Long-range correlations in glasses and glassy fluids, and their connection to glasses' elasticity

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Workshop on Critical Phenomena in Random and Complex Systems

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Outline

Spontaneously broken translational symmetry $\rightarrow$

elasticity and long-range density correlations

D. Forster, "Hydrodynamic Fluctuations, Broken Symmetry, And Correlation Functions"

P.W. Anderson, "Basic Notions of Condensed Matter Physics"

Broken translat. symmetry $\Rightarrow$ long-range correlations

In crystalline solids translational symmetry is broken

$n(\vec{r})$ - density field $\qquad n_0$ - spatially averaged density

$$n(\vec{r}) = n_0 + \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

$\vec{G}$ - reciprocal lattice vectors $\qquad n_{\vec{G}}$ - Bragg-peak amplitudes (order parameters)

Rigid translation: an equivalent but different state

A rigid translation of a crystal by a constant vector $\vec{a}$ produces an equivalent but different state of the crystal. This does not cost any energy/does not require any force.

Under such translation the density field changes:

$$n(\vec{r}) \to n(\vec{r} - \vec{a}) \qquad \equiv \qquad n_{\vec{G}} \to n_{\vec{G}} e^{i\vec{G}\cdot\vec{a}} \quad \text{for} \quad \vec{G} \neq \vec{0}$$

Rigid translations $\equiv$ zero free energy cost excitations (Goldstone modes)

The existence of such zero-free energy excitations is the reflection of a broken translational symmetry.

Long-range density correlations

Density fluctuation for a wavevector close to $\vec{G}$:

$$n(\vec{G}+\vec{q}) = \sum_i e^{i(\vec{G}+\vec{q})\cdot\vec{r}_i} \qquad \delta n(\vec{G}+\vec{q}) = n(\vec{G}+\vec{q}) - \left\langle n(\vec{G}+\vec{q})\right\rangle$$

Bogoliubov inequality $\langle |A|^2\rangle \langle |B|^2\rangle \geq |\langle AB\rangle|^2$

$$A = V^{-1/2}\delta n^*(\vec{G}+\vec{q}) \quad \& \quad B = V^{-1/2}\hat{\vec{n}}\cdot\dot{\vec{g}}(\vec{q}) \quad \text{where} \quad \vec{g}(\vec{q}) = \sum_i m\vec{v}_i e^{-i\vec{q}\cdot\vec{r}_i}$$

$\hat{\vec{n}}$ - an arbitrary unit vector

$$\frac{1}{V}\left\langle |\delta n(\vec{G}+\vec{q})|^2\right\rangle \geq \frac{1}{q^2}\frac{(k_BT)^2\,|n_{\vec{G}}|^2\left(\hat{\vec{n}}\cdot\vec{G}\right)^2}{\lim_{\vec{q}\to 0}\frac{1}{V}\left\langle |\hat{\vec{q}}\cdot \overleftrightarrow{\sigma}(\vec{q})\cdot\hat{\vec{n}}|^2\right\rangle}$$

$\overleftrightarrow{\sigma}(\vec{k})$ - microscopic stress tensor

Small wavevector divergence $\Rightarrow$ long-range correlations in direct space.

GS & M. Ernst, PRB **48**, 112 (1993); H. Wagner, Z. Phys. **195**, 273 (1966)

Dynamic glass transition: dynamics & statics

Dynamic approach

At the dynamic glass transition the relaxation time diverges and the time-dependent density correlation function does not decay:

$$\lim_{t\to\infty} \left\langle \delta n(\vec{k};t)\delta n(-\vec{k}) \right\rangle = nS(k)f(k) > 0$$

$\delta n(\vec{k};t) = \sum_i e^{-i\vec{k}\cdot\vec{r}_i(t)} - \left\langle \sum_i e^{-i\vec{k}\cdot\vec{r}_i(t)} \right\rangle$ - density fluctuation

$S(k)$ - static structure factor $\quad$ $f(k)$ - non-ergodicity parameter

Static (replica) approach (Franz and Parisi, PRL **79**, 2486 (1997))

N particles $\vec{r}_1, ..., \vec{r}_N$ tethered to a quenched configuration $\vec{r}^{\,0}_1, ..., \vec{r}^{\,0}_N$:

$$\text{attractive potential } = -\epsilon \sum_{i,j} w(|\vec{r}_i - \vec{r}^{\,0}_j|).$$

At the dynamic transition non-trivial correlations survive in the $\epsilon \to 0$ limit.

Replicas

Averaging over a distribution of quenched configurations
$\Longrightarrow s$ replicas of the system & $s \to 0$ (or $m = s + \underset{\substack{\uparrow \\ \text{quenched conf.}}}{1}$ & $m \to 1$).

Dynamic glass transition $\equiv$ non-trivial inter-replica correlations:

$$\lim_{\epsilon \to 0} \left\langle \sum_{i,j} e^{i\vec{k}\cdot\vec{r}_{i\alpha} - i\vec{k}\cdot\vec{r}_{j\beta}} \right\rangle = nS(k)f(k)$$

α, β - replica indices $S(k)$ - static structure factor $f(k)$ - non-ergod. parameter

Symmetry transformation hidden in replica approach

Glass can be moved as a rigid body

The system can be tethered to a rigidly shifted quenched configuration:

$$\text{attractive potential } = -\epsilon \sum_{i,j} w(|\vec{r}_i - \vec{r}_j^{\,0} - \vec{a}|).$$

As before: at the dynamic transition nontrivial correlations in the $\epsilon \to 0$ limit.

Physically, nothing changes: we get a glass that is shifted rigidly by $\vec{a}$.

However: (some) replica off-diagonal correlation functions change.

$$\text{For } \alpha > 0 : h_{\alpha 0}(\vec{r}_1, \vec{r}_2) \to h_{\alpha 0}(\vec{r}_1 - \vec{a}, \vec{r}_2)$$

All other pair correlations are unchanged (note: this breaks replica symmetry).

Rigid translations $\equiv$ zero energy cost excitations (Goldstone modes)

The existence of such zero-free energy excitations is the reflection of a randomly broken translational symmetry.

Long-range density correlations

Fourier transform of the joint microscopic density in replicas α and 0:

$$n_{\alpha 0}(\vec{k};\vec{q}) = \sum_{i,j} e^{i\vec{k}\cdot\vec{r}_{i\alpha} - i(\vec{k}+\vec{q})\cdot\vec{r}_{j0}} \qquad \text{(analogue of } n(\vec{G}+\vec{q}) \text{ for crystals)}$$

Bogoliubov inequality $\langle |A|^2\rangle \langle |B|^2\rangle \geq |\langle AB\rangle|^2$

$$A = V^{-1/2}s^{-1}\sum_{\alpha>0}\delta n^*_{\alpha 0}(\vec{k};\vec{q}) \quad \text{where} \quad \delta n_{\alpha 0}(\vec{k};\vec{q}) = n_{\alpha 0}(\vec{k};\vec{q}) - \left\langle n_{\alpha 0}(\vec{k};\vec{q})\right\rangle$$

$$B = V^{-1/2}s^{-1}\sum_{\alpha>0}\hat{\vec{n}}\cdot\dot{\vec{g}}_{\alpha}(\vec{q}) \quad \text{where} \quad \vec{g}_{\alpha}(\vec{q}) = \sum_i m\vec{v}_{i\alpha}e^{-i\vec{q}\cdot\vec{r}_{i\alpha}}$$

$\hat{\vec{n}}$ - an arbitrary unit vector

$$\frac{1}{V}\left\langle |\delta n_{10}(\vec{k};\vec{q})|^2 - \delta n_{10}(\vec{k};\vec{q})\delta n_{20}(-\vec{k};-\vec{q})\right\rangle \geq \frac{1}{q^2}\frac{(k_BT)^2\,(nS(k)f(k))^2\left(\hat{\vec{n}}\cdot\vec{k}\right)^2}{\lim_{\vec{q}\to 0}\frac{1}{V}\langle\Sigma(\vec{q})\rangle}$$

$f(k)$ - non-ergod. parameter

$$\Sigma(\vec{q}) = |\hat{\vec{q}}\cdot \overleftrightarrow{\sigma}_1(\vec{q})\cdot\hat{\vec{n}}|^2 - (\hat{\vec{q}}\cdot\overleftrightarrow{\sigma}_1(\vec{q})\cdot\hat{\vec{n}})(\hat{\vec{k}}\cdot\overleftrightarrow{\sigma}_2(-\vec{q})\cdot\hat{\vec{n}})$$

Long-range density correlations: crystals *vs.* glasses

Crystals

$$\frac{1}{V}\left\langle |\delta n(\vec{G}+\vec{q})|^2 \right\rangle \geq \frac{1}{q^2}\frac{(k_B T)^2\,|n_{\vec{G}}|^2\left(\hat{\vec{n}}\cdot\vec{G}\right)^2}{\lim_{\vec{q}\to 0}\frac{1}{V}\left\langle |\hat{\vec{q}}\cdot\overleftrightarrow{\sigma}(\vec{q})\cdot\hat{\vec{n}}|^2\right\rangle}$$

Small wavevector divergence ⇒ long-range correlations in direct space.

GS & M. Ernst, PRB **48**, 112 (1993); H. Wagner, Z. Phys. **195**, 273 (1966)

Glasses

$$\frac{1}{V}\left\langle |\delta n_{10}(\vec{k};\vec{q})|^2 - \delta n_{10}(\vec{k};\vec{q})\delta n_{20}(-\vec{k};-\vec{q})\right\rangle \geq \frac{1}{q^2}\frac{(k_B T)^2\,(nS(k)f(k))^2\left(\hat{\vec{n}}\cdot\vec{k}\right)^2}{\lim_{\vec{q}\to 0}\frac{1}{V}\left\langle\Sigma(\vec{q})\right\rangle}$$

$f(k)$ - non-ergod. parameter $\quad \Sigma(\vec{q}) = |\hat{\vec{q}}\cdot\overleftrightarrow{\sigma}_1(\vec{q})\cdot\hat{\vec{n}}|^2 - (\hat{\vec{q}}\cdot\overleftrightarrow{\sigma}_1(\vec{q})\cdot\hat{\vec{n}})(\hat{\vec{k}}\cdot\overleftrightarrow{\sigma}_2(-\vec{q})\cdot\hat{\vec{n}})$

Small wavevector divergence ⇒ long-range correlations in direct space.

GS & E. Flenner, PRL **107**, 105505 (2011)

Simplified version of the divergent correlation function

$$\frac{1}{N}\left\langle \left|\delta n_{10}(\vec{k};\vec{q})\right|^2 - \delta n_{10}(\vec{k};\vec{q})\delta n_{20}(-\vec{k},-\vec{q})\right\rangle$$

$$\equiv \frac{1}{N}\left\langle \sum_{i,j} e^{i\vec{k}\cdot\vec{r}_{i1}-i(\vec{k}+\vec{q})\cdot\vec{r}_{j0}} \sum_{l,m} e^{-i\vec{k}\cdot\vec{r}_{l1}+i(\vec{k}+\vec{q})\cdot\vec{r}_{m0}} - \sum_{i,j} e^{i\vec{k}\cdot\vec{r}_{i1}-i(\vec{k}+\vec{q})\cdot\vec{r}_{j0}} \sum_{l,m} e^{-i\vec{k}\cdot\vec{r}_{l2}+i(\vec{k}+\vec{q})\cdot\vec{r}_{m0}} \right\rangle$$

Self (diagonal) part only

$$\frac{1}{N}\left\langle \sum_{i} e^{i\vec{k}\cdot\vec{r}_{i1}-i(\vec{k}+\vec{q})\cdot\vec{r}_{i0}} \sum_{l} e^{-i\vec{k}\cdot\vec{r}_{l1}+i(\vec{k}+\vec{q})\cdot\vec{r}_{l0}} \right\rangle$$

Replacing replicas with $t \to \infty$ limit

Interpreting replica off-diagonal correlation function dynamically

$$\frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot\vec{r}_{i1} - i(\vec{k}+\vec{q})\cdot\vec{r}_{i0}} \sum_l e^{-i\vec{k}\cdot\vec{r}_{l1} + i(\vec{k}+\vec{q})\cdot\vec{r}_{l0}} \right\rangle$$

$$\to \quad \lim_{t\to\infty} \frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot\vec{r}_i(t) - i(\vec{k}+\vec{q})\cdot\vec{r}_i(0)} \sum_l e^{-i\vec{k}\cdot\vec{r}_l(t) + i(\vec{k}+\vec{q})\cdot\vec{r}_l(0)} \right\rangle$$

Connection to the four-point structure factor

$$\frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot\vec{r}_i(t) - i(\vec{k}+\vec{q})\cdot\vec{r}_i(0)} \sum_l e^{-i\vec{k}\cdot\vec{r}_l(t) + i(\vec{k}+\vec{q})\cdot\vec{r}_l(0)} \right\rangle =$$

$$\frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot(\vec{r}_i(t) - \vec{r}_i(0)) - i\vec{q}\cdot\vec{r}_i(0)} \sum_l e^{-i\vec{k}\cdot(\vec{r}_l(t) - \vec{r}_l(0)) + i\vec{q}\cdot\vec{r}_l(0)} \right\rangle \equiv S_4^{\mathrm{F}}(\vec{q},\vec{k};t)$$

This function is a version of a four-point structure factor used to investigate dynamic correlations in glassy fluids!

Four-point functions used to investigate dynamic corrs.

Four-point structure factor: correlations of slow particles

$$S_4(q;t) = \frac{1}{N}\left\langle \sum_i w(\delta\vec{r}_i(t)) e^{-i\vec{q}\cdot\vec{r}_i(0)} \sum_j w(\delta\vec{r}_j(t)) e^{i\vec{q}\cdot\vec{r}_j(0)} \right\rangle$$

$$\delta\vec{r}_i(t) = \vec{r}_i(t) - \vec{r}_i(0), \qquad w(\vec{r}_j(t)) = \theta(a - |\vec{r}_j(t)|)$$

But one could select slow particles in a different way

$$S_4^{\cos}(\vec{q},\vec{k};t) = \frac{1}{N}\left\langle \sum_i \cos(\vec{k}\cdot\delta\vec{r}_i(t)) e^{-i\vec{q}\cdot\vec{r}_i(0)} \sum_j \cos(\vec{k}\cdot\delta\vec{r}_j(t)) e^{i\vec{q}\cdot\vec{r}_j(0)} \right\rangle$$

or one could choose

$$S_4^{\mathrm{F}}(\vec{q},\vec{k};t) = \frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot\delta\vec{r}_i(t)} e^{-i\vec{q}\cdot\vec{r}_i(0)} \sum_j e^{-i\vec{k}\cdot\delta\vec{r}_j(t)} e^{i\vec{q}\cdot\vec{r}_j(0)} \right\rangle$$

BTW, the self-intermediate scattering function $F_s(k;t)$,

$$F_s(k;t) = \frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot\delta\vec{r}_i(t)} \right\rangle \equiv \frac{1}{N}\left\langle \sum_i \cos(\vec{k}\cdot\delta\vec{r}_i(t)) \right\rangle .$$

Different four-point functions are sensitive to different aspects of dynamic correlations

$S_4^{\cos}(\vec{q}, \vec{k}; t)$

$$S_4^{\cos}(\vec{q}, \vec{k}; t) = \frac{1}{N} \left\langle \sum_i \cos(\vec{k} \cdot \delta\vec{r}_i(t)) e^{-i\vec{q}\cdot\vec{r}_i(0)} \sum_j \cos(\vec{k} \cdot \delta\vec{r}_j(t)) e^{i\vec{q}\cdot\vec{r}_j(0)} \right\rangle$$

$S_4^{\cos}(\vec{q}, \vec{k}; t)$ quantifies dynamic heterogeneity in glasses and glassy fluids.

$S_4^{\mathrm{F}}(\vec{q}, \vec{k}; t)$

$$S_4^{\mathrm{F}}(\vec{q}, \vec{k}; t) = \frac{1}{N} \left\langle \sum_i e^{i\vec{k}\cdot\delta\vec{r}_i(t)} e^{-i\vec{q}\cdot\vec{r}_i(0)} \sum_j e^{-i\vec{k}\cdot\delta\vec{r}_j(t)} e^{i\vec{q}\cdot\vec{r}_j(0)} \right\rangle$$

$S_4^{\mathrm{F}}(\vec{q}, \vec{k}; t)$ quantifies (visco)elastic fluctuations in glasses and glassy fluids (it is also sensitive to dynamic heterogeneity).

Simulation details

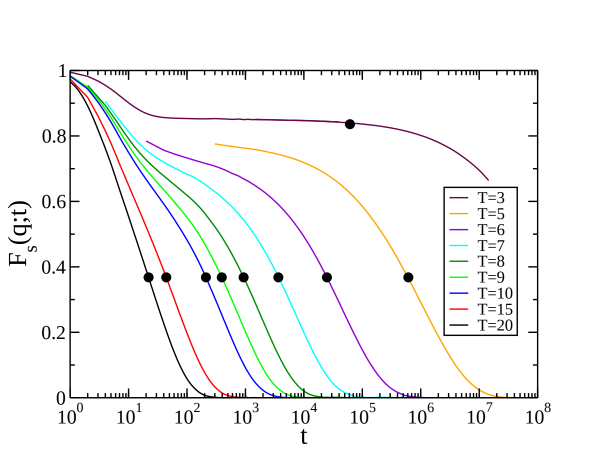
- 50:50 mixture of harmonic spheres

$$V(r) = \begin{cases} \frac{\epsilon}{2}\left(1 - \frac{r}{\sigma_{\alpha\beta}}\right)^2 & \text{if } r \leq \sigma_{\alpha\beta} \\ 0 & \text{otherwise} \end{cases}$$

$\epsilon = 10^4$, $\sigma_{11} = 1.0$, $\sigma_{12} = 1.2$, $\sigma_{22} = 1.4$
number density $n = N/V = 0.675$
"volume fraction" $= \pi \left(0.5N\sigma_{11}^3 + 0.5N\sigma_{22}^3\right)/(6V) = 0.662$

- Very large systems: $N = 100,000$ and $N = 800,000$
- Small wavevectors accessible: $q_{\text{min}} = 0.119$ for the $N = 100,000$ system
- Temperature range: fluid: $5 \leq T \leq 20$; $T_{\text{mct}} = 5.2$, $T_{\text{onset}} \approx 13$
  glass: $T = 3$

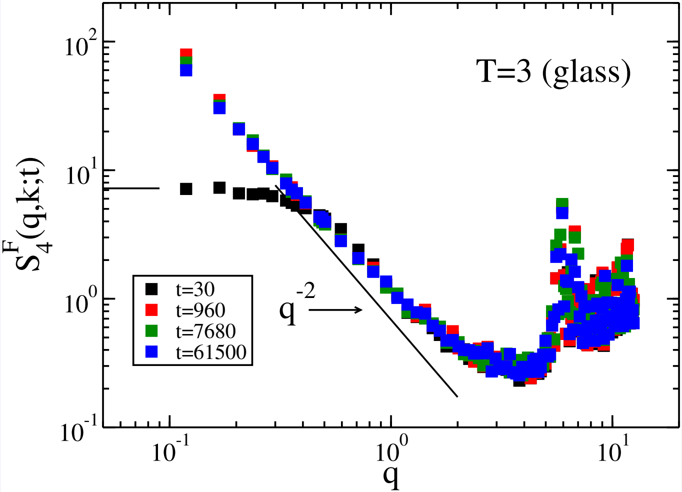
Self-intermediate scattering function $F_s(k;t)$



$T = 5$ - the lowest temperature at which we can equilibrate the fluid;

$$\tau_\alpha(T=5) = 6.14 \times 10^5$$

Long-range correlations in glasses



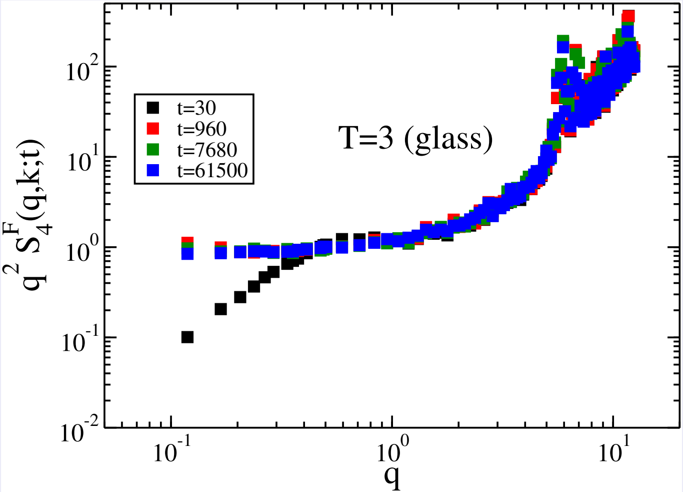
At finite t, $\lim_{q\to 0} S_4^{\rm F}(\vec{q},\vec{k};t)$ is finite and can be calculated independently.

$\lim_{q\to 0} S_4^{\rm F}(\vec{q},\vec{k};t=30)$ - showed as the thin horizontal line.

As $t \to \infty$, $\lim_{q\to 0} S_4^{\rm F}(\vec{q},\vec{k};t) \to \infty$ (in the glass).

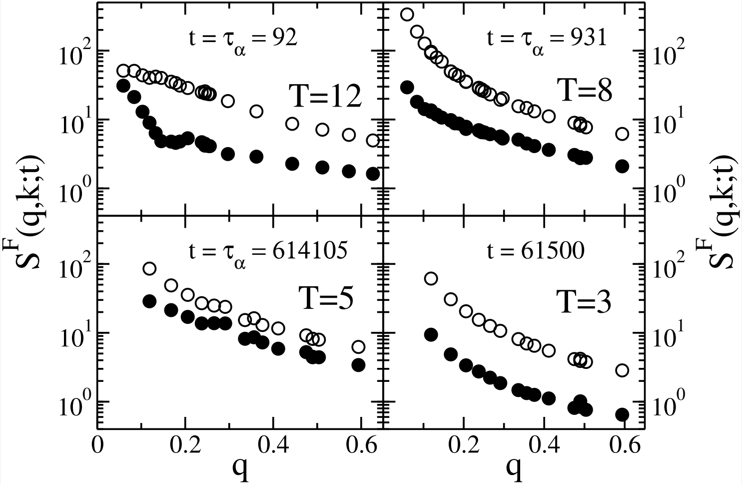
$$S_4^{\rm F}(\vec{q},\vec{k};t) = \frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot(\vec{r}_i(t)-\vec{r}_i(0))-i\vec{q}\cdot\vec{r}_i(0)} \sum_l e^{-i\vec{k}\cdot(\vec{r}_l(t)-\vec{r}_l(0))+i\vec{q}\cdot\vec{r}_l(0)} \right\rangle, \; k=6.1, \; \vec{q}\perp\vec{k}$$

Long-range correlations in glasses



$$S_4^{\mathrm{F}}(\vec{q},\vec{k};t) = \frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot(\vec{r}_i(t)-\vec{r}_i(0)) - i\vec{q}\cdot\vec{r}_i(0)} \sum_l e^{-i\vec{k}\cdot(\vec{r}_l(t)-\vec{r}_l(0)) + i\vec{q}\cdot\vec{r}_l(0)} \right\rangle, \quad k = 6.1, \ \vec{q} \perp \vec{k}$$

Transient viscoelastic fluctuations in glassy fluids



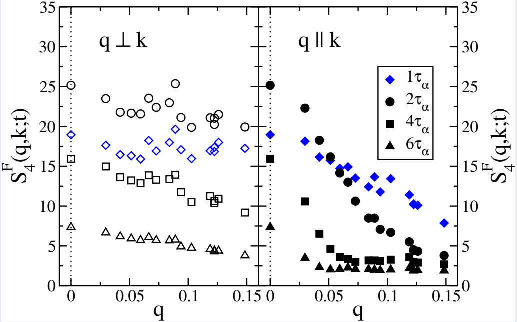
$$S_4^{\mathrm{F}}(\vec{q},\vec{k};t) = \frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot(\vec{r}_i(t)-\vec{r}_i(0))-i\vec{q}\cdot\vec{r}_i(0)} \sum_l e^{-i\vec{k}\cdot(\vec{r}_l(t)-\vec{r}_l(0))+i\vec{q}\cdot\vec{r}_l(0)} \right\rangle$$

$k = 6.1$

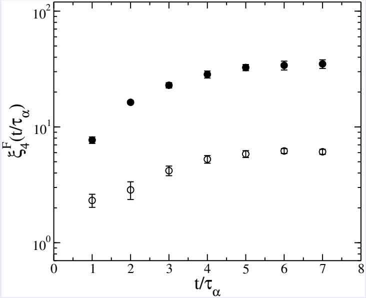
closed: $\vec{k} \parallel \vec{q}$

open: $\vec{k} \perp \vec{q}$

Time-dependence of transient fluctuations



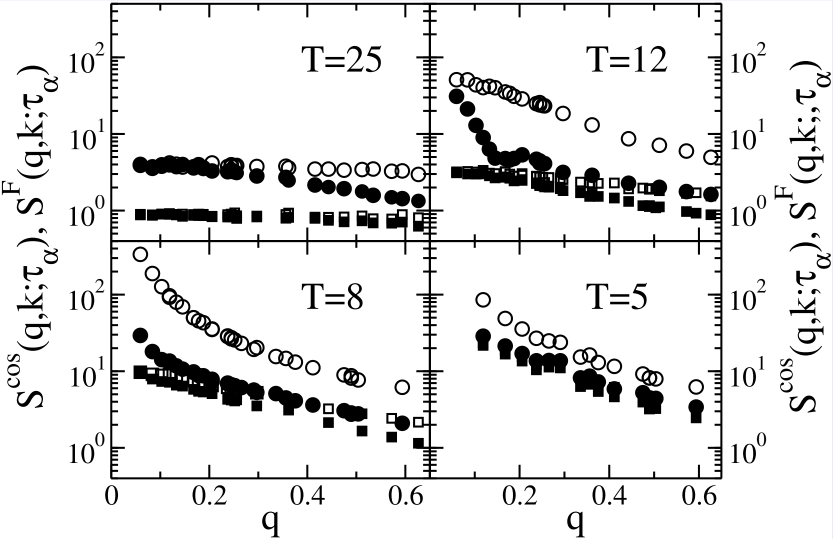
Time dependence of $S_4^{\mathrm{F}}(\vec{q}, \vec{k}; t)$.



close: $\vec{k} \parallel \vec{q}$, open: $\vec{k} \perp \vec{q}$.

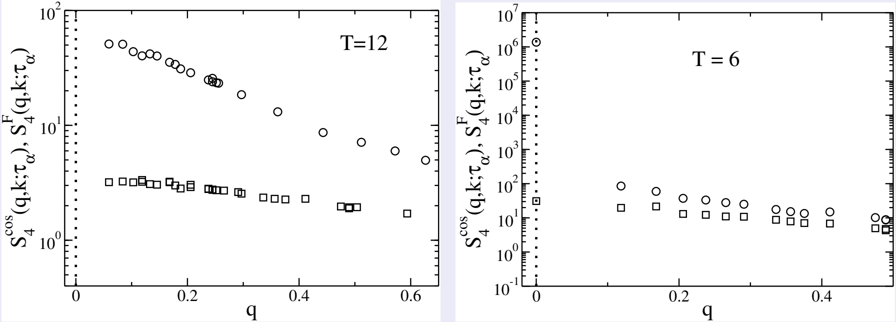
T=15 (above the onset temperature)

Transient viscoelastic correlations *vs.* dyn. heterogen.



circles: S_4^{F}; squares: $S_4^{\cos}$, closed symbols: $\vec{k} \parallel \vec{q}$, open symbols: $\vec{k} \perp \vec{q}$.

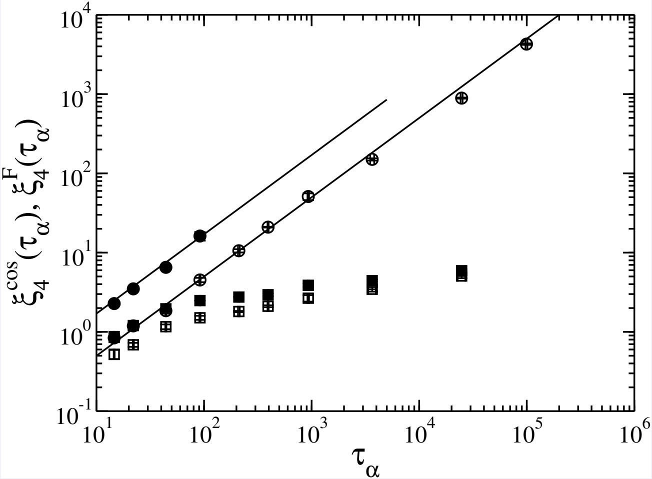
Transient viscoelastic density correlations ($S_4^{\mathrm{F}}(\vec{k};\tau_\alpha)$) *vs.* dynamic heterogeneity ($S_4^{\cos}(\vec{k};\tau_\alpha)$)



circles: S_4^{F}; squares: $S_4^{\cos}$; $\vec{k} \perp \vec{q}$.

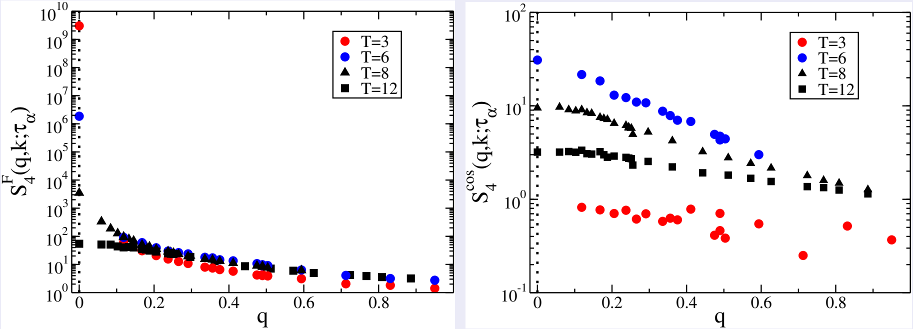
Very different small q limits $\rightarrow$ very different dynamic correlation lengths.

“Viscoelastic length” $\xi_4^{\mathrm{F}}(\tau_\alpha)$ *vs.* dynamic heterogeneity length $\xi_4^{\cos}(\tau_\alpha)$



circles: ξ_4^{F}; squares: $\xi_4^{\cos}$, closed symbols: $\vec{k} \parallel \vec{q}$, open symbols: $\vec{k} \perp \vec{q}$.

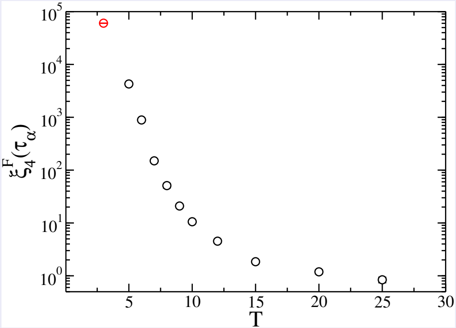
Dynamic fluctuations in glassy fluids *vs.* in glasses

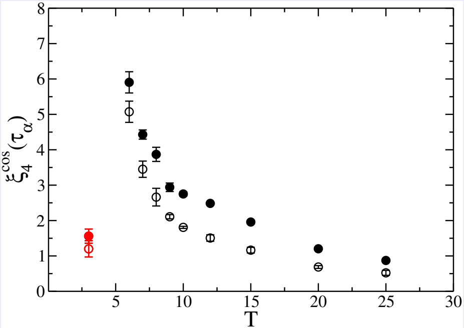


black - glassy fluids; red: glass, at $t = \tau_\alpha(T = 5)$; $\vec{k} \perp \vec{q}$.

Transient “viscoelastic” correlations become long-range in glasses; dynamic heterogeneity correlations decrease in glasses.

Dynamic correlation lengths in glassy fluids *vs.* in glasses



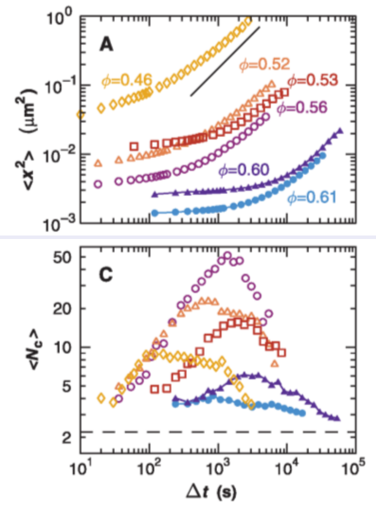


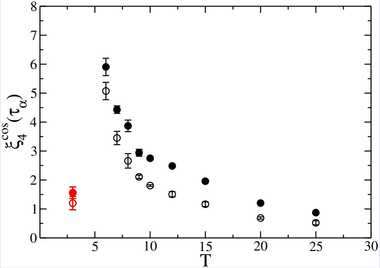
black - glassy fluids; red: glass, at $t = \tau_\alpha(T = 5)$; closed: $\vec{k} \parallel \vec{q}$, open: $\vec{k} \perp \vec{q}$.

Note: in the glass, as $t \to \infty$, $\xi_4^{F}(t) \to \infty$ whereas $\xi_4^{cos}(t)$ is almost t-independ.

Transient "viscoelastic" correlations become long-range in glasses; dynamic heterogeneity correlations decrease in glasses.

Decrease of dynamic heterogeneity at the dynamic glass transition was observed in experiments





← Weeks *et al.*, Science **287**, 627 (2000)

Also seen in:

Ballesta *et al.*, Nature Physics **4**, 550 (2008)

Connection between long-range dynamic correlations and viscoelastic response

Glass transition: divergence of viscosity and emergence of elasticity

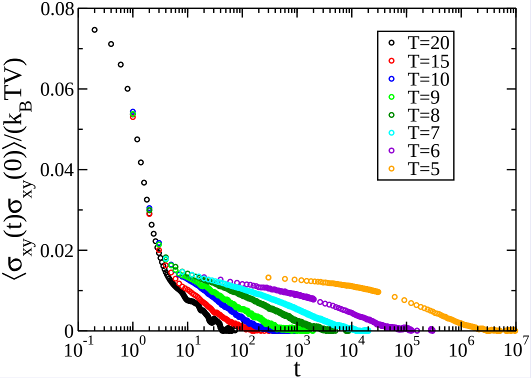
- Are correlations of particle dynamics related to the increase of viscosity and the emergence of elasticity?

Correlations of particle displacements

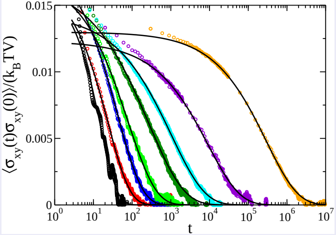
- Correlations in the glass & the signature of elasticity
- Correlations in the fluid & signatures of viscoelasticity

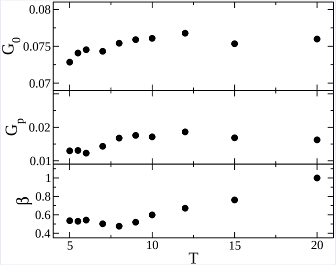
Elijah Flenner & GS, arXiv:1405.0442

Stress tensor auto-correlation function



Long-time part well fitted by a stretched exponential.



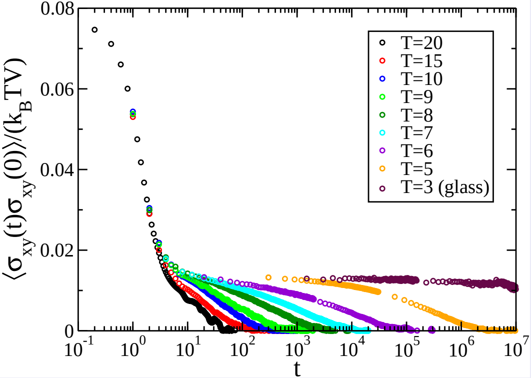


initial value of $\langle \sigma_{xy}(t)\sigma_{xy}(0)\rangle / (Vk_B T) = G_0$

stretched exponential = $G_P \exp\left(-(t/\tau_\sigma)^\beta\right)$

At the lowest temps G_P and β are T-independ.

Stress tensor auto-correlation function



In the glass, $\langle \sigma_{xy}(t)\sigma_{xy}(0)\rangle$ does not decay.

shear modulus $\mu = \lim_{t\to\infty} \frac{1}{Vk_BT} \langle \sigma_{xy}(t)\sigma_{xy}(0)\rangle$

Standard formula for the shear modulus

D. R. Squire, A. C. Holt, and W. G. Hoover, Physica **42**, 388 (1969):

$$\mu = \underbrace{V^{-1}\left\langle B^{xy}\right\rangle}_{\text{Born term}} - \underbrace{(k_B T V)^{-1}\left[\left\langle(\sigma^{xy})^2\right\rangle - \left\langle\sigma^{xy}\right\rangle^2\right]}_{\text{fluctuation term}}$$

where

$$B^{\alpha\beta} = \frac{1}{2}\sum_n \sum_{m\neq n} \frac{(r_{nm}^{\alpha})^2}{r_{nm}^2}\left[(r_{nm}^{\beta})^2 \frac{d^2 V_{nm}(r_{nm})}{dr_{nm}^2} + (r_{nm}^2 - (r_{nm}^{\beta})^2)\frac{1}{r_{nm}}\frac{dV_{nm}(r_{nm})}{dr_{nm}}\right],$$

and $r_{nm}^2 = (r_{nm}^x)^2 + (r_{nm}^y)^2 + (r_{nm}^z)^2$ with $r_{nm}^{\alpha} = r_n^{\alpha} - r_m^{\alpha}$

- Can be calculated for a fluid, a glass or a crystalline solid. In a fluid, it gives 0 (within error bars), in a solid it gives a nonzero result.
- Gives a zero shear modulus unless there are long range density correlations.

Both stress tensor auto-correlation function and the above formula are very difficult (computationally expensive) to calculate in a simulation.

Correlations of particle displacements

Self part of density correlations

$$S_4^{\mathrm{F}}(\vec{q},\vec{k};t) = \frac{1}{N}\left\langle \sum_i e^{i\vec{k}\cdot\delta\vec{r}_i(t)} e^{-i\vec{q}\cdot\vec{r}_i(0)} \sum_j e^{-i\vec{k}\cdot\delta\vec{r}_j(t)} e^{i\vec{q}\cdot\vec{r}_j(0)} \right\rangle$$

$$\delta\vec{r}_i(t) = \vec{r}_i(t) - \vec{r}_i(0)$$

Correlations of transverse displacements

$$S_4^{\perp}(q;t) = \frac{1}{2N}\left\langle \sum_i \delta\vec{r}_i^{\perp}(t) e^{-i\vec{q}\cdot\vec{r}_i(0)} \cdot \sum_j \delta\vec{r}_j^{\perp}(t) e^{i\vec{q}\cdot\vec{r}_j(0)} \right\rangle \qquad \delta\vec{r}_i^{\perp}(t)\cdot\vec{q} = 0$$

$$\delta\vec{r}_i(t) = \vec{r}_i(t) - \vec{r}_i(0)$$

Correlations of transverse displacements

Finite times, small wavevector limit

$$\lim_{q\to 0} S_4^{\perp}(q;t) \quad = \quad \frac{k_B T}{m} t^2$$ due to the momentum conservation

depends on microscopic dynamics!

Note that $\lim_{q\to 0} S_4^{\perp}(q;t) \equiv \lim_{q\to 0} \frac{1}{2N} \left\langle \sum_i \delta\vec{r}_i^{\perp}(t) e^{-i\vec{q}\cdot\vec{r}_i(0)} \cdot \sum_j \delta\vec{r}_j^{\perp}(t) e^{i\vec{q}\cdot\vec{r}_j(0)} \right\rangle$

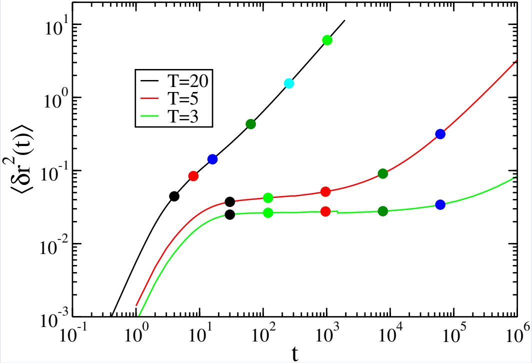
$\neq \frac{1}{2N} \left\langle \sum_i \delta\vec{r}_i^{\perp}(t) \cdot \sum_j \delta\vec{r}_j^{\perp}(t) \right\rangle \equiv 0$ in a $\vec{P}_{\text{total}} = \vec{0}$ ensemble

Finite times, large wavevector limit

$$\lim_{q\to \infty} S_4^{\perp}(q;t) \quad = \quad \frac{1}{3N} \sum_i \left\langle |\delta\vec{r}_i(t)|^2 \right\rangle$$ as t increases, it becomes

proportional to t in the fluid and it saturates in the glass

Correlations of transverse displacements in a glass, in a viscous fluid, and in a moderately viscous fluid

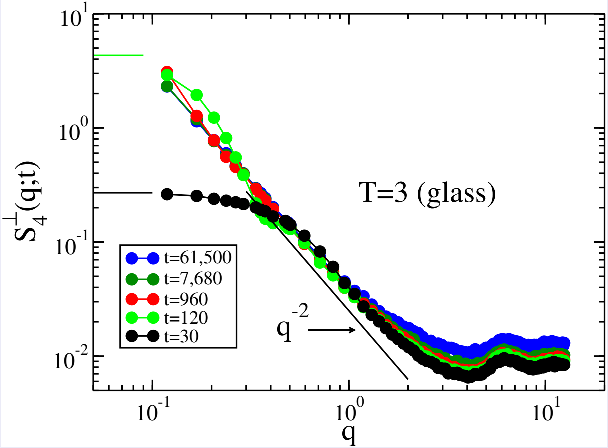


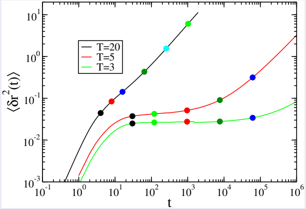
$T = 20$ - a moderately viscous fluid (above T_{onset})

$T = 5$ - the most most deeply supercooled fluid we could equilibrate

$T = 3$ - a glass (quenched from $T = 5$ and well aged); the slight upturn of $\langle \delta\vec{r}^2(t) \rangle$ at the longest times suggests that it is still aging.

Correlations of transverse displacements in a glass

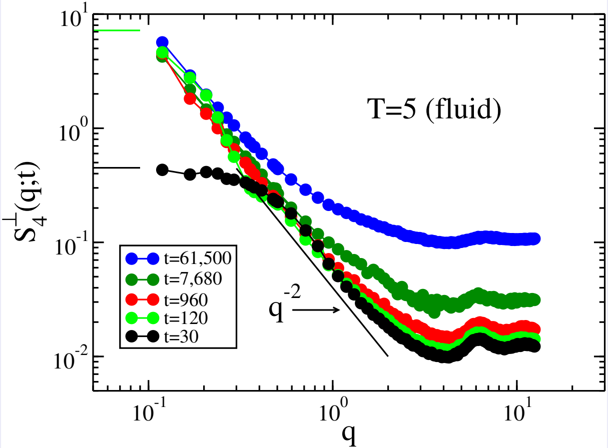


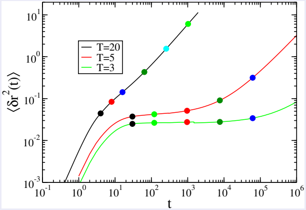


horizontal lines indicate predicted $q \to 0$ limits

At small wavevectors $S_4^{\perp}(q;t)$ saturates, q^{-2} behavior becomes apparent.

Correlations of transverse displacements in a very viscous fluid

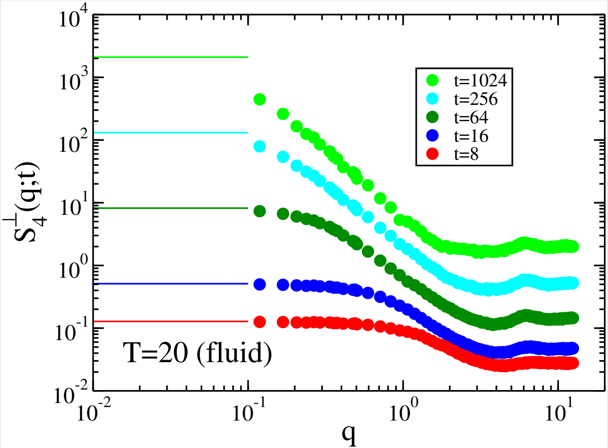


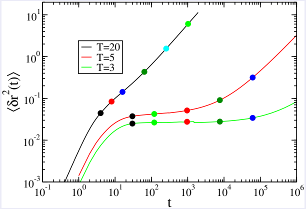


horizontal lines indicate predicted $q \to 0$ limits

At small wavevectors $S_4^{\perp}(q;t)$ exhibits transient q^{-2} behavior.

Correlations of transverse displacements in a moderately viscous fluid





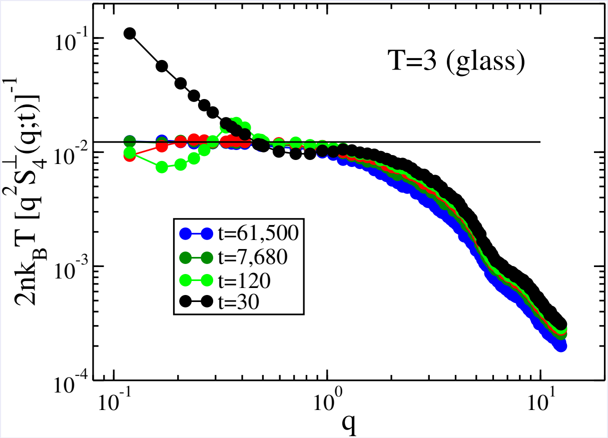
horizontal lines indicate predicted $q \to 0$ limits

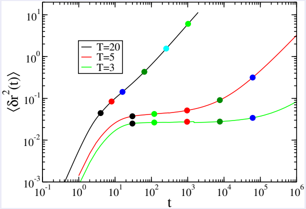
Correlations of transverse displacements and the stress tensor auto-correlation function

Adapting arguments presented in the Supplementary Material to C.L. Klix, F. Ebert, F. Weysser, M. Fuchs, G. Maret, and P. Keim, PRL **109**, 178301 (2012) one can argue that if particles' displacements are bounded (as they are in a glass) then:

$$\lim_{q\to 0}\lim_{t\to\infty}\frac{2nk_BT}{S_4^{\perp}(q;t)q^2} = \lim_{t\to\infty}\frac{1}{Vk_BT}\left\langle\sigma^{xy}(t)\sigma^{xy}(0)\right\rangle = \mu$$

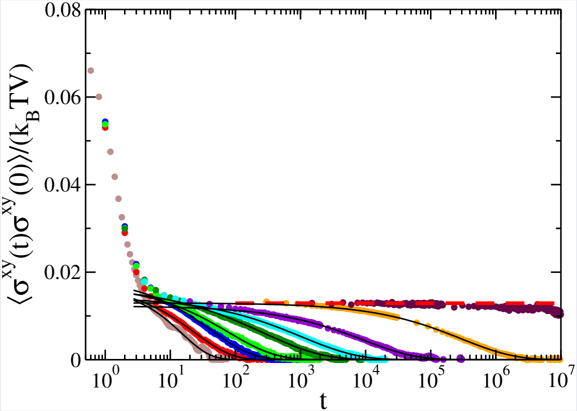
Correlations of transverse displacements in a glass





Saturation of $2nk_BT[S_4^{\perp}(q;t)q^2]^{-1}$ at long times allows us to get an estimate of the shear modulus.

Shear modulus obtained from correlations of transverse displacements agrees well with that calculated from the stress tensor auto-correlation function and from the standard formula.



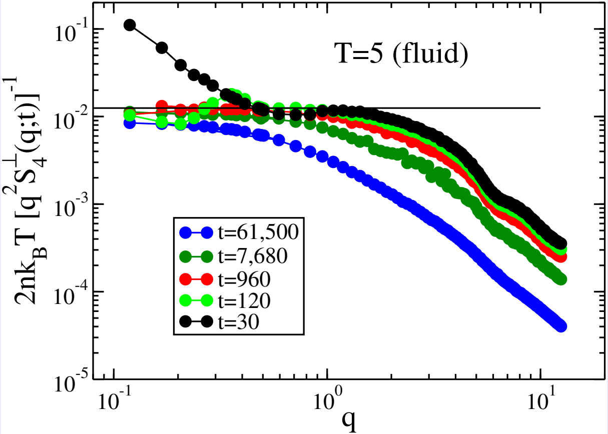
correlations of particle displacements:
$\mu = 0.013 \pm 0.001$

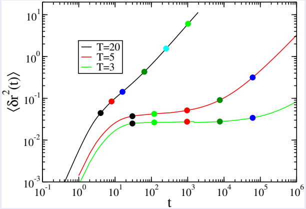
long-time limit of the stress tensor correlations:
$\mu = 0.012 \pm 0.001$

standard formula:
$\mu = 0.010 \pm 0.004$

The particle displacements route allows to use simulations two orders of magnitude shorter than the other two routes.

Correlations of transverse displacements in a very viscous fluid

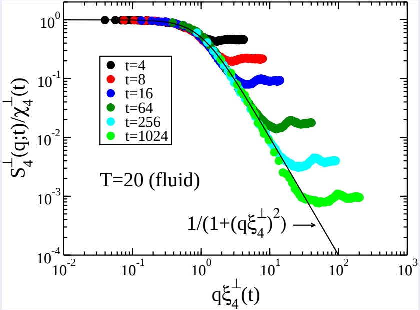


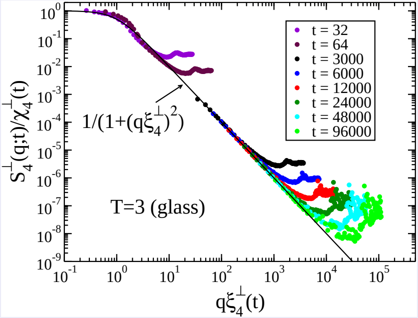


For times in the mean-square-displacement plateau region $2nk_BT[S_4^\perp(q;t)q^2]^{-1}$ is equal to the plateau value of the stress tensor auto-correlation function.

Correlations of transverse displacements: scaling

Rescaling $S_4^\perp(q;t)$, in the fluid and in the glass





$$\chi_4^\perp(t) \equiv \lim_{q\to 0} S_4^\perp(q;t) = \frac{k_B T}{m} t^2$$

Scaling hypothesis

$$\frac{S_4^\perp(q;t)}{\chi_4^\perp(t)} = f(q\xi_4^\perp(t)) \qquad f(x) \sim \frac{1}{1+x^2} \text{ for } x \leq 1 \text{ and } f(x) \sim x^{-2+\eta} \text{ for } x \gg 1$$

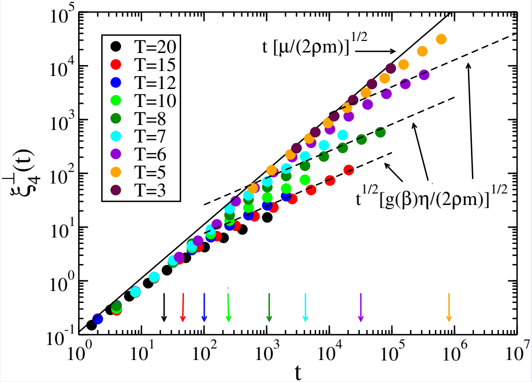
$\eta \approx -0.23 \pm 0.07$ in the fluid and $\eta = 0$ in the glass

Correlation length of transverse displacements

A combination of the scaling form of $S_4^{\perp}(q;t)$:

$$S_4^{\perp}(q;t) = \chi_4^{\perp}(t) f(q\xi_4^{\perp}(t)) \quad \& \quad f(x) \sim x^{-2+\eta} \text{ for } x \gg 1$$

and the formula for the shear modulus: $\mu = \lim_{q\to 0} \lim_{t\to\infty} \frac{2nk_BT}{S_4^{\perp}(q;t)q^2}$ implies that in the glass $\eta = 0$ and $\xi_4^{\perp}(t) \sim t\sqrt{\mu/(2nm)}$.



Glass: $\xi_4^{\perp}(t) \sim t\sqrt{\mu/(2nm)}$

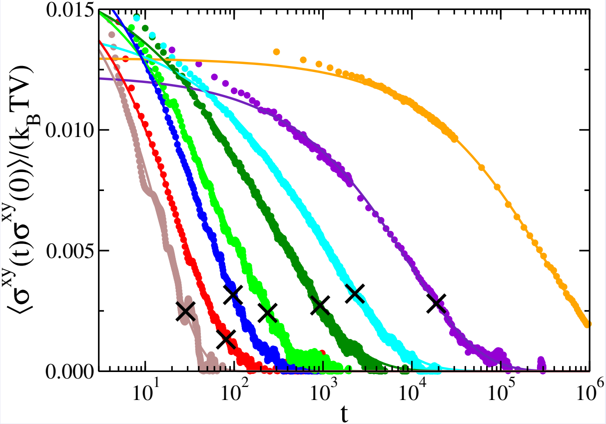
Supercooled fluid:

on intermediate time scales, $\xi_4^{\perp}(t) \sim t\sqrt{\mu/(2nm)}$, where μ is the shear modulus of the glass

at the longest times $\xi_4^{\perp}(t) \propto t^{1/2}$.

Growth of correlation length in the fluid

Empirical observation: for the supercooled fluid, the transition between $\xi_4^\perp(t) \propto t$ and $\xi_4^\perp(t) \propto t^{1/2}$ occurs when $\frac{1}{Vk_BT} \langle \sigma_{xy}(t)\sigma_{xy}(0)\rangle$ is approximately 0.22 G_P (where G_P is the amplitude of the stretched exponential part).

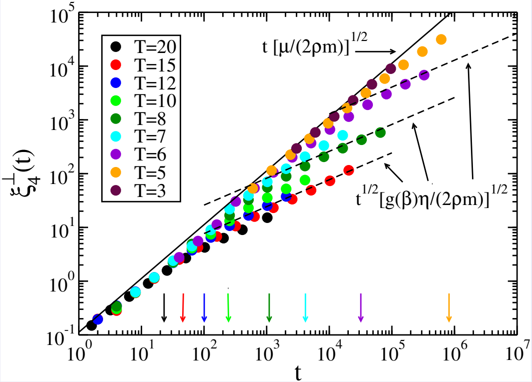


Correlation length of transverse displacements (2)

A combination of the last empirical observation with the dominance of the contribution of the stress tensor auto-correlation function to the viscosity suggests that the amplitude of $t^{1/2}$ dependence is

$$\sqrt{\eta g(\beta)/(2nm)}$$

where η is the fluid's viscosity and $g(\beta)$ is a known function of the stretching exponent β.



Glass: $\xi_4^{\perp}(t) \sim t\sqrt{\mu/(2nm)}$

Supercooled fluid:

on intermediate time scales, $\xi_4^{\perp}(t) \sim t\sqrt{\mu/(2nm)}$, where μ is the shear modulus of the glass.

Supercooled fluid:

asymptotically $\xi_4^{\perp}(t) \sim t^{1/2}\sqrt{\eta g(\beta)/(2nm)}$.

Summary

- Dynamic glass transition implies the existence of long-range density correlations.
- Long-range density correlations can be seen in computer simulations of glasses.
- Pronounced remnants of long-range density correlations can be seen in glassy fluids.

- Shear modulus can be obtained from the small wavevector correlations of particle displacements.
- Solid and fluid: different growth of the correlation length of particle displacements with time.
- Correlations of particle displacements directly reflect (transient) elasticity.

Note: correlations of particle displacements depend on the microscopic dynamics (Newtonian *vs.* Brownian).