Micromechanics and rheology of hard and soft-sphere colloidal glasses
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2. Experimental techniques

2.1: Colloids

The Scottish chemist Thomas Graham discovered (1860) that certain substances (e.g., glue, gelatin, or starch) could be separated from certain other substances (e.g., sugar or salt) by dialysis. He gave the name colloid to substances that do not diffuse through a semipermeable membrane (e.g., parchment or cellophane) and the name crystalloid to those which do diffuse and which are therefore in true solution. Colloidal particles are larger than molecules but too small to be observed directly with the naked eye. Although there are no precise boundaries of size between the particles, colloidal particles are usually on the order of $10^{-6}$ to $10^{-4}$ cm in size. In Fig 2.1 we show the colloidal range compared to the scale of other materials.

One way of classifying colloids is to group them according to the phase (solid, liquid, or gas) of the dispersed substance and of the medium of dispersion. A gas may be dispersed in a liquid to form foam (e.g., shaving lather or beaten egg white) or in a solid to form solid foam (e.g., Styrofoam or marshmallow). A liquid may be dispersed in a gas to form an
aerosol (e.g., fog or aerosol spray), in another liquid to form an emulsion (e.g., homogenized milk or mayonnaise), or in a solid to form a gel (e.g., jellies or cheese). A solid may be dispersed in a gas to form a solid aerosol (e.g., dust or smoke in air), in a liquid to form a sol (e.g., ink or muddy water), or in a solid to form a solid sol (e.g., certain alloys). A further distinction is often made in the case of a dispersed solid.

One property of colloidal systems that distinguishes them from true solutions is that colloidal particles scatter light. If a beam of light, such as that from a flashlight, passes through a colloid, the light scattered by the colloidal particles and the path of the light can therefore be observed. Nowadays colloids are used in wide range of research in different subjects such as condensed matter physics, rheology, chemistry, material science and nanoscience.

2.2: Hard spheres

![Figure 2.2: (a) Hard sphere (PMMA particle), (b) Soft sphere (NIPA particle).](image)

Hard spheres are widely used as model particles in the statistical mechanical theory of fluids and solids. They are defined simply as impenetrable spheres that cannot overlap in space. They mimic the extremely strong repulsion that atoms and spherical molecules experience at very close distances. Hard-sphere systems are studied by analytical means, by molecular dynamics simulations, as well as by the experimental study of certain colloidal model systems, Fig. 2.2(a), [2]. The relevant thermodynamic parameter of hard-sphere suspension is the volume fraction "\( \Phi \)" which is the ratio of the volume occupied by the particles, and the total volume, determined by
\[ \Phi = \frac{N \times V_p}{V_s}, \]  

where \( N \) is the number of particles in suspension, \( V_p \) is the volume of each particle and \( V_s \) is the total volume of suspension.

**Figure 2.3:** Phase diagram of mono-disperse hard spheres as function of volume fractions.

The phase behavior of mono-disperse colloidal suspensions as a function of \( \Phi \) is shown schematically in Fig. 2.3 [3, 4]. At low volume fractions, the system behaves like a dilute gas, that is, there are no structural correlations in the system. As \( \Phi \) is increased, there is short-range order in the particle positions just as in a fluid. At \( \Phi_f \sim 0.49 \), the freezing volume fraction, the system separates into coexisting fluid and crystalline phases. Above \( \Phi_m \sim 0.54 \), the crystal is the thermodynamically stable phase. The crystal becomes denser until it reaches a maximum close packing configuration at \( \Phi \sim 0.74 \). The phases described above are equilibrium phases, where the eventual configuration of the system is determined by equilibrium thermodynamics, that is, the free energy of the system acquires a minimum. This phase behavior was confirmed experimentally by Pusey and van Megen, using suspensions of sterically stabilized PMMA particles (polymethyl methacrylate) [3]. However, the hard sphere systems can also exhibit non-equilibrium behavior. For example, rapid condensation of a hard-sphere fluid to \( \Phi_g = 0.58 \) results in a meta-stable, kinetically trapped state known as a glass, and this volume fraction is termed the glass transition volume fraction [5]. This state persists until \( \Phi_{cp} \sim 0.64 \), the random close packed volume fraction, which is the maximum volume fraction that a large, random collection of spheres can attain without crystalline order [6].
When we have a dilute suspension, particles easily move and exhibit Brownian motion. A Brownian particle's trajectory is parameterized by its self-diffusion coefficient $D$ through the Einstein-Smoluchowsky equation

$$< r^2 > = 2dD\tau \quad (2.2)$$

where $d$ is the number of dimensions of trajectory data. The angle brackets indicate a thermodynamic average over many starting times $t$ for a single particle or over many particles for an ensemble.

The self-diffusion coefficient for isolated Brownian spheres is given by the Stokes-Einstein equation,

$$D = \frac{k_BT}{6\pi\eta_0R} \quad (2.3)$$

Here, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\eta_0$ is the solvent viscosity and $R$ is the particle radius [7].

The characteristic time scale, $\tau_B$, for colloidal suspension is the time required by particle to move its own radius

$$\tau_B = \frac{3\pi\eta_0R^3}{6k_BT} \quad (2.4)$$

This relation is useful for very dilute systems under quiescent conditions. There are no body forces to take into account such as gravity or mechanical or thermal convection. It also neglects the hydrodynamic interactions between the particles that may influence the diffusion and the effective viscosity by several orders of magnitude. Interactions in more concentrated suspensions can be taken into account by substituting the effective viscosity of the material $\eta$ for the solvent viscosity [8].

$$\tau = \frac{3\pi\eta R^3}{6k_BT} \quad (2.5)$$

The difference between Equations (2.4) and (2.5) can be significant. Hence, increasing the concentration can lead to a wide range of timescales in colloidal suspensions [5, 6].
2.3: Soft spheres

Recently, soft particle systems have attracted increasing interest. A typical soft colloidal system is made of poly-N-isopropylacrylamide, sometimes shortened to (PNIPAm) particles, most commonly known as NIPA. These are hydrogel particles, made from a loose network of cross-linked polymers, soluble in water (Fig. 2.2b) [9]. At moderately warm temperatures (typically above 30-35 °C), water acts as a poor solvent for the polymers, and the NIPA particles shrink in size. (The polymers prefer to be close to each other, rather than close to water molecules.) At moderately cool temperatures (typically around 20-25 °C), water acts as a good solvent for the polymers, and the NIPA particles swell so that the polymers can contact as much water as possible. The size change of NIPA particles is typically at least a factor of two in diameter, and thus a factor of eight in volume. Thus by controlling temperature, one can control the volume fraction and thus the behavior of the sample in a direct fashion. However, NIPA particles are very soft, which is a key difference from the previously mentioned hard sphere colloids. If NIPA particles are in suspension at a high concentration, and their size is increased, then they can deform each other, and will no longer be spheres. On the other hand, an advantage of NIPA is that they are mostly composed of water: the polymer is a loose network, and so the particles are closely density-matched to water, and also closely match water’s index of refraction.

2.4: Density function

For microgel particles, a higher degree of crosslinking density is expected inside the particle than in the periphery, as the cross-linker is consumed faster than the monomer during polymerization [10]. This leads to a fuzziness of the particle surface that has to be included when modelling the particles [11, 12]. This can be done by convoluting the radial box profile with a Gaussian, see Fig. 2.4. The density distribution of the particle
can be determined experimentally using static light scattering to determine the particle form factor.

**Figure 2.4:** Structure of PNiPAM microgels. A highly cross-linked core is characterized by a radial box. The crosslinking density decreases with increasing distance to the core described. At $R$ the profile has decreased to half the core density. The overall size obtained by SANS where the profile approaches zero. $R_{\text{SANS}}$ is slightly smaller than the hydrodynamic radius $R_h$ obtained by DLS [11].

### 2.5: Light scattering

Dynamic light scattering has become the standard technique for measuring particle sizes, and we use it in this thesis to determine the average hydrodynamic radius and the size distribution of microgel particles. Dynamic light scattering probes the Brownian motion of suspended particles in solution. The particles diffuse in the solvent with diffusion constants that depend on the size of particles. The light intensity scattered from particles will fluctuate in time as a result of the particle diffusion.
From the temporal intensity autocorrelation function of the scattered light, one can readily derive useful information about particle diffusion, which, in turn, can be related to the particle “average” diameter and sample diameter distribution [13]. For a dilute particle suspension, the inverse relaxation time is related to the Brownian diffusion of the particles via

$$\frac{1}{\tau} = D \cdot q^2 \quad (2.6)$$

Where \(q\) is the scattering vector and \(D\) is the average particle diffusion coefficient given by Stokes Einstein relation,

$$D = \frac{k_B T}{6 \pi \eta_s R_h} \quad (2.7)$$

Here, \(k_B\) is the Boltzmann constant, \(T\) is temperature, \(\eta_s\) is the solvent viscosity, and \(R_h\) is the average particle hydrodynamic radius. The scattering vector \(q\) has magnitude

$$q = \frac{4 \pi n}{\lambda} \sin \frac{\theta}{2} \quad (2.8)$$
where \( n \) is the refractive index of the medium, \( \lambda \) is the wavelength, and \( \theta \) is the scattering angle. By combining equations of 2.6, 2.7 and 2.8, we are able to calculate the average hydrodynamic radius,

\[
R_h = \frac{8\pi k_B T n^2 \tau}{3\lambda^2 \eta} \sin^2 \left( \frac{\theta}{2} \right),
\]

In this formula all parameters on the right side are known except the decay time, \( \tau \), which is determined from the decay of the time correlation function. To measure \( \tau \), we plot the intensity correlation function as a function of time. By fitting the data with an exponential decay, we are able to determine \( \tau \), Fig. 2.6. We use a thermostat to change the temperature of the sample. By this technique it is possible to measure the hydrodynamic radius of microgel particles as a function of temperature.

![Experimental DLS data, filled squares show normalized intensity correlation function as a function of delay time and red line is an exponential fit.](image)

**Figure 2.6:** Experimental DLS data, filled squares show normalized intensity correlation function as a function of delay time and red line is an exponential fit.

### 2.6: Effective volume fraction

In contrast to the case of hard spheres, it is difficult to determine the volume fraction of microgel suspensions. The origin of difficulty is related to the deformable nature of microgels, which means that the volume, as measured, for instance, by light scattering in a dilute dispersion, might not be the same as that in a concentrated dispersion due to the increased osmotic pressure and/or the steric effects exerted...
between particles. To overcome this problem, a common method is to determine the effective volume fraction of microgel dispersions using a relation between the relative viscosity $\eta_{rel}$ under dilute conditions and the effective volume fraction, $\phi_{eff}$. The effective volume fraction is linearly related to the polymer concentration $C$ in wt %, $\phi_{eff} = kC$; the proportionality constant $k$ thus converts between polymer mass concentration and effective volume fraction [14]. We use dynamic light scattering to measure the hydrodynamic radius of the particles as a function of temperature in dilute suspensions, which we plot in Fig. 2.7. The radius changes from $0.42 \pm 0.01 \mu m$ at room temperature to $0.32 \pm 0.01 \mu m$ at $T=40^\circ C$, as determined by regression analysis of the decay of the autocorrelation function of the scattered intensity.

The effective volume fraction of the soft suspension can be estimated at low concentration from its viscosity using the Bachelor expression:

$$\eta_{rel} = \frac{\eta_0}{\eta_s} = 1 + 2.5\phi_{eff} + 5.9\phi_{eff}^2,$$  \hspace{1cm} (2.10)

Here, $\eta_0$ and $\eta_s$ denote the zero-shear viscosity of the suspension and the solvent, respectively. It is important to note that Eqn. 2.10 applies to very dilute suspensions only.

![Figure 2.7: Hydrodynamic radius of microgel particles as a function of temperature as measured by dynamic light scattering.](image-url)
2.7: Rheology

The rheological properties of a material are studied with a rheometer that imposes a shear stress ($\sigma$) and measures the resulting shear strain ($\gamma$) or strain rate ($\dot{\gamma}$) and vice versa. The shear stress ($\sigma$) is defined as a shear force ($F$) per unit area ($A$). The shear strain is the gradient of deformation ($\gamma = \Delta d/\Delta y$). For an ideally elastic material, the work done by the external stress is stored reversibly in the system. For an ideally viscous liquid in contrast the work done by the stress is fully dissipated. Materials with properties between these two extremes are called viscoelastic materials; they exhibit both elastic and viscous properties. In this study, we use a stress-controlled rheometer, “Anton Paar, Physica MCR Series” (Fig. 2.8a) equipped with a cone and plate geometry (Fig. 2.8b). This geometry has the advantage that the shear stress is constant anywhere between the cone and plate. For this geometry, the rheometer calculates the shear stress ($\sigma$), the shear strain ($\gamma$), and the strain rate ($\dot{\gamma}$) from the applied torque and measured angular displacement (velocity) using the following equations:

\[ \sigma = \frac{3M}{2\pi R^3} \]  
\[ \gamma = \frac{\Phi}{\alpha} \]  
\[ \dot{\gamma} = \frac{\dot{\Phi}}{\alpha} \]

where $M$ is the torque applied to the sample, $R$ and $\alpha$ are the radius and the angle of the cone respectively, $\Phi$ is the angular displacement and $\dot{\Phi}$ is the angular speed. Depending on the shear stress profile applied, we can perform both step stress (creep) and oscillatory (dynamic) experiments. In the step stress experiments, a constant stress is applied at $t = 0$ and kept constant for time $t$ ($\sigma(t) = \sigma_0 \Theta(t)$) where $\Theta$ is the Heaviside step function. In an oscillatory experiment, an oscillating shear stress ($\sigma(t) = \sigma_0 e^{i\omega t}$) is applied to the sample [15].
Figure 2.8: (a) Stress-controlled rheometer (Anton Paar, Physica MCR Series). (b) Cone-plate geometry, the cone has a radius of 25 mm and an opening angle of 2°.

2.8: Confocal microscopy

The basic concept of confocal microscopy was originally developed by Marvin Minsky in the mid-1950s (patented in 1957). The Dutch physicist G. Fred Brakenhoff developed a scanning confocal microscope in 1979, while almost simultaneously, Colin Sheppard contributed to the technique with a theory of image formation. Tony Wilson, Brad Amos, and John White nurtured the concept and later (during the late 1980s) demonstrated the utility of confocal imaging in the examination of fluorescent biological specimens. The first commercial instruments appeared in 1987. Confocal microscopy offers several advantages over conventional wide field optical microscopy, including the ability to control depth of field, elimination or reduction of background information away from the focal plane (that leads to image degradation), and the capability to collect serial optical sections from thick specimens. In fact, confocal technology is proving to be one of the most important advances ever achieved in optical microscopy. In most cases, integration between the various components is so thorough that the entire confocal microscope is often collectively referred to as a digital or video imaging system capable of producing electronic images. These microscopes are now being employed for routine investigations on molecules, cells, and living tissues that were not possible just a few years ago [16].
2.9: Resolution

All optical microscopes, including conventional wide field and confocal microscopes, are limited in the resolution that they can achieve by a series of fundamental physical factors. In a perfect optical system, resolution is restricted by the numerical aperture (pinhole) of optical components and by the wavelength of light, both incident (excitation) and detected (emission). The concept of resolution is inseparable from contrast, and is defined as the minimum separation between two points that results in a certain level of contrast between them. In a typical fluorescence microscope, contrast is determined by the number of photons collected from the specimen, the dynamic range of the signal, optical aberrations of the imaging system, and the number of picture elements (pixels) per unit area in the final image. As in wide-field microscopy, resolution at the focal plane is determined by the diameter of the Airy disc (shown in Fig. 2.9a) [17]. Generally, two closely spaced luminous points in the sample plane result into overlapping discs leading to an intensity distribution with two peaks as shown in Fig. 2.9b. A minimum separation is required between the discs to create a reasonable ‘dip’ in between, for the peaks to be resolved - this sets the maximum resolution of the microscope. Following Rayleigh criteria this separation is the full width half maximum (FWHM), FWHM of the airy disc (when the first minimum of an airy disc aligns with the central maximum of the second one) leading to a dip of roughly about 26%, Fig. 2.9c.

![Figure 2.9: Resolution of microscope.](image)

(a) The airy disc of a single particle. (b) The overlapping airy discs of two closely spaced particles and (c) Rayleigh limit for identifying two particles as different objects.

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For the optical setup of most commercially available confocal microscopes this separation in the lateral direction is about 200nm. It is important to note that the precision of determining the position of an imaged object is different from the above discussed resolution. The position of an isolated fluorescent point-like source corresponds to the 'center of mass' of its spatially extended airy disc image. If the disc is about $N$ pixel wide and each pixel is $M$ micrometers across, the center of the disc can be estimated to $\sim M/N$ accuracy, which is higher than the optical resolution. In the present study this uncertainty in detecting the position of a fluorescent particle is close to $\sim 30$nm [18].

References
[1] The origin of picture comes from the website below but we change it a little bit
http://www.newworldencyclopedia.org/entry/File:Spectrum_size.gif