Estimating the length-scale of influence of dynamical heterogeneities in glassy relaxation: Size-dependence study of localized dynamic fluctuations

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We have greatly benefited from inspiring talks with Walter Kob (Montpellier, France)

SUPERCOOLED LIQUIDS

Obtained by cooling a liquid below T_m fast enough to avoid crystallization.

- Static parameters barely change with cooling.

But dramatic **dynamic slowing down. Glassy relaxation.**

- Supercooled liquids are **Dynamically Heterogeneous**: Dynamics vary orders of magnitude from one region of the sample to another.

- Transition to rigidity involves the occurrence of **relaxing regions/ domains whose dimensions and lifetimes increase with the supercooling.** Cooperatively rearranging regions (CRR-Adams&Gibbs theory).

LOOKING FOR RELEVANT RELAXING REGIONS / EVENTS: METABASIN (MB) TRANSITIONS

Archetypal glass former:

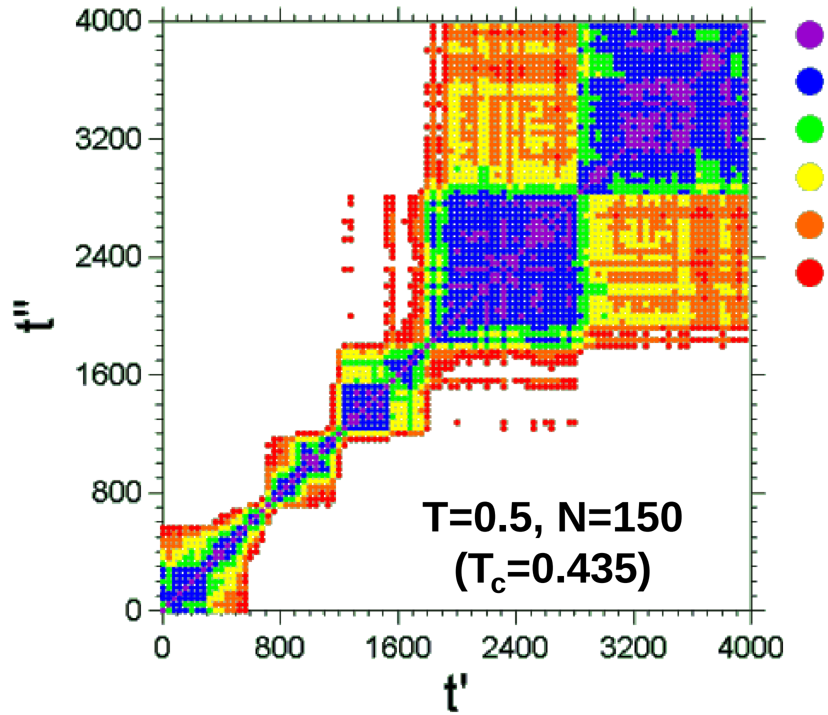
Kob&Andersen Binary Lennard-Jones:
Particles of type A (80%) and smaller of type B (20%)

Small system or sub-system (size N)
Low T. Structural relaxation, τ_α

Distance Matrix (DM; I. Ohmine)):

$$G_s(r,t',t'') = 1/N \sum_i (r_i(t') - r_i(t''))^2$$

$r_i(t)$=position of particle i at time t; square displacements



• Relaxation not smooth but intermittent. Potential energy surface (PES) structured in METABASINS (islands).

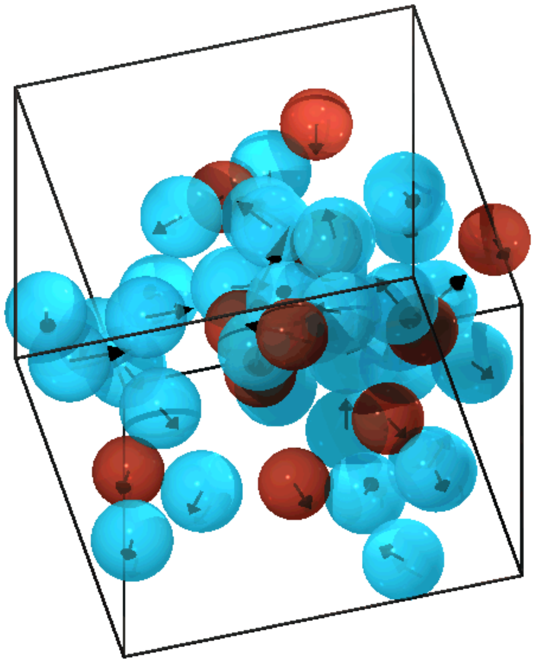
• Transitions between MBs: Fast. $\Rightarrow$ structural α-relaxation.

• $\downarrow$T, MB residence time grows quickly.

• Relaxation events: **d-clusters**

NATURE OF D-CLUSTER EVENTS

MB TRANSITIONS

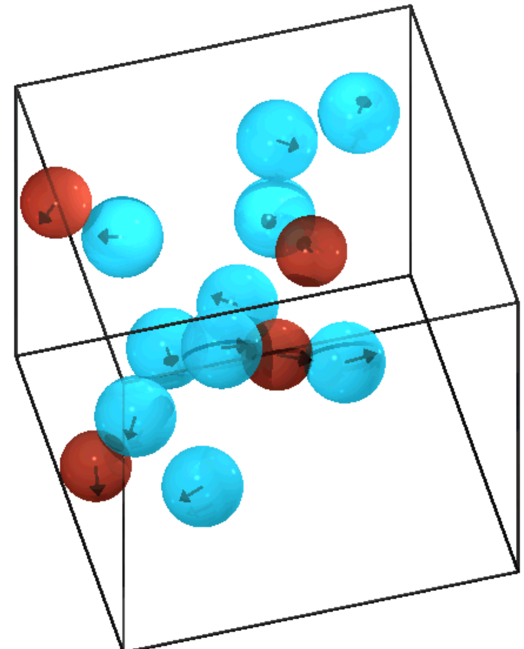


Many particles move collectively (30-60) organized in compact clusters: d-clusters

G.A. Appignanesi, J.A.Rodríguez Fris, R.A. Montani and W. Kob, *Phys. Rev. Lett.* **96**, 057801 (2006).

G.A. Appignanesi, J.A.Rodríguez Fris and M.A. Frechero, *Phys. Rev. Lett.* **96**, 237803 (2006).

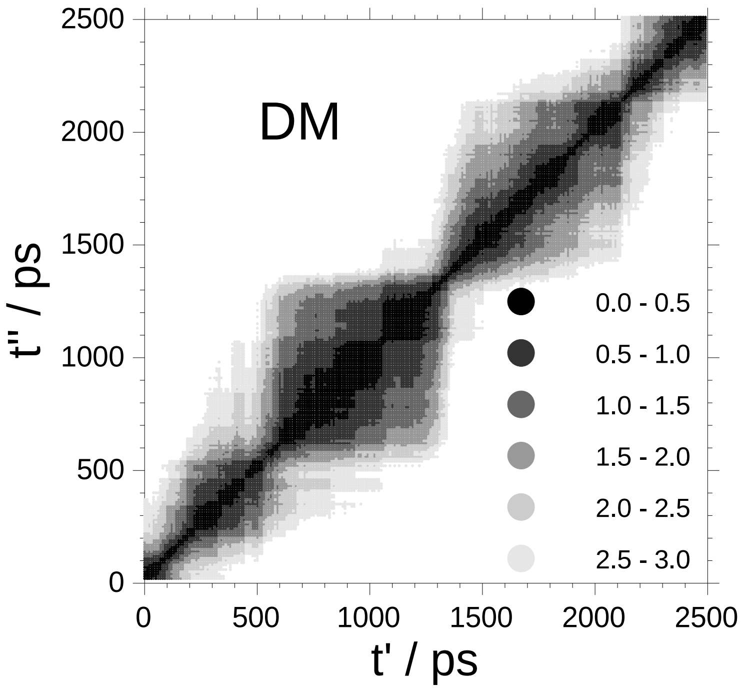
EVENTS WITHIN A MB



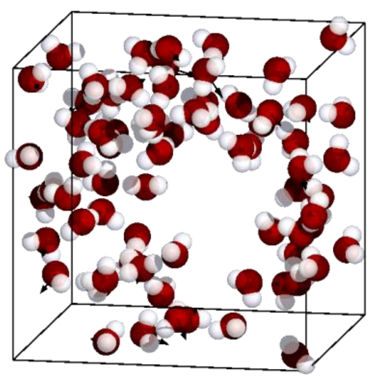
A few particles move collectively

- **The trajectory spends large periods of “inactivity” and suffers rare fast events (dynamical “hot spots”) when a significant portion of the system becomes “active” or mobile: d-clusters.**
- **A series of a few of these events accomplish the α-relaxation.**
- **Potential candidates for the CRRs of Adam&Gibbs.**

SUPERCOOLED WATER



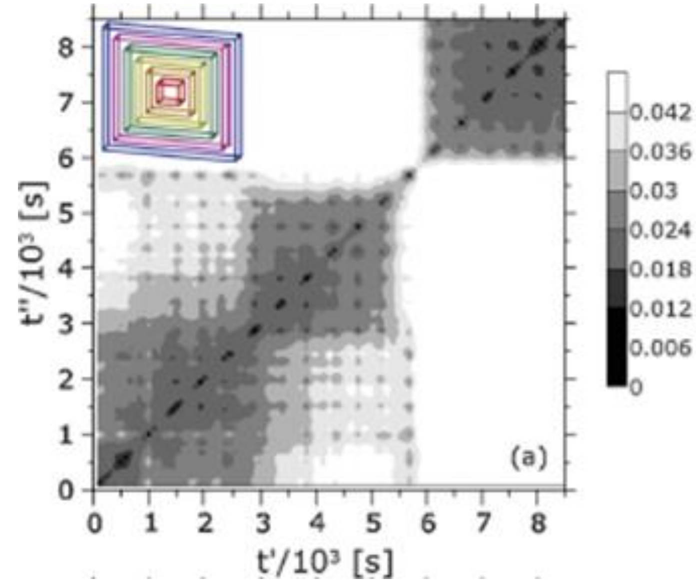
H_2O
SPCE
T=210K

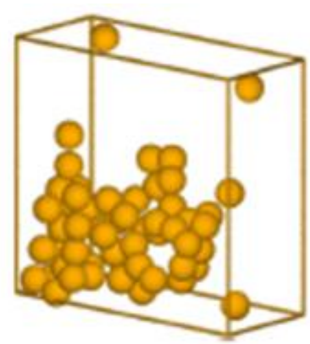


J.A. R. Fris, G.A. Appignanesi, E. La Nave and **F. Sciortino**, *Phys. Rev. E* **75**, 041501 (2007).

COLLOIDAL SUSPENSIONS

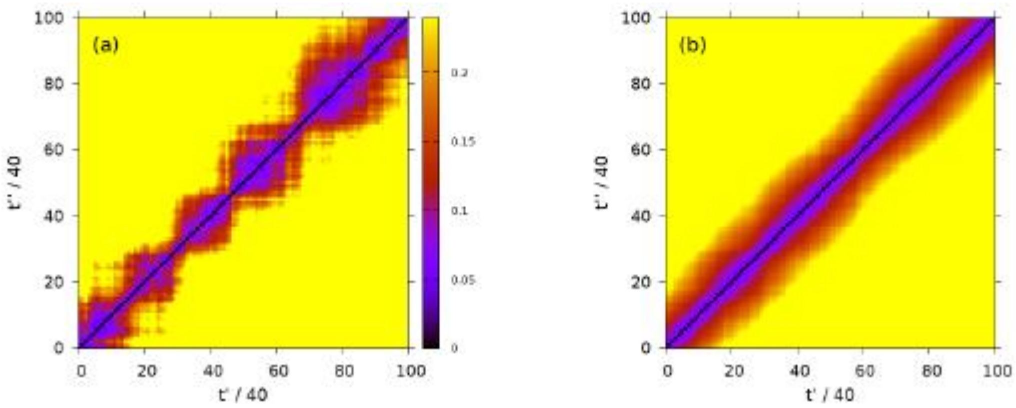
Experimental: Confocal microscopy data (particle tracking). Oder parameter is not T, but packing fraction, ϕ





*J. A. R. Fris, G. A. Appignanesi and **E. R. Weeks**, Phys. Rev. Lett. **107**, 065704 (2011).*

How is the large system limit reached?



Small system (or small sub-system)

Large system (many indep. sub-systems)

Distance matrix: local in both space and time.

$$\Delta^2(t',t'') \equiv \frac{1}{N}\sum_{i=1}^{N} |\vec{r}_i(t') - \vec{r}_i(t'')|^2$$
$$= \langle |\vec{r}_i(t') - \vec{r}_i(t'')|^2 \rangle_{i \in S}$$

MSD: quantity averaged over all time (and all space).

$$M^2(\Delta t) = \langle \Delta^2(t',t'') \rangle_{t''-t'=\Delta t}$$

"Null hypothesis" = Normalized squared deviations from mean value; M^2

Can we use the approach to the large system limit to characterize the spatial scale of dynamical heterogeneities?

The obvious features of are the large fluctuations in the DM

DYNAMIC FLUCTUATIONS STUDY

$$\Omega_S^2(t',t'') = \frac{[\Delta^2(t',t'') - M^2(\Delta t)]^2}{[M^2(\Delta t)]^2}$$

Intermittency measure

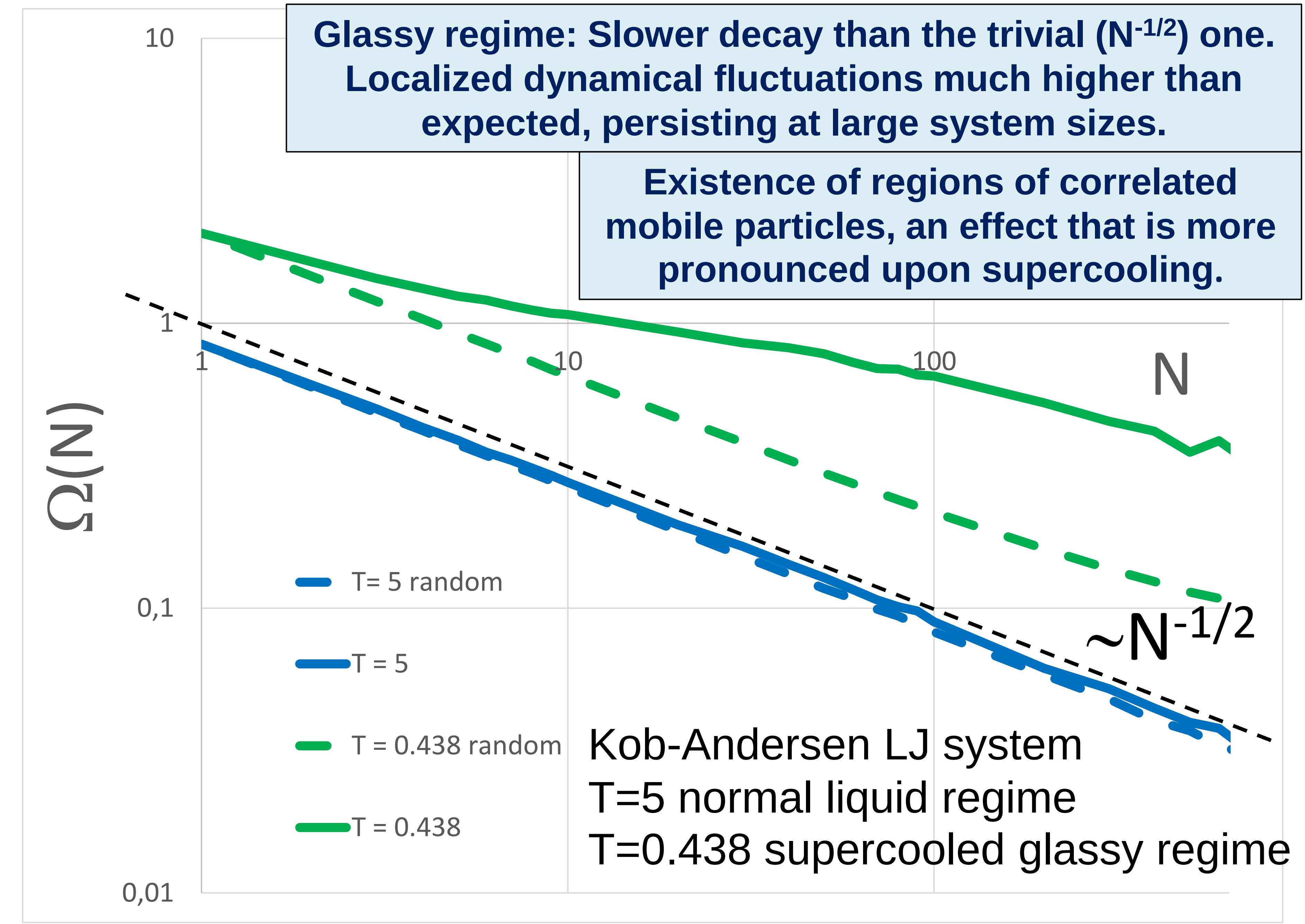
Normalized squared deviations from mean value; M^2 (MSD: expectation for a large system)

Explore sub-systems, s, of size N within a large system (for a total time close to the structural relaxation time (or when the particles have, on average moved one inter-particle distance)

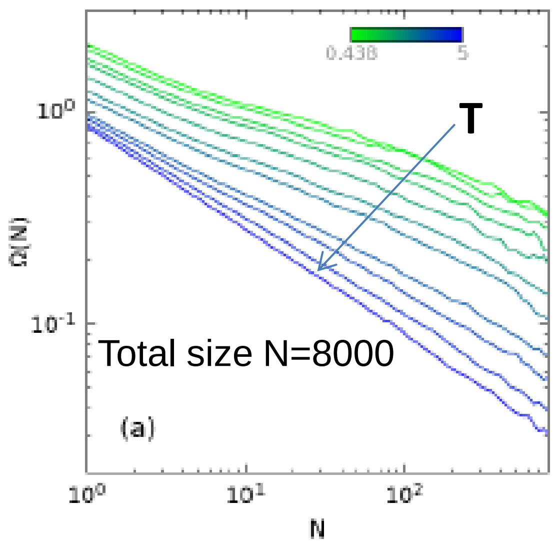
We average $\mathbf{\Omega^2}$ over all time pairs (t', t'') of all subsystems and then take the square root to get a scalar quantity, **Ω(N)**

Ω(N): RATIO OF THE DISPERSION TO THE AVERAGE FOR THE PARTICLE SQUARED DISPLACEMENTS (study on compact sub-systems).

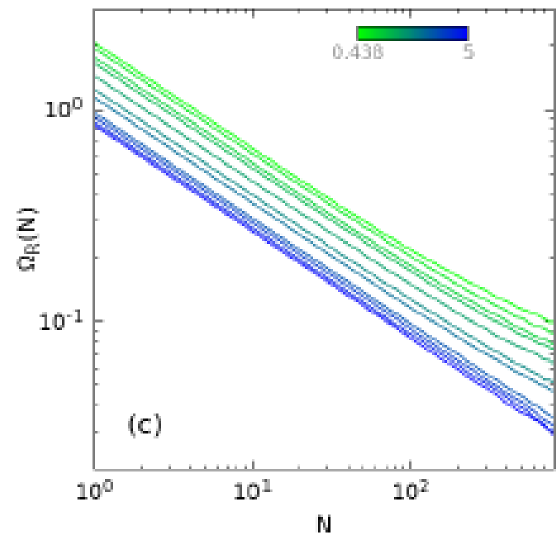
Ω_R(N): N particles randomly chosen within a large system. Non-local, trivial size dependence.



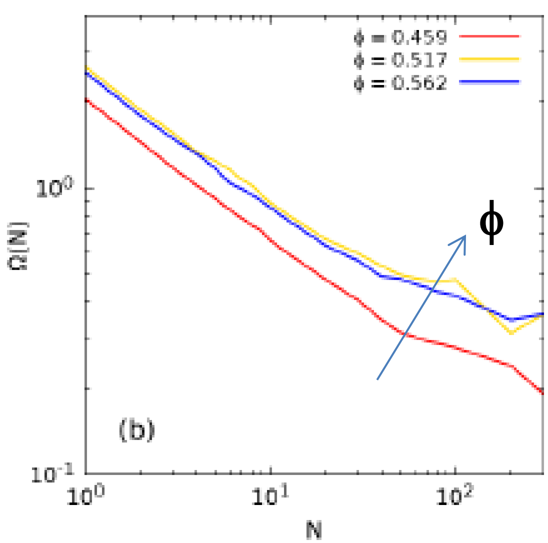
Glassy regime: Slower decay than the trivial (N-1/2) one. Localized dynamical fluctuations much higher than expected, persisting at large system sizes.
Existence of regions of correlated mobile particles, an effect that is more pronounced upon supercooling.
10
1
0,1
0,01
1
10
100
N
Ω(N)
~N-1/2
T= 5 random
T = 5
T = 0.438 random
T = 0.438
Kob-Andersen LJ system
T=5 normal liquid regime
T=0.438 supercooled glassy regime



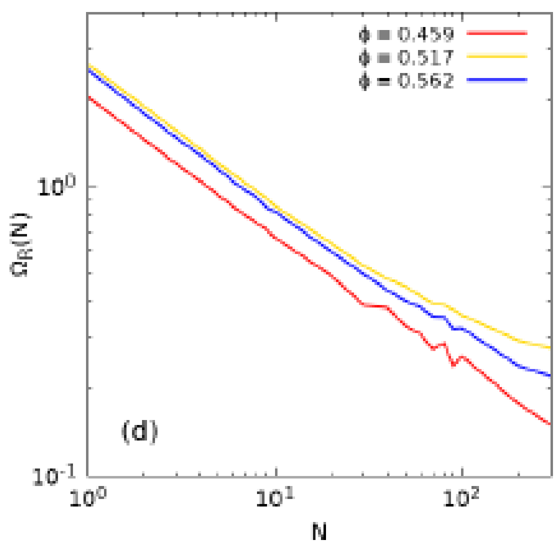
$\Omega(N)$ Kob-Andersen LJ mixture



$\Omega_R(N)$ Kob-Andersen LJ mixture



$\Omega(N)$ Colloidal suspension

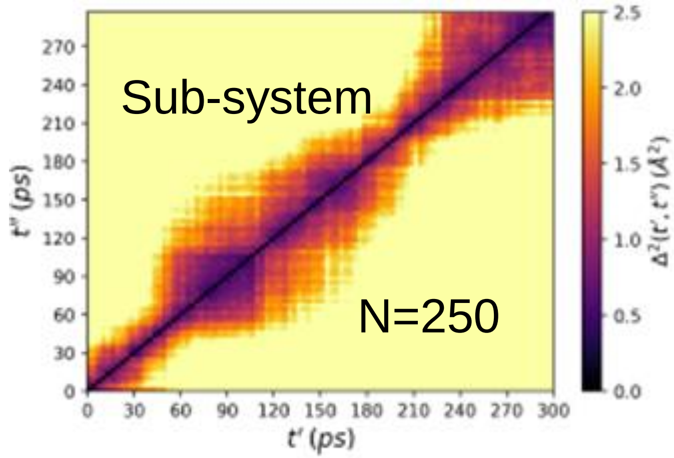


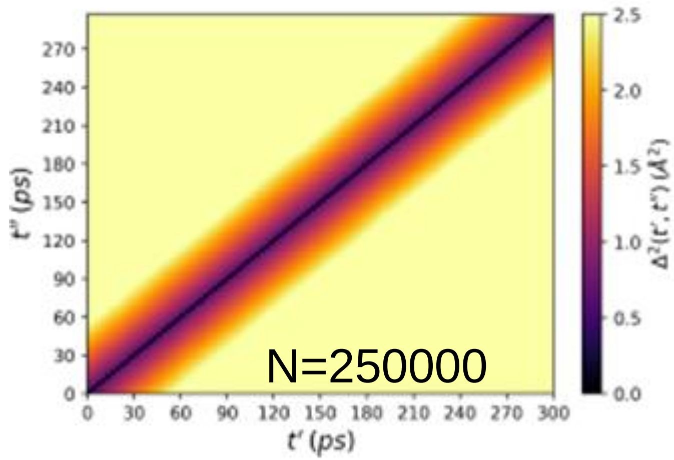
$\Omega_R(N)$ Colloidal suspension

The onset of glassines is marked by spatially localized dynamic fluctuations originating in regions of correlated mobile particles

*J. A. Rodriguez Fris, **E. R. Weeks, F. Sciortino** and G. A. Appignanesi, Phys. Rev. E Rapid Comm. **97**,060601 (2018).*

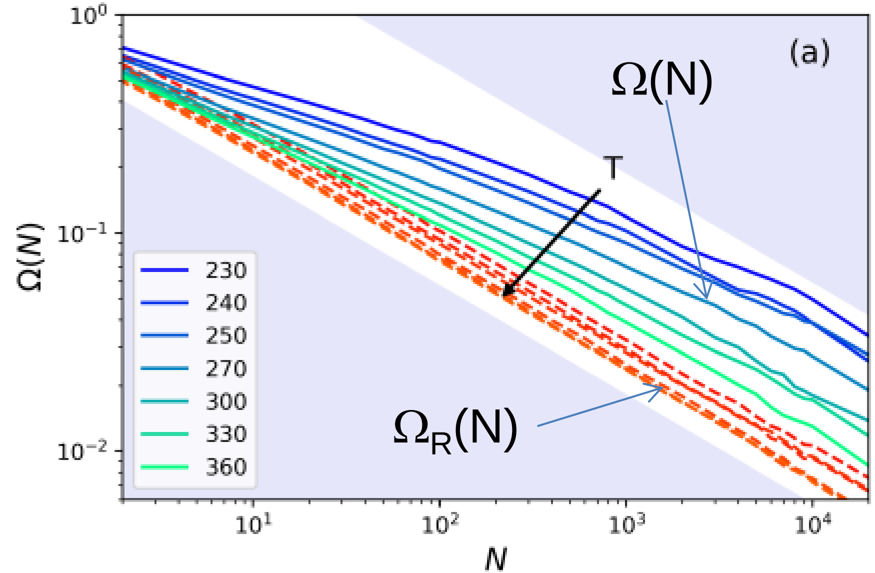
SUPERCOOLED WATER

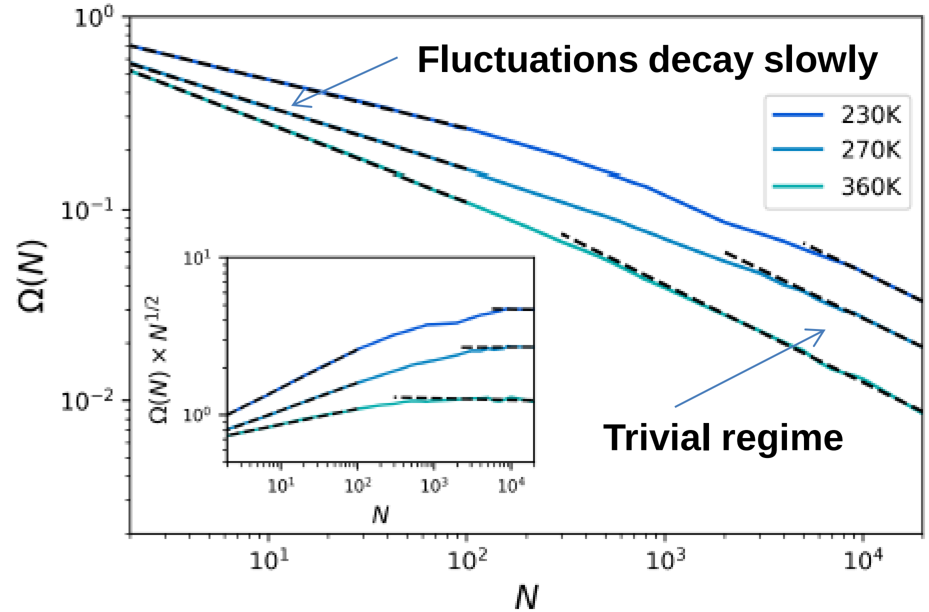




TIP4P/2005; T=230K; ρ=0.95 g/cm^3

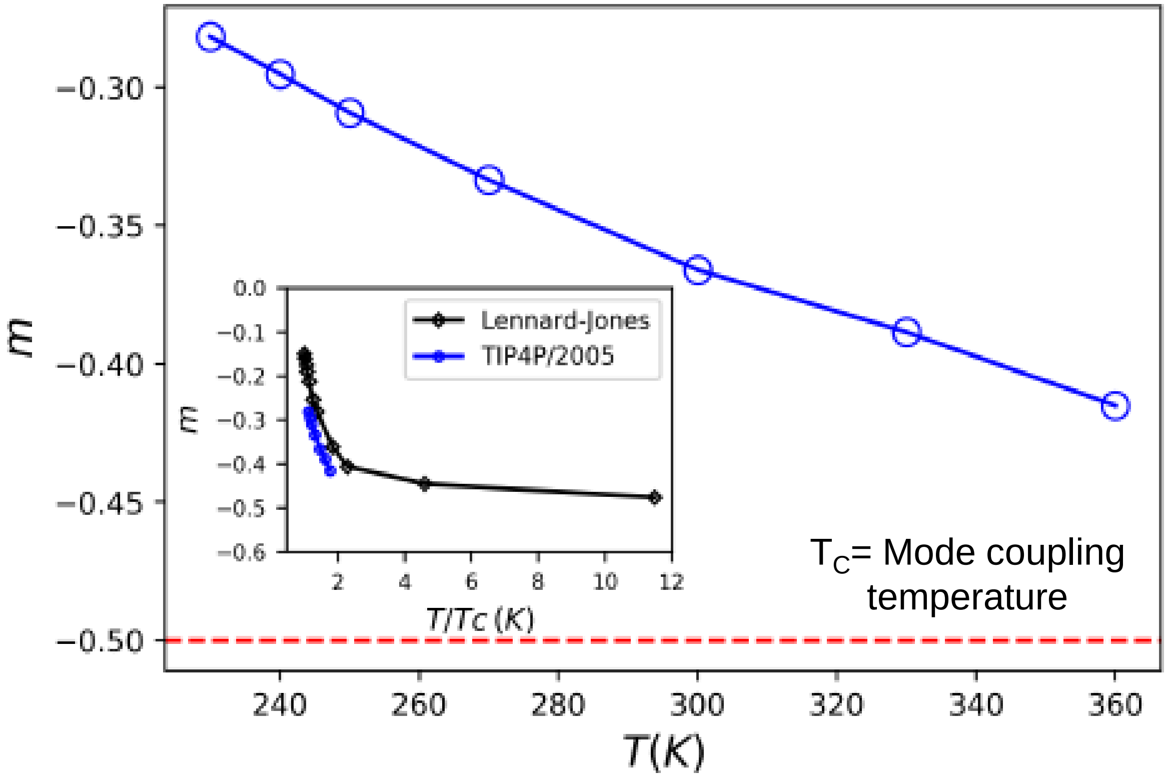
avoids interference of liquid-liquid critical point





First initial slow decay regime (slope m decreases as T is lowered)

Final trivial regime approached at larger N as T is lowered

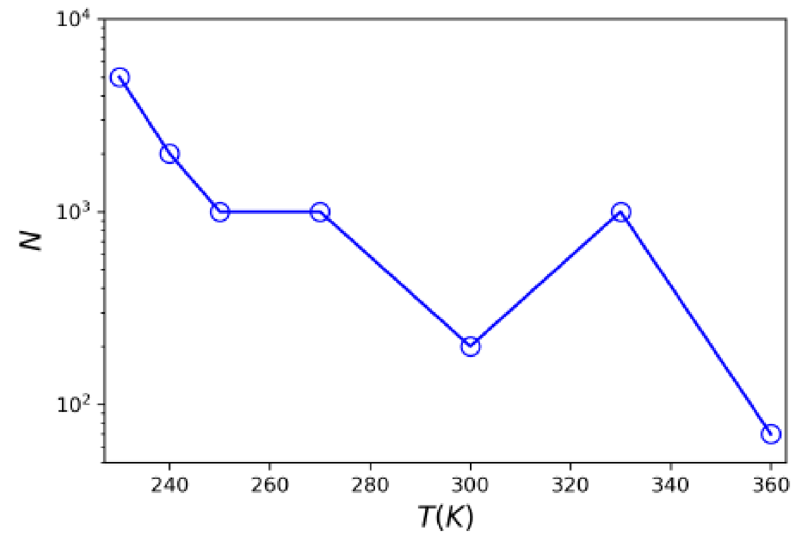


Increase of slope *m* for the initial regime as a temperature decreases

*J. M. Montes de Oca, S. R. Accordino, G. A Appignanesi, **P. H. Handle** and **F. Sciortino**, J. Chem. Phys. **150**, 144505 (2019).*

The lenghtscale of approaching to the trivial $N^{-1/2}$ final regime significantly grows as T decreases (~100 times; >1000 molecules).

Upper limit to the size of correlated mobile regions. Size required to complete average out their influence.



CONCLUSIONS:

- New measure of spatial and temporal dynamic heterogeneity that does not require defining subsets of mobile or immobile particles, but rather looks for fluctuations away from the large system behavior.

- Allows to examine dynamical heterogeneity on a variety of length scales, showing that the approach to the large system limit is slower than would be expected for randomly distributed fluctuations in the dynamics.

- Can be generalized to any other spatially and temporally fluctuating quantities, as long as there is a well-defined null hypothesis based on the large system limit (for example, structure).

- Straightforwardly applied to experimental systems such as the dense colloidal solution we examine; it does not require finite-size scaling, for example.

- **The supercooled glassy regime is characterized by the appearance of regions of correlated mobile particles, which make the system to present significant spatially localized dynamic fluctuations. At low T, it is necessary to reach very large system sizes for a complete cessation of the influence of (to average out) such dynamical heterogeneities.**