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Linear and nonlinear rheology of dense emulsions across the glass and the jamming regimes

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amorphous disordered solids composed of repulsive and deformable soft colloidal spheres.
Based on recent results from simulation and theory, we derive quantitative predictions for the
dependences of the elastic shear modulus and the yield stress on the droplet volume fraction.
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(Some figures may appear in colour only in the online journal)
relax in time. In reality a glass has a finite viscosity (and \( \alpha \)-relaxation in light scattering) that evolves in time, or ages, but the modulus and yield stress will not, for the repulsive (soft and hard) colloidal spheres considered here over relevant time scales.

While many detailed experimental and theoretical studies can be found as \( \phi \) approaches \( \phi_\ell \) from the liquid side [4, 8–13], quantitative studies in which \( \phi \) crosses both \( \phi_E \) and \( \phi_\ell \) are scarce [14]. The very existence of a solid glassy phase has been questioned, and it has even been suggested for hard spheres that the glass and jamming transition are the same \( \phi_E \equiv \phi_\ell \) [15]. Results obtained from experiments on only one type of experimental system have not yet been able to unravel the general question, mainly because it is very difficult to determine exact volume fractions of submicron sized particles [16], as a result of non-zero nanoscopic length scales associated with stabilization. Moreover, the very concept of hard-sphere-like systems has been questioned recently [17] due to the difficulty in designing colloids having a sufficiently sharp repulsive interface.

In this letter, we study the elastic shear modulus and the yield stress of a colloidal model system of (sub)microscale soft repulsive spheres. We discuss the experimental evidence for a solid glass and a jammed state of dense uniform emulsions. Moreover we demonstrate that applying simple theoretical concepts to these technically relevant systems provides accurate quantitative predictions about their linear and nonlinear mechanical properties.

An emulsion is a dispersion of droplets of one liquid in a different immiscible liquid [18]. The nano- to micrometer sized droplets of the dispersed phase can be kept almost indefinitely in a metastable state by decorating their interfaces with amphiphilic surfactant molecules. In emulsions, because of the existence of a thin film of continuous phase between droplets, lubrication is present, so solid–solid friction cannot play a role. In contrast to compressible star polymers or microgels [14, 20, 13, 19], which do not have volume fractions that are precisely defined, in an emulsion, the droplet volume fraction is well defined because the liquid within the droplets is incompressible, even if the droplet interfaces can deform under extreme compression. To prevent droplet coalescence, a short-range, screened electrostatic repulsive interaction, provided by an ionic surfactant, is typically present. For the anionic surfactant, sodium dodecyl sulfate (SDS), at 10 mM concentration in water, the Debye screening length is \( \lambda_D \approx 3.5 \text{ nm} \) [21]. Herein, we interpret measurements of the linear and nonlinear rheology of silicone oil in water emulsions stabilized by 10 mM SDS for droplet radii \( R = 250, 370 \) and 530 nm. Using depletion-induced droplet size segregation [22] the distribution of radii \( R \) of the droplets can be made quite uniform, \( \Delta R/R \sim 10–12\% \), while keeping the polydispersity sufficiently high in order to suppress crystallization [8–12]. The experimental data that we consider for the elastic modulus \( G_E \) and the yield stress \( \sigma_y \) have been published previously, and technical details can be found elsewhere [23, 18].

To provide perspective, we summarize briefly very recent theoretical predictions for the elastic shear modulus and the yield stress in the glass and in the jamming regimes. Theoretical and numerical work by Ikeda et al [25, 26] addresses the glassy dynamics and jamming of soft spheres. The authors lay out a theoretical scenario about how to distinguish between the mechanical response of a glassy system and that of a jammed system. Extensive simulations on idealized spheres that have harmonic repulsions beyond contact were carried out in order to map out the transition. What sets this study apart is their explicit focus on describing the physics of soft colloids crossing all relevant regimes. Most previous attempts for model colloidal systems have either concentrated on the approach to the glass transition \( \phi \leq \phi_E \) [4, 8–13] or on the jamming physics \( \phi > \phi_J \) [2, 3, 27, 29–31]. By considering both, Ikeda et al find that glassy and jammed colloids display qualitatively different characteristics with respect to their mechanical responses.

The details of the transition, however, depend sensitively on the nature of particle elasticity (i.e. repulsive interaction) when particles touch. For very soft spheres, the transition from the glass to a jammed solid is smeared out and phenomenologically disappears [28].

The mechanical properties of the glass are entropically driven and scale with temperature and size as \( \sim k_B T/R^3 \). Ikeda et al suggest the following scaling relation for the yield stress covering the entire glass phase for hard spheres [25]:

\[
\frac{\sigma_y}{k_B T/(2R)^3} \simeq c_1 \left[ 1 + c_2 \left( \phi - \phi_E \right)^{0.7} \right]^{c_3} \left( \phi - \phi_J \right)^{0.8} \tag{1}
\]

with constants \( c_1 \) and \( c_2 \) of order unity. MCT calculations for both the yield stress and the modulus are consistent with this scaling, the parameters \( c_1 \) and \( c_2 \) however strongly depend on the specific approximations made [32–34]. The second term in equation (1) takes account of the expected divergence of \( \sigma_y \) close to the jamming of hard spheres [35, 25]. Since the divergence is avoided for soft spheres, the transition must be somewhat smeared, as it is also apparent in simulation results [25].

We now turn our attention to the packing fraction dependence of the shear modulus above the jamming threshold \( \phi > \phi_J \). In the jamming scenario the modulus is given by a product of the bond strength \( k \) and the excess number of contacts [2, 3] which has been found to scale as \( \Delta Z \propto \sqrt{\phi - \phi_J} \) [36, 37] and thus

\[
G_p = a_1 \frac{k}{\pi R} \sqrt{\phi - \phi_J} \tag{2}
\]

where \( a_1 \) is a constant of order unity [2, 3, 19, 38, 39]. Note that \( \pi R g_0 \) is the spring constant of a particle harmonically bound in a matrix having \( G_p \) [40–42]. When applying a sufficiently large stress \( \sigma_y \) the sample will yield and subsequently flow. Recent simulation work suggests \( \sigma_y \sim \kappa (\phi - \phi_0)^{1.2} [43, 44]^{4} \) which in turn provides expressions for

\[4\] In the supplemental material, figure S3 (available at stacks.iop.org/JPPhysCM/25/502101/mmedia), we compare the model predictions for slightly different scaling exponents, 1 and 1.5, also reported in the literature for harmonic spheres [45, 46].
the yield stress and the yield strain, where \( a_2 \) is a constant

\[
\sigma_y = a_2 \frac{k}{\pi R} (\phi - \phi_1)^{1.2} = (a_2/\alpha_1) G_p \times (\phi - \phi_1)^{0.7}. \tag{3}
\]

\[
\gamma_y = \sigma_y / G_p = a_2 / \alpha_1 (\phi - \phi_1)^{0.7}. \tag{4}
\]

We first compare the theoretical predictions with experimental data for the yield strain, figure 1. The yield strain should be scale invariant and thus the data for different sizes should collapse on a master curve. As shown previously, this is indeed the case for microscale droplets provided the bare droplet volume fraction \( \phi_{eff} = \phi(1 + h/2R)^3 \), where a \( \phi \)-dependent effective thickness \( h \sim 10 \) nm of the interfacial layer is used to account for screened electrostatic interactions between droplet interfaces [23, 18]. Moreover the yield strain should be independent of the bond strength according to equation (4). Indeed, as shown in figure 1, well above \( \phi_1 \) the yield strain rises and the data is consistent with the scaling predicted by equation (4) with \( a_2 / \alpha_1 \sim 0.2 \).

We note that while the concept of an effective volume fraction captures rather well the influence of the interfacial layer for microscale droplets, this approximation is certainly not perfect [24]. This explains for example why the experimental effective jamming density \( \phi_{eff} \sim 0.62 \) [23] is found to be slightly lower than the expected value 0.64 (see also figure 3). The effect is even more pronounced for nanoscale droplets, \( R \leq 100 \) nm, where the size begins to approach the Debye screening length; in this limit disordered nanoemulsions can become elastic solids at bare volume fractions, as low as about \( \phi \sim 0.2 \) [24].

Over 0.60 < \( \phi_{eff} < 0.68 \) the yield strain data are approximately constant, as figure 1. At the very lowest measured 0.58 \( \leq \phi_{eff} \leq 0.60 \), well below \( \phi_{eff} \) and very close to measurements of \( \phi_g, \gamma_y \) is reported to be slightly larger, which would indicate a different scaling of \( G_p \) and \( \sigma_y \) when approaching the jamming transition (i.e. a different \( c_1 \) and \( c_2 \) parameter in equation (1), such that the modulus would rise faster than the yield stress approaching \( \phi_{eff} \)). However this observation could also be due to an increasing uncertainty in the line intersection method on the log–log plot of stress versus strain, which defines the yield point, as the emulsion’s low-strain response begins to transition from dominantly elastic to dominantly viscous [23]. Given the uncertainty in the experiments and analysis, it is reasonable to say that the yield strain is approximately constant for \( \phi_{eff} \) between \( \phi_g \) and \( \phi_{eff} \), at about 0.030 ± 0.005. The same value for \( \sigma_y / G_p \) has been reported by Ballauff, Fuchs and co-workers in a careful study of microgel core–shell particles approaching the glass transition from below [47].

We now return to the discussion of the modulus and the yield stress of an emulsion. The scaling relations equations (2) and (3) have been suggested for harmonic spheres having pair-wise interactions described by \( V(r) = \epsilon(1 - r^2/2R^2)^2 \), where the spring constant is \( k = \epsilon / 2R^2 \) [2, 3, 38, 39, 25].

\[
\gamma_y = \sigma_y / G_p \sim 0.64 \tag{5}
\]

In the limit of small droplet compression \( 1 - r^2/2R \ll 1 \) the potential reduces to the more common form \( V(r) = \epsilon(1 - r^2/2R)^2 \), \( \epsilon = 2C \gamma R^2 \). Here \( \gamma \) is the surface tension. For our case \( \gamma \sim 9.8 \times 10^{-3} \) N m\(^{-1}\) and the characteristic constants are \( C \sim 0.36, \alpha \approx 2.32 \) [36, 37]. For example for \( R = 250 \) nm, \( \epsilon \approx 1.4 \times 10^6 k_B T \). We find for \( k = 3\pi \gamma R/\alpha^3 \),

\[
2R^2 k(r) = \frac{6\alpha^2}{3\alpha} \left( \frac{2R}{r} \right)^5 \left( \frac{2R}{r} \right)^3 - 1 \alpha^{-1}
\]

In a bulk emulsion the interdroplet distance \( r \) set is by the droplet number density which in turn is related to the volume fraction occupied by the oil droplets and thus \( \phi \propto r^{-3} \). At the jamming transition (\( \phi \sim 0.64 \)) the droplets are in direct contact \( r = 2R \) thus \( \phi(\phi_1) \phi^1/3 \) and we can write \( r/2R \approx \phi(\phi_1)^1/3 \) [27]. Combining equations (6) and (2) provides a simple expression for the shear modulus,

\[
G_p / \gamma \sim 6\alpha_1 [\phi/3(\phi - \phi_1)^{0.82} + \phi^{5/3}(\phi - \phi_1)^{1.82}] . \tag{7}
\]

For an estimate of the prefactor \( \alpha_1 \) in equation (7) we compare our model to simulation results for \( G_p \) reported by Lacasse et al [36]. For the comparison we have slightly rescaled the \( \phi \)-values of the simulation data by a numerical factor of 0.978 to have them extrapolate to the same critical value \( \phi_1 = 0.64 \). We find excellent agreement for \( \alpha_1 = 0.25 \pm 0.01 \) as shown in figure 2. This also sets an
Moreover, the scaled G between droplets and the scaling of the coordination number. Remarkably, equations (3) and (7) now provide quantitative analytic predictions for the shear modulus and yield stress of emulsions that can be tested directly against experimental data. In figure 3 we compare the predictions in the jammed state, equations (3) and (7), with the experimental data for the shear modulus and the yield stress. The agreement is remarkable given the difficulty of such a quantitative comparison.

While other formulas exist for predicting the modulus and yield stress of a disordered uniform emulsion as a function of volume fraction [23], they are empirically based and have not, up to now, been derived analytically in a microscopic model that properly incorporates the potential of interaction between droplets and the scaling of the coordination number. Moreover, the scaled Gp(φ) and σγ(φ) are self-consistent in this model (i.e. use the same microscopic parameters) and provide good agreement with both linear and nonlinear numerical simulations of the shear modulus and yield stress. The agreement is given in units of 10⁻¹⁴ (very soft spheres) the glassy phase narrows and the transition is smeared out to an extent that in an experiment or simulation glassy physics and jamming cannot be distinguished any more. For our droplets Tc ~ 10⁻⁷–10⁻⁶ which should allow us to distinguish both regimes. The glass physics and the onset of jamming should not depend on the details of the interaction potential. We can thus attempt to compare the simulation results for Tc = (k_BT)/ε [25].

Next we address the properties in the glass state and the transition from the glass to the jamming physics, which is governed by the particle softness. Ikeda’s measure of softness is given by Tc = (k_BT)/ε [25]. Computer simulations for harmonic spheres show that for values larger than 10⁻⁴ (very soft spheres) the glass phase narrows and the transition is smeared out to an extent that in an experiment or simulation glassy physics and jamming cannot be distinguished any more. For our droplets Tc ~ 10⁻⁷–10⁻⁶ which should allow us to distinguish both regimes. The glass physics and the onset of jamming should not depend on the details of the interaction potential. We can thus attempt to compare the simulation results for Tc = (k_BT)/ε [25]. Computer simulations for harmonic spheres show that for values larger than 10⁻⁴ (very soft spheres) the glassy phase narrows and the transition is smeared out to an extent that in an experiment or simulation glassy physics and jamming cannot be distinguished any more. For our droplets Tc ~ 10⁻⁷–10⁻⁶ which should allow us to distinguish both regimes. The glass physics and the onset of jamming should not depend on the details of the interaction potential. We can thus attempt to compare the simulation results for Tc = (k_BT)/ε [25]. Computer simulations for harmonic spheres show that for values larger than 10⁻⁴ (very soft spheres) the glassy phase narrows and the transition is smeared out to an extent that in an experiment or simulation glassy physics and jamming cannot be distinguished any more. For our droplets Tc ~ 10⁻⁷–10⁻⁶ which should allow us to distinguish both regimes. The glass physics and the onset of jamming should not depend on the details of the interaction potential. We can thus attempt to compare the simulation results for Tc = (k_BT)/ε [25]. Computer simulations for harmonic spheres show that for values larger than 10⁻⁴ (very soft spheres) the glassy phase narrows and the transition is smeared out to an extent that in an experiment or simulation glassy physics and jamming cannot be distinguished any more. For our droplets Tc ~ 10⁻⁷–10⁻⁶ which should allow us to distinguish both regimes. The glass physics and the onset of jamming should not depend on the details of the interaction potential. We can thus attempt to compare the simulation results for Tc = (k_BT)/ε [25]. Computer simulations for harmonic spheres show that for values larger than 10⁻⁴ (very soft spheres) the glassy phase narrows and the transition is smeared out to an extent that in an experiment or simulation glassy physics and jamming cannot be distinguished any more. For our droplets Tc ~ 10⁻⁷–10⁻⁶ which should allow us to distinguish both regimes. The glass physics and the onset of jamming should not depend on the details of the interaction potential. We can thus attempt to compare the simulation results for Tc = (k_BT)/ε [25]. Computer simulations for harmonic spheres show that for values larger than 10⁻⁴ (very soft spheres) the glassy phase narrows and the transition is smeared out to an extent that in an experiment or simulation glassy physics and jamming cannot be distinguished any more. For our droplets Tc ~ 10⁻⁷–10⁻⁶ which should allow us to distinguish both regimes. The glass physics and the onset of jamming should not depend on the details of the interaction potential. We can thus attempt to compare the simulation results for Tc = (k_BT)/ε [25].

5 Simulations for harmonic spheres in the zero-temperature limit [25] are well described by equation (3) with a yield stress parameter σy ≅ 0.03, in fairly good agreement with the estimate reported here. The remaining difference might be due to the different interaction potentials, the different particle size distributions, and due to difficulties in assessing absolute values of the yield stress experimentally with high precision.

6 We note that for simplicity we have neglected an additional weak concentration dependence of r ~ φ⁰.⁰⁵, suggested in [27], and of a and C in the interaction potential V(r) as discussed in [36]. Both effects are due to the rise in the number of contacts Z upon compression and could easily be incorporated in the model.
the experimental data do not scale with the droplet size as suggested by entropic origin of the glass elasticity, equation (1). We are unable to discern whether this is due to limitations of the theory, or due to the experimental difficulties in determining such small values with sufficient accuracy, or both. To resolve this question additional experiments covering a larger range of droplet sizes will be required in the future.

Notwithstanding the above, the present work suggests that the glass and jammed state are well distinguishable for experiments on uniform emulsions. Both the modulus and the yield stress are characterized by a sharp rise close to the jamming transition. This indicates that the smearing of the yield stress are characterized by a sharp rise close to the transition is limited and our emulsion droplets indeed behave as soft spheres with a sufficient stiffness $\epsilon/k_BT$ or bond strength. In reality, emulsion droplets stabilized by an ionic surfactant are slightly more complicated. The presence of the Debye layer will soften the droplet interactions. However, as droplets come into contact, the Debye layer is rapidly compressed and the stiffness increases until it approaches the value $\epsilon/k_BT$ of the elastically coupled droplet core [24]. Our results suggest that this process takes place over a very limited range of concentrations for the droplet sizes $R \geq 250$ nm considered here. The situation might be different when considering smaller droplets [24] or particles having a different interaction potential.

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