National Institutes of Natural Sciences
分子科学研究所
Institute for Molecular Science

Role of length and time scales of dynamic heterogeneities on fragility in various model glasses

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K. Kim and S. Saito, J. Chem. Phys. 138, 12A506 (2013)

Outline

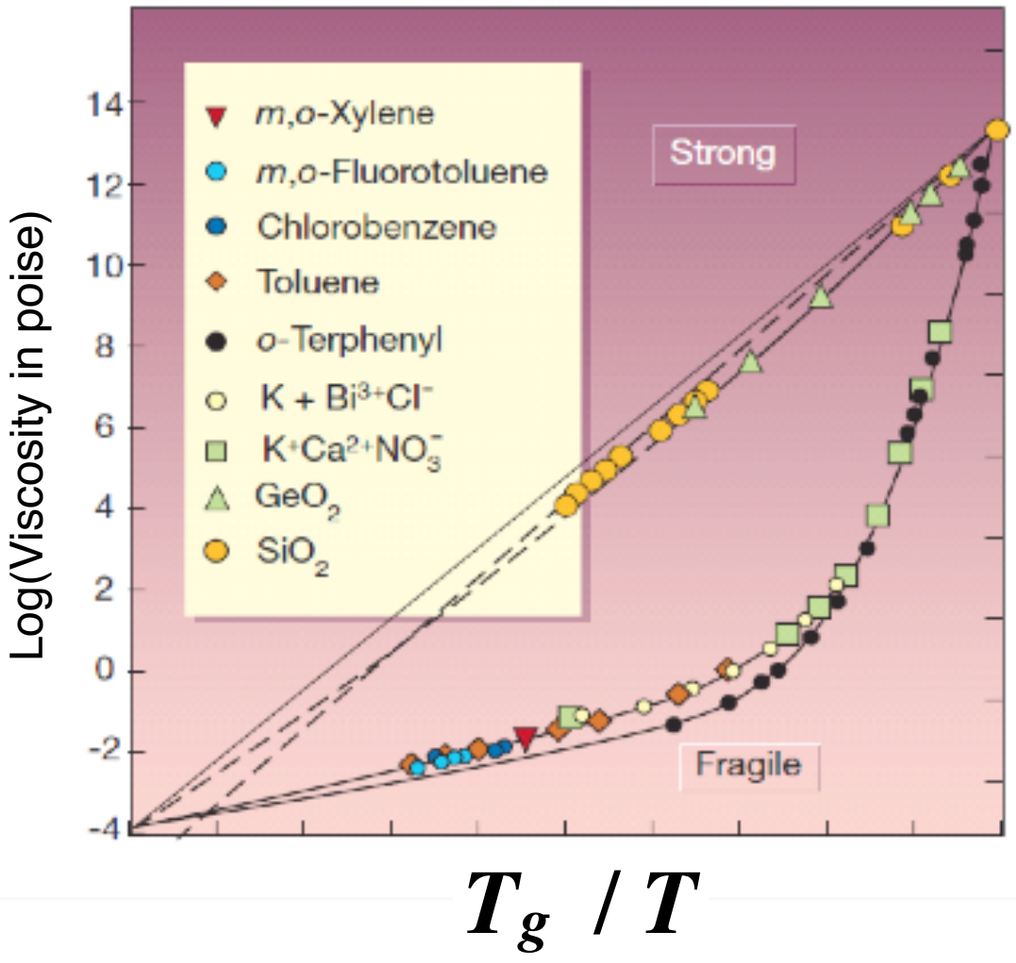
- ✓ Purpose
  - fragility in glass transition
  - dynamic heterogeneities
  - MD for various model glasses

- ✓ Spatiotemporal structures of DH
  - multi-point and multi-time correlations
  - fragility vs. length scale ξ and lifetime τ_{hetero}
  - model detail dependence

- ✓ Summary

Fragility

P. G. Debenedetti and F. H. Stillinger, Nature 410, 259-267 (2001)

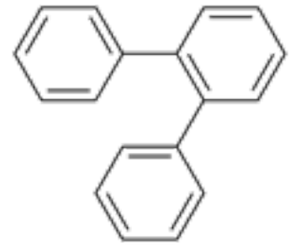


Vogel-Fulcher-Tammann

$$\eta \sim \exp\left[\frac{1}{K(T/T_g - 1)}\right]$$

K: Fragility index

Fragile: o-Terphenyl

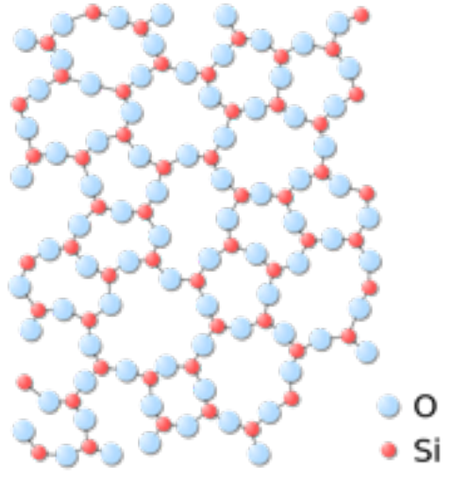


K: large

van der Waals

super-Arrhenius

Strong: SiO_2



K: small

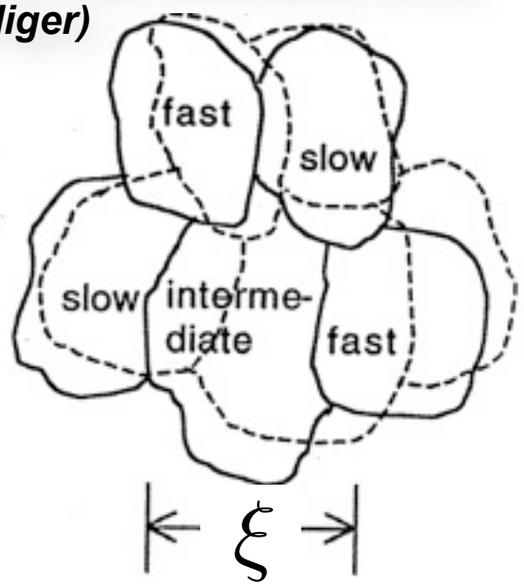
network-formation

Arrhenius

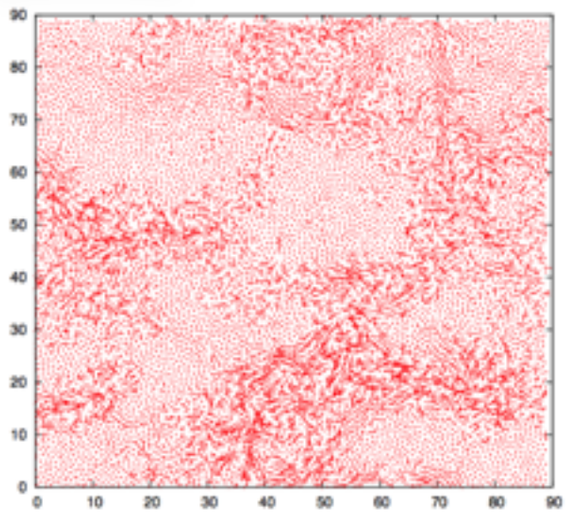
Physical implication of fragility K ?

Simulations visualize Dynamic Heterogeneity (1995～)

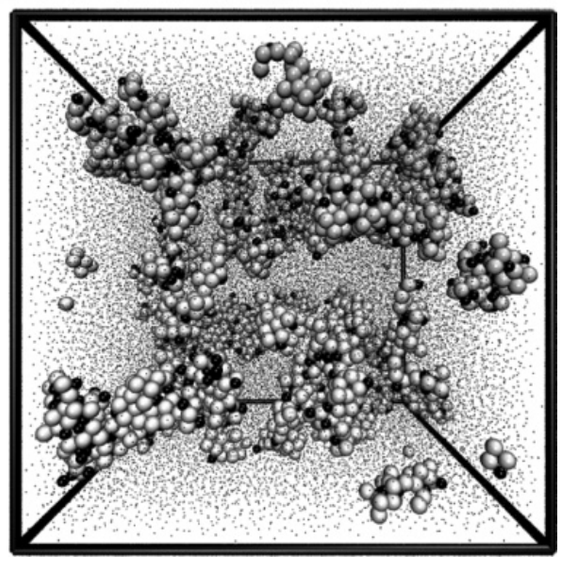
Schematic illustration of DH (Ediger)



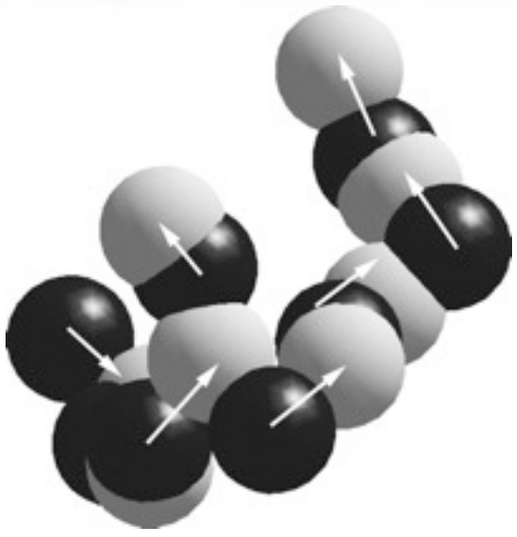
Binary LJ disks (Berthier)



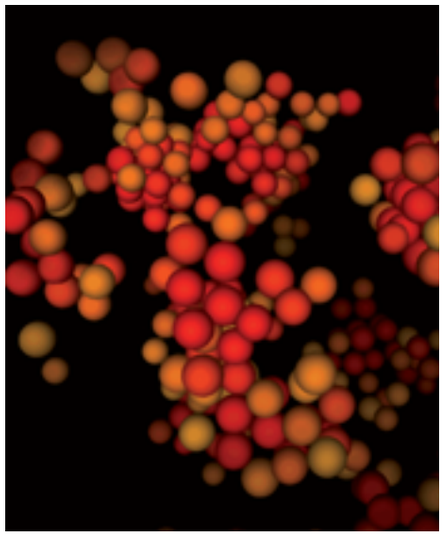
Binary hard spheres (Flenner-Zhang-Szamel)



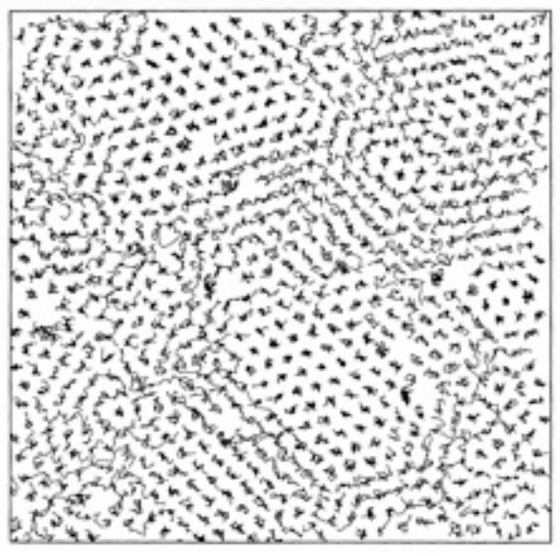
Binary LJ spheres (Donati-Douglas-Poole-Kob-Glotzer)



Polydisperse WCA spheres (Kawasaki-Tanaka)



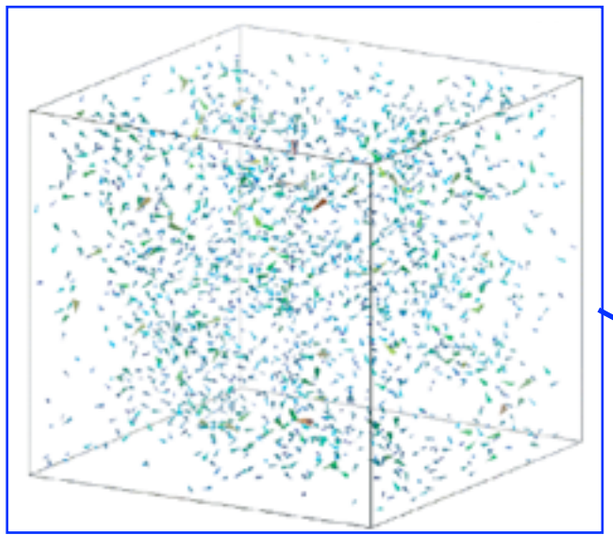
Binary soft disks (Hurley-Harrowell)

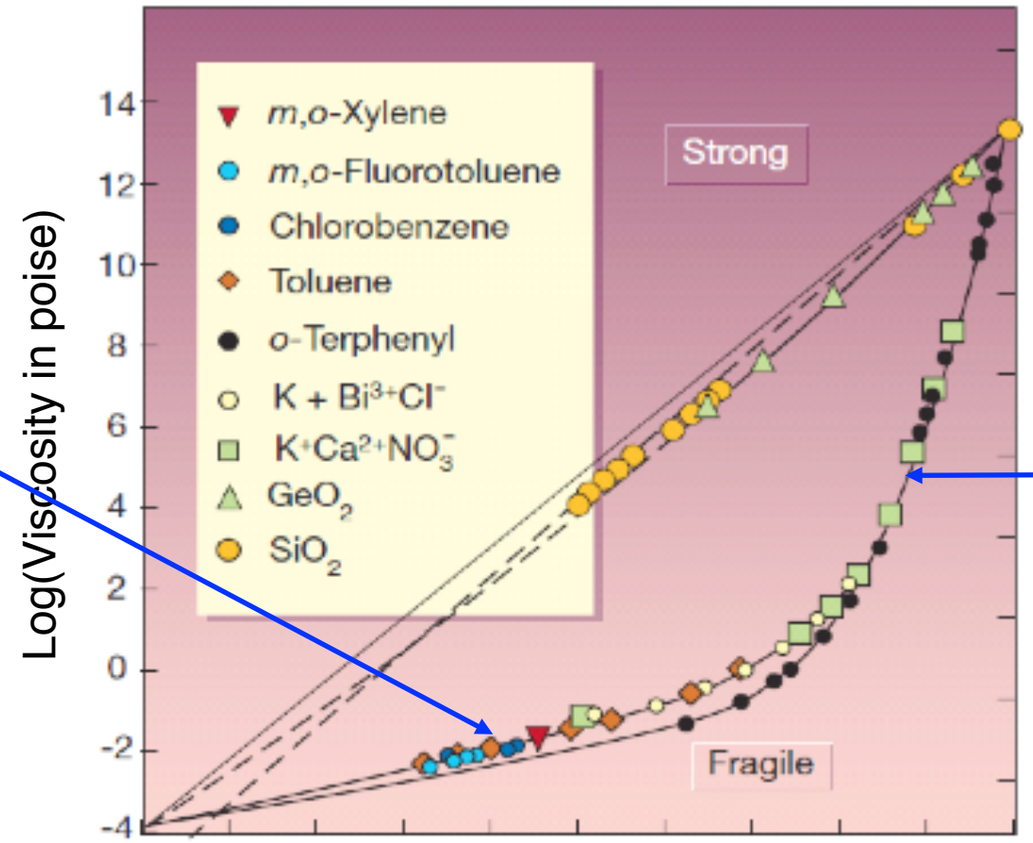


It looks like a universal hallmark, doesn't it?

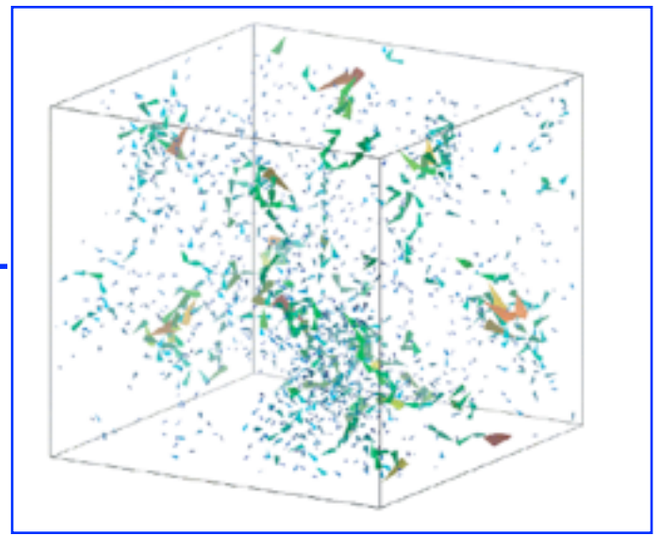
Purpose of this study:
Fragility vs. Dynamic Heterogeneities

P. G. Debenedetti and F. H. Stillinger, Nature 410, 259-267 (2001)





Binary soft spheres (Yamamoto-Onuki)



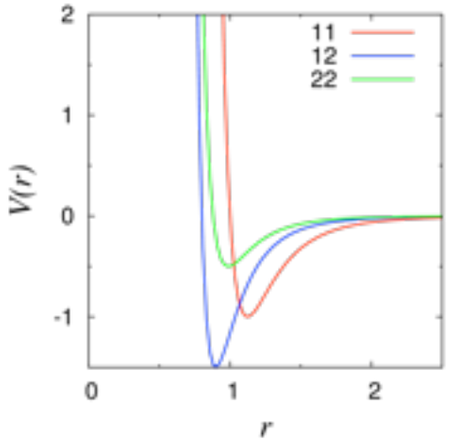
indivisual?
homogeneous?

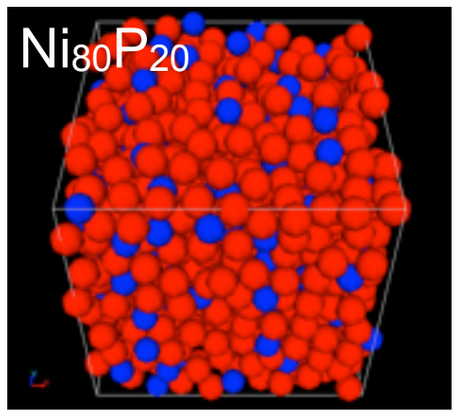
collective?
heterogeneous?

How do collective motions lead to super-Arrhenius?

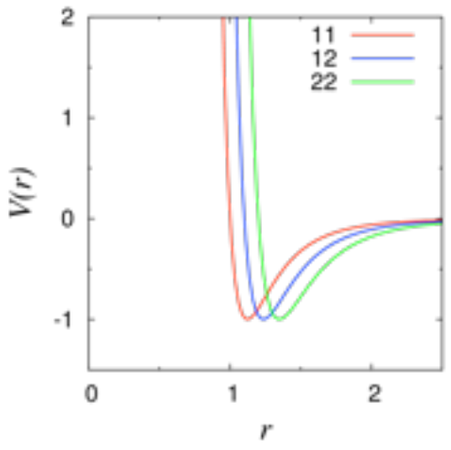
Is the model detail really trivial?

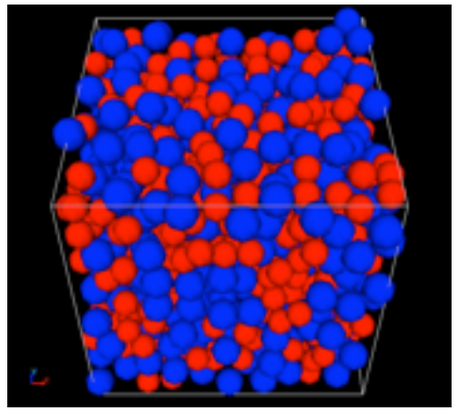
(a) Kob-Andersen LJ model (KALJ)



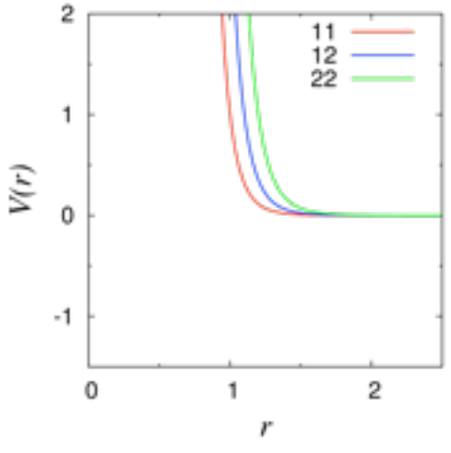


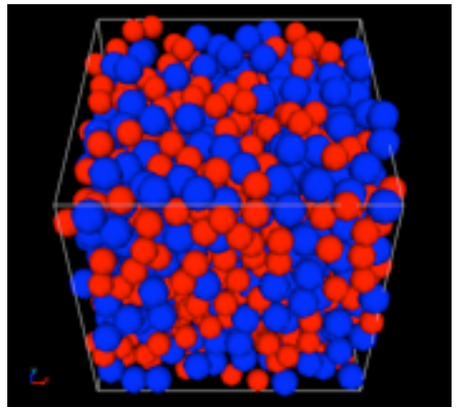
(b) Wahnström LJ model (WAHN)



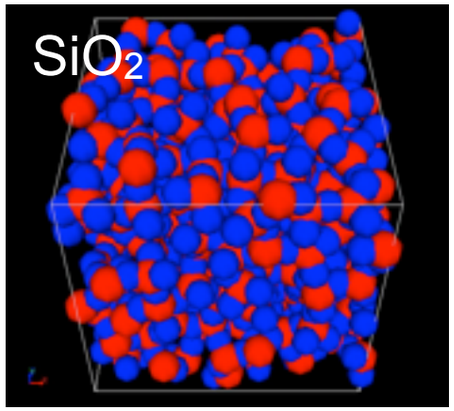


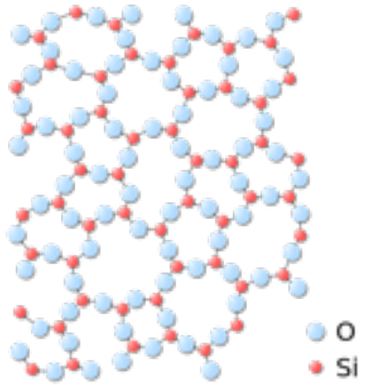
(c) Hiwatari-Hansen softsphere model (SS)

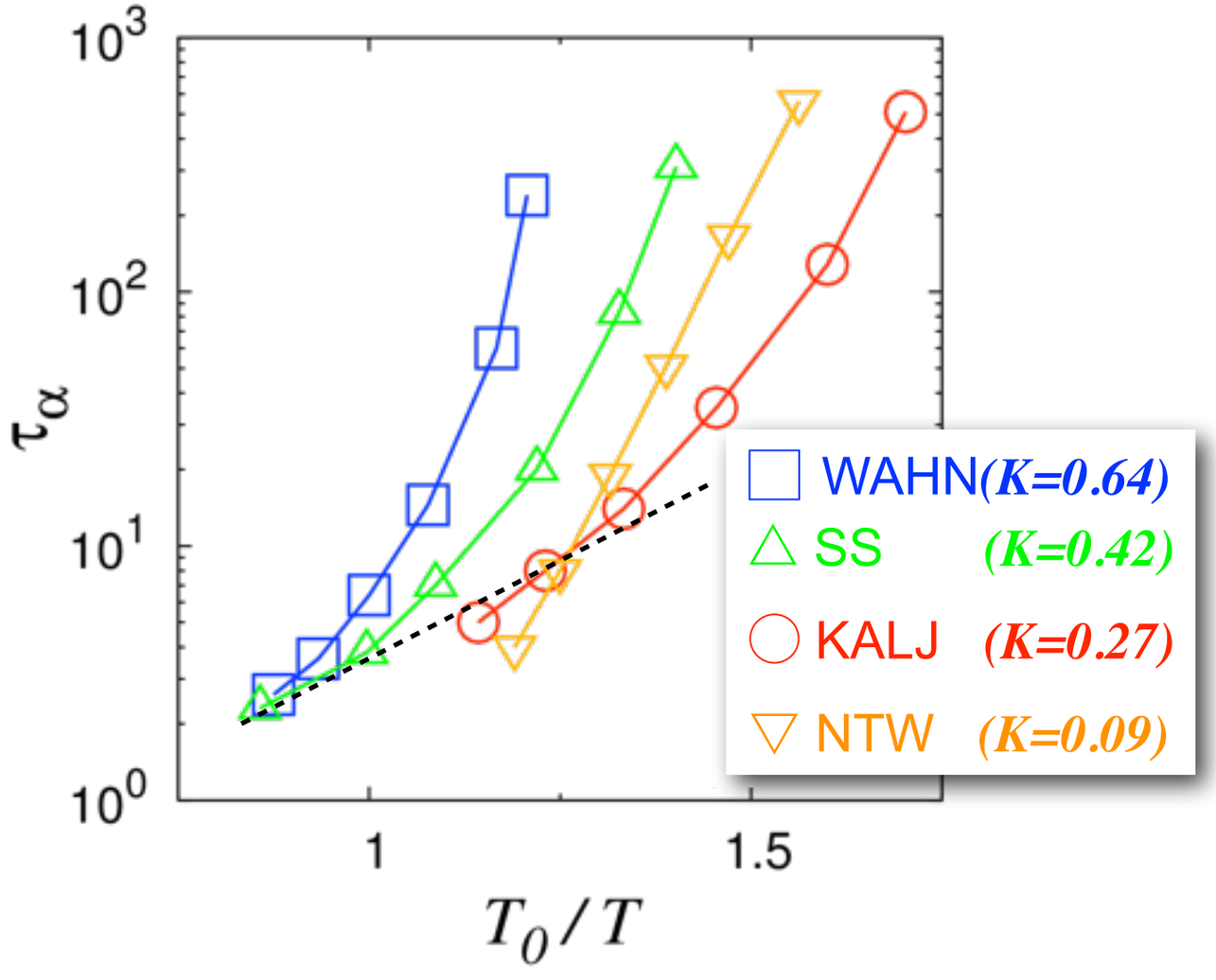




(d) Coslovich-Pastore network model (NTW)



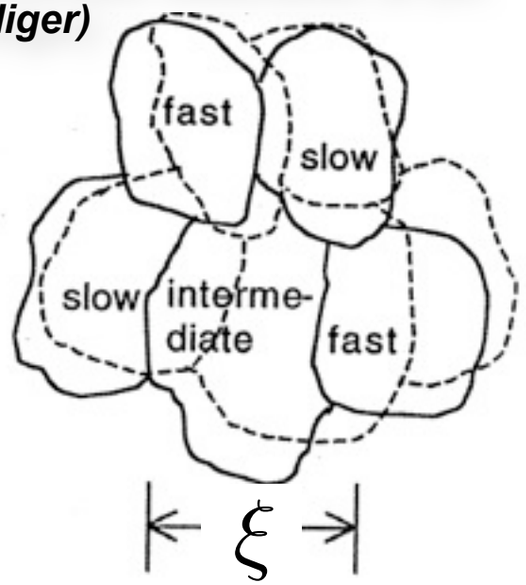


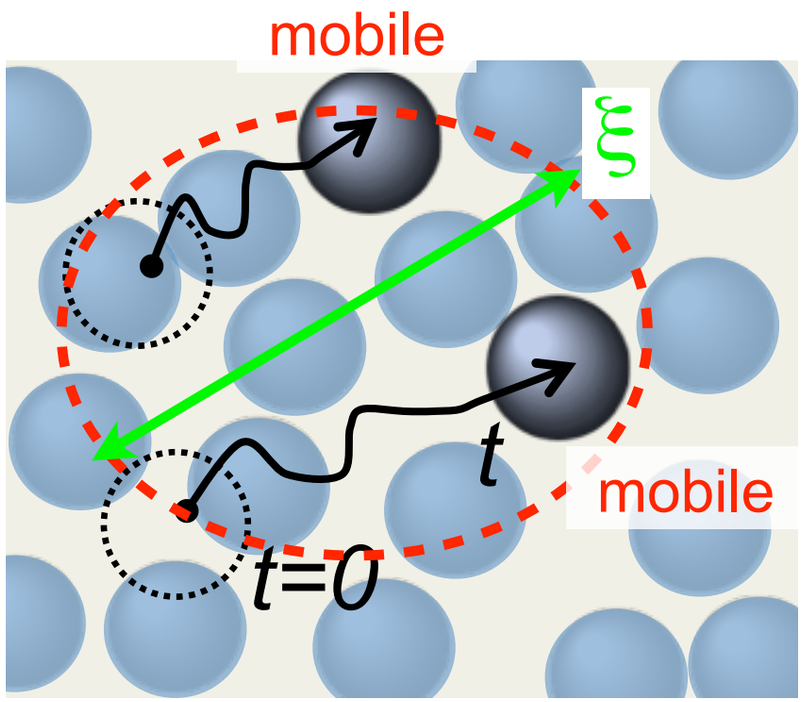


4-point correlations for Dynamic Heterogeneities(2000～)

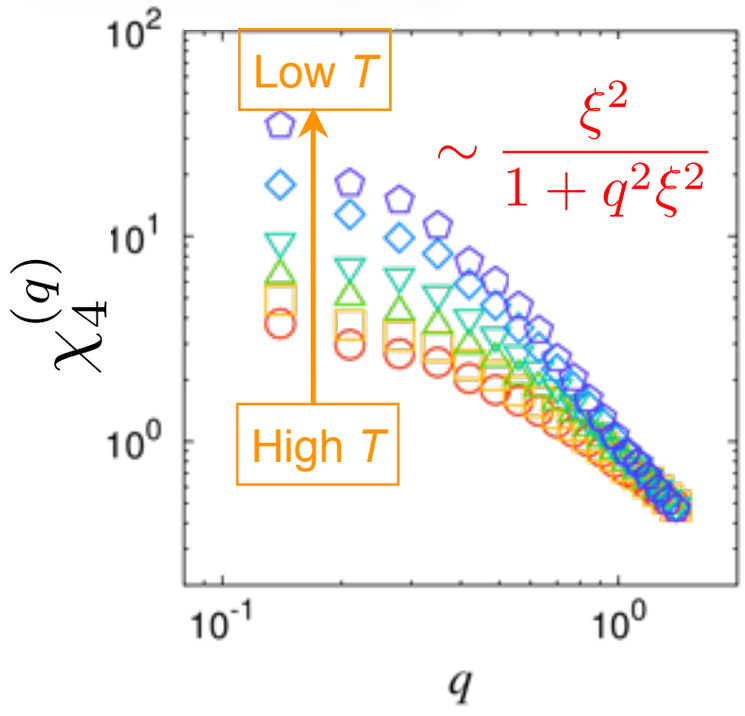
Glotzer, Berthier, Bilori, Chandler, Sastry, Szamel, ...

Schematic illustration of DH (Ediger)





Kim-Saito, JCP(2013)



fluctuations in “local dynamics” $\delta F(k,t)$

$$F_r(k,t) = F(k,t) + \delta F_r(k,t) \qquad F(k,t) = S(k) \times \exp[(-t/\tau_\alpha)^\beta]$$

correlations of fluctuations in 2-point → 4-point

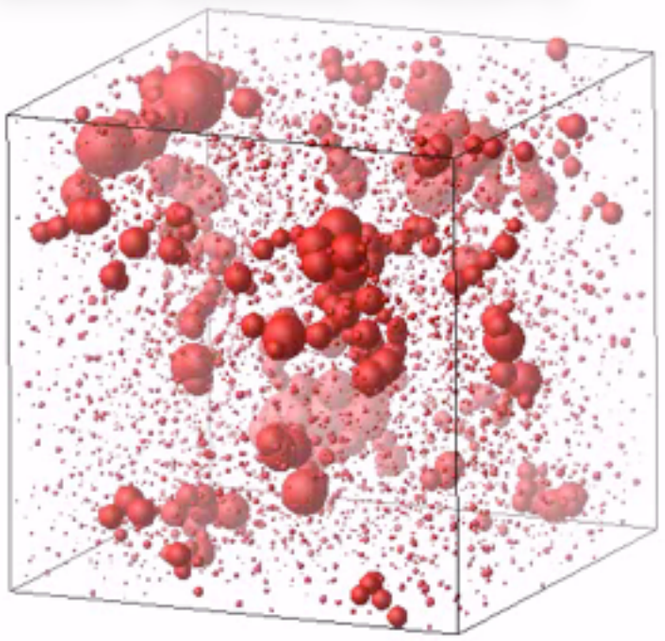
$$\chi_4^{(q)}(k,t) = \langle \delta F_q(k,t) \delta F_{-q}(k,t) \rangle \approx \langle \rho_k(t)\rho_{-k}(t)\rho_k(0)\rho_{-k}(0) \rangle$$

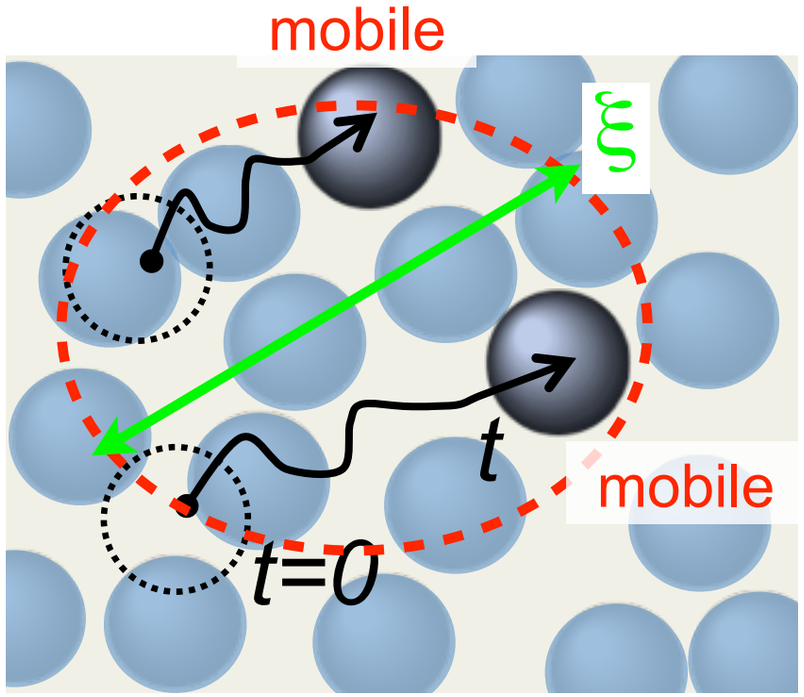
We need 4-point correlations to determine length time scales of DH!!

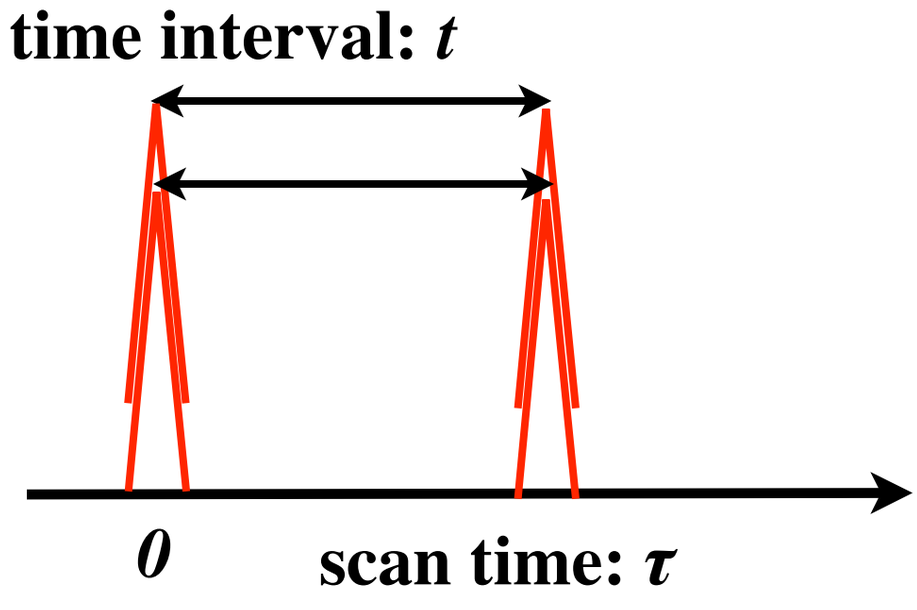
3-time extension of 4-point correlations

Kim-Saito, PRE(2009), JCP(2010), JCP(2013)

Mizuno-Yamamoto, PRE(2011)







Variance of $F(k, t)$ → 4-point (1-time interval)

$$\chi_4(t) \approx \langle \delta F(k,t)^2 \rangle \qquad F(k,t) = S(k) \times \exp[(-t/\tau_\alpha)^\beta]$$

$$\sim \exp[-\tau/\tau_{\rm hetero}]?$$

$$\tau_{\rm hetero} \text{ vs } \tau_\alpha?$$

We need 3-time correlations to determine time scales of DH!!

Lifetime of Dynamic Heterogeneity remains controversial...

✓ $\tau_{\rm hetero} \lesssim \tau_\alpha$

- Perera-Harrowell (binary soft discs)
- Flenner-Szamel (Kob-Andersen LJ)
- Doliwa-Heuer (hard discs)
- Weeks (colloidal glasses)

✓ $\tau_{\rm hetero} \gg \tau_\alpha$ at low T

- Yamamoto-Onuki, Mizuno-Yamamoto (binary soft spheres)
- Leonard-Berthier (fragile KCM model)
- Ediger, Richert, ... (NMR, hole-burning, photo-bleach)
- Orrit, Kaufman, ... (single molecule experiments)

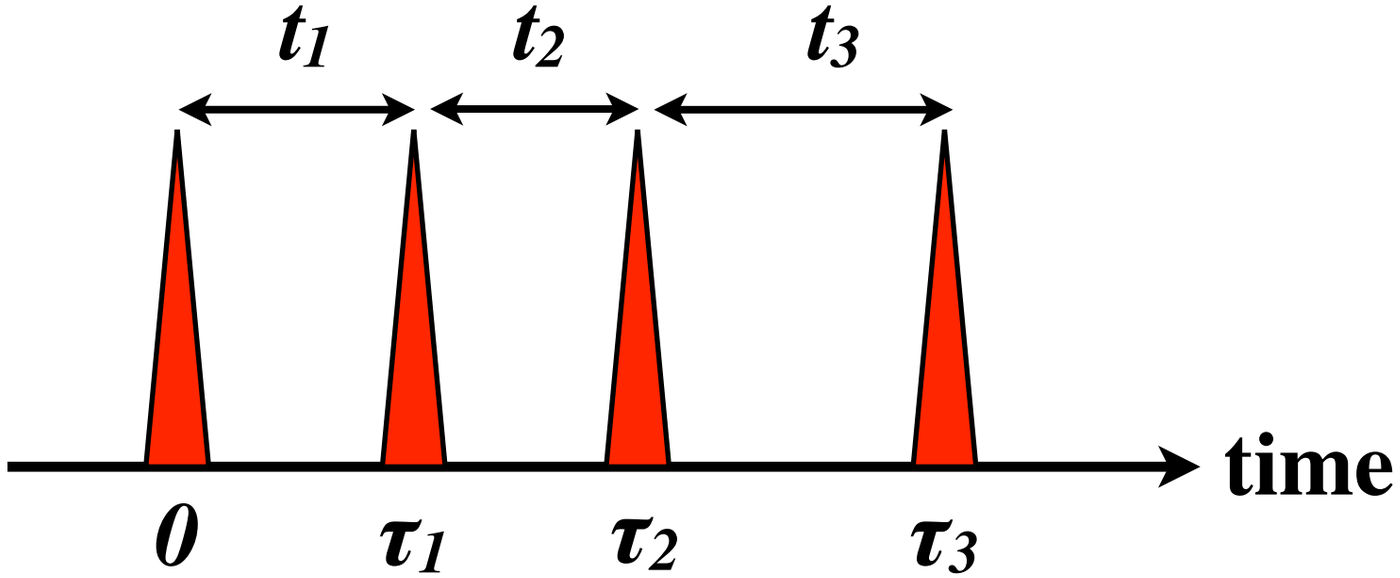
To resolve all controversy, we comprehensively examine multi-time correlation functions!!

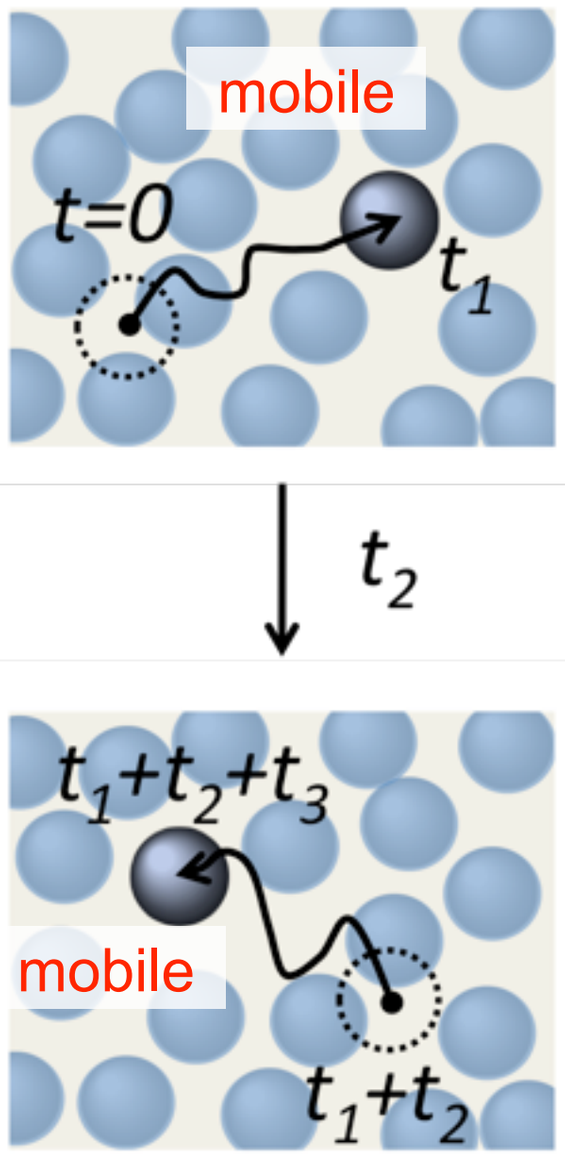
Why use multi-time correlations?: On the analogy of 2D-NMR and 2D-IR spectroscopies

3-time extension of $\chi_4(t)$

$$F_4(k, t_3, t_2, t_1) = \langle \rho_k(\tau_3)\rho_{-k}(\tau_2)\rho_k(\tau_1)\rho_{-k}(0)\rangle$$

$$\Delta F(k, t_3, t_2, t_1) = F_4(k, t_3, t_2, t_1) - F(k, t_1)F(k, t_3)$$





Key strategies:

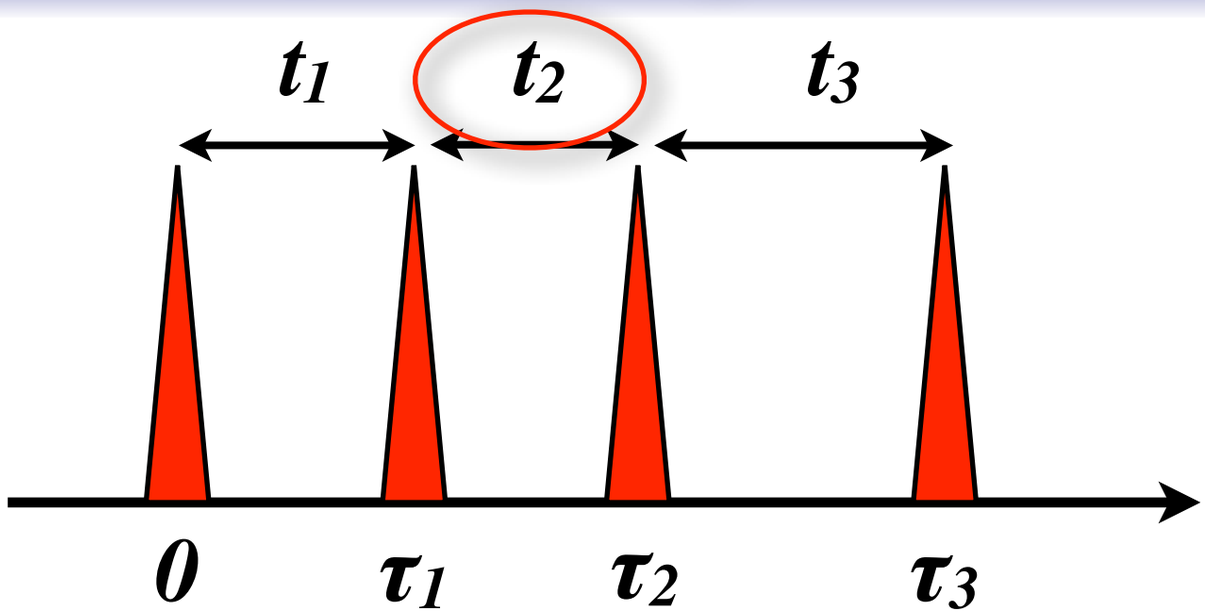
① Analyze couplings of t_1 - t_3 motions

if homogeneous dynamics, $\Delta F \rightarrow 0$

② Change the waiting time t_2

quantify relaxation time of DH τ_{hetero}

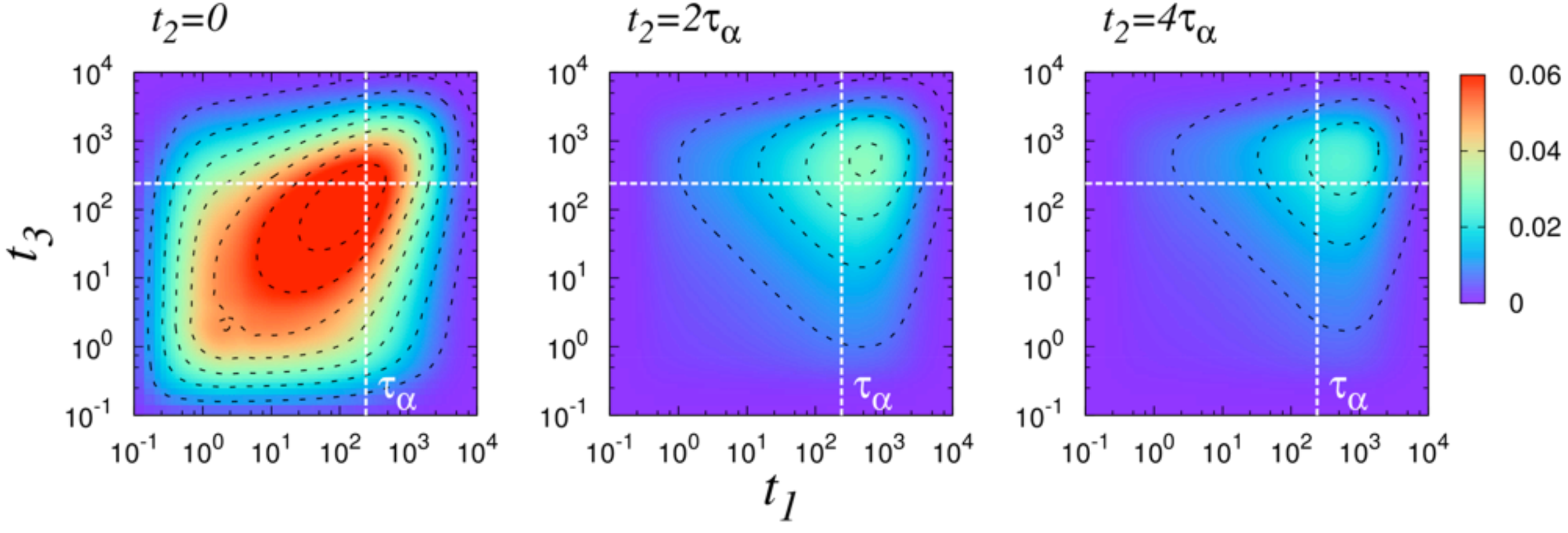
[WAHN fragile glasses] Change the waiting time t_2: How dose Dynamical Heterogeneity decay with time?



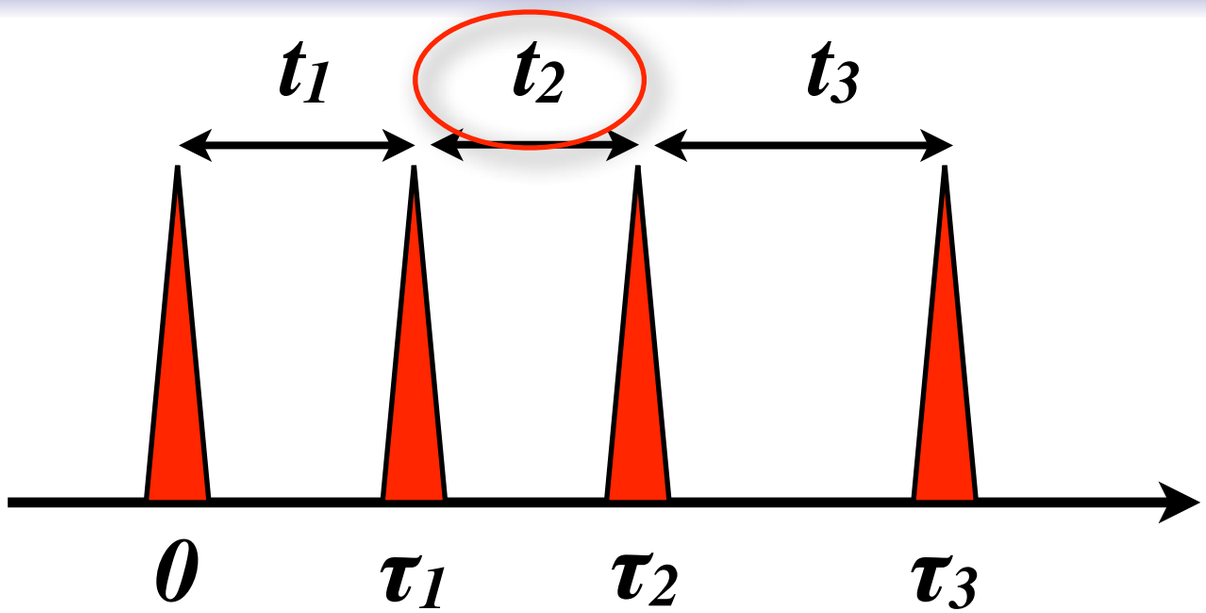
DH still survives for time scale longer than τ_α!!

$$\tau_{\text{hetero}} > \tau_\alpha$$

T=0.58 (low ***T***)



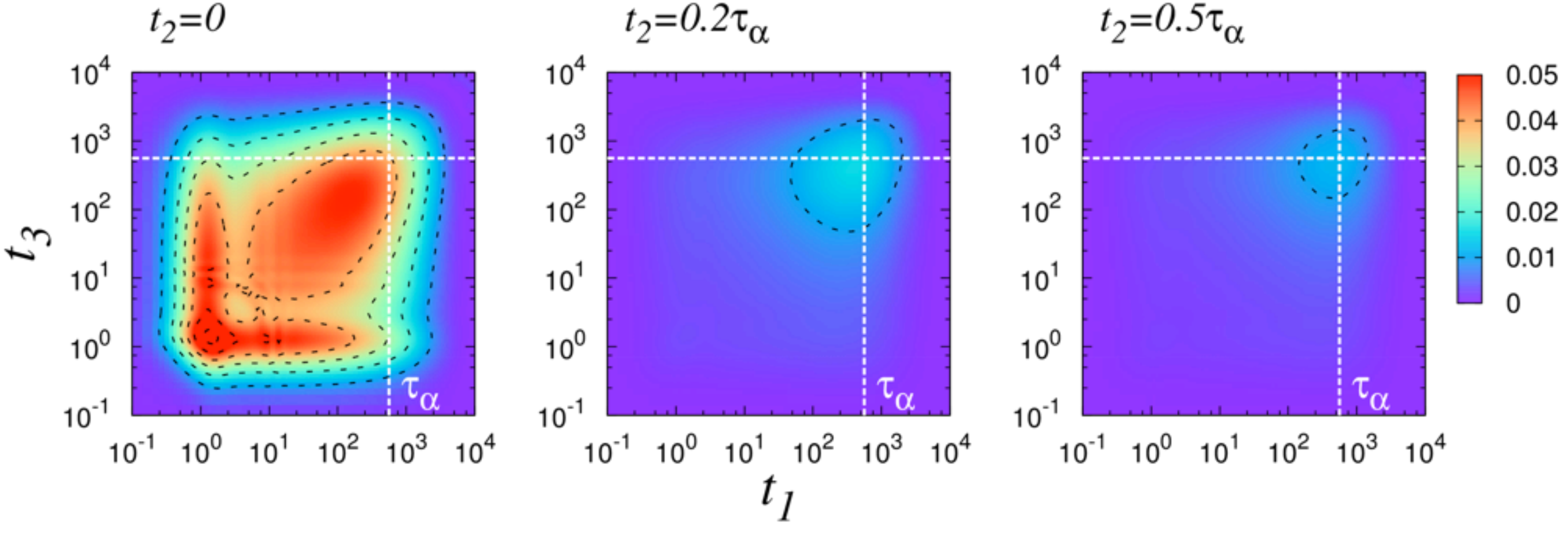
[NTW strong glasses] Change the waiting time t_2: How dose Dynamical Heterogeneity decay with time?



DH decays much faster than τ_α even at low T !!

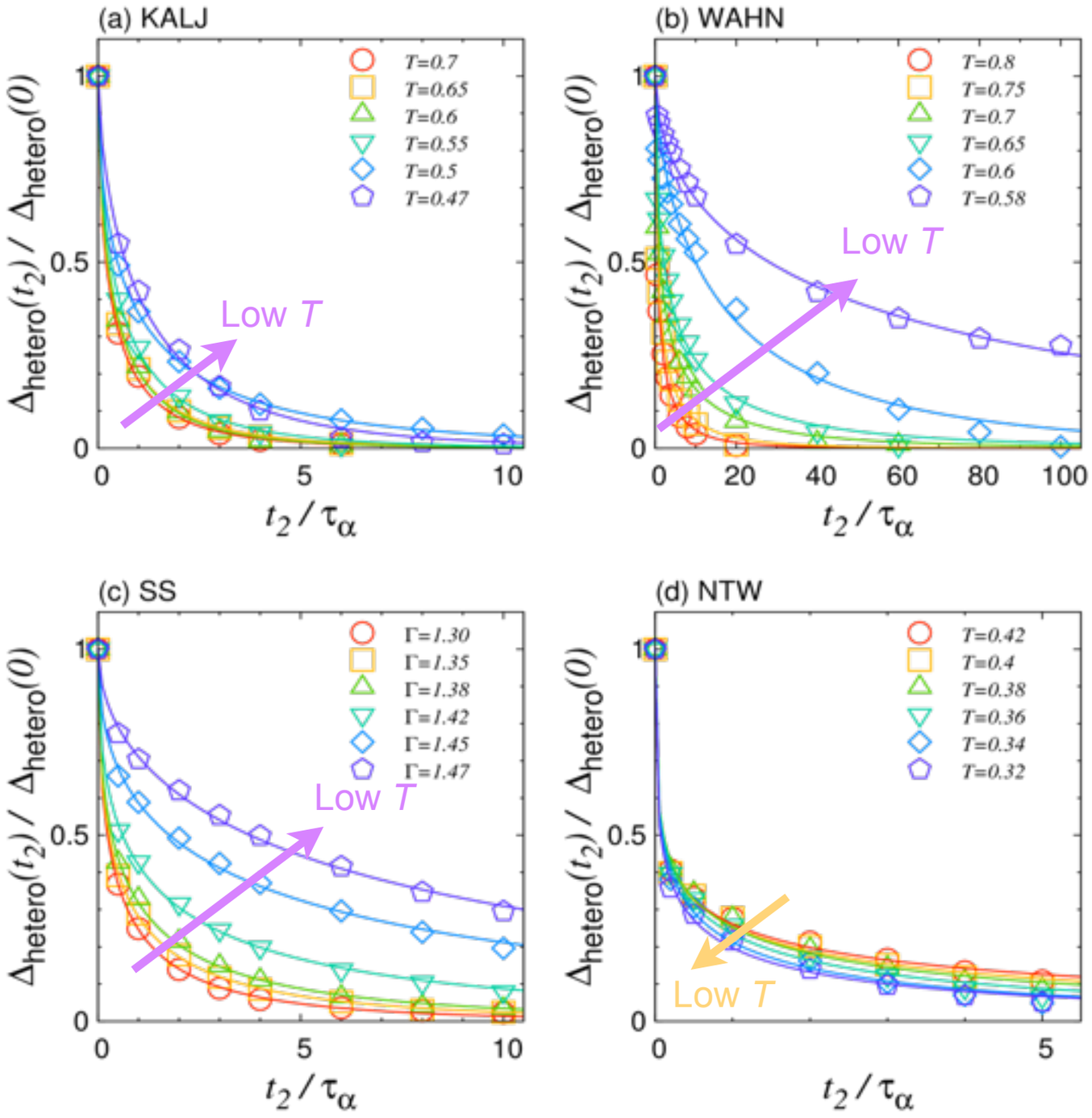
$$\tau_{\text{hetero}} < \tau_\alpha$$

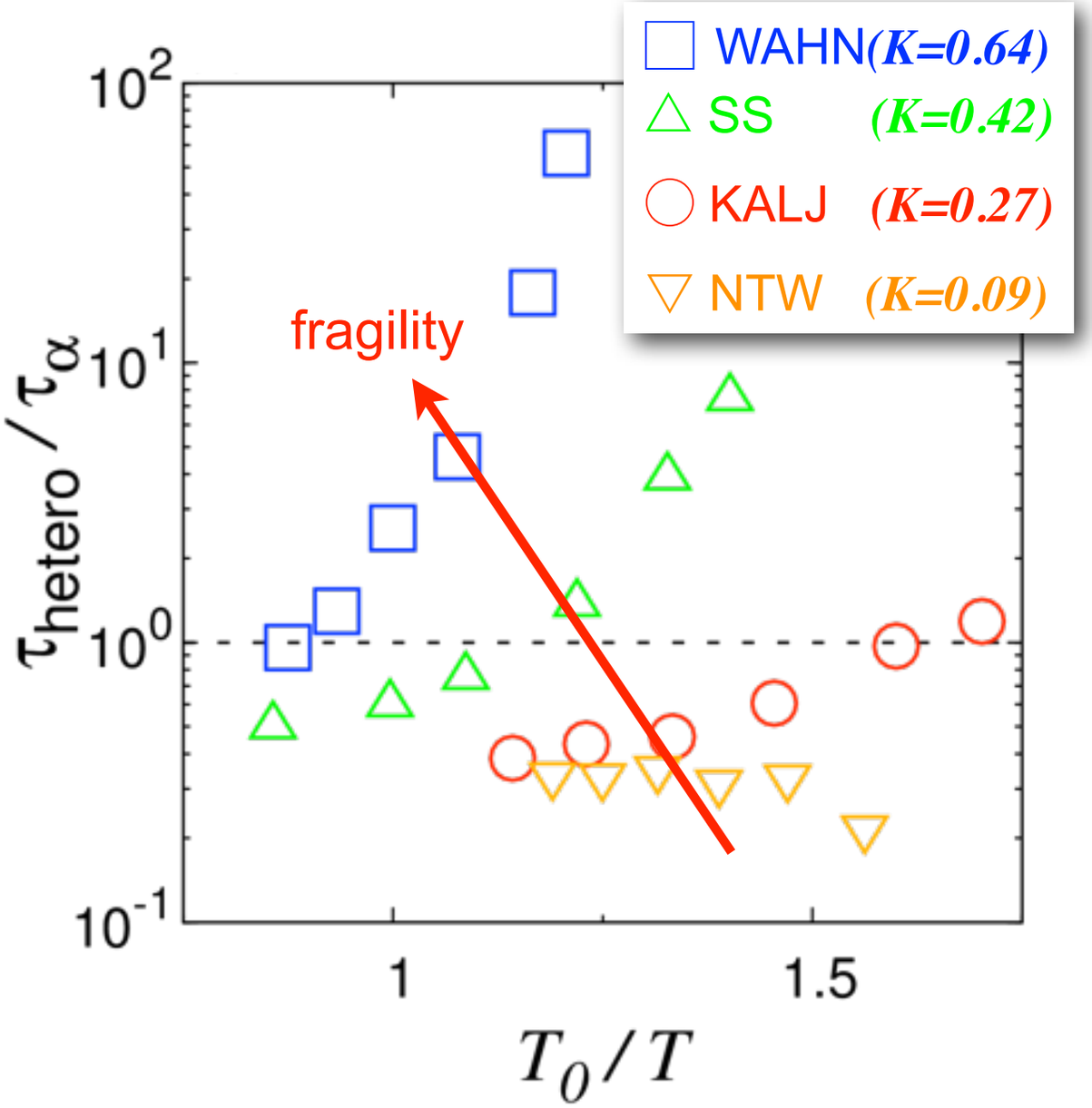
T=0.32 (low T)



Result: Average lifetime τ_{hetero}

"Volume" of heterogeneous dynamics: $\Delta_{\mathrm{hetero}}(t_2) = \int\int \Delta F(k, t_3, t_2, t_1) dt_1 dt_3$

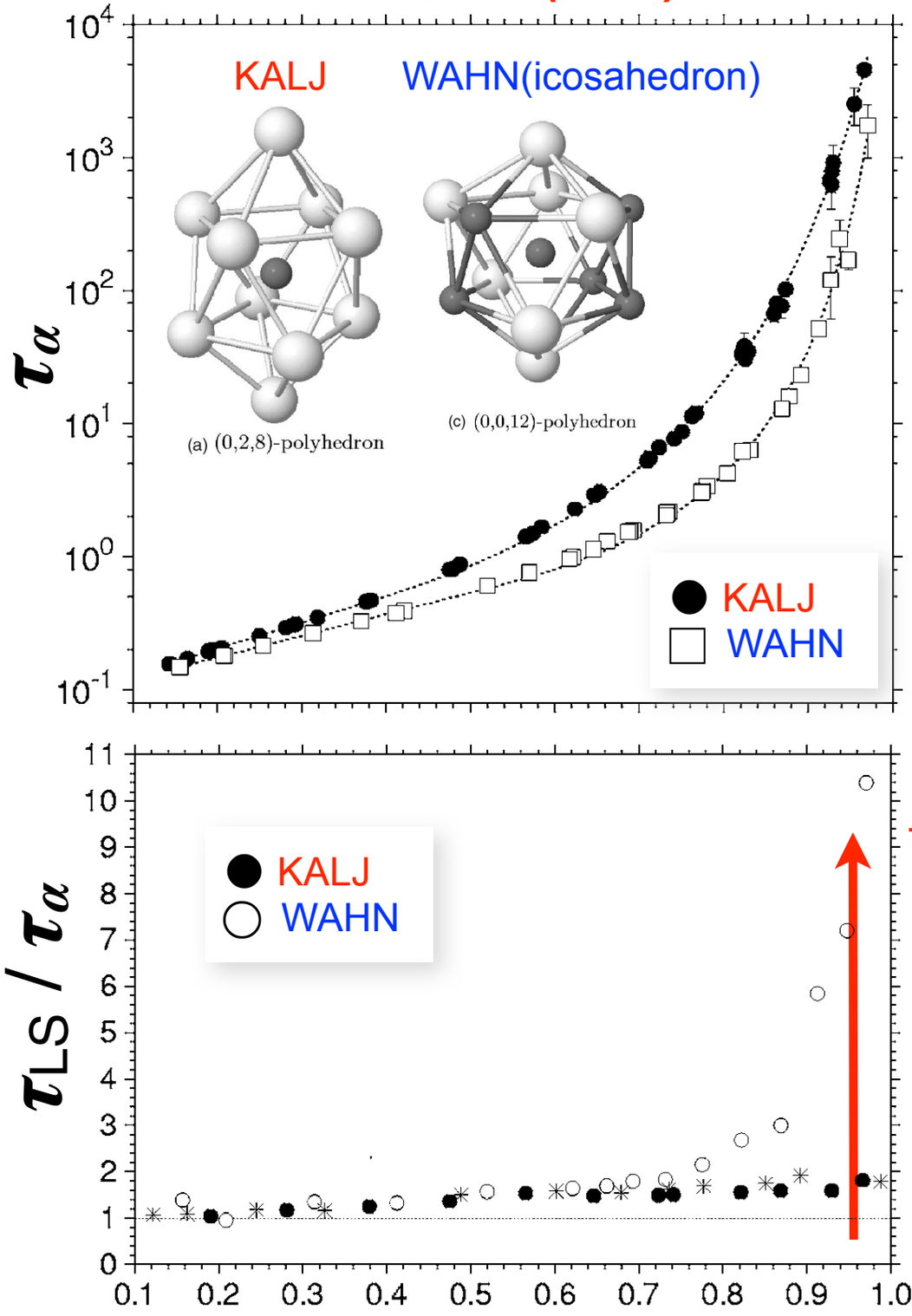




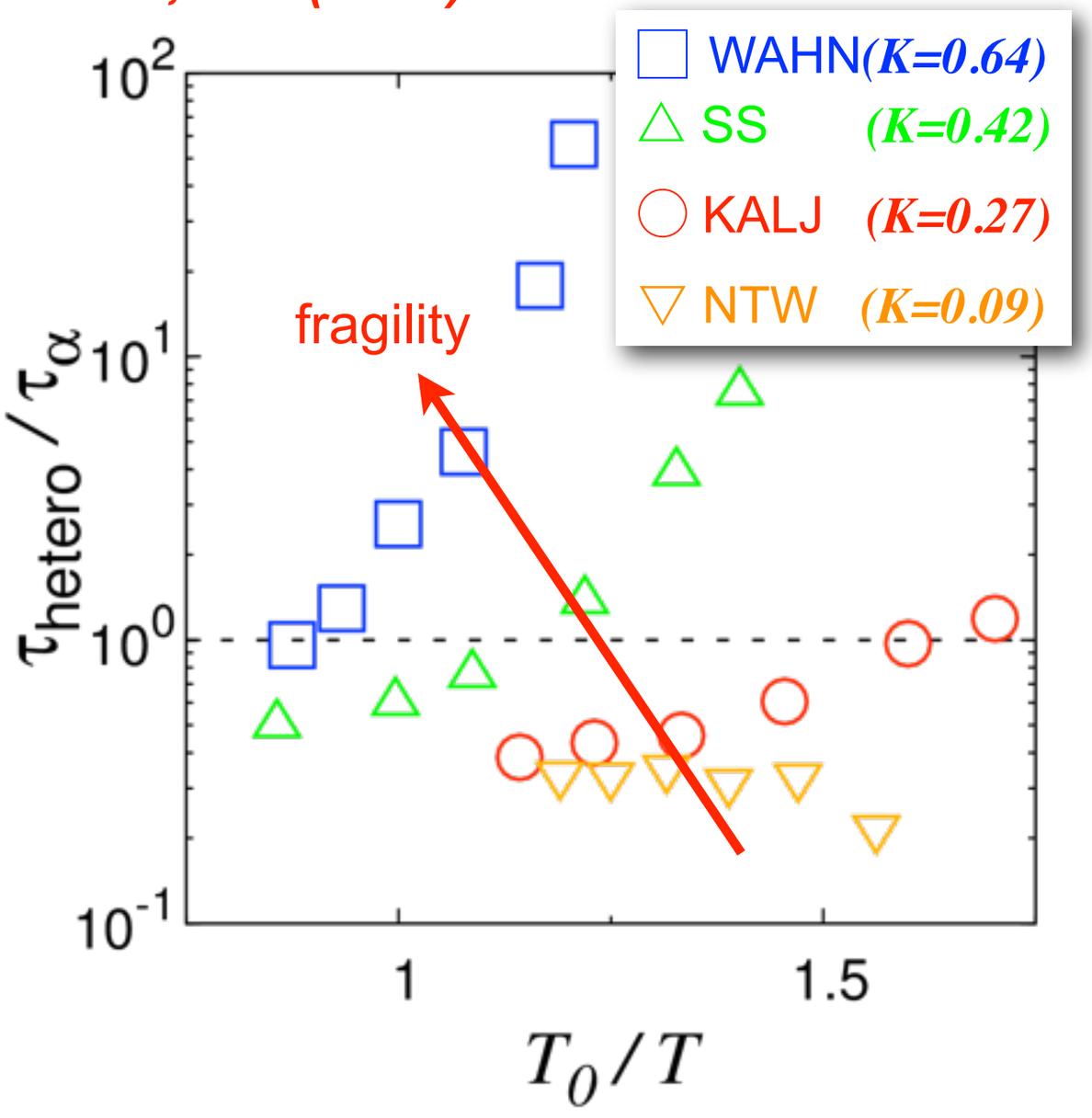
$$\frac{\Delta_{\mathrm{hetero}}(t_2)}{\Delta_{\mathrm{hetero}}(0)} \sim \exp[-(t_2/\tau_{\mathrm{hetero}})^{\beta}]$$

Discussion: Is DH related to Locally Preferred Structures?

Coslovich-Pastore, JCP(2007)



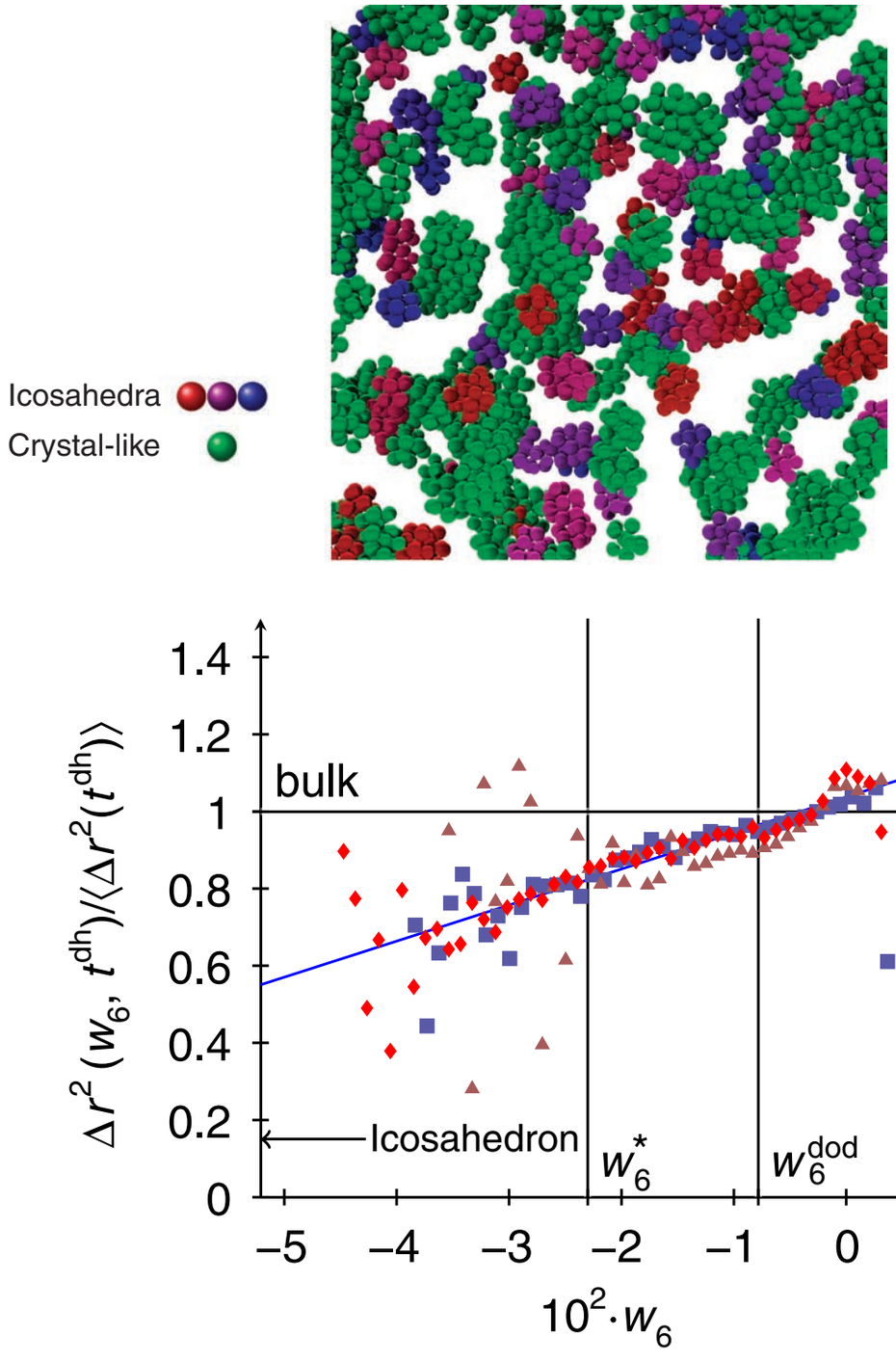
Kim-Saito, JCP(2013)



Are long-lived icosahedral LPSs related to τ_{hetero}?

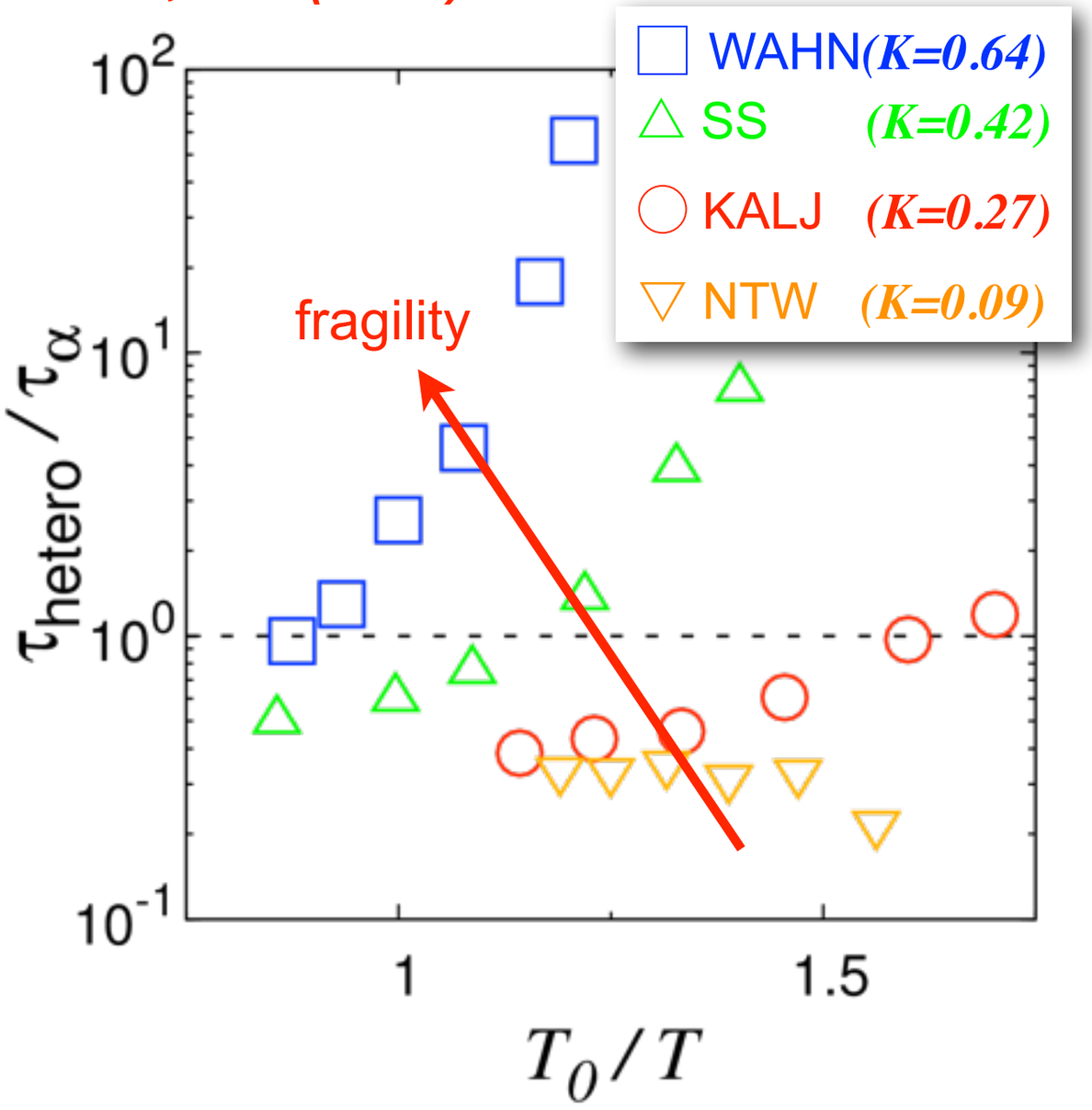
Discussion: Is DH related to Locally Preferred Structures?

Leocmach-Tanaka, Nat. Commun.(2012)



PMMA polydisperse colloids

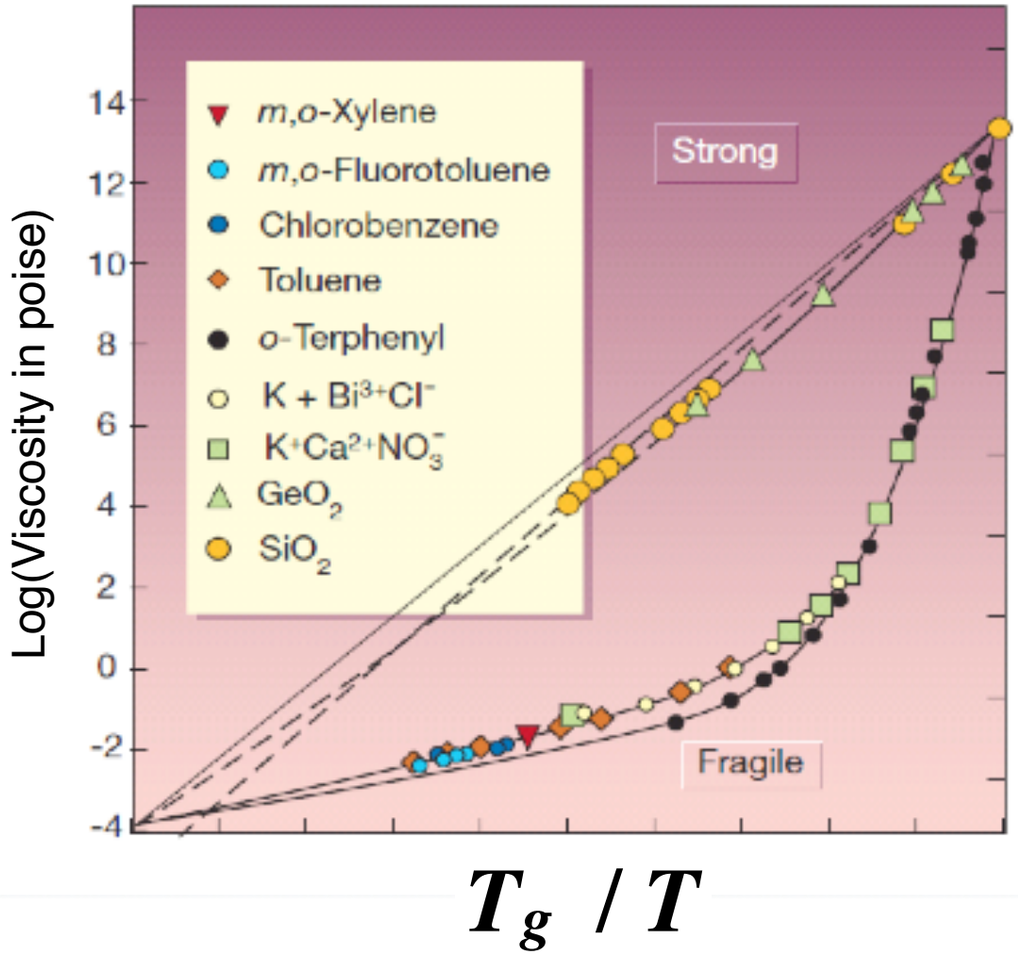
Kim-Saito, JCP(2013)

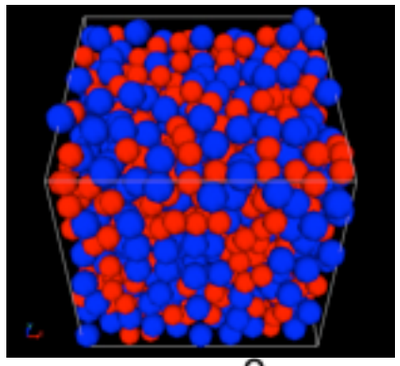


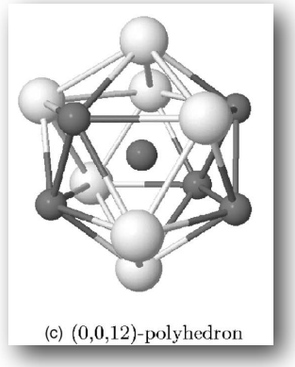
Are long-lived icosahedral LPSs related to τ_{hetero}?

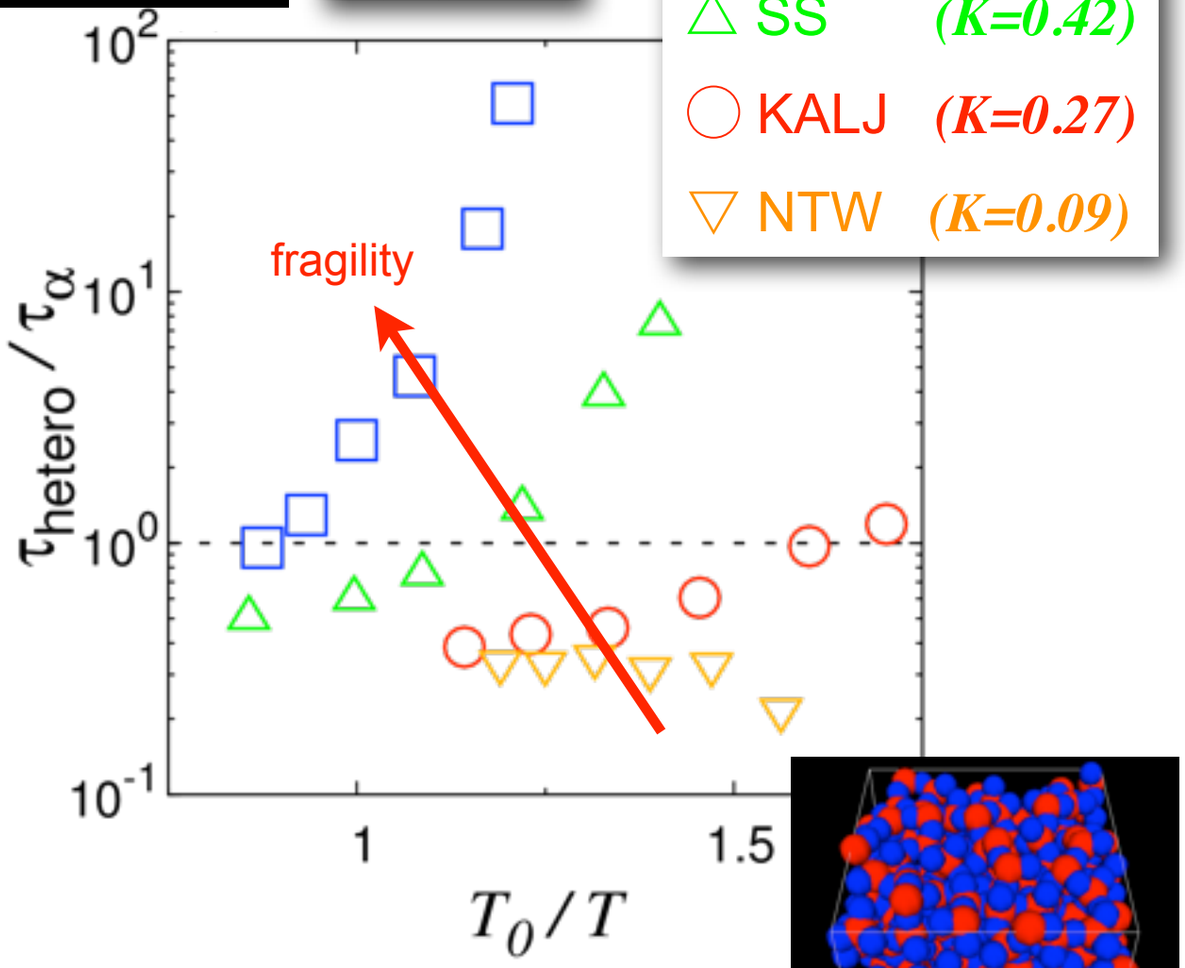
Summary: Dynamic Heterogeneities and Fragility

P. G. Debenedetti and F. H. Stillinger, Nature 410, 259-267 (2001)









K. Kim and S. Saito, J. Chem. Phys. 138, 12A506 (2013)