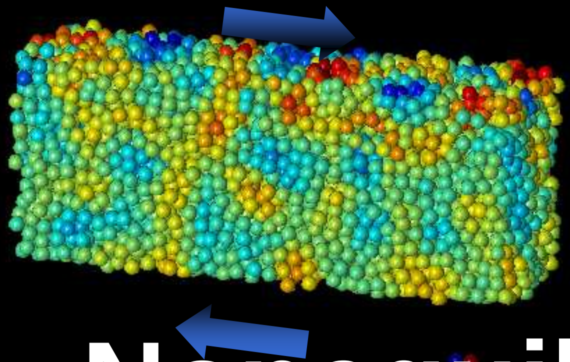
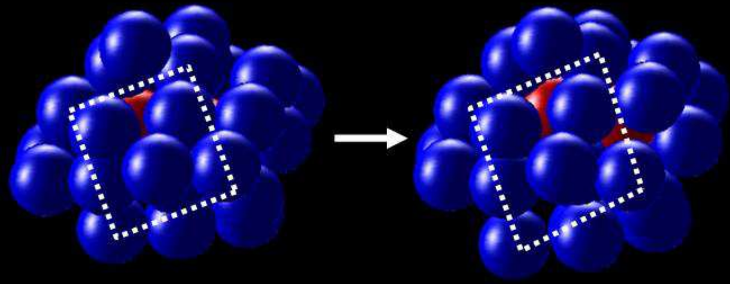
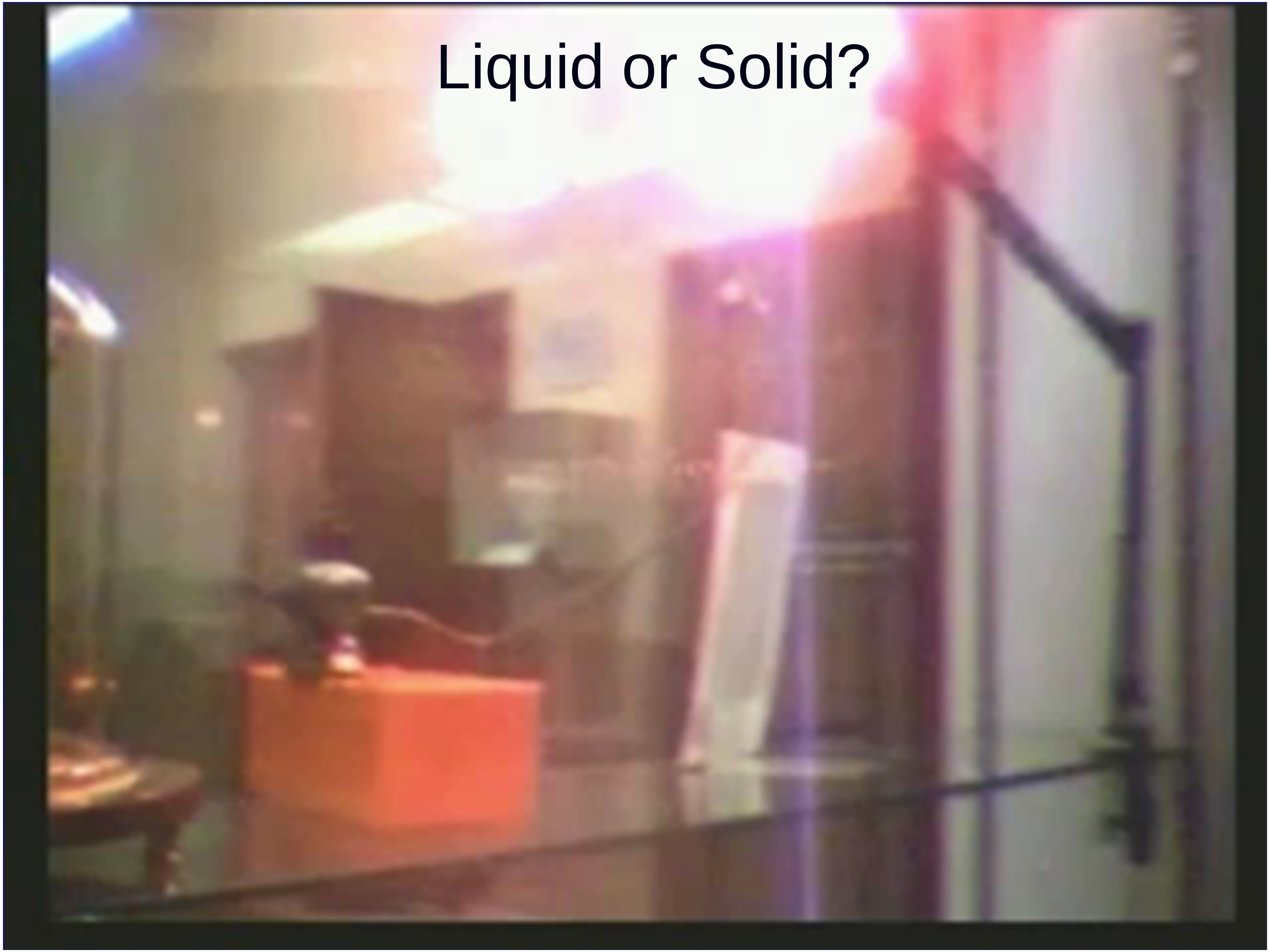


Nonequilibrium transitions in glassy flows

Peter Schall
University of Amsterdam

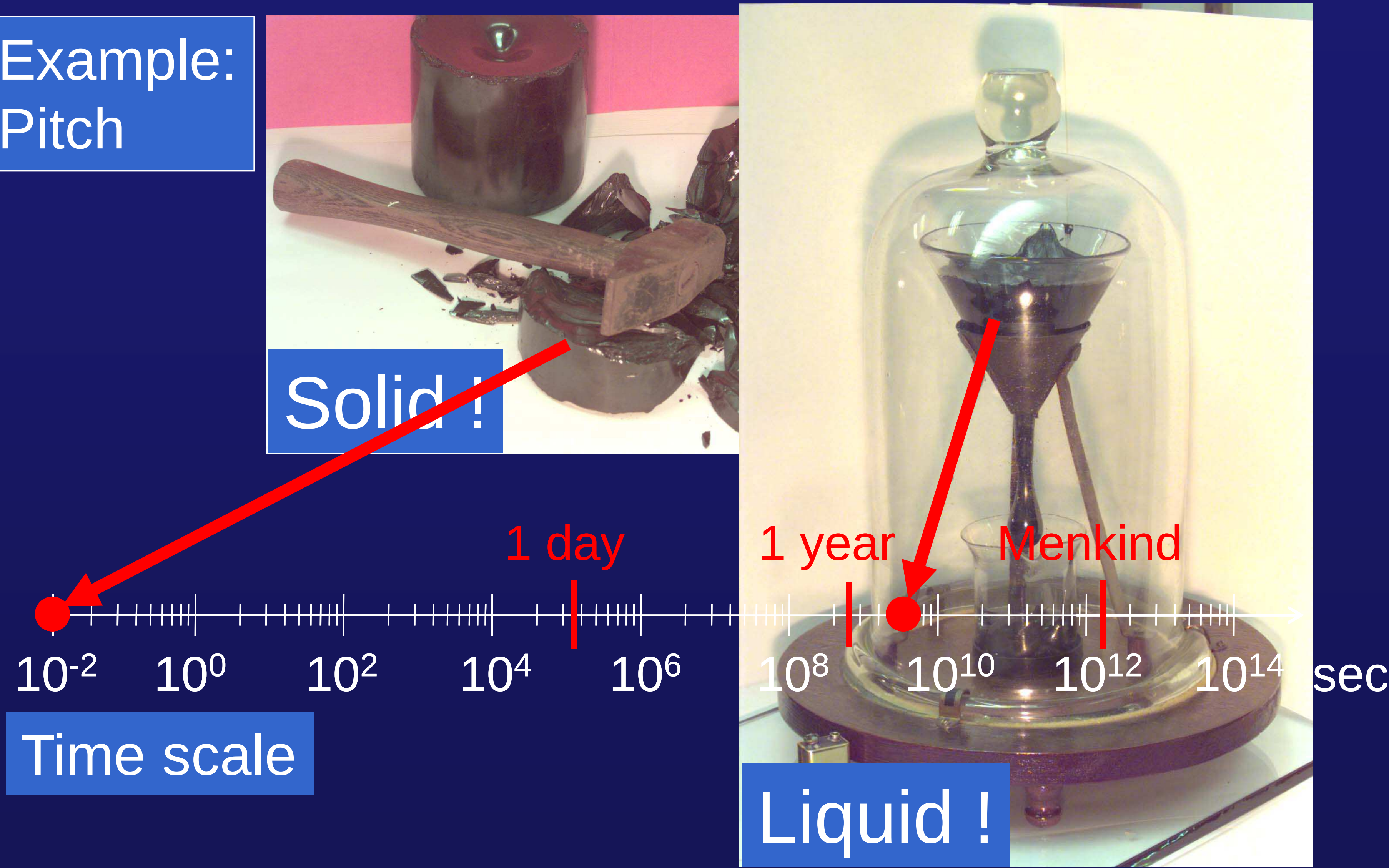


Liquid or Solid?

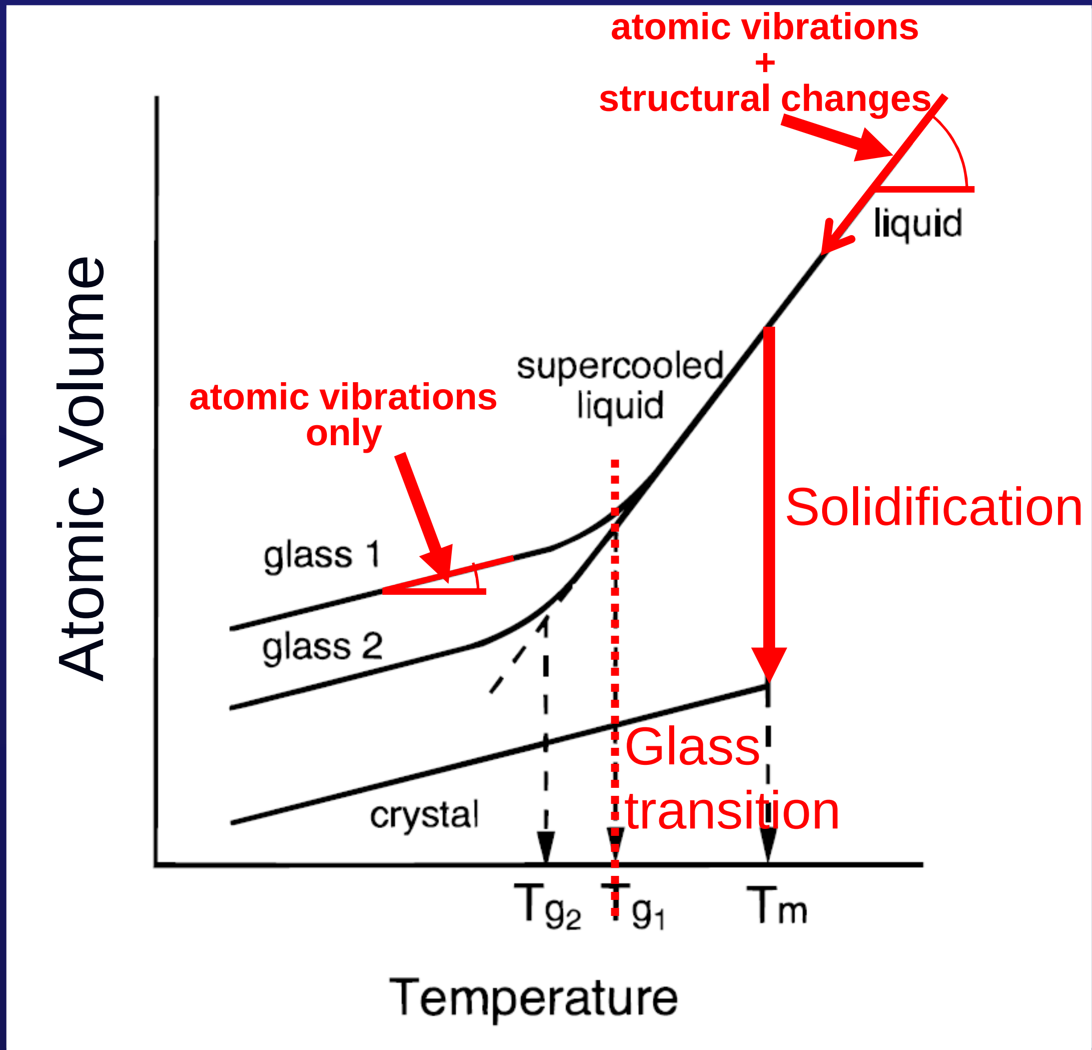


Liquid or Solid?

Example: Pitch



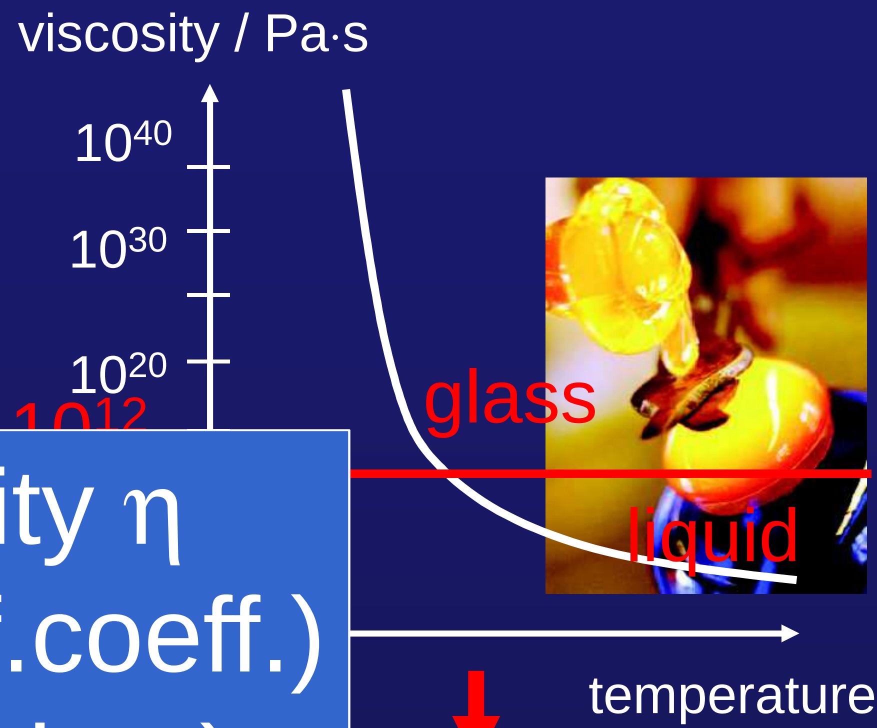
Glasses



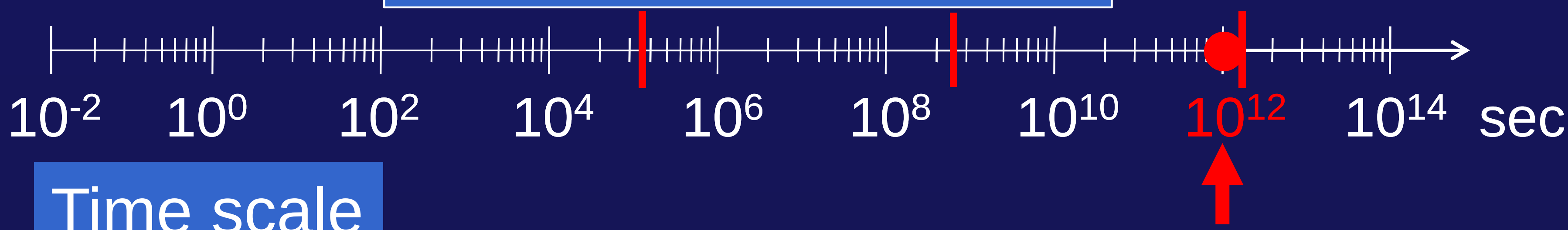
atomic vibrations
+
structural changes
liquid
supercooled
liquid
atomic vibrations
only
Solidification
glass 1
glass 2
Glass
transition
crystal
Atomic Volume
T_{g_2}
T_{g_1}
Tm
Temperature

Viscosity and Diffusion

Macroscopic: Viscosity



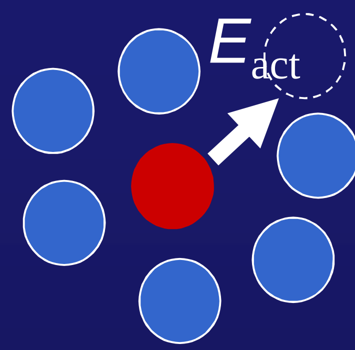
Viscosity η
$\sim 1/D$ (diff.coeff.)
$\sim \tau$ (relax.time)



Time scale

Viscosity and Diffusion

Simple Liquids: Arrhenius

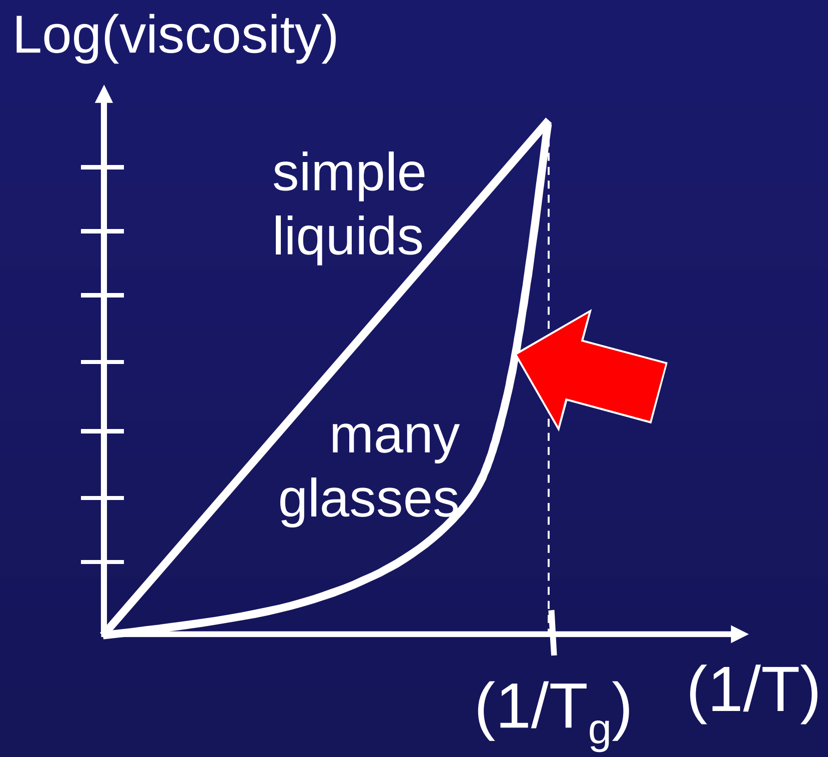


Diffusion coefficient

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

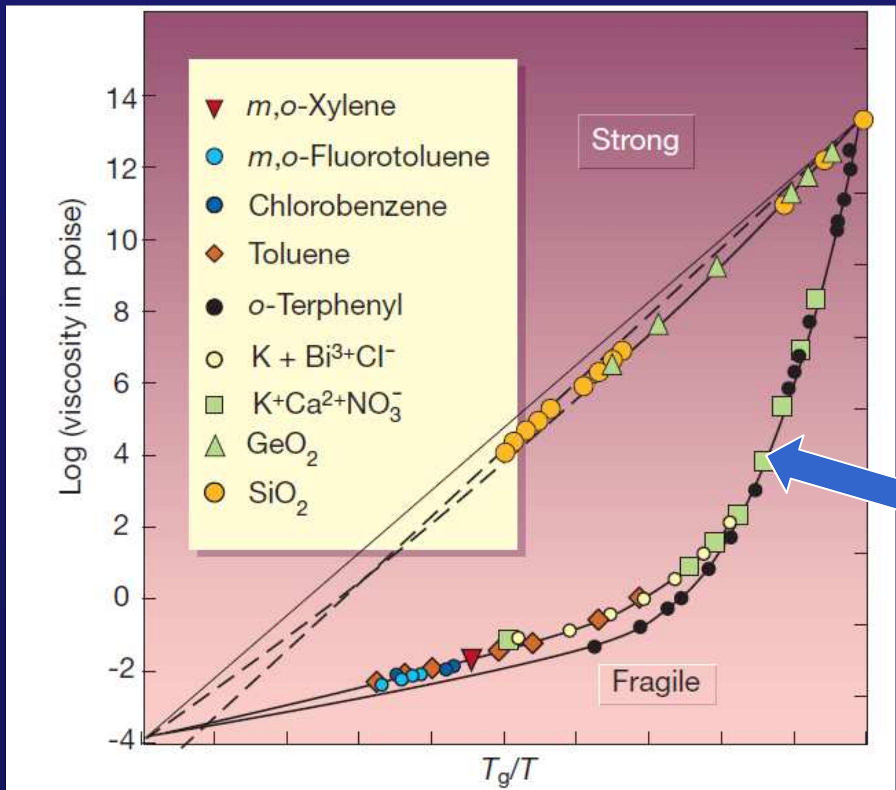
Viscosity

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



Strong and Fragile Glasses

"Angel plot"



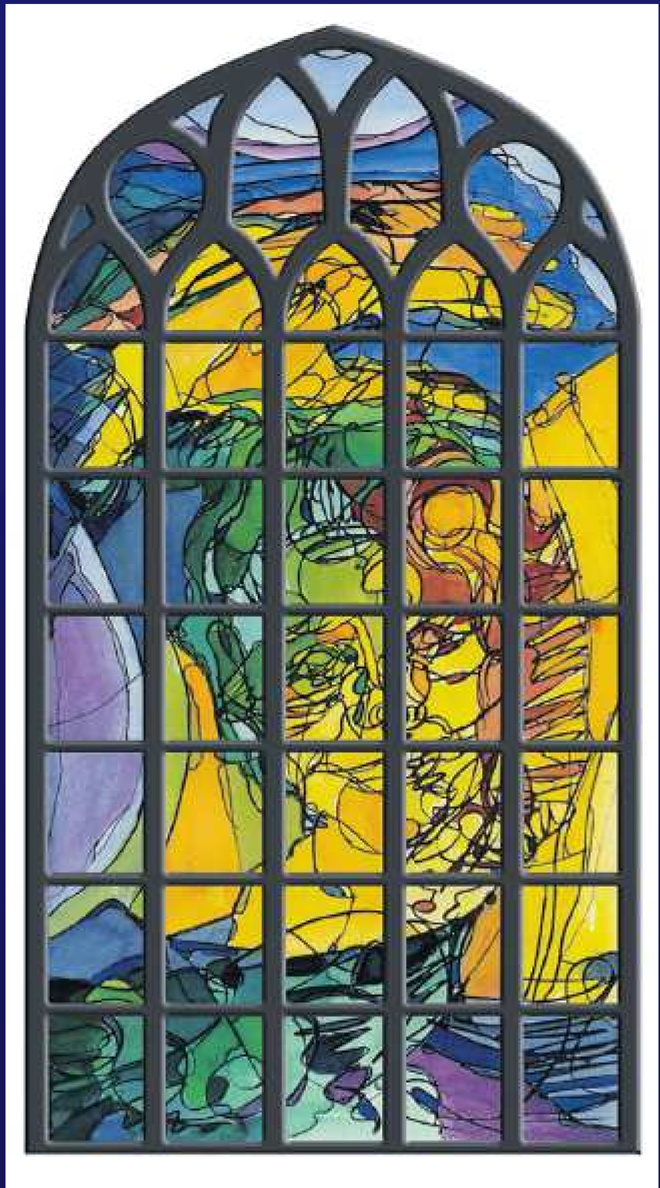
Arrhenius

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

Vogel-Fulcher-Tamman

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

Glass Phenomenology

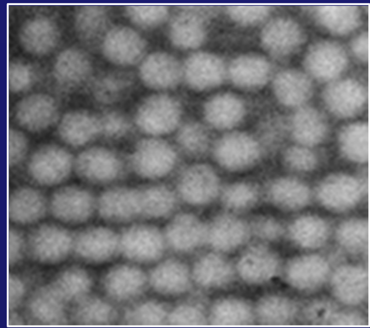


Myth:
Do cathedral glasses flow over centuries?

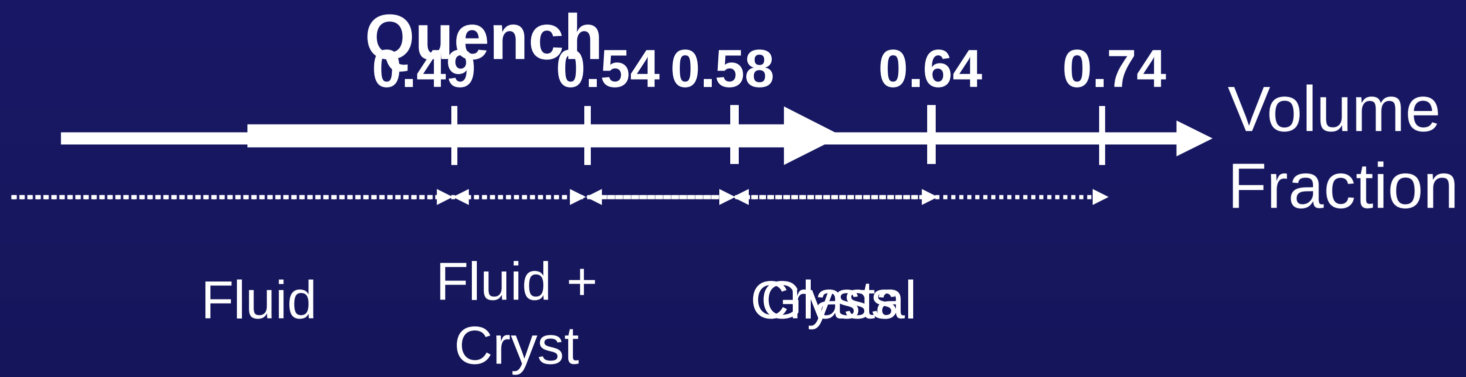
Vogel-Fulcher-Tamman

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

Colloidal Hard Spheres



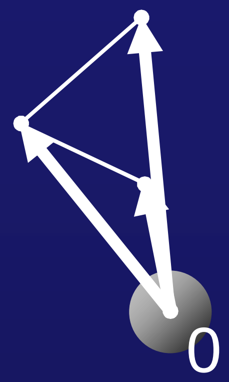
Hard-sphere Phase Diagram

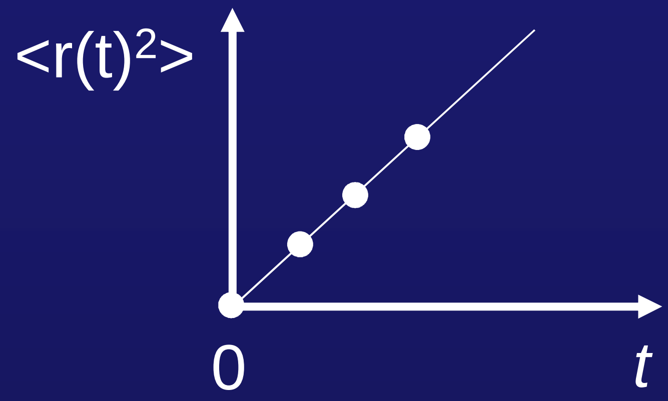


(Alder, Wainwright 1957)

Single Particle Dynamics

Diffusion in liquids





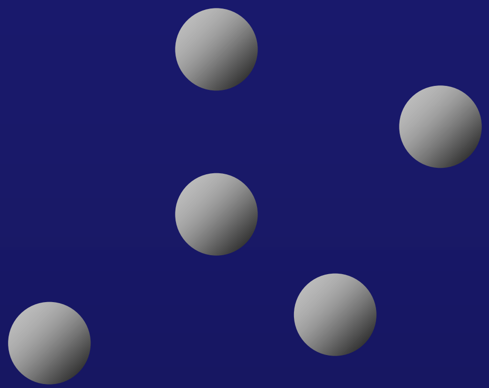
Mean square displacement

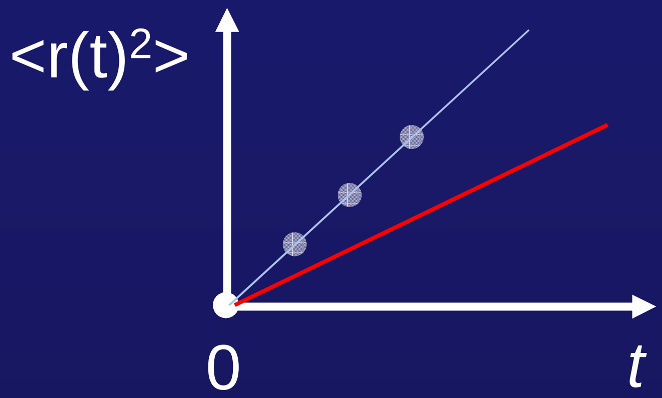
$$< x(t)^2 > = 2Dt$$

Fluctuation-Dissipation $\xi D = k_B T$

Single Particle Dynamics

Dilute suspensions





<u>Einstein (1906):</u>

$$\eta(\phi) = \eta_0 \, (1 + 5/2 \, \phi)$$

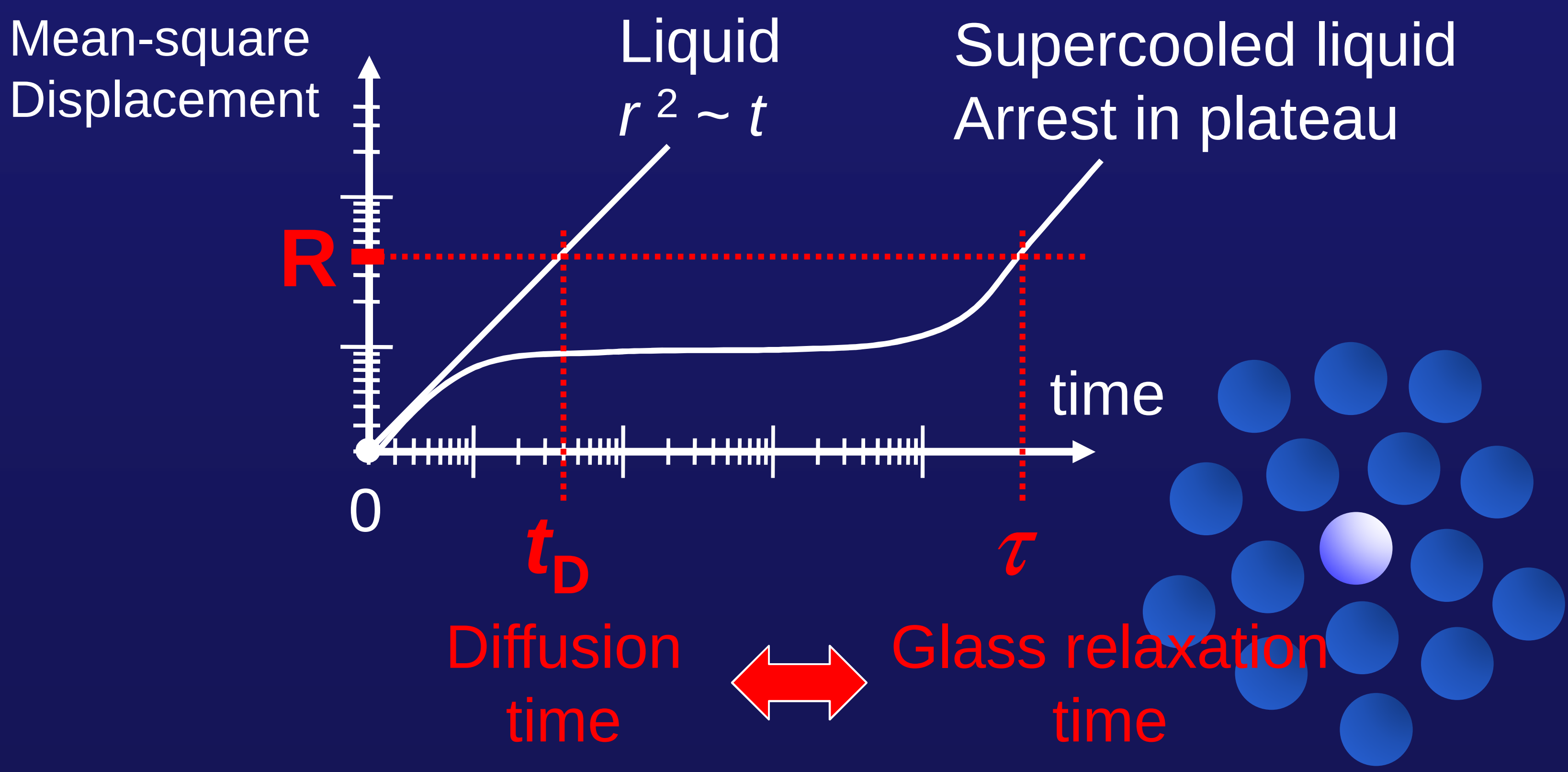
<u>Batchelor (1977):</u>

$$\eta(\phi) = \eta_0 \, (1 + 5/2 \, \phi + 5.9 \, \phi^2)$$

Single Particle Dynamics

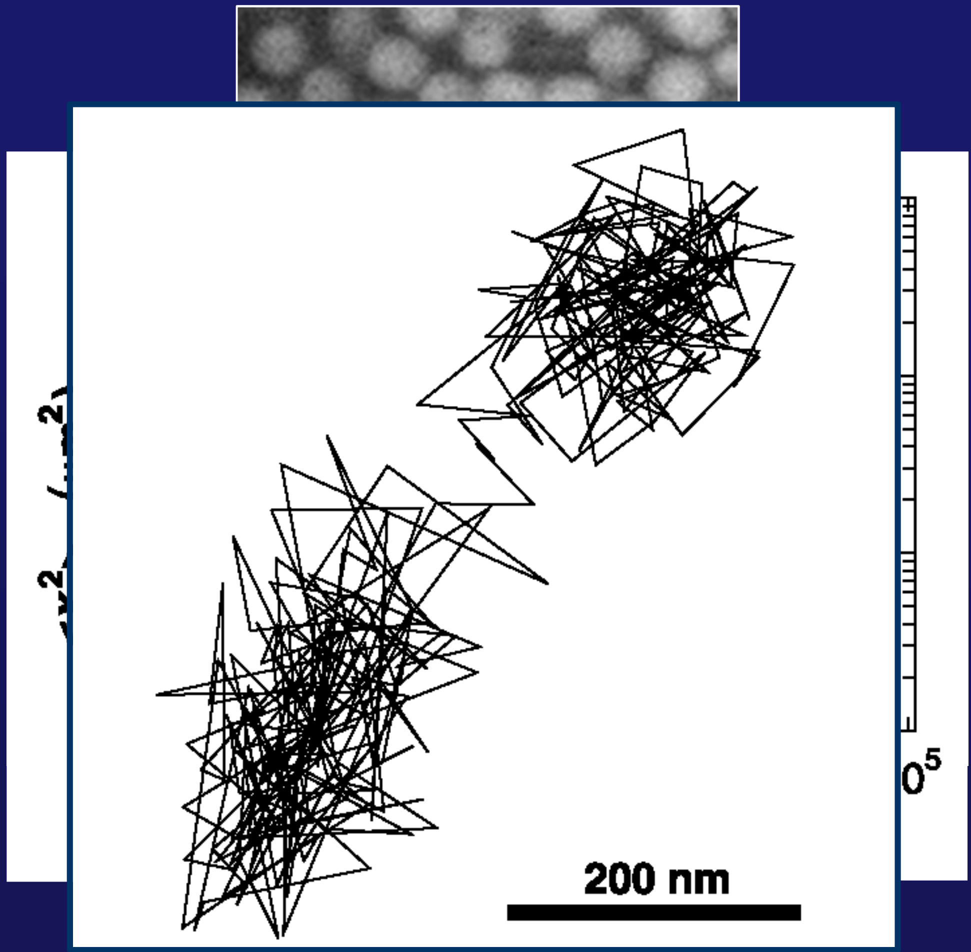
Diffusion

(Molecules or small particles in a supercooled liquid)



Supercooled Liquids

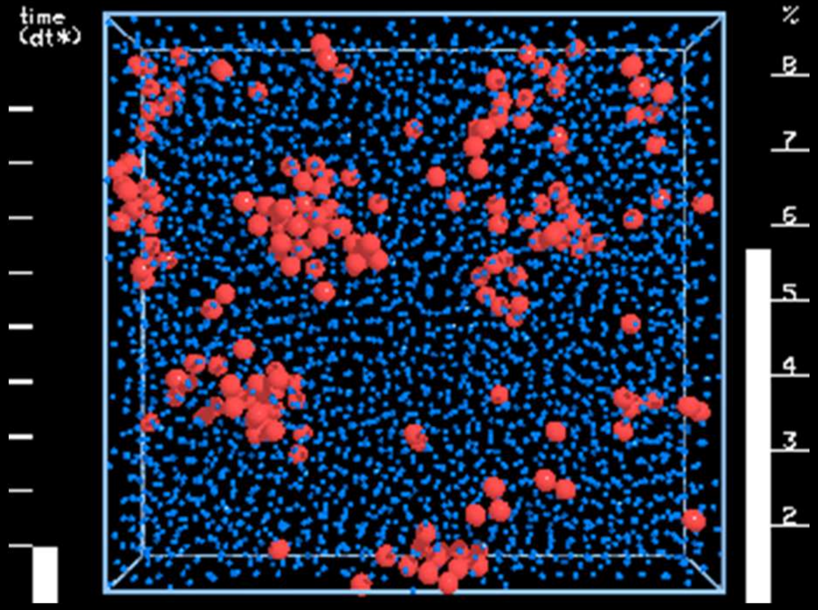
Dynamic Measurements ...



Weeks *et al.*
Science (2000)

Dynamic Heterogeneity

At the glass transition



Packing fraction
ϕ = 58 %

Weeks et al. *Science* 2002

Glassy Flow - Basics

i. **Free volume**

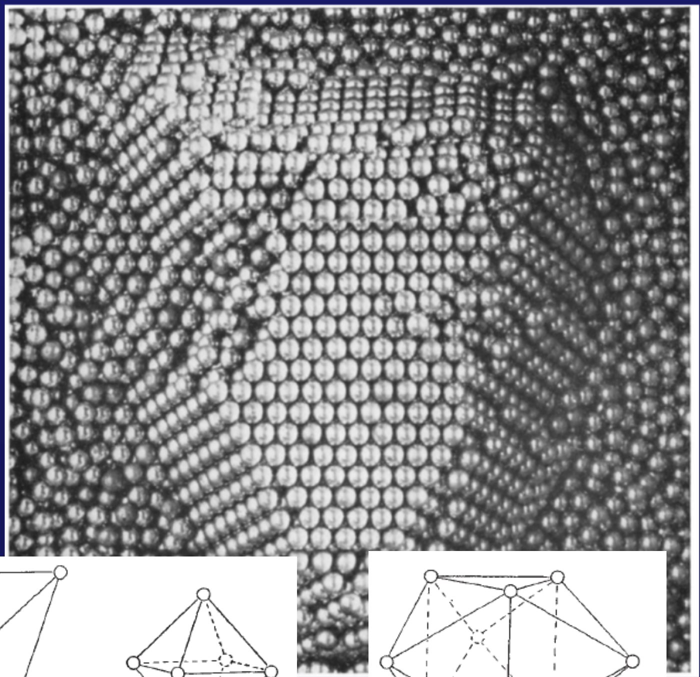
ii. **Correlations**

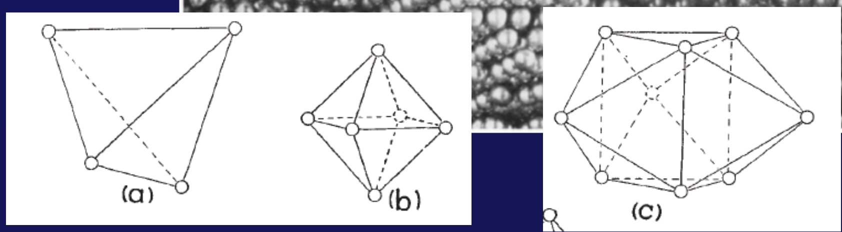
Free Volume Theory

Hard Spheres

Bernal

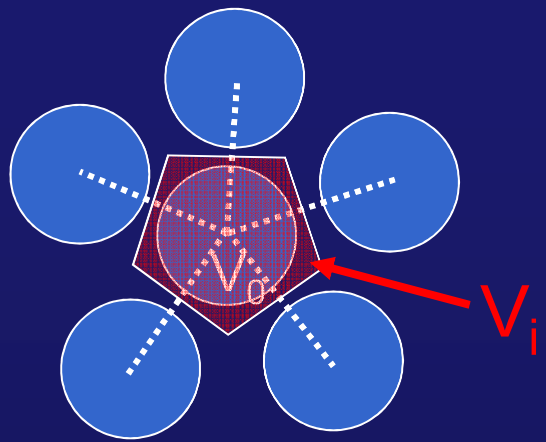
The structure of liquids *et al.* 1960s





Canonical Holes

Free Volume Theory

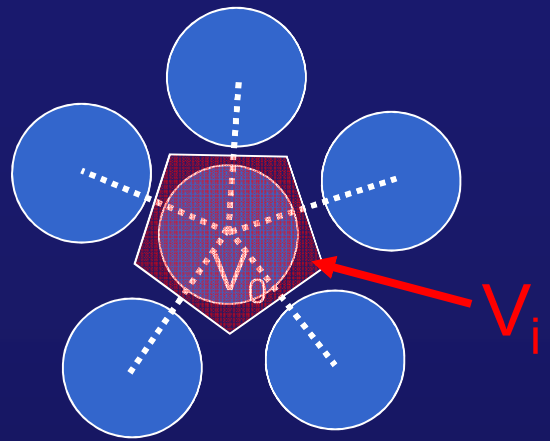


Free Volume $V_f \sim (V_i - V_0)$

Free Volume Theory:

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

Free Volume Theory



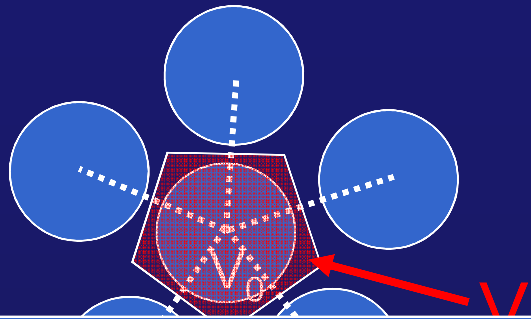
Rearrangements occur if $V_f \sim V_0$

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

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

$\delta \sim 1$

Free Volume Theory



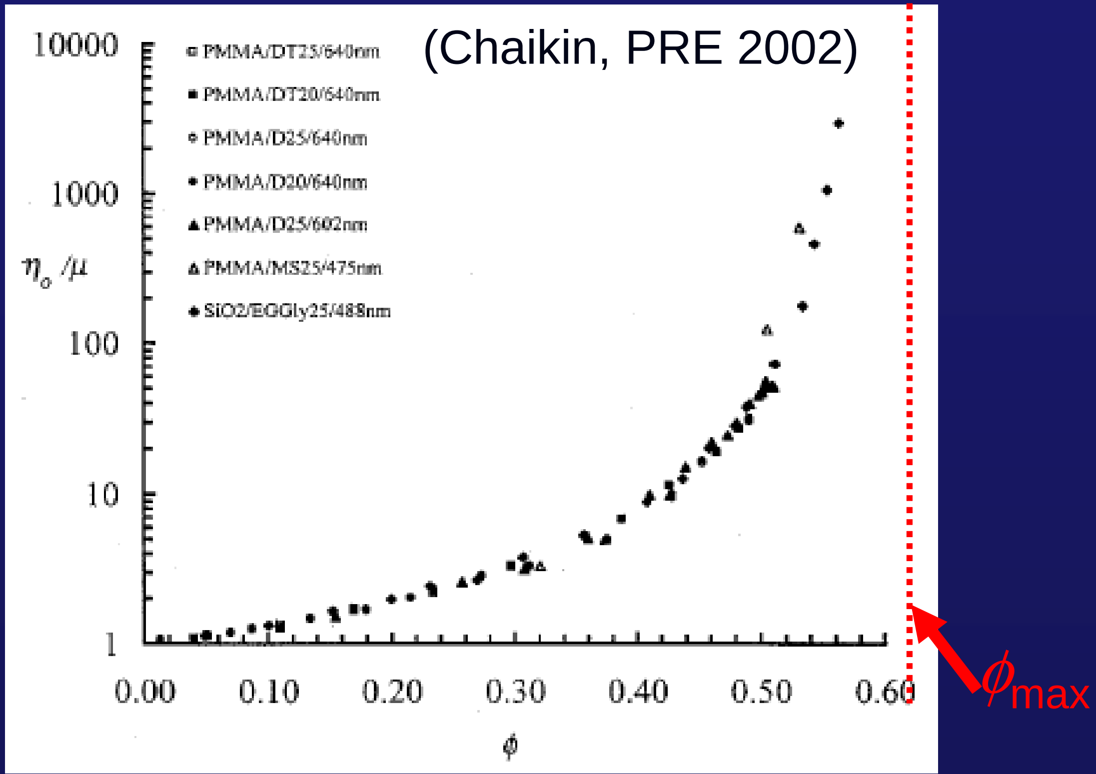
Big success
of free volume theory!

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

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

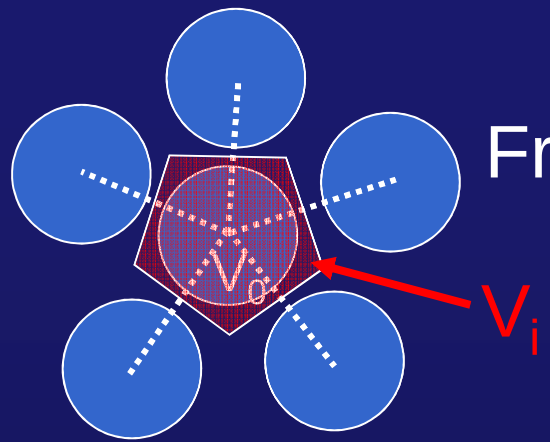
Free Volume Theory

… and suspensions ?



1 / (Temperature) ⟺ Volume fraction ϕ

Free Volume Theory

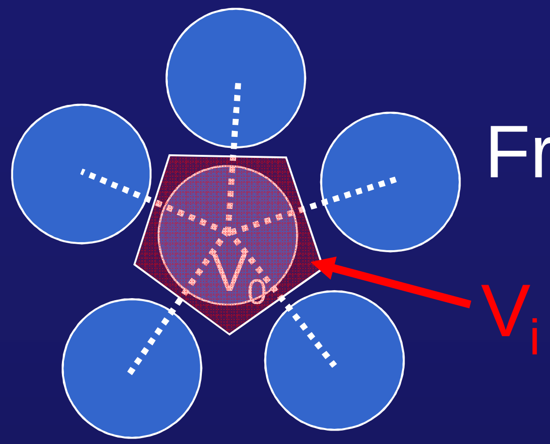


Max. Packing Fraction $\phi_m \sim 0.64$

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

Viscosity: $\eta = ???$

Free Volume Theory

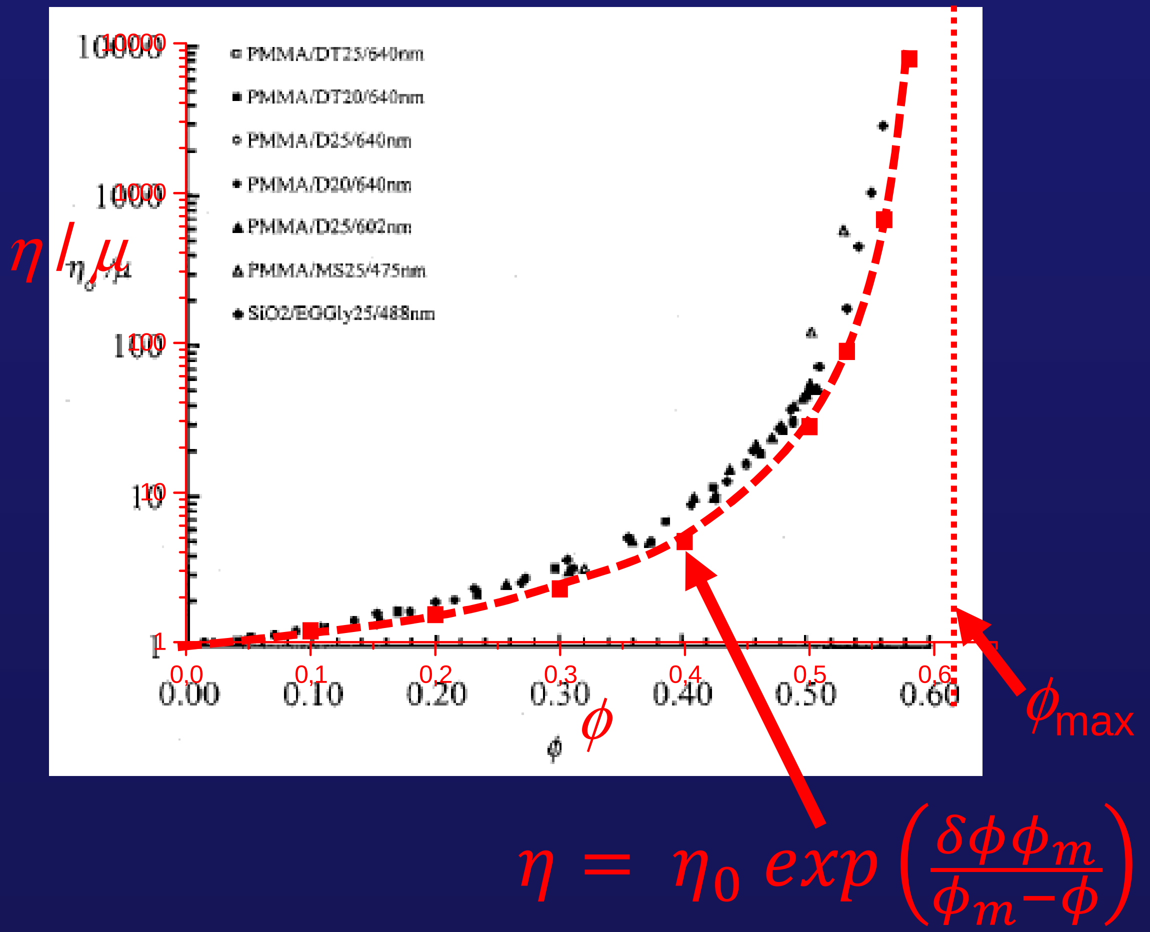


Max. Packing Fraction ϕ_m ~ 0.64

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

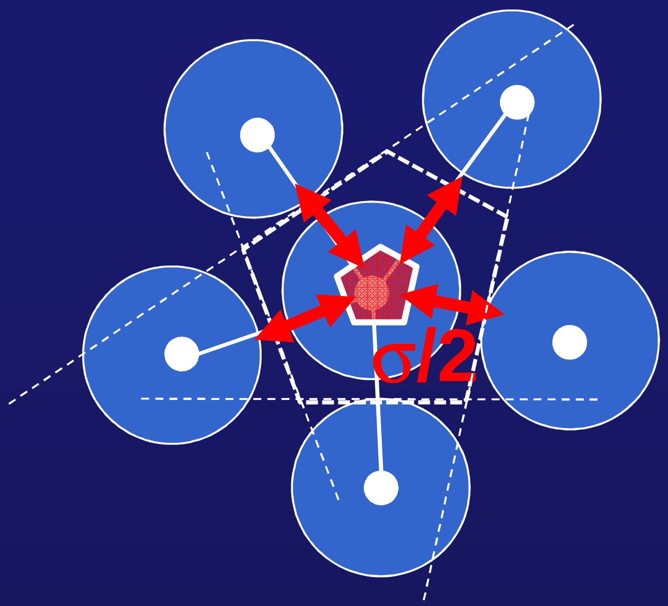
Viscosity: $\eta = \eta_0 \, exp\left(\frac{\delta \phi \phi_m}{\phi_m - \phi}\right)$

Free Volume Theory: Suspensions



(Cheng, Chaikin, PRE 2002)

Free volume → Free energy



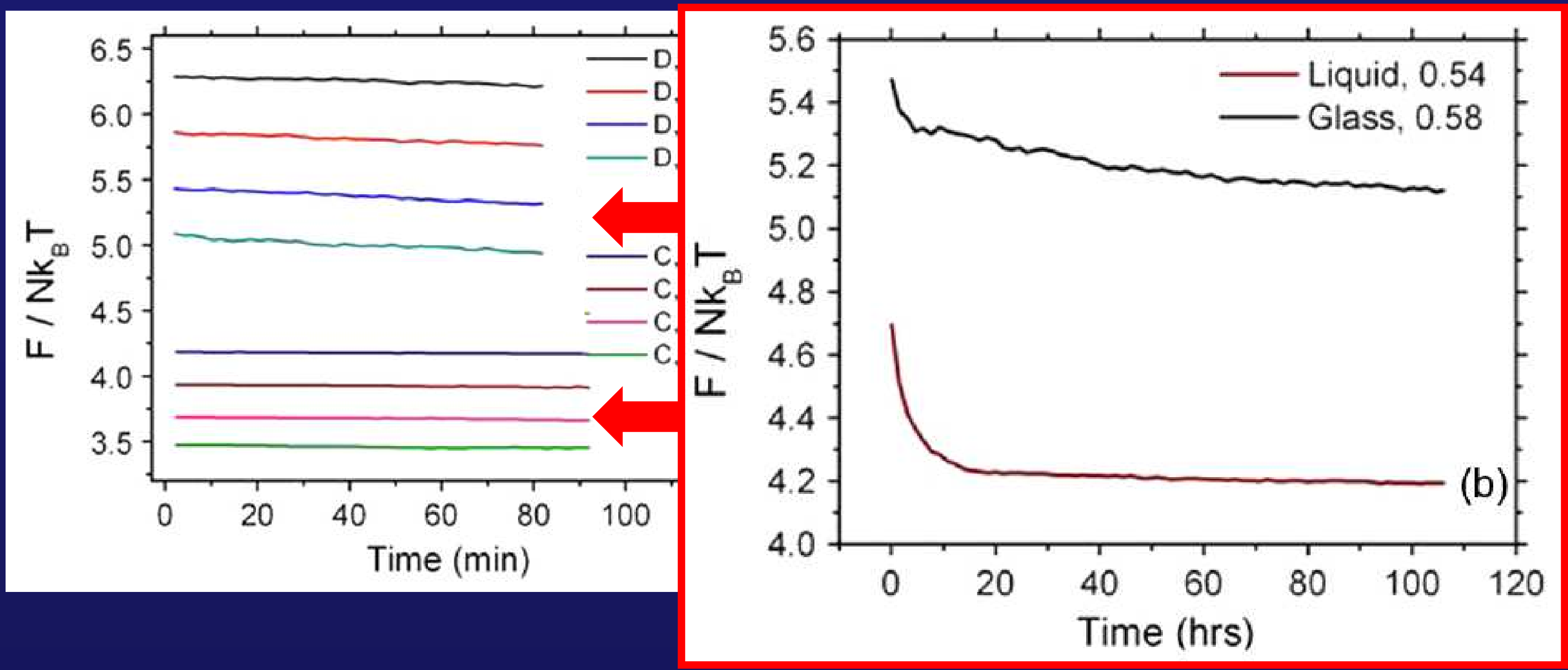
Free Volume

Free energy

$$F = -k_B T \sum_{i=1}^{N} ln\left(\frac{v_{f_i}}{\lambda^3}\right)$$

Zargar, et al. *Phys Rev Lett.* (2013)

Free energy of glasses



Glasses: free energy decrease over time

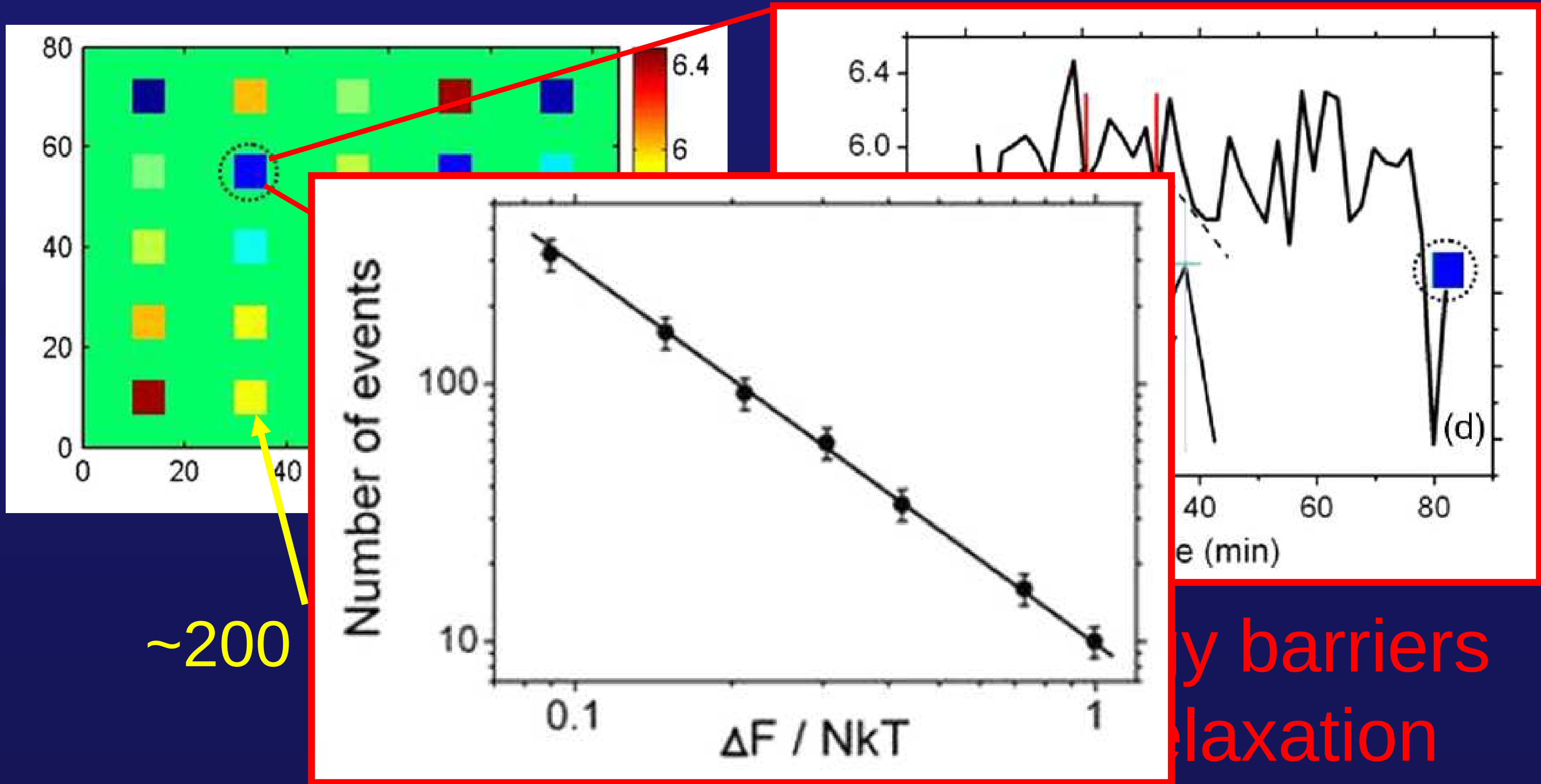
Aging

Zargar, et al. *Phys Rev Lett.* (2013)

Free energy of glasses

Heterogeneity

Relaxation



~200

y barriers

elaxation

$N \sim \Delta F^{-\alpha}, \ \alpha = 1.2$ ~Gutenberg Richter

Glassy Flow - Basics

i. **Free volume**

ii. **Correlations**

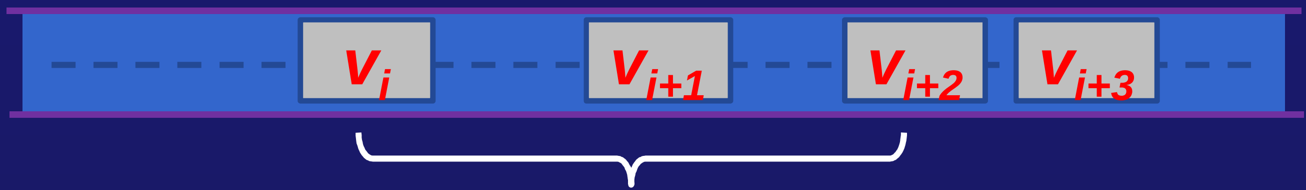
Correlations in Traffic

SHOCKWAVE TRAFFIC JAMS
RECREATED FOR FIRST TIME

Footage courtesy of
University of Nagoya,
Nagoya, Japan

Correlations in Traffic

Correlations in Traffic



Velocity correlations

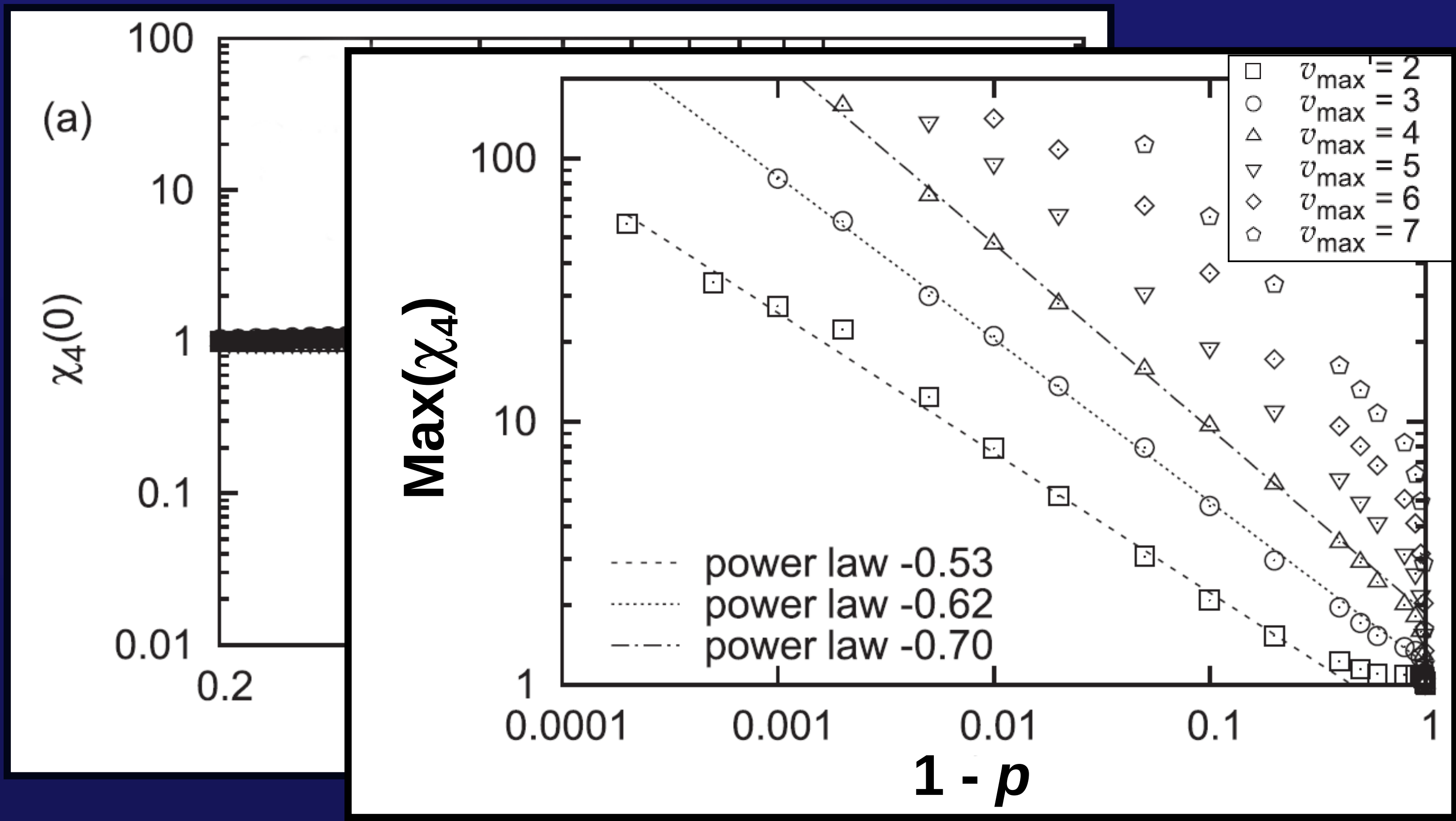
$$C_v(x) = \langle v(i) \cdot v(i+x) \rangle_i - \langle v(i) \rangle^2$$

Dynamic susceptibility

$$\chi \propto \int C_v(x)\, dx$$

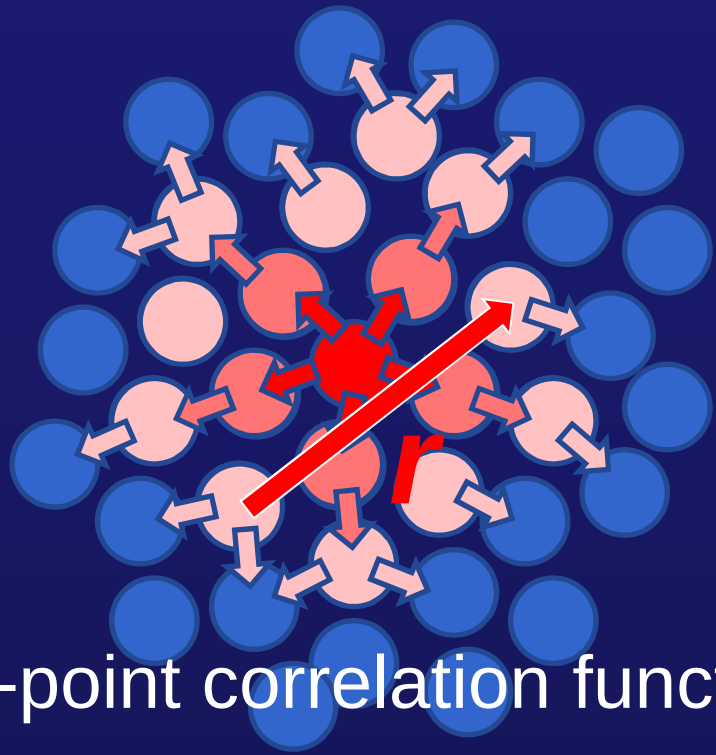
Traffic simulations

Dynamic susceptibility



De Wijn, Miedema, Nienhuis, P.S. *PRL* (2012)

Correlations in glasses



4-point correlation function

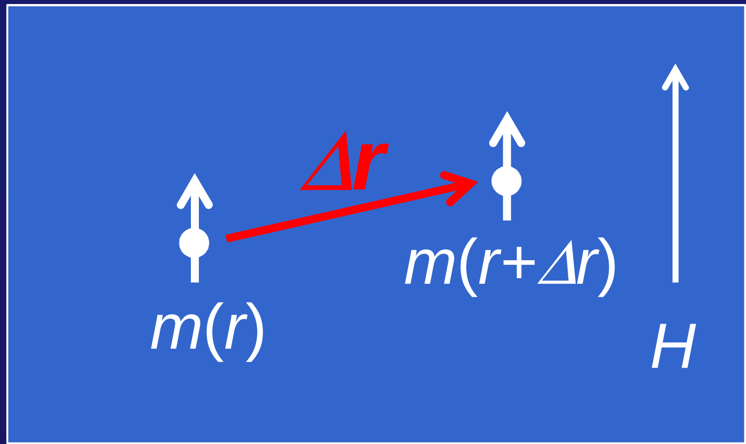
$$G_4(r,\Delta t) = \langle v(0,\Delta t)\cdot v(r,\Delta t)\rangle$$

Dynamic susceptibility

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

Analogy: Magnetic Coupling

Magnetic spins in external field



Correlation function

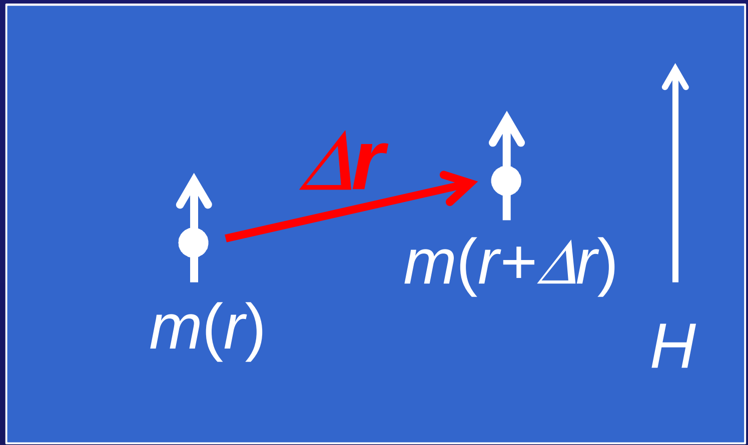
$$C_m(\Delta r) = \langle m(r) \cdot m(r + \Delta r) \rangle_r$$

Susceptibility

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

Analogy: Magnetic Coupling

2nd Order Phase Transitions



Critical Scaling close to T_c

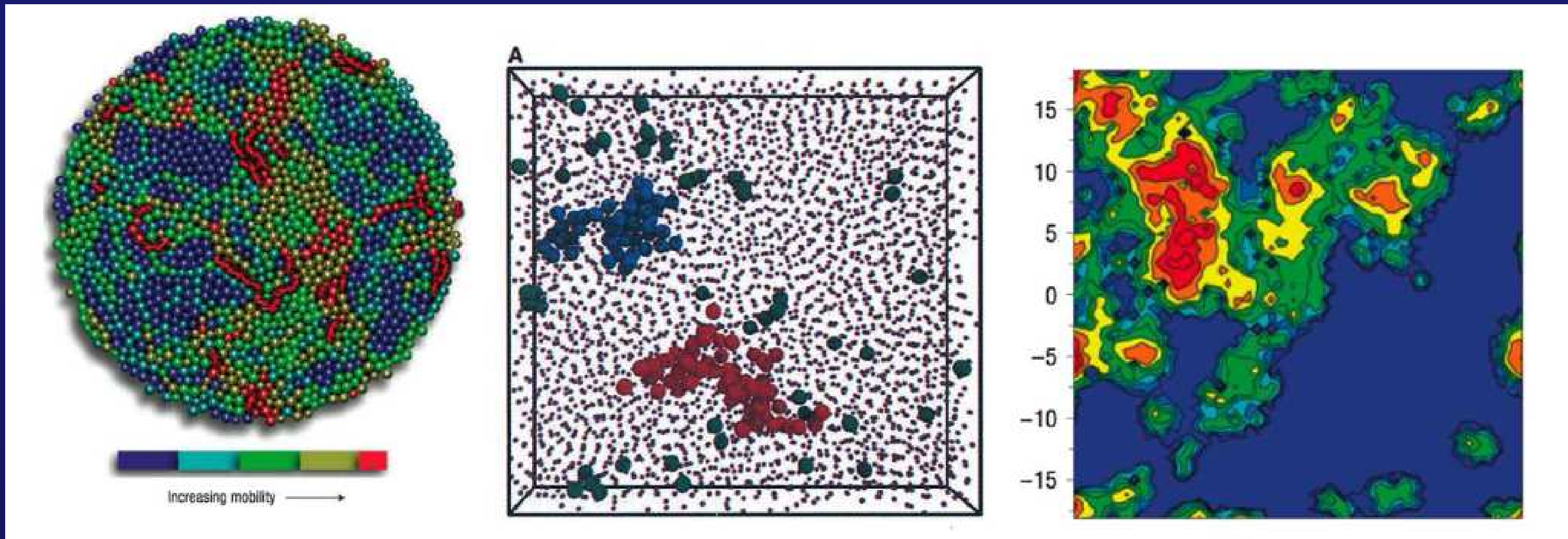
$$C_m(r) \propto r^{-\lambda} \, exp(-r/\xi)$$

Correlation length

Divergence of

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

Glasses: Dynamic correlations



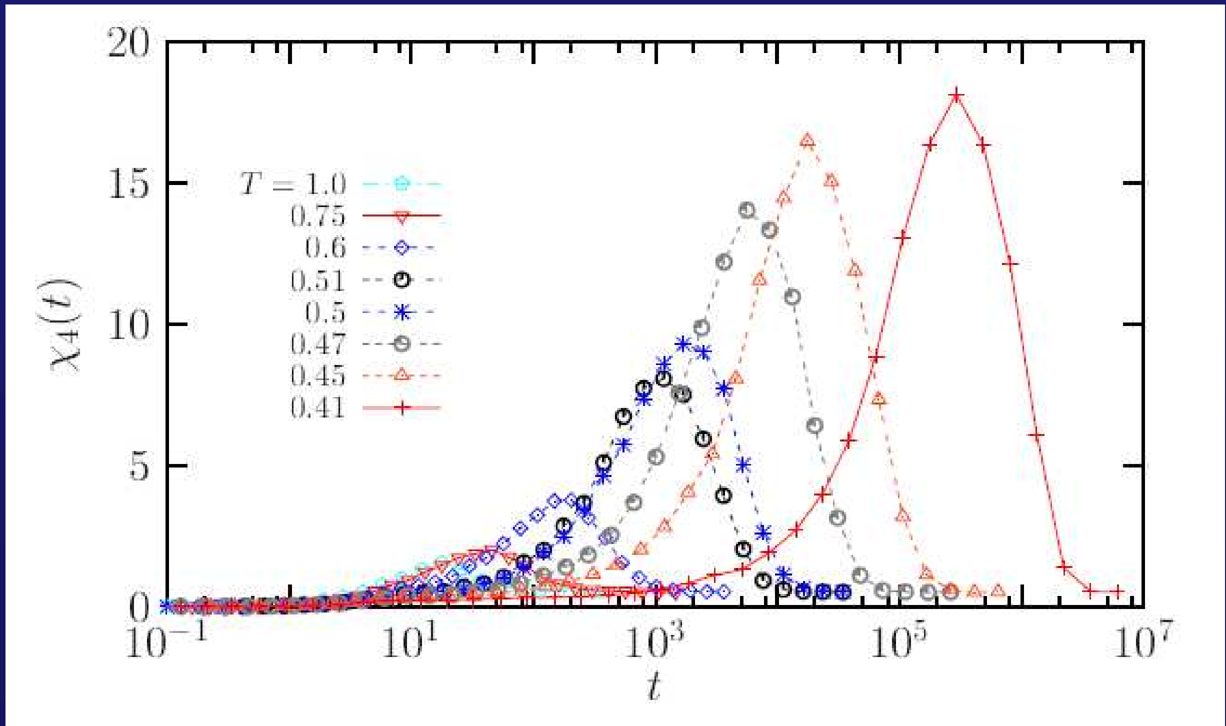
Granular fluid of ball bearings

Colloidal glass

Computer simulation 2D repulsive discs

Dynamic heterogeneity

Glass transition: critical phenomenon?



No true divergence
No dynamic criticality

Summary

- Glasses, Suspensions

  Liquid and Solid, depending on time scale

- Free volume theory

  → Glasses: temperature - viscosity (Vogel-Fulcher)

  → Suspensions: Divergence of viscosity

- Correlations

  Coupling ⇨ Self-Organization?