magnitude of friction observed in experiments.

Here, our aim is to investigate the effect of thermal fluctuations on the frictional response of stiff monolayers, i.e., monolayers with large elastic moduli. In a previous work [9], we had found that the inter-particle interaction regulates how many defects appear in the monolayer as it slides over a substrate. When the interaction strength is so large that no defects appear in the system, the monolayer adopts a type of stick-slip motion which we call a “hopping wave”. This sliding mechanism consists of long periods of virtual motionlessness which are interrupted by the formation of small nuclei of particles that have escaped from their respective substrate wells. These particles subsequently initiate

a cascade of particle hops which eventually encompass the entire system (Fig. 3.1). The “hopping wave” mechanism is of particular note, since it accounts for a sliding phase in which the monolayer remains structurally intact. It also appears to be a feature of systems of this type because the same mechanism was observed under different conditions in an earlier simulation study conducted by Reguzzoni *et al.* [31]. The purpose of our present work is to provide a general and quantitative understanding of the formation of these hopping waves.

3.2 Model

We simulated a two-dimensional array of overdamped particles exposed to an external substrate potential while being driven by a constant force. The particles repel each other via Yukawa interactions and receive random kicks due to the solvent surrounding them. The equation of motion for particle i , with position vector $\mathbf{r}_i$, is therefore

$$\gamma \frac{d\mathbf{r}_i}{dt} = \mathbf{F}_{\text{sub}}(\mathbf{r}_i) + \mathbf{F}_d + \sum_{j \neq i} \mathbf{F}_{\text{yuk}}(|\mathbf{r}_i - \mathbf{r}_j|) + \mathbf{F}_{\text{random}}^i(t). \quad (3.1)$$

The substrate force, $\mathbf{F}_{\text{sub}}(\mathbf{r}_i)$, acting on particle i is the negative gradient of the externally applied potential, $U_{\text{sub}}(\mathbf{r}_i) = -(U_0/9)\{3 + 2[\cos(\mathbf{k}_1\mathbf{r}_i) + \cos(\mathbf{k}_2\mathbf{r}_i) + \cos(\mathbf{k}_3\mathbf{r}_i)]\}$, where the $\mathbf{k}$ -vectors are chosen

from the set $\mathbf{k}_i/||\mathbf{k}|| \in \{(\sqrt{3}/2, 1/2), (-\sqrt{3}/2, 1/2), (\sqrt{3}, 0)\}$ with norm $||\mathbf{k}|| = 4\pi/3a$.

This choice of the $\mathbf{k}$ -vectors produces a hexagonal arrangement of potential wells with a lattice constant a and lattice vectors $\mathbf{g} \in \{(a, 0), (a/2, \sqrt{3}a/2)\}$. The lattice constant of the substrate was set to $a = 6\mu\text{m}$ and the depth of the potential minima was set to $U_0 = 27k_B T$, where k_B is the Boltzmann constant and T is the temperature. As a result, the maximum force that the substrate can exert on a particle in the x direction is $F_{\text{max}} = 24\pi k_B T/a$. The colloidal particles we study are charge-stabilized and therefore repel each other via Yukawa interactions. Two particles separated by a distance r from each other have a potential energy of $U_{\text{yuk}}(r) = \tilde{\Gamma}e^{-\kappa r}/r$, where the inverse screening length, $\kappa = 6.25\mu\text{m}^{-1}$, determines the range of the Yukawa interaction. The coupling parameter $\tilde{\Gamma}$ is related to the effective charge on each colloid. Instead of specifying $\tilde{\Gamma}$, we define the interaction strength as $\Gamma = \tilde{\Gamma}e^{-\kappa a}/a$, which is the potential energy of two particles separated by one lattice constant. The choice of the parameter values used here resulted in the best agreement between simulation and experiment [6, 9]. For particles obeying overdamped Langevin dynamics, at each moment in time a particle experiences an uncorrelated Gaussian random force with zero mean and variance $2k_B T\gamma$. The friction constant γ is related to the diffusion constant of a single particle by the Einstein relation, $\gamma = D/k_B T$. We prepared a rectangular simulation box with periodic boundary conditions compatible with $N = 6400$ hexagonally arranged substrate minima. At the

beginning of each simulation run, we placed a single particle in each well and applied a constant driving force, $\mathbf{F}_d = (F_d, 0)$, in the x direction. The algorithm presented in [39] was employed to simulate the motion of the particles with a time discretization of $\delta t = 10^{-4}$. Data were gathered from 100 runs of 2×10^6 time steps for a multitude of values of Γ and F_d while keeping κ , a , and $F_{\max}$ constant. Before performing measurements, the systems were equilibrated for 10^5 time steps. We used the reduced units $\gamma = k_B T = 1$ and all distances were rescaled by the lattice constant a and all forces by $F_{\max}$.

3.3 Thermal sliding

The stick-slip mechanism mentioned above appears when the inter-particle interaction strength Γ is large enough, in comparison to the substrate potential depth, to preserve the hexagonal structure of the monolayer at all times. The monolayer, if it is to slide, has no other recourse than to form a distortion wave that travels through the system until each particle has moved forwards by one lattice constant. This is accomplished by forming a localized cluster of particles that escape their respective substrate wells. This cluster of hopping particles is the source of a sequence of particle hops that travels through the entire system. After such a “hopping wave” has run its course, the monolayer re-equilibrates and awaits the formation of yet another cluster (see supplementary Videos S1 and S2).

In Fig. 3.2, this process is illustrated for a monolayer driven at two slightly different values of F_d . In the top row of the figure, the average displacement of each particle from its position at $t = 0$ is plotted as a function of time. One can clearly see that the trajectories alternate between a “buildup phase”, in which the monolayer is in the process of forming a hopping wave, and a “slipping phase”, in which a hopping wave travels through the system until each particle has moved forwards by one lattice constant. Although the applied driving forces differ by only a fraction of a percent, the velocity of the monolayer changes almost by a factor 7. Moreover, the regularity with which the hopping waves appear changes drastically.

We can take advantage of the periodicity of the substrate by considering the “periodic position of the center of mass” R (middle row of Fig. 3.2), which is defined as the average displacement in the x direction of each particle from its nearest substrate potential minimum. During the buildup phase, the value of R is equal to the average displacement of the monolayer, d , modulo the lattice constant a . During the slipping phase, the value R does not have a physically meaningful value but the sharp peaks are nonetheless clear indicators of the existence of a hopping wave. The value $R/a = 0.25$ is of particular significance since it is the point of maximum resistance of the substrate. The plots of R vs. γt not only reveal the repetitive nature of the hopping wave mechanism, but

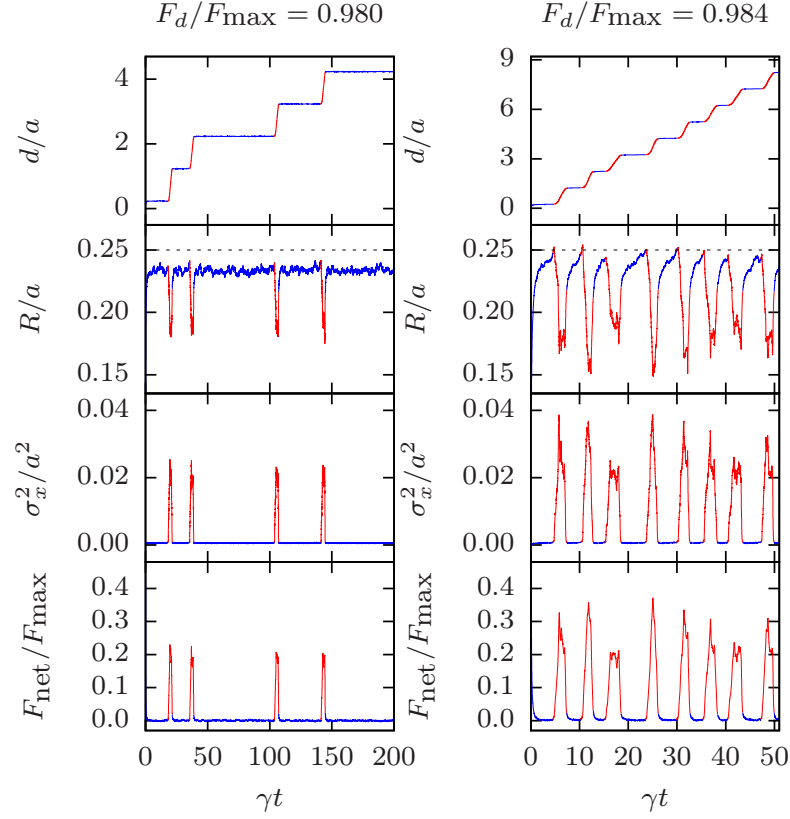


Figure 3.2 Motion of a monolayer with $\Gamma/k_B T = 0.804$. We have depicted (top row) the absolute displacement of the system, d , (middle row) the “periodic position of the center of mass”, R/a , and (bottom row) the net force acting on the monolayer, $F_{\text{net}}/F_{\text{max}}$, as a function of reduced time, γt , for two values of F_d/F_{max} . Panels in the same column belong to the same trajectories. For animations of the data, see Supplementary Videos S1 and S2.

also show that the monolayer in the middle left panel gets pinned by the substrate and takes a variable amount of time to evolve a hopping wave, whereas the buildup phase of the monolayer in the middle right panel consists of an essentially continuous drift towards the point of maximum resistance of the substrate, and shortly thereafter forms a hopping wave.

An examination of the net force acting on the monolayer (bottom row of Fig. 3.2) confirms that the monolayer driven at $F_d/F_{\text{max}} = 0.980$ experiences zero F_{net} for significant periods of time, before a random fluctuation creates a hopping wave. The monolayer driven at a rate of $F_d/F_{\text{max}} = 0.984$, on the other hand, *is perpetually in motion*. This is surprising since the substrate potential is clearly capable of applying a larger restoring force on each particle than F_d , yet the monolayer glides unhindered in the driving direction. In the following section, we will explain the origin of this “thermal sliding”.

3.4 Mapping onto the harmonic crystal

The trajectories in Fig. 3.2 differ primarily in the character and duration of their buildup phases. It also turns out that this part of the trajectories is amenable to analytical treatment. Consider the equation of motion of the periodic center of mass of the monolayer during the buildup phase,

$$\gamma \frac{d\mathbf{R}(t)}{dt} = \mathbf{F}_d + \frac{1}{N} \sum_i \mathbf{F}_{\text{sub}}(\mathbf{r}_i) + \mathbf{F}_{\text{random}}^*(t), \quad (3.2)$$

where the stochastic force $\mathbf{F}_{\text{random}}^*(t)$ is the average random force acting on the particles and is a Gaussian uncorrelated noise with zero mean and variance $2k_B T \gamma / N$. The Yukawa forces cancel due to Newton's third law and so we obtain a stochastic differential equation describing the motion of a Brownian diffuser in a potential defined by the driving force and the average substrate force acting on the monolayer. Since there is no diffusion in the direction perpendicular to the driving force (in the y direction), we merely need to consider the x component of the equation of motion of the system. The only unknown in the equation is the average substrate force acting on the monolayer in the x direction, $F^{\text{eff}}(R) = N^{-1} \sum_i \mathbf{F}_{\text{sub}}^x(\mathbf{r}_i, R)$, which depends on the distribution of the particles' positions $\mathbf{r}_i$ and the instantaneous position of the center of mass.

To treat the buildup phase analytically, we make the following two assumptions:

1. During the buildup phase, the monolayer is in quasi-static thermodynamic equilibrium. It can be expected that this assumption holds because the monolayer creeps along the external potential landscape very slowly during the buildup.
2. The total potential energy of the system can be approximated by a second order Taylor expansion. This approximation is expected to be valid for stiff crystals.

Then, for a given position R , the probability distribution of the particle positions is the equilibrium distribution with the restriction $R = N^{-1} \sum_i r_i^x$,

$$P(\vec{\mathbf{r}}, R) = \frac{\delta(N^{-1} \sum_i r_i^x - R) e^{-\beta U_{\text{tot}}(\vec{\mathbf{r}})}}{Z(R)}, \quad (3.3)$$

where $\beta = 1/k_B T$, δ is the Dirac delta function, and $\vec{\mathbf{r}}$ is a $2N$ -dimensional vector of x and y coordinates of each particle. $U_{\text{tot}}(\vec{\mathbf{r}})$ denotes the total potential energy of the system as a function of all particle positions, and the normalization is given by the $2N$ dimensional integral, $Z(R) = \int d\vec{\mathbf{r}} \delta(N^{-1} \sum_i r_i^x - R) \exp\{-\beta U_{\text{tot}}(\vec{\mathbf{r}})\}$. The normalization and expectation values of such distributions typically defy analytical evaluation, so a further approximation is required.

The second assumption implies that the position of a particle deviates from the location of the center of mass, $\mathbf{R} = (R, 0)$, only by a small displacement, $\mathbf{u}_i$. We can therefore

rewrite the position of each particle as $\mathbf{r}_i = \mathbf{u}_i + \mathbf{R} + \mathbf{R}_i$, where $\mathbf{R}_i$ is the position vector of the substrate minimum closest to the particle i . The center of mass of the monolayer is able to oscillate in the y direction but, by construction, the deviations in the x direction must cancel, $\sum_i u_i^x = 0$. For small $\mathbf{u}_i$, the total potential of the system can then be approximated by a second order Taylor expansion. Although conceptually simple, the following calculation is rather cumbersome, thus, we have detailed every step of the procedure in the SI Appendix S1 and mention only the essential results in the following. The work by Baumgartl *et al.* [53] on this approach is recommended for further reading, and an introduction to the harmonic crystal can be found in Ref. [54]. The second order Taylor expansion of the total potential energy for small $\mathbf{u}_i$ is

$$\begin{aligned} U_{\text{tot}}(R) &= \sum_{j < i} U_{\text{yuk}}(|\mathbf{u}_i - \mathbf{u}_j + \mathbf{R}_i - \mathbf{R}_j|) \\ &\quad + \sum_i [U_{\text{sub}}(\mathbf{u}_i + \mathbf{R}) - F_d u_i^x] - N F_d R \\ &\approx \vec{\mathbf{u}}^T \mathbb{D}(R) \vec{\mathbf{u}} + G(R) \sum_i u_i^x + H(R), \end{aligned} \quad (3.4)$$

where the $2N \times 2N$ interaction matrix $\mathbb{D}(R)$ encodes how each particle interacts with the substrate and with all other particles and $\vec{\mathbf{u}}^T$ is the transpose of the $2N$ dimensional vector of the small displacements of the particle positions. Both in simulation and in this calculation, nearest neighbor cutoffs were used and, hence, the majority of the entries in $\mathbb{D}(R)$ are zero. The function $G(R)$ combines the linear term in the Taylor expansion of the substrate potential and the driving force F_d , and $H(R)$ is the potential energy of the system if all $\mathbf{u}_i$ are zero. Since the interaction matrix is symmetric, it can readily be brought to diagonal form. Using the discrete Fourier transformation, the $2N \times 2N$ matrix $\mathbb{D}(R)$ can be resolved into N 2×2 matrices [53]. The total energy of the system can therefore be rewritten as

$$\begin{aligned} U_{\text{tot}}(R) &= \sum_{\mathbf{q}} \vec{\mathbf{u}}^T(\mathbf{q}) \bar{\mathbb{D}}(\mathbf{q}, R) \vec{\mathbf{u}}(\mathbf{q}) \\ &\quad + \sqrt{N} \bar{u}^x(\mathbf{0}) G(R) + H(R), \end{aligned} \quad (3.5)$$

where $\vec{\mathbf{u}}(\mathbf{q})$ and $\bar{\mathbb{D}}(\mathbf{q}, R)$ are the Fourier transforms of $\mathbf{u}$ and $\mathbb{D}(R)$, respectively, and the sum over $\mathbf{q}$ is the usual sum of the N reciprocal vectors of the Brillouin zone of the substrate lattice. It turns out that the sum over all u_i^x appearing in Eqn. 3.4 is $\sqrt{N} \bar{u}^x(\mathbf{0})$, that is, the x component of the Fourier amplitude assigned to $\mathbf{q} = \mathbf{0}$.

Recasting the total potential in this form allows us to evaluate $Z(R)$, the expectation values of the variances of the particles' positions, and the average force that the substrate exerts on the monolayer for a given value of R . The expectation value of the force exerted

by the substrate in the x direction is

$$\begin{aligned}
F^{\text{eff}}(R) &= \int d\vec{\mathbf{u}} P(\vec{\mathbf{u}}, R) \frac{1}{N} \sum_i \mathbf{F}_{\text{sub}}^x(\mathbf{u}_i, R), \\
&= [NZ(R)]^{-1} \int d\bar{\mathbf{u}}(\vec{\mathbf{q}}) \mathbf{F}_{\text{sub}}^x(\bar{\mathbf{u}}(\vec{\mathbf{q}}), R) \\
&\quad \times \exp \left\{ -\frac{\beta}{2} \sum_{\mathbf{q}} \bar{\mathbf{u}}^T(\mathbf{q}) \bar{\mathbb{D}}(\mathbf{q}, R) \bar{\mathbf{u}}(\mathbf{q}) \right\} \\
&\quad \times \exp \left\{ -\frac{\beta}{2} \left[\sqrt{N} \bar{u}^x(\mathbf{0}) G(R) + H(R) \right] \right\} \delta \left(\frac{\bar{u}^x(\mathbf{0})}{\sqrt{N}} \right), \tag{3.6}
\end{aligned}$$

where $\int d\vec{\mathbf{u}}$ and $\int d\bar{\mathbf{u}}(\vec{\mathbf{q}})$ are $2N$ dimensional integrals over all independent degrees of freedom of the system. The only coordinate appearing in the delta function is $\bar{u}^x(\mathbf{0})$ and therefore the corresponding integral over this degree of freedom is unity. Since the linear term $G(R)$ is only coupled to $\bar{u}^x(\mathbf{0})$ the result of the integration does not depend on $G(R)$. The function $H(R)$ can be pulled out of the integral and cancels with the corresponding term appearing in $Z(R)$. What remains in Eqn. 3.6 is the product of $2N - 1$ Gaussian integrals that can be evaluated individually for each degree of freedom. Having calculated the variances of u^x , u^y , and their cross correlation, we arrive at the result:

$$\begin{aligned}
F^{\text{eff}}(R) &= -F_{\text{max}} \sin \left(\frac{2\pi R}{a} \right) \\
&\quad \times \exp \left\{ -\frac{2\pi^2}{a^2} \left[\sigma_x^2(R) + \frac{1}{3} \sigma_y^2(R) \right] \right\}, \tag{3.7}
\end{aligned}$$

where $\sigma_x^2(R)$ and $\sigma_y^2(R)$ are the expectation values of the variances of the particles from their mean position in x and y directions. It turns out that in the harmonic approximation of the hexagonal lattice, the cross correlation σ_{xy} is 0 which is compatible with our findings from simulation. These variances are directly related to the diagonal elements of the inverse of the dynamical matrix $\bar{\mathbb{D}}(\mathbf{q})$:

$$\sigma_{\mu}^2(R) = \delta_{y\mu} \frac{\bar{\mathbb{D}}_{yy}^{-1}(\mathbf{0}, R)}{N\beta} + \frac{1}{N\beta} \sum_{\mathbf{q} \neq \mathbf{0}} \bar{\mathbb{D}}_{\mu\mu}^{-1}(\mathbf{q}, R), \tag{3.8}$$

where $\mu \in \{x, y\}$. The Kronecker delta $\delta_{y\mu}$ term arises from the fact that the monolayer is free to oscillate in the y direction and ensures that an additional term is added to the sum when $\sigma_y^2(R)$ is calculated.

We find that the expectation values of the effective substrate force and the variances in the particles' displacements are independent of the applied driving force. Furthermore, the formulae for the variances in Eqn. 3.8 can be interpreted as the average value of a function and therefore the effective resistance due to the substrate, F^{eff} , is an

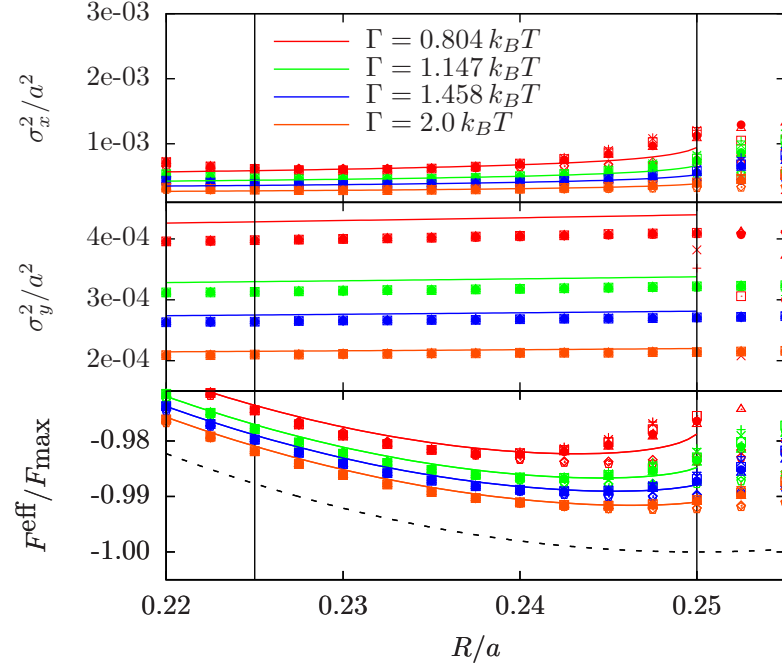


Figure 3.3 Comparison of theoretical prediction (lines) with data gathered from simulation runs (symbols). Symbols and lines of the same color correspond to the same value of Γ , whereas different symbols of the same color correspond to different driving forces. The dashed black line in the bottom panel of the graph is $F^{\text{eff}}(R)$ for $T = 0$ or, equivalently, $\Gamma = \infty$. Vertical black lines limit the region in which the presented theory is applicable.

(essentially) intensive quantity. The functional form of $F^{\text{eff}}(R)$ is similar to the original external potential except that it is exponentially reduced in terms of the variances, $\sigma_\mu^2(R)$, and thus the temperature T . For a sinusoidal substrate, each of the variances increases monotonically as the monolayer travels along the barrier. We included an instruction file, code for a C program, a python script, and a pair of sample files in the SI Appendices S2-S6, with which these formulae can be evaluated.

In Fig. 3.3, we compare the curves generated by Eqns. 3.7 and 3.8 with data obtained from simulation during the buildup phase. We used 4 monolayers of varying interaction strengths Γ , and applied various driving forces close to, but less than F_{max} . As predicted by our calculations, there is a range of R/a in which the driving force does not influence the expectation values of the monolayer, which explains the collapse of the data points of the same color within the indicated region. Furthermore, the lines, which are our theoretical predictions, conform very well with the simulation data. We consider the main source of error to be the truncation of the Taylor expansion at the second order because the theoretical curves become more accurate as the interaction strength is increased. The largest error is incurred in the estimation of $\sigma_y^2(R)$ when $\Gamma/k_B T = 0.804$, for which the average distance between a data point and the curve is 13% and the corresponding error in the estimation of $F^{\text{eff}}(R)$ is 6.6%. Although the region of space in which our formulae are valid may seem small, the monolayers reside in this region for the vast

majority of the time. The harmonic approximation diverges shortly after $R/a = 0.25$ because the curvature of the external potential landscape changes sign and therefore ceases to be a pinning potential. This change of curvature explains why, in simulation, hopping waves form almost immediately after the monolayer reaches that point (see middle right panel of Fig. 3.2).

3.5 Discussion

In the previous section, we mapped the buildup phase of the motion of the monolayer onto the motion of a single overdamped Brownian diffuser subject to an effective substrate force, $F^{\text{eff}}(R)$ (Eqn. 3.2). This effective substrate force is necessarily weaker than the substrate force acting on each particle due to the thermal motion of the particles in the monolayer. The formula for $F^{\text{eff}}(R)$ can be used to find the value of the largest restoring force due to the effective substrate, $F_{\text{max}}^{\text{eff}}$, which delimits two different dynamical regimes. In the first regime, when $F_d > F_{\text{max}}^{\text{eff}}$, the monolayer slides unhindered over an effective substrate. Hence we call this motion “thermal sliding”. In the second regime, when the driving force is lower than the effective barrier, $F_d < F_{\text{max}}^{\text{eff}}$, the monolayer becomes pinned and its center of mass fluctuates about an equilibrium position which can be inferred from Fig. 3.3. In this latter case, a critical number of particles need to be kicked out of their respective potential wells in order to initiate a hopping wave. The time taken to form such a critical cluster needs to be treated within the framework of the classical nucleation theory [31].

The entire trajectory of a monolayer can therefore be resolved into three phases: the buildup phase, the nucleation phase (where applicable), and the hopping wave phase. We expect that the distributions of both the time taken to complete the buildup phase and the time for a hopping wave to travel through the system are Gaussians. Since the convolution of two Gaussian distributions is also a Gaussian, we define $\tilde{t}$ to be the mean time that the monolayer takes to complete the buildup phase plus the mean time the hopping wave takes to travel through the system, and the quantity ζ^2 is the sum of the variances of the aforementioned times. The time taken for nucleation to occur, on the other hand, obeys an exponential distribution with a characteristic time τ . The distribution of the total time, t_{total} , that the monolayer takes to travel forwards by one lattice constant is an exponentially modified Gaussian distribution arising from the convolution of these distributions:

$$\begin{aligned}
P(t_{\text{total}}; \tilde{t}, \tau, \zeta) &= \Pi^{-1} \int_0^\infty dt' \exp \left\{ \frac{t_{\text{total}} - t'}{\tau} \right\} \exp \left\{ -\frac{[t' - \tilde{t}]^2}{2\zeta^2} \right\}, \\
&= \frac{1}{2\tau} \exp \left\{ \tilde{t}/\tau + \zeta^2/2\tau^2 - t_{\text{total}}/\tau \right\} \\
&\quad \times \text{erfc} \left(\frac{\tilde{t} + \zeta^2/\tau - t_{\text{total}}}{\sqrt{2}\zeta} \right), \tag{3.9}
\end{aligned}$$

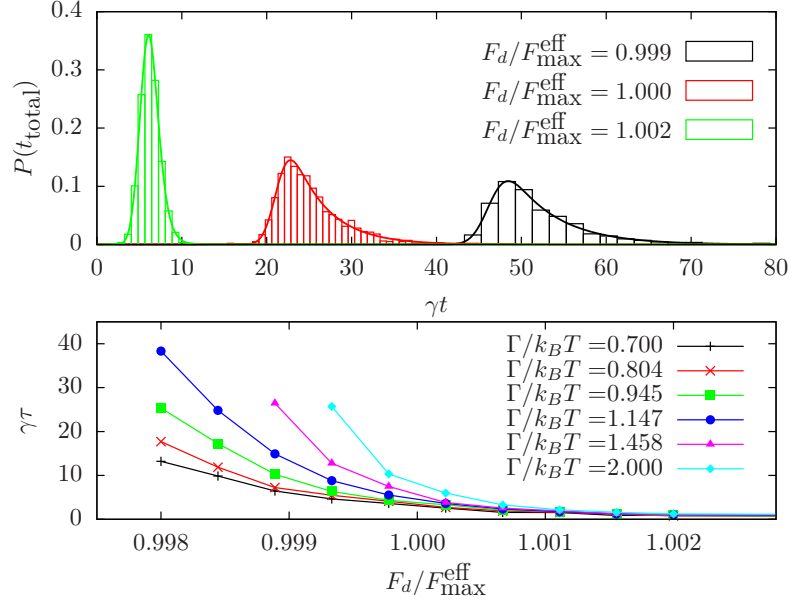


Figure 3.4 Top: Distribution of waiting times between hopping waves for a monolayer with $\Gamma/k_B T = 0.804$ for driving forces below, equal to, and above the effective barrier height, $F_{\text{max}}^{\text{eff}}/F_{\text{max}} = 0.982$. The red and black curves have been shifted horizontally by $15\gamma t$ and $40\gamma t$, respectively, for clarity. Bottom: Nucleation time, $\gamma\tau$ extracted from the distribution of waiting times for multiple monolayers driven at different rates.

where $\text{erfc}(x)$ is the complementary error function and Π is the product of the norms of the distributions. In the top panel of Fig. 3.4, we have plotted the distribution of the waiting times between two successive hopping waves, $P(t_{\text{total}})$, for a monolayer driven with a force less than, equal to, and greater than $F_{\text{max}}^{\text{eff}}$. The data were gathered by finding the time between two successive peaks in the net force acting on the monolayer (see bottom row of Fig. 3.2). The solid lines are fits of Eqn. 3.9 to the data sets, and evidently the tail of the distribution (determined by the value of τ) disappears when F_d becomes larger than $F_{\text{max}}^{\text{eff}}$. In the bottom of Fig. 3.4, we plotted the mean nucleation time τ , gathered from fits of Eqn. 3.9, for different monolayers as a function of the driving force. Due to the exponential dependence of the free energy as a function of the driving force, and the fact that the nucleation barrier is expected to vanish if $F_d > F_{\text{max}}^{\text{eff}}$, one can observe a change of at least 1 order of magnitude in the nucleation time within

a window of 0.4% of $F_{\max}^{\text{eff}}$. The shape of the curves in the bottom of Fig. 3.4 indicates that the dynamical transition from nucleation to thermal sliding is continuous.

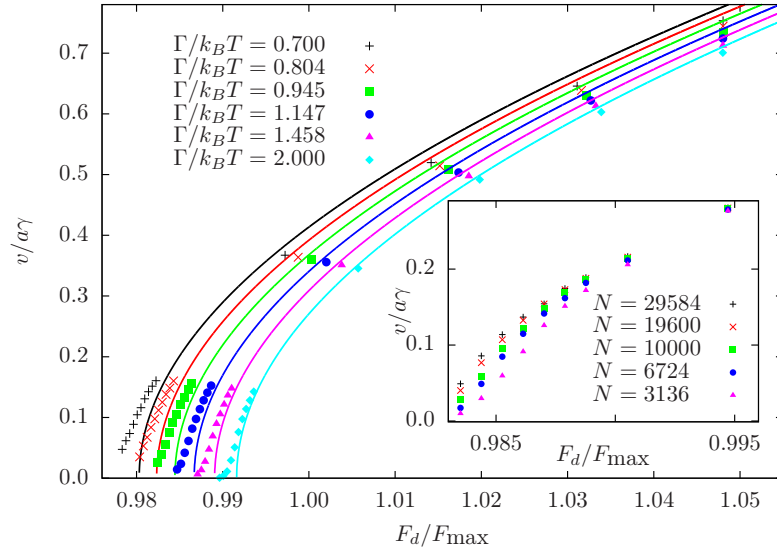


Figure 3.5 Velocity profiles of the simulated monolayers as a function of the reduced driving force $F_d/F_{\max}$. The lines are plots of the function $\gamma v = [F_d^2 - F_{\max}^{\text{eff}}(\Gamma)]^{1/2}$ that terminate at $F_d = F_{\max}^{\text{eff}}(\Gamma)$ and roughly reproduce the velocity of the monolayers when $F_d \gg F_{\max}^{\text{eff}}(\Gamma)$. Inset: Mean velocity of a monolayer with $\Gamma/k_B T = 1.038$ for different system sizes N .

In Fig. 3.5, we have plotted the mean velocity of a number of monolayers driven at rates both above and below their respective effective force barriers. All of the considerations herein lead to the expectation that there are two different scaling regimes of the mean velocity of the monolayer, γv , with respect to the driving force. In the nucleation regime, the value of the mean nucleation time, τ , has the largest influence on the velocity of the monolayer and scales exponentially in the height of the free energy barrier posed by the substrate. The free energy barrier in turn, is influenced by the driving force and thus the velocity is expected to decay exponentially as F_d goes to 0. In the thermal sliding regime, the mean velocity of the monolayer depends primarily on the time the center of mass takes to diffuse along the potential landscape associated with $F^{\text{eff}}(R)$. If one ignores the random force in Eqn. 3.2 and assumes that the variance in the particle positions remains constant, then the first order differential equation for the motion of the monolayer can be solved quite easily. The mean velocity of the monolayer for the thermal sliding regime is then given by $\gamma v = [F_d^2 - F_{\max}^{\text{eff}}(\Gamma)]^{1/2}$. The lines in Fig. 3.5 are plots of this simplification, and conform surprisingly well with the simulation results for $F_d \gg F_{\max}^{\text{eff}}(\Gamma)$, especially with respect to the scaling of γv . As a corollary to this consideration, if, for some reason one were unable to measure velocities in the regime close to $F_d = F_{\max}^{\text{eff}}(\Gamma)$, where velocities tend to be very small, then the obtained data would suggest the existence of a static friction located at $F_d = F_{\max}^{\text{eff}}(\Gamma)$. This apparent static friction obeys Amontons' law, in that the value of $F_{\max}^{\text{eff}}(\Gamma)$ is independent of the contact

area, which in this model is the particle number N , and is, to first order, proportional to the applied load, which is $F_{\max} \propto U_0$ [13, 55]. Nonetheless, we have shown that the atomic details of such monolayers induce a dramatic change in the scaling of the mean velocity close to $F_d = F_{\max}^{\text{eff}}$ and that it decays to small velocities. This finding may have some bearing on the discussion of the molecular origin of static friction found in the literature [31, 38, 55–57].

According to nucleation theory, the mean time of observing a nucleation event is inversely proportional to the product of the nucleation rate and the volume of the system $\tau = [JV]^{-1}$. Therefore, when a collective mechanism is responsible for motion, one expects that an increase of the system size will result in an increase of the monolayer mobility, contrary to the traditional experiences with friction. The mean velocity is expected to converge, however, for sufficiently large volumes or high nucleation rates, due to the appearance of multiple, simultaneous, hopping waves. The inset in Fig. 3.5 is a plot of the mean velocity of a monolayer with $\Gamma/k_B T = 1.038$ as a function of F_d for different system sizes N , and as one can clearly see, the mobility of the monolayer increases with N in the nucleation regime, which is expected to end at $F_{\max}^{\text{eff}}/F_{\max} = 0.9855$, and indeed shortly thereafter, the velocities converge.

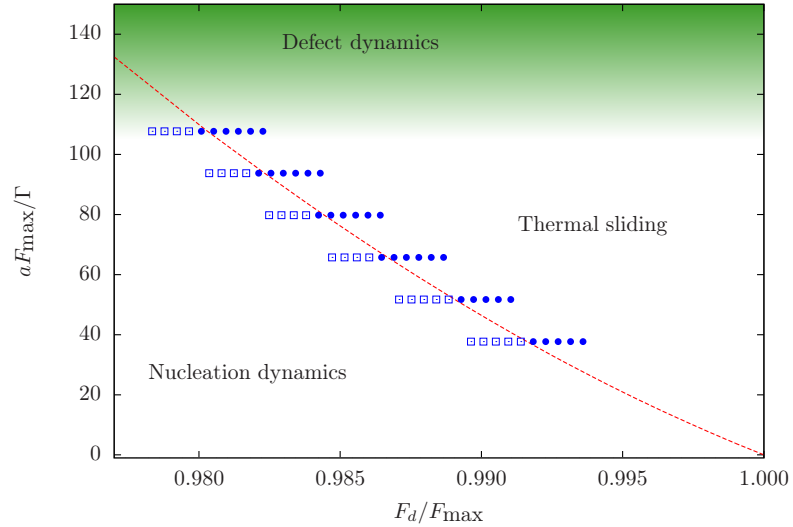


Figure 3.6 Proposed dynamical phase diagram of overdamped monolayers driven by a constant force. The dashed red line is the theoretical demarcation between thermal sliding and nucleation-induced motion $F_{\max}^{\text{eff}}(\Gamma)$ vs Γ^{-1} . Empty boxes denote parameter values for which nucleation of hopping waves was found and filled circles correspond to simulation runs in which thermal sliding occurred. The green gradient indicates the region in which the hopping wave mechanism gives way to defect-induced motion.

We attempted to find a suitable criterion to determine under which conditions the hopping wave mechanism gives way to defect driven motion, but we have been, so far, unsuccessful. We do expect, however, that the ratio of the substrate potential depth

(which favors the formation of defects) and the interaction strength (which penalizes defects) is to first order the main factor in determining whether the system moves through the formation of hopping waves or through correlated defects. Part of the difficulty in finding a cutoff between these two mechanisms stems from the fact that this is a continuous transition, as illustrated in Video S3, which shows that monolayers with $\Gamma/k_B T = 0.4$ produce both hopping wave and defect induced motion. We summarize our findings in Fig. 3.6, where we have plotted $F_{\max}^{\text{eff}}(\Gamma)$ for various values of $aF_{\max}/\Gamma$ (red dashed line) to delineate the nucleation regime from the thermal gliding regime. The symbols indicate interaction strengths and driving forces that we simulated. Empty boxes represent runs in which the net force acting on the monolayer was zero for significant periods of time, as is necessary for nucleation to occur. Filled circles, on the other hand, denote simulations in which the net force was positive virtually all the time, as expected for thermal sliding.

3.6 Conclusion and outlook

In this work, we found that stiff, overdamped monolayers adopt one of two different dynamic phases and developed a quantitative theory describing them. In particular, the velocity of the monolayer can be entirely characterized by the time the center of mass creeps along the effective substrate potential, the time a hopping wave travels through the system, and, where applicable, the mean nucleation time. While the results we presented in this work can be used to determine the first of the aforementioned times, analytical expressions for the hopping wave velocity and the nucleation time need to be developed. With these three quantities, the velocity profiles of the monolayers driven over a commensurate substrate can be reconstructed analytically. The driving force determines which of these times has the largest influence on the velocity of the system and a crossover occurs at $F_d = F_{\max}^{\text{eff}}(\Gamma, F_{\max}, a, \beta)$, which has been computed analytically. For large driving forces, the mean velocity of this model scales as if there existed a static friction and for small forces, we indicated that the mobility has an atypical dependence on the contact area, but a detailed analysis of this finite size effect is still pending.

There are many further studies worthy of consideration. The theory presented herein remains entirely unchanged if a different radially symmetric interaction potential is employed, provided that the particles in the system always repel each other strongly. We can therefore predict that a density dependent dynamical transition occurs for non-monotonic potentials even for large interaction strengths. Although the dynamic phases of the more complex underdamped Langevin dynamics would introduce an additional parameter to the system, it ought to be manageable under the right conditions, particularly

in the “onset of sliding simulations” performed in Refs. [23, 31], in which Nosè-Hoover molecular dynamics and underdamped Langevin dynamics were, respectively, employed.

3.7 Acknowledgments

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Chapter 4

Dynamical phases of attractive particles sliding on a structured surface

4.1 Introduction

The first documented studies of the phenomenon of friction date back to the times of da Vinci, Amontons and Coulomb [58, 59], but the microscopic dynamics underlying the motion of two surfaces in contact with each other is still not fully understood. In the beginning of the last century, Frenkel and Kontorova [12, 17, 19, 52, 60] and later Prandtl [15] and Tomlinson [16] formulated theoretical models to address this issue. Recent advances in experimental techniques were used to study friction at single particle resolution by means of colloidal particles [6], atomic force microscopy [47–50], and quartz crystal microbalance setups [26–28, 51]. Simulations complement the aforementioned studies by providing an opportunity to sample a wide range of precisely tuned parameters [30, 33, 38, 55–57]. In particular, the sliding phases of underdamped [21, 23, 24] and overdamped [61] particles as well as systems with repulsive [62] and with attractive [31, 63] interactions have been studied. In addition to that, the statics and dynamics of monolayers exposed to external potential landscapes with different length scales have also been examined [64, 65].

In our previous works [9, 10], we examined the dynamical response of a monolayer of particles interacting via the purely repulsive Yukawa potential. Like most simple pair potentials, the Yukawa potential depends on two parameters, one of which determines the coupling strength and the other the characteristic length scale of the interaction. Due to the fact that this potential is monotonic, it stands to reason that changing the density, or length scale of the potential, does not change the qualitative behavior of the system. Furthermore, we suggested that our results apply not only to Yukawa particles,

but to all systems in which particles interact with short-ranged, repulsive potentials. The Lennard-Jones (LJ) potential, however, is more complicated in this respect, since it has both a repulsive and an attractive regime and should therefore exhibit more complex dynamical phases. In this work, using a substrate potential with fixed well depth and lattice constant, we examine the frictional response of monolayers with different inter-particle interaction strengths, when the lattice constant of the crystal is greater than, equal to, or less than the lattice constant of the external pinning potential.

If the lattice constant of the LJ monolayer in consideration is equal to or larger than the lattice constant of the underlying surface (harmonic and compressed monolayers), the system behaves similar to the Yukawa case. On the other hand, if the length scale of the Lennard-Jones interactions is smaller than that of the substrate potential (stretched phase), there is an ever present length scale mismatch between the LJ interactions and the external substrate that dramatically changes the dynamics of the system. Not only does the application of a constant driving force create cracks in the monolayer, but, as expected, we find that the attractive interactions increase the mobility of the monolayer. Furthermore, the mobility of the monolayer is non-monotonic in terms of the strength of the interaction: an increase of the attraction strength between the particles at fixed driving force results in an initial decrease of the monolayer velocity, which then starts to grow.

After discussing the simulation details, we present the simulation results, which are divided in two parts; first, we treat the stretched and harmonic monolayers and then the compressed ones. In both cases, we investigate the mobility of the monolayers for various inter-particle interaction strengths and the dynamical phases the monolayer forms when driven over a structured surface.

4.2 Simulation details

We simulated the motion of a two-dimensional monolayer composed of $N = 6400$ particles driven over a structured surface. The size of the simulation box is fixed and chosen so that it can accommodate 80×80 substrate potential minima arranged in a hexagonal lattice with lattice constant a_{sub} . As a result, the ratio of particles to substrate wells, the filling fraction, is unity. The motion of the particles in the system is modeled by overdamped Langevin dynamics [39], which means that at any moment of time their velocity is given by

$$\gamma \frac{d\mathbf{r}_i}{dt} = \mathbf{F}_{\text{sub}}(\mathbf{r}_i) + \sum_{j \neq i} \mathbf{F}_{LJ}(|\mathbf{r}_i - \mathbf{r}_j|) + \mathbf{F}_d + \mathbf{F}_{\text{rand}}(t). \quad (4.1)$$

The substrate force, $\mathbf{F}_{\text{sub}}(\mathbf{r}_i)$, acting on particle i , is the negative gradient of the external potential,

$$U_{\text{sub}}(\mathbf{r}_i) = -\frac{a_{\text{sub}} F_{\text{max}}}{8\pi} [3 + 4 \cos(k_x \mathbf{r}_i^x) \cos(k_y \mathbf{r}_i^y) + 2 \cos(2k_y \mathbf{r}_i^y)], \quad (4.2)$$

where $k_x = 2\pi/a_{\text{sub}}$ and $k_y = 4\pi/\sqrt{3}a_{\text{sub}}$. This choice of k_x and k_y produces a hexagonal arrangement of potential wells with a lattice constant a_{sub} and lattice vectors $\mathbf{g} \in \{(a_{\text{sub}}, 0), (a_{\text{sub}}/2, \sqrt{3}a_{\text{sub}}/2)\}$. The lattice constant of the substrate potential determines the length scale of the substrate, which we set to unity. The prefactor F_{max} is the maximum force that the substrate can exert on a particle in the x -direction and determines the strength of the substrate. We fixed it at $F_{\text{max}} = 8\pi k_B T / 9a_{\text{sub}}$, which corresponds to a substrate potential well depth of $1k_B T$. The particles interact with each other via standard LJ interactions, $\mathbf{F}_{LJ}(|\mathbf{r}_i - \mathbf{r}_j|)$. The corresponding potential energy of two particles separated by distance r is $U_{LJ}(r) = \epsilon [(a_{LJ}/r)^{12} - 2(a_{LJ}/r)^6]$. Here, a_{LJ} is the position of the minimum of the LJ potential and inserting the identity $a_{LJ} = 2^{1/6}\sigma$ into the definition of the LJ potential recovers the more traditional parametrization in which σ is the usual LJ radius of the particle. In order to study the effect of the attractive tails on the dynamics of the monolayer, we varied the inter-particle interaction range a_{LJ} and the interaction strength ϵ . The LJ interactions were truncated at an interparticle separation of $r_c = 2.5a_{LJ}$. In all simulations, we applied a constant driving force, $\mathbf{F}_d = (F_d, 0)$, in the x -direction. The thermal motion of the overdamped particles was simulated by applying a random force $\mathbf{F}_{\text{rand}}(t)$ on each particle, at each moment in time. These forces were uncorrelated in time as well as in their x - and y -components and were represented by Gaussian white noise with zero mean and variance $2\gamma k_B T$, where k_B is the Boltzmann constant, T is the temperature and γ , which also appears in Eq. (4.1), is the viscosity of the fluid the particles were suspended in.

To model the overdamped motion of the particles, we employed the algorithm presented in [39] with a time discretization $\gamma\delta t = 10^{-4}$. For each set of parameters, we performed 5 simulation runs, each of which lasted 5×10^5 time steps. To ensure equilibration, the systems were propagated in time for 2×10^6 time steps, before any measurements were made. The long equilibration times are necessary to ensure that the simulations have converged to the dynamical steady state. We used reduced units in which $\gamma = k_B T = 1$ and, in the following, all distances will be rescaled by the lattice constant of the substrate, a_{sub} , and all forces by F_{max} .

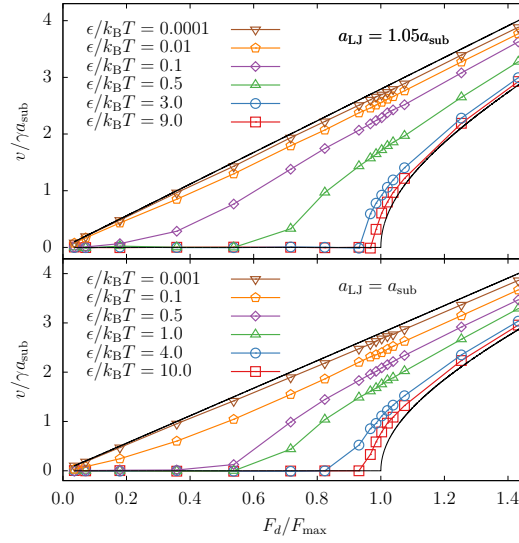


Figure 4.1 Velocity of monolayers with LJ parameter $a_{\text{LJ}} = 1.05a_{\text{sub}}$ (top) and $a_{\text{LJ}} = a_{\text{sub}}$ (bottom) as a function of the driving force F_d for different interaction strengths ϵ . The straight black line, $\gamma v = F_d$, corresponds to the motion of a monolayer in the absence of a substrate. The black curve, $\gamma v = \sqrt{F_d^2 - F_{\text{max}}^2}$ corresponds to the formal solution of the motion of an infinitely stiff monolayer and is the lower bound of the monolayer velocity.

4.3 Results and discussion

4.3.1 Compressed monolayers

First, we consider a relatively dense LJ system, in which the particles have a typical distance equal to or less than the LJ length scale a_{LJ} . We realized this by setting $a_{\text{LJ}} = 1.05a_{\text{sub}}$, in order to obtain purely repulsive interactions between nearest neighbors, and $a_{\text{LJ}} = a_{\text{sub}}$, in order to obtain harmonic interactions. In this case, the energetic groundstate of the system, in the absence of a driving force, is realized by placing one particle in each substrate potential minimum. We expect that the dynamical response of these types of monolayers to a constant driving force will be similar to that of a monolayer composed of Yukawa particles.

The friction of the monolayer is defined by the velocity it adopts when a constant driving force F_d is applied to it. In the absence of an external pinning potential, the monolayer drifts with a velocity $\gamma v = F_d$, which is the maximum speed at which the monolayer can travel. The deviation of the monolayer's average velocity from the free case is the frictional response of the system. In Fig. 4.1, we present the average velocity of different monolayers as a function of the driving force F_d for various inter-particle interaction strengths. The shapes of the curves of the monolayers with $a_{\text{LJ}} = 1.05a_{\text{sub}}$ and $a_{\text{LJ}} = a_{\text{sub}}$ are not only similar to each other, but also match those obtained from simulations of Yukawa particles [9, 10]. As expected, for large values of ϵ , the monolayers are pinned to the substrate until the driving force applied becomes comparable to the

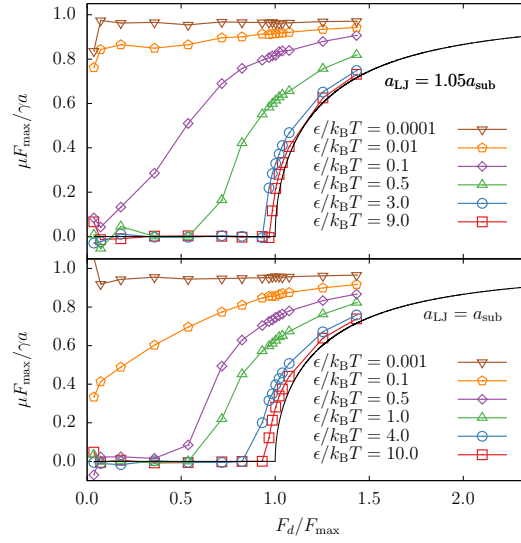


Figure 4.2 Mobility, $\mu = v/F_d$, plotted as a function of the driving force, F_d , for different interaction strengths, ϵ , in reduced units. In the top panel, the LJ parameter is $a_{\text{LJ}} = 1.05a_{\text{sub}}$ and in the bottom panel $a_{\text{LJ}} = a_{\text{sub}}$.

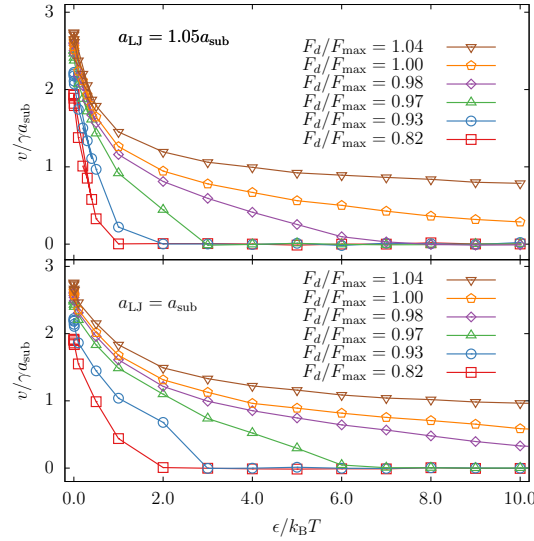


Figure 4.3 Velocity of LJ monolayers at repulsive, $a_{\text{LJ}} = 1.05a_{\text{sub}}$, and harmonic, $a_{\text{LJ}} = a_{\text{sub}}$, length scales as a function of the interaction strength ϵ for different driving force F_d .

maximal force F_{max} that the substrate can exert on a particle. Then, the monolayer slides as a whole with the velocity closely resembling the velocity of a single particle driven over a corrugated substrate [15], $\gamma v = \sqrt{F_d^2 - F_{\text{max}}^2}$.

An alternative, but equivalent, measure of the frictional response of the system is defined by the mobility, which is the ratio of the monolayer velocity and the driving force, $\mu = v/F_d$. When the monolayer is pinned in place, the mobility of the system is zero and it is unity in the absence of an external potential. In Fig. 4.2, we have plotted the mobility of the monolayers for various interaction strengths along with the analytical

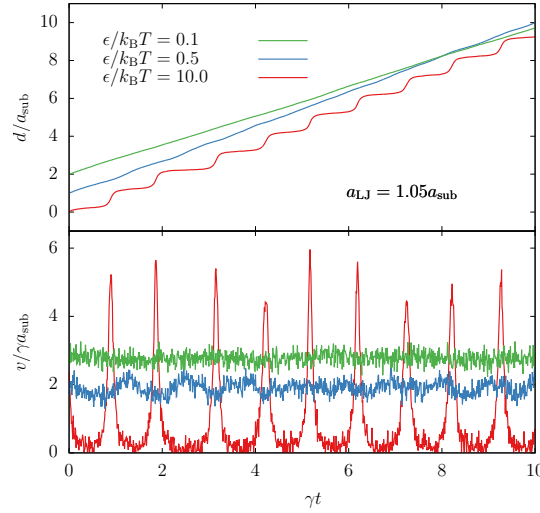


Figure 4.4 Top: Average distance traveled by monolayers for $a_{\text{LJ}} = 1.05a_{\text{sub}}$ and with $\epsilon/k_B T = 0.1, 0.5, 10$ as a function of time. The driving forces were adjusted so that the different monolayers have roughly the same velocity. Each of the curves has been shifted vertically by one unit for clarity. Bottom: Instantaneous velocity of the same representative monolayers obtained from numerical differentiation of the data above. Here, too, each of the curves have been shifted by one for clarity.

solution for a monolayer with infinitely large ϵ [9]. As can be seen in Fig. 4.1, in order to obtain the mobility for small driving forces, one needs to evaluate a small velocity accurately, and then divide this small number by F_d . This procedure is both numerically and statistically unstable, as can be seen for the first few points of each curve in Fig. 4.2.

For both the repulsive and the harmonic monolayers, Fig. 4.3 shows that their velocity decreases monotonically as a function of the interaction strength. This trend can be explained by the fact that stronger interactions suppress the thermal fluctuations, which are necessary to induce motion.

In order to ascertain what types of mechanisms are responsible for the motion in the monolayer, we plotted the average displacement of the particles in a monolayer as a function of time in the top panel of Fig. 4.4, for three different interaction strengths, and for $a_{\text{LJ}} = 1.05a_{\text{sub}}$. The driving forces acting on the monolayers were chosen such that their mean velocities were similar. One can infer the average velocity of each of the monolayers from the average slope of their curves. In the bottom panel of Fig. 4.4, the instantaneous velocity of the system is plotted, also as a function of time and was obtained through numerical differentiation of the d vs t graph. As one can see, the motion of monolayers with large interactions, $\epsilon = 10k_B T$, consists of alternating creeping phases and surges of motion. Monolayers with intermediate interaction strengths, $\epsilon = 0.5k_B T$, perform continuous motion with large fluctuations, and monolayers with small interaction strengths, $\epsilon = 0.1k_B T$, have a virtually constant velocity with small

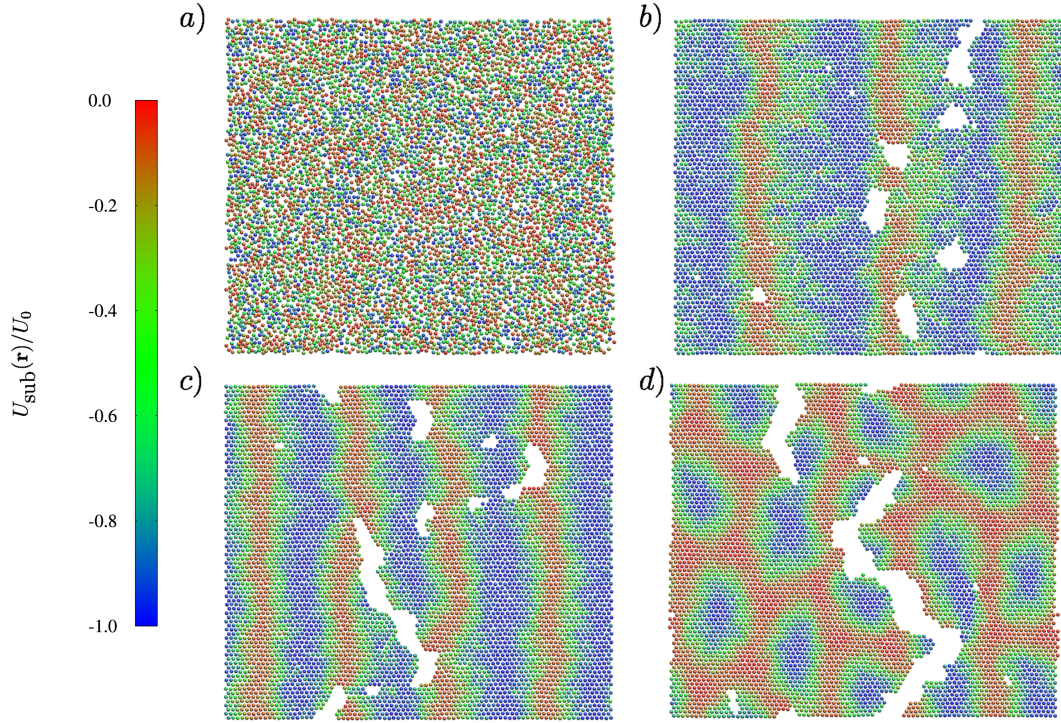


Figure 4.5 Representative configurations of the dynamical phases that LJ monolayers adopt when $a_{\text{LJ}} = 0.95a_{\text{sub}}$, for different interaction strengths. Each of the particles in the system is depicted as a sphere and is colored according to its external substrate potential value as depicted in the color key on the left. The driving force acts from left to right. a) For very small interactions, $\epsilon = 0.1$, the particles barely interact with each other and therefore the particles lose hexagonal order as they slide in an amorphous phase over the substrate. b) As the interaction is increased to intermediate values, $\epsilon = 4.0$, hexagonal order emerges. This order consists of a compromise between the lattice constant of the substrate and that of the LJ interactions. In the y -direction, the monolayer adopts the lattice constant of the substrate. In the x -direction, however, the typical inter-particle spacing is somewhere between a_{LJ} and a_{sub} . c) For large interactions, $\epsilon = 7.0$, the cracks that form become rigid and the relative positions of the particles is a_{LJ} . In the y -direction, however, the monolayer is still stretched. d) Only for very large interparticle interactions, $\epsilon = 10.0$, does the monolayer adopt hexagonal ordering with lattice constant a_{LJ} both in the x - and in y -direction.

fluctuations. In both panels, the curves have been shifted vertically by one, for clarity. Thus, compressed monolayers of LJ particles behave essentially similar to the monolayers composed of purely repulsive Yukawa particles, which were examined extensively in earlier work [9, 10]. The only deviation we find is that the increase of the inter-particle interactions does not result in an initial increase of the mobility (Fig. 4.3) as observed for Yukawa particles. This discrepancy is attributed to the fact that we are considering rather shallow potential wells.

4.3.2 Stretched monolayers

By reducing the LJ parameter to $a_{\text{LJ}} = 0.95a_{\text{sub}}$, we introduce a length scale competition between the substrate, that attempts to assert an inter-particle separation a_{sub} , and the

LJ interaction. We find that even though the length scale mismatch is only 5%, the behavior of the monolayers changes significantly in comparison to the previous cases. As before, we vary the interaction strength, ϵ , and find that it tunes the magnitude of the length scale competition. In the following, we describe the dynamical phases that the monolayers adopt and then proceed to discuss the frictional response of the system. We find that the motion of the monolayer is defined by the structures it forms, which in turn depend upon the compromise between its tendency to be stretched by the substrate and its inclination to contract due to the inter-particle interactions.

4.3.2.1 Dynamical steady-states

In order to compare our results with the $a_{\text{LJ}} \geq a_{\text{sub}}$ case, we initialized all of our simulations by placing a single particle in each substrate minimum. For small ϵ , this configuration is close to the equilibrium state of the system. For intermediate and large interactions, this is less likely to be true. The effects of the initial condition on the dynamics of the monolayer will be discussed in the next section.

In Fig. 4.5, we depicted four representative configurations of the dynamical steady states for different LJ interaction strengths ϵ . Each of the spheres in a configuration represents a particle in the system, and is colored according to its substrate potential value. As indicated by the color key in Fig. 4.5, blue particles reside at the bottom of an external potential well whereas red particles sit at the top of a substrate barrier.

For very small interaction strengths, as one might expect, the particles barely interact with each other and form an amorphous sliding phase (Fig. 4.5a). This amorphous phase consists of a random distribution of particles that are either trapped at the bottom of a substrate potential well (blue) or are currently hopping from one potential well to the next (red). The white spaces in the figure correspond to temporarily unoccupied potential wells that are matched by doubly and triple occupied substrate minima.

In Fig. 4.5b, one can see that, as ϵ increases, the LJ interactions force hexagonal order onto the monolayer. Furthermore, the voids that were randomly distributed before, are now clustered. The reason why these voids appear is that the LJ interaction attempts to impose an inter-particle separation of $a_{\text{LJ}} = 0.95a_{\text{sub}}$, and partially succeeds in doing so, but only through the formation of vacancies. These vacancies tend to cluster in order to minimize the energy penalty associated with them. Perhaps the most striking feature of this dynamical phase is the stripe pattern of the color scheme. The fact that the particles in each column have the same substrate potential value implies that the monolayer has a lattice constant of a_{sub} in the y -direction, whereas the continuous change in coloring along the x -direction suggests that the monolayer is compressed. It appears that the application of a constant driving force helps the monolayer evolve cracks and thereby

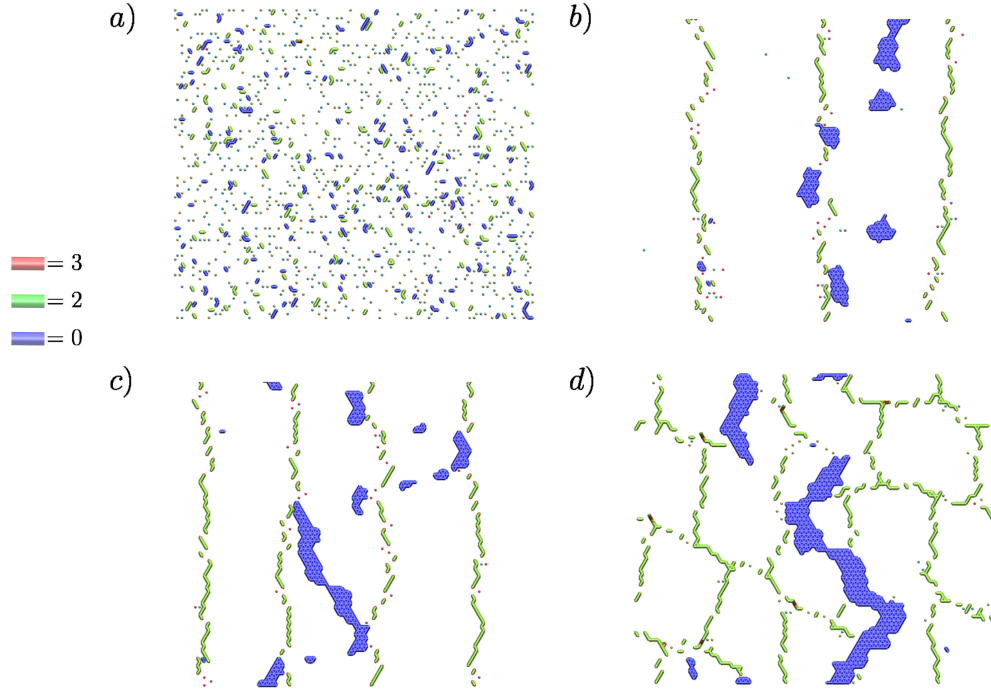


Figure 4.6 Alternative representation of the dynamical phases. After assigning a substrate potential well to each particle in the system, we connected neighboring doubly and triple occupied potential minima by green and red bonds, and the empty substrate potential minima by blue bonds. If a doubly and triple occupied or empty potential well has no neighbors, it is represented by a particle using the same color scheme as the bonds. The network of green bonds correlates with the centers of the red regions in the previous representation and the blue clusters coincide with the location of the cracks in the monolayer.

deform in the x -direction, whereas in the y -direction, perpendicular to the driving force, the substrate is still able to prevent the monolayer from contracting.

For yet larger ϵ , the clustering of the voids, or cracks, in the monolayer increases further and the cracks no longer fluctuate (see V2 and V3 in supplementary materials). Thus, in Fig. 4.5c, only a handful of large cracks remain. Furthermore, there is a very simple consideration that can be used to describe this dynamical phase. Consider a chain of equally spaced particles with inter-particle separation a_{LJ} in a periodic potential with period a_{sub} . This arrangement of particles has a period of $\delta l = a_{\text{sub}} / (a_{\text{sub}} - a_{\text{LJ}})$, which in our case is $\delta l = 20a_{\text{sub}}$. Since the simulation box we considered has a length $80a_{\text{sub}}$ in the x -direction, one can expect that a rigid monolayer with a lattice constant of $0.95a_{\text{sub}}$ in the x -direction should create four stripes, as is the case in this dynamical phase. One can therefore infer that the inter-particle separation in the x -direction conforms to the length scale of the LJ potential and not to that of the substrate. Using this consideration, one can also infer that the average particle separation in the previous dynamical phase (Fig. 4.5b), which exhibits only three stripes, is $0.9625a_{\text{sub}}$ – a compromise between the length scales of the external potential and the LJ interaction.

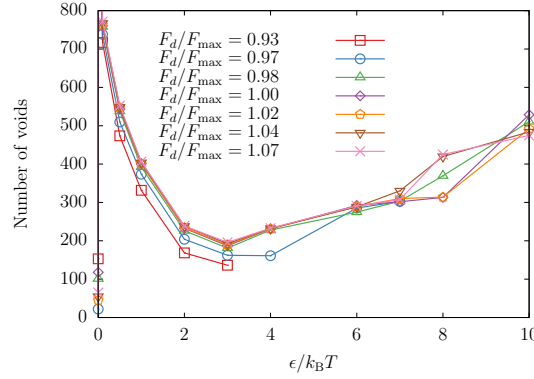


Figure 4.7 Number of unoccupied substrate potential minima as a function of the interaction strength ϵ for various driving forces.

Finally, the dynamical phase in Fig. 4.5d appears only for very large interaction strengths. The colored pattern clearly indicates that the hexagonal lattice formed by the monolayer does not match that of the underlying substrate both in the x - and in the y -direction. The fact that the blue spots form a hexagonal pattern indicates that the length scale of LJ interactions overcomes the influence of the substrate. For animations of these dynamical phases, we refer to the supplementary videos V1-V4.

In order to make the differences between these dynamical phases more apparent, we assigned each particle to the potential well closest to it. By ignoring the external potential wells that are occupied by a single particle, and depicting wells that are empty (blue) or occupied by two or more particles (green and red), the panels in Fig. 4.6 capture the essential structure of the dynamical phases in Fig. 4.5. Two neighboring substrate minima with no particle assigned to them are connected by a blue bond, while isolated, empty substrate minima are represented by blue spheres. The same procedure was repeated for potential wells with two or three particles in them, but these regions are colored green and red, respectively. As can be seen in Fig. 4.6a, the arrangement of empty and doubly and triple occupied lattice sites is essentially random for very small ϵ . The cracks begin to coalesce to larger structures as ϵ increases and the doubly and triple occupied regions, take on the string-like structure that can be expected from a monolayer that is distorted in the x -direction only (Fig. 4.6b and Fig. 4.6c). Finally, when only one or two very large crack regions are visible, the arrangement of doubly occupied potential minima adopts a hexagonal-like structure of its own (Fig. 4.6d). We used this representation in the second panel of the supplementary videos V1-V4 in order to show that the qualitative features of these structures persist over the course of the simulations.

As a preliminary analysis of the structure of the dynamical phases in the system, we calculated the average number of unoccupied substrate potential minima over the course of a trajectory for different interaction strengths and driving forces (blue particles and

bonds in Fig. 4.6). As might be expected, the curves in Fig. 4.7 show that there is a dramatic difference between the complete absence of interparticle interactions ($\epsilon = 0$) and arbitrarily small but finite interaction strengths.

For small values of ϵ , increasing the inter-particle interactions decreases the average number of vacancies in each configuration. This is the case for small ϵ because the particles interact with each other only when they share the same substrate potential well, and when they do, they tend to “stick” together, thereby not only increasing the number of doubly and triple occupied substrate wells, but also unoccupied wells. In the complete absence of the LJ interaction, there is no such energetic preference towards multiple filled substrate wells and therefore fewer vacancies are measured. Then, close to $\epsilon = 3k_{\text{B}}T$, the length scale of the LJ interaction begins to assert itself, and instead of preventing voids from forming, the length scale mismatch between the LJ interactions and the substrate favors the formation of large, vacancy clusters, *i.e.* cracks. The strong overlap of the curves suggests that the dynamical phases that the monolayers adopt depend primarily on the relative strength of the substrate and the LJ interaction, as opposed to the driving force.

In summary, there are four dynamical regimes available to the stretched monolayer. For small interaction strengths, particles in the monolayer display very little order other than that imposed by the substrate. As the interaction strength increases, hexagonal ordering of particles is accompanied by clustering of vacancies in the system. Although these structures still fluctuate, one can clearly see that the LJ interactions start to assert themselves along the direction of the driving force and the monolayer becomes compressed in the x -direction. For larger interactions, the cracks in the configuration become not only very large but also rigid, and the crystal eventually adopts the inter-particle spacing imposed by the LJ interactions in the direction of the driving force. Further increase of the LJ interaction strength causes the monolayer to develop a perfectly hexagonal lattice with a uniform lattice constant in both the x - and y -directions.

4.3.2.2 Frictional response

Although the dynamical phases we described are structurally very different, their velocities are remarkably stationary. To show that the motion of a monolayer is relatively uniform, apart from some noise, we plotted the distance the center of mass of the monolayer has traveled and its instantaneous velocity, as a function of time, in Fig. 4.8. Here, we use the same representative trajectories as in Fig. 4.5. Again, the driving forces were chosen such that the speed of the monolayers is roughly the same. It appears that for attractive monolayers, after they have satisfied the length scale frustration by deforming, glide continuously through space. This is in stark contrast to the harmonic and repulsive cases, where in two out of three sliding phases the motion proceeds through

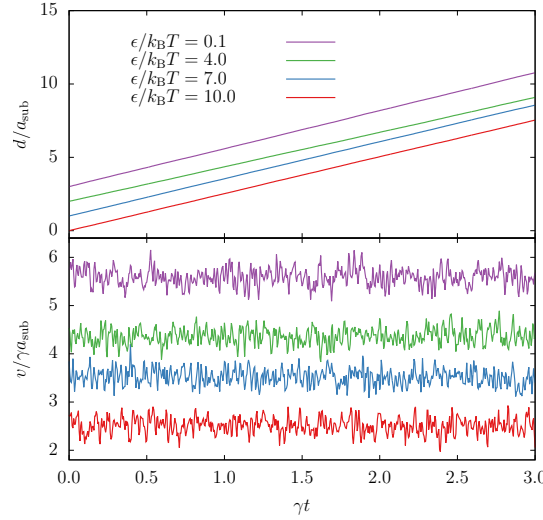


Figure 4.8 Top: Distance the monolayer has traveled as a function of time for LJ monolayers with $a_{\text{LJ}} = 0.95a_{\text{sub}}$. The curves have been shifted vertically by one for clarity. The driving force was adjusted so that the mean velocities are similar. Bottom: Instantaneous velocities of the monolayers obtained from numerical differentiation of the curves above, also shifted by one for clarity.

the creation of local kink-antikink pairs, *i.e.*, local distortions of the hexagonal lattice, which generate large fluctuations in the velocity of the monolayer.

In Figs. 4.9 and 4.10, we present the frictional response of the monolayers as a function of the applied driving force. In order to make the plots less busy, we split them into two panels. In the top panels, we plotted data for monolayers with $\epsilon \geq 3k_{\text{B}}T$. For these values of ϵ , the LJ interactions impose their incommensurate length scale on the system (Figs. 4.5c and 4.5d). There is a jump in the velocity of the monolayer as F_d overcomes some threshold, which we believe is an artifact of the initial configuration. The data points connected by solid lines were obtained from simulation runs in which each particle is placed into its own substrate potential well. During the equilibration phase, in which no measurements were taken, the monolayer needs to form cracks somewhere in the configuration in order to relax into its dynamical steady state. Although it becomes increasingly favorable for the monolayer to contract as ϵ becomes very large, it also takes longer for cracks to appear, since the thermal fluctuations which generate such structural transformations get suppressed as the inter-particle interactions increase. The driving force assists crack formation since for every interactions strength there is a critical value of the driving force for which the monolayers depin within the simulation time. Thus, as the interaction strength grows, so too does the critical driving force necessary for the monolayer to depin. In order to verify that the initial condition we employed is the source of this apparent dynamical arrest, we took configurations from trajectories in which $F_d = 0.93F_{\text{max}}$ and used them as the initial configurations for another set of simulation runs (points connected by dashed lines in Figs. 4.9 and 4.10). As expected,

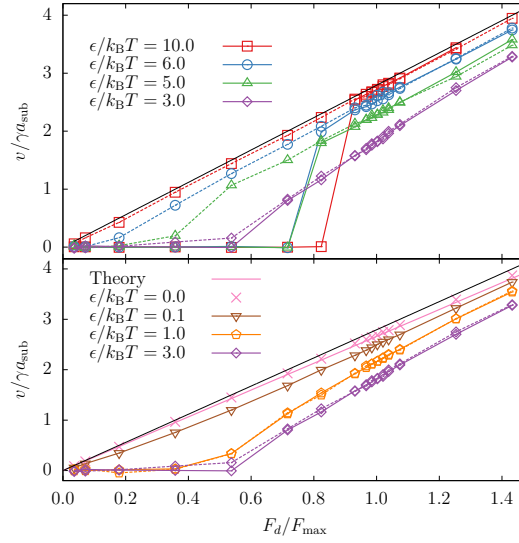


Figure 4.9 Top: Velocities of monolayers as function of the driving force, F_d , for $\epsilon \geq 3k_B T$. Bottom: Velocities of monolayers as function of the driving force, F_d , for interaction strengths $\epsilon = 3k_B T$ and below. The pink line, associated with the $\epsilon = 0$ data, is not a guide to the eye, but is instead the theoretical prediction from [42]. Data points connected by different types of lines (solid or dashed) came from simulations with different initial conditions (see main text).

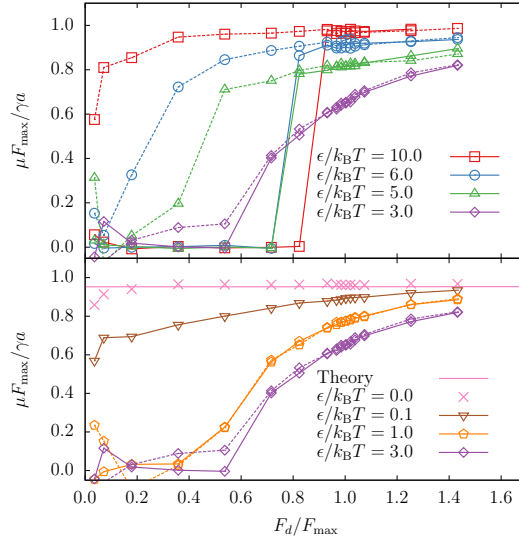


Figure 4.10 Mobility, $\mu = v/F_d$, plotted as a function of the driving force for different interaction strengths ϵ . As in Fig. 4.9, interaction strengths with $\epsilon \geq 3k_B T$ have been plotted in the top panel, and data for $\epsilon \leq 3k_B T$ is presented in the bottom.

the monolayers that were previously pinned throughout the run, were able to slide if cracks were present at the beginning of the simulation. This dynamical hysteresis is caused by the kinetics of crack formation, which we expect to obey a nucleation-like scenario. In the bottom panels, we plotted the data for the monolayers with $\epsilon \leq 3k_B T$. The data for $\epsilon = 3k_B T$ was intentionally included a second time to show that this monolayer has the lowest mobility of all examined interaction strengths. When ϵ is

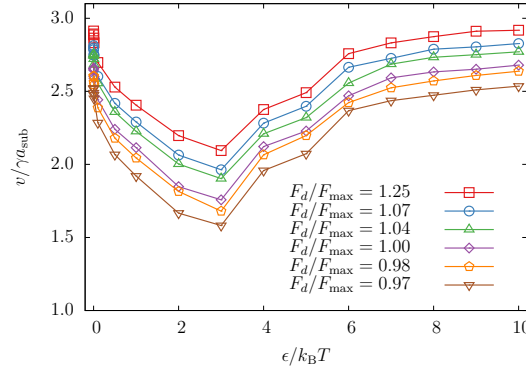


Figure 4.11 Velocity of LJ monolayers with $a_{\text{LJ}} = 0.95a_{\text{sub}}$ as a function of the interaction strength ϵ for different driving force F_d . Unlike its harmonic and repulsive counterparts, the attractive LJ monolayer has a clear global minimum in its mobility at $\epsilon = 3k_{\text{B}}T$ that does not appear to depend on the driving force.

set to zero, the particles do not interact with each other, and therefore, the system is equivalent to the motion of a Brownian particle driven over a sinusoidal potential [9], which can be solved analytically [42]. To compare our simulation results with analytical predictions, we did not connect the data points for the $\epsilon = 0$ data points with lines, but plotted the aforementioned solution (pink lines in the bottom panels labeled “Theory”) instead. Evidently, the prediction agrees very well with simulation results. We point out again that the mobility is prone to be numerically unstable for small driving forces. In order to highlight the scaling of the monolayer velocity as a function of the interaction strength, we plotted the velocity of the monolayer as a function of ϵ for various driving forces F_d in Fig. 4.11. For $\epsilon = 0$, the particles perform completely independent random walks through space. For small, but finite ϵ , the mobility of the monolayer decreases since the particles interact with each other only when they are close, and therefore tend to “stick” to each other when they occupy the same substrate minimum. This effect becomes more pronounced for growing ϵ until some crossover point at which the monolayer begins to assemble domains whose length scale does not match the length scale of the substrate. For interactions beyond this point, the mobility of the monolayer begins to increase as ϵ grows, until, finally, its motion is independent of the substrate and the velocity is given by $\gamma v = F_d$. Thus, the attractive LJ monolayer has a well defined global minimum in the mobility that is flanked by a local maximum at $\epsilon = 0$ and asymptotically approaches $\gamma v = F_d$ as ϵ goes to infinity. This trend is contrary to the behavior of repulsive and harmonic particles as shown in Fig. 4.3, in which the monolayer velocity is, essentially, a monotonically decreasing function bounded by the $\epsilon = \infty$ limit [9].

4.4 Summary and outlook

In this paper, we showed that even a slight length scale mismatch between the inter-particle interactions of a monolayer of particles and the structured surface it is driven over has a dramatic effect on its dynamical phases. For lattice differences resulting in locally repulsive or harmonic inter-particle interactions, we recover, qualitatively, the behavior of Yukawa particles. This therefore suggest that the dynamical behavior of overdamped monolayers of locally repelling particles is independent of the functional form of the potential for large distances. The reason for this behavior is that the external substrate suppresses the influence of a particle on all but the nearest neighbors. On the other hand, for locally attractive particles, the structure that the monolayer adopts consists of a compromise between, in this case, the LJ interactions and the external substrate potential, and it is the ensuing structure that determines the mobility of the system. By tuning the strength of the LJ interactions, we found that the length competition initially reduces mobility, in the amorphous sliding regime, but then enhances mobility as the inter-particle interactions enforce hexagonal order on the system. Although there are two structural transitions the monolayer undergoes as ϵ is varied, almost all of the curves presented herein are smooth, which is an indication that the transitions themselves are continuous, as opposed to Aubry-like [19, 60]. In addition to the two-step assertion of the LJ length scale in the direction parallel and then perpendicular to the driving force, the formation of cracks is essential in resolving the length scale competition. The mechanism underlying the emergence of cracks, the dynamical hysteresis exhibited by the system, and the structural changes parallel and perpendicular to the driving force are not yet fully understood and may form a basis with which to study crack formation and the creation of tribo-films in experiment.

4.5 Acknowledgments

The computational results presented have been achieved using the Vienna Scientific Cluster (VSC). We acknowledge financial support of the Austrian Science Fund (FWF) within the projects P24681-N20 and V 305-N27. The authors would like to thank Georg Menzl and Clemens Moritz for useful discussions.

Chapter 5

Crystallization and flow in active patch systems

Based upon recent experiments in which colloidal particles can be made into active swimmers through the use of laser light, we explore the effect of applying a light pattern on the sample, thereby creating activity inducing zones, or active patches. We simulate a system of interacting Brownian diffusers that become active swimmers if they enter an active patch and analyze the structure and dynamics of the ensuing stationary state. For symmetric activity zones, the system reacts qualitatively similar to a system with a temperature differential. For asymmetric active patches this analogy breaks down because we observe a net flow in the system. The predictions herein can be tested experimentally and may form the basis for a deeper understanding of chemotaxis.

The motion of bacteria, the action of molecular motors along proteins, and the collective motion of flocks are all part of the rapidly growing study of the nonequilibrium statistics of active matter [66]. Recently, a number of soft matter systems have been constructed to probe the collective behaviors of such systems [70]. This work is inspired by the family of experiments in which specially tailored micrometer sized particles can be made into active swimmers by illuminating them with laser light [7, 71]. In the experiments of Bechinger *et al.* [7], micrometer sized silica beads were half-coated with a thin layer of graphite and suspended in a water-lutidine mixture that was kept close to the critical demixing concentration. By pouring this colloidal suspension in a cavity, the particles were confined to a quasi two-dimensional geometry and the sample was then illuminated by laser light. The wavelength of the laser was chosen so that only the carbon coated hemisphere of the silica beads was heated. At sufficiently high light intensity, the carbon half of the beads heated the surrounding solvent to such an extent that local demixing occurred. This created an asymmetric concentration gradient around the bead that induced directed motion perpendicular to the equator connecting the hemispheres. Furthermore, it was shown that the light intensity was directly proportional to

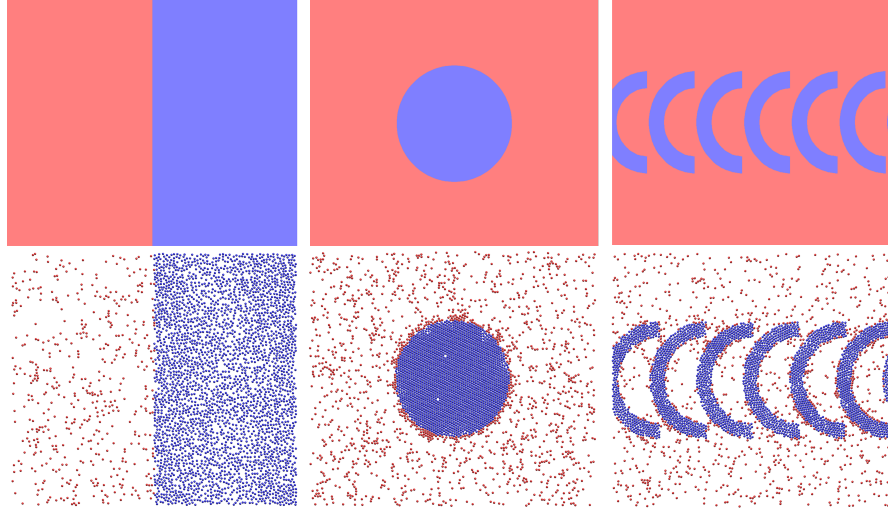


Figure 5.1 The three different types of geometries considered in this work. The red regions correspond to areas that are illuminated by the activity-inducing laser light, and the particles in the blue region perform conventional Brownian diffusion. The bottom row depicts typical configurations of particles for large activity. The particles are colored according to whether or not they are active.

the swimming speed of the particles and it was ascertained that the activity was primarily diffusiophoretic. The aim of this work is to study the effect of partially illuminating the sample, thereby creating an active and an inactive zone. Whenever a particle leaves the illuminated zone, it performs conventional Brownian diffusion. If a particle enters an activity inducing zone it performs active motion in addition to diffusion.

Molecular dynamics simulations discussed in Reference [7], showed that although the colloidal particles are hard spheres, the Weeks–Chandler–Anderson potential [72] more accurately reproduces the radial distribution function obtained from experiment because the quasi two-dimensional geometry that the particles are in allows for a small out of plane overlap. The potential energy between two particles interacting via the WCA potential is

$$U^{\text{WCA}}(r) = \epsilon \left[(r_0/r)^{12} - 2(r_0/r)^6 \right] + \epsilon \text{ for } r < r_0, 0 \text{ otherwise,} \quad (5.1)$$

where r is the interparticle distance. The total potential energy of the system is $U^{\text{tot}} = \sum_{i < j} U^{\text{WCA}}(|\mathbf{r}_i - \mathbf{r}_j|)$ where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the position vectors of the i^{th} and j^{th} particles in the system. The interaction strength between particles was set to $\epsilon = 100k_{\text{B}}T$, where k_{B} is the Boltzmann constant and T is the temperature. The length scale of the interaction potential, r_0 , is related to the Lennard-Jones parametrization by $r_0 = 2^{1/6}\sigma_{LJ}$ and represents the particle diameter. It was also shown that the particles obey overdamped Langevin dynamics without hydrodynamic interactions and therefore the

equation of motion for each particles is,

$$\gamma \dot{\mathbf{r}}_i = \mathbf{F}_i^{\text{WCA}} + \tilde{\mathbf{f}}_i + \gamma v(\mathbf{r}_i) \hat{\mathbf{e}}_i, \quad (5.2)$$

$$\dot{\hat{\mathbf{e}}}_i = \tilde{\mathbf{\Gamma}}_i. \quad (5.3)$$

Here, $\dot{\mathbf{r}}_i$ is the velocity of particle i and γ is the friction constant related to the diffusion constant D_0 of a single particle in the fluid by the Einstein relation $\gamma = k_B T / D_0$, where k_B is the Boltzmann constant. The interparticle force, $\mathbf{F}_i^{\text{WCA}}$, is the negative gradient of the total potential U^{tot} with respect to the coordinates of particle i . The particles experience a random stochastic force $\tilde{\mathbf{f}}_i$, due to the solvent they are in, which was simulated by a Gaussian distribution that is delta correlated in time, and has a variance of $2D_0\gamma^2$. The last term, $v(\mathbf{r}_i)\hat{\mathbf{e}}_i$, is responsible for the active motion of the particle. This force acts along the orientation $\hat{\mathbf{e}}_i$ of the particle with position dependent magnitude $v(\mathbf{r}_i)$. In this work, the magnitude of the active force, $v(\mathbf{r}_i)$, is either a constant v or 0, depending on whether the particle is in the illuminated (red) or unilluminated (blue) region in Figure 5.1. The orientation vector of each particle, $\hat{\mathbf{e}}_i = \{\cos \theta, \sin \theta\}$, performs an independent random walk in θ , such that $\langle \theta(t)\theta(0) \rangle = 2D_r\delta(t)$ and the rotational diffusion constant of the particles obeys the no slip relation, $D_r = 3D_0/r_0^2$.

In all of our simulations, we set $k_B T$, γ , and r_0 to unity. As a result, the bare diffusion constant of the system, D_0 is also unity. We considered a system of 3600 particles with a global (*i.e.* across both zones) number density of $\rho_g = 0.2886$. The system was subject to periodic boundary conditions and the simulations were initialized by arranging the particles in a hexagonal lattice that melts quickly due to the fact that the packing fraction of the system is far from crystallization. The simulation cell had width $L_x = 120r_0$ and a height $L_y = L_x\sqrt{3}/2$. The effect of the interparticle interactions and the phase behavior of the WCA potential can be accounted for by taking advantage of the fact that, for sufficiently high interaction strengths, the WCA potential can be mapped onto a hardsphere system with diameter $\sigma_{\text{HS}}^2 = 2B_2/\pi$ where B_2 is the second Virial coefficient of the WCA potential [73]. For $\epsilon = 100k_B T$, $\sigma_{\text{HS}}^2 = 0.9861r_0$ and therefore, the hard sphere packing fraction of the system is $\eta_g = \rho_g \pi \sigma_{\text{HS}}^2 / 4 = 0.2205$, similar to experiment. The systems were equilibrated for 5×10^6 timesteps and data were then gathered from trajectories of length 1.25×10^7 . We shall consider the three different types of passive zones embedded in an active fluid, as depicted in the top row of Figure 5.1 and analyze the ensuing nonequilibrium stationary state. The passive patches consist of a halfplane of width $L_x/2$, a circle with radius $24r_0$, and six semicircular stripes of width $6r_0$ and outer radius $24r_0$.

In order to compare our results with a more conventional system, and to separate the effect of the activity from a simple increase in the mean square displacement (MSD), we also simulated a system of Brownian particles with position dependent diffusion

constant. Conceptually, this corresponds to a setup in which Brownian particles are subjected to a temperature difference. Typically, the activity of a particle is quantified by its Péclet number, $Pe = r_0 v / D_0$ and in experiments values of about $Pe = 200$ were achieved. The highest activities used in this study correspond to $Pe = 150$ and are therefore well within experimental accessibility. To compare the system with an activity difference to the system with a temperature difference, consider the MSD of a solitary active particle as reported in Refs. [7, 78],

$$\langle \Delta \mathbf{r}^2 \rangle = 4D_0 t + \frac{v^2}{2D_r^2} (e^{-2D_r t} + 2D_r t - 1). \quad (5.4)$$

For short times, this MSD can be approximated by $\langle \Delta \mathbf{r}^2 \rangle = 4D_0 t + (vt)^2$, which is independent of the rotational diffusion constant. On the other hand, in the long time limit the MSD converges to $\langle \Delta \mathbf{r}^2 \rangle = 4 [D_0 + v^2/(4D_r)] t - v^2/(2D_r^2)$. One can therefore associate, for different levels of activity v , a long time diffusion constant $D_A = D_0 + v^2/4D_r$, which is the slope of the mean squared displacement for large t . In the following, the activity of the particles will be given in terms of D_A .

Before we proceed, consider the even simpler reference model of an ideal gas of either active particles or Brownian diffusers whose mobility is position dependent using the half plane geometry in the first column of Figure 5.1. Since the particles in the red region are more mobile than in the blue region, there is a net flow of particles from the more mobile region to the passive region. The system arrives at a stationary state when the density difference has compensated the imposed mobility difference. The stationary state of this system obeys the Smoluchowski equation [76],

$$\Delta [D(x, y)P(x, y, \theta)] + D_r \frac{\partial^2 P(x, y, \theta)}{\partial \theta^2} - \hat{\mathbf{e}} \nabla [v(x, y)P(x, y, \theta)] = 0, \quad (5.5)$$

where Δ and ∇ are the Laplace and gradient operators, respectively. If one imposes a diffusivity difference with no activity, $v(x, y) = 0$, then the equation decouples in position and orientation angle and one obtains the condition $P(x, y)D(x, y) = c$ where c is an integration constant. For a step-like diffusion field $D(x, y)$, one therefore obtains a step-like density profile, and the ratio of the densities grows linearly with the ratio of the diffusion constants. For the active patch system, $D(x, y) = D_0$, and $v(x, y)$ is a step function that is v in the left half of the simulation cell and 0 in the right half. The Smoluchowski equation for an ideal gas of active particles was solved approximately by Löwen *et al.* [77] and predicts that the ratio of the densities in the active and passive zones scale with the square root of the ratio of the long time diffusion constants D_A/D_0 . In Figure 5.2, we plotted the ratio of the densities, $\rho_0/\rho_{H/A}$, in the blue and red regions as a function of the ratio of the respective diffusion constants, $D_{H/A}/D_0$. The brown triangles represent the data obtained from simulations of a diffusivity difference, the

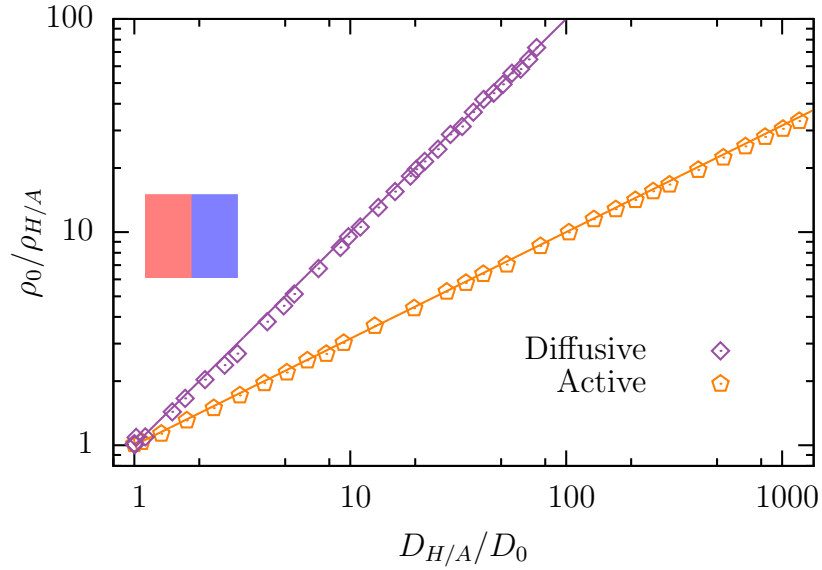


Figure 5.2 Density difference of an ideal gas of particles for a halfplane geometry as a function of an imposed mobility difference that is either due to a larger diffusion constant, D_H/D_0 , (triangles) or activity, D_A/D_0 (pentagons).

orange pentagons were obtained from a system with an activity difference, and the lines are the theoretical predictions of the Smoluchowski equation that correspond well with the simulation data.

Having established the behavior of the ideal gas, we now consider the same boundary for particles with interparticle interactions. Henceforth, in order to account for the excluded volume due to the interparticle interactions, the density differences will be measured in terms of packing fractions $\eta = \rho\pi\sigma_{HS}^2/4$. In Figure 5.3, we have plotted the packing fraction in each zone as a function of the mobility difference for the half plane geometry. For constant particle number, $\eta_{\text{red}}A_{\text{red}} + \eta_{\text{blue}}A_{\text{blue}} = \eta_g A_g$, where A_{red} , A_{blue} , and A_g are the areas of the red, blue and entire system, respectively. In the inset, the ratio of the packing fractions is drawn on a double logarithmic plot and the black lines correspond to the ideal gas solution. Evidently, the interparticle interactions reduce the efficacy with which a mobility difference induces a density difference. In the supplemental video V1, the dynamics of a system with a diffusivity difference is compared to the dynamics of a system with an activity difference. The values of D_H and D_A were chosen such that the density difference for the two systems is the same. Both in the video and in the bottom left panel of Figure 5.1, one can see that the active particles form characteristic dynamical clusters for high levels of activity.

In the case of the half plane, η_g was such that in the limit of very large diffusion differences the density in the blue zone becomes $2\eta_g$, which is below the crystallization of hard disks. Next we consider a passive circle in an active bath (middle column of Figure 5.1). The was chosen to be small enough, so that it was possible to obtain such

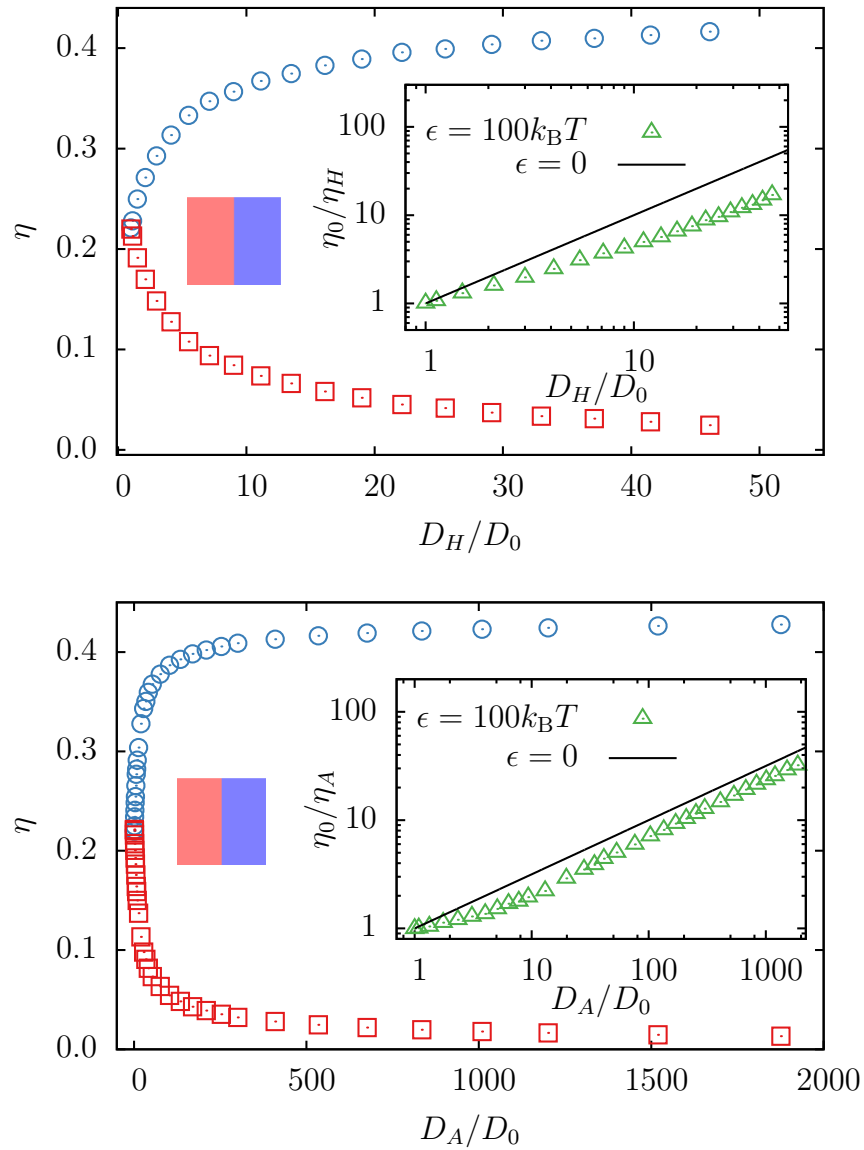


Figure 5.3 Density differences of the half-plane geometry as a function of a temperature difference D_H/D_0 (top) and activity difference D_A/D_0 (bottom). The ratio of the densities is plotted in the insets on a double logarithmic plot and the black lines represent the ideal gas solutions.

large packing fractions in the passive zone that crystallization occurred. One might expect that as the density in the passive zone increases due to rising activity differences, that the mobility of the particles in the passive zone decreases until a freezing transition takes place, after which the particles oscillate about their lattice sites. The hypothesis is confirmed in Figure 5.4, where we plotted the effective diffusion constants of the particles in the active (red squares) and passive (blue circles) particles as a function of the local packing fraction. The long time diffusion constants were obtained by dividing our trajectories into short segments in which no particles cross from one zone to another and then computing the mean square displacements of the particles in each zone separately.

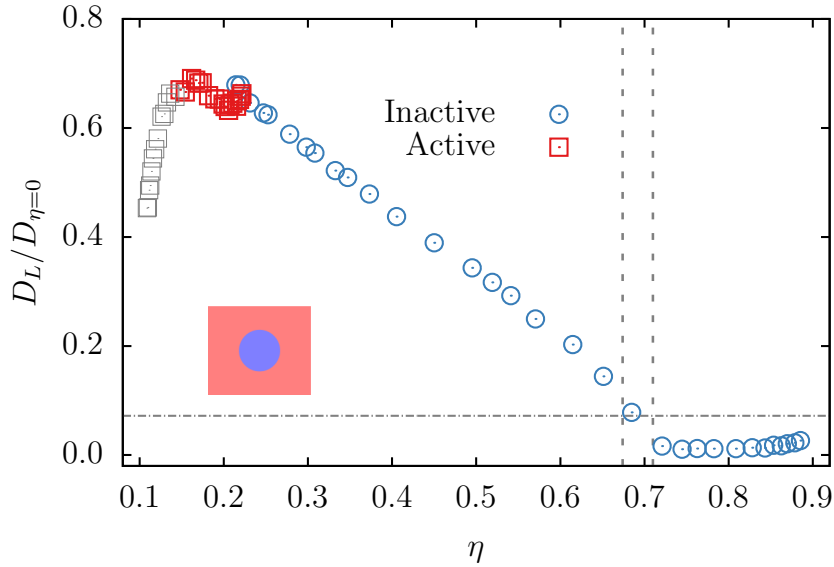


Figure 5.4 Effective diffusion constant of the particles in the active and inactive zones as a function of the packing fraction. The vertical gray lines are the freezing and melting packing fractions for hard disks and the horizontal gray line is the value of the effective diffusion constant at the freezing transition. The data points in gray are the effective diffusion constants of the active particles after crystallization has taken place in the passive zone.

By rescaling the long time diffusion constants of the particles by the diffusion constant in absence of collisions, $D_L/D_{\eta=0}$, we obtained the effective diffusion constant plotted on the y -axis in Figure 5.4. For a dilute system, this ratio is unity by construction. Two independent criteria were used to determine whether crystallization took place and are indicated by the horizontal and vertical lines in the plot. The vertical gray lines represent the packing fraction at which the freezing (left vertical line, $\eta = 0.674$) and the melting transition takes place (right vertical line $\eta = 0.71$) based on the simulation work of Trokhymchuk *et al.* [94] and the density region between these two points correspond to a fluid/solid coexistence regime. The second criterion used to identify the freezing transition is due to Löwen *et al.* [93], who found that the effective diffusion constant of hard disks has a value of $D_L/D_{\eta=0} = 0.072$ (horizontal gray line) at the freezing transition. The data and the two criteria are consistent with a freezing transition. For the particles in the active zone, the measurement of the effective diffusion constant is strongly affected by the presence of the passive zone. For small activity differences, the effective diffusion constant in the red zone increases because the density in that zone decreases. However, for large activity differences, after crystallization has taken place, the active particles travel so quickly that a collision with the boundary of the passive zone is very likely. After such a collision has taken place, the active particles continue to swim in the same direction and persists at the boundary of the crystalline domain. The active particles therefore aggregate at the boundary of the crystalline zone when the

swimming speed is large. This has the effect of reducing the mean square displacement of the particles and therefore one observes a reduction in the effective diffusion constant (gray squares in Figure 5.4) of the particles in the active zone. In the supplemental video V2 and in the snapshot of the configuration in Figure 5.1, one can observe the aggregation of active particles at the boundary of the crystalline domain that leads to this reduction in the effective diffusion constant. To illustrate the aggregation of the active particles at the boundary of the passive zone we plotted the density of the particles as a function of the distance from the center of the circle both for the diffusivity (top) and activity (bottom) induced crystallization in Figure 5.5. For small mobility differences the density in each region is essentially homogenous. For intermediate mobility differences, there is a depletion zone of passive particles (blue data points) that has a width of one particle diameter σ_{HS} that is due to the interactions between particles close to the boundary (we did not observe similar depletion zones in simulations of an ideal gas). For mobility differences crystallization takes place in both cases and the regularly spaced peaks in the density profile of the passive zone reflects the periodic are one particle diameter in width and are a signature of the crystalline domain. The biggest difference between the diffusive and the active case is seen in the density profile outside of the passive circle, after crystallization has taken place. The shoulder in the density profile in the bottom of Figure 5.5 for $D_A = 1876 D_0$ is two particle diameters wide and is a clear indication of the aggregation of active particles at the boundary. The active particles that aggregate at the boundary of the crystalline domain shear and rotate it stochastically, reminiscent of the dynamical clusters formed by bacteria [95]. Finally, since the circular domain is incommensurate with a hexagonal crystal, one regularly observes the appearance of defect and dislocations that travel through the domain and they appear more frequently in the density range of the fluid-solid coexistence. This type of activity difference induced crystallization can easily be achieved experimentally, providing an easy opportunity to study defect and dislocation migration in arbitrarily shaped, hexagonally ordered, domains. Similar simulations and results have been recently published by Magiera *et al.* [96].

The final active patch that we will consider consists of six semicircular passive stripes embedded in an active fluid, as shown in the third column of Figure 5.1. The significant difference between this type of patch and the previous two is that each semicircle has a convex and a concave side, reminiscent of the passive zones considered by Cates *et al.* [97]. It was our expectation that the due to this asymmetry, there would be a net flow of particles and indeed the measurement of the mean velocity of the center of mass in the x direction (*i.e.* from left to right in Figure 5.1), v_{cm} , show that in the presence of asymmetric active patches, the system establishes a net flow. In Figure 5.6, we plotted v_{cm} for a gas of active particles both in the absence and in the presence of interparticle interactions. The plot shows that in both cases, there is a flow and the error bars

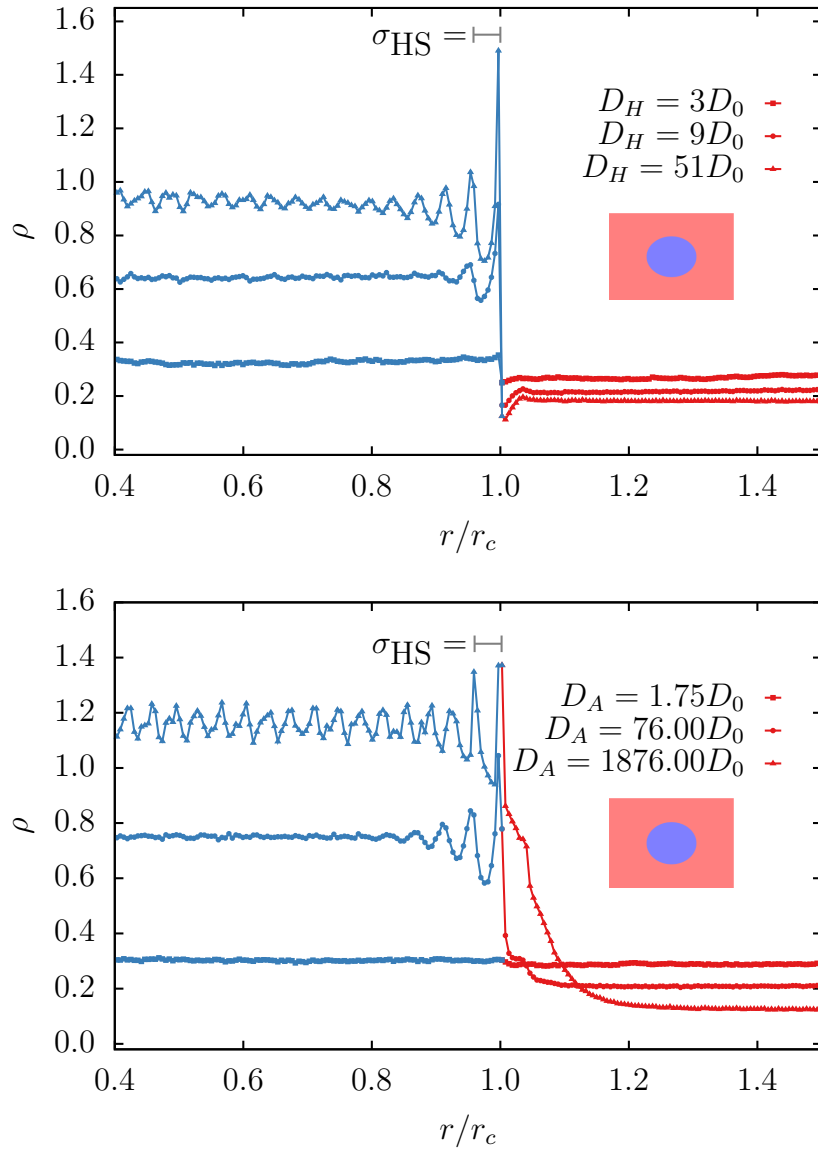


Figure 5.5 Local particle density, $\rho(r)$, as a function of the distance from the center of the circular passive zone, r , for low, intermediate, and high mobility differences. The x axis has been rescaled by the radius of the passive zone $r_c = 24r_0$ and the data points in blue correspond to the density inside the passive circle and the red data points represent the density outside of the passive zone. The effective hardsphere diameter σ_{HS} has been drawn as a guide to the eye.

represent the variance of the observed velocity for 6 independent simulation runs. In the inset of Figure 5.6, we plotted the progression of the center of mass in the x and the y direction as a function of time for a large activity difference and with interparticle interactions. One can see in the inset, that the flow in the x is significantly larger than the typical fluctuation in the y direction and the irregularity in the displacement time graph indicates that the flow is stochastic. The comparison between the ideal active gas and the active hard spheres show that there are two mechanisms at play. In the ideal gas case, the particles enter and exit the passive zone independently from each

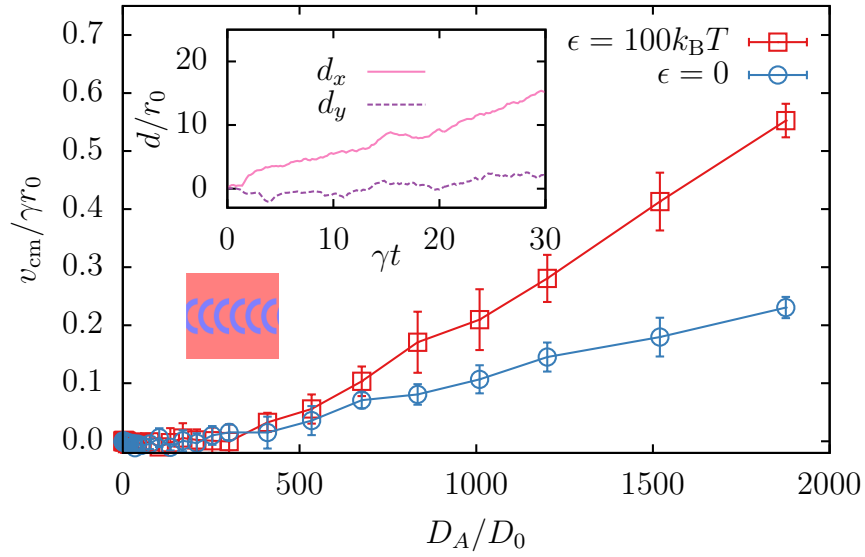


Figure 5.6 Mean velocity of the center of mass of the system as a function of the activity difference. Inset: mean displacement of the center of mass of the hard sphere system in the x - and y -direction for $D_A = 1876 D_0$, as a function of time.

other and therefore the flow is the result of the interaction of the active particles and the geometry of the passive zone. When the interparticle interactions are switched on, the mean velocities are initially the same because the density in the passive zone is comparatively small, so exclusion effects are negligible. As the activity increases, so too does the crowding within the passive zone until, eventually, particles trying to enter the passive zone are kept at the boundary. Therefore, in addition to the geometrically induced flow of the ideal gas case, we observe active particles that are sliding along the convex half of the boundary with greater ease than along the concave half, as can be seen in the supplemental video V3, where a comparison is made between active particles with and without interparticle interactions using the same levels of activity. In the limit of very large activities, the particles in the passive zone crystallize and the ensuing domain acts like a solid boundary, similar to the passive tracers in an active bath that were studied by Caccutto *et al.* [98]. In this final case, the analogy between the system with an activity difference and a temperature difference breaks down completely, since simulations of the latter did not exhibit any flow.

Although a quantitative theory predicting the response of an activity difference is still pending, we have found that particles naturally tend to aggregate in regions of low activity. We examined the behavior of a system of strongly repulsive spheres with an activity difference, and found that they act qualitatively similar to a system with a nonuniform temperature profile, provided that the mobility differences are symmetric. Furthermore, it is possible to induce crystallization if the global density and activity difference are appropriately chosen and the shape of the crystalline domains is entirely

determined by the geometry of the activity field. Mismatches in the curvature of the passive zones, tend to induce a flow in the system, unlike the purely diffusive case.

It is worth noting that this work considers one of the most primitive realizations of active matter. Although one might extend the model to include more complex potentials or include hydrodynamics, the most dramatic change is likely to occur if the shape of the active particles is altered. Active rods, for example, tend to form nematic and smectic phases, but it is unclear how a smectically ordered domain is affected by a bath of active rods swimming around it, especially if the shape of the domain is circular or elliptical. It is likely that a system of rods with an activity difference is a new class of liquid crystal. Finally, it is also expected that inserting particles of arbitrary composition and shape in this system will result in them being pushed into regions of low activity.

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Appendix A

Derivation of the effective potential acting on stiff monolayers driven over commensurate substrates

A.1 Summary

In the following, we shall present a detailed account of our analytical calculation of the total mean force exerted on the center of mass of the colloidal monolayer in the harmonic approximation. For the convenience of those readers that are not anxious to delve into all the details of these derivations, we provide the following quick summary.

For large stiffness of the colloidal layer, i.e., large repulsive Yukawa interaction strength, we regard the build-up phase of a hopping wave as given by a field of small displacement vectors $\mathbf{u}_l$ of the colloidal particles from their ideal lattice sites $\mathbf{R}_l$ on top of a collective rigid translation R of this lattice in the direction x of the external driving force. We argue that during this build-up phase, the monolayer is in quasistatic equilibrium, such that statistical mechanics can be employed to compute the thermally averaged mean force acting on its center of mass. Furthermore, as we assume that the displacements $\mathbf{u}_l$ will be small in relation to the ideal lattice constant of the monolayer, it is justified to employ a harmonic approximation for this task. For periodic boundary conditions, the canonical distribution of the resulting harmonic Hamiltonian factorizes into independent “phonon” contributions, whose energy contributions and covariances are completely determined by the underlying dynamical matrix. It is then straightforward to calculate the averaged covariances σ_{xx} , σ_{xy} and σ_{yy} of the displacement components. To harmonic accuracy, it turns out that these covariances also fully determine the effective total force acting on

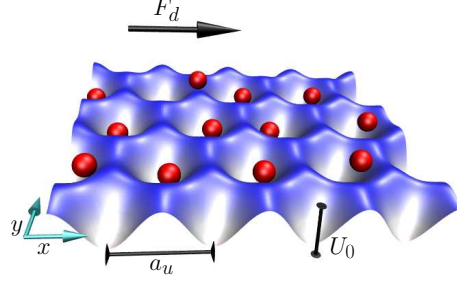


Figure A.1 Schematic view of the potential landscape (A.12). The direction of the external driving force F_d is indicated by an arrow.

the center of mass of the monolayer. The final section provides some useful formulas for a practical numerical implementation.

A.2 Equation of motion of the colloidal monolayer

For overdamped Langevin dynamics, the equations of motion of an N -particle system can be written as

$$\gamma \frac{d\mathbf{r}_p}{dt} = \mathbf{F}_p(\vec{\mathbf{r}}) \quad (\text{A.1})$$

for $p = 0, 1, \dots, N-1$, where the total force

$$\mathbf{F}_p(\vec{\mathbf{r}}) = \sum_{p' \neq p} \mathbf{F}_{\text{yuk}}(\mathbf{r}_{p'} - \mathbf{r}_p) + \mathbf{F}_{\text{sub}}(\mathbf{r}_p) + \mathbf{F}_d + \mathbf{F}_{\text{rand}}^p \quad (\text{A.2})$$

acting on particle p is the sum of the Yukawa forces exerted by all other particles, the substrate force, the external homogeneous force and the Langevin random force, and $\vec{\mathbf{r}}$ is the formal $2N$ -dimensional vector built from all position vectors $\mathbf{r}_0, \dots, \mathbf{r}_{N-1}$. The substrate force, $\mathbf{F}_{\text{sub}}(\mathbf{r}_p)$, acting on particle i is the negative gradient of the externally applied potential, $U_{\text{sub}}(\mathbf{r}_p) = -(U_0/9)\{3 + 2[\cos(\mathbf{k}_1\mathbf{r}_p) + \cos(\mathbf{k}_2\mathbf{r}_p) + \cos(\mathbf{k}_3\mathbf{r}_p)]\}$, where the $\mathbf{k}$ -vectors are chosen from the set $\mathbf{k}_i/\|\mathbf{k}\| \in \{(\sqrt{3}/2, 1/2), (-\sqrt{3}/2, 1/2), (0, 1)\}$ with norm $\|\mathbf{k}\| = 4\pi/a\sqrt{3}$. This choice of $\mathbf{k}$ -vectors produces a hexagonal arrangement of potential wells with a lattice constant a and lattice vectors $\mathbf{g} \in \{(a, 0), (a/2, \sqrt{3}a/2)\}$. For a schematic view of the system see Fig. A.1.

If we perform an average over all N particles,

$$\begin{aligned} \frac{\gamma}{N} \sum_{p=0}^{N-1} \frac{d\mathbf{r}_p}{dt} &= \frac{1}{N} \sum_{p=0}^{N-1} \sum_{p' \neq p} \mathbf{F}_{\text{yuk}}(\mathbf{r}_{p'} - \mathbf{r}_p) \\ &\quad + \frac{1}{N} \sum_{p=0}^{N-1} [\mathbf{F}_{\text{sub}}(\mathbf{r}_p) + \mathbf{F}_d + \mathbf{F}_{\text{rand}}^p] \end{aligned} \quad (\text{A.3})$$

the Yukawa forces cancel in a pairwise manner due to Newton's third law, and we are left with a *single* equation of motion

$$\gamma \frac{d\mathbf{R}}{dt} = \frac{1}{N} \sum_{p=0}^{N-1} \mathbf{F}_{\text{sub}}(\mathbf{r}_p) + \mathbf{F}_d + \frac{1}{N} \sum_{p=0}^{N-1} \mathbf{F}_{\text{rand}}^p \quad (\text{A.4})$$

for the center of mass

$$\mathbf{R} = \frac{1}{N} \sum_{p=0}^{N-1} \mathbf{r}_p \quad (\text{A.5})$$

of the overdamped monolayer, which resembles that of a single overdamped Brownian diffuser in an external potential. The final term in Eqn. (A.4) is the sum of all of the random forces acting on the system. It is Gaussian distributed and has a variance of $2k_B T / \sqrt{N}$.

Although solving the coupled equations of motion for N interacting particles analytically without any approximation is an impossible task, our claim is that there exist a series of approximations that simplify Equation A.4 sufficiently to obtain accurate theoretical predictions. The motion of the center of mass of the monolayer is governed by the constant driving force, the average substrate force, and the total random Langevin force acting on the monolayer. Although the last two forces are trivial, the first, is not. The difficulty lies in the fact that the substrate force acting on the center of mass when it is located at $\mathbf{R}$, $\bar{\mathbf{F}}(\mathbf{R}) = N^{-1} \sum_{p=0}^{N-1} \mathbf{F}_{\text{sub}}(\mathbf{r}_p, \mathbf{R})$ depends on the positions of every particle in the system, which in turn depend upon their mutual interactions as well as the external forces acting on them. We therefore propose a statistical treatment of the problem. If one imagines a trajectory consisting of an arbitrarily large number of buildup phases, then the mean velocity of the monolayer is,

$$\gamma \left\langle \frac{d\mathbf{R}}{dt} \right\rangle = \langle \bar{\mathbf{F}} \rangle_{\mathbf{R}} + \mathbf{F}_d, \quad (\text{A.6})$$

where the average, $\langle \dots \rangle$, is taken over multiple build up phases. So far, no tangible simplification to the system has been made, other than that the motion of the center of mass of the monolayer during the build up phase can be thought of as the motion of a single particle exposed to an effective substrate force $\mathbf{F}_{\text{eff}}(\mathbf{R}) = \langle \bar{\mathbf{F}} \rangle_{\mathbf{R}}$. If the distribution of $\bar{\mathbf{F}}$ is narrow, then it can be replaced by its mean value $\mathbf{F}_{\text{eff}}(\mathbf{R})$ in the equation of motion for the center of mass,

$$\gamma \frac{d\mathbf{R}}{dt} = \mathbf{F}_{\text{eff}}(\mathbf{R}) + \mathbf{F}_d + \bar{\mathbf{F}}_{\text{random}}, \quad (\text{A.7})$$

we justify this simplification *a posteriori* in the supplement S2.

A.3 Quasistatic equilibrium

In order to learn something about the functional form of $\mathbf{F}_{\text{eff}}(\mathbf{R})$, we make two assumptions. First, we assume that configurations from different buildup phases with the same $\mathbf{R}$ are not only statistically independent, but are drawn from the equilibrium distribution of the system. We justify this assumption from the fact that the monolayer travels along the substrate walls very slowly. The second assumption we make is that the interparticle potential is so large that the total potential energy of the system can be approximated by a second order Taylor expansion.

The first assumption is that the monolayer, during the buildup phase, moves so slowly that for a given value of $\mathbf{R}$, the probability of observing a microstate obeys a Boltzmann distribution,

$$d\rho(\vec{\mathbf{r}}, \mathbf{R}) = d^N \mathbf{r} \delta \left(N^{-1} \sum_i \mathbf{r}_i - \mathbf{R} \right) e^{-\beta U_{\text{tot}}(\vec{\mathbf{r}})}, \quad (\text{A.8})$$

where $\beta = 1/k_{\text{B}}T$. In order to obtain analytical results, the needs to be simplified further. The second assumption, which is the topic of the next section, will serve this purpose.

A.4 The harmonic crystal

In the absence of any external potential, colloidal particles that interact with one another via a screened repulsive Yukawa potential U_{yuk} tend to form a triangular lattice. In the present work, the particle density is chosen precisely in such a way that this lattice is commensurate with the hexagonal structure of the underlying substrate. The total potential energy of the resulting system is

$$\begin{aligned} U_{\text{tot}} = & \frac{1}{2} \sum_{p \neq p'}^{N-1} U_{\text{yuk}}(|\mathbf{r}_p - \mathbf{r}_{p'}|) + \sum_{p=0}^{N-1} U_{\text{sub}}(\mathbf{r}_p) \\ & - F_d \sum_{p=0}^{N-1} r_p^x. \end{aligned} \quad (\text{A.9})$$

In order to calculate the Boltzmann average $F^{\text{eff}}(R) = \mathbf{F}_{\text{eff}}^x(R)$ defined by this potential analytically further approximations must be made. Among the most successful and widely used in solid state physics is the harmonic approximation, which rests on the idea that particles residing in a crystal lattice will mostly perform only small amplitude vibrations around their equilibrium positions, such that a second order Taylor expansion

of the potential with respect to the deviations from these equilibrium positions will already capture most of the relevant physics. By imposing periodic boundary conditions (PBCs) and exploiting the resulting translational invariance of the system, the dynamical problem can then be reformulated in terms of certain collective *phonon* variables defined in Fourier space, which are completely decoupled from each other. At least to a good approximation, the whole procedure thus maps the original problem to a non-interacting one, an enormous simplification for dynamical calculations as well as for doing statistical mechanics.

For our present purposes, the instantaneous position $\mathbf{r}_p$ of an individual colloid will be disassembled as follows. Let $\mathbf{R} = (R, 0)$ denote an arbitrary vector, which we will use to describe the global translation of the triangular colloid layer parallel to the direction of the driving force. $\mathbf{R}_p$ denotes the position of the lattice site that the p^{th} particle is assigned to, and $\mathbf{u}_p$ denotes a small residual displacement of the particle with respect to the underlying lattice. Altogether, we then write

$$\mathbf{r}_p = \mathbf{R} + \mathbf{R}_p + \mathbf{u}_p. \quad (\text{A.10})$$

In terms of this parametrization

$$\begin{aligned} U_{\text{tot}} = & \frac{1}{2} \sum_{p' \neq p}^{N-1} U_{\text{yuk}}(|\mathbf{R}_p + \mathbf{u}_p - \mathbf{R}_{p'} - \mathbf{u}_{p'}|) + \sum_{p=0}^{N-1} U_{\text{sub}}(\mathbf{R} + \mathbf{R}_p + \mathbf{u}_p) - F_d \sum_{p=0}^{N-1} u_p^x \\ & - F_d \left(NR + \sum_{p=0}^{N-1} R_p^x \right). \end{aligned} \quad (\text{A.11})$$

Since the substrate potential is periodic in $\mathbf{R}_p$ and the Yukawa potential depends only on the relative distance between two particles, this simplifies to

$$\begin{aligned} U_{\text{tot}} = & \frac{1}{2} \sum_{p \neq p'}^{N-1} U_{\text{yuk}}(|\mathbf{R}_{pp'} + \mathbf{u}_p - \mathbf{u}_{p'}|) + \sum_{p=0}^{N-1} U_{\text{sub}}(\mathbf{R} + \mathbf{u}_p) \\ & - F_d \sum_{p=0}^{N-1} u_p^x - F_d \left(NR + \sum_{p=0}^{N-1} R_p^x \right), \end{aligned} \quad (\text{A.12})$$

where $\mathbf{R}_{pp'} = \mathbf{R}_{p'} - \mathbf{R}_p$ is the difference vector between lattice site p and p' .

In the high coupling limit, when the inter-particle interaction strength is large, the deviations $\mathbf{u}_p$ of the particle positions from the ideal lattice sites $\mathbf{R}_p$ are typically small,

so a second order Taylor expansion

$$\begin{aligned}
U_{\text{tot}} = & \frac{1}{2} \sum_{l,l'=0}^{N-1} \sum_{\mu,\nu} u_l^\mu \phi_{\mu\nu}^{ll'} u_{l'}^\nu + \frac{\pi}{a} F_{\text{max}} \sum_{l=0}^{N-1} \left\{ \cos \frac{2\pi R}{a} \left((u_l^x)^2 + \frac{1}{3} (u_l^y)^2 \right) + \frac{2}{3} (u_l^y)^2 \right\} \\
& + \left(F_{\text{max}} \sin \frac{2\pi R}{a} - F_d \right) \sum_{l=0}^{N-1} u_l^x + C(R, \{\mathbf{R}_p\}), \tag{A.13}
\end{aligned}$$

with respect to $\mathbf{u}_p$ may yield a good approximation to the total energy of the system. Unlike the particle induces p and p' , the indices l and l' denote *lattice site* induces that can be equal to each other in the double sum above, as can be seen in the definition of $\phi_{\mu\nu}^{ll'}$,

$$\phi_{\mu\nu}^{ll'} = \frac{\partial^2}{\partial u_l^\mu \partial u_{l'}^\nu} \sum_{p \neq p'}^{N-1} U_{\text{yuk}}(|\mathbf{u}_p - \mathbf{u}_{p'} + R_{pp'}|) |_{\mathbf{u}_p = \mathbf{u}_{p'} = \mathbf{0}}. \tag{A.14}$$

$C(R, \{\mathbf{R}_p\})$ is the value of the total potential when all $\mathbf{u}_l$ are zero, and $F_{\text{max}} = 24\pi k_B T/a$ is the maximum force the substrate is able to exert. Using the definition of the substrate potential, the 2×2 matrix of the second derivatives of the external substrate

$$\psi(R) = \frac{2\pi F_{\text{max}}}{3a} \begin{pmatrix} 3 \cos \frac{2\pi R}{a} & 0 \\ 0 & \cos \frac{2\pi R}{a} + 2 \end{pmatrix} \tag{A.15}$$

turns out to be diagonal when evaluated at $\mathbf{R} = (R, 0)$. Collecting linear and quadratic terms, we rewrite (A.13) in the compact form

$$\begin{aligned}
U_{\text{tot}} = & \frac{1}{2} \sum_{l,l'=0}^{N-1} \sum_{\mu,\nu} u_l^\mu \bar{\mathbb{D}}_{\mu\nu}^{ll'}(R) u_{l'}^\nu \\
& + \left(F_{\text{max}} \sin \frac{2\pi R}{a} - F_d \right) \sum_{l=0}^{N-1} u_l^x + C(R, \{\mathbf{R}_l\}) \tag{A.16}
\end{aligned}$$

where we have set

$$\bar{\mathbb{D}}_{\mu\nu}^{ll'}(R) \equiv \phi_{\mu\nu}^{ll'} + \delta^{ll'} \psi_{\mu\nu}(R). \tag{A.17}$$

Translational invariance allows to further reduce

$$\frac{1}{2} \sum_{l,l'=0}^{N-1} \sum_{\mu,\nu} u_l^\mu \bar{\mathbb{D}}_{\mu\nu}^{ll'}(R) u_{l'}^\nu = \frac{N}{2} \sum_{l=0}^{N-1} \sum_{\mu,\nu} u_l^\mu \bar{\mathbb{D}}_{\mu\nu}^{l0}(R) u_0^\nu \tag{A.18}$$

Within equilibrium statistical mechanics, our N -particle system is described by the unnormalized probability measure

$$d\rho(\vec{\mathbf{u}}) = d^N \mathbf{u} e^{-\beta U_{\text{tot}}(\vec{\mathbf{u}})}, \quad (\text{A.19})$$

where $\beta = 1/k_B T$, $\vec{\mathbf{u}}$ is the formal $2N$ -dimensional vector built from all displacement vectors $\mathbf{u}_0, \dots, \mathbf{u}_{N-1}$, and $d^N \mathbf{u} = \prod_{l=0}^{N-1} d^2 u_l$. Imposing the constraint that the sum of all the u_l^x be zero amounts to considering the restricted probability measure

$$\begin{aligned} d\rho(\vec{\mathbf{u}}|R) &= d^N \mathbf{u} \delta\left(\sum_l u_l^x\right) e^{-\beta U_{\text{tot}}(\vec{\mathbf{u}})} \\ &= d^N \mathbf{u} \delta\left(\sum_l u_l^x\right) \exp\left\{-\frac{\beta}{2} \vec{\mathbf{u}}^T \tilde{\mathbb{D}} \vec{\mathbf{u}}\right\}. \end{aligned} \quad (\text{A.20})$$

Ensemble averages of observables $A(\{\mathbf{u}_l\})$ are given by

$$\langle A(\vec{\mathbf{u}}) \rangle|_R = \frac{1}{Z(R)} \int d^N \mathbf{u} A(\vec{\mathbf{u}}) d\rho(\vec{\mathbf{u}}|R), \quad (\text{A.21})$$

whose normalization $Z(R) = \int d^N \mathbf{u} d\rho(\vec{\mathbf{u}}|R)$ may be called a restricted canonical partition function.

A.5 Discrete Fourier Transform

In contrast to (A.19), the measure (A.20) is *not* a simple Gaussian one, as the variables $\mathbf{u}_l$ are not independent due to the delta constraint imposed. However, we now show that by virtue of a discrete Fourier transform, (A.20) can actually be factorized into simple components, which clears the way for analytical calculations.

As a prerequisite, we introduce the first Brillouin zone $\mathcal{B}$ of the underlying hexagonal lattice with a total number of $N = N_x N_y$ particles. For simplicity, we choose $N_x = N_y = \sqrt{N}$, and furthermore, without loss of generality, we assume N_x and N_y to be even numbers. By definition, $\mathcal{B}$ consists of all cosets represented by wave vectors that are commensurate with the imposed boundary conditions, two such representatives considered as equivalent if they differ by an arbitrary reciprocal vector. For periodic boundary conditions in both the x and y direction, the allowed representatives are

$$q_x = \frac{2\pi}{a} \frac{n_x}{N_x}, \quad q_y = \frac{4\pi}{\sqrt{3}a} \frac{n_y}{N_y}, \quad (\text{A.22})$$

where n_x and n_y are integers. A convenient choice of a set of representative wave vectors for $\mathcal{B}$ is provided by the Voronoi cell around a point in reciprocal space (see Fig. A.2).

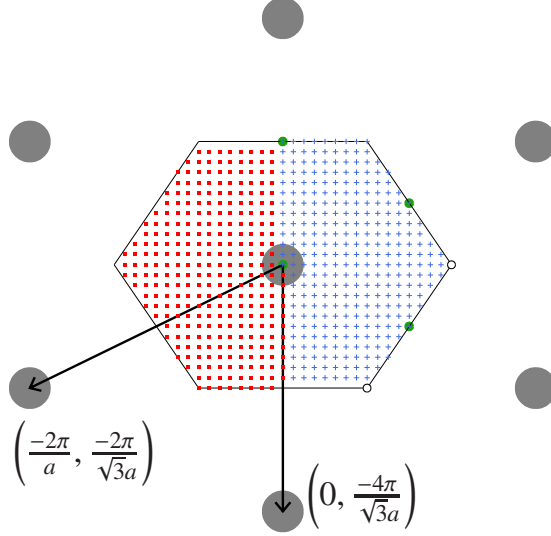


Figure A.2 $\mathbf{q}$ -vectors (points) for a 24×24 hexagonal monolayer. The gray dots are lattice sites belonging to the reciprocal lattice of the original lattice. The four green circles mark the special points defined in Eqn. (A.37) and belong to $\mathcal{B}_0$. The blue crosses belong to $\mathcal{B}_+$ and the red boxes belong to the set $\mathcal{B}_-$. The empty circles at two of the vertices of the small hexagon are points that must be omitted from to avoid double counting, since they differ from already included vertex points by a reciprocal lattice vector.

Now we can introduce the discrete Fourier transform

$$u_l^\mu = \frac{1}{\sqrt{N}} \sum_{\mathbf{q} \in \mathcal{B}} \tilde{u}^\mu(\mathbf{q}) e^{i\mathbf{q}\mathbf{R}_l}. \quad (\text{A.23})$$

We have

$$\sum_{l=0}^{N-1} u_l^x = \frac{1}{\sqrt{N}} \sum_{\mathbf{q} \in \mathcal{B}} \tilde{u}^x(\mathbf{q}) \underbrace{\sum_l e^{i\mathbf{q}\mathbf{R}_l}}_{N\delta(\mathbf{q}, \mathbf{0})} = \sqrt{N} \tilde{u}^x(\mathbf{0}). \quad (\text{A.24})$$

Furthermore

$$\begin{aligned} & \frac{1}{2} \sum_{l, l'=0}^{N-1} \sum_{\mu, \nu} u_l^\mu \bar{\mathbb{D}}_{\mu\nu}^{ll'}(R) u_{l'}^\nu \\ &= \frac{1}{2N} \sum_{l, l'=0}^{N-1} \sum_{\mathbf{q}, \mathbf{q}'} \sum_{\mu, \nu} \tilde{u}^\mu(\mathbf{q}) e^{i\mathbf{q}\mathbf{R}_l} \bar{\mathbb{D}}_{\mu\nu}^{ll'}(R) \tilde{u}^\nu(\mathbf{q}') e^{i\mathbf{q}'\mathbf{R}_{l'}} \\ &= \frac{1}{2} \sum_{\mathbf{q}, \mathbf{q}'} \sum_{\mu, \nu} \tilde{u}^\mu(\mathbf{q}) \underbrace{\left[\frac{1}{N} \sum_{l, l'=0}^{N-1} e^{i\mathbf{q}\mathbf{R}_l} \bar{\mathbb{D}}_{\mu\nu}^{ll'}(R) e^{i\mathbf{q}'\mathbf{R}_{l'}} \right]}_{\equiv \bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, \mathbf{q}', R)} \tilde{u}^\nu(\mathbf{q}'). \end{aligned} \quad (\text{A.25})$$

Using translational invariance, we write

$$\begin{aligned}
\bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, \mathbf{q}', R) &= \frac{1}{N} \sum_{l, l'=0}^{N-1} e^{i\mathbf{q}\mathbf{R}_l} \bar{\mathbb{D}}_{\mu\nu}^{l-l', 0}(R) e^{i\mathbf{q}'\mathbf{R}_{l'}} \\
&= \frac{1}{N} \sum_{l, l'=0}^{N-1} e^{i\mathbf{q}(\mathbf{R}_l + \mathbf{R}_{l'})} \bar{\mathbb{D}}_{\mu\nu}^{l, 0}(R) e^{i\mathbf{q}'\mathbf{R}_{l'}} \\
&= \frac{1}{N} \sum_{l=0}^{N-1} e^{i\mathbf{q}\mathbf{R}_l} \bar{\mathbb{D}}_{\mu\nu}^{l, 0}(R) \underbrace{\sum_{l'=0}^{N-1} e^{i(\mathbf{q}+\mathbf{q}')\mathbf{R}_{l'}}}_{=N\delta_{\mathbf{q}+\mathbf{q}', \mathbf{0}}}
\end{aligned} \tag{A.26}$$

This suggests we define

$$\bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, R) := \sum_{l=0}^{N-1} \bar{\mathbb{D}}_{\mu\nu}^{l, 0}(R) e^{i\mathbf{q}\mathbf{R}_l}. \tag{A.27}$$

Additional symmetry of $\bar{\mathbb{D}}_{\mu\nu}^{ll'}(R)$ under exchange of $l \leftrightarrow l'$ also yields $\bar{\mathbb{D}}_{\mu\nu}^{l, 0}(R) = \bar{\mathbb{D}}_{\mu\nu}^{0, l}(R) = \bar{\mathbb{D}}_{\mu\nu}^{-l, 0}(R)$, and thus

$$[\bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, R)]^* = \sum_{l=0}^{N-1} \bar{\mathbb{D}}_{\mu\nu}^{-l, 0}(R) e^{-i\mathbf{q}\mathbf{R}_l} = \bar{\mathbb{D}}_{\mu\nu}(\pm\mathbf{q}, R), \tag{A.28}$$

i.e., $\bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, R) \in \mathbb{R}$, a fact that could also be anticipated from the manifest reality of

$$\frac{1}{2} \sum_{l=0, l'}^{N-1} \sum_{\mu, \nu} u_l^\mu \bar{\mathbb{D}}_{\mu\nu}^{ll'}(R) u_{l'}^\nu \tag{A.29}$$

$$\begin{aligned}
&= \frac{1}{2} \sum_{\mathbf{q}, \mathbf{q}' \in \mathcal{B}} \sum_{\mu, \nu} \tilde{u}^\mu(\mathbf{q}) \bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}', R) \delta_{\mathbf{q}+\mathbf{q}', \mathbf{0}} \tilde{u}^\nu(\mathbf{q}') \\
&= \frac{1}{2} \sum_{\mathbf{q} \in \mathcal{B}} \sum_{\mu, \nu} \tilde{u}^\mu(-\mathbf{q}) \bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, R) \tilde{u}^\nu(\mathbf{q}).
\end{aligned} \tag{A.30}$$

From the definition of the discrete Fourier transform (A.23) it follows immediately that since the components u_l^μ are real-valued, their Fourier amplitudes must obey

$$\tilde{u}^\mu(-\mathbf{q}) = [\tilde{u}^\mu(\mathbf{q})]^*. \tag{A.31}$$

Thus, if we introduce the complex two-dimensional vector

$$\tilde{\mathbf{u}}(\mathbf{q}) = \begin{pmatrix} \tilde{u}^x(\mathbf{q}) \\ \tilde{u}^y(\mathbf{q}) \end{pmatrix} \tag{A.32}$$

and its adjoint

$$\tilde{\mathbf{u}}^+(\mathbf{q}) = \begin{pmatrix} \tilde{u}^x(-\mathbf{q}) & \tilde{u}^y(-\mathbf{q}) \end{pmatrix}, \quad (\text{A.33})$$

we obtain the compact formula

$$\frac{1}{2} \sum_{l=1,l'}^N \sum_{\mu,\nu} u_l^\mu \bar{\mathbb{D}}_{\mu\nu}^{ll'}(R) u_{l'}^\nu = \frac{1}{2} \sum_{\mathbf{q} \in \mathcal{B}} \tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \bar{\mathbb{D}}(\mathbf{q}, R) \cdot \tilde{\mathbf{u}}(\mathbf{q}). \quad (\text{A.34})$$

The delta function constraint in the measure (A.20) is rewritten as

$$\delta(\tilde{u}^x(\mathbf{0})) = \delta\left(\sqrt{N}\tilde{u}^x(\mathbf{0})\right) = \frac{\delta(\tilde{u}^x(\mathbf{0}))}{\sqrt{N}}. \quad (\text{A.35})$$

Finally, we need to express the volume element $d^N \mathbf{u}$ appearing in the measure (A.20) in terms of the Fourier amplitudes (A.23). Taking the real part of (A.23), we obtain

$$\begin{aligned} u_l^\mu &= \frac{1}{\sqrt{N}} \sum_{\mathbf{q} \in \mathcal{B}} [\Re \tilde{u}^\mu(\mathbf{q}) + i \Im \tilde{u}^\mu(\mathbf{q})] [\cos(\mathbf{q}\mathbf{R}_l) + i \sin(\mathbf{q}\mathbf{R}_l)] \\ &= \sum_{\mathbf{q}} \left[\frac{\cos(\mathbf{q}\mathbf{R}_l)}{\sqrt{N}} \Re \tilde{u}^\mu(\mathbf{q}) - \frac{\sin(\mathbf{q}\mathbf{R}_l)}{\sqrt{N}} \Im \tilde{u}^\mu(\mathbf{q}) \right], \end{aligned} \quad (\text{A.36})$$

which is reminiscent of an orthogonal transformation, except that we seem to have doubled the number of variables. To avoid such a double-counting, note that the reality condition $\tilde{u}^\mu(-\mathbf{q}) = [\tilde{u}^\mu(\mathbf{q})]^*$ implies that $\Re \tilde{u}^\mu(-\mathbf{q}) = \Re \tilde{u}^\mu(\mathbf{q})$ and $\Im \tilde{u}^\mu(-\mathbf{q}) = -\Im \tilde{u}^\mu(\mathbf{q})$, are linearly dependent. The latter condition requires care. By definition, two vectors of the first Brillouin zone are regarded as equal if they differ by a reciprocal lattice vector $\mathbf{G}$. But this implies the possibility that $\mathbf{q}$ and $-\mathbf{q}$ can well be representatives of the same coset of $\mathcal{B}$. A trivial case is the zero vector $\mathbf{Q}_0 = \mathbf{0}$, but in our hexagonal lattice this applies to three more so-called “special high-symmetry vectors”. We shall denote the subset of $\mathcal{B}$ that holds these four vectors

$$\begin{aligned} \mathbf{Q}_0 &= (0, 0), & \mathbf{Q}_1 &= \left(0, \frac{2\pi}{\sqrt{3}a}\right), \\ \mathbf{Q}_2 &= \left(\frac{\pi}{a}, \frac{\pi}{\sqrt{3}a}\right), & \mathbf{Q}_3 &= \left(\frac{\pi}{a}, -\frac{\pi}{\sqrt{3}a}\right), \end{aligned} \quad (\text{A.37})$$

as $\mathcal{B}_0$. Of course, for $\mathbf{Q} \in \mathcal{B}_0$ the Fourier amplitudes $\tilde{\mathbf{u}}(\mathbf{Q})$ must be real as can be directly understood from observing that $\mathbf{Q} \cdot \mathbf{R}_l$ is an integer multiple of π . The residual $N - 4$ elements of the Brillouin zone are given by distinct pairs of representatives $(\mathbf{q}, -\mathbf{q})$ and can now be organized into two subsets $\mathcal{B}_\pm$ of positive and negative “parity” by any

convenient definition. This leads to a partition

$$\mathcal{B} = \mathcal{B}_0 \cup \mathcal{B}_+ \cup \mathcal{B}_- \quad (\text{A.38})$$

of the total Brillouin zone. In Fig. A.2, we have illustrated such a partition of $\mathcal{B}$ into subsets with zero (green circled points), positive (blue points) and negative (red points) parity. In this notation, (A.36) may be rewritten in a more concise way as

$$\begin{aligned} u_l^\mu &= \sum_{\pi(\mathbf{Q}) \in \mathcal{B}_0} \frac{(\pm 1)}{\sqrt{N}} \tilde{u}^\mu(\mathbf{Q}) \\ &+ \sum_{\mathbf{q} \in \mathcal{B}_+} \left[\frac{2 \cos(\mathbf{q} \mathbf{R}_l)}{\sqrt{N}} \Re \tilde{u}^\mu(\mathbf{q}) - \frac{2 \sin(\mathbf{q} \mathbf{R}_l)}{\sqrt{N}} \Im \tilde{u}^\mu(\mathbf{q}) \right]. \end{aligned} \quad (\text{A.39})$$

As this construction reveals, a new set of $2N = 2[4 + 2 \times (N - 4)/2]$ independent real variables is given by

$$\tilde{u}^\mu(\mathbf{Q}), \quad \mathbf{Q} \in \mathcal{B}_0, \quad \mu = x, y \quad (\text{A.40})$$

$$\Re \tilde{u}^\mu(\mathbf{q}), \Im \tilde{u}^\mu(\mathbf{q}), \quad \mathbf{q} \in \mathcal{B}_+, \quad \mu = x, y. \quad (\text{A.41})$$

In terms of these variables, we can rewrite

$$\begin{aligned} \frac{1}{2} \sum_{\mathbf{q} \in \mathcal{B}} \tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \bar{\mathbb{D}}(\mathbf{q}, R) \cdot \tilde{\mathbf{u}}(\mathbf{q}) &= \frac{1}{2} \sum_{\mathbf{Q} \in \mathcal{B}_0} \tilde{u}^\mu(\mathbf{Q}) \bar{\mathbb{D}}_{\mu\nu}(\mathbf{Q}, R) \tilde{u}^\nu(\mathbf{Q}) + \sum_{\mathbf{q} \in \mathcal{B}_+} [\tilde{u}^\mu(\mathbf{q})]^* \bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, R) u^\nu(\mathbf{q}) \\ &= \frac{1}{2} \sum_{\mathbf{Q} \in \mathcal{B}_0} \tilde{u}^\mu(\mathbf{Q}) \bar{\mathbb{D}}_{\mu\nu}(\mathbf{Q}, R) \tilde{u}^\nu(\mathbf{Q}) \\ &+ \sum_{\mathbf{q} \in \mathcal{B}_+} [\Re \tilde{u}^\mu(\mathbf{q}) - i [\Im \tilde{u}^\mu(\mathbf{q})]^*] \bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, R) [\Re u^\nu(\mathbf{q}) + i \Im u^\nu(\mathbf{q})]. \end{aligned} \quad (\text{A.42})$$

In the last line the imaginary contributions must cancel identically for the sum to be real, and we obtain

$$\begin{aligned} \frac{1}{2} \sum_{\mathbf{q} \in \mathcal{B}} \tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \bar{\mathbb{D}}(\mathbf{q}, R) \cdot \tilde{\mathbf{u}}(\mathbf{q}) &= \frac{1}{2} \sum_{\mathbf{Q} \in \mathcal{B}_0} \bar{\mathbb{D}}_{\mu\nu}(\mathbf{Q}, R) \tilde{u}^\mu(\mathbf{Q}) \tilde{u}^\nu(\mathbf{Q}) + \sum_{\mathbf{q} \in \mathcal{B}_+} \bar{\mathbb{D}}_{\mu\nu}(\mathbf{q}, R) [\Re \tilde{u}^\mu(\mathbf{q}) \Re u^\nu(\mathbf{q}) + \Im \tilde{u}^\mu(\mathbf{q}) \Im u^\nu(\mathbf{q})] \\ &= \frac{1}{2} \sum_{\mathbf{Q} \in \mathcal{B}_0} \tilde{\mathbf{u}}^T(\mathbf{Q}) \bar{\mathbb{D}}(\mathbf{Q}, R) \tilde{\mathbf{u}}(\mathbf{Q}) + \sum_{\mathbf{q} \in \mathcal{B}_+} \Re \tilde{\mathbf{u}}^T(\mathbf{q}) \bar{\mathbb{D}}(\mathbf{q}, R) \Re \tilde{\mathbf{u}}(\mathbf{q}) + \sum_{\mathbf{q} \in \mathcal{B}_+} \Im \tilde{\mathbf{u}}^T(\mathbf{q}) \bar{\mathbb{D}}(\mathbf{q}, R) \Im \tilde{\mathbf{u}}(\mathbf{q}). \end{aligned} \quad (\text{A.43})$$

As to the volume element in the measure (A.20), we have

$$d^N \mathbf{u} = J \cdot \prod_{\mathbf{Q} \in \mathcal{B}_0} d^2 \tilde{u}(\mathbf{Q}) \cdot \prod_{\mathbf{q} \in \mathcal{B}_+} d^2 \Re \tilde{u}(\mathbf{Q}) d^2 \Im \tilde{u}(\mathbf{Q}) \quad (\text{A.44})$$

where J is the determinant of the Jacobi matrix of the discrete Fourier transformation, and an additional factor arises from the delta function constraint, since

$$\delta(\tilde{u}^x(\mathbf{0})) = \delta\left(\sqrt{N} \tilde{u}^x(\mathbf{0})\right) = \frac{\delta(\tilde{u}^x(\mathbf{0}))}{\sqrt{N}}. \quad (\text{A.45})$$

Writing down the unnormalized probability measure

$$d\tilde{\rho}(\{\tilde{\mathbf{u}}(\mathbf{q})\}|R) = \prod_{\mathbf{Q} \in \mathcal{B}_0} d^2 \tilde{u}(\mathbf{Q}) \cdot \prod_{\mathbf{q} \in \mathcal{B}_+} d^2 \Re \tilde{u}(\mathbf{q}) d^2 \Im \tilde{u}(\mathbf{q}) \cdot \delta(\tilde{u}^x(\mathbf{0})) e^{-\frac{\beta}{2} \sum_{\mathbf{q} \in \mathcal{B}} \tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \tilde{\mathbb{D}}(\mathbf{q}, R) \cdot \tilde{\mathbf{u}}(\mathbf{q})} \quad (\text{A.46})$$

which obviously factorizes into

$$d\tilde{\rho}(\{\tilde{\mathbf{u}}(\mathbf{q})\}|R) = \prod_{\mathbf{Q} \in \mathcal{B}_0} d\tilde{\rho}^{(0)}(\tilde{\mathbf{u}}(\mathbf{Q})|R) \cdot \prod_{\mathbf{q} \in \mathcal{B}_+} d\tilde{\rho}^{(R)}(\tilde{\mathbf{u}}(\mathbf{q})|R) \cdot d\tilde{\rho}^{(I)}(\tilde{\mathbf{u}}(\mathbf{q})|R) \quad (\text{A.47})$$

as promised, where

$$d\tilde{\rho}(\tilde{\mathbf{u}}(\mathbf{0})|R) = d^2 \tilde{u}(\mathbf{0}) \delta(\tilde{u}^x(\mathbf{0})) e^{-\frac{\beta}{2} \tilde{\mathbf{u}}^T(\mathbf{0}) \tilde{\mathbb{D}}(\mathbf{0}, R) \tilde{\mathbf{u}}(\mathbf{0})}, \quad (\text{A.48})$$

$$d\tilde{\rho}^{(0)}(\tilde{\mathbf{u}}(\mathbf{Q})|R) = d^2 \tilde{u}(\mathbf{Q}) e^{-\frac{\beta}{2} \tilde{\mathbf{u}}^T(\mathbf{Q}) \tilde{\mathbb{D}}(\mathbf{Q}, R) \tilde{\mathbf{u}}(\mathbf{Q})}, \quad \mathbf{Q} \in \mathcal{B}_0 \quad (\text{A.49})$$

$$d\tilde{\rho}^{(R)}(\tilde{\mathbf{u}}(\mathbf{q})|R) = d^2 \Re \tilde{u}(\mathbf{q}) e^{-\beta \Re \tilde{\mathbf{u}}^T(\mathbf{q}) \tilde{\mathbb{D}}(\mathbf{q}, R) \Re \tilde{\mathbf{u}}(\mathbf{q})}, \quad \mathbf{q} \in \mathcal{B}_+ \quad (\text{A.50})$$

$$d\tilde{\rho}^{(I)}(\tilde{\mathbf{u}}(\mathbf{q})|R) = d^2 \Im \tilde{u}(\mathbf{q}) e^{-\beta \Im \tilde{\mathbf{u}}^T(\mathbf{q}) \tilde{\mathbb{D}}(\mathbf{q}, R) \Im \tilde{\mathbf{u}}(\mathbf{q})}, \quad \mathbf{q} \in \mathcal{B}_+. \quad (\text{A.51})$$

A.6 Explicit Formulae

Having fully characterized the coordinate transformation that transforms the dynamical matrix of the harmonic crystal into Fourier space, we now present the explicit form of $\tilde{\mathbb{D}}(\mathbf{q})$. To this end, we make use of the abbreviations,

$$C_x(\mathbf{q}) = \cos\left(\frac{a}{2} q_x\right), \quad S_x(\mathbf{q}) = \sin\left(\frac{a}{2} q_x\right), \quad (\text{A.52})$$

$$C_y(\mathbf{q}) = \cos\left(\frac{a\sqrt{3}}{2} q_y\right), \quad S_y(\mathbf{q}) = \sin\left(\frac{a\sqrt{3}}{2} q_y\right), \quad (\text{A.53})$$

$$f = \frac{2\pi F_{\max}}{3a}, \quad g = \frac{1}{r} U'_{\text{yuk}}(r)|_{r=a}, \quad (\text{A.54})$$

$$h = \left[U''_{\text{yuk}}(r) - \frac{1}{r} U'_{\text{yuk}}(r) \right]_{r=a}. \quad (\text{A.55})$$

The quantities are the result of performing a Fourier transformation on a hexagonal lattice and the quantities in Eqn. (A.55) are the coupling parameters of the particles in the monolayer. These parameters depend upon the first and second derivatives of the substrate potential and the inter-particle interactions. For the Yukawa potential,

$$g = -\frac{\tilde{\Gamma}e^{-\kappa a}}{a^3}[1 + \kappa a] = -\frac{\Gamma}{a^2}(1 + \kappa a), \quad (\text{A.56})$$

$$h = \frac{\tilde{\Gamma}e^{-\kappa a}}{a^3}[3 + 3\kappa a + (\kappa a)^2] = \frac{\Gamma}{a^2}[3 + 3\kappa a + (\kappa a)^2]. \quad (\text{A.57})$$

As in previous work, the coupling strength between two colloids, Γ , is the potential energy between two particles that are separated by one lattice constant. Thus $\Gamma := \tilde{\Gamma} \frac{e^{-\kappa a}}{a}$. We note that for all allowed values of Γ , a , and κ , the absolute value of g is strictly larger than that of h . Furthermore, since these expressions are not quadratic in a , we do not express them in terms of the density of the system, $\rho^{-1} = N^{-1} \frac{\sqrt{3}}{2} a^2$, although that might be a more natural definition.

In terms of this parametrization, we find that

$$\bar{\mathbb{D}}(\mathbf{q}) = \begin{pmatrix} D_0(\mathbf{q}, R) + D_{11}(\mathbf{q}, R) & D_{12}(\mathbf{q}, R) \\ D_{12}(\mathbf{q}, R) & D_0(\mathbf{q}, R) \end{pmatrix} \quad (\text{A.58})$$

where

$$D_0(\mathbf{q}, R) = 4g [2 - C_x^2(\mathbf{q}) - C_x(\mathbf{q})C_y(\mathbf{q})] + 3h [1 - C_x(\mathbf{q})C_y(\mathbf{q})] + f [2 + \cos(2\pi R/a)] \quad (\text{A.59})$$

$$D_{11}(\mathbf{q}, R) = 2h [1 + C_x(\mathbf{q})C_y(\mathbf{q}) - 2C_x^2(\mathbf{q})] - 4f \sin^2(\pi R/a) \quad (\text{A.60})$$

$$D_{12}(\mathbf{q}, R) = \sqrt{3} h S_x(\mathbf{q}) S_y(\mathbf{q}). \quad (\text{A.61})$$

The results we shall derive below will involve the elements of the inverse matrix

$$\bar{\mathbb{G}}(\mathbf{q}, R) := [\beta \bar{\mathbb{D}}(\mathbf{q}, R)]^{-1} = \frac{1}{\beta \det \bar{\mathbb{D}}(\mathbf{q})} \begin{pmatrix} D_0(\mathbf{q}) & -D_{12}(\mathbf{q}) \\ -D_{12}(\mathbf{q}) & D_0(\mathbf{q}) + D_{11}(\mathbf{q}) \end{pmatrix}. \quad (\text{A.62})$$

A.6.1 Calculation of covariances

We now look at the expectation values

$$\sigma_{\mu\nu}(R) = \left\langle \frac{1}{N} \sum_l u_l^\mu u_l^\nu \right\rangle \bigg|_R. \quad (\text{A.63})$$

Since

$$\frac{1}{N} \sum_{l=0}^{N-1} u_l^\mu u_l^\nu = \frac{1}{N^2} \sum_{\mathbf{q}, \mathbf{q}'} \tilde{u}^\mu(\mathbf{q}) \tilde{u}^\nu(\mathbf{q}') \underbrace{\sum_l e^{i(\mathbf{q}+\mathbf{q}')\mathbf{R}_l}}_{N\delta(\mathbf{q}+\mathbf{q}', \mathbf{0})} = \sum_{\mathbf{q}} \tilde{u}^\mu(\mathbf{q}) \tilde{u}^\nu(-\mathbf{q}), \quad (\text{A.64})$$

this reduces to

$$\begin{aligned} \sigma_{\mu\nu}(R) &= \frac{1}{N} \sum_{\mathbf{q}} \langle \tilde{u}^\mu(\mathbf{q}) \tilde{u}^\nu(-\mathbf{q}) \rangle \big|_R \\ &= \frac{1}{N} \sum_{\mathbf{Q} \in \mathcal{B}_0} \langle \tilde{u}^\mu(\mathbf{Q}) \tilde{u}^\nu(\mathbf{Q}) \rangle \big|_R + \frac{1}{N} \sum_{\mathbf{q} \in \mathcal{B}_+} \langle \tilde{u}^\mu(\mathbf{q}) \tilde{u}^\nu(-\mathbf{q}) \rangle \big|_R + \frac{1}{N} \sum_{\mathbf{q} \in \mathcal{B}_-} \langle \tilde{u}^\mu(\mathbf{q}) \tilde{u}^\nu(-\mathbf{q}) \rangle \big|_R \\ &= \frac{1}{N} \sum_{\mathbf{Q} \in \mathcal{B}_0} \langle \tilde{u}^\mu(\mathbf{Q}) \tilde{u}^\nu(\mathbf{Q}) \rangle \big|_R + \frac{2}{N} \sum_{\mathbf{q} \in \mathcal{B}_+} \Re \langle \tilde{u}^\mu(\mathbf{q}) \tilde{u}^\nu(-\mathbf{q}) \rangle \big|_R \\ &= \frac{1}{N} \sum_{\mathbf{Q} \in \mathcal{B}_0} \langle \tilde{u}^\mu(\mathbf{Q}) \tilde{u}^\nu(\mathbf{Q}) \rangle \big|_R + \frac{2}{N} \sum_{\mathbf{q} \in \mathcal{B}_+} \langle \Re \tilde{u}^\mu(\mathbf{q}) \Re \tilde{u}^\nu(\mathbf{q}) + \Im \tilde{u}^\mu(\mathbf{q}) \Im \tilde{u}^\nu(\mathbf{q}) \rangle \big|_R. \quad (\text{A.65}) \end{aligned}$$

To compute these expectation values, we use the well-known formula

$$\frac{\int d^D x x_i x_j e^{-\frac{1}{2} \mathbf{x}^T \mathbf{A} \mathbf{x}}}{\int d^D x e^{-\frac{1}{2} \mathbf{x}^T \mathbf{A} \mathbf{x}}} = A_{ij}^{-1} \quad (\text{A.66})$$

valid for Gaussian integrals, which yields

$$\langle \tilde{u}^\mu(\mathbf{Q}) \tilde{u}^\nu(\mathbf{Q}) \rangle \big|_R = \bar{\mathbb{G}}^{\mu\nu}(\mathbf{Q}, R), \quad \mathbf{Q} \in \mathcal{B}_0 \quad (\text{A.67})$$

$$\langle \Re \tilde{u}^\mu(\mathbf{q}) \Re \tilde{u}^\nu(\mathbf{q}) \rangle \big|_R = \langle \Im \tilde{u}^\mu(\mathbf{q}) \Im \tilde{u}^\nu(\mathbf{q}) \rangle \big|_R = \frac{\bar{\mathbb{G}}^{\mu\nu}(\mathbf{q}, R)}{2}, \quad \mathbf{q} \in \mathcal{B}_+ \quad (\text{A.68})$$

Due to the presence of the delta constraint, special care has to be taken for $\mathbf{Q} = \mathbf{0}$. Since the matrix $\bar{\mathbb{D}}(\mathbf{q}, R)$ is actually diagonal for $\mathbf{q} = \mathbf{0}$ (cf. Eqn. (A.61) below), we have

$$\langle \tilde{u}^\mu(\mathbf{0}) \tilde{u}^\nu(\mathbf{0}) \rangle \big|_R = \begin{cases} 1/\beta \bar{\mathbb{D}}^{yy}(\mathbf{0}, R), & \mu = \nu = y \\ 0, & \text{else} \end{cases} = \begin{cases} \bar{\mathbb{G}}^{yy}(\mathbf{0}, R), & \mu = \nu = y \\ 0, & \text{else} \end{cases} \quad (\text{A.69})$$

In summary, we have shown that

$$\begin{aligned} \sigma_{yy}(R) &= \frac{1}{N} \sum_{\mathbf{Q} \in \mathcal{B}_0} \bar{\mathbb{G}}^{yy}(\mathbf{Q}, R) + \frac{2}{N} \sum_{\mathbf{q} \in \mathcal{B}_+} \frac{\bar{\mathbb{G}}^{yy}(\mathbf{q}, R)}{2} + \frac{2}{N} \sum_{\mathbf{q} \in \mathcal{B}_-} \frac{\bar{\mathbb{G}}^{yy}(\mathbf{q}, R)}{2} \\ &= \frac{1}{N} \sum_{\mathbf{Q} \in \mathcal{B}_0} \bar{\mathbb{G}}^{yy}(\mathbf{Q}, R) + \frac{2}{N} \sum_{\mathbf{q} \in \mathcal{B}_+} \bar{\mathbb{G}}^{yy}(\mathbf{q}, R) \\ &= \frac{1}{N} \sum_{\mathbf{Q} \in \mathcal{B}_0} \bar{\mathbb{G}}^{yy}(\mathbf{Q}, R) + \frac{1}{N} \sum_{\mathbf{q} \in \mathcal{B}_+} \bar{\mathbb{G}}^{yy}(\mathbf{q}, R) + \sum_{\mathbf{q} \in \mathcal{B}_-} \bar{\mathbb{G}}^{yy}(\mathbf{q}, R) \quad (\text{A.70}) \end{aligned}$$

i.e.,

$$\sigma_{yy}(R) = \frac{1}{N} \sum_{\mathbf{q} \in \mathcal{B}} \bar{\mathbb{G}}^{yy}(\mathbf{q}, R). \quad (\text{A.71})$$

In the same way we can show that

$$\sigma_{xx}(R) = \frac{1}{N} \sum_{\mathbf{q} \in \mathcal{B} \setminus \{\mathbf{0}\}} \bar{\mathbb{G}}^{xx}(\mathbf{q}, R). \quad (\text{A.72})$$

and also

$$\sigma_{xy}(R) = \frac{1}{N} \sum_{\mathbf{q} \in \mathcal{B} \setminus \{\mathbf{0}\}} \bar{\mathbb{G}}^{xy}(\mathbf{q}, R). \quad (\text{A.73})$$

However, a closer examination reveals that due to the special structure of the matrix elements

$$\bar{\mathbb{G}}^{xy}(\mathbf{q}, R) = -\frac{\sqrt{3}hS_x(\mathbf{q})S_y(\mathbf{q})}{\beta \det \bar{\mathbb{D}}(\mathbf{q})} \quad (\text{A.74})$$

the sum above actually vanishes. To show this, we first observe that the contributions of all $\mathbf{q}$ -vectors of the types $(q_x, 0)$, $(0, q_y)$ and $(q_x, 2\pi/a\sqrt{3})$ are zero because of the vanishing product of the sine functions $S_x(\mathbf{q})S_y(\mathbf{q})$. The remaining contributions from the wavevectors $\mathbf{q} \in \mathcal{B}_+ \cup \mathcal{B}_-$ can be organized into pairs of (q_x, q_y) , $(q_x, -q_y)$, whose contributions mutually cancel (note that the numerator of (A.74) assumes different signs for the vectors in each couple, whereas the sign of the determinant in the denominator remains the same). In retrospect, the fact that the cross correlation $\sigma_{xy}(R)$ is found to be zero within the harmonic approximation could have been anticipated from the fact that the dynamical matrix is constructed from (i) the sum of a pairwise central potential and (ii) a substrate potential with vanishing mixed second derivatives along the path $(R, 0)$.

In summary we have the covariances

$$\sigma_{xx}(R) = \frac{1}{N} \sum_{\mathbf{q} \in \mathcal{B} \setminus \{\mathbf{0}\}} \bar{\mathbb{G}}^{xx}(\mathbf{q}, R) \quad (\text{A.75})$$

$$\sigma_{yy}(R) = \frac{1}{N} \sum_{\mathbf{q} \in \mathcal{B}} \bar{\mathbb{G}}^{yy}(\mathbf{q}, R) \quad (\text{A.76})$$

$$\sigma_{xy}(R) = 0 \quad (\text{A.77})$$

which are the results announced in Eqn. (8) of the main paper.

A.7 Mean force

By symmetry, the only nonzero component of the total force acting on the center of mass of the monolayer (A.7) located at $\mathbf{R} = (R, 0)$ is along the x -direction. Before averaging, this component of is

$$F^{\text{eff}}(R) = \frac{F_{\text{max}}}{N} \sum_{l=0}^{N-1} \sin[k_x(u_l^x + R)] \cos(k_y u_l^y). \quad (\text{A.78})$$

Here $k_x = 2\pi/a$ and $k_y = 2\pi/a\sqrt{3}$. Using the trigonometric identity $\sin(x + y) = \sin x \cos y + \cos x \sin y$, we rewrite this as

$$\begin{aligned} F^{\text{eff}}(R) &= \frac{F_{\text{max}}}{N} \cos(k_x R) \sum_{l=0}^{N-1} \sin(k_x u_l^x) \cos(k_y u_l^y) + \frac{F_{\text{max}}}{N} \sin(k_x R) \sum_{l=0}^{N-1} \cos(k_x u_l^x) \cos(k_y u_l^y) \\ &= \frac{F_{\text{max}}}{N} \cos(k_x R) \sum_{l=0}^{N-1} \frac{e^{ik_x u_l^x} - e^{-ik_x u_l^x}}{2i} \frac{e^{ik_y u_l^y} + e^{-ik_y u_l^y}}{2} \\ &\quad + \frac{F_{\text{max}}}{N} \sin(k_x R) \sum_{l=0}^{N-1} \frac{e^{ik_x u_l^x} + e^{-ik_x u_l^x}}{2} \frac{e^{ik_y u_l^y} + e^{-ik_y u_l^y}}{2} \\ &= \frac{F_{\text{max}} \cos(k_x R)}{4i} \frac{1}{N} \sum_{l=0}^{N-1} \left[e^{i(k_x u_l^x + k_y u_l^y)} + e^{i(k_x u_l^x - k_y u_l^y)} - e^{i(-k_x u_l^x + k_y u_l^y)} - e^{-i(k_x u_l^x + k_y u_l^y)} \right] \\ &\quad + \frac{F_{\text{max}} \sin(k_x R)}{4} \frac{1}{N} \sum_{l=0}^{N-1} \left[e^{i(k_x u_l^x + k_y u_l^y)} + e^{i(k_x u_l^x - k_y u_l^y)} + e^{i(-k_x u_l^x + k_y u_l^y)} + e^{-i(k_x u_l^x + k_y u_l^y)} \right]. \end{aligned}$$

If we define the four wave vectors

$$\mathbf{k}_{(\pm\pm)} := \begin{pmatrix} \pm k_x \\ \pm k_y \end{pmatrix}, \quad (\text{A.79})$$

we can restate this as

$$\begin{aligned} F^{\text{eff}}(R) &= \frac{F_{\text{max}} \cos(k_x R)}{4i} \frac{1}{N} \sum_{l=0}^{N-1} \left[e^{i\mathbf{k}_{(++)}\mathbf{u}_l} + e^{i\mathbf{k}_{(+-)}\mathbf{u}_l} - e^{i\mathbf{k}_{(-+)\mathbf{u}_l}} - e^{i\mathbf{k}_{(--)}\mathbf{u}_l} \right] \\ &\quad + \frac{F_{\text{max}} \sin(k_x R)}{4} \frac{1}{N} \sum_{l=0}^{N-1} \left[e^{i\mathbf{k}_{(++)}\mathbf{u}_l} + e^{i\mathbf{k}_{(+-)}\mathbf{u}_l} + e^{i\mathbf{k}_{(-+)\mathbf{u}_l}} + e^{i\mathbf{k}_{(--)}\mathbf{u}_l} \right]. \end{aligned} \quad (\text{A.80})$$

To compute the $F^{\text{eff}}(R)$ of the mean net force, we work out the averages

$$\langle e^{i\mathbf{k}_{(\pm\pm)}\mathbf{u}_l} \rangle|_R = \frac{\int d^N \mathbf{u} \delta(\sum u_m^x) \exp \left\{ -\frac{\beta}{2} \vec{\mathbf{u}}^T \tilde{\mathbb{D}} \vec{\mathbf{u}} + i \mathbf{u}_l^T \cdot \mathbf{k}_{(\pm\pm)} \right\}}{\int d^N \mathbf{u} \delta(\sum u_m^x) \exp \left\{ -\frac{\beta}{2} \vec{\mathbf{u}}^T \tilde{\mathbb{D}} \vec{\mathbf{u}} \right\}}. \quad (\text{A.81})$$

At this point it would be straightforward to follow the prescription of the preceding paragraph, i.e., we could rewrite the above integral in terms of the real variables $\Re \tilde{\mathbf{u}}(\mathbf{q})$, $\Im \tilde{\mathbf{u}}(\mathbf{q})$ and utilize the well-known Gaussian formula

$$\frac{\int d^D x e^{-\frac{1}{2} \mathbf{x}^T \mathbf{A} \mathbf{x} + \mathbf{b}^T \cdot \mathbf{x}}}{\int d^D x e^{-\frac{1}{2} \mathbf{x}^T \mathbf{A} \mathbf{x}}} = e^{\frac{1}{2} \sum_{ij} b_i A_{ij}^{-1} b_j}. \quad (\text{A.82})$$

An alternative evaluation proceeds by completion of squares in (A.81). First, slightly symmetrize this expression, rewriting it as

$$\langle e^{i \mathbf{k}_{(\pm\pm)} \cdot \mathbf{u}_l} \rangle_R = \frac{\int d^N \mathbf{u} \delta(\sum u_m^x) \exp \left\{ -\frac{\beta}{2} \tilde{\mathbf{u}}^T \tilde{\mathbb{D}} \tilde{\mathbf{u}} + \frac{i}{2} \mathbf{u}_l^T \cdot \mathbf{k}_{(\pm\pm)} + \frac{i}{2} \mathbf{k}_{(\pm\pm)}^T \cdot \mathbf{u}_l \right\}}{\int d^N \mathbf{u} \delta(\sum u_m^x) \exp \left\{ -\frac{\beta}{2} \tilde{\mathbf{u}}^T \tilde{\mathbb{D}} \tilde{\mathbf{u}} \right\}}. \quad (\text{A.83})$$

With the help of (A.23) and (A.34) this is restated as

$$\begin{aligned} & -\frac{\beta}{2} \tilde{\mathbf{u}}^T \beta \tilde{\mathbb{D}} \tilde{\mathbf{u}} + \frac{i}{2} \mathbf{u}_l^T \mathbf{k}_{(\pm\pm)} + \frac{i}{2} \mathbf{k}_{(\pm\pm)}^T \mathbf{u}_l \\ &= \sum_{\mathbf{q}} \left[\tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \frac{\beta \tilde{\mathbb{D}}(\mathbf{q}, R)}{2} \cdot \tilde{\mathbf{u}}(\mathbf{q}) + \frac{i}{2} \tilde{\mathbf{u}}^+(\mathbf{q}) \frac{\mathbf{k}_{(\pm\pm)} e^{-i \mathbf{q} \mathbf{R}_l}}{\sqrt{N}} + \frac{i}{2} \frac{\mathbf{k}_{(\pm\pm)} e^{i \mathbf{q} \mathbf{R}_l}}{\sqrt{N}} \tilde{\mathbf{u}}(\mathbf{q}) \right] \\ &= -\frac{1}{2} \sum_{\mathbf{q}} [\tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \beta \tilde{\mathbb{D}}(\mathbf{q}, R) \cdot \tilde{\mathbf{u}}(\mathbf{q}) - i \tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \bar{\mathbb{E}}(\mathbf{q}; l) - i \bar{\mathbb{E}}^+(\mathbf{q}; l) \cdot \tilde{\mathbf{u}}(\mathbf{q})], \end{aligned} \quad (\text{A.84})$$

where we have introduced the abbreviation

$$\bar{\mathbb{E}}(\mathbf{q}; l) := \frac{\mathbf{k}_{(\pm\pm)} e^{-i \mathbf{q} \mathbf{R}_l}}{\sqrt{N}}. \quad (\text{A.85})$$

For all nonzero $\mathbf{q}$ we now apply the identity

$$\mathbf{U}^+ \mathbf{D} \mathbf{U} + \mathbf{U}^+ \mathbf{V} + \mathbf{V}^+ \mathbf{U} = (\mathbf{U}^+ + \mathbf{V}^+ \mathbf{D}^{-1}) \mathbf{D} (\mathbf{U} + \mathbf{D}^{-1} \mathbf{V}) - \mathbf{V}^+ \mathbf{D}^{-1} \mathbf{V} \quad (\text{A.86})$$

in the form

$$\begin{aligned} & \tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \beta \tilde{\mathbb{D}}(\mathbf{q}, R) \cdot \tilde{\mathbf{u}}(\mathbf{q}) - i \bar{\mathbb{E}}^+(\mathbf{q}; l) \cdot \tilde{\mathbf{u}}(\mathbf{q}) - i \tilde{\mathbf{u}}^+(\mathbf{q}) \cdot \bar{\mathbb{E}}(\mathbf{q}; l) \\ &= [\tilde{\mathbf{u}}^+(\mathbf{q}) - i \bar{\mathbb{E}}^+(\mathbf{q}; l) \bar{\mathbb{G}}(\mathbf{q}, R)] \cdot \beta \tilde{\mathbb{D}}(\mathbf{q}, R) \cdot [\tilde{\mathbf{u}}(\mathbf{q}) - i \bar{\mathbb{G}}(\mathbf{q}, R) \bar{\mathbb{E}}(\mathbf{q}; l)] + \bar{\mathbb{E}}^+(\mathbf{q}; l) \cdot \bar{\mathbb{G}}(\mathbf{q}, R) \cdot \bar{\mathbb{E}}(\mathbf{q}; l) \\ &= [\tilde{\mathbf{u}}^+(\mathbf{q}) - i \bar{\mathbb{E}}^+(\mathbf{q}; l) \bar{\mathbb{G}}(\mathbf{q}, R)] \cdot \beta \tilde{\mathbb{D}}(\mathbf{q}, R) \cdot [\tilde{\mathbf{u}}(\mathbf{q}) - i \bar{\mathbb{G}}(\mathbf{q}, R) \bar{\mathbb{E}}(\mathbf{q}; l)] + \frac{1}{N} \mathbf{k}_{(\pm\pm)}^T \cdot \bar{\mathbb{G}}(\mathbf{q}, R) \cdot \mathbf{k}_{(\pm\pm)}. \end{aligned} \quad (\text{A.87})$$

Note that the l -dependence has disappeared from the last contribution. On the other hand, due to the delta function constraint, the $\mathbf{q} = \mathbf{0}$ contribution to the above sum

$$\tilde{\mathbf{u}}^+(\mathbf{0}) \cdot \beta \tilde{\mathbb{D}}(\mathbf{0}, R) \cdot \tilde{\mathbf{u}}(\mathbf{0}) - i \tilde{\mathbf{u}}^+(\mathbf{0}) \cdot \bar{\mathbb{E}}(\mathbf{0}; l) - i \bar{\mathbb{E}}^+(\mathbf{0}; l) \cdot \tilde{\mathbf{u}}(\mathbf{0}) \quad (\text{A.88})$$

actually reduces to

$$\beta \bar{\mathbb{D}}^{yy}(\mathbf{0}, R) (\tilde{u}^y(\mathbf{0}))^2 - 2i \tilde{u}^y(\mathbf{0}) \frac{k_{(\pm\pm)}^y}{\sqrt{N}}. \quad (\text{A.89})$$

Since $1/\beta \bar{\mathbb{D}}^{yy}(\mathbf{0}, R) = \bar{\mathbb{G}}^{yy}(\mathbf{0}, R)$ (cf. Eqn. (A.69)), we complete the squares as

$$\begin{aligned} \beta \bar{\mathbb{D}}^{yy}(\mathbf{0}, R) (\tilde{u}^y(\mathbf{0}))^2 - 2i \tilde{u}^y(\mathbf{0}) \frac{k_{(\pm\pm)}^y}{\sqrt{N}} &= \beta \bar{\mathbb{D}}^{yy}(\mathbf{0}, R) \left(\tilde{u}^y(\mathbf{0}) - i \frac{\bar{\mathbb{G}}^{yy}(\mathbf{0}, R) k_{(\pm\pm)}^y}{\sqrt{N}} \right)^2 \\ &\quad + \frac{1}{N} \bar{\mathbb{G}}^{yy}(\mathbf{0}, R) \left(k_{(\pm\pm)}^y \right)^2, \end{aligned} \quad (\text{A.90})$$

which is also independent of l . As anticipated from (A.82), we end up with

$$\langle e^{i\mathbf{k}_{(\pm\pm)} \cdot \mathbf{u}_l} \rangle|_R = \exp \left\{ -\frac{1}{2} \mathbf{k}_{(\pm\pm)}^T \cdot \frac{1}{N} \sum_{\mathbf{q} \neq \mathbf{0}} \bar{\mathbb{G}}(\mathbf{q}, R) \cdot \mathbf{k}_{(\pm\pm)} \right\}. \quad (\text{A.91})$$

Comparison with (A.71)-(A.72) reveals that this can be rewritten in the compact form

$$\langle e^{i\mathbf{k}_{(\pm\pm)} \cdot \mathbf{u}_l} \rangle|_R = \exp \left\{ -\mathbf{k}_{(\pm\pm)}^T \cdot \frac{\bar{\sigma}(R)}{2} \cdot \mathbf{k}_{(\pm\pm)} \right\}, \quad (\text{A.92})$$

where

$$\bar{\sigma}(R) = \begin{pmatrix} \sigma_{xx}(R) & \sigma_{xy}(R) \\ \sigma_{xy}(R) & \sigma_{yy}(R) \end{pmatrix} \quad (\text{A.93})$$

is the 2×2 matrix of covariances.

In applying these results to (A.80), the term $\propto \cos(k_x R)$ is identically zero as could have been anticipated from symmetry arguments, since the contributions from the four different vectors $\mathbf{k}_{(\pm\pm)}$ cancel each other. In the second term $\propto \sin(k_x R)$, it is also clear that the terms for $\mathbf{k}_{(- -)}$ and $\mathbf{k}_{(- +)}$ will give the same result as those for $\mathbf{k}_{(+ -)}$ and $\mathbf{k}_{(+ +)}$, respectively. Thus we are left with

$$\begin{aligned} \langle F_{\text{net}} \rangle|_R &= F_d + \frac{F_{\text{max}} \sin(k_x R)}{2} \left(e^{-\mathbf{k}_{(++)}^T \cdot \frac{\bar{\sigma}(R)}{2} \cdot \mathbf{k}_{(++)}} + e^{-\mathbf{k}_{(+-)}^T \cdot \frac{\bar{\sigma}(R)}{2} \cdot \mathbf{k}_{(+-)}} \right) \\ &= F_d + \frac{F_{\text{max}} \sin(k_x R)}{2} \left(e^{-\frac{1}{2} \sigma_{xx} k_x^2 - \sigma_{xy} k_x k_y - \frac{1}{2} \sigma_{yy} k_y^2} + e^{-\frac{1}{2} \sigma_{xx} k_x^2 + \sigma_{xy} k_x k_y - \frac{1}{2} \sigma_{yy} k_y^2} \right), \end{aligned} \quad (\text{A.94})$$

i.e.,

$$F^{\text{eff}}(R) = -F_{\text{max}} \sin(k_x R) \cosh(\sigma_{xy} k_x k_y) \exp \left\{ -\frac{1}{2} (\sigma_{xx} k_x^2 + \sigma_{yy} k_y^2) \right\}. \quad (\text{A.95})$$

Reverting to the former definitions $k_x = 2\pi/a$ and $k_y = 2\pi/a\sqrt{3}$, we end up with

$$F^{\text{eff}}(R) = -F_{\text{max}} \sin\left(\frac{2\pi a}{R}\right) \cosh\left(\frac{4\pi^2}{\sqrt{3}a^2}\sigma_{xy}\right) \exp\left\{-\frac{2\pi^2}{a^2}\left[\sigma_{xx} + \frac{\sigma_{yy}}{3}\right]\right\} \quad (\text{A.96})$$

Taking advantage of the fact that σ_{xy} is zero, we finally obtain,

$$F^{\text{eff}}(R) = -F_{\text{max}} \sin\left(\frac{2\pi a}{R}\right) \exp\left\{-\frac{2\pi^2}{a^2}\left[\sigma_x^2 + \frac{\sigma_y^2}{3}\right]\right\} \quad (\text{A.97})$$

as presented in Equation 7 of the main paper.

A.8 Data analysis

In this section, we present a detailed description of how data were obtained from simulations and compared to the theoretical results obtained in the previous part of the appendix.

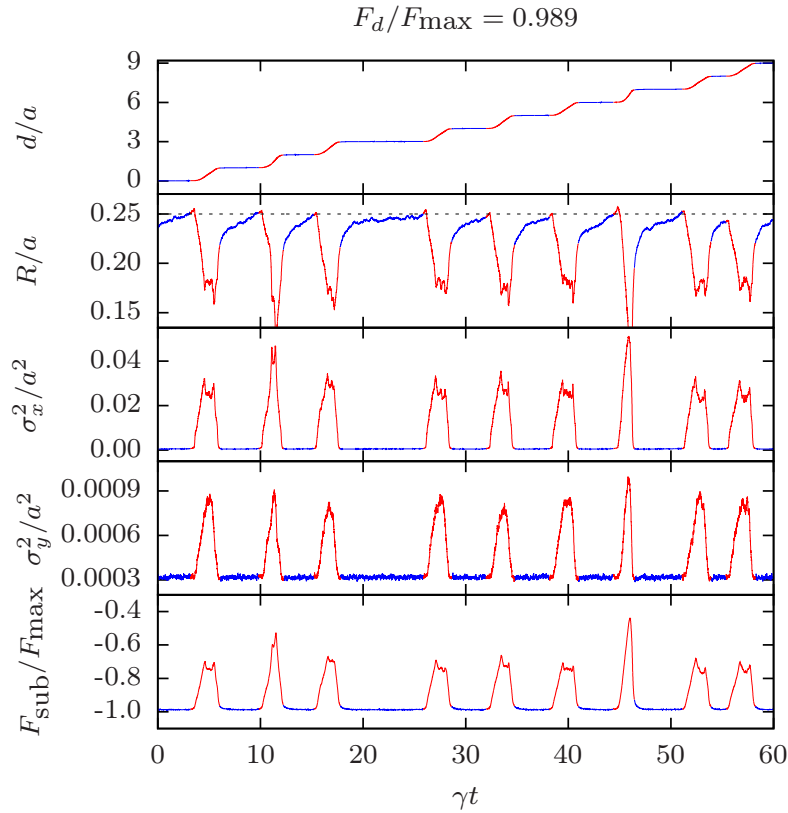


Figure A.3 Total displacement (first panel), periodic center of mass (second panel), variance of the relative displacements of particles, $\mathbf{u}_i$, in the x and y directions (third and fourth panels), and the net substrate force acting on the monolayer (fifth panel), all plotted as a function of time for part of a trajectory. The inter-particle interaction strength is $\Gamma/k_B T = 1.147$ and the driving force $F_d/F_{\text{max}} = 0.989$. The data points are plotted in blue if the monolayer is undergoing a buildup phase.

As a representative example, we use a part of the trajectory of a monolayer with $\Gamma/k_B T = 1.147$, driven by a force $F_d/F_{\max} = 0.989$. Standard trajectories used for the article were twice as long as the fragment considered here. Similar to the main article, Figure A.3 presents the total displacement, the periodic center of mass, the variances of the particle positions, and the net substrate force acting on the monolayer. Data drawn in blue belong to the build up phase, whereas data belonging to configurations in which a hopping wave is traveling through it are colored in red. The periods of rapid motion (hopping waves) are characterized either by the rapid change of total displacement (top) or spikes in all of the remaining quantities. The buildup phase coincides with plateaus in the total displacement and regions with relatively small changes in other quantities. We used the arbitrarily cutoff, $\sigma_x^2/a^2 < 0.85 \times 10^{-4}$ in order to differentiate between the two phases.

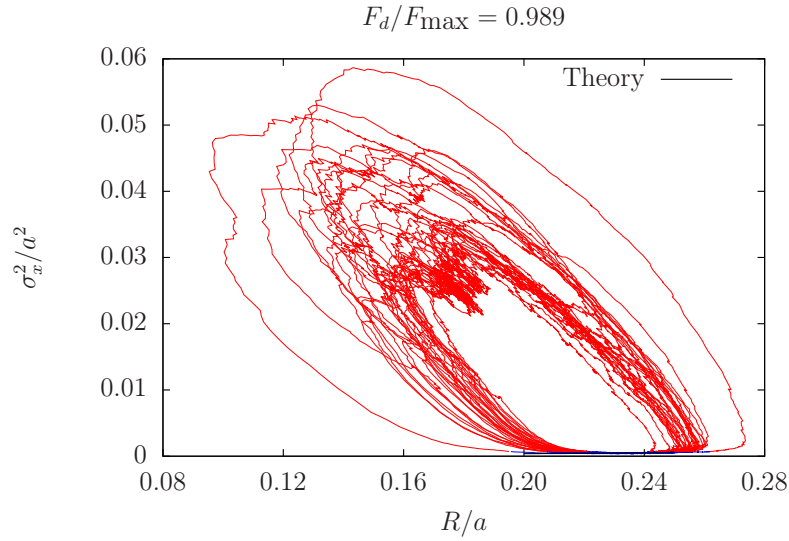


Figure A.4 Variance of the relative displacements of particles, $\mathbf{u}_i$, in the x direction, σ_x^2 , as a function of the periodic position of the center of mass, R . The inter-particle interaction strength is $\Gamma/k_B T = 1.147$ and the driving force $F_d/F_{\max} = 0.989$.

As can be seen in Figure A.4, where σ_x^2 is plotted as a function of the periodic position of the center of mass, values that correspond to the buildup phase are all bundled in a small region of R . In Figure A.5, we zoomed in on this region and present σ_x^2 , σ_y^2 and F_{sub} , all as a function of R . The theoretical predictions of the mean value of these quantities has been plotted next to the data. Furthermore, our theory predicts that, in the buildup phase, these distributions are independent of the applied driving force. In Figure A.6, we compare the simulation results for a trajectory of a monolayer driven by $F_d/F_{\max} = 0.987, 0.989$, and 1.002 with the theoretical prediction. Evidently, the distributions of the substrate forces of these monolayers overlap strongly.

We have plotted, in Figure A.7, a histogram of the net substrate force $F_{\text{sub}}(R)$ acting on the monolayer with the intention not only to show that the theoretical prediction is very close to its expectation value, but that the distribution is also very narrow. As

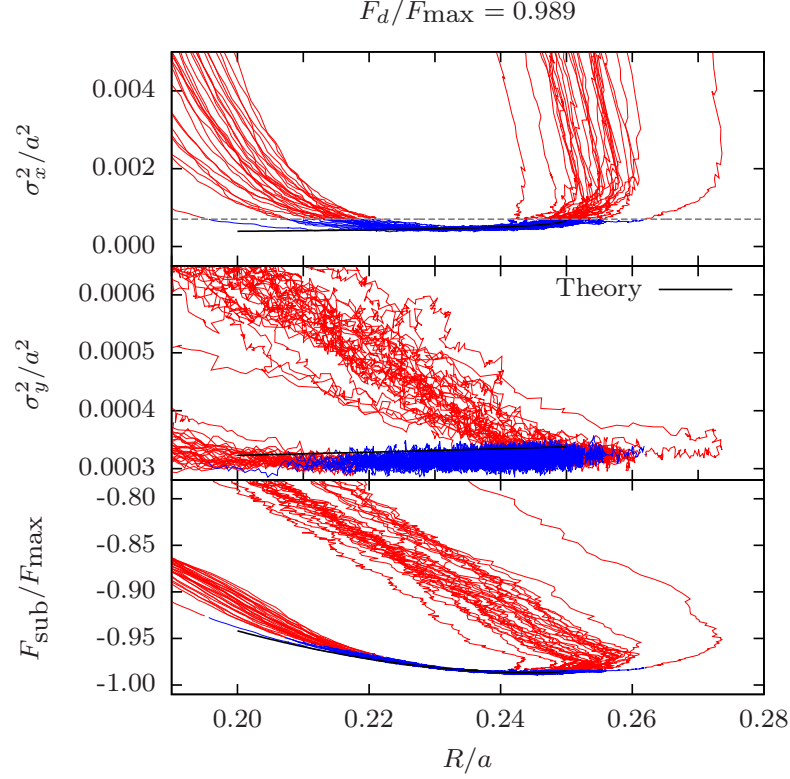


Figure A.5 Variances of the relative displacements of particles, $\mathbf{u}_i$, in the x and y directions and the net substrate force acting on the monolayer as a function of the periodic position of the center of mass, R , restricted the buildup phase. The inter-particle interaction strength is $\Gamma/k_B T = 1.147$ and the driving force $F_d/F_{\max} = 0.989$. The theoretical predictions are indicated by the solid black lines. The threshold value of σ_x^2 used to differ between the phases is denoted by the dashed gray line which is located at $\sigma_x^2/a^2 = 8.5 \times 10^{-4}$.

a result, one can, to a good approximation, use $F^{\text{eff}}(R)$ as the effective substrate force acting on the monolayer.

So far, we have only considered driving forces $F_{\max} > F_d > F_{\max}^{\text{eff}}$, where $F_{\max}^{\text{eff}}$ is the maximum restoring force of $F^{\text{eff}}(R)$. In this parameter regime, the monolayer is able to drift up to $R = 0.25a$, but also remain in quasi-static equilibrium as it does so. If the driving force is below $F_{\max}^{\text{eff}}$, the monolayer gets pinned by the effective substrate at the position R_0 such that $F^{\text{eff}}(R_0) + F_d = 0$. The monolayer then oscillates about R_0 for a while until a small group of particles spontaneously form a critical “hopping cluster” (red particles in the video) which then initiates a hopping wave. In Figure A.8, we have plotted the position of the periodic center of mass for the monolayer with $\Gamma/k_B T = 1.147$, driven at rates below $F_{\max}^{\text{eff}}/F_{\max} = 0.9867$. Using our analytical formula for $F^{\text{eff}}(R)$, we found the corresponding value of R_0 numerically and plotted it as the black dashed line in the graph. Each of the monolayers oscillates for a while about R_0 before creating a hopping wave, as predicted.

For the results presented in the article, we considered a total of 6 different values of Γ driven with 10 different F_d . For each pair Γ and F_d values, 100 independent trajectories

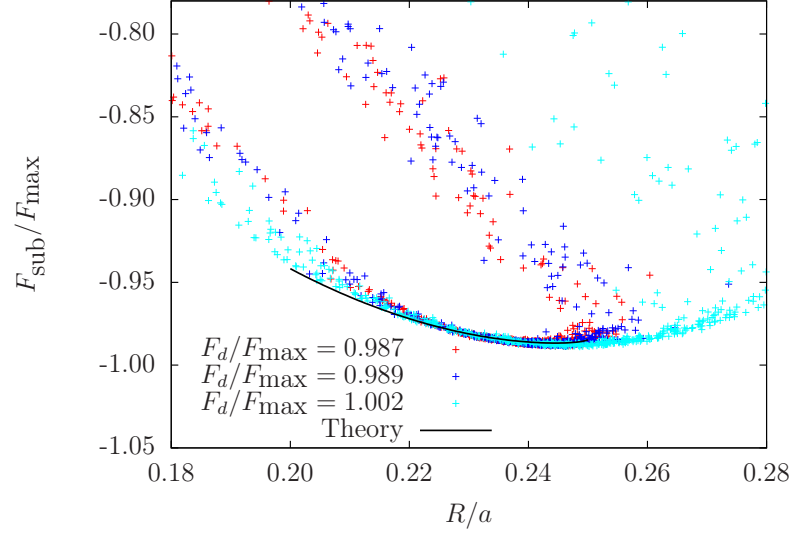


Figure A.6 Net substrate force acting on the monolayer driven by $F_d/F_{\max} = 0.987, 0.989$, and 1.002 as a function of the periodic position of the center of mass, R . The inter-particle interaction strength is $\Gamma/k_B T = 1.147$. The theoretical prediction is indicated by the solid black line.

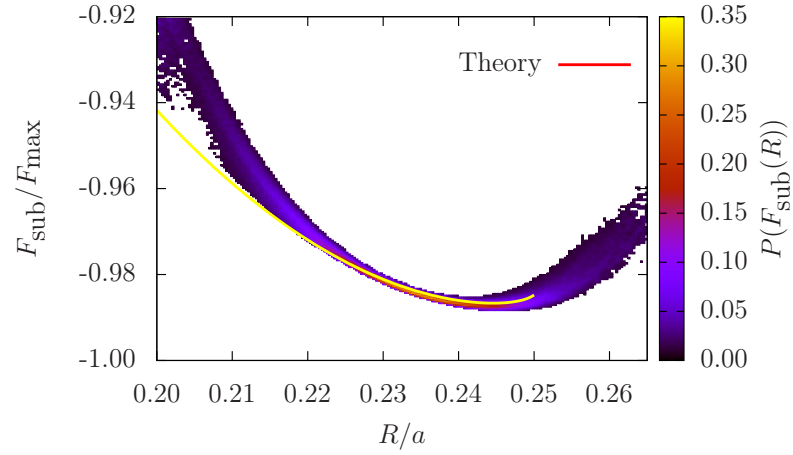


Figure A.7 Distribution of the average substrate forces for multiple build up phases, gathered from 100 trajectories and several values of the driving forces, as a function of R . The yellow line indicates the theoretical prediction for $F^{\text{eff}}(R)$.

were generated and analyzed.

A.9 System size dependence

As described in the supplement S1, the effective force acting on the monolayer,

$$F^{\text{eff}}(R) = -F_{\max} \sin\left(\frac{2\pi R}{a}\right) \times \exp\left\{-\frac{2\pi^2}{a^2} \left[\sigma_x^2(R) + \frac{1}{3}\sigma_y^2(R)\right]\right\}, \quad (\text{A.98})$$

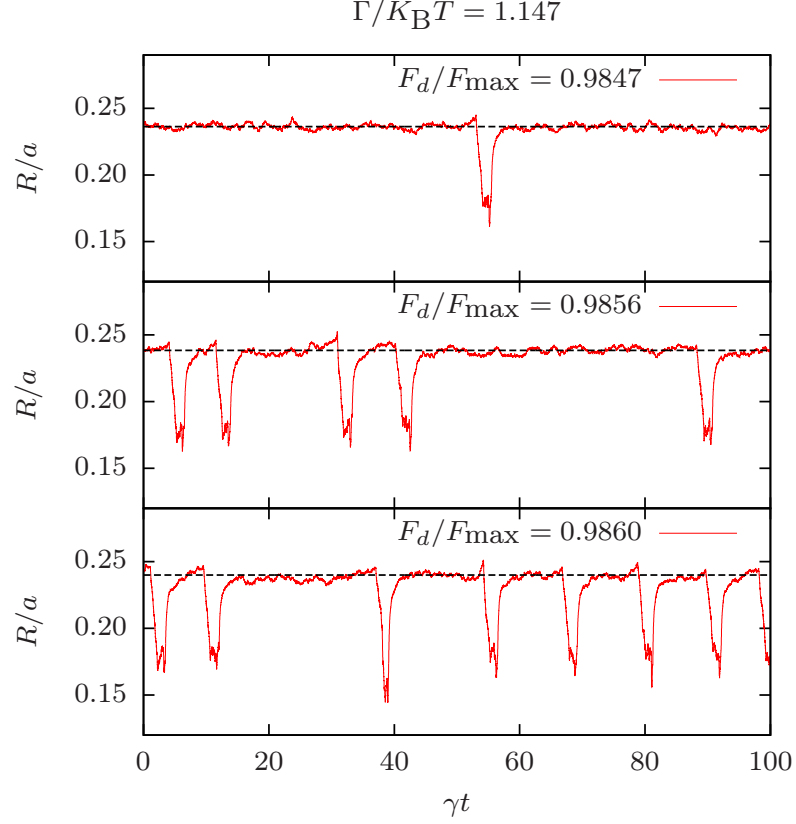


Figure A.8 Periodic center of mass, R , as a function of time for a monolayer driven by $F_d/F_{\max} = 0.9847, 0.9856$, and 0.9860 , all of which are less than $F^{\text{eff}}(\Gamma)$, where $\Gamma/k_{\text{B}}T = 1.147$. Dashed lines indicate theoretical predictions for the position R_0 , at which the monolayers become pinned.

is a function of the variances,

$$\sigma_{\mu}^2(R) = \delta_{y\mu} \frac{\bar{\mathbb{D}}_{yy}^{-1}(\mathbf{0}, R)}{N\beta} + \frac{1}{N\beta} \sum_{\mathbf{q} \neq \mathbf{0}} \bar{\mathbb{D}}_{\mu\mu}^{-1}(\mathbf{q}, R), \quad (\text{A.99})$$

which are sums of the elements of the dynamical matrix $\mathbb{D}(\mathbf{q})$ divided by the particle number. These variances can be interpreted as the mean value of the continuous function $\bar{\mathbb{D}}(\mathbf{q}, R)$ discretized to N equally spaced points. The number of particles in the system determines how fine the “mesh” is. Naturally, the value of the variances converges as N becomes large and in the limit of infinitely large N , the sum over $\mathbf{q}$ becomes an integral. According to our formula, the continuous function $\mathbb{D}_{\mu\mu}^{-1}(\mathbf{q}, R)$ has to be evaluated at the N $\mathbf{q}$ -vectors compatible with a simulation of N particles. In order to trace the convergence of the solution to an infinitely large system, we have plotted, in Figure A.9, our predictions for the effective force acting on the monolayer. Evidently, we considered a system size (indicated by a circle) which is quite close to the limit of an infinitely large system.

As was stated in the paper, the entire trajectory of the monolayer can be resolved into

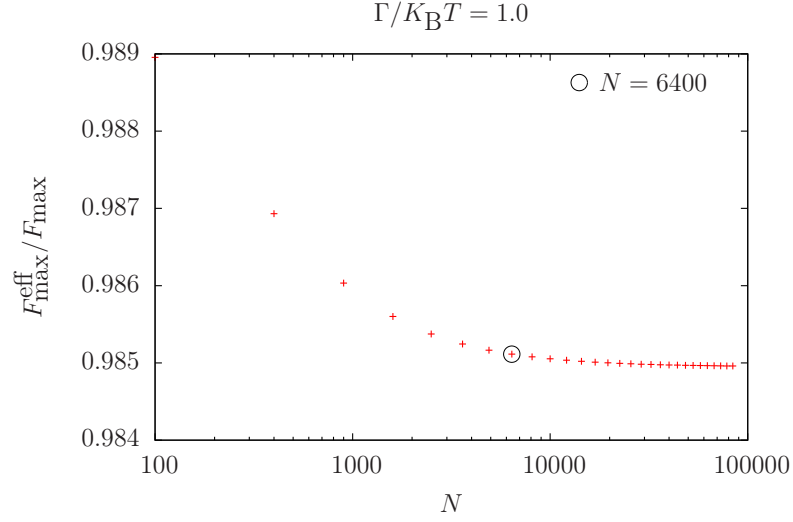


Figure A.9 Theoretical predictions for the effective force acting on the monolayer as a function of the number particle number N .

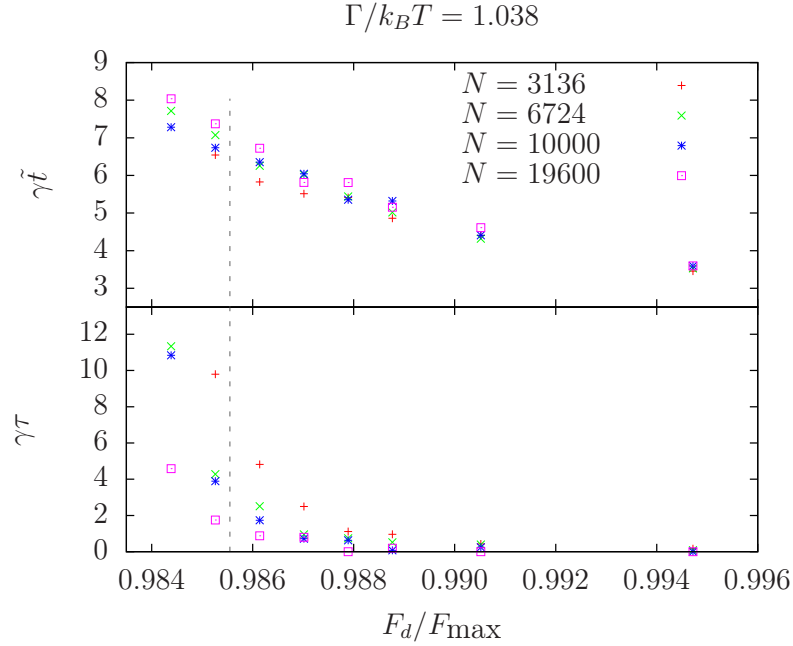


Figure A.10 Top: Average time the buildup phase plus the hopping wave takes to travel through the system as a function of driving force F_d for different system sizes N . Bottom: Average time the system takes to nucleate a hopping wave also as a function of F_d and N . The dashed line is located at $F_{\max}^{\text{eff}}$.

three times: the drifting time due to the effective substrate $\tilde{t}_1$, the nucleation time τ , and the hopping wave time $\tilde{t}_2$. The mean velocity of the monolayer is exactly equal to $\gamma v = a / (\tilde{t}_1 + \tilde{t}_2 + \tau) = a / (\tilde{t} + \tau)$. The time $\tilde{t}_1$, which is the time that the monolayer needs to reach R_0 if $F_d < F_{\max}^{\text{eff}}$ or $R = 0.25a$ if $F_d > F_{\max}^{\text{eff}}$, can be calculated by evaluating the integral using the appropriate limits of integration,

$$\tilde{t}_1 = \int \frac{dR}{F_d + F^{\text{eff}}(R)} \quad (\text{A.100})$$

and is independent of N in the manner discussed above. The hopping wave time is roughly $\tilde{t}_2 = a\sqrt{N}/v_{\text{wave}}(F_d)$, where $v_{\text{wave}}(F_d)$ is the velocity with which the radius of the hopping wave expands and is expected to monotonically increase with the driving force. The dependance on N stems from the fact that the hopping wave has to cover larger distances as the system size increases. Finally, the average nucleation time, τ is predicted to be proportional to the inverse system size $\tau \propto N^{-1}$ and scales exponentially in the free energy barrier associated with forming a critical cluster of hopping particles. This free energy barrier, in turn, depends on F_d and is expected to vanish if it exceeds $F^{\text{eff}}(R)$. Determining the exact functional form of these three times would require the determination of a series of proportionality terms, such as the kinetic prefactor, the surface tension due to a hopping wave, and the hopping wave velocity. Although this is feasible, such a detailed analysis is beyond the scope of this work and would be tantamount to solving the entire model in this parameter range. We are, nonetheless, able to make some predictions.

As a result of the aforementioned considerations, the mean velocity of the monolayer is predicted to scale very differently with the driving force and system size in the two dynamical regimes that were explored in this work. Since τ is minuscule or 0 in the thermal sliding regime, and most of the time is spent in the build up phase, $\tilde{t}_1$ determines the mean velocity. As a result, the expression $\gamma v = \sqrt{(F_d)^2 - (F_{\text{max}}^{\text{eff}})^2}$ is quite accurate in reproducing the velocity of the monolayer. In the nucleation regime, the average nucleation time, τ , is the dominant time and therefore the velocity of the monolayer increases with system size and increases exponentially as F_d grows. In both regimes, the time the hopping wave takes to travel through the system scales with $\sqrt{N}$ and F_d , but its contribution to the velocity is small since the other two times are much larger than $\tilde{t}_2$. As a result we expect, that $\tilde{t}$ should *increase* slightly as the system size grows, whereas the nucleation time τ should *decrease* by a large amount for growing system sizes. Our expectations are confirmed in Figure A.10. Finally, from the shape of the curves, the bottom panel also illustrates that the transition from nucleation dynamics to thermal sliding is continuous.

Appendix B

Curriculum vitae

Current occupation: PhD student in the group of Professor Christoph Dellago.
Specialization: Computational and statistical physics.
Research interests: Atomic friction, phase transitions, rare events, soft matter, driven systems, and bio-physics.

Particulars:

- Born on 25/09/1983, in Vienna, Austria.
- Canadian citizen.
- Currently living in Vienna, Austria.

Education:

- Graduation at Jakarta International School (2002).
- BSc/MSc in physics from the University of Vienna (2010).

Fields of expertise:

- Developing and implementing advanced code to simulate multi body systems.
- Statistical mechanics, thermodynamics, and computational physics.

Publication list:

- Jaffar Hasnain, Swetlana Jungblut, and Christoph Dellago. “Dynamic phases of colloidal monolayers sliding on commensurate substrates”, *Soft matter* (cover, 2013), **9**, 5867-5873.
- Jaffar Hasnain, Swetlana Jungblut, Andreas Tröster, and Christoph Dellago. “Frictional dynamics of stiff monolayers: from nucleation dynamics to thermal sliding”, *Nanoscale* (2014), **6**, 10161-10168.
- Jaffar Hasnain, Swetlana Jungblut, and Christoph Dellago. “Dynamical phases of attractive particles sliding on a structured surface”, *J Phys Condens Matter*. (2015), **27**, 194122.

Conference and summer schools attended:

- SFB TR6 Summer School on Soft Matter, "**Physics of colloidal suspensions and granular media**", September 27 - October 09, 2010.
- **8th liquid matter conference**, September 6-10, 2011, poster.
- **Comploids conference on complex colloids**, August 22, 2012.
- **Comploids conference on complex colloids**, May 14-18, 2013.
- Contributed talk at the **9th liquid matter conference**, July 21-25, 2014.
- **Berkeley Mini Stat Mech Meeting**, January 9-11, 2015, poster.

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