Static and dynamical properties of classical one-dimensional and two-dimensional finite size systems

Statische en dynamische eigenschappen van klassieke één- en tweedimensionale eindige systemen

Proefschrift voorgelegd tot het behalen van de graad van doctor in de wetenschappen aan de Universiteit Antwerpen te verdedigen door

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Chapter 1

Introduction

The self-organization of inorganic particles is important for both fundamental research as in the fabrication of nano-structured particle systems. Ordered systems as colloids and complex plasmas play a more and more important role as model systems for the study of different phenomena in condensed matter physics as glass formation, crystallization, nucleation and melting because they are accessible for real-space imaging. By manipulating the particles in the correct way, the inter-particle interaction can be controlled almost unlimited. The expectation is that the study of those systems will lead to a better understanding of electro- and magneto-rheological fluids [1]. These systems also made it possible to study fundamental thermodynamical phenomena like e.g. dissipation, melting, freezing, glass transition and Brownian dynamics. With the view on applications there are a lot of possibilities. The formation of big arrays of ordered organic and inorganic building blocks is one of the most exciting fields in materials science and technology. Previously, periodic structures were produced using lithographic processes, but the disadvantage of this top-down technique is that it is quite expensive, complicated and time intensive. Alternatively one can opt for a bottom-up technique. For example isotrope self-organizing colloids can be used as a mask in a lithographic process [2]. The size of the nanoparticles can be determined by the empty space in the colloidal crystals which are determined by the interaction between the colloidal particles. By varying the interaction between the particles, pyramid, ring and rod like structures can be formed [3]. Chemical physicists want to understand how the inter-particle interaction determines the crystal structure and speed of crystallization. Biochemists want to crystallize proteins whose structure can be determined. Nanotechnologists want to know how colloids and nanoparticles can self-assemble to a specific structure, like e.g. the diamond lattice and this for potential applications e.g. in photonics. Metallurgists want to predict which alloys will form the best metal glasses [4] and which structural changes are responsible for the formation of glasses [5]. Previous studies where mostly directed to isotropic systems with identical particles. Recently, a lot of systematic studies were initiated with mixtures of particles [6], growth of templates and anisotropic inter-particle interactions. However there are limits to the structures that can be assembled from isotropic particles. This resulted recently in considerable interest in the development of methods to fabricate colloidal particles with an anisotropy in their shape [7] and/or in their interaction [8].
In this thesis we will give in the first chapter an overview of typical examples and experimental systems of classical confined systems which exhibit Wigner crystallization. In the second chapter we will describe three models of the most relevant experimental systems for this thesis and the numerical methods used to obtain its relevant properties. Here several methods as molecular dynamics, Monte Carlo, and Langevin dynamics are briefly introduced.

In chapter 3, the frequency spectrum of a system of classical charged particles interacting through a Coulomb repulsive potential and which are confined in a two-dimensional (2D) parabolic trap is studied. It is shown that, apart from the well known center-of-mass and breathing modes, which are independent of the number of particles in the cluster, there are more ‘universal’ modes whose frequencies depend only slightly on the number of particles. To understand these modes, the spectrum of excitations as a function of the number of particles is compared with the spectrum obtained in the hydrodynamic approach. The modes are classified according to their averaged vorticity and it is shown that these ‘universal’ modes have the smallest vorticity and can be described by a hydrodynamic behavior.

In chapter 4, a system of classical charged particles interacting through a Coulomb repulsive potential which are confined in a two-dimensional parabolic trap is studied. We allow one or two particles, called defect particles, to have a different mass and/or charge than the other particles. The structure of the whole system depends on the mass and the charge of the defects and the total number of particles in the system. The groundstate configurations are investigated and phase diagrams are constructed, which explain the recent experimental results of Grzybowski et al. Ref. [54]. We found that several of the experimental configurations are metastable and that replacing the Coulomb inter-particle potential by an inversely quadratic has only little effect on the results.

In chapter 5, a system of classical charged particles confined in a two-dimensional trap and interacting through a competing short-range attractive and long-range repulsive potential is studied. The structure of the system strongly depends on the interaction range of the short-range attraction potential and the total number of particles. Depending on the appropriate choice of parameters for the attractive potential, the particles organize themselves in bubbles, stripe phases and ringlike configurations, or combinations of them. Detailed phase diagrams are presented for systems consisting of $N = 2$ up to $N = 6$ particles. General rules are derived for the different subsequent transitions between those configurations and how the ground state configuration of a large system can be deduced from the one of a small number of particles.

In chapter 6, the dynamics of topological defects in 2D clusters of charged classical particles interacting through a screened Coulomb potential are investigated through the Molecular Dynamics (MD) simulation technique. The formation of dislocations and their dynamics is central to our understanding of crystalline materials. Thermal effects are
1.1 Wigner crystals

Paul Wigner predicted in 1934, that electrons crystallize and form a lattice if the density of a three-dimensional (3D) electron gas is lowered beyond a certain critical value \[9\]. This is because at low densities the potential energy dominates the kinetic energy and the spatial arrangement of the electrons becomes important. To minimize their potential energy electrons form a body-centered-cubic (bcc) lattice. This regime is called the classical regime because quantum effects can be neglected. The state of an uniform electron thought to play a critical role in the nucleation of these defects. The particles are confined by a harmonic potential and coupled with an Anderson heat reservoir. We investigate cooling rate effects on the formation of grain boundaries and the dynamics of them by decreasing the temperature of the heat reservoir linear in time. We found that: i) the mobility of defects strongly depends on the number of nearest neighbors and the nature of those defects, ii) geometrically induced defects have different dynamics than other defects because of spontaneous pinning of the defects at the corners of the hexagon, and iii) if the cooling speed is large enough, the system will no longer be in thermodynamic equilibrium and a glass-like structure is formed.

In chapter 7, a binary system of classical charged particles interacting through a dipole repulsive potential and confined in a 2D hardwall trap is studied by Brownian dynamics simulations. We found that the presence of small particles stabilizes the angular order of the system as a consequence of radial fluctuations of the small particles. There is an optimum in the increased rigidity of the cluster as function of the number of small particles. The small (i.e. defect) particles melt at a lower temperature compared to the big particles and exhibit a reentrant behavior in its radial order that is induced by the inter-shell rotation of the big particles.

In chapter 8, the diffusion of charged massive particles in a one-dimensional (1D) channel is investigated using the Langevin Dynamics (LD) simulations. Molecular diffusion in unidimensional channel structures (single-file diffusion) is important to understand the behavior of, e.g., colloidal particles in porous materials (zeolites) and superconducting vortices in 1D channels. We analyze different regimes based on the hierarchy of the interactions and damping mechanisms in the system and we show that, contrary to previous findings, single file diffusion depends on the inter-particle interaction and could be suppressed if the interaction is strong enough displaying a subdiffusive behavior slower than \(r^{1/2}\), in agreement with recent experimental observations in colloids and charged metallic balls.

In chapter 9, I looked for strategies to estimate the dissipated work through a refinement of the Jarzynski and Crooks theorem obtained in Ref. [92].
1. Introduction

gas at zero temperature is characterized by the Wigner-Seitz radius \( r_s = a/a_B \), where \( a \) is the average inter-particle distance and \( a_B \) the Bohr radius.

Let consider the 2D case. The classical regime is mainly determined by the Coulomb interaction. The importance of the Coulomb interaction is determined by the coupling parameter \( \Gamma = \frac{\langle V \rangle}{\langle K \rangle} \) which is defined as the ratio of the mean potential energy \( \langle V \rangle = \frac{e^2}{\langle 1/r \rangle} = e^2 \sqrt{\pi n_e} \) to the mean kinetic energy \( \langle K \rangle = k_B T \). Where \( n_e \) is the electron density, \( e \) the electron charge, \( k_B \) the Boltzmann constant, and \( T \) the temperature. The potential energy can be seen as an indication of the order of the system while the kinetic energy can be seen as an indication of disorder. In the low temperature quantum regime one has \( \langle K \rangle = E_F = \frac{\pi h^2 n_e}{m} \) and consequently \( \Gamma = r_s = r_0/a_B \), with \( n_e = 1/\pi r_0^2 \) the electron density, \( a_B \) the Bohr radius, and \( r_0 \) the inter-particle distance. According to the value of \( \Gamma \) three different regimes can be distinguished. When \( \Gamma < 1 \), the potential energy is lower with respect to the kinetic energy and the system will behaves as an ideal gas. In this regime the Coulomb interaction is of minor importance and this regime is realized for high density at high temperature. For \( 1 < \Gamma < 100 \) the electrons are correlated and the system behaves liquid-like. For \( \Gamma > 100 \), which is the low-density low-temperature regime, the Coulomb potential energy dominates over the kinetic energy and there are strong correlations between the electrons, which is expected to drive the system through a phase transition to an ordered state, i.e. a periodic crystalline array.

The quest for the observation of such a Wigner crystal has been the object of very intense and continuous work. Experimental observations of a 3D Wigner lattice of electrons has not yet been realized. Electrons in materials like e.g. metals and semiconductors not only feel there mutual repulsion but are also influenced by the ‘imperfect’ host lattice in which they move. Defects, impurities and similar imperfections destroy such a 3D Wigner lattice. Therefore, one has looked for alternative systems in which such Wigner crystallization can be realized. In 1971 Crandall and Williams [10] proposed to look for such Wigner lattice in the 2D system of electrons above a liquid helium surface, where the conditions for crystallization can be realized much more easily and also because of the almost ideal character of the system, i.e. no complicated band structure is present like in real metals, absence of impurities and imperfections, and the inherent low temperature.

After the theoretical prediction of the possibility of the existence of a Wigner lattice on the helium surface [11] the fundamental problem arises: how to observe such a Wigner lattice? The electron solid is lighter, much less dense and is also much less strongly bound than a normal solid, so that different experimental techniques have to be used in order to detect whether or not the 2D electron system is in the ordered phase. Eight years later in 1979, the first discovery of Wigner crystallization of electrons on the surface of liquid helium was reported by Grimes and Adams in Ref. [12] at Bell laboratories (Murray Hill, N.J., USA).

Experimental investigations of classical Wigner crystals have made considerable
progress since the first discovery of Wigner crystallization. Examples of electrons in quantum dots \[13\], particles in colloidal suspensions \[14, 15\] and in confined plasma crystals \[16, 44, 45, 19\] can exhibit such classical Wigner crystal-like ordered structures. Various similar systems, such as laser-cooled ions in a trap \[20\] which is realized by electric and magnetic fields, trapped ions cooled by laser techniques \[21\], ions in a radio-frequency (RF) trap (Paul trap) \[22, 23\] or a Penning trap \[24, 25, 26\] which can also serve as an illustration of 3D Coulomb clusters \[27, 28, 29\].

Other related systems, which exhibit Wigner crystal-like ordering are the following: the vortex clusters in an isotropic superfluid \[30\], vortices in superfluid He \[31, 32\], vortices in a Bose-Einstein condensate stirred with a laser beam \[33\], in superconducting grains \[34\], even in biological systems \[35, 36\] have many common features with those of 2D charged particles \[37\].

Electron and ion crystals, for example, electrons in quantum dots and ions in a penning and Paul traps, are atomic scale crystals. Macroscopic crystals have many advantages for the detailed study of the Wigner Crystal, because of the macroscopic size and ease of optical observation of their structure (i.e. the position of such particles can be detected and followed in time). Furthermore, several parameters can be controlled over a wide range of parameters. Examples are complex plasmas, and colloidal systems.

Following experimental systems will be discussed in detail in the following sections: i) Dynamic self-assembly of millimeter-size magnetic disks at a liquid-air interface was reported by the G. M. Whitesides’ group from Harvard University in Ref. \[39, 40\]. Macroscopic 2D Wigner islands, consisting of charged metallic balls above a plane conductor were studied and ground state, metastable states and saddle point configurations were found experimentally by Prof. M. Saint Jean’s group at the University of Paris 6 \[38\]. ii) The dust particles in a plasma, or in other words dusty plasmas, interact with each other through a screened Coulomb interaction. These particles can be confined in a 2D plane which can be used to study Wigner crystallisation. iii) Colloidal paramagnetic particles interacting with each other through a dipole interaction organize themselves in regular patterns if a magnetic field is applied perpendicular to their 2D confinement.

1.2 Electrons above liquid He

In this system electrons are confined in 2D above a helium interface \[41\]. The electrons are attracted towards the surface by an image charge of the electrons in the liquid due to the dielectric difference between vacuum and He and are pushed to the He-surface by a perpendicular electric field. The penetration into the liquid is avoided due to a potential energy barrier at the surface (i.e. He does not like extra electrons). A liquid-solid phase transition will occur at sufficient low temperature. The main difference with the
1. Introduction

Figure 1.1: Configurations of (a) 2, (b) 8 and (c) 20 dimples (appearing as dark spots) on a helium surface in an external potential of cylindrical symmetry. (From Ref. [42].)

A very fundamental and unique property, related to this small density was observed in this system in 1979 [12]: the formation of an electron crystal.

If one applies a strong electric field perpendicular to the helium surface, the system becomes unstable and the homogeneous electron distribution is destroyed. The electrons become localized in a regular array of pockets, or ‘dimples’, which constitute a macroscopic analogue of the microscopic Wigner crystal. These many-electron dimples, each of which contains up to $10^7$ electrons with a typical diameter of the order of 1 mm, can be considered as macroscopic particles and the Coulomb repulsion between the many-electron dimples leads to an ordering in a ring configuration as is shown in Fig. 1.1 for 2, 8 and 20 dimples on the surface of liquid Helium [42].

It is not only possible to trap electrons above the surface of liquid helium, but also to trap charged particles, or ‘ions’, just below the surface of liquid helium. These ions are created by removing (resulting in a positive ion) or adding (resulting in a negative ion) an electron from or to the helium. As is the case with electron pools trapped above the surface of liquid helium, the trapped ions provide us with simple 2D systems of particles with precisely known (Coulomb) interactions. Such systems are model systems which allows one to carry out experiments analogous to 2D plasma physics and on the behavior of condensed matter in two dimensions. The large effective mass of an ion means that the ion system is always in the classical limit.
1.3 Complex plasmas

More than 99% of the visible matter in our universe is in the plasma state. A plasma is a state where the particles of a material are ionized. Typically, a plasma has three kinds of components: the positively charged ions, the negative electrons and neutral particles. The plasma state is often termed “the fourth state of matter” because adding energy to a solid converts it first to a liquid, then to a gas, and finally to a plasma. In contrast with the other phases which are separated by a phase boundary, the plasma state is not separated by a phase boundary from the gas phase. The transition between gas and plasma is a continuous one.

A complex plasma is formed after the introduction of a fourth component into the plasma namely dust. Dust in this context, refers to nano/microscopic particles with all shapes and sizes ranging from a few nanometers up to tens of microns. Defining a plasma as a collection of positive and negative charges that are not atomically bound to each other, we encounter two possibilities. Most commonly, the charges have abundant kinetic energy and can easily pass their neighbors, much like molecules in a gas. That’s termed a weakly coupled plasma. In less common strongly coupled plasma, charged particles have a kinetic energy much smaller than the electrostatic potential energy between its neighbors. The best-known strongly coupled plasmas included the interiors of stars and laser-cooled ion aggregates. In stellar interiors, the ratio $\Gamma$ of electrostatic to kinetic energy is large because of high density and small inter-particle spacing. In laser cooling experiments, $\Gamma$ is large because the ion temperature is so low.
In a *strongly coupled plasma*, immersed nano/microscopic particles (‘dust’), can form ordered structures, i.e. they crystallize in a Wigner lattice, under proper conditions. The ordered solid phase of dusty plasmas was first predicted theoretically by H. Ikezi in 1986 [43] and then observed experimentally as plasma crystals in 1994 [44, 45, 19]. A few typical topics which were studied are the following: (i) the different structures in the crystal phase, especially under an additional dipole field [44, 45, 19]; (ii) the structure and the order-disorder phase transition [46, 47], which may serve as a macroscopic model system for melting in two or three dimensions; (iii) the features of the liquid phase [48]; (iv) the defect properties and dynamics [49]; (v) the microscopic motion and collective excitations in the melting and liquid states [50]; (vi) the anomalous diffusion in the melting and liquid states [50], etc.

Dust particles in a plasma collect a high number of ions and electrons from their surroundings onto their surfaces. Due to the much lower mobility of the heavier ions, the dust particles are hit on the average by more electrons which results in a negatively charg-
1.3. Complex plasmas

The mobility of the electrons can be hundreds of time larger than that of the ions. The ions will form a positive cloud of ions around the particles (see Fig. 1.2) resulting in a screened Coulomb interaction between the particles, where this screening is the result of the positive ion cloud. Because these dust particles are negatively charged they can be confined by an electrostatic confinement $E_c$ in the horizontal direction preventing the particle from escaping. Depending on the plasma parameters single- or multi-layers are formed. The interplay of the cylindrical confinement and screened Coulomb interaction will then lead to the formation of a hexagonal structure. The interparticle spacing is determined by the number of dust particles inserted into the plasma and the plasma conditions and is typically in the sub-millimeter region. The most important forces acting in the vertical direction on the dust particles are the: ion drag force, thermophoretic force, gravity, the dipolar effect, the anisotropic pressure and an external applied electric field. To confine the dust sheet vertically all forces have to be balanced.

A typical experimental set-up and configuration are shown in Fig. 1.3. Large dust crystals can have sizes corresponding to hundreds of interparticle distances in the horizontal plane, with up to ten layers in the vertical direction. Dust crystals with only a small number of particles ($N < 200$) are called dust clusters (or Coulomb clusters). Since the number of particles is reduced, dust clusters exhibit many unique physical properties not found in large crystals. In contrast to large clusters, the particles in dust clusters ($N < 40$) tend to arrange themselves into a single layer with shell structures due to the cylindrical symmetry in a typical confinement potential. Such individual clusters are called cluster rings. For intermediate dust clusters ($200 > N > 40$), the particles on the outer rings form a hexagonal lattice. The structural configuration of these particles can be catalogued in a periodic table by listing the number of particles in each ring [103].

Examples of complex plasmas

Dusty plasmas occur both in cosmic and terrestrial surroundings. Examples of dusty plasmas are found in nature, space, and in industrial devices. Ironically, work on dusty plasmas has been carried out over the years by groups with entirely opposite motivations. Initially, industrial scientists and engineers worked feverishly to eliminate dust from plasma-processing devices. Meanwhile, physicists doing basic plasma research to get dust into plasmas so that they could study its effects. As is often the case, researchers in these varied disciplines barely knew of each other’s existence, rarely talked with each other or attended the same meetings, and seldom published in the same journals. Eventually, however, they were brought together by the realization that they were investigating the same basic phenomena. Nowadays they share in plasma-source development and diagnostic techniques.
Noctilucent clouds

A fascinating example of a naturally occurring dusty plasma are noctilucent clouds, that is as the name suggests literally "shine at night". These atmospheric cloud formation form in the dry polar mesosphere (80-110 km) above sea level and are believed to be composed of ice-coated dust particles. At this lower reach of the ionosphere, free electrons can attach to the ice particles (typically 50 nm across) to form a dusty plasma. The clouds are never visible at daylight sky. Only after sunset, when the sun has dipped 6 to 16 degrees below the horizon, the sun is still lit, exposing the blue-white tendrils spread across the sky. Therefore, they can generally only be seen within the 50-65 degrees latitude region in both hemispheres and they only occur during the summer months when the atmosphere at these high altitudes is much colder than in the winter (150 K rather than 240K). They were first observed in 1885, about two years after the powerfull eruption of the Krakatoa volcano, but so far still remain an enigma.

Saturn rings

Over the past 20 years, the publication rate on the subject of dusty plasmas has grown exponentially, spurred by two watershed discoveries. The first occurred in the early 1980’s. Images of Saturn’s rings taken by Voyager 2 revealed certain features in the B ring that were probably as mysterious to modern planetary scientists as the rings themselves were to Galileo in 1610. The Voyager images revealed a pattern of nearly radial “spokes” rotating around the outer portion of Saturn’s (see figure 1.4) dense B ring. As the spacecraft approached the planet, the spokes first appeared dark against the bright background. But as Voyager 2 withdrew from the Saturnian system, the spokes appeared brighter than the material around them.

This observation, that the spoke material scatters sunlight more effectively in the forward direction, indicated that the material is a fine dust. Perhaps the most interesting aspect of the discovery of the spokes was that they are not stationary structures. Indeed, they develop remarkably fast, with new spokes forming in as little as five minutes. This short dynamical time scale rules out explanations based solely on gravitational effects, indicating that the dust particles are affected by electromagnetic fields.

Killer particles

In the production process of micro-electronic devices many production steps involve plasmas. The presence of dust particles (or killer particles) in the plasma chamber can lead to the deposition of dust particles on the substrate which can cause voids, delamination, and interconnect shortcuts. To avoid this killer particles, some solutions are known to involve plasma-chamber designs that exploit various forces on particles to divert them toward the
1.3. Complex plasmas

Figure 1.4: (Left) Noctilucent clouds are suspension of ice crystals coated particles at extremely high altitude. And as the name sugests, noctilucent clouds literally shine at night. The clouds are formed in the very dry part of the atmosphere such as the polar mesosphere [Courtesy of Pekka Parviainen, Polar Image]. (Right) Dynamic spokes in Saturn’s B ring, the wide bright ring just inside the prominent dark Cassini ring. The square fields at left are successive detailed images of the same orbiting physical region (yellow square), taken at roughly 10-minute intervals by Voyager 2 in 1981. The observed pattern of nearly radial ”spokes,” appearing dark against a bright background as the spacecraft approaches from the Sun side, changes quite rapidly. New spokes form in as little as five minutes, which suggests that the fine dust particles that compose them are affected by electromagnetic fields. (Courtesy Calvin J. Hamilton.)

Figure 1.5: (Left) An enlarged image of a grain of salt on a section of a microprocessor indicates the smallness and complexity of the electrical network. [Courtesy of Intel] (Right) dust impurities are well known to lower the performance of fusion magnetic confinement devices and leads to safety hazards due to the accumulation of radioactive tritium. (From EFDA-JET)

vacuum pump. There have also been changes in the method of coupling radio frequency (RF)-energy to the plasma. Rather than relying solely on capacitive coupling, manufac-
turers now commonly also use inductive coupling to power a plasma-processing reactor. As a result, the electric fields are too weak to levitate particles large enough to cause killer defects on etched wafers.

The discovery by the semiconductor industry that RF-powered plasmas can levitate dust particles turned out to be a boon for basic plasma physicists, who study such phenomena as waves and instabilities in ionized gases. Plasma physicists had heard astronomers talk of dusty plasmas in space, and they were eager to study them. The laboratory experimenter, however, has the difficulty that dust particles, unlike plasma ions and electrons, are so massive that they fall rapidly to the bottom of the chamber due to gravity. Experimenters needed a way to fill a volume of plasma with particles.

Then came Selwyn's unexpected discovery at IBM, N.Y., USA. When he was carrying out a routine measurement with laser-induced fluorescence, to determine the concentrations of reactive gases in a plasma, Selwyn shined his laser into the plasma. He attempted measurement of weak optical fluorescence that was overwhelmed by scattering of the incident light. The laser light was illuminating clouds of micron-sized particles electrically suspended in the plasma above the wafer (see Fig. 1.5). Selwyn found that particles actually formed and grew in the gas phase, aggregating material from gases that were thought to have been exhausted by the vacuum pump. Then, at the fateful moment when the plasma-generating RF power was switched off, the particles fell and contaminated the wafer. Selwyn's discovery revealed that much of the particle contamination responsible for costly yield losses was happening not just anywhere in the clean rooms, but inside the plasma reactors.

Immediately after the appearance of his paper in 1989 [51], plasma experimenters worldwide realized how they could levitate particles in an RF-generated plasma. Soon, other laboratory methods of filling a plasma volume were developed as well. One can, for example, maintain a dusty plasma by constantly showering dust particles in from above.

**Dust in fusion plasmas**

Much of plasma physics is devoted to developing controlled nuclear fusion. Igniting a fusion plasma requires heating deuterium and tritium nuclei to temperatures above 100 million Kelvin. At such high temperatures, however, any solid material is vaporized and highly ionized. Therefore nobody expected that dust particles could exist in a fusion plasma, much less that they could be a source of concern. It turns out, however, that a magnetically confined fusion plasma is in many ways dominated by the conditions at its edges, where it comes near material surfaces. The outer portions of the plasma typically have temperatures hundreds of times cooler than its center. In this more benign edge plasma, solid particles can survive briefly. Indeed, inspection of the bottom of magnetic-confinement fusion devices after periods of operation shows the presence of fine dust
1.4 Stainless-steel balls on a plane conductor

The experimental setup of this experiment as was realised by Coupier et al. [53] is shown in Fig. 1.6. It is composed of unique millimeter sized conducting balls. These balls are placed between two electrodes of a condensator. The lowest electrode is made from silicium and the top electrode from indium thin oxide (ITO). The inox conducting balls have a radius of $R = 0.4 \text{ mm}$ and mass $m = 2.15 \text{ mg}$. The balls become charged after applying a potential difference between the bottom and top electrode in the order of $kV$. As shown in Fig. 1.6, the potential difference results in a negative electrostatic charging of the top surface of the bottom electrode and the confinement frame and consequently of the balls itself on top of this surface. In this way the particles will be pushed inside by the confinement and repelled from each other by an electrostatic force. The interparticle interaction in this experiment can be well described by a modified Bessel function $K_0$, i.e., similar to the inter-vortex interaction in superconductors as was shown in Ref. [53]. An effective temperature was induced by a mechanical shaking produced by loud speakers.

Recently, the group of prof. Saint-Jean (University of Paris 6) studied the diffusion of macroscopic charged metallic balls moving in a circular channel such that mutual passing was forbidden. A typical example of the experimental system is given in Fig. 1.7. Diffusion of particles in a narrow channel where mutual passage is forbidden, and thus the sequence of particles remains the same over time, is known as single file diffusion (SFD). The authors found that the system of interacting balls exhibited a subdiffusive behavior slower than predicted for SFD ($t^{1/2}$). The $t^{1/2}$-behavior was previously observed in colloidal systems. In Chapter 8, I will discuss these experimental results further and give a theoretical explanation for it. Recent advances in nanotechnology has stimulated a growing interest in SFD, in particular, in the study of transport in nanopores. Separation, catalysis, and drug release all rely upon the controlled transport through microscopic channels.

1.5 Self-assembled aggregates of magnetized disks

An interesting experiment [54] was performed by Grzybowski et al. at the university of Harvard, where the self-assembly of millimeter-sized, magnetized disks floating on a
liquid-air interface, and rotating under the influence of a rotating external magnetic field was considered. Spinning of the disks results in a hydrodynamic repulsion between them, while the rotating magnetic field produces an average confining potential acting on all disks. The interplay between hydrodynamic and magnetic interactions between the disks leads to the formation of ordered patterns, which shows that it can be considered as a dynamic self-assembling system. All the disks in this experiment were identical, except for one or two which had a larger radius than the others. These results which inspired us to extend our previous work on classical systems to systems with one or two defects and to see if the obtained static configurations resemble the experimental dynamic self-assembled ordered structures. Below will give a short description of the experimental setup.

In Fig. 1.8 the schematic setup of the system is shown. Under the fluid, a rotating rectangular magnet is placed with an angular velocity of (200 – 1200 rpm). The distance between the top of the magnet and the fluid-air interface is \( H = 10 \) mm. On this fluid-
1.6 Magnetic fluids

A magnetorheological (MR) fluid is a field-responsive fluid that changes its properties under the application of an external magnetic field. Magnetic fluids are composed of micro-sized paramagnetic particles suspended in a non-magnetic carrier. Paramagnetic particles don’t have a net dipole moment in the absence of an external magnetic field. If these particles can form large-scale clusters and so overcome the thermal forces trying to break them apart, one speaks about super-paramagnetic particles. If an external magnetic field is applied, these particles will align in the direction of the magnetic field. By changing the external magnetic field it is possible to change the magnetic dipole of the particles and so the size of the inter-particle interaction and viscosity of the sample. If the external magnetic field is removed, the paramagnetic colloids lose their magnetization and the magnetic properties of the fluid are lost. In a Ferro fluid on the other hand, the particles are nano-meter sized ferromagnetic particles which have a permanent dipole. Because the
Figure 1.8: Schematic experimental setup of a rotating magnet experiment. (left) Disks are attracted to the center by the rotating magnet. Above is a qualitative profile showing the radial component of the magnetic force. In the middle the profile of the magnetic force $F_m$ is shown acted on a point object. Below a qualitative energy profile for an object located at the liquid-air interface. (Right) inter-disk interaction: (a-b) The rotating magnet induces a rotation of the disks; (c) Rotating disks create current fields in the surrounded liquid resulting in a repelling force between the magnets. (From Ref. [54])

dipole-dipole interaction between the particles is very weak, no large aggregates are found. Ferro fluids however have some interesting surface properties under the application of an external magnetic field, which makes them an interesting study object.

In this thesis we will consider only 2D fluids where the magnetic field is aligned perpendicular to the surface. In this way a magnetic dipole is induced by an external magnetic field perpendicular to the surface resulting in a dipole interaction between the particles. Small clusters of paramagnetic particles were investigated by R. Bubbeck et.al. [97] who used super-paramagnetic colloids confined in 2D cavities with quadratic, hexagonal or circular shapes. At low temperatures and in the case of circular cavities the clusters are found not to crystallize in a triangular lattice (Wigner crystal), but are arranged in a shell
Figure 1.9: A few typical configurations obtained by the rotating magnet experiment in which one larger particle is introduced. The arrows indicates the possible transitions from one state to another. (From Ref. [54])

Figure 1.10: Typical configuration of a 2D confined cluster of particles interacting through dipole interaction obtained R. Bubbeck et al. (From Ref. [57]).

structure. Accordingly, it was pointed out that such systems may be a ”realization” of a 2D Thomson atom where the structure as a function of the particle number can be analyzed in terms of a Mendeleev-type table. A typical configuration is shown in Fig. 1.10 which was studied theoretically in [56]. A possible application of super-paramagnetic particles one can find in photonic crystals. The problem with the current photonic devices is there limited tunability, their slow response on external stimuli and the difficulty to integrate them in an existing photonic system. Recently, researchers at the University of California used super-paramagnetic colloidal nanoclusters to construct photonic crystals
that overcome these challenges. diffracted ambient light by the photonic crystal will display peaks across the visible spectrum depending on the size of the nanoclusters and the strength of the applied magnetic field. a photonic crystal of magnetite particles is shown in fig. 1.11.

1.7 Paul trap for ions

A linear Paul trap and its realization is presented schematically in Fig. 1.12. A quadrupole field perpendicular to the trap axis (z-direction) is generated by four electrodes mounted such that by applying a RF-voltage of the same phase to diagonal electrodes, but with a phase shift of 180° with respect to the nearest electrodes. Each electrode is sub-divided into three parts such that a positive dc-voltage can be applied to the eight end-pieces. While this dc-voltage leads to static confinement along the z-direction, it leads to a defocusing force in the radial plane perpendicular to this axis. The radial and axial confinement can be controled by appropriate choices of the dc and RF-voltages and RF-frequency defining the parameters:

$$a = \eta \frac{8QU_{dc}}{m\omega_r^2z_0^2},$$  \hspace{1cm} (1.1)

$$q = \frac{2QU_{rf}}{m\omega_r^2r_0^2},$$  \hspace{1cm} (1.2)
1.7. Paul trap for ions

Figure 1.12: (a) Sketch of the linear trap used in the experiments of Ref. [58]. A quadrupole electric field is applied on the four electrodes. (b) Experimental setup of a Paul trap. (From Ref. [58])

Figure 1.13: Two-dimensional projection of a single species crystal of $^{24}Mg^+$ ions. The Coulomb crystals contains 500 ions for a series of different axial potentials. In all pictures, the rf voltage was constant, while the dc voltages $U_{dc}$ on the eight end-pieces was changed from (a) $U_{dc} = 0.01V$ to (c) 10V. (From Ref. [58])
1. Introduction

**Figure 1.14:** Images of fluorescence from a bi-crystal consisting of $^{40}\text{Ca}^+$ ions and $^{44}\text{Ca}^+$. (a) Fluorescence from the $^{40}\text{Ca}^+$ ions in the crystal. (b) Fluorescence from the $^{44}\text{Ca}^+$ ions in the crystal. (c) Combined image. (From Ref. [58])

where $\omega_{rf}$ and $U_{rf}$ are the frequency and amplitude of the RF-field, respectively, $m$ is the mass of the ion, $Q$ is the ion charge, $U_{dc}$ is the voltage applied to the end-pieces, $z_0$ and $r_0$ are the trap dimensions and $\omega$ is a positive geometric parameter dependent on $z_0$ and $r_0$. One can show that if $a$ and $q$ lie within certain stability regions stable single ion motion exist. Most of the time the motion is complex but when $q < 0.4$ a single ion not too far from the trap center will feel an effective harmonic potential:

$$\Phi(z,r) = \frac{1}{2}m(\omega_z^2z^2 + \omega_r^2r^2)$$

(1.3)

where $\omega_z$ and $\omega_r$ are the oscillation frequencies along the $z$-axis and in the radial plane, respectively, given by

$$\omega_z = \frac{1}{2}\omega_{rf}\sqrt{a},$$

(1.4)

$$\omega_r = \frac{1}{2}\omega_{rf}\sqrt{\frac{1}{2}(q^2 - a)}.$$  

(1.5)
In the radial plane, the ions will in addition to the force from the effective potential above, be subjected to a fast oscillating force at the RF-frequency, but it can be shown that the amplitude of the corresponding motion (often named micro-motion) always will be much smaller than the distance of the ion from the z-axis when \( q < 0.4 \).

**Ion Wigner crystals**

We know from section 1.2 that ordered states are formed, due to the combination of the trapping forces and the Coulomb repulsion, when \( \Gamma = E_{pot}/E_{kin} > 100 \). The potential energy of the ions with respect to their nearest neighbor at a distance given by the Wigner-Seitz radius \( a \), and \( E_{kin} \) is the average kinetic energy of the ions at temperature \( T \).

In general temperatures of \( T < 10 \text{ mK} \) are needed for crystallization. Even lower temperatures are found to be needed to obtain spatially ordered structures of two ion species that are simultaneously trapped.

The structure of the formed crystal depends on the trapping potential, and the number of different ion species. For a single ion species, the ideal crystalline structure is body-centered-cubic (bcc) in the limiting case of an infinite crystal. Such structures are only observed in the centers of the cold ion ensembles consisting of about \( 105 - 106 \) ions, while for smaller amounts of ions, the ions organize themselves in a near-hexagonal structure inside concentric shells which are spheroidal. In Fig. 1.13, images of the fluorescence from pure \( ^{24}\text{Mg}^+ \) ion crystals obtained by an image-intensified CCD-camera are shown. In these 2D projections of the Coulomb crystals, light from separate shells is observed (without any clear indication of the near-hexagonal in-shell ordering).

In the case of two-species crystals, the structures are more complicated. Since the potential given by Eq. (1.3) depends on the mass and charge of the trapped ions, two different ion species will normally separate radially as has been studied earlier in detail in the case of \( ^{24}\text{Mg}^+/^{40}\text{Ca}^+ \) bi-crystals. In Fig. 1.14, an image of a bi-crystal, consisting of two singly charged isotopes of calcium, is shown. Here, one clearly observes how the lighter \( ^{40}\text{Ca}^+ \) (Fig. 1.14 (a)) ions segregate around the trap axis in a close to cylindrical structure, while the heavier \( ^{44}\text{Ca}^+ \) (Fig. 1.14 (b)) ions form a surrounding shell structure with a spheroidal outer boundary. Fig. 1.14 (c) show the combined image of (a) en (b).

The density of the individual ion species is constant.

**1.8 Colloidal systems with competing interaction**

Competing attractive and repulsive interactions generate domain patterns in a wide variety of two- and three-dimensional systems in nature [59, 60]. In biology, liquid regions of biological membranes are formed by lipid bilayers and membrane proteins. The width
1. Introduction

Figure 1.15: (a) Elongated chains of dust grains like these appearing in the early stages of planet formation around a young protostar, according to a microgravity experiment inside a rocket. (From J. Blum, Braunschweig Technical University) (b) Particles in a floating gaseous disk collide induced by Brownian motion forming planetary seedlings. (From NASA/JPL-Caltech/G.Melnick) (c) Circular droplets of magnetic domains in mixed films. (d) After critical composition $\chi = 0.3$ the structure changes to stripes (From Ref. [71]) (e) A bubble of self-assembled cobalt nano-particles. (inset e) Fourier transform of (e). (f) Super-lattice of bubbles from self-assembled cobalt nano-particles. (From Ref. [69])

of the liquid domains depends on the competition between line tension and electrostatic dipolar repulsion. In magnetic materials the domain structure with alternating spin orientation originates from the competition between short-range exchange interaction and long-range dipole interaction [62]. In antiferromagnetic materials, or layered transition metal oxides, holes interact through a competing long-range and short-range potential [63, 64]. These competitions generate charge ordering and have possible relations to the mechanism of high-temperature superconductivity in doped cuprates [65] and bismuthates [?]. In materials science experiments with colloidal systems, combined with theoretical predictions, may lead to the design of novel soft materials and to a deeper un-
1.8. Colloidal systems with competing interaction

Figure 1.16: Confocal microscope images of colloid-polymer mixtures at different volume fractions. From left to right: $\phi_c = 0.080$, 0.094, and 0.156. The attractive part of inter-particle potential is the same in all samples. Images (a) and (b) contain clusters while (c) shows a cluster phase.

Understanding of the glass and gel states of matter [66]. In space, particles floating within a gaseous disk (Fig. 1.15 (b)) collide because of their constant thermal agitation, known as Brownian motion. Gravitational attraction is negligible for tiny dust grains, so they stick only through electrostatic van der Waals forces and repel each other by a Coulombic force. In Fig. 1.15 (a) loose aggregates of particles are shown with many branches in a complex network, like a portion of a spider’s web. This seedlings are seen as the building blocks for new planets. Another example are the dispersion properties of chemical synthesized cobalt nanoparticles which were studied experimentally [67] and are shown in Fig. 1.15 (e-f). The cobalt particles organize themselves in bubbles (Fig. 1.15 (e)) where each bubble is part of a super-lattice (Fig. 1.15 (f)).

Besides presenting a rich variety of cluster types and showing an excellent model for technological applications, colloidal systems have the added advantage of the facility to control the interaction between particles and of real time imaging of their configuration through video microscopy. A wide variety of activities studying colloidal systems were developed in order to understand the structure and dynamic of different kind of systems, such as colloidal particles interacting through a short-range attractive and long-range repulsive potential [68, 69, 70, 71]. In Ref. [71] domain-shape instabilities are investigated in a 2D binary mixture of near-critical composition, a monomolecular film confined to an air-water interface and composed of a phospholipid and cholesterol. Depending on the composition of the film a bubble like or stripe like phase is formed (Fig. 1.15 (c-d)). In Ref. [69] typical configurations of colloidal poly methyl methacrylate (PMMA) particles are investigated. The short-range attractive potential is induced by adding poly(styrene), a nonadsorbing polymer. In Fig. 1.16 typical configurations are shown. Depending on the volume fraction $\phi_c$ of colloidal PMMA particles, they organize themselves in a cluster phase (bubbles) or a network phase (stripes). Another experiment is a binary system of
super-paramagnetic colloidal particles that are confined to a two-dimensional water-air interface and exposed to an external magnetic field perpendicular to the interface showed diverse configurations [3]. Moreover, the authors observed that clustering appeared only for one type of particles, instead of the whole system. Recently, several models were developed having a small number of interacting particles in order to understand the behavior of colloidal systems as a function of temperature [72, 73, 74]. Different melting scenarios were studied extensively in systems consisting of charged particles for a range of inter-particle interaction types and trap types, such as charged particles confined by a circular hard-wall potential interacting by a repulsive dipole potential [75]. Other experimental realizations of systems with competing interactions are the dynamic self-assembly of rings of charged metallic spheres [76, 77], pattern formation in dynamical systems [78] and crystallization and aggregation in a colloid-polymer suspension [79].
2.1 Monte Carlo

Monte Carlo simulation methods are statistical simulation methods, where statistical simulation is defined in quite general terms to be any method that utilizes sequences of random numbers to perform the simulation. Monte Carlo methods have been used for decades, but only in the past several decades has the technique gained the status of a full-fledged numerical method capable of addressing the most complex applications. The name “Monte Carlo” was coined by Metropolis (inspired by Ulam’s interest in poker) during the Manhattan Project of World War II, because of the similarity of statistical simulation to games of chance, and because the capital of Monaco was a center for gambling and similar pursuits. Monte Carlo simulations are now used routinely in many diverse fields.

Conventional discretization methods solve in general directly the partial differential equations which describes the underlying physical or mathematical system. Assuming that the evolution of the physical system under investigation can be described according to a probability density function (PDF), Monte Carlo simulation can proceed by sampling this PDF. In this way for many applications their is even no need to write down the differential equations that describe the behavior of the system. The only requirement is that the physical (or mathematical) system be described by pdf’s. Many simulations are then performed (multiple ”trials” or ”histories”) and the desired result is taken as an average over the number of observations (which may be a single observation or perhaps millions of observations). In many practical applications, one can predict the statistical error in this average result, and hence an estimate of the number of Monte Carlo trials that are needed to achieve a given maximum error.

From classical physics we know that the average value of a variable $A$ is given by:

$$< A > = \frac{\int_{\Omega} P(p^n, r^n) A(p^n, r^n) dp^n dr^n}{\int_{\Omega} P(p^n, r^n) dp^n dr^n},$$

(2.1)

where $p^n$ and $r^n$ represent the momenta of the $n$ particles respectively and $P(p^n, r^n)$ the PDF. Equation 2.1 gives the average value of the observable $A$, averaged over the points $(p^n, r^n)$ in the volume $\Omega$ in phase space. If the kinetic energy is a quadratic function of the
momenta the integration over momenta can be carried out analytically. The most difficult problem is then to compute the average function \( A(\mathbf{r}^n) \) and the problem reduces to:

\[
\langle A \rangle = \frac{\int_{\Omega} P(\mathbf{r}^n) A(\mathbf{r}^n) d\mathbf{r}^n}{\int_{\Omega} P(\mathbf{r}^n) d\mathbf{r}^n}, \tag{2.2}
\]
or in discrete form:

\[
\langle A \rangle = \frac{\sum_{i=1}^{N} P(r_i) A(r_i)}{\sum_{i=1}^{N} P(r_i)}, \tag{2.3}
\]

where \( N \) is the number of states and \( Z = \sum_{i=1}^{N} P(r_i) \) is the partition function. Because it is not possible to compute the above equation exactly, because of the high number of states, one has to find another method for calculating the average value of the observable. One of these other methods is the Monte Carlo metropolis method which will sample the PDF.

The most often used algorithm today is the Metropolis algorithm which has been introduced by Nicolas Metropolis and co-authors in 1953. A Monte Carlo method consists of two stages. First a trial move bringing the system from the initial state \( o \) to the state \( n \) according to the properties of the distribution of a Markov chain. Having the Markov property means that given the present state, the future states are independent of the past states. The transition probability in a Markov chain of going from the initial state \( o \) to the state \( n \) is normally represented by \( \alpha(o \rightarrow n) \). The second stage is the decision to either accept or reject the trial move from \( o \) to \( n \) by \( \text{acc}(o \rightarrow n) \). The transition probability of going from state \( o \) to \( n \) is then:

\[
\mathcal{W}(o \rightarrow n) = \text{acc}(o \rightarrow n) \alpha(o \rightarrow n). \tag{2.4}
\]

If one wants to be sure to be in equilibrium, the average number of accepted trial moves for leaving state \( o \) must be exactly equal to the number of accepted trial moves from all other states \( n \) to state \( o \). To be sure that the system is in equilibrium it is convenient to impose a much stronger condition; namely that the average number of accepted moves from \( o \) to any other state \( n \) is exactly canceled by the number of reverse moves. This detailed balance can be written as:

\[
P(o) \mathcal{W}(o \rightarrow n) = P(n) \mathcal{W}(n \rightarrow o), \tag{2.5}
\]

where \( P(o) \) is the probability to be in a given state \( o \). If \( \alpha \) is symmetric we can rewrite Eq. (2.5) as:

\[
P(o) \text{acc}(o \rightarrow n) = P(n) \text{acc}(n \rightarrow o). \tag{2.6}
\]
From these equations follows that:

\[
\frac{\mathcal{W}(o \to n)}{\mathcal{W}(n \to o)} = \frac{P(n)}{P(o)} = e^{-\frac{H(n)}{k_B T}} Z e^{-\frac{H(o)}{k_B T}} = e^{-[H(n) - H(o)]/k_B T},
\]

(2.7)

(2.8)

(2.9)

where \( H \) represent the Hamiltonian of the system. In order to satisfy these conditions Metropolis et al. [80] choose for the following scheme:

\[
\text{acc}(o \to n) = \begin{cases} 
P(n)/P(o) & \text{if } P(n) < P(o) \\ 1 & \text{if } P(n) \geq P(o) \end{cases}
\]

(2.10)

(2.11)

The last thing to explain now is how to decide whether a trial move is accepted or rejected. Suppose that \( H(n) > H(o) \) than according to Eq. (2.9) the move is accepted with a probability:

\[
\text{acc}(o \to n) = \exp(-[H(n) - H(o)]) < 1
\]

(2.12)

It is essential that the random displacement should not introduce a bias into the sampling. The efficiency of the algorithm depends on the random number generator and on the choice of the random displacements. When the displacement is very small almost every move will be accepted, but it will take a large number of moves to cover the whole available phase space. When the displacement is very large the acceptance ratio will be very small.

A big advantage of the Metropolis method is that only the energies need to be calculated, neglecting the real time evolution of the system. In this way it is possible to get average values of observables depending only on the system configurations. In order to determine quantities, which depend also on the particle velocities, it is possible to introduce some improvements in the technique, but usually one prefers to use other numerical methods, e.g. Molecular Dynamics (MD) simulations.

### 2.2 Molecular Dynamic simulation

We call molecular dynamics (MD) a computer simulation technique where the time evolution of a set of interacting atoms is followed by integrating their equations of motions. These equations of motions mostly follow the Newton law and are given by:

\[
F_i = m_i a_i
\]

(2.13)
for each particle $i$ in a system constituted of $N$ particles. Where $m_i$ is the particle mass, $a_i = d^2 r_i / dt^2$ its acceleration, and $F_i$ the force acting on the particles due to the other particles and/or external forces. These equations are solved by time integration based on finite difference methods, where the time step is discretized on a finite grid, with the time step $\Delta t$ as the distance between two consecutive grid points. If one knows the position and their time derivatives at time $t$, the scheme gives the same quantities at a later time $t + \Delta t$. By iterating this procedure, the time evolution of the system can be followed for long times. In contrast with the Monte Carlo method, Molecular dynamics is a deterministic technique because after knowing all initial coordinates (positions, velocities, and forces), the trajectories of the particles are completely determined. On the other hand, molecular dynamics is a statistical mechanics method, because like Monte Carlo, it is a way to obtain a set of configurations distributed according to some statistical distribution function, or statistical ensemble. Physical quantities are represented by averages over configurations distributed according to a certain statistical ensemble. This set of configurations can be obtained using MD. A physical quantity is than obtained by averaging an instantaneous value of a quantity during a MD run. The link between the microscopic behavior and thermodynamics is then given by statistical physics. In the case that one would run a simulation for infinite time, one would be able to sample the full phase space density, and in this limit would yield the thermodynamic properties. In practice simulations are not infinite and one has to estimate when the sample of the phase space is good or not. Therefore MD can be used for estimating thermodynamic properties if the sampling occurs in a proper way. MD is nowadays a very important tool to study e.g. liquids, defects, fractures, surfaces, friction, clusters, biomolecules and electronic properties and dynamics. Further MD can be used to study non-equilibrium processes, and can be an efficient tool for finding a global minimum by overcoming the local minimum with the simulated annealing method. Simulated annealing is a well-known stochastical method for global optimization that is inspired to thermodynamics. It combines the fast convergence speed of the Metropolis algorithm at high temperature with the high probability of finding the optimal solution at low temperature. The basic idea is to start from a very high temperature and then to slowly lower it. This approach is the computer analogue of the thermal process, called annealing (hence the name), used in condensed matter physics to obtain solids with low energy states, for example in steel production and crystallization processes. By mean of the simulated annealing procedure the system is given the opportunity to surmount energetic barriers around the local minima and to explore larger portions of the phase space in the search for the global minimum.

The physical model determines the interaction between the particles and other external forces acting on them. The potential $V(r_1, r_2, ..., r_N)$ is a function of the positions of the particles. If the forces acting on each particle are independent of the velocities, the forces
can be derived as the gradient of the potential with respect to the particle positions:

\[ F_i = -\nabla r_i V(r_1, r_2, ..., r_N). \]  (2.14)

This form implies the conservation law of total energy \( E = K + V = \text{constant} \), where \( K \) is the instantaneous kinetic energy. Because the potential is very important a lot of research is directed to the development of it. Beside the potential also the integration scheme to integrate the equations of motions are of major importance. Next, we will discuss the Verlet integration scheme.

Integration scheme

The most commonly used time integration algorithm is probably the so-called Verlet algorithm. The idea is to write two third-order expansions for the positions \( r(t) \), one forward and one backward in time giving the following equations:

\[
\begin{align*}
    r(t + \Delta t) &= r(t) + v(t)\Delta t + (1/2)a(t)\Delta t^2 + (1/6)b(t)\Delta t^3 + O(\Delta t^4), \\
    r(t - \Delta t) &= r(t) - v(t)\Delta t + (1/2)a(t)\Delta t^2 - (1/6)b(t)\Delta t^3 + O(\Delta t^4),
\end{align*}
\]

where \( v \) are the velocities, \( a \) the accelerations, and \( b \) the third derivative with respect to \( t \).

Adding these two expressions gives:

\[
    r(t + \Delta t) = 2r(t) - r(t - \Delta t) + a(t)\Delta t^2 + O(\Delta t^4),
\]

which is the basic form of the Verlet algorithm. From Newton's law we know that the acceleration \( a(t) \) is nothing else than the force divided by the mass and we got:

\[
    a(t) = -(1/m)\nabla V(r(t)).
\]

because the higher terms from the 4th order are neglected, this algorithm is called a fourth order algorithm. A problem with this variant of the Verlet algorithm can be that the velocities are not calculated directly. However, they are not needed for the time evolution but their information is sometimes important. One could calculate in that case the velocities from the position using:

\[
    v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t} \quad (2.15)
\]

Probably the best way to implement this algorithm is the use of the following form:

\[
\begin{align*}
    r(t + \Delta t) &= r(t) + v(t)\Delta t + (1/2)a(t)\Delta t^2, \\
    v(t + \Delta t/2) &= v(t) + (1/2)a(t)\Delta t, \\
    a(t + \Delta t) &= -(1/m)\nabla V(r(t + \Delta t)), \\
    v(t + \Delta t) &= v(t + \Delta t/2) + (1/2)a(t + \Delta t)\Delta t, \quad (2.16)
\end{align*}
\]
where position, velocity and acceleration are calculated at the same time. This is also the method used for the calculation of most of the dynamical properties in the following of this thesis.

**Heat bath**

In the constant temperature method proposed by Andersen [81] the system is coupled to a heat bath that imposes the correct temperature by contacting it with a large heat bath. Under those conditions, the probability of finding the system in a given energy state is given by the Boltzmann distribution. The coupling to a heat bath is represented by stochastic impulsive forces that act occasionally on randomly selected particles. These stochastic collisions with the heat bath can be considered as Monte Carlo moves that transport the system from one constant energy shell to another. Between stochastic collisions, the system evolves at constant energy according to the normal Newtonian laws of motion. The stochastic collisions ensures that all accessible constant-energy shells are visited according to their Boltzmann weight.

So if we want to model a collision with a heat bath, we should first select the strength of the coupling to the heat bath. This coupling strength is determined by the frequency of stochastic collisions, $\nu$. If successive collisions are uncorrelated, then the distribution of time intervals between two successive stochastic collisions, $P(t; \nu)$, is of the Poisson form:

$$P(t; \nu) = \nu \exp[-\nu t]$$  \hspace{1cm} (2.17)

where $P(t; \nu)$ is the probability that the next collision will take place in the interval $[t, t + dt]$. A simulation at constant temperature consist then of the following steps:

- Integrate the equations of motions over a time $\Delta t$.
- Select randomly particles to undergo a collision with the heat bath with probability $\nu \Delta t$ in a time interval $\Delta t$.
- If a particle is selected its velocity will be set according to the Maxwell-Bolzmann distribution corresponding with the desired temperature $T$.

### 2.3 Langevin Dynamics

The simulation technique we will describe in this section is an extention of molecular dynamics simulations with an additional random term. In classical molecular dynamics simulation the Newton equations of motion are solved ignoring the surrounding medium.
If however the particles are suspended in a liquid medium a lot of other forces due to friction and interactions with the molecules of the surrounding medium will act on the particle. One of the possible ways to solve this problem is by solving the traditional Newton equations including all the interactions between the liquid molecules and the suspended particle. The problem found here is a timescale separation problem, which occurs when one form of motion in the system is faster (the molecules) than another (suspended particles). Because the motion of the solvent are little of interest the solution of our problem will be to omit them from the simulation, and to model their effect by a combination of random forces and friction terms. In the case the system is in thermal equilibrium with a heat bath the motion of the suspended particles can be properly described by the Langevin equations.

The Langevin equation is a stochastic differential equation in which two force terms are added to Newton’s second law in order to approximate the effects of neglected degrees of freedom: one term presents the friction force which is proportional to the velocity of the particle and the other one a random force. Both forces should be in equilibrium since the random term removes kinetic energy out of the system and the random force adds energy to the system.

The first theoretical basis of this theory of simplifying the equations of motion, and removing the rapidly varying degrees of freedom was given by Zwanzig in 1960 and by Mori in 1965. They introduced the "projection operators" in order to obtain a "reduced description" of the system. The aim of this approach was to divide the phase-space into two parts, namely the interesting and uninteresting degrees of freedom. The aim is to end up with an equation involving only the set of interesting variables and not the others.

The formal equations of motion for Langevin dynamics for an one-dimensional system is given by:

\[
\begin{align*}
m \, dv &= -m\gamma v \, dt + F(x) \, dt + dR(t), \\
dr &= v \, dt,
\end{align*}
\]

where the first term at the right side is the friction term with \( \gamma \) the friction constant and \( m \) the particle mass, the second term is the interaction term and the third term \( R \) is the stochastic term. \( R \) is a stochastic process known as a Wiener process. A Wiener process is characterized by the following three facts:

1. \( R(t) \) is normally distributed for \( t \geq 0 \);
2. \( \langle R(t) \rangle = 0 \) for \( t \geq 0 \);
3. \( R(0) = 0 \)
The spread of the distribution of $R(t)$ is coupled to the friction by the fluctuation-dissipation theorem which balance the dissipated energy due to the friction with added energy of the random term by the following expression:

$$\langle R(t)R(t+\tau) \rangle = 2m\gamma k_BT\tau$$

The differential form for the Langevin equations in Cartesian coordinates is:

$$m_i \frac{d^2 r_i}{dt^2} = -m_i \sum_j \Gamma_{ij} \frac{dr_j}{dt} + f_i(r_i) + \xi_i,$$

where the subscript $i$ denotes the particle number, $\Gamma_{ij}$ is a $3 \times 3$ friction matrix, $f(r) = -\nabla V(r)$ and $\xi_i$ is a random force, often called noise. In most cases the friction matrix is diagonal and isotropic, which simplify the form of Eq. (2.18) to:

$$m_i \frac{d^2 r_i}{dt^2} = -m_i \gamma_i \frac{dr_i}{dt} + f_i(r_i) + \xi_i,$$

with $\gamma_i$ the friction coefficient of the $i^{th}$ particle.

Without memory of the history of the system, the noise is not correlated in time and gaussian distributed. The correlation is, thereby, given by:

$$\langle \xi_{ik}(t)\xi_{jl}(t+\tau) \rangle = 2m_i\gamma_i k_BT \delta_{ij}\delta_{kl}\delta(\tau),$$

where $k$ and $l$ indicate the Cartesian vector components, $\delta_{ij}$ is the Kronecker delta and $\delta(\tau)$ is the Dirac delta function.

### 2.4 Brownian Dynamics

Brownian dynamics (BD) is a simplified version of Langevin dynamics and corresponds to the limit where no average acceleration takes place during the simulation run. This approximation can also be described as 'overdamped' Langevin dynamics, or as Langevin dynamics without inertia. The equation of motion is then given by:

$$0 \approx -m\gamma v dt + F(x) dt + dR(t),$$

where $F(x)dt$ describes the force as calculated from the particle interaction potentials; $m\gamma v dt$ describes the velocity-dependent friction; and $R(t)$ is a random noise term. As on average no acceleration is assumed to take place, the sum of the time average of these terms is zero.
2.5 Model systems

2.5.1 Colloidal dipole particles

In this model, like the experiment of Ref. [82], the particles are confined by a circular hard wall potential ($V_P = 0$ for $r \leq R$ and $V_P = \infty$ for $r > R$). Like the results of the experiment shown in Fig. 1.10, the particles interact through a repulsive dipole potential $V(\vec{r}_i, \vec{r}_j) = q_i q_j / |\vec{r}_i - \vec{r}_j|^3$, where $q_i = M_i \sqrt{m_0 / 4\pi}$ is the ‘charge’ and $\vec{r}_i$ the coordinate of the $i^{th}$ particle. For a given type of inter-particle interaction and external confinement, only three parameters characterize the order of the system namely: i) the number of big particles $N_B$, ii) the number of small particles $N_S$ (also called defect particles), and iii) the coupling parameter $\Gamma$. In the experiment the diameter of the big particles is twice the diameter of the small particles [82], therefore we have chosen the charge of the small particles to be $1/8$th of the charge of the big particles. We define the characteristic energy of the inter-particle interaction for dipole clusters as $E_0 = q^2 / a_0^3$, where $a_0 = 2R / N_B^{1/2}$ is the average distance between the big particles. In the present calculation we define the coupling parameters as $\Gamma = q^2 / a_0^3 k_B T$, where $k_B$ is the Boltzmann constant and $T$ the temperature of the medium.

The ratio of the particle velocity relaxation time versus the particle position relaxation time is very small due to the viscosity of water and consequently the motion of the particles is diffusive and overdamped. In our simulations we will neglect hydrodynamic interactions. Following [83] we rewrite the stochastic Langevin equations of motion for the position of the particles as those for Brownian particles:

$$\frac{d\vec{r}_i}{dt} = \frac{D_i}{k_B T} \left\{ \sum_{j=1}^{N} \frac{dV(\vec{r}_i, \vec{r}_j)}{d\vec{r}} + \frac{dV_P(\vec{r}_i)}{d\vec{r}} + \frac{\vec{F}_L^i}{m_i} \right\},$$

where $D_i$ is the self-diffusion coefficient and $m_i$ is the particle mass of the $i^{th}$ particle, and $\vec{F}_L^i$ is the randomly fluctuating force acting on the particles due to the surrounding media. In the numerical solution of Eq. (9.4) we took a time step $\Delta t \leq 10^{-4} / (n D_B)$, where $n = N_B / (\pi R^2)$ is the density of the big particles. The radius of the circular vessel is $R = 36 \mu m$ and the self-diffusion coefficient of the big particles $D_B = 0.35 \mu m^2/s$ is taken from the experiment [82]. As the self-diffusion constant is inversely proportional to the particle diameter (from the Stokes-Einstein relation $D = k_B T / 8 \pi \nu a$, with $\nu$ the viscosity of the fluid and $a$ the particle diameter) we took $D_S = 0.7 \mu m^2/s$ for the small particles.
2. Model System and Numerical Approach

2.5.2 Rotating magnets

An experiment of rotating magnets at a liquid air interface is shown in Fig. 1.8. In Ref. [54] an empirical Hamiltonian for the experimental system was proposed, namely:

\[ H = \sum_i c_1(H, M) r_i^2 + \sum_{i<j} c_2(\omega, a_1, a_2, \rho) \frac{1}{|r_i - r_j|^2}. \] (2.23)

The first term is the confinement potential due to the rotating magnet. The confinement strength \( c_1 \) depends on the magnetization \( M \) of the magnet and its distance \( H \) from the interface. The second term describes the hydrodynamic repulsion between the disks. The coefficient \( c_2 \) depends on the angular velocity \( \omega \) of the magnet, the radii of the particles \( a_1 \) and the defect(s) \( a_2 \), and the density \( \rho \).

Motivated by this empirical Hamiltonian, we consider a system with \( N \) point-like classical particles interacting through a more general \( 1/r^n \) potential. The particles are free to move in two-dimensions but are confined by a parabolic trap centered at the origin. The general Hamiltonian of the system for particles with different masses and charges is:

\[ H = \frac{1}{2} \sum_{i=1}^{N} m_i^* \omega_0^2 r_i^2 + \frac{1}{\varepsilon} \sum_{i<j} q_i^* q_j^* \frac{1}{|r_i - r_j|^{n}}, \] (2.24)

where \( m_i^* \) is the effective mass of the particle and \( q_i^* \) its charge, \( \omega_0 \) the radial confinement frequency, and \( \varepsilon \) the dielectric constant of the medium the particles are moving in. The Hamiltonian can be transformed to a dimensionless form using the following units: \( r_0 = (2 Q^2 / M \varepsilon \omega_0^2)^{1/(1+n)} \) for the length and \( E_0 = M \omega_0^2 r_0^2 / 2 \) for the energy. \( M \) and \( Q \) represent the reference mass and charge. After rescaling we can write the Hamiltonian in dimensionless form

\[ H = \sum_{i=1}^{N} m_i r_i^2 + \sum_{i<j} q_i q_j \frac{1}{r_i - r_j}, \] (2.25)

with \( m_i = m_i^* / M \) and \( q_i = q_i^* / Q \) respectively the rescaled mass and charge of particle \( i \). We take \( m_i = 1 \) and \( q_i = 1 \) for all particles except one or two.

2.5.3 Stainless Steel balls

In the experiment of stainless steel balls we model the inter-particle interaction by a simplification of the \( K_0 \) potential. The Langevin equation for a system of \( N \) interacting particles is given by:

\[ m \frac{d^2 \vec{r}_i}{dt^2} = -\alpha \frac{d\vec{r}_i}{dt} + \frac{q_i^2}{\varepsilon} \sum_{j \neq i}^{N} \frac{e^{-|\vec{r}_i - \vec{r}_j|/\kappa}}{|\vec{r}_i - \vec{r}_j|} + \vec{F}_L, \] (2.26)
where $t$ is the time, $q$ is the particle charge, $\alpha$ is the friction, $m$ stands for the particle mass, $\vec{r}_i$ is the coordinate of the $i^{th}$ particle, $1/\kappa = \lambda$ is the screening length, and $\vec{F}_L$ is the random force which obeys the conditions: $\langle F(t) \rangle = 0$ and variance $\langle F(t)F(t') \rangle = k_B T$. The damping coefficient is given by $\nu = \alpha/m$. In dimensionless units this equation reads:

$$\frac{d^2 \vec{r}'_i}{dt'^2} = -\nu \frac{d \vec{r}'_i}{dt'} + \sum_{j \neq i} e^{-|\vec{r}'_i - \vec{r}'_j|/\kappa'} \frac{\vec{r}'_i - \vec{r}'_j}{|\vec{r}'_i - \vec{r}'_j|} + \vec{F}'_L(t), \quad (2.27)$$

where the time $t'$ is given in units of $(r_0/q)\sqrt{me/\kappa}$, the damping coefficient $\nu'$ is given in units of $(1/t')$, where $\eta'$ is the friction, $r' = r/r_0$, $T' = k_B T$ and $\vec{F}'_L(t)$ is the dimensionless random force. Because increasing $r_0$ is the same as increasing $\kappa$ we will fix $\kappa' = 1$. Because the friction $\nu'$ scales with time we will fix $\nu' = 10000$. Further all the primes will be omitted. In our simulation the hydrodynamic interactions are neglected.

### 2.5.4 Competing interactions

In this model system we are interested to study the effect of the competition of a short range attraction and a long range repulsion on the configurations in a finite system. We considered a system with $N$ point like classical particles interacting through a repulsive Coulomb potential and an attractive exponential potential as in Refs. [118, 119]. The particles move in two dimensions where they are confined by a parabolic potential trap centered at the origin. The general dimensionless Hamiltonian of the system is written as

$$H = \sum_{i=1}^{N} \vec{r}'^2_i + \sum_{i<j} \left( \frac{1}{|\vec{r}'_i - \vec{r}'_j|} - Be^{-\kappa'|\vec{r}'_i - \vec{r}'_j|} \right), \quad (2.28)$$

using the following units: $r' = (2q^2/me\omega_0^2)^{1/2}$ for the length, $E' = m\omega_0^2 r_0^2/2$ for the energy with $m$ the mass of the particles and $\omega' = \omega_0/\sqrt{2}$ for the frequency with $\omega_0$ the strength of the confinement potential. Note that the strength of the confinement potential in combination with the strength of Coulomb repulsive part of the inter-particle interaction determine the length and energy scale. The first term is the confinement potential, the second the repulsive part of the inter-particle potential and the last the attractive part. The exponential term is determined by two parameters $B$ and $\kappa$, where $B$ determines the strength and $\kappa$ the interaction range of the attractive part of the inter-particle potential. Notice that the repulsive part is long range while the attractive part is short range.
2.5.5 Coulomb interaction

We consider the classical 2D system consisting of charged particles which are laterally confined by a parabolic potential and interact through the Coulomb potential. The system is described by the Hamiltonian

\[ H = \frac{1}{2} m^* \omega_0^2 \sum_{i=1}^{N} r_i^2 + \frac{1}{\varepsilon} \sum_{i<j}^{N} \frac{e^2}{|r_i - r_j|}, \]  

(2.29)

where \( m^* \) is the effective mass of the particle, \( e \) the particle charge, \( \omega_0 \) is the confinement frequency, and \( \varepsilon \) is the dielectric constant of the medium where the particles are moving in. If we choose \( r_0 = (e^2/\varepsilon m^* \omega_0^2)^{1/3} \) as length unit and \( E_0 = m^* \omega_0^2 r_0^2 \) as energy unit \([108]\), the Hamiltonian can be expressed in dimensionless form as:

\[ H = \frac{1}{2} \sum_{i=1}^{N} r_i^2 + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}. \]  

(2.30)

Above model is used to model the dust particles in dusty plasma experiments.

2.6 Bounding dissipation in stochastic models

In equilibrium statistical physics is the microscopic foundation of thermodynamics built around the concept that the entropy is equal to the logarithm of the phase volume. To make this theory accessible for out-equilibrium, this theory was extended to the regime of linear irreversible thermodynamics. This method had the disadvantage only to work for systems near equilibrium. For systems far from equilibrium new techniques had to be found and people started investigating fluctuation \([84, 85, 86, 87]\) and work \([88, 89, 90, 91, 92]\) theorems, which point to the existence of exact equalities valid independent of the distance to equilibrium. One of these theorems was the work theorem of Jarzynski and Crooks.

However, these work and fluctuation theorems are very interesting for the study of small systems, they don’t provide additional information about the average delivered work and entropy production. Recently, the microscopically exact value of the average work has been obtained in a set-up similar to the work theorem of Jarzynski and Crooks \([92]\). Here they describe a system by a) Hamiltonian \( H(\lambda, \gamma) \), where \( \lambda \) represents the phase-space coordinates \( \lambda = (p, q) \), nl. the positions and momenta, and where \( \gamma \) is an external control parameter (e.g. an external field or volume). If one changes \( \gamma \) from an initial value to a final value, the second law of thermodynamics stipulates that the average work \( \langle W \rangle \) of going from equilibrium state \( A \) to equilibrium state \( B \), is at least equal to the free energy
difference between these two states: \( \langle W \rangle \geq \Delta F = F_B - F_A \). The average work used for bringing the system to the new equilibrium position is than equal to: \( \langle W \rangle - \Delta F \) which is called the dissipated work. This amount of energy is random because of the randomness of the initial state. By performing than repeated experiments starting from different initial coordinates, one can sample in principle the probability density \( \rho(\lambda; t) \) for a system to be in a certain micro-state \( \lambda \) at a certain time \( t \). After, one considers the time-reversed scenario of starting at the final value of the control parameter \( \gamma \) and going back to the initial value of \( \gamma \) while and measuring the phase-space density \( \tilde{\rho}(\lambda; t) \). The dissipated work \( \langle W \rangle - \Delta F \) is than given by:

\[
\langle W \rangle - \Delta F = k_B T \int d\lambda \rho(\lambda; t) \ln \frac{\rho(\lambda; t)}{\tilde{\rho}(\lambda; t)}. \tag{2.31}
\]

Above equation fully reveals exactly the microscopic nature of the dissipation, and is valid even for a system far out of equilibrium. The disadvantage is that it requires full statistical information on all the microscopic degrees of freedom of the system. In this thesis I will try to find strategies to calculate good estimates of the dissipated work of the system using only a limited number of degrees of freedom.
2. Model System and Numerical Approach
Chapter 3

Eigenmode Spectrum

The frequency spectrum of a system of classical charged particles interacting through a Coulomb repulsive potential and which are confined in a two-dimensional parabolic trap is studied. It is shown that, apart from the well-known center-of-mass and breathing modes, which are independent of the number of particles in the cluster, there are more ‘universal’ modes whose frequencies depend only slightly on the number of particles. To understand these modes, the spectrum of excitations as a function of the number of particles is compared with the spectrum obtained in the hydrodynamic approach. The modes are classified according to their averaged vorticity and it is shown that these ‘universal’ modes have the smallest vorticity and follow the hydrodynamic behavior.

3.1 Introduction

Classical clusters of repulsive particles confined in traps are both theoretically and experimentally a study object for many decades due to their applicability to a wide variety of systems. Recently, there has been considerable theoretical and experimental progress in the study of mesoscopic systems consisting of a finite number of charged particles confined in a parabolic trap. These systems are composed of a finite number of charged classical particles which can move in a two-dimensional (2D) plane and are confined in the plane by an external applied potential. They are the classical analogue of the 2D quantum dot. Typical experimental realizations of such systems are electrons on the surface of liquid helium [93], electrons in quantum dots [94], plasma’s with dust particles [16], ion traps [22], vortices in superfluids [30], confined ferromagnetic particles [95], charged metallic balls above a plane conductor [96] and colloidal crystals [95, 97]. The 2D charged clusters also resemble the problem of charge distribution studied by Mayer [98] and by Thomson in his “plum-pudding” model of the atom [99, 100].

Such Coulomb clusters with a finite number of particles (typical $N < 100$) have been extensively studied during the past few years. Theoretically, the configurations [101, 102], the transitions to metastable states [102, 103], normal modes [104] and the melting properties have been studied.

Recently, also experimentally the dynamical properties of Coulomb clusters have been studied in which a selective excitation of modes was performed [105, 106]. The successful extraction of the excitation spectrum from the thermal Brownian motion of the
particles in the cluster [107] apparently shows the usefulness of such 2D finite Coulomb clusters with a small number of particles being an ideal tool for comparison with detailed modelling.

Motivated by the experimental ability of selectively excitation of modes, we performed a detailed study of the spectrum of a Coulomb cluster and trace the dependence of the modes on the number of particles and compare the spectrum with the hydrodynamic treatment.

This chapter is organized as follows: In section 3.1 we present our simulation method for the discrete system and in section 3.3 the hydrodynamic approach. In section 3.4 the results of both models are compared, and the vorticity of the different modes are calculated. In section ?? our conclusions are formulated.

### 3.2 Discrete system simulation

We consider the classical 2D system consisting of charged particles which are laterally confined by a parabolic potential and interact through the Coulomb potential. The system is described by the Hamiltonian

\[ H = \frac{1}{2} m^* \omega_0^2 \sum_{i=1}^{N} r_i^2 + \frac{1}{\varepsilon} \sum_{i<j}^{N} \frac{e^2}{|r_i - r_j|}, \quad (3.1) \]

where \( m^* \) is the effective mass of the particle, \( \omega_0 \) is the confinement frequency, and \( \varepsilon \) is the dielectric constant of the medium where the particles are moving in. If we choose \( r_0 = (e^2/\varepsilon m^* \omega_0^2)^{1/3} \) as length unit and \( E_0 = m^* \omega_0^2 r_0^2 \) as energy unit [108], the Hamiltonian can be expressed in dimensionless form as:

\[ H = \frac{1}{2} \sum_{i=1}^{N} r_i^2 + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}. \quad (3.2) \]

To find the minimum energy configuration we used the Monte Carlo simulation technique extended with a Newton optimization technique, as first used in Ref. [104]. In order to be sure to have found the ground state configuration, one has to run the Monte Carlo simulation routine many times starting with a different initial random configuration. The spectrum of all system excitations and the corresponding particle velocities for every excitation mode were defined via the diagonalization of the dynamical matrix, which is given by:

\[ \frac{\partial H}{\partial r_{\alpha,i} \partial r_{\beta,j}}, \quad (3.3) \]

with \( \alpha \) and \( \beta = x, y \) and \( i,j \) denoting the particle number.
To be sure that the obtained configuration is a stable one, the lowest eigenvalue of the
dynamical matrix is checked to be positive.

The obtained excitation spectrum for clusters containing up to \( N = 100 \) particles is
shown in Fig. 3.1. The solid curve approximately indicates the upper limit of this spec-
trum. The two frequencies which are independent of the number of particles are clearly
seen: the center-of-mass mode with \( \omega = 1 \) and the breathing mode with \( \omega = \sqrt{3} \), in-
dicated by the black arrows. However a close inspection reveals that more horizontal
lines are present, some of them are indicated by the open arrows in Fig. 3.1. The exist-
tence of such modes which frequency is almost independent of the number of particles
is better seen in the frequency histogram shown in Fig. 3.2, or in the positive values of
the derivative of it shown in Fig. 3.3. The histogram was calculated taking into account
the frequencies for all systems with different number of particles ranging from 2 to 100.
Peaks in Fig. 3.2 and 3.3 indicate that in the considered system there are excitation modes
with a frequency which almost does not depend on the number of particles in the cluster.
As shown in the next section, they are related to the excitation frequencies in the hydro-
dynamic approach where all frequencies are independent of the number of particles.

### 3.3 Hydrodynamic approach

The hydrodynamic approach for 2D dots in a perpendicular magnetic field for various
circular confinements was developed in Ref. [115]. As shown in the appendix, the global,
static properties of the cluster, like the cluster energy and its radius, as obtained with the

![Figure 3.1: Excitation spectrum (the frequency is in units of \( \omega_0 \)).](image)
3. Eigenmode Spectrum

Figure 3.2: Density of states (DOS) obtained by using an averaging over intervals with $\Delta \omega / \omega_0 = 0.04$. Clusters are considered with particles from $N = 2$ to $N = 200$.

Figure 3.3: The positive values of the histogram derivative shown in Fig 3.2. The arrows mark the states which coincide with the hydrodynamic model labelled with the integer numbers $(j, m)$.

The hydrodynamic model agrees rather well with the results obtained from the simulations for the discrete model. This motivate us to compare also the dynamical properties like the frequency spectrum for both models. The hydrodynamic model is based on the solution of the Laplace equation for the potential created by the electrons. Spheroidal coordinates are used with boundary conditions ensuring a constant chemical potential inside the dot.
The solution leads to the static electron density (in $r_0^{-2}$ units)

$$\rho_0 = \frac{3N}{2\pi R^2} \sqrt{1 - r^2/R^2},$$

(3.4)

and the chemical potential

$$\mu = R^2,$$

(3.5)

where

$$R = \left(\frac{3\pi N}{4}\right)^{1/3}$$

(3.6)

is the hydrodynamic dot radius in our scaled variables.

The excitations of the system are described by the linearized continuity equation for small density deviations $\rho(t)$ from the equilibrium density distribution and for the particle velocities $v(t)$, the equation of motion in the simplest Drude approximation, and the Laplace equation for potential deviation $\phi(t)$ with the corresponding boundary conditions, namely,

$$\frac{\partial}{\partial t} \rho + \nabla (\rho_0 v) = 0,$$

(3.7a)

$$\frac{d}{dt} v = \nabla \phi,$$

(3.7b)

$$\nabla^2 \phi = 0,$$

(3.7c)

$$\frac{\partial \phi}{\partial z} = 2\pi \rho.$$  

(3.7d)

According to the scaling used the time is measured in $\omega_0^{-1}$ units, and the velocity in $r_0^{-1}$ units. Besides, charge conservation is assumed.

Assuming the usual exponential time dependence $\exp(-i\omega t)$ of all small deviations ($\rho(t)$, $\phi(t)$, and $v(t)$) we arrive at a time independent set of equations. According to the solution presented in Ref. [115], this problem is diagonalized in spheroidal coordinates.

The electron density in the dot (in polar coordinates $r = (r, \theta)$) for a specific excitation mode is given by the expression:

$$\rho(\tau, \theta) = \frac{1}{\tau} P_j^m(\tau) e^{im\theta}, \quad \tau = \sqrt{1 - r^2/R^2},$$

(3.8)

and the corresponding frequency reads

$$\omega_{jm}^2 = \frac{4}{\pi L_j^m} \{ j(j+1) - m^2 \}.$$

(3.9)
Here the symbol $P_j^m(x)$ stands for the Legendre polynomial of the first kind, and

$$L_j^m = 2\frac{\Gamma\left(\frac{j+|m|+1}{2}\right)\Gamma\left(\frac{j-|m|+1}{2}\right)}{\Gamma\left(\frac{j+|m|+1}{2}\right)\Gamma\left(\frac{j-|m|+1}{2}\right)},$$  \hspace{1cm} (3.10)

where $\Gamma(x)$ is the Gamma function. All modes are marked by two integers: the non negative number $j$ and the orbital number $m$, which gives the number of nodes in the orbital part of the density. The difference between these numbers is even. Thus, one can write $j = |m| + 2k$, where the non negative integer radial number $k$ actually gives the number of density nodes along the radius.

In the asymptotic region of large $m$ and $k$ values, a more simple expression for the frequencies can be obtained. Replacing the Gamma functions in Eq. (3.10) by their Stirling asymptotic expression one can easily obtain that in this region the frequencies are given by:

$$\omega_{jk}^2 \approx \frac{4}{\pi} \sqrt{j^2 - m^2} \approx \frac{8}{\pi} \sqrt{k|m|}.$$  \hspace{1cm} (3.11)

The spectrum of the cluster excitations as it is given by Eq. (3.9) is shown in Fig. 3.4.

In contrast to the averaged properties of the cluster, which coincide for the discrete and the hydrodynamic models rather well (see the Appendix), the more detailed characteristics of the dot are much more sensitive to the choice of the model. One of those sensitive characteristics is the spectrum of excitations, and as seen from first sight the spectrum obtained by the numerical simulation of the discrete system (Fig. 3.1) and the one obtained from the continuous hydrodynamic model (Fig. 3.4) differ very much.
Comparing these two spectra we notice two essential differences. First, the spectrum in the hydrodynamic approach extends up to infinite while the frequencies of the discrete model is confined to a restricted frequency interval. Next, the spectrum of the hydrodynamic model has a gap ($0 < \omega < 1$) where there are no excitation levels at all while in the case of the discrete model this gap is filled with levels (see Fig. 3.1).

The physical origin of the first discrepancy is evident. The excitations with large frequencies correspond to large $m$ and $k$ numbers, or a large number of azimuthal and radial nodes in the mode density function of expression (3.8). They can not all be realized in the discrete model due to the finite number ($N$) of electrons and as a consequence there are only $2N$ eigenmodes. Assuming an equidistant location of particles in the dot we can estimate the number of radial nodes as $k \approx \sqrt{N/12}$, and the number of azimuthal nodes as $m \approx \sqrt{3N/16}$. Inserting these expressions into Eq. (3.11), which is valid for large frequency values, we obtain an estimation for the maximum frequency

$$\omega_{\text{lim}} \sim N^{1/4}.$$  \hspace{1cm} (3.12)

Thus, only in the region $\omega \ll \omega_{\text{lim}}$ one can expect a coincidence of the hydrodynamic spectra and the one from the discrete model.

Note that the upper frequency limit for the discrete model (see the solid curve in Fig. (3.1)) was obtained numerically by fitting the above expression, giving:

$$\omega_{\text{lim}} = 1.17 N^{1/4}.$$  \hspace{1cm} (3.13)

The second difference, the gap in the hydrodynamic spectrum, has also a clear physical reason. Due to the finite dimensions of the dot, the actual wavelengths of excitations are limited from above, what leads to a frequency limitation from below. Moreover, in the hydrodynamic model the electrons are considered as a charged liquid which doesn’t resist shear deformations. Consequently, various types of rotating excitations are possible, and all of them have zero frequency. Mathematically this fact follows from Eq. (3.7). Namely, there are numerous solutions of the aforementioned equation set with $\rho (t) = \phi (t) = 0$ and the excitation velocity obeying the equation

$$\nabla (\rho_0 v) = 0,$$  \hspace{1cm} (3.14)

which are excitations with zero current divergence. Thus, in the hydrodynamic approach the zero level frequency is multiple degenerate and contains all rotating modes. On the other hand it is easy to check (it follows from Eq. (3.7b)) that all other hydrodynamic modes (with $\omega \neq 0$) obey the condition

$$\text{rot} \ v = 0,$$  \hspace{1cm} (3.15)

or equivalently have zero vorticity.
In the discrete model (where all electrons are arranged into a finite size Wigner crystal) there is a resistance to shear deformations. Thus, the aforementioned hydrodynamic zero frequency level is split, and redistributed over the complete frequency range. This leads to the idea to classify the modes in the discrete model according to their vorticity. Only the modes with small vorticity can be expected to be close to their hydrodynamic analogs.

3.4 Vorticity

In the discrete model the local vorticity can be defined approximately using the triangle composed of an electron at point $r_0$ and its two closest neighbors (at points $r_1$ and $r_2$) as depicted in Fig. 3.5. We define the local vorticity as the following integral of the rotor of the velocity over the above triangle area:

$$\gamma(r_0) = \frac{1}{S} \int d^2 r (\text{rot} \mathbf{v})_z = \frac{1}{S} \oint_C d\mathbf{r} \mathbf{v}$$

$$\approx \frac{1}{2S} \left( v_2 r_1 + v_3 r_2 + v_1 r_3 - v_1 r_2 - v_2 r_3 - v_3 r_1 \right).$$

(3.16)

We define a global vorticity for a specific mode as the absolute value of the above local vorticity averaged over all electrons.

As an example, the above global vorticity is shown in Fig. 3.6 for a $N = 50$ particle cluster as a function of frequency. The vorticities for clusters with different number of particles in are similar. It is remarkable that there is an evident gap in the region $0 < \omega < 1$ with large vorticity. In this region there are no modes with small vorticity what agrees with our earlier assertion that these modes are originating from the degenerate zero frequency level of rotating modes of the hydrodynamic model. Some of these rotating modes are shown in Fig. 3.7 and correspond with the downward arrows in the vorticity plot of Fig. 3.6. In the region $\omega > 1$ the modes with a rather small vorticity are clearly seen. Four of them indicated by arrows are the same modes which are marked in Figs. 3.1

**Figure 3.5:** The definition of the approximate local vorticity.
and 3.6. One may expect that the frequencies of these modes have to be rather close to those ones obtained in the hydrodynamic model. To confirm this statement we present in Fig. 3.8 the frequency of the modes from the discrete model with the smallest vorticity (black circles on the plot) and compare them with the lowest frequencies obtained in the hydrodynamic model which are indicated by the horizontal lines. We see that with increasing number of electrons the frequencies from the discrete model and those from the hydrodynamic model start to coincide. This further confirmed by the close similarity of the electron velocity distribution for both models which are shown in Fig. 3.9. In the first two columns the velocities of the discrete model are presented for a 50 and 150 particle system respectively, and in the third column the velocity distribution of the hydrodynamic
3. Eigenmode Spectrum

Figure 3.8: Comparison of the frequencies of the hydrodynamic model (horizontal lines) and the low vorticity modes of the discrete model (dots) as function of the number of particles.

model. This velocity distributions can be useful to extract these modes from future experimental data. In Figs. 3.8 and 3.9, and in Fig. 3.3 as well, the hydrodynamic modes are indicated by two integers \( \{j, m\} \). Thus, we showed clearly that low vorticity marks from the spectrum of the discrete model tends very slowly to its hydrodynamic analog when the number of particles is incremented.

The last question which we still have to answer is the behavior of the modes in the discrete model in the frequency gap. For this purpose we counted the number \( n_g \) of those modes in the \( 0 < \omega < 1 \) region. It’s dependence on the number of particles in the cluster is shown in Fig. 3.10. The dashed curve shows the asymptotic behavior of this quantity for a large number of particles in the cluster. The latter was obtained by fitting the calculated data using a logarithmic scale in the region \( N = 120 \div 200 \), and the expression of this curve reads

\[
 n_g \approx 4.7 N^{0.47}.
\]

Thus, the number of modes in the gap increases with the number of particles. Nevertheless, as the total number of modes increases as \( 2N \), the relative number of modes in the frequency gap is

\[
 n_g / 2N \approx 2.3 N^{-0.53} \to 0,
\]

and decreases. Moreover, the averaged density of modes can be estimated as

\[
 2N / \omega_{\text{lim}} = 2N / 1.17 N^{1/4} \sim N^{3/4},
\]
Figure 3.9: Velocity distribution for the coinciding modes in the discrete and the hydrodynamic model. In the first two columns the velocities of a 50- and 150-particle system are presented, respectively. These results are compared in the third column with the one from the hydrodynamic model. The contour plot in the third column shows the density of particles.

while the density of modes in the frequency gap actually is given by Eq. (3.17). So, we see that as the number of particles grows, the ratio of the density of modes in the gap to the averaged density tends to zero as well, and consequently, in this sense the discrete model tends to the hydrodynamic model as well.
3.5 Conclusions

In this chapter we performed a detailed study of the spectrum of Coulomb clusters, traced it's dependence on the number of particles, and compared the results with the hydrodynamic approach. We found out that it is convenient to classify the discrete model modes according to their global vorticity.

In the frequency region $0 < \omega < 1$ only modes with large vorticity are present. They originate from the degenerate hydrodynamic state corresponding to zero frequency, where all possible rotations of the liquid droplet are included. As the number of particles is incremented the density of modes in this region becomes negligible as compared with the total averaged density in the cluster.

In the region $\omega > 1$ there are modes with a rather small vorticity. As the number of particles in the cluster grows, the frequencies of these modes tend to their analogues in the hydrodynamic model. The velocity distributions of the hydrodynamic model pretty well coincide with the distributions obtained in the discrete model for the above modes with small vorticity, and thus, they may be useful for experimental purposes.

3.6 The energy and the radius of the cluster

In this appendix we consider the behavior of two global properties of the cluster — the averaged energy per particle $E_0/N$ and the maximum radius of the cluster.

The averaged energy per particle for the discrete model is shown by the solid curve

Figure 3.10: Number of modes in the $0 < \omega < 1$ frequency gap as function of the number of particles. The dashed curve shows the $N \to \infty$ asymptotic behavior.
3.6. The energy and the radius of the cluster

in Fig. 3.11. The dashed curve shows the same quantity, which was calculated in the hydrodynamic model integrating the chemical potential (see Eq. (3.5)) over the number of particles in the cluster, namely,

\[ E_0(N) = \int_0^N \mu(N') dN' = \left( \frac{3\pi}{4} \right)^{2/3} \int_0^N N'^{2/3} dN' \]

\( = a_0 N^{5/3}, \quad a_0 = \frac{3}{5} \left( \frac{3\pi}{4} \right)^{2/3} \approx 1.06. \)  \hspace{1cm} (3.20)

Thus, in the hydrodynamic approach the energy per particle is \( a_0 N^{2/3}. \)

In the inset of Fig. 3.11 the difference between these energies is shown by the solid curve. We see that it increases with the number of particles in the cluster. The physical origin of this discrepancy is the crystallization energy. Following the idea of the local density approximation, it can be estimated by averaging the crystallization energy for the homogeneous crystal over the surface area occupied by the cluster. The crystallization energy per particle for the homogeneous crystal was obtained in Ref. [116], and for the hexagonal lattice it is:

\[ E_{cr}^{(hom)} / N = c_0 \sqrt{\rho}, \quad c_0 \approx 1.96. \]  \hspace{1cm} (3.21)

Now replacing the homogeneous density in the above equation by the density of the cluster (3.4) and averaging it over the cluster we obtain the following expression for the aver-

**Figure 3.11:** Energy per particle in the cluster: solid curve – discrete model, dashed line – hydrodynamic model Eq. (3.20). Inset: solid curve – crystallization energy per particle, dashed curve – Eq. (3.22), short dashed curve – the ratio of the above quantities.
age crystallization energy:

\[
E_{cr} = c_0 \int_{r \leq R} d^2 r \rho_0^{3/2}(r) = \frac{c_0(3N)^{3/2}}{R \sqrt{2\pi}} \int_0^1 drr (1 - r^2)^{3/4}
\]

[3.22]

\[
= \frac{\sqrt{2} c_0 (3N)^{3/2}}{7 \sqrt{\pi}} \left( \frac{4}{3\pi N} \right)^{1/3} \approx 0.87 N^{7/6}.
\]

The averaged crystallization energy per particle \(E_{cr}/N\) is shown in the inset of Fig. 3.11 by the dashed curve. We see a rather good coincidence of this quantity with the above considered difference of cluster energies per particle of both models shown in the same inset by the solid curve. At least the difference of these two curves (the ratio of the two curves is given in the inset by the dotted line) does not depend on the number of particles.

Next we consider the maximum radius of the cluster which for the discrete model is shown in Fig. 3.12 by the solid curve. The same quantity for the hydrodynamic model (see Eq. (3.6)) is shown by the dashed curve. Although both curves demonstrate the same behavior, they differ quantitatively: the radius calculated in the hydrodynamic model is larger. Such a behavior for the behavior of the cluster radius is typical for various confinement potentials (see, for instance Ref. [117] and Ref. [114], where a system of charged particles confined by a Coulomb potential was studied). It is remarkable that the difference of the maximum radii calculated in both models (shown by the dotted line) doesn’t depend on the number of particles in the cluster for a large \(N\) and the ratio becomes relatively small the large \(N\).

**Figure 3.12:** Maximum radius of the cluster: solid curve – discrete model, dashed curve – hydrodynamic model Eq. (3.6), short dashed curve – the difference between the above quantities.
The physical origin of this discrepancy is related to the same crystallization phenomena, and can be explained as follows. Let us assume that the crystallization is just the replacement of the liquid droplet by a regular hexagonal lattice of electrons. If there are $N$ electrons in the dot, then there are $\sqrt{N/3}$ along the radius and $2\sqrt{3N}$ along its perimeter. We also assume that these electrons along the cluster perimeter are made of a thin outer ring of liquid droplet of width $h$ which has the same amount of charge, namely,

$$2\sqrt{3N} = 2\pi \int_{R-h}^{R} r dr \rho_0(r) = 3N \int_{1-h/R}^{1} drr\sqrt{1-r^2},$$

$$\approx N(h/R)^{3/2},$$

(3.23)

what leads to

$$h = \left( \frac{3}{2N} \right)^{1/3} R = \left( \frac{9\pi}{8} \right)^{1/3} \approx 1.52.$$  

(3.24)

Now if we put these outer particles on a circle with a radius coinciding with the averaged charge position on the above thin ring of the droplet we will obtain the following contraction of the droplet caused by crystallization:

$$\Delta R = \frac{\int_{R-h}^{R} drr(R-r)\rho_0(r)}{\int_{R-h}^{R} drr\rho_0(r)} \approx \frac{3}{5} h = 0.91,$$

(3.25)

which is in good agreement with the dotted line in Fig. 3.12.
3. Eigenmode Spectrum
Chapter 4

Influence of a defect particle on the structure of a classical two-dimensional cluster

A system of classical charged particles interacting through a Coulomb repulsive potential which are confined in a two-dimensional parabolic trap is studied. We allow one or two particles, called defect particles, to have a different mass and/or charge than the other particles. The structure of the whole system depends on the mass and the charge of the defects and the total number of particles in the system. The ground-state configurations are investigated and phase diagrams are constructed, which explain the recent experimental results of Grzybowski et al. [Phys. Rev. E 64, 11603 (2001)]. We found that several of the experimental configurations are metastable and that replacing the Coulomb interparticle potential by an inversely quadratic one has only little effect on the results.

4.1 Introduction

Classical clusters of repulsive particles confined in traps are both theoretically and experimentally a study object for many decades due to their applicability to a wide variety of systems. These systems are composed of a finite number of charged classical particles which can move in a two-dimensional (2D) plane and are confined in the plane by an external applied potential. They are the classical analogon of the 2D quantum dot. Typical experimental realizations of such systems are electrons on the surface of liquid helium [93], plasma’s with dust particles [16], ion traps [22], vortices in superfluids [30], confined ferromagnetic particles [95], charged metallic balls above a plane conductor [96] and colloidal crystals [15]. The 2D charged clusters also resemble the problem of charge distribution studied by Mayer [98] and by Thomson in his “plum-pudding” model of the atom [99, 100].

When the particles are confined to a parabolic trap, there is a competition between the bulk triangular lattice and the circular confinement potential that tries to force the charged particles into ringlike configurations. Those configurations were systematically studied in Ref. [102] and a Mendeleev-type of table for these classical atomlike structures was constructed. The spectral properties of the groundstate configurations were presented in Refs. [104, 109] and generalized to screened Coulomb [110, 111] and logarithmic [110, 100, 112, 113] interparticle interactions.
Recently, an interesting experiment [54] (as explained in the introduction) was performed where the self-assembly of millimeter-sized, magnetized disks floating on a liquid-air interface, and rotating under the influence of a rotating external magnetic field was considered. Spinning of the disks results in a hydrodynamic repulsion between them, while the rotating magnetic field produces an average confining potential acting on all disks. The interplay between hydrodynamic and magnetic interactions between the disks leads to the formation of ordered patterns, which shows that it can be considered as a dynamic self-assembling system. All the disks in this experiment were identical, except for one or two which had a larger radius than the others. These results which inspired us to extend our previous work on classical systems to systems with one or two defects and to see if the obtained static configurations resemble the experimental dynamic self-assembled ordered structures.

Recently, a theoretical study of the structure and melting of clusters consisting of two-species of charged particles with the same mass was reported [114]. The system is identical to the one studied here with the exception that a fraction of the particles had a charge which was twice as large as the others. The particles were found to arrange themselves in rings where those with a larger charge were expelled to the edge of the trap.

Here we will show that allowing the ‘defect’ particles to have a different mass and/or charge dramatically modifies the obtained configurations and we found that the defect particles can reside anywhere in the cluster depending on their mass and charge. The obtained results will be summarized in phase diagrams. We also found that the introduction of the defect particle leads to an increase of the number of metastable states, some of which were observed in Ref. [54].

This chapter is organized as follows. In section 4.2 our model system is introduced. The results for one and two defects are shown in sections 4.3 and 4.4, respectively. In these sections also a comparison with the experimental results of Ref. [54] is given. Our conclusions are presented in section 5.6.

4.2 Model system

In Ref. [54] an empirical Hamiltonian for the experimental system was proposed, namely

\[
H = \sum_i c_1(H,M) r_i^2 + \sum_{i<j} c_2(\omega, a_1, a_2, \rho) \frac{1}{|r_i - r_j|^2}.
\]  

(4.1)

The first term is the confinement potential and is due to the rotating magnet. The confinement strength \( c_1 \) depends on the magnetization \( M \) of the magnet and its distance \( H \) from the interface. The second term describes the hydrodynamic repulsion between the disks. The coefficient \( c_2 \) depends on the angular velocity \( \omega \) of the magnet, the radii of the particles \( a_1 \) and the defect(s) \( a_2 \), and the density \( \rho \).
Motivated by this empirical Hamiltonian, we consider a system with \( N \) point-like classical particles interacting through a more general \( 1/|r|^n \) potential. The particles are free to move in two-dimensions but are confined by a parabolic trap centered at the origin. The general Hamiltonian of the system for particles with different masses and charges is

\[
H = \frac{1}{2} \sum_{i=1}^{N} m_i^* \omega_0^2 r_i^2 + \frac{1}{\varepsilon} \sum_{i<j}^{N} \frac{q_i^* q_j^*}{|r_i - r_j|^n},
\]

where \( m_i^* \) is the effective mass of the particle and \( q_i^* \) its charge, \( \omega_0 \) the radial confinement frequency, and \( \varepsilon \) the dielectric constant of the medium the particles are moving in.

The Hamiltonian can be transformed to a dimensionless form using the following units: \( r_0 = \left( \frac{2Q^2}{M \varepsilon \omega_0^2} \right)^{1/(1+n)} \) for the length and \( E_0 = M \omega_0^2 r_0^2 / 2 \) for the energy. \( M \) and \( Q \) represent the reference mass and charge. After rescaling we can write the Hamiltonian in dimensionless form

\[
H = \sum_{i=1}^{N} m_i r_i^2 + \sum_{i<j}^{N} \frac{q_i q_j}{|r_i - r_j|^n},
\]

with \( m_i = m_i^* / M \) and \( q_i = q_i^* / Q \) respectively the rescaled mass and charge of particle \( i \).

We take \( m_i = 1 \) and \( q_i = 1 \) for all particles except one or two.

To find the minimum energy configuration we used the Monte Carlo simulation technique extended with a Newton optimisation technique, as first used in Ref. [104]. This last technique increases the convergence and the accuracy of the local minimum. In order to be sure to have found the groundstate configuration, one has to run the Monte Carlo simulation routine many times starting with a different initial random configuration. To be sure that the obtained configuration is a stable one, each particle was moved around its ‘equilibrium’ position and the force on the particle and the energy of the configuration was monitored.

### 4.3 Systems with one defect

The inter-particle potential was taken to be Coulombic (i.e. \( n = 1 \) in Eq. (4.2)). The stable configurations were studied as function of the charge and mass of the defect particle which was embedded in a system of \( N \) identical particles. The results for the groundstate configuration are summarized in phase diagrams which for \( N = 3, \ldots, 7 \) are shown in Figs. 4.1(a-e). The obtained groundstate configurations can be classified in three groups: (i) closed ring configurations with the defect in the center and the other particles forming a ring around it, which is realized in the upper left part \( (m \gg q) \) of the phase diagram, (ii) open ring configurations in which the outer ring around the defect is not closed, and (iii) cluster configurations in which the defect is not situated in the center and the other
Influence of a defect particle on the structure of a classical two-dimensional cluster

Figure 4.1: (a-e) Phase diagrams for the groundstate configuration of a classical cluster with $N = 3, \ldots, 7$ particles and a single defect particle. The insets show the typical configurations in each region of the phase diagram. (f) The energy difference of all stable configurations with the energy of the closed ring configuration as a function of the charge of the defect for $N = 5$ particles and fixed $m/M = 2.4$.

Particles are grouped in a cluster opposite to the position of the defect, as realized in the lower right part ($m \ll q$) of the phase diagram.

One can see that the complexity of the phase diagrams increases, in general, with the number of particles. However, there is always a closed ring configuration and a cluster configuration. A closed ring configuration is the groundstate when the defect has a large mass. The defect with a large mass can lower its confinement energy by moving to the center of the trap. However, when the charge becomes large, the repulsive inter-particle interaction energy increases, which is minimised when the particle is situated at the edge of the system, which leads to the formation of a cluster configuration. This competition between the confinement energy and the inter-particle energy determines the ground state. Notice that the phase boundary between both phases is almost linear and the slope of this boundary decreases with increasing number of particles. This means that, when we start from a system in a groundstate cluster configuration, putting an extra particle will move
4.3. Systems with one defect

the defect even further away from the center in order to minimize the Coulomb repulsive energy. This costs extra confinement energy, which can lead to a transition from a cluster configuration to a closed ring configuration with the defect in the center.

The phase diagrams only show the groundstate configurations, but several metastable configurations can be realized at the same time. An example is shown in Fig. 4.1(f) where the energy difference of all stable configurations with respect to the closed ring configuration for 5 particles and a single defect is plotted as a function of the defect charge for fixed $m/M = 2.4$. Notice that: i) configurations which are the groundstate in a certain region can still be a metastable state outside that region, and ii) stable configurations can be realized which never become the groundstate.

Notice that in the system with 5 particles and 1 defect four ground state configurations are possible, while for the 6 particle system only two configurations exist. However, for small values of the defect charge, the cluster configuration is also realized but only in a very narrow region. This remarkable phase boundary can be understood as follows. If one starts from the cluster configuration with a large defect charge, and diminishes the charge slowly, the defect will move closer to the center. At some point the cluster configuration will not be the ground state configuration anymore, the closed ring configuration will take over. However, the cluster configuration becomes a metastable configuration. When the defect charge becomes very small, the defect sits almost in the center, close to the central particle. These two particles will now act as one effective particle. From previous work [102] we know that the ground state configuration of 6 identical particles is (1,5) (1 particle in the center with a ring of 5 particles around it), and consequently the cluster configuration becomes the groundstate again.

Also in the phase diagram for 7 particles and 1 defect one can see this sharp boundary for small values of the defect charge. Again the central particle and the defect behave as a single particle with almost unit charge. However, an extra phase exists in comparison with the 6 particle system, in which the groundstate configuration for a large defect charge has two central particles.

We compared the results of our simulations with the recent experimental results of Ref. [54]. Although this experiment describes a dynamical system we were able to reproduce the experimentally observed configurations with our static theory. As it is non-trivial to derive from the experiment the appropriate values for $m/M$ and $q/Q$, we had to make a good choice. In the experiment also slightly different configurations were observed for different disk diameters and angular velocity of the magnet. Therefore, a one to one agreement with the experiment is impossible. However, the best qualitative agreement was obtained for $m/M = 4$ and $q/Q = 4.4$, which we fixed in all subsequent comparison with the experiment of Ref. [54]. Fig. 4.2 shows the groundstate configuration and the first metastable state for systems with 2 up to 24 particles (which was also the largest system in the experiment) for Coulomb interaction and for a $1/r^2$ repulsive interaction
between the particles. A good qualitative agreement with the configurations shown in Figs. 4 and 5 of Ref. [54] is obtained. As already mentioned in Sec. 4.2, in Ref. [54] it is argued that the interaction potential between the disks is of the form $1/r^2$. However, one can notice that there are only minor differences between the configurations for a $1/r^2$ interaction and a Coulomb interaction.

From the empirical Hamiltonian (4.1) one can see that the confining strength $c_1$ only depends on the magnetization $M$ of the magnet and its distance $H$ from the interface, and is thus equal for all disks, including the one with the larger diameter. In our model this would result in an equal mass for all particles. We want to stress that both $m/M$ and $q/Q$ had to differ from 1 in order to be able to reproduce the experimental configurations. However, we believe that the empirical Hamiltonian must be slightly changed. The confinement force of each disk in the experiment depends on its magnetic moment. The magnetic moment of a disk is proportional to its volume, and thus it depends on the square of the disk radius, $a^2$. Therefore, the coefficient $c_1$ in the empirical Hamiltonian has also to depend on $a$, in contrast to what was claimed in Ref. [54].

From their experimental results, the authors deduce 6 qualitative rules (written in italic below) which describe the formation of the different patterns. We will comment on each of them using our theoretical results.

1. *The largest disk (i.e. a defect particle) occupies the central position on the axis of rotation of the magnet.* From the phase diagrams in Fig. 4.1 we know that only when the mass of the defect is large in comparison with its charge, the defect will occupy the central position. Therefore changing some experimental parameters like the disk radius or the angular velocity of the magnet may lead to a different configuration. For example, as $c_1$ depends on $a$, decreasing the radius of the largest disk may lead to a cluster configuration.

2. *Smaller disks (i.e. the identical particles) organize into shells around the large disk (i.e. the defect particle).* The formation of shells is also clearly observed in our numerical results.

3. *The larger the size difference between the defect and the other disks, the simpler the morphology of the aggregates.* As $c_1$ depends on $a$, increasing the size difference corresponds approximately with increasing the mass of the defect particle. In the phase diagrams this means that one moves upwards (away from the linear phase boundary). It is clear from our phase diagrams (Fig. 4.1) that this leads to simpler configurations.

4. *Shells are populated consecutively, i.e., the second shell fills, only after the first shell is completed.* From our theoretical results we can indeed deduce that first the first shell is populated up to 10 particles before the second shell is formed. However,
from Fig. 4.2 one can see that the formation of the second shell starts with particles positioned between the defect and the outer ring and a clear distinction between first and second shell is not always possible. Around 18-19 particles and beyond a closed second shell is formed.

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**Figure 4.2:** The groundstate and first metastable configurations for one defect and \( N = 2, \ldots, 24 \) particles. Results are shown for \( 1/r^2 \) and Coulomb interaction potentials. The mass and charge of the defect particle is fixed to \( m/M = 4 \) and \( q/Q = 4.4 \).
5. When the size of an atom (i.e. the whole system) is not too large, the occupancies of the shells can be predicted by simple geometric considerations (polygon method). We want to stress that the polygon method gives only the correct configuration for certain systems and that for systems with a small number of particles even open ring configurations are observed. The polygon method will work better if the closed ring configuration is the groundstate. Experimentally, this can be achieved by increasing the radius of the defect particle.

6. Closed ring structures are more stable than open ring structures. We found that the stability regions for open-shell configurations are indeed smaller than the region in which the closed ring structure is the groundstate.

4.4 Systems with two defects

Also experimental results were reported in Ref. [54] for systems containing two defects. For our simulations with two defects we used the same values for $m/M = 4$ and $q/Q = 4.4$ as before. We reproduced most of the experimental configurations by our simulations. In the experimental paper Ref. [54] several stable configurations were found. Our numerical results shown in Fig. 4.3 must be compared with the first 7 rows in Fig. 6 of Ref. [54] which match exactly with these experimental results. The particles organize into groups on either side of the axis joining the defect particles. All possible combinations are allowed (i.e. $n$ particles on one side of the axis joining the two defect particles and $N - n$ on the other side), provided that the number of particles in one group does not exceed 7. Note indeed that for the system with 8 particles, experimentally as well as theoretically, always at least one particle is situated at each side of this line. Not all numerically obtained groundstates for 5 up to 8 particles were observed experimentally. Those corresponding to the open ring configurations, which are shown in the right column of Fig. 4.3, were not reported in Ref. [54]. It is not obvious why these ground state configurations where not reported in Ref. [54] and why the experimental systems seems to be trapped into a metastable configuration.

The numerical configurations from 9 up to 32 particles and two defects are shown in Fig. 4.4 and should be compared with the results shown in Figs. 6 and 7 of Ref. [54]. Experimentally the last open ring configuration is found for 11 small disks, while numerically it is found for 10 particles. Experimentally, starting from 12 disks, many polymorphic configurations were observed and only representative examples are shown. Also numerically many metastable configurations were found with very simular structures, which, for limited amount of space, are not reported here.
4.5 Conclusions

The groundstate structure of classical identical pointlike particles with one or two defect particles with different mass and charge, interacting through a Coulomb or $1/r^2$ potential and confined in a parabolic potential, was studied. We showed that in the presence of one defect particle the groundstate depends strongly on the charge and mass of the defect.

**Figure 4.3:** The groundstate and first metastable configurations for two defects and $N = 2, \ldots, 8$ particles. Results are shown for a $1/r^2$ interaction potential. The mass and charge of the defect particle is fixed to $m/M = 4$ and $q/Q = 4.4$. For the groundstate the energy per particle is given, and for the metastable states the energy difference with the groundstate is given.
Figure 4.4: The groundstate configurations for two defects and $N = 9, \ldots, 32$ particles. Results are shown for a $1/r^2$ interaction potential. The mass and charge of the defect particle is fixed to $m/M = 4$ and $q/Q = 4.4$. 

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particle: closed ring, open ring and cluster configurations are found. Interesting phase diagrams were constructed.

A good qualitative agreement was obtained with recent experimental results [54] for systems with both one and two defects. It is interesting to note that the experimental parameters were chosen rather nicely in a region of the phase diagram with many possible states, namely close to the linear phase boundary between the closed ring and cluster configuration. In our simulations we fixed only once the mass and charge of the defect particle in order to explain all the obtained configurations.
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Chapter 5

Structure of a 2D cluster with competing interaction

A system of classical charged particles confined in a two-dimensional trap and interacting through a competing short-range attraction and long-range repulsion potential is studied. The structure of the system strongly depends on the interaction range of the short-range attraction potential and the total number of particles. Depending on the appropriate choice of parameters for the attractive potential, the particles organize themselves in bubbles, stripe phases and ringlike configurations, or combinations of both of them. Detailed phase diagrams are presented for systems consisting of $N = 2$ up to $N = 6$ particles. General rules are derived for the different subsequent transitions between those configurations and how the ground state configuration of a large system can be deduced from the one of a small number of particles.

5.1 Introduction

In the introduction we showed that competing attractive and repulsive interaction are responsible for diverse two- and three-dimensional systems in nature.

Recently, it became clear that the pattern formation in the above systems displays common structural features. These common features, like the spatial modulation, suggest a universal approach for explaining the behavior of these systems. In recent molecular dynamics simulations [118, 119, 120, 121] simplified models with different types of interaction potential were performed and lead to a good agreement with the experimental observed patterns. The goal of these simulations was to control these self-organized patterns by adjusting a small number of physical parameters. This is important in order to understand these self-assembled systems and to control the size, orientation, and structure of the formed patterns. Notice that all theoretical studies until now were done for infinite systems.

In the modern age of nanoscience, the study of finite size effects has become very important. Often the nano-system is put on a surface and motion is limited in two dimensions (2D). This motivated us to apply an extra confinement potential to a 2D system and study the effect of a boundary on the patterns generated by the competing interactions. The system under study in this chapter is composed of a finite number of classical particles which interact through a repulsive Coulomb potential and an attractive exponential
potential and move in a 2D plane where the motion is confined by a parabolic potential. The competition between the short-range attraction and the long-range repulsion potential will generate a spontaneous spatial modulation of the particles. We found that the particles will organize themselves in various different phases like bubble phases (particles are organized in different bubbles), stripe phases (particles are organized in different lines on a ring), rings (particles are organized in different rings around the center) or combination of those phases depending on the strength and interaction range of the short-range potential, the strength of the confinement potential, and the number of particles.

The chapter is organized as follows. In Sec. II our model system is introduced. The results for a small system are presented in Sec. III, those for an intermediate systems in Sec. IV, and for large systems in Sec. V. Our conclusions are presented in Sec. VI.

5.2 Model system

With our model system we are interested to study the effect of the competition of a short range attraction and a long range repulsion on the configurations in a finite system. We considered a system with $N$ point like classical particles interacting through a repulsive Coulomb potential and an attractive exponential potential as in Refs. [118, 119]. The particles move in two dimensions where they are confined by a parabolic potential trap centered at the origin. The general dimensionless Hamiltonian of the system is written as

$$H = \sum_{i=1}^{N} r_i^2 + \sum_{i<j}^{N} \left( \frac{1}{|r_i - r_j|} - B e^{-\kappa |r_i - r_j|} \right),$$

using the following units: $r' = (2q^2/m\varepsilon\omega_0^2)^{1/2}$ for the length, $E' = m\omega_0^2 r_0^2/2$ for the energy with $m$ the mass of the particles and $\omega' = \omega_0/\sqrt{2}$ for the frequency with $\omega_0$ the strength of the confinement potential. Note that the strength of the confinement potential in combination with the strength of Coulomb repulsive part of the inter-particle interaction determine the length and energy scale. The first term is the confinement potential, the second the repulsive part of the inter-particle potential and the last the attractive part. The exponential term is determined by two parameters $B$ and $\kappa$, where $B$ determines the strength and $\kappa$ the interaction range of the attractive part of the inter-particle potential. Notice that the repulsive part is long range while the attractive part is short range. But in the present work the ranges of the potentials should be compared with the finite size of our system.

To find the minimum energy configurations we used the Monte Carlo simulation technique extended with a Newton optimization technique [104]. This last technique increases the convergence and the accuracy of local minima. In order to be sure to have found the
5.3 Small number of particles

In the following, phase diagrams for the configuration of small clusters are presented as a function of the inter-particle potential parameters. In order to understand these phase diagrams better, it is useful to investigate the interaction potential first. The curves in Fig. 5.1 show the position $r$ of the extrema of the interaction potential between two particles for different $\kappa$-values as function of $B$. Each curve corresponds with two extrema, a minimum and a maximum, which join together at some minimum value of $B$. At this point the extrema disappears. For $B$-values below this point the attractive part of the potential becomes too small to compete with the repulsive part and the inter-particle potential is purely repulsive. The distance between both extrema is inversely proportional to $\kappa$. Notice that the qualitative behavior is similar for low and high $\kappa$. For $\kappa = 0$, the range of the attractive part of the potential becomes independent of the distance between the par-

![Figure 5.1: Position of the extrema of the inter-particle potential as function of $B$ for different $\kappa$ values. The full curves correspond to a minimum and the dashed curves to a maximum. The insets show the potential energy as function of the distance between the particles for $B = 2$ and $B = 6$ with $\kappa = 1.5$.](image)

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5.3 Small number of particles

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particles and doesn’t affect the structure of the system. In the other limit, if $\kappa$ is very large, the range of the attractive potential becomes too short and will be unable to affect the structure of the system either. So one can expect a transition region in ($\kappa, B$)-space, where the attractive potential strongly competes with the repulsive Coulomb potential resulting in transitions between different particle configurations. Also one can expect that these transitions will appear around the same values in ($\kappa, B$) for different number of particles in the parabolic trap, because the transitions are determined by the mean inter-particle distance and this mean inter-particle distance is approximately independent of the number of particles in a parabolic trap. The configurations were studied as function of $\kappa$ and $B$. The results for the ground state configurations are summarized in phase diagrams for $N = 2, \ldots, 6$ particles. In order to label the configurations, we use the following notation $\{ n(k)^{s,b}; m(l,d) \}$, where the numbers between brackets, $k$, $l$ and $d$, give the number of particles per shell in a stripe or bubble and $n$ and $m$ the number of bubbles or stripes with the same configuration. The letters $s$ and $b$ stand respectively for the stripe and the bubble configuration. For example the notation $\{ 2(2)^{s}; 2(3)^{b} \}$ in Fig. 5.15 means that there are 2 stripes of two particles and 2 bubbles of 3 particles. Let us first discuss the result for $N = 2$, presented in Fig. 5.2. From the analysis of the inter-particle potential we know that when $B$ is sufficiently large, the inter-particle potential has a minimum and a maximum, and consequently two configurations are possible: one in which the particles are close to each other and one in which they repel each other. The latter is only stable because of the

![Figure 5.2: Phase diagram for the ground state configurations of a classical cluster with $N=2$ particles. The insets shows the typical configurations in each region of the phase diagram.](image-url)
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presence of the confinement potential. The former we call the high (H) and the latter the low (L) density ring configuration, notated as $2H$ and $2L$, respectively. The first order phase boundary between both phases is given by the solid curve in Fig. 5.2, which to a good approximation can be represented by the line $B = 2.9\kappa - 5.0$. This line ends in a critical second order transition point $(\kappa, B) = (5,8.6)$. Notice that for low $B$-values one can go continuously from one configuration to the other.

In Fig. 5.3 we investigate a 3-particle system. The particles are arranged on a ring with different densities on both sides of the transition line, i.e. the $(3)^L$ and the $(3)^H$ configuration. The thin lines in Fig. 5.3 are equiradius lines for the ring configuration. The configuration in the low density region is determined by the Coulomb repulsive part of the inter-particle interaction as found in previous simulations [102]. The configuration in the high density region is determined by the competition of the attractive and repulsive part of the inter-particle interaction. The boundary between the low and high density configuration regions is a triple line (to a good approximation given by $B = 2.80\kappa - 5.40$) which ends in a critical point $(\kappa, B) = (4,1.6,8)$, below which no transitions occur. Exactly on the triple line, the $\{(1), (2)^b\}$-bubble configuration coexist with both ring configurations, as shown in Fig. 5.4. For this $\kappa$-value and $B$-range, 3 stable configurations are found which go through a single point on the triple line. In the bubble configuration on the triple line, two particles are grouped in a bubble and separated from the third particle by the Coulomb potential.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{phase_diagram}
\caption{Phase diagram for the ground state configurations of a classical cluster with $N=3$ particles. The insets show typical configurations in each region of the phase diagram. On the bold line three phases coexist and is therefore a triple line which ends up in a critical point. The thin lines are equiradius lines for the ring configuration.}
\end{figure}
Figure 5.4: The energy of all stable configurations, of a classical cluster with $N = 3$ particles, as function of the amplitude $B$ of the attractive potential.

Figure 5.5: The distance between the 2-particle stripe and a third particle and between the particles in the stripe following the transition line from high $\kappa$ to the critical point.

Fig. 5.5 shows the distance between two particles in the bubble and the distance between the bubble and a third particle as function of $\kappa$ following the bubble configuration on the triple line until the critical point is reached. If $\kappa$ increases following the transition line, the distance between bubble and particle become equal to the distance between a particle and another effective defect particle with double charge and mass. This limit is plotted in Fig. 5.5 and is equal to $D = 1.145$. In the other limit if $\kappa$ decreases and goes to the critical point, the distance between the particles in the bubble and between the particle
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Figure 5.6: Eigenfrequencies (upper figures) and distance of each particle to the center of the confinement potential (lower figures) of a 3-particle system as function of $\kappa$ for three different values of $B$. The insets show the corresponding eigenmodes. The center of mass mode and the one shown in the inset of the right figure are two fold degenerate. The curves for $B = 6.8$ are going through the critical point.

and the bubble become equal or in other words the bubble configuration becomes equal to the ring configuration. One can conclude that the triple line doesn’t end up in a triple point where the high and low density ring configuration coexist with the bubble phase. Instead, but that all those phases become identical. In the eigenfrequency and radius plot in Fig. 5.6 for $B = 8$ we see that the transitions on the triple line are of first order. Following the transition region to smaller $B$- and $\kappa$-values, we found that the lowest non zero eigenfrequency goes to zero at the critical point indicating a second order transition as shown in Fig. 5.6 for $B = 6.8$, which shows the eigenfrequencies for $B$-values near the critical point. Note that not a single but two frequency branches become zero indicating that the second order derivative in the critical point is zero in more than one direction, which is consistent with the fact that the 3 configurations become the same in this point. Decreasing $\kappa$ and $B$ further leads to an increase in the lowest non zero eigenfrequency and no transitions occur. In this region one can go in a continuous way from the $(3)^L$-configuration to the $(3)^H$-configuration. The radii in Fig. 5.6 for $B = 6$ and equiradii lines in Fig. 5.3 illustrate the phase transition before and after this critical point. The positions of the particles exhibit a jump at the first order transition. Notice also that the frequency
of the breathing mode, the mode where all particles vibrate simultaneously in the radial
direction (see insets of Fig. 5.6), becomes large in the high density region due to the
strong mutual interaction.

In the 4-particle system (see Fig. 5.7) we have a similar high and low density region in which the particles are located on a ring. But the transition region is much richer, due to the fact that we can combine different number of particles in bubbles of different sizes. The first order phase boundaries are given to a good approximation by \( B = 2.7\kappa - 4.3 \), \( B = 2.8\kappa - 4.6 \) and \( B = 3.0\kappa - 5.0 \) (The second expression represents two transition lines which only slightly differs) which join together in a critical point at \((\kappa, B) = (4.0, 6.6)\). Just like for the bubble phase in the 3-particle system, the 3 bubble phases of the 4-particle system can transform continuously (through a second order transition) into the same ring configuration. As a consequence all the phase boundaries must join in a single point, leading to the markable feature that in this point 4 phases become the same. The inclination of the lowest phase boundary is almost the same as for the 3-particle system. This behavior can be understood as follows: the formation of a two particle bubble, by increasing \( B \) or decreasing \( \kappa \), is independent of the number of particles but is determined by the interaction between two particles in a bubble. At high \( \kappa \) values the system is in the low density ring configuration. The interaction range of the attractive potential is too small to compete with the Coulomb potential. The system behaves as interacting through a Coulomb repulsion and trapped in a parabolic confinement potential. By decreasing \( \kappa \), the short-range potential becomes strong enough to compete with

![Figure 5.7](image)

**Figure 5.7:** Phase diagram for the ground state configurations of a classical cluster with \( N=4 \) particles. The straight lines indicate the first order transitions and the dashed line the second order transition. The insets depict typical configurations in each region of the phase diagram.
the Coulomb potential and bubble configurations are possible. The bubble configuration, with two particles grouped into a bubble, becomes the ground state by further decreasing $\kappa$. Such a bubble can be viewed as an effective defect particle with multiple charge and mass as was studied in Ref. [122]. Therefore the distance between the two other particles increases slightly and prevents them to group in another bubble. This process continues until all particles are grouped in a single bubble, i.e. the high density $(4)^H$ state. Notice that the phase diagram only shows the ground state configurations, but several metastable configurations can exist at the same time. These configuration are illustrated in Fig. 5.8, where the energy of the different stable states are plotted as function of $\kappa$ for fixed $B$. Notice that the state $\{2(2)^b\}$ becomes the ground state only over a very small $\kappa$-region which is shown in one of the insets of Fig. 5.8. This is in contrast with a three particle system where we found a triple line where three phases coexist. In a 4-particle system, the critical point, i.e. the second order phase transition, is extended from a single point to a line in the high density region, which stops in the critical point $(B, \kappa) = (20.4, 8.6)$. In the $4 < \kappa < 8.5$ region this line is closely approximate by the line $B = 2.4\kappa - 0.8$. This line is absent in the 3-particle system because this system forms a Wigner lattice in the ground state which is proven to be very stable. In a 4-particle system, the particles form a ring and the triangular structure is lost. These particles on the ring are more free to move in comparison with particles in a triangular structure and this causes the system to undergo, in the high density configuration, a second order transition by grouping two opposite particles in the center of the parabolic confinement to minimize the energy. Fig. 5.9 shows that the first non-zero eigenfrequency goes to zero at the second order transi-
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Figure 5.9: The non-zero eigenfrequencies for a 4-particle system, as function of the interaction range $\kappa$ with $B = 10$.

The other transitions occur through first order transitions. In a 5-particle system there is again a transition region which separates a high and low density ring configuration with a second order transition line in the high density ring configuration. The first order phase boundaries are given to a good approximation by $B = 2.6\kappa - 3.4$, $B = 2.7\kappa - 3.6$.

Figure 5.10: Phase diagram for the ground state configurations of a classical cluster with $N=5$ particles. The straight line shows the first order transitions and the dashed lines the second order transition. The insets show the typical configurations in each region of the phase diagram.
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Figure 5.11: The energy of all stable configurations, of a classical cluster with 5 particles, as function of the interaction range $\kappa$ of the attractive potential.

$B = 2.8\kappa - 4.0$, $B = 2.9\kappa - 4.5$ and $B = 2.9\kappa - 4.7$ which join together in a critical point at $(\kappa, B) = (3.5, 5.7)$. The second order transition line in the region $2 < \kappa < 10$ is closely approximated by the line $B = 2.9\kappa - 0.7$. In the critical point this second order line joins the first order line similar to what was found for the 4-particle system (see Fig. 5.7). Making the comparison between the 4- and 5-particle phase diagrams, the inclination of the second order transition line in the phase diagram is increased and the first order transition region is extended to smaller $\kappa$-values. The first order transition region is extended due to the increased number of possible configurations which is proportional to the number of particles squared. The inclination of the second order transition line is increased due to the increasing diameter of the ring. This increasing diameter results in a weaker confinement of the particles on the ring and allows a second order transition at lower $\kappa$-values. Notice that all phase boundaries join together in a single critical point $(\kappa, B) = (3.5, 5.7)$. This is because if one follows the phase transition lines for decreasing $\kappa$, the particle configurations resemble more and more the (5)-ring configuration (this behavior is similar to the one of a 3-particle system as seen in Fig. 5.6) and become this configuration at the joining point. The different phases in Fig. 5.10 can be easily understood intuitively as an increased clustering of the particles and finally for small $\kappa$ a collapse into a single bubble. The energies of all the states are given as function of $\kappa$ in Fig. 5.11. Notice that from all of the 9 stable configurations only 6 are realized as ground state configurations.

The phase diagrams for $N = 6$ system (see Fig. 5.12) is qualitatively different from the previous cases. There is only a short second order transition line, which at a first glance is unexpected. In comparison with previous systems, there is one particle in the center...
Figure 5.12: Phase diagram for the ground state configurations of a classical cluster with $N=6$ particles. The insets show the typical configurations in each region of the phase diagram.

of the configuration preventing a second order transition in the ground state configuration $(1,5)^H$. However, the ring configuration (6), without a particle in the center (which is the ground state in a small region), can go through a second order phase transition in which the particles group themselves in bubbles of two. The ground state configuration for a very large value of $\kappa$ is the $(1,5)^L$-configuration. The first order phase boundaries are given to a good approximation by $B = 3.2\kappa - 6.3$, $B = 2.9\kappa - 5.3$, $B = 2.2\kappa - 3.0$ (representing two phase lines) and $\bar{B} = 2.5\kappa - 2.6$ (representing two phase lines). In contrast to the previous systems, one can see two critical second order joining points for the first order phase transition lines at $(\kappa, B) = (3.5, 6.3)$ and $(\kappa, \bar{B}) = (4.0, 6.5)$. This is because also the (6)-configuration exists as a ground state in a small region around the joining points of the phase transition lines. Therefore, if one follows the phase transition region for decreasing $\kappa$, the configuration can go in a continuous way to the (1,5)- or the (6)$^H$-configuration, leading to the critical point. One can see that the most circulatory configurations go to the (6)-configuration and the other to the (1,5)-configuration. Finally in Fig. 5.13 the energies of all the possible stable configurations are plotted as function of $\kappa$. With increasing $\kappa$ we found the following ground states: 1, 2, 5, 6, 9, 10, 12 and 15, where the number corresponds to the curves in the upper figure of Fig. 5.13 and the corresponding configurations are shown in the lower figures of Fig. 5.13.
Figure 5.13: The energy of all stable configurations, of a classical cluster with 6 particles, as function of the interaction range \( \kappa \) of the attractive potential. The corresponding configurations are depicted in the lower figures.
Figure 5.14: (a) Number of stable states, (b) energy difference of the metastable states with respect to the ground state, (c) the distance of the particles to the center, and (d) eigenfrequencies of the ground state of a 10-particle system as function of $B$ for $\kappa = 4$. The vertical lines mark the different regions: I ring, II stripe, III bubble and IV cluster phases. Subdivisions in a region are marked with a short dashed line.
5.4 Intermediate number of particles

In this section we want to see if we can infer the behavior of larger systems from our knowledge of the few particle systems of previous section. Therefore, we will take a closer look to the 10-, 20- and 30-particle systems. In previous section we found that the number of possible stable states increases very rapidly with increasing number of particles, e.g. 9 in Fig. 5.11 for $N = 5$ and 21 in Fig. 5.13 for $N = 6$. There is also a corresponding increase of the number of possible phases as ground state. Therefore, for systems with more particles it becomes almost impossible to construct a detailed phase diagram. To obtain still information about the influence of changing $B$ on the system we make a cross section in $(\kappa, B)$-space at $\kappa = 4$. In this paragraph the influence of changing $B$ on the ground state of a 10-particle system is studied and $\kappa$ is fixed at 4. In Fig. 5.14, the number of stable states, the energy differences of the metastable states with the

![Diagram](image)

**Figure 5.15:** Snapshots of the ground state configuration for a $N = 10$-particle system with $\kappa = 4$. The different regions refer to Fig. 5.14.
Figure 5.16: (a) Number of stable states and (b) the distance of the particles to the center and (c) eigenfrequencies of the ground state of a 20-particle system as function of $B$ with $\kappa = 4$. The vertical dashed lines mark different types of configurations in the ring and the bubble region.
ground state, the distance of the particles of the ground state configuration to the center of the confinement potential, and the eigenfrequencies of the ground state configuration are given as function of $B$. We distinguished 4 main regions which are separated by the full vertical lines: region $I$ corresponds to low density ring configurations, $II$ to stripe configurations, $III$ to bubble configurations, and $IV$ to high density ring configurations. The snapshots of Fig.5.15 are labelled with the region number to which the configuration belongs. In region $I$ the ground state configurations are ring configurations. Different ring configurations are found as function of $B$ and therefore region $I$ is subdivided, marked by the short dashed lines in Fig. 5.14. For $B = 0$ the $(2,8)^L$-ring configuration is the ground state. If one increases $B$, the system changes slightly by rotating the inner particles with respect to the other particles, through a second order transition. If one increases $B$ further, the particles redistribute themselves over different rings in order to form first the $(1,9)^L$-configuration and subsequently the $(10)^L$-ring configuration by promotion of the particles from the inner shell to the outer shell. Next, the $(10)^L$-ring configuration undergoes a second order transition and the particles group themselves in stripes of two particles on a ring (or pentagon) and form the $\{5(2)^s\}$-stripe configuration, immediately followed by another first order transition and form the $\{2(2)^s,2(3)^s\}$-stripe configuration (in which the particles are grouped in stripes of 2 or 3 particles which are roughly situated on a rectangle). These stripe phases constitute region $II$. In region $III$ bubble phases are formed: the particles in the two 3-particles stripes form two 3-particles bubbles resulting in the $\{2(2)^b,2(3)^b\}$-configuration followed by a transition to the $\{2(3)^b,(4)^b\}$-configuration. The system consists now of two bubbles of three particles and one bubble of four particles. This last configuration is very symmetric and stays the ground state over a certain $B$-range, indicated by the two dashed lines in Fig. 5.14 around $B = 8$. Finally, if one increases the amplitude of the attractive potential further, the particles redistribute themselves over larger bubbles until all particles are grouped in one bubble in region $IV$ in order to form the $(2,8)^H$ deformed ring-like configuration. Also this high density ring configuration undergoes a first order transition, marked by a dashed line in Fig. 5.14, to the final ground state configuration $(3,7)^H$. Notice, that qualitatively the transitions occur through the same mechanism as found in smaller systems. Moreover, the clustering of the particles in bubbles occurs around similar values for the parameters of the attractive part of the inter-particle potential as found in smaller system. Constructing a complete phase diagram from the Monte Carlo simulations is very time consuming, as the number of stable configurations can be very large. This is illustrated in Fig. 5.14(a) for $N = 10$ and $\kappa = 4$ where $B$ is varied with steps of $\Delta B = 0.1$. We preformed 50,000 trials and used the criterium that two states are taken to be different if $\Delta E = 10^{-7}$. Around $B = 8$ a peak appears which is exactly in the bubble phase region $III$, where metastable states are easily formed by redistributing particles between the bubbles and rotating the bubbles with respect to each other. For small $B$ (region $I$) the number of stable states is small be-
Figure 5.17: Snapshots of the ground state configuration for a $N = 20$-particle system with $\kappa = 4$. The different regions refer to Fig. 5.16

cause the system is close to a normal Coulomb cluster. For larger values of $B$ (region IV), the total number of stable states stays large. Notice that the energy differences between ground state and the metastable states (shown in Fig. 5.14(b)) become larger after region III. This implies that the stability of the metastable states decreases for increasing $B$ and the number of stable states decreases. The same quantities as in Fig. 5.14 are shown in Fig. 5.16 but now for a 20-particle system. Note the increase, an order of magnitude, in the number of stable states for $B > 7$ (Fig. 5.16(a)) as compared to the $N = 10$ case. Snapshots of configurations for different $B$ are shown in Fig. 5.17. As for $N = 10$, we can distinguish four main types of configurations (I low density rings, II stripes, III bubbles, and IV high density rings) are present and marked by full vertical lines in Fig. 5.16. Subdivisions are marked by short dashed lines. From both figures, one can see that the particles first redistribute themselves over different rings until the $(3,17)^L$-ring configuration in region I. Notice that in contrast to $N = 10$, for $N = 20$ two well developed ring are observed. Next in region II, the particles on the outer ring group themselves in stripes
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5.4.1. Intermediate number of particles

Figure 5.18: The distance of the particles to the center of a 30-particle system as function of $B$ with $\kappa = 4$. The vertical dashed lines mark the redistribution of the particles over different rings ($B < 6.7$) and the bubble region ($6.7 < B < 29$).

through a second order transition. Note that the stability of the stripe phase is reduced tremendously: in Fig. 5.16 it is marked by one vertical line. The only stripe phase in this region is the $\{(3);2(3)^5;(11)^5\}$-configuration. The outer particles form almost a perfect ring, however a detailed investigation of the interparticle distances shows the existence of two curved stripes of 3 particles and one long curved stripe of 11 particles. By further increasing $B$, particles group in bubbles in region III through first order transitions. The width of this region has clearly increased in comparison with the 10-particle case. The chaotic behaviour of the radii of the particles in region III (shown in Fig. 5.16(c)) indicates a fast redistribution of the particles between the different bubbles with changing $B$. The number of particles with a radius smaller than 1 clearly increases for increasing $B$, which shows that the number of particles in the central bubble grows until all particles are grouped into the $(1,7,12)^H$-ring configuration in region IV. Only around $B = 9$, a surprisingly stable configuration exist, which corresponds with the small dip in the number of stable configurations (see Fig. 5.16(a)). This configuration is triangular and consists of 2 clusters of 7 particles and one with 6 particles (see Fig. 5.17). On the other hand, one can see from Fig. 5.16(b) that around $B = 7.5$ the energy difference of the 5-particle bubbles configuration is rather large. If one looks at the eigenfrequencies one can see, for higher $B$, that the first non-zero eigenfrequency becomes larger. This means that the bondings between the particles become stiffer which can be explained by the higher particle density of the system. For the 30-particle system we limit the discussion and show the distances of the particles to the center as a function of $B$ in Fig. 5.18 for $\kappa = 4$. Fig. 5.19 shows a
few snapshots of ground state configurations for different $B$ values. Again the four regions are marked. Many more different low density ring configurations are found in region $I$: with increasing $B$ the particles jump from the inner rings to the outer ring. The stripe phase region $II$ is again a very small region and on the scale of Fig. 5.18 is reduced to a single line. The stripe phase $\{(7)^5; (13)\}$ around $B = 6.7$ consists of a bent stripe in the center and a closed ring around it. The stability region of the bubble phase region $III$ now has even more increased, because it takes longer before all particles are grouped in the central bubble. Eventually, the high density ring configuration $(1, 5, 10, 14)^H$ is reached around $B = 29$.

From the above it is clear that with increasing number of particles the stability region of the stripe phases decreases while it increases for the bubble phases.
5.5 Large systems

The series $N = 10, 20, 30$ already gives us an idea of the richness of the possible realizable configurations which are a consequence of the competition between the confinement potential and the repulsive and attractive parts of the inter-particle interaction. To illustrate the increased complexity with $N$ we consider as a final example the 100-particle system. We show in Fig. 5.20 snapshots of ground state configurations for 5 different $B$ values with $\kappa$ fixed at 4. For small $B$, we find again the low density ring configuration (note even the onset of the hexagonal structure in the center). Increasing $B$ leads to a clustering of different rings in bands, as shown in the configuration for $B = 6$ in Fig. 5.21. With a further increase in $B$, these bands break up, resulting in the equivalent of a stripe phase (see the configuration for $B = 7$ in Fig. 5.20). After the stripe phase, many different bubble phases are obtained.

From previous analysis of intermediate size and large systems we can formulate some general rules for different transitions between regions from the low to the high density configuration: i) the particles redistribute to higher and less shells through first order transitions, ii) the particles group in stripes located on shells through a second order transition, iii) the particles in these stripes collapse into bubbles through first order transitions; iv) the particles organize themselves in bubbles of different sizes and finally all particles are grouped in a single bubble through first order transitions. These transitions to bubbles occur for similar parameters of the attractive part of the inter-particle potential as found for smaller systems. Finally, we want to investigate if we can predict even more properties of a large system with the obtained knowledge about smaller systems, since from Fig. 5.1 in Sec. III we expected that the transitions occur around the same parameters. As an example we want to predict for which $B$-value a 100 particle system consists mainly
of 3-particle bubbles at $\kappa = 6$. From the phase diagram for a 6-particle system (Fig. 5.12) we find that 3-particle bubbles are formed at $\kappa = 6$ for $B = 13.5$. The ground state configuration for 100 particles for the same parameters is shown in Fig. 5.21. The ground state configuration was obtained from 100 different trials. Note that the system is organized in small bubbles. These bubbles can be seen as effective particles with multiple charge and mass which interact through a Coulomb repulsive potential. These particles organize themselves in rings around the center of the central confinement potential. The average number of particles is found to be 2.77 particles per bubble which is very close to the predicted number of 3 particles per bubble using the phase diagram of a small system. This example shows that we can understand and predict some of the behavior of larger systems starting from our knowledge of small systems. For larger systems, a bubble can be treated as an effective particle having multiple charge and mass. The subsequent multitype particle system is the finite analogon of the alloy problem.

5.6 Conclusions

In this chapter we investigated a system of classical charged particles with competing short-range attraction and long-range repulsion potential which are confined in a two-dimensional parabolic trap. A rich variety of different configurations were obtained, the number of which increases with the number of particles. Transitions between the different configurations are centered around a strip located near $B \approx 2.5\kappa - 3.5$. This strip separates two identical ring configurations with different density, i.e. the low and high density
ring configuration. The inclination of the smallest $B$ first order phase boundary of this region doesn't depend on the number of particles in the system, but only on the individual interaction between the two particles. The width of the transition region is determined by the number of particles in the system because a deeper local potential minimum is needed to group all particles together in a single bubble. If one follows the ground state configuration starting from the low density configuration to the high density configuration through the transition region, we found that the particles are successively grouped in bubbles. This grouping is almost independent of the number of particles and occurs around the same parameters of the attractive part of the inter-particle potential. The existence of a second order transition in this high density region depends on the structure of the configuration. It doesn't appear in configurations with a triangular structure. For systems with more particles, the number of stable configurations grows very rapidly with $N$. With increasing the attractive part of the interaction potential, intermediate size and large systems all pass through four main phases: low density ring configurations, stripe phases, bubble phases and finally the high density ring configuration. The global qualitative behavior can be deduced from systems with a small number of particles for which we presented the full $(B, \kappa)$ phase diagram. The transition between a stripe phase and a bubble phase occurs through a first order transition. The transition between a ring configuration and the stripe phase through a second order transition.
5. Structure of a 2D cluster with competing interaction
Chapter 6

Dynamics of topological defects and the effects of the cooling rate on finite-size 2D screened Coulomb clusters

The formation of dislocations and their dynamics is central to our understanding of crystalline materials. Thermal effects are thought to play a critical role in the nucleation of these defects. Here, the dynamics of topological defects in two-dimensional (2D) clusters of charged classical particles interacting through a screened Coulomb potential are investigated through the Molecular Dynamics (MD) simulation technique. The particles are confined by a harmonic potential and coupled with an Anderson heat reservoir. We investigate cooling rate effects on the formation of grain boundaries and the dynamics of them by decreasing the temperature of the heat reservoir linear in time. We found that: i) the mobility of defects strongly depends on the number of nearest neighbors and the nature of those defects, ii) geometrically induced defects have different dynamics than other defects because of spontaneous pinning of the defects at the corners of the hexagon. and iii) if the cooling speed is large enough, the system falls out of equilibrium and a glass like structure is formed.

6.1 Introduction

When a liquid is cooled, it can solidify in two very different ways. It can form an ordered crystal or become a glass, depending on the cooling rate. For slow cooling rates, the system will crystallize in a metastable state containing defects close to the ground state. A liquid undergoes a glass transition when crystallization is avoided during the cooling process. Or in other words, when the cooling rate exceeds the relaxation time scale of the system, the system will be out of equilibrium and it undergoes a glass transition.

An important aspect in the formation of crystals is the dynamics of defects during the cooling process. Understanding the nature of glass formation is an important practical issue that goes far beyond window glass. Glassy pharmaceuticals are more rapidly available than crystals. Saccharide glasses are being used to preserve biological structures (tissues, cells, and enzymes) for storage and transportation. All synthetic polymers form solids that are at least partially amorphous; the properties of materials and devices made from polymers thus depend on the molecular motions responsible for the glass transition. Breakthroughs in our understanding of the glass transition may also have an impact on related fields, including protein dynamics and the flow of granular materials.
6. Dynamics of topological defects and the effects of the cooling rate on finite-size 2D screened Coulomb clusters

The phenomenology of crystals and glass formation has been known for decades [124, 125], but we are still far from understanding the relevant features of molecular motion. Experiments have not allowed us to directly measure how a molecule moves relative to a particular neighbor in a glass or to observe which local structures are prone to reorganization. This is the reason who one started studying two dimensional systems with charged particles like e.g. colloids [126] and dusty plasma’s [16] which display similar phase behavior as atoms and molecules with the added advantage that the micrometer size of the particles and their slower dynamics make them accessible for real space imaging [127].

In a recent study of a 3D system consisting of hardspheres [128] dynamical heterogeneities were found. Shortly after this experiment a new experiment showed [129] that fast moving particles were organized in clusters. The behavior of the formed clusters indicated a very inhomogeneous relaxations. This correlated motion can play a critical role in the dynamics of the sample near the glass transition, and its consequences must be incorporated in any theoretical treatment. In this work we want to investigate if similar effects that depend on the cooling rate are present in finite 2D systems. One of the questions we wants to answer is: ”can we find the analogue of a glass transition in a 2D finite systems?”.

In contrast to theoretical work, where it is possible to find the ground state for such a finite system with a limited number of particles, experimentalist always find a metastable state of the system when cooling and annealing the system to a very low temperature. Despite this limitation, a very good agreement between experiment and theory was found for the dynamical properties like melting [102, 123] and reentrant behavior [?, 130], and for the static properties like shell structure formation [102]. It was also found that melting of a large (i.e. N = 150) two dimensional cluster was initiated by topological defects organized at the six corners of a hexagon which were called geometrically induced defects [103].

But, important questions regarding the dynamics of defects and cooling rate effects in these finite 2D systems are remained unanswered. In this chapter we investigate the importance of defect dynamics in finite two dimensional systems during the cooling process and on the formation of crystals or glasses by measuring single defect diffusion and the potential energy of the system. In contrast to previous theoretical studies in which the melting properties of two-dimensional Coulomb clusters were studied [133], we investigate here the effects of the cooling rate on the defect dynamics. Up to now, only one experimental study of defect dynamics was reported for a 3D spherical colloidal crystal [131] where it was found that the defects assemble into scars.

In this chapter we will first show the different diffusion mechanisms that are active and the effect of a boundary in a finite 2D system during the formation of crystals, i.e. by slowly cooling the system. Further we show that if the cooling rate is increased beyond the relaxation times of the system a glass-like structure is formed.
6.2 Model system

We study a 2D model system of $N$ equally charged particles and confined in a parabolic potential interacting through a repulsive screened Coulomb.

\[
V = \sum_{i=1}^{N} \frac{1}{2m} \omega_0^2 r_i^2 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} q^2 e^{-\kappa |\vec{r}_i - \vec{r}_j|}/|\vec{r}_i - \vec{r}_j|, \tag{6.1}
\]

where $m$ is the mass of the particle, $r_i = (x_i, y_i)$ is the vector position of the $i$th particle, and $\kappa$ the inverse screening length. If we take as units for length $r' = (q^2/\gamma)^{1/3}$, for energy $E' = \gamma r'^2$ and for time $t' = \sqrt{2}/\omega_0$ with $\gamma = m \omega_0^2/2$, the potential energy can be expressed in dimensionless form:

\[
V = \sum_{i=1}^{N} r_i^2 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} e^{-\kappa |\vec{r}_i - \vec{r}_j|}/|\vec{r}_i - \vec{r}_j|. \tag{6.2}
\]

All the results are given in dimensionless units. The dimensionless inverse screening length is chosen $\kappa = 5$.

We simulate the cooling of the system by performing molecular dynamics simulations in which the system is coupled to a heat bath as was proposed by Andersen [134]. We decrease the temperature $T(t)$ of the heat reservoir linearly in time i.e., $T(t) = T_i - \gamma t$ with $\gamma$ the cooling rate of the system, $t$ the time, and $T_i$ the initial temperature. Further the equation of motion is integrated with the velocity form of the Verlet algorithm with time step $\Delta t = 10^{-3} - 10^{-4}$. The thermostat is a stochastic collision procedure which randomly substitutes the velocities of the particles according to a Boltzmann distribution that corresponds to the temperature of the heat bath. To improve the statistics we start from 50 different uncorrelated initial positions and average all the results over these 50 independent runs.

The cooling of the system is continued until the temperature of the heat bath is zero. The final obtained configuration is further relaxed using the Newton optimization technique [133]. The Newton optimisation method is similar to molecular dynamics simulations at zero temperature but with increased efficiency.

A defect is defined as a particle which does not have six nearest neighbours. The defects in the system are characterized in different ways. We call a particle with 5 nearest neighbours as a negative or a 5-fold coordinated defect (with topological charge -1) and a particle with 7 nearest neighbours as a positive or 7-fold coordinated defect (with topological charge +1). Furthermore, defects can arrange themselves as dislocations or disclinations. A dislocation consists of an equal number of tightly bound positive and negative defects with a zero total topological charge, a disclination is an array of defects with a total charge of +1. The number of disclinations in a finite two dimensional clusters...
is determined by Euler’s theorem and is equal to six. These six defects can be considered as geometrically induced defects. The other defects will be called randomly induced defects in this chapter.

6.3 The simulation

In order to analyse single defect diffusion, a new variable was constructed, as was proposed by S. Ratynskaia et al. [132]. At every time step the cumulative sum $\xi_j = \sum_{i=1}^{j} \delta \xi_i$ of the azimuthal position displacements is calculated for each particle, with $\delta \xi_i = r_i \delta \phi_i$. Here $r_i$ is the distance from the center of the cluster at time $i \delta t$, and $\delta \phi_i$ is the increment in the azimuthal angle from time $(i-1) \delta t$ to $i \delta t$. The choice of the quantity $\xi_j$ is motivated by the fact that the azimuthal displacement is not limited by the boundary in contrast to the radial displacement. A measure which characterizes the azimuthal diffusion of each particle is now given by $\Delta \xi_j(\tau) = \xi_j + \tau / \delta t - \xi_j$ over the time lag $\tau = 0.1$, which we call the azimuthal diffusion parameter. In the calculation of the azimuthal diffusion parameter we only take into account the inner particles of the cluster. The azimuthal diffusion of the defects is obtained by averaging this azimuthal diffusion parameter over particles with the same number of nearest neighbours.

6.4 Defect dynamics during slow cooling

A lot of research in the past was directed to the study of low dimensional crystals. However very little is known about the formation of crystals and the defect dynamics during the cooling process. Here we investigate how defects are diffusing and relaxing during the cooling process.

As reference system we choose a 200 particle system which is large enough to see already semi-bulk effects, but small enough to obtain results within an acceptable time period. To be sure that all particles are initially uncorrelated at the beginning of the simulation we started at a sufficiently high temperature $T = 0.1$. A relatively simple quantity to study during the cooling process is the average proportion of 7-fold and 5-fold coordinated defects in the system. We show in Fig. 6.1 the defect density as function of temperature. The red dashed line presents the density of the 5-fold coordinated defects, the blue dotted line the 5-fold coordinated defects and the black full line the other particles. As expected, the number of defects decreases during the cooling process because the system tries to form a crystalline structure in order to minimize its potential energy.

How do these defects vanish in the system? A first insight is given by investigating the defect density as function of the radial position for three fixed temperatures as shown in the insets of Fig. 6.1. For high temperature (Fig. 6.1(c) - liquid phase) the number of
Defect dynamics during slow cooling

When cooling down the system, we notice from Fig. 6.1(a) that beside a reduction of the defect density we also observe that the defects migrate from the center of the system to the outer shells. The crystalisation is indicated by the oscillations in the density profile curves as function of the radial coordinate indicating shell formation. Note from Fig. 6.1(c) that the onset of the crystallization process takes place in the center.

Why does crystalisation start from the center of the system? The reason can be found in Ref. [123] where it was shown that in a system 2D consisting of a finite number of repelling particles which are held together by a circular harmonic potential, the cluster patterns are determined by the need to balance the tendency to form a triangular lattice against the formation of a compact circular shape. These defects were called geometrically induced defects and are introduced due to the packing of the triangular lattice into a region with a circular boundary and located at the six corners of a hexagon. Here the melting was initiated by topological defects located at the corners of a hexagon. In our case we cool the system to zero temperature from an initial temperature $T = 0.1$. First the system crystalizes in the center and ends with a symmetry breaking at the six corners of a hexagon. The existence of geometrically induced defects is clearly visible in Fig. 6.1 where the density curve of the 5-fold coordinated defects is almost an equidistance of the 7-fold coordinated defect density curve. By analysing this more closely we found that on average their are six 5-fold coordinated defects more than 7-fold coordinated defects as should be according to Euler theorem. Now we will investigate the possible different defect dynamics and the mechanisms that lead to an annihilation of defects. Therefore we analysed the azimuthal diffusion of the different kind of defects. In Fig. 6.2 the azimuthal diffusion of the defects for a system consisting of 200 particles is plotted. We can clearly distinguish three phases marked by the vertical black dotted lines: The fluid phase ($III$) where the azimuthal diffusion of the 5-fold coordinated defects is larger than the diffusion of the 7-fold coordinated defect and the neutral particles; the crystalized phase ($I$) where the azimuthal diffusion of the 5-fold coordinated (blue dotted line) and the 7-fold coordinated (red dashed line) defects particles are equal, and the transition phase ($II$) where the crystallization of the neutral particles starts and where the diffusion of the 7-fold coordinated particles changes its behaviour.

In order to understand the differences between the diffusion curves for neutral, 5-fold and 7-fold coordinated particles in the fluid region we have to consider two properties, first the number of nearest neighbors and secondly the preferential triangular structure. If we look at the nearest neighbors only, we expect a larger diffusion for the low coordinated particles because they have by definition less nearest neighbors and are consequently less confined by there neighboring particles. However if we look at region $III$ we see that the diffusion of the 7-fold coordinated defects is only slightly lower than the diffusion of the neutral particles which is unexpected. To explain this behavior we have to take into
Figure 6.1: Probability of finding neutral and defect particles as function of temperature for a cooling rate of $\gamma = 10^{-4}$. The red dashed line shows the 7-fold coordinated defects and the blue dotted line the 5-fold coordinated defects. The inverse screening length of the particles is $\kappa = 5$. The insets labeled with (a),(b)and(c) show the density profile as function of radial distance at $T=0.1, T=0.5$ and $T=0.9$, respectively.

account the distortion of the triangular lattice by 7-fold coordinated particles which leads to a higher mobility of the particles around the distortion. We can conclude that the distortion of the lattice by the positive defects compensates the effect of a lower coordination number leading to similar diffusion properties as for neutral particles.

If we cool down the system further till region I, the diffusion of the 7-fold coordinated particles is now equal to the diffusion of the 5-fold coordinated particles because the 7-fold coordinated particles form now an alternating chain of 5-fold and 7-fold coordinated particles. If the neutral particles start crystalysing the geometrically induced defects will occupy the 6 corners of a hexagon. Those defects will be pinned at those corners because of geometrical considerations and are less mobile than the randomly induced defects. Because the netto charge of a geometrical induced disclination is always -1, the 5-fold coordinated defects will be pinned first. This disclination will grow by adding 5-7 fold coordinated pairs forming a chain of alternating 5-fold and 7-fold coordinated defects. As a result, the motion of the 7-fold coordinated defect is now coupled with the motion of the 5-fold coordinated defects. Therefore the diffusion of the 7-fold coordinated defects is first decreasing and than increasing with decreasing temperature, which is a clear reentrant behavior of the azimuthal diffusion of 7-fold coordinated defects. To investigate the pinning phenomenon more closely we tried to make a distinction between geometrically and randomly induced defects because we expected the geometrically induced defects to be less mobile and more stable than randomly induced defects. Therefore we investi-
gated the diffusion of defects in a smaller system, where the number of randomly induced defects are smaller and the geometrical defects are more predominant. In Fig. 6.3 the diffusion of defects in a system consisting of 100 particles is given. Here we found the azimuthal diffusion of the 5-fold coordinated defects to be smaller than the diffusion of the neutral particles. This can be explained as follows: as explained before geometrically induced defects find their origin in the competition between the triangular structure and the circular boundary. Furthermore a structure with on average six 5-fold coordinated at the corners of a hexagon is leading to a system with much lower energy than a system without those geometrically induced defects. Here we found that pinning of geometrically induced defects results in a lower azimuthal diffusion of those defects with respect to randomly induced defects in the system. In addition this proves that the diffusion mechanism in small system differs from the diffusion in larger systems.

6.5 Formation of a glass

So far we discussed the dislocation dynamics during a show cooling. Here, in this section we will show the importance of the cooling speed on the formation of crystals and glasses.

Like mentioned before the temperature of the system is decreased lineair in time by decreasing the temperature of the heat reservoir. This heat reservoir is strongly coupled

![Figure 6.2](image-url)

*Figure 6.2:* (color online) The azimuthal diffusion of a system consisting of 200 particles as function of temperature. The red dashed line show the 7-fold coordinated defects and the blue dotted line the 5-fold coordinated defects and the strait black line indicates the result for the other particle.
to the system so that the system is cooled at very high cooling rates will follow the temperature of the heat reservoir (A weakly thermal coupled system results only in more noisy results because the timescale of the coupling become larger than the timescale of the cooling).

Often in the literature the glass transition is determined as the point where the total energy-temperature curve is bending. Because in our case the external work on the system is zero and the kinetic energy is linearly decreasing with temperature due to the strong thermal coupling, it is appropriate to look for a bend in the potential curve.

In Fig. 6.4 the potential as function of the temperature is given for all cooling rates investigated for a 200 particle system. For decreasing cooling rate the system approaches the behaviour given by the blue dotted curve. This limit is reached when the cooling of the system is sufficiently slow such that its potential energy can attain its minimum. If a system exceeds this critical cooling rate the system equilibrium and a glass transition occurs.

To show the influence of the cooling rate on the glass transition, Fig. 6.5 shows the glass transition temperature and the number of defects after cooling as function of the cooling rate. A small increase of the glass transition temperature is found as function of small cooling rates but a sudden increase occurs if a critical cooling rate is reached. This behavior is explained by the fact that for high cooling rates the system is no longer in thermodynamic equilibrium and consequently the system is no longer able to minimalize its potential energy. If the cooling rate is large enough the system will reach a configuration with maximal energy and number of defects which is indicated by the red dash dot line in the potential curve.
6.6 Conclusions

We have performed a molecular dynamics simulation of a screened Coulomb clusters in order to investigate the roll of defect dynamics during the formation of crystals and the influence of the cooling rate on the formation of glasses.

Our analysis on the formation of crystals show that defects are vanishing in the center first and are pinned at the corner of a hexagon at zero temperature. There were found two diffusion mechanism were found depending on the nature of the defects which were called geometrically and randomly induced defects. The geometrically induced defects
are shown to be less mobile in comparison with the randomly induced defects by measuring the single defect diffusion.

Our analysis of the formation of glasses show a cooling rate dependency of the glass structure. A glass was formed when the cooling rate is so high that the relaxation times of the system at the glass transition temperature is no longer able to equilibrate.

The formation dynamics during cooling and the dynamic nature of the dislocations will have to be accounted for in the design of novel nano and mesoscale materials.

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Chapter 7

Induced order and reentrant melting in classical two-dimensional binary clusters

A binary system of classical charged particles interacting through a dipole repulsive potential and confined in a two-dimensional hardwall trap is studied by Brownian dynamics simulations. We found that the presence of small particles stabilizes the angular order of the system as a consequence of radial fluctuations of the small particles. There is an optimum in the increased rigidity of the cluster as function of the number of small particles. The small (i.e. defect) particles melt at a lower temperature compared to the big particles and exhibit a reentrant behavior in its radial order that is induced by the intershell rotation of the big particles.

7.1 Introduction

Melting and crystallization are fundamental processes in nature and have been widely studied. Charged particles systems like e.g. colloids [126] and dusty plasma’s [16] display similar phase behavior as atoms and molecules with the added advantage that the micrometer size of the particles and their slower dynamics make them accessible for real space imaging [127]. Most of the previous research was directed towards one-component systems. Recently, in a theoretical study in Ref. [114] the complexity of the system was increased by investigating systems with two types of particles of different radii and different effective charge confined in a parabolic trap. A recent experimental study [135] concentrated on oppositely charged colloidal particles confined in a cavity and found a remarkable diversity of new binary structures. In this chapter we consider a finite size binary system of repulsive particles which are confined to move in two dimensions (2D). The circular hard wall confinement potential competes with the 2D Wigner crystal structure [9] and leads to ring like arrangements for the particles [12, 102]. Previously it was shown experimentally [15] and theoretically [?] that single component systems exhibit a remarkable re-entrant melting behavior. In the present binary system we assume a large difference in the size and ‘charge’ of the particles and therefore the smaller particles can be considered as ‘defects’ which disturb the order of the big particles [122]. We found that these defect particles have a pronounced effect on the melting behavior of the system.
and results in an unexpected stabilization of the ordered phase and a new reentrant melting behavior. The possibility of stabilization was also addressed in the theoretical study of Ref. [114] in the case of few binary Coulomb clusters confined in a parabolic trap.

The present study is motivated by the experiment of Ref. [82] where the melting behavior of a binary system of paramagnetic colloidal spheres (with different radii) confined in 2D circular cavities was studied. The coupling parameter could be tuned by changing the applied magnetic field strength. They found that: 1) the shell-like structure of the system depends strongly on the relative number of big $N_B$ and small particles $N_S$, and 2) the melting process takes place in several stages where first the small particles and afterwards the big particles become delocalized.

### 7.2 Model system

In our model, like the experiment of Ref. [82], the particles are confined by a circular hard wall potential ($V_P = 0$ for $r \leq R$ and $V_P = \infty$ at $r > R$). Like in the experiment, the particles interact through a repulsive dipole potential $V(\vec{r}_i, \vec{r}_j) = q_i q_j / |\vec{r}_i - \vec{r}_j|^3$, where $q_i = M_i \sqrt{m_0 / 4\pi}$ is the ‘charge’ and $\vec{r}_i$ the coordinate of the $i^{th}$ particle. For a given type of interparticle interaction and external confinement, only three parameters characterize the order of the system: the number of big particles $N_B$, the number of small particles $N_S$ (also called defect particles) and the coupling parameter $\Gamma$. In the experiment the diameter of the big particles is twice the diameter of the small particles [82], therefore we have chosen the charge of the small particles to be $1/8^{th}$ of the charge of the big particles. As a representative example we will discuss in the following the results for clusters with 16 and 17 big particles. We define the characteristic energy of the interparticle interaction for dipole clusters as $E_0 = q^2 / a_0^3$, where $a_0 = 2R/N_B^{1/2}$ is the average distance between the big particles. In the present calculation we define the coupling parameters as $\Gamma = q^2 / a_0^3 k_B T$, where $k_B$ is the Boltzmann constant and $T$ the temperature of the medium.

The ratio of the particle velocity relaxation time versus the particle position relaxation time is very small due to the viscosity of water and consequently the motion of the particles is diffusive and overdamped. In our simulations we will neglect hydrodynamic interactions. Following [83] we rewrite the stochastic Langevin equations of motion for the position of the particles as those for Brownian particles:

$$\frac{d\vec{r}_i}{dt} = \frac{D_i}{k_B T} \left\{ \sum_{j=1}^{N} \frac{dV(\vec{r}_i, \vec{r}_j)}{d\vec{r}} + \frac{dV_P(\vec{r}_i)}{d\vec{r}} + \frac{\vec{F}_L^i}{m_i} \right\}, \quad (7.1)$$

where $D_i$ is the self-diffusion coefficient and $m_i$ is the particle mass of the $i^{th}$ particle, and $\vec{F}_L^i$ is the randomly fluctuating force acting on the particles due to the surrounding...
media. In the numerical solution of Eq. (1) we took a time step \( \Delta t \leq 10^{-4} / (nD_B) \), where \( n = N_B / (\pi R^2) \) is the density of the big particles. The radius of the circular vessel is \( R = 36 \, \mu m \) and the self-diffusion coefficient of the big particles \( D_B = 0.35 \, \mu m^2/s \) is taken from the experiment [82]. As the self-diffusion constant is inversely proportional to the particle diameter (from the Stokes-Einstein relation \( D = k_B T / 8 \pi \nu a \), with \( \nu \) the viscosity of the fluid and \( a \) the particle diameter) we took \( D_S = 0.7 \, \mu m^2/s \) for the small particles.

Before starting the Brownian dynamics we find first the ground state configuration using the Monte Carlo technique as in Ref. [104].

In order to characterize the angular order of the system, we calculate the angular diffusion of the particles over a 30 min x 1000 time interval. The relative angular diffusion coefficient can be written as

\[
D_\theta = \left\{ \langle \Delta \theta(t)^2 \rangle - \langle \Delta \theta(t) \rangle^2 \right\} / t, \tag{7.2}
\]

where \( \langle \rangle \) refers to a time averaging, and the mean relative angular displacement rotation of the first shell \( \theta_1(t) \) relative to the second \( \theta_2(t) \) one is defined as \( \Delta \theta(t) = |\theta_2(t)| - |\theta_1(t)| \). The mean squared radial diffusion (MSRD) coefficient is

\[
\Delta R^2 = \frac{1}{N} \sum_{i=1}^{N} \left( \langle r_i(t)^2 \rangle - \langle r_i(t) \rangle^2 \right) / a_0, \tag{7.3}
\]

which is a measure of the radial order in the system. The MSRD is calculated separately for the big and the small particles.

### 7.3 Results

We found that all the interesting melting properties for small binary clusters are present in the \( N_B = 16 \) and \( N_B = 17 \) systems. In the insets of Fig. 7.1 the ground state configurations for these systems are shown with zero ((a) and (e)), one ((b) and (f)), three ((c) and (g)) and six ((d) and (h)) small particles. In a 16-particle system with less than 9 small particles (left column in Fig. 7.1), one can see that the big particles form a shell structure with 4 particles in the inner shell and 12 particles localized at the edge of the hard wall. The small particles fill up the vacancies between the big particles. The difference of charge between the big particles and the small particles is so large, that the small particles are expelled from the outer ring. The (4,12)-configuration is a magic number configuration and is exactly the same configuration as one finds without small particles [136]. (For 9 or more small particles the magic configuration is lost and the big particles form a non-magic configuration.) In a 17-particle system (right column in Fig. 7.1) with no small particles, the big particles form the (5,12)-configuration. However, by adding 2...
small particles to the system, the ground state configuration of the big particles changes into the (4,13)-configuration. The reason for this change in the ground state is that the (5,12)-configuration is a non-magic number configuration and by adding small particles the system tries to adjust to a more triangular lattice. In order to study the melting of the binary clusters we performed Brownian dynamics simulations for several values of the coupling constant $\Gamma$. First we show how the angular melting properties change by adding small particles. Afterwards we deal with the radial melting properties.

### 7.3.1 Angular melting

The relative angular diffusion coefficients as function of $\Gamma$ for a system with 16 and 17 big particles for different number of small particles are shown in Fig. 7.1. We notice

![Figure 7.1:](image)

Figure 7.1: (color online) Left column: system containing 16 particles. From top to bottom the number of small particles increases from 0, 1, 3, 6. Right column: system containing 17 particles. Right scale: the relative angular diffusion coefficient (given with error bars) as function of $\Gamma$. Left scale: the $\Delta R^2$ for the small particles (red bullets) and the big particles (black squares) in the binary cluster as function of $\Gamma$. The insets show the corresponding groundstate configuration at $T = 0$. 
from Fig. 7.1(a), for the magic number cluster (4, 12) without small particles, that the relative angular diffusion curve starts to differ from zero around \( \Gamma \approx 1000 \). For larger values of \( \Gamma \), both shells do not rotate relative to each other (i.e. they are locked), which is a typical behavior for a magic number configuration. One can see that adding small particles influences drastically the relative angular melting temperature: the value of the coupling constant \( \Gamma \) at which the angular order between both rings is lost moves to smaller values. This is shown more clearly in Fig. 7.2: the black squares show the \( \Gamma \) value at which the relative angular diffusion coefficient exceeds the value 100 as a function of the number of small particles in a cluster consisting of 16 big particles. One can see that adding even a few small particles can reduce the critical \( \Gamma \) value with a factor of ten. This leads to a first conclusion that adding small particles stabilizes angular order (i.e. it increases the rigidity of the cluster). This unexpected increase in angular order is induced by the vibrations of the small particles. The vibrating small particles, which are mostly situated between the inner and outer shell, lock both shells with respect to each other and stabilize the angular order. Notice the occurrence of a relatively large critical value of \( \Gamma \) for 6 small particles. This can be explained in terms of vacancies. Between the big particles there are only 5 vacancies. When 6 small particles are added to the system, two small particles have to occupy the same vacancy (see inset of Fig. 7.1(g)). This distorts the triangular structure and reduces the angular order, leading to a smaller angular melting temperature. If one increases the number of small particles further, the angular stabilization is restored. One can conclude that on average small particles stabilize the angular order, but the increase in angular melting temperature with respect to a cluster without small particles depends on the positioning of the small particles in the vacancies.

Adding small particles does not only influence the angular melting temperature, but also the height of the plateau in the angular diffusion coefficient (shown by the red triangles in Fig. 7.2 at \( \Gamma = 20 \)). The height of the plateau indicates how fast the shells are rotating with respect to each other. There exists an optimum number of small particles for this angular stabilization (corresponding to a minimum in this curve), which in this case is obtained for \( N_S = 8 \) at which the relative angular diffusion coefficient is reduced with a factor of two with respect to a system without small particles. Note also that the small dip in the relative angular diffusion coefficient for the system without small particles around \( \Gamma \approx 8 \) is a sign of the reentrant behavior as studied before in Ref. [?] and observed in the experiment of R. Bubeck et al. [15].

Next, we examine how these angular melting properties are modified for the non-magic cluster with 17 big particles (see right column in Figs. 7.1 and 7.3). Without small particles, the relative angular order is lost at much smaller temperatures than for a magic number configuration. Adding one small particle does not affect this melting temperature substantially for this particular system, as it will sit in the center of the cluster. However, adding more than three small particles has an even stronger influence on the melting
temperature for angular melting (shown by the black squares in Fig. 7.3) in comparison with the magic-number configuration. Again we found an optimum number of small particles for angular stabilization, which in this case also occurs for 8 small particles (see the minimum in the curve with red triangles in Fig. 7.3).

### 7.3.2 Radial melting

In order to describe the melting in the radial direction we calculated $\Delta R^2$ as a function of $\Gamma$. The $\Delta R^2$ of the big particles in the binary cluster is shown by the black squares in Fig. 7.1. Notice that the radial melting of the big particles sets in around $\Gamma = 10$ which is independent of the number of small particles. In the limit of $\Gamma$ to zero, $\Delta R^2$ approaches $N_B/72$, which is exactly the theoretical limit for the $\Delta R^2$ of a system of completely uncorrelated particles in a cavity with hard walls. Notice that the $\Delta R^2$ curve of the big particles in Fig. 7.1, exhibits an increase of the inclination around $\Gamma = 10 - 20$ as a function of the number of small particles. To analyze this further, we show in Figs. 7.2 and 7.3 the $\Delta R^2$ of the big particles at $\Gamma = 20$ as a function of the number of small particles (green dots) for 16 and 17 big particles, respectively. This $\Delta R^2$ curve shows a linear increase which can be understood as follows: as the angular motion of the big particles is tempered by the small particles, most of the kinetic energy of the particles is directed into the radial direction. Summarizing we can conclude that the radial melting temperature of the big particles is independent of the number of small particles, but that the thermal fluctuations of the angu-

![Figure 7.2:](image-url) (color online) System containing 16 particles. Black squares: critical $\Gamma$ where the angular diffusion of the big particles is exceeding the value 100. Red triangles: height of the plateau of the angular diffusion curve measured at $\Gamma = 20$. Green dots: height of the $\Delta R^2$ of the big particles measured at $\Gamma = 20$. Pink pentagons: Melt temperature of the small particles.
lar motion of the big particles is compensated by an increase of $\Delta R^2$. Comparing the $\Delta R^2$ of the big particles with the $\Delta R^2$ of the small particles (the red dotted curves in Fig. 7.1) it is seen that the radial melting of the small particles sets in at a smaller temperature than the radial melting of the big particles. This confirms the experimental observation [82] that the small particles become delocalized at a larger value of the coupling constant than the big particles. From the $\Delta R^2$ of the small particles we notice that the radial melting of the small particles depends on the number of small particles. Figs. 7.2 and 7.3 (pink pentagons) show the critical $\Gamma$ value where $\Delta R^2$ becomes larger than 0.01 as a function of the number of small particles for a 16 and 17 particle system, respectively. The $\Delta R^2$ curves show that the radial melting temperature increases as function of the number of small particles. This is a consequence of the induced distortion of the triangular lattice by the small particles which is proportional to the number of small particles. The influence of this distortion is clearly visible in the $\Delta R^2$ curve (pink pentagons in Fig. 7.2), just like for the angular melting temperature (black squares). For 6 small particles, at least 2 particles have to occupy a single vacancy which distorts significantly the triangular lattice of the big particles in comparison to the occupancy of only 1 small particle per vacancy. This leads also to a weaker pinning of the small particles and consequently a smaller melting temperature (i.e. a larger critical coupling constant). Since the interaction energy of the small particles (with charge $= q_0/8$) is less than the interaction energy of the big particles, we can expect that the critical coupling constant at which the small particles melt is between 8 times (for 1 small particle in the cluster) and 64 times (in the limit that the interaction is completely dominated by small particles) the critical coupling constant for the big particles. One can verify in Fig. 7.1 that this is indeed the case.

An unusual behavior is found for the radial melting behavior of the small particles which is found not to occur in a single step. The $\Delta R^2$ (red dotted curves in Fig. 7.1

![Figure 7.3](color online) The same as Fig. 7.2 but now for a cluster consisting of 17 big particles.
for 16 and 17 big particles) increases suddenly at a specific $\Gamma$ value. However, it does not reach its maximum value immediately. This means that the small particles at this temperature do not move freely throughout the system, but hop between the vacancies. By further decreasing $\Gamma$ we even observe a decrease in the $\Delta R^2$ before it reaches the theoretical limit of $N_B/72$, in which case the small particles move uncorrelated through the system. In contrast to the mono dispersive cluster where only an angular reentrant behavior was observed [?], we find here a new reentrant behavior but now in the radial melting of the small particles. This reentrant melting occurs exactly at the $\Gamma$ value where the relative angular diffusion coefficient increases strongly. When at large $\Gamma$ the small particles temper the relative angular motion of the shells, we notice now that for smaller $\Gamma$ values it is the complete angular melting which restricts on its turn the radial motion of the small particles.

### 7.4 Conclusion

In conclusion, we investigated the melting behavior of a classical two-dimensional binary cluster. We showed that defect particles in such a binary cluster stabilize the angular order of the cluster. An optimum value for the number of small particles was found for this increased angular stabilization. This tempering of the angular motion of the big particles is compensated by an increase of the radial motion of the big particles. The melting process in a binary cluster takes place in several steps where first the small particles and then the big particles become delocalized with increasing temperature. Due to the radial diffusion of the small particles, the relative intershell rotation of the big particles is reduced with respect to a system without small particles. Further, with an increase of temperature, the diffusion of the big particles switches on that leads to the stabilization of the radial motion of the small particles and a reentrant behavior of the small particles occurs.
Chapter 8

Single file diffusion of interacting particles in a one-dimensional channel

Molecular diffusion in unidimensional channel structures (single-file diffusion) is important to understand the behavior of, e.g., colloidal particles in porous materials (zeolites) and superconducting vortices in 1-dimensional (1D) channels. Here the diffusion of charged massive particles in a 1D channel is investigated using the Langevin Dynamics (LD) simulations. We analyze different regimes based on the hierarchy of the interactions and damping mechanisms in the system and we show that, contrary to previous findings, single file diffusion depends on the inter-particle interaction and could be suppressed if the interaction is strong enough displaying a subdiffusive behavior slower than $t^{1/2}$, in agreement with recent experimental observations in colloids and charged metallic balls.

8.1 Introduction

Diffusion of particles in a narrow channel where mutual passage is forbidden, and thus the sequence of particles remains the same over time, is known as single file diffusion (SFD). Recent advances in nanotechnology has stimulated a growing interest in SFD, in particular, in the study of transport in nanopores. Separation, catalysis, and drug release all rely upon the controlled transport through microscopic channels. Furthermore, SFD is also related to surface growth phenomena. The concept of SFD was introduced few decades ago in bio-physics, to account for the transport of water and ions through molecular-sized channels in membranes [137]. They found that the movement of one molecule of water or ions in the membrane was associated with the movement of others in the same direction. Particle transport across membranes is a crucial intermediate step in almost all biological and chemical engineering processes [137]. The theoretical grounds of SFD were developed in several early studies on 1D transport of particles in pores [138, 139, 140, 141, 142, 143, 144]. Since the mutual passage of particles is prohibited in single-filing (SF) systems, the movements of particles are correlated, because the displacement of a given particle over a long distance drives the motion of other particles in the same direction. Such systems were generally modeled by an infinite set of particles
with hard wall interaction. The correlation in SF systems is reflected in the long-time behavior of the mean square displacement (MSD) which has been predicted for an infinite system to be:

$$\langle \Delta x^2 \rangle = 2F \sqrt{t}, \tag{8.1}$$

where $F$ is the SF mobility and $t$ is the time [140]. In contrast to two-dimensional (2D) and three-dimensional (3D) self-diffusion, SFD cannot be described by a diffusion coefficient or, in other words, does not obey Fick’s law [139]. More recently, it was shown that this behavior is also encountered in overdamped systems with arbitrary repulsive interactions, providing the correlation length between the particles is of finite range [145].

An assembly of “nonpassing” particles diffusing on a one-dimensional periodic substrate was shown [147] to undergo SFD for both noisless (i.e., ballistic) and stochastic dynamics. In the thermodynamic limit (when the density of particles $\rho = N/L$ is constant, where $N$ is a number of particles moving on a segment $L$, and $L, N \to \infty$), for a ballistic single file (bSF) the MSD is

$$\langle \Delta x^2 \rangle \propto \langle | v | \rangle t. \tag{8.2}$$

Thus a bSF particle diffuses as a Brownian particle with normal diffusion coefficient $D = \langle | v | \rangle t/(2\rho)$. For a stochastic single file (sSF) of Brownian particles with damping constant $\eta$ and temperature $T$, the MSD exhibits anomalous diffusion (8.1).

The SFD can be observed in experiments on diffusion of molecules in zeolite molecular sieves (see, e.g., [146]). Zeolites with unconnected parallel channels may serve as a good realization of the theoretically investigated one-dimensional systems. Molecular diffusion of tetrafluoromethane in zeolite AlPO$_4$-5 was studied by pulsed field gradient NMR spectroscopy [148]. The channel diameter, as resulting from a structure analysis by X-ray diffraction, was of the order of 0.73 nm, whereas the diameter of the CF$_4$ molecules was 0.47 nm. Thus the mutual passage of molecules was excluded. An analysis done in [148] showed that in a zeolite channel, the movement of an isolated particle, after a short ballistic period, was determined by the stochastic interaction with the channel walls yielding diffusional behavior, and the MSD was shown to obey the anomalous diffusion law (8.1).

Because the SF condition is hard to fulfill experimentally for, e.g., atomic systems, experimentalists used micro-meter sized colloidal particles in narrow channels. A well-defined SFD model was created [149] by confining paramagnetic colloidal spheres of 3.6 $\mu$m in a set of circular trenches (7 $\mu$m in width and 33 to 1608 $\mu$m in diameter) fabricated by photolithography. Using a video microscopy, the trajectories of individual colloidal particles were followed over long periods of time. The long-time observations ($\sim 8$ hours) revealed a SFD behavior characterized by MSD defined by Eq. (8.1) (with deviations for short and very long times which we will discuss below).
Recently, SFD was experimentally realized even in a macroscopic system where it was easy to fulfill the SF condition and to observe optically the motion of particles. This was realized by Coupier et al. [53], who studied the diffusion of macroscopic charged metallic balls (of radius $R = 0.4$ mm and mass $m = 2.15$ mg) interacting electrostatically and moving in a circular channel such that mutual passing was forbidden, while mechanical shaking induced an effective temperature. The interparticle interaction in the experiment [53] was well described by a modified Bessel function $K_0$, i.e., similar to the inter-vortex interaction in superconductors. The authors found that the system of interacting balls exhibited a subdiffusive behavior slower than predicted for SFD (Eq. (8.1)) and observed in colloidal systems.

The aim of this chapter is to investigate the effect of the inter-particle interaction on SFD, to understand the experimentally observed subdiffusive behavior, and to analyse the obtained results with respect to the existing studies on SFD.

8.2 Model

To study the diffusion in a 1D chain of interacting particles we used Langevin dynamics simulations and model the interparticle interaction by a screened Coulomb potential. The Langevin equation for a system of $N$ interacting particles is given by:

$$m \frac{d^2 \vec{r}_i}{dt^2} = -\alpha \frac{d\vec{r}_i}{dt} + \frac{q^2}{\kappa} \sum_{j=1}^{N} e^{-|\vec{r}_i - \vec{r}_j|/\kappa} + \vec{F}_L,$$

(8.3)

where $t$ is the time, $q$ is the particle charge, $\alpha$ is the friction, $m$ stands for the particle mass, $\vec{r}_i$ is the coordinate of the $i$th particle, $1/\kappa = \lambda$ is the screening length, and $\vec{F}_L$ is the random force which obeys the conditions: $\langle F(t) \rangle = 0$ and variance $\langle F(t)F(t') \rangle = k_B T$. The damping coefficient is given by $\nu = \alpha/m$. In dimensionless units this equation reads as:

$$\frac{d^2 \vec{r}'_i}{dt'^2} = -\nu \frac{d\vec{r}'_i}{dt'} + \sum_{j=1}^{N} \frac{e^{-|\vec{r}'_i - \vec{r}'_j|/\kappa'}}{\kappa'} + \vec{F}'_L(t),$$

(8.4)

where the time $t'$ is given in units of $(r_0/q)\sqrt{me/\kappa}$, the damping coefficient $\nu'$ is given in units of $(1/t')$, where $\eta'$ is the friction, $r' = r/r_0$, $T' = k_B T$ and $\vec{F}'_L(t)$ is the dimensionless random force. Because increasing $r_0$ is the same as increasing $\kappa$ we will fix $\kappa' = 1$. Because $\nu'$ scales with time we will fix $\nu' = 10000$. Further on the primes will be omitted.

In our simulation we will neglect hydrodynamic interactions.
8.3 Results and discussion

We consider a chain of $N$ (we typically took $N = 50$; but we checked that our results did not change when we used longer chains, e.g., $N = 100$) interacting particles, and we impose periodic boundary conditions at the ends of the chain. Before we started with our numerical simulation we first checked the validity of our one-dimensional (1D) model by comparing it with a quasi 1D (Q1D) system (i.e., the particles are confined in a parabolic well), and we found it to be identical to our 1D model as long as the condition of SFD was fulfilled (i.e., that the particles are not able to pass each other). We used a cutoff for the interaction between the particles at long distances such that for the highest particle density the particle cannot interact with itself through the cyclic boundary conditions.

In order to characterize the diffusion of the system we calculated the mean square displacement (MSD) as follows:

$$\Delta X^2(t) = \frac{1}{N} \sum_{i=1}^{N} \left[ \langle x_i(t)^2 \rangle_{\tau} - \langle x_i(t) \rangle_{\tau}^2 \right]$$

where $\langle \ldots \rangle_{\tau}$ refers to the time averaging from the initial time $\tau = t_0$ till $\tau = t$ and $N$ to the number of particles.

The variation of the MSD as a function of time is given in a log-log plot in Fig. 8.1 for three values of the particle density $\rho = 2, 1, \text{and } 0.5$. The diffusion of a single ball is known to possess a Gaussian distribution (see, e.g., [145]) and after an initial $t$ increase at short times, a transition to a $\sim t^1$ behavior at long times takes place. For a particle embedded in a chain satisfying the SF condition, theoretical and experimental studies suggest that after an initial fast growth, the diffusion stabilizes for a long time displaying a subdiffusive $t^{1/2}$ behavior. We define a crossover time $\tau_c$ as the transition from the short time to the long time behavior. This crossover from short- to long time behavior is found for all particle densities investigated and is marked by a line separating regions I (fast diffusion) and II (MSD $\sim t^{1/2}$) in Fig. 8.1. Note that similar crossover was found analytically [150, 151] for the long time diffusion of hard rods hopping in an infinite 1D lattice (1D exclusion model). For short times a particle in the SF regime does not see its neighboring particles in most cases and performs a regular random walk leading to a $t^1$ behavior. Only after a certain time $\tau_c$, which can be interpreted as the time a particle needs to meet one of its nearest neighbors and to realize that it can not cross this particle, the long-time behavior (i.e., regime II) sets in. We found that the crossover time from regime I to II is significantly shifted to larger values of time when the density of the particles decreases which agrees with the findings of a recent experiment with colloids [149].

Contrary to the analytical predictions for hard rods and colloids, where only two regimes were investigated, we found also a third and even fourth regime for longer simulation time. This third regime was recently experimentally observed by Coupier et al.
8.3. Results and discussion

Figure 8.1: (Color online) The average MSD (in log-log scale) of a ball embedded in a single file of $N = 50$ particles for different particle densities. At high particle density, $1/\rho = 2$ (a), the MSD has four different regimes: regime I is an initial fast grow at short times characterized by $\sim t^2$ behavior. The crossover, i.e., the crossover time $\tau_c$, to regime II is shown by the dashed vertical line. Second regime (II) is the subdiffusive behavior typical for overdamped particles (e.g., colloids) and stochastic SFD. Regime III corresponds to the suppressed diffusion, due to the interparticle interaction, even below the $t^{1/2}$. Finally, regime IV is related to the center-of-mass motion of the chain as a whole. For lower particle density, $1/\rho = 1$ (b), the crossover time $\tau_c$ shifts towards longer times. Decreasing the particle density from $1/\rho = 2$ to $1/\rho = 1$, which means that the interaction becomes effectively weaker, is accompanied by an increase of the power of $t^\alpha$ in regime III in the MSD from $\alpha = 0.35$ to $\alpha = 0.45$. For even lower particle density, $1/\rho = 0.5$ the role of the interparticle interaction diminishes, and as a result the system displays a $t^{1/2}$ behavior typical for overdamped systems.

[53] where they found a sub-diffusive behavior slower than $t^{1/2}$. Although not mentioned
by the authors, a similar slowing down of the diffusion for long times was observed also in the experimental study with colloids [149]. As one can see in Fig. 2(A) of [149], for times from $\sim 10^2$ to $\sim 10^3$ s the diffusion is indeed characterized by a subdiffusive behavior $\sim t^{1/2}$, while for times longer than $10^3$ s the MSD starts to decrease thus becoming slower than $t^{1/2}$. The results of our calculations (see Fig. 8.1) clearly show that increasing the particle density favors the appearance of the third region characterized by a subdiffusive behavior with the MSD $\sim t^\alpha$ where $\alpha < 1/2$. Moreover, the larger the density, the smaller becomes $\alpha$ (see Figs. 8.1 (a) and (b); note that for low particle densities region III disappears, Fig. 8.1 (c)). Note that additionally we found that at very long time for a high particle density a forth regime appears (regime IV in Fig. 8.1(a)). In this regime all particles move together as a single massive “particle” with mass equal to the sum of the masses of all individual particles, due to the strong coupling between the particles. This center-of-mass motion is not related with the SFD and will not be discussed here.

Since the role of the interaction between particles becomes more important with increasing density of the particles, our results suggest that the appearance of the regime III, characterized by a subdiffusion behavior slower than $t^{1/2}$, is perhaps a consequence of the interparticle interaction. On the one hand, this result agrees with the observed subdiffusive behavior in the SFD experiments of metallic balls [53] and colloids [149] but, on the other hand, it seems to contradict the findings of previous theoretical studies which showed that the long-time MSD behavior did not depend on the nature of the interparticle interaction [145].

In order to clarify this issue, we will analyze the role of the interparticle interaction in case of a 1D chain of particles under different conditions. Let us first consider the simplest case of massive particles with the interparticle distance $a_0$ much larger than the particle radius $R$ interacting through a hard-core potential during a collision, at very low temperature when the interaction with a medium or a substrate is negligible. Because of the condition $a_0 \gg R$, particles behave as free particles most of the time and thus undergo ballistic SF diffusion with the MSD $\sim t$ (see Eq. (8.2)). This case is illustrated in Fig. 2(a). For higher temperature, particles experience many collisions with the medium (see Fig. 2(b)) before they collide with another particle resulting in stochastic SF diffusion with MSD $\sim t^{1/2}$ (see Eq. (8.1)). Similar behavior is typical for non-interacting particles moving in a viscous medium characterized by a damping $\eta \gg m$, i.e., the overdamped regime (Fig. 2(c)). These are all ideal systems where only one dominating mechanism responsible for particle motion is taken into account and all others are disregarded. However, real systems are usually much more complex and involve a complex hierarchy of interactions and damping mechanisms. For instance, assume interacting particles moving in a medium (Fig. 2(d)). We consider two different regimes. The first regime corresponds to low temperature, $\eta \gg m$, and $| -\eta v_i | \gg f_i^{\text{int}}$, where $v_i$ is the $i$th particle’s velocity, and $f_i^{\text{int}}$ is the force of interaction of the $i$th particle with all other particles. In
8.3. Results and discussion

![Diagram]

**Figure 8.2:** (Color online) Schematic plot of a 1D chain of particles illustrating different regimes of diffusion: ballistic particles interacting with each other through a hard-core potential during a collision, i.e., ballistic SF with the MSD $\langle \Delta x^2 \rangle \sim t^1$ (a); stochastically driven particles, i.e., stochastic SF with the MSD $\langle \Delta x^2 \rangle \sim t^{1/2}$ (b); overdamped motion of non-interacting particles, subdiffusive behavior with $\langle \Delta x^2 \rangle \sim t^{1/2}$ (c); overdamped motion of interacting particles, subdiffusive behavior with $\langle \Delta x^2 \rangle \sim t^{1/2}$ [145] (d); strongly interacting particles in the presence of damping, diffusion is suppressed, $\langle \Delta x^2 \rangle \sim t^{\alpha}$ with $\alpha < 1/2$ (e); infinitely strong interaction (rigid body limit), no diffusion $\langle \Delta x^2 \rangle \equiv 0$ (f).

In this case, the particle motion is mainly governed by the damping force $-\eta v_i$ rather than by the force due to the interparticle interaction $f_i^{\text{int}}$, i.e., the interaction is weak. From this it follows that the details of the interparticle interaction potential are not important as soon as the moving particles are overdamped. This conclusion suggests that the finding of Ref. [145] that the long-time asymptotic behavior of the MSD is independent of the nature of interactions is true only in the overdamped regime.

The second regime assumes that $| -\eta v_i | \lesssim f_i^{\text{int}}$, i.e., that the interaction is not weak. What is the behavior of the MSD in this case? Our calculations suggest that if the in-
terparticle interaction becomes stronger and thus more important in the hierarchy of the mechanisms which influence the particle’s motion, the diffusion in such a system is suppressed. In this case the system can no longer be referred to as an overdamped system, because the damping becomes less important than the interaction. This can be illustrated by a chain of balls linked by a spring with stiffness $K$ which is placed into a viscous medium with a damping $\eta$ (see Fig. 2(e)). Note that in the limiting case of an infinitely stiff spring ($K \to \infty$) the chain moves as a rigid body without any diffusion, i.e., the MSD $\langle \Delta x^2 \rangle \equiv 0$ (Fig. 2(f)) (for an infinite chain, this means that particles do not move at all; in case of a chain of finite number of particles, the system still can move as a whole (i.e., the center-of-mass motion) but, of course, we can easily distinguish between this regime and the subdiffusion). In case of a particle trapped by two neighbors (which do not move) the MSD can be shown [53] to be inversely proportional to $K$: $\langle \Delta x^2(t) \rangle \sim k_B T / K$, thus the MSD $\sim t^0$. For large but finite interaction strengths, the diffusion of interacting particles in a 1D channel is suppressed, and it is characterized by the MSD $\sim t^{\alpha}$, where $0 < \alpha < 1/2$ in the overdamped case, and $0 < \alpha < 1$ in the underdamped case. Note that according to our results the transition to the subdiffusive behavior can occur from the ballistic regime with the MSD $\sim t$ (but not necessarily from the overdamped regime with the MSD $\sim t^{1/2}$). In this case the $\sim t^{1/2}$ behavior is not necessarily indicative of an overdamped regime but is just an intermediate regime between the initial fast diffusion and the subdiffusive behavior with $\alpha < 1/2$. Thus, our analysis eliminates the “contradictions” noticed in Ref. [53] between the experimentally observed subdiffusive behavior slower than $t^{1/2}$ and the theoretical predictions of the $t^{1/2}$ behavior, and it explains the results observed in the experiments [149, 53].

In conclusion, we studied the role of the interparticle interaction in the long time behavior of the FSD in a 1D chain of interacting massive particles. Unlike in overdamped systems where the long-time behavior of the mean squared displacement $\Delta x^2(t)$ was shown to be independent of the nature of the interaction between the particles, we found that when the interparticle interaction becomes strong and thus more important in the hierarchy of the mechanisms driving the particle’s motion, the long time diffusion behavior depends on the interaction and can lead to a subdiffusive behavior with MSD $\sim t^\alpha$ where $\alpha < 1/2$. Our analysis resolves the seemingly contradictions between the earlier theoretical studies and the results of recent experimental studies on SFD in colloids and submillimeter metallic balls and agrees with the results of those experiments. Our results can also be applied to other 1D systems of interacting particles which are subject to SFD. In particular, it can be useful for a better understanding of the 1D channelling of vortices in superconductors which interact in a similar way as the system considered in the present study.

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8. Single file diffusion of interacting particles in a one-dimensional channel
In the second chapter we already mentioned that according to the second law of thermodynamics the average mechanical work \( \langle W \rangle \) needed to move a system in contact with a heat bath at temperature \( T \), from one equilibrium state \( A \) to another equilibrium state \( B \) is at least equal to the free energy difference between these two states: \( \langle W \rangle = \Delta F = F_B - F_A \). The work of going from state \( A \) to \( B \) depends on how the transition is realised. To obtain this work often an external parameter \( \lambda \) is changed in time. The delivered average work can then be written as:

\[
\langle W \rangle = \int_{\lambda_A}^{\lambda_B} d\lambda \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_{\lambda},
\]

(9.1)

where \( H \) represents the Hamiltonian of the system. If we change the control parameter very slowly, one approaches the quasistatic limit were \( \langle W \rangle = \Delta F \), which can be seen as a thermodynamic integration scheme. The difference between the average mechanical work \( \langle W \rangle \) and the difference in free energy \( \Delta F \) is often referred to as the dissipated work. By varying the external control parameter the system can be brought far out of equilibrium. The problem in the past was that most techniques were only valid near equilibrium. For systems far from equilibrium new techniques had to be found and people started investigating fluctuation [84, 85, 86, 87] and work [88, 89, 90, 91, 92] theorems, which show the existence of exact equalities valid independent of the distance to equilibrium. One of these theorems was found in Ref. [92] based on the work theorem of Jarzynski and Crooks. They derived that the dissipated work \( \langle W \rangle - \Delta F \) is given by:

\[
\langle W \rangle - \Delta F = k_B T \int d\lambda \rho(\lambda;t) \ln \frac{\rho(\lambda;t)}{\tilde{\rho}(\lambda;t)},
\]

(9.2)

where \( \rho \) and \( \tilde{\rho} \) are the phase space densities of the system measured at the same intermediate but otherwise arbitrary point in time, in the forward and backward protocol, respectively. Further we will refer all the quantities measured in the backward process with the superscript tilde.

The goal of the following chapter is to estimate \( \rho \) by coarse graining. Because \( \rho \) is an estimate quantity the equality of Eq.(9.2) changes to the inequality:

\[
\langle W \rangle - \Delta F \geq k_B T \int d\lambda \rho(\lambda;t) \ln \frac{\rho(\lambda;t)}{\tilde{\rho}(\lambda;t)},
\]

(9.3)
where \( p(\lambda; t) \) represents the estimate for the phase-space density \( \rho(\lambda; t) \). An interesting question is now how this inequality can be verified experimentally. One possibility are experiments of dusty plasma’s as we will show in this chapter. Further, we will discuss the best coarse graining strategies which can be applied in an experimental setup. The varied external control parameter will be the strength of the parabolic confinement. We consider overdamped motion which justifies the use of Brownian dynamics simulations.

### 9.1 Brownian dynamics simulations

Because the motion is overdamped their is no velocity correlation between two successive time steps. This simplifies the sampling of \( \rho \) in that sense that the velocities can be ignored. In our simulations we will neglect hydrodynamic interactions. Following [83] we rewrite the stochastic Langevin equations of motion for the position of the particles as those for Brownian particles:

\[
\frac{d\vec{r}_i}{dt} = \frac{D}{k_B T} \left\{ \sum_{j=1}^{N} \frac{dV(\vec{r}_i, \vec{r}_j)}{d\vec{r}} + \frac{dV_P(\vec{r}_i)}{d\vec{r}} + \frac{\vec{F}_L^i}{m_i} \right\},
\tag{9.4}
\]

where \( D \) is the self-diffusion coefficient, and \( m_i \) is the particle mass of the \( i^{th} \) particle, and \( \vec{F}_L^i \) is the randomly fluctuating force acting on the particles due to the surrounding media. In the numerical solution of Eq. (9.4) we took a time step \( \Delta t \leq 10^{-4}/(nD) \), where \( n = N/(\pi R^2) \) is the density of the particles. The radius of the circular vessel is taken \( R = 36 \, \mu m \) and the self-diffusion coefficient of the big particles \( D = 0.35 \, \mu m^2/s \) is taken from the experiment [82].

### 9.2 Parabolic confinement

We consider a classical 2D system consisting of charged particles which are laterally confined by a parabolic potential and interacting through the Coulomb potential. The system is described by the Hamiltonian

\[
H = \frac{1}{2} m^* \omega^2 \sum_{i=1}^{N} r_i^2 + \frac{1}{\epsilon} \sum_{i<j}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|},
\tag{9.5}
\]

where \( m^* \) is the effective mass of the particle, \( e \) the particle charge, \( \omega = \alpha \omega_0 \) is the confinement frequency, \( \omega_0 \) a reference frequency, \( \alpha \) the ratio between confinement frequency and the reference frequency, and \( \epsilon \) is the dielectric constant of the medium where the particles are moving in. If we choose \( r_0 = (e^2/\epsilon m^* \omega_0^2)^{1/3} \) as length unit and
9.2. Parabolic confinement

\[ E_0 = m^* \omega_0^2 r_0^2 = k_B T \] as energy unit [108], the Hamiltonian can be expressed in dimensionless form as:

\[ H = \frac{1}{2} \alpha \sum_{i=1}^{N} r_i^2 + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}. \]  

(9.6)

Initially we will only consider one particle and the Hamiltonian reduces to:

\[ H = \alpha r^2. \]  

(9.7)

The equilibrium probability of finding a particle at a certain coordinate \( q = (x,y) \) is given by the Boltzmann distribution:

\[ p(q; \alpha) = \exp[-\beta H(q, \alpha)]/Z_\alpha, \]

(9.8)

\[ = \frac{\beta \alpha}{2\pi} \exp[-\frac{\beta \alpha}{2}(x^2 + y^2)], \]  

(9.9)

where \( Z_\alpha \) is the partition function and \( \beta = 1/k_B T \). During our simulation we will change the control parameter \( \alpha \), which determines the strength of the confinement, in a continuous way from \( \alpha = 1 \) to \( \alpha = 2 \). Since the position doesn’t change during an instantaneous quench the work in the forward process can be calculated as:

\[ \langle W \rangle = \int dxdy[H(x,y; \alpha = 2) - H(x,y; \alpha = 1)]p(x,y; \alpha) = 1 \]  

(9.10)

The free energy difference can be calculated by taking the logarithm of the ratio of the partition functions at \( \alpha = 2 \) and \( \alpha = 1 \) giving:

\[ \Delta F = \ln(Z_{\alpha=2}/Z_{\alpha=1}) = \ln(2). \]  

(9.11)

The dissipated work for an instantaneous quench is then:

\[ \langle W \rangle - \Delta F = \int d\lambda_\alpha \rho(\lambda_\alpha; t) \ln \frac{\rho(q,t; \alpha)}{\tilde{\rho}(q,t; \alpha)} \]

(9.12)

\[ = \int \frac{1}{2\pi} \exp[-\frac{x^2 + y^2}{2}] \ln \exp \frac{x^2 + y^2}{2} = 1 - \ln(2) \]  

(9.13)

Because the dissipated work at an instantaneous quench is maximal we will refer to it as the exact quench limit. Following Eq. (9.17 we can estimate the dissipated work by estimating the phase-space density at an arbitrary point in the forward process, i.e. \( \alpha \)-value, and at the same arbitrary point in the backward process. Because we consider an overdamped Brownian particle, i.e. no velocity correlation between successive time steps, it is sufficient to sample the probability distribution \( \rho(p,t; \alpha) \) which gives the probability
9. Dissipation in a 2D cluster

of the system to be in a certain micro-state at a certain time. In computer simulations and experiments the probability distribution has to be discretized and sampled by performing repeated experiments or simulations starting from different initial coordinates.

The choice of the total number of discrete grid bins $N_G$ in 2D turned out to be very important on the estimated value of the dissipated work. An optimal choice was found when $N_S/N_G = c$ is satisfied, where $N_S$ is the number of simulations, and $c$ a constant which has to be determined at the beginning of the simulations. This can be understood as follows: one would expect that the quality of the approximation of the phase-space density $\rho$ increases with the number of grid bins $N_G$ and the number of simulations $N_S$. If however the ratio between the number of simulations and grid bins is not large enough a too low resolution of a certain point in phase-space is obtained resulting in a bad estimate of the phase-space.

In Fig. 9.1 the estimated dissipation is plotted as function of the number of simulations for a particle in a 2D parabolic confinement together with the analytical obtained quench limit indicated by the dashed line. From this graph one can see that the estimated value of the dissipation very slowly approaches the exact quench limit as function of the number of simulations.

So far we only calculated and simulated the dissipation during an instantaneous quench. Now we calculate the dissipated work as function of the quench time $\tau$ using Eq. (9.1) and Eq. (9.17). In order to improve the statistics for Eq. (9.17) we smoothed the probability distribution $\rho(q,t;\alpha)$ after coarse graining which lead to an improvement of 10%. Further we improved the statistics by taking the average of the dissipated work

![Figure 9.1: The solid line is the dissipative work as estimated from the relative entropy as function of the number of simulations.](image)

$\Delta F$
obtained by applying Eq. (9.17) at 10 different values of the control parameter \( \alpha \) leading to a serious noise reduction dissipation-quench time curve. In Fig. 9.2 the dissipated work is plotted as function of the quench time \( \tau \). The dotted line again indicates the exact quench limit, the thick line the dissipated energy as directly obtained from the simulation, and the thin line the dissipated work as estimated from the relative entropy. \( p(p, t; \alpha) \) that was coarse grained with 500000 simulations.

As intermediate conclusion we can say that Eq. (9.17) gives a good estimate for the dissipated work, but that the exact quench limit cannot be reached within a reasonable number of simulations. It is always lower than the theoretical upper bound.

![Figure 9.2: Dissipation of Brownian particles in a harmonic 2D potential. The thick line is the dissipative work as directly obtained from simulation. The thin line indicates the estimated work obtained from the relative entropy.](image)

**Figure 9.2:** Dissipation of Brownian particles in a harmonic 2D potential. The thick line is the dissipative work as directly obtained from simulation. The thin line indicates the estimated work obtained from the relative entropy.
Summary

In this thesis I investigated the dynamical and static properties of classical one-dimensional and two-dimensional finite size systems.

In chapter 3 a detailed study of the spectrum of Coulomb clusters was performed. I traced its dependence on the number of particles, and compared the results with the hydrodynamic approach. I found out that it is convenient to classify the discrete model modes according to their global vorticity. In the frequency region $0 < \omega < 1$ only modes with large vorticity are present. They originate from the degenerate hydrodynamic state corresponding to zero frequency, where all possible rotations of the liquid droplet are included. As the number of particles is incremented the density of modes in this region becomes negligible as compared with the total averaged density in the cluster. In the region $\omega > 1$ there are modes with a rather small vorticity. As the number of particles in the cluster grows, the frequencies of these modes tend to their analogues in the hydrodynamic model. The velocity distributions of the hydrodynamic model pretty well coincide with the distributions obtained in the discrete model for the above modes with small vorticity, and thus, they may be useful for experimental purposes.

In chapter 4, the groundstate structure of classical identical pointlike particles with one or two defect particles with different mass and charge, interacting through a Coulomb or $1/r^2$ potential and confined in a parabolic potential, was studied. I showed that in the presence of one defect particle the groundstate depends strongly on the charge and mass of the defect particle: closed ring, open ring and cluster configurations are found. Interesting phase diagrams were constructed. A good qualitative agreement was obtained with recent experimental results [54] for systems with both one and two defects. It is interesting to note that the experimental parameters were chosen rather nicely in a region of the phase diagram with many possible states, namely close to the linear phase boundary between the closed ring and cluster configuration. In our simulations I fixed only once the mass and charge of the defect particle in order to explain all the obtained configurations.

In chapter 5, I investigated a system of classical charged particles with a competing short-range attraction and a long-range repulsion potential which are confined in a two-dimensional parabolic trap. A rich variety of different configurations was obtained, the number of which increases with the number of particles. Transitions between the dif-
different configurations are centered around a strip located near $B \approx 2.5\kappa - 3.5$, where $B$ is the strength and $\kappa$ the screening length of the attractive part of the inter-particle potential. This strip separates two identical ring configurations with different density, i.e. the low and high density ring configuration. The inclination of the smallest $B$ first order phase boundary of this region doesn’t depend on the number of particles in the system, but only on the individual interaction between the two particles. The width of the transition region is determined by the number of particles in the system because a deeper local potential minimum is needed to group all particles together in a single bubble. If one follows the ground state configuration starting from the low density configuration to the high density configuration through the transition region, I found that the particles are successively grouped in bubbles. This grouping is almost independent of the number of particles and occurs around the same parameters of the attractive part of the inter-particle potential. The existence of a second order transition in this high density region depends on the structure of the configuration. It doesn’t appear in configurations with a triangular structure. For systems with more particles, the number of stable configurations grows very rapidly with $N$. With increasing the attractive part of the interaction potential, intermediate size and large systems all pass through four main phases: low density ring configurations, stripe phases, bubble phases and finally the high density ring configuration. The global qualitative behavior can be deduced from systems with a small number of particles for which I presented the full $(B,\kappa)$ phase diagram. The transition between a stripe phase and a bubble phase occurs through a first order transition. The transition between a ring configuration and the stripe phase through a second order transition.

In chapter 6, I have performed a molecular dynamics simulation of a screened Coulomb cluster in order to investigate the roll of defect dynamics during the formation of crystals and the influence of the cooling rate on the formation of glasses. Our analysis on the formation of crystals shows that defects are vanishing in the center first and are pinned at the corner of a hexagon at zero temperature. Two diffusion mechanisms were found depending on the nature of the defects which were called geometrically and randomly induced defects. The geometrically induced defects are shown to be less mobile in comparison with the randomly induced defects by measuring the single defect diffusion. Our analysis of the formation of glasses shows a cooling rate dependency of the glass structure. The formation dynamics during cooling and the dynamic nature of the dislocations will have to be accounted for in the design of novel nano and mesoscale materials.

In chapter 7, I investigated the melting behavior of a classical two-dimensional binary cluster. I showed that defect particles in such a binary cluster stabilize the angular order of the cluster. An optimum value for the number of small particles was found for this increased angular stabilization. This tempering of the angular motion of the big particles is compensated by an increase of the radial motion of the big particles. The melting
process in a binary cluster takes place in several steps where first the small particles and then the big particles become delocalized with increasing temperature. Due to the radial diffusion of the small particles, the relative intershell rotation of the big particles is reduced with respect to a system without small particles. Further, with an increase of temperature, the diffusion of the big particles switches on which leads to the stabilization of the radial motion of the small particles and a reentrant behavior of the small particles occurs.

In chapter 8, I studied the role of the interparticle interaction in the long time behavior of the single file diffusion (SFD) in a 1D chain of interacting massive particles. Unlike in overdamped systems where the long-time behavior of the mean squared displacement \( \Delta x^2(t) \) was shown to be independent of the nature of the interaction between the particles, I found that when the interparticle interaction becomes strong and thus more important in the hierarchy of the mechanisms driving the particle’s motion, the long time diffusion behavior depends on the interaction and can lead to a subdiffusive behavior with MSD \( \sim t^\alpha \) where \( \alpha < 1/2 \). Our analysis resolves the seemingly contradictions between the earlier theoretical studies and the results of recent experimental studies on SFD in colloids and submillimeter metallic balls and agrees with the results of those experiments. This results can also be applied to other 1D systems of interacting particles which are subject to SFD. In particular, it can be useful for a better understanding of the 1D channelling of vortices in superconductors which interact in a similar way as the system considered in the present study.

In chapter 9, I looked for strategies to estimate the dissipated work through a refinement of the Jarzynski and Crooks theorem obtained in Ref. [92] by:

\[
\langle W \rangle - \Delta F = k_B T \int d\lambda \rho(\lambda;t) \ln \frac{\rho(\lambda;t)}{\tilde{\rho}(\lambda;t)},
\]

where \( \rho \) and \( \tilde{\rho} \) are the phase space densities of the system measured at the same intermediate but otherwise arbitrary point in time, in the forward and backward protocol, respectively. The goal was to estimate \( \rho \) by coarse graining. When \( \rho \) is an estimated quantity the equality of Eq. (9.17) changes to the inequality:

\[
\langle W \rangle - \Delta F \geq k_B T \int d\lambda p(\lambda;t) \ln \frac{p(\lambda;t)}{\tilde{\rho}(\lambda;t)},
\]

where \( p(\lambda;t) \) represent the estimate of the phase-space density \( \rho(\lambda;t) \). An interesting question is now how this inequality can be verified experimentally. One possibility are through experiments on dusty plasma’s as I showed. The best coarse graining strategies were discussed which can be applied in an experimental setup.
In deze thesis heb ik de dynamische en statische eigenschappen van klassieke één- en twee-dimensionale eindige systemen onderzocht.

In hoofdstuk 3, werd een gedetailleerde studie van het spectrum van Coulomb clusters uitgevoerd. Ik ben de invloed van het aantal deeltjes op het spectrum nagegaan, en de resultaten vergeleken met deze bekomen via een hydrodynamische aanpak. Het bleek nuttig te zijn de modes bekomen uit het discrete model in te delen aan de hand van hun globale vorticiteit. In het frequentiegebied tussen nul en de massacentrum-mode zijn enkel modes met een grote vorticiteit aanwezig. Deze corresponderen met de ontaarde hydrodynamische toestanden die corresponderen met de frequentie nul. Indien het aantal deeltjes toeneemt wordt de mode-dichtheid in dit gebied verwaarloosbaar in vergelijking met de totale gemiddelde dichtheid in de cluster. In het gebied waar \( \omega \) groter is dan de massacentrum-mode vindt men vooral modes met een kleine vorticiteit. Indien het aantal deeltjes in de cluster toeneemt, neigen de frequenties in deze modes naar deze bekomen in het hydrodynamisch model. Voor deze modes komt de snelheidsdistributie van het hydrodynamisch model zeer goed overeen met die bekomen in het discrete model.

In hoofdstuk 4 heb ik de grondtoestand van klassieke identieke punt-deeltjes met één of twee defectdeeltjes met verschillende massa en lading onderzocht. Als interactie tussen de deeltjes werd een Coulomb of \( 1/r^2 \) potentiaal genomen en opgesloten in een parabolische potentiaal. Hier heb ik aangetoond dat afhankelijk van de lading en massa van de defect deeltjes de grondtoestand verschillende configuraties kan aannenen, zoals de gesloten ring, open ring en cluster configuratie. Een goede kwalitatieve overeenkomst werd bekomen met de experimentele resultaten in Ref. [54] voor systemen met zowel één als twee defecten. Het is interessant te vermelden dat de experimentele parameters mooi gekozen waren in een gebied waar meerdere toestanden mogelijk waren, namelijk dicht bij de fasegrens tussen de gesloten ringconfiguratie en de clusterconfiguratie. In onze simulaties heb ik enkel de massa en lading van het defectdeeltje vastgelegd om de bekomen resultaten te verklaren.

In hoofdstuk 5 heb ik systemen met klassieke geladen deeltjes interagerend door middel van een concurerende korte dracht aantrekkings- en lange dracht afstotingspotentiaal in een parabolische opsluiting onderzocht. Een rijke variëteit aan verschillende configuraties
werd bekomen, met een toenemend aantal in functie van het aantal deeltjes. De transities tussen de verschillende configuraties zijn gecentreerd rond een strip gelocaliseerd rond \( B \approx 2.5\kappa - 3.5 \), waar \( B \) staat voor de sterkte en \( \kappa \) voor de afscherm lengte van het aantrekkingsgedeelte van de interdeeltjespotentiaal. Deze strip scheidt twee identieke ring configuraties van elkaar met verschillende dichtheid. De breedte van dit transitiegebied wordt bepaald door het aantal deeltjes in het systeem omdat een dieper potentiaalminimum vereist is om alle deeltjes te groeperen in een bubble. Indien men de grondtoestand configuratie volgt van de lage dichtheidsconfiguratie naar de hoge dichtheidsconfiguratie doorheen het transitiegebied, vond ik dat de deeltjes openvolgend gegroepeerd werden in bubbles. Deze groepering is bijna onafhankelijk van het aantal deeltjes en gebeurt rond dezelfde parameters van aantrekkingsgedeelte van de interdeeltjespotentiaal. De aanwezigheid van een tweede orde transitie in dit hogedichtheidsgebied hangt af van de structuur van de configuraties en gebeurt niet voor configuraties met een Wigner structuur. Voor systemen met meerdere deeltjes groeit het aantal stabiele configuraties zeer snel in functie van het aantal deeltjes. Indien men het aantrekkingsgedeelte van de interactiepotentiaal versterkt, passeren middelgrote en grote systemen door de volgende vier hoofdfasen: de lage dichtheid ringconfiguratie, de strip fase, de bubble fase en uiteindelijk de hoge dichtheid ringconfiguratie. Het globale kwalitatief gedrag van deze systemen kan afgeleid worden van systemen met een kleiner aantal deeltjes waarvoor ik het volledige \( (B, \kappa) \) fasediagram heb voorgesteld. De transities tussen een strip configuratie naar een bubble configuratie gebeurt via een eerste orde transitie en de transitie van de ringconfiguratie naar de stripconfiguratie via een tweede orde transitie.

In hoofdstuk 6 heb ik de rol van de defect dynamica gedurende de vorming van kristallen en de invloed van de koelsnelheid op de vorming van een glas onderzocht aan de hand van moleculaire dynamica simulaties. Onze analyse op de vorming van kristallen toont aan dat de defecten tijdens het koelprocedé eerst verdwijnen in het centrum en vervolgens vastpinnen op de hoeken van een hexagon rond temperatuur nul. Twee verschillende diffusie mechanismen werden gevonden afhankelijk van de natuur van de defecten die we random en geometrisch geïnduceerde defecten hebben genoemd. De geometrisch geïnduceerde defecten bleken minder mobiel te zijn in vergelijking met de random geïnduceerde defecten. Onze analyse toonde verder aan dat de koelsnelheid een grote invloed heeft op de vorming van de glasstructuur. In het ontwerp van nieuwe nano- en mesoschaal materialen moet gedurende het koelen rekening gehouden worden met de vormingsdynamica en de natuur van de dislocatiedynamica.

In hoofdstuk 7 heb ik het smeltgedrag van een klassieke tweedimensionale binaire cluster onderzocht. Er werd aangetoond dat de defectdeeltjes in zulke binaire clusters de angulaire orde van de cluster stabiliseren. Een optimale waarde van het aantal kleine deeltjes werd gevonden met betrekking tot de angulaire stabilisatie. Deze onderdrukking van de angulaire beweging van de andere grotere deeltjes werd gecompenseerd door een
toename van de radiale beweging van deze deeltjes. Het smeltproces in een binaire cluster gebeurt in verschillende stappen waar eerst de kleinere deeltjes en vervolgens de grotere deeltjes gedelocaliseerd worden bij toenemende temperatuur. Door de radiale diffusie van de kleinere deeltjes is de relatieve interschilrotatie van de grote deeltjes gereduceerd ten opzichte van een systeem met identieke deeltjes. Indien men verder de temperatuur verhoogt, wordt de diffusie van de grote deeltjes geactiveerd resulterend in een stabilisatie van de radiale beweging van de kleinere deeltjes, en een re-entrant gedrag van de kleinere deeltjes.

In hoofdstuk 8 heb ik de rol van interdeeltjesinteractie op het lange tijdsgedrag van "enkel rij diffusie" (ERD) onderzocht in een 1D keten van interagerende massieve deeltjes. In tegenstelling tot andere overgedempte systemen waar het langetijdsgedrag van de gemiddelde gekwadrateerde verplaatsing $\Delta x^2(t)$ onafhankelijk bleek te zijn van de natuur van de interactie tussen de deeltjes, vond ik dat de inter-deeltjes interactie sterk het lange tijdsgedrag beïnvloeden in het geval van ERD. Dit leidt tot subdiffuus gedrag $\sim t^{\alpha}$, met $\alpha < 1/2$. Deze analyse ziet er uit als een contradictie tussen de eerdere theoretische studies, maar de resultaten van recente experimenten over ERD in colloïds en submillimeter metallische balletjes bevestigen onze theoretisch resultaten. Deze resultaten kunnen ook toegepast worden op andere 1D systemen van interagerende deeltjes die onderworpen zijn aan ERD.

In hoofdstuk 9 heb ik onderzoek gedaan naar strategieën om het gedissipeerde werk te schatten aan de hand van een verfijning van het Jarzynski en Crooks theorema zoals bekomen in Ref. [92]:

$$\langle W \rangle - \Delta F = k_B T \int d\lambda \rho(\lambda;t) \ln \frac{\rho(\lambda;t)}{\tilde{\rho}(\lambda;t)},$$  \hspace{1cm} (9.16)

met $\rho$ en $\tilde{\rho}$ de dichtheid van de faseruimte van het systeem gemeten op hetzelfde maar een willekeurig punt in de tijd, respectievelijk in het voorwaartse en achterwaartse protocol. Het doel was om $\rho$ te schatten door middel van "coarse graining". Indien $\rho$ een geschatte kwantiteit is verandert de gelijkheid van bovenstaande vergelijking in de volgende ongelijkheid:

$$\langle W \rangle - \Delta F \geq k_B T \int d\lambda \rho(\lambda;t) \ln \frac{\rho(\lambda;t)}{\tilde{\rho}(\lambda;t)},$$  \hspace{1cm} (9.17)

waarbij $\rho(\lambda;t)$ de geschatte dichtheid van de faseruimte voorsteld. Een interessante vraag is dan hoe we deze ongelijkheid experimenteel kunnen verifiëren. Eén van de mogelijkheden zijn stoffige plasma experimenten besproken in de introductie. In dit hoofdstuk zijn de beste coarse graining strategieën onderzocht die ook toegepast kunnen worden bij een experimentele analyse.
SAMENVATTING
## List of Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>0D</td>
<td>Zero dimensional</td>
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<tr>
<td>1D</td>
<td>One dimensional</td>
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<td>AC</td>
<td>Alternating Current</td>
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<td>Two dimensional</td>
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<td>Three dimensional</td>
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<td>body-centered-cubic</td>
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<td>CCD</td>
<td>Charged-coupled device</td>
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<td>DC</td>
<td>D Current</td>
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<td>Mean Squared Radial Displacement</td>
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<td>PDF</td>
<td>Probability distribution function</td>
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<td>RF</td>
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<td>Single File diffusion</td>
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REFERENCES


[108] Here $\omega_0$ is unit of frequency, where previously $\omega_0/\sqrt{2}$ was used.
REFERENCES


Curriculum Vitae

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Education

2003–2008 DEPARTMENT OF PHYSICS, UNIVERSITY OF ANTWERP
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1998–2002 DEPARTMENT OF INDUSTRIAL SCIENCE AND TECHNOLOGY, KATHOLIC HIGH SCHOOL OF LIMBURG
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Employment

10/2003–present PhD student, Condensed Matter Theory Group, University of Antwerp, Belgium (Head of the research group: Prof. Dr. François Peeters).
Publications

List of publications attached at the end.

Major Talks

15/09/2006 : K. Nelissen, B. Partoens, and F.M. Peeters- Dynamics of topological defects and the effects of the cooling rate on large two-dimensional screened Coulomb clusters, Workshop on Diagnostics and Simulation of Dusty Plasmas, Kiel, Duitsland.

Teaching experience

- Exercises: quantum mechanics: 2th Bachelor Physics.
- Practicum: Parallel computing.

Computer skills

Operating systems: Windows, Linux
Office: Word, Exell, Access, PowerPoint
Programming Languages: C/C++, Fortran, Python, java, bash scripting, perl
Parallel programming: MPI, OpenMP, multi threading
PSE’s: Mathematica, MATLAB, Maple, Comsol
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Electronic Egineering: Ledit
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Language Proficiency

Dutch(native), English (fluent), French (good), German(basic)

Interests and Hobbies

Piano, Squash, swimming
List of publications

Refereed journals


