メニュー

1. イントロダクション・ガラス転移とは

2. 流体力学から分子運動論まで:
モード結合理論超入門

3. ランダム一次転移理論(RFOT):
ガラスの平均場描像

4. ガラス理論の検証

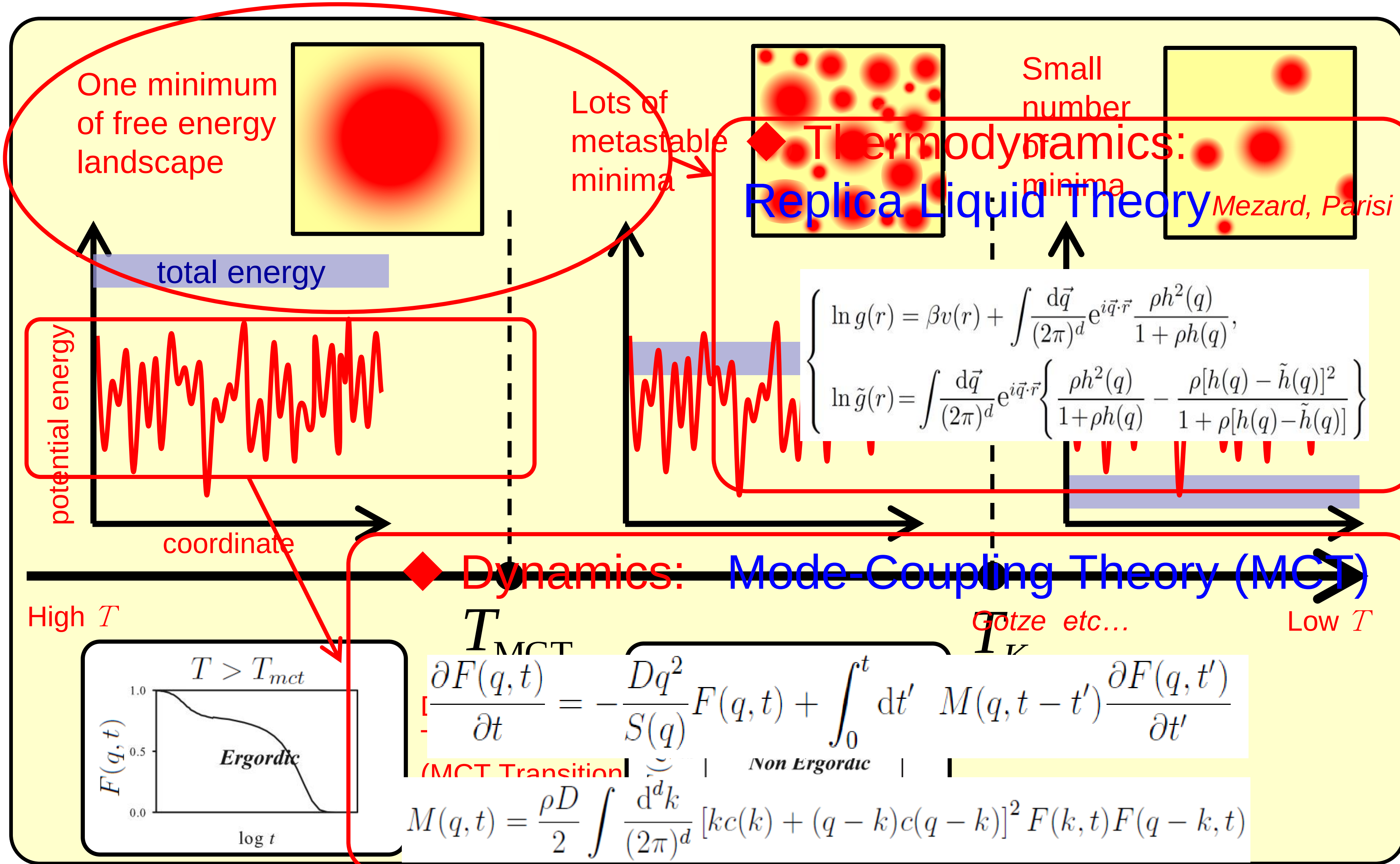
5. 最近の研究から

最近の研究から

- ***Glass transition at high dimensions***
- ***Long ranged systems***
- ***Jamming transition***
- ***Randomly pinned glass transition***

Glass transition at high dimension

• Introduction



◆ Thermodynamics: Replica Liquid Theory *Mezard, Parisi*

$$\begin{cases} \ln g(r) = \beta v(r) + \displaystyle\int \frac{\mathrm{d}\vec{q}}{(2\pi)^d} e^{i\vec{q}\cdot\vec{r}} \frac{\rho h^2(q)}{1+\rho h(q)}, \\ \ln \tilde{g}(r) = \displaystyle\int \frac{\mathrm{d}\vec{q}}{(2\pi)^d} e^{i\vec{q}\cdot\vec{r}} \left\{ \frac{\rho h^2(q)}{1+\rho h(q)} - \frac{\rho[h(q)-\tilde{h}(q)]^2}{1+\rho[h(q)-\tilde{h}(q)]} \right\} \end{cases}$$

◆ Dynamics: Mode-Coupling Theory (MCT) *Gotze etc…*

$$\frac{\partial F(q,t)}{\partial t} = -\frac{Dq^2}{S(q)} F(q,t) + \int_0^t \mathrm{d}t' \; M(q,t-t') \frac{\partial F(q,t')}{\partial t'}$$

$$M(q,t) = \frac{\rho D}{2} \int \frac{\mathrm{d}^d k}{(2\pi)^d} \left[k c(k) + (q-k) c(q-k) \right]^2 F(k,t) F(q-k,t)$$

Glass transition at high dimension

- ***Introduction***

If RFOT scenario is correct,

- *MCT should work better in Higher Dimensions*

- *MCT should work better for Long-Ranged Systems*

- *Dynamic (MCT) transition point should mark the qualitative change of the free energy landscape (inherent structures)*

Glass transition at high dimension

- ***MCT vs MD at d=4***

MD for 4d Hard Sphere Fluid

- Density (Volume fraction) φ is a sole parameter

- Nucleation rate is small van Meel, Frenkel, Charbonneau *PRE* **79**, (2009) 030201

  Monatomic (1-component) glass former!

MCT for 4d Hard Sphere Fluid

$$\frac{\partial F(q,t)}{\partial t} = -\frac{Dq^2}{S(q)} F(q,t) + \int_0^t \mathrm{d}t' \; M(q,t-t') \frac{\partial F(q,t')}{\partial t'}$$

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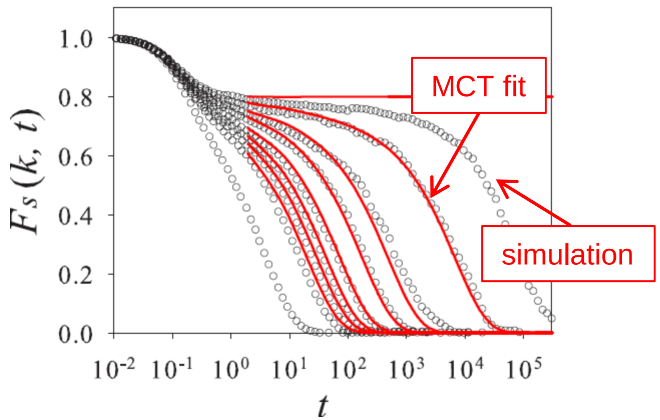
Glass transition at high dimension

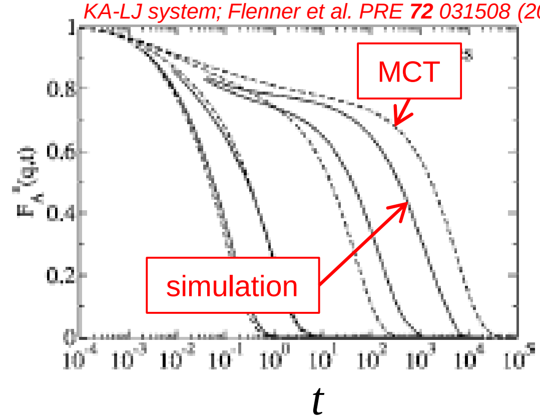
● MCT vs MD at d=4

d=4

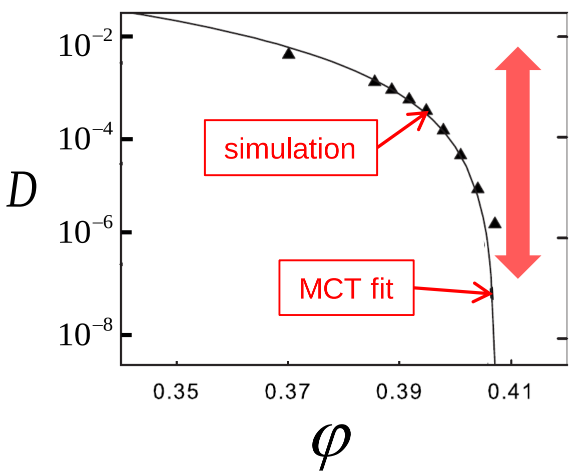
d=3



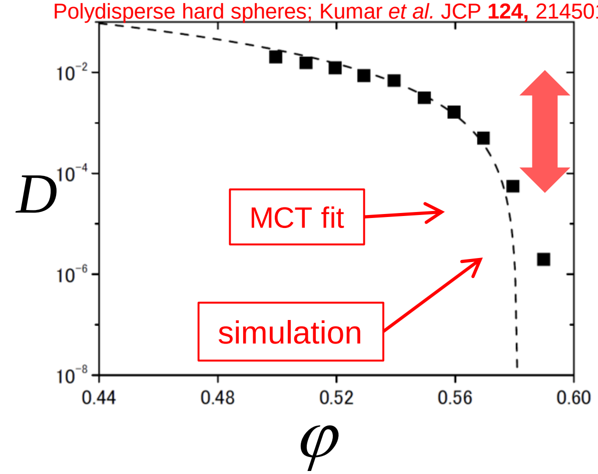
*KA-LJ system; Flenner et al. PRE **72** 031508 (2005)*



Density correlation (self part)



Polydisperse hard spheres; Kumar *et al.* JCP **124,** 214501 **(**2006)



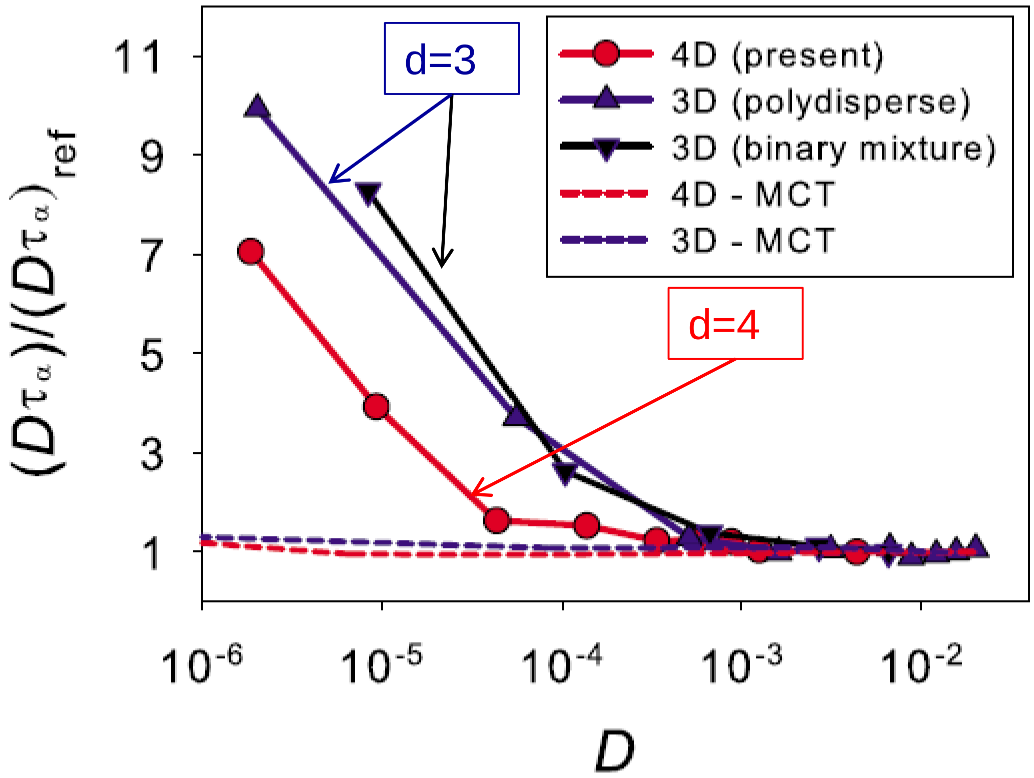
Diffusion correlation

$$D \propto |\varphi - \varphi_{mct}|^{\gamma}$$

Glass transition at high dimension

● MCT vs MD at d=4

Violation of Stokes-Einstein relation



MCT is more mean-fieldy in 4d!

Glass transition at high dimension

● *MCT vs Replica Theory at high d's*

MCT vs. Replica theory in $d = 3$

◆ MCT in arbitrary dimensions

$$\frac{\partial F(q,t)}{\partial t} = -\frac{Dq^2}{S(q)} F(q,t) + \int_0^t \mathrm{d}t' \;\; M(q,t-t') \frac{\partial F(q,t')}{\partial t'}$$

$$M(q,t) = \frac{\rho D}{2} \int \frac{\mathrm{d}^d k}{(2\pi)^d} \left[k c(k) + (q-k) c(q-k) \right]^2 F(k,t) F(q-k,t)$$

◆ Replica Theory with Hyper-Netted Chain *Parisi and Zamponi Rev. Mod. Phys.* ***82*** *789 (2010)*

$$\begin{cases} \ln g(r) = \beta v(r) + \displaystyle\int \frac{\mathrm{d}\vec{q}}{(2\pi)^d} \mathrm{e}^{i\vec{q}\cdot\vec{r}} \frac{\rho h^2(q)}{1+\rho h(q)}, \\ \ln \tilde{g}(r) = \displaystyle\int \frac{\mathrm{d}\vec{q}}{(2\pi)^d} \mathrm{e}^{i\vec{q}\cdot\vec{r}} \left\{ \frac{\rho h^2(q)}{1+\rho h(q)} - \frac{\rho[h(q)-\tilde{h}(q)]^2}{1+\rho[h(q)-\tilde{h}(q)]} \right\} \end{cases}$$

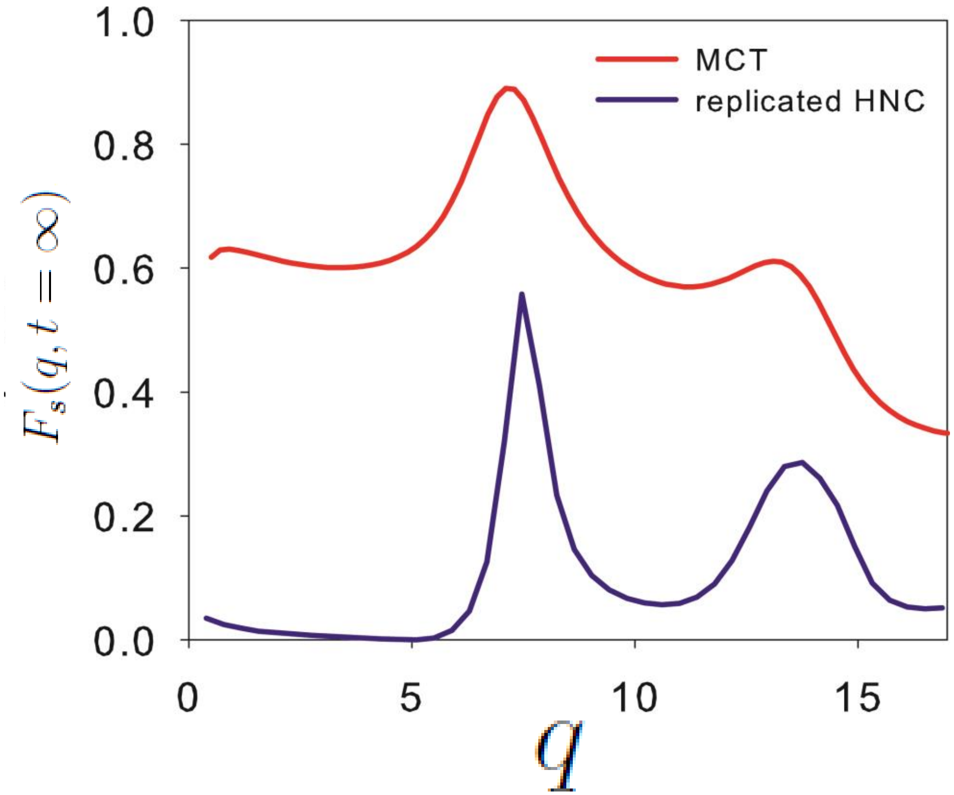
Regular HNC equation

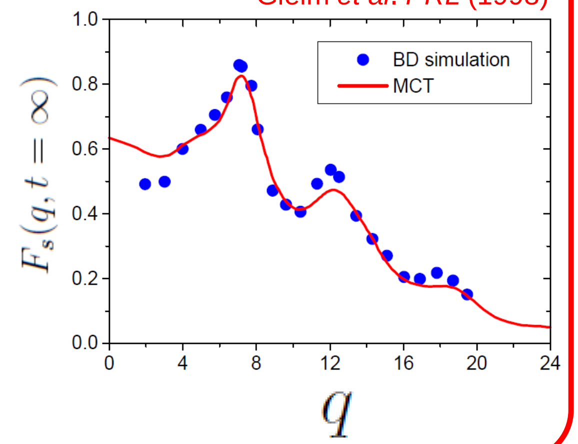
HNC equation between replicas

Glass transition at high dimension

- ***MCT vs Replica Theory at high d's***

MCT vs. Replica theory in $d = 3$





MCT wins over Replica. But maybe simply because HNC is a bad approximation.

Glass transition at high dimension

● *MCT vs Replica Theory at high d's*

MCT vs. Replica theory in $d = \infty$

In $d = \infty$, static input is given by a single Mayor function: $c(q) = -\left(\frac{2\pi}{q}\right)^{d/2} J_{d/2}(q)$

◆ MCT in arbitrary dimensions

$$\frac{\partial F(q,t)}{\partial t} = -\frac{Dq^2}{S(q)} F(q,t) + \int_0^t \mathrm{d}t' \; M(q, t-t') \frac{\partial F(q,t')}{\partial t'}$$

$$M(q,t) = \frac{\rho D}{2} \int \frac{\mathrm{d}^d k}{(2\pi)^d} \left[kc(k) + (q-k)c(q-k)\right]^2 F(k,t) F(q-k,t)$$

◆ Replica Theory with Cage Expansion

*Parisi and Zamponi Rev. Mod. Phys.**82** 789 (2010)*

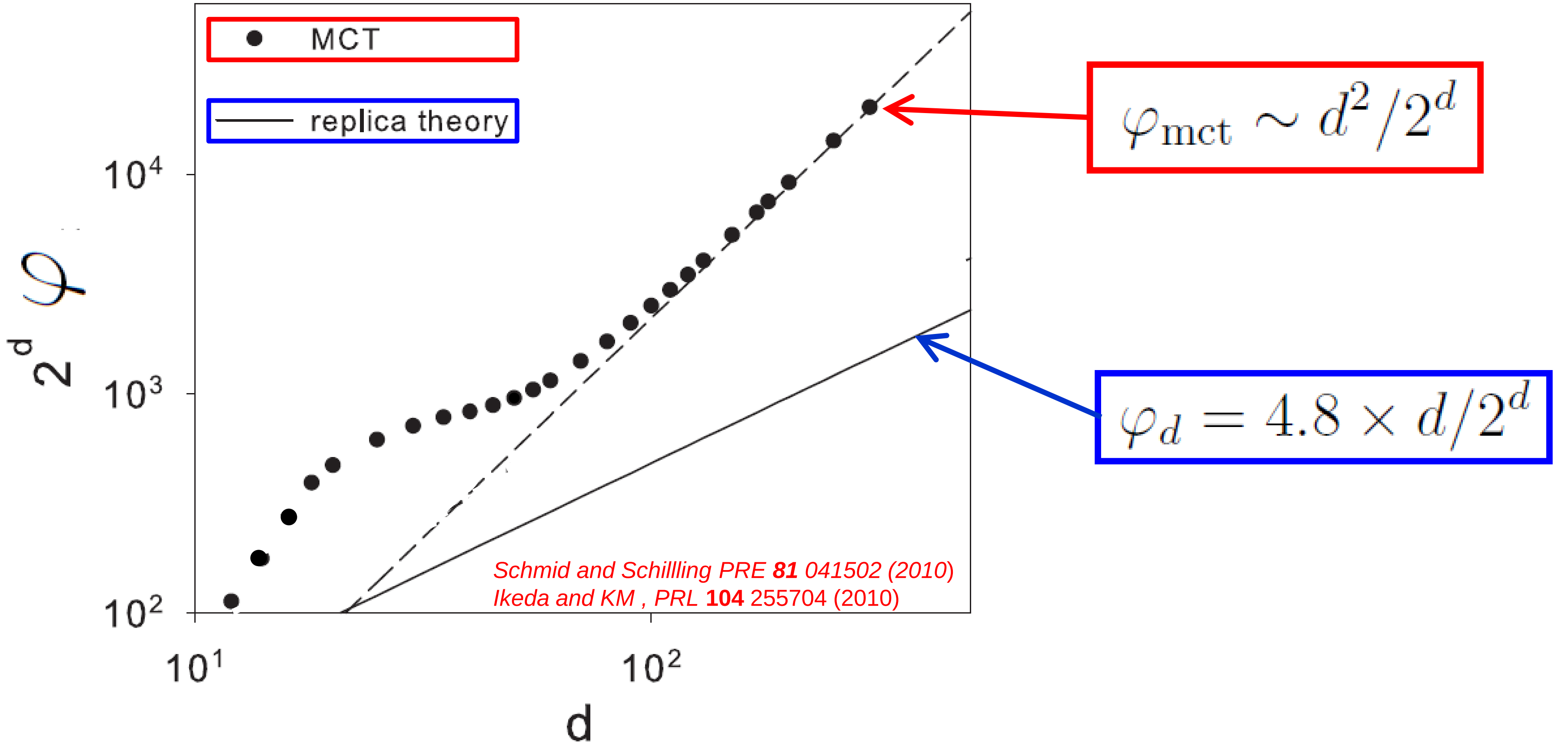
$F(q, t=\infty) \propto \exp\left[-Aq^2\right]$ Gaussian assumption

$$\frac{1}{A} = -\frac{\rho}{d} \int \mathrm{d}^d r \; \log\left[1 - \int \frac{\mathrm{d}^d q}{(2\pi)^d} \mathrm{e}^{-iqr - Aq^2} c(q)\right] \int \frac{\mathrm{d}^d q'}{(2\pi)^d} \mathrm{e}^{-iq'r - Aq'^2} q'^2 c(q')$$

Glass transition at high dimension

● *MCT vs Replica Theory at high d's*

MCT vs. Replica theory in $d = \infty$

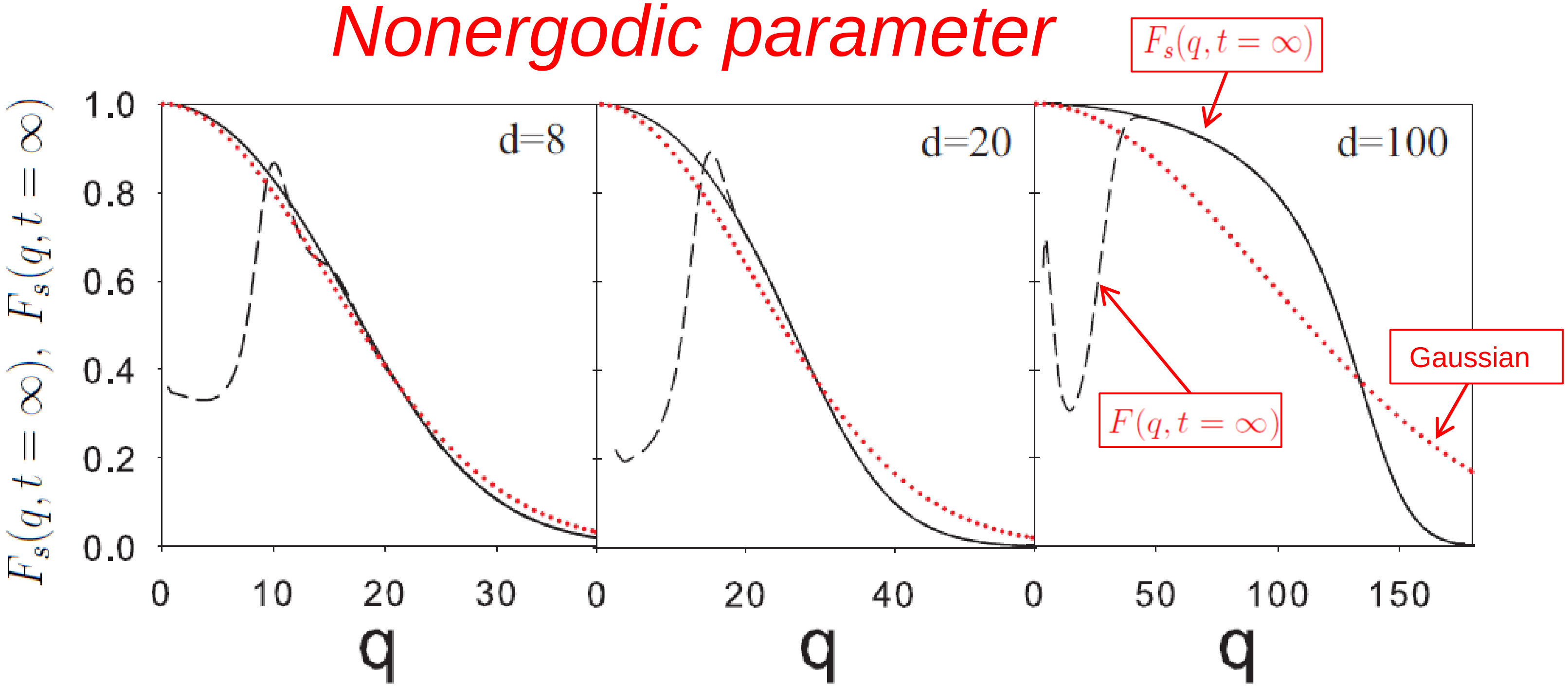


Glass transition at high dimension

● *MCT vs Replica Theory at high d's*

MCT vs. Replica theory in $d = \infty$

Nonergodic parameter



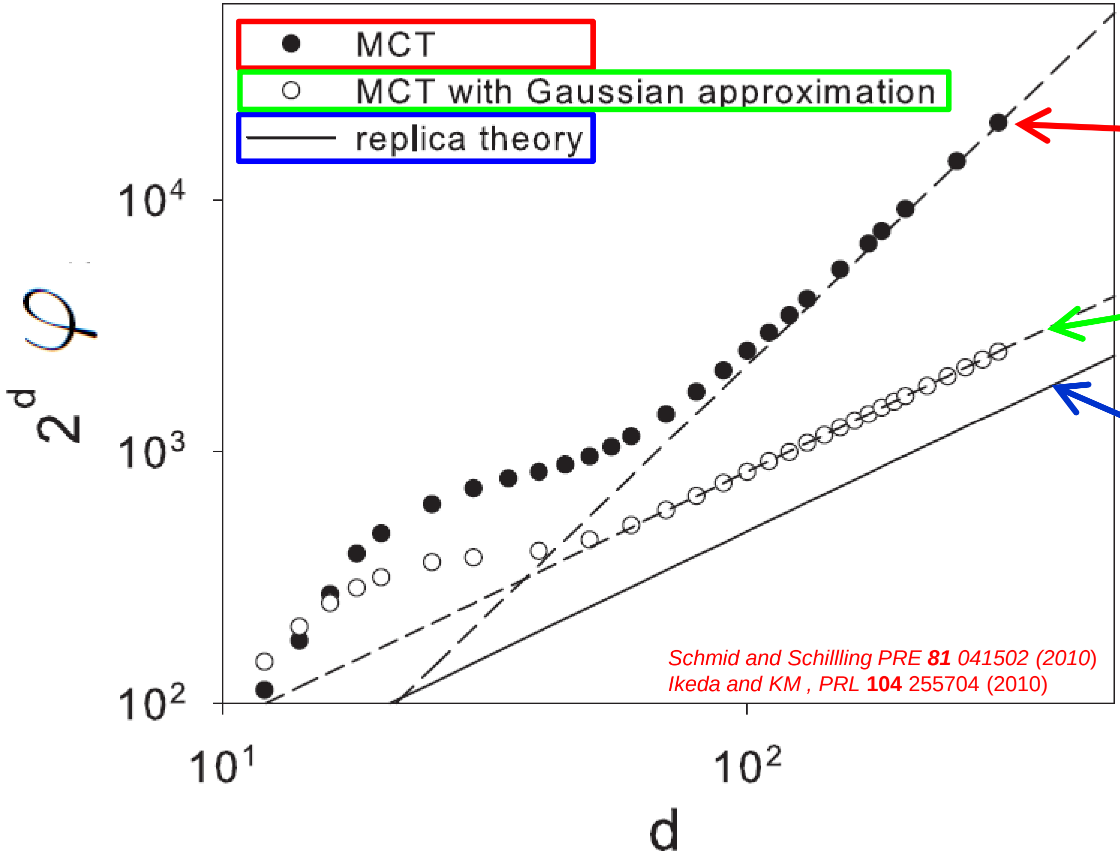
MCT predicts non-Gaussian shape

Replica assumes Gaussian shape a priori

Glass transition at high dimension

● MCT vs Replica Theory at high d's

MCT vs. Replica theory in $d = \infty$



$$\varphi_{\mathrm{mct}} \sim d^2/2^d$$

$$\varphi^{G}_{mct} = 8.27 \times d/2^d$$

$$\varphi_d = 4.8 \times d/2^d$$

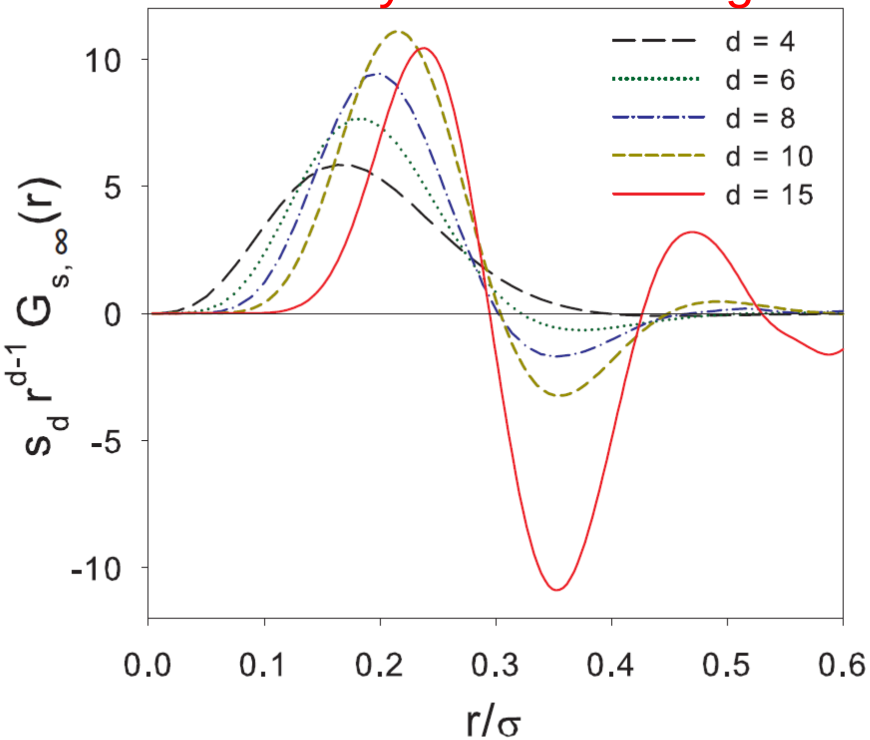
Glass transition at high dimension

● *MCT vs Replica Theory at high d's*

MCT vs. Replica theory in $d = \infty$

This discrepancy is due to failure of MCT!

Non-Gaussian (and squashed) shape of *F(q, t)* is WRONG because inevitably leads to a negative value in its real space representation.



Fourier transform of $F(q, t = \infty)$

$$G_s(r) \propto \langle \delta(r - \Delta R) \rangle$$

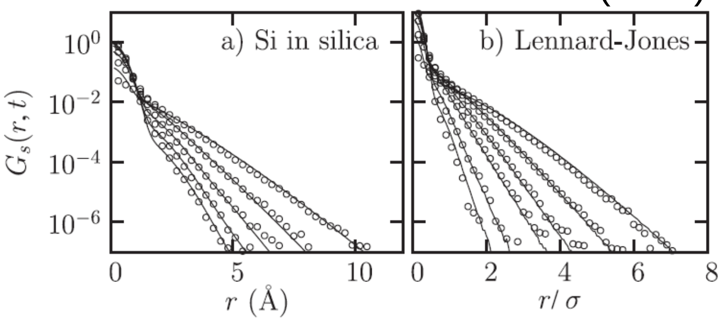
Probability distribution of a tagged particle (van Hove function).

Glass transition at high dimension

● *Recent progresses*

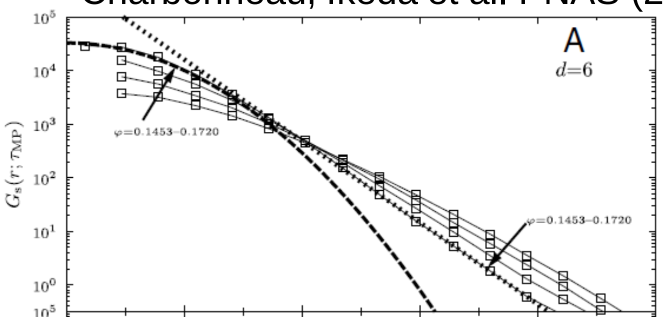
Non-Gaussian long tails due to Rare Hoppings

Chaudhuri et al. PRL (2007)



$d = 3$

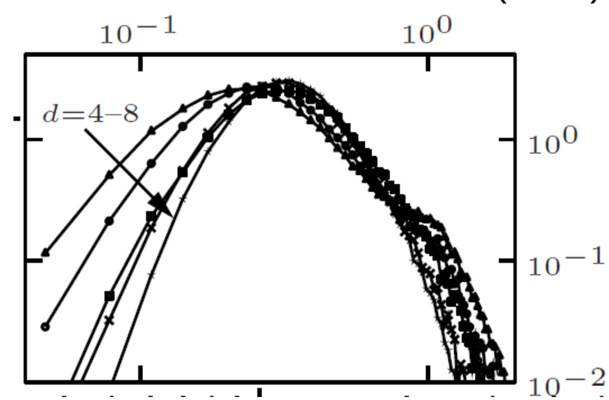
Charbonneau, Ikeda et al. PNAS (2012)



r

$d = 6$

Charbonneau et al. arXiv (2012)



r

$d = 4 \sim 8$

Glass transition at high dimension

- ***Recent progresses***

Violation of the Stokes-Einstein law

Ginzburg criteria for glass (Biroli Bouchaud, 2007)

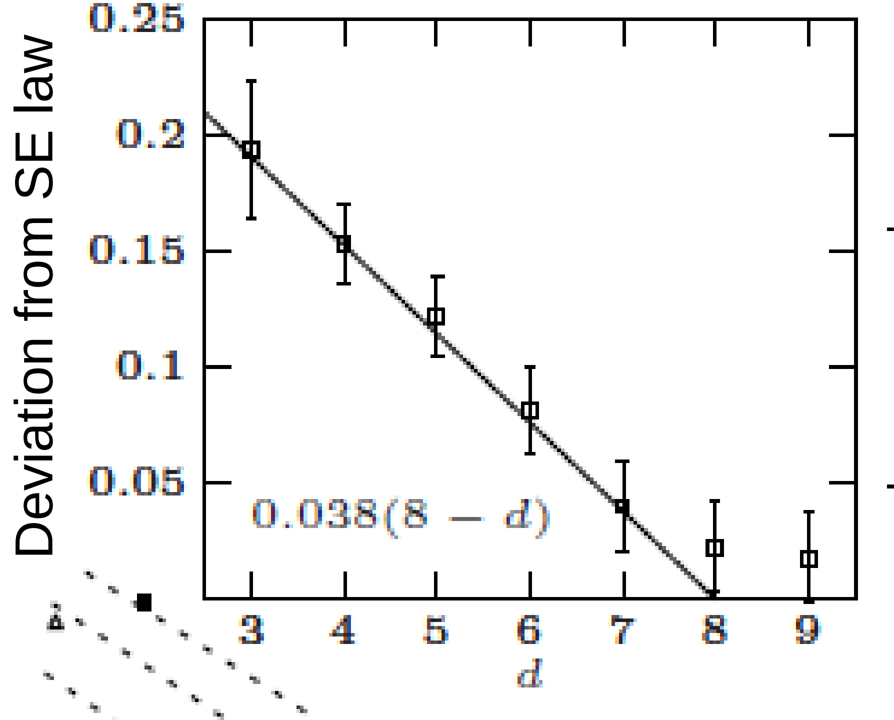
$$\left\langle \delta F^2(k,t) \right\rangle << \left\langle F(k,t) \right\rangle^2 \xi^d$$

$$\Leftrightarrow \quad \xi^4 << \xi^{d-4}$$

upper-critical dimension

$$d_c = 8$$

Charbonneau et al. arXiv (2012)



Glass transition at high dimension

- ***Recent progresses***

Exact Replica Theory Calculation at High d's without Gaussian ansatz (Kurchan Zamponi 2012, arXiv)

$$\boxed{\varphi_d = 4.8 \times d/2^d}$$

Remain unchanged…

最近の研究から

- *Glass transition at high dimensions*
- *Long ranged systems*
- *Jamming transition*
- *Randomly pinned glass transition*

Long Ranged Systems

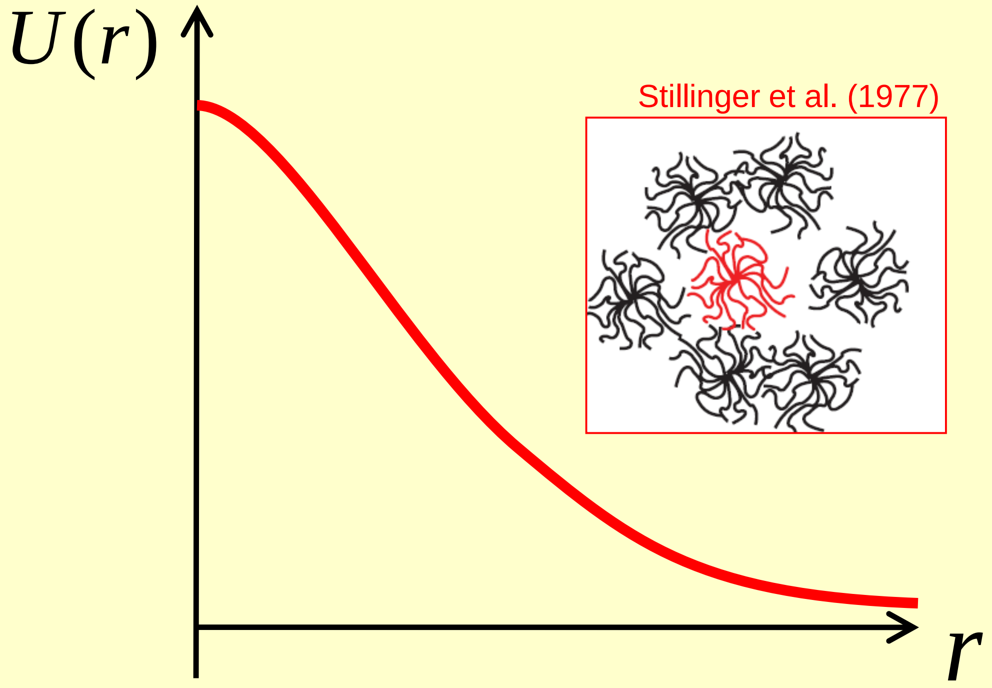
If RFOT scenario is correct,

- *MCT should work better in Higher Dimensions*
- *MCT should work better for Long-Ranged Systems*
- *Dynamic (MCT) transition point should mark the qualitative change of the free energy landscape (inherent structures)*

Long Ranged Systems

Long-ranged Potential = Dense Ultra-Soft Potential

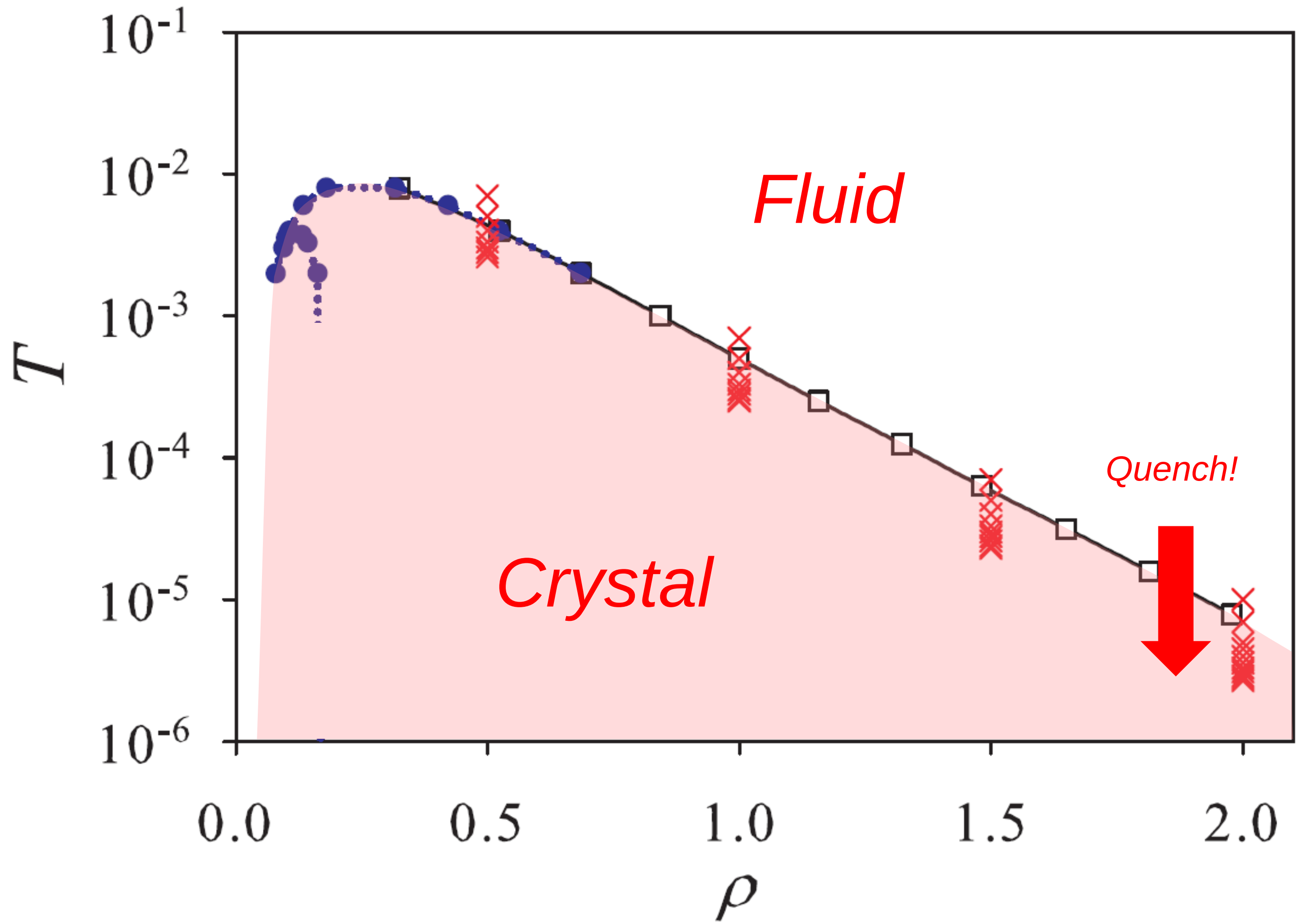
Gaussian Core Model (GCM)



$$U(r) = \varepsilon \exp\left[-\frac{r^2}{\sigma^2}\right]$$

Long Ranged Systems

Phase Diagram of Monatomic GCM

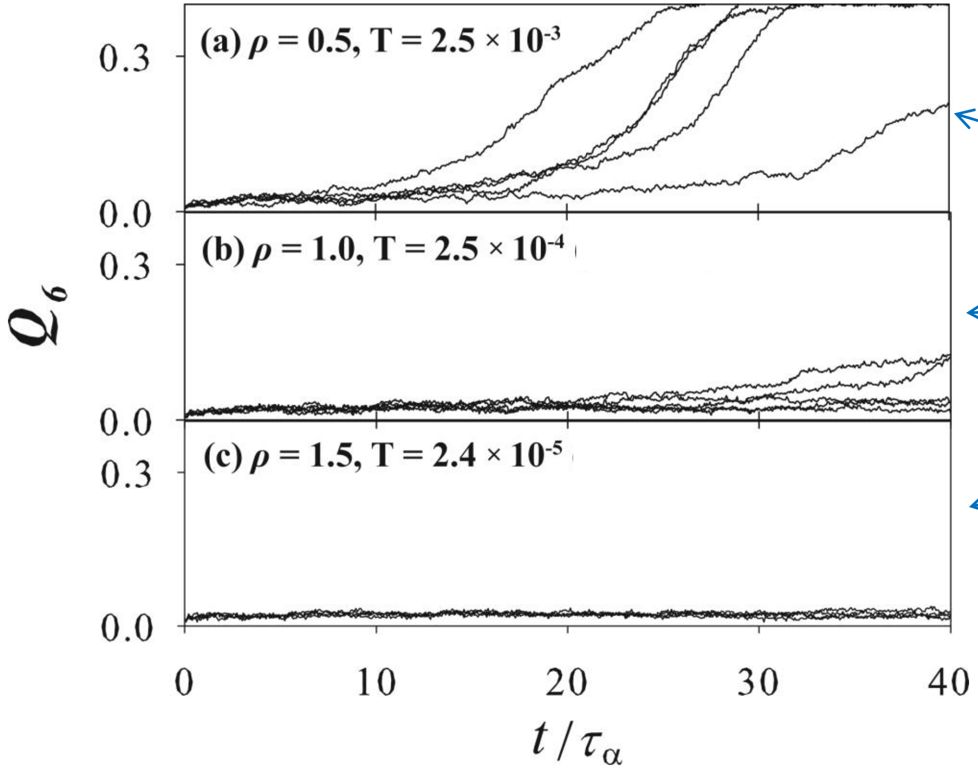


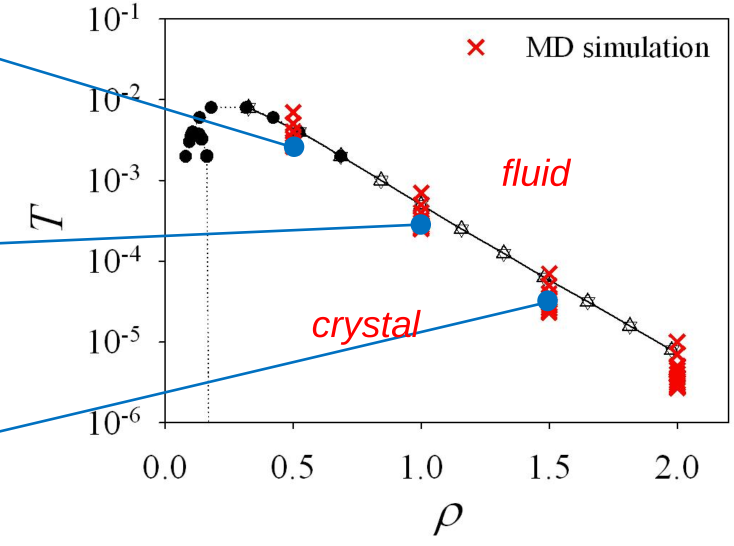
Long Ranged Systems

Monatomic GCM vitrifies!

And MCT works unprecedentedly well!!

And dynamic heterogeneities are weak!!!





Long Ranged Systems

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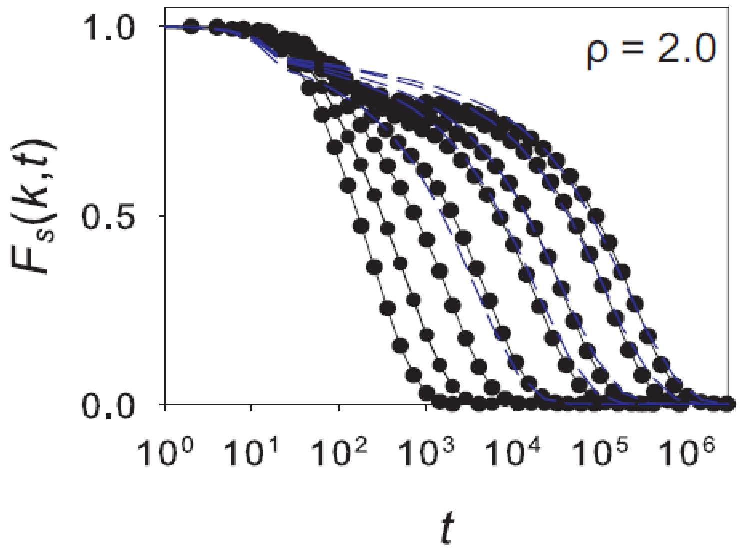
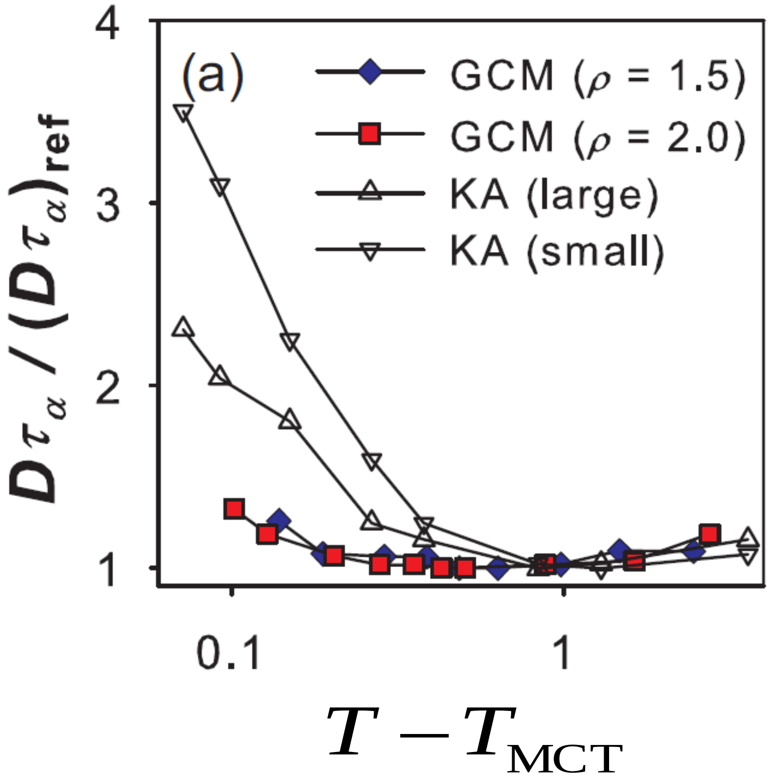


	KA LJ	GCM (ρ = 1.5)	GCM (ρ = 2.0)
T_{mct} (simulation+fitting)	0.435	0.202×10^{-5}	0.266×10^{-6}
T_{mct} (theory)	0.922	0.266×10^{-5}	0.340×10^{-6}
Deviations	112 %	33 %	28 %

Long Ranged Systems

Monatomic GCM vitrifies!
And MCT works unprecedentedly well!!
And dynamic heterogeneities are weak!!!

Weaker violation of Stokes-Einstein relation



Long Ranged Systems

Monatomic GCM vitrifies!

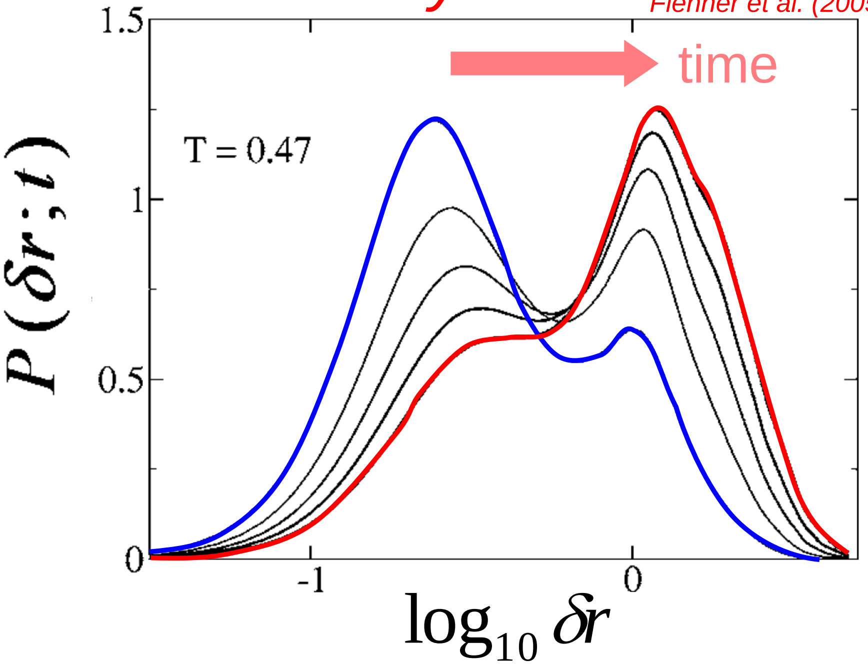
And MCT works unprecedentedly well!!

And dynamic heterogeneities are weak!!!

Distribution of the Particle Displacement δr

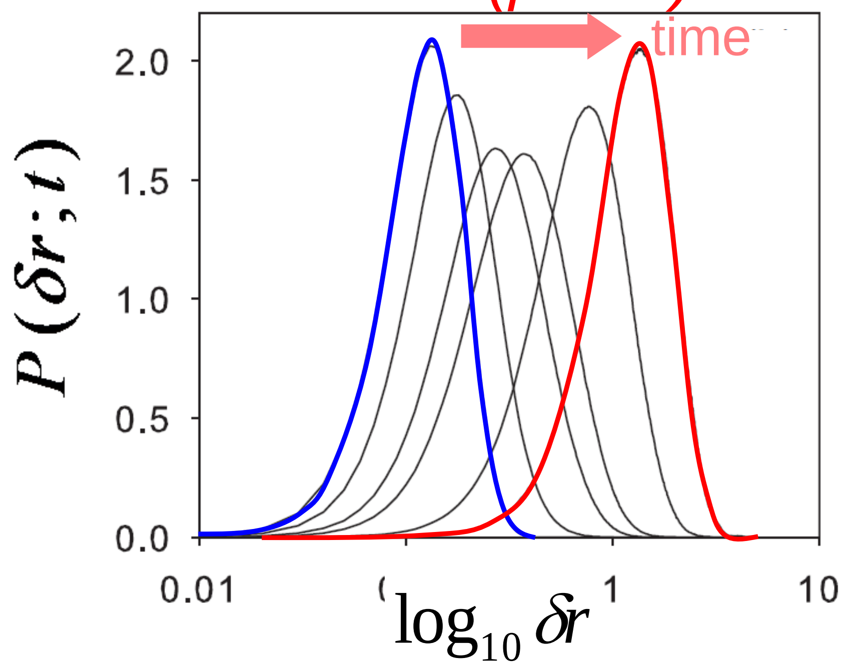
KA-LJ system

Flenner et al. (2005)



Bimodal distribution of fast and slow particles

GCM (ρ=2.0)

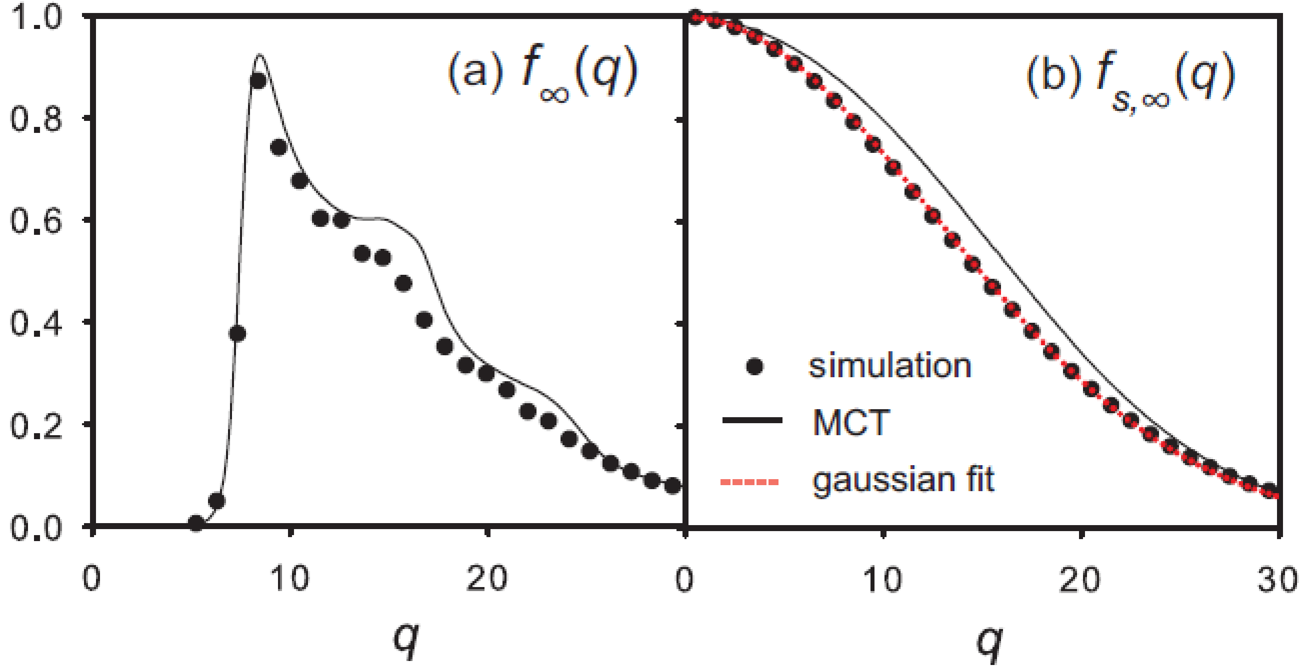


Single-peaked and Gaussian shape

Long Ranged Systems

Whereas GCM becomes more mean-field-like, MCT may start deteriorating, as the density increases

Debye-Waller factors of MCT become anomalous (non-Gaussian) at high densities!?

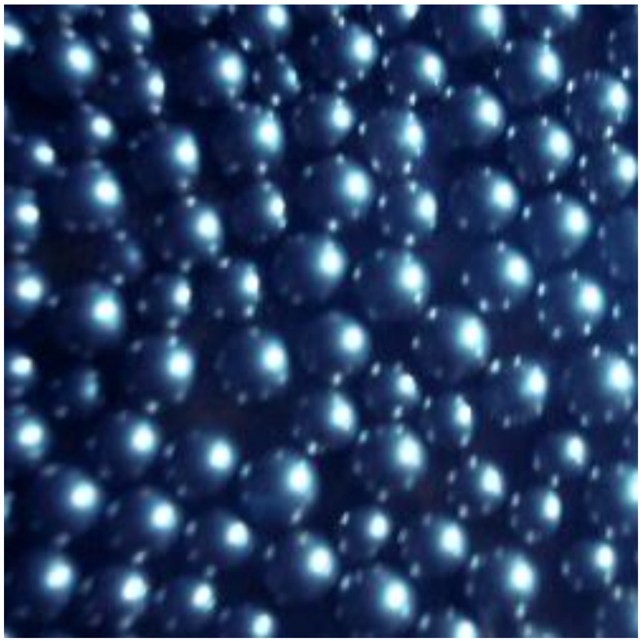


最近の研究から

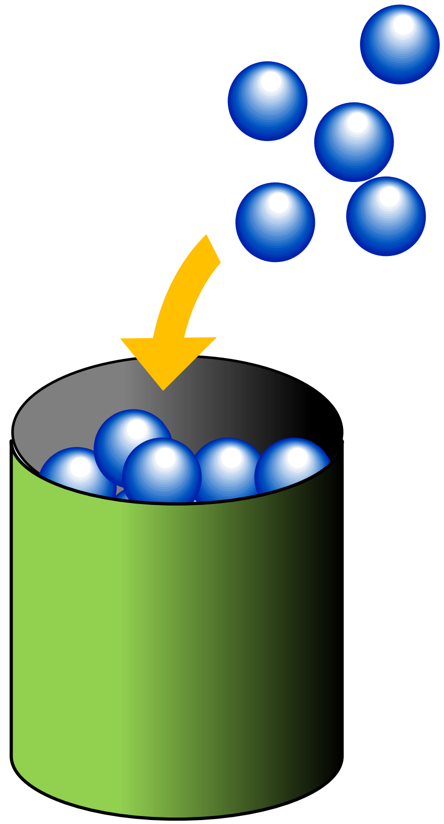
- *Glass transition at high dimensions*
- *Long ranged systems*
- *Jamming transition*
- *Randomly pinned glass transition*

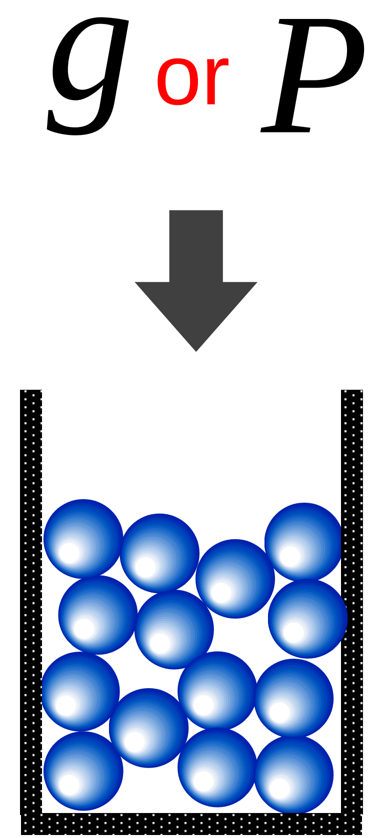
Jamming Transition

What is the Jamming Transition?



H. Tanaka's homepage

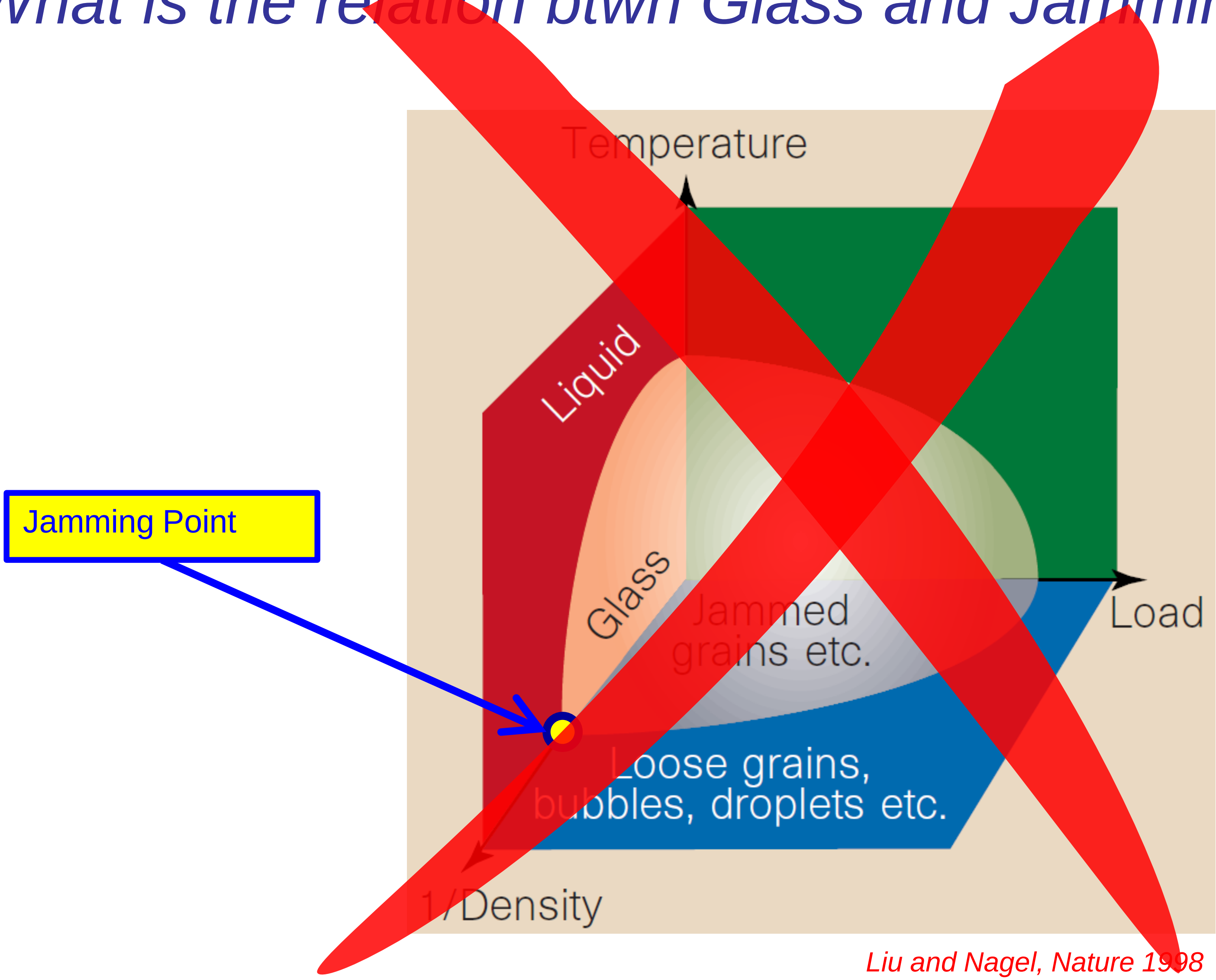




The volume fraction (density) of the hard balls poured into a jar randomly is always about $\varphi_{\mathrm{J}} \approx 64\%$ *!!*

Jamming Transition

What is the relation btwn Glass and Jamming Transition?



Liu and Nagel, Nature 1998

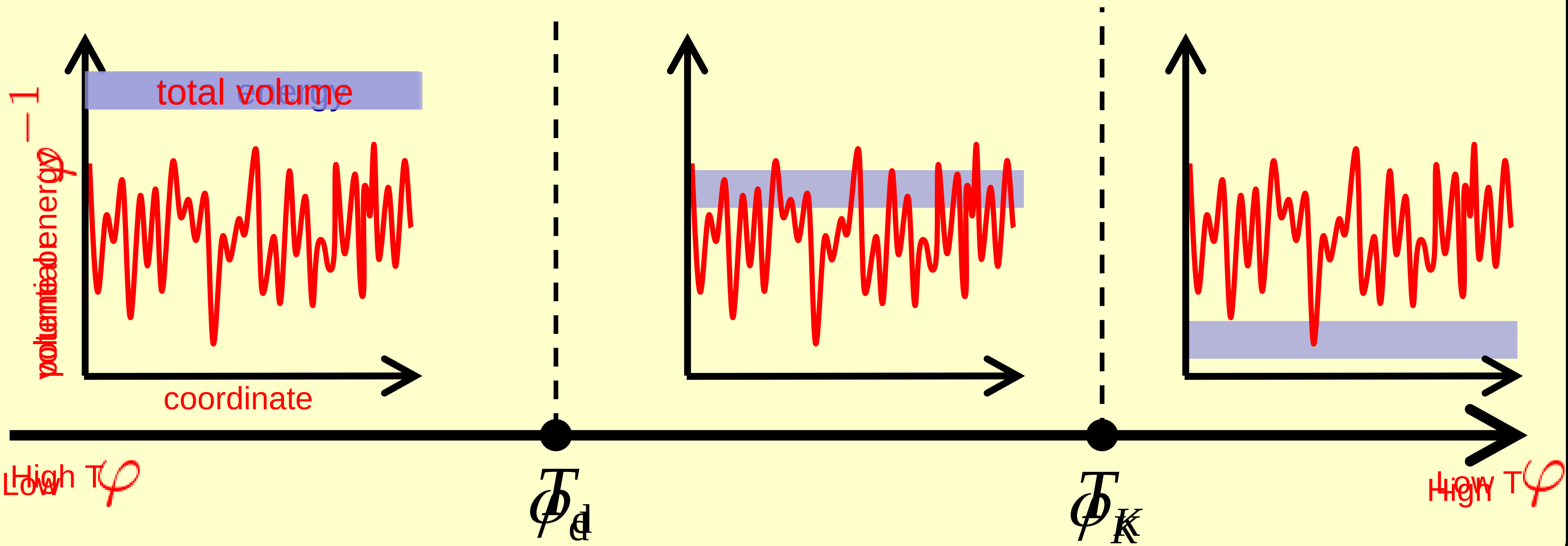
Jamming Transition

Mean Field "Theories" of the Glass transition

If we use

(P, V) *or* (P, φ) *instead of* (T, E)

density

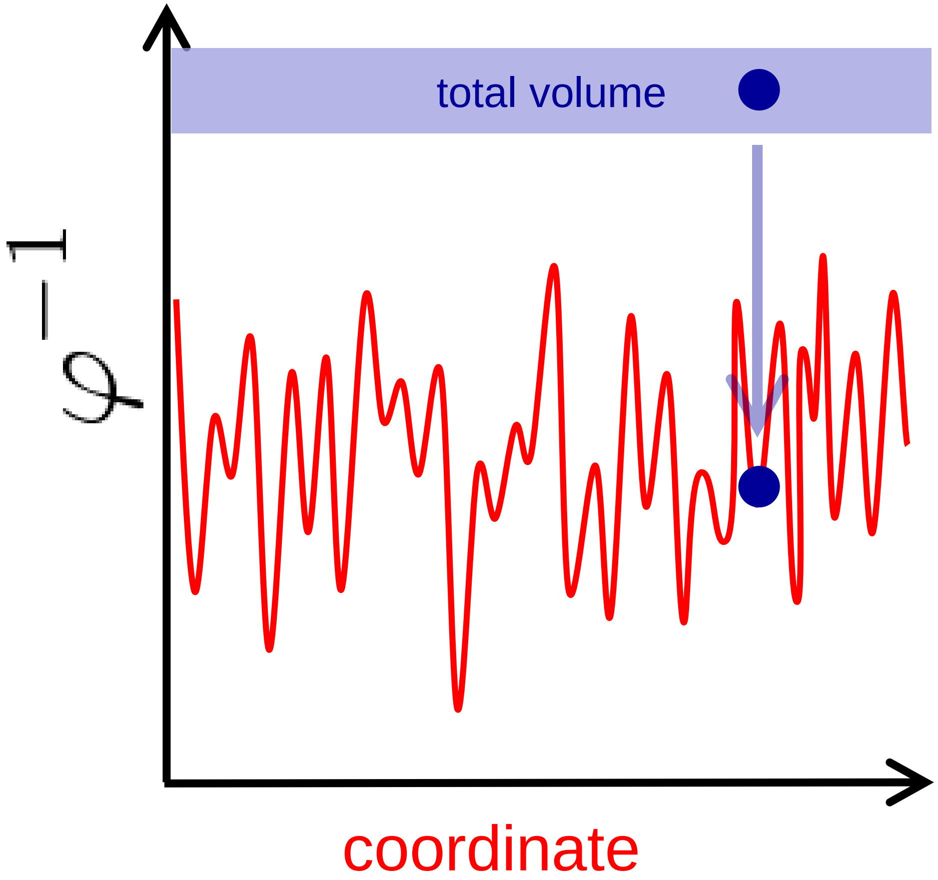


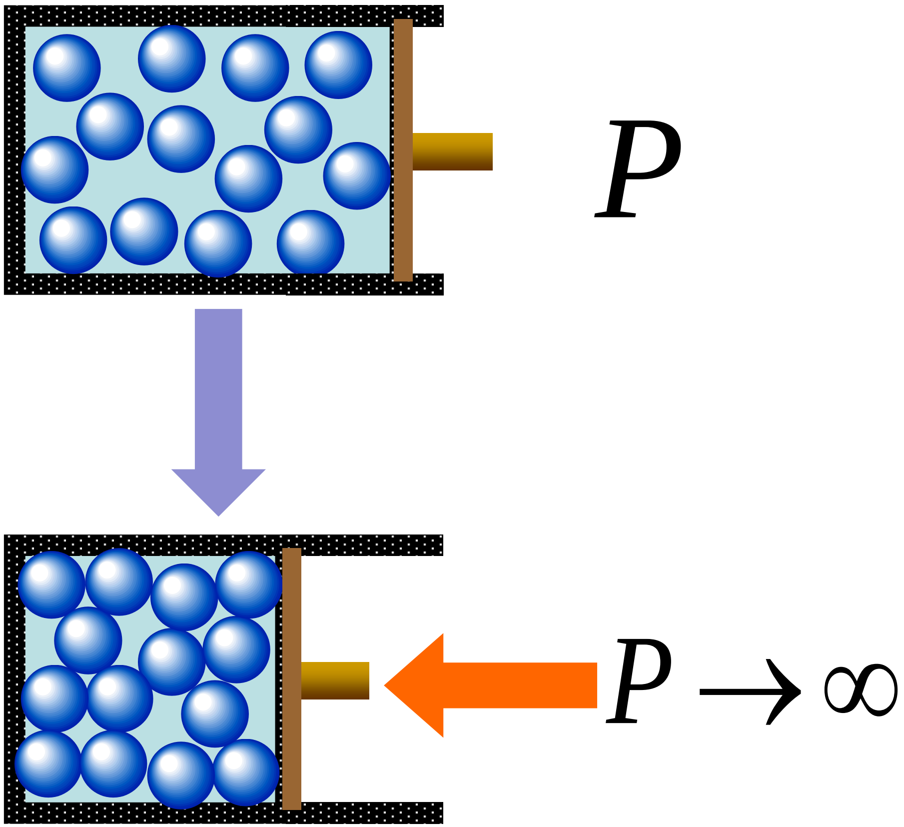
Dynamic (MCT)
transition point

Thermodynamic
transition point

Jamming Transition

Visualize the "Energy" Landscape

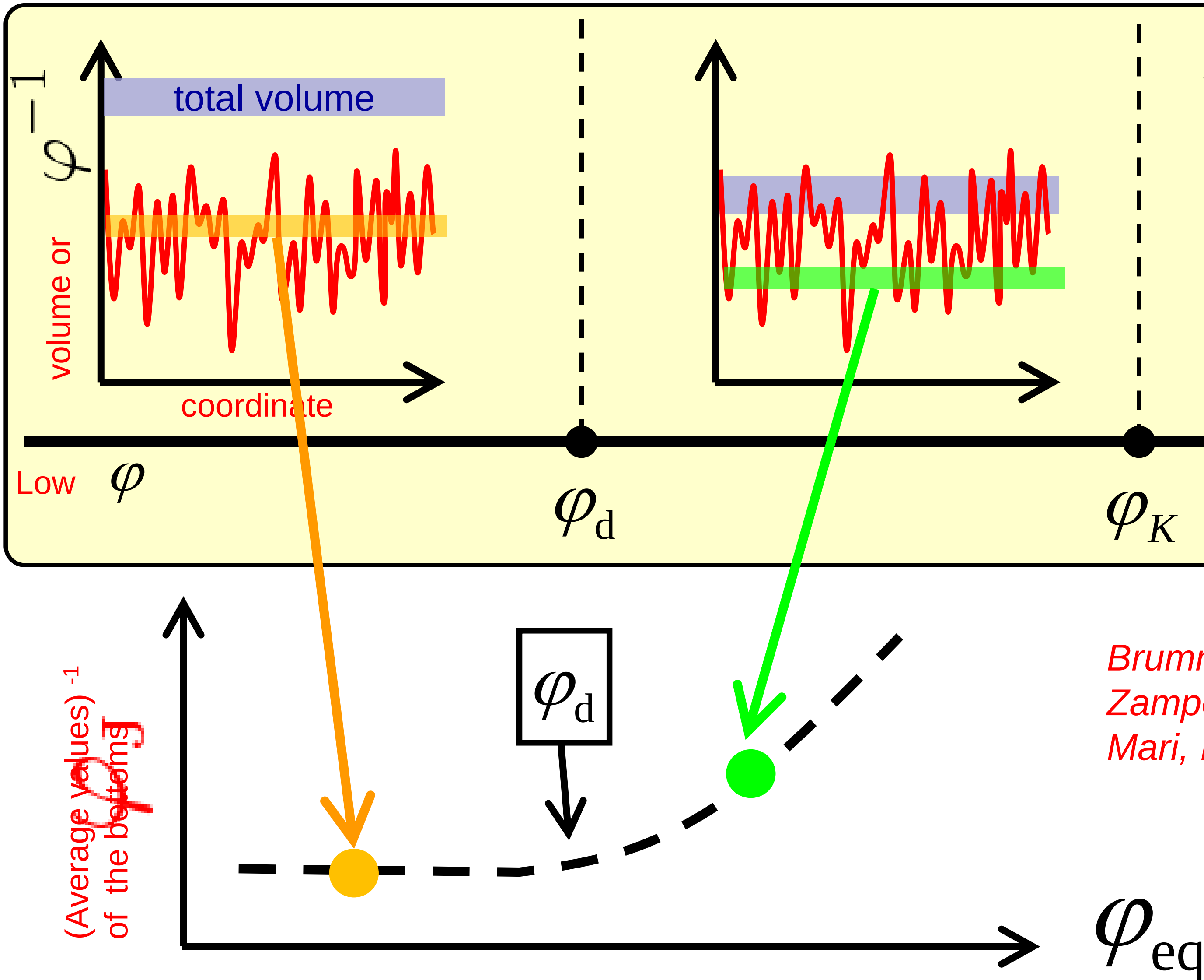




This is nothing but the Jamming transition

Jamming Transition

The average will be lowered as density increases



Brummer, Reichman (2005)
Zamponi, Parisi (2009)
Mari, Krzakala, Kurchan (2009)

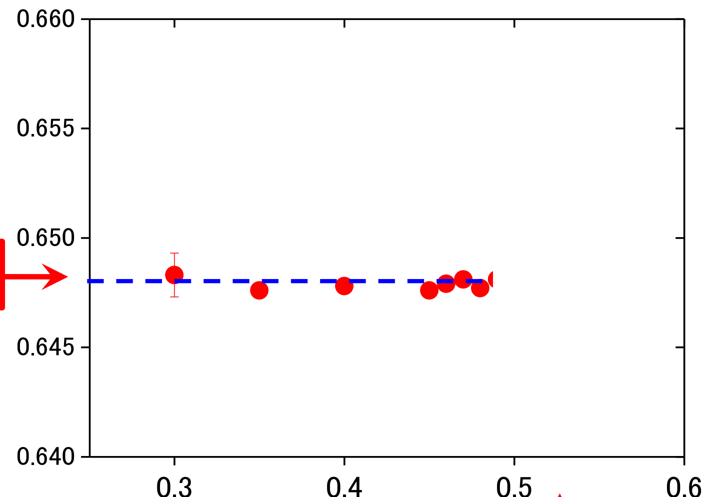
Jamming Transition

Initial density dependence of jamming transition points

Ozawa, Kuroiwa, Ikeda, and KM, PRL (2012)

Binary Hard Spheres with size ratio 1.4 and composition ratio 0.5:0.5

d=3



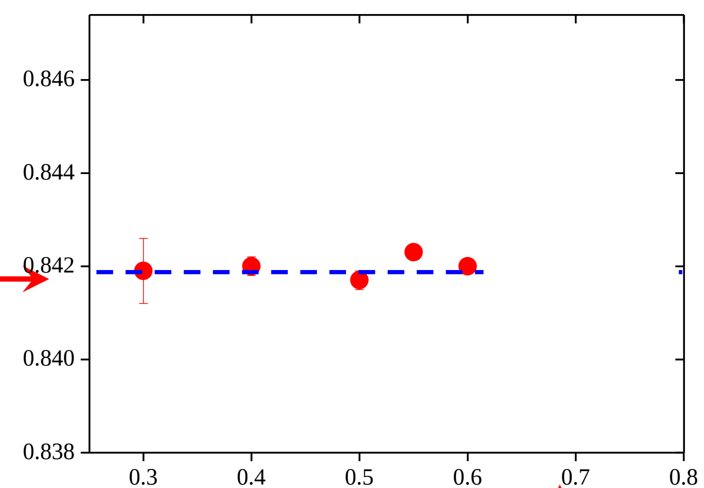
φ_J

$\varphi_J \approx 0.648$

φ_{eq}

$\varphi_d = 0.52$

d=2



φ_J

$\varphi_J \approx 0.842$

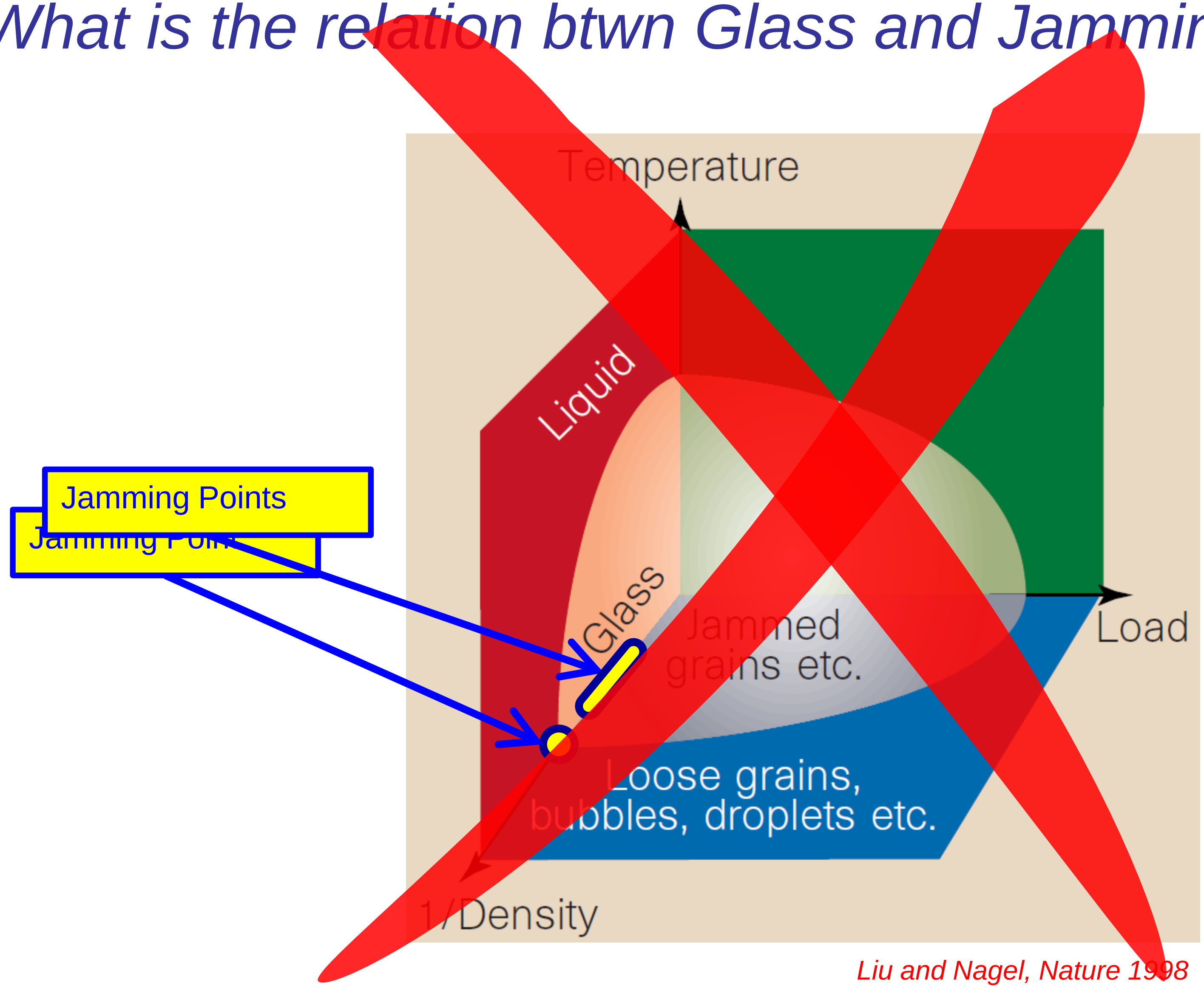
φ_{eq}

$\varphi_d = 0.69$

See also Chaudhuri, Berthier, Sastry, PRL **104** (2010) 165701
Pica Ciammarra, Canigrio, Candia, Soft Matter **6** (2010) 2957

Jamming Transition

What is the relation btwn Glass and Jamming Transition?

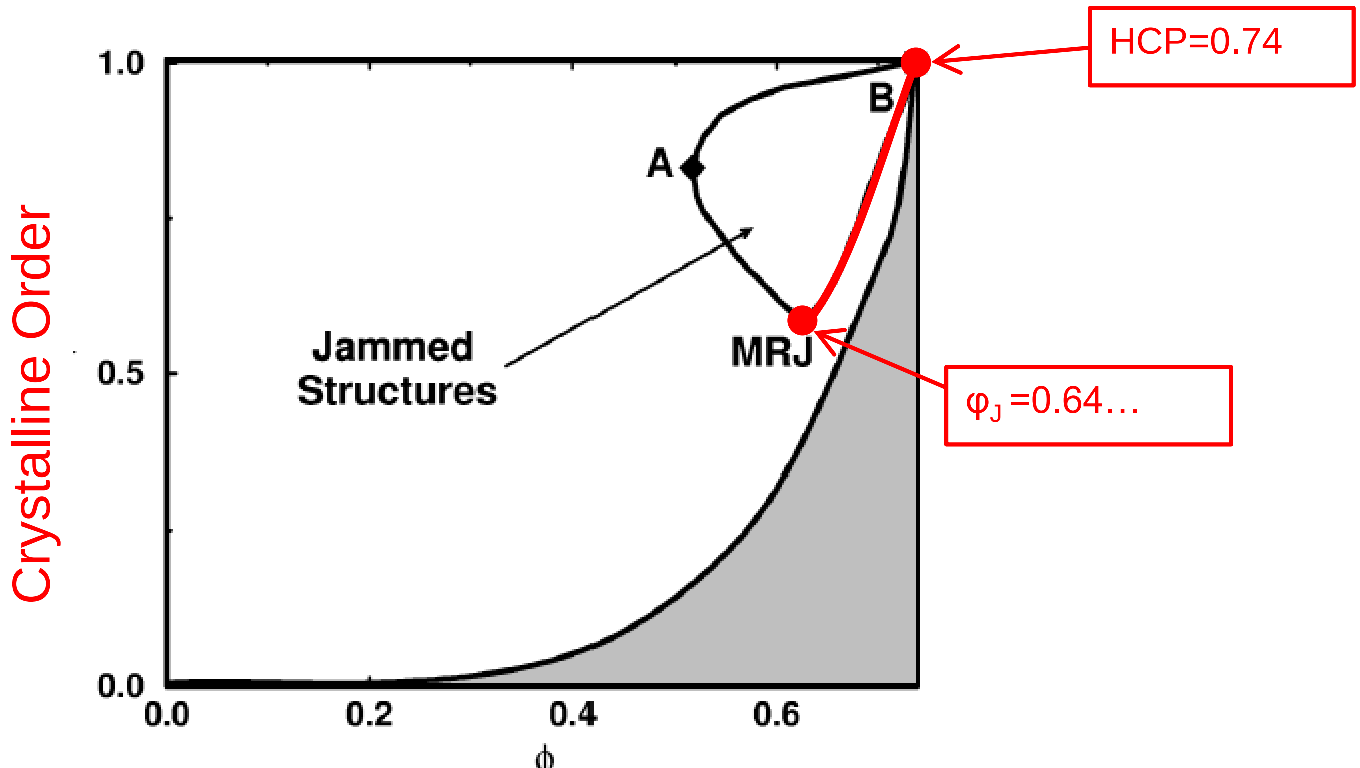


Liu and Nagel, Nature 1998

Jamming Transition

What is the jammed packing denser than 0.648? Is this just a less random (or more ordered) packing?

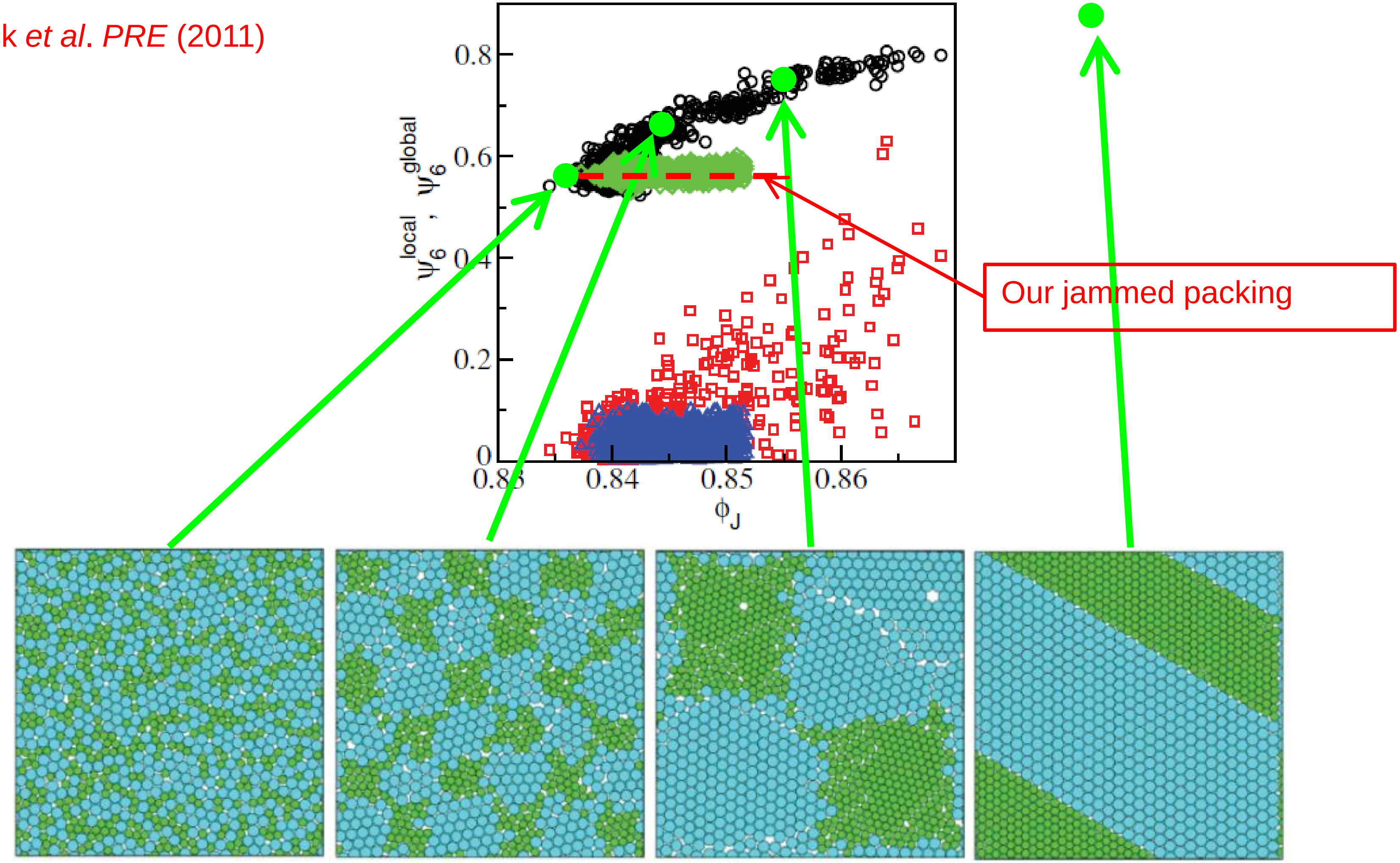
S. Torquato et al., PRL (2000)



Jamming Transition

Orientational Order Parameters

Schreck *et al*. *PRE* (2011)

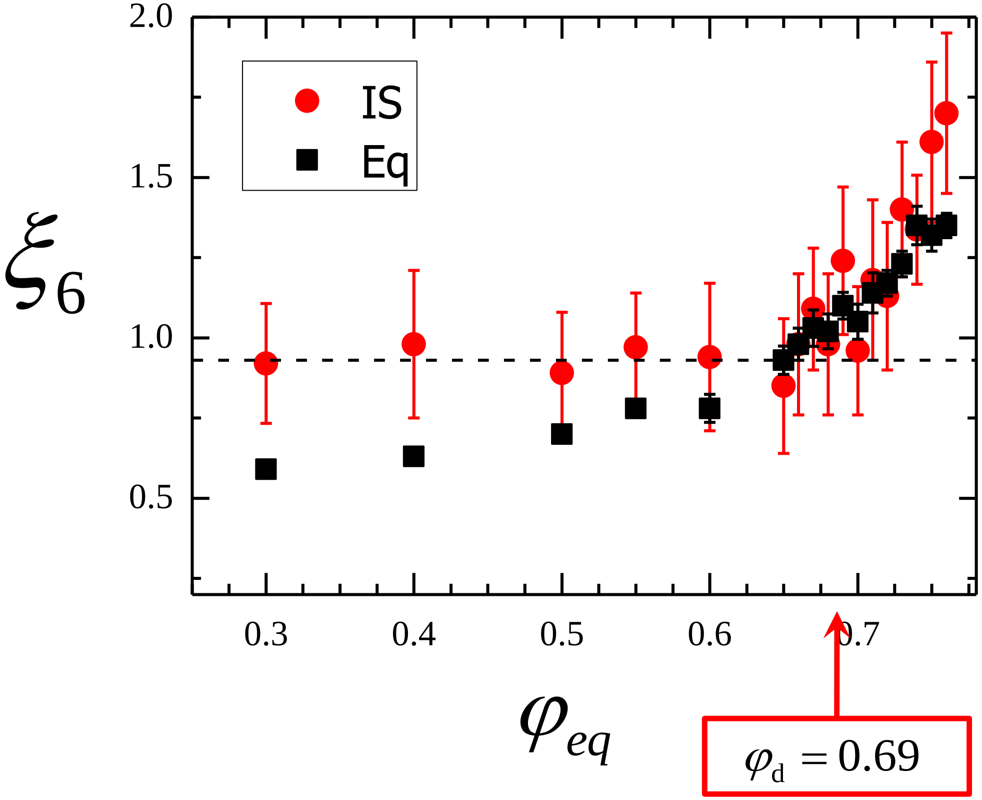


Jamming Transition

Hidden length

Ozawa, Kuroiwa, Ikeda, and KM, PRL (2012)

$$g_6(r) = \langle \delta\Psi_6(r)\delta\Psi_6(0)\rangle = \exp[-r/\xi]$$



Jamming Transition

What is the jammed packing denser than 0.648? Is this just a less random (or more ordered) packing?

For the ordered crystal, the density can not exceed φ=0.74 of HCP packing (Kepler, 1611)

For the disordered jammed state, can the density exceed φ=0.648 without being polluted by crystalline order?

Jamming Transition

Conclusions

Dynamic transition point marks the qualitative change of the free energy landscape (inherent structures)

More puzzles than answers…

- *What is the configurational properties beyond dynamic transition point?*
  Does any "amorphous-order" grow beyond $\varphi=0.648$??

- *Why does the mean field theory work so well quantitatively? Is it just fortuitous?*

最近の研究から

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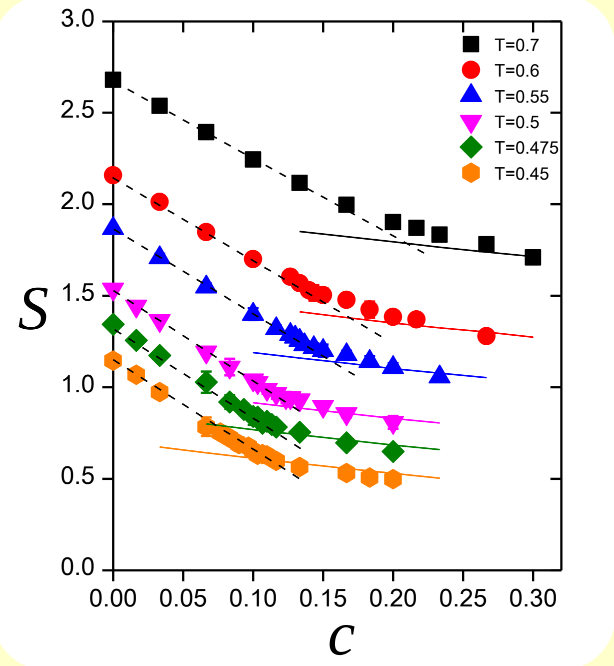
- ***Randomly pinned glass transition***

Thermodynamic Glass Transition of Randomly Pinned Systems



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(talk at UCGP 02/02/2015)

ACKNOWLEDGEMENTS

Collaboration

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Nagoya University

Funded by

Fluctuation & Structure

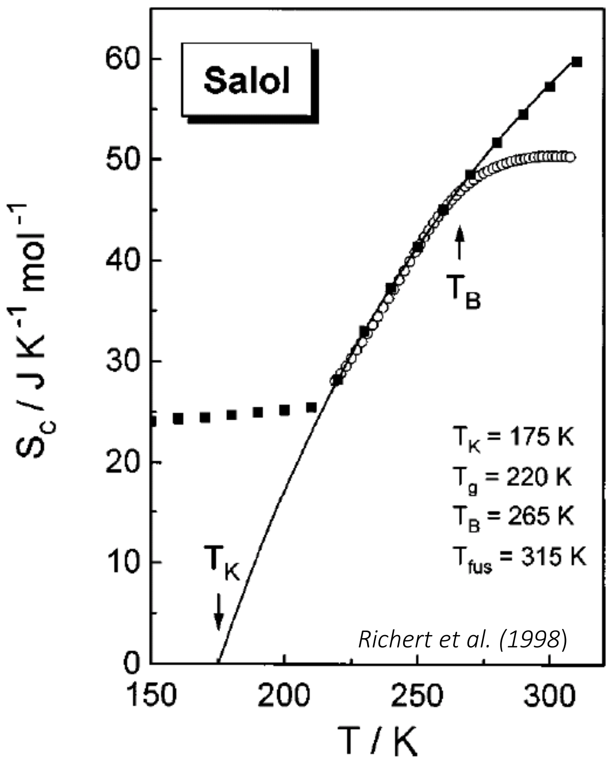
科研費

KAKENHI

INTRODUCTION

- Does the *(thermodynamic) Glass Transition Point* exit?

Configuratinal (residual) entropy



Yes!

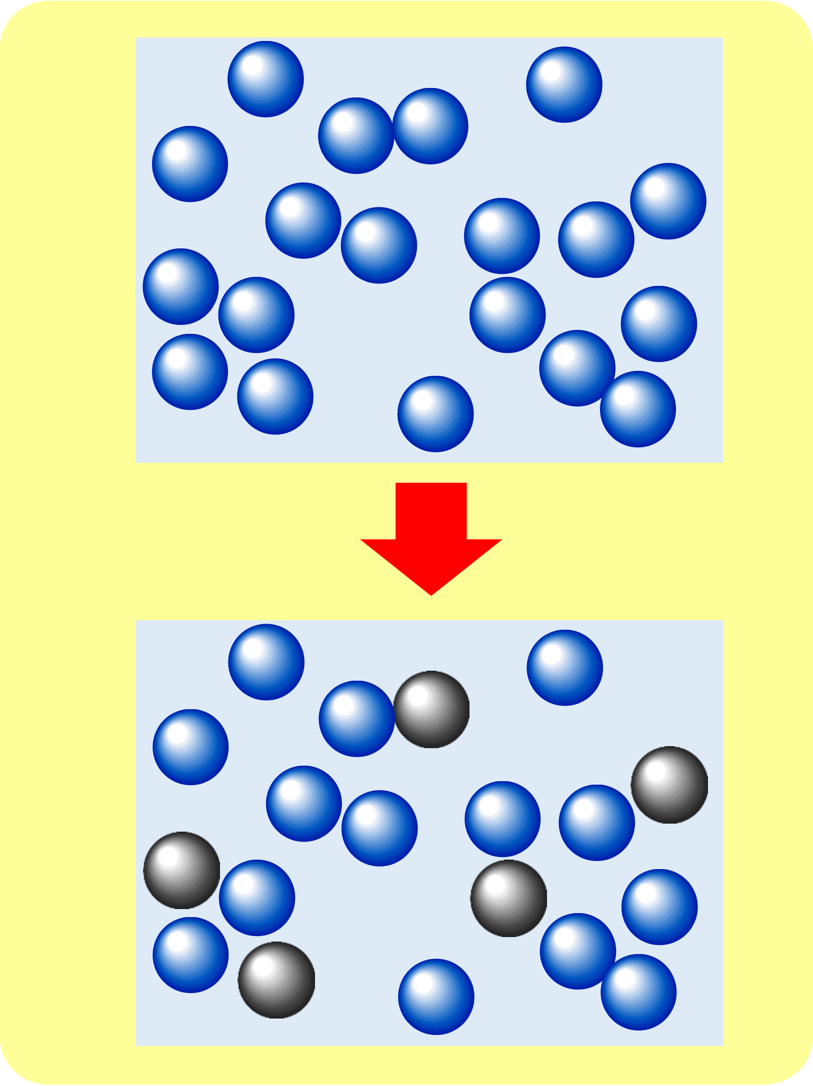
Adam-Gibbs theory
Random First Order Transition(RFOT)
etc…

No!

Purely Kinetic scenarios
Frustration pictures
etc…

Randomly Pinned Glass Transition

Kim (2000), Krakoviack(2005), KM and others (2009~)



1. Randomly distribute all particles

2. Let them run till equilibrated

3. Quench (pin) a fraction of particles while leave others moving

4. Take ensemble and sample averages

Randomly Pinned Glass Transition

Cammarota and Biroli (2012)

p-spin mean field model with random pinning

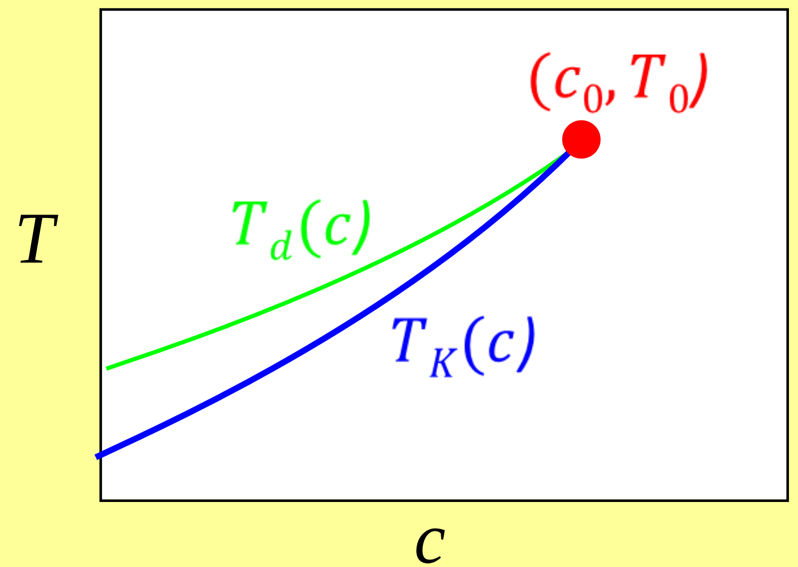
$$H = -\sum_{i,j,k} J_{ijk} s_i s_j s_k$$

$$\langle J_{ijk} \rangle = 0, \qquad \langle J_{ijk}^2 \rangle = \frac{3!}{2N^2}$$

- T_K (ideal glass) and T_d (dynamic) transition line rise as c (density of pinned spins) increases.

- They meet and terminate at the end point

Cammarota et al. (2012)

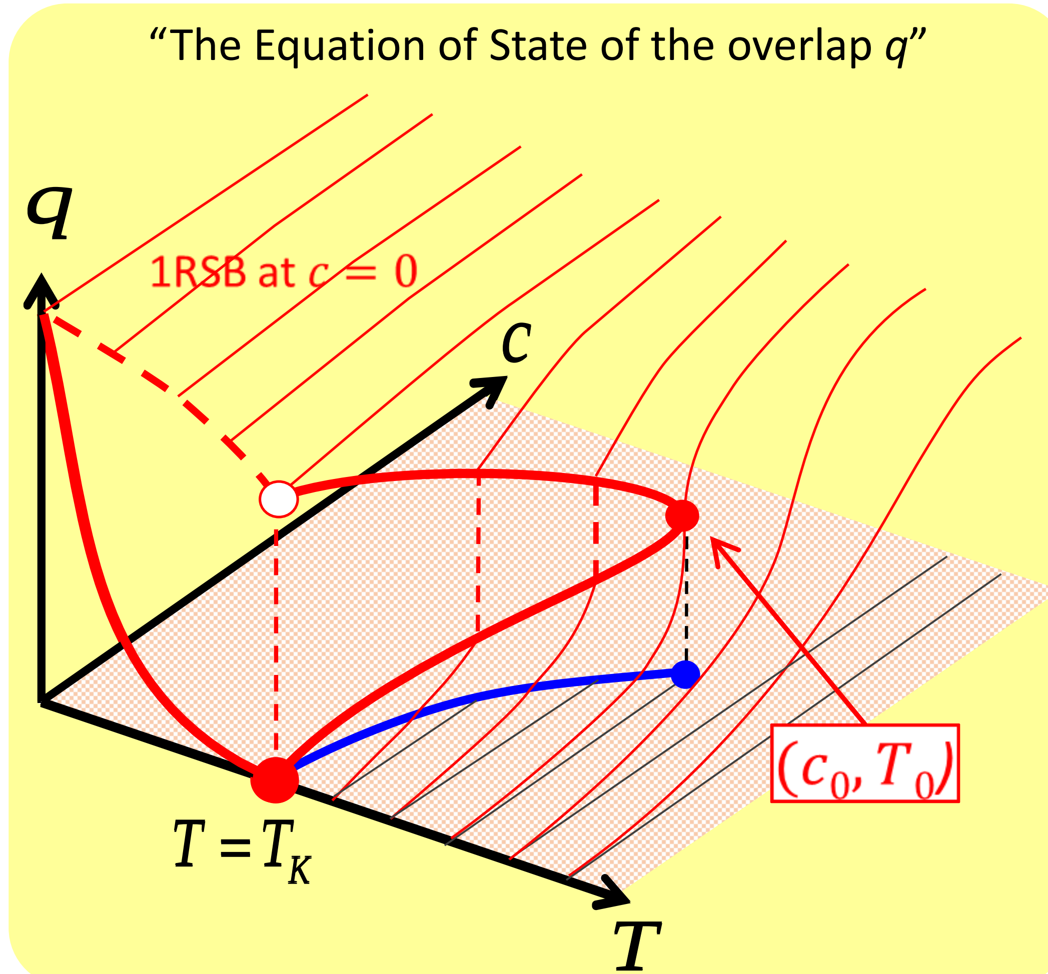


Randomly Pinned Glass Transition

Cammarota and Biroli (2012)

The ideal glass transition is a mix of 1RSB + 1st order transitions

- The overlap q discontinuously jumps at T_K
- The configurational entropy S_c vanishes at T_K
- The end point (c_0, T_0) is of the universality class of Random Field Ising Model



Randomly Pinned Glass Transition

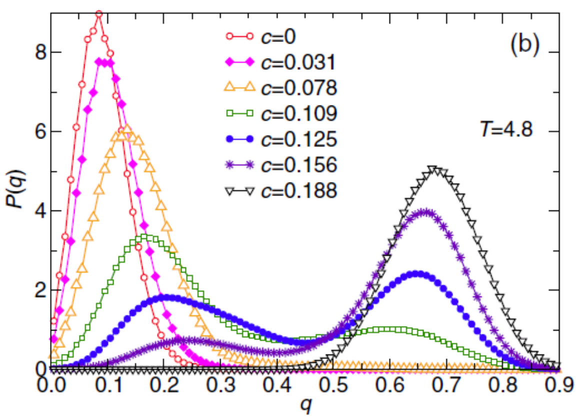
Kob and Berthier (2013)

Replica Exchange Simulation for harmonic binary system

Overlap $$q = \frac{1}{N'}\sum_{i=1}^{N'} n_i^{\alpha} n_i^{\beta}$$

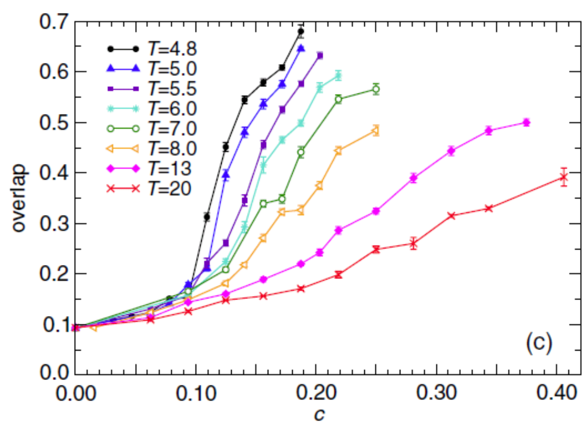
Distribution of q

Double peaked:
The 1st order transition in finite sized box



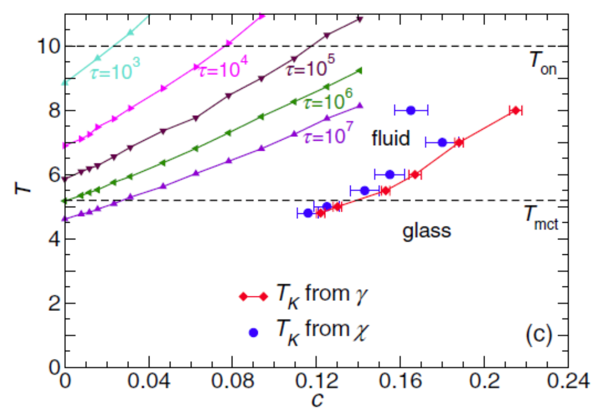
Averaged overlap q

Discontinuous jump



Phase diagram

Ideal glass!



Kob et al. (2013)

Randomly Pinned Glass Transition

AGENDA

1. Overlap q: discontinuously jump at T_K

2. Configurational Entropy S_c : vanishing at T_K

3. Dynamic Transition (spinodal) line T_d :

   merging with T_K at large c

Randomly Pinned Glass Transition

Model and Simulation Method

System: Kob-Andersen LJ binary mixture

N=300 (and 150)

Simulation methods:

Thermodynamics: Replica Exchange

Dynamics (at higher T): MC

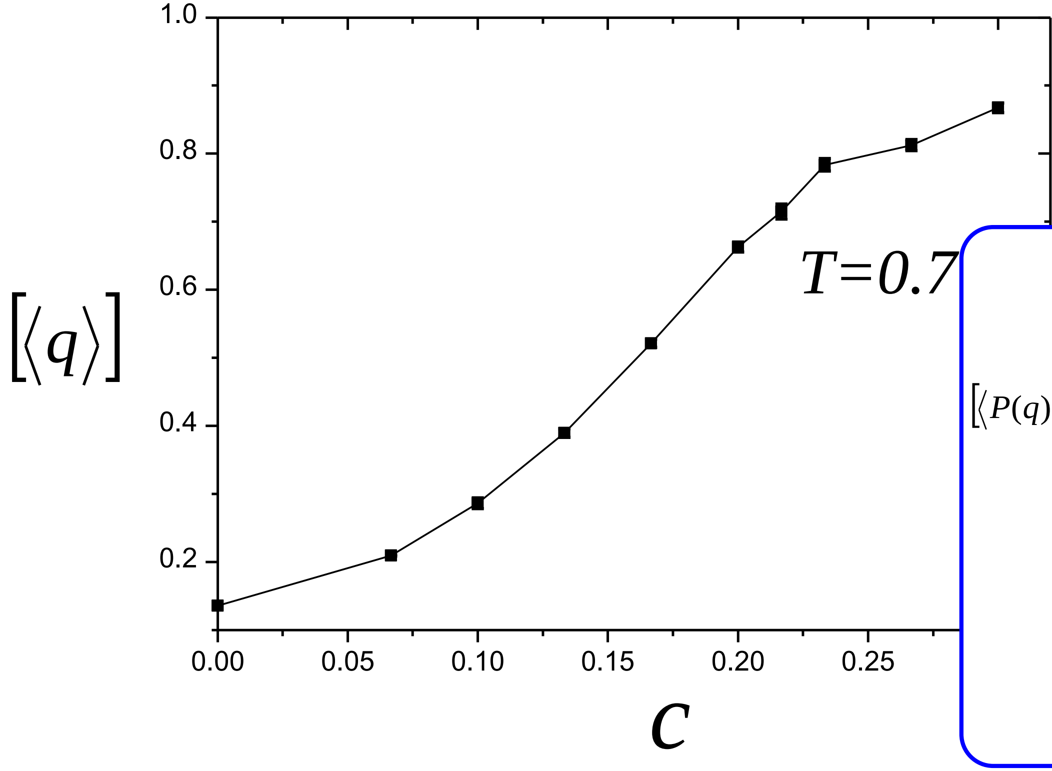
and

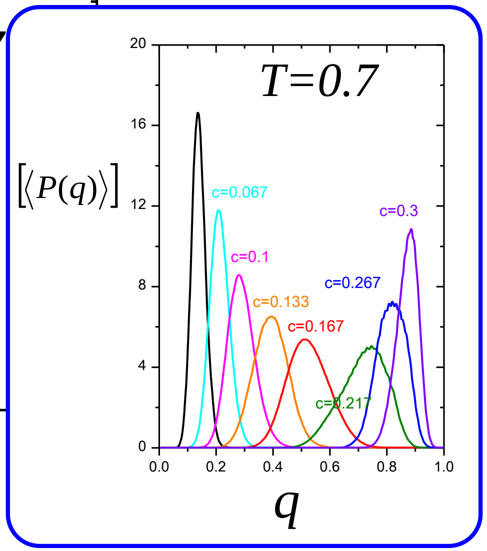
Thermodynamic Integration

Randomly Pinned Glass Transition

Overlap $$q = \frac{1}{N}\sum_{i,j}^{N} \theta\left(a - \left|R_i^{\alpha} - R_j^{\beta}\right|\right) \qquad (a = 0.3)$$

Averaged Overlap

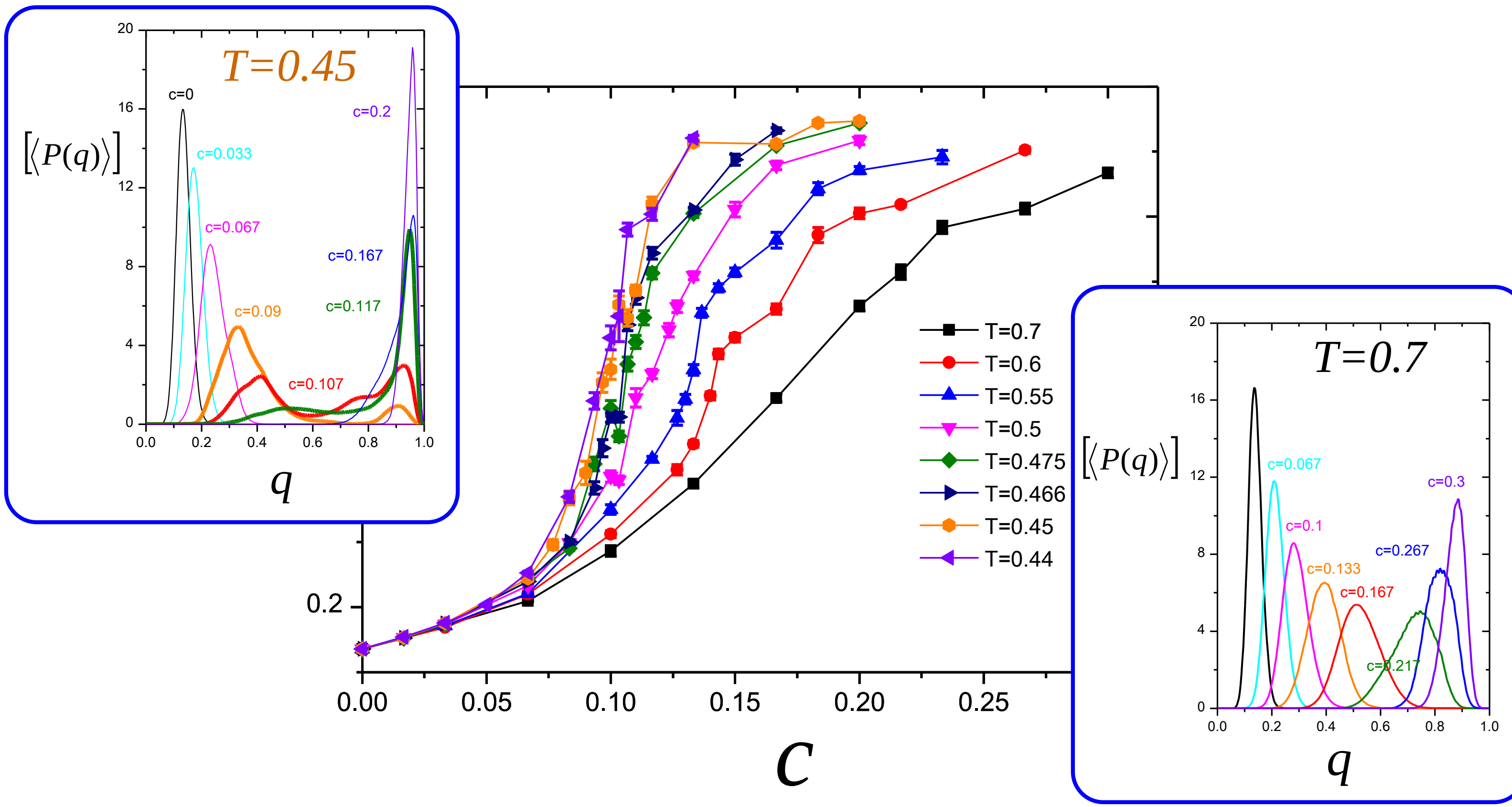




Randomly Pinned Glass Transition

Overlap $q = \frac{1}{N}\sum_{i,j}^{N} \theta(a - |R_i^\alpha - R_j^\beta|)$ $(a = 0.3)$

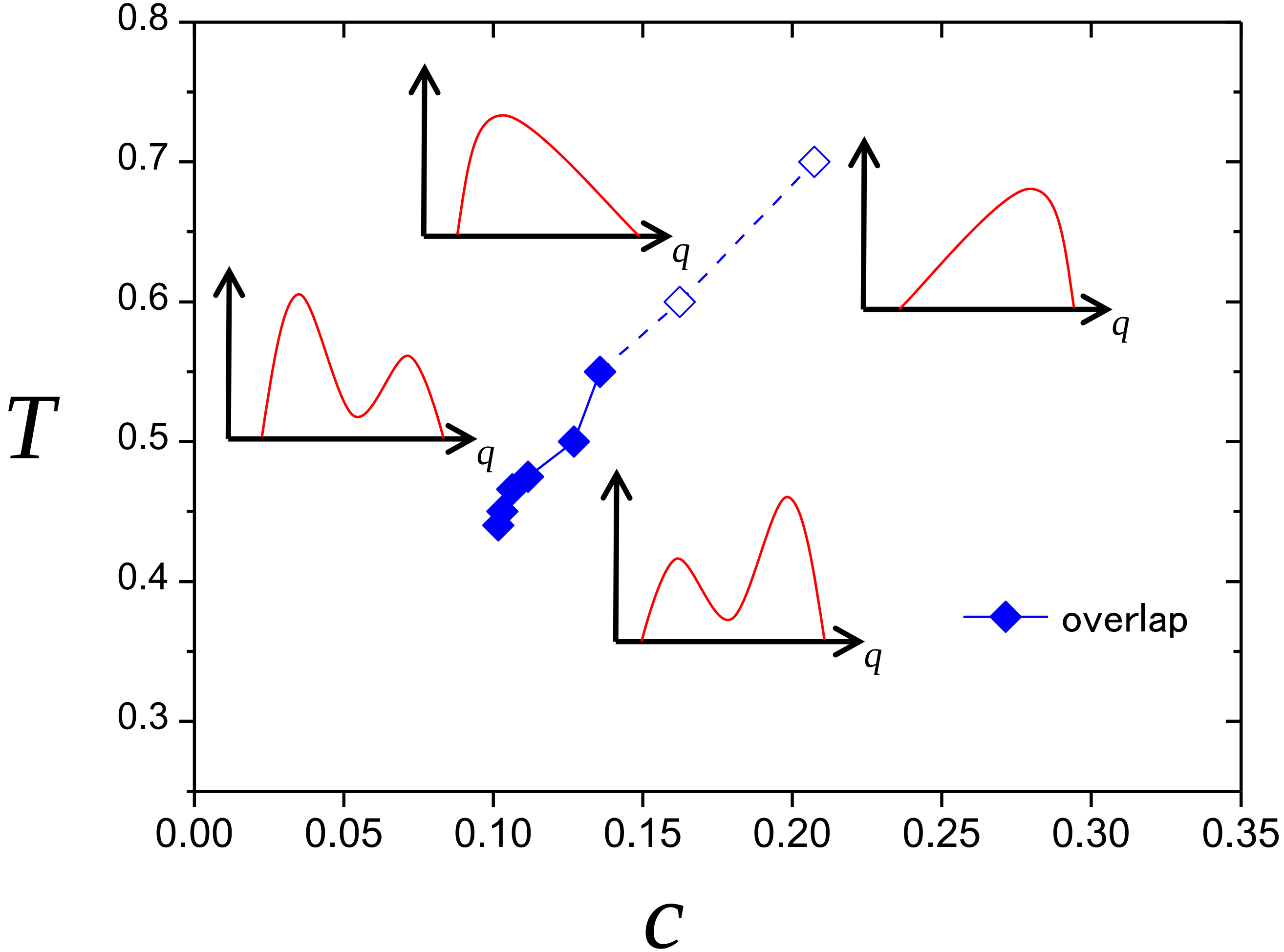
Averaged Overlap



Randomly Pinned Glass Transition

Phase Diagram

$T_K(c)$ obtained as a point $\left[\langle P(q)\rangle\right]$ becomes symmetric



Randomly Pinned Glass Transition

AGENDA

1. Overlap q: discontinuously jump at T_K

2. Configurational Entropy S_c : vanishing at T_K

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   merging with T_K at large c

Randomly Pinned Glass Transition

Total Entropy of Pinned System

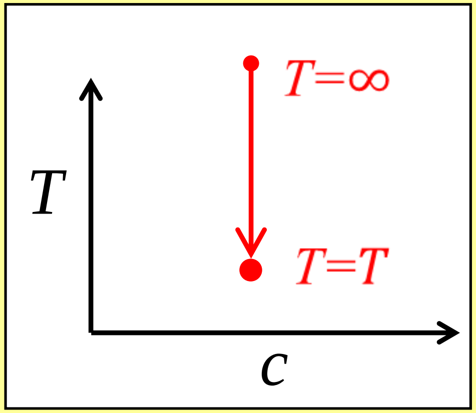
Thermodynamic Integration Method: *Sciortino et al (1999), Coluzzi et al. (2000)*

1. Integrate over a given pinned configuration $\vec{S}$

$$S(\vec{S},\beta)=S(\vec{S},0)+\beta\langle U\rangle(\vec{S},\beta)-\int_0^\beta \mathrm{d}\beta'\ \langle U\rangle(\vec{S},\beta')$$

2. Average over pinned configurations

$$S(\beta)=\left[S(\vec{S},\beta)\right]$$



Vibrational Entropy of Pinned System

1. Harmonic approximation around the inherent structures e_{IS}

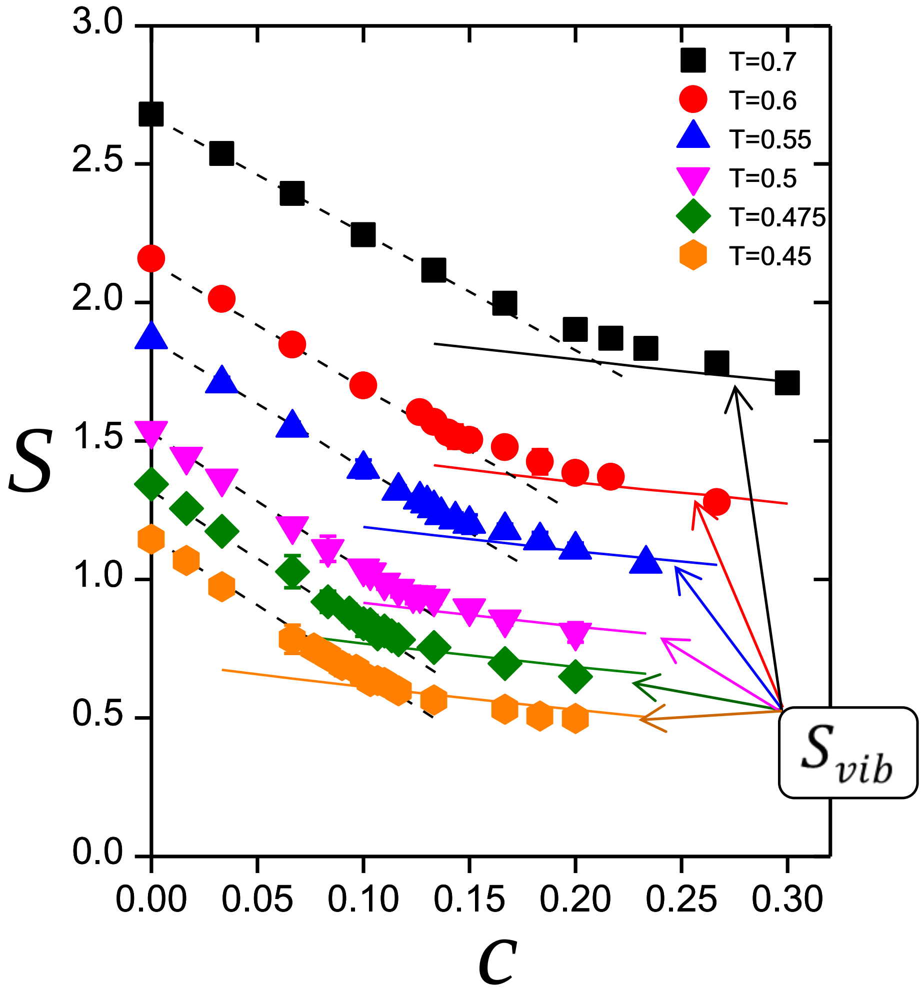
$$S_{\mathrm{vib}}(\vec{S},\beta)=\sum_a \{1-\log(\beta\hbar\omega_a)\}(\vec{S})$$

2. Average over pinned configurations

$$S_{\mathrm{vib}}(\beta)=\left[S_{\mathrm{vib}}(\vec{S},\beta)\right]$$

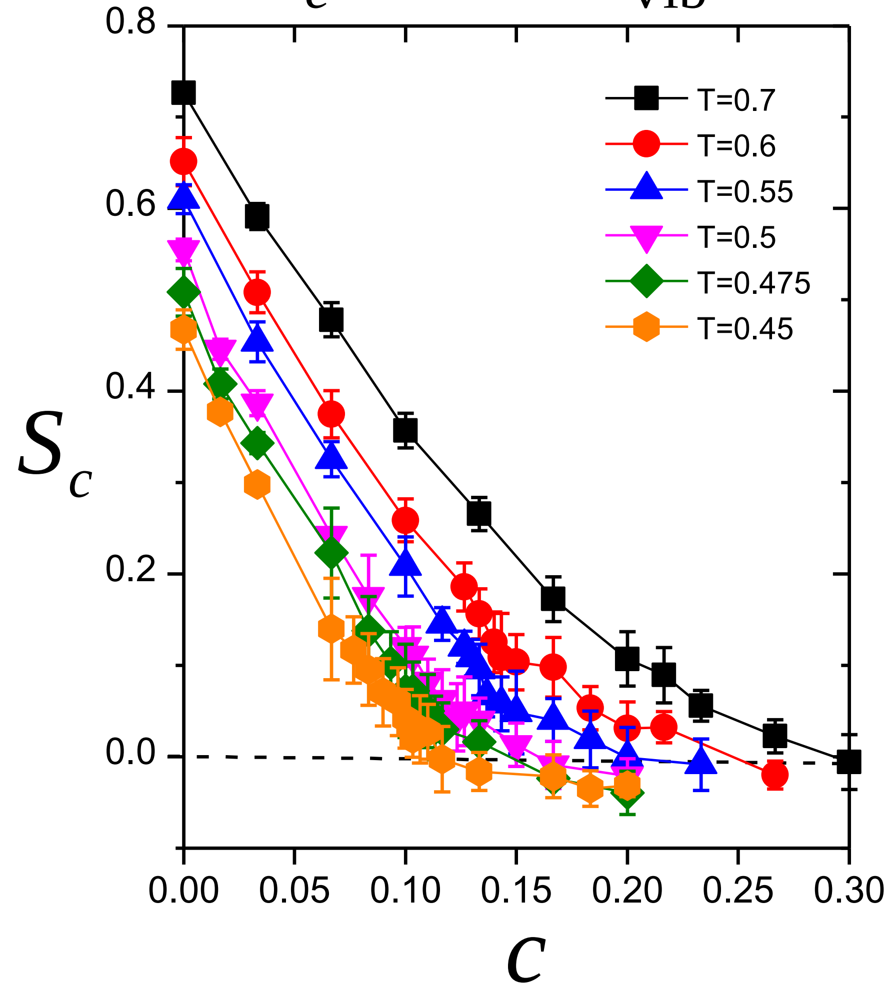
Randomly Pinned Glass Transition

Total Entropy



Configurational Entropy

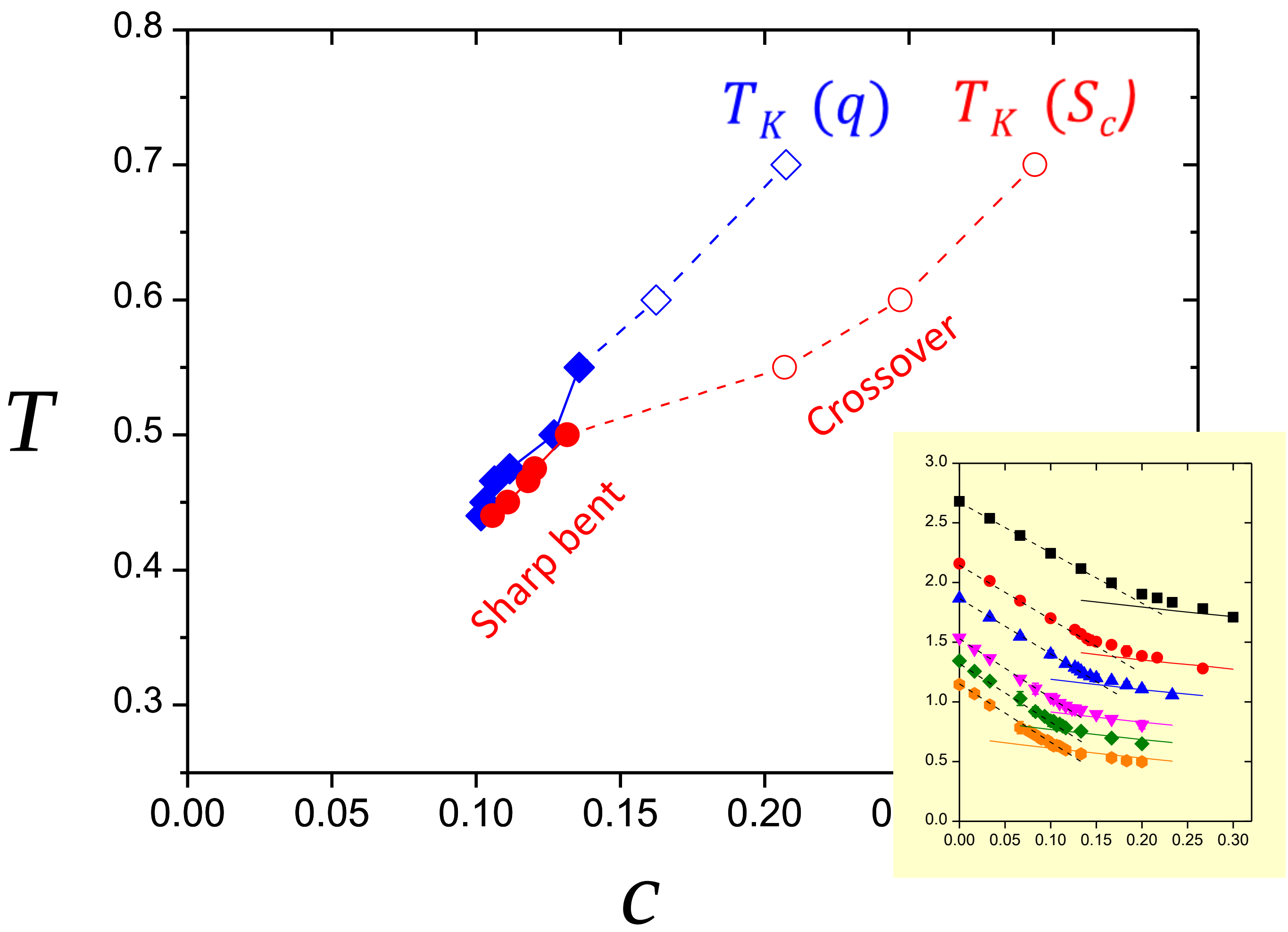
$$S_c = S - S_{\mathrm{vib}}$$



Randomly Pinned Glass Transition

Phase Diagram

$T_K(c)$ obtained as a point where $S_c = 0$



Randomly Pinned Glass Transition

AGENDA

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3. Dynamic Transition (spinodal) line T_d :

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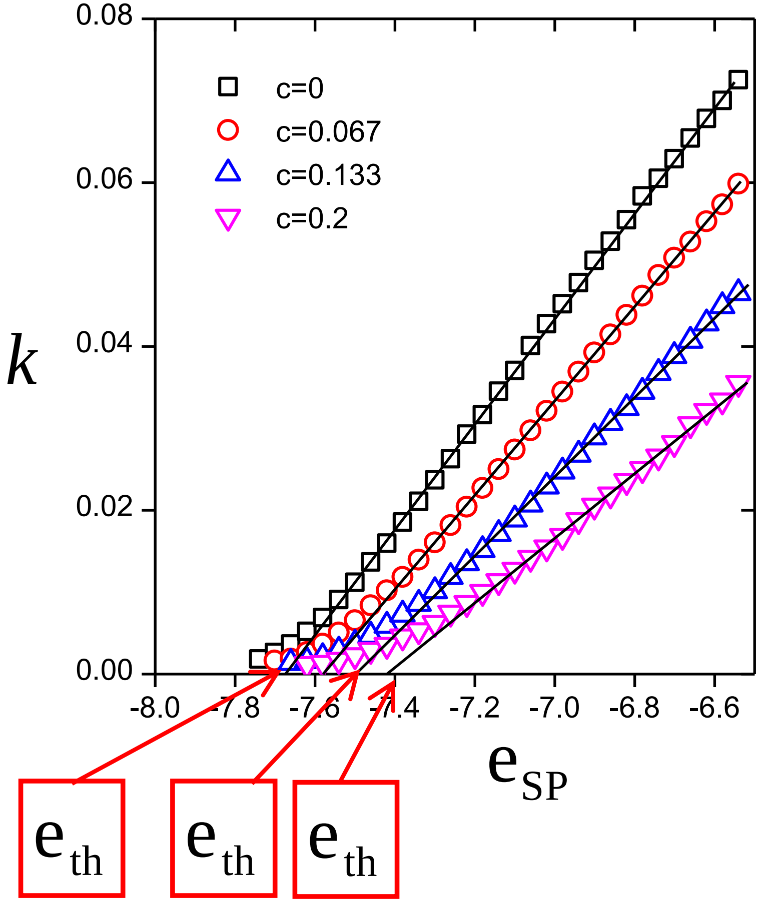
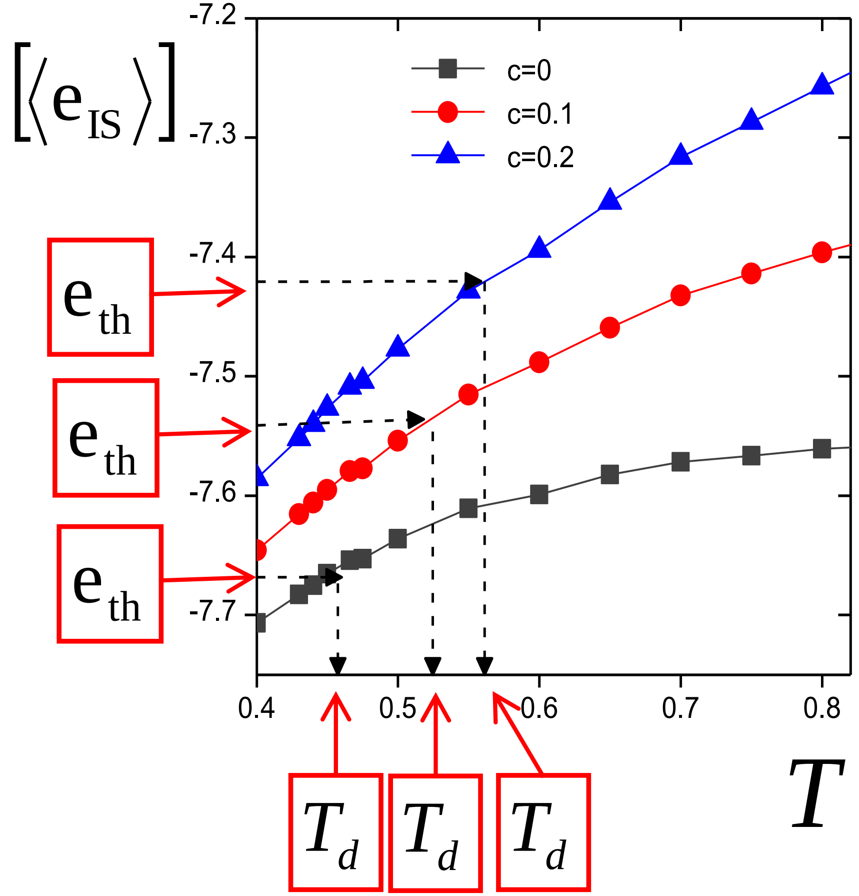
Randomly Pinned Glass Transition

The dynamic (MCT) transition T_d (Angelani et al., Broderix et al. 2000)

# of saddles

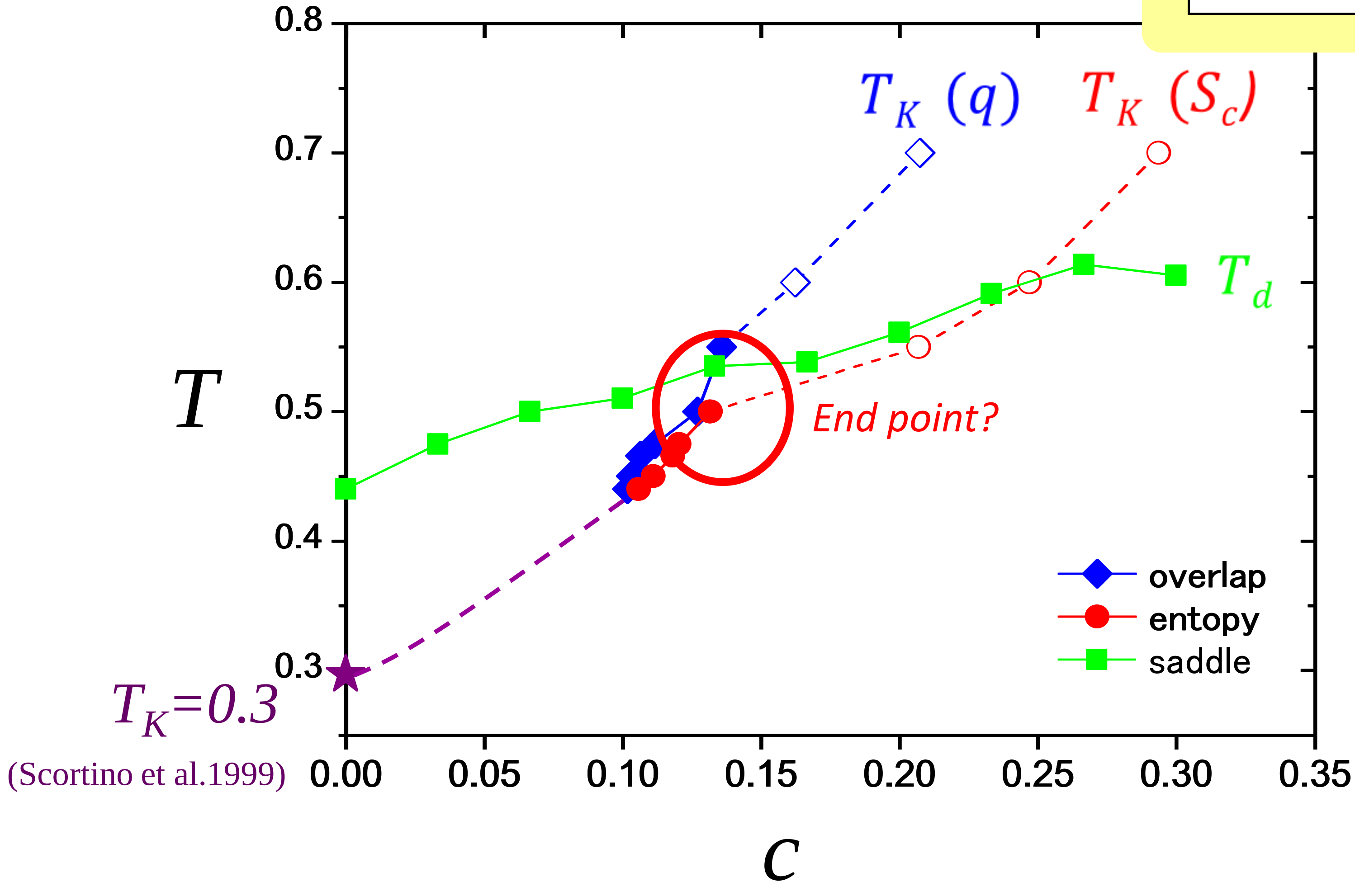


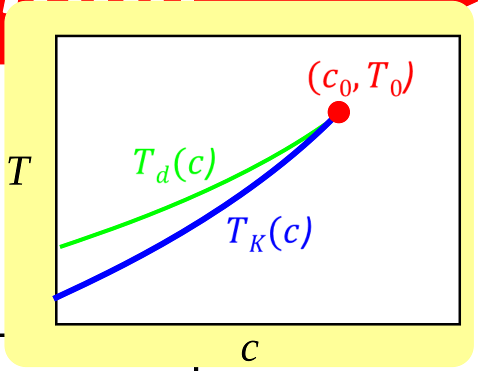
Inherent Structures



Randomly Pinned Glass Transition

Phase Diagram





Randomly Pinned Glass Transition

CONCLUSIONS

The first experiments *in silico*
to detect the ideal glass at T_K *and* $Sc = 0$
Strong support for RFOT

More questions than answers

- Growing *static* length(s) at T_K?
- RFIM universality at the end point?
- Slow dynamics: *A3 singularity? Adam-Gibbs violation?*
- and more…