Growing Length and Time Scales in Glass Forming Liquids

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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

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

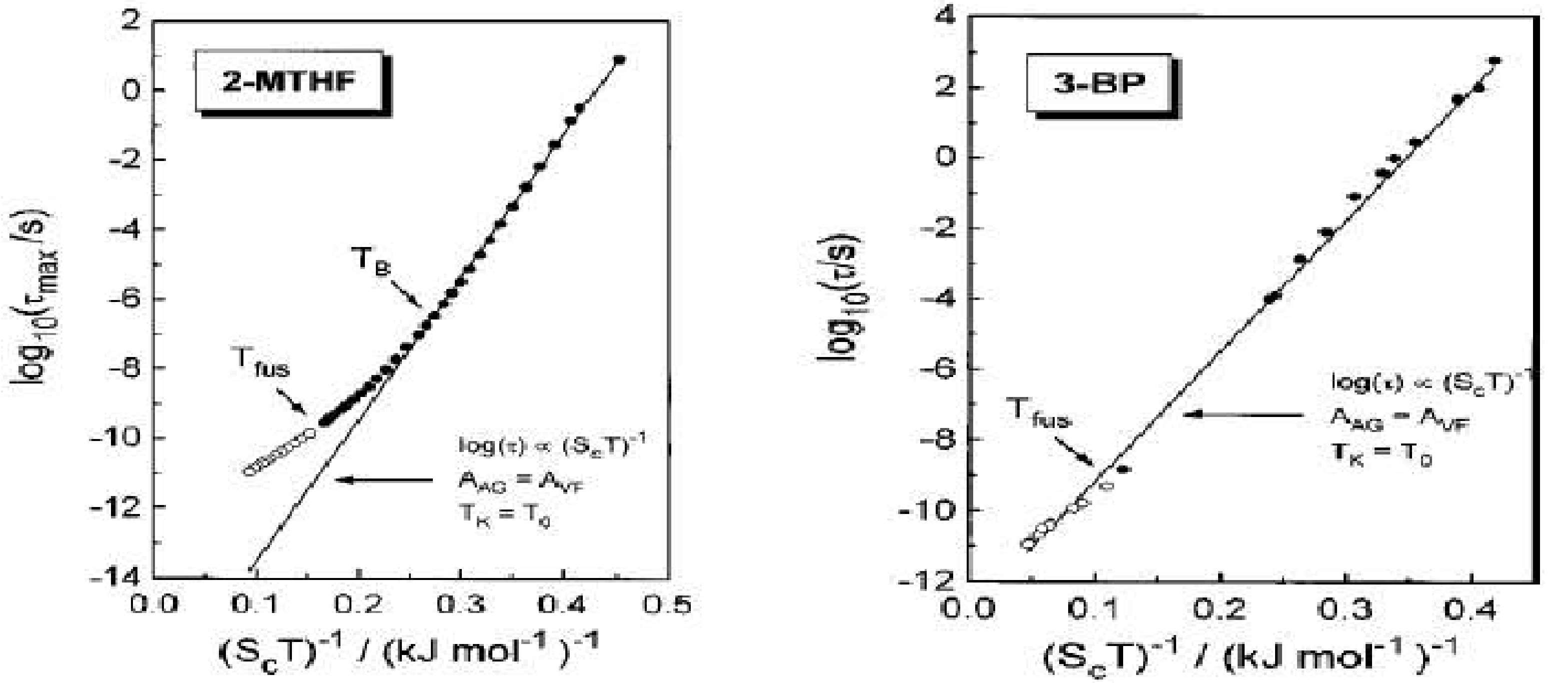
Vogel-Fulcher-Tammann (VFT) Form
"Fragile" liquid

Viscosity = 10^{13} 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



Experimental demonstration of the validity of the Adam-Gibbs relation

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

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 $T_0 = T_K$?

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".

Many proposals:

Dynamical correlation length: size of "clusters" of "fast" particles, correlation length of inhomogeneous mode coupling theory,….

Static correlation length: "mosaic" length, "point-to-set" correlation length, correlation length of equivalent spin-glass model, ….

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.

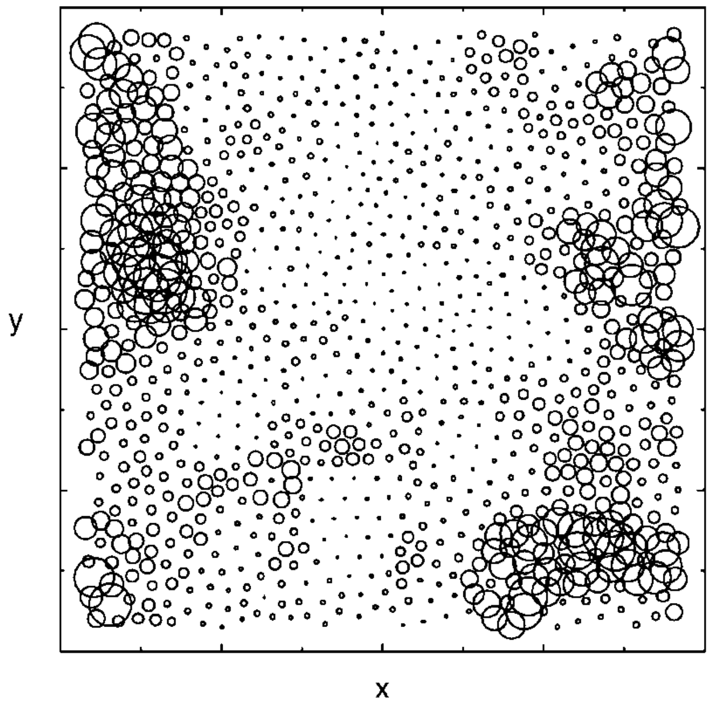
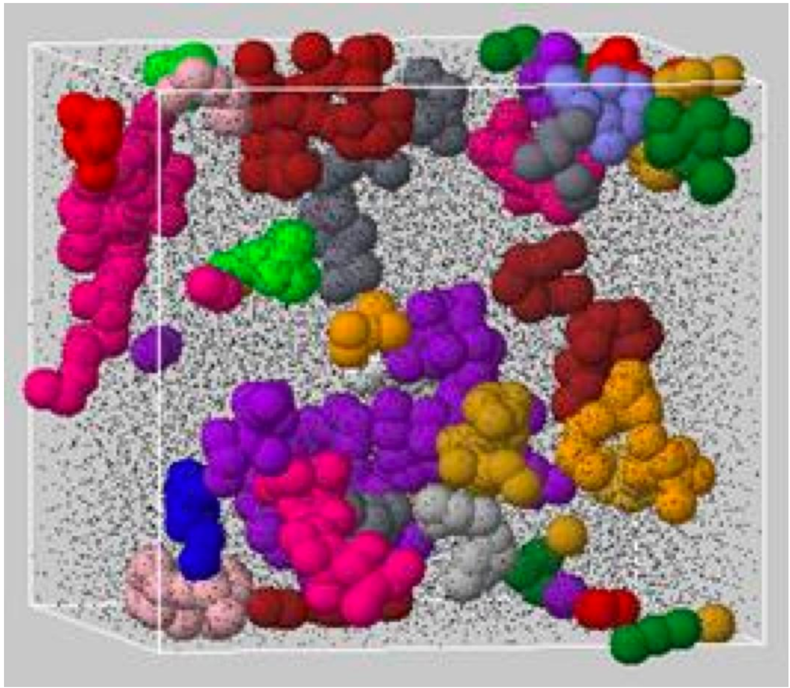


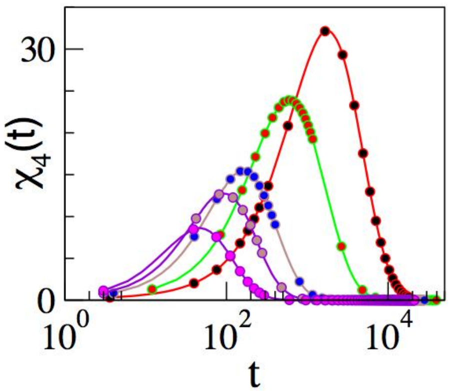
FIG. 3. The spatial distribution of propensities at $T = 0.4$ calculated using 1000 runs. A circle of radius $\langle \Delta r_i^2 \rangle_{ic}$ has been drawn about the initial position of each particle i.

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 →





Dynamical 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 $t = \tau(T)$.
- $\chi_4^p(T) \equiv \chi_4(t=\tau)$ 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.

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

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 $f(x) \to 1$ as $x \to \infty$, $f(x) \propto x^{\gamma/\nu}$ as $x \to 0$.

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 $g(x) \to 1$ as $x \to \infty$, $g(x) \propto x^z$ as $x \to 0$.

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 $g_2(t) \equiv \langle Q(t) \rangle$.

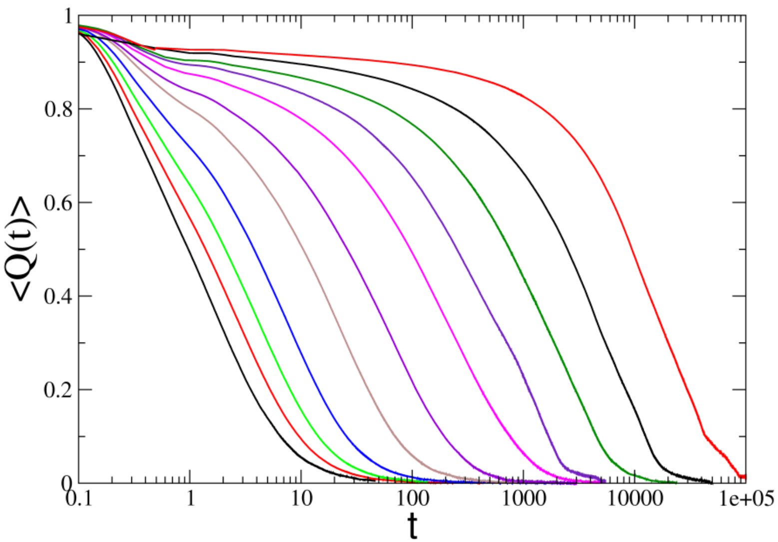
Donati *et al* (2002)

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

Four-point susceptibility:

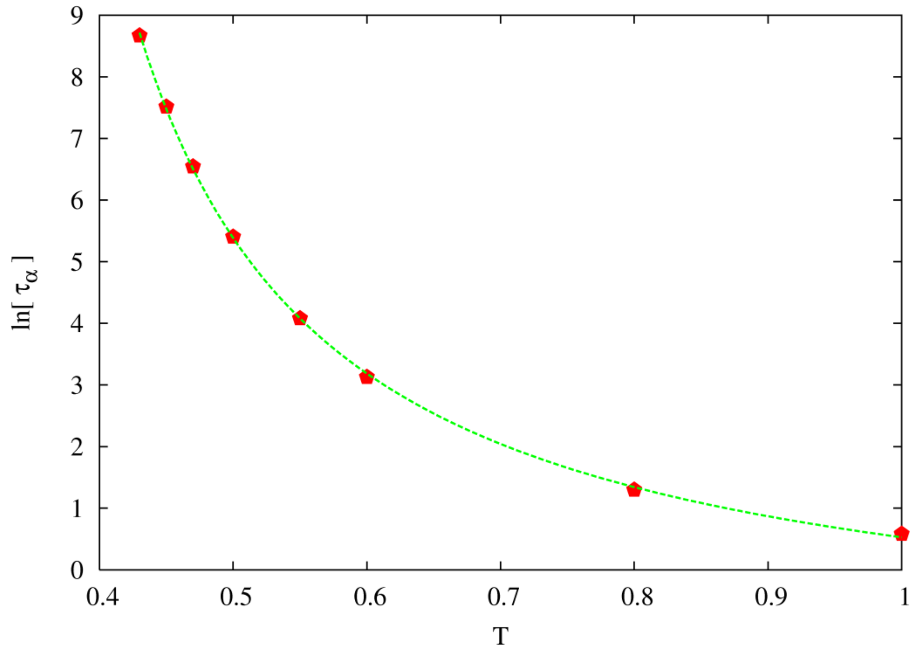
$\chi_4(t) = \frac{1}{N}[\langle Q^2(t) \rangle - \langle Q(t) \rangle^2]$.

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 $\tau_\alpha(T)$.



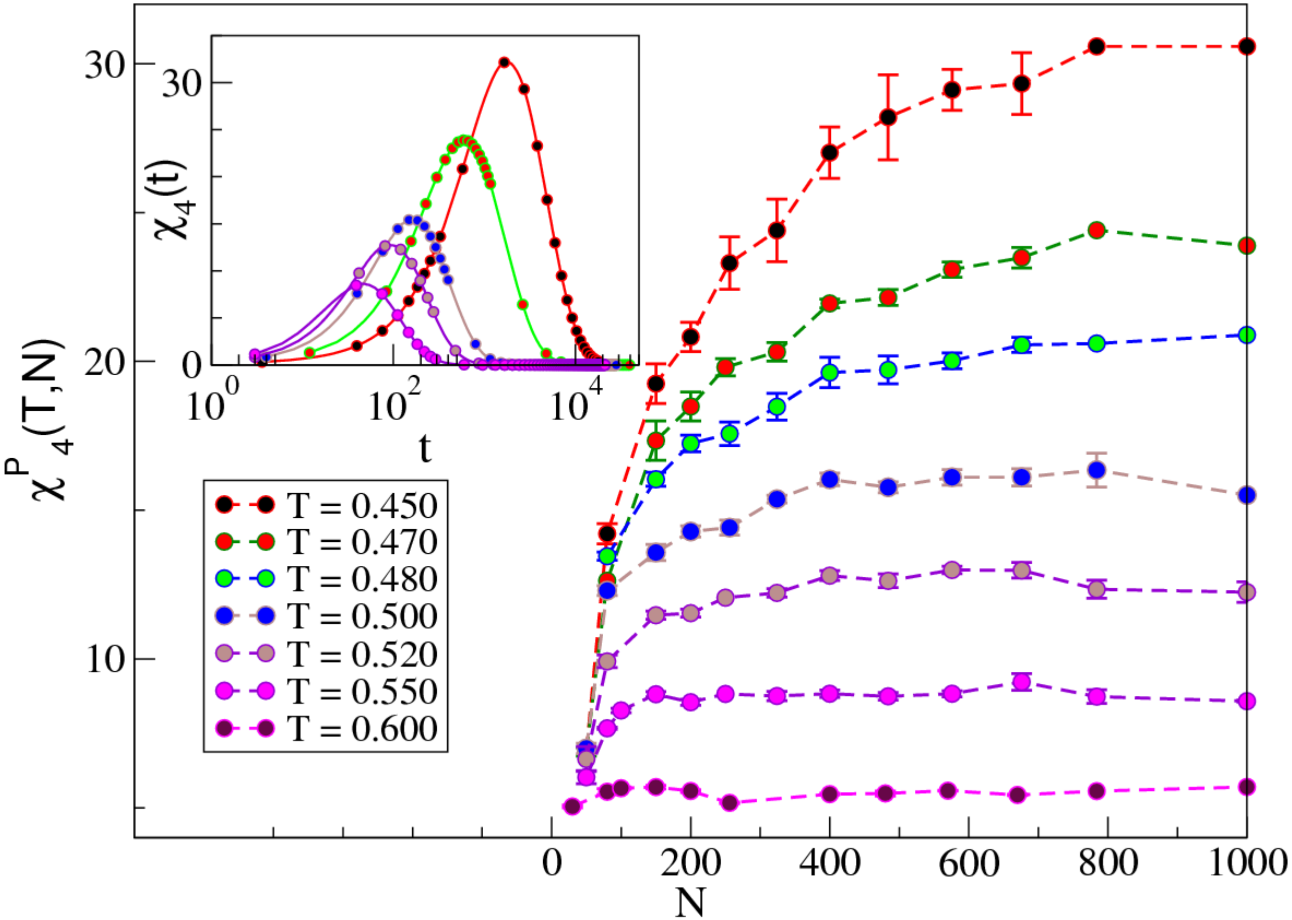
VFT Fit for the temperature dependence of the relaxation time

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

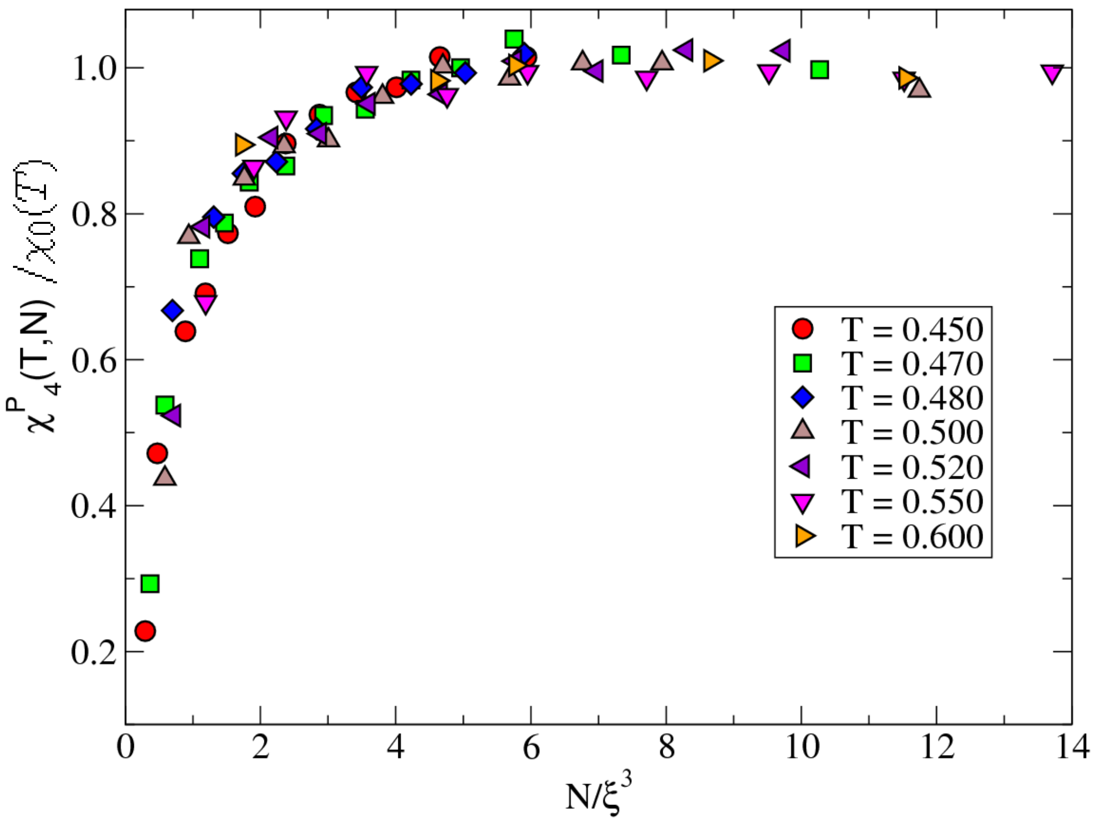


Inset:
Time-dependence
of χ_4 at different
temperatures
(N=1000)

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

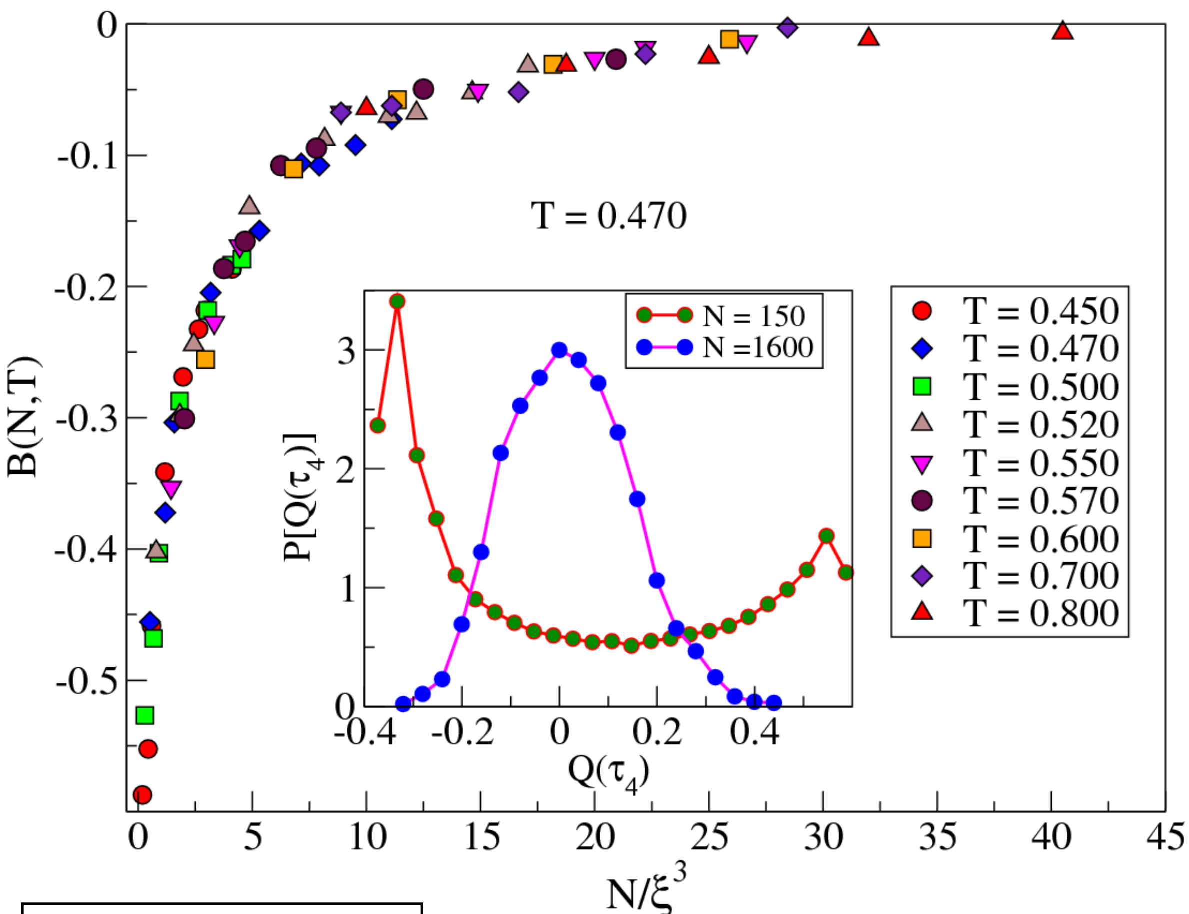
χ_4^p increases with N and then saturates.

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 $f(x) \to 1$ as $x \to \infty$, $f(x) \propto x^{\gamma/\nu}$ as $x \to 0$.

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

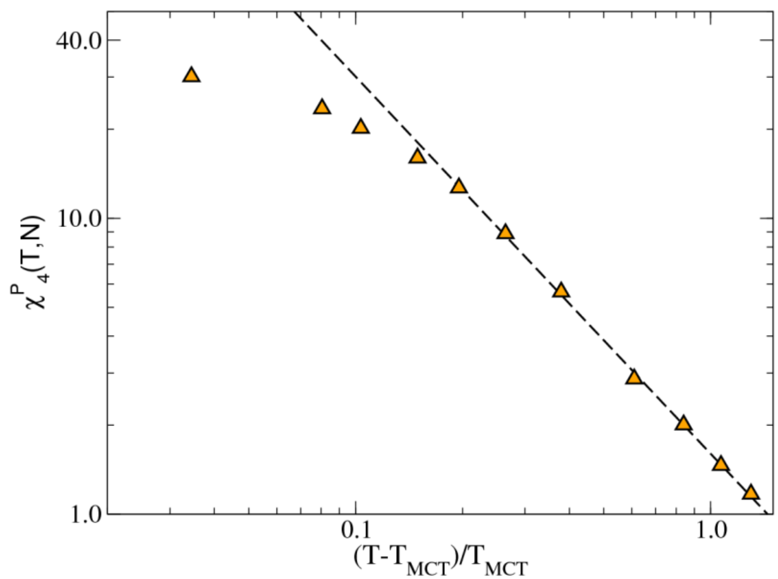
Binder Cumulant

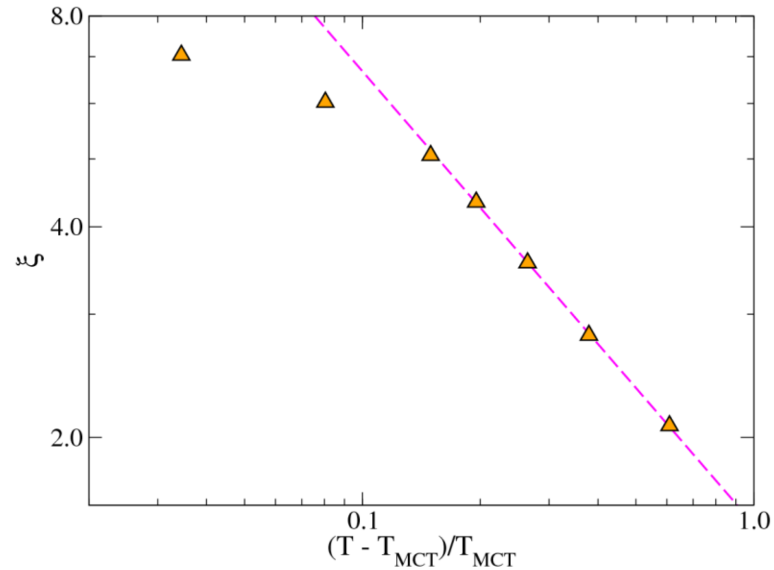
$$B(N,T) = \frac{<[Q(\tau_4) - <Q(\tau_4)>]^4>}{3<[Q(\tau_4) - <Q(\tau_4)>]^2>^2} - 1$$

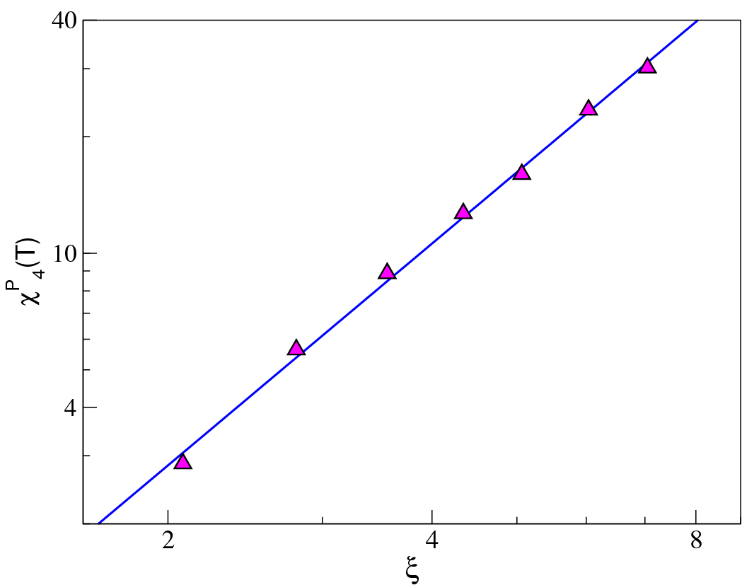
$$B(N,T) = g(N/\xi^3(T))$$

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

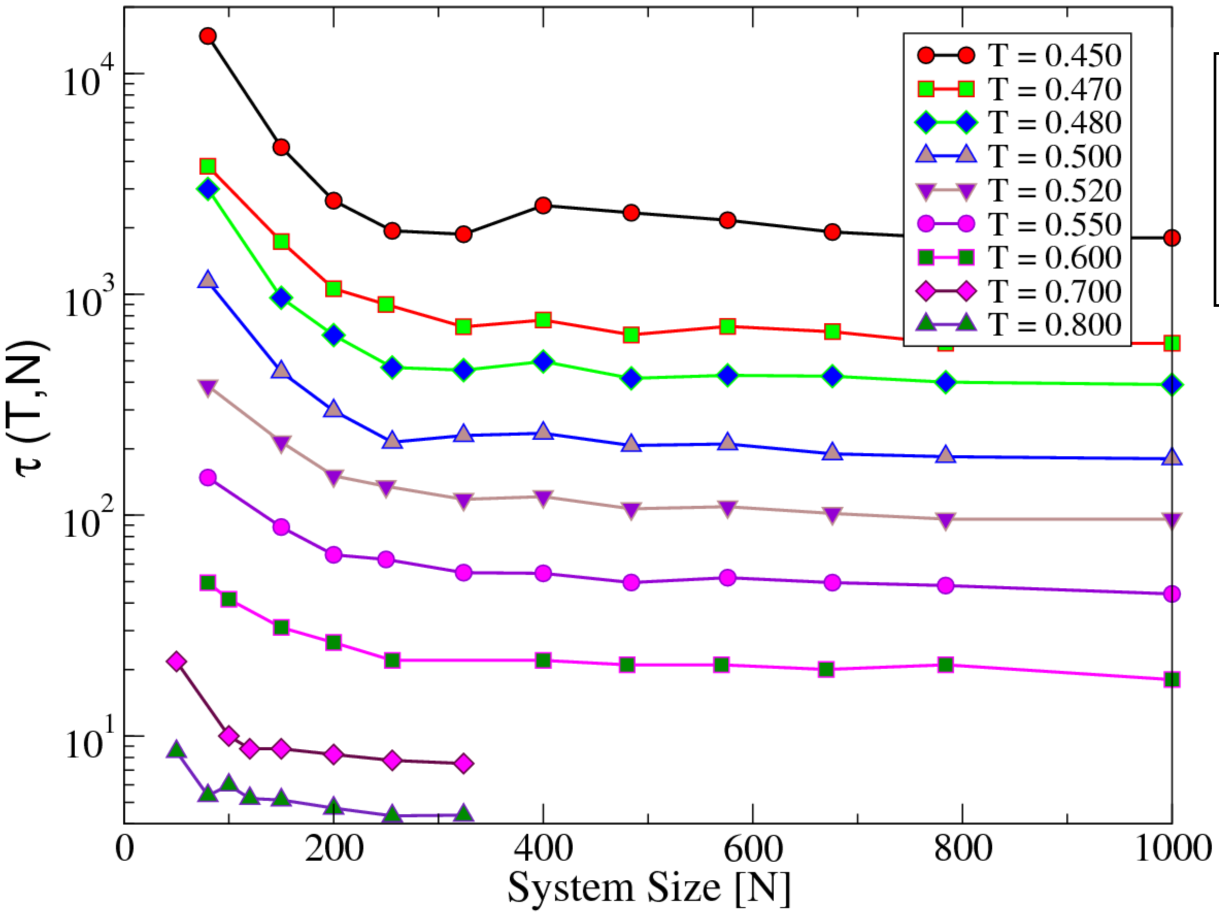
$$P[Q(\tau)] = \langle \delta(Q(\tau) - \sum_i w(|\mathbf{r}_i(t_0) - \mathbf{r}_i(t_0+\tau)|)) \rangle$$







$$\chi_4^p(T) \propto \left[(T - T_c)/T_c\right]^{-1.3}$$
$$\xi(T) \propto \left[(T - T_c)/T_c\right]^{-0.65}$$
$$\chi_4^p(T) \propto \left[\xi(T)\right]^2$$



Dependence of the relaxation time on T and N

Expected finite-size scaling form:

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

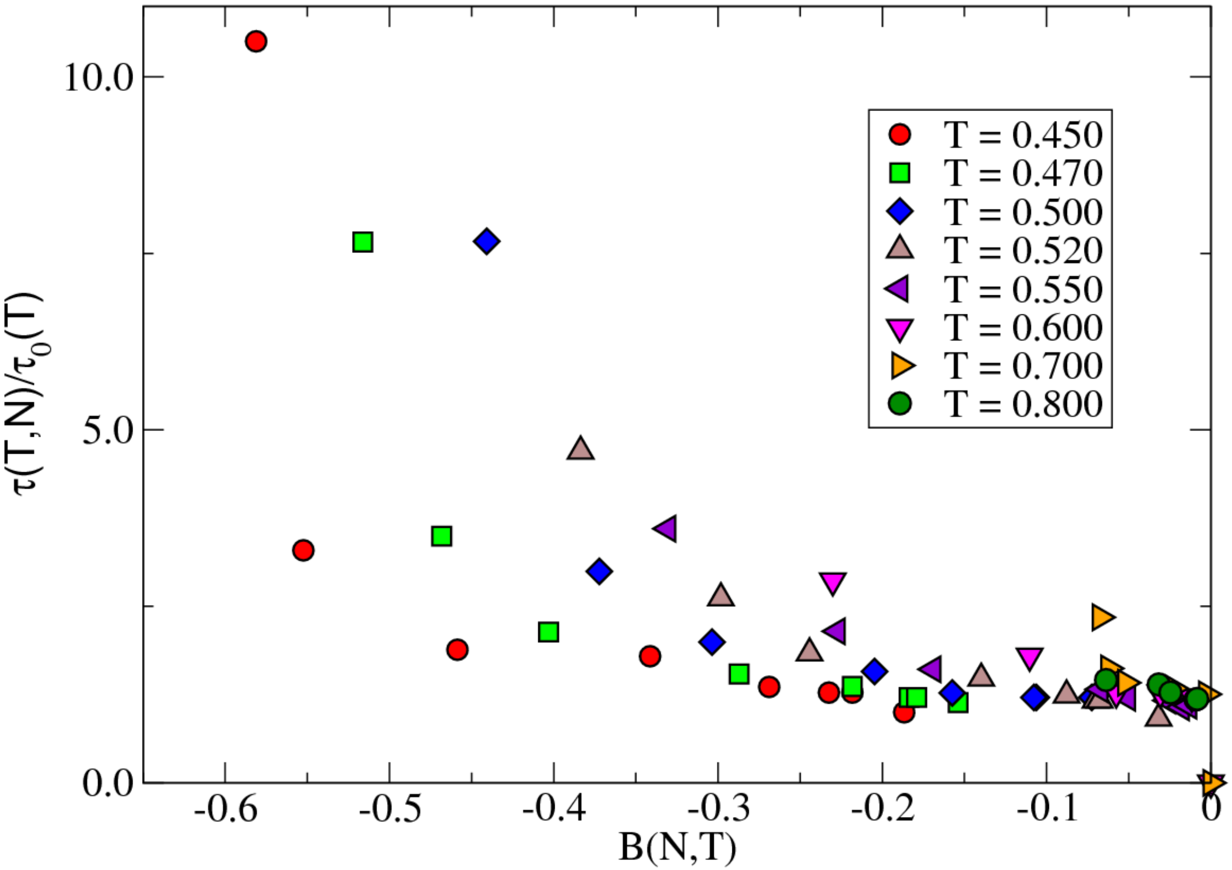
with g(x) increasing with x

Kim and Yamamoto (2000)

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

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

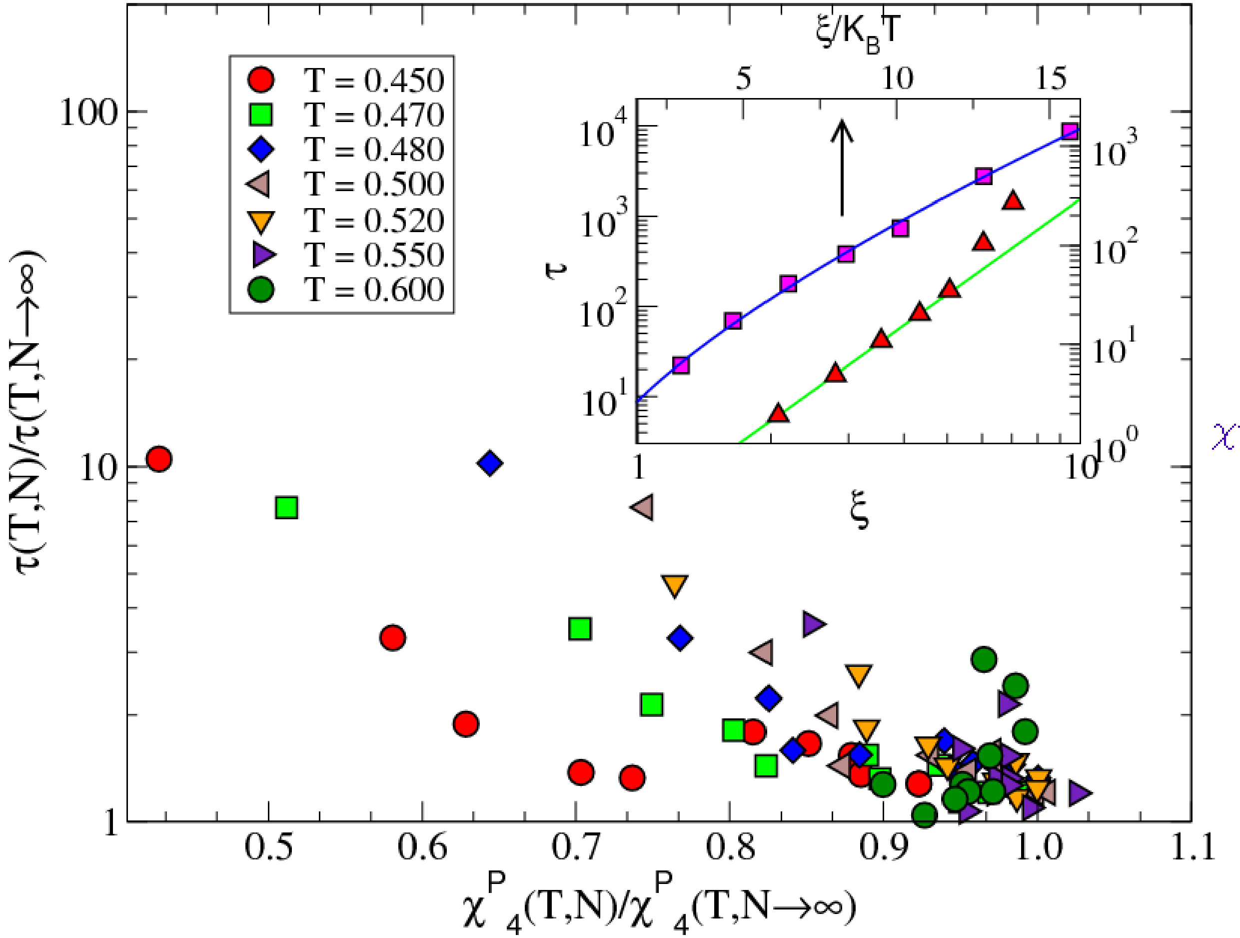
Does the relaxation time scale with the same correlation length?



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

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

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



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

$$\chi_4^p(T,N) = \chi_4^p(T, N \to \infty) g[N/\xi^3(T)]$$

A plot of $\tau(T,N)/\tau_0(T)$ vs.

$$\chi_4^p(T,N)/\chi_4^p(T, N \to \infty)$$

for different T and N should collapse to the same scaling curve

Inset: Dependence of relaxation time on correlation length

$$\tau(T, N \to \infty) \propto [\xi(T)]^z, \quad z \simeq 3.6$$ IMCT

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

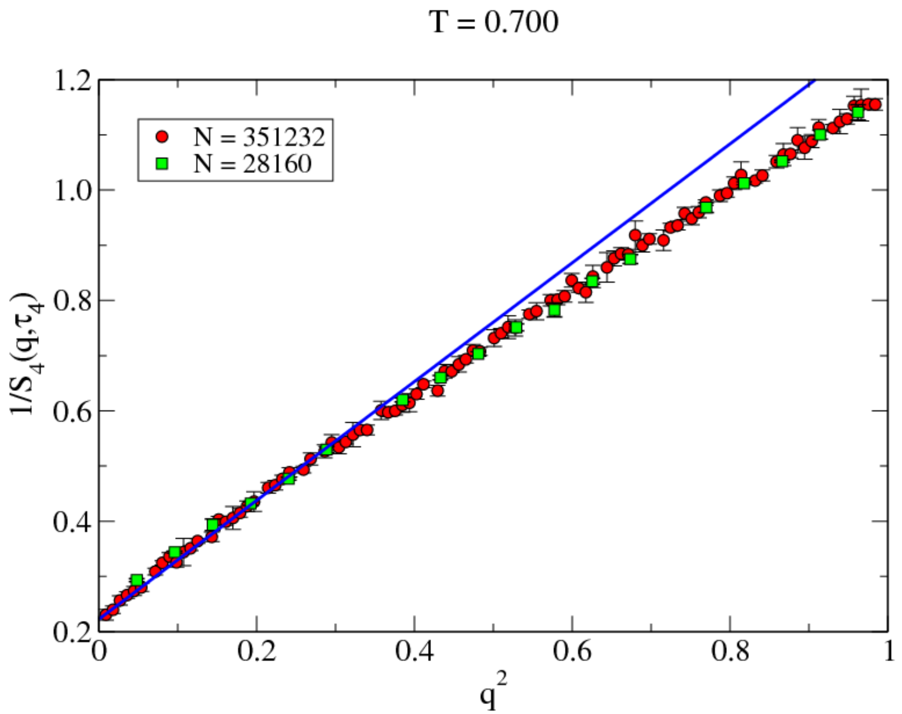
A different way of determining the correlation length $\xi(T)$

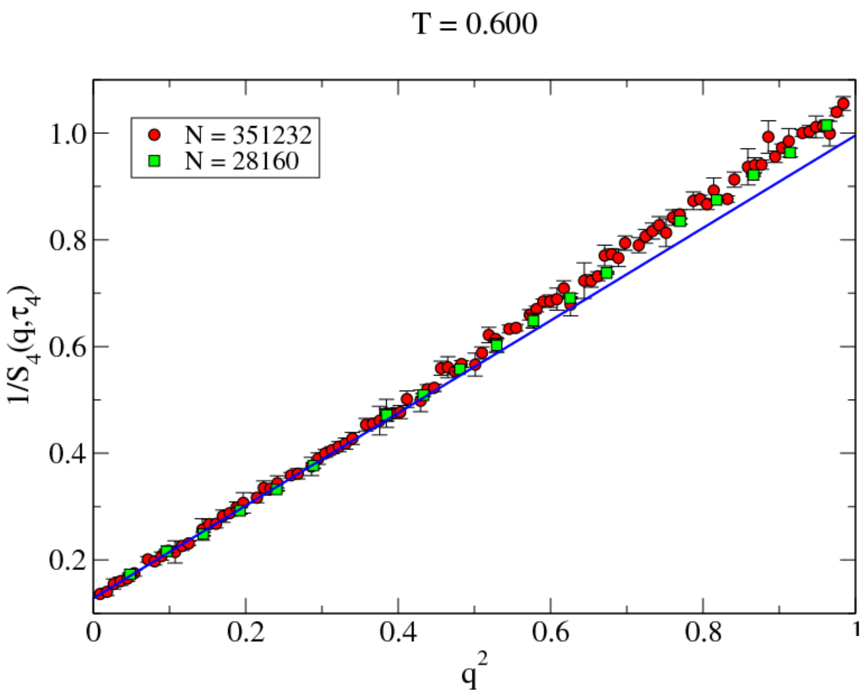
Berthier (2004),
Berthier *et al* (2007)

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

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

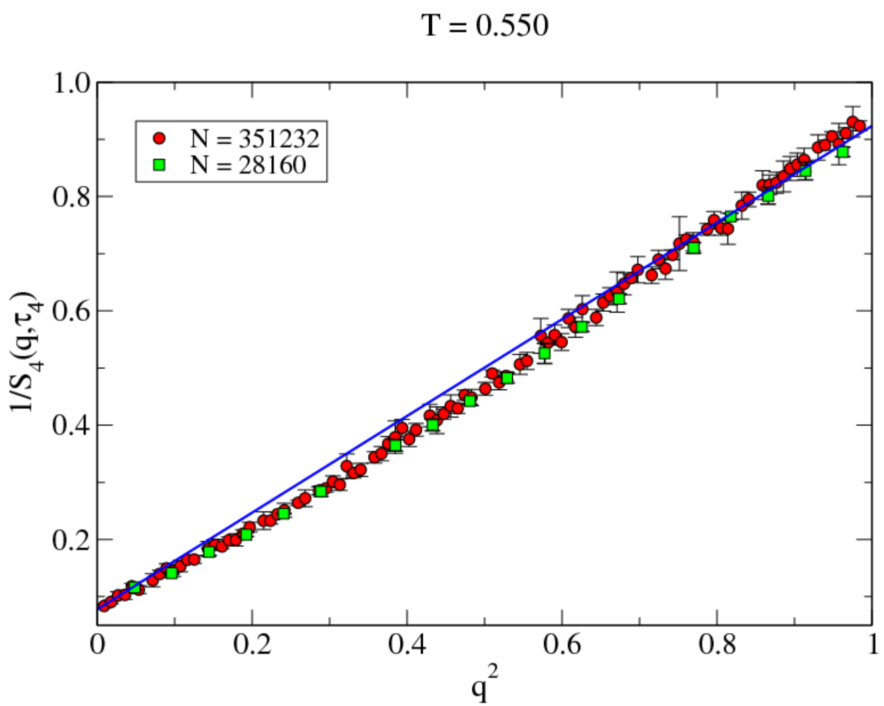
Ornstein-Zernike Form: $S_4(q,\tau) = \chi_4^p(T)/[1+q^2\xi^2]$ as $q \to 0$

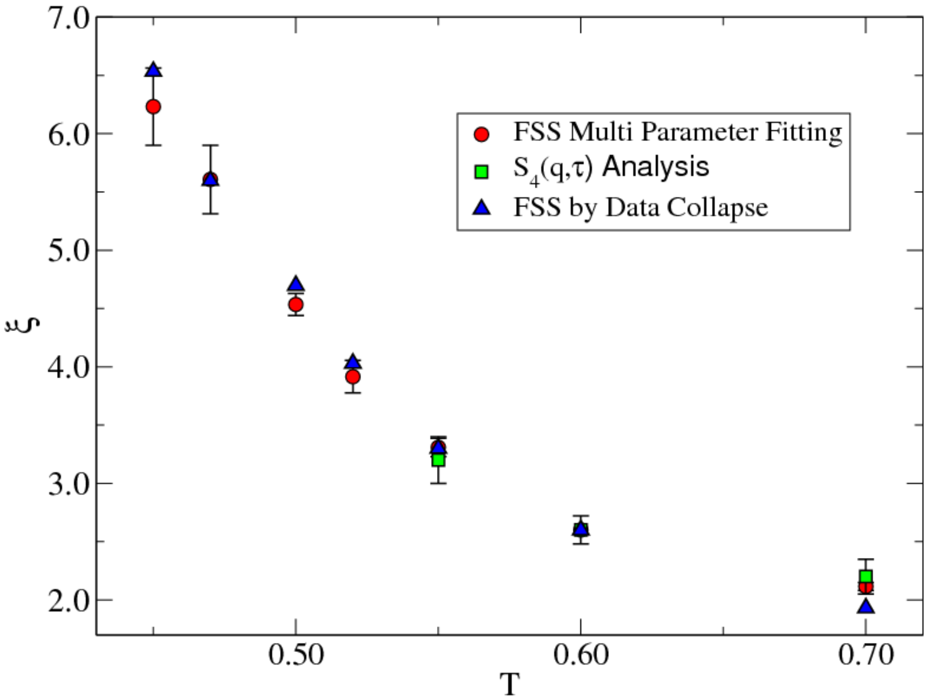




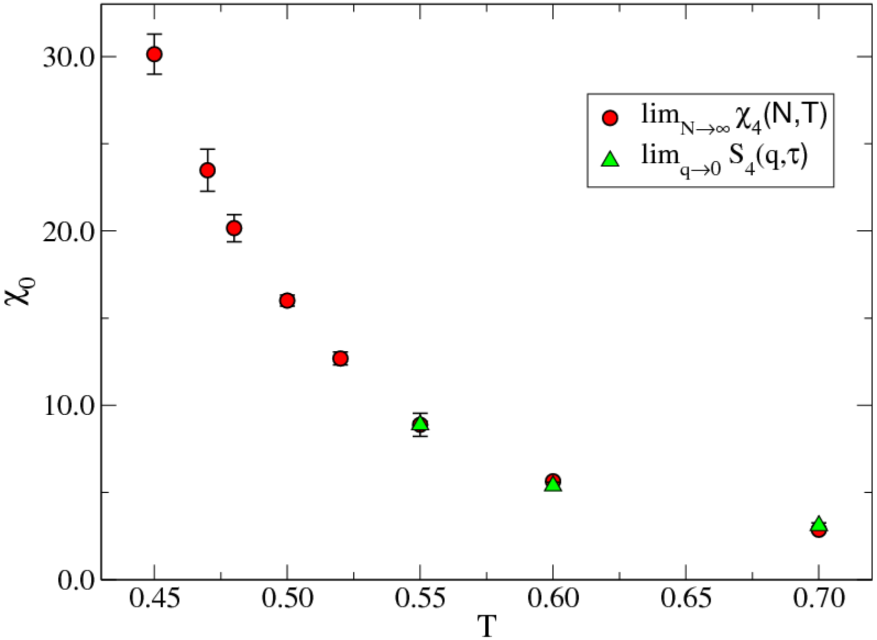
Need very large systems for reliable estimation of the correlation length at low T

Results for the correlation length are in good agreement with those obtained from finite size scaling





FSS results for the correlation length scaled down by 1.4%



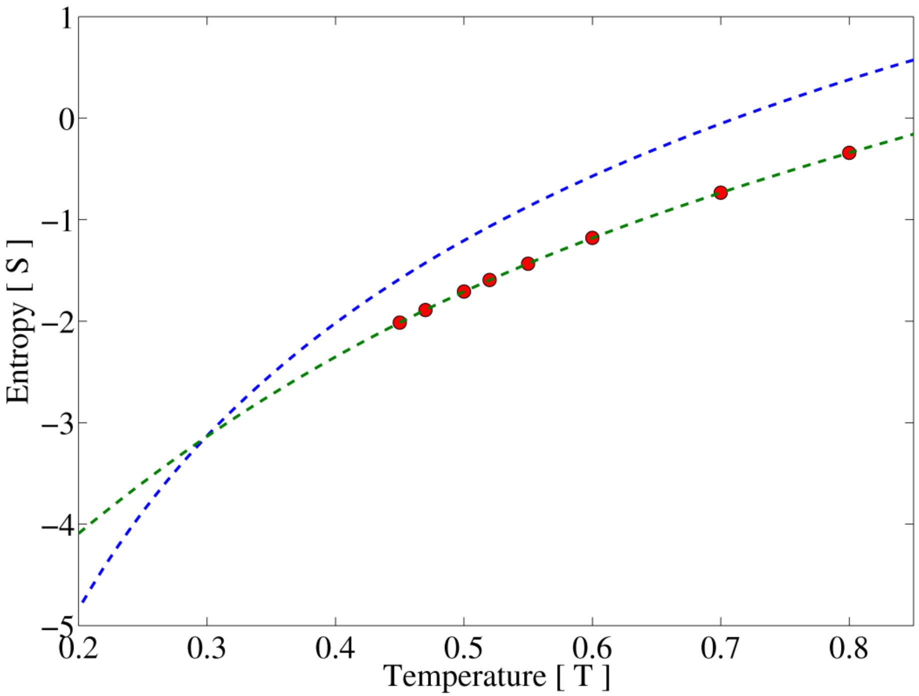
Values of $S_4(q \to 0, \tau)$ scaled down by 1.45 (?)

Calculation of the configurational entropy

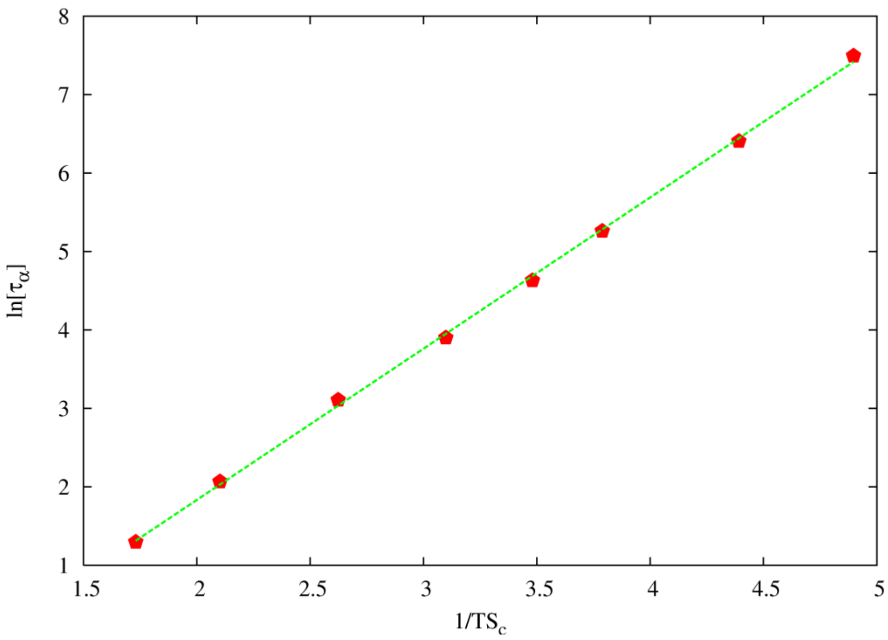
$$S_c(T) = S_{liq}(T) - S_{basin}(T)$$

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

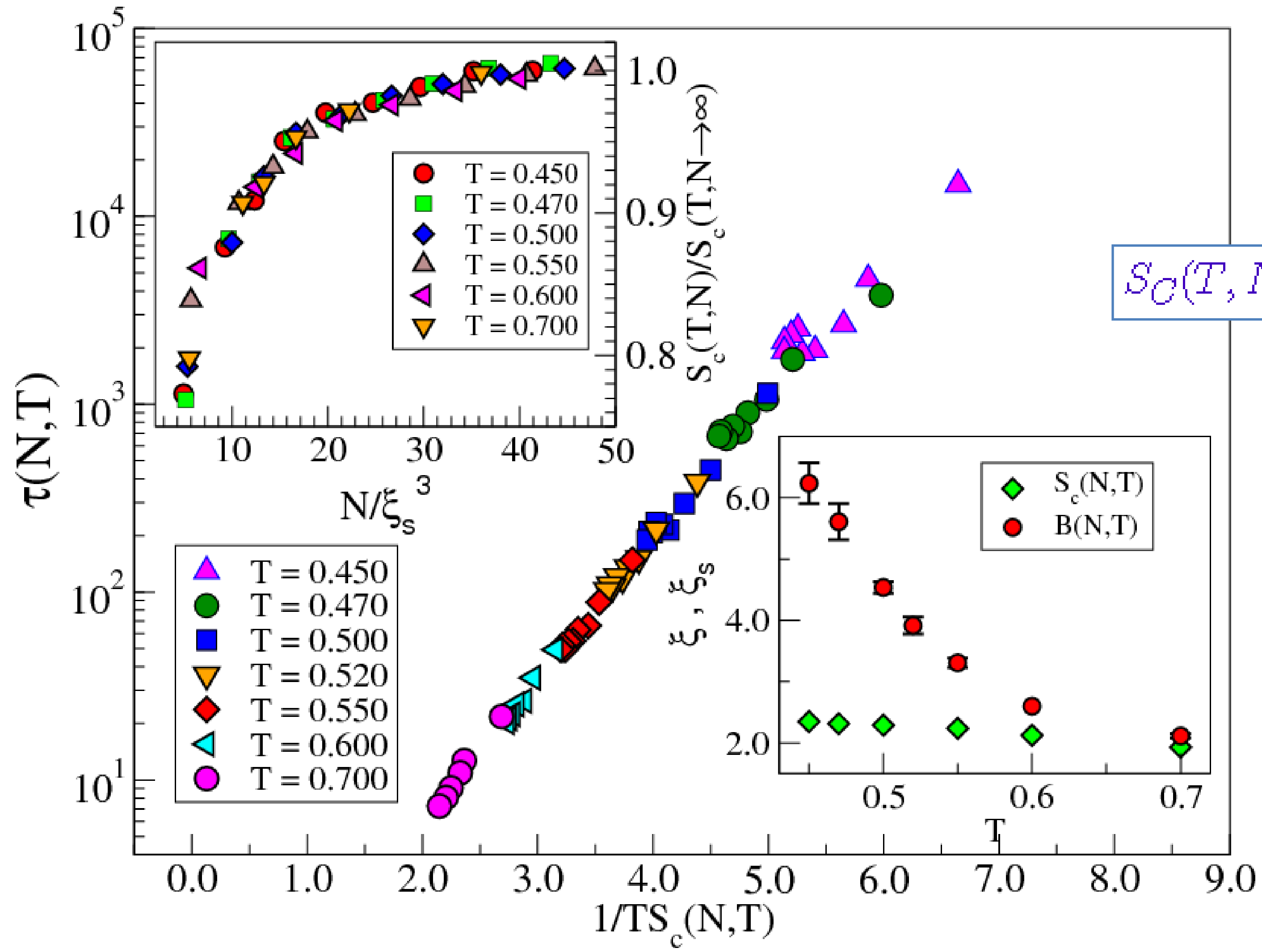
$S_{basin}(T)$ is the entropy of vibrations in the basin of an "inherent structure"



Determination of the Kauzmann temperature



Verification of Adam-Gibbs relation



Insets:

FSS for $S_C(T,N)$

$$S_C(T,N) = S_C^0(T) f[N/\xi_s^3(T)]$$

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

Comparison with predictions of existing theories

A. Inhomogeneous mode coupling theory (IMCT)

- The observed behavior of the four-point susceptibility and the associated correlation length is qualitatively consistent with predictions of IMCT, but the exponent values appear to differ from IMCT predictions.

- The observed system-size dependence of the relaxation time can not be understood from IMCT [D. Reichman: MCT predicts an oscillatory dependence of the relaxation time on sample size].

- The observation that the dependence of the relaxation time on both T and N is well described by the Adam-Gibbs relation at temperatures higher than the mode-coupling transition temperature is not consistent with IMCT.

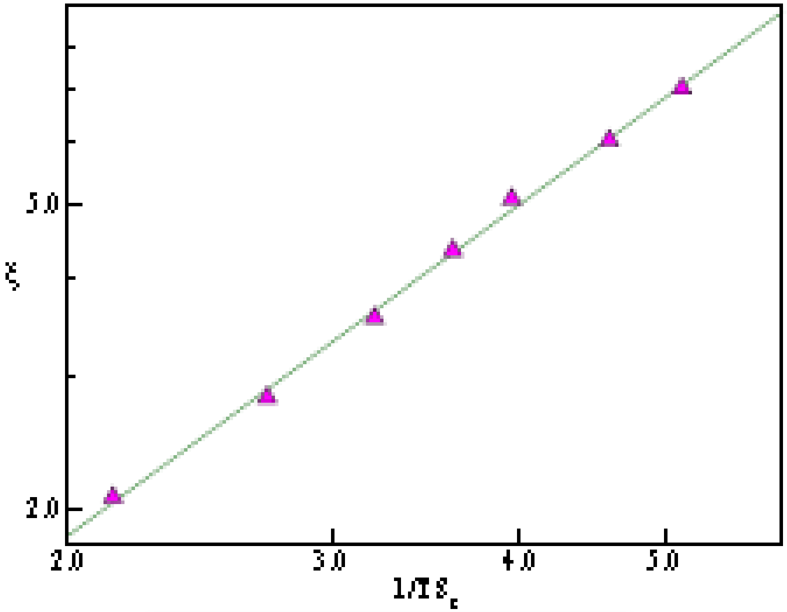
B. Random first-order transition (RFOT) theory

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 $\exp[(\Delta F)^{\psi}_{max}/(k_BT)]$, with $\psi \leq 1$.



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

In the "entropic nucleation" picture, the "mosaic scale" is given by

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

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

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

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

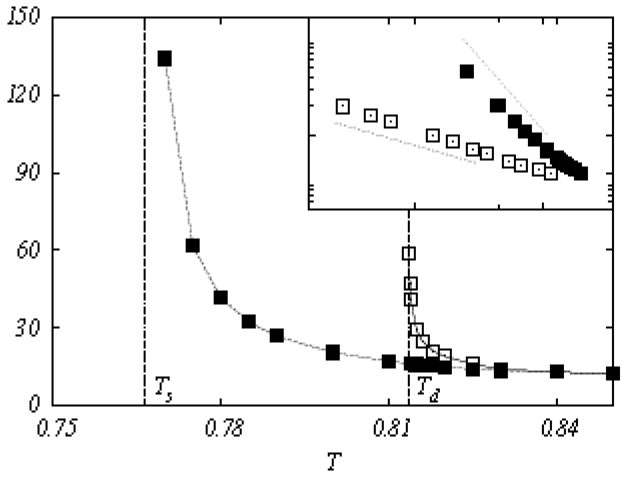
The values of θ and ψ are close to those obtained by Capaccioli *et al* (2008) from analysis of experimental data near the laboratory glass transition temperature.

Also, similar results for the T-dependence of the entropy of a CRR.

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

Talks of Cavagna and Wolynes

C. Kac Glass Model Calculation, Franz and Montanari (2007):



- Dynamic ("heterogeneity") and static ("mosaic") length scales.
- Relaxation at length scales smaller than the dynamic length scale requires activated processes.
- Provides rationalization of the observed increase in relaxation time with decreasing N for small N.

Does not explain the observed Adam-Gibbs dependence of the relaxation time on the configurational entropy in the large system-size limit at temperatures much above the mode-coupling transition temperature.

Summary

1. The dependence of $\chi_4^P(T,N)$ 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, suggesting that the growth of the relaxation time is not governed solely by this 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.