CONFINEMENT AS A TOOL TO PROBE AMORPHOUS ORDER

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In collaboration with:
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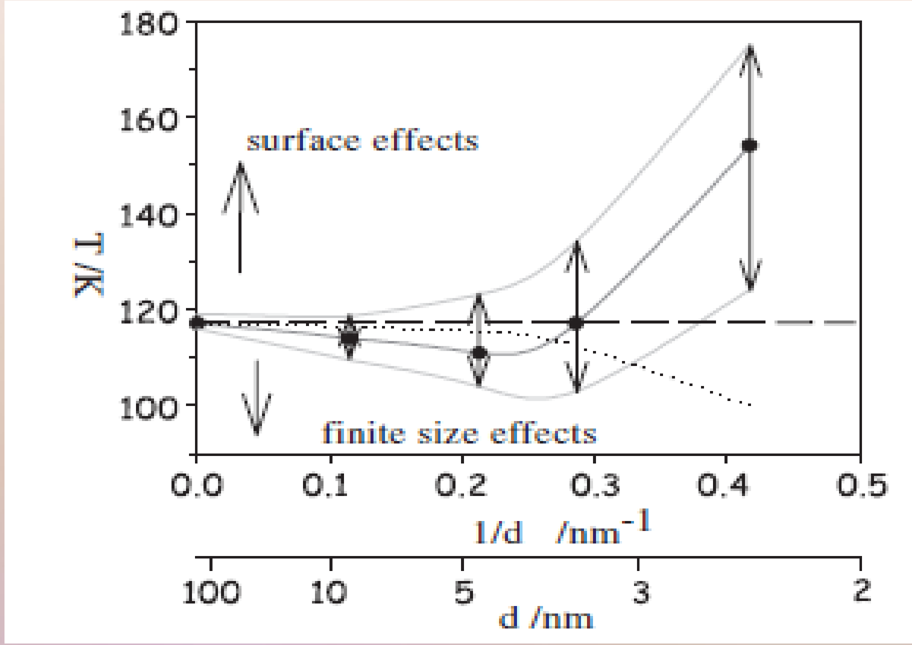
Kyoto, Japan, 19th July 2013

Does confinement enhances or depresses the tendency to form a glass ?



Confinement: reduction of the volume available to the liquid

- Jackson C L and McKenna G B, Chem. Mater. 8, 2128–37 (1996)
- C. Alba-Simionesco, *et al*, J. Phys. Condens. Matter 18 (2006) R15.

Fig: Glass transition temperature Tg, obtained from calorimetric measures, versus pore diameter “d” for toluene confined in nanopores. Non monotonic behaviour!

Competing effects

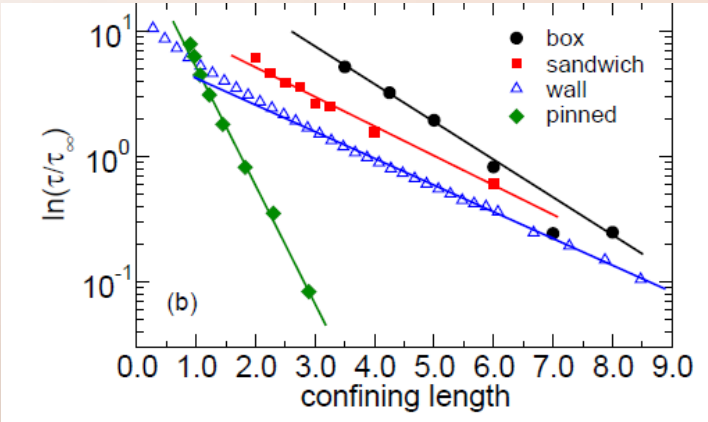
“Cut-off” effect $\tau_{bulk} = \exp(\xi^{\psi}/T)$

diameter of the pore $d < \xi \Rightarrow \tau(d) < \tau_{bulk}$

Interaction with boundaries

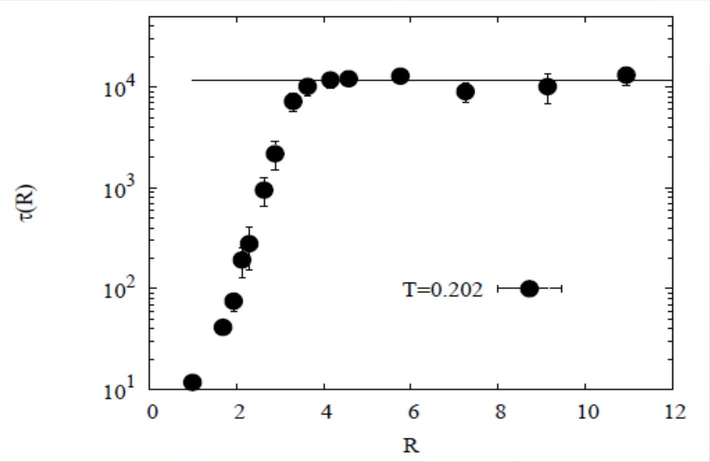
Slowing down of the system

Competing effects in simulations



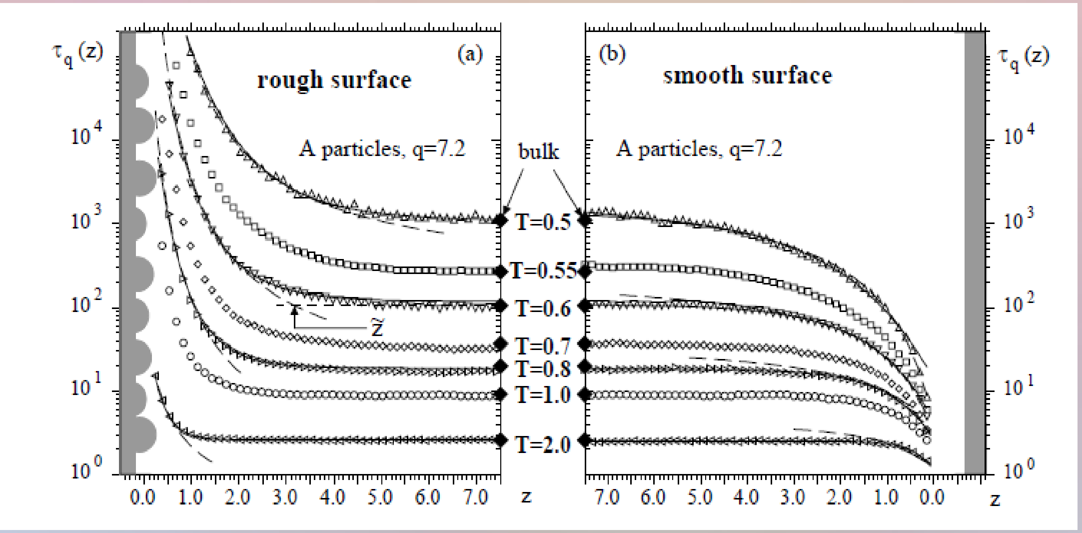
Boundary influence: smaller cavities are slower.

L. Berthier and W. Kob, Physical Review E 85, 011102 (2012)



“Cut-off” effect: smaller cavities are faster.

A. Cavagna, T. S. Grigera, and P. Verrocchio,
J. Chem.Phys. 136, 204502 (2012)



P. Scheidler, W. Kob, K. Binder, 2002 Europhys. Lett. 59 701

Local relaxation time varying the distance from the wall

Effect on confinement on the tendency to form a glass

↓

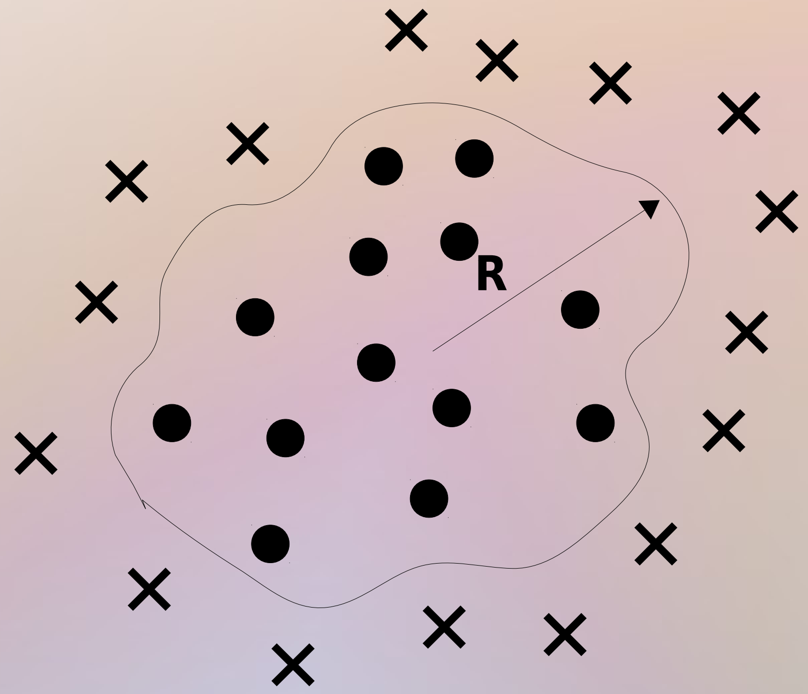
Definition and behaviour of static length-scales which are defined via "gedanken" confinement experiments

↓

Difference and similarities between "amorphous" and "random" boundary conditions in the confining cavity

Amorphous boundary conditions: Point-to-set correlation length

Configurational entropy $$\sigma_c(f) = \frac{1}{N}\log(\mathcal{N}(f))$$ <u>Exponential number of amorphous states at low temperature</u>



Free energy gain for the nucleation of a new amorphous state in a glass-forming liquid

$$\Delta F(R) = Y_{PS}R^{\theta} - T\sigma_c R^3$$

(Kirkpatrick,Thirumalai,Wolynes, *Phys.Rev.A*, 1989)

Probability of finding the cavity, after equilibration, in the same amorphous state of the frozen boundaries

$$p_{in}(R) = \frac{1}{1+e^{-\beta\Delta F(R)}}$$

(Biroli,Bouchaud, *J.Chem.Phys*, 2004)

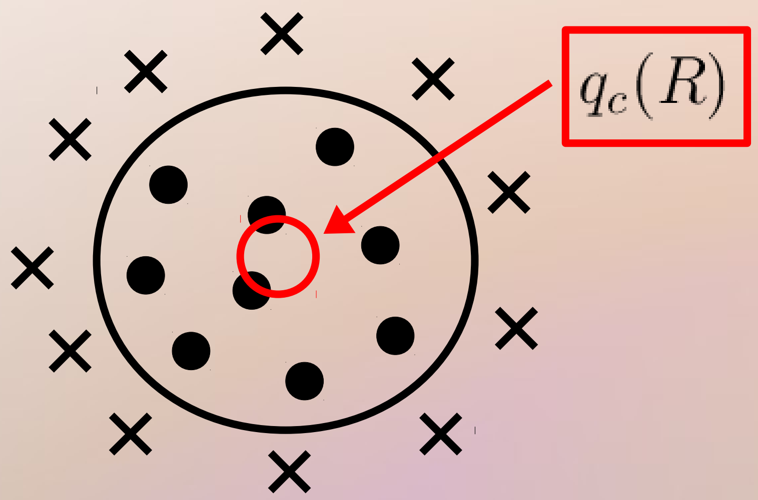
× **Frozen** particles

● **Free** particles

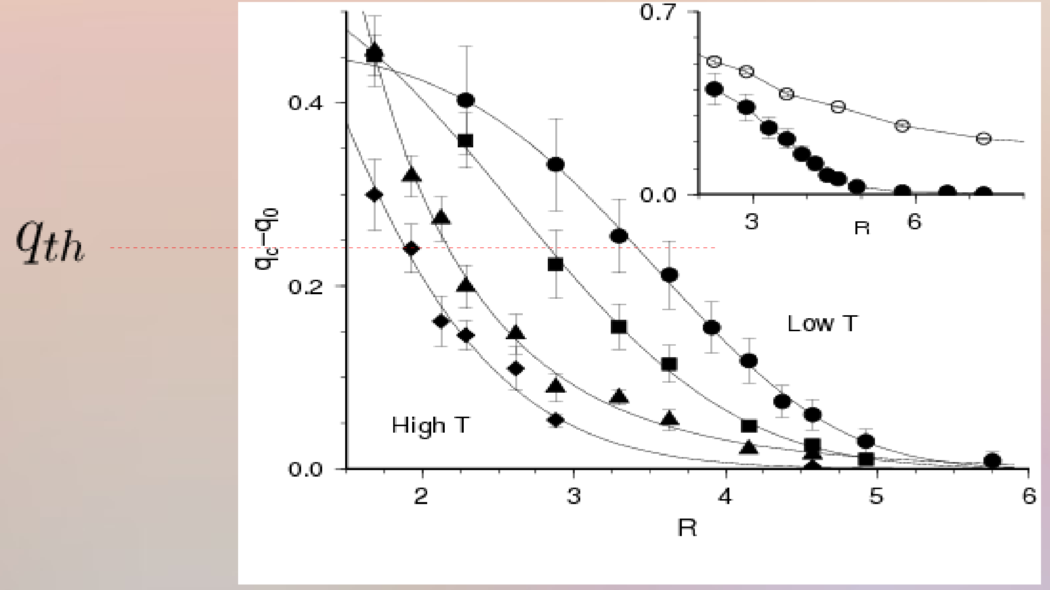
<u>Point-to-set length</u>:
crossover from ergodic (large R) to non ergodic (small R) cavities

$$\ell_{PS} = \left(\frac{Y}{T\sigma_c}\right)^{\frac{1}{d-\theta}}$$

Point-to-set correlations length in simulations
Crossover to a glass state



Overlap at the center of the cavity: average correlation between configurations equilibrated under the influence of amorphous boundaries



A threshold value of the overlap can be conventionally fixed

$$q_c(R) > q_{th} \qquad \text{GLASS}$$

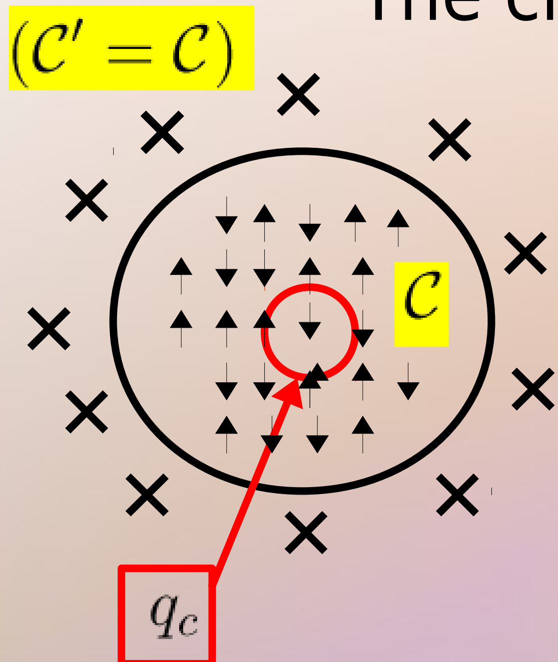
$$q_c(R) < q_{th} \qquad \text{LIQUID}$$

Biroli, Bouchaud, Cavagna, Grigera, Verrocchio, *Nature Physics*, 2008

L. Berthier and W. Kob, PRE 85, 011102 (2012)

Hocky, Markland, Reichman, *PRL*, 2012

Analytic results in a Kac glass model: The crossover becomes a transition

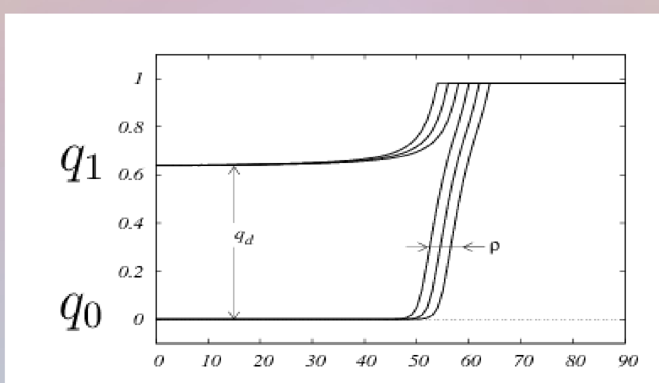


3d Kac model: fully connected p-spin model with effective interaction range γ and space dependent overlap field q(x)

$$\overline{F(R,\beta) = \frac{1}{Z(\beta)} \sum_{\mathcal{C}'} e^{-\beta H[\mathcal{C}']} f(R,\beta|\mathcal{C}')}$$

$$F[q(x)] = \gamma^d \int_{q(r>R)=1} d^d x \; (-\nabla^2 q(x) + V(q(x)))$$

At small enough temperatures: $\delta F / \delta q = 0 \longrightarrow q_1(x), q_0(x)$



$$F(q_1) - F(q_0) = \underbrace{\sigma_c R^3 - \beta Y_{PS} R^\theta}_{\text{Cavity configurational entropy}} = 0$$

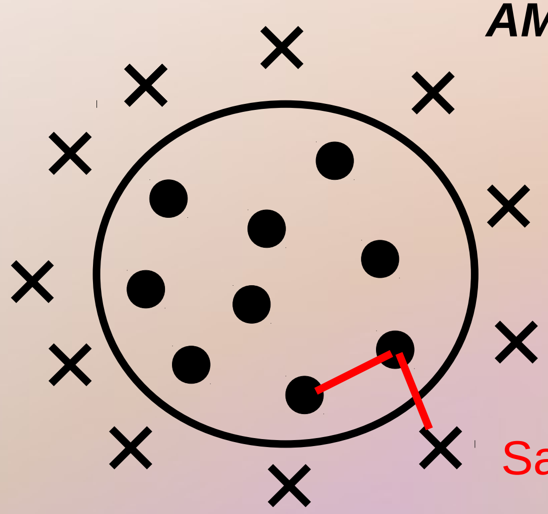
$$\ell_{PS} = \left(\frac{Y_{PS}}{T \sigma_c} \right)^{\frac{1}{d-\theta}}$$

$$\ell_{PS} \sim (T - T_K)^{-1}$$

Discontinuous overlap jump at the point-to-set: **glass formation in small cavities!**

Franz, Montanari, J. Phys. A Math. Theor. 40, (2007)

Beyond the point-to-set length: Removal of amorphous boundaries



AMORPHOUS BOUNDARY CONDITIONS

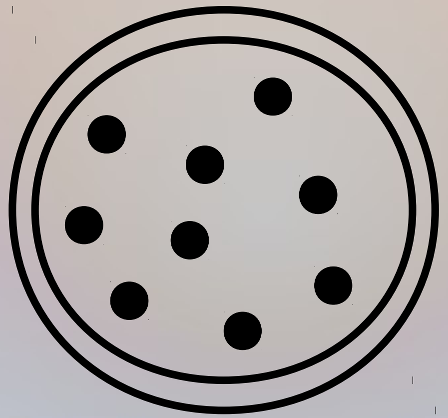
1) Equilibrate a sample
2) Freeze all particles outside sphere R
3) Equilibrate only inside sphere R

... experimentally a hard task !

Same chemical interaction between inner liquid and boundaries

TAKE FEATURLESS BOUNDARIES: JUST CONFINEMENT!

Confinement:
reduction of the volume available to the glass-former (hard walls, boundaries of a different material,etc...)

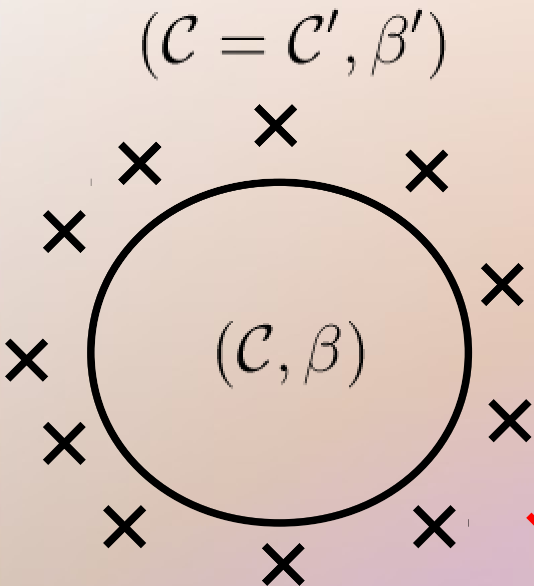


$$\ell_C = ?$$

$R > \ell_C$ LIQUID

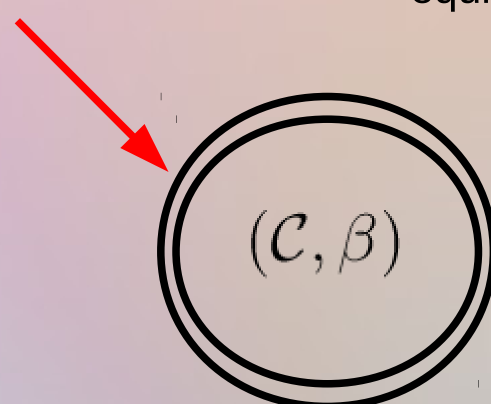
$R < \ell_C$ GLASS

Kac glass model with featureless boundaries



$$F(R,\beta,\beta') = \overline{\frac{1}{Z(\beta')}\sum_{\mathcal{C}'} e^{-\beta' H[\mathcal{C}']} f(R,\beta|\mathcal{C}')}$$

Average free energy cost to keep the configuration at β inside the cavity constrained to a configuration equilibrated at β' outside the cavity



CONFINEMENT

$\beta' = 0$

$$F(R,\beta,m) = \gamma^d \int d^d x[-(1-m)\nabla^2 q_1(x) - m\nabla^2 q_0(x) + V(q_0(x), q_1(x), m)]$$

Two possible equilibrium values of overlap between configurations inside the cavity
1RSB scenario

Kac glass model with random boundaries: definition of the confinement length

Configurational Entropy

$$F(q_0, q_1, R, \beta, m) = F(q_0, R, \beta, m=1) + (m-1)\overbrace{\tilde{F}(q_0, q_1, R, \beta)}$$

$$\delta\tilde{F}/\delta q_1 = 0 \;,\; \delta\tilde{F}/\delta q_0 = 0$$ → ***Solutions!***

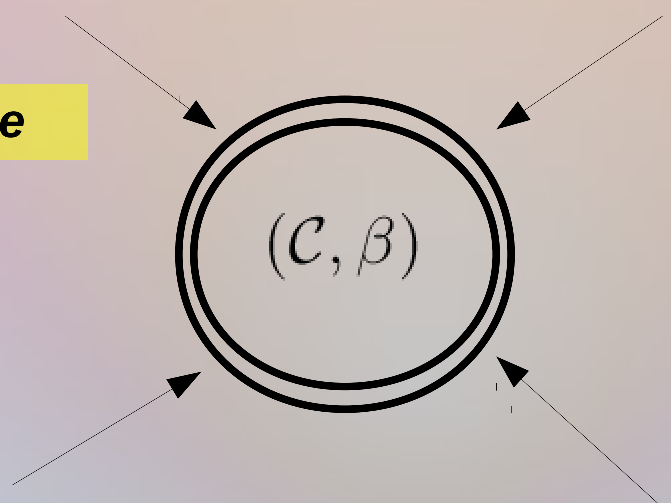
$$\tilde{F}(q_0, q_1, R, \beta, m) = \sigma_c R^3 - \beta Y_C R^\theta = 0$$ ⇒

$$\ell_C = \left(\frac{Y_C}{T\sigma_c}\right)^{\frac{1}{d-\theta}}$$

Confinement length

Transition to a glass state

By squeezing the volume available to the system the configurational entropy vanishes: glass state



$$Y_C \lesssim Y_{PS}$$

$$\theta_C = \theta_{PS} = 2$$

Kac glass model with random boundaries: definition of the confinement length

Configurational Entropy

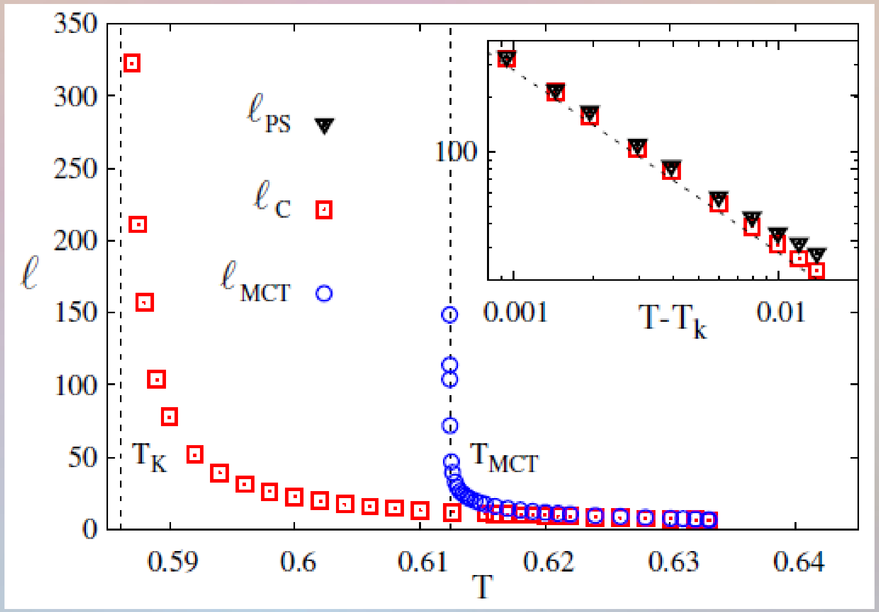
$$F(q_0,q_1,R,\beta,m) = F(q_0,R,\beta,m=1) + (m-1)\overbrace{\tilde{F}(q_0,q_1,R,\beta)}$$

$$\delta\tilde{F}/\delta q_1 = 0\ ,\ \ \delta\tilde{F}/\delta q_0 = 0$$ → ***Solutions!***

$$\tilde{F}(q_0,q_1,R,\beta,m) = \sigma_c R^3 - \beta Y_C R^\theta = 0$$ ⇒

$$\ell_C = \left(\frac{Y_C}{T\sigma_c}\right)^{\frac{1}{d-\theta}}$$

Confinement length



$$\ell_C \sim \ell_{PS} \sim (T-T_K)^{-1}$$

Kac glass model with random boundaries: definition of the confinement length

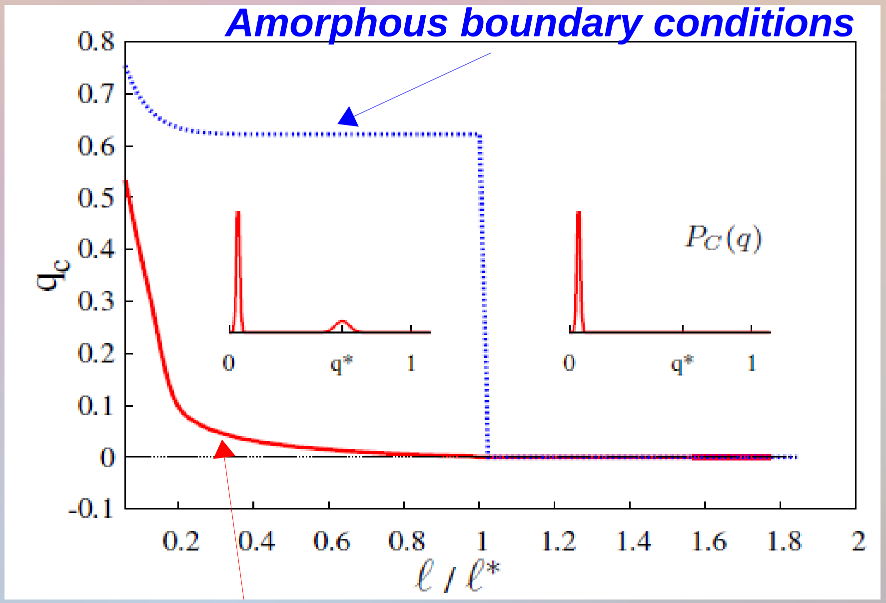
Configurational Entropy

$$F(q_0, q_1, R, \beta, m) = F(q_0, R, \beta, m=1) + (m-1)\overbrace{\tilde{F}(q_0, q_1, R, \beta)}$$

$$\delta \tilde{F}/\delta q_1 = 0\ ,\ \ \delta \tilde{F}/\delta q_0 = 0$$ → ***Solutions!***

$$\tilde{F}(q_0, q_1, R, \beta, m) = \sigma_c R^3 - \beta Y_c R^\theta = 0 \quad \Longrightarrow \quad \ell_C = \left(\frac{Y_c}{T\sigma_c}\right)^{\frac{1}{d-\theta}}$$

Confinement length



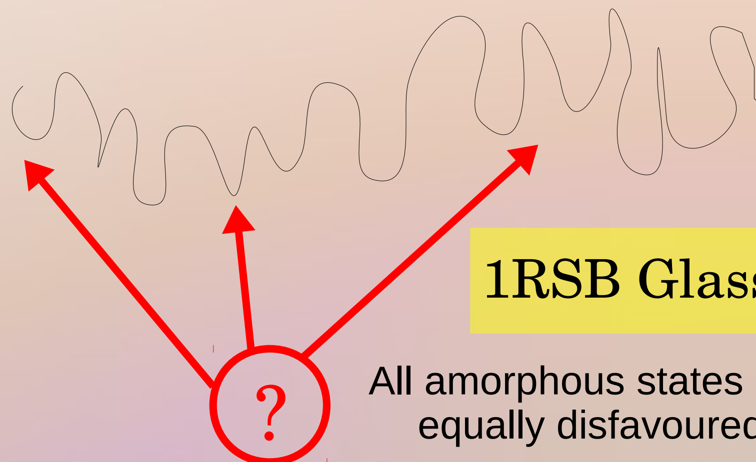
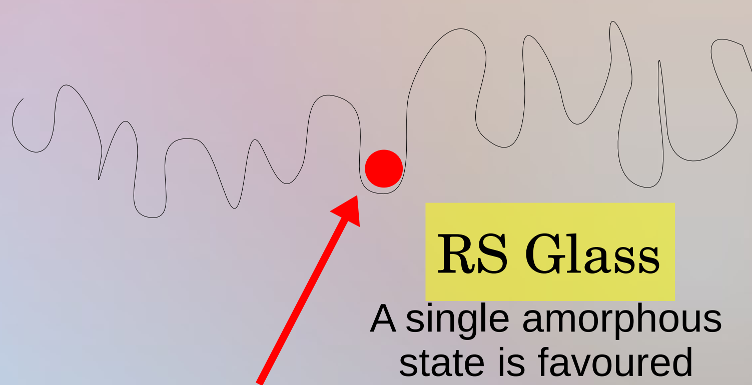
Random boundary conditions

Different behaviour of the overlap with random boundaries!

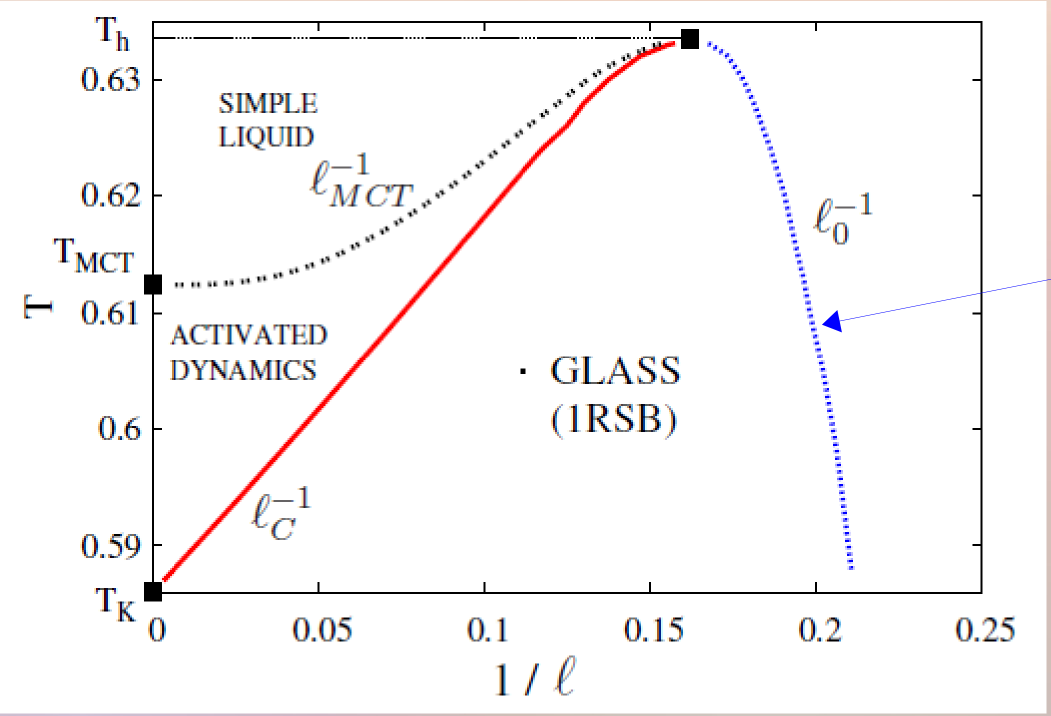
1) Smooth growth of the average overlap at the centre of the cavity

2) Bimodal distribution of the overlap ruled by parameter “m”, 1RSB phase

Random vs Amorphous boundary conditions

	Glass (ℓ^*)	**Activated Dynamics** (ℓ_{MCT})	**Simple Liquid**
Random boundary conditions	 **1RSB Glass** All amorphous states are equally disfavoured $\{q_0, q_1, m<1\}$	q_0 stable, q_1 metastable; q_1 ***Not favoured by boundaries***	
Amorphous boundary conditions	 **RS Glass** A single amorphous state is favoured $\{q_1\}$	q_0 stable, q_1 metastable; q_1 ***Favoured by boundaries***	

Kac glass model with random boundaries: Phase diagram



For small values of the cavity radius we find a ***continuous transition*** to a trivially blocked state!

Confinement:
C. Cammarota, G. Gradenigo and G. Biroli, **arXiv 1305.3538**

Phase-diagram with randomly pinned particles:
C. Cammarota, G. Biroli, J. Chem. Phys. 138, 12A547 (2013)

Conclusions

- Point-to-set length and confinement length behave in the same way.

- Pure geometric confinement induce amorphous order

- Glassy state induced by confinement is rather different than the glass induce by amorphous boundary conditions.
Confinement is more similar to cooling.

Perspectives

- Inclusion of finite range correction in the Kac model

- Behaviour of the confinement lenght in system with realistic interaction

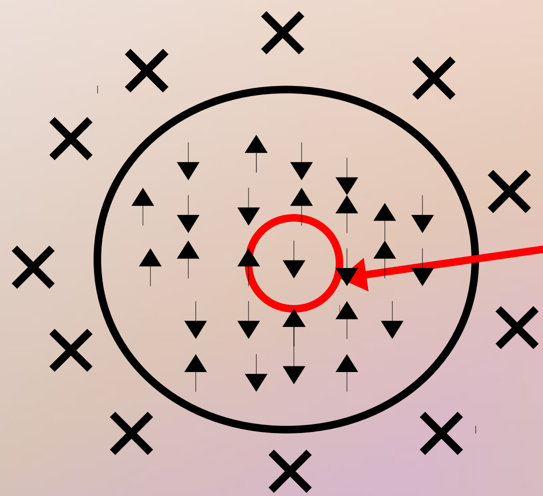
- Experimental/numerical test of results in small cavities: bimodal distribution of overlap?

- Experimental/numerical study of the relaxation time under confinement?

Analytic results in a Kac glass model: The crossover becomes a transition

Franz, Montanari, J. Phys. A Math. Theor. 40, (2007)

Kac model: fully connected p-spin model with effective interaction range γ



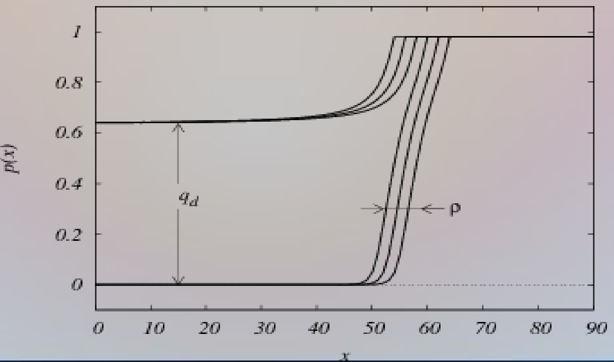
$$\overline{q_c(R)} \sim \int_{q(x)=1;|x|>R} \mathcal{D}q \; e^{-\beta F[q(x)]} \; q(0)$$

$$F[q(x)] = \gamma^d \int d^d x(-\nabla^2 q(x) + V(q(x)))$$

Free energy difference between high and low overlap solutions

$$\Delta F(R) = Y_{PS} R^{\theta} - T\sigma_c R^3 \quad \ell_{PS} = \left(\frac{Y}{T\sigma_c}\right)^{\frac{1}{d-\theta}}$$

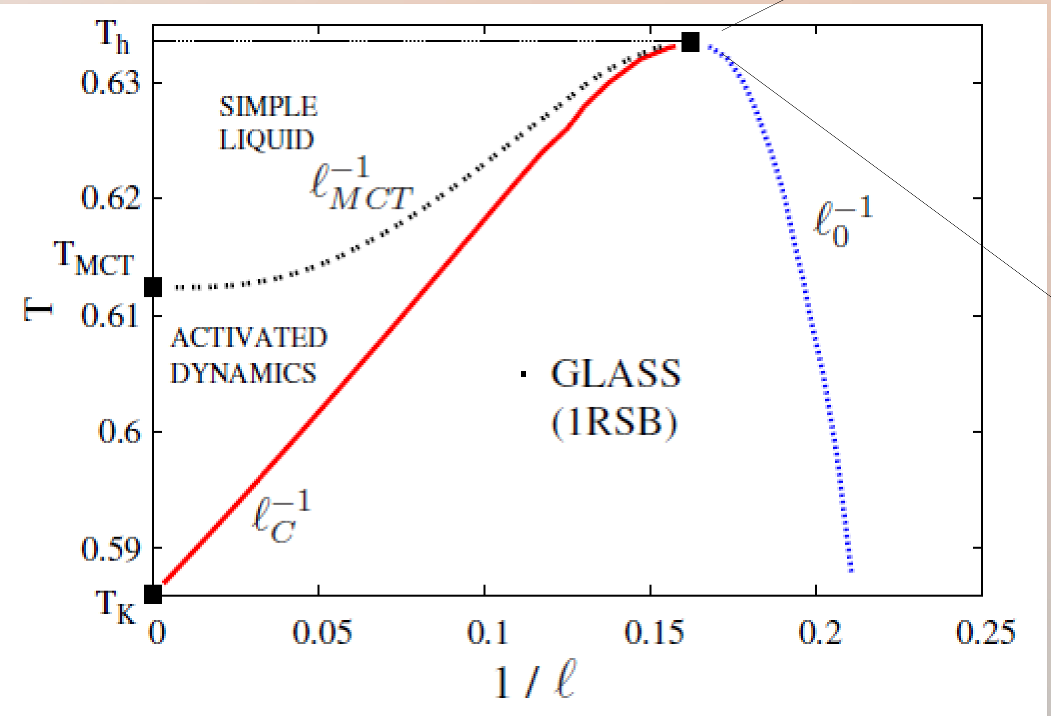
Confinement with amorphous boundary conditions: ***increase of the glass transition temperature***

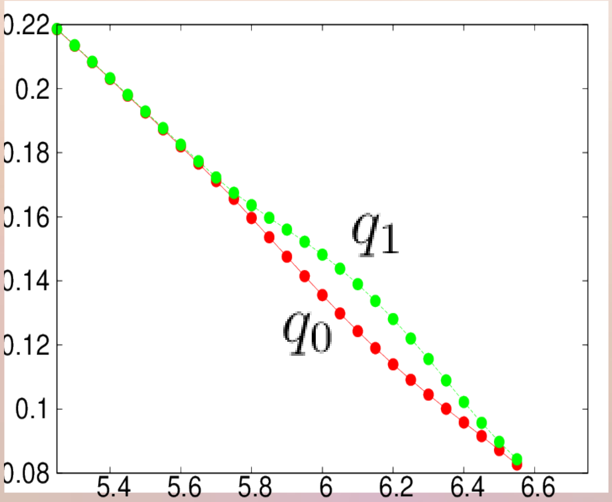


Point-to-set

$$\ell_{PS} \sim (T - T_K)^{-1}$$

Kac glass model with random boundaries: Phase diagram





For small values of the cavity radius we find a ***continuous transition*** to a trivially blocked state!

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