Thermal fluctuations, mechanical response, and hyperuniformity in jammed solids

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Jamming problem

- Jamming problem can be formulated most clearly at T=0.
- Randomly packed athermal spheres show a number of non-trivial critical behaviors:
  - Freq. of disordered mode

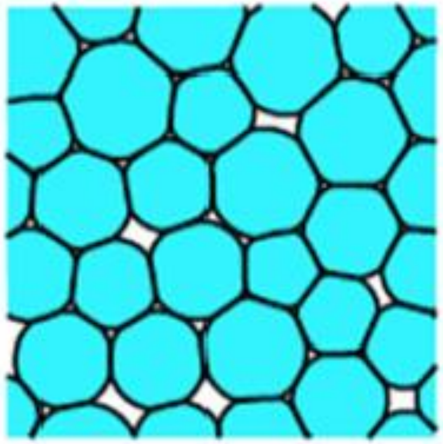
    $$\omega^* \propto (\Delta\varphi)^{0.5}$$

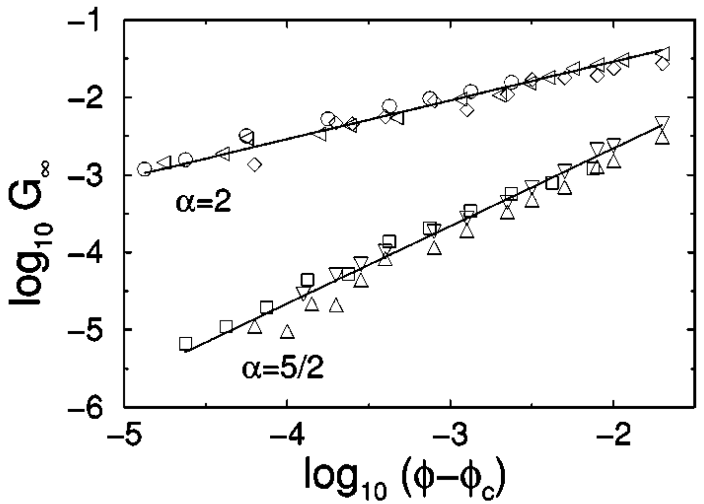
  - Shear modulus

    $$G \propto (\Delta\varphi)^{0.5}$$

  - Yield stress

    $$\sigma_Y \propto (\Delta\varphi)$$

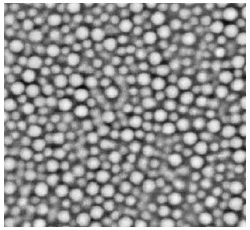




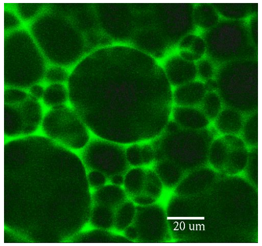
[O'Hern, Silbert, Liu, Nagel…]

Jammed spheres at finite T

◆ Jamming criticality is also expected to play a role in spheres subjected to thermal fluctuation. Examples are:



PMMA colloids



Oil-in-water emulsion

◆ Modeling

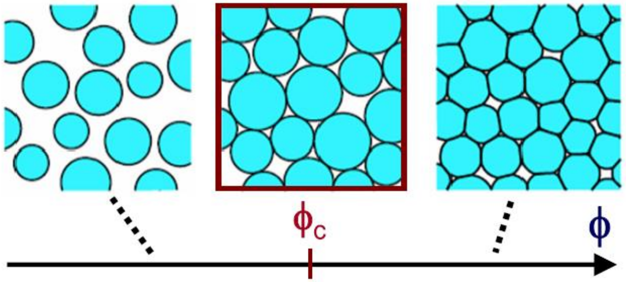
- ◆ Randomly packed harmonic spheres

$$v(r_{ij}) = \frac{\epsilon}{2}(1 - r_{ij}/\sigma)^2 \Theta(\sigma - r_{ij})$$

- ◆ MD simulation at finite temperature

$$k_B T/\epsilon = 10^{-5},\ 10^{-6},\ 10^{-7},\ 10^{-8}$$

- ◆ Analysis of the caging dynamics



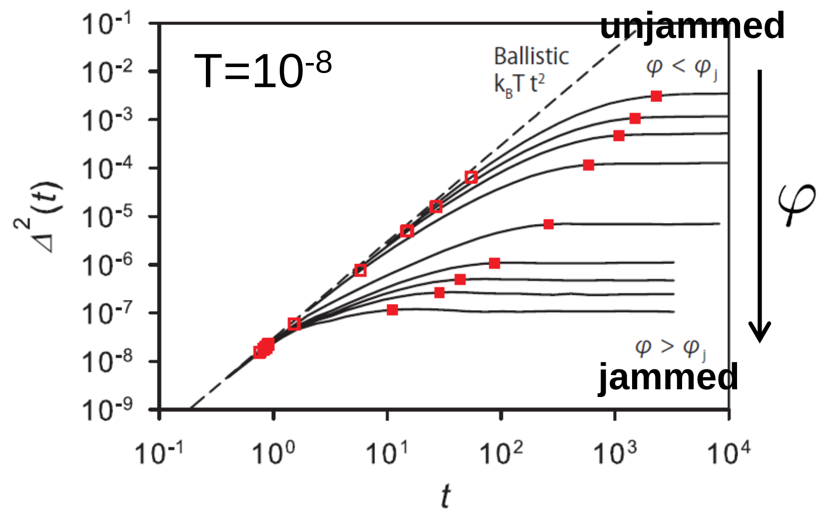
[Ikeda, Berthier, Biroli 2013]

Mean square displacement

- Mean square displacement shows caging dynamics at finite temperature

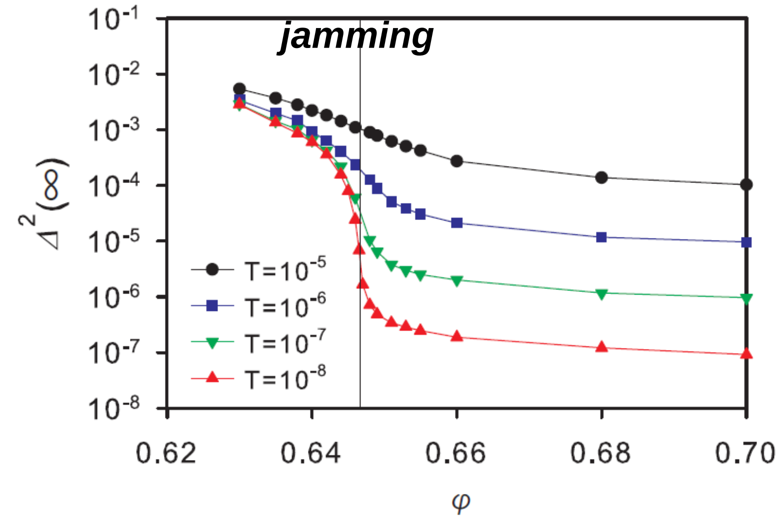
$$\Delta^2(t) = \frac{1}{N'}\sum_{i=1}^{N'}\langle|\Delta r_i(t)|^2\rangle$$

  - Short time – Ballistic
  - Long time – Plateau



- Compression decreases the plateau height.

- It is a bit difficult to discuss the signature of the jamming criticality from this plot.



Timescale (short)

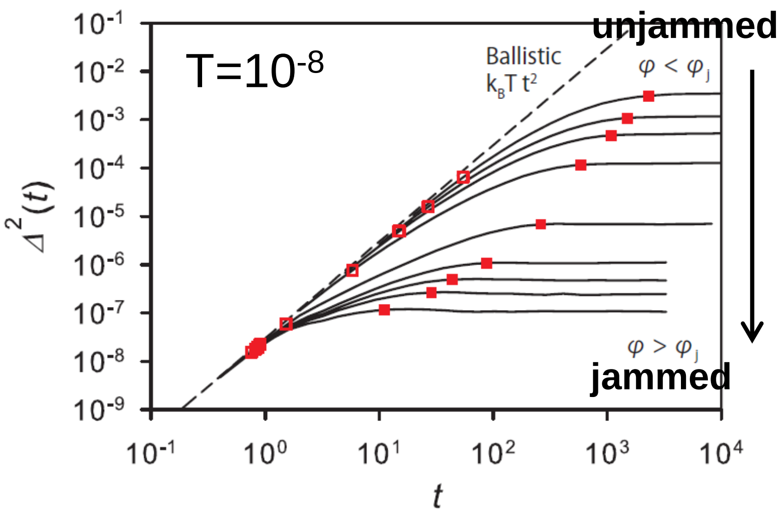
- Time scale at which the MSD deviates from the ballistic behavior.
  - [Unjammed] Two body collision (can be described by Enskog theory)

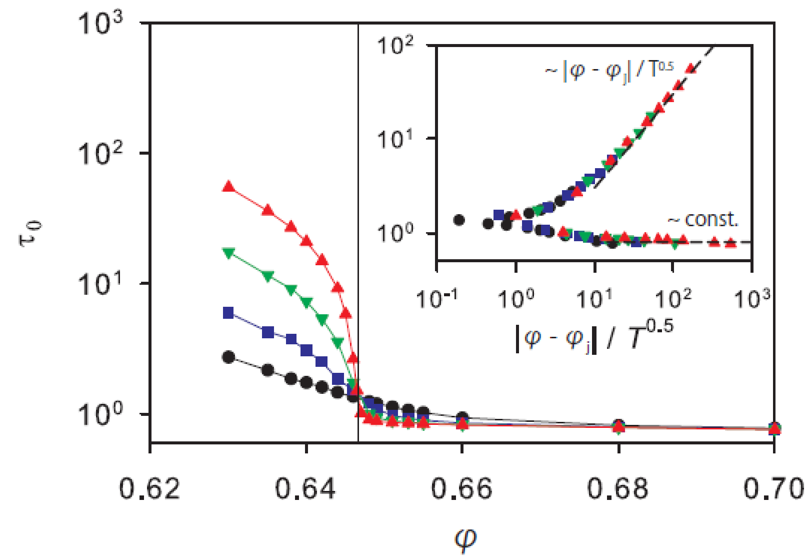
$$\frac{1}{\tau_0} \approx \frac{8\rho g(\sigma^+)}{3}\sqrt{\frac{\pi T}{m}} \sim \frac{\sqrt{T}}{|\varphi - \varphi_J|}$$

  - [Jammed] Two body vibration (can be described by Einstein Frequency)

$$\frac{1}{\tau_0} \approx \sqrt{\frac{\rho}{3m}\int dr g(r)\nabla^2 v(r)} \sim \text{const}$$

  - **Microscopic time scale strongly depends on density**



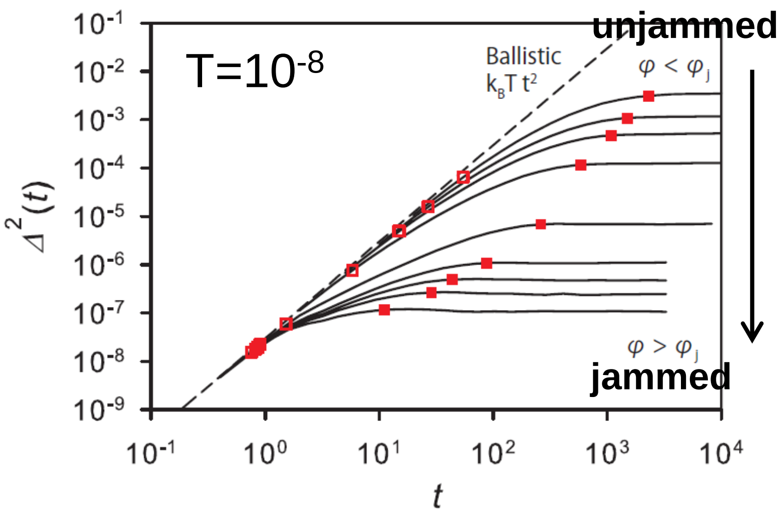


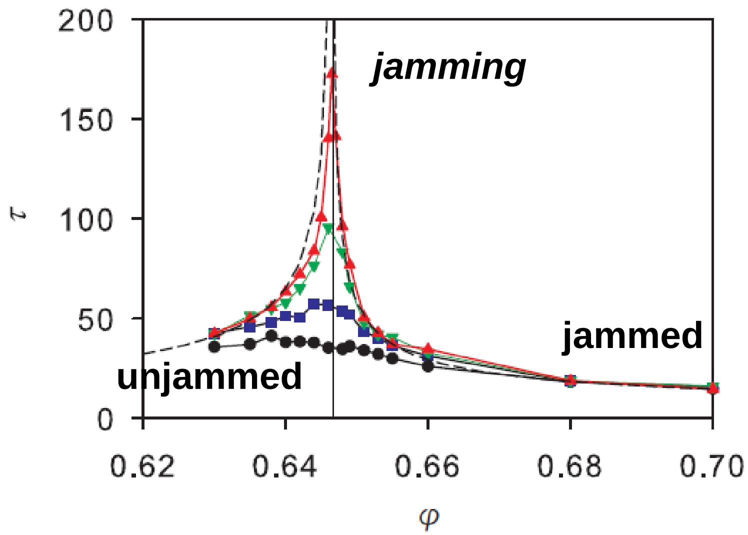
Timescale (long)

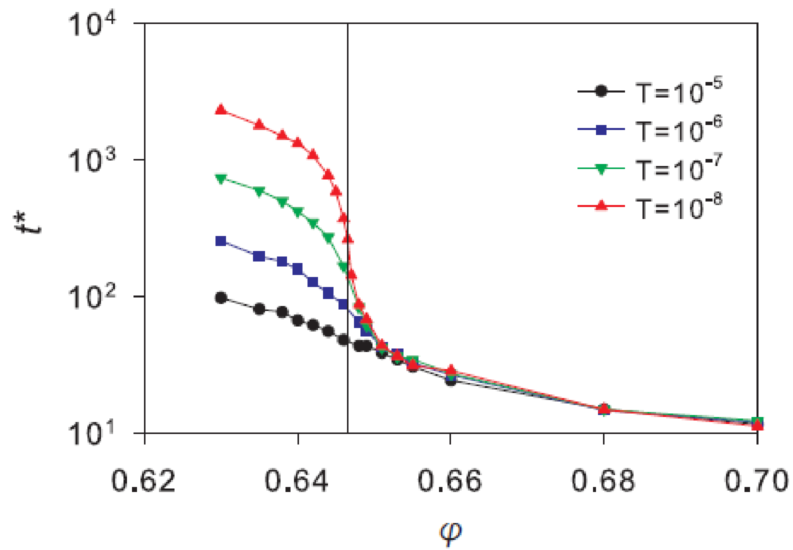
- Time scale at which the MSD shows plateau

- To see the impact of the collective motions, we renormalize the long time by the short time.

$$\tau(\varphi, T) \equiv \frac{t^\star}{\tau_0}$$

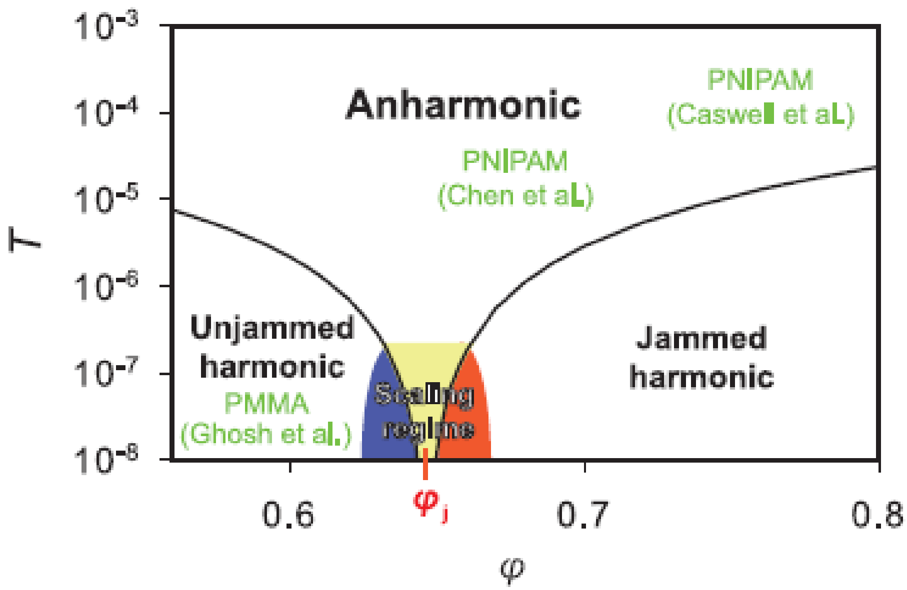


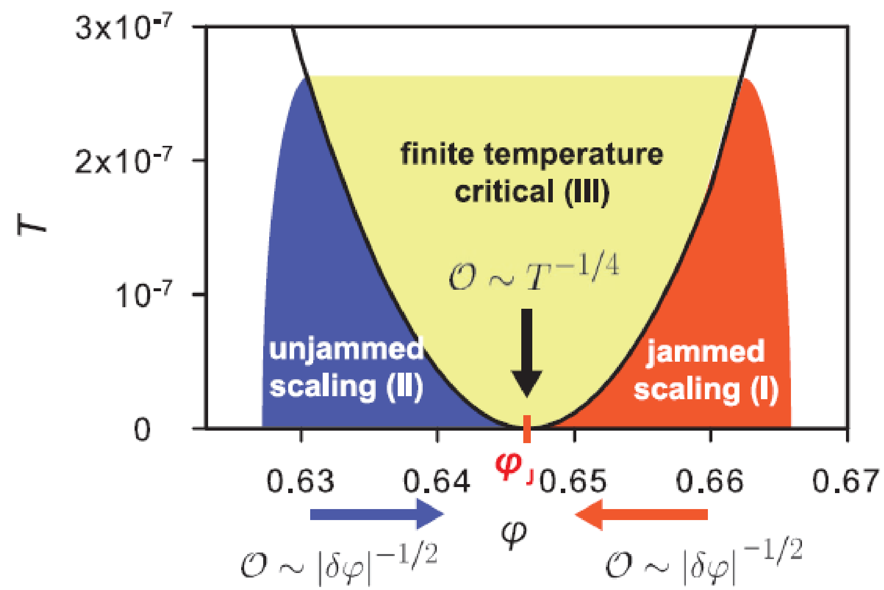




Jammed spheres at finite T

- At high temperature, criticality seems to be smeared out.
- **From renormalized quantities, we determined scaling regime**

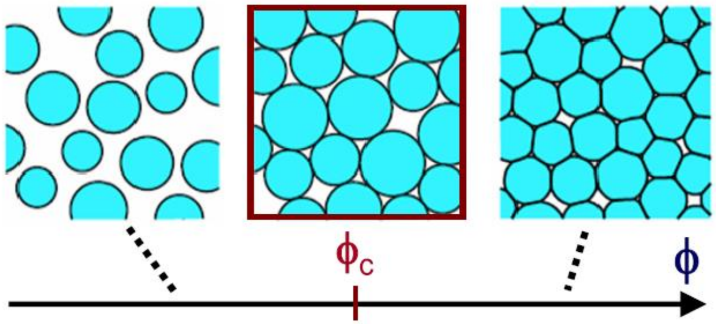




This work

- Harmonic spheres at around the J point.

$$v(r_{ij}) = \frac{\epsilon}{2}(1 - r_{ij}/\sigma)^2 \Theta(\sigma - r_{ij})$$



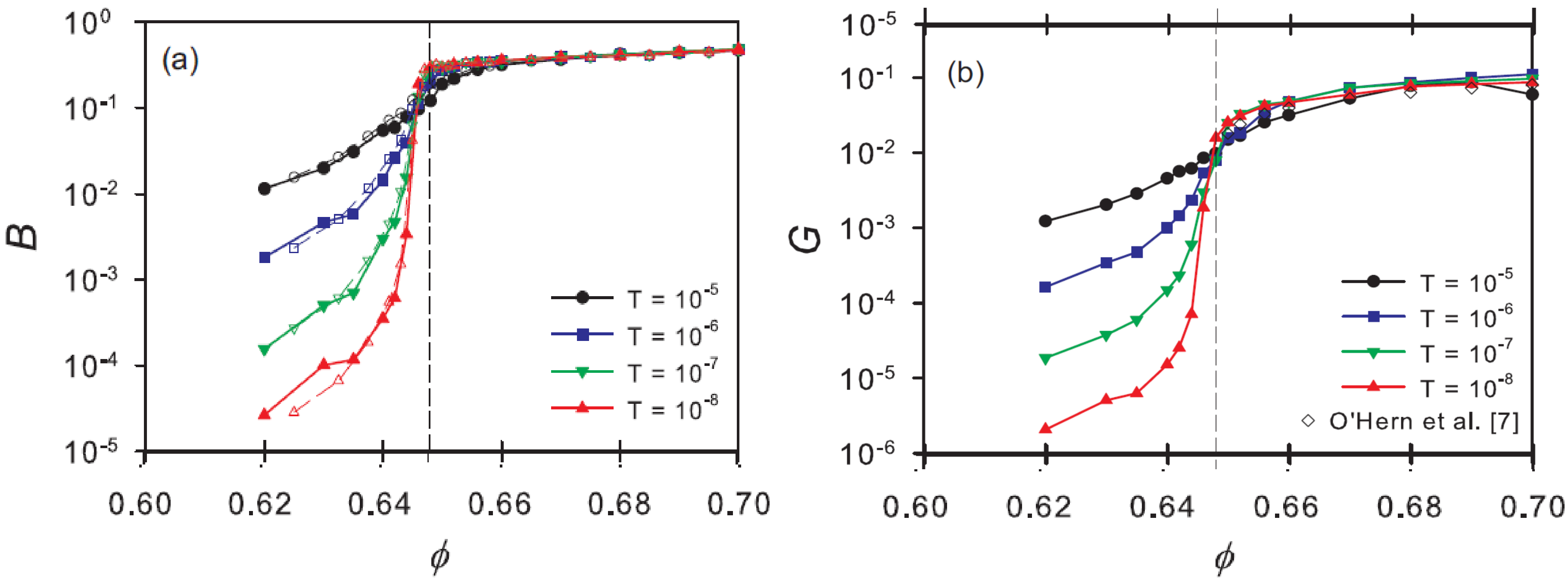
- Temperature:

$$k_B T/\epsilon = 10^{-5},\ 10^{-6},\ 10^{-7},\ 10^{-8}$$

- **Extend the analysis to:**
  - **Macroscopic mechanical moduli**
  - ***k* dependence of moduli**
  - **Static structure factor**

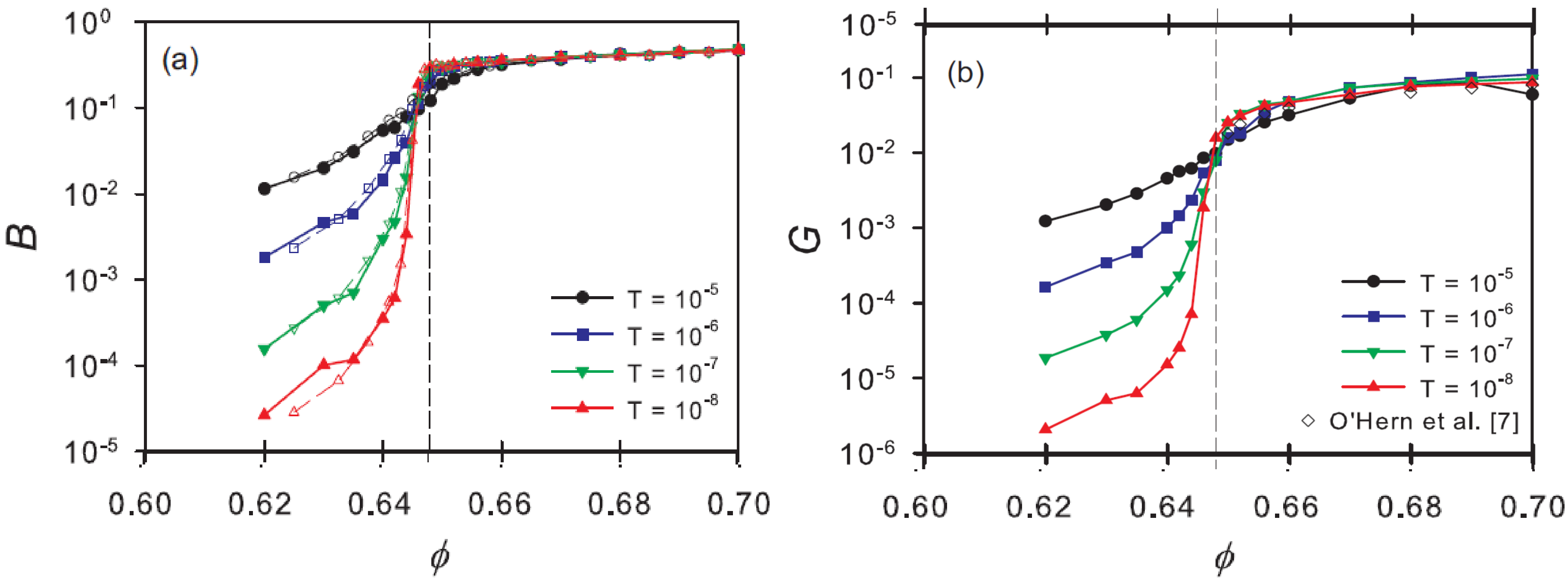
Macroscopic Moduli

Bulk and shear modulus



◆ Moduli are calculated through (1) fluctuation of the pressure, (2) density dependence of the pressure, (3) fluctuation of the displacement fields. All results agree.

Bulk and shear modulus



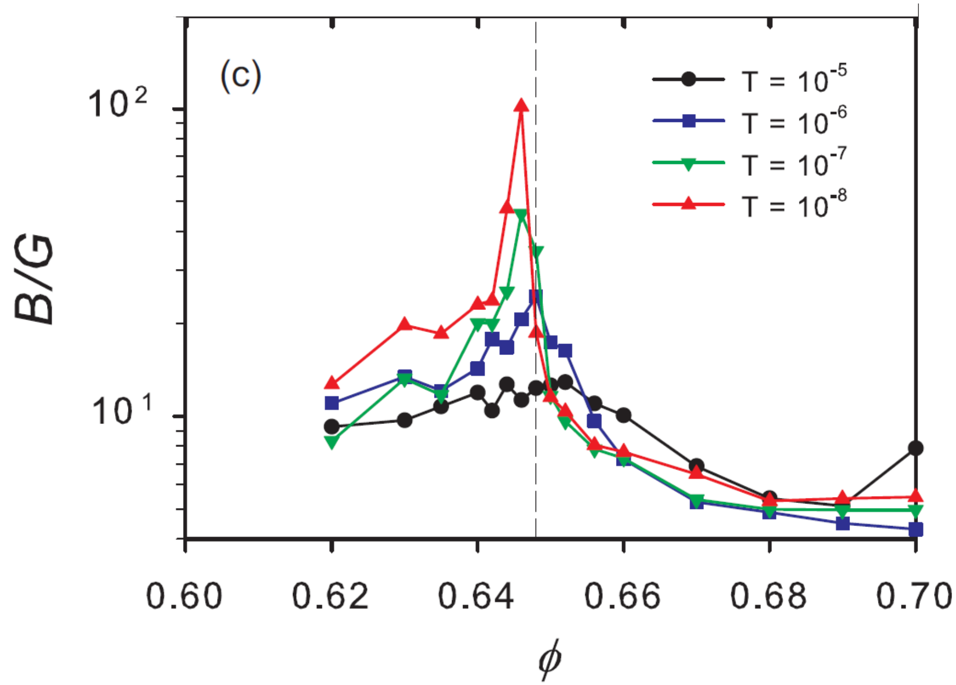
- Unjammed: Proportional to temperature

$$B \propto T(\Delta\varphi)^{-2} \qquad G \propto T(\Delta\varphi)^{-\kappa} \quad (\kappa \sim 1.41...)$$

- Jammed: Independent from temperature

$$B \sim \text{const.} \qquad G \propto (\Delta\varphi)^{0.5}$$

Bulk/Shear ratio



- Divergence of B/G, a signal of the jamming criticality, appears only at very low temperature, say $T < 10^{-6}$:
  - Consistent with the observation in caging dynamics

k dependence of the moduli

Definitions

- Displacement field: $$\vec{u}_{\vec{k}} = \sum_j \vec{u}_j \exp(-i\vec{k}\cdot\langle\vec{R}_j\rangle) \qquad \vec{u}_i = \vec{R}_i - \langle\vec{R}_i\rangle$$
- Longitudinal/Transverse : $$\vec{u}_{\vec{k}} = \hat{k} u_{L,\vec{k}} + \vec{u}_{T,\vec{k}}$$
- Structure factor

$$S_L(k) = \frac{k^2}{N}\langle u_{L,\vec{k}} u_{L,-\vec{k}}\rangle, \xrightarrow{\text{k} \to \text{0 plane wave description}} S_L(k) = \frac{\rho T}{B + \frac{4}{3}G}$$

$$S_T(k) = \frac{k^2}{N}\langle \vec{u}_{T,\vec{k}} \cdot \vec{u}_{T,-\vec{k}}\rangle \longrightarrow S_T(k) = \frac{\rho T}{G}$$

[Klix, Ebert, Weysser, Fuchs, Maret, Keim, 2012]

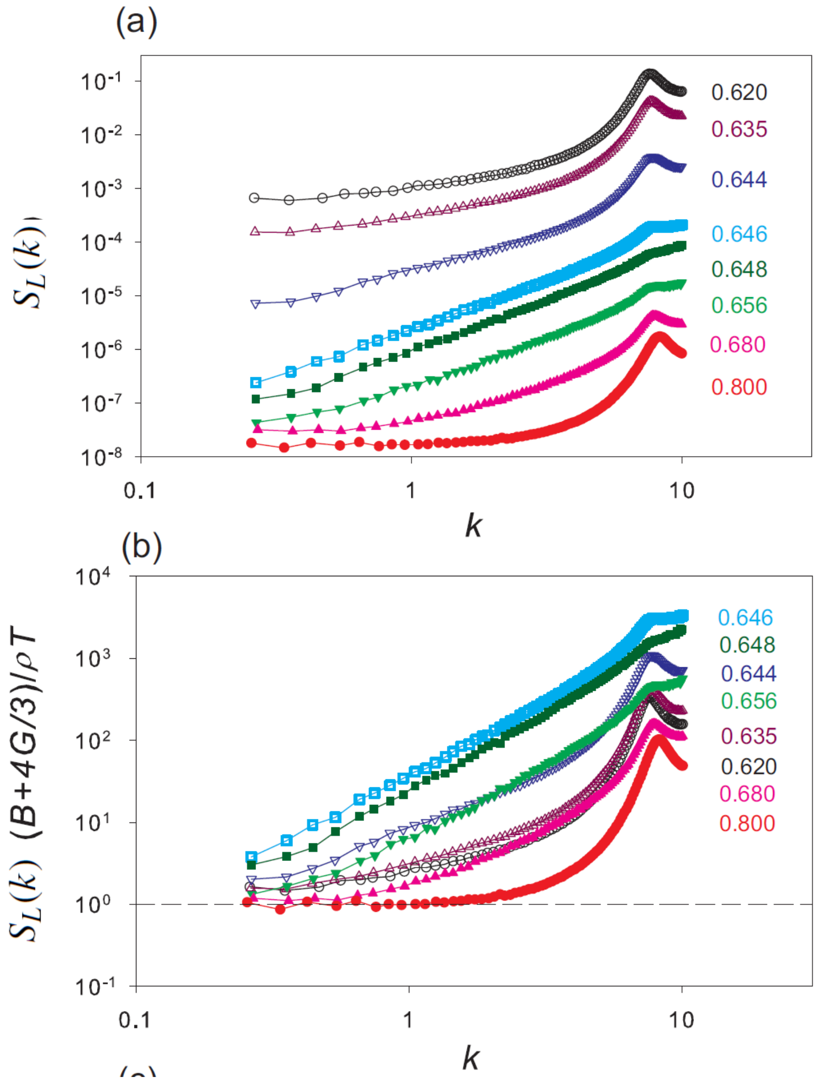
Longitudinal

- Fluctuation decreases with compression.
- Flat behavior at higher and lower densties, but

$$S_L(k) \propto k^2$$

at the jamming

- Renormalize: $S_L(k)$ are converging to the macroscopic modulus
- Characteristic wave vector shows non-monotonic behavior across the jamming density.



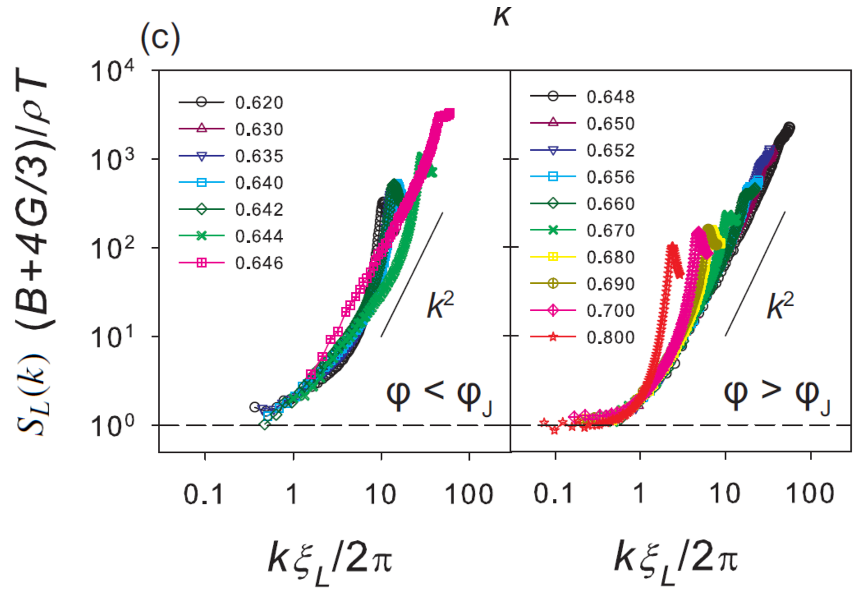
Longitudinal

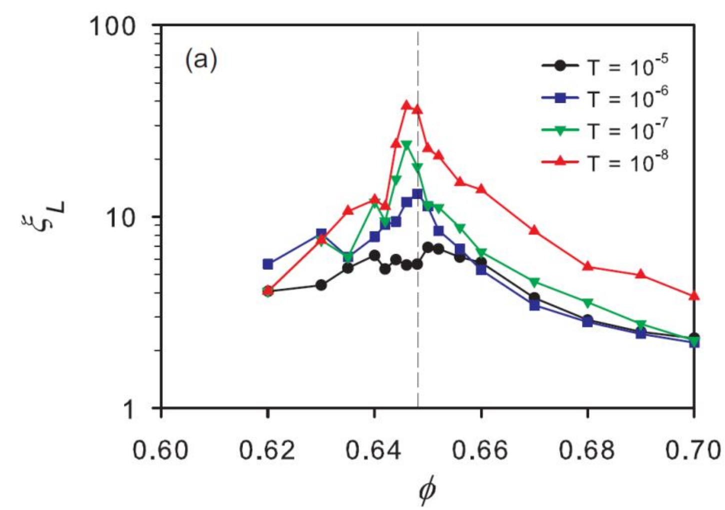
- Scaling analysis assuming

$$S_L(k) \approx \frac{\rho T}{B + \frac{4}{3}G} F(k\xi_L)$$

- The length characterizes the breakdown of usual plane wave description.

- The length diverges from the both sides of the jamming at lower T, and remain microscopic at higher T.

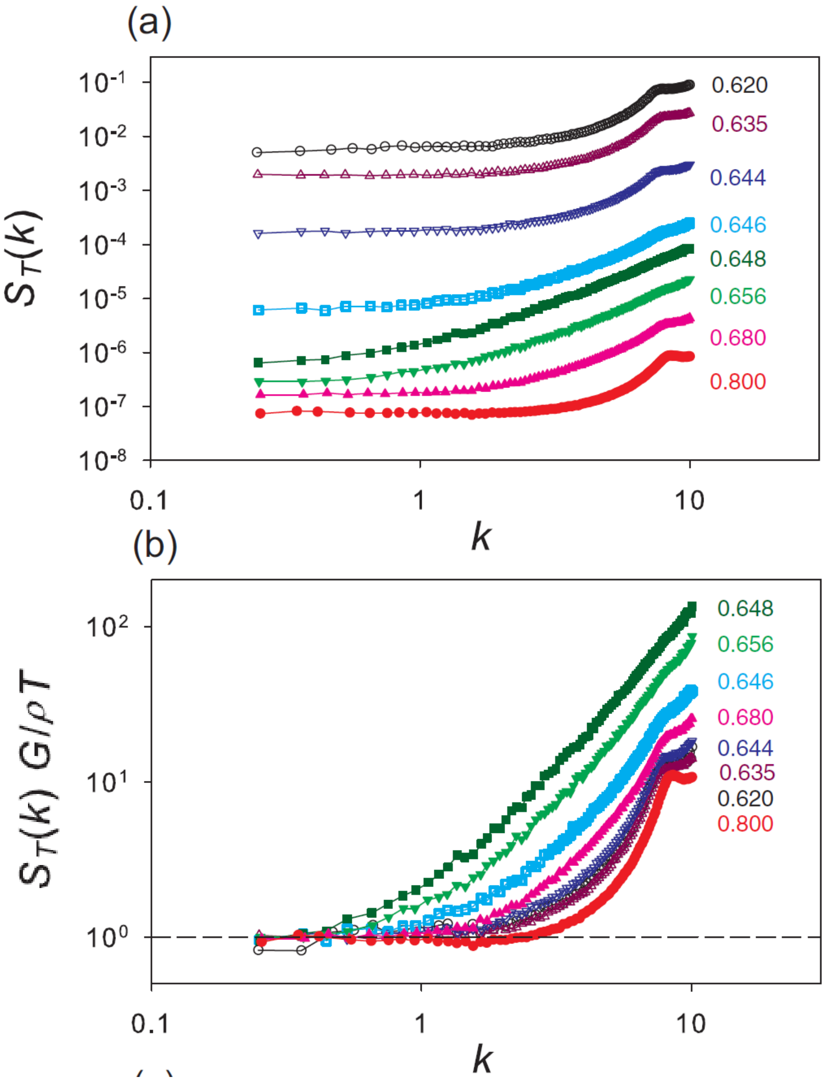




Transverse

- Similar behavior as the longitudinal one, though the k-dependence is little bit weak
  - At all the densities, $S_T(k)$ are converging to the macroscopic modulus.
  - However characteristic wave vector shows non-monotonic behavior across the jamming density.
  - At the jamming density,

$$S_T(k) \propto k^2$$

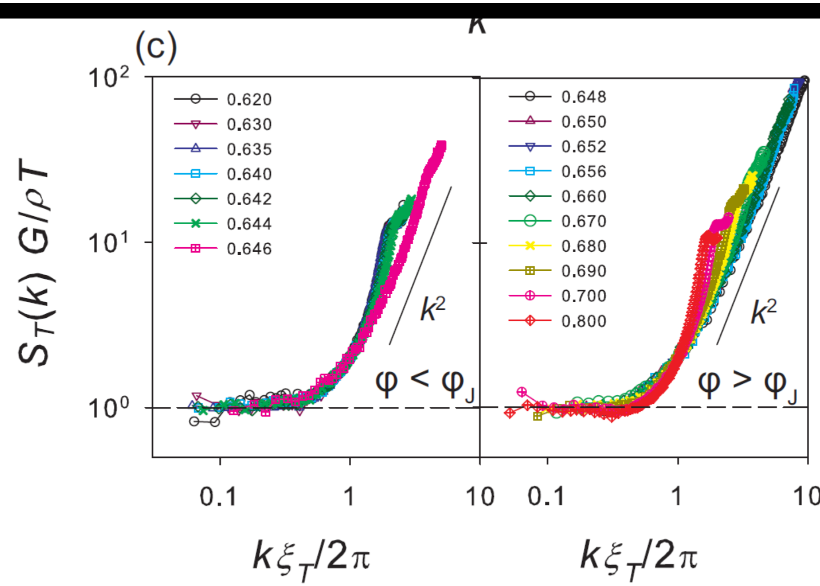


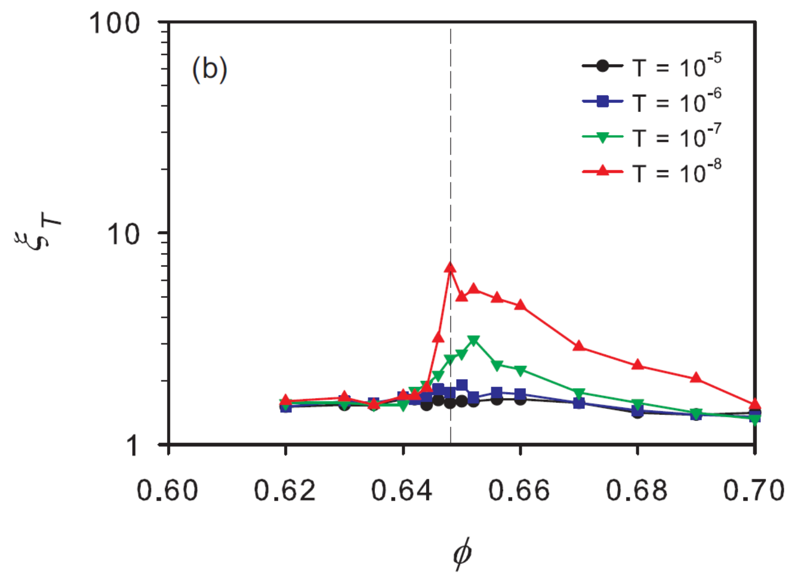
Transverse

- Scaling analysis assuming

$$S_T(k) \approx \frac{\rho T}{G} H(k\xi_T)$$

- The transverse length is shorter and its density dependence is weaker than the longitudinal ones.





Discussion 1

◆ The longitudinal & transverse lengths characterizing the breakdown of the usual plane wave description diverges from the both sides of the jamming.

◆ This is in sharp contrast to the recent statement by Xu et al., "***Transverse phonon doesn't exist in hardsphere glasses***".

[Wang, Xu et al PRL 2015]

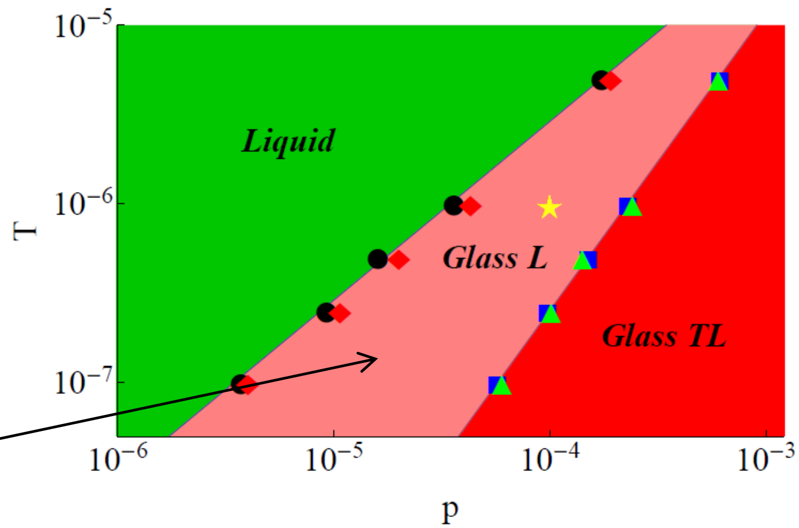


FIG. 3: (color online). Phase diagram including the glass transition (circles with the line $T_g \sim p$) and jamming-like transition (squares with the line $T_j \sim p^{5/3}$). The diamonds and triangles locate the crossover temperatures T_L ($\omega_{IR}^L = 0$) and T_T ($\omega_{IR}^T = 0$), respectively. The star marks the location of the state shown in Fig. 2(f).

Discussion 2

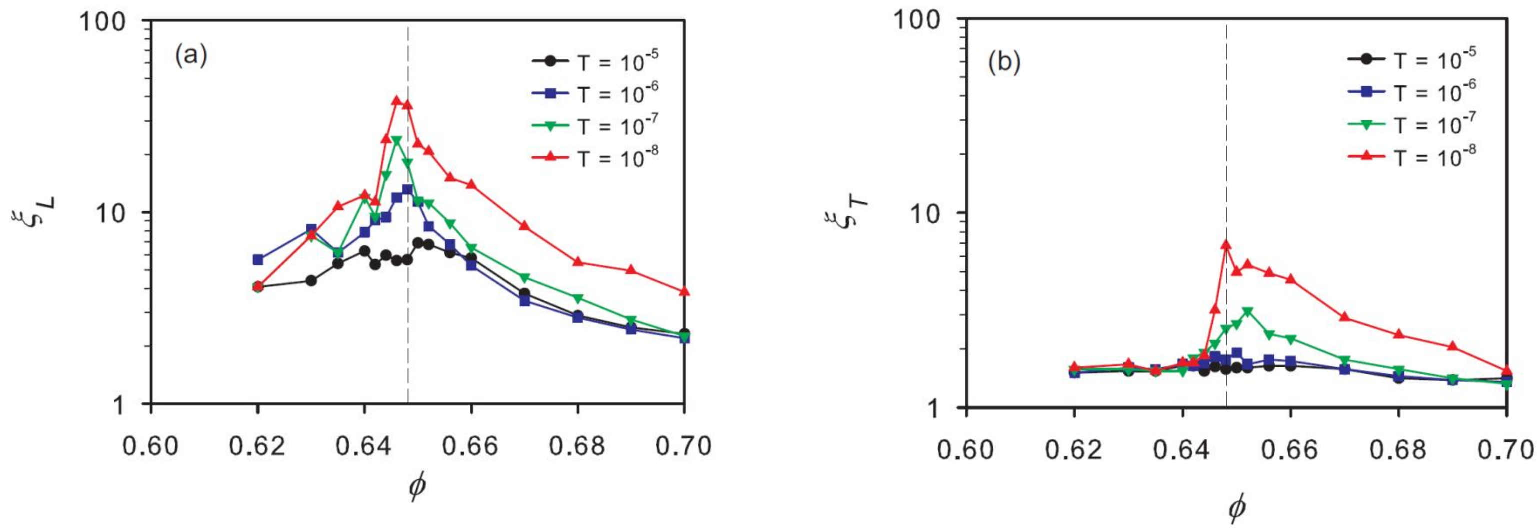
◆ The longitudinal & transverse lengths characterizing the breakdown of the usual plane wave description diverges from the both sides of the jamming.

◆ = Longitudinal and transverse length of phonon at w*?

$$\xi_L^* \propto (\varphi - \varphi_J)^{-0.5} \qquad \xi_T^* \propto (\varphi - \varphi_J)^{-0.25}$$

[Silbert et al 2006]

◆ We couldn't fit our data with these exponents.



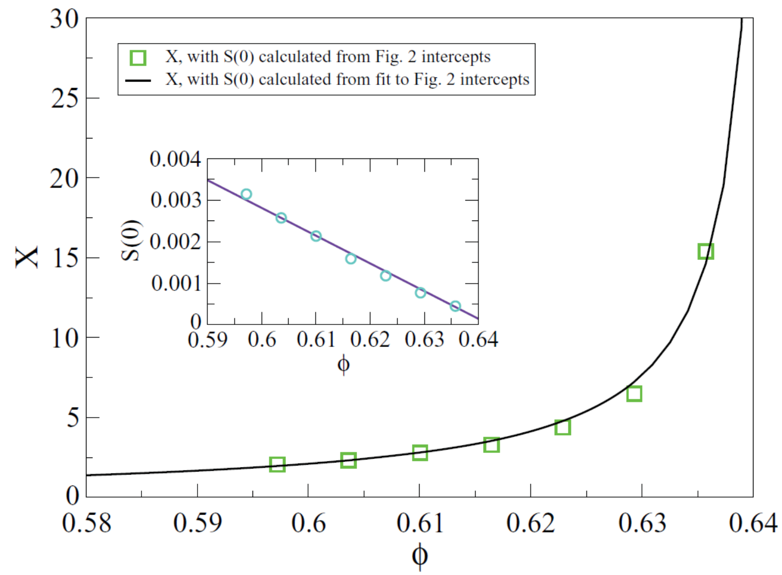
Discussion 3

- **“Non-equillibrium index”**
  - In liquid state

$$\lim_{k\to 0} S(k) = \frac{\rho T}{B}$$

  - “Non-equilibrium index” was introduced by Torquato et al.

$$X \equiv \lim_{k\to 0} \frac{S(k)B}{\rho T} - 1$$



  - **Diverging X at around the Jamming → “It strongly indicates that the jammed glassy state for hard spheres is fundamentally nonequilibrium in nature”**

[Hopkins, Stilinger, Torquato 2012 and more]

Discussion 3

$$S(k) = \frac{1}{N}\langle \rho_{\vec{k}} \rho_{-\vec{k}} \rangle \qquad \rho_{\vec{k}} = \sum_j \exp(-i\vec{k}\cdot\vec{R}_j),$$

- In solid: $S(k) = S_\delta(k) + S_0(k),$

$$S_\delta(k) = \frac{1}{N}\langle \delta\rho_{\vec{k}} \delta\rho_{-\vec{k}} \rangle \qquad S_0(k) = \frac{1}{N}\langle \rho_{\vec{k}} \rangle \langle \rho_{-\vec{k}} \rangle$$

$$\delta\rho_{\vec{k}} = \sum_j [-i\vec{k}\cdot\vec{u}_j + O(k^2)] \exp(-i\vec{k}\cdot\langle\vec{R}_j\rangle).$$

$$\approx \; S_L(k)$$

→ Bulk modulus

Discussion 3

- **"Non-equillibrium index"**
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$$\lim_{k\to 0} S(k) = \frac{\rho T}{B}$$

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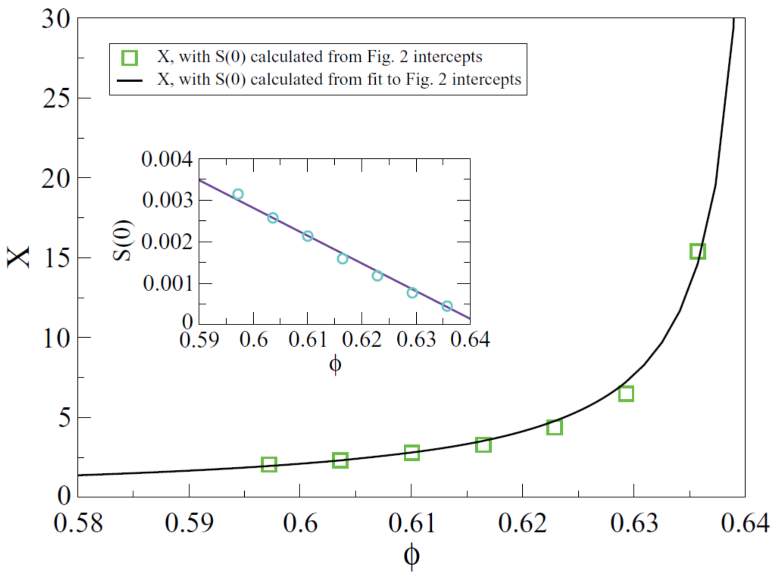


- **Our results: The fluctuation formula for solids works perfectly.**
  - Even if the solids are formed through *equilibrium phase transitions,* X would be able to take a non-zero value

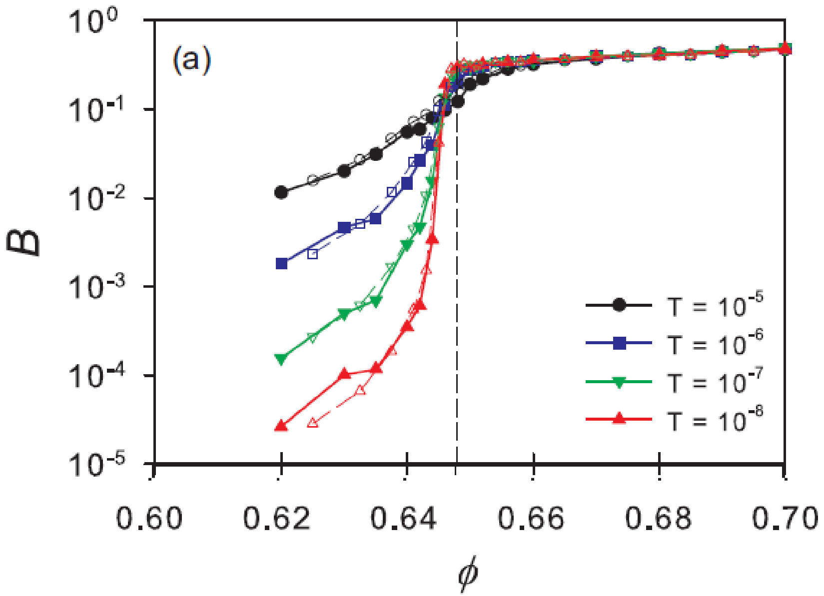
Discussion 3

◆ Bulk modulus is evaluated through the fluctuation of pressure. (bold-line)

$$B = P + \frac{\langle W_2 \rangle}{V} - \frac{\langle P^2 \rangle - \langle P \rangle^2}{T} V + \frac{2}{3}\rho T - \frac{T\gamma_V^2}{\rho c_V},$$

◆ Bulk modulus from the derivative of the pressure against the density (dashed)

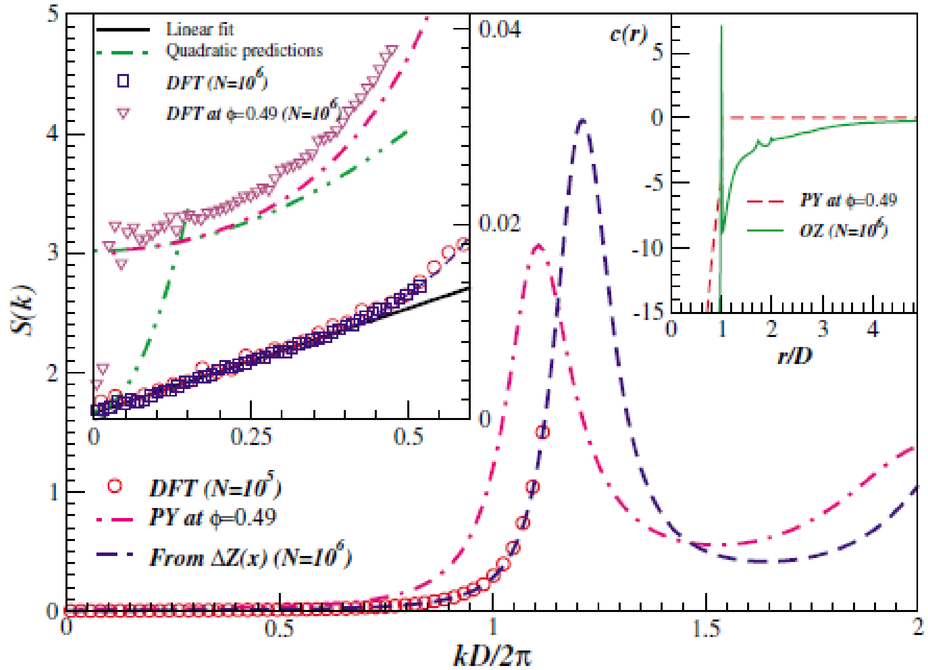
$$B = -V\left(\frac{\partial P}{\partial V}\right)_T$$



◆ **Again, the fluctuation formula works perfectly**

Static structure factor

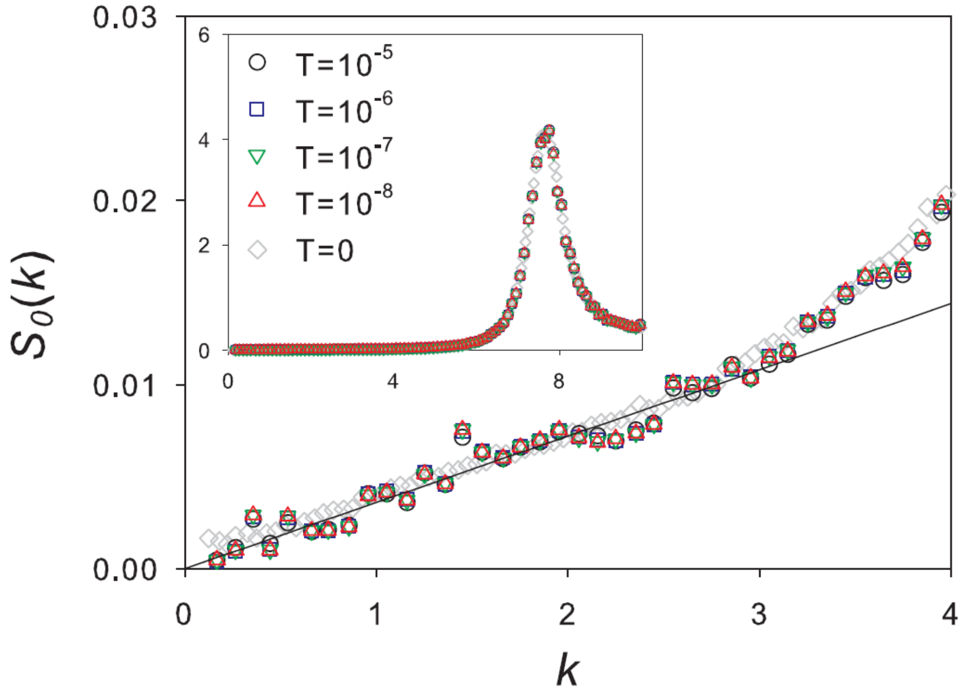
Hyperuniformity



◆ S(k) ~ k (seems going to zero at k = 0) is observed at the jamming of hardspheres. [Donev, Stillinger, Torquato, 2005]

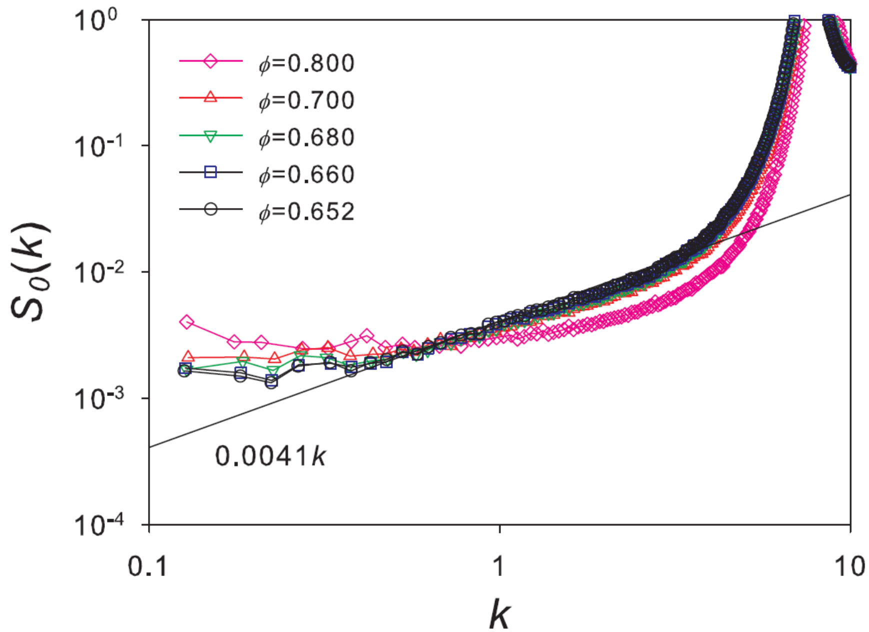
◆ Avoid some confusions: Hyperuniformity (S_0) is NOT related to the compressibility (S_{delta}) of the jammed spheres

Temperature dependence



- Hyperuniformity is very much robust against the thermal fluctuation
  - Sharp constrast to other critical quantities

Density dependence



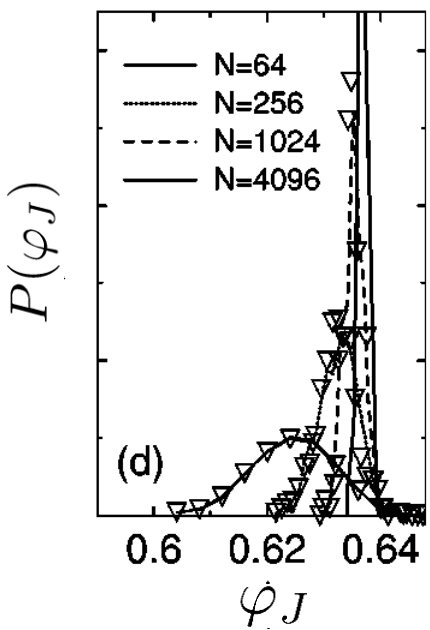
- Prepared a large system (N=512000) at T=0 and calculated S(k).
- (1) Hyperuniformity in intermediate *k* is very much robust against the density change!
- (2) Strict hyperuniformity at k → 0 is not observed even at the jamming! (Sharp contrast to other critical quantities)

A similar conclusion is reached in [Wu, Olsson, Teitel, 2015]

Discussion

- Strict hyperuniformity should be observed…?
- Problem is related to the distribution of the jamming density

(athermal) $S(k \to 0) = N^{-1} \lim_{k \to 0} |\rho_k|^2 \sim N[\Delta\varphi_J]^2$

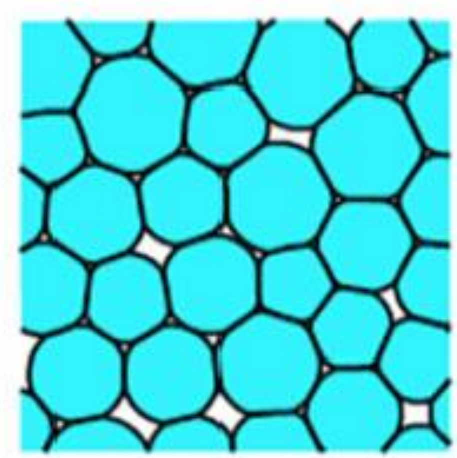


Width of the distribution

$$w = w_0 N^{-\Omega}$$

$$\Omega = 0.55 \pm 0.03$$

[O'Hern et al, 2003]



- It seems natural not to have the strict hyperuniformity…

Conclusion

- Fluctuation formula works perfectly for the estimate of mechanical moduli → Non-equillibrium index is not required

- k-dependent moduli is characterized by the scaling laws

$$S_\delta(k) \approx \frac{\rho T}{B + \frac{4}{3}G} F(k\xi_L), \quad F(x \ll 1) = 1, \quad F(x \gg 1) \propto x^2. \qquad S_T(k) \approx \frac{\rho T}{G} H(k\xi_T) \quad H(x \ll 1) = 1, \quad H(x \gg 1) \propto x^2$$

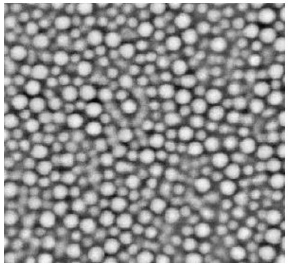
The lengths characterize the breakdown of the usual continuum mechanics with macroscopic mechanical moduli.

- The length diverges from the both sides of the jamming at T→0, but the lengths remain microscopic at higher T

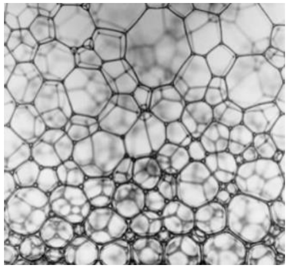
- Hyperuniformity seems not to be directly related to the jamming criticality itself.
    - Strict hyperuniformity (S(k→0) =0) is not observed even at the jamming.
    - Protocol dependence? Slow quenching give a different result?

Jamming problem

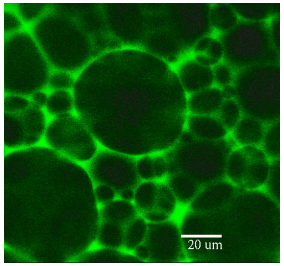
- Not clear in thermal soft particles:
  - Colloids, Emulsions, etc



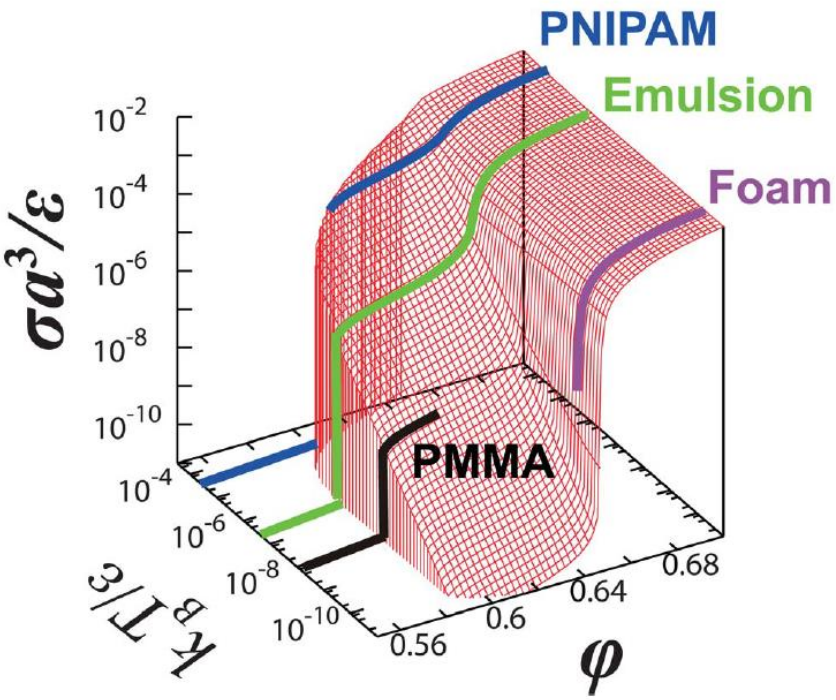
PMMA colloids



Aqueous foam



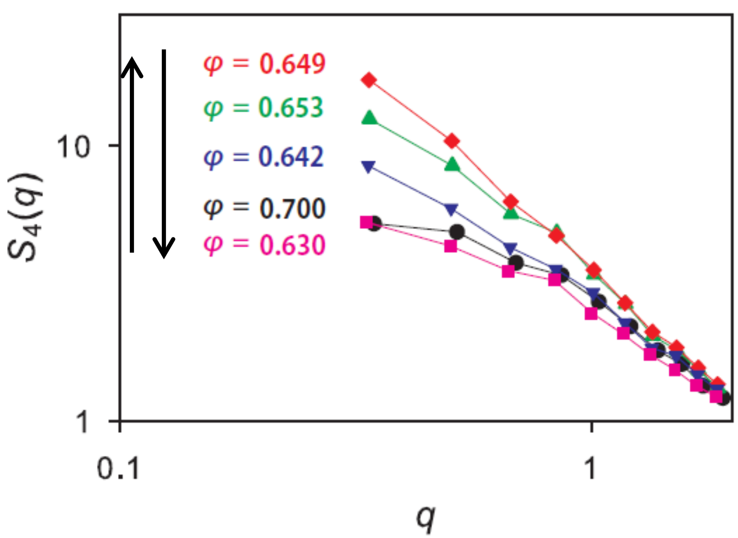
Emulsions



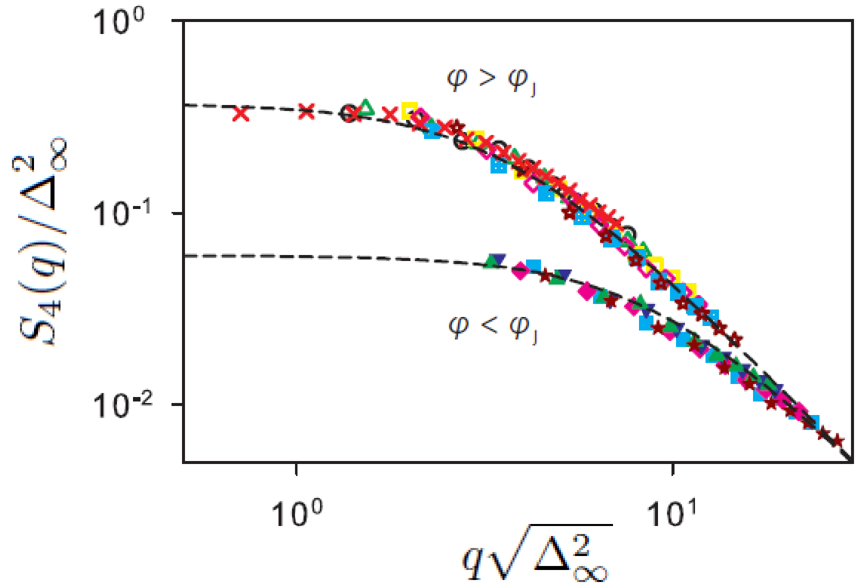
Dynamic heterogeneity

- Structure factor of displacements in vibration

$$S_4(q,t) = \frac{1}{N}\sum_{i,j=1}^{N} \langle |\mu_i(t)\mu_j(t)\exp(i\vec{q}\cdot\vec{r}_{ij})| \rangle$$



Scaling analysis



$$\tau \sim \Delta_\infty^2 \sim \xi_4^2$$

$$\xi_4 \sim |\varphi - \varphi_J|^{-1/4}$$

Insight into experiments

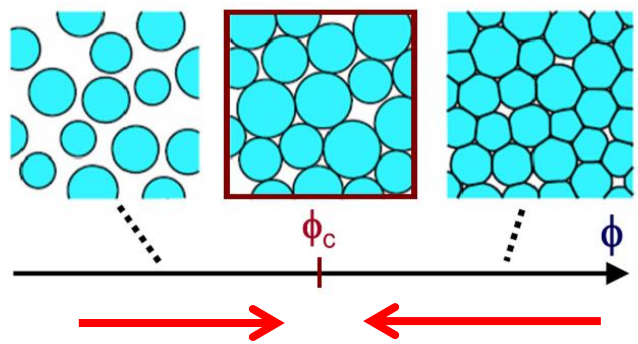
- **In simulations, we have used "temperature" to control :**

$$k_B T/\epsilon \qquad \tau_T = \frac{\xi a^2}{k_B T} \qquad \sigma_T = \frac{k_B T}{a^3}$$

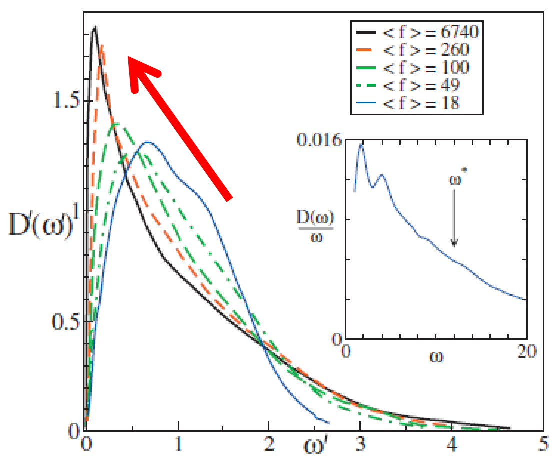
- **But in experiments, temperature is almost always fixed at the room temperature. Instead, "particle softness" and "particle size" is controllable.**

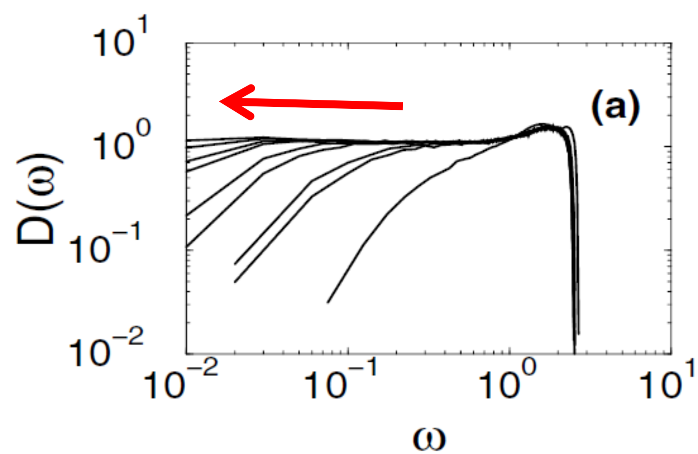
Within harmonic approx.

- Diagonalization of hessian of the potential energy (alike for unjammed) shows **excess of low frequency modes**.



[Silbelt, Liu, Nagel (2005)]
[Brito, Wyart (2009)]





$$\omega^* \propto (\phi - \phi_c)^{\Omega} \qquad \Omega = 0.48 \pm 0.03$$

Critical slowing down

- Renormalized quantities
  - To see the time scale for the collective motion, we renormalize the long time by ballistic time.

$$\tau(\varphi, T) \equiv \frac{t^\star}{\tau_0}$$

  - Likewise, we define microscopic length scale

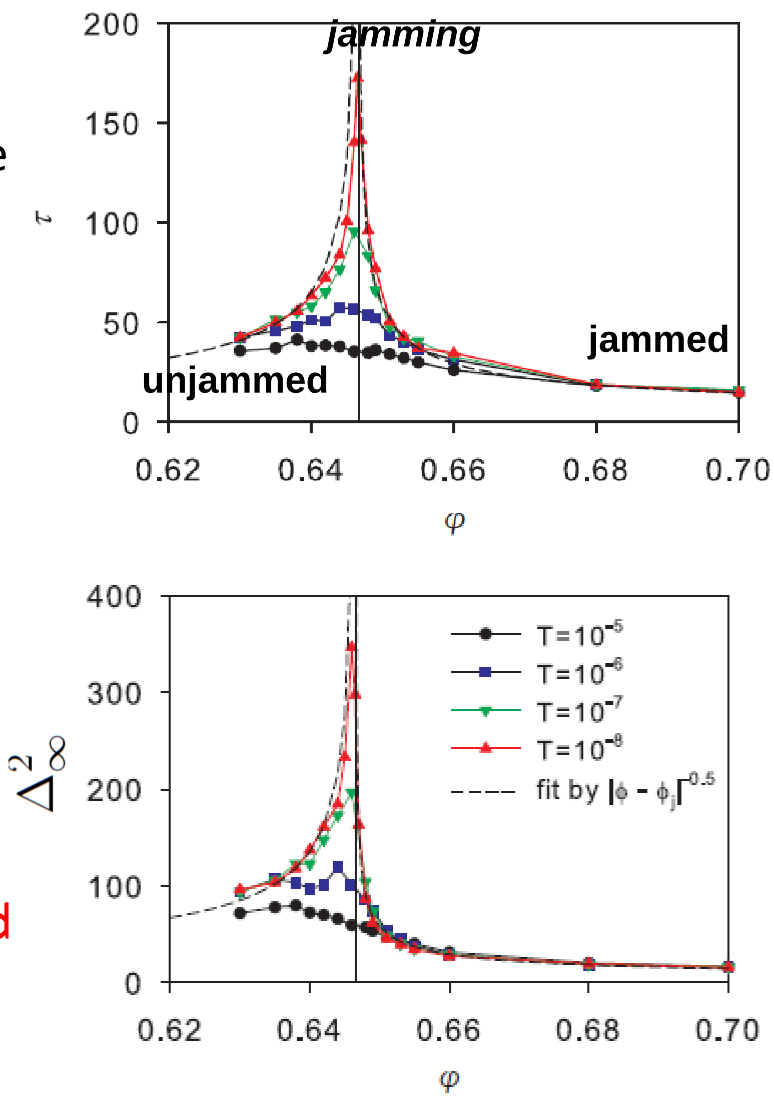
$$\delta = \sqrt{T}\tau_0$$

Then we focus on

$$\Delta^2_\infty(\varphi, T) = \frac{\Delta^2(\infty)}{\delta^2}$$

  - **They shows critical slowing down and associated large vibration.**

$$\tau \sim \Delta^2_\infty \sim |\varphi - \varphi_J|^{-1/2}$$



Discussion 1

- "Non-equilibrium index" is ill-defined,

$$X \equiv \lim_{k \to 0} \frac{S(k)B}{\rho T} - 1$$

[Hopkins, Stilinger, Torquato 2012 and more]

because bulk modulus is related to the thermal fluctuation part.

- Even if the solids are formed through *equilibrium phase transitions,* X would be able to take non-zero value

- X actually diverges in low T in Lennard-Jones glass, however it is just 1/T.