International School on Glass Formers and Glasses
JNCASR, Bengaluru

Changes in the Structure due to Temperature and Relaxation

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Structure Property Relationship

- Drastic changes in the properties, such as viscosity with temperature, do not seem to be reflected in the structure (Grand Challenge – C. A. Angell).
- High-order correlations cannot be readily measured (see poster by Claudio Maggi).
- Small changes in the pair correlation; they can be measured, if you do the experiment carefully and with patience.

Changes in the Pair-Density Function

- Highly accurate PDF measurement ($10^{7\text{-}8}$ ct.)
  - EDXD, synchrotron radiation with 2D detector, *in-situ* measurement
- Small changes in PDF
  - With temperature, structural relaxation.
- Interpretation
  - Atomic level stresses.
  - Universal critical strain
  - Glass transition.

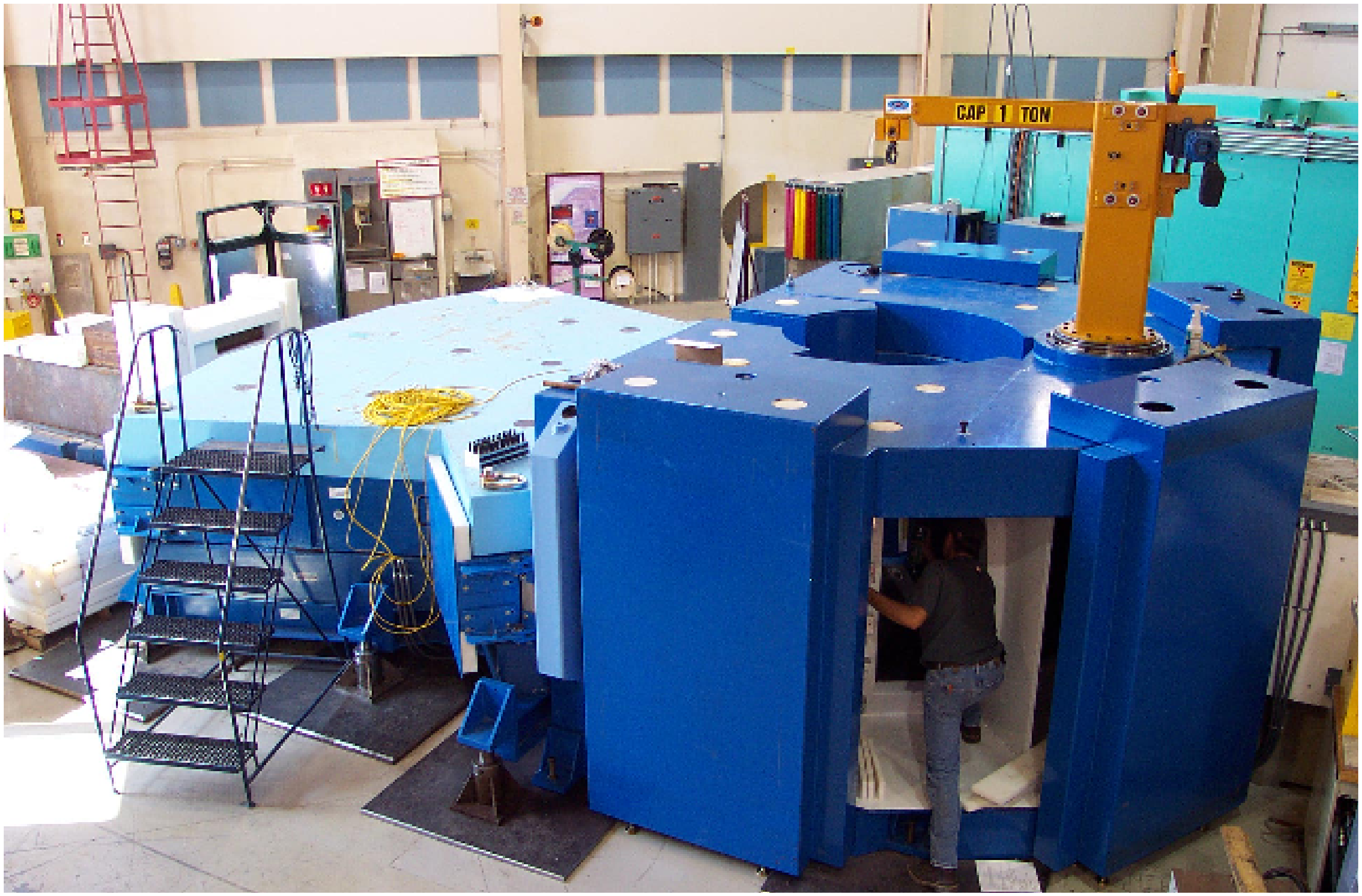
How to Measure PDF Accurately

- High statistical accuracy
- Wide *Q* range

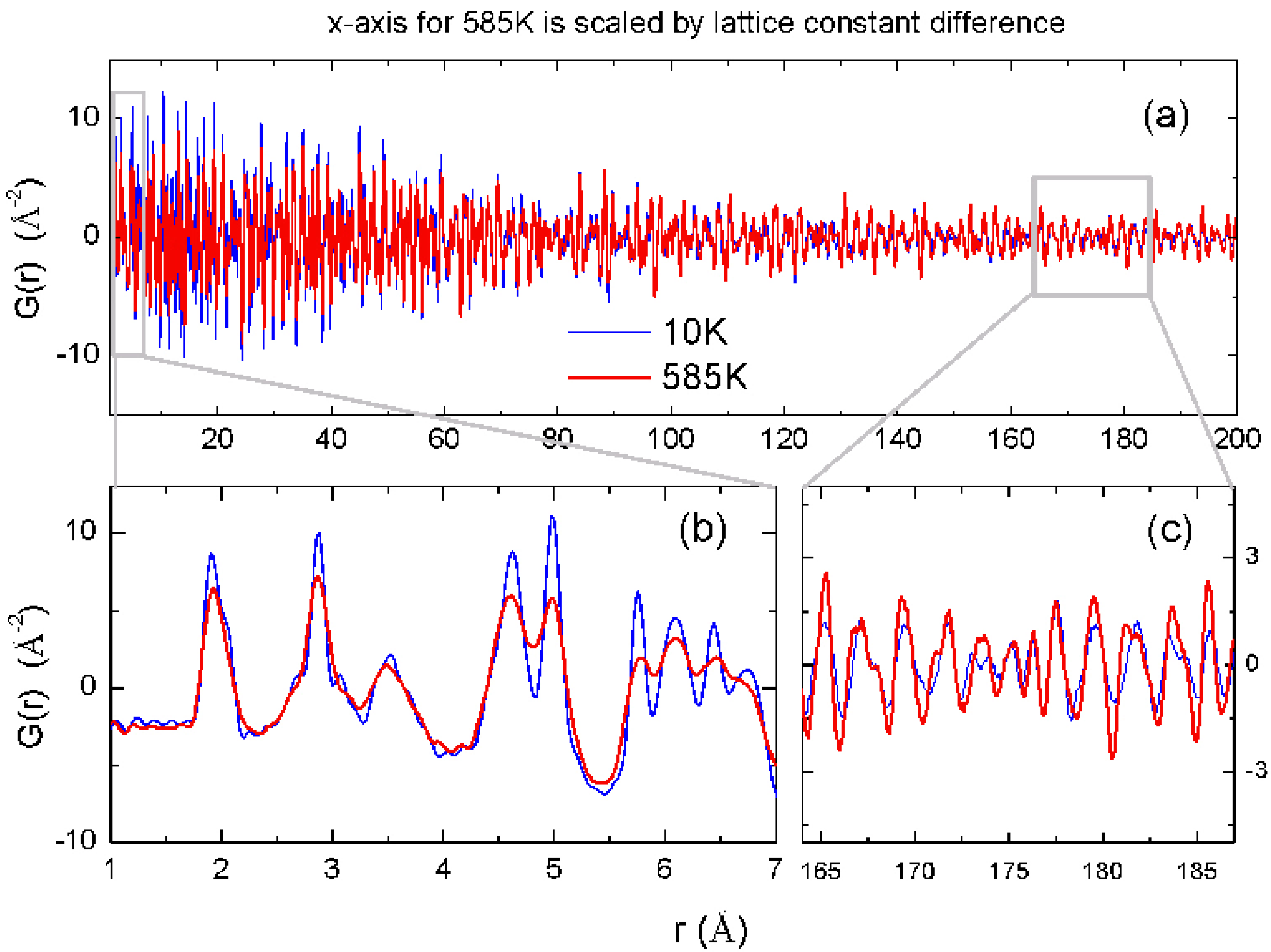
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)\,dQ \qquad Q = \frac{4\pi}{\lambda}\sin\theta < \frac{4\pi}{\lambda}$$

- With Mo radiation 16 Å^{-1}, but with synchrotron radiation and pulsed neutron up to 50 Å^{-1} or more.
- Stable set-up, *in-situ* measurement.

High-resolution pulsed neutron scattering spectrometer, NPDF, LANSCE, Los Alamos National Lab.



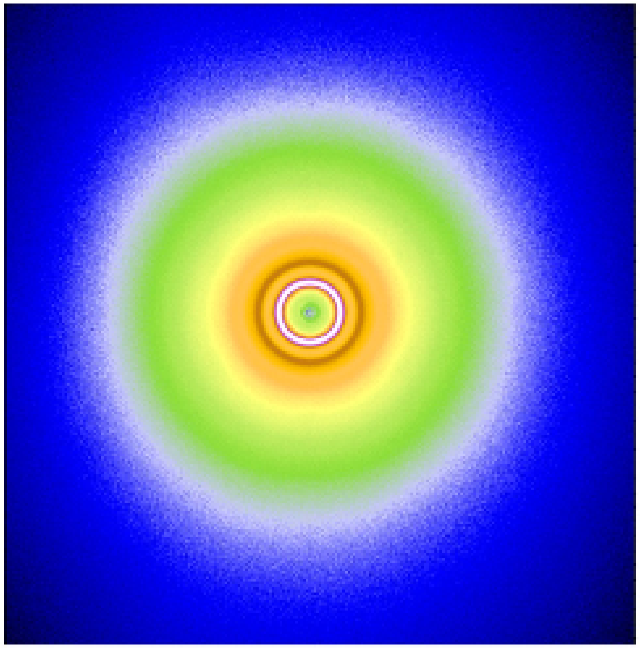
- High Q resolution $\Delta Q/Q = 0.0015$, high real space resolution for PDF.

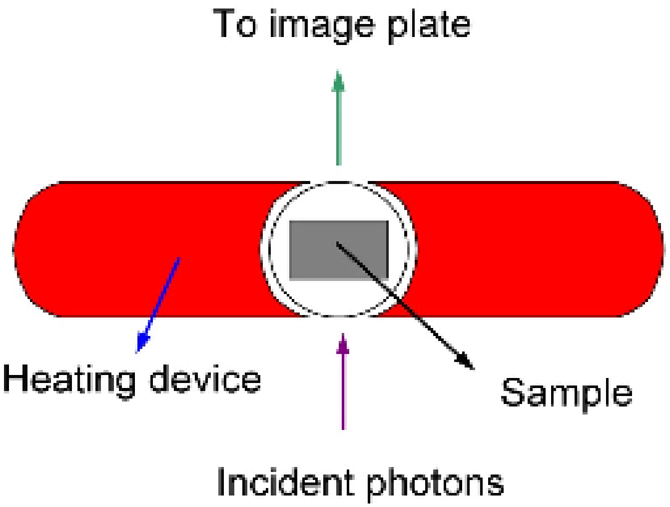


- Local and intermediate structure of $LiNiO_2$ (PRB **71**, 064410 (2005)).

Effect of Temperature

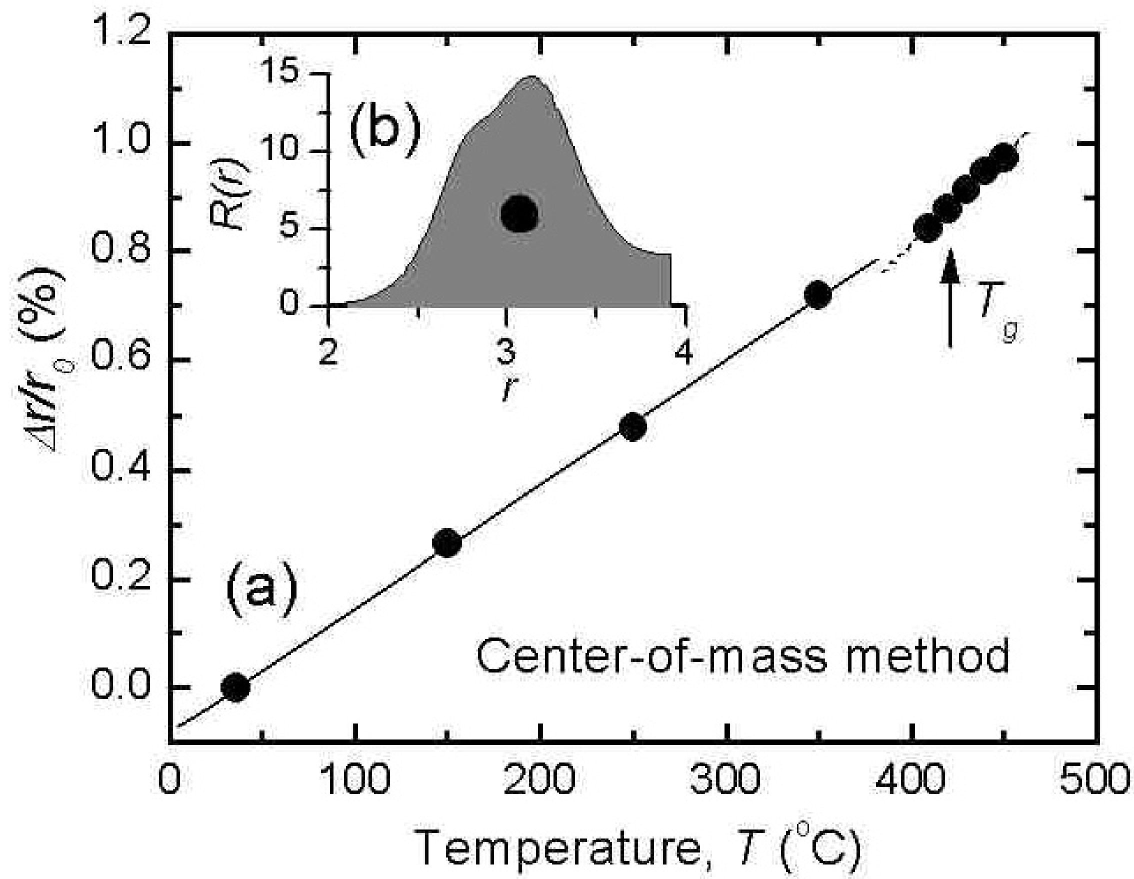
- High energy x-ray diffraction with a 2D detector.





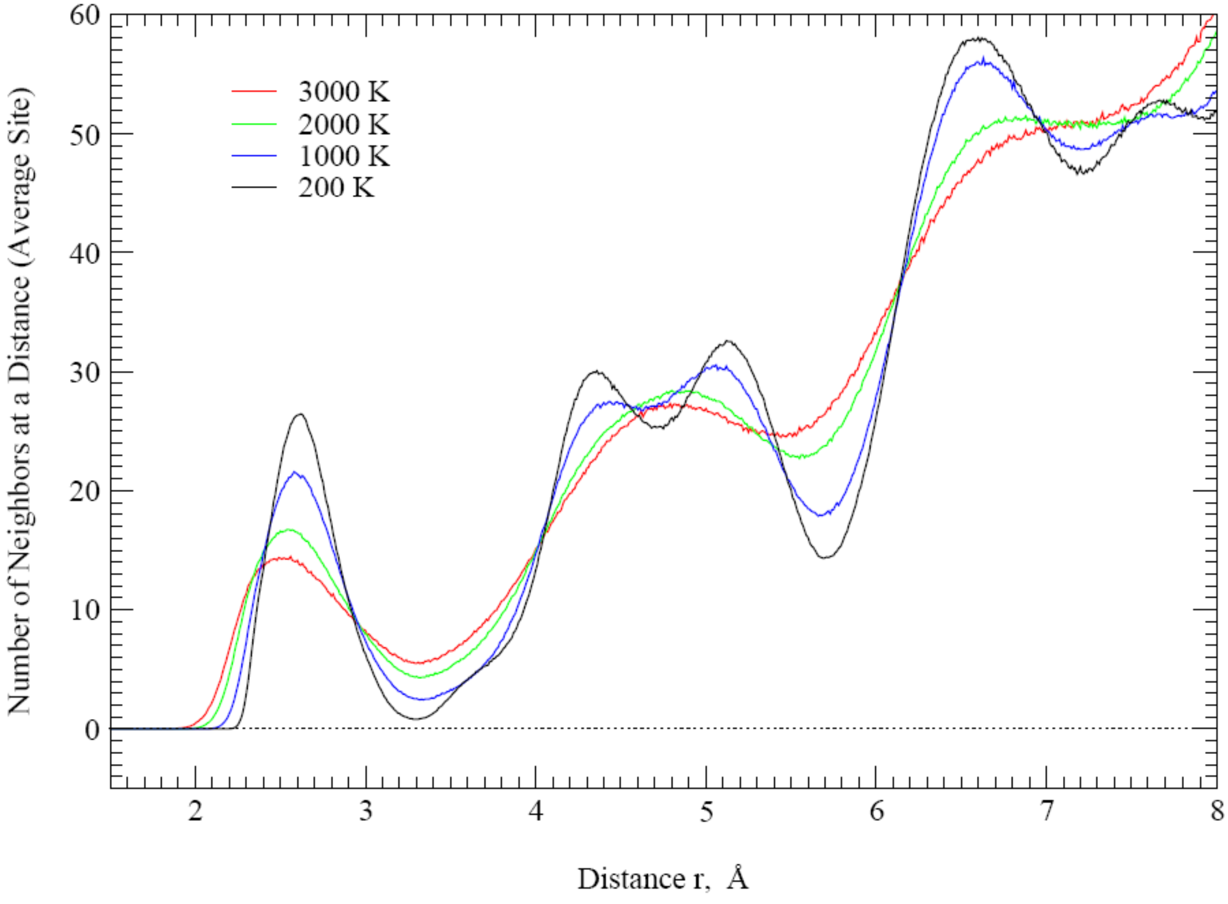
- Thermal expansion coefficient;

- α = 1.80 x 10^{-5}
- α = 3.28 x 10^{-5} (macroscopic).

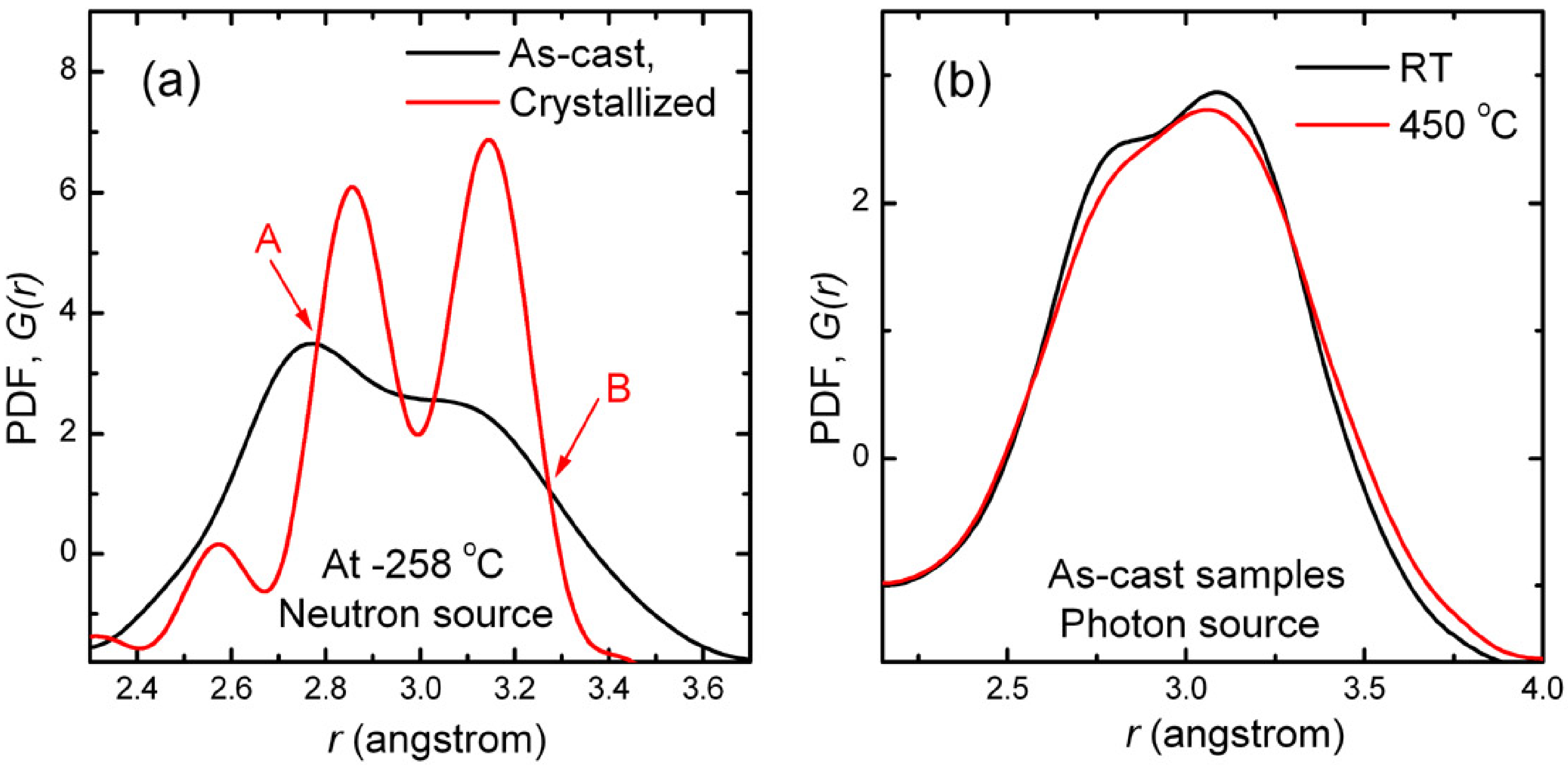


PDF and Temperature

- The PDF peak width increases with temperature, reflecting increased atomic vibration.

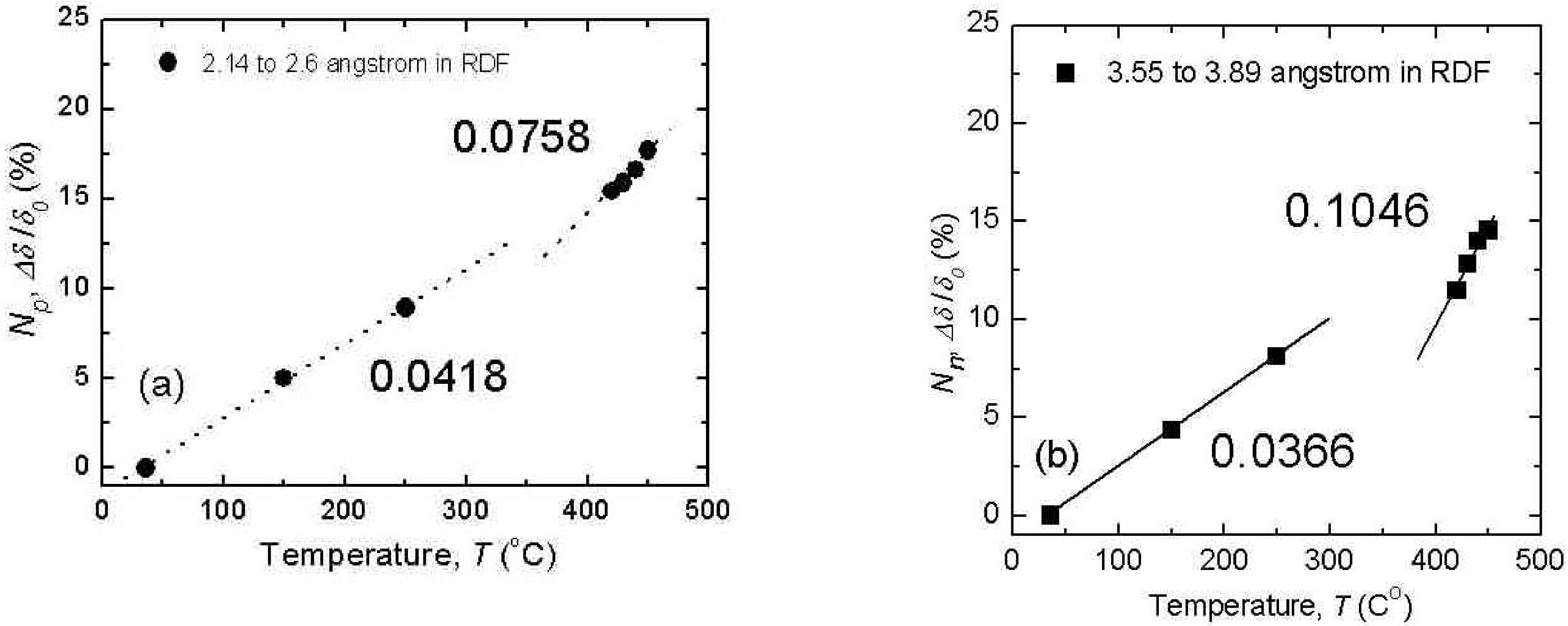


Simulated PDF of iron



(a)
As-cast,
Crystallized
A
B
At -258 °C
Neutron source
PDF, G(r)
r (angstrom)
8
6
4
2
0
2.4
2.6
2.8
3.0
3.2
3.4
3.6
(b)
RT
450 °C
As-cast samples
Photon source
PDF, G(r)
r (angstrom)
2
0
2.5
3.0
3.5
4.0

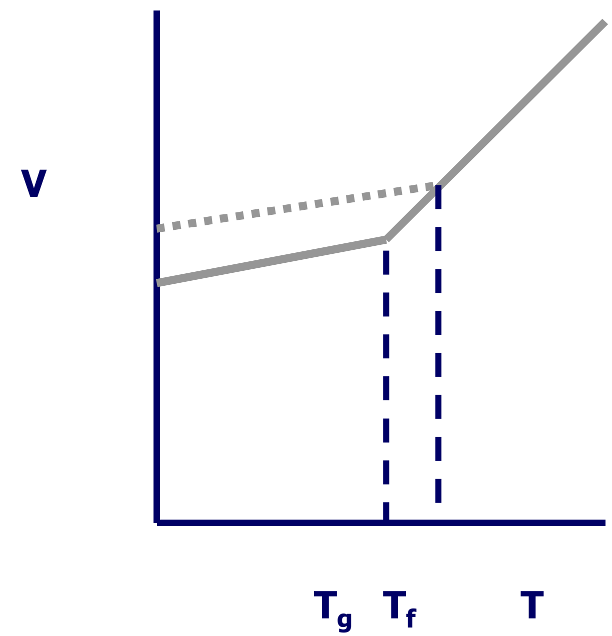
Change in the area with temperature



- The change in the first peak is symmetric, reflecting the harmonic potential, and not hard-sphere-like.

Changes in the Structure due to Structural Relaxation

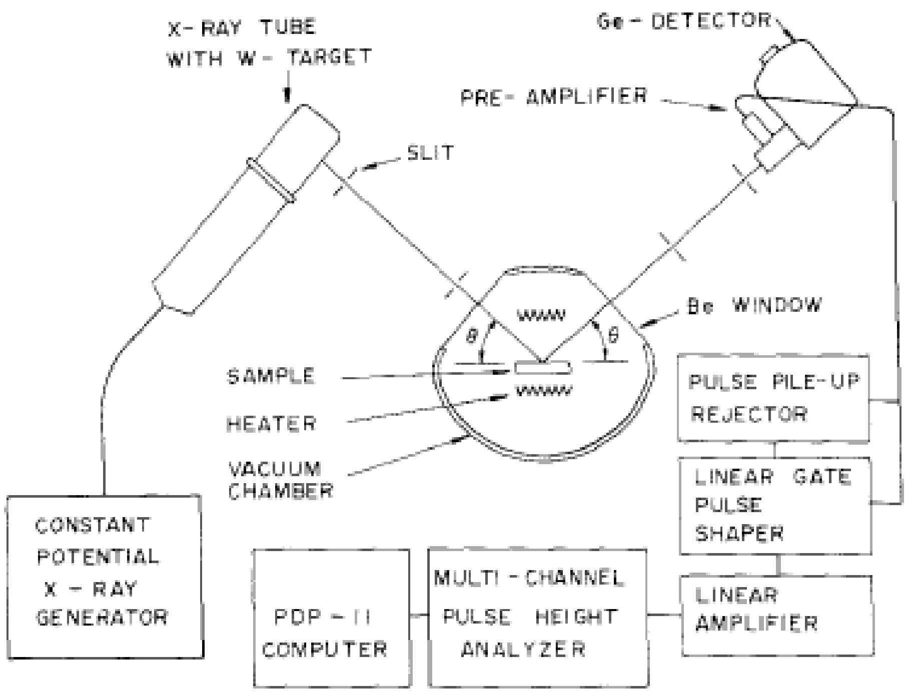
- Small volume change (~0.5%).
- Significant changes in the properties. $\Delta H/\Delta V \sim 10$ eV.
- Significant changes in the structure are happening. How do we observe and describe them?

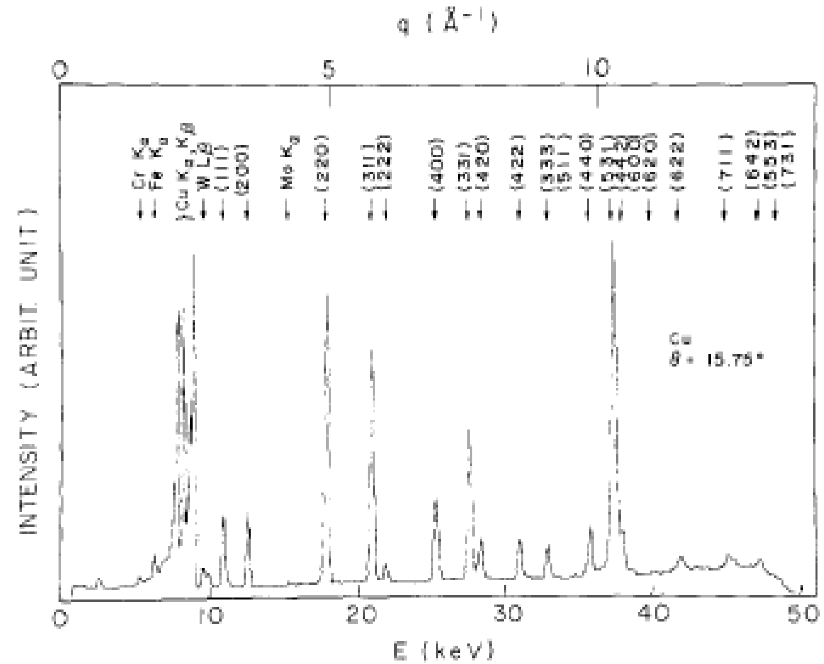


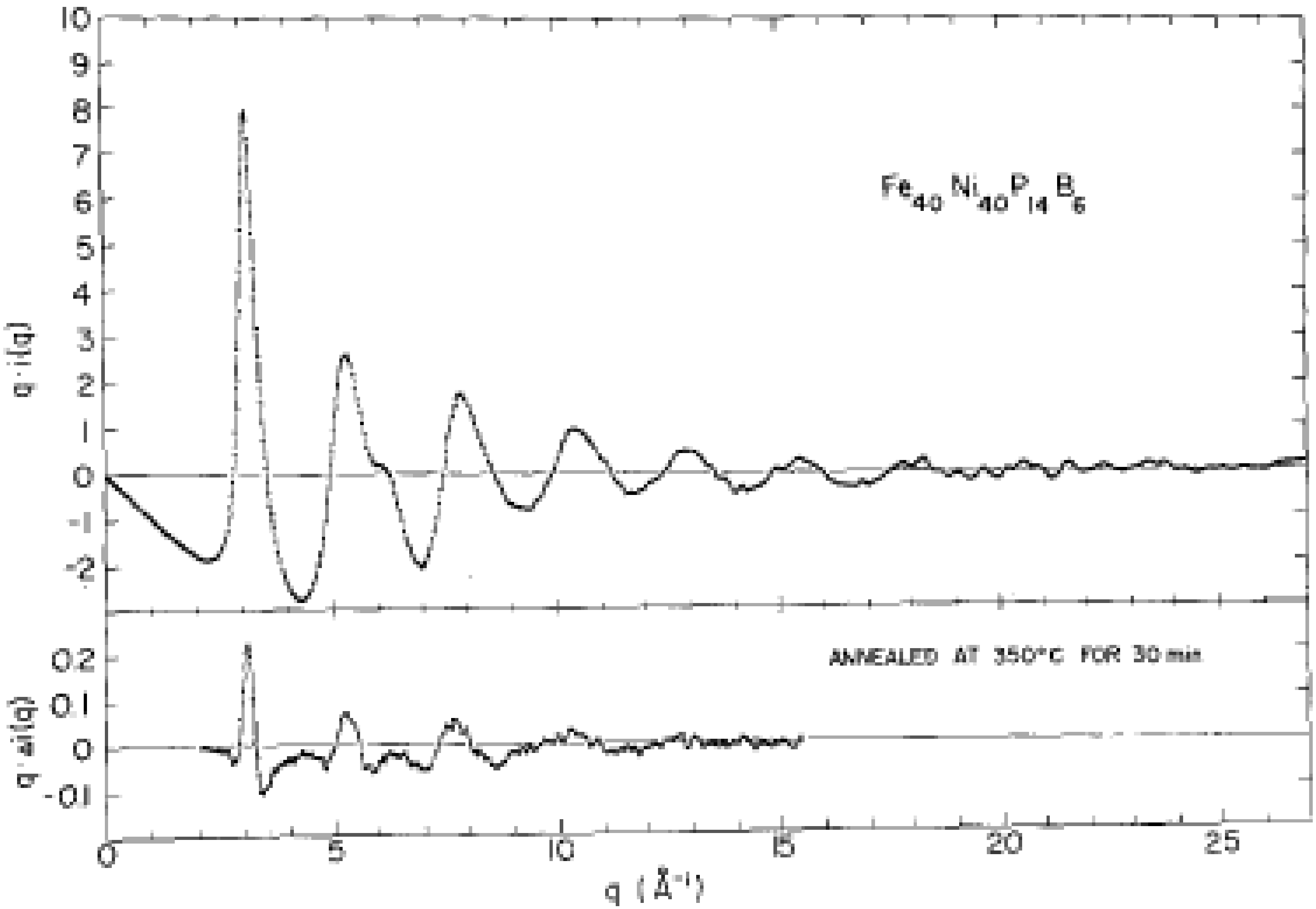
Energy-Dispersive X-ray Diffraction

- Spectroscopic diffraction measurement with white x-rays.

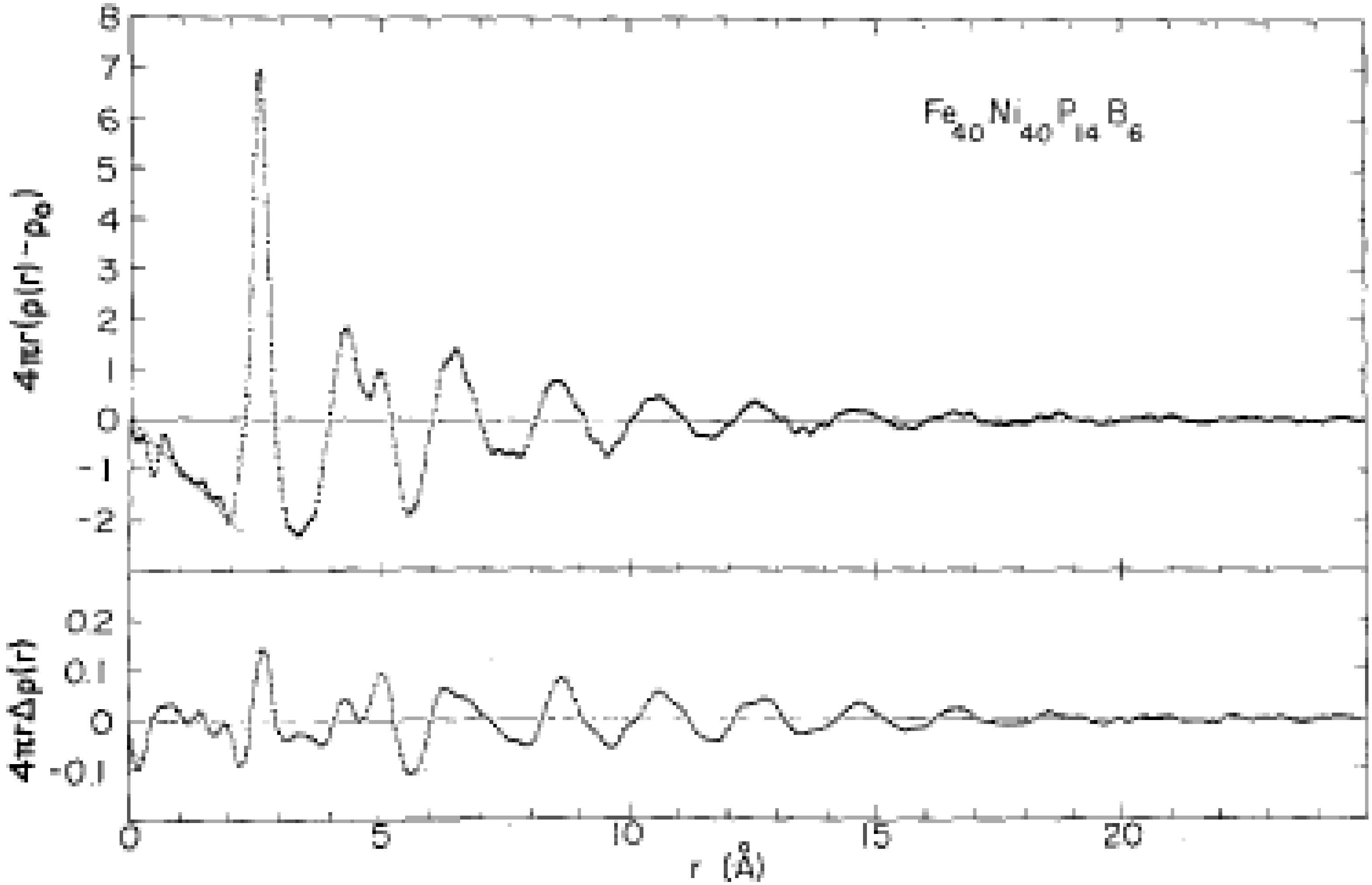
T. Egami, *J. Mater. Sci*. **13**, 2587 (1978)



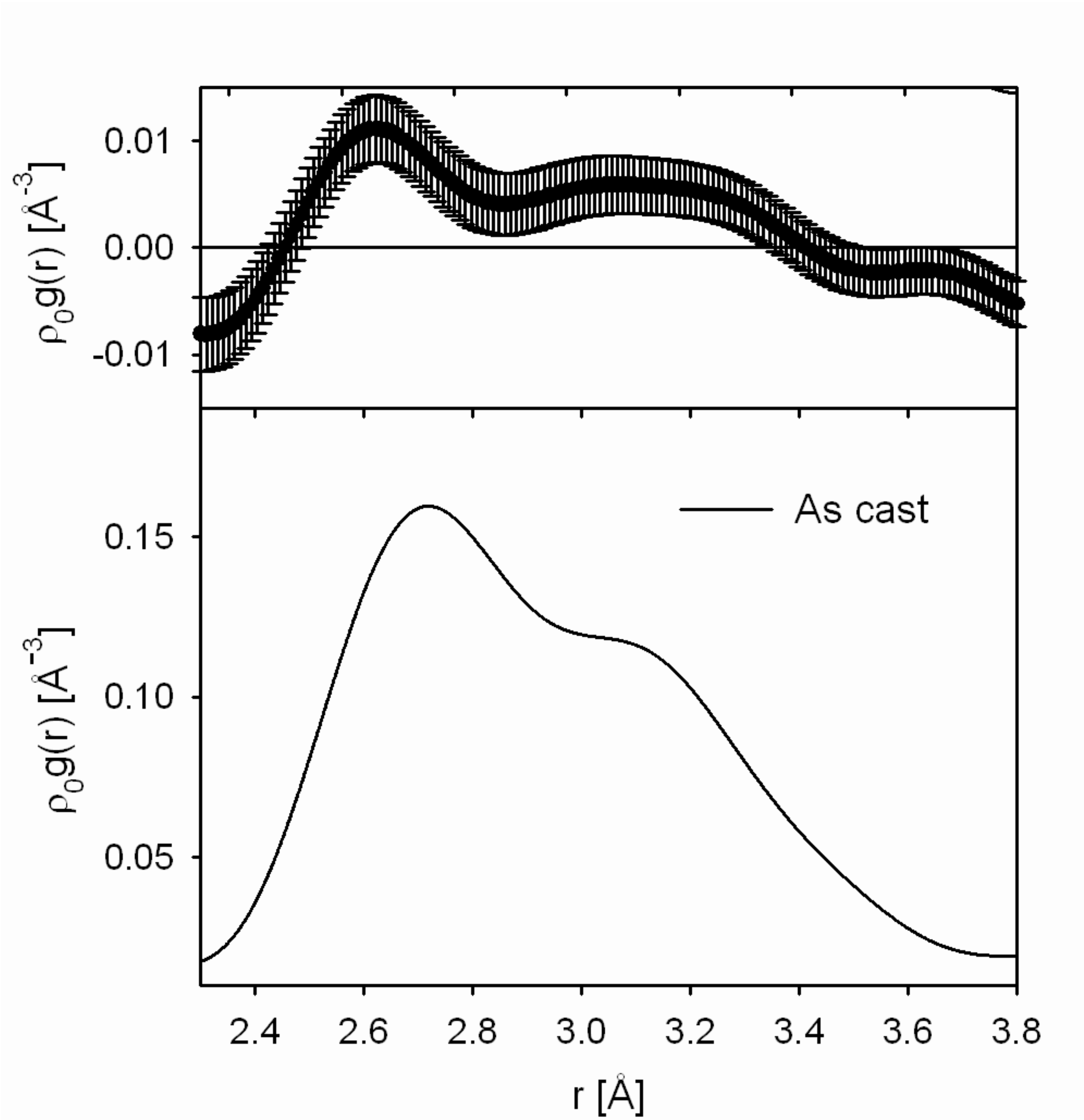




$Fe_{40}Ni_{40}P_{14}B_6$
ANNEALED AT 350°C FOR 30 min
q · i(q)
q · Δi(q)
q (Å⁻¹)



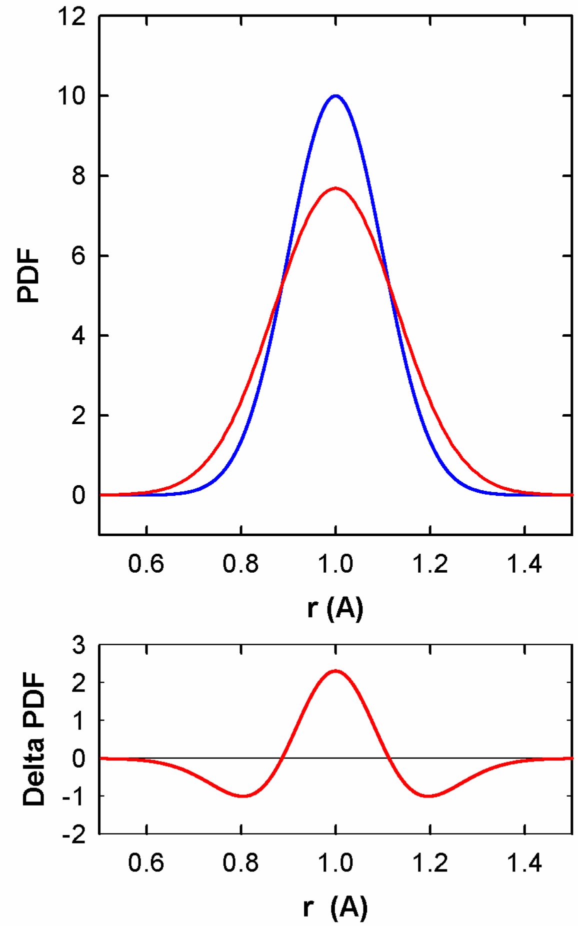
$Fe_{40}Ni_{40}P_{14}B_6$
$4\pi r(\rho(r)-\rho_0)$
$4\pi r\Delta\rho(r)$
8
7
6
5
4
3
2
1
0
-1
-2
0.2
0.1
0
-0.1
0
5
10
15
20
r (Å)



0.01
0.00
-0.01
$\rho_0 g(r)$ [Å^{-3}]
As cast
0.15
0.10
0.05
$\rho_0 g(r)$ [Å^{-3}]
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
r [Å]

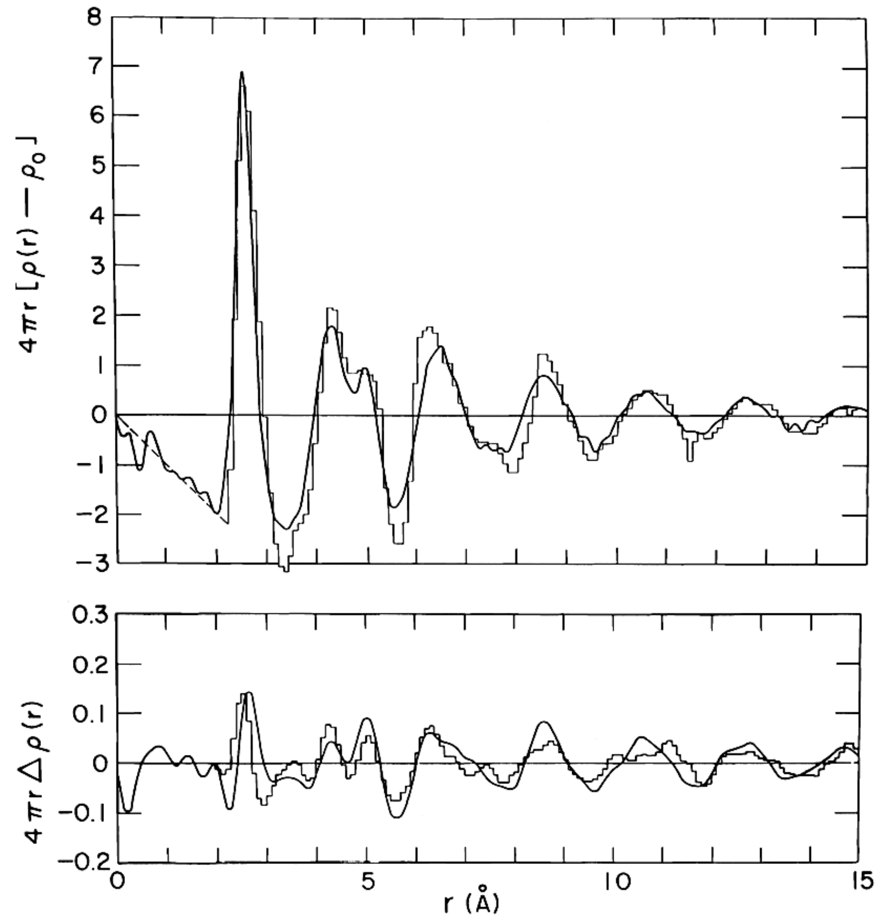
Change in the PDF due to Structural Relaxation

- Even though the change in $\Delta\ell/\ell$ is 0.2%, PDF changes 2 – 7 %.
- Little shift in the peak position; stays in the minimum of the interatomic potential.
- The coordination number remains largely unchanged.
- 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

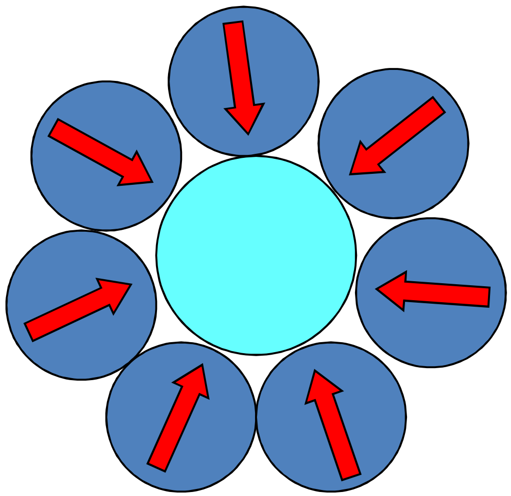
- Reduction in $<\Delta N_C^2>$, and $<p^2>$.
- Change in the PDF; 30% change in $<p^2>$.
- 30% change in the fictive temperature.



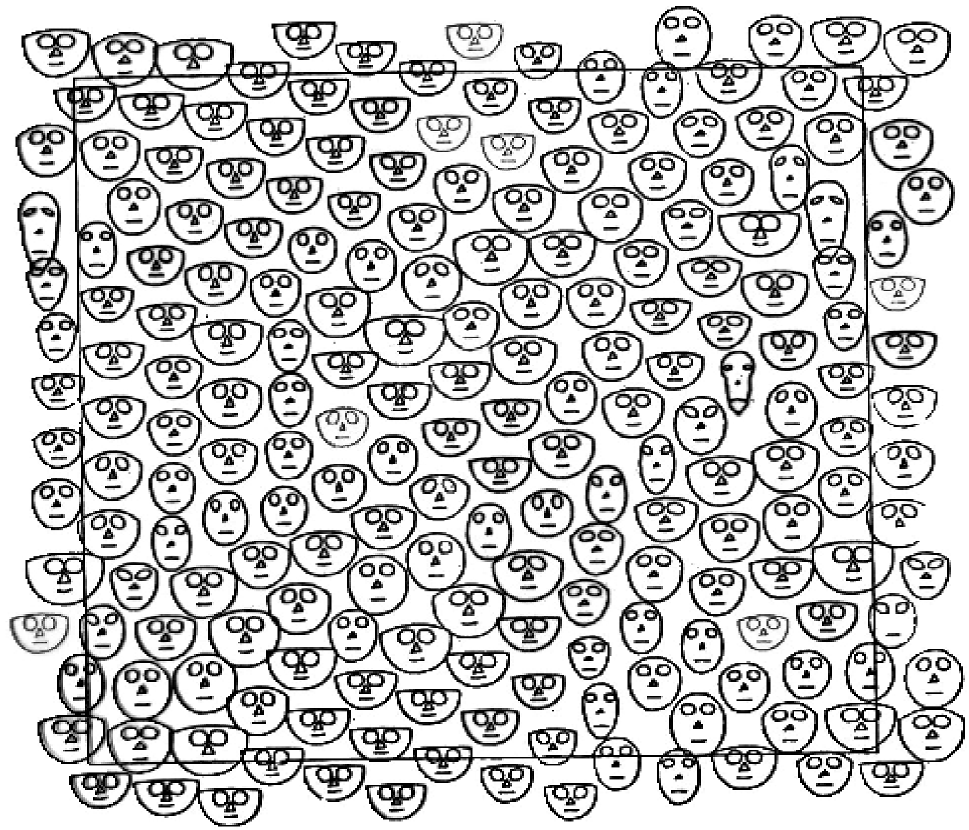
T. Egami, *J. Mater. Sci.* **13**, 2587 (1978), D. Srolovitz, T. Egami, and V. Vitek, *Phys. Rev. B* **24**, 6936 (1981)

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).

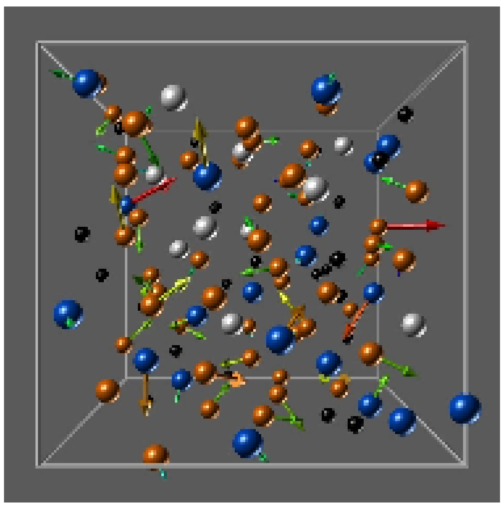


- Atomic level stresses relate the local topology to the local energy landscape.

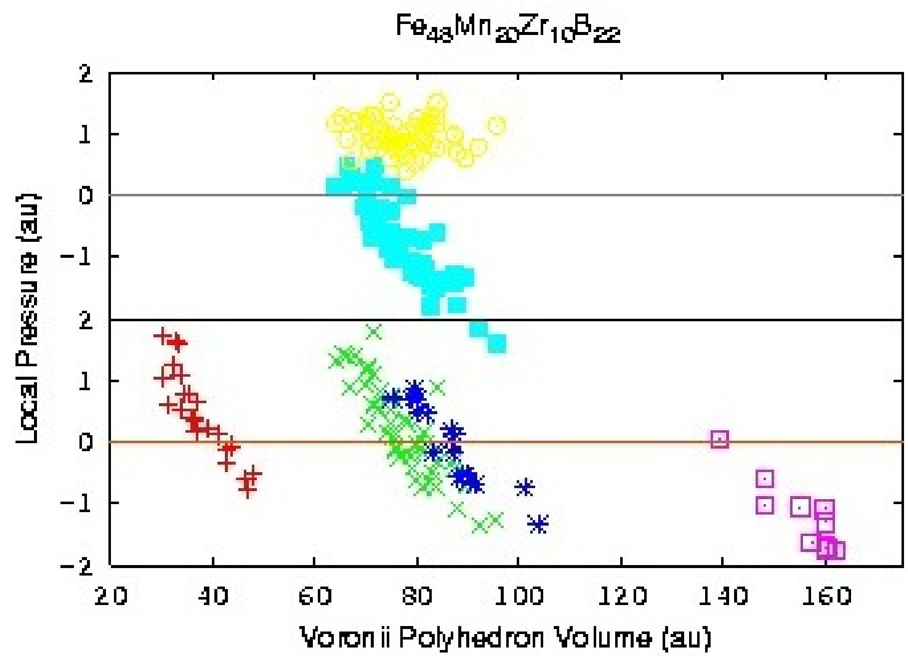
Atomic Level Stresses from the First Principles

Nielson (PRL **50**, 697 (1983); Filippetti PRB **61**, 8433 (2000)

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



$Fe_{48}Mn_{20}Zr_{10}B_{22}$



D. Nicholson and G. M. Stocks

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

Atomic Level Stresses

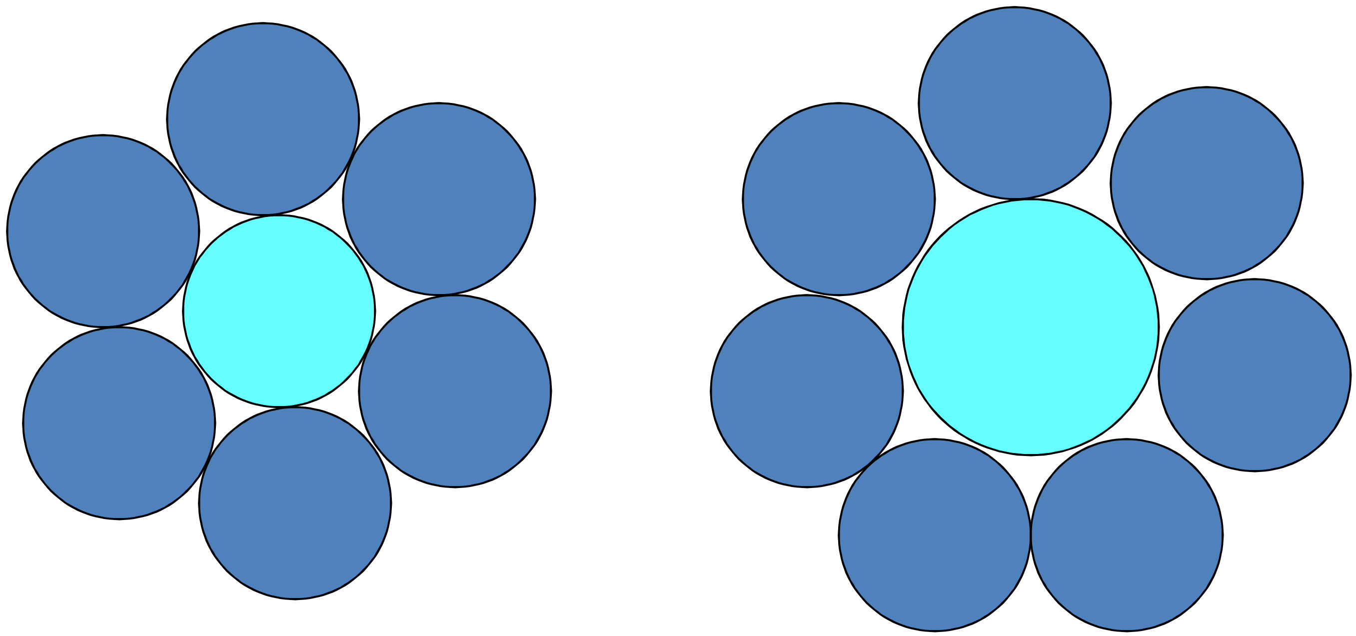
- If an an atom is in an *ideal* environment, $f_{ij} = 0$, so $\sigma_i = 0$.

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

- Stress describes the deviation from the ideal state; **<unhappiness>**.
- Topological deviations.

Stress fluctuations = Topological fluctuations

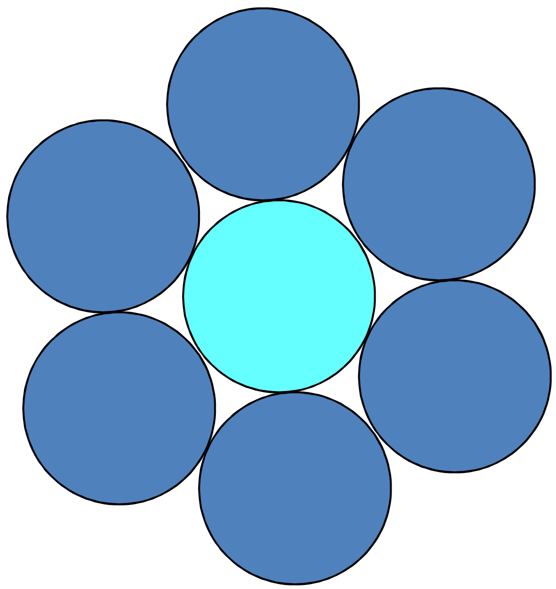
Atomic size and local coordination



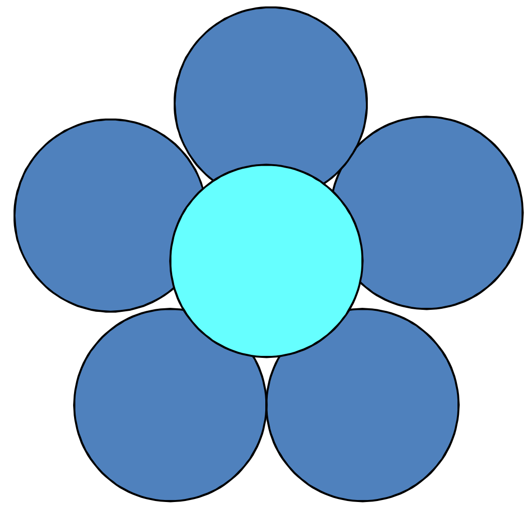
- A large atom has more neighbors………

Origin of the Atomic-Level Stresses

- The origin is the mismatch between the **local topology and the atomic size**.



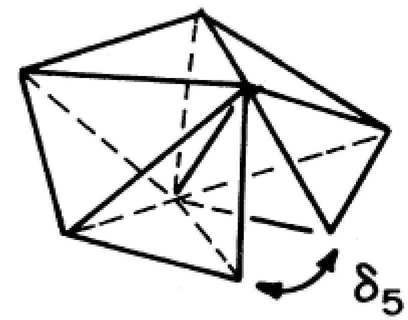
P = 0



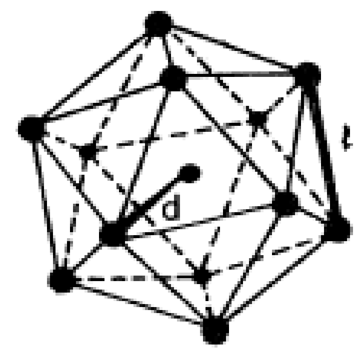
P > 0

Topology and Geometry

- Putting five tetrahedra together makes pentagonal bipyramid, with distortion (δ_5 = 7.4°).
- Putting twenty tetrahedra makes icosahedron, but each tetrahedron is distorted.
- Thus the local packing and global packing are not compatible; the structure is frustrated.



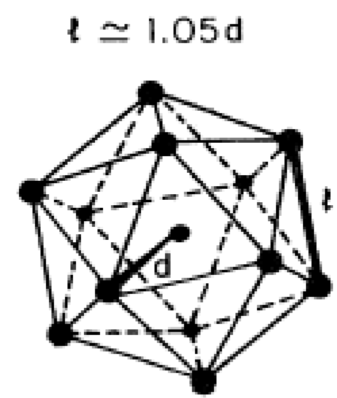
$\ell \simeq 1.05d$



ICOSAHERON IN FLAT SPACE
(a)

Curvature in 4D

- Euclidian space is a flat surface in 4-dimensional space.
- If we make the 4D surface curved, icosahedron can be made without strain.
- Space can be filled by tetrahedra if the space is curved.
- The real structure can be described by locally curved space (M. Klemann, F. Sadoc, D. R. Nelson, G. Tarjus).
- Local curvature is equivalent to local atomic level strain.
- Strain cannot be uniquely defined, but stress can be.



ICOSAHERON IN FLAT SPACE
(a)

Connection with MCT and DFT

- MCT and DFT consider only the density, $n(\mathbf{r})$, as a variable, but we consider the stress, (strain) tensor, $\bar{\bar{\sigma}}_i$, (B. Chakraborty).
- Atomicity enters as local frustration that causes local incompatibility (E. Kröner), and deviates from continuum mechanics).
- Slowdown occurs because of the atomicity.
- The local incompatibility is characterized by the minimum universal strain.

Viscosity

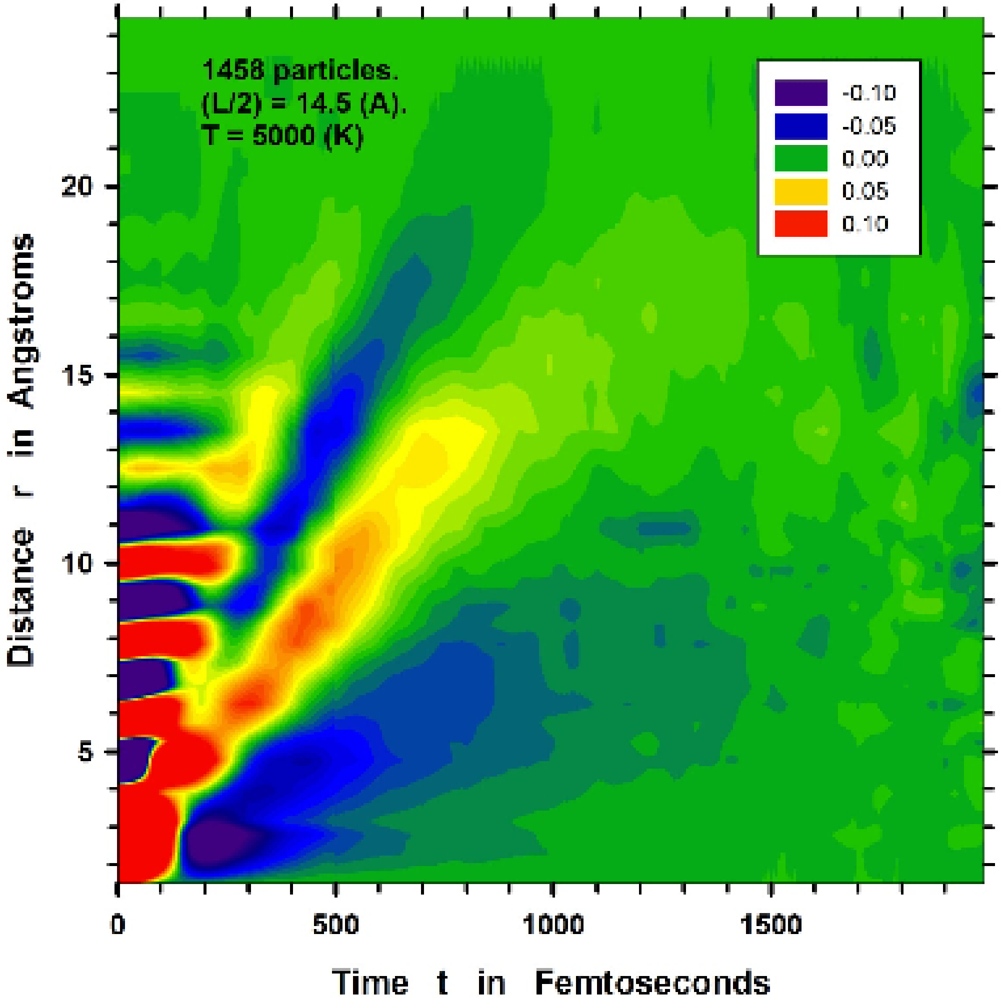
- Green-Kubo equation (fluctuation-dissipation theorem);

$$\eta = \frac{kT}{V}\int \left\langle \sigma^{xy}(0)\sigma^{xy}(t)\right\rangle dt$$

- In terms of the atomic level stresses,

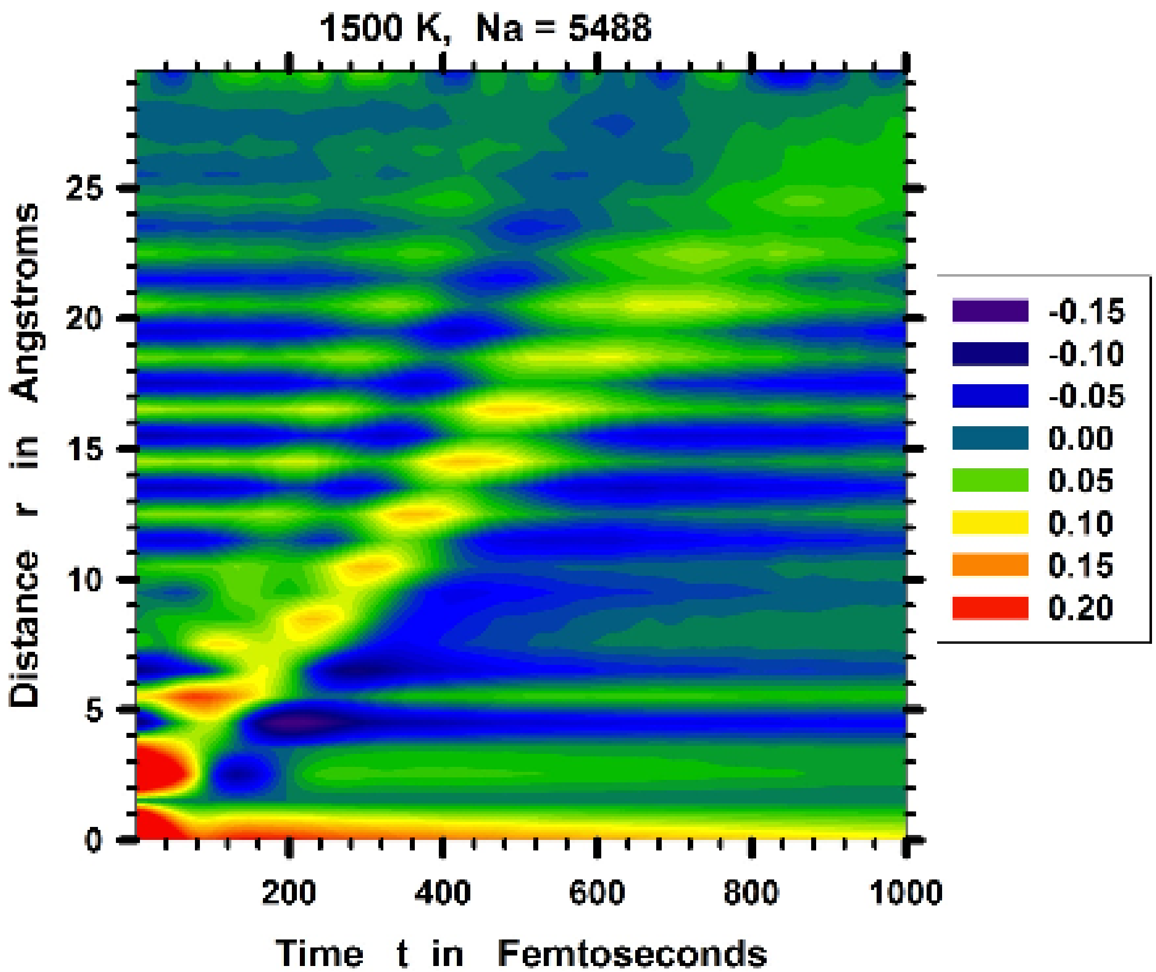
$$\eta = \frac{kT}{V}\int \sum_{i,j}\Omega_i\Omega_j \left\langle \sigma_i^{xy}(0)\sigma_j^{xy}(t)\right\rangle dt$$

$$\Sigma(r,t) = \iint \left\langle \sigma^{xy}(\boldsymbol{r}',0)\sigma^{xy}(\boldsymbol{r}'',t)\right\rangle \delta\left(r - \left|\boldsymbol{r}' - \boldsymbol{r}''\right|\right) d\boldsymbol{r}' d\boldsymbol{r}''$$



- Liquid iron.
- T = 5000 K
- T_g = 800 K, T_{CO} = 2300 K
- L and T waves are seen.

$$\Sigma(r,t) = \iint \left\langle \sigma^{xy}(\boldsymbol{r}',0)\,\sigma^{xy}(\boldsymbol{r}'',t) \right\rangle \delta\left(r - \left|\boldsymbol{r}' - \boldsymbol{r}''\right|\right) d\boldsymbol{r}' d\boldsymbol{r}''$$



- Correlation developing over both **time and space: That is why viscosity changes so much.**

- Currently developing the theory.

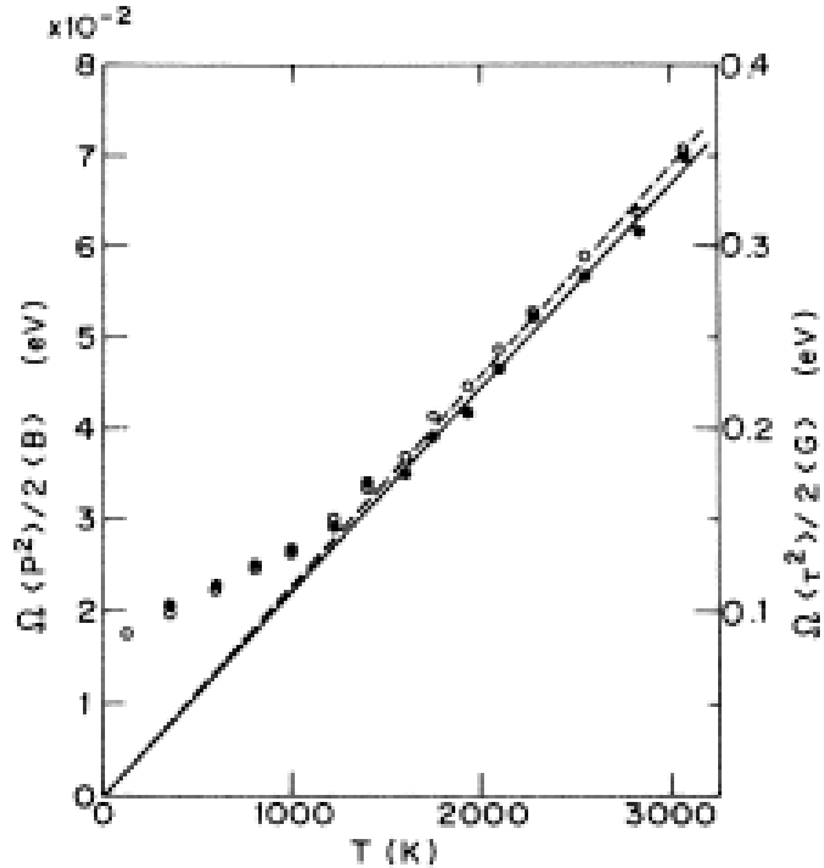
Local structural fluctuation in liquid

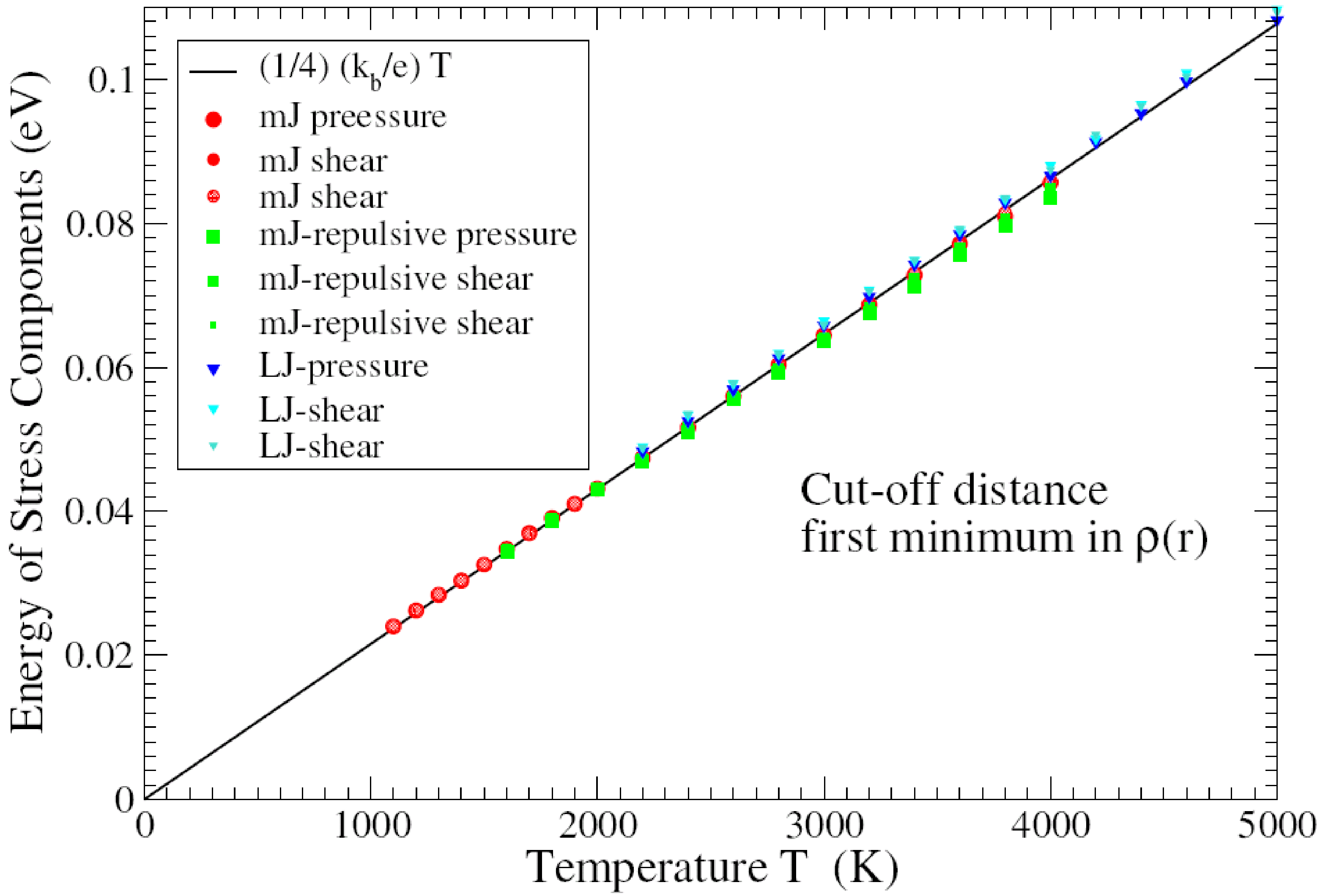
- Temperature dependence of the local stress fluctuation (T. Egami and D. Srolovitz, *J. Phys. F*, **12**, 2141 (1982))

- S.-P. Chen, T. Egami and V. Vitek, *Phys. Rev. B* **37**, 2440 (1988). At high temperatures;

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

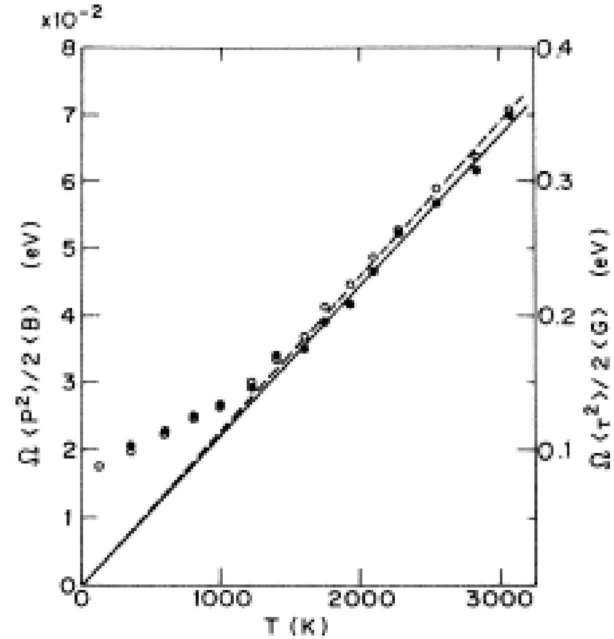
$$\frac{V}{10G}\left\langle \tau^2 \right\rangle = \frac{VG}{10}\left\langle \varepsilon_s^2 \right\rangle = \frac{kT}{4}$$





- $E_{el} = 3kT/2$ for various inter-atomic potentials.
- Atomic-level stress is an excellent bridge between thermodynamics and structure.

Glass Transition



- High-temperature equation,

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

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

- But that is physically impossible because of jamming.

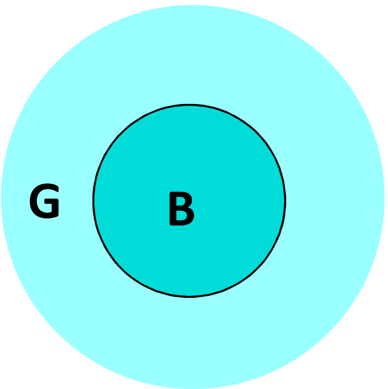
- There must be a minimum strain.

Self-Energy in the Glassy State

- Energy of local fluctuation in volume is given by Eshelby theory (T. Egami and D. Srolovitz, *J. Phys. F*, **12**, 2141 (1982)),

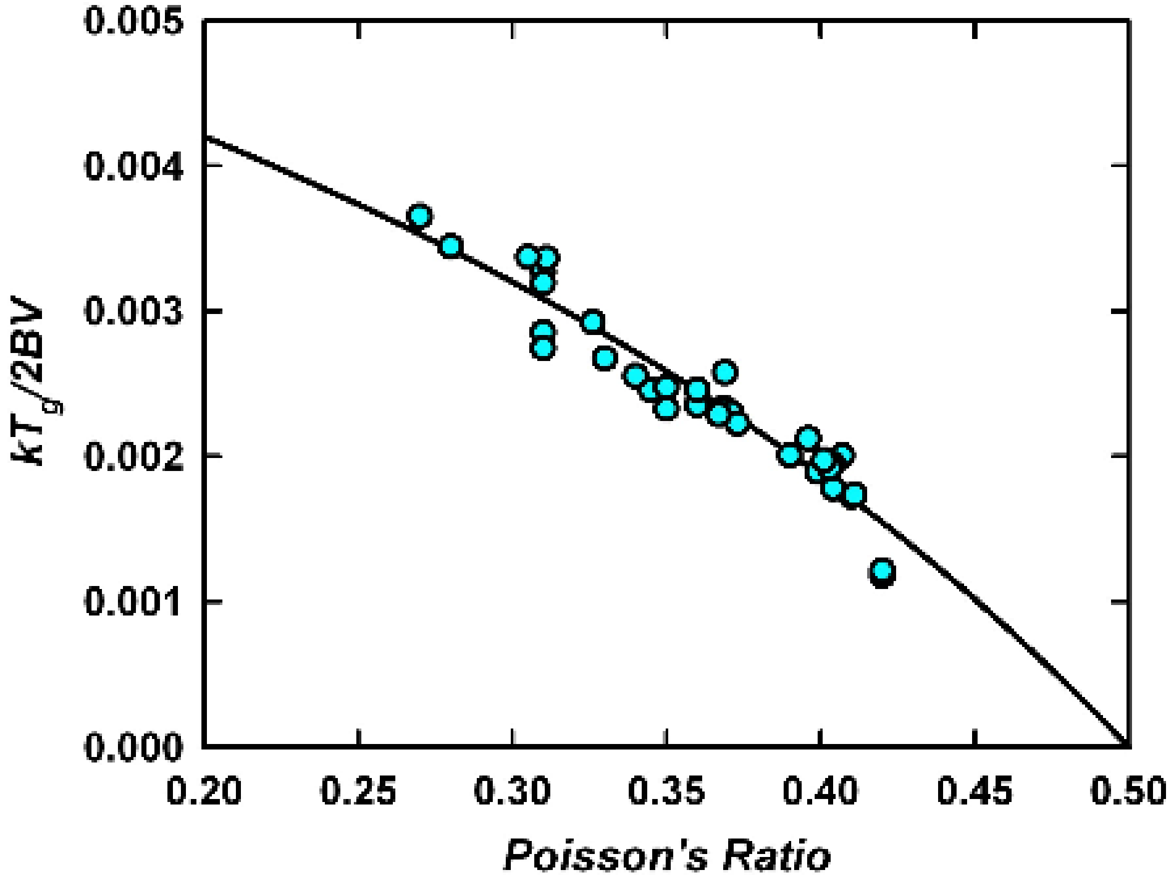
$$E_v = \frac{BV}{2K_\alpha}\left(\varepsilon_{v,T}\right)^2,$$

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



- This energy was compared to the glass transition temperature of many alloys.

$$E_v = \frac{BV}{2K_\alpha}\left(\varepsilon_v^{T,crit}\right)^2 = \frac{kT_g}{4}$$



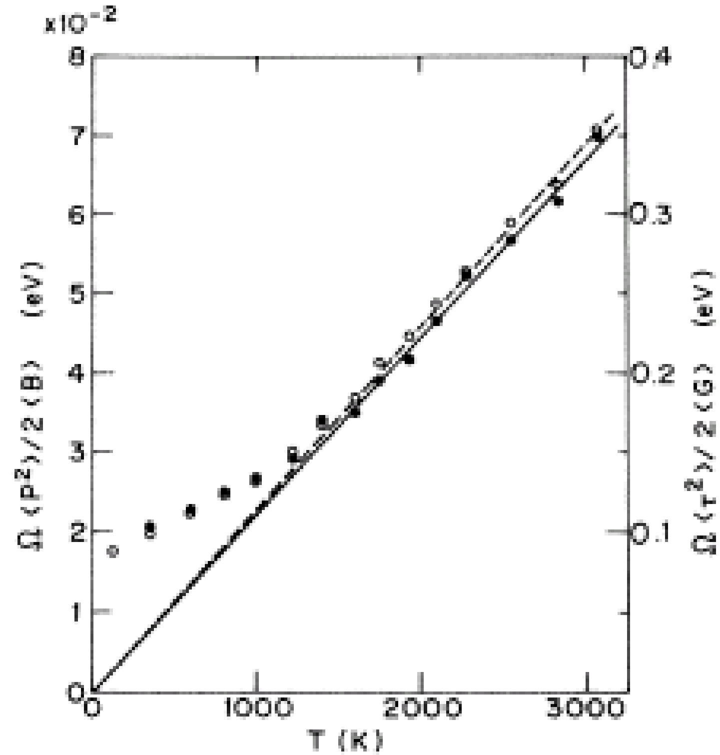
- Glass transition temperature is equal to the energy of local density fluctuation with the long-range stress field at a critical strain level. $\varepsilon_{v,T}$ = 0.095 ± 0.004 (4%).

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

Universal Minimum Strain

- The value of $\varepsilon_v^{T,crit}$ = 0.095, is universal regardless of composition.

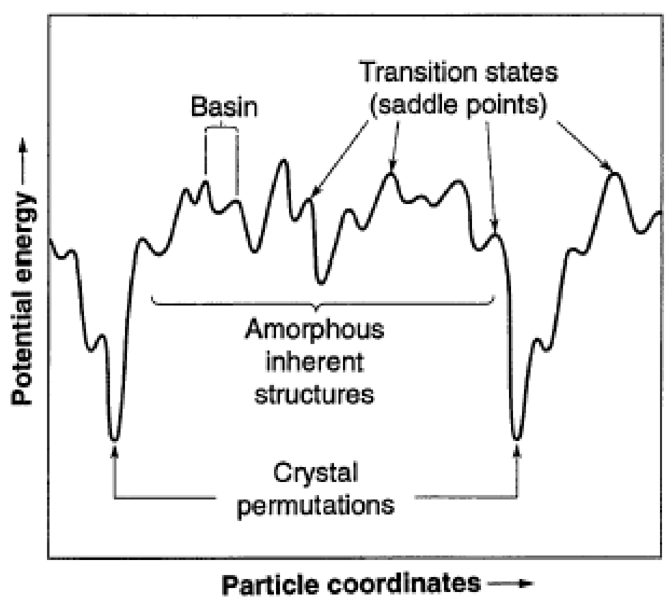
$$kT_g = \frac{2BV}{K_\alpha}\left(\varepsilon_v^{T,crit}\right)^2$$

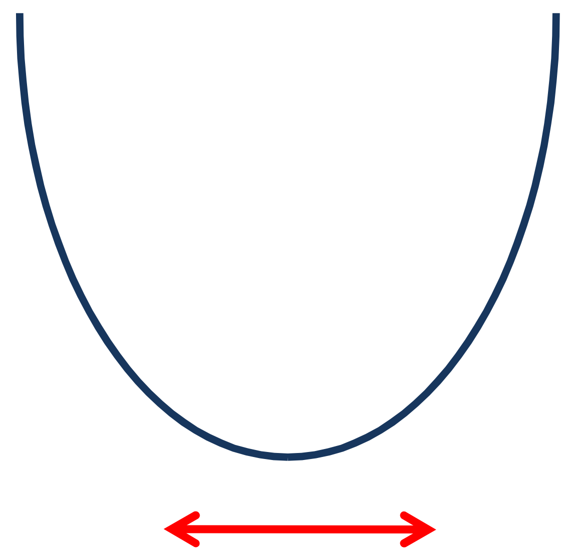


Universal Minimum Local Strain

- Depth of the valley in the energy landscape.

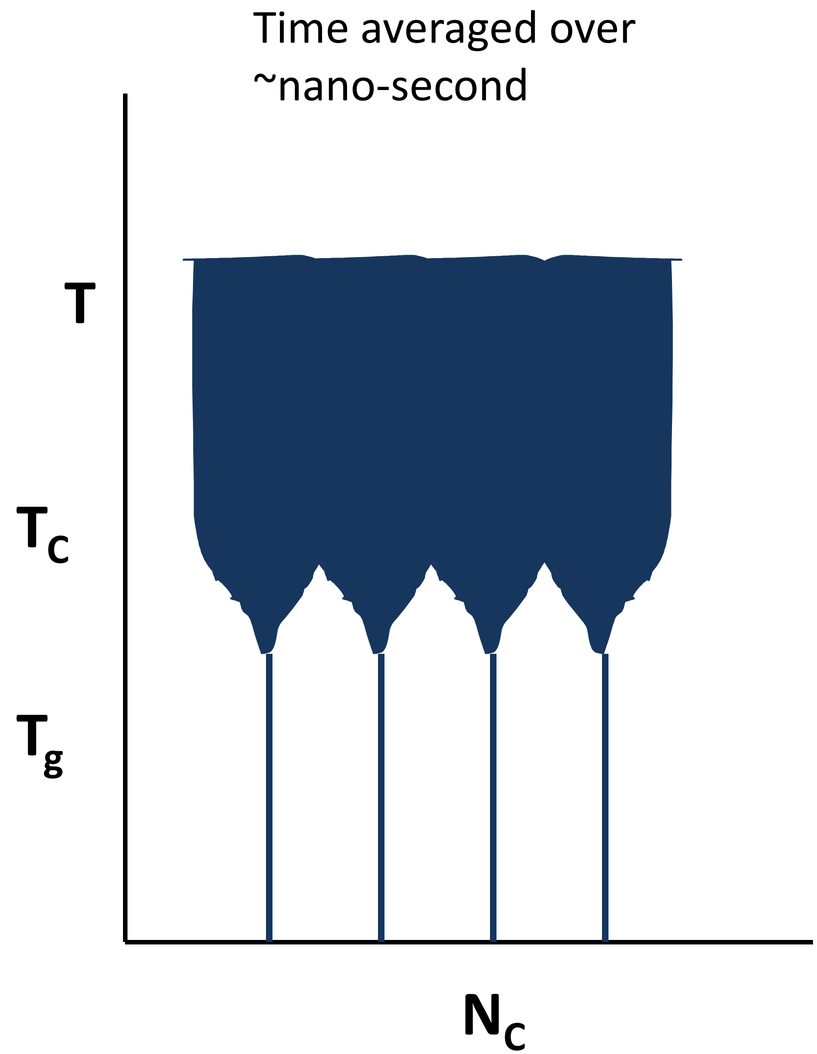
- If the strain is too large the local topology becomes unstable, and change.





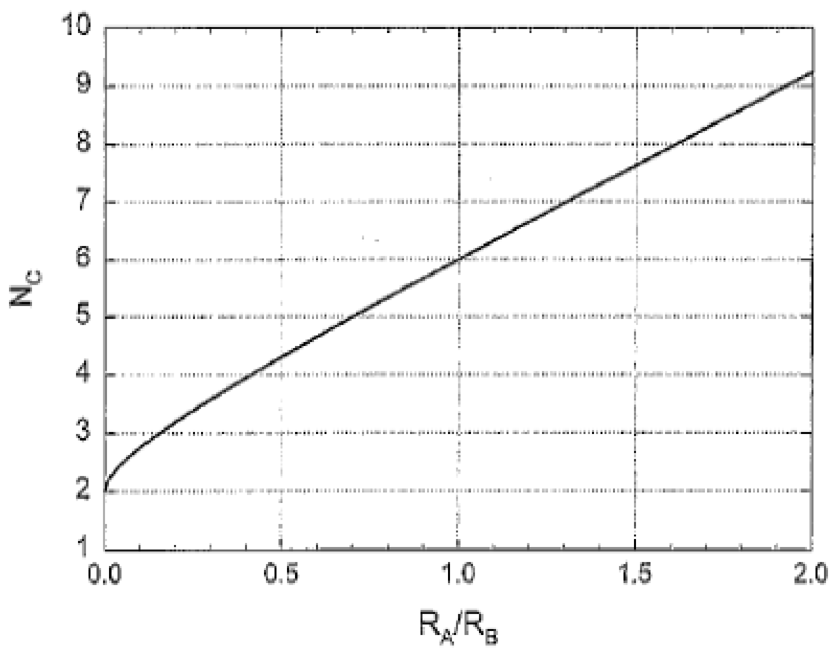
“Quantization” Effect

- 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**.

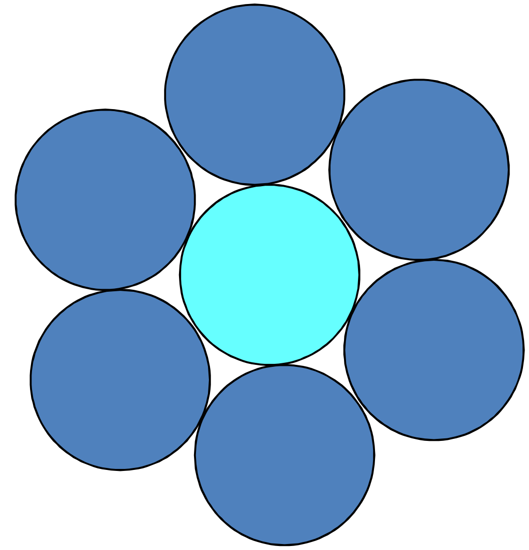


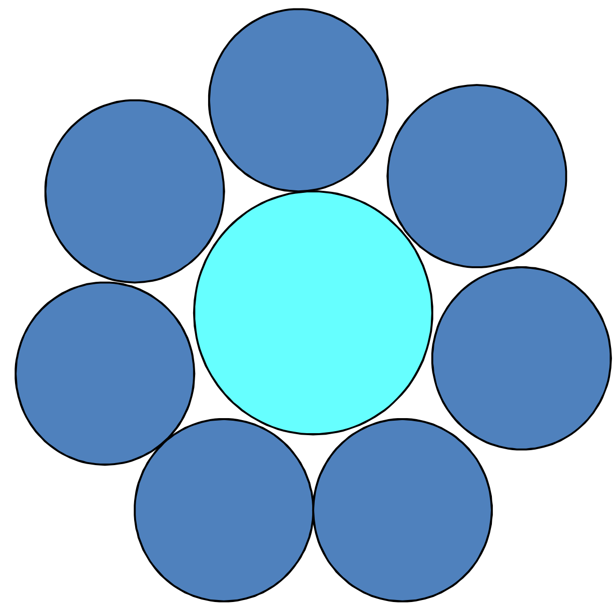
Local Topology and Geometry

- Close packing around the atom.



$$N_C = \frac{2\pi}{\theta_{A-B}} = \frac{\pi}{\sin^{-1}(R_B/(R_A + R_B))}$$





Critical Strain

$$\sin^{-1}\left(\frac{1}{1+x}\right)=\frac{\pi}{N_C}$$

$$x_n=\frac{1}{\sin\left(\frac{\pi}{n}\right)}-1$$

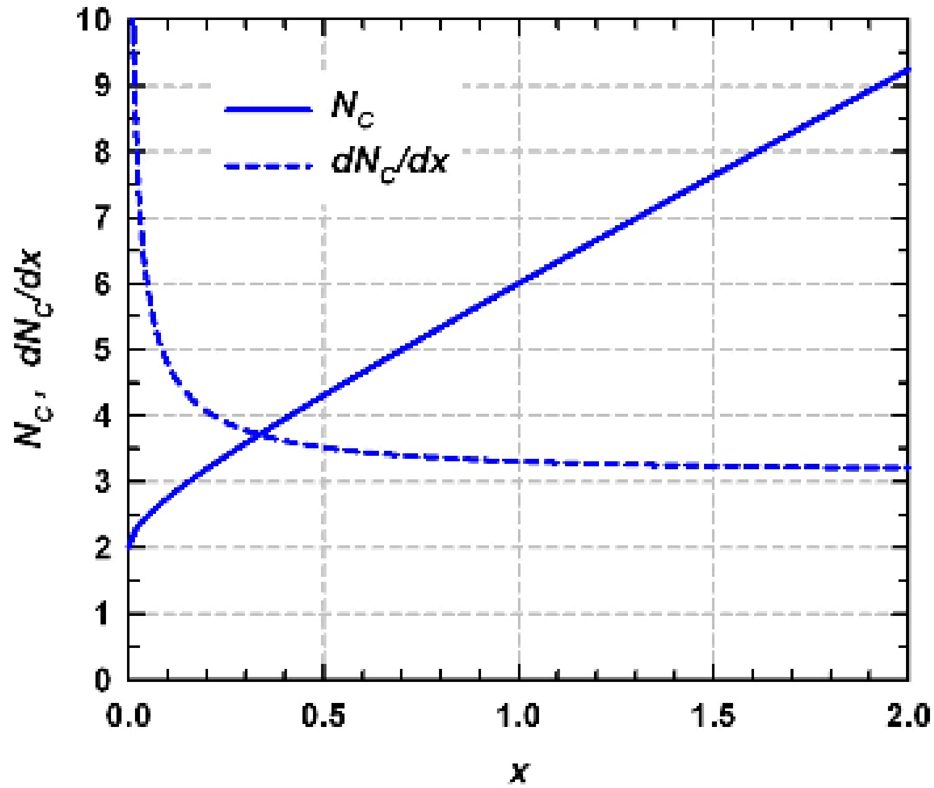
$$\frac{dN_C}{dx}=\frac{N_C^2\sin^2\left(\frac{\pi}{N_C}\right)}{\pi\cos\left(\frac{\pi}{N_C}\right)}$$

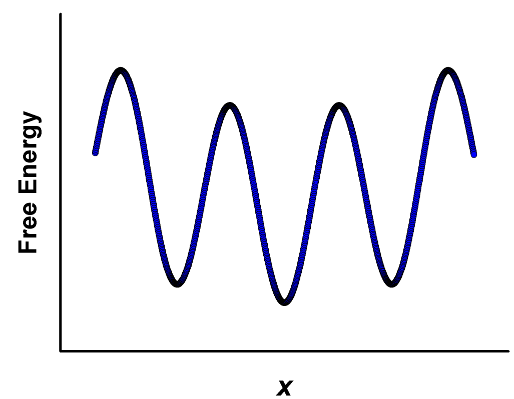
- Critical value of x corresponding to $dN_C = 0.5$;

$$\Delta x_{crit}=\frac{1}{2}\frac{dx}{dN_C}=0.151$$

- Critical shear strain:

$$\varepsilon_s^{crit}=\frac{1}{\sqrt{2}}\varepsilon_{crit}^{\gamma 1}=0.131$$

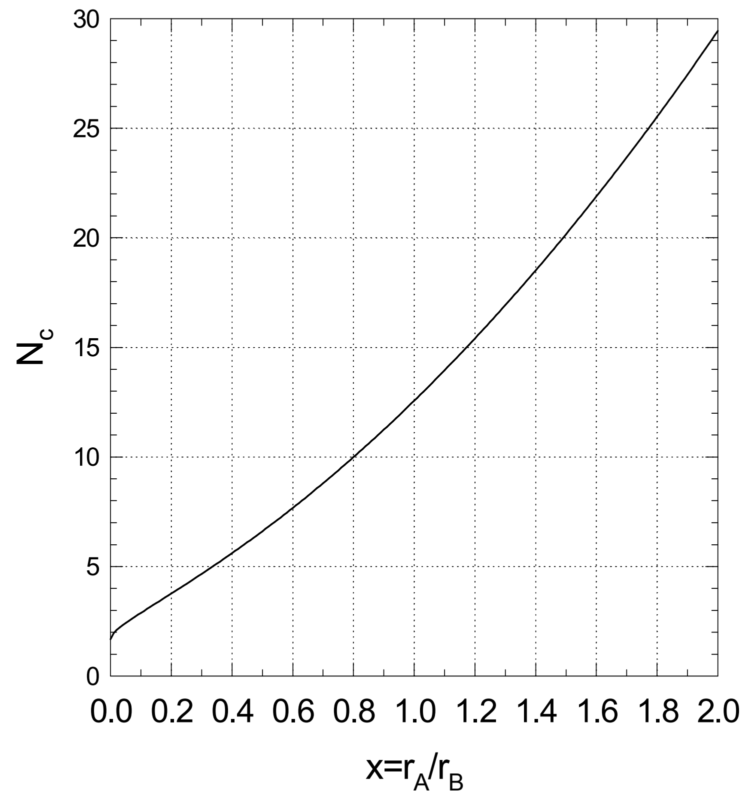




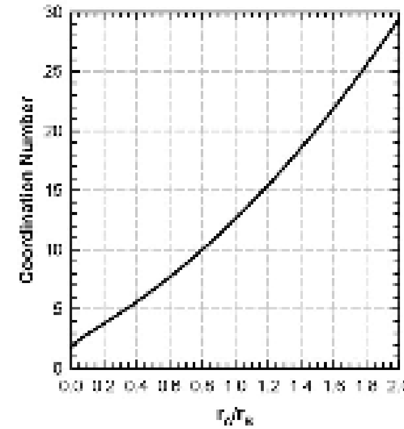
Local topology of metallic glass

- Place an A atom with the radius r_A in the liquid of B.
- There is an equilibrium coordination number as a function of $x = r_A/r_B$.

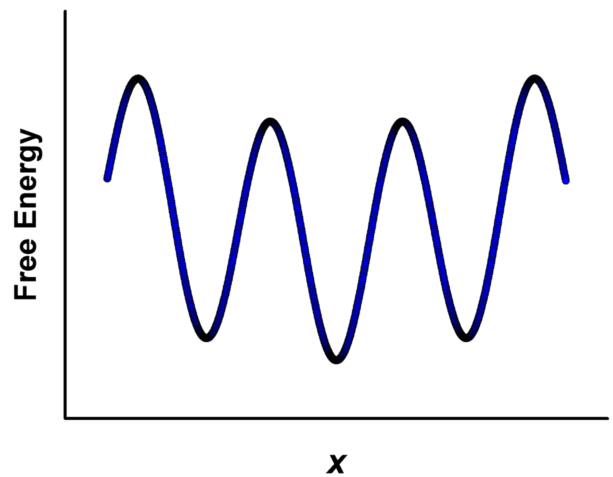
$$N_C^A(x) = 4\pi\left[1-\frac{\sqrt{3}}{2}\right] \Big/ \left[1-\frac{\sqrt{x(x+2)}}{x+1}\right]$$

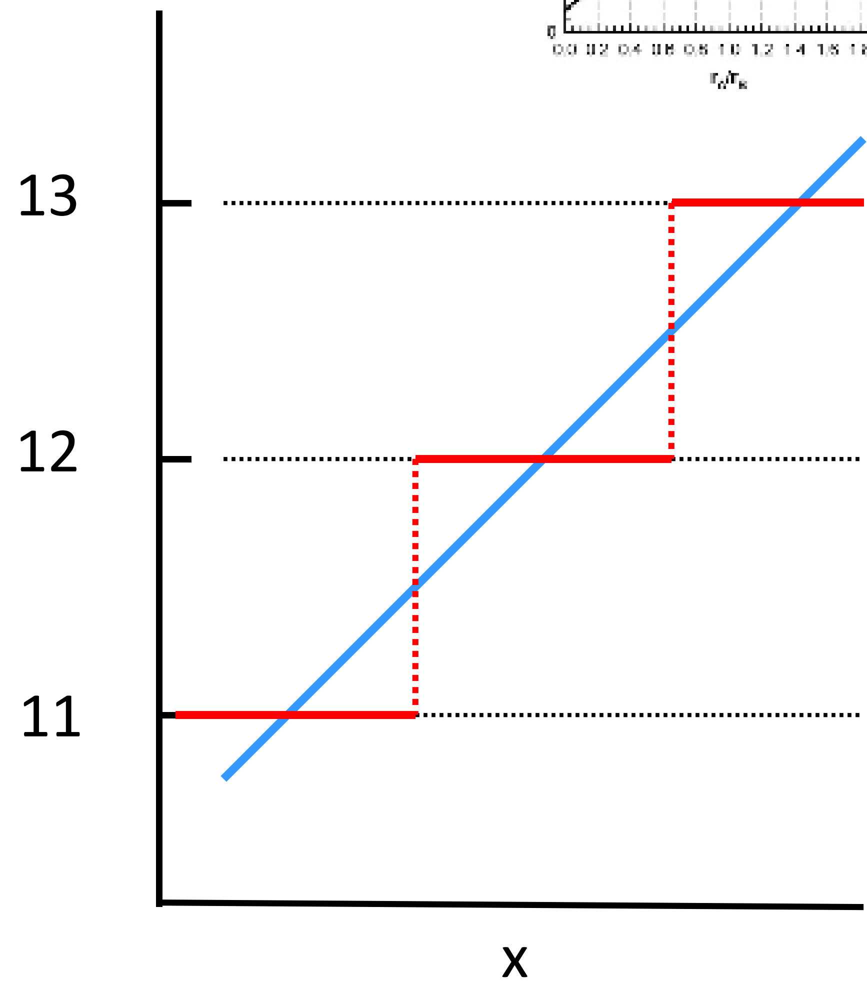


Local topological instability



- 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.

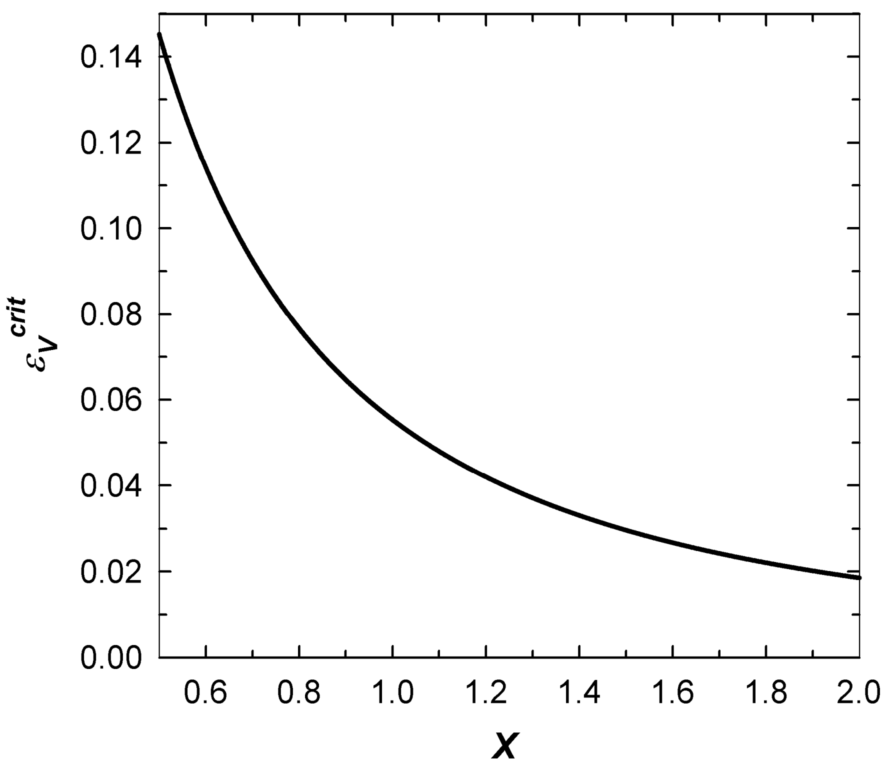
- The instability condition:

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

- For a monoatomic system (x = 1),

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

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

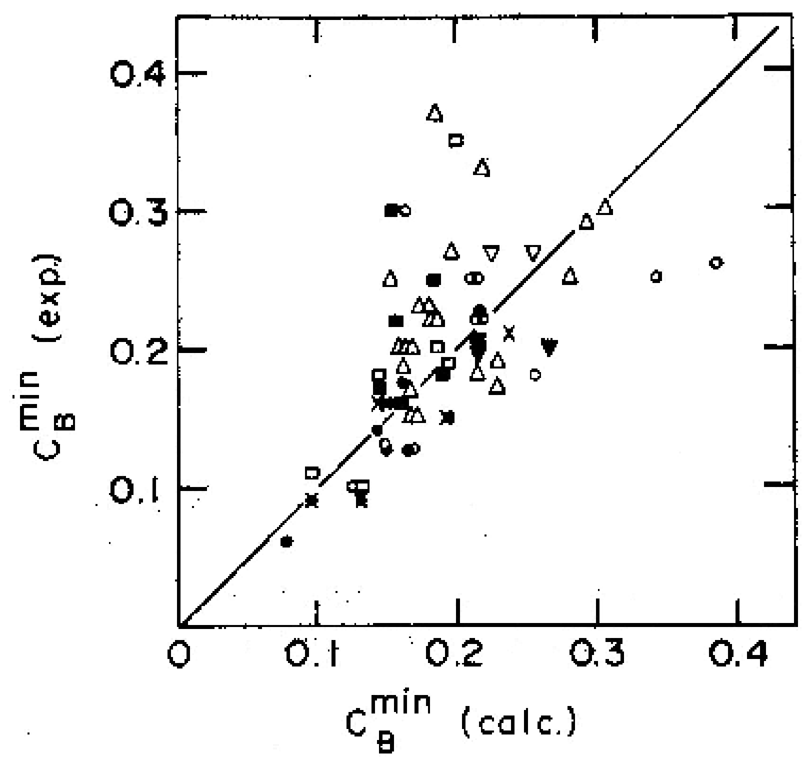


Composition limit for binary glass

- This leads to the composition limit (T. Egami and Y. Waseda, *J. Non-Cryst. Solids*, **64**, 113 (1984)),

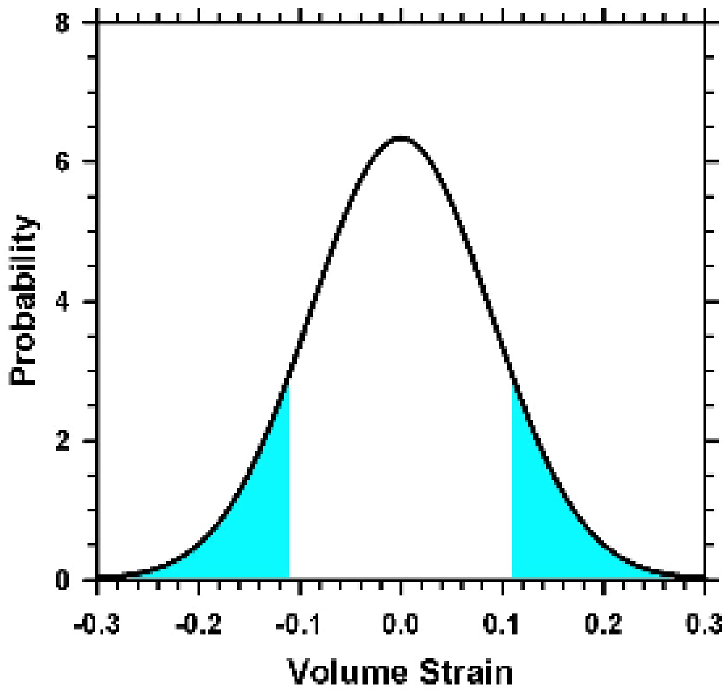
$$c_B^{\min} = 0.1\frac{V}{|\Delta V|}; \quad \Delta V = V_A - V_B$$

- Tested for a large number of alloy systems.



Liquid-Like Sites (Free-Volume)

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



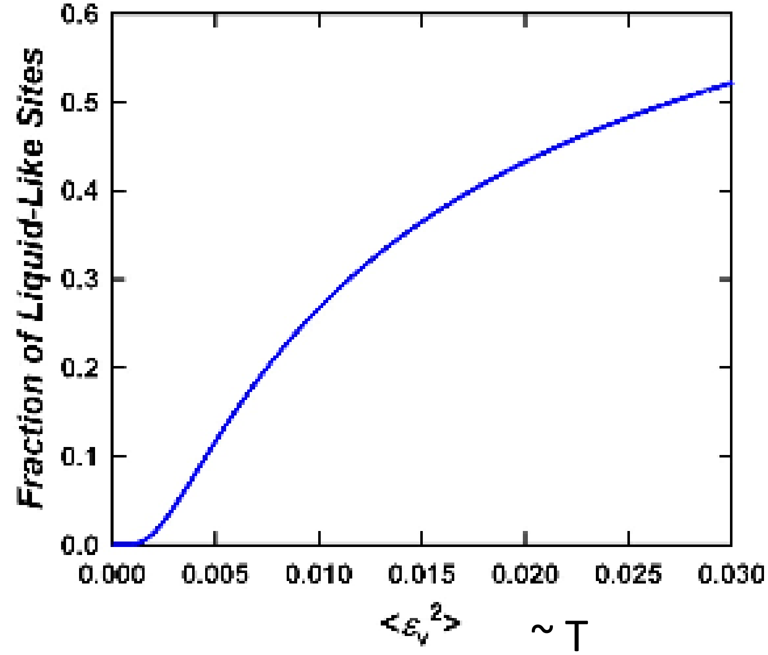
Free volume element

Percolation of the Liquid-like Sites

- Total fraction of the liquid-like sites:

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

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



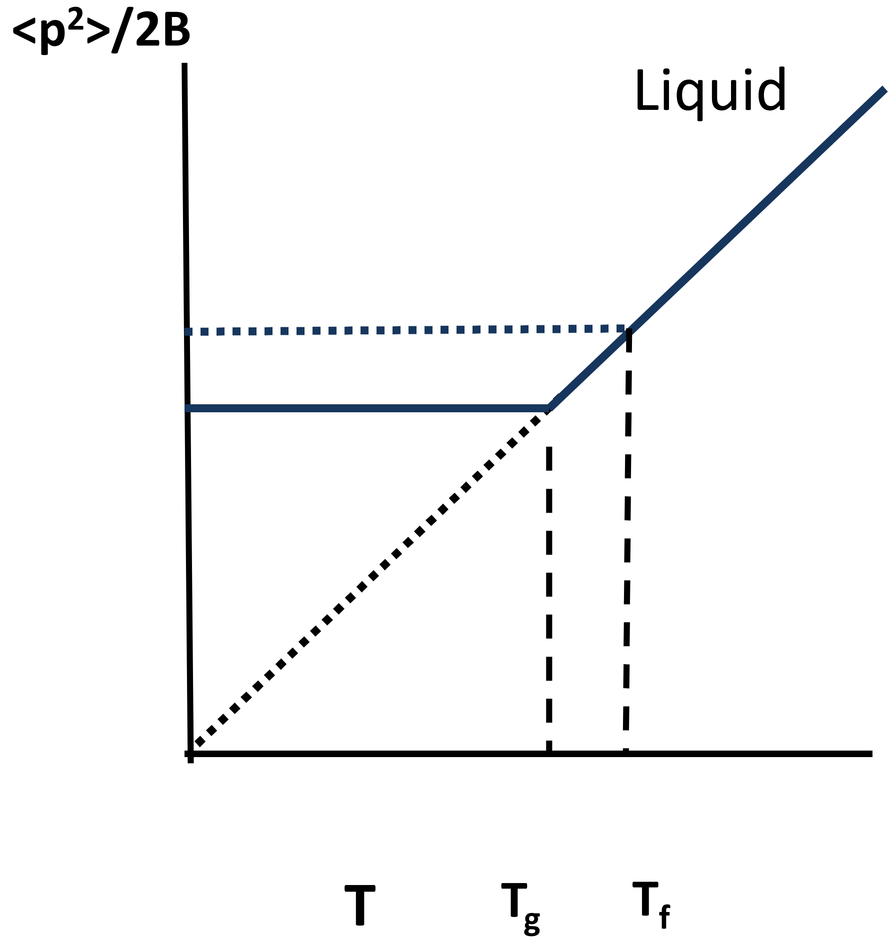
- For $\varepsilon_{v,T}$ = 0.095 ± 0.003

$$p(liq) = 0.243$$

- 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)

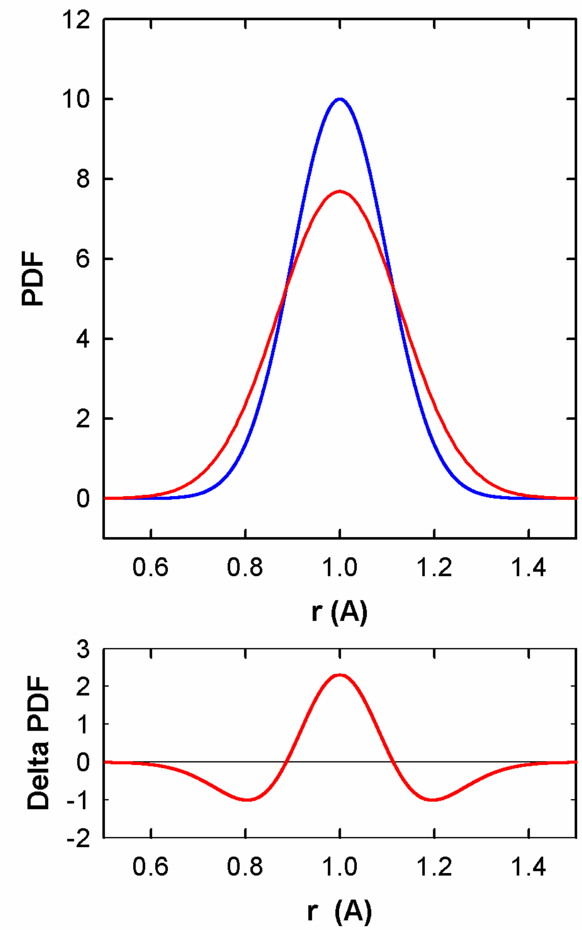
Structural Relaxation

- Rapid cooling traps the system to a high level of stresses.
- Structural relaxation = relaxation of the atomic level stresses.
- Distribution of P becomes narrower.



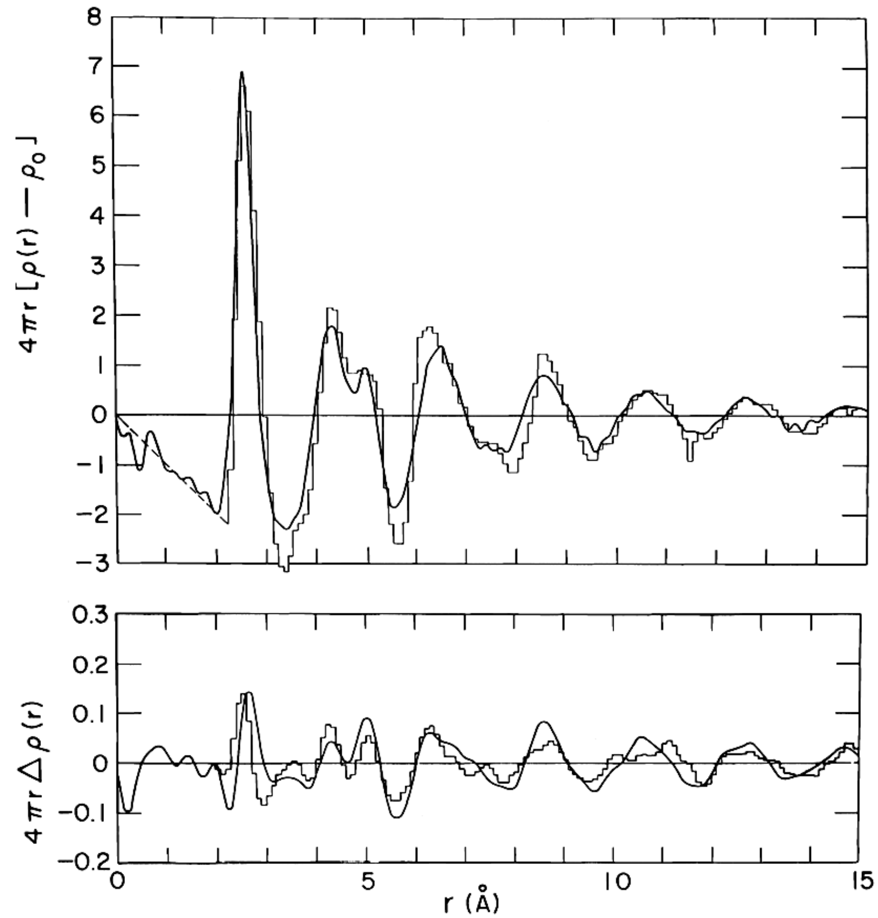
Change in the PDF due to Structural Relaxation

- 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 $<\Delta N_C^2>$, and $<p^2>$.
- Change in the PDF; 30% change in $<p^2>$.
- 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)

Conclusions

- **Changes in the PDF** due to structural relaxation can be observed by careful x-ray diffraction.
- Relaxation reduces the PDF peak width without shifting the peak.
- Relaxation can be explained in terms of **reduction in the distribution of atomic-level stresses**.
- **Atomic level stresses** describe local topology and connect them with **local energy landscape**.
- The self-energy of the atomic level stresses follows the **equipartition theorem** for various potentials.
- Freezing of the atomic-level stress fluctuation defines the **glass transition**. The equation thus deduced agrees with experiment with high accuracy.