STRUCTURE AND DEFECTS OF HARD-SPHERE COLLOIDAL CRYSTALS AND GLASSES

A DISSERTATION PRESENTED
BY
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TO
THE DEPARTMENT OF PHYSICS

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE SUBJECT OF
PHYSICS

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
MAY 2013
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ABSTRACT

Colloidal particles provide convenient and useful building blocks for creating ordered and disordered structures with length scales on the order of a micrometer. These structures are useful materials in their own right, and also serve as excellent scale models for exploring properties of atomic materials that would otherwise be inaccessible to direct experiment. In this dissertation, we explore structure formation in hard-sphere colloidal systems using templated sedimentation techniques, and then use colloidal crystals and glasses formed in this way to study the development of extended defects in single crystals and shear defects in glasses. We find that it is possible to form large, defect-free colloidal single crystals extremely rapidly by centrifugation onto a deterministic template. On non-deterministic templates, we find a critical deposition flux above which the material always crosses over to forming a glass. With this understanding of the effects of template and deposition flux, we designed and tested amorphous templates that allow us to make colloidal glasses by sedimentation under gravity, as well as more complex structures. In face-centered cubic colloidal single crystals grown on (100) templates, extended defects (dislocations and stacking faults) can nucleate and grow if the crystal exceeds a critical thickness that depends on the lattice misfit with the template spacing. We account for the experimental observations of the density of misfit dislocations using the Frank-van der Merwe theory, adapted for the depth-dependent variation of lattice spacing and elastic constants that results from the gravitational pressure. In the second part of the thesis, we report the first results of a detailed study of reversible and irreversible deformation of colloidal glasses. We show that shear defects exist and are active in both sheared and quiescent colloidal glasses and that these defects behave as Eshelby inclusions. We observe a decrease in the shear modulus of the glass, which corresponds to a small dilatation, which, in turn, lowers the activation barrier for shear.
For Dad,
who started me on “mystery number” problems
around the same time he taught me to fish,
who inspired me to start running marathons,
and who still helps me with my homework.
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Acknowledgements

Graduate school is a big project. Many, many thanks are due. And not just for the wonderful seven years I’ve spent at Harvard working toward my Ph.D. I am so grateful to be a professional scientist and so fortunate that it’s my job to do the most fun, enjoyable, and rewarding work I can imagine (and then share it with others!).

Thank you, all of you, so very much for helping me get so far. And thank you for all the help and support that you will undoubtedly provide in the future.

Huge thanks to my wonderful parents, Rick and Laura Jensen, for three decades (and counting!) of love, support, encouragement, guidance, and just being great parents. I could not have done this without you. Thank you! And you can expect that I’ll still call home for writing tips (Mom), math/physics help (Dad), and advice about navigating The Academy (both!). I’m also proud to say that my father and I are both coauthors on my first publication, and I hope we manage to collaborate professionally again in the future.

To my little brother, Rory: We’ve come a long way from spending summers stick-fighting and building forts in the woods! It’s been great to grow up with you, and even now we keep discovering new things we have in common. Thanks also for teaching me extremely basic concepts of graphic design to improve my figures and presentations, and for occasional photoshopped work, including the dedication and last page of this book.

I have benefitted from many excellent teachers, mentors, research supervisors, colleagues, and
students over the years. In some kind of roughly chronological order, thanks to: John A. Chandler (1933-2007), who welcomed a 16-year-old into his UMASS chemistry class; David Hansen, who taught me organic chemistry and supervised my first lab research job the summer after high school; Steve Gullans, who got my dad into bioinformatics research, and welcomed me to join that research effort for two summers; David Wilkinson (1935-2002), who got me started in experimental physics and for whom WMAP is named; Olgica Bakajin, with whom I did microfluidics research for a summer at LLNL; William Happer, my undergraduate advisor and mentor, whose wisdom, spirit, and continued encouragement have made me a better physicist; Jon Twichell, my group leader during my two-year “pre-doc” at MIT Lincoln Laboratory, and ever a mentor and friend; Erik Duerr, Simon Verghese, George Turner, Alex MacKintosh, and all the rest of Group 83 also for that two-year period before graduate school, and for providing me an ongoing scientific creative outlet; David Nelson, the theorist of my committee, always reliable for thoughtful discussion (and impeccable blackboard technique!); Rick Heller and Michael Brenner, with whom I taught some great undergraduate classes; all the students of The Physics of Music and Sound, AP282, and Science and Cooking, for helping me become a much better teacher; the masters, students, and staff of Kirkland House for welcoming me into their community for so many years; Peter Schall and his group in Amsterdam for constant collaboration and inviting me to visit the lab for months at at time in 2010 and soon again in 2013; and all of my great summer or semester research students: Emily Margolis, Anjali Bhatt, Dan Pennachio (who took much of the (100) crystal data discussed in Chapters 3 and 4), Emma Thomas, and Saraf Nawar.

In graduate school I had two advisors, Frans Spaepen and David Weitz. In many ways their research styles are completely different, but they complement each other extremely well. I have benefitted tremendously from working with both of them at the interface of materials science and soft condensed matter physics. Their technical input has been invaluable, but I’ve learned much more from them than technical skills. Dave taught me how essential it is to know and be able to communicate why my work is not just interesting – lots of things are interesting – but important. He taught me how to write good papers in an organized way. Perhaps most significantly, I’ve learned a lot from Dave about the many different ways in which one can be a successful scientist.
I deeply appreciate that he encourages all of his advisees to find the path that is right for them – in science, or otherwise – and then does everything he can to help each of us succeed in whatever we choose.

In addition to being one of my Ph.D. advisors, Frans Spaepen has also been an exceptional mentor throughout graduate school. I have no doubt that he will continue to be there for me as I move forward in my career, ever ready with sage advice, good humor, and a seemingly infinite willingness to review material that we’re pretty sure I should already know. (Often these discussions begin with, “As you learned in 282...” and a smile.) He is truly a pleasure to write papers with; while we occasionally disagree on style, he’s an exceptional writer, and I learned a lot writing with him. Frans, I can’t begin to thank you for everything I have learned from you and for the support you have given me throughout our time together. I just hope it has been as fun and rewarding for you as it has for me!

I have had wonderful lab- and office-mates over the years in both the Materials Science Group and the Weitzlab, including Ingo Ramsteiner, Tom Kodger, Emily Russell, Demet Tatar, Emily Redston, Yunzhuo Lu, Hyerim Hwang, Zsolt Tserdik, and many, many more! I benefitted from many useful discussions with Mike Aziz, Joanna Aizenberg, and David Clarke. Christina Andujar and Barbara Sewall – you keep these groups running smoothly – thank you! I also have to thank the Materials Science Group and its alumni (the “Oldtimers”) for creating a wonderful community and inspiring me to learn to play softball for the annual Oldtimers Softball Game and Picnic, even though the “Young Moduli” have lost every year I played. Oldtimers beware – I’ll be on your team soon! In the lab I worked particularly closely with Maria Persson Gulda; we started in Frans’s group at the same time and she was a constant companion, loyal friend, and partner-in-crime from beginning to end of both of our Ph.D.s. It would not have been the same without you! Marc Heggen, Nobutomo Nakamura, and Eric Maire visited Frans’s group for extended stays at various times and were a tremendous pleasure to work with, and I’m thrilled that our collaborations continue. Daniel Recht falls into practically every category I’m thanking: college buddy, summer student at LL, officemate and fellow grad student in the Materials Science Group, co-author, and also my roommate for six years. Most of all, though, I thank Dan for being such a good friend.
(And I also thank him and his wife Emily Eames for putting up with my eccentricities around the apartment!)

Thanks to everyone in the Harvard Physics Department for taking me in seven years ago and looking after me all this time, especially Sheila Ferguson, Maggie McFee, Carol Davis, Melissa Franklin, Lisa Cacciabauda, Jacob Barandes, Jay McNeil, Stuart McNeil, Dayle Maynard, Bonnie Currier, Bill Walker, and Jim MacArthur. Thanks to Stan Cotreau for running an exceptional machine shop, giving endless good design advice, teaching me to weld, and putting up with all of us in the shop. Thanks to all my fellow grad students, especially the members of Team 266 (including our pinch-hitters): Josh Dorr, Jason Dowd, Jerome Fung, Yejin Huh, Tracy Slatyer, Tess Williams, Matt Barr, Brendan Shields, and Phil Richerme. Our puppet show was epic.

To all the rest of my friends and family: you have been amazing, and I thank you for all of your contributions, large and small. My paternal grandfather, Roderick Emil Jensen, was also a career scientist and ever an inspiration. Several of my younger cousins are studying physics, which is exciting and inspirational for me; I wish you all the best, whatever interests you pursue!

Thanks to Tudor Dimofte, my best friend for well over a decade, and always up for an adventure. Huge thanks to Corwin, who has been a constant source of support and encouragement, proofread this thesis, and provided software algorithm design and programming help, particularly with the numerical free volume calculation and FSP amorphous template design; and to Cecilia: you’re my two best friends in Cambridge, and I can’t thank you enough for being there for me, making me dinner all the time, and providing me with copious access to cats.

Thanks to my jujitsu students, teachers, and friends, for providing a much-needed outlet and patiently understanding when the dissertation made me disappear for months on end.

Thanks are also certainly due to all the places that fed and caffeinated me throughout graduate school, most especially Cafe Rustica and Porter Square Books. Also thanks to Kate Marron and Becca Schneider for helping me maintain my health and wellness throughout grad school.

Last, but not least, thank you to all those who provided financial support for this work: the Harvard University Department of Physics, the DoD via their NDSEG Fellowship, the NSF MRSEC at Harvard, the Women’s Travel Club, and P.E.O. via their Scholar Award. Some fabrication work
was done at the Center for Nanoscale Systems (CNS) at Harvard, a member of the NSF-supported National Nanotechnology Infrastructure Network (NNIN).

This thesis was typeset using \LaTeX, starting from the template that is freely available at https://github.com/suchow/.
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List of Included Publications

This dissertation is based on the following publications, as well as new work that has not yet been incorporated into any other paper:


The author also contributed to the following related publications.


We are also continuing additional work that is a direct followup to the results reported in this dissertation, particularly focused on the detailed structure of shear defects in glasses, and expect to prepare those results for publication later in 2013.
Colloidal particles provide convenient and useful building blocks for creating ordered and disordered structures with length scales on the order of nanometers to micrometers. These structures can be useful materials in their own right, and can also serve as scale models for exploring fundamental properties of atomic materials. Perfect crystals of colloidal particles are useful as optical-wavelength photonic materials \cite{50}, frameworks for hierarchical materials \cite{70,71}, templates for inverse-opal structures \cite{30}, and as experimental models for exploring the static and dynamic properties of atomic crystals \cite{61,62}. Colloidal glasses, on the other hand, are also useful as materials that can generate structural color \cite{42} and as models for understanding universal properties of amorphous materials \cite{11,12,63}.

We first introduce colloidal materials and some of the current challenges in colloid structure
formation, then describe the fundamental physics problems that we address in this work using colloids as experimental model materials.

1.1 Colloidal materials

Colloids are soft materials consisting of solid particles surrounded by a continuous fluid. Colloids of all sorts are ubiquitous in our everyday experience, with examples including paint, ink, milk, and ice cream [13]. Colloidal particles can come in any shape. Recent works study cubes and octahedra [31, 58], nano-octopods [47], dumbbells [52], multi-sphere clusters [43], and buckled or form fitting shapes [59], with sizes ranging from nanometers to micrometers.

This size is important because an essential characteristic of colloids is that they are thermal, meaning that the solid particles can move and rearranges spontaneously driven only by Brownian motion. This distinguishes them from granular materials, which can be structurally similar to densely-packed colloids, but are fundamentally athermal systems and undergo internal rearrangements only in response to an external driving force.

Colloidal particles can interact via a combination of charge effects, depletion attractions, or other, more complex interactions [51, 56], or can be hard such that they do not interact at all beyond an infinite repulsion on contact. Increasing interest in self-assembly at the colloidal length scale is spurring the development of more and more complex colloid structures as enabled by advances in synthesis techniques [72].

While the complexity of available colloid shapes and interactions is growing rapidly, monodisperse, hard-sphere colloidal particles continue to provide deep insights into the physics of structure formation and the relation between microscopic structure and large-scale properties. This relatively simple system possesses a rich phase space and demonstrates many of the phenomena commonly observed in much more complex systems. Hard spheres exhibit entropy-driven phase transitions as a functions of volume fraction or packing fraction, \( \phi \), including a first-order melting/crystallization phase transition and a glass transition on rapid quenching. The phase diagram for hard spheres, with examples of various phases from our work, is shown in Figure 1.1.
With increasing volume fraction, hard spheres form crystals and glasses. Fluid $0.494$ Fluid + Crystal $0.545$ Crystal $\sim 0.58$ Glass $0.64$ $0.74$

**Figure 1.1:** The phase diagram for hard spheres, with examples from our work demonstrating each phase. Traditionally, large crystals can only be formed very slowly, giving the particles time to find their lowest energy configuration (the crystal), and glasses require very rapid quenching from an initially-dilute colloid liquid in order to avoid crystallization.

### 1.2 Experimental system used in this work

We use 1.55-μm-diameter colloidal silica particles with a polydispersity <3.5% in a mixture of dimethyl sulfoxide (DMSO, 62.8% by volume), deionized water (36.0% by volume), and fluorescein-NaOH dye solution (1.2% by volume). The fluid phase has a viscosity $\eta = 1.6$ mPa·s and matches the index of refraction of the particles. The dye solution is 3% by weight fluorescein-NaOH in water and enables fluorescent imaging of the sample. Thanks to the index-matching between the particles and their surrounding fluid, we are able to take optical images deep in the colloid with minimal light loss due to scattering.

The particles we use are specially-filtered Sicaster plain particles purchased from Micromod. We receive the particles in pure water at a concentration of 50 mg/mL, or 2.5% by volume. The raw particle stock contains a small population of ~800nm-diameter particles, which we usually remove by fractionation prior to preparing the index-matched colloid. Scanning electron microscope (SEM) images of the raw particle stock are shown in Figure 1.2.

Silica particles acquire a negative surface charge in aqueous environments, but adding the fluorescein sodium salt has the additional important effect of reducing the Debye screening length.
Figure 1.2: SEM images of the raw particle stock we receive from Micromod\ref{footnote:micromod}; the bottom image was taken at a 5.25× higher magnification than the top. The particles have an average diameter of 1.55 μm; the very small and very large particles (including particle clusters) present in the raw stock are removed prior to our experiments. These images were taken for the author by Tom Kodger.
to less than 10 nm so that the particles interact as hard spheres. We checked for possible charge effects that could cause deviations from hard-sphere behavior by comparing crystals of the same height sedimented using our standard colloid mixture and using one with 10 mM NaCl added, and found no difference in the interparticle spacings. Had there been any residual charging not screened by the fluorescein-NaOH, we would have expected to see a reduction of the interparticle spacing with the addition of high-concentration NaCl salt.

1.3 Colloids as model materials

The essential challenge of the science of materials is to relate the properties of a material to its underlying structure. Additionally, an understanding of how and why this structure forms is also paramount. However, elucidating the details of these relationships at the atomic scale can be very difficult.

An ideal experiment would allow us to observe all relevant length and time scales of the problem simultaneously, following the individual motions and interactions of atoms and groups of atoms while simultaneously observing the bulk behavior of the material. Unfortunately, atoms are simply too small and move too quickly to do this. Glasses are particularly tricky. The very disordered nature that is responsible for the unique properties of amorphous materials also makes them more difficult to study than their crystalline counterparts. Even techniques like transmission electron microscopy (TEM) that can image individual atoms in crystals cannot resolve this level of detail in structures that lack crystalline symmetry.

However, by using hard-sphere colloids as scale models of atomic crystals and glasses, we are able to perform exactly the ideal experiment. These are materials in which the relevant length and time scales are observable in 3D and real time using optical microscopy. We create colloidal crystals and glasses as generic examples of these broad classes of materials: powerful experimental tools for directly probing the physics that relates the microscopic structure and dynamics to the large-scale materials properties.

This sort of analog physical modeling has a rich history. In the late 1940s, Bragg and colleagues created a two-dimensional “bubble raft” model of atoms in a metal out of tiny (≤1 mm),
monodisperse soap bubbles floating on the surface of a soap solution. This model provided the first experimental realization of crystal defects, including vacancies, impurities, and dislocations, as well as the first direct observation of the role dislocations play in mediating plastic deformation in crystals. As Bragg wrote, “The assemblages [of bubbles] show structures which have been supposed to exist in metals, and simulate effects which have been observed”.

Similar insights into the structure and dynamics of glasses were harder to come by. In 1979, Argon created a 2D amorphous bubble raft using a mixture of two sizes of bubbles to frustrate crystallization. Using this model, he made the first experimental observation of a “shear defect” or “shear transformation zone” (STZ). Like the dislocations observed for the first time in Bragg’s bubble raft, shear defects were hypothesized to exist in amorphous materials and to play a similar role in mediating plastic deformation in glasses as dislocations do in crystals.

However, both the crystalline and amorphous bubble experiments were limited to 2D, while the atomic materials they were supposed to model exist largely in 3D. (Bragg did create some multilayered crystal bubble structures, but had no way to image the layers in 3D.) Furthermore, the bubble rafts were relatively short lived because the bubbles begin to pop after some time, so longer relaxation or deformation experiments were impossible.

Meanwhile, macroscopic hard spheres were being used to model the three-dimensional structure, if not dynamics, of crystals, glasses, and interfaces. Notably, the random close-packing experiments of Bernal and Finney [4,25,26] provided the first statistically significant insights into a real-space amorphous structure. However, these 3D models only demonstrated static structure; they did not allow any insight into dynamics.

With the colloid model, however, we achieve the best of both worlds: dynamic, three-dimensional structures that can be optically imaged in 3D and real time under conditions of quiescence of applied deformation.

1.4 CONTENTS OF THIS DISSERTATION

The work that comprises this dissertation uses hard-sphere colloidal materials to explore structure and defects of crystals and glasses, particularly working toward an experimental model of the
detailed mechanisms of deformation in amorphous materials. Chapter 2 describes in detail the experiments and essential analyses, with particular emphasis on new tools, apparatus, and techniques that were developed as part of this work. The most significant of these inventions are a 3D calibration device for measuring the pixel-to-micrometer conversion factor of the confocal microscope, improvements to the apparatus for applying shear deformation to a dense colloid while imaging the colloid in 3D, and a new data processing technique for tracking particles more accurately than existing methods.

In Chapter 3, we explore the mechanisms of structure formation in monodisperse, hard-sphere colloids, with particular focus on templated sedimentation techniques. We demonstrate controlled growth of face-centered cubic (FCC), monodisperse hard-sphere colloidal crystals by centrifugation at up to 3000g onto FCC (100) templates, about 500 times faster than previously believed possible. Such rapid deposition rates generally result in an amorphous sediment; surprisingly, however, growth onto (100) templates results only in single crystals with few or no extended defects. By contrast, we find that deposition onto flat, (111), or (110) templates results in rapid disordering to an amorphous sediment if the dimensionless flux (particle volume fraction \( \times \) Peclet number) exceeds a critical value. This crystalline-to-amorphous crossover results from the degeneracy of possible stacking positions for these orientations. No such degeneracy exists for growth onto (100), on which a crystal can be grown defect-free at high dimensionless flux to arbitrary thickness. This understanding of the crystalline-to-amorphous crossover also enables us to form colloidal glasses much more slowly than previously believed possible. We achieve this by sedimentation at super-critical dimensionless flux onto specially-designed amorphous templates that initiate crystalline-amorphous crossover from the very first layer of particles. This understanding also enables more complex structures; as an example, we demonstrate the first amorphous-crystalline interface template, on which a perfect colloidal crystal and colloidal glass can be grown side-by-side.

Next, we use this understanding of the physics of colloid structure formation to create perfect crystals and glasses as experimental models of atomic materials. In Chapter 4, we study the nucleation and growth of extended defects (dislocations, stacking faults) due to strain caused by lattice mismatch with the templates in FCC colloidal crystals grown on (100) templates. Although
the crystals are defect-free as-formed, after growth extended defects can nucleate and grow if the
crystal exceeds a critical thickness that depends on the lattice misfit with the template spacing.
The experimental observations of the density of misfit dislocations are accounted for by the Frank-
van der Merwe theory adapted for the depth-dependent variations in both the lattice spacing and
the elastic constants that result from the gravitational pressure of the colloid.

Finally, in Chapter 5 we report the first results of a detailed study of reversible and irreversible
deformation of colloidal glasses. We observe both the individual particle and bulk dynamics of the
glass under conditions of quiescence and applied shear strain. We show that shear defects exist and
are active in both sheared and quiescent colloidal glasses. We characterize these defects as Eshelby
inclusions, and show that the theoretical framework of Eshelby inclusions agrees quantitatively
with our experimental observations. We measure the shear modulus of the glass, and find that it is
exquisitely sensitive to particle density. We show that the energy required to activate a shear defect
is consistent with the available thermal energy. These defects are a thermally-activated deformation
mode of the system. We find that local density fluctuations can lower the shear modulus for a local
region, thus lowering the activation barrier for shear defect activation in that region.

An appendix containing details of experimental procedures follows the main work, and is
intended to be a useful reference for anyone wishing to perform similar experiments.
Experimental apparatus and analysis methods

The confocal microscope is the key piece of equipment that enables our study of the structure and dynamics of colloidal materials. In recent years, confocal microscopes combined with computers for image acquisition and analysis \([28,46]\) have become powerful tools for making high-precision 3D measurements in physics and biology \([53,54]\). Confocal microscopes differ from conventional optical microscopes in that they have a pinhole positioned at the conjugate focus of the objective lens. This pinhole ensures that only light coming from the image plane will pass through to the detector; any out-of-focus light will be rejected, as shown in Figure 2.1. As a result, the confocal microscope is able to capture high-resolution images deep inside a sample. We obtain three-dimensional images of our colloids by stepping the image plane along the optical (z) axis and acquiring a two dimensional image at each z-position.
Confocal Microscopy of Colloids

• Confocal pinhole rejects any out-of-focus light
•Rastering mirrors (not shown) allow x-y scanning
• Shifting the focus depth allows scanning in z
• Result: 3D, real time, trackable images of 50k-500k particles

Not in image plane
in image plane

Laser (488nm)

Microscope Objective

PMT

Pinhole

Dichroic Mirror

Figure 2.1: Schematic diagram of a laser point-scanning confocal microscope. Any out-of-focus light (drawn schematically as red dashed lines) coming from above or below the image plane is rejected by the confocal pinhole and will not be detected by the photomultiplier tube (PMT). Raster mirrors, not drawn, allow scanning in the x-y plane (orthogonal to the optical axis).
To get the clearest possible images at the greatest depth, it is important that the sample be as transparent as possible. To achieve this transparency, we use colloids in which the fluid phase is index of refraction matched to the silica particles. The fluid is also dyed for fluorescence imaging. The number of particles whose trajectories can be followed depends on the size of the particles, their packing fraction, and the speed and resolution of the microscope. For our 1.55-μm-diameter silica colloidal particles, we are able to image up to half a million particles in a single stack. For dynamic experiments, we limit the stacks to about 50,000 particles to achieve higher time resolution.

In this chapter, we describe the essential experimental tools and analysis methods that we use for our colloid experiments, with particular emphasis on new tools designed and built for this work, including a simple device we invented to calibrate simultaneously the x, y, and z pixel-to-micrometer conversion factors for a confocal microscope and the miniature shear cell apparatus used for colloid deformation experiments on the microscope. For an excellent review of the confocal microscopy of colloids, see Ref. [54].

Following the description of the experiments, we describe the analytic methods we use to process the image data. Each experiment generates tens or hundreds of gigabytes of image data. The initial analysis of these data consists of locating the positions of the individual particles in each image stack, linking these positions into particle trajectories. Again, the description will focus on new software tools that were created for this work.

More specific details, including experimental procedures, can be found in Appendix A.

2.1 A THREE-DIMENSIONAL CALIBRATION DEVICE FOR THE CONFOCAL MICROSCOPE

Confocal microscopes are powerful tools, but they are only useful for accurate 3D measurements if the pixel-to-micrometer conversion factors are known accurately in all three dimensions. This is particularly difficult along the optical axis (z-direction), because scanning in this direction is performed by a different physical mechanism than in the x- and y-directions. It is essential to reconcile the two physically different x-y and z scanning mechanisms to ensure that distance measurements in all directions are consistent. Although the microscope software uses nominal pixel-to-micrometer conversion factors, we find that these can be incorrect by as much as 40% in the z-direction.
Depending on the microscope, the x-y images are taken either all at once by a CCD array or by a raster scan of the plane. We use Leica SP5 laser point-scanning confocal microscopes, which operate by the latter mechanism. Additionally, the Leica SP5 confocal microscopes that we use have two modes for scanning in z: so-called “z-wide,” in which the entire objective lens turret moves vertically, and “z-galvo,” in which the objective remains stationary and the sample stage moves. The z-galvo stage offers faster and more precise scan steps, but is limited to a travel of ±250 μm and a total sample weight of about 200 grams. The z-wide mode, on the other hand, uses a fixed sample stage. This mode does not limit the sample size or weight. However, acquisition is slower, and when using the z-wide mode we always observe a periodic stretching and compression in the z-direction with a period of roughly 7 μm. We can correct for the 7 μm striping during data processing, but when possible we use the z-galvo stage to avoid this problem. Example x-y and y-z cross-sections of a typical raw data image stack acquired using the z-galvo stage are shown in Figure 2.2.

We invented a simple device for calibrating the x, y, and z pixel-to-micrometer conversions for a confocal microscope. The device is constructed to hold a 2D reference pattern of known length scale at a precise angle on the microscope. By taking a 3D image of the angled pattern and comparing it to the known dimensions of the reference, we can simultaneously determine the pixel-to-micrometer conversion factors in all three dimensions.

A detailed schematic of the calibrator is shown in Figure 2.3. The device consists of a 30° angled wedge mounted on a base plate. There is a large opening in the base plate for viewing. The point of the wedge extends slightly over the opening. The wedge and base are both made of aluminum. The wedge was machined using sine bars to ensure the accuracy of the angle. A large-area, 0.17mm-thick coverslip, glued in place, entirely covers and seals the bottom of the device. This creates a viewing window and a reservoir that can be filled with a dyed fluid for fluorescence microscopy. The entire device weighs about 87 grams when filled.

We created a 2D reference pattern by etching a square array of dots into a 22x50x0.17mm glass slide, using standard microlithographic techniques. Each dot is separated by 1.63 μm from its
Figure 2.2: Horizontal (x-y) (top) and vertical (y-z) (bottom) slices through a typical confocal image stack. Because the z-direction (vertical) coincides with the optical axis, the image resolution is worse in this direction.
Figure 2.3: Schematic drawings of the calibrator. (a) Side view, with reference pattern slide (R) shown held in place on the 30° wedge by the metal bracket, and the microscope objective (M.O.) below the reference pattern. The inset shows a not-to-scale magnified view of the edge of the patterned slide close to – but not touching – the glass viewing window at the bottom of the calibrator. An example of a cross-sectional image plane is drawn as a dashed horizontal line. (b) Top view of the calibrator, without the reference pattern slide and holding bracket.
nearest neighbors. For imaging, the reference pattern is immersed in an index-matched fluid consisting of 37.2% water and 62.8% dimethyl sulfoxide (by volume) containing fluorescein-NaOH dye for fluorescence imaging. As a result, the pattern of dots appears dark against a bright background. The entire square pattern measures about 5 mm on each side.

To use the reference pattern with the calibrator, we cleaved the glass so that the reference pattern extended to the edge of the slide, and then mounted the slide pattern-side down on the device with a flat bracket. The slide is positioned so that the reference pattern is mechanically decoupled from the viewing window. This is easily achieved by cleaving the slide at a slight angle so that only a corner far from the reference pattern makes contact with the window. Figures 2.4 and 2.5 show examples of the assembled calibrator prior to use. Both of these examples show a backing slide being used to stabilize the patterned reference slide, but we find that this is not usually necessary.

![Figure 2.4: Assembled calibrator, perspective view from above. The reference patterns are clearly visible due to Bragg diffraction. A thicker glass slide can be used to reinforce the reference pattern slide, as in this example, but the reinforcement is usually not necessary.](image)

Once the patterned coverslip is in place, several milliliters of the dye solution are added so
Figure 2.5: Calibrator assembled without the large-area coverslip to seal the bottom, view from below.
that the array of dots is entirely submerged. Wetting usually also occurs between the coverslip and the 30° wedge, which has the effect of making the coverslip adhere tightly to the wedge. At this point, the holding bracket is no longer required; capillary forces alone hold the reference pattern to the calibrator. An example of the calibrator in use on the confocal microscope is shown in Figure 2.6.

![Figure 2.6: The same calibrator setup as in Figure 2.4, but now in use on the confocal microscope. The bottom edge of the reference pattern is submerged in the dye fluid. The bright spot above the center of the objective lens is from the dye fluorescing as the microscope acquires images.](image_url)

The entire device is set onto the sample stage of the confocal microscope, oriented so that the axes of the calibrator (shown in Figure 2.3) are aligned with the corresponding microscope image axes. The base plate of the calibrator fits easily onto the sample stage of the microscope, and is mechanically stable during imaging.

The reference pattern is imaged in three dimensions and a stack of cross-sectional images is generated that shows the angled reference pattern in 3D. In this orientation, the separation in the x-direction is reduced to \( \Delta x = 1.63 \, \mu m \times \cos 30° \), while the separation \( \Delta y = 1.63 \, \mu m \) between reference dots along the y-direction is unchanged. Adjacent columns of dots are separated in z by
\[ \Delta z = 1.63 \mu m \times \sin 30^\circ. \]

We show details of confocal images of the reference pattern in Figure 2.7, both (a) in a flat \((0^\circ)\) configuration to show the square pattern, and (b-c) two different cross sections of the pattern mounted at \(30^\circ\) on the calibrator. In this small example, the cross sections are separated by \(n = 36 \pm 1\) pixels in \(z\), corresponding to \(m = 5\) columns of dots. Hence, in this example, each pixel in \(z\) corresponds to \(m \Delta z/n = 0.113 \pm 0.003 \mu m/\text{pixel}\), which is about 10\% smaller than the conversion factor used by the microscope software, \(0.1259 \mu m/\text{pixel}\).

**Figure 2.7:** Details of the reference pattern imaged on the confocal microscope. (a) The square reference pattern at \(0^\circ\) (flat), surrounded by fluorescently-dyed fluid. (b) A cross-section through the reference pattern held at \(30^\circ\) by the calibrator in a pool of the same fluid. (c) The same field of view as (b), 5 rows of dots and 36 scan steps higher in \(z\). Bright regions in the images indicate the presence of the dyed fluid; dark sections indicate the glass of the patterned slide.

Usually, larger image stacks are used to achieve higher precision. Figure 2.8 shows \(z\)-direction calibration data obtained over a larger stack with scope and resolution chosen to match those of an upcoming experiment. In this example, we performed calibration measurements scanning both up and down the angled reference pattern, as inconsistency between the scanning directions could indicate mechanical instability. Within the measurement uncertainty, we find no difference between the two scanning directions, nor do we see any deviation from a straight line along the length of the scans.

By fitting a straight line to the data, we obtain the calibrated pixel-to-micrometer conversion factor. For the data obtained while scanning up, we find a conversion of \(0.1149 \pm 0.0002 \mu m/\text{pixel}\), and for scanning down we obtain \(0.1146 \pm 0.0002 \mu m/\text{pixel}\).
**Figure 2.8:** Measured calibrator dot positions over a larger range than the example of Figure 2.7. The calibrated pixel-to-micrometer conversion factor is the slope of a straight-line fit to these data. Horizontal error bars indicate a z-level measurement uncertainty of ±1 pixel, which translates into a ±0.0002 μm/pixel uncertainty in computing the calibrated conversion factor.
We have used this calibration device to determine the pixel-to-micrometer conversion for several confocal microscopes in our laboratories, varying the scanning method (sample motion versus objective lens motion), scan speed, and resolution (over a range of nominal pixel-to-micrometer conversion values). We find that the x-y conversion is usually accurate, but that the z conversion can vary significantly between different microscopes and between different scanning methods on the same microscope. We find that the z conversion can differ by as much as 40% from the nominal value used by the confocal microscope software. For a given microscope and scanning method, however, neither the scanning rate nor the resolution affect the result, and the calibrated conversion factors are usually consistent over many months. The source of the miscalibration remains unclear; as it is consistent over time, it seems likely to be a software problem rather than a hardware malfunction. However, since the microscope software often uses an incorrect pixel-to-micrometer conversion, an independent calibration is essential to ensure accuracy of results.
2.2 MINIATURE SHEAR CELL FOR DEFORMATION EXPERIMENTS

In order to perform deformation experiments on colloidal materials, we designed and built a new “miniature shear cell” (MSC) that has a number of advantages over the larger shear cell designs previously used by our group [63]. A detailed schematic is shown in Figure 2.9. The MSC weighs approximately 180g with a sample loaded on it, making it small and light enough to go on the z-galvo stage of the confocal microscope.

![Schematic of the miniature shear cell (MSC)](image)

**Figure 2.9:** Schematic of the miniature shear cell (MSC), drawn to scale. (A) shows an expanded view, with top views of the top and the base, aligned with the post as they would be when assembled. (B) shows a side view of the assembled MSC, including the piezoelectric actuator, the screw used to attach the post and adjust its height, and the template slide sealing the bottom of the reservoir.

The MSC is designed so that either a fully-assembled, filled sample cell can be mounted directly on it, or so that the MSC’s own built-in reservoir can be used as a sample cell directly integrated into the shear apparatus. In the latter configuration, a template slide is affixed directly...
to the base of the MSC using Norland optical adhesive, sealing the bottom of the reservoir to create the sample cell as in Figure 2.10. Then, the rest of the apparatus is assembled as in Figure 2.9. Most of our deformation experiments were performed using the integrated reservoir, with a BOATS amorphous template to ensure reliable glass formation (described in Section 3.2).

![Picture of Miniature shear cell (MSC) partially assembled on the confocal microscope, with base plate, template slide (visible sealing the sample reservoir at right), and piezoelectric actuator attached.](image)

**Figure 2.10:** Miniature shear cell (MSC) partially assembled on the confocal microscope, with base plate, template slide (visible sealing the sample reservoir at right), and piezoelectric actuator attached.

Shear is applied to the sample by means of a fine metal TEM grid 3 mm in diameter that is affixed to the bottom of the hollow post. The post is connected via the top of the MSC to a P-780 closed-loop piezoelectric actuator drive. The actuator is computer controlled via RS232 serial communication; a Matlab program handles all of the communication and control.

The piezoelectric actuator can achieve a maximum displacement of 80 μm with an accuracy of ±5 nm. A #2-56 screw enables simple vertical motion of the post; one-eighth of a complete turn corresponds to a vertical displacement of 57 micrometers. A large hole perpendicular to the long axis of the post ensures that the volume above and below the grid is easily accessible to the colloid.

For deformation experiments, the grid is positioned at a fixed height above the template and embedded firmly in dense colloidal material. This defines the shear gap. Another advantage of the MSC design is that the entire apparatus can be assembled prior to introducing the colloid, and
then the colloid structure can be formed directly in situ by sedimentation onto the template (see Chapter 3).

Figure 2.11: Miniature shear cell (MSC) assembled and awaiting a sample. After the colloid sample is loaded into the reservoir, the reservoir is carefully covered with parafilm to limit evaporation of the fluid. Because water evaporates more quickly than DMSO, any significant evaporation degrades the index match between the fluid and the particles.

Figure 2.11 shows the MSC fully assembled and ready for the reservoir to be filled with a sample. Figure 2.12 shows a low-magnification horizontal confocal image just prior to an experiment. The TEM grid and the outline of the template patterns are visible. During the deformation experiment, the grid is displaced parallel to the bottom of the sample cell, thus applying a bulk shear strain to the material in the gap. Simultaneously, we use the confocal microscope to capture high-resolution, three-dimensional images of the colloid structure as it evolves over time.
Figure 2.12: Large field-of-view image of the TEM grid in place over the template. The template pattern is printed in four sections, which are visible in the background. The honeycomb-like shadows result from residual lens oil on the underside of the template.
2.3 Iterative Particle Locating

Once the experiment is complete, the first analysis step is to convert each three-dimensional image into a list of particle locations. Standard algorithms exist for precise locating of spherical objects in 3D images. The development and implementation of these particle locating algorithms has been the subject of previous studies [14, 26, 41]. For all of the work described in this thesis, we use the publicly-available Matlab implementation described in Ref. [28] for basic particle locating. However, we find that we can improve on the accuracy and completeness of the particle locations by using a new iterative locating method that we developed.

The particle locating algorithm begins by bandpass-filtering the raw 3D image to remove high-frequency noise and subtract any overall intensity gradients in the background. Then, the feature finding software searches the filtered images for compact “bright spots” corresponding to the approximate particle size in pixels. The feature finding implementation we use adds an additional refinement step to increase the precision of the particle locations, as described in the reference, and those authors report location uncertainty of about 1/10 of a pixel, which corresponds to 15-20 nm in our experiments [28].

However, a single pass through the raw data usually fails to locate the particles perfectly, particularly for densely packed colloids. Some real particles are missed and some fictitious are found. While the locating algorithms can be tuned by adjusting the input parameters, there is a tradeoff between missing fewer particles and finding fewer fictitious particles. Optimizing the parameters such that neither type of error is too large results in a non-ideal data set with a some of each type of error.

To solve this problem, we developed an iterative particle locating algorithm that is able to find all of the particles in a sample with few or no double hits. For a typical data set, we estimate <0.2% of the particles are found twice, and these doubles can be subsequently consolidated in a straightforward way. The steps of this process are described below, and illustrated for an example image stack in Figure 2.13.

For the first pass through the data, we use the filtering and feature-finding software of Ref. [28] on the original image stacks in the standard way, but with parameters that deliberately err on the
side of missing particles to avoid as much as possible double-counting any particle. On this first pass, we usually locate roughly 95% of the particles in the sample, leaving the remaining 5% to be found in subsequent iterations. Figure 2.13(a) shows a small section of an x-y slice of raw data, (b) the same data after filtering, and (c) the locations of particles found in this slice marked as black + symbols overlaid on the raw data. Note that one particle in the middle was missed; this can be difficult to catch by eye but will become very obvious as the iterative procedure progresses.

Next, we generate a new “raw” image stack by using the particle coordinates we already have, combined with an estimate of the particle size in pixels, to delete the particles that have already been found from the original raw image. The result is a new image of residual raw data that shows only those particles that have not yet been found. An example is shown in Figure 2.13(d). The particles that were missed are usually fairly sparse in the new residual raw data, making them much easier for the software to locate than when they were surrounded by a dense packing of other particles.

We filter the residual raw image (Figure 2.13(e)) and locate the remaining particles using the same particle location settings as in the first pass, with the exception that we set a strict total intensity criterion for a bright spot to be considered a “real” particle. This cutoff is important because there may be some residual small bright spots in the image from particles that were already found but were not completely deleted from the original image. However, these regions are significantly smaller than the real particles, so there is no ambiguity in distinguishing them from real particles.

This process is repeated until no more particles are found. The second pass usually finds nearly all of the particles missed by the first iteration. Figure 2.13(f) shows all of the particles located in the first two passes, with the additional particles found in the second pass marked by white × symbols. For a typical image stack containing 50,000 particles, the iterative locating completes in four to six iterations.
Figure 2.13: A demonstration of iterative particle locating on a small section of an image stack. (a) An x-y slice through the raw data. (b) The same slice after filtering to remove noise and any overall background. (c) Particles found after the first locating pass, marked as black + symbols superimposed on the raw data. A particle close to the center was missed. (d) The same slice through the new raw residuals data after the already-found particles have been deleted from the raw image. The missed particle is now very easy to pick out. (e) The filtered residual data. (f) The same as (e), but with white × symbols added for particles found in the second iteration.
2.4 Basic Structural Analyses

Once we have the locations of all of the particles contained in an image stack, there are several analyses that we regularly use to characterize the static structure of the colloid.

2.4.1 Radial Distribution Function, \( g(r) \), and Particle Size Dispersion

The radial distribution function (RDF) or pair correlation function, \( g(r) \), plots the probability of finding a particle at a given radial distance, \( R \), away from any other particle. We calculate the RDF of a colloid by first measuring the interparticle separations between all pairs of particles (carefully avoiding the edges of the image volume), and then plotting the histogram of these separations divided by \( R^2 \). The normalization by \( R^2 \) is required because the absolute number of neighbors at a given radial distance \( R \) will, in general, increase as the surface area of a sphere of radius \( R \). It is the usual convention to further normalize the overall amplitude so that the RDF goes to 1 for large \( R \). Examples from our work of measured radial distribution functions for an FCC colloidal crystal and a colloidal glass are shown in Figures 2.14 and 2.15. The latter figure also shows the data from Finney’s random close-packing experiment using perfectly monodisperse quarter-inch steel ball bearings [25], rescaled to have the same sphere size and number of particles as our colloid data. We find remarkable agreement between Finney’s experiment and ours, although the greater polydispersity of our colloids is evident in the breadth of our peaks compared with Finney’s.

As demonstrated in Figures 2.14 and 2.15, the size and position of the peaks in the radial distribution yields information about the large scale structure of the material. The first peak provides information about the particles and their nearest neighbors. For the analyses in this work, we will define a particle’s nearest neighbors as any particle that is closer than the first minimum of \( g(r) \).

In a densely-packed system, the location of the first peak is the mean particle diameter. According to the manufacturer, our silica particles have an average diameter \( 2R = 1.55 \mu \text{m} \), which agrees well with our RDF measurements from our densest samples. If there is no uncertainty in the particle positions, the shape of the first peak is simply the convolution of the distribution of
**Figure 2.14:** The measured RDF of an FCC colloidal single crystal. Also shown are the peak positions and heights for an ideal FCC crystal with the same first-neighbor distance [55].

**Figure 2.15:** (black line and dots) The measured RDF of a colloidal glass formed by sedimentation onto a BOATS amorphous template (see Section 3.3). (red dashed line) The measured RDF from Finney’s random close-packing experiment using perfectly monodisperse quarter-inch steel ball bearings [25], rescaled to have the same sphere size and number of particles as our colloid data. The colloid data peaks are wider due to the small dispersion of particle sizes.
particle radii with itself. Thus, the width of the first peak can be used to make a measurement of the particle polydispersity. In the case where there is some uncertainty in the particle locations, we can at least put an upper bound on the size dispersion.

If we assume that the particle radii are normally distributed, then the first peak of \( g(r) \) will also have a Gaussian form, making the calculation of polydispersity straightforward. The polydispersity measured in this way for our particles equals the standard deviation of the distribution of the particle radii divided by the mean radius, \( \sigma / \bar{R} = 0.035 \), which corresponds to \( \sigma = 0.054 \, \mu m \). The average volume of the particles, \( \Omega \), is derived from the third moment of the distribution function. For a normal distribution, this gives \( \bar{\Omega} = \frac{\pi}{6} \left[ (2\bar{R})^3 + 3(2\bar{R}) \sigma^2 \right] = 1.96 \, \mu m^3 \), which is slightly larger than \( \frac{\pi}{6} (2\bar{R})^3 = 1.95 \, \mu m^3 \). This effect becomes more significant as the polydispersity increases. Any calculations involving the average particle volume must take this into account.

### 2.4.2 Voronoi volume, \( V \)

The Voronoi volume of any individual particle in a collection of monodisperse particles is all of the space that is closer to the center of that particle than to any other particle. Computing Voronoi volumes is a way of dividing space among the particles, and the sum of all of the individual Voronoi volumes must add up to the entire sample volume, \( V_{total} \). In other words, the average Voronoi volume is given by

\[
V = \left( \frac{\sum_{i=1}^{N} V_i}{N} \right) = \frac{V_{total}}{N} = \frac{1}{n},
\]

where \( N \) is the total number of particles and \( n \) is the number density of particles. Thus, the inverse of an individual particle’s Voronoi volume is a direct measure of the local density at that particle.

We compute the Voronoi tessellation of the sample and the Voronoi volume for every particle using standard Matlab functions, but with the following constraint: any particle whose Voronoi cell would close outside of the measured sample volume, or within 1 \( \mu m \) of the edge of the measured volume, has its Voronoi volume set to zero. These particles are too close to the edge to be sure that we can measure their position and the positions of their neighbors accurately, and they may indeed be missing neighbors that were not included in the imaged volume. Setting the Voronoi volumes of the edge particles to zero additionally serves as an identifier for these particles so that they can
be excluded from future analyses as needed.

Note that for polydisperse samples, the above definition of Voronoi volume is no longer appropriate. A new definition that takes into account the particle size is required. There are numerous ways to define a polydisperse Voronoi tessellation. These include Voronoi S regions, where the boundaries between the regions are defined as being equidistant from the surfaces of the spheres rather than from their centers, and the radical plane construction, in which the space that belongs to the Voronoi cell of particle \( i \) with radius \( r_i \) is defined as all points whose distance to \( i \), \( d_i \) satisfies the following relation [60]:

\[
d_i^2 - r_i^2 < d_j^2 - r_j^2 \quad \forall \, j \neq i
\]  

The radical plane construction is somewhat simpler than the the S region construction because the boundaries between Voronoi cells are flat planes, and the neighbor connectivity in the radical plane construction is identical to what it would have been with the traditional definition of Voronoi volumes [60]. These are both useful properties for some calculations, particularly in calculating the individual particle free volume as described in Section 2.4.4.

The dual of the Voronoi tessellation is the Delaunay tessellation, which divides all space into tetrahedral simplices (in 3D) whose vertices are particle centers and whose edges connect nearest neighbors.

### 2.4.3 Volume fraction, \( \phi \)

The overall volume fraction, \( \phi \), of a colloid is defined as the total volume occupied by the particles divided by the total sample volume, \( V_{\text{total}} \), and is related to the average Voronoi volume, \( V \), by the average particle volume, \( \bar{V} \):

\[
\phi = \frac{N \bar{\Omega}}{V_{\text{total}}} = \frac{\bar{\Omega}}{V}
\]  

In our samples, we measure the volume fraction by dividing the average particle volume by the average Voronoi volume, excluding particles near the edge of the image volume and taking into account the polydispersity of the particles.
2.4.4 Free volume

For any two hard spheres, their centers can never be closer than the sum of their radii. From the perspective of any individual particle, this creates an impenetrable “exclusion sphere” around each of its neighbors. If these neighbors are packed tightly around the particle of interest, it may have little or no “wiggle room” in which it could move before colliding with one of its neighbors. On the other hand, if the neighbors are packed more loosely, the particle may have significant potential mobility.

The free volume of a particle is defined as precisely that region of space in which the particle’s center can move given the constraints imposed by the present locations of its neighbors. Unlike the Voronoi volume and volume fraction, which are measures only of the particle density, the free volume provides additional information about local structure and whether the particle can actually access the space around it. Free volume theory was proposed by Turnbull to describe self-diffusion in glasses \[68\], and this theory was later extended by Spaepen to explain how shear defects might occur during plastic deformation of glasses \[64\].

As an example, we show a disordered collection of monodisperse hard disks in Figure 2.16(a). The center of each disk is marked by a white dot. Because these are monodisperse disks, the neighboring particles’ centers can not approach any closer to each other than twice the disk radius, \(2R\), as shown in Figure 2.16(b). The motion of each particle is constrained by those around it. By superimposing the exclusion disks of all of the neighbors of a given particle as in Figure 2.16(c), the free volume of that particle becomes readily apparent as all of the space around the particle center that is not covered by any exclusion disk. In Figure 2.16(d), the exclusion disks for all of the particles are shown so that the free volume regions for each particle are apparent. Some particles have very little free volume, while others have much more volume in which they may move.

We developed two ways of calculating the free volume of every particle in a hard-sphere colloid. The first is a numerical calculation in which we discretize space and reconstruct the excluded and free volume around each particle. Then, starting from the particle’s center, the software maps out the free volume by exploring space one voxel at a time, never examining one voxel more than
Figure 2.16: A schematic of monodisperse hard disks illustrating free volume (or free area, in this 2D case). (a) A collection of hard disks, whose centers are marked with a white dot. As they are not close-packed, they are free to move until they run into their neighbors. (b) No particle center can approach closer than twice a disk radius, \(2R\), to another disk. This defines an impenetrable region, or exclusion disk, that limits the free motion of the other particles. (c) The exclusion disks of all the neighbors of a particular particle. The space around the particle’s center that is not covered by an exclusion disk is accessible to the particle. This is its free volume region. (d) All exclusion disks are shown, illustrating the variation in size and shape of the free volume regions for each particle.
twice. Although developed independently, the approach is similar to that of Ref. \[19\]; however, our approach differs in that it makes no approximations at the edges of the free region and is robust even for very complicated free volume shapes.

We used this method to compute the free volume for every particle in a colloidal glass during deformation. Interestingly, although free volume is not strictly conserved, the average free volume of the entire sample is very nearly constant. In Figure 2.17, we show the free volume distributions for a series of time steps during deformation as well as the mean distribution over all time, plotted on a semilog scale. Interestingly, the free volume distribution appears to be fit well by two exponentials, consistent with Turnbull’s prediction that the free volume in a glass should be exponentially distributed \[68\]. Further results of this study are reported in Section 5.7.

The numerical free volume calculation is, in principle, accurate to arbitrary precision, as the discretization into voxels can be done at any resolution. However, the higher the precision, the slower the calculation, and so we also wrote software to compute the free volume of an arbitrary arrangement of hard spheres analytically using the algorithm invented by Sastry et al. \[60\]. The problem of analytically computing the volume of the complicated shape left over after a union of exclusion spheres is difficult. However, Sastry’s algorithm uses the geometry of the Voronoi and Delaunay tesselations to break down the problem. We describe the method very briefly here, but refer the reader to the original paper for a very thorough discussion of the algorithm.

To calculate the free volume for a given particle, its coordinates are removed from the list of particles, and the Voronoi and Delaunay tesselations are computed with that particle missing. By definition, either tesselation fills all of space, and so the entire free volume region of the particle of interest must be contained within a union of Delaunay simplices. Further, the Delaunay simplices that contain part of the contiguous free volume region can be identified as those whose corresponding Voronoi vertices are also in the free region and are connected by Voronoi edges that are also entirely in the free region (the condition for a contiguous region). Starting from the Voronoi vertex corresponding to the Delaunay simplex that contains the particle’s original coordinates, we identify those simplices that contain parts of a contiguous free volume region by following the Voronoi edges from vertex to vertex until they cross into an excluded region.
Figure 2.17: The free volume distribution over time (colored points) and the mean for all times (black line). Although there are local fluctuations in the free volume, the total free volume and distribution of free volumes is fairly constant. The fact that the free volume distribution appears straight (in two regions) on a semilog scale is consistent with the predictions of Turnbull and Cohen [68].
Once these simplices containing the free volume are identified, they are further subdivided into 24 subsimplices, each of which is a right tetrahedron that intersects one and only one exclusion sphere. Now the geometry is easy; the free volume contributed by each of the subsimplices is straightforward to calculate. Thus, the calculation is reduced to adding up the contributions from all of the subsimplices. Unlike the numerical calculation, this method runs reasonably quickly even for large colloid samples, and yields an exact result.

Although in our case we are working with monodisperse hard spheres, the algorithm is completely general for polydisperse hard spheres, as long as the size of each individual sphere is known. We implemented the software using the radical plane Voronoi construction described above so that it can be used to compute the free volume of any collection of spheres. In the case of monodisperse spheres, the radical plane construction reduces to the standard Voronoi definition.

2.5 Particle tracking

To study the dynamics of a colloidal crystal or glass, we need the particle positions over time. Each image stack from the confocal microscope corresponds to a snapshot of the system in time. Acquiring many stacks over time enables us to observe individual particle trajectories over time for each particle contained within the image volume. These trajectories form the basis of many of the analyses in the chapters to follow. The final step in the basic data analysis of a dynamics experiment is to link the particle locations into trajectories over time. Tracking the particles requires different software from that used in the particle locating step.

We wrote new particle tracking software in Matlab. The software takes the particle coordinate lists for two consecutive times, converts the coordinates from pixels to micrometers according to a user-specified conversion factor (see Section 2.1 above for a description of the confocal calibrator, or Section A.4 for the calibration procedures), and then compares the particle locations between the two times to identify each individual particle at both times. To determine which particle is which over time, the software matches particles based on the simple principle of minimizing the displacement. Although expressed differently, this algorithm is mathematically identical to that described in Ref. [28].
If a particle has no match at the later time, it is likely that it has passed outside of the image volume, and so its trajectory may end before the end of the experiment. Similarly, particles may move into the image volume, and these will have trajectories that start some time after the beginning of the experiment. During the initial analysis, we keep track of all located particles, regardless of the length of their trajectories. However, we may subsequently remove from the data set particles with only a few time points in their trajectories. Such particles are usually located near the edge of the image volume where the locating is noisier. Furthermore, most dynamic analysis cannot be performed on particles with short-lived trajectories.
Large, defect-free crystals and slow-sedimented glasses: Complex structures from simple spheres

Earlier, we introduced the importance of developing an understanding of how colloidal crystals and glasses form. Here, we discuss the roles of sedimentation flux and substrate pattern boundary conditions in controlling structure formation for both hard-sphere colloidal crystals and glasses by epitaxial growth onto both patterned and flat substrates.
3.1 Rapid growth of large, defect-free colloidal crystals by centrifugation

A quick, convenient method for growing large, perfect crystals is desirable. Common colloidal crystal growth methods require very slow growth rates to avoid formation of an amorphous sediment and often produce structures with a high number of defects [16,17,24,33,38,40,75]. Some of the difficulty can be overcome by using a template, a patterned substrate that directs the initial crystal growth. Templates can be used both in convective assembly, which has produced crystals quickly but of limited thickness [40], and in sedimentation, which can produce large crystals but only at slow growth rates to avoid defects and amorphization [24,33,57,69]. A technique to grow quickly large, defect-free colloidal single crystals is essential for their further development as useful materials.

Here, we demonstrate rapid growth of large, hard-sphere, face-centered cubic (FCC) colloidal single crystals by centrifugation up to 3000 g onto an FCC (100) template. We never observe an amorphous sediment for this growth orientation, even at 3000 g where the crystal grows at \( \sim 10 \, \mu m/s \). By contrast, high-flux deposition onto other substrates results in a crossover to an amorphous sediment due to stacking degeneracy. On the (100) template, the single crystals can be grown defect-free; following growth, however, extended defects can develop depending on the total crystal thickness and the template lattice spacing. This defect nucleation and growth process is discussed in details in Chapter 4. Our results provide a scalable technique for rapidly producing arbitrarily large colloidal crystals free from extended defects and suggest a mechanism for creating other colloidal structures that can be described by deterministic layering.

3.1.1 Experiments

Initially, the colloidal suspension has a uniform particle volume fraction, \( \phi_0 \). Over time, the particles sediment due to their difference in density with the fluid phase, \( \Delta \rho = 0.94 \, g/cm^3 \). In our experiments, we grow dense colloidal structures by sedimentation either under gravity or in a centrifuge, and subsequently observe the resulting structure in a confocal microscope. Under gravity, the sedimentation velocity is \( u_s = 0.75 \, \mu m/s = 2.7 \, mm/h \). Under centrifugation, this velocity increases linearly with the centrifugal acceleration, since even at 3000 g the Reynolds number remains

39
low. The Peclet number, which is the ratio of the rate of sedimentation to that of diffusion, is given by $Pe = \Delta \rho g_s \bar{R}^4 / (k_B T)$, where $g_s$ is the acceleration during sedimentation, $\bar{R}$ is the mean particle radius, and $k_B T$ is the thermal energy. At $g_s = 1g$ and room temperature, $Pe = 0.83$, so that the rates of sedimentation and diffusion are similar. We test the effects of deposition flux on crystal formation by varying $g_s$ from 25g to 3000g for $\phi_0 = 0.29\%$ and by varying $\phi_0$ up to 3\% for sedimentation at 1g. In all cases, sedimentation is complete prior to imaging.

The sample cell consists of a metal tube \sim 1 cm in diameter, glued onto a 0.17-mm-thick glass coverslip. To make crystal templates in the coverslips, we use photolithography to mask the desired pattern and reactive ion etch directly into the bare glass. The resulting template is an array of cylindrical holes approximately 500 nm in depth, with a diameter slightly less than that of the colloidal particles. We fabricate templates to match the three densest crystal planes of the FCC lattice: (111), (100), and (110), shown in Figure 3.1.

Hexagonal close-packed planes can occupy three distinct stacking positions, as shown in Figure 3.1a, and are designated as A, B, and C. In face-centered cubic (FCC) crystals they occur in the sequence $ABCABC...$ and are (111) planes. In hexagonal close-packed (HCP) crystals they occur in the sequence $ABABAB...$ and are (0002) planes. Hard-sphere FCC and HCP crystals have the same density. Because for hard spheres the B and C stacking positions are energetically degenerate on the A-layer of the (111) plane, growth on such templates usually does not produce a pure FCC crystal, but rather a random hexagonal close-packed (RHCP) sequence of A, B, and C stacking positions.

(111) crystal planes have the highest in-plane density; (100) and (110) crystal planes have, respectively, 13\% and 39\% lower in-plane density than (111). On all templates the nearest-neighbor distance is 1.63 \mu m \cite{61}. Consequently, all templates produce FCC crystals that differ only in orientation. Each patterned template measures a few millimeters on each side, and is surrounded in the sample cell by flat, unetched glass. The entire sample cell can be spun in an Eppendorf Centrifuge 5702 RH, which produces a maximum centrifugal acceleration of $g_s = 3000g$.

After deposition, all samples are imaged from below in three dimensions using a Leica SP5 point-scanning confocal microscope. Because the fluorescein-NaOH dye is in the fluid phase, the
Figure 3.1: Schematic of stacking sequences for (a) (111), (b) (100), and (c) (110) planes in an FCC crystal. The circles show the particle size to scale in relation to the template lattice parameter. In the (111) orientation, the $B$ and $C$ stacking positions are degenerate on the $A$-layer. All of these templates generate FCC crystals that differ only in orientation.

particles appear dark against a bright background. All image stacks are taken far from the edges of the template and from the sample cell walls to avoid possible boundary effects. We locate the particle centers in three dimensions using standard particle location software.

3.1.2 Results

Using a (100) crystal template, we obtain FCC single crystals all the way to the top of the sediment for all $g_s$ and $\phi_0$. The crystals are grown 13-70 $\mu$m thick, limited only by the total number of particles placed in the sample cell. By increasing $\phi_0$ we grow taller crystals; our tallest to date is 100 $\mu$m thick, grown at 100$g$ from $\phi_0 = 0.44\%$. Surprisingly, we never observe an amorphous sediment above the (100) template, even at 3000$g$ when the crystal grows at $\sim 10$ $\mu$m/s. A horizontal confocal image slice through the 18th layer of particles in a perfect FCC crystal grown at 3000$g$ on a (100) template is shown in Figure 3.2.

Deposition onto other substrates can result in a crossover from a crystalline to amorphous sediment depending on the deposition conditions. We refer to FCC, HCP, and RHCP ordered structures equally as “crystals” to distinguish them from amorphous packings, even though RHCP is not strictly periodic due to its $ABC$ stacking disorder. We define amorphous or disordered
Figure 3.2: Horizontal confocal image of Layer 18 of a perfect FCC colloidal crystal grown by centrifugation onto a (100) template at 3000g with initial volume fraction $\phi_0 = 0.29\%$. The image has lateral dimensions of 155.0 $\mu$m.
packings as dense, isotropic structures that lack long-range periodicity.

On a (111) template, we obtain crystals in sedimentation at 1g with $\phi_0 = 0.29\%$, but under centrifugation conditions the same initial volume fraction produces structures that rapidly degrade into an amorphous sediment. The template constrains the first layer of particles to form a perfect crystal plane. Under centrifugation conditions, after the first layer we next observe a few RHCP layers at the bottom of the sediment; then, crossover to amorphous begins. Patches of particles settle into a stacking position different from their surroundings and form a local stacking fault. The number of ordered layers deposited before this crossover begins varies; sometimes, significant local stacking faults occur as early as the second layer. In subsequent layers, the boundaries between these patches and the surrounding crystal become sources of disorder. Once disorder is established locally, everything above it is amorphous and the disordered region spreads laterally as the sediment accumulates. Ultimately, the amorphous sediment spreads throughout the sample.

A typical layer-by-layer sequence at the onset of crystalline-to-amorphous crossover for a sample with $\phi_0 = 0.29\%$ centrifuged at 100g onto a (111) template is shown in Figure 3.3. In this example, the first 7 layers of the crystal have the RHCP stacking sequence ACACABC, and significant local faulting begins around layer 8. By layer 23 the crystal has all but disappeared.

We also tested the effect of increased initial volume fraction during sedimentation at 1g onto the (111) template. For $\phi_0 = 2\%$, we observe crossover to the amorphous state initiated by local stacking faults, as with the centrifuged samples. However, we also see some homogeneous nucleation of small RHCP crystallites in the bulk amorphous material. For $\phi_0 \geq 3\%$ at 1g we observe crossover to amorphous but no subsequent crystal nucleation.

Deposition onto a flat, featureless surface produces a sediment of which the first layer is polycrystalline with a predominantly (111) texture. The (111) plane is the densest packing of spheres in two dimensions and hence favored as the first layer structure, but occasional (100) domains exist as well. For $\phi_0 = 0.29\%$, sedimentation at 1g onto a flat substrate results in a polycrystalline RHCP structure. For $\phi_0 = 3\%$ at 1g, however, the (111) texture rapidly degrades to an amorphous sediment by local stacking faults in the same way as the (111) templated crystals,
Figure 3.3: Layer-by-layer horizontal confocal image slices showing the onset of crystalline-amorphous crossover in a colloid sample centrifuged at 100g onto a (111) template from an initial volume fraction $\phi_0 = 0.29\%$. Labels indicate the stacking positions of the particles relative to Layer 1 which is templated in the A position (see Figure 3.1). Each image has lateral dimensions of 155.0 $\mu$m. Consecutive layers are separated by 1.2 $\mu$m.
with additional disorder initiated at grain boundaries. Centrifuging a colloid with $\phi_0 = 0.29\%$ onto a flat substrate results in a noticeably higher occurrence of (100) texture in the first layer, even though the (111) texture still dominates. Although these centrifuged samples also cross over to forming an amorphous sediment, the native (100) regions are remarkably robust against disordering, and persist vertically until they are displaced by spreading adjacent disordered regions. The first and tenth particle layers of such a sample are shown in Figure 3.4.

![Figure 3.4](image)

**Figure 3.4:** (left) First layer of an untemplated colloidal polycrystal grown by centrifuging a colloid with $\phi_0 = 0.29\%$ on a flat surface at 100g, showing spontaneously occurring (111) and (100) texture. (right) The same area at Layer 10, where crossover to amorphous is proceeding both from the original grain boundaries and by local stacking faults in the (111) regions. These images are not representative of the relative amounts of (111) and (100) texture in the overall sample, of which less than 10% is (100). Each image has lateral dimensions of 77.5 μm.

Deposition onto (110) templates produces FCC crystals at 1g and low $\phi_0$. However, (110) is a significantly less dense crystal plane and never appears as a spontaneously occurring texture on a flat surface. With centrifugation or high $\phi_0$ we observe degradation of order above the (110) templates by insertion of stacking fault planes along the direction where the pattern is less dense, perpendicular to the longer in-plane neighbor separation. This local disordering ultimately leads to the formation of an amorphous sediment.

Although we usually remove the small population of 800-nm-diameter particles that exist
in the raw particle stock, we see interesting effects when these are left in. For crystals grown at 1g we see only a small number of these particles in the interior of the crystal as substitutional impurities. Instead, most of them are excluded from the crystal as it grows, and are concentrated in the colloidal liquid fan just above the sediment. In centrifuged crystals, however, many of the small particles are trapped interstitially in the octahedral holes of the FCC crystal, while the number that occupy lattice sites remains roughly constant. This trapping process could extend the usefulness of colloidal crystals as experimental models to such phenomena as impurity trapping during rapid solidification of a melt front [67]. This result also suggests that centrifugation of carefully designed colloids having a bimodal size dispersion may produce interesting new crystals, a possibility that we are currently investigating.

3.1.3 Role of critical flux and substrate pattern in determining crystal-to-amorphous crossover

We can quantitatively characterize all experiments by a dimensionless particle flux, defined as \( \phi_0 Pe \), where \( \phi_0 \) is the initial volume fraction of the particles and \( Pe = \Delta \rho g a R^4 / (k_B T) \) is the Peclet number of the particles as described above [33]. This quantity accounts for the effects of particle concentration, sedimentation velocity, and thermal equilibration, and enables useful comparison between experiments with different particle types and fluid phase compositions. Our experimental results for deposition onto (100), flat, (111), and (110) substrates are compared with the results of Davis et al. [17] and Hoogenboom et al. [33] for deposition onto flat, featureless substrates in Table 3.1. We summarize the resulting structures for the various deposition fluxes and substrate patterns in Figure 3.5, in which solid symbols indicate a crystalline sediment and open symbols indicate an amorphous one. That Davis et al.’s amorphous result occurs at an anomalously low dimensionless flux compared with other data likely stems from the 6% polydispersity of their colloidal particles.

For our samples with polydispersity <3.5%, we observe crystalline-amorphous crossover above \( \phi_0 Pe \approx 0.02 \) in all cases except for growth on the (100) template, which always produces single crystals. On flat substrates, where a (111) texture dominates, and on (111) templates, hard-sphere
Figure 3.5: Overview of the structures obtained as a function of substrate type and dimensionless flux. Legend: ● This work, crystalline; ○ This work, amorphous; ■ Hoogenboom et al., crystalline [33]; □ Hoogenboom et al., amorphous [33]; ▲ Davis et al., crystalline [17]; △ Davis et al., amorphous [17].
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<th>$\phi_0$</th>
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Table 3.1: Sedimentation results sorted by their dimensionless flux, $\phi_0Pe$, where $\phi_0$ is the initial volume fraction of the dispersion and $Pe = \Delta \rho g_s R^4 / (k_B T)$ is the Peclet number of the particles. Dimensionless flux values for Hoogenboom et al. [33] are computed from $\phi_0$ and $Pe$ values reported in that reference; values for Davis et al. [17] are calculated based on particle and fluid phase properties reported in that work.

crystal growth suffers from a stacking degeneracy, as shown in Figure 3.1. Starting from a layer in which the particles occupy $A$-positions, the next layer of particles has a choice of two stacking positions ($B$ or $C$) that are distinct but energetically degenerate for hard spheres. As a result, local stacking faults form easily, and the edges of the faults initiate the onset of disorder. Once this disorder is established at high dimensionless flux, a crystalline structure cannot be recovered and the amorphous region spreads upwards and outwards as deposition continues.

By contrast, the (100) template has no stacking degeneracy, and we observe no amorphous crossover at least up to a dimensionless flux of $\phi_0Pe = 7.2$, roughly 500 times faster than the limiting rate on other substrates. We expect that much higher growth rates are possible. For
growth in this orientation, each layer of particles precisely determines the center locations of the subsequent layer, as shown in Figure 3.1. We refer to this as deterministic layering; each layer precisely fixes the next. As there is no mechanism for the onset of disorder, successive layers can nucleate randomly while the overall crystal remains perfect. Furthermore, the (100) plane is quite dense and thus resistant to insertion of interstitial particles. In principle, (110) also has no stacking degeneracy, but because it is significantly less dense than (100) or (111), it does not sufficiently constrain the incoming particles in-plane. As a result, growth on a (110) template is susceptible to local disordering by insertion of additional particles and consequently to crossover to an amorphous sediment at high dimensionless flux.

A similar orientation-dependence of defect structure and amorphous crossover at high growth rates has been observed in atomic crystals that have a low stacking fault energy, such as silicon [15]. In pulsed-laser melting and regrowth experiments of substrates with different orientations, a maximum growth rate is observed above which crossover to an amorphous solid occurs. Below this critical velocity, growth in the [001] direction forms defect-free crystals, while rapid growth in the [111] direction results in significant local stacking faults, the density of which increases with growth velocity. These experiments also point to the possible use of colloidal materials as kinetic models for non-equilibrium materials.

3.2 CONTROLLED GLASS FORMATION BY HIGH-FLUX SEDIMENTATION ONTO AMORPHOUS TEMPLATES

While the previous section focused on crystal formation, sometimes amorphous structures are desired. Studies of the colloidal glass transition [34], structural relaxation and aging of glasses [8,73], and deformation of amorphous materials [5,63] require consistent, reliable production of amorphous structures.

Traditionally, colloidal glasses have been made by centrifugation at very high flux, far above the minimum flux required for amorphous crossover. This method has a number of drawbacks. It requires either that the sample cell can fit in a centrifuge and be strong enough to withstand centrifugation or that the glass be centrifuged in some other container and then transferred to the
experimental setup, thus subjecting the glass to large and uncontrolled deformations prior to the experiment. Also, in most glassy systems the quench rate during glass formation effects the final glass structure, and so we expect the deposition flux to have a similar effect on the final structure of the glass. The ability to form colloidal glass structures over a large range of fluxes could be useful in achieving a variety of glass structures.

Toward this end, and using our understanding of the crystal-amorphous crossover, we have designed amorphous templates that produce stable, monodisperse, hard-sphere colloidal glasses without centrifugation. We designed and tested two different amorphous template designs, shown in Figure 3.6.

The first template design, the “Frans Spaepen Pattern” (FSP), enforces maximum (111) $B/C$ stacking disorder in the first layer (similar to the macroscopic experiment described in [55]). This guarantees that the crystalline-amorphous crossover process begins as completely as possible from the very first layer. Although all the particles in the first layer sit at the same depth on a purely FSP template, ordering in the $z$-direction disappears within a few layers, and the sample becomes fully amorphous.

The second amorphous template design is the “Based on a True Story” (BOATS) template. This template was based on a reconstruction of a cross section through an actual colloidal glass sample that had been formed by centrifugation. The BOATS template has the effect of creating disorder on the length scale of the particles, which prevents ordering in any dimension from the very first layer.

Both of these amorphous templates work well for forming colloidal glasses by sedimentation, as long as the dimensionless flux is above the critical flux to ensure crossover. In our colloid system, this can be achieved at $1g$ by starting with $\phi_0 \geq 3\%$, or from a lower initial volume fraction by centrifugation.

Other methods of creating a substrate with roughness on the length scale of the particle size can also work, but the FSP and BOATS templates have the advantage that the lithographic process by which they are made is robust and repeatable, and produces templates that are etched directly into the glass coverslip that will form the bottom of the sample cell. We have also tried other
Figure 3.6: The two amorphous template designs created for this work. (a) The “Frans Spaepen Pattern” (FSP) template, which enforces complete B/C stacking disorder in the very first layer of sediment. (b) The “Based on a True Story” (BOATS) template, which is a reconstruction of a cross section through an actual colloidal glass sample that had been formed by centrifugation. The BOATS template creates disorder on the length scale of the particles, preventing ordering in any direction from the very first layer.
methods including spin-coating a layer of slightly larger, highly polydisperse silica spheres glued down with a thin layer of PMMA, and simply sandblasting the coverslip to achieve a rough surface. Examples of these sorts of rough substrates are shown in Figure 3.7. Both of these roughening techniques can cause imaging problems, as in the first case the PMMA is not index-matched to the rest of the system and so casts shadows in the confocal images wherever a small clump of glue forms, and the sharp edges in the sandblasted substrate also tend to scatter light because of the slight index mismatch between the coverslip and the water/DMSO fluid mixture.

3.2.1 Effect of deposition flux on glass density and amorphous crossover

In most glass-forming systems, the final structure of the glass depends on the quench rate at which the solid glass is formed from a liquid melt \( \phi_0 \). Atomic glasses formed at higher quench rates tend to have a lower density than glasses formed more slowly. We expect that the same should be true for colloidal glasses, and indeed find that the glasses formed at dimensionless fluxes just above the critical crossover flux (e.g. \( \phi_0 = 3.5\% \text{ at } 1g \)) have high final volume fractions, usually 62-63\%, close to the maximum of random close packing (64\%). By contrast, glasses formed at much higher flux (e.g. by centrifugation at \( \sim 2000g \) from somewhat lower initial volume fractions, \( \phi_0 \approx 0.3\% \)) usually have final volume fractions close to that of the glass transition, \( \phi = 58\% \). Unfortunately, the results of a preliminary study to elucidate a more detailed relationship between the deposition flux and the resulting glass density were inconclusive.

As part of this study, we examined the first-layer grain structure for deposition onto flat surfaces at varying flux. While the first layer on a flat surface has a predominantly (111) texture, as mentioned above, the typical 2D grain size decreases with increasing deposition flux. Since grain boundaries also contribute to the crystalline-amorphous crossover, when the grains become small disordering at the boundaries dominates over the \( B/C \) stacking disorder crossover mechanism, and this results in a faster crossover with fewer crystalline layers at high deposition flux.
Figure 3.7: Two alternative methods of creating a rough substrate on which to form a glass. (a) A layer of 3-μm-average-diameter, highly polydisperse silica spheres glued to a coverslip with a thin layer of PMMA polymer. (b) A coverslip that has been sandblasted. Both of these roughening techniques work for creating colloidal glasses, but cause imaging problems in the confocal microscope and so are not ideal for our experiments.
3.2.2 Compound structures: Amorphous-crystalline interface

Our understanding of the effects of boundary conditions and flux on the resulting structure reveal that there are fluxes at which the resulting structure is determined only by the boundary conditions. This opens up the possibility of creating more complex, hybrid structures that include interfaces between different phases.

We have designed a template that juxtaposes a perfect FCC crystal side-by-side with a glass, creating a nearly-vertical crystal-amorphous interface. As the colloid is deposited onto this template and the interface structure grows, the interface line moves toward the crystalline side, so that the glass takes over more and more of the volume, similar to the spread of the amorphous regions we observed during crystal-amorphous crossover on non-deterministic templates. The interface is approximately a close-packed (111) crystal plane, but varies somewhat in position and is not a single plane. The template pattern and examples of horizontal cross-sections at various heights are shown in Figure 3.8.

One intriguing feature of the amorphous-crystalline interface is that within about 100 μm of the interface, the particle density of the amorphous sediment shows a periodic fluctuation with height. This fluctuation has exactly the same period as the (100) crystal plane spacing in the adjacent crystalline region, but is precisely 180° out of phase with the crystal.

The density of particle centers as a function of distance from the template near the interface is plotted in Figure 3.9 separately for the crystal and the glass at least 20 μm laterally away from the interface on each side. Particles on both sides of the interface first appear at the same height, which is expected because the template pattern fixes the first layer of particles. As expected, on the crystal side, the particles lay in planes with a spacing equal to $1/\sqrt{2}$ times the lattice spacing set by the template, with no particle centers in between layers.

On the amorphous side, after the first layer, the particle center positions become more disordered as they can take a range of positions. Far from the interface, after a few micrometers there is no longer any detectable layering; the frequency of centers versus height is roughly constant. However, near the interface, the density of particle centers in the glass versus height establishes
Figure 3.8: Confocal microscope images of a colloid structure grown on the amorphous-crystalline interface template. (a) At the bottom, the template itself, with a (100) crystal template at left matched up precisely with an FSP amorphous template at right. The template pattern appears bright because the holes are filled with fluorescent dye solution. (b) The first layer of particles, following the holes of the template pattern exactly. (c-d) Horizontal layers at about 10 and 20 μm above the first layer, respectively. Note that the glass progressively encroached onto the crystalline side as the material was deposited.
a perfectly periodic fluctuation about a mean value. We might expect some effect of the crystal structure on the amorphous sediment right at the interface, but as these are hard-sphere particles, we would not expect any long-range effects. The cause of this phenomenon is unknown.

![Histogram of z-coordinates](image)

**Figure 3.9:** The density of particles centers versus z height near the amorphous-crystalline interface, for the crystal side (blue) and the amorphous side (green). It is unknown why the amorphous side maintains a periodicity exactly equal to that on the crystalline side, but 180° out of phase.

In future work, we would like to use this interface template to study in detail the structure and dynamics of the crystalline-amorphous interface, as well as how the interface evolves over time as the structure is allowed to equilibrate.
3.3 Conclusion

When growing colloidal structures epitaxially onto a patterned substrate, the deposition rate (dimensionless flux), template pattern, and the relation between the template spacing and the crystal thickness determine the resulting structure. A detailed understanding of these parameters makes it possible to grow perfect crystals more rapidly than previously believed. This may also be a method for creating non-equilibrium colloidal structures in a controlled way.

In this chapter, we report the growth of large, defect-free, FCC colloidal single crystals by centrifugation onto (100) templates at growth rates up to \(\sim 10 \text{ \mu m/s} \). This rapid crystal growth is possible because deposition onto a (100) template gives incoming particles no choice of position; the layering is completely deterministic. In principle there is no limit to the size of the (100)-oriented FCC crystal that can be grown in this manner, and much higher deposition rates may be possible. Recent numerical simulations have produced similar results [48]. Our results point to a method both for rapid, reliable production of large three-dimensional colloidal crystals, and also for building any other colloidal structures that can be described by deterministic layering of densely-packed planes.

High-flux deposition onto a (111) template, which provides the particles with two degenerate stacking positions, or a (110) template, which lacks sufficient in-plane density to fix the incoming particle positions, rapidly disorders into an amorphous sediment. We find that on flat, (111), and (110) substrates, the transition to an amorphous sediment occurs if the dimensionless flux exceeds \(\phi_0 Pe \approx 0.02\).

We investigated the defect formation in these crystals in detail by measuring the densities of extended defects as a function of crystal thickness; these results are discussed in Chapter 4.

Complementary to our understanding of how colloidal crystals can be formed far faster than previously believed possible is an understanding of how colloidal glasses can be formed at relatively lower fluxes than previously thought. As long as the dimensionless flux during deposition exceeds the critical flux for amorphous crossover of 0.02 and the bottom substrate is non-deterministic, a glass will form; to form only an amorphous sediment without any crystalline layers, an amorphous template can be used that initiates crossover from the very first layer. We designed and tested
two such templates: one that enforces complete (111) $B/C$ stacking disorder from the very first layer, and another that recreates a horizontal cross section of a previously-created and imaged glass sample that serves to create roughness on the length scale of the particles.

With this understanding of the fundamental physics of structure formation by sedimentation of simple hard sphere colloids and these template designs (several of which are shown in photograph of Figure 3.10), we next use the colloidal materials that we can make using these techniques as experimental models for studying the properties of atomic crystals and glasses.
**Figure 3.10:** Photographs of colloid templates. Crystalline templates appear colorful due to Bragg diffraction, while the amorphous templates do not.
Strain-induced nucleation and growth of extended defects in FCC colloidal crystals

In Chapter 3, we described a mechanism by which perfect FCC colloidal crystals can be grown by rapid deposition onto a (100) template. While we find that the as-formed crystal can be free of extended defects, such as dislocations or stacking faults, we observe in certain cases that after some time, extended defects nucleate at the top of the crystal and grow down into the bulk. Whether or not this occurs depends, for a given spacing template spacing, on the total height of the crystal. Eventually, the crystal reaches an equilibrium concentration of extended defects.

We show that the formation of these defects can be understood by the classical Frank-van der Merwe theory [27], adapted using the equation of state of the hard-sphere colloids to account for the pressure-induced variation of lattice spacing and elastic constants with depth.
4.1 Strain-induced defect nucleation and growth

While growth on (100) templates results in single crystals for all dimensionless fluxes, we observe that some of these crystals contain extended defects: stacking faults and dislocations (Shockley partials with \( \vec{b} = \frac{2}{3}(112) \)). During low-flux deposition, defects can result from impurities in the suspension during growth, but most defects nucleate after crystal growth is complete, driven by the strain that arises from a slight lattice mismatch between crystal and template. This lattice mismatch can be accommodated by the introduction of misfit dislocations at the interface. Growth at high dimensionless flux kinetically suppresses both mechanisms. Due to the pressure head from the particles above, the lattice parameter of the unconstrained crystal and its compressibility decrease with increasing depth. Whether or not misfit dislocations nucleate depends on the misfit strain and the thickness of the crystal, which must exceed a critical value, \( h_c = 26 \text{ } \mu \text{m} \) [27, 44, 61].

To study the defect density as a function of total crystal thickness, we prepared a series of FCC colloidal single crystals of various thicknesses by centrifugation onto (100) templates, as described above. We identify the stacking faults in reconstructed images of otherwise perfect FCC crystals by marking particles with HCP-type local coordination [61]. The edges of these stacking fault planes are the dislocations. The average linear distance between dislocation lines at the crystal-template interface, \( \Lambda \), is determined from the number of HCP-coordinated particles, \( N_{SF} \), by computing the average distance between the \( \{111\} \) stacking fault planes. This is given by \( \Lambda = 4\sqrt{2}V_c/(a^2N_{SF}) \), where \( V_c \) is the volume of the crystal and \( a \) is the average interparticle spacing. We show both a horizontal confocal image slice and a three-dimensional reconstruction of the stacking fault planes in a crystal grown to a super-critical \( (h > h_c) \) thickness in Figure 4.1.

The equation of state for hard spheres can be written as

\[
P V = Z(\phi) k_B T, \tag{4.1}
\]

where \( P = P(u) \) is the pressure, \( V = V(u) \) is the volume per particle, \( \phi = \phi(u) \) is the volume fraction, and \( Z(\phi) = Z(\phi(u)) \) is the compressibility factor, all of which are functions of depth in the
Figure 4.1: (a) Confocal image of a horizontal section through a colloidal FCC crystal grown to a total thickness of 42.9 μm on a (100) template. Because the crystal thickness exceeds the critical thickness, it acquired a significant concentration of stacking faults. (b) Three-dimensional reconstruction of stacking faults in the same crystal, with particles shaded according to their depth in the crystal. Stacking faults are identified as pairs of planes with local HCP coordination.
crystal, \( u \). We define the coordinate system such that \( u = 0 \) corresponds to the top of the crystal (at crystal/liquid coexistence), and the positive \( u \) direction points down into the crystal (parallel to gravity). The pressure at a depth \( u \) exerted by the weight of the crystal above is:

\[
P(u) = (\Delta \rho) g_s \int_{-\infty}^{u} \phi(u') du',
\]

(4.2)

In this case, \( g_s = 1g \) because the crystal is allowed to equilibrate outside of the centrifuge after crystal formation.

The equation of state becomes then:

\[
\phi(u) \cdot Z(\phi(u)) = \frac{\bar{\Omega} \Delta \rho g}{k_B T} \int_{-\infty}^{u} \phi(u') du',
\]

(4.3)

where \( \bar{\Omega} = 1.96 \ \mu m^3 \) is the average particle volume (refer to Section 2.4.1). The quantity \( l = \left( \frac{\Omega \Delta \rho g}{k_B T} \right)^{-1} = 0.23 \mu m \) is the gravitational length of a particle. Differentiating both sides with respect to \( u \) yields a differential equation for the volume fraction:

\[
\phi'(u) = l \left( \frac{\partial \phi}{\partial u} \right) \left( Z(\phi(u)) + \phi(u) \frac{\partial Z}{\partial \phi} \right)
\]

(4.4)

The equation of state for hard spheres has been the subject of numerous theoretical and numerical studies \cite{[1],[2],[29]}. For our FCC colloidal crystals, the compressibility factor for dense, hard-sphere crystals proposed by Hall \cite{29} is appropriate:

\[
Z = \frac{12 - 3\beta}{\beta} + 2.557696 + 0.1253077\beta + 0.1762393\beta^2 - 1.053308\beta^3 + 2.818621\beta^4 - 2.921934\beta^5 + 1.118413\beta^6
\]

(4.5)

where \( \beta(\phi) = 4 \left( 1 - \frac{3\sqrt{2}\phi}{\pi} \right) \). Using this expression for \( Z(\phi) \) and the initial condition of crystal-liquid coexistence \( \phi(0) = 0.545 \), we numerically solve the differential equation for \( \phi(u) \). Figure 4.2 shows the calculated volume fraction and corresponding interparticle spacing \( a(u) \) as a function of depth in the crystal. Even with polydispersity, the relation between the average nearest neighbor distances and the volume fraction is still that of the monodisperse FCC lattice: \( a(u) = \left( \frac{4}{3} \pi R^3 \frac{\sqrt{2}}{\phi(u)} \right)^{1/3} \).
For greater crystal depths, the system asymptotically approaches close packing ($\phi_{CP} = 0.740$, $a_{CP} = 1.55 \, \mu m$).

Figure 4.2 also shows the depth-dependence of the bulk modulus, $K$:

$$K(u) = -V \left( \frac{\partial P}{\partial V} \right) = -V(u) \left( \frac{\partial P}{\partial u} \right) \left( \frac{\partial V}{\partial u} \right)^{-1} = \Delta \rho \, g \, \phi^2(u) \left( \frac{\partial \phi}{\partial u} \right)^{-1} \quad (4.6)$$

In Figure 4.3 we compare the measured Voronoi volume averaged over entire crystals of various heights to the results of these calculations. Agreement is best with the data from those thick crystals ($h > h_c$) most relaxed by the introduction of misfit dislocations as established by direct observation of the confocal images. That the data of the unrelaxed crystals lie above the curve can be attributed mostly to the expansion of the lattice by the template.

We can use the continuum theory for misfit dislocations in epitaxial thin crystals [27, 32, 44, 61] to calculate the expected linear density of dislocations, $\Lambda^{-1}$, as a function of the thickness of the colloidal crystals. The elastic strain energy resulting from the misfit, $\epsilon_0$, can be relieved by the insertion of dislocations (Shockley partials), resulting in a total elastic strain

$$\epsilon_{el}(u) = \epsilon_0 - \epsilon = a_t - a(u) - b \cos(\alpha) \Lambda^{-1}. \quad (4.7)$$

where $a_t = 1.63 \, \mu m$ is the template interparticle spacing (constant) and $a(u)$ is the depth-dependent nearest neighbor spacing in a crystal unconstrained by a template. The strain relieved by the misfit dislocations, $\epsilon$, consists of $b \cos(\alpha) = a(u)/3$, the component of the Burgers vector of a Shockley partial dislocation parallel to the template, and the linear dislocation density, $\Lambda^{-1}$. Since all the stacking faults are \{111\} planes, $\cos \alpha = 1/\sqrt{3}$.

The elastic energy per unit area stored in a strained film of thickness $du$ at depth $u$ is

$$dU_{el} = \epsilon_{el}^2 Y \, du, \quad (4.8)$$

where $Y = Y(u)$ is the depth-dependent biaxial modulus. The total elastic energy per unit area in
Figure 4.2: Calculated properties of an unconstrained FCC colloidal crystal as a function of depth in the crystal: (top) volume fraction, $\phi(u)$, and corresponding particle Voronoi volume, $V(u)$, and interparticle spacing, $a(u)$; (bottom) the bulk modulus, $K(u)$. 
Figure 4.3: Average particle volume versus total crystal thickness. Each symbol corresponds to a crystal grown either by centrifugation (■) or by sedimentation (▲). The calculated values (solid line) are based on the hard-sphere equation of state (see text).
a film of thickness $h$ is:

$$U_{el} = \int_{0}^{h} Y(u) \left( \frac{a_t - a(u)}{a(u)} - \frac{a(u)}{3} \Lambda^{-1} \right)^2 \, du. \quad (4.9)$$

The energy cost of having $\Lambda^{-1}$ dislocations per unit length in the interface is given by the cylindrical integral:

$$U_I = \Lambda^{-1} \int_{0}^{\pi} \int_{r_c}^{r_{out}} \frac{\mu b^2}{\pi^2 (1 - \nu)} \frac{1}{r} \, drd\theta, \quad (4.10)$$

where $r_c = b/4 = \frac{a(h)}{4\sqrt{3}}$ is the effective dislocation core radius, $r_{out}$ is the outer radius of the dislocation strain field and is approximately equal to $h$ for a dislocation at the crystal-template interface, $\mu = \mu(u)$ is the depth-dependent shear modulus, and $\nu$ is Poisson’s ratio. While the biaxial and shear moduli vary with depth in the crystal, we assume that Poisson’s ratio remains roughly constant throughout the crystal, consistent with simulation results for hard sphere crystals.

Note that the expression in Equation (4.10) differs from the classical theory by a factor of four due to the large difference in stiffness between the colloidal crystal and the glass template (1 versus $10^{11}$ Pa), which makes the latter rigid, and hence strain-free, in the calculation. This is incorporated into the dislocation energy calculation by introducing an image dislocation of the same magnitude and strain, which doubles the strain and quadruples the strain energy density in the colloidal half-crystal with respect to a dislocation in a homogeneous colloidal crystal.

By approximating the colloidal crystal as an isotropic, elastic medium, the biaxial and shear moduli can be expressed in terms of the bulk modulus and Poisson’s ratio: $Y(u) = \frac{3(1-2\nu)}{1-\nu} K(u)$ and $\mu(u) = \frac{3(1-2\nu)}{2(1+\nu)} K(u)$. Minimization of the total energy, $U = U_{el} + U_I$, with respect to the defect density, $\Lambda^{-1}$, yields an expression for the equilibrium defect density:

$$\Lambda^{-1}(h) = \frac{3 \int_{0}^{h} K(u) (a_t - a(u)) \, du - \frac{3}{4\pi^2 (1+\nu)} \int_{0}^{\pi} \int_{r_c}^{r_{out}} K(u) a^2(u) \frac{1}{r} \, drd\theta}{\int_{0}^{h} K(u) a^2(u) \, du} \quad (4.11)$$

By substituting $u = h - r \sin \theta$ into the cylindrical integral, this expression can be evaluated to predict the equilibrium defect density as a function of total crystal height. For our particles, this
predicts a critical thickness, corresponding to \( \Lambda^{-1} = 0 \), of \( h_c = 26 \mu m \), below which defect formation is suppressed. We plot our experimental measurements (points) and the calculated physical defect density (solid line) in Figure 4.4, and find good agreement. The measured values of \( \Lambda^{-1} \) for crystals with supercritical thickness all lie below the calculated equilibrium values, indicating that the strain relaxation at the time of the measurements was still incomplete. Nucleation and growth of dislocations get exponentially slower as relaxation proceeds due to the decreasing driving force; the kinetics of these processes have been studied in detail in colloidal crystals by Schall et al. [61]. The supercritical data may be slightly high because of the presence of non-dislocation-related defects, which could not be quantitatively removed from the calculation of \( \Lambda^{-1} \). The subcritical crystals are all dislocation-free, even though they occasionally contain other types of imperfections.

![Figure 4.4: Linear density of dislocations, \( \Lambda^{-1} \), versus total crystal thickness. Points indicate experimental data from colloidal single crystals obtained by centrifugation (■) and by low-flux sedimentation (▲). The gray line represents the values calculated from Eq. [4.11].](image)

By decreasing the nearest-neighbor distance of the template and depositing onto such tem-
plates at high dimensionless fluxes so that defect nucleation is suppressed during growth, it should be possible to form arbitrarily large crystals entirely free of extended defects. Using a template designed with a slightly smaller lattice spacing, we have already made crystals greater than 50 \( \mu \text{m} \) tall in which extended defects do not form.

4.2 Conclusion

We investigated the defect formation in crystals formed by deposition onto (100) templates at various dimensionless fluxes in detail by measuring the densities of extended defects as a function of crystal thickness and could account for these results using the Frank-van der Merwe continuum theory adapted for the hard sphere equation of state.
Local shear transformations in deformed and quiescent colloidal glasses

The atomic-scale mechanisms by which glasses, which lack the translational symmetry of crystals, undergo elastic, anelastic, and plastic deformation are still not understood. For the plastic deformation of metallic glasses, theory \[2, 64\] and simulation \[6, 24, 89\] predicted the existence of “shear defects” or “shear transformation zones” (STZs) that mediate plastic deformation, as dislocations do in crystals. The bubble raft experiments of Argon \[8\] provided the first experimental evidence for STZs in a 2D amorphous structure, and recent experiments on colloidal glasses \[11, 12, 83\] identified STZs in 3D systems as localized regions of high irreversible strain. However, much remains unknown about these shear defects, including whether they already exist in the absence of applied strain, and how their population evolves with time and increasing strain.
Here, we show that shear defects exist in both sheared and unsheared (quiescent) colloidal glasses. These defects conform with Eshelby’s solution \[ \text{22, 23} \] of the elastic strain field of a sheared inclusion and its surroundings. When a bulk uniform shear strain is applied to the glass beyond the yield point of the material, a population of these defects transforms irreversibly as shear transformation zones (STZs), biased in the direction of the applied shear. Further, we show that the energy required to activate the Eshelby inclusions is consistent with the available thermal energy, which supports our interpretation of these inclusions as a major deformation mode of the system.

As part of this study, we use the strain fluctuations during quiescence to measure the shear modulus as a function of depth in the material. We find that the modulus is exquisitely sensitive to even very small density gradients and varies as a function of depth in our colloid glasses. For purely quiescent samples, the shear modulus is constant in time. After a deformation cycle, however, the shear modulus becomes uniform throughout the material, indicating that the glass was forced to dilate in order to undergo shear. Subsequent quiescent measurements reveal that the depth-dependence of the modulus is restored over time as the glass relaxes.

5.1 Deformation Experiments

We apply shear deformations to colloidal glasses while simultaneously imaging them in 3D using a confocal microscope. The sample cell consists of a metal reservoir \( \sim 1 \text{ cm in diameter} \), glued onto a 0.17mm-thick glass coverslip. The coverslip is patterned with an amorphous template that serves to prevent crystallization in the first layers of the sample during glass formation, as described in Section \[ \text{3.2} \]. We prepare colloidal glasses directly in the sample cell via high-flux sedimentation at \( 1g \) \( (\phi_0 Pe = 0.03, \text{ where } \phi_0, \text{ the initial volume fraction, is about } 3.5\%) \) onto the amorphous template \[ \text{36} \]. After sedimentation is complete, the compact sediment has a thickness of about 250 \( \mu \text{m} \). The sample cell is fixed to the microscope stage, and does not move over the course of the experiment.

We use a computer-controlled piezoelectric actuator to apply the shear deformation. The actuator has a maximum travel of 80 \( \mu \text{m} \) and an accuracy \( \pm 5 \text{ nm} \) in the \( y \)-direction. It is mechanically coupled to the glass by a fine metal transmission electron microscope (TEM) grid that is
embedded deep in the glass sample during sedimentation, about 200 μm below the surface of the sediment. The shear gap, Δz, is defined by the separation between the bottom of the embedded grid and the amorphous template. We experimented with gaps ranging from about 40-90 μm; in the experiments reported here, the gap was Δz = 45 μm. Placement of the grid deep in the sample ensures good contact between the glass and the grid, as the glass completely surrounds the grid and fills the space above and below it. For more details on the construction of the shear cell apparatus, see Section 2.2.

The entire shearing setup is assembled and aligned prior to the colloid glass formation, as shown in Figures 5.1 and 5.2. The post holding the metal grid is hollow and perforated so that the volume above the grid is completely open to the surrounding fluid. As the glass grows by sedimentation up around the grid. The sedimentation is complete within about two hours, and then the glass is allowed to relax for approximately six more hours before the shear experiment begins. For the quiescent experiments reported here, the sample preparation is exactly the same, but no strain is applied to the glass.

All image stacks are taken far from the edges of the template and from the sample cell walls to avoid possible boundary effects. During deformation experiments, we take two image stacks at each time step: a low-resolution stack that spans the entire shear gap from the TEM grid at top to the amorphous template at bottom, and a high-resolution image stack in the middle of the shear gap, about 10 μm away from either top or bottom of the gap. The low-resolution images allow us to monitor the entire shear gap and watch for any boundary slip or shear band effects that might affect the actual applied strain, while the high-resolution stack provides the data that we use for our detailed analyses. Figure 5.3 gives an example of these images. It takes about 5.5 minutes to acquire both stacks and we repeat the scans every 6 minutes. This is fast enough at the strain rates used in our experiments for each image stack to represent a snapshot of the particle configuration at that time.

We locate the particle centers in three dimensions using standard particle location software [28], run iteratively to minimize missed or double-located particles as described in Section 2.3.
Figure 5.1: The miniature shear cell (MSC). (top) Photograph of the MSC during setup on the confocal microscope. (bottom) Schematic of the assembled shear cell, drawn to scale. The screw enables precise vertical adjustment of the post. The bottom of the post is hollowed out, and the TEM grid is attached to the bottom rim. The template slide seals the bottom of the sample reservoir.
Figure 5.2: A not-to-scale detail of the sample reservoir configuration in the miniature shear cell, indicating the bulk strain profile.
Figure 5.3: Example of the raw data, showing the high-resolution image stack embedded in the low-resolution stack that spans the entire gap from stationary template to the moving TEM grid. Part of one of the TEM grid bars is visible in cross-section at the top of the image ($y \sim 40-48 \mu m$). The highest peaks of the amorphous template are just visible as dark bumps at the bottom of the image.
Once the particles have been located in the image stacks, we convert the coordinates from units of pixels to micrometers using an experimentally calibrated conversion factor as described in Section 2.1. Finally, we link the particle locations over time into 3D trajectories, allowing for trajectories that begin or end as particles near the edge move in or out of the field of view. These particle trajectories provide the basis for all further analyses of local and global deformation dynamics of the material.

We deform the glass at various strain rates and to various maximum strains, then reverse the deformation at an equal, but opposite, strain rate until the bulk strain is zero. We performed plastic deformation experiments to 5% and 10% maximum strain, and at strain rates of $2 \times 10^{-5}$ s$^{-1}$ and $5 \times 10^{-5}$ s$^{-1}$. Here, we focus on the results of the longest and slowest of these experiments: 10% maximum strain at $2 \times 10^{-5}$ s$^{-1}$. All of these strain rates are slow enough to ensure homogeneous deformation so that we observe no shear bands, and the maximum strains easily exceed the yield point of the material ($\gamma_{\text{yield}} \approx 2\%$). For comparison, we also observe quiescent glasses with no applied strain but otherwise the same experimental conditions.

5.2 Glass deformation results

We measure the applied strain in the glass in three ways: the externally-applied deformation, the bulk material strain, and the average local strain. We find close agreement between all three ways of measuring the strain.

First, the externally-applied bulk applied strain, $\gamma_{\text{applied}}(t)$, is equal to the displacement of the piezoelectric actuator over time, $y_{\text{piezo}}(t)$, divided by the shear gap, $\Delta z$. Next, we consider the deformation profile, which consists of the individual particle displacements as a function of height in the sample; see Figure 5.4, first column. We find that the deformation profile is straight, confirming that the bulk deformation experienced by the sample was simple shear, as expected. We fit a straight line to these data at each time point, the slope of which provides the second measure of bulk strain in the material.

Third, we use the method of Falk and Langer [24] to calculate the local strain for each individual particle. In this method, we use the vector displacements of each particle’s nearest
Figure 5.4: Evolution of strain and strain field correlations in the colloidal glass at several points during a shear experiment. The time and bulk strain corresponding to each row are indicated in Figure 5.8. Column 1: The deformation profile (particle height versus displacement) for all particles. Column 2: Top-view reconstructions showing only those particles with individual strain $|\epsilon_{yz}| > 0.1$, colored according to their strain, at each time step during the strain experiment. On strain reversal, some of the particles that acquired a high positive strain return to a low-strain state, and so disappear from the reconstruction. Column 3: Cross-sections in the y-z plane of the $\epsilon_{yz}$ strain correlations at the same times, showing the evolution of the quadrupolar signature.
neighbors from a reference time, $t_{ref}$, to some later time, $t$, to sample the displacement field, $\vec{u}$, in the vicinity of that particle. Nearest neighbors are defined as all particles closer to the particle of interest than a distance equal to the first minimum of the pair distribution function, $g(r)$, and only neighbors that meet this criterion at both $t_{ref}$ and $t$ are considered in the calculation. The position vector of the $n$th neighbor over time, $\vec{r}_n(t)$, is computed with the central particle defining the origin of the coordinate system at each time.

From the positions, we compute all components of the affine deformation tensor, $\overline{\pi}$, that best describes how that region has changed since the reference time using the formulae of Falk and Langer, included here for completeness:

$$\alpha_{ij} = \sum_k X_{ik} Y_{jk}^{-1} - \delta_{ij}$$  \hspace{1cm} (5.1)

where

$$X_{ij} = \sum_n r_n^i(t) \times r_n^j(t_{ref})$$  \hspace{1cm} (5.2)

$$Y_{ij} = \sum_n r_n^i(t_{ref}) \times r_n^j(t_{ref})$$  \hspace{1cm} (5.3)

By separating this tensor into its symmetric and antisymmetric parts, we obtain the components of the strain, $\epsilon_{ij}$, and rotation, $\omega_{ij}$, tensors for each individual particle.

Figure 5.5 shows top-view reconstructions of the individual particles with the highest magnitude strains in the direction of applied shear over an entire experiment. For comparison, the top-view reconstruction series from the same experiment for the $\epsilon_{xy}$ and $\epsilon_{xz}$ strain components, in which there is no bulk strain, are shown in Figures 5.6 and 5.7.

The average of all of the individual particle shear strains provides the third measure of the bulk strain experienced by the sample, $\langle \epsilon_{yx} \rangle = \gamma/2$. In Figure 5.4, column 1 shows the bulk deformation as seen in the deformation profile, and column 2 shows a top-view reconstruction of
Figure 5.5: Top-view reconstructions showing only those particles with individual strain $|\epsilon_{yz}| > 0.1$, colored according to their strain, during the strain experiment. On strain reversal, some of the particles return to a low-strain state and disappear from the reconstruction. Others become irreversibly locked into their high-strain states; other regions must undergo high negative strains (blue) in order to return the sample to zero bulk strain.
Figure 5.6: A similar reconstruction series as in Figures 5.5 and 5.7 but for the $\epsilon_{xy}$ strain component.
Figure 5.7: A similar reconstruction series as in Figures 5.5 and 5.6, but for the $\epsilon_{xx}$ strain component.
the individual particle strains $\epsilon_{yz}$ in the direction of applied shear at the maximum applied strain, $\gamma_{\text{max}} = 10\%$. Note that the individual particle strains can significantly exceed the bulk strain, and that some even oppose the direction of the applied strain.

The bulk deformation over the course of a shear experiment, measured in these three ways, is plotted in Figure 5.8. We observe excellent agreement between these three separate measures. Further, we use the measurement of the other strain components to confirm that there is no bulk x-y or x-z shear strain (orthogonal to the applied shear). These measurements are also plotted in Figure 5.8(c). We also use these metrics to confirm that there is no bulk deformation or drift at all in the quiescent experiments.

Figure 5.8: The bulk shear strain, $\gamma$, over time during a deformation experiment. The strain is measured in three ways: (1) (red dashed line) the applied strain, $\gamma_{\text{app}}$, equal to the actuator displacement divided by the gap height; (2) (blue squares) the bulk strain measured by fitting the deformation profile; and (3) (black triangles) the average of all of the individual particle strains, $2\langle\epsilon_{yz}\rangle$. For comparison, the average strains orthogonal to the applied strain, $2\langle\epsilon_{xy}\rangle$ and $2\langle\epsilon_{xz}\rangle$, are shown as black solid and dot-dashed lines, respectively.
Although the bulk strain experienced by the glass during deformation is uniform, locally the individual particle strain is highly heterogeneous. We look for patterns in the local particle strain by computing the unnormalized three-dimensional spatial correlation \([11,12]\) of the strain fluctuations, 
\[
C_\epsilon(\Delta r) = \langle \epsilon_\delta(\mathbf{r}) \epsilon_\delta(\mathbf{r} + \Delta \mathbf{r}) \rangle,
\]
where \(\epsilon_\delta(\mathbf{r}) = \epsilon(\mathbf{r}) - \langle \epsilon(\mathbf{r}) \rangle\) is the measured local strain minus the bulk strain. Over time, a strong quadrupolar signature develops in the strain correlations, which remains even after the bulk strain is completely reversed. As the bulk strain approaches zero, however, the strain correlation decays more quickly with distance from the center of the inclusion. We attribute this to the presence of inclusions of opposite sign (directly visible as blue particle clusters in the final spatial reconstructions of Figure 5.4). An inclusion of either sign will contribute positively to the quadrupolar correlation signature, but a negative inclusions nearby an inclusion of positive sign will tend to cancel out the longer-range strain field effects.

The correlations of the \(\epsilon_{yz}\) strain component (corresponding to applied strain) are shown in column 3 Figure 5.4 as they evolve over time during the course of the experiment. At each time, we show the cross section through the 3D correlation corresponding to that strain component (in this case, y-z). For consistency and so that the evolution of the quadrupole is evident, we use a fixed color scale for all of these plots, chosen to show clearly the correlation corresponding to maximum bulk strain. However, with a smaller dynamic range, the quadrupole signature is faintly visible even in the first measurement, at which time no strain had been applied yet.

As a control, we also make the same measurements on a colloidal glass sample with no applied strain (quiescent). The sample preparation and setup are identical; the main difference is the lack of externally-applied stress, although we are unable to verify experimentally that the total colloid sediment heights are exactly identical. We observe significantly less motion in the quiescent sample, but the glass still shows clear signs of active shear defects throughout. A summary of the quiescent glass is shown in Figure 5.9, with the same information at the same time intervals as Figure 5.4.
Figure 5.9: Evolution of strain and strain field correlations in a colloidal glass under quiescent conditions. The time intervals are chosen to match those of Figure 5.4, although these times have no particular significance in this experiment. Column 1: The deformation profile (particle height versus displacement) for all particles. Column 2: Top-view reconstructions showing only those particles with individual strain $|\varepsilon_{xy}| > 0.03$, colored according to their strain, at each time step during the strain experiment. Column 3: Cross-sections in the x-y plane of the $\varepsilon_{xy}$ strain correlations at the same times, showing the evolution of the quadrupolar signature. The length scales for the Column1 plots are identical between both figures, so the deformation profiles can be directly compared. Columns 2 and 3 have different color scales than in Figure 5.4 so that the dynamics are visible.
5.3 **Eshelby inclusions in colloidal glass**

This quadrupolar signature in the local strain indicates the presence of Eshelby inclusions: local, high-strain regions that are coupled elastically to the surrounding medium. Eshelby originally proposed such inclusions as a mechanism of plastic deformation of an otherwise elastic medium; in the plastic deformation of amorphous materials, these are known as as “shear defects” or “shear transformation zones” (STZs). This quadrupolar signature in the strain correlations was already recently observed in a density-matched PMMA colloidal glass under steady-state homogeneous deformation [11].

![Diagram of Eshelby inclusion process](image)

**Figure 5.10:** The hypothetical sequence of creating an Eshelby inclusion in an elastic medium. A spherical inclusion of volume \( v_0 \) is removed from the material, plastically deformed to a new state with unconstrained strain \( \epsilon^T \) and zero stress, and then forced back into its original position and configuration in the elastic matrix. Subsequent elastic relaxation of the matrix and the inclusion results in a bulk plastic deformation of the entire material mediated by the inclusion.

We compare our experimental results to Eshelby’s calculation of the three-dimensional displacements for a spherical inclusion with an unconstrained transformation shear strain \( \epsilon^T_{yz} = \gamma/2 \) and inclusion radius \( a \) in an isotropic elastic medium with dimensionless elastic constant \( c = 1/(4(4 - \nu)) \). Here, \( \nu \) is Poisson’s ratio for our colloidal glass, taken to be 1/3 [36, 58]. The final shear strain inside the inclusion when it is embedded in the elastic matrix is
\[ \epsilon_{yz}^0 = \gamma \frac{4 - 5\nu}{15(1 - \nu)} \]  

(5.4)

For such an inclusion, the displacements at distances \( r = \sqrt{x^2 + y^2 + z^2} \) outside the inclusion are

\[
\begin{align*}
  u_x &= \epsilon_{yz}^0 a^3 \left\{ 6c(r^2 - a^2) \left( \frac{5xyz}{r^7} \right) \right\} \quad (5.5) \\
  u_y &= \epsilon_{yz}^0 a^3 \left\{ -\frac{z}{r^3} + 6c(r^2 - a^2) \left( \frac{5y^2z}{r^7} - \frac{z}{r^5} \right) \right\} \quad (5.6) \\
  u_z &= \epsilon_{yz}^0 a^3 \left\{ -\frac{y}{r^3} + 6c(r^2 - a^2) \left( \frac{5yz^2}{r^7} - \frac{y}{r^5} \right) \right\} \quad (5.7)
\end{align*}
\]

This result holds if the elastic constants are uniform throughout the matrix and the inclusion. The full deformation tensor is \( \alpha_{ij} = \frac{\partial u_i}{\partial y_j} \), as usual, and, as above, the strain tensor \( \overline{\epsilon} \) is the symmetric part of \( \overline{\alpha} \). Although we calculate all of the deformation components, we particularly focus on the shear strain corresponding to the interior strain of the inclusion, in this case, the y-z component. Considering both the interior and exterior strain of an ideal inclusion, the complete analytic expression for the y-z component of the strain in the y-z plane is:

\[
\epsilon_{yz}(r) = \begin{cases} 
  \epsilon_{yz}^0, & r < a \\
  \epsilon_{yz}^0 a^3 \left( 9a^2c - (2 + 3c)r^2 - 15c(7a^2 - 5r^2) \cos (4\theta) \right), & r \geq a
\end{cases} \quad (5.8)
\]

This strain field is a quadrupole aligned with the yz plane. We plot the results of the autocorrelation of this analytic solution for the strain field extended over a finite volume and compare with the correlation calculated from the data in Figure 5.11(a) and (b). These show good quantitative agreement with our experimental data, indicating that the Eshelby theoretical framework is a good description of the local strain fluctuations in the colloidal glass.

Interestingly, when we compute the strain correlations for the other shear strain directions (\( \epsilon_{xz} \) and \( \epsilon_{xy} \)), we also observe a quadrupolar signature in the correlation cross section corresponding to the shear plane. Although the Eshelby solution does have non-zero strain components in the other shear directions, those do not have a quadrupolar signature. Rather, the observed signature
Figure 5.11: Strain correlations (a) at the maximum applied bulk strain ($\gamma_{yz,max} = 10\%$, $t = 5040$ seconds), (b) at the same time, but for $\varepsilon_{xy}$, with zero bulk strain, and (c) for a single, ideal Eshelby inclusion of radius $a = 2.25$ $\mu$m, elastic constant $c = 0.107$ embedded in an infinite elastic medium.

indicates the presence of shear transformation zones operating orthogonal to the applied strain, even though there is no bulk strain in these directions. The inclusions are activated thermally, with an equal number in opposite directions, so that there is no net strain.

For ease of comparison, the correlations of $\varepsilon_{yz}$ (corresponding to applied strain), $\varepsilon_{xz}$, and $\varepsilon_{xy}$ strain components as they evolve over time during the course of the experiment are shown in Figures 5.12, 5.13, and 5.14. For each component, we show the cross section through the 3D correlation that corresponds to that strain component. All figures are shown with the same color scale to make clear the evolution of the correlation. The color scale is set with respect to the average squared strain at the time of maximum bulk strain; the color limits are $\pm \langle \varepsilon_{yz}^2(t_{max}) \rangle / 10$. 

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Figure 5.12: $\epsilon_{y2}$ strain correlations evolving over the course of a strain experiment.
Figure 5.13: $\epsilon_{xx}$ strain correlations evolving over the course of a strain experiment.
Figure 5.14: $\epsilon_{xy}$ strain correlations evolving over the course of a strain experiment.
Figure 5.15: For comparison, ε_{xy} strain correlations in a purely quiescent sample evolving over the same time intervals.
5.4 Characterizing the population of shear defects

The strain correlations provide insight into the characteristics of the population of shear defects present in the material. The length scale of the quadrupole field is determined only by the size of the inclusion, so the analytical results shown in Figure 5.11 allow us to measure the average size of the shear defects by matching the peaks of the correlations. We find an average inclusion radius of about $\bar{a} = 2.3 \mu m$, slightly larger than the first minimum of the radial distribution function. Note that there is likely a range of inclusion sizes, but this indicates that the population is dominated by fairly small inclusions.

There is also likely a range of inclusion internal strains, but we can not get an average inclusion strain, $\tau_{ij}^0$, from the correlation measurement because we do not know how many defects are present in the imaged volume, nor precisely how they may be interacting. The fact that the correlation shows a single, symmetric quadrupole indicates that the inclusions are fairly well separated and uniformly distributed. If we can consider their strain fields not to interact significantly (at least at the early times), then the strain energy from the entire population is simply the sum of the energy contributed by each inclusion. However, without knowing how many defects there are, this still does not allow us to measure the average inclusion strain.

However, we can directly inspect the local strain fields to identify shear defects as irreversible regions of high local strain, and in at least some instances we can directly observe the Eshelby quadrupole strain field around the defect. An example of this is shown in Figure 5.16.

While it is inefficient to find shear transformation zones by inspection, this sort of “eyeball testing” can provide valuable information about the population of shear defects and allow us to at least put some upper bounds on the strain of the defect core. For example, we consider the x-y shear defects that are active in the glass with no applied strain in any direction. Even with our shortest time interval (360 seconds) and no applied strain, there is a clear quadrupole signature in the strain correlation, indicating thermally-activated defects. These early-time quadrupole signatures are difficult to see in the correlation evolution plots of Figures 5.12–5.14 because of the fixed color scale. In Figure 5.17a and b, we show the first correlation of Figure 5.14 first (a) with the same
Figure 5.16: Reconstruction of a y-z cross section through a shear defect (opaque spheres) and its immediate surroundings (semi-transparent spheres) showing alternating positive and negative strains around the core in a quadrupole pattern. Dashed white lines are drawn as guides to the eye.
color scale as in Figures 5.12–5.14 and then (b) with a color scale normalized to these data, so that the color limits in (b) are $\pm (e_{xy}^2(t = 360s))/10$.

The strain correlation reveals that shear defects were active in the unstrained glass during this time interval and dominated the local strain in the material. We further know from the correlation that the average radius of the active defects was a little larger than the first nearest neighbor shell. Therefore, we should be able to see at least the highest-strain defects in a direct reconstruction of the individual particles with highest strain.

In Figure 5.17 images (c)-(f) show reconstructions of the particles whose individual strain magnitude exceeded a cutoff value, $|\epsilon_{xy}| > c$, from the same time as the correlations in (a) and (b), 360 seconds from the reference time. The cutoff values shown are $c = 0.04, 0.03, 0.025$, and $0.02$, respectively. By gradually lowering the cutoff for what constitutes a “high strain” particle, we see that clusters comprising at least a complete nearest neighbor shell do not clearly until all particles with strains of about $\epsilon > 0.025$ are shown. Thus, we can estimate an upper bound of the internal strain for the largest magnitude defects (at this time) of about $\epsilon^0 = 0.025$. Although a rough estimate, this at least gives us some idea of the magnitude of internal strain in thermally-activated inclusions, which will be useful in estimating their energy.

5.5 Measurement of the shear modulus of the glass as a function of depth

Before we can make an estimate of the energetic cost required to activate the shear defects that we have observed in the glass, however, we need to know the elastic constants of the glass. As this is an isotropic material, there are only two independent elastic moduli. We take Poisson’s ratio, $\nu$, to be approximately $1/3$, and constant throughout the material consistent with previous observations [35, 36, 63].

We measure the shear modulus as a function of height in the glass by examining the strain field fluctuations while the glass is quiescent; we report data both from a purely quiescent experiment and during the periods of quiescence before and after a deformation experiment. For a glass with no externally-applied stress, we expect that any local strain fluctuations with be the result of thermal energy. Thus, we expect to see an exponential distribution of strain energies, whose form will
Figure 5.17: Finding shear defects by inspection. (a) The $\epsilon_{xy}$ strain correlation at $t = 360$, with color scale set as in Figure 5.14 (same as the first image of that figure). (b) The $\epsilon_{xy}$ strain correlation at $t = 360$, with color scale limits set at $\pm \langle \epsilon_{xy}^2(t = 360s) \rangle / 10$. The clear quadrupole reveals that shear defects were active in the material during this time interval, and that they had an average radius slightly larger than a first neighbor shell. (c)-(f) Reconstructions of the particles whose individual strain magnitude exceeded a cutoff value, $|\epsilon_{xy}| > c$, from the same time as the correlations in (a) and (b), 360 seconds from the reference time. The cutoff values shown are $c = 0.04, 0.03, 0.025$, and 0.02, respectively. No strain was applied to the glass during this time interval, but the axes are labelled to be consistent with other figures.
depend on the available thermal energy, \( k_B T \), and the shear modulus, \( \mu \), of the material (for shear strain fluctuations).

Following the method of Reference 63, we coarse-grained the \( \epsilon_{yz} \) shear strain by dividing the sample into boxes with side length \( s = 3 \mu m \), and computed the total elastic energy in each box, equal to \( E = (\mu/2)(2\langle \epsilon_{yz} \rangle^2)s^3 \). These energies are exponentially distributed such that \( \ln (p(E)) = -\mu(E/(\mu k_B T)) \). By plotting the normalized energy distributions for different heights, and fitting these with lines on a semi-log scale, we obtain the shear modulus as a function of height in the glass. An example of such a measurement and the resulting dependence of the shear modulus on height is shown in Figure 5.18.

We find that the shear modulus changes significantly over a few tens of micrometers, going from roughly 6 Pa at the bottom of the imaged region to between 1-2 Pa near the top. We expect the shear modulus to increase with increasing density or packing fraction, so it is not surprising to find a depth dependence in our colloid due to the pressure of the particles above. We also previously calculated this dependence for hard-sphere colloidal crystals in Chapter 4. What is remarkable here is that the change in packing fraction over this range is so small as to be nearly undetectable, which demonstrates how exquisitely sensitive the shear modulus is to even very small volume fluctuations.

In Figure 5.19 we show all of the modulus-versus-depth plots aggregated together for 50 measurements taken every 360s for 5 hours in a purely quiescent sample. The reference state for each strain measurement is the previous time step (\( \Delta T = 360 \) seconds). Although there is some noise, and perhaps a small trend toward softening, for the quiescent sample, the shear modulus is mostly constant over time.

In the sheared samples, however, we observe something very different. In a typical series of deformation experiments, we perform several experiments to varied maximum strain and at different strain rates, with periods of quiescence separating the experiments. In Figure 5.20, we plot the shear modulus versus height during these periods of quiescence prior to any deformation and in between deformation cycles. As above, in these cases, the reference state for the strain measurement is the previous time step (\( \Delta T = 360 \) seconds).
Figure 5.18: An example of a measurement of shear modulus as a function of height. (top) Semi-log plot of distributions of normalized strain energies. Each curve represents data from a different height in the sample. Dashed lines show exponential fits to each curve; the slope of each of these lines (on the semilog plot) is the shear modulus measured at that height. (bottom) Shear modulus versus height measured from the data in the upper graph. Such variation in modulus results from the very slightly greater glass density at lower heights in the sample, and demonstrates how exquisitely sensitive to density the shear modulus is.
Figure 5.19: Shear modulus, $\mu$, versus height in the sample for a purely quiescent glass, measured every 360s for 18000s. Lines are colored in groups of 10 according to time, with the earliest measurements purple, then blue, green, yellow, and red the latest times. Although there seems to be a small trend toward overall softening of the glass with time, for the most part the dependence of modulus on height remains the same.
Figure 5.20: Shear modulus, $\mu$, versus height in the sample for a purely quiescent glass, measured over 360s intervals during periods of quiescence between deformation experiments. Colors indicate sequences of consecutive times; the first measurement in each sequence is represented by squares, the second by triangles, and the third (if it exists) by circles. The quiescent sequences come at the very beginning of the experiment, prior to any applied strain (purple), and after deformation cycles with $\gamma_{max} = 5\%$ strain at $\dot{\gamma} = 5 \times 10^{-5}$ s$^{-1}$ (blue), after $\gamma_{max} = 10\%$ strain at $\dot{\gamma} = 5 \times 10^{-5}$ s$^{-1}$ (green), after $\gamma_{max} = 10\%$ strain at $\dot{\gamma} = 2 \times 10^{-5}$ s$^{-1}$ (orange), and after $\gamma_{max} = 5\%$ strain at $\dot{\gamma} = 5 \times 10^{-5}$ s$^{-1}$ (red).
Before any deformation has been applied, the glass shows a very similar variation of shear modulus with height as the purely quiescent sample. Immediately after a deformation cycle, we find that modulus is very nearly constant with height, and reduced to a minimum value. Over time, as the glass relaxes, the modulus recovers toward its original values. As the deformation series continues, the modulus recovers more and more slowly.

As the shear modulus depends sensitively on the packing fraction, the reduction of the shear modulus, particularly at the lower depths, indicates that the shear deformation is causing the glass to dilate and become less dense throughout. After the deformation is complete, the glass relaxes by eliminating this excess volume, which we observe as an increase in the shear modulus.

5.6 Energy required for activation of an inclusion

The energetic cost of activating a shear defect is determined by the elastic constants of the material (Poisson’s ratio, \( \nu \), and the shear modulus, \( \mu \)), the size of the defect (volume \( v_0 = \frac{4}{3} \pi a^3 \)), and the internal strain of the defect, represented either as the unconstrained transformation strain, \( \epsilon^T \), or the final internal strain as constrained by the bulk elastic matrix, \( \epsilon^0 = \epsilon^T \left( \frac{2(4-5\nu)}{15(1-\nu)} \right) \). \( a \), \( \epsilon^0 \), and \( \nu \) determine the strain tensor \( \epsilon_{ij} \) both inside and outside the inclusion, as discussed earlier in Section 5.3, while \( \mu \) enters in the calculation of the energy. In an isotropic, elastic medium, the energy density, \( w \), stored in such a strain field is [66]

\[
w = \mu \sum_{i,j} \epsilon_{ij}^2 + \frac{\mu\nu}{1-2\nu} \left( \sum_k \epsilon_{kk} \right)^2
\]  

(5.9)

The total elastic strain energy, \( E_{el} \), is the integral of \( w \) over all space. Eshelby solved this problem for a general ellipsoidal inclusion and then for several particular examples [22]. In the case of a spherical inclusion he found that

\[
E_{el} = \frac{8}{3} \pi a^3 \mu \left( \frac{7 - 5\nu}{15(1-\nu)} \right) (\epsilon^T)^2
\]  

(5.10)

For the reasonable estimates we made above for properties of a typical inclusion, \( a \approx 2.3 \) and \( \epsilon^0 \approx 0.025 \), and for the elastic constants of the glass, \( \nu = 1/3 \) and \( \mu \approx 4 \) Pa (at an intermediate
height in the unstrained material), $E_{el} = 3 \times 10^{-20}$ Joules, or $7k_B T$. This is a reasonable energy range that we would expect to see some active defects that are thermally activated.

Note, however, that this energy depends strongly on the precise size and strain of the inclusion, and linearly on the shear modulus. We certainly observe somewhat larger and significantly higher strain defects, whose energetic cost is significantly higher. During deformation, some of this can be supplied by the work, $W_{ext}$, done by the externally applied force that causes the bulk strain,

$$W_{ext} = \sigma v_0 \epsilon^T = \frac{4}{3} \pi a^3 \sigma \epsilon_0 \frac{15(1 - \nu)}{2(4 - 5 \nu)}$$

where $\sigma$ is the stress of the external matrix. Although we do not measure stress in our experiments, we can estimate as the stress at yield, which we measure to be $\gamma_0 \approx 0.02$ [19], multiplied by the shear modulus during strain. Hence, $\sigma \approx \mu \gamma_0 \approx 0.04$, which translates to $W_{ext} = 1 \times 10^{-19}$ Joules, or 27 kT. This would enable, for example, shear defects of the same size but more than twice the internal strain than those of our energy estimate above. However, this still does not account for all of the defects we observe, some of which have internal strains close to $\epsilon^0 \approx 0.1$ for similar or slightly larger sizes.

We have seen that the shear modulus is extremely sensitive to volume fraction, especially in this very dense system that is close to close packing. We observed this sensitivity directly in Section 5.3 above, and also found this in our equation of state calculations in Chapter 4. (Although those calculations were based on an equation of state for hard-sphere crystals [29], for which the properties diverge at cubic close packing rather than random close packing, a generally similar variation of modulus with depth would be expected for hard-sphere glasses.)

Thus, small local volume fluctuations can produce large fluctuations in the shear modulus, creating soft spots in the material where the energetic barrier to shear transformation is greatly reduced. We conclude this chapter with some first results examining the free volume of a shear defect leading up to and immediately after transformation. We find that the free volume may be a useful indicator of a developing shear transformation zone.
5.7 Free volume of a shear transformation zone

As described in Section 2.4.4, the free volume of a hard sphere at any time is a direct measure of the volume accessible for that sphere to move into given the exclusion constraints of its neighbors. Unlike other density and volume metrics, such as volume fraction or Voronoi volume, the free volume provides information not just about how much volume there is per particle but also whether the particle could potentially use that volume for motion. Further, the free volume is particularly sensitive to very small density fluctuations. Here, we present some preliminary results examining the free volume of a shear transformation zone leading up to its transformation.

We calculated numerically the free volume for every particle in a colloidal glass during deformation. In Figure 5.21, we focus on a particular shear defect, chosen because it was well-separated from other high-strain regions so that the core of the inclusion was clear by inspection. The red dashed line shows the average free volume in the entire sample, which is nearly constant over the time interval shown. The average free volume of the shear defect, however, changes significantly over time, fluctuating first about the mean and then growing steadily to a maximum of \( v_f = 0.16 \mu m^3 \) in the time leading up to the shear transformation.

We can make a simple estimate of what an average free volume of 0.16 \( \mu m^3 \) means by roughly converting that to a volume fraction. The zero-free-volume reference state is random close-packing, which has a volume fraction \( \phi_{RCP} = \Omega/V_{RCP} \), where \( \Omega = 1.96 \mu m^3 \) is the average particle volume and \( V_{RCP} \) is the Voronoi volume at random close-packing. If we naively simply add the average free volume as if it were additional Voronoi volume, then in the vicinity of the shear defect the effective local volume fraction would be \( \phi_{eff} = \frac{\Omega}{V_{RCP}+v_f} = 60.8\% \) for this simple estimate. The average for the entire sample, on the other hand, corresponds to a volume fraction of about 62.5\%. This is a significant reduction in the region of the defect, which seems to have facilitated the shear defect activation.

Just after the cluster reaches its maximum average free volume, the defect transforms and simultaneously gives up most of its free volume, returning to a dense, immobile state with an average free volume significantly below the average for the bulk material. With the extra volume
Figure 5.21: (black line and points) The average free volume versus time for a cluster of particles that was identified by eye as a shear defect: a local region of high plastic strain that underwent an irreversible shear transformation between time 21 and 22. Leading up to the transformation event, the average free volume in the vicinity of the defect increased until the transformation occurred; after that, the defect lost or used up its free volume, and became irreversibly locked into its new configuration. By contrast, the average free volume for the bulk sample remained very nearly constant over this time interval (red dashed line).
gone, the cluster becomes locked into its new configuration, and hence remained an irreversible transformation.

5.8 **Reversible and Irreversible Deformation**

We have mentioned our related work studying irreversible deformation and the onset of yield in hard-sphere colloidal glasses \[49\], but for the most part that work has not been included in this dissertation. However, the shear experiments reported in this chapter provide an interesting insight into reversible elastic deformation in the glasses, so we do include that briefly here.

In Figure 5.22, we plot both the average local strain in the glass (as in Figure 5.8 above, but without doubling to convert to \( \gamma \)) during on complete strain cycle, and we also plot the root mean squared of the strain. As we saw above, the strain energy is proportional to \( \epsilon^2 \), so we can think of this latter plot as representing the strain energy. Both the strain and RMS strain plots start a value of zero at the reference time, by definition.

The RMS strain plot shows a number of interesting features. First, just from thermal fluctuations, at the first time step there is noticeable strain energy in the glass, even though there has not yet been any applied strain. (We also saw this directly earlier when we examined the strain field fluctuations and shear defects active without any applied strain.) From there, the RMS strain increases with increasing strain, which is sensible.

After the bulk strain reaches its maximum and begins to reverse back to zero, remarkably, the RMS strain also decreases for some time before it begins to increase again. We understand this as the recovery of the elastic and anelastic reversible strain stored in the material on strain reversal. Once the glass reaches its yield point going in the opposite direction, the total strain energy begins to increase again.
Figure 5.22: The average shear strain, $\langle \epsilon_{yz} \rangle$ (circles), and the root mean squared shear strain, $\langle \epsilon_{yz}^2 \rangle$ (squares) during a deformation experiment to $\gamma_{max} = 10\%$ at $\dot{\gamma} = 2 \times 10^{-5}$ 1/s. Remarkably, the RMS strain – which is proportional to the strain energy – decreases for some time on strain reversal before beginning to increase again, indicating recovery of elastic strain energy.
5.9 Conclusion

In this chapter, we reported experiments using confocal microscopy and digital image processing to follow the individual trajectories of monodisperse, hard-sphere particles in a colloidal glass as an experimental model for amorphous metals. We observed both the individual particle and bulk dynamics of the glass under conditions of quiescence and applied shear strain. We showed that shear defects exist and are active in both sheared and quiescent colloidal glasses. We characterized the defects as Eshelby inclusions, and showed that the strain field calculated for Eshelby inclusions in an elastic matrix agrees quantitatively with our experimental observations. We estimated the size and strain of typical, thermally-activated inclusions. We also measured the shear modulus as a function of height in the glass, and observed that the shear modulus decreases and becomes more uniform throughout the material as a result of applied shear deformation, likely due to dilation of the glass during strain. We showed that the energy required to activate the shear defects is consistent with the available thermal energy. Finally, we presented first results that the free volume leading up to a shear transformation may be a good indicator of a developing shear defect.

The result of this chapter provided a deeper physical understanding of the detailed physics of shear transformation zones in glasses, but there is still much to learn. The theoretical framework of Eshelby inclusions in turn provides insight into the local, physical mechanism of shear defect formation and their role in the deformation of glasses. We plan to use the Eshelby framework not just to analyze shear defects, but to identify them in an efficient, automated way by fitting the displacement fields in the colloidal glass to those predicted for in and around an Eshelby inclusion. This will enable us to make a more statistically significant study of the population of shear defects, their activation energies, and the local volume fluctuations that may be lowering the barrier to activation.
This dissertation has explored structure and defects in colloidal crystals and glasses, keeping in mind the potential applications of these materials while probing fundamental physics questions about structure-property relations in materials.

Chapter 1 introduced colloidal materials and the fundamental physics questions we address using colloids as experimental models. Chapter 2 introduced the experimental system and measurements in detail, particularly describing new tools and techniques that were developed for this work.

In Chapter 3, we explored the mechanisms of structure formation in colloidal systems, with particular focus on templated sedimentation techniques. We found that in epitaxial growth of colloidal materials, the boundary condition set by the bottom substrate and the dimensionless flux
(volume fraction \times \text{Peclet number}) determined the resulting structure. Further, we found that on deterministic templates, only the boundary condition matters, so that perfect crystals can be formed at arbitrarily high flux. We also found that the critical flux for creating an amorphous structure on non-deterministic templates was not as high as previously believed. We designed amorphous templates that initiate the amorphous crossover from the very first layer, and showed that these can reliably produce colloidal glasses by sedimentation above the critical flux without any need for centrifugation.

Next, we used this understanding of the physics of colloid structure formation to create perfect crystals and glasses as experimental models of atomic materials. In Chapter 4, we studied the extended defects (dislocations and stacking faults) that can nucleate and grow in FCC crystals formed on (100) templates if the crystal exceeds a critical thickness that depends on the lattice misfit with the template spacing. The experimental observations of the density of misfit dislocations are accounted for by the Frank-van der Merwe theory, adapted for the depth-dependent variation of lattice spacing and elastic constants that results from the gravitational pressure.

Finally, in Chapter 3 we reported the first analyses of detailed experiments exploring the specific, local mechanisms of deformation in a colloidal glass. We showed that shear defects exist and are active in both sheared and quiescent colloidal glasses and characterized the defects as Eshelby inclusions. Using our measurements of the shear modulus of the glass and the average defect size, along with a rough measurement of the internal strain of the defect, we showed that the energy required to activate the shear defects is consistent with the available thermal energy. Furthermore, we found that a local reduction in the shear modulus resulting from local dilatation can lower the energetic barrier for shear defect activation.

There is much more we can learn from these deformation experiments. Now that we know something about the population of shear defects present in a colloidal glass, we are focusing on using the Eshelby framework to identify and characterize individual shear defects. We are also looking more closely at the local strain and energy recovery on strain reversal to better understand the elastic response and the onset of plastic deformation in the glass.

Additionally, this work suggests a number of directions for further study. There is more we
would like to understand about glass formation using amorphous templates. We hypothesize that deposition flux should have an effect on the final structure or overall density of a templated glass, but our preliminary results have been inconclusive. With Saraf Nawar, we are experimenting with interstitial trapping, attempting to grow binary hard-sphere crystals by rapid sedimentation, and growing templated crystals with a new particle system. With Emily Redston, we are pursuing a more detailed study of the structure and dynamics of a vertical amorphous-crystalline interface using the template described in Section 3.2.2.

All of these studies are possible because we can control structure formation in monodisperse, hard-sphere colloids, and because colloidal crystals and glasses work so well as experimental models of atomic crystals and glasses. These relatively simple materials will undoubtedly continue to provide deep insights into the the fundamental physics of more complex materials for many years to come.
Experimental Details

This appendix contains a great deal of wisdom that’s too detailed for introduction: useful numbers, specific procedures, some tips and tricks, and a few things that you just shouldn’t do even if they seem like a good idea at the time. I hope these suggestions help make your experiments go smoothly. Good luck!
A.1 Some useful numbers related to this work

Particle diameter (specified by Micromod, and checked with SEM and by measuring the sedimentation velocity in pure water): \( d = 1.55 \mu m \).

Particle radius: \( R = 0.775 \mu m \)

Particle volume: \( \Omega = \frac{4}{3} \pi R^3 = 1.95 \mu m^3 \)

Particle density (approximate): \( \rho = 2.1 \text{ g/cm}^3 \)

Density difference (in water/DMSO): \( \Delta \rho = 0.94 \text{ g/cm}^3 = 940 \text{ kg/m}^3 \)

Buoyant mass (in water/DMSO): \( \Delta m = \Omega \Delta \rho = 1.8 \times 10^{-15} \text{ kg} \)

Weight of a single particle (in water/DMSO): \( (\Delta m) g = 1.8 \times 10^{-14} \text{ N} \)

Boltzmann’s constant: \( k_B = 1.38 \times 10^{-23} \text{ J/K} \)

Thermal energy, room temperature (293K): \( k_B T = 4.05 \times 10^{-21} \text{ J} \)

Gravitational length (in water/DMSO): \( l^* = \frac{k_B T}{(\Delta m)g} = 0.23 \mu m \)
A.2 Photolithographic process for the fabrication of templates in glass coverslips

(Revised 01/16/13 from the 05/26/2007 version originally written by Peter Schall.)

1. Cleaning of the glass slides

Sonicate cover slips for at least 10 minutes in acetone, move quickly into methanol and sonicate for at least another 10 minutes.

2. Spin coating

Spin coat Microprime Primer, followed immediately by Shipley S1805 photoresist. Each should be spun for 5 seconds at speed 500 rpm followed by 40 seconds at speed 4000 rpm. (This is typically spinner standard Recipe 4, but check each time.) Cure at 115°C for 3.5 min (hot plate).

3. Exposure

Expose slides using the OL-3 MJB3 Mask Aligner for 0.5-2.5 sec. The required exposure time varies depending on the size of the holes in the chrome mask and the power of the UV lamp that day.

Hints: Poor contact between the coverslip and the mask is the most common problem that ruins templates at this stage; watch for Newton rings as the glass is raised into “Contact” with the mask as a sign of good contact. Dust between the mask and the glass is another problem – especially from bits of the glass coverslip edges breaking off. These can cause poor contact or, worse, damage the chrome mask. Finally, be sure that the chrome side of the mask faces down when it’s on the mask aligner (which means it faces up when you place it on the mask holder).

4. Development and pattern checking

Prepare side-by-side small (100 mL) beakers with

1. 15 mL MF351 developer mixed with 75 mL water (1:5 ratio)

2. pure water for rinsing

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Develop exposed slides for 60-90 seconds in the developer. Using [plastic] tweezers, swish the slide gently in the developer at the beginning and end of the development to help wash away the photoresist. Transfer the slide to water and swish to rinse off any residual photoresist/developer. Dry with compressed air.

Check pattern under optical microscope. Make sure the light is coming from the upper light source; this has a yellow filter so that the coverslip can be returned to the developer solution if needed.) Use this step to calibrate exposure and development times, and repeat steps 3 and 4 on the remaining coverslips.

5. **Hard bake**

   Hard bake the photoresist onto the coverslips by heating at 115°C for 10 min (hot plate).

6. **Reactive ion etching (RIE) – WEEKDAYS 6AM-8PM ONLY!!!**

   Use the STS ICP RIE. Log in to the machine both using the main cleanroom tool login AND at the etcher itself as “Other” with your CNS user name and password.

   First, condition the chamber in two steps using the predefined recipe O2CLEAN for 20 minutes. Next, condition the chamber by running “Spaepen etch2” for 5 minutes.

   Affix samples to a carrier wafer (white) using the thermal paste (white and messy). It is very important to completely cover the back side of the slides, as any exposed glass will be etched and become cloudy. Run “Spaepen etch2” for 12 minutes (adjust time as necessary depending on results). Vent the load lock and re-position the carrier wafer so that it is in position. To strip the remaining photoresist, run “O2 Clean” for 3 minutes.

7. **Clean the coverslips, again**

   Use acetone, methanol or isopropanol, and lots of cleanroom paper towels to clean the thermal paste off of the slides (the paste will wipe off with acetone). Also clean the carrier wafer and put it away. Next, repeat Step 1 (sonication cleaning) to completely clean all of the thermal paste and residual photoresist off of the coverslips.

8. **Enjoy your templates!**
A.3 Template making – detailed procedure

This section is a highly-detailed version of the steps required to make templates, intended as a thorough reference for the reader.

It is possible for one person to make templates in one day, but the process is much more easily done over two days with two people working together on the first day to do everything leading up to etching (steps 1-5). With two people, the lithography process is much faster, less exhausting, and produces much more consistent results. The exposure and development steps can take a very long time, and the etching requires a specific time reservation and must be done between 6am-8pm on weekdays, so planning to etch on a different day relieves any time constraint. Also, fewer templates get broken due to fatigue-induced user error. The etching and final clean up can easily be done by one person on the second day.

Before entering the cleanroom - what can be done ahead

Before going into the cleanroom, gather everything you will need for template making. This includes:

- Cleanroom notebook and pen
- Procedure summary printout (in plastic cover)
- Template mask(s)
- #1.5 glass coverslips (usually 22x50mm)
- Teflon coverslip racks (10-slide rack and 7-slide rack)
- 500 mL beakers (x2)
- Tweezers (ideally 1 plastic, 1 metal)
- Permanent marker
- Optional useful items: extra tweezers, glass scribe, hefty metal tweezers, your own safety glasses
Ideally, do this the day before, so that it doesn’t add extra time to the fabrication day (which will be long enough!). All of the equipment should fit into one cleanroom box.

A few notes about this item list:

The procedure summary should either be printed on cleanroom paper or encased in a clear plastic sleeve to prevent paper dust from contaminating the cleanroom.

Only bring the masks with you that you intend to use; this helps to protect the other masks and saves on space.

Plastic tweezers are much better at holding glass than metal, so these are highly recommended for handling the glass coverslips. Metal tweezers are much more likely to drop or break the slides. However, the plastic tweezers will melt on the 115°C hotplate, so metal tweezers are required for steps involving the hot plate. It is useful also to have a hefty pair of metal tweezers for lifting the coverslip racks out of the cleaning solutions.

As part of pre-cleanroom preparation, it’s useful to pre-label the two 500 mL beakers with your name, phone number, “in cleanroom” (unless you expect to be elsewhere during slide cleaning), and “Acetone” and “Methanol”, respectively. Fill the racks with coverslips, and keep these in the beakers for now.

All chemicals required for template making are stocked by the cleanroom, and can be found in the cabinet below the bench where they should be used. These are: acetone, methanol, isopropanol, Microprime Primer, Shipley S1805 Photoresist, MF351 Developer, and thermal contact paste. All supplies not mentioned above are also provided by the cleanroom, including: small (100 mL) plastic beakers, eye droppers, paper towels, and aluminum foil.

All approximate supply amounts and times below are given for processing 17 coverslips (both racks full).

A.3.1 Step 1: Clean the coverslips

Place a coverslip rack (full) into a 500 mL beaker, and fill with enough acetone to cover the top of the coverslips (about 300 mL). Sonicate for ≥10 minutes. Meanwhile, put about the same volume of methanol into the other 500 mL beaker. At the end of the 10 minutes, transfer the coverslip
rack into the methanol beaker without allowing the acetone to dry on the glass. Sonicate for $\geq 10$
more minutes in the methanol.

Remove the coverslip rack from the methanol, allowing the fluid to drain back into the beaker.
Blow dry the coverslips with compressed air. (They can remain in the rack for drying.)

To save time, during the final sonication, start setting up a spinner for Step 2.
Step 1 usually takes about 40 minutes.

A.3.2 Step 2: Spin Coat with Photoresist

Set up a spinner with the largest chuck whose vacuum ridges will be completely covered by a
coverslip (so it will hold vacuum). Check that the hole though the center of the chuck is clear of
any residual photoresist.

Choose standard Recipe 4 on the spinner and check the steps of the recipe; these should be
5 seconds at 500 rpm followed by 40 seconds at 4000 rpm, followed by nothing else. Pro tip: “Step
Terminate” is the button to change the duration of a step in the spin recipe.

Test the spin recipe to make sure that the spinner holds vacuum and everything goes as
planned. Use an extra coverslip straight out of the box for this in case something goes terribly
wrong and the glass gets broken.

Set up a pair of small plastic beakers, labelled, with the chemicals needed for spin coating:
one with $\sim 10$ mL of Microprime Primer and the other with about $\sim 15-20$ mL of Shipley S1805
Photoresist.

Using the spinner recipe above, spin coat each of the clean coverslips first with Microprime
Primer, followed by a coat of Shipley S1805 Photoresist. (So each slide gets spun twice in a row.)
The primer helps the photoresist wet the glass.

After spinning the photoresist, transfer to the 115°C hot plate for 3.5 minutes. (An older
version of this recipe called for a 110°C hotplate, but the spinner bench hotplate is permanently
set to 115°C. I don’t believe it matters.)

If you have two people, it works well to have one person spinning and transferring to the hot
plate and the other keeping track of the baking time and recording everything in the notebook.
Use a permanent marker to number the coverslips as they come off the hot plate to keep track of which one is which as well as which side is up. Place the slides in labelled petri dishes (usually two per dish), photoresist up.

With two people, Step 2 takes about 1 hour. This can be a good point to take a short break, as steps 3-5 all get done together and can take a few hours, depending on the number of template patterns you are planning to make and whether you encounter any difficulties with the mask aligner or development.

A.3.3 Step 3: Mask exposure

If you have two people, do steps 3 and 4 concurrently. If working alone, set up the developer solutions for step 4 now, and take each coverslip through steps 3 and 4 until you are completely confident about the exposure settings.

We usually use the OL-3 MJB3 Mask Aligner (the orange one). It works well and is the simplest aligner to use, which works well for us because we have a very simple process. Most any of the mask holders will work for our masks, so you will likely not have to change it. Use the substrate chuck that has 9 holes in a square pattern. It should not have a vacuum seal ring on it; if the substrate chuck has a flexible plastic ring around it, remove the ring and put it away in its drawer before continuing.

Clean the mask with acetone, followed immediately by isopropanol (without allowing the mask to dry in between), then blow dry with compressed air. Set the mask onto the mask holder chrome side up so that the chrome side will be down when set on the mask aligner. Roughly align the mask pattern with the substrate chuck so that you the center of the chuck is roughly under the center of the template pattern. (This is just for convenience, and is not strictly necessary.)

Bring the substrate into hard contact with the mask, and expose the pattern for 0.5-2.5 seconds, depending mostly on the size of the holes in the mask and the UV lamp power (which is posted on the wall). On each coverslips, pattern several templates by bringing the coverslip back out from under the mask, moving the slide to a new position, bringing this new area into contact with the mask, and exposing again. (The previously-exposed areas will be under solid chrome, and
hence protected from receiving any additional UV light.) You may want to use different exposure times for each individual template pattern to try a range of template hole sizes. On a 22mmx50mm coverslip, you can fit about 6 copies of the large double templates (such as (100) or Σ5), and 2 rows of about 8 copies of the small single templates (such as BOATS, Am-C, or FSP).

For the first slide, explore a range of exposure times around where you think the ideal time will be based on previous experiments. Before exposing any other coverslips, develop this one and check the pattern under the optical microscope adjacent to the developing station (step 4) to determine the ideal exposure conditions. Repeat these steps until you are satisfied with the exposure settings for this mask. At this point, you can go ahead and expose patterns onto the rest of the slides before developing them, but I recommend developing and checking the pattern once in a while just in case anything is starting to go wrong systematically. (This is a point where it is ideal to have a second person developing slides and checking patterns concurrently while the first does the mask aligning and exposure.)

Each mask is different. If using more than one, the steps for determining the ideal exposure time must be repeated for each mask. This can be very time consuming, so plan accordingly when deciding what templates to make in a given cleanroom session.

Hints: Poor contact between the coverslip and the mask is the most common problem that ruins templates at this stage; watch for Newton rings as the glass is raised into “Contact” with the mask as a sign of good contact. Be careful about dust between the mask and the glass – especially from chips of the glass coverslip breaking off. These can cause poor contact or, worse, damage the chrome mask.

A.3.4 Step 4: Photoresist development and pattern checking

Prepare two side-by-side small (100 mL) plastic beakers. In one, mix 15 mL MF351 photoresist developer with 75 mL water (a 1:5 mixture). Fill the other with pure water for rinsing. (And label everything well.) Note that the photoresist developer bench, which is directly across from the OL-3 MJB3 Mask Aligner, requires a face shield for use. It’s useful to set this up near the timers and near one of the compressed air blowers.
Check the pattern under optical microscope. Make sure the light is coming from the upper light source; this has a yellow filter so that the coverslip can be returned to the developer solution if needed.) Compare the different exposure times to choose a time or range of times that work best. If the features seem indistinct, or like the photoresist didn’t all come off from the pattern, return the coverslip to the developer for an additional 20-30 seconds. Strange-looking features that don’t replicate the mask pattern or templates that are partially washed out are likely caused by poor mask contact. Use this step to calibrate exposure and development times, and repeat steps 3 and 4 on the remaining coverslips.

If you are satisfied with the exposure and development settings, and not changing masks, it’s ok not to check every slide; however, do check a slide every now and then just to make sure that nothing is starting to go wrong systematically.

Steps 3 and 4 together, for a single mask, with good luck and everything working well, take at least 1.5 hours. It can take much longer if you have any problems with the aligner, or you are planning to use multiple masks (which requires determining different exposure and development times). For this reason, it’s a good idea to allow a lot of time for this step; best of all, plan to end the day just after this with Step 5 (which is very short), and to etch on a following day.

A.3.5 Step 5: Hard Bake

Hard bake the photoresist onto the coverslips by heating at 115°C for 10 min (hot plate). (This exact time is not critical.) This hardens the photoresist so that it will be more resistant to reactive ion etching and hence produce sharper features.

After the hard bake, return each coverslip – patterned side up – to its petri dish.

Step 5 is quick; if you can fit all of your coverslips onto a single hot plate, you can do it in 10 minutes.

This is a very good time to take a long break, or to stop for the day. If you do, stack the petri dishes containing the slides and wrap them well in aluminum foil so that they will be protected from light (which can damage the resist). Label them well, and leave them on the shelf in the yellow-light part of the cleanroom (near the door).
A.3.6 Step 6: Reactive ion etching (RIE)

We use the STS ICP RIE for etching templates directly into the glass. Our recipe – Spaepen Etch 2 – is a variation on a standard SiO$_2$ nitride etch. The etch recipe details are below.

I recommend reserving the etcher for 3 hours.

After logging in to your etching reservation, log in on the etcher computer itself by selecting the login type “Other” and entering your CNS username and password (or whatever you have chosen for your login credentials). Run the standard recipe O2CLEAN for 20 minutes, followed by Spaepen Etch 2 for 5 minutes to clean and condition the chamber. This whole step takes about 40 minutes.

Meanwhile, prepare the first slides for etching. Start with just one or two coverslips in case the etch parameters aren’t quite right yet. (Occasionally the etcher will be much less or much more powerful than last time, so the first etched slides will be for testing the etch parameters.) Coat the backside of the coverslip with a thin layer of thermal paste (provided by the cleanroom), and affix it to one of the transparent wafer-shaped slide carriers. At absolute minimum, the thermal paste must cover the area behind the templates, because any region that is not pasted to the slide carrier will “burn” and become cloudy on the back side. However, an excess of thermal paste around the coverslips will also burn and leave dark brown lines on the carrier. Ideally, the back side of the coverslip is completely coated and makes good contact with the carrier, but little or no excess thermal paste sticks out around the edges.

Etch 12 minutes (± about a minute, depending on the behavior etcher that day) using Spaepen Etch 2. If happy with the results, you can then strip the remaining photoresist by running O2CLEAN for 3 minutes. (This will not etch the glass.) The resist will also come off later in the final cleaning step with acetone and methanol, but it’s a good idea to O2CLEAN the first couple of batches at least so that you can see immediately how the templates are turning out.

If needed, repeat with just one or two slides per etch until you are happy with the etching conditions and results. After that, feel free to cram as many coverslips onto the carrier wafer as you like.

Etch.
A.3.7 Step 7: Final clean

Bring the carrier wafer back to the sonication bench. Using cleanroom towels and copious amounts of acetone followed by isopropyl alcohol or methanol, clean as much of the thermal paste off of the coverslips as possible. This cleaning will remove the numbers labeling the slides, so keep careful track of which slide is which and what orientation it’s in. Put the coverslips back into the coverslip racks that they started the process in, and mark the coverslip rack with a permanent marker so you know what order the slides are in.

There is likely still some residual thermal paste on the templates after this. Repeat Step 1 (sonication in acetone, methanol) as a final cleaning and drying step. Finally, re-label the slides with a permanent marker.

The boxes that the coverslips come in make great template storage boxes.

A.3.8 Step 8: Enjoy your templates!

Use an optical microscope (such as the one in the optics room) to evaluate the template quality. The best templates have large, well-defined holes that come close to touching or just touch.

A.4 How to use the calibrator

The simple device we invented for measuring the pixel-to-micrometer scaling on the confocal microscope is described in detail in Section 2.1 above, as well as in Ref. 57. What follows here is a detailed procedure for how to actually use the device.

A.4.1 How to take calibration data on the confocal microscope

This procedure assumes that the calibrator is already assembled with the reference pattern slide in place (since this only needs to be done once). If you are assembling the calibrator for the first time, or replacing the calibrator slide, see Section A.4.3 below for assembly instructions.

Place the calibrator on the confocal microscope so that it is secure on the stage. Add the fluorescently dyed DMSO/water mixture into the reservoir at least until the bottom edge of the
Figure A.1: The calibrator in use.
reference grid slide is completely submerged. Refer to Figure A.1.

The precise amount of fluid doesn’t matter, and you don’t need to fill the reservoir. It is important to use the water/DMSO mixture that matches the index of refraction of silica so that the calibration measurement is not affected by any refractive effects. We usually use supernatant left over from concentrating colloid suspensions, which does contain a trace concentration of silica colloidal particles. These trace particles are useful during alignment to make sure that the imaging settings are reasonable.

First, determine the approximate location in x, y, and z of the reference pattern. Use a low magnification, long-working-distance objective for this rough alignment, such as the 10x air objective. Find the x-y position where the reference pattern slide is closest to the bottom of the reservoir. Without moving in x-y from this position, lower the objective turret completely and then use the Mark & Find module in the confocal software to mark this x-y position.

Switch to the objective lens that you will use for your actual experiment. (Often this is the 100x oil objective.) Return to the marked x-y position, and raise the objective lens until the reference pattern slide comes into view. Be careful not to exceed the maximum working distance of the objective lens!

If you are unable to find the reference pattern slide, it may be that the slide is positioned too far from the bottom of the reservoir. Try repeating the rough alignment with the low magnification objective, again looking for the lowest point of the reference slide. If you still can’t see the reference pattern with the higher magnification objective, you may need to reposition the reference pattern slide. See Section A.4.3 for instructions on how to do this.

If you have already used the calibrator in its current assembly, you may already have an idea of where the reference pattern is. If so, you can skip the rough alignment step and proceed straight to the higher magnification objective. For the calibrator configuration that KEJ set up, the reference pattern is about 40 micrometers above the bottom of the reservoir.

Once you can see the dots of the reference pattern clearly, set the scan angle in the x-y image settings to 90° and then adjust the angle so that a column of dots is perfectly vertical on the screen. This ensures that the reference pattern is aligned with the coordinate axes of the confocal
microscope.

Finally, take an image stack of the reference pattern. Set the resolution, scan rate, z-step size, and other parameters of the calibration stack to be as close as possible to what you will use or have just used in your experiment, so that you can be confident that the measured calibration will be correct for your experiment.

A.4.2 How to Analyze Calibration Data

There are various ways that you might automate the calibration process, but I’ve found it easiest simply to measure the calibration by hand.

Make a graph of dot center position in micrometers versus its center position in pixels as in Figure 2.8. and then fit a straight line to these data. The slope of the line is the calibrated pixel-to-micrometer conversion factor. This works equally well for all three axes.

A.4.3 Calibrator Assembly and Setup

Setting up the calibrator for the first time is straightforward but takes a little care, especially in handling the reference pattern slide. However, once the calibrator is assembled with the reference pattern in place, it should never need adjustment and can be used indefinitely. (Or, at least, until someone drops it.)

First, screw the wedge onto the base. Then, glue a large-area coverslip to the bottom side of the base in order to seal the reservoir. Very loosely attach the small metal bracket to the wedge with the two small screws.

Take a slide (usually a #1.5 22mm-by-50mm coverslip) patterned with the calibration reference grid, and cut the glass so that the new edge cuts through one of the reference patterns. Make additional cuts as necessary to ensure that the desired reference pattern will be easy to identify and, when installed, will be close to but not quite touching the bottom of the reservoir.

For an example of this, see Figure A.2. Here, the reference patterns are clearly visible; due to Bragg refraction, they appear colored. The upper row of reference patterns has a larger spacing of 1.70 $\mu$m between dots, so I cut away the end of this row at an angle so that only the end of
the lower row is available. This has a spacing of 1.63 μm between dots. The rest of the slide edge is carefully cut so that no part sticks out significantly farther than the region with the reference pattern, as this could prevent the reference pattern from being close enough to the bottom of the reservoir for imaging.

![Image of assembled calibrator](image)

**Figure A.2:** Assembled calibrator, perspective view from above. The reference patterns are clearly visible due to Bragg diffraction. A thicker glass slide can be used to help support the reference pattern slide, as in this example, but this is not necessary.

Complete the assembly of the calibrator by holding the reference pattern slide so that the pattern faces down (toward the reservoir) and sliding the other end of it under the metal holding bracket. Gently place a fingertip on the reference pattern slide against the wedge, and slide it down until it just stops moving. At this point, the cut edge is just contacting the bottom of the reservoir, but the reference pattern slide should not be bent at all. Optionally, you can use a thicker blank slide as a backing to reinforce the reference pattern slide. The assembly examples in Figures A.2
and \[A.3\] both show a backing slide in use, but I find it’s not actually necessary to prevent the reference pattern slide from bending.

Don’t tighten down the metal bracket yet! Rather, use the calibrator for the first time with the metal bracket still loose, but be sure to allow a little of the reservoir fluid to wet between the wedge and the reference pattern slide. This will cause the slide to adhere tightly to the wedge by capillary forces, but it will still be adjustable along the wedge, so that if you need to make adjustments during the initial use that’s easy to do. Once you are happy with the positioning of the reference pattern slide, only then gently tighten down the screws of the metal holding bracket. Take care not to over tighten them, as you could break the reference pattern slide.

Once the calibrator is set up and secured, it can be used indefinitely without further adjustment.

A.4.4 QUICK WAYS TO CHECK YOUR CALIBRATION, OR WHAT TO DO IF YOU DIDN’T TAKE CALIBRATOR MEASUREMENTS WITH YOUR EXPERIMENT

A WORD OF CAUTION

These are last-resort suggestions. You should make a true calibration measurement before and/or after your confocal experiment. However, if you didn’t, there are ways to use colloid position data to estimate what the calibration should be. It’s not ideal to try to calibrate measurements based on your data; furthermore, these techniques require making assumptions about the structure or dynamics of your colloid. So use the suggestions of this section only with caution, and if you don’t have any way to make an independent calibration measurement.

CALIBRATION USING THE DIRECTIONAL RADIAL DISTRIBUTION FUNCTION, \(g(\vec{R})\)

By looking at the radial distribution function \(g(R)\) of your colloid sample, you may be able to see immediate evidence that there is a calibration problem. Symptoms of poor calibration include peaks that are asymmetric or have a strong shoulder, or extra peaks that don’t seem to correspond to any reasonable structure. For some crystal structures and orientations, the nearest neighbor
Figure A.3: Calibrator assembled without the large-area coverslip to seal the bottom, view from below.
peak may look perfect even when there is a calibration problem, but subsequent peaks will show the symptoms of the mis-calibration.

If you know what structure you expect to have, you can re-calibrate the distance measurements by computing the directional radial distribution function $g(\vec{R})$. By comparing the locations of the first few peaks in $g(x)$, $g(y)$, and $g(z)$, you can check the relative calibration of the microscope in all directions. KEJ wrote Matlab software to do this; see the software list and summary at the end of the thesis in Appendix ??.

If your colloid structure is truly isotropic, then the radial distribution function $g(\vec{R})$ should look identical in all directions, starting with the very first peak. If that peak is shifted for one of the directions, then you have a mis-calibration in that directions. For example, if the first peak in $g(z)$ is at a 10% larger distance than the first peak in $g(x)$ or $g(y)$, then you know that the pixel-to-micrometer conversion factor is 10% too large in the z-direction, and you can correct accordingly.

If your colloid is not isotropic, but has a known structure, the technique of comparing $g(\vec{R})$ along the coordinate axes can also be used. However, care must be taken to work out what the $g(\vec{R})$ peaks should be along the different directions, as they may not be the same. For example, in a templated FCC crystal grown in the (100) orientation, there is no nearest-neighbor peak in the z-direction. Rather, nearest neighbors exist only in the x-y plane, but there is a second neighbor ($\sqrt{2}$) peak in all directions, so this can be used for the calibration.

We used this calibration technique before the calibrator was built. The crystal structure data from Chapter 3 was calibrated in this way, as well as some of the glass deformation data analyzed in Chapter 5.

**Other Calibration Methods**

In a more dilute sample, the colloid structure may not be sufficiently well defined to use the calibration technique of the previous section. The problem then becomes even more difficult. If the motion of the particles is expected to be isotropic, then it may be possible to calibrate the length scales by comparing the displacement distribution in each direction, as another symptom of
mis-calibration is a much greater apparent mobility is some directions than others. Note that this requires a density-matched sample, so that gravity does not affect the motion.

It should also be possible to calibrate based on a 3D image of a known object included in the sample, such as a large sphere. This may be a simpler method than using the calibrator, but requires a different setup and may not be as accurate, depending on the size of the reference object and how precisely its dimensions are known.

A.5 Procedure for Deformation Experiments

A.5.1 Sample Preparation and Loading

In order to perform deformation experiments on a colloidal glass, it is first necessary to load the glass into a shear cell with good contact at the top and bottom of the shear gap.

I designed and machined a miniature shear cell (MSC) that is small and light enough to go on the z-galvo stage of the confocal microscope. The MSC weighs approximately 180g with a sample loaded on it. See Figure A.4 for a detailed schematic.

The MSC is designed so that it can either be used with a sample cell assembled and filled separately and then mounted in the MSC, or so that it can be used with its own built-in sample cell. Most of my deformation experiments were performed in the latter configuration, with a BOATS amorphous template as the bottom of the sample reservoir. The template is affixed to the bottom of the sample cell using Norland optical adhesive, cured under UV light for at least 20 minutes (more typically a few hours). This creates a sample cell directly integrated into the shear apparatus.

Once the glue has cured and the template is attached to the bottom plate, we start to assemble the full MSC. The next piece is the piezo drive, which itself is the largest and heaviest piece of the entire apparatus. At this point, while the template pattern is still easily visible from above, I put the partially-assembled MSC on the confocal microscope and rough-align the microscope objective with the template pattern (Figure A.4). I mark this x-y stage location in the confocal software so that I can easily return the MSC to the same position, facilitating later alignment.

Next, I take the MSC back off of the microscope, and attach the top arm with post (see
Figure A.4: Shear cell schematic.
Figure A.5: Miniature shear cell (MSC) partially assembled, with base plate, template (visible at right with microscope objective lens below), and piezo unit attached.
schematic in Figure A.4, and photograph in Figure A.6. The base of the post is hollowed out, and a copper TEM grid is glued across the bottom with Norland optical glue. The hollowed region is further perforated by large holes drilled perpendicular to the post, so that when submerged in a colloidal suspension the entire volume above and below the grid is easily accessible to the colloid. A 2-56 screw enables simple vertical motion of the post; one-eighth of a complete turn corresponds to a vertical displacement of 57 micrometers.

![Image](image.jpg)

**Figure A.6:** Miniature shear cell (MSC) assembled.

I pipette the colloid suspension at an initial volume fraction of $\phi_0 = 3.5\%$ into the reservoir. The exact volume introduced determines how high the sediment will be; typically, I add about $\sim 300\mu$L. I put the assembled and filled MSC back on the confocal microscope and return the x-y stage to the same alignment as previously noted, so that I know the objective lens is just below the template even though I can no longer see through to the lens.
I now begin final positioning of the top grid at the desired gap height above the template. Starting with the 10x air objective, which has a maximum field of view of a couple of millimeters, I bring the template into view on the microscope, and then shift the focus a couple hundred micrometers above the template. The precise lens position is unimportant because the 10x air objective has a very large depth of field. At this point, I can see the faint shadow of the template. By turning the vertical motion screw, I bring the top grid down until I can see it clearly in the microscope; see Figure A.7 for an example of this. This view allows me to verify that the grid is level and intact, and what parts of the template it is positioned over.

I center the image on a representative section of the template. I add Parafilm around the top of the sample reservoir to limit evaporation of the colloid fluid phase. I also wrap some Parafilm tightly at the base of the height adjustment screw for side-to-side stability during the shear experiment. Figure A.8. All that remains before setup is complete is the final positioning of the grid.

I switch to the 100x oil-coupled objective, which I will use for the experiment. Since I already know that the objective lens is aligned with the template, and further aligned under the top grid, I can finish positioning the grid with confidence that I won’t crash the objective or break the grid with the sample. (See Section A.6 for more commentary on what can go wrong.) I again bring the template pattern into view, and then position the objective lens focus about 80 micrometers above the template – about 10 μm below the maximum working distance of the lens. I then turn the screw in order to bring the top grid down into the field of view. Once I see the grid, I move the focal plane to correspond to the top of the desired gap height, and very slowly bring the grid down the rest of the way into position.

From the moment the colloid is added to the sample reservoir, the particles are sedimenting onto the template. However, the entire procedure of positioning the grid takes less than half an hour, during which time the sediment will only have grown a small amount. The exact height at that point depends on the initial volume fraction, but for any of our experiments the compact sediment has not yet grown up anywhere close to the gap height by the time positioning is finished.
Figure A.7: Large field-of-view image of the TEM grid in place over the template. The template pattern is printed in four sections, which are visible in the background. The honeycomb-like shadows result from residual lens oil on the underside of the template.
Figure A.8: Miniature shear cell (MSC) assembled and ready for use.
This means that the entire setup is in place before the sediment grows. I then leave the setup for six to eight hours so that sedimentation is complete before I begin deformation experiments. By forming the glass by high-flux sedimentation with the top grid already in place, the grid is automatically embedded deep within the glass, and so makes a stable contact with the top of the shear gap.

A.5.2 Deformation experiments

Once the glass is fully sedimented, everything is in place for deformation experiments. I finalize my choice of location where I will acquire image stacks during deformation, and set up the stack sequence for the experiment. Typically, I take a high-resolution full-gap stack prior to beginning any experiments so that I have a baseline structure all the way from the template into the top grid. If quiescent or relaxation data is desired, I might take many of these full-gap stacks over time.

For a deformation experiment, I acquire two distinct image stacks at each time step: a low-resolution (dz ≈ 0.75µm/pixel) rough image stack spanning the entire gap height, and a high-resolution (dz ≈ 0.08µm/pixel) over a limited field of view in the center of the sample, away from the boundary conditions at the top and bottom of the shear gap. The former allows me to monitor the overall deformation and be sure that there is no wall slip at the template or the grid, or shear banding in the sample.

I use a Matlab program to control the piezo stage via an RS232 communication bus. The software has a graphical interface and is straightforward to use for simple shear or single shear cycles (an excursion at a fixed rate to a maximum strain and return to zero at the same strain rate). More complex stain patterns are possible by hard-coding the desired strain sequence into the software. The software will show the programmed strain pattern prior to starting. As the experiment progresses, the actual measured piezo position is plotted every several minutes on the screen. Both the requested and actual realized positions are recorded automatically by the software. A typical complex-shear experiment setup is shown in Figure A.9.

As seen in the Figure, a complex shear sequence consists of several shear excursions to various strains and at various strain rates, with a quiescent time in between experiments usually lasting
Figure A.9: Shear cell software screenshot.

1000-2000 seconds.

Once the shear experiment is complete, I export the confocal data as TIFF images and save the measured piezo position data. The sample can potentially be used again, either as-is or by raising the top grid all the way up, remixing the colloid, replacing the grid, and re-sedimenting. I do not recommend attempting to remix the sample while the grid is in place (see Section A.6 for more details).
A.6 What not to do

Sometimes disaster strikes. Samples are destroyed. Hearts are broken. My goal here is to help you avoid some pain by describing some of the ways things have gone horribly wrong for me at times.

Don’t drop your sample. This goes without saying. However, it did not stop me from trying to take images of it anyway. They didn’t look good.

Turn the laser on. The power, the key, and in the confocal software. Unfortunately, the confocal software won’t tell you when the interlock key isn’t turned, so pay attention. Otherwise terrible things can happen. See Figure A.10 for evidence thereof.

“And as a result, the sharks got smarter.”
Figure A.10: This is an example of what can happen when you forget to turn the laser on and crash the sample. Don’t do this.
Figure A.11: This is an example of what can happen when you stab through the TEM grid with a pipette and then crack the template while trying to flatten the grid back out. Don’t do this either.
References


[45] We purchase specially-filtered Sicaster plain particles from Micromod. www.micromod.de


Why is everything glass?

Whether natural or synthetic, the primary ingredient in glass is silica (silicon oxide). The obsidian and pumice of this lava flow contain about 75% silica, like most window glass does in a hot, molten state, silica's atoms tend to stick together and create webs of molecules that slow down the movement of all atoms. The surface of this lava flow cooled off before its atoms had time to organize into crystals, so we are left with glass instead.

CRystal
Organized atoms in crystals

GLASS
Disorganized atoms in glass and obsidian

OBSIDIAN
Solid glass with inclusions