Micromechanics and rheology of hard and soft-sphere colloidal glasses
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4. Rheology of hard and soft-sphere colloidal glasses

In this chapter, we investigate the macroscopic rheology of hard and soft sphere suspensions using large-amplitude oscillatory shear (LAOS). We investigate dense soft sphere suspensions in which the particles are jammed and exhibit permanent contact and compare the rheology with those of hard sphere suspensions around the glass transition. We use large-amplitude oscillatory shear (LAOS) measurements to determine the strain-dependent viscoelastic moduli and yield stress. A recent scheme is applied to interpret LAOS data in terms of a sequence of physical processes [1], revealing different characteristics of yielding, flow, and structural rejuvenation in the two systems. While for hard spheres, yielding and flow is governed by the breaking and rejuvenation of the nearest neighbour cage, for soft spheres, the particle compliance gives rise to a much more gradual yielding. We address the effect of particle softness directly by measuring the single-particle modulus with atomic force microscopy, and link it to the suspension modulus via the pair correlation function determined by microscopy. This allows us to bridge from particle scale to macroscopic suspension rheology.

4.1: Introduction

The rheological behavior of hard and soft - sphere suspensions is of interest because they can form the basis for understanding the behavior of a wide range of systems such as soft pastes, micelles, foams and emulsions that are important for applications [2]. Contrary to hard spheres that have been used a lot as models to investigate the structure, dynamics, and rheology of dense suspensions [3], soft deformable particles have been used as models only relatively recently. Hard spheres have provided conceptually simple model systems to understand the mechanical properties of dense suspensions. Because their size is fixed and the volume of the particles is conserved, in principle the flow properties can be understood based on volume exclusion: the motion
of a particle is confined by the cage formed by its nearest neighbours [4]. With increasing particle volume fraction, the available space for particle motion gets increasingly small, leading to divergence of the viscosity at volume fractions \( \sim 0.64 \), where this available volume vanishes [2]. Contrary to hard spheres, soft particles can deform and adjust themselves and can therefore attain volume fractions larger than hard spheres. At low concentrations, these particles exhibit rheological behavior similar to that of hard spheres. Several similarities in the rheology of soft- and hard sphere suspensions have been reported [5, 6-14]. While the comparison might be relatively successful for these low and intermediate volume fractions, however, it must fail at higher concentration where the soft particles start to deform: The high concentration leads to permanent contacts of the particles that strongly affect the rheological behavior of the suspension.

A well-known tool to probe the linear and nonlinear rheology of suspensions is large amplitude oscillatory shear (LAOS). A new analysis scheme was recently introduced that allows interpretation of LAOS data as a sequence of physical processes [1]: The deformation cycle is interpreted in terms of straining, yielding, flow, and structural rejuvenation. This decomposition provides insight into the physics of yielding and flow, and allows us to elucidate differences in the rheology of hard and soft particles suspensions. These differences are a direct result of the different compliance of the particles. An important challenge then is to link the particle compliance directly to the macroscopic suspension rheology. In principle, by considering the effective deformation of a particle in its dense environment, the macroscopic suspension modulus can be directly calculated [15]: in dense soft particle suspensions, particles exhibit permanent contact with each other: every particle is indented by its nearest neighbors, and their elastic contact [16] ultimately determines the macroscopic compressibility and shear rigidity of the suspension [17]. Therefore, it should be possible to link the observed rheological properties directly to the softness of the particles.

In this chapter, we investigate the rheology of dense hard and soft-sphere suspensions using LAOS to elucidate elastic straining, yielding, and flow. Oscillatory shear is used to determine the strain-dependent viscoelastic moduli and yield stress, allowing us to study the effect of the particle softness/hardness on the rheological behavior. We then analyse
the full time-dependent stress-strain data in detail to obtain insight into the sequence of elastic straining, yielding, flow and dissipation. Strong differences between hard and soft spheres are observed in the cage elasticity, as well as the nature of yielding. While for hard spheres yielding is linked with cage breaking, for soft spheres the much more gradual yielding appears to be a result of the long-range relaxation modes, with the local cage remaining largely intact. This interpretation is in agreement with the microscopic observations of long-range correlated relaxation modes in soft-sphere glasses presented in chapter 5. To connect the macroscopic rheology with the microscopic particle softness, we measure the single-particle modulus directly with atomic force microscopy, and use the pair correlation function determined with confocal microscopy to link single-particle and suspension moduli. We show that the simple Hertz model of elastic contact provides a good, quantitatively accurate description of the shear modulus.

4.2: Samples and rheological test

As hard-sphere samples, we use poly-methylmethacrylate (PMMA) particles with a radius of 0.13 \( \mu \text{m} \) suspended in cisdecahydronaphthalene (cis-decalin), see also sec. 3.2. As soft sphere samples we use poly isopropylacrylamide (PNiPAM) microgel particles, with a hydrodynamic radius of \( R = 506 \text{ nm} \) at room temperature, suspended in water. The particles are suspended in a 0.233 \( m \text{M} \) solution of NaCl that screens particle charges. Concentrated hard and soft sphere suspensions are prepared by diluting samples centrifuged to sediment. Hard-sphere suspensions are prepared with volume fractions \( \phi = 0.57, 0.59, 0.61 \) and 0.63, assuming a volume fraction of \( \phi_{\text{max}} = 0.64 \) in the centrifuged sediment. For the soft spheres, we measure the effective volume fraction by using the Bachelor expression as described in sec. 3.2.

We diluted suspensions centrifuged to a sediment to obtain samples with effective volume fractions \( \phi_{\text{eff}} = 1.66, 1.90, 1.96, 2.02, \) and 2.13. In order to plot data for hard and soft-sphere samples in one diagram, we also calculated relative volume fractions, where we normalized by \( \phi_{\text{max}} \), the volume fraction of the suspension after centrifugation. An overview over the soft sphere samples are given in table 4.1. We used large amplitude
oscillatory shear measurements on a stress-controlled rheometer equipped with cone and plate geometry as described in sec. 3.3.

<table>
<thead>
<tr>
<th>$\phi_{\text{eff}}$</th>
<th>1.66</th>
<th>1.90</th>
<th>1.96</th>
<th>2.02</th>
<th>2.13</th>
</tr>
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<tr>
<td>$\phi_{\text{eff}}/\phi_{\text{max}}$</td>
<td>0.78</td>
<td>0.89</td>
<td>0.92</td>
<td>0.95</td>
<td>1.0</td>
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Table 4.1: Volume fractions of the soft sphere samples used in this work: Effective volume fraction, $\phi_{\text{eff}}$, and volume fraction normalized to the value after centrifugation $\phi_{\text{eff}}/\phi_{\text{max}}$.

4.3: Results and discussion

4.3.1: Strain sweeps and constant strain rate sweeps

![Figure 4.1](image)

**FIG. 4.1:** The normalized storage modulus $G'$ (closed symbols) and loss modulus $G''$ (open symbols) during oscillatory shear on hard (a) and soft sphere samples (b). (a) Constant strain rate sweep at a strain rate of $\dot{\gamma}_0 = 0.1$ s$^{-1}$ for hard sphere samples with varying volume fractions. (b) Strain sweeps at a frequency of 1 rad s$^{-1}$ for soft sphere samples with varying volume fractions.
We first show the storage and loss moduli $G'$ and $G''$ as a function of strain amplitude $\gamma_0$ in Fig. 4.1. To compare hard and soft spheres, the moduli have been normalized by $R^3/k_b T$. As expected for dense suspensions, $G'$ is always larger than $G''$ in the linear regime indicating predominately elastic behavior of the suspensions. We find that the deeply jammed soft-sphere suspensions have overall higher moduli than the dense hard-sphere suspension and the difference in magnitude between the storage and loss modulus is more pronounced, indicating the predominant elastic component of the SS suspensions compared to the hard spheres. We attribute these properties to the interactions between the soft spheres in the dense suspension. At high effective volume fractions, the soft particles deform and exhibit permanent contacts (Fig. 4.2a), and consequently the mechanical properties of the particle contact determine the rheological properties of the suspension. The elastic modulus of PNIPAM particles is of the order of several kPa [18]; this modulus starts to be on the order of the modulus of the most concentrated suspensions we investigate here. In contrast, the Young's modulus of PMMA particles is several MPa, many orders of magnitude larger than that of the suspension so that these particles are not noticeably deformed (Fig. 4.2b), and the internal elasticity of the particles will not have any noticeable effect on the elasticity of the concentrated suspension. This particle softness is reflected in the concentration dependence of the moduli as shown in Fig. 4.3.

**FIG. 4.2:** (a) SEM image of dried nanocomposite microgel particles [32], (b) Confocal microscope image of the hard sphere sample at a volume fraction $\sim$0.60.
FIG. 4.3: The normalized magnitude of the storage modulus $G'$ (closed symbols) and loss modulus $G''$ (open symbols) in the linear regime, for the HS and SS samples, plotted as a function of $\phi/\phi_{\text{max}}$. The red dotted line is a guide to the eyes. The black solid curve is a fit of the Krieger-Dougherty equation to the data. The black dashed line indicates the prediction by Kobelev and Schweizer (2005).

While the HS suspension (closed squares and diamonds) shows a strong dependence that suggests a divergence at $\phi_{\text{max}}$ according to the Krieger-Dougherty relation $(1 - \frac{\phi}{\phi_{\text{max}}})^{-2.5k}$ (black line) [2, 19], the SS suspension exhibits a much weaker dependence that does not show any signature of divergence. We associate this much weaker dependence with the compliance of the soft particles. We note that this dependence is also in qualitative agreement with recent theory based on activated barrier hopping by Kobelev and Schweizer (2005).

4.3.2: Linking particle softness and suspension rheology

To address the effect of the particle softness quantitatively, we measured the modulus of individual soft particles directly, and used the suspension structure factor to link directly the particle and suspension moduli [15]. According to Hertzian theory [16], the elastic energy $u$ of two contacting spherical elastic bodies varies with the depth of indentation, $\Delta = r - 2R$, according to [20]:

\[ u = \frac{1}{2} k (r - 2R)^2 \]
where $E_p$ is the particle’s elastic modulus and $r$ the distance between the particle centres. In concentrated suspensions, particles indent each other, and their mutual interaction gives rise to macroscopic rigidity. The resulting high-frequency elastic modulus is given by [15, 17]:

$$G_\infty = \frac{2\pi}{15} n^2 \int_0^{2R} g(r) \frac{d}{dr} \left[ r^4 \frac{du(r)}{dr} \right] dr;$$  \hspace{1cm} (4.2)

where $n$ is the particle density and $g(r)$ the pair correlation function; the latter indicates the probability of finding particle centres separated by $r$. We measured the Young’s modulus of individual soft particles directly using atomic force microscopy. A typical load-displacement curve is shown in Fig. 4.4.

**FIG. 4.4:** Measurement of the elastic modulus of soft particles by atomic force microscopy. The indentation force is shown as a function of indentation depth. The red curve shows the measurement; the green curve shows a fit with the modulus $E = 5.2$ kPa.
Repeated measurements performed on several different particles yield a particle elastic modulus of $E_p = 5 \pm 0.2 \text{kPa}$ corresponding to $1.5 \pm 0.06 \times 10^5 \left( kT/R^3 \right)$. This modulus starts indeed to be on the order of the modulus of the most concentrated suspensions investigated here.

To link the single particle modulus directly to the suspension modulus, we determined the pair correlation function by microscopic imaging. We used confocal microscopy to image $\sim 4 \times 10^4$ particles in a $65 \mu m$ by $65 \mu m$ by $20 \mu m$ volume and determine their centres with an accuracy of $0.02 \mu m$ in the horizontal, and $0.05 \mu m$ in the vertical direction. We then calculated the pair correlation function directly from the particle positions. Pair correlation functions for different volume fractions are shown in Fig. 4.5; these show characteristic nearest and higher-order neighbour peaks. With increasing volume fraction, these peaks shift to smaller distances, indicating the increasing compliance of the particles. Assuming isotropic and homogeneous squeezing of the particles, one expects that the first peak of the pair correlation function varies with volume fraction as $r_m = 2 R (\phi_c / \phi)^{1/3}$, where $\phi_c \sim 0.64$ is the volume fraction at close packing 1.

**FIG. 4.5:** Pair correlation function of jammed soft sphere suspensions with volume fraction $\phi$= 2.13 (red), 2.02 (violet), 1.96 (blue), 1.9 (green) and 1.66 (black). Inset: Scaling of the position of the first peak of $g(r)$ with the particle volume fraction.
To test this prediction, we plot the position of the first peak of $g(r)$ as a function of $\phi^{-1/3}$ in Fig. 4.5 (inset). We also indicate the expected dependence with a dashed line. Indeed, the data follows the expected relation, in good agreement with the above prediction. We can now use the measured pair correlation function and the particle modulus to calculate the high-frequency shear modulus according to Eqn. 4.2. By solving the integral numerically, we obtain the modulus as a function of $\phi$, which we indicate by red dots in Fig. 4.6a. Also shown are experimental values of the shear modulus measured at increasing frequency. These have been taken from the measurement presented in Fig. 4.6b where the frequency dependence of the shear modulus has been determined. Overall, the data shows reasonable agreement with the predicted values: both the volume fraction dependence and absolute magnitude are reasonably well described. The observed exponential volume fraction dependence of the modulus is also in good agreement with previous work [15]. We therefore conclude that the simple extrapolation Eqn. 4.2 provides a reasonably accurate prediction of the modulus of soft sphere suspensions.

Fig. 4.6: (a) Suspension elastic modulus as a function of volume fraction: calculated high-frequency modulus (red dots) and measured moduli at 0.16 Hz (green triangle), 0.8 Hz (blue diamonds) and 8.1 Hz (yellow stars). (b) Frequency dependence of the shear modulus at a strain of 1.5% with varying volume fractions on soft sphere samples.
4.3.3: Non-linear elasticity: Lissajous curves

To obtain insight into the yielding and flow behavior, we investigated the full stress-strain raw data during a steady-state oscillatory cycle at a given frequency and amplitude. Examples of stress-strain responses are shown in Fig. 4.7; the top row shows results for soft spheres, and the bottom row for hard spheres, with strain amplitude increasing from left to right. In both cases, at small strain amplitude, this curve is an ellipse, indicating linear response. The aspect ratio of the ellipse reflects the ratio $G'/G''$; the higher skewness observed for the soft sphere suspension then indicates directly its higher elastic component. At larger strain amplitude, distinct nonlinear response is observed. To interpret this nonlinear behavior, we follow the analysis by Rogers et al. (2011) and decompose the entire cycle into a sequence of straining, followed by yielding and viscous flow, to final structural relaxation (Fig. 4.8).

**FIG. 4.7:** Lissajous curves (blue) for the SS sample with $\phi_{eff}/\phi_{max} = 0.92$ (a-d) and the HS sample (red curves) with $\phi/\phi_{max} = 0.92$ (e-h). Stress versus strain data for steady state cycles in the linear regime (a and e) and the nonlinear regime (b, c, d, f, g and h), with increasing strain amplitude from left to right.
Fig. 4.8: Schematic view illustrating the intro cycle regimes illustrated here

The crosses show reversal points, open and closed circles depict static yielding point and maximum stress, respectively. Hard (a) and soft sphere suspension (b).

The initial elastic straining is characterized by the local cage modulus, which we define from the slope of the stress-strain curve at vanishing stress:

$$G_{cage} = \frac{d\sigma}{dy} \bigg|_{\sigma=0}; \quad (4.3)$$

The resulting cage modulus is shown in Fig. 4.9 together with the shear moduli reproduced from Fig. 4.1.

FIG. 4.9: Apparent cage modulus as a function of strain amplitude overlaid on the shear moduli data of Fig. 1 for hard (a) and soft spheres (b). The cage modulus coincides with $G$ in the linear regime, while it persists to higher strains.
Both overlap at small strain amplitude, indicating that the cage modulus dominates the suspension rheology. As the strain amplitude increases and the storage modulus decreases, the cage modulus remains approximately constant. This indicates that even at high strain, there is pronounced elastic behavior of the cages; this elastic behavior is lost when averaging over the entire straining cycle. Comparing hard and soft spheres, we notice a slight dip of $G_{\text{cage}}$ for the hard, and a persistent constant value for the soft spheres, indicating the persistent stiffness of the cages in the concentrated soft sphere suspension.

At later stages in the cycle, however, these cages break and the material yields and starts to flow. The cumulative strain acquired until the point of yielding is known as the yield strain. To determine it, we measure the strain acquired from the lower reversal point to the point of maximum stress. The resulting values are shown as a function of strain amplitude in Fig. 4.10 c and d. Open symbols indicate the strain acquired until the first stress overshoot, and closed symbols indicate the absolute maximum of stress, see Fig. 4.10 a and b. Assuming an entirely elastic response from the lower to the upper reversal point, the total acquired strain would be $2\gamma_0$. On the other hand, for a viscous material, the maximum stress occurs at maximum strain rate, in the middle between the two reversal points, and the acquired strain is $\gamma_0$. Fig. 4.10 shows that the data first follows the straight line corresponding to $2\gamma_0$; therefore, the maximum stress is caused by an elastic process. This trend continues for the soft spheres (closed symbols) up to high strains indicating that the stress maximum is always caused by elastic processes. In contrast, for hard spheres, the data follows the line corresponding to $\gamma_0$ at higher strain amplitudes, indicating that the stress maximum is caused by a viscous process. At the same time, the yield strain continues to rise with a lower power. The data indicates a power law with index 0.2 (dashed line) similar to the one observed by Rogers et al. (2011) for soft microgel pastes. For the soft spheres, this data is inconclusive. Thus, the main difference in the behavior of the acquired strain is the strong elastic component that dominates the yielding of the soft spheres up to high strains. To elucidate the yielding process in more detail, following Rogers et al. (2011), we determine the static yield stress as the maximum stress overshoot, and the dynamic yield stress at the point of zero instantaneous shear
rate; these stresses are generally associated with cage breaking and cage reformation (see [21, 22] for a recent discussion on the yield stress).

They are shown as a function of strain amplitude in Fig. 4.11. At low strain amplitude, these two stresses are indistinguishable, and yielding has not taken place yet. Only at higher strain amplitudes, the two stresses become different, indicating that yielding has occurred. For the hard spheres, a clear difference between static and dynamic yield stress is observed for strains higher than $\gamma_0 \sim 10\%$, indicating breaking and reformation of the nearest neighbor cage, in agreement with earlier work [4].

**FIG. 4.10: Yield strain in the Lissajous cycle.**

(a,b) Lissajous cycles for three characteristic amplitudes illustrating the definition of the cumulative strain for hard (a) and soft-sphere suspensions (b). (c,d) Cumulative strain at the point of maximum stress as a function of strain amplitude, $\gamma_0$, for hard (c) and soft spheres (d). The behavior of ideal elastic and ideal viscous material is indicated by the solid lines labeled $2\gamma_0$ and $\gamma_0$, respectively. Dashed line indicates a power law with exponent 0.2.
FIG. 4.11: Yield stress (a, b) Lissajous curves illustrating the static and dynamic yield stress, defined as the maximum elastic stress and the stress at the strain reversal point, and the flow sequence in between for hard (a) and soft-sphere suspensions (b). (c, d) Static and dynamic yield stress as a function of strain amplitude, $\gamma_0$, for hard (c) and soft spheres (d). Dashed line indicates a power law with exponent 0.2.

For the soft spheres at intermediate strains, however, differences are much more gradual and a clear distinction emerges only at larger strain. We interpret this gradual yielding with long-range structural relaxations that are predominant in these soft-sphere materials [23] as we will show by direct Confocal microscopy observation in chapter 5. We observe clear differences in the relaxation modes of hard and soft-sphere glasses: while the former are short ranged, in qualitative agreement with the simple cage-breaking picture, the latter are much more long-ranged, in agreement with the much more gradual yielding behavior observed here. Motivated by Fig. 4.11d, we hypothesize that long-range coordinated relaxation occurs over an extended regime of intermediate strain amplitudes.
5% < γ₀ < 50%, before the nearest neighbour cage is broken. This seems plausible considering the strong compliance of the soft particles. In the latest stage, for both hard and soft spheres the stresses appear to rise with a power law with exponent 0.2 (dashed line), in agreement with the behavior observed by Rogers et al. (2011) for soft microgel pastes.

Another possible way to determine the yield stress \[21, 22\] is from the intersection of \(G'\) and \(G''\) in Fig. 4.1. The yield stress is then determined from the crossover of the normalized \(G'\) and \(G''\) using \(\sigma_y = G'y_y\), where \(y_y\) is the yield strain and \(G'\) is taken in the linear response regime. To compare with the yield stresses of the Lissajous analysis, we plot the yield stresses as a function of volume fraction in Fig. 4.12. The figure compiles data for HS and SS samples from this work and other work reported \[11, 24\]. The yield stress determined from the Lissajous analysis (Fig. 4.12) is indicated by diamonds; it roughly agrees with the yield stresses determined from the crossover of \(G'\) and \(G''\) (red dots and blue squares).

**FIG. 4.12:** Overview of yield stress data for HS (squares) and SS samples (circles) from this work and from literature, (Le Grand and Petekidis, 2008; Pham et al., 2008) plotted as a function of \(\phi/\phi_{\text{max}}\). The dotted line is a guide to the eyes. Yield stresses from the Lissajous analysis are indicated as diamonds.
**FIG. 4.13:** Stress as a function of strain rate in the flow regime of the cycle. The dashed area indicates approximately the regime beyond the yield stress (dashed horizontal lines) where yielding has taken place. Closed symbols indicate hard, and open symbols soft spheres. The data indicates maybe a slight shear thickening.

Furthermore, we note that the HS samples exhibit yield stresses in the range of a few \( k_B T/R^3 \), reflecting the fact that the moduli result from the entropic interactions of the particles; this was exactly the reason for scaling the stresses in this way: for hard sphere colloids subject to thermal agitation, the only stress scale is \( k_B T/R^3 \).

For the deeply jammed SS samples, yield stresses are much higher, ranging from 50 to 300 Pa, reflecting the fact that there is another stress scale in the system: that of the deformable particles themselves. Comparing to previous work, we find that the previously reported values [11, 24] for HS suspensions lie close to the values obtained in this work, while the literature value for a SS suspension [11] at much lower volume fraction is in good agreement with our data; this extrapolation also shows that at lower volume fraction the SS suspensions start to behave similarly to HS suspensions, as was discussed previously. After yielding, flow of the material takes place; this part of the Lissajous curves indicates the way the material starts to flow. We therefore plot the stress as a function of strain rate for points between the yield point and the strain reversal point (see Fig. 4.11 a and b) in Fig. 4.13; closed and open symbols indicate data of hard and soft spheres,
respectively. Flow occurs for stresses larger than the yield stress, indicated by dashed horizontal lines; the grey area then indicates the flow regime. The curves for different strain amplitudes exhibit good overlap for hard spheres as expected. However, the curves appear shifted for the soft spheres; this shift might again indicate the gradual yielding of the soft sphere suspension, which depends on the amount of strain.

4.3.4: Dissipated Energy

Another important parameter is the area enclosed by the Lissajous curves, which indicates the energy dissipated during one oscillation cycle. To look at the dissipated energy in more detail, we show the normalized dissipated energy as a function of strain amplitude in Fig. 4.14. Three different regimes in the scaling of $P$ can be distinguished. At small strain, $P$ increases as $P \propto \gamma^2$. At intermediate strains, where yielding of the material takes place, the scaling of $P$ increases to a larger power.

**Fig. 4.14:** Dissipated energy $P$ of hard sphere (a) and soft sphere suspensions (b) as a function of strain amplitude $\gamma_0$ calculated from the area of the Lissajous curves (solid lines), and from the LAOS parameters according to eqn. 4.4. The volume fractions 0.57, 0.59, 0.61 and 0.63 (hard spheres) and 1.66, 1.96 and 2.13 (soft spheres) are as indicated. The prediction from the Lissajous parameters according to eq. 4.6. is indicated by dashed lines.
Finally, at large strain far in the nonlinear regime, the scaling of $P$ decreases again to a power close to $P \propto \gamma$. A power of 2 in the linear regime is in agreement with the expected dissipated energy [25]:

$$P = \pi \gamma^2 G''; \quad (4.4)$$

The fact that the scaling is not exactly $P \propto \gamma^2$ can be explained by the slight increase of $G''$ at low $\gamma_0$ (Fig. 4.1a). The stronger increase of $P$ at yielding is linked with the onset of structural relaxation and goes hand in hand with the increase of $G''$. Finally, the almost linear dependence $P \propto \gamma$ observed in the nonlinear regime is related to the decrease of $G''$, which decreases roughly as $G'' \propto \gamma_0^{-1}$. Upon increasing the volume fraction, the whole curve of $P$ is shifted upwards, indicating more dissipated energy but presumably no change in the overall yielding mechanism. Furthermore, the dissipated energy of the SS samples is larger than that of the HS samples over the whole strain range. This can be explained by considering that dissipation originates from movement of the interstitial fluid through the pores between particles. Hard spheres do not deform themselves, and the only drainage of liquid is through the interstitial pores in between the particles. However, when the soft particles are deformed, some liquid needs to drain through the mesh of the particles themselves. Because of the small dimension of this mesh size compared to the particle size; this can lead to a high dissipation. It is instructive to link the dissipated energy directly to the rheological LAOS parameters determined above. The amount of dissipation during an oscillatory cycle is set by the phase angle between stress and strain. This phase angle can be approximated by

$$\sin \delta = \left(1 - \frac{\sigma_{dy}}{\gamma_0 G_{cage}}\right); \quad (4.5)$$

using a simple geometric relation [1]. We show the approximated phase angle as a function of strain amplitude in Fig. 4.15a.
FIG. 4.15: (a) Phase angle as a function of strain amplitude for hard and soft spheres. (b) Storage and loss moduli, $G'$ and $G''$ reconstructed from Fig. 4.1 (symbols) and calculated using the extrapolated phase angle (dashed lines). Good agreement is observed, except at small strains where some deviation occurs.

It increases from $\delta = 0^\circ$ at small strain to values approaching $90^\circ$ as expected. The resulting storage and loss moduli, $G' = (\sigma_0 / \gamma_0) \cos(\delta)$ and $G'' = (\sigma_0 / \gamma_0) \sin(\delta)$ are compared with the values of soft spheres from Fig. 4.1b in Fig. 4.15b. Good agreement is observed at large strain. Some deviation in $G''$, however, occurs at small strain. Using Eqns. 4.4 and 4.5, we can now link the dissipated energy directly to the Lissajous parameters determined above. It follows that

$$P = \pi \sigma_0 \left( \gamma_0 - \left( \frac{\sigma_{dy}}{G_{cage}} \right) \right); \quad (4.6)$$

The resulting values of the dissipated energy are indicated by dashed lines in Fig. 4.14. Good agreement is observed at high strain, while larger deviations occur at small strain, in line with the deviations of the loss modulus shown in Fig. 4.15.

4.4: Conclusion

We have investigated the behavior of dense hard sphere (HS) and soft sphere (SS) suspensions under oscillatory shear. In contrast to the HS, for which thermal particle
collisions lead to effective yield stresses of the order of $kT/R^3$, the modulus of the jammed SS suspension arises from the permanent contact of the particles. The suspension modulus can be accounted for by using Hertzian theory with a single-particle modulus determined by atomic force microscopy. The soft nature of the particles leads to higher yield strain, and a more gradual yielding, in contrast to the distinct yielding observed for hard-sphere suspensions. We associate this gradual yielding with long-range relaxation modes in soft glasses, and contrast it to the local cage breaking associated with the yielding of hard sphere glasses. At the high volume fractions probed here, a deformation of the SS sample involves deformation of the particles as well, which gives rise to an increased elasticity and dissipated energy. Dissipated energy curves show very similar power law regimes for HS and SS suspensions, $P \propto \gamma^2$ in the linear regime, and $P \propto \gamma$ in the nonlinear regime, but the dissipated energy of the soft spheres is around two orders of magnitude larger than that of the HS suspension. We associate this with the drainage of liquid through the mesh size of the deformed soft NIPA particle.

References