Soft Self-assembly and Densest Packings in Colloidal Models

by

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Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the Graduate School of Duke University

2017
Abstract

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Abstract

Inspired by the beauty of various materials with distinct structures and functions in nature, researchers have been dedicating themselves to discover new ways of creating functional artificial materials to fulfill the increasingly various needs in life. Self-assembly, categorized into the ‘bottom-up’ method, is an important approach in building man-made crystals. Elegant and useful structures have been obtained by colloidal self-assembly, including triangular, kagome and square lattices in two-dimensional systems and hexagonal layered structures and color-tunable structures in three-dimensional systems. However, the self-assembly process itself has not yet been fully understood, both thermodynamically and dynamically. Three major challenges in this field are: a) given a set of conditions and parameters of the system, what is the equilibrium assembly structure? b) given a predetermined structure, how should we design particles to self-assemble it? c) how to avoid possible kinetic barriers to assembly complex structures? This dissertation will focus on answering some of the above questions using statistical mechanics approaches and then provide some guidance to colloidal experiments. More specifically, we first study a quasi-two-dimensional, binary colloidal alloy that exhibits liquid—solid and solid—solid phase transitions, focusing on the kinetics of a diffusionless transformation between two crystal phases. Experiments are conducted on a monolayer of magnetic and nonmagnetic spheres suspended in a thin layer of ferrofluid and exposed to a tunable magnetic field. A theoretical model of hard spheres with point dipoles at their
centers is used to guide the choice of experimental parameters and characterize the underlying materials physics. When the applied field is normal to the fluid layer, a checkerboard crystal forms; when the angle between the field and the normal is sufficiently large, a striped crystal assembles. As the field is slowly tilted away from the normal, we find that the transformation pathway between the two phases depends strongly on crystal orientation, field strength, and degree of confinement of the monolayer. In some cases, the pathway occurs by smooth magnetostrictive shear, while in others it involves the sudden formation of martensitic plates. Secondly, we examine the densest packing structures and their assembly dynamics for hard spheres of diameter $\sigma$ within cylinders of diameter $D$. We extend the identification of close packings up to $D = 4.00\sigma$ by adapting Torquato—Jiao’s adaptive-shrinking-cell formulation and sequential-linear-programming (SLP) technique. We identify 17 new structures, almost all of them chiral. Beyond $D \approx 2.85\sigma$, most of the structures consist of an outer shell and an inner core that compete for being close packed. In some cases, the shell adopts its own maximum density configuration, and the stacking of core spheres within it is quasiperiodic. In other cases, an interplay between the two components is observed, which may result in simple periodic structures. In yet other cases, the very distinction between the core and shell vanishes, resulting in more exotic packing geometries, including some that are three-dimensional extensions of structures obtained from packing hard disks in a circle. Although in such a system phase transitions formally do not exist, marked structural crossovers can nonetheless be observed. Over the range $\sigma \leq D \leq 2.82\sigma$, we find in simulations that structural crossovers echo the structural changes to the densest packing sequence. We also observe that the out-of-equilibrium self-assembly depends on the compression rate. Slow compression approximates equilibrium results, while fast compression can skip intermediate structures. Crossovers for which no continuous line-slip exists are found to be dynamically unfavorable, which is the source of this difference.
results from colloidal sedimentation experiments at low diffusion rate are found to be consistent with the results of fast compressions, as long as appropriate boundary conditions are used. The similitude between compression and sedimentation results suggests that the assembly pathway does not here sensitively depend on the nature of the out-of-equilibrium dynamics. We also examine the behavior of different correlation lengths in such quasi-one-dimensional systems via transfer matrix method. Non-monotonicity of the correlation lengths is observed, as has been identified in the assembly simulations. For the quantities that have a Delta distribution function at infinite pressure, the corresponding correlation lengths vanish as the pressure increases, due to the suppression of fluctuations. For quantities that grow non-monotonically, the decrease of correlation lengths always corresponds to the structural crossovers in the system. As another approach to obtain quasi-one-dimensional assemblies, we examine the focusing of nanoparticles in acoustic standing waves. To perform this study, we build an acoustic focusing chamber containing opposing piezoelectric transducers to rapidly focus particles of different size into highly parallel patterns and visualized this process in real time using dark field microscopy. We select gold as a model material because its high density and low compressibility, making it an ideal candidate for investigating the limits of particle acoustophoresis. To extend our results, we use our theoretical model to estimate, for the first time, the minimum pressure amplitude necessary to concentrate nanoparticles of any composition. Finally, to overcome the limitations of focusing of acoustic standing waves, we develop a simple UV light-based method to controllably induce the aggregation of particles for their rapid concentration below the theoretical size limit at a given pressure amplitude. Lastly, we study the Gardner transition in polydisperse crystals and identify the aging effect by measuring the mean squared displacement as a function of time.
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7.2 \( \Delta(t,0) \) for (a) \( P_d = 0.01 \) and (b) 0.03 at different \( \varphi \) in units of \( \bar{\sigma} \). Circles represent \( \Delta(t,0) \) as a function of time and lines represent the corresponding \( \Delta_{AB} \).

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List of Abbreviations and Symbols

Symbols

\( \theta \) magnetic field tilt angle  
\( U \) system energy  
\( N \) particle number  
\( r_{ij} \) distance between particle \( i \) and \( j \)  
\( \sigma \) particle diameter  
\( U_{\text{HS}} \) hard sphere potential  
\( U_{\text{dd}} \) magnetic interaction potential  
\( U_g \) gravitational energy  
\( \vec{m} \) effective dipole moment  
\( \vec{r} \) unit vector  
\( \mu_f \) ferrofluid magnetic permeability  
\( \chi_B \) material bulk magnetic susceptibility  
\( \varphi \) volume fraction of nanoparticles  
\( \mu_0 \) vacuum permeability  
\( \bar{\chi} \) effective magnetic susceptibility  
\( v_i \) particle volume  
\( V \) system volume  
\( H_z (H_x) \) the vertical (in-plane) component of the external field in air  
\( \partial i^{(\xi)} \) neighbors of particle \( i \) within a cutoff radius \( \xi \)
\( \hat{\rho} \) density mismatch between particles and the fluid

\( T^* \) reduced temperature

\( T \) temperature

\( \beta \) inverse temperature, \( \beta = \frac{1}{k_B T} \)

\( k_B \) Boltzmann constant

\( \alpha \) effective susceptibility

\( r_{\text{sim}} \) cutoff radius for the pair interaction

\( P \) pressure

\( \varrho \) density

\( r_{\text{AVBMC}} \) cutoff for AVBMC

\( r_{\text{clu}} \) cutoff for cluster volume move

\( \Delta x \) particle move step size

\( \Delta \ln V \) volume move step size

\( F^{\text{id}} \) ideal gas free energy

\( \Lambda \) thermal de Broglie wavelength

\( \eta \) packing fraction

\( \psi \) azimuthal angle

\( \Phi_4 \) modified square order parameter

\( \epsilon \) strain tensor

\( \vec{q} \) wave vectors of the fundamental Fourier peaks

\( r \) particle position

\( \lambda \) cylindrical lattice vector

\( v_u \) unit cell volume

\( D \) cylinder diameter

\( (l, m, n) \) phyllotactic notation

\( \xi \) correlation length
\( \gamma \) compression rate

\( g(r) \) radial distribution function

\( \theta_6 \) hexagonal structural parameter

\( \Phi_6 \) 2D hexatic order parameter

\( \text{Rt} \) ratio of settling time to diffusion time for a particle

\( v_{\text{set}} \) settling velocity

\( D_{\text{diff}} \) diffusion constant

\( g \) gravitational acceleration

\( \rho_p (\rho_m) \) particle (solvent) density

\( \mu \) shear viscosity

\( \rho^* \) reduced number density, \( \rho^* = N\sigma^3/V \)

\( H \) separation between two parallel lines

\( \theta(x) \) Heaviside step function

\( Z_{\text{NPT}} \) isobaric partition function

\( \Delta(t, t_w) \) mean squared displacement

\( t_w \) waiting time

\( \Delta_{AB} \) distance between two different copies, \( A \) and \( B \)

\( u(r) \) pair interaction

\( \Phi \) acoustic contrast factor

\( E_{\text{ac}} \) acoustic energy density

\( c_p (c_f) \) speed of sound in the particle (fluid)

\( f_{\text{PZT}} \) drive frequency of the PZT transducer

\( m \) mass

\( \lambda_{\text{aw}} \) acoustic wavelength
<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVBMC</td>
<td>aggregation-volume-bias Monte Carlo</td>
</tr>
<tr>
<td>Cb</td>
<td>checkerboard crystal</td>
</tr>
<tr>
<td>DI</td>
<td>deionized</td>
</tr>
<tr>
<td>DRIE</td>
<td>deep reactive-ion etching</td>
</tr>
<tr>
<td>ECMC</td>
<td>event-chain Monte Carlo</td>
</tr>
<tr>
<td>Hex</td>
<td>hexagonal striped crystal</td>
</tr>
<tr>
<td>EOS</td>
<td>equation of state</td>
</tr>
<tr>
<td>FCC</td>
<td>face centered cubic</td>
</tr>
<tr>
<td>FFC</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>Fl</td>
<td>fluid</td>
</tr>
<tr>
<td>FWHM</td>
<td>full-width-at-half-maximum</td>
</tr>
<tr>
<td>HS</td>
<td>hard sphere</td>
</tr>
<tr>
<td>HS1</td>
<td>Hudson Structure One</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>MSD</td>
<td>mean squared displacement</td>
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<td>NN</td>
<td>nearest-neighbor</td>
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<tr>
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<td>next-nearest-neighbor</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PVA</td>
<td>polyvinyl alcohol</td>
</tr>
<tr>
<td>PZT</td>
<td>lead zirconate titanate</td>
</tr>
<tr>
<td>q1D</td>
<td>quasi-one-dimensional</td>
</tr>
<tr>
<td>RFOT</td>
<td>Random First Order Transition theory</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SK</td>
<td>Sherrington-Kirkpatrick</td>
</tr>
<tr>
<td>SLP</td>
<td>sequential linear programming</td>
</tr>
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</table>
2D two-dimensional
3D three-dimensional
Acknowledgements

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Introduction

One of the most fascinating magic of nature is the beauty of various materials with distinct structures and functions. Examples include diamond, salt, wood, bone and so on. Since the very ancient age of human beings, people have been utilizing different materials from nature to fulfill their various needs for life, which is usually considered as the major distinction between human beings and other animals. However, human beings is not a species that can be satisfied ever. Since the industrial revolution in 1760s, science and technology have been extraordinarily developed, especially the engineering capability with materials. People now have reached the age where we can go beyond nature and it has been a long time that researchers dedicated themselves to discover new ways of creating functional artificial materials to fulfill the increasingly various needs.

Two major strategies are widely used in building man-made crystals: ‘top-down’ and ‘bottom-up’. The former usually includes lithography and moulding techniques and the latter usually refers to (directed) self-assembly [7]. Colloidal soft matter, whose strength of interaction potential is in the order of thermal fluctuations (a few $k_B T$) and size ranging from nanometer to micrometer [8], serves as a great building
block in this area because that its real-space position can be monitored through microscopy and its inter-particle interactions can be tuned [9]. Colloidal self-assembly is then analogous to designing architectures in microscale and abundant structures have been obtained, including the triangular [10, 11], kagome [7, 12] and square lattices [7] in (quasi-) two-dimensional systems, hexagonal layered structures [13], different types of binary ionic crystals [14, 15], color-tunable crystals [16, 17] in three dimensions, and helical structures [18–21] in quasi-one-dimensional systems. The term “soft” is used to denote the fact that these systems react much more sensitively to mechanical perturbations, as compared to atomic or molecular materials [8]. A good example would be a granular system of small mooncakes within a box.

Since the famous talk by Prof. Feynman in 1959 [22], people have been dreaming of manipulating chemical structures atom by atom, while not yet gained much progress. Colloids, usually termed colloidal suspensions, instead offers an alternate approach to this dream, because of several reasons: colloidal particles being a several order of magnitude larger, having relatively mild interactions between particles and experimentally more controllable. However, instead of manipulating the system in a microscopic way, people are more interested in colloidal self-assembly, during which a system consisting of disordered particles forms an organized structure because of particle interactions. Thus the self-assembly structures can often be easily tuned by different system parameters. Common examples include the self-assembly of oppositely charged particles [14, 15, 23] and magnetic particles [7, 24].

Instead of exploring the parameter space in colloidal self-assembly randomly, people have been seeking for design rules that control colloidal self-assembly, and one major challenge for the past decade in the field is to properly design particles to self-assemble into predetermined crystals [25]. Patchy particles, which are particles with anisotropic interactions, are considered the “elementary brick of tomorrow’s self-assembled materials” [25], probably due to its possibilities for various decorations on
the particle shapes and interactions. Recent experimental [12] and theoretical [26–29] efforts have been made to reveal these underlying design rules.

![Figure 1.1](image)

**Figure 1.1**: Hard sphere potential $U$ as a function of particle separation $r$. $U = \infty$ if particles overlap (spheres on the left), $U = 0$ otherwise (spheres on the right).

Being individually resolvable and having a “reaction time” convenient for experimental observation, colloidal soft matter systems serve as great playgrounds for statistical mechanics, the central question of which is to predict macroscopic properties by examining the microscopic details of the system [9]. The hard sphere model, which has been important in this field, is a simple model describing particle interactions which prohibits particle overlaps (Fig. 1.1). The simplest soft matter systems are colloidal suspensions, which usually consist of spherical, rigid particles, such as polystyrene, silica and poly(methyl methacrylate) (PMMA) particles [9]. These systems can thus be theoretically studied by the hard sphere model. This model has been extensively examined because of its dual physical generality and mathematical elegance. For instance, it helps predict the absolute crystal-nucleation rate in hard colloidal suspensions [30], explain both the ordering of binary alloys [31–33] and the persistence of disorder in metallic glass formers [34].
Packing problems, i.e., identifying optimal configurations of a set of hard geometric objects in space without overlap, are NP-hard optimization problems [35]. Studies of hard sphere packings can usually predict self-assembly structures not only for colloidal systems with purely hard interactions, but also those with other types of interactions at high pressures. Mathematical demonstrations of the optimality of these packings present prestigious challenges to surmount. In two dimensions, the triangular lattice of disks in which each touches six others has long been known to be the close packed arrangement [36], but the proof of the Kepler conjecture for hard spheres in three dimensions was only recently obtained [37] (with much fanfare [36]), and in higher dimensions demonstrations are an absolute scarcity [38, 39]. Although mathematical proves are usually difficult, different computational schemes have been developed to search for densest packing candidates, such as simulated annealing [40], genetic algorithms [32] and sequential-linear-programming technique [41]. Generally there exists a large amount of possible self-assembly structures, which essentially prohibits enumerations and the importance of densest packing structures is that they can often provide useful insights into the equilibrium assembly structures. Moreover, many of them are indeed densest packings that are predicted by numerical results [32].

Although the densest packing structures are themselves both elegant and useful, their assembly pathways can be just as important. While failure to assemble optimal structures often results in gel or glass formation, ordered suboptimal outcomes, including limit periodic structures [42] and quasi-crystals [43], are also observed. Conceptually, the dynamical accessibility of structures is often couched in terms of geometrical frustration [44–47]. If the locally preferred organization in the disordered phase is compatible with the globally optimal structure, the system is deemed unfrustrated and assembly is presumed facile. A classic example is a system of two-dimensional hard disks. Locally, the disks spontaneously form equilateral tri-
angles, which can easily organize into the globally optimal triangular lattice. By contrast, a mismatch between the two types of order, i.e., a geometrically frustrated system, places hurdles on the path to assembly. Three-dimensional spheres, for instance, locally form perfect tetrahedra, but their optimal packings (face-centered cubic, hexagonal close-packed, etc.) require the inclusion of geometrical features other than tetrahedra, thus giving rise to a rich set of assembly intermediates [30, 48–50].

A counterpart to this effect is that a suboptimal structure may sometime form more efficiently and reliably than the optimal one, simply because the assembly pathway to the former is less geometrically frustrated than the latter.

Another important topic in self-assembly and statistical mechanics is phase transitions, and self-assembly can often be studied in terms of transitions from disordered to ordered phases. Depending of the continuity of the derivative of the system free energy $F$ with respect to the coupling constants of the dynamical degrees of freedom (e.g. pressure) [51], phase transitions can be classified into two types: it is said to be a first order phase transition if the derivative is discontinuous, and a continuous phase transition otherwise. Interestingly, the phase behaviors of the system sometimes depend on the dimensionality and confinements. A well-known example is that genuine phase transitions formally do not exist in quasi-one-dimensional systems with short-range interactions because the free energy cost of creating defects is small, i.e., of $\mathcal{O}(N^0)$ for a system of size $N$ [52–54], as rigorously shown by Mermin and Wagner [55] as an extension of van Hove’s work [52]. As another example, the liquid-vapor type phase separation or demixing of binary fluid mixtures under confinements between two parallel walls is seriously modified compared to those in three-dimensional systems [56]. An important tool to control the self-assembly process is then by calculating the phase diagram of the system. To efficiently obtain the desired ordered structures, one needs to be sitting at the right spot in the phase diagram, otherwise, particles do not assemble or significant kinetic barriers may occur.
The theme of this thesis is to try to connect different aspects in colloidal self-assembly to better understand this process, both from thermodynamics and dynamics points of view, and from experimental, theoretical and computational approaches. I here focus mainly on self-assemblies under external fields and in restricted geometries. More specifically, self-assembly of magnetic particles in quasi-two-dimensions, hard sphere packings in quasi-one-dimensional systems, focusing of nanoparticles in quasi-one-dimensional confinements are examined. Last but not least, for researchers working on packing problems, it is almost unavoidable to deal with the glass problem. Here in the last chapter, I present the recently on-going work on the Gardner transition in polydisperse crystals with a separate introduction written at the beginning of that chapter.
Phase Transformations in Binary Colloidal Monolayers

In this chapter, we present the collaborative work with Prof. Yellen’s and Prof. Socolar’s groups at Duke University, in which we study both fluid-solid and solid-solid transformations that occur in a mixture of magnetic and nonmagnetic colloidal particles immersed in a thin aqueous solution of magnetic nanoparticles (ferrofluid) and exposed to an external magnetic field. ¹

2.1 Theoretical Model

The magnetic particles used in experiments consist of magnetic nanograins uniformly distributed inside an inert, spherical micron-sized polymer matrix. They thus behave as a homogeneous continuum on the micron scale, allowing for the assignment of an effective magnetic permeability, $\mu_m$ or $\mu_n$, for magnetic or nonmagnetic particles, respectively. The nonmagnetic particles have similar composition, but do not contain magnetic nanograins. Both types of particles are immersed in an aqueous ferrofluid of

¹ This chapter is adapted from the paper: Phase transformations in binary colloidal monolayers, *Soft Matter*, 11 (12), 2404-2415, (2015). My contribution to this work includes performing simulations, calculations of the phase diagram and critical insights into the experimental results.
magnetic nanograins, whose concentration tunes the average magnetic permeability $\mu_f$. In the following, the ferrofluid is assumed to be homogeneous.

**Figure 2.1**: Phases of binary colloidal monolayers. (a) Magnetic particles (red) and nonmagnetic particles (blue) are depicted in the checkerboard crystal phase at low tilt angles and striped crystal phase at high tilt angles. Experimental images corresponding to the cartoons in (a) are provided in (b) the checkerboard crystal in a tilt angle of $\theta = 0^\circ$ and (c) the striped crystal in a tilt angle of $\theta = 60^\circ$. Magnetic particles have average diameter of 2.8 $\mu$m, and nonmagnetic particles have diameter of 3.1 $\mu$m. Particles are immersed a ferrofluid with 1% volume fraction of magnetic nanoparticles. Scale bars are 10 $\mu$m. (d) Calculated minimal potential energy configuration as a function of tilt angle and negative susceptibility ratio, $-\chi_mv_m/\chi_nv_n$, for a perfectly confined 2D system with equal bead size and particle number densities. Note the natural log scale on the horizontal axis. Gravity and image dipoles were not included in this calculation. The susceptibility ratio can be tuned by changing the nanoparticle concentration in the ferrofluid. Experiments and simulations in this work were performed at $-\chi_mv_m/\chi_nv_n = 1$ (solid gray line). Note that for $3 \lesssim \chi_mv_m/\chi_nv_n \lesssim 3.7$ (e.g., dashed gray line), decreasing the tilt angle transforms an equimolar striped crystal into a hexagonal crystal with a 2:1 ratio of magnetic to nonmagnetic particles through an intermediate chain phase. This change in crystal stoichiometry suggests that the solid-solid transition should be accompanied by long-range particle diffusion.
2.1.1 Dipolar potential energy

From classical magnetostatics we know that a homogeneous sphere of magnetically susceptible material produces the field of a point dipole when exposed to a uniform magnetic field. The potential energy of the binary colloid system placed in an external magnetic field is thus modeled by taking the particles to be induced point dipoles at the centers of hard spheres, with the effective susceptibility determined by the permeability difference between a sphere and the surrounding fluid. The system potential energy $U$ is thus taken to be the sum of hard sphere interactions and magnetic interactions between the induced point dipoles. The gravitational energy associated with out-of-plane buckling is also considered. For $N$ particles, we thus have

$$U = \sum_{i<j}^N [U_{HS}(r_{ij}) + U_{dd}(r_{ij}) + U_g(r_i)] \quad (2.1)$$

where $r_{ij}$ is the distance between particles $i$ and $j$, and hard sphere exclusion is complete up to the particle surface at $(\sigma_i + \sigma_j)/2$ for particles of diameter $\sigma$. Dipolar interactions are given by the classical expression,[57]

$$U_{dd}(r_{ij}) = -\frac{\mu_t}{4\pi r_{ij}^3} \left[ 3 (m_i \cdot \hat{r}_{ij})(m_j \cdot \hat{r}_{ij}) - m_i \cdot m_j \right], \quad (2.2)$$

where $m_i$ and $m_j$ are the effective dipole moments and $\hat{r}$ is a unit vector. The ferrofluid magnetic permeability $\mu_t$ is assumed to be a function of the material bulk magnetic susceptibility $\chi_B$ and the volume fraction of nanoparticles $\varphi$,

$$\mu_t = \mu_0 (1 + \varphi \chi_B), \quad (2.3)$$

where $\mu_0$ is the vacuum permeability.

The effective magnetic susceptibility of a particle submersed in the ferrofluid is
given by
\[ \bar{\chi}_i = 3 \left( \frac{\mu_i - \mu_f}{\mu_i + 2\mu_f} \right), \] (2.4)
leading to the effective dipole moment
\[ \mathbf{m}_i = \bar{\chi}_i v_i \mathbf{H}_i, \] (2.5)
where \( v_i \) is the particle volume. When \( \mu_f \) lies between \( \mu_n \approx \mu_0 \) and \( \mu_m > \mu_0 \), the nonmagnetic particles are effectively diamagnetic (\( \bar{\chi}_n < 0 \)), while the magnetic particles are paramagnetic (\( \bar{\chi}_m > 0 \)).

No sufficiently accurate, direct measurements of the difference in susceptibilities between each particle type and the ferrofluid are available. We can, however, estimate the ratio of the two moments in an equimolar mixture by noting that the observed checkerboard phase is a potential energy minimum when the susceptibility ratio \( \chi_m v_m / \chi_n v_n = -1 \) and the tilt angle \( \theta \) is small (see Fig. 6.1d and Sec. 2.2.1). In experiments, we focus on systems where the largest checkerboard crystals assemble, and we thus reasonably assume that \( \chi_m v_m / \chi_n v_n = -1 \) for the rest of the experimental and numerical analyses.

2.1.2 Self-consistent magnetic moments and image dipoles

The magnetic moment of a given particle should be calculated from the total field at its center, which is the sum of the applied field and the field created by neighboring particles:
\[ \mathbf{m}_i = \bar{\chi}_i v_i \left[ \frac{\mu_0}{\mu_f} H_z \hat{z} + H_x \hat{x} + \sum_{j \in \partial i(\xi)} \frac{3(\mathbf{m}_j \cdot \hat{r}_{ij})\hat{r}_{ij} - \mathbf{m}_j}{4\pi r_{ij}^3} \right], \] (2.6)
where \( H_z \) (\( H_x \)) is the vertical (in-plane) component of the external field in air and \( \partial i(\xi) \) denotes the set of neighbors of particle \( i \) within a cutoff radius \( \xi \).
Such computations are possible, but numerically expensive, so we first evaluate their relevance. Self-consistent calculations of the effect of nearest-neighbor fields on the magnetic moments reveal that they generate only small contributions to the potential energy. The only structure with a non-negligible change in potential energy is the incommensurate stripe phase, but even in this case the zero-temperature phase boundary shifts by only a few degrees, from 41° to 49° (see Fig. 6.2). For computational efficiency, we therefore ignore the field created by other particles when calculating the magnetic moments in Monte Carlo simulations.

The presence of a magnetic permeability mismatch at the fluid-glass interface gives rise to image dipoles. The difference in magnetic permeabilities of the ferrofluid and the confining glass results in an additional field felt by the particles. Consider a point dipole with magnetic moment \( \mathbf{m} = (m_x, m_y, m_z) \) located at \( \mathbf{r} = (x_0, y_0, z_0) \) within the ferrofluid. Let the bottom glass slide be in the plane \( z = 0 \) and the coverslip be in the plane \( z = h \). The field within the ferrofluid at \( \mathbf{r} = (x, y, z) \) is thus a sum of the magnetic field of the real dipole and the fields of two image dipoles located at \( \mathbf{r}_{\text{im}}^{(1)} = (x_0, y_0, 2h - z_0) \) and \( \mathbf{r}_{\text{im}}^{(2)} = (x_0, y_0, -z_0) \) with magnetic moment:

\[
\mathbf{m}_{\text{im}} = \left( \frac{\mu_f - \mu_0}{\mu_f + \mu_0} \right) (m_x, m_y, -m_z).
\]

(2.7)

The inclusion of image dipoles in potential energy calculations produces slightly different minimum energy phase boundaries, but again the phase transition sequence is not qualitatively affected (Fig. 6.2), which justifies ignoring their effect in simulations.

2.1.3 Gravitational effects

A gravitational contribution must be included when the experimental cell height is larger than one particle diameter. For a density mismatch \( \bar{\rho}_i \) between particles of
Figure 2.2: Minimal energy structures at various field tilt angles \( \theta \). Energies were calculated using different values of glass slide to coverslip distance \( h \), and \( h = 1.00 \) corresponds to a perfect 2D confinement. For each buckling height, the effects of image dipoles and self-consistently determined magnetic moments were included in the energy calculation. In panels (a), (d), and (g) image dipoles were included and self-consistently determined moments were used. In panels (b), (e), and (h) no image dipoles were included and self-consistently determined moments were used. In panels (c), (f), and (i) no image dipoles were included and the magnetic moments were fixed by the external field alone.
type $i$ and the ferrofluid, we take

$$U_g(r_i) = \bar{\rho}_i v_i g r_i \cdot \hat{z},$$  \hspace{1cm} (2.8)$$

where $v_i$ is the volume of a bead of type $i$ and the $z = 0$ plane is at a distance $\sigma_m/2$ above the bottom glass slide. In our experiments, the density of the nonmagnetic beads is closely matched with that of the fluid, but the magnetic beads are more dense, hence: $\bar{\rho}_n = 0$ and $\bar{\rho}_m = 350 \text{ kg/m}^3$.

2.1.4 Reduced temperature

In order to directly compare simulations, in which the temperature is varied, with experiments, in which the applied field is controlled, we define a reduced temperature as the ratio of thermal energy to dipolar potential energy in the system:

$$T^* \equiv \frac{4\pi k_B T \alpha^2}{\mu_0 H^2 \sigma^3},$$  \hspace{1cm} (2.9)$$

where $T = 298 \text{ K}$ is the ambient temperature, $k_B$ is the Boltzmann constant, $\sigma = (\sigma_m + \sigma_n)/2$ is the average particle diameter, and $\alpha$ is an effective susceptibility that accounts for experimental features that are not modeled directly and corrections to the dipole moment approximations mentioned above.

2.2 Numerical Methods

Different methods were used to extract quantitative and qualitative information from the variants of the theoretical model. The numerical and simulation details are provided in this section.

2.2.1 $T = 0$ phase diagram

The minimal potential energy structures as a function of $\theta$ and $-\chi_m v_m/\chi_n v_n$ were determined from a set 65 two-dimensional structures of equal-sized magnetic and
nonmagnetic particles, i.e., $\sigma_m = \sigma_n$. This set includes rings, chains and crystals that were either presented in Ref. 59, manually constructed, or predicted by a genetic algorithm.[60] Potential energy and magnetic moment calculations were performed using the same methods as in Ref. 59. Magnetic moments were self-consistently determined by solving Eq. (2.6) using a cutoff radius of $r_m = 1.1 \sigma$. The overall potential energy calculation used no cutoff radius for the rings and cutoff radii of $500 \sigma$ and $100 \sigma$ for the chains and crystals, respectively. Gravity and image dipoles were neglected, and, for non-stoichiometric crystals, additional particles were assigned zero potential energy, as in the ideal gas limit.[59] Other parameters used in the calculations are presented in Table 2.1. Note that performing the energy calculations with different values of $\sigma$, $|H|$, and $\chi_B$ does not change the location of the phase boundaries in the tilt angle-susceptibility ratio phase diagram.

<table>
<thead>
<tr>
<th></th>
<th>Fig. 6.2</th>
<th>Fig. 6.1d</th>
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<tr>
<td>$\sigma_m$</td>
<td>$2.8 \mu m$</td>
<td>$1.0 \mu m$</td>
</tr>
<tr>
<td>$\sigma_n$</td>
<td>$3.1 \mu m$</td>
<td>$1.0 \mu m$</td>
</tr>
<tr>
<td>$\mu_m$</td>
<td>$1.5$</td>
<td>$2$</td>
</tr>
<tr>
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<td>$1$</td>
<td>$1$</td>
</tr>
<tr>
<td>$\chi_B$</td>
<td>$19.5$</td>
<td>$11.65$</td>
</tr>
<tr>
<td>$</td>
<td>H_0</td>
<td>$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>$1.0%$</td>
<td>-</td>
</tr>
<tr>
<td>$\psi$</td>
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<td>-</td>
</tr>
<tr>
<td>$r_m$</td>
<td>$20.1 \sigma_n$</td>
<td>$1.1 \sigma$</td>
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<tr>
<td>$r_u$</td>
<td>$30.1 \sigma_n$</td>
<td>see Sec.2.2.1</td>
</tr>
</tbody>
</table>

Table 2.1: Parameters used in potential energy calculations for Fig. 6.1d and Fig. 6.2.

Comparisons of potential energies with and without self-consistent fields and image dipoles were made for seven types of structures. Here again, energy calculations were performed in the high-field limit, in which the gravitational energy is negligible. Three buckling heights were then considered, corresponding to slide to coverslip separations $h = \sigma_n$, $1.17 \sigma_n$, and $1.37 \sigma_n$. 

14
For calculations in which magnetic moments were self-consistently determined, Eq. (2.6) was solved using the Jacobi method with a cutoff radius of $r_m = 20.1 \sigma_n$. Convergence of the energy to within 0.1% was obtained within three iterations. For all cases, the total potential energy per particle was calculated using a cutoff radius of $r_u = 30.1 \sigma_n$. The two cutoff radii were chosen so as to minimize computation time while yielding an error of $\leq 0.1\%$ in the potential energy. The values of the parameters used in calculations are presented in Table 2.1.

The values of $\varphi$ and $\chi_B$ were chosen such that the magnetic moments of the magnetic and nonmagnetic particles are equal and opposite in the limit of infinite dilution. This results in the checkerboard crystal being stable at $\theta = 0$ (Fig. 1d). Note that because both the magnetic moments and the dipole energy are functions of the product $\varphi \chi_B$, calculations performed with any values of $\varphi$ and $\chi_B$ that satisfy the magnetic moment condition above result in identical system energies.

The value of $\mu_m$ in experiment is not known precisely. For the structures observed experimentally (depicted in Fig. 6.2), energy calculations were performed with $\mu_m = 1.5$, which accounts well for the tilt angles at which transitions should occur.

2.2.2 Finite $T$ simulations

The phase diagram and hysteresis loop calculations were obtained from systems in perfect 2D confinement. For simplicity and efficiency, two additional approximations were made. First, the magnetic and nonmagnetic particles were chosen to have the same diameter, $\sigma$. Second, the magnetic moments were not calculated self-consistently, but kept fixed (see Sec. 2.1.2 for a detailed discussion). The first approximation was only made for the phase diagram calculation and the second one was made for all simulations. It was empirically observed from comparing the results with experiments that the errors introduced by these approximations can be accounted for by rescaling the fitting factor $\alpha$. 

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In order to keep the error on the numerical energy calculations within 0.1%, the cutoff radius for the pair interaction $r_{\text{sim}}$ was chosen to be half the simulation box size, i.e., a given particle is considered to interact with $\sim N \pi / 4$ particles. To further improve the computational efficiency, energy calculations for the solid phase used Ewald summation (see, e.g. Ref. 61, Ch. 6, App. F). For the fluid phase, however, in the system size regime considered the approach is less efficient than real-space radial truncation.

2.2.3 Equations of state

The fluid and the crystal equations of state (EOS) were determined by measuring density $\rho$ as a function of pressure $P$ from constant $NPT$ Monte Carlo (MC) simulations. Simulations with $N = 400$ particles were averaged over $4 \times 10^6$ MC cycles following an initial equilibration of $10^6$ MC cycles. Each MC cycle consists of $N$ particle moves and one volume move, on average. In order to efficiently treat strongly associated particles at low densities ($\rho \lesssim 10^{-2}$) and temperatures ($T \lesssim 0.14$), aggregation-volume-bias MC (AVBMC)[62] and cluster volume moves[63] are substituted for half of the standard local displacements and volume moves. We used $r_{\text{AVBMC}} = 1.2\sigma_{ij}$ as the cutoff for the AVBMC and $r_{\text{chu}} = 1.05\sigma_{ij}$ as the cutoff for the cluster volume move, where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. The maximal step size $\Delta x$ and $\Delta \ln V$ for displacements and volume moves, respectively, were tuned every 1000 MC cycles, in order to keep the acceptance rates of both types of moves between 30% and 40%.

2.2.4 Phase diagram

The system free energy was obtained through thermodynamic integration (see, e.g. Ref. 64, Ch. 10). For the fluid, an equimolar mixture of ideal gases is used as the reference free energy

$$F^{\text{id}}(\rho) = N k_B T \left[ \ln \left( \frac{\rho \Lambda^2}{2} \right) - 1 + \frac{\ln(2\pi N)}{2N} \right], \quad (2.10)$$
where the thermal de Broglie wavelength $\Lambda$ is here set equal to $\sigma$. For the solid, an Einstein crystal with area fraction $\eta = 0.739$ was used instead. We found that the Einstein crystal limit is recovered for a spring constant of $2000k_BT/\sigma^2$ for the different state points studied.

The fluid-solid coexistence densities at a given $T$ were determined from a parametric curve of the chemical potential, $F/N + P/\rho$, and $P$ for each phase as a function of density. Phase coexistence takes place at the intersection of the two curves. Note that the fluid-checkerboard crystal coexistence region obtained here is consistent with an earlier, lower-precision calculation.[65]

2.2.5 Dynamical Monte Carlo

The simulation results for both the hysteresis loop and the martensitic transformation, dynamical Monte Carlo simulations, i.e., using only local single-particle displacements, were performed at constant $NVT$ and for $N = 400$.

The hysteresis loop of Fig. 6.4 was determined at a fixed area fraction $\eta = 0.46$ in a 2D system. The order parameter was averaged over 2000 MC cycles for each $T$ ($H$). The reduced temperature was changed by $\Delta T = 0.004$ every 2000 MC cycles between $T^* = 0.023 - 0.075$, $\Delta T = 0.015$ every 2000 MC cycles between $T^* = 0.075 - 0.135$, and $\Delta T = 0.03$ every 2000 MC cycles between $T^* = 0.135 - 0.375$.

For the martensitic transformation simulation, the full Hamiltonian for particles with diameter ratio $\sigma_m : \sigma_n = 2.8 : 3.1$ (Section 2.1) was used. Both perfectly 2D and quasi-2D systems were considered. In the former, particle centers were constrained to only move in the $z = \sigma_n/2$ plane; in the latter, the particles were allowed to move between hard walls separated by a distance $h = 1.1\sigma_n$. The external field was tilted from $0^\circ$ to $50^\circ$ with a tilt rate of $2.5^\circ/2000$ MC cycles. To straightforwardly compare the simulation results with the experiments, images and movies were colored using the same protocol as used in experiments (See Section 2.3.4 and Movie S4).
2.3 Experimental Methods

Colloidal monolayers were formed by placing an equimolar (1:1) binary mixture of spherical 2.8 μm diameter magnetic (M-270 Dynabeads®, Life Technologies™) and 3.1 μm nonmagnetic particles (Fluro-Max R0300, Thermo Fischer) immersed in a ferrofluid (EMG705, Ferrotec, Bedford, NH) between a glass slide and a coverslip. Both magnetic and nonmagnetic particles have a size dispersity of less than 3%. To reduce adhesion between particles and surfaces, the glass slides and coverslips were coated with polyethyleneglycol (PEG) by silanization with 10kD silane-polyoxyethylene-carboxylic acid (PG2-CASL-10k, NANOCS, New York, NY). The ferrofluid susceptibility was controlled by adjusting the volume fraction of magnetic nanoparticles in the final suspension to ~ 1%.

A 1.9 μL aliquot of fluid mixture was sealed in between the glass surfaces with Loctite marine epoxy. Uniform magnetic fields were applied by passing currents through air-core solenoids (Fisher Scientific, Pittsburgh, PA). Microscopy was performed with a DM LM fluorescent microscope (LEICA, Bannockburn, IL) using a 40X air-immersion objective and a combination of brightfield and fluorescent filter cubes (Chroma Technology). Videos were recorded with Retiga 2000R camera (Qimaging, Surrey, Canada). The field ramp was produced by a combination of vertical and horizontal solenoids controlled with Labview (National Instruments, Version 2010, Austin, TX). Image processing was performed using MATLAB (Mathworks, Version 2011, Natick, MA). Details about the image processing and data analysis methods[62, 63] are provided in Section 2.3.4.

2.3.1 Phase diagram

The fluid-solid transition was studied in a vertical magnetic field, with samples prepared at various η. (See Fig. 5.) Each cooling-heating cycle lasted 512 minutes.
The magnetic field was adjusted with the square root of time, which results in the inverse reduced temperature changing linearly with time. The time-dependence of the magnetic field over a single cycle was thus

\[
H = \begin{cases} 
0.5\sqrt{t} \, \hat{z}, & 0 \leq t \leq 256 \\
0.5\sqrt{512-t} \, \hat{z}, & 256 \geq t \leq 512 
\end{cases}
\]  

(2.11)

where the field strength is in Oe and time is in minutes. An image of the system was taken every minute. An example of the fluid-solid transition in an effective cooling-heating cycle at \( \eta = 0.43 \) is demonstrated in Movie S1.

### 2.3.2 Magnetostriction

Magnetostriction experiments proceed by adding a weak, in-plane magnetic field to a vertical field of 9.5 Oe, hence the total external magnetic field was

\[
H_0 = H_z \, \hat{z} + H_x \sin(2\pi ft) \, \hat{x},
\]

(2.12)

where \( H_z = 9.5 \) Oe, \( H_x = 2.1 \) Oe. The cycling frequency \( f = 5.0 \times 10^{-4} \) Hz was chosen such that the crystal had sufficient time to equilibrate, and it corresponds to the polar field tilt angle reaching 12.5° from 0° in \( 2.00 \times 10^3 \) s.

The magnetostriction dependence on the polar tilt angle (Fig. 6.6d) was determined from a square section of the system consisting of 6×6 nonmagnetic particles within a crystallite (Fig. 6.6b). In order to reduce the influence of other factors, such as crystal size and orientation, we only analyzed crystals containing more than 250 particles and with their 10 axis parallel to the \( x \)-axis (azimuthal angle \( \psi = 0^\circ \)). During each of the eight replicates, an image of the system was taken every 50 s, and their analysis gave consistent results.

The magnetostriction dependence on the crystal orientation, or azimuthal angle \( \psi \), was determined from crystallites with more than 250 particles. Crystals with similar orientation (\( \Delta \psi < 5^\circ \)) were grouped together and crystal growth was repeated
until every group had at least five data sets. Within each group, the average relative extension ratio at $\theta = 12.5^\circ$ was calculated (Fig. 6.6e) from images of the system taken every 20 s. An example of magnetostriction dependence on both $\theta$ and $\psi$ is presented in Movie S3.

2.3.3 Martensitic transformation

More than 10 martensitic transformation experiments were performed to verify the consistency of the different martensitic transformation pathways, and an image was taken every 30 s for analysis in each experiment. The image processing and particle identification protocol described in Section 2.3.4 was used to determine the particle coordinates. The particle bonds were then characterized using the method described in Section 2.3.5. In Figure 2.7 and Movies S8, S10, S12, and S13, the particles are artificially colored according to their bond type for visualizing the details in the martensitic transformation process.

2.3.4 Modified square order parameter

Experimental measurements of $\Phi_4$ were obtained from images taken during the cooling-heating cycle that were preprocessed using background subtraction and noise reduction, following the method developed by Crocker et al.[66] A two-step particle identification was then performed: (i) nonmagnetic particles were identified by finding the local intensity maximum of the particle center; (ii) magnetic particles were identified by first locating the dark rim of the particle edge, and then checking that the intensity of the tentative particle center is within a properly chosen range. Visual inspection of multiple images reveals that this identification protocol correctly determines $> 98\%$ of the particle coordinates. For Movies S8, S10, S12, and S13, the remaining particles were manually corrected.

Neighbors, i.e., particles within $1.3\sigma_m$ of each other, are then identified. This
definition deliberately excludes second-nearest neighbors in a square lattice. Given a particle \( k \) with \( n \) neighbors, the local order around particle \( k \) is analyzed in terms of a modified square order parameter

\[
\Phi_{4,k} \equiv \begin{cases} 
0, & n \leq 2 \\
\frac{1}{n} \sum_{j \in \partial k(\Phi)} \exp(4i\theta_{j,k}), & n > 2,
\end{cases}
\]  
(2.13)

where \( \partial k(\Phi) \) denotes the set neighbors (within \( r_{\Phi} = 1.3\sigma_m \) of particle \( k \)), and \( \theta_{j,k} \) is the acute angle between the \( x \) axis and the bond between particle \( k \) and its \( j^{th} \) neighbor. This definition allows us to differentiate between the checkerboard crystal phase (\( n = 4 \) in the bulk, \( n = 3 \) at the boundary, hence \( \Phi_{4,k} \neq 0 \)) and the chain phase (\( n = 2 \) in the bulk, \( n = 1 \) at the boundary, hence \( \Phi_{4,k} = 0 \)). An illustration of this calculation is given in Fig. 6.3. The global order parameter is then defined as the average of \( \Phi_{4,k} \) over all particles,

\[
\Phi_4 \equiv \frac{1}{N} \sum_{j=1}^{N} \Phi_{4,k},
\]  
(2.14)

where \( N \) is the total number of particles in the field of view.

2.3.5 Particle bond characterization

Types of particle bonds, rather than a local order parameter, were used to quantify the martensitic transformation. When \( r_{ij} < 1.2\sigma_{ij} \), two particles are deemed bonded. If the bond formed by a pair of like particles lies within \( 20^\circ \) from the in-plane field component, then it is considered to be a martensitic bond; if a bond is between a pair of unlike particles, then it is considered to be an austenitic bond. The number and distribution of bonds is used to characterize the formation of phases in the martensitic transformation process.
2.3.6 Reciprocal lattices

The reciprocal lattices were obtained by computing the Fourier transform of experimental and simulation images. To eliminate artifacts created by the image boundary, the real-space images were first processed with a Gaussian kernel function \( \exp\left\{-\frac{[(x - x_0)^2 + (y - y_0)^2]}{2\sigma^2}\right\} \), where \((x_0, y_0)\) is the center of the image and \(\sigma = 1000\). A Fast Fourier Transform (FFT) was then performed on the processed images using Matlab (R2011b).

2.4 Results

Results for assembly and phase transformation of the experimental and the theoretical models are presented in this section.

2.4.1 Phase diagram in a vertical field

To study the transformation between bulk solid phases without interference from edge effects and defect-mediated transitions, we first developed a protocol for build-
ing large, well ordered single crystals. This endeavor requires a quantitative understand-
ing of the fluid-solid phase transition, which is achieved by directly comparing experimental results with the phase diagrams obtained by Monte Carlo simulations.

Figure 6.4b shows the simulated phase diagram in the plane of reduced temperature $T^*$ and area fraction $\eta$ for dipolar hard spheres under 2D confinement. The corresponding experimental results are obtained by continuously varying the magnitude $H$ of a vertical magnetic field for samples with different $\eta$. A bond-orientational order parameter $\Phi_4$ (defined in Section 2.3.4) tracks the first-order freezing and melting transitions as the field strength is cycled between 0 and 8 Oe (Fig. 6.4a and Movies S1 and S2). The center of the hysteresis loop is used to estimate the melting point at a given $\eta$. In agreement with simulations, the melting field strength is roughly independent of $\eta$ at $0.1 < \eta < 0.4$, as evidenced by the plateau of Fig. 6.4b, but decreases at high $\eta$. Matching the experimentally observed transitions to the computed phase diagram at several different area fractions gives a fitting factor $\alpha = 2.4 \pm 0.3$, for Eq. (2.9)

In the fluid-solid coexistence regime, we expect that large regular crystals should form at values of $H$ and $\eta$ near the neck of the phase diagram around $T^* = 0.12$. The small density difference between the two phases in that regime helps anneal crystal defects. Preparing monolayers with $\eta \geq 0.60$ was too difficult to achieve because of the high viscosity of these solutions, but reasonably large crystals were nonetheless grown near the phase boundary at $\eta = 0.51$ and $H = 5$ Oe (Fig. 6.5e). Crystals with more than 500 particles, such as those in Fig. 6.1, formed within hours and were taken as the starting points for studies of magnetostriction and martensitic transformations.
Figure 2.4: Fluid-solid phase transitions of binary colloidal monolayers in a vertical field. (a) Experimental and simulated hysteresis curves. Up (down) pointing triangles correspond to experimental data, while the red (black) dashed curve corresponds to the numerical simulation results for the increasing (decreasing) magnetic field. The triangle colors represent the \( \Phi_4 \) bond orientation order parameters, following the color scheme used in (b). Simulation results (dots connected with dashed lines) are superimposed. (insets) Typical experimental images with each particle colored according to its individual \( \Phi_4 \) value. Hysteresis curves are obtained with a field ramp rate that grows with the square-root of time, corresponding to a linear temperature ramp. (b) Phase diagram from simulations shows the fluid (Fl), fluid-checkerboard crystal coexistence (Fl/Cb), checkerboard crystal (Cb), and hexagonal striped crystal (Hex) phases. Black dots and connecting lines indicate the simulated phase boundaries. The colored bars represent the system \( \Phi_4 \) bond order parameter taken from the heating/cooling cycles of part (a) at four different area fractions. The left and right colored bars at each particle concentration represent the cooling and heating processes, respectively. Particles are immersed in a ferrofluid with 1% volume fraction of magnetic nanoparticles. The numerical fitting parameter is \( \alpha = 2.4 \pm 0.3 \). The color scheme is the same as Fig. 6.3.
Figure 2.5: Crystal growth in a constant vertical field. The dependence of crystal growth on area fraction is demonstrated for (a) $\eta = 0.20$, (b) $\eta = 0.33$, and (c) $\eta = 0.41$ at a field strength of $H = 6$ Oe. The dependence of crystal growth on field strength is demonstrated for (d) $H = 2.5$ Oe, (e) $H = 5$ Oe, and (f) $H = 7.5$ Oe at a particle area fraction of $\eta \sim 0.51$. In each experiment, the magnetic field was held constant for six hours. The largest crystals were found to grow at $\eta \sim 0.51$ and $H = 5$ Oe.

2.4.2 Tilting the field at small angles: magnetostriction

Tilting the magnetic field away from the vertical induces magnetostrictive compression for tilt angles $\theta > 0^\circ$. Experimentally, a strong vertical field (9.5 Oe) is applied, in order to reduce thermal motion, and a weak in-plane sinusoidal magnetic field is supplemented. The in-plane component was set to oscillate at $5.00 \times 10^{-4}$ Hz, so that the crystal had sufficient time to equilibrate. Repeating experiments at rates
corresponding to oscillation periods between $2.00 \times 10^3$ s to $5.00 \times 10^3$ s gave comparable results (Fig. 6.5f), suggesting that our experiments were performed at (or near) thermodynamic equilibrium.

Figure 6.5 illustrates the magnetostriction coefficient for different $\theta$ and crystal orientations, $\psi$, relative to the in-plane component of the field. The components of the 2D strain tensor are given by $\varepsilon_{xx} = (a_f - a_i)/a_i$, $\varepsilon_{yy} = (b_f - b_i)/b_i$, $\varepsilon_{xy} = c/a_i$, and $\varepsilon_{yx} = d/b_i$, where $a_i$ and $b_i$ are the unstressed ($\theta = 0^\circ$) lattice constants in the $x$ and $y$ directions, respectively, and $a_f$, $b_f$, $c$, and $d$ are measured in the final state (Fig. 6.5a), using the original lattice in the experimental image. The non-magnetic particles at the corners of the rectangle depicted in Fig. 6.5b were used for the measurements. Both $a_i$ and $b_i$ are approximately equal to $\sqrt{2}(\sigma_m + \sigma_n)/2$. We find that dilation ($\varepsilon_{xx} + \varepsilon_{yy}$), rotation ($\varepsilon_{xy} - \varepsilon_{yx}$), and transverse shear ($\varepsilon_{xy} + \varepsilon_{yx}$) are all negligible. Figure 6.5 thus only depicts the extension ratio (or longitudinal shear) $E = \varepsilon_{xx} + \varepsilon_{yy}$, which results from Joule magnetostriction. Negative values indicate that the crystal is compressed along the direction of the in-plane field. For $\psi = 0^\circ$ (a field aligned with the 10 crystal direction) the magnetostriction is maximal, exceeding 10%, which is an order of magnitude larger than that observed in giant magnetostrictive materials;[67] by contrast, for $\psi = 45^\circ$ (a field along the 11 crystal direction), magnetostriction is suppressed (see Movie S3). To test the accuracy of our measurement of Joule magnetostriction, the reciprocal lattice obtained via Fast Fourier Transform (FFT) of the real-space images was also analyzed. The peaks at the corners of the rectangle in Fig. 6.5c were used to calculate the magnetostriction coefficient. The difference between the real- and reciprocal-space results is within experimental uncertainty.
Figure 2.6: Magnetostriction of binary colloidal crystals. Experiments were performed in a magnetic field with a constant vertical component of 9.5 Oe and a sinusoidally varying horizontal field with a magnitude of 2.1 Oe and a frequency of $5 \times 10^{-4}$ Hz. (a) General deformation of a rectangle. The black rectangle with lengths $a_i$ and $b_i$ represents the unstressed state, and the blue shape represents the deformed state with lengths, $a_f$, $b_f$, $c$, and $d$. An example experimental region used for measuring the magnetostriction effect is illustrated in both (b) real-space and (c) reciprocal-space. The Joule magnetostriction coefficient, defined as the extension ratio $E$ is plotted in (d) as a function of the tilt angle for fixed crystal orientation $\psi = 0^\circ$, and (e) as a function of the crystal orientation for a fixed tilt angle $\theta = 12.5^\circ$. The insets in (d) illustrate an exaggerated crystal compression for small and large tilt angles for a fixed $\psi = 0^\circ$. The insets in (e) illustrate the field direction relative to the crystal orientation for $\psi = 2.5^\circ$ and $\psi = 32.5^\circ$, respectively, with fixed $\theta = 12.5^\circ$. The extension ratio as a function of tilting frequency is illustrated in (f), where $1/f$ corresponds to the period of the in-plane sinusoidal wave. The black arrow indicates the tilting frequency that is used for obtaining the data in panels (d) and (e).

2.4.3 Large tilt angles: martensitic transformations

To explore the transformation from checkerboard to striped crystal, we applied a rotating magnetic field with constant angular frequency and field strength. For $\theta > 15^\circ$, the crystal undergoes a diffusionless transformation through a combination of compression, shear, and slip along the 10 or 11 lattice directions. Video microscopy and numerical simulations reveal a variety of possible combinations of these different
elements (Fig. 2.7). For a fixed $T$ (constant $H$), the chosen pathway indeed depends
on the initial crystal orientation, field strength, and degree of planar confinement.
Note that the latter two factors are related because out-of-plane motion is suppressed
near the melting transition, where the gravitational cost of buckling is large compared
with the energy gain of forming dimers.

To characterize the different experimental transformation pathways, we first con-
sider the behavior of systems where the motion is perfectly confined to a 2D plane,
which are only accessible in simulation. In this case, for all field strengths the tran-
sition at $\psi = 0^\circ$ proceeds through continuous longitudinal shear (see Fig. 2.7(a-d)
and Movie S4 for the high field cases, and Movie S5 for the low field cases), while at
$\psi = 45^\circ$ zigzags form and gradually straighten into horizontal stripes (see Fig. 2.7(m-
p) and Movie S6 for the high field cases, and Movie S7 for the low field cases).
These pathways are qualitatively different from those observed in experiments (see
Fig. 2.7(e-l), and (q-x)), in which perfect 2D confinement is not accessible. Although
we cannot precisely quantify the amount of experimental buckling, we can estimate
it by comparing the distance between adjacent particle centers relative to the diam-
eter of the particle. This analysis suggests that in most experiments the buckling
angle between two adjacent particles was in the range of $5^\circ$ to $15^\circ$ relative to the
plane. When a similar amount of out-of-plane motion (buckling) is allowed in sim-
ulation, we find markedly improved agreement with experiment and thus conclude
that confinement plays a key role in tuning the transformation pathway.

Each row in Fig. 2.7 shows the crystal transformations for different tilt angles $\theta$
and crystal orientations $\psi$. The first and fourth rows depict the simulated transfor-
mation for strict 2D confinement. The second and fifth rows depict the experimental
transformation in a strong field. The third and sixth rows depict the corresponding
experimental transformations in a weak field.

Experimental observations of the transition from checkerboard to striped phase

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Figure 2.7: False color experimental and simulation images of the martensitic transformation from a checkerboard crystal phase to a striped crystal phase for different crystal orientations and field strengths. Each row shows a sequence of images from a single experiment or simulation in which the tilt angle of the field was monotonically increased. For visualization purposes, the particles with at least one martensitic bond are falsely colored red (pink) if they are magnetic (nonmagnetic), while particles with only austenitic bonds are colored dark blue (light blue) if they are magnetic (nonmagnetic). Simulated transformations under perfect 2D confinement and experimental transformations at both strong (12 Oe) and weak (5 Oe) fields are shown for each of the two crystal orientations $\psi = 0^\circ$ and $\psi = 45^\circ$. By setting $h = 1.11 \sigma_n$ in simulations (Movies S9 and S11), better agreement with experiment is obtained, which highlights the role of confinement in the transformation dynamics. In all experiments, the tilt rate of the field $0.008^\circ$/s.
for two field strengths and two initial crystal orientations are shown in Fig. 2.7. The experimentally observed transformation pathway for a strong field and $\psi \approx 0^\circ$ proceeds first through magnetostrictive compression, and then by shear, resulting in the diagonal lines of dimers visible in Fig. 2.7g. Adjacent dimer lines then align and coalesce to form the striped phase of Fig. 2.7h. (See experimental Movie S8 and simulation Movie S9, which allows buckling, unlike the simulation of Fig. 2.7c). These transformations are smooth and homogeneous. By contrast, the transformation for $\psi \approx 45^\circ$ proceeds through a sequence of abrupt slips, giving rise to the vertical lines of nearly horizontal dimers visible in Figs. 2.7r and 2.7s. In most cases, the dimer line nucleates at a defect site and is facilitated by a local lattice expansion, which opens up free space for adjacent columns to shift and for dimer lines to zip up. Isolated dimer lines first form throughout the crystal, typically appearing every few columns. Dimer lines and monomer lines then coalesce into trimers or quadrtrimers (see experimental Movie S10 and simulation Movie S11), depending on the spacing between nearby dimer lines, and finally form horizontal stripes (Fig. 2.7t). The sudden coordinated line slips result in structures that resemble martensitic plates.[68, 69] For weaker fields, the features observed at strong fields remain qualitatively discernible, but the coherence of the dimer lines is weakened, as displayed in Figs. 2.7k and 2.7w (see experimental Movies S12 and S13, and simulation Movies S14 and S15). We attribute this effect to the increased importance of gravity relative to the dipole interactions, which suppresses buckling and thus hybridizes the pathways with those of perfectly confined systems. The perfectly 2D confined systems, which can only be probed via simulations, show little evidence of a dimer phase, as may be expected given that dimer formation in the experimental system involves buckling (see Figs. 2.7c and 2.7o).

Fourier transforms of the experimental images (see insets in Fig. 2.7 and Movies S8, S10, S12, and S13) confirm the rotational symmetries of the different interme-
diates and show evidence of ordering at wavenumbers present in neither the initial checkerboard nor the final striped phase. For $\psi \approx 0^\circ$, the system is first continuously sheared. Let $\mathbf{q}_1 = (q_1, 0)$ and $\mathbf{q}_2 = (0, q_2)$ be the wave vectors of the fundamental Fourier peaks. During the magnetostriction, $q_1$ grows and $q_2$ shrinks. As dimer lines form, diffuse Fourier peaks appear at $\pm (-q_1, q_2)/2$ (Fig. 2.7g and Movie S8), indicating the emergence of a dimer configuration with a unit cell twice as large as the (sheared) checkerboard. As the field is tilted further, however, both the peaks at $(-q_1 \pm q_2)/2$ and at $q_1$ are extinguished, a signature of the striped phase. While trimer or quadrimer patterns may also exist, we see no clear evidence of ordering at the wavenumbers associated with them.

For $\psi \approx 45^\circ$, the rectangular symmetry of the Fourier pattern is retained throughout the transformation, and Fourier peaks remain fixed in position, indicating that there is no overall shearing or compression of the lattice (see Movie S10). Let $\mathbf{q}_3 = (1, 1)q$ and $\mathbf{q}_4 = (1, -1)q$ be the wave vectors of the fundamental Fourier peaks in the checkerboard phase in this orientation. The presence of an ordered dimer configuration is then signaled by the emergence of Fourier peaks at $(\mathbf{q}_3 + \mathbf{q}_4)/4 \pm (\mathbf{q}_3 - \mathbf{q}_4)/2 = (1/2, \pm 1)q$ (see Fig. 2.7s and Movie S10), which then vanish as the dimers join to form longer chains and eventually extended stripes.

Fourier images of the striped phase display two columns of peaks at $q_x \approx \pm 2q$. The peaks at nonzero values of $q_x$ show no evidence of different spacings for the two stripe types. Though potential energy calculations indicate that an incommensurate phase is the ground state for a tilt angle of $50^\circ$, the Fourier images indicate that at finite temperatures the system does not display this feature.

2.5 Conclusions

We have observed several different types of fluid-solid and solid-solid transformations in a binary system of magnetic and nonmagnetic spheres. By exploring the mech-
anism behind fluid-solid transformation, we were able to optimize the experimental conditions so that a large single domain checkerboard lattice can grow within a few hours. By probing the solid-solid transformations with a tilted magnetic field, we also found that the diffusionless transformation from a checkerboard to a striped phase can be selected by choosing the applied field strength and the orientation of the initial crystal with respect to the tilt direction of the applied field. For high fields, the different pathways both pass through intermediate states dominated by buckled dimers before reaching the striped phase. Because of the slow relaxation timescales along the transformation pathway, we suspect that the experiment is not performed in the quasistatic regime. Dimer formation and alignment may thus be a far from equilibrium feature. We note, however, that potential energy calculations suggest that at least two different dimer phases may be stable at certain tilt angles (see Fig. 6.2). At low temperatures (or high field strengths), phases of trimers, quadrimeres, etc. may also play a role if the field can be tilted sufficiently slowly. For the relatively rapid tilt rates employed in our experiments, the high degree of order observed quite far from equilibrium is rather remarkable.

In general, the ability to switch among different pathways could enable the control of functional characteristics of engineered materials, including their capacity for heat exchange and susceptibility to shape change along the transformation. The binary magnetic system described here also opens the way for studying other dynamical processes in alloys. For instance, changing the ferrofluid susceptibility would enable the investigation of solid-solid transitions that require long-range diffusion, such as the transformation from a striped crystal to a hexagonal crystal[59] with $n_m/n_n = 2$ (see Fig. 6.1d).
In this Chapter, we examine the possible densest packing structures of hard spheres within cylinders of different diameters $D$ by adapting Torquato-Jiao’s adaptive-shrinking-cell formulation and sequential-linear-programming (SLP) technique. \footnote{This chapter is adapted from the paper: Hard sphere packings within cylinders, *Soft Matter*, 12 (9), 2505-2514, (2016). And this work is also done by collaborations with Prof. Socolar’s group. Data relevant to this work have been archived and can be accessed at https://doi.org/10.7924/G8SF2T3Z}

3.1 Sequential Linear Programming Method

In order to identify close packings of HS in cylinders, we adapt the SLP method of Torquato and Jiao [70] to this geometry. For convenience, we describe configurations using cylindrical coordinates with $z$, $r$, and $\theta$ representing the axial, radial and angular components, respectively. For our search procedure, we consider a fixed number of spheres in a finite cylinder with periodic boundary conditions that match the top of the cylinder to the bottom with a twist. In other words, the entire volume of the cylinder is taken as a unit cell with a one-dimensional periodicity. The infinite

In this Chapter, we examine the possible densest packing structures of hard spheres within cylinders of different diameters $D$ by adapting Torquato-Jiao’s adaptive-shrinking-cell formulation and sequential-linear-programming (SLP) technique.\footnote{This chapter is adapted from the paper: Hard sphere packings within cylinders, *Soft Matter*, 12 (9), 2505-2514, (2016). And this work is also done by collaborations with Prof. Socolar’s group. Data relevant to this work have been archived and can be accessed at https://doi.org/10.7924/G8SF2T3Z}
structure consists of spheres centered at

\[ \mathbf{r}_{ij} = \mathbf{r}_i + n_j \mathbf{\lambda}, \quad (3.1) \]

where \( \mathbf{r}_i \) \((i = 1, 2, \ldots)\) are the particle positions within a unit cell, \( n_j \in \mathbb{Z} \), and \( \mathbf{\lambda} = (\lambda_r, \lambda_\theta, \lambda_z) \) is the lattice vector. For our system, \( \lambda_z \) is the height of the unit cell, \( \lambda_\theta \) is the twist angle, and \( \lambda_r = 0 \). Note that for helical structures, the twist angle is necessary because \( \Delta \theta \) between two successive particles in a helix may not be a rational fraction of \( 2\pi \). The volume of a unit cell is thus

\[ v_u = \pi (D/2)^2 \lambda_z, \quad (3.2) \]

and the lattice packing fraction can be expressed as

\[ \eta = \frac{N v_s}{v_u}, \quad (3.3) \]

where \( N \) is the number of particles in a unit cell and \( v_s \) is the volume of a sphere of diameter \( \sigma \).

At each optimization step, we allow the \( N \) particles in the unit cell to move as well as changes to the unit cell height, \( \lambda_z \), and twist angle, \( \lambda_\theta \). Denoting particle displacements \( \Delta \mathbf{r} \), the matrix specifying changes to the unit cell \( \mathbf{\epsilon} \), the new particle positions \( \mathbf{r}^n \), and the new lattice vector \( \mathbf{\lambda}^n \), we have

\[ \mathbf{\lambda}^n = (\mathbf{I} + \mathbf{\epsilon})\mathbf{\lambda} \quad (3.4) \]

\[ \mathbf{\epsilon} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \epsilon_\theta & 0 \\ 0 & 0 & \epsilon_z \end{bmatrix} \quad (3.5) \]

\[ \mathbf{r}^n = (\mathbf{r}_r + \Delta r_r, \mathbf{r}_\theta + \Delta r_\theta, (1 + \epsilon_z)(\mathbf{r}_z + \Delta r_z)) . \quad (3.6) \]

Note that the twist angle is not continuously shearing the particles within the unit cell, but is only a property of the boundary conditions. It thus only appears in \( \mathbf{r}^n \) for boundary particles.
In order to find the maximum packing density we must solve the following problem:

minimize \( v_u \)

subject to

\[
\begin{align*}
  r_{ij}^n & \geq \sigma, \forall ij \text{ neighbor pairs}, \\
  r_{ir} + \Delta r_{ir} + \sigma/2 & \leq D/2, \forall i = (1, 2, ..., N).
\end{align*}
\] (3.7, 3.8)

The first condition corresponds to the hard-sphere constraint and the second to the hard-wall constraint. Because during the optimization \( D \) is fixed, minimizing \( v_u \) is equivalent to minimizing \( \lambda_z \). The packing problem then becomes a standard constrained optimization problem, and the constraints can be linearized (by Taylor expansion), allowing the use of linear-programming solvers [70, 71]. The optimization problem at each step then becomes

minimize : \( \epsilon_z \)

subject to

\[
\begin{align*}
  r_{ij}^n & \geq \sigma, \forall ij \text{ neighbor pairs} \\
  r_{ir} + \Delta r_{ir} + \sigma/2 & \leq D/2, \forall i \\
  |\Delta r_{ir}| & \leq \Delta r_{ir}^{\text{upper}}, \forall i \\
  |\Delta r_{i\theta}| & \leq \Delta r_{i\theta}^{\text{upper}}, \forall i \\
  |\Delta r_{iz}| & \leq \Delta r_{iz}^{\text{upper}}, \forall i \\
  |\epsilon_{\theta}| & \leq \epsilon_{\theta}^{\text{upper}} \\
  |\epsilon_z| & \leq \epsilon_z^{\text{upper}},
\end{align*}
\] (3.9-3.15)

with algorithmic bounds that are sufficiently small so as to limit large particle overlaps, which are a consequence of linearization and are eliminated by counterproductively expanding the unit cell, but not so small so as to slow down convergence.
Here, optimal bounds on particle displacements and volume changes are found to be roughly $\Delta r_{\text{upper}} = \Delta r_{z,\text{upper}} = \epsilon_{z,\text{upper}} = 0.001\sigma$, and $\Delta r_{\theta,\text{upper}} = \epsilon_{\theta,\text{upper}} = 0.001$ radians.

The overall packing optimization can thus be done sequentially, meaning that the optimal solution for a given step is used as input for the subsequent one, until convergence is achieved. Operationally, we accept a solution as having converged when the difference between two iterations $|\Delta v_u| < v_{\text{tol}}$, where $v_{\text{tol}} = 10^{-6}$. Note that because this criterion is independent of the unit cell size, the final unit cell volume is determined less precisely for smaller system sizes, but this effect is negligible on the scale of the figures and of the other numerical results reported here.

Recall that for periodic structures, close packing can only be obtained when $N = n_cN_c$, where $n_c$ is a positive integer and $N_c$ is the number of particles in the unit cell. For regimes where the densest structure is known (and periodic), i.e., at small diameters, we choose $n_c \geq 3$. For the rest of the diameter range, however, no systematic studies have previously been undertaken, and only a few structures have been proposed [72, 73]. Where $N_c$ is not a priori known, we resort to scanning system sizes with $N = 48$ to $N = 150$. If the close packing is actually periodic with $N_c \leq 150$, it is identified properly, and the $N$ that yields the highest density is an integer multiple of $N_c$. One can then check factors of this $N$ to identify $N_c$. For systems where the close packed arrangement is not periodic or where $N_c > 150$, the algorithm finds the best periodic approximant within this regime of $N$.

### 3.2 SLP Results

Using the SLP method, we identified candidate structures for HS close packing from $D = 2.16\sigma$ to $D = 4.00\sigma$. For $D \leq 2.862$, we reproduce previously reported results [2] (Fig. 3.1), but we obtain denser structures than Mughal et al. for $2.862\sigma < D < 2.873\sigma$ (Fig. 3.2 inset). This discrepancy is likely due to the difference in system sizes between the two studies. The structures obtained for this regime in Ref. [2] had
Figure 3.1: Close packing densities for $2.16\sigma \leq D \leq 2.86\sigma$. Configurations are depicted at density maxima. Yellow particles are part of a same helix. In this regime, the results are in complete agreement with those of Ref. [1]. Figure 3.2 presents results for $D \geq 2.86\sigma$.

unit cells with either $N = 7$ or 15 particles, while our system size varies from $N = 24$ to 150, and the densest structures are found to have $50 \leq N \leq 85$. The origin of this strong system size dependence likely lies in the complex periodicity, i.e., the large $N_c$, of the packings in this regime, or to their potential aperiodicity. (We come back to this point in Section 3.3.)

SLP identifies 17 distinct structures and their deformations over $2.873\sigma \leq D \leq 4.00\sigma$ (Fig. 3.2). The structures depicted in Figure 3.2 are local maxima in $\eta(D)$. Most of the structures in this regime have two well-defined layers: an outer shell and an inner core. In structures for which this definition makes geometrical sense, the
outer shell is comprised of particles that are touching the wall, or nearly so, and which form a corrugated cylinder of diameter roughly $D - \sigma$ that contains the particles comprising the inner core. Because many of the outer shells are themselves close packings of spheres disks on the inner surface of the cylinder, they can be described using the phyllotactic notation for helices, $(l, m, n)$, with $l = m + n$ and $m > n$, where $l$, $m$ and $n$ are the number of helices, using the three possible helix definitions (Fig. 3.3) [1]. The parameters defining some of these helical outer shells are listed in Table 3.1. For simplicity, we denote below structures with the helix whose height difference, $\Delta z$, between two successive particles within that helix is minimal, and $\Delta \theta$ is thus the angular coordinate difference between two successive particles within that helix (Fig. 3.3a). Based on these definitions, we note that $\lambda_z = (N_s/l)\Delta z$ and $\lambda_\theta = \text{mod} \ 2\pi ((N_s/l)\Delta \theta)$, where $N_s$ is the number of shell particles in the unit cell.

Intermediate structures can be obtained by continuously transforming local density maxima. Some are uniform radial expansions (or compressions) of these structures, accompanied with a compression (or expansion) in $z$, while other structures undergo a line-slip, which is a slip between two helices, keeping the relative position of the other helices constant [2]. Because a helix can be defined in three different ways (Fig. 3.3), each maximal density structure presents up to six corresponding line-slip possibilities (two directions for each type of slip), although symmetry can reduce this number.

In the following subsections we present an overview of different $D$ regimes over which the packings we obtain share a number of structural features.

3.2.1 Structures for $D < 2.86\sigma$

In this regime, all the structures are periodic and have a simple mathematical description. Most of them are simple helices. The last two structures, however, are non-helical and contain an inner core (Fig. 3.1). HS close packing for $2.71486\sigma \leq$
Table 3.1: Structural parameters and properties of close packed outer shells for different cylinder diameters. Quantities are rounded to the last digit.

<table>
<thead>
<tr>
<th>Notation</th>
<th>$D/\sigma$</th>
<th>$\Delta\theta$</th>
<th>$\Delta z/\sigma$</th>
<th>Chirality</th>
<th>Number of helices</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6,5,1)</td>
<td>2.8652</td>
<td>1.1167</td>
<td>0.1538</td>
<td>chiral</td>
<td>1</td>
</tr>
<tr>
<td>(6,6,0)</td>
<td>3.0000</td>
<td>1.0472</td>
<td>0.0000</td>
<td>achiral</td>
<td>/</td>
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<tr>
<td>(7,4,3)</td>
<td>3.0038</td>
<td>0.9365</td>
<td>0.4268</td>
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<td>3</td>
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<tr>
<td>(7,5,2)</td>
<td>3.0623</td>
<td>0.9697</td>
<td>0.2759</td>
<td>chiral</td>
<td>2</td>
</tr>
<tr>
<td>(7,6,1)</td>
<td>3.1664</td>
<td>0.9507</td>
<td>0.1309</td>
<td>chiral</td>
<td>1</td>
</tr>
<tr>
<td>(8,4,4)</td>
<td>3.2630</td>
<td>0.7854</td>
<td>0.5000</td>
<td>achiral</td>
<td>4</td>
</tr>
<tr>
<td>(8,5,3)</td>
<td>3.2888</td>
<td>0.8357</td>
<td>0.3706</td>
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<td>3</td>
</tr>
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<td>0.8976</td>
<td>0.0000</td>
<td>achiral</td>
<td>/</td>
</tr>
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</tr>
<tr>
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<td>0.7220</td>
<td>0.4434</td>
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<td>4</td>
</tr>
<tr>
<td>(9,6,3)</td>
<td>3.5818</td>
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<td>0.3267</td>
<td>chiral</td>
<td>3</td>
</tr>
<tr>
<td>(8,8,0)</td>
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<td>0.7854</td>
<td>0.0000</td>
<td>achiral</td>
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<tr>
<td>(9,7,2)</td>
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</tr>
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<td>1</td>
</tr>
<tr>
<td>(10,5,5)</td>
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<td>achiral</td>
<td>5</td>
</tr>
<tr>
<td>(10,6,4)</td>
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<td>0.3971</td>
<td>chiral</td>
<td>4</td>
</tr>
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<td>(10,7,3)</td>
<td>3.8800</td>
<td>0.6771</td>
<td>0.2917</td>
<td>chiral</td>
<td>3</td>
</tr>
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<td>(9,9,0)</td>
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<td>0.6981</td>
<td>0.0000</td>
<td>achiral</td>
<td>/</td>
</tr>
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<td>0.6738</td>
<td>0.1883</td>
<td>chiral</td>
<td>2</td>
</tr>
</tbody>
</table>

$D \leq 2.74804\sigma$ has $D_5$ symmetry with a close packed inner core, and can be constructed as a packing of spindles of nearly regular tetrahedra. The optimal structure for $2.74804\sigma \leq D \leq 2.8481\sigma$ has instead a unit cell of 11 particles – an inner particle sandwiched between two staggered five-particle rings – that is reminiscent of a stacking of ferrocene molecules. Note, however, that neither the inner core nor the outer shell of this last structure are separately close packed.

3.2.2 Structures for $2.86\sigma \leq D < 2.988\sigma$

For $D \geq 2.86\sigma$, packings do not have simple analytical descriptions. The competition between the inner core and the outer shell becomes more complex, because the two layers have different packing requirements, and neither of them systematically wins. For $2.86\sigma \leq D \leq 2.988\sigma$, the inner core dominates. To see why, note that a core
Figure 3.2: Close packing densities for $D = 2.85 - 4.00\sigma$. Configurations are depicted at the density maxima. Yellow particles are part of a same helix or its line-slip structure, as described by the phyllotactic notation, and red particles are hoppers (see text for details). Note that some configurations do not have a well-defined helical structure. The inset shows the difference between Mughal et al.’s (red triangles) and the current (blue circles) results for $2.86\sigma < D < 2.875\sigma$.

A particle can only fit into a shell formed by a horizontal layer of 6 spheres when $D \geq 3\sigma$. For $D < 3\sigma$, a core sphere can only fit if these 6 spheres form a helix around it. Every core particle must thus be at the center of a six-particle helix, which limits its freedom to move within the inner core. For instance, for a perfect (6,5,1) outer shell, for which $D = 2.8652\sigma$, the spacing between two turns of the six-particle helix that forms the outer shell is $6\Delta z = 0.9228\sigma < \sigma$. If the outer shell were itself close packed, then three six-particle helices would only accommodate a single inner particle, leaving large gaps between inner particles. A denser structure is instead obtained by deforming the outer shell in order to accommodate a denser inner core.

As $D$ approaches $3\sigma$, core particles become increasingly free to move. For $2.97\sigma < D < 3.00\sigma$, the close packed outer shell is a line-slip structure of (7,4,3). The perfect
Figure 3.3: There exists three different ways to define a helix, and thus six possible line-slip structures. Yellow particles are part of a same helix. This configuration is an example of a \((l, m, n) = (7, 5, 2)\) helix, where \(l = 7\) can be obtained by counting the particle number of the top layer (c), \(m\) is depicted in (b), and \(n\) in (a). In the text, we select the convention depicted in (a) to denote helices.

\((7,4,3)\) outer shell at \(D = 3.0038\sigma\) has an inner core spacing of \(\frac{7}{3}\Delta z = 0.9959(1)\sigma\), which is barely smaller than a particle diameter. Hence, for \(2.97\sigma < D < 2.988\sigma\), although the overall structure remains dominated by the inner core, the outer shell barely differs from a close packed, line-slip structure of \((7,4,3)\).

3.2.3 Structures for \(2.988\sigma \leq D \leq 3.42\sigma\)

For \(2.988\sigma \leq D\), the inner core is sufficiently large to allow core particles to move freely within an outer shell, thus greatly reducing their constraint on the outer shell. Note that the lower end of this range is smaller than \(3\sigma\) because the close packed shell for \(2.988\sigma \leq D < 3.000\sigma\) is a line-slip structure of \((7,4,3)\), for which no six outer particles are ever in the same plane. They can thus wrap an inner core without difficulty. Close packed structures from that point on and up to \(D = 3.42\sigma\) are found to almost always form a close packed outer shell, independently of the inner core. The local density maxima in Figure 3.2 for this regime indeed all correspond
to the diameters of close packed outer shells (Table 3.1).

Out of the sequence, the structure with a (8,4,4) outer shell is particularly noteworthy. As for all outer shells with \( m = n = \frac{1}{2} l \), this helical structure is achiral — two of the three possible helical directions are equivalent, and \( \Delta z = \sigma / 2 \). As a result, the outer shell consists of straight columns when viewed from the top of the cylinder. The top view of (8,4,4) outer shell and its core is thus very similar to the close packing of hard disks in a circle (Fig. 3.4a). Two other structures are found to have this property (Fig. 3.4b and c), but the structure with the (8,4,4) outer shell is the only one that is close packed. Note that a similar phenomenon would likely be observed for a structure with a (10,5,5) outer shell were it to be close packed (which it is not).

![Figure 3.4](image)

**Figure 3.4:** Comparison between disks in a circle and the top view of spheres in a cylinder at (a) \( D = 3.613\sigma [3] \) (circle) and \( D = 3.25\sigma \) (cylinder), (b) \( D = 3.813\sigma [3] \) (circle) and 3.43\( \sigma \) (cylinder), and (c) \( D = 3.924\sigma [4] \) (circle) and 3.58\( \sigma \) (cylinder). Red particles are hoppers. The cylinder outer shells consist of straight columns and only the top layer of particles is visible, so the resulting packings look similar to those of disks in a circle. Note that because the height of neighboring columns is shifted by 0.5\( \sigma \), the cylinder diameter is smaller than that of the circle and projecting particles onto the cylinder base reveals overlaps.
The case $D = 3.00\sigma$ is also remarkable. The outer shell is then a close packed structure with staggered six-particle rings, i.e., (6,6,0). The spacing between two rings is $\Delta_\perp = \sigma\sqrt{3} - 1 \approx 0.8556\sigma$. Although core particles placed between the planes of the rings can shift off the cylinder axis, they cannot shift enough to allow a periodic packing of the core with no gaps between successive core spheres. This phenomenon illustrates the difficulty of searching for close packed structures in this regime. Close packed structures may indeed be quasiperiodic and thus not correspond to any finite $\lambda_z$ or $N_c$. In the present context, a quasiperiodic structure consists of a periodic shell and a column of core particles with an average vertical separation that is irrational with respect to the height of the unit cell of the shell. Our numerical approach then at best provides a periodic approximant of that structure. In order to consider this issue more carefully, we present an alternate algorithm for studying this regime in Section 3.3.

3.2.4 Structures for $D > 3.42\sigma$

For $D > 3.42\sigma$, many of the close packed outer shells are not observed. Instead of remaining disordered or quasiperiodic, the inner core then forms nearly ordered structure, which imposes many defects on the outer shell. For some of the packings, the defects are so large that they enable the two shells to interpenetrate. The structures in this regime are thus not clearly dominated by any one of the two layers, hence neither of the two shells is typically close packed. For instance, of $l$-particle staggered ring structures, $(l,l,0)$, only $l = 6$, 7 and 9 are observed. For $l = 6$ and 7, the inner core is so small that only a lightly zig-zagging chain of particles fits within it; for $l = 9$, the inner core is large enough that a staggered three-particle ring structure fits. For $l = 8$, however, the zig-zagging structure is not very dense, and a two-particle flat pair does not fit. The packing structure thus ends up having a completely different organization: a dense triple helix inner core and an tortuous
outer helical shell of eight particles.

The competition between the two shells does not only result in defective compromises, but also yields two novel types of structures. First, some structures are analogous to three-dimensional extensions of packing of hard disks in a circle (Fig. 3.4b and c). Although the roughly straight columns formed by these structures gives their top view a two-dimensional feel, they are not simple stacks of these packings. As can be seen in Figure 3.4, projections of particles onto the cylinder base reveals overlaps. The outer shell is an (imperfect) triangular lattice rather than a square lattice, and the outer rings are not flat but form zig-zags. As a result the same three-dimensional version fits in a cylinder with a smaller diameter than the corresponding two-dimensional circle. Second, some structures cannot be neatly divided into shells. For instance, for $3.55\sigma \leq D \leq 3.61\sigma$, although both layers are dense the gap between them is sufficiently large to allow outer particles to hop back and forth between the two shells, keeping $\eta$ unchanged (Fig. 3.4c and Fig. 3.2).

Table 3.1 indicates that four ten-fold ($l = 10$) outer shells could potentially be observed for $D \leq 4.00\sigma$. Yet only one appears in the phase sequence, as the last structure. The other three structures are missing, because for $3.62\sigma \leq D \leq 3.94\sigma$ the inner core is just large enough to accommodate a triple helix, and thus a nine-fold helical outer shell better accommodates this inner shell than a ten-fold one.

As discussed in Sec. 3.2, for $3.00\sigma \leq D \leq 3.42\sigma$, the incommensurability of the two shells may result in structures that are not periodic. Close packed structures thus cannot be obtained using a finite periodic unit cell, which makes the numerical search for packings by SLP extremely challenging (if not impossible) for some regions, e.g. $3.00\sigma \leq D \leq 3.05\sigma$. By contrast, for $D > 3.42\sigma$ the strong interaction between the two shells forces the two to share a same periodicity in some ranges of $D$ (see Supplementary Table S1). There therefore exist in those regions dense periodic structures that can be identified with relative computational ease. The vastness of
the configurational space to sample at this point, however, reduces the confidence with which truly close packed structures are then identified.

3.3 Sinking Algorithm for $2.988\sigma \leq D \leq 3.42\sigma$

SLP results suggest that for $2.988\sigma \leq D \leq 3.42\sigma$ packings may be quasiperiodic. Despite their relatively simple geometrical description, the true densest structures are then beyond the reach of our numerical algorithm because SLP relies on periodic boundary conditions. Systematically extrapolating the SLP results to infinite system size could sidestep this difficulty, but the range of computationally accessible system sizes is here insufficient for such extrapolation to be of much numerical significance. We thus consider a more directed approach to analyze the infinite-system size limit of these packings. This approach, however, rests on assumptions about the overall structure of packings that are not rigorously justified, and is found to be suboptimal in a few instances.

We first assume that packings in this regime have an outer shell that is close packed along the cylinder wall (see Fig. 3.5). For $D = 3\sigma$, for instance, the densest outer shell is the (6,6,0) structure. Note, however, that even this seemingly straightforward case would be mathematically nontrivial to demonstrate. The structure cannot be argued to be the densest possible based on the local packing density, because a closed hexagon (or triangle) of spheres on the cylinder surface minimizes the covered area when one diameter of the hexagon is vertical rather than horizontal as in the (6,6,0) structure (Fig. 3.6). Rigorously proving that (6,6,0) shell is close packed for $D = 3\sigma$ thus remains an open problem. We nonetheless persist in this direction and next assume that each successive core particle falls to its lowest possible position without perturbing the outer shell. These assumptions are broadly consistent with the SLP results, and should allow for slightly denser structures to be obtained by sidestepping the periodicity and finite-size constraints of that algorithm.

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Figure 3.5: Perfect, close packed outer shells: (a) stacked layers of 6 spheres each (6,6,0), (b) a 7-particle triple helix (7,4,3), and (c) a 7-particle double helix (7,5,2).

Figure 3.6: The cylinder surface area occupancy for bent hexagons with different orientations for $D = 3\sigma$. The area coverage is minimized for $\theta = \pi/6$ and is maximal for $\theta = 0$, even though it is the latter structure that gives rise to the (6,6,0) outer shell.
For convenience, in the following we define the shell density, \( \rho_s \), as the number of shell spheres per unit length along the cylinder axis. As the cylinder diameter \( D \) expands from a perfect, close packed shell, the shell could expand radially and compress axially, but it is always preferable for a line slip to emerge instead [74]. It is an exercise in geometry to analytically generate these structures. The density of the inner core, \( \rho_\infty \), is then computed as follows. (i) We sample all of the possible heights for a periodic starting point within the helix periodicity, looking for a combination of \( r \) and \( \theta \) that maximizes \( r \) while obeying the hard sphere and hard wall constraints. (ii) Given the position of a sphere in the core, we then assume the best way to pack the next higher sphere is to place it at the lowest possible position without moving any sphere in the shell or already placed in the core. Each core sphere thus touches the core sphere below it and two spheres of the outer shell. (iii) We iterate this step until the density of the core can be determined to within the desired numerical accuracy.

Overall, we thus assume that the core density is optimized by maximizing the radial coordinates of the inner particles, and especially the first one. This last assumption is made with no loss of generality for the cases in which the core is quasiperiodic, as in such cases every height of a core particle relative to the shell structure is approached with arbitrary accuracy in the infinite system; the value obtained for \( \rho_\infty \) does not depend on the location of the initial particle. We also assume that a locally densest packing ensures a globally densest packing. This last assumption is known not to be true in general. For random-sequential addition, for instance, it is known to fall far short of the close packing[75]. The highly constrained nature of our growth algorithm, however, here does give access to very high density structures.

In the special case \( D = 3\sigma \), the procedure can be described by a map. Recall that \( \Delta_\perp = \sigma \sqrt{\sqrt{3} - 1} \) is the spacing between successive layers of the shell. Consider
a core sphere at a generic specified height \( z_1 \) that is moved as far as possible off of the cylinder axis and is therefore touching two shell spheres. Let \( \mathbf{x}_1 \) be the position of this sphere and \( \mathbf{x}_2 \) be the position of the core sphere that sits just above it. Let 
\[
a_i = \{z_i/\Delta_\perp\},
\]
where \( \{\cdot\} \) denotes the fractional part, indicate the relative height of the \( i \)th sphere with respect to the shell layers just below and just above it. We construct the map \( M(a) \) that relates \( a_2 \) to \( a_1 \). This map can then be iterated to determine the locations of all of the spheres in the core:

\[
z_{i+1} = z_i + (1 + \{a_2 - a_1\})\Delta_\perp.
\] (3.16)

If the map converges to a fixed point or a limit cycle, the core is periodic. We will see, however, that this map is either quasiperiodic or has an extremely long period.

Figure 3.7 shows the possible locations \( \mathbf{x}_1 \) for a sphere within one layer. The cyan circular arc shows the possible locations for a sphere that touches two adjacent shell spheres in a same layer. The magenta arc shows the possible locations for a sphere that touches two adjacent spheres in different layers. The purple arc shows the same locations as the cyan arc, but shifted up one layer and rotated accordingly by \( \pi/6 \) about the cylinder axis. The portions of these arcs shown with thick blue and red curves (along with the positions related by the hexagonal rotations and reflections) are the possible locations of a core sphere within the depicted layer.

The placement, \( \mathbf{x}_2 \), of the sphere that rests on top of the sphere at \( \mathbf{x}_1 \) must lie on a piecewise arc of the type shown in Fig. 3.7, displaced one or two layers upward, and rotated so as to be as close to diametrically opposite \( \mathbf{x}_1 \) as possible. Inspection of the possible rotations and reflections reveals that the choice leading to the densest structure is a reflection through the plane containing the cyan arc in Fig. 3.7, followed by a rotation by \( 7\pi/6 \) about the cylinder axis and a translation upward by \( \Delta_\perp \), as shown in Fig. 3.8.

The map \( M(a) \) is determined by finding the value of \( a_2 \) along the upper curve
Figure 3.7: Possible locations of a core sphere within a layer. The large disks are cross sections of the confining cylinder, and are separated by $\Delta_\perp$. The core sphere must be centered on a point on one of the thick blue curves or the short, thick red curve. See text for details.

(green/orange in Fig. 3.8) that is exactly $\sigma$ away from $a_1$ on the lower curve (blue/red). $M(a)$ has the form of a circle map:

$$M(a) = \{a + \omega + f(a)\}, \quad (3.17)$$

where $\omega$ is a constant and $f(a)$ is a periodic function with unit period and zero mean. Numerical computation of the map yields $\omega = 0.163887$ and the function $f(a)$ shown in Fig. 3.9. Note the scale on the vertical axis; deviations from a line with unit slope are quite small. The slope of $M(a)$ lies within the range (0.8689, 1.1533) everywhere, hence the map is monotonic and thus invertible, which means that it cannot be chaotic [76].

For a circle map with a small amplitude nonlinearity, the generic behavior is
Figure 3.8: Placement of a core sphere. A point $P$ on the blue or red curve indicates a possible placement of a sphere center. The sphere above it lies on the point on the green or orange curve that is a distance $\sigma$ from $P$. See text for details.

Quasiperiodic [76]. In the present case, we confirm the quasiperiodicity to a high degree of accuracy, i.e., we detect no exponential convergence to a limit cycle, and we determine the asymptotic density $\rho_\infty$ by fitting the values of $\rho_n = n/z_n$ to the form

$$\rho_\infty = \rho_n + c/n,$$

(3.18)

where $c$ is a fitting constant. More precisely, we compute $z_n$, the height of the $n^{\text{th}}$ sphere in the core, taking $z = 0$ to be a point at the center of a layer of the outer
shell and beginning with $z_1 = 0$. We then extract the sequence of $z_n$ values for which the $n^{th}$ sphere sets a new record for coming closest to lying exactly in the plane of a layer, but is just below that plane, i.e., points for which $a_n$ comes ever closer to unity. Note that if the sequence were converging to a periodic limit cycle, this procedure would either yield a finite sequence or one that exponentially approaches a value different from unity. Figure 3.10 shows $\rho_n - \rho_\infty$ as a function of $n$ for the sequence of best approximants, where $\rho_\infty$ has been adjusted to get a straight line on the log-log plot. We find the best fit to be obtained for $\rho_\infty \approx 1.0043324(1)/\sigma$, which is slightly denser than for a simple stack of spheres on the cylinder axis, $1/\sigma$. The total number of spheres per unit of cylinder length is thus $\rho_s + \rho_\infty = 8.0169578(1)/\sigma$, corresponding to $\eta = 0.593849(1)$, which is denser than $\eta = 0.593661(1)$ obtained.
from the SLP algorithm, as expected.

For $D \neq 3\sigma$, the lack of reflection symmetry in the helical shells and the presence of line slips complicate the construction of a map from one core sphere height to the next. We instead perform brute force numerical computations of the core packing algorithm for $n$ spheres and take the core density to be $\rho_n = n/z_n$. The core density, $\rho_\infty$, is obtained by fitting the numerical results to Eq. (3.18), as above. The joint core and shell packing fraction, $\eta(D)$, is then obtained with a resolution of $\Delta D = 0.001\sigma$ (see Fig. 3.11).

For most values of $D$, the sinking algorithm gives structures with a higher packing fraction than the SLP algorithm, but differences that are typically less than 0.1%, which suggests that the SLP algorithm performs remarkably well in this regime. The most significant structural difference between the two algorithms is observed for $3.003\sigma \leq D \leq 3.017\sigma$, where the sinking algorithm identifies structures with
a (7,4,3) outer shell, while the SLP algorithm produces a (6,6,0) outer shell. The packing fraction difference between these two structures is small, but well above our numerical precision. The discrepancy may thus result from the former structure not being as easily accessible in the SLP search than the latter for our choice of algorithmic parameters and initial conditions.

At the level of precision considered for the SLP study ($\Delta D = 0.01\sigma$), the sinking algorithm is found not to win outright at three points: $D = 3.04\sigma$, $D = 3.27\sigma$, and $D = 3.40\sigma$ (see Table 3.2). We find that two distinct mechanisms are at play, which can be seen through consideration of the linear density ratio between the SLP and the sinking algorithms separately for the shell, $\rho_s$, and for the core, $\rho_\infty$ (Fig. 3.11 inset). Interestingly, we find that $\rho_s^{\text{SLP}} / \rho_s^{\text{sink}} \leq 1$ at $3.04\sigma$ and $3.40\sigma$. This indicates that a denser core is obtained at the expense of having a slightly perturbed (and less dense) outer shell. At $3.27\sigma$, some shell spheres instead do not touch the cylinder wall (taking over some of the empty core space), which increases both the shell and the core densities. (For $D = 3.09 - 3.10\sigma$, the SLP also identifies a denser outer shell than the one used in the sinking algorithm, but in these cases the denser core obtained by the sinking algorithm more than compensates for this difference.) The effect of the coupling between the outer shell and the inner core may be due to the proximity of a change to the shell symmetry ($D \approx 3.04\sigma$), or to the end of this regime ($D \approx 3.40\sigma$), but finer resolution studies would be needed to make more definitive statements. It is also unclear whether this coupling is strong enough to make the close packed structures periodic. SLP identifies unit cells that contain at least $55 \leq N \leq 80$ spheres, but larger cells are certainly possible.

3.4 Conclusion

In this study, we have extended the range of known HS close packings in cylinders of diameters $D = 2.862\sigma$ to $D = 4.00\sigma$ by adapting the SLP method of Ref. [70]
Table 3.2: Density differences between SLP and sinking structures for points where the former is denser than the latter.

<table>
<thead>
<tr>
<th>$D/\sigma$</th>
<th>$(\rho_s^{SLP} - \rho_s^{sink})/\sigma$</th>
<th>$(\rho_{\infty}^{SLP} - \rho_{\infty}^{sink})/\sigma$</th>
<th>$\eta_s^{SLP} - \eta_s^{sink}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.04</td>
<td>$-6.4 \times 10^{-6}$</td>
<td>$1.259 \times 10^{-5}$</td>
<td>$9.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>3.27</td>
<td>$2.9 \times 10^{-6}$</td>
<td>$4.510 \times 10^{-4}$</td>
<td>$2.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>3.40</td>
<td>$-7.9 \times 10^{-3}$</td>
<td>$9.254 \times 10^{-3}$</td>
<td>$7.2 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Figure 3.11: Packing results for the SLP (blue circles) and the sinking (solid line) algorithms are in fairly close agreement, but the quasiperiodic phases identified by the latter are typically denser. The biggest differences are in the choice of optimal shell morphology around $D = 3.01\sigma$ and $D = 3.35\sigma$. The phase sequence for the sinking algorithm is (7,4,3), (6,6,0), (7,4,3), (6,6,0), (7,5,2), (7,6,1), (8,4,4), (8,5,3), (7,7,0) and (8,6,2), from left to right (separated by dashed lines). The inset shows the shell $\rho_s^{SLP}/\rho_s^{sink}$ (red triangles) and core $\rho_{\infty}^{SLP}/\rho_{\infty}^{sink}$ (blue circles) linear density ratio as a function of $D$. See text for details.

...to this geometry and by developing a sinking algorithm. We have identified 17 new structures, most of them chiral, along with their continuous deformation. We also distinguish ranges of cylinder diameters over which different types of packings are...
observed. Most notably, around $D = 3\sigma$ the outer shell is both fairly independent of the inner core and close packed, and both algorithms provide strong numerical evidence that many of the packings are quasiperiodic.

Although our study ended at $D = 4.00\sigma$, we expect the competition between different shells to persist even once three and four of them develop. For $D \gg 4\sigma$, however, the bulk FCC limit should eventually be recovered. The shell area should thus eventually form but a thin wrapping of a FCC core. Based on the analogy with packing of disks within a circle [77], however, we don’t expect this phenomenon to develop before $D \gtrsim 20\sigma$, which is far beyond the regime that can be reliably studied with existing numerical methods.

In closing, it is important to recall the difference between packings and their assembly from local algorithms, such as the Lubachevsky-Stillinger algorithm [78] and other slow annealing approaches that mimic self assembly. Although optimal, some of the packings may be dynamically hard to access (or even inaccessible) via self-assembly, which can be important in simulations and colloidal experiments. This question will be the object of a future publication.
Assembly of Hard Spheres in a Cylinder

After identifying the densest packing structures, we now focus on the self-assembly kinetics of the system because assembly pathways can be just as important as the desired ordered structure. In this Chapter, we use specialized MC simulations to obtain the structural diagram of this system, and then examine the kinetically favored pathways to different assembly structures and possible experimental realizations.¹

4.1 Computational Method

We consider a system of $N$ hard spheres of diameter $\sigma$, confined within a hard cylinder of fixed diameter $D$ and variable height $\lambda_z$. The system is under periodic boundary conditions along $z$ with an angular twist at the boundary. In this setup, a periodic packing is described by

$$r_{i\alpha} = r_i + n_{\alpha} \lambda_i,$$

(4.1)

¹ This chapter is adapted from the paper: Assembly of hard spheres in a cylinder: a computational and experimental study, *Soft Matter*, (2017), DOI: 10.1039/C7SM00316. And this work is a collaboration with López’s group at Duke University. Data relevant to this work have been archived and can be accessed at http://doi.org/10.7924/G82Z13F1
where \( \mathbf{r}_{i\alpha} \) is the position of the \( i \)th particle within the \( \alpha \)th unit cell, \( n_\alpha \in \mathbb{Z} \), and \( \mathbf{\lambda} = (\lambda_r, \lambda_\theta, \lambda_z) \) is the lattice vector with subscripts \( r, \theta \) and \( z \) denoting the axial, radial and angular components of cylindrical coordinates, respectively. Hence, \( \lambda_\theta \) is the twist angle at the periodic boundary and \( \lambda_z \) is the unit cell height. For all the systems studied here, \( \lambda_z = 0 \).

Monte Carlo (MC) simulations are run in the isothermal-isobaric (constant-NPT) ensemble. Pressure \( P \) is kept constant by standard logarithmically-sampled volume moves on \( z \) [79], while temperature, \( T \), is a trivial scaling factor for hard interactions. Particles evolve through random local displacements that are accepted following the Metropolis criterion, and so is the twist angle \( \lambda_\theta \). The step size of the various MC moves is tuned to ensure an acceptance ratio between 30% to 40%. The remaining simulation parameters are chosen differently, depending on whether equilibrium or compression simulations are performed, as described below.

4.1.1 **Equilibrium simulations**

Confinement hinders structural relaxation, especially at high pressures. In order to accelerate equilibration, we adapt the event-chain Monte Carlo (ECMC) scheme [80] to the cylinder geometry, which accelerates sampling by up to four orders of magnitude at the highest pressure studied. ECMC is a rejection-free sampling scheme that allows an arbitrarily long chain of particles to be displaced in a single move, while preserving algorithmic balance. In general, one first randomly selects a particle and a vector \( \mathbf{v} \) for displacing it. After colliding with another particle, the initial one is immobilized and the second particle is displaced until it itself collides, and so on. The procedure terminates once one of the components of the sum of individual displacements reaches a given \( l \). Choosing \( l \) to be comparable to the size of the simulation box ensures that a collective displacement is achieved.

In order to adapt this scheme to cylindrical confinement, we restrict \( \mathbf{v} \) to have
\[ |v_r/v_z| \leq 0.5, \text{ so that particle displacements lie mainly along } z; \ l = \lambda_z \text{ is also chosen along } z; \text{ and if a particle collides with the wall of the cylinder before reaching another particle, it is reflected by the plane tangent to the collision point. The detailed procedure is as follows.} \]

1. Randomly select particle \( i \in [1, N] \) and displacement vector \( \mathbf{v} \), such that \( v_r/v_z \in [-0.5, 0.5] \) and \( v_\theta \in [0, 2\pi] \).

2. For all \( j \neq i \), calculate the distance \( d_{ij} \) that \( i \) would travel along direction \( \mathbf{v} \) before hitting \( j \), and find \( j^{\min} = \arg\min_j d_{ij} \). (A cell list is used to accelerate this step.) Calculate also the distance \( d_{\text{wall}} \) that \( i \) would travel before hitting the cylinder wall.

3. Denoting the \( z \) component of the cumulative displacements \( z_{\text{cum}} \), calculate \( d_{\text{move}} = \min(d_{\text{wall}}, d_{ij^{\min}}, l - z_{\text{cum}}) \).

   - If \( d_{\text{move}} = d_{\text{wall}} \), move particle \( i \) to the wall by \( d_{\text{wall}} \), reflect \( \mathbf{v} \), and then go back to step 2;
   - If \( d_{\text{move}} = d_{ij^{\min}} \), move particle \( i \) up to its collision point with \( j^{\min} \) by \( d_{ij^{\min}} \), replace \( i \) by \( j^{\min} \), and then go back to step 2;
   - If \( d_{\text{move}} = l - z_{\text{cum}} \), move particle \( i \) by \( l - z_{\text{cum}} \) and terminate.

In large systems, relatively small volume moves are conducted as otherwise they are rejected with high probability. In order to further improve their computational efficiency, we keep track of the minimum collision distance between particles in the \( z \) direction, \( z_{\text{max}} \equiv \max_i z_{ij}, i \neq j \), where \( z_{ij} = \sqrt{\sigma^2 - r_{ij}^2 + (r_{iz} - r_{jz})^2}/\Delta z_{ij} \) with \( \Delta z_{ij} = (r_{iz} - r_{jz}) \). For a system without overlap, we thus obtain:

\[
|z_{ij}^2| = \frac{\sigma^2 - (r_{ij}^2 - \Delta z_{ij}^2)}{\Delta z_{ij}^2} \leq 1, \quad \forall i, j. \tag{4.2}
\]
Because the numerator in Eqn. (4.2) does not contain $\Delta z_{ij}$, each volume move rescales $1/z_{\text{max}}$ linearly with $\lambda_z$, and as long as $z_{\text{max}} \leq 1$ no overlap occurs. This simple bookkeeping keeps the computational cost of volume moves of $\mathcal{O}(1)$. For systems initially prepared far from equilibrium, the frequency of volume moves should not be too high in order to maintain an efficient balance with particle moves. We find that having each MC average $N/60$ volume, one ECMC, $N$ particle, and 10 twist angle moves ensures fast and reliable equilibration.

As a check of equilibration, simulations are initialized from at least two different conditions: (i) disordered configurations at a low packing fraction, $\eta = 0.05$; and (ii) lattice configurations of the densest packings for the cylinder diameter considered. Around the structural crossovers, lattice configurations of intermediate order types are additionally used as starting points. Note that structural crossovers here refer to changes in structure due to changing pressure. In all cases, equilibration is run over $1.0 \times 10^7$ MC steps before observables, such as density, are sampled over $5.0 \times 10^6$ MC steps. The final system is deemed equilibrated if the different preparation protocols provide numerically consistent results. Numerical estimates of the equations of state are then obtained by interpolating the simulated equilibrium points at a given cylinder diameter.

We sample $\sigma \leq D \leq 2.82\sigma$ with a typical resolution of $0.33\sigma$. Because the structural correlation length, $\xi$, grows significantly as pressure increases – especially for achiral structures – a sufficiently large $N$ is used to prevent self-correlations with the periodic image. We find $N = 3000$ to suffice over the $P$ and $D$ regime sampled, which keeps the equilibrium unit cell height reasonably large, i.e., $\lambda_z \gtrsim 15\xi$. Additional trial runs with $N = 5000$ and 10000 for certain $D$ validate this choice.
4.1.2 Assembly simulations

The impact of the compression rate on assembly is studied by MC pressure annealing. Simulations all start from a disordered, low-density structure at \( \eta = 0.05 \). The unitless pressure, \( P_{\text{init}}^* \equiv \beta P \sigma^3 = 1.0 \) is then ramped up to \( P_{\text{max}}^* = 50 \), in steady increments after each MC cycle. The compression rate, \( \gamma = (P_{\text{max}}^* - P_{\text{init}}^*)/t_{\text{MC}} \), where \( t_{\text{MC}} \) is the number of MC cycles. We consider the assembly of systems under fast and slow compressions, \( \gamma = 4.90 \times 10^{-4} \) and \( \gamma = 2.45 \times 10^{-7} \), respectively, over the full range of cylinder diameters studied above. We also consider the impact of intermediate rates \( 1.63 \times 10^{-5} \leq \gamma \leq 2.45 \times 10^{-7} \) for \( D = 2.20 \sigma \). To explore the role of the cylinder boundary in experiments, simulations with a hard bottom under fast compression are additionally performed.

For assembly simulations, we use \( N = 60 \), which approximates the experimental system size, and eliminate ECMC moves because they do not correspond to a physical (local) dynamics. Each MC cycle thus averages one volume, \( N \) particle, and 10 twist angle moves. We explore the diameter range \( 2.00 \sigma \leq D \leq 2.82 \sigma \) with a resolution of \( 0.01 \sigma \), and consider 20 assembly simulations for each \( D \) because different structures can assemble for a same \( D \). Below \( 2 \sigma \), assembly is as trivial as the optimal structure. Above \( 2.71486 \sigma \) [6] at high pressures, structures with inner particles that do not touch the cylinder wall assemble. The complexity of the structural crossovers between these structures goes beyond the scope of this work, but in order to reach the assembly boundary of the last helix-based structures at finite pressures, our study extends up to \( 2.82 \sigma \). For \( D = 2.2 \sigma \), which is examined in finer detail, 300 simulations are performed for each compression rate.

4.1.3 Correlation length calculation

Different correlation lengths, \( \xi \), could be considered in this system, each capturing different types of order [81]. For example, correlations between the radial and lon-
itudinal coordinates of particles along the cylinder could be computed separately. These various correlation lengths, however, are expected to be proportional to one another, varying only at the level of a (structure-dependent) prefactor. The asymptotic critical scaling of these various lengths should therefore remain universal.

Here, we specifically consider correlations between fluctuations in the $z$ direction, which is most relevant for describing the different helical structures. More precisely, we choose a $\xi$ that characterizes the spatial decay of the axial component of the pair correlation function, $g(r)$,

$$g(z) = \frac{1}{\rho} \left\langle \frac{1}{N} \sum_{i<j} \delta(|r_{iz} - r_{jz}| - z) \right\rangle,$$

where $\rho = N/V_{in}$, and $V_{in} = \pi [(D - \sigma)/2]^2 \lambda z$. This function effectively projects particle positions onto the $z$ axis of the cylinder, before computing the standard pair correlation function. The correlation length is then obtained from a logarithmic fit of the exponential decay of the peaks of $g(z)$,

$$g(z) = 1 + Ae^{-z/\xi},$$

where the prefactor $A$ is fitted along $\xi$. Note that for the systems studied here, the first few peaks have to be discarded from the analysis because preasymptotic corrections can hide the exponential decay at short length scales, while peaks at large $z$ are discarded once they become comparable to the statistical noise. An exponential decay over more than two decades is then typically obtained (see Fig. 4.1).

4.1.4 Structural parameter

For the $D$ regime considered here, structures without inner particles can be described as a rolled two-dimensional sheet of (nearly) close-packed hard spheres. We devise a structural parameter, $\theta_0$, that measures the orientation of a hexagon on this sheet.
Figure 4.1: Radial decay of the axial component of the pair correlation function at $P^* = 6.0$ for $D = 2.40\sigma$. Green circles denote the points used to fit Eq. (4.4), and the straight line shows the results for a decay length $\xi = 2.83\sigma$. (Inset) Linear-scale oscillations of $g(z)$.

relative to the $x$-$y$ plane, i.e., the plane perpendicular to the $z$ axis of the cylinder:

$$\theta_6 \equiv \left\langle \arg\left[\sum_{k=1}^{N_{nn}} \exp(i6\theta_{jk})\right] \right\rangle,$$

(4.5)

where $N_{nn}$ is the number of nearest neighbors within $1.3\sigma$ of particle $j$, and $\theta_{jk}$ is the bond angle between the $x$-$y$ plane and the bond connecting particle $j$ to its nearest neighbor $k$. Note that although no complete hexagon can be found when unrolling the structure of narrow cylinders, $\theta_6$ nonetheless captures structural differences between different packings. Changes to $\theta_6$ are thus more revealing than its absolute value. For disordered structures, however, $\theta_6$ presents no clear signature, and is thus not reported.

To detect ordering at low pressures, we use instead the two-dimensional hexatic
order parameter:

\[
\Phi_6 = \left\langle \frac{\sum_{k=1}^{N_{nn}} \exp(i6\theta_{jk})}{N_{nn}} \right\rangle.
\] (4.6)

For \(D > 2.00\sigma\), an inflection point in the equations of state is observed for \(P^* \approx 8\), which hints at the existence of a crossover between ordered and disordered configurations. We find \(\Phi_6 = 0.7\) to be a geometrical threshold comparable to this pressure. For the sake of convenience we thus consider structures to be ordered when \(\Phi_6 \geq 0.7\).

4.1.5 Structural notation

The patterns on the unrolled sheets can be described using a phyllotactic notation: \((l, m, n)\) with \(l = m + n\) and \(m \geq n\), where \(l\), \(m\) and \(n\) are then number of helices along the three possible helical directions. In particular, \((l, l, 0)\) corresponds to piles of staggered rings [6, 82]. To identify the dominant helical symmetry without visual inspection and detect the onset of structural changes, we calculate typical \(\theta_6\) for various structures (Table 4.1). Note that \(\theta_6\) differs for the two isomers of a chiral structure, but their sum is always \(\pi/3\).

<table>
<thead>
<tr>
<th>Structure</th>
<th>(\theta_6/\text{rad})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3,2,1)</td>
<td>(\arctan(\sqrt{3}/5) \approx 0.3335)</td>
</tr>
<tr>
<td>(3,3,0)</td>
<td>(\arctan(0) = 0.0000)</td>
</tr>
<tr>
<td>(4,2,2)</td>
<td>(\arctan(\sqrt{3}/3) \approx 0.5236)</td>
</tr>
<tr>
<td>(4,3,1)</td>
<td>(\arctan(\sqrt{3}/7) \approx 0.2426)</td>
</tr>
<tr>
<td>(4,4,0)</td>
<td>(\arctan(0) = 0.0000)</td>
</tr>
<tr>
<td>(5,3,2)</td>
<td>(\arctan(\sqrt{3}/4) \approx 0.4086)</td>
</tr>
<tr>
<td>(5,4,1)</td>
<td>(\arctan(\sqrt{3}/9) \approx 0.1901)</td>
</tr>
<tr>
<td>(6,3,3)</td>
<td>(\arctan(\sqrt{3}/3) \approx 0.5236)</td>
</tr>
</tbody>
</table>

The unrolled sheet is decorated with perfect equilateral hexagons only for a few special \(D\). Intermediate structures show a slip between two helices, keeping the relative positions of the other helices constant. Three different line-slips can thus arise, one for each of the three helices. As a result, a structure \((l, m, n)\) can line-slip into \((l \pm 1, m \pm 1, n)\), \((l \pm 1, m, n \pm 1)\) and \((l, m \pm 1, n \mp 1)\). Following Ref. [6], we
denote intermediate line-slip structures as \( (l, m, n) \), \( (l, m, n) \) and \( (l, m, n) \), where the bold number identifies the helix that does not change during the transformation.

Note that in the regime \( 2.71486\sigma \leq D \leq 2.82\sigma \), a structure with particles along the cylinder core emerges, which is beyond the phyllotactic regime. We denote it instead by its point group symmetry, \( D_5 \).

4.2 Experimental Method

The experimental assemblies considered here are obtained by sedimenting polystyrene (PS) particles into cylindrical pores on a polyvinyl alcohol (PVA) film (Fig. 4.2). Instead of a compression rate, the tuning parameter is here \( Rt = \frac{t_{set}}{t_{diff}} \), where \( t_{set} \) is the time for particles to settle a distance \( \sigma \) and \( t_{diff} \) is the time for the particles to diffuse a distance \( \sigma \):

\[
t_{set} = \frac{\sigma}{v_{set}} = \frac{18\mu}{g\sigma(\rho_p - \rho_m)} \quad (4.7)
\]

\[
t_{diff} = \frac{\sigma^2}{D_{diff}} = \frac{3\pi\mu\sigma^3}{k_B T} \quad (4.8)
\]

\[
Rt = \frac{t_{set}}{t_{diff}} = \frac{6k_B T}{\pi g\sigma^4(\rho_p - \rho_m)}, \quad (4.9)
\]

where \( v_{set} \) is the settling velocity, \( D_{diff} \) is the diffusion constant, \( g \) is the gravitational acceleration, \( \rho_p \) is the particle density, \( \rho_m \) is the solvent density and \( \mu \) is the shear viscosity. \( Rt \gg 1 \) corresponds to thermal fluctuations being significant during the settling, and is thus equivalent to slow compression rates.

To make the PVA film, we first spin coated AZ 9260 positive photoresist (AZ Electronic Materials USA Corp.) on a 3-inch silicon wafer (Addison Engineering, Inc.). The wafer was then soft baked at 110°C for 65 seconds and exposed to UV light (Karl Suss MA6/BA6) through a chrome-printed photomask (PhotoSciences, Inc.) with an array of well-defined circles of differing diameters at 13.5 mW/cm².
Figure 4.2: Schematic diagram of the experimental setup. PS particles suspended in non-aqueous solvent mixture are sedimenting into a porous PVA film.

for 140 seconds. Afterwards, the wafer was submerged in AZ 400K developer (AZ Electronic Materials USA Corp.), diluted 1:4 in deionized (DI) water for 180 seconds to form cylinders of crosslinked photoresist [83], and then rinsed with DI water and dried with nitrogen gas. This last step was repeated until the uncrosslinked photoresist was completely removed. An SPTS Pegasus Deep Silicon Etcher was used afterwards to perform the deep reactive-ion etching (DRIE). The wafer was then thoroughly cleaned to remove the photoresist. To prepare the PVA solution, 40g PVA powder (98% hydrolyzed; Sigma-Aldrich, Co.) was dissolved in 400mL DI water at 200°C, and 16mL glycerol (VWR International, LLC) was added to the solution. The PVA solution was then cast into a solid film as the negative mold of the etched wafer. The film was then gently removed from the wafer. The presence of glycerol rendered the film more elastic to help with the removal.

Monodisperse PS particles of two different diameters (6.4µm, 7.7µm from Spherotech, Inc.) were used for sedimentation into the PVA film. The PS particles were first re-suspended in a non-aqueous solvent mixture, consisting of ethanol, glycerol and Tween 20 (Sigma-Aldrich, Co.). Three different solvent mixtures were used, as listed
in Table 4.2. To estimate the shear viscosity of mixtures, the Gambill method \cite{84} is used. Then $v_{\text{set}}$ and $D_{\text{diff}}$ are calculated from Stoke’s law and the Stoke-Einstein relation, respectively.

Table 4.2: Non-aqueous solvent mixtures used to re-suspend PS particles and properties of particles with $\sigma = 7.7\mu \text{m}$ in these mixtures.

<table>
<thead>
<tr>
<th>Mix.</th>
<th>EtOH : Gly : Tween 20</th>
<th>$v_{\text{set}}/\mu \text{m} \cdot \text{s}^{-1}$</th>
<th>$D_{\text{diff}}/\mu \text{m}^2 \cdot \text{s}^{-1}$</th>
<th>$R_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1mL : 0.2mL : 1µL</td>
<td>0.1</td>
<td>$1 \times 10^{-15}$</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>1mL : 0.4mL : 1µL</td>
<td>0.03</td>
<td>$0.5 \times 10^{-15}$</td>
<td>$2.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>1mL : 0.6mL : 1µL</td>
<td>0.01</td>
<td>$0.3 \times 10^{-15}$</td>
<td>$3.9 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

A small segment was separated from the rest of the PVA film using a 6.00 mm biopsy punch (Ted Pella, Inc.), and the punched PVA film piece was placed into the lid of a 1.5mL Eppendorf tube. The re-suspended particle mixture was then pipetted into the container directly above the PVA film.

To sinter particles, the segmented PVA film was first taken out of the suspension using metallic tweezers and then gently submerged in ethanol to wash off particles on the surface of the PVA film. The PVA film was placed on a glass slide, covered with a Petri dish to prevent dust accumulation and dried overnight at 25°C. The glass slide was subsequently placed on a hot plate at 85°C, covered with a Petri dish to sit for 20 minutes. After sintering the particles, the PVA film was dissolved by 0.5mL DI water at 75°C in a glass scintillation vial (VWR International, LLC). The assembled fibrils were finally observed by scanning electron microscope (SEM) (FEI XL30 ESEM) with an accelerating voltage around 7kV.

Experiments with $D_1 = 2.20(10)\sigma$, $D_2 = 2.25(10)\sigma$ and $D_3 = 2.70(10)\sigma$ were conducted. For $D_1$ and $D_2$, we find that Mixture 1 (see Table 4.2) suffices to assemble ordered structures, even with such a small Rt, but for $D_3$ a larger Rt is needed. Note that for $D_3 = 2.70(10)\sigma$, the cylinder diameter is so large that core particles start to play a role in the assembly, which makes the formation of ordered single layer structures (i.e., without core particles) difficult. A larger Rt would thus be
necessary to avoid the formation of defects by core particles. The height of the cylindrical pores mainly depends on the DRIE time and an average $\lambda_z$ of $65 \mu m$ was observed. Experimental structures are matched to simulations by comparing the cylinder diameters and side-views alone. The measured $D/\sigma$ is first used to search for candidate structures, and then the phyllotactic indexes $l$, $m$ and $n$ are identified by visual inspection. Note, however, that the cylinder diameters are difficult to accurately determine due to edge effects of SEM imaging. Because more secondary electrons leave the sample at edges, rims of the pores appear brighter and are hard to pinpoint. The experimental $D$ was thus further calibrated by comparing with simulation predictions. The resulting error on $D$ then prevents the direct match of the experimental results to the phase boundaries obtained from the simulation sequences.

4.3 Results and Discussion

In this section, we first present the equilibrium and assembly simulation results. We then relate these observations to the sedimentation experiments. As shown by Van Hove [52], phase transitions formally do not exist in this system. We thus obtain “structural diagram” (and not phase diagrams) that summarizes the continuous yet relatively sharp changes to the system structure that take place as a function of cylinder diameter and pressure. Note that because temperature is but a trivial scaling factor in systems with hard interactions, it is not considered here.

4.3.1 Equilibrium results

Qualitatively, our equations of state agree with earlier published results. For $D < 2\sigma$ they are featureless, while for $D \geq 2\sigma$, inflection points are observed at intermediate pressures [85] (Fig. 4.3). For $D < 2\sigma$, complete quantitative agreement is also obtained, but for larger $D$, discrepancies are observed. For instance, at $D = 2.20\sigma$
we observe the inflection point at $P^* = 13.6$, while earlier work reported this feature at $P^* = 15$ [5, 85] (Fig. 4.3 inset). Simulations with and without ECMC and torsional moves suggest that our enhanced sampling gives rise to a more robust equilibration in this hard-to-sample crossover regime.

![Figure 4.3](image)

**Figure 4.3**: Equations of state for $D = 1.50, 2.00, 2.20$ and $2.40\sigma$. The y axis is the reduced number density $\rho^* = N\sigma^3/V$. For $D < 2\sigma$, no inflection point is observed in this pressure range. (Inset) Comparison with earlier results for $D = 2.20\sigma$ (red downward triangles) and $D = 1.50\sigma$ (red squares) [5] clearly show that sampling in the crossover regions for $D > 2\sigma$ is more efficient.

Figure 4.4a shows that the correlation length, $\xi$, generally increases with $P^*$. At low $D$, it grows monotonically (see, e.g., $D = 1.50\sigma$ in Fig. 4.4a), which is qualitatively similar to what happens at $D = \sigma$ [54]. For $D > 2\sigma$, however, the growth of $\xi$ is non-monotonic, and jumps in $\xi$ grow increasingly sharp with $D$. Interest-
Figure 4.4: Pressure evolution of (a) the correlation length $\xi$, (b) the structural parameter $\theta_6$ and (c) the order parameter $\Phi_6$, for different $D$. As explained in the text, $\theta_6$ is not reported for disordered states, while $\Phi_6$ is not reported for $D < 2\sigma$. Note that the sharp changes in the quantities coincide for different $D$ (dashed lines).

ingly, these non-monotonic regions accompany the inflection points in the equations of state. Although the jumps in $\xi$ are reminiscent of a phase transition, they are clearly not. The volume integral of the pair correlator is the susceptibility, $\chi$, which would diverge at a second-order phase transition, but here only peaks. Hence, even though phase transitions are formally impossible in a finite-pressure (quasi-)one-
dimensional system with short-range interactions, clear crossovers between distinct structural regimes persist. The increasing sharpness of these jumps with $D$ is likely an echo of the first-order transition obtained in bulk three-dimensional systems, i.e., for $D \to \infty$.

The non-monotonic behavior of $\xi$ is accompanied by marked structural changes. For instance, the non-monotonicity of $\xi$ for $D = 2.40\sigma$ corresponds to the system transitioning from an achiral double helix, i.e., (4,2,2), to a chiral single helix, i.e., (4,3,1). The systematic decrease of $\xi$ after the crossover reveals that as a new structural order develops its spatial extent momentarily shrinks. In other words, the increased packing efficiency enables the order to loosen. For achiral structures, however, the opposite is observed. For $(l, l, 0)$ and $(l, l/2, l/2)$, $\xi$ grows much quicker than for chiral structures, and as a result $\xi$ increases (instead of decreasing) when the system goes from chiral to achiral (see, e.g., $D = 2.20\sigma$ in Fig. 4.4a). This effect is expected to be an artifact of our specific choice for $\xi$. The correlation functions for helical structures with more peak splitting in $g(z)$ experience increased fluctuations. By opposition, structures with more particles in the same $z$ plane display longer range spatial correlations. The $D$ evolution of $\xi$ at $P^* = 10$ clearly captures the net result (Fig. 4.5). The correlation length displays multiple peaks, corresponding to distinct structures and to the systematic change in $\xi$ when a new order develops. Note that all the peaks for $D > 2.00\sigma$ correspond to achiral structures.

In absence of genuine phase transitions, the structural parameter $\theta_6$ is expected to change continuously. Structural changes, however, are here so sharp that even with a resolution of $\Delta P^* = 0.01$, the quantity appears to jump. We can thus confidently rely on it to distinguish different structural regimes. Remarkably, between structural crossovers, $\theta_6$ changes only very slowly (see Fig. 4.4b). Although continuous line-slip pathways between structures do exist, they do not seem to contribute significantly to the finite pressure equilibrium behavior. Otherwise, $\theta_6$ would change steadily. If
Figure 4.5: Structural correlation length, $\xi$, at $P^* = 10$ for different $D$. For achiral structures with $D > 2\sigma$, i.e., those with $(l,l,0)$ and $(l,l/2,l/2)$, $\xi$ is systematically larger than for chiral structures. Although $\xi$ is generally expected to grow with $D$, the rich set of structural intermediates gives rise to a non-monotonic behavior in this regime.

Line-slip structures do play a role at finite pressures, it is thus only very close to the structural crossovers. A clearer understanding of their effect is, however, beyond the resolution of our simulations.

As shown in Fig. 4.4, all three quantities $\xi$, $\theta_6$ and $\Phi_6$, abruptly change together for $2\sigma < D \leq 2.82\sigma$. These changes also correspond to inflections in the equations of state. Figure 4.6a summarizes these results as solid lines. The contrast with $D < 2\sigma$, for which all quantities evolve smoothly and monotonically with pressure is marked. The distinction is reminiscent of the featureless equations of state for $D < 2\sigma$ and the simplicity of the corresponding zigzag order.

For $2\sigma < D \leq 2.82\sigma$, the sequence of helical symmetries at finite $P^*$ system-
atically follows that observed in the densest packings. Hence, starting from one state point, one obtains the same helical morphology by increasing (or decreasing) either $D$ or $P^\ast$. Although our simulation scheme is unable to equilibrate configurations in structural crossovers with $P^\ast \gtrsim 16$, we can use this observation to infer that the sequence of structures remains the same for $16 \lesssim P^\ast < \infty$. Structural transitions in the densest packings at $P = \infty$ [6, 82] can thus be used to extrapolate the equilibrium results (dashed lines in Fig. 4.6). The correspondence between pressure and diameter is also physically interesting because the effective interaction between finite-pressure hard spheres is not a step function at contact, but decays logarithmically with distance [86, 87]. From the structural robustness, we conclude that (free-)energy minima in this regime are fairly insensitive to the precise form of the (effective) interaction form. Crudely speaking, because the average gap between hard spheres scales as $\sim \frac{1}{P^\ast}$, spheres have an effective diameter $\sigma^\ast > \sigma$. Increasing pressure decreases the average interparticle gap and thus $\sigma^\ast$, hence giving rise to a comparable phase sequence as increasing $D/\sigma$ in this regime (Fig. 4.6a). Note, however, that the non-monotonic $\xi$ behavior for $D < 2\sigma$ in Figure 4.5 is not observed in the pressure evolution of $\xi$ (see, e.g. $D = 1.5\sigma$ in Figure 4.4a), which hints that this correspondence may only apply within a specific diameter regime.

At higher $D$, the structural complexity of the high-pressure packings also affects the robustness of the structural sequence. For instance, (5,5,0) does not appear between (5,4,1) and $D_5$ at $D = 2.80\sigma$; (5,5,0) appears to be only stable at high pressures. The boundaries of (5,5,0) in Fig. 4.6a are indeed all dashed. (Boundaries are here estimated by the results at $P^\ast = \infty$, and by knowing that (5,5,0) cannot be stabilized in the accessible pressure range for $P^\ast \lesssim 16$.) The instability of (5,5,0) at higher $D$ and lower $P^\ast$ might be related to the ease of forming an inner core under thermal excitation, which naturally give rise to $D_5$. The optimal packings observed at higher $D$ might suffer a similar fate.
Figure 4.6: (a) Structure diagram for $\sigma < D \leq 2.82\sigma$. Because the zigzag regime extends all the way to $D = \sigma$, the $D < 2\sigma$ region is featureless. Note that the disordered regime only has meaning for $D \geq 2\sigma$, because no well-defined order-disorder crossover exists for $D < 2\sigma$. The points at $P = \infty$ are the densest packing results from Ref. [6]. Finite pressure transition lines are obtained as described in the text. Structures that dominate the assembly of systems with (b) $\gamma = 4.9 \times 10^{-4}$ and (c) $\gamma = 2.45 \times 10^{-7}$ with periodic boundary conditions, and (d) $\gamma = 2.45 \times 10^{-7}$ with hard boundaries. Differences between these the sequences are much more than just a shift in $D$. For instance, a new structure, $(6,3,3)$, assembles only under fast compressions. Note that phase intervals labeled by non-line-slip structures also include the corresponding line-slip structures.
4.3.2 Simulation assembly results

Compressing a system sets a timescale, $\tau_{\text{comp}} \sim \gamma^{-1}$, for equilibration. Because the equilibration timescale is itself determined by the timescale for structural rearrangement, $\tau_\alpha \sim e^{\beta P \Delta V}$, where $\Delta V$ is an activation volume, a finite-rate compression is expected to trap the system in an intermediate structure around a pressure for which $\tau_\alpha \gtrsim \tau_{\text{comp}}$. In a (quasi-)one-dimensional system, because $\Delta V$ is microscopic and because for $2\sigma < D \leq 2.82\sigma$ a cut through the phase diagram at fixed pressure is roughly equivalent to the high-density phase sequence, one might naively expect the assembly phase sequence to closely follow the densest packing sequence, only shifted in $D$. The results, however, reveal a much richer behavior.

Assuming $\Delta V \sim \sigma^3$ and knowing that at $P^* = 16$ reaching equilibrium is computationally challenging, gives $\tau_\alpha \sim 10^7$ as a typical timescale for a slow compression. For $\gamma = 2.45 \times 10^{-7}$, we thus expect the assembly sequence to correspond to a cut through the phase diagram at $P^* \sim 16$. Yet, a couple of discrepancies are observed (Fig. 4.6b). Compared to the equilibrium results in Fig. 4.6a, (4,3,1), which occurs after (4,2,2) at equilibrium, is here found between (3,3,0) and (4,2,2), while (5,3,2) is missing altogether. If the assembly sequence is a rough cut through the phase diagram, then it is not at a fixed pressure. In order to obtain a microscopic understanding of this effect, we consider the two outliers in more details. For $2.28\sigma < D \leq 2.32\sigma$, even at such a slow compression, the crossover from (3,3,0) to (4,2,2) is not observed, suggesting that $\Delta V$ might be larger than for other transformations. Line-slips can continuously and easily transform one structure into another, hence it is natural to assume that structural crossovers should proceed via this route. The effect is indeed reminiscent of a martensitic transformation. It can also explain why $\Delta V$ is large for transforming (3,3,0) into (4,2,2): no single line-slip transformation between the two is possible. A line-slip through (3,3,0) instead brings the system from (3,3,0)
to (4,3,1). The same process accounts for the absence of (5,3,2). No single line-slip can transform (4,4,0) into (5,3,2), and thus (5,4,1) assembles even though (5,3,2) is the equilibrium structure. Additional evidence that $\Delta V$ is large for the (3,3,0) to (4,2,2) crossover is that (4,2,2) emerges around the point at which (3,3,0) disappears at equilibrium.

Because order develops slowly as pressure increases, fast compressions should lead to a cut through the phase diagram around the first structural crossover at $P^* \approx 8$, which corresponds to a timescale $\tau_\alpha \lesssim 5 \times 10^3$. Results for $\gamma = 4.9 \times 10^{-4}$ indicate that structure skipping in this regime is in fact quite pronounced. For instance, (3,3,0) and (4,4,0) disappear. For $2.16\sigma \leq D \leq 2.26\sigma$, (4,2,2) assembles because the system first gets trapped in (3,2,1), and then transforms into (4,2,2) through (3,2,1). As a result (3,3,0) is skipped. Similarly, (4,2,2) is skipped because (3,3,0) transforms into (4,3,1) via (3,3,0). Other structures show the same effect, the most remarkable of which being the transformation of (5,3,2) via (5,3,2) into (6,3,3), which is not a densest packing for any $D$.

Surprisingly, (4,2,2) assembles even in regimes for which (3,2,1) does not appear in the structural diagram. It is key, however, to recall that $\Phi_6 \geq 0.7$ is chosen as a somewhat arbitrary criterion for ordering. Here, (3,2,1) does not appear in Fig. 4.6a for $2.20\sigma < D \leq 2.26\sigma$, because then $\Phi_6 \leq 0.7$ for that structure. Under such a quick compression, even the weak local order in the disordered regime, i.e., the liquid order, can thus affect assembly, which is reminiscent of a geometrical frustration mechanism. As a result, a shift of the structural sequence to smaller $D$ is observed, in contradiction to our initial expectation. More importantly, this provides a new pathway for assembling dense packings in this regime. One can obtain the densest packing by quick compression, letting the system fall out of equilibrium at low densities and thus skip intermediate structure(s), rather than go through a slow crossover at high pressure.
The \( \gamma \) dependence of the assembly sequence suggests that the compression rates select different crossover mechanisms. This dependence is a consequence of \( \Delta V \) being different for each transition pathway. Generally, three line-slips are possible for each helical structure, and we expect the one with the smallest \( \Delta V \) to be most favorable. If the dynamically favorable structure is not thermodynamically stable, however, its assembly probability should depend on \( \gamma \). For example, for \( D = 2.20\sigma \), (3,2,1) forms at low pressures, while both (3,3,0) and (4,2,2) are accessible via line-slips ((4,3,1) simply does not fit within a \( D = 2.20\sigma \) cylinder). Figure 4.7 shows how the assembly probabilities for these two structures change with \( \gamma \). Faster compressions clearly make (3,3,0) less likely and instead favor (4,2,2). The line-slip via (3,2,1) has a smaller \( \Delta V \), and hence is dynamically more favorable. To understand this effect, we analyze the above result with the densest packing sequence for \( 2.039\sigma \leq D < 2.1545\sigma \), i.e., (3,2,1), (3,2,1) and (3,2,1) (see Table 1 from Ref. [6]). We find that the dynamically favored line-slip ((3,2,1) in this case) is the one that appears next to the current structure ((3,3,0) in this case) in the densest packing sequence. This mechanism, which also applies for other phyllotactic structures, reflects the importance of the packing efficiency for these transformations.

Interestingly, of all the crossovers in the equilibrium structural diagram only passing from (2,2,0) to (3,2,1) is dynamically favorable. As a result, the boundary between these two structures is invariant of \( \gamma \), while most of the other equilibrium structures at intermediate pressures can be skipped by fast compression. Figure 4.8 summarizes the dynamically favorable pathways by red dotted arrows. Note that no dotted arrow points to (3,3,0) and (4,4,0), so these two structures are not expected to assemble under quick compression.

All the simulation results mentioned above are for systems under periodic boundary conditions. In experiments, however, the cylinders are finite, with a hard bottom. Based on the results from the sequential deposition algorithm in cylinders [88], we
Figure 4.7: Probability of forming (3,3,0) and (4,2,2) at $D = 2.20\sigma$ as a function of compression rate. Although (3,3,0) is the equilibrium structure, it is not as dynamically favorable as (4,2,2). As a result, the assembly probability of (3,3,0) decreases as $\gamma$ increases.

expect this effect to play a role in assembly. We thus perform an additional series of fast compressions with hard boundaries (Fig. 4.6d). The flat bottom clearly favors structures with planar staggered rings, $(l,l,0)$, which would otherwise not form under fast compression. In addition, between the $(l,l,0)$ regimes, only phyllotactic structures with $n = 1$ assemble. The absence of (4,2,2), (5,3,2) and (6,3,3) likely results from their mechanical instability under these conditions.

4.3.3 Experimental realization

To validate our model and examine potential issues that could arise in experiments, we consider the assembly of micron-sized PS particles in cylindrical pores by sedimentation. Calibrating the experimental $D$ from simulation predictions suggests
that $D_1 = 2.25(10)\sigma$, $D_2 = 2.50(10)\sigma$ and $D_3 = 2.75(10)\sigma$. As expected, different helical structures assemble at different $D$ (see Fig. 4.9). Experimentally, (3,3,0), (4,4,0) and (5,5,0) dominate the assembly (Fig. 4.9b d and h). Considering that the experimental $\lambda_z \approx 10\sigma$, assembly in a flat-bottom cylinder (Fig. 4.6d) explains this observation. Yet some outliers from the simulation results are also found: (4,2,2) and (5,3,2) (Fig. 4.9a and e), most notably. Their presence in experiments might due to the density difference between particles and Mixture 3 being so small that the pressure at which these structures become mechanically unstable is not reached. Note that the assembly of (5,3,2) is a signature of fast compression, which is consistent with $R_t \ll 1$ for the three experimental mixtures.
Figure 4.9: SEM images of structures assembled through sedimentation experiments. Grey spheres are PS particles while blue spheres are simulation results with (a) (4,2,2), (b) (3,3,0), (c) (4,3,1), (d) (4,4,0), (e) (5,3,2), (f), (g) (5,4,1) and (h) (5,5,0) structures. a, b and c have $D_1 = 2.20(10)\sigma$, d, e and f have $D_2 = 2.25(10)\sigma$ and g and h have $D_3 = 2.70(10)\sigma$. Scale bars represent 20$\mu$m.

It is important to note that although sedimentation of particles onto a flat-bottom cylinder shares great similarities with the sequential-deposition algorithm [88], signif-
icant differences exist. In the sequential-deposition algorithm, particles are deposited
to the lowest possible positions one by one based on a randomly generated bottom
template. Particles are then held fixed and are not affected by the deposition of
subsequent particles. In experiments, however, template particles can become me-
chanically unstable. For example, for $D = 2.2\sigma$, a template of two particles settling
on the cylinder bottom generally forms, but rearrangements can happen as a third
particle sediments (Fig. 4.10). As a result, the base template tends to consist of
as many particles as possible, and $(l, l, 0)$ structures with staggered rings and $(l, l - 1, 1)$ structures are strongly favored. Yet some outliers are nonetheless observed
in experiments. Because the gravitational pull on the particles is relatively weak,
frictions with the cylinder wall and bottom can stabilize some of the templates.

![Figure 4.10: Possible rearrangements of a template. The template may be (a) mechanically unstable due to the addition of an additional particle, and (b) a new template of a three-particle ring thus forms.](image)

4.4 Conclusions

In this study, we have calculated the equilibrium structural behavior and out-of-
equilibrium assembly of hard spheres confined to cylinders of diameter $\sigma < D \leq 2.82\sigma$. At equilibrium, significant structural crossovers were identified, and for a given
cylinder diameter the structural sequence upon changing $P^*$ and $D$ correspond. This
suggests that the optimal packings are fairly robust to the effective interaction type in this diameter regime. Although the out-of-equilibrium assembly sequence depends on the compression (or sedimentation) rates and the choice of boundary conditions, the equilibrium behavior provides key insight into the results. Interestingly, mechanisms akin to geometrical frustration and martensitic transitions are found to play a role in the assembly process.

Another interesting observation is that, although assembling densest packings for a given diameter can be difficult, the naive solution of following the equilibrium pathway may not always be optimal. For a system with multiple solid phases, one might aim for a continuous and diffusionless pathway connecting two solids, to avoid intermediate structures.

Based on our experimental observations, assemblies of structures without inner particles by sedimentation are straightforward, and thus \( R_t \approx 1 \times 10^{-3} \) suffices to obtain certain ordered structures. To assemble more complex structures for larger \( D \), however, a much larger \( R_t \) (using either smaller or better density matched particles) would be necessary. For smaller particles, however, \( D/\sigma \) would be even more difficult to control. To recover the infinite system results, the templating impact of the cylinder bottom should be avoided by increasing the experimental \( \lambda_z \).

In closing, we have here only considered assembly in fairly small cylinder diameters, but the phase morphology becomes increasingly complex as the diameter grows. One expects that even richer assembly processes might then be at play.
Correlation Lengths via Transfer Matrix Method

As mentioned in the previous two Chapters, the system we have been studying is a strongly confined quasi-one-dimensional (q1D) system, which can be solved exactly via transfer matrix method. In this chapter, we solve both systems of hard disks between two parallel lines and hard spheres within a cylinder, and focus on the non-monotonicity of the correlation length which is observed in the previous Chapter.

5.1 Transfer Matrix Method

Two types of q1D systems are considered in this Chapter: \( N \) hard disks of diameter \( d \) confined between two parallel lines a distance \( H \) apart, and \( N \) hard spheres of diameter \( d \) confined within a cylinder of diameter \( D \). For notational convenience, we refer to these two families of systems as being 2D and 3D systems, respectively. And two regimes are considered: systems with nearest-neighbor (NN) interactions only and systems with next-nearest-neighbor (NNN) interactions.
5.1.1 Systems with NN interactions

We first consider models with only NN interactions. Choosing 2D systems with $H \leq (1 + \sqrt{3}/2)d$ guarantees that only NN disks can come in contact. Without loss of generality, we choose the lines to be parallel to the $x$ axis and set the origin halfway between those two lines. The available space in $y$ for the disk centers is then $h = H - d$, and the isobaric partition function reads [89]

$$Z_{NPT} = \frac{1}{\Lambda^{2N} (\beta F)^{N+1}} \prod_{i=1}^{N} \int_{-h/2}^{h/2} dy_i \exp \left[ -\beta F \sum_{j=1}^{N-1} \sigma_2(y_j, y_{j+1}) \right],$$

(5.1)

where $\Lambda$ is the thermal De Broglie wavelength, $F = P_x H$ is a force associated with the longitudinal pressure $P_x$, and $\sigma_2(y, y') = \sqrt{d^2 - (y - y')^2}$ is the contact distance between two neighboring particles along the $x$ direction.

Defining the kernel function

$$K_2(y, y') \equiv \exp \left[ -\beta F \sigma_2(y, y') \right],$$

(5.2)

allows the partition function to be rewritten as

$$Z_{NPT} = \text{Tr}(K_2^N),$$

(5.3)

where the trace of $K_2$ is the sum over all eigenvalues $\lambda_k$ with corresponding eigenfunctions $u_k(y)$ that satisfy

$$\int_{-h/2}^{h/2} dy K_2(y, y') u_k(y) = \lambda_k u_k(y').$$

(5.4)

In the thermodynamic limit, $N \to \infty$, $\text{Tr}(K_2^N)$ is dominated by $\lambda_{\text{max}}^N$. The Gibbs free energy per particle is then

$$\beta g = \lim_{N \to \infty} \frac{-\ln Z_{NPT}}{N} = 2 \ln \Lambda + \ln(\beta F) - \ln \lambda_{\text{max}},$$

(5.5)
the equation of state for the linear density of particles, \( \rho_l = N/L \),

\[
\frac{1}{\rho_l} = \frac{1}{\beta F} - \left( \frac{\partial \ln \lambda_{\text{max}}}{\partial \beta F} \right)_{\beta,N}
\]

\[
= \frac{1}{\beta F} + \frac{1}{\lambda_{\text{max}}} \int_{-h/2}^{h/2} \text{d}y_{\text{max}}(y) \int_{-h/2}^{h/2} \text{d}y'_{\text{max}}(y') K_2(y, y') \sigma(y, y'),
\]

and the probability distribution function of the \( y \) coordinate, \( u^2_{\text{max}}(y) \).

The spatial correlation between the \( y \) coordinate of two particles is

\[
g_y(i, j) = \langle (y_i - \langle y_i \rangle)(y_j - \langle y_j \rangle) \rangle
\]

\[
= \langle y_i y_j \rangle - \langle y_i \rangle \langle y_j \rangle = \langle y_i y_j \rangle,
\]

noting that confinement symmetry gives \( \langle y \rangle = 0 \). In terms of the kernel eigenvalues and eigenfunctions, we have [90]:

\[
g_y(i, j) = \sum_{k=1}^{\infty} \left( \frac{\lambda_k}{\lambda_{\text{max}}} \right)^{|i-j|} \left[ \int_{-h/2}^{h/2} \text{d}y_{\text{max}}(y) y u_k(y) \right]^2
\]

\[
= \sum_{k=1}^{\infty} \left( \frac{\lambda_k}{\lambda_{\text{max}}} \right)^{|i-j|} I_k^2,
\]

where \( \lambda_{k2} \) is the second largest eigenvalue with \( I_k \neq 0 \). Because q1D systems are expected to decay exponentially at large distances, i.e., \( g_y(i, j) \sim \exp(-|i - j|/\xi_y) \) with correlation length \( \xi_y/\rho_l \) for \( |i - j| \to \infty \), we have \( \xi_y = [\ln(\lambda_{\text{max}}/|\lambda_{k2}|)]^{-1} = [\ln(\lambda_0/|\lambda_1|)]^{-1} \).

For 3D systems, the same formalism allows us to derive the partition function in terms of cylindrical coordinates—radial \( r \) and angular components \( \varphi \)—[89]

\[
Z_{\text{NPT}} = \frac{1}{\Lambda^3 N (\beta F)^N} \prod_{i=1}^N \int_0^w \text{d}q_i \int_{-\pi}^\pi \text{d}\varphi_i \exp \left[ -\beta F \sum_{j=1}^{N-1} \sigma_3(q_j, q_{j+1}, \varphi_j, \varphi_{j+1}) \right],
\]

where \( w = (D - d)/2, \varrho \equiv r^2, F = P_x \pi (D/2)^2 \) and

\[
\sigma_3(q, q', \varphi, \varphi') = \sqrt{d^2 - q - q'} + 2\sqrt{q q'} \cos(\varphi - \varphi').
\]
The kernel $K_3(\varrho, \varrho', \varphi, \varphi')$ then becomes

$$K_3(\varrho, \varrho', \varphi, \varphi') \equiv \exp \left[ -\beta F \sigma_3(\varrho, \varrho', \varphi, \varphi') \right], \quad (5.10)$$

with a corresponding eigenequation

$$(\hat{H}\phi_k)(\varrho', \varphi') = \int_0^{w^2} d\varrho \int_{-\pi}^{\pi} d\varphi K_3(\varrho, \varrho', \varphi, \varphi') \phi_k(\varrho, \varphi)$$

$$= \lambda_k \phi_k(\varrho', \varphi'). \quad (5.11)$$

It can easily be shown that

$$\hat{H} \left( i \frac{\partial}{\partial \varphi} \phi_k(\varrho, \varphi) \right) = i \frac{\partial}{\partial \varphi} (\hat{H}\phi_k(\varrho, \varphi)), \quad (5.12)$$

which guarantees that the solution can be written with separated variables, i.e.,

$$\phi_k(\varrho, \varphi) = \phi_{k,r}(\varrho) \exp(-ia_k \varphi), \text{ with } a_k \text{ satisfying}$$

$$i \frac{\partial}{\partial \varphi} \phi_k(\varrho, \varphi) = a_k \phi_k(\varrho, \varphi). \quad (5.13)$$

The periodic boundary condition $\phi_k(\varrho, \varphi) = \phi_k(\varrho, \varphi + 2\pi)$ further quantizes $a_k$ to integer values. Because $\phi_{max}^2(\varrho, \varphi)$ is the probability density for $\varrho$ and $\varphi$, and the system is cylindrically symmetric, $\phi_{max}(\varrho, \varphi) = \phi_{max,r}(\varrho)$ and $a_{max} = 0$. Eq. (5.11) can thus be simplified as

$$\int_0^{w^2} d\varrho K'_3(\varrho, \varrho') \phi_{max,r}(\varrho) = \lambda_{max} \phi_{max,r}(\varrho') \quad (5.14)$$

with

$$K'_3(\varrho, \varrho') = \int_{-\pi}^{\pi} d(\varphi - \varphi') K_3(\varrho, \varrho', \varphi - \varphi'). \quad (5.15)$$

Note that Eq. (5.14) is valid for all $\phi_k(\varrho, \varphi)$ with $a_k = 0$. The simplification thus expresses both $\lambda_{max}$ and the equation of state from the solution of a simple one-dimensional eigenproblem.
The spatial correlation for the angular component of the 3D system can be extracted from

\[ g_{\phi}(i,j) = \langle \phi_i \phi_j \rangle - \langle \phi_i \rangle \langle \phi_j \rangle = \langle \phi_i \phi_j \rangle \]

which gives

\[ g_{\phi}(i,j) = \sum_{k=1}^{\infty} \left( \frac{\lambda_k}{\lambda_{\text{max}}} \right)^{|i-j|} \left[ \int_0^{\omega^2} d\varphi \int_{-\pi}^{\pi} d\varphi \phi_{\max}(\varphi,\varphi) \phi_k(\varphi,\varphi) \right]^2. \]

with \( \langle \varphi \rangle = 0 \) by symmetry. The solutions \( \phi_k(\rho,\varphi) \), give \( \xi_{\phi} = \left[ \ln(\lambda_0/|\lambda_1|) \right]^{-1} \). Similarly, correlations of the radial components are

\[ g_r(i,j) = \sum_{k=1}^{\infty} \left( \frac{\lambda_k}{\lambda_{\text{max}}} \right)^{|i-j|} \left[ \int_0^{\omega^2} d\varphi \sqrt{\rho} \phi_{\max,r}(\varphi,\rho) \phi_k(\rho,\rho) \int_{-\pi}^{\pi} d\varphi e^{-ia_k\varphi} \right]^2 \]

\[ = \sum_{k=1}^{\infty} \left( \frac{\lambda_k}{\lambda_{\text{max}}} \right)^{|i-j|} I_k^2. \]

Because \( a_k \) is an integer, the only terms that contribute, i.e., \( I_k^2 \neq 0 \), have \( a_k = 0 \). The correlation length can thus be expressed as \( \xi_r = \left[ \ln(\lambda_0/|\lambda_1|) \right]^{-1} \), where the eigenvalues of Eq. (5.14) rather than those of Eq. (5.11) are used.

5.1.2 Systems with NNN interactions

For 2D systems with NNN interactions, the formalism of Ref. 81 gives

\[ Z_{NPT} = \frac{1}{\beta F} \prod_{i=1}^{N} \int_0^{h/2} ds_i e^{-\beta F s_i} \int_{-h/2}^{h/2} dy_i e^{-\beta F} \sum_{j=1}^{N-1} \sigma_2(y_i,y_{i+1}) \prod_{k=2}^{N-1} \Theta_k, \]

where the separation between neighboring disks along the \( x \) axis is denoted

\[ s_i = \begin{cases} x_i & i = 1 \\ x_i - x_{i-1} - \sigma_2(y_i,y_{i-1}) & i \geq 2 \end{cases} \]

and a collection of Heaviside step functions, \( \theta \), accounts for the NNN interactions

\[ \Theta_k \equiv \theta(s_k + s_{k+1} + \sigma_{2,k,k+1} + \sigma_{2,k-1,k} - \sigma_{2,k-1,k+1}) \]

\[ = \theta(x_{k+1} - x_k - \sigma_{2,k-1,k+1}), \]
where we denote $\sigma_{2,i,j} = \sigma_2(y_i, y_j)$ for short.

Upon sequentially performing the integrations in Eq. (5.18), the thermodynamic limit of the integration kernel approaches an eigenfunction corresponding to the largest eigenvalue of the integration equation

$$e^{-\beta F(s_2 + \sigma_{2,1,2})} \int_0^\infty ds_1 \int_{-h/2}^{h/2} dy_0 \Theta_1 u'_k(y_1, y_0, s_1) = \lambda_k u'_k(y_2, y_1, s_2).$$

The kernel for this system

$$K'_2(y_0, y_1, y_2, s_1, s_2) = \exp[-\beta F(s_2 + \sigma_{2,1,2})] \Theta_1$$

gives the free energy $\beta g = -\ln \lambda_{\text{max}} + O(1/N)$, and, similarly to Eq. (5.6), we obtain

$$\frac{1}{\rho_1} = \int_0^\infty ds \int_{-h/2}^{h/2} dy_1 \int_{-h/2}^{h/2} dy_2 e^{\beta F(s + \sigma_{2,1,2})} \times$$

$$u'_\text{max}(y_1, y_2, s) u'_\text{max}(y_2, y_1, s) / B[u'_\text{max}, u'_\text{max}]$$

(5.23)

with

$$B[u'_k, u'_m] = \int_0^\infty ds \int_{-h/2}^{h/2} dy_1 \int_{-h/2}^{h/2} dy_2 e^{\beta F(s + \sigma_{2,1,2})} u'_k(y_1, y_2, s) u'_m(y_2, y_1, s).$$

(5.24)

Preserving more variables in the eigenfunction allows the extraction of correlation lengths for different order types. As for the NN expression, we have $\xi_y = [\ln(\lambda_0/|\lambda_1|)]^{-1}$, but we also obtain the correlation length for the longitudinal separation between neighboring disks, $\xi_{s+\sigma_2} = [\ln(\lambda_0/|\lambda_2|)]^{-1}$.

The NNN case for 3D systems is akin to that of 2D systems, replacing the eigenfunctions $u'_k(y, y', s)$ by $\phi'_k(\varphi, \varphi', \varphi, s)$, where $\varphi$ is the difference between the angular components of neighboring spheres. Because no closed form for this expression is available, however, all the integral equations must then be solved numerically, which makes investigation of this case particularly numerically challenging. The study of such high-dimensional eigenequations is thus beyond the scope of the current work.
The above integral equations can be solved numerically after discretizing the arguments of the kernel. We only describe below the case of 2D systems with NNN interactions, but the same procedure is followed for all three cases considered here. Discretizing Eq. (5.21) then gives

\[ \Delta y \Delta s \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} K'_2(i \Delta y, y_1, y_2, j \Delta s, s_2) u_k'(y_1, i \Delta y, j \Delta s) = \lambda_k u_k'(y_2, y_1, s_2), \quad (5.25) \]

where \( \Delta y = h/n_1 \), and similarly \( u'_k = u'_k(l \Delta y, m \Delta y, n \Delta s) \). A total of \( n_1^2 n_2 \) simultaneous equations then define the square matrix \( K \), and solving Eq. (5.21) is equivalent to diagonalizing \( K \). Although this operation is not possible for arbitrarily high limits of integration on \( s \), the Tonks-like exponential decay of \( u'_k(y, y', s) \) beyond \( s_{\text{max}} = d - \sigma_2(y, y_{i-1}) \) gives \( u'_k(y, y', s) = u'_k(y, y', s_{\text{max}}) e^{-\beta F(s - s_{\text{max}})} \) for \( s > s_{\text{max}} \). The integration beyond \( s_{\text{max}} \) can thus be performed analytically. Equation (5.25) then becomes

\[ \Delta y \Delta s \sum_{i=1}^{n_1} \left\{ \sum_{j=1}^{n_2} \left[ K'_2(i \Delta y, y_1, y_2, j \Delta s, s_2) \theta(s_{1\text{max}} - j \Delta s) u'_k(y_1, i \Delta y, j \Delta s) \right] 
\right. 
\left. + K'_2(i \Delta y, y_1, y_2, s_{1\text{max}}, s_2) \frac{1}{\beta F \Delta s} \times u'_k(y_1, i \Delta y, s_{1\text{max}}) \right\} = \lambda_k u'_k(y_2, y_1, s_2), \quad (5.26) \]

where \( \Delta s = s'_{\text{max}}/n_2 \) and \( s'_{\text{max}} = d - \sigma_2(0, h) \).

At high pressures, the disks are close to the boundaries with high probability, and thus both the probability density and \( u'_k(y, y') \) have most of their weight near the confining lines. The effect is especially pronounced for \( h > \sqrt{3}/2 \). In order to minimize \( n_1 \) and \( n_2 \) needed to obtain a given accuracy, we then perform a change of variables \( y(t) = at + bt \tanh(ct) \) and \( y(\pm 1) = \pm h/2 \). Defining \( f(t) = \frac{dy}{dt} = a + b \cosh^2(ct), \)
then Eq. (5.21) becomes

\[ \exp(-\beta F(s_2+\sigma_2,1,2)) \int_0^\infty ds_1 \int_{-1}^1 dt_0 f(t_0) \Theta_1 u_k'(y_1(t_1), y_0(t_0), s_1) = \lambda_k u_k'(y_2(t_2), y_1(t_1), s_2), \]

(5.27)

and similarly \( \Delta y \) in Eqs.(5.25) and (5.26) becomes to \( \Delta t = 2/n_1 \). As suggested in Ref. 81, \( a, b \) and \( c \) should be chosen such that two thirds of the \( |y| \) grid points lie within \([\sqrt{3}/4, h/2] \) in that regime. We here find \( b = h/2, a = h/2 - b \tanh(c) \) and \( c \approx 6 \) to provide sufficient accuracy in this regime. For the 2D and 3D NN regimes the eigenequation is one-dimensional, hence the accuracy of the solution can be maintained at high pressures by increasing the number of grid points used in the discretization.

We validate our numerical approach by comparing 2D results for \( \xi_y \) obtained from the NN and the NNN calculations, noting that our NN results are indistinguishable from those previously reported [90]. Agreement between the two approaches is excellent at low pressures, but a discrepancy of up to \( \sim 2\% \) develops as pressure increases (Fig. 5.1). This mismatch results from the growing sharpness in the form of the eigenfunctions as pressure increases, which reduces the numerical accuracy of the NNN calculation. The error, however, is quantitatively fairly modest and thus should not qualitatively alter our analysis.

5.2 Results and Discussion

5.2.1 Numerical solution

In this section, numerical results for various correlations in 2D and 3D systems are reported. The results are discussed within the broader context of ordering in q1D systems.
Figure 5.1: Comparison between the NN calculation and the NNN calculation for $\xi_y$ for $H = 1.5d$. (Inset) The ratio between the two quantities reaches a bit more than 2% at the highest pressure considered here.

5.2.2 2D Systems

In 2D systems, we investigate the behavior of two correlation lengths: $\xi_y$ and $\xi_{s+\sigma_2}$ (Fig. 5.2). The former increases monotonically as both pressure and $H$ increase, and its only notable feature is the presence of an inflection point at low pressures. The latter, by contrast, presents a much richer behavior, evolving non-monotonically with both $P_x$ and $H$. The behavior of $\xi_{s+\sigma_2}$ is reminiscent of the decay of the standard pair correlation function in systems under cylindrical confinement that have been studied numerically [91]. In order to determine if $\xi_{s+\sigma_2}$ captures a similar phenomenon we consider whether or not this feature accompanies changes to equilibrium structures.
Figure 5.2: (a) Evolution of $\xi_y$ for varying $P_x$ with $H = 1.5$, 1.8 and 1.9$d$, and (inset) for varying $H$ with $P_x = 5$, 10 and 15. Evolution of $\xi_{x+\sigma_2}$ for varying (b) $P_x$ and (c) $H$. $\xi_y$ grows monotonically as both $P_x$ and $H$ increase, while non-monotonicity is observed for $\xi_{x+\sigma_2}$. For $H = 1.9d$, this non-monotonicity corresponds to a structural crossover between straight-chains and zig-zags, while for the other two, it is a reflection of the vanishing correlation length. For different $P_x$, $\xi_{x+\sigma_2}$ first peaks, then starts growing again around where the NNN interactions emerge.

In 2D systems with $H < (1 + \sqrt{3}/2)d$, only two equilibrium order types can form: straight chains and zig-zags, but for $(1 + \sqrt{3}/2)d < H \leq 2d$ an additional buckled zig-zag order emerges at high pressures [81]. The structural crossover from zig-zag to buckled zig-zag order was studied by Godfrey and Moore [81], who noted that $\xi_{x+\sigma_2}$ grows non-monotonically in the vicinity of this crossover. However, the low-pressure regime, in which the straight-chain to zig-zag crossover should occur, was not considered. Here, for $(1 + \sqrt{3}/2)d < H \leq 2d$, we see clearly that $\xi_{x+\sigma_2}$ also grows non-monotonically at low pressures (Fig. 5.2b). As a hint of the presence of a structural crossover, we consider the evolution of $\xi_{x+\sigma_2}$ with density, $\rho_l$. We find that $\xi_{x+\sigma_2}$ peaks around $\rho_l \approx 1$ (Fig. 5.3), which is the maximum linear density of a straight chain. Systems with $\rho_l > 1$, must therefore have a significant zig-zag order. Note that for $\rho_l < 1$, particles can fluctuate between the two lines freely, and the linear order grows smoothly. When $\rho_l > 1$, by contrast, significant zig-zag defects develop because the relaxation of defects require an increase in volume and thus $\xi_{x+\sigma_2}$ decreases. The non-monotonicity of $\xi_{x+\sigma_2}$ actually reflects the competition between linear and zig-zag orders. For $\rho_l > 1$, if we consider zig-zag particles as defects, we would expect that the
Figure 5.3: Parametric plot of the evolution of $\xi_{s+\sigma_2}$ for varying $H$ and $P_x$. For a fixed $H$ or $P_x$, increasing $P_x$ or $H$ both result in increasing $\rho_l$. The correspondence between $H$ and $P_x$ is obvious. Both curves peak around $\rho_l = 1$, where the system crosses over from straight-chain and to zig-zag order.

correlation length for zig-zag ordering to be dominant once the defect concentration, $x_1 \gtrsim 0.5$. The longitudinal distance between neighbors is then 0.5 for the zig-zag order and 1 for the linear order. We thus have $(1 - x_1) \cdot 1 + x_1 \cdot 0.5 = \rho_l^{-1}$ for $\rho_l > 1$. For $H = 1.9d$, $\xi_{s+\sigma_2}$ grows again around $\rho_l = 1.43$ (Fig. 5.3b) and the corresponding $x_1 = 0.6$.

For $H < (1 + \sqrt{3})d$, however, the situation is markedly different. In this regime, although $\xi_{s+\sigma_2}$ grows at low pressures, it quickly reaches a maximum and then steadily decays as pressure increases. This behavior is inconsistent with an ordering crossover. It rather reflects the fact that fluctuations in interparticle distances completely vanish at high pressures in this regime. To better understand this point, consider for instance a perfect zig-zag structure, which is the most densely packed structure in
this $H$ regime. This structure has $\langle s + \sigma_2 \rangle = s + \sigma_2 = 0$, $\forall i$, hence $g_{s+\sigma_2}(i,j) \equiv 0$, $\forall i, j$ and $\xi_{s+\sigma_2} = 0$. As pressure increases, the correlation function vanishes because fluctuations become suppressed as a result of the probability distribution function trivially concentrating to $\lim_{\rho \to \infty} P(s + \sigma_2; H) = \delta(0)$. This contrasts with the behavior at $(1 + \sqrt{3}/2)d < H \leq 2d$, where $\lim_{\rho \to \infty} P(s + \sigma_2; H)$ condenses to the sum of two delta functions, and thus does not completely eliminate fluctuations. Another way of understanding this phenomenon stems from the fact that correlation functions generally decay as $g = A e^{-|i-j|/\xi}$ at large distances. For systems with $g = 0$ and $A \neq 0$, we would have $\xi = 0$. Hence, although the system is strongly correlated at high pressures, $\xi_{x+\sigma_2}$ is not a suitable measure of correlations in the NN regime. Non-monotonic growth of $\xi_{s+\sigma_2}$ can also be observed with increasing $H$ at fixed pressure (Fig. 5.2c). The position at which it first peaks varies with $P_x$ and is known from the above analysis to not correspond to structural modifications. The following minimum forms a kink near $H = (1 + \sqrt{3}/2)d \approx 1.866d$ that only weakly depends on $P_x$, and echoes the change in behavior in going from NN to NNN interactions described above. A correspondence between $P_x$ and $H$ is expected to follow from the knowledge that the average spacing between particles scales as $\sim \frac{1}{\beta P_x}$. The effective particle diameter $d'$ thus decreases as $P_x$ increases. Note that changing $P_x$ or $H$ would both result in a different $\rho_1$. Thus by choosing $\rho_1$ as a common parameter, the evolution of $\xi_{s+\sigma_2}$ with $P_x$ and $H$ can be mapped onto the same plane and their correspondence can then be seen clearly.

5.2.3 3D Systems

We expect 3D systems to behave similarly as their 2D counterparts in the NN regime, i.e., $D < (1 + \sqrt{3}/2)d$. Helicity is then weak and the densest packing structures in 3D are essentially the same as in 2D [40]. Hence $\xi_\varphi = [\ln(\lambda_0/|\lambda_1|)]^{-1}$ is simply the 3D counterpart to $\xi_y$. Three-dimensional correlation lengths, $r\cos\varphi$ and $r\sin\varphi$, which
are more directly equivalent to the $y$ correlation in 2D, are indeed precisely the same as for $\varphi$, as can be seen in Eq. (5.17).

![Graph showing correlation lengths](image)

**Figure 5.4:** Evolution of $\xi_{\varphi}$ as the longitudinal force varies with $D = 1.5$ and $1.8d$ and (inset) as the cylinder diameter varies with $P_x = 5$ and 10. $\xi_{\varphi}$ grows monotonically as both $F$ and $D$ increases. It is always smaller than $\xi_y$ at the same pressure because of the additional degree of freedom.

By comparing Figs. 5.4 and 5.2a, we note that $\xi_{\varphi}$ is smaller than $\xi_y$ at a same pressure. The additional degree of freedom indeed weakens correlations somewhat, but its growth nonetheless remains monotonic as both pressure and diameter increase. By contrast to $\xi_y$, however, no obvious inflection point is observed. Upon changing from linear chain to zig-zag order, $y$ (or $r$) changes while $\varphi$ remains constant for each particle. In other words, for $y$, linear particles at the center of the cylinder are considered as defects for a zig-zag order, while for $\theta$, they are not.

We also consider the correlation length for the radial component, $\xi_r$. As expected, it grows at low pressures (Fig. 5.5), but just like $\xi_{x+\sigma_2}$ in the NN regime it peaks
Figure 5.5: Evolution of $\xi_r$ as the longitudinal force varies for $D = 1.866d$. It grows at low pressures, while systematically decreases to 0 at infinite pressure because of the Delta probability density for $r$ at close packing, which is illustrated as (inset) $\langle r^2 \rangle/w^2$ converging to 1 at infinite pressure.

and then systematically decreases as pressure increases. The underlying reason is also the same. At infinite pressure, all particles are forced to touch the cylinder wall for maintain mechanical stability, i.e., $r_i = w, \forall i$, thus no defects in $r$ can be generated and $\xi_r = 0$. To illustrate this effect, we calculate $\langle r^2 \rangle/w^2$ as a function of pressure (Fig 5.5 inset) and it is clear that the quantity converges to unity with increasing pressure. We expect a similar behavior for this correlation function for narrow pores up to $D < 2.71486d$ [92, 93], in which all particles touch the cylinder wall at high pressure. Beyond that range, however, we expect that $\xi_r$ should diverge just like $\xi_{s+\sigma_2}$ does once it reaches $H > (1 + \sqrt{3})d$. Note the vanishing correlation length is also observed in hard squares with restricted rotations confined between two parallel lines. The correlation length of the square rotation angle only diverges
when \( H = (2\sqrt{2} - 1)d \), as close-packed densities for configurations with two different square rotation angles are the same, and thus the probability density for the rotation angle is the sum of two delta functions [94].

5.3 Conclusion

We have examined the behaviors of different correlation lengths for hard disks confined between two parallel lines and hard spheres within a cylinder. Because different correlation lengths capture different types of order, they display distinct pre-asymptotic behaviors and some of these lengths are also found to have scale trivially. The length \( \xi_{s+\sigma} \), which measures the correlation of longitudinal separations between neighboring disks in 2D, grows non-monotonically in the NNN regime as the pressure or the confinement width varies. This non-monotonicity follows the crossover between straight chain and zig-zag order. A similar phenomenon is also observed for hard spheres within wider cylindrical pores. While under wider confinements the structural crossovers are quite sharp, the one observed in this study is rather smooth and rounded, as expected. Only once a q1D system reaches the bulk limit, does the structural crossover become a genuine phase transition.

The lengths \( \xi_y \) and \( \xi_\phi \) both increase monotonically as the pressure or the confinement width increases. However, for \( \xi_{s+\sigma} \) in the NN regime and \( \xi_r \), its behavior is non-monotonic and it does not diverge because it then becomes single valued. In general, for a geometrically confined system, different spatial correlations may behave distinctly and one needs to identify a suitable correlation length for characterizing the structural crossovers.
In this chapter, we present another collaborative work\textsuperscript{1} with Prof. Wiley’s and Prof. López’s groups, in which we try to concentrate nanoparticles by acoustic standing waves. As mentioned in Chapter 4, one possible experimental realization of hard sphere packings within cylinders is by sedimenting particles into cylindrical holes, while concentrating nanoparticles by acoustic standing waves is also expected to be another candidate because q1D confinements can be generated by primary radiation forces. Here we examine the capabilities and limitations of this experimental approach.

6.1 Brief Description

In this study, we investigate the theoretical and empirical limitations of acoustic radiation forces to concentrate nanoparticles of a given size and composition. To perform this study, we built an acoustic focusing chamber containing opposing piezoelectric

\textsuperscript{1} My contribution to this work includes the development of the theoretical model, experimental data analysis and critical insights into the experimental results
Figure 6.1: Schematic of the device used to acoustically concentrate nanoparticles. (A) Gold nanoparticles suspended in water are (B) focused to nodes of the acoustic standing wave generated by two vertical piezoelectric transducers.

transducers to rapidly focus particles of different sizes into parallel patterns (Fig. 1A-B). We selected gold as a model material, due to its high density (19.3 g/cc) and low compressibility (5.5 x 10^{-12} Pa^{-1}). These properties give gold nanoparticles a high acoustic contrast factor (Φ) in water, and thus a strong potential to migrate to the pressure node, making it an ideal candidate for investigating the limits of
acoustophoresis [95].

6.2 Results and Discussion

Our approach to concentrate gold nanoparticles relies on superposing acoustic standing waves created with two lead zirconate titanate (PZT) piezoelectric transducers facing opposite to one another inside an acrylic chamber. In an acoustic standing wave, particles experience a primary radiation force from the acoustic potential $U$, which leads to the concentration of particles around the potential minima. To provide insights into and probe the limits of this technique, we developed a theoretical model to investigate the dynamics and equilibrium assembly of the system. In this model, standing waves form planes with one-dimensional periodicity. Setting the oscillatory direction along the $x$-axis, we obtain:

$$U = -\frac{1}{2} V E_{ac} [f_1 - \frac{3}{2} f_2 + \Phi \cos(2kx)] \quad (6.1)$$

and thus the acoustic force felt by a particle is

$$F = k V E_{ac} \Phi \sin(2kx), \quad (6.2)$$

where

$$E_{ac} = \frac{P^2}{4 \rho c_l^2} \quad (6.3)$$

$$f_1 = 1 - \frac{\rho t c_l^2}{\rho p c_p^2} \quad (6.4)$$

$$f_2 = \frac{2(\rho_p - \rho_t)}{2\rho_p + \rho_t} \quad (6.5)$$

$$\Phi = f_1 + \frac{3}{2} f_2 \quad (6.6)$$

$$k = \frac{2\pi f_{PZT}}{c_l} \quad (6.7)$$
The variables are listed in Table 6.1. Depending upon the sign of $\Phi$, particles focus either to the nodes (of constant pressure) or the antinodes (with the highest pressure fluctuations) of the standing wave [96].

By considering solely Brownian motion, Stokes drag and the primary radiation force, which is valid for perfectly formed acoustic standing waves in the limit of a dilute concentration of nanoparticles (the hard-core repulsion is ignored), the dynamical evolution of the probability $\hat{p}(\hat{x}, \hat{t})$ for a particle to be at position $\hat{x}$ at time $\hat{t}$ conditional on $\hat{p}(\hat{x}, 0)$ can be described by the dimensionless Smoluchowski equation:

$$\frac{\partial}{\partial \hat{t}} \hat{p}(\hat{x}, \hat{t}) = \hat{D}(\frac{\partial^2}{\partial \hat{x}^2} - \hat{\beta} \frac{\partial}{\partial \hat{x}} \hat{F}) \hat{p}(\hat{x}, \hat{t}),$$

(6.8)

where

$$\hat{x} = 2kx$$

(6.9)

$$\hat{t} = 2kv_0 t$$

(6.10)

$$\hat{D} = 2k \frac{D}{v_0}$$

(6.11)

$$\hat{F} = \frac{1}{2kv_0^2} F$$

(6.12)

$$\hat{\beta} = \beta mv_0^2.$$
The variables are also listed in Table 6.1 and \( v_0 \) is an arbitrary scaling constant, which can be chosen such that \( \beta = 1 \).

Because \( \hat{p} \) is real and \( U \) is even, the Fourier series expansion gives:

\[
\hat{p}(\hat{x}, \hat{t}) = \sum_{n=-\infty}^{\infty} c_n(\hat{t}) e^{in\hat{x}}, \text{ with real } c_n = c_n^*,
\]

which can be inserted into Eqn. (6.8) to obtain the tridiagonal recurrence relation:

\[
\frac{\partial}{\partial \hat{t}} c_n = \frac{1}{2} \hat{D} \beta n d c_{n-1} - D n^2 c_n - \frac{1}{2} \hat{D} \beta n d c_{n+1}, \quad \forall n
\]

with

\[
d = \frac{1}{2v_0^2} V E_{ac} \Phi.
\]

In experiments, particles are initially uniformly distributed, i.e.

\[
\hat{p}(\hat{x}, 0) = 1/(2\pi)
\]

(without loss of generality, we can consider the system behavior over a single period), which sets the initial conditions for Eqn. (6.8) and Eqn. (6.14) to be:

\[
c_0(0) = \frac{1}{2\pi}
\]

\[
c_{n \neq 0}(0) = 0.
\]

We then numerically solve for \( \hat{p} \) by the continued fractions method [97]. To characterize the system dynamics and compare the theoretical predictions with experimental results, we measure the full-width-at-half-maximum (FWHM) of the particle distribution, \( p(x, t) \).

Note that the stationary solution to Eqn. (6.8), i.e., for \( t = \infty \), is the Boltzmann distribution, i.e., \( p(x) = A \exp(-\beta U(x)) \), where \( A = \int_{-\pi/k}^{\pi/k} \exp(-\beta U(x)) dx \) is a normalization factor which does not affect the FWHM. To determine the cutoff for the
Fourier series, \( n_c \), for \( n \) in Eqn. (6.14), we compare the FWHM for the equilibrium distribution and \( p(x, t = 10000s) \) for different \( n_c \). We find that for \( P = 87.5 \text{ kPa} \) (\( \hat{\beta}d \approx 1.1 \)), 175 kPa (\( \hat{\beta}d \approx 4.2 \)), 350 kPa (\( \hat{\beta}d \approx 16.9 \)) and 700 kPa (\( \hat{\beta}d \approx 67.6 \)), \( n_c = 4, 8, 16 \) and 28 are sufficient to keep the numerical error below 0.2%.

This model provides the theoretical FWHM as a function of time, and thus we estimated the characteristic time, \( t_c \), for focusing gold nanoparticles to the pressure node. We define the characteristic time \( t_c \) as the time at which the FWHM of the particle distribution approaches the value

\[
\text{FWHM}(t = t_c) = \frac{[\text{FWHM}(t = 0.1) + \text{FWHM}(t = \infty)]}{e} \tag{6.20}
\]

The equilibrium time was set to be \( 2t_c \), and we measured the corresponding equilibrium FWHM for different pressure amplitudes.

To experimentally verify these equilibrium-focusing times, we generated standing wave fields with different pressure amplitudes. We found that pressure amplitudes could not be reproducibly generated above the limits of the transducers, i.e., at around 700 kPa and thus we chose to examine the system under pressures of 175 kPa, 350 kPa and 700 kPa. After the experimental equilibrium time, we acquired dark-field images of the concentrated gold nanoparticles in the chamber. Trends in the experimental results agreed well with theoretical predictions (Fig. 6.2A, B). After \( 2t_c \), the FWHM did not systematically decrease, which matches our theoretical predictions. With 50 nm particles (Fig. 6.2B, left column), we did not observe the formation of patterns over the experimental range of acoustic pressures (i.e., up to 700 kPa; Fig. 6.2B, top row). Although, we note that our model suggests the ability to focus 50 nm, or smaller, nanoparticles with higher pressures, it is not achievable in our experimental setup because of the device limitation. While our model predicts a relatively small FWHM in the pressure range considered here for 50 nm particles, the theoretical equilibrium particle distribution was essentially flat, i.e., the difference
between the maximum and minimum of the distribution is small, and hence particle focusing was not observed (Fig. 6.2B (bottom row)). On applying a pressure of 350 kPa, we observed signs of particle concentration along the nodes of the standing wave (Fig. 6.2B (middle row)), forming distinct patterns separated by a half of the acoustic wavelength, $\frac{1}{2} \lambda_{aw}$. Increasing the applied pressure further produced tighter nodes. With 200 nm particles, we observed patterning at all experimental pressures (Fig. 6.2B right column), and the patterns formed were closer packed than those observed with 100 nm particles (Fig. 6.2B middle column).

To further verify our model, we compared the experimental and theoretical equilibrium FWHM values of gold nanoparticles of different sizes at different pressure amplitudes. Theoretical distributions for both 100 nm (Fig. 6.3(A-D) for 87.5, 175, 350 and 700 kPa, respectively) and 200 nm (Fig. 6.3(I-L) for 87.5, 175, 350 and 700 kPa, respectively) gold nanoparticles exhibited qualitative agreement with experimental distributions (Fig. 6.3E-H and M-P). Generally, as shown in Figure 6.3Q&R, experimental FWHM were systematically larger than those predicted by our model;

Figure 6.2: Acoustophoresis of spherical gold nanoparticles. A) Theoretical plot of the equilibrium FWHM for different acoustic pressures and different gold nanoparticle diameters. B) Dark-field images of 50, 100 and 200 nm gold particles (left to right) in an acoustic standing wave with pressure amplitudes of 700, 350 and 175 kPa (top to bottom) after equilibrium was reached. All scale bars are 40 µm.
however for the case of the 100 nm particles, this discrepancy decreased with increasing acoustic pressures. Further, we observed a better agreement between our model and experiments with 200 nm particles than with 100 nm particles.

We attribute the discrepancy between the experiments and our model to the fact that we assumed that our system is solely influenced by primary acoustic radiation forces, Brownian motion (thermal fluctuations) and Stokes’ drag. However, in the range of pressure amplitudes used in this work, other factors such as acoustic streaming and secondary radiation forces, also referred to as Bjerknes forces, can contribute to the dispersion of nanoparticles [95]. Other than these effects, for low pressures, the discrepancy may also have resulted from the flatness of the particle distribution and the quality of the images (Fig. 6.3F&G). The qualitative agreement between the FWHM and the acoustic pressure amplitude in our model suggests that the contribution of these confounding factors is relatively small in our system, and that the tie between pressure amplitude and particle concentration is well-understood.

Next, we investigated the kinetics of the system by measuring the FWHM centered about a pressure node over time. We assumed the initial particle distribution (at \( t = 0 \)) was uniform, and then solved Eqn. (6.8) to characterize the system dynamics for the duration of acoustic manipulation by calculating the FWHM as a function of time. For this work, we studied the dynamics of 200 nm gold nanoparticles subject to pressure amplitudes of 87.5, 175 and 350 kPa. By solving Eqn. (6.8) for \( p(x, t) \), we obtained theoretical particle distributions at different times (Fig. 6.4A-C). We then verified the system dynamics by acquiring dark-field images at regular time intervals from a fixed region of the chamber, and we compared our experimental observations (Fig. 6.4D-F) with grayscale solutions for particle distribution \( p(x, t) \) at different times. To validate the reproducibility of the measurements, we conducted three experiments for each pressure amplitude and plotted FWHM versus time of focusing for each experiment.
Figure 6.3: Equilibrium focusing of gold nanoparticles. Theoretical equilibrium distributions for 100 nm (A-D) and for 200 nm gold nanoparticles (I-L) at pressures 87.5, 175, 350 and 700 kPa respectively. The white and black regions demarcate regions of maximum and minimum concentration, respectively. Corresponding equilibrium dark-field images from representative experiments for 100 nm (E-H) and 200 nm (M-P) gold nanoparticles at 87.5, 175, 350 and 700 kPa, respectively. Graphs of the equilibrium FWHM as a function of pressure amplitude predicted by the model from a Boltzmann distribution (red curve) versus experiments (black symbols) for (Q) 100 nm and (R) 200 nm gold nanoparticles. Scale bars are 40 µm.
The concentration of gold nanoparticles at the nearest pressure node increased with time until equilibrium was reached (Fig. 6.4G), and the experimental results generally exhibited good agreement with theoretical predictions. We observed a nearly stable equilibrium FWHM at the predicted timescales for the experimental pressure amplitudes. Theoretically, smaller sized nanoparticles could be focused and a narrower FWHM could be achieved with use of higher applied acoustic pressures. As discussed earlier, this could not be realized in our experiments due to the limitations of our device, i.e., the nodes become less stable at higher pressures due to acoustic streaming, and the voltages required to achieve higher acoustic pressures are above the tolerance of the transducers.

Our theoretical solutions for equilibrium focusing and system dynamics consider gold nanoparticle distributions in two dimensions. However, the blurriness observed in experimental images (e.g., Fig. 6.3D-F) suggests that particles were not in the same plane. Particles out of the focus plane contribute differently to the FWHM measurements and thus can cause errors. However, high-depth-of-view objectives can increase the precision of these experimental FWHM values. Overall, our results indicate acoustic radiation forces can be used to concentrate gold nanoparticles of a given size using an appropriate pressure amplitude; however, with limitations in the pressure amplitudes generated in these devices and the effect of the acoustic streaming, there are corresponding limits to the size of particles that can be focused to a certain FWHM via bulk acoustic standing waves.

To overcome this limitation, we developed a UV-light-activated aggregation technique to concentrate nanoparticles below the theoretical limit at a given pressure amplitude. We added a photoacid, pyranine, to the colloidal solution, which increases the acidity of the solution upon exposure to UV light [98]. The increased acidity alters the surface charge of the nanoparticles past the isoelectric point [99]. This reduces the electrostatic particle-particle interactions, thus allowing the particles to
Figure 6.4: Kinetics of concentrating 200 nm gold nanoparticles under pressure of 350 kPa. Theoretical distribution of gold nanoparticles after A) 0 sec, B) 30 sec and C) 60 sec of exposure to an acoustic standing wave. The white and black regions demarcate regions of maximum and minimum concentration, respectively. Experimental images of gold particles after D) 0 sec, E) 30 sec and F) 60 sec of exposure to an acoustic standing wave. G) Plot of theoretical and experimental FWHM over time after exposure to an acoustic standing wave. Images were acquired at regular time intervals until equilibrium timescale of patterning. All scale bars are 40 $\mu$m.

Flocculate during their Brownian fluctuations, increasing the magnitude of acoustic primary radiation force acting on the aggregates and thus increasing their ability to focus. To verify this experimentally, the nanoparticles were subjected to a 700 kPa acoustic pressure amplitude and dark-field images are taken at 300 and 360 sec for 80 nm and 60 nm particles before the photo acid generator was activated (Fig. 6.5A&C, respectively). This acoustic pressure was sufficient to focus the nanoparticles to an equilibrium FWHM of 121 $\mu$m and 140 $\mu$m for 80 nm and 60 nm particles respectively. After irradiation with a UV light source, the FWHM decreased to 105 $\mu$m and
61 \mu m for 80 nm and 60 nm particles, respectively (Fig. 6.5B, D-F). This experiment shows that the UV-induced aggregation of nanoparticles allowed for an increase in the concentration of the nanoparticles within the acoustic node beyond what can be achieved with acoustophoresis alone. This result also implies that if aggregation of nanoparticles occurs during an acoustic focusing experiment, the degree of focusing that would be achieved is beyond what would be predicted by our acoustophoresis model because particle-particle interactions are ignored.

Figure 6.5: UV activated aggregation. Dark-field images of (A&B) 80 nm and (C&D) 60 nm gold nanoparticles focused at 700 kPa. Images of gold nanoparticles focused at equilibrium times (A&C) before UV irradiation and (B&D) after UV irradiation. FWHM plots of the E) 80 nm and F) 60 nm gold nanoparticles, showing a cross sectional projection about the pressure node.

We can generalize our findings from gold nanoparticles to describe the minimum acoustic pressure amplitude necessary to focus nanoparticles of various sizes and compositions (described by the acoustic contrast factor, $\Phi$) to the pressure (anti-
We found that for pressures with predicted equilibrium FWHM smaller than or equal to 1/8 of the acoustic wavelength, $\lambda_{aw}$ ($(1/8)\lambda_{aw} = 60.5 \, \mu m$ in this work), reproducible patterning of particles could be observed. We thus define the minimum focusing pressure as the pressure which gives an equilibrium FWHM to be $(1/8)\lambda_{aw}$. We tested the validity of our model by comparing 3 sets of particles with different contrast factors and diameters (Fig. 6.6B). The applied acoustic pressure amplitude was kept constant at 700 kPa and particle diameters were chosen above and below the predicted threshold for focusing. Polystyrene, silica and gold were chosen for comparison because the contrast factors of these particles span three orders of magnitude.

No observable focusing occurred with the 300 nm polystyrene and 100 nm silica particles as expected, and focusing was observed for the 500 polystyrene and 200 nm silica with FWHMs of 139.7 $\mu m$ and 89.2 $\mu m$ respectively. Although the larger set of particles focused as expected, their FWHMs were much larger than the model predicts, 18 $\mu m$ for the 500 nm polystyrene and 20 $\mu m$ for the 200 nm silica. This discrepancy may be due to the fact that these particles do not scatter as brightly in our dark field microscope, limiting our ability to precisely measure the FWHM. Our experiments, did however, agree qualitatively with our model as particles above the particle diameter limit focused at 700kpa and those below the threshold failed expectedly.

Sinha and coworkers have previously reported the ability to focus 5 nm particles with bulk acoustic waves using a device similar to the one in this report [100], yet our model indicates the minimum particle size which could be focused with such a device is 60nm. Our results suggest that what was actually focused in that work were aggregates rather than individually dispersed nanoparticles. Indeed, Sinha and coworkers focused diamond nanoparticles in water without a surfactant, and other work has shown that diamond nanoparticles for stable aggregates with diameters of
Figure 6.6: A) Plot Describing the Minimum Pressure Amplitude to Focus Particles of Various Compositions. Plot of the required applied acoustic pressure to focus particles of various sizes to a FWHM of 60.5 μm in water as a function of acoustic contrast factor. The experimental limit of our device is 700 kPa and is represented by the shaded region. B) Experimental data testing the limit of acoustic focusing for different particle compositions. The dashed line represents focusing to a FWHM of 60.5 μm at 700 kPa.
100-200 nm under such conditions, even after powerful and extensive sonication [99]. Although the images in the paper by Sinha and coworkers are not of sufficient magnification to distinguish between individual 5-nm nanoparticles and larger aggregates, focusing of such larger aggregates would be consistent with our theoretical model and experimental results [99].

6.3 Conclusions

With this work we aimed to clarify to what extent a nanoparticle of a given size and composition could be focused with a bulk acoustic wave by developing a theoretical model for predicting the time-dependent focusing of nanoparticles subject to an acoustic standing wave. The predictions of this model matched well with the observed time-dependent and equilibrium focusing of gold nanoparticles, and established that the smallest gold nanoparticle size that could be focused was 60 nm in diameter. As gold has one of the highest acoustic contrast factors for nanoparticles in water, this size represents a lower limit for the diameter of nanoparticles that can be focused with a standing acoustic wave. These results were extended to establish what was the minimum size nanoparticle that could be focused as a function of acoustic contrast factor (i.e., for different nanoparticle compositions), and again these predictions were confirmed experimentally for silica and polystyrene nanoparticles. Finally we demonstrated that UV-induced aggregation of nanoparticles with could be used to overcome Brownian motion and allow nanoparticles to aggregate to an extent beyond that predicted by our model. We hope that the model and results reported here will allow researchers considering the use of acoustic forces for manipulation of nanoparticles to be more aware of the limits of this technique and plan accordingly.
6.4 Methods and Materials

6.4.1 Gold nanoparticles

The gold nanoparticles used in this study were spherical with diameters of 50, 100 and 200 nm (corresponding to G-50-100, G-100-100 and G-200-100, Cytodiagnostics) with narrow dispersity (i.e., coefficients of variance ≤10%). The nanoparticles were used in the concentrations supplied by the vendor, $3.51 \times 10^{10}$, $3.84 \times 10^9$ and $1.91 \times 10^9$ particles/mL for the 50, 100 and 200 nm particles respectively, in suspensions of 0.1 mM PBS stabilized with citric acid. Prior to each experiment, particles were agitated in an ultrasonic bath (Branson 2510) for 30 min to disperse aggregates.

6.4.2 Device fabrication and experimental setup

We built a square, resonating chamber similar to chambers described previously (Fig. 6.1A) [101]. Briefly, the chamber was constructed from transparent acrylic (Plexiglas, McMaster-Carr, Co.) that was laser-cut into a square frame with an inner dimension 31 mm x 31 mm, a wall thickness of 5 mm and a height of 6 mm. Two PZT transducers (30 x 10 x 1 mm, 841-WFB, with a resonant frequency of 2.91 MHz, APC International) were fixed onto two opposing inner chamber walls using cyanoacrylate adhesive (Elmer’s Products, Inc.). Electrical leads were soldered onto the transducers in a manner that prevented contact with the liquid inside of the chamber. Finally, we glued the acrylic chamber onto a 1.0 mm thick glass substrate (Nexterion Glass B, Schott, AG) using a silicone adhesive. We actuated the transducers with a 3.062 MHz AC signal from a waveform generator (AFG 3022C, Tektronix), amplified by a power amplifier (25A250AM6, Amplifier Research) to generate 126 linear pressure nodes within the chamber. We correlated the drive voltages supplied to the PZT transducers with apparent pressure amplitudes using a method described previously [101].
We analyzed gold nanoparticles with a dark field microscope (BX51, Olympus) fitted with a 20x objective (UPlanFL N, 0.50 numerical aperture, Olympus) and high-speed camera (SC30, Olympus), and acquired images using a constant exposure time of 4.5 msec. For each experiment, we pipetted 1 mL of the stock nanoparticle suspension (undiluted) into the chamber, we allowed the particles to settle under gravity for 15-30 min (corresponding to the 200—50 nm particles), and we focused the microscope on the settled layer of nanoparticles. This time was not sufficient to allow all of the particles to settle, as we experimentally observed only a subset of particles settling at that time.

6.4.3 Model to predict Gold nanoparticle patterning

The dimensionless Smoluchowski equation was numerically solved as a Fourier series [97] using MATLAB, and the FWHM as a function of time was then obtained over a duration of 1000 seconds with a resolution of 1 second. The assumptions of our model include: (1) a uniform distribution of particles inside the chamber at time \( t = 0 \); (2) acoustic radiation forces, Brownian motions and Stokes drag are the dominating forces governing the dynamics of nanoparticle movement (i.e., we ignored other factors). The equilibrium state was characterized by the Boltzmann distribution.

6.4.4 Equilibrium time for focusing of Gold nanoparticles, data acquisition and analysis

We used our model to determine the equilibrium timescale for concentrating each size of particle at different pressure amplitudes. We define the characteristic time \( t_c \) as the time at which the FWHM of the particle distribution approaches the value

\[
\text{FWHM}(t = t_c) = \left[ \text{FWHM}(t = 0.1) + \text{FWHM}(t = \infty) \right]/e. \tag{6.21}
\]

Then the equilibrium time was set to be \( 2t_c \).
To verify this equilibrium time experimentally, we tuned the drive voltage of the waveform generator to generate pressure amplitudes of 175, 350 and 700 kPa, and we acquired images after the $2t_c$. For each combination of conditions, we imaged nanoparticles patterns at five positions and from three independent experiments.

We characterized the equilibrium focusing of gold nanoparticles by measuring the FWHM of the distribution of the grayscale intensity for experimental snapshots. We used a custom code written in MATLAB to segment each image into multiple rectangular regions of interest, each 2.5 $\mu$m x 250 $\mu$m. For each segment, the grayscale intensity was averaged over rows of pixels and then the distribution of grayscale intensities was fitted to a Gaussian distribution to locate the peak of the distribution. To eliminate the error caused by the meandering of the particle line, the peaks of different segmentations were aligned before obtaining the average of the grayscale intensity distribution of the whole raw image. This distribution was then subtracted by its lowest value to adjust the base to zero. We then determined the peak intensity value, the half-maximum and its corresponding $x$-coordinates, from which we calculated the equilibrium FWHM. We repeated this procedure for each image, computed the mean and standard deviation from images acquired for each particle size and each acoustic pressure, and we plotted those values along with the values predicted by our model.

6.4.5 Kinetics of acoustic patterning of 200 nm Gold particles, data acquisition and analysis

We studied the kinetics of particle concentration using 200 nm particles and at pressure amplitudes of 87.5, 175 and 350 kPa. We used our model to predict the variation of FWHM of the pressure node of gold nanoparticles as a function of time over the entire duration of acoustic manipulation. We programmed the camera to acquire frames at regular intervals, which varied depending upon the pressure amplitude.
(typically 1 sec for 350 kPa and 5 sec for 87.5 kPa), until equilibrium conditions were reached, with a delay of 5 sec prior to acoustic actuation. We characterized the kinetics of particle concentration by measuring the FWHM of sequentially focused gold nanoparticles from 10 frames for each pressure amplitude, and from a 381 µm x 242 µm region of interest in each frame. We repeated the experiments three times for each pressure amplitude, and we plotted the variation of FWHM with time for each experiment. The data analysis from the images was the same as for equilibrium experiments.

6.4.6 UV activated aggregation

To increase the acoustic concentration, the particles were suspended in a 1mM pyranine (Tokyo Chemical Industry, Japan). After the nanoparticles were focused to equilibrium, the sample was exposed to 365 nm UV light with a power density of ca. 36 mW cm for 10 seconds while under an acoustic field. Dark field images were taken before and after UV activation.
7 Gardner Transition in Polydisperse Crystals

As we have shown in Chapter 4, thermodynamic equilibrium structures cannot always be obtained easily and kinetics sometimes plays a key role in self-assembly. In specific, even the FCC structure is not trivial to assemble because of geometric frustrations and thus dense hard sphere fluids could form disordered glassy states under quick quench in volume. In this chapter, we present the preliminary results for the on-going work on the Gardner transition in polydisperse crystals.

7.1 Introduction

Establishing a theoretical description for the glass problem has been a key challenge in condensed matter physics for decades now. Conventional strategies based on perturbations around either the ideal gas limit or an ideal lattice both fail because the interactions are strong and an equilibrium reference system is missing [102]. An alternate method for treating the glass problem is solving it in infinite dimensions \((d \to \infty)\) and using \(1/d\) as a small parameter, hoping to recover the low-dimensional behavior this way. Following this strategy, the Random First Order Transition (RFOT) theory for the glass transition developed by Kirkpatrick, Thiru-
malai and Wolynes in the 80s [103–109] was recently assessed. The replica approach proposed by Parisi and Zamponi [110, 111] was indeed transformed into an exact $d = \infty$ solution [112–114] and many features of the RFOT scenario were found to be exact in that limit. The practical importance of this solution was strengthened by the observation that glass properties do not depend sensitively on dimension, as recent computational efforts have made clear [115–118].

The traditional view of the free energy landscape of glasses, which follows the RFOT scenario, is that it consists of simple basins (local free energy minima) corresponding to (meta)stable glass state. Two types of relaxations then exist: vibrational excitations within the simple basin and jumps between free energy basins [119, 120]. However, mechanical marginality [121–123], which is accompanied with very soft vibrational modes [123, 124] in some glasses, cannot be explained by such a simple description. The infinite-dimensional result predicts instead the existence of a Gardner transition within the glass state [114, 125], beyond which the smooth basins become as rough as the glass states in the Sherrington-Kirkpatrick (SK) model [126].

For long, renormalization group results have suggested that a Gardner-like transition should disappear in spaces of low dimensions [127]. Recent numerical studies have nonetheless detected strong hints of its existence in a three-dimensional hard sphere glass [128, 129], which has motivated revisiting the renormalization group analysis and led to the discovery of a non-perturbative fixed point. These results strongly suggest that the detection of the Gardner transition should be possible in experiments.

Here, we propose a different type of systems in which a Gardner-like transitions should be possible. Consider a polydisperse crystal near jamming (Fig. 7.1). Just as in the monodisperse amorphous solids, particles under compression have different possible choices of neighbors in which to come into contact. Rather than arising from the self-induced disorder of a glass, however, it is the particle size polydispersity that
is at play. This multiplicity of choices roughens the free energy landscape. We thus follow a procedure similar to that developed in Ref. [129] to locate the Gardner transition in a polydisperse crystal.

Figure 7.1: Schematic compression of a polydisperse crystal. The lattice order is maintained until particles can differentiate between larger and smaller neighbors in their collisions, which is the case as long as the spacing between particles is larger than the system polydispersity. Further compression traps the system into different local minima. For example, different choices of contacts for the black particle bifurcate the system into A and B. The same situation happens for the blue and pink particles into $A_1$, $A_2$ and $B_1$, $B_2$, respectively. A continued branching process is expected, but is not shown here.
7.2 Methods

7.2.1 Preparation of the crystal

The polydisperse crystal studied in this work is based on a binary structure, the Hudson Structure One (HS1) [130], whose unit cell has four larger particles, 12 smaller particles and orthorhombic periodicity with dimensions of $a = 7.27300$, $b = 10.89540$ and $c = 18.92019$. To introduce polydispersity, the diameter $\sigma$ of every particle is scaled by a random variable $R$:

$$\sigma_i = \sigma_{i}^{\text{HS1}} \times R,$$

(7.1)

where $\sigma_{i}^{\text{HS1}}$ is the diameter for particle $i$ in HS1 and $R$ is a Log-normal distributed random variable with unit mean and standard deviation $P_d$. Note that Log-normal is chosen so as to avoid having negative diameters. Here, $P_d = 0.01$ and 0.03 are considered. To limit finite-size effect, the system size is expanded by $5^3$ to have the particle number $N = 2000$, before introducing the polydispersity.

7.2.2 Simulation methods

The simulations are initialized from a perfectly close-packed HS1 binary crystal at the packing fraction $\varphi_{\text{cp}} \approx 0.757$, and the unit cell is increased to eliminate overlaps that result from the polydispersity. Isothermal-isobaric, constant $NPT$, Monte Carlo (MC) simulations are then run to reach a target $\varphi$. Pressure $P$ is kept constant by standard logarithmically-sampled volume moves. Because the initial configurations are well-ordered, dense structures, conventional MC moves with a ratio between particle moves and volume moves being $N : 10$ suffice to efficiently compress the system. From the target density, constant volume, constant $NVT$ simulations are performed using only a local Metropolis dynamics. The step sizes of different MC moves are tuned to ensure an acceptance ratio between 40% and 50%.
Mean squared displacement calculation

A standard order parameter for glasses is the mean squared displacement,

\[
\Delta(t, t_w) = \frac{1}{N} \sum_{i=1}^{N} \langle |\mathbf{r}_i(t + t_w) - \mathbf{r}_i(t_w)|^2 \rangle, \tag{7.2}
\]

where \( t_w \) is the waiting time after the target pressure or density is reached and \( \mathbf{r}_i \) is the position of particle \( i \). Before and after the Gardner transition, the behavior of \( \Delta(t, t_w) \) is different. After the Gardner transition the MSD ages, but does not beforehand.

To detect the transition in the polydisperse HS1 crystal, we thus measure the time evolution of \( \Delta(t, t_w = 0) \) for different packing fractions. For \( P_d = 0.01, \phi = 0.710, 0.720, 0.730, 0.735, 0.740 \) and \( 0.745 \) are studied; for \( P_d = 0.03, \phi = 0.680, 0.690, 0.700, 0.710 \) and \( 0.715 \) are studied.

The plateau of \( \Delta(t, 0) \) for systems before the Gardner transition are obtained by averaging over \( \Delta(t > 10^5, 0) \). For systems after the Gardner transition, by construction \( \Delta(t, 0) \) does not converge after \( 5 \times 10^7 \) MC cycles, and an estimate of the early plateau is approximated at \( \Delta(10^4, 0) \). Note, however, that a clearer estimate could be obtained by considering systems with a series of \( t_w \neq 0 \).

The long-time limit of \( \Delta(t, t_w) \) quickly becomes computationally unattainable once the system reaches the Gardner phase. To more clearly reveal the effect of aging, we obtain the equilibrium \( \Delta(t \to \infty, t_w \to \infty) \) from the distance \( \Delta_{AB} \) between two different copies, \( A \) and \( B \), with the same \( \phi \) and particle polydispersity, compressed from the same initial configuration, but using a different stochastic trajectory

\[
\Delta_{AB}(t) = \frac{1}{N} \sum_{i=1}^{N} \langle |\mathbf{r}_i^A(t) - \mathbf{r}_i^B(t)|^2 \rangle. \tag{7.3}
\]

Note that \( \Delta_{AB}(t) \) is calculated after aligning the centers of mass of the two copies, and 300 realizations of disorder are used in the averaging for both \( \Delta(t, t_w) \) and
\( \Delta_{AB} \). In addition, the introduction of polydispersity would change the original aspect ratio of the crystal, making the system impossible to reach the densest packing limit \( (\varphi \approx 0.757) \) if maintaining the original aspect ratio. Although we are still far from that limit and the \( P_d \) considered here are small, anisotropic volume moves are performed. In the calculation of \( \Delta_{AB}(t) \), in contrast, to reduce the effect of the difference in aspect ratio, volume moves are isotropic to ensure that \( A \) and \( B \) have the same system dimensions.

**Pressure calculation**

The system pressure \( P \) is calculated from the virial. In general, for a polydisperse system, this would include the calculation of \( N(N-1)/2 \) distinct pair distribution functions. Hard interactions, however, allow a rescaling that simplifies the relationship to a single distribution function. Defining the rescaled quantities:

\[
\bar{r}_{ij} = \frac{r_{ij}}{(\sigma_i + \sigma_j)/2} \quad (7.4)
\]

\[
\bar{u}_{ij} = \begin{cases} 
\infty, & \bar{r}_{ij} < 1 \\
0, & \bar{r}_{ij} \geq 1
\end{cases} \quad (7.5)
\]

\[
\bar{f}_{ij} = -\nabla \bar{u}_{ij}, \quad (7.6)
\]
where $r_{ij}$ is the distance between particles $i$ and $j$, we can indeed rewrite the virial as

$$
\beta P = \rho + \frac{\beta}{3V} \left\langle \sum_{i<j} \mathbf{f}_{ij} \cdot \mathbf{r}_{ij} \right\rangle
$$

(7.7)

$$
= \rho + \frac{\beta}{3V} \sum_{i<j} \langle \mathbf{f}_{ij} \cdot \mathbf{r}_{ij} \rangle
$$

(7.8)

$$
= \rho + \frac{\beta \rho^2}{3} \frac{1}{N(N-1)} \sum_{i<j} \int \mathbf{f}_{ij} \cdot \mathbf{r}_{ij} \tilde{g}(\mathbf{r}_{ij}) d\mathbf{r}_{ij}
$$

(7.9)

$$
= \rho + \frac{4\beta \pi \rho^2}{3} \frac{1}{N(N-1)} \sum_{i<j} \left[ \frac{1}{2} \sum_{i<j} \tilde{g}(\mathbf{r}_{ij}) d\mathbf{r}_{ij} \right] \left[ (\sigma_i + \sigma_j)/2 \right]^3
$$

(7.10)

$$
= \rho + \frac{4\beta \pi \rho^2 k_B T}{3} \frac{1}{N(N-1)} \sum_{i<j} \left[ \frac{1}{2} \sum_{i<j} \tilde{g}(\mathbf{r}_{ij}) d\mathbf{r}_{ij} \right] \left[ \frac{1}{2} \right]^3
$$

(7.11)

where $\tilde{g}(\bar{r})$ is a uniform rescaled pair distribution function and the contact value $\tilde{g}(1^+)$ is extrapolated from the first few non-zero values of $\tilde{g}(\bar{r})$ using a quadratic fit.

Note that Eqn. (7.11) reduces to the monodisperse case when $\sigma_i = \sigma_j = \sigma$, $\forall i, j$.

Once the target $\varphi$ is reached, $2 \times 10^5$ MC cycles are run to equilibrate the system. The distribution function $\tilde{g}(\bar{r})$ is then sampled every 100 MC cycles, and both $\tilde{g}(1^+)$ and the pressure are then calculated at every sampled cycle. Except for the two largest $\varphi$, $P$ converges, which is taken as the equilibrium value. For the two largest $\varphi$ the last recorded value of (out-of-equilibrium) $P$ is reported.

### 7.3 Results

Figure 7.2a shows $\Delta(t, t_w)$ in units of the average diameter $\bar{\sigma} = \sum_i \frac{1}{N} \sigma_i$, as a function of time for $P_d = 0.01$ at different $\varphi$. For $\varphi = 0.710$ and $0.720$, $\Delta(t, t_w)$ plateaus quickly and $\Delta_{AB}$ matches the equilibrium $\Delta(\infty, t_w)$. For $\varphi = 0.730, 0.740$ and $0.745$, $\Delta_{AB}$ is not reached after $5 \times 10^7$ MC cycles. The aging effect becomes increasingly
obvious as the packing fraction increases. The results suggest that the Gardner transition is $\varphi_G = 0.72(1)$ for $P_d = 0.01$ and $\varphi_G = 0.69(1)$ for $P_d = 0.03$.

**Figure 7.2**: $\Delta(t,0)$ for (a) $P_d = 0.01$ and (b) 0.03 at different $\varphi$ in units of $\bar{\sigma}$. Circles represent $\Delta(t,0)$ as a function of time and lines represent the corresponding $\Delta_{AB}$.

**Figure 7.3**: $\Delta_{AB}$ and (early) plateau values of $\Delta(t,t_w)$ for (a) different pressures and (b) packing fractions for $P_d = 0.01$ (blue) and 0.03 (red). Vertical lines denote $P = 1/P_d$.

Figure 7.3a shows $\Delta_{AB}$ versus the (early) plateau values of $\Delta(t,t_w)$ as a function of reduced pressure $P^* = \beta P \bar{\sigma}^3$. An obvious splitting of these two quantities is observed around the Gardner transition. As expected, the crystal begins to feel its polydispersity at $P^*$ around $1/P_d$, because the average gap between particles is

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roughly $\sim \frac{1}{P}$. Although the pressure for the two largest $\varphi$ are not trustable, the trend shown here is clear. The same phenomenon is also shown in Figure 7.3b for different packing fractions.
Bibliography


Biography

Lin Fu was born on June 30th, 1988, in Yunfu, Guangdong, China, and spent 4 years of childhood in his hometown, after which his family moved to Shunde. He grew up with his family until the age of sixteen. From 2004 to 2007, he attended the Li Zhaoji Middle School in Shunde, Guangdong, China. After that he spent four exciting and wonderful years at Sun Yat-sen University, Guangzhou, Guangdong, China, where he got his B.S. in chemistry from Department of Chemistry in 2011. In August 2011, he went to the graduate school at Duke University, Durham, North Carolina, United States. He is to receive his Ph.D. in physical chemistry from Duke University in the March of 2017.

Publications

