

Introduction to Metallic Glasses: How they are different/similar to other glasses

T. Egami

- Model System of Dense Random Packing (DRP)
 - Hard Sphere vs. Soft Sphere
- Glass transition
- Universal behavior

History: Experiment

- Observations of “amorphous metals” by low temperature deposition or electro-plating; never confirmed to be glassy.
- Rapid cooling (“splat-quenching”) of Au-Si by Pol Duwez (1960).
- Confirmation through thermal measurement by David Turnbull; observation of the glass transition.
- More stable alloys (Pd-Si-Cu, etc.) by Turnbull group.
- Commercialization by Allied Chemical (1973).
- Spurt of research (magnetic and other properties) in 70s.
- Discovery of bulk metallic glasses in 90s.

BMG



History: DRP Concept

- Demonstration of extensive supercooling by D. Turnbull (1952).

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VOLUME 20, NUMBER 3

MARCH, 1952

Kinetics of Solidification of Supercooled Liquid Mercury Droplets

DAVID TURNBULL

General Electric Research Laboratory, Schenectady, New York

(Received September 21, 1951)

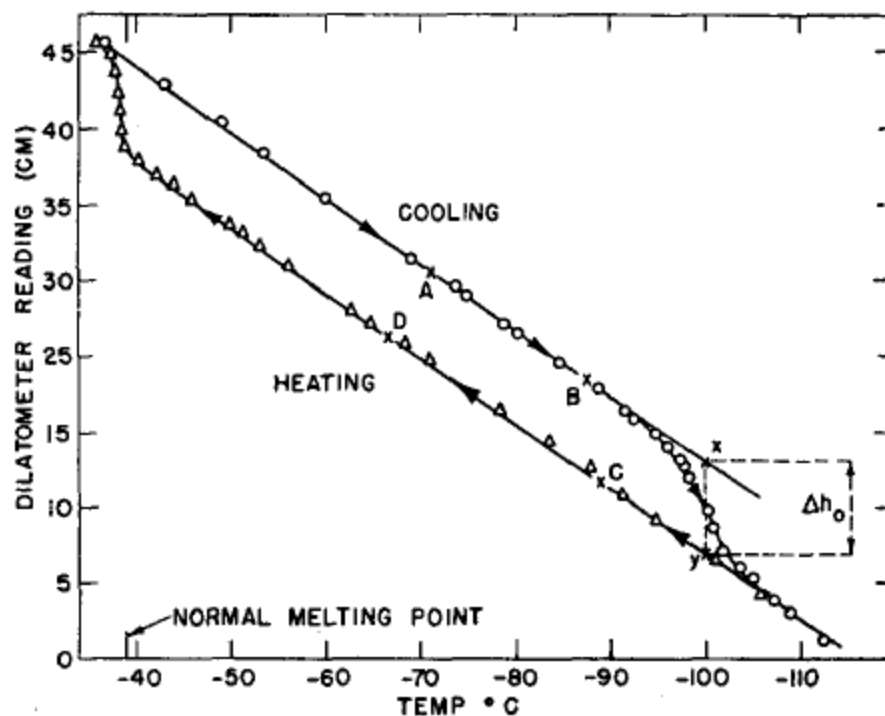


FIG. 2. Cooling-heating cycle for dispersion of Hg(St)-coated Hg droplets.

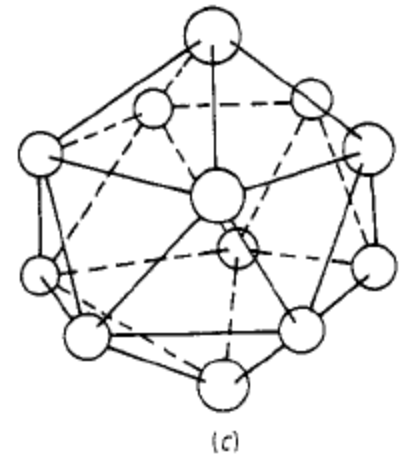
- Idea of icosahedral clusters by C. Frank (1952).

Proc. R. Soc. Lond. A 1952 **215**, 43-46

SUPERCOOLING OF LIQUIDS

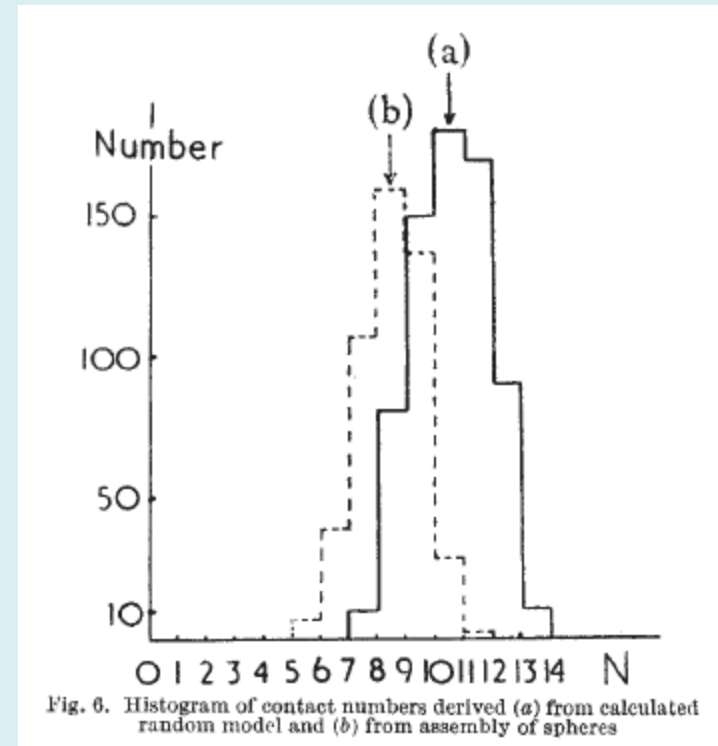
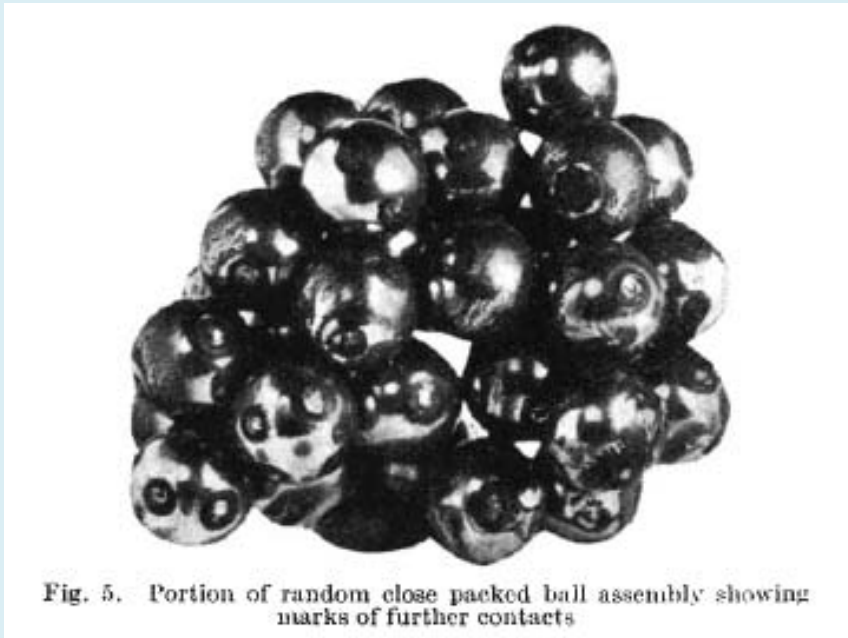
BY F. C. FRANK

H. H. Wills Physics Laboratory, Bristol University



The theoretical argument is misleading also. Consider the question: 'In how many different ways can one put twelve billiard balls in simultaneous contact with one, counting as different the arrangements which cannot be transformed into each other without breaking contact with the centre ball?' The answer is *three*. Two which come to the mind of any crystallographer occur in the face-centred cubic and hexagonal close-packed lattices. The third comes to the mind of any good schoolboy, and is to put one at the centre of each face of a regular dodecahedron. That body has five-fold axes, which are abhorrent to crystal symmetry: unlike the other two packings, this one cannot be continuously extended in three dimensions. You will find that the outer twelve in this packing do not touch each

- DRP model by Bernal (1960).



Dense and Loose Packing

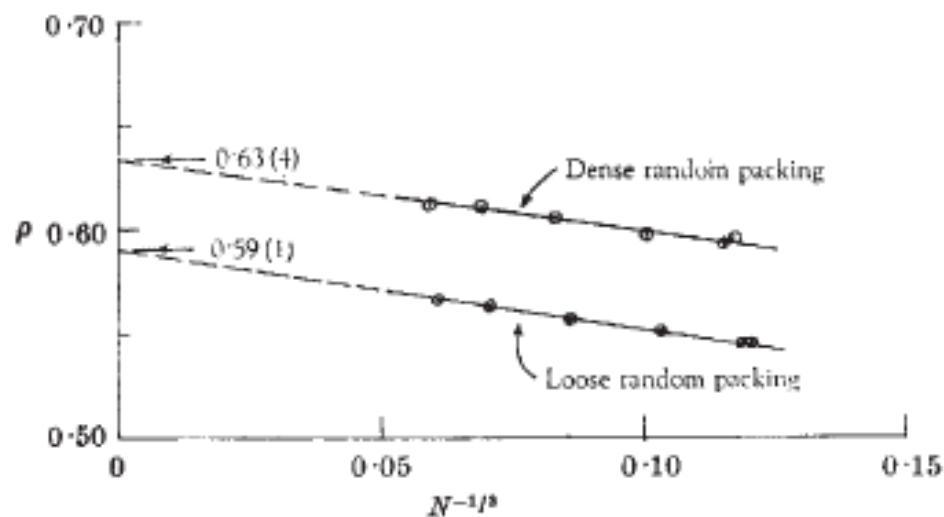


Fig. 1. Packing density for steel balls in glass flasks. Packing density (ρ) versus $N^{-1/3}$. N is the number to fill the flask

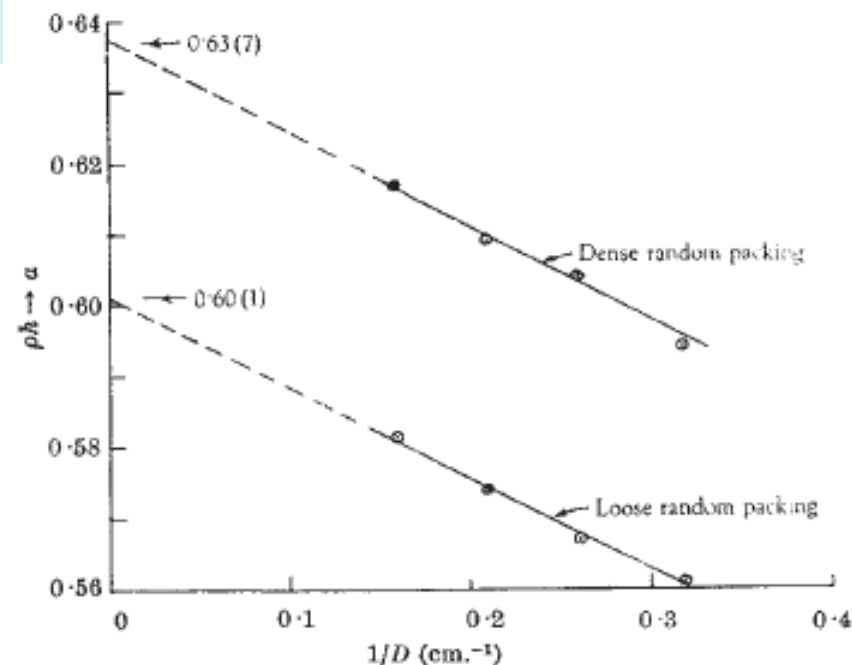
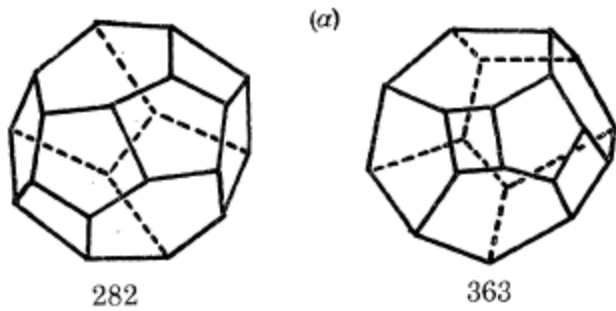


Fig. 3. Packing density in cylinder of 'infinite' length obtained from extrapolations as in Fig. 2, plotted against reciprocal of diameter. Packing density $\rho_h \rightarrow \alpha$ versus $1/D$. D is diameter of cylinder



- Analysis by J. Finny (1970).

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†

Crystallography Department, Birkbeck College, London, W.C. 1

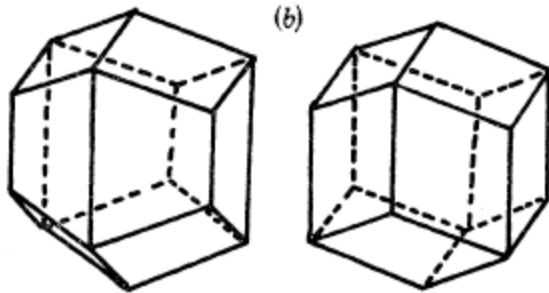


FIGURE 2

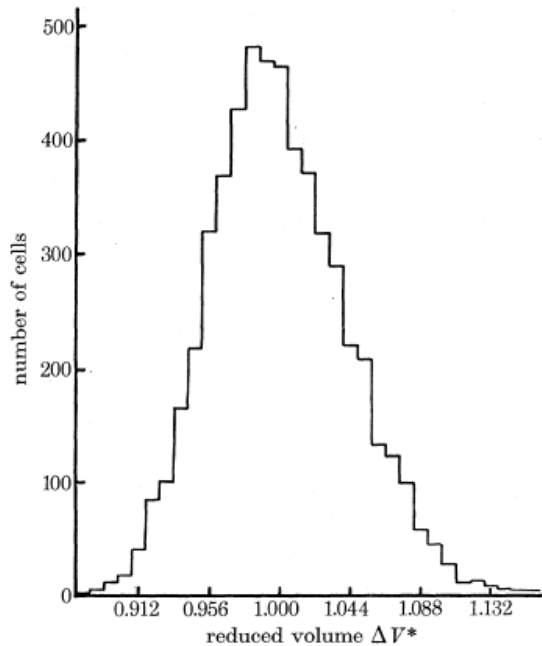
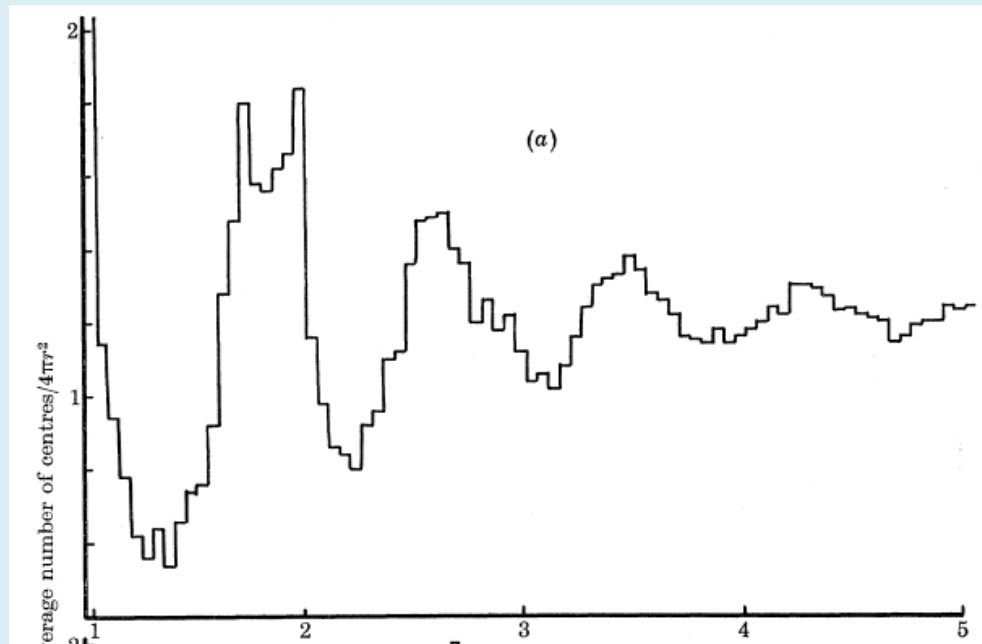
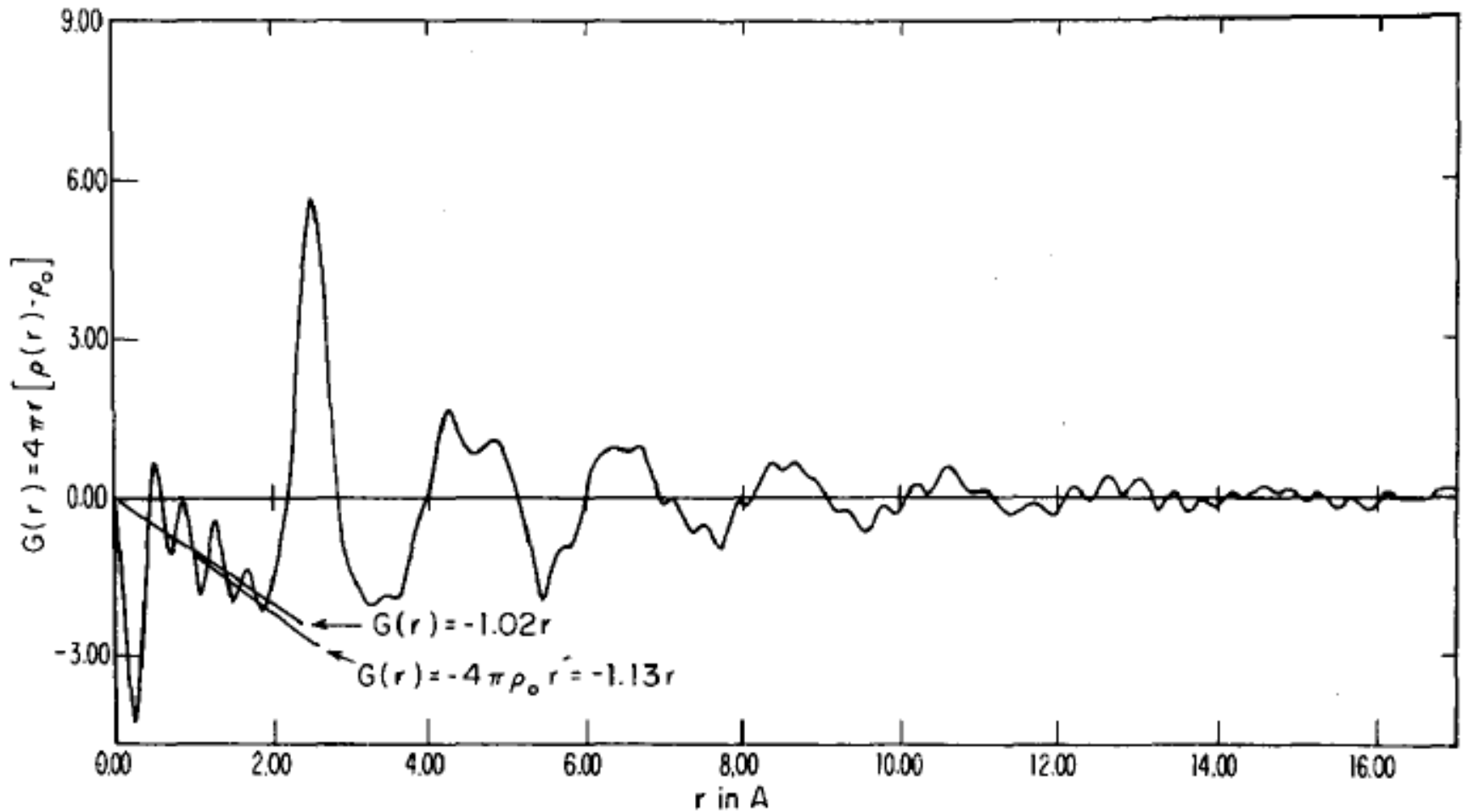


FIGURE 3. Cell volume distribution for the large model. $V^* = 0.0088$.

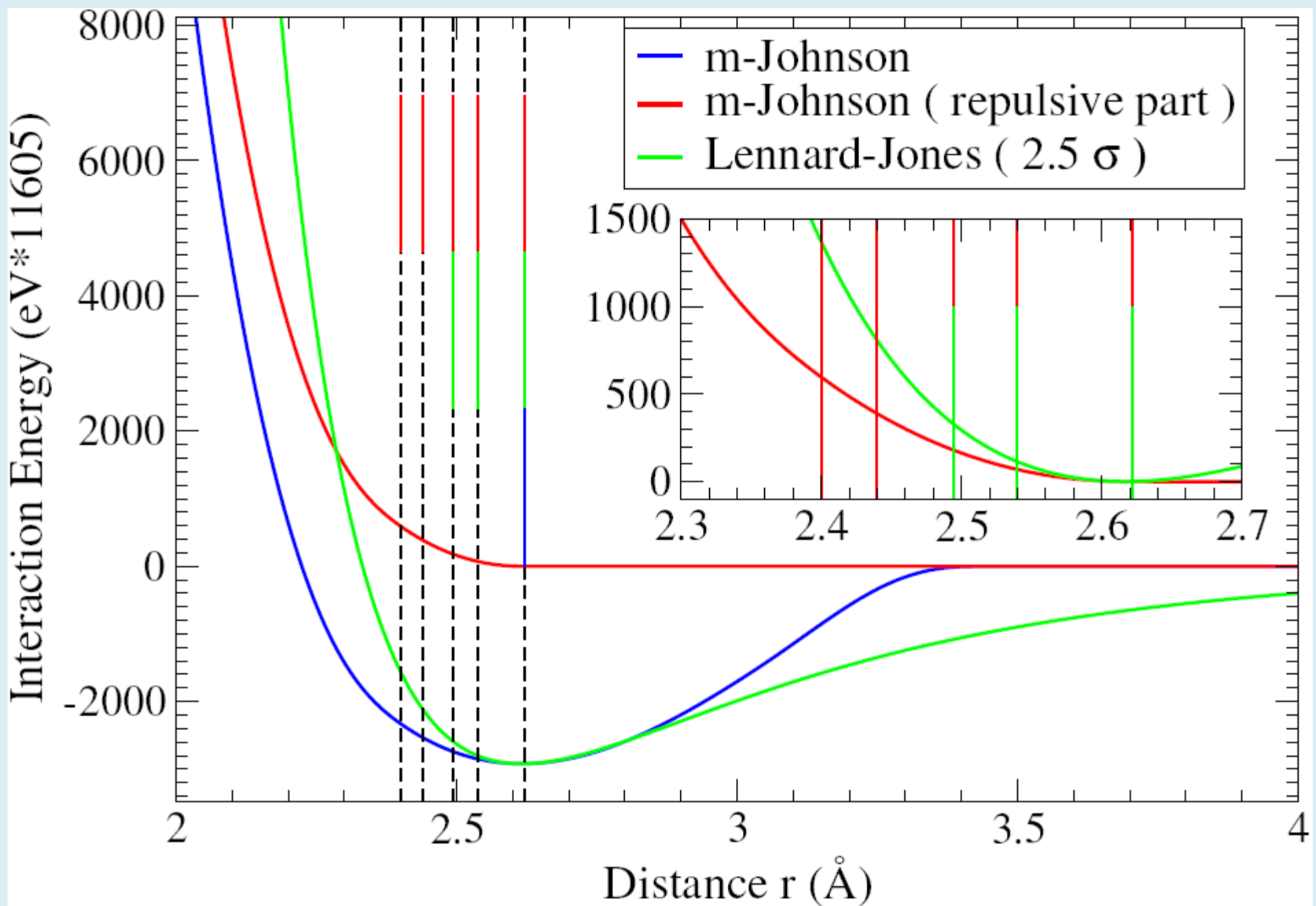


- Diffraction by S. Cargill (1971).



Hard-Sphere vs. Soft-Sphere

- The question of the potential: Probably not fundamental, but too often clouds the discussion.
- HS model is pathological, and this influences the results.
- LJ potential is not soft enough.
- Metallic potential is dominated by Friedel oscillation, and is much more harmonic.

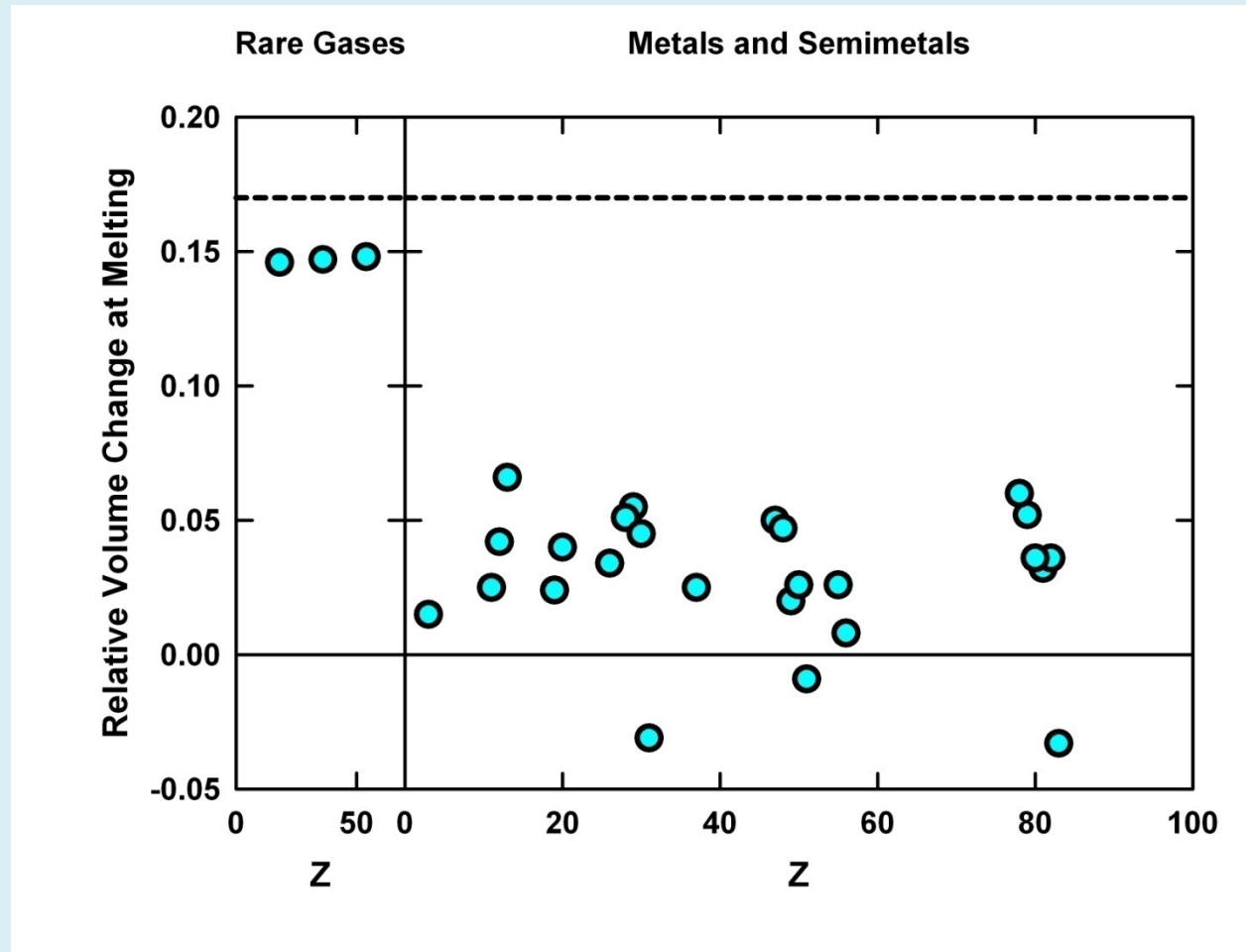


Soft Potential

- Small thermal expansion (small Grüneisen constant).
- Phase separation at low density or high temperature (below the tri-critical point).
- Weak effect of pressure and temperature.
Tendency to keep identity; characteristic local structure, etc.

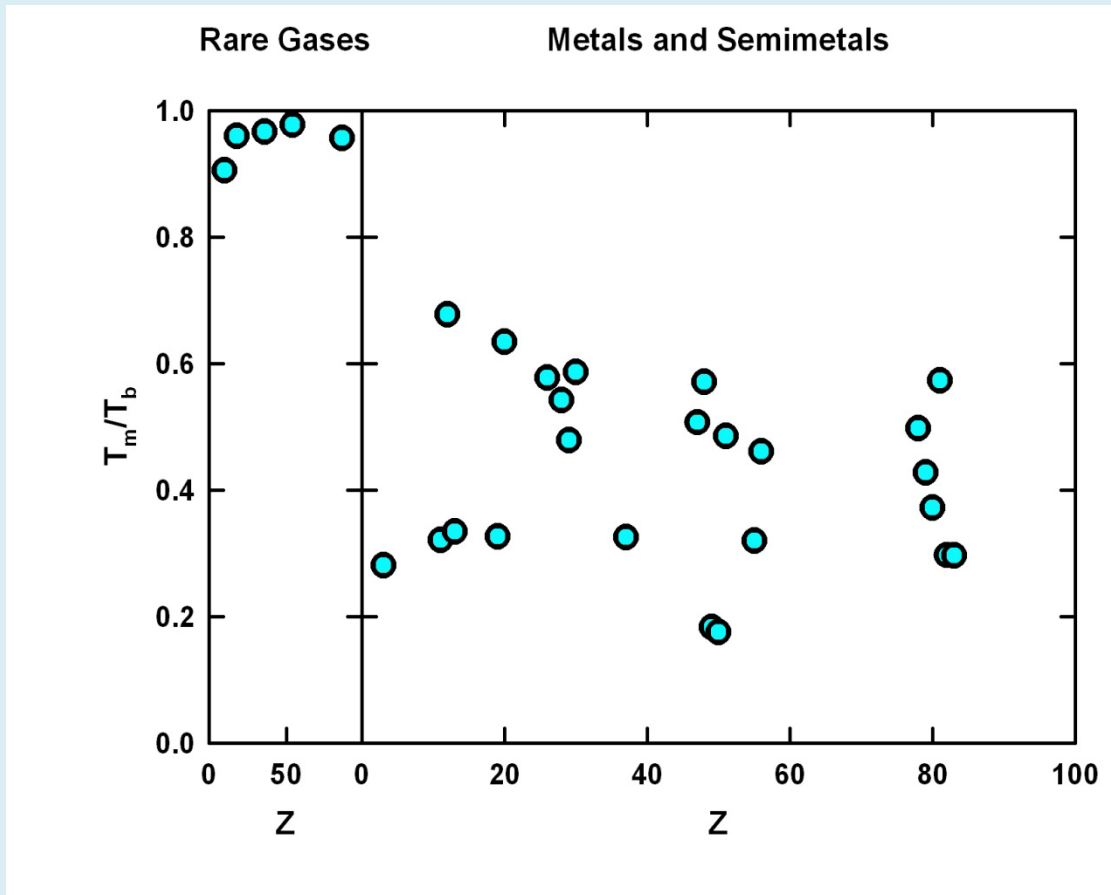
Density Change at Melting

$P = 0.74$ for f.c.c.
 $P = 0.64$ for DRP

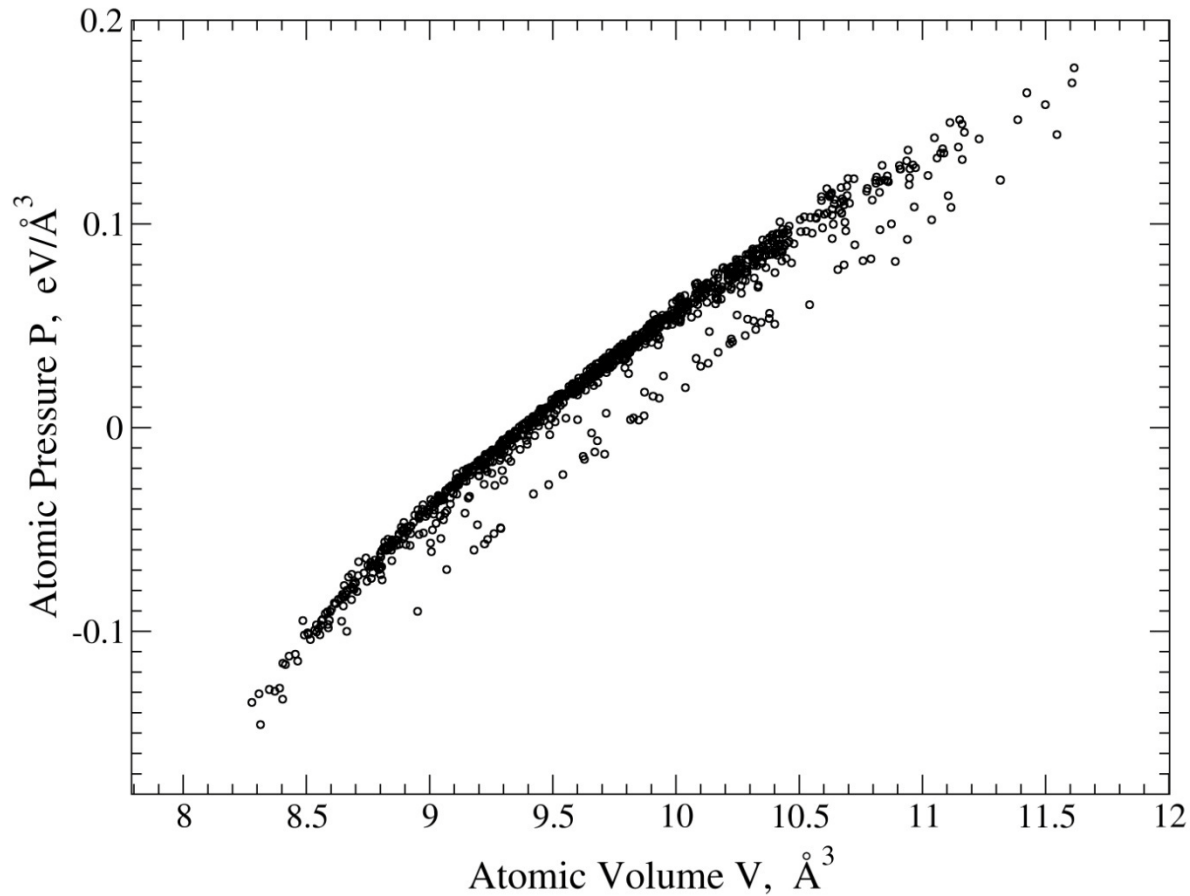


- 17% change for hard-sphere model, and LJ systems.
- Much smaller changes for metals.

T_m/T_b Ratio

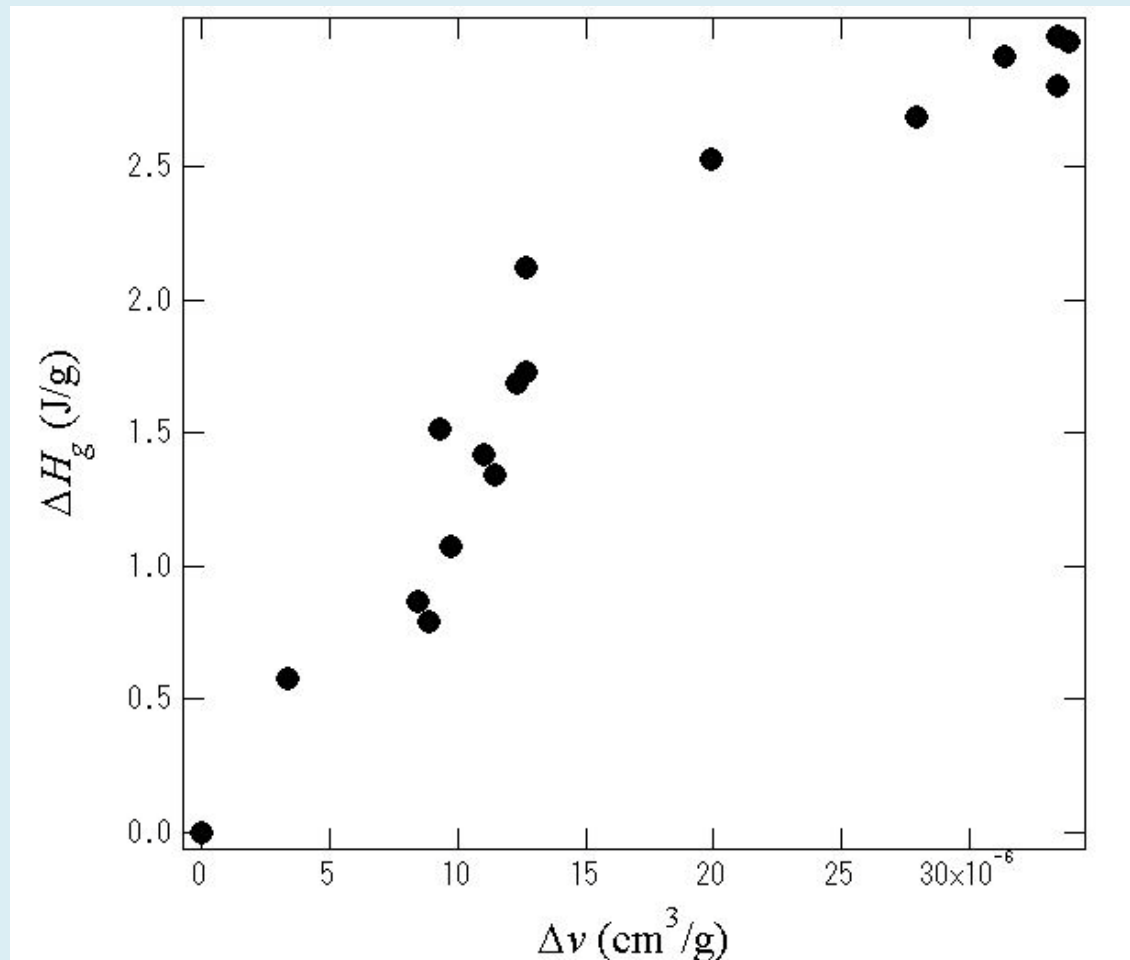


- Potential is wide, relative to the depth.



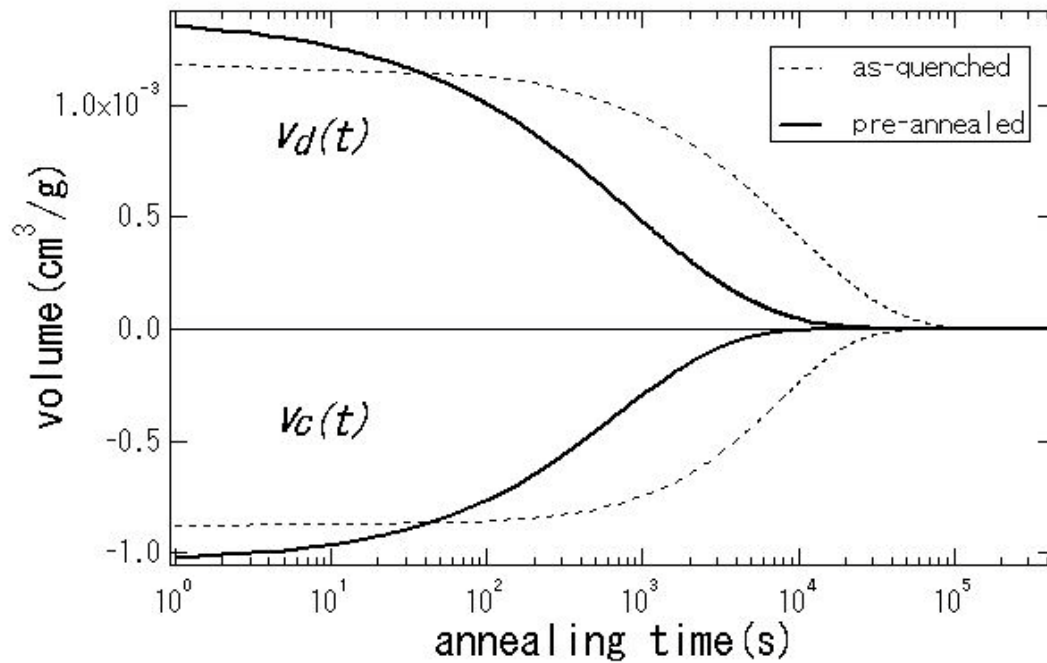
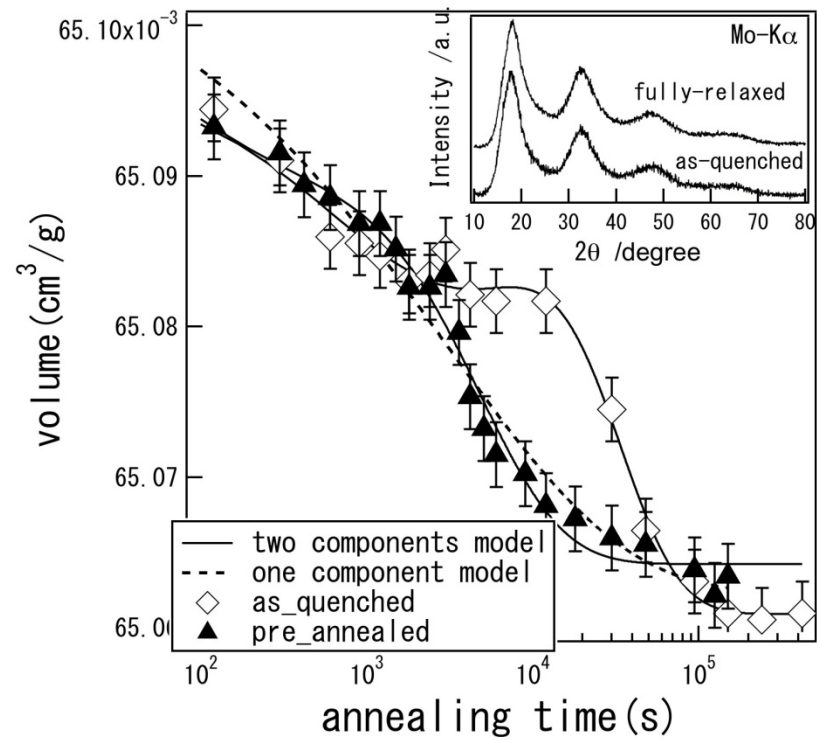
$$V(P) = V(0) + \frac{dV}{dP} \langle P \rangle + \frac{1}{2} \frac{d^2V}{dP^2} \langle P^2 \rangle + \dots$$

- Positive and negative local density fluctuations.
- Volume change only due to anharmonicity.



$$\Delta H/\Delta V \approx 140 \text{ kJ/cm}^3 = 12.6 \text{ eV/atom}$$

M. Kohda, O. Haruyama and T. Egami, *Phys. Rev. B*, **81**, 092203 (2010)

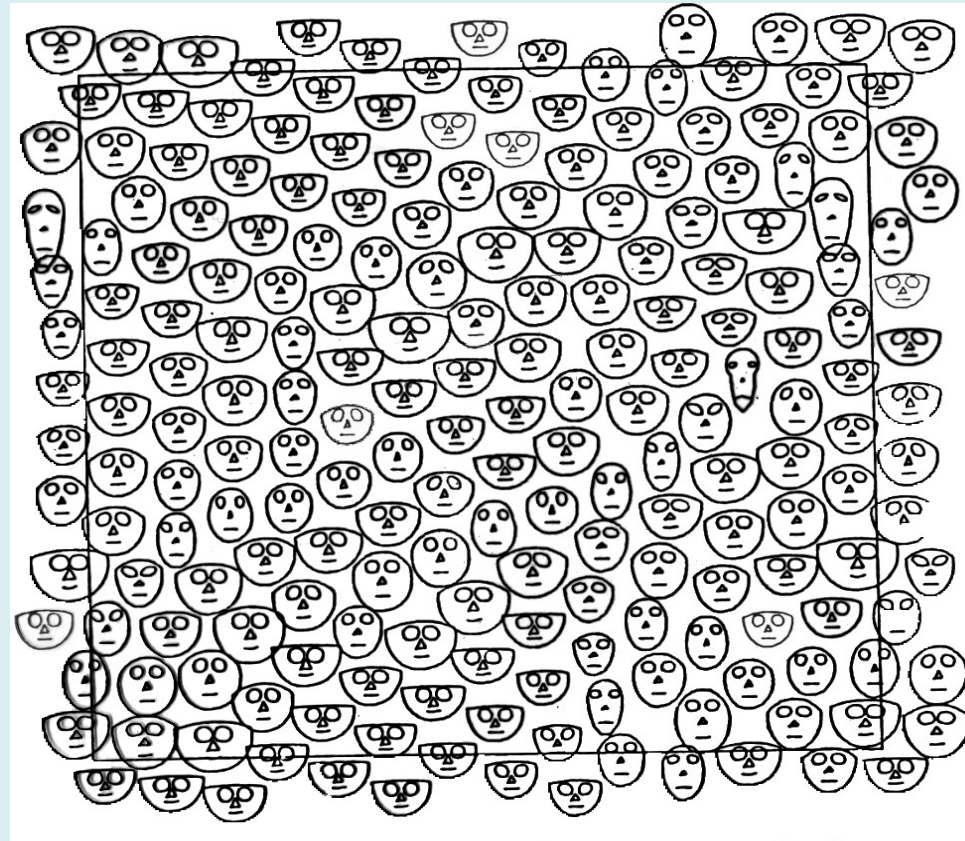
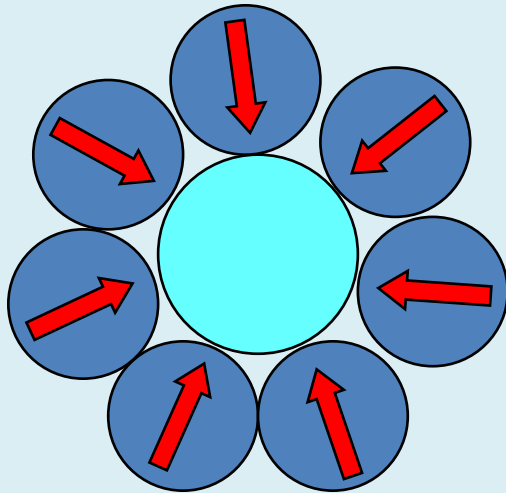


Volume Change

- In soft potential systems the volume change (free volume) does not indicate the defect volume.
- Density fluctuations contribute to the volume change only to the second order.
- Conventional “defect” theories (free volume) assumes defect $\sim 1\%$, but in reality $\sim 25\%$ (corresponding to the reduction on the shear elastic modulus due to anelastic effect).

Atomic Level Stresses and Strains

$$\sigma_i^{\alpha\beta} = \frac{1}{\Omega_i} \sum_j f_{ij}^{\alpha} \cdot r_{ij}^{\beta}$$



T. Egami, K. Maeda and V. Vitek, *Phil. Mag.* **A41**, 883 (1980).

- Atomic level stresses relate the local topology to the local energy landscape.

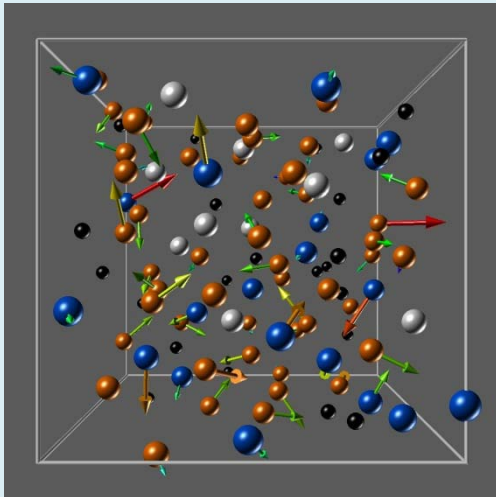
Periodicity vs. Aperiodicity



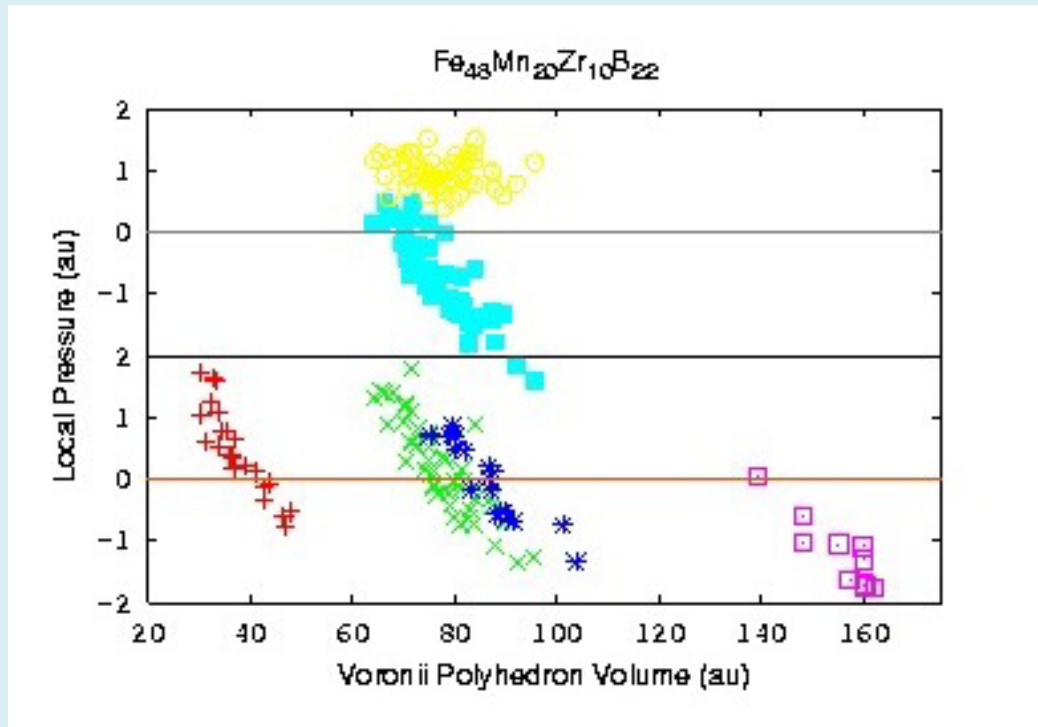
Atomic Level Stresses from the First Principles

Nielson (PRL **50**, 697, 1983); Vitek and Egami (phys. stat. sol. (b) **144**, 145, 1987)

$$\sigma_{\alpha\beta} = - \sum_{\varepsilon_i < \varepsilon_F} \frac{\partial}{\partial x_\alpha} \psi^\dagger \frac{\partial}{\partial x_\beta} \psi - \delta_{\alpha\beta} (\varepsilon_{xc} - V_{xc}) - \frac{1}{4\pi e^2} [E_\alpha E_\beta - \frac{1}{2} \delta_{\alpha\beta} E^2]$$



$\text{Fe}_{48}\text{Mn}_{20}\text{Zr}_{10}\text{B}_{22}$



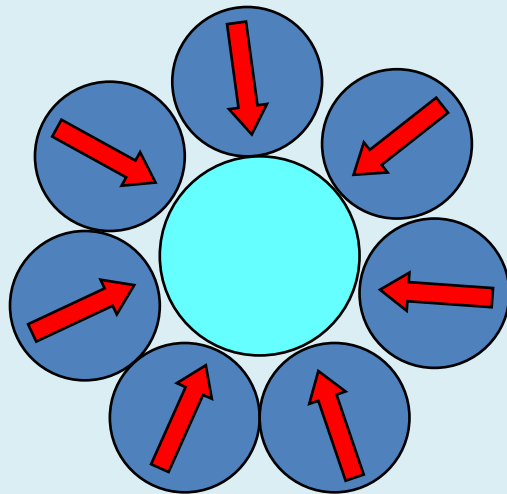
D. Nicholson and G. M. Stocks

- Integrated stress for unit cell
- Results will provide check for local stress

Atomic Level Stresses and Strains

$$\sigma_i^{\alpha\beta} = \frac{1}{\Omega_i} \sum_j f_{ij}^{\alpha} \cdot r_{ij}^{\beta}$$

$$\sigma_i^{\alpha\beta} \approx -\frac{1}{\Omega_i} \sum_j K (r_{ij} - r_0) r_{ij}^{\alpha} \cdot r_{ij}^{\beta}$$

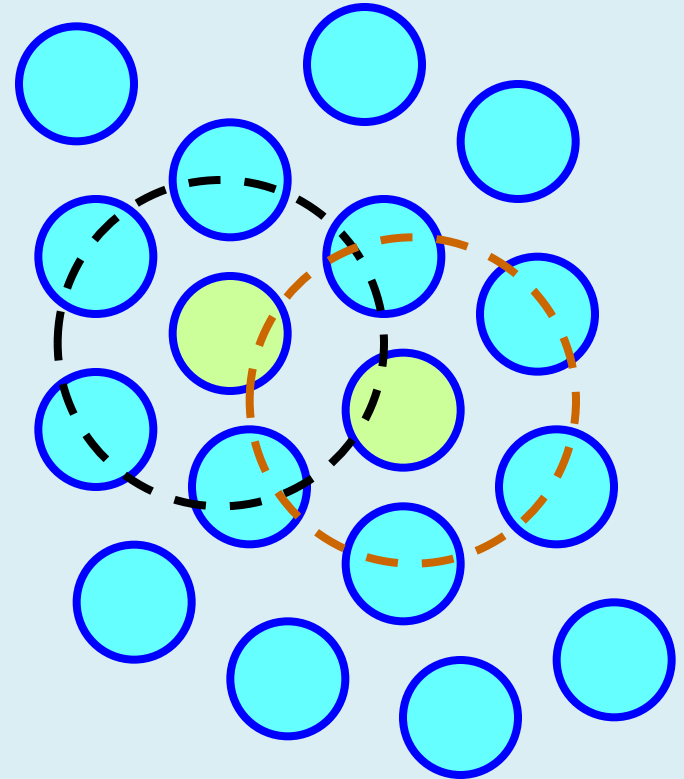


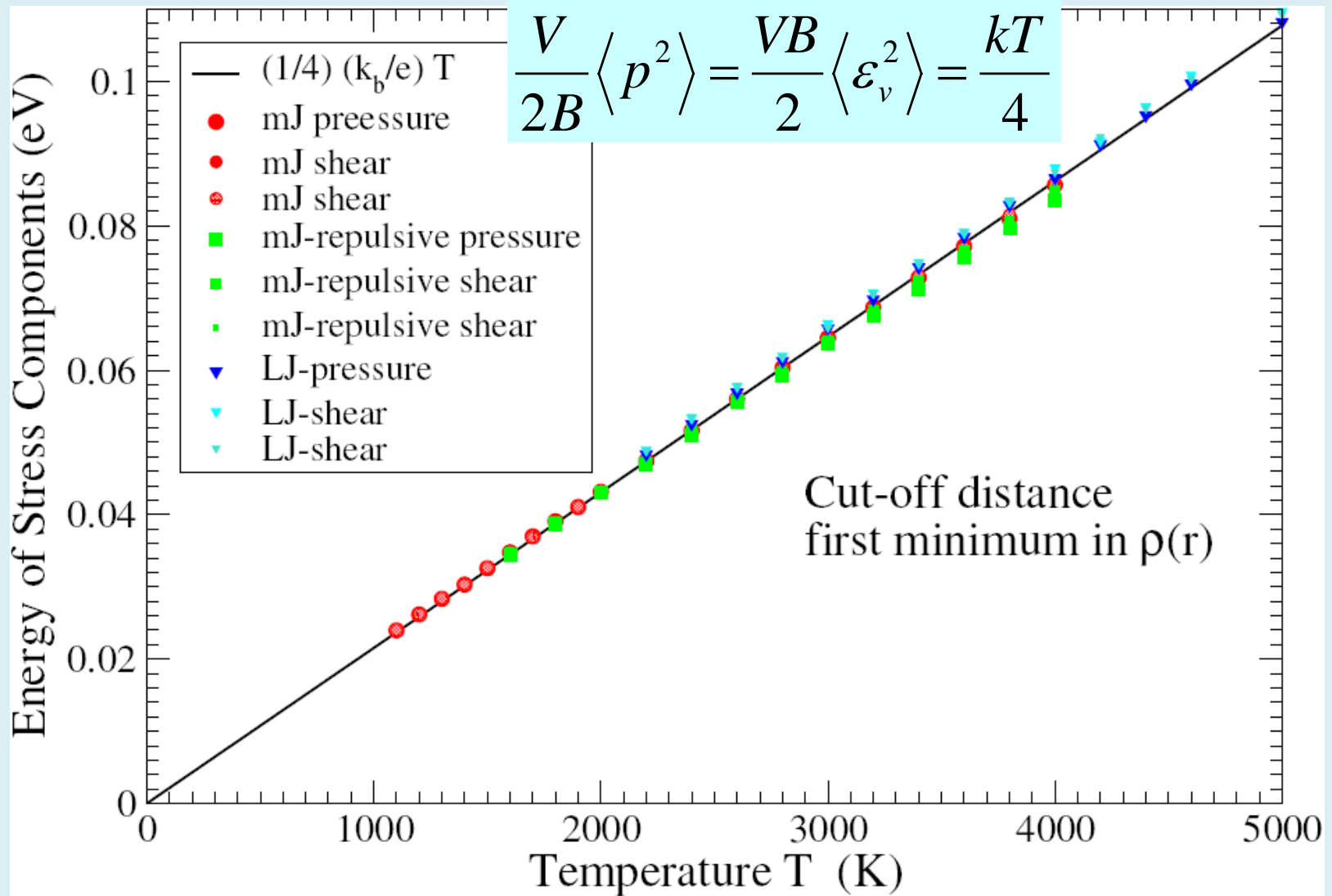
- $r_{ij} = 0$ defines the “ideal glass” that cannot be achieved.
- Symmetry and extent of deviation from the ideal state.
- Strain cannot be defined without the reference, but stress can.

T. Egami, K. Maeda and V. Vitek, *Phil. Mag.* **A41**, 883 (1980).

Vibrations of the Neighbor Shells

- Vibrations of the nearest neighbor shells are **nearly orthogonal to each other.**
- They can be the basis for the statistical mechanics of the liquids.
- They can be described in terms of the atomic-level stresses.





- Equal to $kT/4$ for various potentials.

V. A. Levashov, R. S. Aga, J. R. Morris and T. Egami, *Phys. Rev. B*, **78**, 064205 (2008)

Dynamic PDF

- Dynamic structure factor:

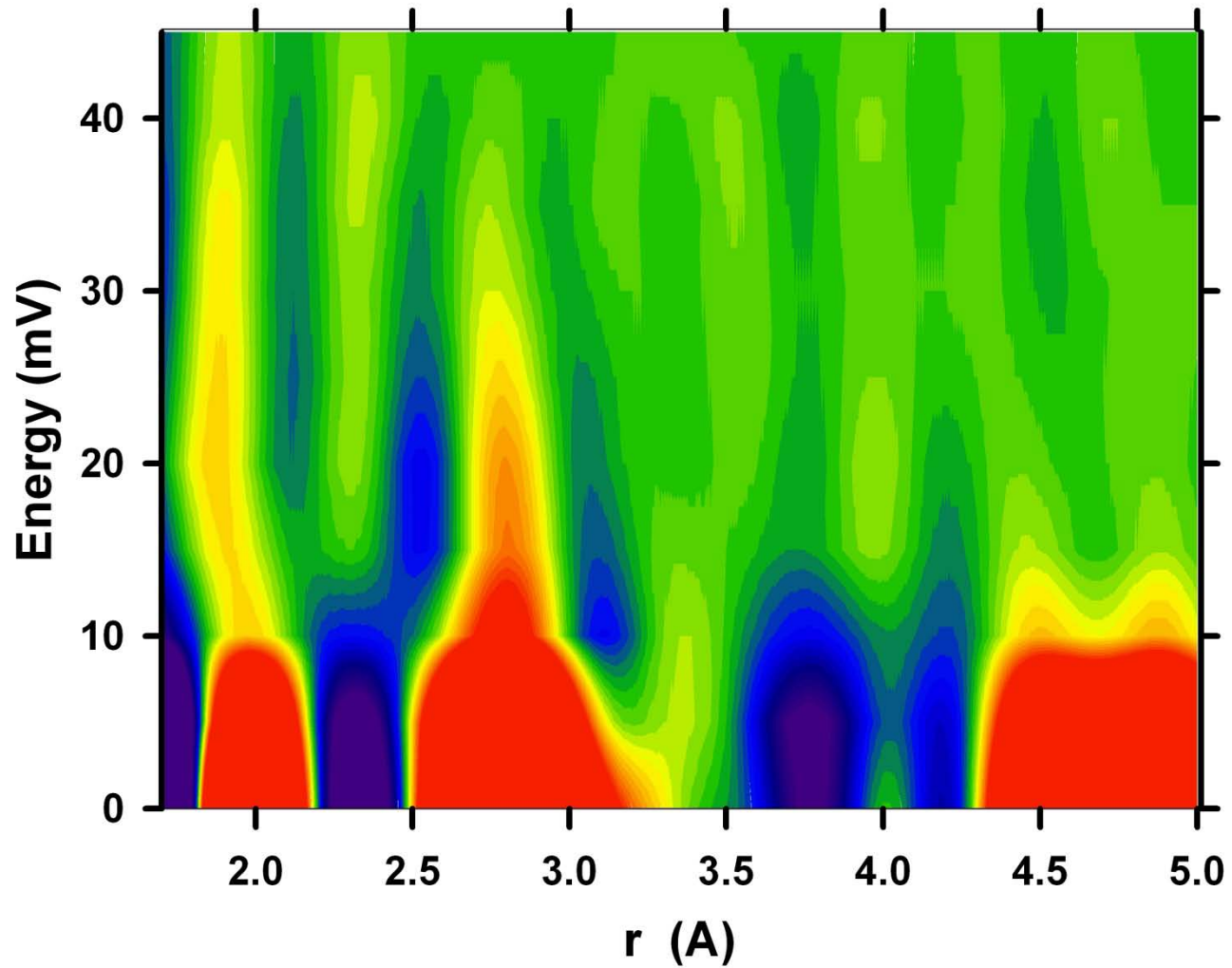
$$S(\mathbf{Q}, \omega) = \frac{1}{N \langle b \rangle^2} \sum_{\nu, \mu} b_{\nu} b_{\mu} \int \left\langle \left\langle e^{i\mathbf{Q} \cdot (\mathbf{R}_{\nu}(0) - \mathbf{R}_{\mu}(t))} \right\rangle \right\rangle e^{-i\omega t} dt$$

- Dynamic PDF

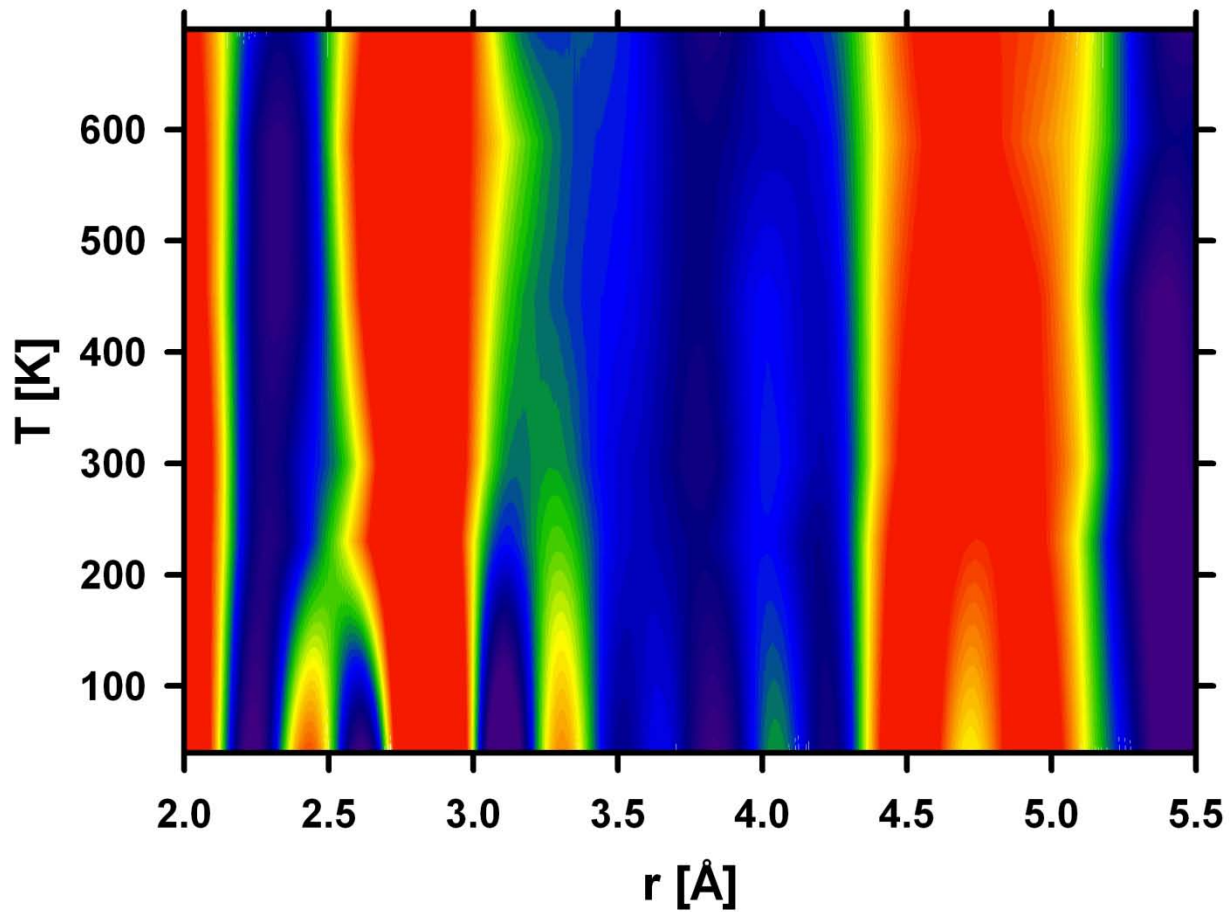
$$\begin{aligned} \rho(\mathbf{r}, \omega) &= \int S(\mathbf{Q}, \omega) e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{Q} \\ &= \frac{1}{N \langle b \rangle^2} \sum_{\nu, \mu} b_{\nu} b_{\mu} \int \delta(\mathbf{r} - [\mathbf{R}_{\nu}(0) - \mathbf{R}_{\mu}(t)]) e^{i\omega t} dt \end{aligned}$$

Dynamic PDF

T = 450K

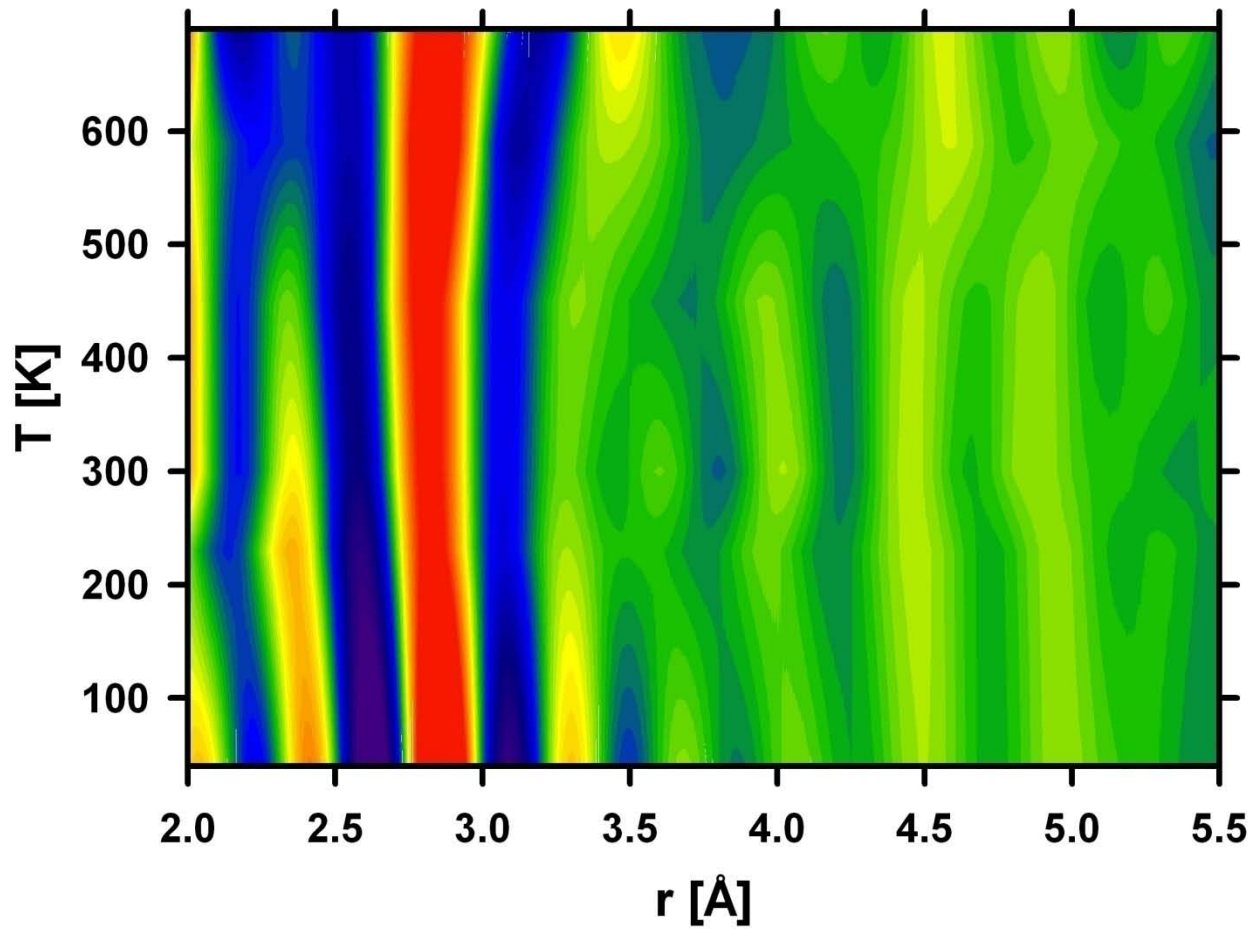


-5 to 5 meV

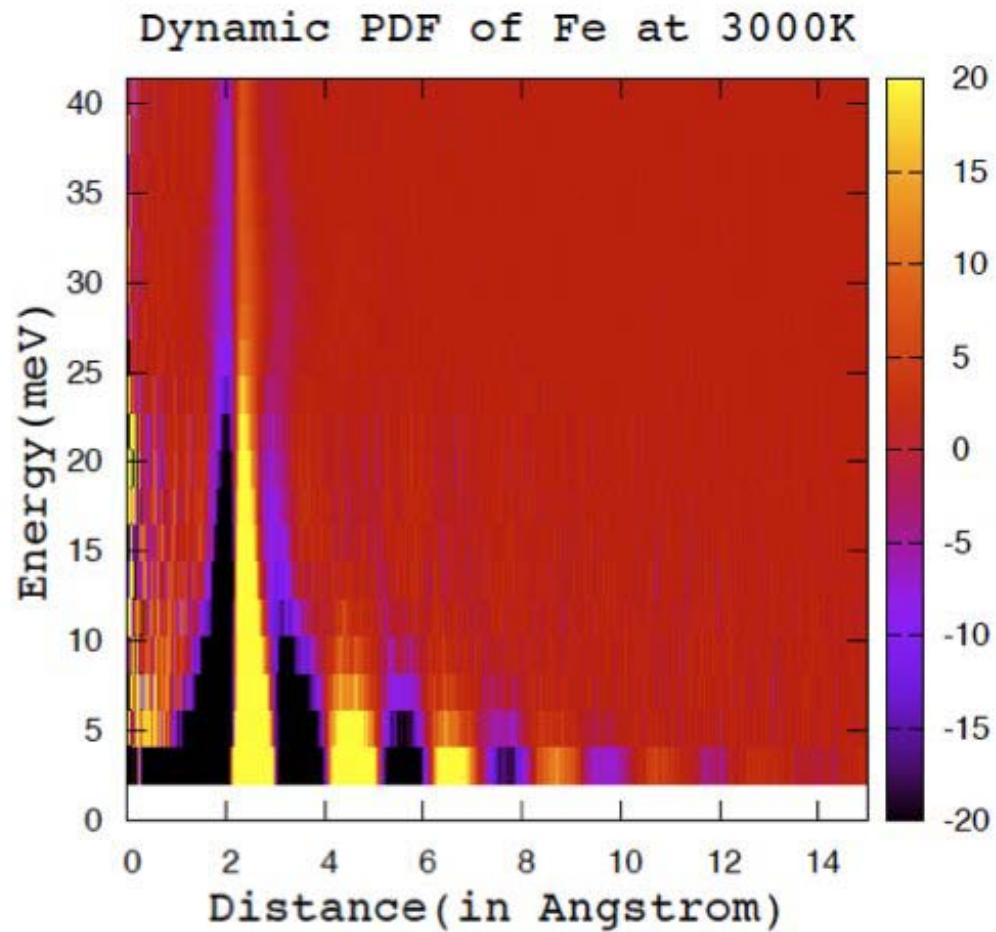


Average (Static) Structure

10 to 20 meV



Dynamic PDF

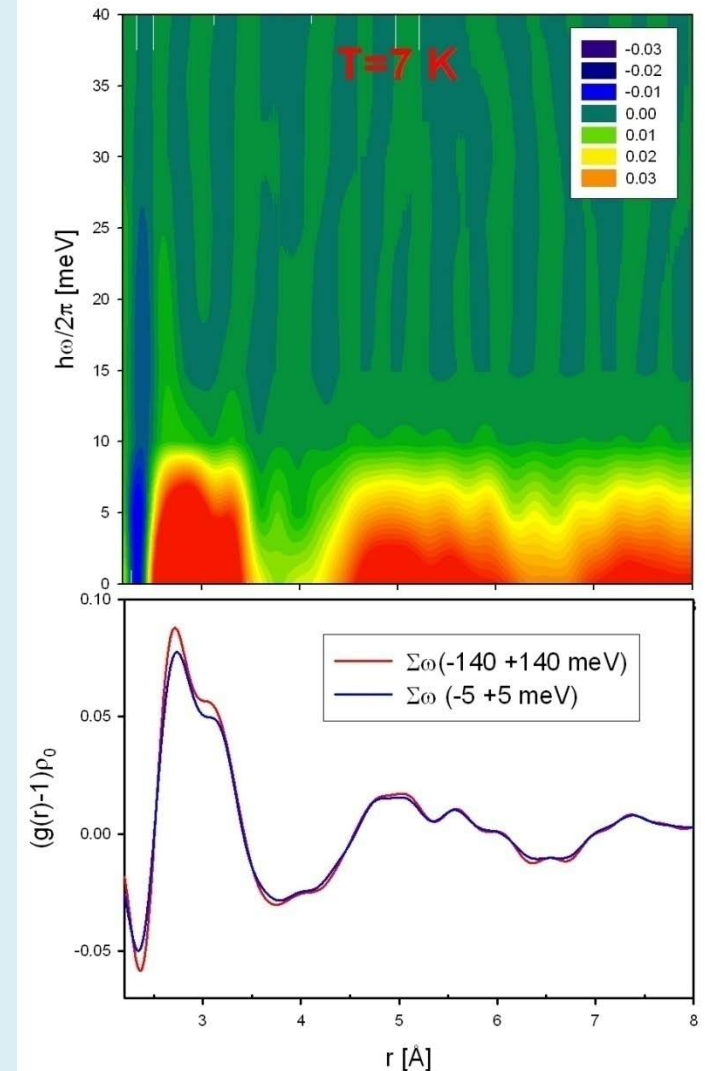
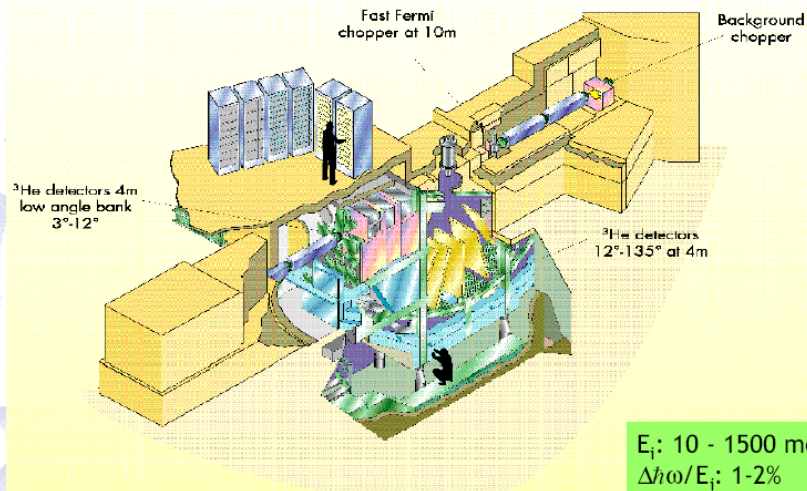


- Only the NN are dynamic above 10 meV.

DPDF of Bulk Metallic Glasses

- Metallic glass $Zr_{50}Cu_{40}Al_{10}$
- Measurement at MARI, ISIS.

A chopper spectrometer on a pulsed source - MARI



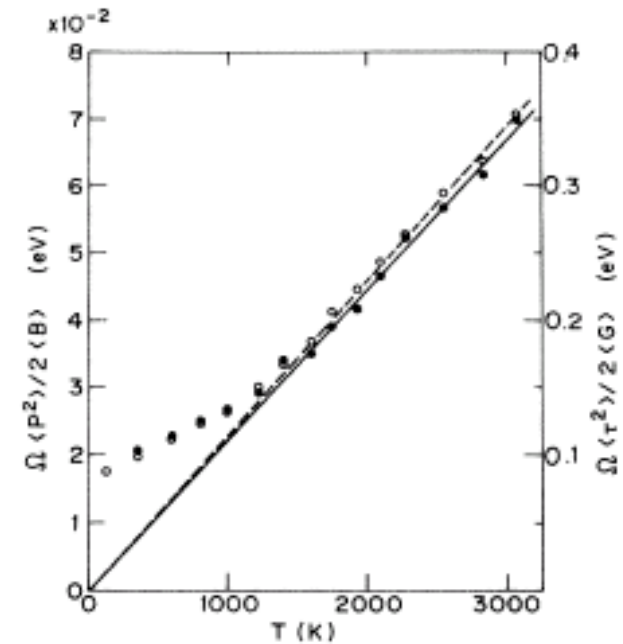
Glass Transition

- High-temperature equation,

$$\frac{V}{2B} \langle p^2 \rangle = \frac{VB}{2} \langle \varepsilon_v^2 \rangle = \frac{kT}{4}$$

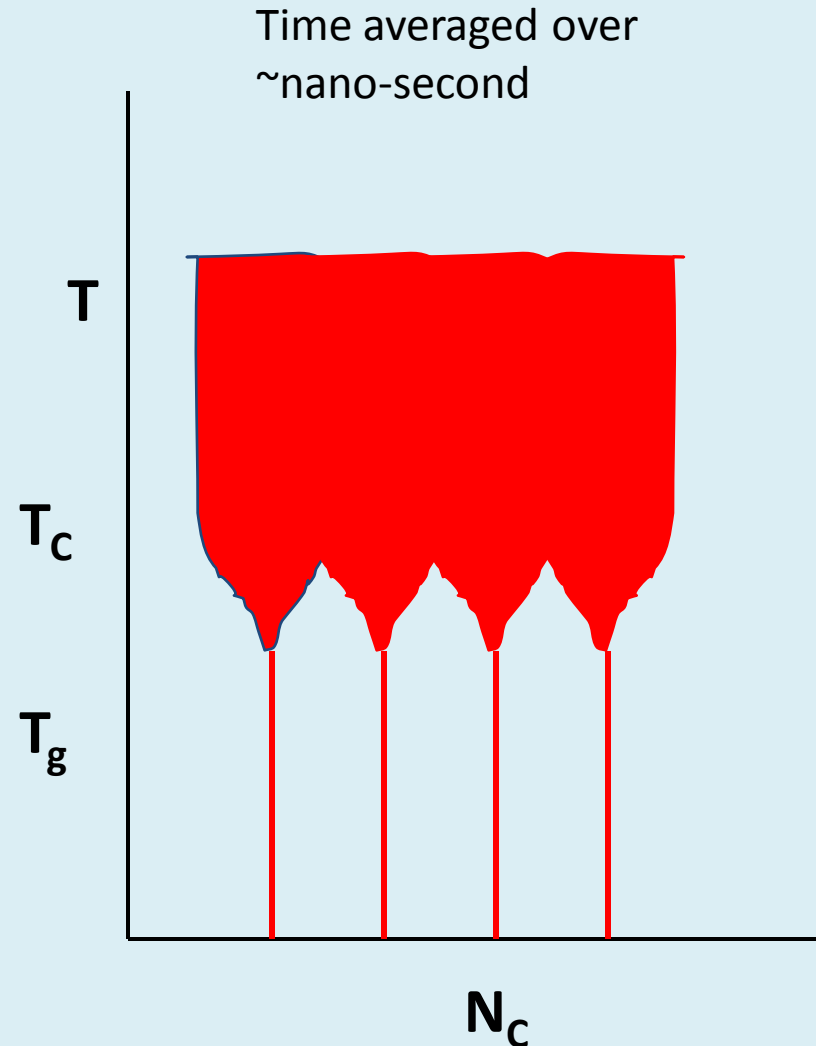
extrapolates to $\varepsilon_v = 0$ at $T = 0$; all neighbors at the bottom of the potential.

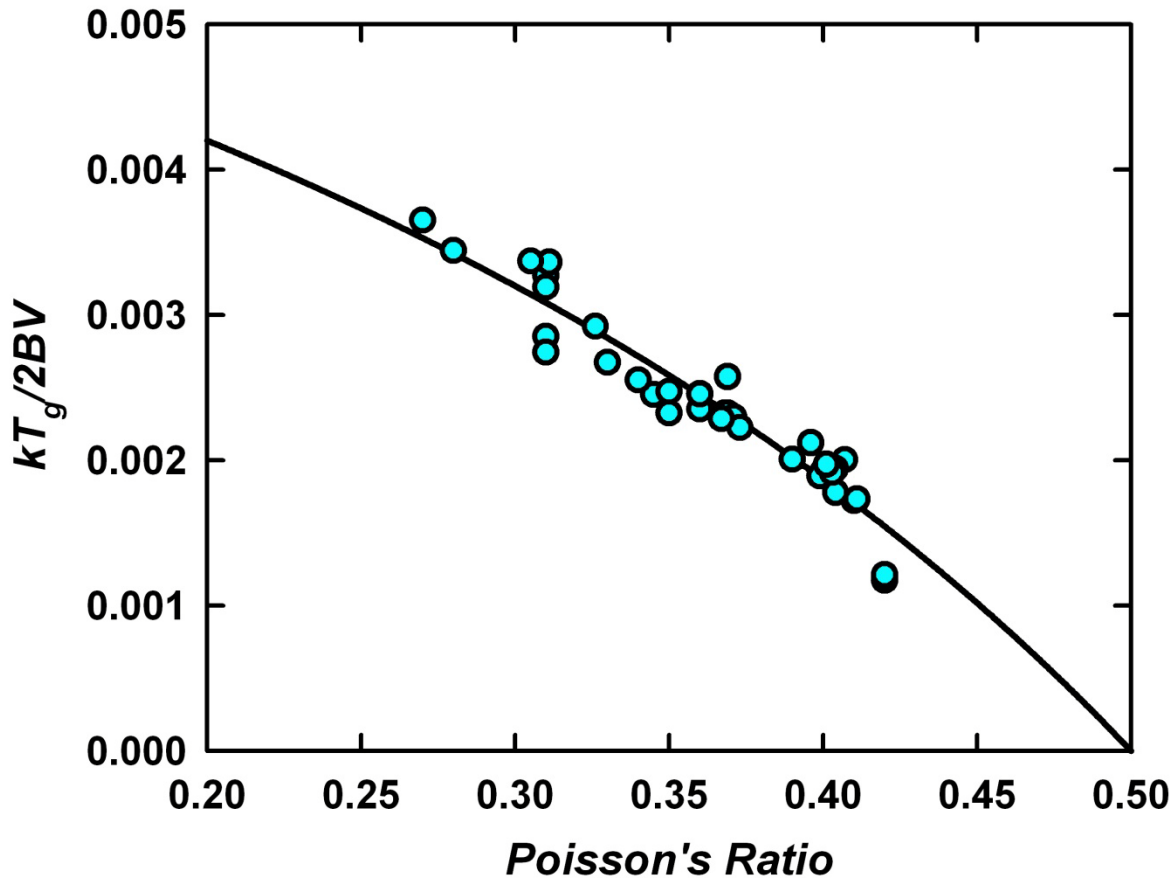
- But that is physically impossible because of jamming.
- There must be a minimum strain.



“Quantization” Effect

- N_C continuously fluctuates at high T , and a short time average is a non-integer.
- As the system freezes local N_C becomes an integer.
- This process of “quantization” is the heart of the **glass transition**.





$$kT_g = \frac{2BV}{K_\alpha} \left(\varepsilon_v^{T,crit} \right)^2$$

$$\frac{kT_g}{2BV} = \frac{1}{K_\alpha} \left(\varepsilon_v^{T,crit} \right)^2$$

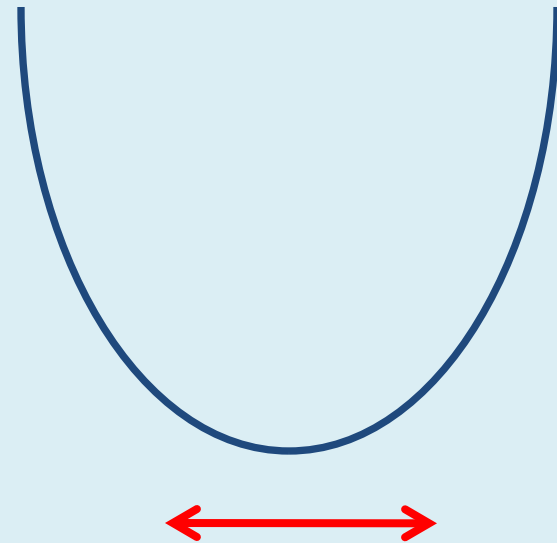
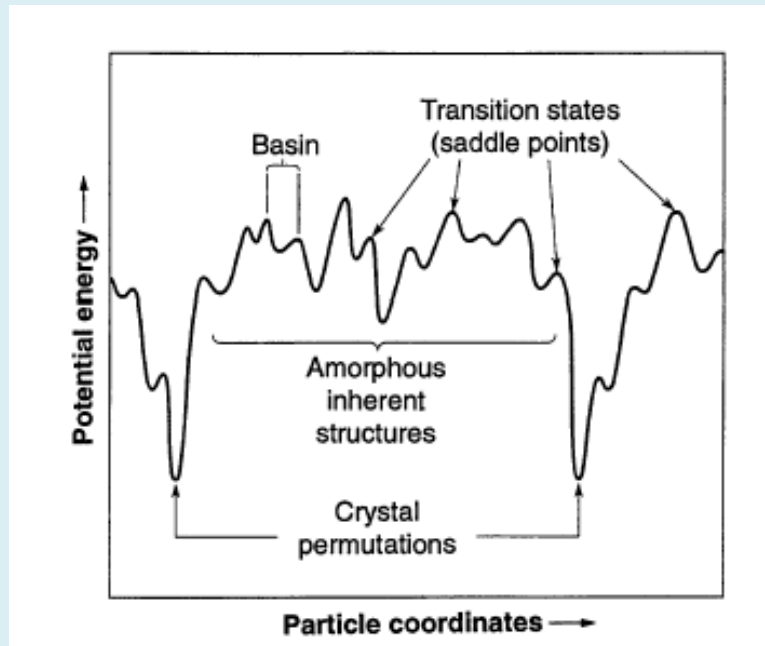
$$K_\alpha = \frac{3(1-\nu)}{2(1-2\nu)}$$

- Glass transition temperature is equal to the energy of local density fluctuation with the long-range stress field at a critical strain level.
 $\varepsilon_{v,T} = 0.0917 \quad 0.003$ (4%).

T. Egami, S. J. Poon, Z. Zhang and V. Keppens, *Phys. Rev. B* **76**, 024203 (2007).

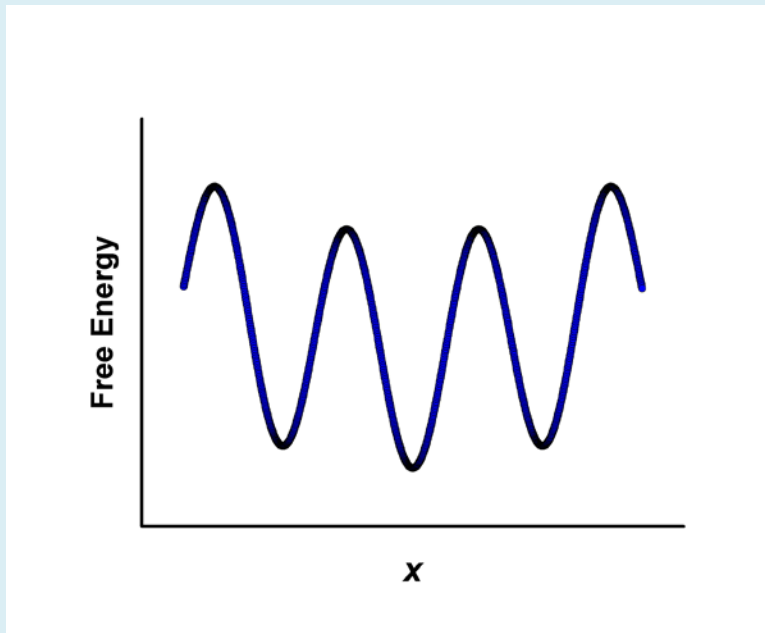
Universal Minimum Local Strain

- Depth of the valley in the energy landscape.
- If the strain is too large the local topology becomes unstable, and change.

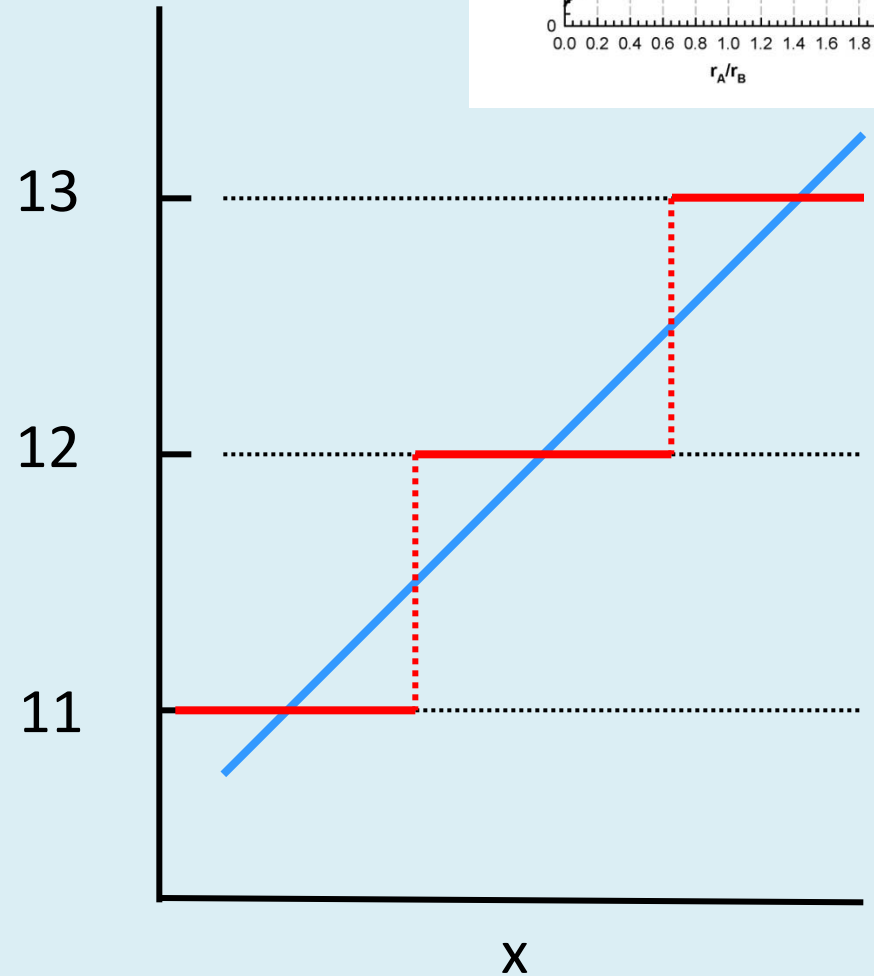
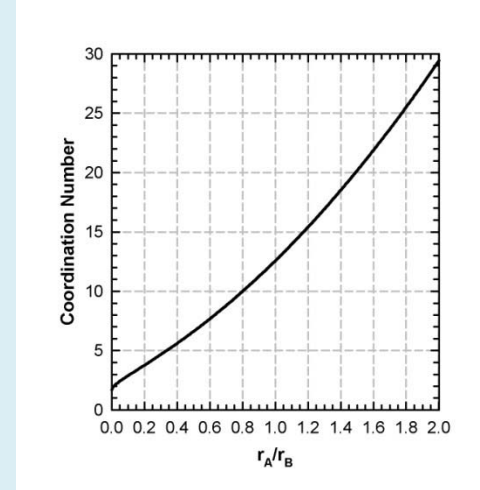


Local topological instability

- Since the coordination number is an integer, there is a range of values of x over which a particular coordination number is stable.



Local energy landscape



Topological instability condition

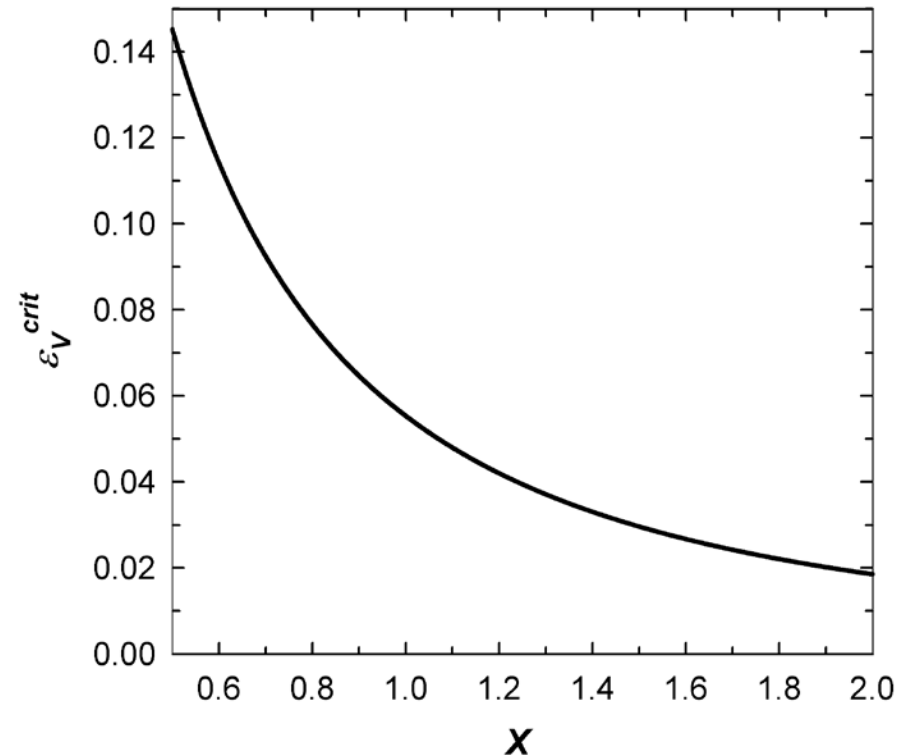
- If the radius of the A atom is changed, when the corresponding N_C changes by ~ 0.5 , the atomic cage around the A atom becomes unstable.
- The instability condition:

$$\Delta x_C = \frac{1}{2} \left/ \frac{\partial N_C^A(x)}{\partial x} \right.$$

- For a monoatomic system ($x = 1$),

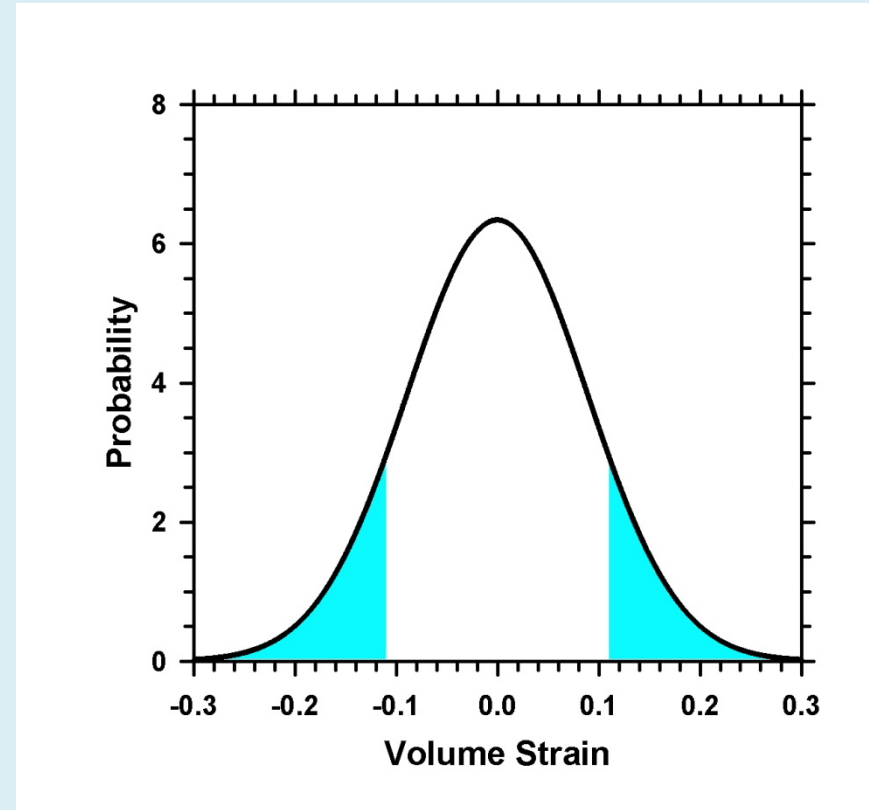
$$\varepsilon_V^{crit} = \frac{3}{2} \Delta x_C = \frac{6\sqrt{3}-9}{8\pi} = 0.0554$$

$$\varepsilon_V^{crit} = 3\Delta x_C = \frac{6\sqrt{3}-9}{4\pi} = 0.111$$



Liquid-Like Sites (Free-Volume)

- Local environment unstable at certain sites with the volume strain larger than 11%.
- Free-volume (n) ($\epsilon_v > 0.11$) and anti-free-volume (p) ($\epsilon_v < -0.11$) defects [Cohen and Turnbull, 1959]
- They define the liquid-like sites.



Free volume element

Percolation of the Liquid-like Sites

- Total fraction of the liquid-like sites:

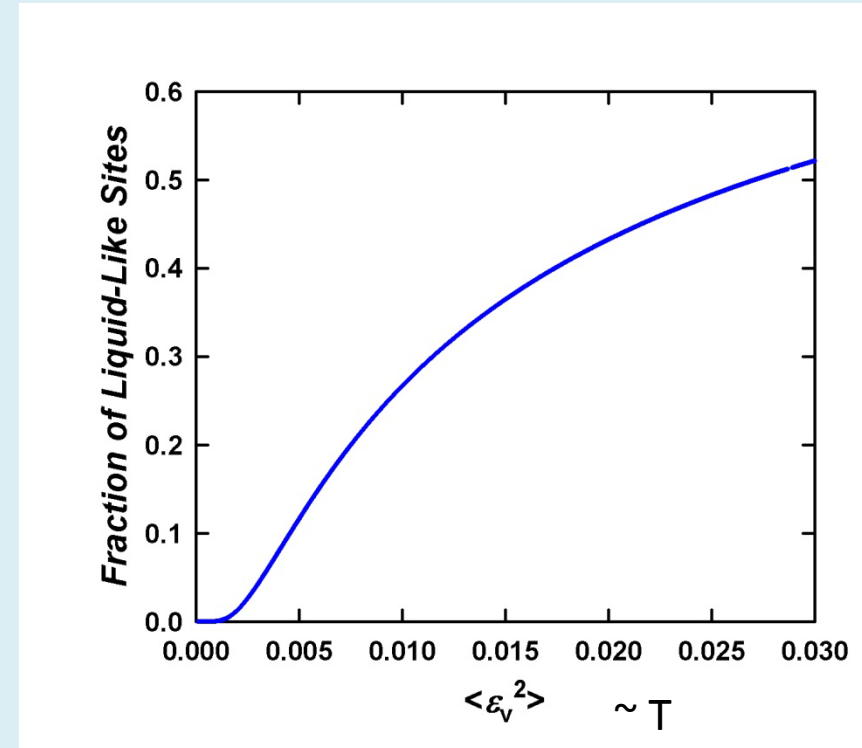
$$p(liq) = CE(y_c) = \frac{2}{\sqrt{\pi}} \int_{y_c}^{\infty} e^{-y^2} dy$$

$$y_c = \frac{\varepsilon_v^{crit}(L)}{\sqrt{2} \langle \varepsilon_v^2 \rangle^{1/2}}$$

- For $\varepsilon_{v,T} = 0.095 \quad 0.003$

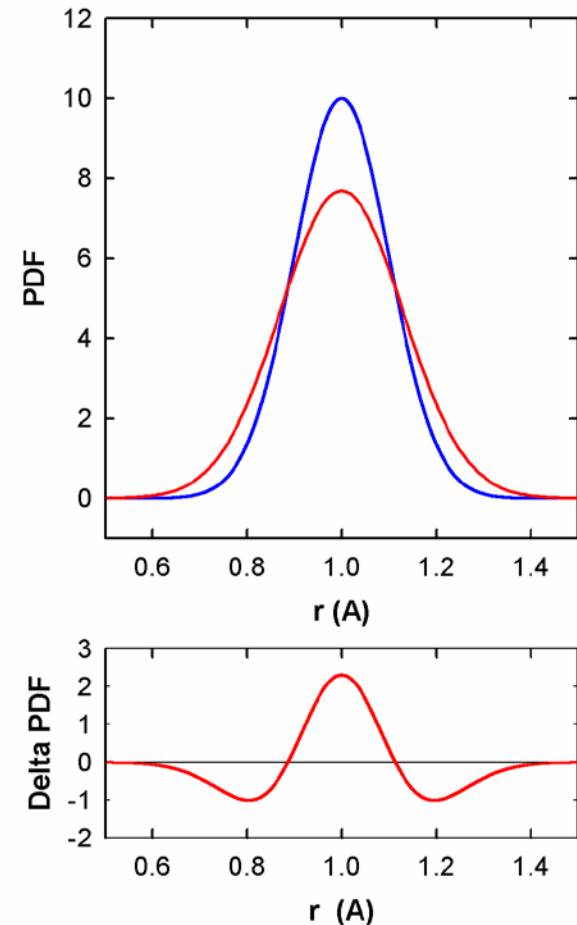
$$p(liq) = 0.243$$

- Percolation concentration for DRP is 0.2: Glass transition occurs by percolation of the liquid-like sites [M. H. Cohen and G. Grest, Liquid-glass transition, a free-volume approach, *Phys. Rev. B* **20**, 1077-1098 (1979)]



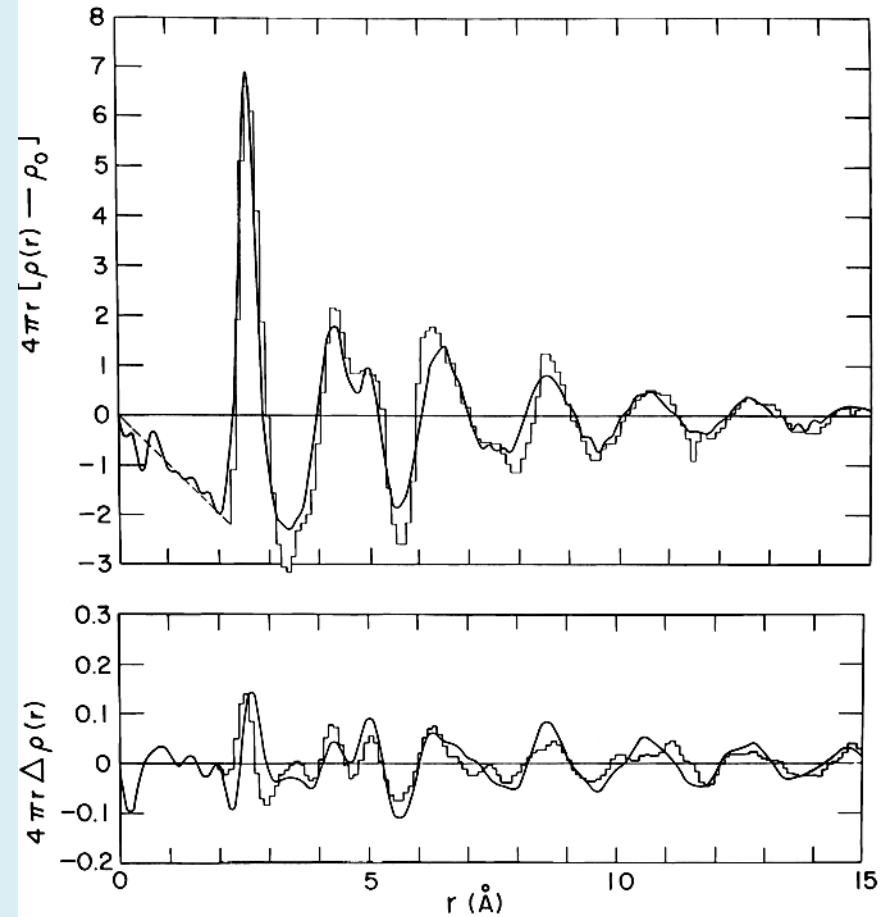
Change in the PDF due to Structural Relaxation

- The coordination number remains unchanged.
- Little shift in the peak position; stays in the minimum of the interatomic potential.
- The N.N. peak becomes sharper; short and long bonds disappear.
- Less dense regions (free volume) as well as dense regions (anti-free volume) disappear as a result of relaxation.



Structural Relaxation

- Reduction in $\langle \Delta N_C^2 \rangle$, and $\langle p^2 \rangle$.
- Change in the PDF; 30% change in $\langle p^2 \rangle$.
- 30% change in the fictive temperature.



T. Egami, *J. Mater. Sci.* **13**, 2587 (1978), D. Srolovitz, T. Egami, and V. Vitek, *Phys. Rev. B* **24**, 6936 (1981)

Conclusion I

- Metallic glasses are characterized by harmonic potentials. Not HS-like.
- Density fluctuations both positive and negative.
- At HT vibrational modes are strongly localized to the NN. Thus they can be well described by the dynamics of atomic level stresses.
- Atomic level fluctuations extrapolate to zero at $T = 0$, but intercepted by topological frustration.

- The minimum atomic level strain can be calculated by the argument of local topological instability.
- This allows the calculation of T_g , which agrees well with the data.
- The local topological instability condition could be universal.
- This also relates to the mechanism of deformation to be discussed later.