Micromechanics and rheology of hard and soft-sphere colloidal glasses

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3. Sample preparation and data acquisition

3.1: Synthesis

PNIPAM microgel particles have been synthesized using a precipitation polymerization method [1]. Typically, NIPAM monomer and the cross linking agent methylene-bis-acrylamide (BIS) are mixed in water under a nitrogen atmosphere [2]. Different amount of sodium dodecyl sulfate in water are used as surfactant to control particle size. Potassium persulfate (KPS)-water solution is added to the reactor to initiate polymerization. To prepare the particles for imaging by confocal microscopy, we have added fluorescein dye that makes them visible under fluorescent imaging. A dye solution is prepared using 5(6)-Amino-tetramethylrhodamine (ATMR) dissolved in DMSO and a separate solution is prepared with 1-Ethyl-3-[3-dimethylaminopropyl] Carbodiimide Hydrochloride (EDC) dissolved in water. The reaction is kept at 70 °C for 4h. After cooling down the solution to room temperature, we filter it. Finally, we centrifuge the solution and remove the supernatant in order to increase the volume fraction of the colloidal suspension. Fig. 3.1 shows a schematic of the synthesis steps used to make the particles.

Table 3.1 shows the amount of chemical material used. To introduce electric charges to PNIPAM particles, one can make copolymer microgels by incorporating different monomers. Typically, PNIPAM-co-acrylic acid (AAC) [3] microgels are negatively charged while PNIPAM-co-allylamine [4] microgels are positively charged in a neutral pH environment.

<table>
<thead>
<tr>
<th>Nipam</th>
<th>AAC</th>
<th>BIS</th>
<th>KPS</th>
<th>SDS</th>
<th>EDC</th>
<th>ATMR</th>
<th>MDSO</th>
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<td>0.06</td>
<td>0.05</td>
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<td>4</td>
<td>1</td>
<td>2</td>
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<td>(mg)</td>
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</tr>
</tbody>
</table>

*Table 3.1: Materials and their amount used for the microgel synthesis. The amount of SDS changes the size of the particles.*
3.2: Preparation of hard and soft-sphere glasses

We prepare hard-sphere colloidal glasses by suspending PMMA (polymethylmethacrylate) spheres in a mixture of cisdecahydronaphthalene (cis-decalin) and cycloheptylbromide (CHB) that matches both their refractive index and density. These particles have a radius of $R=0.13 \, \mu m$ (used in chapter 4) and $R = 0.65 \, \mu m$ (used in chapter 5), with a polydispersity of $\sim 10\%$ to avoid crystallization, and are sterically stabilized with a layer of grafted poly-12-hydroxystearic acid (PHSA), 10nm in length. We prepared suspensions with volume fractions between $\phi = 0.54$ and 0.6 around the hard-sphere glass transition by diluting suspensions centrifuged to a sediment. Soft colloidal glasses are prepared using the synthesized poly-N-isopropylacrylamide (pNIPAM) microgel particles with a cross linker density of 2%wt, suspended in water. These particles swell in water at room temperature, but shrink and undergo a reversible volume phase transition at $T \sim 32^\circ C$. This allows to change the particle size and to control the packing fraction directly with temperature [5, 6]. We prepared dense PNIPAM suspensions by centrifuging the suspension to a sediment, similar to the hard-sphere samples. We define the effective volume fraction $\phi_{eff} = n V_{ss}$, where $n$ is the number density of the particles, and $V_{ss} = 4\pi R^3/3$ is the volume of the undeformed particle in dilute suspension [5, 7]. We calibrate the measurement of $\phi_{eff}$ by diluting the final samples by a known amount, using the Bachelor expression (2.10) to determine the volume fraction of the diluted suspension. From its viscosity, and then extrapolating back to the concentrated suspension, using the known

Figure 3.1: Particle synthesis scheme.
amount by which the suspension was diluted. This gives an effective volume fraction of \( \phi_{\text{eff}} = 0.91 \) for the centrifuged suspension at room temperature, larger than the close-packing limit \( \phi_{\text{cp}} = 0.64 \), indicating that the particles overlap and have adjusted their size during centrifugation. This volume fraction decreases to \( \phi_{\text{eff}} = 0.52 \) when we raise the temperature to \( T = 34.6^\circ C \).

### 3.3: Rheological measurements

The rheological measurements presented in chapter 4 are performed on a stress-controlled Physica MCR rheometer (Anton Paar) with a cone and plate geometry (diameter: 25 mm, angle: 2° for the constant strain rate sweeps; diameter: 49.95 mm, angle: 1° for the strain sweeps). A solvent trap is used around the sample to prevent solvent evaporation. Using the solvent trap, the results were found to be reproducible (i.e., unaffected by evaporation) for at least two hours; none of the measurements presented below takes longer than that. All measurements were performed at \( T = 20^\circ C \). A fixed protocol was used to obtain a reproducible initial state: after loading, a conditioning step is applied where the sample is pre-sheared at 100 s\(^{-1}\) for one minute and left to equilibrate for 15 seconds before starting the measurements [8].

We performed conventional strain sweeps on the soft sphere samples and constant strain rate sweeps on the hard sphere samples. We checked that the different methodology does not influence the results presented here. The strain sweeps were performed at a constant frequency \( \omega = 1 \text{ rad s}^{-1} \), probing the sample at a fixed timescale \( t = 1/\omega \), while increasing the strain amplitude \( \gamma_0 \) from 0.001 to 1. In the constant strain rate (CSR) sweep tests [9], both frequency \( \omega \) and strain amplitude \( \gamma_0 \) are varied at the same time to keep the strain rate \( \dot{\gamma}_0 = \omega \gamma_0 \) constant. This has advantages if one wants to probe the internal relaxation time \( \tau \) of the material. The CSR sweeps were performed at strain rates of \( \dot{\gamma}_0 = 0.1 \text{ s}^{-1} \) and 1.0 s\(^{-1}\). The strain \( \gamma_0 \) was varied from 0.01 to 1 for both strain rates, while the frequency was varied from 10 to 0.1 rad s\(^{-1}\) for \( \dot{\gamma}_0 = 0.1 \text{ s}^{-1} \) and from 100 to 1 rad s\(^{-1}\) for \( \dot{\gamma}_0 = 1 \text{ s}^{-1} \). Using the raw stress and strain data, we determined Lissajous curves by plotting strain versus stress in a steady state oscillation cycle at fixed strain amplitude and frequency. In addition to this traditional rheological analysis, in chapter 4, we also analyse
the raw data of the steady-state cycles in a new framework of Rogers et al. (2011); this analysis allows a physical interpretation of the LAOS cycle. This is in contrast to the more traditional techniques such as the Chebychev analysis, where one concludes on effective strain hardening/softening based on “Chebychev coefficients”, or the Fourier analysis, where the higher harmonics of the stress response give some insight into the yielding; in both cases, the physical insight into the mechanism of yielding and flow is limited. In contrast, by applying the new method by Rogers, we obtain direct insight into the straining and yielding mechanisms. We determine the cage modulus from the slope of the stress-strain curve at zero stress, and the static and dynamic yield stresses as the stress values at the maximum stress overshoot and the strain reversal point, respectively. This analysis yields new insight into the rheology of soft and hard-sphere suspensions, and allows us to interpret rheology differences in terms of the particle softness.

3.4: Observation of quiescent glasses

To observe the dynamics of quiescent colloidal glasses (chapter 5), we construct sample cells as follow. We use a cylindrical hole in the middle of a cover slide as sample container. The height of this cylindrical container, i.e. the thickness of the cover slide, is 1mm. This sample cell is filled with the colloidal suspension and subsequently sealed by cover glasses to prevent any evaporation. To initialize the samples we add a small stirrer bar to each hard-sphere sample to rejuvenate it by stirrer rotation. For the soft sphere samples we rejuvenate the samples by heating and then shaking. We start our measurements at a certain time after the shear melting for all the samples. Therefore, we insure the same protocol for initializing both systems. To control the temperature, we put a styrofoam box joined with a heater and thermometer around the microscope stage; this way we control the temperature in the range between 24 °C and 40 °C. We use confocal microscopy to acquire 2D images of the system in the field of view. We then use the standard IDL software to find the positions of the particles and follow their motion in time. The schematic of the setup is shown in Fig. 3.2.
Figure 3.2: (a) Schematic view of the sample cell. (b) Sample cell mounted on the confocal microscope including heater fan and controller to warm up temperature inside. (c) The microscope is enclosed inside a Styrofoam box to insure homogeneous constant temperature.

3.5: Indentation setup

To investigate the initial stages of plastic flow, in chapter 6, we used an indentation setup analogous to the nanoindentation setup that has been used extensively in the deformation of atomic glasses. We prepared an amorphous film of colloidal particles by rapidly quenching silica particles from a dilute suspension onto a cover slip in a centrifuge. In order to avoid boundary induced crystallization, the cover slip surface has been roughened by sintering a 5 μm thick layer of polydisperse colloidal particles on top. Finally, we obtain an amorphous film about 48 μm thick, with a volume fraction which is well above the glass transition value of hard spheres. We use an ordinary sewing needle to indent the colloidal glass. We determine by optical microscopy that this needle has an almost hemispherical tip with a radius of 38 μm. The length scale ratios below the tip diameter, colloidal particle size and thickness of the film are comparable to those used in the nanoindentation of atomic glasses.

3.6: Data acquisition

We image the colloidal particles in the colloidal glass using an objective with a magnification of 100x and a numerical aperture of 1.4. The Zeiss LSM 5 microscope uses a line scanner to illuminate a section of the sample line by line, at a maximum of 120 frames per second (fps). The position of the focal plane, Z, is controlled by a pięzo-element on while the objective is mounted. For 3D imaging, an image stack is acquired by rapidly
varying the height of the objective using the piëzo and simultaneously taking 2D images. We typically image a \( 67 \times 67 \times 30 \, \mu\text{m}^3 \) volume by taking 300 images at a spacing of 0.1 \( \mu\text{m} \) in the \( z \) direction. At a scan speed of 20fps, it takes 15 s to acquire a \( z \)-stack. For 2D imaging, we fix the position of the objective such that its focal plane is, at least, 7 \( \mu\text{m} \) away from the boundaries, and acquire a time series of images. Typically, the images are acquired at a rate of 6 fps to follow the motion of particles in the glass.

### 3.7: Image processing and particle tracking

![Figure 3.3: (a) Raw confocal image, (b) filtered image, (c) Tracked image, (d) trajectory of one particle](image)

To calculate and analyse the particle motion of the particle in our colloidal suspension, we determine the particle positions in each frame; we do this by image processing of the recorded images using an algorithm developed by Crocker and Grier [10]. This allows us to find individual particles and determine their trajectories. We start with the raw confocal image, Fig. 3.3a, use a spatial band pass filter that smooths the image and subtracts the background, Fig. 3.3b. We set a parameter to find particle features, and we check whether
the positions of the particle centres are ready in the centre of the imaged particles, Fig. 3.3c. We connect particle coordinates in time to determine their trajectories. Fig. 3.3d shows the trajectory of a single particle. We export particle coordinates and their trajectories to the MATLAB software for further analysis.

### 3.8: Particle motion and strain calculation

We start with a set of particle positions as a function of time and use the displacements between subsequence frames to compute the closest possible approximation to a local strain tensor in the neighborhood of each particle. To define that neighborhood, we use the first minimum of the pair correlation function, which we choose to be the interaction range “$r_0$”, (see Fig. 1.2). The local strain is then determined by minimizing the mean-square difference between the actual displacements of the neighboring particles relative to the central one and the relative displacements that they would have if they were in a region of uniform deformation $\Gamma$ (Fig. 3.4).

![Figure 3.4:](image)

**Figure 3.4:** (a) Finding the neighbour that we should take to account for calculate local strain, (b) Deformation of the cage and displacement of centre particle in time, (c) calculate distance between particles and centre particle in time $t$ and $t + \Delta t$.

That is, we define

$$D^2(t, \Delta t) = \sum_n \sum_i (r_n^i(t) - r_0^i(t))^2 - \sum_j (\delta_{ij} + \Gamma_{ij}) \times \left( r_n^i(t - \Delta t) - r_0^i(t - \Delta t) \right)^2,$$  (3.1)

where the indices $i$ and $j$ denote spatial coordinates and the index $n$ runs over the particles within the interaction range of the reference particle, $n=0$. $r_n^i(t)$ is the $i$th component of
the position of the \( n \)th particle at time \( t \). We then find the \( \Gamma_{ij} \) that minimizes \( D^2 \) by calculating

\[
X_{ij} = \sum_{n}[r_{n}^{i}(t) - r_{0}^{i}(t)] \times [r_{n}^{j}(t - \Delta t) - r_{0}^{j}(t - \Delta t)], \quad (3.2)
\]

\[
Y_{ij} = \sum_{n}[r_{n}^{i}(t - \Delta t) - r_{0}^{i}(t - \Delta t)] \times [r_{n}^{j}(t - \Delta t) - r_{0}^{j}(t - \Delta t)]. \quad (3.3)
\]

\[
\Gamma_{ij} = \sum_{k} X_{ik} Y_{jk}^{-1} - \delta_{ij} \quad (3.4)
\]

The minimum value of \( D^2(t, \Delta t) \) is the local deviation from affine deformation during the time interval \( [t - \Delta t, t] \), [11]. The local strain tensor is the symmetric part of the deformation tensor.

\[
\varepsilon_{ij} = \frac{1}{2} (\Gamma_{ij} + \Gamma_{ij}^T). \quad (3.5)
\]

References