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Density of States of Colloidal Glasses

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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 uncertain and remains a point of discussion, the fact is that the dynamics becomes very slow around a volume fraction of \( \phi = 0.58 \) [13]. We use poly-methylmethacrylate (PMMA) particles, of diameter, \( \sigma = 1.3 \) \( \mu \)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 \( \mu \)m \( \times \) 100 \( \mu \)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 \( \mu \)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, \( \tau_B = \eta d^2/k_B T = 0.75 \) sec, where \( \eta \) is the solvent viscosity. The mean-square displacement per particle \( \langle \delta r \rangle^2 \) 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
The mean-square displacement. The full line is a
inset, where the plateau is not so evident. Right: pressure
have been measured. The same plot in log-log scale is shown in
0.60 shows a plateau over which the soft modes in the system
obtain the DOS before large-scale rearrangements happen.
ange 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 pres-
ture 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

computed from the volume fraction using an empirical
equation of state for the colloidal hard spheres, for example
[17], $p = -(k_B T / \nu) \phi^2 \frac{d^2}{dx^2} \ln \left( \left[ \phi_{\max} / \phi \right]^{1/3} - 1 \right)^2$, with
$\nu$ 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 reason-
able 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 di-
rectly 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 com-
bined effects of damping, anharmonicity and hydrody-
namic 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,

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

where $\langle \cdot \cdot \rangle$ denotes the average over the period of mea-
surement, which is about 175 sec. Diagonalizing $D_{ab}$ we
obtain the normal modes, and the corresponding eigen-
values $\lambda_a$. 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 \( \omega/\rho \). 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 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.

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

FIG. 3 (color online). Left: Density of states shown for the volume fractions, \( \phi = 0.58 \). The frequency axis is in the unit of \( \mu m^{-1} \). 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.

FIG. 4 (color online). The two-dimensional eigenvector fields. The volume fraction is \( \phi = 0.60 \). Frequencies (\( \mu m^{-1} \)) 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.
We have 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 $\delta r_i = 1.5 \, \mu\text{m}$ 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.

\[
\vec{V} = \sum_a c_a \vec{v}_a \quad \text{with} \quad \sum_a c_a^2 = 1. \tag{3}
\]

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 $\lambda_a \geq \tilde{\lambda}$ 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 $p \to \infty$). 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.