Experimental and numerical evidences of growing lengthscales escorting the glass transition

Ludovic Berthier

Laboratoire des Colloïdes, Verres et Nanomatériaux
Université de Montpellier II & CNRS

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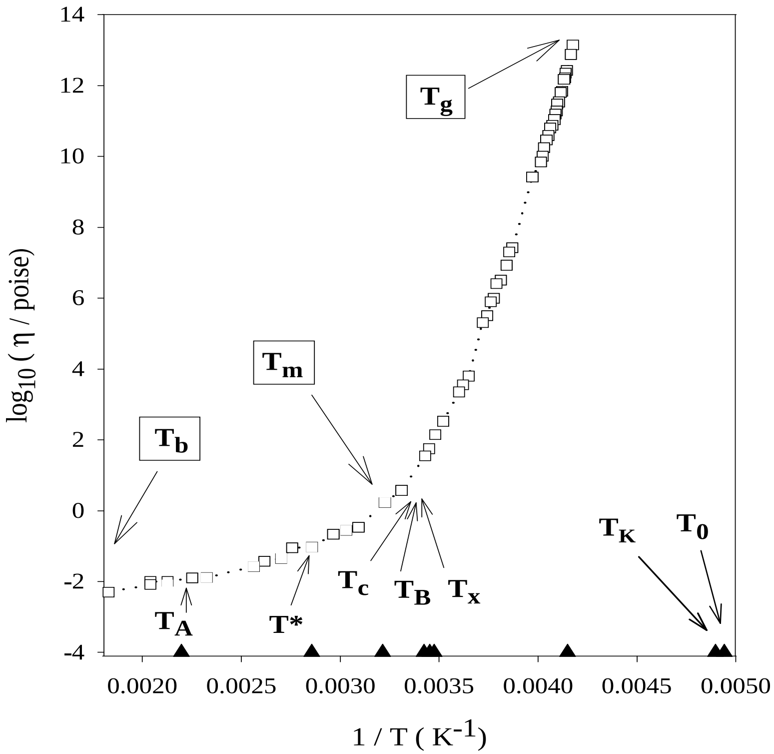
with G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, J.P. Garrahan, D. L’Hôte, F. Ladieu,

S. Léonard, M. Pierno, S. Whitelam.

Glassy materials

• Many materials (hard & soft matter) are glassy. Amorphous structure with slow dynamics, $t_{\rm rel} \sim t_{\rm exp}$.

• How do we understand slow dynamics beyond "mean-field" theories?



[Tarjus, Kivelson, '00]

• Canonical example: supercooled liquids. Yet, unsolved problem.

• First step: Macroscopic behaviour.

Slowing down ('jamming'): $\eta = \eta(T)$.

Non-linear response: $\eta = \eta(\dot{\gamma})$.

Aging: $\eta = \eta(t_{\rm w})$.

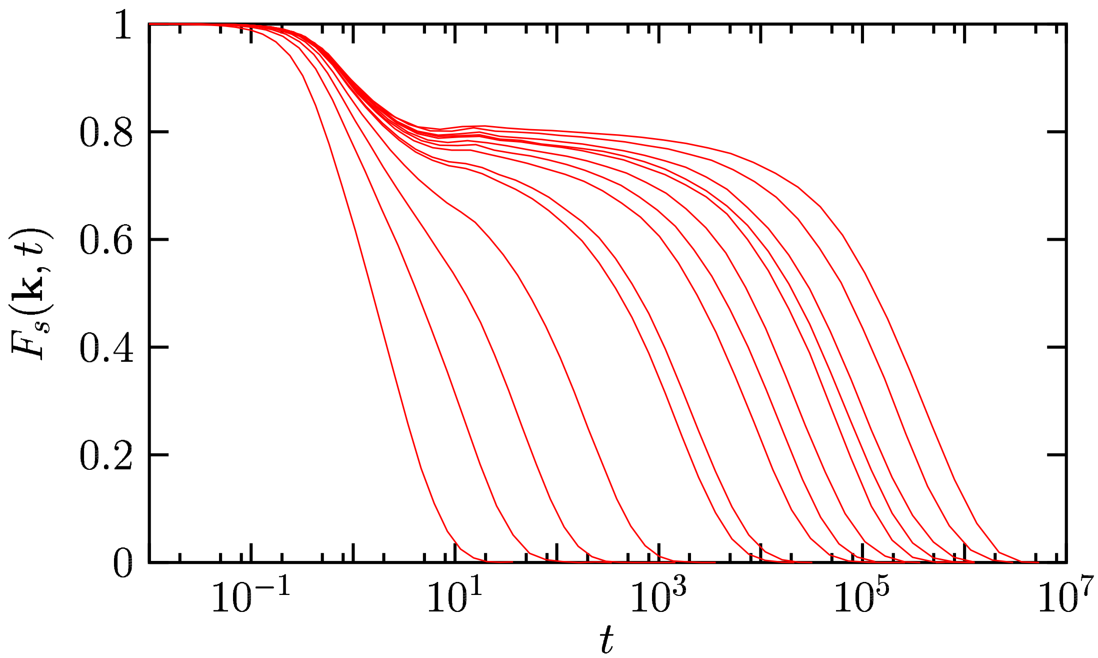
Memory and rejuvenation effects, etc.

• Macroscopic phenomenological theories (e.g. Free volume).

Averaged microscopic behaviour

- Second step: Averaged microscopic dynamics.

- Self intermediate scattering function in a LJ supercooled liquid, $F_s(\mathbf{k},t) = \langle \frac{1}{N} \sum_i \exp\left(j\mathbf{k} \cdot [\mathbf{r}_i(t) - \mathbf{r}_i(0)]\right) \rangle$, displays stretched relaxation.



- ‘Microscopic’ mean-field theory (e.g. trap models).

Dynamic heterogeneity

- Definition: Spatio-temporal fluctuations of the local dynamical behaviour

Manifestation 1: Wide or stretched relaxations distributions.

Manifestation 2: Non-Gaussian individual particle displacements

Manifestation 3: Decoupling; Stokes-Einstein relations breakdown

- Characterization: Need for correlation functions that probe more than two points in space and time.

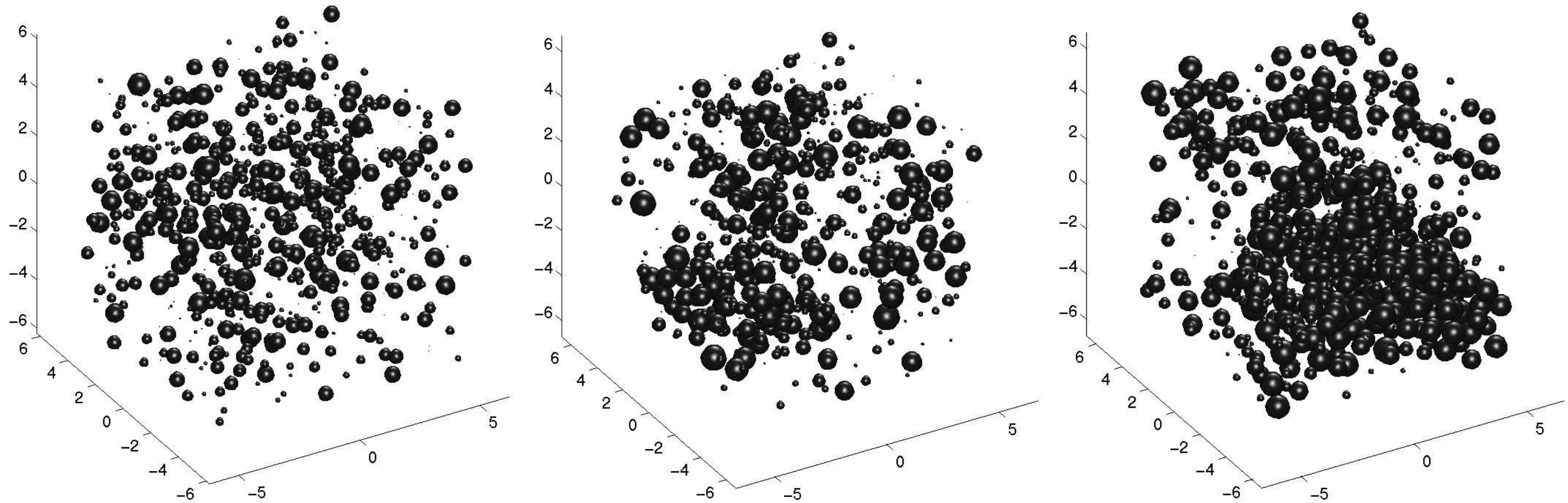
- Lifetime of dynamic heterogeneity: Experimentally ‘easy’ because no spatial resolution needed: ‘4-time’ correlations (NMR, solvation, hole-burning...):

$$C_4(t_1, t_{\rm w}, t_2) = \langle P_i(0; t_1) P_i(t_1 + t_{\rm w}; t_1 + t_{\rm w} + t_2) \rangle$$

- Crucial missing information: lengthscales?

Spatial dynamic correlations

- Snapshots of local fluctuations of $F_s(\mathbf{k},t) = \langle e^{i\mathbf{k}\cdot[\mathbf{r}_m(t)-\mathbf{r}_m(0)]} \rangle$ in a LJ supercooled liquid [Berthier, PRE ’04].



- Local dynamics becomes spatially correlated as T decreases.

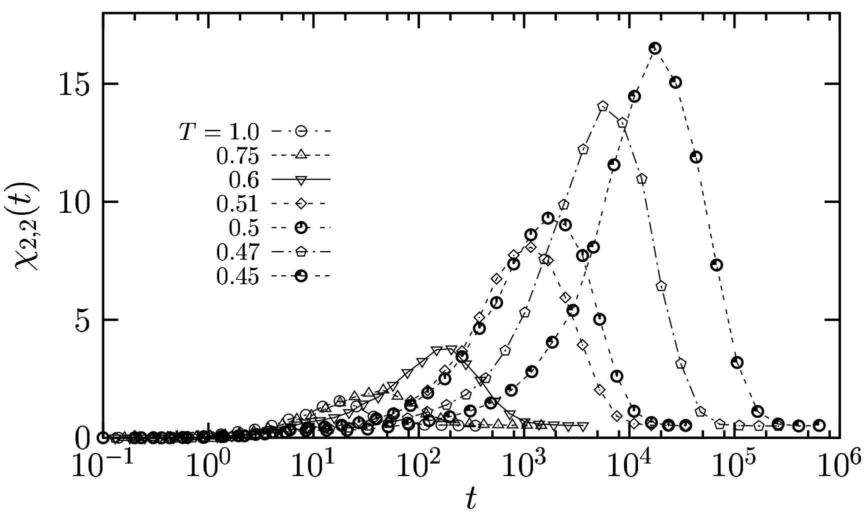
Multi-point correlations

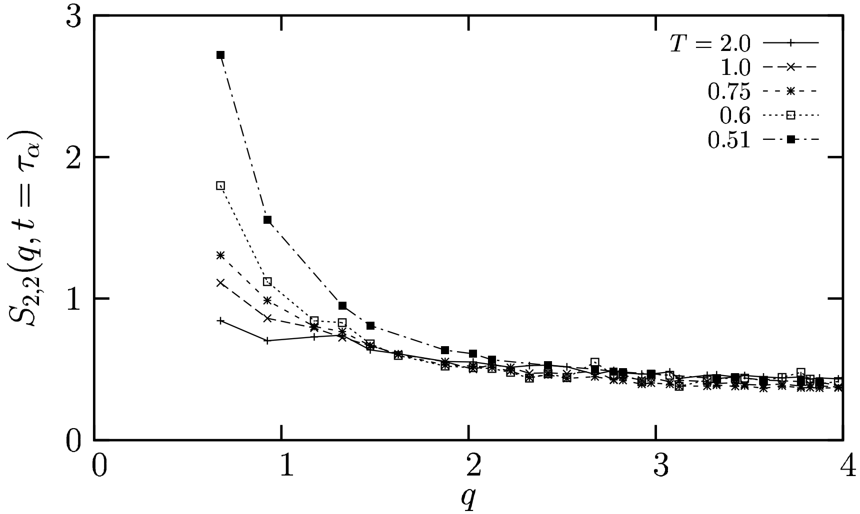
- Structure factor of dynamic heterogeneity is a 2-time, 2-point correlation:

$$S_{2,2}(\mathbf{q},t) = \left\langle \frac{1}{N} \sum_{m,n} \delta F_m(\mathbf{k},t) \delta F_n(\mathbf{k},t) e^{i\mathbf{q}\cdot[\mathbf{r}_m(0)-\mathbf{r}_n(0)]} \right\rangle,$$

where $\delta F_m(\mathbf{k},t) = e^{i\mathbf{k}\cdot[\mathbf{r}_m(t)-\mathbf{r}_m(0)]} - F_s(\mathbf{k},t)$.

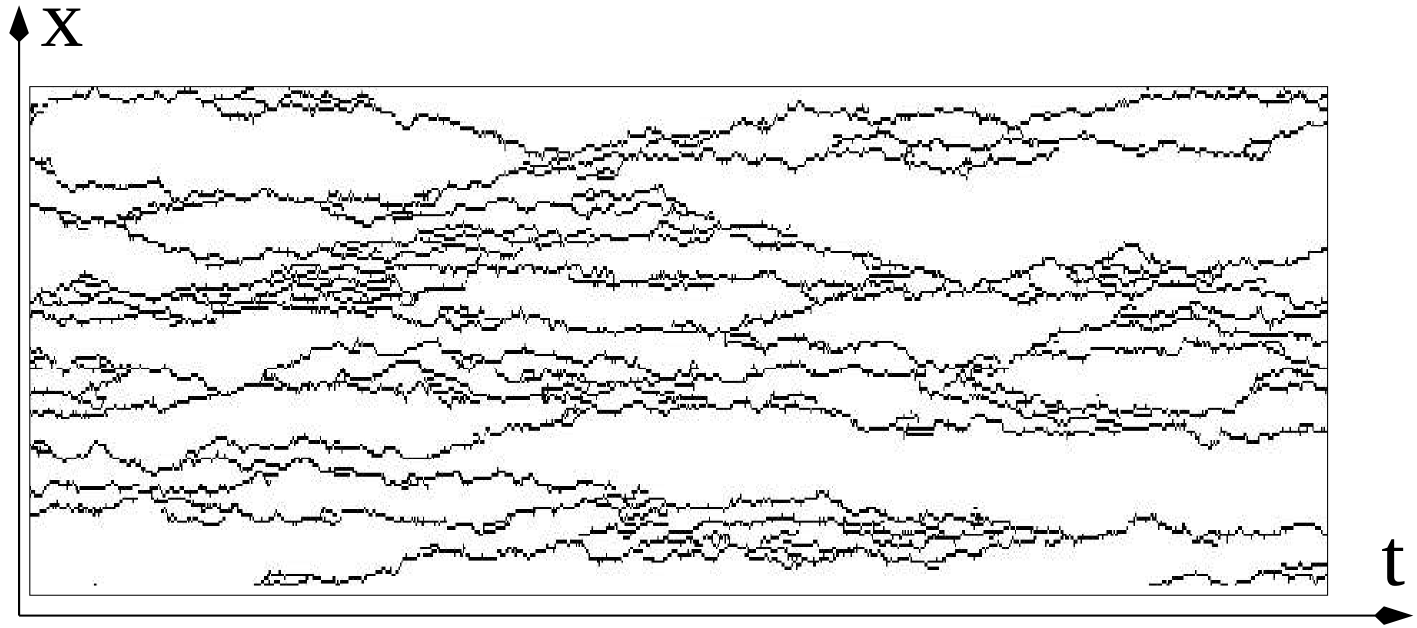
- $\chi_{2,2}(t) = S_{2,2}(\mathbf{q}=0,t)$ is a "four-point" dynamic susceptibility ("$\chi_4(t)$").





Coarse-grained models

• Kinetically constrained spin model (e.g. FA model): dynamics of a coarse-grained mobility field [cf JP Garrahan's talk].

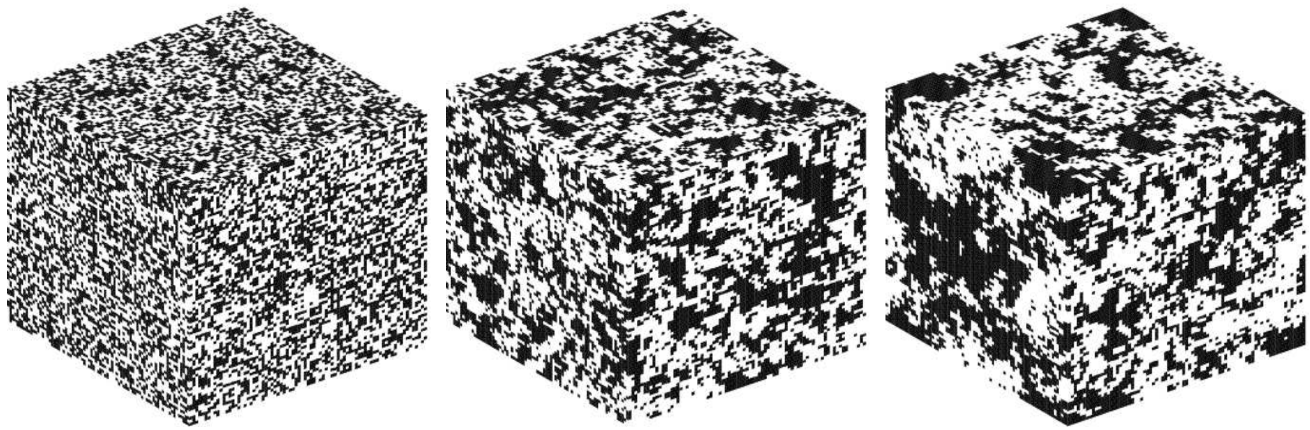


• Dynamics is heterogeneous in space and time.

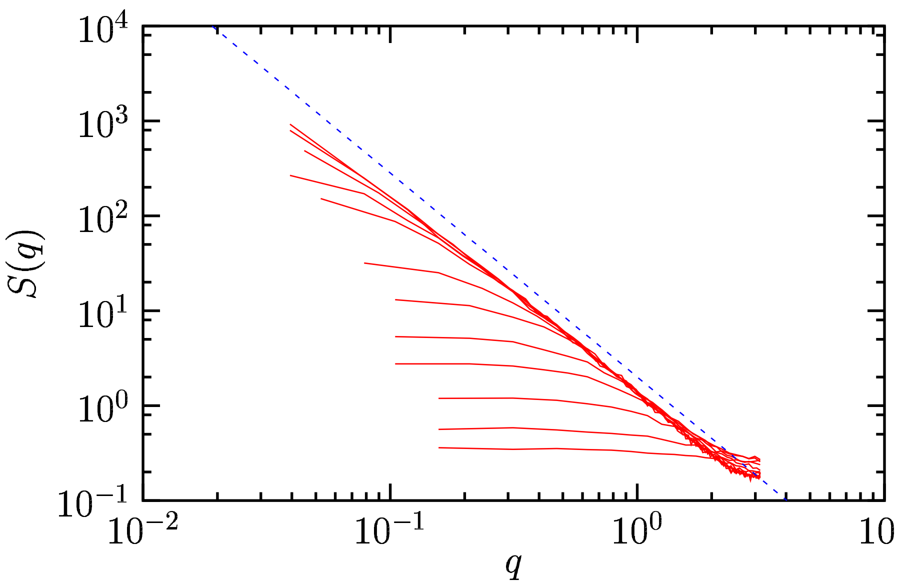
• Temporal and spatial extensions of the "bubbles" diverge when $T \to 0$.
[Whitelam *et al.*, PRL '04 - PRE '05].

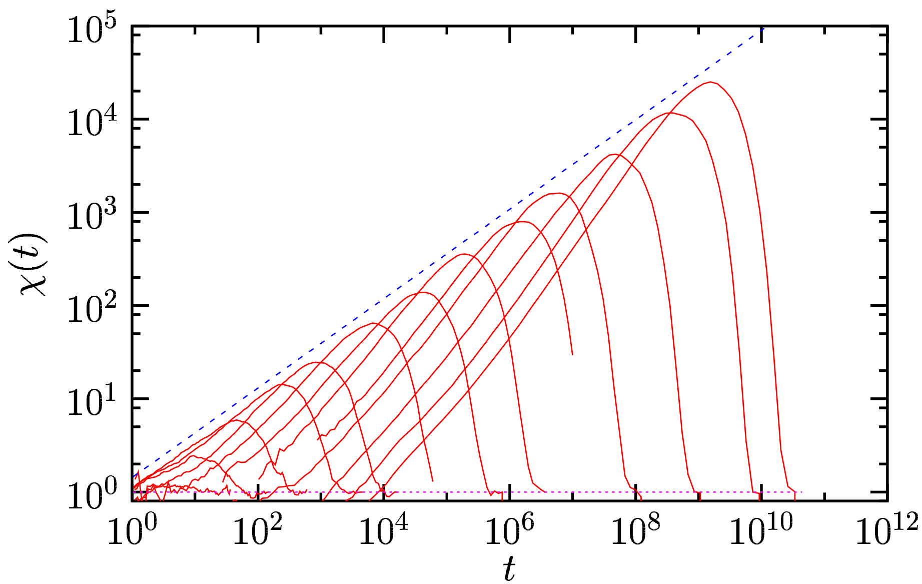
Dynamic critical fluctuations

- $P_i(t) = 0, 1$ (b, w), at time τ such that $\langle P_i(\tau) \rangle = 0.5$ in $d = 3$ FA model.



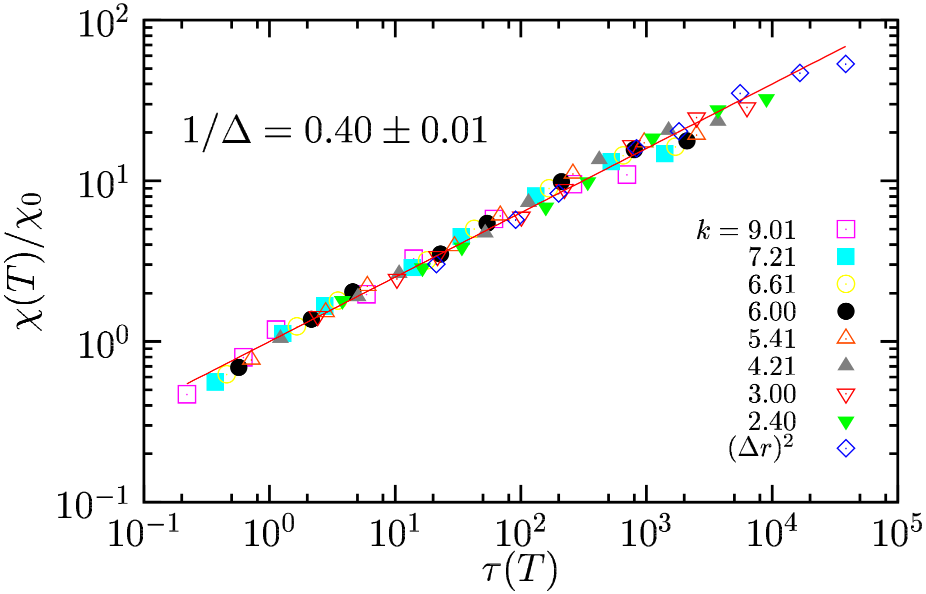
- $S(q) = \sum_{k,l} e^{iq(k-l)} \left[\langle P_k P_l \rangle - \langle P_k \rangle^2 \right]$ and $\chi = S(q = 0)$.

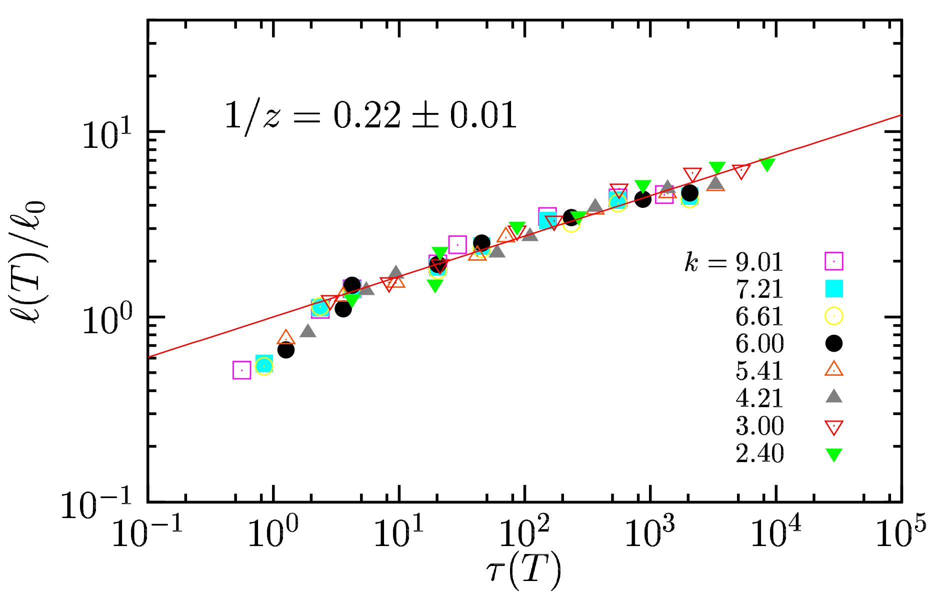




Universal dynamic scaling

- Dynamic scaling in LJ supercooled liquid [Whitelam *et al.*, PRL '04].





- Power law scalings, $\chi \sim \tau^{1/\Delta}$ and $\ell \sim \tau^{1/z}$, as predicted by RG.
- Numerical values of the exponents close to $3d$ FA model: coincidence?

Problem

- Several detailed theoretical predictions for growing lengthscales and susceptibilities.

- Numerical works are limited to $t \sim 10^{-7}$ sec and $T \gg T_g$.

- Spontaneous fluctuations of the dynamics are hard to measure experimentally in molecular liquids (colloids?): spatio-temporal resolution needed.

- No experimental evidence for growing lengthscales, dynamic scaling, time/temperature/pressure dependences.

- Experiments are really needed!

A solution

- Induced fluctuations are more easily measured than spontaneous ones.

- Use fluctuation-dissipation theorems to relate spontaneous to induced fluctuations.

- $C(t) = \delta A(t)\delta A(0)$; $F(t) = \langle C(t) \rangle$. Then define:

$$\chi_x(t) = \frac{\partial F(t)}{\partial x},$$

with $x = T$, P, ρ...

- $\chi_x(t)$ is an experimentally accessible multi-point dynamic susceptibility.

[Berthier, Biroli, Bouchaud, Cipelletti, El Masri, L'Hôte, Ladieu, Pierno, Science '05]

Why χ_x?

- For Newtonian dynamics in the NPT ensemble,

$$k_B T^2 \chi_T(t) = N\langle \delta C(t) \delta H(0) \rangle$$

where $H(t)$ is the enthalpy.

- With $NC(t) = \rho \int d^3\vec{r} c(\vec{r}, t)$ and $NH(t) = \rho\sqrt{k_B c_P} T \int d^3\vec{r}\hat{h}(\vec{r}, t)$,

$$\sqrt{\frac{k_B}{c_P}} T \chi_T(t) = \rho \int d^3\vec{r} \left\langle \delta c(\vec{r}, t) \delta \hat{h}(\vec{0}, 0) \right\rangle$$

- Similarly for colloidal particles,

$$\sqrt{\rho k_B T \kappa_T} \rho \chi_\rho(t) = \rho \int d^3\vec{r} \left\langle \delta c(\vec{r}, t) \delta \hat{\rho}(\vec{0}, 0) \right\rangle$$

- Growing χ_x due to a growing dynamic lengthscale: spatial correlations between local dynamic and structural (enthalpy/density) fluctuations.

Link with $\chi_{2,2}$?

- Yes!

$$\chi_{2,2}(t)|_{NPT} = \chi_{2,2}(t)|_{NPH}(t) + \frac{k_B}{c_P} T^2 \chi_T^2(t)$$

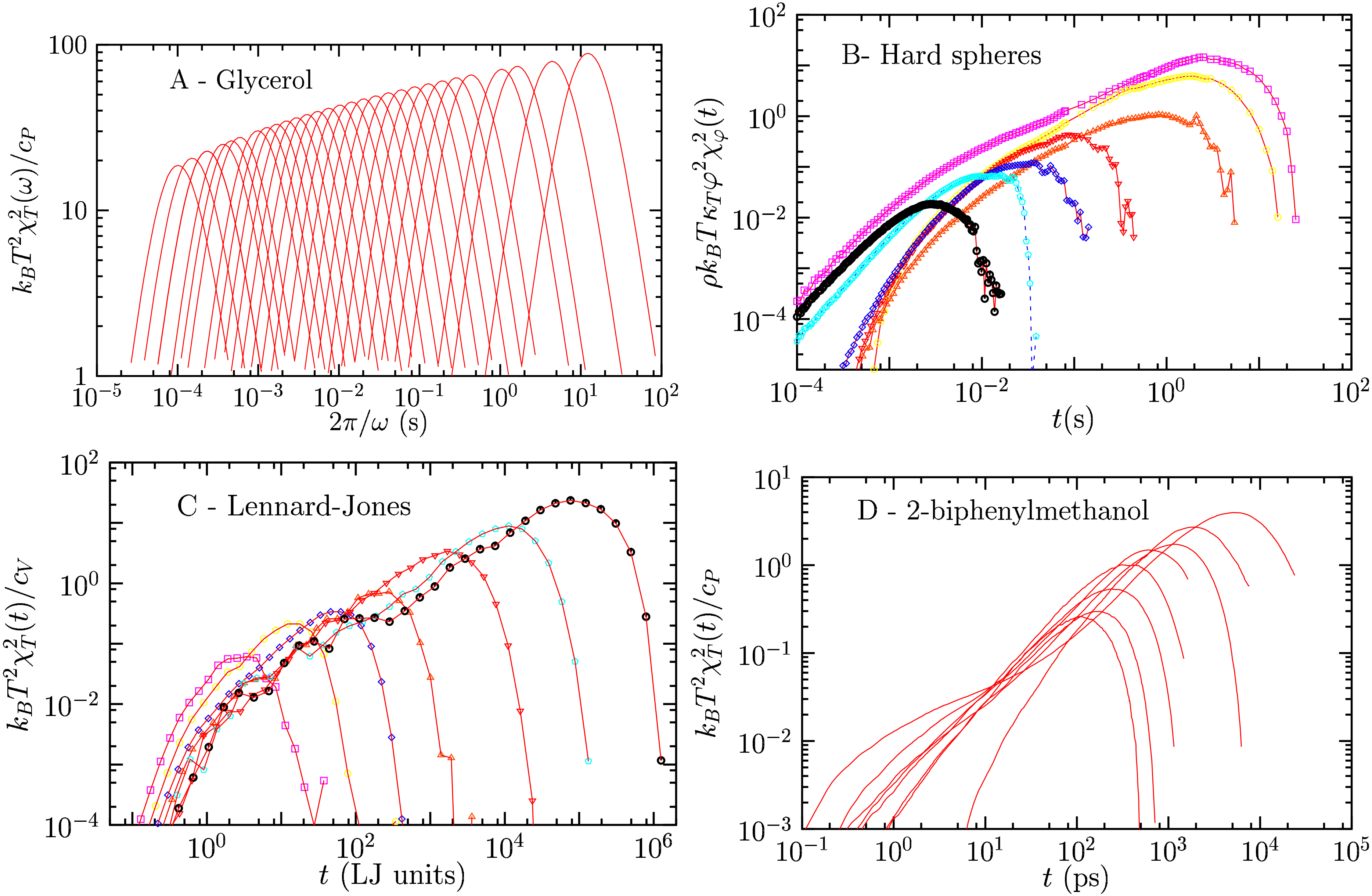
cf. [Lebowitz, Percus & Verlet, Phys. Rev. ’67]

- χ_T provides a rigorous lower bound to $\chi_{2,2}$,

$$\chi_{2,2}(t)|_{NPT} \geq \frac{k_B}{c_P} T^2 \chi_T^2(t)$$

- Numerical simulations indicate that $k_B T^2 \chi_T^2 / c_P$ is a good quantitative estimate of $\chi_{2,2}$, both in strong (BKS silica) and fragile (binary LJ) liquids.

Measuring dynamic fluctuations



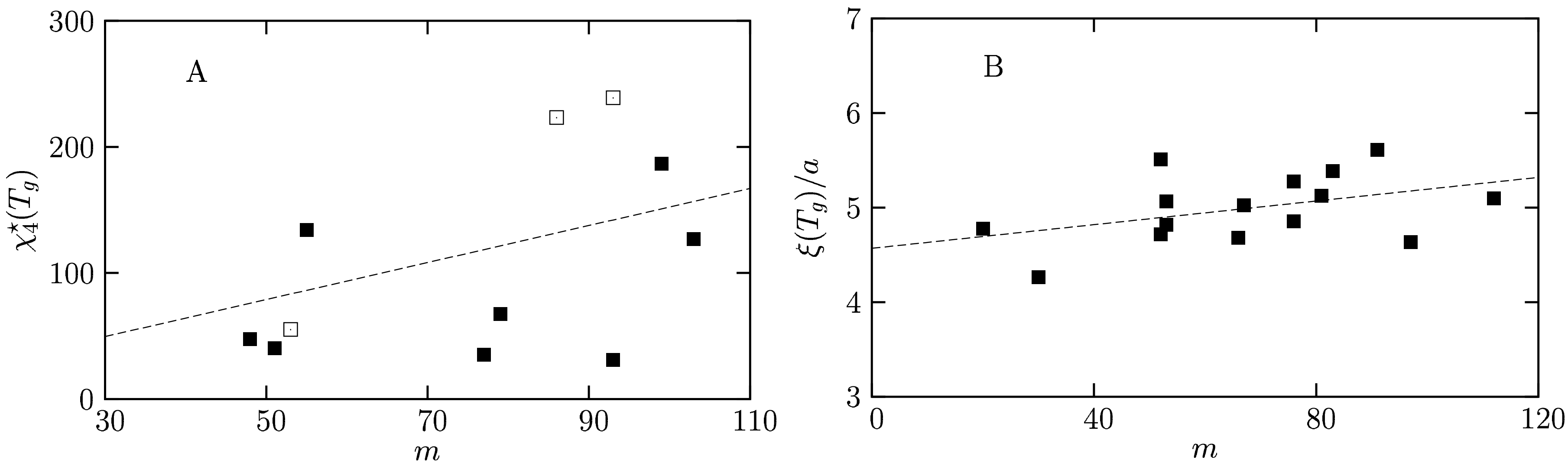
Growing dynamic lengthscales

- $\chi^*_{2,2}(T) \approx \left(\frac{\xi}{a}\right)^{\zeta}$, with $\zeta = 2 - 4$, a is a molecular lengthscale.

- For glycerol ($T_g = 185$ K), $\xi = 0.9$ nm at 232 K to $\xi = 1.5$ nm at 192 K

Similar to Ediger's 4D NMR data: $\xi_{\rm het} = 1.3 \pm 0.5$ nm at 199 K.

- If $F(t) = \mathcal{F}(t/\tau_\alpha)$, $\chi^*_{2,2}(T_g) \approx [\mathcal{F}'(1)]^2 \frac{k_B}{c_P} \left(\frac{\partial \ln \tau_\alpha}{\partial \ln T}\Big|_{T_g} \right)^2$.



Conclusions

- Spatial dynamic correlations are central to understand glassy dynamics

- Multi-point dynamic susceptibilities characterizing dynamic heterogeneity are now experimentally accessible

- Dynamic heterogeneity has a structural origin (enthalpy or density fluctuations).

- Dynamical fluctuations increase as $T \to T_g$

- Dynamic lengthscales increase weakly up to about 4-6 molecular diameters at the glass transition

- More experimental work is needed to characterize important lengthscales in various supercooled liquids