Systematic Analyzes on Growing Time / Length Scales in the Dynamics of Supercooled Liquids

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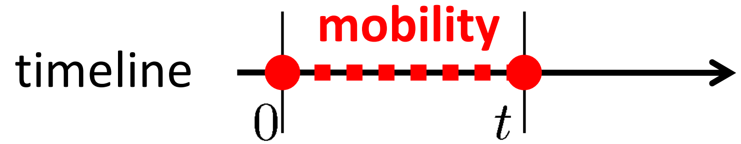
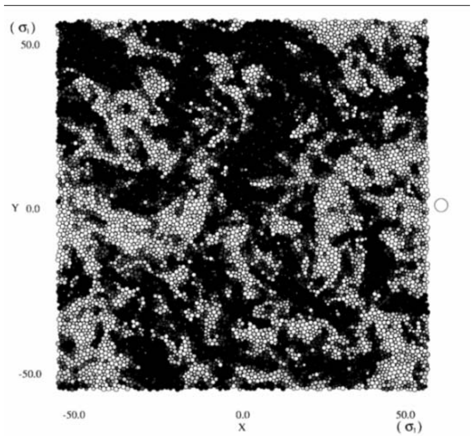
Outline

1. Quick Review on Dynamic Heterogeneity (DH)
2. Critical Slowing-Down vs. Glass Transition
3. Lifetime of DH in Supercooled Liquids

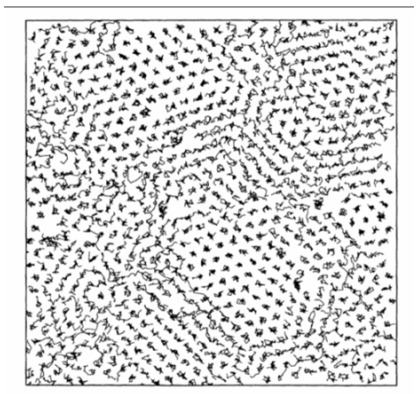
Dynamic Heterogeneity (DH)



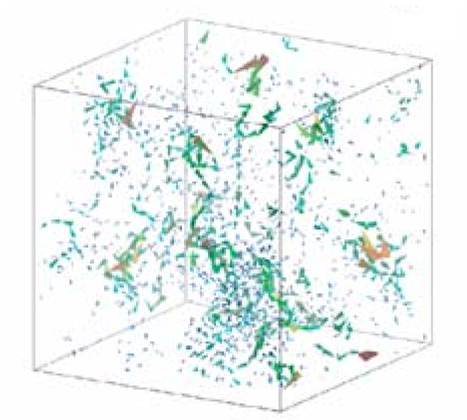
Binary soft disks(Muranaka-Hiwatari)



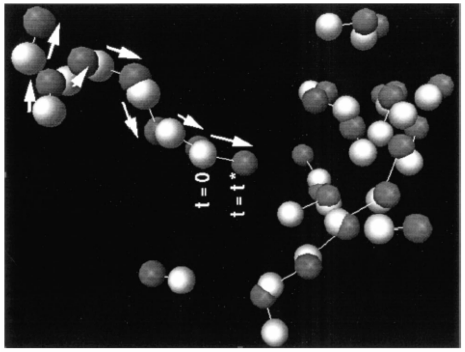
Binary soft disks (Harrowell)



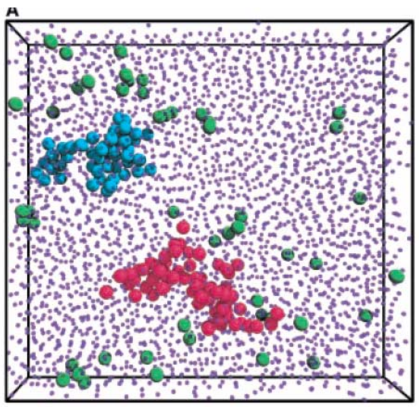
Binary soft spheres (Yamamoto-Onuki)



Binary Lennard-Jones particles
(Donati-Poole-Kob-Glotzer)

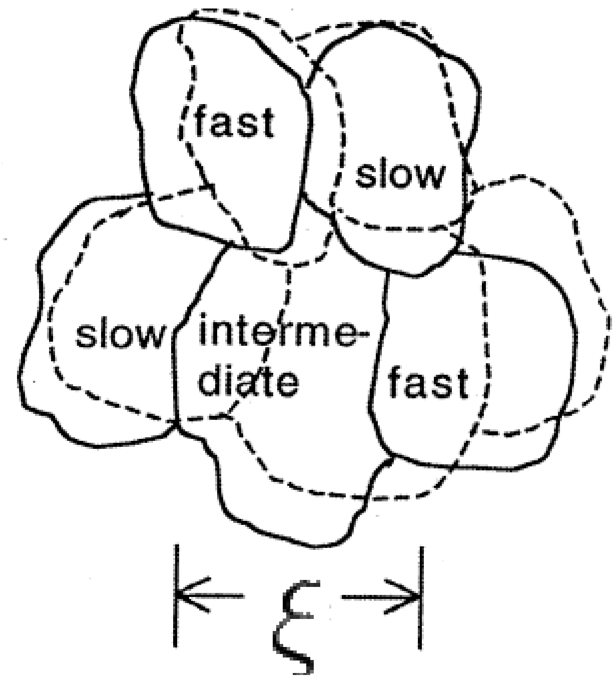


Colloidal suspensions (Weeks-Weitz)



Important Properties of DH

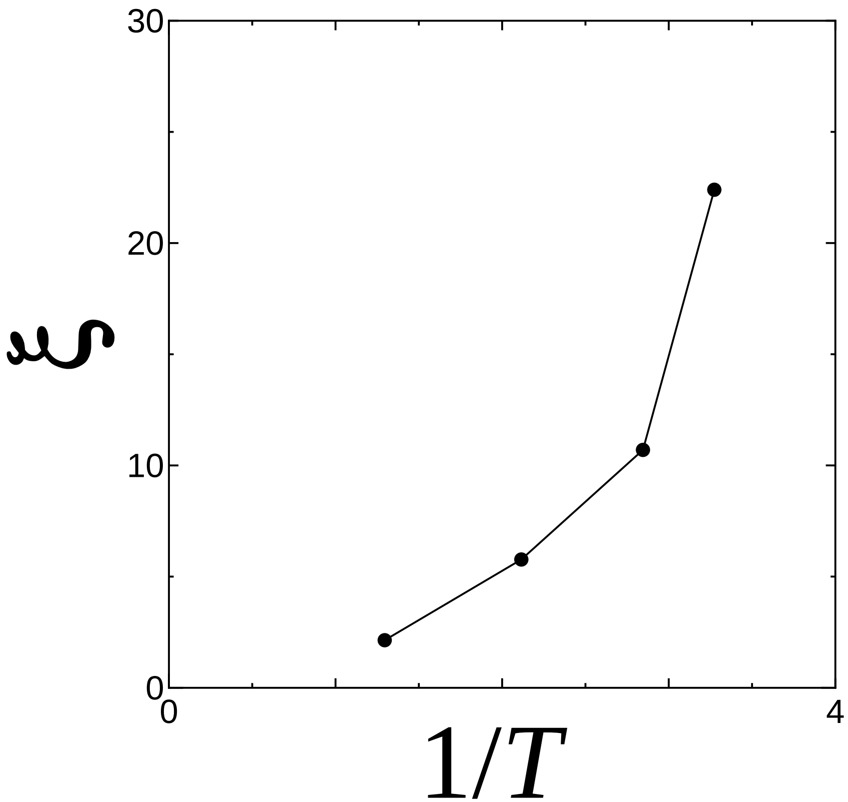
Schematic illustration of DH (Ediger)



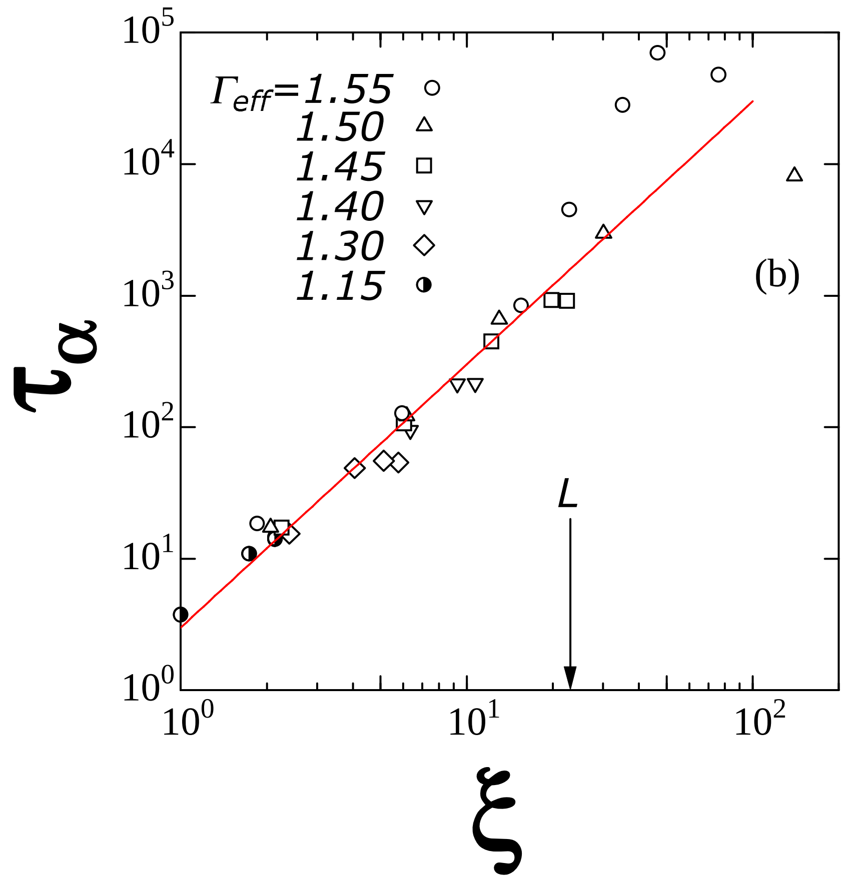
1. *Size of DH* -> ξ
2. *Intensity of DH* -> χ_4
3. *Lifetime of DH* -> τ_{hetero}
   (cf. spin glass)

ξ : "size" of DH

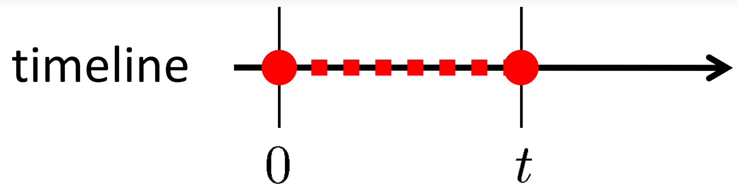
Yamamoto-Onuki PRE(1998)



$$\tau_\alpha \sim \xi^z, (z = 2)$$



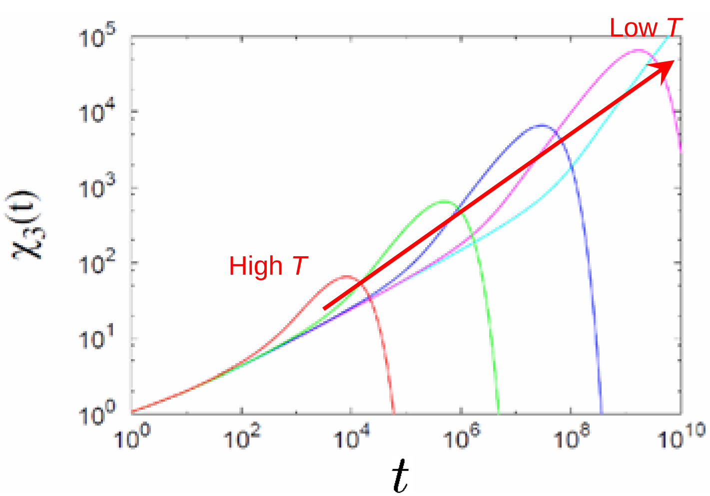
χ_4: "intensity" of DH

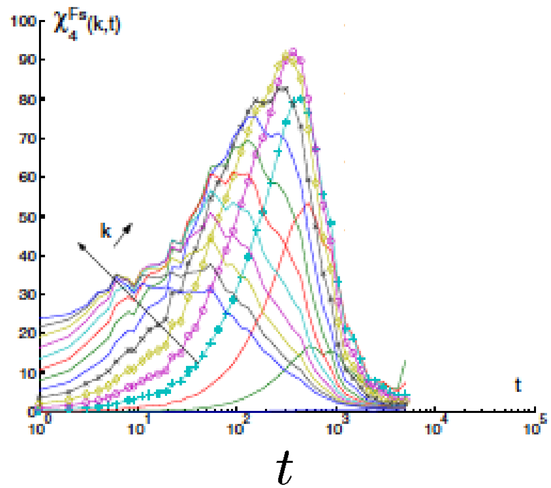


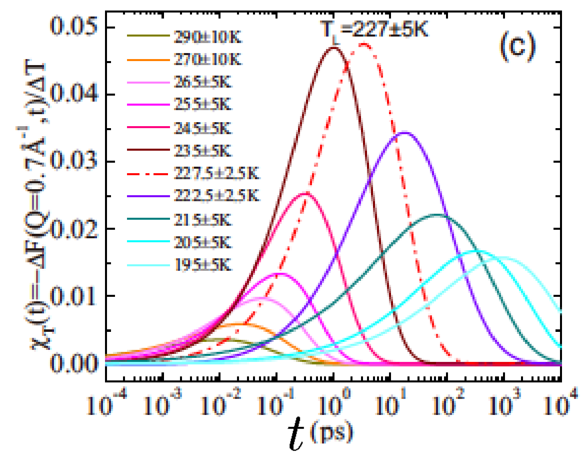
Inhomogeneous MCT
Biroli *et al*., PRL (2006)

Sheared Granular Materials
Dauchot *et al*., PRL (2005)

Supercooled Water
Chen *et al*., PRE (2009)







τ_{hetero}: “lifetime” of DH

VOLUME 81, NUMBER 22 PHYSICAL REVIEW LETTERS 30 NOVEMBER 1998

Heterogeneous Diffusion in Highly Supercooled Liquids

Ryoichi Yamamoto and Akira Onuki
Department of Physics, Kyoto University, Kyoto 606-8502, Japan
(Received 13 July 1998)

The diffusivity of tagged particles is demonstrated to be heterogeneous on time scales comparable to or less than the stress relaxation time $\cong \tau_\alpha$ in a highly supercooled model liquid. The particle motions in the relatively active regions dominantly contribute to the mean square displacement, giving rise to a diffusion constant larger than the Stokes-Einstein value. The van Hove self-correlation function $G_s(r,t)$ is shown to have a large r tail which can be scaled in terms of $r/t^{1/2}$ for $t \lesssim 3\tau_\alpha$. Its presence indicates heterogeneous diffusion in the active regions. However, the diffusion process becomes homogeneous on time scales longer than the life time of the heterogeneity structure ($\sim 3\tau_\alpha$). [S0031-9007(98)07758-8]

space-time correlations of local particle diffusivity

$$S_{\mathcal{D}}(q,t,\tau) = \langle \mathcal{D}_q(t_0 + \tau, t)\mathcal{D}_{-q}(t_0, t)\rangle$$

$$\boxed{\tau_{\rm hetero} \simeq 3\tau_\alpha}$$

τ_{hetero}: "lifetime" of DH

PHYSICAL REVIEW E 70, 052501 (2004)

Lifetime of dynamic heterogeneities in a binary Lennard-Jones mixture

Elijah Flenner and Grzegorz Szamel
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80525, USA
(Received 27 May 2004; published 29 November 2004)

A four-time correlation function was calculated using a computer simulation of a binary Lennard-Jones mixture. The information content of the four-time correlation function is similar to that of four-time correlation functions measured in NMR experiments. The correlation function selects a subensemble and analyzes its dynamics after some waiting time. The lifetime of the subensemble selected by the four-time correlation function is calculated, and compared to the lifetimes of slow subensembles selected using two different definitions of mobility, and to the α relaxation time.

$$\boxed{\tau_{\rm hetero} \simeq \tau_\alpha}$$

INSTITUTE OF PHYSICS PUBLISHING — JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **17** (2005) S3571–S3577 doi:10.1088/0953-8984/17/45/050

Lifetime of dynamic heterogeneity in strong and fragile kinetically constrained spin models

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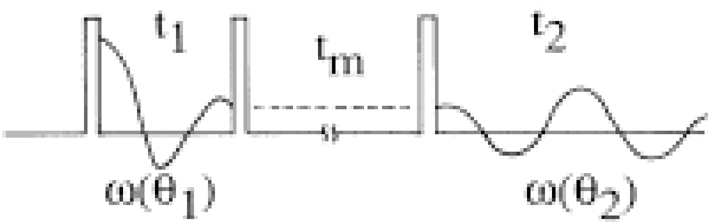
Online at stacks.iop.org/JPhysCM/17/S3571

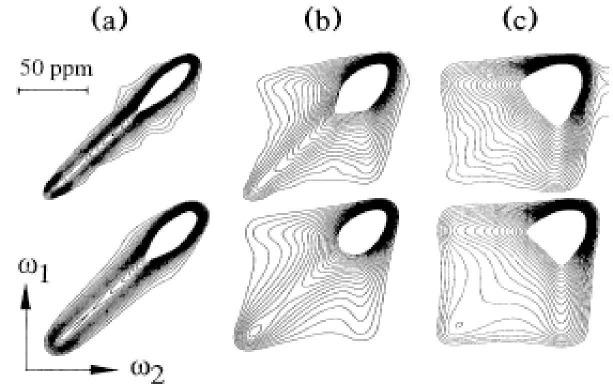
Abstract
Kinetically constrained spin models are schematic coarse-grained models for the glass transition which represent an efficient theoretical tool to study detailed spatio-temporal aspects of dynamic heterogeneity in supercooled liquids. Here, we study how spatially correlated dynamic domains evolve with time and compare our results to various experimental and numerical investigations. We find that strong and fragile models yield different results. In particular, the lifetime of dynamic heterogeneity remains constant and roughly equal to the alpha relaxation time in strong models, while it increases more rapidly in fragile models when the glass transition is approached.

$$\boxed{\tau_{\rm hetero} \simeq 6\tau_\alpha}$$

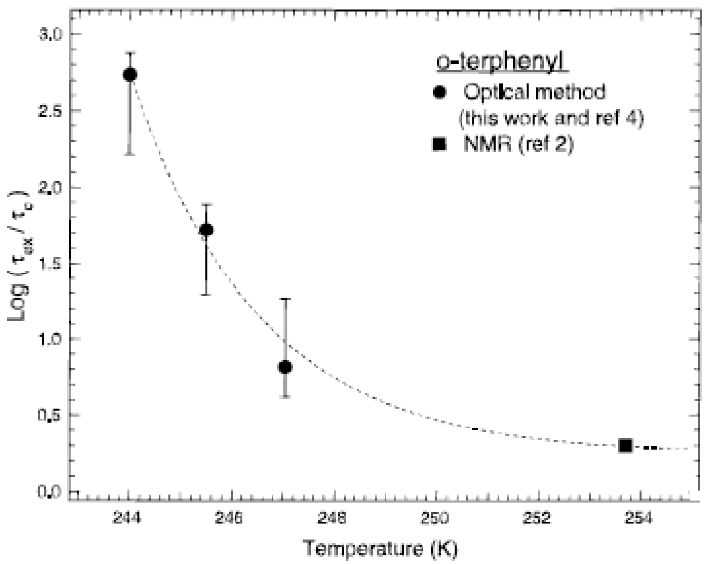
τ_{hetero}: "lifetime" of DH

K. Schmidt-Rohr and H. Spiess, PRL (1991)
2D-NMR





CY. Wang and MD. Ediger, JPCB (1999)
Hole Burning



$$\boxed{\tau_{\text{hetero}} \geq 100\tau_\alpha}$$

$$(\text{at } T_g + 1\text{K})$$

Open questions related to DH

1. *True identity of DH*
   a. *Any correspondence with static properties?*
   b. *Anything to do with other pictures (AG, CRR, medium-range order, bond-orientation order, mosaic, domain, …) ?*

2. *Role of DH*
   a. *DH plays some roles near GT?*
   b. *Any proper theories bridging between growing length scale (ξ) and growing time scales (τ_{hetero}, τ_α)?*
   c. *Something fundamental to GT? or just a by-product of GT?*
   d. *DH suppresses or enhances microscopic dynamics at low T?*

Critical Slowing-Down ('60 - early'70)

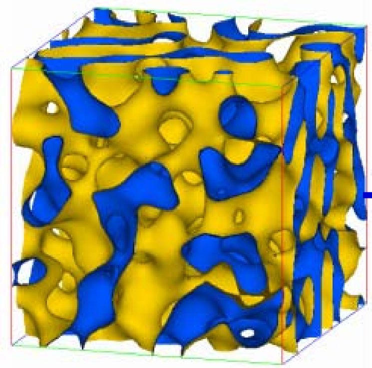
fluctuations in "order parameter" M

$$M(\vec{r},t) = \langle M \rangle + \delta M(\vec{r},t)$$

time-space correlation (2-point)

$$\langle \delta M(\vec{q},t)\delta M^*(\vec{q},0)\rangle \sim \langle |\delta M(\vec{q},0)|^2\rangle \times f_{\rm relax}(-t/\tau_q)$$

(figure taken from H. Tanaka's HP)



System

$$\chi_q \sim \frac{\xi^2}{1+\xi^2 q^2}$$

OZ form

(small $q=q_\xi$)

MC approx. is reliable near CP

MCT for CP (Kawasaki)

$$\tau_{q=q_\xi} \sim \xi^2 \times h(\xi)$$

$$(\tau_{q=k_m} \sim const.)$$

This is so-called critical slowing-down. Growing length scale directly leads to the slowing-down at small q, but nothing happens at microscopic q.

Glass Transition

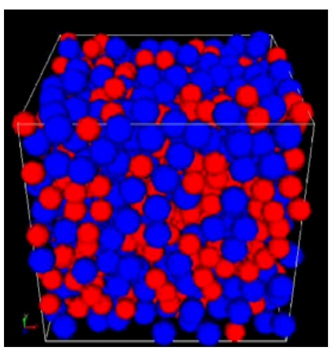
fluctuations in "density" ρ

$$\rho(\vec{r},t) = \bar{\rho} + \delta\rho(\vec{r},t)$$

time-space correlation (2-point)

$$F(\vec{k},t) = \langle \delta\rho(\vec{k},t)\delta\rho^*(\vec{k},0)\rangle \simeq \underline{\langle |\delta\rho(\vec{k},0)|^2\rangle} \times f_{\mathrm{relax}}(-t/\underline{\tau_k})$$

MC approx. reliable for microscopic *k*??



System

$$\boxed{S(\vec{k})}$$

Structure factor (microscopic *k*=k_m)

MCT for glass (Götze)

No growing length scale, but time scale associated with microscopic k slows down.

$$\boxed{\tau_\alpha \equiv \tau_{k=k_m} \sim \exp\left(\frac{C}{T-T_c}\right)}$$

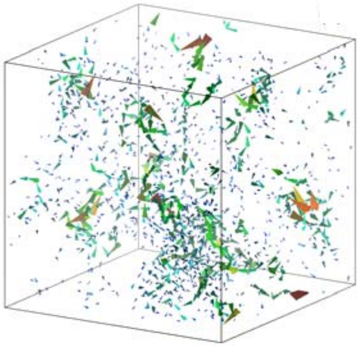
Search for LRCs in Glass Transition

fluctuations in "local dynamics" Q_t $(\text{ex.} \quad bb, \Delta r^2(t), F(k_m, t), Q(t), \cdots)$

$$Q_t(\vec{r}, t_0) = \langle Q_t \rangle + \delta Q_t(\vec{r}, t_0)$$

time-space correlation (4-point)

$$\langle \delta Q_t(\vec{q}, t_s) \delta Q_t^*(\vec{q}, 0) \rangle \sim \underline{\langle |\delta Q_t(\vec{q}, 0)|^2 \rangle} \times f_{\text{relax}}(-t_s / \underline{\tau_{4,q}})$$



System

$$\boxed{\chi_{4,q} \sim \frac{\xi^2}{1 + \xi^2 q^2}}$$

OZ-like form (small $q = q_\xi$)

any physics behind this ??

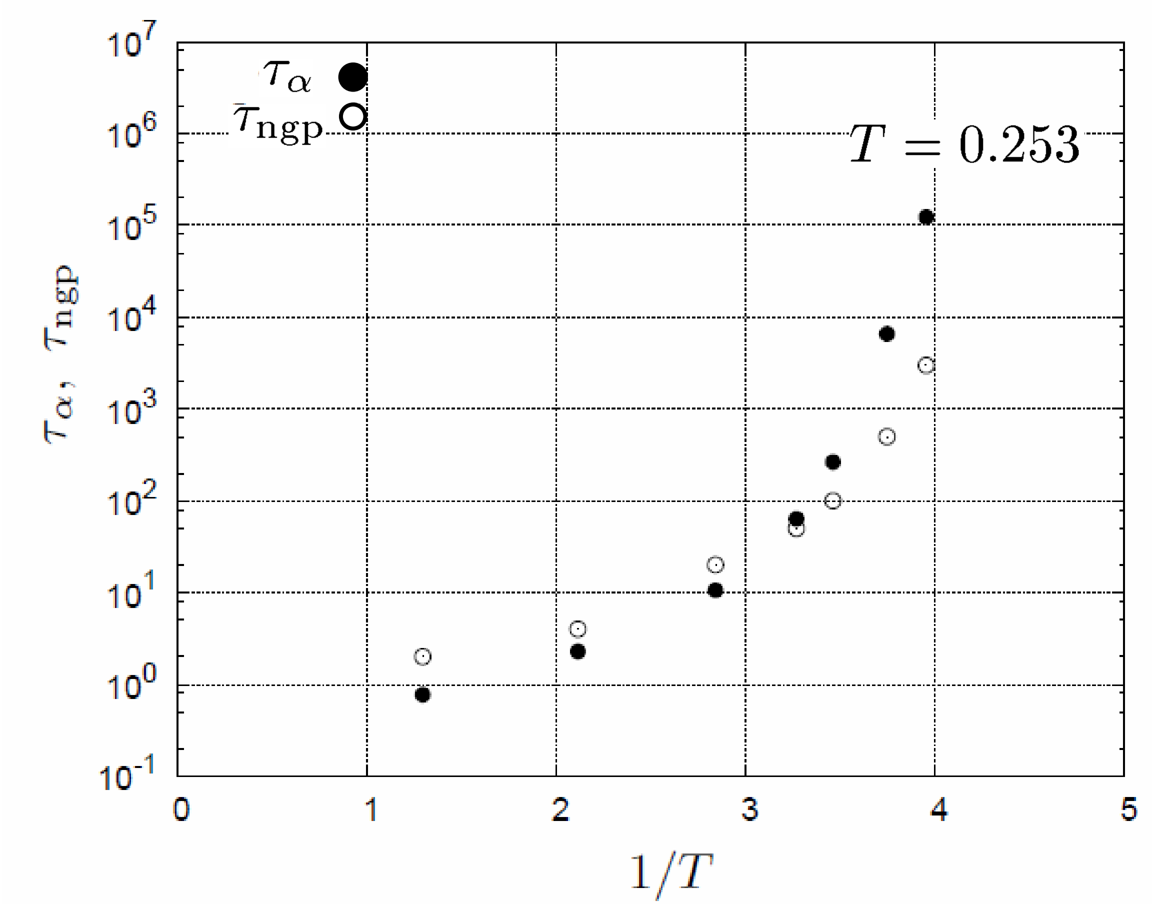
$$\tau_{\text{hetero}} (\equiv \tau_{4,q=q_\xi}) \sim \xi^z$$

$$\tau_\alpha \quad \text{vs.} \quad \tau_{\text{hetero}}$$

Present System

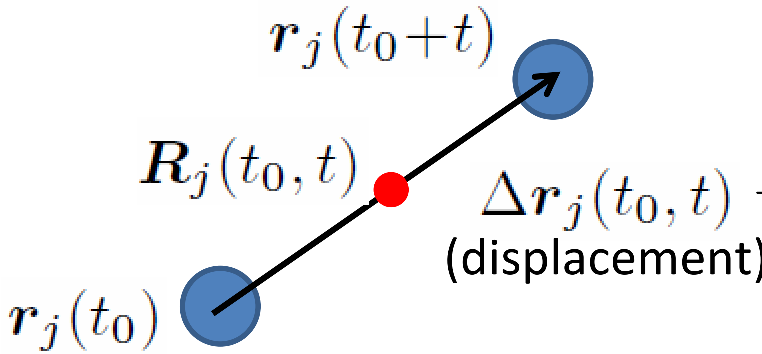
Mizuno-Yamamoto
arXiv:1006.3704

50/50 binary mixture of small and large (1:1.2) soft spheres
(3D, Total *N* is 10,000 or 100,000)



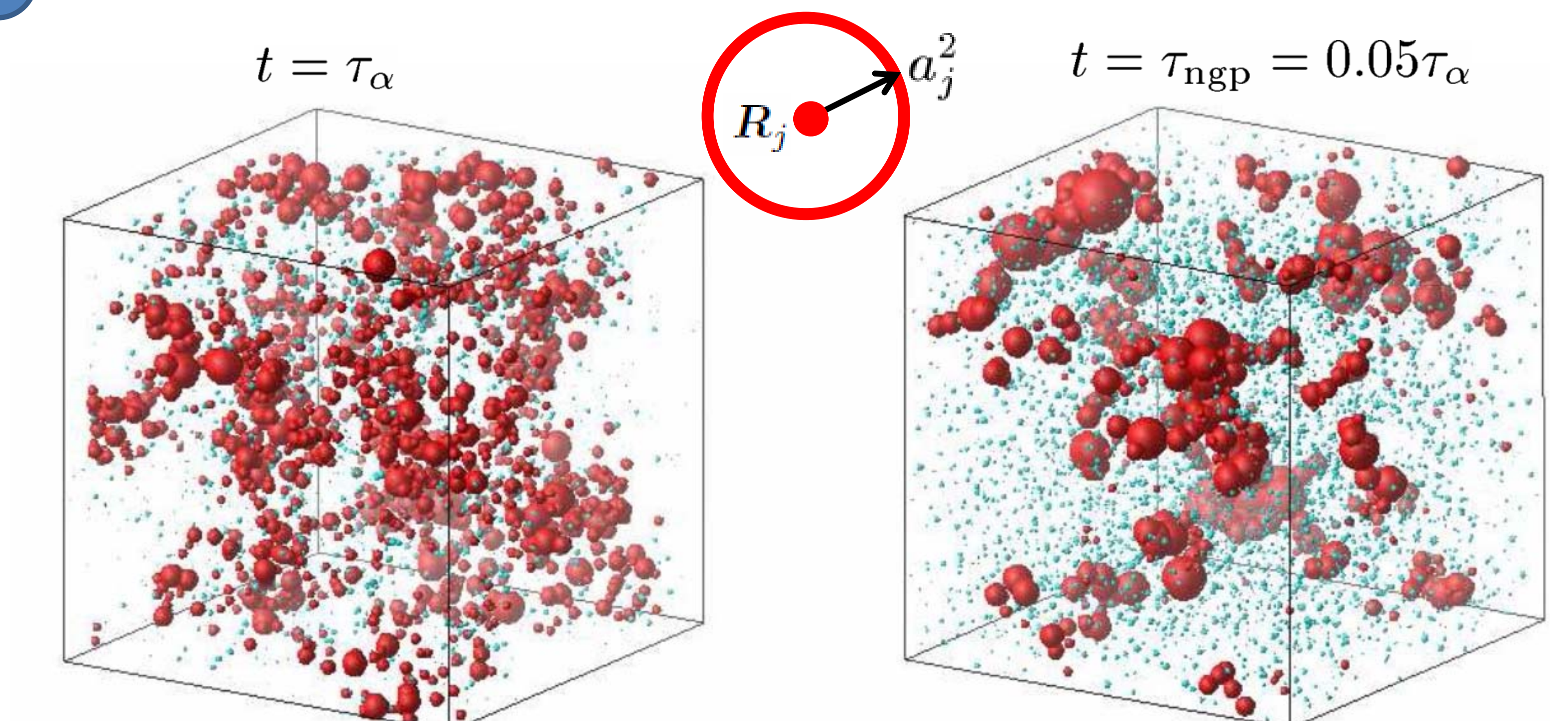
Order Parameter: local particle-diffusivity

Mizuno-Yamamoto
arXiv:1006.3704



LPD

$$\boxed{a_j^2(t_0,t) = \frac{|\Delta\vec{r}_j(t_0,t)|^2}{\langle\Delta r^2(t)\rangle}}$$



Visualization of LPD at $T=0.253$

Space-Time correlations of LPD

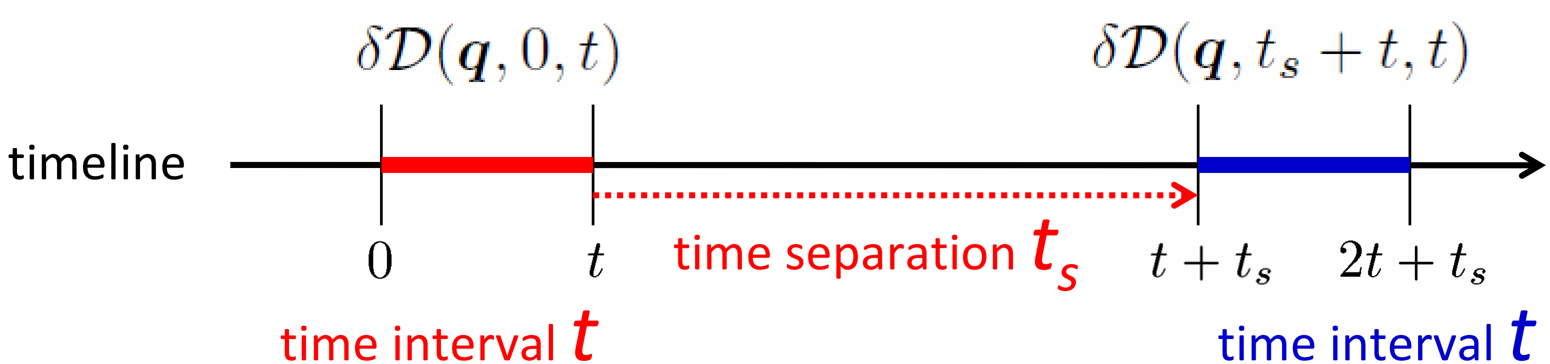
Mizuno-Yamamoto
arXiv:1006.3704

q-wavevector Fourier component of spatial fluctuations at t_0 in "local particle diffusivity" defined with a time interval t RY (PRL 1998, 2010)

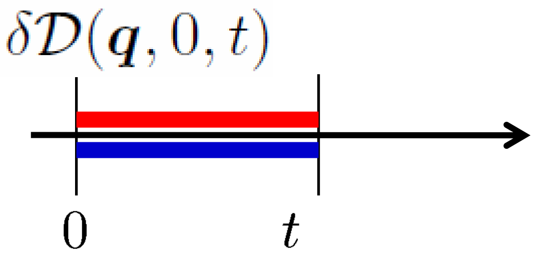
$$\delta\mathcal{D}(\boldsymbol{q}, t_0, t) = \sum_{j=1}^{N_1} (a_j^2(t_0, t) - 1) \exp[-i\boldsymbol{q} \cdot \boldsymbol{R}_j(t_0, t)]$$

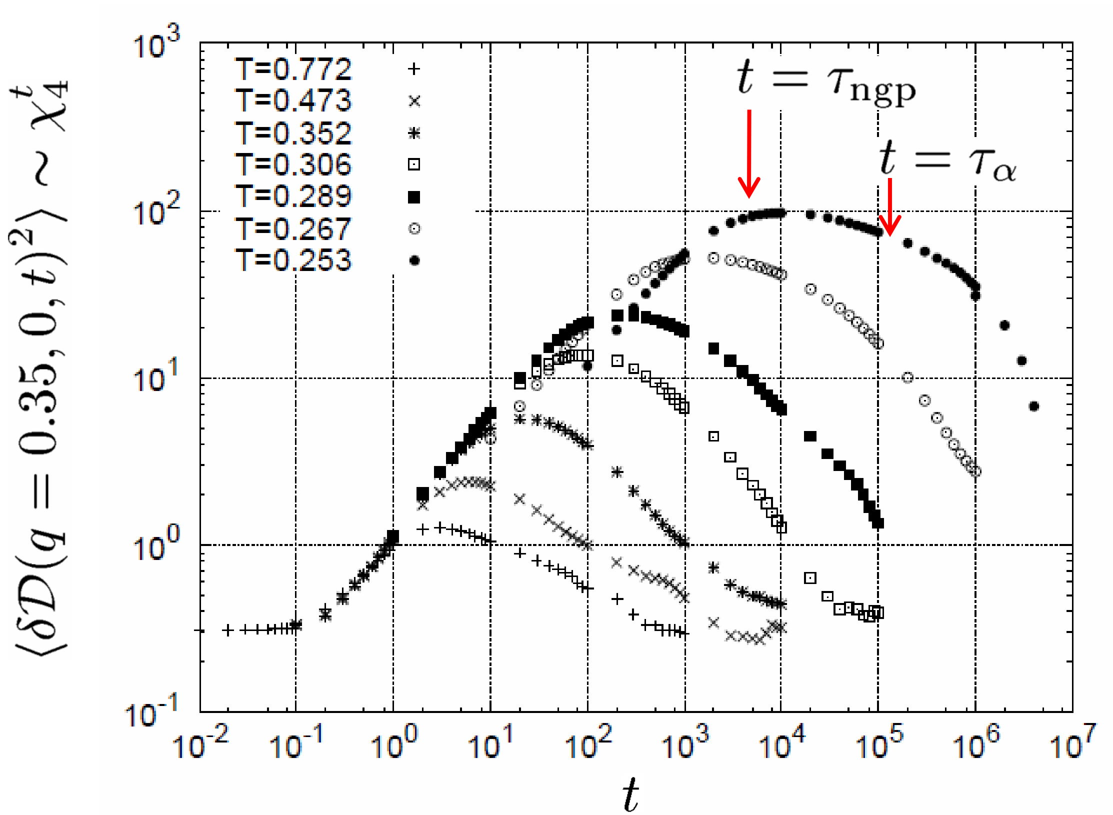
4-points (times) space-time correlation function

$$S_{\mathcal{D}}(q, t_s, t) = \langle \underline{\delta\mathcal{D}(\boldsymbol{q}, t_s + t, t)}\, \underline{\delta\mathcal{D}(\boldsymbol{q}, 0, t)} \rangle$$



χ_4: equal time correlations of LPD

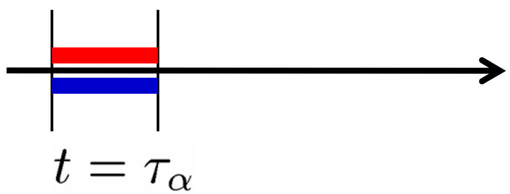




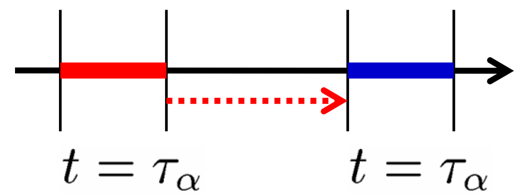
Lifetime of dynamic heterogeneity (DH)

Mizuno-Yamamoto
arXiv:1006.3704

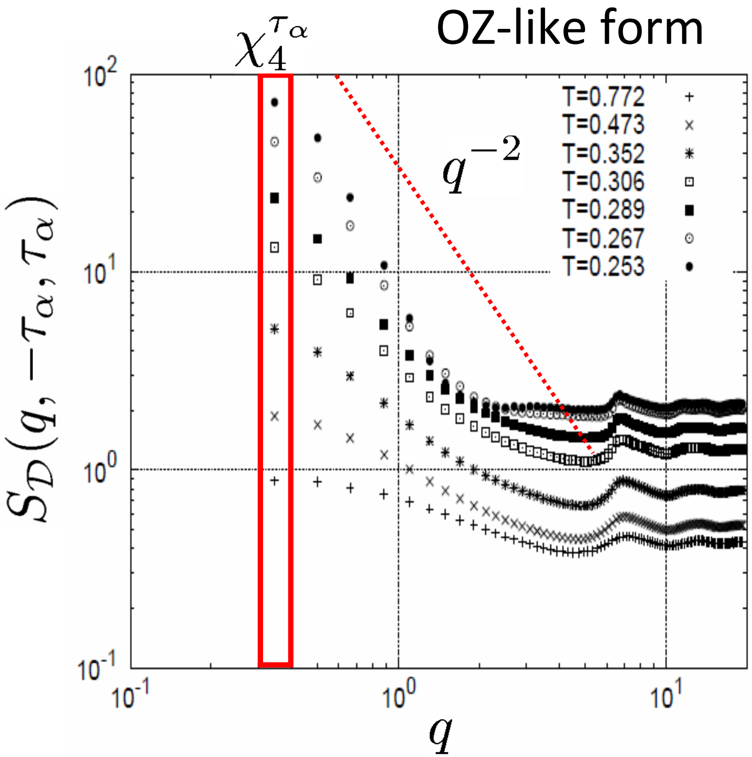
equal time corr.

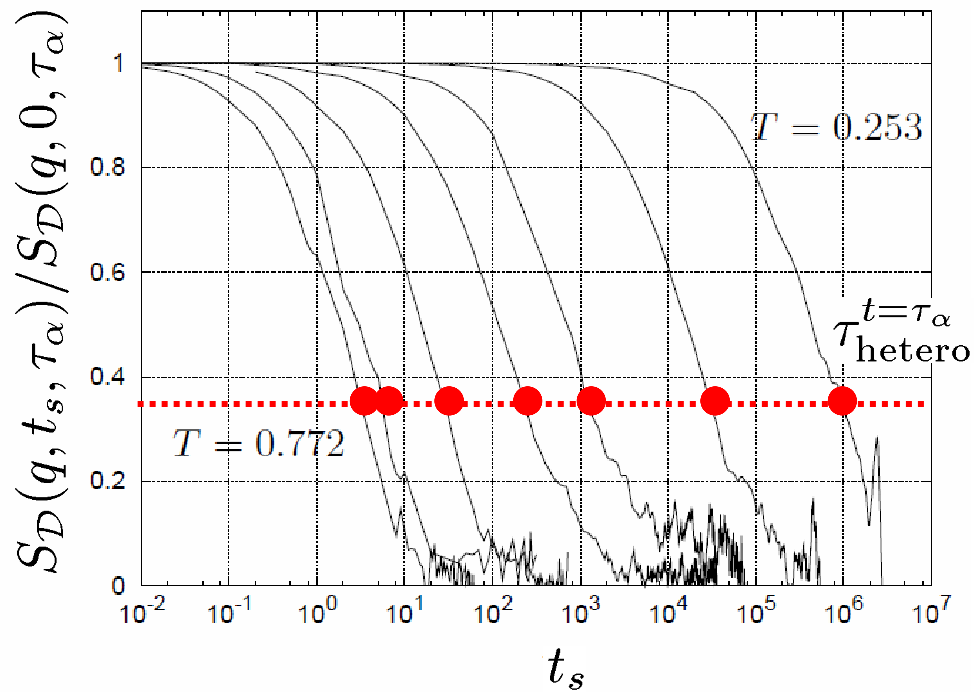


corr. between $t_s > 0$



OZ-like form

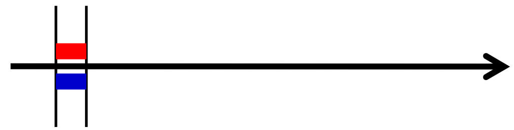




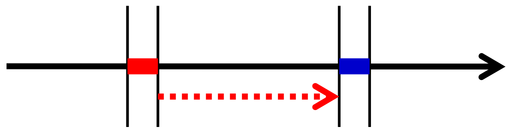
Lifetime of dynamic heterogeneity (DH)

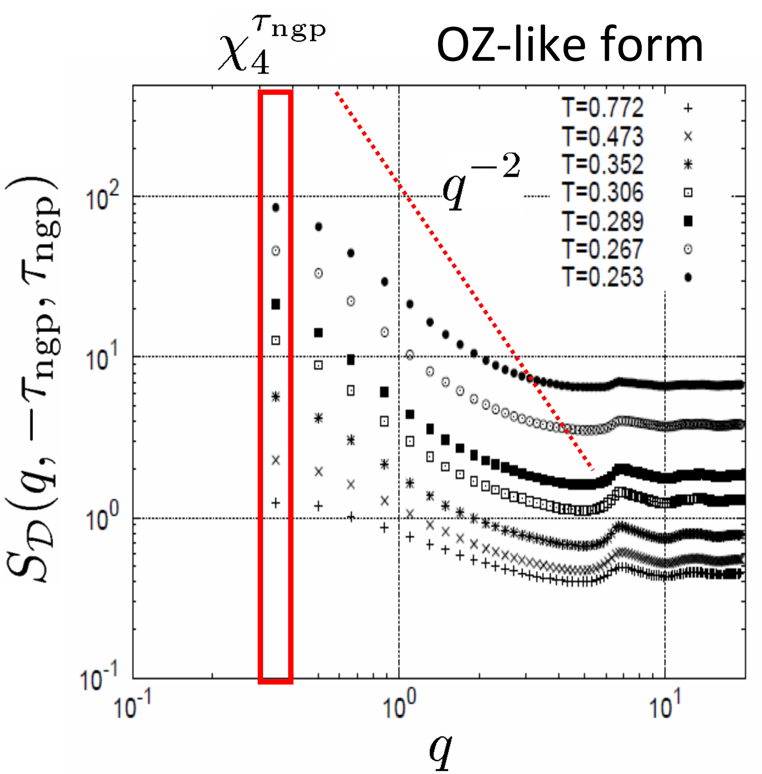
Mizuno-Yamamoto
arXiv:1006.3704

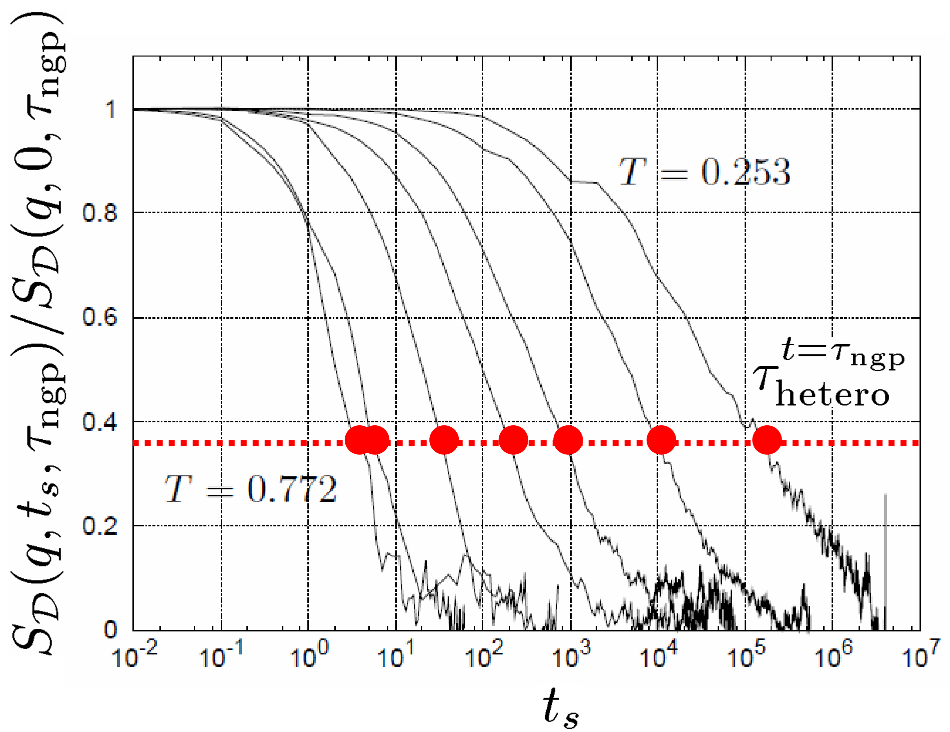
equal time corr.



corr. between $t_s > 0$

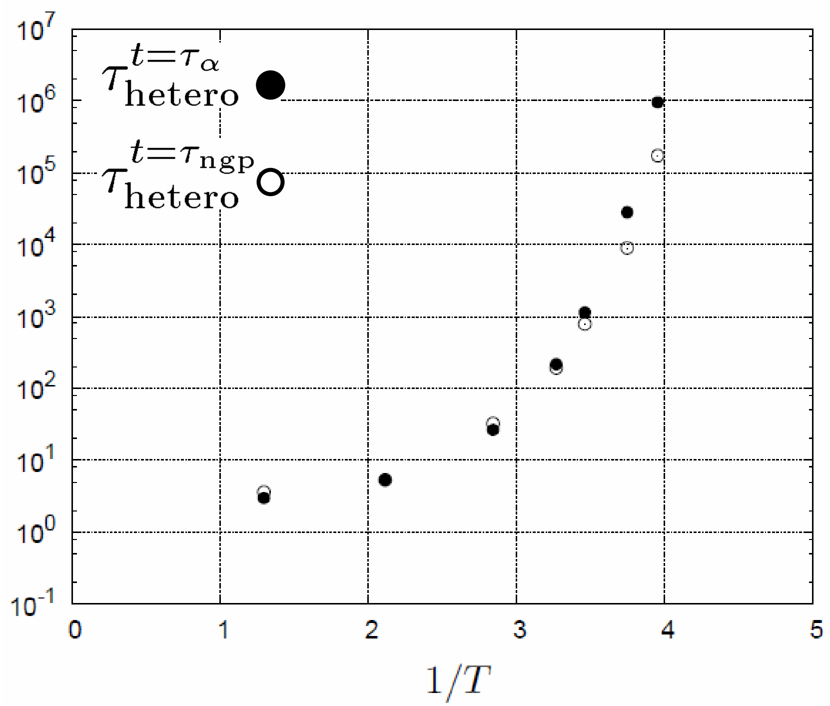


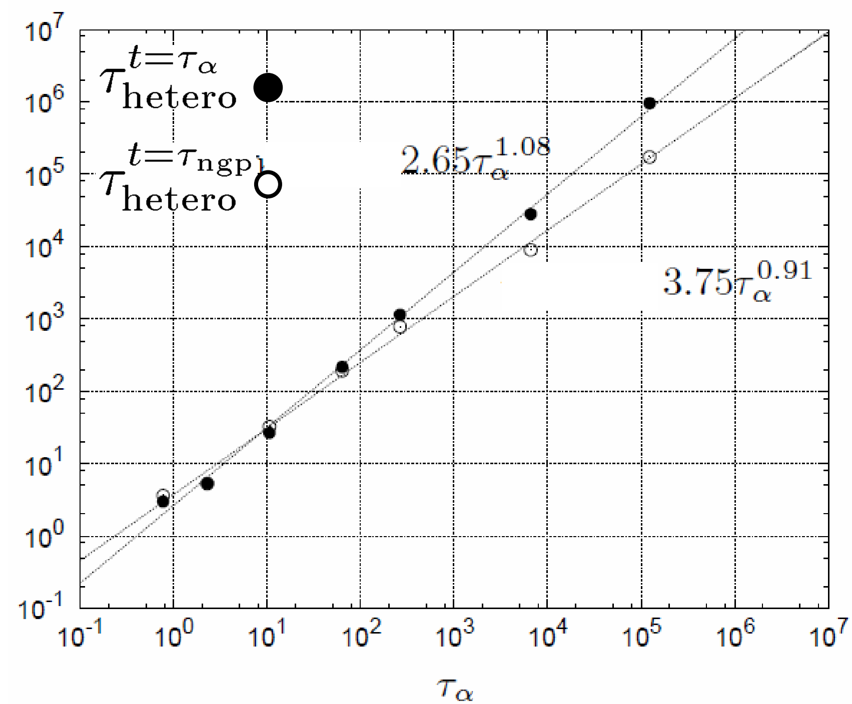




Scaling Analysis

Mizuno-Yamamoto
arXiv:1006.3704





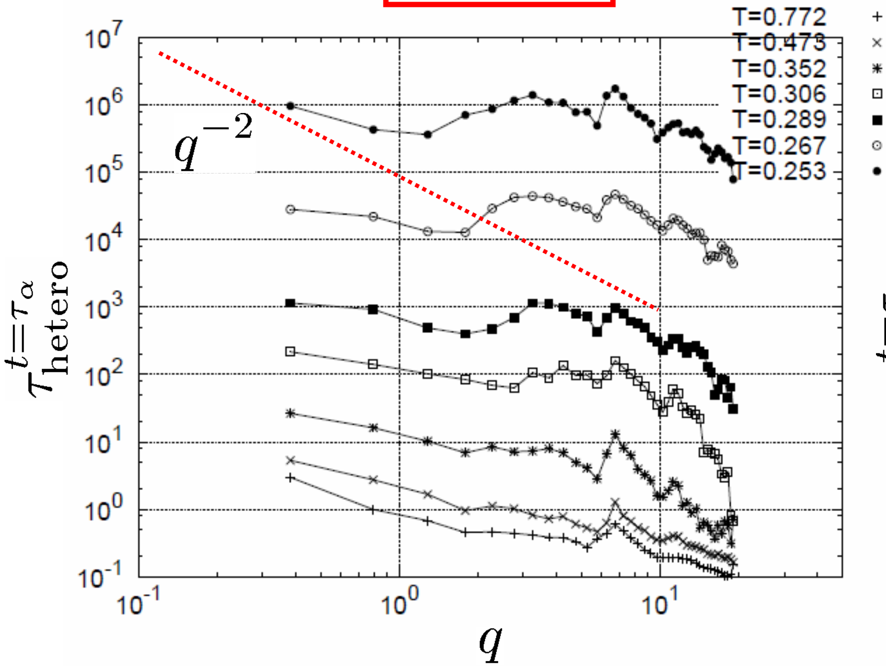
$$\tau_{\mathrm{hetero}}^{t=\tau_\alpha} = 2.65\tau_\alpha^{1.08}$$

$$\tau_{\mathrm{hetero}}^{t=\tau_{\mathrm{ngp}}} = 3.75\tau_\alpha^{0.91}$$

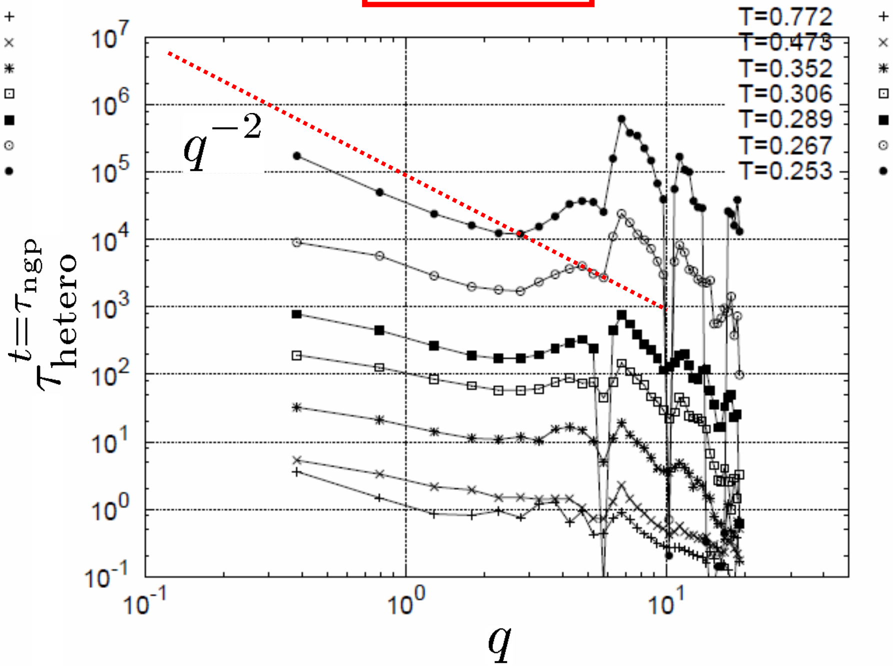
q-dependence of DH-lifetime (collective)

$$\delta\mathcal{D}(\vec{q}, t_0, t) = \sum_{j=1}^{N} \left(\left[\frac{|\Delta\vec{r}_j(t_0,t)|^2}{\langle \Delta r^2(t) \rangle} \right] - 1 \right) \exp[-i\vec{q}\cdot\vec{R}_j(t_0,t)]$$

$t = \tau_\alpha$



$t = \tau_{\mathrm{ngp}}$

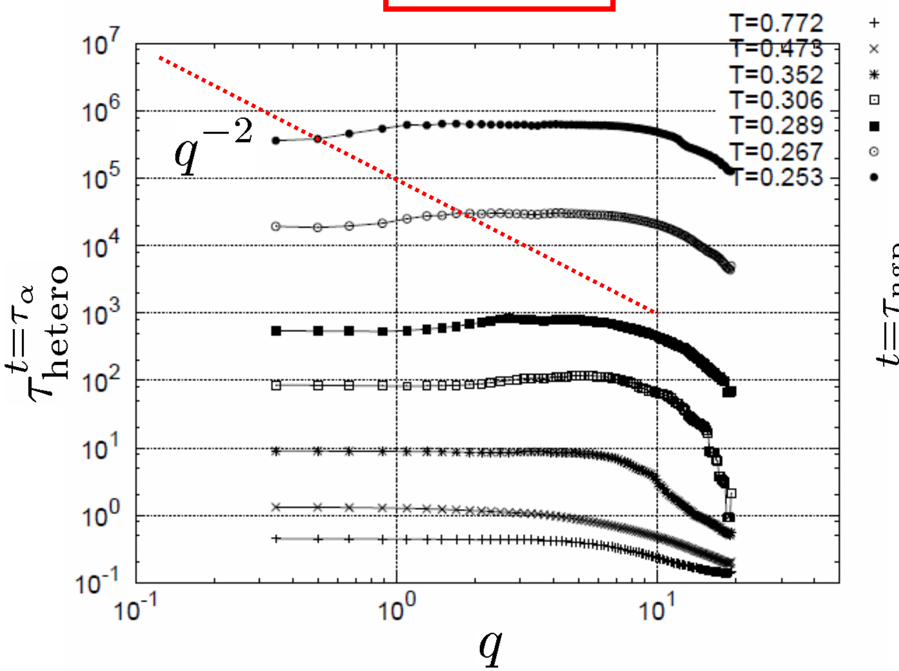


This result suggests that DH evolves in time in diffusion-like manner

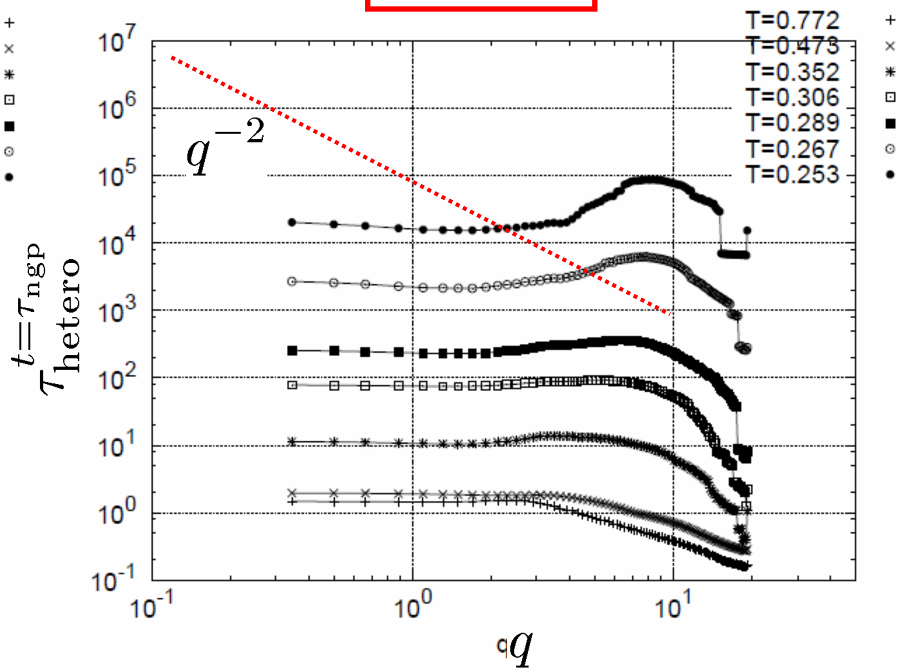
q-dependence of DH-lifetime (self)

$$\delta\mathcal{D}_j(\vec{q},t_0,t)=\left(\left[\frac{|\Delta\vec{r}_j(t_0,t)|^2}{\langle\Delta r^2(t)\rangle}\right]-1\right)\exp[-i\vec{q}\cdot\vec{R}_j(t_0,t)]$$

$t=\tau_\alpha$



$t=\tau_{\mathrm{ngp}}$



This may also be acceptable because the meaning of *q* is quite different from the collective case

Multi-time density correlation function

q-wavevector Fourier component of spatial fluctuations at t_0 in "local particle diffusivity" defined with a time interval *t* RY (PRL 1998, 20[illegible])

$$\boxed{\delta\mathcal{D}(\vec{q},t_0,t) = \sum_{j=1}^{N}\left(\left[\frac{|\Delta\vec{r}_j(t_0,t)|^2}{\langle\Delta r^2(t)\rangle}\right]-1\right)\exp[-i\vec{q}\cdot\vec{R}_j(t_0,t)]}$$

(collective)

q-wavevector Fourier component of spatial fluctuations at t_0 in "local density relaxation" defined with a time interval *t*

$$\delta F^{\vec{k}}(\vec{q},t_0,t) = \frac{1}{N}\sum_{j=1}^{N}\left(\exp[-i\vec{k}\cdot\Delta r_j(t_0,t)] - F(k,t)\right)\exp[-i\vec{q}\cdot\vec{r}_j(t_0)]$$

(collective)

or

$$\delta F_j^{\vec{k}}(\vec{q},t_0,t) = \left(\exp[-i\vec{k}\cdot\Delta r_j(t_0,t)] - F_s(k,t)\right)\exp[-i\vec{q}\cdot\vec{r}_j(t_0)]$$

(self)

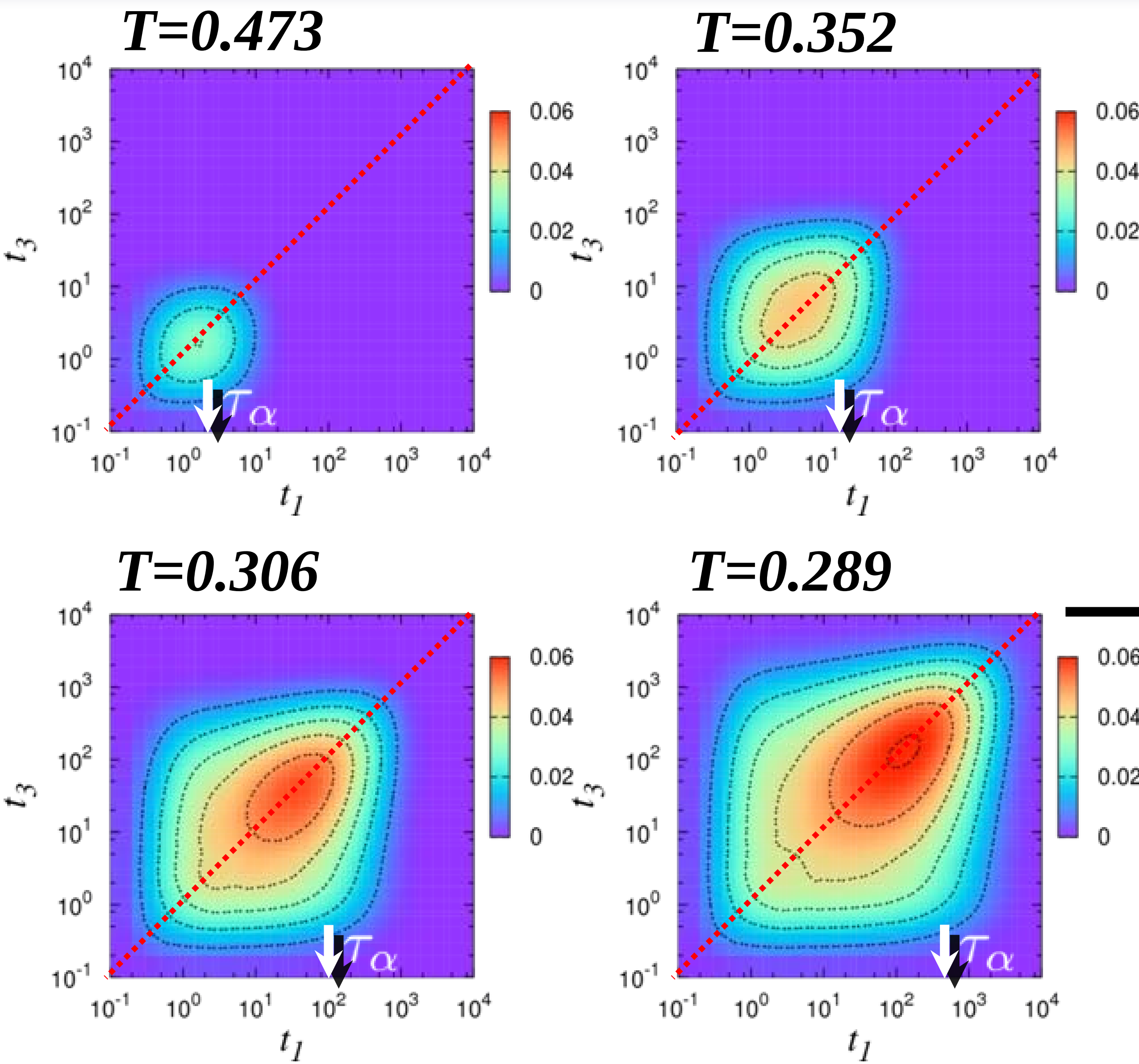
q --> 0 Kim-Saito (PRE 2009)

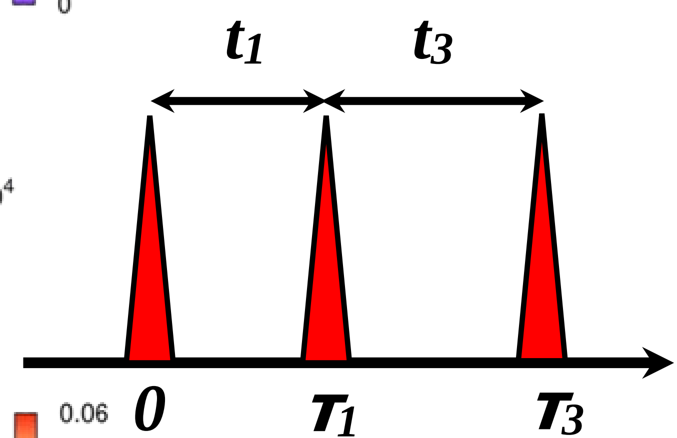
$$\boxed{\delta F_j^{\vec{k}}(t_0,t) = \left(\cos[\vec{k}\cdot\Delta r_j(t_0,t)] - F_s(k,t)\right)}$$

(self)

2D plot of ΔF(t_3, t_2=0, t_1)

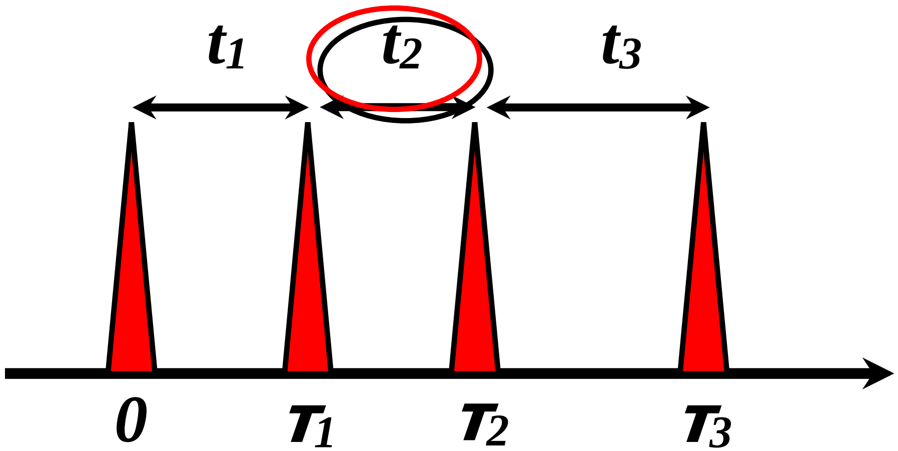
Kim-Saito (PRE 2009)



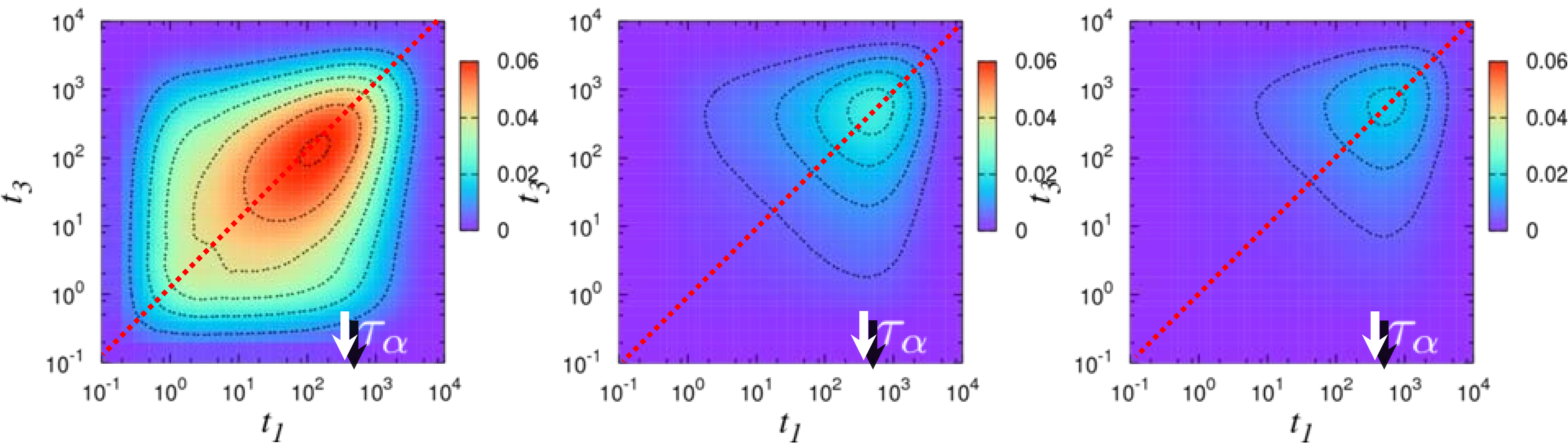


Lifetime of Dynamical Heterogeneity

Kim-Saito (PRE 2009)



T=0.289

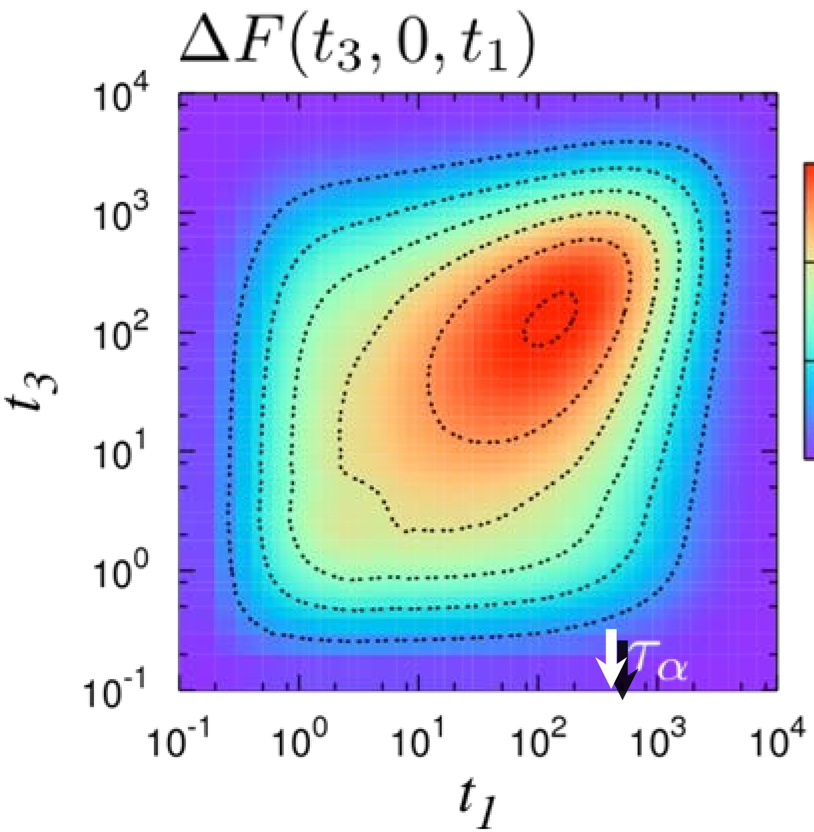


$t_2 = 0$ $\qquad$ $t_2 = \tau_\alpha$ $\qquad$ $t_2 = 2\tau_\alpha$

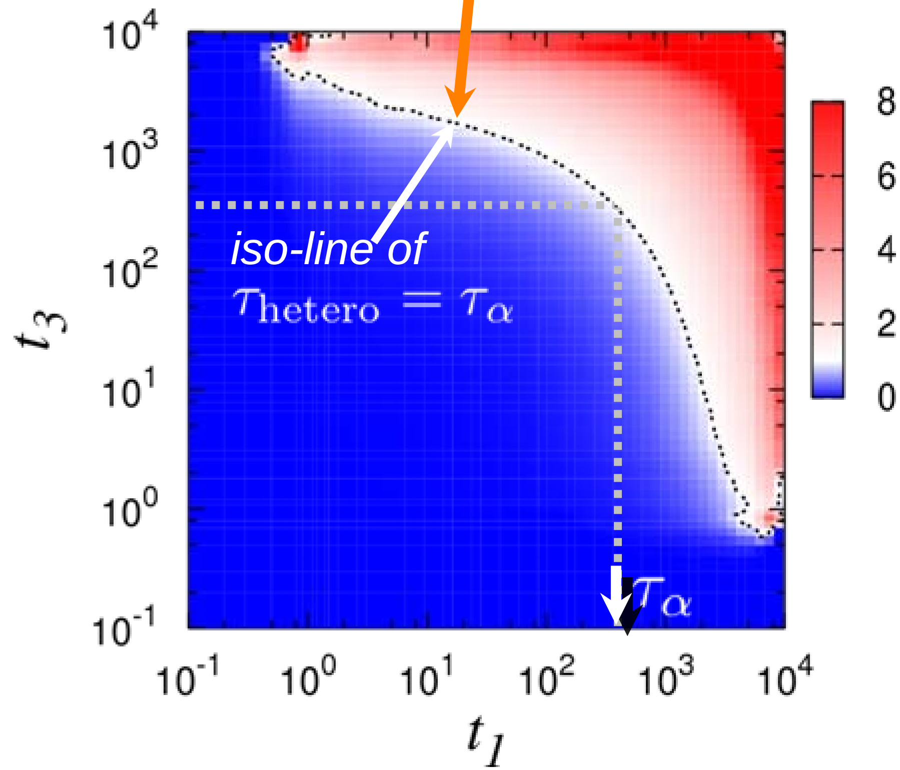
Relaxation time $\tau_{hetero}(t_3, t_1)$

Kim-Saito (PRE 2009)

T=0.289



α-relaxation time scale:
$\tau_{\rm hetero} \simeq \tau_\alpha$



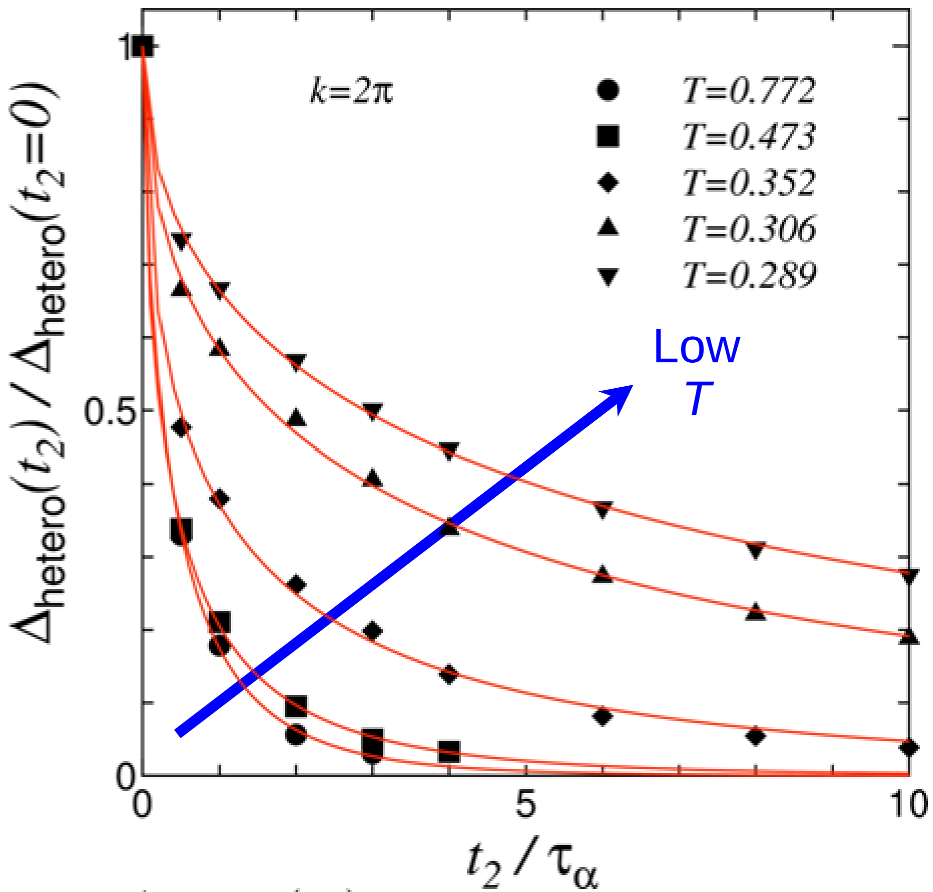
$$\tau_{\rm hetero} : \frac{\Delta F(t_3, \tau_{\rm hetero}, t_1)}{\Delta F(t_3, 0, t_1)} = e^{-1}$$

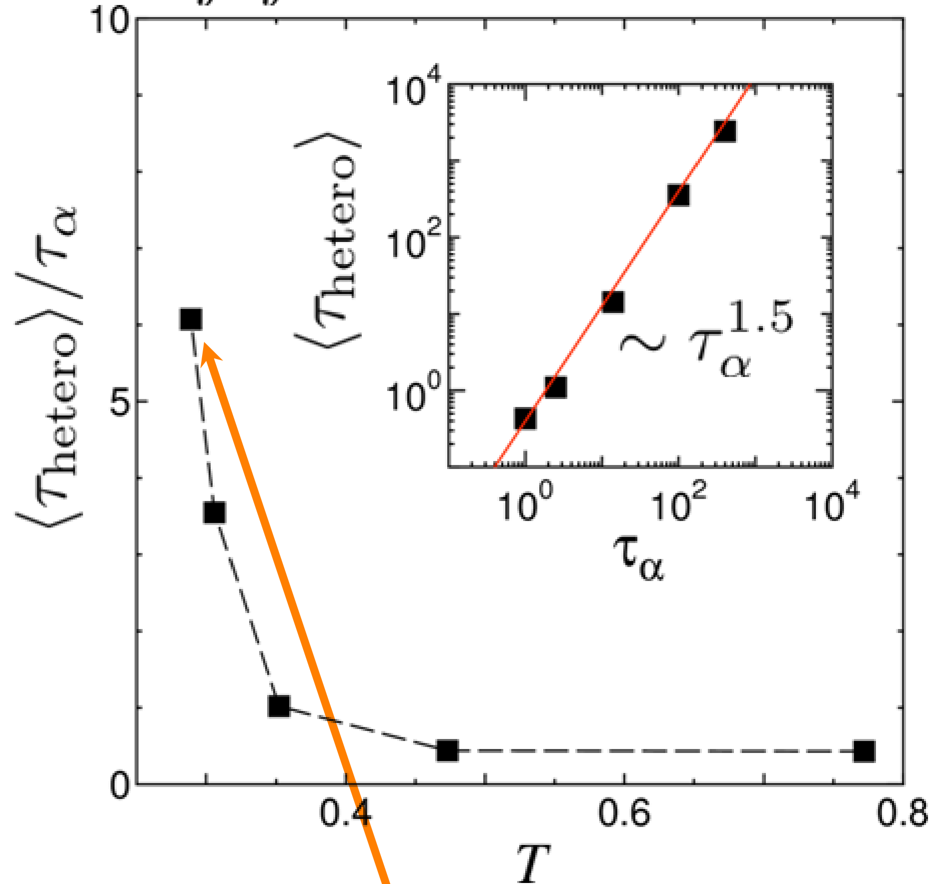
Average lifetime of Dynamical Heterogeneity

Kim-Saito (PRE 2009)

“Volume” of heterogeneous dynamics:

$$\Delta_{\text{hetero}}(t_2) = \int\int \Delta F(t_3, t_2, t_1)\, dt_1 dt_3$$



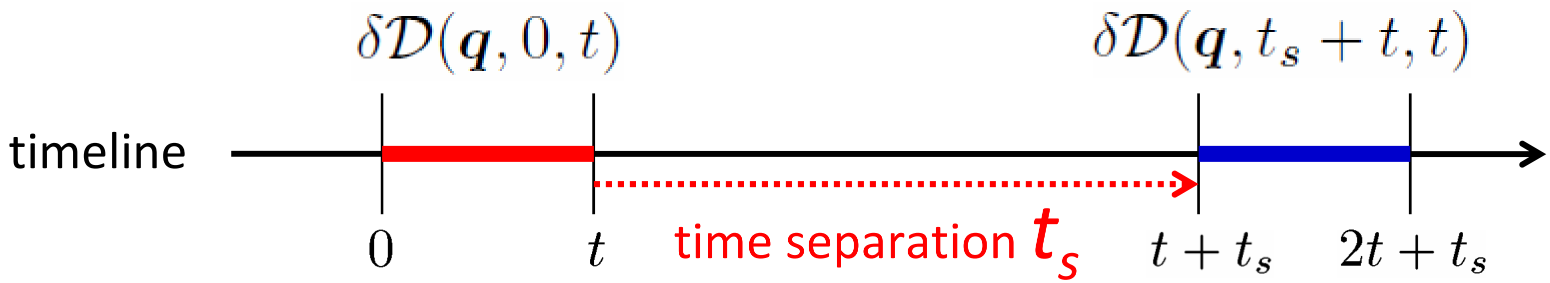


$$\frac{\Delta_{\text{hetero}}(t_2)}{\Delta_{\text{hetero}}(t_2=0)} \sim \exp[-(t_2/\langle\tau_{\text{hetero}}\rangle)^{\beta}]$$

$$\boxed{\langle\tau_{\text{hetero}}\rangle \simeq 6\tau_\alpha} \quad \beta \simeq 0.6$$

Summary

$$\delta\mathcal{D}(\vec{q},t_0,t)=\left(\sum_{j=1}^{N}\left[\frac{|\Delta\vec{r}_j(t_0,t)|^2}{\langle\Delta r^2(t)\rangle}\right]-1\right)\exp[-i\vec{q}\cdot\vec{R}_j(t_0,t)]$$



Present study

$$\tau_{\text{hetero}}^{t=\tau_\alpha}=2.65\tau_\alpha^{1.08}$$

$$\tau_{\text{hetero}}^{t=\tau_{\text{ngp}}}=3.75\tau_\alpha^{0.91}$$

$$\tau_{\text{hetero}}=1/(q^2D_{\text{hetero}})$$

Kim-Saito (2009)

$$\tau_{\text{hetero}}\sim\tau_\alpha^{1.5}$$

So far, numerical results support …

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

suggesting that DH may strongly affect dynamical properties near GT.

Open questions related to DH

1. *True identity of DH*
   a. *Any correspondence with static properties? -> Tanaka, ...*
   b. *Anything to do with other pictures (AG, CRR, medium-range order, bond-orientation order, mosaic, domain, ...) ?*
2. *Role of DH*
   a. *DH play some roles near GT? -> YES*
   b. *Any proper theories bridging between growing length scale (ξ) and growing time scales (τ_{hetero}, τ_{α})? -> so far, NO*
   c. *Something fundamental to GT? or just a by-product of GT?*
      -> hopefully fundamental, but can be a by-product
   d. *DH suppresses or enhances microscopic dynamics near GT?*
      -> collective motions should enhance it