Density of states of colloidal glasses

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Published in: Physical Review Letters

DOI: 10.1103/PhysRevLett.104.248305

Citation for published version (APA):
Although the exact localization of glass transition is un-
surprisingly long length scales.

are collective "swirling" particle motions that extend over
goes deeper into the glass phase. The observed soft modes
emerge in the vibrational density of states, with a

gap at low frequencies that disappears as the pressure
becomes infinite.

frequency modes that are very different in nature from the usual acoustic vibrations of ordinary solids.

We find that the vibrational modes of a colloidal glass experimentally, and find soft low-

These modes extend over surprisingly large length scales.

PACS numbers: 82.70.Dd, 63.50.−x, 64.70.pv

The glass transition is perhaps the greatest unsolved
problem in condensed matter physics [1]: the main ques-
tion is how to reconcile the liquidlike structure with solid-

dynamics becomes very slow around a volume fraction of

We use poly-methylmethacrylate (PMMA) particles, of diameter, \( \sigma = 1.3 \, \mu m \), with a poly-
dispersity 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 miscoscopy. We use a mixture of cyclohexyl-
benzene 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 behav-
or 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 behav-
or; 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 sam-
ple 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 1/15th of the
Brownian time, \( \tau_B = \eta d^2/k_BT = 0.75 \, sec \), 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 experimen-
tal time-window, each particle moves in a "cage" consti-
tuted 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 fit from the equation of state as a function of the plateau value of the mean-square displacement vs the pressure. The latter can be obtained as follows. Denoting $u_a(t)$ the components of the particle displacements from the average position along the confocal plane $u_a(t) = \langle [x_i(t) - \langle x_i \rangle, (y_i(t) - \langle y_i \rangle) \rangle$, 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 $\langle \cdot \cdot \cdot \rangle$ 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,
\[ \omega_a = \sqrt{1/\lambda_a} \] (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 low-frequency eigenvector field, we calculated the orientational correlation function defined as the scalar product \( \langle \vec{v}_i, \vec{v}_j \rangle \), 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 (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 \( \vec{V} \) with eigenvalue \( \lambda \) 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 \( \vec{V} \) in terms of \( V_a \) as

![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 \( \phi = 0.54, 0.57, 0.58, 0.59, 0.60 \). The frequencies along the horizontal axis are scaled by the pressure.](image1)

![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.](image2)
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.