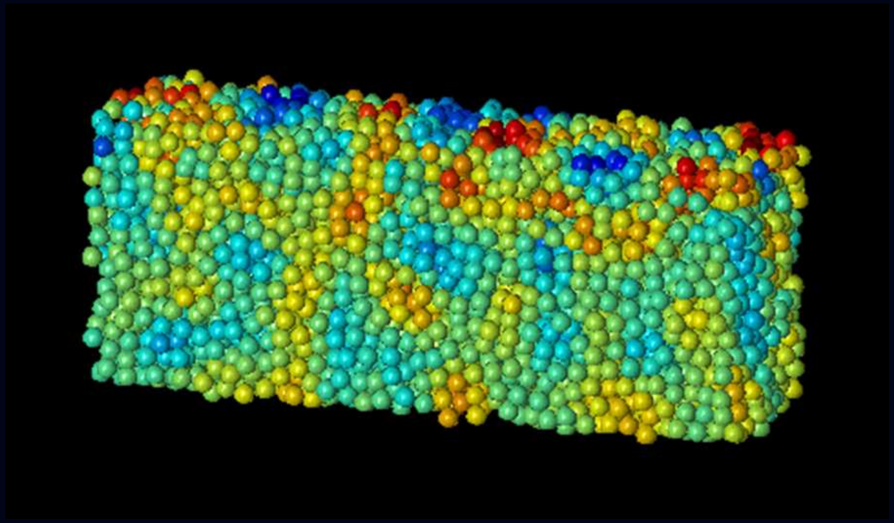
JMBC Workshop

Jamming and glassy behavior in colloids

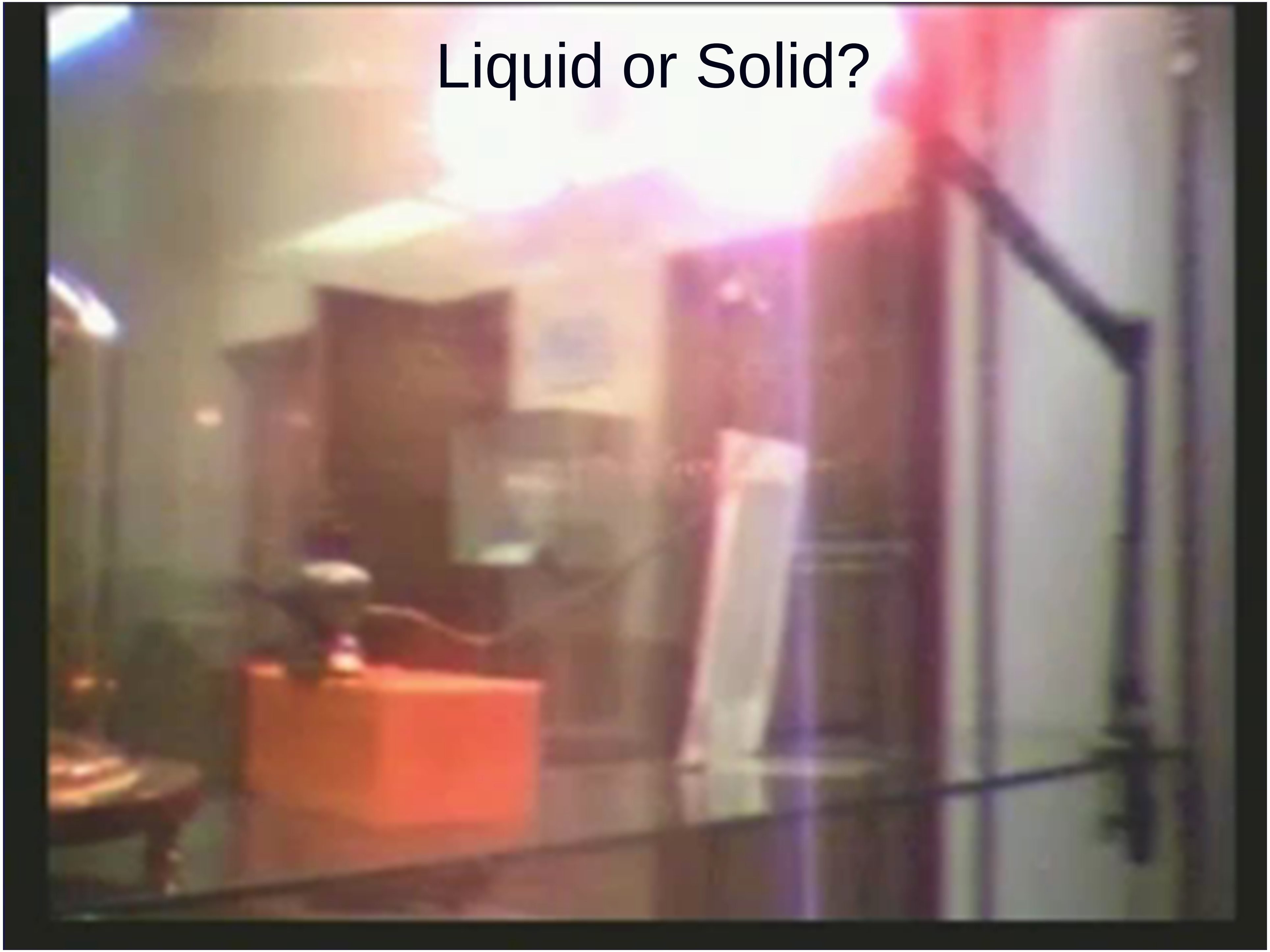
Peter Schall
University of Amsterdam



Jamming and glassy behavior in colloids

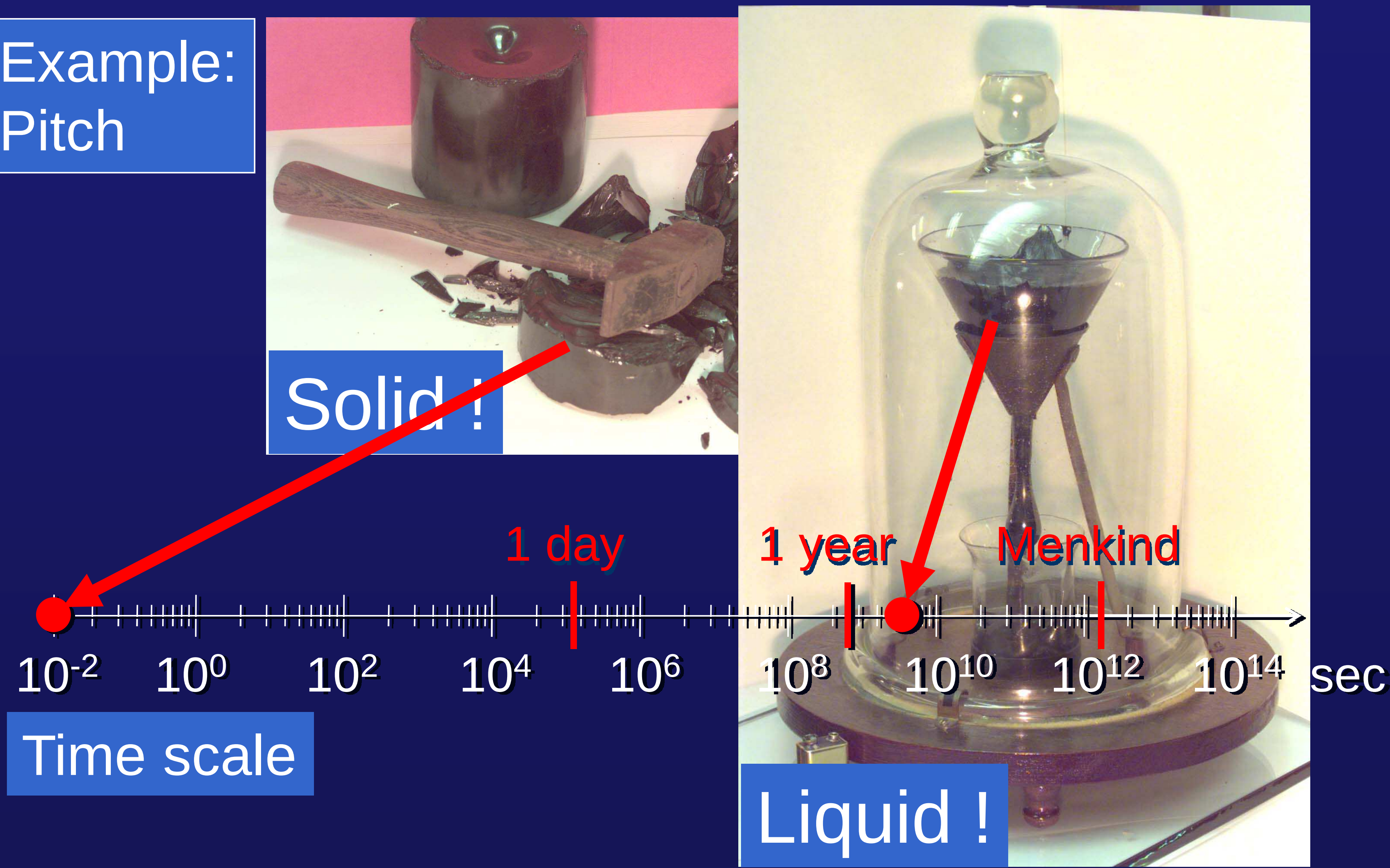
1. Glasses: Some concepts
2. Flow of Glassy Materials
3. Insight from Colloidal Glasses

Liquid or Solid?



Liquid or Solid?

Example: Pitch



Fundamental Transition

Elastic solid → **Viscous Liquid**

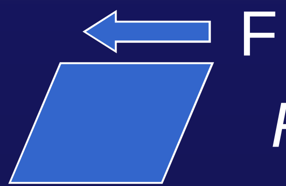
Elastic solid
Reversible, Memory
Elastic Modulus μ

Viscous Liquid
Irreversible, random
diffusive, Viscosity η

<u>Symmetry change</u>

Temporal symmetry

Elastic

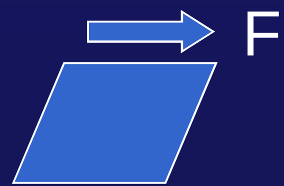


$F(-t) = F(t)$

Energy storage

Plastic

$F(-t) = - F(t)$

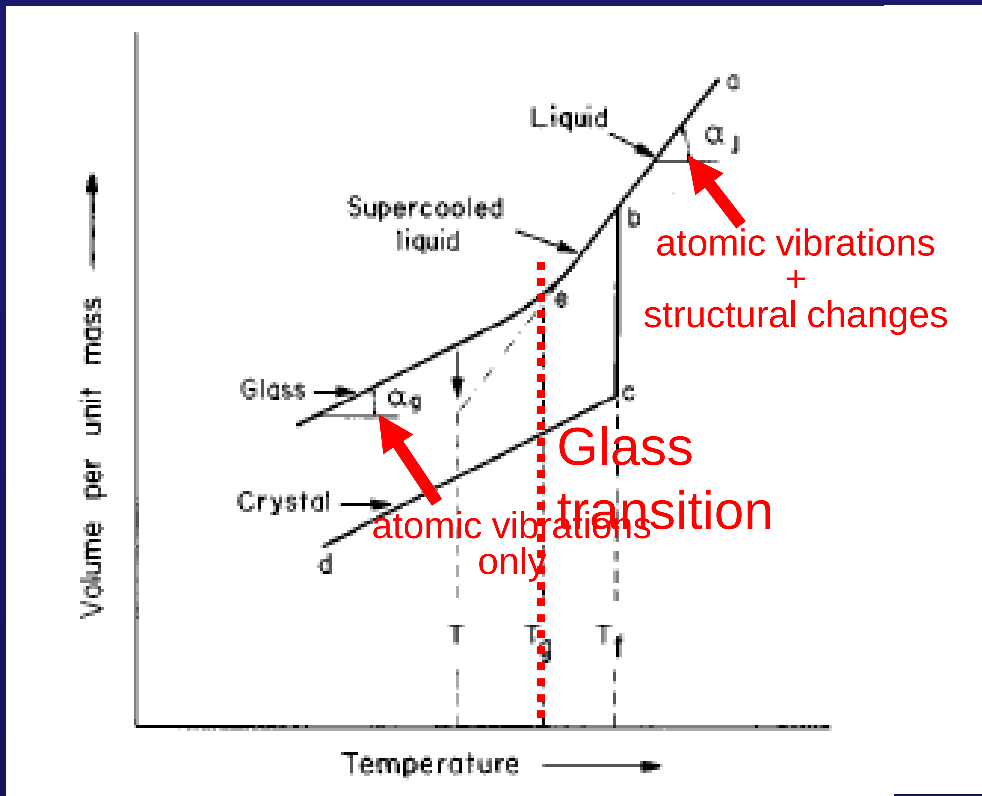


Energy loss


Dynamic Arrest

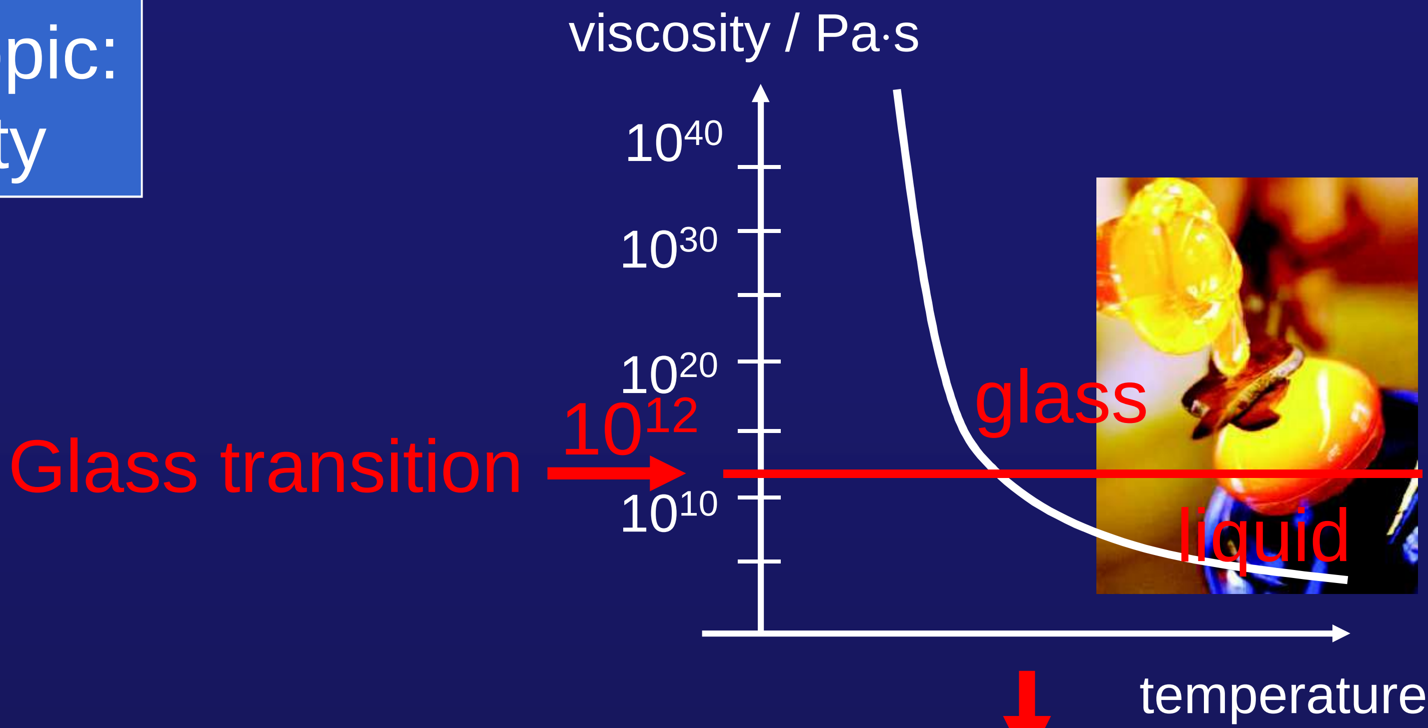
Glass Formation

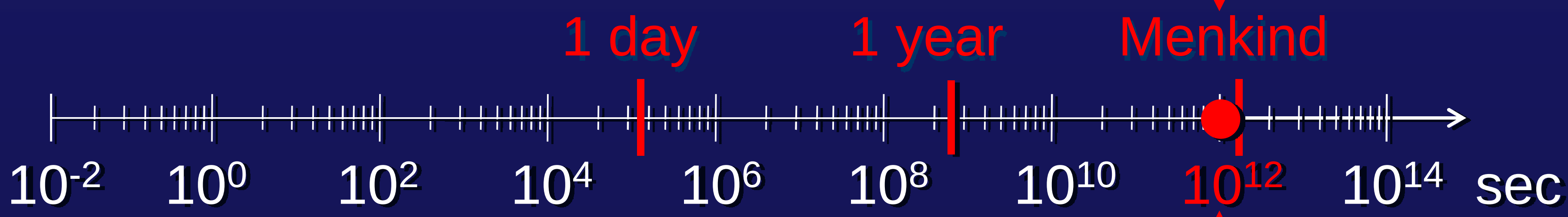
Cooling from Liquid



Viscosity and Diffusion

Macroscopic: Viscosity

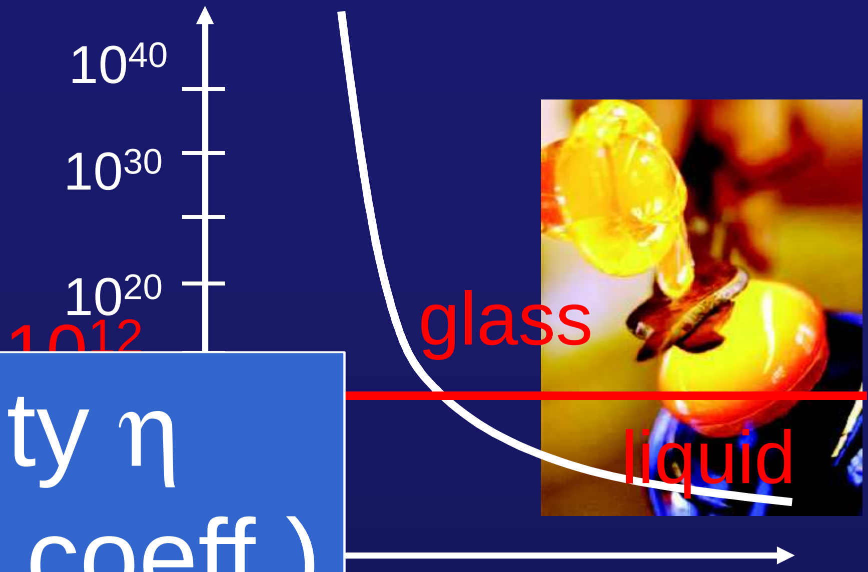




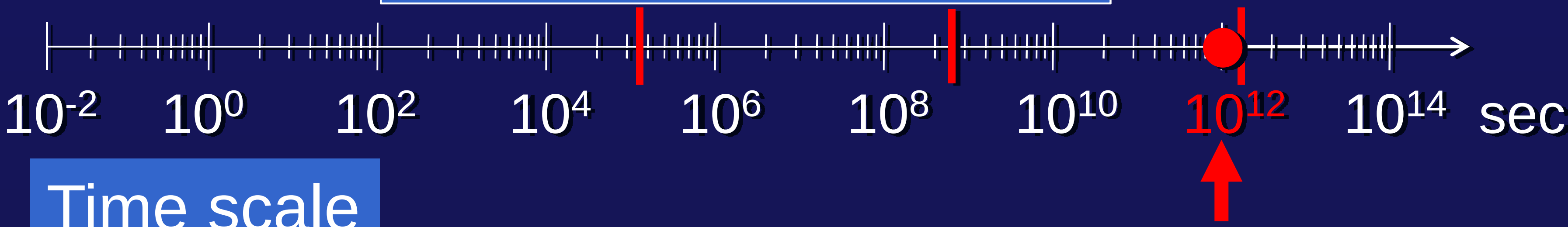
Time scale

Viscosity and Diffusion

Macroscopic: Viscosity



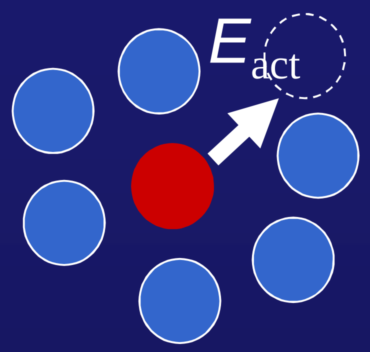
Viscosity η
~ 1/D (diff.coeff.)
~ τ (relax.time)



Time scale

Viscosity and Diffusion

Simple Liquids: Arrhenius

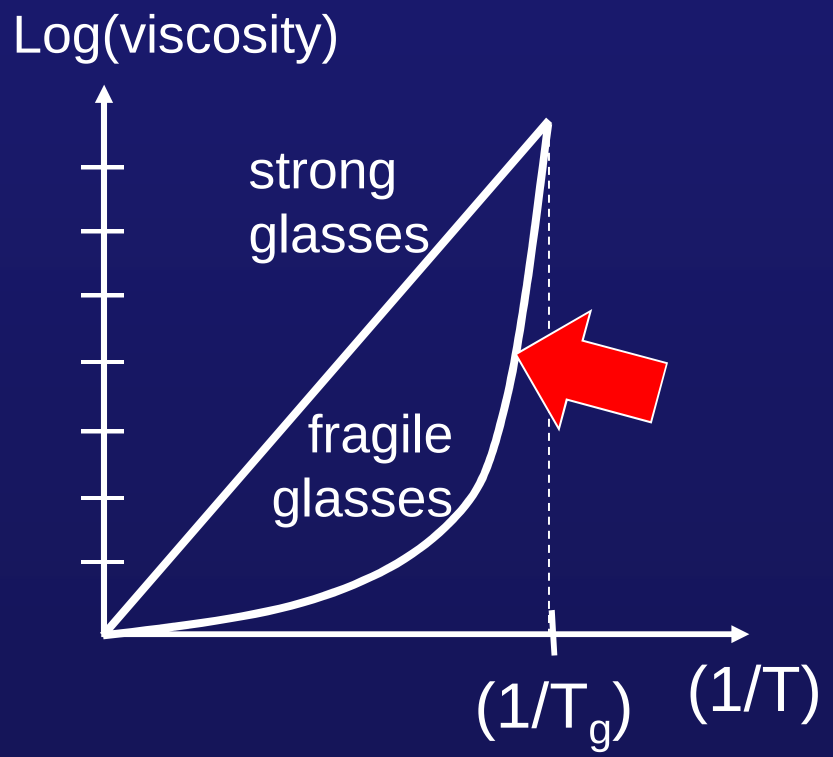


Diffusion coefficient

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

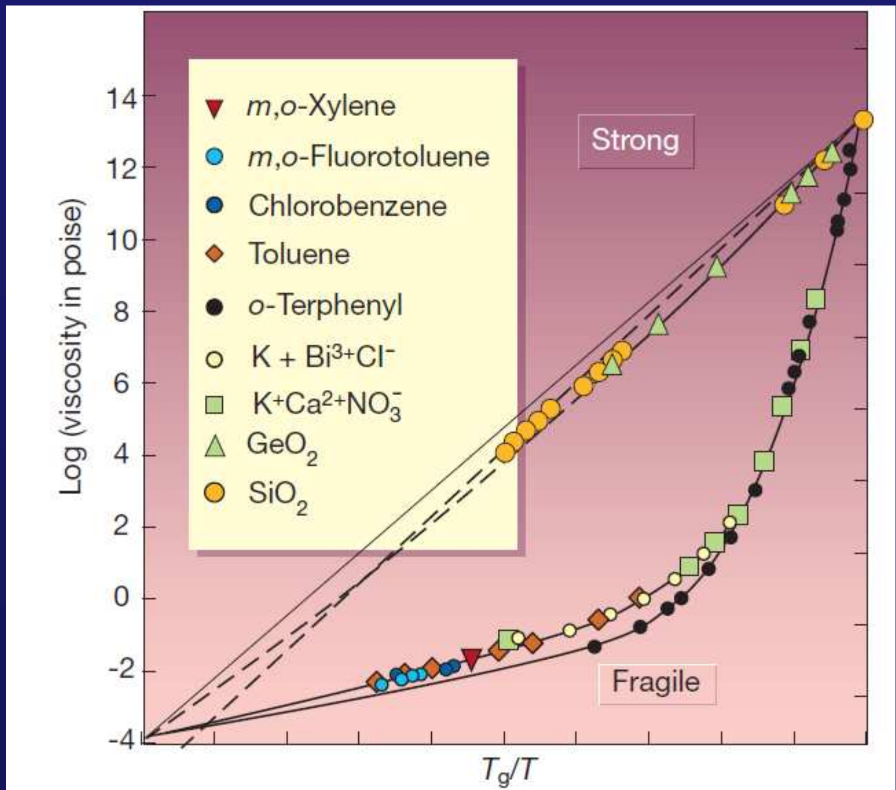
Viscosity

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



Strong and Fragile Glasses

“Angel plot“



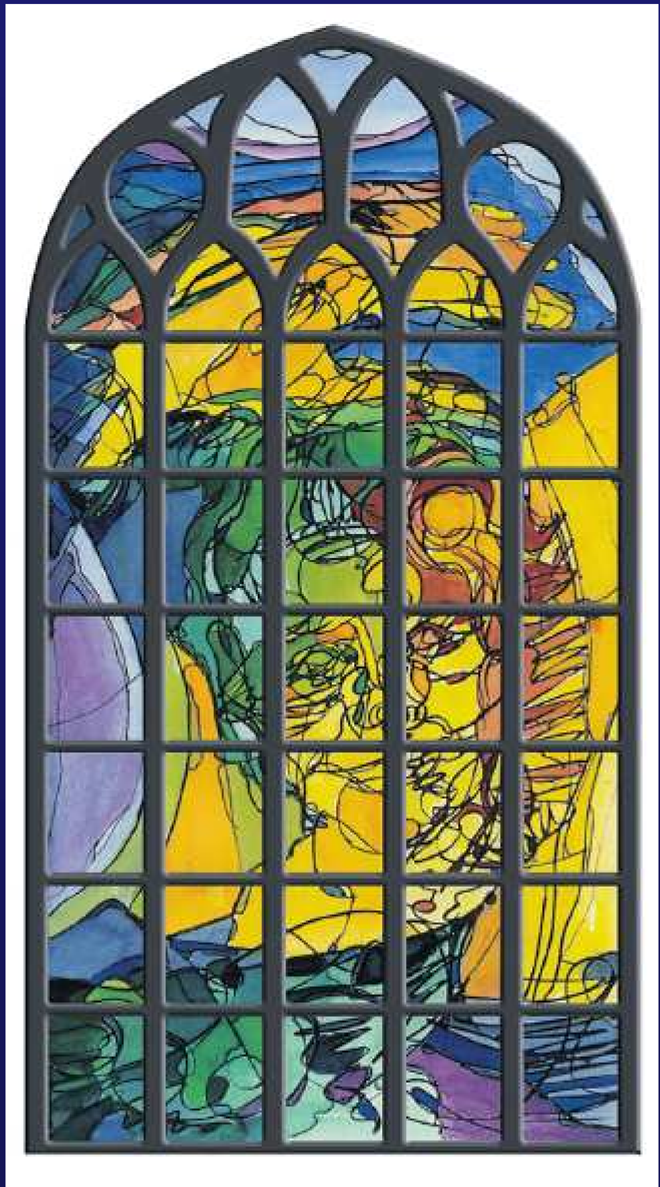
Arrhenius

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

Vogel-Fulcher-Tamman

$$\eta = \exp(A + \frac{B}{T - T_0})$$

Vogel-Fulcher-Tamman



Myth:
Do cathedral glasses flow over centuries?

Vogel-Fulcher-Tamman

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

Vogel-Fulcher-Tamman

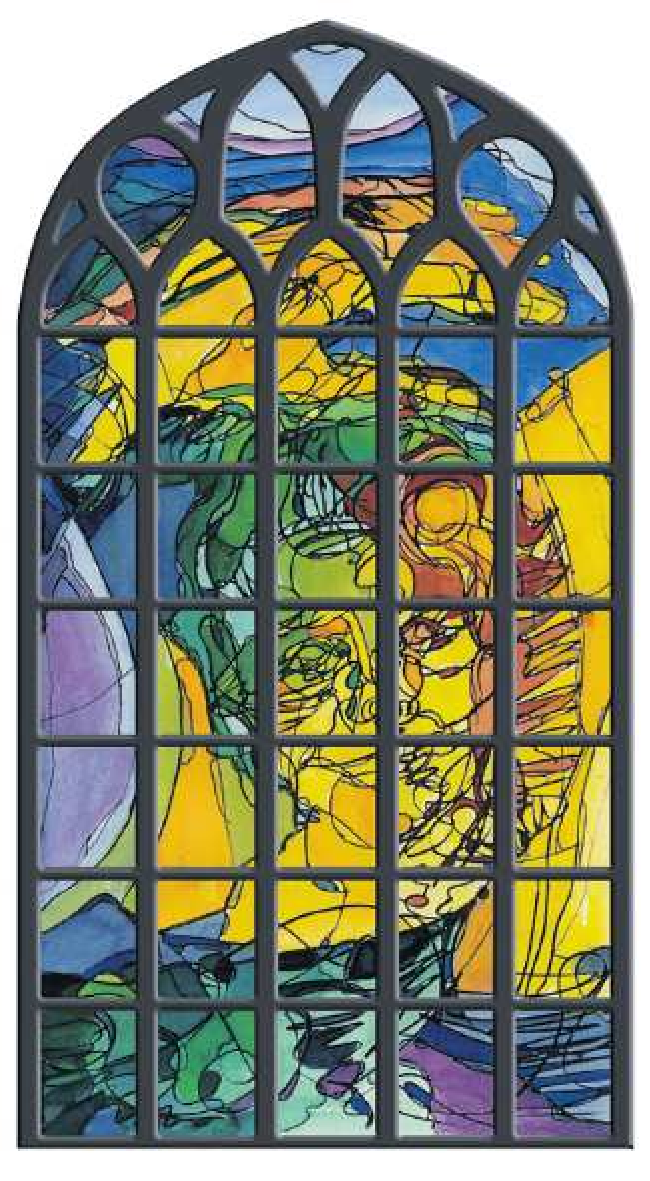


Table I. Typical compositions (wt %) and VFT parameters[a] of window glasses.

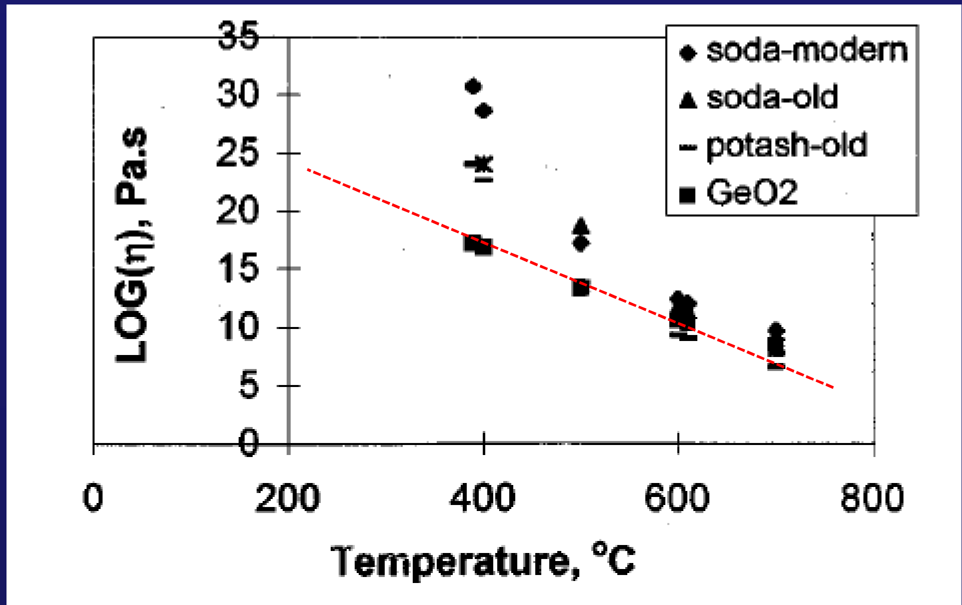
	Modern	Medieval glasses
SiO_2	73.2	45–75
Na_2O	13.4	0.1–18
CaO	10.6	1.0–25
Al_2O_3	1.3	0.8–2.0
K_2O	0.8	2.0–25
MgO	0.7	0.8–8.0
Fe_2O_3	0.1	0.3–2.1
MnO	···	0.3–2.3
P_2O_5	···	2.5–10
A	−2.6	−4.2[a]
B	4077.7	5460.9[a]
T_0	254.7	196.3[a]

[a]Yellow glass of the Gatien Cathedral, Tours (France).

Vogel-Fulcher-Tamman

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

Vogel-Fulcher-Tamman



Your turn!

Vogel-Fulcher-Tamman

Relaxation time: 10^{32} years!

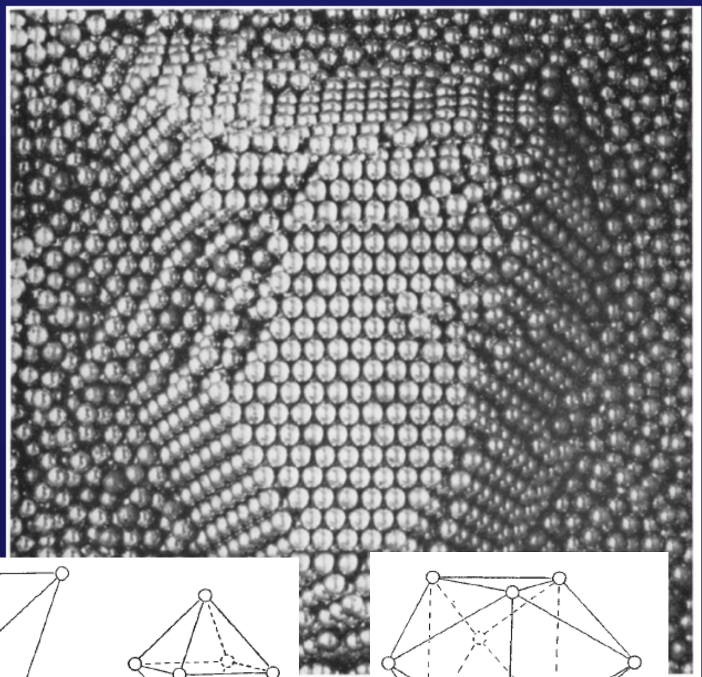
>> age of the universe 10^{10} years

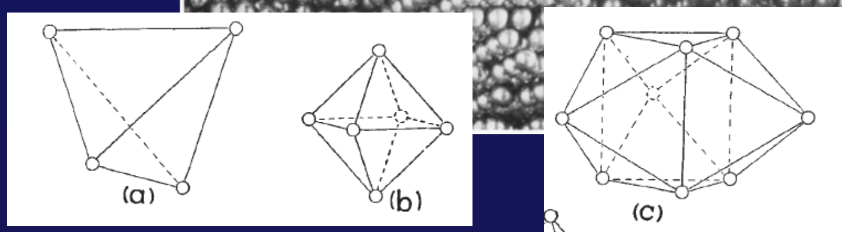
Free Volume Theory

Hard Spheres

Bernal

The structure of liquids *et al.* 1960s





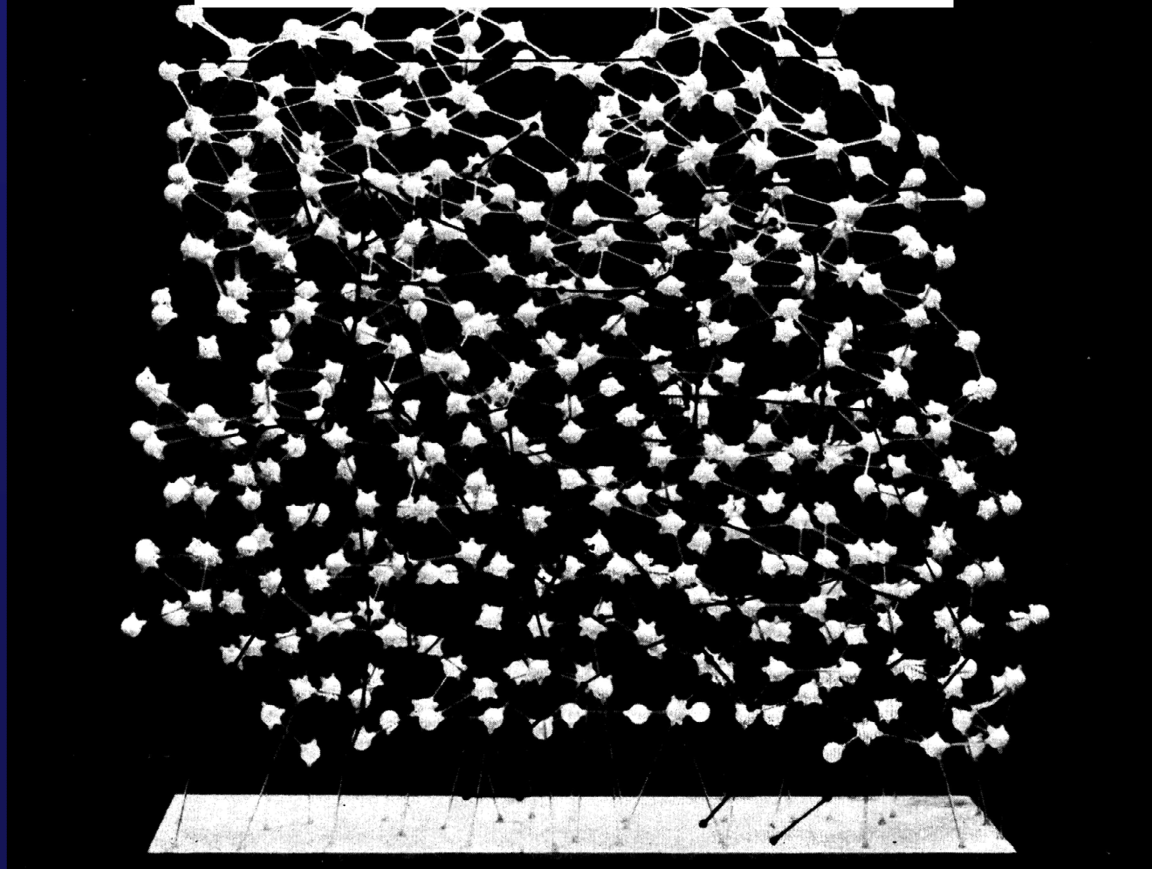
Canonical Holes

Model systems: Hard spheres

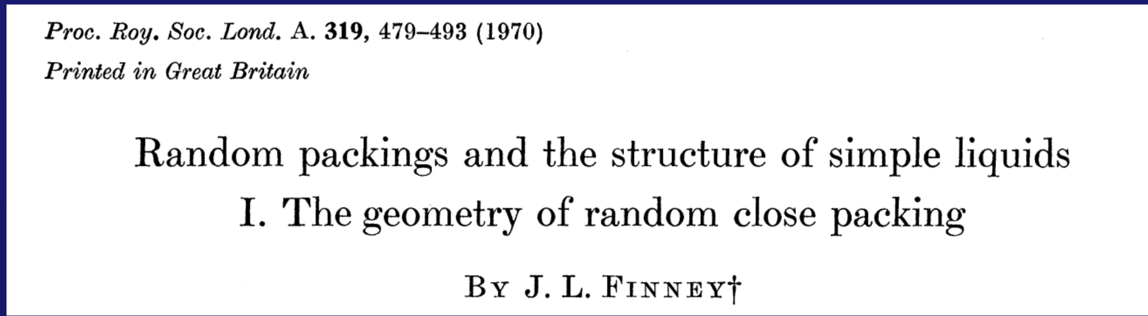
THE BAKERIAN LECTURE, 1962

The structure of liquids

BY J. D. BERNAL, F.R.S.



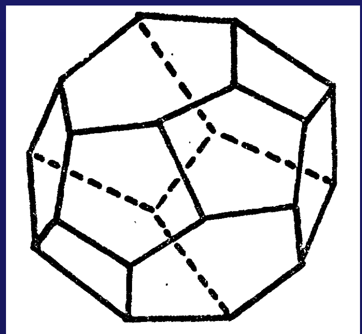
Model systems: Hard spheres

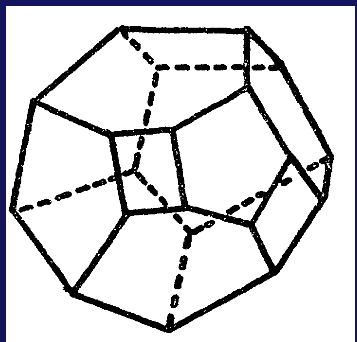

Proc. Roy. Soc. Lond. A. **319**, 479–493 (1970)
Printed in Great Britain

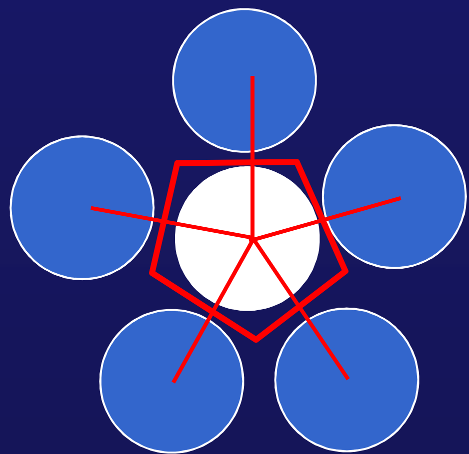
Random packings and the structure of simple liquids
I. The geometry of random close packing

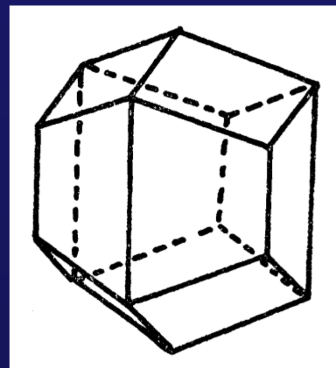
By J. L. Finney†

Voronoi Volume









Model systems: Hard spheres

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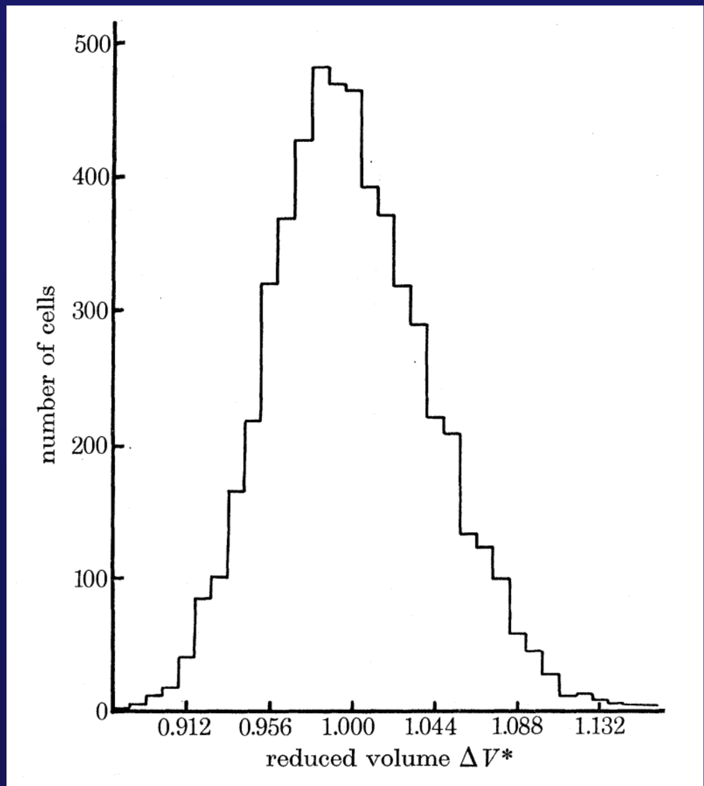
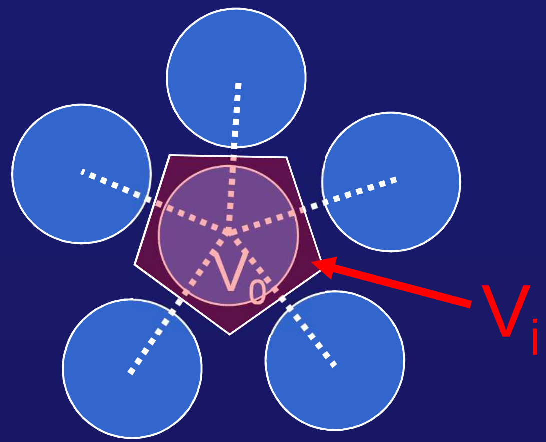


Voronoi Volume Distribution

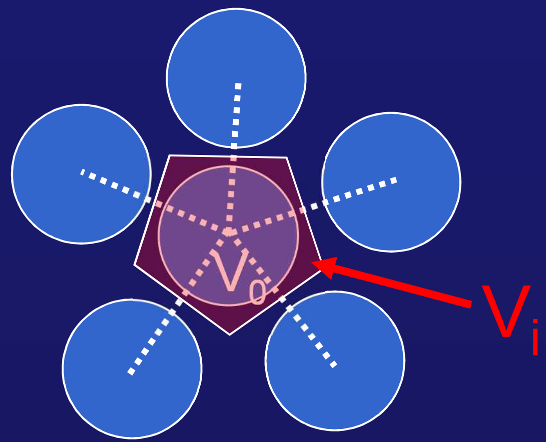
Free Volume Theory



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

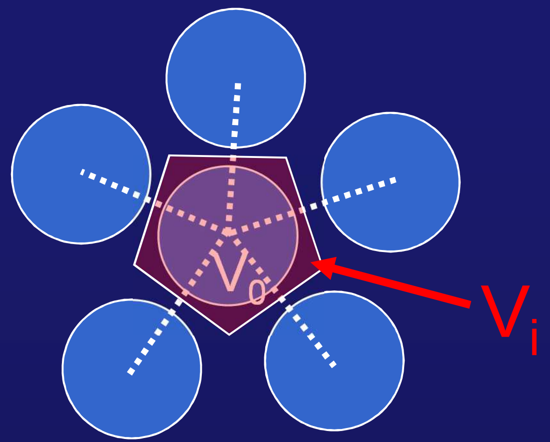


Rearrangements occur at $V_f > \delta V_0$

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

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

Free Volume Theory



Free volume from thermal expansion

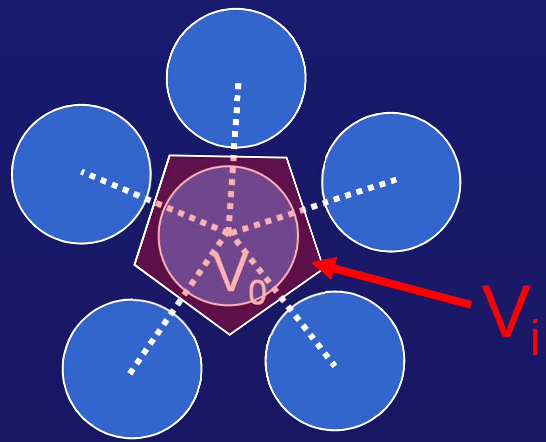
$V_f = 0$ at $T = T_0$

⇩

$V_f(T)$, $\eta(T)$???

Your turn!

Free Volume Theory

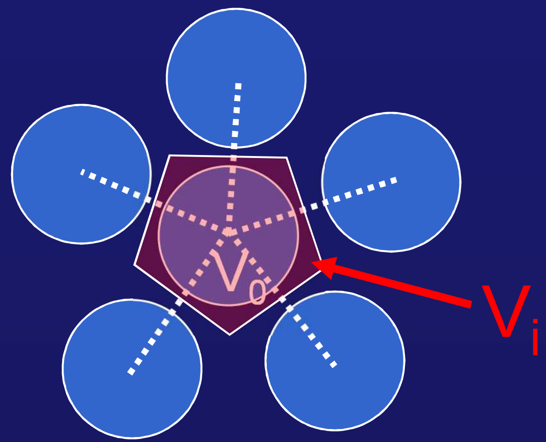


Free volume from thermal expansion

$V_f = 0$ at $T = T_0$

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

Free Volume Theory



Free volume from thermal expansion

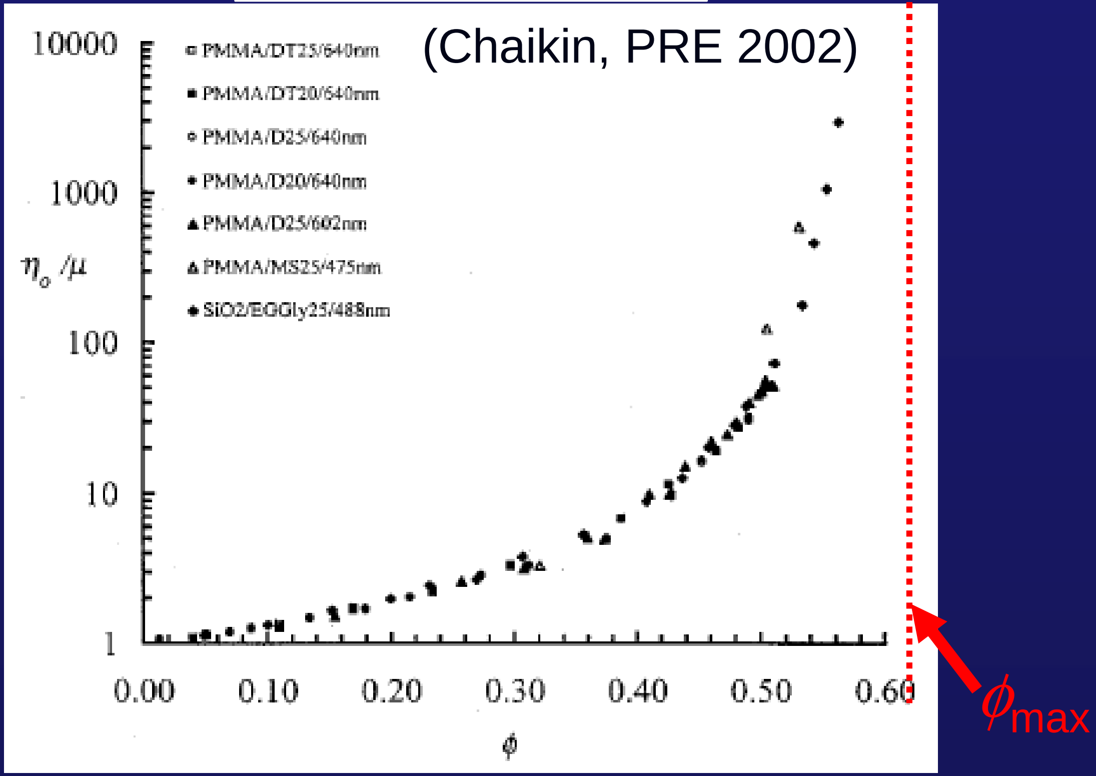
$$\frac{\langle V_f \rangle}{V_0} \propto T - T_0$$

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

Big success of free volume theory!

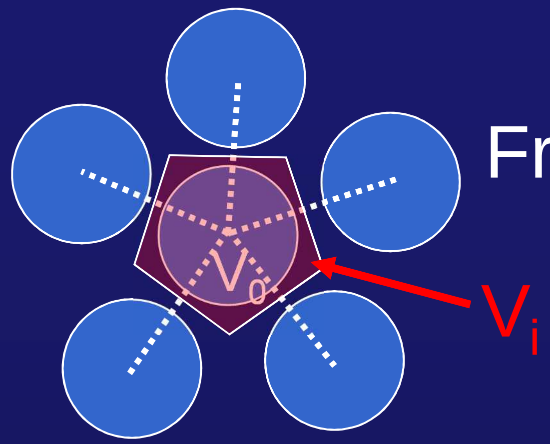
Free Volume Theory

Suspensions



1 / (Temperature) ⟺ Volume fraction ϕ

Free Volume Theory



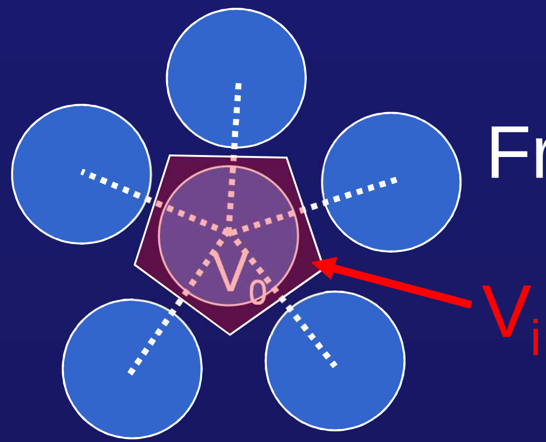
Max. Packing Fraction $\phi_m \sim 0.64$

Free volume: $\frac{v_f}{v_0} = ???$

Viscosity: $\eta = ???$

Your turn!

Free Volume Theory

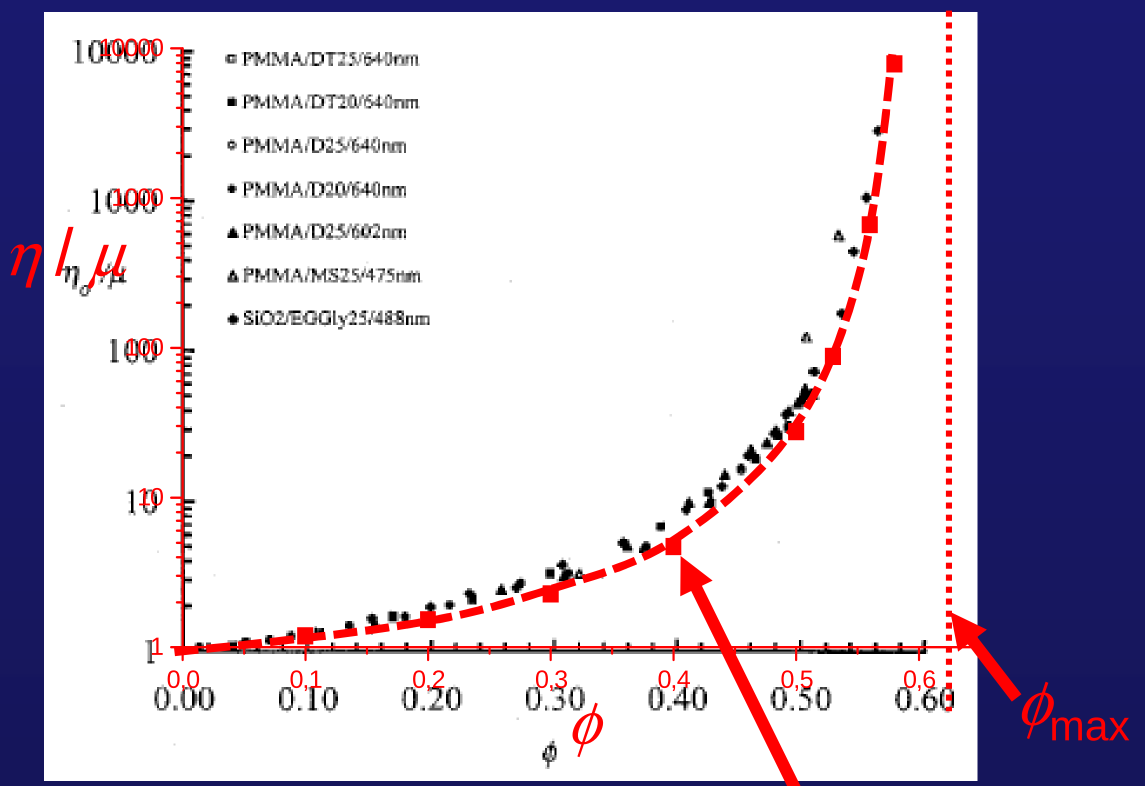


Max. Packing Fraction $\phi_m \sim 0.64$

Free volume: $$\frac{v_f}{v_0} = \frac{1}{\phi} - \frac{1}{\phi_m} = \frac{\phi_m - \phi}{\phi \phi_m}$$

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)

Dynamic correlations

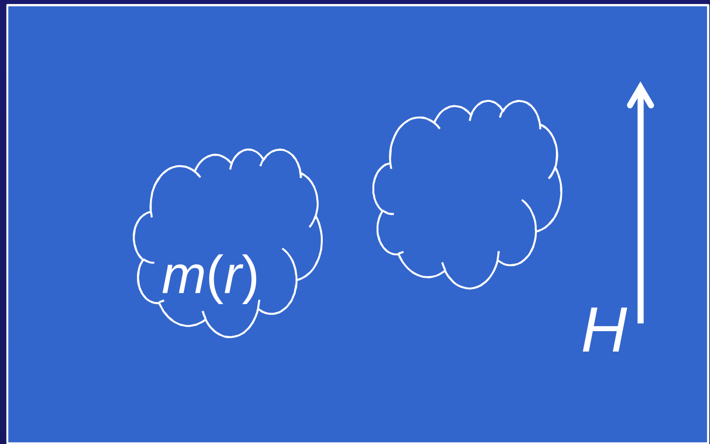
$T \rightarrow T_g$ ⇨ Increasing cooperativity

Adam & Gibbs (1965)

Analogy to 2nd order phase transitions?
... but viscosity not singular

Dynamic correlations

2nd Order Phase Transitions



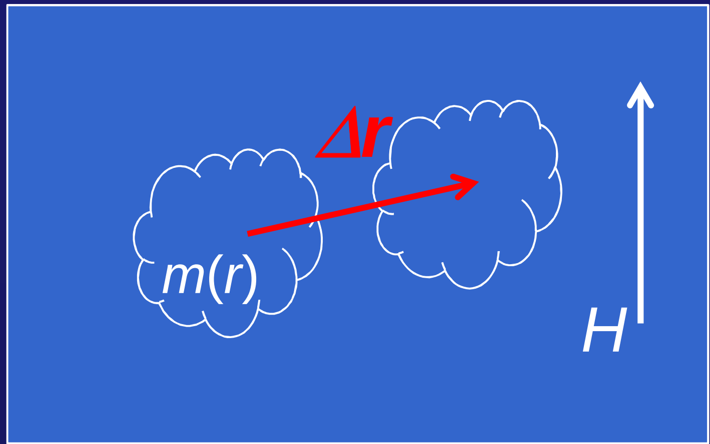
Order Parameter

Magnetization $M = \int m(r)\, dV$

Local Magnetic Moment $m(r)$

Dynamic correlations

2nd Order Phase Transitions



Correlation function

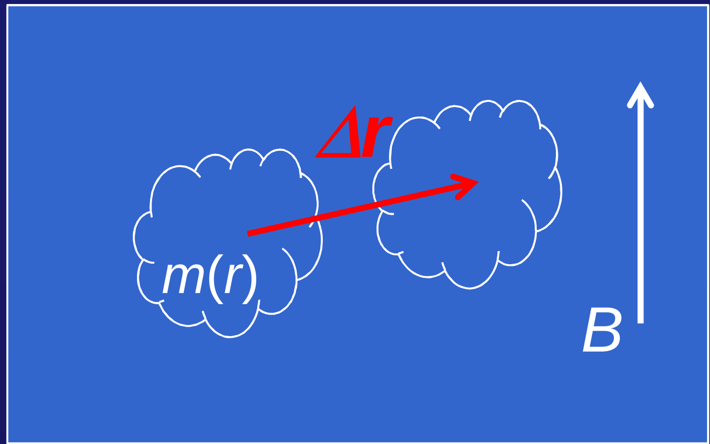
$$C_m(\Delta r) = \langle m(r) \cdot m(r + \Delta r) \rangle_r$$

Susceptibility

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

Dynamic correlations

2nd Order Phase Transitions



Critical Scaling close to T_c

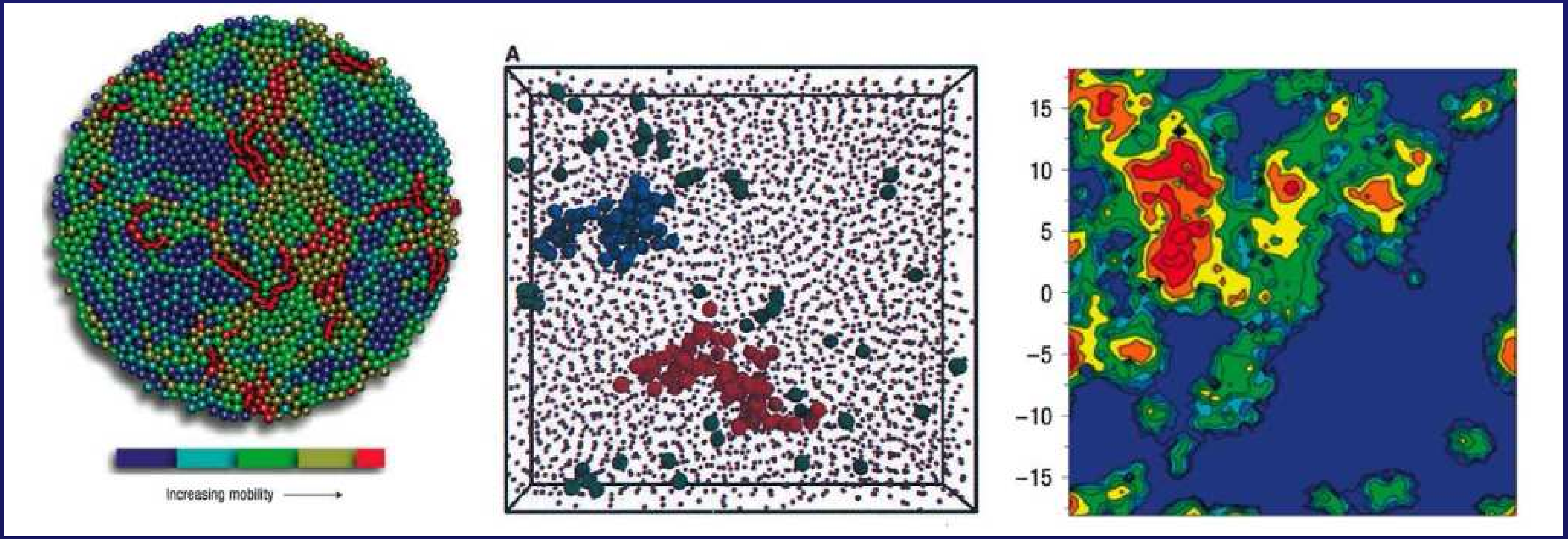
$$C_m(r) \propto r^{-\lambda} \, exp(-r/\xi)$$

Correlation length

Divergence of

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

Dynamic correlations



Granular fluid of ball bearings

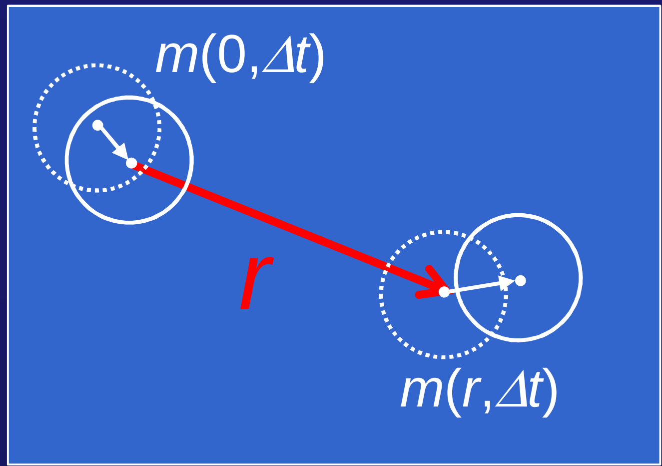
Colloidal glass

Computer simulation 2D repulsive discs

Glass transition as critical phenomenon?

Dynamic correlations

Dynamic correlation function



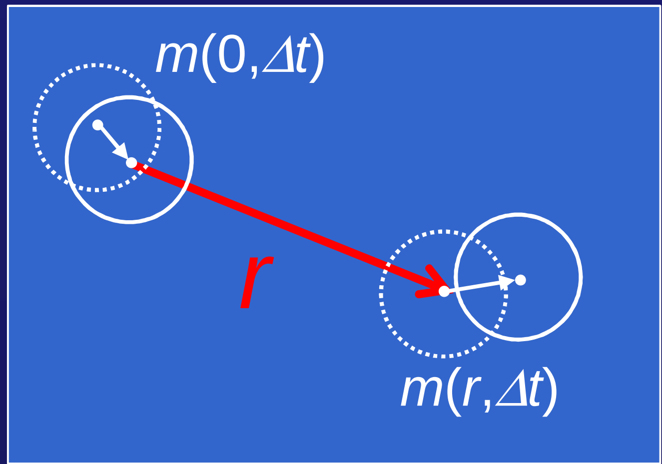
4-point correlation function

Glotzer et al. 1999

Biroli, Dauchot, Berthier,
PRL 2005, 2008, 2009

Dynamic correlations

Dynamic correlation function



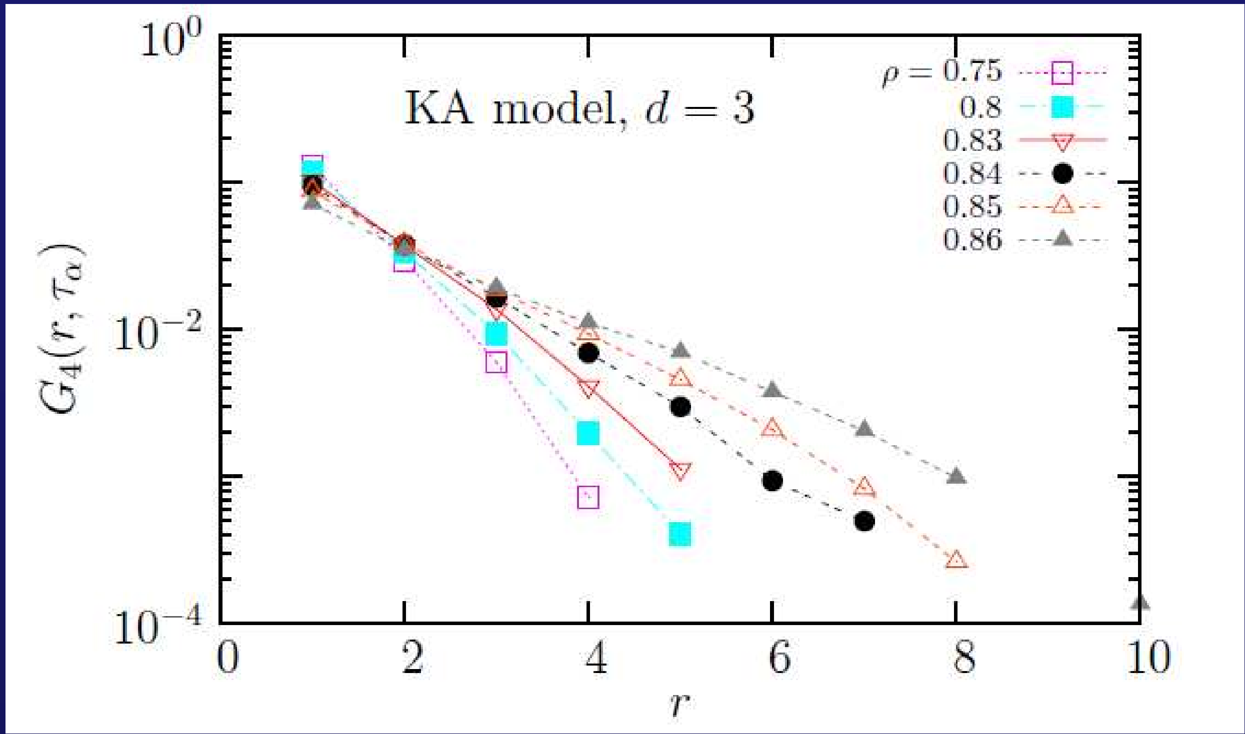
4-point correlation function

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

Dynamical criticality?

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

Glass transition: critical phenomenon?

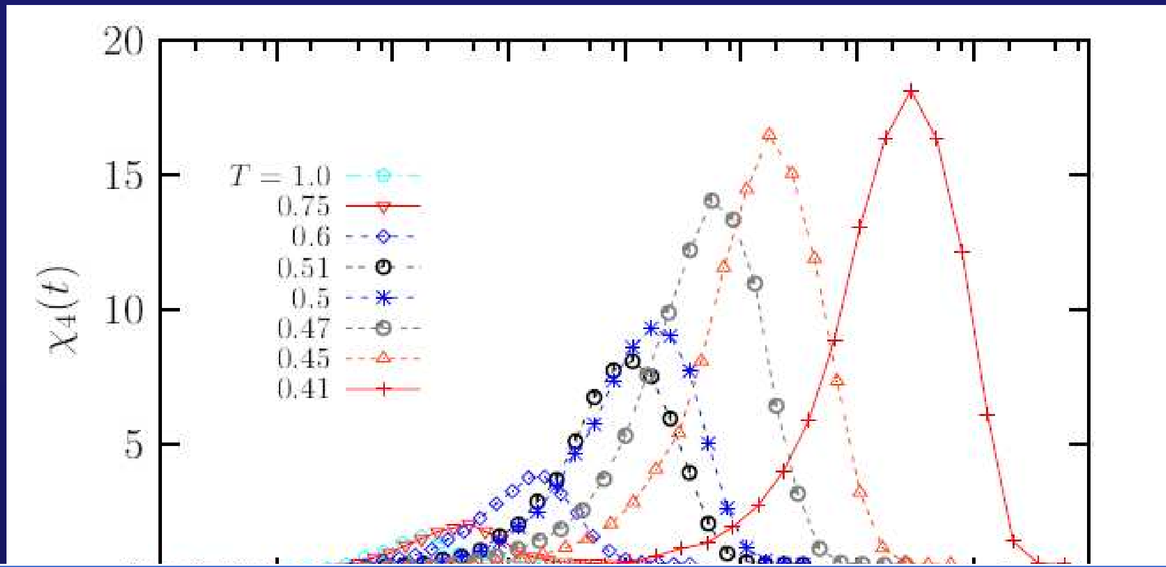


Berthier *et al.* PRL 2003

Dynamical criticality?

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

Glass transition: critical phenomenon?



No evidence of true divergence

~~Dynamical criticality?~~

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

Summary

Amorphous materials
Liquid and Solid, depending on time scale

Empirical relations for viscosity:
Vogel-Fulcher

Free Volume Theory
→ Success in deriving Vogel Fulcher relation

Dynamic heterogeneity
→ No true divergence of correlations