ガラス系における低エネルギー励起と緩和

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乱れたまま固まったモノ

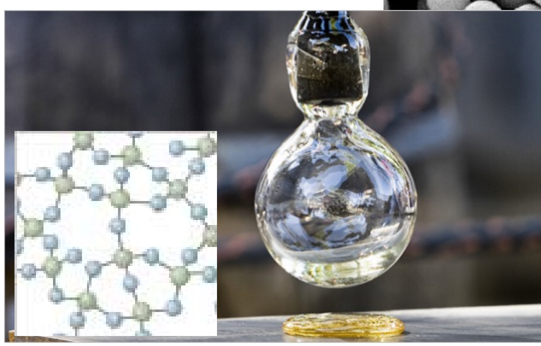
コロイドガラス

粉体

ペースト

渋滞

ガラス



* 幅広い空間スケールで存在する乱れた固体状態

* 遅い動力学・非線形応答などの興味ある現象

* 秩序の欠如・非平衡性 → 理論的な扱いの困難さ

Outline

1. Broad introduction to glass problems

2. Low energy vibrations of glasses

Mizuno-Shiba-Ikeda PNAS 2017
Shimada-Mizuno-Wyart-Ikeda PRE(R) 2018

3. Ideal glass transition of randomly pinned systems

Ozawa-Kob-Ikeda-Miyazaki PNAS 2015
Ozawa-Kob-Ikeda-Miyazaki PRL 2018

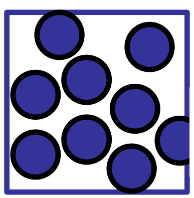
What is glass?

Liquid

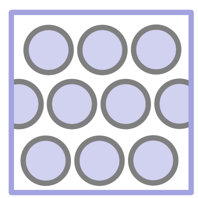
Crystal

Glass

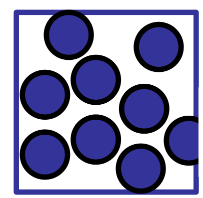
Structure



Disordered



Ordered



Disordered

Fluidity

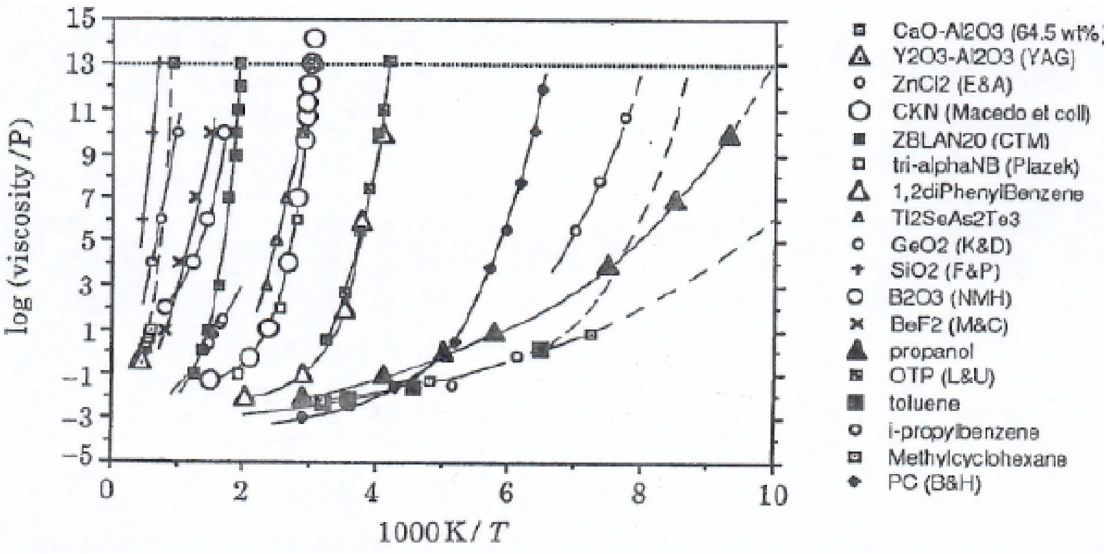
Flow

No flow

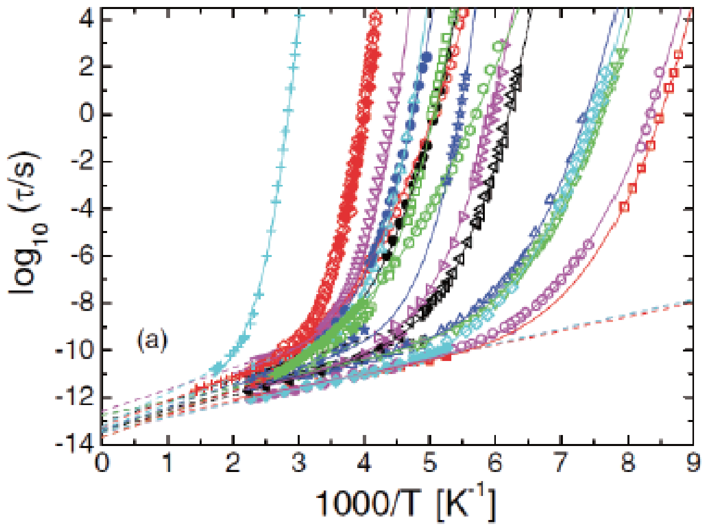
No flow

Glass transition

Viscosity vs 1/Temp.



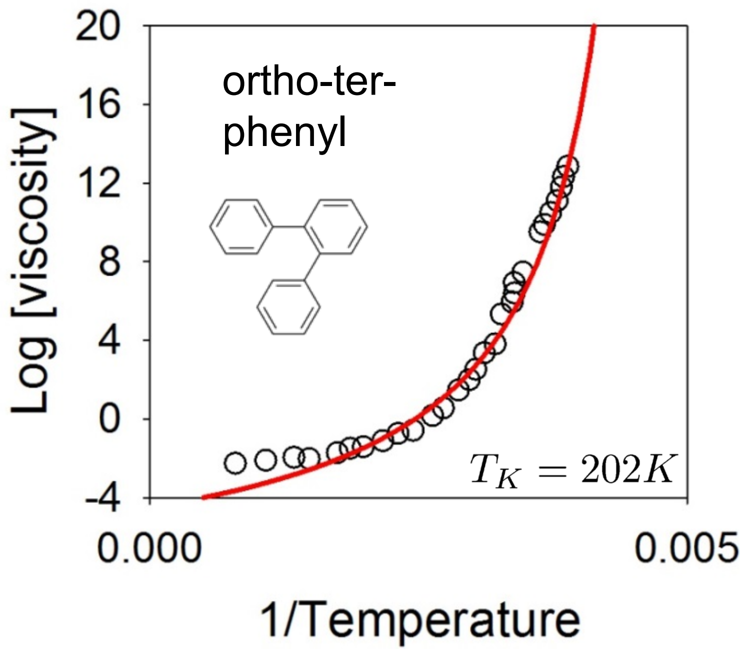
Relax. Time vs 1/Temp.



◆ **Dramatic slowing down of the dynamics with decreasing temperature**

- ◆ When the relaxation times become larger than the experimental time scale, liquid practically becomes solid.

Glass transition



$$\eta \sim \exp\left(\frac{A}{T - T_K}\right)$$

(Vogel-Fulcher-Tamman則)

- **Slowing down of the dynamics can be well fitted by the diverging function**
  - Suggests the phase transition at T_K
  - But, no experimental results at around T_K...

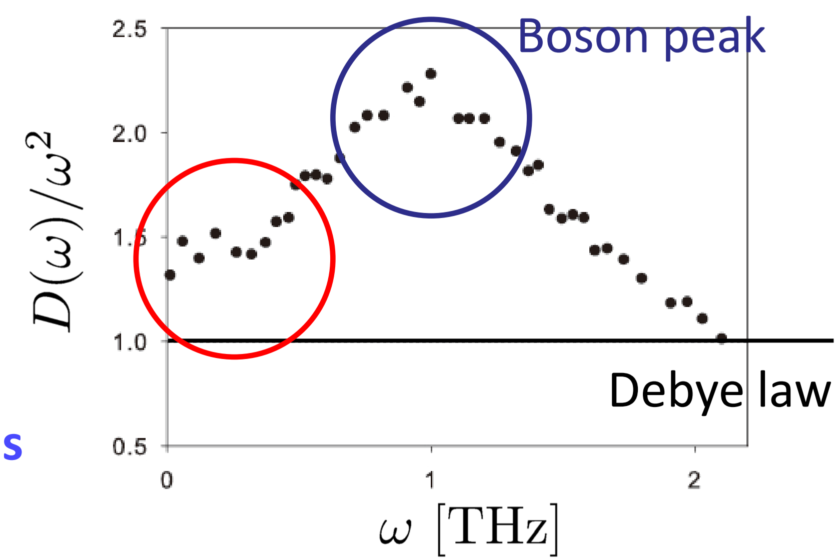
Vibration of glass

- **Macroscopic solids obey the elasticity equation**

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} = (\lambda + \mu)\vec{\nabla}\vec{\nabla}\cdot\vec{u} + \mu\nabla^2\vec{u}$$

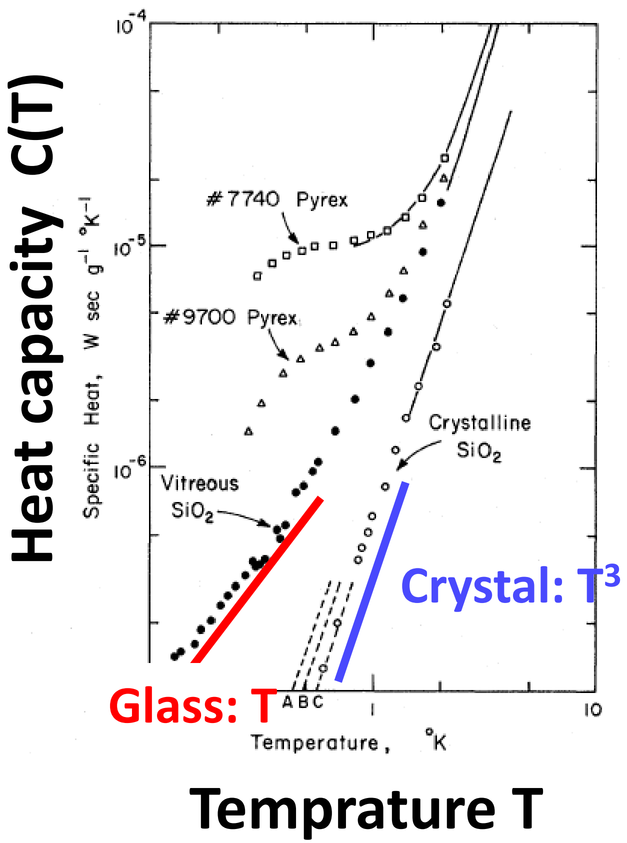
  - Plane wave solutions (Phonon)
  - Vibrational density of states (vDOS) follow **Debye law** $D(\omega) \propto \omega^2$

- **vDOS of real glasses**
  - Example: Glycerol, measured by scattering experiments
  - **Peak at around 1 THz is called Boson peak.**
    → "excess" of low energy vibrations
  - **Not so much was known for lower frequency region.**



Monaco-Giordano, PNAS 2009

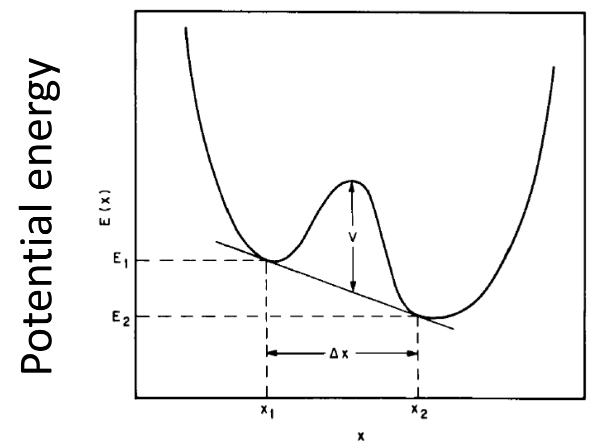
Heat capacity in low T regime



C ~ T at T < 1 K

Zeller, Pohl PRB 1971

Two-level system scenario:



Coordinates for some group of atoms

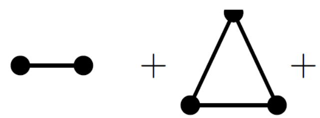
If double-well structure is present in the energy landscape, transitions between two states may take place (thermal activation or tunneling), which gives the additional contribution to the heat capacity

Anderson et al./Phillips 1971

Big Questions

Q1 *Glass transition (thermodynamic transition to glass) exists?*

Hamiltonian $U = \sum_{i}^{N} \sum_{j>i}^{N} v(r_{ij})$

$-\beta F = \rho(1 - \log \rho) +$ 

virial expansion

Yes, in infinite dimension: Mean-field theory

Parisi-Urbani-Zamponi, "Theory of simple glasses" (2020)

Not known, in finite dimension

Berthier-Biroli, Review of Modern Physics (2011)

Q2 *Anomalous solid state properties of glass can be understood?*

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} = (\lambda + \mu(\vec{r}))\nabla\nabla \cdot \vec{u} + \mu(\vec{r})\nabla^2 \vec{u}$$

$$P(\mu) \sim \exp\left(-\frac{(\mu - \mu_0)^2}{2\sigma^2}\right)$$

Phenomenological mean-field theory

Glass → Solid with spatially fluctuating elasticity

Can predict boson peak

Can not predict low T anomalies

e.g. Schirmacher-Scopigno-Ruocco JNCS 2015

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Ozawa-Kob-Ikeda-Miyazaki PRL 2018

Q. How glasses approach the continuum limit?

Numerical simulation on BIG system

Mizuno-Shiba-Ikeda, PNAS, 114, E9767 (2017).

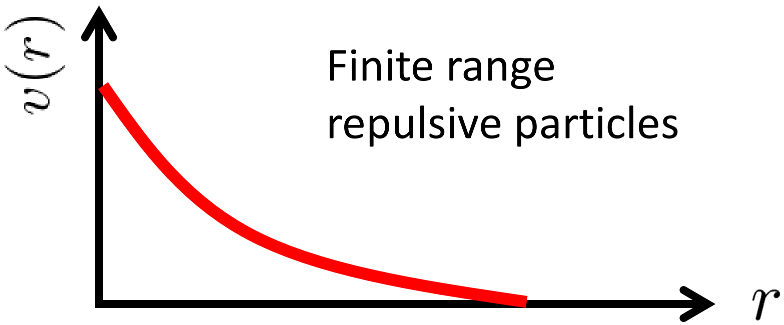
Model

Model

$$U = \sum_{i}^{N} \sum_{j>i}^{N} v(r_{ij})$$

From N = 16,000 up to 2,048,000

Periodic boundary condition



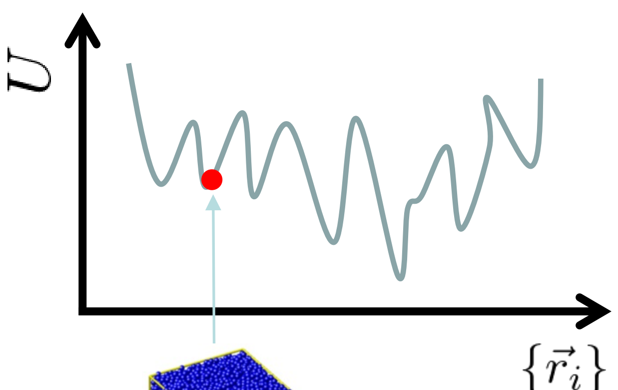
Preparation of glass

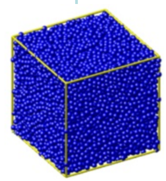
From fully random initial configuration, we perform the energy minimization

e.g. steepest descent $$\frac{d\vec{r}_i}{dt} = -\gamma \frac{\partial U}{\partial \vec{r}_i}$$

This gives a local minimum, which is a glass.

Different initial configuration gives different local minimum, but we focus on the universal properties





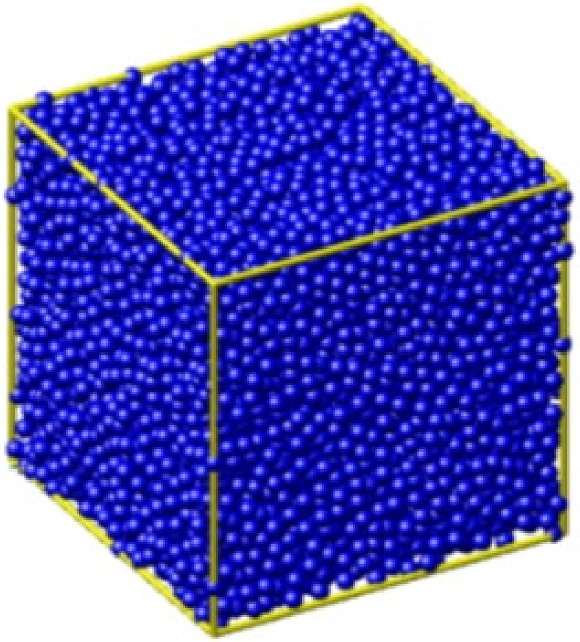
Model

- Focus on harmonic dynamics around a local minimum

$$\vec{r}_i = \vec{r}_{i,0} + \vec{u}_i$$

$$\frac{d\boldsymbol{u}}{dt} = \mathbf{H}\boldsymbol{u} + O(u^3) \quad H_{ij} = \frac{\partial^2 U}{\partial \vec{r}_i \vec{r}_j}$$

dynamical matrix

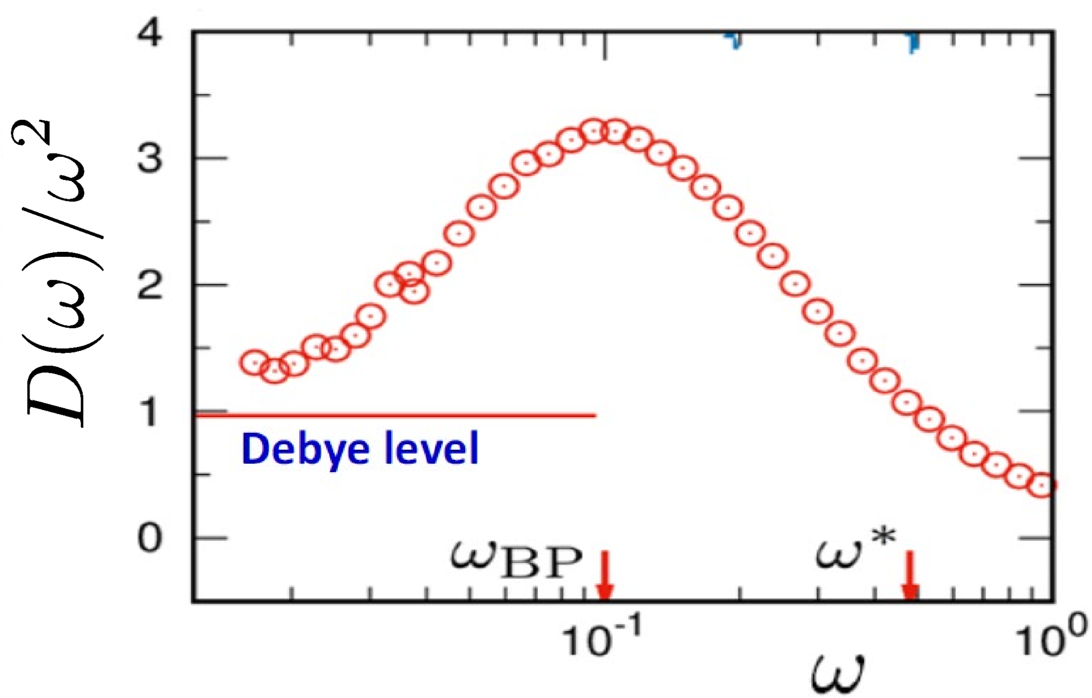


- Diagonalize the dynamical matrix numerically.

$$\mathbf{H}\boldsymbol{e}_k = \lambda_k \boldsymbol{e}_k$$ k-th eigenmode

$$D(\omega) = \sum_k \delta(\omega - \sqrt{\lambda_k})$$ vibrational density of states

vDOS



- We found the Boson peak.
- In further low frequency regime, vDOS approaches to the Debye level, but only slowly.

analyze carefully

Analysis of the modes

Participation ratio of vibrational mode *k*:

Mazzacurati, Ruocco, Sampoli, EPL 1996

$$P^k = \frac{1}{N} \frac{1}{\sum_{j=1}^{N} \left(\boldsymbol{e}_j^k \cdot \boldsymbol{e}_j^k \right)^2}$$

1. Only one particle vibrates:

$$\boldsymbol{e}_1^k = 1, \quad \boldsymbol{e}_j^k = 0 \ (j = 2, 3, ..., N) \quad \Rightarrow \quad P^k = \frac{1}{N}$$

2. All the particles vibrate equivalently:

$$\boldsymbol{e}_j^k = \frac{1}{\sqrt{N}} \quad (j = 1, 2, ..., N) \quad \Rightarrow \quad P^k = 1$$

Fraction P^k of total particles participate in the vibrational mode *k*

Analysis of the modes

Phonons (elastic waves) in isotropic medium under periodic boundary:

$$\boldsymbol{e}_j^{\boldsymbol{k},\sigma} = \frac{\boldsymbol{p}_{\boldsymbol{k},\sigma}}{\sqrt{N}} \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j^0),\ \omega_{\boldsymbol{k},\sigma} = c_\sigma|\boldsymbol{k}|,\ c_\sigma = \sqrt{M_\sigma/\rho},$$

$\boldsymbol{k} = (2\pi/L)(i,j,k)$: wave vector

Expansion by phonon modes (Fourier expansion) of vibrational mode *k*:

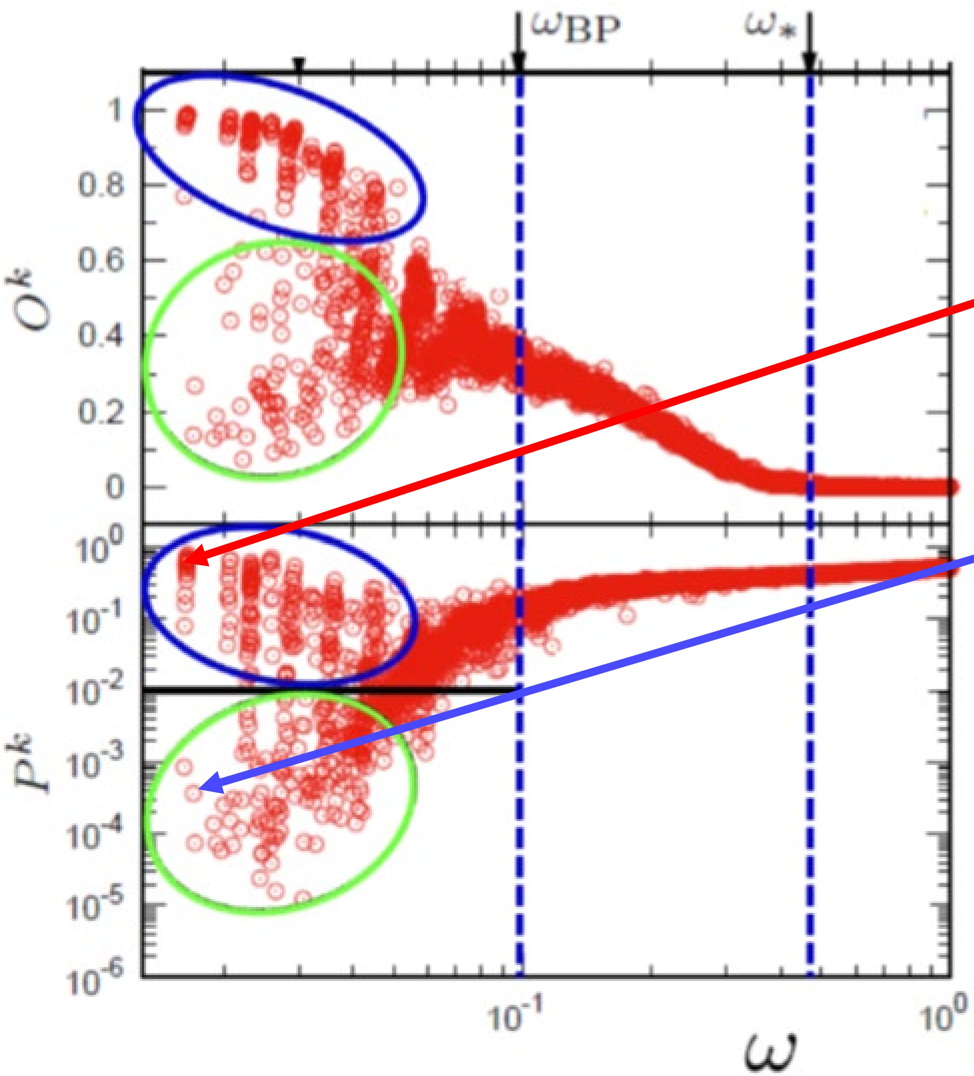
$$\boldsymbol{e}_j^k = \sum_{\boldsymbol{k},\sigma} A_{\boldsymbol{k},\sigma}^k \boldsymbol{e}_j^{\boldsymbol{k},\sigma} \Rightarrow O_{\boldsymbol{k},\sigma}^k = \left|A_{\boldsymbol{k},\sigma}^k\right|^2,\quad \sum_{\boldsymbol{k},\sigma} O_{\boldsymbol{k},\sigma}^k = 1$$

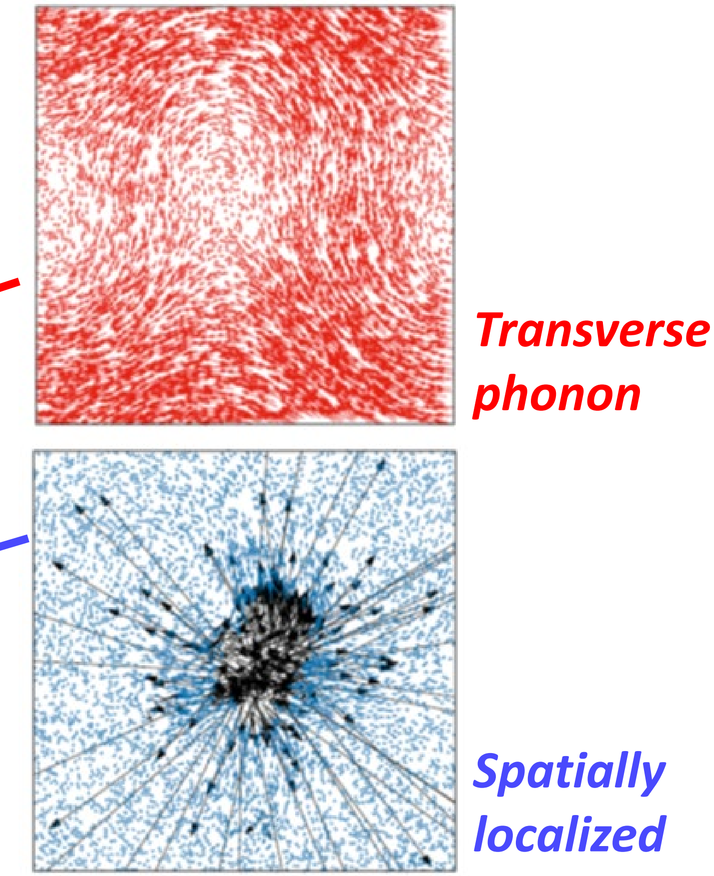
Overlap of vibrational mode *k*, with phonons:

$$O^k = \sum_{\left\{\boldsymbol{k},\sigma;\ O_{\boldsymbol{k},\sigma}^k \geq \frac{N_m}{3N-3}\right\}} O_{\boldsymbol{k},\sigma}^k = \begin{cases} 1 & \text{: Phonon} \\ 0 & \text{: Non-phonon} \end{cases}$$

$$(N_m = 100)$$

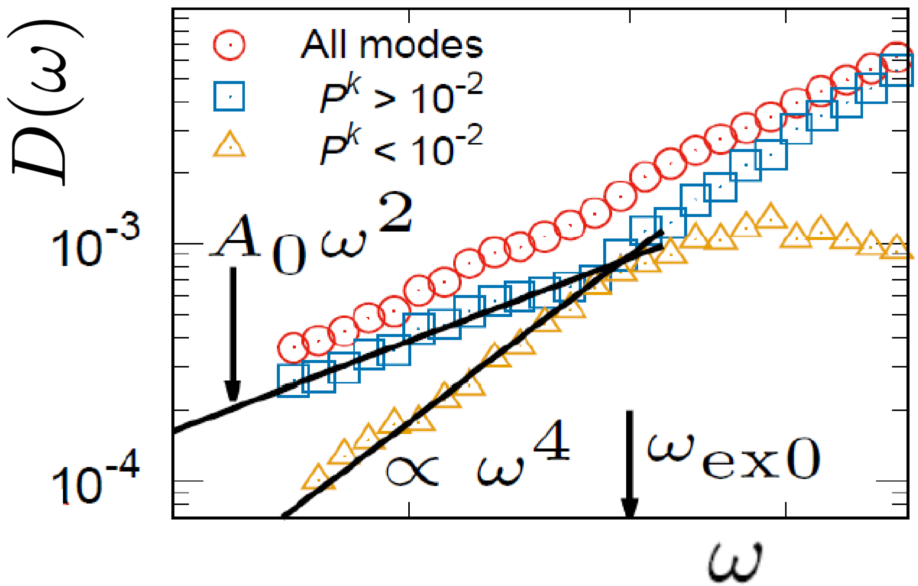
Analysis of the modes

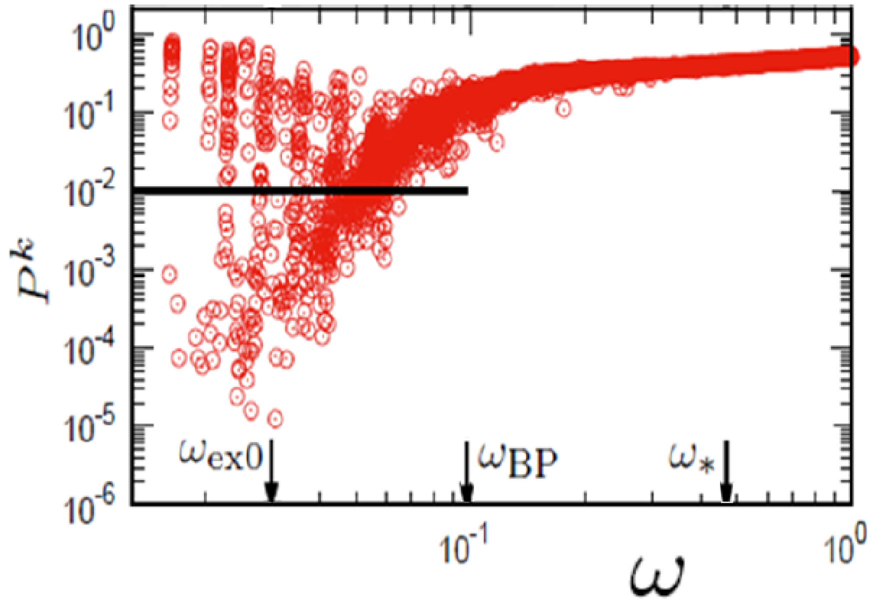




Phonon modes and **localize modes** coexist in low frequency regime

Phonon and localized modes



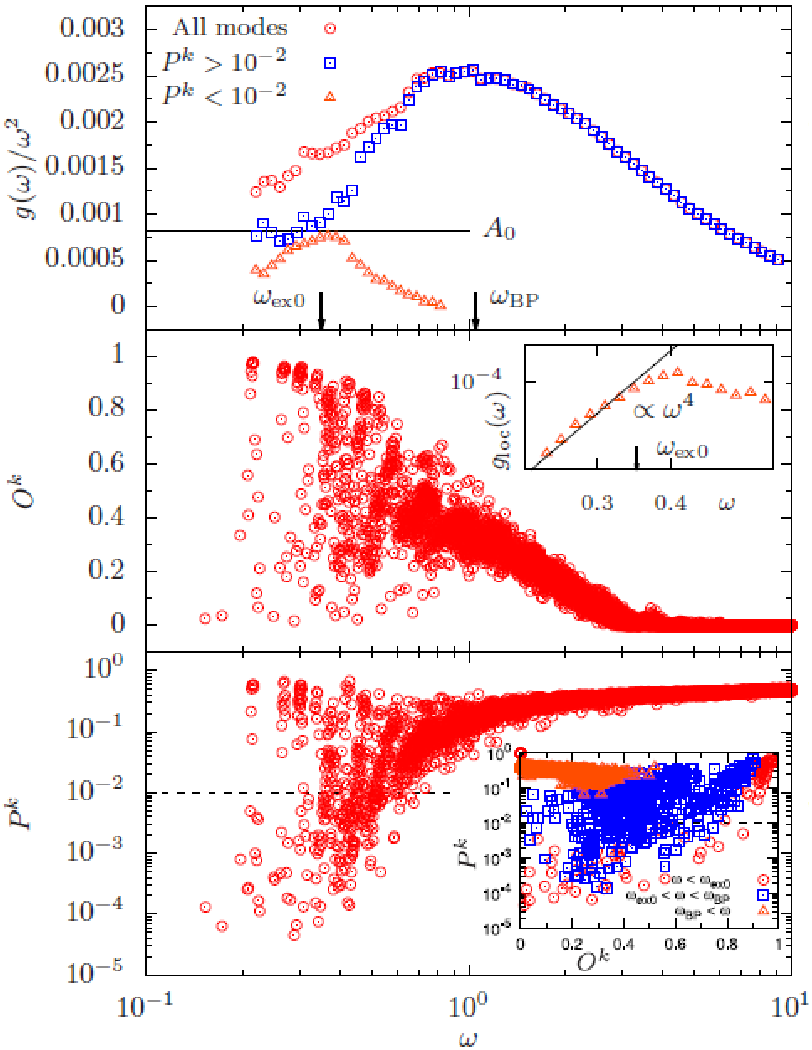


$$D(\omega) = \underbrace{D_{ex}(\omega)}_{A_0\omega^2} + \underbrace{D_{loc}(\omega)}_{\propto \omega^4}$$

Debye law

Non-Debye law of localized modes

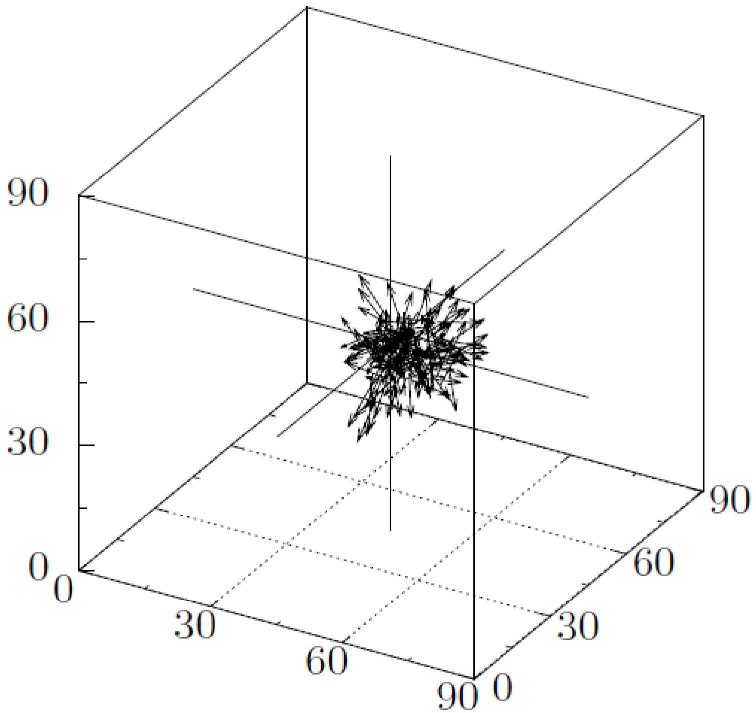
Lennard-Jones glass



$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Localized modes are universally present in many different glasses

Shimada-Mizuno-Ikeda, Phys. Rev. E 97, 022609.



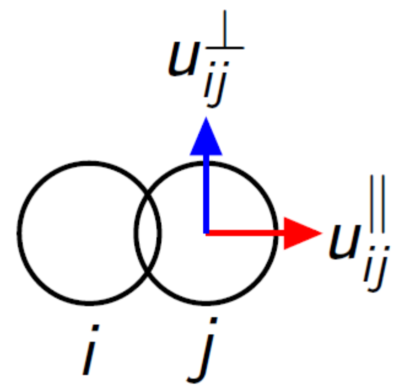
Q. How particles vibrates in the localized modes?

Shimada-Mizuno-Wyart-Ikeda, Phys. Rev. E 98, 060901(R).

Vibrational energy

For an eigenvector $\boldsymbol{e}^k$, the energy between an interacting pair $\langle ij \rangle$ is

$$\delta E_{ij}^k = \left(u_{ij}^{\parallel}\right)^2 + \frac{-f_{ij}}{r_{ij}}\left(u_{ij}^{\perp}\right)^2 ,$$



parallel: > 0

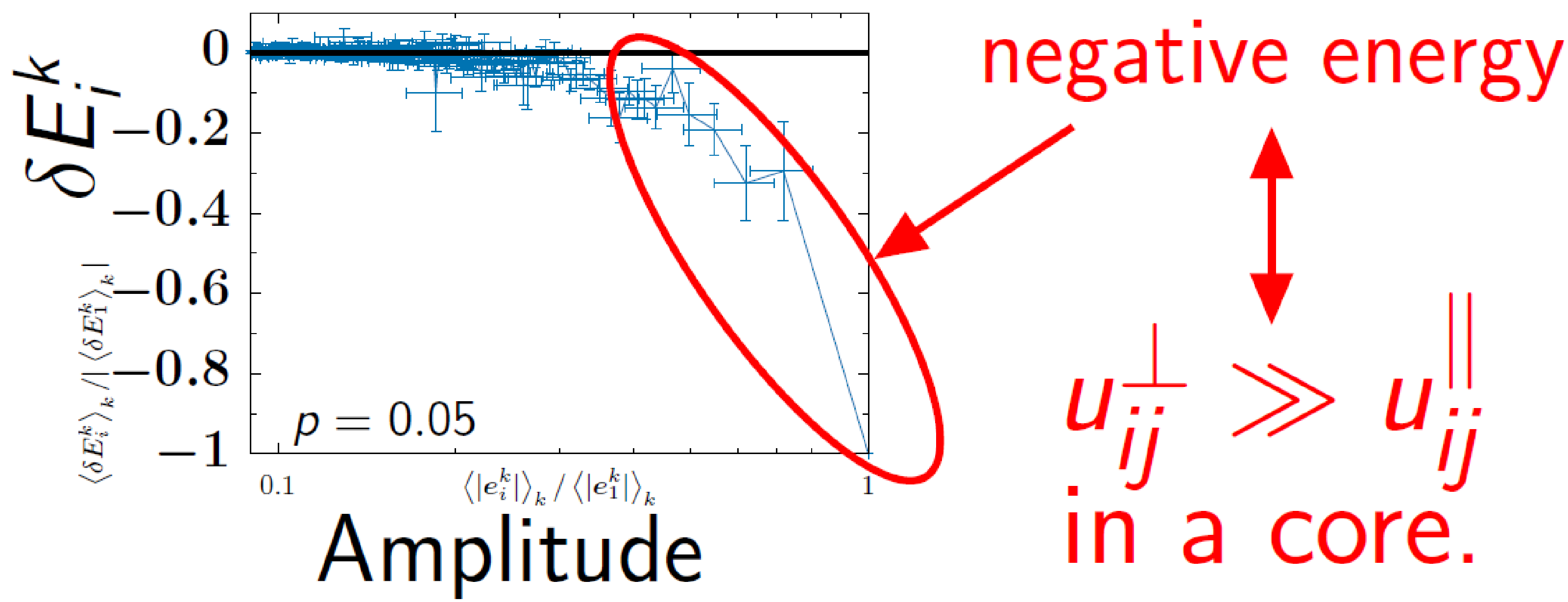
perpendicular: < 0

where r_{ij} is the distance and f_{ij} is the force between the pair ($f_{ij} > 0$ for repulsion).

Vibrational energy

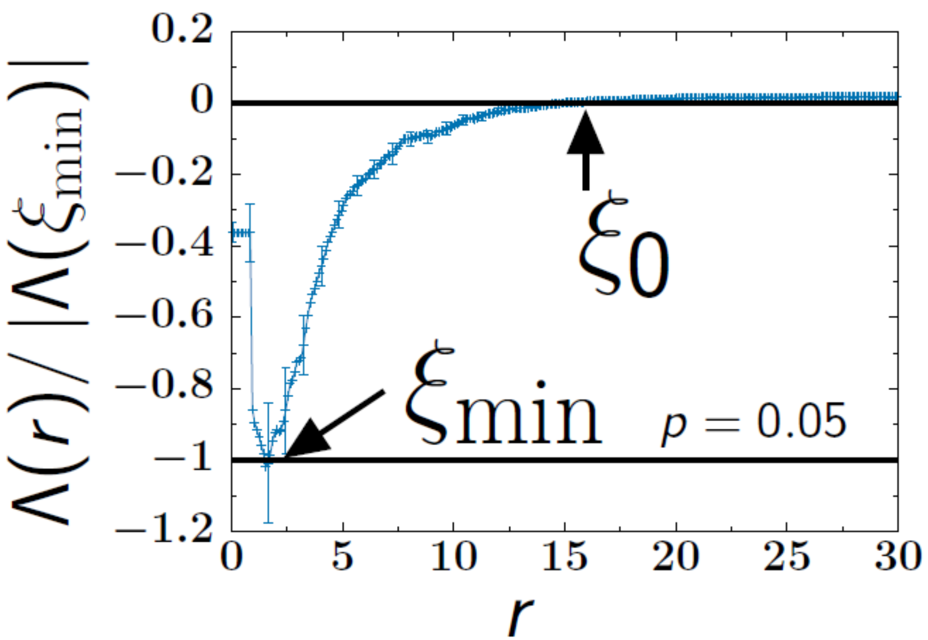
The vibrational energy for i-th particle is

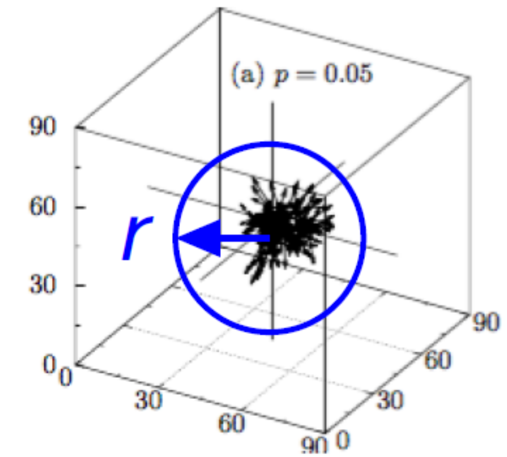
$$\delta E_i^k = \frac{1}{2} \sum_{j \in \partial i} \delta E_{ij}^k .$$



Vibrational energy

$$\Lambda(r) \equiv \left\langle \sum_{r_i \leq r} \delta E_i^k \right\rangle_k .$$





*** Core part has negative energy → Unstable**

*** Far-field part has positive energy → Stabilize the core**

Summary

- We use large-scale numerical simulation to study the low frequency vibrations of structural glasses.

- Low frequency part of vDOS is

$$D(\omega) = \underbrace{D_{\rm ex}(\omega)}_{\propto\, \omega^2} + \underbrace{D_{\rm loc}(\omega)}_{\propto\, \omega^4}$$

Phonon **Localized mode**

- Localized mode = Unstable core, which is stabilized by the far-field component (supported by the surrounding medium)

- Localized modes are “gapless” modes
  - Glass has weak spots which do not have characteristic energy scale – “Glass is marginally stable solid”

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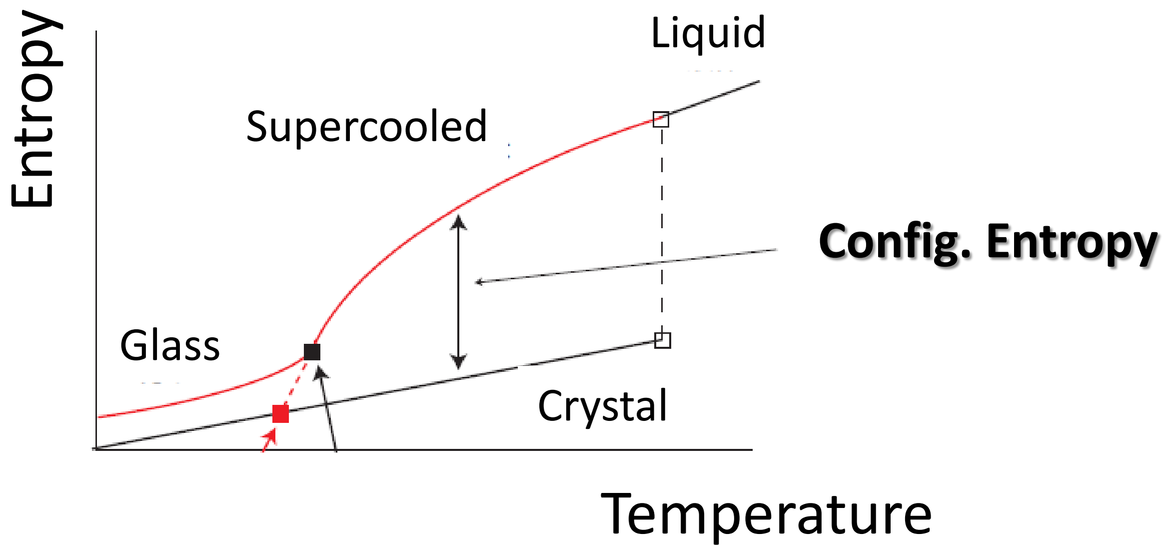
Glass transition

- Heat measurement of supercooled liquids



- Experimentally, configurational entropy is defined as

$$S_c \equiv S_{\text{liquid}} - S_{\text{vibration}} \approx S_{\text{liquid}} - S_{\text{crystal}}$$

  - Estimates of number of different configurations

Glass transition

Increase of the viscosity and decrease of the config. entropy can be fitted with functions with *same critical temperature*

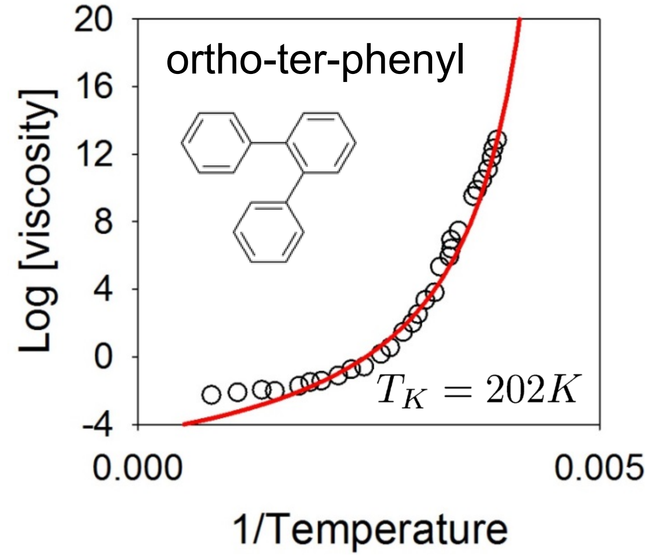
$$\eta \sim \exp\left(\frac{A}{T - T_K}\right)$$

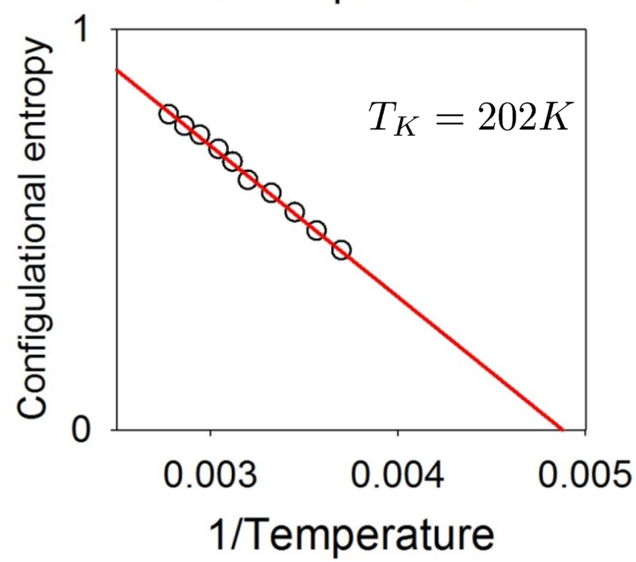
$$S_c \sim 1 - T_K/T$$

→ Indicate the existence of equilibrium glass transition

→ **Ideal glass transition = Viscosity diverges & Config. entropy becomes zero in equilibrium**

But, we are still far from T_K...

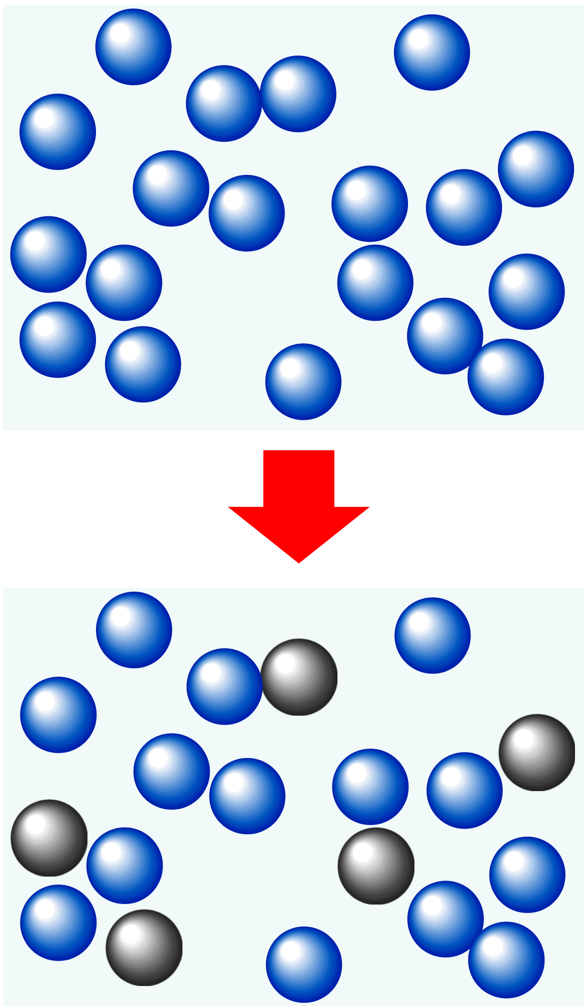




Q. Glass transition can exists in finite dimension?

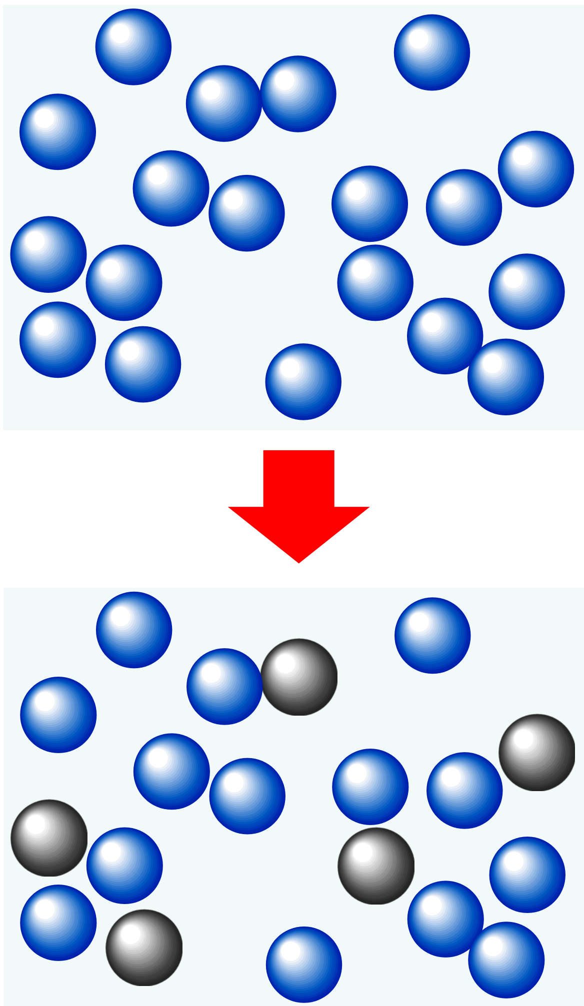
Ozawa-Kob-Ikeda-Miyazaki, PNAS 112, 6914 (2015).
Ozawa-Kob-Ikeda-Miyazaki, PRL 121, 205501 (2018).

Random pinning



- Equilibrate a liquid at temperature *T*
- Pin some fraction of particles (fraction *c*). Then consider thermodynamics of remaining mobile particles at *T*
- Of course, the liquid freezes at *c* = 1.
- Q. Does the liquid freezes even at *c* < 1 ?
  - Glass transition using *c* as a control parameter

Why random pinning?



- Positions of pinned particles are taken from equilibrium configurations
  - We do not “insert” pin particles
- Thus, the pinning does not disturb structure
  - **If the original liquids are equilibrated, we do not need to equilibrate the pinned system**

[Kob & Berthier, PRL 2013]

Simulation

- Two component Lennard-Jones (system size: N=300, 1200)

$$u_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right],$$

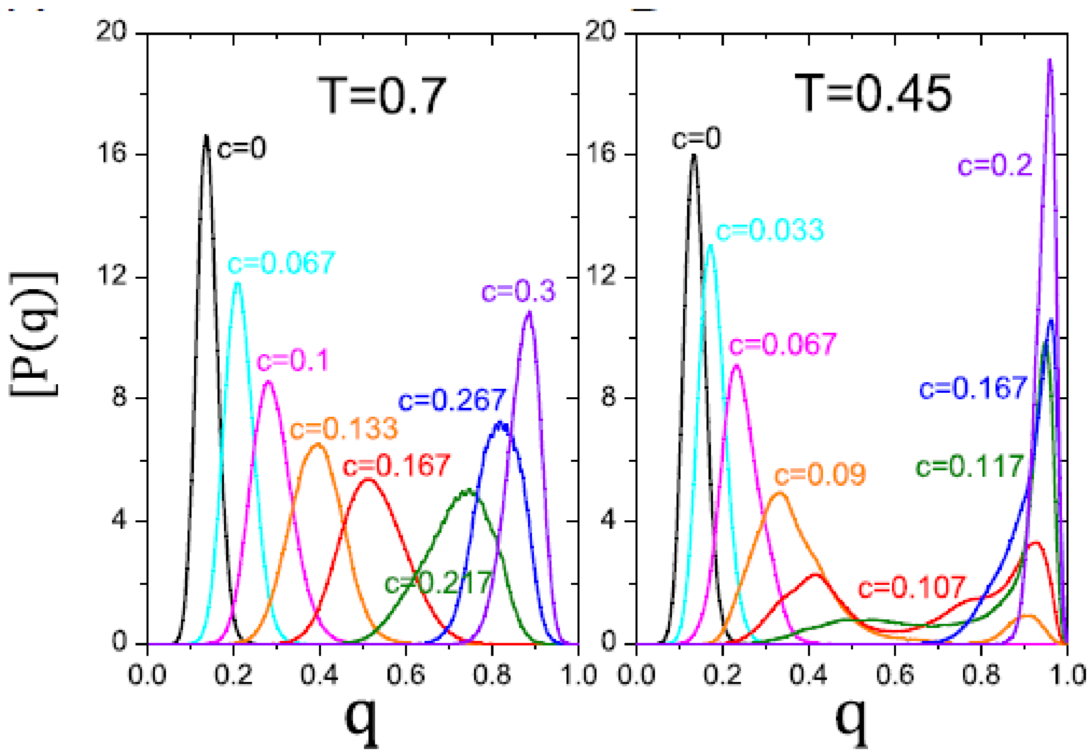
- Equilibrate the fluid state without pinning
- Select particles randomly with the probability *c* and pin them.
- Replica exchange MC simulation of the mobile particles to calculate various equilibrium physical quantities.
- Perform many different realization of pinning and average over them

Overlap

$$q_{\alpha\beta} = \sum_i \theta(a - |\vec{r}_i(\alpha) - \vec{r}_i(\beta)|)$$

a = 0.3

Prob. distribution of q



- Sample configurations appearing in the different replicas

$$\{\vec{r}_i(\alpha)\},\ \{\vec{r}_i(\beta)\}, \cdots$$

- Measure the similarities between them

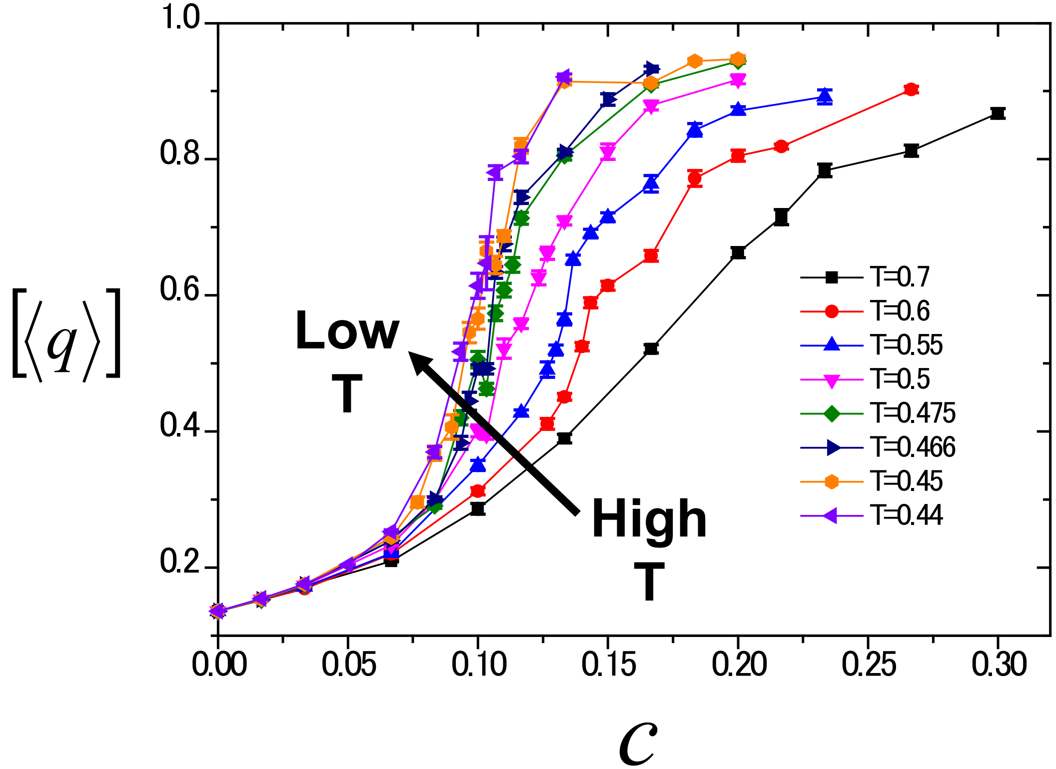
- High T: Smooth change
- Low T: Discontinuous change

Overlap

$$q_{\alpha\beta} = \sum_i \theta(a - |\vec{r}_i(\alpha) - \vec{r}_i(\beta)|)$$

a = 0.3

Average of q



◆ Sample configurations appearing in the different replicas

$$\{\vec{r}_i(\alpha)\},\ \{\vec{r}_i(\beta)\}, \cdots$$

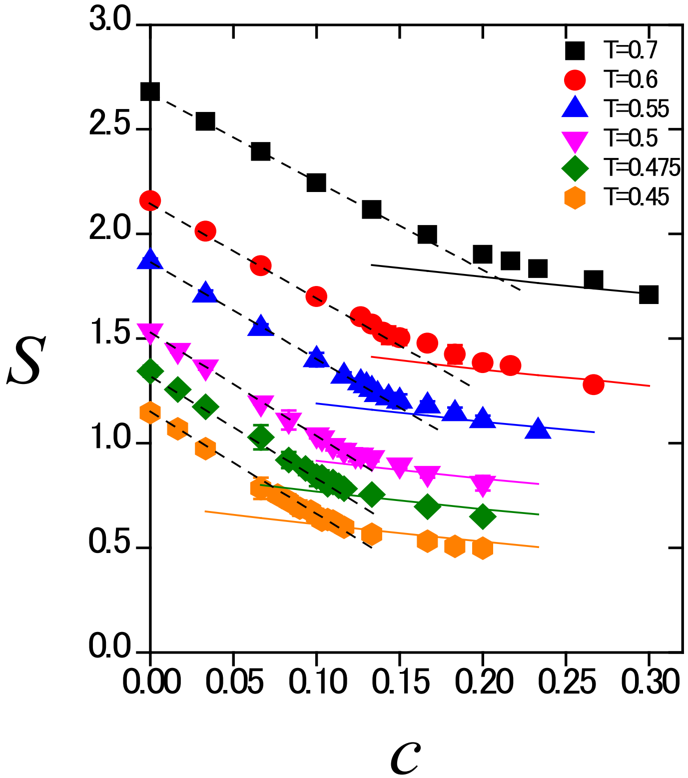
◆ Measure the similarities between them

◆ **Phase transition into the frozen state takes place at low T**

Entropy

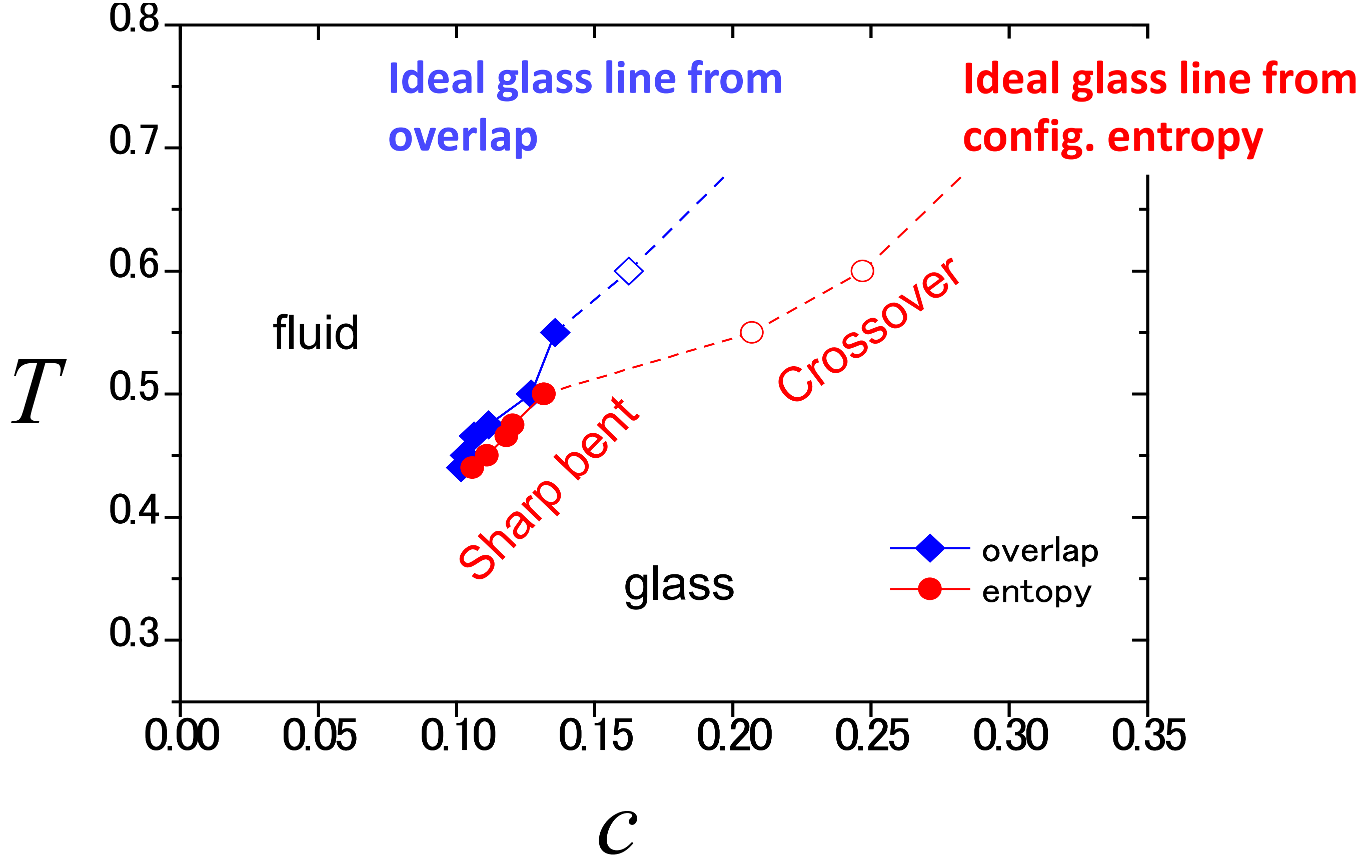
- Calculate entropy

$$S(\beta_*) = S(0) + \int_0^{\beta_*} \frac{\partial S}{\partial \beta} d\beta$$



- Bending of the entropy at $c < 1$ → **Phase transition is accompanied with the bending of entropy → Ideal glass!**

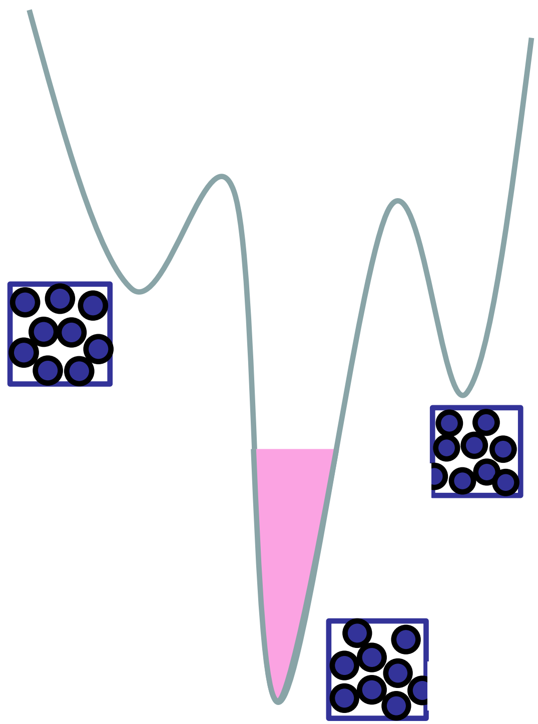
Phase diagram



◆ At lower T, the overlap and entropy approach give the same glass transition temperature → **Clear ideal glass transition**

Nature of the glass

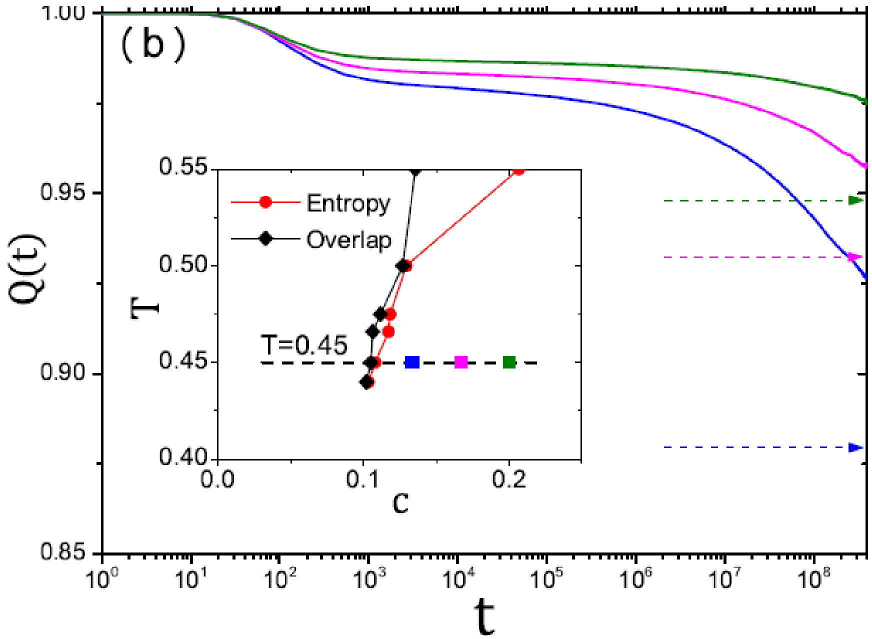
◆ Traditional expectation on the glass phase: (Harmonic) vibration around the most stable amorphous configuration



Dynamics

- Time evolution of the overlap $$q(t) = \sum_i \theta(a - |\vec{r}_i(t) - \vec{r}_i(0)|)$$

$a = 0.3$



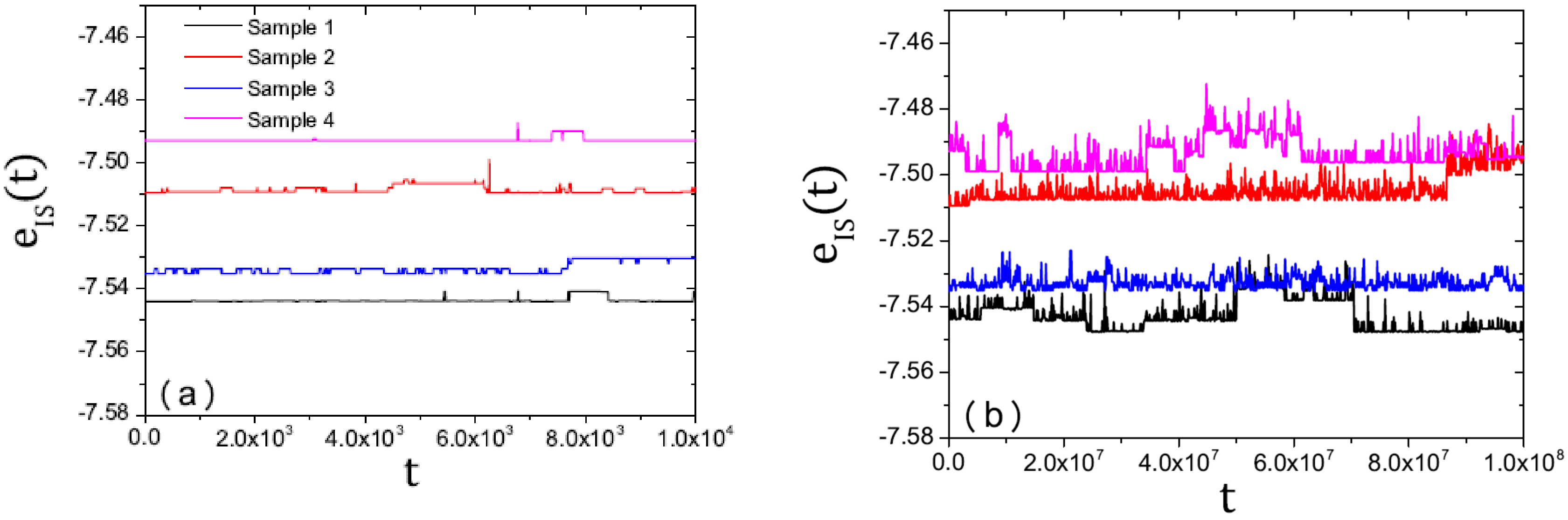
Dashed vectors:
Long time limit evaluated by the replica exchange MC

- Plateau at intermediate time scale is originated from the small vibration around a single configuration.
- **Not vibrational relaxation is present in the long time regime**

Dynamics

◆ Starting from the instantaneous configurations in the MC simulations, we perform energy minimization to find the nearest local minima

→ Time series of local minima



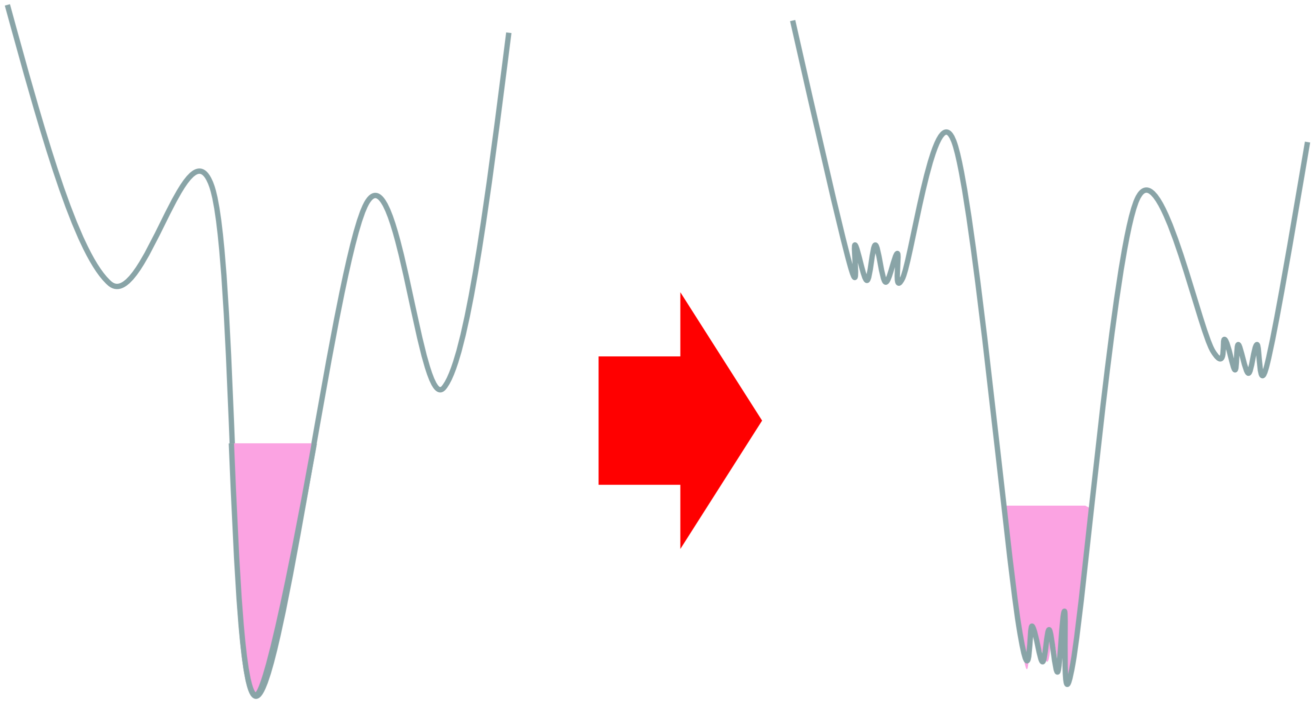
◆ Short time: Basically, stay in the same local minimum

◆ Long time: Explore many different local minima

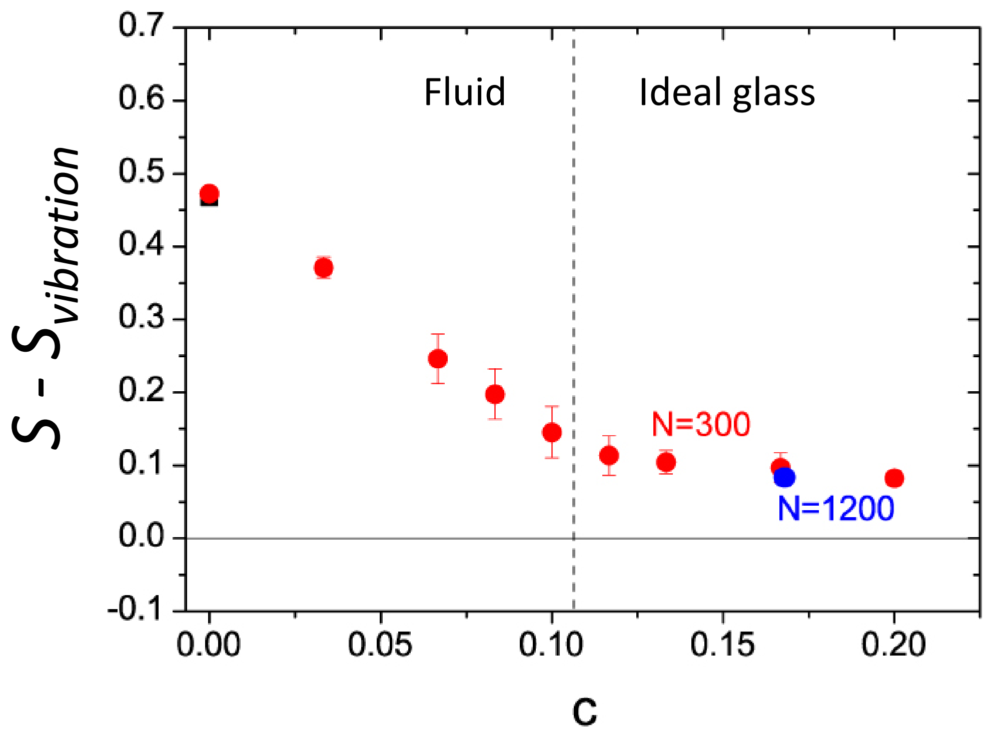
Nature of the glass

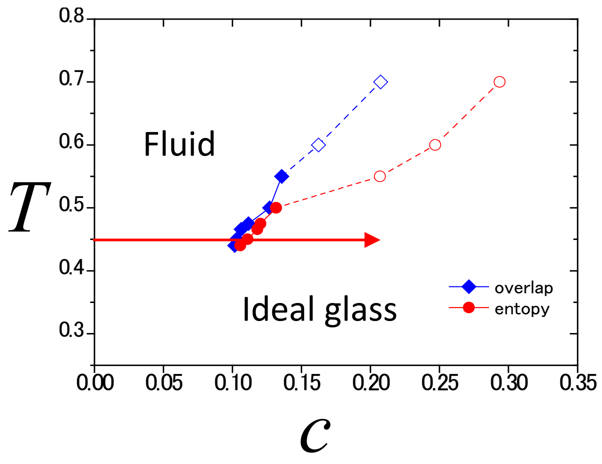
◆ Traditional view on the glass phase: Harmonic vibration around the most stable amorphous configuration

◆ Results mean that many (slightly different) configurations contribute to a single ideal glass state!



Analysis of the entropy





◆ Indeed, simple vibration cannot explain the entropy of the glass phase ($S - S_{vib} \sim 0.1$)

Summary

Vibration

◆ Low frequency part of vDOS is

$$D(\omega) = \underbrace{D_{\rm ex}(\omega)}_{\propto\, \omega^2} + \underbrace{D_{\rm loc}(\omega)}_{\propto\, \omega^4}$$

Localized mode

◆ Localized mode = Unstable core, which is stabilized by the far-field component (supported by the surrounding medium)

◆ Glass is marginally stable solid.

Glass transition

◆ Entropy bending and overlap jump take place simultaneously.
→ Ideal glass state exists in the randomly pinned fluids.

◆ Non-vibrational dynamics are observed in the glass phase, giving the additional contribution to the glass entropy.