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Rheology of concentrated soft and hard-sphere suspensions

K. van der Vaart,^{a)} Yasser Rahmani, and Rojman Zargar

Institute of Physics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

Zhibing Hu

Department of Physics, University of North Texas, Denton, Texas 76203

Daniel Bonn and Peter Schall^{b)}

Institute of Physics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

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Synopsis

We present a detailed comparison of the rheology of concentrated hard and soft-sphere suspensions using a variety of techniques including large-amplitude oscillatory shear (LAOS). While the soft spheres are jammed and exhibit permanent contact, the hard-sphere suspensions are below close packing where particle collisions lead to an effective modulus. Oscillatory shear measurements are used 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 [Rogers *et al.*, J. Rheol. **55**, 435–458 (2011a)], revealing different characteristics of yielding, flow, and structural rejuvenation in the two systems. While for hard spheres, yielding and flow are governed by the breaking and rejuvenation of the nearest neighbor 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 linking it to the suspension modulus via the pair correlation function determined by microscopy. © 2013 The Society of Rheology. [http://dx.doi.org/10.1122/1.4808054]

I. INTRODUCTION

Suspensions of particles are 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 in addition are also important for applications [Larson (1998)]. Contrary to hard spheres (HSs) that have been used a lot as models to investigate the structure, dynamics, and rheology of dense suspensions [Fuchs and Ballauff (2005)], soft deformable

^{a)}Present address: LHE, École Polytechnique Fédérale de Lausanne, Switzerland.

^{b)}Author to whom correspondence should be addressed; electronic mail: P.Schall@uva.nl

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particles have been used as models only relatively recently. HSs 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 neighbors [Pusey (2008)], and with increasing particle volume fraction, the available space for particle motion gets increasingly small, leading to divergence of the viscosity at volume fractions ~ 0.64 , where this available volume vanishes [Larson (1998)]. Contrary to HSs, soft particles can deform and adjust themselves, and can therefore attain volume fractions larger than those of HSs. At low concentrations, these particles exhibit a behavior similar to that of HSs. Several similarities between soft-sphere (SS) and HS suspensions have been reported [Mason and Weitz (1995); Senff and Richtering (2000); Deike et al. (2001); Cloitre et al. (2003); Crassous et al. (2005); Crassous et al. (2008); Carrier and Petekidis (2009); Le Grand and Petekidis (2008); Helgeson et al. (2007); Vlassopoulos (2004)]. 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, which strongly affect the rheological behavior of the suspension.

A well-known tool to probe the linear and nonlinear rheology of suspensions is largeamplitude oscillatory shear (LAOS). A new analysis scheme was recently introduced that allows interpretation of LAOS data as a sequence of physical processes [Rogers et al. (2011a, 2011b); Rogers and Lettinga (2012)]: 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 determination of important parameters such as the local cage modulus, static and dynamic yield stresses and the flow curve. Its application to suspensions of hard and soft particles would allow insight into their different rheology and yielding that is a direct result of the elastic properties of the constituent particles. An important challenge then is to link the microscopic singleparticle modulus 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 [Seth et al. (2006)]. In dense soft particle suspensions, particles exhibit permanent contact with each other: Every particle is indented by its nearest neighbors, and their elastic contact [Hertz (1881)] ultimately determines the macroscopic compressibility and shear rigidity of the suspension [Zwanzig and Mountain (1965)]. Therefore, it should be possible to link the observed rheological properties directly to the softness of the particles.

In this paper, we investigate the rheology of dense HS and SS suspensions by using LAOS to elucidate elastic straining, yielding, and flow. We focus on the concentrated regime, where the soft particles deform and exhibit permanent contacts, and compare the rheology with that of HSs below close packing, where strong caging dominates the suspension rheology. 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. Taking advantage of the recent scheme introduced by Rogers *et al.* (2011a), we then analyze 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 HS and SS are observed in the cage elasticity, as well as the nature of yielding. While for HSs yielding is linked with cage breaking, for SSs 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 recent microscopic observations of long-range correlated relaxation modes in SS glasses

[Maccarrone *et al.* (2010); Rahmani *et al.* (2012)]. 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.

II. EXPERIMENTAL METHODS

A. Samples

As HS samples, we use poly-methylmethacrylate (PMMA) particles suspended in *cis*-decahydronaphthalene (*cis*-decalin). The particles have a radius of R = 127 nm, with a polydispersity of 12%, to prevent crystallization. Particles are sterically stabilized with a layer of grafted poly-12-hydroxystearic acid (PHSA), 10 nm in length, to prevent aggregation. As SS samples we use poly-isopropylacrylamide (PNiPAM) microgel particles, with a hydrodynamic radius of R = 506 nm at room temperature, suspended in water. The particles were prepared using 3.8 g NIPA and 0.07 g crosslinker BIS (~2 wt.%). These particles swell in water; in their swollen state, their density closely matches that of the solvent. The particles are suspended in a 0.233 mM solution of NaCl that screens particle charges.

Concentrated HS and SS suspensions are prepared by diluting samples centrifuged to a sediment at a centrifugation speed of 5500 rpm. HS suspensions were prepared with volume fractions $\phi = 0.57$, 0.59, 0.61 and 0.63, assuming a volume fraction of ϕ_{max} = 0.64 in the centrifuged sediment. For the SSs, the volume fraction is no longer a good measure of the particle concentration because the particle size adjusts and the particle volume is not fixed. We instead define the effective volume fraction $\phi_{eff} = nV_{ss}$, where *n* is the number density of the particles, and V_{ss} is the volume of the undeformed particle in dilute suspension. We calibrate the measurement of ϕ_{eff} by using the Batchelor expression [Batchelor (1977)] for HSs

$$\eta_{\rm rel} = \eta_0 / \eta_{\rm s} = 1 + 2.5 \phi_{\rm eff} + 5.9 \phi_{\rm eff}^2, \tag{1}$$

to directly link viscosity and volume fraction [Senff and Richtering (1999); Mattsson *et al.* (2009)]. Here, η_0 and η_s denote the zero-shear viscosity of the suspension and the solvent, respectively. We diluted suspensions centrifuged to a sediment to obtain samples with effective volume fractions $\phi_{eff} = 1.66$, 1.90, 1.96, 2.02, and 2.13. In order to plot data for HS and SS samples in one diagram, we also calculated relative volume fractions, where we normalized by ϕ_{max} , the volume fraction of the suspension after centrifugation. An overview over the SS samples is given in Table I.

B. Rheology

The measurements 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 (CSR) 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 2 h; none of the measurements presented below take longer than that. All measurements were performed at T = 20°C. A fixed protocol was used to obtain a reproducible initial state: After loading, a conditioning step is applied where the sample is presheared at 100 s^{-1}

TABLE I. Volume fractions of the soft-sphere samples used in this work: Effective volume fraction, ϕ_{eff} , and volume fraction normalized to the value after centrifugation $\phi_{\text{eff}}/\phi_{\text{max}}$.

$\phi_{ m eff}$	1.66	1.90	1.96	2.02	2.13
$\phi_{\rm eff}/\phi_{\rm max}$	0.78	0.89	0.92	0.95	1.0

for 1 min and left to equilibrate for 15 s before starting the measurements; while aging takes place in these suspensions, we found this protocol to give reproducible results [Abou *et al.* (2003)].

We performed conventional strain sweeps on the SS samples and CSR sweeps on the HS 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 γ_0 from 0.001 to 1. In the CSR sweep tests [Wyss *et al.* (2007)], both frequency ω and strain amplitude γ_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 τ of the material; however, as pointed out by Erwin *et al.* (2010), this technique may give erroneous results when applied to the nonlinear regime. The CSR sweeps were performed at strain rates of $\dot{\gamma}_0 = 0.1 \text{ and } 1.0 \text{ s}^{-1}$. The strain γ_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. The raw data of the steady-state cycles were analyzed as sequence of physical processes in the framework of Rogers *et al.* (2011a): We determined 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 SS and HS suspensions, and we interpret this difference in terms of the particle softness.

III. RESULTS AND DISCUSSION

A. Strain sweeps and CSR sweeps

We first show the storage and loss moduli G' and G'' as a function of strain amplitude γ_0 in Fig. 1. To compare HSs and SSs, the moduli have been normalized by R^3/k_bT . As expected for dense suspensions, G' is always larger than G'' in the linear regime indicating predominantly elastic behavior of the suspensions. We find that the deeply jammed SS suspensions have overall higher moduli than those of the dense HS suspension and the difference in magnitude between the storage and the loss modulus is more pronounced, indicating the predominant elastic component of the SS suspensions compared to the HSs. We attribute these properties to the interactions between the SSs in the dense suspension. At high effective volume fractions, the soft particles deform and exhibit permanent contacts, 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 [Hashmi and Dufresne (2009)]; 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



FIG. 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 $\dot{\gamma}_0 = 0.1 \text{ s}^{-1}$ 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.

deformed, 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. 2. While the HS suspension (closed squares and diamonds) shows a strong dependence that suggests a divergence at ϕ_{max} according to the Krieger–Dougherty relation $(1 - \frac{\phi}{\phi_{\text{max}}})^{-2.5k}$ (black line) [Larson (1998); Cheng *et al.* (2002)], 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. This dependence is also in qualitative agreement with recent theory based on activated barrier hopping by Kobelev and Schweizer (2005). For HSs, suspension moduli and their volume



FIG. 2. 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 ϕ/ϕ_{max} (see Table I for the absolute volume fractions of soft spheres). 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).

fraction dependence can vary due to differences in the thickness of the stabilizing layer [Mewis and Wagner (2012)].

B. 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 the particle and suspension moduli [Seth *et al.* (2006)]. According to Hertzian theory [Hertz (1881)], the elastic energy u of two contacting spherical elastic bodies varies with the depth of indentation, $\delta = r - 2R$, according to Johnson (1985)

$$u = \frac{8}{15} \sqrt{\frac{R}{2}} E_{\rm p} \,\delta^{2.5},\tag{2}$$

where E_p is the particle's elastic modulus and *r* the distance between the particle centers. 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 [Zwanzig and Mountain (1965); Seth *et al.* (2006)]

$$G_{\infty} = \frac{2\pi}{15} n^2 \int_0^{2R} g(r) \frac{d}{dr} \left[r^4 \frac{du(r)}{dr} \right] dr, \tag{3}$$

where *n* is the particle density and g(r) the pair correlation function; the latter indicates the probability of finding particle centers 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. 3. Repeated measurements performed on several different particles yield a particle elastic modulus of $E_p = 5\pm0.2$ kPa corresponding to $1.5\pm0.06 \times 10^5 (kT/R^3)$. This modulus starts indeed to be on the order of the modulus of the most concentrated suspensions investigated here. To link this particle modulus



FIG. 3. Measurement of the elastic modulus of soft particles by atomic force microscopy. The indentation force, *F*, is shown as a function of indentation depth, δ . The jagged curve shows the measurement; the smooth curve is a fit in the grey area with the Hertzian relation $F = (4/3)E^*R^{1/2}|\delta|^{3/2}$, where E^* is the combined modulus of tip and particle, yielding a particle modulus of $E_p = 5.2$ kPa.



FIG. 4. (a) Pair correlation function of jammed soft-sphere suspensions with volume fraction (from left to right) $\phi = 2$:02, 1.96, 1.9, and 1.66. Inset: Scaling of the position of the first peak of g(r) with the particle volume fraction. (b) Suspension elastic modulus as a function of volume fraction: calculated high-frequency modulus (dots) and measured moduli at 0.16 Hz (triangle), 0.8 Hz (diamonds), and 8.1 Hz (stars).

directly to the suspension modulus using Eqs. (2) and (3), we determined the pair correlation function by microscopic imaging. We used confocal microscopy to image $\sim 4 \times 10^4$ particles in a $65 \times 65 \times 20 \,\mu m$ volume and determine their centers with an accuracy of $0.02 \,\mu\text{m}$ in the horizontal and $0.05 \,\mu\text{m}$ 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(a); these show characteristic nearest and higher-order neighbor 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 $r_{\rm m} = 2R(\phi_{\rm c}/\phi)^{1/3}$, where $\phi_c \sim 0.64$ is the volume fraction at close packing.¹ 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(a) (inset). We also indicate the expected dependence with a dashed line. Indeed, the data follow the expected relation in good agreement with the above prediction. We note that shrinkage of the SSs, besides resulting from particle contacts, can also arise from osmotic pressure effects; such interactions have been discussed for micelles and star polymers, see Vlassopoulos et al. (2001).

We can now use the measured pair correlation function and the particle modulus to calculate the high-frequency shear modulus according to Eq. (3). By solving the integral numerically, we obtain the modulus as a function of ϕ , which we indicate by red dots in Fig. 4(b). Also shown are experimental values of the shear modulus measured at increasing frequency. Overall, the data show 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 [Seth *et al.* (2006)]. We therefore conclude that the simple estimation of the suspension modulus using Eq. (3) provides a reasonably accurate prediction of the modulus of SS suspensions.

¹We note that an additional weak volume fraction dependence arises from the change of the number of nearest neighbors, or equivalently the height of the first peak of g(r) [Seth *et al.* (2006)]. This additional weak dependence, however, is unimportant for the limited range of volume fractions investigated here.



FIG. 5. Lissajous curves (top) for the SS sample with $\phi_{eff}/\phi_{max} = 0.92$ (a–d) and the HS sample (bottom) 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)–(d) and (f)–(h)], with increasing strain amplitude from left to right.

C. Nonlinear elasticity: Lissajous curves

To obtain insight into the yielding and flow behavior, we investigated the full stressstrain raw data during a steady-state oscillatory cycle at a given frequency and amplitude. Examples of stress-strain responses are shown in Fig. 5; the top row shows results for SSs, and the bottom row for HSs, 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 SS 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.* (2011a) and decompose the entire cycle into a sequence of straining, followed by yielding and viscous flow, to final structural relaxation. 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

$$G_{\text{cage}} = d\sigma/d\gamma|_{\sigma=0}.$$
(4)

The resulting cage modulus is shown in Fig. 6 together with the shear moduli reproduced from Fig. 1. 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 HSs and SSs, we notice a slight decrease of G_{cage} for the hard, and a persistent constant value for the SSs, indicating the smaller free space inside the cages of the concentrated SS suspensions besides their similar normalized density ϕ/ϕ_{max} .

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. 7. Open symbols indicate the strain acquired until the first stress



FIG. 6. 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.

overshoot, and closed symbols indicate the absolute maximum of stress, see inset. 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 γ_0 . Figure 7 shows that the data first follow the straight line corresponding to $2\gamma_0$; therefore, the maximum stress is caused by an elastic process. This trend continues for the SSs (closed symbols) up to high strains indicating that the stress maximum is always caused by elastic processes. In contrast, for HSs, the data follow the line corresponding to γ_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 indicate a power law with index 0.2 (dashed line) similar to the one observed by Rogers *et al.* (2011a). For the SSs, these data are unconclusive. Thus, the main difference in the behavior of the acquired strain is the strong elastic component that dominates the yielding of the SSs up to high strains.



FIG. 7. Cumulative strain at the point of maximum stress as a function of strain amplitude for hard (a) and soft spheres (b). The behavior of ideal elastic and ideal viscous material is indicated by the solid lines labeled $2\gamma_0$ and γ_0 , respectively. Dashed line indicates a power law with exponent 0.2. Insets show the corresponding points within the Lissajous cycle.



FIG. 8. Static and dynamic yield stress defined from the maximum elastic stress and the stress at the strain reversal point for hard (a) and soft-sphere suspensions (b). Dashed line indicates a power law with exponent 0.2. Insets show the corresponding points within the Lissajous cycle.

To elucidate the yielding process in more detail, following Rogers et al. (2011a), 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 Moller et al. (2009) and Denn and Bonn (2011) for a recent discussion on the yield stress]. They are shown as a function of strain amplitude in Fig. 8. At low strain amplitude, these two stresses are indistinguishable, because yielding has not taken place yet. Only at higher strain amplitudes, the two stresses become different, indicating that yielding has occurred. For the HSs, a clear difference between static and dynamic yield stress is observed for strains higher than $\gamma_0 \sim 0.1$, indicating breaking and reformation of the nearest neighbor cage, in agreement with earlier work (Pusey, 2008). For the SSs 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 known to be predominant in these SS materials: Recent light scattering [Maccarrone et al. (2010)] and confocal microscopy studies [Rahmani et al. (2012)] provide clear evidence of the difference of the relaxation modes of HS and SS glasses: While former are short ranged, in qualitative agreement with the simple cage-breaking picture, latter are much more long-ranged, in agreement with the much more gradual yielding behavior observed here. Indeed, Fig. 8(b) suggests that long-range coordinated relaxation occurs over an extended regime of intermediate strain amplitudes $0.05 < \gamma_0 < 0.5$ before the nearest neighbor cage is broken, a consequence of the strong compliance of the soft particles. In the latest stage, for both HSs and SSs 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. (2011a).

Another possible way to determine the yield stress [Moller *et al.* (2009); Denn and Bonn (2011)] is from the intersection of G' and G'' in Fig. 1. The yield stress is then determined from the crossover of the normalized G' and G'' using $\sigma_y = G'\gamma_y$, where γ_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. 9. The figure compiles data for HS and SS samples from this work and other work reported [Pham *et al.* (2008); Le Grand and Petekidis (2008)]. The yield stress determined from the Lissajous analysis (Fig. 9) is indicated by diamonds; it roughly



FIG. 9. 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 ϕ/ϕ_{max} (see Table I for the absolute volume fractions of soft-spheres). The dotted line is a guide to the eyes. Yield stresses from the Lissajous analysis are indicated as diamonds.

agrees with the yield stresses determined from the crossover of G' and G'' (red dots and black squares). 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 HS 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 [Pham et al. (2008); Le Grand and Petekidis (2008)] for HS suspensions lie close to the values obtained in this work, while the literature value for an SS suspension [Le Grand and Petekidis (2008)] is at much lower volume fraction but does roughly extrapolate on 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. We note that the yield stress depends also weakly on frequency; for the concentrated SS suspensions, we find an increase of the yield stress by $\sim 25\%$ when we increased the frequency by an order of magnitude.

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 inset in Fig. 8) in Fig. 10; closed and open symbols indicate data of HSs and SSs, respectively. Flow occurs for stresses larger than the yield stress, indicated by dashed horizontal lines; the gray area then indicates the flow regime. The curves for different strain amplitudes exhibit good overlap for HSs as expected. However, the curves appear shifted for the SSs; this shift again indicates the gradual yielding of the SS suspension, which depends on the amount of strain.

D. 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



FIG. 10. Stress as a function of strain rate in the flow regime of the cycle for hard (closed symbols) and soft spheres (open symbols). The gray area indicates approximately the regime where yielding has occurred (dashed horizontal line; yield stress).

amplitude in Fig. 11. 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. Finally, at large strain far in the nonlinear regime, the scaling of *P* decreases to a power close to $P \propto \gamma$. A power of 2 in the linear regime is in agreement with the expected dissipated energy [Tschoegl (1989)]

$$P = \pi \gamma_0^2 G''. \tag{5}$$

The fact that the scaling is not exactly $P \propto \gamma^2$ can be explained by the slight increase of G'' at low γ_0 [Fig. 1(a)]. 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



FIG. 11. Dissipated energy *P* of hard-sphere (a) and soft-sphere suspensions (b) as a function of strain amplitude γ_0 , calculated from the area of the Lissajous curves (solid lines), and from the LAOS parameters according to Eq. (7). 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.

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 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. HSs 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

$$\sin \delta = (1 - (\sigma_{dy} / \gamma_0 G_{\text{cage}})) \tag{6}$$

using a simple geometric relation [Rogers *et al.* (2011a)]. We show the approximated phase angle as a function of strain amplitude in Fig. 12(a). It increases from $\delta = 0^{\circ}$ at small strain to values approaching 90° 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 SSs from Fig. 1(b) in Fig. 12(b). Good agreement is observed at large strain. Some deviation in G'', however, occurs at small strain. Using Eqs. (5) and (6), we can now link the dissipated energy directly to the Lissajous parameters determined above. It follows that

$$P = \pi \sigma_0 (\gamma_0 - (\sigma_{dy}/G_{\text{cage}})). \tag{7}$$

The resulting values of the dissipated energy are indicated by dashed lines in Fig. 11. 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. 11. We note that because Eq. (7) connects the dissipated energy directly to the cage modulus [Rogers *et al.* (2011a)], this yields an alternative explanation of the different magnitude of dissipated energy of SS and HS suspensions: Following Eq. (7) a higher value of G_{cage} should directly lead to higher dissipated energy, which is indeed observed for the SSs as shown in Fig. 11.



FIG. 12. (a) Phase angle as a function of strain amplitude for hard and soft spheres. (b) Storage and loss moduli, G' and G'', of soft spheres reconstructed from Fig. 1 (symbols) and calculated using the extrapolated phase angle (dashed lines). Good agreement is observed, except at small strains where some deviation occurs.

IV. CONCLUSION

We have investigated the behavior of dense HS and SS suspensions under oscillatory shear. By using a new scheme to analyze oscillatory shear data, we have demonstrated the different physical processes in the straining, yielding and flow of concentrated HS and SS suspensions. 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 contacts of the particles. This suspension modulus can be accounted for using Hertzian theory with a single-particle modulus determined by atomic force microscopy. The compliance of the SSs leads to a high elastic component in the yielding, a smooth volume fraction dependence of the moduli, and a gradual yielding behavior that contrasts with the distinct yielding observed for HS suspensions. We associate this gradual yielding behavior with long-range relaxation modes in SS suspensions, and contrast it to the local cage breaking associated with the yielding of HS glasses. At the high volume fractions probed here, a deformation of the SS sample involves deformation of the particles as well, giving rise to an increased elasticity and dissipated energy. This high elasticity gives also rise to much higher yield stresses and strains of SS suspensions compared to the HSs. 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 SSs 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.

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