Soft modes and strings
from cold to hot

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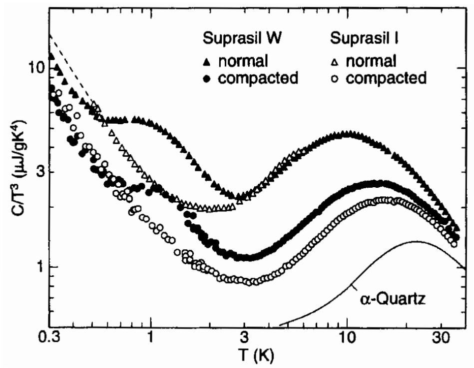
Introduction

- Glasses and amorphous materials are structurally disordered.
- Force constant disorder results from structural disorder and internal stresses.
- Nearest neighbour order in general similar to crystal.
- Glassy spectrum at higher frequencies similar to cystalline one.
- Elastic constants similar to crystalline ones, normally somewhat lower.

Glassy properties

- Vibrations, Boson peak, sound wave damping, localization.
- Two-level systems (tunnelling).
- Diffusion mechanism, isotope effect, activation volume, dynamic heterogeneity.

Specific Heat of Amorphous Silica



two-level systems (tunnelling)

$$E = \sqrt{\Delta + \Delta_0}$$
$$\Delta_0 \sim \hbar \omega e^{-\lambda}$$
$$\lambda = g/\hbar \sqrt{m E_b d}$$

standard tunnelling model

localized motion

$N \sim 10^{-6}$

harmonic vibrations, Boson peak

$$I_{\text{inelastic}}(\omega) \propto g(\omega)/\omega^2$$

dynamical matrix: ω^2, $\mathbf{e}_{i,\alpha}$

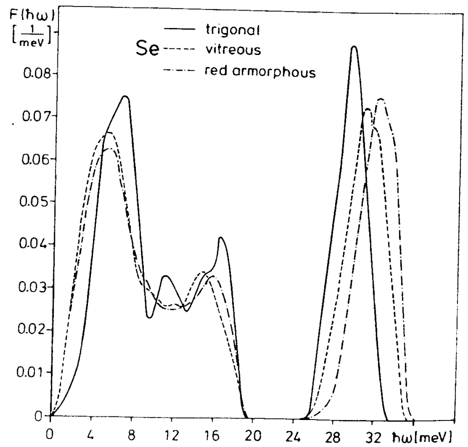
continuum of modes

e.g. random matrix models

extended modes

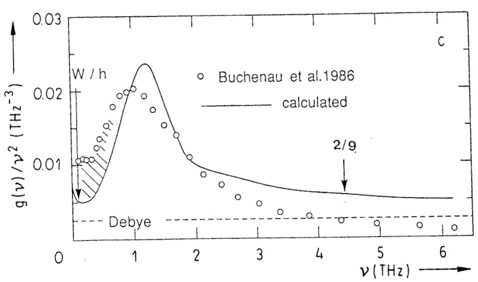
$N \sim 10^{-2}$

Vibrations



Gompf, J. Phys. C. S. **42**, 539 (1981)

- vibrational densities of state:
  similar for glasses and their crystalline counterparts
- similar near neighbour structure
- the elastic constants are similar



Buchenau, PRB **34**, 5665 (1986)

- excess of low frequency vibrations:
  Boson peak
- maximum in specific heat

random matrix realisations

$$D^{mn}_{\alpha\beta} = \frac{\partial^2 u(|\mathbf{R}^m - \mathbf{R}^n|)}{\partial R^m_\alpha \partial R^n_\beta} = \sum_\sigma m\omega(\sigma)^2 e(\sigma)^m_\alpha e(\sigma)^n_\beta \tag{1}$$

$$Z(\nu) = \left\langle \frac{1}{3N-3} \sum_\sigma \delta(\omega - \omega^\sigma) \right\rangle \tag{2}$$

dynamical matrix is $N \times N$ but has N eigenvalues
$========>$ additional information needed

too weakly restricted random matrix has negative eigenvalues
too strongly restricted random matrix reflects ad-hoc restrictions

softpotential model

assumption:

- some groups of atoms show a soft local vibration
- their structure does not strongly depend on their vibrational frequency.

$$V(x) = \epsilon \left[\eta (x/a)^2 + t (x/a)^3 + (x/a)^4 \right] \quad (3)$$

low frequency limit: $p(\eta, t) = p_0 |\eta|$

$=======>$ universal behavior
$m_{eff} > 10m$
coupling to phonons strong and not proportional to ω^2
$\Phi - \delta\Phi \approx 0$

note: in fcc, hcp $f_{parall} >> 0$ but $f_{vert} < 0$
local stress leads to cancellation of force constants

Boson Peak and sound waves

- split modes into sound waves and local modes
  $H = H_{\rm sw} + H_{\rm lm} + H_{\rm int} + H_{\rm anh}$
- interaction between local modes via sound waves
  $g_{\rm ex} \propto \omega$
  unstable modes
- remove instability by anharmonicity
  $g_{\rm ex}$ universal shape
  $g_{\rm ex} \propto \omega^4$ for $\omega \longrightarrow 0$
  $g_{\rm ex} \propto \omega$ for $\omega > \omega_{\rm BP}$
  tunnelling states
- scatter sound waves on $g_{\rm ex}$

Weakly Interacting Oscillators I

$$U_{\text{tot}}(x_1, x_2, ..., x_s) = \sum_i \frac{k_i}{2} x_i^2 - \frac{1}{2} \sum_{i,j \neq i} I_{ij} x_i x_j + \frac{1}{4} \sum_i A_i x_i^4, \qquad A_i > 0$$

$k_i = m\omega_i^2$ e. g. $g_0(\omega) = 3\omega^2 \quad \omega \leq 1$

$I_{ij} = g_{ij} J / r_{ij}^3 \qquad J = \Lambda^2/\rho/v^2$

$$M_1 \ddot{x}_1 = -k_1 x_1 + \sum_{j \neq 1} I_{1j} x_j - A_1 x_1^3 \qquad \text{low frequency oscillator}$$

$$M_j \ddot{x}_j = -k_j x_j + \sum_{i \neq j} I_{ji} x_i - A_j x_j^3, \qquad j \neq 1 \qquad \text{high frequency oscillator}$$

$$M_1 \ddot{x}_1 = -(k_1 - \kappa) x_1 - A_1 x_1^3 = -\frac{dU_{\text{eff}}(x_1)}{dx_1}$$

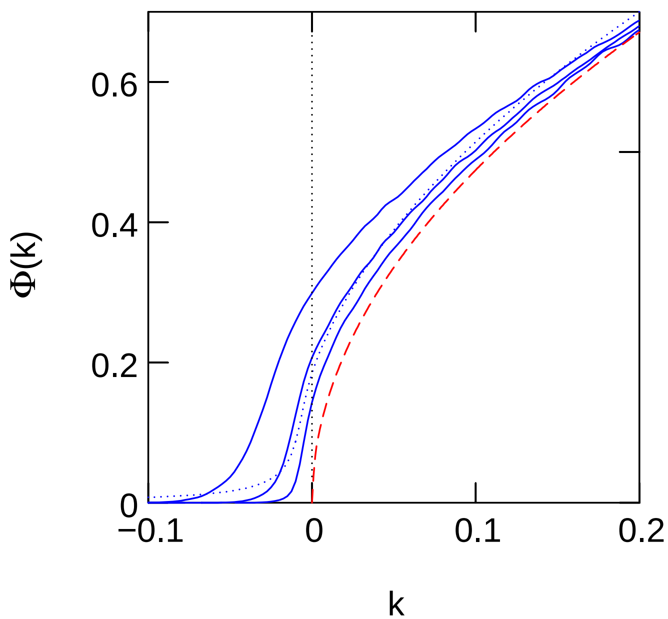
$$\kappa = \sum_{j \neq 1} \frac{I_{1j}^2}{k_j} \simeq \frac{I^2}{M\omega_0^2}$$

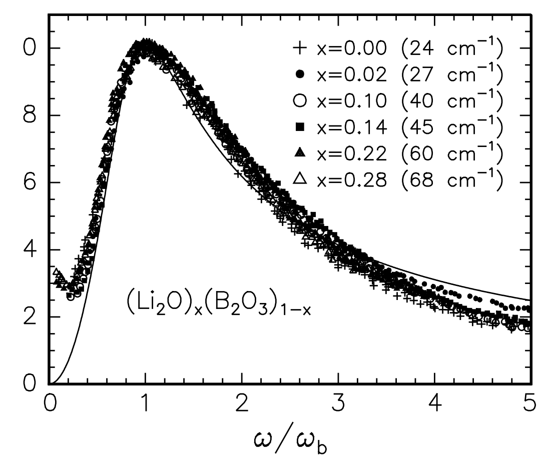
Boson Peak

$$U_{\rm tot} = \sum_i \frac{M_i\omega_i^2}{2}x_i^2 + \frac{1}{4}\sum_i A_i x_i^4 + \frac{1}{2}\sum_{i,j\neq i} I_{ij}x_i x_j .$$

interaction ===> harmonic instability anharmonicity ===> stabilisation

====> universal shape of boson peak

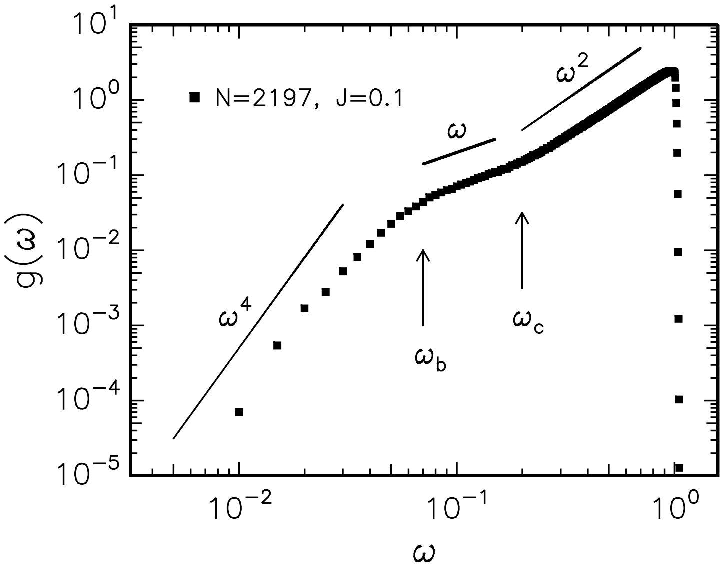




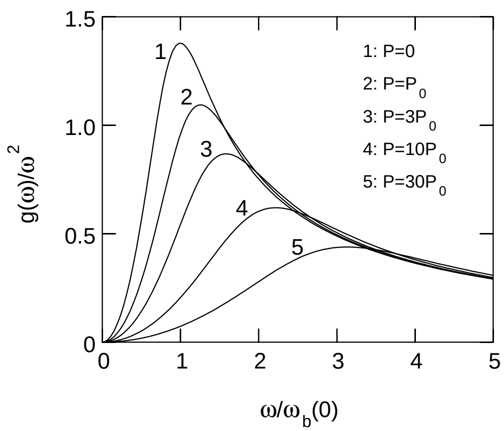
Gurevich *et al.*, PRB **67**, 094203 (2003)

Boson peak intensity

$$U_{\rm tot} = \sum_i \frac{k_i}{2} x_i^2 - \frac{1}{2}\sum_{i,j\neq i} I_{ij} x_i x_j + \frac{1}{4}\sum_i A_i x_i^4 - \sum_i f_i x_i - \frac{1}{2}\sum_{i,j\neq i} \Delta I_{ij} x_i x_j$$



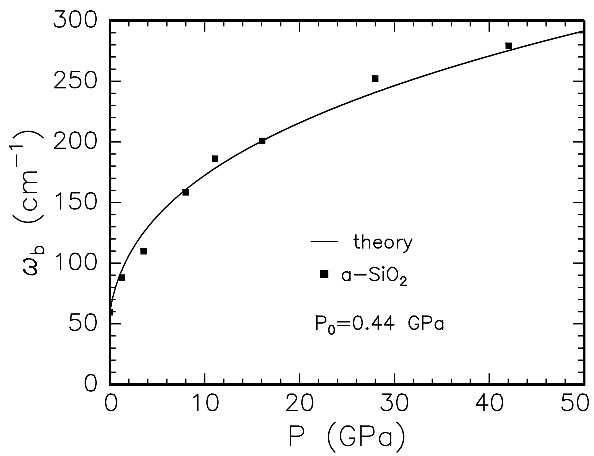
pressure



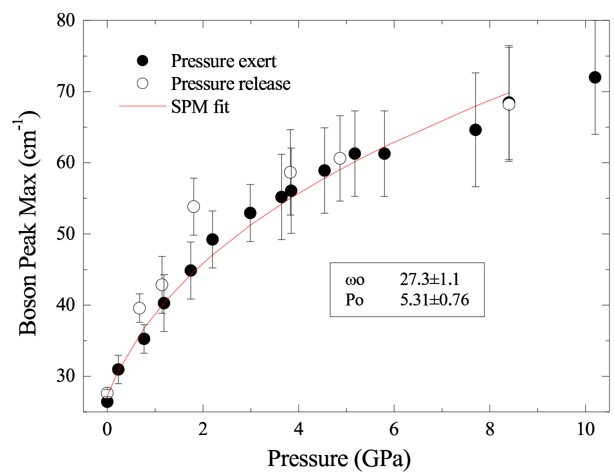
$$I(\omega_{\rm BP}) \propto \omega_{\rm BP}^{-1}$$

Gurevich *et al.*, PRB **71**, 014209 (2005)

Boson Peak Pressure Experiment



SiO



As_2S_3

experiment: Hemley et al. (1997)

experiment: Andrikopoulos et al. (2006)

Boson Peak and sound waves

T-matrix scattering approximation, Z. Phys. B **21**, 255 (1975), averaged over Boson Peak excess spectrum

$$S(q,\omega) \propto \Im G(q,\omega) \propto \Im \frac{1}{m\omega^2 - m\omega_0(q)^2 + \Sigma(q,\omega)}$$

$\Re\Sigma$: shift
$\Im\Sigma$: width

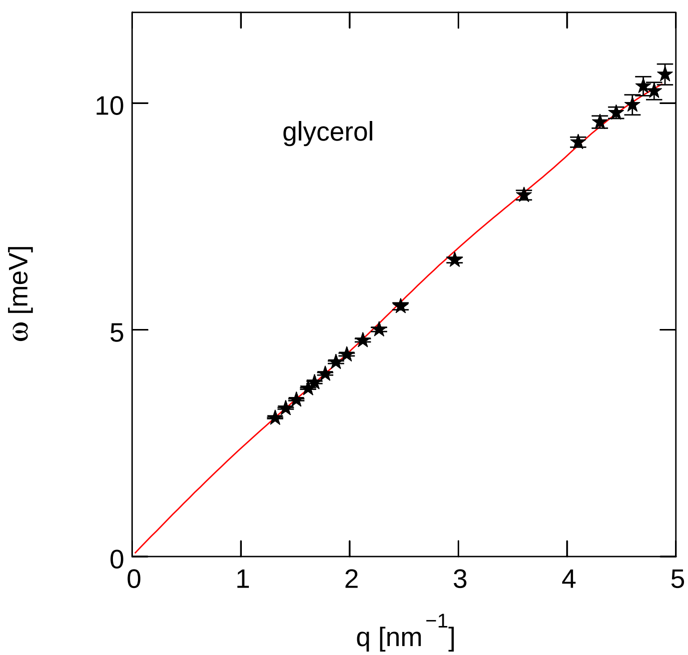
$$\Sigma(q,\omega) = \int_s g_{\rm BP}(\omega_s) t_s(q,\omega)\, d\omega_s$$

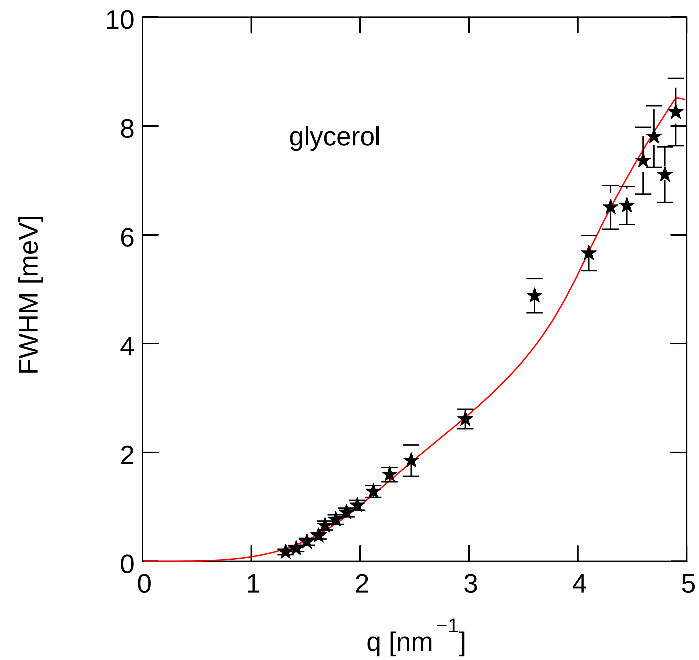
$$t_s(q,\omega) \approx \frac{|\langle q|\delta l|s\rangle|^2}{m\left(\omega^2 - \omega_s^2 - i2\omega_s\gamma_s(\omega)\right)}$$

$|\langle q|\delta l|s\rangle|^2 \propto q^2, q^4$

$\gamma_s(\omega) \propto \omega, \omega^3$
$\omega_0(q), \omega_{\rm BP}$ plus 2 or more parameters

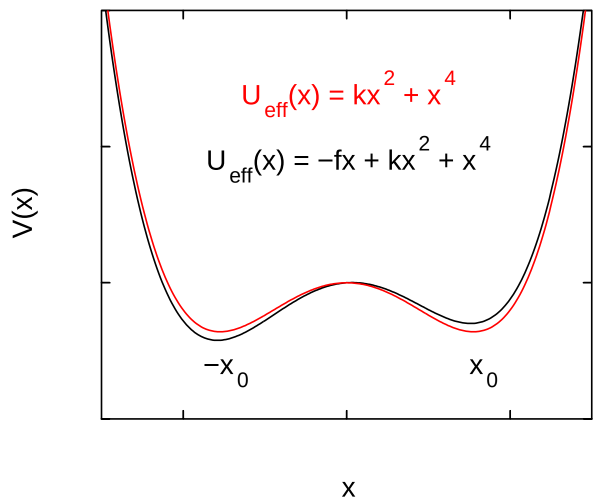
Boson Peak and sound waves,glycerol





fit to G. Monaco and V. M. Giordano, PNAS **106**, 3659 (2009).

Two Level Systems



$$\Delta_0 \approx W \exp\left(-S/\hbar\right)$$

$$S = \int_{-x_0}^{x_0} |p| dx = 2 \int_{0}^{x_0} \sqrt{2M\left[U_{\rm eff}(x) + V\right]} dx$$

$$\Delta = 2 f x_0 = 2f\sqrt{|k|/A}$$

$$E = \sqrt{\Delta_0^2 + \Delta^2}$$

standard tunnelling model recovered (+log corrections)

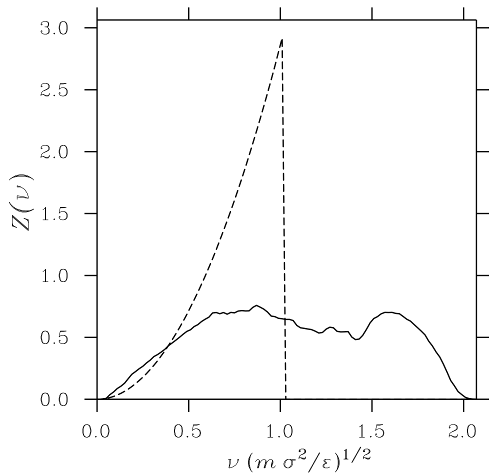
consistent set of parameters for TLS and BP

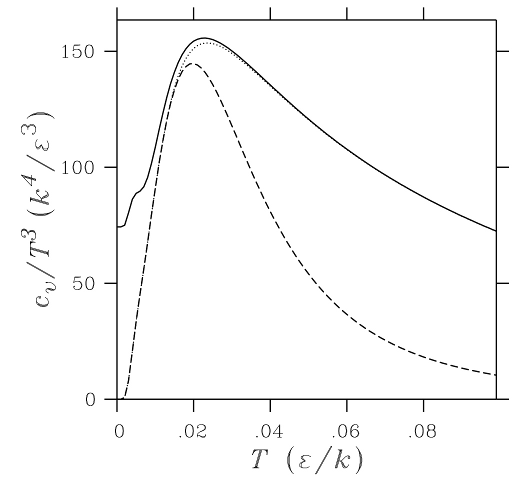
$n_{\rm TLS} \sim 10^{-7}$

$C = \frac{\bar{P}\gamma^2}{\rho v^2} \sim 10^{-4}$

Computer Simulation: Vibration

$V(r) = 1/r^6 +$ cutoff correction

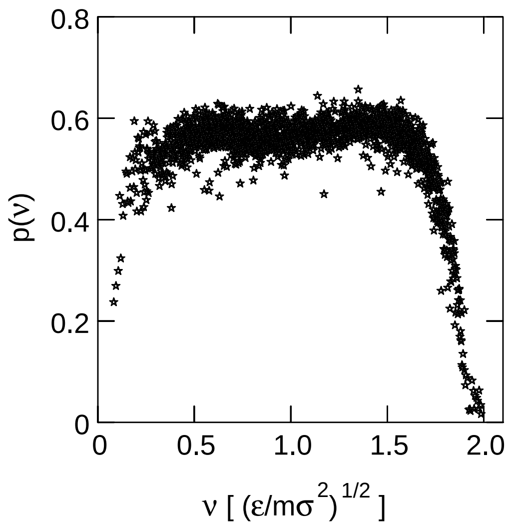




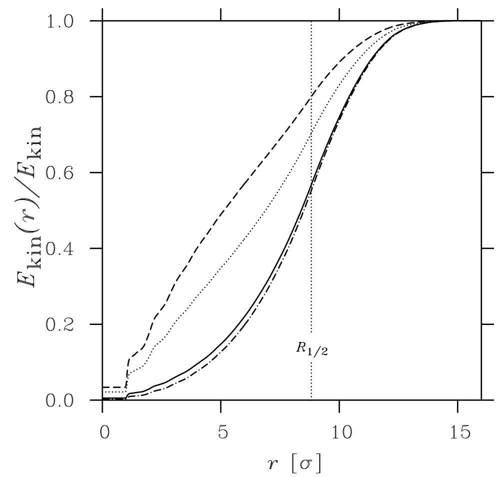
HRS + Oligschleger, PRB **53**, 11469

Computer Simulation: Vibration II

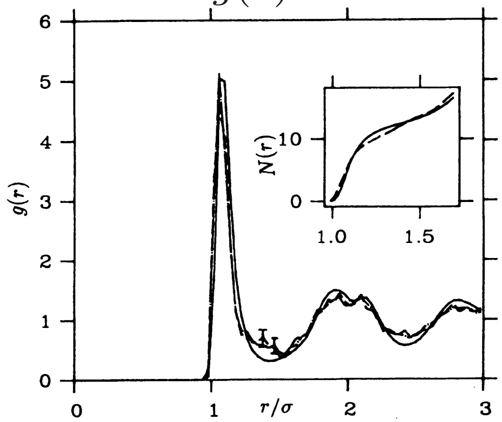
$$p = \left(N \sum_j |\mathbf{e}^j|^4 \right)^{-1}$$



HRS + Laird, PRB **44**, 6747

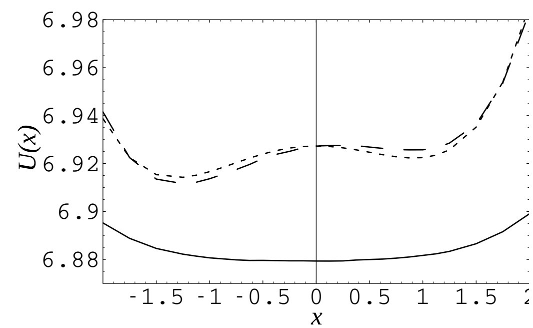


Computer Simulation: Vibration III



HRS + Laird, PRB **44**, 6747

$$\mathbf{R}^n = \mathbf{R}_0^n + x\mathbf{e}^n$$

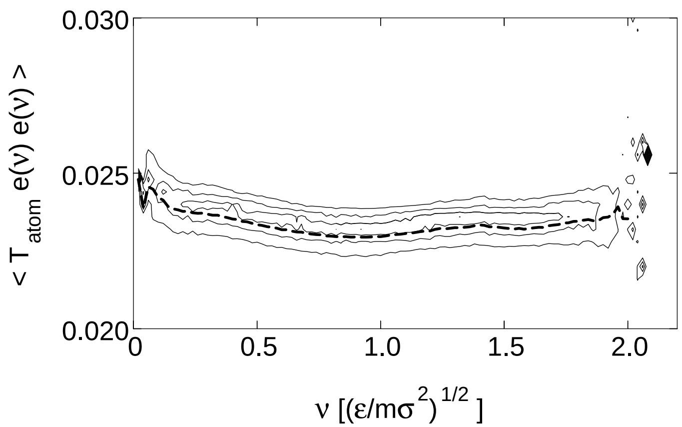


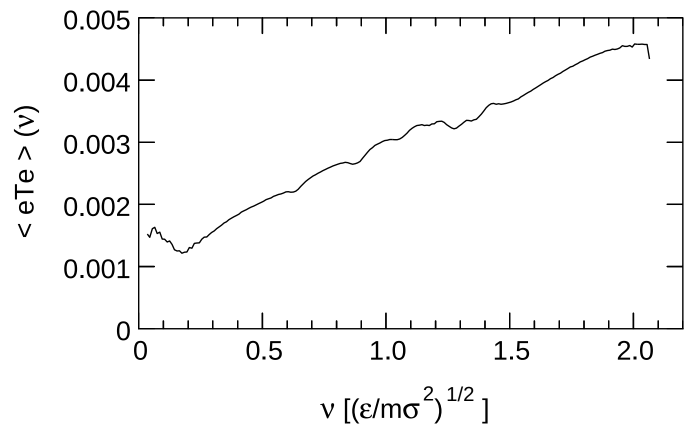
Luchnikov, PRB **62**, 3184

Classification of Structures ?

Voronoi-Delaunay tesselation; e.g. tetrahedricity

$$T(\nu) = \langle \frac{1}{N} \sum_n T^n_{\text{atomic}} \mathbf{e}^n(\nu) \mathbf{e}^n(\nu) \rangle \qquad \mathcal{T}^{mn}_{\alpha\beta} = \frac{\partial^2 \langle T \rangle}{\partial R^m_\alpha \partial R^n_\beta}$$

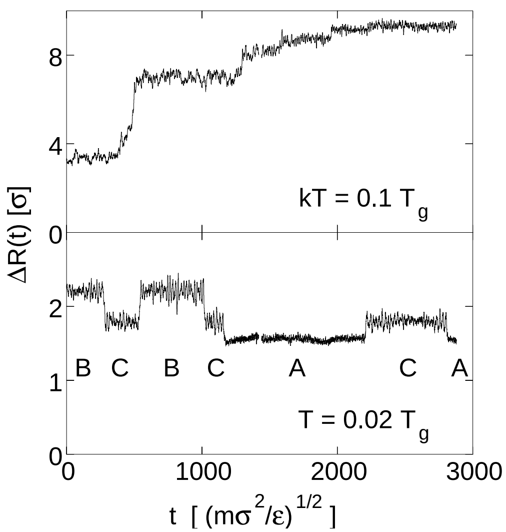




Jumps and Diffusion

total displacement

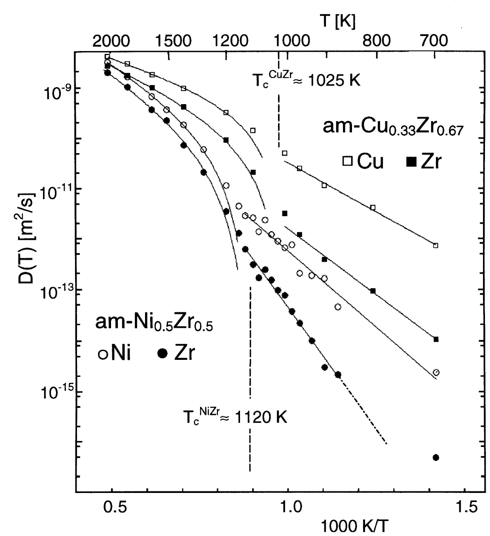
$$R(t) = \sqrt{\sum_n (\mathbf{R}^n(t) - \mathbf{R}^n(0))^2}$$



Oligschleger + HRS, PRB **59**, 811 (1999)

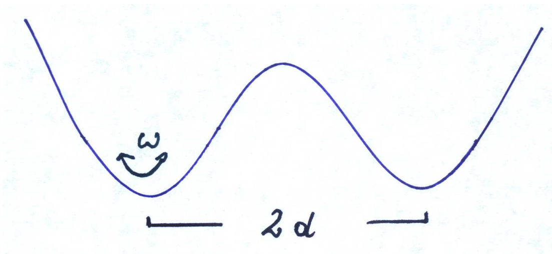
diffusion coefficient

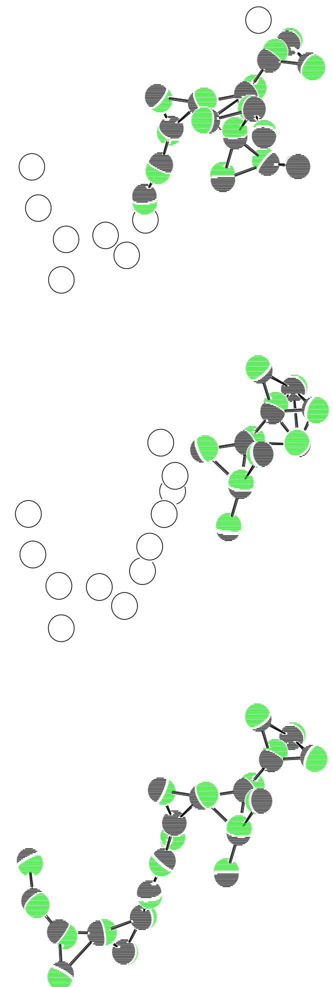
$$D = \lim_{t\to\infty} \frac{1}{6t} \langle |\mathbf{R}^n(t) - \mathbf{R}^n(0)| \rangle$$

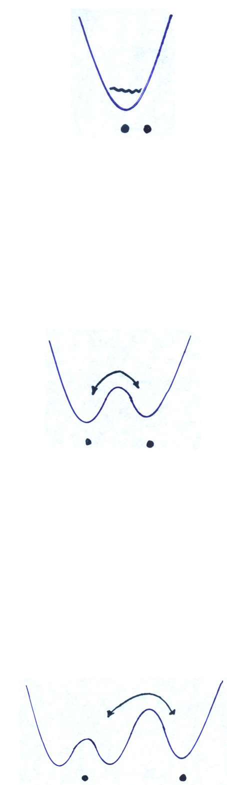


Faupel *et al.*, Rev. Mod. Phys. **75**, 237 (2003)

Quasi-Localized Vibrations and Jumps







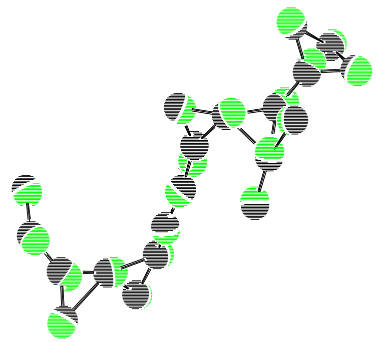
$$E^{\mathrm{m}} \approx g\,\mathbf{d}\,\underline{\underline{G^{-1}}}\,\mathbf{d}$$

$$\approx g\,d^2\,\omega_{\mathrm{QLV}}^2$$

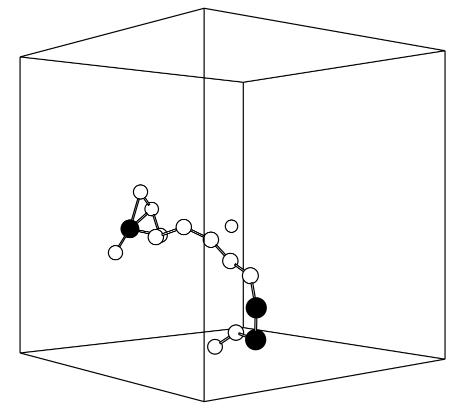
$$G^{\ell\ell}_{\alpha\beta} = \int d\omega\,\frac{e^{\ell}_{\alpha} e^{\ell}_{\beta}}{\omega^2}\,Z^{\ell}(\omega)$$

Cooperative Jumps

glass

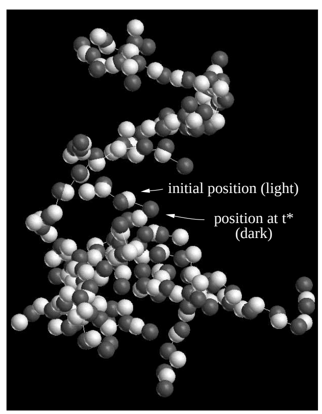


Soft sphere glass, $T = 0.15T_g$
Schober *et al.* (1993)

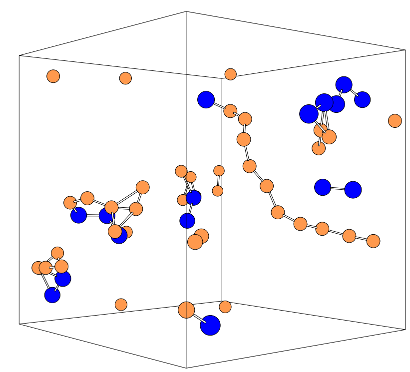


CuZr, T= 350 K ($\Delta R > 0.0075$ nm)
Gaukel, thesis (1998)

melt



binary Lennard-Jones
Donati *et al.* (1998)



CuZr, T= 1200 K ($\Delta t = 6.5$ ps)
Schober *et al.* (1997)

Dimension

$$G_{\alpha\beta}(j) = \frac{\sum_n |\Delta\mathbf{R}^n(j)|^\mu \, (R_\alpha^n - R_\alpha^{\mathrm{CM}})(R_\beta^n - R_\beta^{\mathrm{CM}})}{\sum_n |\Delta\mathbf{R}^n(j)|^\mu}.$$

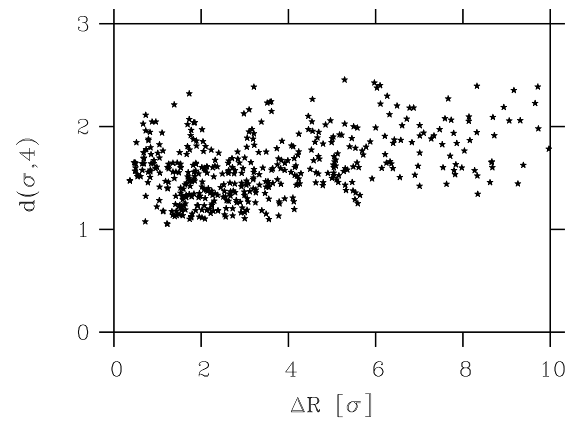
where we take the exponents $\mu = 2$ and $\mu = 4$, and

$$\mathbf{R}^{\mathrm{CM}} = \frac{\sum_n |\Delta\mathbf{R}^n(j)|^\mu \, \mathbf{R}^n}{\sum_n |\Delta\mathbf{R}^n(j)|^\mu}.$$

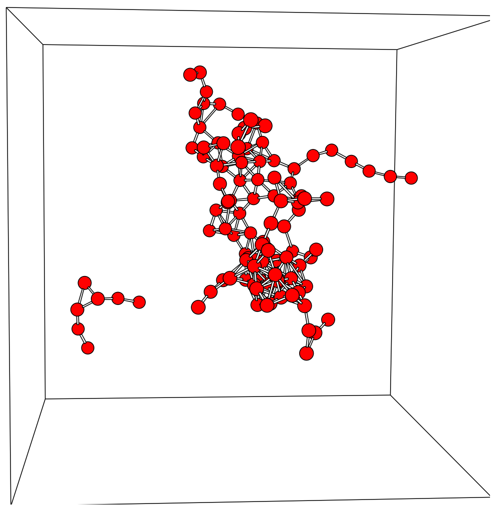
eigenvalues: $\rho^i(j,\mu)$ and average gyration radius

$$R_{\mathrm{gyr}}(j,\mu) = \sqrt{\frac{1}{3}\sum_i \rho^i(j,\mu)}.$$

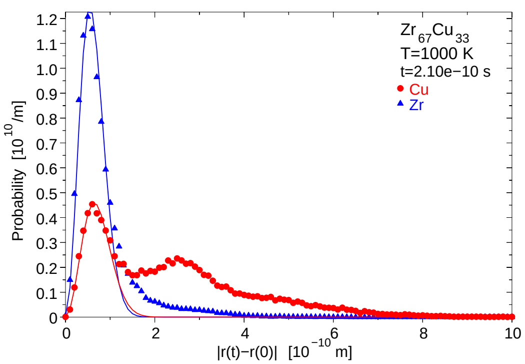
$$d(j,\mu) = \sum_i \rho^i(j,\mu) \;/\; \max \rho^i(j,\mu)$$



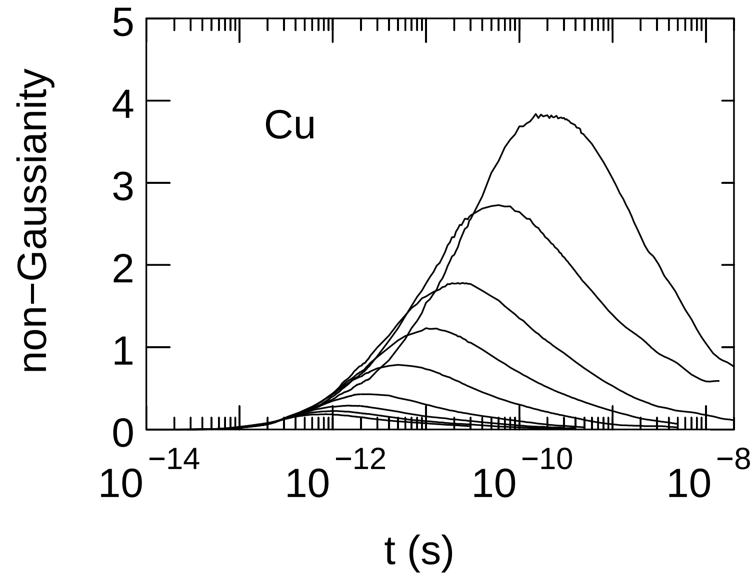
Dynamic Heterogeneity



$$\alpha_2(t) = \frac{3\left\langle \left(\Delta R^i(t)\right)^4 \right\rangle}{5\left\langle \left(\Delta R^i(t)\right)^2 \right\rangle} - 1$$

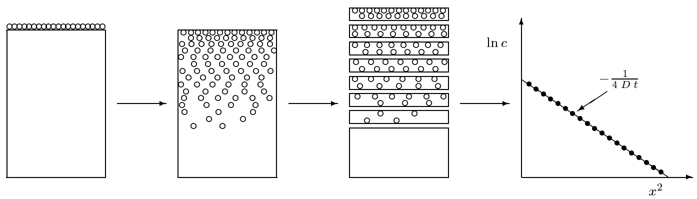


auto-correlation function



T =800, 900,1000, 1100, 1200 .... 2000 K

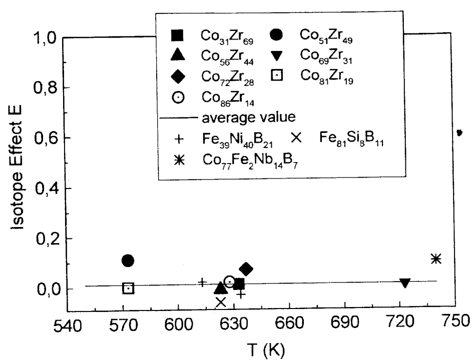
Isotope Effect



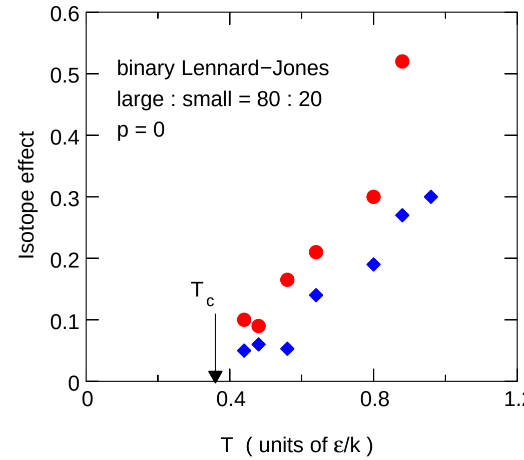
$$D = \frac{1}{\sqrt{m_{\mathrm{eff}}}} D^*$$

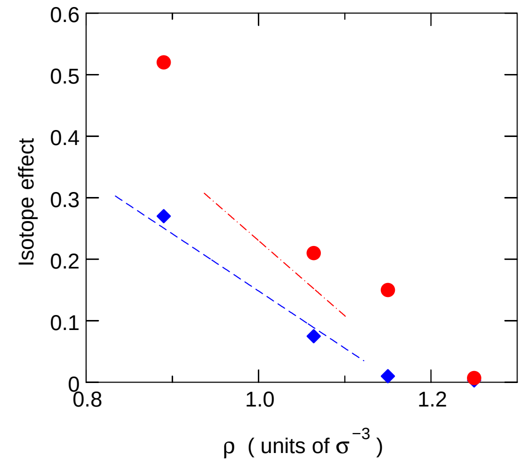
$$(m_{\mathrm{eff}})_\alpha = m_\alpha + (n-1)\overline{m}$$

$$E = \frac{D\alpha/D_\beta - 1}{\sqrt{m_\beta/m_\alpha - 1}} \qquad E \to \frac{1}{n}$$



Faupel *et al.* 1990 ff





Schober, Solid St. Comm. **119**, 73 (2001)

Pressure Dependence

$$V_{\text{act}} \approx -kT \left[\frac{\partial \ln D}{\partial p}\right]_T$$

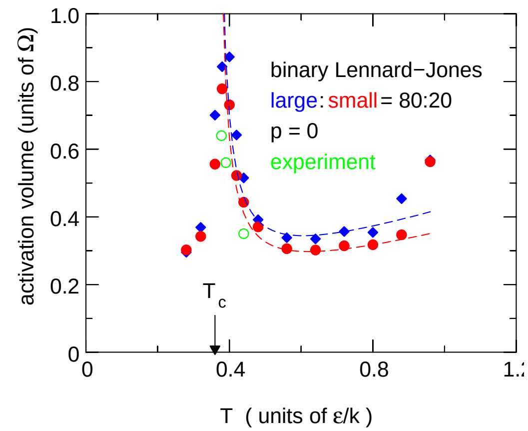
$$V_{\text{act}}^{\text{MCT}} \sim -kT \left[\frac{\partial \ln D_0^{\text{MCT}}}{\partial p} - \frac{\gamma}{(T-T_c)} \frac{\partial T_c}{\partial p}\right]_T$$

crystal

$$V_{\text{act}} \approx \left[\frac{\partial E^m + E^f}{\partial p}\right]_T$$

$V_{\text{act}} \approx \Omega$ vacancy diffusio n

$V_{\text{act}} \approx 0$ interstitial diffusion



glass

experiment: $V_{\text{act}} = 0.1\Omega .....\Omega$

liquid

$$D^{\text{VFT}} = D_0^{\text{VFT}} e^{-E^{\text{VFT}}/k(T-T_0)}$$

$$====> V_{\text{act}}^{\text{VFT}} \sim \left[\frac{E^{\text{VFT}}}{(T-T_0)^2} \frac{\partial T_0}{\partial p}\right]_T$$

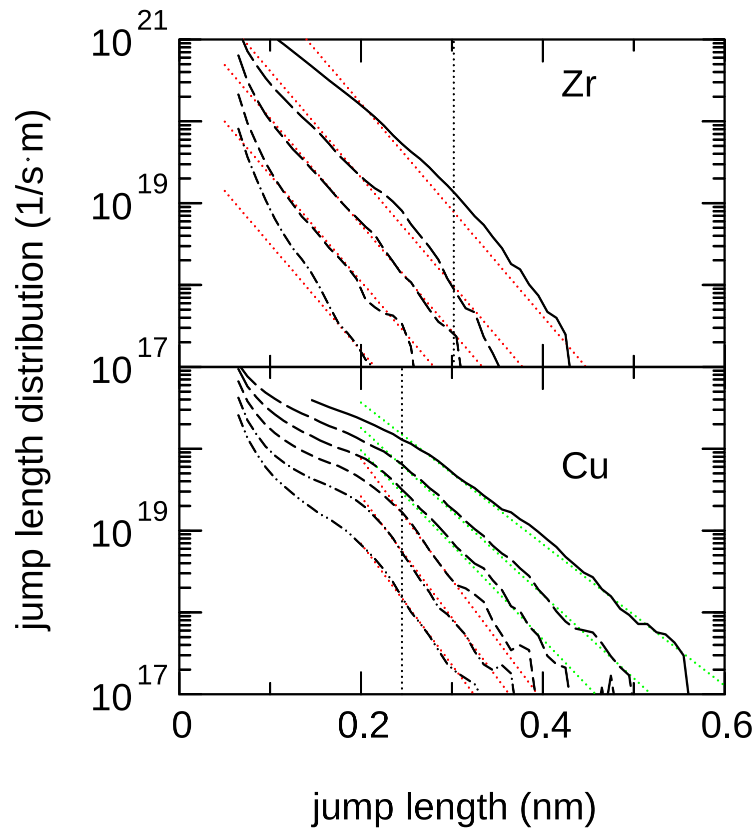
$$D^{\text{MCT}} = D_0^{\text{MCT}} (T - T_c)^{\gamma}$$

$\frac{\partial \ln D_0^{\text{MCT}}}{\partial p}$: plateau

$\frac{\gamma}{(T-T_c)} \frac{\partial T_c}{\partial p}$: cusp

H. R. Schober, Phys. Rev. Lett. **88**, 145901 (2002)

Atomic Jump Length in $Cu_{33}Zr_{67}$ I

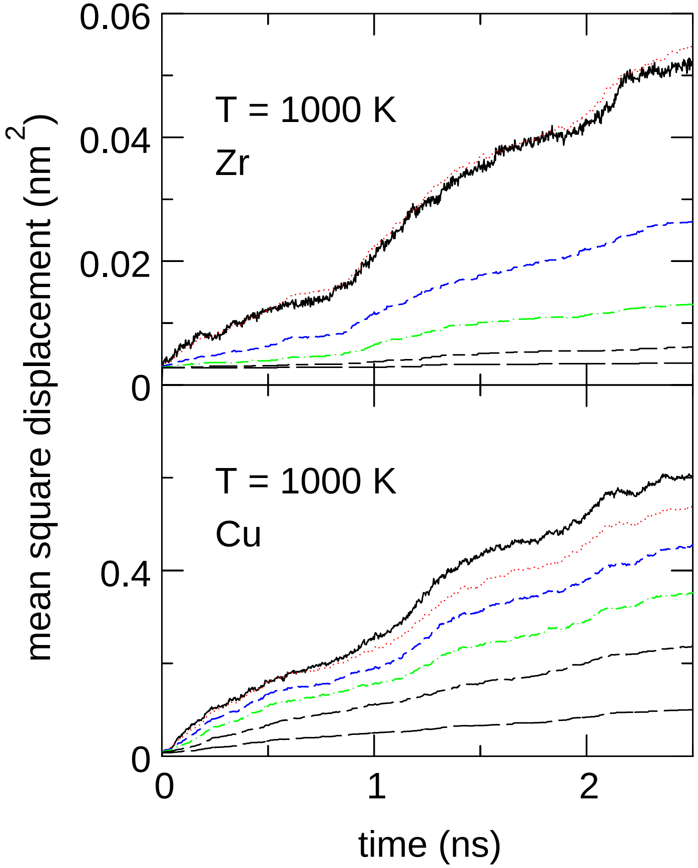


T = 1400, 1200, 1100, 1000, 900, (800) K

$$P_{\mathrm{jump}}(T,\ell) = A_{\mathrm{jump}} e^{-E_{\mathrm{jump}}/kT} e^{-\ell/\ell_{\mathrm{jump}}}$$

$$P^{\mathrm{Cu}}_{\mathrm{ljump}}(T,\ell) = B^{\mathrm{Cu}}_{\mathrm{ljump}} e^{-\ell/\ell_{\mathrm{ljump}}(T)} \quad T > T_{\mathrm{c}}$$

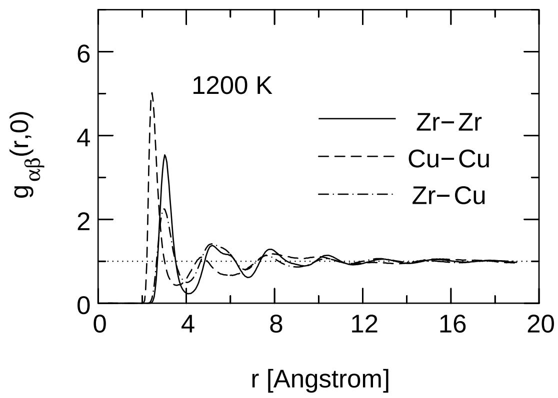
Atomic Jump Length in $Cu_{33}Zr_{67}$ II



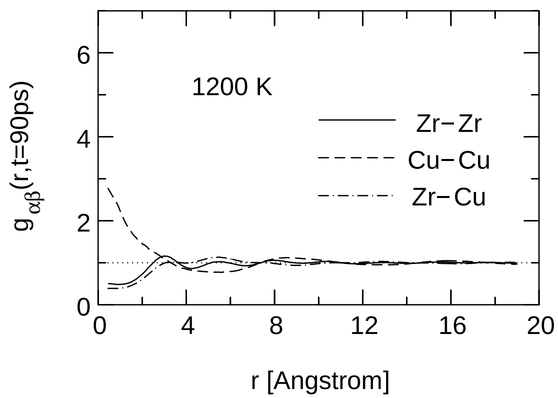
$\ell > 0.06$ nm
$\ell > 0.10$ nm
$\ell > 0.15$ nm
$\ell > 0.20$ nm
$\ell > 0.25$ nm

Paircorrelation: self-hole

$T = 1200$ K

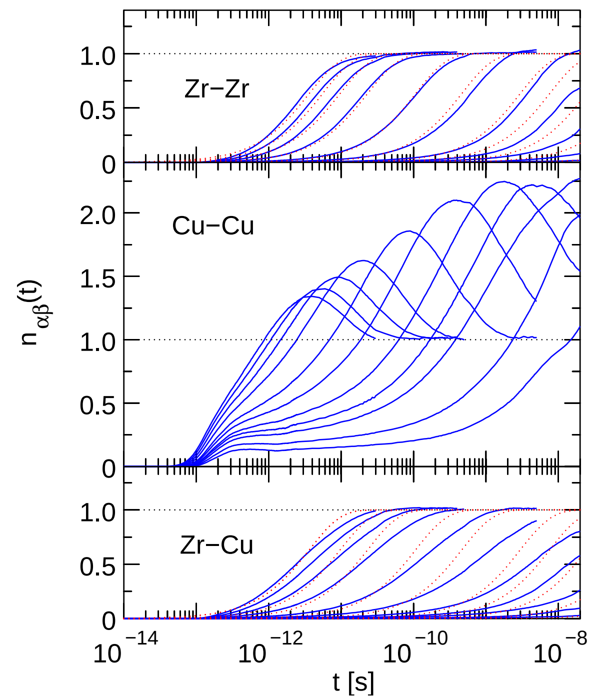


$t = 90$ ps

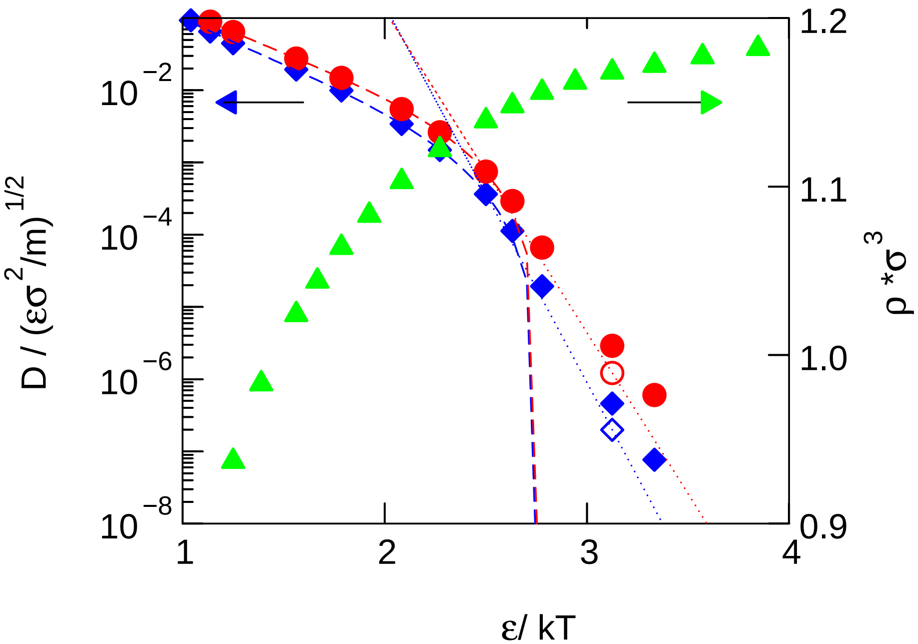


filling of self-hole with time

$T =$ 2000, ... 700 K



Diffusion in the binary Lennard-Jones system



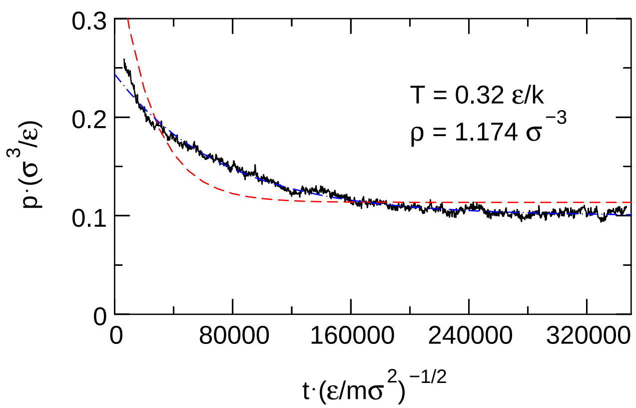
$T_g \approx 0.35\epsilon/k$

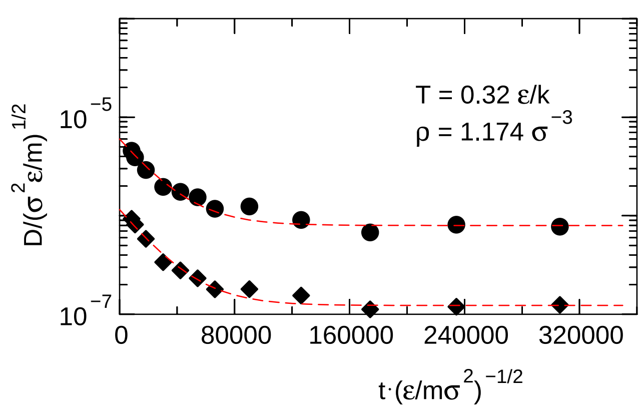
MCT fit:
$T_c = 0.36\epsilon/k$,
$\gamma = 1.87$ and 2.02

Schober, PCCP 6, 3654 (2004)

Ageing

binary Lennard-Jones system, quench from T_c to $\approx 0.9T_c$





$$p(t) = p_{\mathrm{inh}} + p_{\mathrm{def}} c_{\mathrm{def}}(0) e^{-\alpha_{\mathrm{def}} t}$$

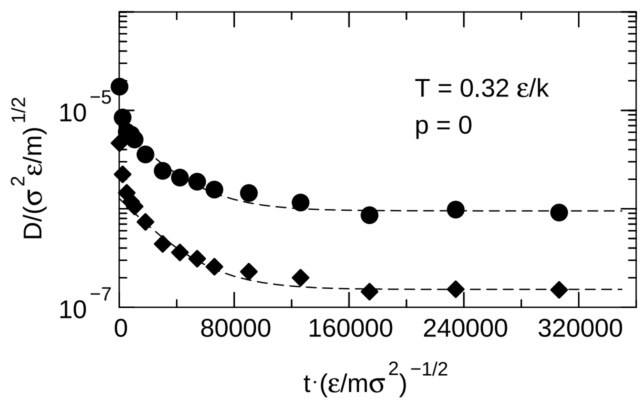
$$\alpha_{\mathrm{def}} = 1.38 \cdot 10^{-5}$$

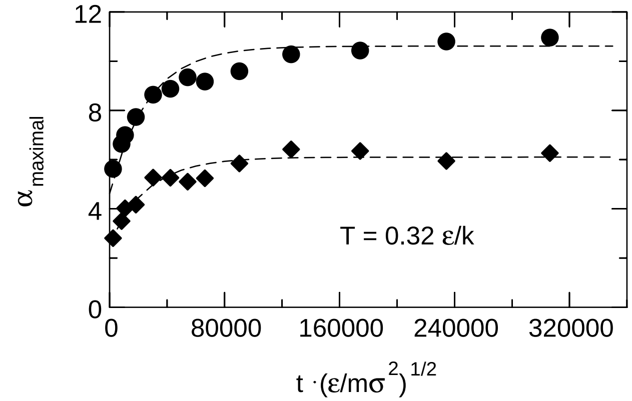
$$D(t) = D_{\mathrm{inh}} + D_{\mathrm{def}} c_{\mathrm{def}}(0) e^{-\alpha_{\mathrm{def}}} t$$

$$\alpha_{\mathrm{def}} = 4.27 \cdot 10^{-5}$$

Schober, PCCP **6**, 3654 (2004)

Ageing II





$$\alpha_2(t) = \alpha_2^{\mathrm{inh}} + \alpha_2^{\mathrm{def}} c_{\mathrm{def}}(0) e^{-\alpha_{\mathrm{def}} t}$$

$$D(t) = D_{\mathrm{inh}} + D_{\mathrm{def}} c_{\mathrm{def}}(t)$$

$$D(t) = D_{\mathrm{inh}} + D_{\mathrm{def}} c_{\mathrm{def}}(0) e^{-\alpha_{\mathrm{def}} t}$$

Schober, PCCP **6**, 3654 (2004)

Summary

- diffusion in the glass and undercooled melt is highly collective
- pressure derivative follows mode coupling theory
- no preferred jump length
- smooth transition jump $\longrightarrow$ flow
- dynamic heterogeneity
- different aging of density and dynamics
- correlation quasi local vibrations — jumps