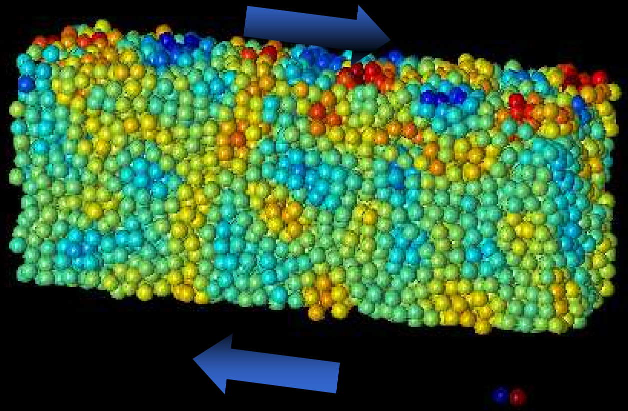
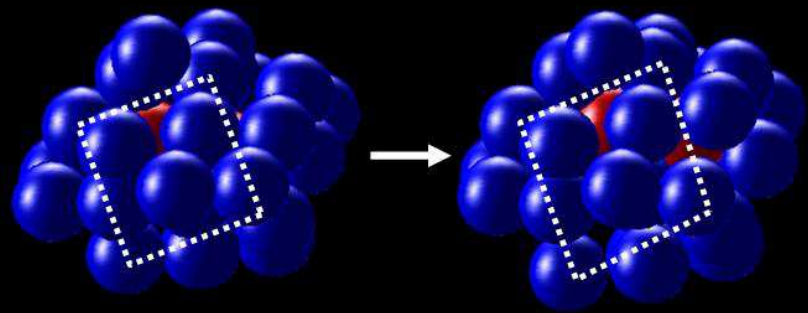
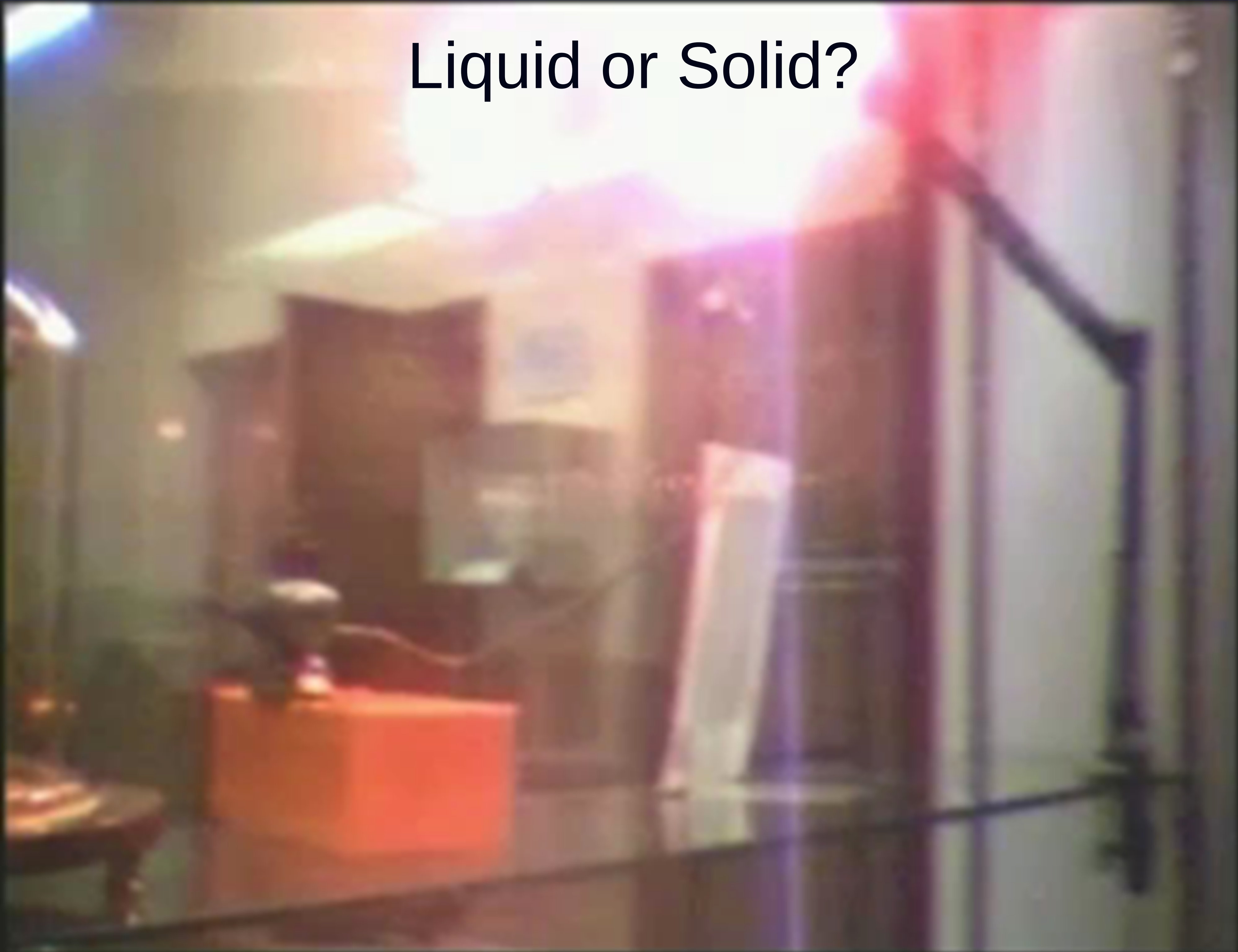


Flow of Glasses

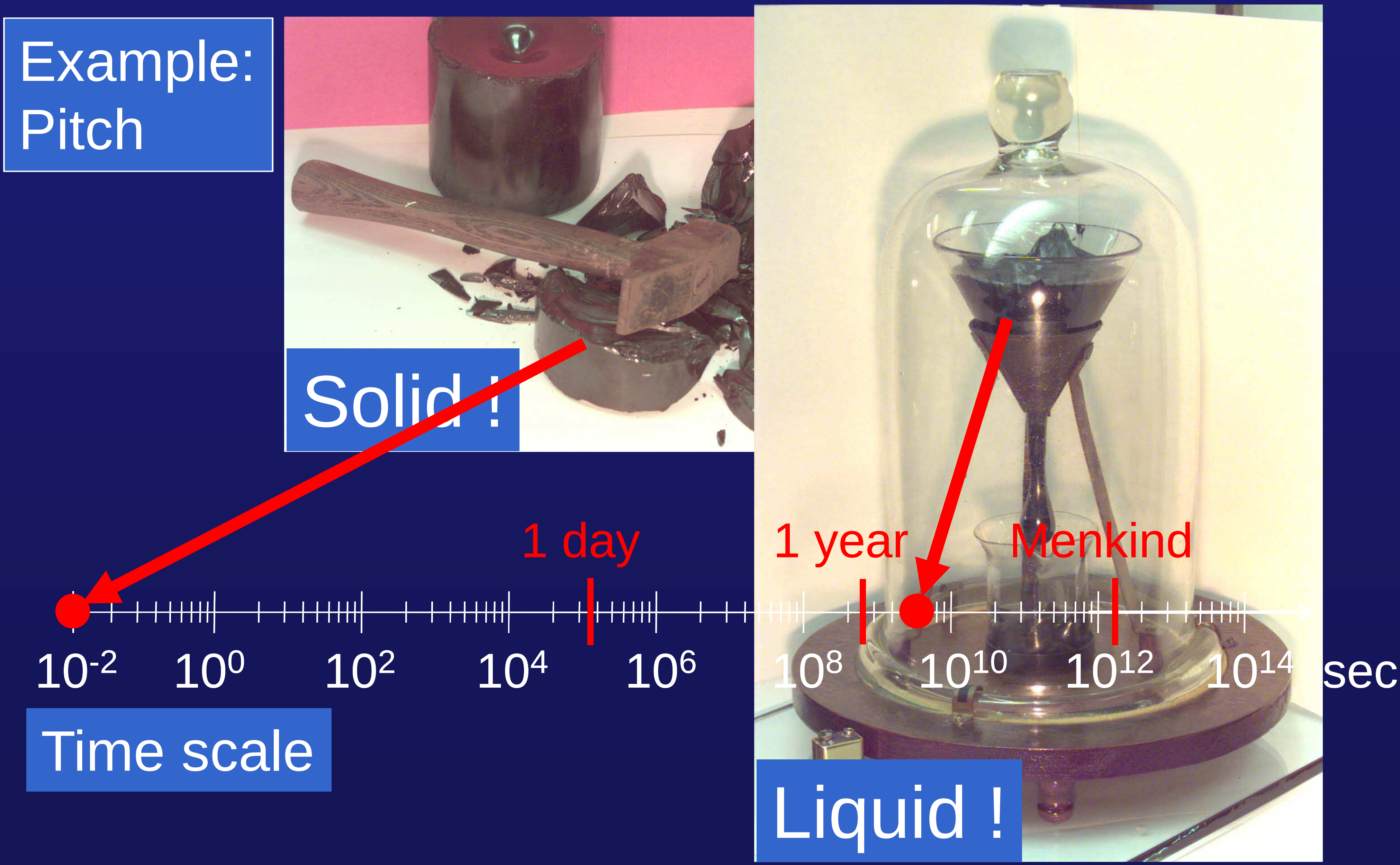
Peter Schall
University of Amsterdam



Liquid or Solid?



Liquid or Solid?



Fundamental Transition

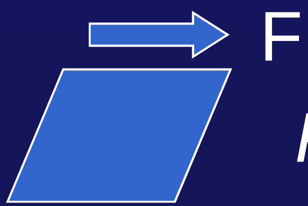
Elastic solid → Viscous Liquid

Elastic Modulus μ — diffusive, Viscosity η

<u>Symmetry change</u>

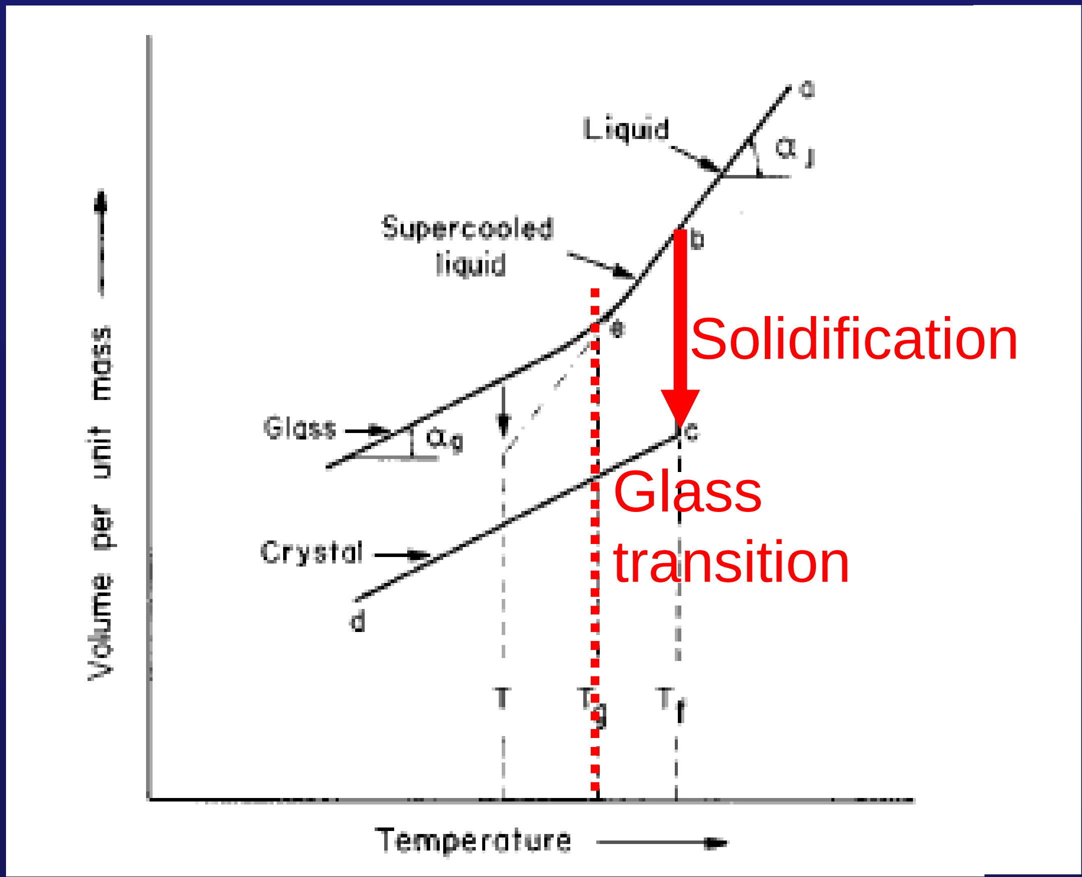
Temporal symmetry

Elastic	Plastic
$F(-t) = F(t)$	$F(-t) = - F(t)$
Energy storage	Energy loss



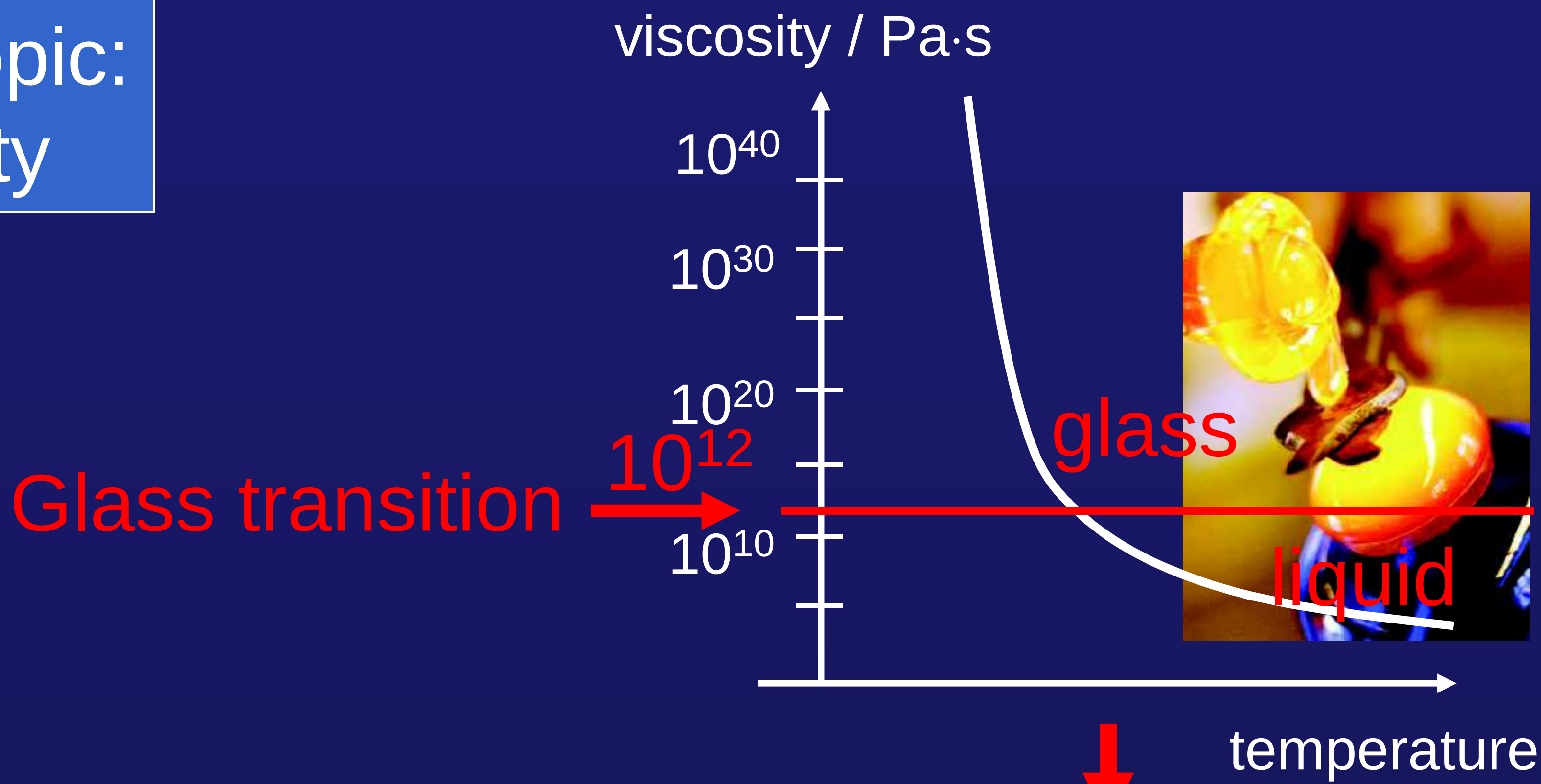
Glass Formation

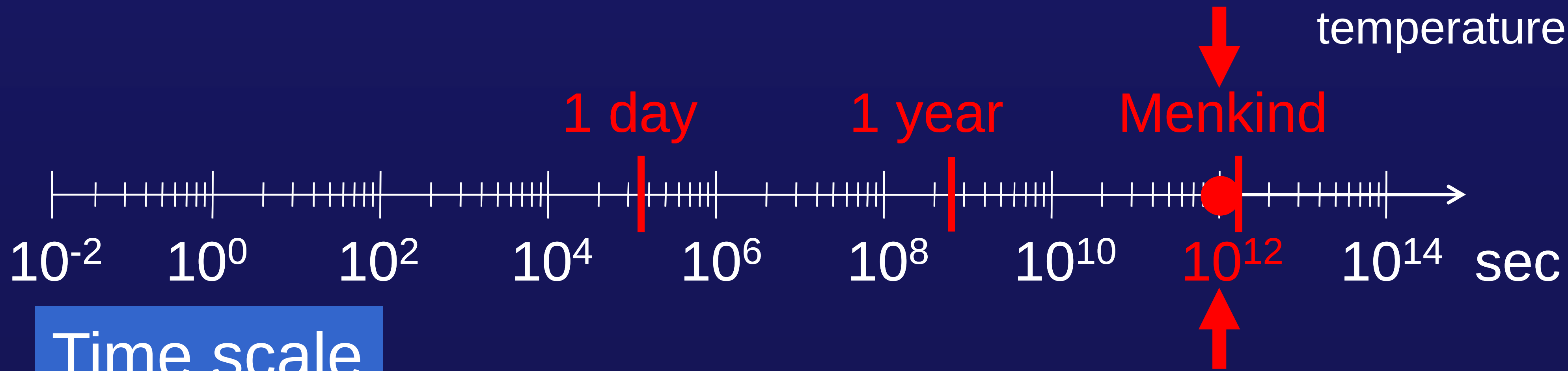
Cooling from Liquid



Viscosity and Diffusion

Macroscopic: Viscosity

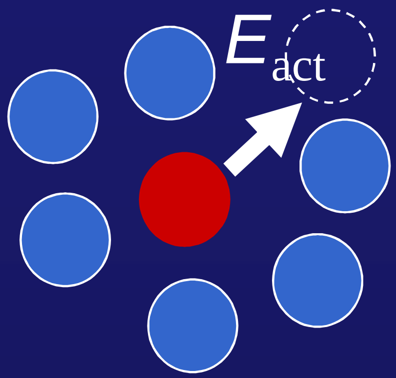




Time scale

Viscosity and Diffusion

Simple Liquids: Arrhenius

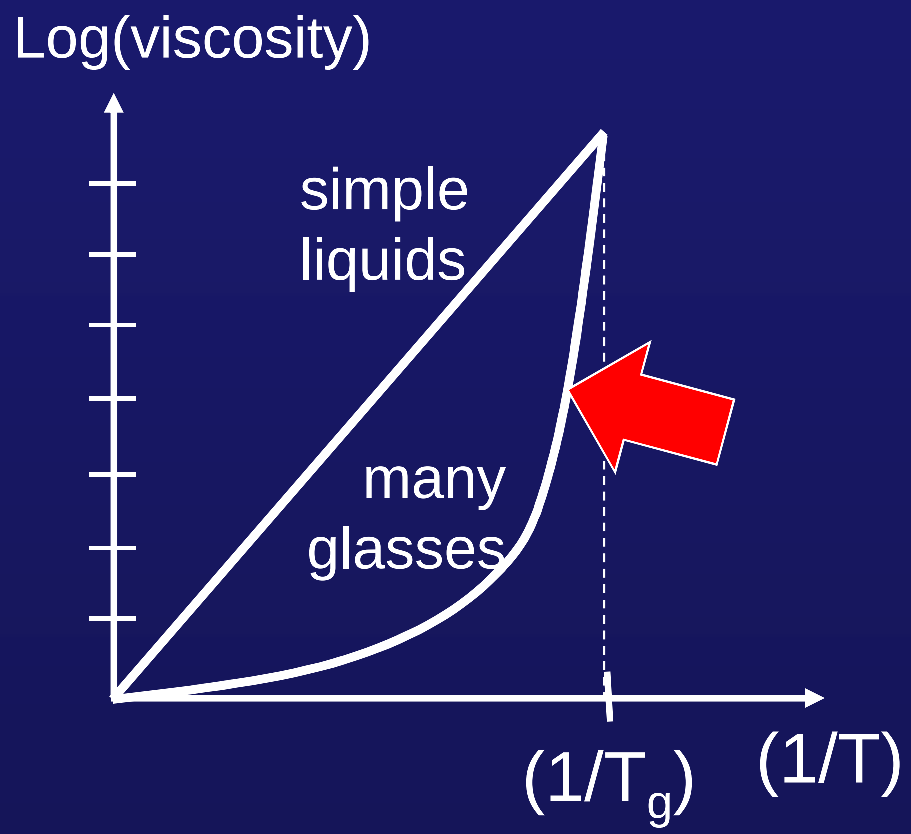


Diffusion coefficient

$$D \sim D_0\, e^{(-E_{act}/k_B T)}$$

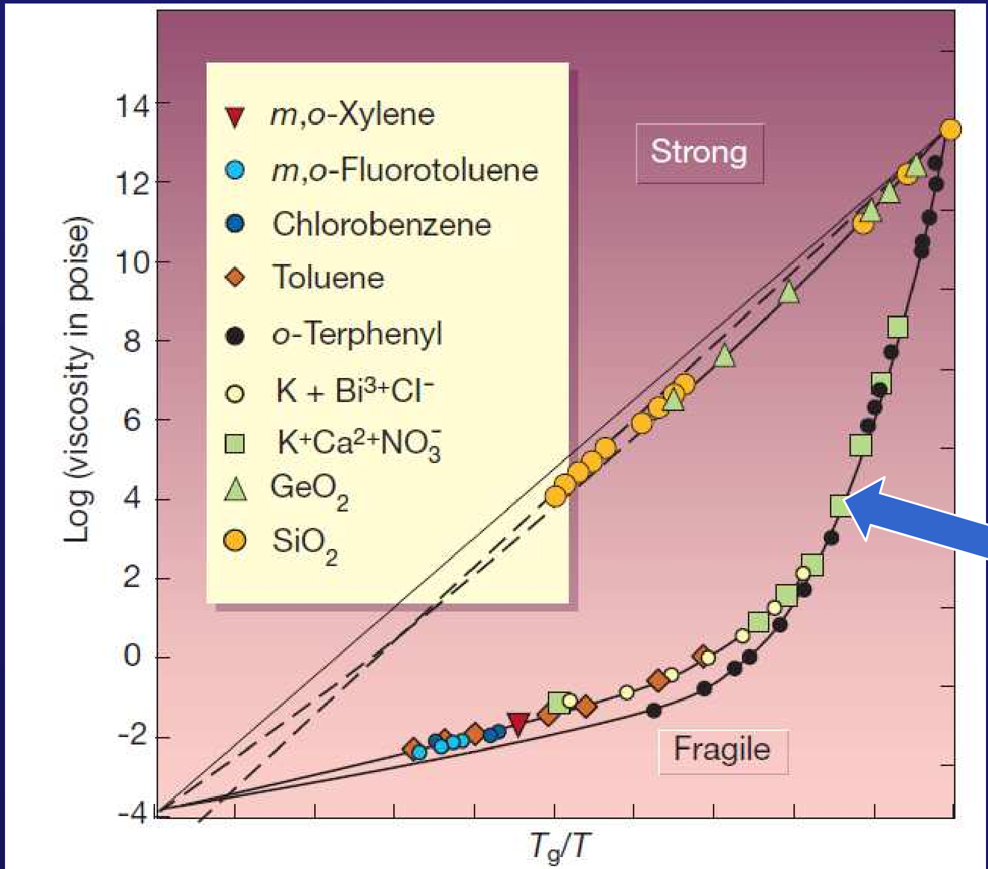
Viscosity

$$\eta \sim \eta_0\, e^{(E_{act}/k_B T)}$$



Strong and Fragile Glasses

"Angel plot"



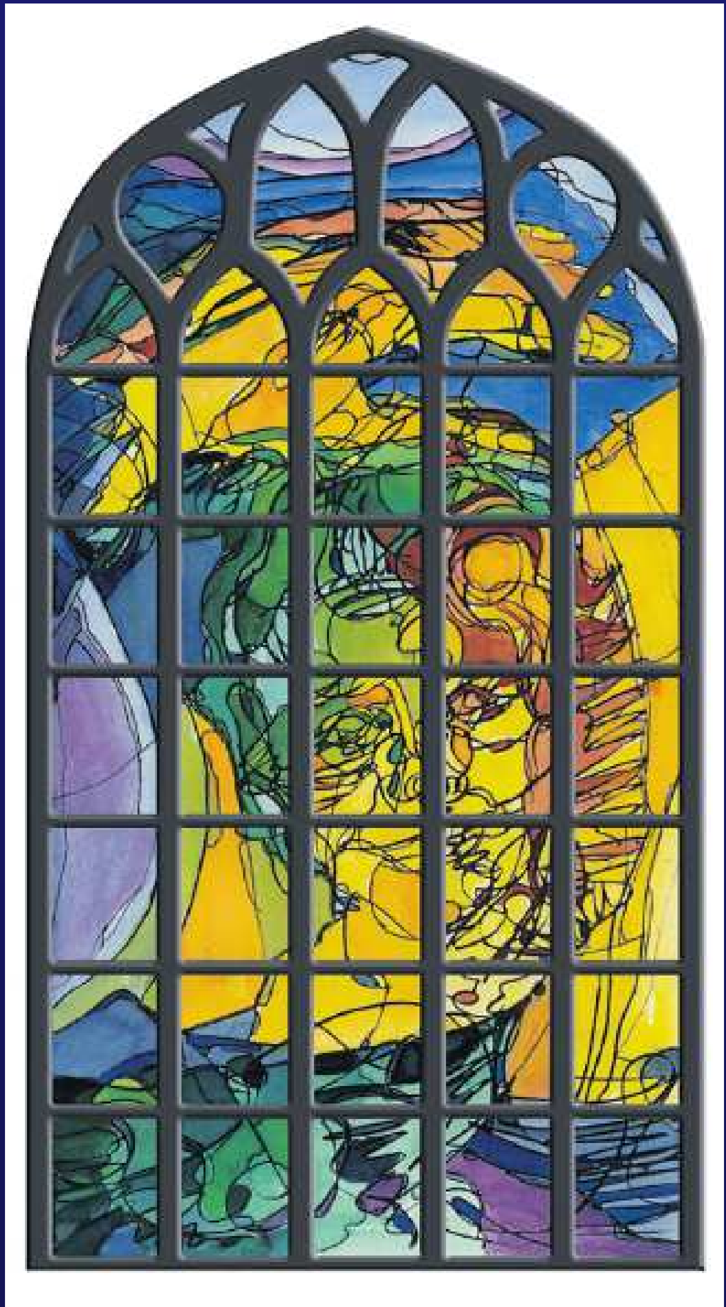
Arrhenius

$\eta = \eta_0 \exp(E/k_B T)$

Vogel-Fulcher-Tamman

$$\eta = \eta_0 \exp\left(\frac{B}{T-T_0}\right)$$

Glass Phenomenology



Myth:
Do cathedral glasses flow over centuries?

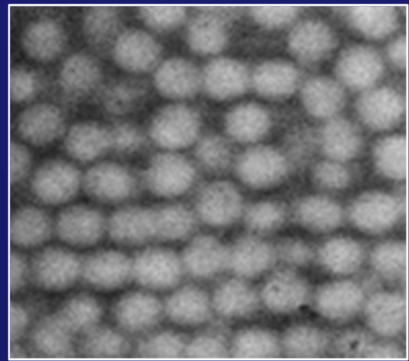
NO!

Vogel-Fulcher-Tamman

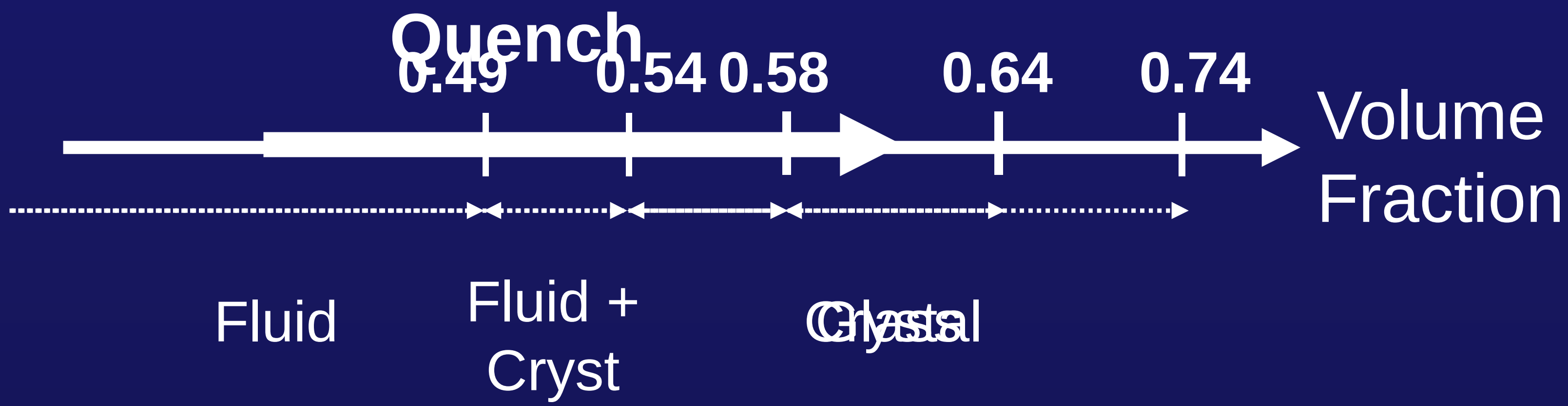
$$\eta = \eta_0 \, exp\left(\frac{B}{T - T_0}\right)$$

→ Relax. Time > 10^{18}s

Hard-Sphere Suspensions



Hard-sphere Phase Diagram

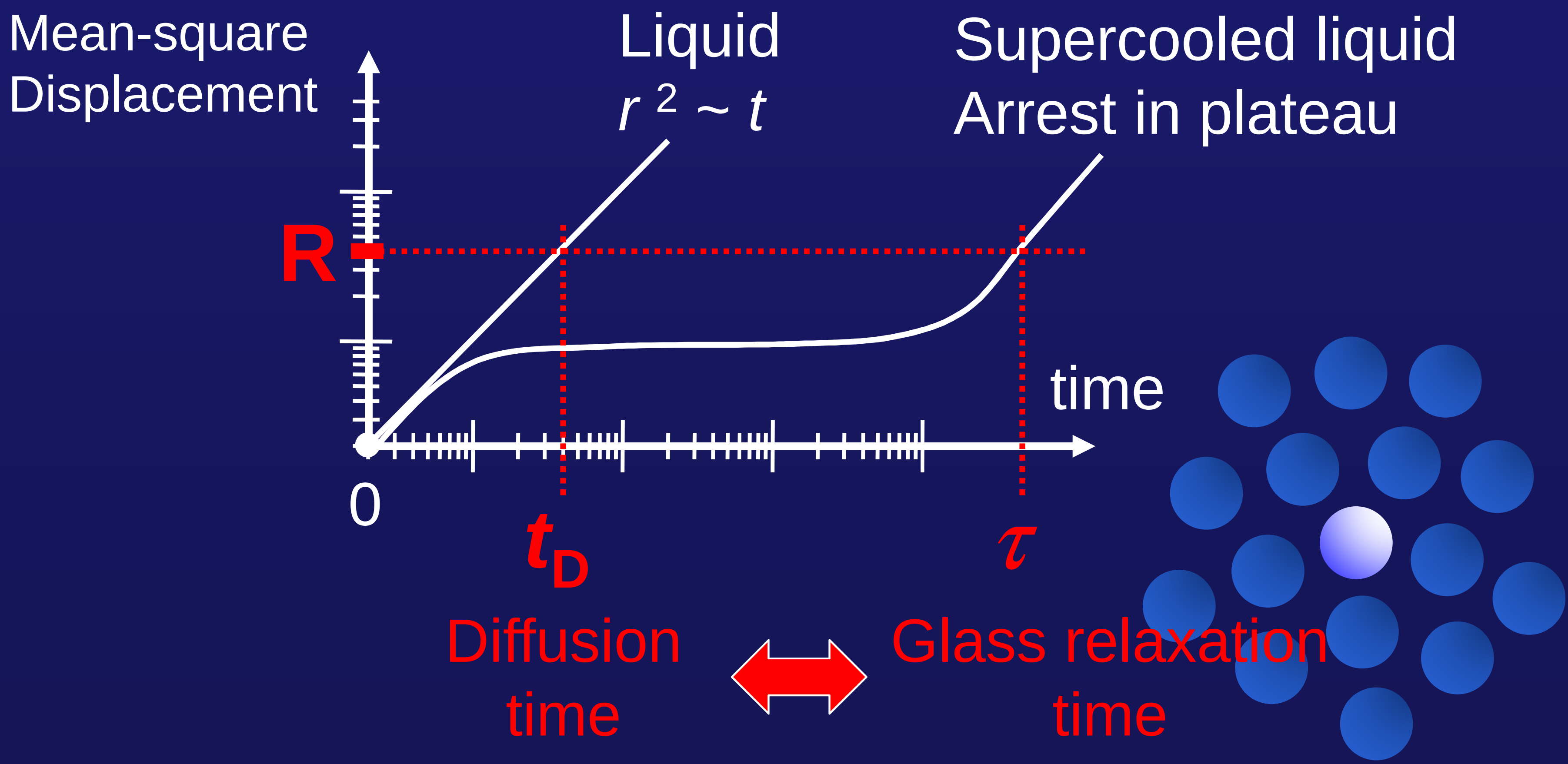


(Alder, Wainwright 1957)

Single Particle Dynamics

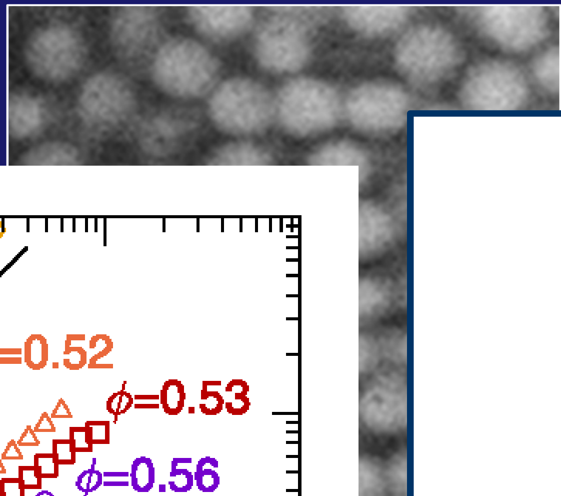
Diffusion

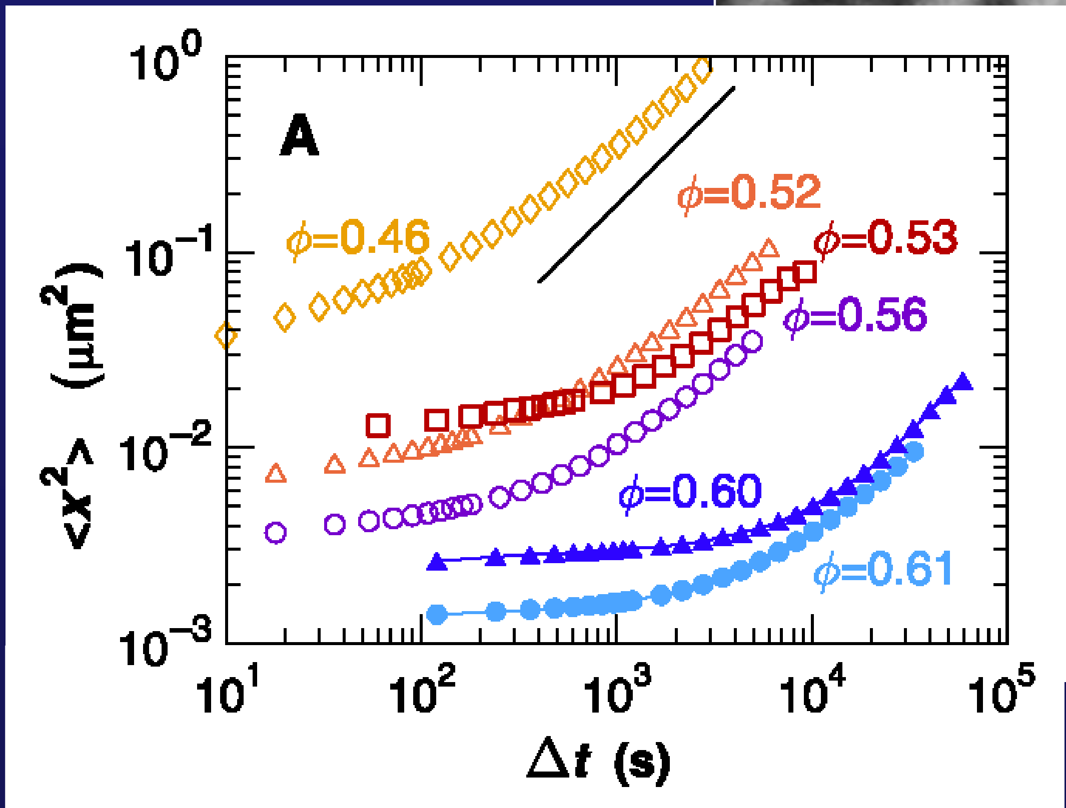
(Molecules or small particles in a supercooled liquid)

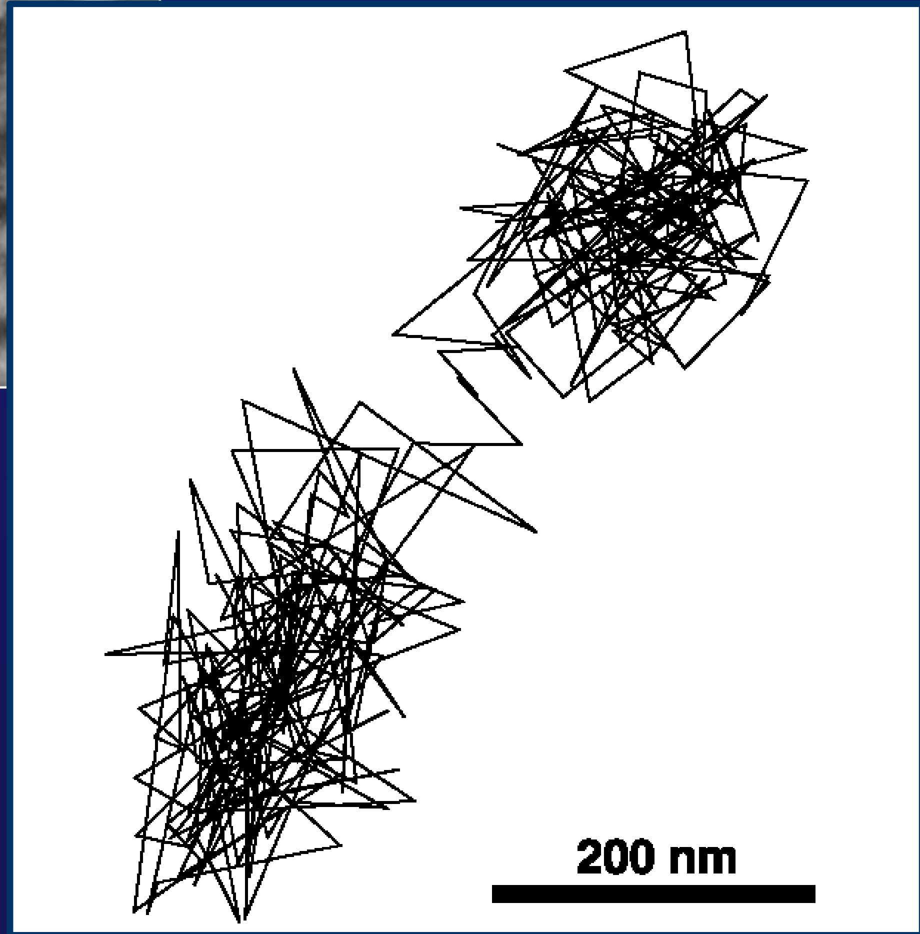


Supercooled Liquids

Dynamic Measurements ...

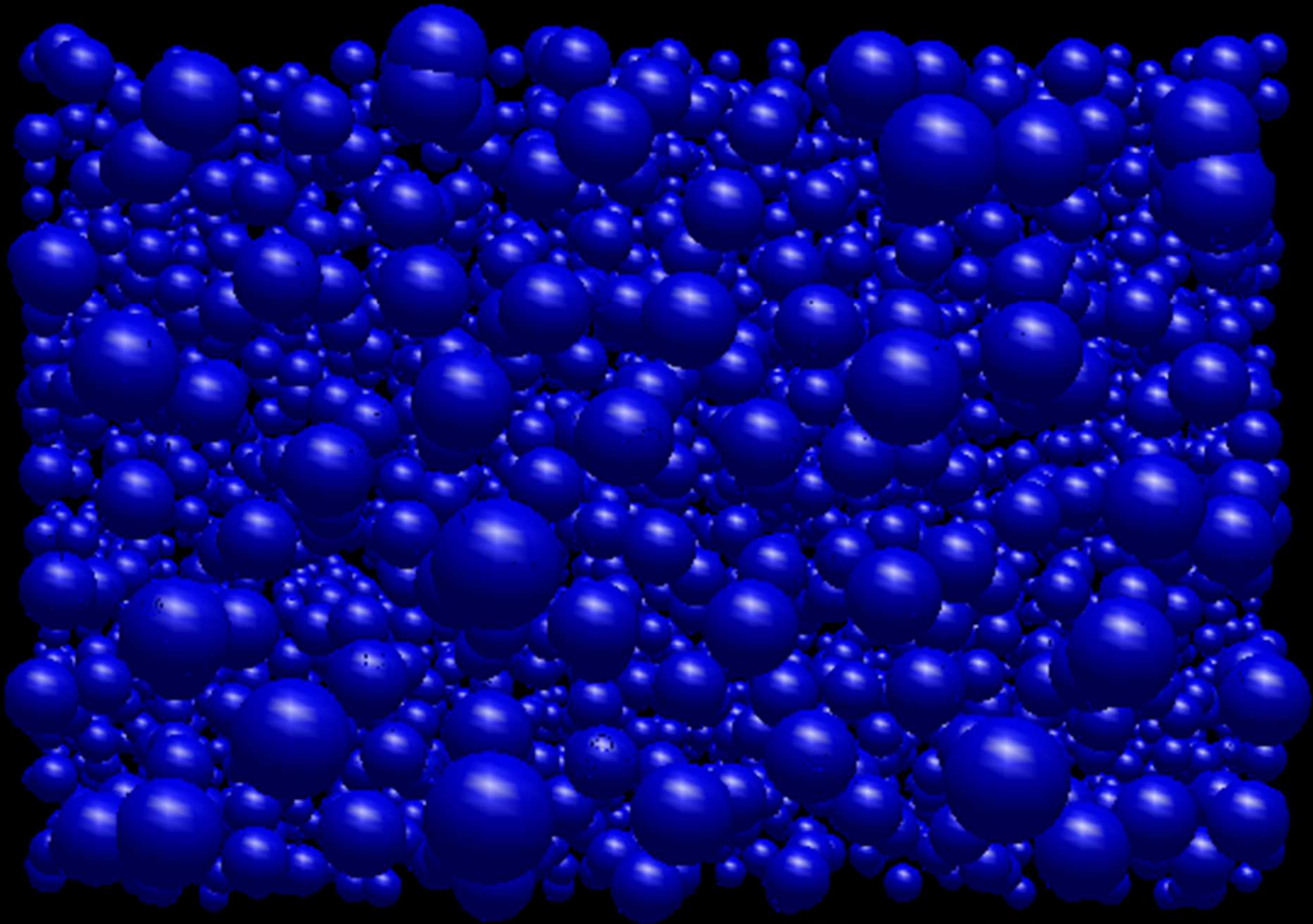






Weeks *et al.* Science (2000)

Insight into Flow Phenomena …



Harvard MRSEC, **Schall,** Spaepen, Weitz

Food

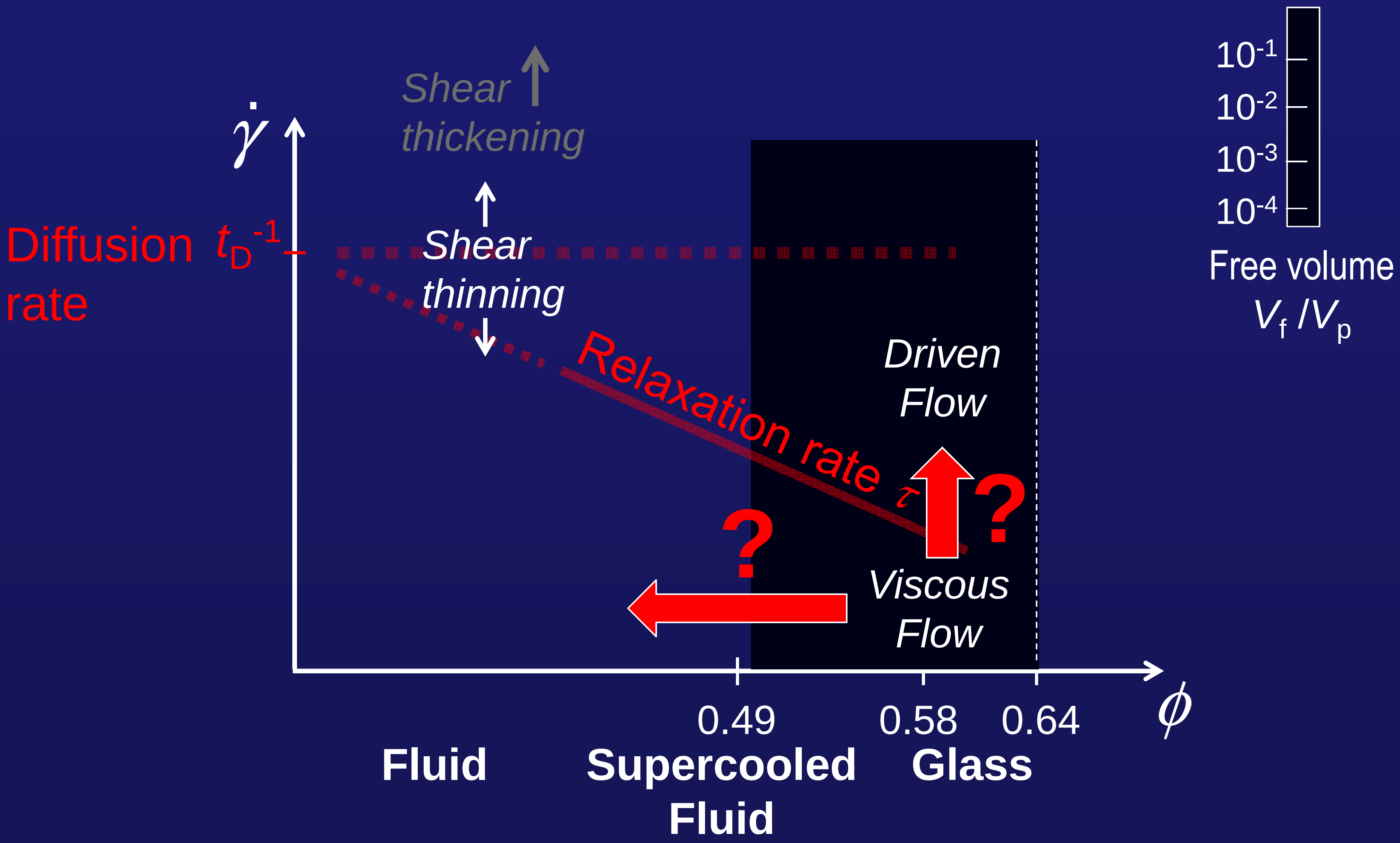
Personal care products

… and Applications

Paint

Processing Construction

Suspension Flows



Glassy Flow - Basics

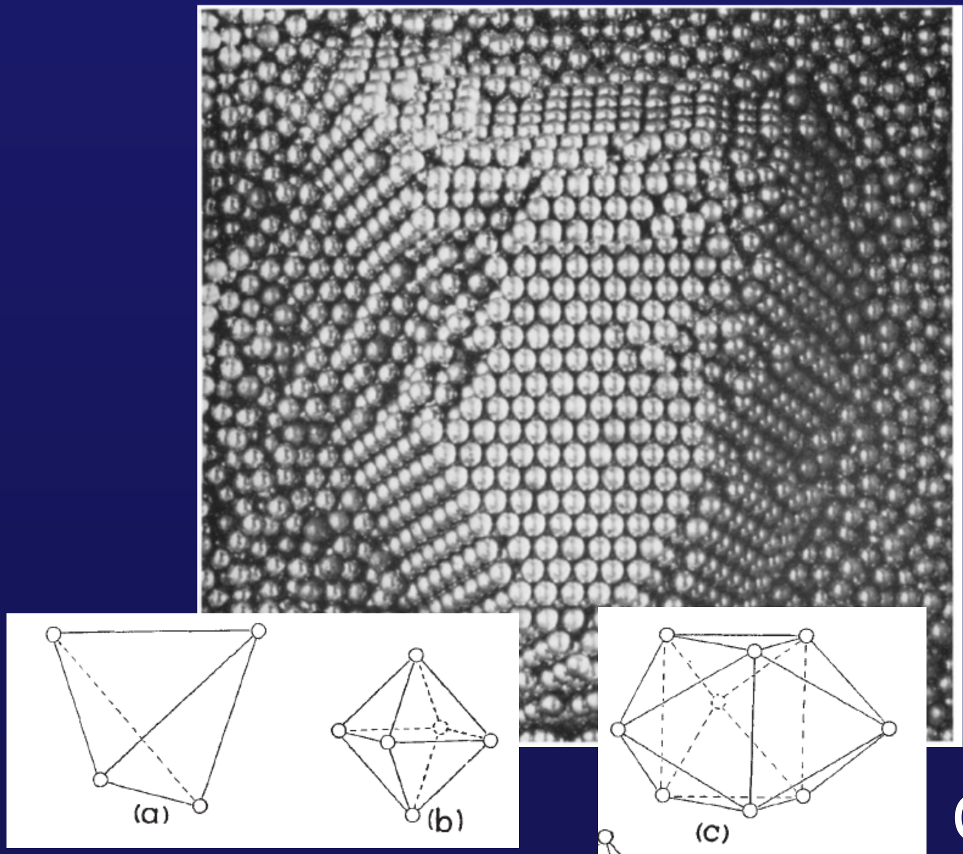
i. **Free volume**

Free Volume Theory

Hard Spheres

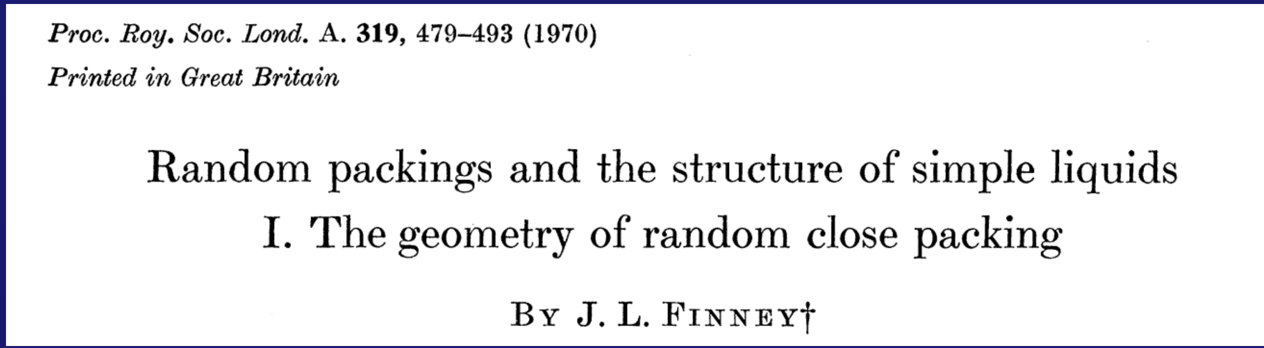
Bernal

The structure of liquids *et al.* 1960s



Canonical Holes

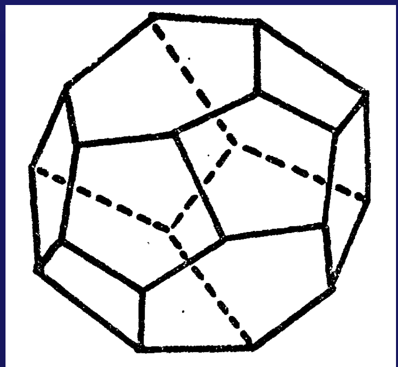
Model systems: Hard spheres

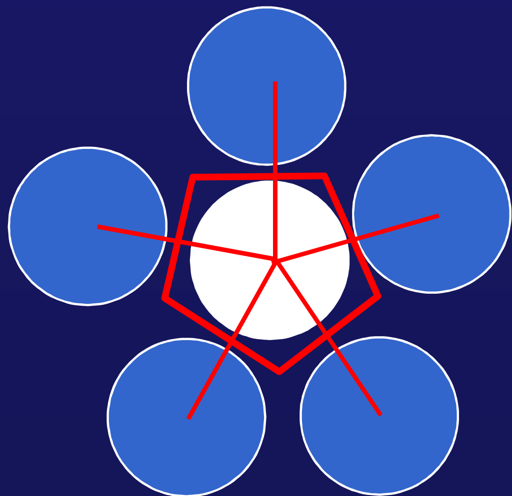

Proc. Roy. Soc. Lond. A. **319**, 479–493 (1970)
Printed in Great Britain

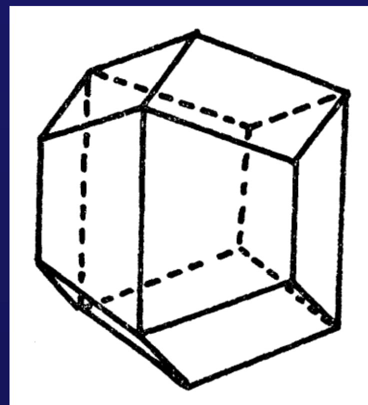
Random packings and the structure of simple liquids
I. The geometry of random close packing

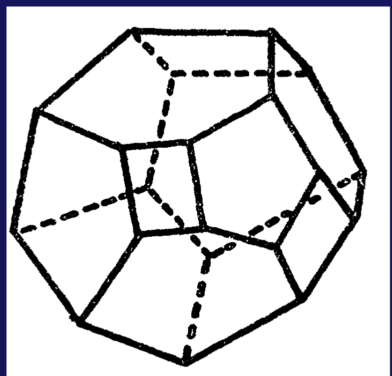
By J. L. Finney†

Voronoi Volume

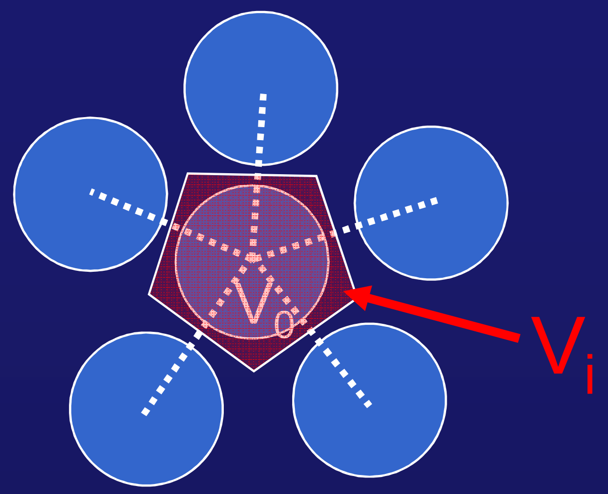








Free Volume Theory

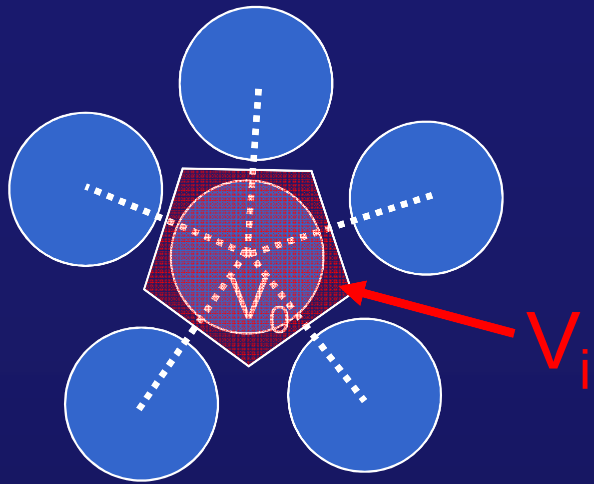


Free Volume $V_f \sim (V_i - V_0)$

Free Volume Theory:

$P(V_f) \sim \exp(-V_f / \langle V_f \rangle)$

Free Volume Theory



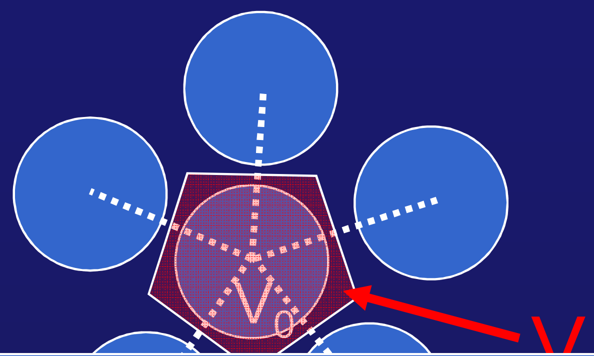
Rearrangements occur if $V_f \sim V_0$

Viscosity $\eta \sim P\,(V_f \sim V_0)^{-1}$

$\sim \exp(+\delta V_0/\langle V_f \rangle)$

~1

Free Volume Theory



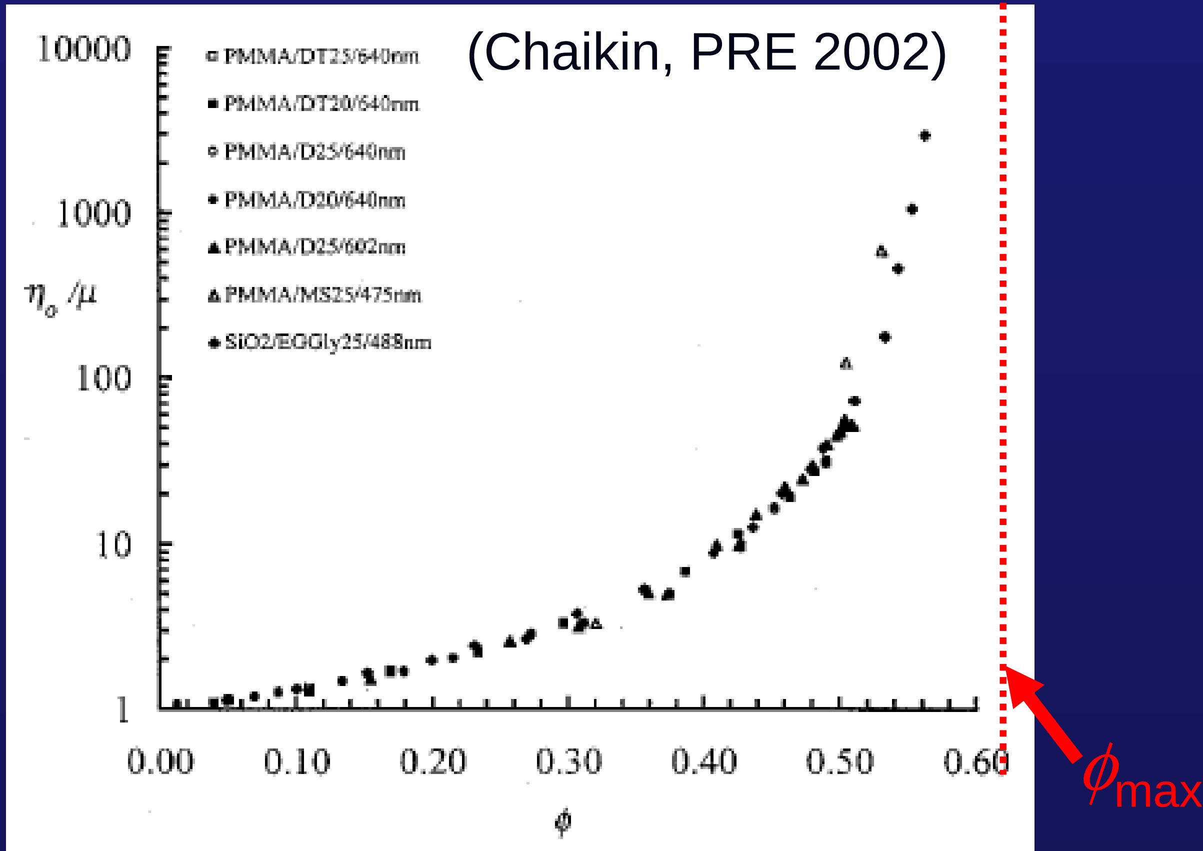
Big success
of free volume theory!

$$\frac{\langle V_f \rangle}{V_0} \propto T - T_0$$

Viscosity $\eta = \eta_0 \, exp\left(\frac{B}{T - T_0}\right)$

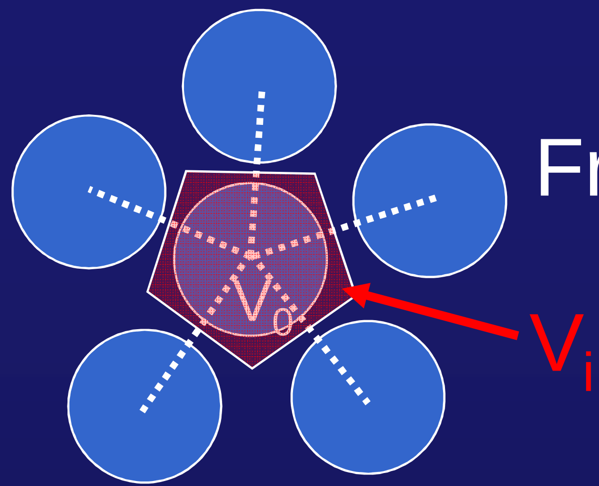
Free Volume Theory

Suspensions



1 / (Temperature) ⟺ Volume fraction ϕ

Free Volume Theory

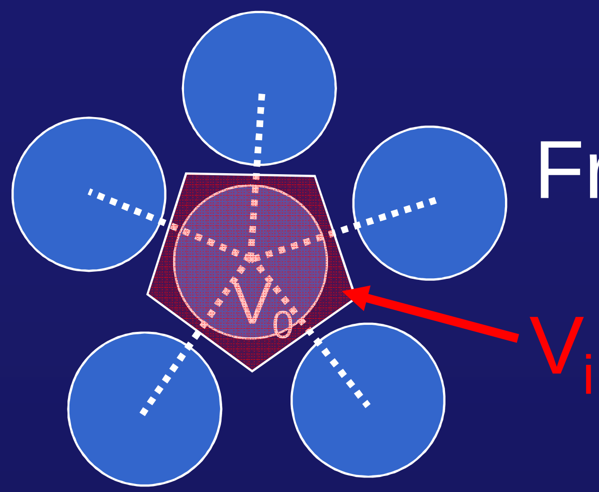


Max. Packing Fraction $\phi_m \sim 0.64$

Free volume: $\frac{\langle V_f \rangle}{V_0} = ???$

Viscosity: $\eta = ???$

Free Volume Theory

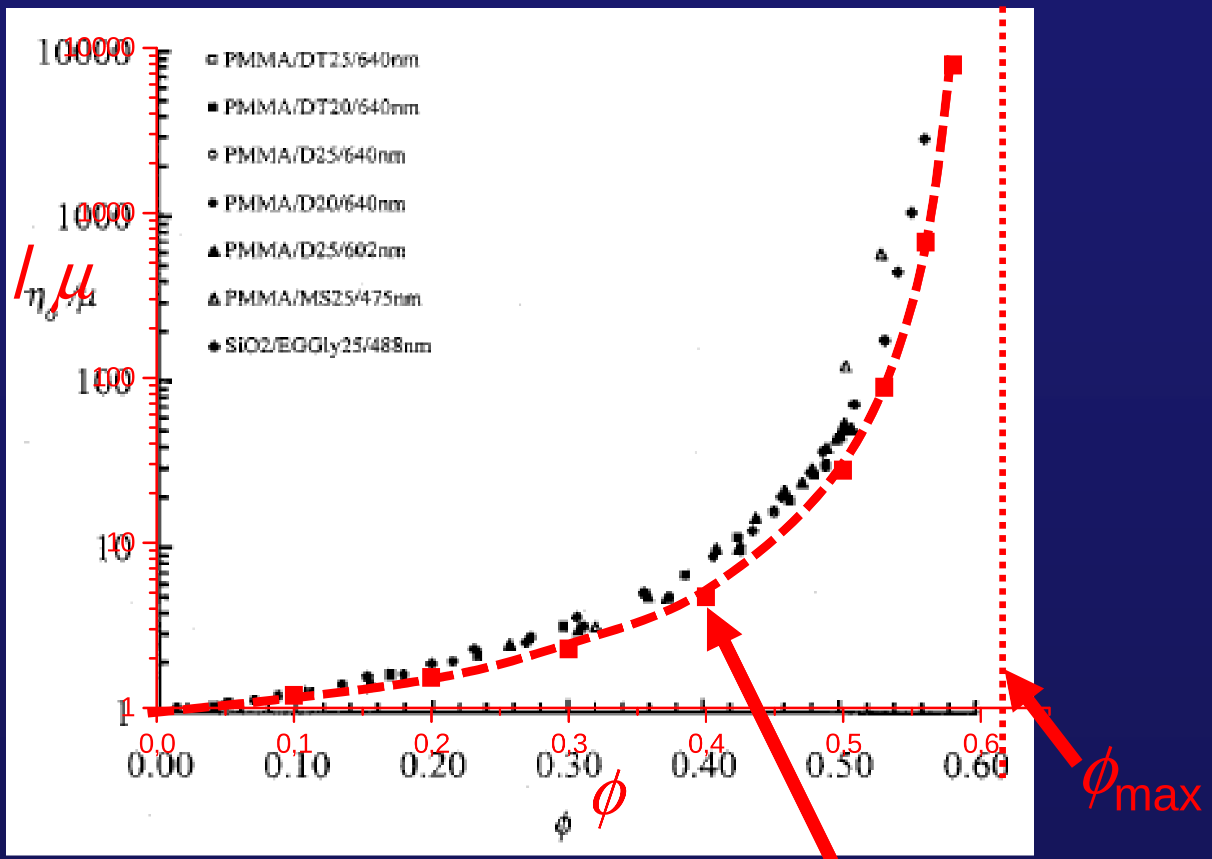


Max. Packing Fraction $\phi_m \sim 0.64$

Free volume: $$\frac{\langle V_f \rangle}{V_0} = \frac{1}{\phi} - \frac{1}{\phi_m} = \frac{\phi_m - \phi}{\phi \phi_m}$$

Viscosity: $$\eta = \eta_0 \, exp\left(\frac{\delta \phi \phi_m}{\phi_m - \phi}\right)$$

Free Volume Theory: Suspensions



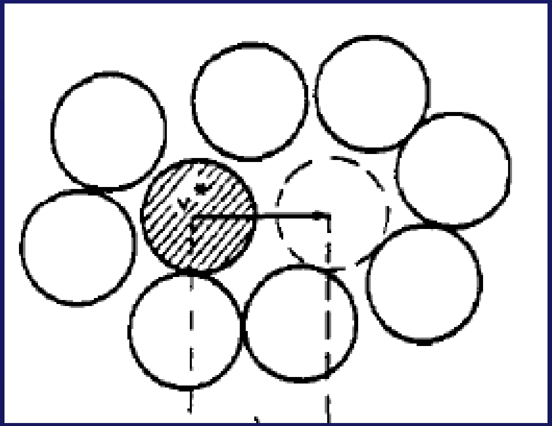
$$\eta = \eta_0 \, exp\left(\frac{\delta\phi\phi_m}{\phi_m - \phi}\right)$$

(Cheng, Chaikin, PRE 2002)

Flow : Constitutive description

$$\dot{\gamma} = \left(\text{Fraction f of flow spot} \right) \cdot \left(\text{Strain per STZ} \right) \cdot \left(\text{Jump Rate} \right)$$

(Spaepen Acta Met. 1977)



1. Free volume Theory

$$f = \int_{v^*}^{\infty} p(v)dv = exp\left(-\frac{\gamma v^*}{v_f}\right)$$

2. Strain per STZ

$$\varepsilon_0 \sim 1$$

3. Jump Rate

$$R = \nu_0 \, exp\left(-\frac{\Delta G}{kT}\right)$$

Applied Stress σ

$$\nu_0 exp\left(-\frac{\Delta G - \tau\Omega/2}{kT}\right) \quad \text{(forward)}$$

$$\nu_0 exp\left(-\frac{\Delta G + \tau\Omega/2}{kT}\right) \quad \text{(backward)}$$

Flow : Constitutive description

$$\dot{\gamma} = \left(\text{Fraction f of flow spot} \right) \cdot \left(\text{Strain per STZ} \right) \cdot \left(\text{Jump Rate} \right)$$

(Spaepen Acta Met. 1977)

$$\dot{\gamma} = f \cdot \epsilon_0 \cdot \nu_0 \cdot sinh\left\{\frac{\sigma\Omega}{2kT}\right\} exp\left\{-\frac{\Delta G}{kT}\right\}$$

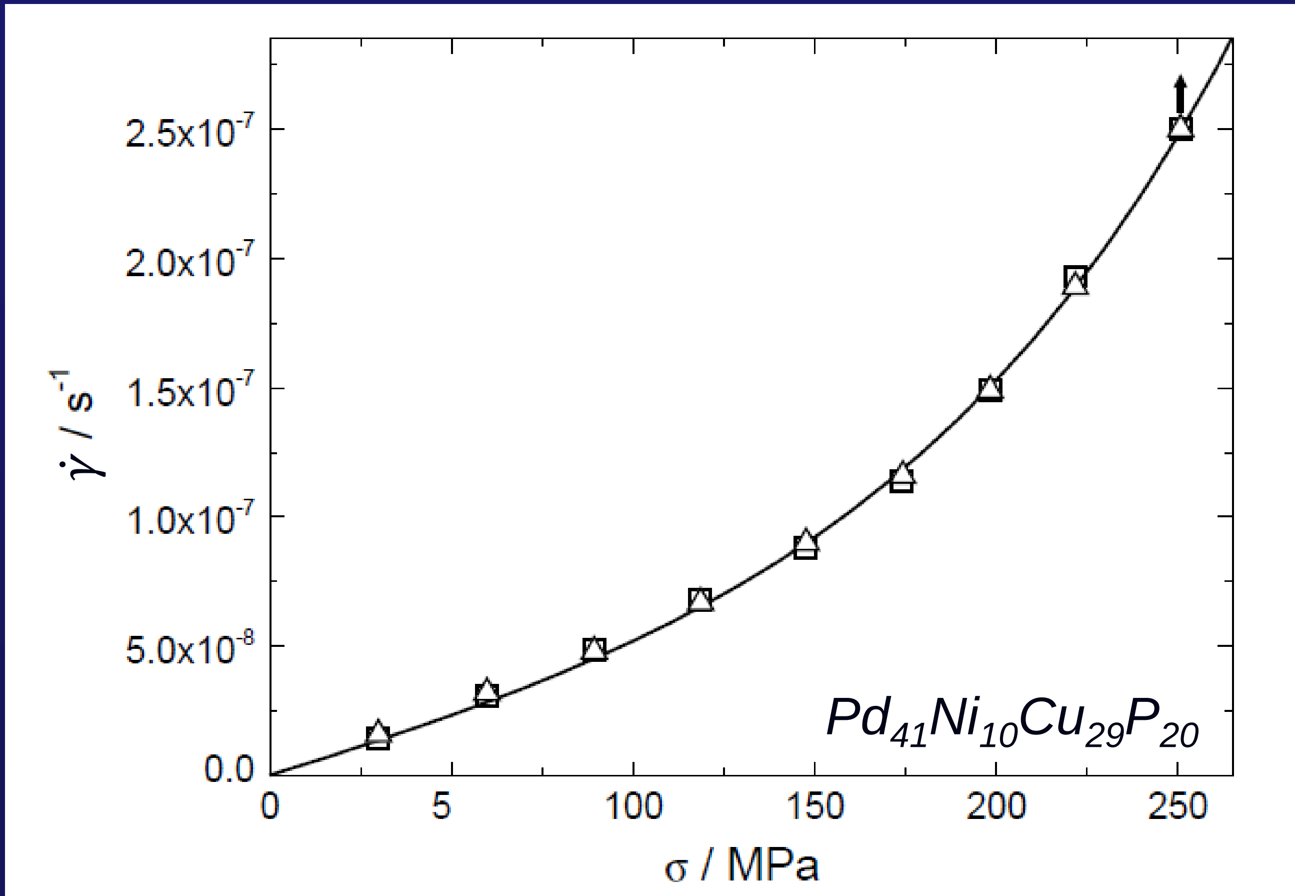
$$= f \cdot \epsilon_0 \cdot \nu_0 \cdot \frac{\sigma\Omega}{2kT} exp\left\{-\frac{\Delta G}{kT}\right\}$$

sinh(x) ~ x

$$\propto \boldsymbol{\sigma}$$

Flow : Constitutive description

Models Creep of Bulk Metallic Glass



Heggen *et al.* 2003

T = 550K

Local Correlation

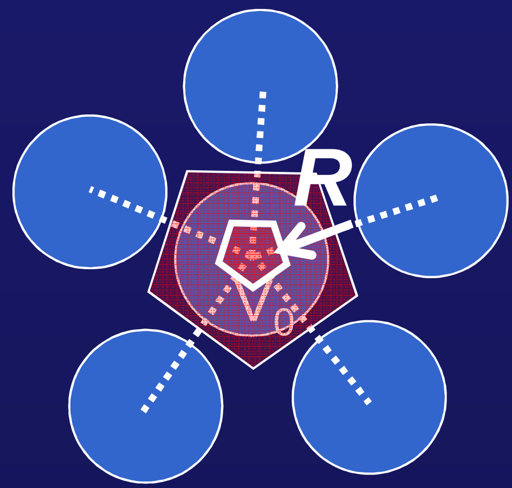
Shear Modulus ⟺ **Free Volume**

From thermal fluctuations

$<\varepsilon_{ij}^2>_t$

$$k_B T = \frac{1}{2}\,\mu <\varepsilon_{ij}^2>_t$$

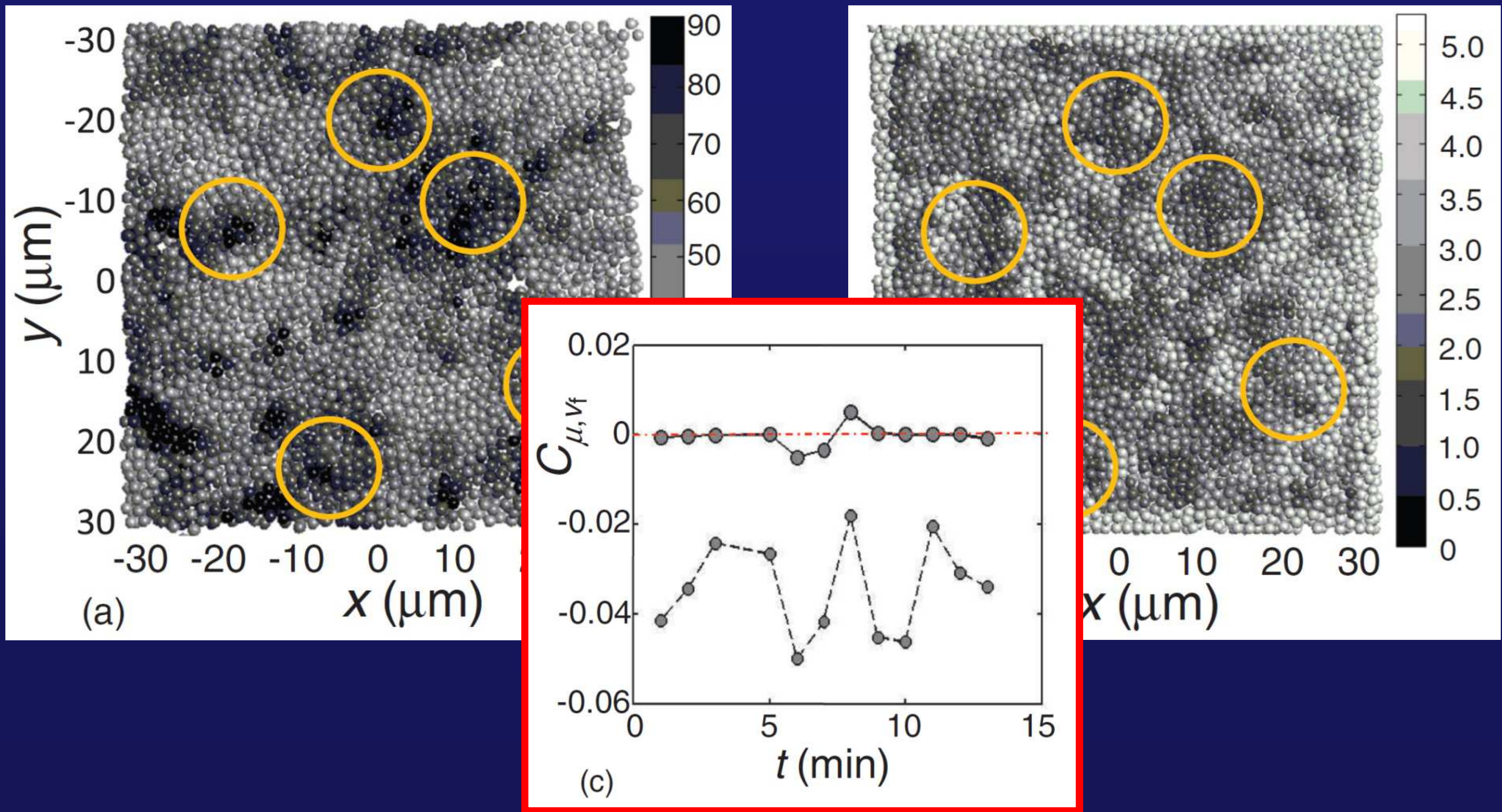
From Voronoi volume



Rahmani *et al. Phys Rev. E* (2014)

Local Correlation

Shear Modulus μ [$k_B T/R^3$]   Free Volume V_f [$10^{-3}V_0$]



Rahmani *et al. Phys Rev. E* (2014)

Glassy Flow - Basics

i. **Correlations**

$T \rightarrow T_g$ ⇨ Increasing cooperativity

Adam & Gibbs (1965)

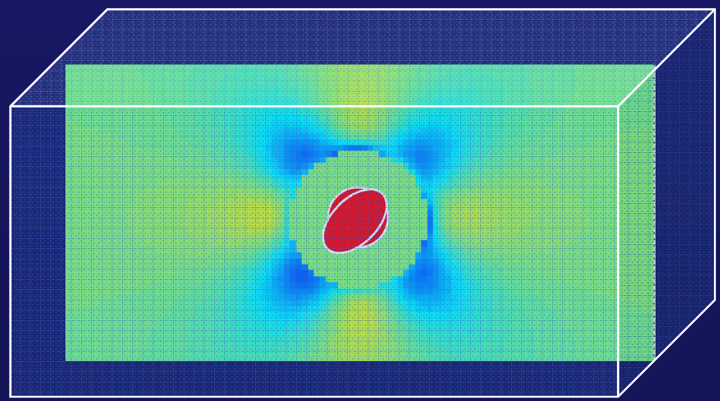
Elastic Field

The determination of the elastic field of an ellipsoidal inclusion, and related problems

By J. D. Eshelby

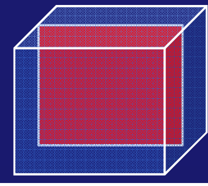
Department of Physical Metallurgy, University of Birmingham

(*Communicated by R. E. Peierls, F.R.S.—Received* 1 *March* 1957)



Elastic continuum

Elastic Field



Displacements

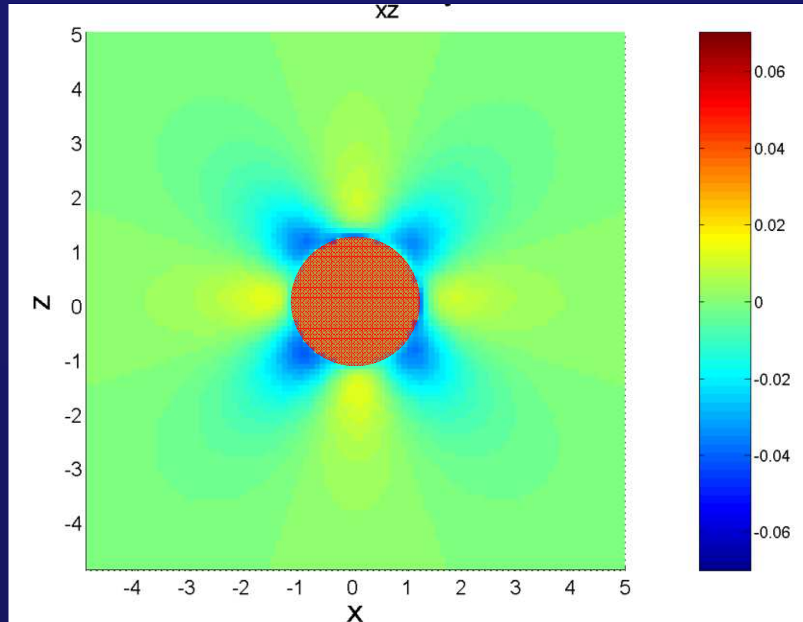
$$u_1 = Aa^3\left\{\frac{x_3}{r^3} + 6c(r^2 - a^2)\left(\frac{5x_1^{\,2}x_3}{r^7} - \frac{x_3}{r^5}\right)\right\}$$

$$u_2 = Aa^3\left\{6c(r^2 - a^2)\left(\frac{5x_1x_2x_3}{r^7}\right)\right\}$$

$$u_3 = Aa^3\left\{\frac{x_1}{r^3} + 6c(r^2 - a^2)\left(\frac{5x_1x_3^{\,2}}{r^7} - \frac{x_1}{r^5}\right)\right\}$$

(Hutchinson 2006)

Strain Field

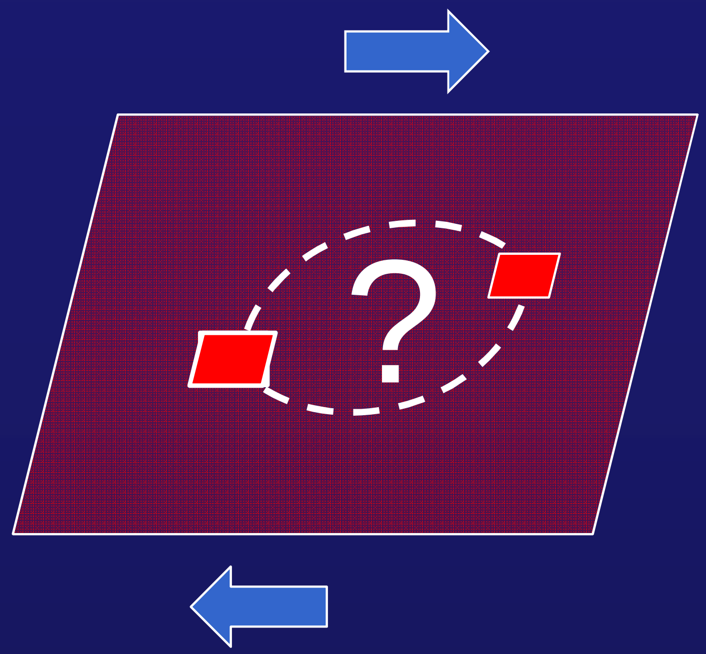


Strain Field $\epsilon_{xz} \propto \frac{1}{r^3}$

→ long-range

→ Correlations between flow spots?

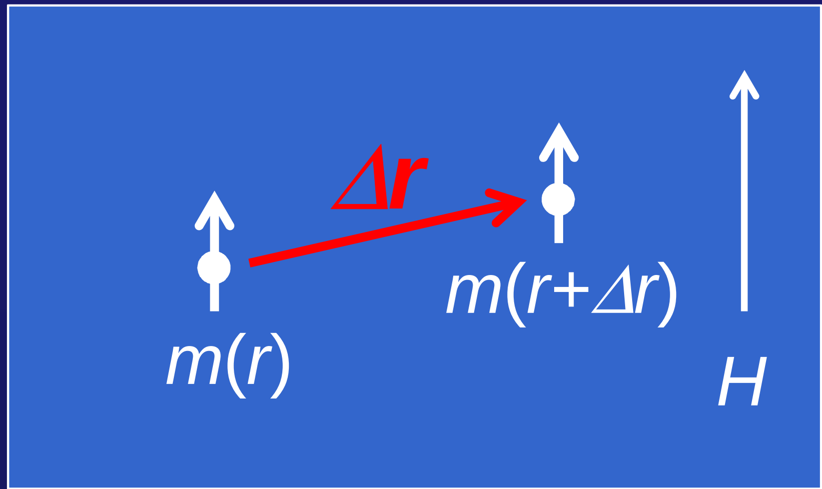
Elastic Correlations



Internal coupling in external field

Analogy: Magnetic Coupling

Magnetic spins in external field



Correlation function

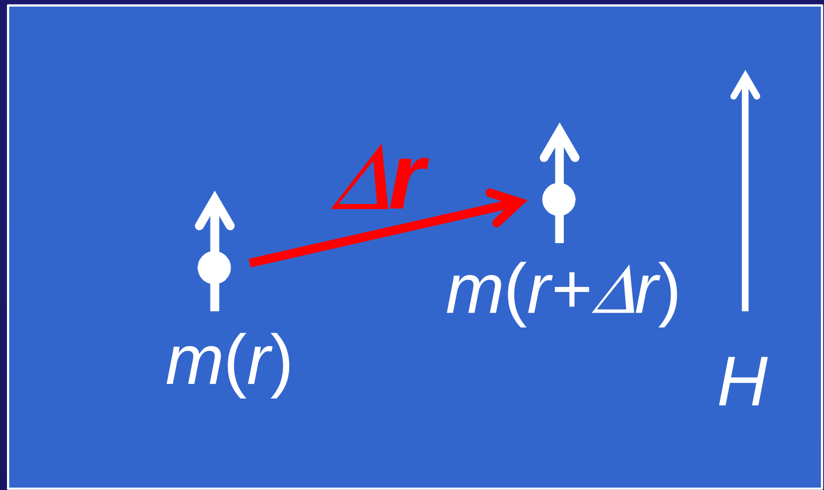
$$C_m(\Delta r) = \langle m(r) \cdot m(r + \Delta r) \rangle_r$$

Susceptibility

$$\chi_m = \int C_m(r)\, dV$$

Analogy: Magnetic Coupling

2nd Order Phase Transitions



Critical Scaling close to T_c

$$C_m(r) \propto r^{-\lambda} \, exp(-r/\xi)$$

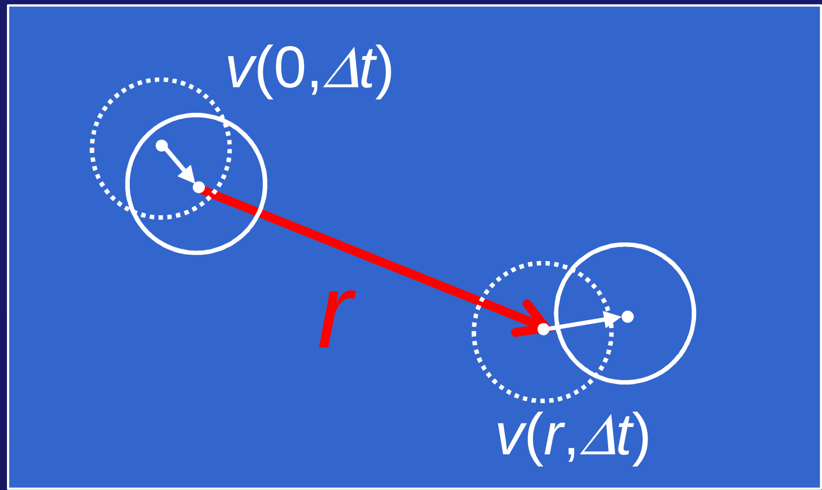
Correlation length

Divergence of

- Correlation length $\xi \propto |T - T_c|^{-\nu}$
- Susceptibility $\chi_m \propto |T - T_c|^{-\mu}$

Glasses: Dynamic correlations

Dynamic correlation function



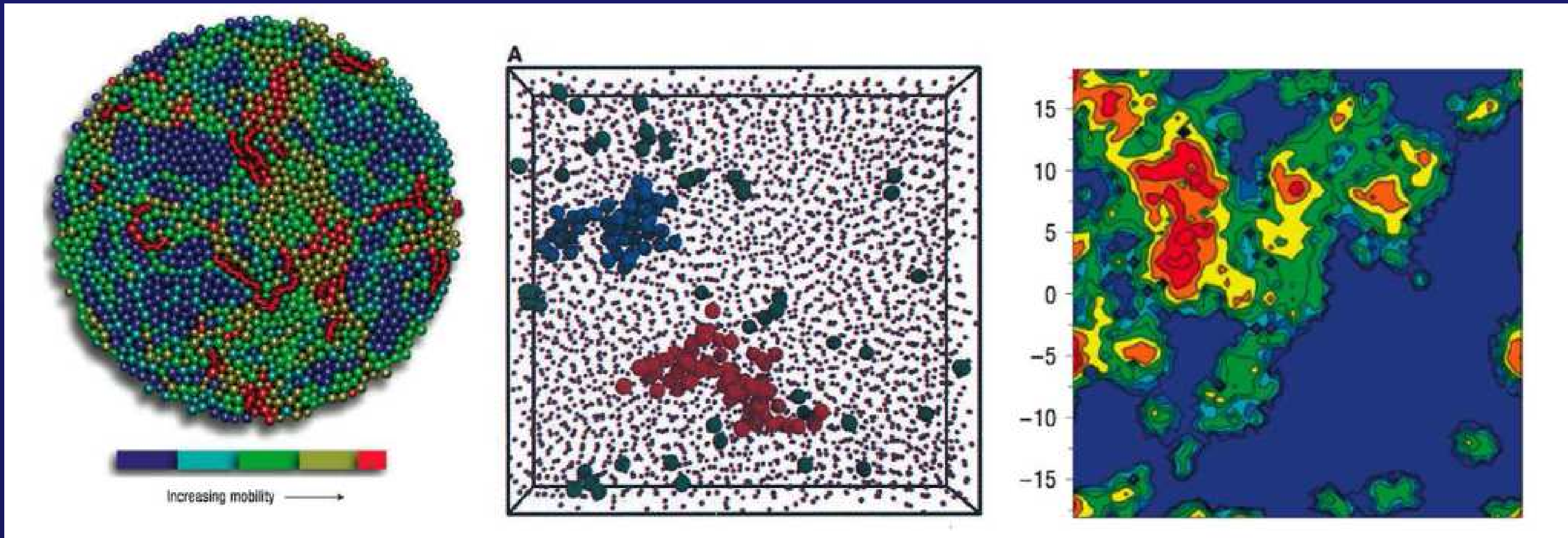
4-point correlation function

$$G_4(r,\Delta t) = \langle v(0,\Delta t) \cdot v(r,\Delta t) \rangle$$

Dynamic susceptibility

$$\chi_4 = \int G_4(r,\Delta t)\, dr$$

Glasses: Dynamic correlations



Granular fluid of ball bearings

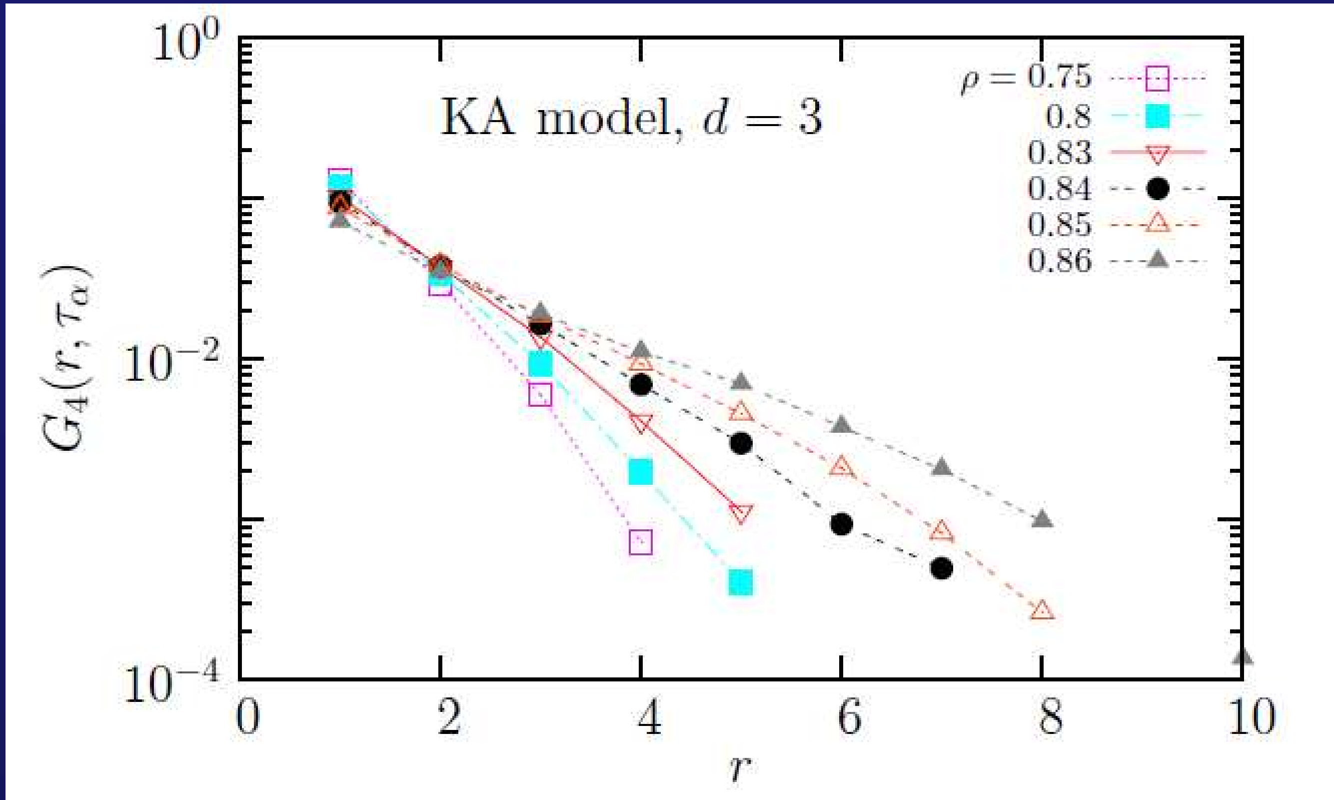
Colloidal glass

Computer simulation 2D repulsive discs

Dynamical criticality?

$$G_4 \propto r^{-\lambda}\ e^{-r/\xi_4}$$

Glasses: Dynamic correlations

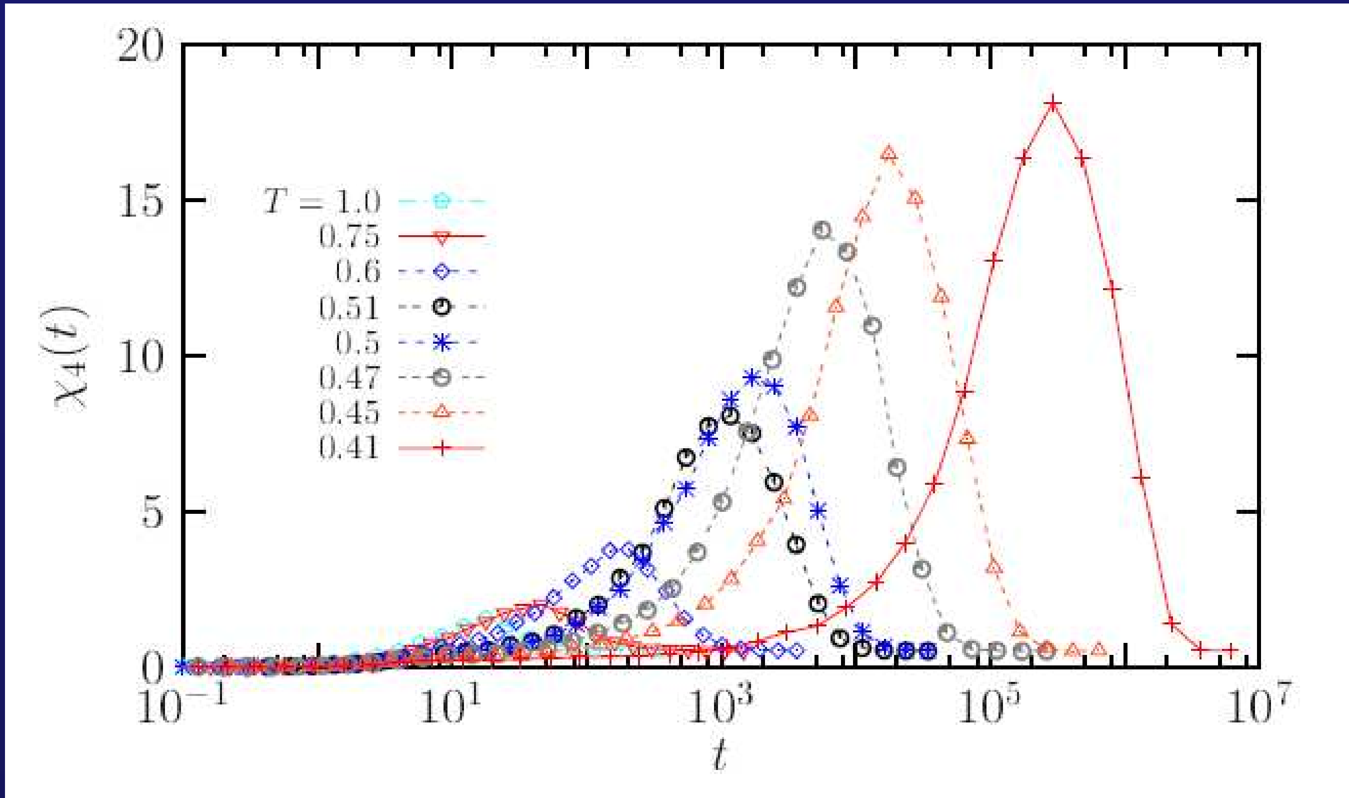


Berthier *et al.* PRL 2003

Dynamical criticality?

$$G_4 \propto r^{-\lambda} \; e^{-r/\xi_4}$$

Glass transition: critical phenomenon?



No true divergence for quiescent glass

Summary

- Glasses
  Liquid and Solid, depending on time scale
- Flows
  Liquid/Glassy, Flow rate ~ t_D^{-1}, τ_D^{-1}
- Structural ingredient
  Free volume ⟺ local modulus
- Correlations
  Elastic field ⇨ Coupling ⇨ Self-Organization?