Elasticity of Arrested Short-Ranged Attractive Colloids: Homogeneous and Heterogeneous Glasses

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We evaluate the elasticity of arrested short-ranged attractive colloids by combining an analytically solvable elastic model with a hierarchical arrest scheme. This new approach allows us to discriminate the microscopic (primary particle-level) from the mesoscopic (cluster-level) contribution to the macroscopic shear modulus. The results quantitatively predict experimental data in a wide range of volume fractions and indicate in which cases the relevant contribution is due to mesoscopic structures. On this basis we propose that different arrested states of short-ranged attractive colloids can be meaningfully distinguished as homogeneous or heterogeneous colloidal glasses in terms of the length scale which controls their elastic behavior.

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Suspensions of short-ranged attractive colloidal particles are the object of intense study due to their technological applications (proteins, paints, etc.), as the constituent blocks of nanomaterials, as well as model systems to investigate phase behavior and dynamical arrest of condensed matter [1]. A landscape of phases has been observed upon varying the volume fraction ϕ or the interaction parameters [2], and, as a matter of fact, extended regions of the phase diagram are still poorly understood. In very dense suspensions ($\phi > 0.5$) the arrested states are spatially homogeneous (i.e., the typical linear size of structural heterogeneity is smaller than the particle diameter R_0). Particles are immobilized within the range of attraction, giving rise to bonds that are persistent under strain in the linear regime, and the high density leads to (attractive) glassy states [3]. For $0.2 < \phi < 0.5$, the situation is complicated: arrested states can only occur thanks to pronounced structural heterogeneities, typically on length scales larger than R_0. Therefore, they are more related to gelation [4], rather than to the caging typical of crowded random media [5]. However, such arrested states are also hardly classifiable as classic network gels in view of the different morphology and stress-bearing mechanisms. For them, different microscopic phenomena should be considered and a new theoretical framework, able to account for the strong spatial heterogeneities and currently still missing, would be desirable. A crucial point, mostly neglected in recent studies, is that arrested states occurring at different volume fractions and attraction strengths do display dramatically diverse mechanical and rheological properties [6]. That is why their characterization is of true interest in technological applications and material design.

In this Letter we propose a new, more *down to earth*, approach to characterize arrested short-ranged attractive colloids, based on their mechanical response. The problem being extremely hard to tackle, we rely on a simplified picture: We combine an analytically solvable elastic model with a hierarchical arrest scheme and provide a first attempt to discriminate the microscopic (primary particle-level) from the mesoscopic (cluster-level) contribution to the macroscopic elasticity. The predictions are given in terms of the shear modulus, a quantity that can be measured in a rheometer, and are directly compared with experimental results. In spite of the crude, but physically grounded assumptions, we are able to show, for the first time, that where structural heterogeneities such as clusters are present, the measured macroscopic elasticity differs by orders of magnitude from the one of the homogeneous glass because it is strongly dominated by the intercluster contribution. Our approach offers, therefore, a new insight into the physics of arrested attractive colloidal suspensions, especially in the range $0.2 < \phi < 0.5$, hitherto poorly understood. We propose that homogeneous and heterogeneous arrested states can be distinguished in terms of the length scale $\tilde{R}_0$, which controls the macroscopic elastic modulus.

Model and predictions.—We study a suspension of colloidal particles interacting via a short-range attraction, as the one typically induced by depletion using nonadsorbing polymer [1], well above percolation, so that a finite shear modulus is always detectable. As a first step towards rationalizing the mechanical response of arrested, dense attractive colloids, and in the fundamental lack, at present, of alternative approaches, we use a simplified, although physically grounded, scenario. We consider that, by reducing the volume fraction from the very dense homogeneous glass case, the attractive interactions will start to produce small aggregates, with the aggregation being soon arrested by the glassy environment. This mechanism leads to compact aggregates of relatively small linear size [7,8]. In order to distinguish the single-particle contribution to elasticity from the mesoscopic one, we therefore consider coarse-grained entities, i.e., *renormalized particles*. Their effective interactions are directly responsible for the macroscopic properties of the system. This scheme can be associated to a double-ergodicity-breaking scenario where the arrest occurs in the form of a cluster-glass transition [9–11]. A *sine qua non* is that further coalescence of the clusters, leading to phase separation, is prevented on the observation time scale [10]. We distinguish between the macroscopic elasticity of the system G, the intracluster elasticity G_g resulting from mutual interactions between primary particles, and the intercluster elasticity G_c, resulting from mutual interactions between clusters.

Let us first consider the case of a homogeneous attractive glass in the low-temperature and high-density ($\phi > 0.5$) region of the phase diagram. Here we focus on the first linear regime reported in rheological measurements [12], which is due to bond breaking and, for strong attractions, extends nearly up to strains of a few percent. Hence, we follow the Cauchy-Born approach developed in [13] for amorphous solids and obtain the elasticity from a free energy expansion around a *stressed* (quenched) reference state $\{R\}$ where all particles are *labeled*. The expansion reads $\delta F \equiv F(\{r\}) - F(\{R\}) \simeq \sum_{ij}[\partial F/\partial r_{ij}]\delta r_{ij} + \frac{1}{2}\sum_{ij,kl}[\partial^2 F/\partial r_{ij}\partial r_{kl}]\delta r_{ij}\delta r_{kl}$, where the sums run over all interacting pairs of particles (bonds) and the derivatives are evaluated at relative distances $\{\mathbf{R}_{ij}\}$ in the quenched reference state. Because of the purely internal nature of the stresses, the first term in the right-hand side does not contribute to the macroscopic elasticity [13,14]. In the case of central forces, considering a pair interaction with a deep minimum $\epsilon \gg k_B T$, the bond stiffness is defined by $\kappa \simeq \partial^2 F/\partial r_{ij}^2$ (evaluated at the minimum), and the Born-Huang (BH) terms become $\delta F = \frac{1}{2}\kappa\sum_{ij}(\delta r_{ij})^2$. If we express such deviations in terms of a smooth displacement field $\mathbf{u}_{ij}$ [13], with central forces only the longitudinal component $u_{ij}^{\parallel}$ is nonzero. Upon neglecting higher order terms, the deformation free energy reads $\delta F \simeq \frac{1}{2}\kappa\sum_{ij}(u_{ij}^{\parallel})^2$. Under the assumption that all pairs of particles are much localized near the minimum of the potential well and that displacements are affine, we take the continuum limit of the microscopic $u_{ij}^{\parallel}$ in terms of the macroscopic strain tensor $\mathbf{e}$, $\langle u_{ij}^{\parallel}\rangle = \mathrm{Tr}[(\mathbf{R}_{ij} \otimes \mathbf{R}_{ij}) \cdot \mathbf{e}/R_{ij}]$, with $\langle u_{ij}^{\parallel} - \langle u_{ij}^{\parallel}\rangle\rangle^2 \ll \langle u_{ij}^{\parallel}\rangle^2$, to obtain $\delta F \simeq \frac{1}{2}\kappa\sum_{ij}\{\mathrm{Tr}[(\mathbf{R}_{ij} \otimes \mathbf{R}_{ij}) \cdot \mathbf{e}/R_{ij}]\}^2$. For the quenched reference configuration $\{R\}$, in the case of uncorrelated disorder, the summation over bonds can be replaced by the total number of contacts, which introduces the average coordination number $z(\phi)$ in the final expression of the deformation free energy. We then derive the off-diagonal components of the stress tensor [15]

$$\sigma_{\alpha\beta} \equiv \frac{\partial \delta F}{\partial e_{\alpha\beta}} \simeq 2\rho z(\phi)\kappa \frac{\partial}{\partial e_{\alpha\beta}} \left\langle \left(\frac{R_{ij}^{\alpha} R_{ij}^{\beta}}{R_{ij}}\right)^2 e_{\alpha\beta}^2 \right\rangle_{\Omega}, \qquad (1)$$

where $\langle\cdots\rangle_{\Omega} = (4\pi)^{-1}\int\cdots d\Omega$. Hence the shear modulus of an arrested phase of volume fraction $\phi = \rho\pi R_0^3/6$, with mean particle diameter $\simeq R_0$, is given by $G_g = (2/5)\pi^{-1}\phi z(\phi)\kappa R_0^{2-d}$. The evaluation of the coordination number $z(\phi)$ in dense glassy systems is still controversial. Since at high densities also attractive systems are likely to be dominated by excluded-volume repulsion [16], we estimate the number of short-range contacts involved in the mechanical bonds from $z(\phi)$ of a purely replusive glass. That is, we integrate the radial distribution function (rdf) of the dense (hard-sphere) liquid precursor, $g(r)$, within a shell of width $l^{\dagger}$. A reasonable choice for repulsive systems is $l^{\dagger} \sim 0.03$ which allows us to recover $z \sim 6$ at random close packing [17]. We thus obtain the shear modulus as a function of the rdf:

$$G_g \simeq (48/5)\pi^{-1}\kappa R_0^{2-d}\phi \int_0^{l^{\dagger}} (1 + l)^2 g(l;\phi) dl, \qquad (2)$$

where $l = (r - R_0)/R_0$ and $l^{\dagger} \simeq 1/30$. For $g(r)$ near contact ($l < 0.1$) we use liquid theory valid in the dense hard-sphere fluid [18] and we calculate κ using the Asakura-Oosawa (AO) potential [19]. Our predictions have been compared to the experimental data of Ref. [12] for an attractive colloidal glass ($\phi \simeq 0.6$). The shear modulus was measured as a function of the attraction strength, i.e., the reduced polymer concentration c_p/c_p^*. For strong enough attraction (and fully elastic response), the affine approximation is more realistic and our prediction gives an accurate estimate of the measured shear modulus [20]. We have checked that the agreement does not significantly change upon varying $l^{\dagger}$.

For a more stringent test of the model where the bond-stiffness and the local structure of the glass are well-defined, we performed molecular dynamics simulations of deeply quenched glasses obtained from different models for supercooled liquids. We subjected the glass to shear strain and extracted stress-strain curves [20]. The agreement obtained in the linear regime is remarkable, indicating that the model is quantitatively predictive and that the nonaffine rearrangements are actually small in the strong-attraction or deep quench limit, in agreement with our assumptions [20].

For the more dilute regime, we now consider local aggregation of the colloidal particles to form beads (clusters), which, in turn, arrest due to either caging or residual attraction, as in the double-ergodicity breaking scenario mentioned above [9–11]. The clusters are viewed as compact (spherical or quasispherical) renormalized particles of diameter $\tilde{R}_0$, whose effective volume fraction ϕ_c may be identified with the one determined by the smallest spheres enclosing them (i.e., ϕ_c significantly larger than ϕ). If the cluster linear size is larger than the particle diameter by a factor say less than 10, each contact between clusters is likely to reduce to a single colloid-colloid bond. Upon neglecting: (i) the breakup probability within the cluster, and (ii) the effect of long-range repulsion, the effective interaction between clusters obviously reduces to the bare colloid-colloid interaction, in agreement with [10].

Further, the mean coordination will change to $z(\phi_c)$, but its form can be still determined as in Eq. (2) if ϕ_c is in the dense glassy regime dominated by mutual impenetrability. Hence, for the modulus of the cluster glass we can write,

$$G_c \simeq (2/5)\pi^{-1}\phi_c z(\phi_c)\tilde{\kappa}\tilde{R}_0^{2-d} \tag{3}$$

with $\tilde{\kappa} \simeq \kappa$ under the assumption of small clusters. Equation (3) gives the elastic modulus of the material, where the macroscopic elasticity is dominated by the mesoscopic level. We test our scheme using the extensive experimental data of Ref. [7] for a system of colloidal silica particles with polystyrene as depletant in organic solvent (decalin), where the ratio of the polymer gyration radius to R_0 is the same as in the experiments of [12]. For two values of c_p/c_p^*, they vary ϕ in the range 0.2–0.4. The system is a dense gel of compact clusters ($\phi \simeq 0.5$ inside the cluster), whose diameter $\tilde{R}_0/R_0 \sim 5$ is determined from the Debye-Bueche plot. For a fixed c_p/c_p^*, they find $\tilde{R}_0/R_0$ and the volume fraction inside the clusters not to significantly change with ϕ, i.e. ϕ_c increasing linearly with ϕ. This indicates that in this case our assumptions on the structure are reasonable. The assumption that the spheres enclosing the clusters are densely packed yields $\phi_c \simeq 0.64$ at the largest value of ϕ, allowing for a physically reasonable estimate of ϕ_c in the range of ϕ considered. Using the experimental measurement of $\tilde{R}_0/R_0$ we can therefore calculate G_c from Eq. (3). In Fig. 1 we plot the values of the shear modulus measured at 1 Hz in [7] for two different attraction strengths, together with our predictions of G_g from Eq. (2) [21] and of G_c from Eq. (3), as function of ϕ and ϕ_c. The excellent agreement between our estimate and experiments in Fig. 1 clearly indicates that, differently from the case previously considered, now is G_c that dominates the macroscopic elasticity of the system. We have checked that the uncertainty on ϕ_c does not significantly affect this result. For lower attractions, the system will gradually cross over towards the repulsive case.

We now consider the results recently reported in [8], for a different arrested AO system in the heterogeneous glass regime, studied at a fixed $\phi = 0.4$ and upon varying c_p/c_p^*. In the experiments, they used light scattering and microscopy to estimate the length scale of structural heterogeneities up to $c_p/c_p^* \simeq 2$. We have used this experimental input to calculate the prediction of our model for this system. Again for densely packed clusters (i.e., with volume fraction in the range 0.58–0.64) we estimate $\phi_c \sim 0.6$ (and check that variation around this value does not significantly change our outcomes). In Fig. 2 we compare G_c to the experimental measurements: G_c (solid line) shows a remarkable agreement with G_{exp} and turns out again to dominate the elastic response (see in comparison G_g, dashed line). Also here the comparison with experiments has been done at low frequencies and for fully elastic response.

The results just discussed lead us to sketch in Fig. 3 a new qualitative *phase diagram* for the arrested states of short-range attractive colloidal suspensions. As a function of ϕ and k_BT/ϵ, where ϵ is the depth of the attractive well, we locate the arrested states in the region where the system displays a nonzero measurable elastic modulus G (the continuum line divides fluid from solid states as discussed, e.g., in [22]). At high enough ϕ and large attractions, such *state* (*homogeneous glass*) is characterized by an elastic modulus dominated by the interparticle elasticity ($\tilde{R}_0/R_0 = 1$). Upon lowering ϕ, aggregation starts to produce mesoscopic structural heterogeneities and the mechanical response of the system crosses over towards a regime dominated by the intercluster elasticity (*heterogeneous glass*) ($\tilde{R}_0/R_0 \gg 1$). The two regimes will be distinguished by a significant variation of the elastic modulus of the material (Fig. 1). Our diagram suggests for the first

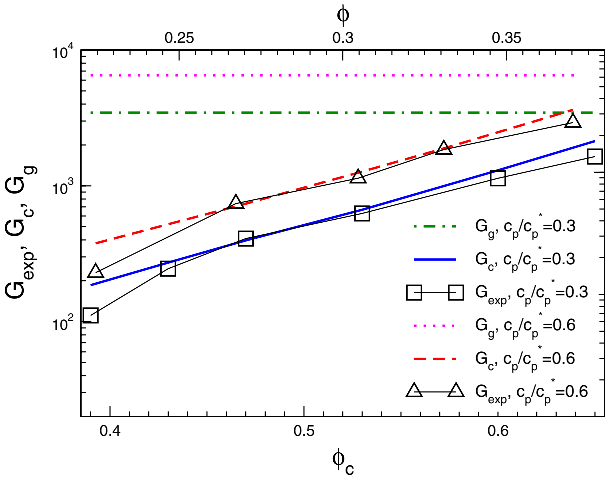

FIG. 1 (color online). Shear modulus as a function of ϕ_c for the experimental data from [7] and for the model prediction from Eqs. (2) and (3). $\tilde{R}_0/R_0 = 5.5$ and polymer-to-colloid size ratio $\xi = 0.078$ from [7] (upper x axis: ϕ for $c_p/c_p^* = 0.3$).

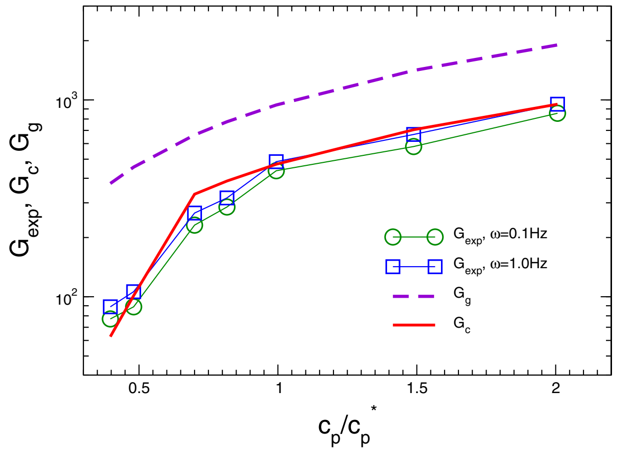

FIG. 2 (color online). The shear modulus as a function of c_p/c_p^* from Ref. [8] (symbols), with polymer-to-colloid size ratio $\xi = 0.08$ and $\tilde{R}_0/R_0$ from experiments. Lines: model prediction from Eq. (2) (dashed) and (3) (full).

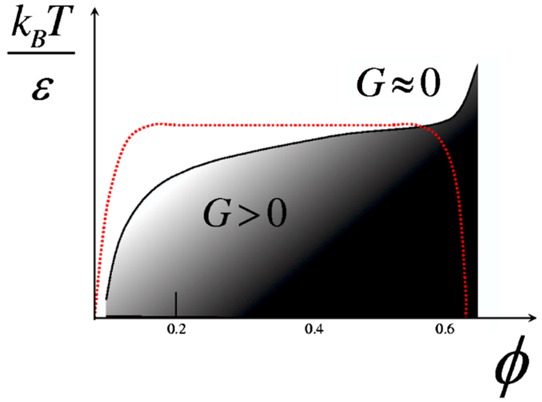

FIG. 3 (color online). Arrested states characterized in terms of the typical length scale $\tilde{R}_0/R_0$ of the mechanically relevant structural heterogeneities. Color gradient from $\tilde{R}_0/R_0 \gg 1$ (light) to $\tilde{R}_0/R_0 \simeq 1$ (dark). Fluid-solid transition (solid line) and spinodal (dotted line) also indicated.

time a distinction between arrested states of attractive colloidal suspensions in terms of a well-defined, directly measurable quantity, the elastic shear modulus. When the structure of the material is known in some detail, such distinction can provide information on which part of the structure is relevant to the elastic behavior. Upon further lowering the volume fraction ($\phi \lesssim 0.2$), we expect the elastic response to be dominated by a different length scale, associated to the weakly connected networklike mesoscopic structure and strongly dependent on ϕ [4]. Because of lower connectivity, nonaffinity is likely to be more pronounced and lead to a sensibly lower shear modulus (Fig. 1). At very low ϕ arrested states may be due to effective directional interactions arising at mesoscopic length scales, leading to open network structures [23], where buckling strongly affects the macroscopic elasticity.

Conclusions.—We have proposed that dramatic differences, observed at different volume fractions in the mechanical response of arrested, dense attractive colloids, originate from the presence of structural heterogeneities. We have presented a first attempt to estimate the shear modulus of glassy systems where structural heterogeneities as clusters are present. Being the problem extremely hard to tackle, we have to rely on a rather simplified picture. In spite of this, we have been able to show in two different experimental systems that the measured macroscopic elasticity is strongly dominated by the intercluster contribution. This first novel approach can pave the way to a meaningful distinction between different glassy states, on the basis of the length scale $\tilde{R}_0$ dominating their elastic response. $\tilde{R}_0$ varies with volume fraction and attraction strength due to the arising of structural heterogeneities. However, whereas the characterization of structural heterogeneities requires detailed structural information and is therefore often elusive, the variation of $\tilde{R}_0$ is unambiguously signalled by significant variation of the elastic modulus. Therefore we propose that homogeneous and heterogeneous arrested states can be distinguished in terms of the length scale $\tilde{R}_0$, which controls the macroscopic elastic modulus.

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