UNIVERSITY OF PISA
Ph.D. graduate school in Physics

Mutual Information in molecular liquids

Supervisor
Prof. Dino Leporini

Phd student
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Outline of the presentation

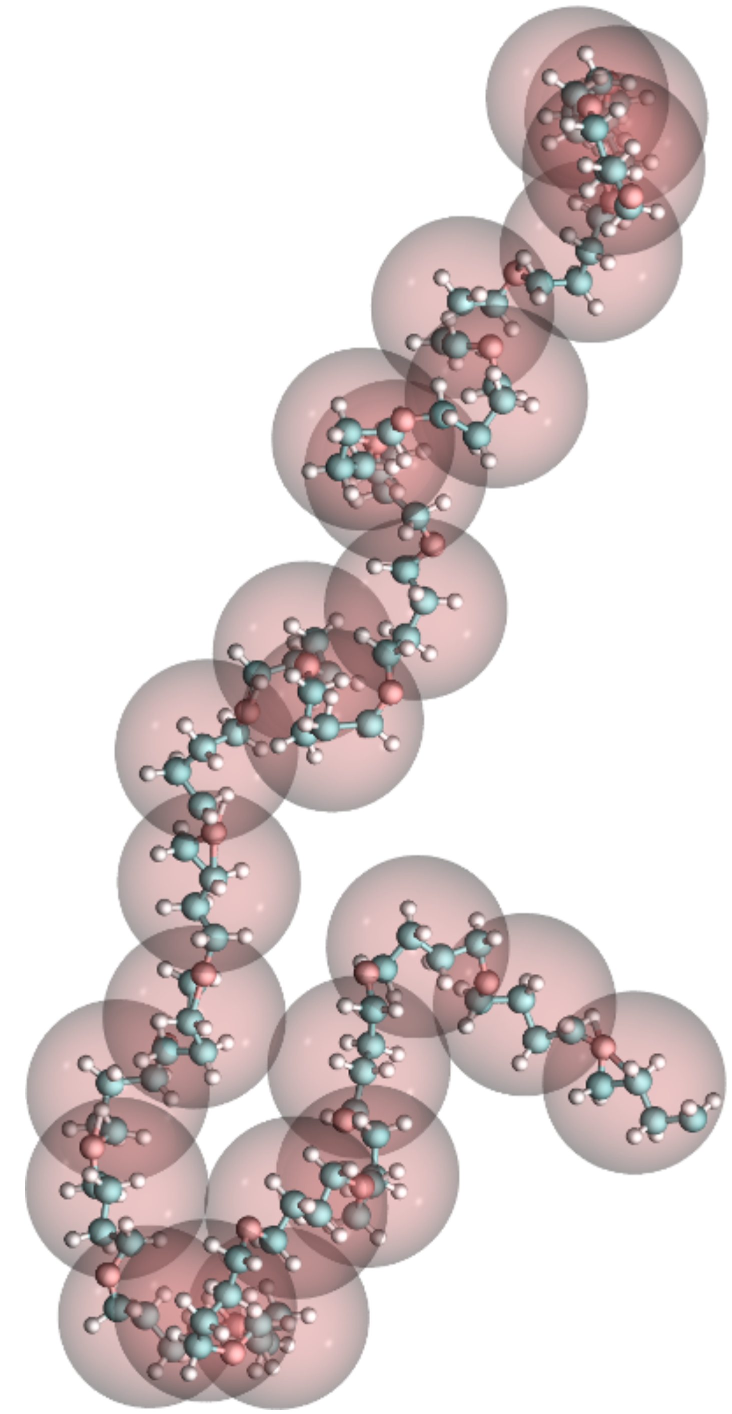
- ***Context***

  - *Glass transition*
  - *Investigated system and method*

- ***Displacement-Displacement correlation***

  - *Average number of MI-correlated particles*
  - *Standard deviation*
  - *Correlation with structure*

- ***Conclusion and future work***



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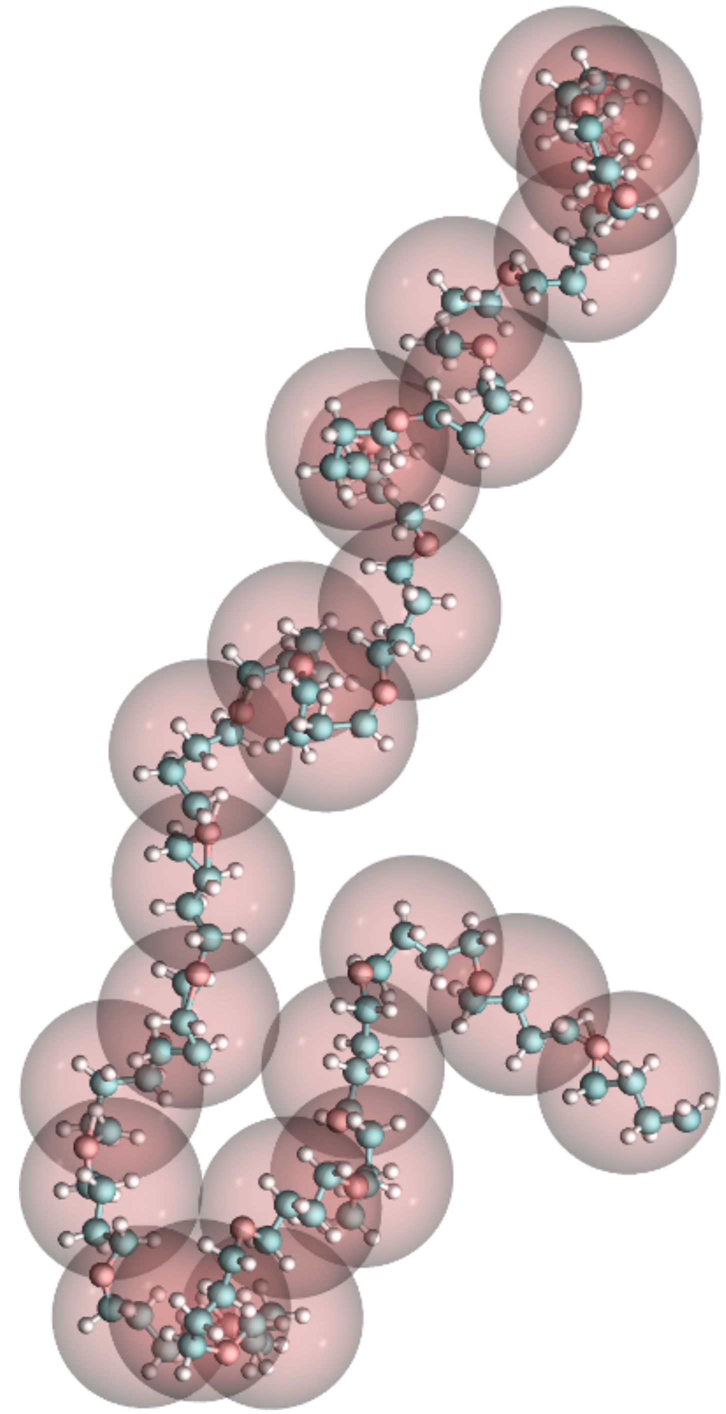
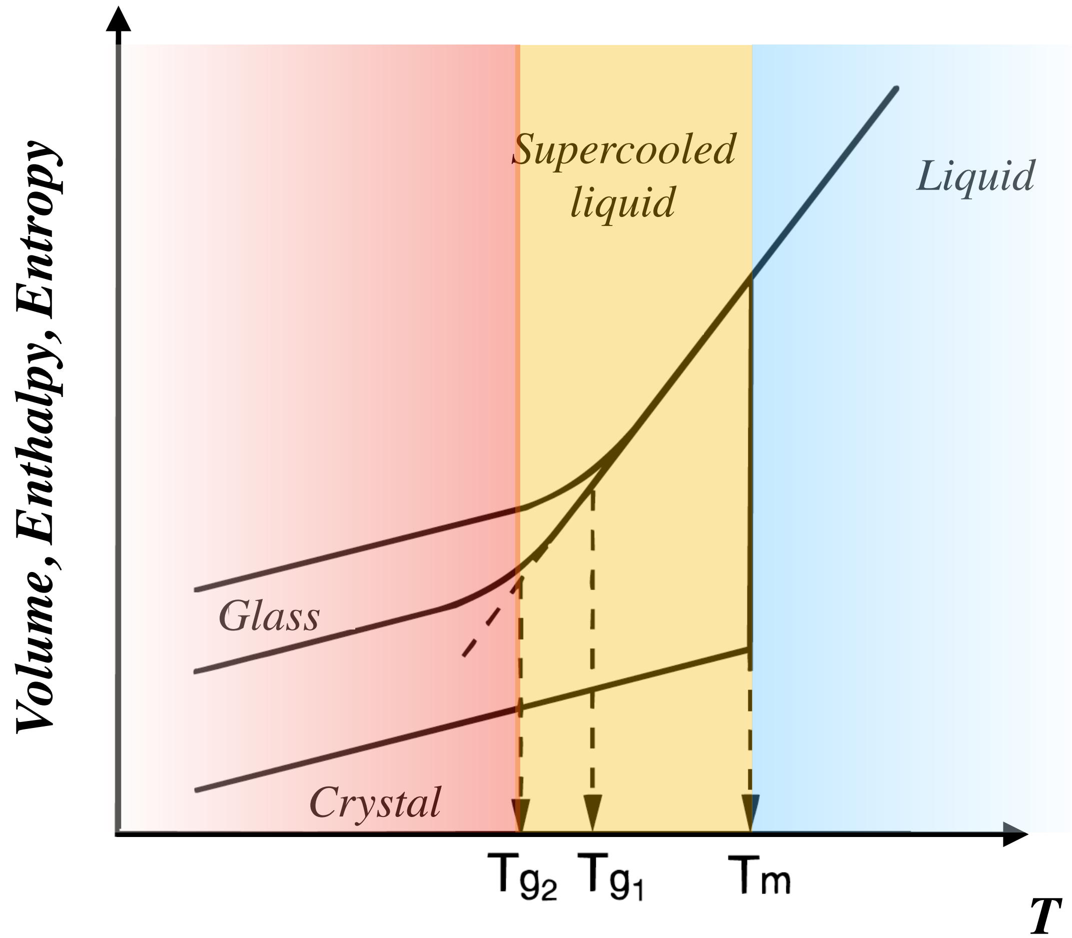
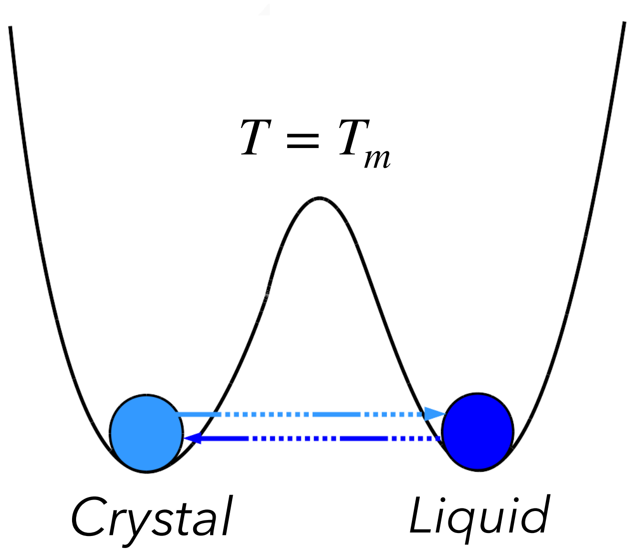


Liquids cooled fast enough avoid crystallization and fall out of equilibrium





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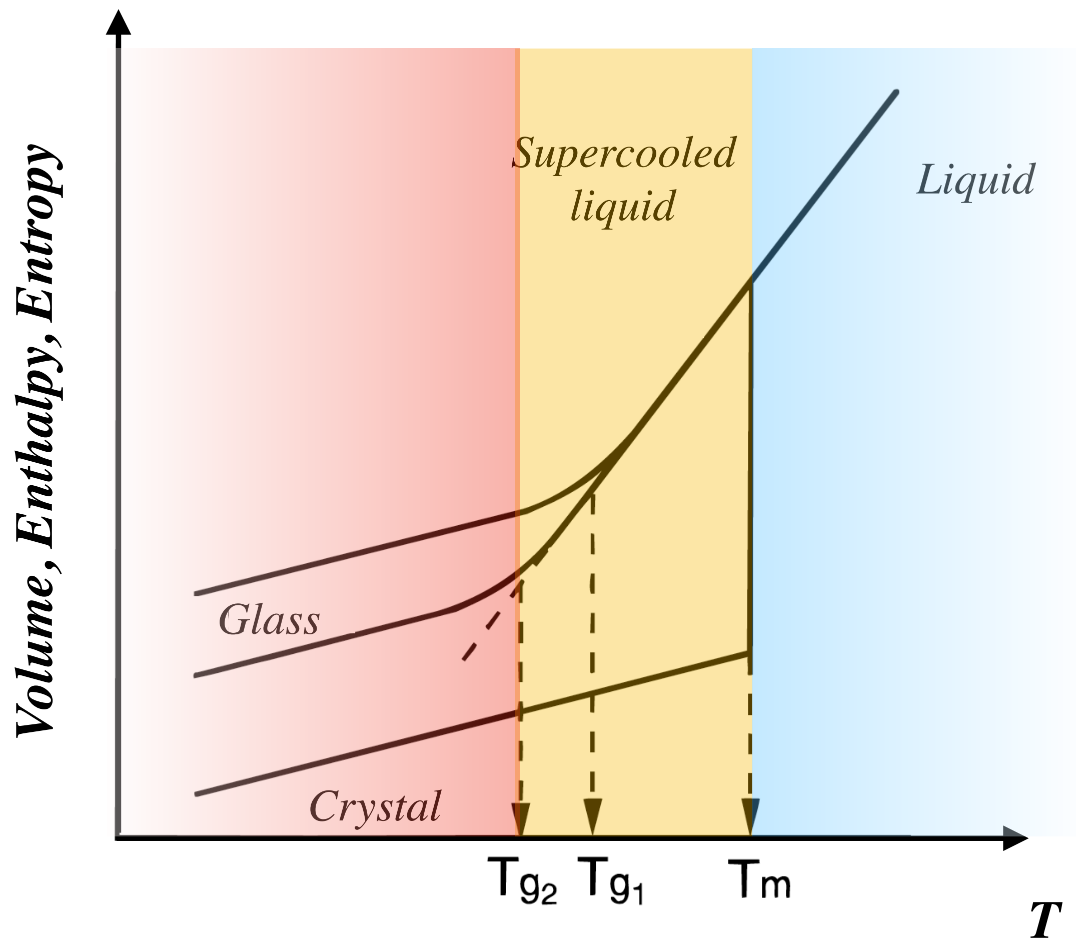

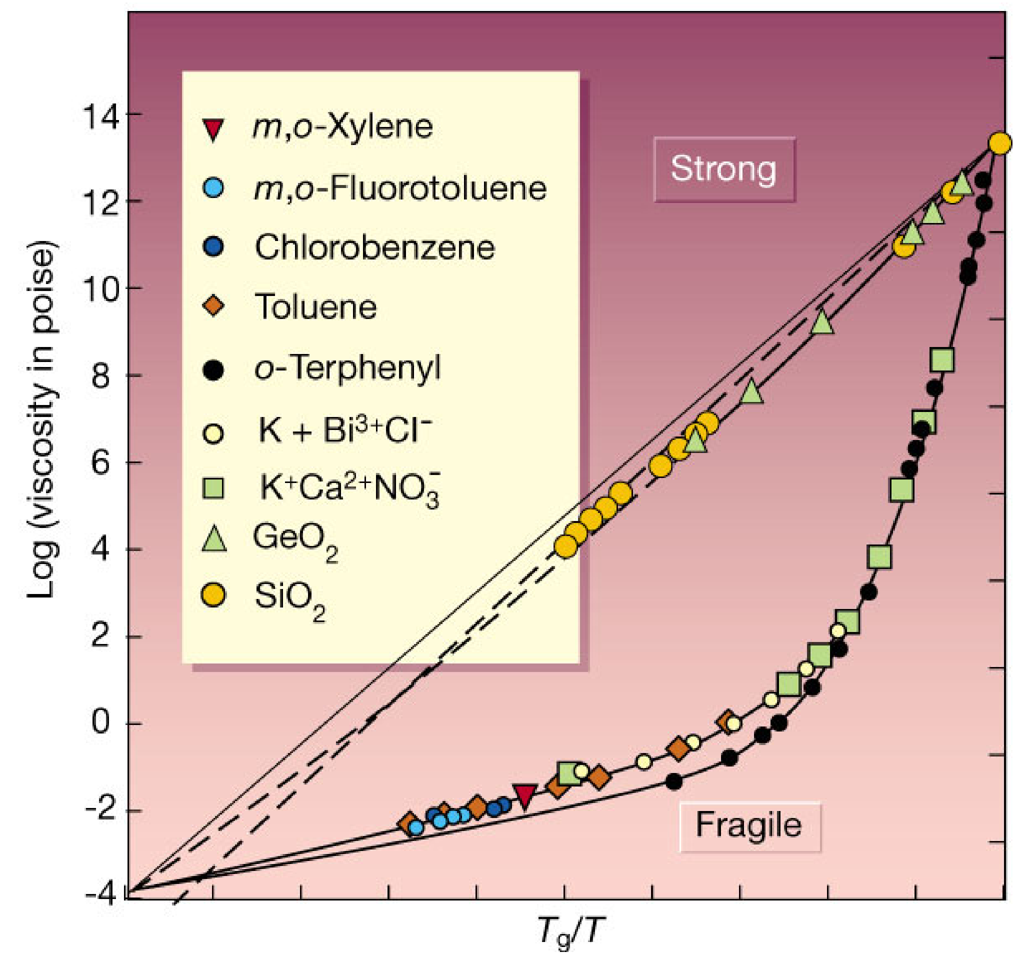

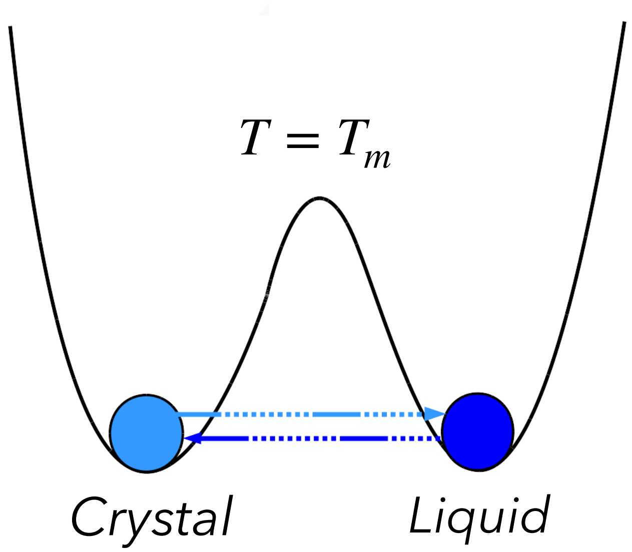

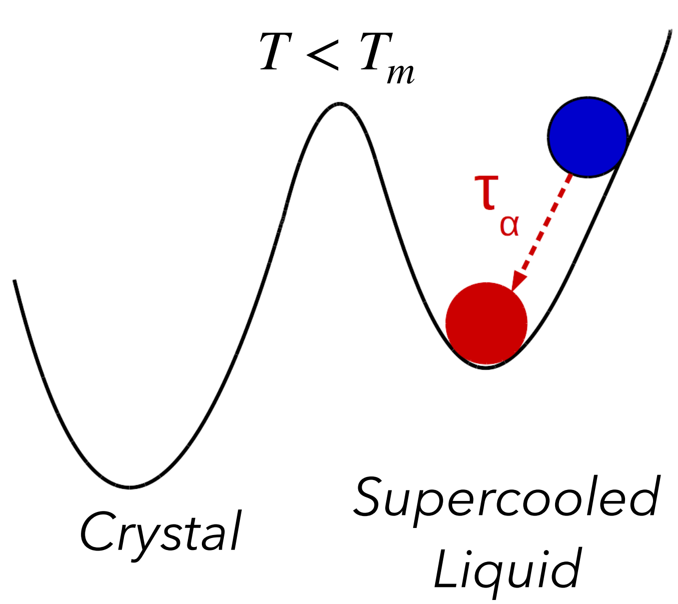

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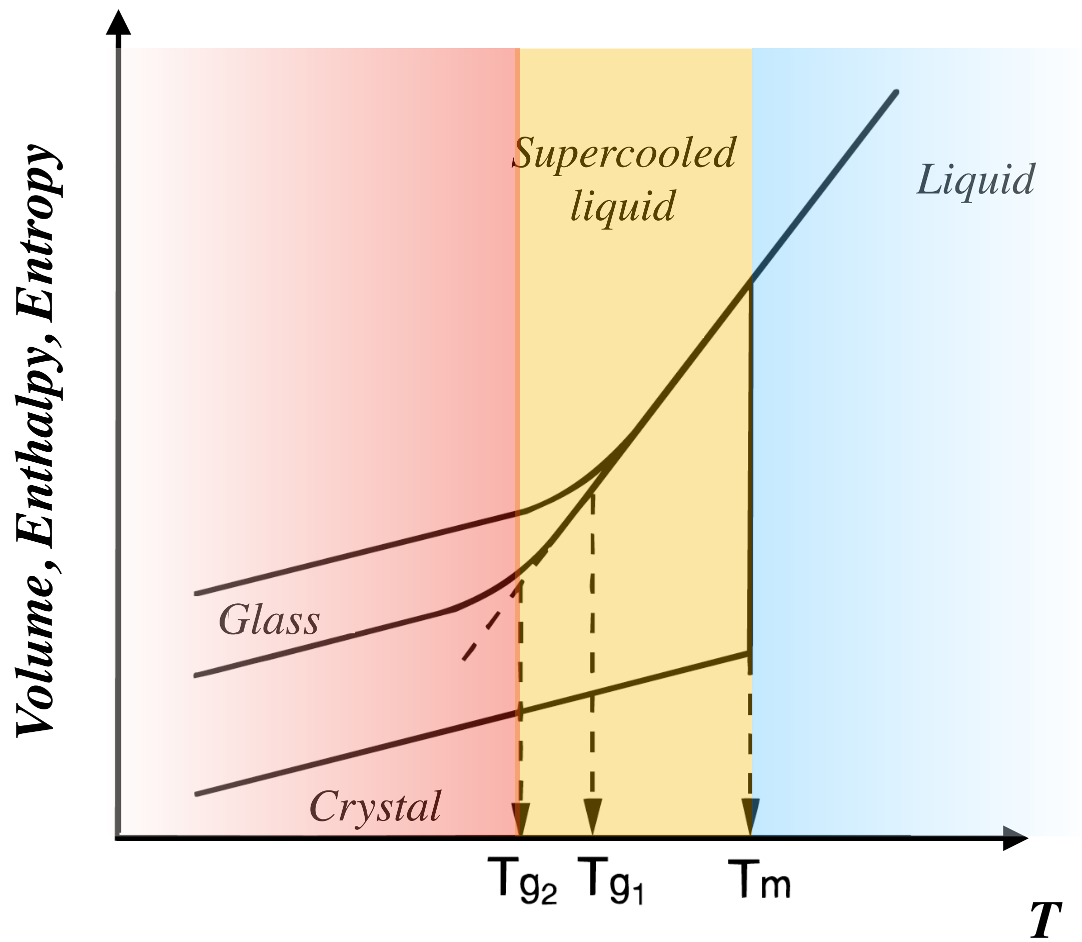
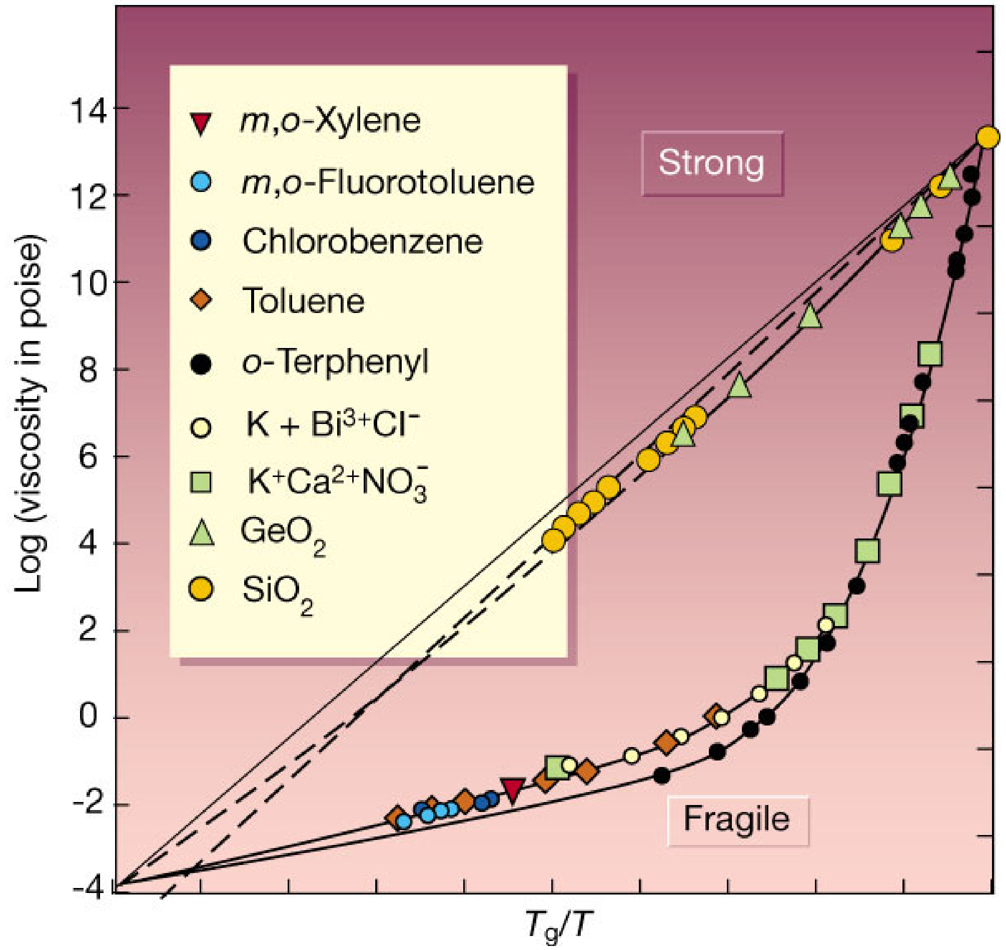
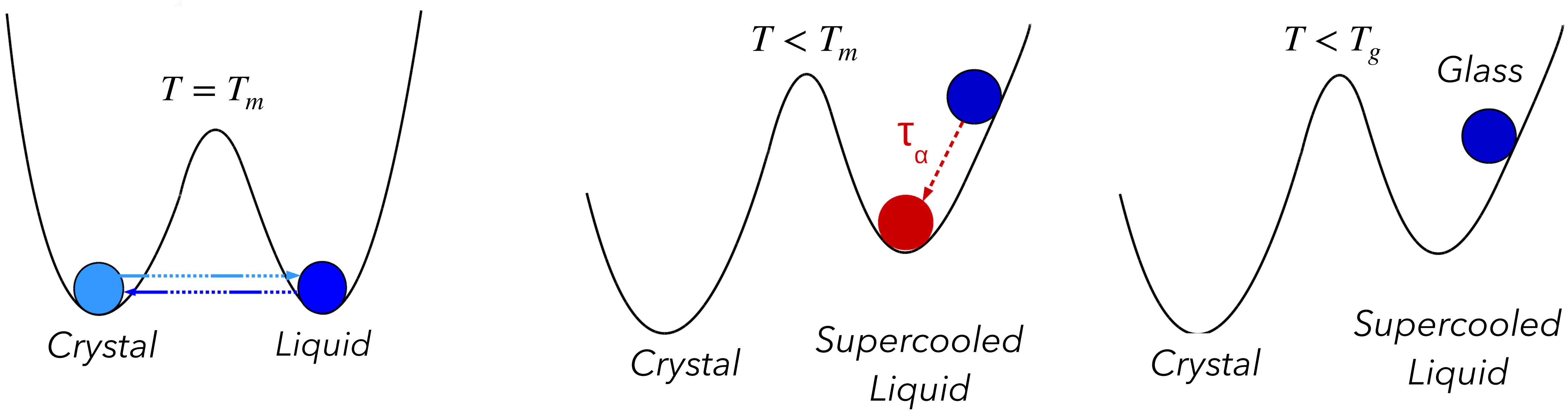






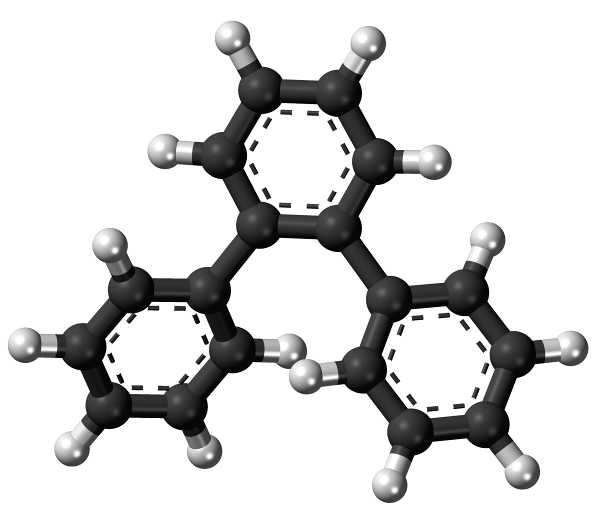
Structure does not change undergoing the glass transition

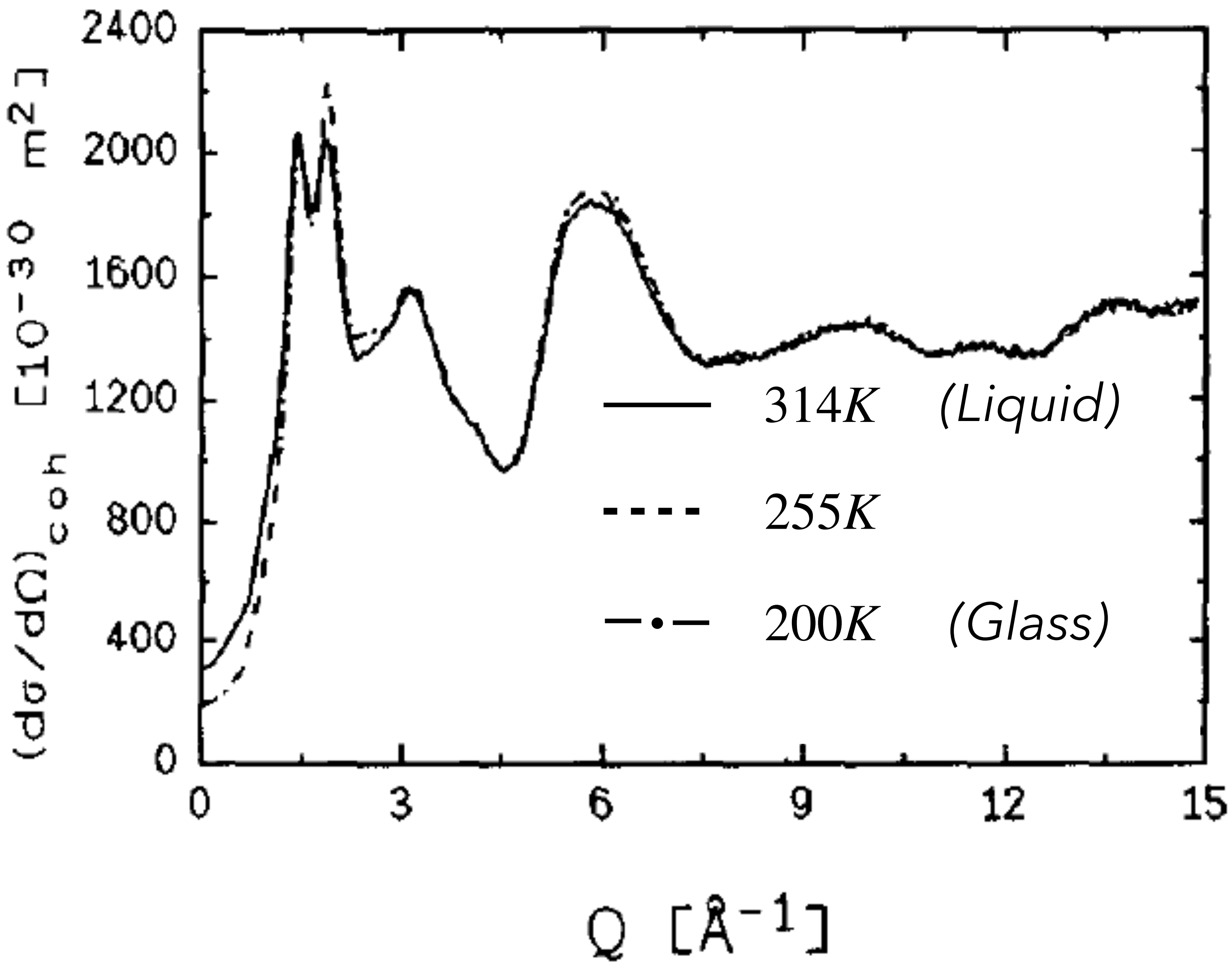
Static structure factor

$$S(\mathbf{q}) = \frac{1}{N} \left\langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}} \right\rangle$$

$$\rho_{\mathbf{q}} = \sum_{i=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_i}$$

Orto-terphenyl

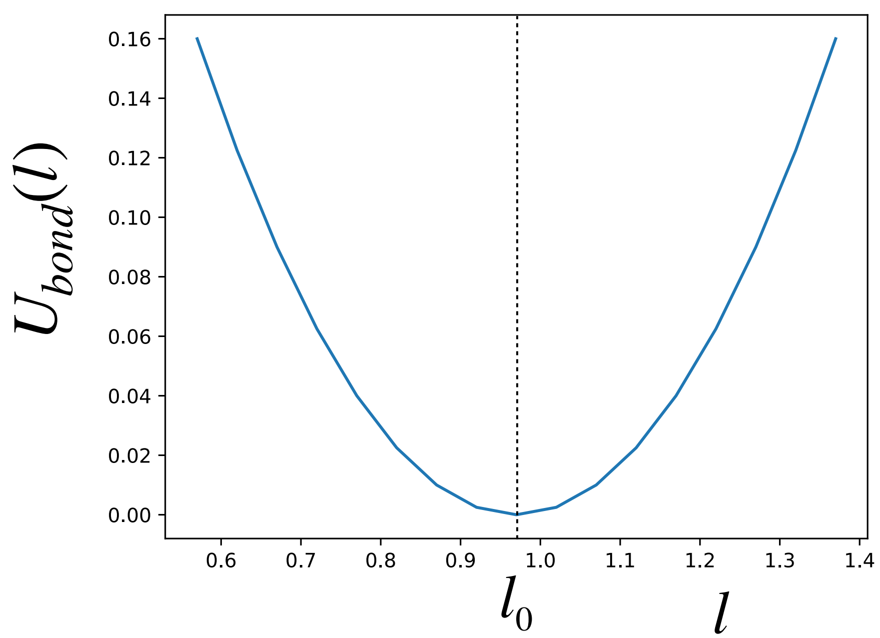




Coarse-grained polymeric model offer a good framework for numerical simulation

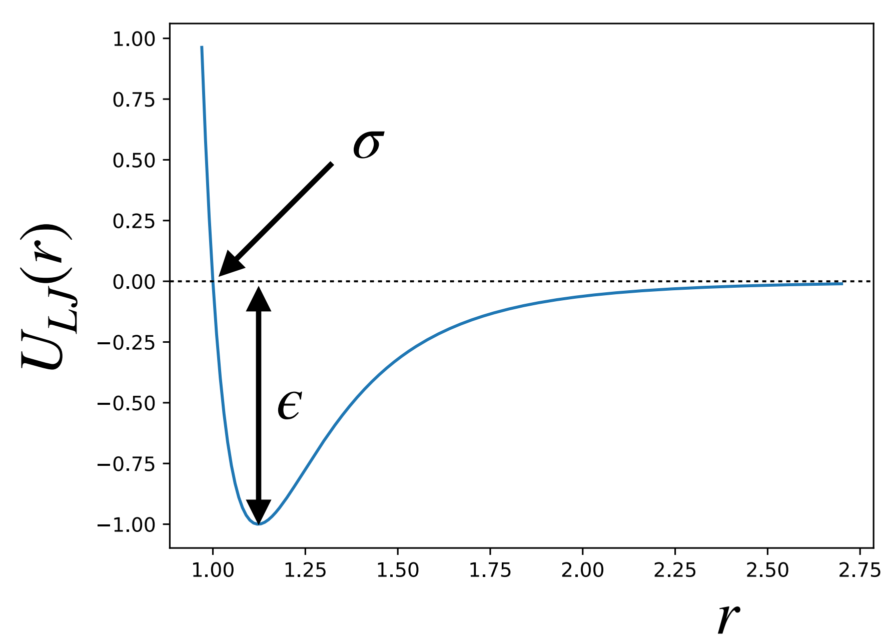
<u>Bond interaction</u>

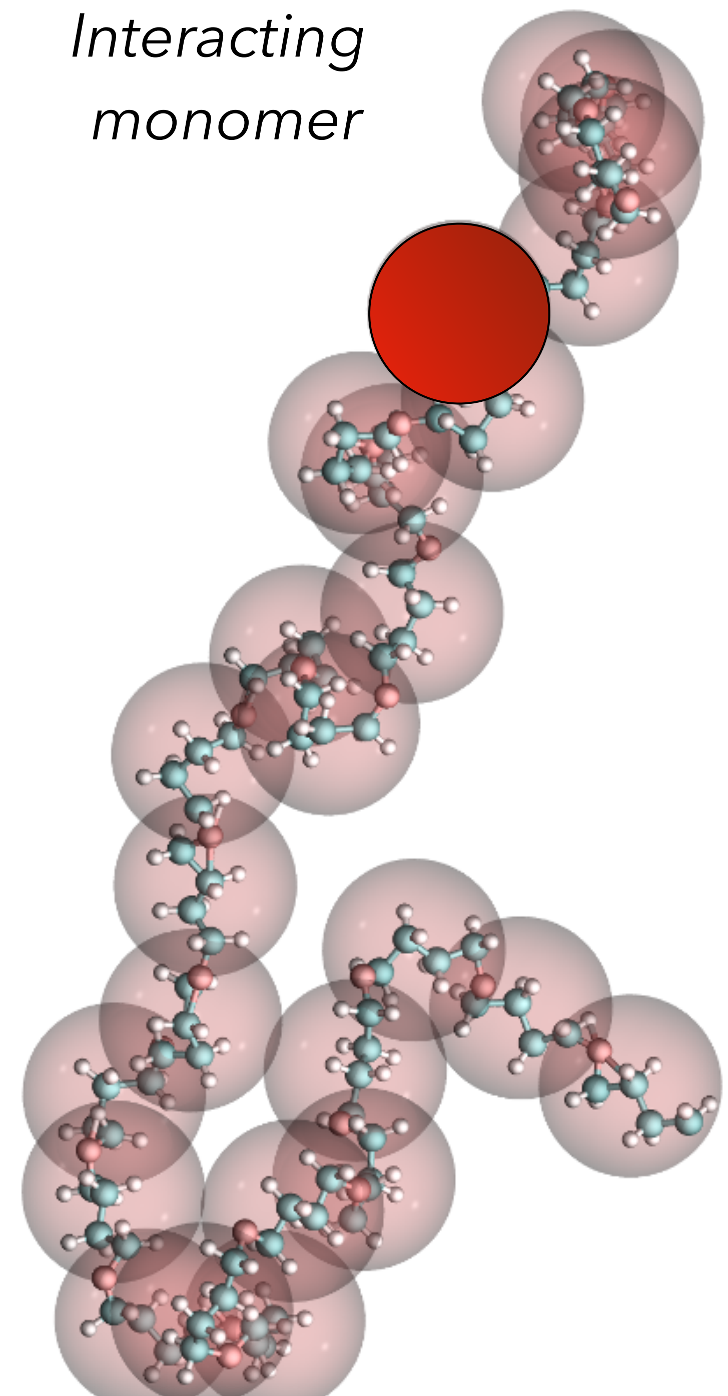
$$U_{bond}(l) = k(l - l_0)^2$$



<u>Lennard-Jones Interaction</u>

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

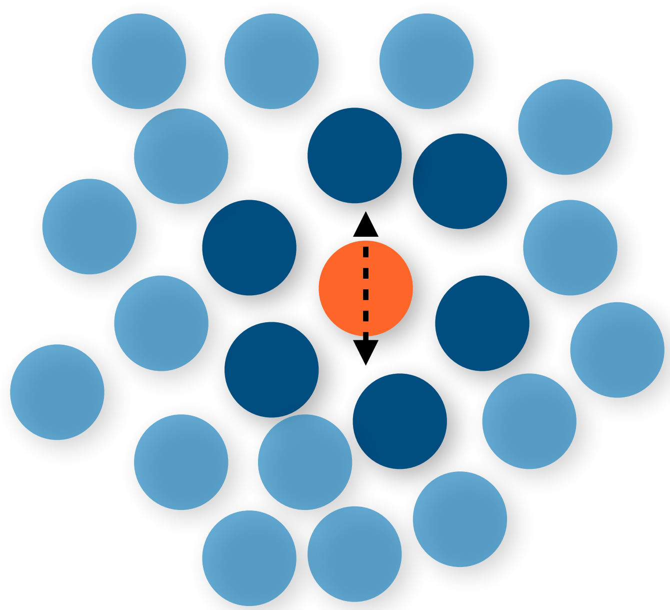




Monomer dynamics is characterized by MSD and ISF

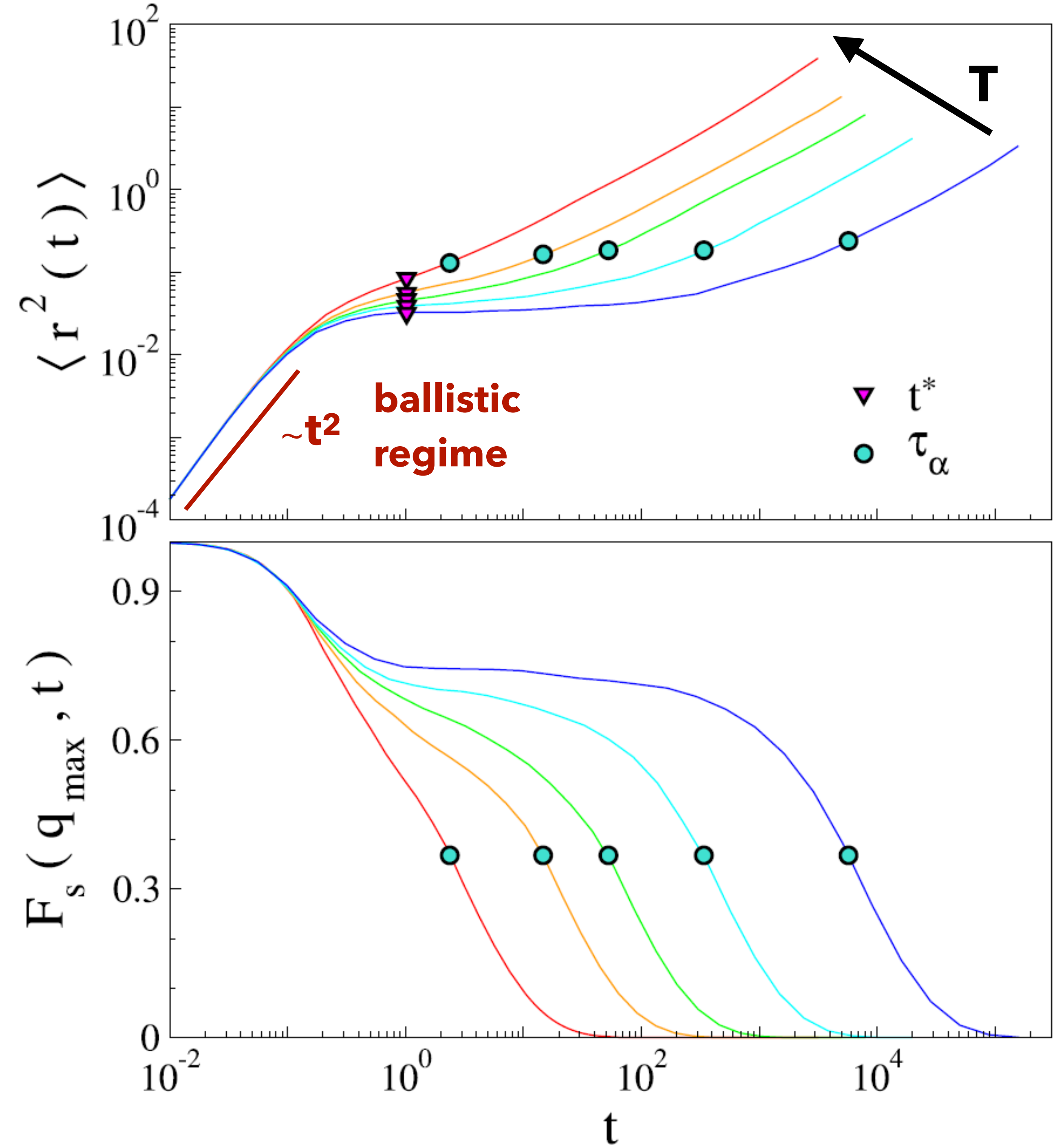
Mean Square Displacement

$$\langle \delta r^2(t) \rangle = \frac{1}{N} \sum_{j=1}^{N} \left\langle || \mathbf{r}_j(t) - \mathbf{r}_j(0) ||^2 \right\rangle$$



Intermediate scattering function

$$F_s(\mathbf{q}, t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_j(t) - \mathbf{r}_j(0)]} \right\rangle$$



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S. Bernini, F. Puosi, and D. Leporini, J. Phys. Condens.Matter 29, 135101 (2017).

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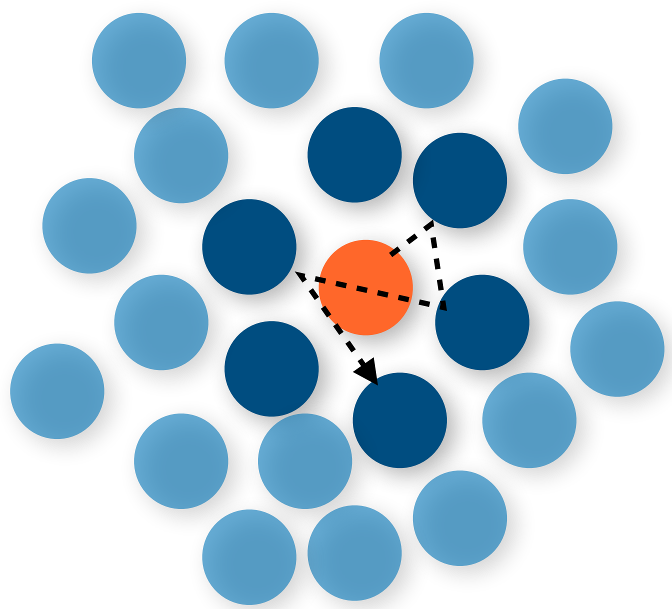

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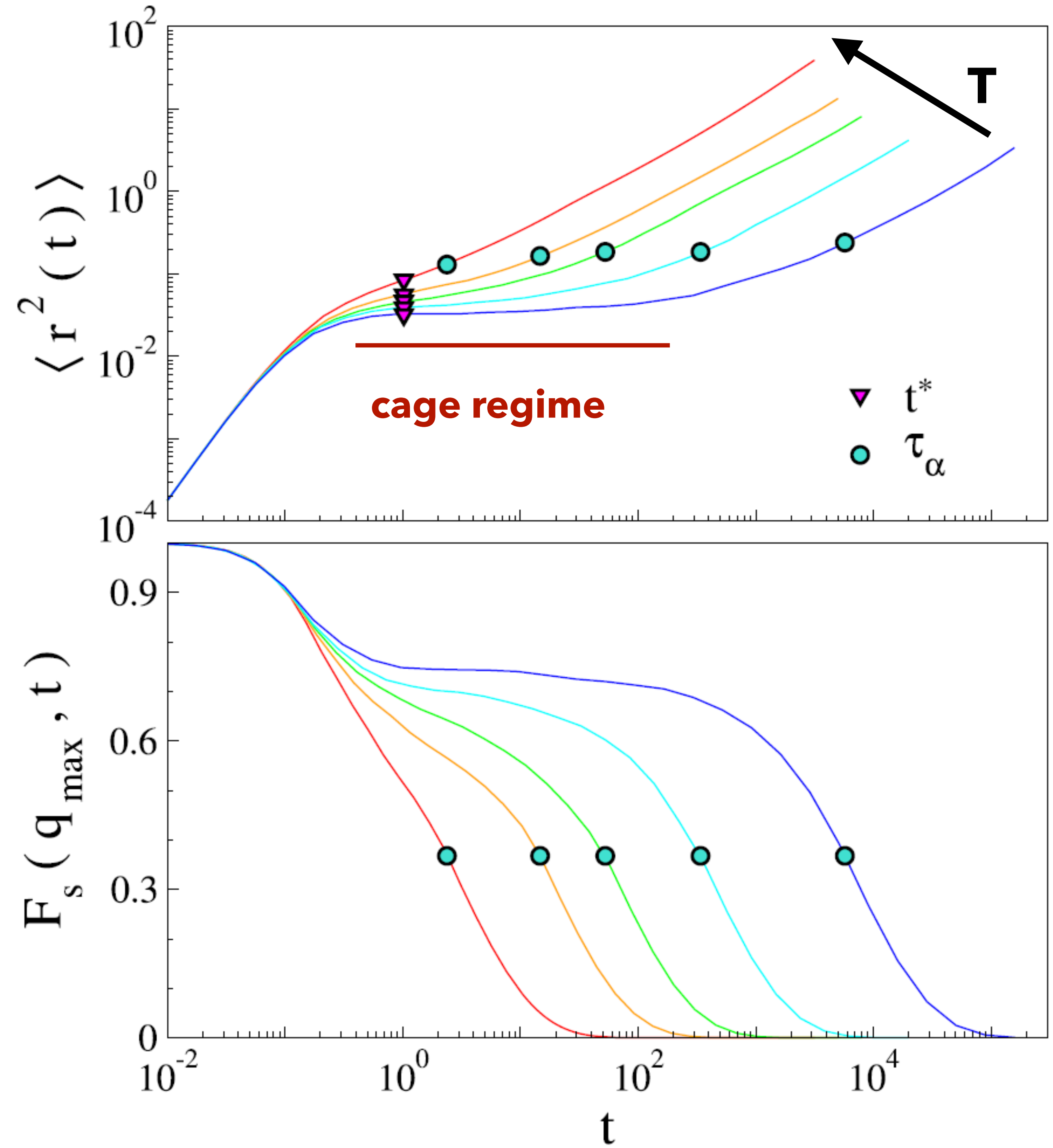

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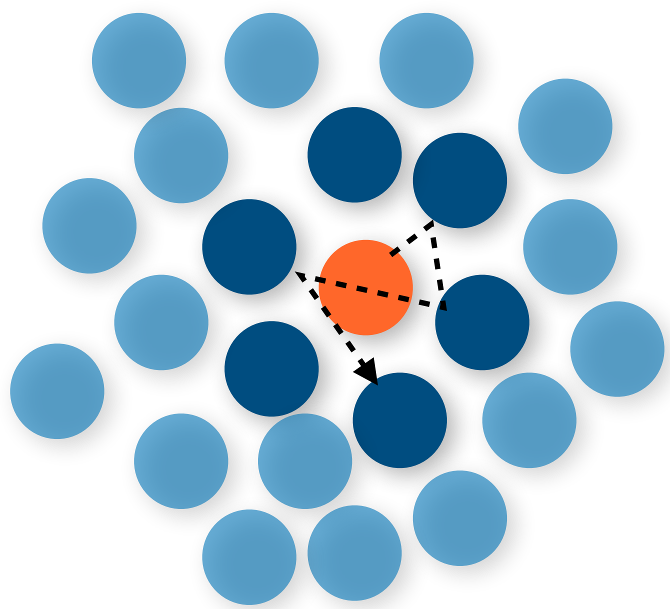

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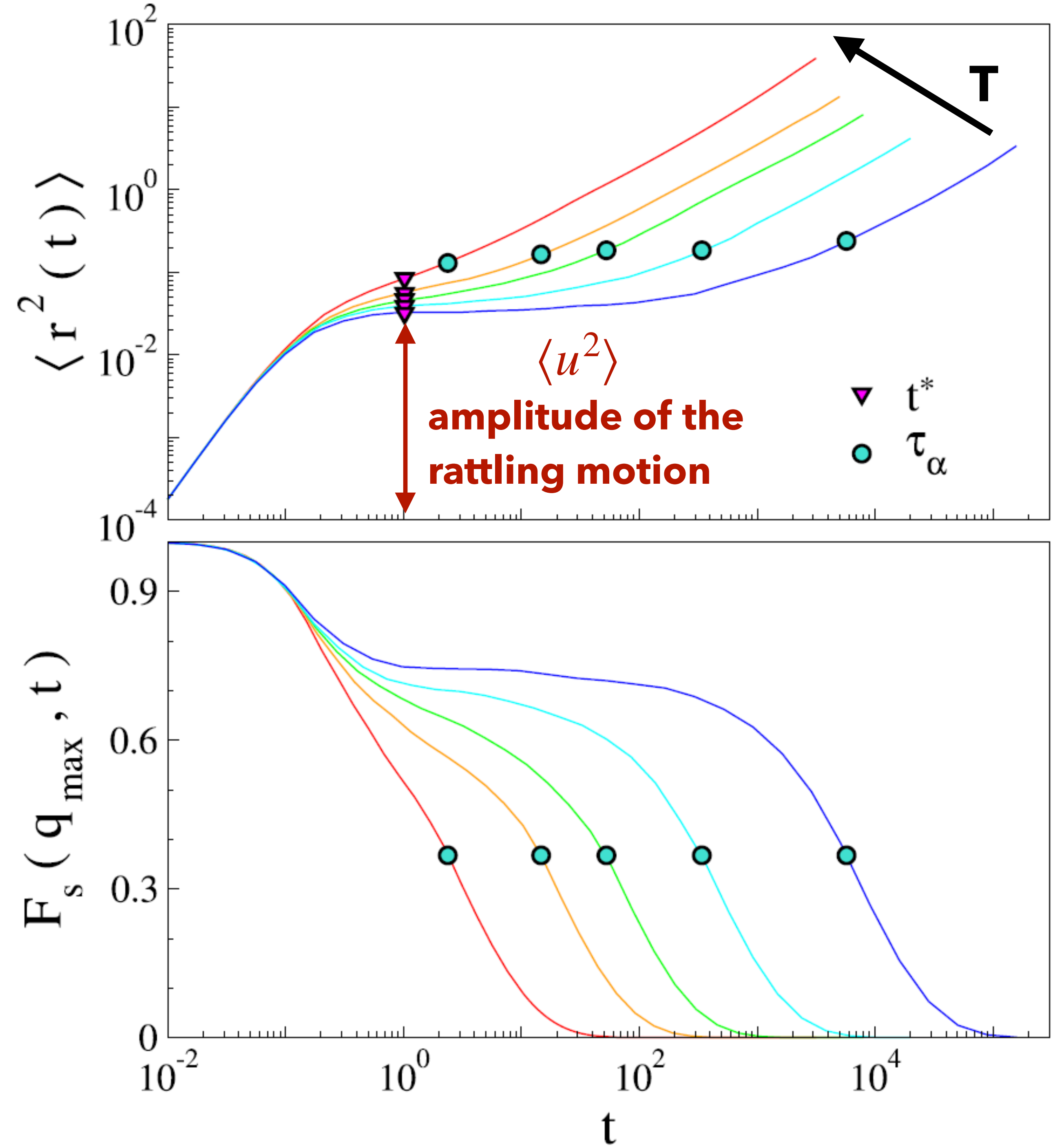

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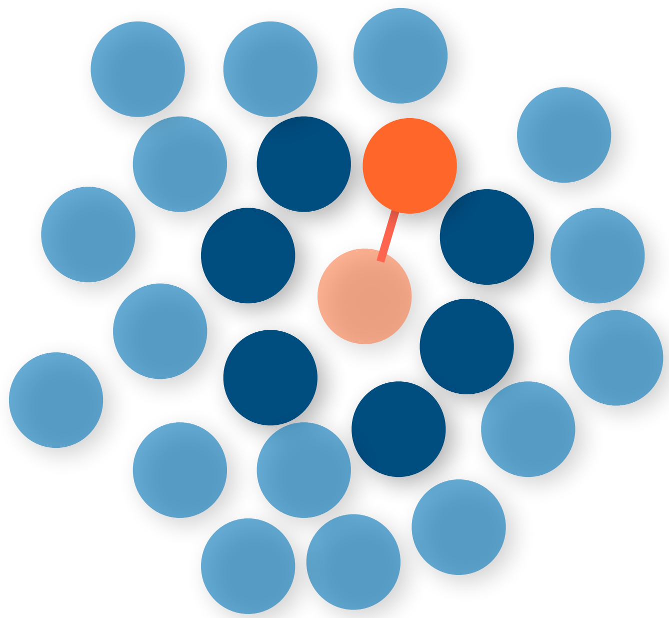
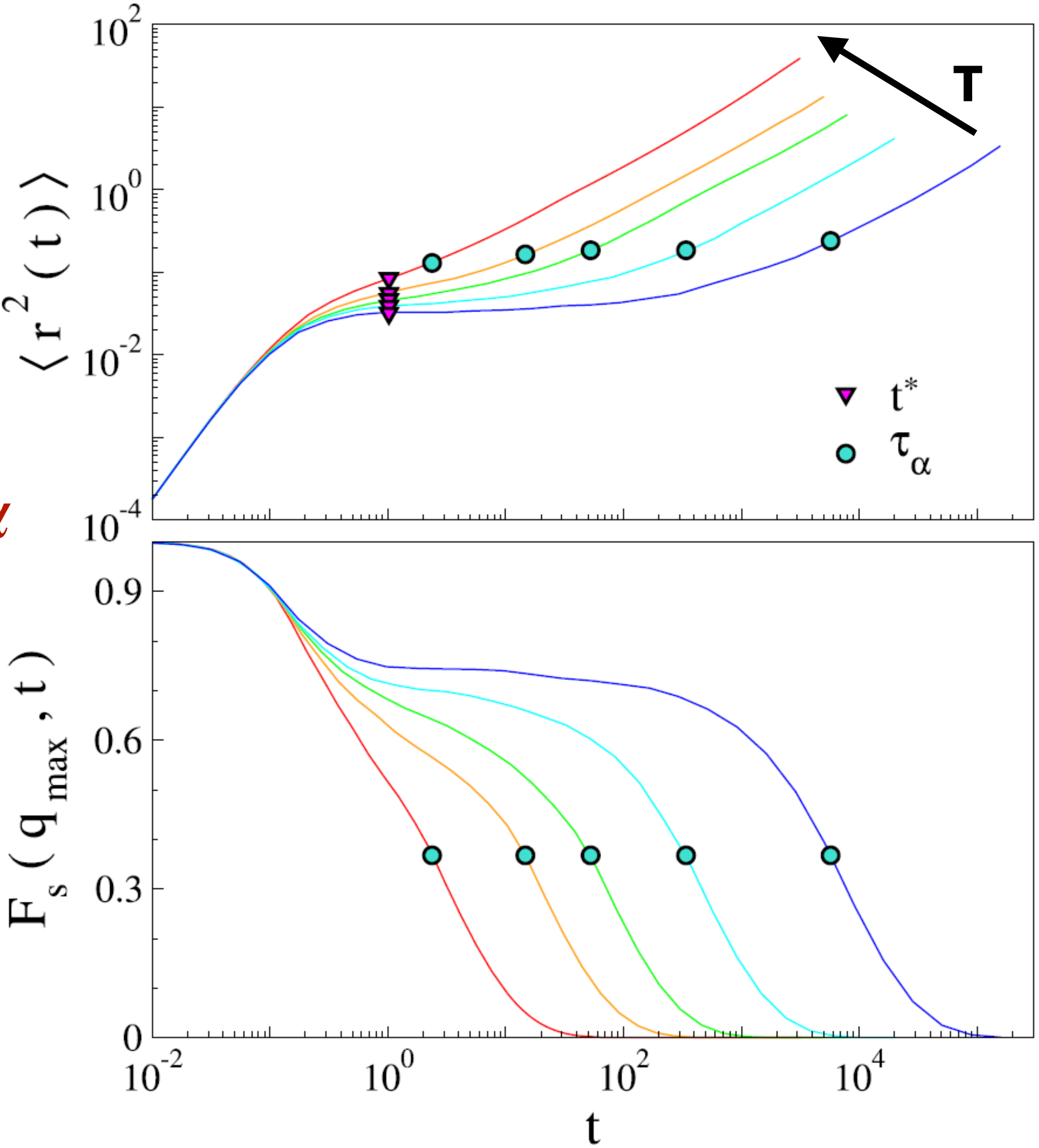


$\sim \tau_\alpha$

Intermediate scattering function

$$F_s(\mathbf{q}, t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_j(t) - \mathbf{r}_j(0)]} \right\rangle$$

$$F_s(q_{max}, \tau_\alpha) = 1/e$$



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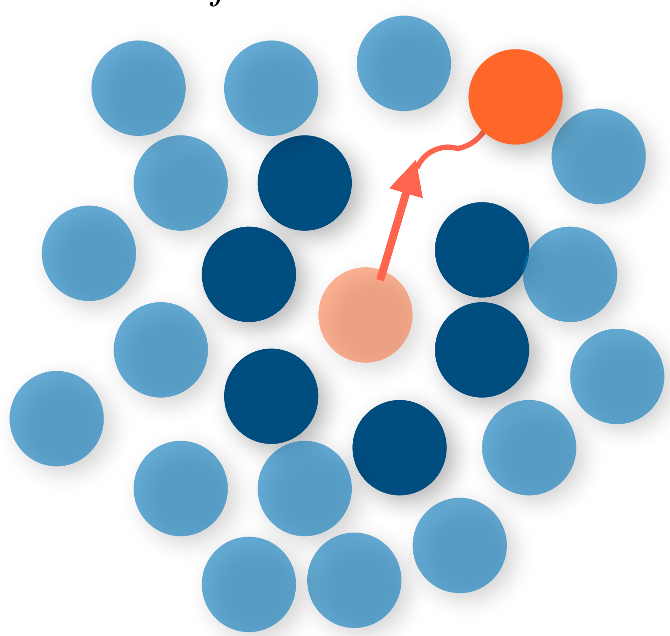

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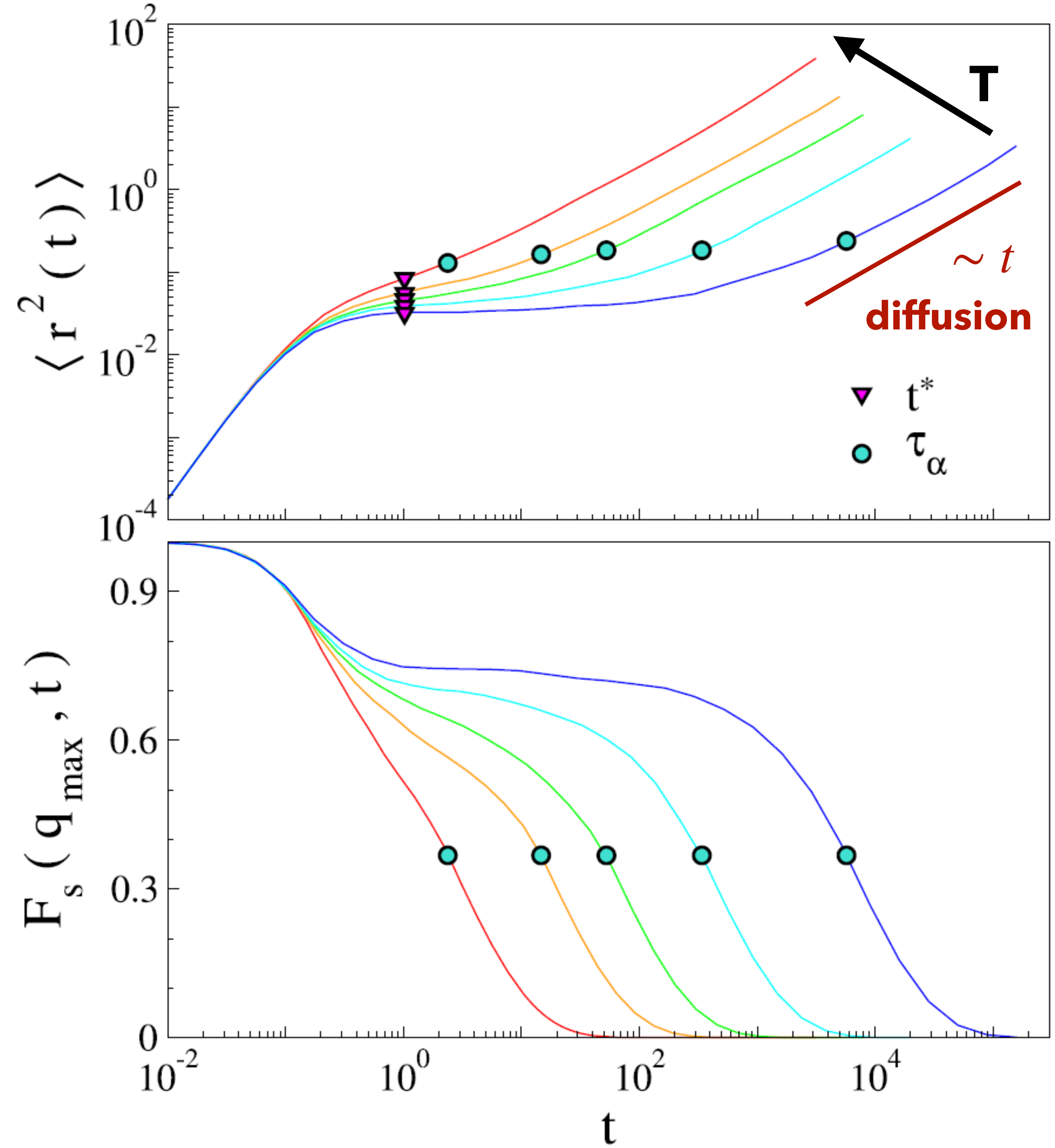

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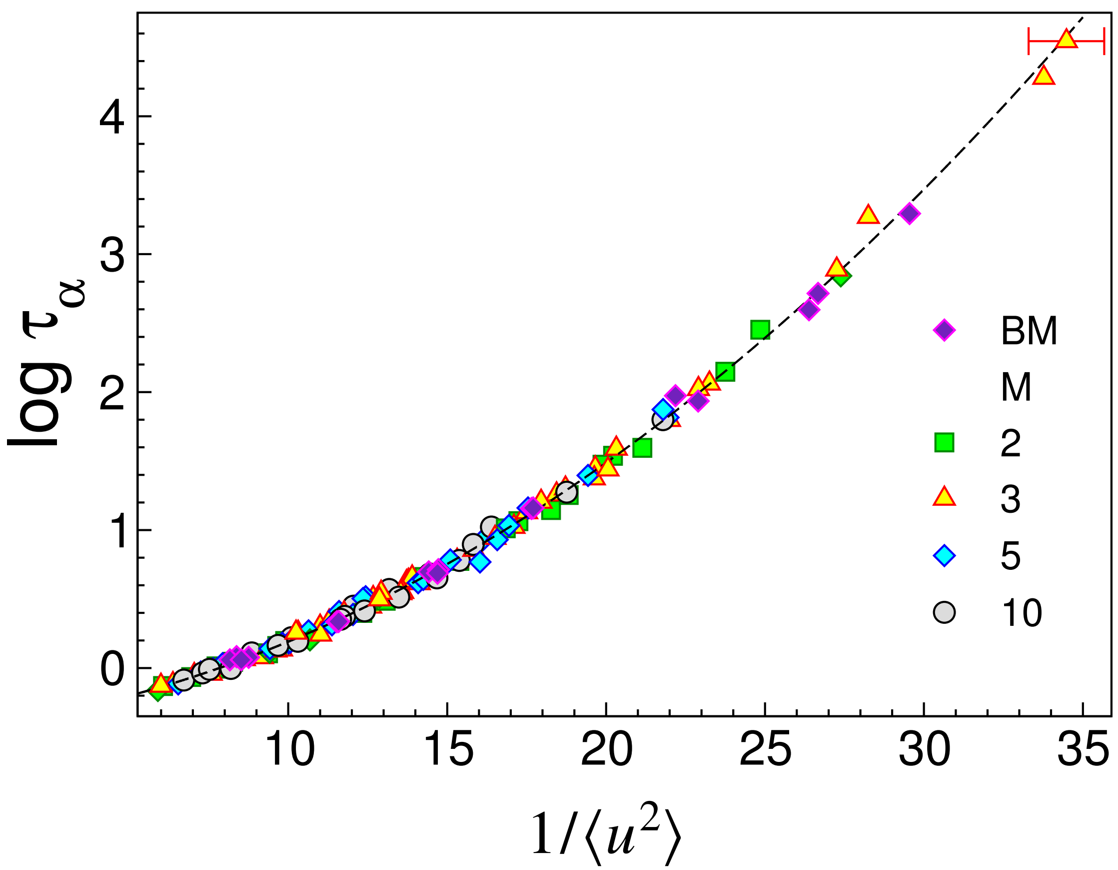
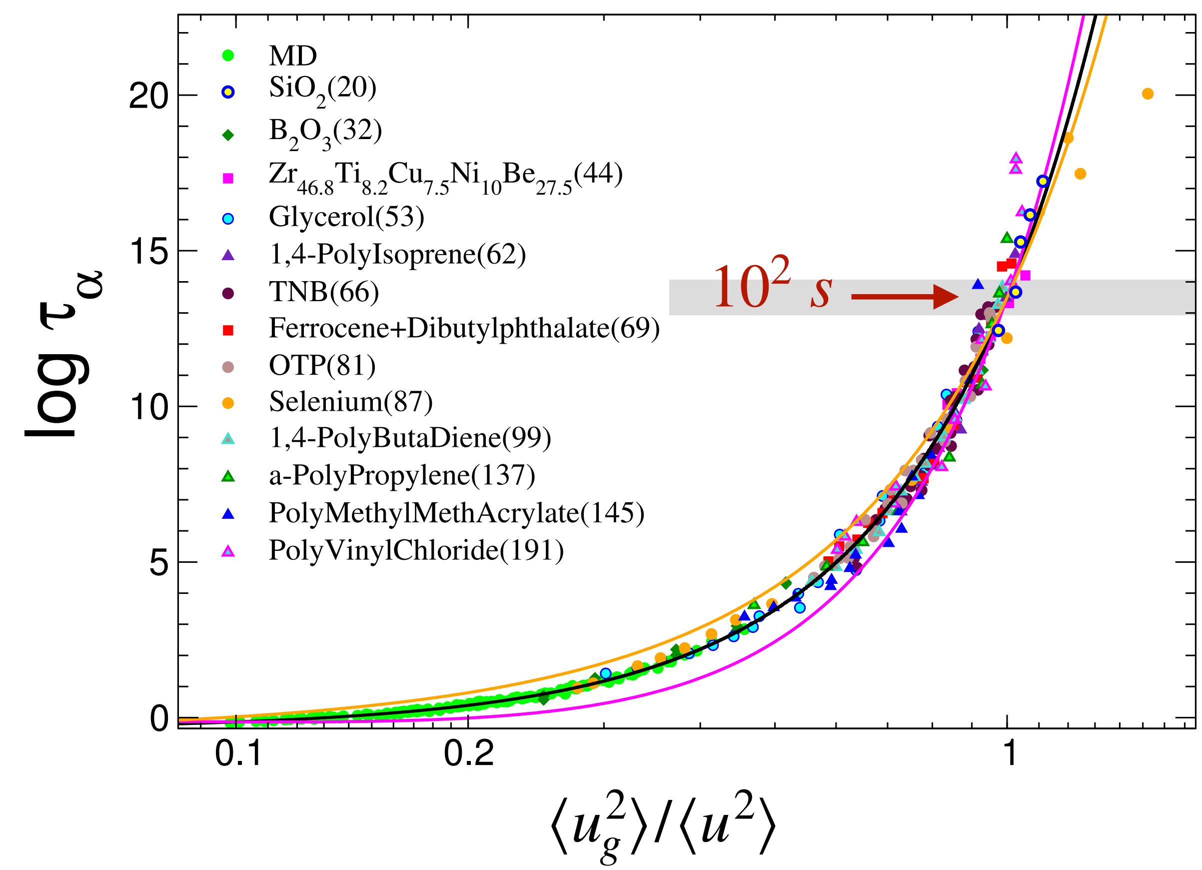
Fast mobility ($<u^2>$) and relaxation (τ_α) are correlated

Molecular dynamics simulations



$$\log \tau_\alpha = \alpha + \beta \left(\frac{1}{\langle u^2 \rangle} \right) + \gamma \left(\frac{1}{\langle u^2 \rangle} \right)^2$$

Experiments



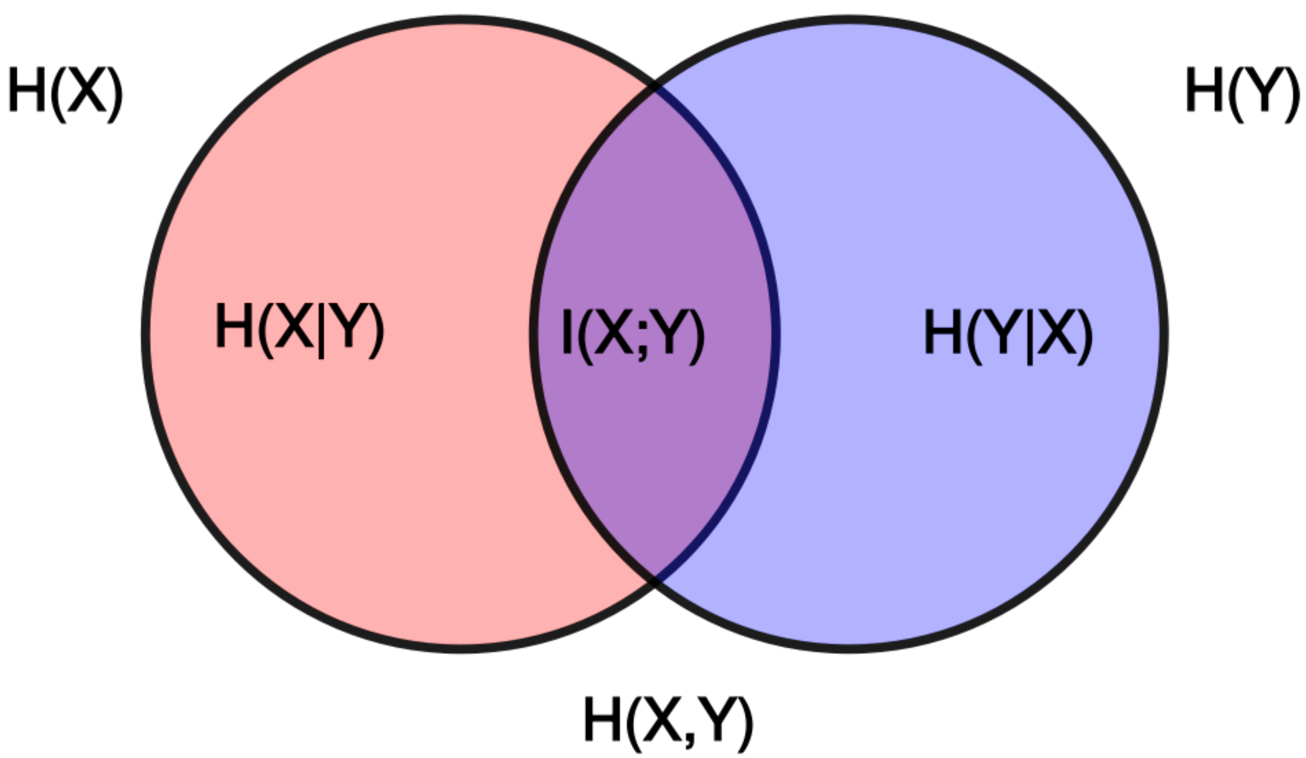
$$\log \tau_\alpha = \alpha + \beta \left(\frac{\langle u_g^2 \rangle}{\langle u^2 \rangle} \right) + \gamma \left(\frac{\langle u_g^2 \rangle}{\langle u^2 \rangle} \right)^2$$

Mutual information gives the general degree of dependence between two random variables

<u>Shannon Entropy</u>

$$H(X) = -\int dx\ p(x)\log p(x)$$

it quantify the randomness of a random variable



X and Y, random variables with joint probability distribution $p(x, y)$

$$H(X, Y)$$

if X and Y are independent

$$p(x, y) = p(x)p(y)$$

$$H(X, Y) = H(X) + H(y)$$

if not

$$I(X, Y) = H(X) + H(Y) - H(X, Y)$$

<u>Mutual Information</u>

Mutual information gives the general degree of dependence between two random variables

X and Y, random variables with joint probability distribution $p(x, y)$

<u>*Shannon Entropy*</u>

$$H(X) = -\int dx\ p(x) \log p(x)$$

it quantify the randomness of a random variable

$$H(X, Y)$$

if X and Y are independent

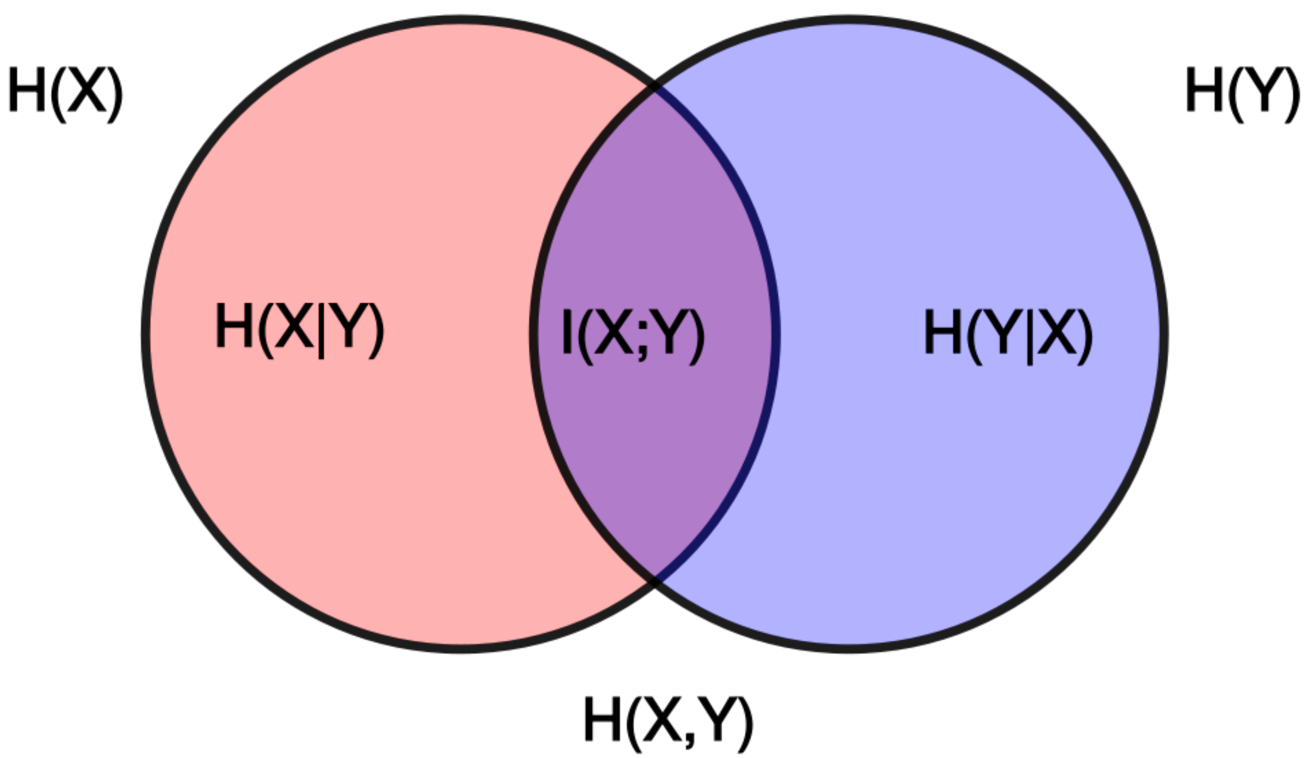
$$p(x, y) = p(x)p(y)$$

$$H(X, Y) = H(X) + H(y)$$

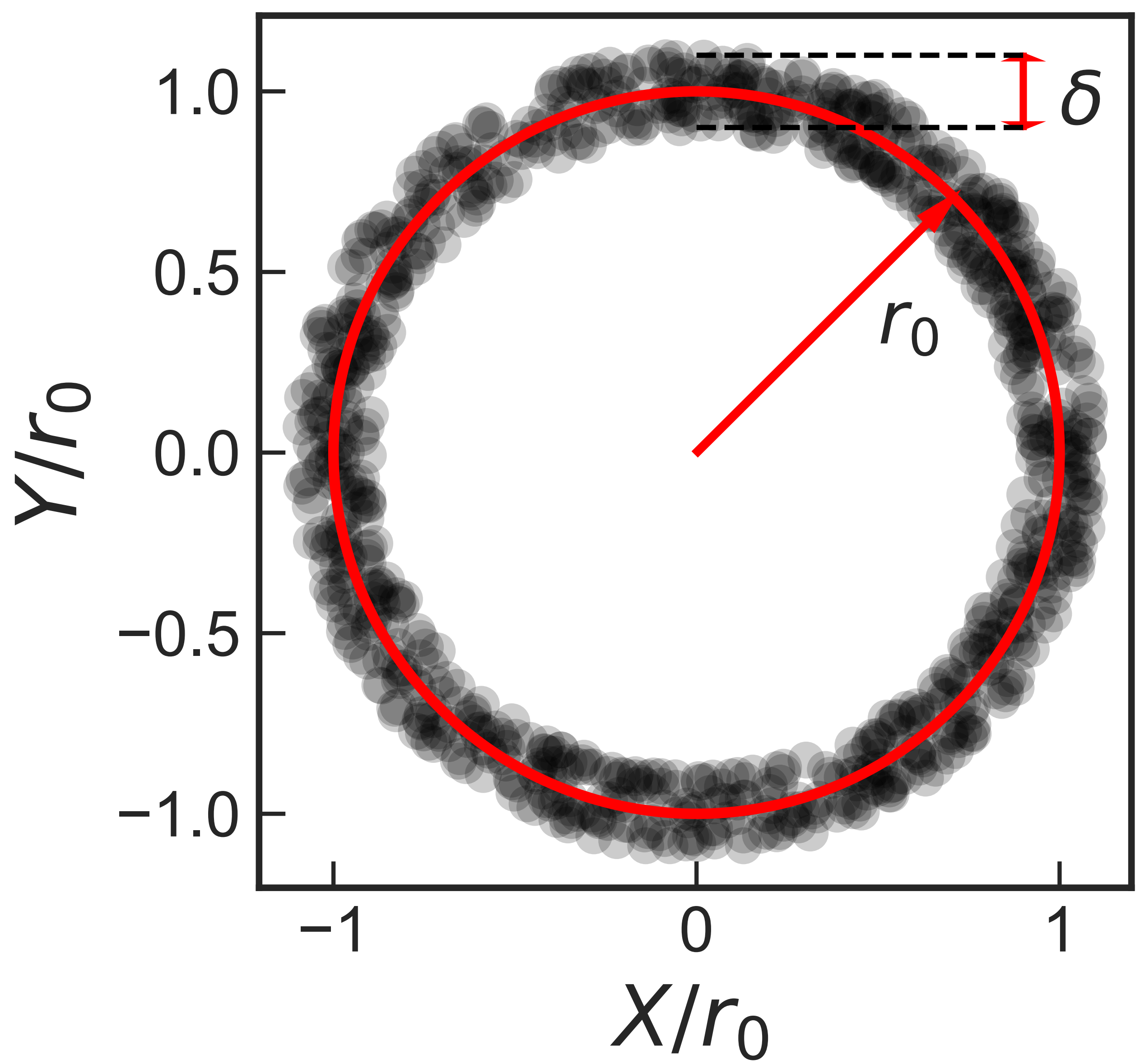
if not

$$I(X, Y) = \int\int dxdy\ p(x, y) \log \left[\frac{p(x, y)}{p(x)p(y)} \right]$$

<u>*Mutual Information*</u>



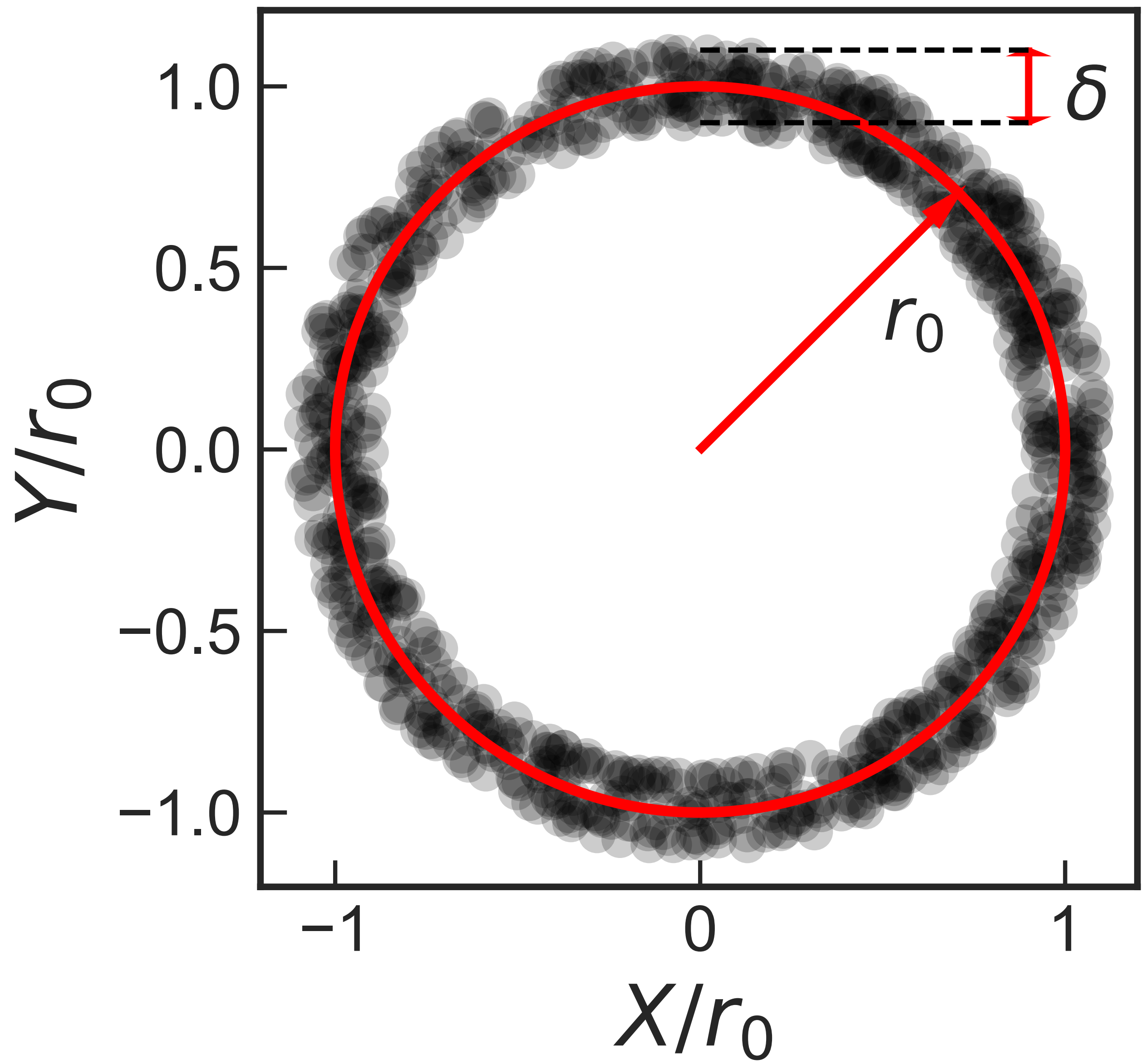
Are X and Y dependent on each other?



<u>*Pearson correlation coefficient*</u>

$$C(X,Y) = \frac{\langle (x - \langle x \rangle)(y - \langle y \rangle) \rangle}{\sigma_X \sigma_Y} = ?$$

Are X and Y dependent on each other?

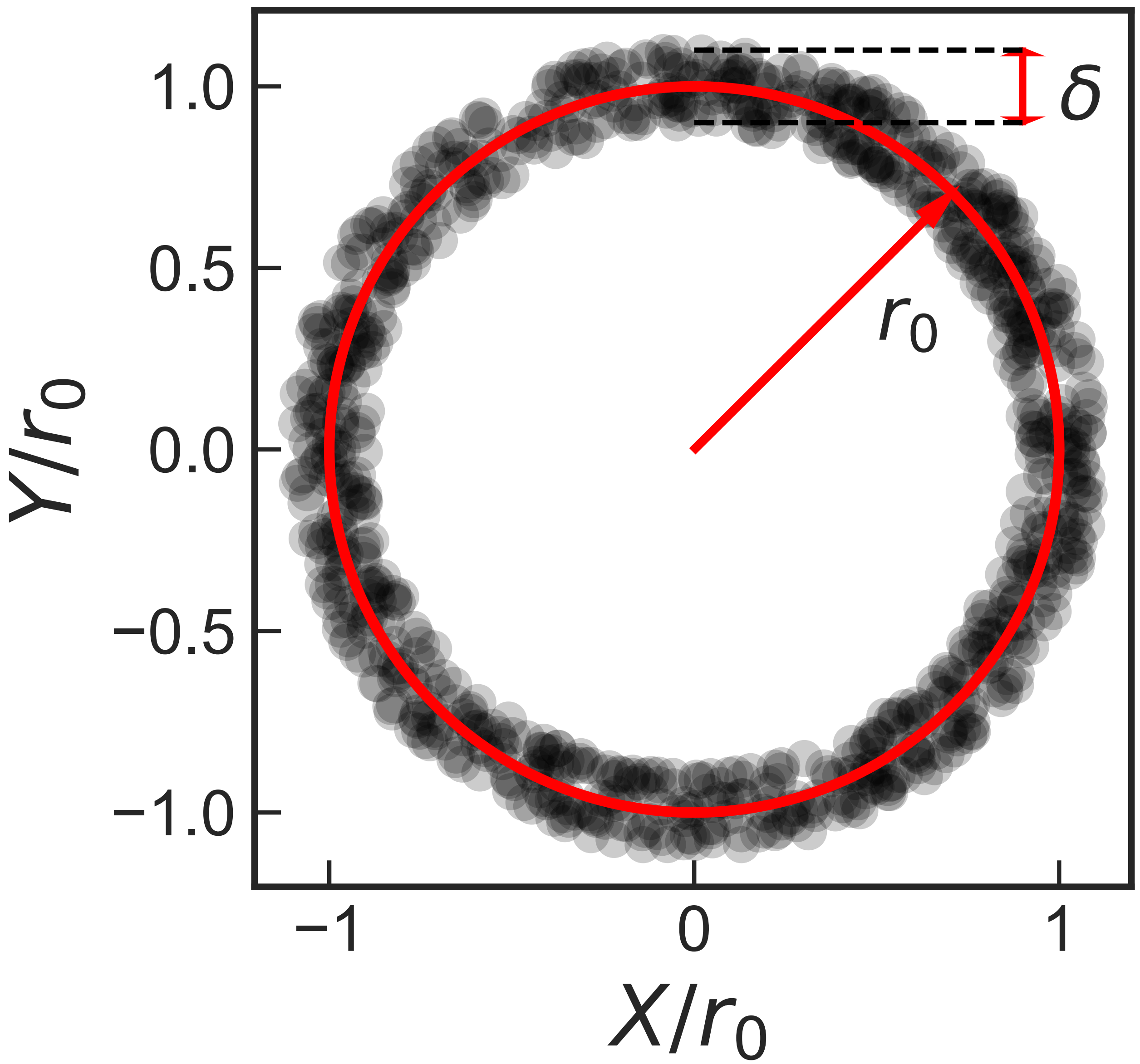


Pearson correlation coefficient

$$C(X,Y) = \frac{\langle (x-\langle x\rangle)(y-\langle y\rangle)\rangle}{\sigma_X \sigma_Y} = 0$$

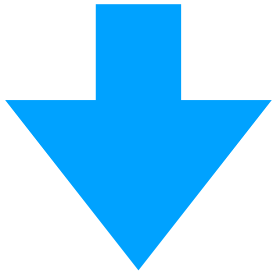
X and Y are independent !?

Are X and Y dependent on each other?



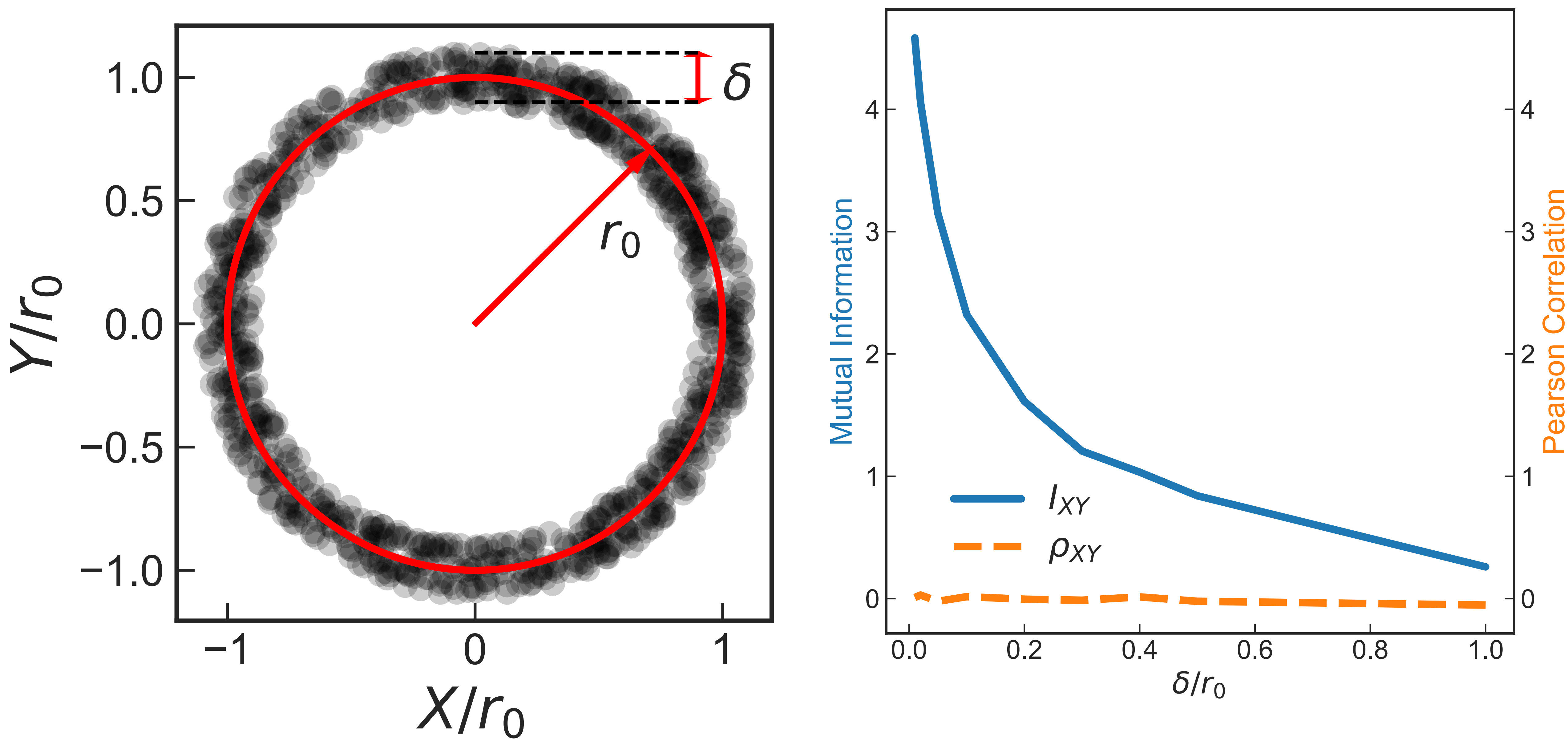
Pearson correlation coefficient

$$C(X, Y) = \frac{\langle (x - \langle x \rangle)(y - \langle y \rangle) \rangle}{\sigma_X \sigma_Y} = 0$$



~~X and Y are independent !?~~

Are X and Y dependent on each other?



$$I(X, Y) \neq 0$$

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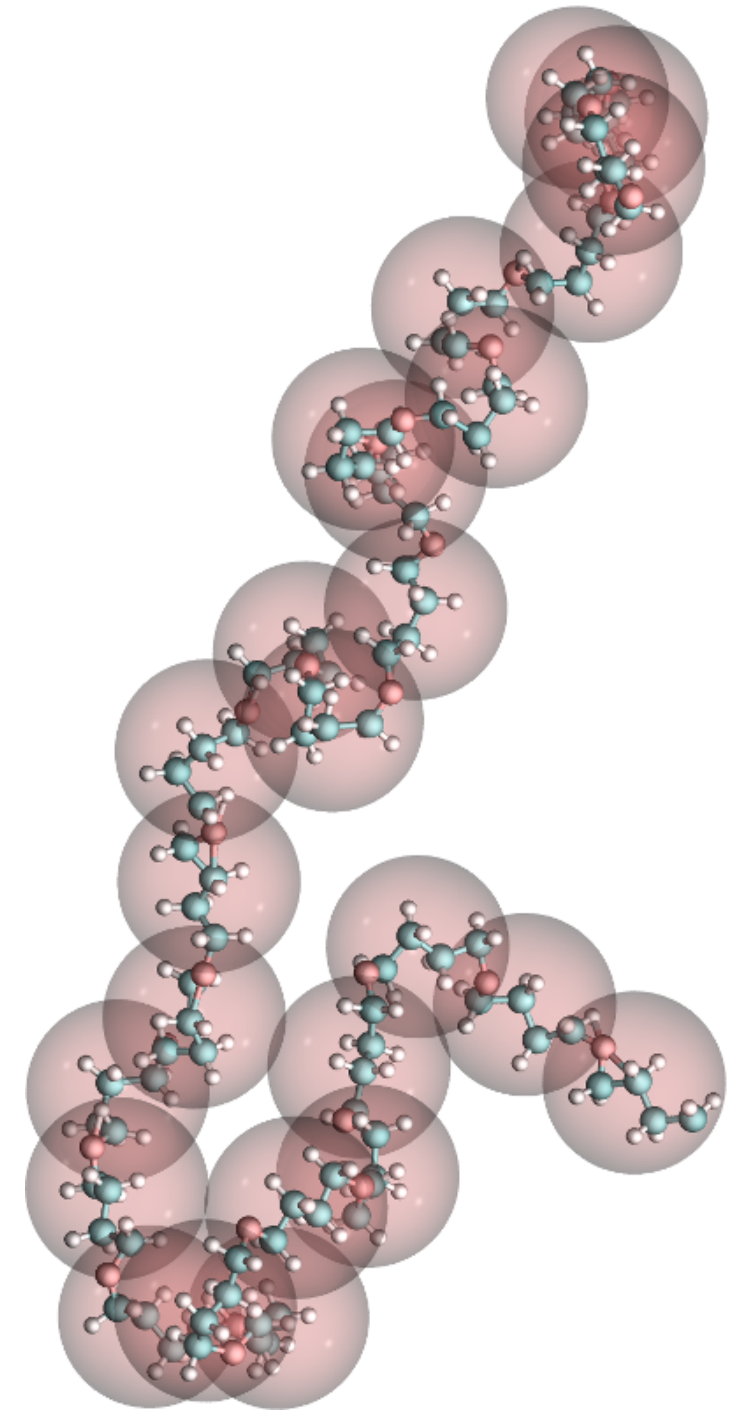
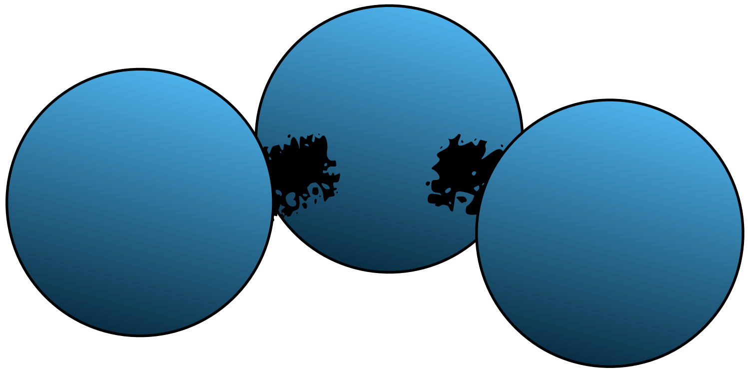
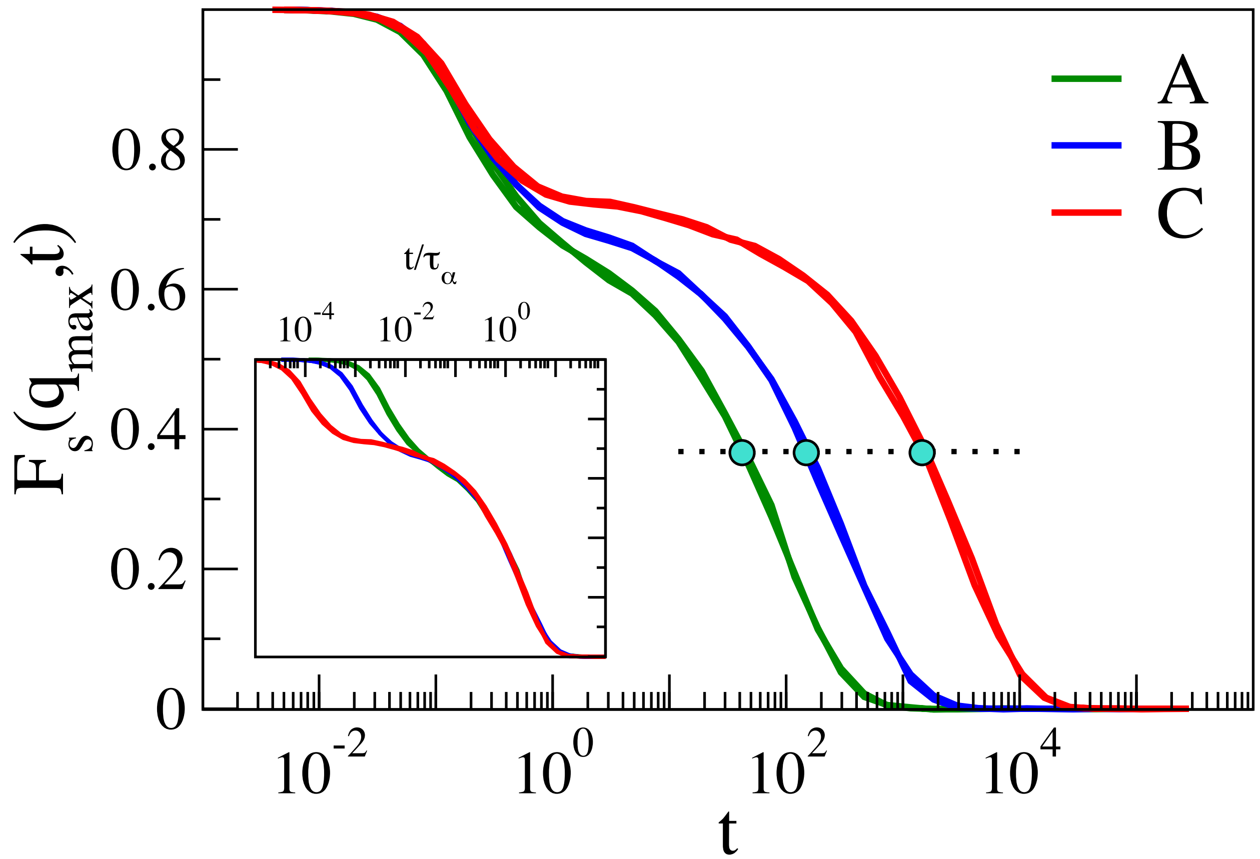
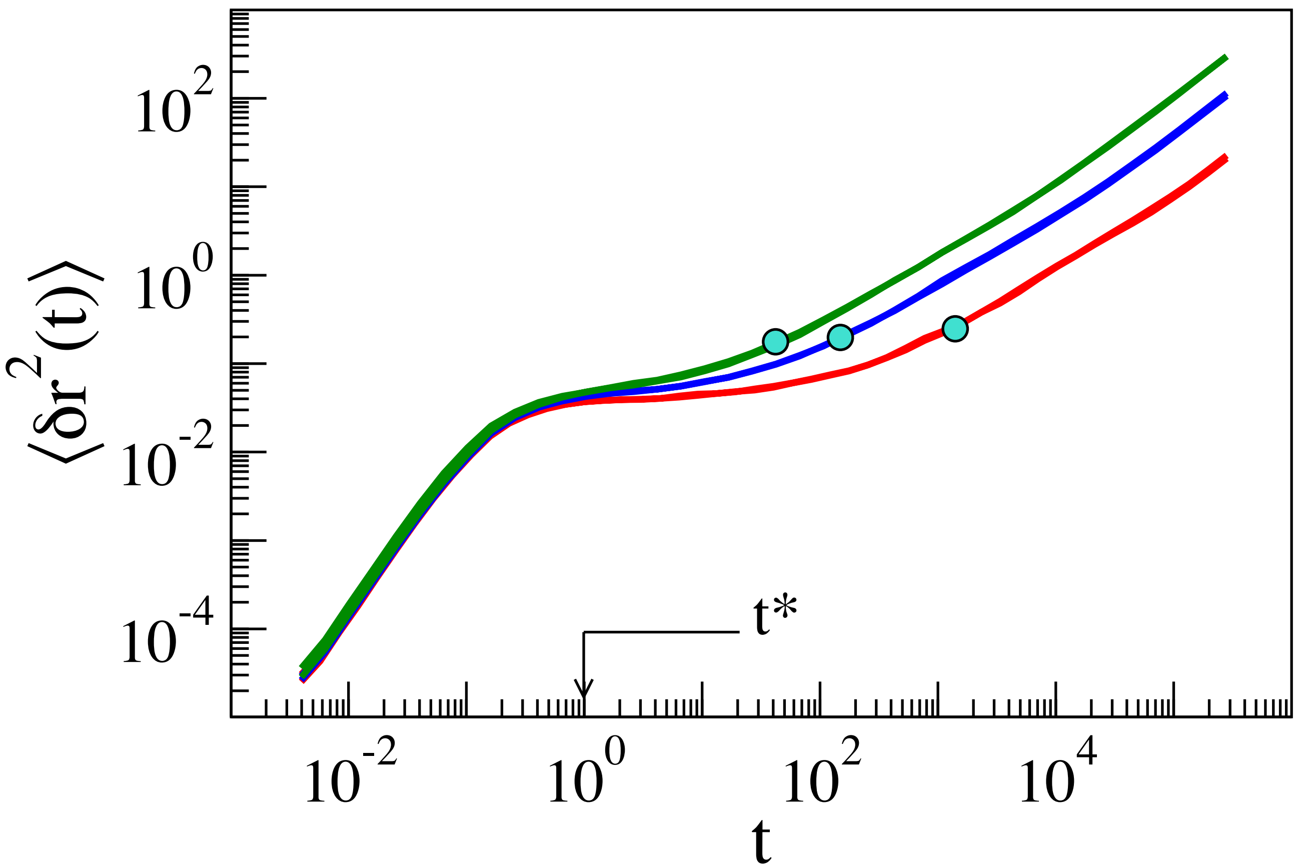


We built three set of iso-relaxing states

Molecular liquid of trimers

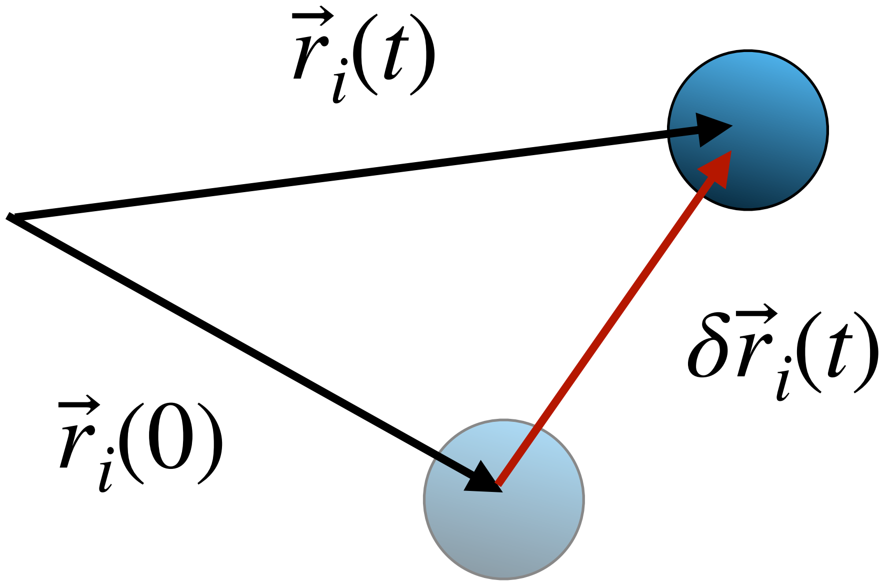




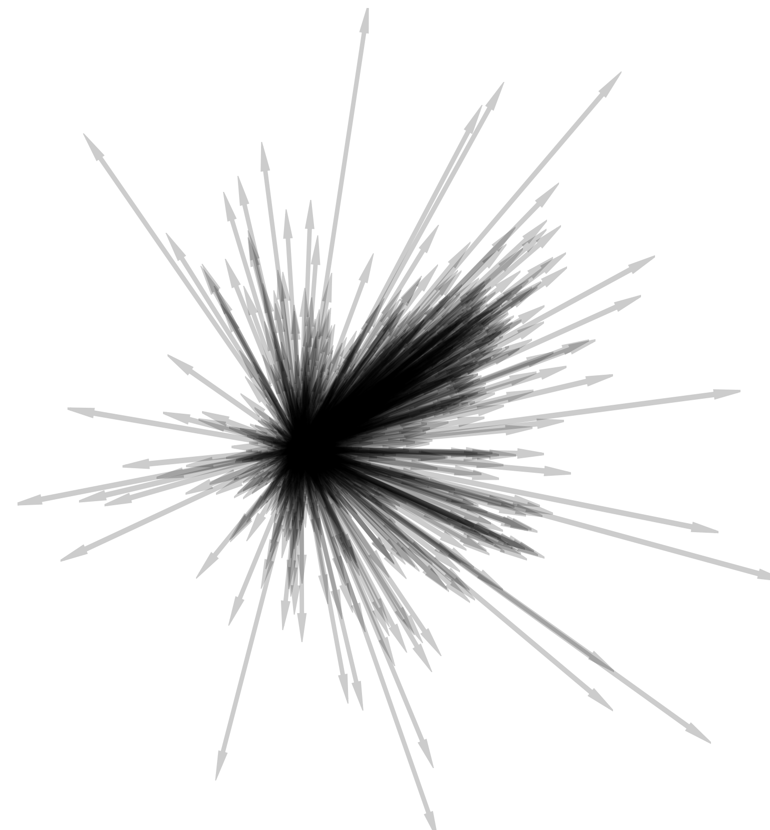


A	**B**	**C**
$\rho = 1.01\ T = 0.47$	$\rho = 1.01\ T = 0.435$	$\rho = 1.01\ T = 0.42$
$\rho = 1.05\ T = 0.60$	$\rho = 1.03\ T = 0.49$	$\rho = 1.05\ T = 0.51$

We investigate displacement correlation between pairs of particle through mutual information



Displacement distribution in the iso-configurational ensemble

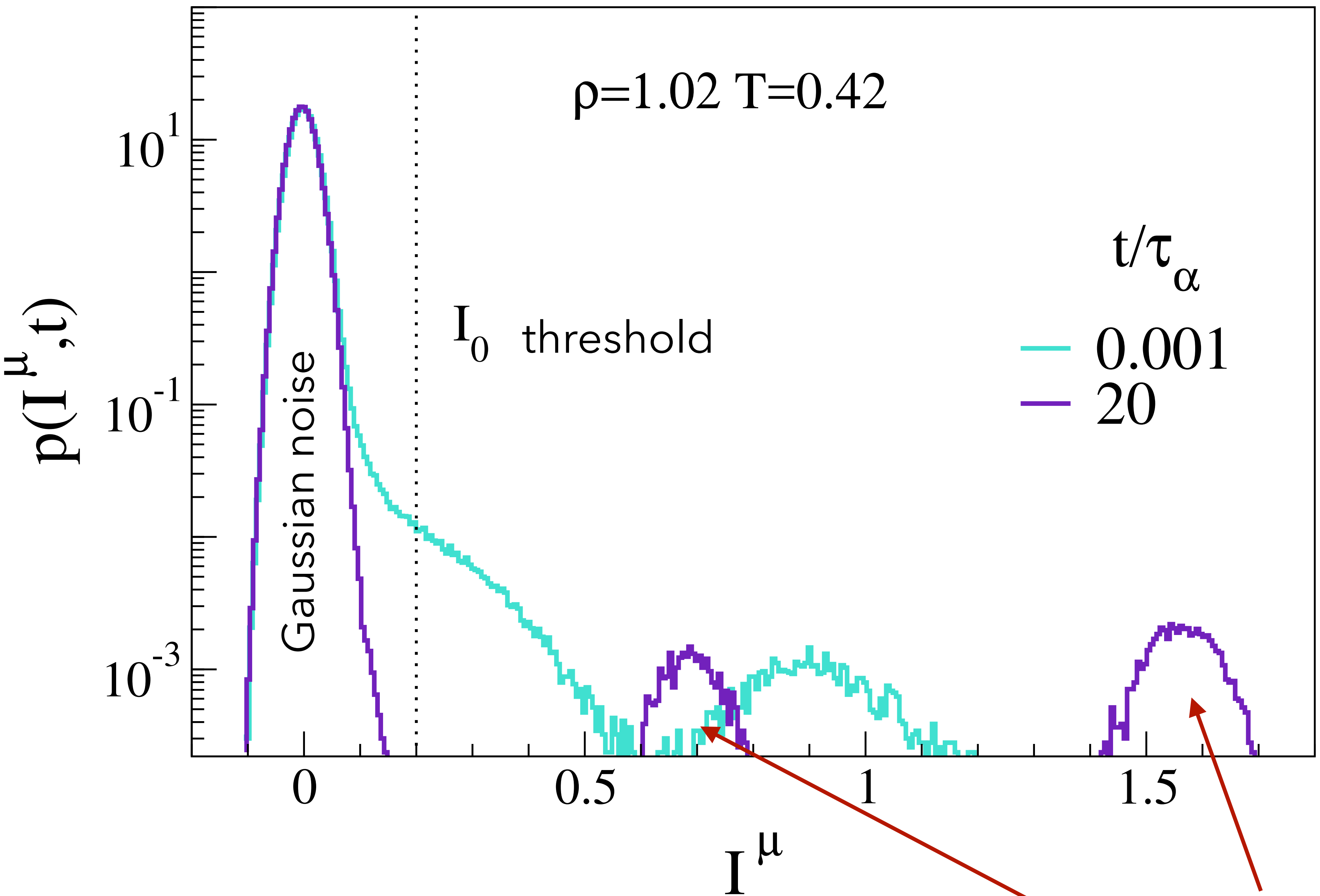


Iso-configurational ensemble

- *Take an equilibrated configuration*
- *Erase all the velocities*
- *Re-assign velocities according to a M-B at the same temperature*

$$I_{ij}(t) = I(\delta\vec{r}_i(t), \delta\vec{r}_j(t))$$

Particles above threshold are said to be significantly correlated



Neighbors in the chain

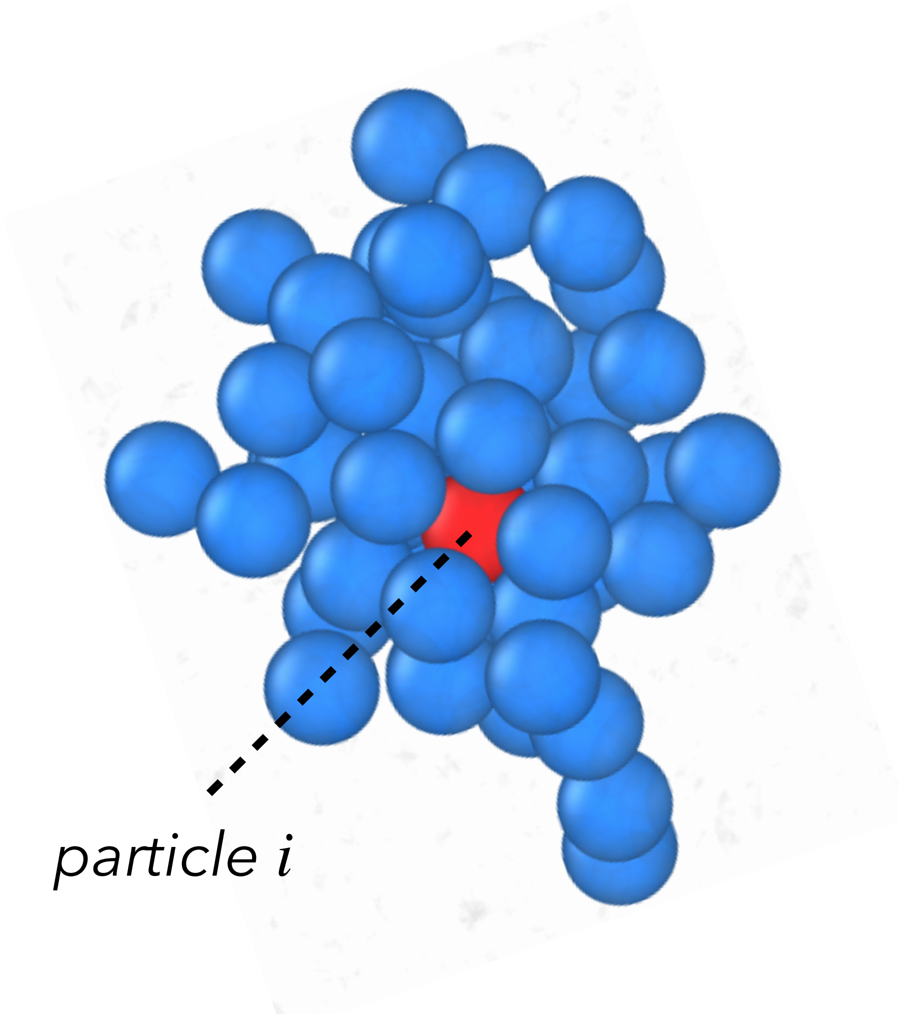
μ

starting configuration

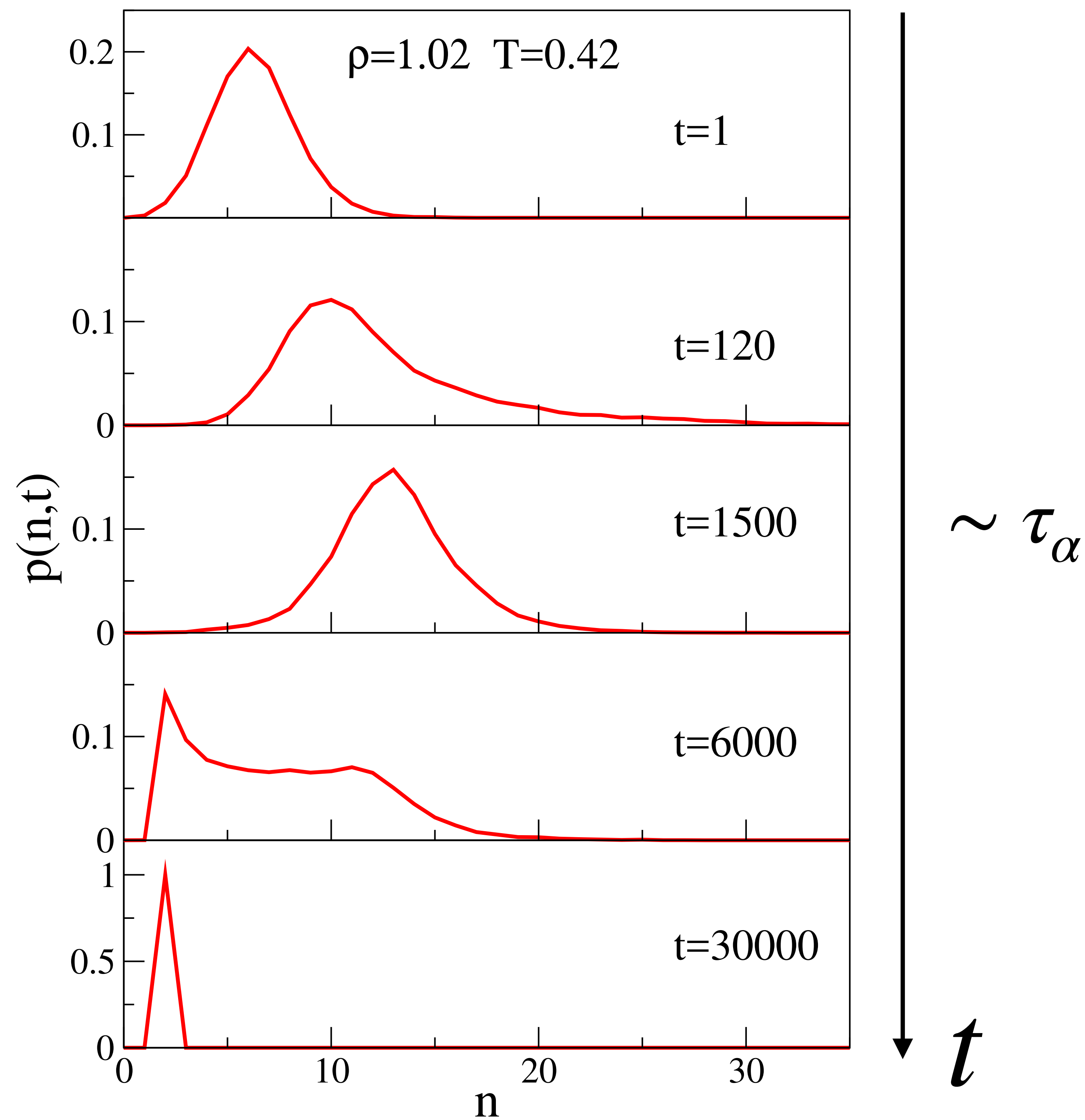
I^{μ}_{ij} *is a* $N \times N$ *matrix*

$(N = 3999)$

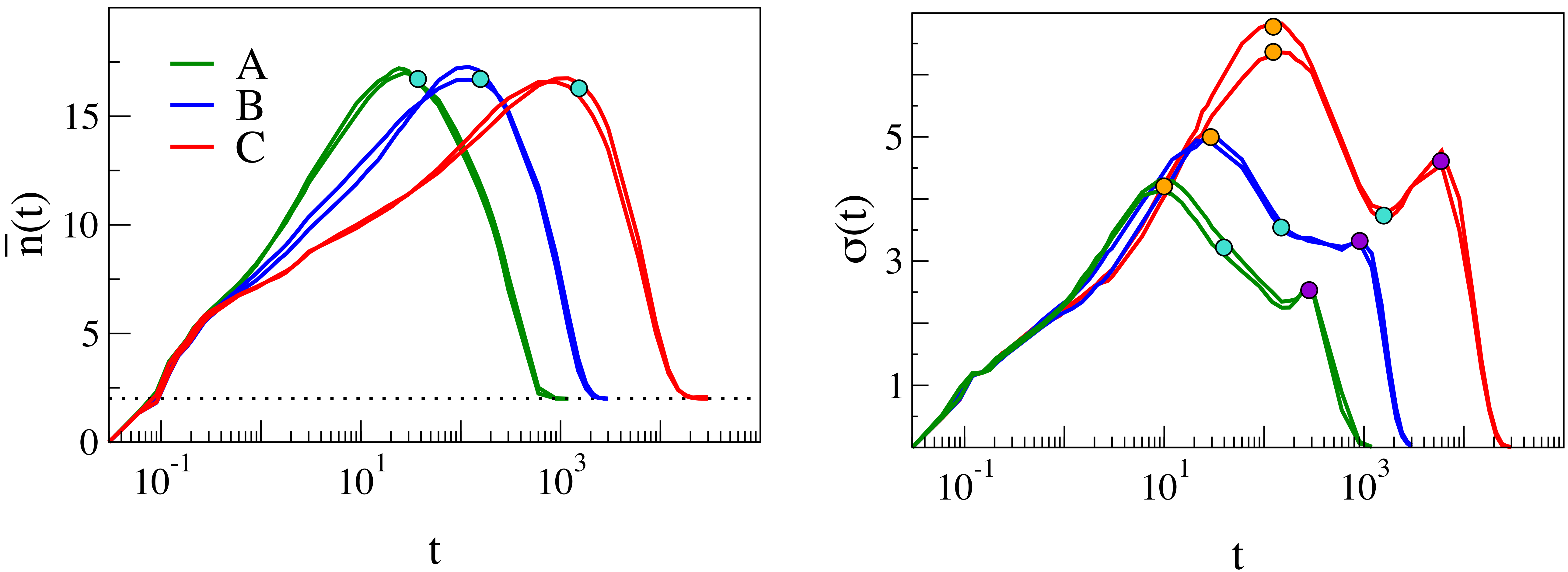
At each time we can compute the distribution of the number of particle correlated to a tagged one



n_i *correlated particles at time t*



The distribution can be characterized by its mean value and standard deviation



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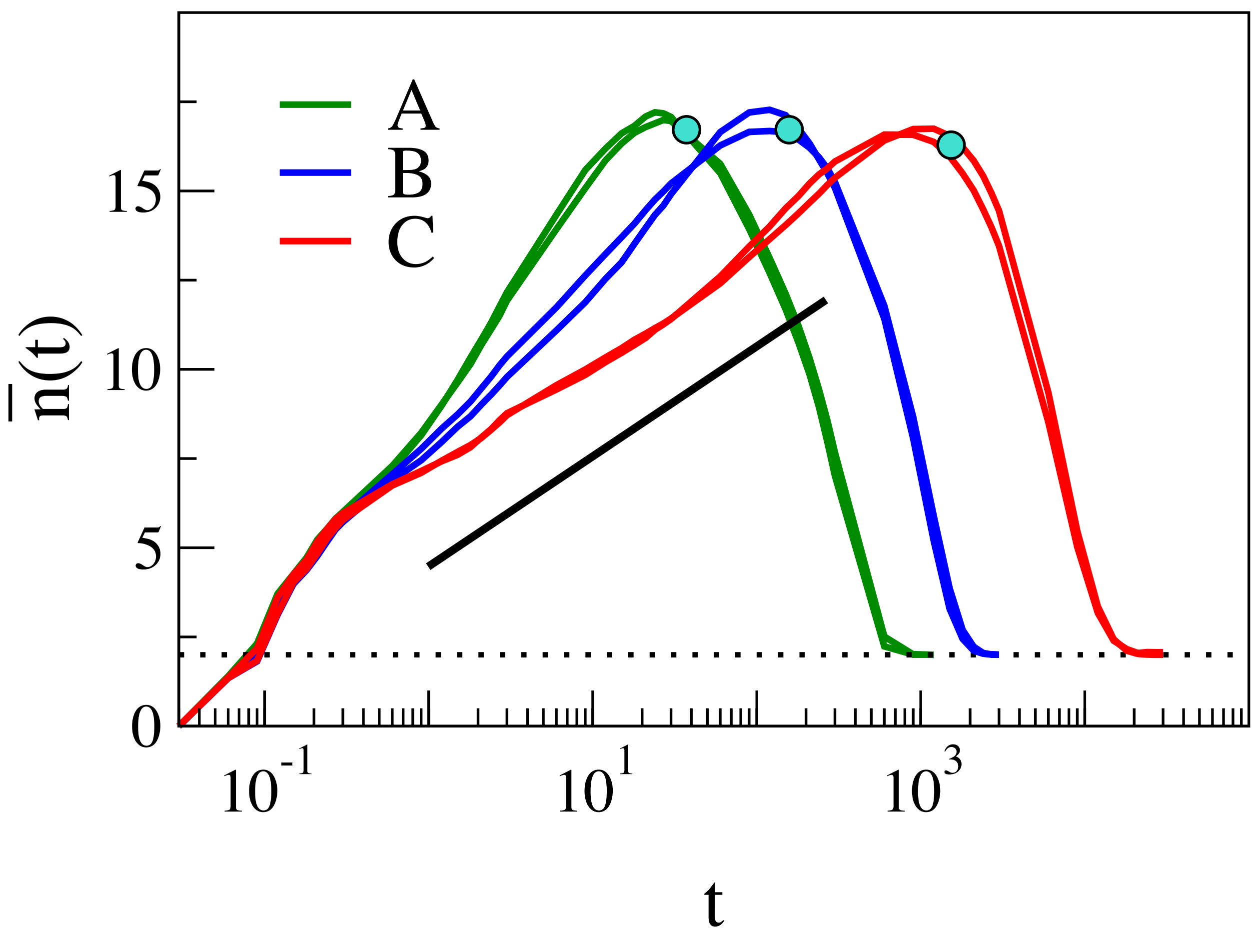
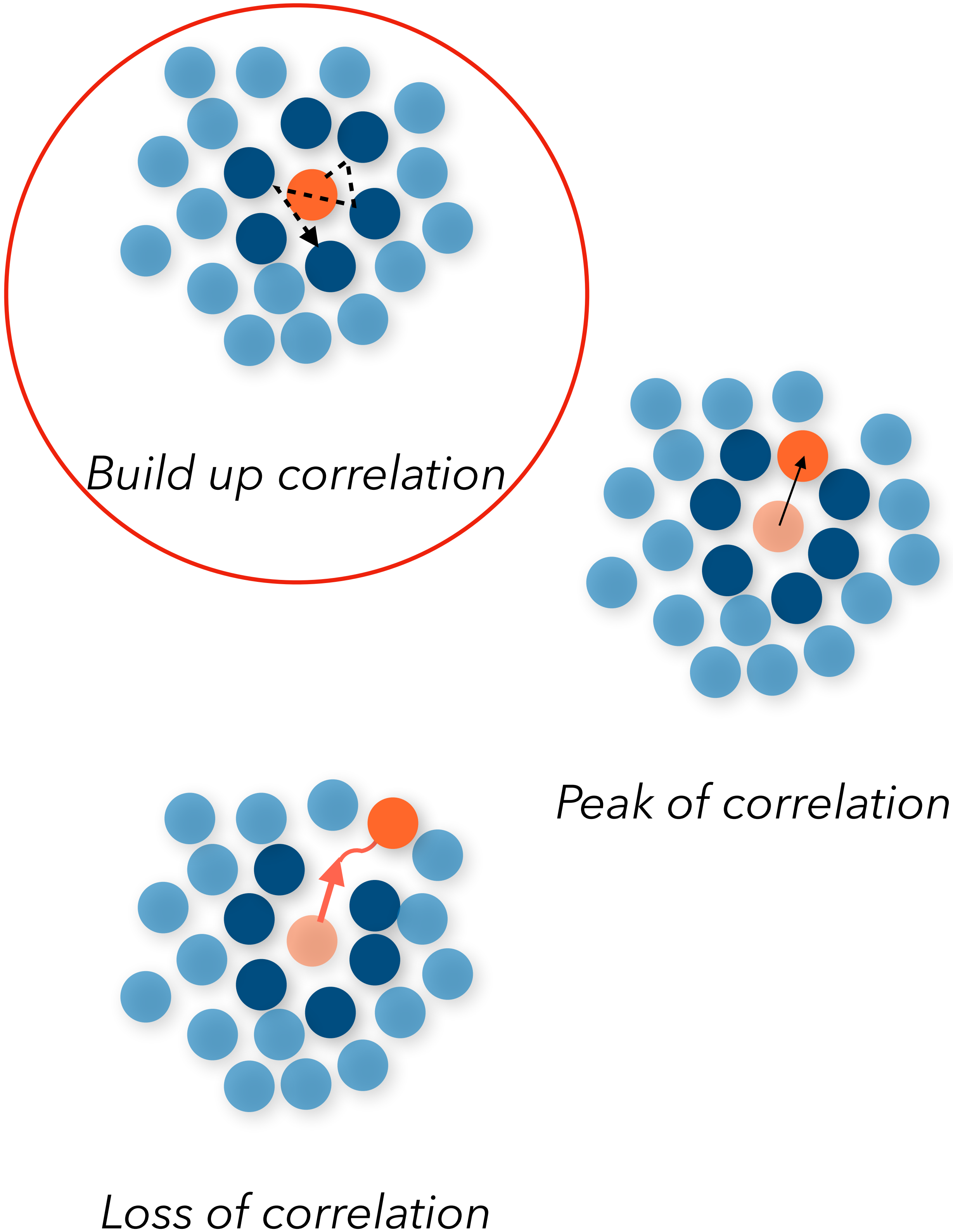


The maximum value of $\overline{n}(t)$ do not increase with τ_α



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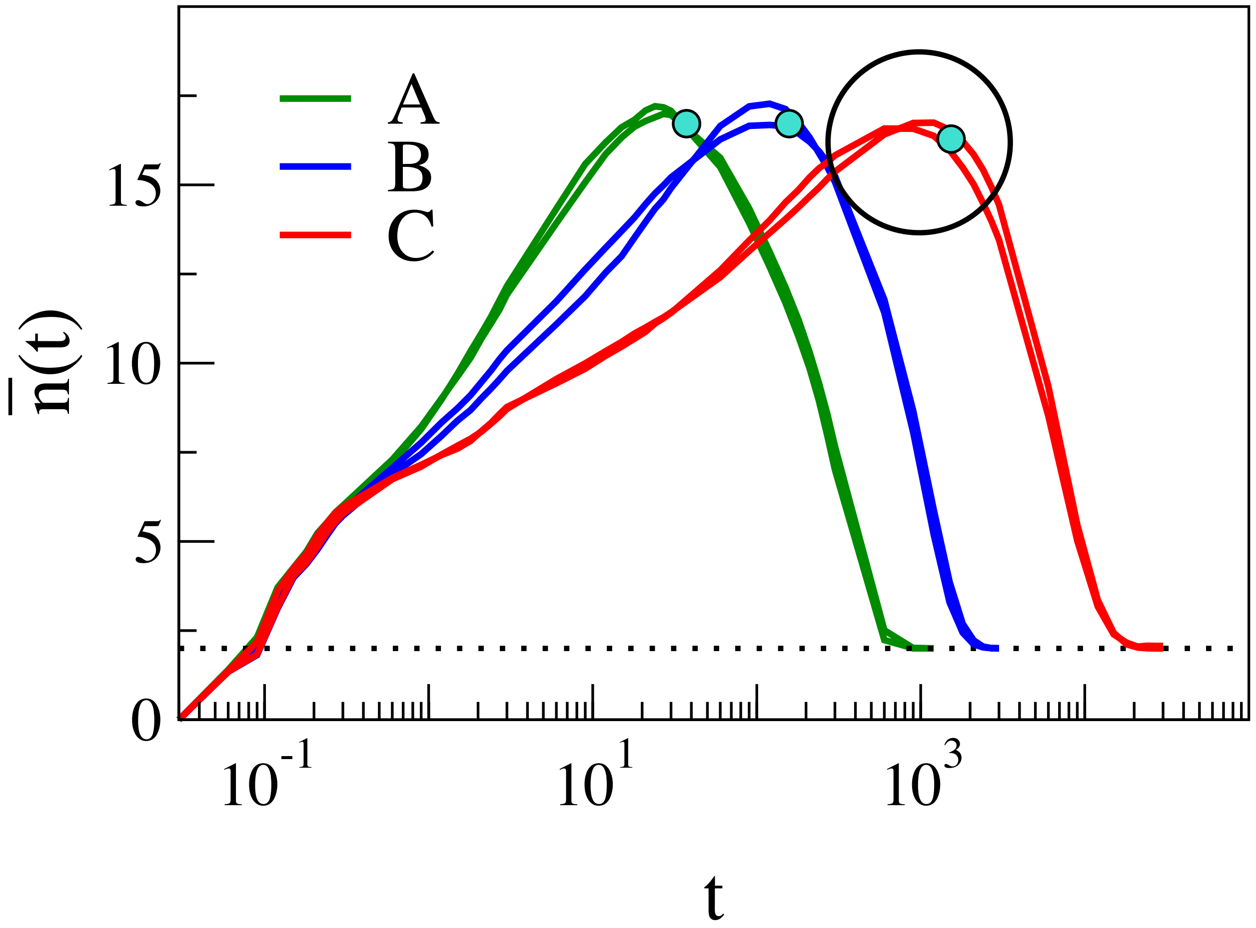

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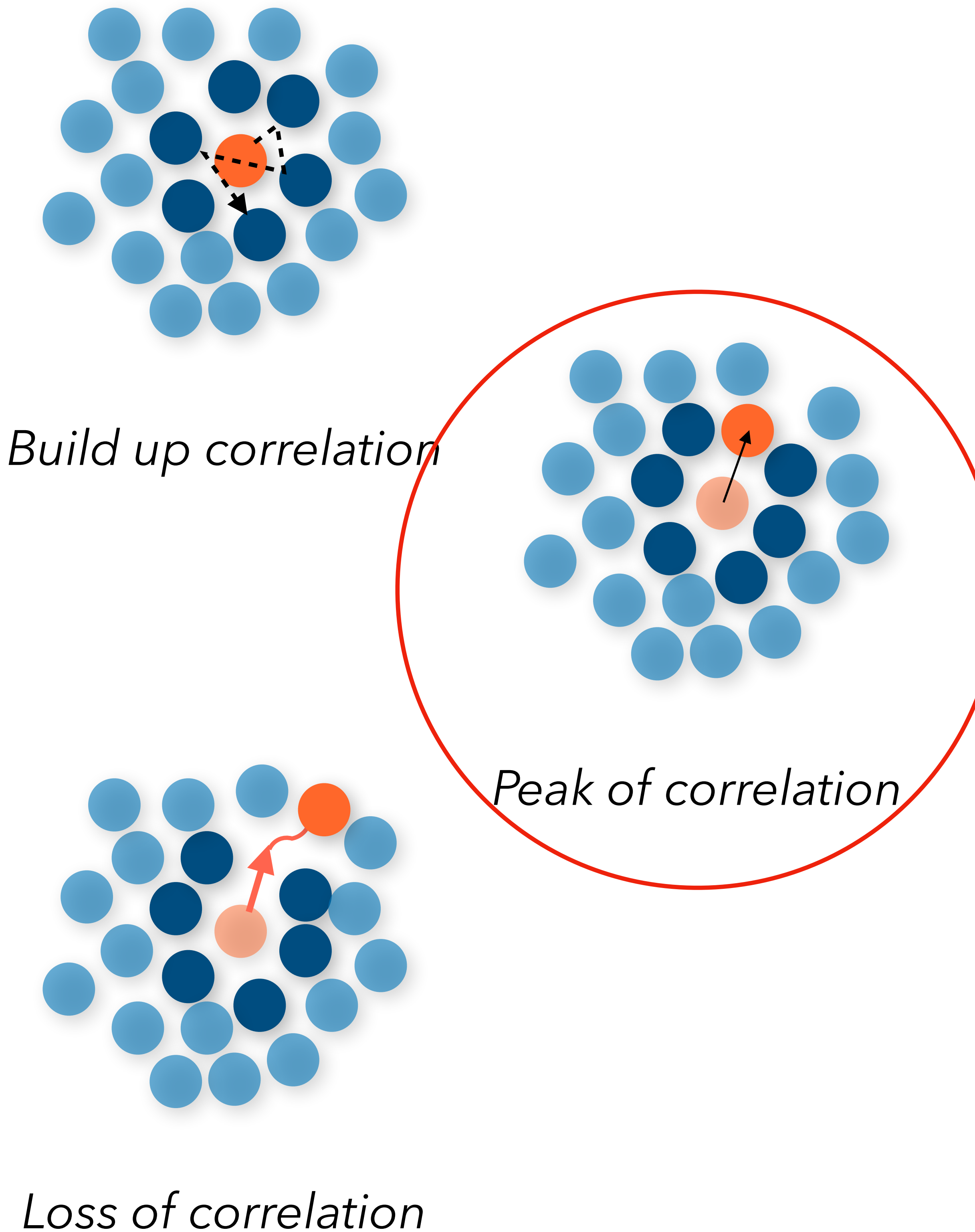

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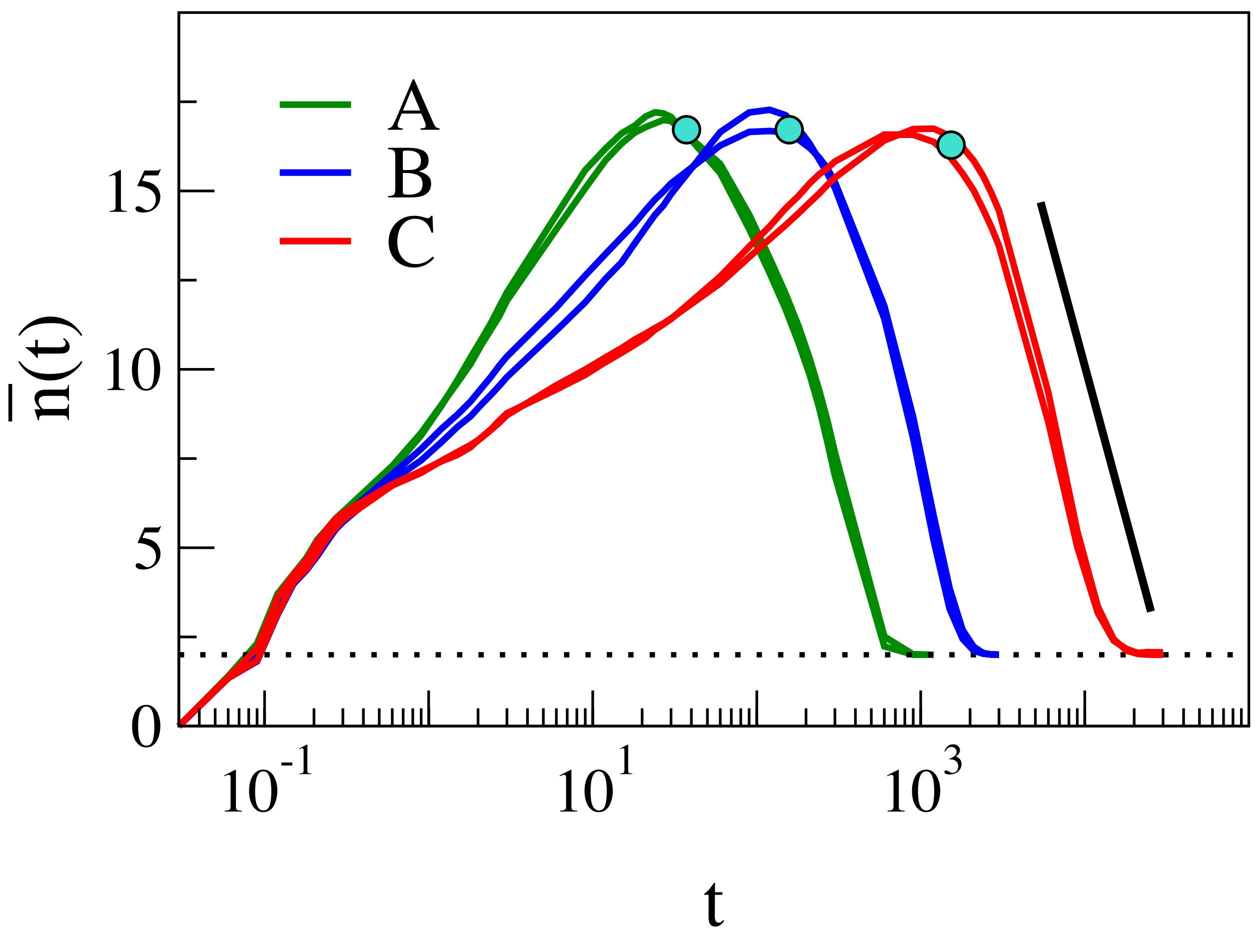

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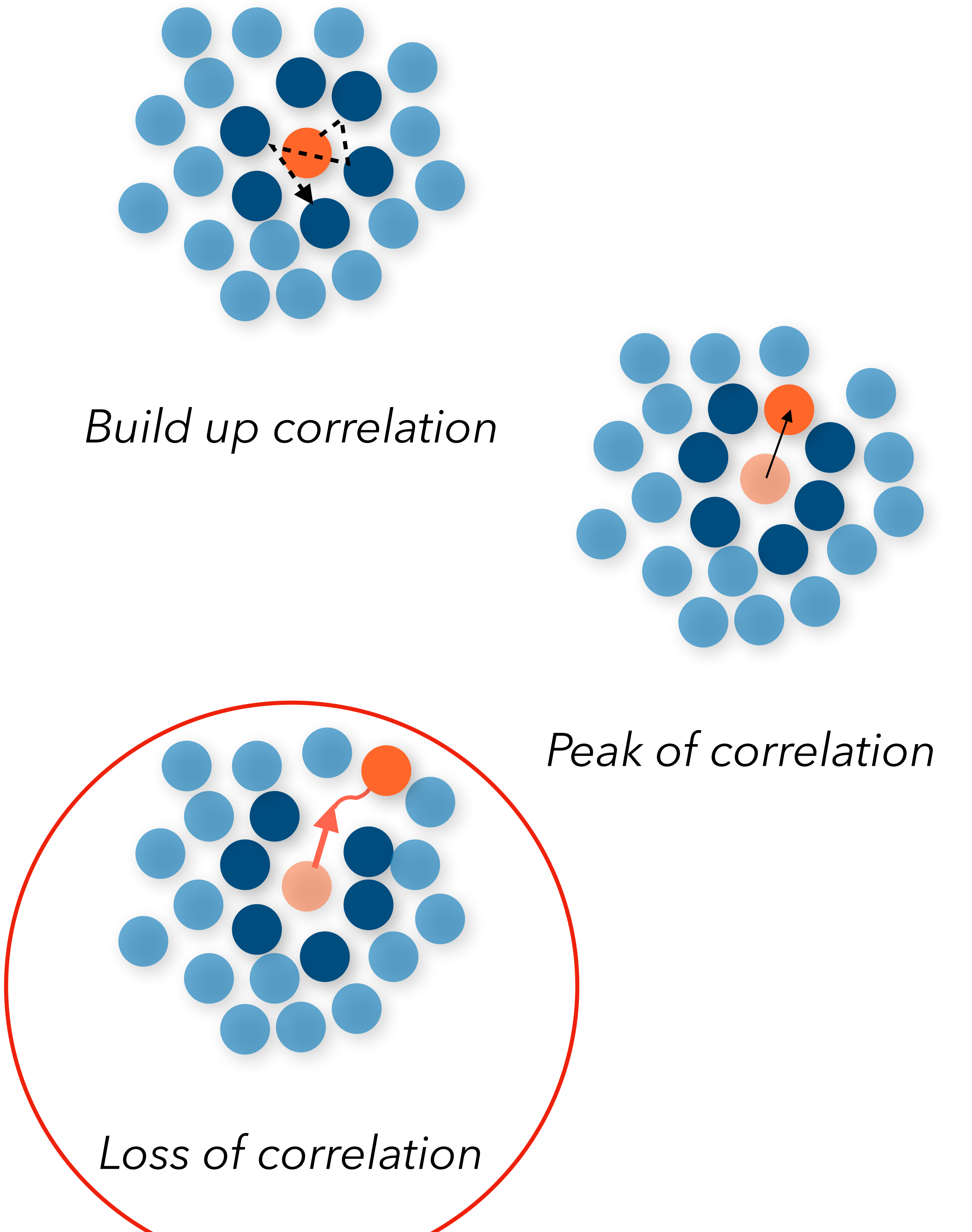

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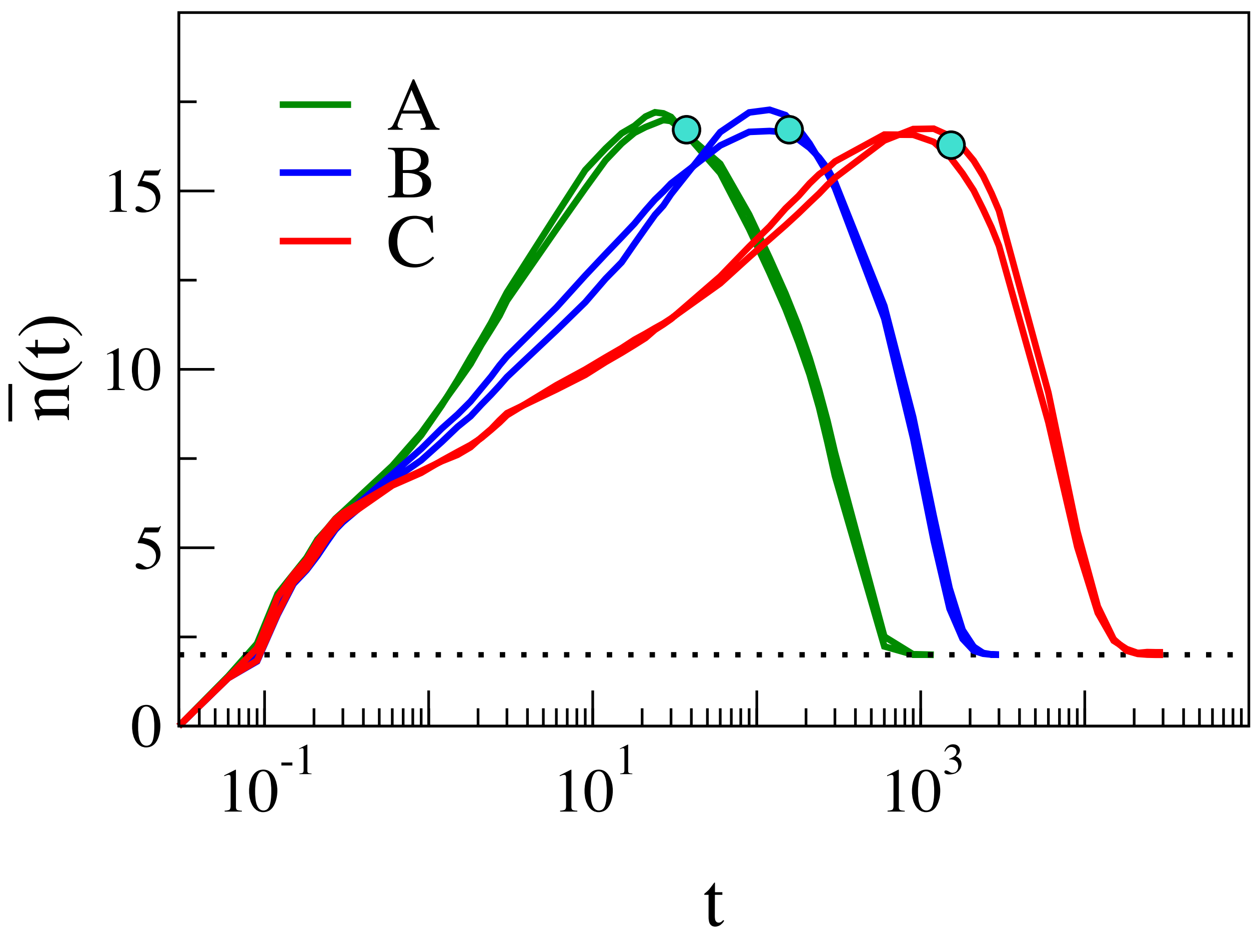
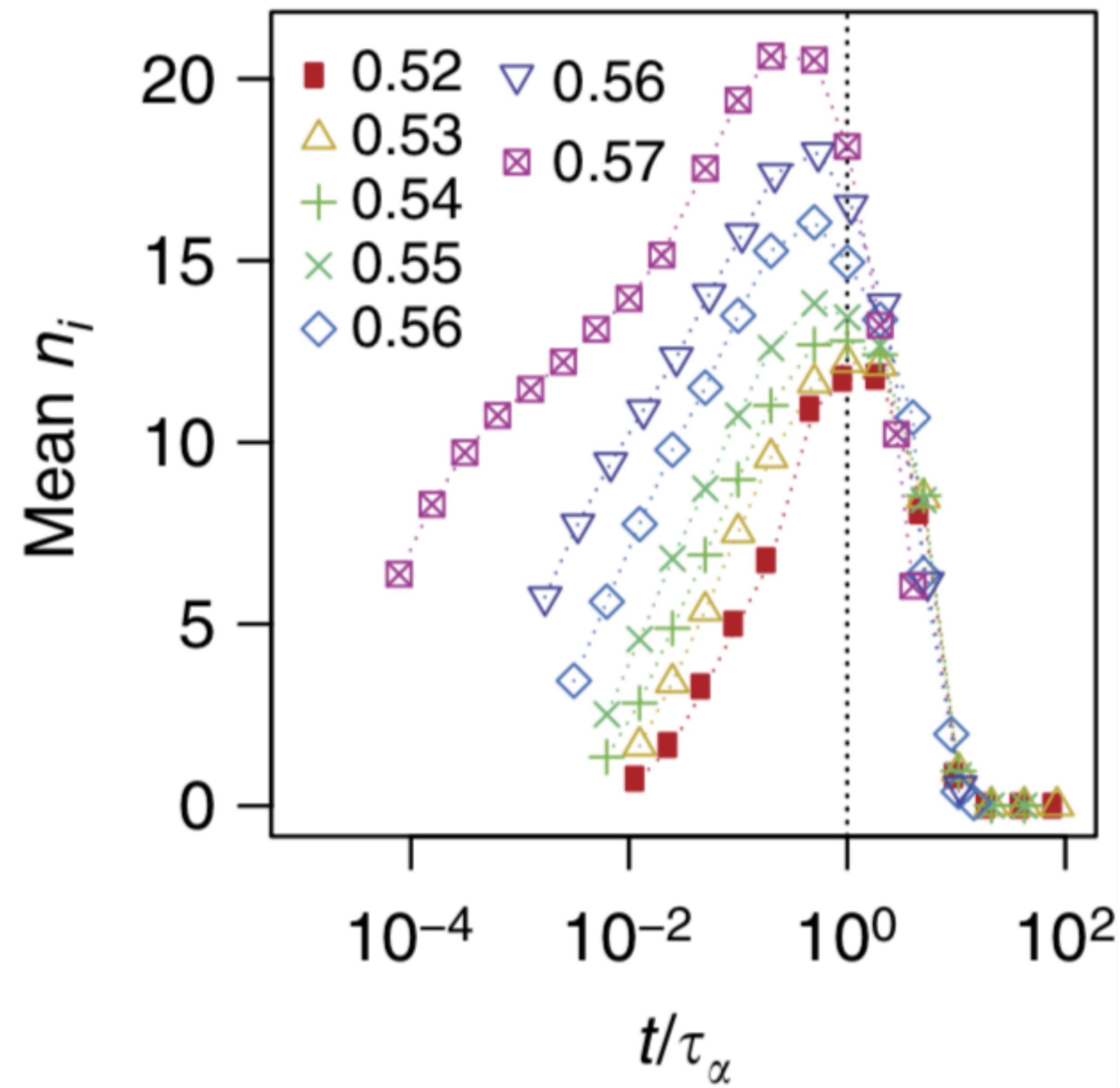


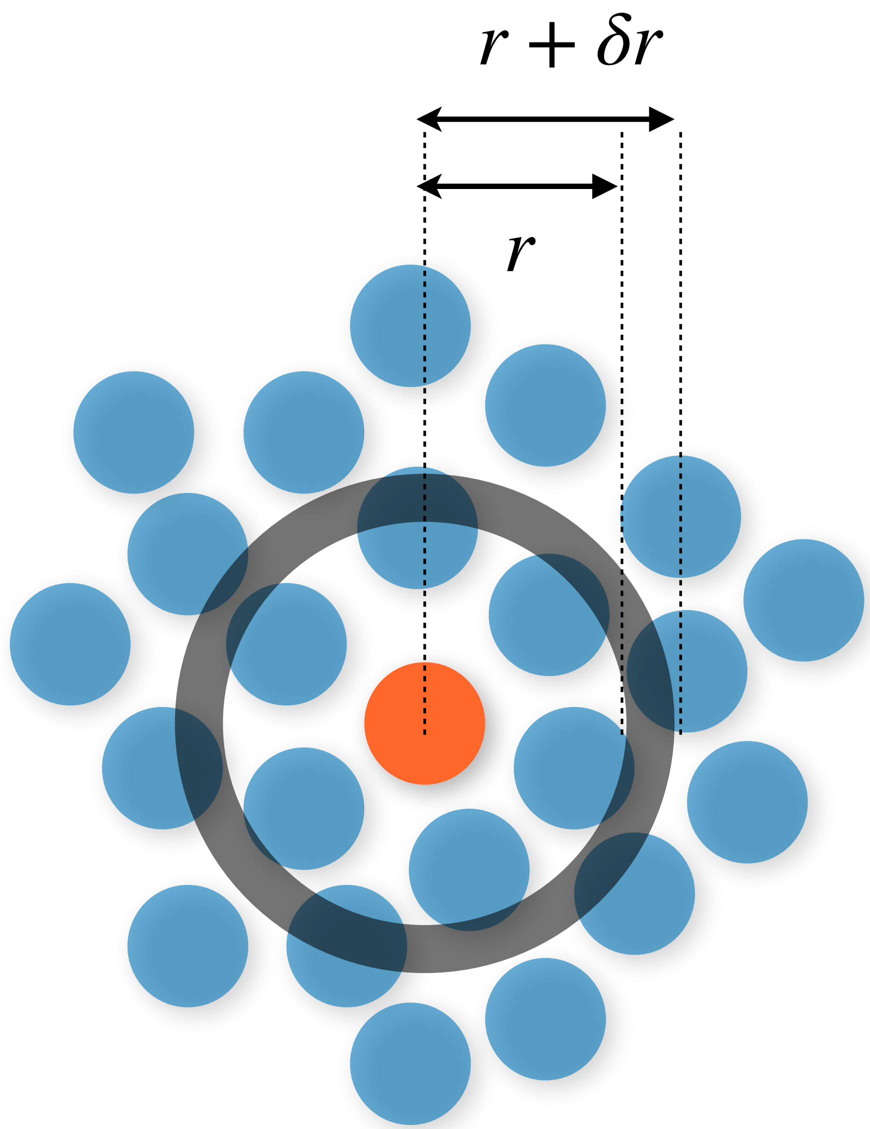
The maximum value of $\bar{n}(t)$ do not increase with τ_α



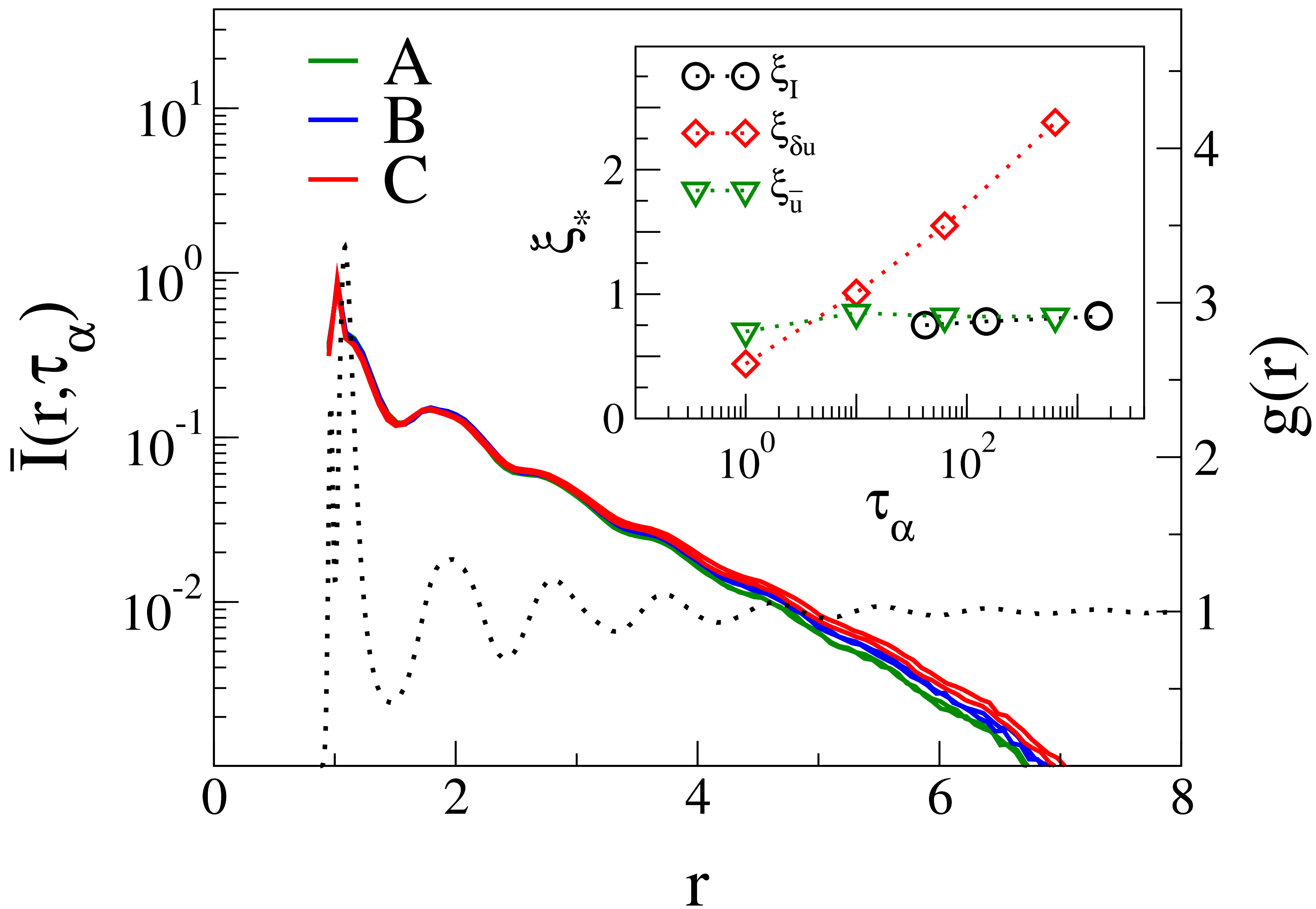
A. J. Dunleavy *et al.* , Nature Communications 6, 6089 (2015)

Loss of correlation

Mutual information correlation length increases weakly approaching the glass transition



A. Tripodo, A. Giuntoli, M. Malvaldi, and D. Leporini, SoftMatter , (2019)

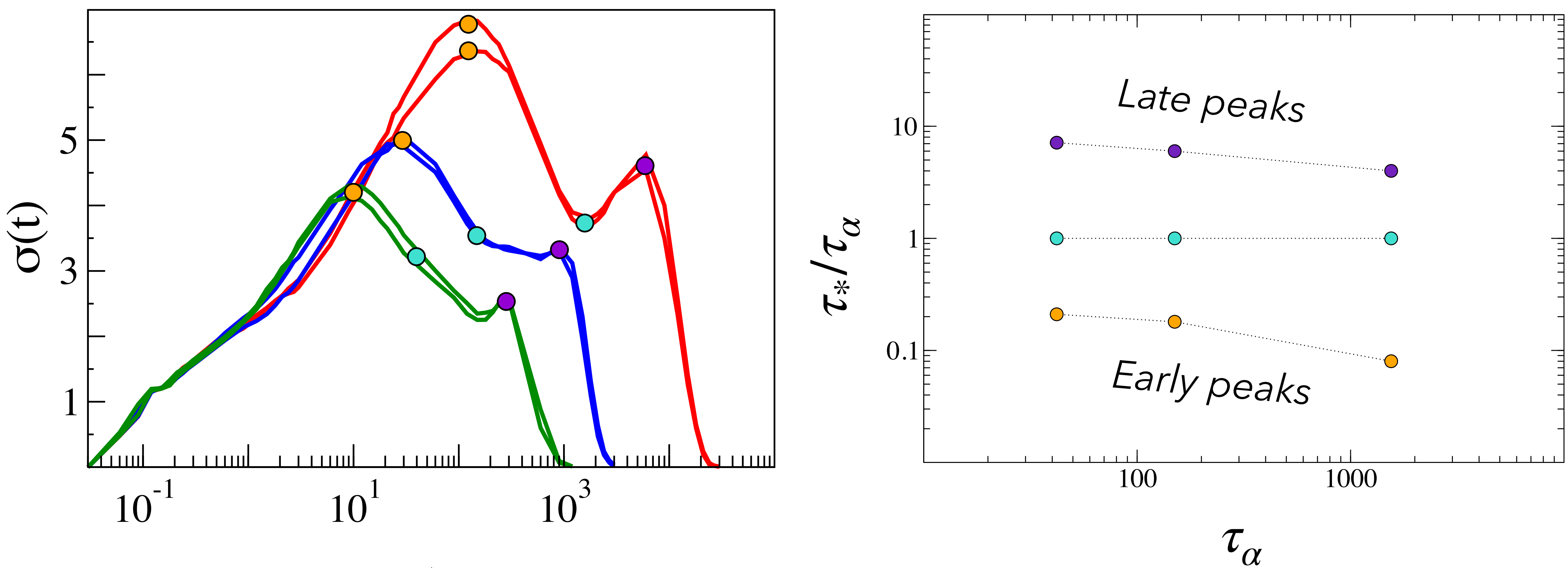


Conventional displacement correlation functions

$$C_{\bar{u}}(r,t) = \langle \hat{\mathbf{u}}_i(t_0,t) \cdot \hat{\mathbf{u}}_j(t_0,t) \rangle \longrightarrow \xi_{\bar{u}}$$

$$C_{\delta u}(r,t) = \frac{\langle \delta u_i(t_0,t)\delta u_j(t_0,t) \rangle}{\langle [\delta u(t_0,t)]^2 \rangle} \longrightarrow \xi_{\delta u}$$

Standard deviation reveals two length scales

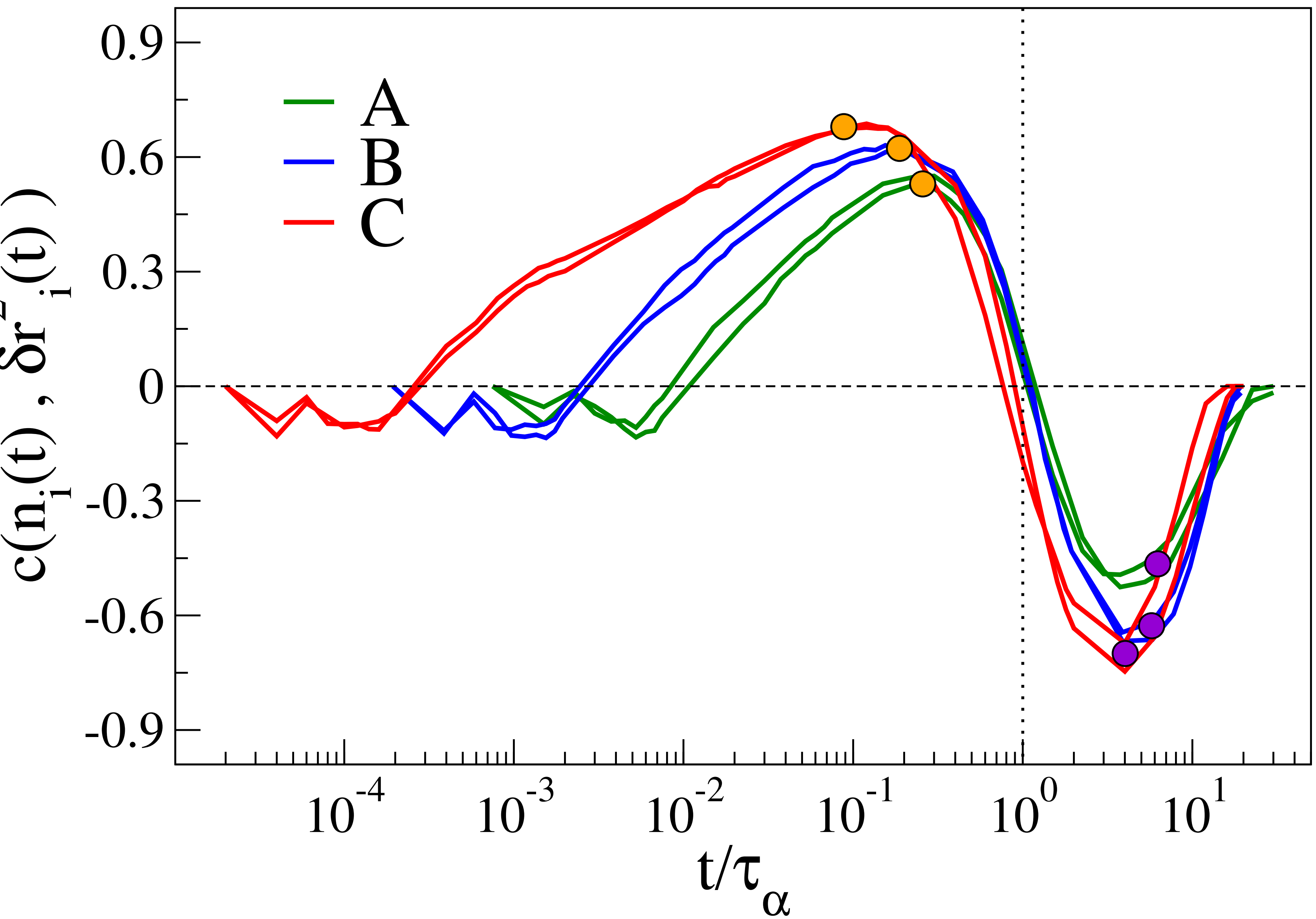


we need to characterize monomers on the basis of $n_i(t)$

High $n_i(\tau_{early})$ implies high mobility
High $n_i(\tau_{late})$ implies low mobility

Pearson correlation coefficient:

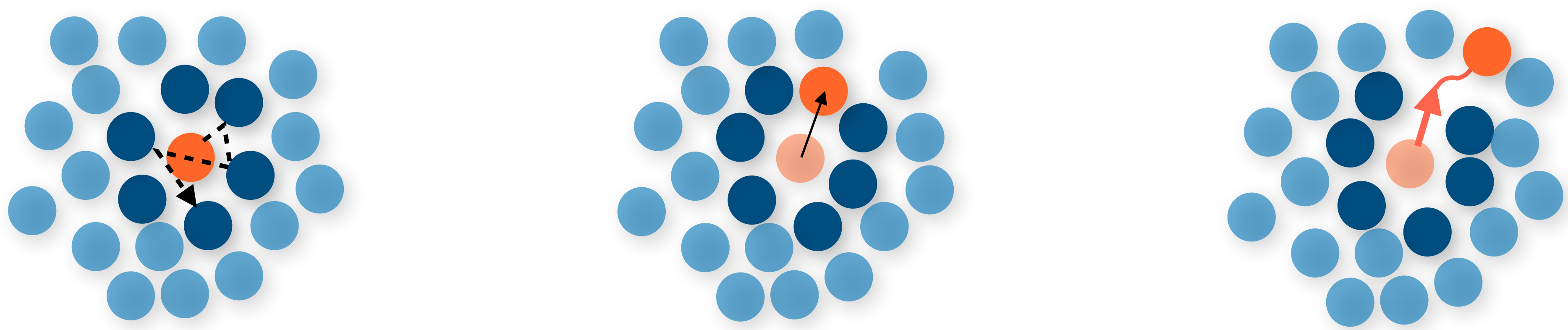
$$c(n_i(t), \delta r_i^2(t)) = \frac{\langle (n_i(t) - \langle n_i(t) \rangle)(\delta r_i^2(t) - \langle \delta r_i^2(t) \rangle) \rangle}{\sigma_{n_i} \sigma_{\delta r_i^2}}$$



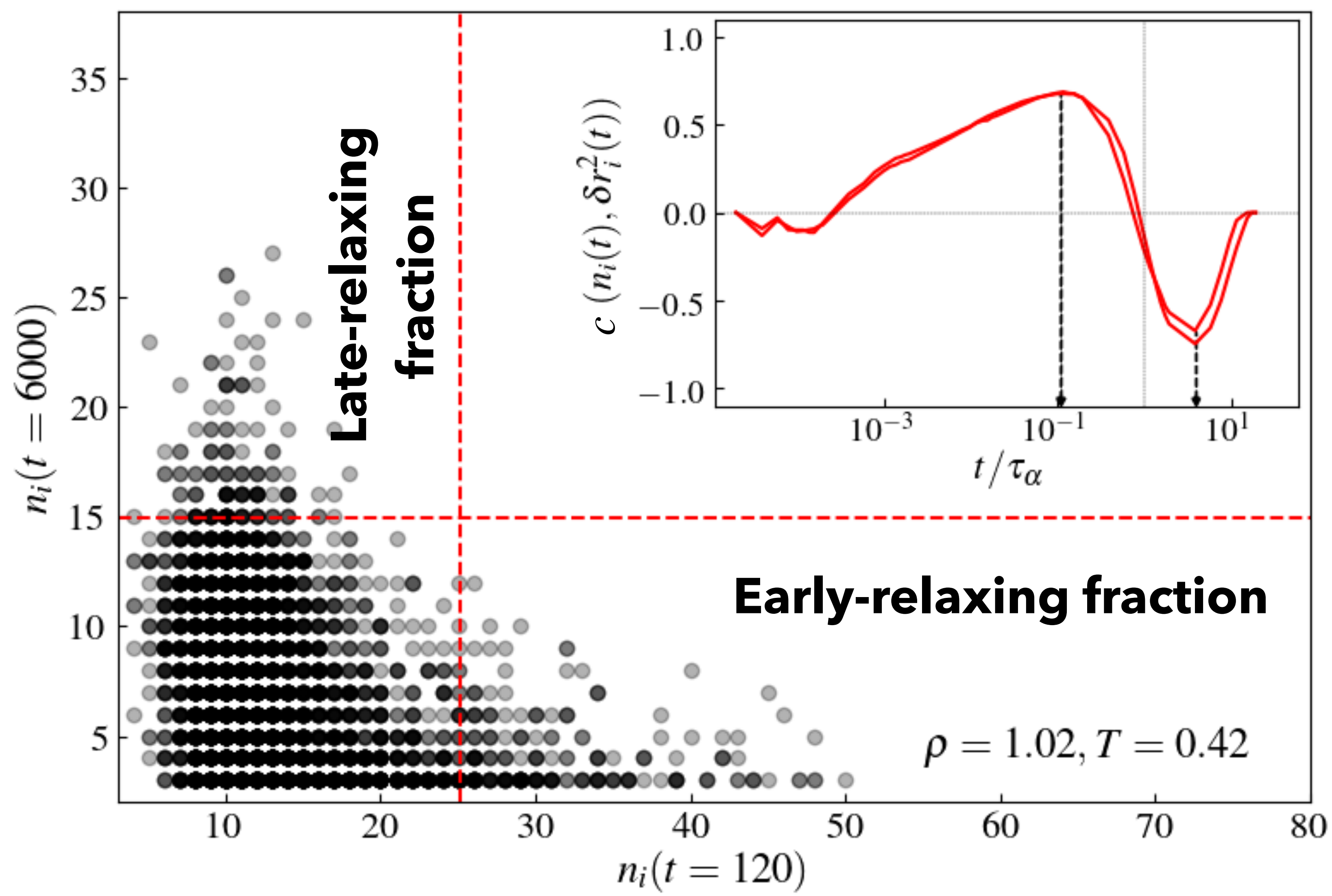
Propensity:

$$\delta r_i^2(t) = |r_i(t) - r_i(0)|^2$$

τ_{early} and τ_{late} mark two modes of relaxation



Build up correlation | *Peak of correlation* | *Loss of correlation*

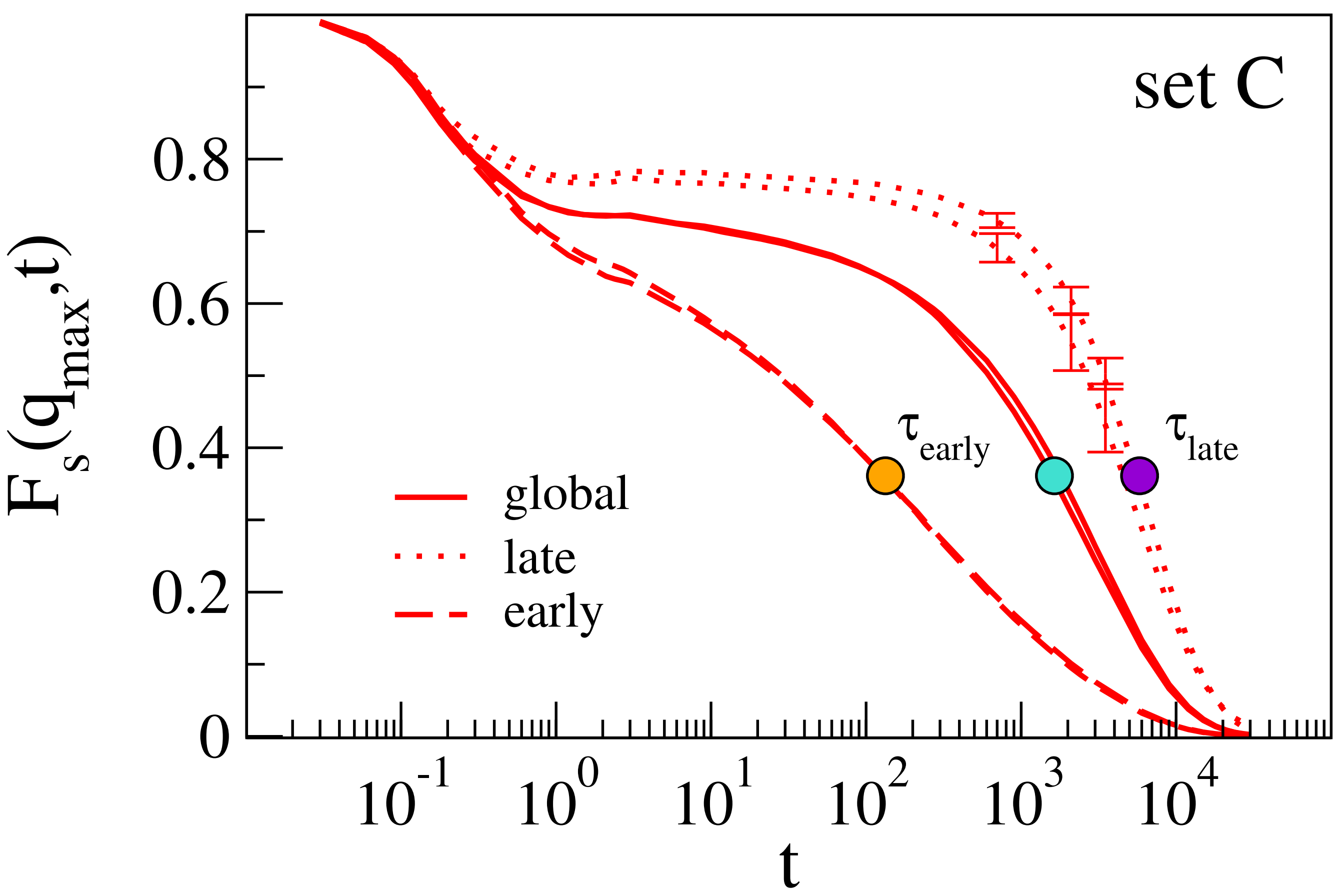


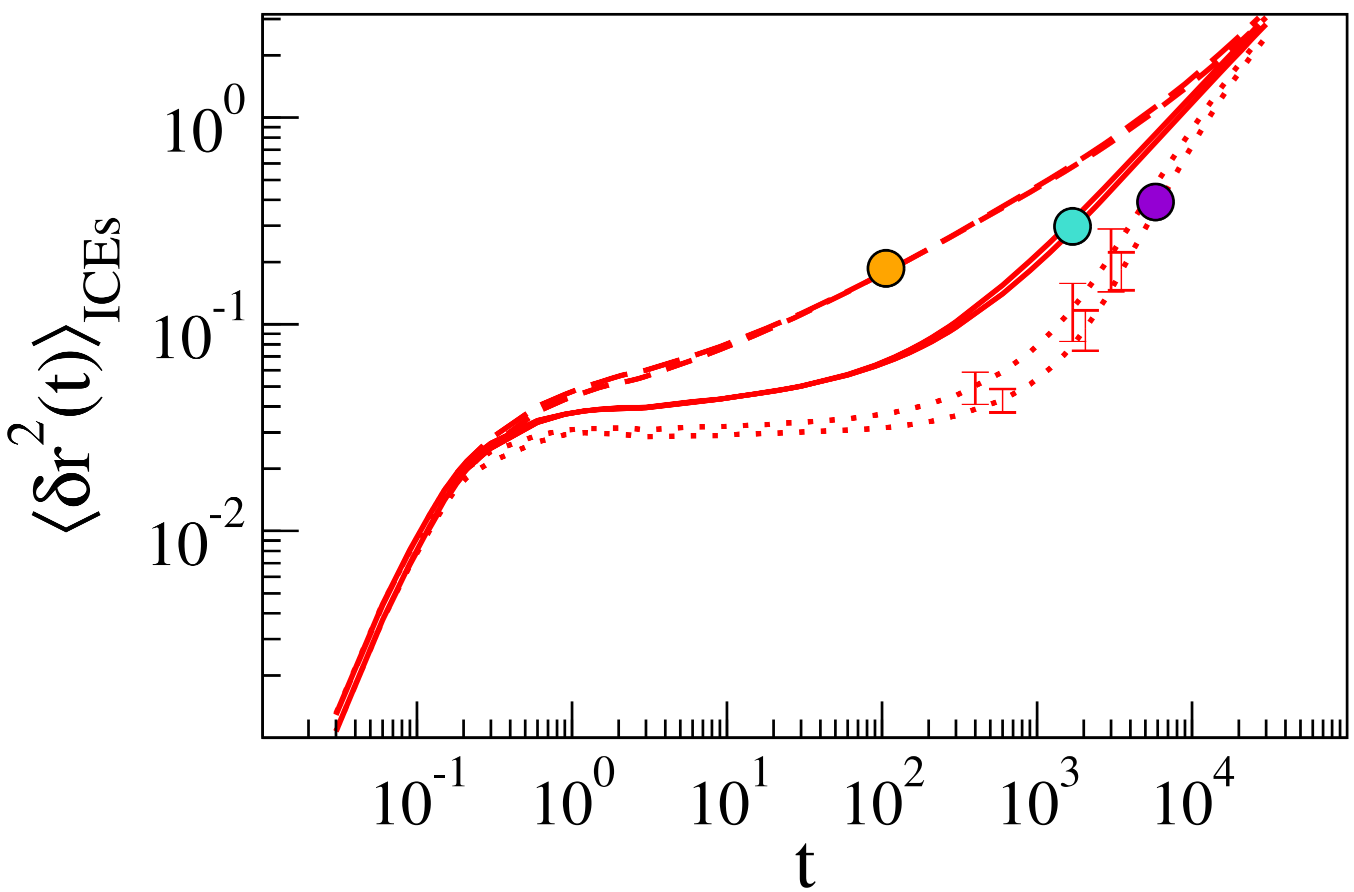
Isolate these two modes

Threshold

$\langle n_i \rangle + 2\sigma_{n_i}$

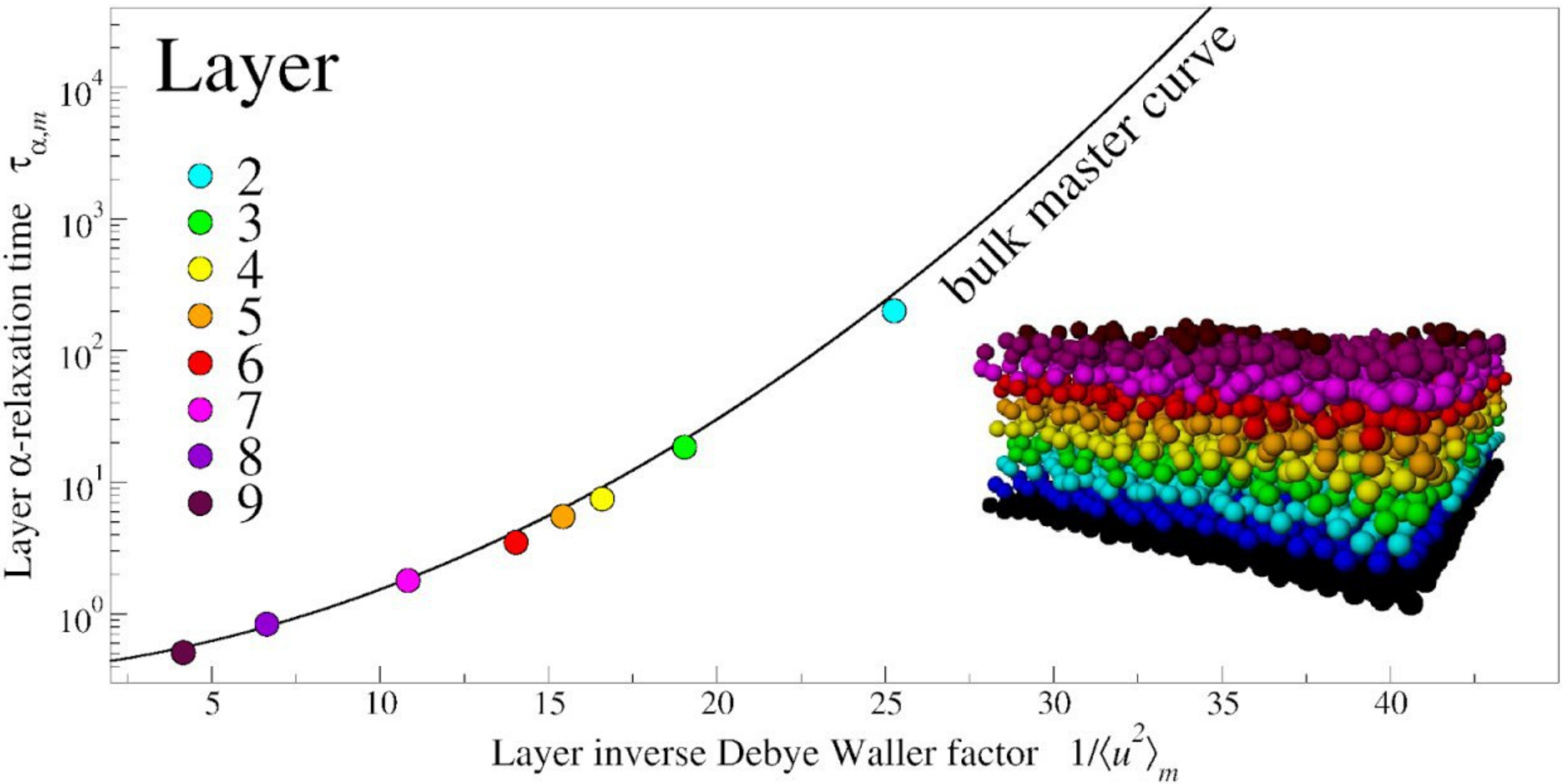
τ_{early} and τ_{late} are the structural relaxation times of the two fractions





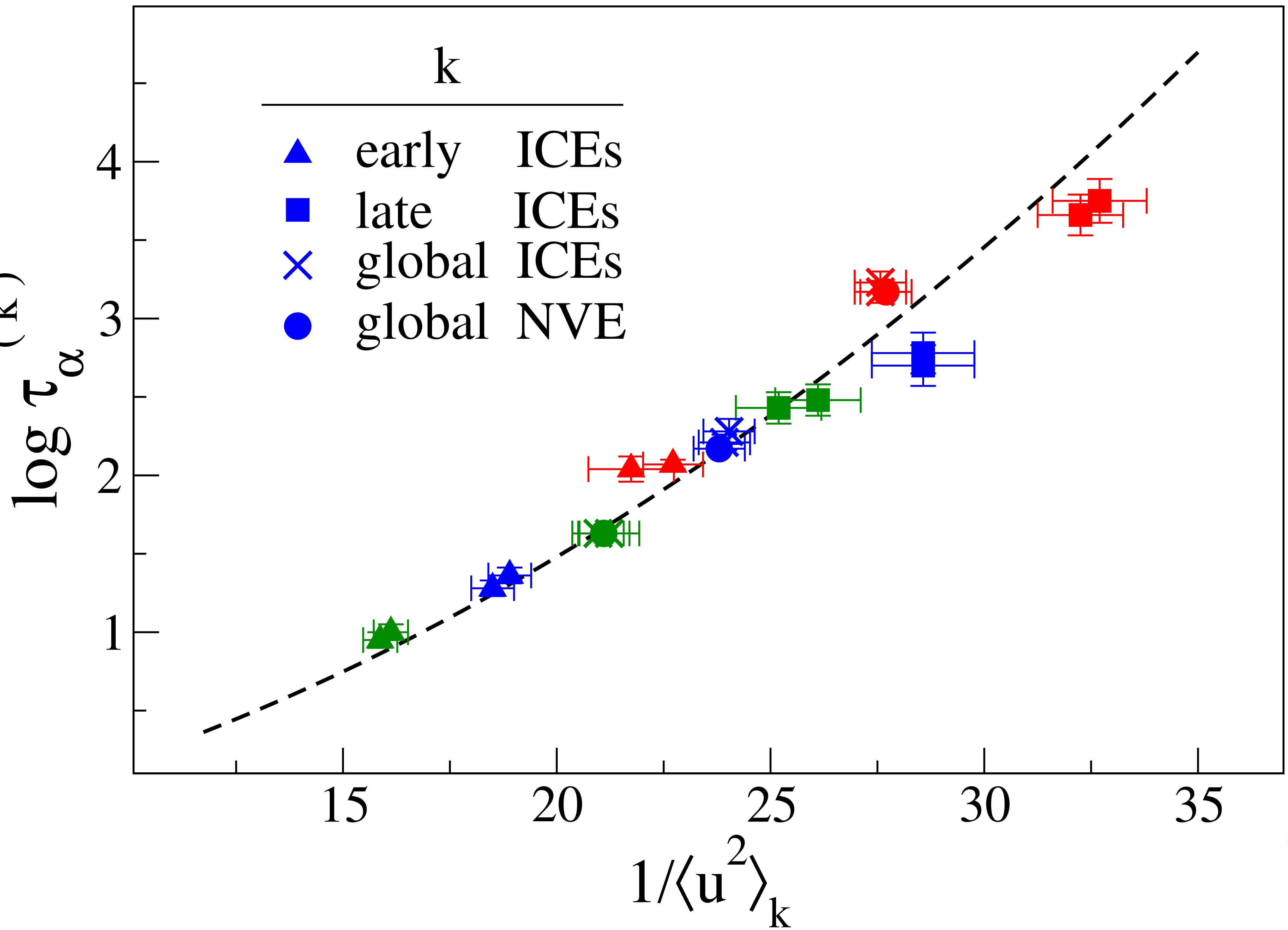
~ equal curves even for the fractions → ***Scaling***

Scaling has already proven to hold for subset of particles of a bulk system



M. Becchi, A. Giuntoli, and D. Leporini, SoftMatter 14, 8814 (2018)

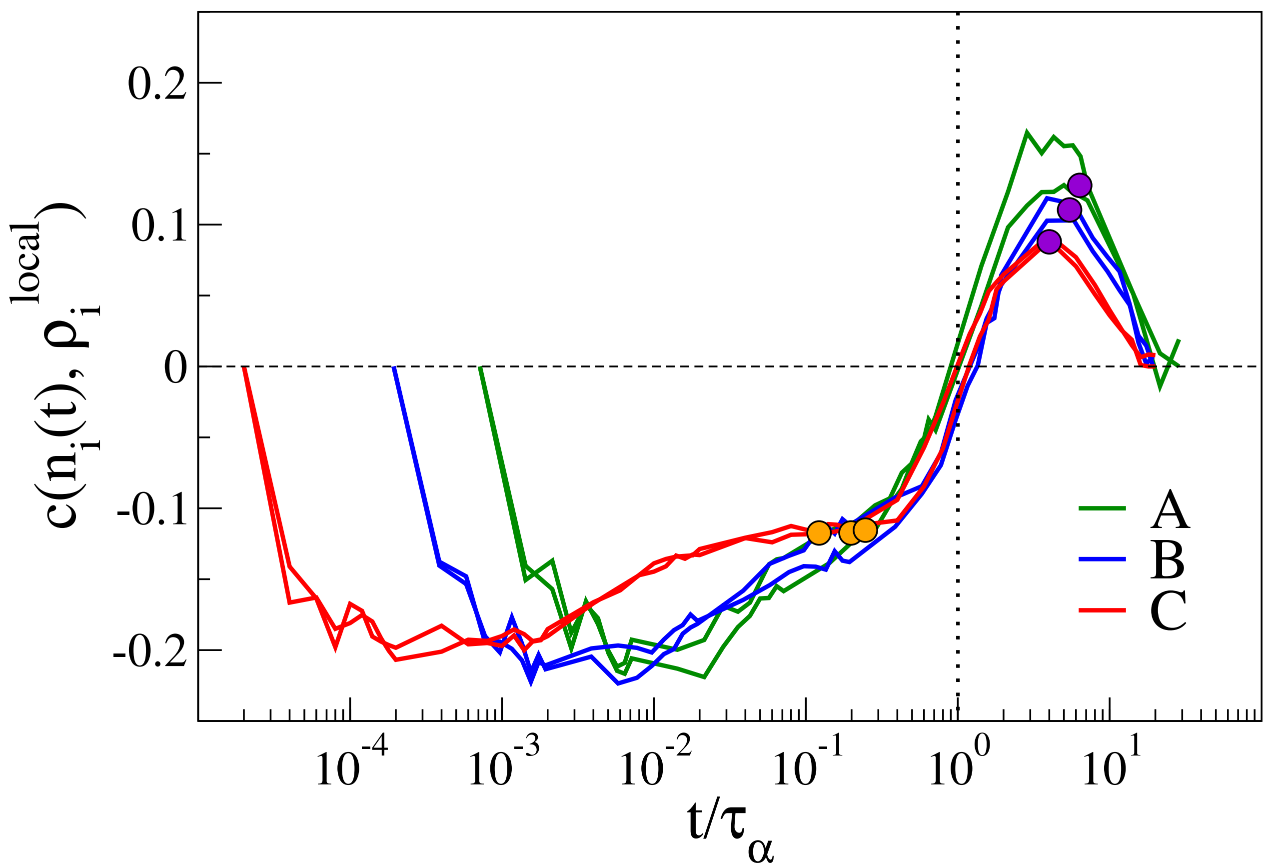
Scaling holds for the early and late-relaxing fractions

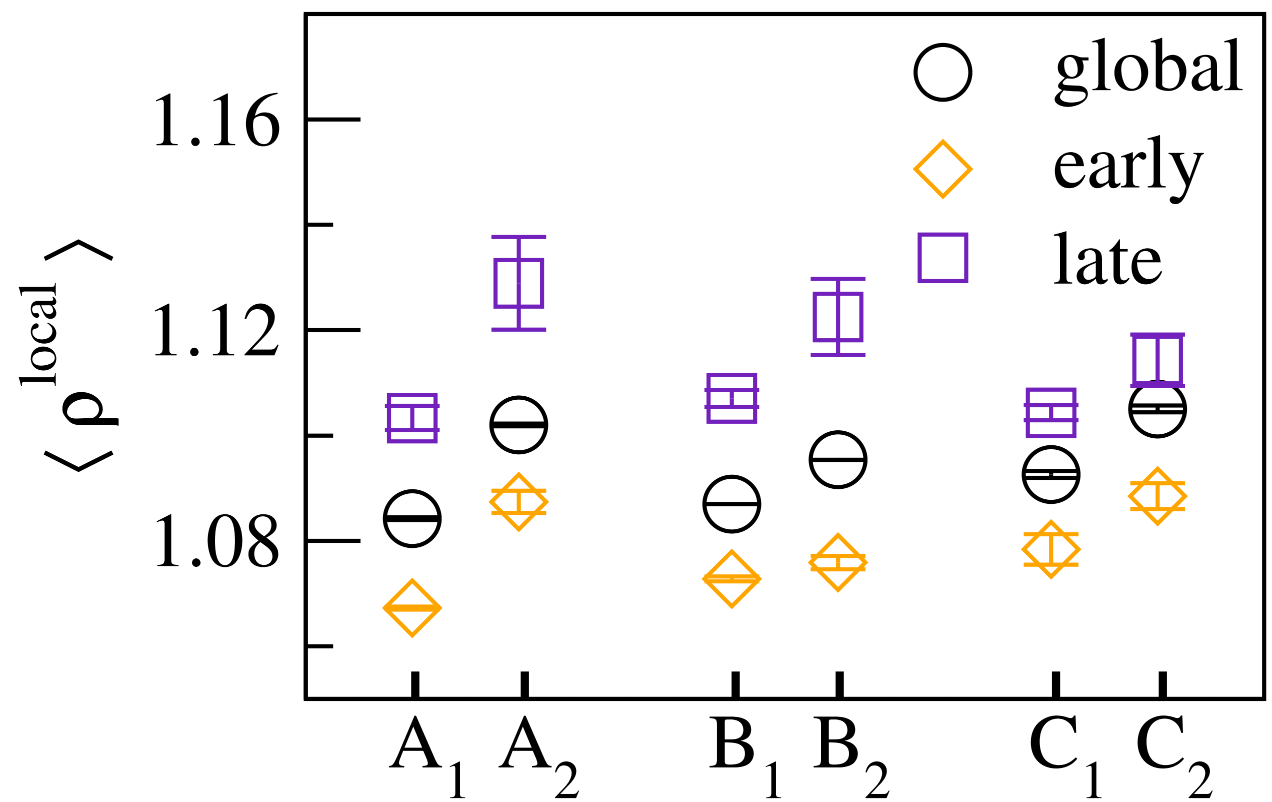


$$\log \tau_\alpha = \alpha + \beta \left(\frac{1}{\langle u^2 \rangle} \right) + \gamma \left(\frac{1}{\langle u^2 \rangle} \right)^2$$

Local structure correlates with the two populations

- ***Local density***



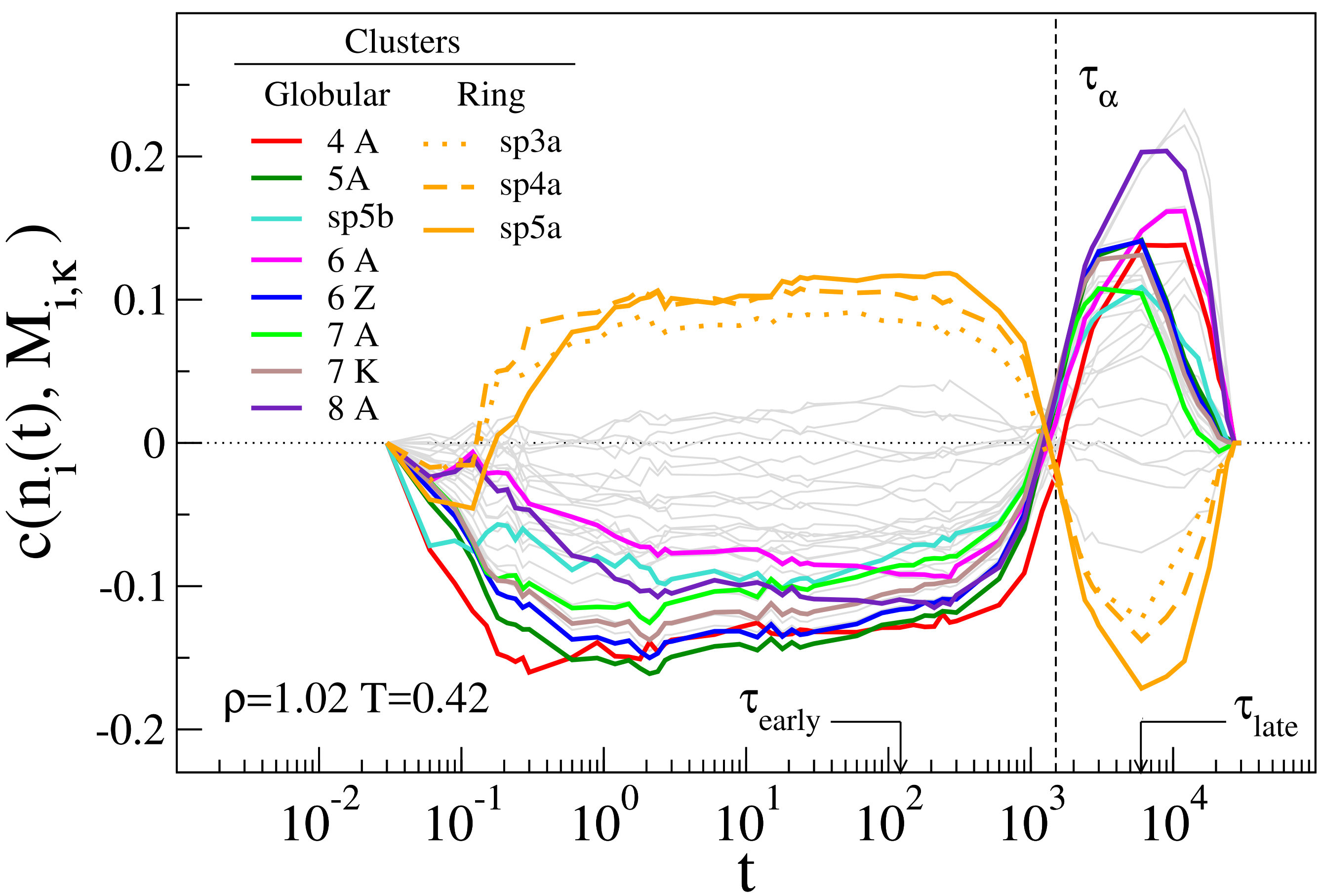


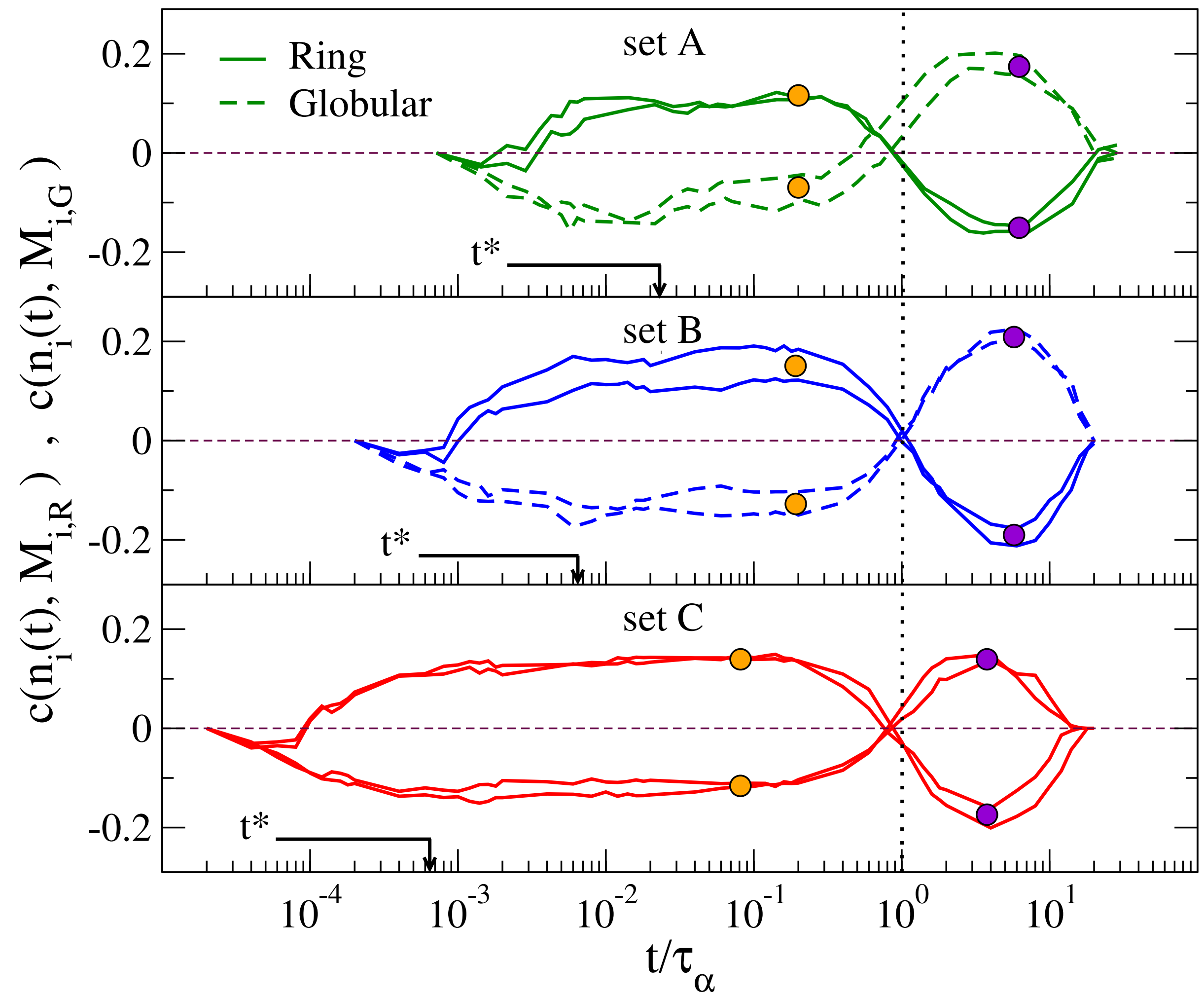
$$c(n_i(t), \delta r_i^2(t)) = \frac{\langle (n_i(t) - \langle n_i(t) \rangle)(\rho_i(t) - \langle \rho_i(t) \rangle) \rangle}{\sigma_{n_i} \sigma_{\rho_i}}$$

Average over populations for all the states

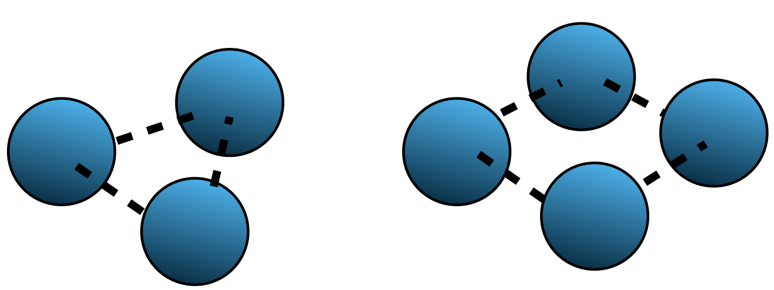
Local structure correlates with the two populations

- ***Topological characterization of local structure***

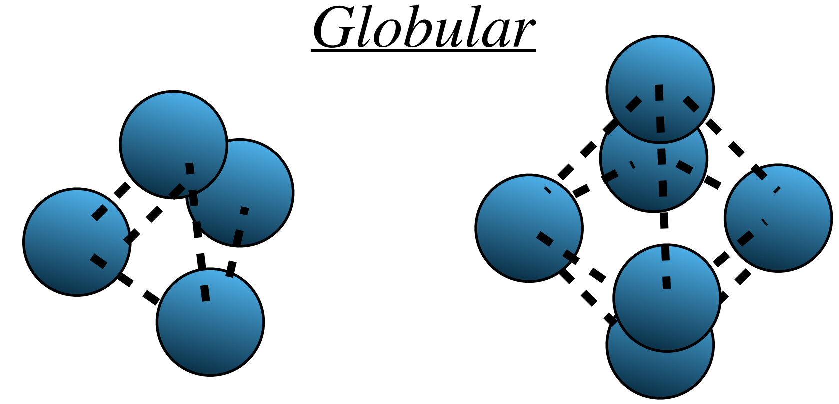




Rings



Globular



Outline of the presentation

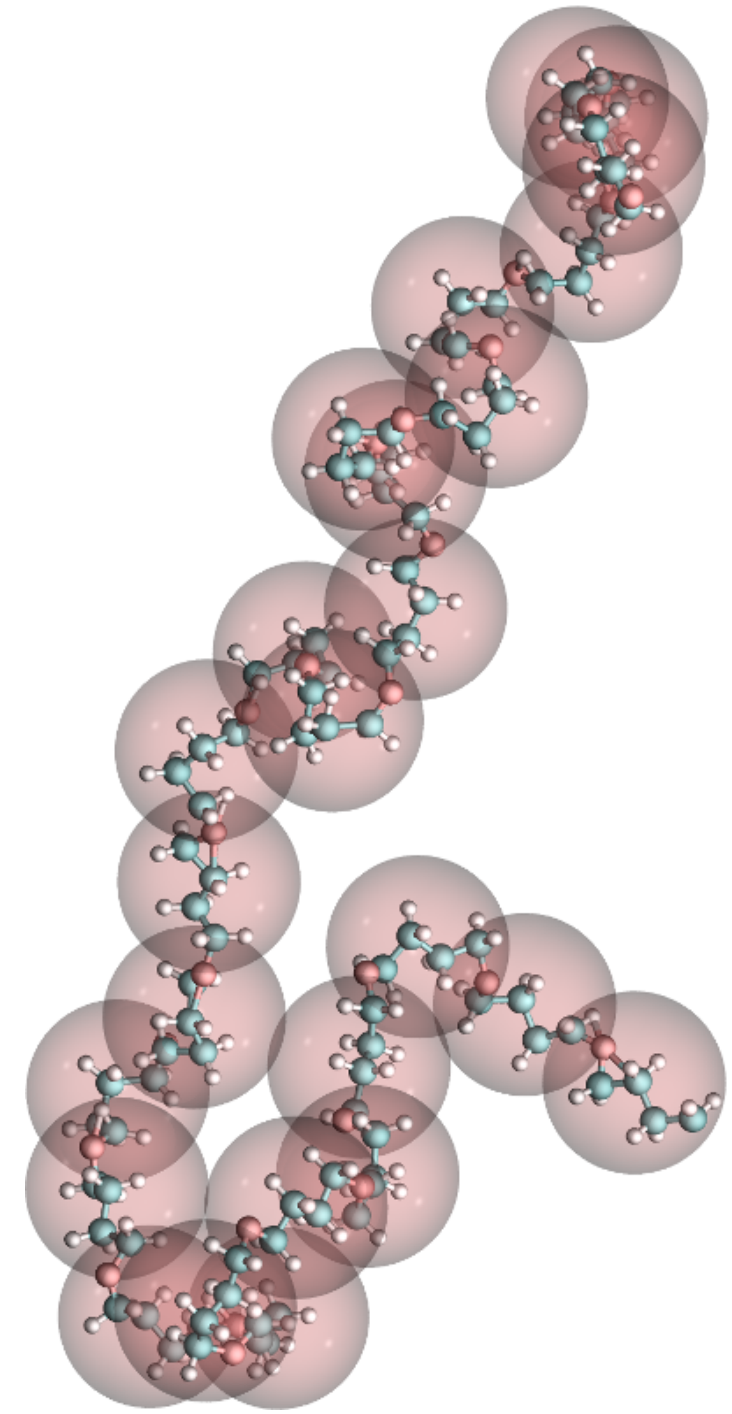
- ***Context***

  - *Glass transition*
  - *Investigated system and method*

- ***Displacement-Displacement correlation***

  - *Average number of MI-correlated particles*
  - *Standard deviation*
  - *Correlation with structure*

- ***Conclusion and future work***



Conclusion and future work

- ***Investigated displacement-displacement correlation of pair of particle through mutual information***

- ***Average number of correlated particle → MI length scale***

A. Tripodo, A. Giuntoli, M. Malvaldi, and D. Leporini, SoftMatter , (2019)

- ***Standard deviation → Two modes of relaxation and scaling***

Soon-to-be-published

In the immediate future

- ***Correlation of the modulus of the displacement***
- ***Connection of τ_{late} with τ_{ee}***