# Length Scales Related to Alpha and Beta Relaxation in Glass Forming Liquids

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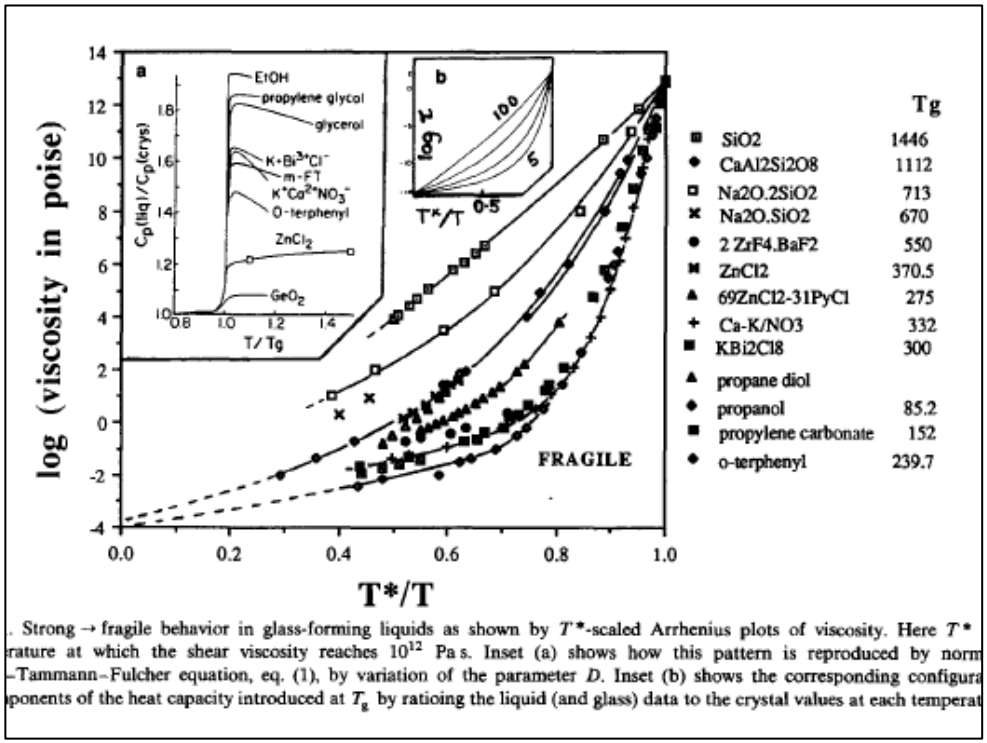
KITP , Santa Barbara, May 2010

# Outline

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

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

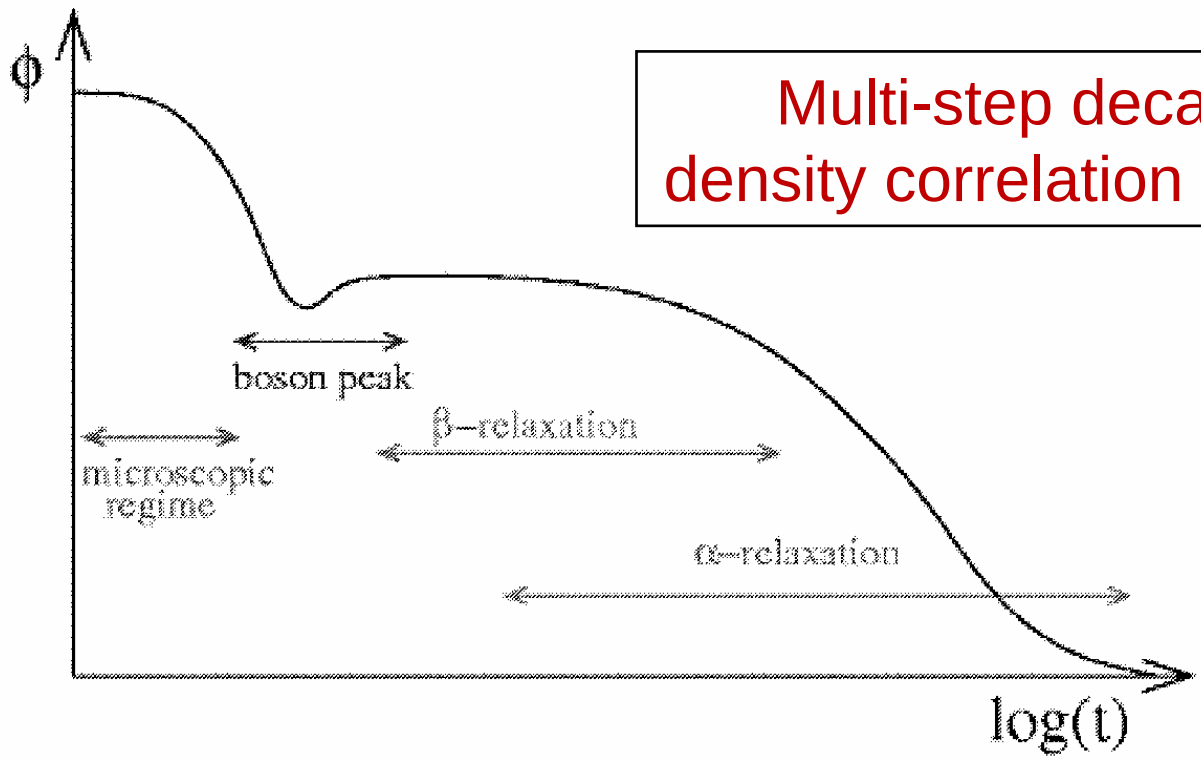



. Strong → fragile behavior in glass-forming liquids as shown by $T^*$-scaled Arrhenius plots of viscosity. Here $T^*$ rature at which the shear viscosity reaches $10^{12}$ Pa s. Inset (a) shows how this pattern is reproduced by norm –Tammann–Fulcher equation, eq. (1), by variation of the parameter $D$. Inset (b) shows the corresponding configura ponents of the heat capacity introduced at $T_g$ by ratioing the liquid (and glass) data to the crystal values at each temperat

Existence of growing **length scales** near the glass transition??

Many proposals, but no clear answer

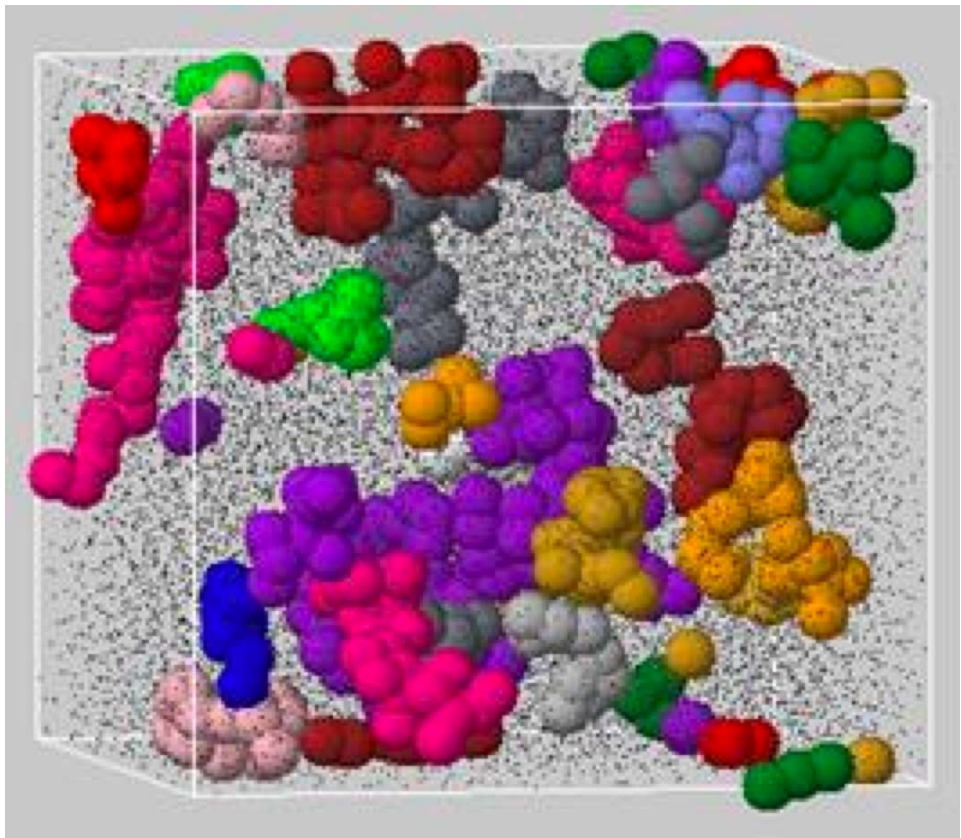
# Non-Debye relaxation of fluctuations in supercooled liquids




Multi-step decay of density correlation function

Connection between short-time (beta regime) and long-time (alpha regime) dynamics ??

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



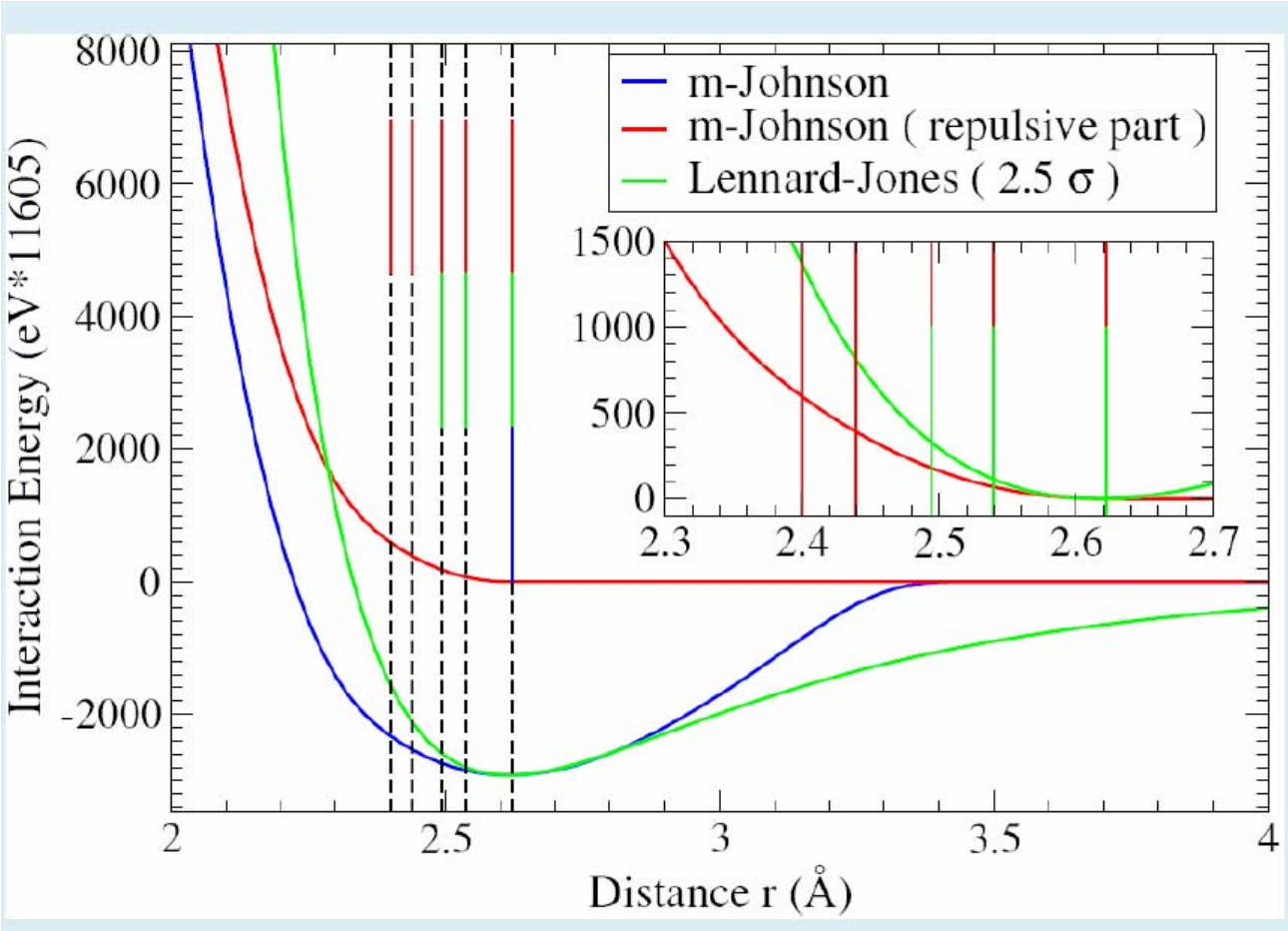
Particles color-coded
according to
the distance moved

# Relevance to metallic glasses?

Studies of the “glass transition”: The main interest is in understanding the **dynamics of the supercooled liquid** as the glass transition is approached from the liquid side.

Studies of metallic glasses: The main interest is in understanding the **structural and mechanical properties of the glassy state**.

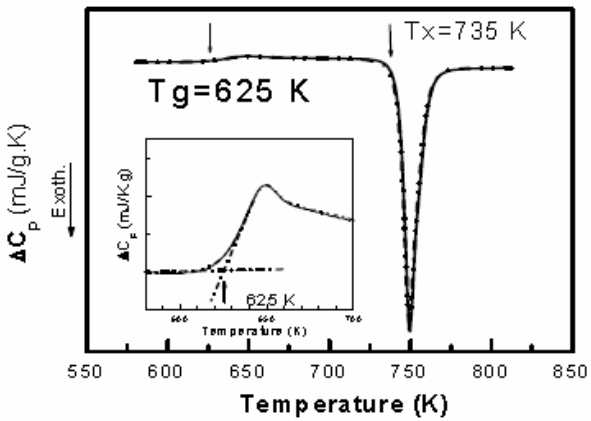
- Inter-particle potential in metallic glasses is not very different from those used in studies of supercooled liquids.




From the talk of T. Egami

- Some met glass systems can be maintained in the supercooled liquid state for long times

$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit4)




From the talk of W.H. Wang

**Bulk specimens allow effective physical properties measurements and stable supercooled liquid state**

- **ΔT=110 K**
- **No phases separation**
- **High GFA**

How do the properties of the met glass depend on the temperature of the liquid from which it is quenched ?

The glass obtained by quenching from the supercooled liquid at temperature T is one of the "**inherent structures**" (local minima of the potential energy) sampled by the liquid at temperature T.

Many studies suggest a close connection between the dynamics of the liquid and properties of the inherent structures sampled by it.

If the dynamics of the liquid can be understood from the properties of the inherent structures, then it should be possible to obtain useful Information about the properties of a metallic glass from those of the liquid from which it is quenched.

PRL 104, 205704 (2010) PHYSICAL REVIEW LETTERS week ending 21 MAY 2010

# Probing a Critical Length Scale at the Glass Transition

Majid Mosayebi, Emanuela Del Gado, Patrick Ilg, and Hans Christian Öttinger
*Polymer Physics, ETH Zürich, Department of Materials, CH-8093 Zürich, Switzerland*
(Received 30 March 2010; published 21 May 2010)

We give evidence of a clear structural signature of the glass transition, in terms of a static correlation length with the same dependence on the system size, which is typical of critical phenomena. Our approach is to introduce an external, static perturbation to extract the structural information from the system's response. In particular, we consider the transformation behavior of the local minima of the underlying potential energy landscape (inherent structures), under a static deformation. The finite-size scaling analysis of our numerical results indicate that the correlation length diverges at a temperature $T_c$, below the temperatures where the system can be equilibrated. Our numerical results are consistent with random first order theory, which predicts such a divergence with a critical exponent $\nu = 2/3$ at the Kauzmann temperature, where the extrapolated configurational entropy vanishes.

This work suggests that it is possible to define a characteristic length scale from the transformation behavior of an inherent structure (metallic glass?) under a static deformation, and this length scale grows as the temperature of the liquid from which the inherent structure (glass?) was obtained is decreased.

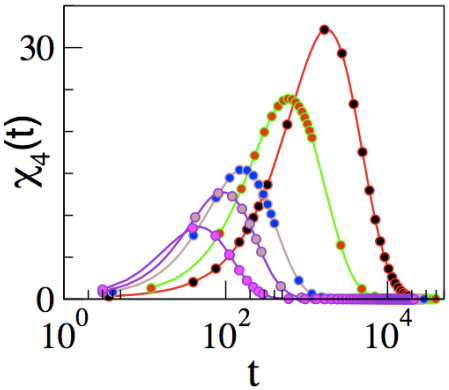
Connection between **dynamic heterogeneity** in supercooled liquids and "**weak spots**" in metallic glasses?

Dynamic heterogeneity: Coexistence of "slow" and "fast" regions.

"Weak spots": Liquid-like sites (Egami)
Shear Transformation Zones (Falk)
"Rattlers" (O'Hearn)
"Clusters" with low activation barrier (Rodney)
Non-affine regions (Sengupta)
Localized eigenvectors of the Hessian matrix with small eigenvalues (Harrowell, Reichmann)

Methods developed in studies of dynamic heterogeneity may be useful in studies of "weak spots" in metallic glasses.

# 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 $T_c$.

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

$$\tau(T) \sim \left(\frac{T-T_c}{T_c}\right)^{-\delta} \sim \xi^{\delta/\nu}$$

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 Analysis of Four-point Susceptibility

Smarajit Karmakar, CD, Srikanth Sastry, PNAS **106**, 3675 (2009)

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

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

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

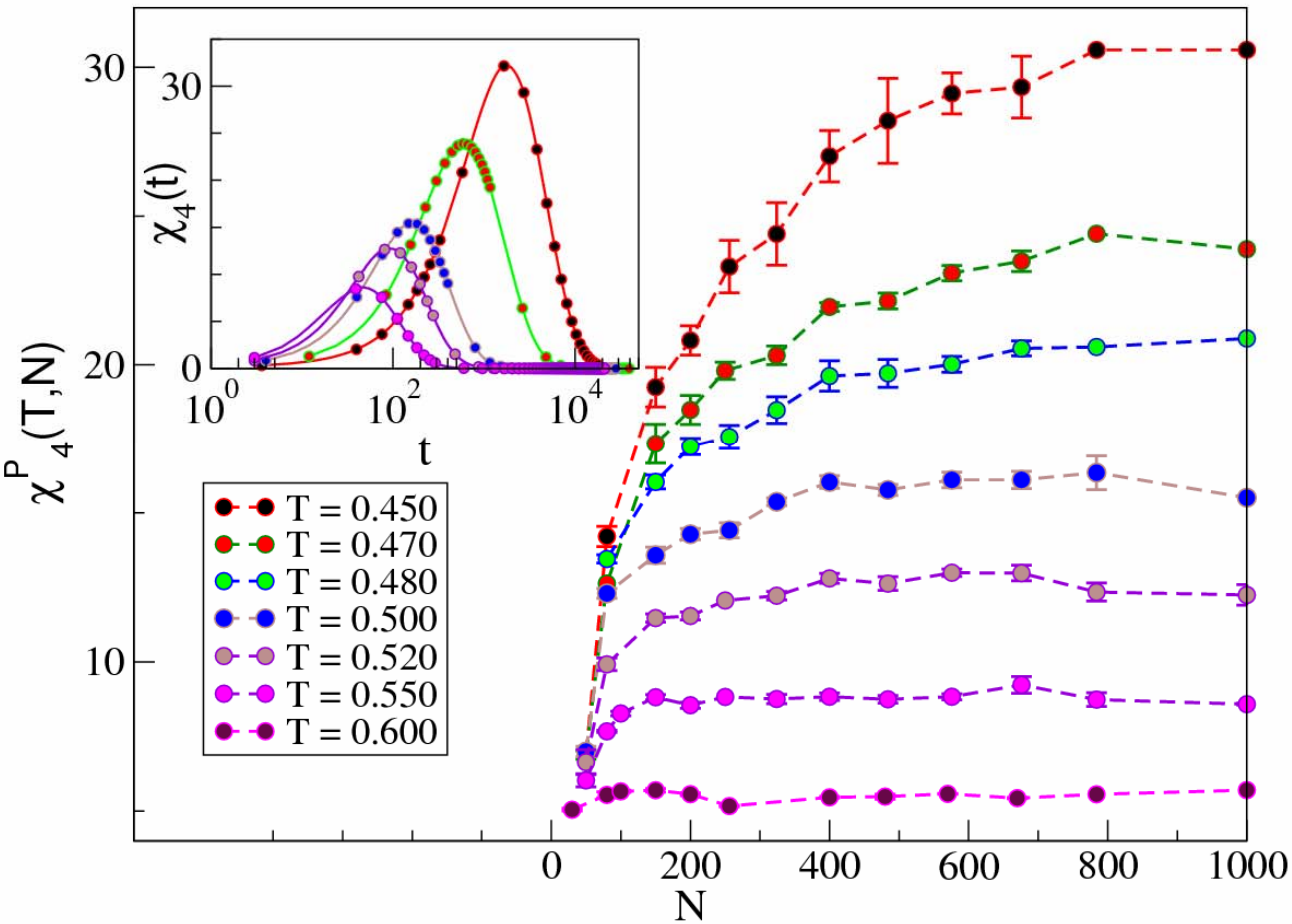
Number density $\rho = 1.2$

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.

# $T$- and $N$-dependence of $\chi_4$

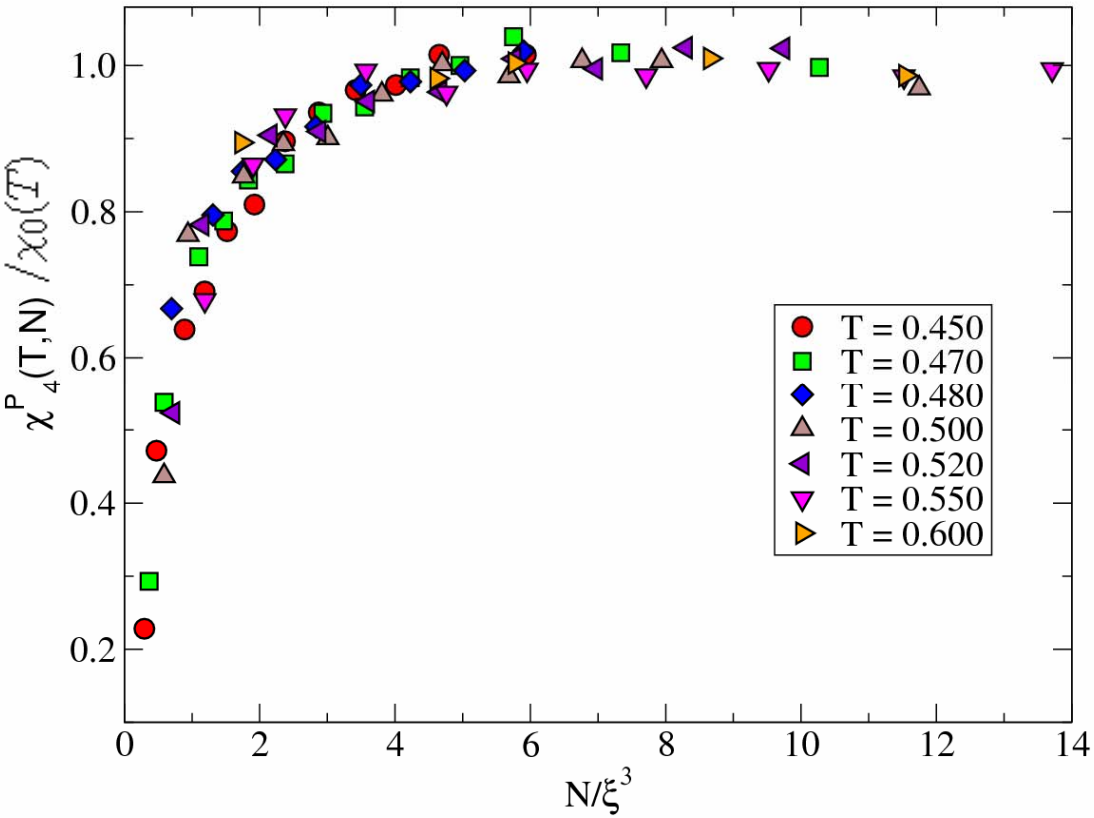



Inset: Time-dependence of $\chi_4$ at different temperatures (N=1000)

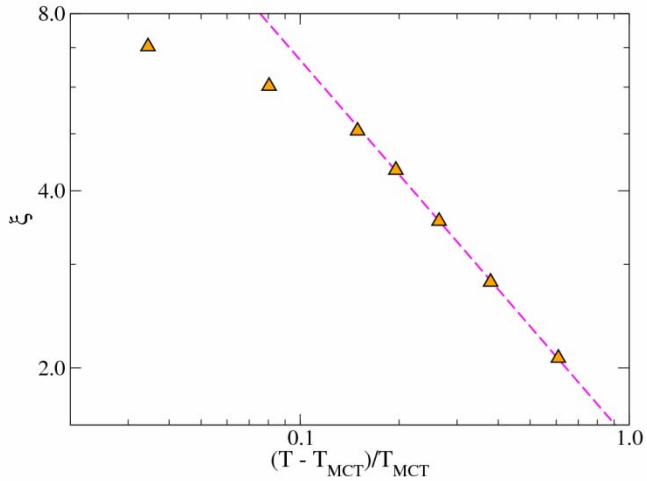
$N$-dependence of $\chi_4^p(T,N)$ for $T = 0.45,\ 0.47,\ 0.48,$ $0.50,\ 0.52,\ 0.55,\ 0.60$, from top to bottom

$\chi_4^p$ increases with $N$ and then saturates.

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




Results for correlation length confirmed from analysis of four-point structure function




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

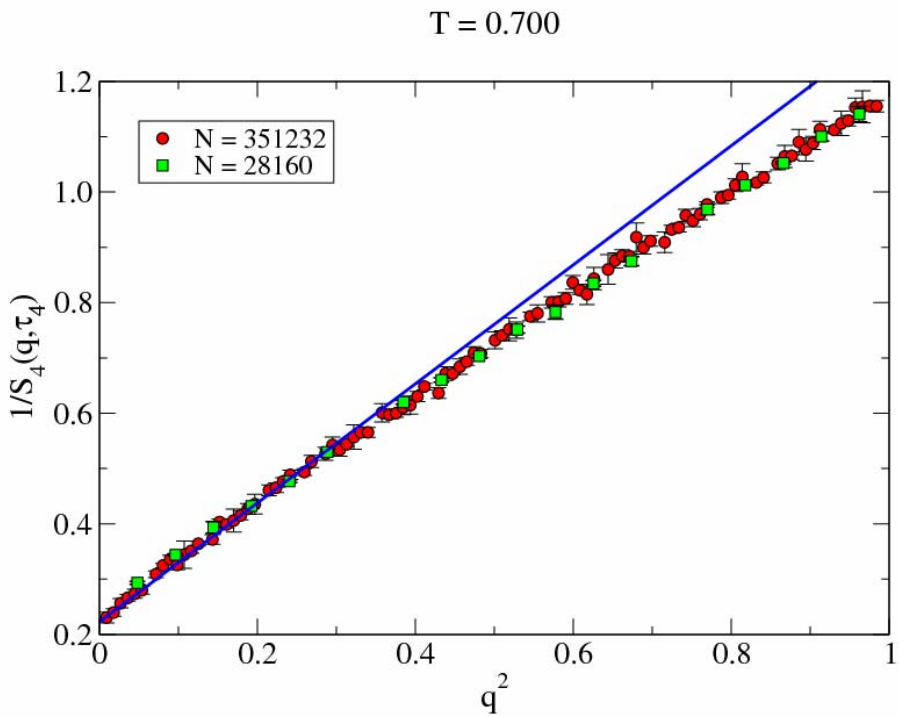
# A different way of determining the correlation length $\xi(T)$

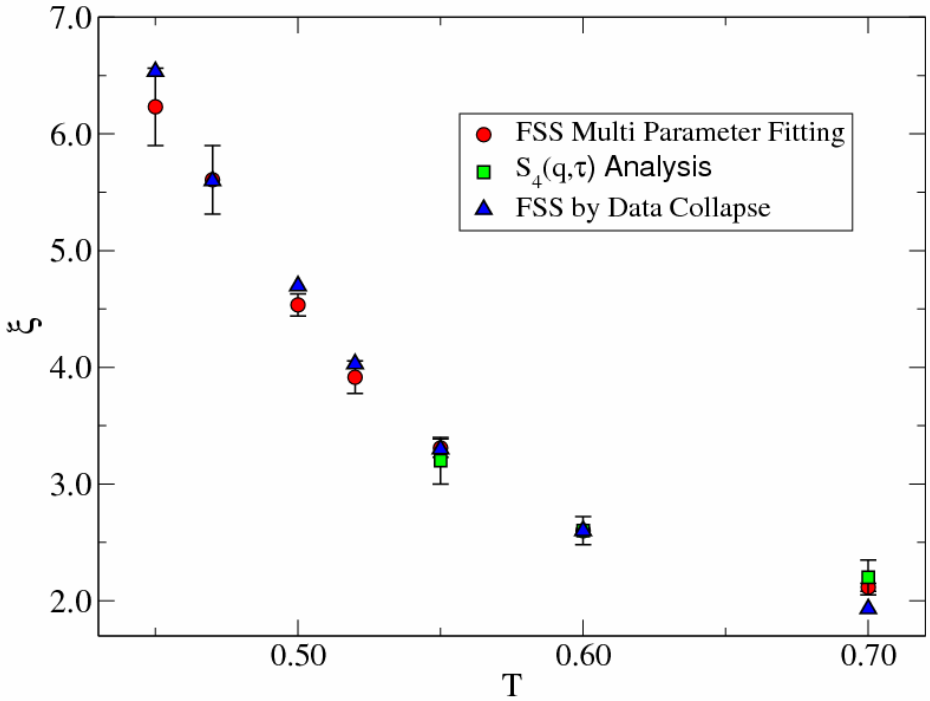
Berthier (2004),
Berthier *et al* (2007)

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

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

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



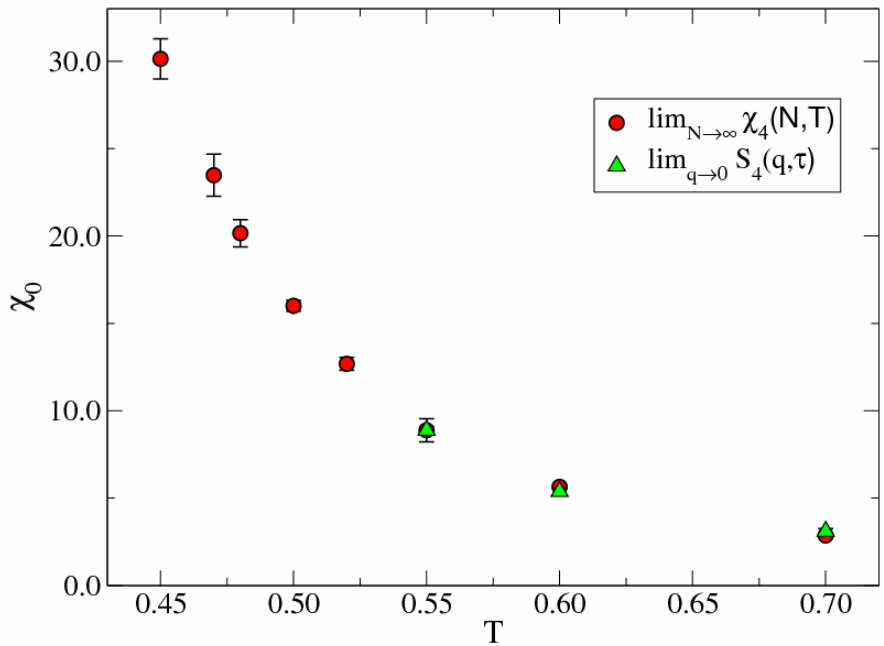


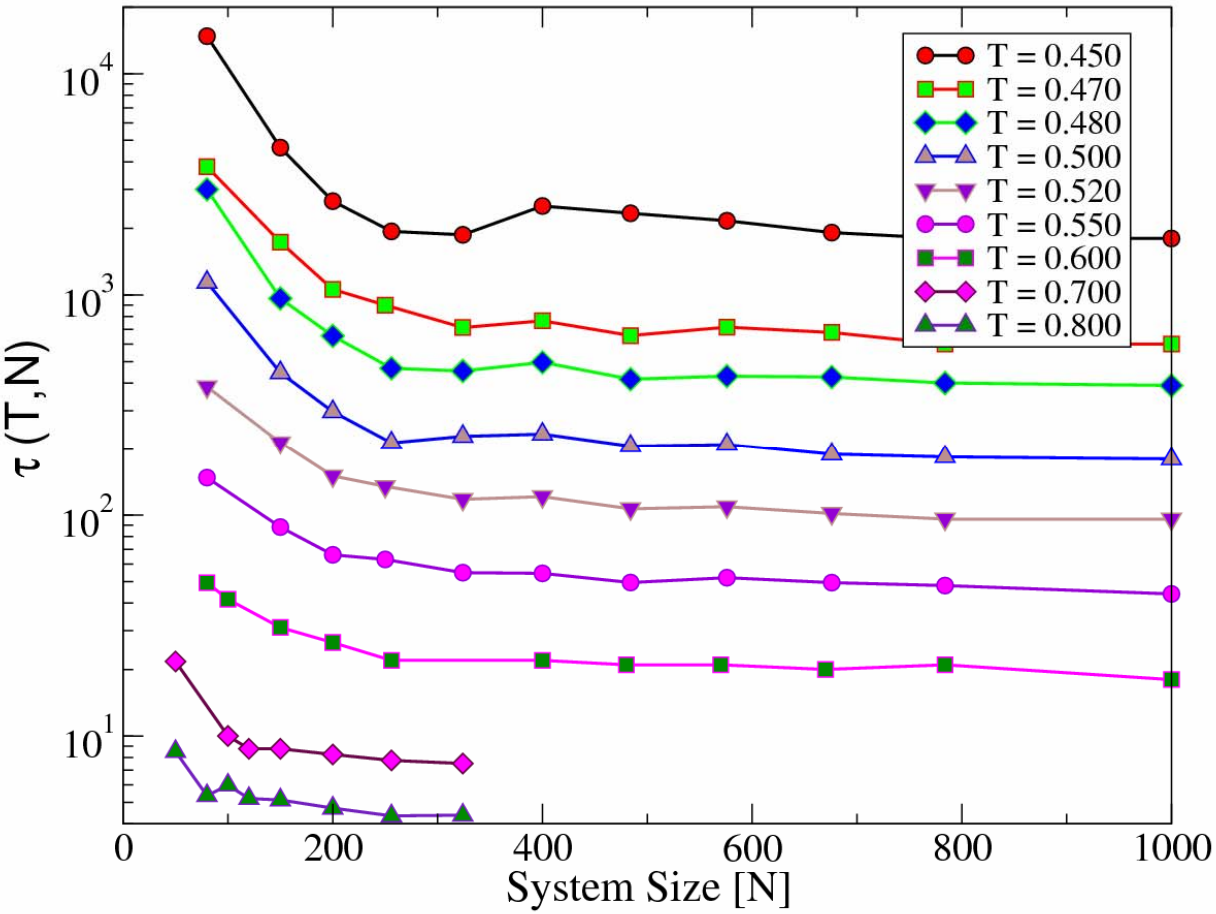

Good agreement with FSS results

Exponent values are inconsistent with the predictions of IMCT

S. Karmakar, CD and S. Sastry, Phys. Rev. Lett. (in press)

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






Dependence of the $\alpha$ relaxation time on T and N

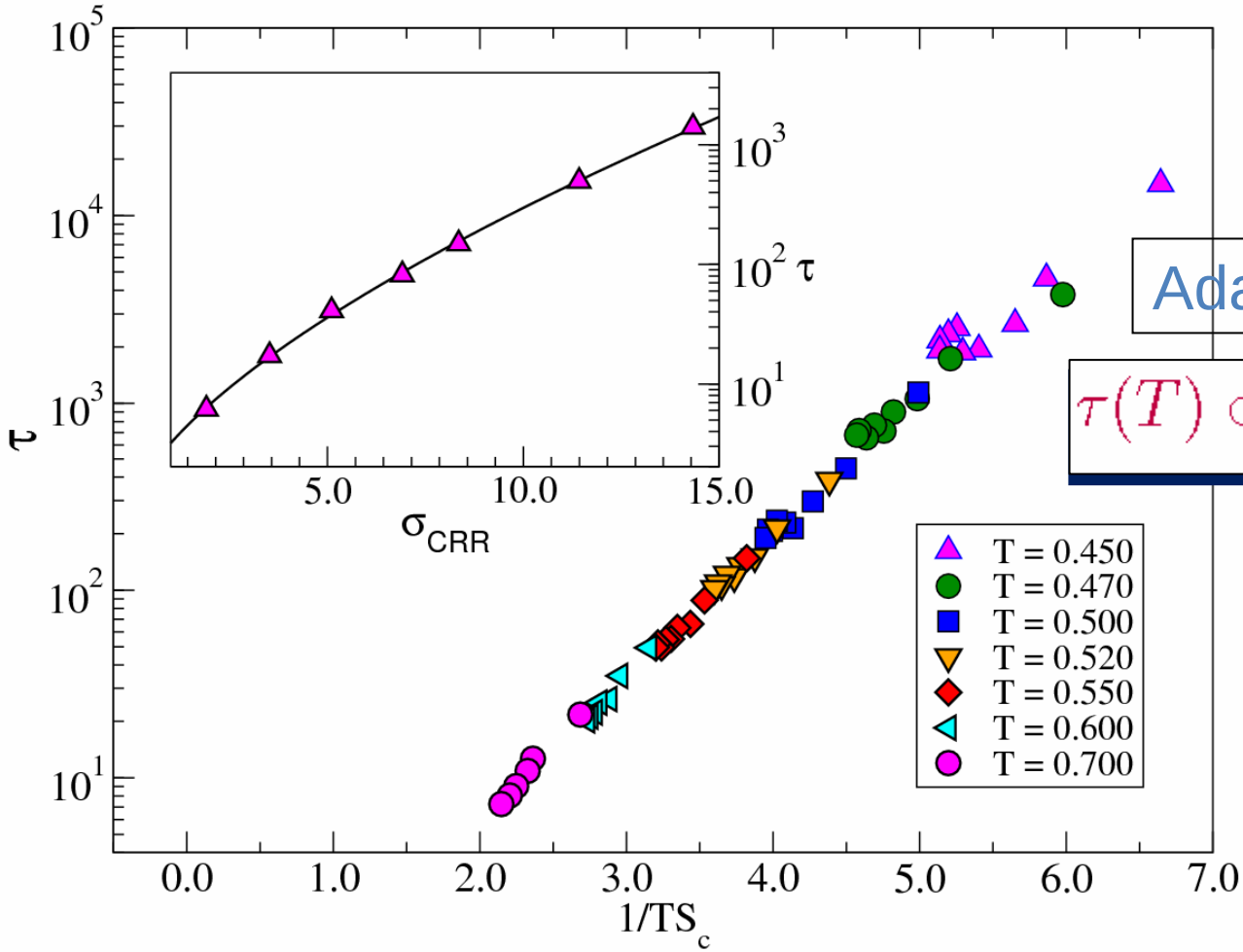
Expected finite-size scaling form:

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

with g(x) increasing with x

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

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




Adam-Gibbs Relation

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

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

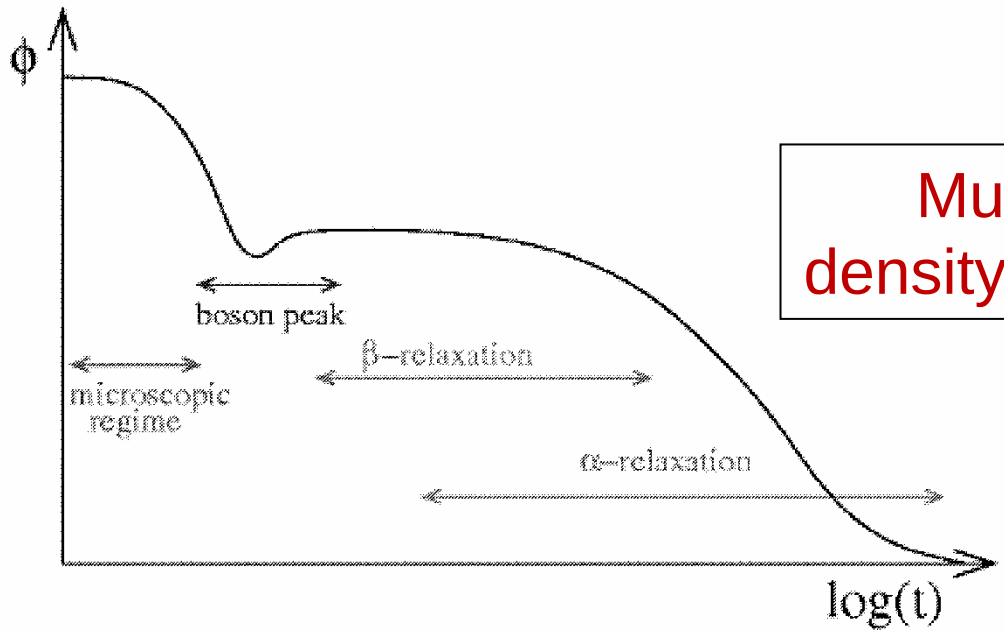
# Summary

1. The dependence of $\chi_4^{\rho}(T,N)$ on T and N exhibits the expected finite-size scaling behaviour, confirming the existence of a growing dynamic 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 $\alpha$ 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.

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



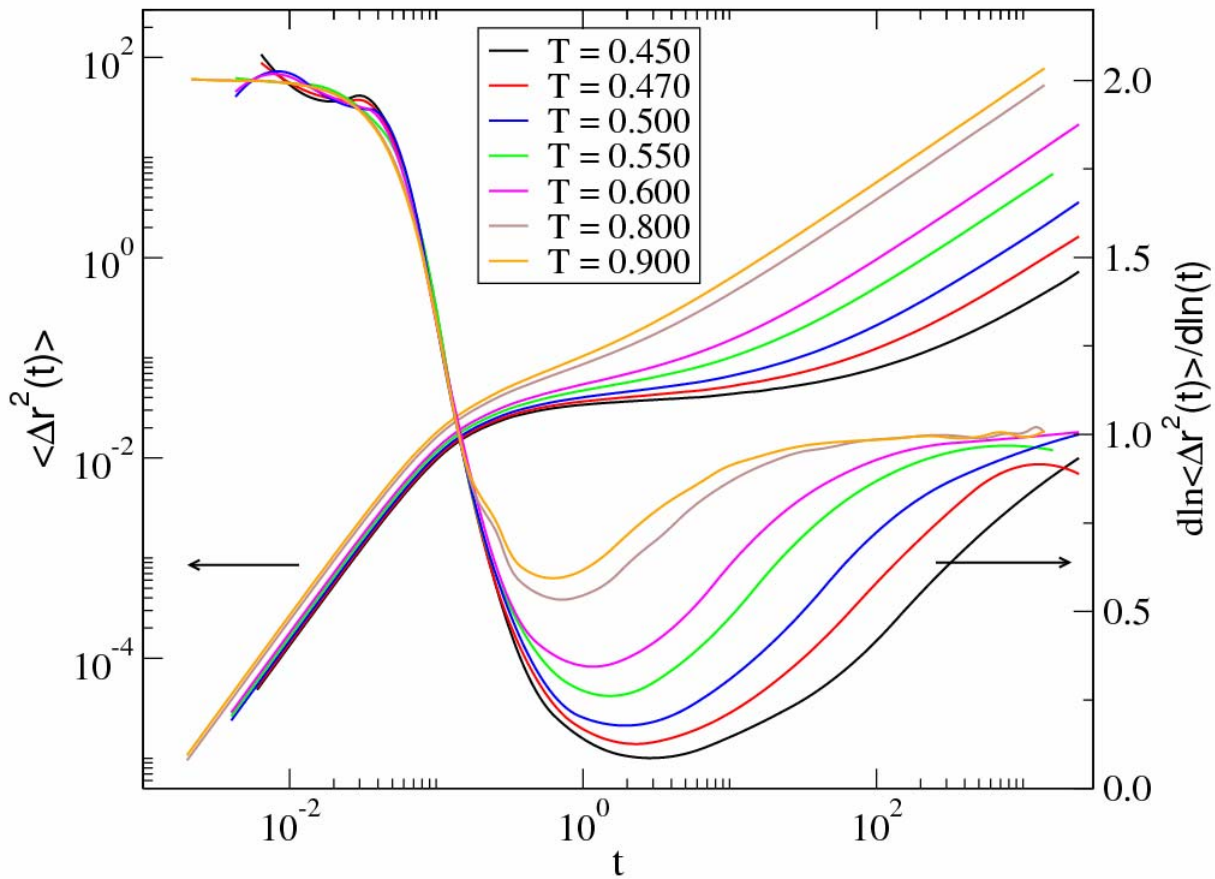

Multi-step decay of density correlation function

Short-time $\beta$ relaxation: 'caging' regime.

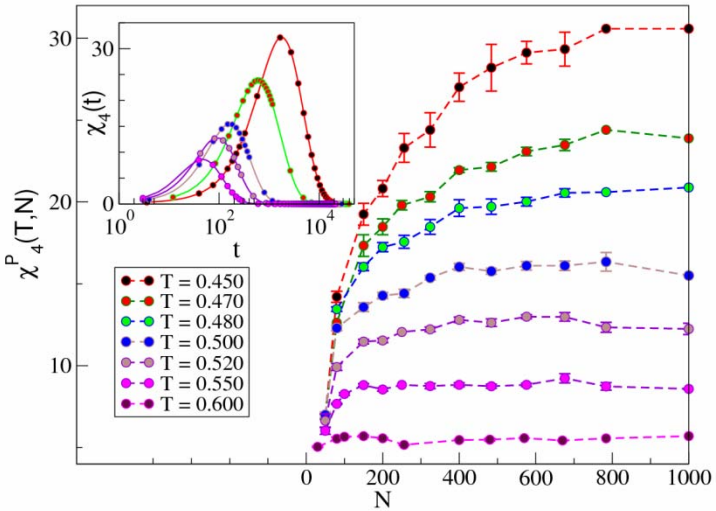
Transient formation of 'cages' by the neighbors of a particle.

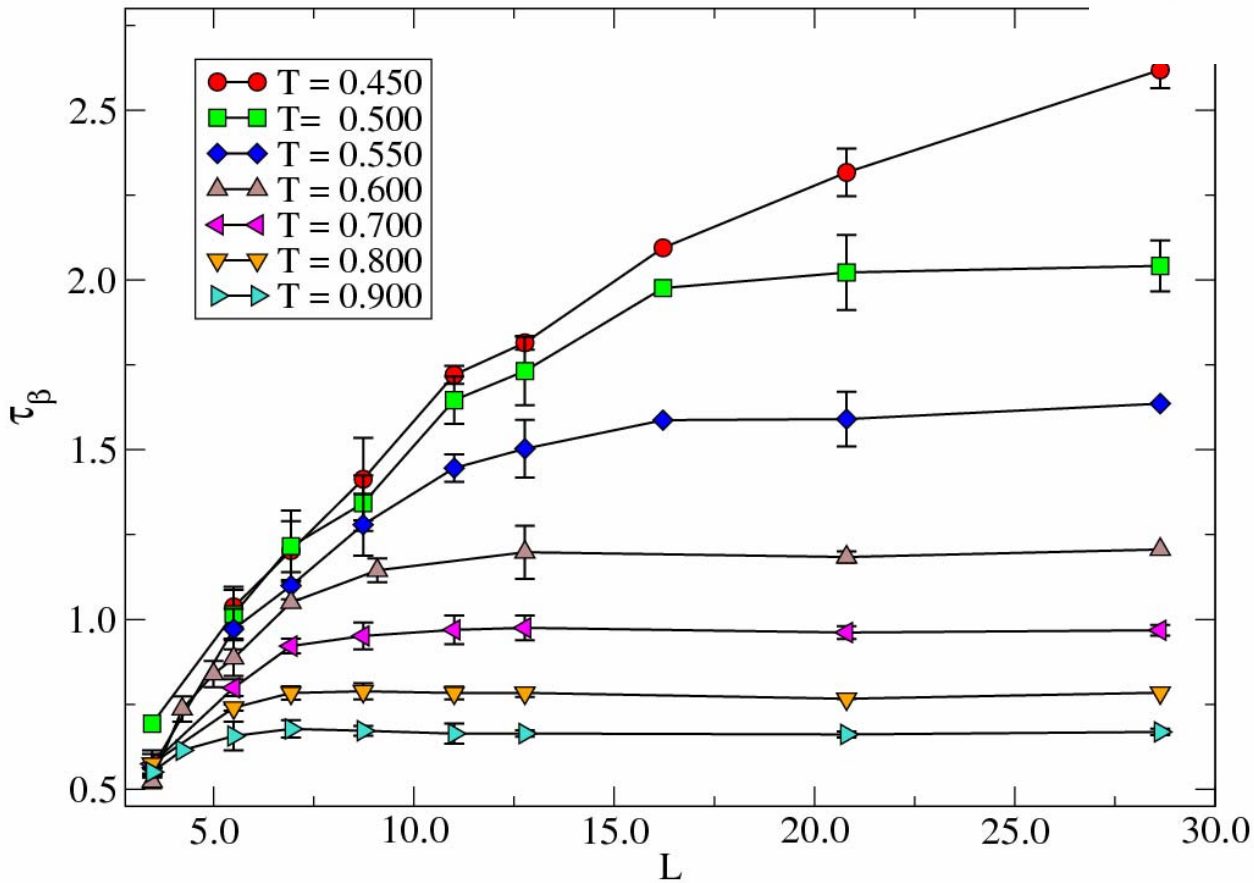
# Time scale of $\beta$ relaxation: Time at the minimum of $\frac{d \ln \langle |\Delta \mathbf{r}|^2 \rangle}{d \ln t}$

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



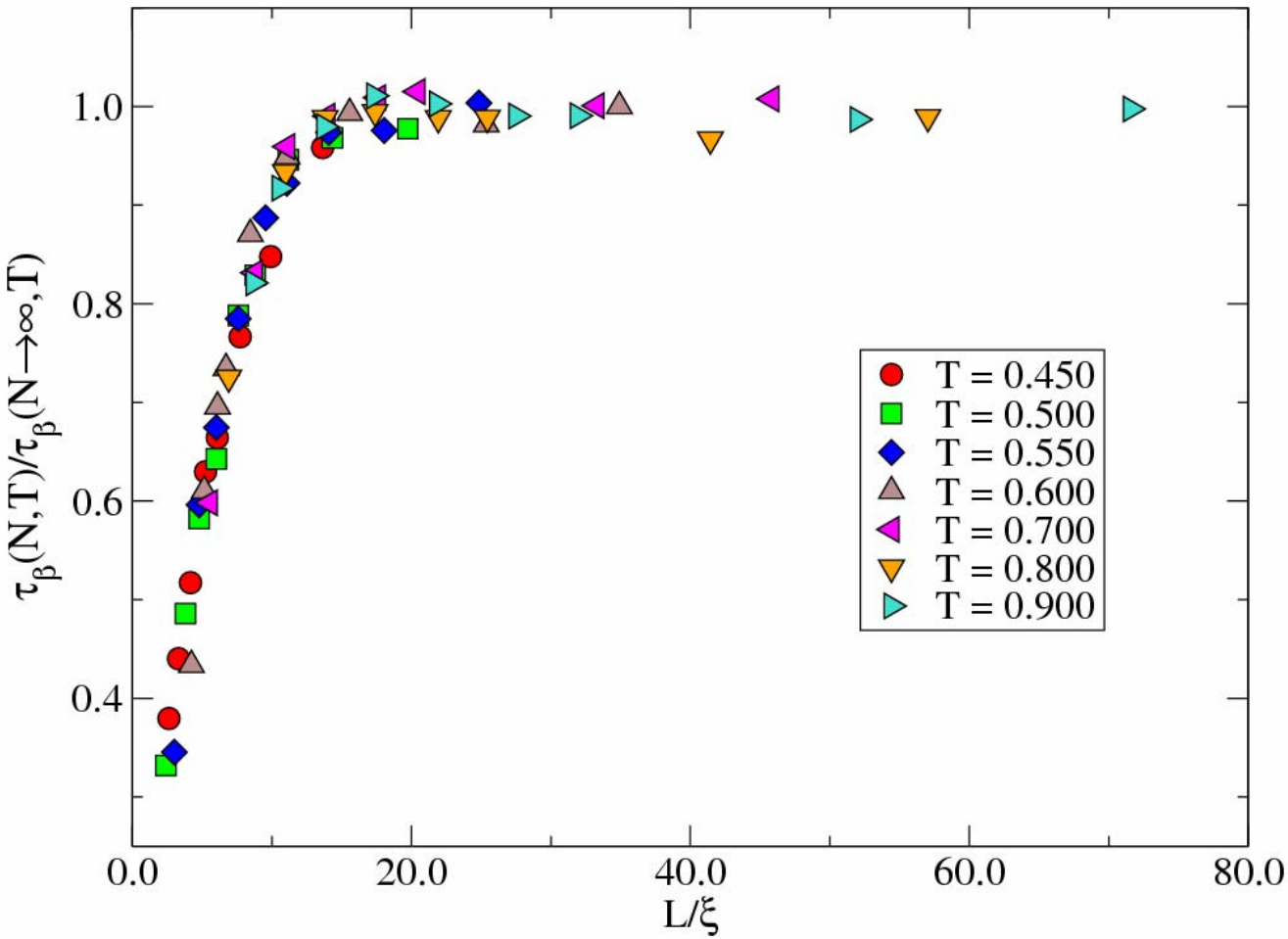
## Dependence of $\tau_\beta$ ,the time scale of $\beta$ relaxation, on T and L



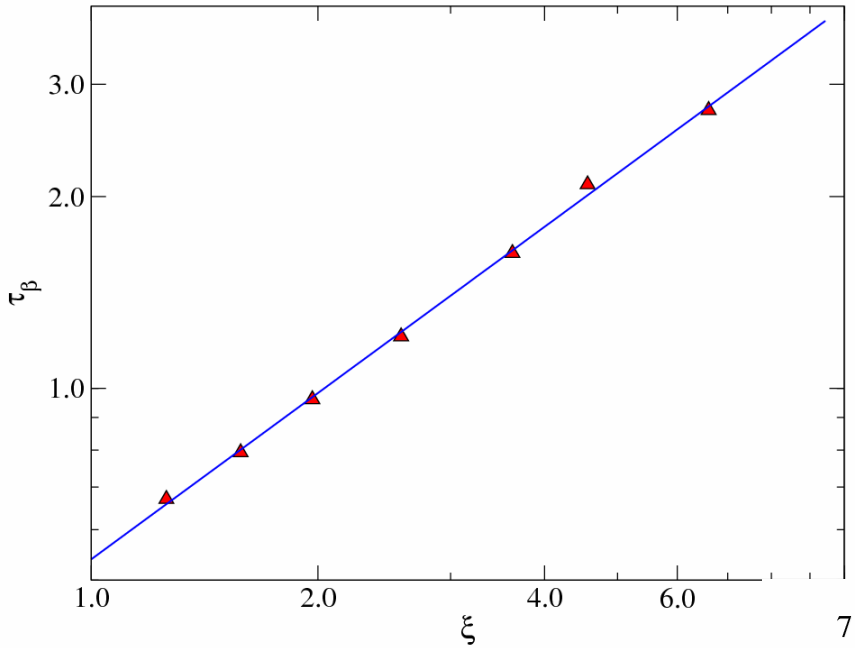




Strong dependence on system size at low temperatures

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



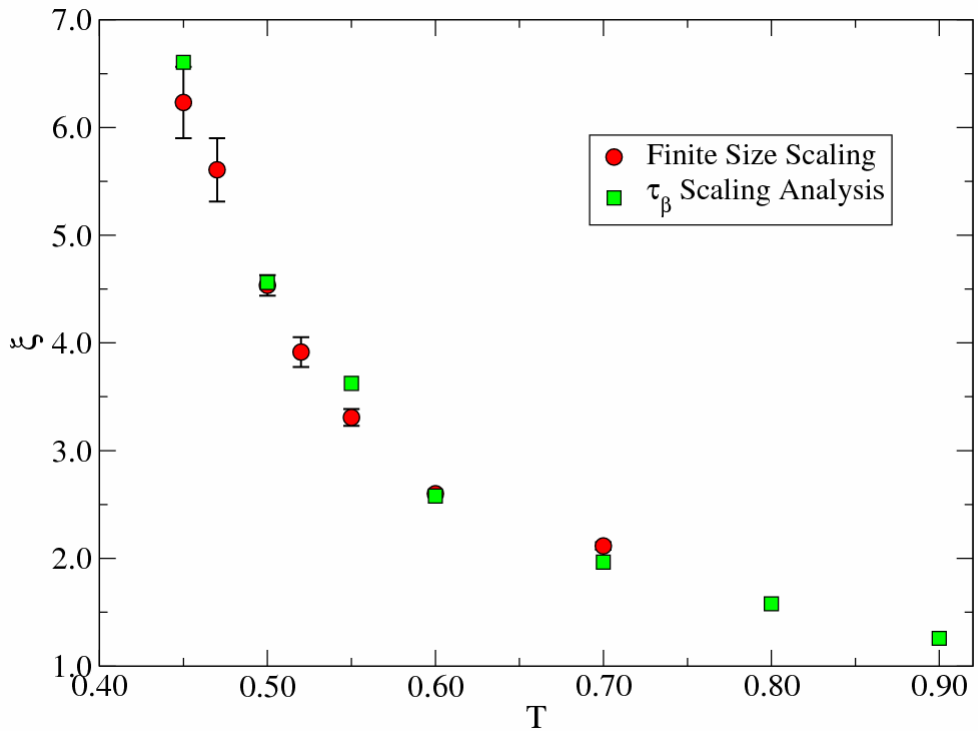

$$\tau_\beta(T, N) = \tau_\beta(T, N \to \infty) f(N/\xi^3)$$




$$\tau_\beta(T) \propto \xi(T)^z, \;\; z \simeq 0.9$$

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

- Dynamics in the short-time, $\beta$ - relaxation regime is governed by a growing dynamic length scale.

  Inhomogeneous mode-coupling theory (Berthier *et al*., 2006) predicts the presence of a growing length scale in the short-time dynamics. The observed value of the exponent for the growth of this length scale is **different** from the prediction of IMCT.

- 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 $\alpha$ relaxation.

  A similar connection has been suggested in Widmer-Cooper *et al.* Nature Physics **4**, 711 (2008), in Brito and Wyart, JSTAT L08003 (2007), and in Candelier *et al.* arXiv0912:0193.