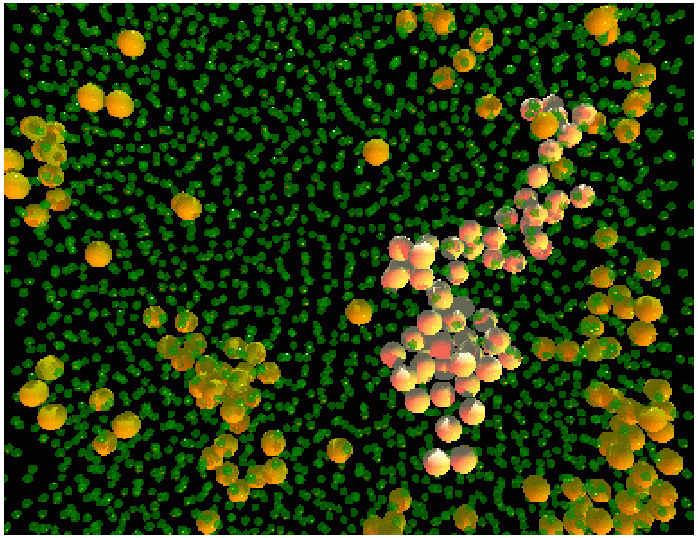
Inhomogeneous Mode Coupling Theory and Dynamic Heterogeneity



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(Talk at Blore 01/09/2010)

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See G. Biroli et al. *Phys. Rev. Lett.* **97**, 195701 (2006).

OVERVIEW

Lecture 1: Dynamic Heterogeneity

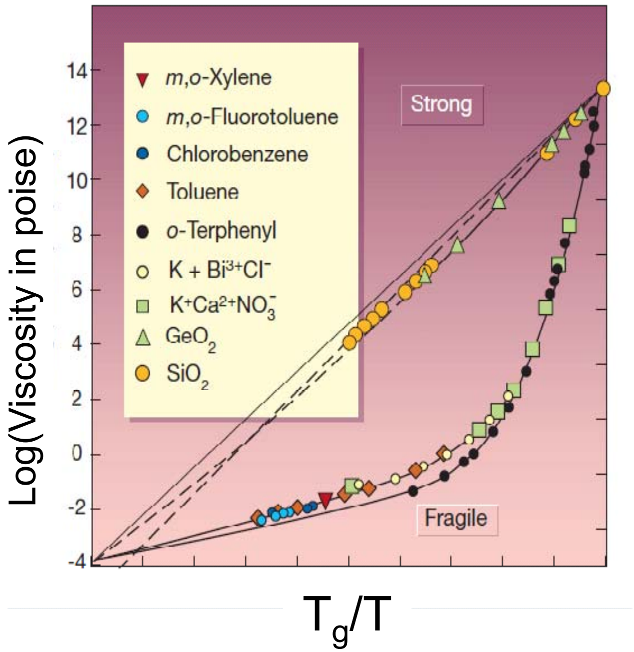
- Motivation
- What causes the slow dynamics?
- Dynamic heterogeneity
- Dynamic heterogeneity and hidden length scale
- Various scenarios of dynamic heterogeneity

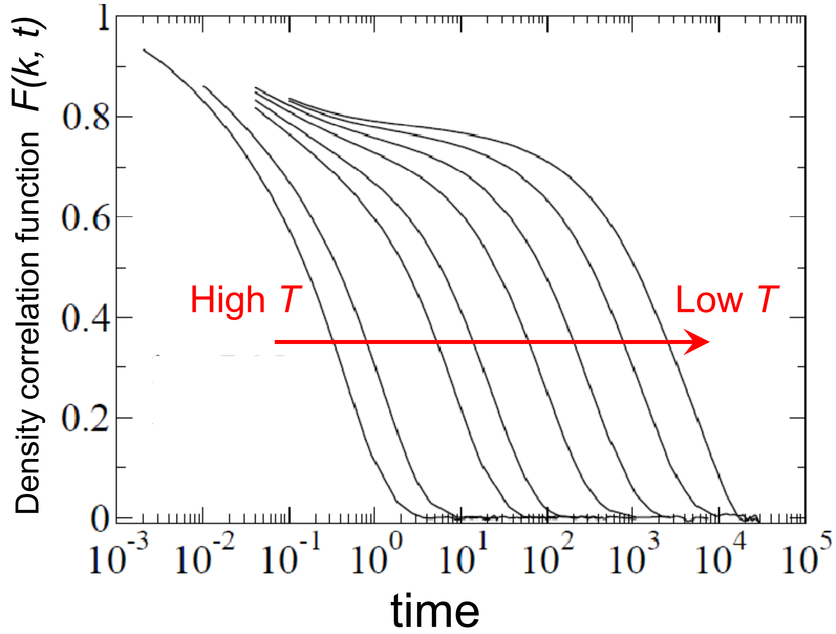
Lecture 2: Inhomogeneous MCT

- Mode-Coupling Theory reloaded
- Inhomogeneous Mode Coupling Theory
- Comparison with simulations
- Where are we and what should we look at?

MOTIVATIONS

What is the glass transition?





Drastic slowing down of supercooled liquids at low temperature

MOTIVATIONS

What is the glass transition?

Important unanswered questions

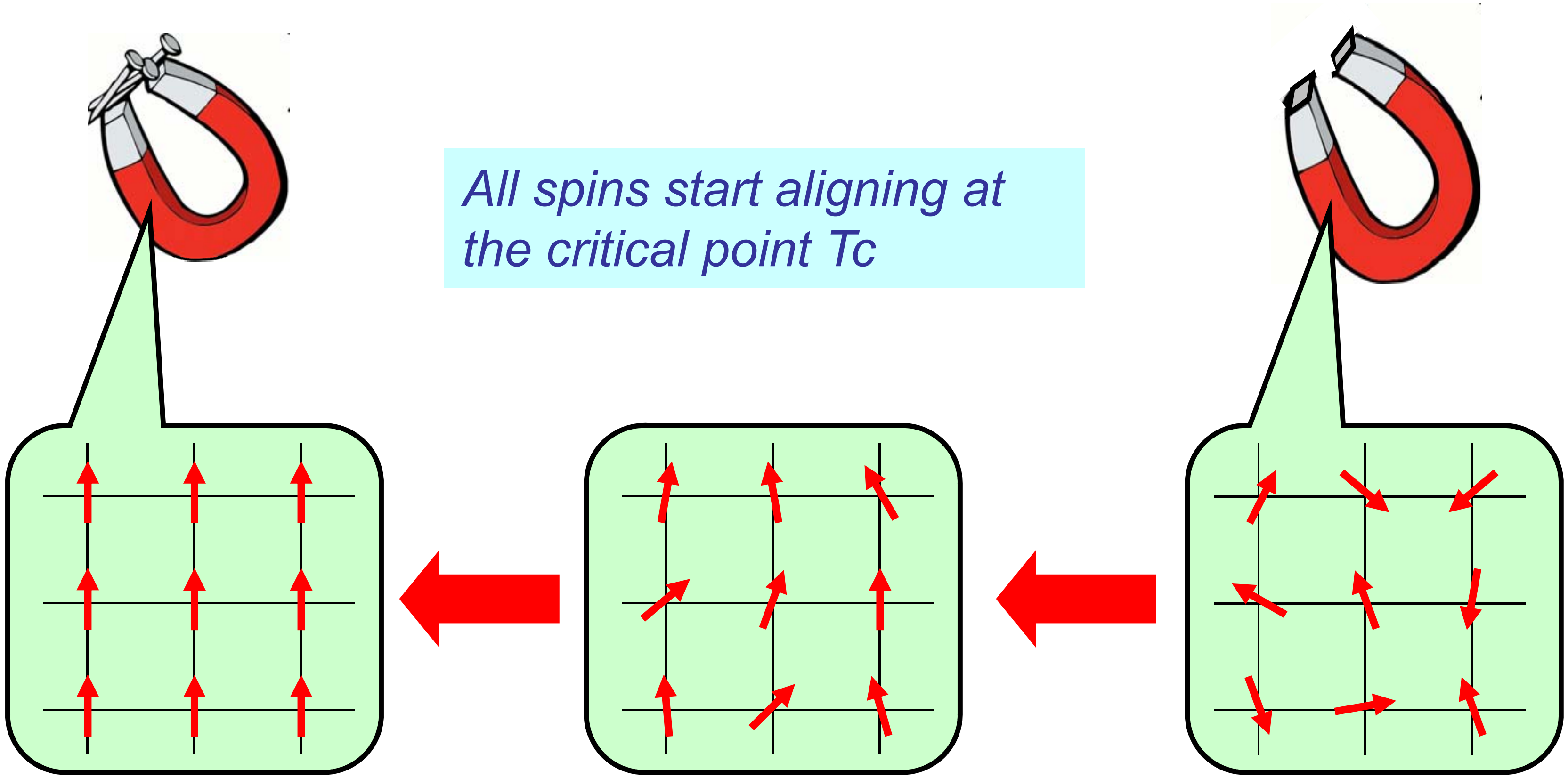
- The glass transition point exists?
  If so, is this purely dynamic
  or any underlying thermodynamic transition escorting slow dynamics?

- What causes the slow dynamics?
  Any characteristic length scale controlling the collective motion?

What causes the slow dynamics?

Conventional Critical Phenomena (2nd order phase transition)

Ferro/Para-magnetic phase transition



Low temperature | $T = T_C$ | *High temperature*

What causes the slow dynamics?

Conventional Critical Phenomena (2nd order phase transition)

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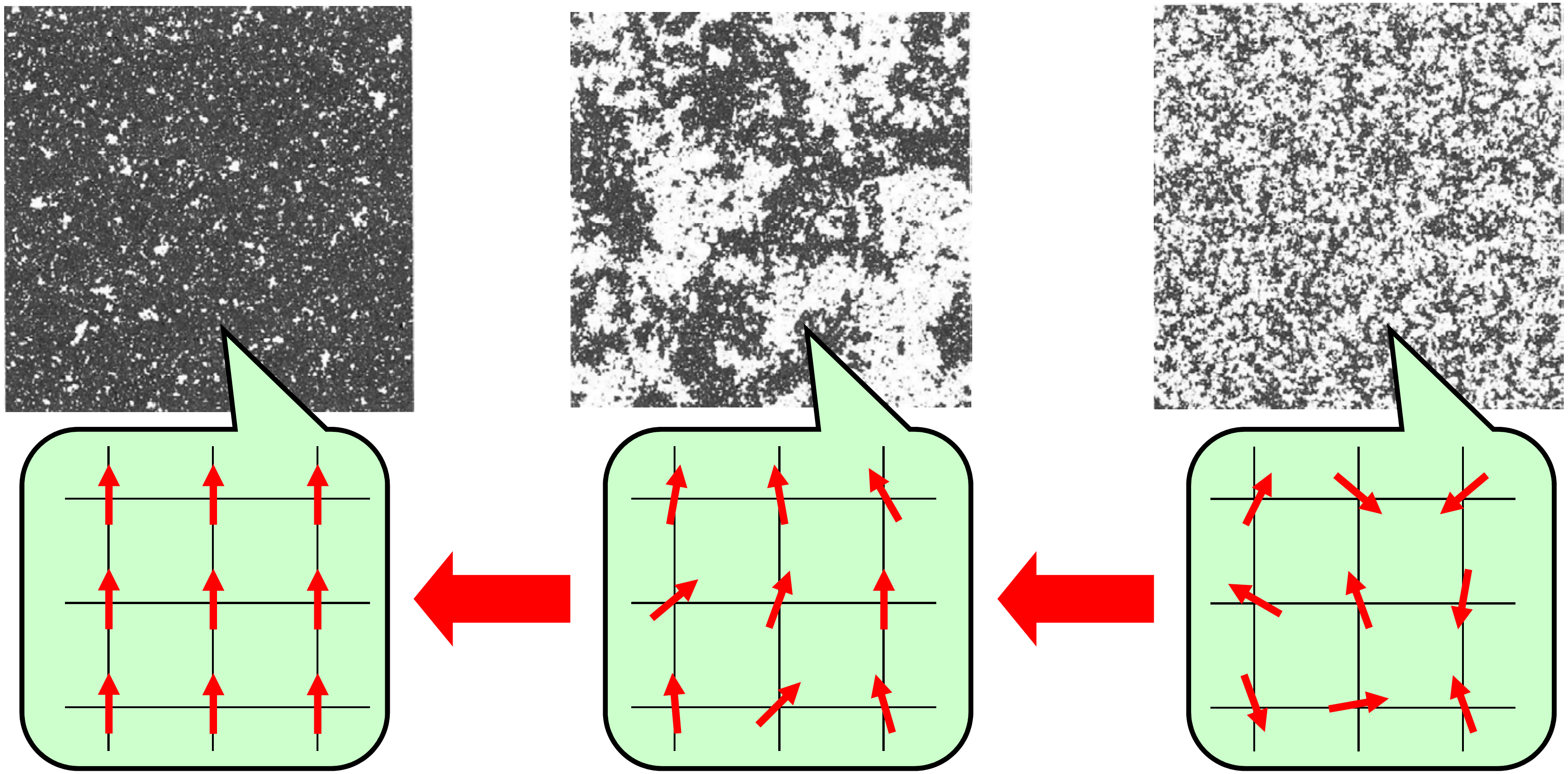

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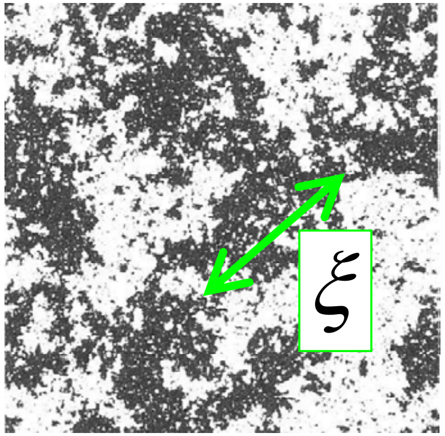

Correlation function of the order parameter

$$G(r) = \langle M(r)M(0)\rangle \approx \exp[-r/\xi]/r^{\tau}$$

$M(r)$ *: the order parameter (magnetization)*

$$\xi = |T - T_c|^{-\nu} \qquad (\nu = 1/2,\ \text{Mean field theory})$$

Characteristic size (correlation length) of fluctuations diverges!

What causes the slow dynamics?

Conventional Critical Phenomena (2nd order phase transition)

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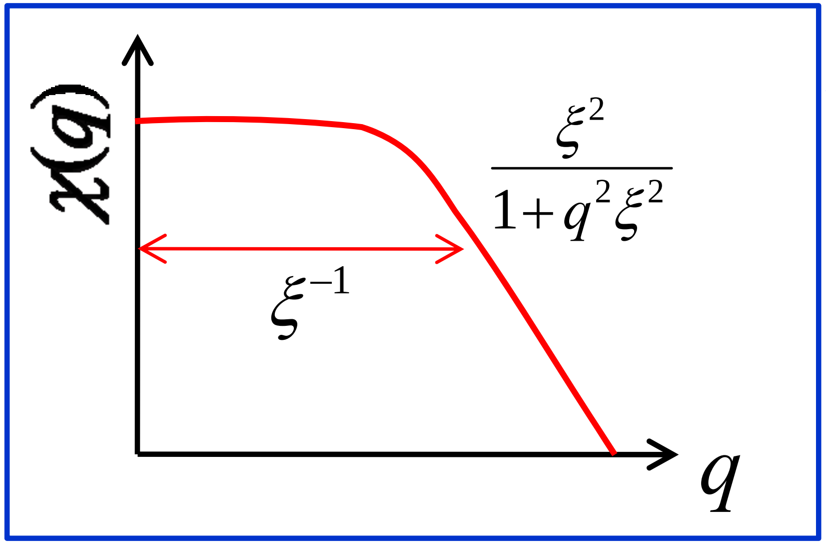


$\chi(q)$: Fourier transform of *G*

Orstein-Zernike like behavior

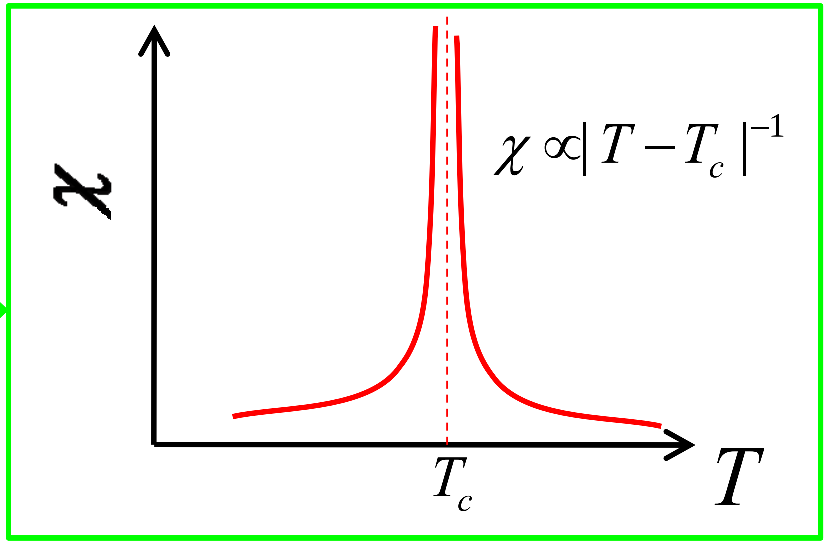
$$\chi(q) = \frac{\xi^2}{1+q^2\xi^2}$$

with ξ increasing as *T* lowered

$$\chi \equiv \chi(q=0) \propto \xi^2$$

Integral of *G(r)* over space

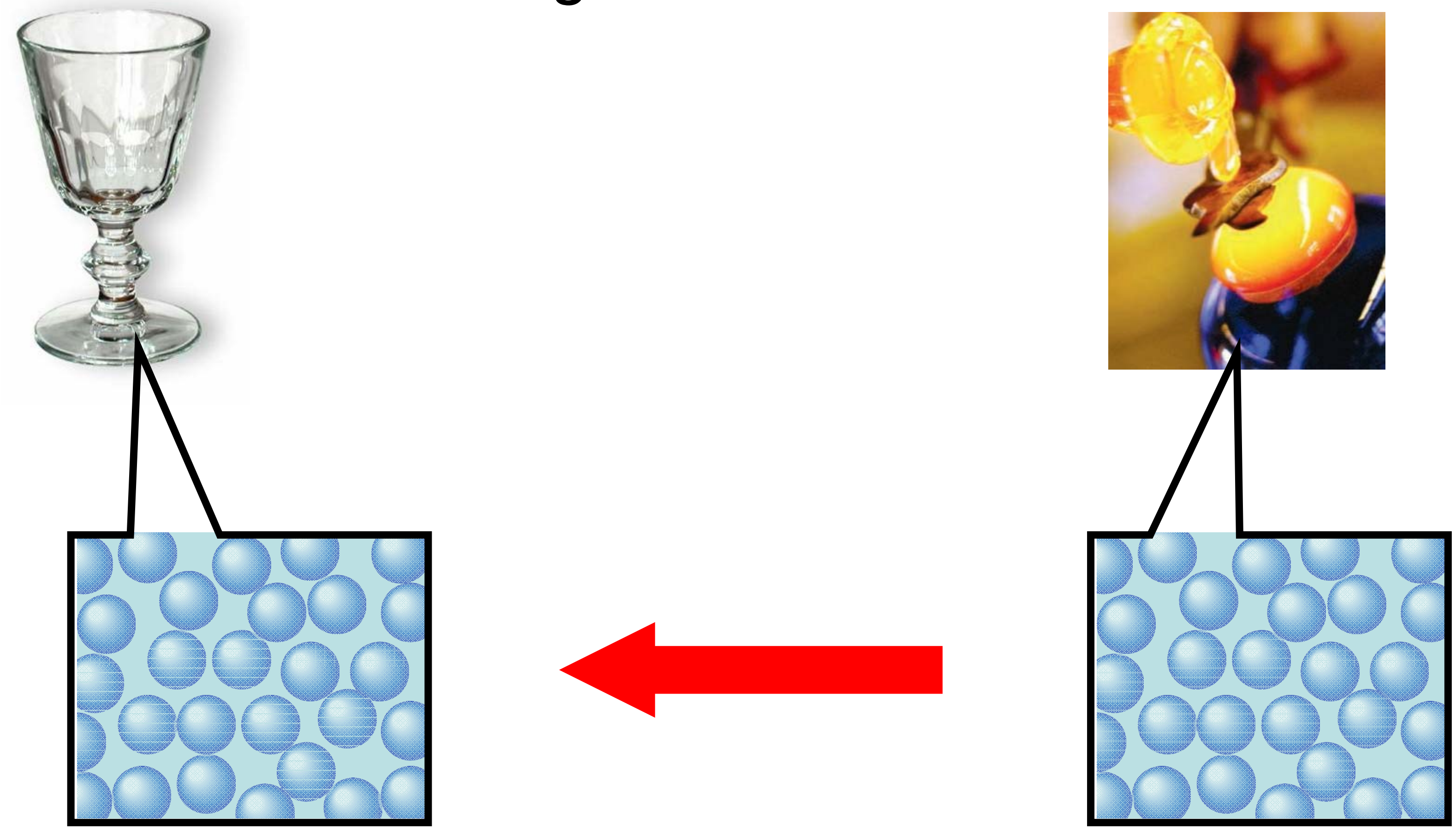
Its amplitude diverges at Tc.



What causes the slow dynamics?

For the glass transition...

Where is the sign of "transition" hidden?



Low temperature near T_g

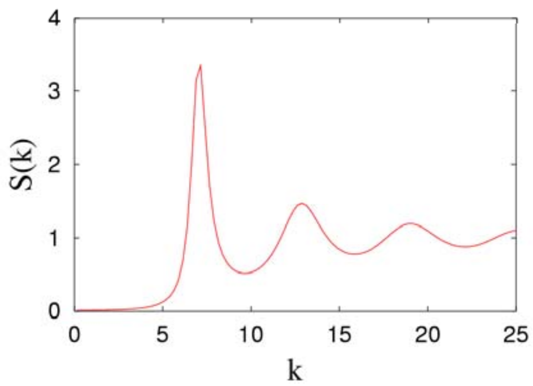
High temperature

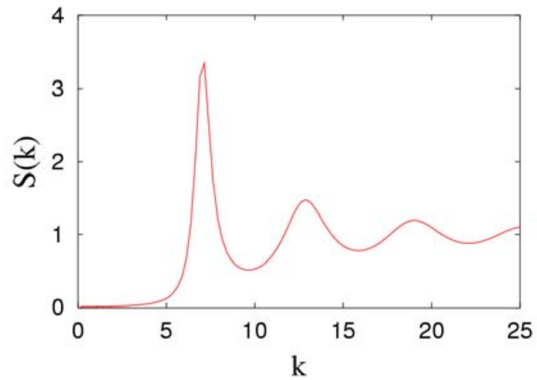
What causes the slow dynamics?

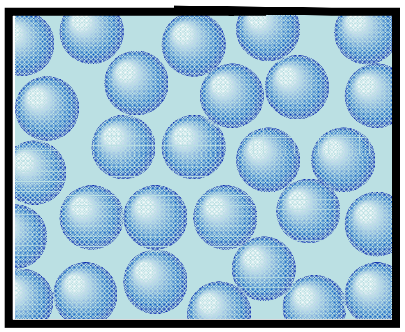
For the glass transition...

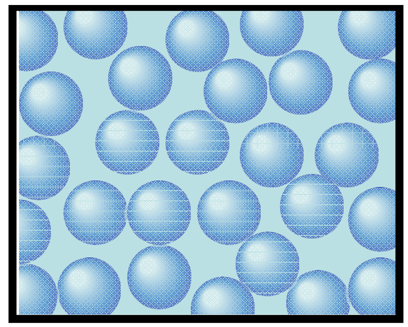
Where is the sign of "transition" hidden?

$S(k) =$ Fourier transform of $\langle \rho(r)\rho(0) \rangle$









Low temperature near T_g

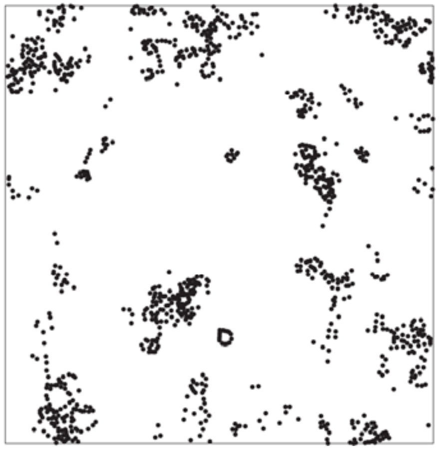
High temperature

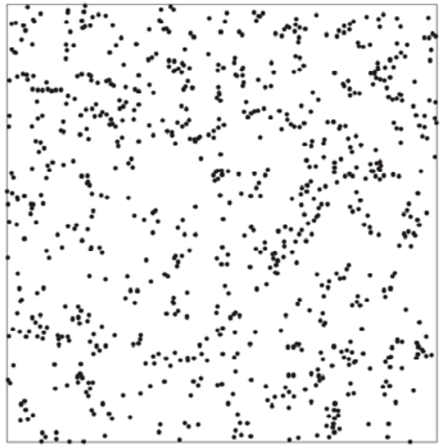
What causes the slow dynamics?

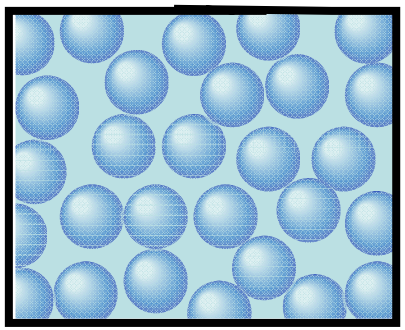
For the glass transition...

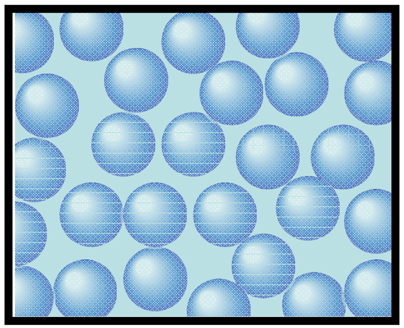
Where is the sign of “transition” hidden?

Motion of atoms









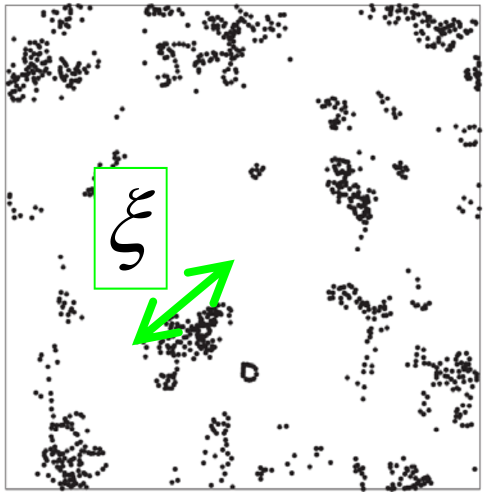
Low temperature near T_g

High temperature

Dynamic Heterogeneity

Dynamic Heterogeneities in Simulations

(Yamamoto et al. '98)



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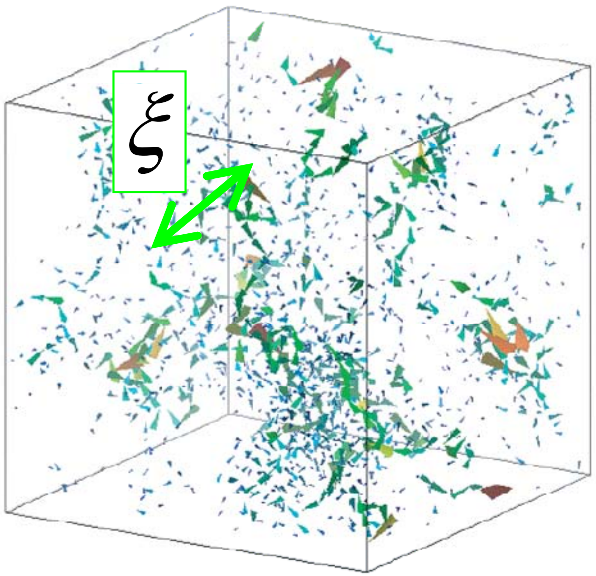
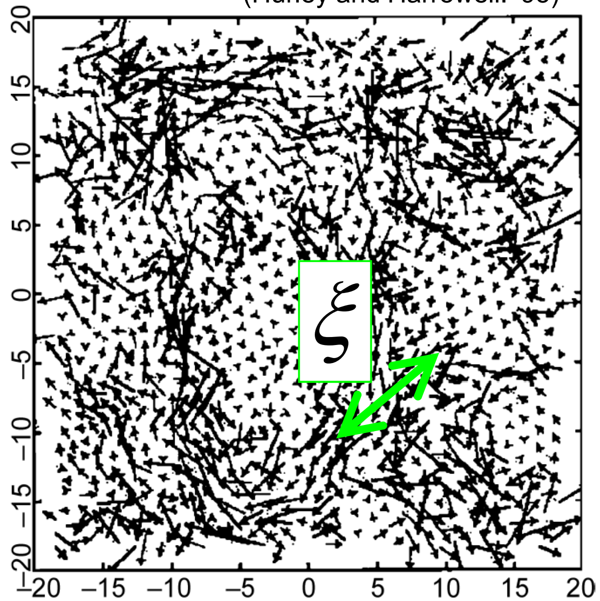


(Hurley and Harrowell. '95)

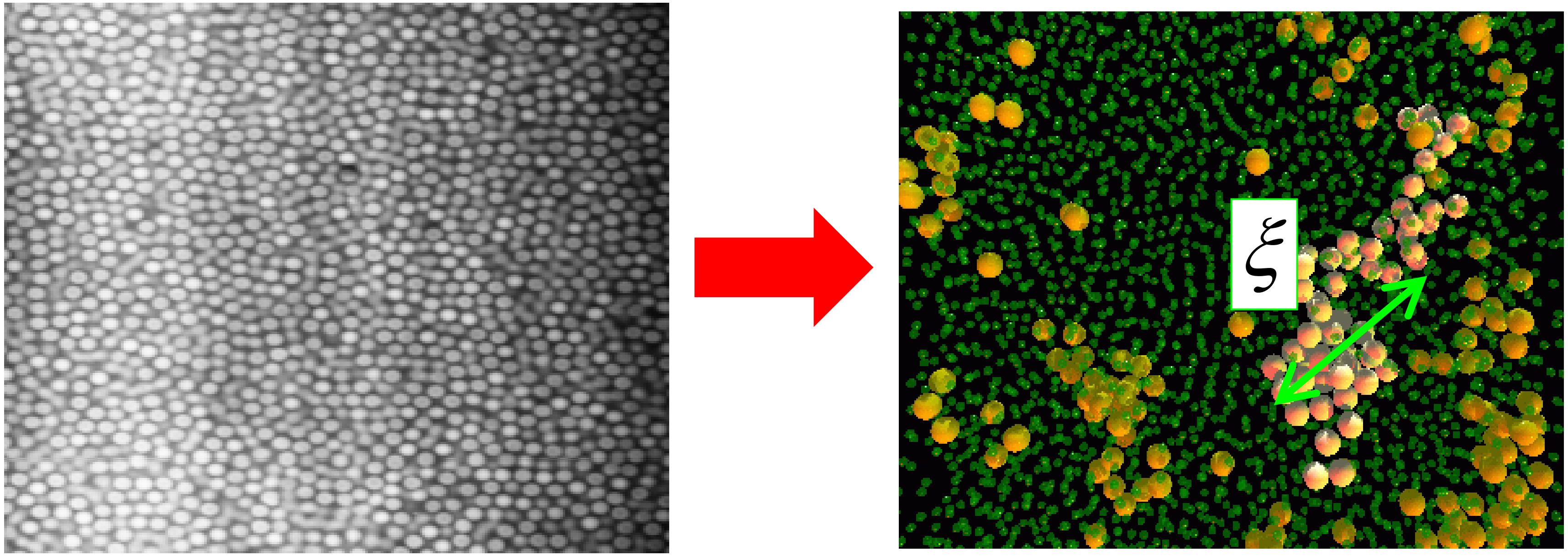


Dynamic Heterogeneity

Dynamic Heterogeneities in Experiments

Colloidal suspension

(Week et al. ’00)



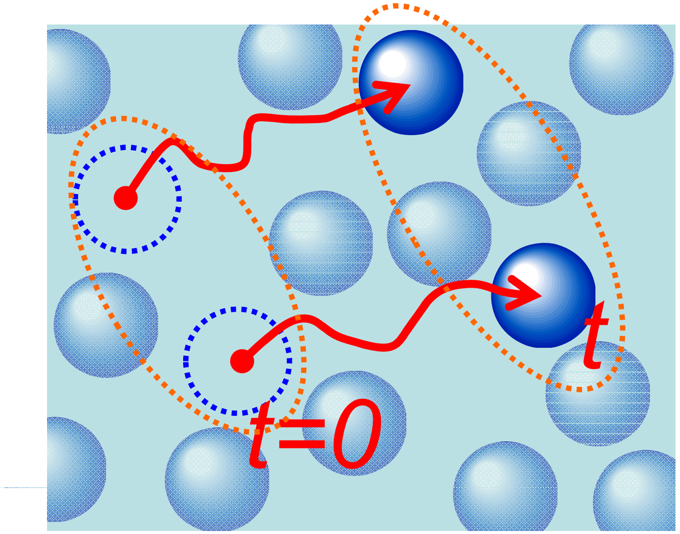
Dynamic heterogeneity and hidden length scale

How to quantify the dynamic heterogeneity?

Nonlinear susceptibility

or

4 point correlation function



Density-density correlation function (2-point)

$$F(k,t) = \langle \rho_k(t)\, \rho_{-k}(0) \rangle \equiv \langle \hat{F}(k,t) \rangle$$

4-point density correlation function

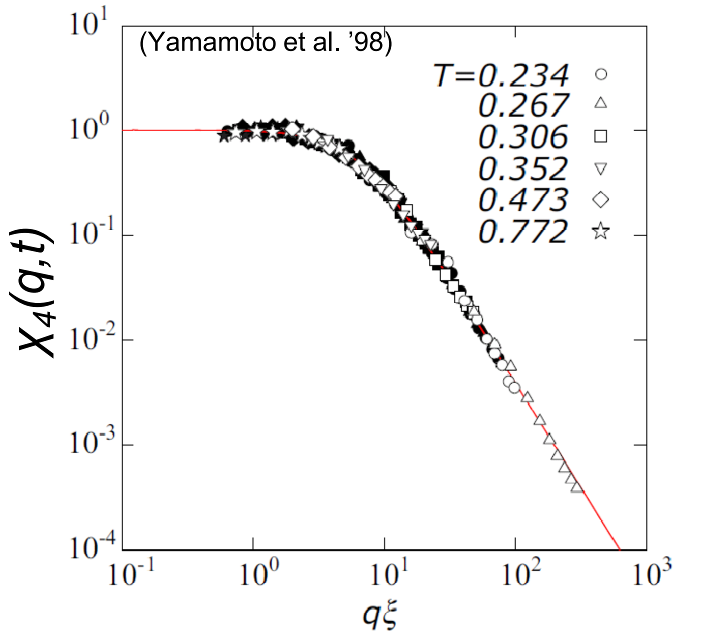
$$G_4(r,t) \approx \langle \rho(r,t)\rho(r,0)\rho(0,0)\rho(0,t) \rangle$$

or

$$\chi_4(t) \approx \int dr\ G_4(r,t) \Leftrightarrow \langle \delta\hat{F}^2(k,t) \rangle$$

Dynamic heterogeneity and hidden length scale

The 4 point correlation function



$\chi_4(q,t)$: Fourier transform of $G_4(r,t)$

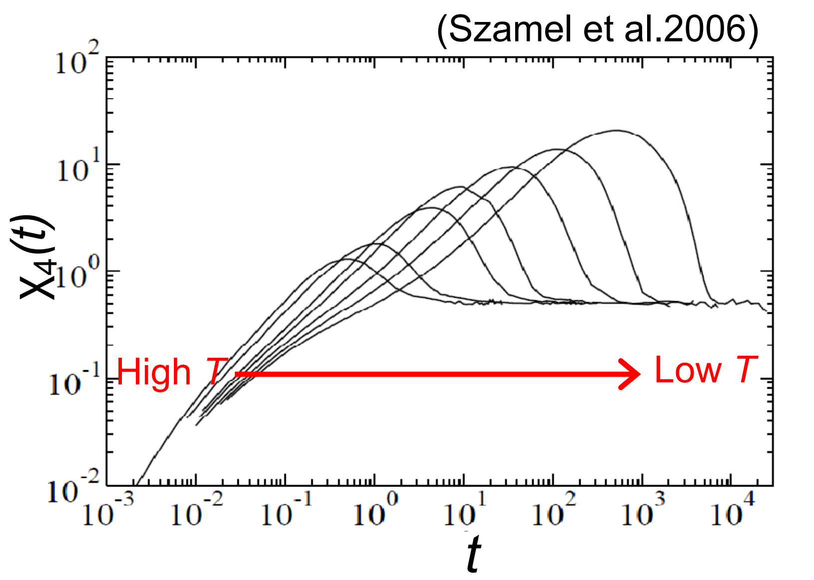
Orstein-Zernike like behavior

$$\chi_4(q,t) \approx \frac{\xi^2}{1+q^2\xi^2} \quad ?$$

with ξ increasing as T lowered

$$\chi_4(t) = \chi_4(q=0,t)$$

Integral of $G_4(r, t)$ over space
Its amplitude grows as T lowered, reflecting a growing length scales.



Various scenarios of dynamic heterogeneity

What is the origin of the dynamic heterogeneity?
Static or purely dynamic?

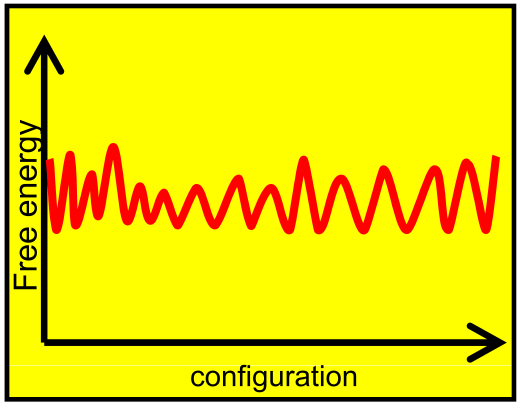
Various scenarios of the glass transition

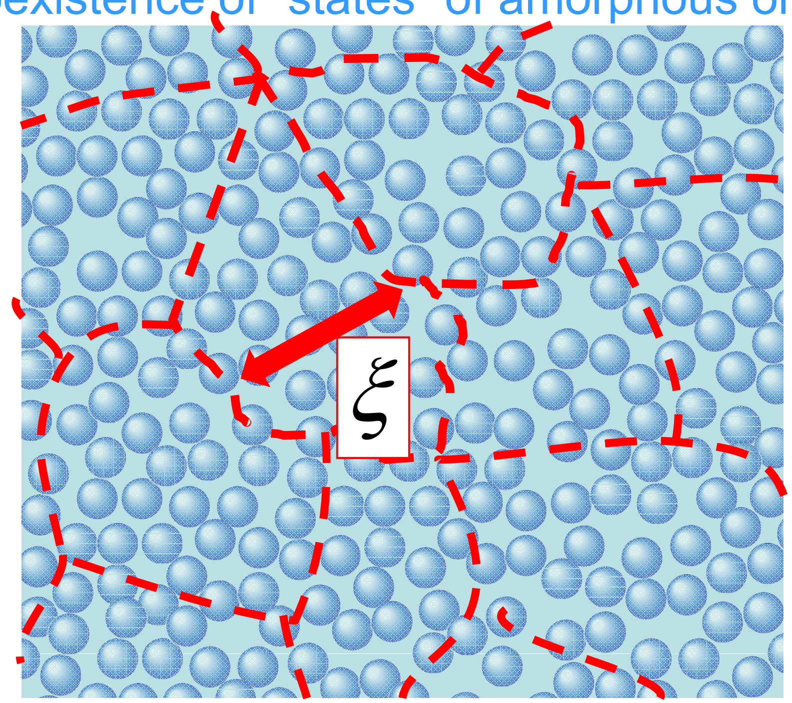
- *Landscape (mosaic) pictures*
- *Frustration picture*
- *Purely dynamic picture*
- *Mode-Coupling Theory*
- *etc…*

Dynamic Heterogeneity

Landscape (mosaic) pictures

Such as
Random First Order Transition theory (RFOT) (G. Biroli's talk)





DH is originated from the static amorphous order

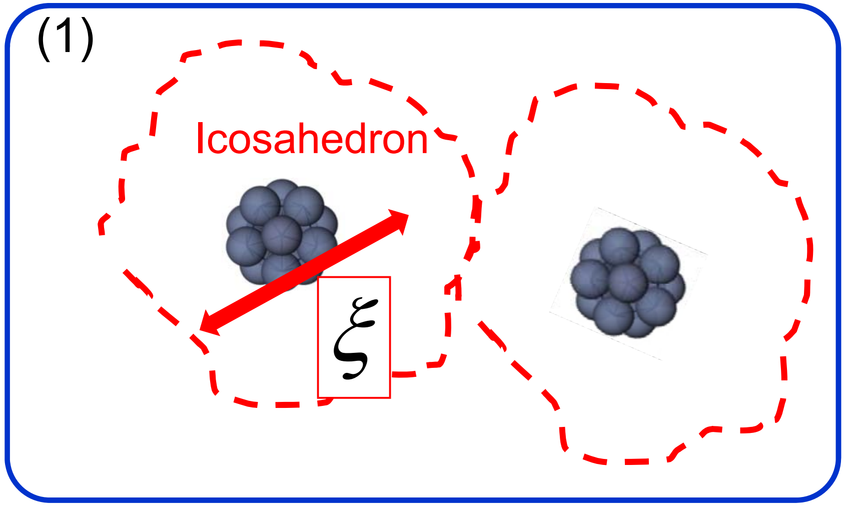
Dynamic Heterogeneity

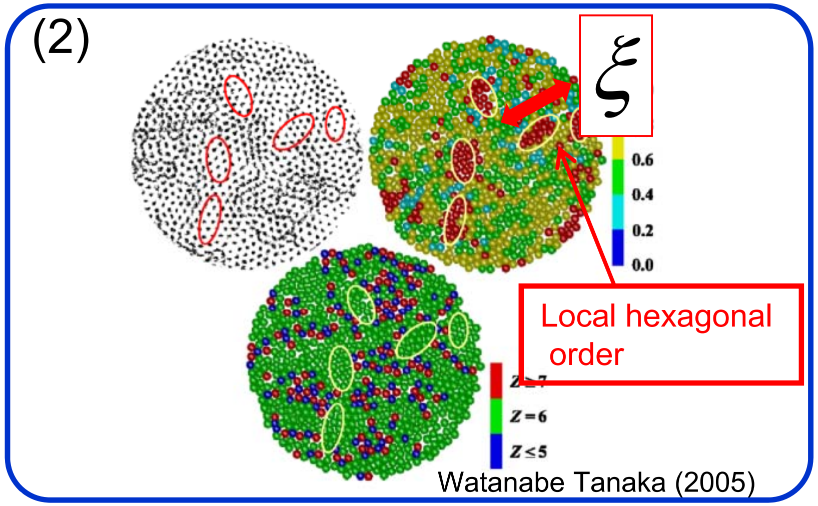
Frustration picture

(1) *Frustration-limited domain*（Tarjus, *et al.* 1996)

(2) *Medium-Range Crystalline Order*（Tanaka 2006-)

Locally favorable orders such as icosahedral or local crystalline order are incompatible with global crystalline order and thus slow dynamics results





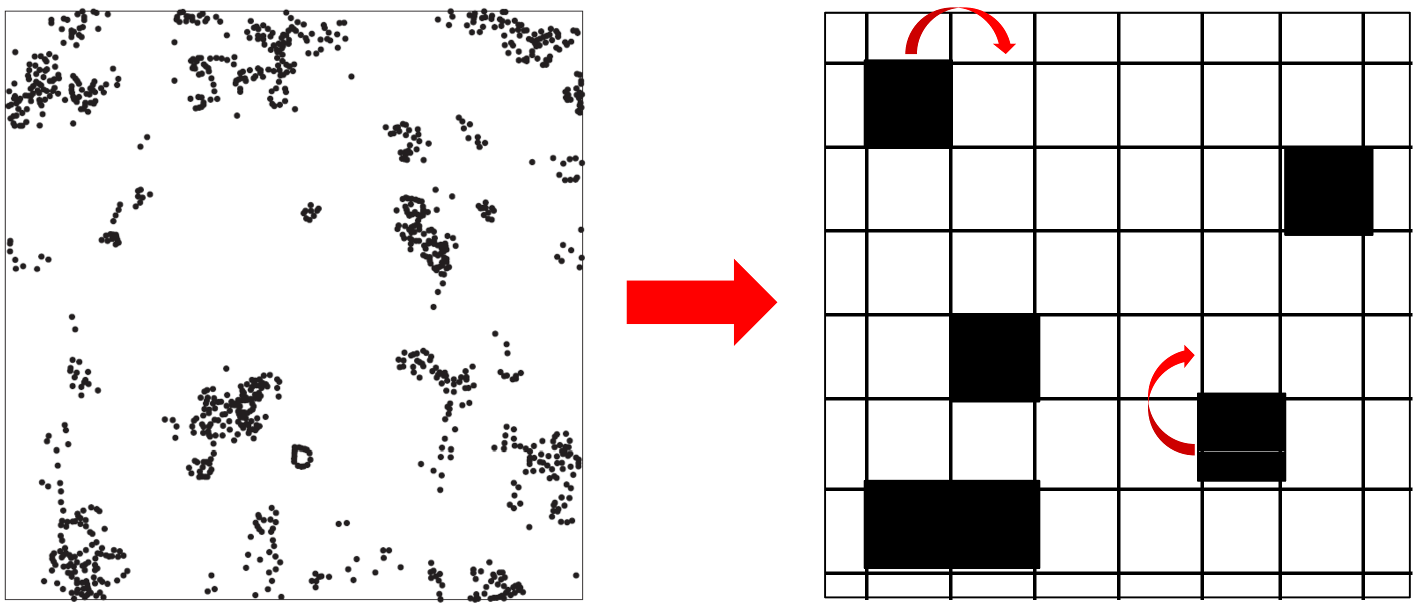
DH is originated from the locally favored static order

Dynamic Heterogeneity

Purely dynamic picture (R. Jack's talk)

Kinetically constrained model (KCM) (Frederickson, Andersen, Garrahan, Chandler…)

Example: Frederickson-Andersen model (1985)



Simulation ***Coase graining***

Ideal-gas-like defects move around with a nontrivial dynamic rules

Dynamic Heterogeneity

Purely dynamic picture (R. Jack's talk)

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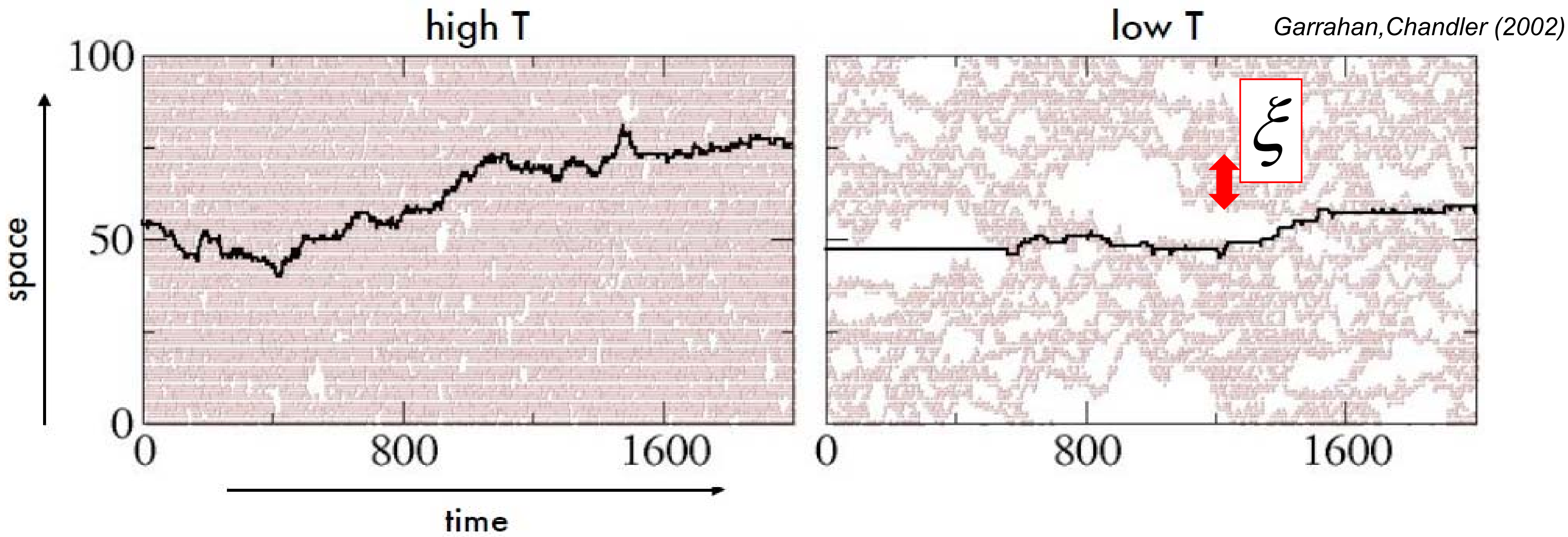
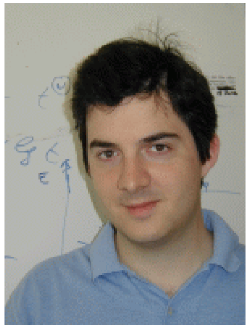
Example: Frederickson-Andersen model (1985)



DH is the spatio-temporal pattern of defects

Dynamic Heterogeneity

Mode-Coupling Theory



To be continued to Lecture 2

OVERVIEW

Lecture 1: Dynamic Heterogeneity

- Motivation
- What causes the slow dynamics?
- Dynamic heterogeneity
- Dynamic heterogeneity and hidden length scale
- Various scenarios of dynamic heterogeneity

Lecture 2: Inhomogeneous MCT

- Mode-Coupling Theory reloaded
- Inhomogeneous Mode Coupling Theory
- Comparison with simulations
- Where are we and what should we look at?

Mode-Coupling Theory Reloaded

Mode Coupling Theory (MCT)

"Only" first principles theory of the glass transition

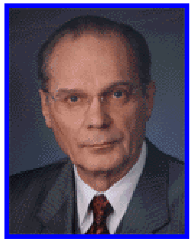
$$\frac{\partial F(k,t)}{\partial t} = -\frac{Dk^2}{S(k)}F(k,t) - \int_0^t dt' M(k,t-t')\frac{\partial F(k,t')}{\partial t'}$$

Structure factor

Memory function (taking care of multibody collisions)

$$M(k,t) = \int dq\, V(q,k-q) F(q,t) F(k-q,t)$$

A function of structure factor



Gotze *et al.* (1984)

Quick Derivation of MCT

STARTING POINT: Diffusion equation for density field with interactions

$$\frac{\partial\rho(r,t)}{\partial t} = -D\nabla\cdot\left\{\nabla\rho(r,t) + \frac{1}{k_B T}\rho(r,t)\nabla\int dr'\,V(r-r')\rho(r,t)\right\} + \nabla\cdot\eta(r,t)$$

Step 0: Let's simplify the equation

$$\dot{x}(t) = -\gamma\, x(t) + \lambda\, x^2(t) + \eta(t)$$

with $\langle\eta(t)\eta(t')\rangle = 2k_B\gamma\delta(t-t')$

Quick Derivation of MCT

Step 1: Multiply x(0) from the right, and then take the average over ensemble

For $C_2(t) = \langle x(t)x(0) \rangle$

$$\frac{\partial C_2(t)}{\partial t} = -\gamma\, C_2(t) + \lambda C_{2,1}(t)$$

where $C_{2,1}(t) = \langle x^2(t)x(0) \rangle$

Step 2: From the reversibility of time

$$C_{2,1}(t) = C_{1,2}(t) \equiv \langle x(t)x^2(0) \rangle$$

Step 3: Take the time derivative of $C_{1,2}(t) \equiv \langle x(t)x^2(0) \rangle$

$$\frac{\partial C_{1,2}(t)}{\partial t} = -\gamma\, C_{1,2}(t) + \lambda C_{2,2}(t)$$

where $C_{2,2}(t) = \langle x^2(t)x^2(0) \rangle$

Quick Derivation of MCT

Step 4: Solving the equation formally for $C_{1,2}(t)$

$$C_{1,2}(t) \approx \lambda \int_0^t dt' \exp\left[-\gamma(t-t')\right] C_{2,2}(t')$$

Step 5: Plug this back to equation for $C_2(t)$

$$\frac{\partial C_2(t)}{\partial t} = -\gamma\, C_2(t) + \lambda^2 \int_0^t dt' \exp\left[-\gamma(t-t')\right] C_{2,2}(t')$$

Step 6: Gaussian approximation for $C_{2,2}(t)$

$$C_{2,2}(t) = \left\langle x^2(t) x^2(0) \right\rangle \approx 2\left\langle x(t) x(0) \right\rangle^2 = 2C_2^2(t)$$

Quick Derivation of MCT

Step 7: Also the simple relaxation can be approximated as

$$\exp\left[-\gamma\, t\right] \approx C_2(t)$$

Step 8: Now arrived at equation closed in terms of $C_2(t)$!

$$\frac{\partial C_2(t)}{\partial t} = -\gamma\, C_2(t) - 2\lambda^2 \int_0^t dt'\, C_2^2(t-t')\, \frac{\partial C_2(t')}{\partial t'}$$

Step 9: Translate back to the original variables. Voila!!

$$\frac{\partial F(k,t)}{\partial t} = -\frac{Dk^2}{S(k)} F(k,t) - \int_0^t dt'\, M(k,t-t')\, \frac{\partial F(k,t')}{\partial t'}$$

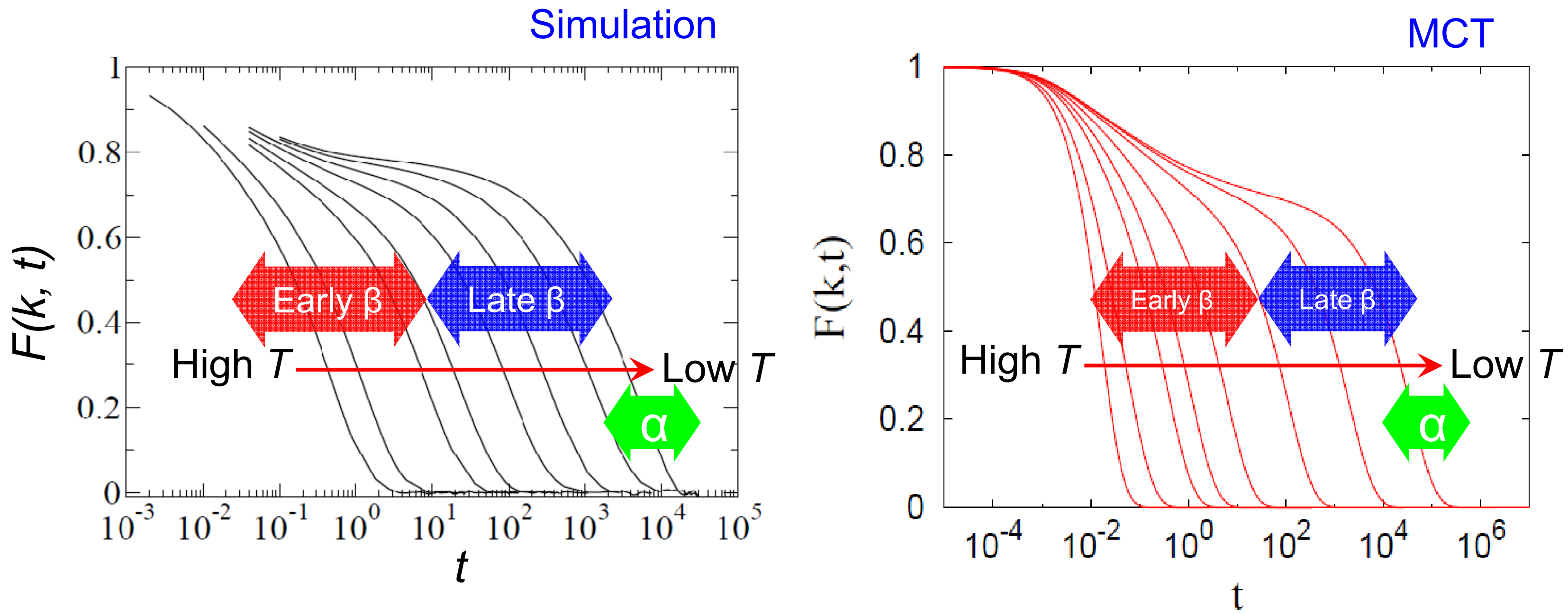
Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

MCT can Predict 2-step relaxation



Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

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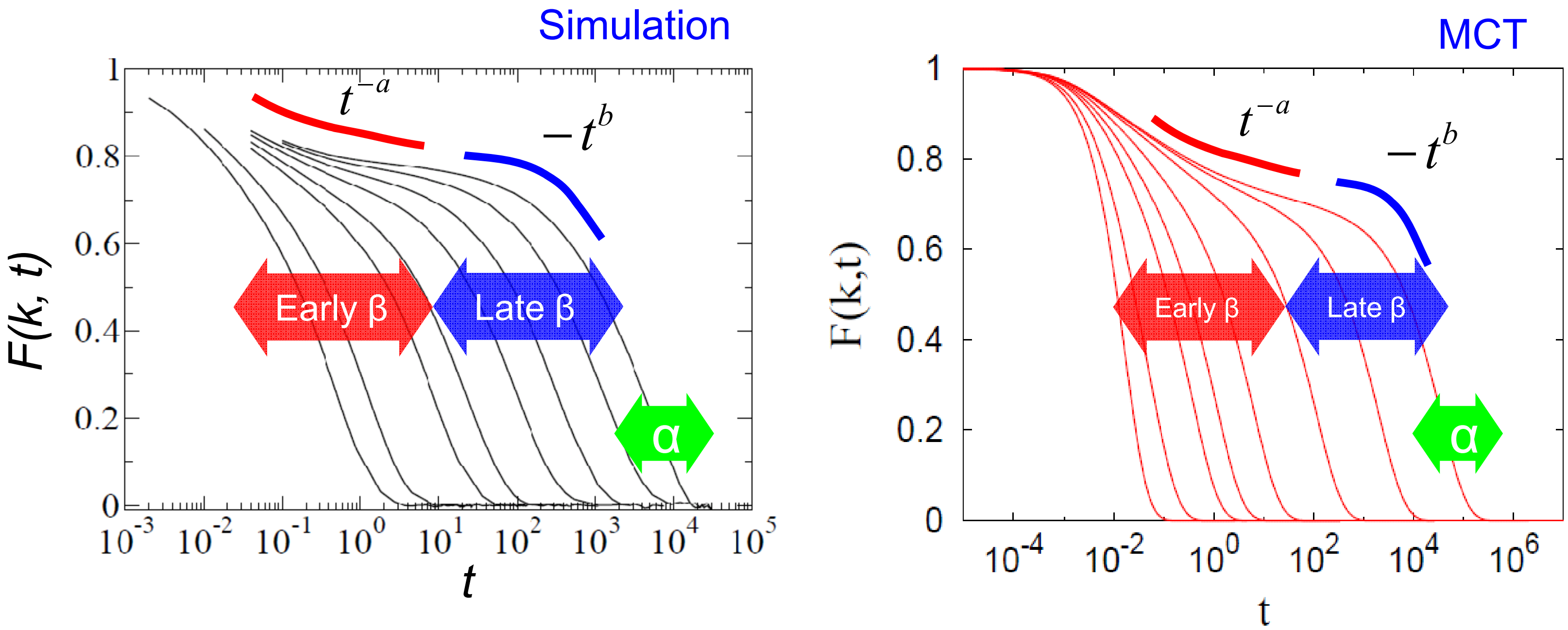


Algebraic β relaxation (von Schweidler law)

For a hard sphere colloidal glass

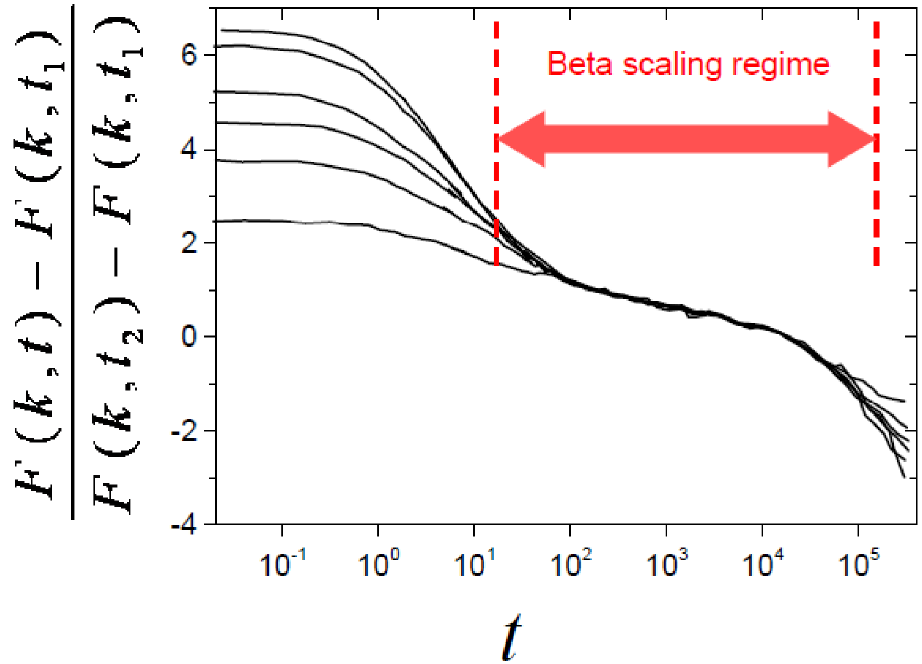
Experiment: $a = 0.328, \quad b = 0.646$

MCT: $a = 0.312, \quad b = 0.583$

Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

MCT can Predict 2-step relaxation



(Gleim and Kob '00)

Algebraic β relaxation (von Schweidler law)

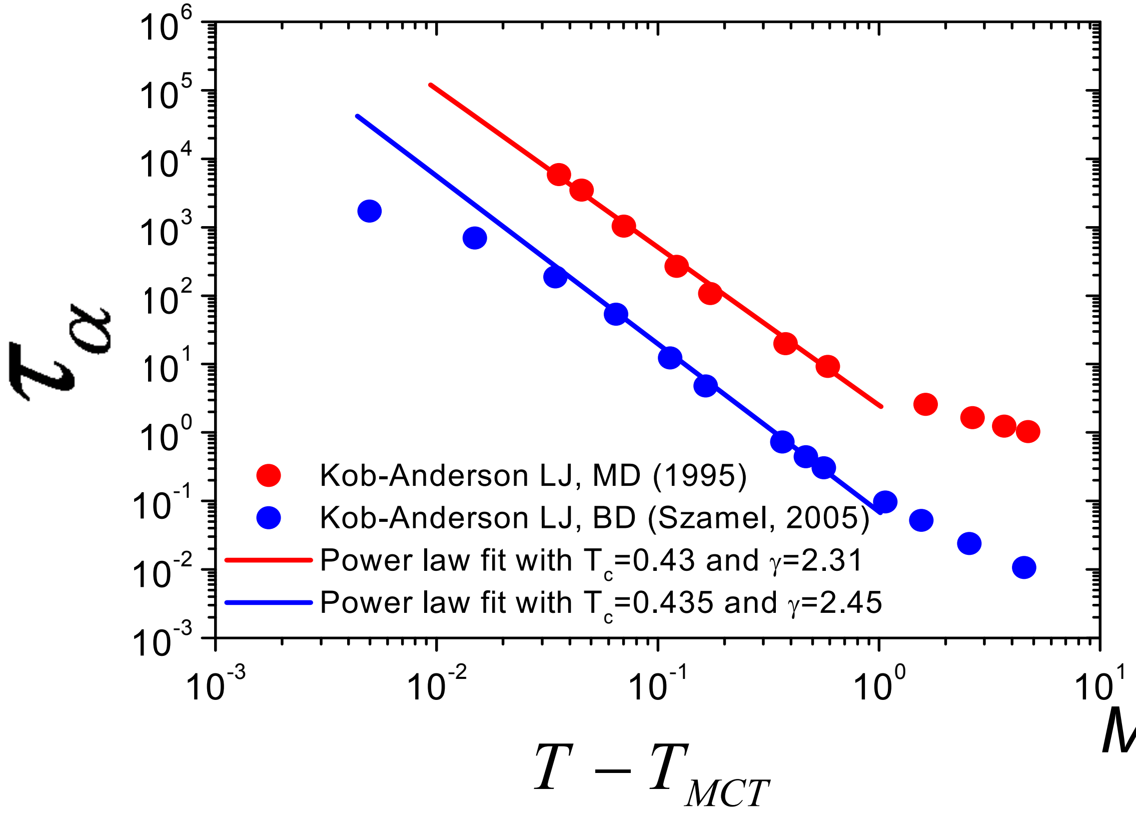
For a hard sphere colloidal glass
(van Megen 1995)

Experiment: $a = 0.328, \quad b = 0.646$
MCT: $a = 0.312, \quad b = 0.583$

Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

MCT can predict power law of α relaxation time and viscosity



$$\tau_\alpha \propto \left| T - T_{\mathrm{MCT}} \right|^{-\gamma}$$

$$\eta \propto \left| T - T_{\mathrm{MCT}} \right|^{-\gamma}$$

with $\gamma = \dfrac{1}{2a} + \dfrac{1}{2b}$

MCT predicts $\gamma = 2.46$

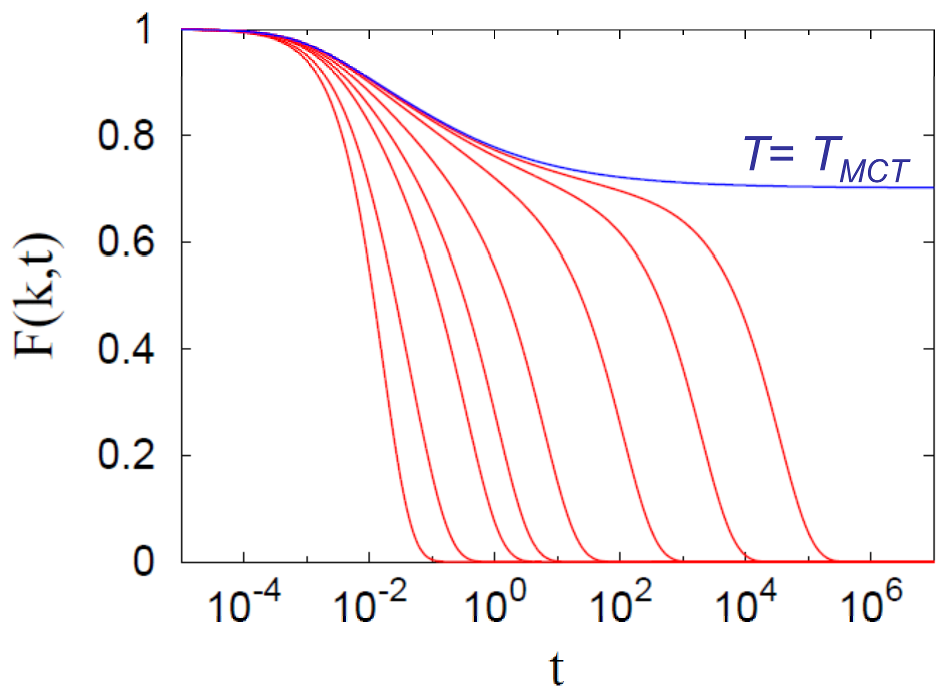
(for LJ binary system,

Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

MCT can't go beyond T_{MCT} (> T_g)

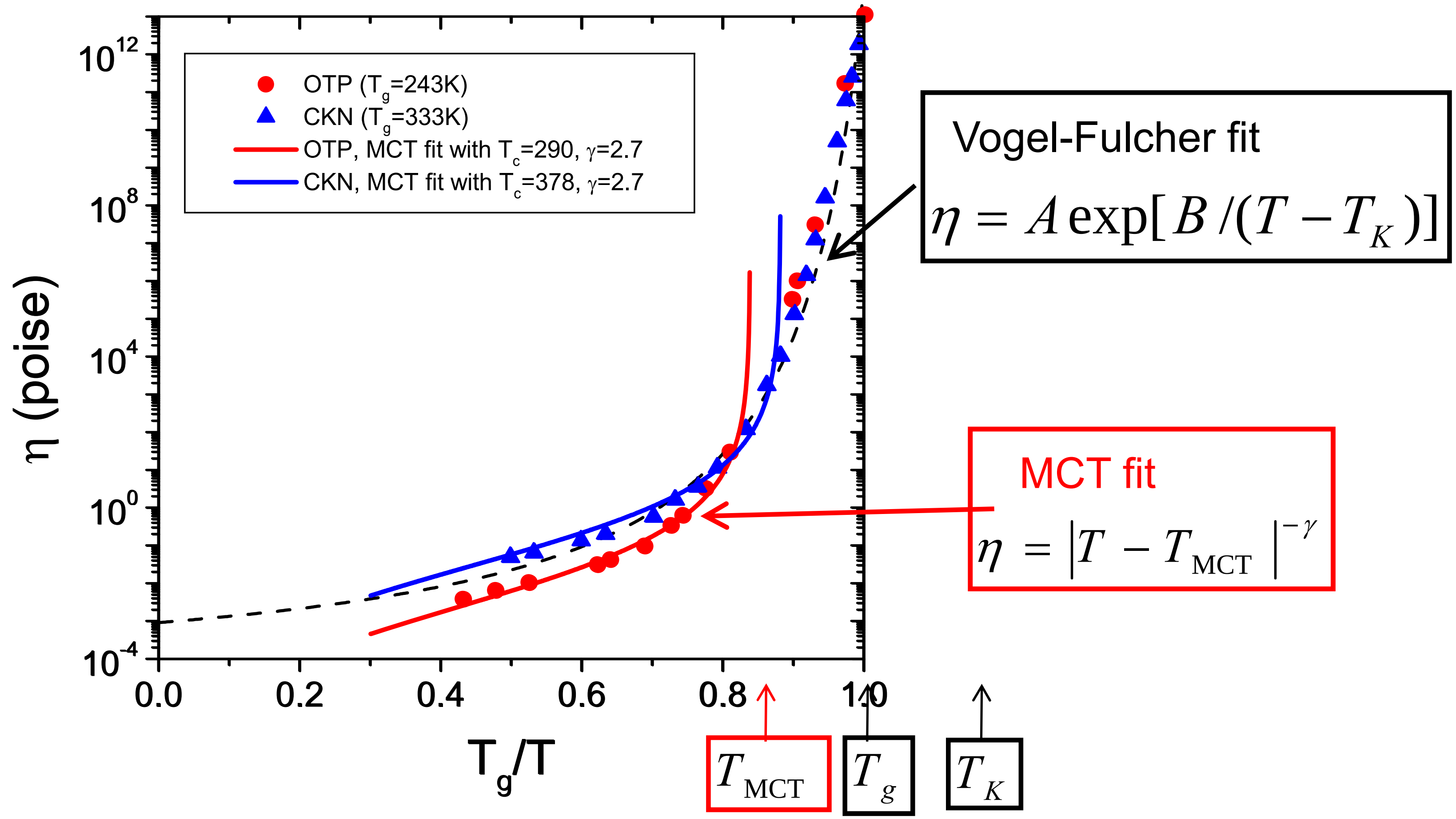
Predict a spurious non-Ergodic transition at T_{MCT}.



Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

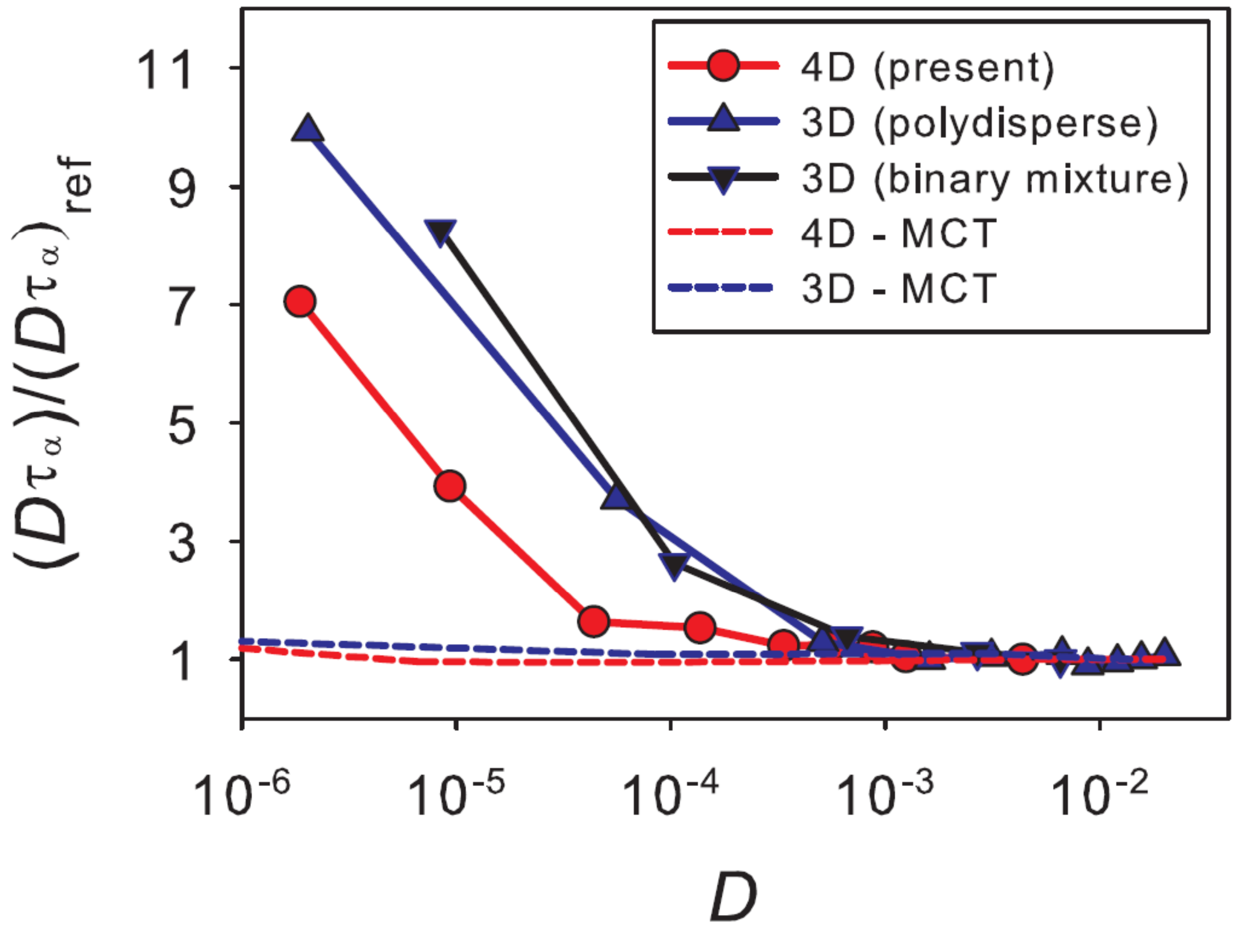
MCT can't go beyond T_{MCT} (> T_g)



Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

MCT can't explain Stokes-Einstein Law $D \propto \frac{1}{\tau_\alpha}$

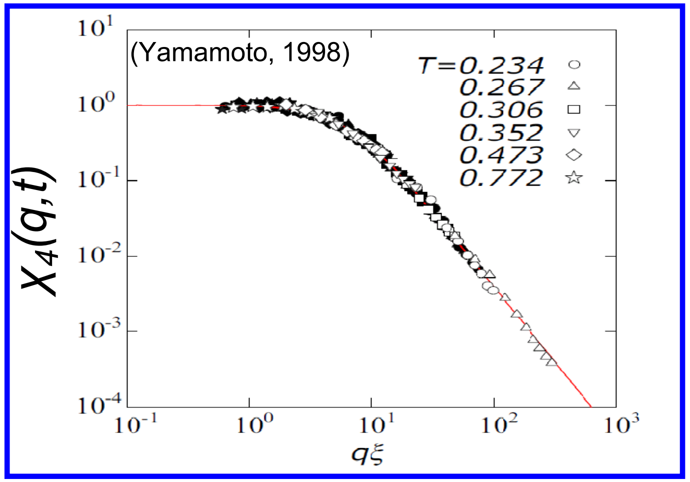


Mode-Coupling Theory Reloaded

Cans and Cant's of MCT

And can MCT describe Dynamic Heterogeneity?

Simulation



MCT

?

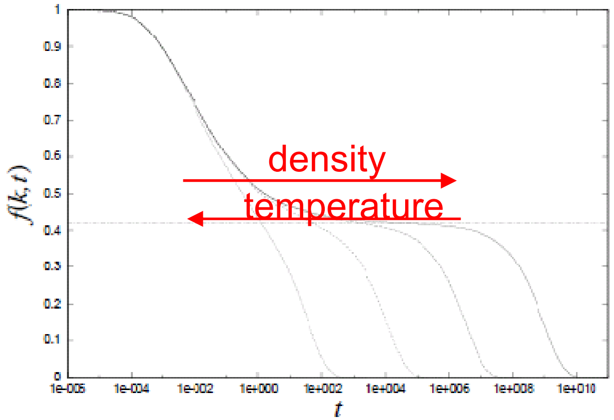
Mode-Coupling Theory Reloaded

Can MCT describe Dynamic Heterogeneity?

Mode-Coupling Theory

$$\frac{\partial F(k,t)}{\partial t} = -\frac{Dk^2}{S(k)} F(k,t) - \int_0^t dt' M(k,t-t') \frac{\partial F(k,t')}{\partial t'}$$

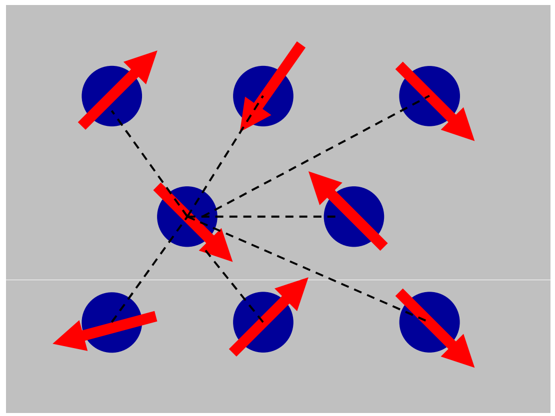
Memory function
$$M(k,t) \propto F^2(q,t)$$



p-spin spherical spin model (Mean Field Model) (p=3)

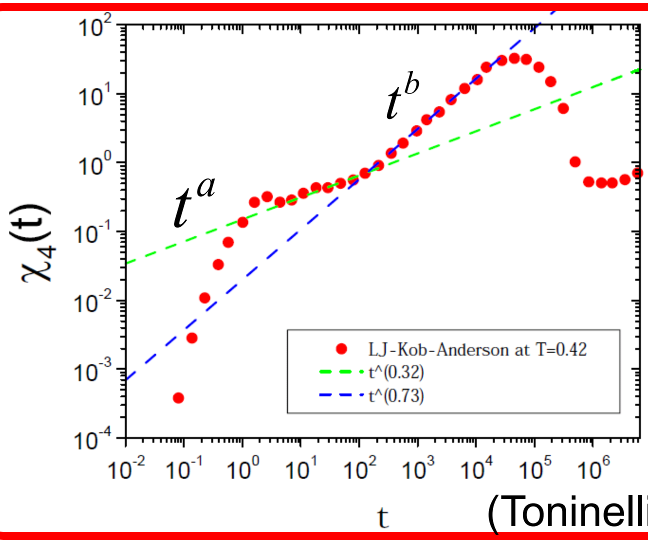
$$\frac{\partial \phi(t)}{\partial t} = -\gamma\phi(t) - \int_0^t dt' \lambda^2 \phi^2(t-t') \frac{\partial \phi(t')}{\partial t'}$$

$$\phi(t) = \langle S(t)S(0) \rangle$$



Mode-Coupling Theory Reloaded

Can MCT describe Dynamic Heterogeneity?



(Toninelli et al. '05)

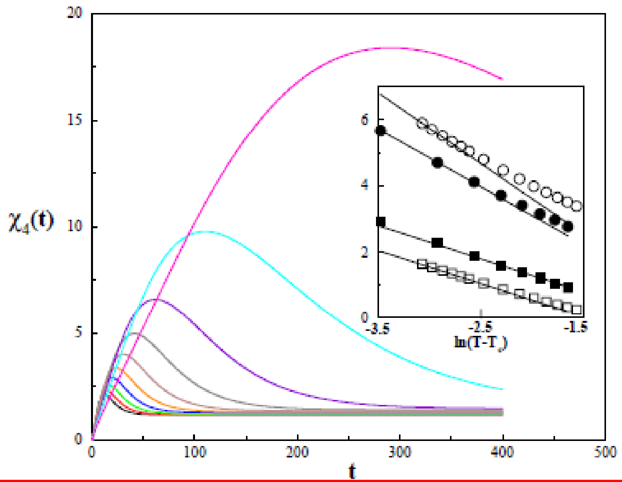
$\chi_4(t)$: Integral of $G_4(r, t)$ over space

Dynamical exponents are very similar to what MCT predicts!

p-spin Mean Field Model (p=3)

$$\chi_4(t) \approx \left\langle S^2(t) S^2(0) \right\rangle$$

Preliminary results shows the growing 4-point correlation function!



(Franz et al. '00)

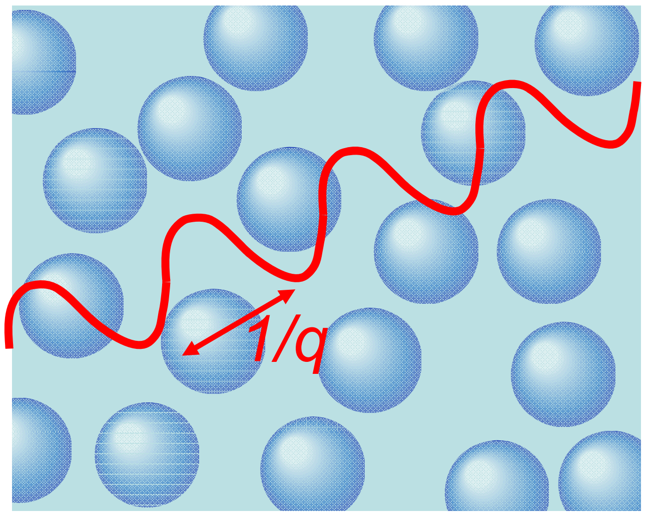
INHOMOGENEOUS MCT

Calculate Nonlinear Susceptibility using MCT

Instead of calculating the 4 point correlation function (it is too complicated), we shall calculate *the 3 point correlation function*

$$\chi_3(k,q,t) = \langle \rho(k,t)\rho(q,t)\rho(-k-q,0) \rangle$$

Hamiltonian $H_{tot} = H + \varepsilon\rho_q$ Pinning field



$$F(k_1,k_2,t) = \langle \rho(k_1,t)\rho(k_2,0) \rangle$$

Linear response theory says

$$\chi_3(k,q,t) \approx \frac{\partial F(k,k+q,t)}{\partial \varepsilon}$$

Need to construct MCT for $F(k_1,k_2,t)$

INHOMOGENEOUS MCT

Calculate Nonlinear Susceptibility using MCT

Basic Idea

Linear Response Theory says

$$H_{tot} = H + xF$$

$$\langle x(t) \rangle_F = \int_{-\infty}^{t} dt' \, \chi(t-t') F(t') \quad \text{with} \quad \boxed{\chi(t) = \langle x(t) x(0) \rangle_{eq}}$$

Change of *x* due to *F* can be described by correlation function at equilibrium

or

The 1st moment of *x* in the presence of *F* can be written by the 2nd moment of x in the absence of *F*.

or

The 2nd moment of *x* in the absence of *F* can be written by the 1st moment of x in the presence of *F*.

or

The *3rd* moment of *x* in the absence of *F* can be written by the *2nd* moment of x in the presence of *F*.

INHOMOGENEOUS MCT

Calculate Nonlinear Susceptibility using MCT

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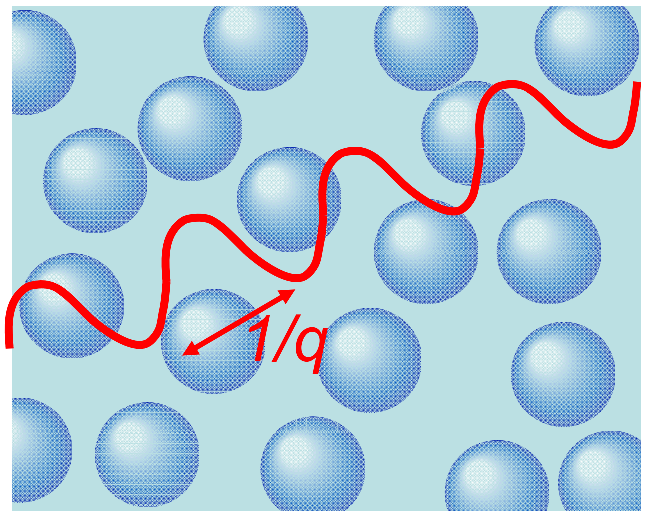
Hamiltonian $H_{tot} = H + \varepsilon\rho_q$

Pinning field



$$F(k_1,k_2,t) = \langle \rho(k_1,t)\rho(k_2,0) \rangle$$

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$$\chi_3(k,q,t) \approx \frac{\partial F(k,k+q,t)}{\partial \varepsilon}$$

Need to construct MCT for $F(k_1,k_2,t)$

INHOMOGENEOUS MCT

Calculate Nonlinear Susceptibility using MCT

MCT in the presence of the pinning field (thus w/o translational invariance)

$$\frac{\partial^2 F(k_1,k_2,t)}{\partial t^2} + \Omega^2(k_1,q)\, F(q,k_2,t) + \nu \frac{\partial F(k_1,k_2,t)}{\partial t} + \int_0^t dt'\, M(k_1,q,t-t') \frac{\partial F(q,k_2,t')}{\partial t'} = 0$$

with

$$\Omega^2(k_1,k_2) = \frac{k_B T}{m} k_1 \cdot q_1 \left\langle \sum \mathrm{e}^{i(q_1-q_2)R_j} \right\rangle S^{-1}(q_2,k_2)$$

$$M(k_1,k_2,t) = k_1 V(k_1,q_1,q_2) \times \left\{ F(q_1,q_3,t)F(q_2,q_4,t) + F(q_1,q_4,t)F(q_2,q_3,t) \right\} V(k_2,q_3,q_4) \frac{1}{k_2}$$

INHOMOGENEOUS MCT

Calculate Nonlinear Susceptibility using MCT

$$\frac{\partial^2 \chi_3(\mathbf{q}_1,\mathbf{q}_2;t)}{\partial t^2} + \Omega_0^2(\mathbf{q}_1)\chi_3(\mathbf{q}_1,\mathbf{q}_2;t) + \Omega_1^2(\mathbf{q}_1,\mathbf{q}_2)F(\mathbf{q}_2,t) + \nu\frac{\partial \chi_3(\mathbf{q}_1,\mathbf{q}_2;t)}{\partial t'}$$
$$+ \int_0^t \mathrm{d}t'\ M_0(\mathbf{q}_1,t-t')\frac{\partial \chi_3(\mathbf{q}_1,\mathbf{q}_2;t')}{\partial t'} + \int_0^t \mathrm{d}t'\ M_1(\mathbf{q}_1,\mathbf{q}_2;t-t')\frac{\partial F(\mathbf{q}_2,t')}{\partial t'} = 0$$

with

$$M_0(\mathbf{k},t) = \frac{k_\mathrm{B}T}{2mn}\int\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}V_\mathbf{k}^2(\mathbf{q},\mathbf{k}-\mathbf{q})F(k,t)F(|\mathbf{q}-\mathbf{k}|,t)$$

$$M_1(\mathbf{k}_1,\mathbf{k}_2;t) = \frac{k_\mathrm{B}T}{2mn}\int\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\Big[\ V_{\mathbf{k}_1}^2(\mathbf{q},\mathbf{k}_1-\mathbf{q})F(k,t)F(|\mathbf{k}_1-\mathbf{q}|,t)\frac{\mathbf{k}_1\cdot\mathbf{k}_2}{k_2^2}S(q_0)$$
$$+2k_1V_{\mathbf{k}_1}(\mathbf{q},\mathbf{k}_1-\mathbf{q})\chi_3(\mathbf{q},\mathbf{q}_0+\mathbf{q};t)F(|\mathbf{k}_1-\mathbf{q}|,t)V_{\mathbf{k}_2}(\mathbf{k}_1-\mathbf{q},\mathbf{q}_0+\mathbf{q})\frac{1}{k_2}\Big]$$

$$\Omega_0^2(\mathbf{k}) = \frac{k_\mathrm{B}Tk^2}{mS(k)}$$

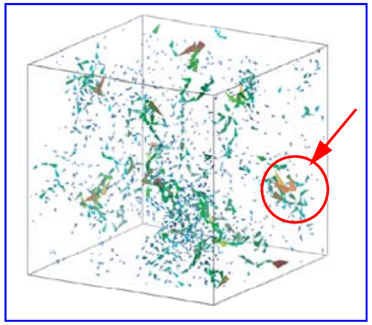
$$\Omega_1^2(\mathbf{k}_1,\mathbf{k}_2) = \frac{k_\mathrm{B}T}{m}S(q_0)\left\{k_1^2 - \frac{\mathbf{k}_1\cdot\mathbf{k}_2}{S(k_2)}\right\}$$

INHOMOGENEOUS MCT

For *q=0:* Integral over space:

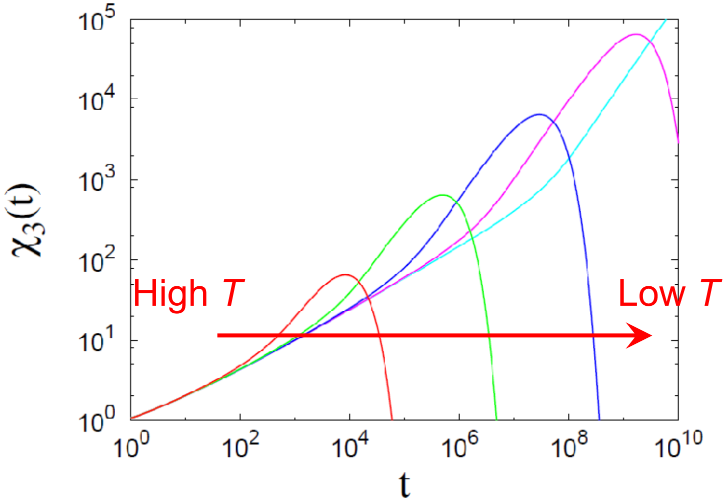
$$\chi_3(t) = \chi_3(k, q=0, t)$$

$\propto$ A number of particles in a "cluster"



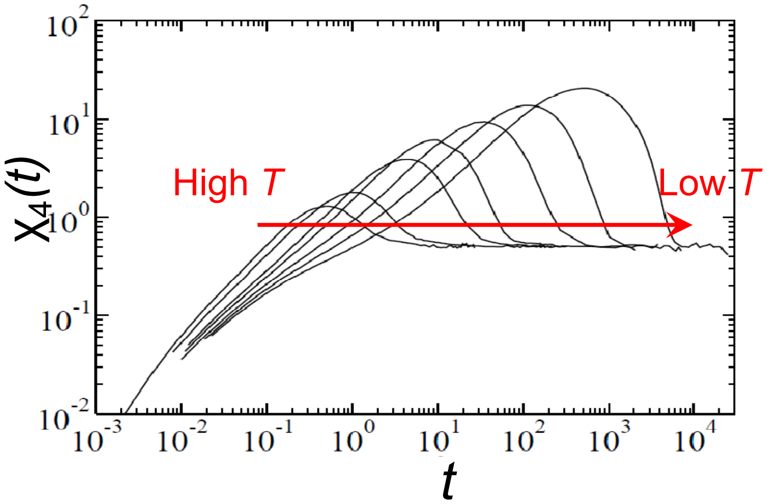
$\chi_3(t)$ IMCT

(A simplified model calculation)



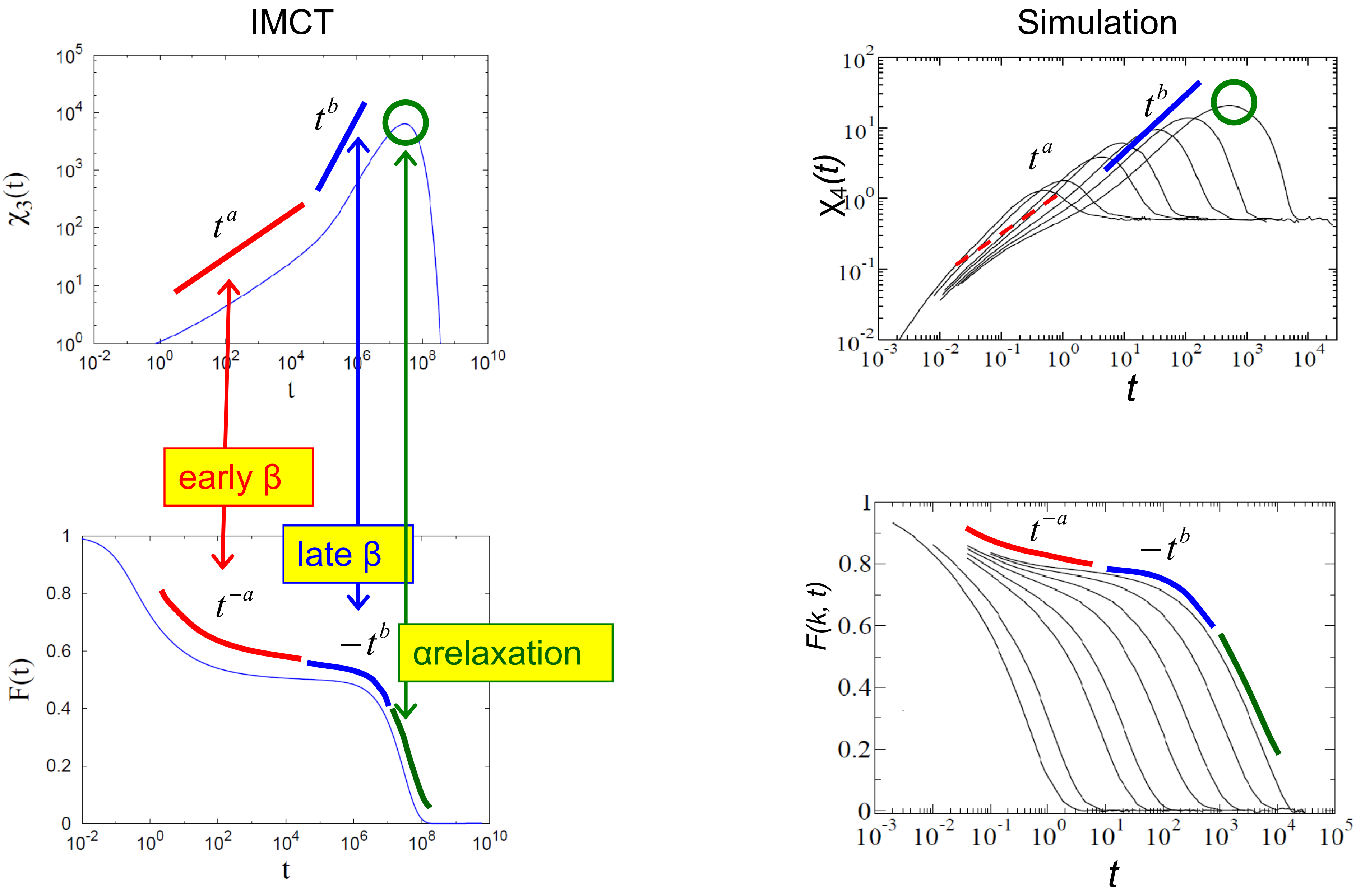
$\chi_4(t)$ Simulation

for a colloid, (Szamel et al.2006)



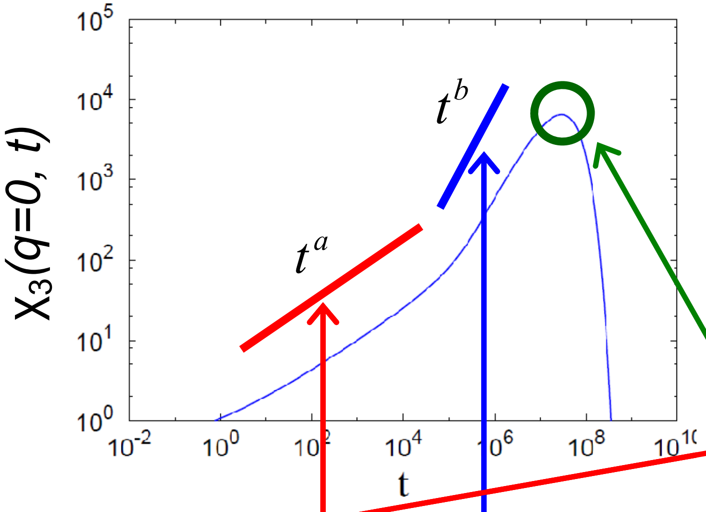
Cluster size / length scale grow as *T* lowered.

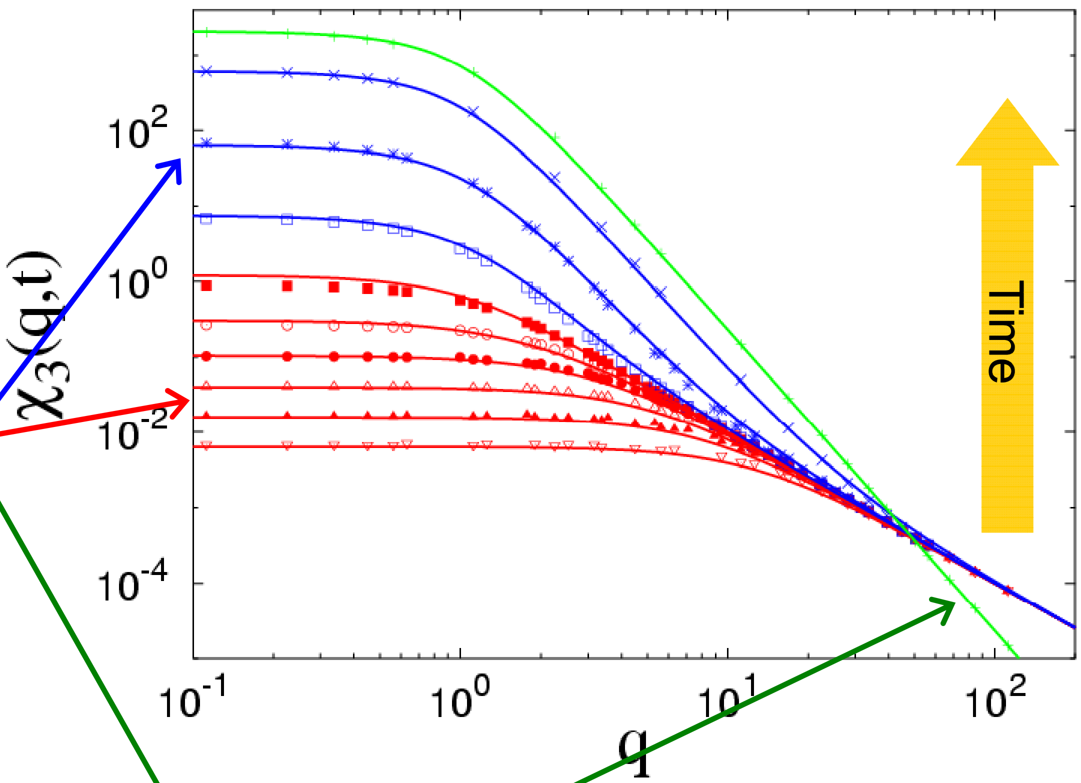
INHOMOGENEOUS MCT



INHOMOGENEOUS MCT

For *q≠0:* Length scale dependence:





early β

$$\chi_3(q,t) \propto \frac{\xi^2}{1+q^2\xi^2}$$

$$\xi(t) \propto t^{a/2}$$

late β

$$\chi_3(q,t) \propto \frac{B(t)}{1+q^2\xi^2 + A(t)q^4\xi^4}$$

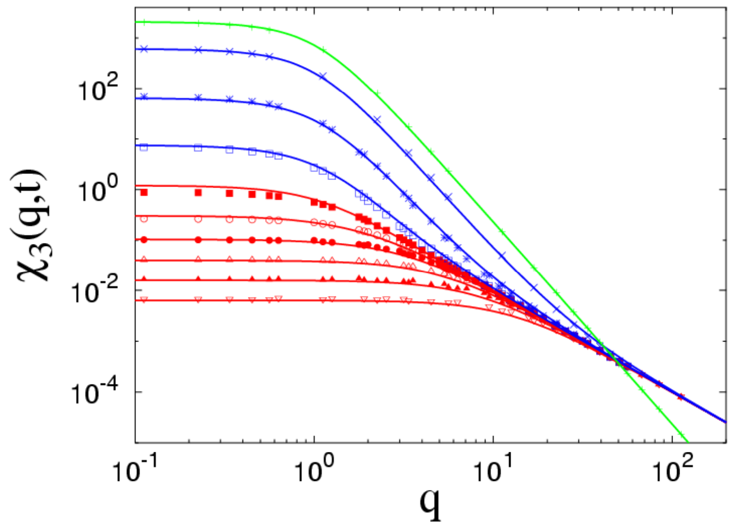
αrelaxation

$$\chi_3(q,t) \propto \frac{\xi^4}{1+q^2\xi^2 + Cq^4\xi^4}$$

$$\xi(t) \propto |T - T_{\mathrm{MCT}}|^{-1/4}$$

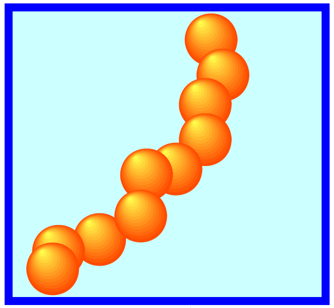
INHOMOGENEOUS MCT

For *q≠0:* The cluster morphorogy:



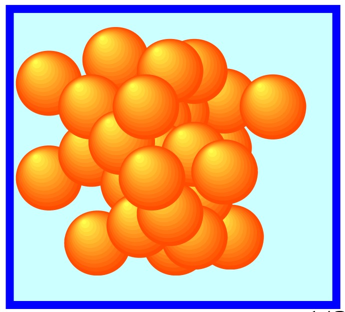
early β → late β → α relaxation

Real glasses for d=3



$\xi(t) \propto N$

(Donati et al, 1998)



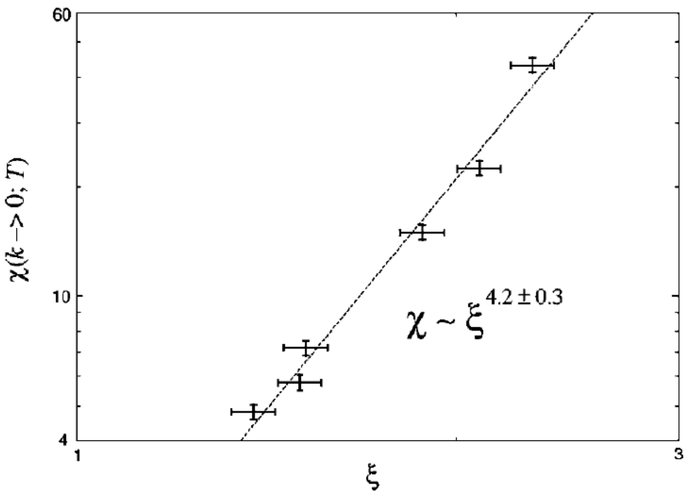
$\xi(t) \propto N^{1/3}$

(Appignanessi et al, 2006)

COMPARISON WITH SIMULATIONS

Stein and Andersen,
Phys. Rev. Lett. 101 (2008) 267802
Lenard Jones binary system

$$\chi(q=0, t=\tau_\alpha) = \xi^{2-\eta}$$



IMCT	MD simulation
$2-\eta=4$	$2-\eta=4.2\pm0.3$

$$\xi(t=\tau_\alpha) = |T - T_{\mathrm{MCT}}|^{-\nu}$$

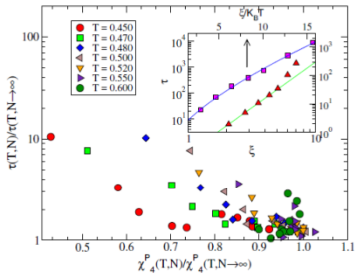
$\nu = 1/4$	$\nu = 0.27 \pm 0.03$

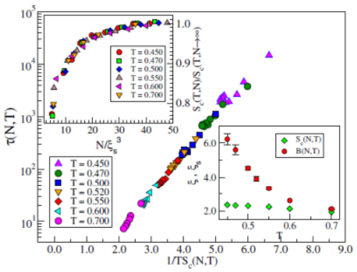
$$\chi(q=0, t=\tau_\beta) = \xi^{2-\eta}$$

$2-\eta=2$	$2-\eta=2.05\pm0.26$

COMPARISON WITH SIMULATIONS

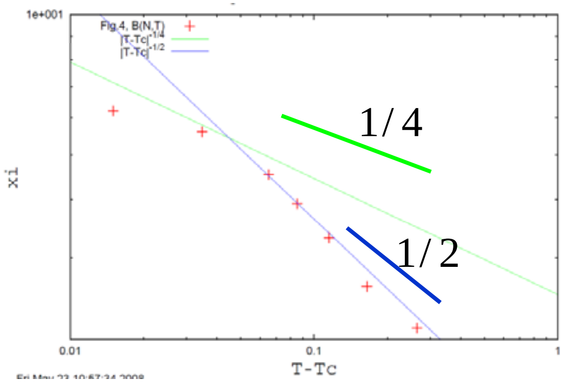
Karmakar, Dasgupta, Sastry
PNAS. 106 (2000) 3675
Lenard Jones binary system

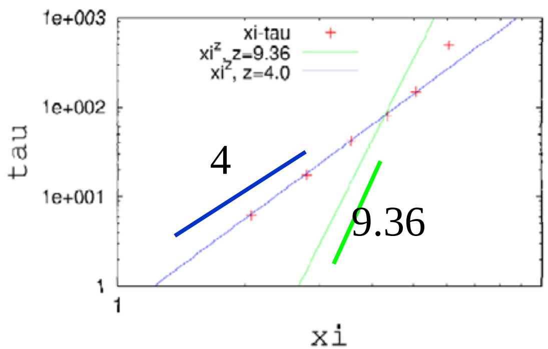




$$\xi(t=\tau_\alpha) = |T - T_{\text{MCT}}|^{-\nu}$$

IMCT	MD simulation
$\nu = 1/4$	$\nu \approx 0.5$





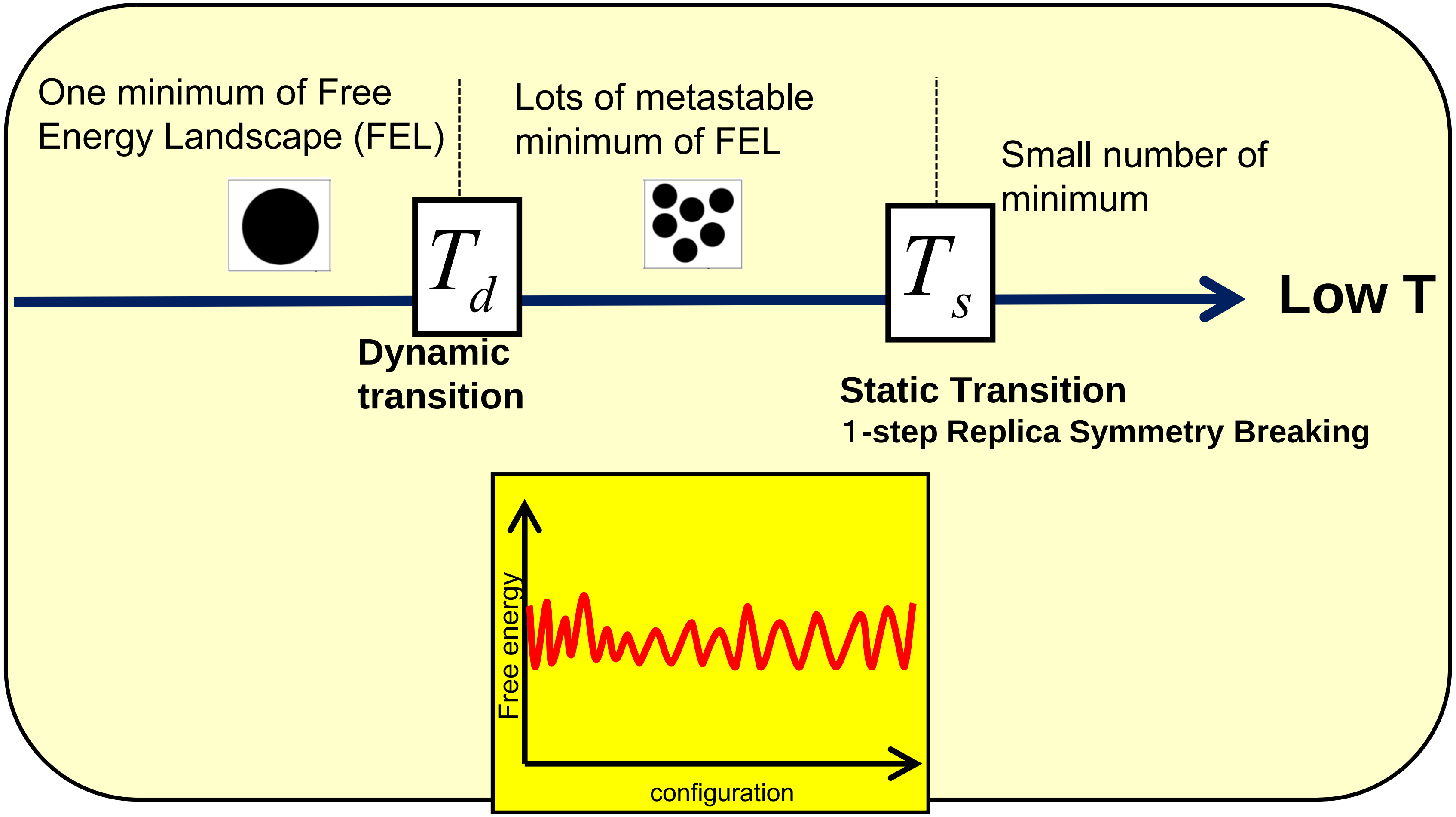
$$\tau_\alpha = \xi^z$$

$z = 9.36$ $\quad$ $z \approx 4$

Summary 1: Where are we?

MCT is often referred to as a mean field theory

p-spin(p=3) spherical model (mean field model)



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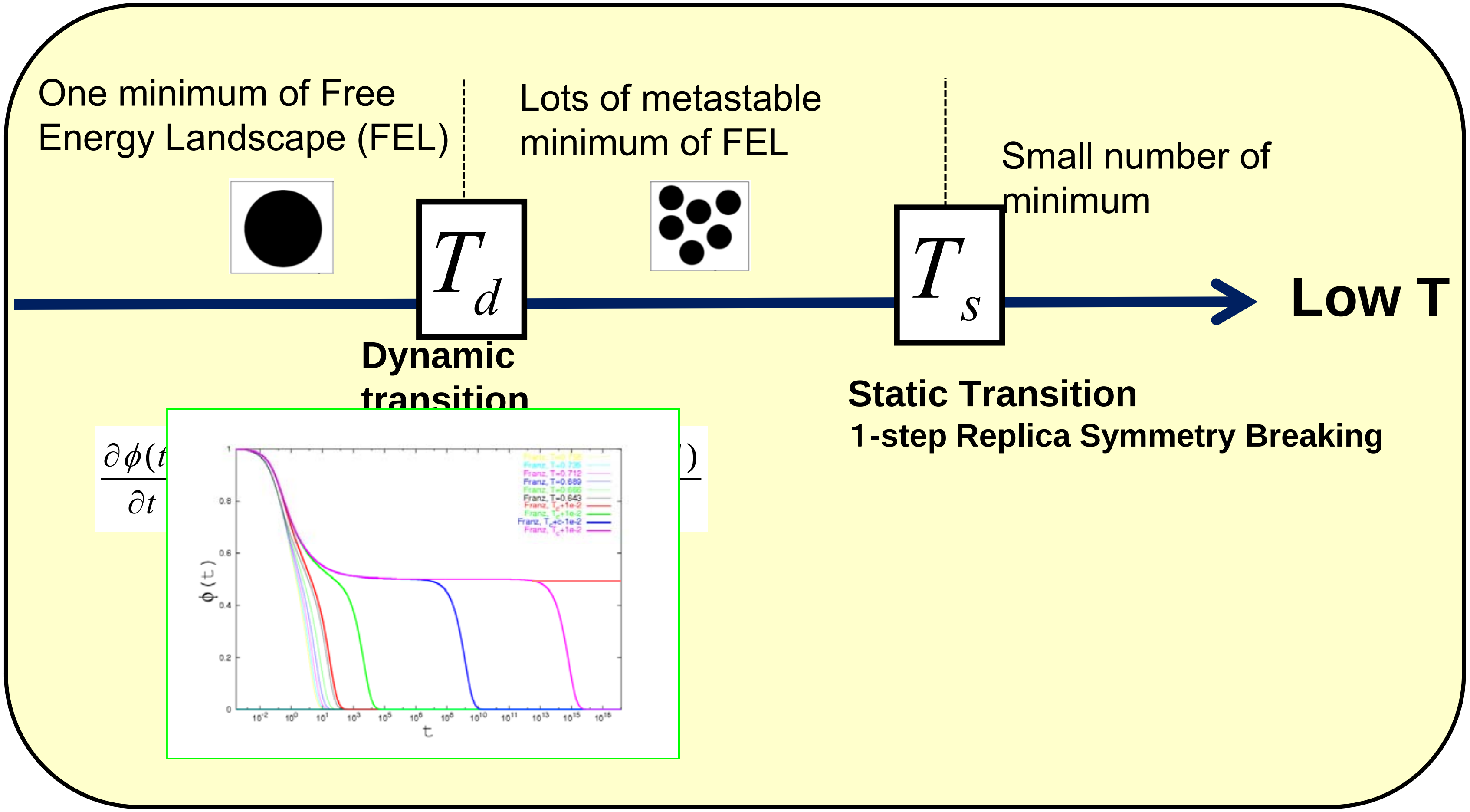
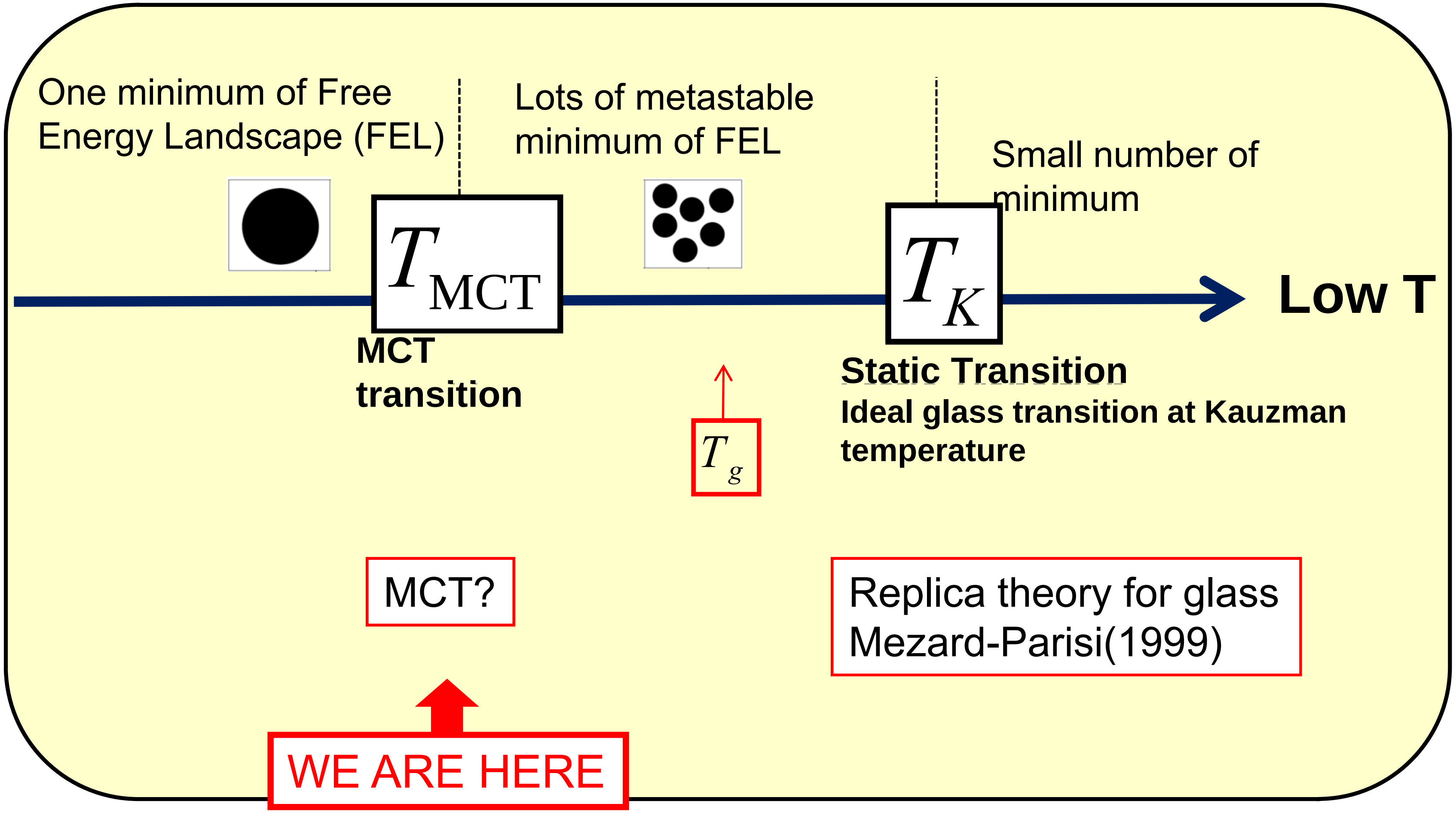


Summary 1: Where are we?

MCT is often referred to as a mean field theory

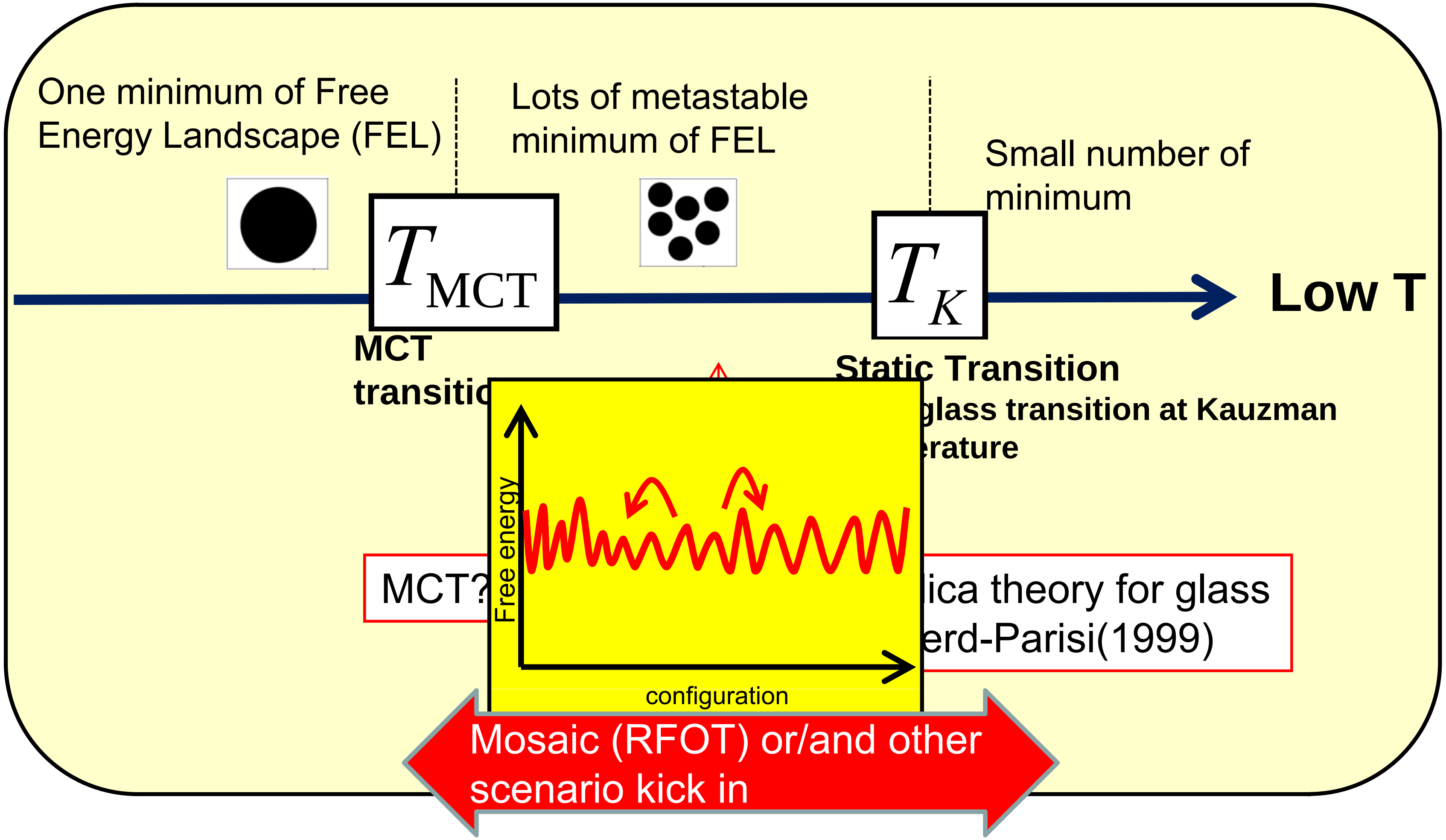
Mean Field picture of the Glass Transition



Summary 1: Where are we?

MCT is often referred to as a mean field theory

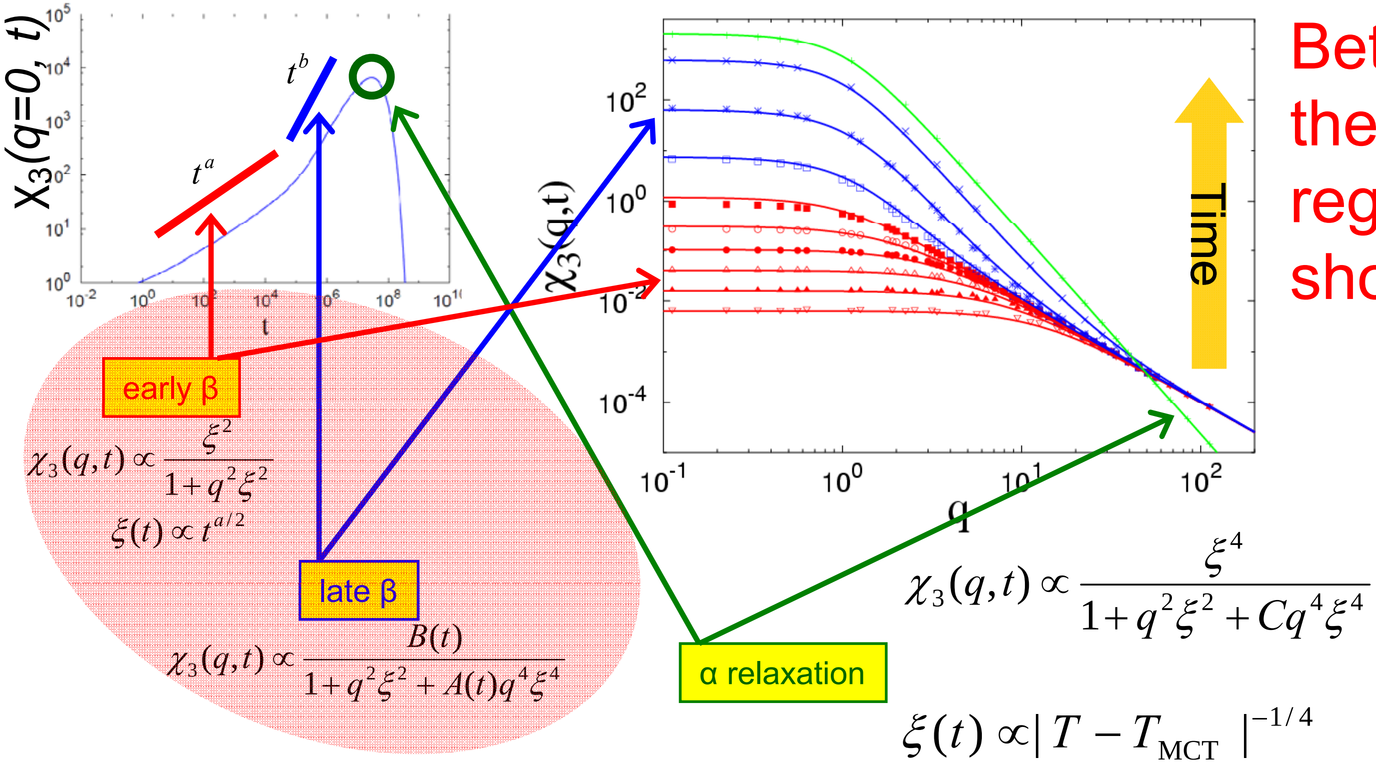
In the real glass… Activation processes round off the MCT transition



Summary 2: What should we look at?

(1) α relaxation regime is a meeting point of various scenario.

Look at β regime!

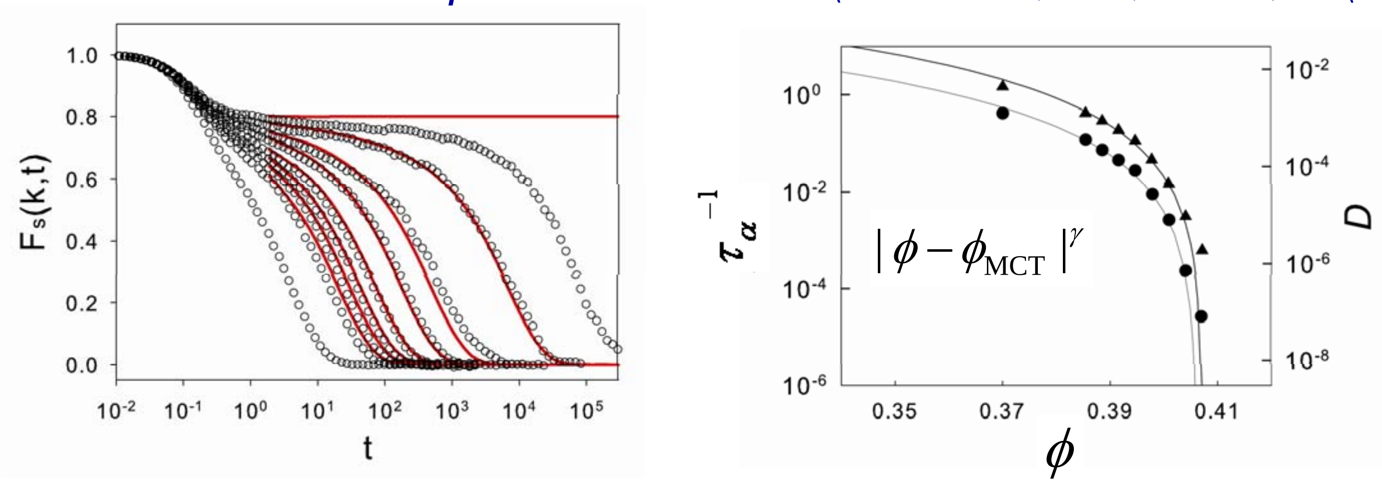


Better place to check the theory is the β regime, where MCT should work better.

Summary 2: What should we look at?

(2) If MCT is really a mean field theory of the glass, it should work better at higher dimension.
Go and check the higher dimension!

MD simulation for Hard Sphere Fluid in 4d *(Charbonneau, Ikeda, vanMeel, KM (2009))*



MCT works better!