June 29th (Fri.), 2018

Yukawa Institute for Theoretical Physics, Kyoto University, Japan

Rheology of disordered particles — suspensions, glassy and granular materials
10:15-11:05, 40mins. talk and 10mins. discussion

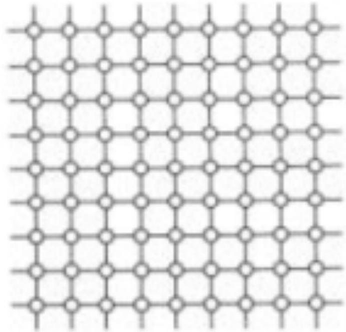
Vibrational properties and phonon transport of amorphous solids

Hideyuki Mizuno, Hayato Shiba, Atsushi Ikeda

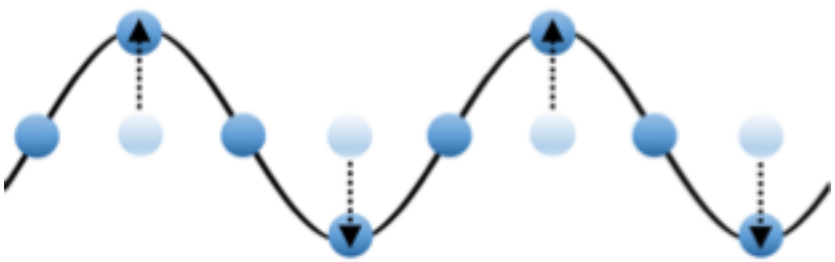
The University of Tokyo, Tohoku University

Background
Vibrational properties of amorphous solids

Crystals (lattice structure)

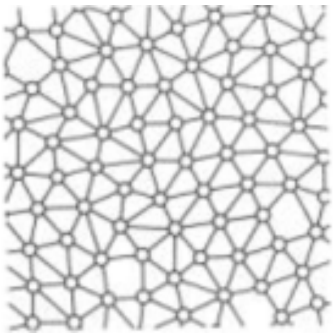


Molecules vibrate around lattice structure

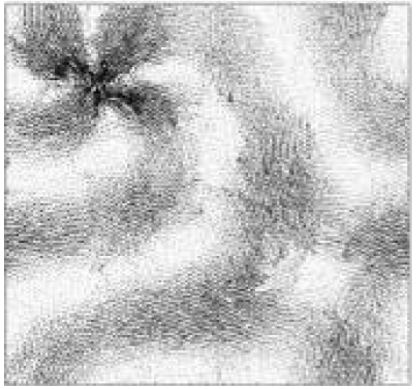


Vibrational modes are phonons

Amorphous solids (amorphous structure)



Molecules vibrate around amorphous structure

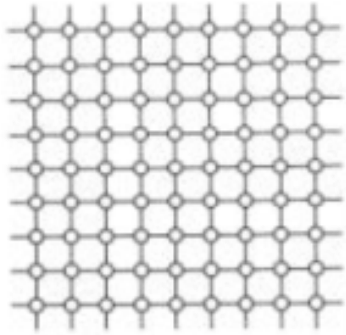


Tanguy et al., EPL 2010

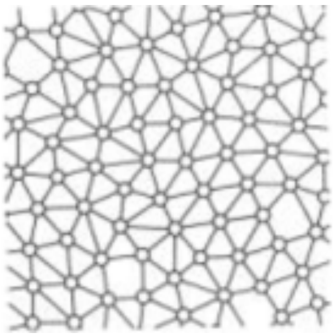
Some modes are localized
-> These modes are non-phonons

Background
Vibrational properties of amorphous solids

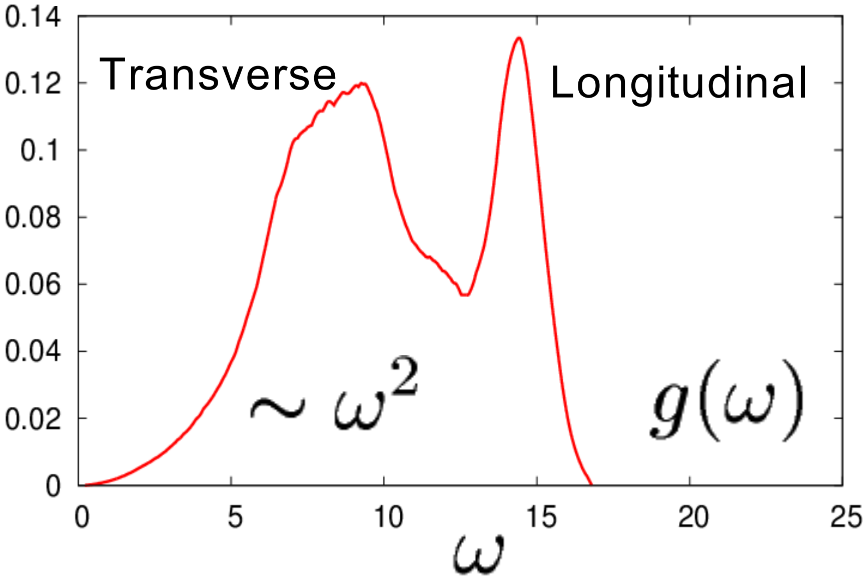
Crystals (lattice structure)

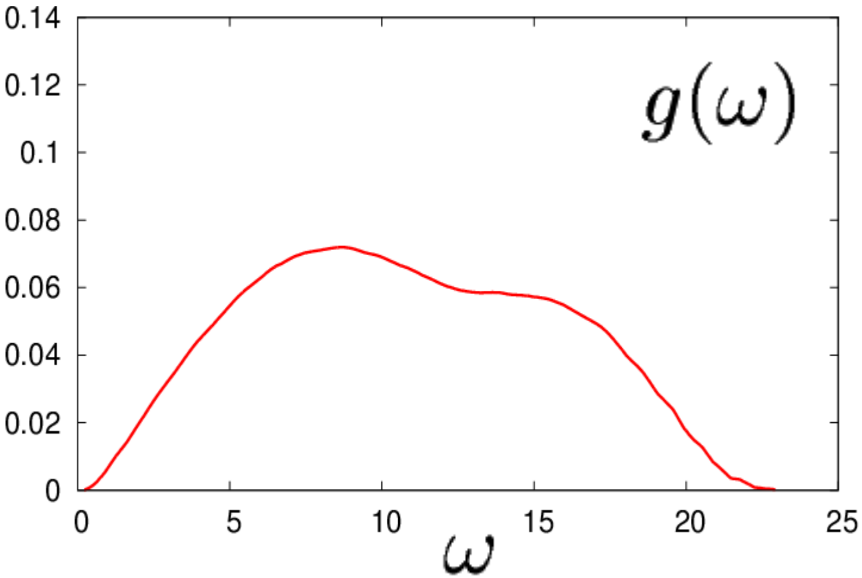


Amorphous solids (amorphous structure)



Vibrational density of states (one component Lennard-Jones system)





Background
Excess low-ω vibrational modes in amorphous solids

Excess over Debye-theory prediction (Boson peak) is observed in many glasses (amorphous solids)

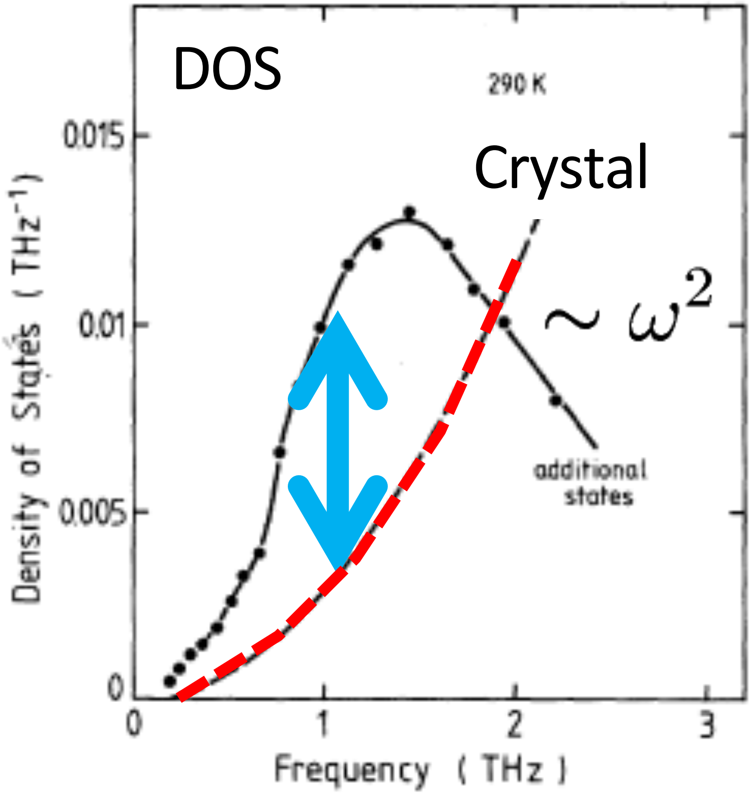
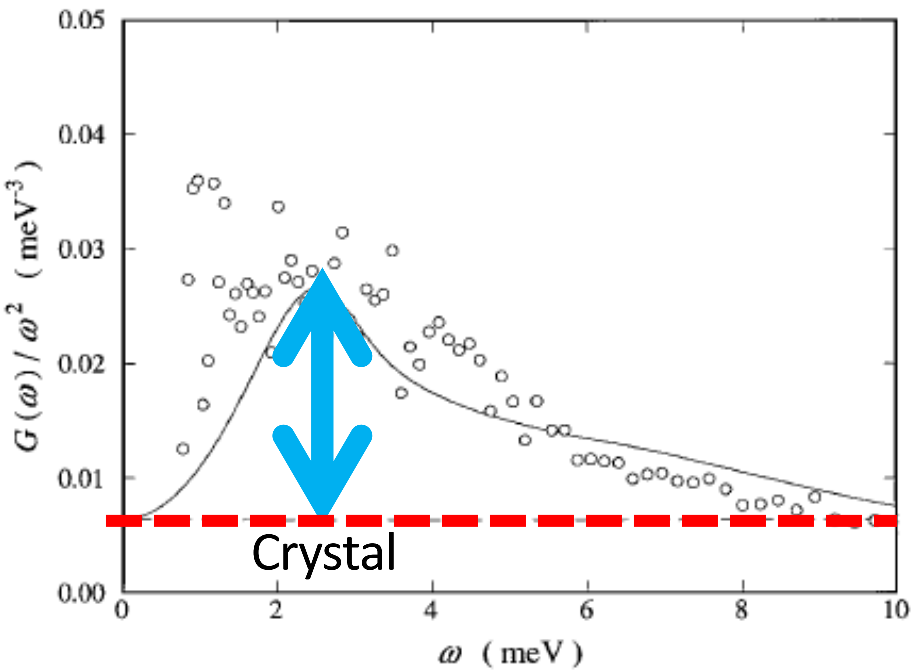


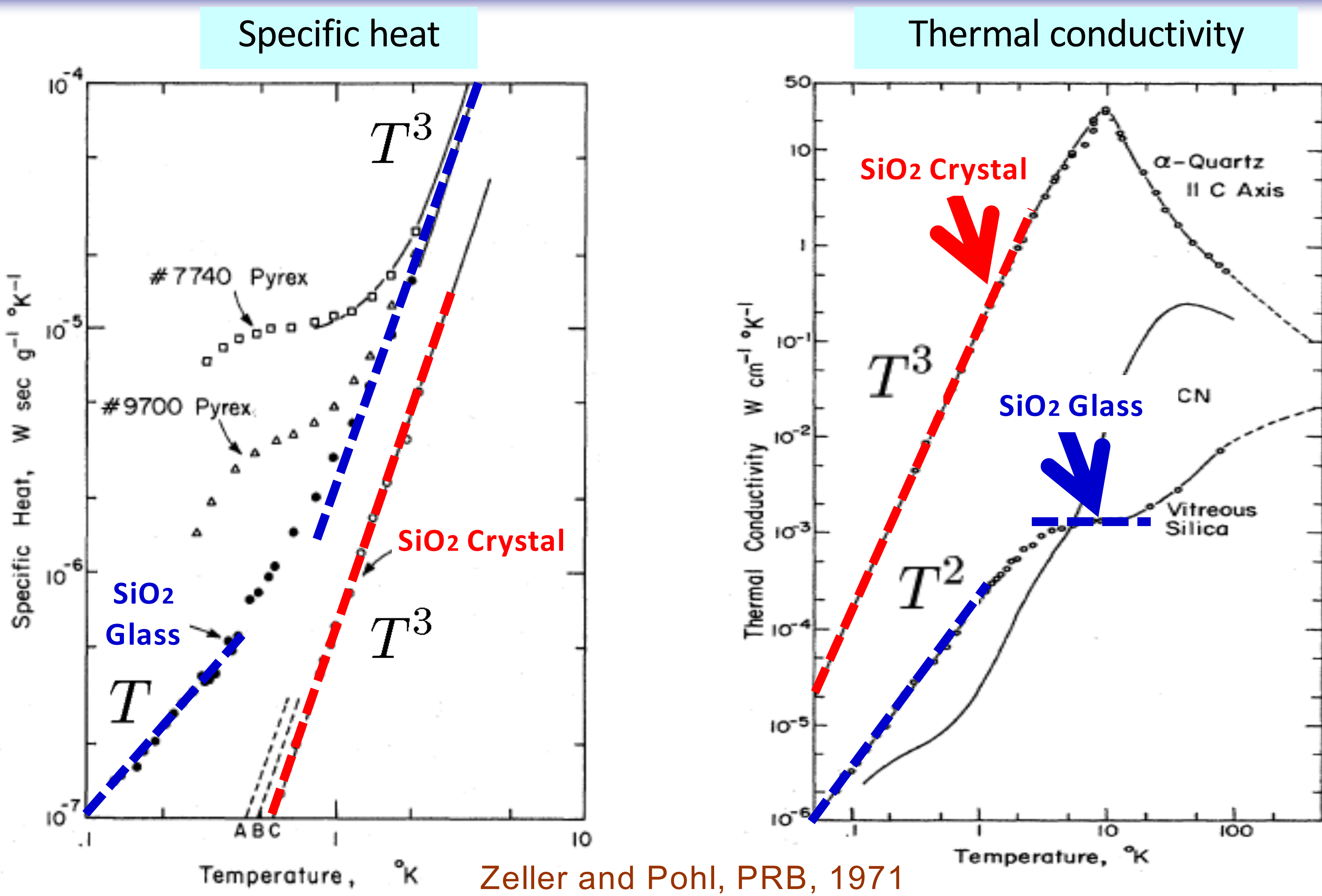
FIG. 6. Density of states of additional modes in vitreous silica compared to the Debye density of states.

Buchenau et al., PRL 1984



Yamamuro et al., JCP 1996

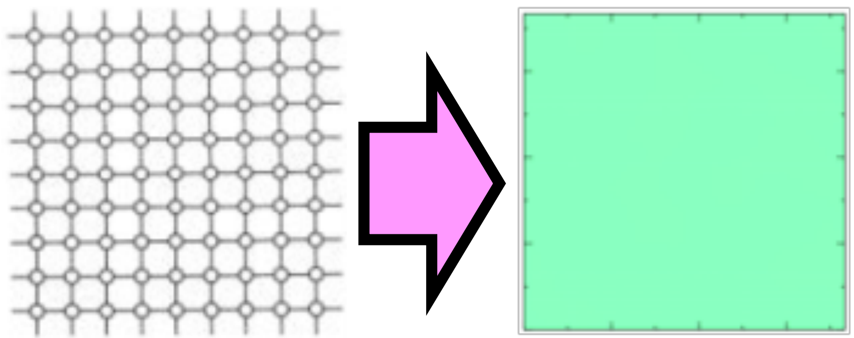
Background
Low-*T* thermal properties of amorphous solids



Zeller and Pohl, PRB, 1971

Background
Extension of Debye theory: Elastic heterogeneities

Crystals : Debye theory

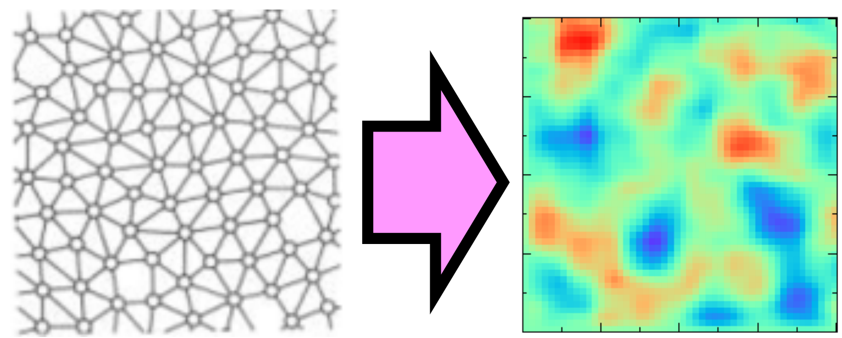


- Homogeneous elastic media
- Elastic mechanics predict phonons（or acoustic waves）as vibrational modes
- This explains heat capacity of crystals （T cubed behavior） $C \sim T^3$

$$-\omega^2 u_i(\mathbf{r},\omega) = \sum_j \partial_j \tilde{\sigma}_{ij}(\mathbf{r},\omega)$$

$$\tilde{\sigma}_{ij} = \frac{1}{\rho}\sigma_{ij} = \tilde{K}\delta_{ij}\mathrm{Tr}\{\epsilon\} + 2G\hat{\epsilon}_{ij}$$

Amorphous solids: Extended Debye theory



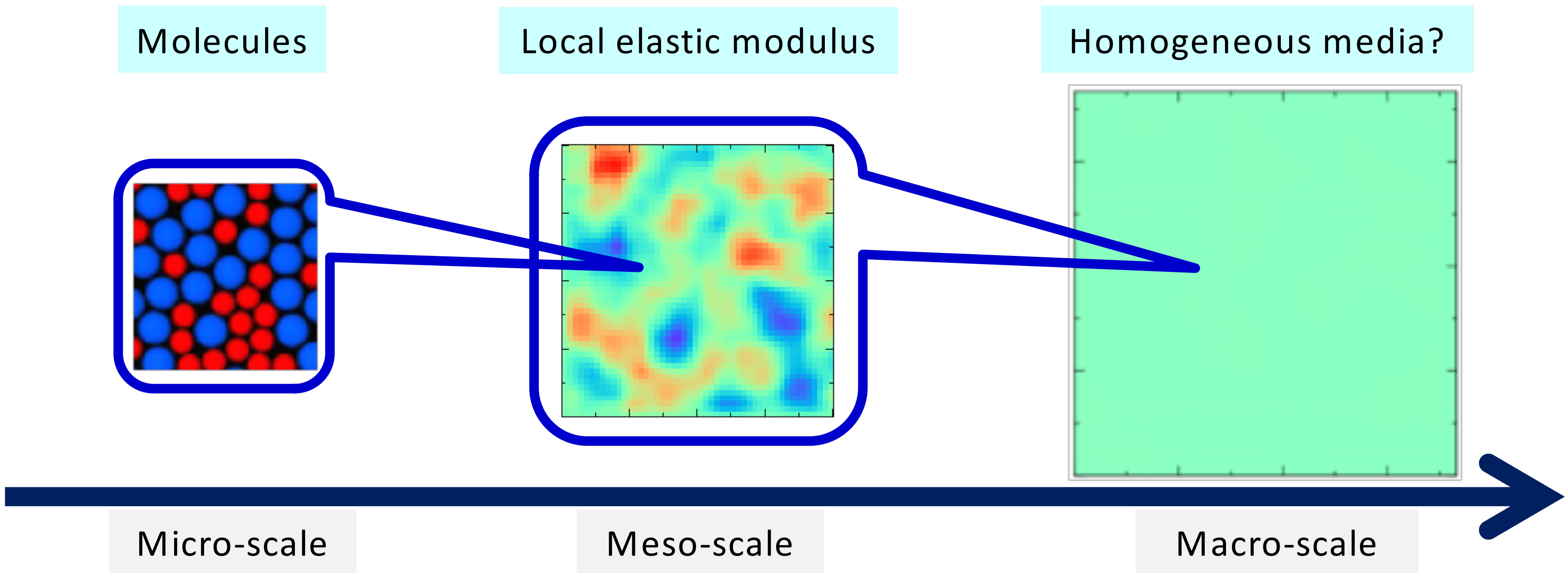
- Heterogeneous elastic media
- Vibrational modes are deformed to non-phonon modes by elastic heterogeneities
- This predicts heat capacity larger than Debye prediction ⇒ Thermal properties of amorphous solids (Boson peak)

$$\tilde{\sigma}_{ij} = \frac{1}{\rho}\sigma_{ij} = \tilde{K}\delta_{ij}\mathrm{Tr}\{\epsilon\} + 2\tilde{G}(\mathbf{r})\hat{\epsilon}_{ij}$$

Heterogeneous modulus

Schirmacher et al., EPL 2006, PRL 2007

Background
Multi-scale structure of amorphous solids



At meso-scale, local elastic modulus fluctuates in the space.

-> Elastic heterogeneities control thermal properties of amorphous solids

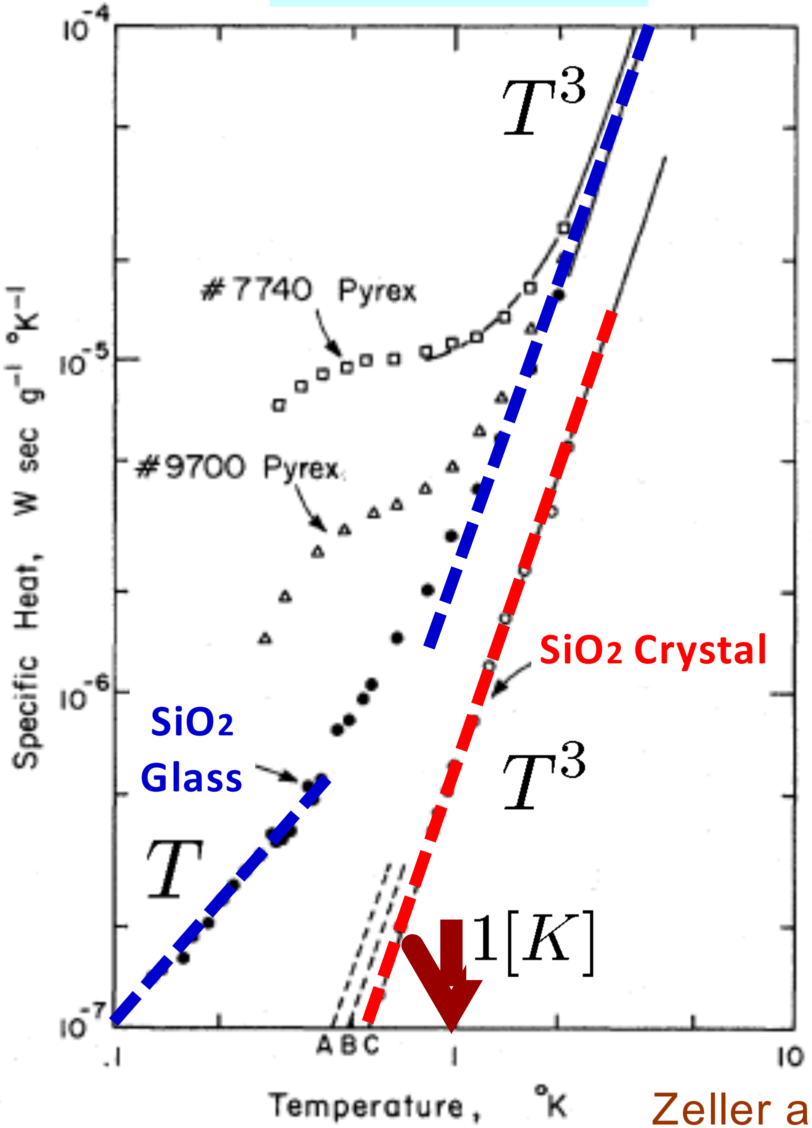
Mizuno, Mossa, Barrat, EPL 2013, PNAS 2014, PRB 2016

At macro-scale (continuum limit), amorphous solids behave as homogeneous elastic media?

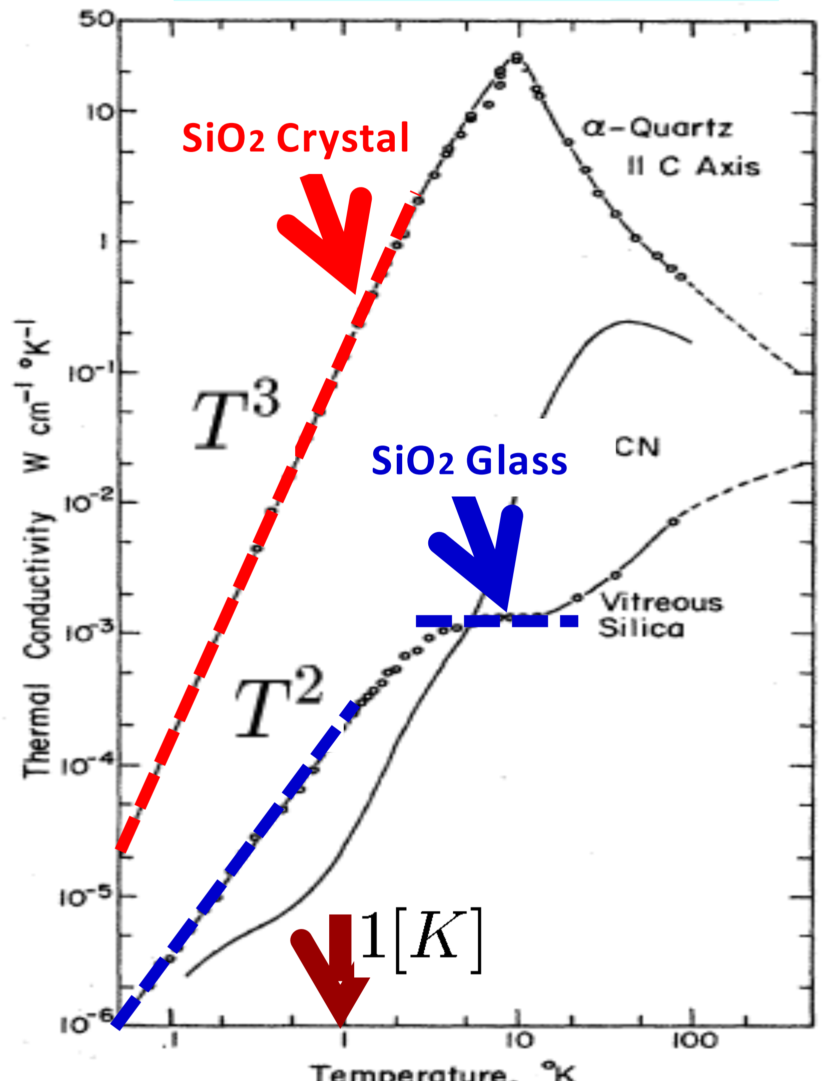
Mizuno, Shiba, Ikeda, PNAS 2017

Background
Low-T thermal properties of amorphous solids

Specific heat



Thermal conductivity



Zeller and Pohl, PRB, 1971

Contents

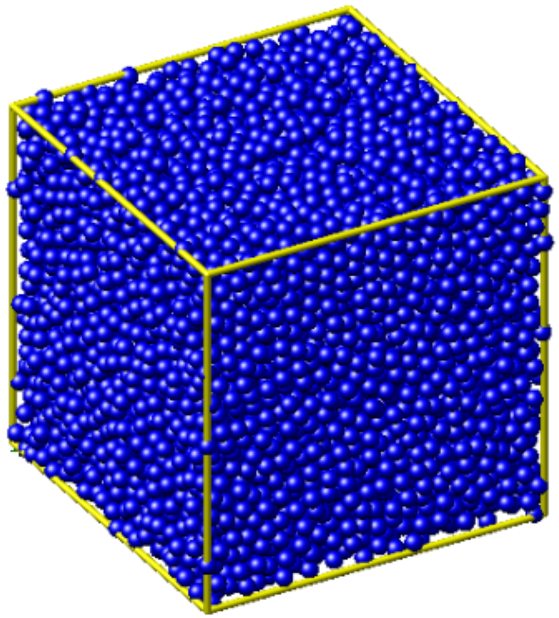
Questions

- What is nature of low-frequency vibrations of amorphous solids?
- What laws do they obey?

We perform molecular-dynamics simulations on a simple model amorphous solid

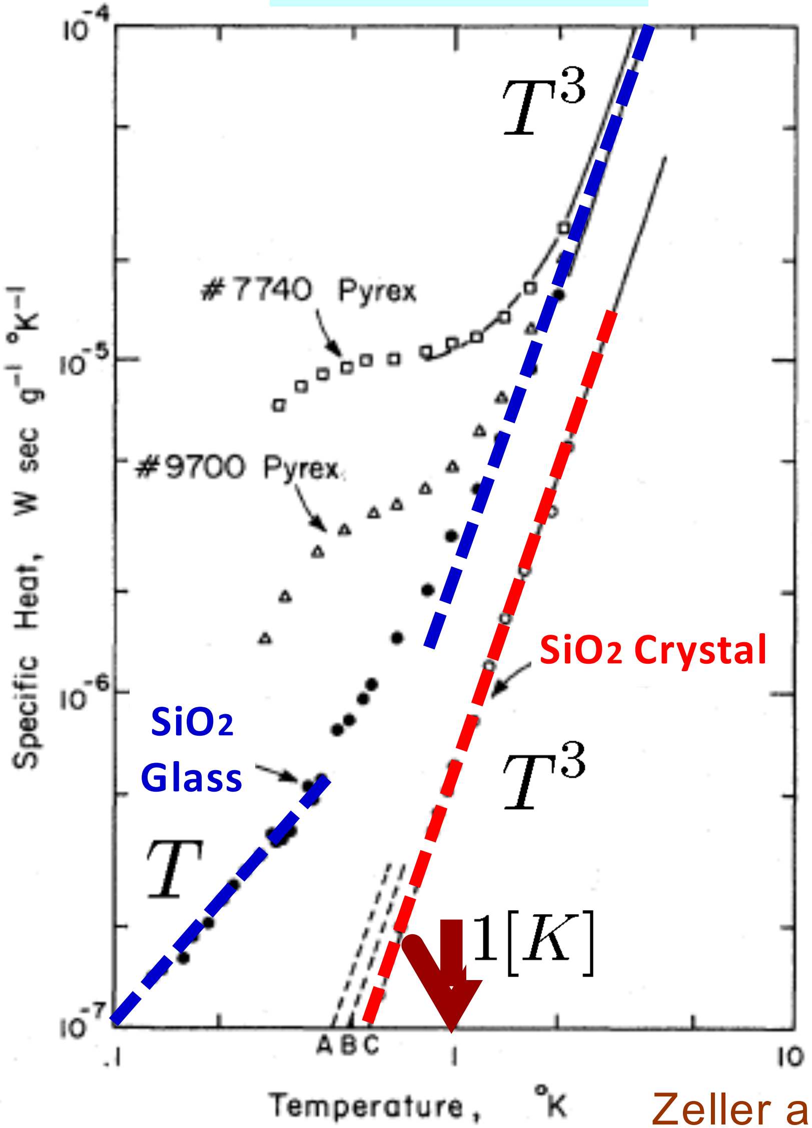
- ✓ Molecules interact through harmonic pair potential
- ✓ System size : up to 4,096,000
- ✓ Periodic boundary condition in all the directions

$$\phi(r_{ij}) = \begin{cases} \frac{\varepsilon}{2}\left(1 - \frac{r_{ij}}{\sigma}\right)^2 & (r_{ij} < \sigma) \\ 0 & (r_{ij} \geq \sigma) \end{cases}$$



Background
Low-*T* specific heat of amorphous solids

Specific heat



Zeller and Pohl, PRB, 1971

Within the harmonic approximation

$$C(T) \simeq 3k_B\rho \int \left(\frac{\hbar\omega}{k_BT}\right)^2 \exp\left(-\frac{\hbar\omega}{k_BT}\right) \underline{g(\omega)}d\omega$$

vDOS

Low-temperature thermal properties are controlled by low-frequency vibrations:

$$\omega < k_BT/\hbar$$

$$T = 10[K] \rightarrow \omega \lesssim 1[\mathrm{THz}]$$
$$T = 1[K] \rightarrow \omega \lesssim 0.1[\mathrm{THz}]$$
$$T = 0.1[K] \rightarrow \omega \lesssim 0.01[\mathrm{THz}]$$

Background
Two level system / Soft potential model

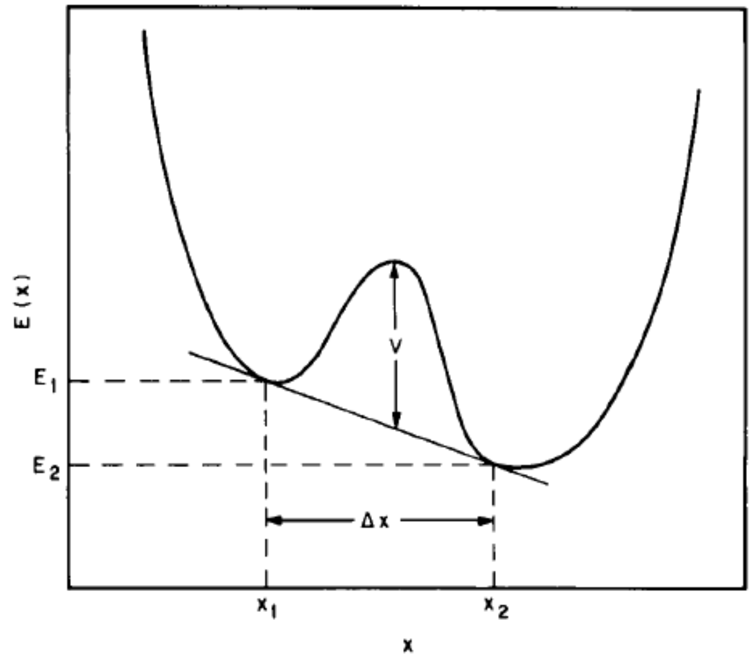
$$C(T) = \alpha T + \beta T^3$$

Debye theory
-> Phonons

Additional, non-phonon modes exist in amorphous solids
-> **Two level system**, presumably considered as **localized motions of particles**
-> $C \sim T$ is explained

Anderson, et al., Phil. Mag., 1972

Two level system



Energy E of the system as a function of a generalized coordinate x, measuring position along a line connecting two nearby local minima of E.

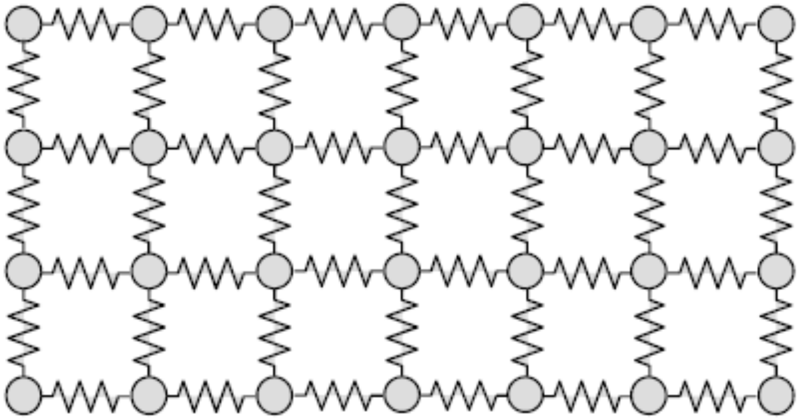
$$C = k\int_0^\infty n(\Delta E)\times\left\{\left(\frac{\Delta E}{kT}\right)^2\frac{\exp(-\Delta E/kT)}{[1+\exp(-\Delta E/kT)]^2}\right\}d(\Delta E)$$

$$\sim \frac{\pi^2}{6}k^2 T n(0)$$

Density of two level system with very low energy barriers

Vibrational modes analysis

Spring-mass model



$$\boldsymbol{u} = \boldsymbol{r} - \boldsymbol{r}_0$$

✓ Linearized equation of motion

$$\ddot{\boldsymbol{u}} = -\left(\frac{\partial^2 \Phi}{\partial \boldsymbol{r} \partial \boldsymbol{r}}\right)_0 \boldsymbol{u}$$

✓ Diagonalize Hessian matrix : (3N × 3N matrix)

$$\boldsymbol{e}^k \left(\frac{\partial^2 \Phi}{\partial \boldsymbol{r} \partial \boldsymbol{r}}\right)_0 \boldsymbol{e}^k = {\omega^k}^2$$

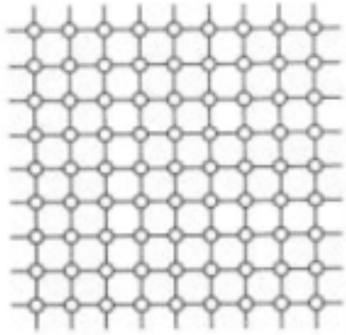
✓ Vibrational modes (normal modes, eigen modes)

- Eigen frequencies: ω^k
- Eigen vectors: $\boldsymbol{e}^k = \{\boldsymbol{e}_1^k, \boldsymbol{e}_2^k, ..., \boldsymbol{e}_N^k\}$

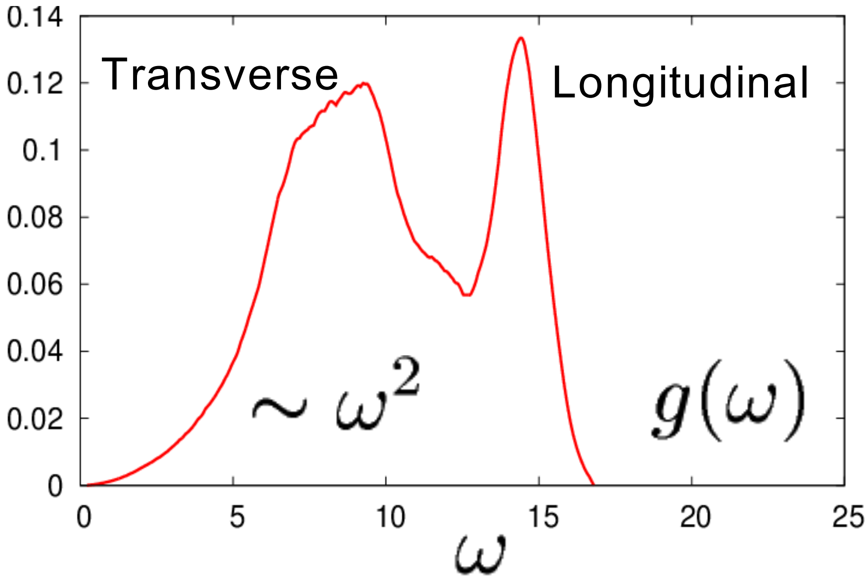
$$k = 1, 2, ..., 3N$$

Vibrational modes in Lennard-Jones **crystals**

Crystals (lattice structure)

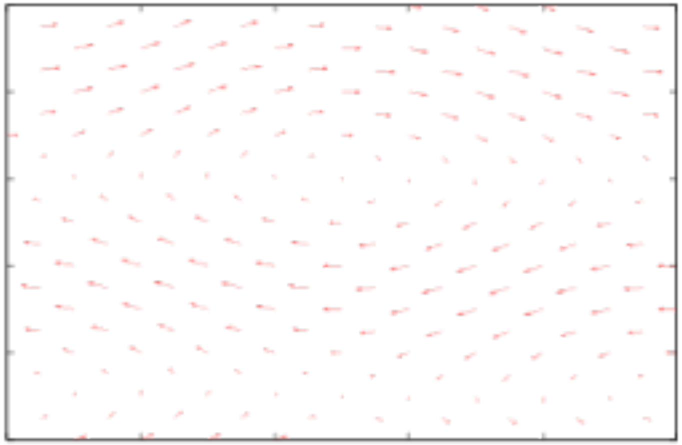


Vibrational density of states

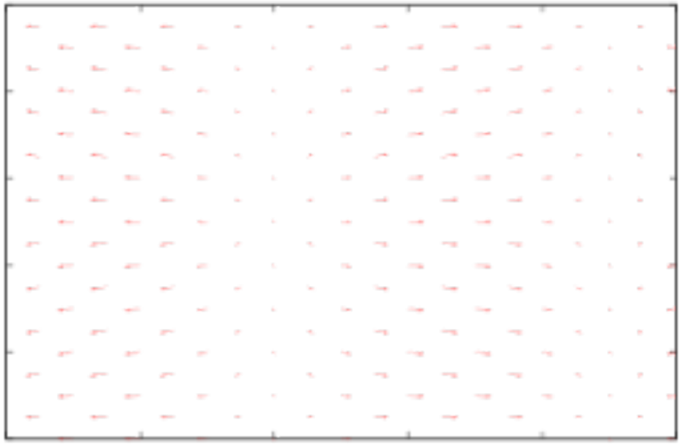


Eigen vectors: $\boldsymbol{e}^k = \{\boldsymbol{e}_1^k, \boldsymbol{e}_2^k, \ldots, \boldsymbol{e}_N^k\}$

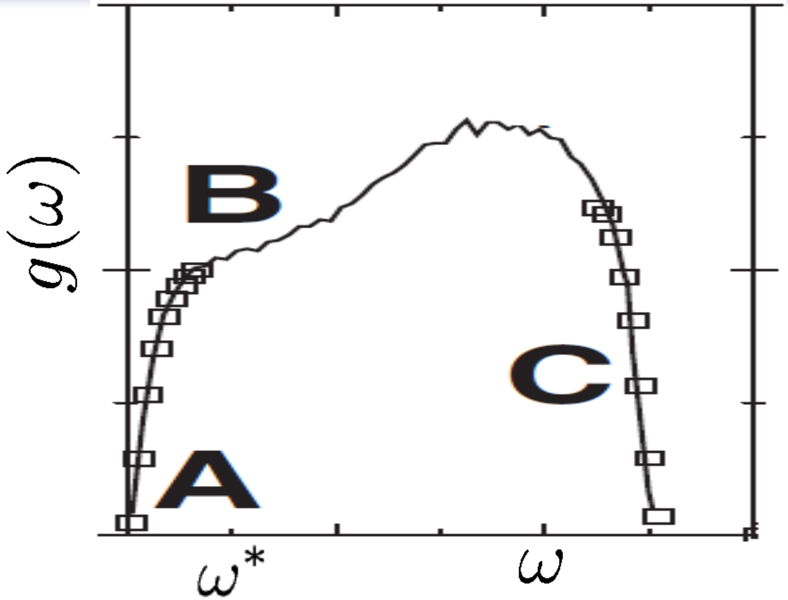
Transverse phonon



Longitudinal phonon

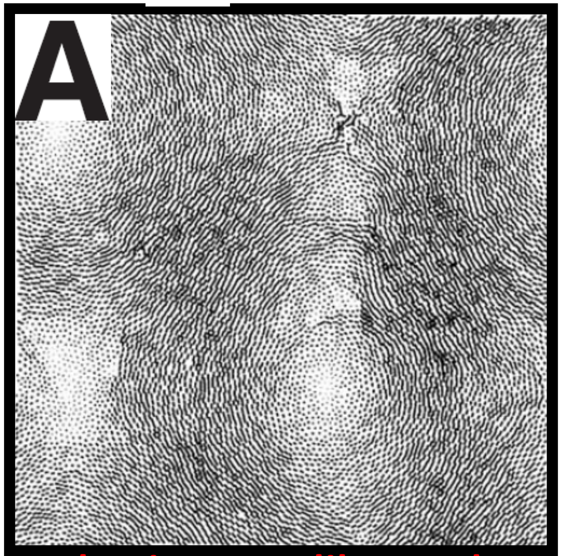


Vibrational modes in **simple amorphous solid**

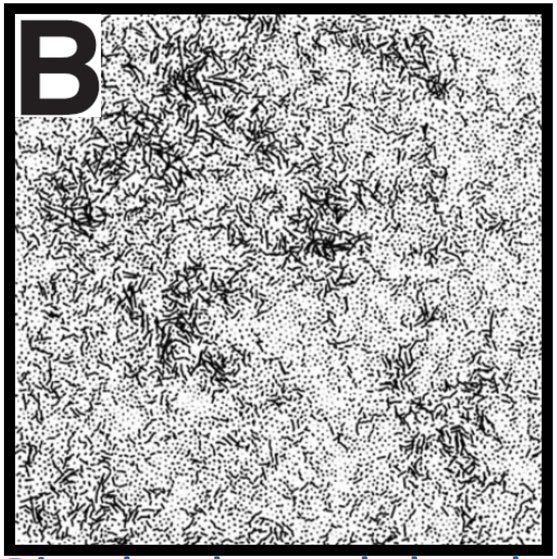


Silbert, Liu, Nagel, PRE 2009

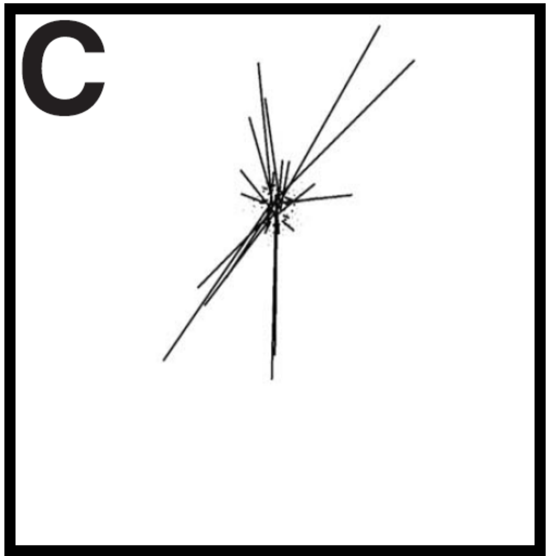
- **A, Debye-like regime :**
  Elastic-wave-like modes
- **B, Plateau regime :**
  Disordered extended modes
- **C, High frequency regime :**
  Highly localized modes



Elastic-wave-like mode

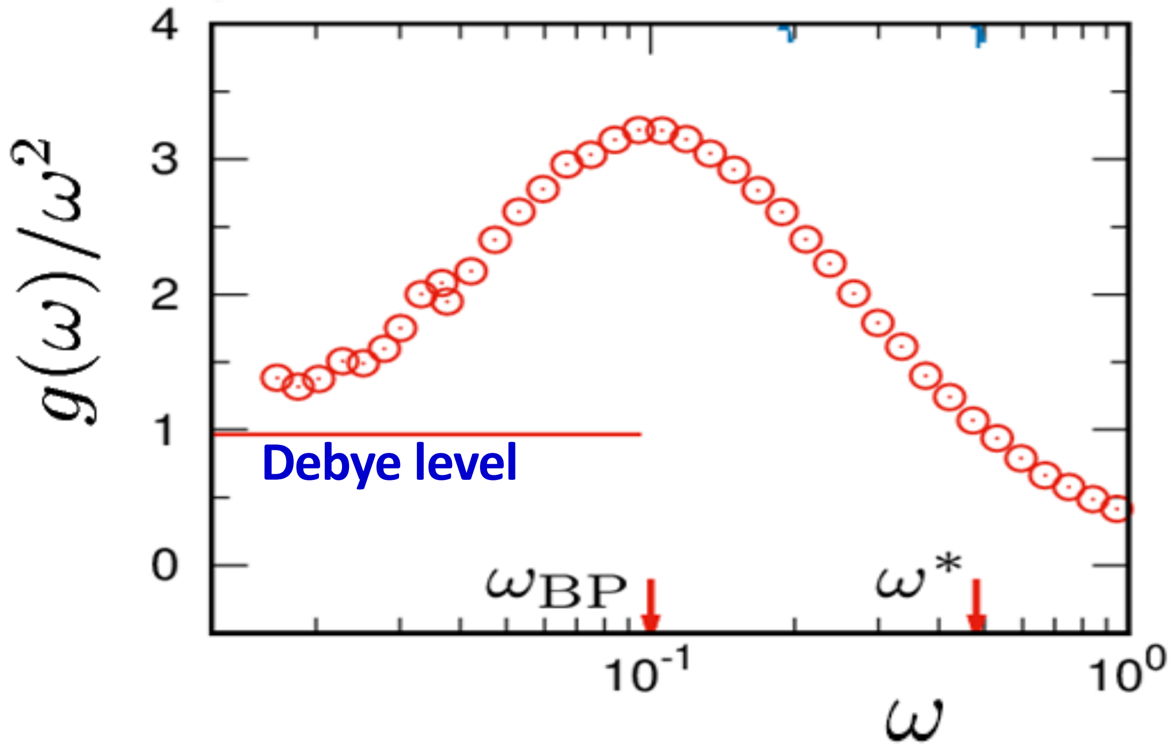


Disordered extended mode



Highly localized mode

Vibrational density of states



- ✓ We observe the **boson peak** around ω = 0.1.
- ✓ Reduced vDOS goes towards the Debye level, but does not converge in our frequency regime.

Characterize each vibrational mode: Phonon order parameter

Phonons in isotropic medium under periodic boundary:

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

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

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

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

Phonon order parameter:

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

$(N_m = 100)$

Characterize each vibrational mode: Participation ratio

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:

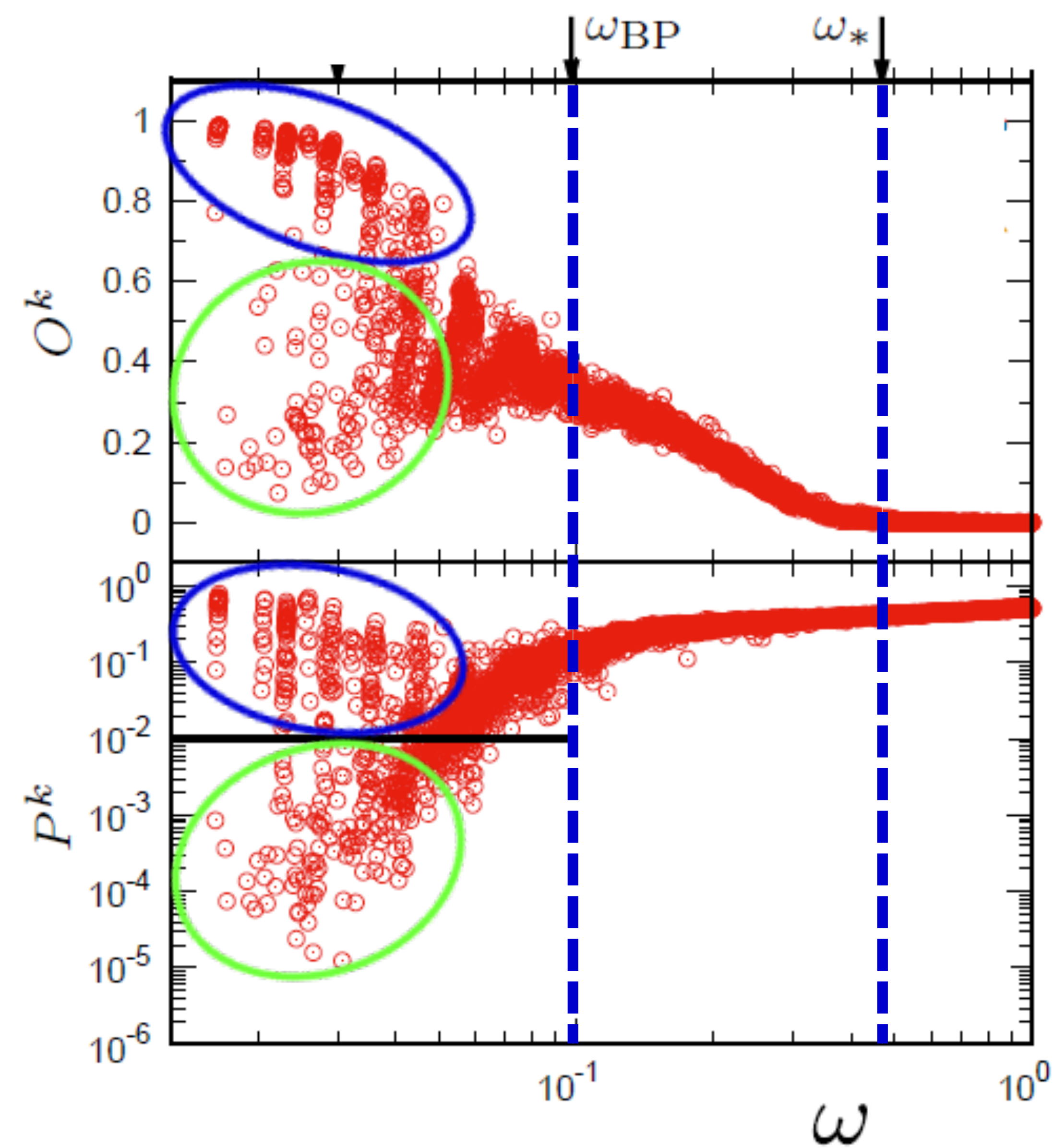
$$\boldsymbol{e}_1^k = 1, \quad \boldsymbol{e}_j^k = 0 \ (j = 2, 3, ..., N) \ \Rightarrow \ P^k = \frac{1}{N}$$

2. All the particles vibrate equivalently:

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

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

Vibrational modes



At ω > ω* :

Non-phonon, extended vibrational nature

-> Disordered extended mode

At ω ~ ωBP < ω* :

Hybrid character of phonon and disordered mode

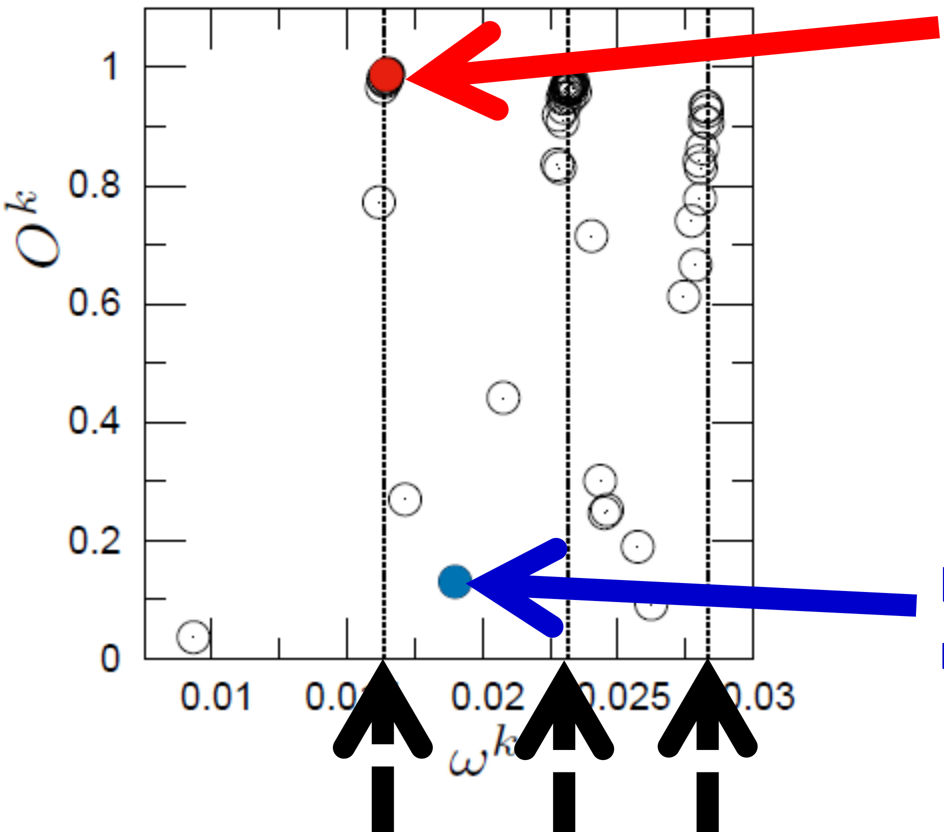
At ω < ωBP :

Mixture of phonon mode and soft localized mode

-> Consistent with the idea of two-level system

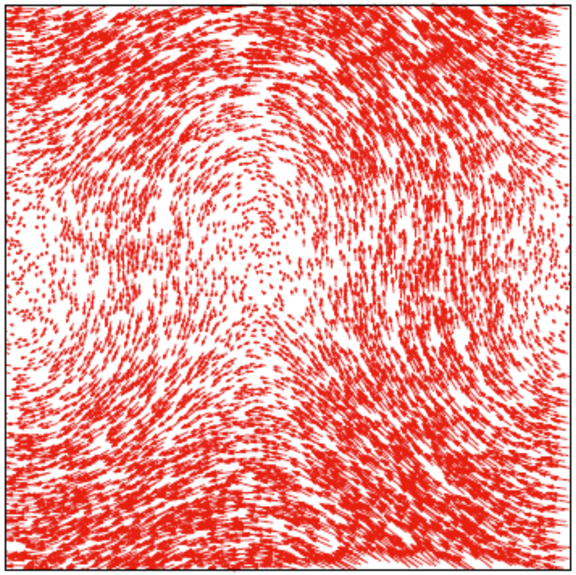
Close up to the low-frequency regime

N = 2,048,000, L = 114

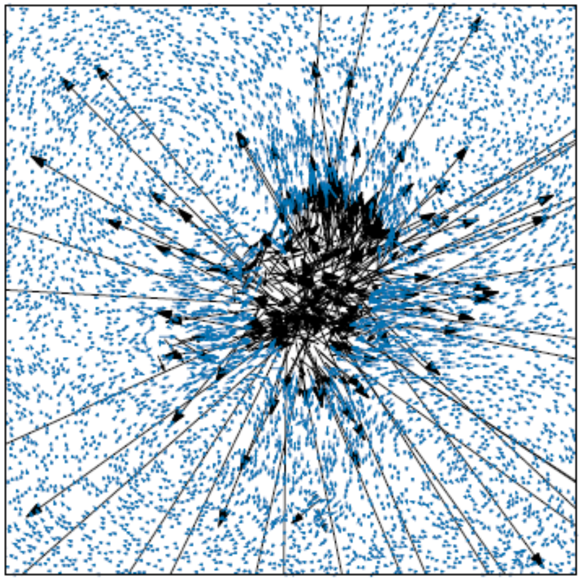


Phonon mode

$\lambda = L$



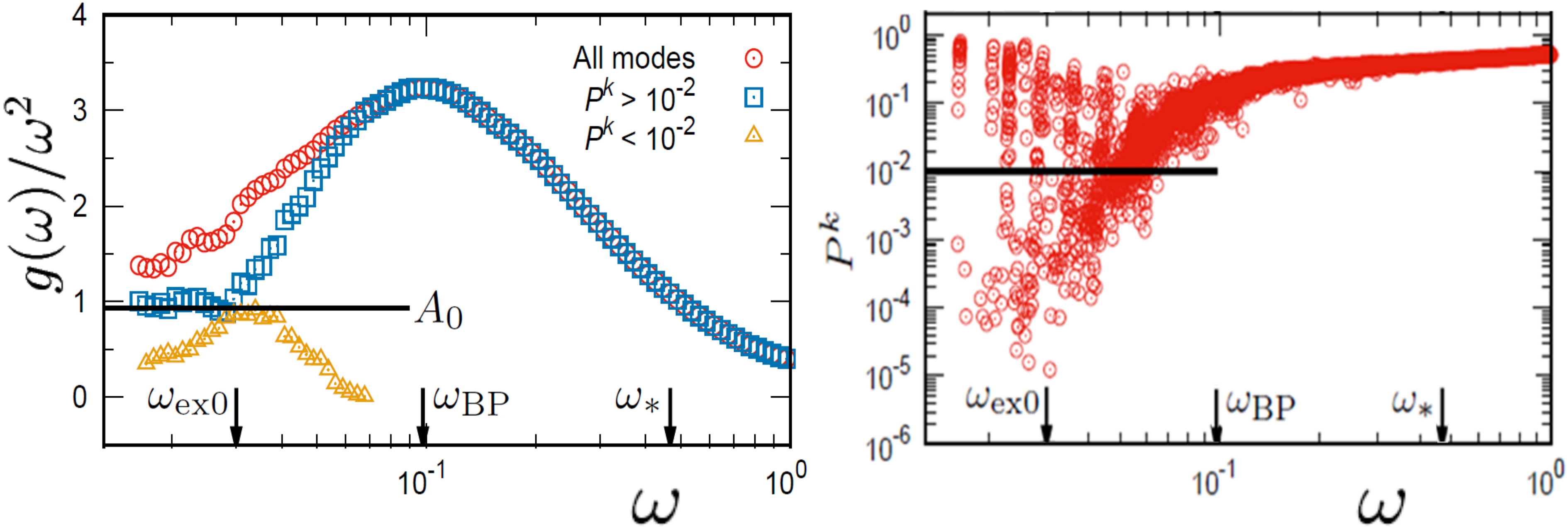
Localized mode



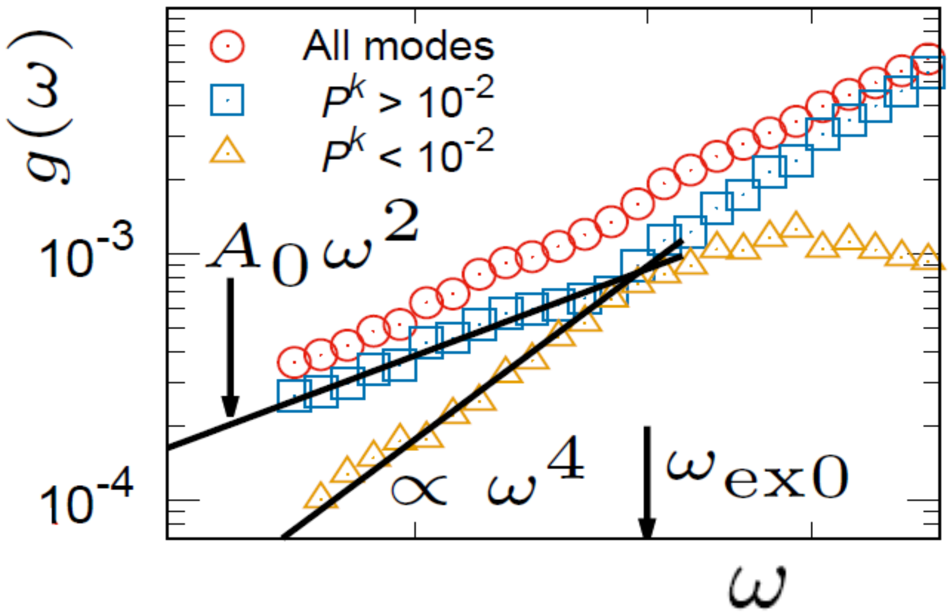
$$\omega_{\boldsymbol{k},\sigma} = c_\sigma \frac{2\pi}{L} \sqrt{i^2 + j^2 + k^2}$$

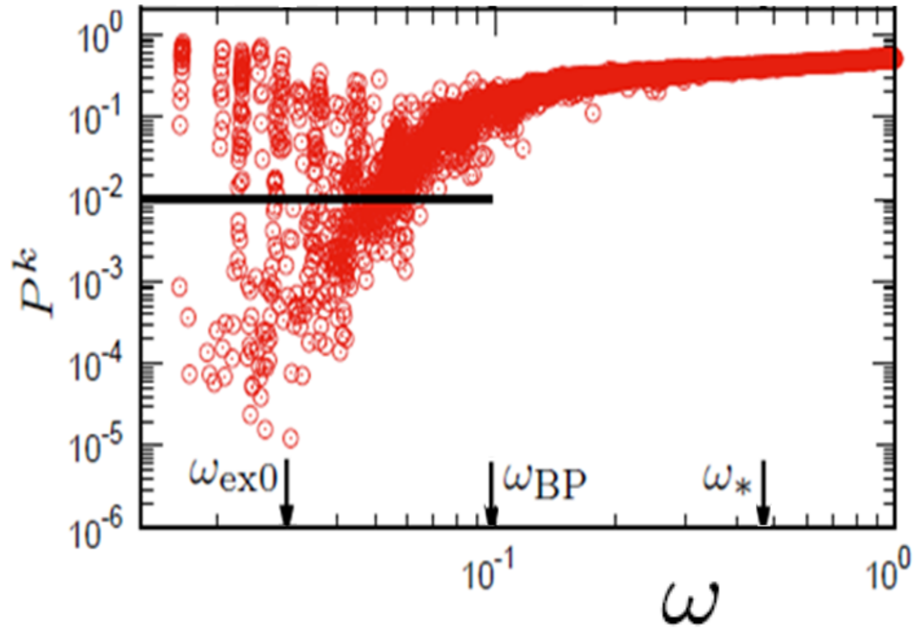
✓ Non-phonon, localized modes sit between different phonon energy levels

Vibrational density of states



Vibrational density of states





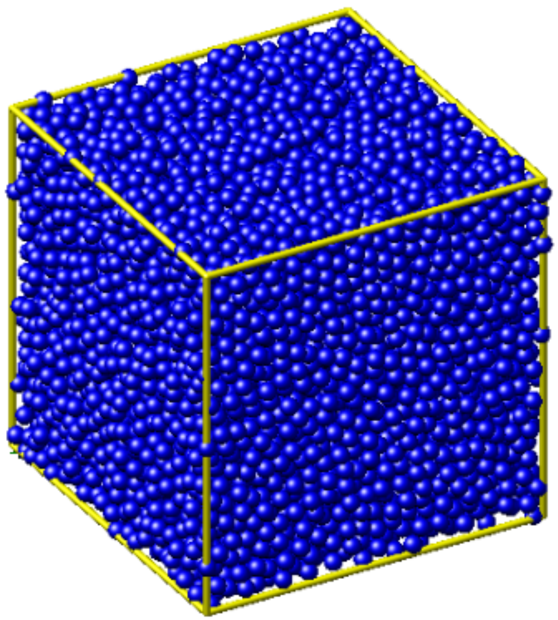
$$g(\omega) = \underbrace{g_{ex}(\omega)}_{A_0\omega^2} + \underbrace{g_{loc}(\omega)}_{\propto \omega^4} \rightarrow A_0\omega^2 \quad (\omega \rightarrow 0)$$

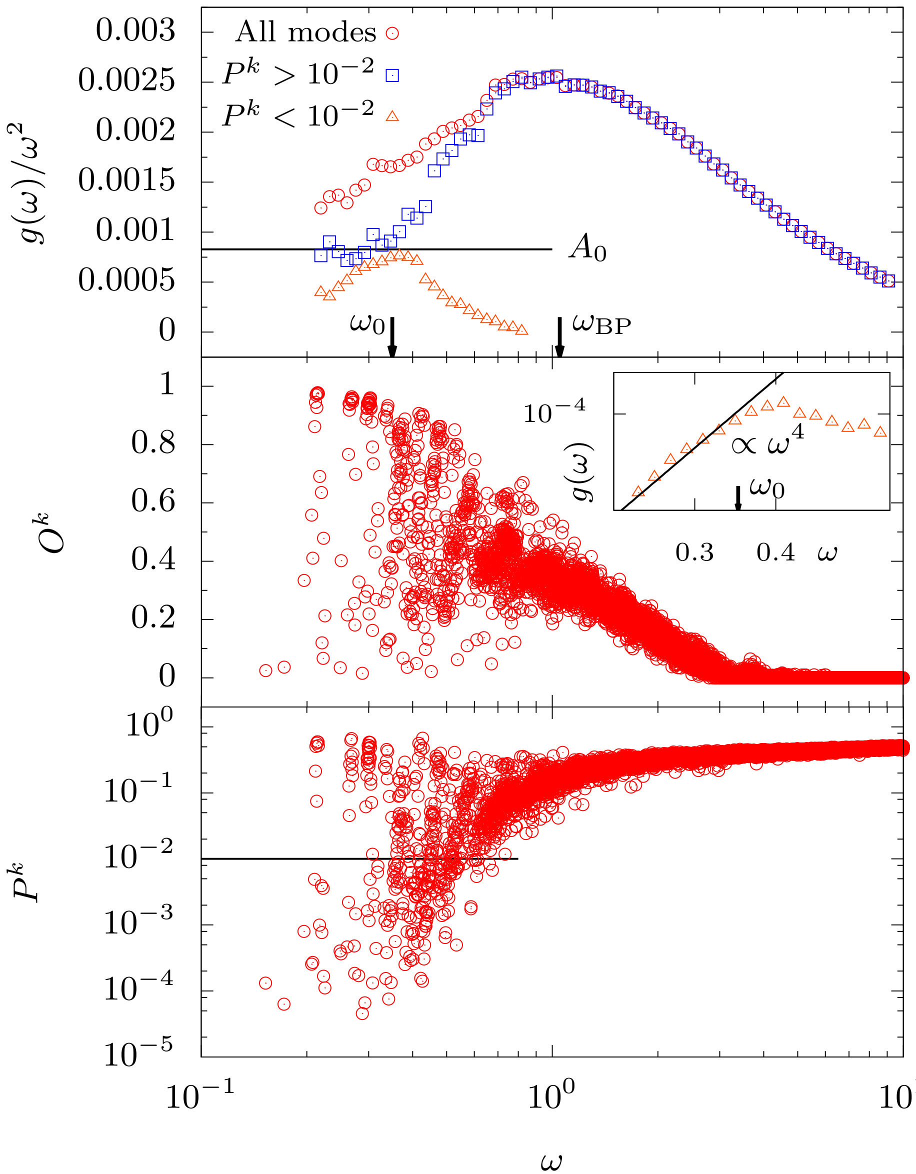
Debye law

Non-Debye law of localized modes

Vibrational modes in **Lennard-Jones glass**

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





Mixture of phonons and soft localized modes is observed in LJ glass

Shimada, Mizuno, Ikeda, PRE 2018

Conclusion

Questions

- What is nature of low-frequency vibrations of amorphous solids?
- What laws do they obey?

✓ Mixture of phonons and soft localized modes

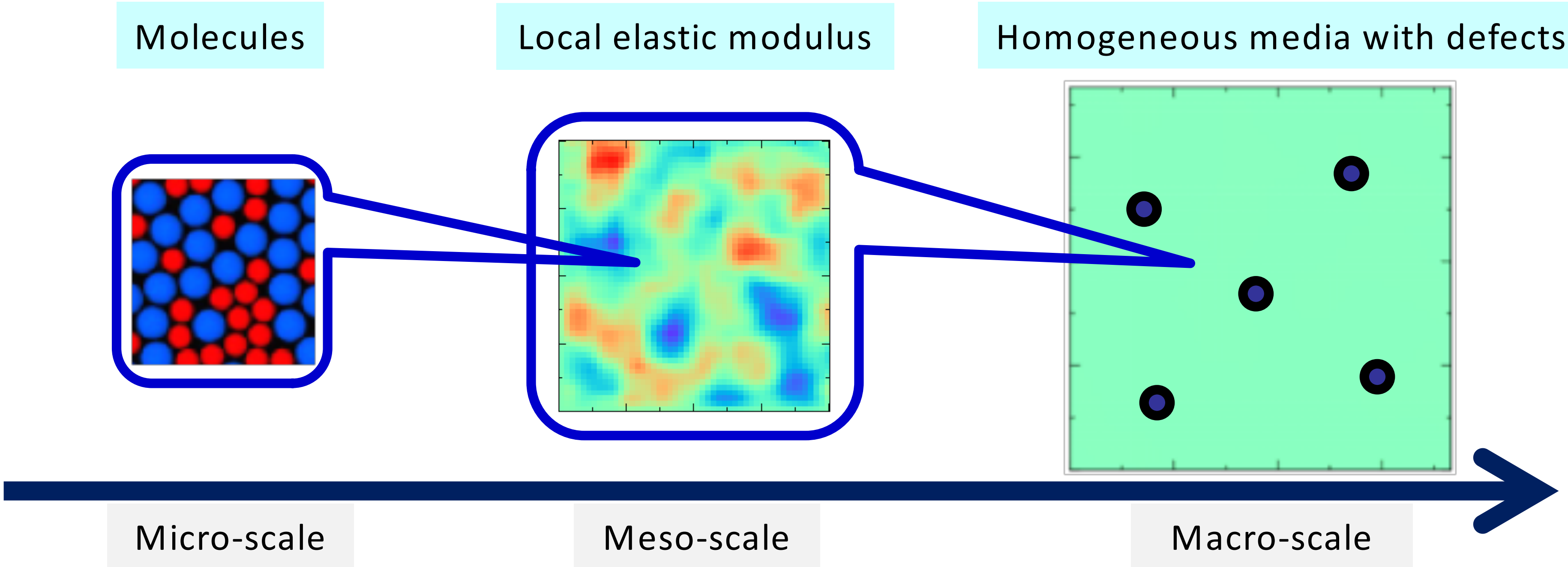
✓ Phonons follow Debye law, while localized modes follow non-Debye scaling law (ω4 law)

✓ This seems consistent with TLS/SPM picture

✓ In the continuum limit, glasses do NOT behave as homogeneous elastic media, but rather they behave as **elastic media with ``defects"**

Mizuno, Shiba, Ikeda, PNAS (2017)

Conclusion

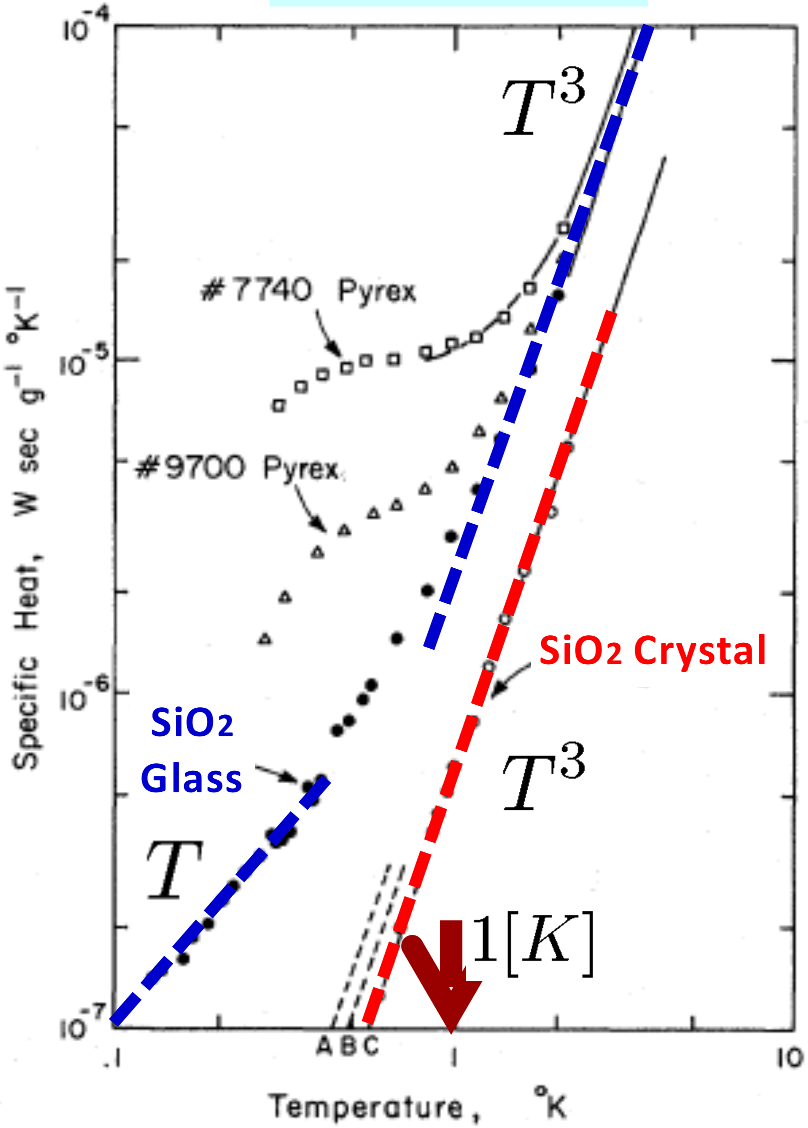


At macro-scale (continuum limit), amorphous solids are essentially different from normal solids (elastic media).

✓ プレスリリース (東大・ 東北大)、ガラスと通常の固体の本質的な違いを発見

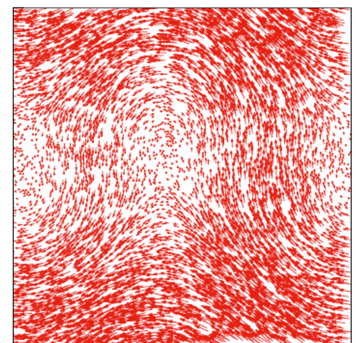
Low-T specific heat
Can we explain linear-T term by localized modes?

Specific heat



Continuum limit

Phonon modes



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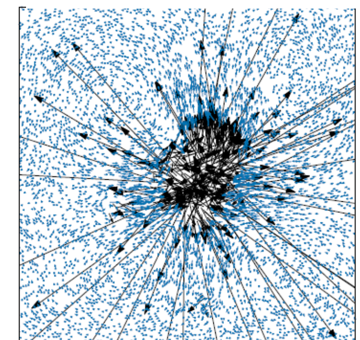
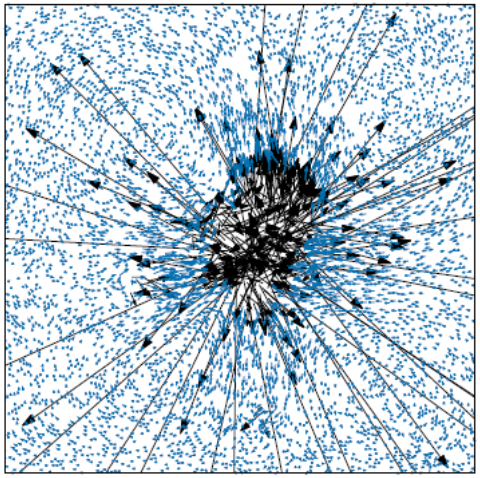
Localized modes



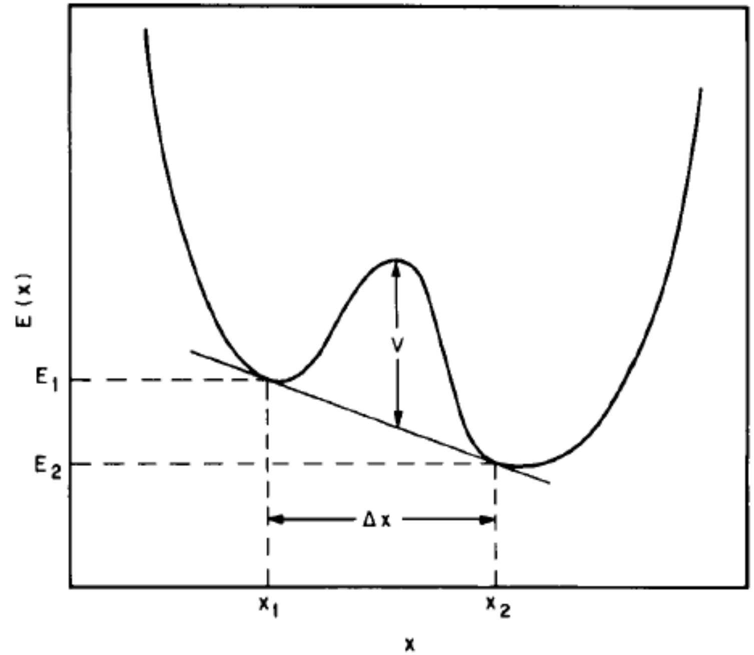
$$C(T) = \underline{\alpha T} + \underline{\beta T^3}$$

Low-T specific heat
Can we explain linear-T term by localized modes?

Localized modes



Two level system



E of the system as a function of a generalized coordinate x, easuring position along a line connecting two nearby local minima f E.

- Do two-level tunneling transitions happen in the localized modes?
- What is role of non-Debye law?

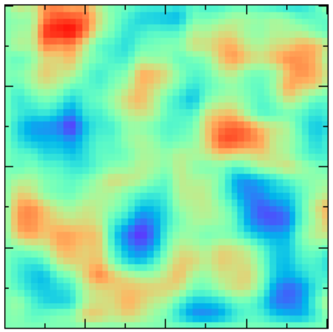
$$C = k \int_0^\infty n(\Delta E) \times \left\{ \left(\frac{\Delta E}{kT} \right)^2 \frac{\exp(-\Delta E/kT)}{[1+\exp(-\Delta E/kT)]^2} \right\} d(\Delta E)$$

$$\sim \frac{\pi^2}{6} \underline{k^2 T n}(0)$$

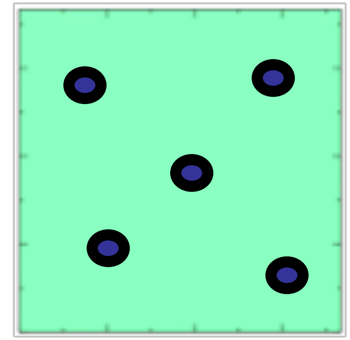
Anderson, et al., Phil. Mag., 1972

Localized mode is key to understand amorphous solids

Local elastic modulus



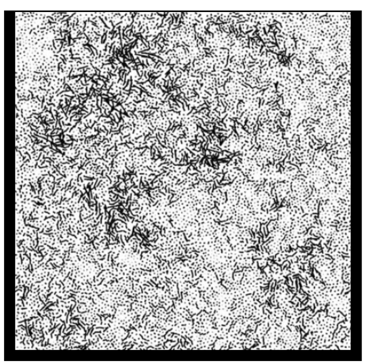
Homogeneous media with defects



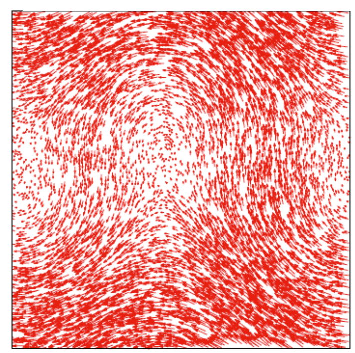
Meso-scale

Macro-scale

Disordered extended modes

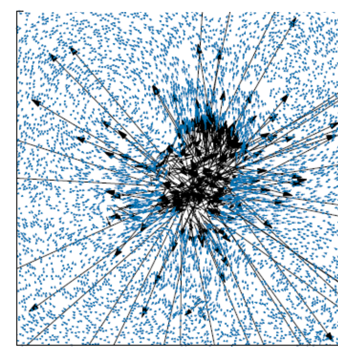


Phonon modes



+

Localized modes



ω_{BP} ω_{ex0} **Continuum limit**