Bridging the gap between Mode coupling theory and Random first order transition theory

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Mode Coupling Theory and Glass Transition (Recap from Bagchi+Miyazaki+Sciortino)

Generalized Langevin equation for the density-density correlation

$$\ddot{\Phi}(q,t) + \frac{q^2}{\beta m S(q)}\Phi(q,t) + \int_0^t \eta_{ll}(q,(t-t'))\dot{\Phi}(q,t')dt' = 0$$

$$\eta_{ll}(q,t) = \frac{k^2}{Nmk_BT} < \sigma^*_{zz}(q) e^{iQLt} \sigma_{zz}(q) >$$

$$\eta_{ll}(q,t) = \gamma\delta(t) + \int dk \int dp V(\mathrm{k},\mathrm{p},\mathrm{q})\Phi(k,t)\Phi(p,t)$$

$$\approx \gamma\delta(t) + \lambda\Phi(q,t)\Phi(q,t)$$

$V(k,q,p) \rightarrow$ coupling between longitudinal viscosity and structural relaxation

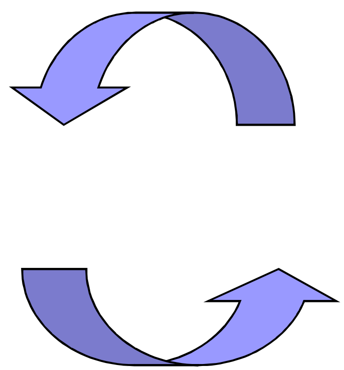
Mode Coupling Theory and Glass Transition (Recap from Bagchi+Miyazaki+Sciortino)

Generalized Langevin equation for the density-density correlation

$$\ddot{\Phi}(q,t) + \frac{q^2}{\beta m S(q)}\Phi(q,t) + \gamma\dot{\Phi}(q,t)$$

$$+ \int_0^t \int dk \int dp V(\mathbf{k},\mathbf{p},\mathbf{q})\Phi(k,t-t')\Phi(p,t-t')\dot{\Phi}(q,t')dt' = 0$$

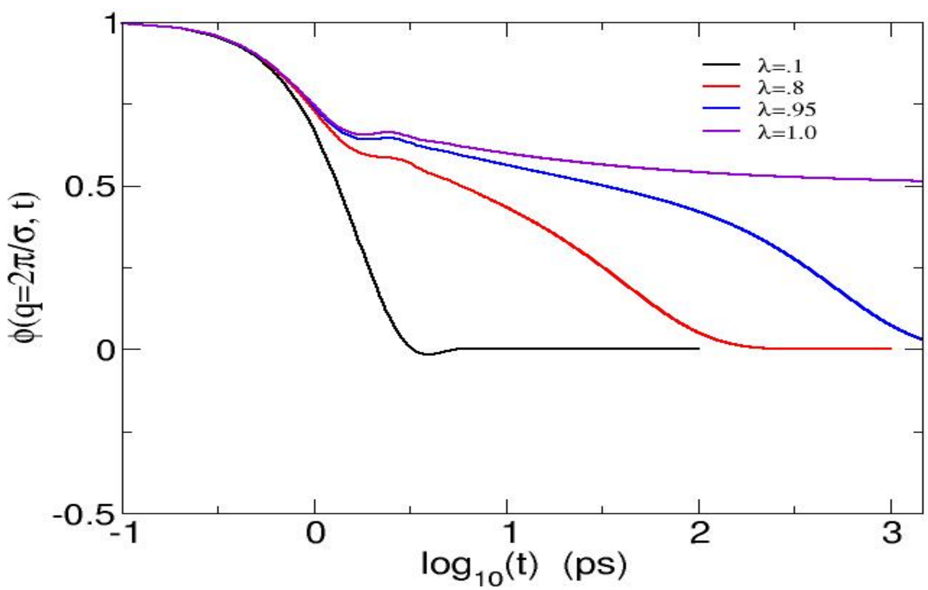
$$\Phi(q,z) = \cfrac{1}{z + \cfrac{\langle \omega_q^2 \rangle}{z + \eta_{ll}(q,z)}}$$

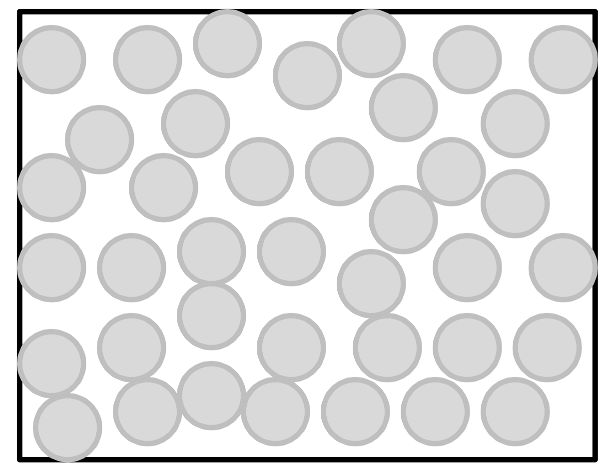


$$\eta_{ll}(q,z) = \gamma + \lambda \mathcal{L}\left\{\Phi^2(q,t)\right\}$$

Feedback Mechanism

Arrest in Structural Relaxation



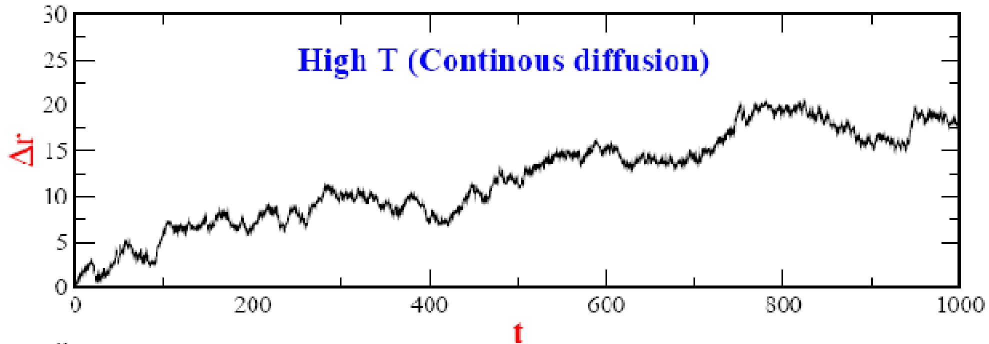


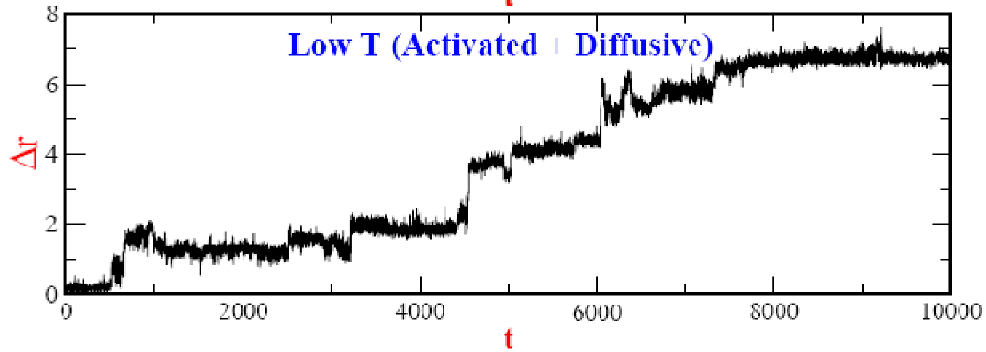
Caging → Glass Transition (1984)

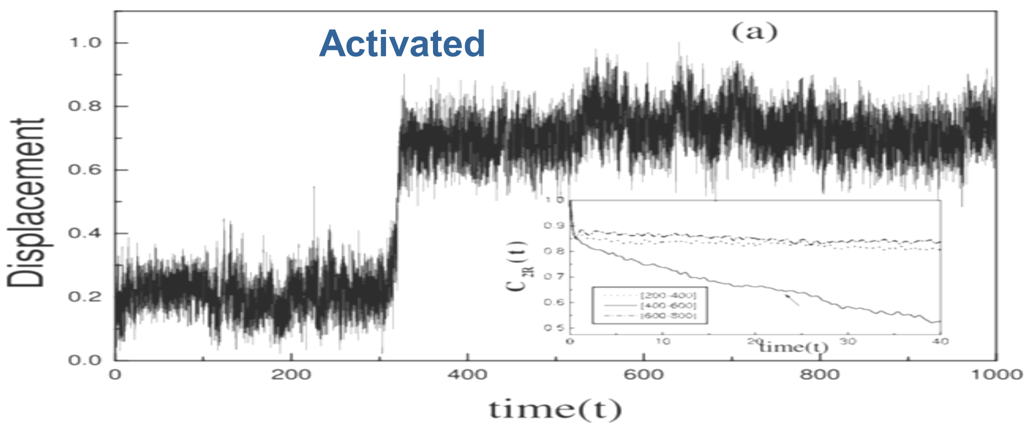
Leutheusser, PRE, **29**, 2765 (1984)
Bengtzelius, Gotze, Sjolanler, J. Phys. C: **17**,5915 (1984)

•Critical point (T_c) 30-50K above the glass transition temperature

Trajectories in Supercooled Liquids







Extended MCT

Gotze & Sjogren , Z. Phys. B ,65, 415 (1987)

Take higher order terms in the expansion

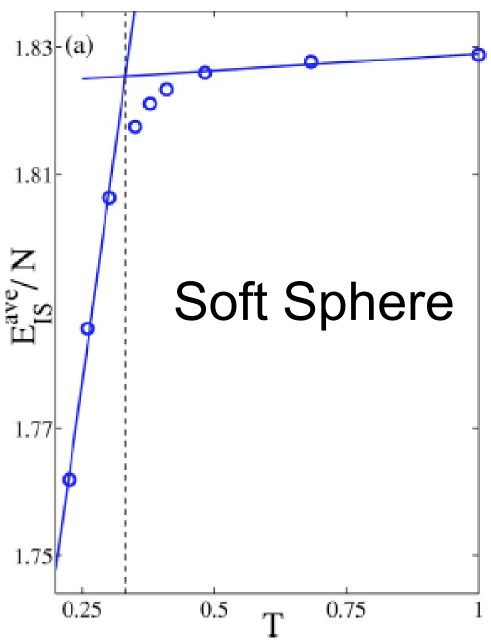
$$\Phi(q,z) = \frac{1}{z + \dfrac{<\omega_q^2>}{z + \eta_{ll}(q,z)}} \rightarrow \Phi(q,z) = \frac{1}{z + \dfrac{<\omega_q^2>}{z + \eta_{ll}(q,z)} + \delta}$$

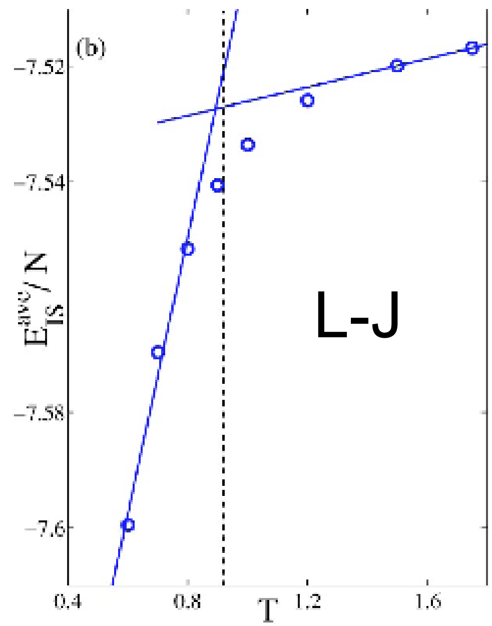
$\delta \rightarrow$ coupled to density relaxation

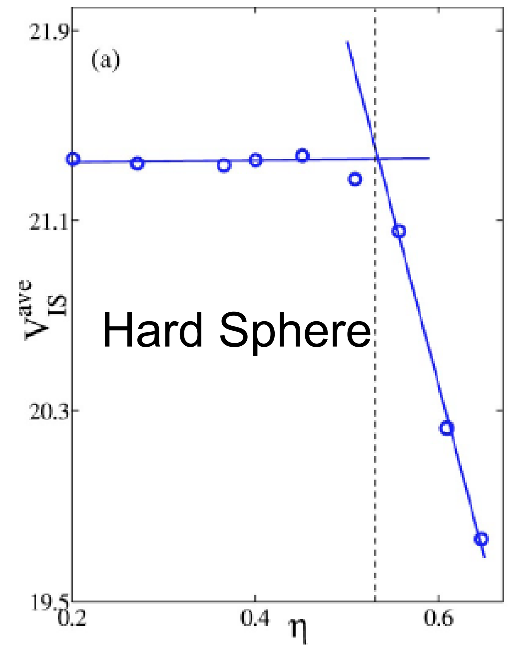
Higher order terms cannot describe activated dynamics

MCT transition temperature ??

Microscopic MCT transition temperature (T_c^0) or density (ρ_c^0)





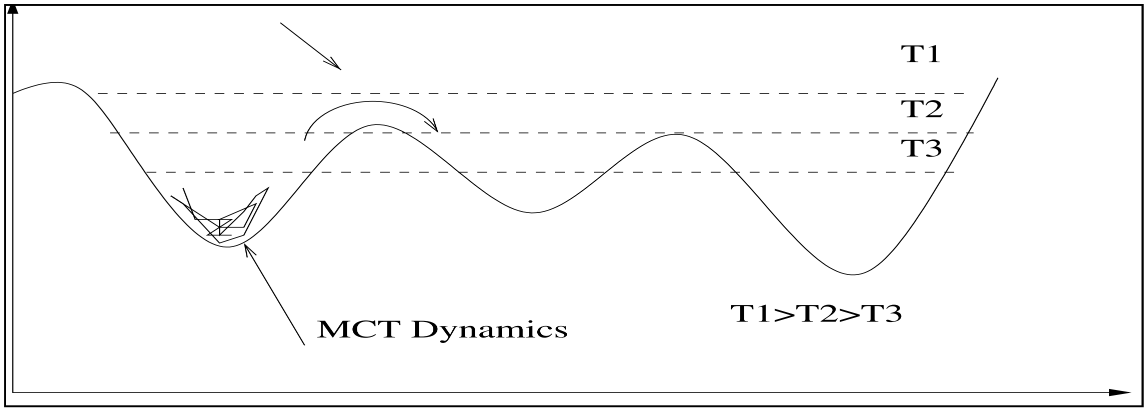


$T^o_c \approx T_L$ → Landscape properties first change

Sastry et al. (Nature, **393** 354 (1998)

Brumer and Reichman (PRE **69,** 041202 (2004)

MCT transition temperature ?



However

$$\tau \sim \left[\left(T - T_c^{fit} \right) / T_c^{fit} \right]^{-\gamma}$$

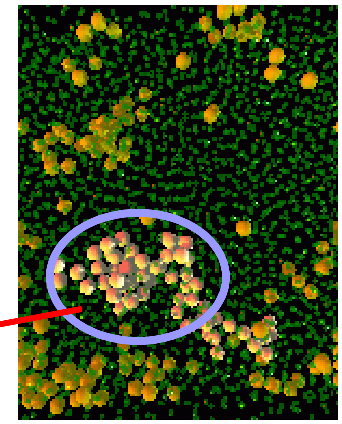
T_c^{fit} → MCT Scaling relation breaks down

What happens to the dynamics between $T^{o}_{c} > T > T^{fit}_{c}$

- Simulations → presence of activated dynamics below T_L
- Why dynamics still follows MCT prediction below T^{o}_{c} ???
- Is there a sharp crossover from diffusive (MCT) to activated dynamics ??
- Most simulation studies are in this domain

Random First Order Transition Theory (RFOT)

Experiments in colloids E. R. Weeks



Above T_g Entropically favoured liquid droplet nucleates.

Driving force→ **Entropy**

$$\Delta F(r) = 4\pi\sigma_K(r)r^2 - \frac{4\pi}{3}(r/a)^3 Ts_c$$

Sharpe interface

↑ ↓

Surface wetting-diffused interface

↑ ↗ ↗ → ↘ ↓

Lowering of surface tension $\sigma(r) = \sigma_0(a/r)^{1/2}$

Xia and Wolynes, PRL, **86,** 5526 (2001) ; Lubchenko and Wolynes, JCP, **119,** 9088 (2003)

Random First Order Transition Theory (RFOT)

$$\Delta F^*(r) = \frac{3\pi\sigma^2{}_0 r_0}{T s_c}$$

Adam-Gibbs

$$s_c = \Delta c_P(T)\frac{T - T_K}{T_K}$$

$$\Delta F^*(r) = \frac{3\pi\sigma^2{}_0 r_0}{T\Delta c_P}\frac{T_K}{T - T_K} = k_B T D \frac{T_K}{T - T_K}$$

VFT

Fragility parameter $D \propto 1/\Delta c_P$

$$P_{hop} = exp(-\Delta F^* / k_B T)$$

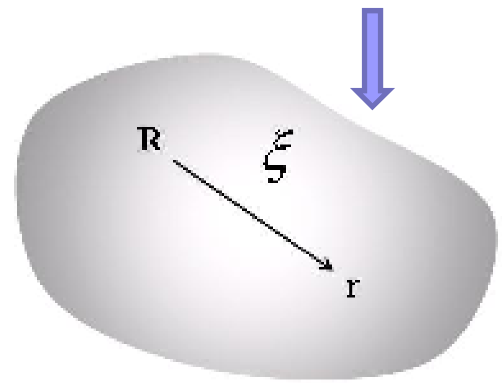
$$\xi / a = \left(\frac{3\sigma_0 a^2}{2T s_c}\right)^{2/3} \approx \frac{2.0}{s_c{}^{2/3}}$$

Xia and Wolynes, PRL, **86,** 5526 (2001) ; Lubchenko and Wolynes, JCP, **119,** 9088 (2003)

Mesoscopic event (Activated dynamics) →Change in microscopic density

Co-operatively rearranging region (CRR)

CRR



Single activated event effects the whole region within a CRR

$$\frac{\partial \rho_{hop}(r,t)}{\partial t} = \frac{1}{V}\int_V dR\,\Theta\left(\left(r-R\right)<\xi\right)P_{hop}\left(R\right)$$

$$\times\left[\int dt' \int dr' G\left(r-r', t-t'\right)\partial\rho\left(r', t'\right) - \partial\rho\left(r,t\right)\right].$$

Bridging the gap……
MCT+RFOT and Structural Relaxation

Master Equation –

$$\frac{\partial\rho(r)}{\partial t} = P_{hop}(R)\times\frac{1}{V}\int_V \Theta\left(\left(r-R\right)<\xi\right)$$

$$\times\left[\int dt'\int dr' G\left(r-r',t-t'\right)\partial\rho\left(r',t'\right)-\partial\rho(r,t)\right]$$

$$-\int dt'\int dr' K_{MCT}\left(r-r',t-t'\right)\partial\rho\left(r',t'\right).$$

Dynamic Structure factor-

$$\Phi\ (q,z) = \frac{1}{z+K^{R}(q,z)}$$

Renormalizion of memory Kernel via hopping event

$$\Phi(q,z) = \frac{1}{z + K^R(q,z)}$$

$$= \frac{1}{z + K_{hop}(q,z) + K_{MCT}(q,z)}$$

$$K_{MCT}(q,z) = \Im\left(\left\{K^R(q,z)\right\}\right) = \frac{<\omega_q^{\ 2}>}{z + \eta_1(q,z)}$$

$$K_{hop}(q,z) = P_{hop}\frac{v_o}{v_P}\left(G(q,z) - 1\right)$$

$$\Phi(q,t) = \Phi_{MCT}(q,t) \times \Phi_{hop}(q,t)$$

Information required

Activated part

Configuration entropy per bead- s_c=2.65 k_B

Kauzmann Temperature T_K=175K

Region participating in hopping- correlation length

MCT part

Static structure factor ---we do not have for realistic systems

F_{12} model- We need to know the non-ergodic **transition temperature**.

Burmer and Reichman (PRE **69,** 041202 (2004)- Non-ergodic transition
-Where inherent structure energy changes
-Sastry et al. (Nature, **393** 354 (1998) – Change of Inherent structure energy and stretching parameter correlated.
Non-ergodic transition, T=278K (Dreyfus *et al.* PRL **69**, 3666 (1992))
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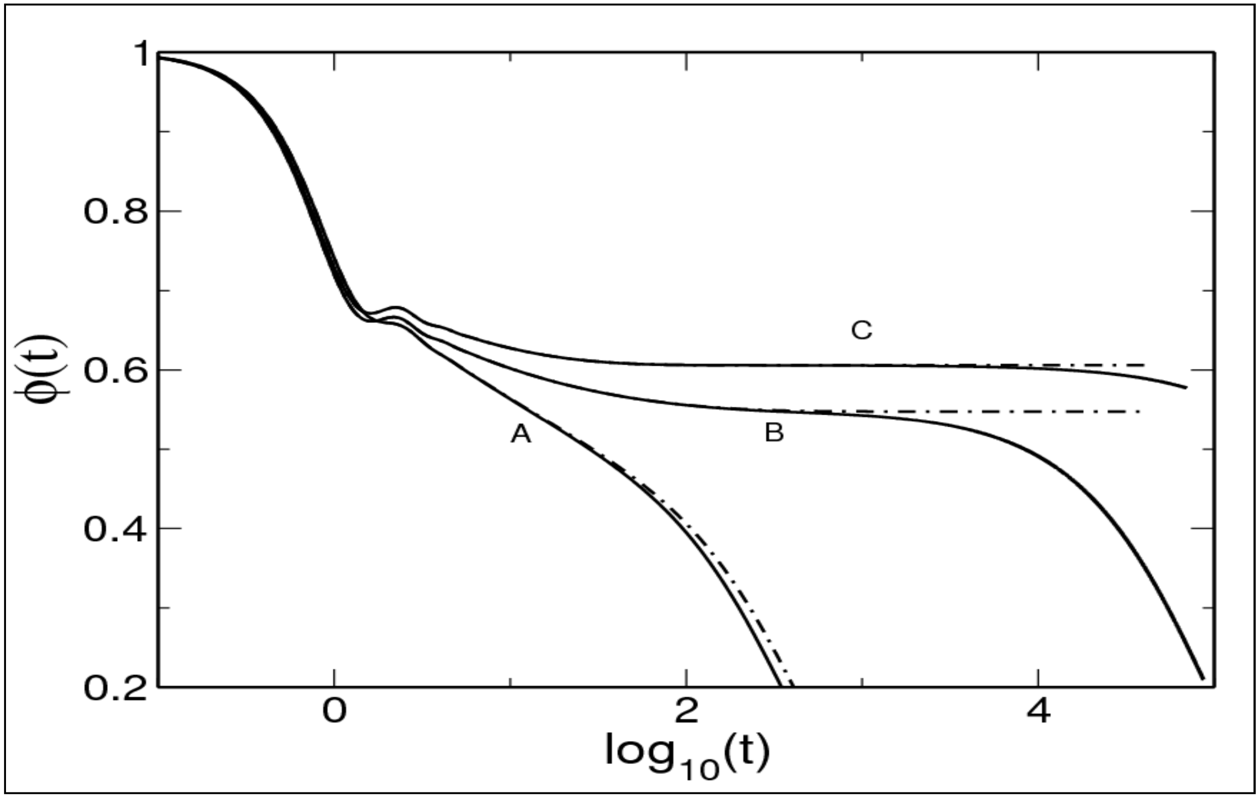
Structural Relaxation below T_c



Ergodic – non-ergodic transition avoided

Bhattacharyya, Bagchi, Wolynes, PRE, **72** 031509, (2005) Are they (MCT and Activated dynamics) just acting as parallel decay channels ???

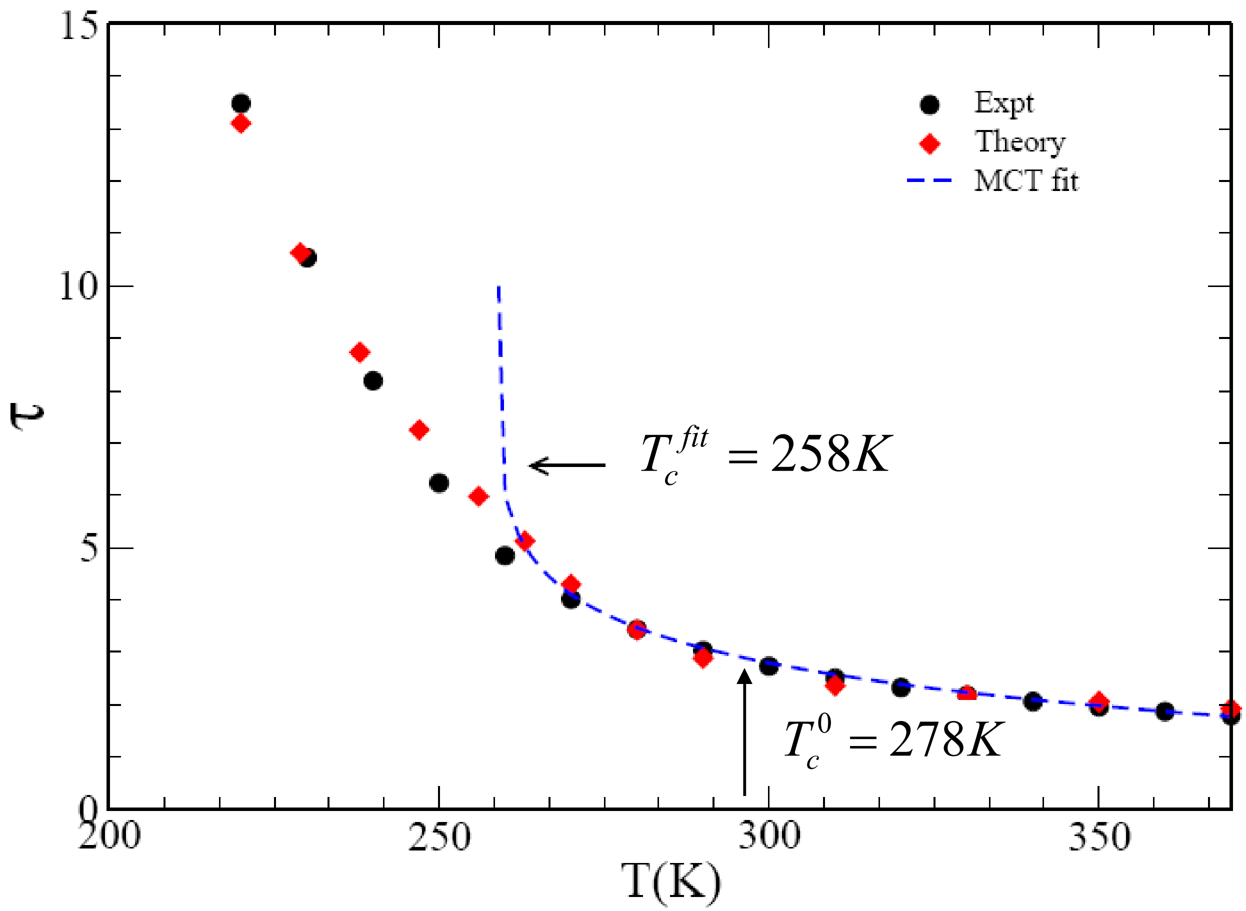
$$\Phi(q,t) = \Phi_{MCT}(q,t) \times \Phi_{hop}(q,t)$$

Growth of relaxation time with supercooling

$$\tau_{MCT} : \left[\left(T - T_c^{\,fit}\right) / T_c^{\,fit}\right]^{-\gamma}$$

$$\tau_{hop} \propto exp(B / (T - T_K))$$

T-dependence of τ_α (Salol)



T^o_c=278K

T^{fit}_c =258K (Prediction)

Bhattacharyya, Bagchi, Wolynes, PNAS, **105** 10677, (2008)

Why does MCT still seem to work between $T^{o}_{c} > T > T^{fit}_{c}$?

$$\phi_{MCT}(z) = \frac{1}{z + \dfrac{<\omega_q^2>}{z + \eta_l(z)}}$$

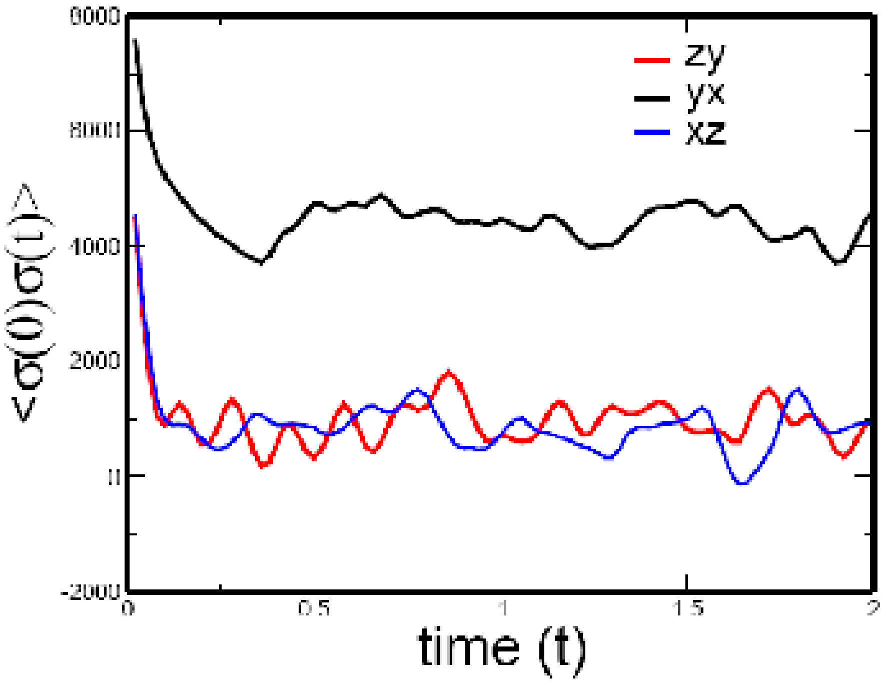
$$\eta_l(z) = \gamma + \lambda \mathrm{L}\left\{\phi^2(t)\right\}$$

Hopping → Softening of Longitudinal Viscosity → Relaxation of the MCT part

$$T < T_c^0, \qquad \tau^{-1}{}_{MCT} \sim \frac{2\tau^{-1}{}_{hop}}{(f_q^2\lambda - 1)}$$

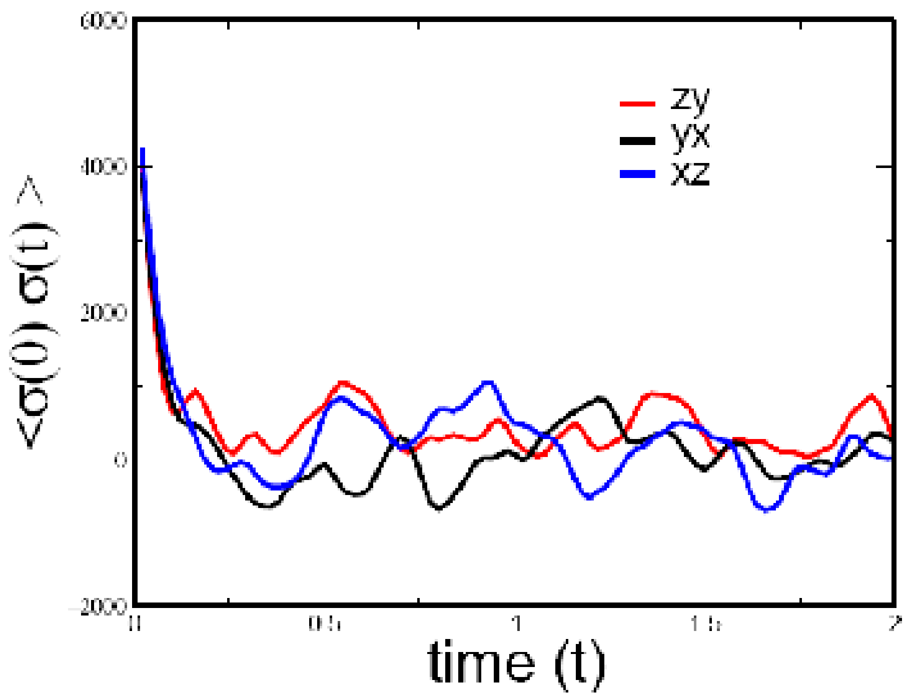
Hopping induced diffusive dynamics

Hopping Induced Relaxation of Local Stress-auto correlation



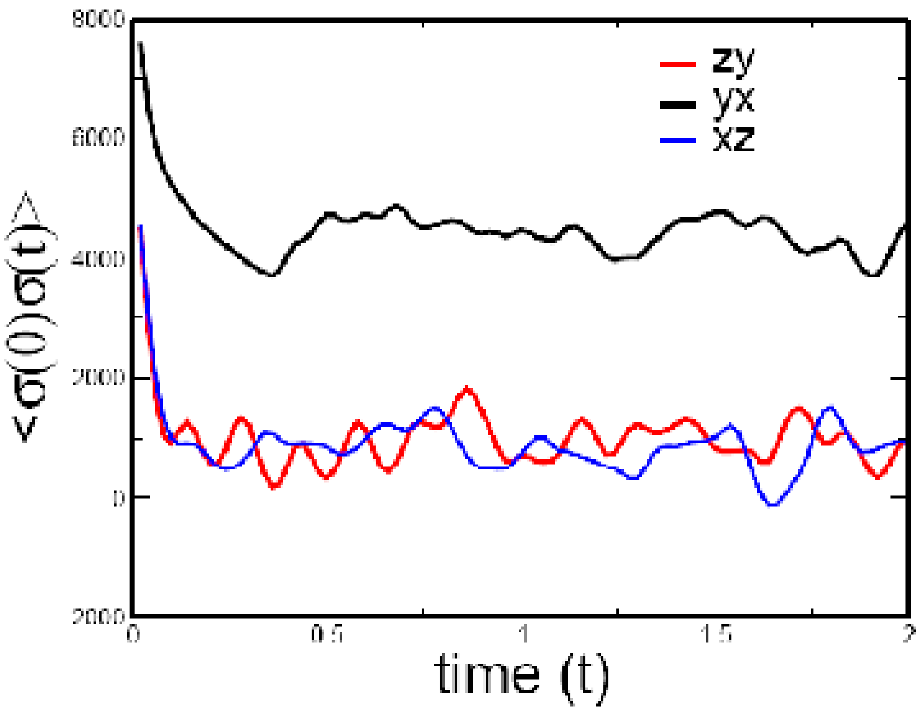
Before hopping

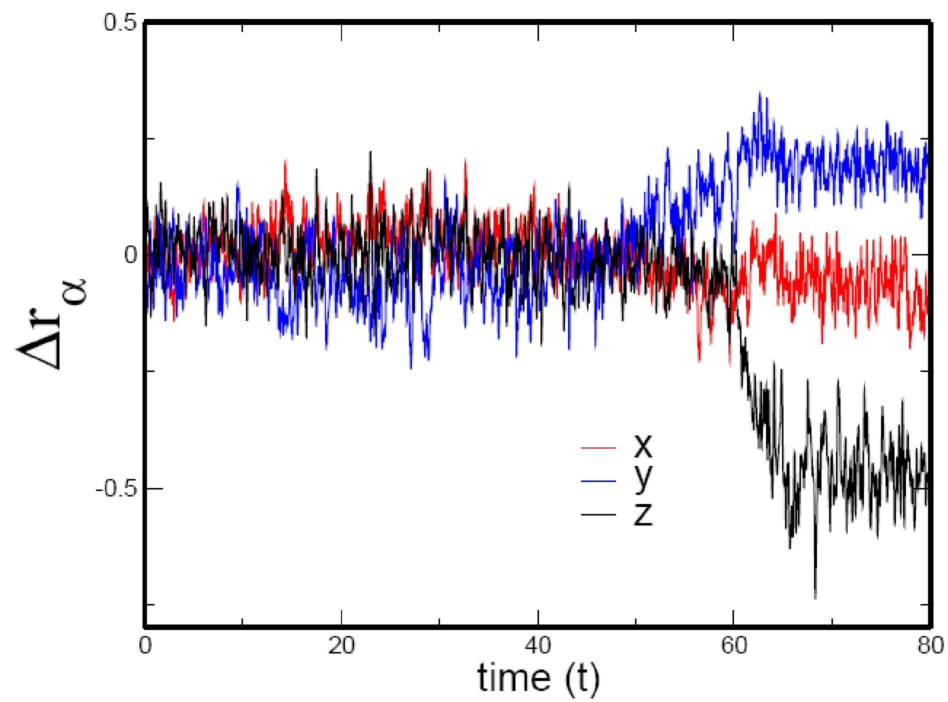
After hopping



Bhattacharyya and Bagchi PRL, **89** 025504-1, (2002)

Correlation between Anisotropy in Stress and Direction of Particle Hopping



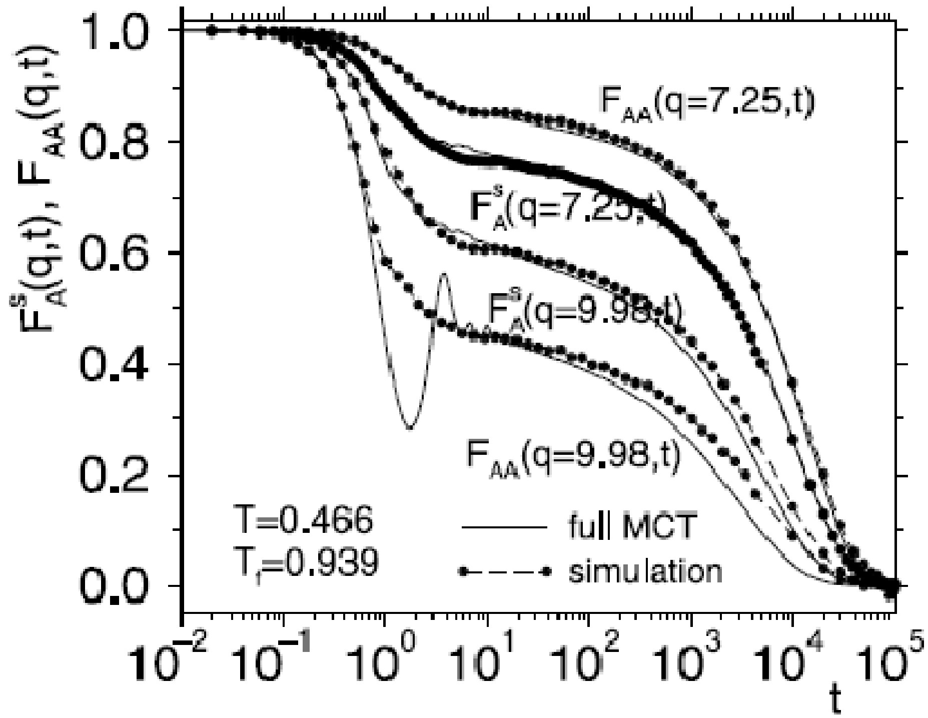


Bhattacharyya and Bagchi PRL, **89** 025504-1, (2002)

Hopping increases local temperature

Puzzle-Dynamics well described by λ calculated at higher effective T !!!!

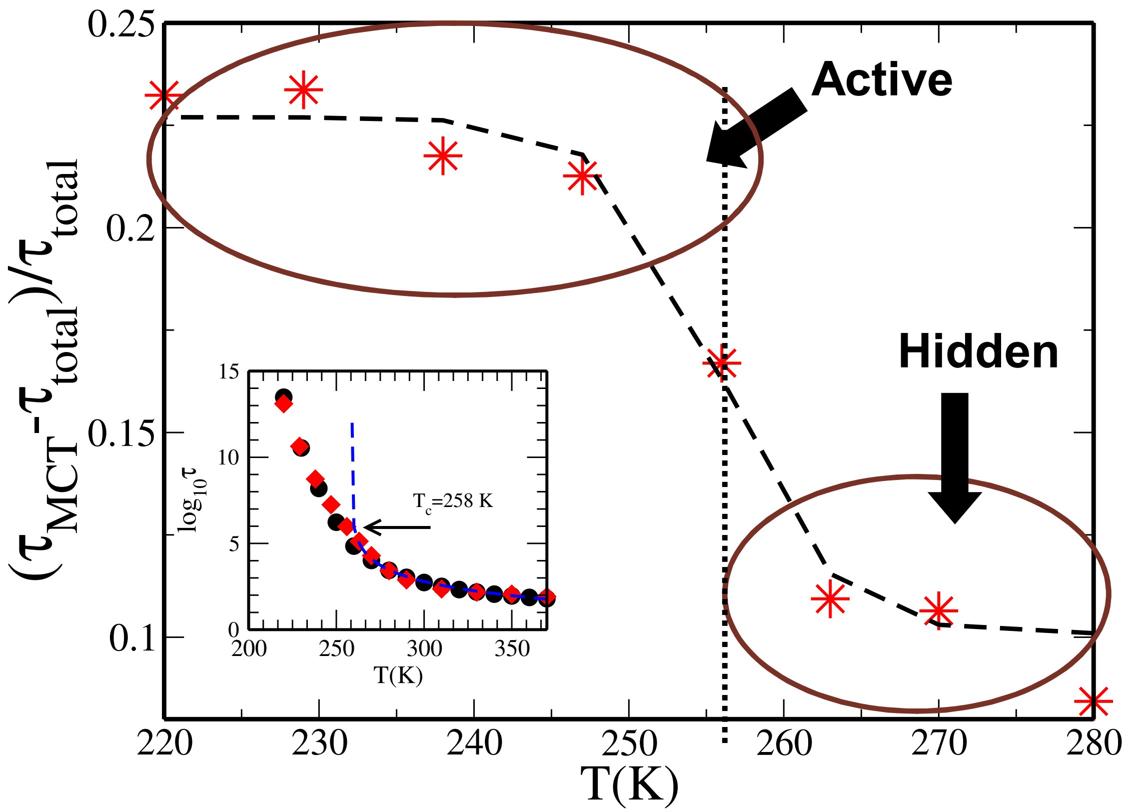
$$\eta_l(z) = \gamma + \lambda < \omega_q^2 > \mathrm{L}\left\{\phi^2(t)\right\}$$



Hopping → Increases the local temperature

W. Kob, M. Nauroth, F. Sciortino J. of Non-Cryst. Solids **307–310** 181–187 (2002)

Why does MCT breakdown ?



Gradual change of the dynamics from diffusive to activated

$$\tau^{-1}_{MCT} ; \frac{2\tau^{-1}_{hop}}{(f_q^{\,2}\lambda - 1)}$$

$$(f_q^{\,2}\lambda - 1) << 2 \rightarrow \text{Hidden}$$

$$(f_q^{\,2}\lambda - 1) >> 2 \rightarrow \text{Active}$$

Connection with Landscape Picture

Sastry et al. (Nature, **393** 354 (1998))

- Hidden role of hopping → Landscape influenced regime

- Active role of hopping → Landscape dominated regime

Wavenumber (q)- dependence of relaxation time

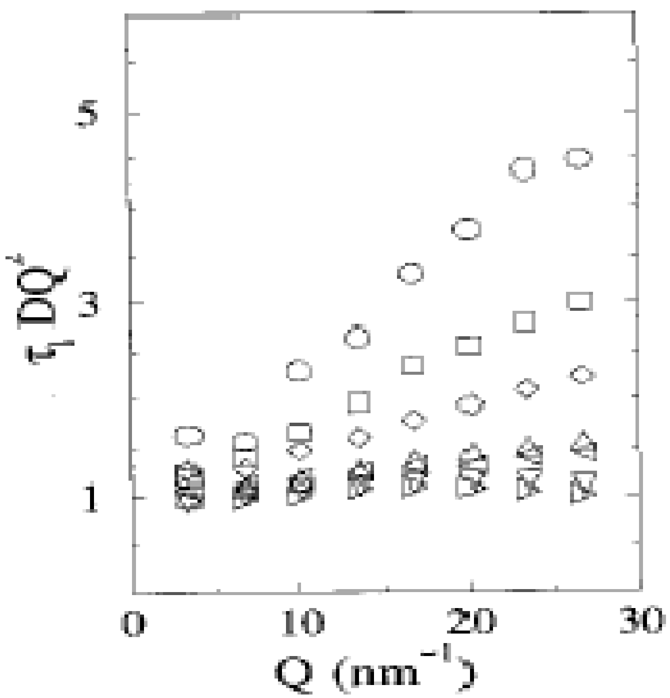
- MCT→ Diffusive dynamics → Ficks law → quadratic ***q*** dependence

$$\tau_{MCT}(q) \propto q^{-2}$$

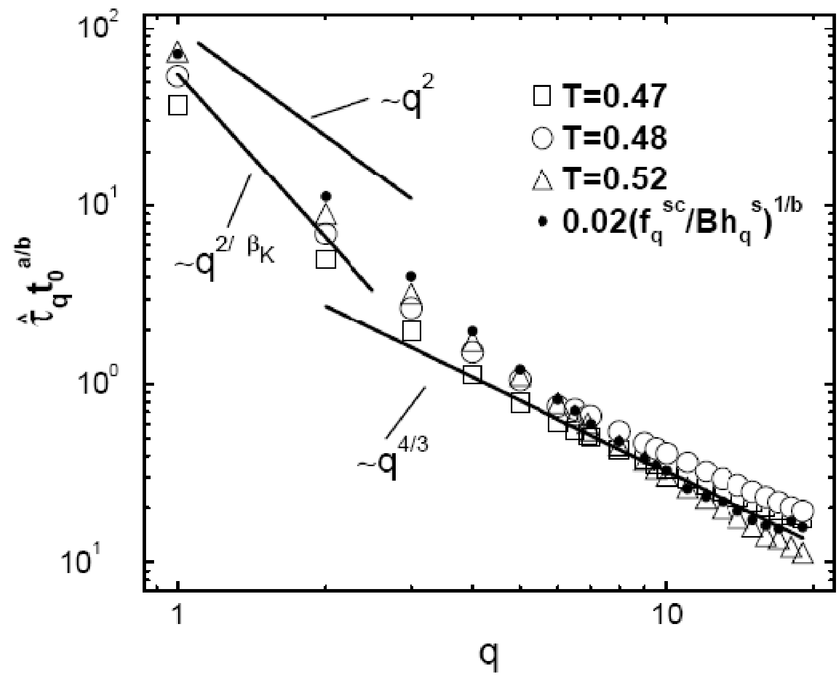
- Activated dynamics → Jump diffusion model → ***q*** independent dynamics

$$\tau_{hop}(q) \propto q^{0}$$

Simulation studies of q- Dependence of timescale at different T



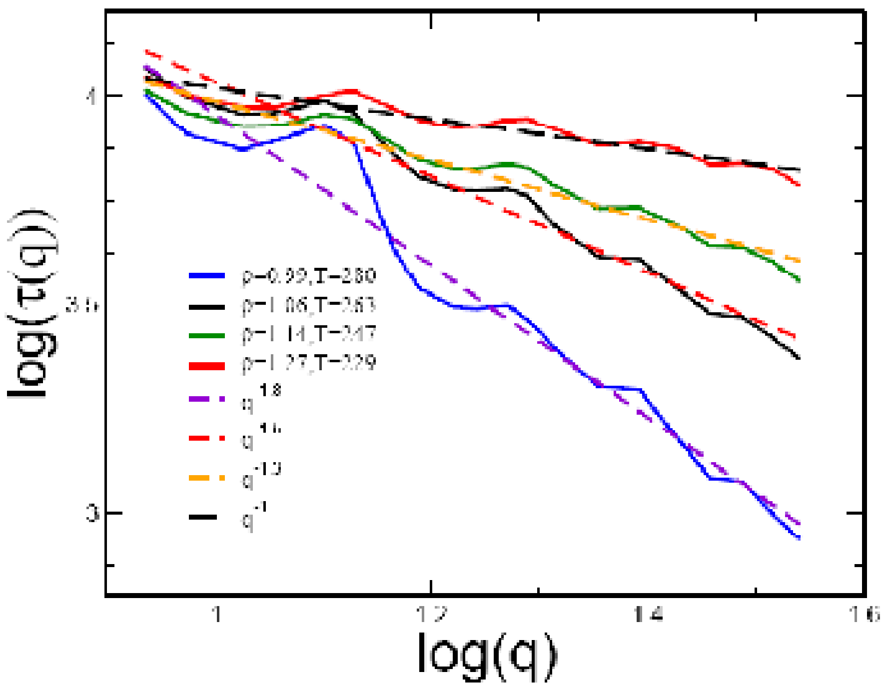
Sciortino *et al*. PRE **54** 6331 (1996)



Bennemann, Baschnagel, Paul, Eur. Phys. J. B **10** 323 (1999)

Weaking of q- dependence of timescale as T is lowered

$$\phi(q,t) = a(q)\exp(-(t/\tau(q))^{\beta(q)}$$



$$\tau(q) \propto q^{-\alpha}$$

T $\downarrow$ → α $\downarrow$

Bhattacharyya, Bagchi, Wolynes arXiv:0902.4078 (2009)

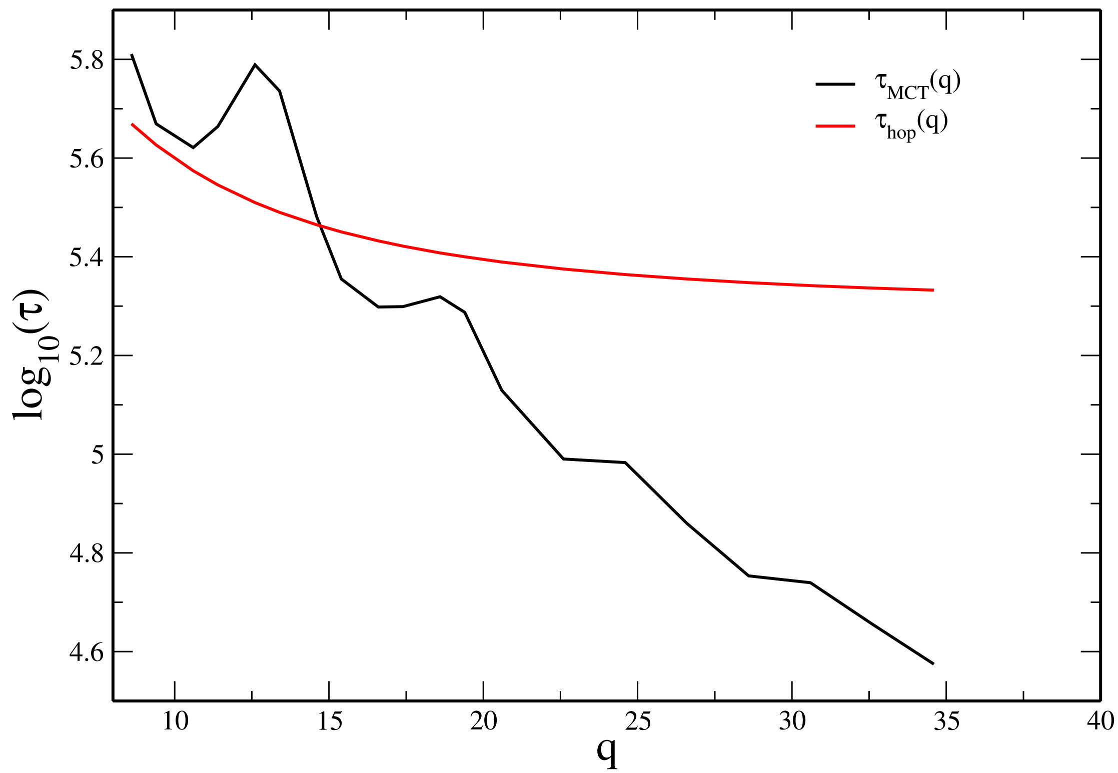
What causes Gradual weakening of q-dependence of relaxation time ?

Weakening of q-dependence of hopping induced MCT dynamics

or

Gradual change of dynamics in the crossover regime

Wavenumber dependence of hopping induced diffusive dynamics

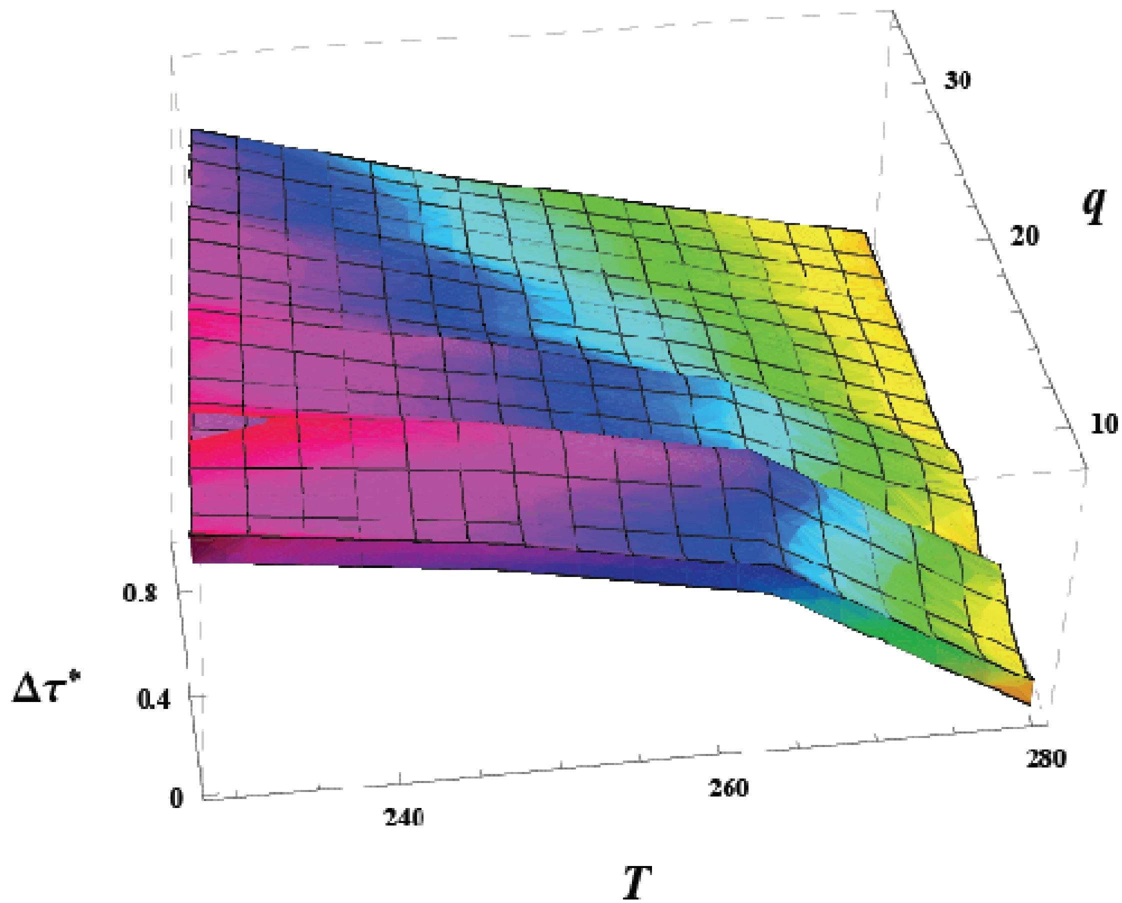


$$\tau^{-1}{}_{MCT} \;;\; \frac{2\tau^{-1}{}_{hop}}{(f_q{}^2\lambda - 1)}$$

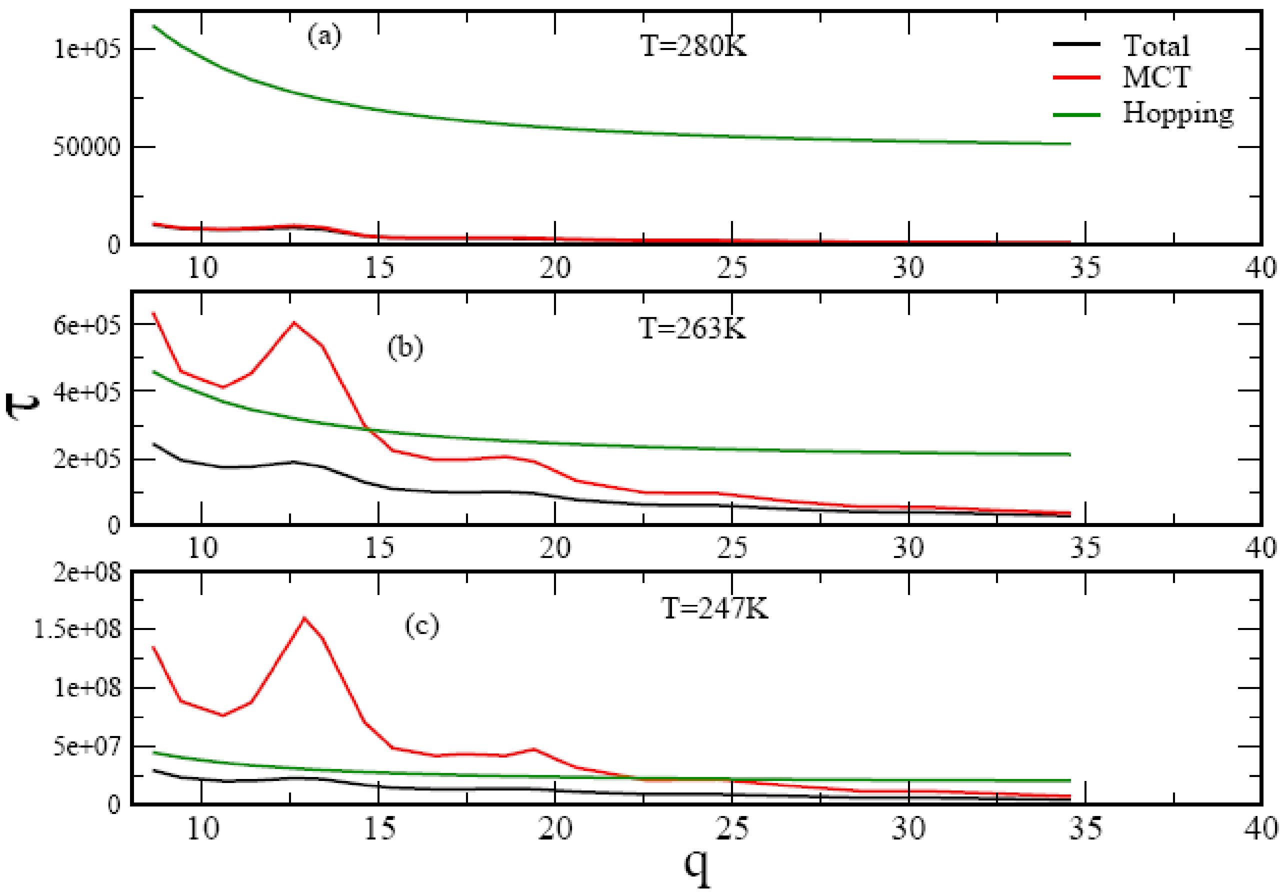
$$f_q \rightarrow DWF$$

Hopping induced MCT dynamics retains its wavenumber dependence

Wavenumber dependence of gradual crossover



Bhattacharyya, Bagchi, Wolynes arXiv:0902.4078 (2009)

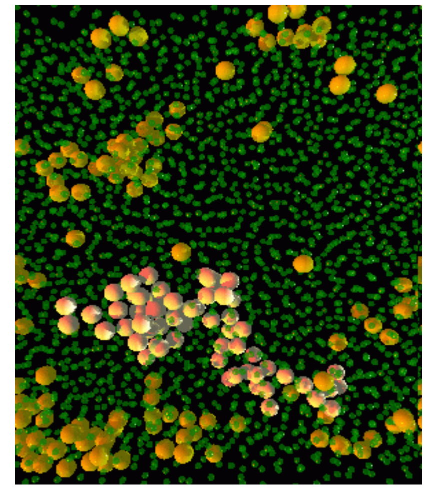


Wavenumber dependence of crossover

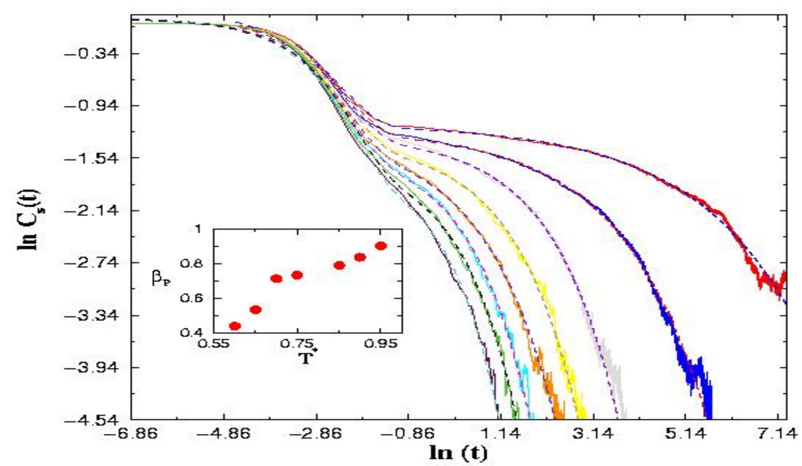
⇩

Gradual weakening of q- dependence of relaxation time

Dynamic Heterogeneity



- Heterogeneity grows with supercooling
- Stretched dynamics, stretching parameter β → measure of heterogeneity
- MCT describes homogeneous theory



Heterogeneity in RFOT

Range of barriers ΔF^*

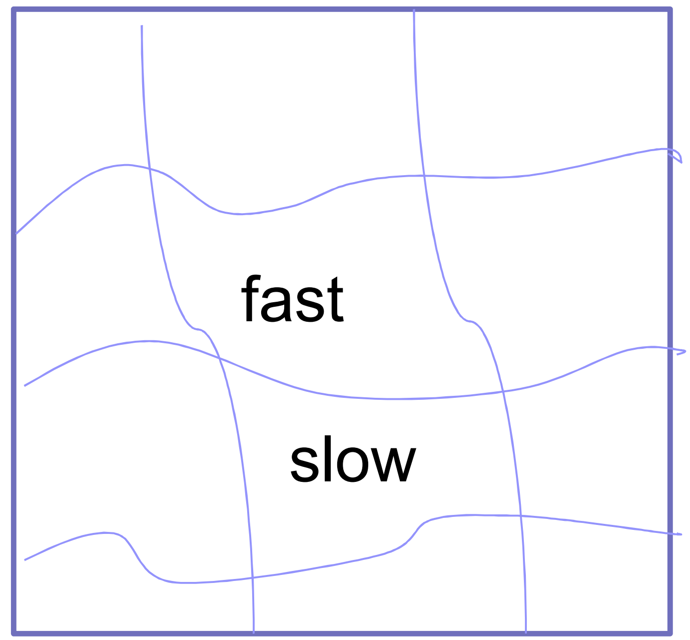
Assume $P(\Delta F^*) \rightarrow$ Gaussian

$$\Delta F^*(r) = \frac{3\pi\sigma^2{}_0 r_0}{T s_c}$$

$$\frac{\delta \Delta F^*}{\Delta F^*} \approx \frac{\delta s_c}{s_c}$$

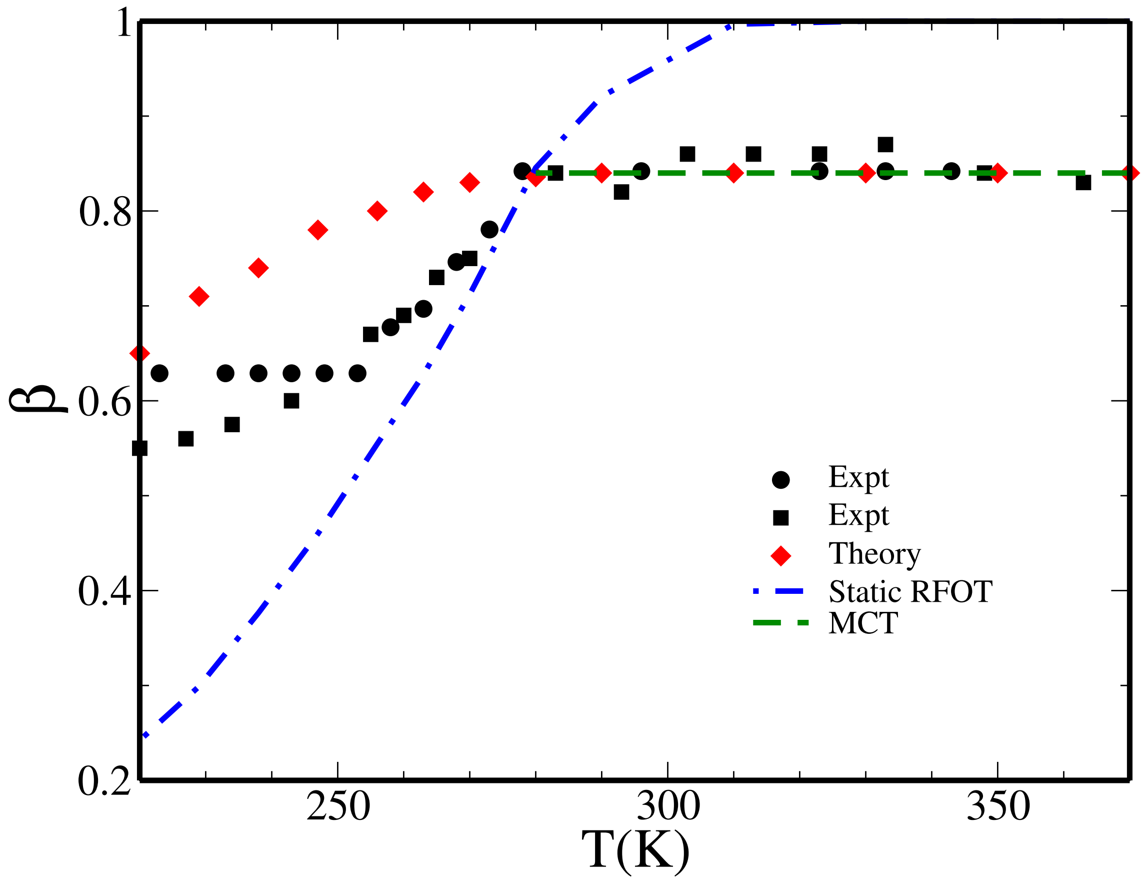
$$\delta s_c \propto \sqrt{\Delta c_P \xi^3}$$

Mosaic Structure



More Fragile liquids $\rightarrow$ higher $\Delta c_P \rightarrow$ wider $P(\Delta F^*)$

T-Dependence of β (Salol)



$$\beta_{hop} \square \ \beta_{MCT+hop}$$

Modified Barrier Height Distribution

$$e^{-\left(t/\tau_{\alpha}\right)^{\beta}} = \int_{0}^{\alpha} e^{-\left(t/\tau\right)} P(\tau)d\tau$$

Stretched Exponential dynamics

↓

Distribution of timescale.

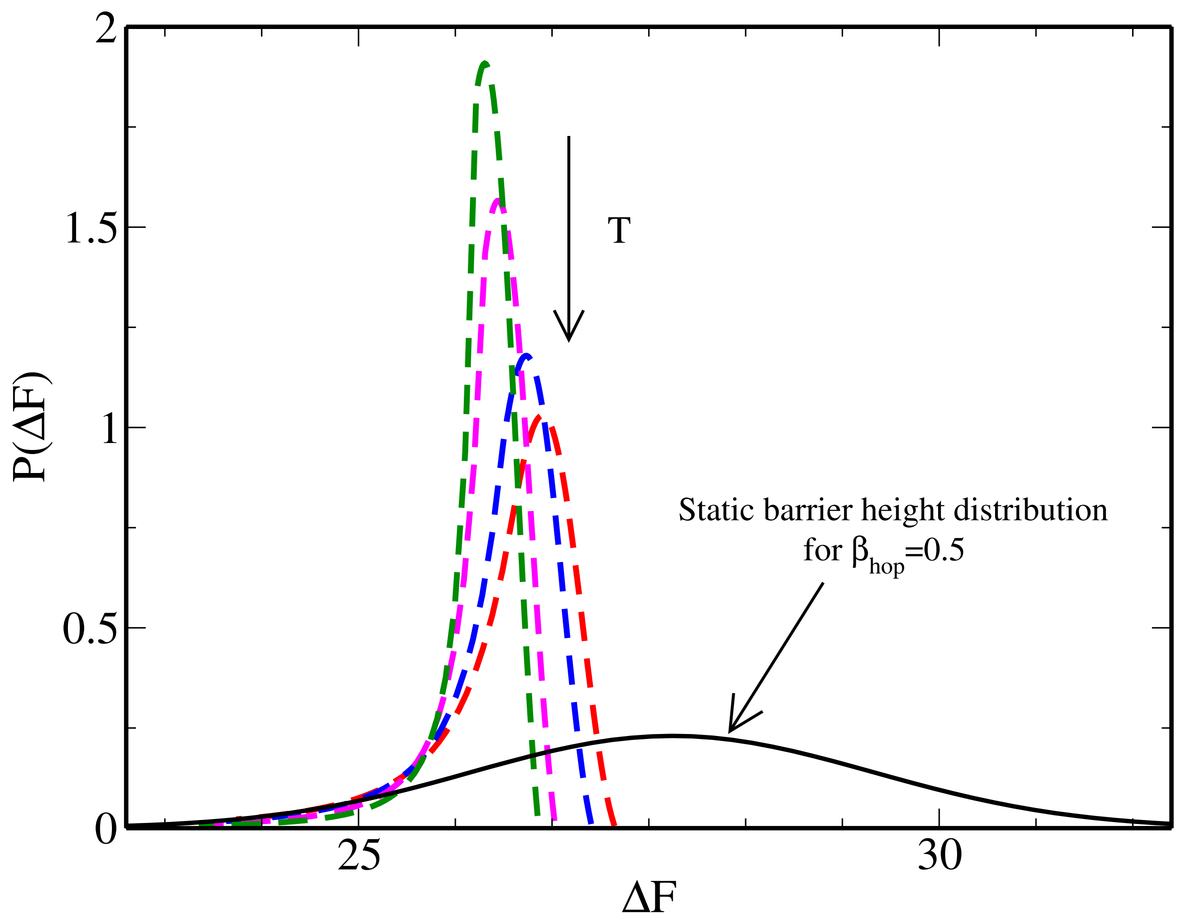
$$P(\Delta F)d\Delta F = P(\tau)d\tau$$

↓

Modified distribution of barrier height

$$\tau \approx \frac{\tau_0}{(\alpha+1)} \exp(\Delta F / k_B T)$$

Renormalized (by MCT) Barrier Height Distribution - Function of MCT Timescale



MCT → renormalizes barrier height distribution.

Distribution depends on MCT timescale.

Bhattacharyya, Bagchi, Wolynes, PNAS, **105** 10677, (2008)

Facilitation

Mosaic Structure

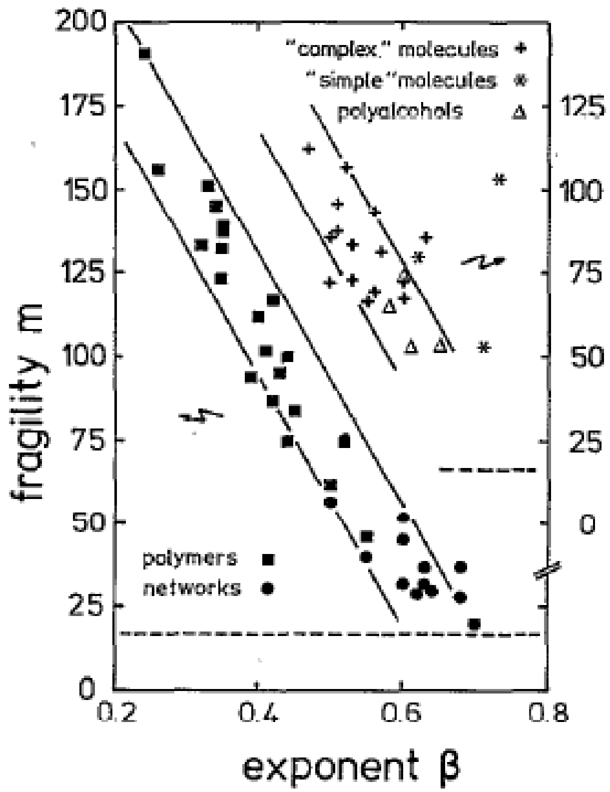
MCT induces interaction
between fast and slow regions

- MCT dynamics facilitates the activated dynamics by lowering the effective barriers.
- Faster MCT dynamics → greater facilitation
- MCT decreases the heterogeneity
- Renormalized barrier distribution → mean field estimate of dynamic heterogeneity

Fragility and Dynamic Heterogeneity

Correlation mentioned by Gilles Tarjus

Bohmer *et al* J. Chem. Phys. **99** 4201 (1993)



$$m = 16 + 590 / D$$

Experimental observation

More fragile → Larger stretching parameter

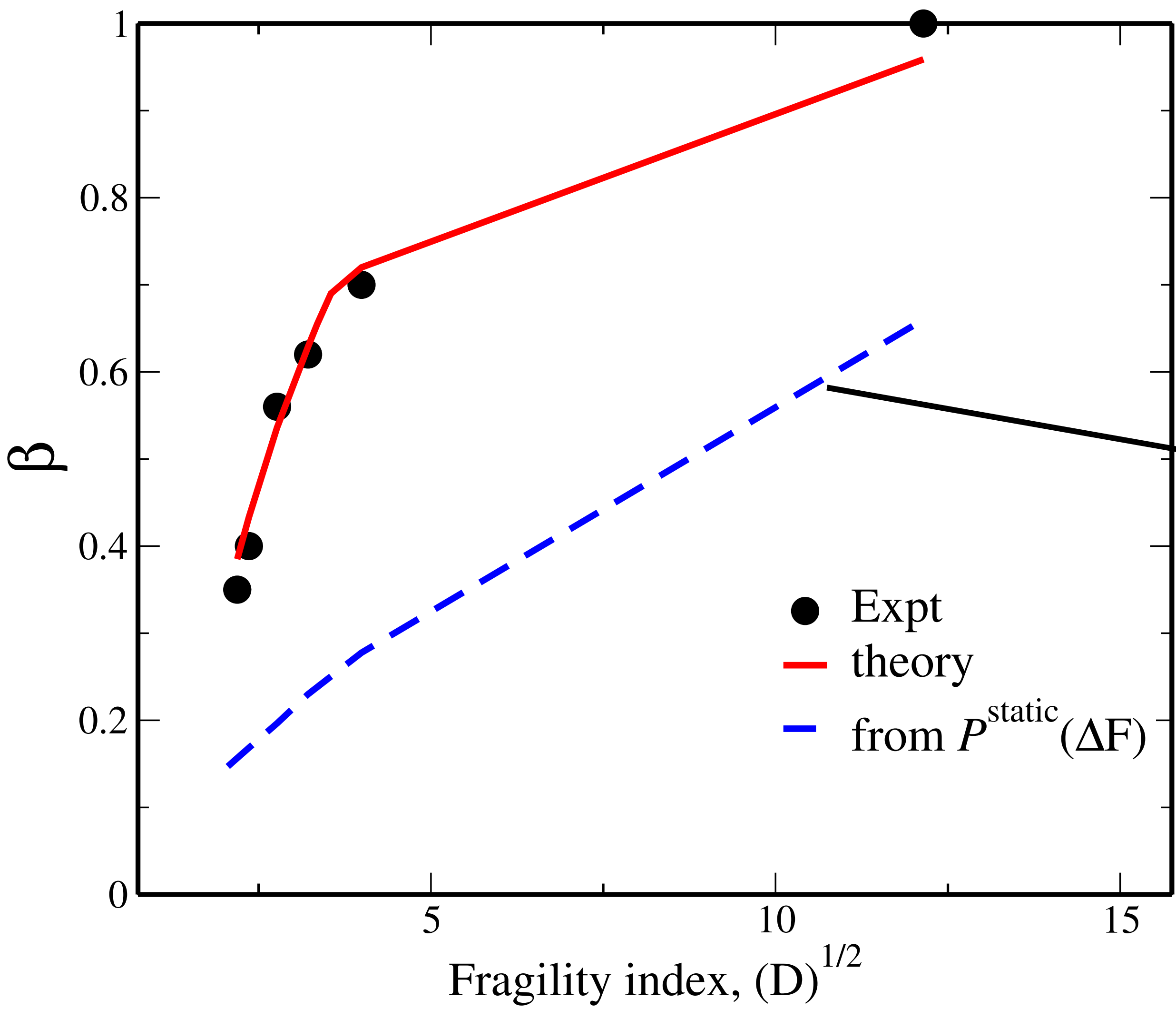
Fragile liquid →Rugged energy landscape→ wider barrier height distribution

$$\Phi(t) = \int e^{-t/\tau(\Delta F^*)} P(\Delta F^*) d\Delta F^*$$

$$\beta_{hop} = \left[1 + \left(\frac{\Delta F^*{}_o(T)}{2k_B T \sqrt{D}} \right)^2 \right]^{-1/2}$$

Xia and Wolynes, PRL, **86,** 5526 (2001)

Fragility and Stretching Parameter



$$\beta_{hop} = \left[1 + \left(\frac{\Delta F^{*}{}_{o}(T)}{2 k_B T \sqrt{D}} \right)^2 \right]^{-1/2}$$

Renormalized barrier height distribution reduces heterogeneity

Glass transition and Growing correlation length

Correlation length → peak height of four point susceptibility χ_4(t)

C. Dasgupta et al, Europhys. Lett. 15, 307(1991).

χ_4(t) = response of a two-point correlation F(t) to an external field
Fluctuation dissipation theorem

$$\chi_x(t) = \frac{\partial F(t)}{\partial x}$$

Berthier et al Science, **310** 1797 (2005)

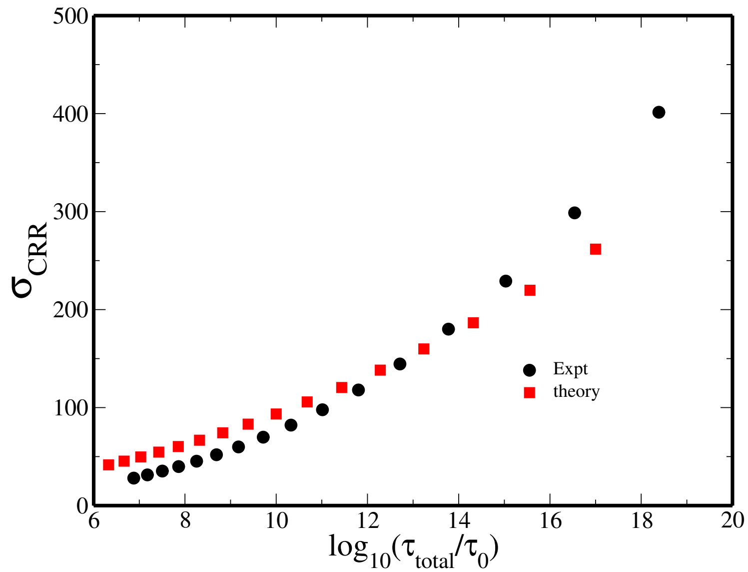
$$F(t) = \phi(t) \propto \exp(-(t/\tau_\alpha)^\beta)$$

$$N_{CRR}(T) = \rho\xi^d = \frac{k_B}{\Delta C_P}\frac{\beta(T)}{e^2}\left(\frac{d\ln\tau_\alpha}{d\ln T}\right)^2$$

Number of particles in a CRR

Growth of Complexity

$$\sigma_{CRR}(T) = \frac{S_c}{k_B} N_{CRR} = \frac{S_c}{\Delta C_P} \frac{\beta(T)}{e^2} \left(\frac{d \ln \tau_\alpha}{d \ln T} \right)^2$$



Adam-Gibbs → $\sigma_{CRR}(T) \quad T-indep$

RFOT → $\sigma_{CRR}(T) \propto \log(\tau)$

Expt and Present theory → $\sigma_{CRR}(T)^{\psi} \propto \log(\tau)$

Dynamical correlation length different from static correlation

Capaccioli, Ruocco, Zamponi, J. Phys. Chem. B 112 10652 (2008)

Bhattacharyya, Bagchi, Wolynes, PNAS, **105** 10677, (2008)

Summary

- Interplay between activated and diffusive dynamics
- **Hidden** role → Hopping induced diffusive dynamics T< T^{o}_{c}
  → **Landscape influenced regime**
- **Active** role of hopping → Breakdown of MCT→ **Landscape dominated regime**
- MCT renormalizes barrier height distribution → Picks up lower barriers.