Study of a glass-forming liquid in a confined geometry : correlation lengths and interfaces of amorphous states

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CEA, Saclay, 30th June 2011

PLAN OF THE TALK

Introduction

Thermodynamics of a constrained cavity:
point-to-set correlation length.

Random First Order Theory (RFOT) in the spherical cavity: finite size corrections

Consolidation

RFOT in “sandwitch” geometry

Point-to-set vs penetration length

Advances

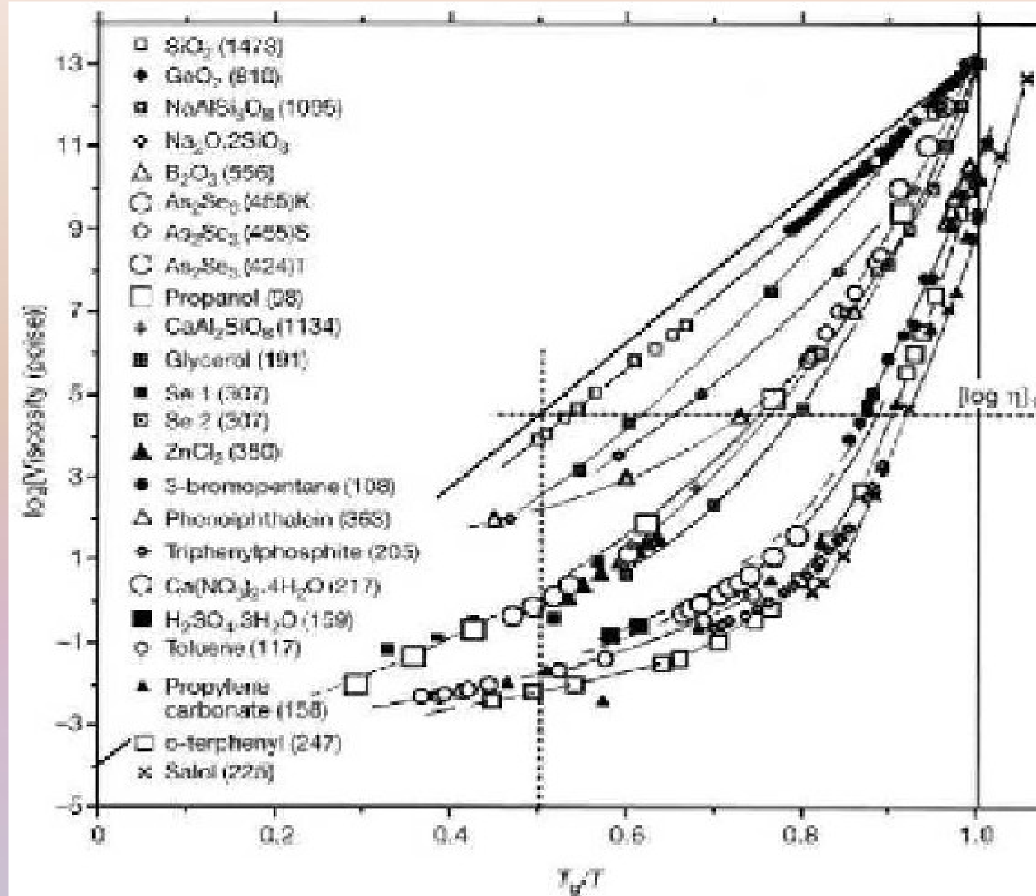
Energy of interfaces in spherical cavity ?

Pinning of interfaces in the sandwitch geometry

Stiffness exponent

Conclusions

GLASS TRANSITION: DYNAMICAL ARREST



... but today : <u>Thermodynamics</u>

<u>Static correlation lenghts</u>

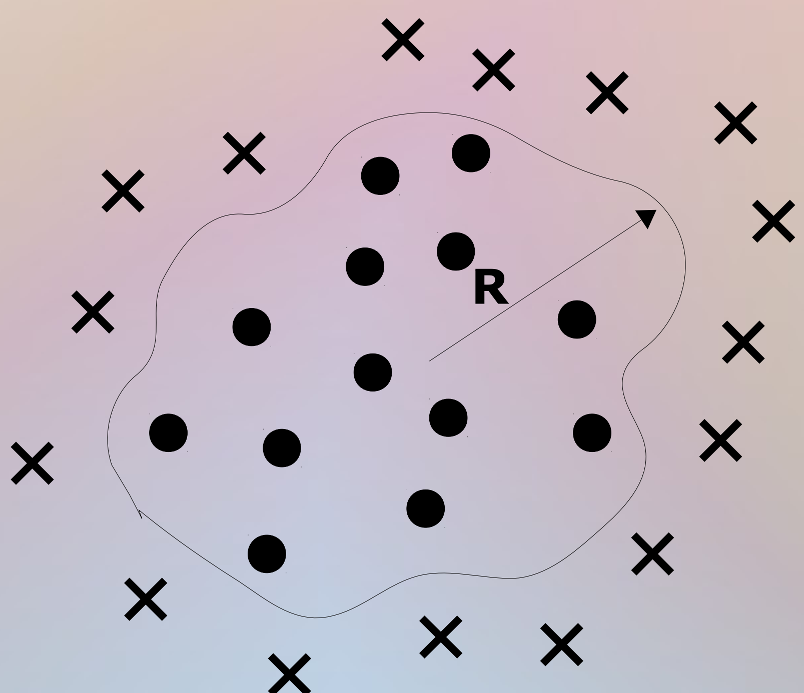
Random First Order Theory: Cooperatively rearranging regions

Glass-forming liquid: below Mode Coupling equilibration via <u>activated events</u>

<u>Configurational Entropy</u>

$$\sigma_c(f) = \frac{1}{N} \log(\mathcal{N}(f))$$

Number of metastable states



<u>SIZE OF AMORPHOUS DROPLETS</u>

Gain $\delta f_+ = \sigma_c R^d$

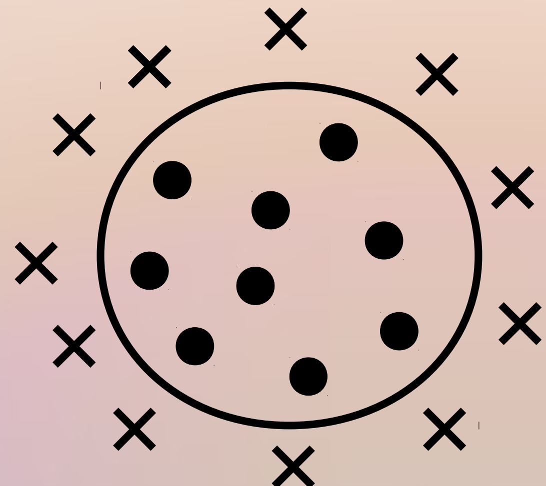
Cost $\delta f_- = \beta \Upsilon R^\theta$

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

Random First Order Theory: Thermodynamics of a constrained cavity

1) Out of the cavity particles are frozen in equilibrium state β

2) Let the system equilibrate ***only*** inside the cavity



3) Equilibrium state β act as random pinning field at the borders

4) Which is the probability to find particles *inside the cavity* ***still*** in state β ?

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

$$Z(R) = e^{-\beta f^* R^d} + e^{-\beta f^* R^d + \sigma_c R^d - \beta \Upsilon R^\theta}$$

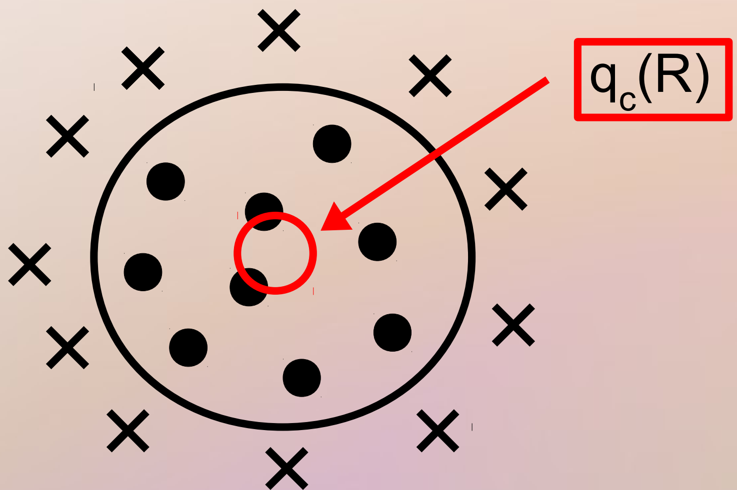
$$p_{in}(R) = \frac{1}{1 + e^{\sigma_c R^d - \beta \Upsilon R^\theta}}$$

$$\xi = \left(\frac{\Upsilon}{T \sigma_c} \right)^{1/(d-\theta)}$$

$$p_{in}(R) \sim \Theta(Y - T \sigma_c R^{d-\theta})$$

Poin-to-set correlation length

Random First Order Theory:
Point-to-set correlation function

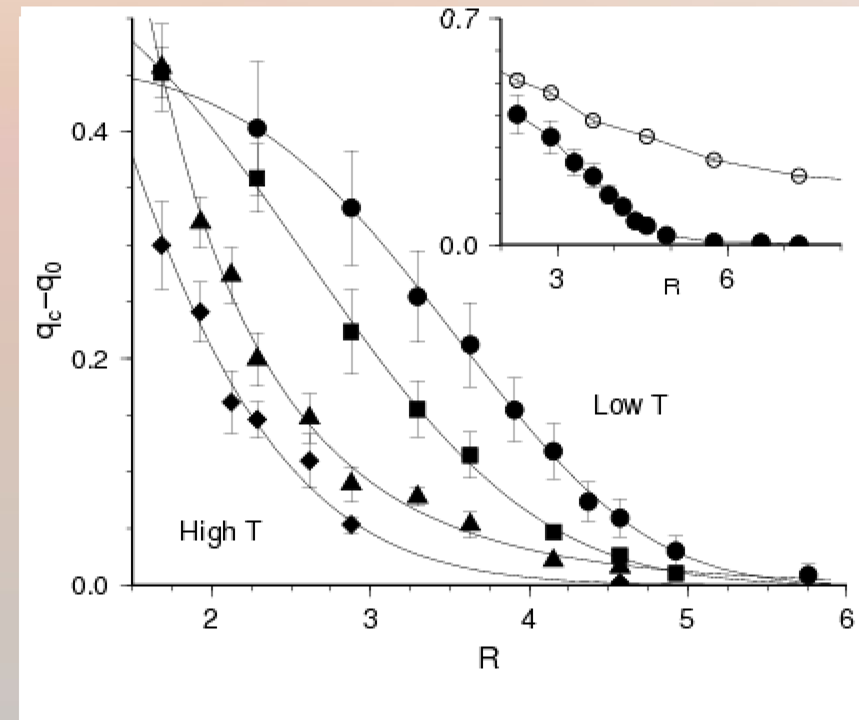


Numerical experiment with a binary mixture of **soft-spheres** in **3d.**

Simulation box is divided in “small” cells
$n_i(t)$ = occupation number at time t.

$$q_c(R) = \frac{1}{N_v} \sum_{i \in v} \langle n_i(0) n_i(\infty) \rangle$$

1 RSB scenario ; two values of overlap

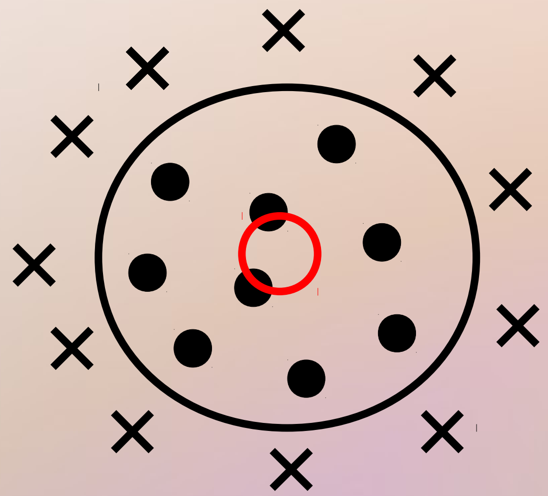


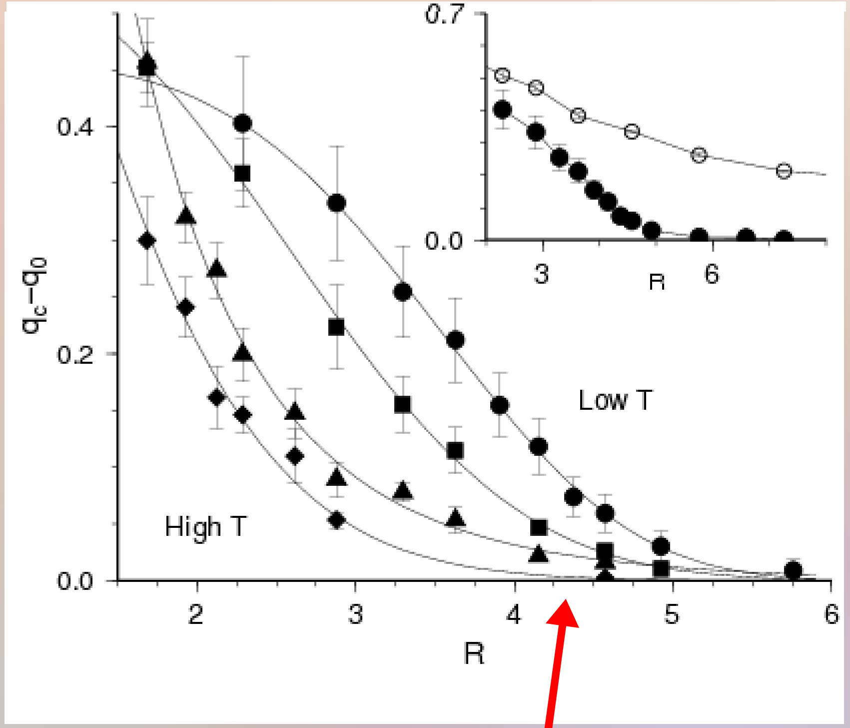
(Biroli *et al.*, *Nature Physics*, 2008)

(Cavagna,Grigera, Verrocchio, *PRL*, 2007)

$$q_c(R) = p_{in}(R) q_1 + p_{out}(R) q_0$$

Random First Order Theory: Point-to-set correlation function





Numerical experiment with a binary mixture of **soft-spheres** in **3d.**

Simulation box is divided in “small” cells

$n_i(t)$ = occupation number at time t.

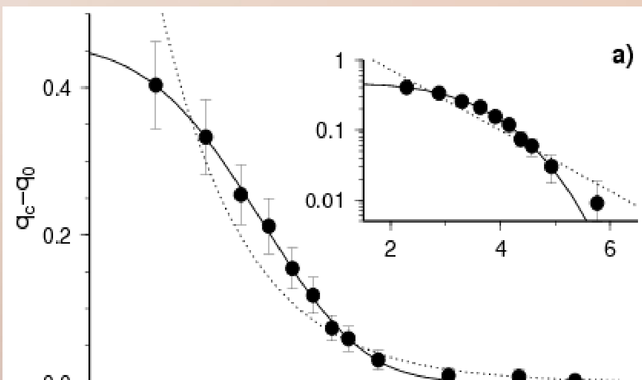
NOT REALLY STEPWISE

$$q_c(R) = \frac{1}{N_v} \sum_{i \in v} \langle n_i(0) n_i(\infty) \rangle$$

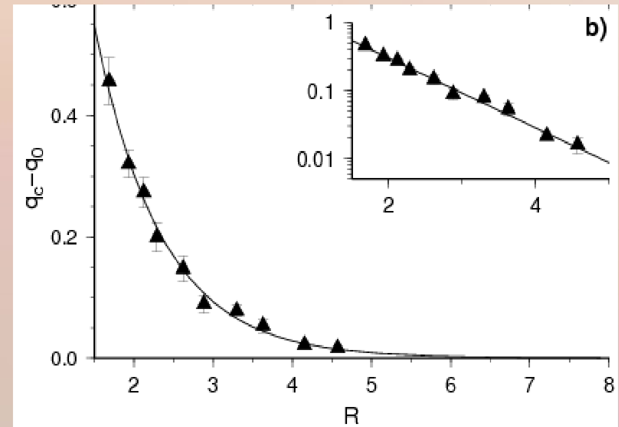
$$q_c(R) = p_{in}(R) q_1 + p_{out}(R) q_0$$

$$q_c(R) \sim p_{in}(R) \sim \Theta(Y - \sigma_c T R^{d-\theta})$$

Random First Order Theory:
Finite-size corrections, fluctuating surface tension



Low Temperature
Non-exponential decay



High Temperature
Exponential decay

$$q_c(R) \sim \exp[-(R/\xi_{ps})^\zeta]$$

<u>Finite size effect: surface tension fluctuations</u>

$$q_c(R) \sim \int_0^\infty d\Upsilon P(\Upsilon)\Theta(\Upsilon - T\sigma_c R^{d-\theta})$$

$$\zeta = \nu(d-\theta)$$

$$\nu \nearrow \quad \langle(\Upsilon - \overline{\Upsilon})^2\rangle \to 0$$

Measure of ν

C.Cammarota *et al.*, *J.Stat.Mech*,2009

Random First Order Theory:
Open questions

Evidence of this surface tension ?
Evidence of thermodynamic states ?

$$\xi = \left(\frac{\Upsilon}{T\sigma_c}\right)^{1/(d-\theta)}$$

<u>Measure of microspic surface tension fluctuations from Inherent Structures</u>

C.Cammarota *et al., J.Chem.Phys.,*2009
C.Cammarota *et al., J.Stat.Mech,*2009

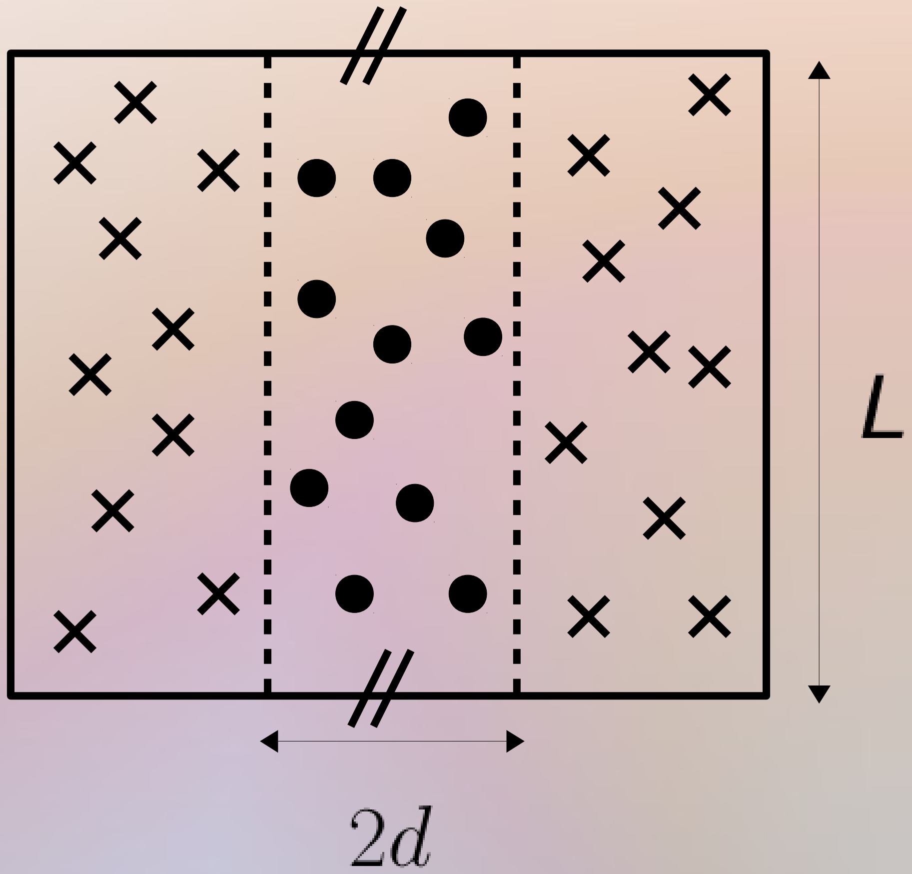
$$q_c(R) \sim exp[-(R/\xi)^{\nu(d-\theta)}]$$

Non-exponentiality:
artifact of the spherical geometry ?

<u>Measure of static length-scales in glass-forming lquids: always simple exponentials</u>

Scheidler,Kob, Binder, *EPL,* 2002 Berthier, Kob*, arXiv,* 2010

Random First Order Theory: “sandwitch” geometry.



Sandwitch cavity: two lengths
L = simulation box side
2d = distance between hard walls

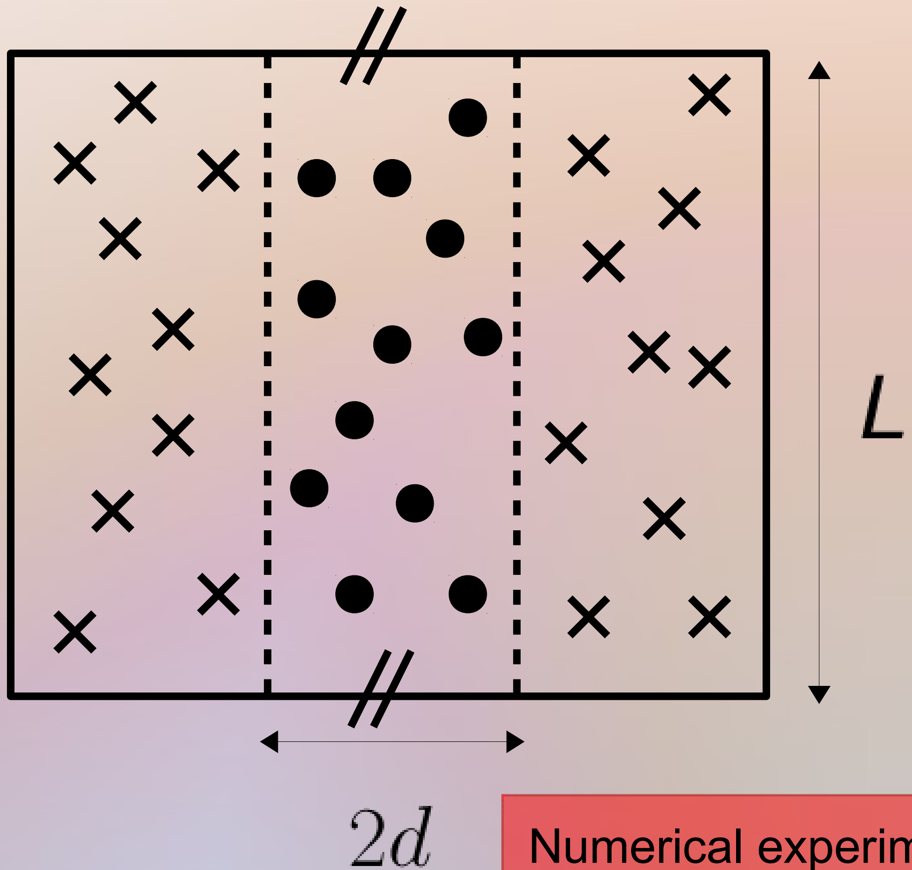
Spherical cavity: one length
R = radius of the cavity

3d Soft spheres binary mixture

$$V = \sum_{i>j}^{N} \left[\frac{\sigma_{\mu(i)} + \sigma_{\mu(j)}}{|\mathbf{r}_i - \mathbf{r}_j|} \right]^{12}$$

$$\sigma_2/\sigma_1 = 1.2$$

Random First Order Theory: "sandwitch" geometry.



Sandwitch cavity: two lengths
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$$V = \sum_{i>j}^{N} \left[\frac{\sigma_{\mu(i)} + \sigma_{\mu(j)}}{|\mathbf{r}_i - \mathbf{r}_j|} \right]^{12}$$

$$\sigma_2/\sigma_1 = 1.2$$

Numerical experiment

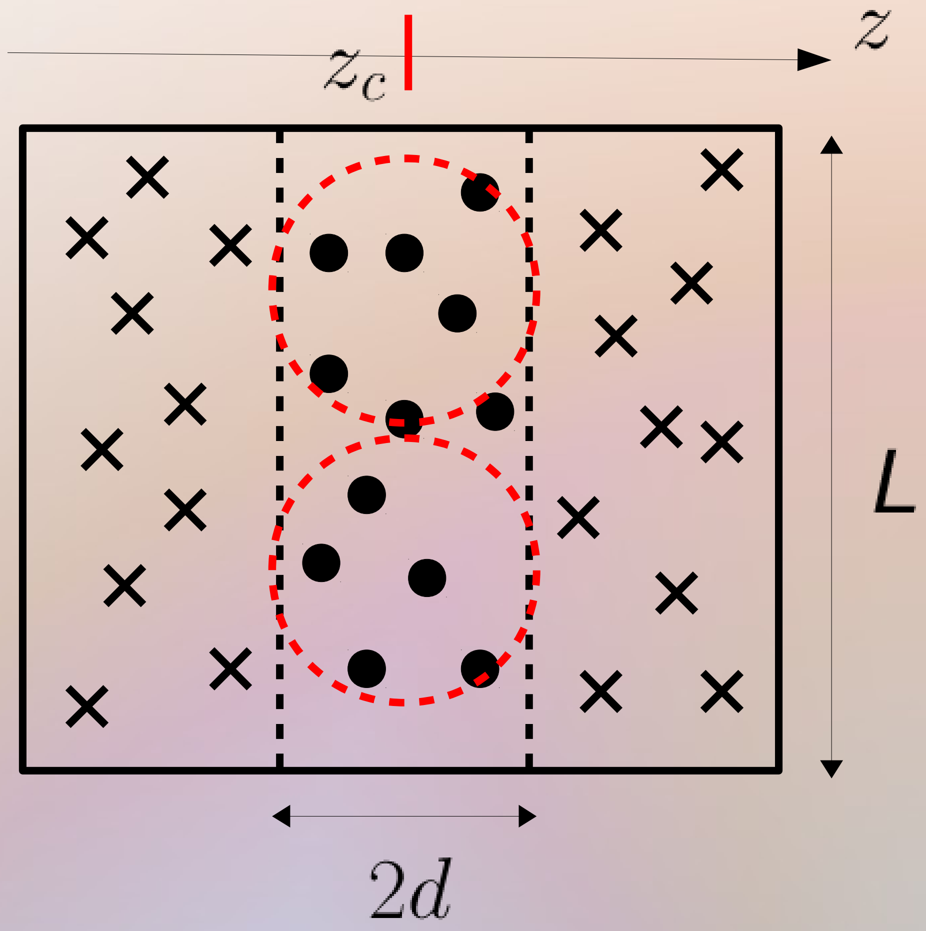
1) Equilibrate all particles

2) Freeze particles outside the cavity

3) Ri-equilibrate particles in the cavity subject to random boundary conditions

4) Calculate point-to-set correlation function

Random First Order Theory: "sandwitch" geometry.



$$q_{z_c}(d) = \frac{1}{N_v} \sum_{i \in z_c} \langle n_i(0) n_i(\infty) \rangle$$

Spherical cavity rearrangements

$$\delta f_+ = T \sigma_c R^3$$
$$\delta f_- = \Upsilon R^\theta$$

Assume **ISOTROPIC** excitations in the sandwitch

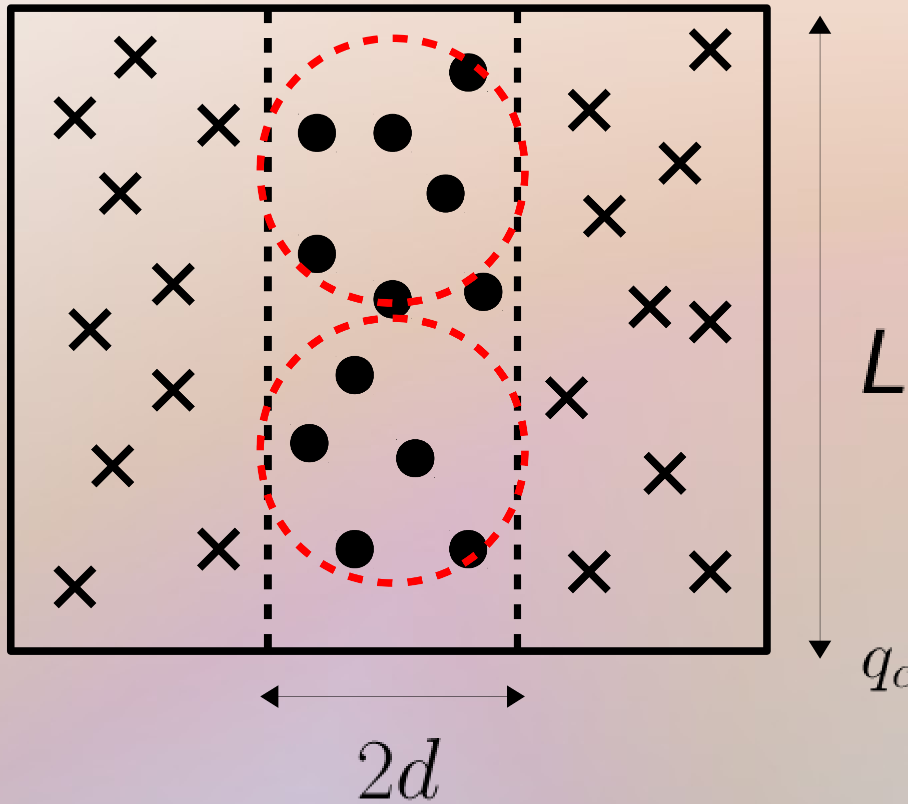
Sandwitch cavity rearrangements

$$\delta f_+ = M T \sigma_c d^3$$
$$\delta f_- = \Upsilon M d^\theta$$

$$M = L^2 d / d^3 = (L/d)^2$$

Number of isotropic amorphous excitations in a sandwitch

Random First Order Theory: "sandwitch" geometry.



$$q_{z_c}(d) = \frac{1}{N_v} \sum_{i \in z_c} \langle n_i(0) n_i(\infty) \rangle$$

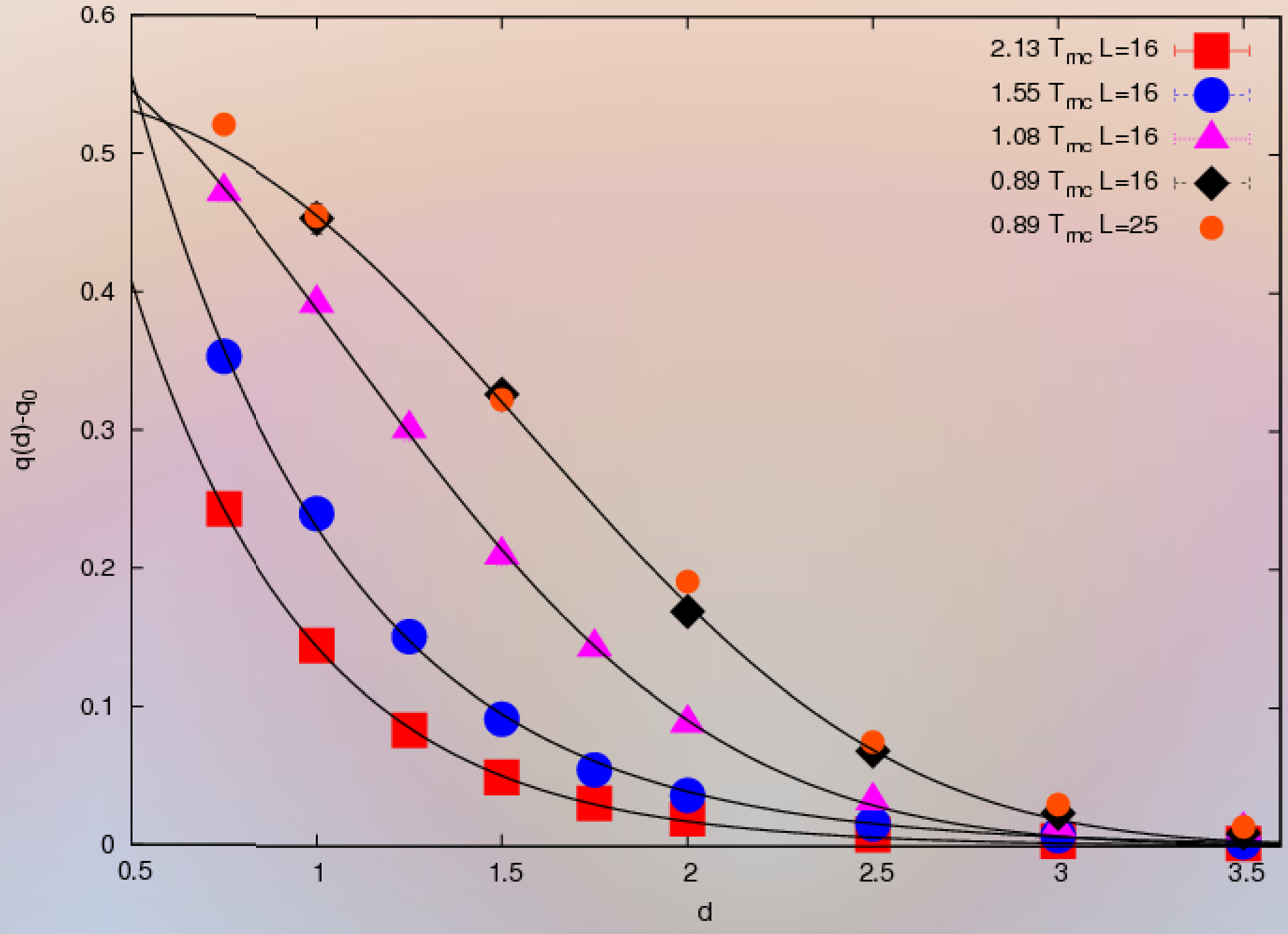
Point-to-set is non exponential for Spherical cavity …

$$q_c(R) \sim \int d\Upsilon P(\Upsilon) \frac{1}{1 + e^{\sigma_c R^3 - \beta \Upsilon R^\theta}}$$

… we can expect the same for liquid confined by two walls !

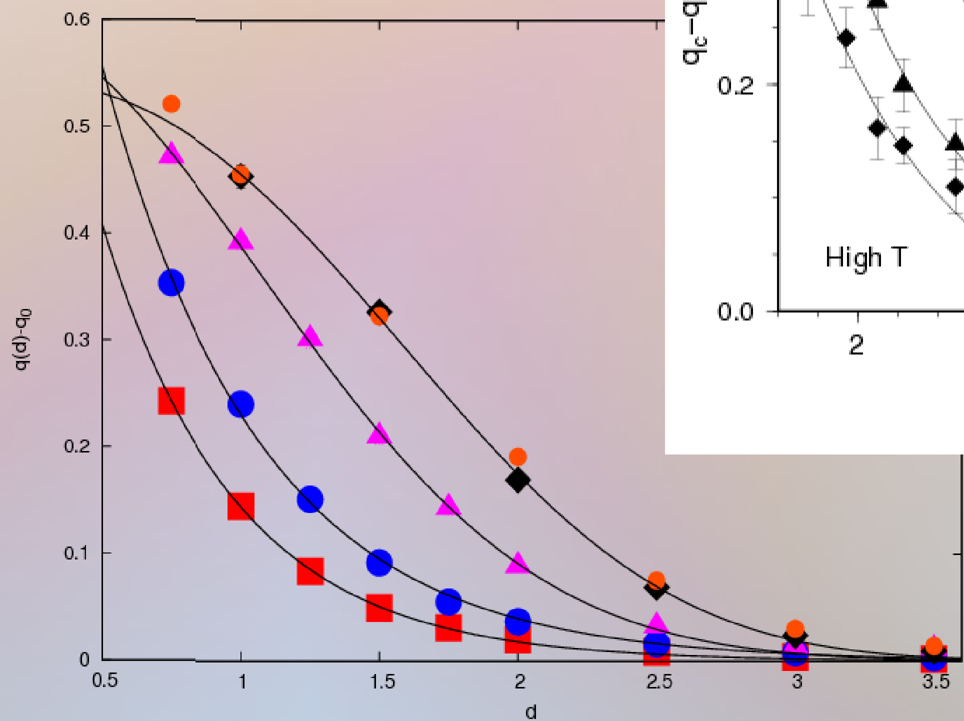
$$q_{z_c}(d, M) \sim \int d\Upsilon P(\Upsilon) \frac{1}{1 + e^{M(\sigma_c d^3 - \beta \Upsilon d^\theta)}}$$

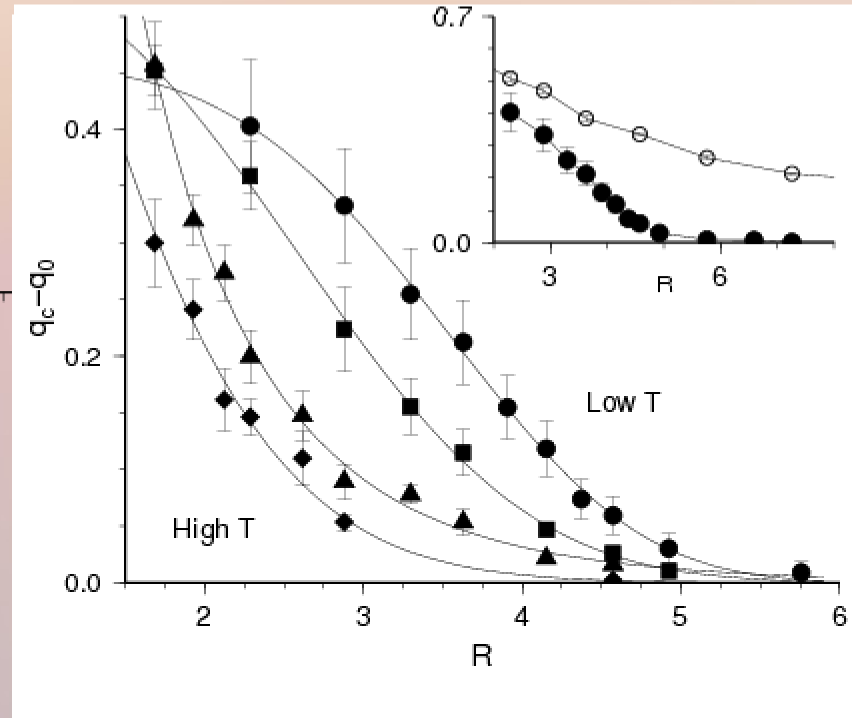
"Sandwitch" geometry :
point-to-set correlation function



“Sandwitch” geometry : point-to-set correlation function

Sandwitch

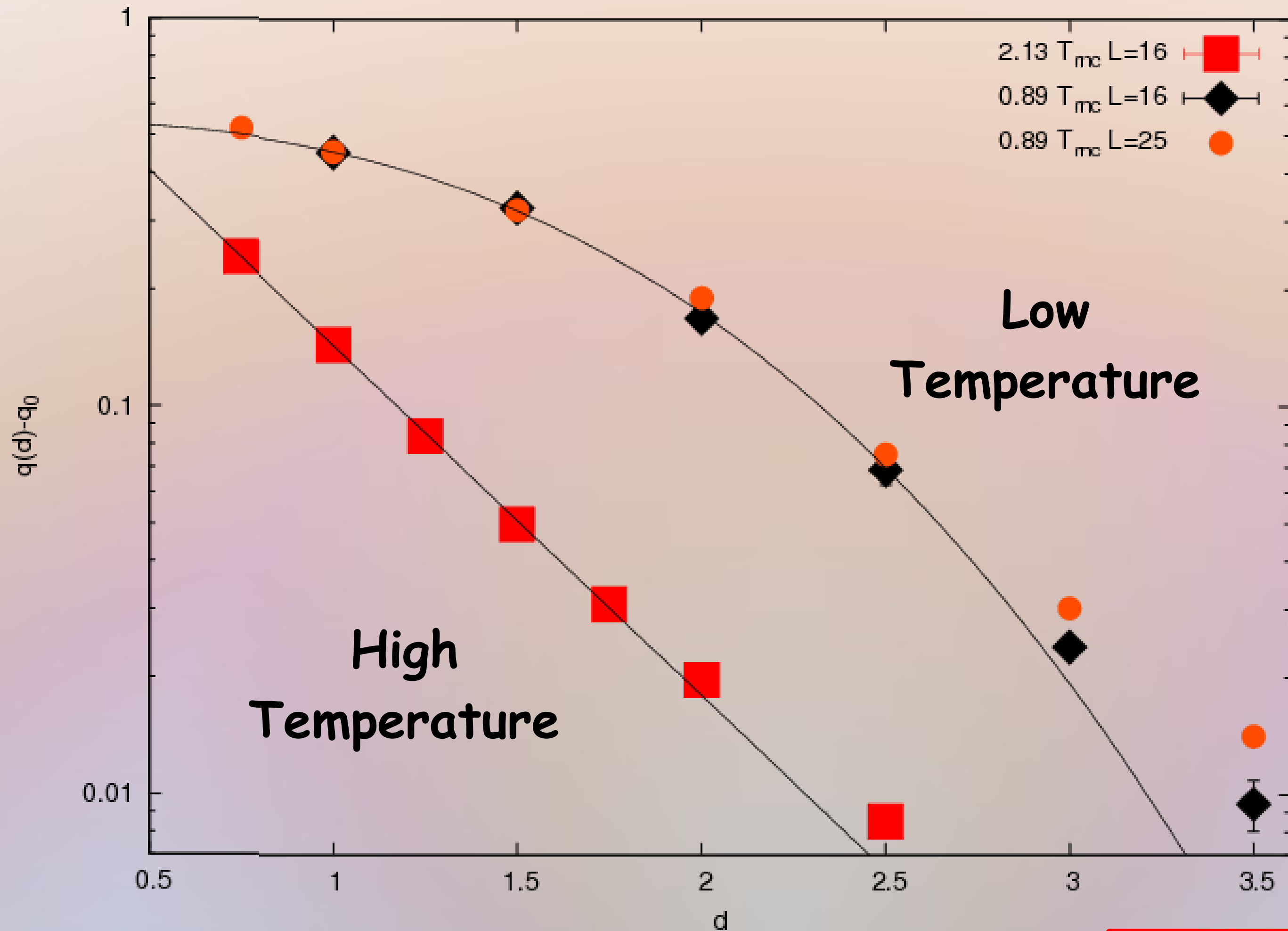




Sphere

Same temperatures !

Point-to-set correlation function



Sphere

$\zeta = 4.0 \pm 0.6$

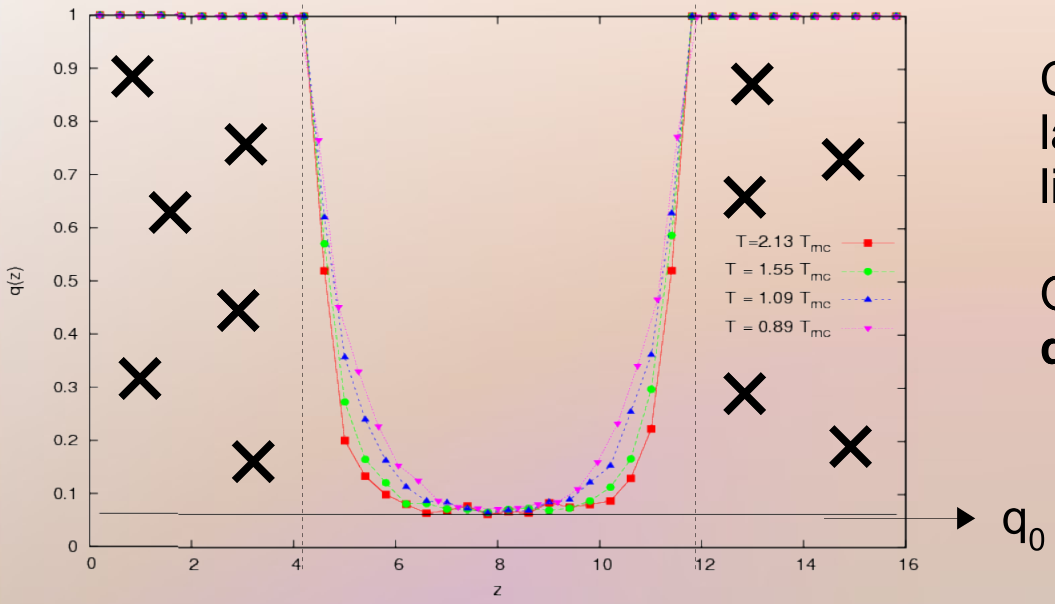
Non-exponentiality

$$q_c(R) \sim \exp[-(R/\xi_{ps})^{\zeta}]$$

Sandwitch

$\zeta = 2.7 \pm 0.2$

Penetration length: simple exponential decay

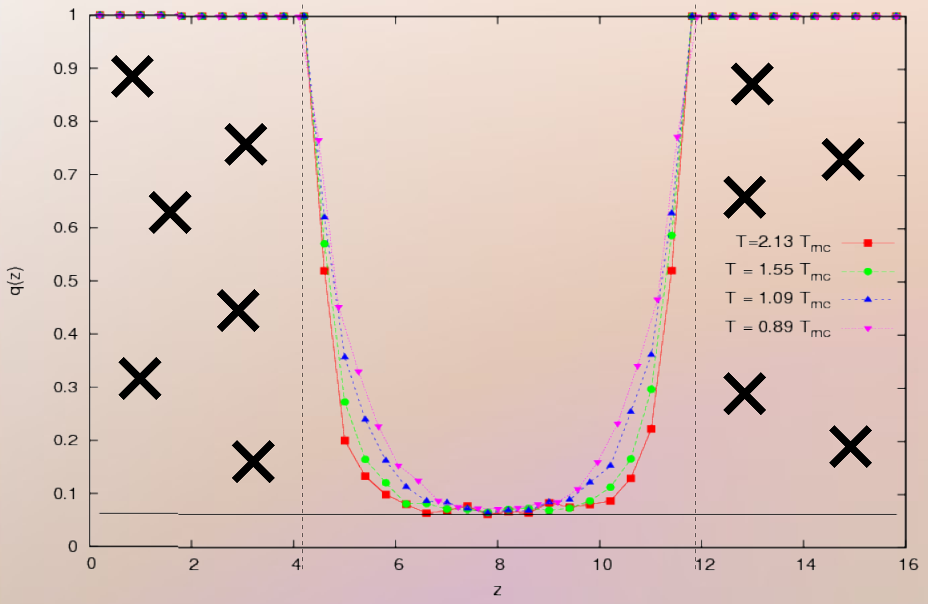


Consider at each temperature large cavities equilibrated to the liquid state.

Overlap at the center

$q(z_c) = q_0 = 0.062876$

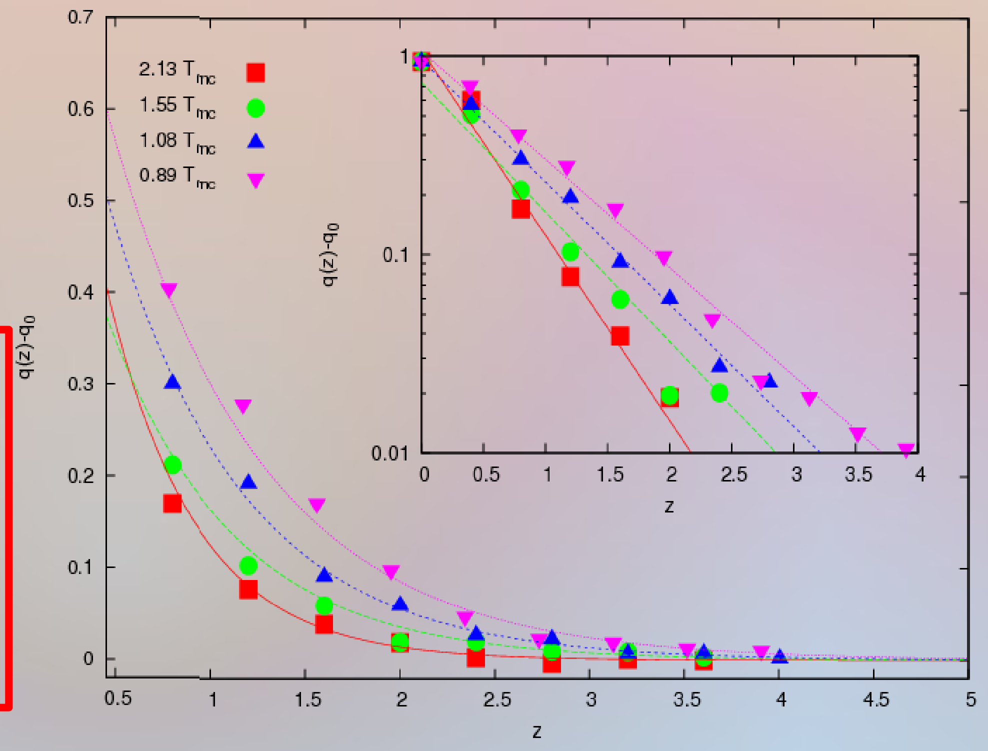
Penetration length: simple exponential decay



Influence of a **single wall** in the liquid

Consider at each temperature large cavities equilibrated to the liquid state.

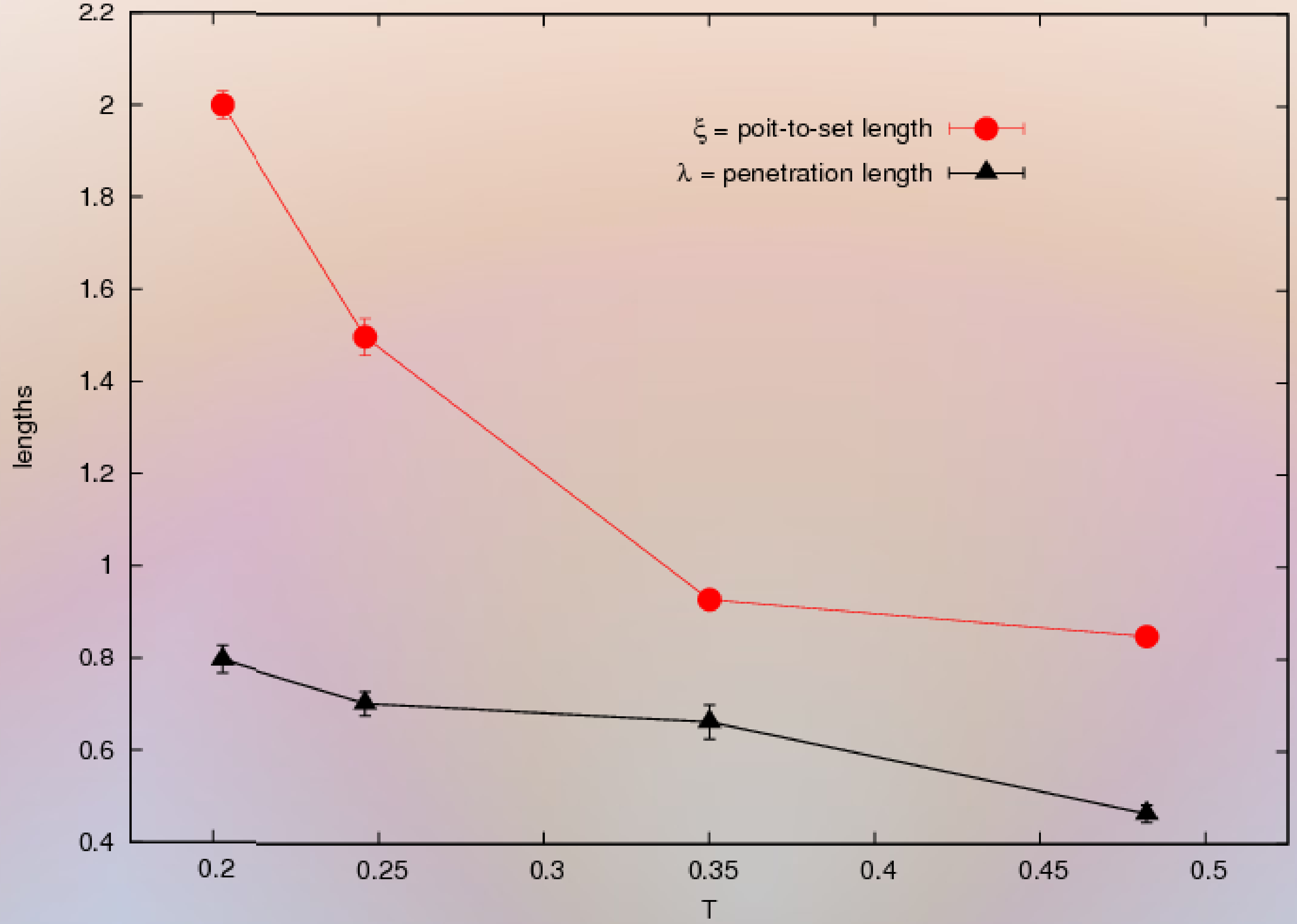
Overlap at the center
$q(z_c) = q_0 = 0.062876$



Overlap decay **exponentially** moving away from a wall at **every temperature**

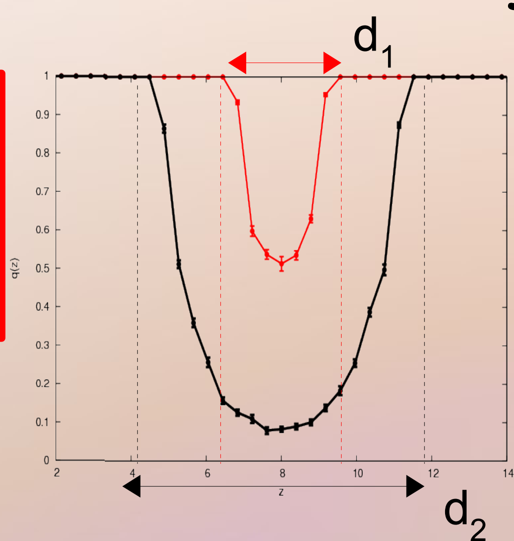
$$q(z - z_0) = Ce^{-(z-z_0)/\lambda}$$

Point-to-set lenght vs Penetration length



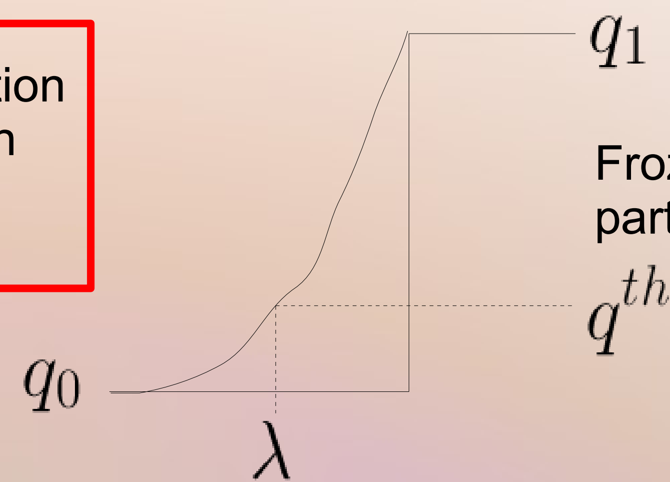
Point-to-set lenght vs Penetration length

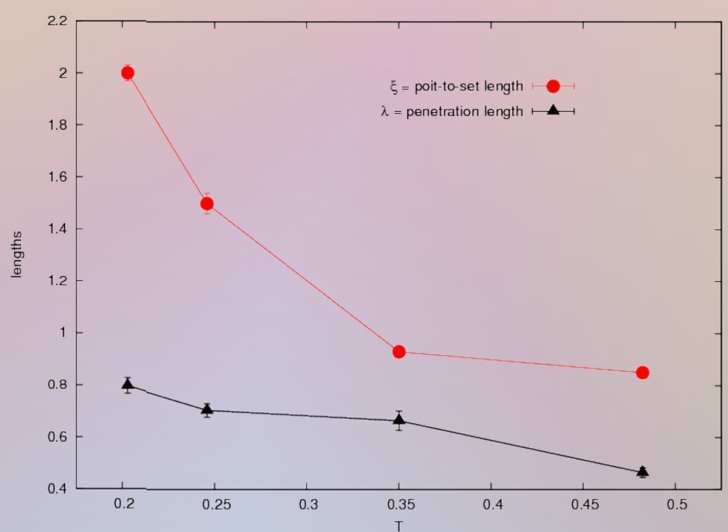
Point-to-set Length
ξ_{PS}



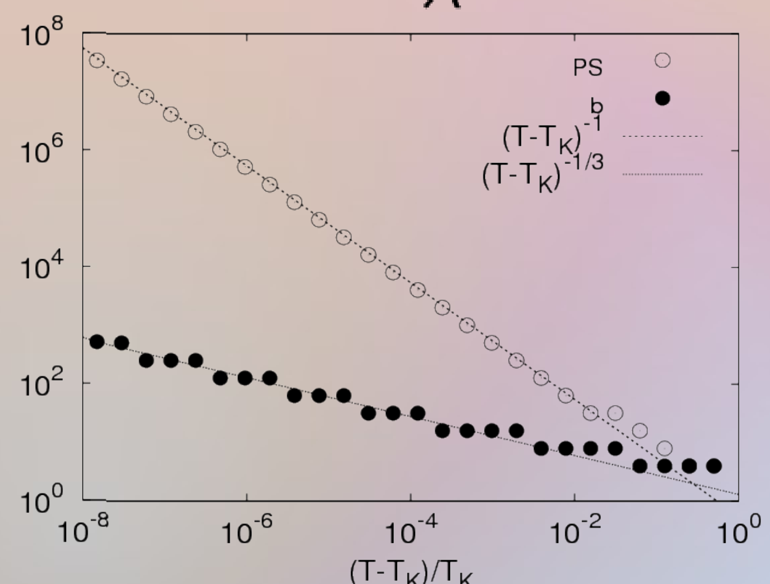
$d_1 < \xi_{PS} < d_2$

Penetration Length
λ





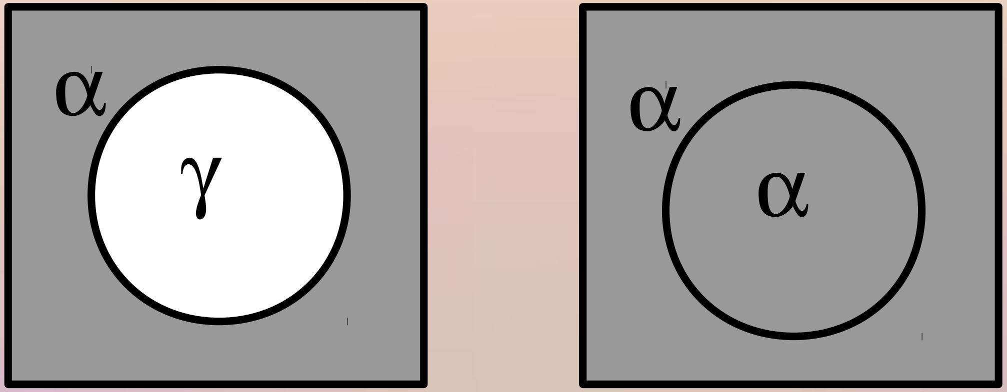
Numerical results on a glass-forming liquid (unpublished)



Analytical results from RG on a finite dimensional model with RFOT transition (Cammarota *et al.,* PRL, 2010)

Energy cost of interfaces: spherical cavity ?

Consider cavieties completely uncorrelated from random boundary.
An interface must be there hidden somewhere … can we measure its energy ?



$\langle E_{\alpha\gamma}\rangle - \langle E_{\alpha\alpha}\rangle = ?$

Energy cost of interfaces: spherical cavity ?

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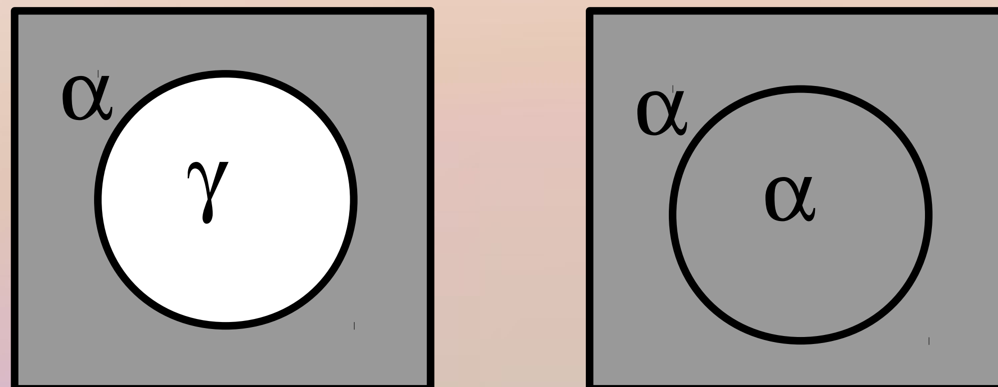


$\langle E\alpha\gamma\rangle$ - $\langle E\alpha\alpha\rangle$ = ?

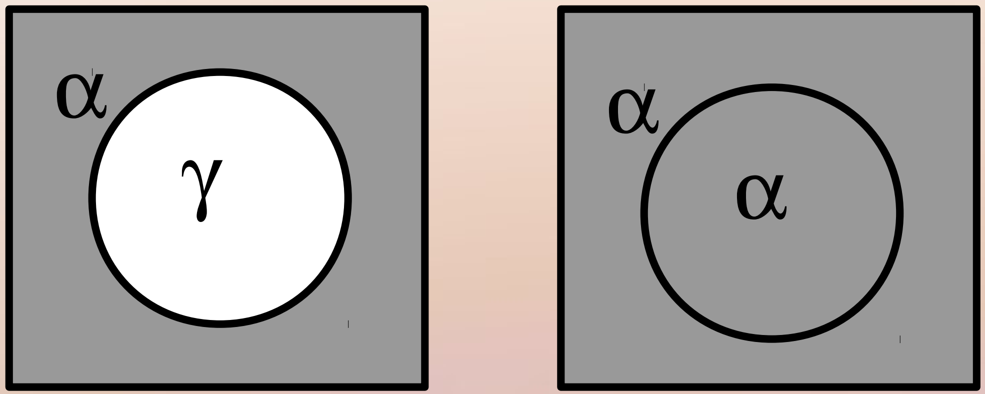
Let us assume that thermodynamics is “insensitive” to a hard wall within the system...

$$\langle E\rangle = \frac{1}{\mathcal{Z}}\int \mathcal{D}\mathbf{X}\,\mathcal{H}(\mathbf{X})e^{-\beta\mathcal{H}(\mathbf{X})} = \frac{1}{\mathcal{Z}}\int \prod_{i=1}^{M} d\mathbf{x}_i \prod_{j=M+1}^{N} d\mathbf{r}_j e^{-\beta\tilde{\mathcal{H}}(\mathbf{X},\mathbf{R})}\tilde{\mathcal{H}}(\mathbf{X},\mathbf{R})$$

$$\tilde{\mathcal{H}}(\mathbf{X},\mathbf{R}) = \mathcal{H}(\mathbf{X},\mathbf{R}) + \sum_i v_{in}(\mathbf{x}_i) + \sum_i v_{out}(\mathbf{r}_i)$$

$$\mathbf{X} = \{\mathbf{x}_1,\ldots,\mathbf{x}_M\} \quad \mathbf{R} = \{\mathbf{r}_{M+1},\ldots,\mathbf{r}_N\}$$

Energy cost of interfaces: spherical cavity ?



<Eαγ - Eαα> = ?

1) Sample all equilibrium configurations in the cavity and keep fixed the outside particles.

$$\mathcal{Z}(\mathbf{X}_{out}) = \int \prod_{i \in in} d\mathbf{x}_i \; e^{-\beta \widetilde{\mathcal{H}}(\mathbf{X}^{in}, \mathbf{X}^{out})}$$

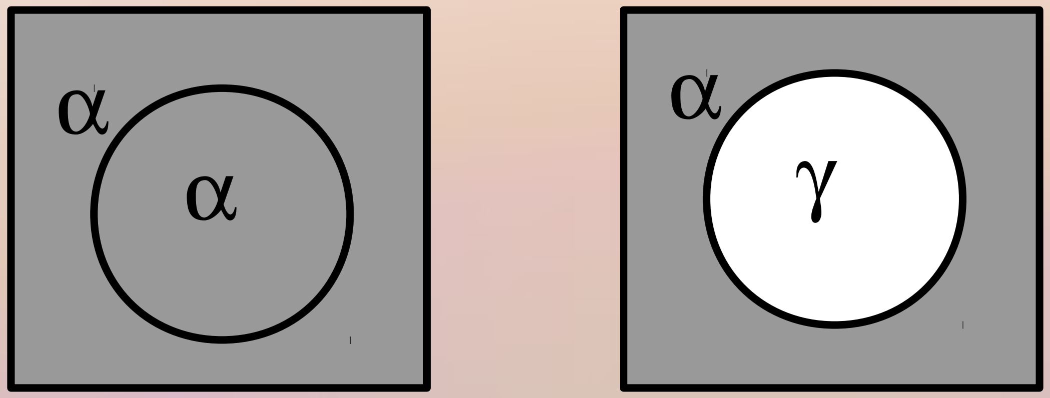
$$\langle E \rangle_{\mathbf{X}^{out}} = \frac{1}{\mathcal{Z}(\mathbf{X}_{out})} \int \prod_{i \in in} d\mathbf{x}_i \, \widetilde{\mathcal{H}}(\mathbf{X}^{in}, \mathbf{X}^{out}) \, e^{-\beta \widetilde{\mathcal{H}}(\mathbf{X}^{in}, \mathbf{X}^{out})}$$

2) Sample **a set** pinning configurations with Boltzmann weigth

$$\overline{\langle E \rangle} = \frac{1}{\mathcal{Z}} \int \prod_{j \in \; all} d\mathbf{x}_j \; \langle E \rangle_{\mathbf{X}^{out}} \; e^{-\beta \widetilde{\mathcal{H}}(\mathbf{X}^{in}, \mathbf{X}^{out})}$$

$$\overline{\langle E \rangle} = \frac{1}{\mathcal{Z}} \int \Big(\prod_{j \in \; out} d\mathbf{x}_j \Big) \mathcal{Z}(\mathbf{X}_{out}) \; \langle E \rangle_{\mathbf{X}^{out}} = \langle E \rangle$$

Energy cost of interfaces: spherical cavity ?

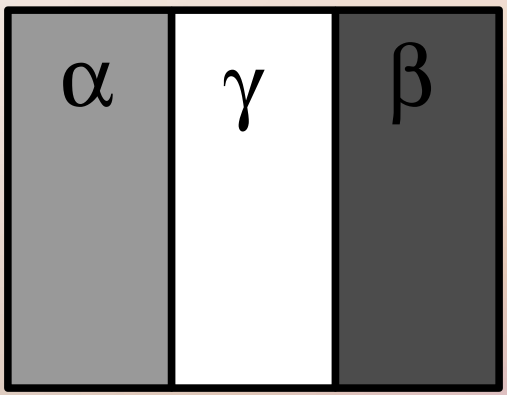


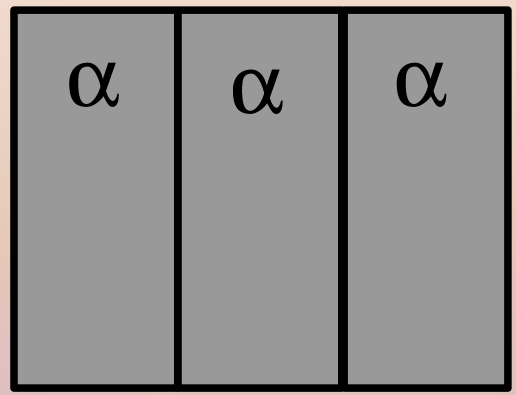
$$\langle E \rangle - \overline{\langle E \rangle} = 0$$

Quenched average equals equilibrium average !

<u>No measure of surface energy from the spherical cavity</u>

Energy of interfaces: sandwitch cavity





$$\langle E\rangle - \overline{\langle E\rangle} = \ ?$$

$$\langle E\rangle^{out}_{\alpha,\beta} = \frac{1}{\mathcal{Z}_{out}} \int \prod_{i\in in} d\mathbf{x}_i\, \tilde{\mathcal{H}}(\mathbf{X}^{out}_{\alpha,L}, \mathbf{X}^{in}, \mathbf{X}^{out}_{\beta,R})\, e^{-\beta\tilde{\mathcal{H}}(\mathbf{X}^{out}_{\alpha,L},\mathbf{X}^{in},\mathbf{X}^{out}_{\beta,R})}$$

$$\mathcal{Z}_{out} = \int \prod_{i\in in} d\mathbf{x}_i\ e^{-\beta\tilde{\mathcal{H}}(\mathbf{X}^{out}_{\alpha,L},\mathbf{X}^{in},\mathbf{X}^{out}_{\beta,R})}$$

2) Sample **independently two set** of pinning configurations with Boltzmann weigth

$$\overline{\langle E\rangle} = \frac{1}{\mathcal{Z}^2} \int \prod_{i_\alpha\in\ all} d\mathbf{x}^\alpha_i \prod_{j_\alpha\in\ all} d\mathbf{x}^\beta_j\, \langle E\rangle^{out}_{\alpha,\beta}\, e^{-\beta\tilde{\mathcal{H}}(\mathbf{X}^{out}_\alpha,\mathbf{X}^{in}_\alpha,\mathbf{X}^{out}_\alpha)}\ e^{-\beta\tilde{\mathcal{H}}(\mathbf{X}^{out}_\beta,\mathbf{X}^{in}_\beta,\mathbf{X}^{out}_\beta)}$$

3) Integrating over “internal” coordinates does not allow to single out $\mathcal{Z}_{out}$

Measure of interface energy cost

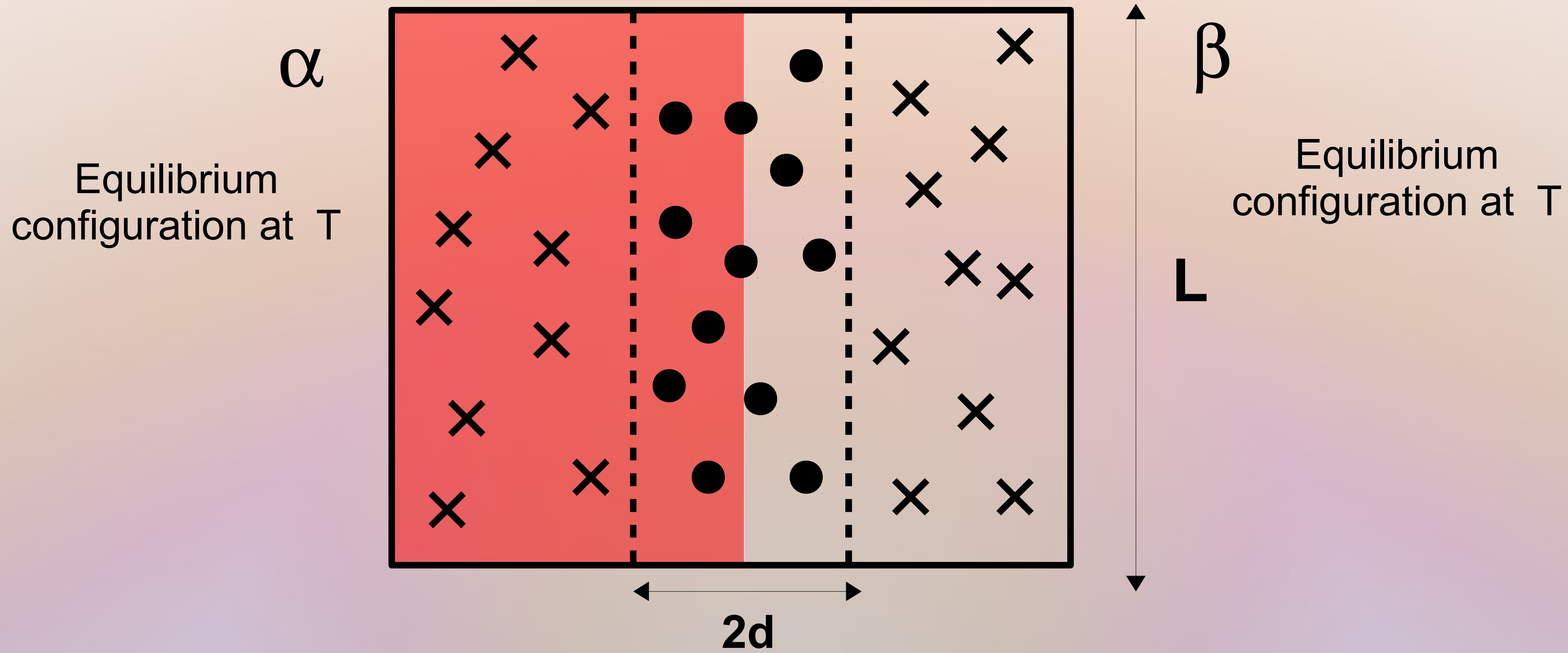
Equilibrium configuration at T

Equilibrium configuration at T

Match two configurations of the liquid equilibrated <u>independently</u> at the

same temperature **T** .

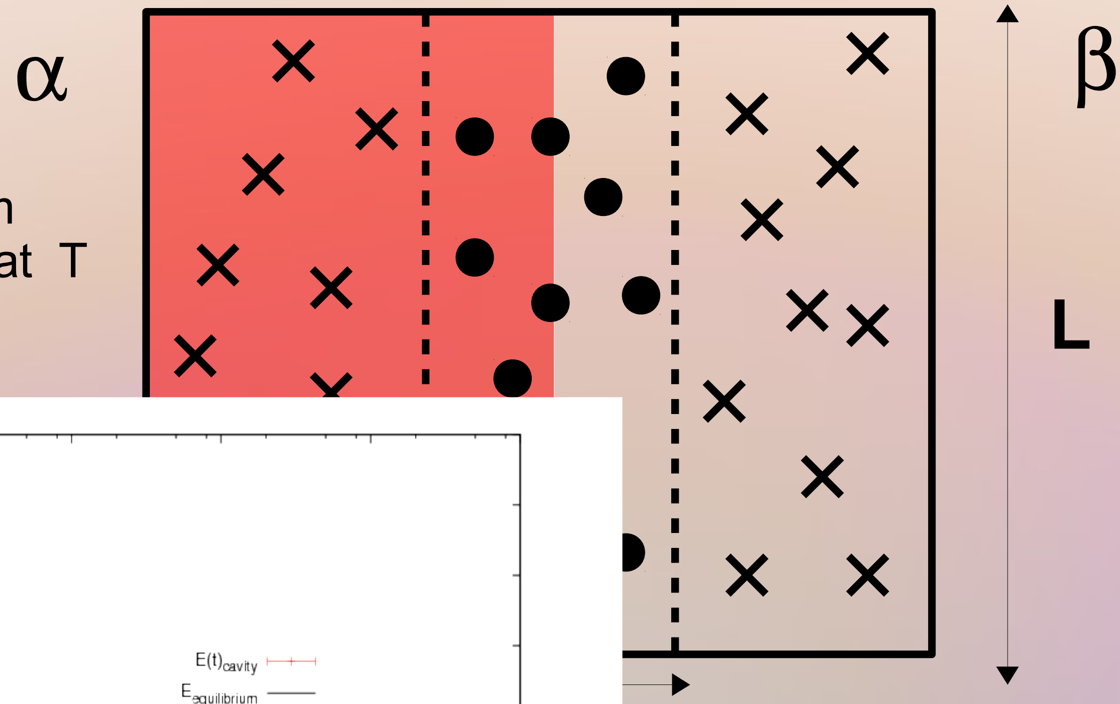
Measure of interface energy cost



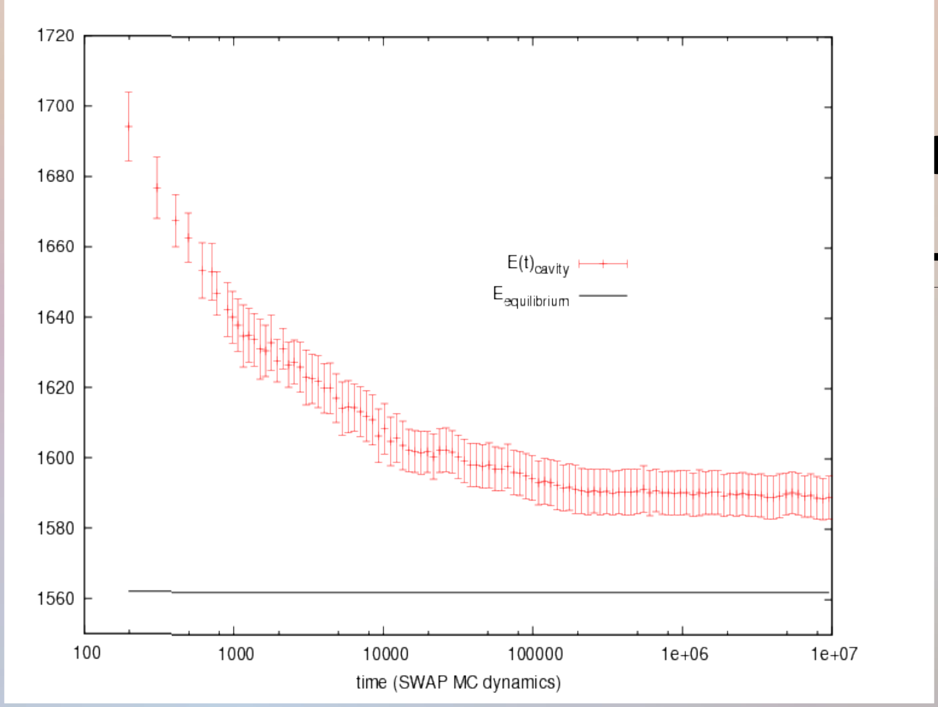
Fix particles in the **boundaries**, acting now as a random pinning field, and equilibrate particles inside the cavity, until a stationary value of the energy is reached

Measure of interface energy cost

Equilibrium configuration at T

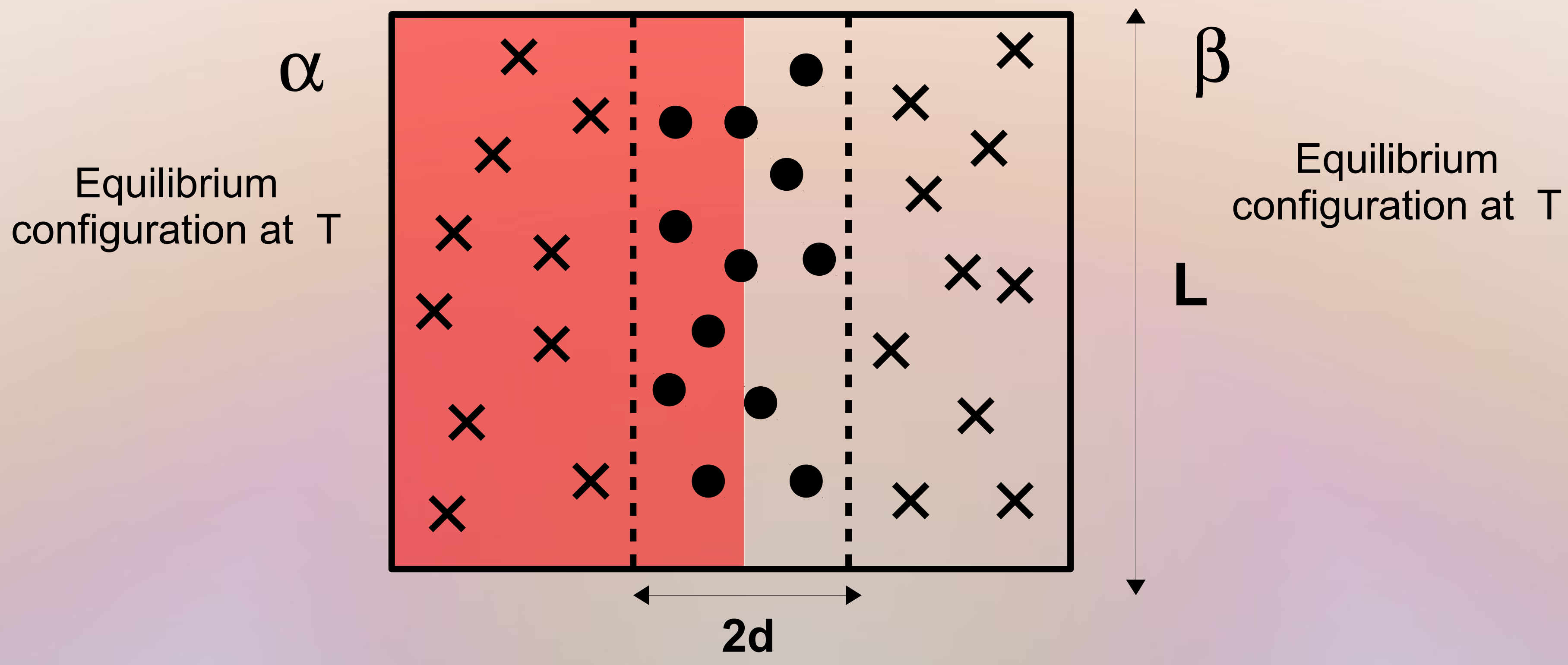


Equilibrium configuration at T



Hard equilibration !

Measure of interface energy cost

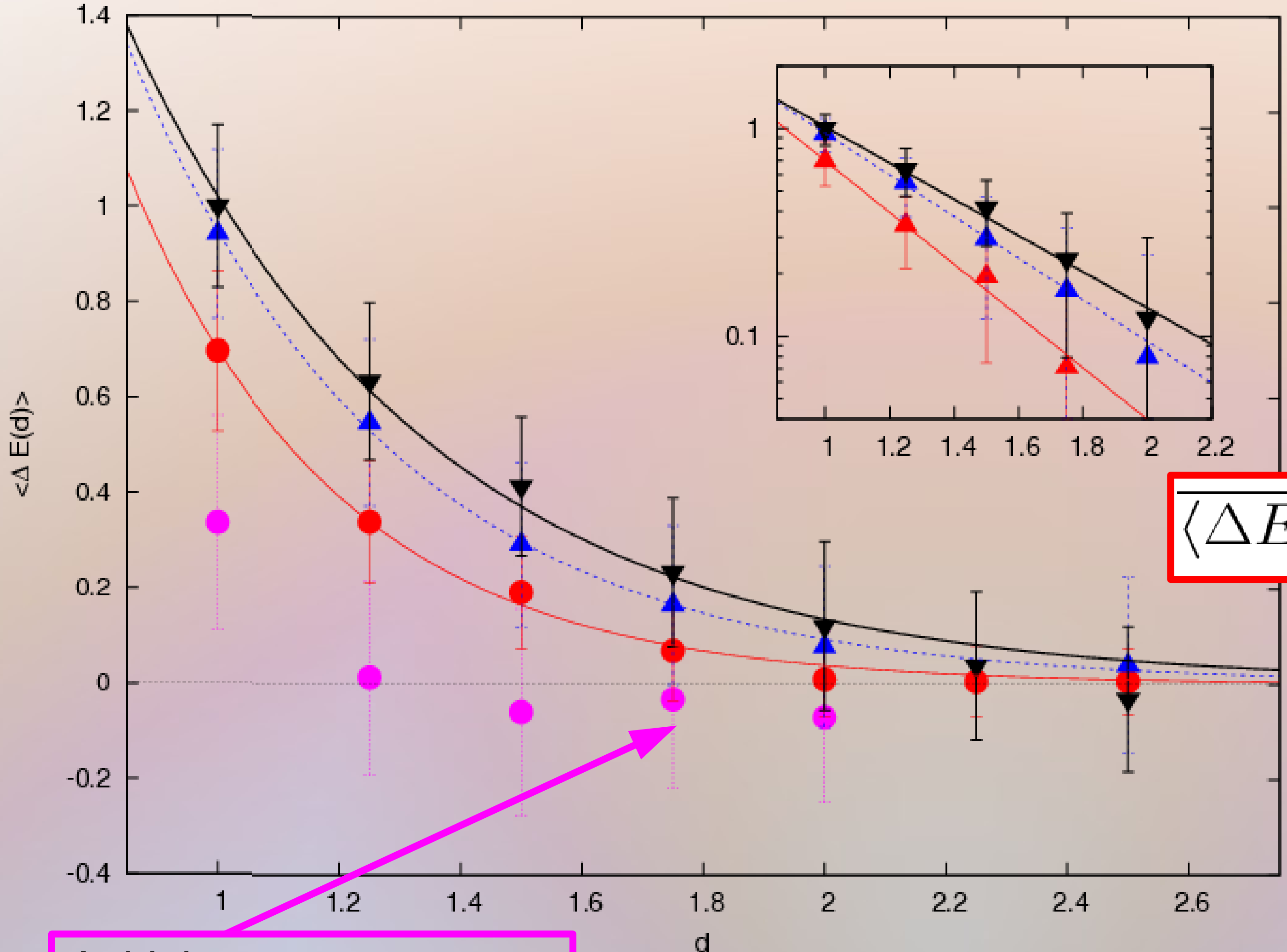


Fix particles in the **boundaries**, acting now as a random pinning field, and equilibrate particles inside the cavity, until a stationary value of the energy is reached

$$\overline{\langle \Delta E(d) \rangle} = \overline{\langle E(d) \rangle} - \langle E \rangle$$

Analitic study in Kac model: (Franz,Zarinelli, *J.Stat.Mech*,2010)

Measure of interface energy



Exponential decay !

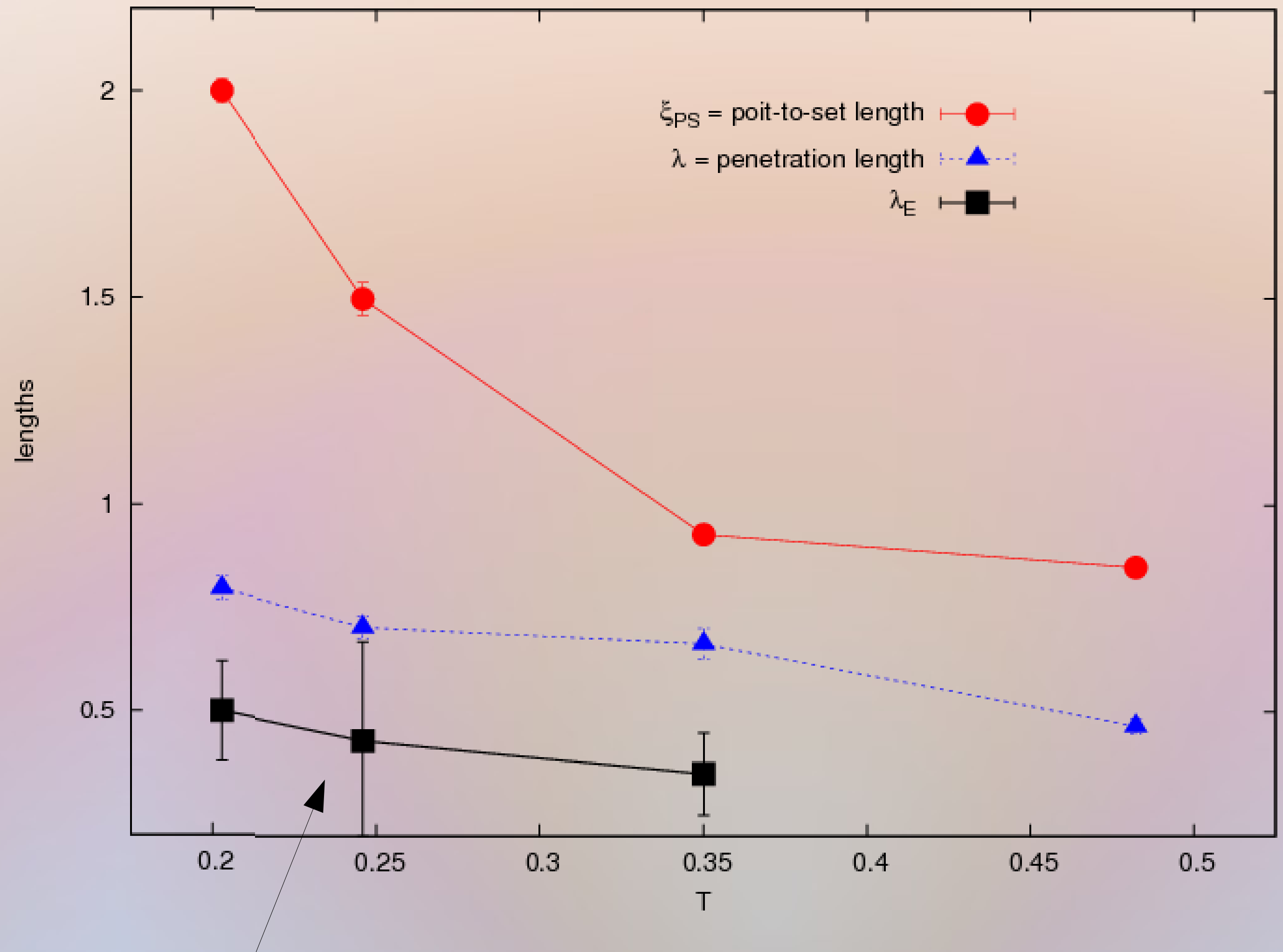
$$\overline{\langle \Delta E(d) \rangle} \sim e^{-d/\lambda_E}$$

At high temperature vanishing energy cost … no more states

Equilibrium energy cost of matching different states !

(Franz,Zarinelli, *J.Stat.Mech*, 2010)

Point-to-set, penetration and interface energy length



λ_E for energy decay close related to penetration length !

Stiffness Exponent from inteface energy ?

General expression for energetic cost of an inteface

1) $$\overline{\langle \Delta E(d,L) \rangle} \sim L^{\theta}\, g(d/L, d/\lambda)$$

2) In the limit d, λ << L $$\lim_{L\to\infty} \frac{\overline{\langle \Delta E(d,L) \rangle}}{L^2} = \mathrm{const}$$

3) The only coiche left is : $$g(d/L, d/\lambda) = \left(\frac{d}{L}\right)^{2-\theta} \tilde{g}(0, d/\lambda)$$

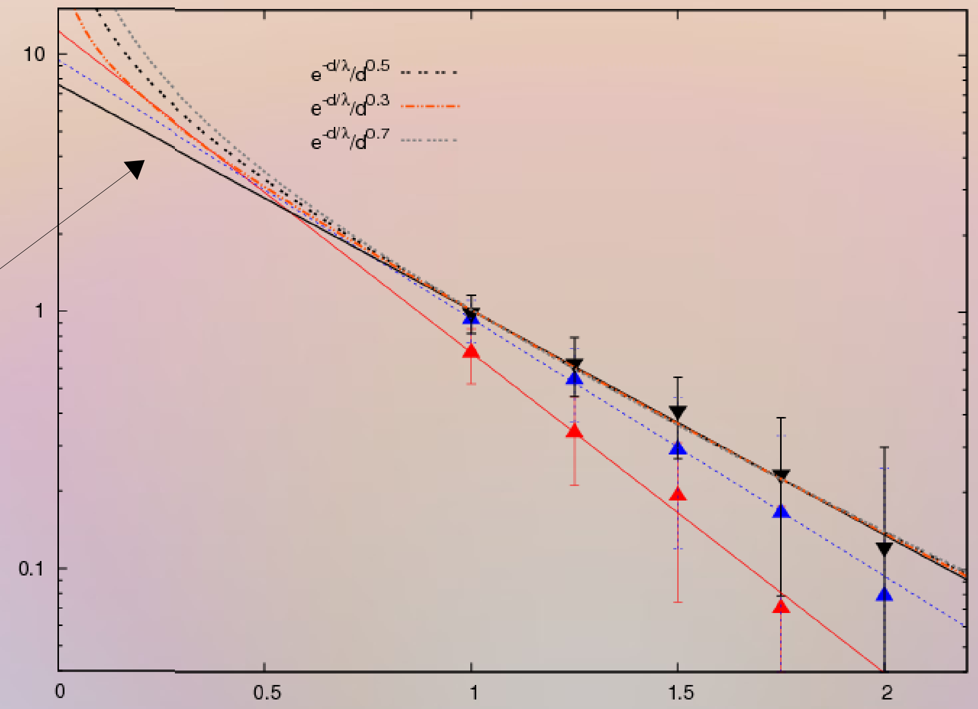
4) And a reasonable one : $$\tilde{g}(0, d/\lambda) \sim \exp(-d/\lambda)$$

$$\overline{\langle \Delta E(d,L) \rangle} \sim L^2\, \frac{\exp(-d/\lambda)}{d^{2-\theta}}$$

Stiffness Exponent from inteface energy ?

Stiffness exponent undecidable from our data !

Fit with different power laws are equally good for our data



Need to probe larger values of the penetration length !

$$\overline{\langle \Delta E(d, L) \rangle} \sim L^2 \, \frac{\exp(-d/\lambda)}{d^{2-\theta}}$$

CONCLUSIONS AND PERSPECTIVES

Measure of the **point-to-set** correlation function in the **sandwich** geometry.
Consistency with result in the spherical cavity: <u>non-exponential behaviour</u>

Comparison of **point-to-set** and **penetration** lengths:
Qualitative agreement with theoretical predictions

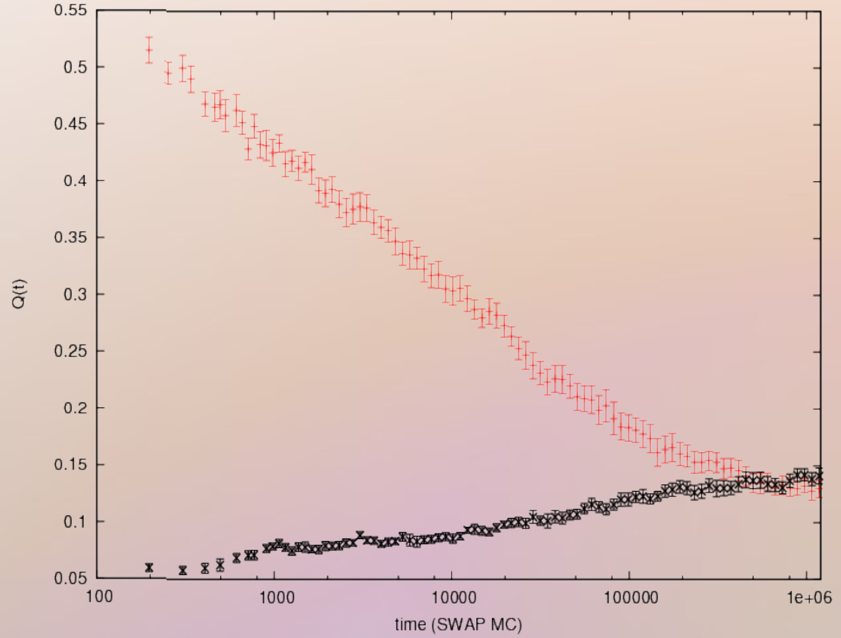
Sandwich geometry allows one to measure the **energy of amorphous interfaces**: amorphous states are there !

Need to go to **lower temperatures** to measure the **stiffness exponent** !

THANKS !

EQUILIBRATION OF THE CAVITY: YOUNG TEST

SWAP (non local)
Monte Carlo dynamics



Large cavity

Small cavity