

Aneesur Rahman (1927- 87)



Pioneered the application of computational methods in studies of condensed matter systems.

His 1966 paper, “Correlations in the Motion of Atoms in Liquid Argon” [*Phys Rev* **136**: A405] introduced the method of *Molecular Dynamics*.

Algorithms developed by him are still in use.

Born in Hyderabad, India; undergraduate education in Cambridge University. D.Sc. from Louvain University, Belgium in 1953. Worked at Osmania University, Hyderabad (1953-57); TIFR, Mumbai (1957-60); **Argonne National Laboratory (1960-85)** and University of Minnesota (1985-87).

The American Physical Society annually awards the **Aneesur Rahman Prize** for outstanding achievement in computational research.

Growing Length and Time Scales in Glass Forming Liquids

Chandan Dasgupta
Centre for Condensed Matter Theory
Department of Physics, Indian Institute of Science

With

Smarajit Karmakar (Weizmann Institute),
Srikanth Sastry and Shiladitya Sengupta (JNCASR, Bangalore)

Golden Jubilee Conference, IIT Kanpur, February 2010

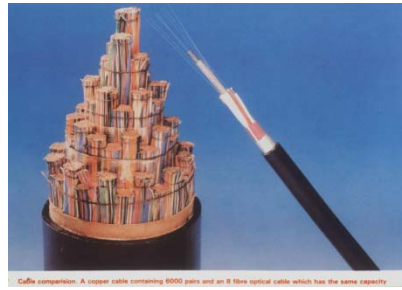
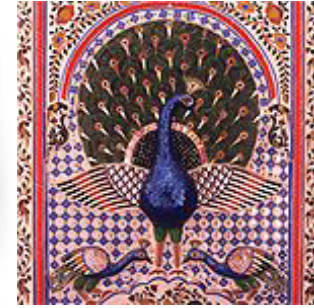
Outline

- Introduction
- Dynamic heterogeneity in glass-forming liquids
- Growing dynamic length scale from four-point susceptibility
- Growing length scale in the short-time dynamics
- Conclusions

Reference:

S. Karmakar, C. Dasgupta and S. Sastry, Proceedings of the National Academy of Sciences USA (PNAS) **106**, 3675 (2009); submitted for publication (2009); and in preparation.

MANY DIFFERENT FORMS OF GLASSES



Cable comparison. A copper cable containing 1000 pairs and an 8 fibre optical cable which has the same capacity.



Slide from
Sri Sastry



Glass: Disordered solid-like state obtained by rapidly cooling a liquid to a temperature lower than the **equilibrium crystallization temperature**

The glassy state is metastable

Examples:

- ❖ Oxide glasses (silica, Germanium glass,....)
- ❖ Chalcogenide glasses (GeSbTe, AgInSbTe,.....)
- ❖ Metallic glasses (Fe-Cr-Mo-C-B, Mg-Cu-Tb,....)
- ❖ Polymer glasses (polystyrene, poly-vinyl-acetate,..)
- ❖ Colloidal glasses
- ❖ Simple molecular glasses (ortho-terphenyl, salol,..)

Viscosity increases by 14-16 orders of magnitude as the temperature of a supercooled liquid is decreased by about 100 degrees

$$\eta(T) \propto \exp[E_0/(k_B T)]$$

Arrhenius behaviour: “strong” liquid

$$\eta(T) \propto \exp[BT_0/(T - T_0)]$$

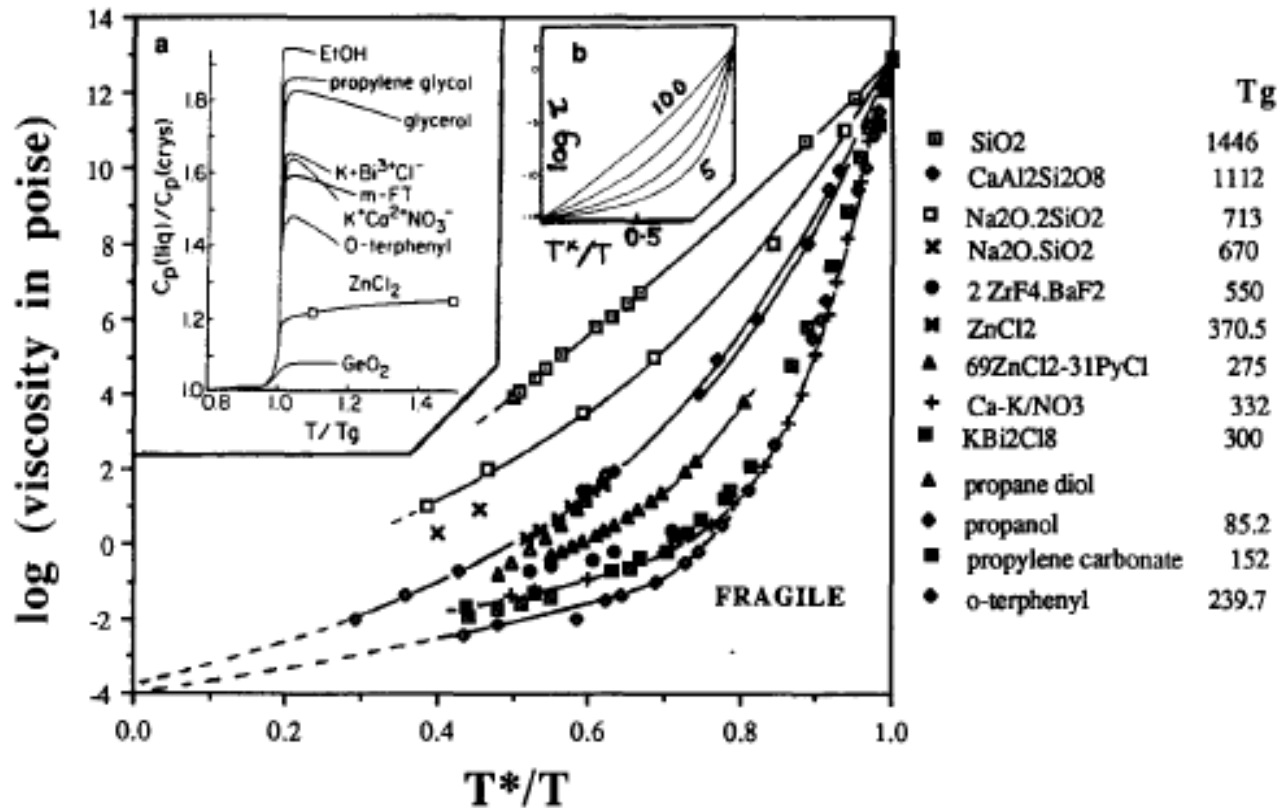
Vogel-Fulcher-Tammann (VFT) Form
“Fragile” liquid

Viscosity = 10^{18} poise at the experimentally defined glass transition temperature, T_g

The “excess entropy”, defined as the difference between the entropy of the supercooled liquid and the crystalline solid, extrapolates to zero at the “Kauzmann Temperature” T_K which is close to T_0

$$\tau(T) \propto \exp[A/\{TS_{ex}(T)\}]$$

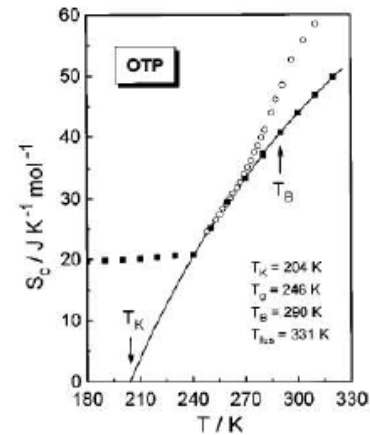
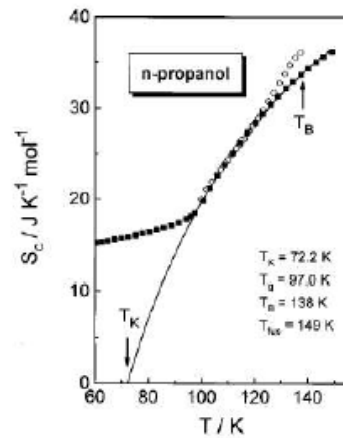
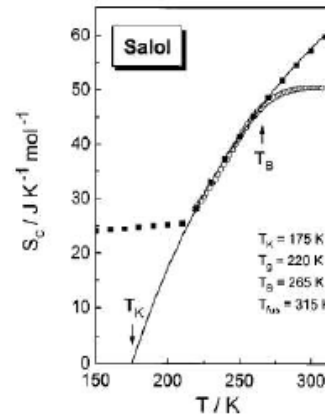
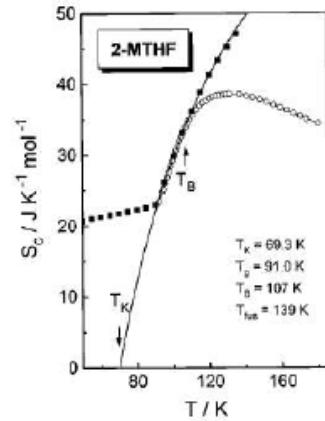
Adam-Gibbs Relation



.. Strong \rightarrow fragile behavior in glass-forming liquids as shown by T^* -scaled Arrhenius plots of viscosity. Here T^* is the temperature at which the shear viscosity reaches 10^{12} Pa s. Inset (a) shows how this pattern is reproduced by the modified Arrhenius equation, eq. (1), by variation of the parameter D . Inset (b) shows the corresponding configurational entropy components of the heat capacity introduced at T_g by ratioing the liquid (and glass) data to the crystal values at each temperature.

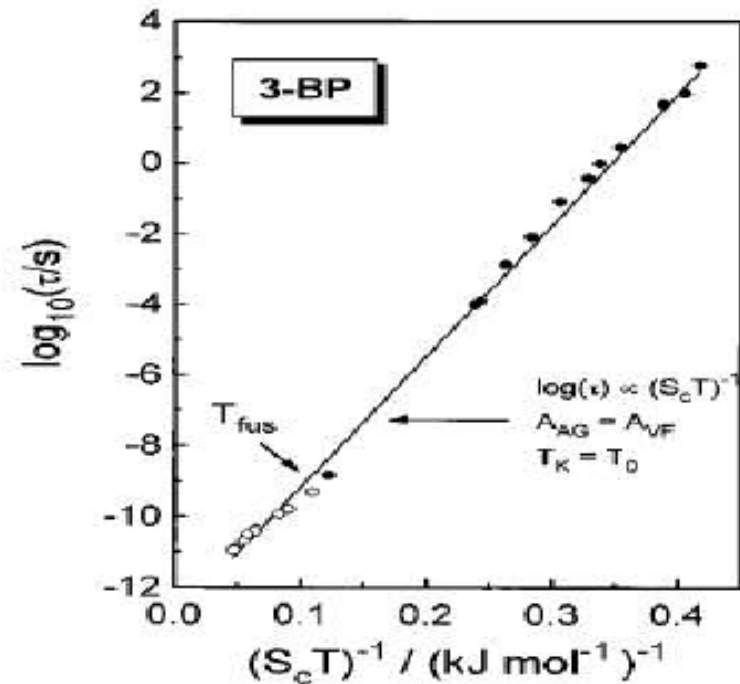
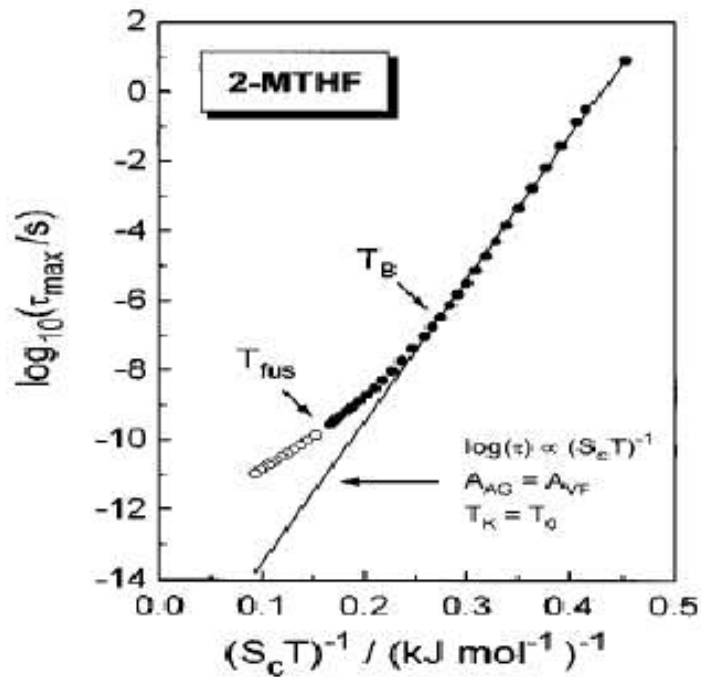
Viscosity as a function of temperature: "Angell Plot"

From: C. A. Angell, J. Non-cryst. Solid, **131-133**, 13 (1991)



Kauzmann "Paradox": Experimental data

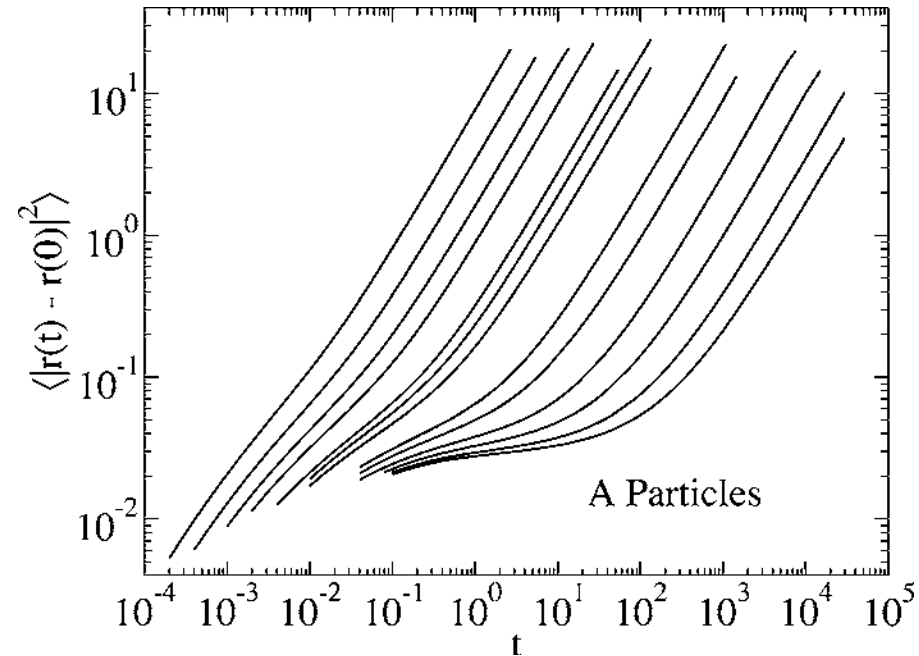
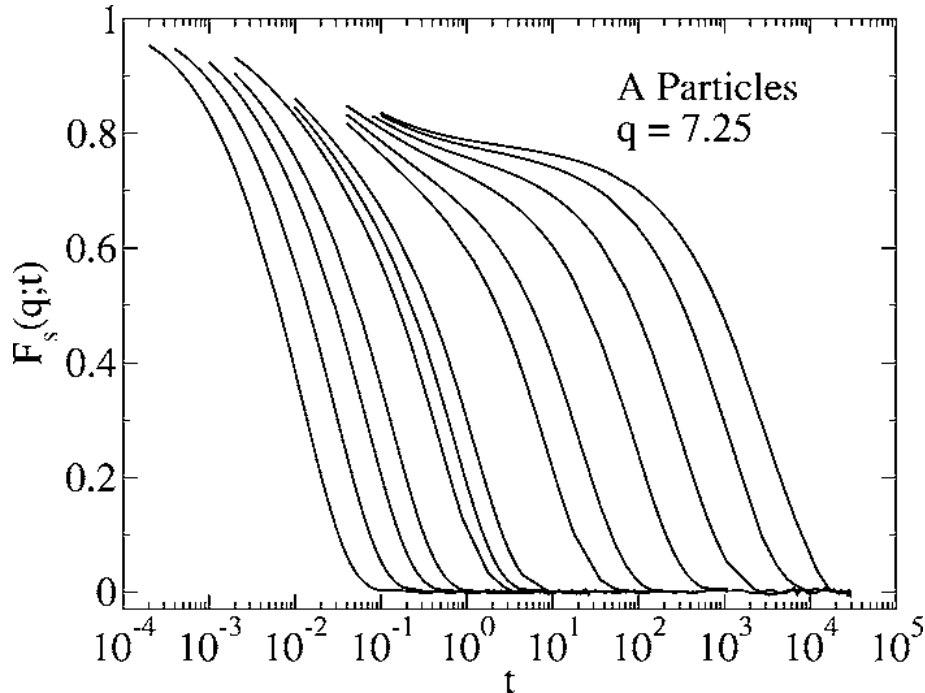
From: R. Richert and C. A. Angell, J. Chem. Phys. **108**, 9016 (1998)



Experimental demonstration of the validity of the Adam-Gibbs relation

From: R. Richert and C. A. Angell, J. Chem. Phys. **108**, 9016 (1998)

Multi-step relaxation in supercooled liquid



E. Flenner and G. Szamel, Phys. Rev. E **72**, 011205 (2005)

Short time: β relaxation
Long time: α relaxation

Mode Coupling Theory

[Leutheusser, Götze, Mazenko, Das, ...]

Mass density $\rho(\mathbf{r}, t)$ and momentum density $\mathbf{g}(\mathbf{r}, t)$.

Equations of fluctuating hydrodynamics:

$$\begin{aligned}\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{g} &= 0, \\ \frac{\partial g_i}{\partial t} &= - \sum_j \nabla_j \left[\frac{g_i g_j}{\rho} \right] - \rho \nabla_i \frac{\delta F}{\delta \rho} - \sum_j L_{ij}^0 \frac{g_j}{\rho} + \theta_i.\end{aligned}$$

F is an appropriate free energy functional, L_{ij}^0 is the “bare” damping matrix, and θ_i is a Gaussian noise satisfying the fluctuation-dissipation relation.

Mode coupling approximation: Treatment of the nonlinearities at the one-loop self-consistent level.

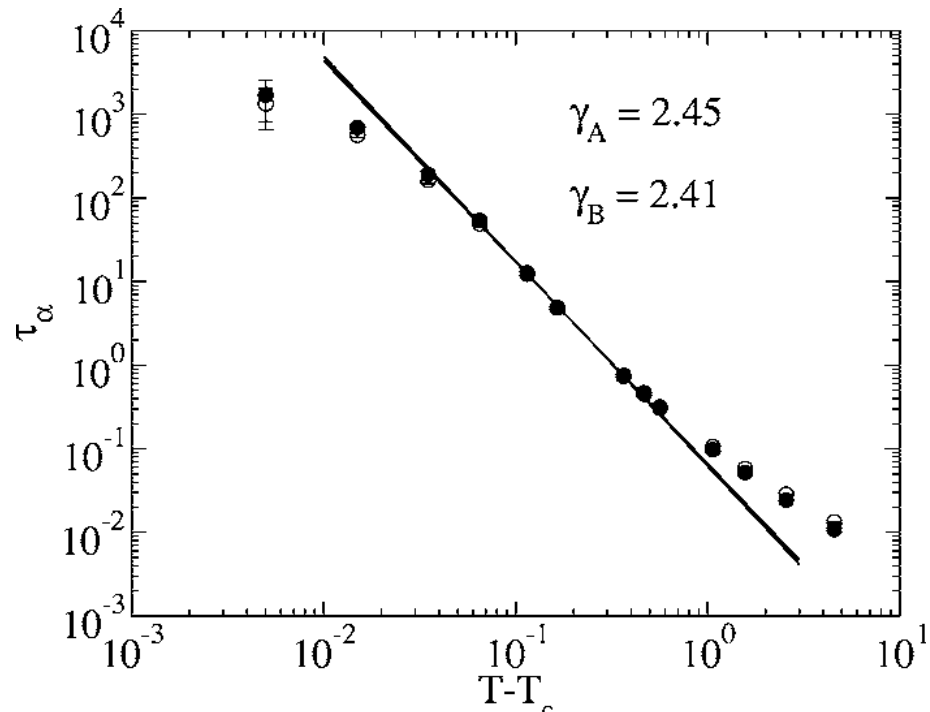
Mode Coupling Theory provides a qualitatively correct description of the dynamics in the weakly supercooled regime

“Ideal” MCT: Divergence of η at T_c

Experiments: $T_c > T_g$, $\eta(T_c) \approx 10^2$ poise, crossover in dynamics near $T = T_c$

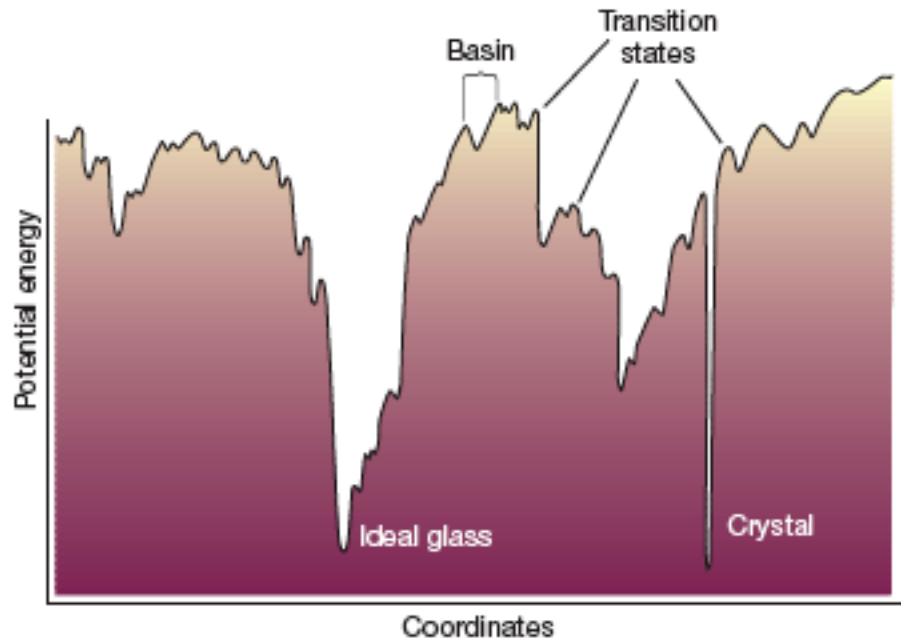
$$T_x > T_c > T_g > T_0 \simeq T_K$$

Thermodynamic Glass Transition at $T_0 = T_K$?



Energy landscape picture

- Disordered liquid structure implies many local energy minima.
- Lowering temperature, the local minima sampled get deeper, and it gets harder to go from one to the other.
- Increasing viscosity.
- Configurational entropy \sim logarithm of number of sampled local energy minima



From Srikanth Sastry

Partition Function $Q(N, \rho, T)$

$$= \int d\Phi \Omega(\Phi) \exp[-\beta(\Phi + F_{bas}(\Phi, T))]$$

[Exclude IS's with large crystallites]

$S_c(\Phi) \equiv k_B \ln \Omega(\Phi)$ **is the configurational entropy of inherent structures at energy Φ .**

$$S_c(T) = \int d\Phi S_c(\Phi) P(\Phi, T)$$

$S_c(\Phi)$ and $S_c(T)$ can be determined numerically by appropriate sampling methods

- Numerically determined $S_c(T)$ extrapolates to zero at $T = T_K \simeq T_0$ extracted from VFT fits to dynamical data
- Adam-Gibbs relation is satisfied within numerical accuracy

Existence of a growing **length scale** near the glass transition??

Adam-Gibbs theory *postulates* the existence of a growing length scale that represents the size of “cooperatively rearranging regions”.

Recently, many experimental, numerical and theoretical studies have investigated the existence of a length scale associated with **dynamical heterogeneity** that describes the spatial heterogeneity of the local relaxational kinetics in supercooled liquids.

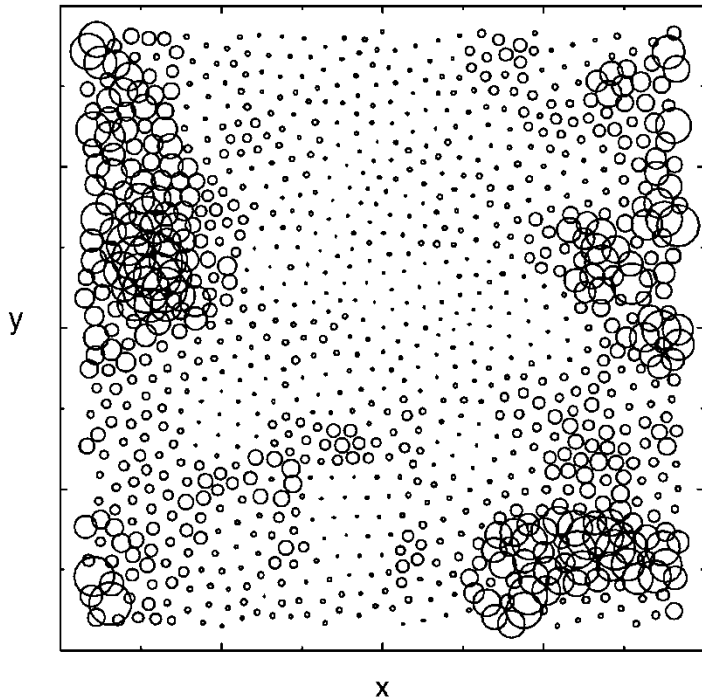
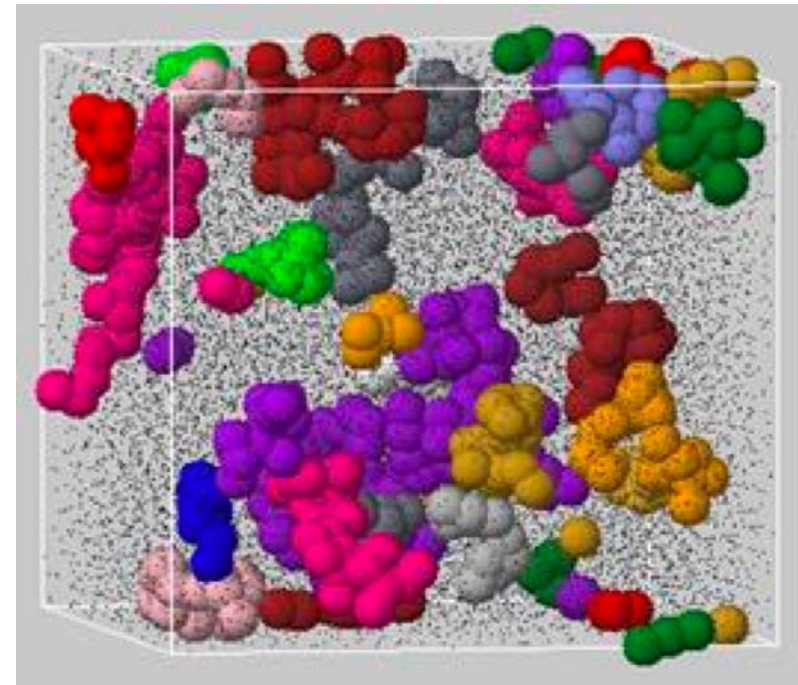


FIG. 3. The spatial distribution of propensities at $T = 0.4$ calculated using 1000 runs. A circle of radius $\langle \Delta r_i^2 \rangle_{ic}$ has been drawn about the initial position of each particle i .

Dynamical heterogeneity in the spatial distribution of “propensity for motion”

From: A. Widmer-Cooper and P. Harrowell, Phys. Rev. Lett. 93, 135701 (2004).

Particles color-coded according to the distance moved \rightarrow



Dynamic Heterogeneity:

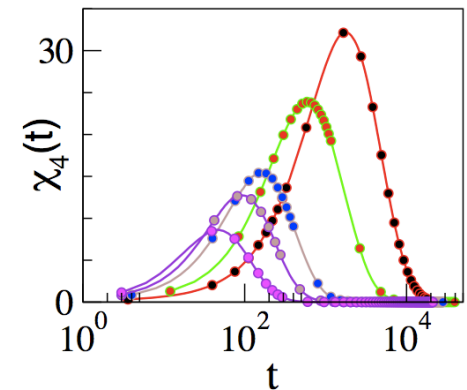
Four-point Correlation function:

$$g_4(\mathbf{r}, t) = \langle \delta\rho(0, 0)\delta\rho(0, t)\delta\rho(\mathbf{r}, 0)\delta\rho(\mathbf{r}, t) \rangle \\ - \langle \delta\rho(0, 0)\delta\rho(0, t) \rangle \langle \delta\rho(\mathbf{r}, 0)\delta\rho(\mathbf{r}, t) \rangle$$

[CD, Indrani, Ramaswamy and Phani (1991)]

$$\chi_4(t) = g_4(\mathbf{k} = 0, t)$$

- $\chi_4(t)$ peaks at $t = \tau(T)$. $\tau \propto \alpha$ -relaxation time
- $\chi_4^p(T) \equiv \chi_4(t = \tau)$ and $\tau(T)$ increase as T is decreased toward the “**mode-coupling transition temperature**” T_c .



Biroli and Bouchaud (2004); Berthier, Biroli, Bouchaud, Kob, Miyazaki, Reichman (2006):

Growth of $\chi_4^p(T)$ and $\tau(T)$ is associated with a **dynamical correlation length** $\xi(T)$ that grows as T is decreased toward T_c .

$$\xi(T) \sim \left(\frac{T - T_c}{T_c}\right)^{-\nu}, \quad \chi_4^p(T) \sim \left(\frac{T - T_c}{T_c}\right)^{-\gamma} \sim \xi^{\gamma/\nu} \quad \tau(T) \sim \left(\frac{T - T_c}{T_c}\right)^{-\delta} \sim \xi^{\delta/\nu}$$

Crossover to “activated dynamics” is believed to occur in three-dimensional systems at a temperature slightly higher than T_c .

The system-size dependence of $\chi_4^p(T)$ and $\tau(T)$ in the temperature range in which they exhibit power-law growth should exhibit **finite-size scaling** similar to that observed near a continuous phase transition.

Finite size scaling

In a system with a dominant, large correlation length $\xi(T)$, (e.g. near the critical point of systems exhibiting a second order phase transition), the dependence of thermodynamic quantities on the system size L is determined by $L/\xi(T)$.

Susceptibility $\chi(T, L) = \chi_0(T) f[L/\xi(T)]$, with $\chi_0(T) \propto (T - T_c)^{-\gamma}$, and $f(x) \rightarrow 1$ as $x \rightarrow \infty$, $f(x) \propto x^{\gamma/\nu}$ as $x \rightarrow 0$.

Plots of $\chi(T, L)/\chi_0(T)$ vs. $L/\xi(T)$ for different N, T should collapse to the same scaling curve.

Finite size dynamic scaling:

Relaxation time $\tau(T, L) = \tau_0(T) g[L/\xi(T)]$, with $\tau_0(T) \propto [\xi(T)]^z$, and $g(x) \rightarrow 1$ as $x \rightarrow \infty$, $g(x) \propto x^z$ as $x \rightarrow 0$.

Molecular Dynamics Simulations

Kob-Andersen binary (80:20) Lennard-Jones mixture

$$\epsilon_{AA} = 1.0, \epsilon_{BB} = 0.5, \epsilon_{AB} = 1.5;$$

$$\sigma_{AA} = 1.0, \sigma_{BB} = 0.88, \sigma_{AB} = 0.80.$$

Number density $\rho = 1.2$

Temperature range: $0.45 \leq T \leq 1.0$

Number of particles: $40 \leq N \leq 1000$

Newtonian dynamics simulations in (N,V,T) ensemble with periodic boundary conditions.

$Q(t) = \sum_i w(|\mathbf{r}_i(0) - \mathbf{r}_i(t)|)$ where

$w(r) = 1$ if $r \leq a(= 0.3)$, $= 0$ otherwise.

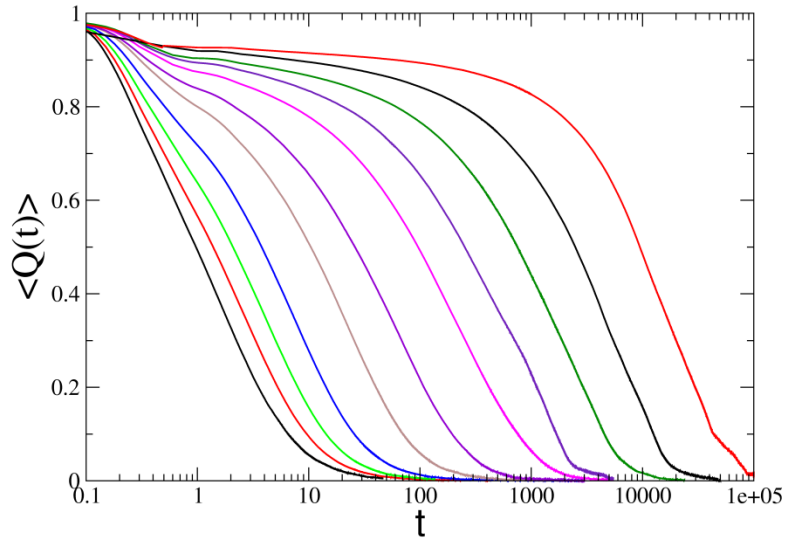
“Overlap” function $g_2(t) \equiv \langle Q(t) \rangle$.

Analogous to the “self”-part of the two-point density correlation function

Four-point susceptibility:

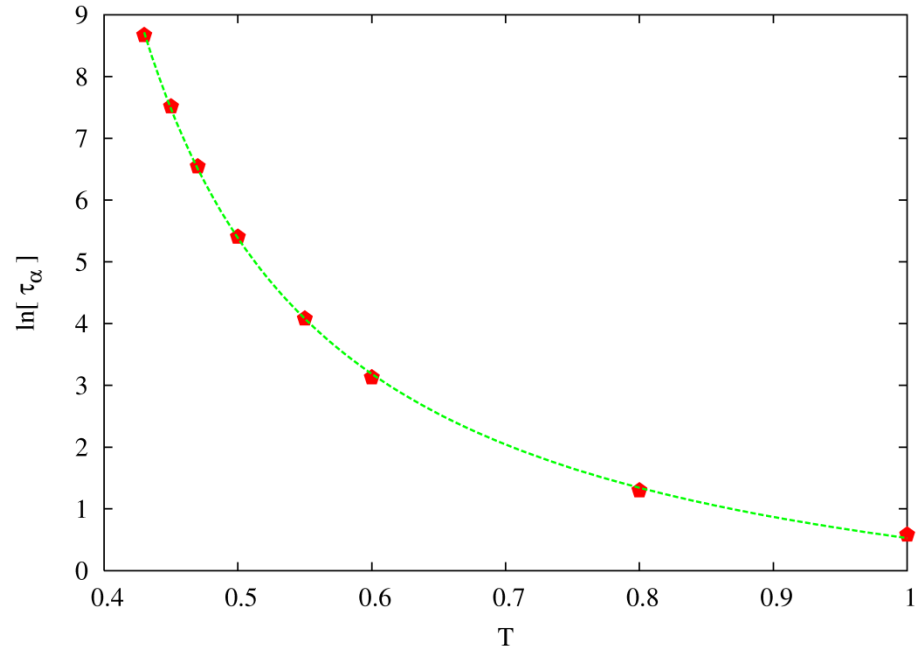
$$\chi_4(t) = \frac{1}{N} [\langle Q^2(t) \rangle - \langle Q(t) \rangle^2].$$

Results of MD simulations



Relaxation of overlap function

$g_2(t)$ fitted to stretched exponential form,
 $g_2(t) = g_0 \exp[-(t/\tau_\alpha)^\beta]$, to obtain $\tau_\alpha(T)$.



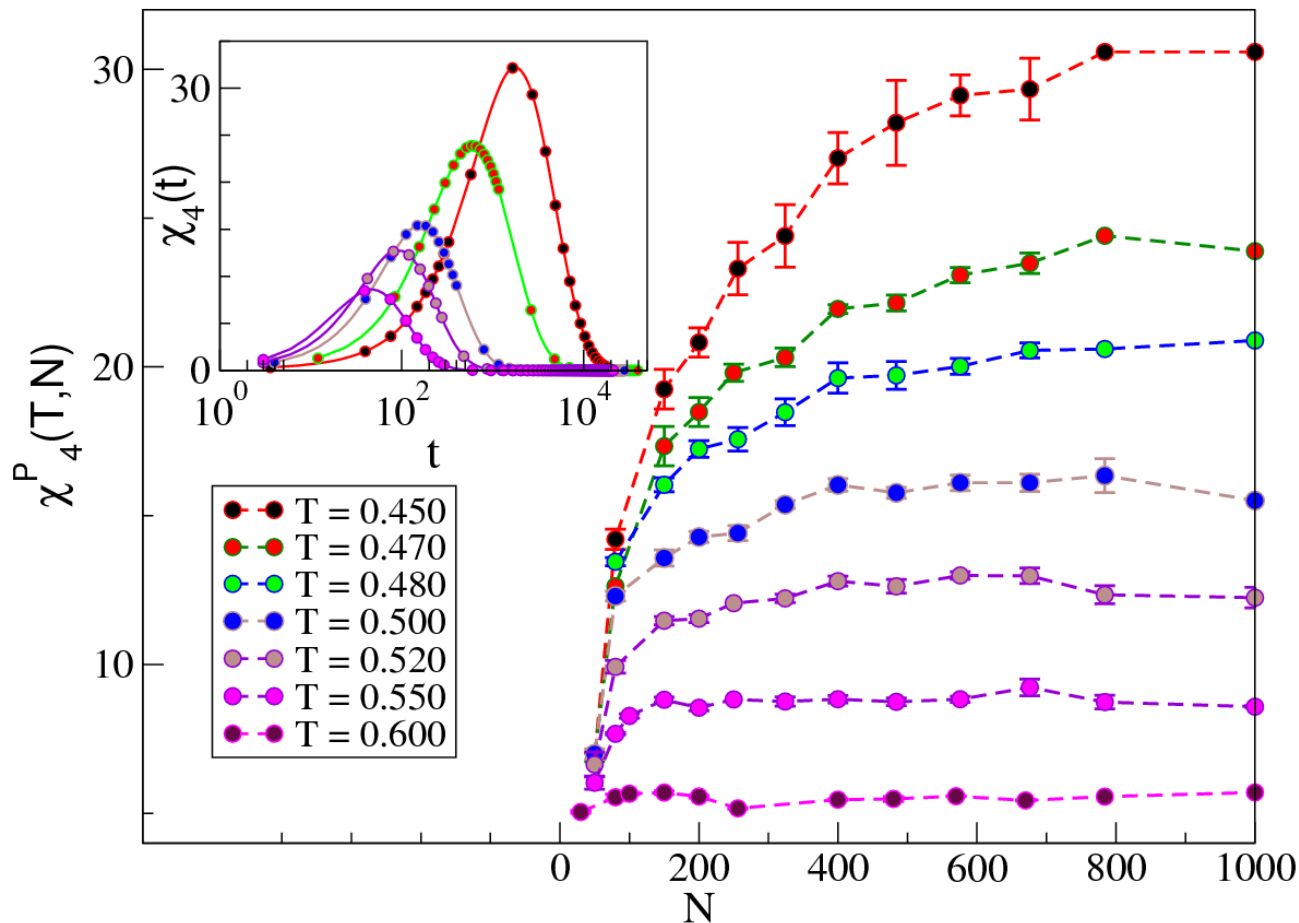
VFT Fit for the temperature dependence of the relaxation time

$$T_0 = 0.3$$

“Mode-coupling” fit:

$\tau_\alpha(T) \propto (T - T_c)^{-\delta}$ with $T_c \simeq 0.43$ and
 $\delta \simeq 2.4$ for $0.47 \leq T \leq 1.0$.

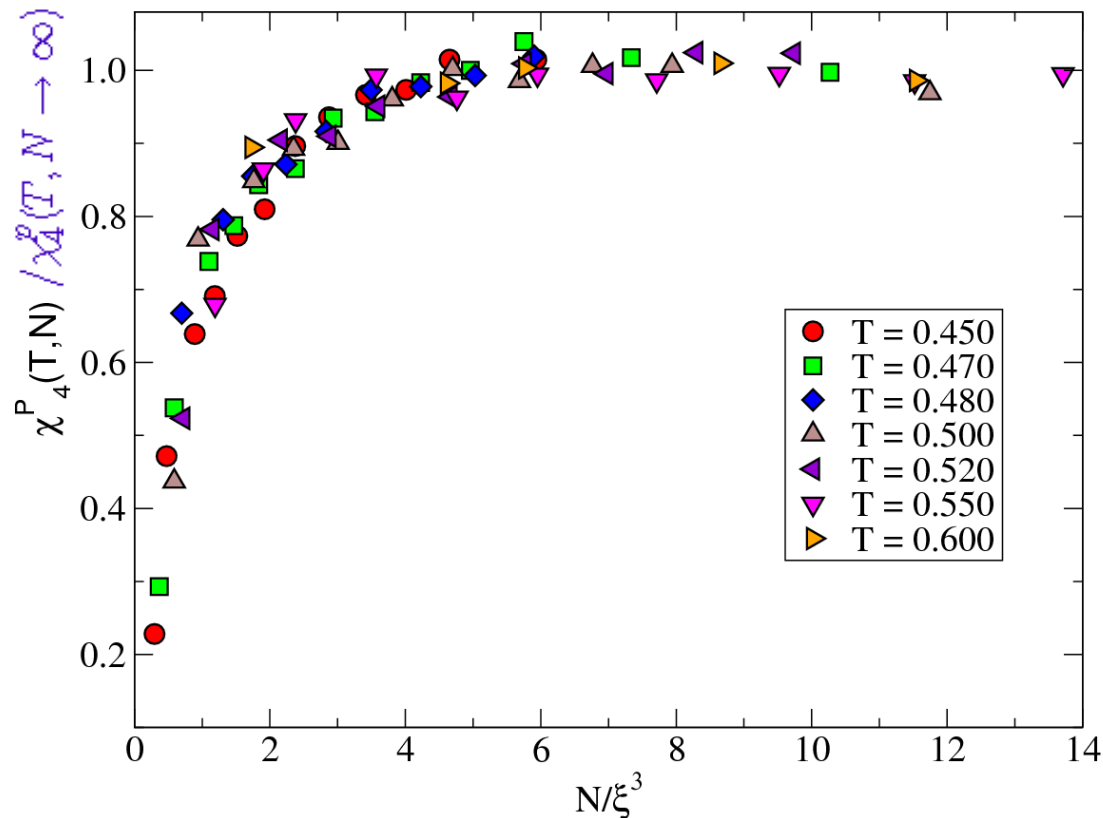
T - and N -dependence of χ_4



N -dependence of $\chi_4^p(T, N)$ for $T = 0.45, 0.47, 0.48, 0.50, 0.52, 0.55, 0.60$, from top to bottom

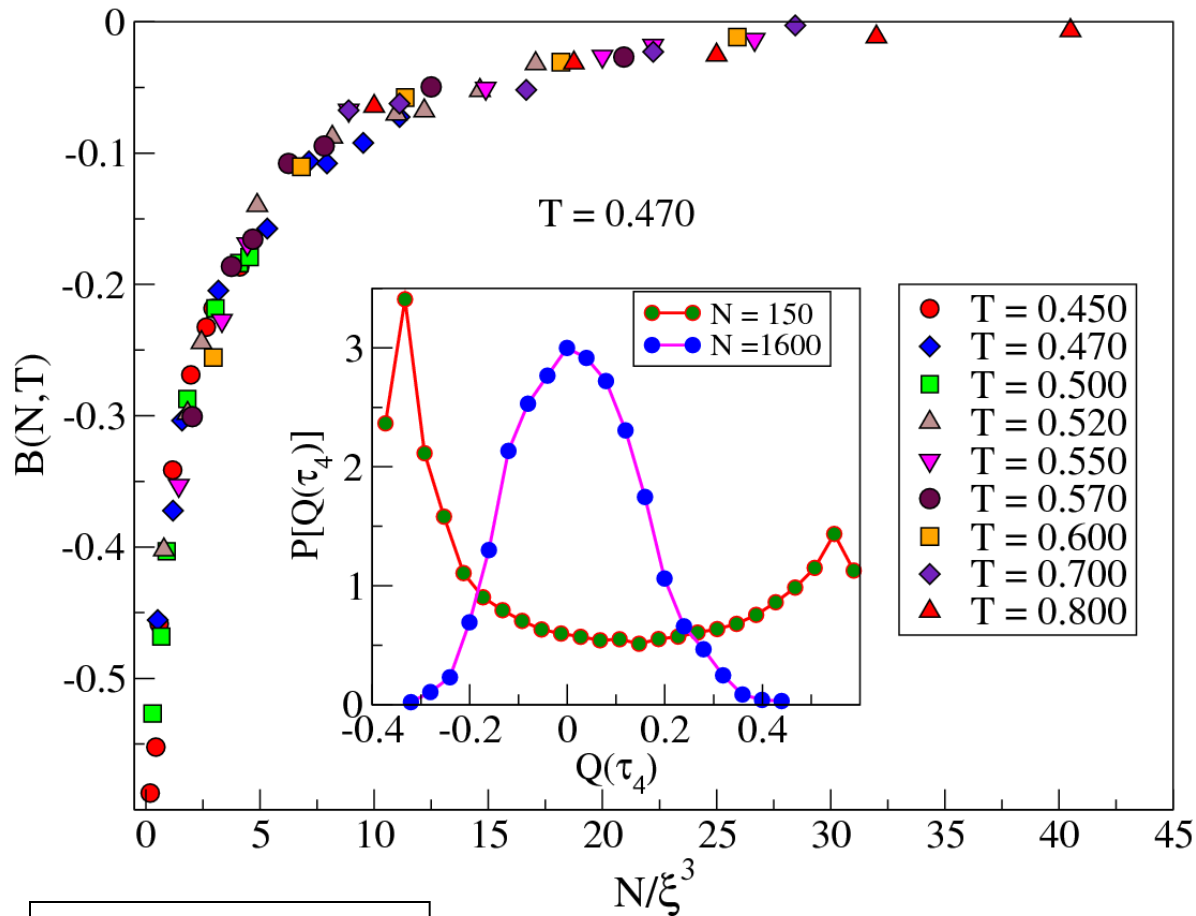
χ_4^p increases with N and then saturates.

Finite-size scaling for $\chi_4^p(T, N)$



$\chi_4^p(T, L) = \chi_0(T) f(L/\xi(T))$, with $\chi_0(T) \propto (T - T_c)^{-\gamma}$,
and $f(x) \rightarrow 1$ as $x \rightarrow \infty$, $f(x) \propto x^{\gamma/\nu}$ as $x \rightarrow 0$.

Plots of $\chi_4^p(T, L)/\chi_0(T)$ vs. $L/\xi(T)$ or N/V_ξ with $V_\xi = \xi^3$ for different N, T should collapse to the same scaling curve.



Finite-size scaling
of the
Binder Cumulant

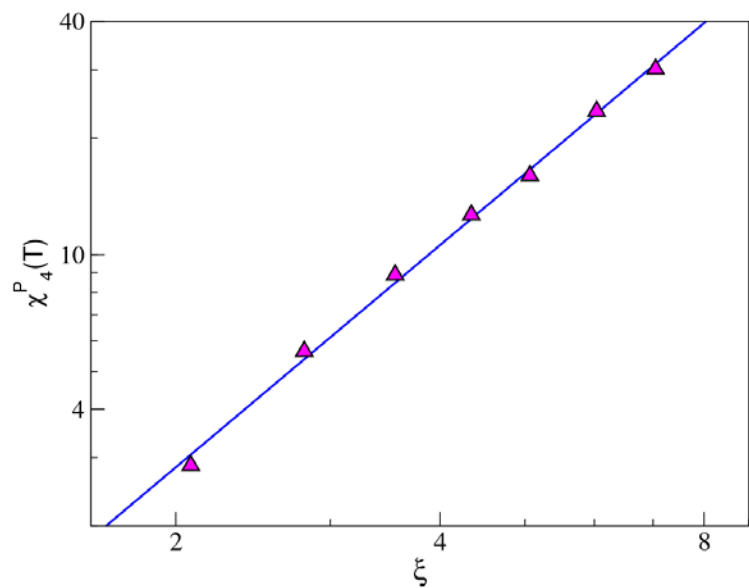
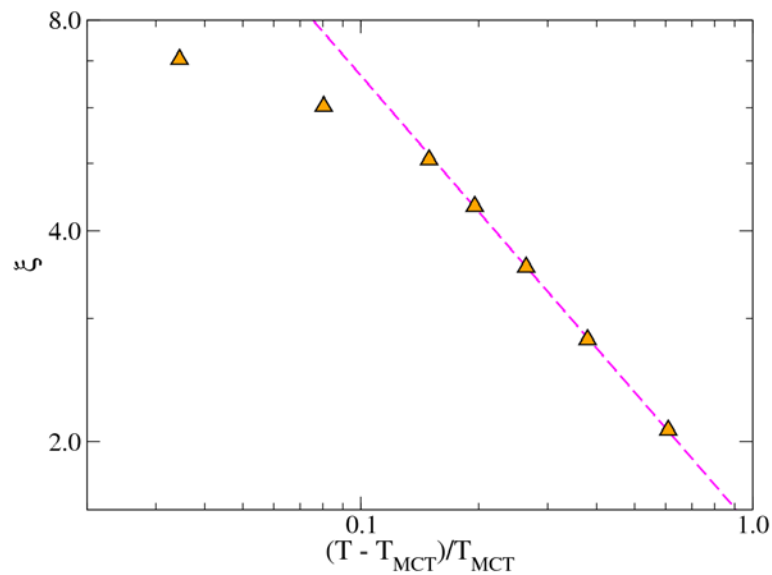
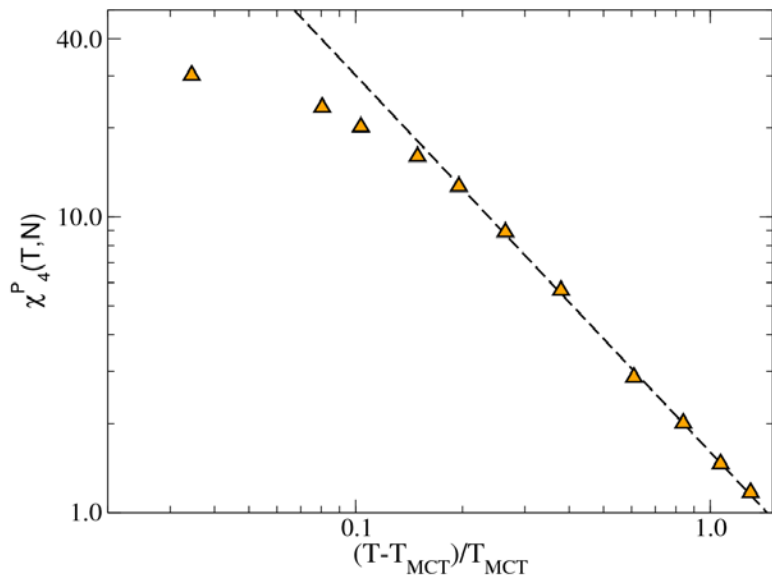
Binder Cumulant

$$B(N, T) = \frac{\langle [Q(\tau_4) - \langle Q(\tau_4) \rangle]^4 \rangle}{3 \langle [Q(\tau_4) - \langle Q(\tau_4) \rangle]^2 \rangle^2} - 1$$

$$B(N, T) = g(N/\xi^3(T))$$

Inset: Probability Distribution of $Q(\tau)$

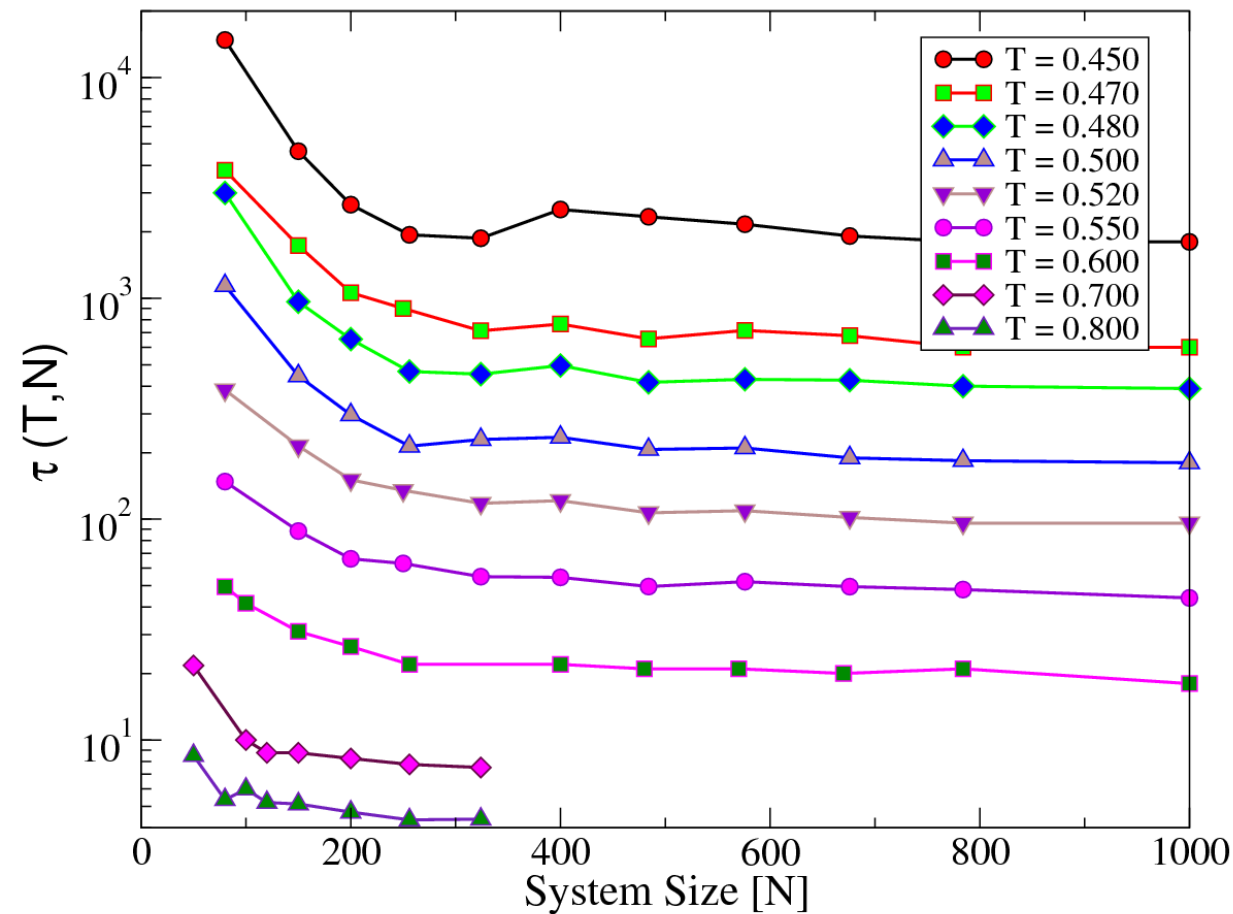
$$P[Q(\tau)] = \langle \delta(Q(\tau) - \sum_i w(|\mathbf{r}_i(t_0) - \mathbf{r}_i(t_0 + \tau)|)) \rangle$$



$$\chi_4^p(T) \propto [(T - T_c)/T_c]^{-1.3}$$

$$\xi(T) \propto [(T - T_c)/T_c]^{-0.65}$$

$$\chi_4^p(T) \propto [\xi(T)]^2$$



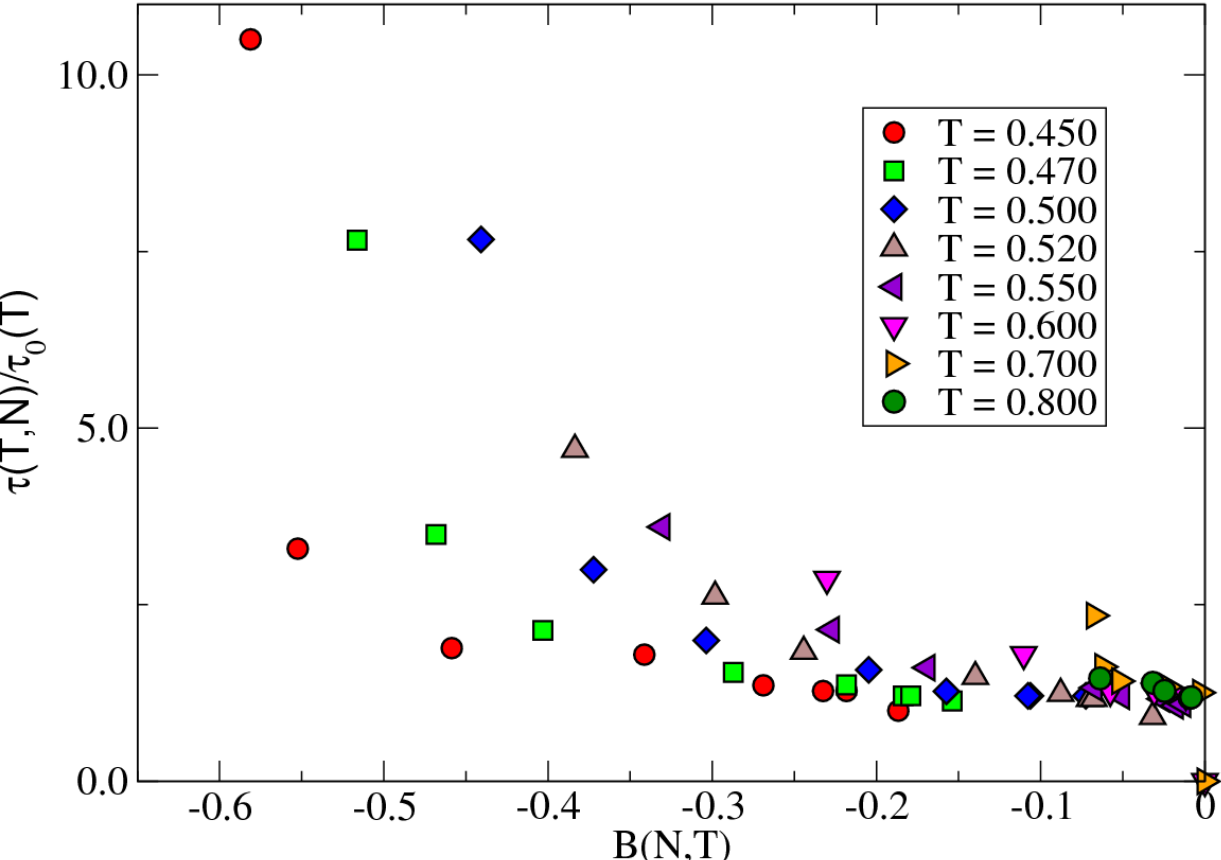
Dependence of the α relaxation time on T and N

Expected finite-size scaling form:
 $\tau(T, N) = [\xi(T)]^z g(N/\xi^3)$
 with $g(x)$ increasing with x

$\tau(T, N)$ *decreases* with increasing N for small values of N !

This behaviour is **inconsistent** with standard finite-size dynamical scaling

Does the relaxation time scale with the same correlation length?



$\tau(T, N)$ **does not** scale with correlation length $\xi(T)$

$$\tau(T, N) = \tau_0(T) f[N/\xi^3(T)]$$

$$B(T, N) = g[N/\xi^3(T)]$$

A plot of $\tau(T, N)/\tau_0(T)$ vs. $B(T, N)$ for different T and N should collapse to a single scaling curve

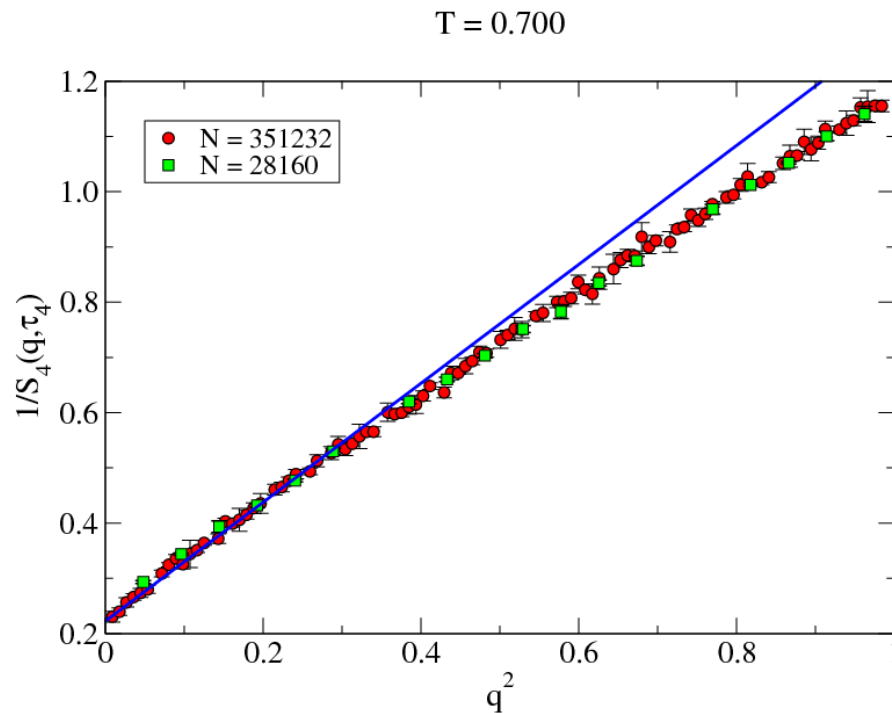
A different way of determining the correlation length $\xi(T)$

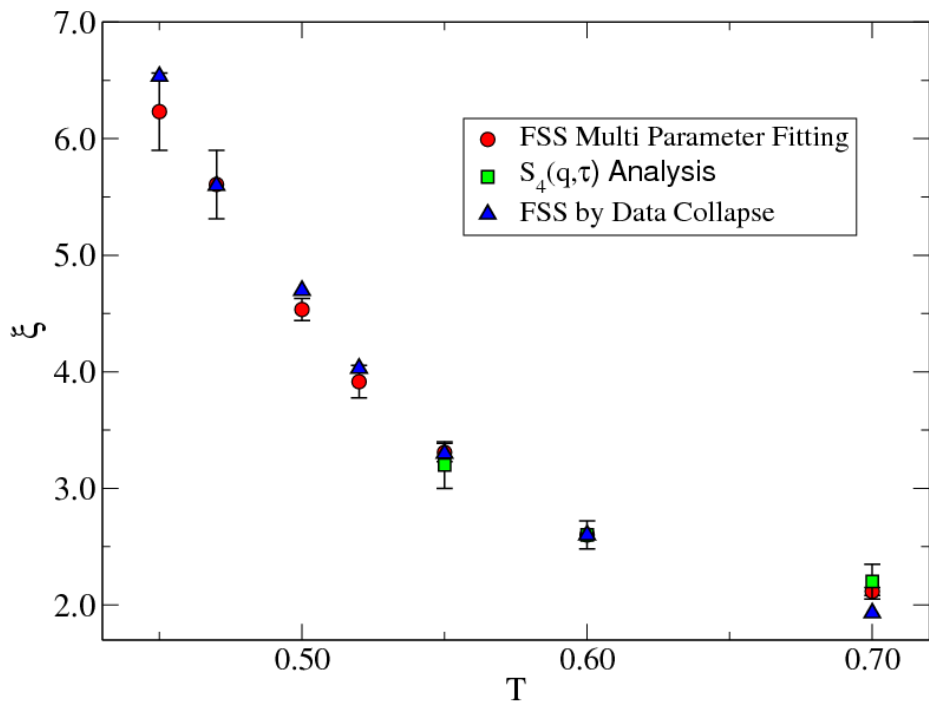
$$S_4(q, t) = \frac{1}{N} \langle \tilde{Q}(\mathbf{q}, t) \tilde{Q}(-\mathbf{q}, t) \rangle$$

Berthier (2004),
Berthier *et al* (2007)

$$\tilde{Q}(\mathbf{q}, t) \equiv \sum_{i=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_i(0)} w(|\mathbf{r}_i(0) - \mathbf{r}_i(t)|)$$

Ornstein-Zernike Form: $S_4(q, \tau) = \chi_4^p(T) / [1 + q^2 \xi^2]$ as $q \rightarrow 0$

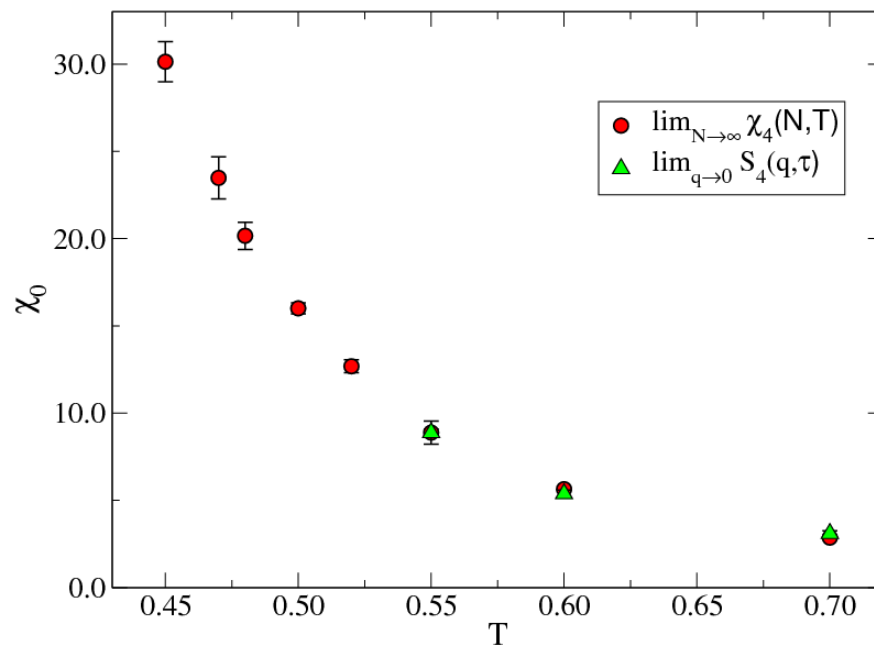




FSS results for the correlation length scaled down by 1.4%

Values of $S_4(q \rightarrow 0, \tau)$ scaled down by 1.45 (?)

Good agreement with the results obtained from finite-size scaling

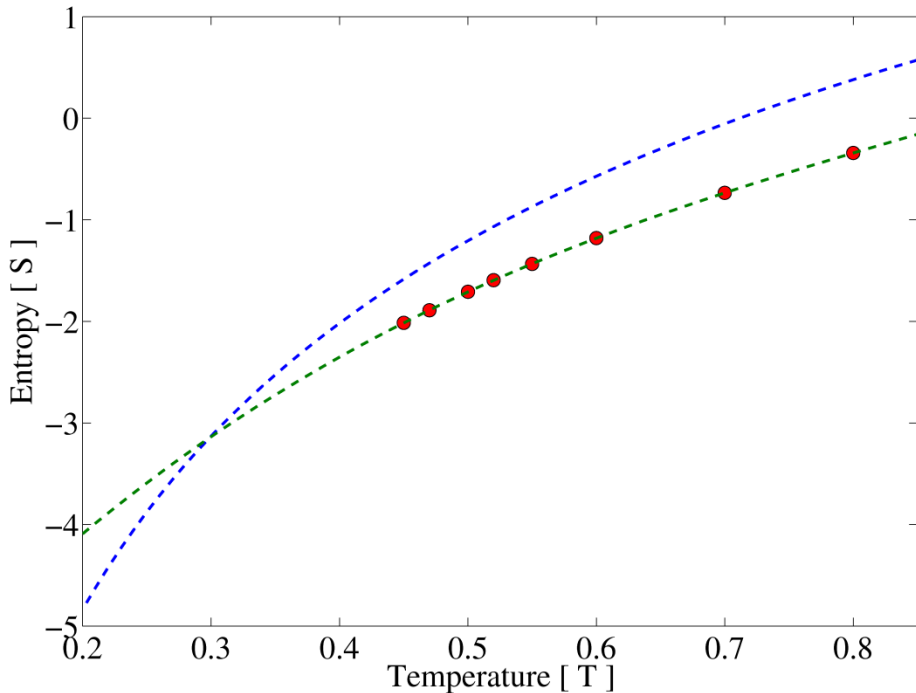


Calculation of the configurational entropy

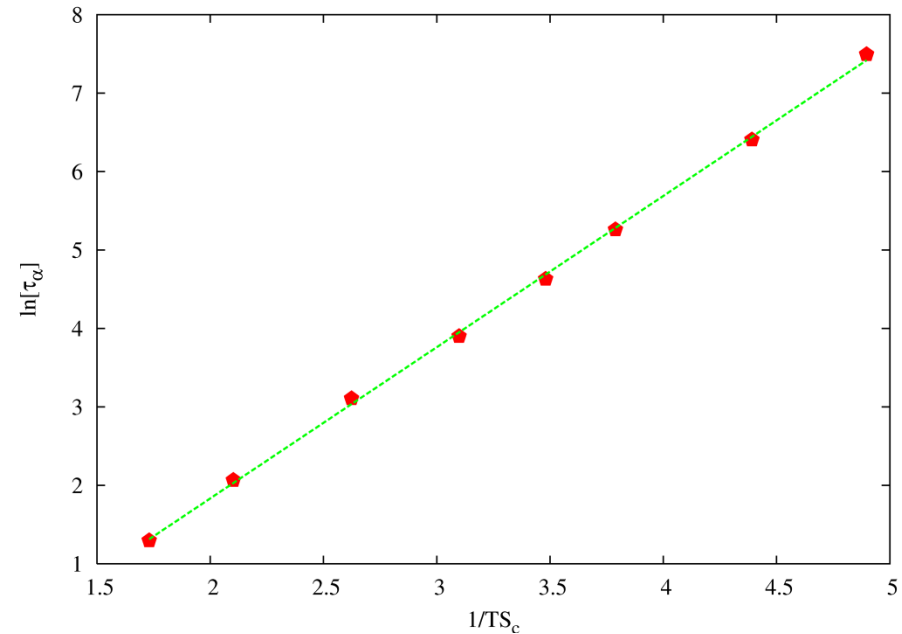
$$S_c(T) = S_{liq}(T) - S_{basin}(T)$$

$S_{liq}(T)$ is the entropy of the liquid at temperature T

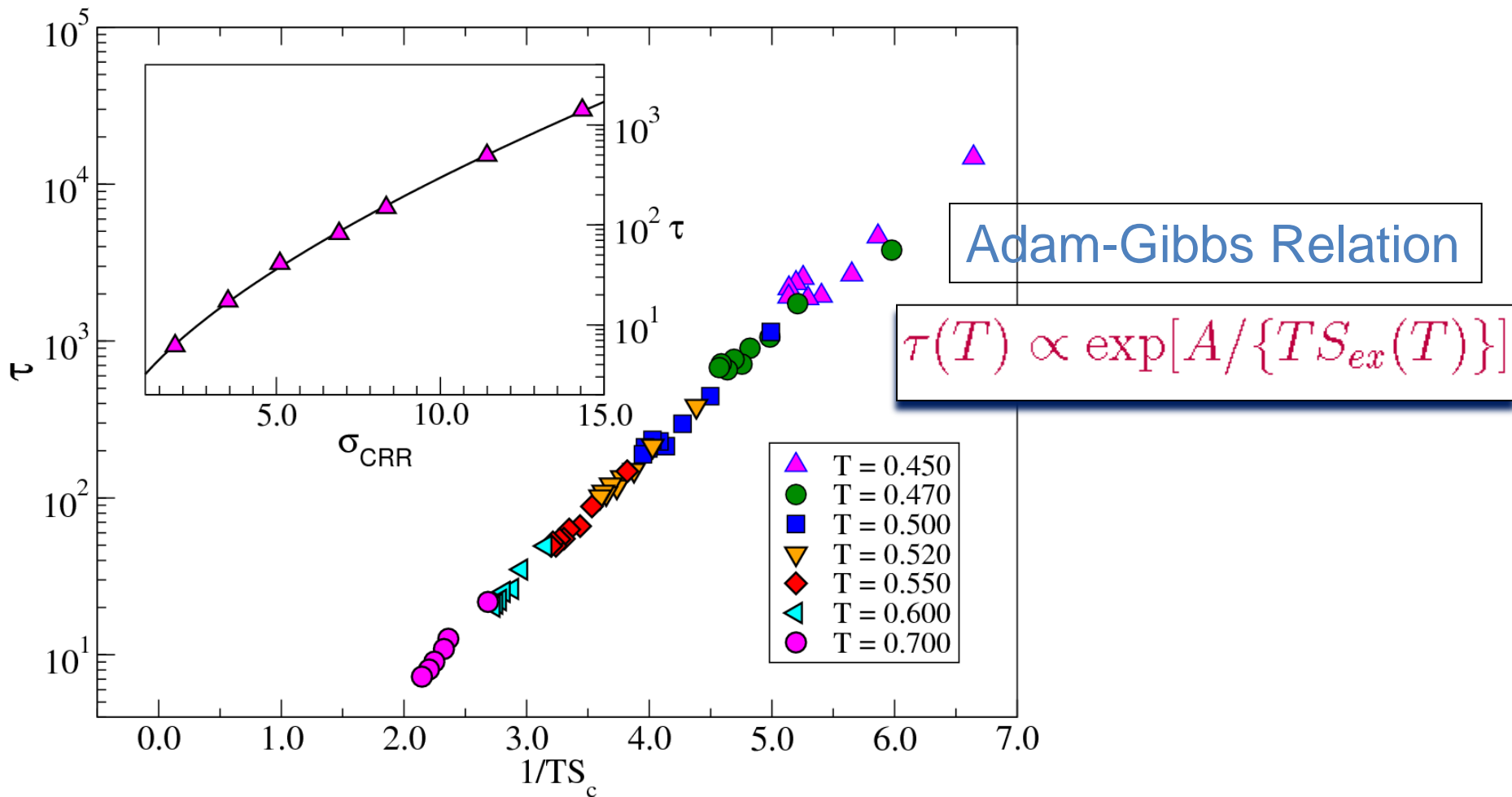
$S_{basin}(T)$ is the entropy of vibrations in the basin of an “inherent structure”



Determination of the Kauzmann temperature



Verification of Adam-Gibbs relation



The dependence of the α relaxation time on both T and N is well described by the Adam-Gibbs relation

Random First Order Transition (RFOT) Theory

[Wolynes, Kirkpatrick, Thirumalai, Biroli, Bouchaud,]

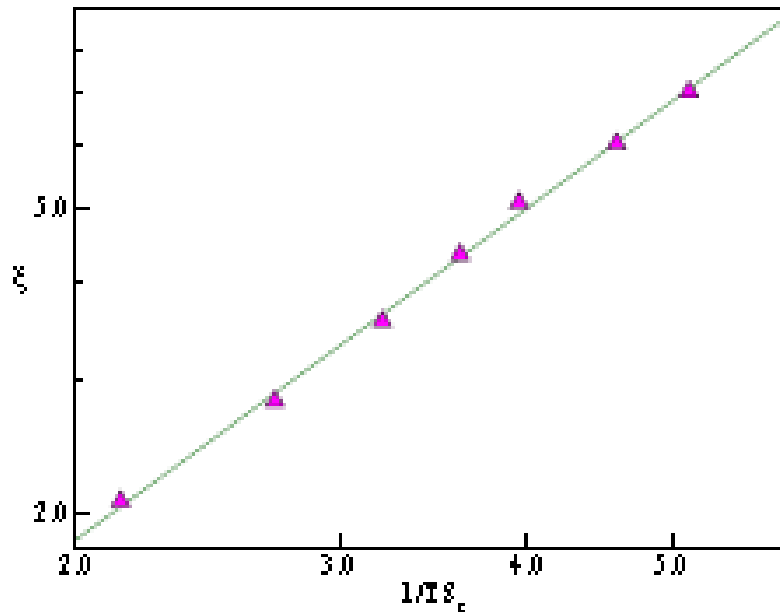
Entropic nucleation and “mosaic structure”

Extensive configurational entropy $S_c(T)$ provides an entropic mechanism for the formation of a “mosaic” structure consisting of “droplets” of different “phases”. Free energy cost of nucleating a “droplet” of *any possible* phase $\mathcal{B} \neq \mathcal{A}$ in phase \mathcal{A} is given by

$$\Delta F = -TS_C r^d / V + \sigma r^\theta$$

where r is the size of the droplet, V is the volume, σ is a generalized surface tension, and $\theta \leq d - 1$.

The barrier $(\Delta F)_{max}$ for nucleation of a different phase is the maximum of ΔF as a function of r , and the relaxation time is assumed to be proportional to $\exp[(\Delta F)_{max}^\psi / (k_B T)]$, with $\psi \leq 1$.



$$\xi(T) \propto 1/[TS_c]^{1.4}$$

Interpretation according to RFOT Theory

The values of θ and ψ are close to those obtained by Capaccioli *et al* (2008) from analysis of experimental data near the laboratory glass transition temperature.

In the “entropic nucleation” picture, the “mosaic scale” is given by

$$\xi(T) \propto 1/[TS_c(T)]^{1/(d-\theta)}$$

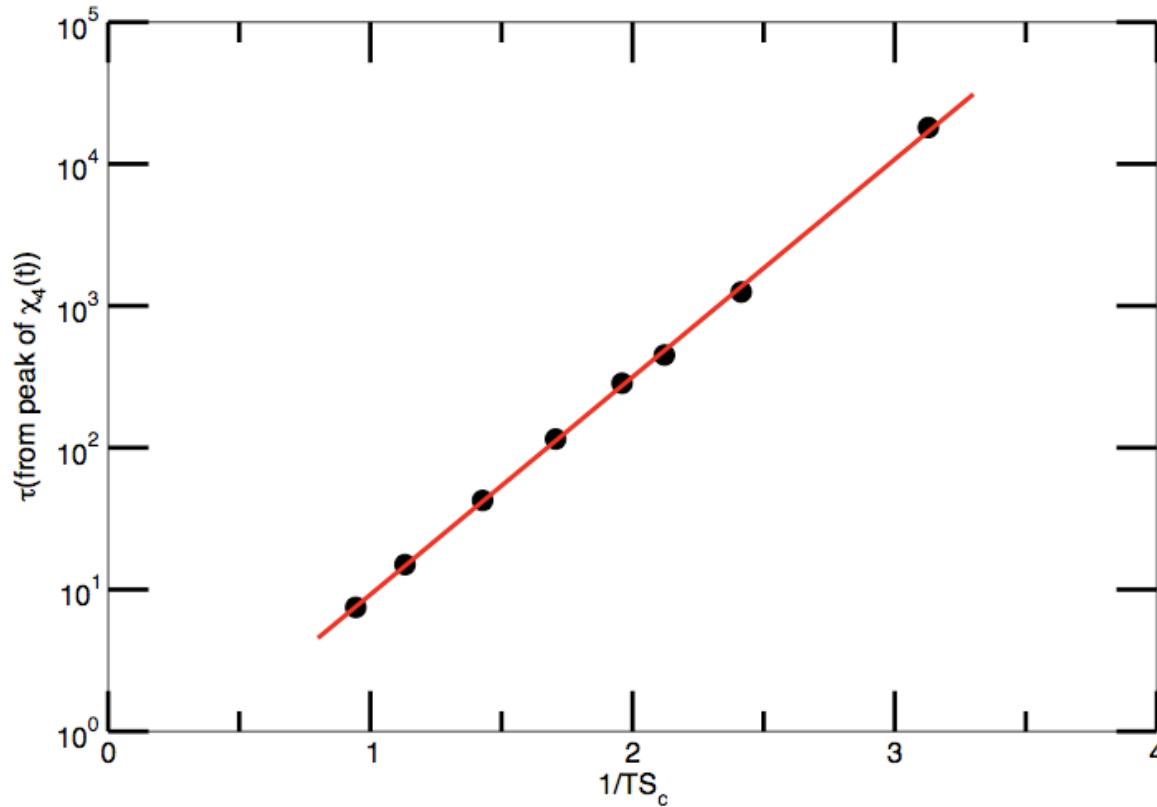
$$\theta \simeq 2.3 > d - 1 ?$$

$$1/(d - \theta) \simeq 1.4 \rightarrow \theta \simeq 2.3 > d - 1$$

$$\tau(T, N \rightarrow \infty) \propto \exp[K(\xi/k_B T)^\zeta], \quad \zeta \simeq 0.7$$

$$\zeta = \theta\psi \rightarrow \psi \simeq 0.3$$

Does the Adam-Gibbs relation work in other dimensions?



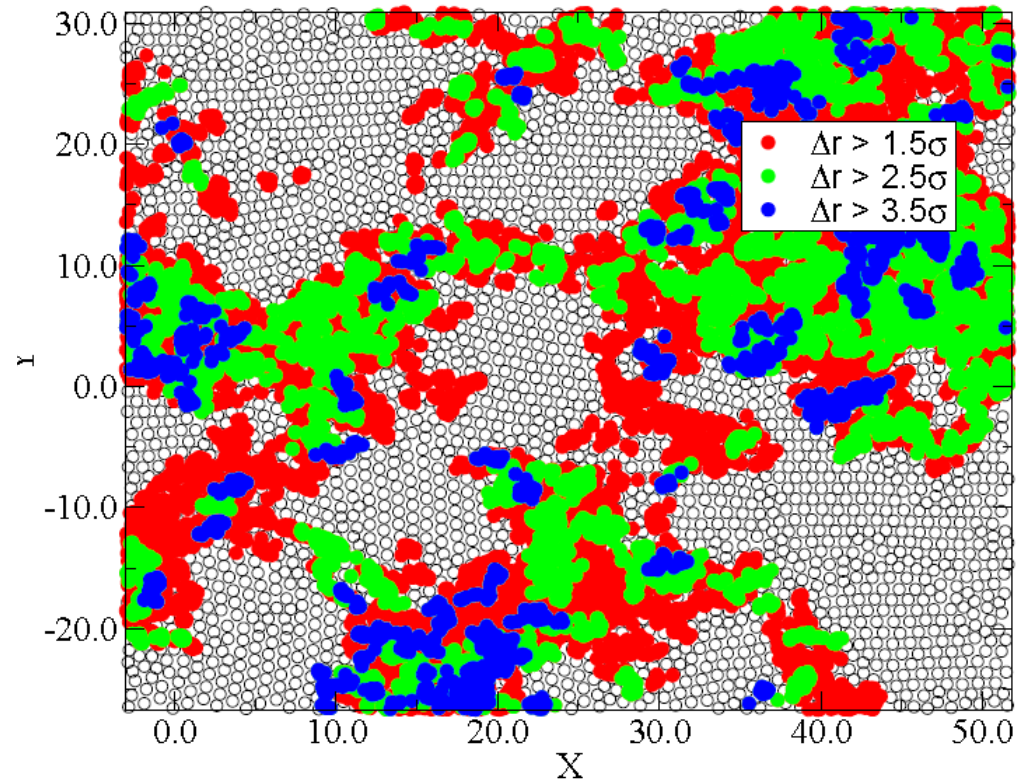
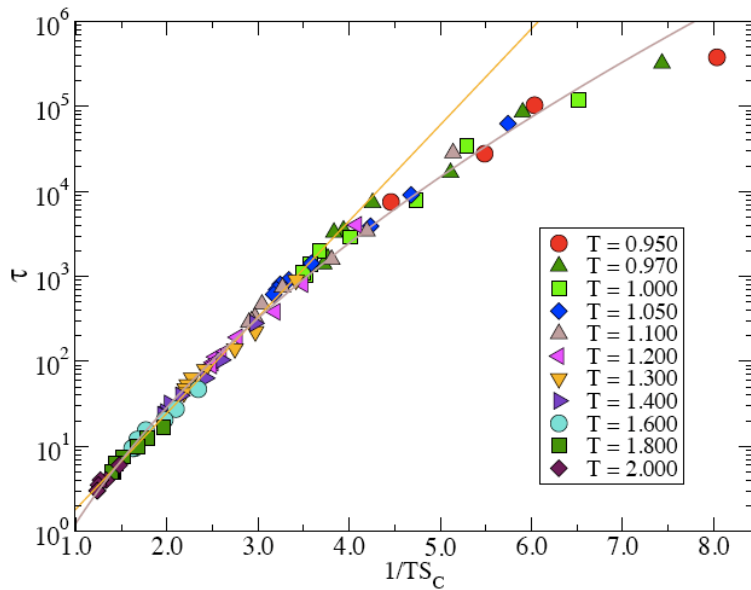
Kob-Andersen model in four dimensions

RFOT Theory:

$$\tau \propto \exp[C / (TS_c)^\alpha]$$

$$\alpha = \frac{\theta\psi}{d - \theta}$$

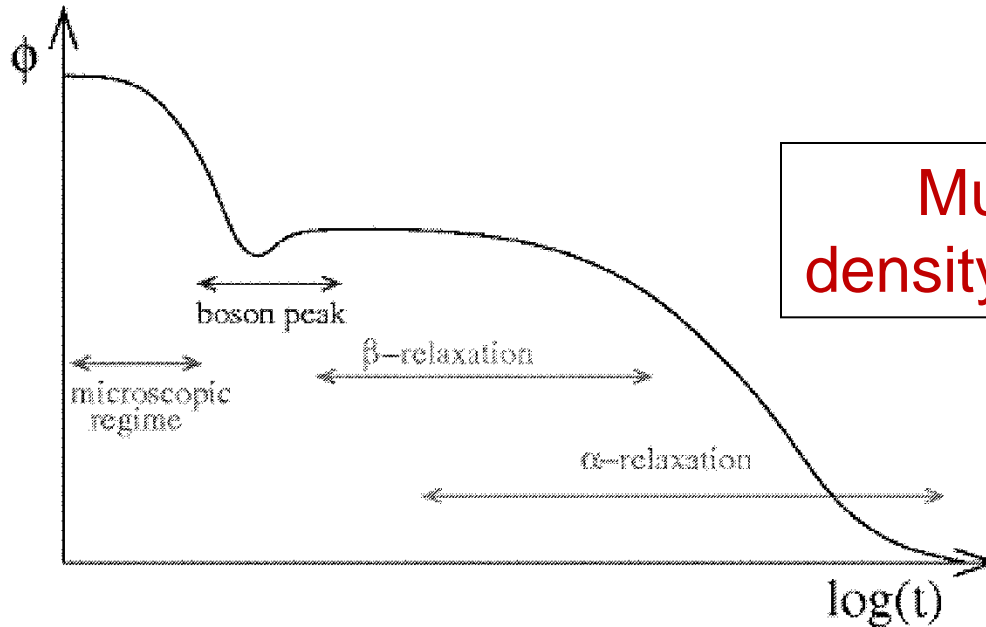
Kob-Andersen model in two dimensions



Adam-Gibbs relation does not work !

New physics from the formation of crystalline patches?

Is there a characteristic time scale in glassy dynamics that exhibits dynamic finite-size scaling with the correlation length $\xi(T)$?



Multi-step decay of density correlation function

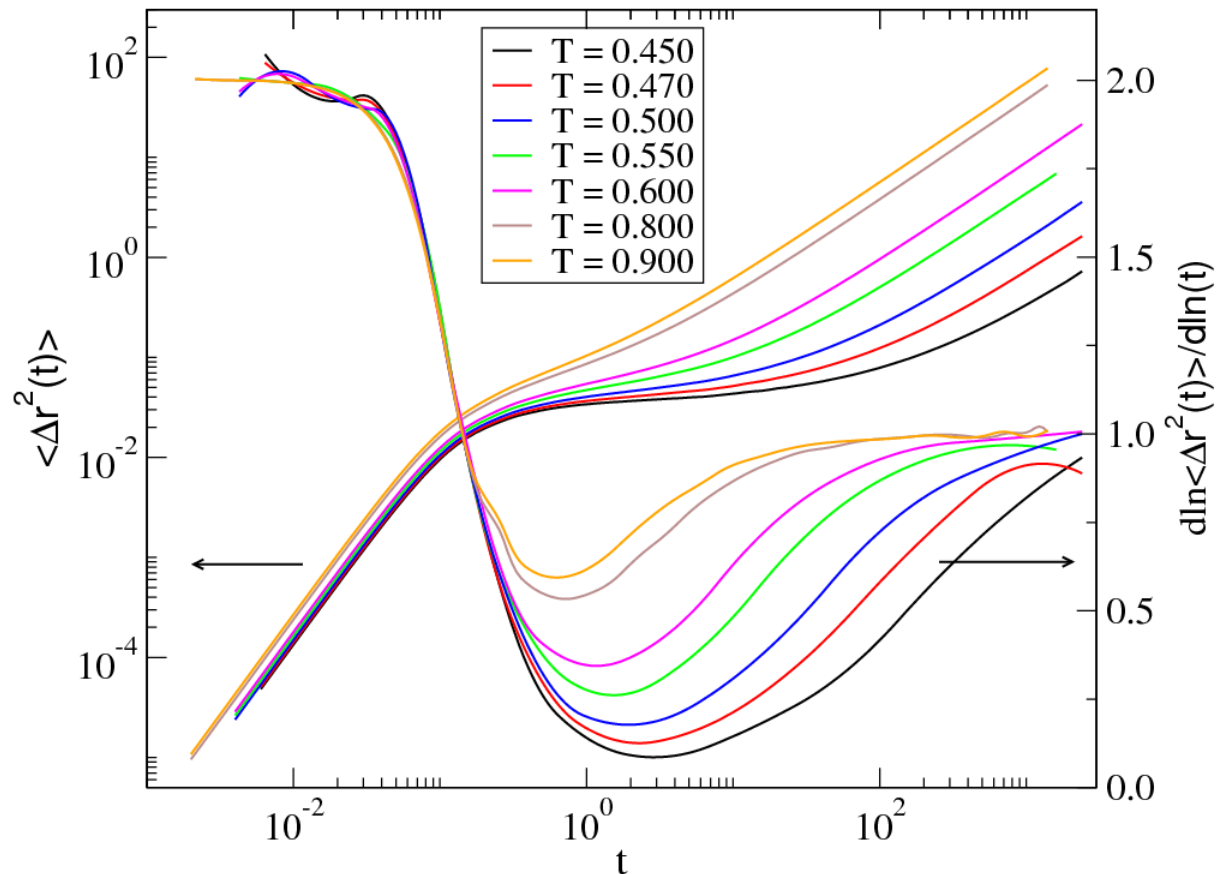
Short-time β relaxation: 'caging' regime.

Transient formation of 'cages' by the neighbors of a particle.

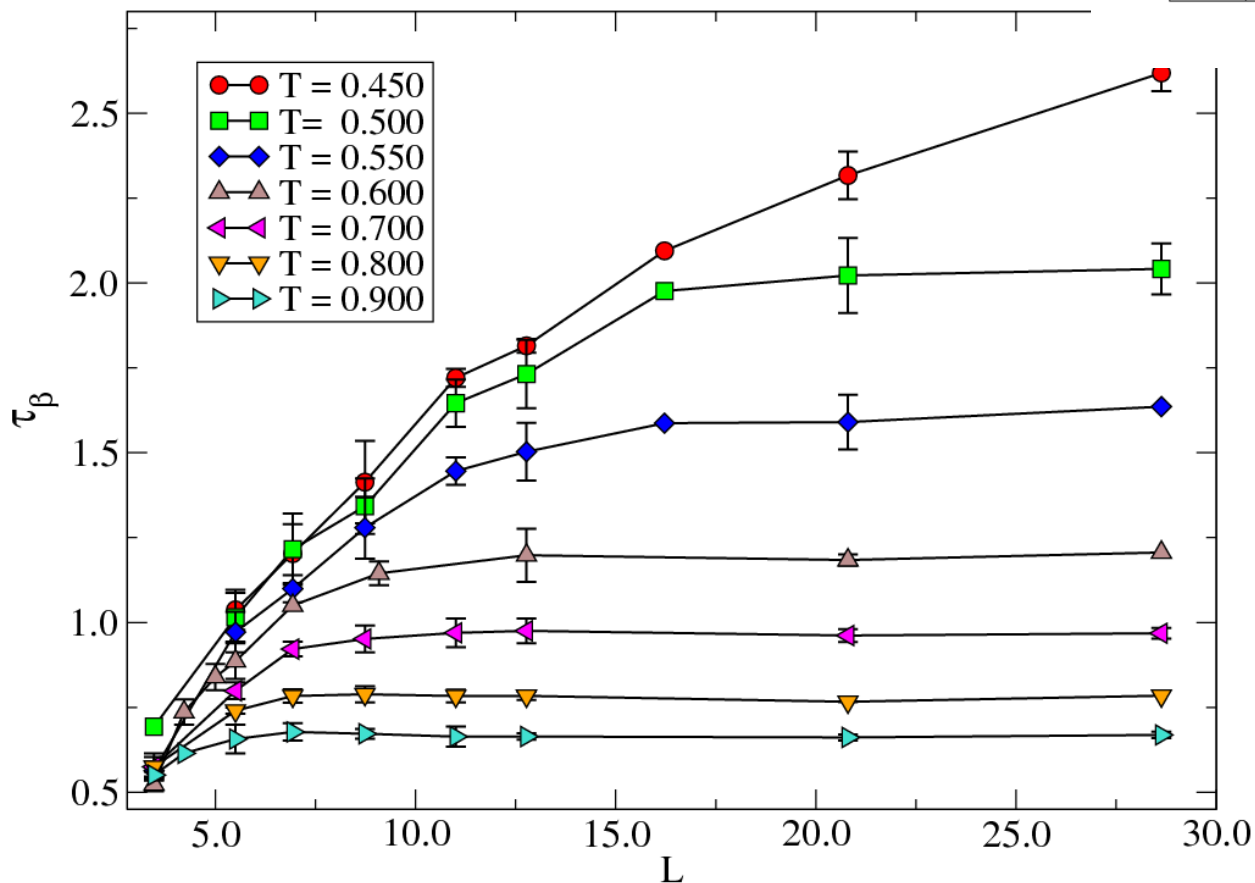
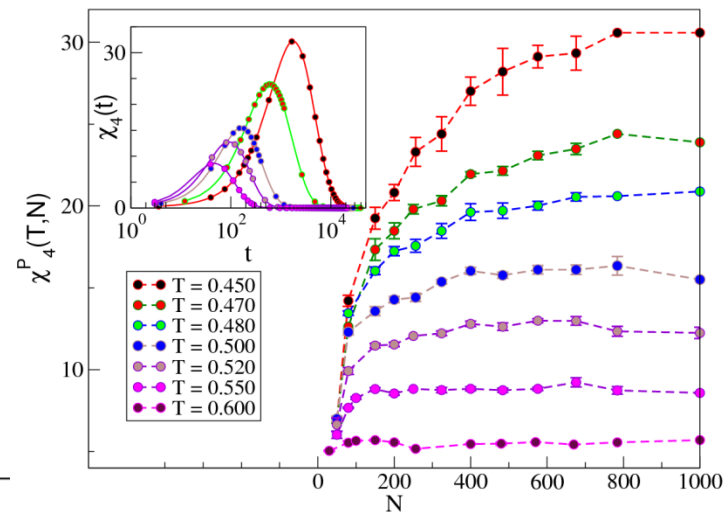
Time scale of β relaxation: Time at the minimum of

$$\frac{d \ln \langle |\Delta \mathbf{r}|^2 \rangle}{d \ln t}$$

[Stein and Andersen, PRL **101**, 267802 (2008)]

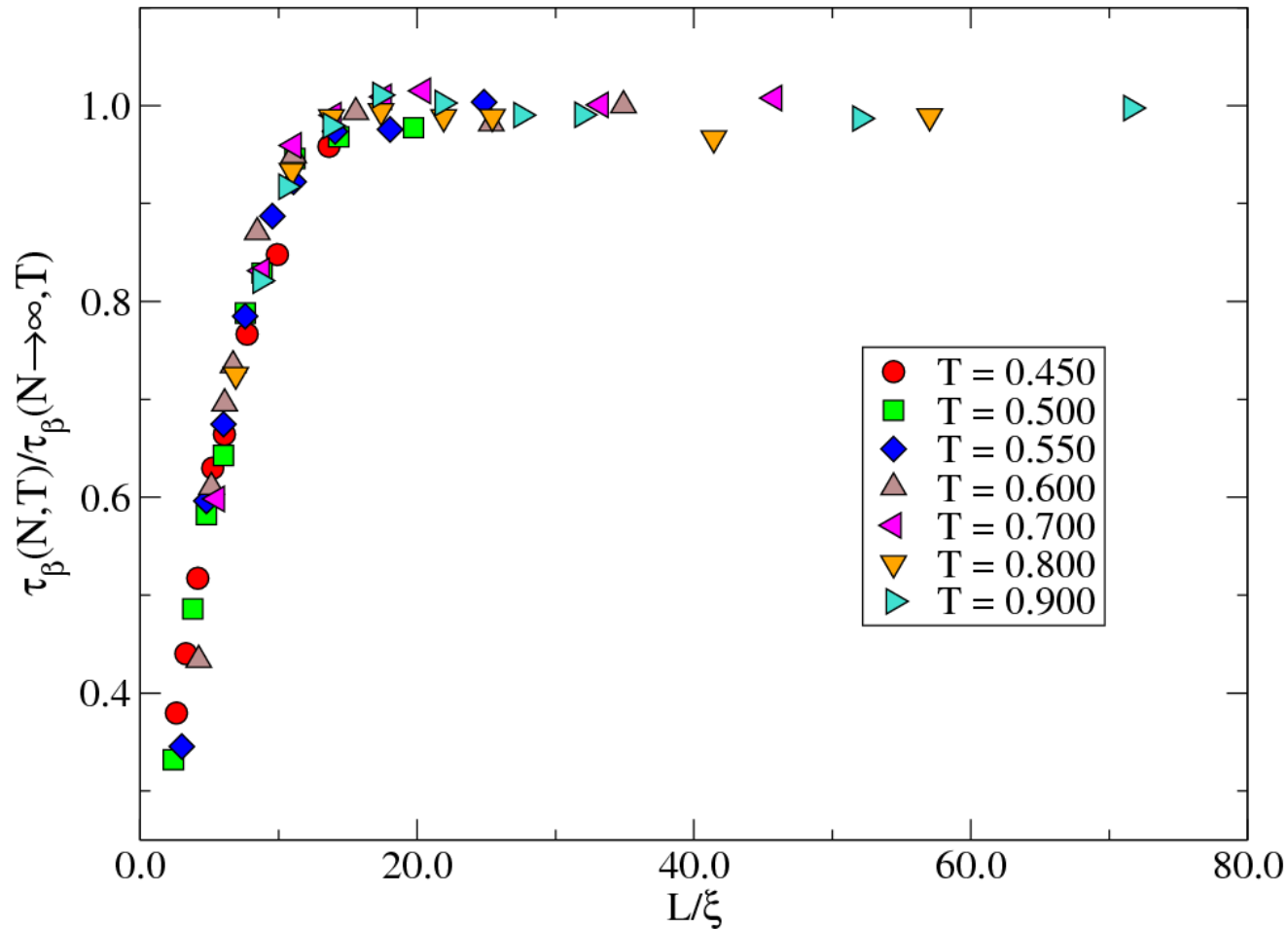


Dependence of τ_β , the time scale of β relaxation, on T and L

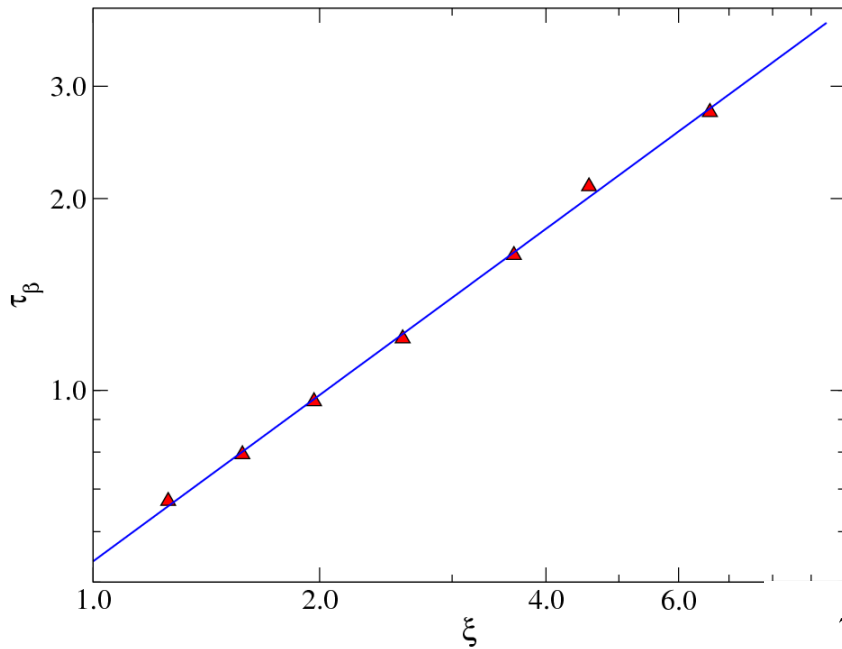


Strong dependence on system size at low temperatures

Finite-size scaling for $\tau_\beta(T, N)$



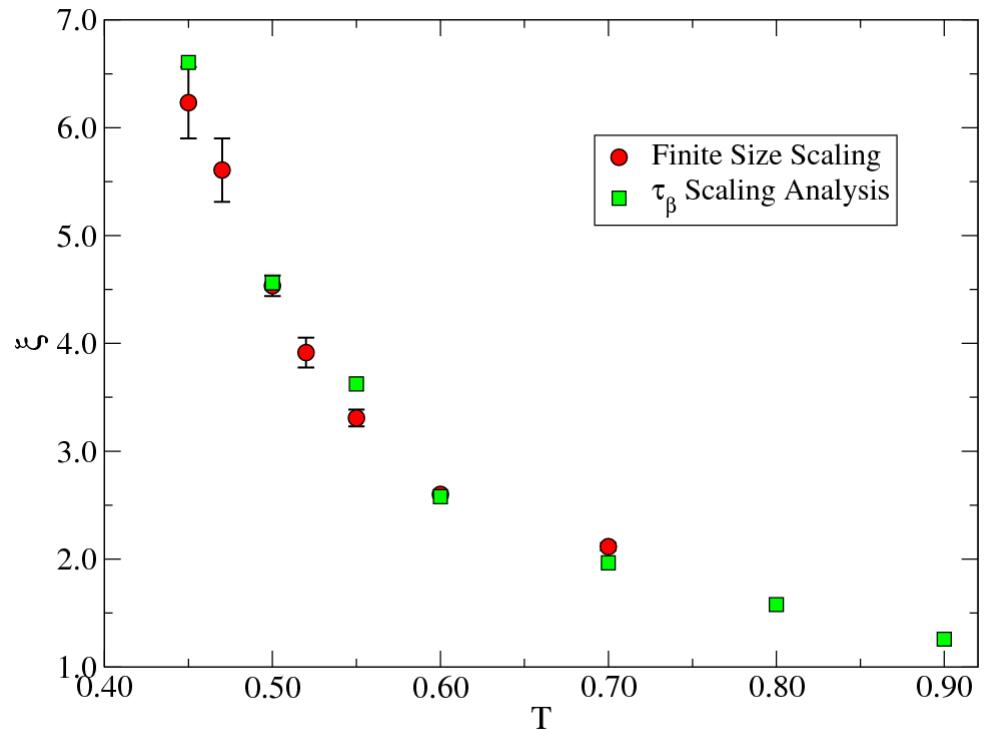
$$\tau_\beta(T, N) = \tau_\beta(T, N \rightarrow \infty) f(N/\xi^3)$$



$$\tau_{\beta}(T) \propto \xi(T)^z, \quad z \simeq 0.9$$

First clear demonstration of dynamic finite-size scaling in the dynamics of a realistic glass-forming liquid.

Length scale is the **same** as that obtained from the finite-size scaling analysis of $\chi_4^p(T, N)$



Conclusions

1. The dependence of $\chi_4^2(T, N)$ on T and N exhibits the expected finite-size scaling behaviour, confirming the existence of a growing dynamical correlation length.
2. The dependence of $\tau(T, N)$ on T and N is not consistent with the expected finite-size scaling behaviour, indicating that the growth of the relaxation time is not governed solely by the growing correlation length.
3. The dependence of the relaxation time on the configurational entropy is well described by the Adam-Gibbs relation as both T and N are varied, indicating that the configurational entropy plays a crucial role in determining the relaxation time even for T much higher than the mode-coupling transition temperature.

Conclusions (contd.)

4. Dynamics in the short-time, β - relaxation regime is governed by a growing dynamic length scale.

This length scale is the **same** as the dynamic correlation length obtained from the finite-size scaling of $\chi_4^p(T, N)$, suggesting a close connection between short-time dynamics and dynamic heterogeneity at the time scale of α relaxation.

Need to combine aspects of mode coupling theory and “activated dynamics” for a complete picture.