Glass elasticity from particle trajectories: supplementary material

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This supplementary material contains technical details of the theoretical approach (part I) and of the simulations (part II).

I: THEORETICAL DETAILS

Starting point of our approach are the variables of an ergodic fluid, especially the velocity fluctuations of N point-particles $\mathbf{v_q}(t) = (1/\sqrt{N}) \sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i(t)} \dot{\mathbf{r}}_i(t)$. Their correlation tensor is $\mathbf{K}(\mathbf{q},t) = \langle \mathbf{v}^*_{\mathbf{q}}(t)\, \mathbf{v_q}(0)\rangle$, with initial value $\mathbf{K}(\mathbf{q},0) = \frac{k_BT}{m}\mathbf{1}$. The collective displacement field $\mathbf{u_q}(t)$ shall obey

$$\frac{\partial}{\partial t}\mathbf{u_q}(t) = \dot{\mathbf{u}}_{\mathbf{q}}(t) = \mathbf{v_q}(t)\ , \tag{6}$$

so that collective displacement differences in a fluid are given by

$$\Delta\mathbf{u_q}(t) = \int_0^t dt'\ \mathbf{v_q}(t')\ . \tag{7}$$

Equations of motion (EOM) of displacement correlation functions thus follow from the familiar results on $\mathbf{K}(\mathbf{q},t)$ [14] based on the Zwanzig-Mori projection operator formalism. We consider $\mathbf{C}(\mathbf{q},t)$, the tensor of collective mean-squared displacement differences defined by

$$\mathbf{C}(\mathbf{q},t) = \langle \Delta\mathbf{u}^*_{\mathbf{q}}(t)\, \Delta\mathbf{u_q}(t)\rangle = 2\int_0^t dt'(t-t')\mathbf{K}(\mathbf{q},t'). \tag{8}$$

Its EOM follow straightforwardly after overdamping as appropriate for colloidal dispersions:

$$\mathbf{C}(\mathbf{q},t) + \frac{D_0q^2}{k_BTn}\ \int_0^t dt'\ \tilde{\mathbf{G}}(\mathbf{q},t-t')\ \mathbf{C}(\mathbf{q},t') = 2D_0\,t\ \mathbf{1}\ \ , \tag{9}$$

with the short time diffusion coefficient D_0, and stress kernels generalizing the (inverse) fluid isothermal compressibility κ^T to finite wave vectors and frequencies: $\tilde{\mathbf{G}}(\mathbf{q},t) = \mathbf{G}(\mathbf{q},t) + (1/\kappa^T_q)\hat{\mathbf{q}}\hat{\mathbf{q}}$. Here, $\kappa^T_q = S_q/(k_BTn)$ is given by the equilibrium fluid structure factor. The time-dependent stress kernels

$$\mathbf{G}(\mathbf{q},t) = (n/k_BT)\langle \boldsymbol{\sigma}_{\mathbf{q}}(t_{\mathcal{Q}})^*\boldsymbol{\sigma}_{\mathbf{q}}\rangle\ , \tag{10}$$

where $t_{\mathcal{Q}}$ indicates absence of conserved modes, are built with the stress tensor elements containing the interparticle forces (see Ch. 9.3, 9.4 in [14] and Ch. 3.3 in [34])

$$\boldsymbol{\sigma}_{\mathbf{q}} = \frac{i}{q\sqrt{N}}\ \sum_{j=1}^{N}\ \mathbf{F}_j\ e^{i\mathbf{r}_j\cdot\mathbf{q}} = \underbrace{\frac{-1}{\sqrt{N}}\ \sum_{j=1}^{N}\ \frac{\mathbf{F}_j(\mathbf{r}_j\cdot\mathbf{q})}{q}}_{\boldsymbol{\sigma}_0} + \mathcal{O}(q)\ . \tag{11}$$

They reduce to the rheological stress auto-correlation functions in the limit of vanishing wave vector

$$\mathbf{G}(t) = \lim_{q\to 0}\mathbf{G}_{\mathbf{q}}(t) = \frac{n}{k_BT}\ \langle \boldsymbol{\sigma}_0(t)^*\ \boldsymbol{\sigma}_0\rangle\ . \tag{12}$$

These definitions and formally exact results will now be applied to glass, which is taken to be a non-ergodic state, where the time dependent stress kernels take finite values at infinite time [34]:

$$\mathbf{G}(\mathbf{q}, t\to\infty) \to \mathbf{G}_\infty(\mathbf{q})\ , \tag{13}$$

which predicts from Eq. (9)

$$\mathbf{C}(\mathbf{q}, t\to\infty) \to \mathbf{C}_\infty(\mathbf{q}) = 2\frac{k_BTn}{q^2}\ (\mathbf{G}_\infty(\mathbf{q}))^{-1}\ \ . \tag{14}$$

Displacement differences stay below a finite limit for all times. This non-ergodic state is a solid one, and its displacement field can be obtained by integrating Eq. (6) giving Eq. (1) in the main text. The approximation $e^{i\mathbf{q}\cdot\mathbf{r}_i(t)} = e^{i\mathbf{q}\cdot\bar{\mathbf{r}}_i} + \mathcal{O}(\mathbf{q}\cdot\mathbf{u}_i(t))$ can be made.

Particles still locally move around their time-averaged positions, which can be measured by displacement functions defined as

$$\hat{\mathbf{C}}(\mathbf{q},t) = \langle \mathbf{u_q}(t)^*\ \mathbf{u_q}\rangle^{\mathrm{glass}}. \tag{15}$$

The superscript 'glass' indicates that averaging is done in a restricted phase space set by the glassy state. As the so obtained displacement fluctuations are ergodic, time and ensemble averages agree, and the $\hat{\mathbf{C}}(\mathbf{q},t)$ are auto-correlators [20]. Because of Eq.(6), taking a time derivative of $\hat{\mathbf{C}}(\mathbf{q},t)$ leads to velocity fluctuations which do not become non-ergodic at the glass transition owing to time-reversal symmetry [34]. This gives, again neglecting terms of order $\mathcal{O}(\mathbf{q}\cdot\mathbf{u}_i(t))$,

$$\frac{\partial}{\partial t}\hat{\mathbf{C}}(\mathbf{q},t) = -\frac{1}{2}\ \frac{\partial}{\partial t}\mathbf{C}(\mathbf{q},t) \tag{16}$$

and thus the EOM of the displacement correlation functions $\hat{\mathbf{C}}(\mathbf{q},t)$ in glass can straightforwardly be obtained from Eq. (9) except for an integration constant. In order for $\hat{\mathbf{C}}(\mathbf{q},t)$ to approach zero at long times, this integration constant has to be chosen such that

$$\hat{\mathbf{C}}(\mathbf{q},t) = \frac{1}{2}\ (\mathbf{C}_\infty(\mathbf{q}) - \mathbf{C}(\mathbf{q},t))\,. \tag{17}$$

The equal time variance $\hat{\mathbf{C}}(\mathbf{q},t=0) = \frac{1}{2}\mathbf{C}_\infty(\mathbf{q})$ follows, which is the equipartition theorem Eq. (2) in the main text using Eq. (14) and definition (15).

II: SIMULATIONAL DETAILS

We simulated a binary mixture of hard discs undergoing Brownian motion using the algorithm proposed by Scala et al. [35]. The system is made up of $N = 1000$ particles, with a diameter ratio of small to big disks $d_s/d_b = 0.7$ and equal number concentrations $x_s = x_b = 1/2$ at a total packing fraction of $\varphi = \frac{\pi N}{4V}(x_s d_s^2 + d_b^2 x_b)$. A detailed analysis of the structural relaxation close to its glass transition can be found in Ref. [23].

The dispersion relations and elastic moduli were obtained as explained in the letter from 10^4 equally spaced snap-shots along one equilibrated simulation trajectory for times up to Δt. Following the method of Alder et al. [36] we also determined the integrated time dependent shear modulus

$$\eta_{xy}(t) = \frac{1}{2k_B TV}\frac{d}{dt}\left\langle \left(\sum_{coll\in[0;t]} \Delta r_{ij}^y(t_c)\Delta p_{ij}^x(t_c)) \right)^2 \right\rangle . \tag{18}$$

Here the sum runs over all collisions up to time t and $\Delta\mathbf{r}_{ij}(t_c)$ denotes the relative distance and $\Delta\mathbf{p}_{ij}(t_c)$ the momentum transfer of two particles at the collision at time t_c [37]. The brackets $\langle ... \rangle$ denote the average over different simulation runs. The integrated shear modulus was determined for 600 independent, equilibrated initial configurations at $\varphi = 0.81$ and for 150 for all other packing fractions. Equilibration was assumed when the correlation functions became independent on the waiting time. The differentiation in Eq. (18) was done numerically, as was the second one to obtain $G(t)$ from $\eta_{xy}(t) = \int_0^t dt' G(t')$. Finally, a seven point running average was performed on the data for $G(t)$. The Kohlrausch fit to the data points at $\varphi = 0.80$ was performed in the intervall $[1.0; 10^4]/(D_0 n^2)$.

For each packing fraction, the shear moduli in Fig. 2 contain the statistical average of 100 independent simulation runs with different trajectory lengths. We calculated the displacement auto-correlation functions (Eq. (3)) and performed a fit with the function $A \cdot q^2$ for $q \lesssim 0.7$, from which we infer the shear moduli and the errobars in Fig. 2.

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