# Universal nature of particle displacements close to the glass and jamming transitions

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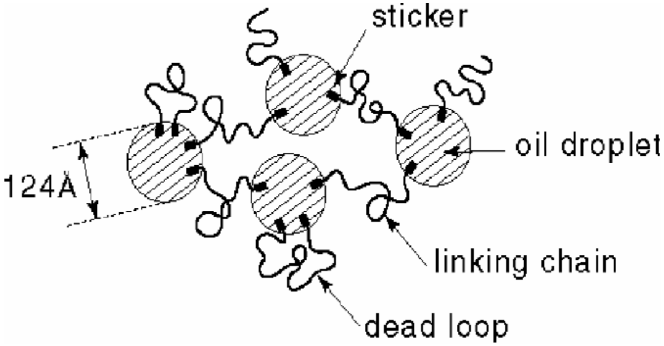
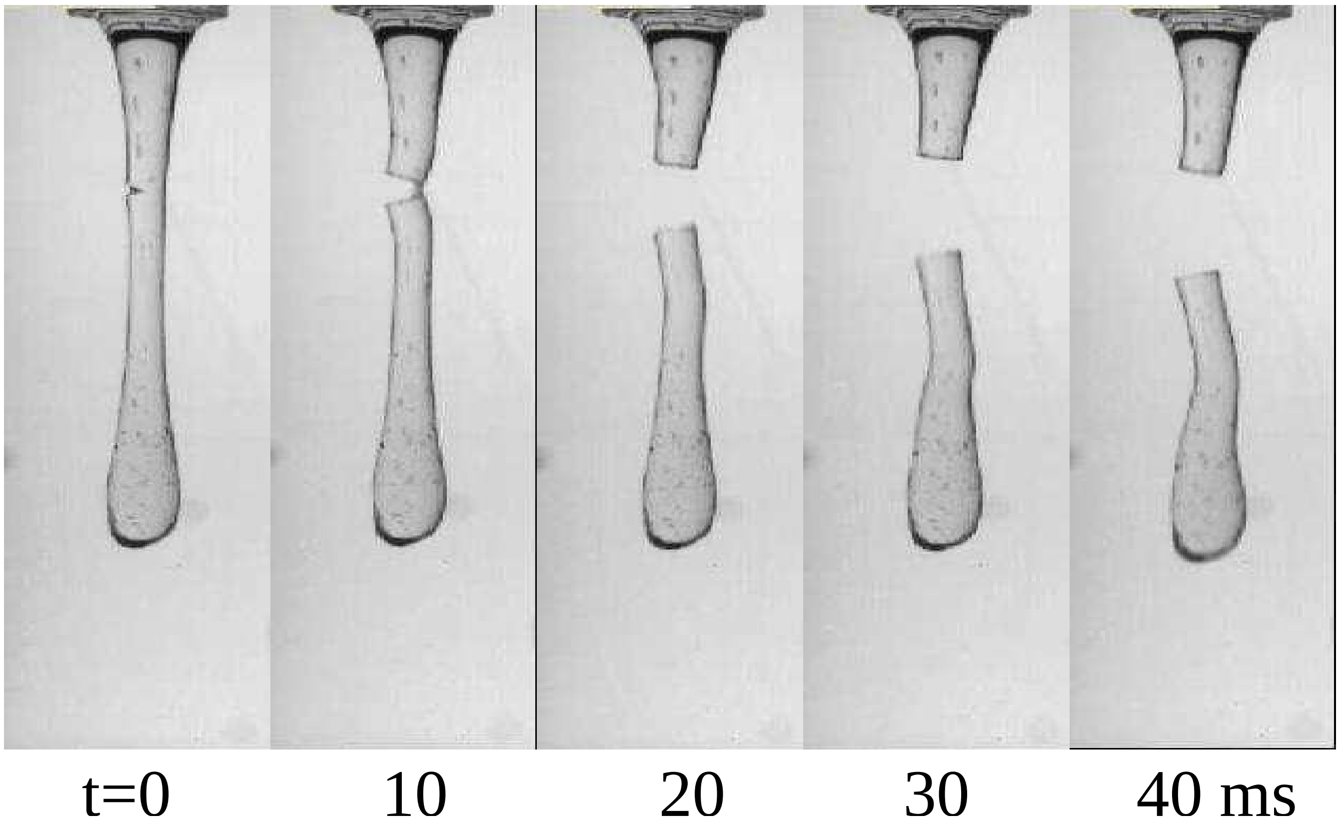
Talk at 'Mechanical behaviour of glassy materials' – Vancouver, July 23, 2007

with P. Chaudhuri, P. Hurtado, R. Jack, W. Kob

# Mechanics of glassy materials




Oil droplet in water $+$ telechelic polymers
$=$ Transient Network fluid.
Gel with non-linear rheological behaviour.
[Appell, Porte, Mora, Montpellier]

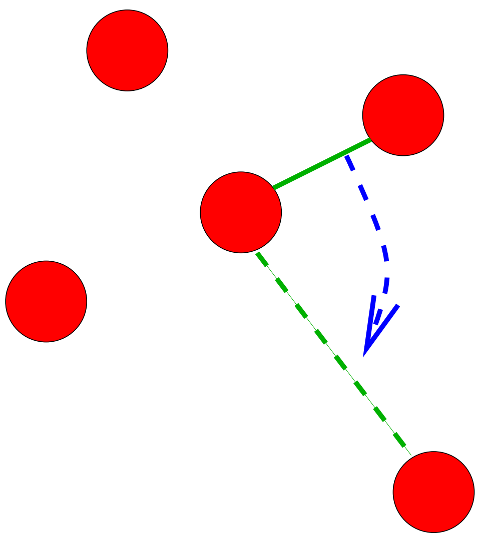


# Hybrid MC/MD simulations

- 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: $\tau_{\text{link}}^{-1} \min(1, \exp[-\Delta V_{\text{fene}}/k_B T])$.

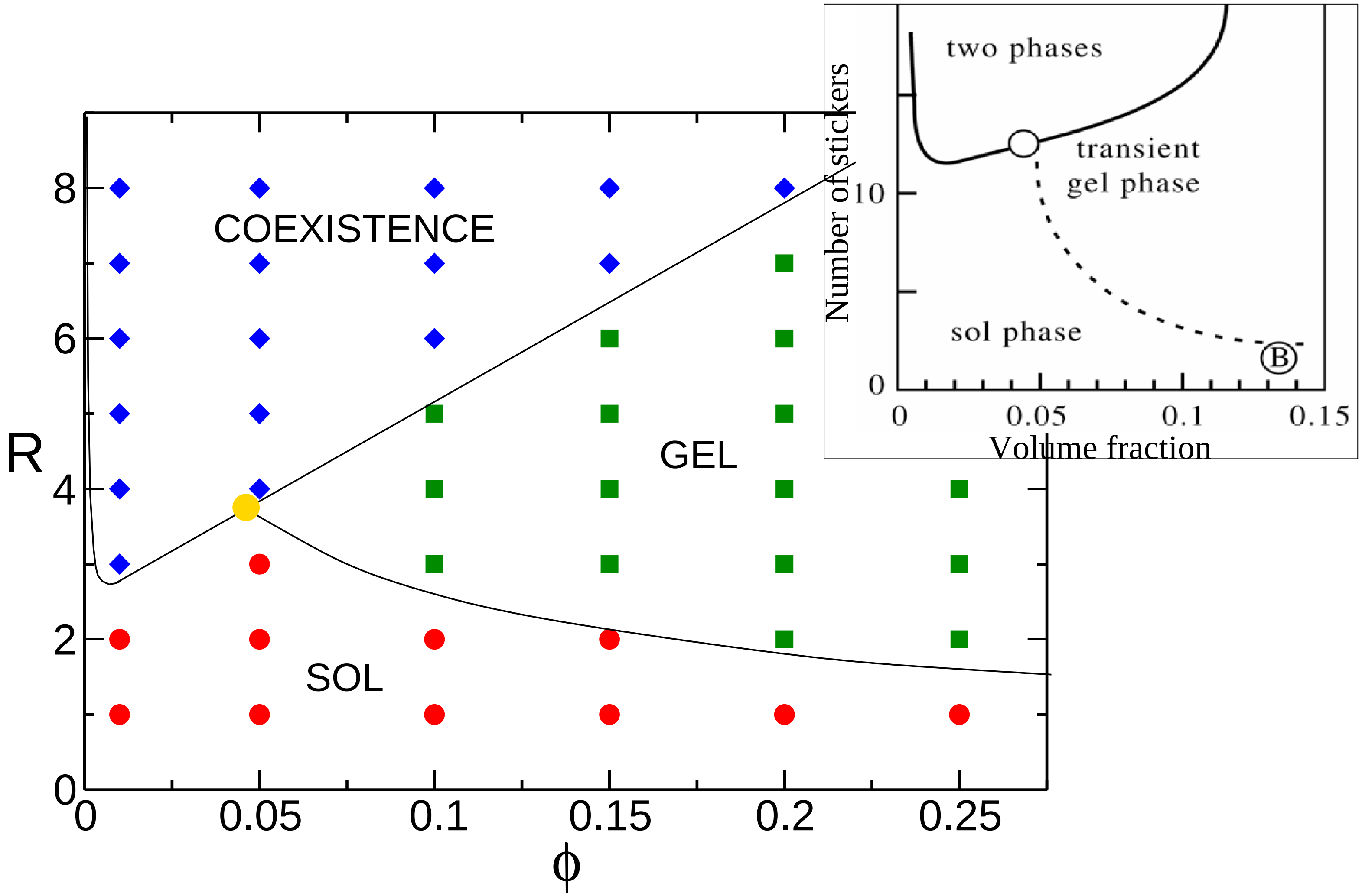
- Control parameters:

  $\phi$: droplet volume fraction;

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

  $\tau_{\text{link}}$: attempt timescale for sticker escape.

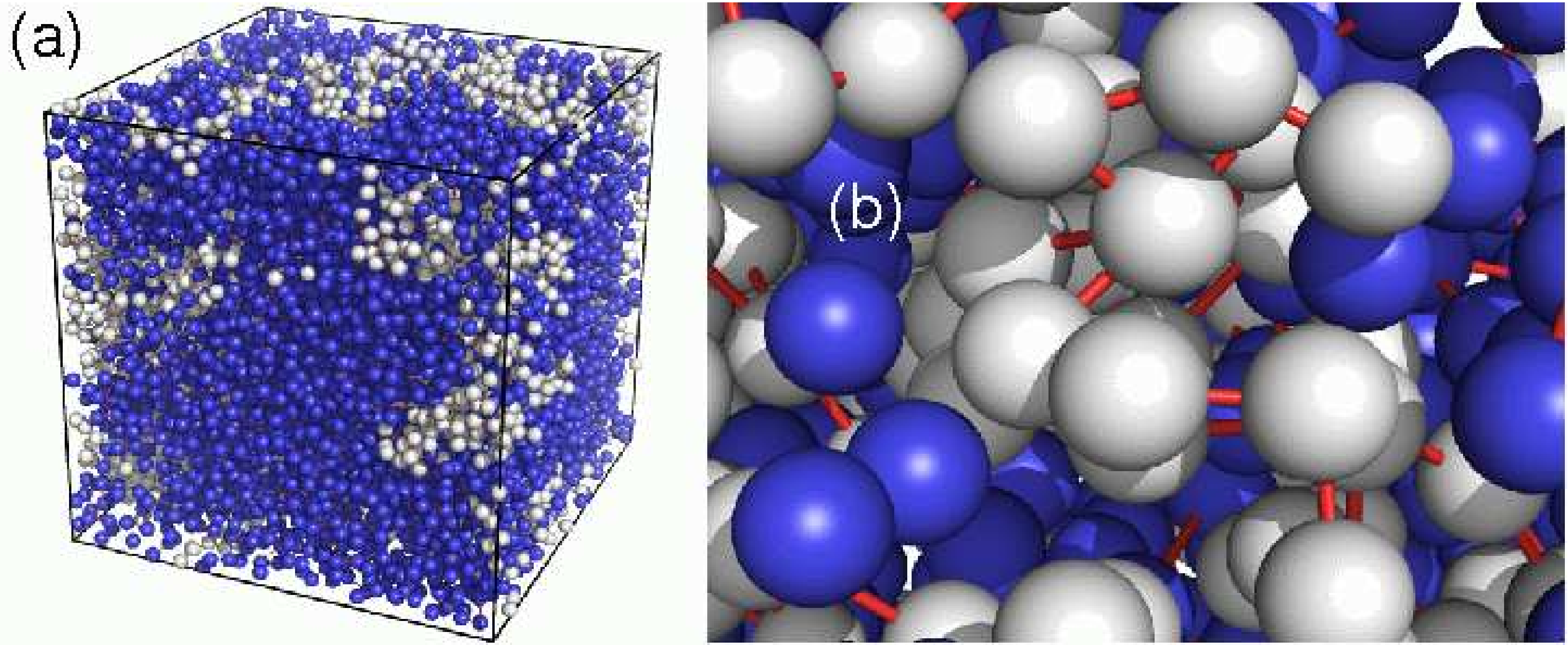
# Equilibrium phase diagram




- Equilibrium results in agreement with experiments.

[Hurtado, Berthier, Kob, PRL ’07]

# Gelation = geometric percolation




$\phi = 0.2,\ R = 2$

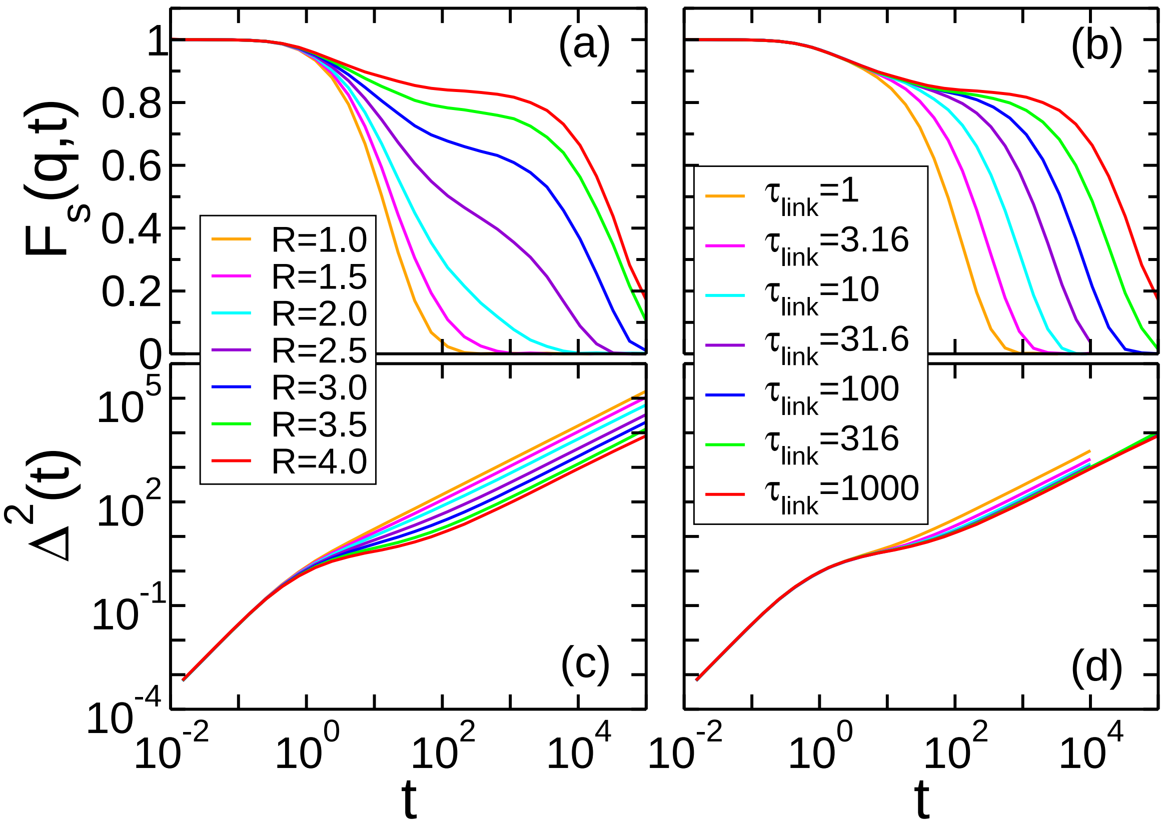
- Homogeneous overall structure, but fractal network of connected droplets

# Glassy dynamics in gels

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

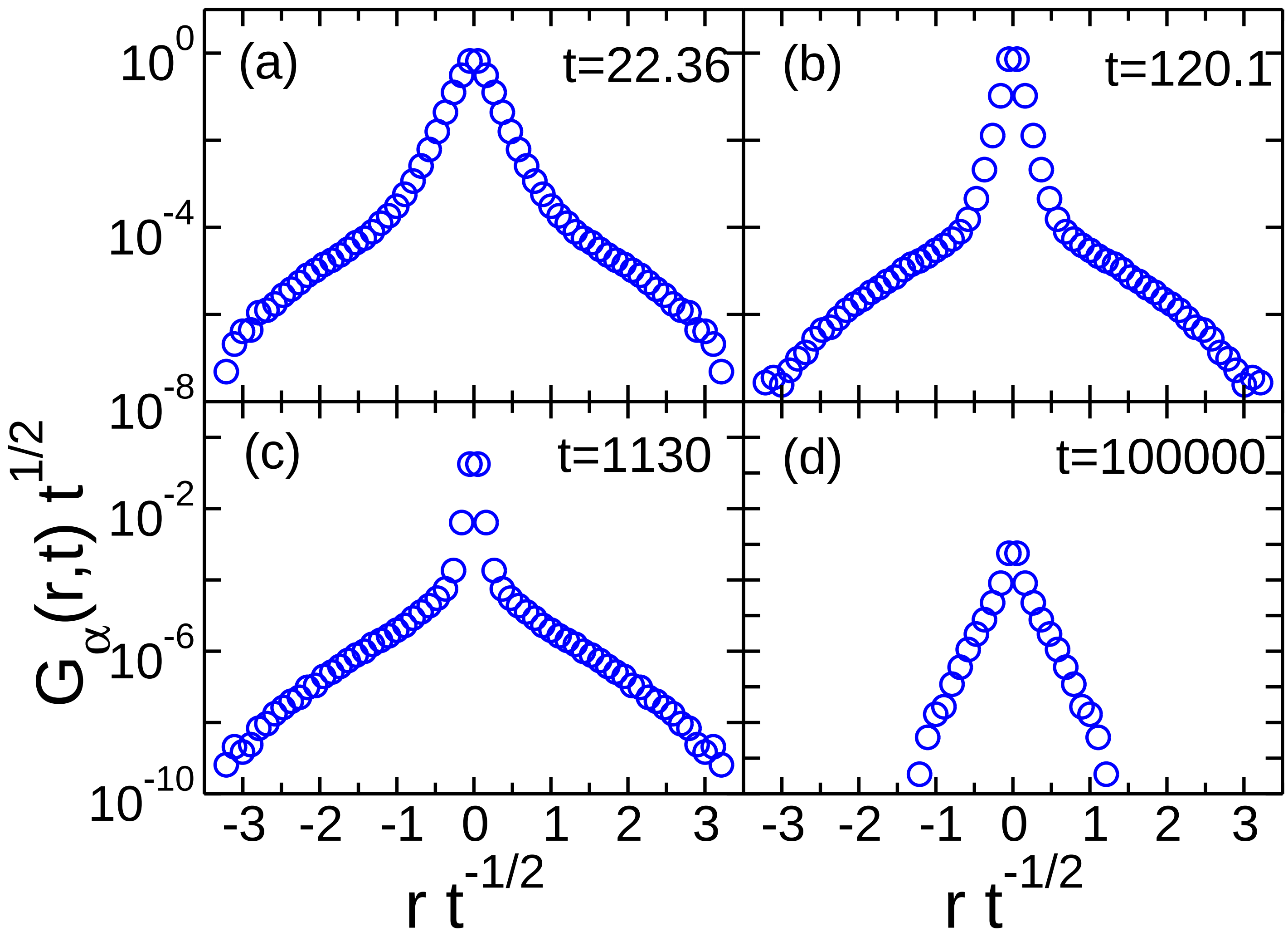
- Structure → Dynamics percolation = plateau = viscoelasticity $\neq$ glass transition.

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



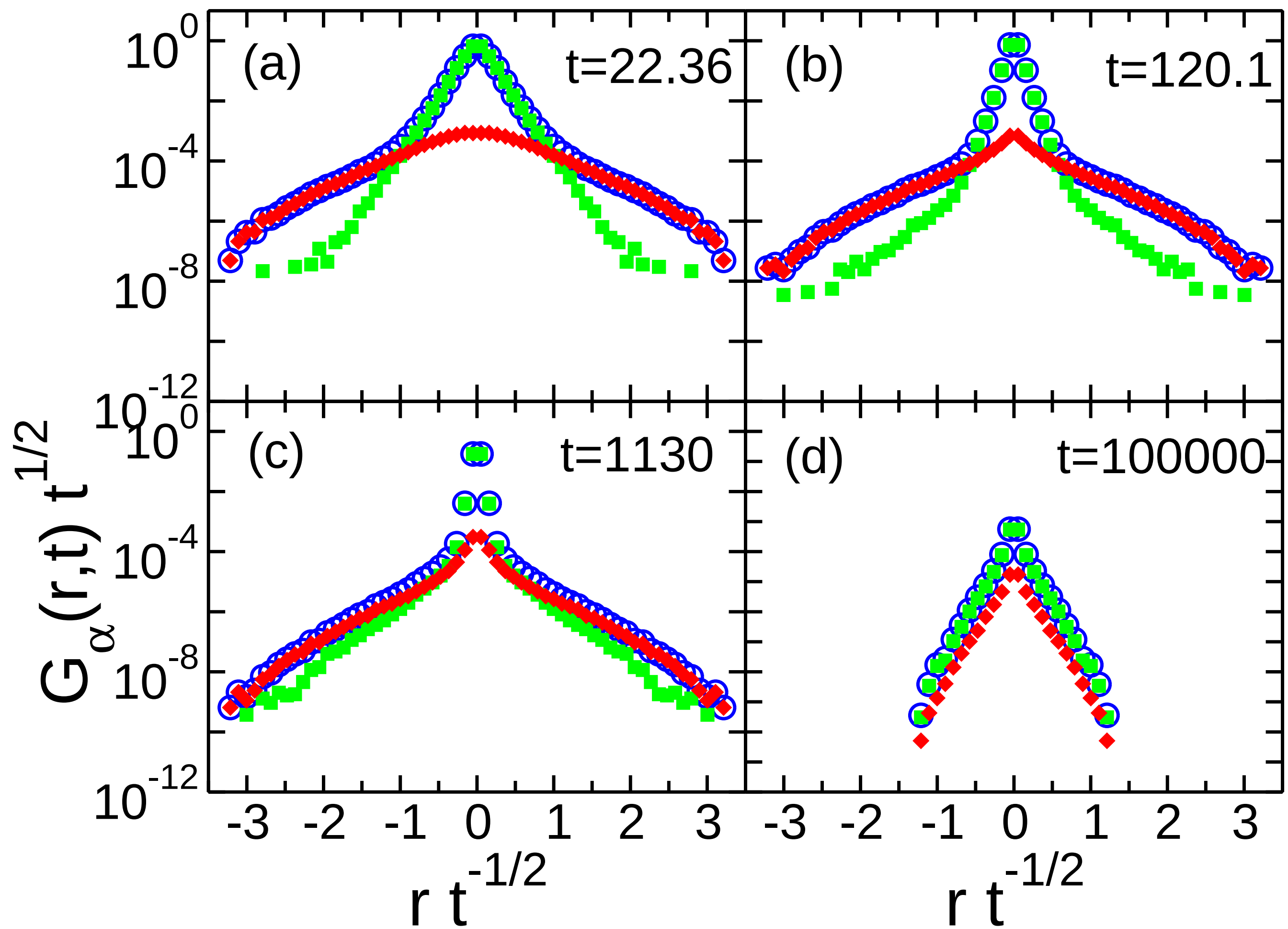

- But something's wrong: $F_s(q,t) \neq \exp(-q^2\Delta(t)^2/6)$. Decoupling!

# Dynamic heterogeneity in gels




- Non-Gaussian, “bimodal” distributions of particle displacements.

# Dynamic heterogeneity in gels




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

# 2-family dynamical model

- Assume 2 families of particles, $A$ ("arrested", $c_A$) and $M$ ("mobile", $c_M = 1 - c_A$).

- $p_\alpha(t)$: probability that a particle in $\alpha$ switches for the first time to $\bar{\alpha}$ at time $t$; $P_\alpha(t) = \int_t^\infty dt' p_\alpha(t')$ is a persistence function; $p_\alpha(t) = \exp(-t/\tau_\alpha)/\tau_\alpha$.

- $g_\alpha(\mathbf{r}, t)$: van-Hove function for particles within family $\alpha$ in the interval $[0, t]$; $\Delta_\alpha \equiv p_\alpha(t) g_\alpha(\mathbf{r}, t)$; $g_M \sim \exp(-r^2/(4D_M t))$; $g_A \sim \exp(-r^2/a^2)$.

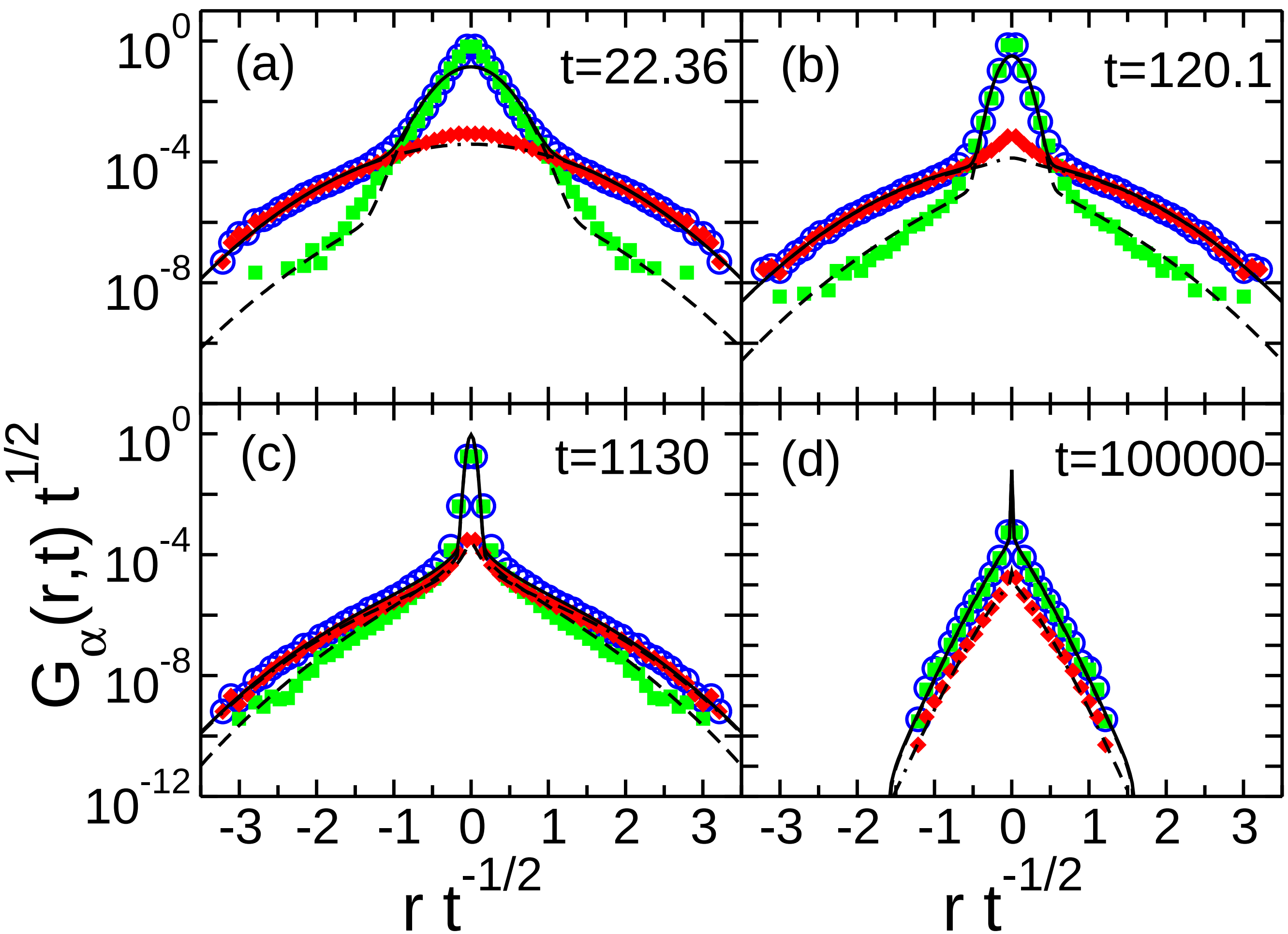
- Dynamic evolution:

$$G_\alpha(\mathbf{r}, t) = P_\alpha(t) g_\alpha(\mathbf{r}, t) + \int_0^t dt' \int d\mathbf{r}' p_\alpha(t') g_\alpha(\mathbf{r}', t') G_{\bar{\alpha}}(\mathbf{r} - \mathbf{r}', t - t')$$

- Solved in the Fourier-Laplace domain. Free parameters are $(c_A, D_M, a, \tau_A)$. Only $\tau_A$ is not fixed (but consistent) by simulations.

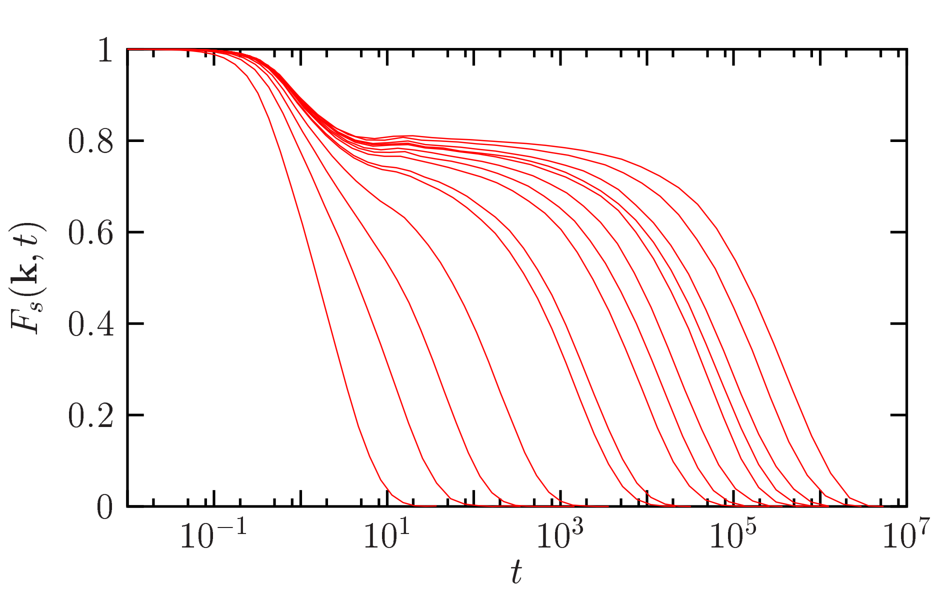
$$G_\alpha(\mathbf{q}, s) = \frac{\tau_\alpha \Delta_\alpha(\mathbf{q}, s) + \tau_{\bar{\alpha}} \Delta_\alpha(\mathbf{q}, s) \Delta_{\bar{\alpha}}(\mathbf{q}, s)}{1 - \Delta_\alpha(\mathbf{q}, s) \Delta_{\bar{\alpha}}(\mathbf{q}, s)}$$

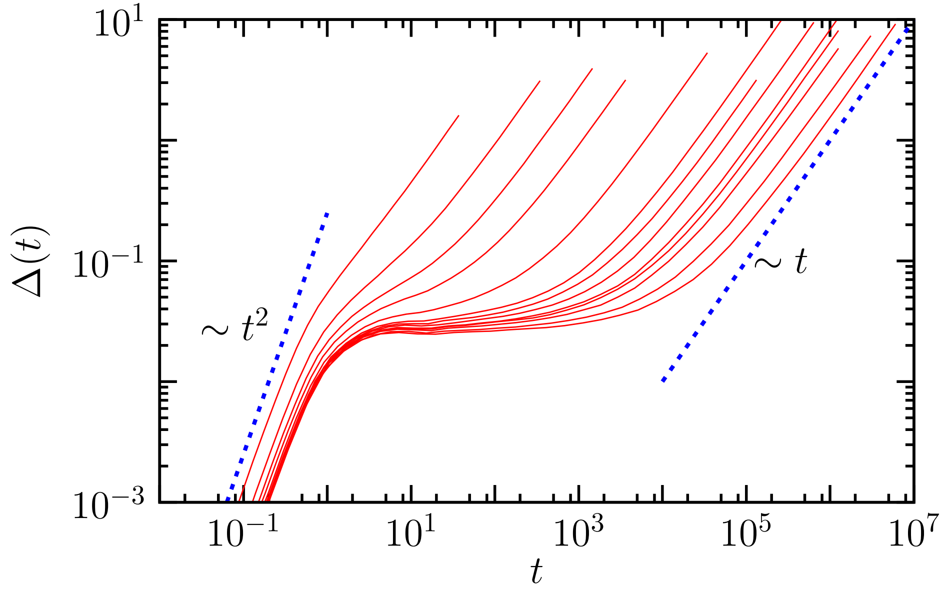
# Dynamic heterogeneity in gels




- Excellent fits throughout the gel phase for $G_M$, $G_A$ and $G_s = c_A G_A + (1 - c_A) G_M$, for all $t$'s beyond microscopic: experiments?

# Dynamics of supercooled liquids




- Dramatic slowing down as $T$ decreases.

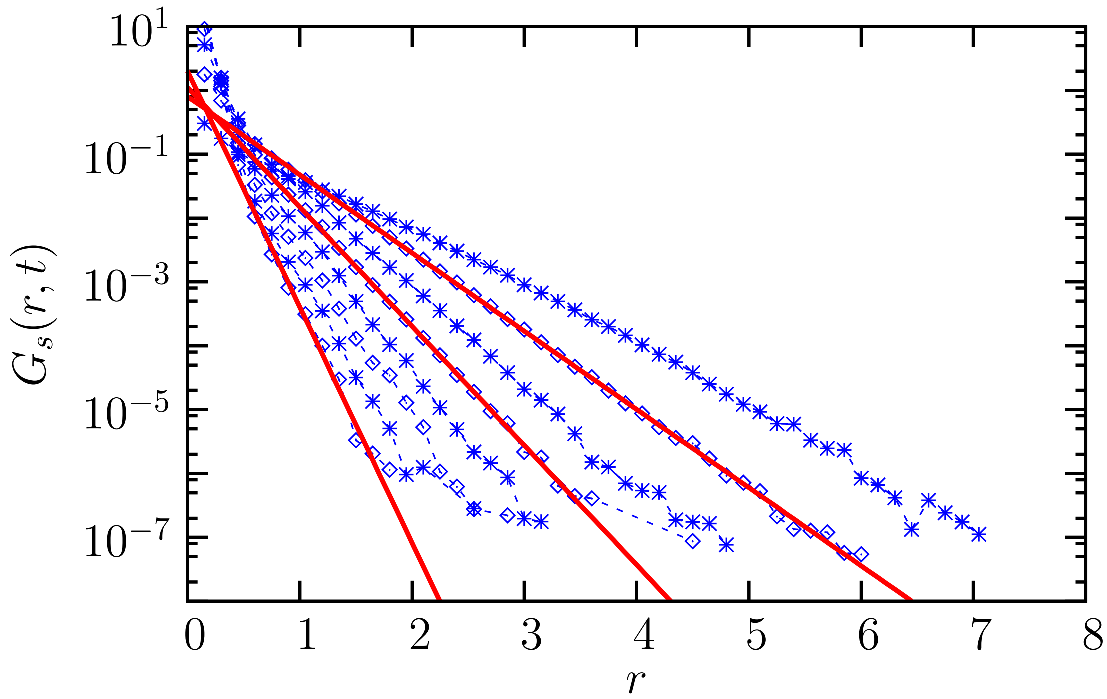
- Computer simulations record the dynamics over 9 decades, for simple liquids, a bit less for more complex structures (e.g. silica $SiO_2$).

- Something's wrong again: $F_s(q,t) \neq \exp(-q^2 \Delta(t)^2/6)$. Decoupling!
But structure provides no clue.

# Dynamic heterogeneity in liquids

• Non-Gaussian distribution of particle displacements in a supercooled liquid.

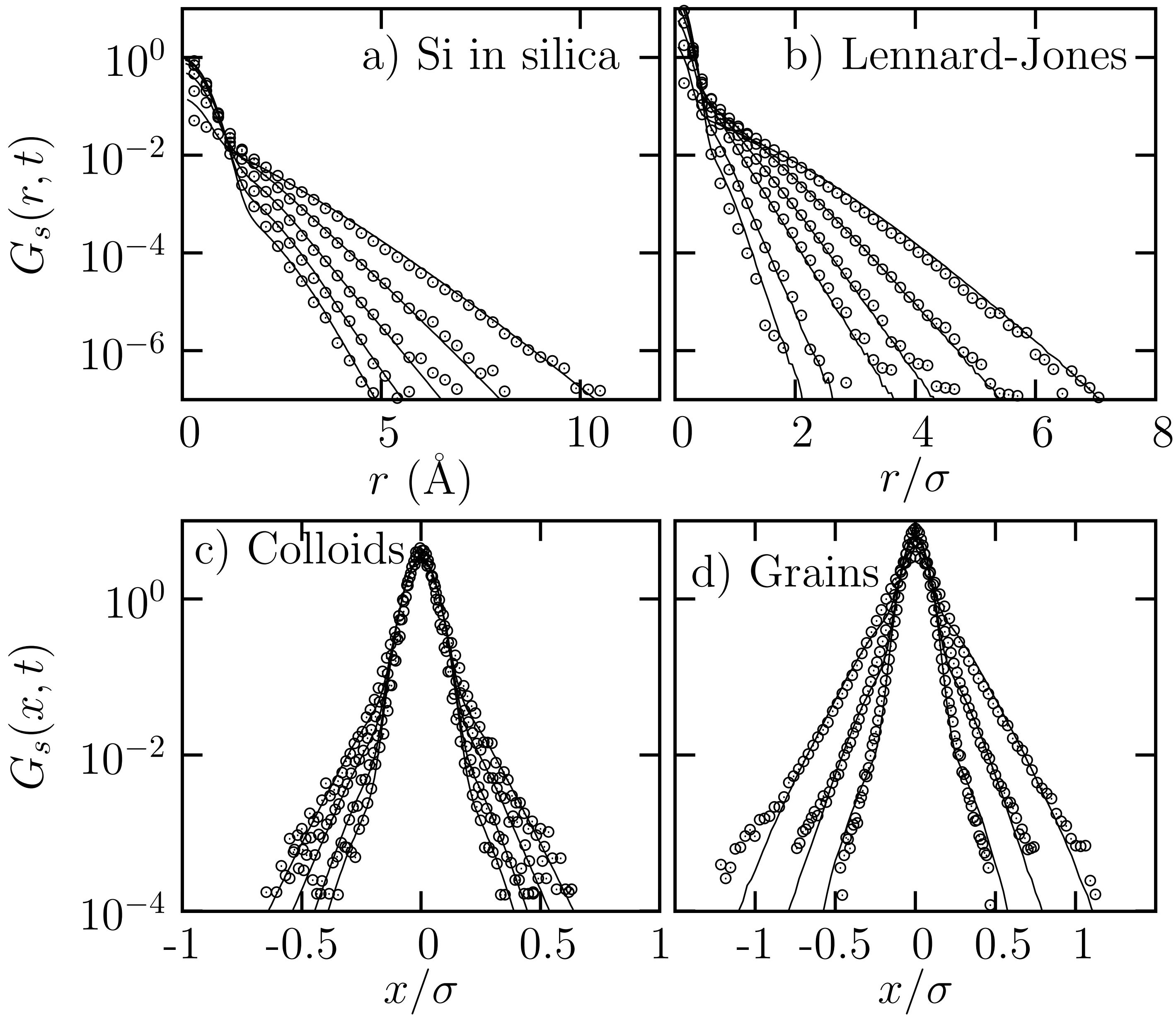
• Gaussian part for small $r$, exponential tails at large distance.




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

• A new, universal dynamical feature characterizing the dynamics of glass-forming liquids.

# This behavior is truly universal



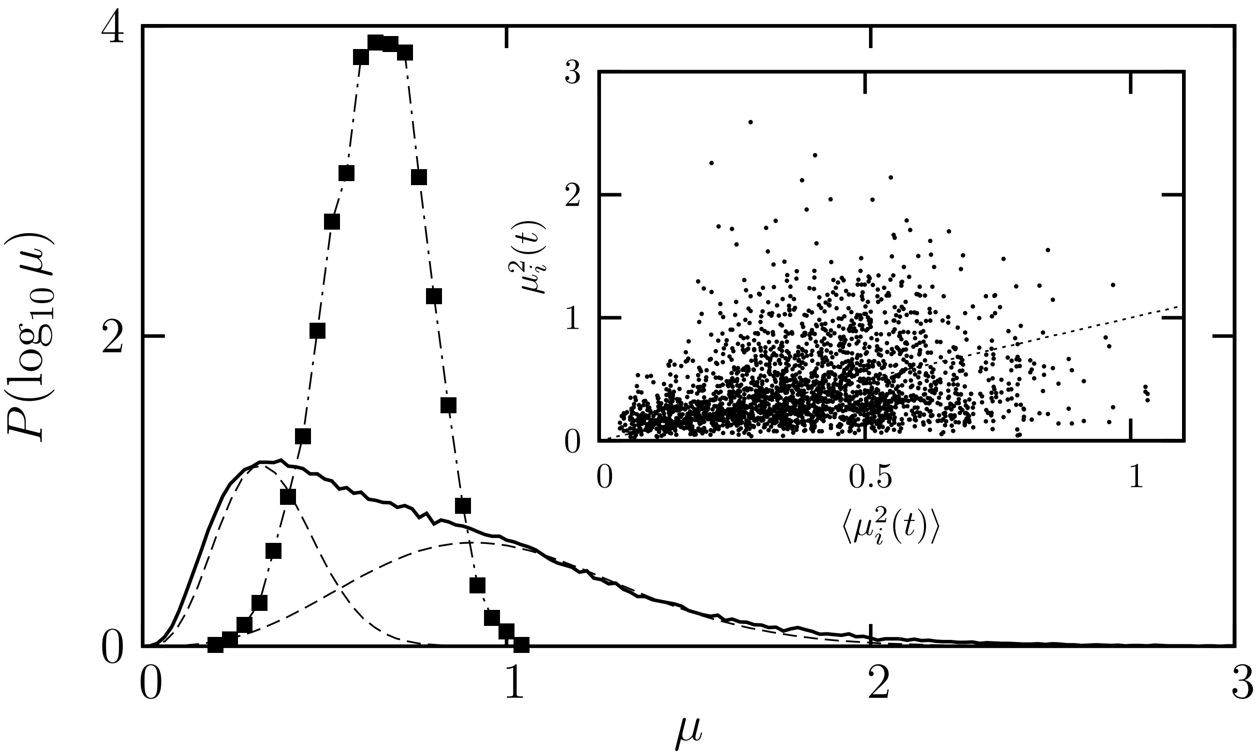
# Structure or dynamics?

- Harrowell *et al.* define the 'propensity' $\langle \mu_i(t) \rangle = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)| \rangle$ by averaging at constant structure at $t = 0$.

- structure $\rightarrow$ propensity replaces structure $\rightarrow$ dynamics

- What about propensity $\rightarrow$ dynamics? Predictability?

[Berthier, Jack arXiv:0706.1044]




- Fast/slow character lost.

- Single particle dynamics unpredictable!

# Predictability at large lengthscales

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

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

- Simulations indicate $\delta(\tau_\alpha)/\Delta(\tau_\alpha) < 4$ %: dynamical origin.

- Repeat for global fluctuations: $C(t) = \frac{1}{N}\sum_i \mu_i(t)$:

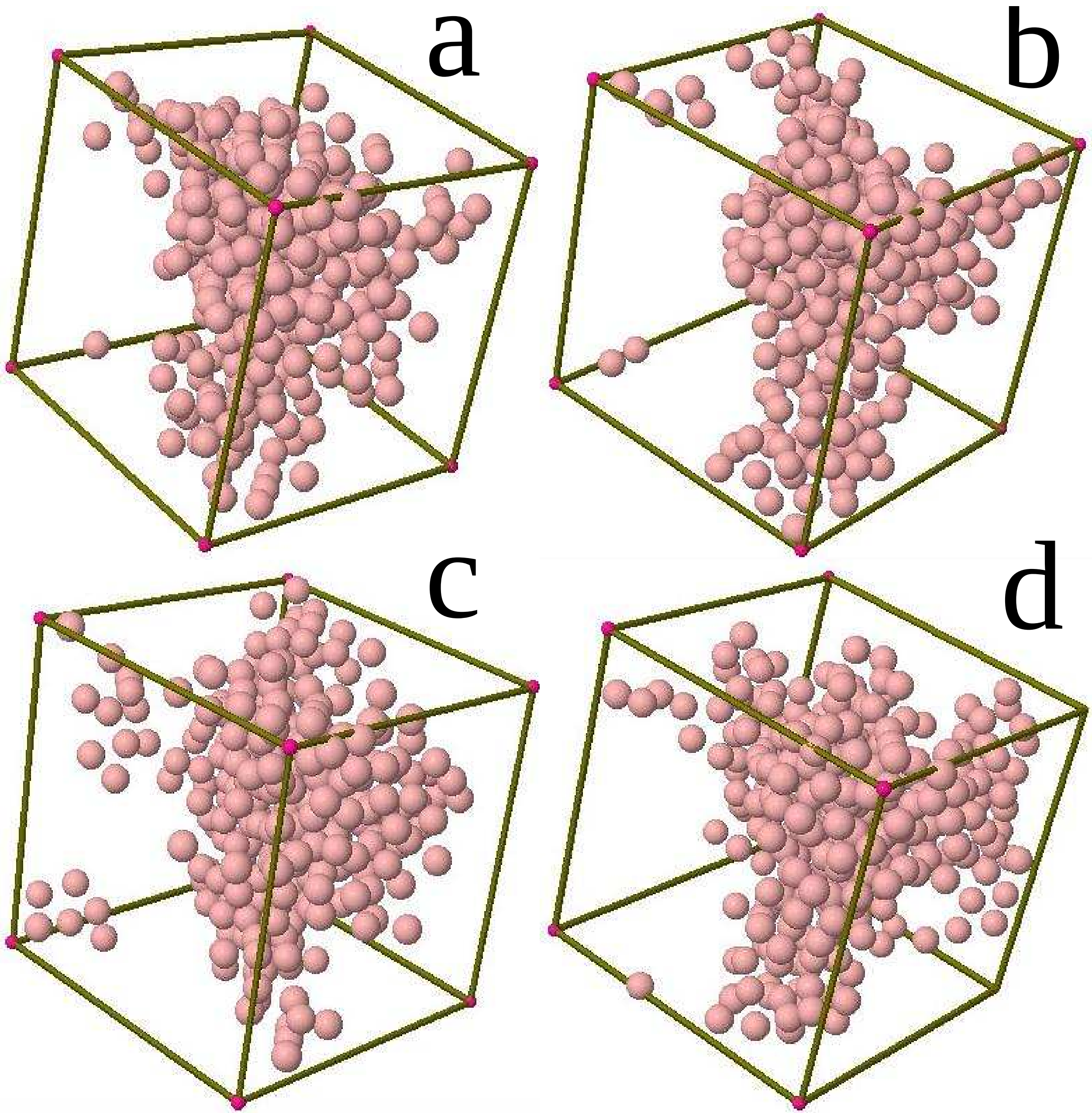
$\chi_4(t) = N\{\mathbb{E}\left[\langle C^2(t) \rangle\right] - \mathbb{E}^2\left[C(t)\right]\} = \Delta_4^{\mathrm{iso}}(t) + \delta_4(t)$

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

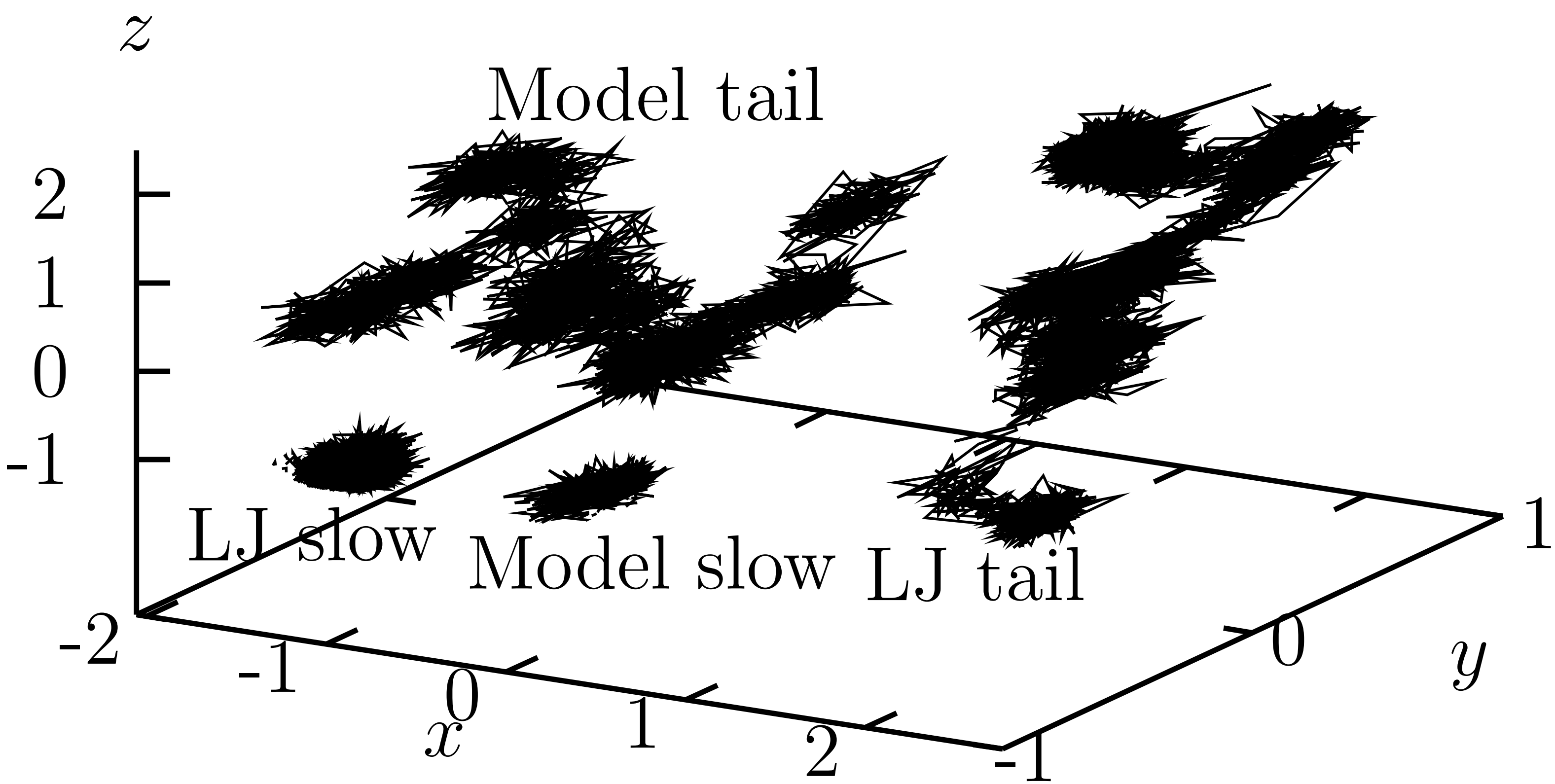
- Dynamic heterogeneity dynamical in essence at single particle level, but structural origin of fast and slow domains. [Berthier, Jack, arXiv:0706.1044]

- Coarse-grained dynamics $\approx$ propensity

# Predictability at large lengthscales



# Dynamical microscopic origin




- Particles perform random walks at random times, “CTRW”, with specific properties. [Montroll, Bouchaud, Odagaki, Heuer, Langer, Berthier *et al.*, EPL ’05, & Chaudhuri *et al.*, arXiv: :0707.0319].

# Modified CTRW

- $G_s(\mathbf{r},t) = \sum_{n=0}^{\infty} \pi_n(t) f_n(\mathbf{r})$.
- $\pi_0(t) = P(t)$ is a persistence function; $P(t) = \int_t^\infty dt' p(t')$; $f_0(\mathbf{r}) = f_{\mathrm{vib}}(\mathbf{r})$ for vibrations.
- $\pi_1(t) = \int_0^t dt' p(t') \Psi(t-t')$; $\Psi(t) = \int_t^\infty \psi(t')$; $\psi(t)$ is the distribution of exchange times; $f_1(\mathbf{r}) = [f_0(\mathbf{r}) \otimes f_{\mathrm{jump}}(\mathbf{r})] \otimes f_{\mathrm{vib}}(\mathbf{r})$.
- $\pi_2(t) = \int_0^t dt' \pi_1(t') \psi(t-t')$; $f_2(\mathbf{r}) = [f_1(\mathbf{r}) \otimes f_{\mathrm{jump}}(\mathbf{r})] \otimes f_{\mathrm{vib}}(\mathbf{r})$ , etc.
- Solution: $G_s(\mathbf{q},s) = P(s) f_0(\mathbf{q}) + \dfrac{p(s) f_0(\mathbf{q}) f(\mathbf{q}) [1-\psi(s)]}{s[1-f(\mathbf{q})\psi(s)]}$,

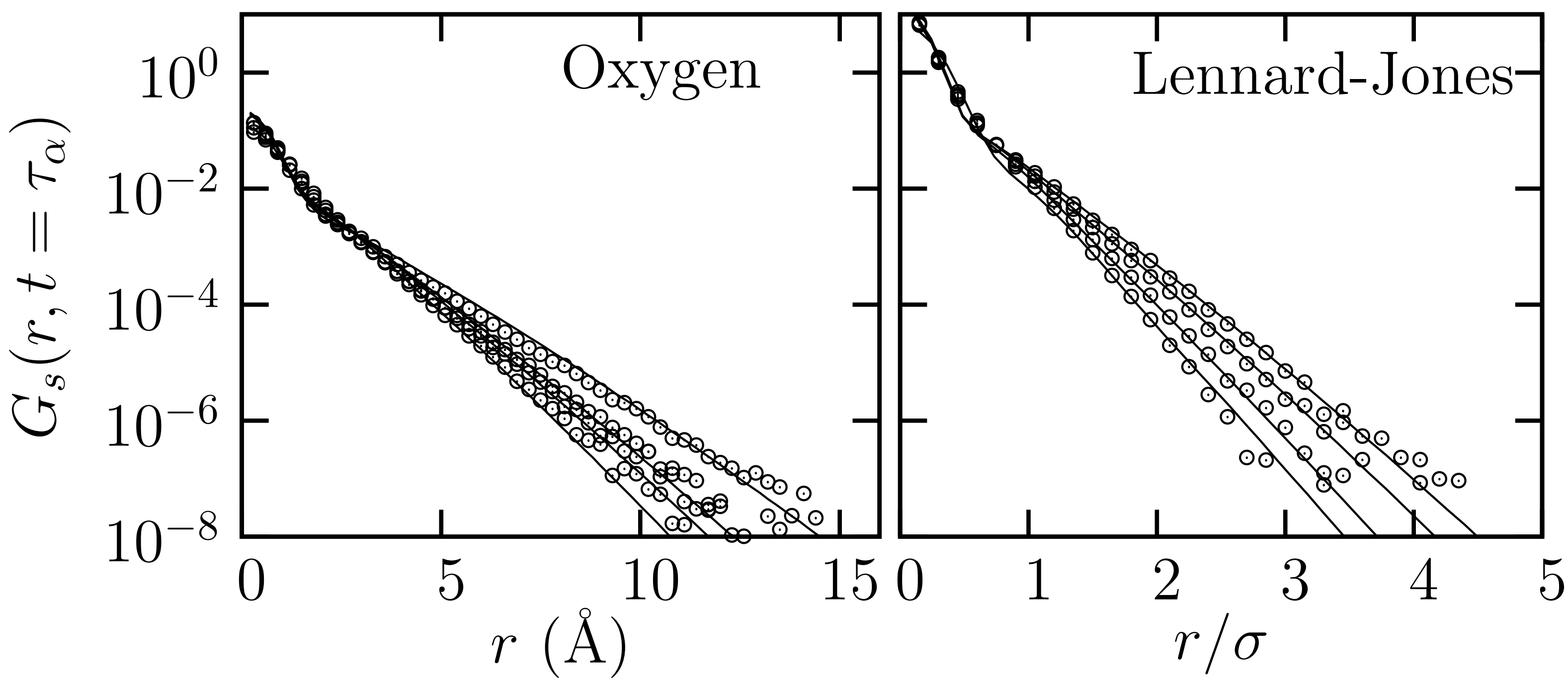
with $f(\mathbf{q}) = f_{\mathrm{vib}}(\mathbf{q}) f_{\mathrm{jump}}(\mathbf{q})$.
- Timescales: $p(t) = \exp(-t/t_1)/t_1$ and $\psi(t) = \exp(-t/t_2)/t_2$.
- Lengthscales: $f_{\mathrm{vib}} \sim \exp(-r^2/\sigma_1^2)$ and $f_{\mathrm{jump}} \sim \exp(-r^2/\sigma_2^2)$.

# Fitting data in real materials

$$G_s(r,t) = P(t) f_{\rm vib}(r) + \frac{4\pi}{r} \int_0^\infty dq \frac{q \sin(qr) f(q) f_0(q)}{(1-f(q))^{\frac{t_2}{t_1}} - 1} \left( e^{-t/t_1} - e^{-t(1-f(q))/t_2} \right)$$

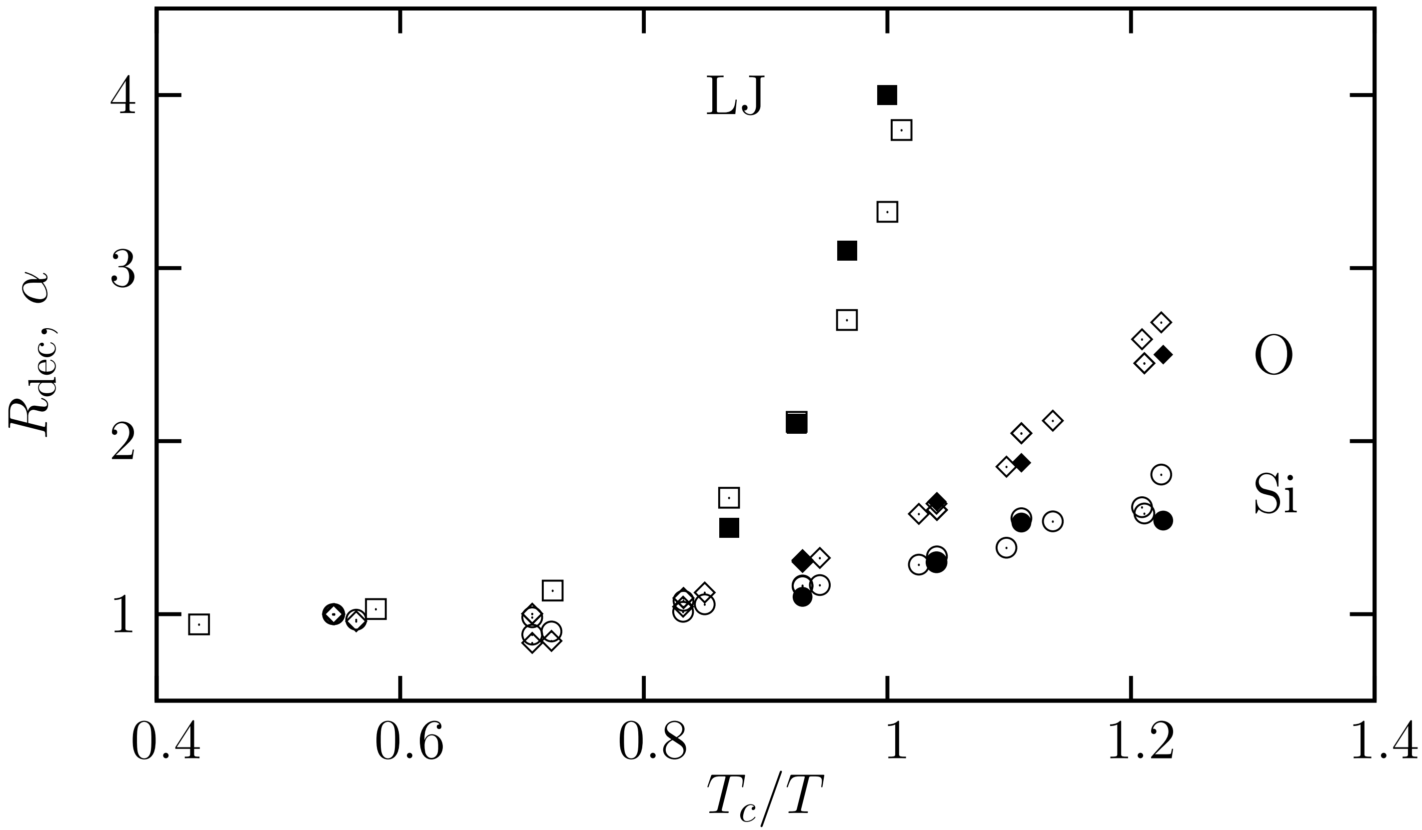
The last integral is not nice, but it generically (saddle-point) leads to an exponential tail (with log-corrections).

- Using ($\sigma_1$, $\sigma_2$, $t_1$, $t_2$), data for liquids, colloids and grains can be fitted for many ($t$, $T$, $\varphi$).



# Decoupling re-interpreted

- $\alpha = t_1/t_2$ from fitting the data vs. $R_{\text{dec}} = \dfrac{D_s(T)\tau_\alpha(T)}{D_s(T_0)\tau_\alpha(T_0)}$: translational decoupling measured in simulations.
- Clear link between exponential tail and decoupling.



# Conclusions

- Slow dynamics in gels and glassy materials

- Dynamically heterogeneous behaviour is commonly observed

- Single particle dynamic heterogeneity results from structure in gels, is purely dynamical in glasses

- Simple stochastic models can be devised to capture generic behaviours in gels and glasses

- Lengthscales are important...

- More experimental data are needed to confirm exponential tail, link with spatial correlations, microscopic calculations, etc.