Emergence of long-range correlations and rigidity at the dynamic glass transition

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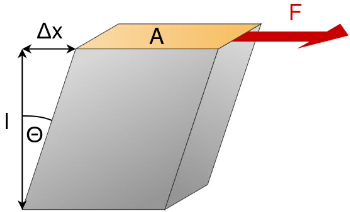
Outline

Solid: elastic response to a shear deformation



Max Born (1939):
“The difference between a solid and a liquid is that the solid has elastic resistance to a shearing stress while a liquid does not.”

non-zero shear modulus μ:

$$\mu = \frac{F/A}{\Delta x/I}$$

Free energy of a deformed system

Consider an N-particle system in a box of volume V; particles interact via potential $V(r)$. The non-trivial part of the free energy of this system is

$$F = -k_B T \ln \int_V \frac{d\vec{r}_1 \ldots d\vec{r}_N}{V^N} \exp\left(-\frac{1}{k_B T} \sum_{i<j} V(r_{ij}) \right).$$

Now, let's deform the box with shear strain γ. Then, one would integrate over a deformed volume,

$$F(\gamma) = -k_B T \ln \int_{V'} \frac{d\vec{r}_1 \ldots d\vec{r}_N}{V^N} \exp\left(-\frac{1}{k_B T} \sum_{i<j} V(r_{ij}) \right).$$

Mathematically, one can change the variables $x' = x - \gamma y$; $y' = y$; $z' = z$ and then one integrates over the undeformed box:

$$F(\gamma) = -k_B T \ln \int_V \frac{d\vec{r}'_1 \ldots d\vec{r}'_N}{V^N} \exp\left(-\frac{1}{k_B T} \sum_{i<j} V\left(\sqrt{(x'_{ij} + \gamma y'_{ij})^2 + y_{ij}^2 + z_{ij}^2} \right) \right).$$

Note: the shear strain γ appears now in the argument of V.

General formula for shear modulus

Expanding the free energy in the shear strain one gets:

$$F(\gamma) = F(0) + N\sigma\gamma + \frac{1}{2}N\mu\gamma^2 + \ldots$$

σ - shear stress μ - shear modulus

$$\mu = \frac{1}{N}\left[\left\langle \sum_{i<j} y_{ij}^2 \frac{\partial^2 V(r_{ij})}{\partial x_{ij}^2} \right\rangle - \frac{1}{k_B T}\left(\left\langle \left(\sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}}\right)^2 \right\rangle - \left\langle \sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right\rangle^2\right)\right]$$

Squire, Holt and Hoover, Physica **42**, 388 (1969)

- $\frac{1}{N}\left\langle \sum_{i<j} y_{ij}^2 \frac{\partial^2 V(r_{ij})}{\partial x_{ij}^2} \right\rangle \leftarrow$ the Born term
- $\frac{1}{N}\left(\left\langle \left(\sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}}\right)^2 \right\rangle - \left\langle \sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right\rangle^2\right) \equiv N\left(\langle \sigma^2 \rangle - \langle \sigma \rangle^2\right) \leftarrow$

  stress fluctuations

General formula for shear modulus

Expanding the free energy in the shear strain one gets:

$$F(\gamma) = \quad F(0) \quad + \quad N\sigma\gamma \quad + \quad \frac{1}{2}N\mu\gamma^2 \quad + \quad \dots$$

σ - shear stress μ - shear modulus

$$\mu = \frac{1}{N}\left[\left\langle \sum_{i<j} y_{ij}^2 \frac{\partial^2 V(r_{ij})}{\partial x_{ij}^2} \right\rangle - \frac{1}{k_B T}\left(\left\langle \left(\sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right)^2 \right\rangle - \left\langle \sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right\rangle^2 \right)\right]$$

Squire, Holt and Hoover, Physica **42**, 388 (1969)

- In the thermodynamic limit the free energy density is shape-independent:

$$\lim_{\infty} \frac{F(0)}{N} = \lim_{\infty} \frac{F(\gamma)}{N}$$

- However, the shear modulus is finite: $\lim_{\infty} N^{-1} \left.\frac{\partial^2 F(\gamma)}{\partial \gamma^2}\right|_{\gamma=0} \neq 0$

General formula for shear modulus

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σ - shear stress μ - shear modulus

$$\mu = \frac{1}{N}\left[\left\langle \sum_{i<j} y_{ij}^2 \frac{\partial^2 V(r_{ij})}{\partial x_{ij}^2} \right\rangle - \frac{1}{k_B T}\left(\left\langle \left(\sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right)^2 \right\rangle - \left\langle \sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right\rangle^2 \right)\right]$$

Squire, Holt and Hoover, Physica **42**, 388 (1969)

- This formula is applicable to both crystals and glasses.
- Can also be evaluated for fluids; computer simulations showed that for fluids this formula gives $\mu = 0$ (as it should).
- It can be proved that for systems with short range interactions, the above formula gives $\mu = 0$ unless there are long-range density correlations (Bavaud *et al.*, J. Stat. Phys. **42**, 621 (1986)).

General formula for shear modulus

Expanding the free energy in the shear strain one gets:

$$F(\gamma) = F(0) + N\sigma\gamma + \frac{1}{2}N\mu\gamma^2 + \ldots$$

σ - shear stress μ - shear modulus

$$\mu = \frac{1}{N}\left[\left\langle \sum_{i<j} y_{ij}^2 \frac{\partial^2 V(r_{ij})}{\partial x_{ij}^2} \right\rangle - \frac{1}{k_B T}\left(\left\langle \left(\sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right)^2 \right\rangle - \left\langle \sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right\rangle^2 \right)\right]$$

Squire, Holt and Hoover, Physica **42**, 388 (1969)

- The above formula was a starting point of a calculation of glass shear modulus by H. Yoshino and M. Mezard (PRL **105**, 015504 (2010)); see also H. Yoshino, JCP **136**, 214108 (2012).
- Goal: investigate the existence of long range density correlations and derive an alternative formula for the shear modulus.

Broken translational symmetry

In crystalline solids translational symmetry is broken

The average density $n(\vec{r})$ is a periodic function of $\vec{r}$:

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

where $\vec{G}$ are reciprocal lattice vectors.

Rigid translation: an equivalent but different state

By translating a crystal by a constant vector $\vec{a}$ we get 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 correlations

Density fluctuations for wavevectors close to $\vec{G}$ diverge

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

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

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

$\overleftrightarrow{\sigma}(\vec{k})$ - microscopic stress tensor $\hat{\vec{n}}$ - an arbitrary unit vector

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

Displacement field and its long-range correlations

Slowly varying deformation

Infinitesimal uniform translation: $n(\vec{r}) \to n(\vec{r}) - \vec{a} \cdot \partial_{\vec{r}} n(\vec{r})$

Infinitesimal deformation with a slowly varying $\vec{a}(\vec{r})$: $n(\vec{r}) \to n(\vec{r}) - \vec{a}(\vec{r}) \cdot \partial_{\vec{r}} n(\vec{r})$

Microscopic expression for the displacement field

$$\vec{u}(\vec{k}) = -\frac{1}{\mathcal{N}} \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} \frac{\partial n(\vec{r})}{\partial \vec{r}} \underbrace{\sum_i \delta(\vec{r} - \vec{r}_i)}_{\text{microscopic density}} \qquad \mathcal{N} = \frac{1}{3V} \int d\vec{r} \left(\frac{\partial n(\vec{r})}{\partial \vec{r}} \right)^2$$

If $\delta n(\vec{r}) = -\vec{a}(\vec{r}) \cdot \partial_{\vec{r}} n(\vec{r})$, then $\left\langle \vec{u}(\vec{k}) \right\rangle = \vec{a}(\vec{k})$.

Long-range correlations of the displacement field

Bogoliubov inequality $\Longrightarrow$

$$\frac{1}{V} \left\langle |\hat{\vec{n}} \cdot \vec{u}(\vec{k})|^2 \right\rangle \geq \frac{1}{k^2} \frac{(k_B T)^2}{\lim_{\vec{k}\to 0} \frac{1}{V} \left\langle |\hat{\vec{k}} \cdot \overleftrightarrow{\sigma}(\vec{k}) \cdot \hat{\vec{n}}|^2 \right\rangle}$$

This can be used to show that $\vec{u}(\vec{k};t)$ is a slow (hydrodynamic) mode
$\rightarrow$ G. Szamel & M. Ernst, Phys. Rev. B **48**, 112 (1993).

Macroscopic force balance equation

Macroscopic force balance equation

In the long wavelength ($k \to 0$) limit we have the following relation between a transverse displacement $\vec{a} = a_x(k_y)\hat{\vec{e}}_x$ and the external force (per unit volume) needed to maintain this displacement:

$$\vec{F} = F_x(k_y)\hat{\vec{e}}_x = \lambda_{xxyy} a_x(k_y) k_y k_y \hat{\vec{e}}_x \qquad \lambda_{xxyy} \equiv \mu \leftarrow \text{shear modulus}$$

Microscopic force balance equation

Transverse non-uniform displacement

Infinitesimal transverse deformation with a slowly varying $\vec{a}(\vec{r}) = \vec{a}(\vec{k})e^{i\vec{k}\cdot\vec{r}}$:

$$n(\vec{r}) \to n(\vec{r}) - \vec{a}(\vec{r})\cdot\partial_{\vec{r}}n(\vec{r}) = n(\vec{r}) - \vec{a}(\vec{k})e^{i\vec{k}\cdot\vec{r}}\cdot\partial_{\vec{r}}n(\vec{r}),\ \vec{a}\perp\vec{k}$$

External force needed to maintain deformed density profile

External potential needed to maintain the density profile change:

$$\int d\vec{r}_2 \left(\frac{\delta V^{\text{ext}}(\vec{r}_1)}{\delta n(\vec{r}_2)}\right)\left[-\vec{a}(\vec{k})e^{i\vec{k}\cdot\vec{r}_2}\cdot\partial_{\vec{r}_2}n(\vec{r}_2)\right]$$

External force on the system (per unit volume):

$$\begin{aligned}\vec{F}(\vec{k}) &= -\frac{1}{V}\int d\vec{r}_1 e^{-i\vec{k}\cdot\vec{r}_1}n(\vec{r}_1)\partial_{\vec{r}_1}\int d\vec{r}_2\left(\frac{\delta V^{\text{ext}}(\vec{r}_1)}{\delta n(\vec{r}_2)}\right)\left[-\partial_{\vec{r}_2}n(\vec{r}_2)\right]\cdot\vec{a}(\vec{k})e^{i\vec{k}\cdot\vec{r}_2} \\ &= -\frac{1}{V}\int d\vec{r}_1 d\vec{r}_2 e^{-i\vec{k}\cdot\vec{r}_1}\left(\partial_{\vec{r}_1}n(\vec{r}_1)\right)\left(\frac{\delta V^{\text{ext}}(\vec{r}_1)}{\delta n(\vec{r}_2)}\right)\left[\partial_{\vec{r}_2}n(\vec{r}_2)\right]\cdot\vec{a}(\vec{k})e^{i\vec{k}\cdot\vec{r}_2}\end{aligned}$$

Microscopic force balance equation → shear modulus

Shear modulus

External force on the system (per unit volume):

$$\vec{F}(\vec{k}) = -\frac{1}{V}\int d\vec{r}_1 d\vec{r}_2 e^{-i\vec{k}\cdot\vec{r}_1}\left(\partial_{\vec{r}_1} n(\vec{r}_1)\right)\left(\frac{\delta V^{\text{ext}}(\vec{r}_1)}{\delta n(\vec{r}_2)}\right)\left[\partial_{\vec{r}_2} n(\vec{r}_2)\right]\cdot\vec{a}(\vec{k})e^{i\vec{k}\cdot\vec{r}_2}$$

Long wavelength ($k \to 0$) limit:

$$\vec{F} = F_x(k_y)\hat{\vec{e}}_x = \underbrace{0}_{\text{no force needed to shift rigidly}} + \underbrace{0}_{\text{symmetry}} + \mu a_x(k_y)k_y k_y \hat{\vec{e}}_x + \ldots$$

Comparison with macroscopic force balance equation allows us to identify shear modulus:

$$\begin{aligned}\mu &= -\frac{k_B T}{2V}\int d\vec{r}_1 \int d\vec{r}_2 \,(y_{12})^2 \left(\partial_{\vec{r}_1} n(\vec{r}_1)\right)\left(\frac{\delta(-\beta V^{\text{ext}}(\vec{r}_1))}{\delta n(\vec{r}_2)}\right)\left(\partial_{\vec{r}_2} n(\vec{r}_2)\right)\\ &= \frac{k_B T}{2V}\int d\vec{r}_1 \int d\vec{r}_2 \,(y_{12})^2 \left(\partial_{x_1} n(\vec{r}_1)\right) c^{\text{cr}}(\vec{r}_1,\vec{r}_2)\left(\partial_{x_2} n(\vec{r}_2)\right)\end{aligned}$$

$c^{\text{cr}}(\vec{r}_1,\vec{r}_2)$ - direct correlation function of the crystal

Shear modulus

$$\mu = \frac{1}{N}\left[\left\langle \sum_{i<j} y_{ij}^2 \frac{\partial^2 V(r_{ij})}{\partial x_{ij}^2} \right\rangle - \frac{1}{k_B T}\left(\left\langle \left(\sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right)^2 \right\rangle - \left\langle \sum_{i<j} y_{ij} \frac{\partial V(r_{ij})}{\partial x_{ij}} \right\rangle^2 \right)\right]$$

Squire, Holt and Hoover, Physica **42**, 388 (1969)

$$\mu = \frac{k_B T}{2V} \int d\vec{r}_1 \int d\vec{r}_2 \, (y_{12})^2 \, (\partial_{x_1} n(\vec{r}_1)) \, c^{\mathrm{cr}}(\vec{r}_1, \vec{r}_2) \, (\partial_{x_2} n(\vec{r}_2))$$

$c^{\mathrm{cr}}(\vec{r}_1, \vec{r}_2)$ - direct correlation function of the crystal

G. Szamel & M. Ernst, Phys. Rev. B **48**, 112 (1993).

Static description of a glass: replica approach

How to "construct" a glass

Franz and Parisi (PRL **79**, 2486 (1997)):

An N-particle system $\vec{r}_1, ..., \vec{r}_N$ coupled to a quenched configuration $\vec{r}^{\,0}_1, ..., \vec{r}^{\,0}_N$:

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

For low enough temperature or high enough density/volume fraction, as $\epsilon \to 0$ the system may remain trapped in a metastable state correlated with the quenched configuration $\Longrightarrow$ dynamic glass transition.

It is convenient to average over quenched configurations: replicas

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

System correlated with the quenched configuration
$\Longrightarrow$ non-trivial correlations between different replicas.

Appearance of non-trivial inter-replica correlations
$\Longrightarrow$ dynamic glass transition (identified with the mode-coupling transition).

OZ equations: a way to implement replica approach

Pair correlation functions: m replicas

$h_{\alpha\beta}(r)$: pair correlation function involving particles in replicas α and β

Ornstein-Zernicke (OZ) equations known from equilibrium stat. mech.

$$h_{\alpha\beta}(\vec{r}_1,\vec{r}_2) = c_{\alpha\beta}(\vec{r}_1,\vec{r}_2) + n\sum_{\gamma}\int d\vec{r}_3 c_{\alpha\gamma}(\vec{r}_1,\vec{r}_3)h_{\gamma\beta}(\vec{r}_3,\vec{r}_2)$$

$c_{\alpha\beta}$: direct correlation function

Replica symmetry: $h_{\alpha\alpha} = h$ & $c_{\alpha\alpha} = c$ for $\alpha \neq \beta$: $h_{\alpha\beta} = \tilde{h}$ & $c_{\alpha\beta} = \tilde{c}$

$m \to 1$ limit

$$h(\vec{r}_1,\vec{r}_2) = c(\vec{r}_1,\vec{r}_2) + n\int d\vec{r}_3 c(\vec{r}_1,\vec{r}_3)h(\vec{r}_3,\vec{r}_2)$$ standard OZ equation

$$\int d\vec{r}_3(\delta(r_{13}) - nc(\vec{r}_1,\vec{r}_3))\tilde{h}(\vec{r}_3,\vec{r}_2) = \tilde{c}(\vec{r}_1,\vec{r}_2) + n\int d\vec{r}_3\tilde{c}(\vec{r}_1,\vec{r}_3)h(\vec{r}_3,\vec{r}_2) - n\int d\vec{r}_3\tilde{c}(\vec{r}_1,\vec{r}_3)\tilde{h}(\vec{r}_3,\vec{r}_2)$$

Additional relations (closure relations) between h's and c's needed!

Symmetry transformation hidden in replica approach

Glass can be moved as a rigid body

Imagine repeating the Franz-Parisi construction with a rigidly shifted system, $\vec{r}_i \to \vec{r}_i + \vec{a}$ (with the quenched configuration kept in its original position):

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

As before: $\epsilon \to 0$, metastable state $\Longrightarrow$ replica off-diagonal correlations.

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 transformation $h_{\alpha 0}(\vec{r}_1, \vec{r}_2) \to h_{\alpha 0}(\vec{r}_1 - \vec{a}, \vec{r}_2); c_{\alpha 0}(\vec{r}_1, \vec{r}_2) \to c_{\alpha 0}(\vec{r}_1 - \vec{a}, \vec{r}_2)$ leaves Ornstein-Zernicke equations unchanged.

Its existence is the reflection of a broken translational symmetry.

Displacement field

Slowly varying deformation

Infinitesimal uniform translation: $h_{\alpha 0}(\vec{r}_1, \vec{r}_2) \to h_{\alpha 0}(\vec{r}_1, \vec{r}_2) - \vec{a} \cdot \partial_{\vec{r}_1} h_{\alpha 0}(\vec{r}_1, \vec{r}_2)$

Infinitesimal deformation with a slowly varying $\vec{a}(\vec{r}_1)$:

$$h_{\alpha 0}(\vec{r}_1, \vec{r}_2) \to h_{\alpha 0}(\vec{r}_1, \vec{r}_2) - \vec{a}(\vec{r}_1) \cdot \partial_{\vec{r}_1} h_{\alpha 0}(\vec{r}_1, \vec{r}_2)$$

Displacement field

$$\vec{u}(\vec{k}) = -\frac{1}{\mathcal{N}} \int d\vec{r}_1 e^{-i\vec{k}\cdot\vec{r}_1} \int d\vec{r}_{21} \frac{\partial h_{\alpha 0}(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} \underbrace{\sum_{i,j} \delta(\vec{r}_1 - \vec{r}_i^{\,\alpha}) \delta(\vec{r}_2 - \vec{r}_j^{\,0})}_{\text{microscopic two-replica density}}$$

$$\mathcal{N} = \frac{1}{3} \int d\vec{r}_{21} \left(\frac{\partial h_{\alpha 0}(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} \right)^2$$

If $\delta h_{\alpha 0}(\vec{r}_1, \vec{r}_2) = -\vec{a}(\vec{r}_1) \cdot \partial_{\vec{r}_1} h_{\alpha 0}(\vec{r}_1, \vec{r}_2)$ then $\left\langle \vec{u}(\vec{k}) \right\rangle = \vec{a}(\vec{k})$.

Long-range correlations

Long-range correlations of the displacement field

Bogoliubov inequality $\Longrightarrow$

$$\frac{1}{V}\left\langle |\hat{\vec{n}}\cdot\vec{u}_\alpha(\vec{k})|^2\right\rangle \geq \frac{1}{k^2}\frac{(k_BT)^2}{\lim_{\vec{k}\to 0}\frac{1}{V}\left\langle |\hat{\vec{k}}\cdot\overleftrightarrow{\sigma}_\alpha(\vec{k})\cdot\hat{\vec{n}}|^2\right\rangle}$$

where $\hat{\vec{n}}$ is an arbitrary unit vector and $\overleftrightarrow{\sigma}_\alpha$ is the (microscopic) stress tensor in replica α.
Note: This is identical to the inequality derived for crystalline solids.

Long-range density correlations

$$\frac{1}{V}\left\langle |\hat{\vec{n}}\cdot\vec{u}_\alpha(\vec{k})|^2\right\rangle$$
$$= \frac{1}{V\mathcal{N}^2}\int d\vec{r}_1 \ldots d\vec{r}_4 \hat{\vec{n}}\cdot\frac{\partial h_{\alpha 0}(\vec{r}_1,\vec{r}_2)}{\partial \vec{r}_{21}}\hat{\vec{n}}\cdot\frac{\partial h_{\alpha 0}(\vec{r}_3,\vec{r}_4)}{\partial \vec{r}_{43}} n_{\alpha 0,\alpha 0}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)e^{-i\vec{k}\cdot\vec{r}_{13}}$$

Replica off-diagonal four-point correlation function $n_{\alpha 0,\alpha 0}$ is long-ranged.

Macroscopic force balance equation

Macroscopic force balance equation

For an isotropic solid, in the long wavelength ($k \to 0$) limit we have the following relation between a transverse displacement $\vec{a} = a_x(k_y)\hat{\vec{e}}_x$ and the external force (per unit volume) needed to maintain this displacement:

$$\vec{F} = F_x(k_y)\hat{\vec{e}}_x = \lambda_{xxyy} a_x(k_y) k_y k_y \hat{\vec{e}}_x \qquad \lambda_{xxyy} \equiv \mu \leftarrow \text{shear modulus}$$

Microscopic force balance equation

Transverse displacement $\vec{a}(\vec{r}) \to$ change of inter-replica correlations

Infinitesimal deformation with a slowly varying $\vec{a}(\vec{r}_1)$:

$$h_{\alpha 0}(\vec{r}_1,\vec{r}_2) \to h_{\alpha 0}(\vec{r}_1,\vec{r}_2) - \vec{a}(\vec{r}_1)\cdot\partial_{\vec{r}_1} h_{\alpha 0}(\vec{r}_1,\vec{r}_2)$$

Inter-replica force needed to maintain these correlations

Inter-replica potential needed to maintain these correlations:

$$\sum_{\beta>0}\int d\vec{r}_3 d\vec{r}_4 \left(\frac{\delta V_{\alpha 0}(\vec{r}_1,\vec{r}_2)}{\delta h_{\beta 0}(\vec{r}_3,\vec{r}_4)}\right)_n \left[-\vec{a}(\vec{r}_3)\cdot\partial_{\vec{r}_3} h_{\beta 0}(r_{34})\right]$$

Force (per unit volume) on replica α:

$$\vec{F}_\alpha(\vec{k}) = -\frac{n^2}{V}\int d\vec{r}_1 \ldots d\vec{r}_4 e^{-i\vec{k}\cdot\vec{r}_{13}} \left(\partial_{\vec{r}_1} h_{\alpha 0}(r_{12})\right) \sum_\beta \left(\frac{\delta V_{\alpha 0}(\vec{r}_1,\vec{r}_2)}{\delta h_{\beta 0}(\vec{r}_3,\vec{r}_4)}\right)_n \left(\partial_{\vec{r}_3} h_{\beta 0}(r_{34})\right)\cdot\vec{a}(\vec{k})$$

Microscopic force balance equation $\rightarrow$ shear modulus

Shear modulus

Force (per unit volume) on replica α:

$$\vec{F}_\alpha(\vec{k}) = -\frac{n^2}{V}\int d\vec{r}_1 ... d\vec{r}_4 e^{-i\vec{k}\cdot\vec{r}_{13}} \left(\partial_{\vec{r}_1} h_{\alpha 0}(r_{12})\right) \sum_\beta \left(\frac{\delta V_{\alpha 0}(\vec{r}_1,\vec{r}_2)}{\delta h_{\beta 0}(\vec{r}_3,\vec{r}_4)}\right)_n \left(\partial_{\vec{r}_3} h_{\beta 0}(r_{34})\right)\cdot \vec{a}(\vec{k})$$

Long wavelength ($k \rightarrow 0$) limit:

$$\vec{F} = F_x(k_y)\hat{\vec{e}}_x = \underbrace{0}_{\text{no force needed to shift rigidly}} + \underbrace{0}_{\text{symmetry}} + \mu a_x(k_y) k_y k_y \hat{\vec{e}}_x + ...$$

Comparison with macroscopic force balance equation allows us to identify shear modulus:

$$\mu = -\frac{n^2 k_B T}{2V}\int d\vec{r}_1 ... \int d\vec{r}_4 \,(y_{13})^2 \left(\frac{\partial h_{10}(\vec{r}_1,\vec{r}_2)}{\partial x_1}\right)$$
$$\times\left(\left(\frac{\delta(-\beta V_{10}(\vec{r}_1,\vec{r}_2))}{\delta h_{10}(\vec{r}_3,\vec{r}_4)}\right)_n - \left(\frac{\delta(-\beta V_{10}(\vec{r}_1,\vec{r}_2))}{\delta h_{20}(\vec{r}_3,\vec{r}_4)}\right)_n\right)\left(\frac{\partial h_{10}(\vec{r}_3,\vec{r}_4)}{\partial x_3}\right)$$

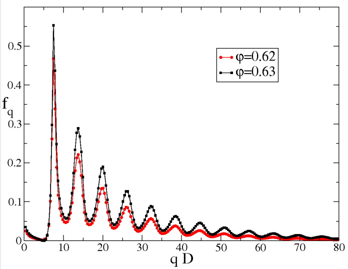
Shear modulus: numerical results

Needed: a theory to calculate replicated correlation functions

Cardenas, Franz and Parisi (JCP **110**, 1726 (1999)) used replicated hyper-netted chain (HNC) integral equation approach (a.k.a. HNC closure).

For hard-sphere interaction replica off-diagonal correlation functions $\tilde{h}$ appear discontinuously at the dynamic transition $\phi_d = 0.619$.

Non-ergodicity parameter $f(q)$



replica approach: $f(q) = \dfrac{n\tilde{h}(q)}{S(q)}$

mode-coupling theory:

$$\lim_{t\to\infty} F(q;t)/S(q) = f(q)$$

$F(q;t)$: intermediate scattering function
$S(q)$: static structure factor

Comparison with simulations

$\Longrightarrow f(q)$ is too small.

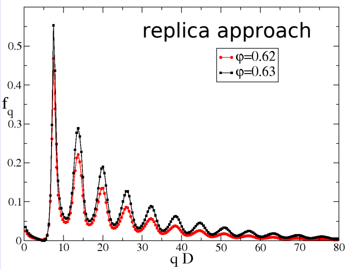
Shear modulus: numerical results

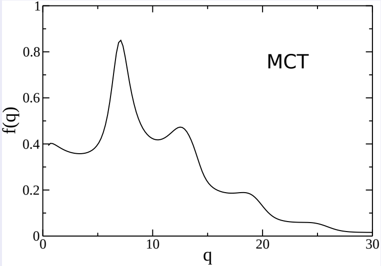
Needed: a theory to calculate replicated correlation functions

Cardenas, Franz and Parisi (JCP **110**, 1726 (1999)) used replicated hyper-netted chain (HNC) integral equation approach (a.k.a. HNC closure).

For hard-sphere interaction replica off-diagonal correlation functions $\tilde{h}$ appear discontinuously at the dynamic transition $\phi_d = 0.619$.

Non-ergodicity parameter $f(q)$





An alternative closure (G. Szamel, Europhys. Lett. **91**, 56004 (2010))

Metastable state ≡ state with vanishing currents

pair distribution: $n_{\alpha\beta} = n^2(h_{\alpha\beta}+1)$ Brownian Dynamics, $D_0 = 1$, $k_BT = 1$

$$0 = \partial_t n_{\alpha\beta}(\vec{r}_1,\vec{r}_2;t) = -\partial_{\vec{r}_1}\cdot\vec{j}_{\alpha,\beta}(\vec{r}_1,\vec{r}_2;t) - \partial_{\vec{r}_2}\cdot\vec{j}_{\beta,\alpha}(\vec{r}_2,\vec{r}_1;t)$$

Assumption: currents vanish ($\alpha \neq \beta$) $\Longrightarrow$

$$0 = \vec{j}_{\alpha,\beta}(\vec{r}_1,\vec{r}_3) = -\partial_{\vec{r}_1} n_{\alpha\beta}(\vec{r}_1,\vec{r}_3) + \int d\vec{r}_2\vec{F}(\vec{r}_{12}) n_{\alpha\alpha\beta}(\vec{r}_1,\vec{r}_2,\vec{r}_3)$$

$$0 = \vec{j}_{\beta,\alpha\alpha}(\vec{r}_1,\vec{r}_2,\vec{r}_3) = -\partial_{\vec{r}_3} n_{\alpha\alpha\beta}(\vec{r}_1,\vec{r}_2,\vec{r}_3) + \int d\vec{r}_4\vec{F}(\vec{r}_{34}) n_{\alpha\alpha\beta\beta}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)$$

$$\partial_{\vec{r}_1}\partial_{\vec{r}_3} n^2\tilde{h}(\vec{r}_1,\vec{r}_3) \equiv \partial_{\vec{r}_1}\partial_{\vec{r}_3} n_{\alpha\beta}(\vec{r}_1,\vec{r}_3) = \int d\vec{r}_2\vec{F}(\vec{r}_{12}) \int d\vec{r}_4\vec{F}(\vec{r}_{34}) n_{\alpha\alpha\beta\beta}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)$$

$n^{\mathrm{irr}}_{\alpha\alpha\beta\beta}$ - one-particle irreducible part of $n_{\alpha\alpha\beta\beta}$:

$$\partial_{\vec{r}_1}\partial_{\vec{r}_3} n^2\tilde{c}(\vec{r}_1,\vec{r}_3) = \int d\vec{r}_2\vec{F}(\vec{r}_{12}) \int d\vec{r}_4\vec{F}(\vec{r}_{34}) n^{\mathrm{irr}}_{\alpha\alpha\beta\beta}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)$$

Equation for the non-ergodicity parameter

Closure: expressing $\tilde{c}$ in terms of $\tilde{h} = S(q)f(q)/n$

A factorization approximation for $n^{\text{irr}}_{\alpha\alpha\beta\beta}$ inspired by an earlier analysis of similar equilibrium correlations results in the following equation for $\tilde{c}$:

$$\tilde{c}(q) = \frac{1}{2q^2}\int \frac{d\vec{q}_1 d\vec{q}_2}{(2\pi)^3}\delta(\vec{q}-\vec{q}_1-\vec{q}_2)\left(\hat{\vec{q}}\cdot[\vec{q}_1 c(q_1)+\vec{q}_2 c(q_2)]\right)^2 S(q_1)S(q_2)f(q_1)f(q_2)$$

Self-consistent equation for non-ergodicity parameter $f(q)$

Using this closure in the replica off-diagonal OZ equation gives an equation for $f(q)$ identical to that derived using mode-coupling theory:

$$\frac{f(q)}{1-f(q)} = \frac{nS(q)}{2q^2}\int \frac{d\vec{q}_1 d\vec{q}_2}{(2\pi)^3}\delta(\vec{q}-\vec{q}_1-\vec{q}_2)\left(\hat{\vec{q}}\cdot[\vec{q}_1 c(q_1)+\vec{q}_2 c(q_2)]\right)^2 \times S(q_1)S(q_2)f(q_1)f(q_2)$$

Mode-coupling theory's equation for $f(q)$ is re-derived using a static approach.

This version of replica approach is consistent with mode-coupling theory.

Shear modulus: numerical results

Needed: a theory to calculate $\left(\frac{\delta(-\beta V_{10}(\vec{r}_1,\vec{r}_2))}{\delta h_{10}(\vec{r}_3,\vec{r}_4)}\right)_n$ and $\left(\frac{\delta(-\beta V_{10}(\vec{r}_1,\vec{r}_2))}{\delta h_{20}(\vec{r}_3,\vec{r}_4)}\right)_n$

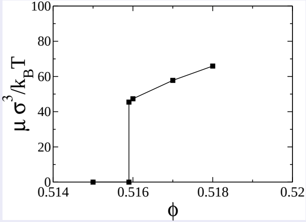
- An approximate relation between replica off-diagonal potentials and the change of the direct correlation functions:

$$n^2 \delta c_{\alpha 0}(\vec{r}_1, \vec{r}_2) = -n_{\alpha 0}(\vec{r}_1, \vec{r}_2) \beta V_{\alpha 0}(\vec{r}_1, \vec{r}_2)$$

- Direct correlation functions can be expressed in terms of replica off-diagonal correlations through Ornstein-Zernicke equations.

Shear modulus: numerical results

Results - shear modulus



Hard sphere potential; static structure calculated using Percus-Yevick structure factor.

Discontinuous appearance of the shear modulus at the dynamic glass transition.

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

Summary

- Crystalline solid: broken translational symmetry
  $\Longrightarrow$ Goldstone modes, long-range correlations & elasticity
- An alternative expression for the shear modulus
- Glassy (amorphous) solid:

  randomly broken translational symmetry
  $\Longrightarrow$ Goldstone modes, long-range correlations & elasticity
- An alternative expression for the shear modulus of glasses
- Discontinuous appearance of the shear modulus at the dynamic glass transition

Origin of rigidity in solids: broken translational symmetry

Crystals

G. Szamel & M. H. Ernst,
“Slow modes in crystals: A method to study elastic constants",
Phys. Rev. B **48**, 112 (1993)

C. Walz & M. Fuchs,
“Displacement field and elastic constants in nonideal crystals”,
Phys. Rev. B **81**, 134110 (2010)

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“On the coarse-grained density and compressibility of a non-ideal crystal”, in preparation

Glasses

G. Szamel & E. Flenner,
“Emergence of Long-Range Correlations and Rigidity at the Dynamic Glass Transition",
Phys. Rev. Lett. **107**, 105505 (2011)