Dynamic heterogeneity: Experimental and numerical results

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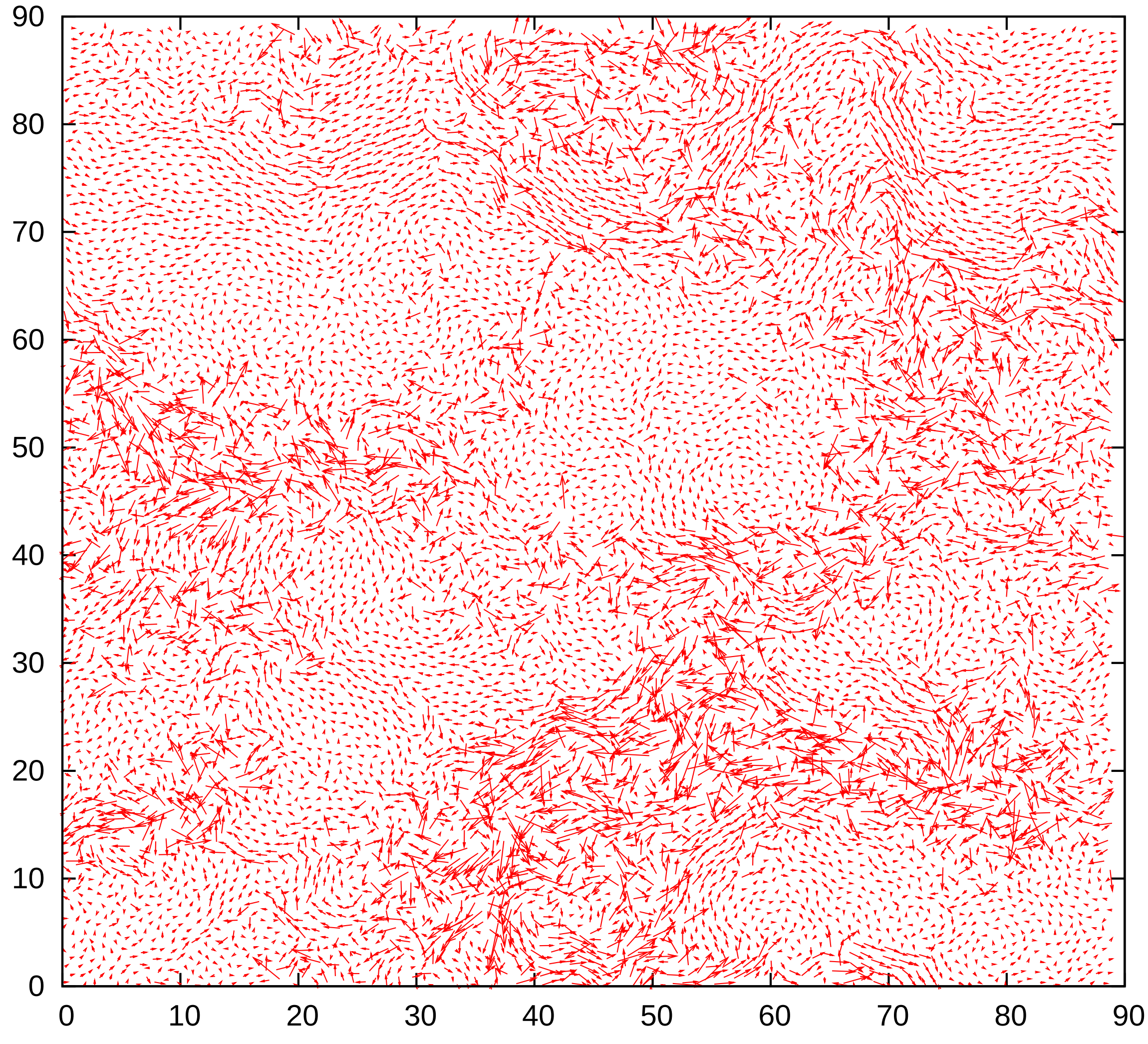
School on glass-formers and glasses – Bangalore, Jan 4 - 20, 2010

Acknowledgments

- Generic ideas, illustrated by results obtained with:

C. Alba-Simionesco,
G. Biroli, J.-P. Bouchaud,
D. Chandler,
L. Cipelletti, P. Chaudhuri,
C. Dalle-Ferrier,
D. El Masri,
J. P. Garrahan,
P. Hurtado,
R. Jack, M. Kilfoil,
W. Kob, F. Ladieu,
D. L'Hôte, P. Mayer,
K. Miyazaki,
M. Pierno, D. Reichman,
G. Tarjus, C. Thibierge,
C. Toninelli, S. Whitelam,
M. Wyart, G. Yongxiang.



Outline

Lecture 1

- Broad introduction to glass-formers
- Microscopic aspects of the dynamics
- Dynamic heterogeneity at the particle level
- Application to gels

Lecture 2

- Clusters, etc.
- Four-point correlation functions
- More dynamic susceptibilities
- Structure or dynamics?

A broad introduction to glass-formers

Glass-formers & glasses

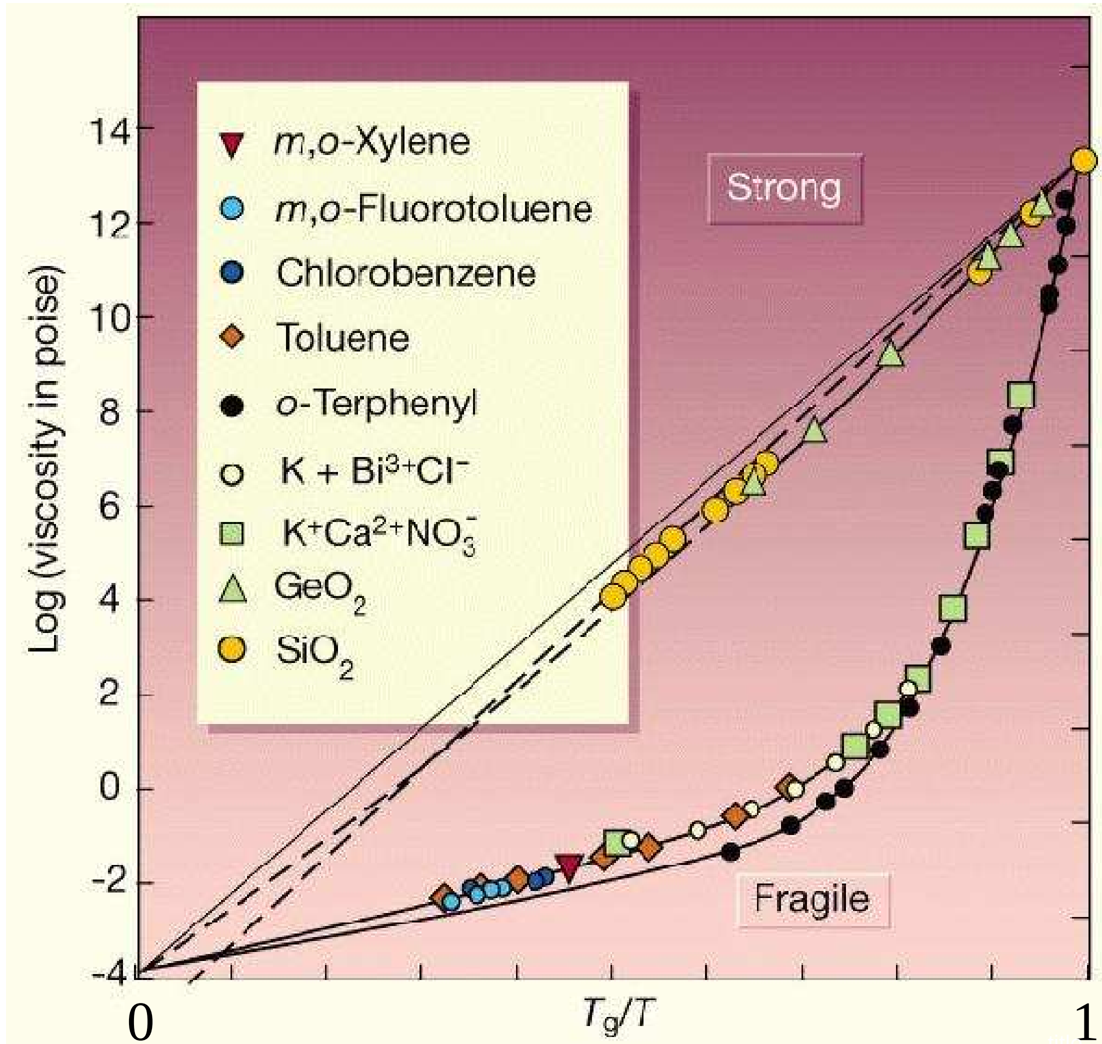
- Many materials (hard & soft) are glassy. Amorphous structure with slow dynamics, $t_{\rm rel} \sim t_{\rm exp}$. E.g. structural glasses [Debenedetti, Stillinger '01]

- Angell and Tarjus.

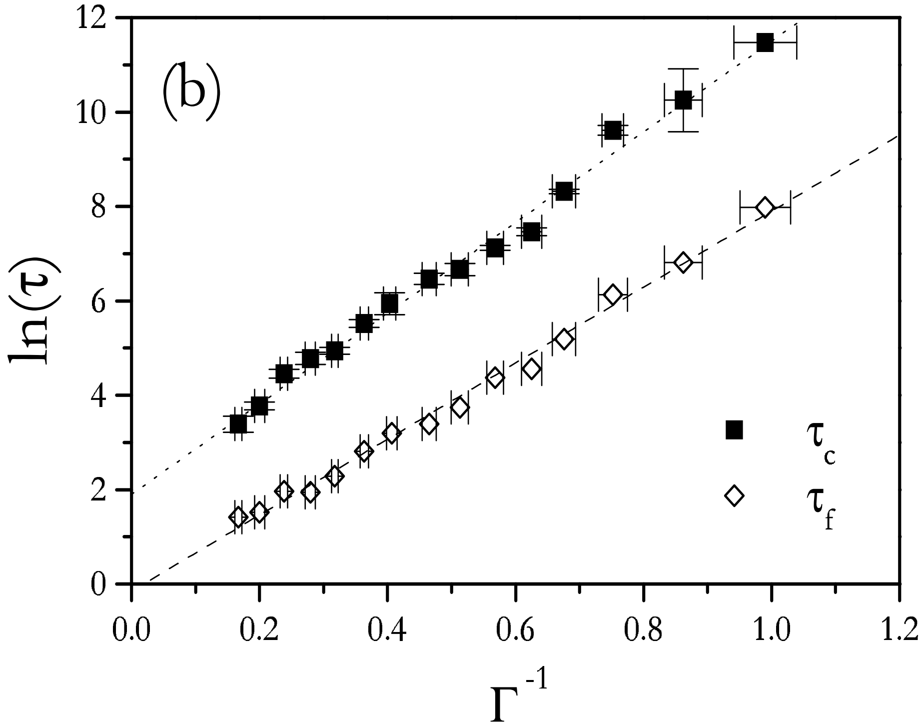
- Glass 'transition' $\eta(T_g) = 10^{13}$ Poise

- How to describe structural relaxation?

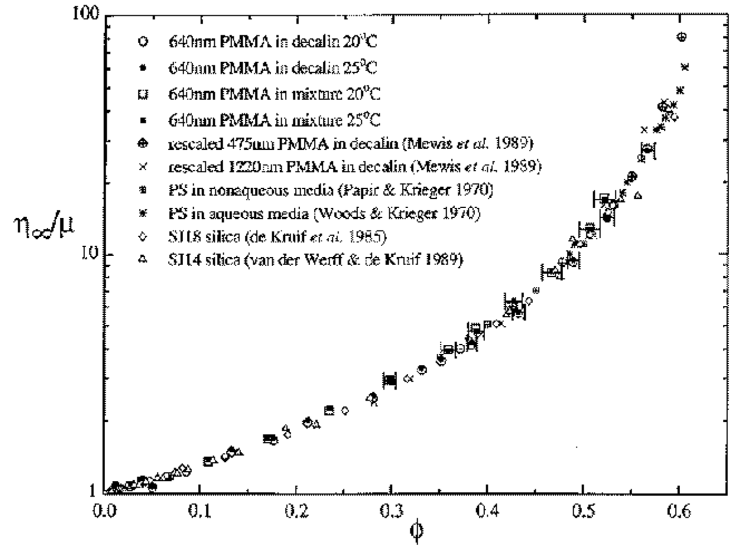
- Microscopic mechanisms, relevant fluctuations, length scales?



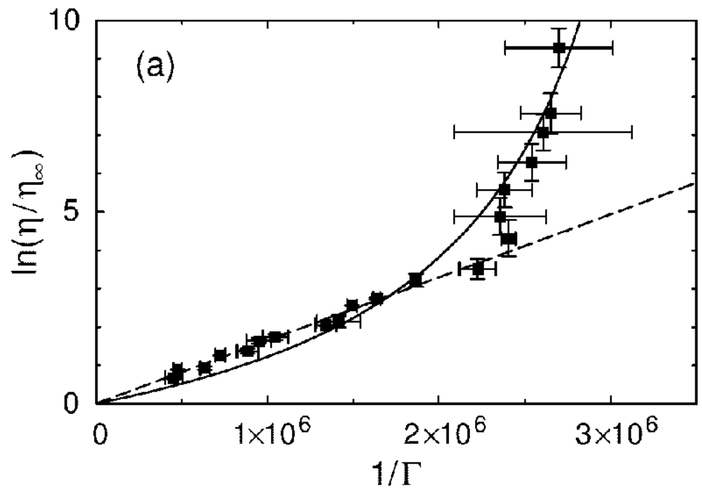
More 'jamming' transitions



Vibrated grains [Philippe & Bideau, EPL '02]



Colloids [Phan *et al.*, PRE '96]



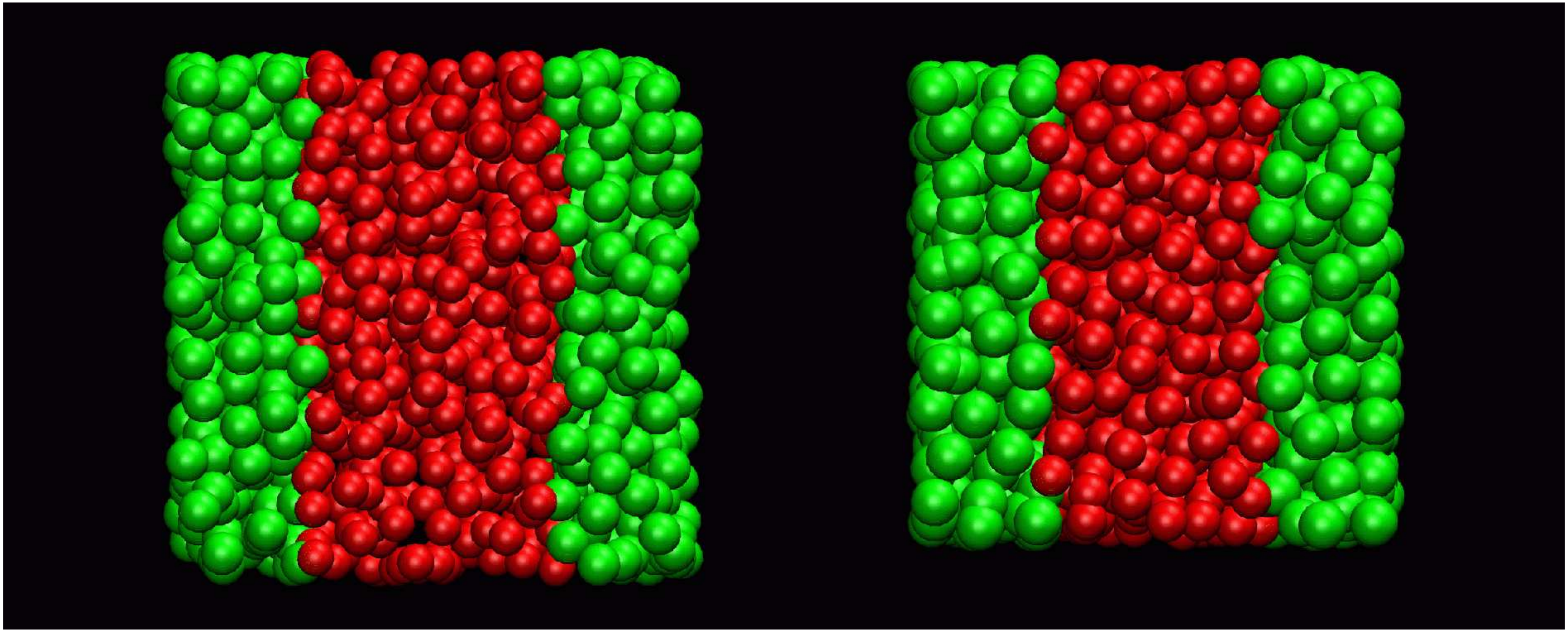
Sheared foam [Langer, Liu, EPL '00]

- Dense assemblies of grains, colloids and bubbles stop flowing. Sollich.

The glass conundrum

A liquid flows

A glass does not



- Why don't glasses flow? How do viscous liquids flow?

A challenging field

- Broad variety of materials made of:

Atoms – Molecules – Spins – Droplets – Colloids – Bubbles – Grains

- Many transitions from an ergodic/fluid phase to a non-ergodic/glassy phase are empirically well-known.

- But poorly understood! Disorder, non-ergodicity, off-equilibrium, experimental difficulties, etc.

- Most of them are not even ‘transitions’ in a statmech sense.

- Rich phenomenology to be studied and explained: rheology, aging, memory, rejuvenation, hysteresis, non-linear response, effective temperatures, etc.

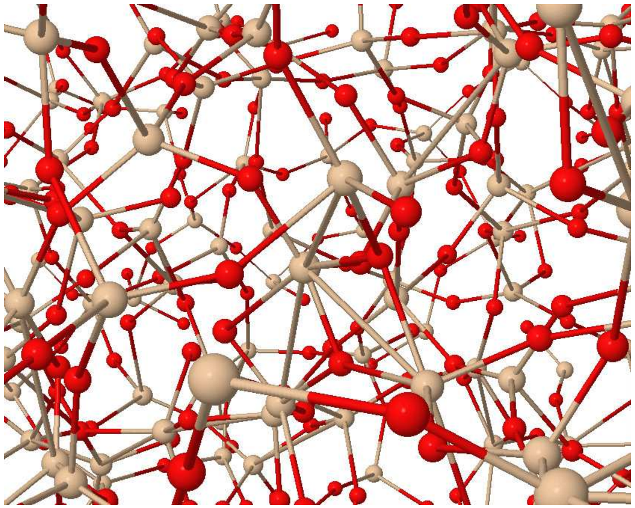
Slow dynamics in glassy materials: Microscopic aspects

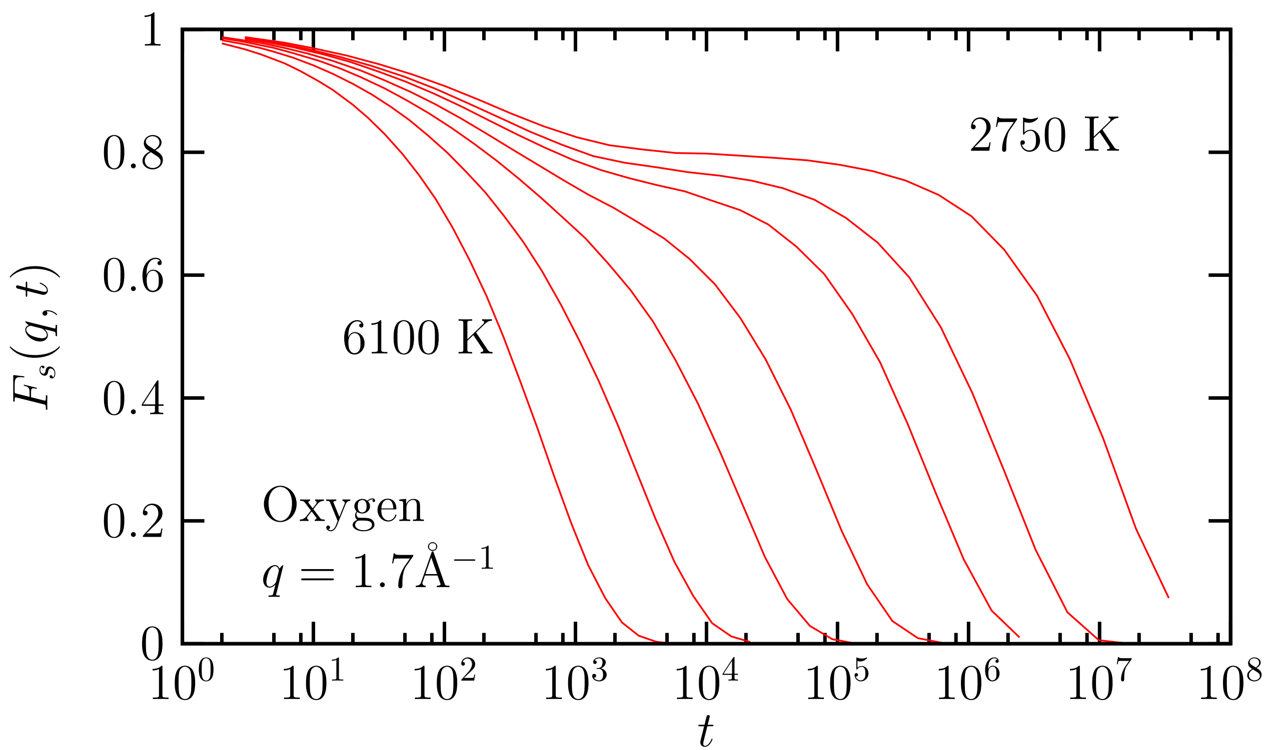
Microscopic dynamics

- We want to understand the dynamics at a microscopic level.

E.g., self-intermediate scattering function $F_s(q,t) = \langle e^{i\mathbf{q}\cdot(\mathbf{r}_n(t)-\mathbf{r}_n(0))}\rangle$ in a silica melt SiO_2: slow atomic motions. Kob.

- Broad distributions, stretched exponential: $F_s \sim \exp[-(t/\tau_\alpha)^\beta]$, $\beta < 1$.

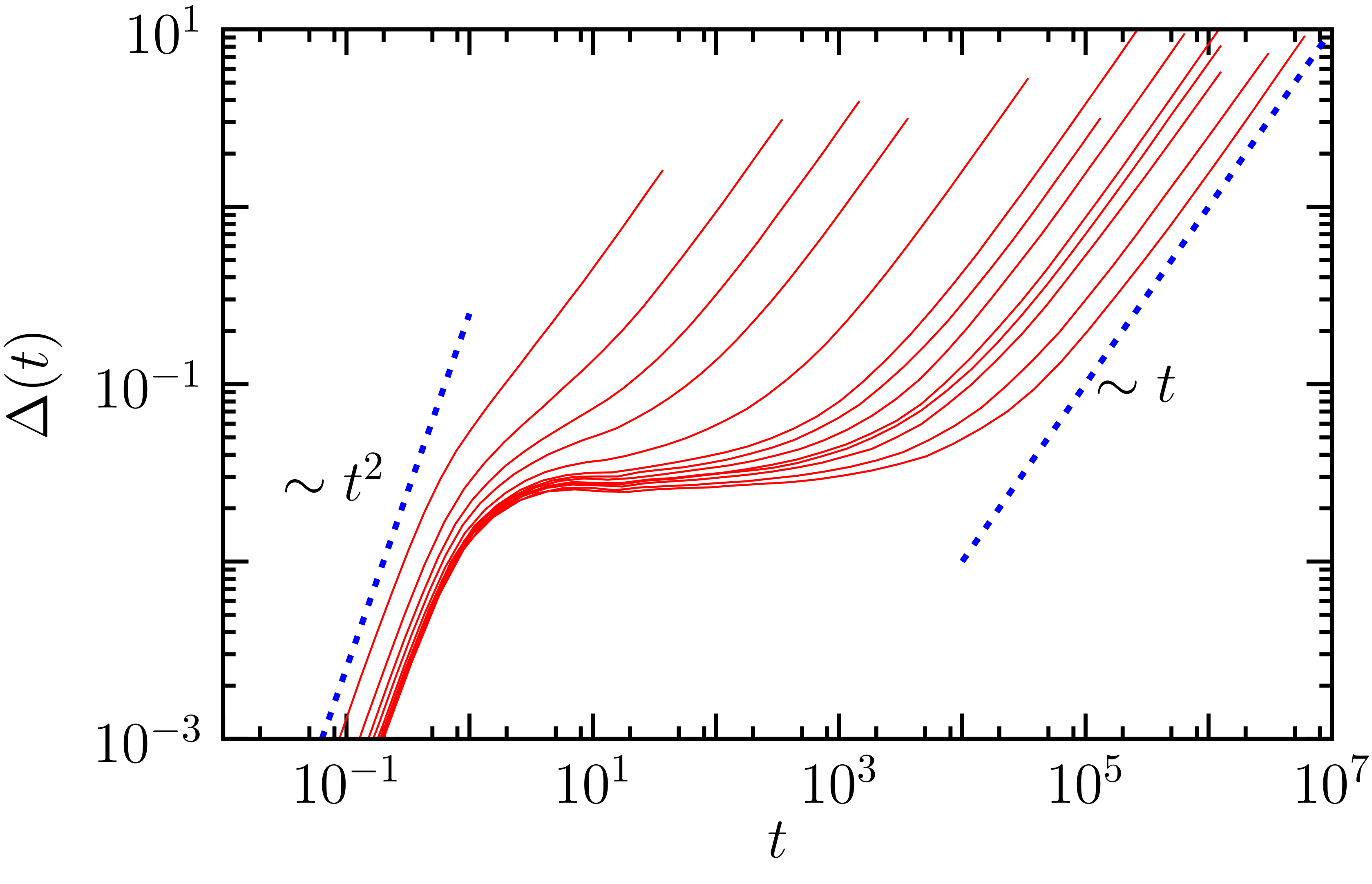




[Berthier, PRE '07]

Averaged displacements

Mean-squared displacement, $\Delta(t) = \langle|\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2\rangle$, in a Lennard-Jones mixture: non-Fickian dynamics at intermediate times.

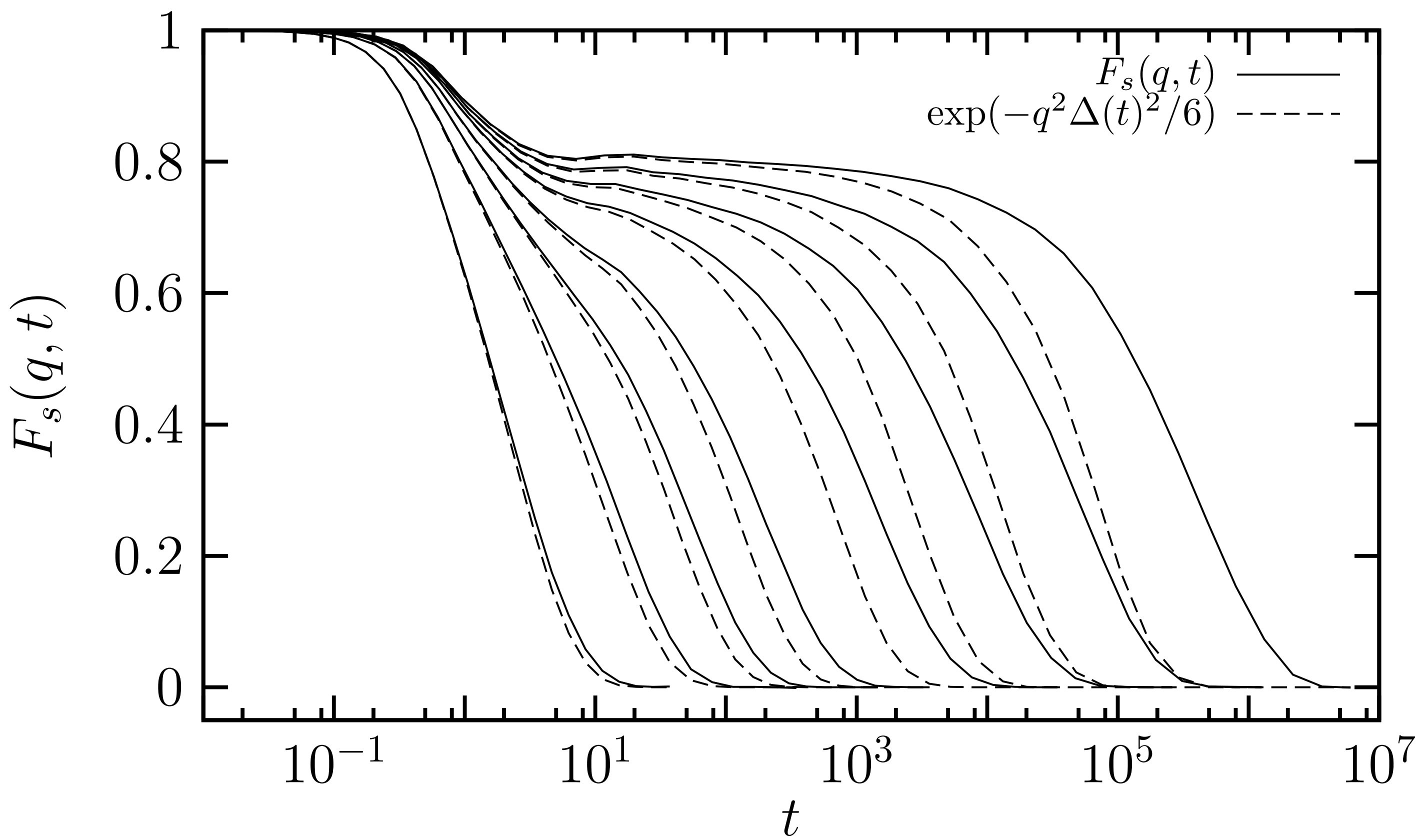


Fickian (Gaussian) dynamics

- Fickian diffusion implies: $G_s(x,t) = (4\pi D_s t)^{-1/2} \exp(-x^2/4D_s t)$.
- Implies simple diffusion: $\Delta(t) = 3\langle x^2 \rangle = 3 \int_{-\infty}^{\infty} dx G_s(x,t) x^2 = 6 D_s t$.
- $F_s(q,t) = \left(\int_{-\infty}^{\infty} dx e^{i q_x x} G_s(x,t) \right)^3 = e^{-q^2 D_s t} = e^{-q^2 \Delta(t)/6}$
- Same information content from $\Delta(t)$ and $F_s(q,t)$.
- Dispersion relation $\tau(q) = \dfrac{1}{q^2 D_s}$.
- 'Non-Gaussian parameter', $\alpha_2(t) = \dfrac{\langle x^4 \rangle}{3\langle x^2 \rangle} - 1$, is zero for a Gaussian process, also quite popular.

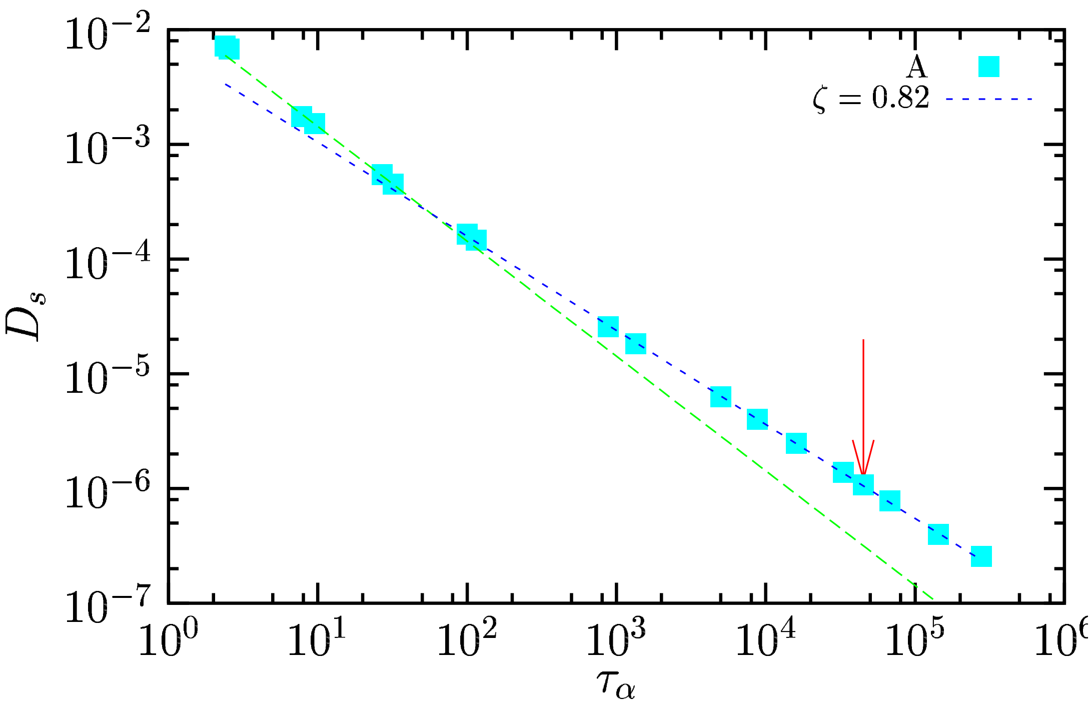
Non-Gaussian local dynamics

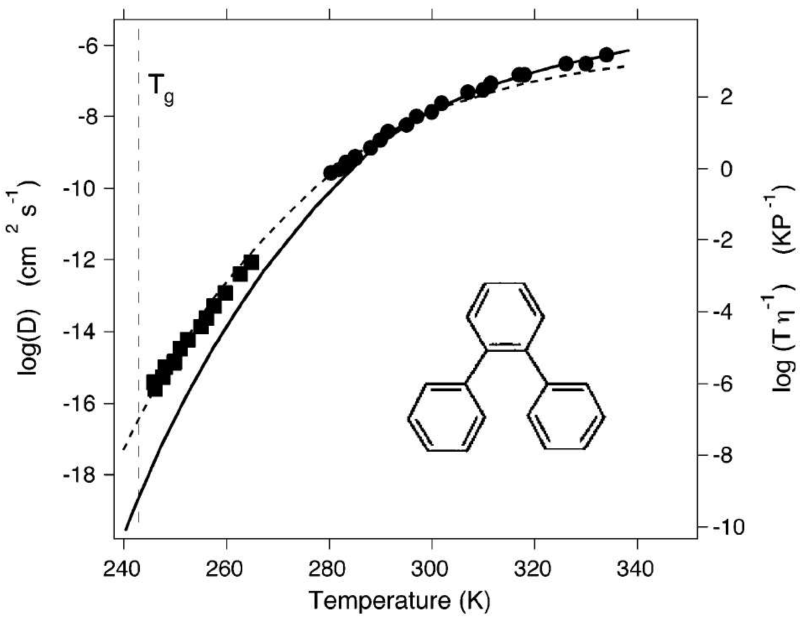
• Comparison of $F_s(q,t)$ and $\exp(-q^2\Delta(t)/6)$: non-Gaussian diffusion at low temperatures. Viscous liquids are ‘different’.



• Suggests that $\tau_\alpha(q_0,T) \approx \eta(T)$ and $D_s(T)$ behave differently with temperature, they ‘decouple’.

Decoupling phenomena





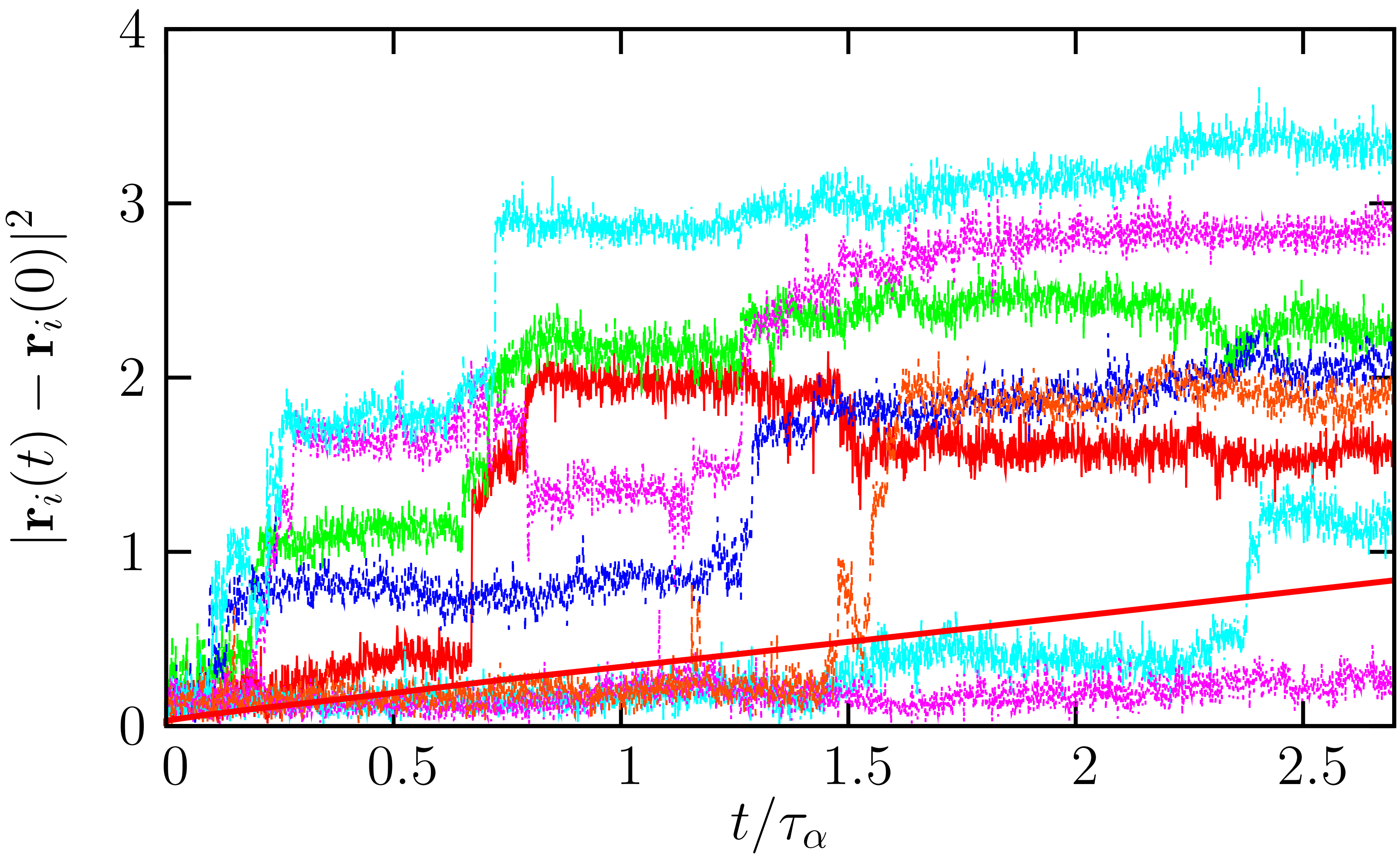
[Mapes *et al.*, JCP ’06]

- $D_s \sim \tau_\alpha(q_0, T)^{-\zeta}$, with $\zeta \approx 0.82 < 1$ in LJ mixture. Fractional Stokes-Einstein relation in OTP: $D_s \sim (T/\eta)^\zeta$, $\zeta \approx 0.82 < 1$.

- Importance of statistical distributions and microscopic fluctuations. New constraints for theories (e.g. MCT). Decoupling has been widely studied.

Dynamic heterogeneity at the single particle level

‘Intermittent’ dynamics (movie)

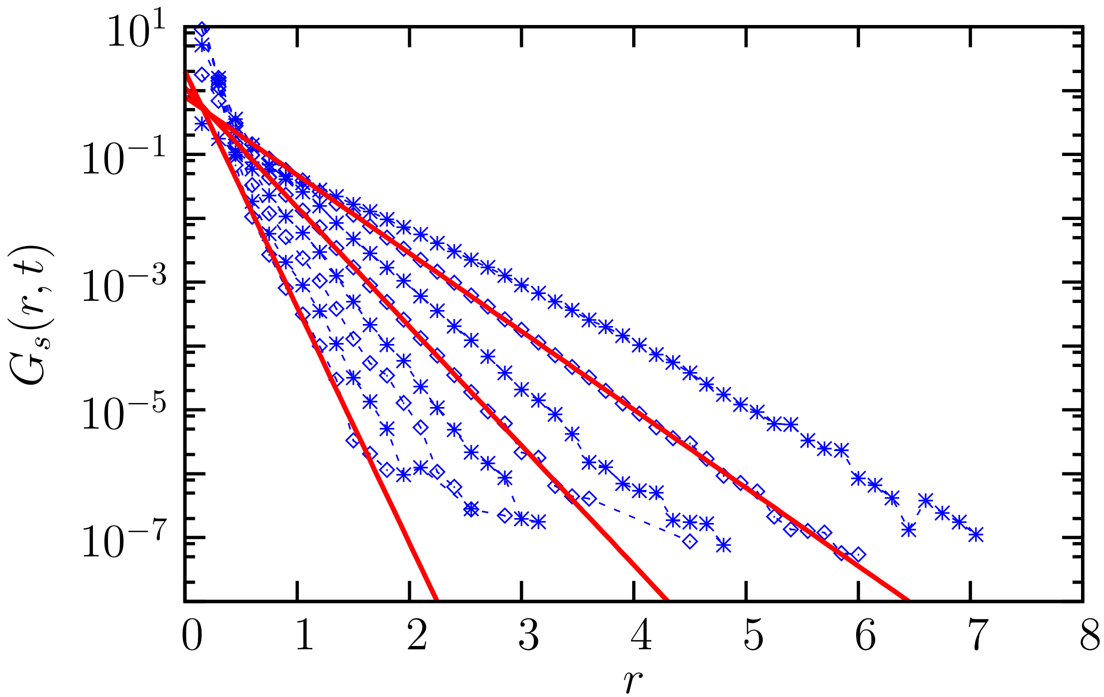


- This information cannot be captured by averaged statistical correlators.
- Need for temporally and spatially resolved experiments/simulations.

Dynamic heterogeneity in liquids

• Non-Gaussian distribution of particle displacements in a supercooled liquid.
$G_s(r,t) = \langle \delta(r - |r_i(t) - r_i(0)|) \rangle$

• Gaussian part for small r, exponential tails at large distance.



[Chaudhuri, Berthier, Kob, PRL'07]

• Coexistence of fast/slow populations of particles. 'Historical' definition of dynamic heterogeneity: Hundreds of papers, several reviews (Ediger).

• The exponential tail is the analog, in space, of stretched exponential decay of time correlation functions. Theoretical explanation? MCT?

A random walk picture

- Particles perform random walks at random times, or “Continuous Time Random Walk” (CTRW).

[Lax, Scher, Bouchaud, Odagaki, Berthier *et al.* EPL ’05, Chaudhuri *et al.* PRL’07]

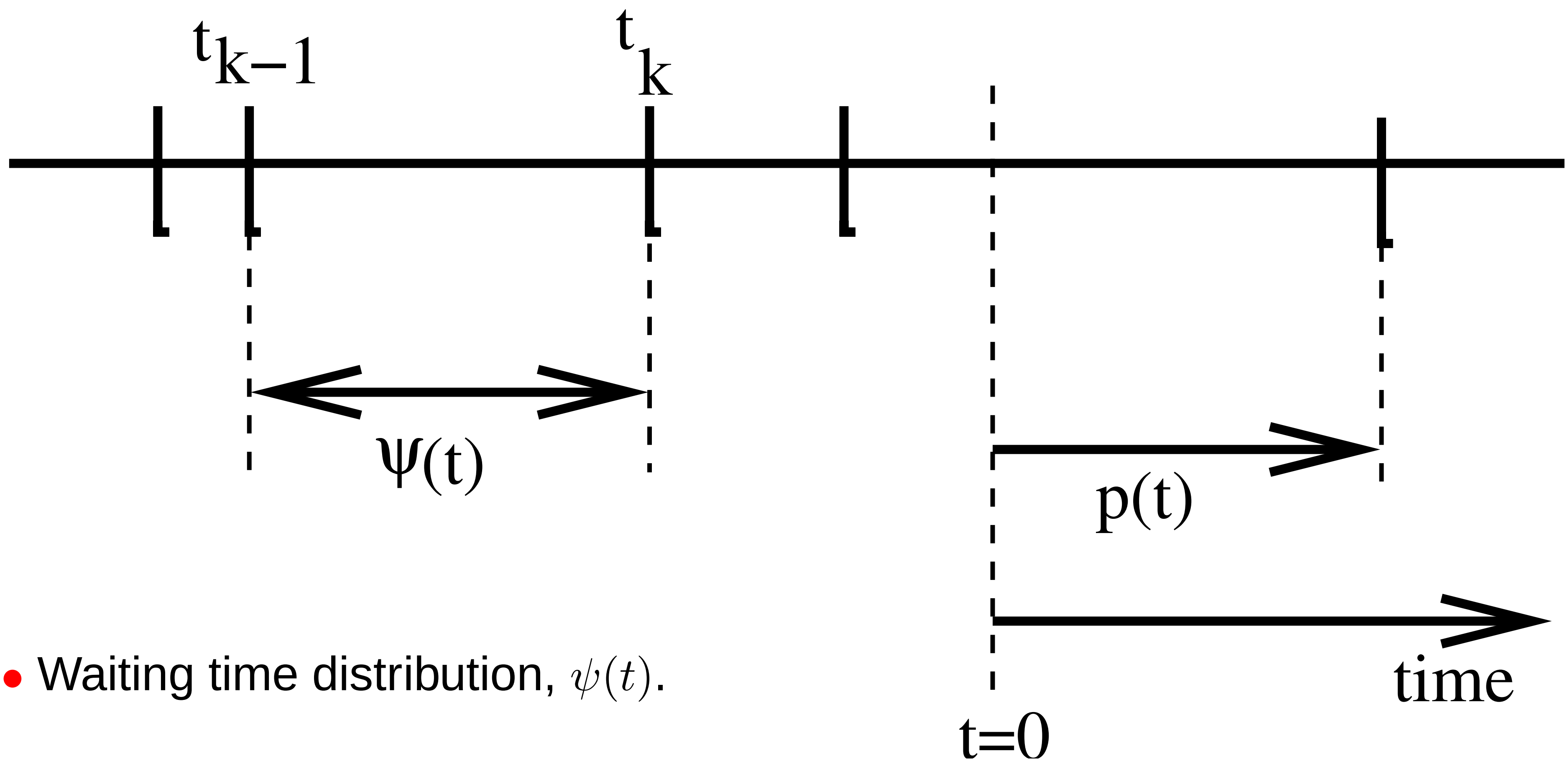
- Compute $G_s(r,t)$ using standard formalism of CTRW.

- Generically (saddle-point) leads to an exponential tail (with log-corrections) for van Hove distribution.

- Conclusion: intermittent jump dynamics in supercooled liquids is responsible for exponential tail of van-Hove distributions.

Set up for computation

- Consider a stationary continuous time random walk. Measurement of displacement starts at arbitrarily chosen $t = 0$.



- Waiting time distribution, $\psi(t)$.

Standard CTRW

- $G_s(\mathbf{r},t) = \sum_{n=0}^{\infty} p(n,t) f(n,\mathbf{r})$.
- $p(0,t) = \int_t^\infty dt' p(t')$, time to the 1rst jump; $f(0,\mathbf{r}) = f_{\text{vib}}(\mathbf{r})$.
- $p(1,t) = \int_0^t dt' p(t')\Psi(t-t')$; $\Psi(t) = \int_t^\infty \psi(t')$; $\psi(t)$ is the waiting time distribution; $f(1,\mathbf{r}) = [f(0,\mathbf{r}) \otimes f_{\text{jump}}(\mathbf{r})] \otimes f_{\text{vib}}(\mathbf{r})$.
- $p(n+1,t) = \int_0^t dt' p(n,t')\psi(t-t')$; $f(n+1,\mathbf{r}) = [f(n,\mathbf{r}) \otimes f_{\text{jump}}(\mathbf{r})] \otimes f_{\text{vib}}(\mathbf{r})$.
- Solution: $G_s(\mathbf{q},s) = \left(\frac{1-p(s)}{s}\right) f_{\text{vib}}(\mathbf{q}) + \frac{p(s) f_{\text{vib}}(\mathbf{q}) f(\mathbf{q})[1-\psi(s)]}{s[1-f(\mathbf{q})\psi(s)]}$,

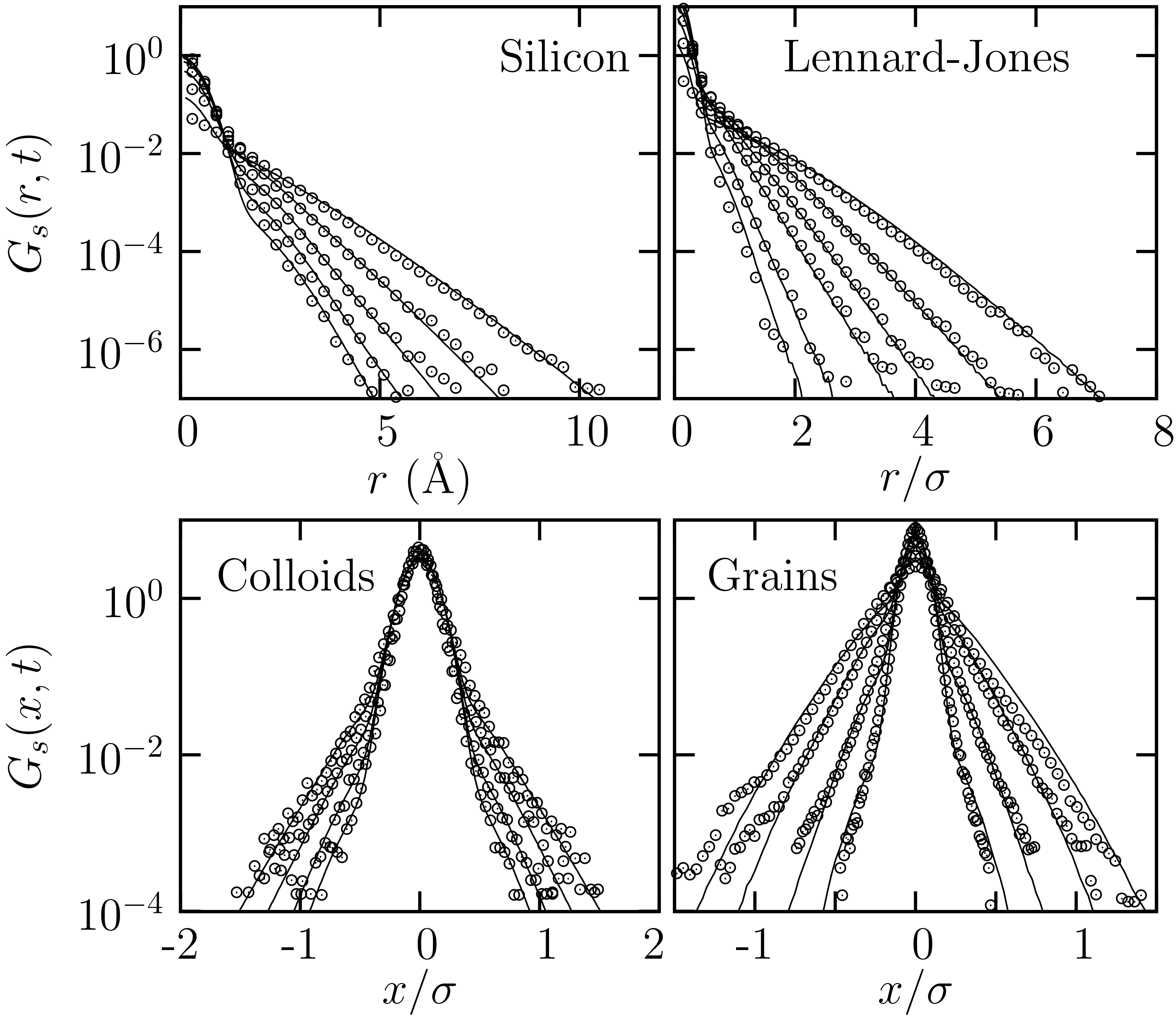
with $f(\mathbf{q}) = f_{\text{vib}}(\mathbf{q}) f_{\text{jump}}(\mathbf{q})$ [Tunaley, PRL '74].

- Feller relation: $p(t) = \frac{\int_t^\infty dt' \psi(t')}{\int_0^\infty dt' t' \psi(t')} \rightarrow \langle t \rangle_p = \frac{\langle t^2 \rangle_\psi}{\langle t \rangle_\psi}$.

First jump gives more weight to large waiting times.

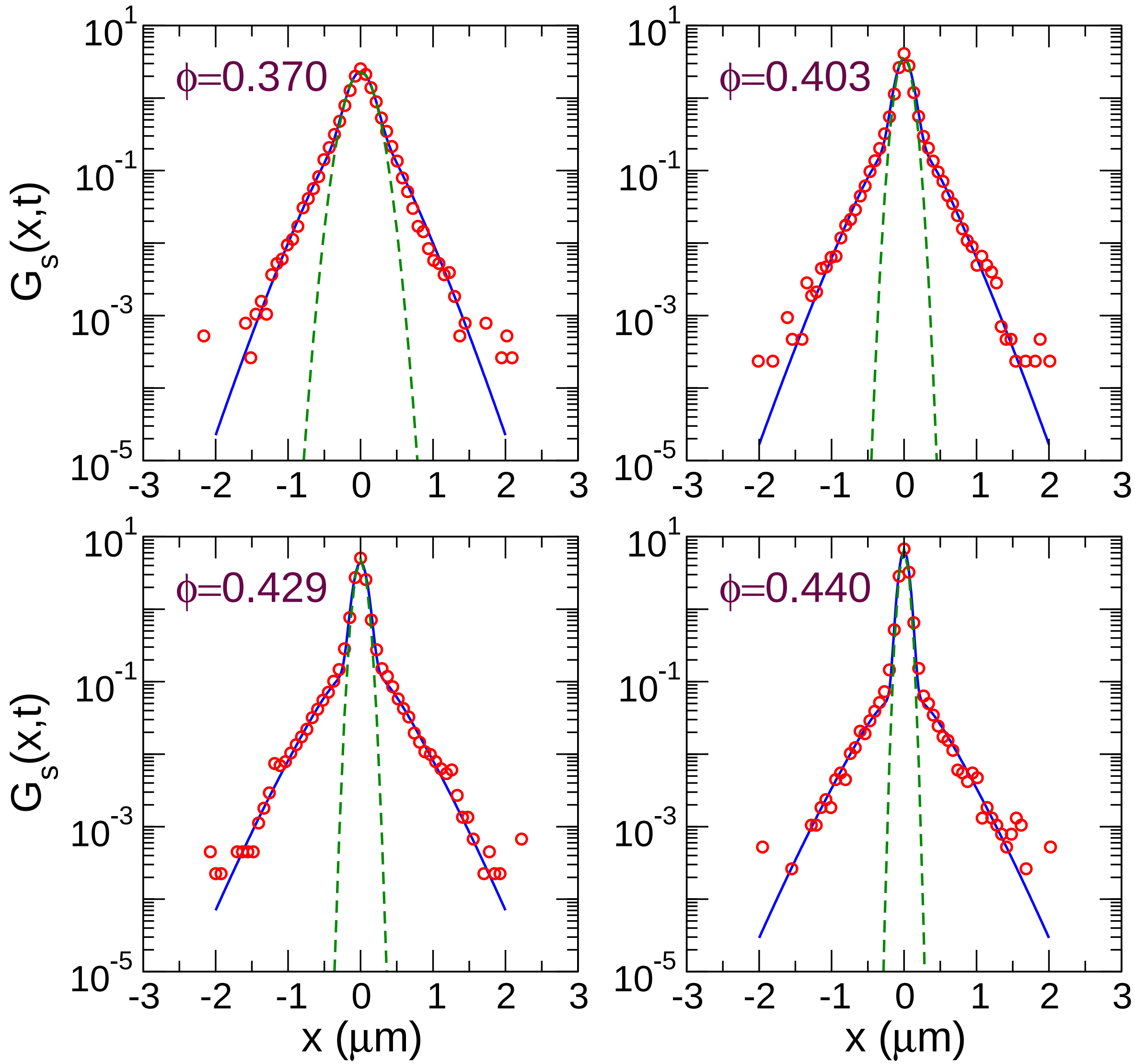
Fitting data in real materials

- Waiting time distributions are not known! $\rightarrow$ Simplified CTRW model.
- Timescales: $p(t) = \exp(-t/t_1)/t_1$ and $\psi(t) = \exp(-t/t_2)/t_2$; $t_1 > t_2$.
- Lengthscales: $f_{\rm vib} \sim \exp(-r^2/\sigma_1^2)$ and $f_{\rm jump} \sim \exp(-r^2/\sigma_2^2)$.
- Using (σ_1, σ_2, t_1, t_2), data for liquids, colloids and grains can be fitted for many (t, T, φ).
- Typically, we find $\sigma_2 \approx \sigma_1$.



Silicon
Lennard-Jones
Colloids
Grains
$G_s(r,t)$
$G_s(x,t)$
r (Å)
r/σ
x/σ
x/σ
10^0
10^{-2}
10^{-4}
10^{-6}
0
5
10
0
2
4
6
8
-2
-1
0
1
2
-1
0
1

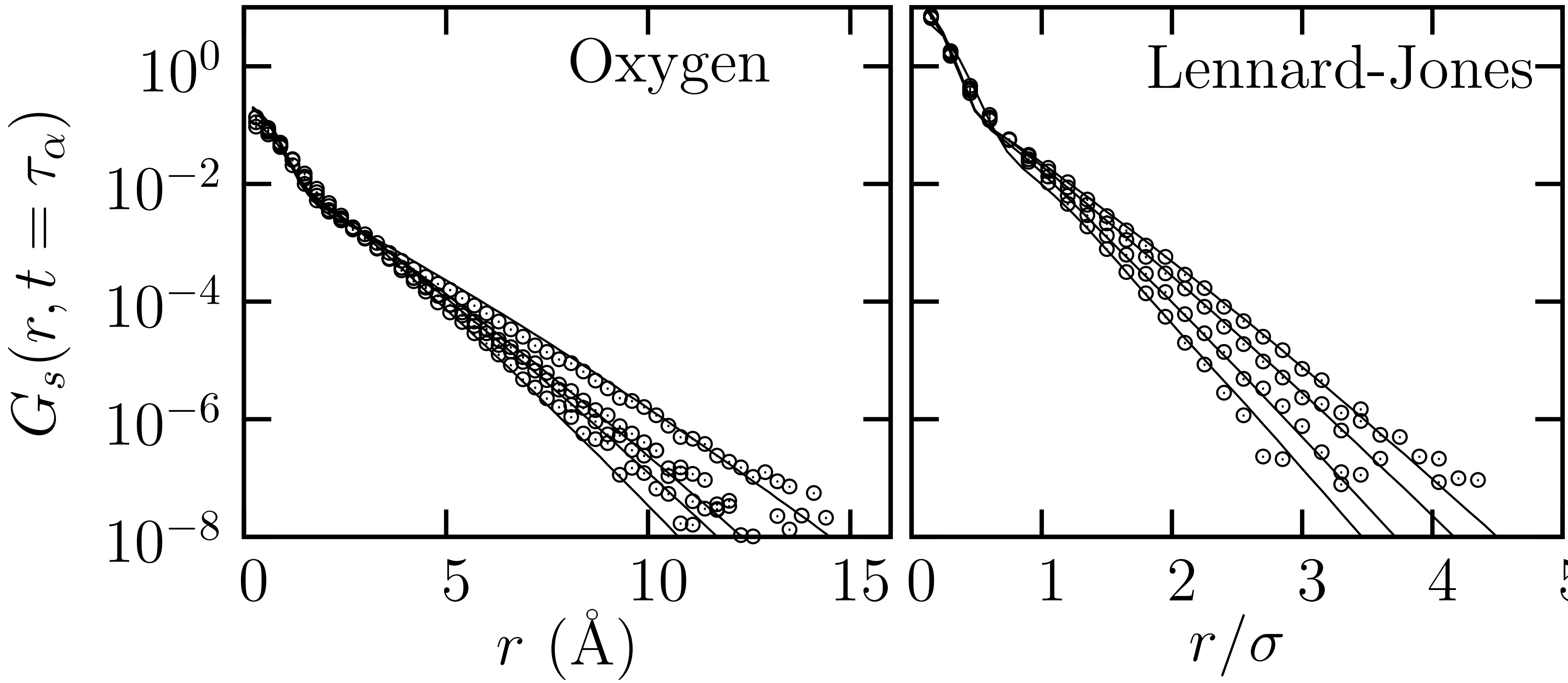
... even in colloidal gels



[Chaudhuri, Gao, Berthier, Kilfoil, Kob, JPCM ’08]

Temperature evolution

- Distributions get broader at low temperature.



- Waiting time distributions get broader (in model, t_1/t_2 increases).

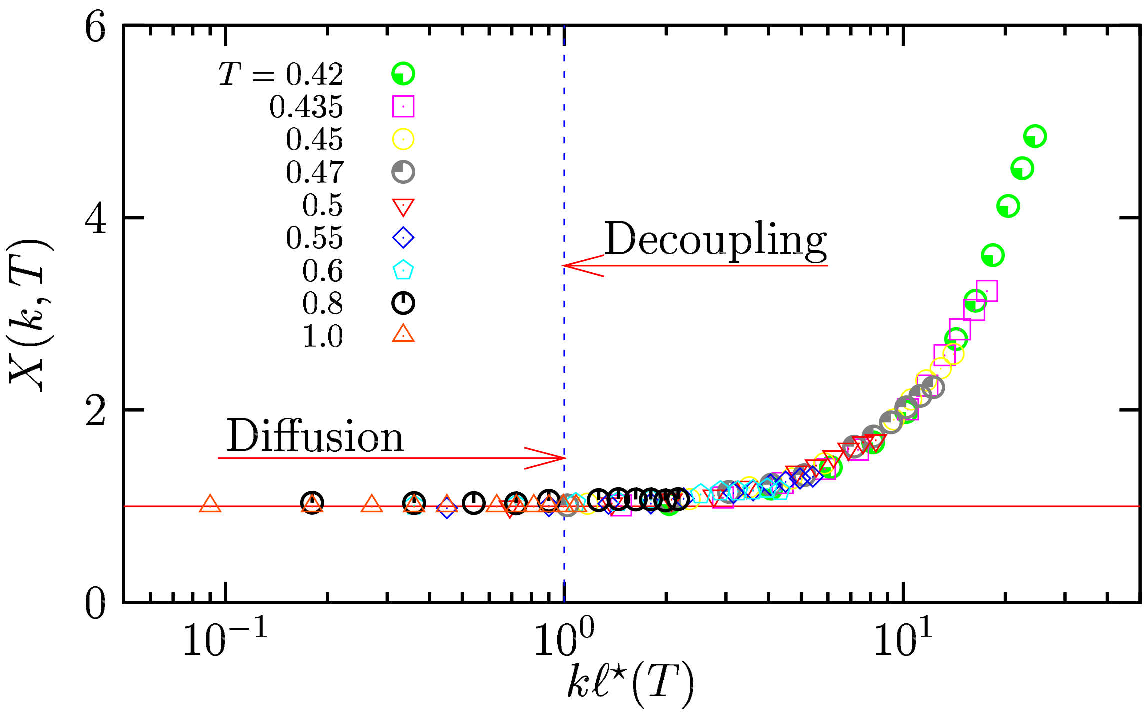
The Fickian lengthscale

- CTRW solution shows that $\tau(q) \approx t_1 + \frac{t_2}{q^2}$, with $t_2 \sim 1/D_s$. That is, $\tau(q) \times q^2 D_s \approx 1 + (q\ell^\star)^2$, with $\ell^\star = \sqrt{t_1 D_s}$ is a 'Fickian lengthscale', above which the diffusion equation holds [Berthier, Chandler, Garrahan, EPL '05].

- Broad waiting time distributions $\to t_1 \gg t_2$.
Dynamic heterogeneity $\to$ large $\ell^\star$.

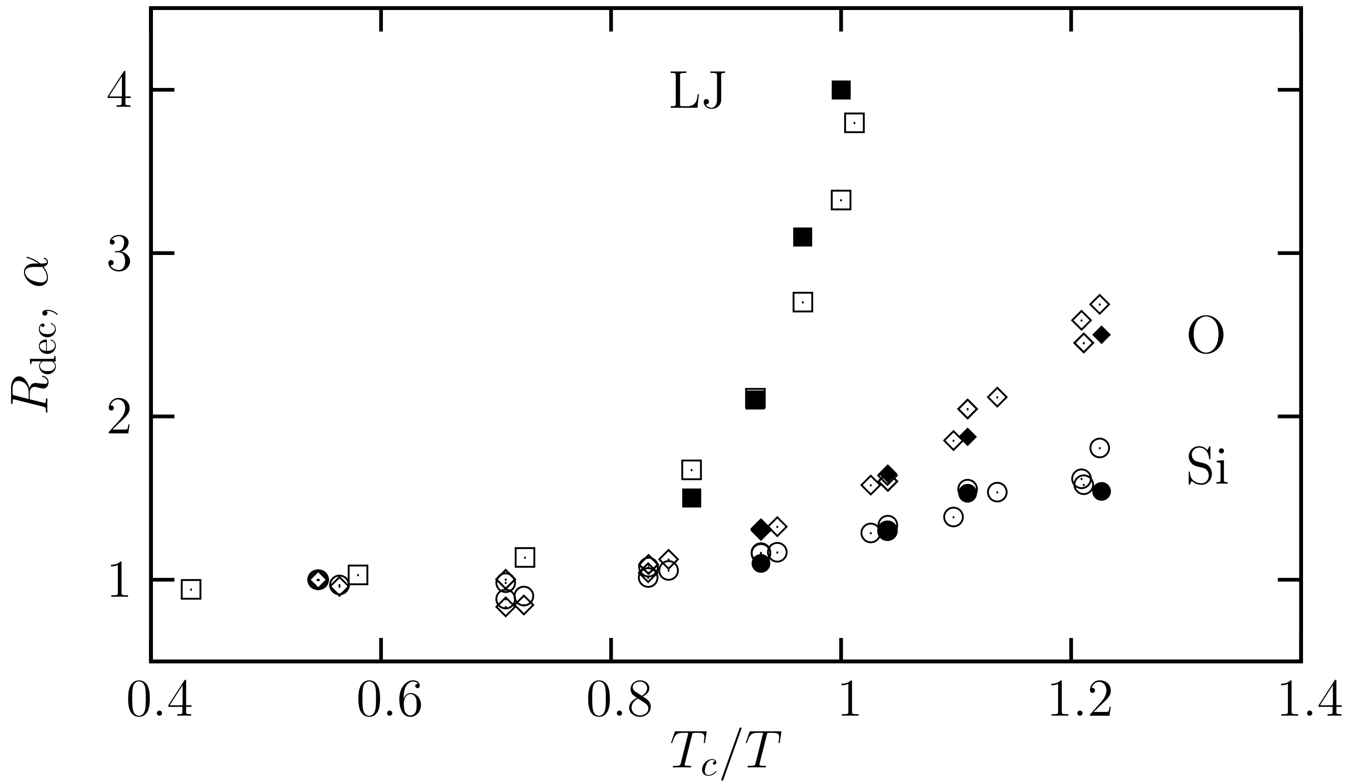
- New length scale $\ell^\star$ is observed in MD simulations [Berthier, PRE '04].

- Experiments are (were?) being performed [Ediger et al.]



Decoupling re-interpreted

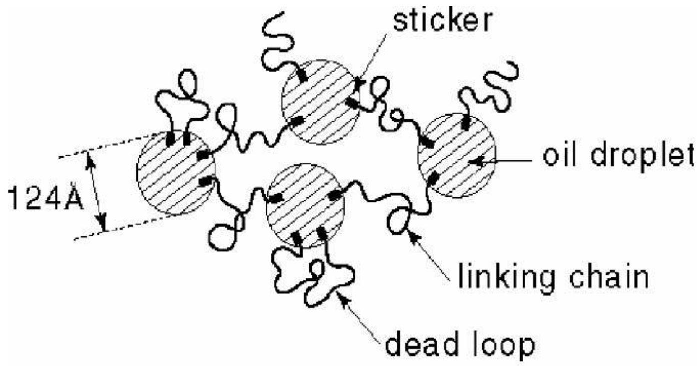
• Compare $\alpha = t_1/t_2$ from fitting van-Hove data, to $R_{\rm dec} = \dfrac{D_s(T)\tau_\alpha(T)}{D_s(T_0)\tau_\alpha(T_0)}$, a measure for translational decoupling.



• Clear link between intermittency, $G_s(x,t)$ tails, broad waiting time distributions, and decoupling.

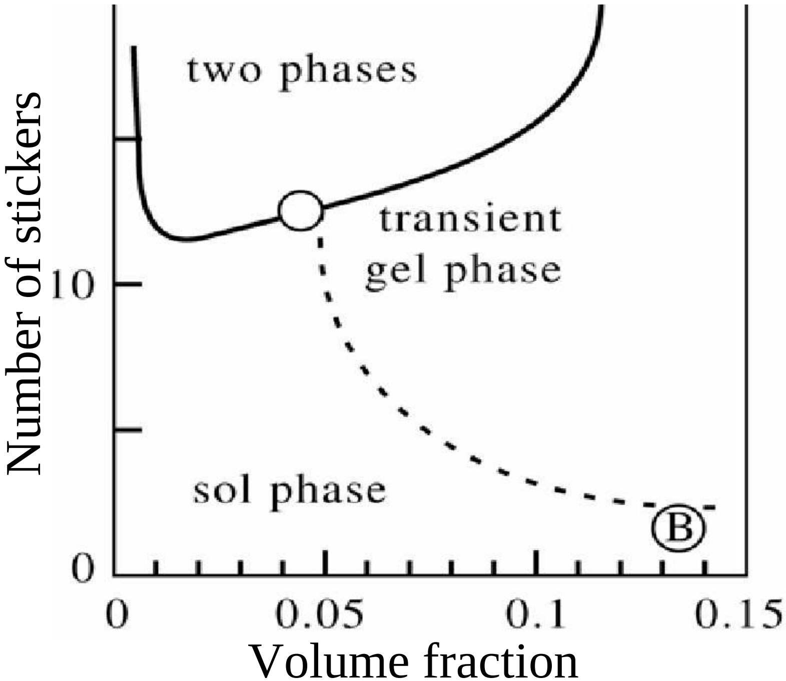
A simple application:
Dynamic heterogeneity in gels

Dynamic heterogeneity in gels

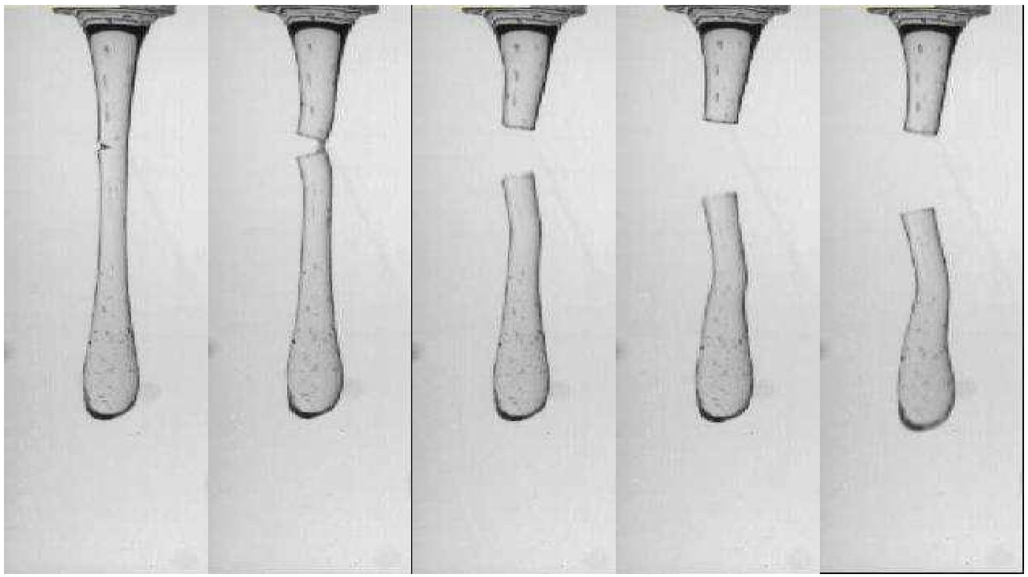


- Model system for complex transient network fluid. A soft solid, a gel, with highly non-linear rheology. Sciortino.

- Fractures? Percolation? Gelation? Banding? Gel dynamics? Heterogeneity?



[Porte, Appell *et al.*, several papers]

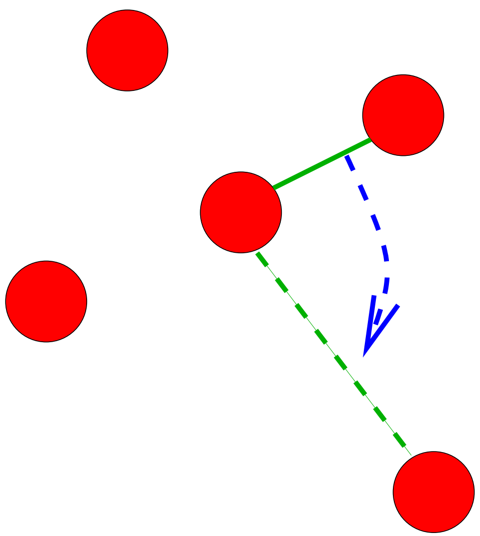


Hybrid MC/MD simulations

- Configuration: $\{\mathbf{r}_i(t), \mathbf{v}_i(t)\}$ for droplets; connectivity matrix $\{C_{ij} = \#\ \text{polymers linking}\ i\ \text{and}\ j\}$ for polymers.

- Solve Newton's equations for droplets with total Hamiltonian:

$$\mathcal{H} = \frac{1}{2} m \sum_{i=1}^{N} \mathbf{v}_i^2 + \sum_{i=1}^{N} \left(C_{ii}\epsilon_{\text{loop}} + \sum_{j>i} \left[V_{\text{soft sphere}}(r_{ij}) + C_{ij} V_{\text{fene}}(r_{ij}) \right] \right)$$



- Evolve the connectivity matrix $\{C_{ij}\}$ with Monte Carlo dynamics. Acceptance rate: $\tau_{\text{link}}^{-1} \min(1, \exp[-\Delta V_{\text{fene}}/k_B T])$.

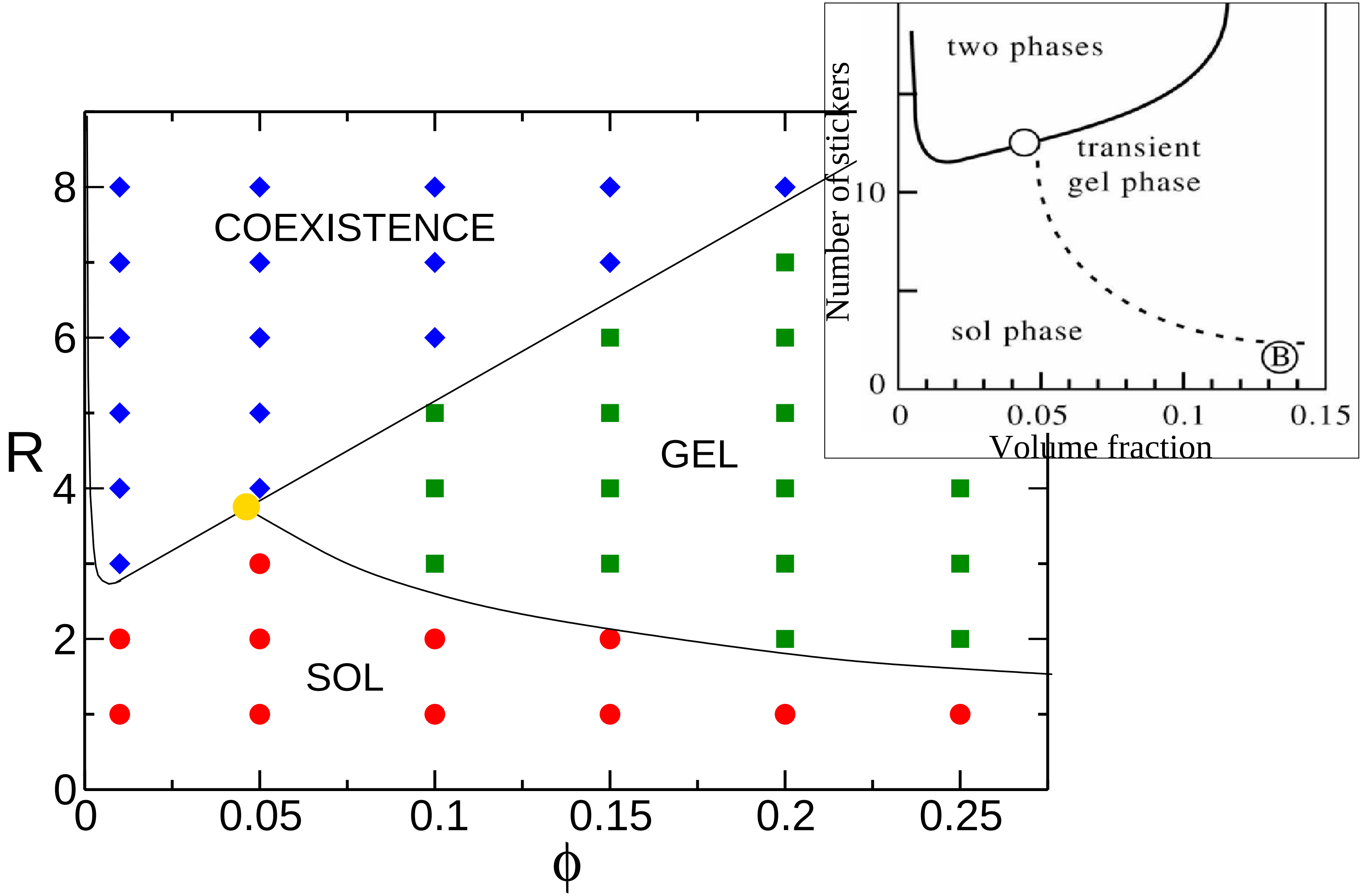
- Control parameters

  ϕ: droplet volume fraction;

  $R = 2N_{\text{p}}/N$: number of stickers per droplet;

  τ_{link}: attempt timescale for sticker escape.

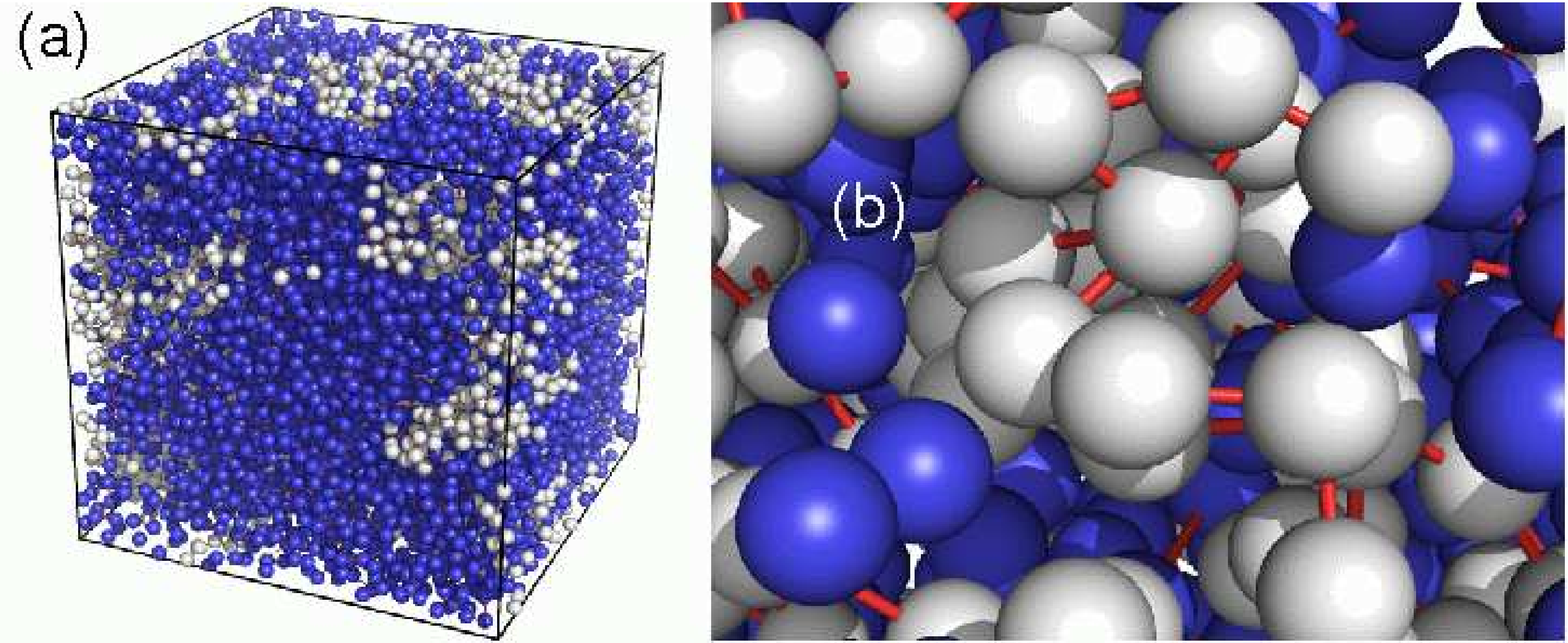
Equilibrium phase diagram



- Equilibrium results in agreement with experiments.

[Hurtado, Berthier, Kob, PRL ’07]

Gelation = geometric percolation



$\phi = 0.2,\ R = 2$

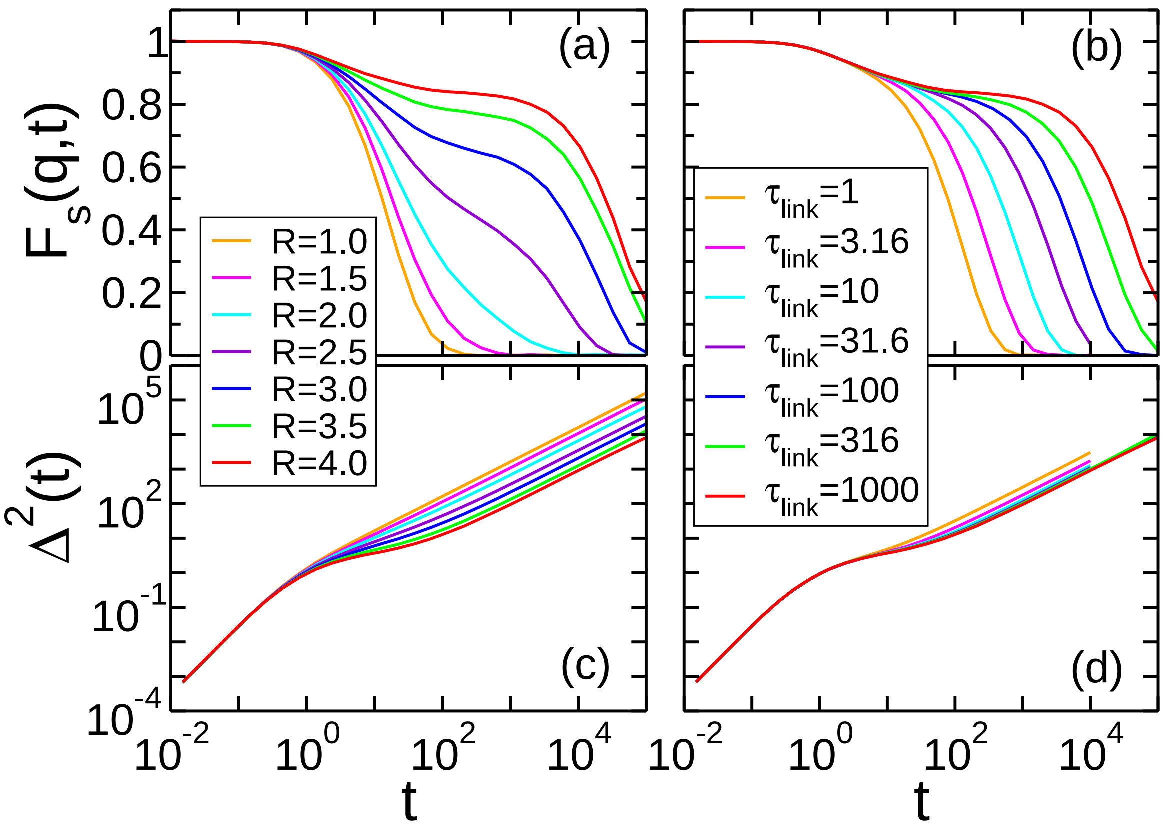
- Homogeneous overall structure, but fractal stress-sustaining network at thermal equilibrium.

‘Slow’ dynamics in gels

• Self intermediate scattering function, $F_s(q,t) = \langle e^{i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))}\rangle$, mean squared displacement, $\Delta^2(t) = \langle |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2 \rangle$.

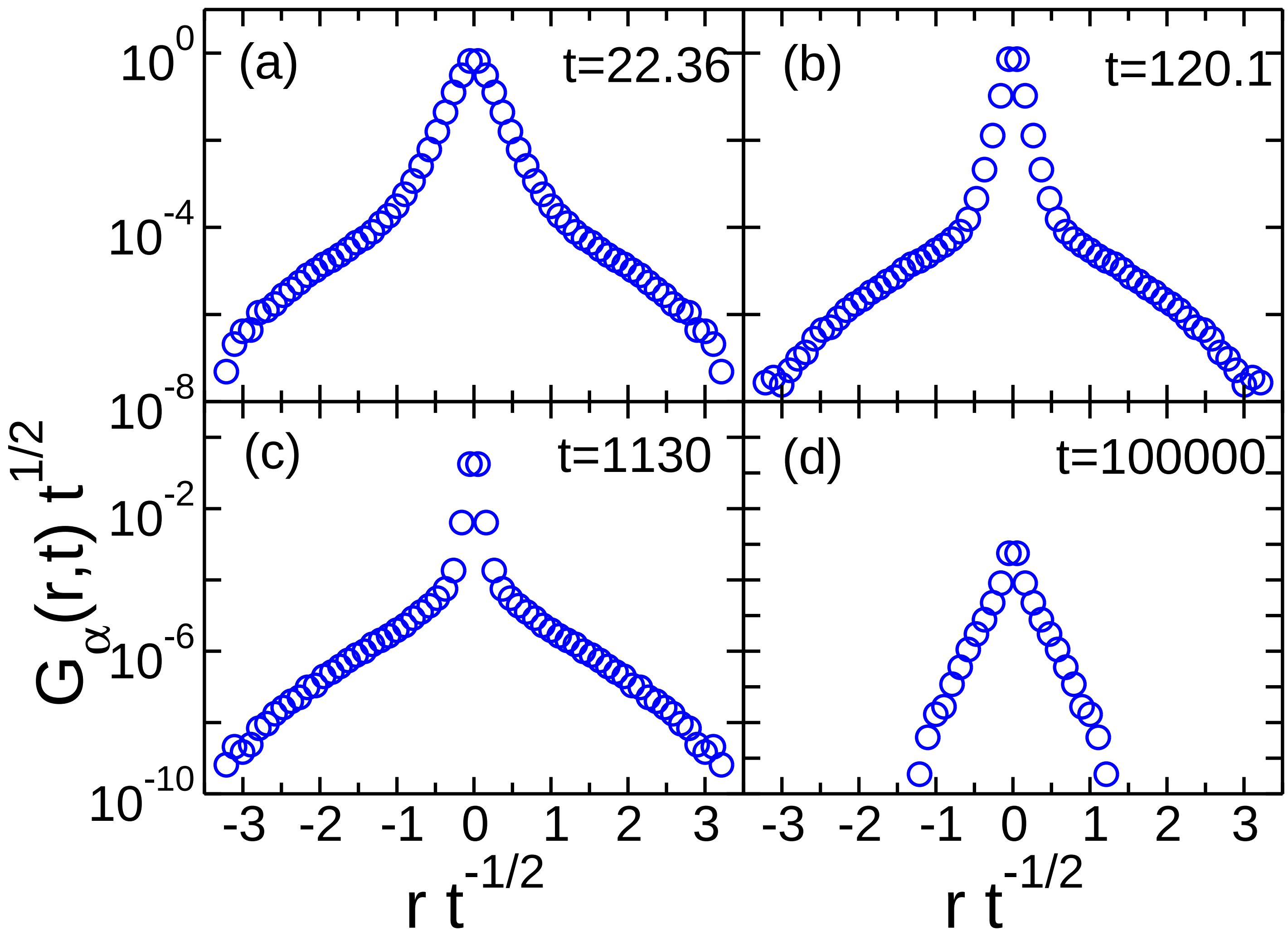
• Structure → Dynamics percolation = plateau = viscoelasticity $\neq$ glass transition.

• $\tau_{\rm link}$ controls the long-time dynamics in the gel.



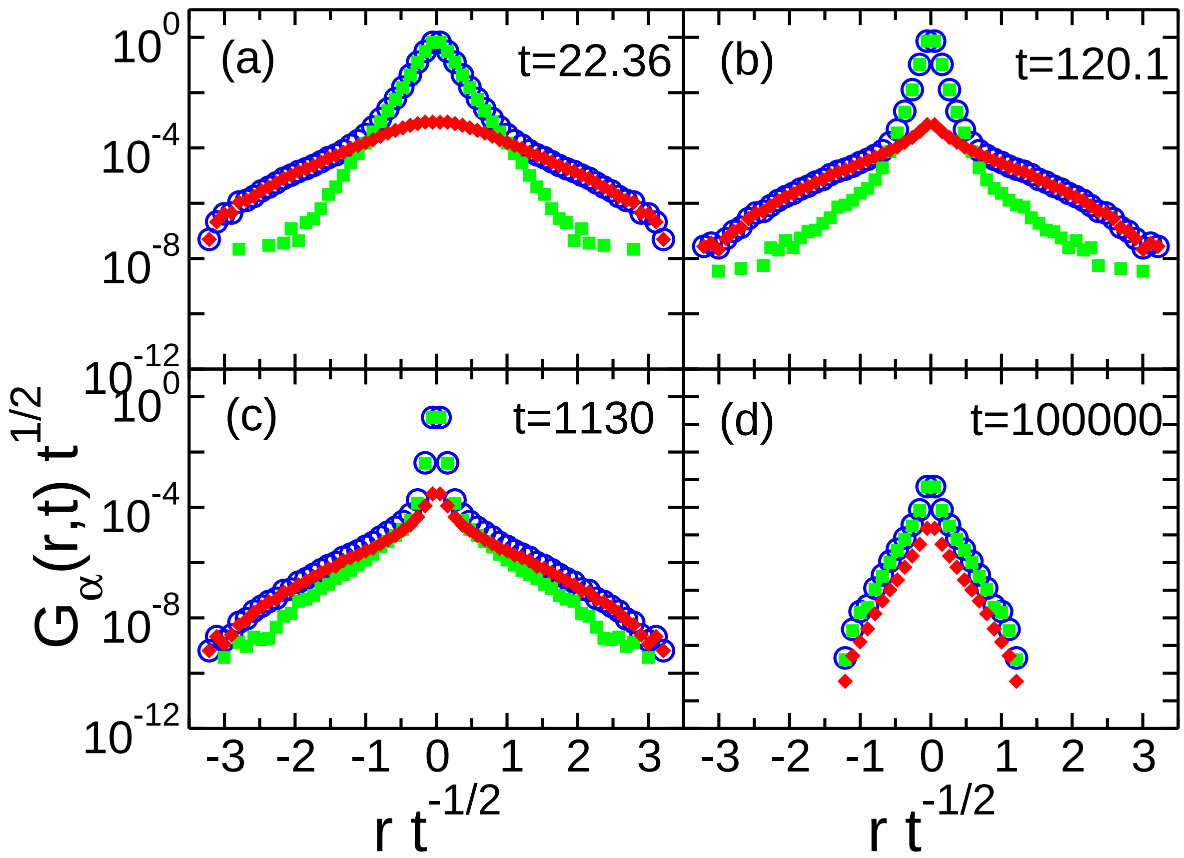
• But: $F_s(q,t) \neq \exp(-q^2\Delta(t)^2/6)$. Non Gaussian effects, ‘decoupling’.

Dynamic heterogeneity in gels



- Non-Gaussian, ‘bimodal’ distributions of particle displacements.

Heterogeneity is structural



● Coexistence of an "arrested" gel and “freely” diffusing droplets, with dynamic exchange between the 2 populations → Simple modelling.

● Fundamentally different from supercooled liquids.

Conclusion Lecture 1

- Understanding the microscopic aspects of the glass formation through atomic motions.
- Viscous liquids are different.
- Single particle diffusion strongly non-Fickian.
- Intermittent jumps and broad distributions: stretched exponential decays (time) and exponential tails (space).
- Anomalous dispersion relation and Fickian lengthscale.
- Decoupling phenomena.
- A (simpler) application of these tools to a gel system.

- I did not address the microscopic origin of these behaviours.

Acknowledgments

- Generic ideas, illustrated by results obtained with:

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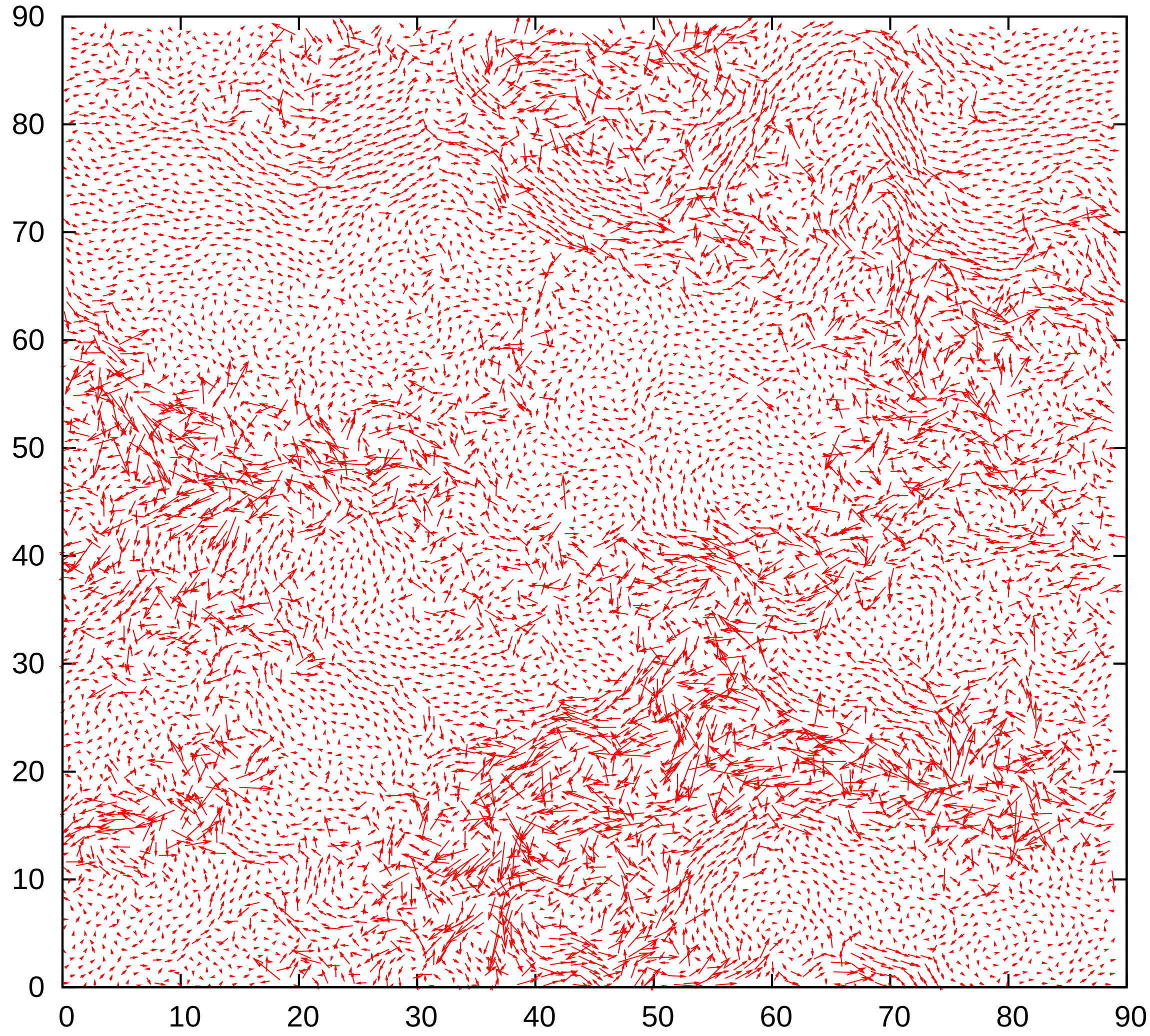

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- Four-point correlation functions
- More dynamic susceptibilities
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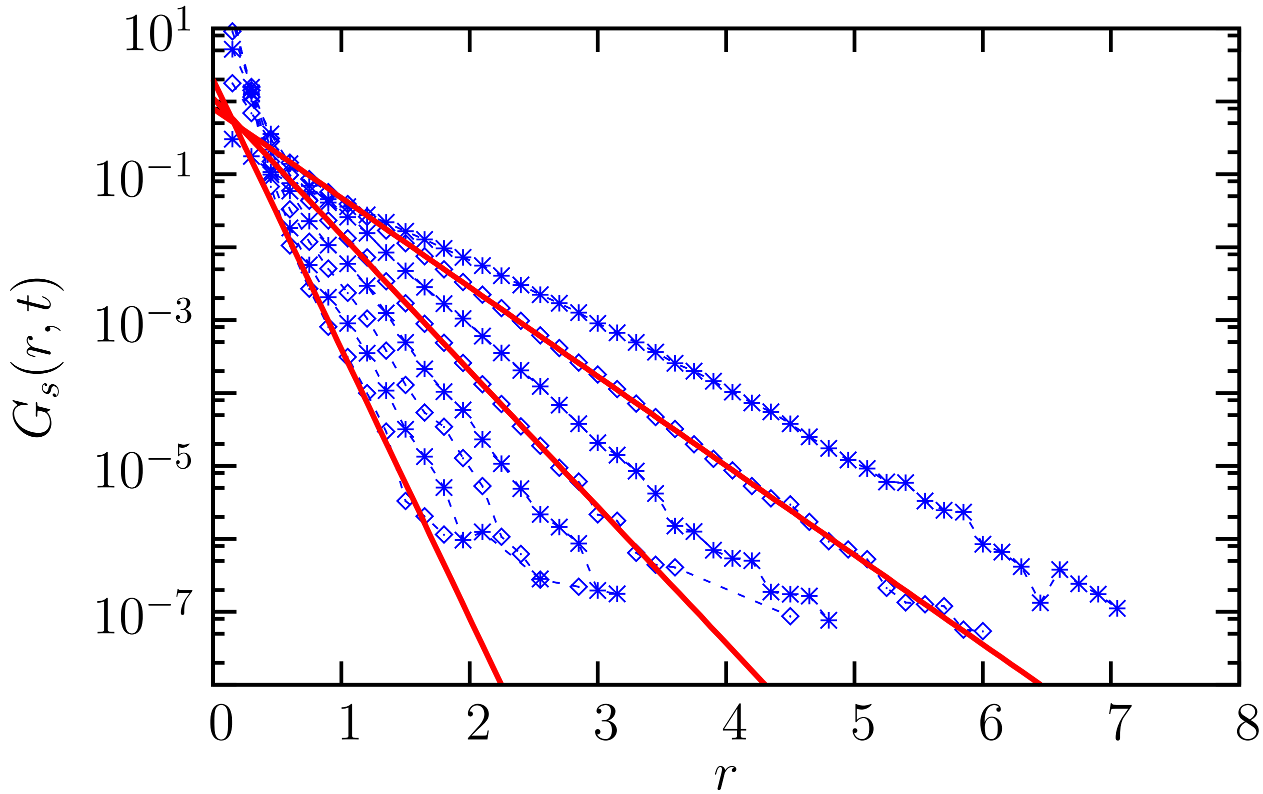
Spatial aspect of dynamic heterogeneity: Clusters

Dynamic 'populations'

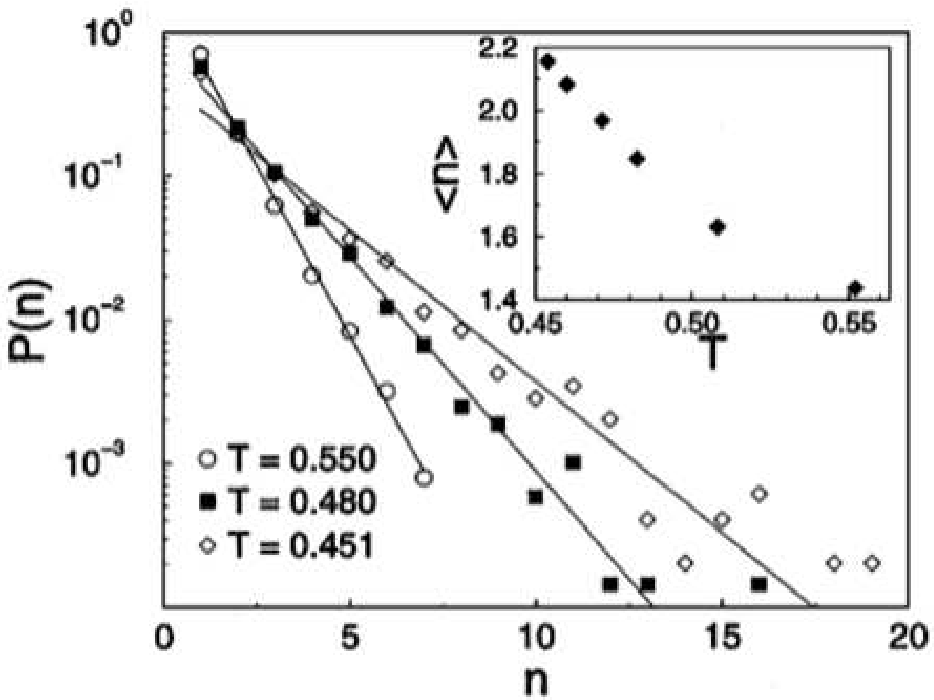
- Non-Gaussian distribution of particle displacements in a supercooled liquid. Where are the particles in the tail?



- Coexistence of fast/slow populations of particles.
- Thresholding, e.g. $\mu_i(t = t^\star) = |r_i(t^\star) - r_i(0)| > \epsilon$, to identify populations.

Clustering

• Use cluster analysis to study sub-populations.



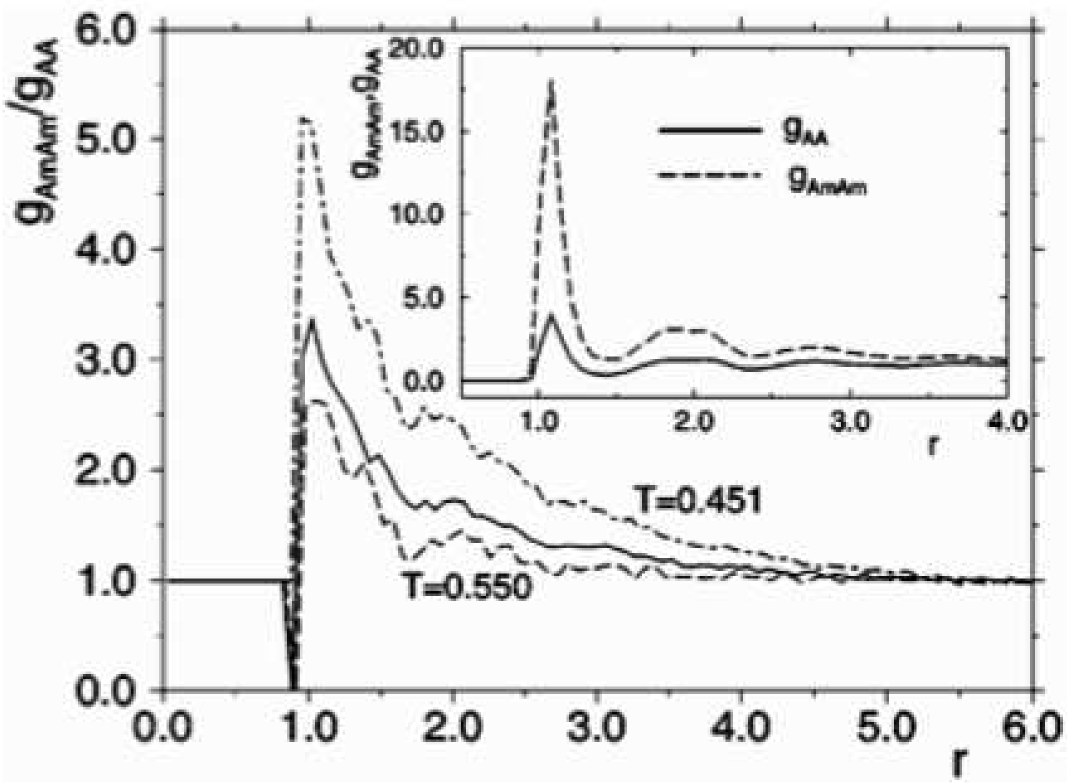
[Donati *et al.*, PRL '98].

• Identify 'strings', 'cooperatively rearranging regions', 'democratic clusters', etc. Very many contributions but no consensus?

• Problems: Clusters are reconstructed a posteriori; thresholding not easily treated theoretically; comparisons between systems hard.

Structure of mobile regions

• What is the structure of regions with distinct mobilities? Partial structure factors of dynamic mixtures ('four-point' functions).



[Donati *et al.*, PRE '99].

• Clear indications that particles with similar mobilities increasingly cluster in space as T decreases.

Four-point functions:
Defi nitions and results

Mobility field and its fluctuations

- Define mobility field: $f(\mathbf{r},t) = \sum_i f_i(t)\delta(\mathbf{r}-\mathbf{r}_i)$, and its fluctuating part: $\delta f(\mathbf{r},t) = f(\mathbf{r},t) - \langle f(\mathbf{r},t)\rangle$.

- E.g. $f_i(t) = \exp[i\mathbf{k}\cdot(\mathbf{r}_i(t)-\mathbf{r}_i(0))]$, or $f_i(t) = \exp[-(\mathbf{r}_i(t)-\mathbf{r}_i(0))^2/a^2]$, etc.

- No thresholding; comparisons between different systems become easy; theory can handle the following four-point correlations.

- Four-point structure factor: $g_4(\mathbf{r},t) = \langle \delta f(\mathbf{0},t)\delta f(\mathbf{r},t)\rangle$.

- In Fourier space: $S_4(\mathbf{q},t) = \langle f(\mathbf{q},t) f(-\mathbf{q},t)\rangle$.

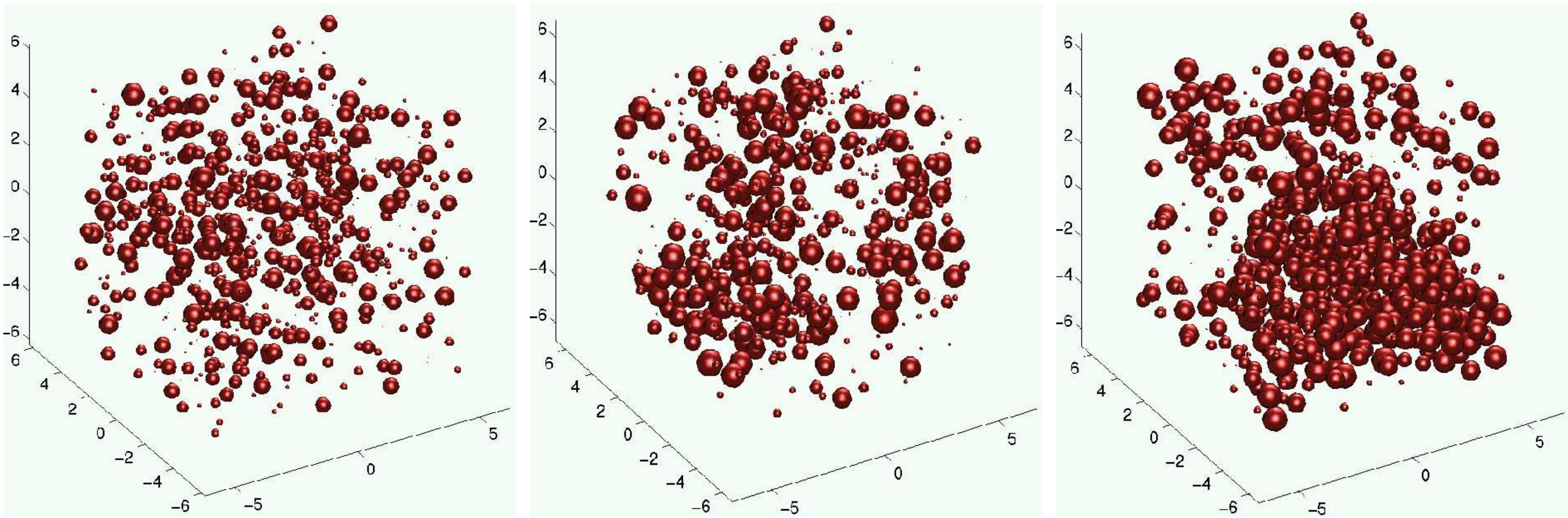
- Susceptibility:

$$\chi_4(t) = \int g_4(\mathbf{r},t)d\mathbf{r} = N\left[\left\langle \left(\frac{1}{N}\sum f_i(t)\right)^2\right\rangle - \left\langle \frac{1}{N}\sum f_i(t)\right\rangle^2\right].$$

- These functions are the analog for $f(\mathbf{r},t)$ of $g(r)$, $S(q)$, and κ_T from density fluctuations $\rho(\mathbf{r},t) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i)$ of a liquid. Kob.

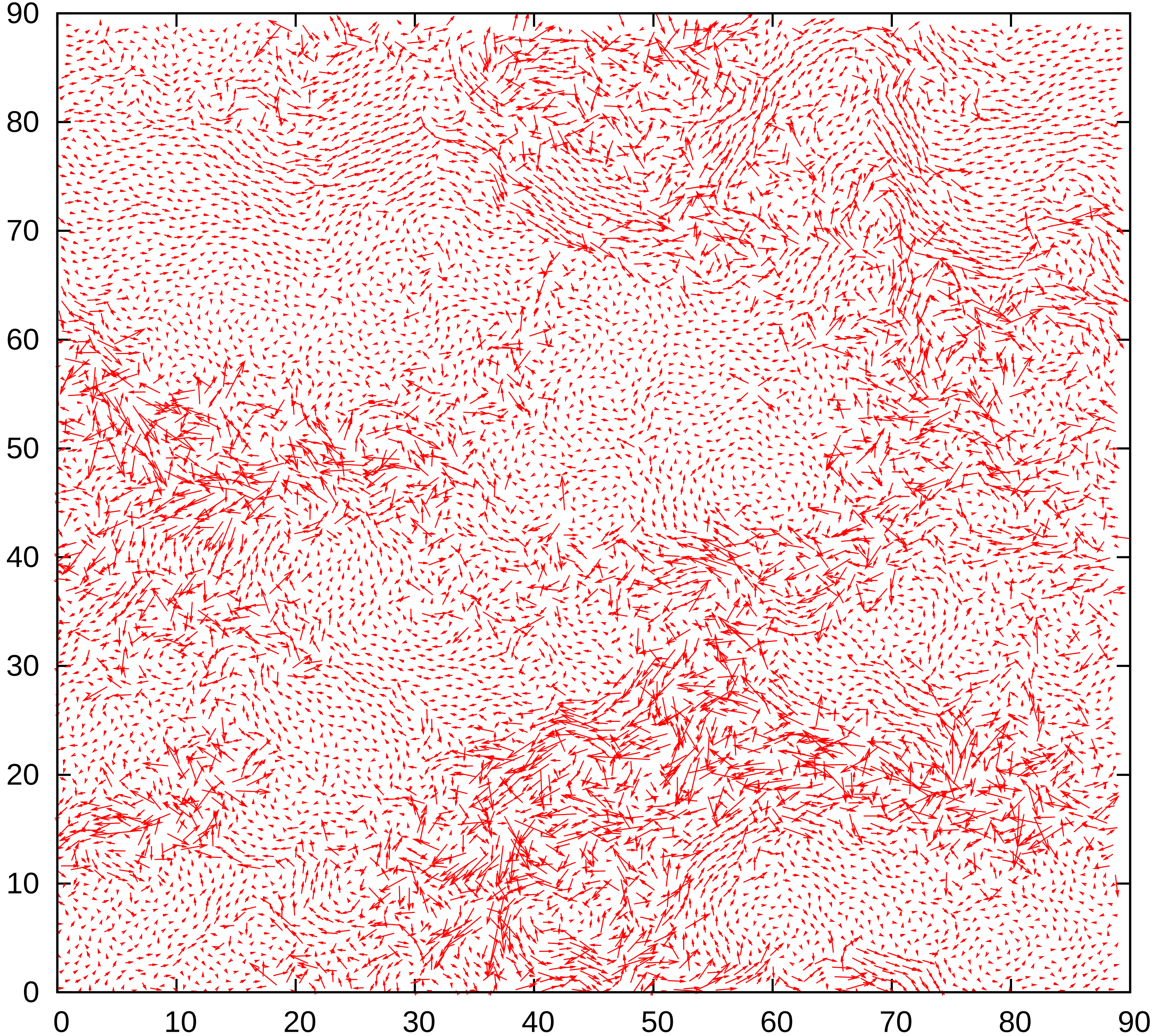
Spatially heterogeneous dynamics

• Snapshots of $\delta F_j(\mathbf{k},t) = e^{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]} - F_s(\mathbf{k},t)$, for $t \approx \tau_\alpha$.
[Berthier, PRE'04].



• Local dynamics becomes spatially correlated as T decreases.

• Similar snapshots of mobility fields have been published for liquids, colloids, granular materials, etc.



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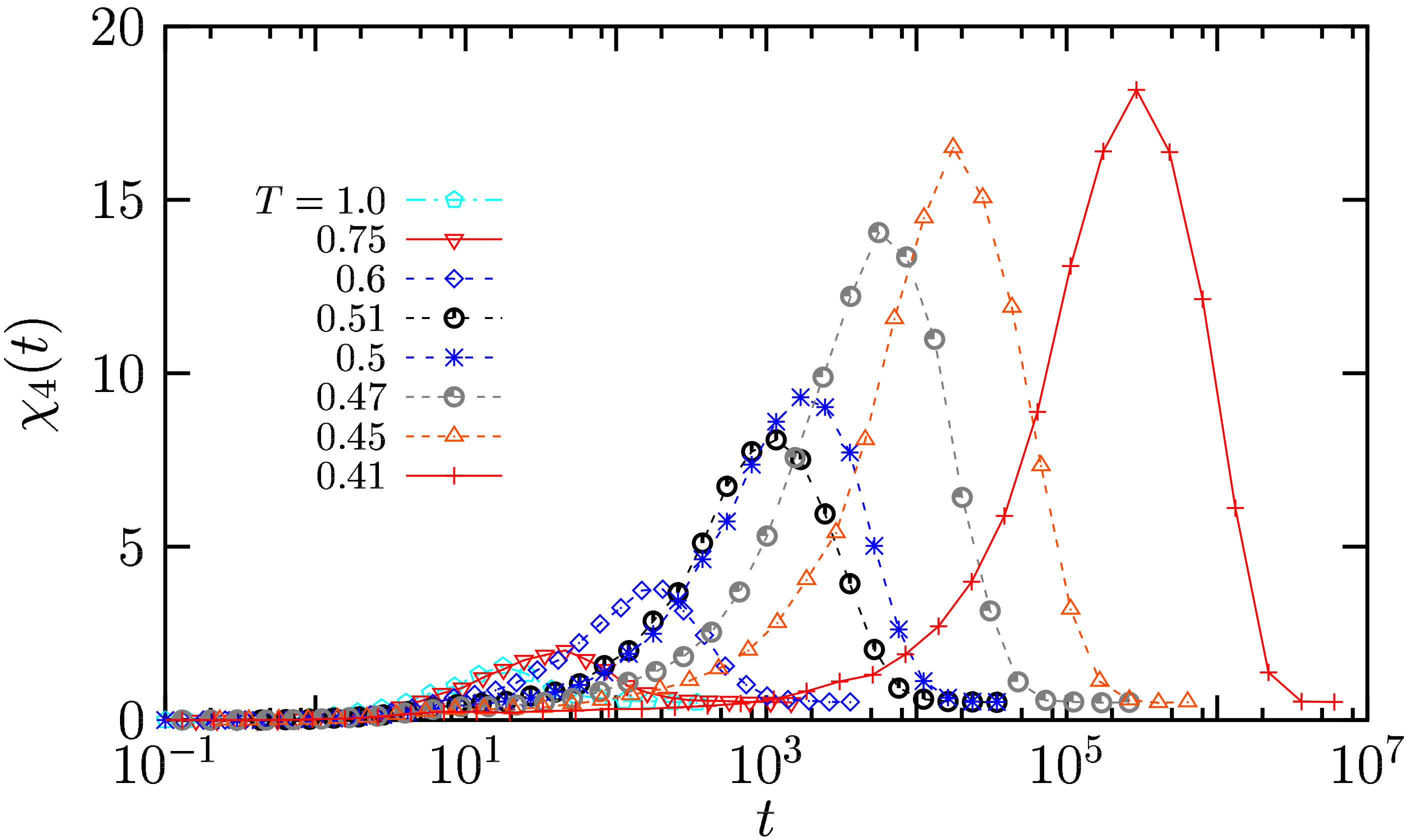
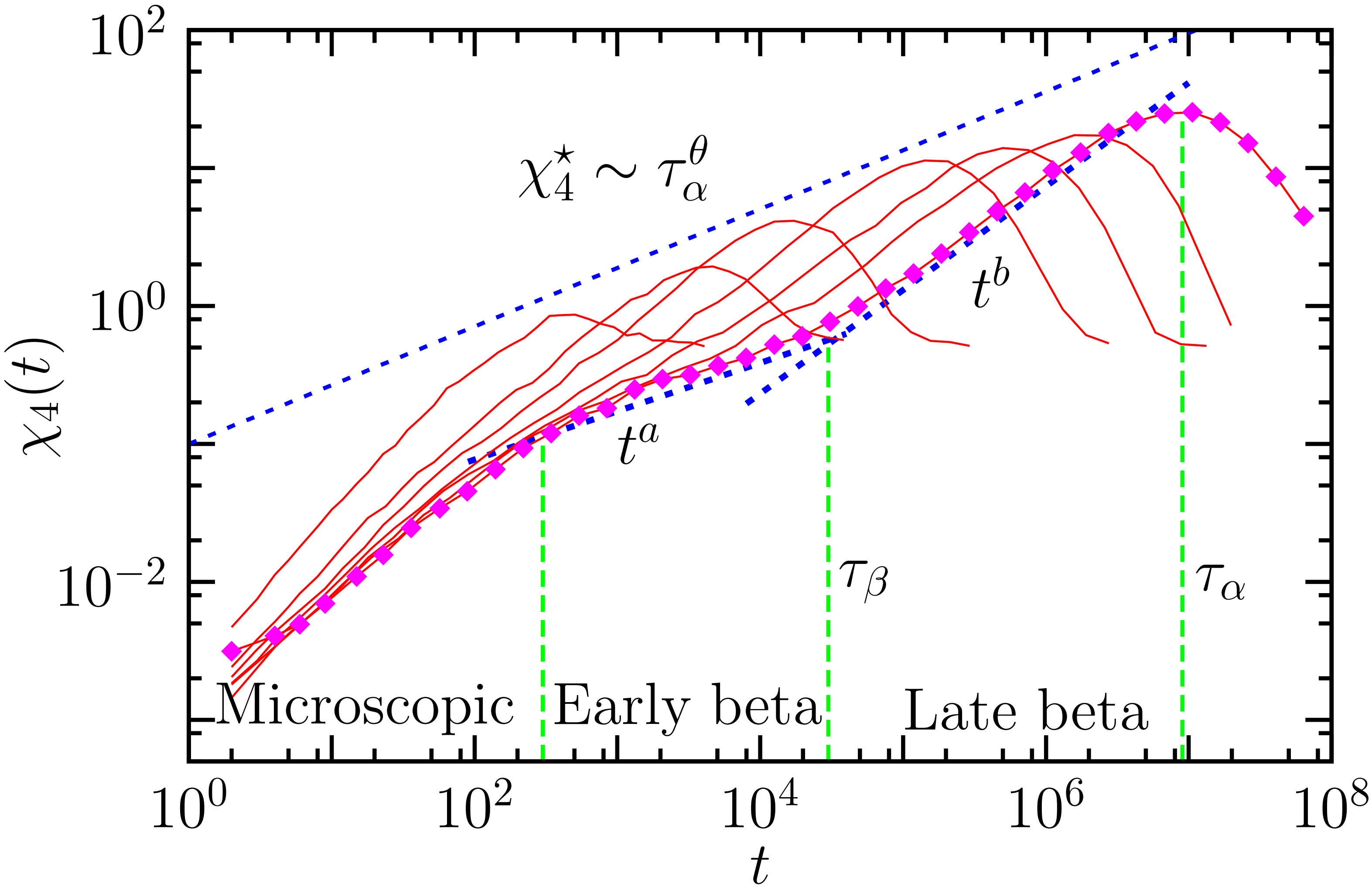
Growing χ_4 in simulations

$\chi_4 = N\langle \delta F(k, t \approx \tau_\alpha)^2 \rangle$ is a ‘correlation volume’.



• Growing χ_4 reveals that dynamics is increasingly spatially heterogeneous at low temperature. Viscous liquids are ‘different’.

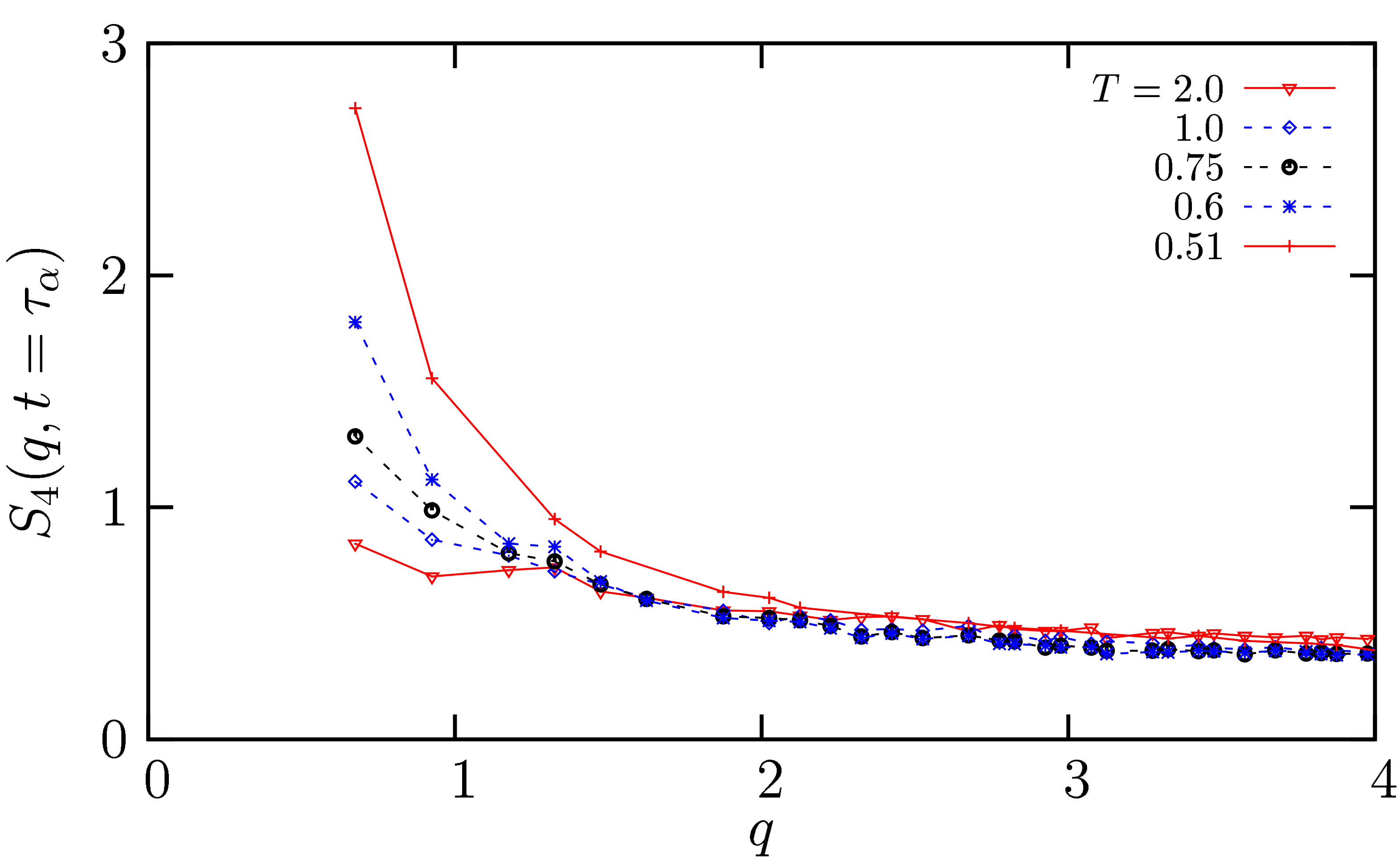
Behaviour of $\chi_4(t)$



- Comparison to theoretical predictions (MCT, KCM, RFOT) is possible

[Toninelli *et al.*, PRE '05]. Miyazaki, Jack, Biroli, Franz.

Growing lengthscale in simulations



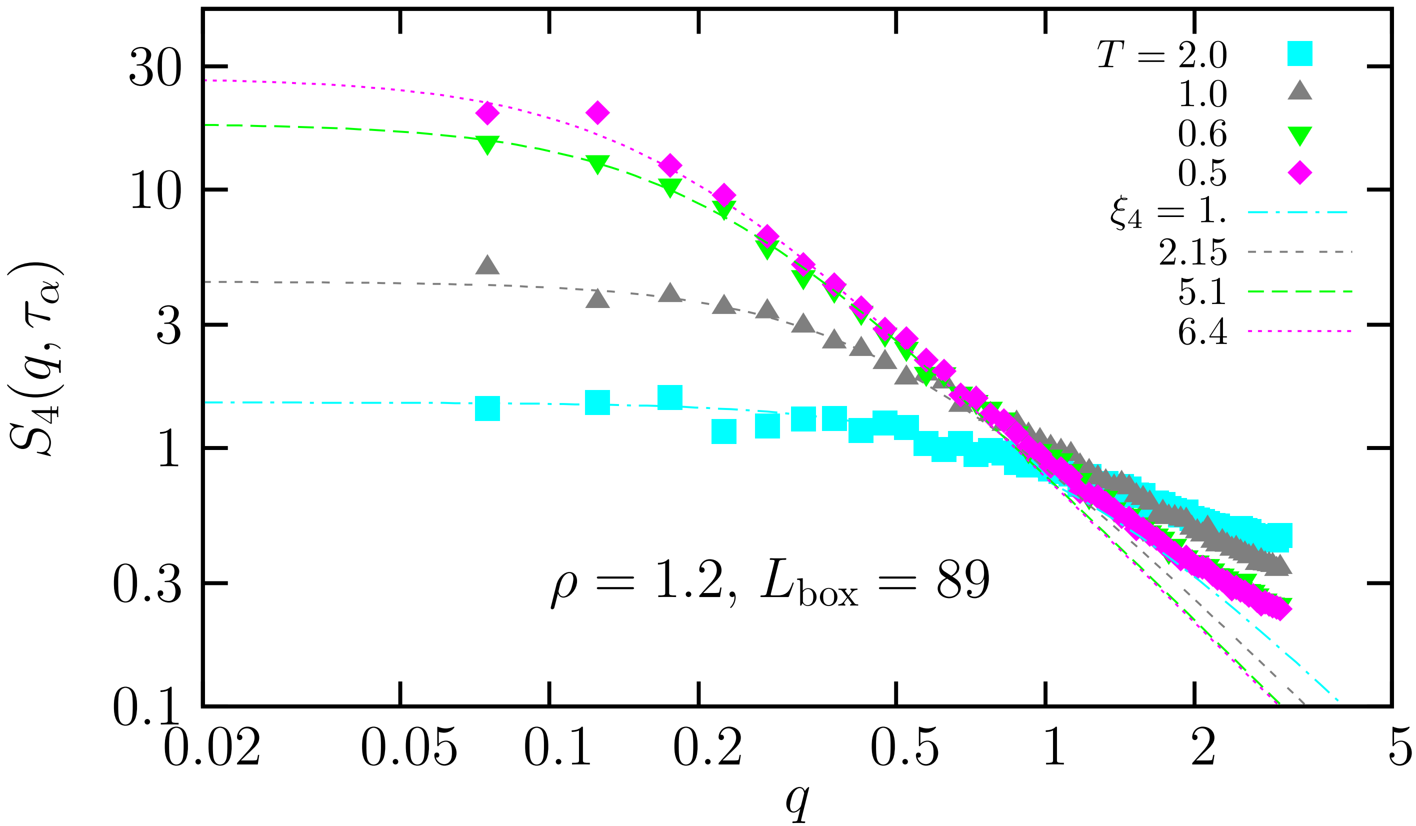
- Simulations with $N = 1000$ particles, $L_{\rm box} = 9.4$, $q_{\rm min} = 2\pi/L_{\rm box} \approx 0.67$.
- Large peak at $q = 0$ indicates growing lengthscale, ξ_4. Measurement?

Growing length in simulations

- If not enough data, use scaling to get ξ_4. E.g. $S_4(q,t) \approx \dfrac{S_0}{1+(q\xi_4)^2}$.

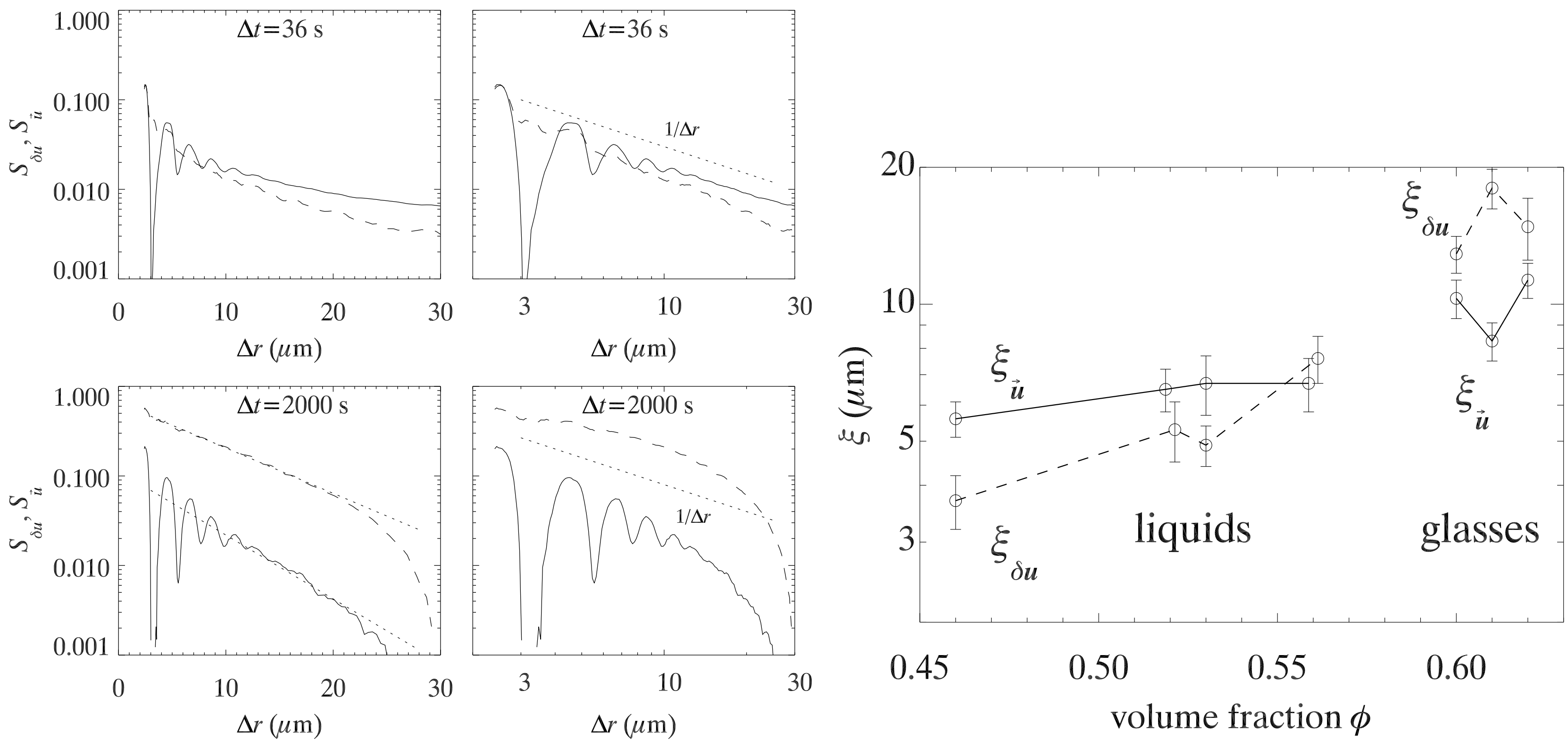
- No consensus on functional form, no agreed measurement of ξ_4.

(Stein/Andersen, $N = 27,000$, Karmakar *et al.*, $N = 300,000$). Hard!



Growing length in experiments

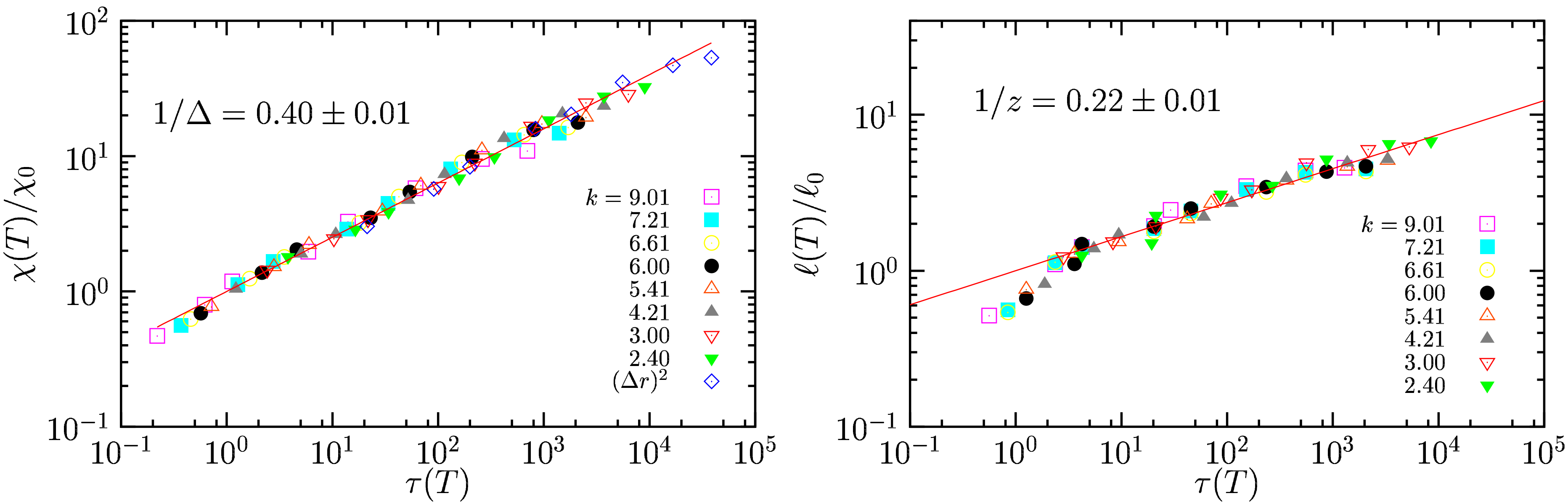
- Eric Weeks has measured $g_4(r,t)$ in colloidal systems using confocal microscopy. [Weeks et al., JPCM '07]



- Simulations and experiments indicate $\xi_4 \approx 5$ particle diameters after 5 decades of slowing down.

Dynamic scaling

• Dynamic scaling in LJ supercooled liquid [Whitelam, Berthier, Garrahan, PRL '04]. Power laws: $\chi \sim \tau^{1/\Delta}$ and $\ell \sim \tau^{1/z}$.



• Predicted by RG analysis of coarse-grained kinetically constrained spin models [Whitelam *et al.* PRL '04 - PRE '05] and mode-coupling theory [Biroli, Bouchaud, EPL '05]. Coincidence?

• What happens closer to T_g? Hard to measure.

More multi-point dynamic susceptibilities

Multi-point response functions

- Experiments (in liquids) only access averaged correlations: $\langle F(t) \rangle$.
- We define the linear response functions:

$$\chi_T(t) = \frac{\partial}{\partial T} \langle F(t) \rangle$$

$$\chi_\rho(t) = \frac{\partial}{\partial \rho} \langle F(t) \rangle$$

$\Rightarrow \chi_x(t)$ [with $x = T, \rho$] are experimentally accessible multi-point dynamic susceptibilities quantifying dynamic heterogeneity in glass-formers.

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

Spontaneous & induced fluctuations

- χ_T / χ_ρ: part of the dynamic fluctuations induced by energy / density fluctuations:

$$\chi_4(t) = \chi_4^{NVE}(t) + \frac{k_B}{c_V} T^2 \chi_T^2(t) + \rho^3 k_B T \kappa_T \chi_\rho^2$$

- χ_T / χ_ρ provide a rigorous lower bound to χ_4:

$\chi_4(t) \geq \frac{k_B}{c_V} T^2 \chi_T^2(t)$ for molecular liquids.

$\chi_4(t) \geq \rho^3 k_B T \kappa_T \chi_\rho^2$ for colloidal hard spheres.

- Theory and simulations of strong and fragile glasses and hard spheres show that the bounds are good approximations. Experiments become feasible.

[Berthier *et al.*, JCP (I+II) '07]

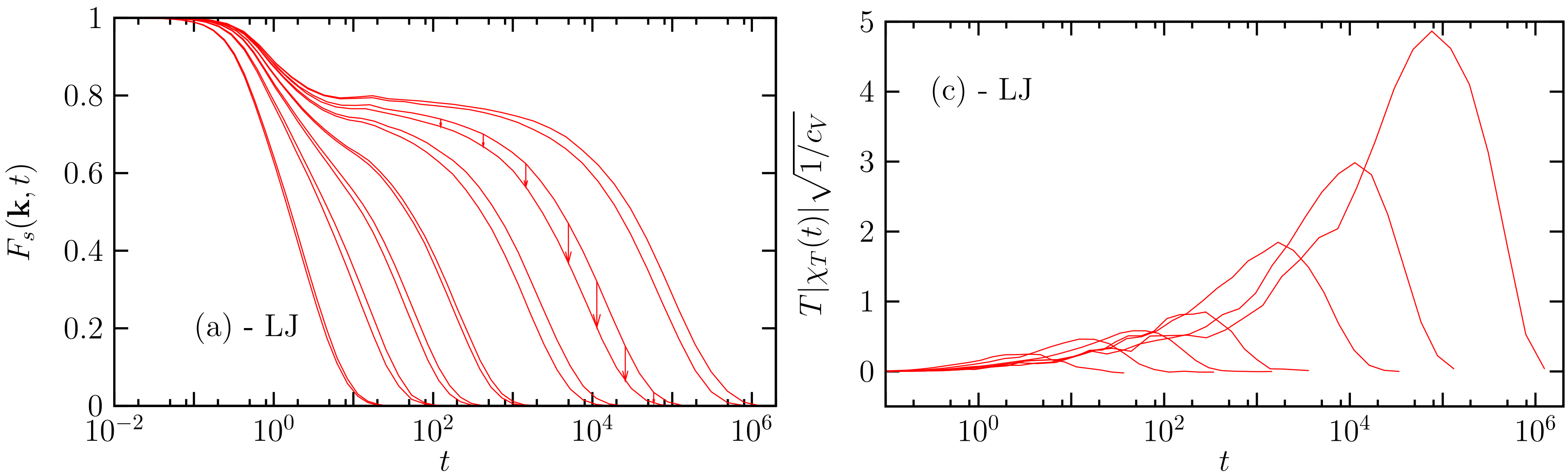
[Dalle-Ferrier *et al.*, PRE'07]

How to measure $\chi_T(t)$?

• $\chi_T(t)$ can be estimated by finite difference (but check linear response):

$$\chi_T(t) = \frac{\partial F_T(t)}{\partial T} \approx \frac{F_{T+\delta T}(t) - F_T(t)}{\delta T}.$$

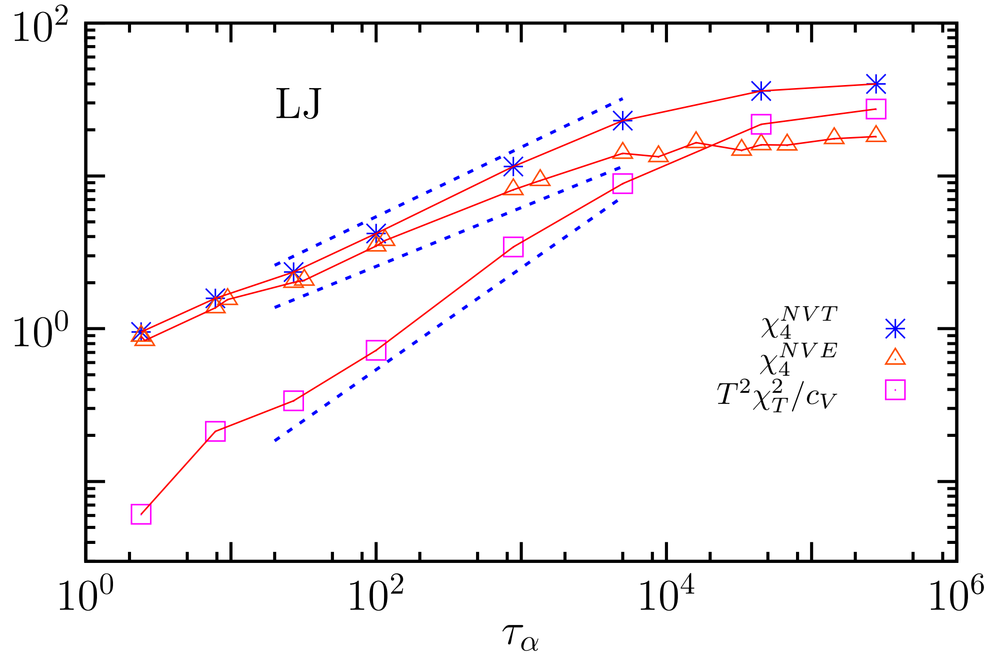
• Works with any two-time dynamical correlator, dielectric susceptibility, mechanical compliance, etc.

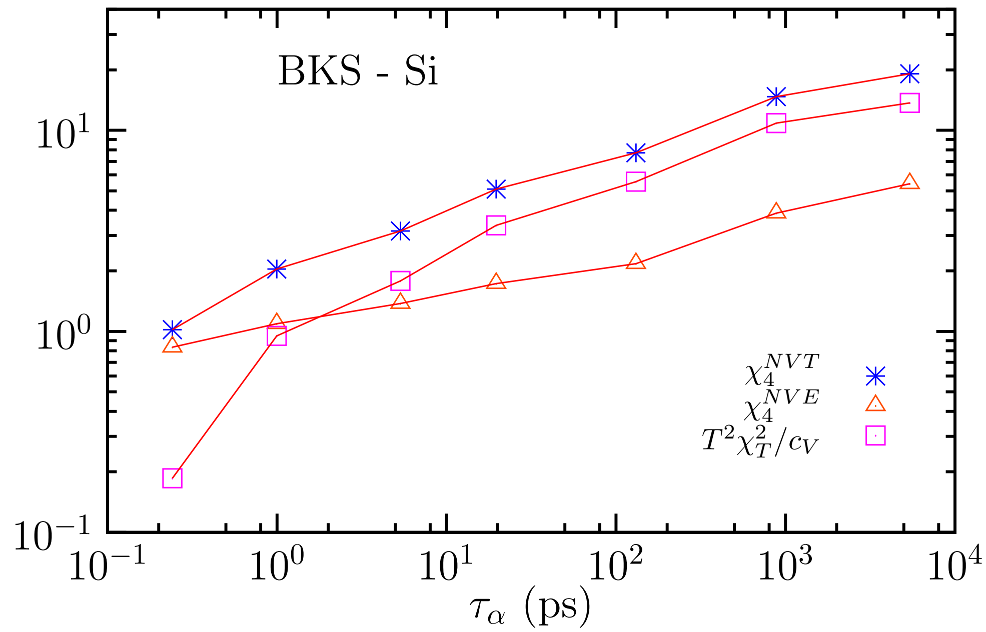


• Simulations of a LJ glass-former: $\chi_T(t)$ has a growing peak when T decreases: Growing dynamic fluctuations and related lengthscales.

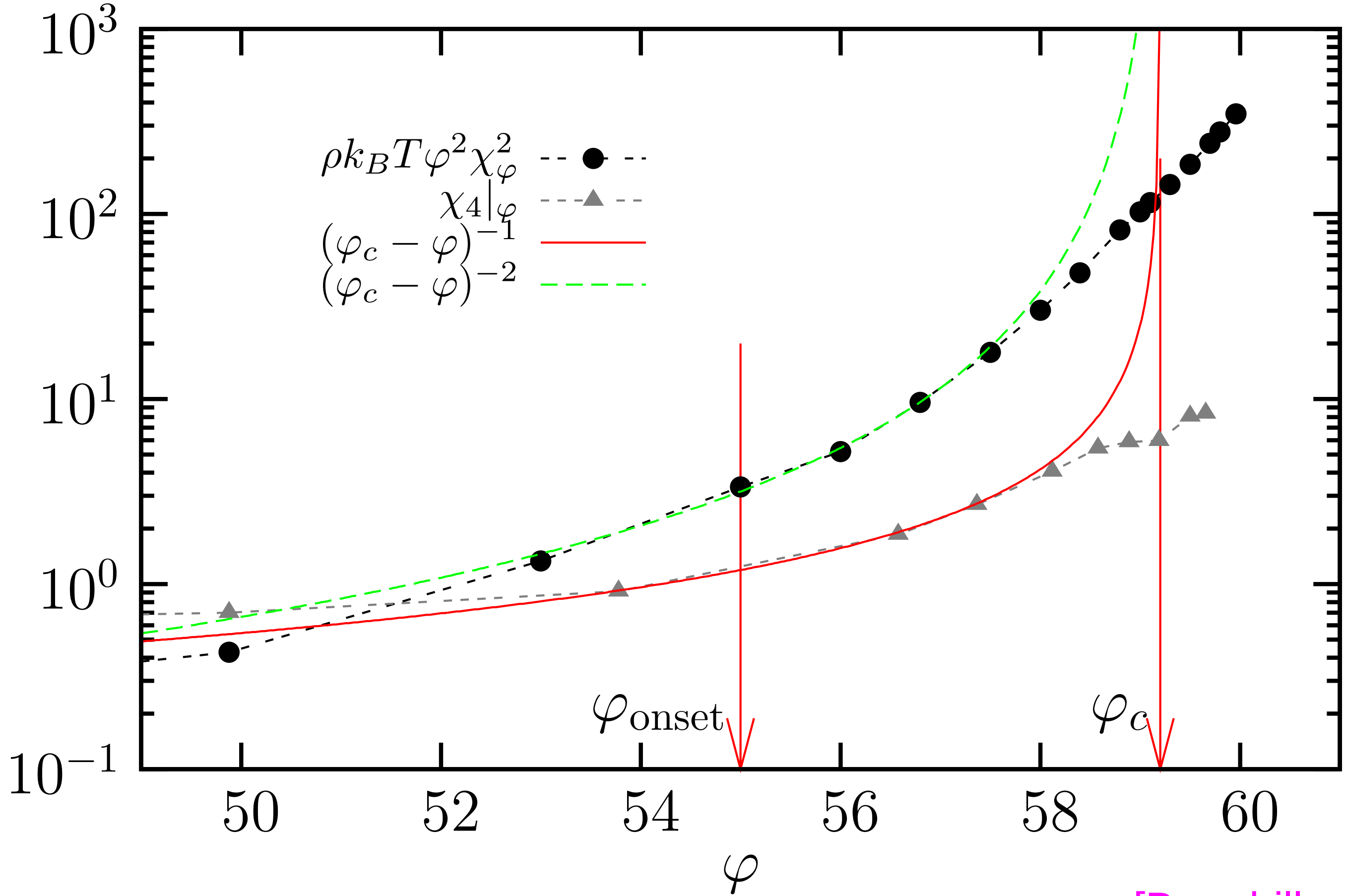
Reliable estimate of χ_4?

- Yes!
- Numerical simulations of fragile Lennard-Jones and strong BKS silica models.
  [Berthier *et al.*, JCP '07]
- Measure independently all contributions to χ_4^{NVT}.
- The term with χ_T^2 dominates at low T. Good news for experiments close to T_g.
- Dynamic heterogeneity mostly triggered by energy fluctuations.





Colloidal hard spheres



[Brambilla *et al.*, PRL '09]

- χ_4 can be safely estimated from response function $\chi_\varphi = \partial F(t)/\partial\varphi$ in colloidal particles.

Physical content of $\chi_T(t)$

- For Newtonian dynamics in the NVT ensemble,

$$k_B T^2 \chi_T(t) = N\langle \delta F(t) \delta E(0) \rangle,$$

where $E(t)$ is the energy (dynamic fluctuation-dissipation relation).

- With $NF(t) = \rho \int d^3\vec{r} f(\vec{r},t)$ and $NE(t) = \rho \sqrt{k_B c_V} T \int d^3\vec{r} \hat{e}(\vec{r},t)$,

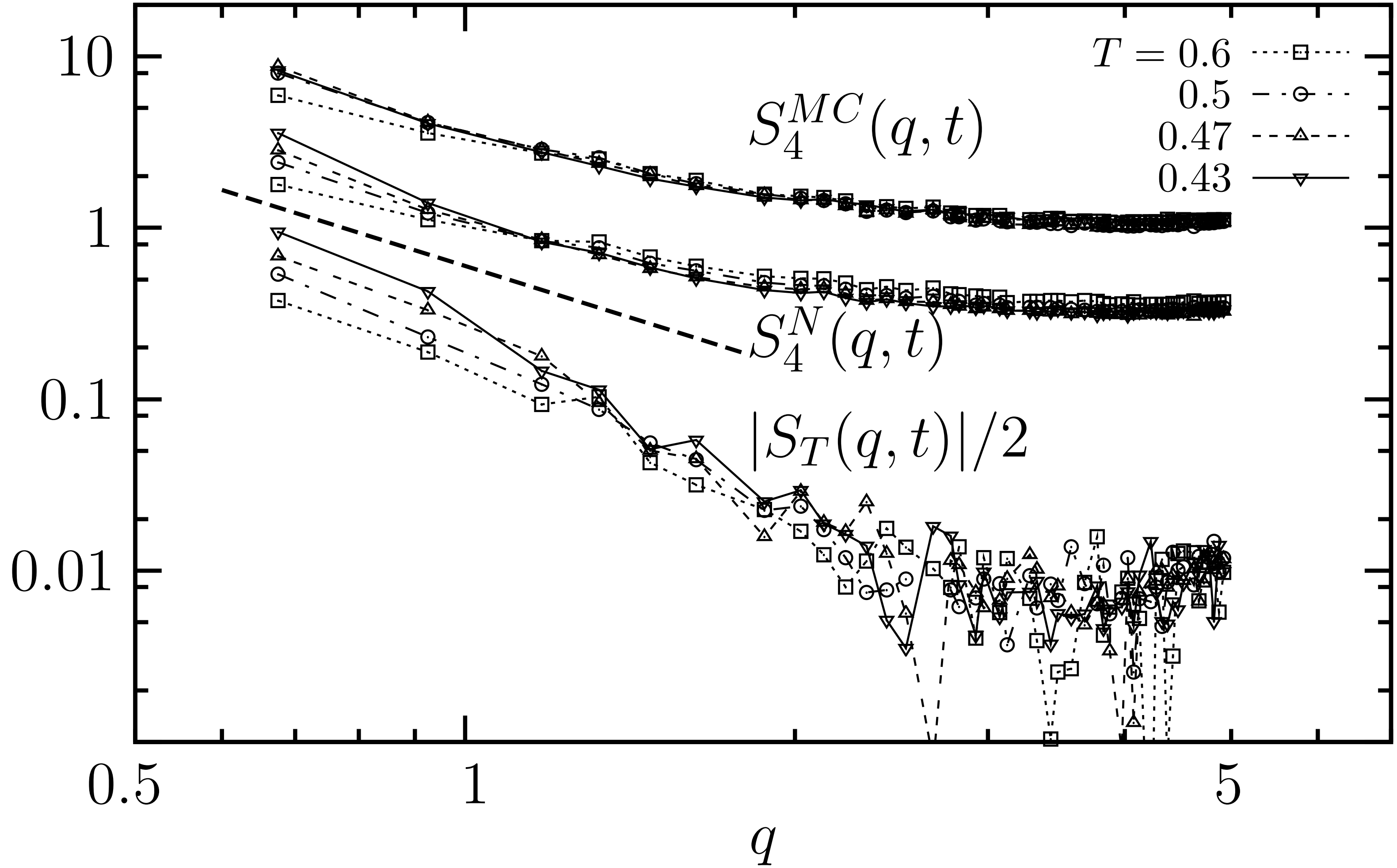
$$\sqrt{\frac{k_B}{c_V}} T \chi_T(t) = \rho \int d^3\vec{r} \left\langle \delta f(\vec{r},t) \delta \hat{e}(\vec{0},0) \right\rangle \approx \left(\frac{\xi_T}{a} \right)^{d_s}.$$

- Similarly for colloidal particles,

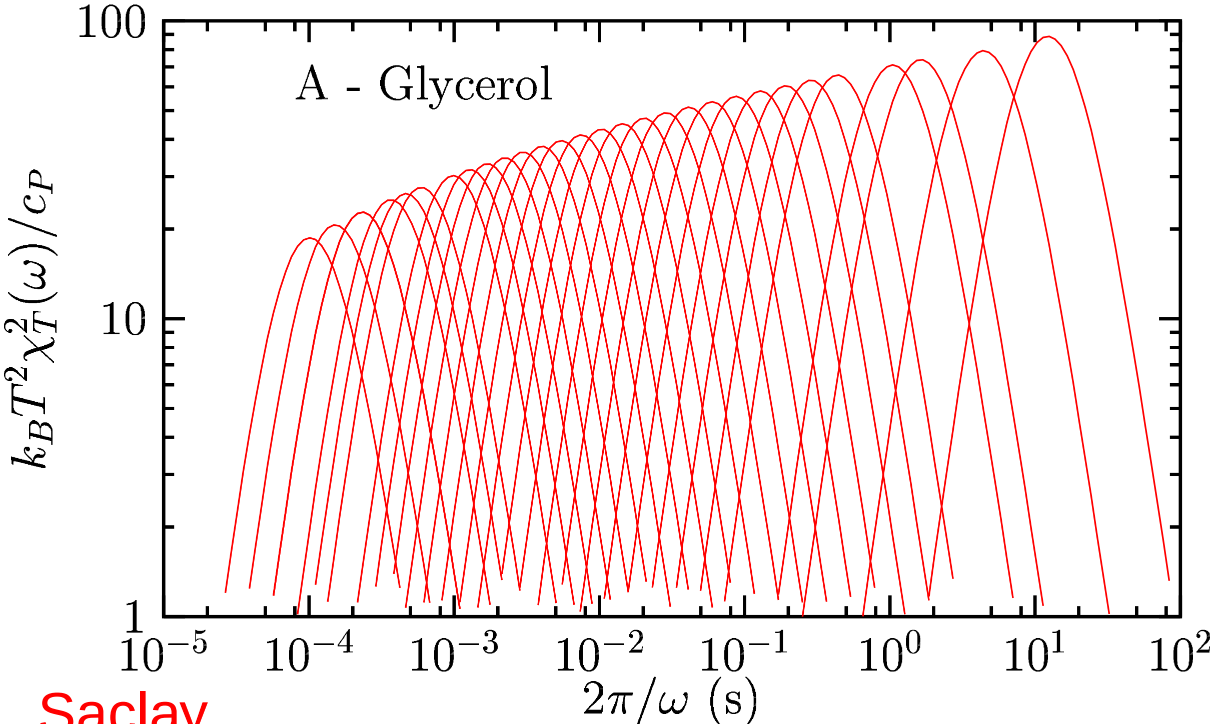
$$\sqrt{\rho k_B T \kappa_T} \varphi \chi_\varphi(t) = \rho \int d^3\vec{r} \left\langle \delta f(\vec{r},t) \delta \hat{\rho}(\vec{0},0) \right\rangle.$$

- Growing $\chi_T(t)$ directly reveals a growing dynamic lengthscale ξ_T: spatial correlations between local dynamic and energy fluctuations.

Another lengthscale?

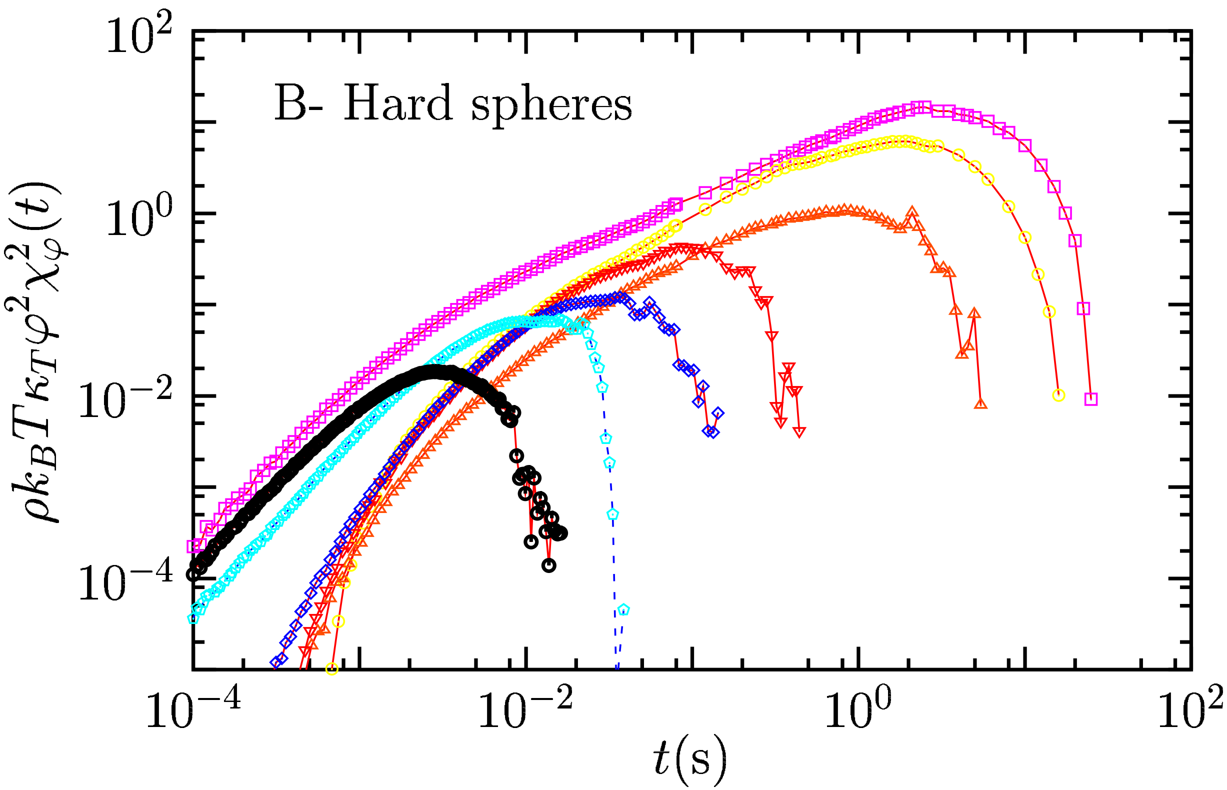


• Theory: No. Data compatible with $\xi_4 \approx \xi_T$, but hard to know for sure. More work needed here.



Saclay

Montpellier



- Dynamic lengthscale grows with viscosity
- Few hundreds of molecules move cooperatively at T_g.

[Berthier *et al.*, Science '05]

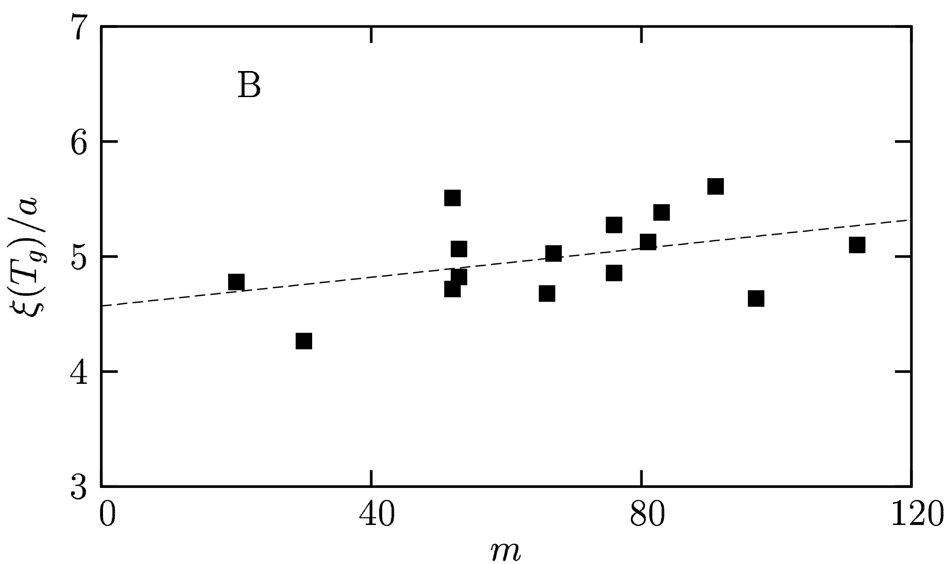
Growing length near T_g

- $\chi_4^*(T) \approx \left(\frac{\xi}{a}\right)^{d_s}$, with $d_s = 2 - 4$, 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

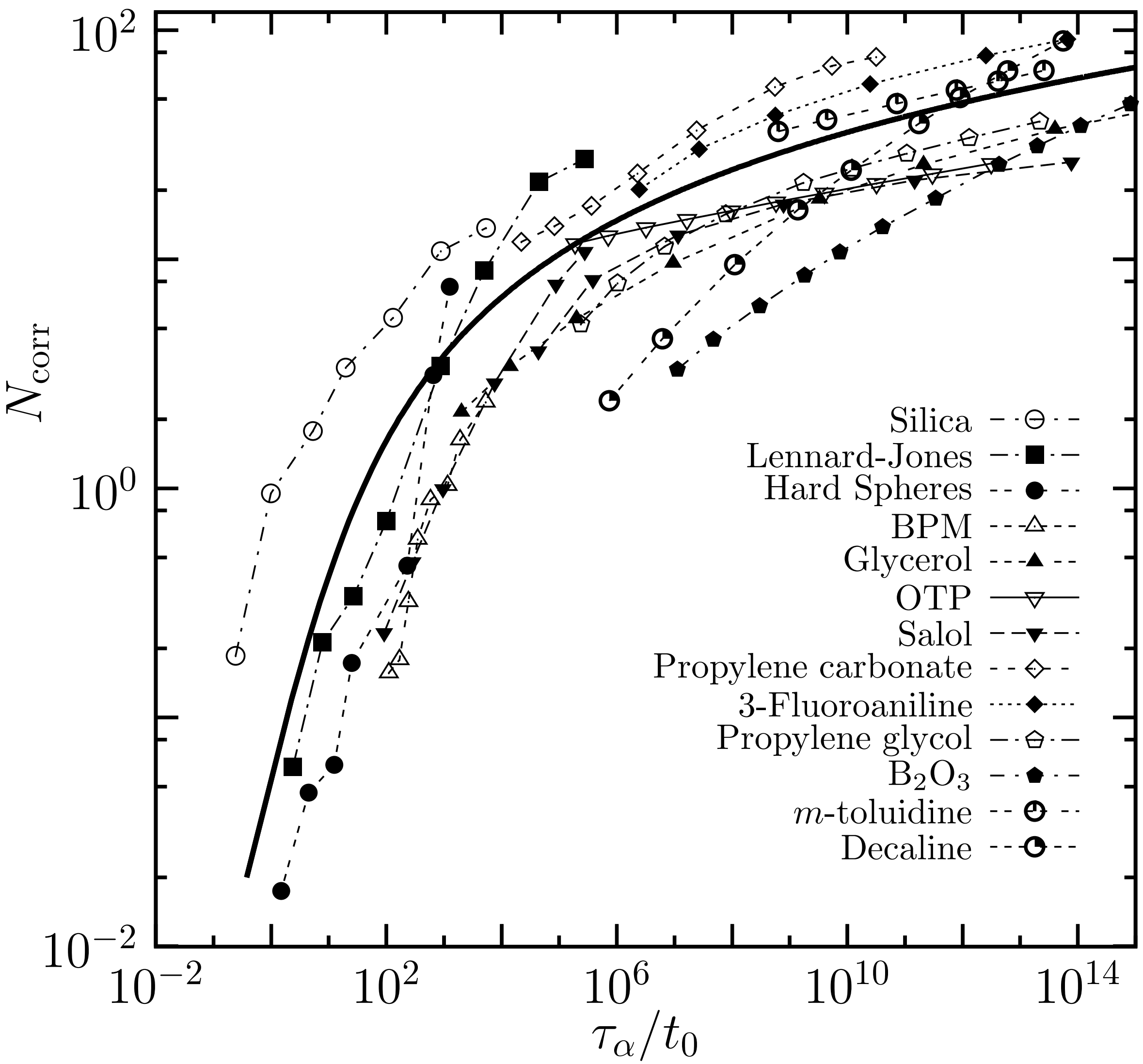
Similar to Ediger's 4D NMR data: $\xi_{\rm het} = 1.3 \pm 0.5$ nm at 199 K.

- If $F(t) = \mathcal{F}(t/\tau_\alpha)$, $\chi_4^*(T_g) \approx [\mathcal{F}'(1)]^2 \frac{k_B}{c_P} \left(\frac{\partial \ln \tau_\alpha}{\partial \ln T}\Big|_{T_g} \right)^2$.



Few hundreds of molecules move cooperatively at T_g.

Evolution of dynamic lengthscale



- $N_{\rm corr} \equiv \chi_4 \propto \chi_T^2$ from temperature derivative for many different liquids. [Dalle-Ferrier *et al.*, PRE '07]

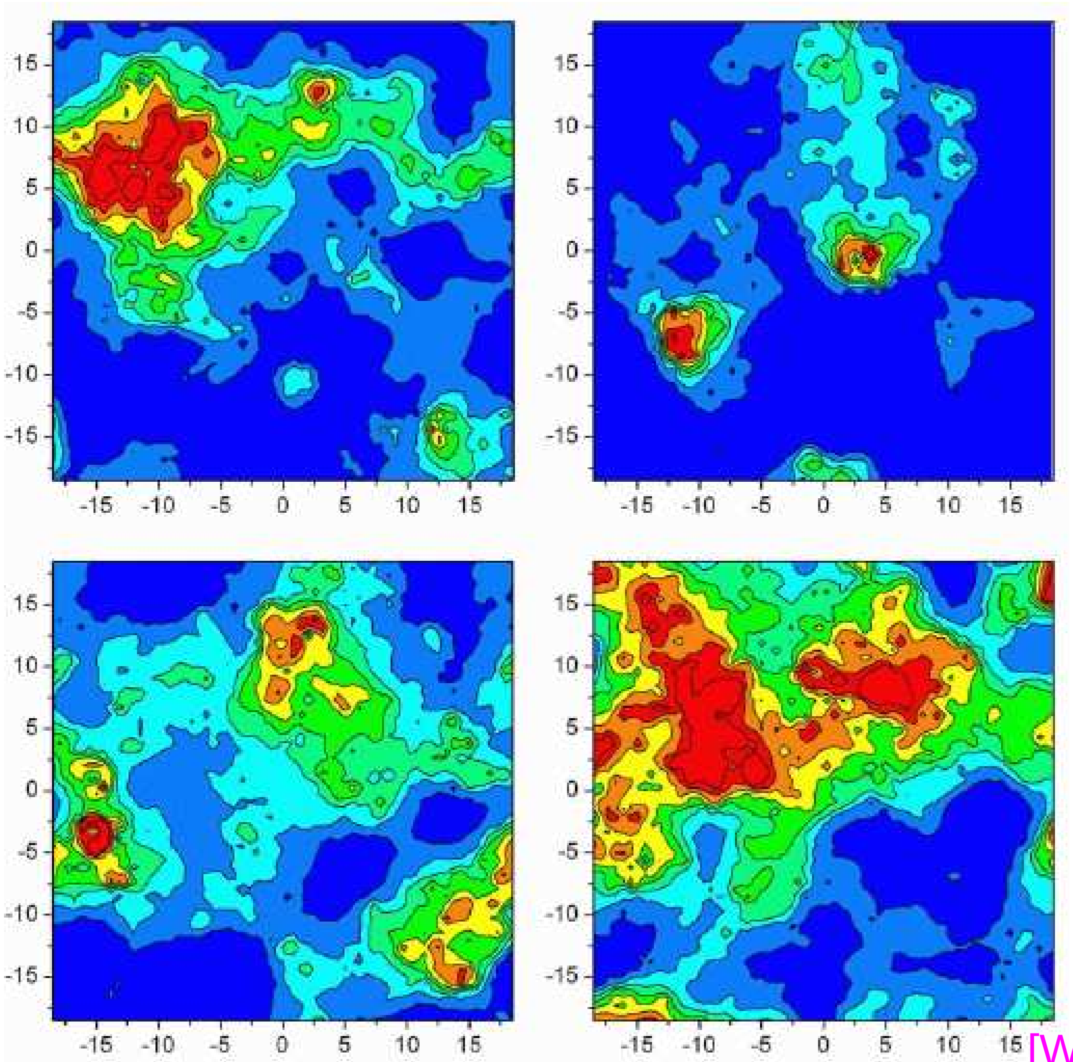
- Crossover from algebraic to logarithmic growth.

- ξ_4 does not 'diverge'.

Structure or dynamics?

Isoconfigurational ensemble

- 'Propensity' $\langle \mu_i(t) \rangle_{\mathrm{iso}} = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)| \rangle_{\mathrm{iso}}$ by averaging at constant initial structure.

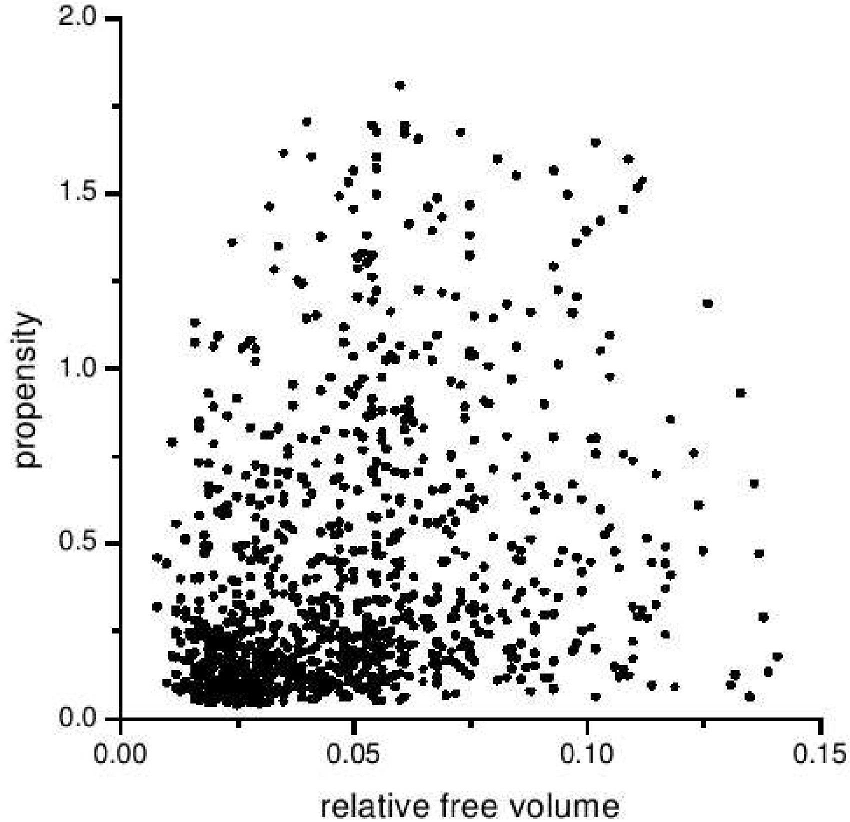


[Widmer-Cooper *et al.*, PRL '04]

Correlation is not prediction

- Propensity fluctuations show that 'something' in the structure causes 'some' dynamic heterogeneity.

- Echoes a long list of 'correlation' between structural and dynamical fluctuations. Not necessarily causal, not necessarily meaningful...



[Widmer-Cooper *et al.*, JPCM '04]

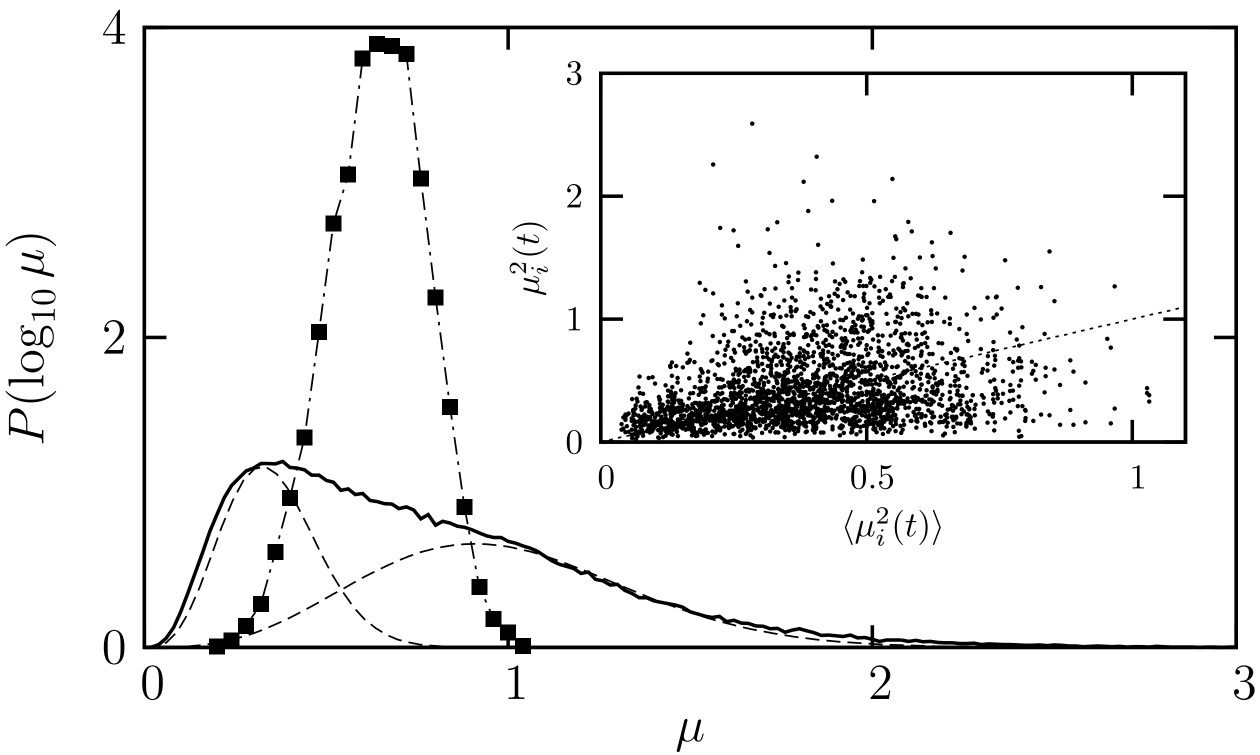
- Harrowell and coworkers report strong (almost predictive) correlation between propensity fluctuations and vibrational properties (mode spectrum). No consensus. Barrat.

Structure or dynamics?

- Harrowell *et al.* replaced the structure $\rightarrow$ dynamics problem by structure $\rightarrow$ propensity.

- What about propensity $\rightarrow$ dynamics? What about predictability?
[Berthier, Jack, PRE '07]

- Let's start with single particle dynamics: $\mu_i = |\mathbf{r}_i(t) - \mathbf{r}_i(0)|$, $\langle \mu_i \rangle_{\rm iso}$.



- Fast/slow character lost.

- Correlation is not prediction.

- Single particle dynamic heterogeneity is not predictible from the structure.

Predictability at large lengthscales

- $\Delta(t) = \mathbb{E}\left[\langle \mu_i^2(t)\rangle_{\rm iso}\right] - \mathbb{E}^2\left[\mu_i(t)\right] = \Delta^{\rm iso}(t) + \delta(t)$

$\Delta^{\rm iso}(t) = \mathbb{E}\left[\langle \mu_i^2(t)\rangle_{\rm iso} - \langle \mu_i(t)\rangle_{\rm iso}^2\right]$ at constant structure (dynamical origin)
$\delta(t) = \mathbb{E}\left[\langle \mu_i(t)\rangle_{\rm iso}^2\right] - \mathbb{E}^2[\mu_i(t)]$ propensity fluctuations (structural origin)

- Simulations indicate $\delta(\tau_\alpha)/\Delta(\tau_\alpha) < 4$ %: dynamical origin of single particle heterogeneity. Don't try to explain fast/slow particles from their local structure!

- Decompose also global fluctuations: $F(t) = \frac{1}{N}\sum_i \mu_i(t)$:
$\chi_4(t) = N\{\mathbb{E}\left[\langle F^2(t)\rangle_{\rm iso}\right] - \mathbb{E}^2\left[C(t)\right]\} = \Delta_4^{\rm iso}(t) + \delta_4(t)$

- $\delta_4(\tau_\alpha)/\chi_4(\tau_\alpha)$ grows rapidly and ≈ 35 % at lowest temperature: structure is back!

- Dynamic heterogeneity dynamical in essence at single particle level, but structural origin of fast and slow domains. [Berthier, Jack, PRE '07]

Conclusion Lecture 2

- Increasing lengthscale of dynamic heterogeneity with viscosity.

- Multi-point dynamic susceptibilities to quantify early observations of clusters.

- Can be measured and compared in different systems, analyzed by theory, simulations and experiments.

- Crossover from early power law growth to modest logarithmic increase: length scales remain modest even at T_g.

- Tools are now commonly used outside the glass transition field: granular problems, jamming of soft particles, colloidal gels, etc.

- Many open problems were discussed.
Tarjus, Miyazaki, Jack, Biroli, Franz, many of your posters.