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## Density of States of Colloidal Glasses

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Glasses are structurally liquidlike, but mechanically solidlike. Most attempts to understand glasses start from liquid state theory. Here we take the opposite point of view, and use concepts from solid state physics. We determine the vibrational modes of a colloidal glass experimentally, and find soft low-frequency modes that are very different in nature from the usual acoustic vibrations of ordinary solids. These modes extend over surprisingly large length scales.

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The glass transition is perhaps the greatest unsolved problem in condensed matter physics [1]: the main question is how to reconcile the liquidlike structure with solidlike mechanical properties. In solids, structure and mechanics are related directly through the vibrational density of states (DOS) of the material [2]. To see whether similar ideas could be used for glasses, a first step is to determine the density of states of a glass that is solid mechanically, but has no crystalline ordering.

Recent theory shows that randomly packed, frictionless hard spheres form a system with no redundant mechanical constraints. Because of this, a small perturbation, like, for example, breaking a particle contact, may induce rearrangements at all scales [3–5]: the system is “critical” in this sense [6,7]. It has been argued that the marginality of the system has dramatic consequences for the vibrational spectrum [8]: in stark contrast to the well-known phonon modes in solids [9–12], a broad band of floppy modes emerges in the vibrational density of states, with a gap at low frequencies that disappears as the pressure becomes infinite.

In this Letter we measure, for the first time, vibrational eigenstates of colloidal glasses and supercooled liquids. We consider colloidal hard spheres that are subject to thermal agitation, allowing us to follow the “vibrational” motion of particles that are trapped in cages constituted by their neighbors. This is done at different random dense packing configurations around the glass transition. We obtain the density of modes from a normal-mode analysis of particle displacements measured using confocal microscopy. We find that the vibrational spectrum has many soft low-frequency modes [8], more abundant and different in nature from the usual acoustic vibrations of ordinary solids. This results in an anomalous low-frequency peak in the density of states which approaches zero frequency as one goes deeper into the glass phase. The observed soft modes are collective “swirling” particle motions that extend over surprisingly long length scales.

Hard-sphere colloidal systems exhibit a glass transition. Although the exact localization of glass transition is un-

certain and remains a point of discussion, the fact is that the dynamics becomes very slow around a volume fraction of  $\phi_{\text{glass}} = 0.58$  [13]. We use poly-methylmethacrylate (PMMA) particles, of diameter,  $\sigma = 1.3 \mu\text{m}$ , with a polydispersity in size of about 5% that prevents crystallization within the time scale of our experiments. Particles are sterically stabilized to prevent aggregation and are dyed with rhodamine which makes them visible using (confocal) fluorescence microscopy. We use a mixture of cyclohexylbromide and decalin as our solvent, to match the density and index of refraction of the particles. The organic salt TBAB (tetrabutylammoniumbromide) is used to screen possible residual charges. To verify the hard-sphere behavior we allow the system to crystallize by waiting weeks or months, and measure the crystallization density, a very sensitive measure for deviations from the hard-sphere behavior; it agrees to within a fraction of a percent to that of true hard spheres.

Two-dimensional images were acquired using a fast confocal microscope (Zeiss LSM live) in a field of view of  $100 \mu\text{m} \times 100 \mu\text{m}$ . Following around 2000 particles in real time allows us to reconstruct all particle trajectories (Fig. 1). The 2D slice was taken at a distance of 25–30  $\mu\text{m}$  away from the coverslip, deep enough to avoid the effects of confinement [14]. To ensure reproducibility, each sample is measured a few times, and for each volume fraction 2 to 3 samples are measured. The time interval between each image is 0.05 sec, which is approximately  $1/15^{\text{th}}$  of the Brownian time,  $\tau_B = \eta d^3/k_B T \approx 0.75 \text{ sec}$ , where  $\eta$  is the solvent viscosity. The mean-square displacement per particle  $\langle(\delta r)^2\rangle$  as a function of time shows a plateau when plotted on a log-lin scale, indicating that in our experimental time-window, each particle moves in a “cage” constituted by neighboring particles. The plateau value decreases with increasing volume fraction of the suspension, because the particle motion is more restricted (Fig. 2). Clearly, measurement times have to be long enough for soft modes (if present) to be visible, yet short enough that the system stays within a basin. The very existence of a plateau in our measured mean-squared displacement shows that there is a

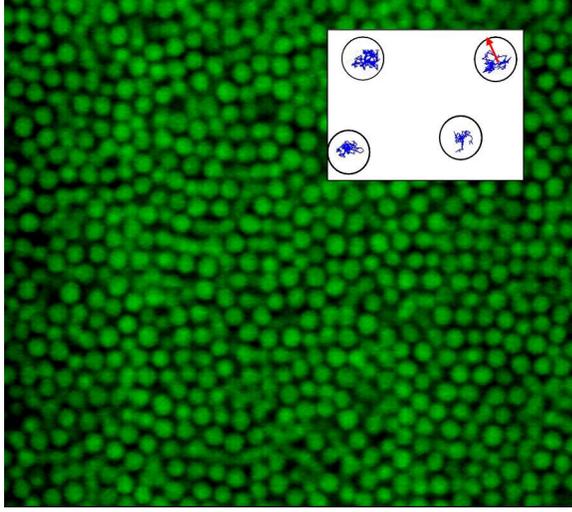


FIG. 1 (color online). A two-dimensional image of the colloidal suspension at a volume fraction 0.60 acquired by confocal microscopy. The field of view is  $100 \times 100 \mu\text{m}$ . The inset shows a few typical particle trajectories, which show that we obtain the DOS before large-scale rearrangements happen.

range of time scales for which local equilibrium can be justified and the soft modes can be measured, without many activated events taking place.

As shown in [15], if there is a proliferation of soft modes above a low-frequency gap, the value of the plateau in the mean-squared displacement is dominated by the soft modes just above the gap, leading to an anomalous scaling of the plateau with pressure. Although each individual high frequency vibrational mode will have a squared amplitude that scales as  $p^{-2}$ , the dominant effect here should be that the new modes appear as the gap closes with increasing pressure. An estimate of the pressure dependence on the gap then leads [15,16] to the prediction that the plateau value of the mean-squared displacement scales with pressure as  $p^{-3/2}$ . This scaling can be tested directly in our experiments by plotting the plateau value of the mean-square displacement vs the pressure. The latter can be

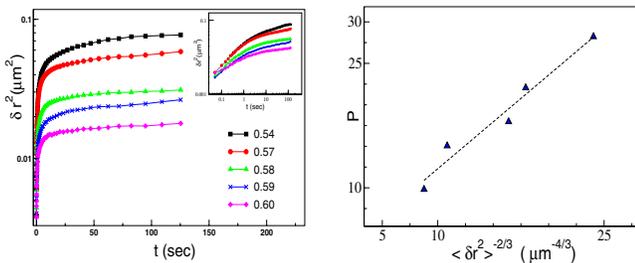


FIG. 2 (color online). Left: Mean-square displacement versus time at different volume fractions  $\phi = 0.54, 0.57, 0.58, 0.59, 0.60$  shows a plateau over which the soft modes in the system have been measured. The same plot in log-log scale is shown in the inset, where the plateau is not so evident. Right: pressure from the equation of state as a function of the plateau value of the mean-square displacement. The full line is a  $P^{-3/2}$  fit.

computed from the volume fraction using an empirical equation of state for the colloidal hard spheres, for example [17],  $p = -(k_B T/v)\phi^2 \frac{d}{d\phi} \ln[(\phi_{\text{max}}/\phi)^{(1/3)} - 1]^3$ , with  $v$  the volume per particle. Fitting the data, it is clear that they are indeed compatible with the anomalous scaling proposed by [15,16] (Fig. 2). This is the first indication that soft modes are present in the system.

It is worthwhile noting here that if we make the reasonable assumption that the system is in local equilibrium during the time interval associated with the plateau, then the values of the squared-displacements are independent of the dynamics, which may go from overdamped to purely ballistic, and even contain hydrodynamic interactions. What *does* depend on the nature of the dynamics is the actual time dependence of the displacements, but not their statistical distribution. As an analogy: over- and under-damped Langevin dynamics in a harmonic well are very different, but their statistical distribution of displacements is the same.

We now turn to the experimental determination of the DOS of our colloids. There are two standard methods to obtain the density of modes of such a system. Spatial Fourier analysis of displacements has been successfully applied to colloidal crystals [9]. However, it is inapplicable here, since it relies on the periodicity of the lattice. Secondly, one can calculate the Fourier transform of the velocity autocorrelation function, provided one uses a method with high time resolution [18,19], higher than we can achieve here.

Here we use a new method in which we directly analyze the normal modes of the vibrations in the cages from the displacement correlations. If the system were harmonic, undamped and without hydrodynamic interactions, the DOS obtained from velocity autocorrelations and our method would coincide. However, in the former method all the spatial information is lost. The strength of the present analysis using confocal measurements lies in directly visualizing the collective modes at low frequencies and therefore gaining information about the nature of such modes. But the price to pay is the exclusion of the combined effects of damping, anharmonicity and hydrodynamic interactions which results in a frequency scale that is somewhat different from the real frequencies of a damped anharmonic system. In our method, the DOS is obtained as follows. Denoting  $u_a(t)$  the components of the particle displacements from the average position along the confocal plane  $u_a(t) = \{(x_i(t) - \langle x_i \rangle), (y_i(t) - \langle y_i \rangle)\}$ , we obtain the displacement correlation [20–22] matrix (of dimension twice the number of observed particles) as,

$$D_{ab} = \langle u_a(t)u_b(t) \rangle, \quad (1)$$

where  $\langle \cdot \cdot \cdot \rangle$  denotes the average over the period of measurement, which is about 175 sec. Diagonalizing  $D_{ab}$  we obtain the normal modes, and the corresponding eigenvalues  $\lambda_a$ . We express the results in terms of the relevant quantities,

$$\omega_a = \sqrt{1/\lambda_a}, \quad (2)$$

which are the temporal frequencies the system would have if it were harmonic and undamped.

The resulting density of states is shown in Fig. 3. Because “hard” modes are expected to have eigenvalues proportional to the pressure, we scale out this effect by plotting the DOS in terms of scaled frequencies  $\omega/p$ . The rescaled cumulative density of states (Fig. 3) shows that, in agreement with [15,20], the gap in the rescaled variables closes with increasing pressure. This is also the reason for the anomalous scaling of the plateau in the mean-squared displacement. Hence we conclude that indeed there is a proliferation of soft modes when the system becomes glassy.

What do the soft modes look like? The two-dimensional eigenvector field corresponding to a single frequency shows the emergence of large vortexlike structures (Fig. 4), indicating that the low-frequency soft modes consist in fact of a large scale swirling motion of the particles. To the contrary, for higher frequencies, the eigenvector field tends to look random. To quantify the order in the low-frequency eigenvector field, we calculated the orientational correlation function defined as the scalar product  $(\vec{v}_i \cdot \vec{v}_j)$ , where  $\vec{v}_i$  and  $\vec{v}_j$  are the two-dimensional eigenvector components corresponding to the  $i$ th and  $j$ th particle for a single eigenmode. The result for eigenmodes in the different parts of the spectrum are shown in Fig. 5. The low-frequency soft modes involve motion correlated over many (tens of) interparticle distances and thus extend over large length scales. One surprise is that the correlations characterizing the soft modes are very weakly dependent on volume fraction and hence on pressure (Fig. 5), suggesting that the large correlation length stays finite in the large-pressure limit. The negative part (anticorrelation) of the correlation function (Fig. 5) becomes slightly more pronounced upon increasing the volume fraction. To be able to see the swirling motion disappearing completely one presumably has to go to even lower volume fractions

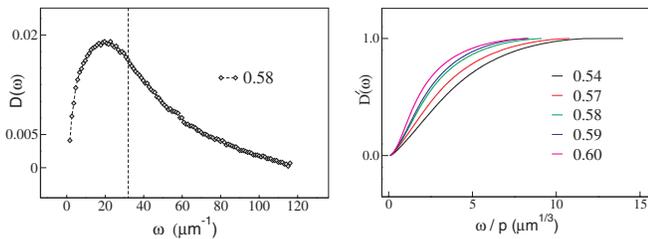


FIG. 3 (color online). Left: Density of states shown for the volume fractions,  $\phi = 0.58$ . The frequency axis is in the unit of  $\mu\text{m}^{-1}$ . The dashed line shows the upper-limit of frequency  $\omega_0$  until which the spectrum is reliable. Right: Closure of the gap: cumulative density of states  $D'(\omega) = \int D(\omega)d\omega$  at different volume fractions respectively  $\phi = 0.54, 0.57, 0.58, 0.59, 0.60$ . The frequencies along the horizontal axis are scaled by the pressure.

(equilibrium fluid phase), where the present method of analysis no longer applies.

As was pointed out to us by Henkes, Brito, and van Saarloos [23] the finite resolution of the microscope leads to a significant uncertainty in the high frequency tail of the calculated DOS. Roughly, the error in the DOS becomes important when the value of the matrix elements of the displacement correlation matrix becomes on the order of the square of the resolution of the microscope (estimated to be 30 nm [14]). The corresponding upper limit of the of frequency  $\omega_0$  up to which the spectrum is reliable is indicated in Fig. 3. The eigenvector fields presented here all correspond to frequencies below  $\omega_0$ .

One possible caveat of our analysis is the following. In our experimental setup we measure the displacements of particles in a small and two-dimensional slice of the real system, and we diagonalise a submatrix of the full correlation matrix. This is not only due to an experimental, but also to a numerical limitation: diagonalizing the full correlation matrix is an impossible task. The problem is not hopeless, because our slice is typical of all others and will give statistically equal results. In particular, the mean-squared displacement per particle and per spatial dimension is the same when restricted to a slice and in the whole system. One can say more: consider an eigenvector  $\tilde{V}$  with eigenvalue  $\tilde{\lambda}$  of the restricted covariance matrix, involving only the measured particles and their motion along the confocal plane. The eigenvectors of the full system  $\{V_a\}$  form a complete basis so we can expand  $\tilde{V}$  in terms of  $V_a$  as

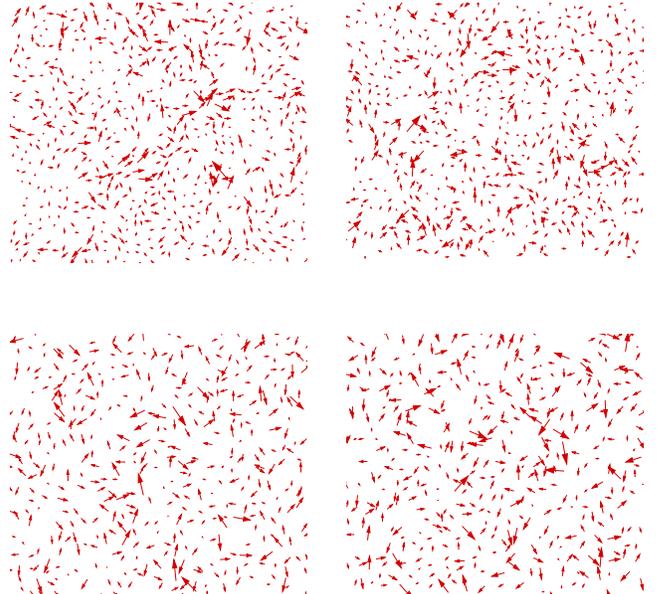


FIG. 4 (color online). The two-dimensional eigenvector fields. The volume fraction is  $\phi = 0.60$ . Frequencies ( $\mu\text{m}^{-1}$ ) from left to right, top: 1.01, 3.40, bottom: 10.4, 18.5. The length scale associated with swirling structures (top left corner) is about 34 microns. Large displacements (big arrows) in the eigenvector field are mostly seen always at low frequencies and are often an isolated event.

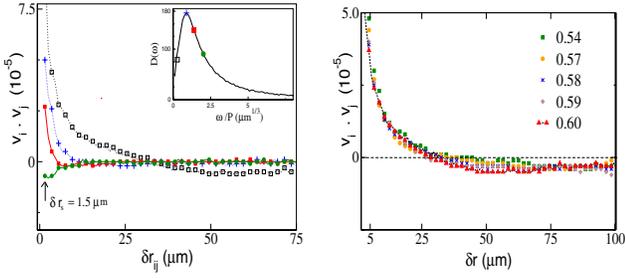


FIG. 5 (color online). Left: The average scalar product  $\vec{v}_i \cdot \vec{v}_j$ , for a vol. fraction 0.60. This has been computed for eigenmodes in different parts of the spectrum, as shown in  $D(\omega)$  in the inset. Lowest frequency modes have a long tail with a negative part characterizing the swirling motion. The shortest interparticle distance  $\delta r_s = 1.5 \mu\text{m}$  is indicated by the arrow. Right: The orientational correlation function for the lowest frequency modes for different packing fractions  $\phi = 0.54, 0.57, 0.58, 0.59, 0.60$ . The general shape of the modes seems only very weakly dependent on the packing fraction.

$$\tilde{V} = \sum_a c_a V_a \quad \text{with} \quad \sum_a c_a^2 = 1. \quad (3)$$

One has  $\tilde{\lambda} = \sum_a c_a^2 \lambda_a$ , which can also be written as  $\sum_a c_a^2 (\tilde{\lambda} - \lambda_a) = 0$ . It is clear from this and the fact that eigenvalues are positive that the existence of a large eigenvalue  $\tilde{\lambda}$  for the restricted problem implies the existence of a large eigenvalue  $\lambda_a \geq \tilde{\lambda}$  for the complete problem, or, equivalently,  $\omega_a \leq \tilde{\omega}$ . Each soft mode of the restricted problem implies the existence of—and has a large projection over—soft modes of the complete system. In particular, a mode with  $\tilde{\omega} = 0$  in the restricted problem implies a mode  $\omega = 0$  in the true system. Although we do not expect that the spectrum associated with a large two-dimensional slice coincides exactly with that of the full system, we may be certain that the soft modes we observe are indeed a reflection of all the soft modes of the full system. Another argument is that the vibration we observe in our slice is induced by the global soft modes. As mentioned above,  $D(\omega)$  has a sharp peak at a gap value  $\omega^*(p)$ , below which there are very few modes ( $\omega^*(p)$  goes to zero as  $p \rightarrow \infty$ ). The mean-squared displacement is dominated at high pressures by the peak value contribution [15]  $\langle (\delta r)^2 \rangle \sim \frac{D(\omega^*)}{\omega^*}$ . Thus, at large pressure, *essentially all* the motion of each particle is given by a combination of the soft modes just above the gap, i.e., those having  $\omega \sim \omega^*(p)$ .

In conclusion, we have argued that the normal modes of a restricted set of particles gives information on the whole system. Thanks to this, a well-established technique such as confocal microscopy can be used to study global vibrational properties of the system, which contain very detailed information on the geometry of the configurations. The above strategy can be applied for much more complex colloidal systems, e.g., with interactions other than hard-sphere repulsions. Here, we have reported an excess of low-frequency modes in a colloidal hard-sphere system around the glass transition volume fraction. These modes

show large-scale correlations in the velocities of particles, extending over many particle diameters. The existence of soft modes had been predicted for ideal hard spheres on the basis of theoretical considerations. Our experimental study shows that they do exist in glassy colloidal suspensions, probably the most studied system in the field of glassy dynamics. These vibrational modes signal the onset of macroscopic elasticity and give a microscopic insight in the collectivity of the particle dynamics near the glass transition. Following particles for longer times will further allow us to assess the relevance of the low-frequency soft modes to long time, activated dynamics near the glass transition.

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