KITP Conference on Glass Physics, June 21-25

Local Dynamics of Liquids and the Glass Transition

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Supported by DOE-BES

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Spallation Neutron Source

- $1.4B
- 5 times the second best source in power.

JINS

•Built by the state of Tennessee
•Belongs to UTK
•Completed this July
•Frontier of interdisciplinary research
•UT/ORNL collaboration
•Users welcome

Outline

- Dynamics of metallic liquid
  - Equipartition theorem with the dynamics of atomic-level-stresses.
- Glass transition
  - Loss of ergodicity due to topological frustration.
  - Universal critical strain for the glass transition.
  - Local topological instability.
- Jump in specific heat at T_g.
- Density of “defects” by x-ray diffraction.
- Implications.

Atomic Dynamics

- Normal mode obtained by diagonalizing the dynamical matrix (Born and Huang):

$$D_{ij}^{\alpha\beta} \quad , \quad D_{ij}^{\alpha\beta} = \frac{\partial^2 E}{\partial r_i^{\alpha} \partial r_j^{\beta}}$$

- Similar analysis has been made for liquids and glasses.
- However, in the liquid state ***D*** is time-dependent.
- In high-temperature liquids modes are more localized.

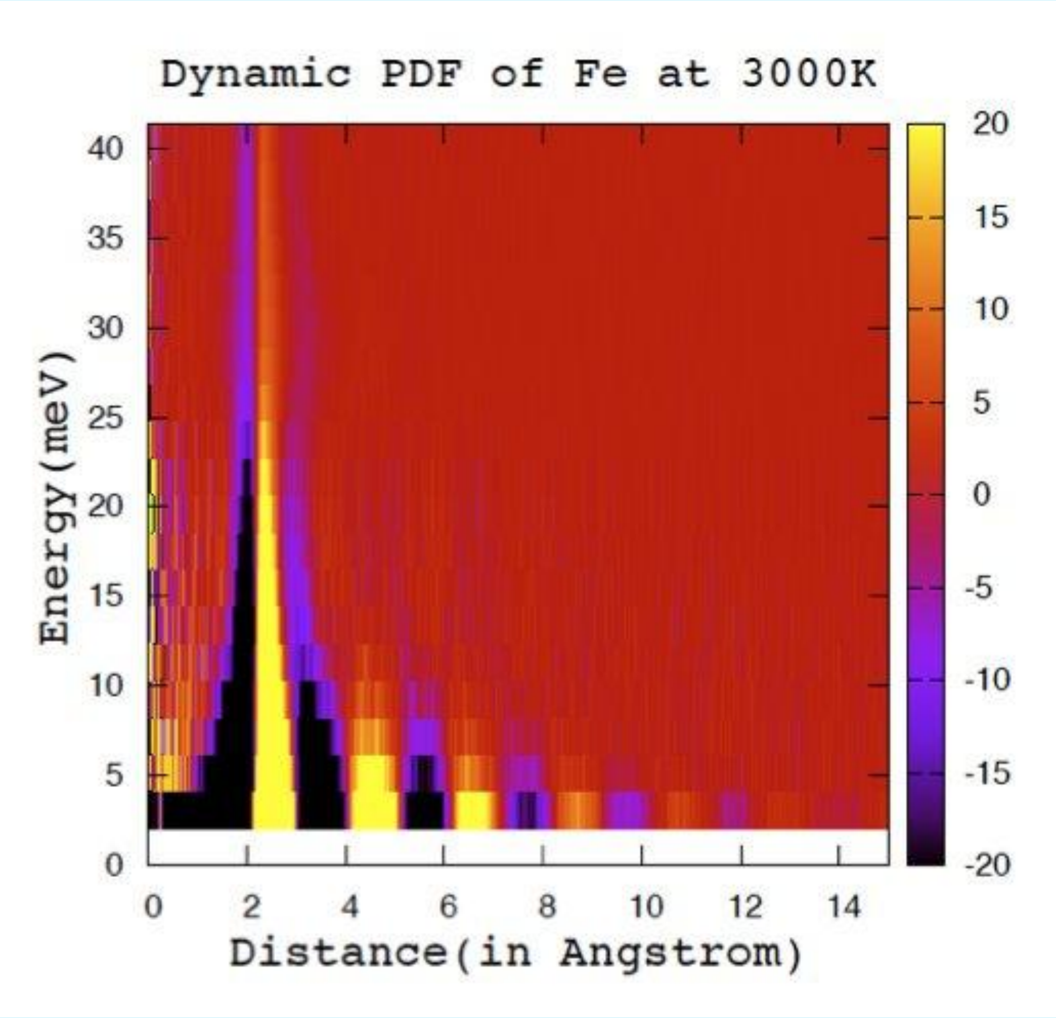
Dynamic PDF

- 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

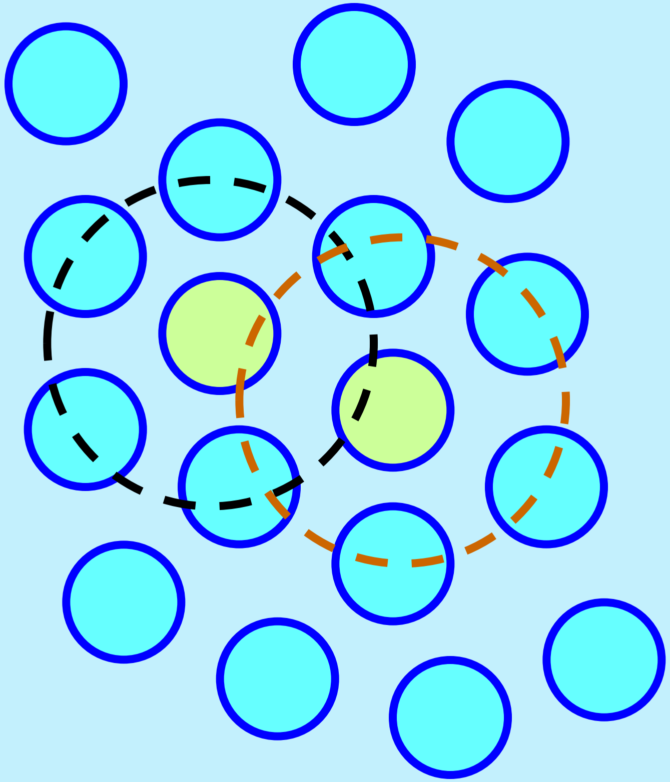
$$\rho(\mathbf{r},\omega) = \int S(\mathbf{Q},\omega)\, e^{i\mathbf{Q}.\mathbf{r}}\,d\mathbf{Q}$$
$$= \frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu} b_\nu b_\mu \int \delta\left(\mathbf{r}-\left[\mathbf{R}_\nu(0)-\mathbf{R}_\mu(t)\right]\right) e^{i\omega t}\,dt$$



- Only the NN are dynamically correlated above 10 meV.

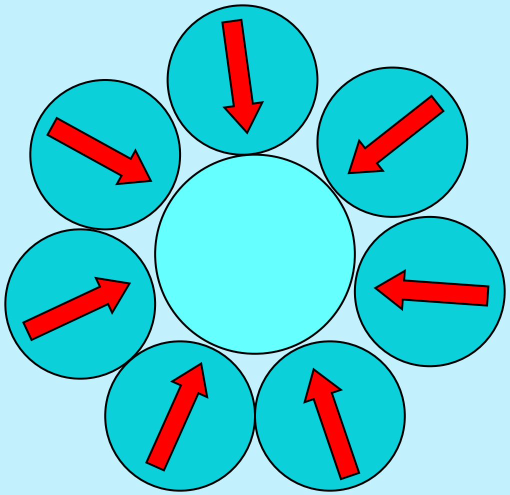
Vibrations of the Neighbor Shells

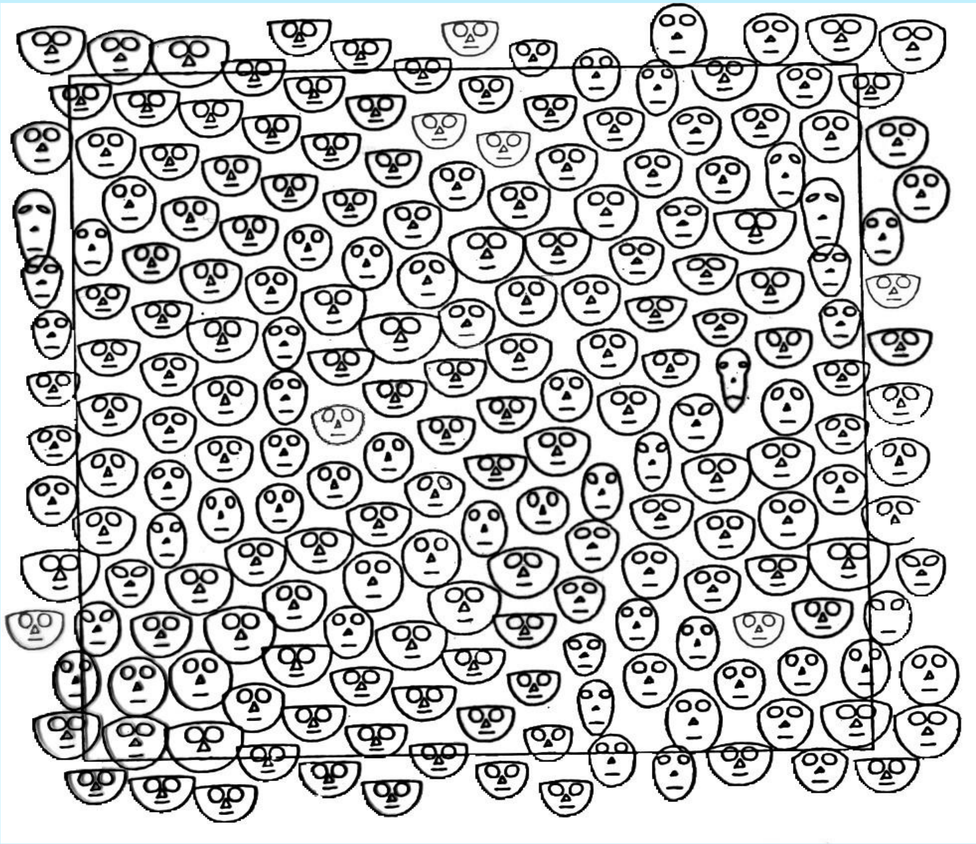
- Vibrations of the nearest neighbor shells are **nearly orthogonal to each other**.
- They can be the basis for the statistical mechanics of the liquids.
- They can be described in terms of the atomic-level stresses.



Atomic Level Stresses and Strains

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





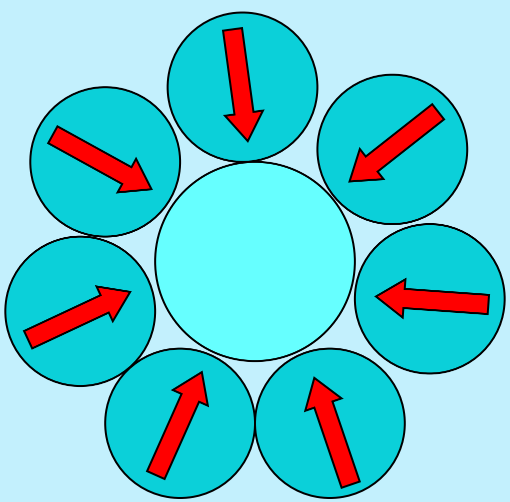
T. Egami, K. Maeda and V. Vitek, *Phil. Mag*. **A41**, 883 (1980).

- Atomic level stresses (pressure and five shear stresses) relate the local topology to the local energy landscape.

Atomic Level Stresses and Strains

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

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

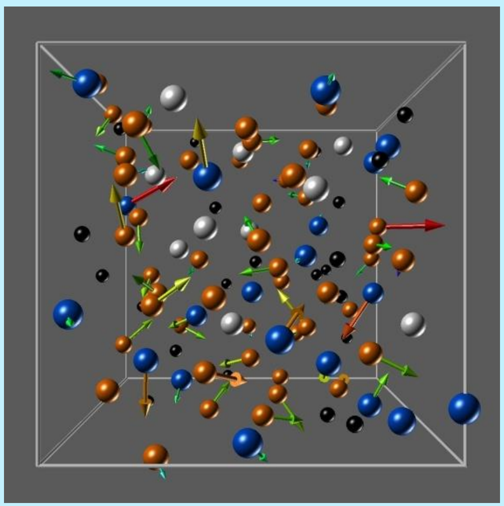


- ***r_{ij}*** = 0 defines the “ideal glass” that cannot be achieved.
- Symmetry and extent of deviation from the ideal state.
- Strain cannot be defined without the reference, but stress can.

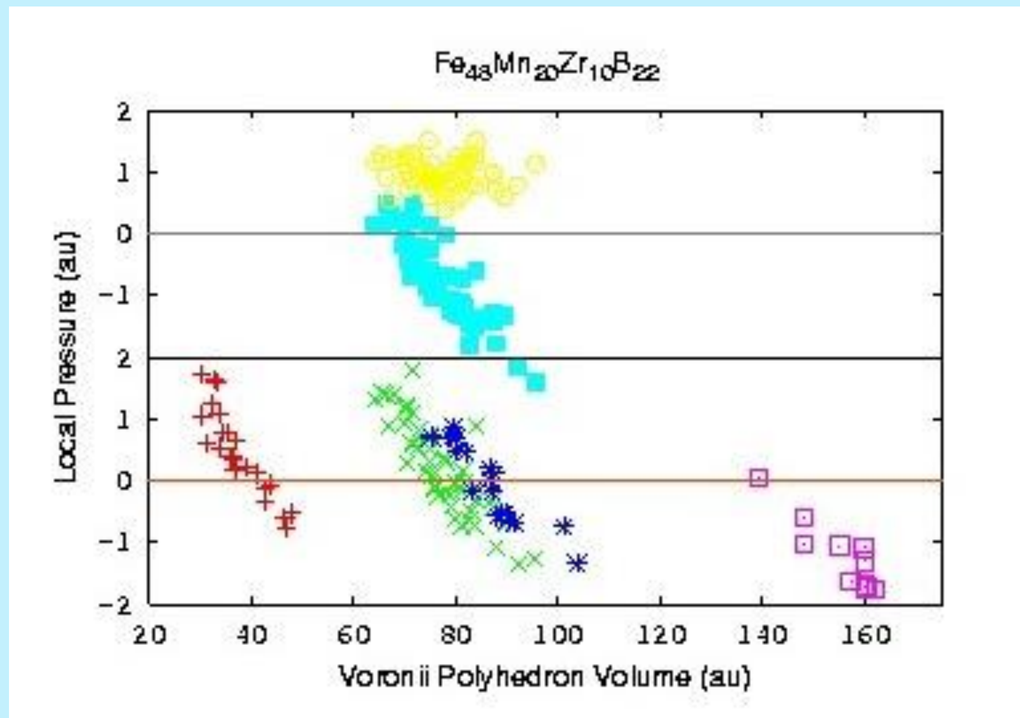
Atomic Level Stresses from the First Principles

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

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



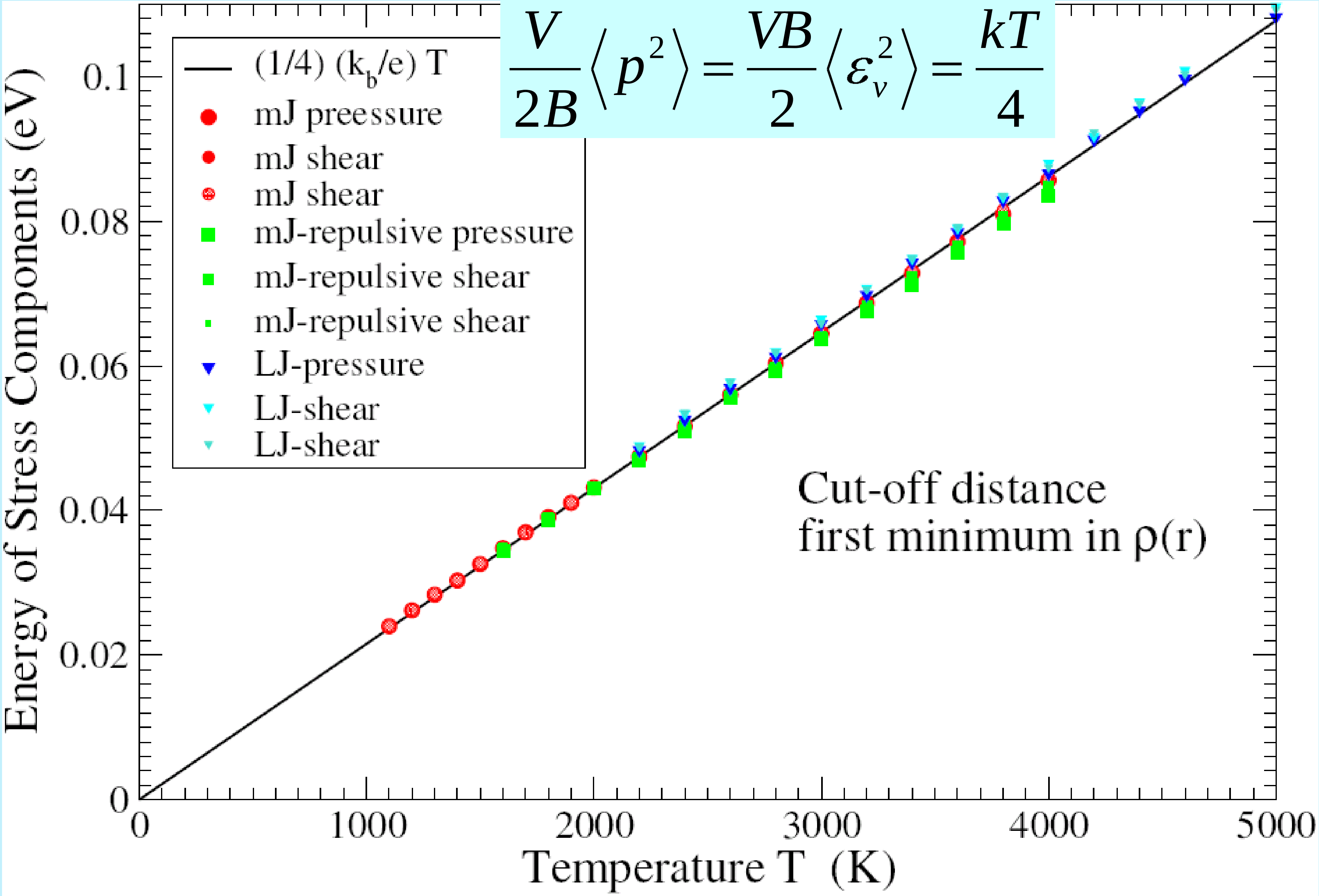
$Fe_{48}Mn_{20}Zr_{10}B_{22}$



D. Nicholson and G. M. Stocks

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

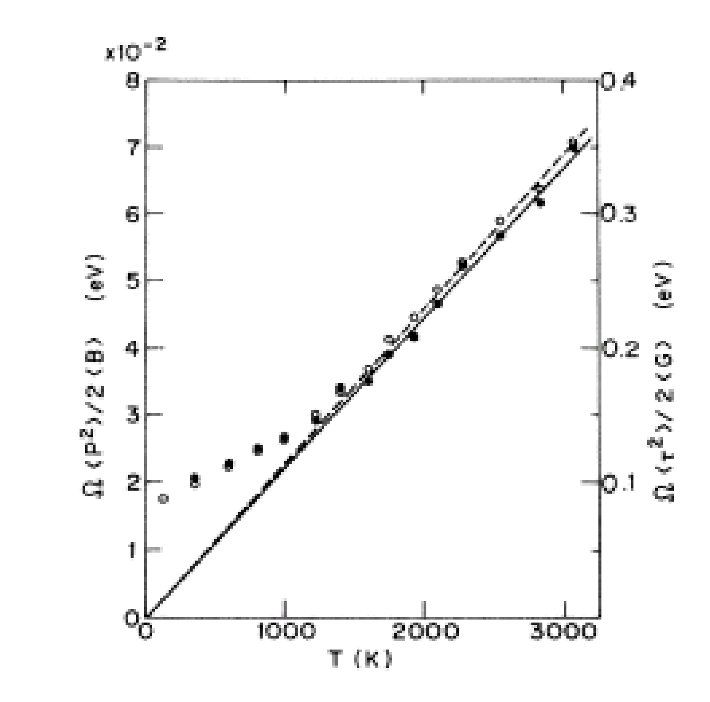
$$\frac{V}{2B}\left\langle p^2 \right\rangle = \frac{VB}{2}\left\langle \varepsilon_v^2 \right\rangle = \frac{kT}{4}$$



- 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)

Glass Transition



- High-temperature equation,

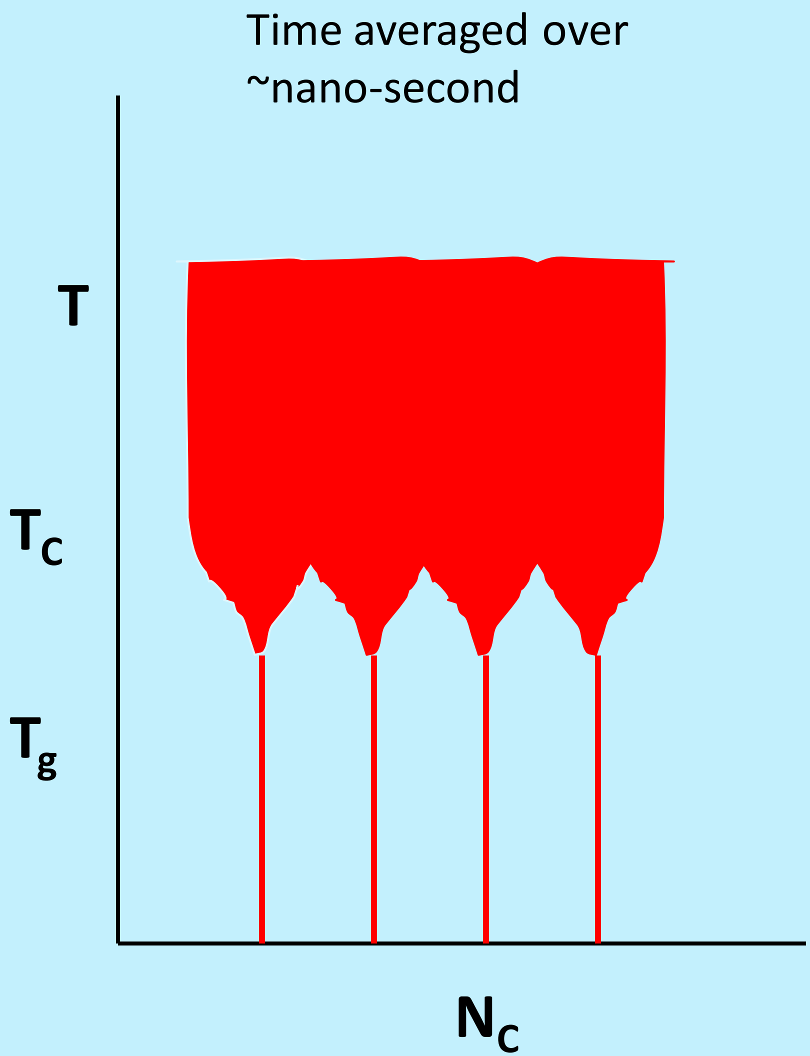
$$\frac{V}{2B}\left\langle p^2\right\rangle = \frac{VB}{2}\left\langle \varepsilon_v^2\right\rangle = \frac{kT}{4}$$

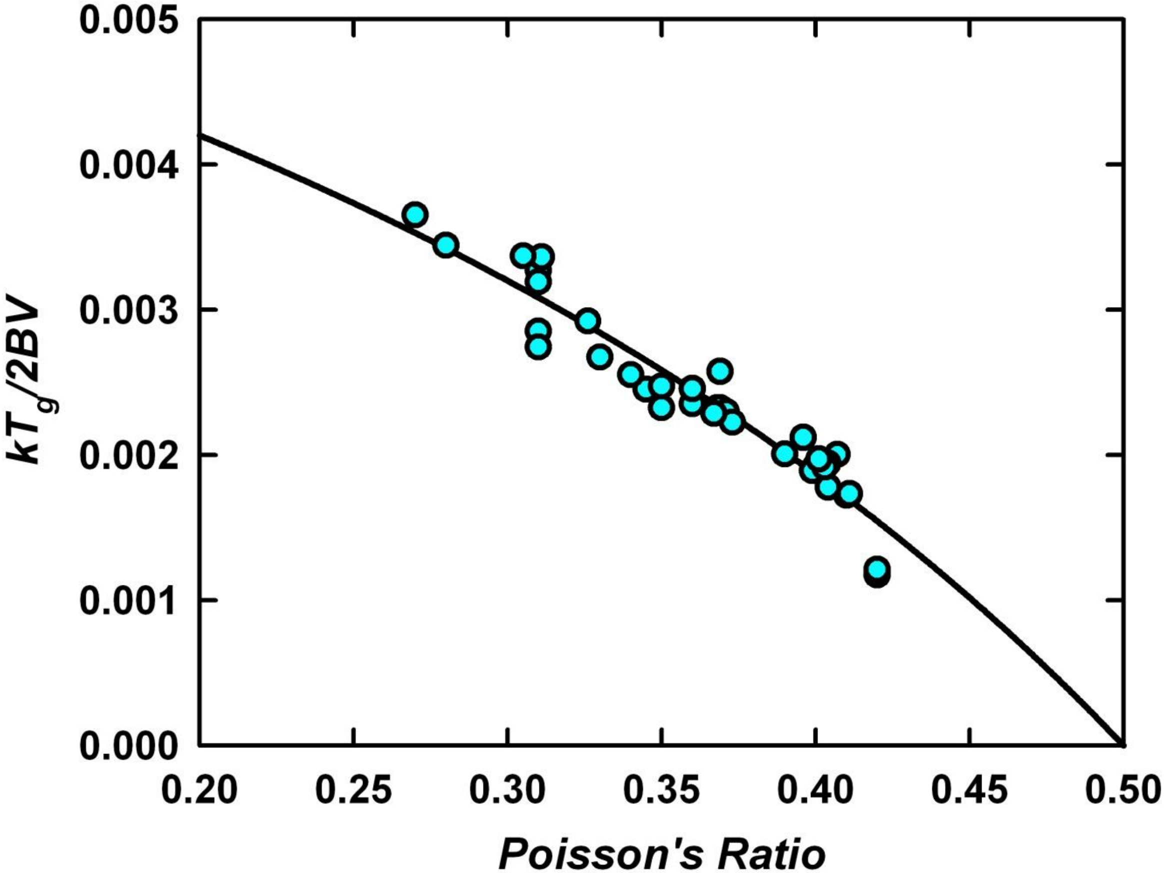
extrapolates to $\varepsilon_v = 0$ at $T = 0$; all neighbors at the bottom of the potential.

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

“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**.





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

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

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

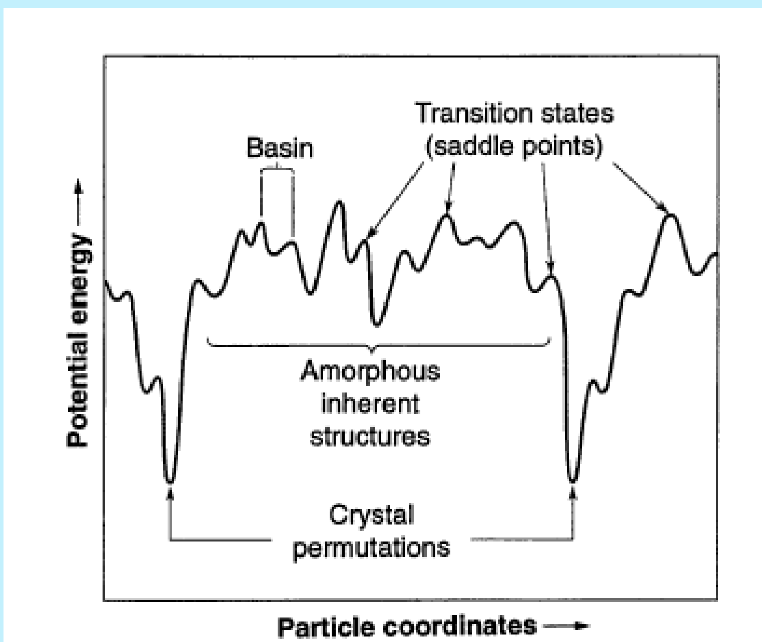
- Glass transition temperature is equal to the energy of local density fluctuation with the long-range stress field at a critical strain level. $\varepsilon_{v,T}$ = 0.0917   0.003 (4%).

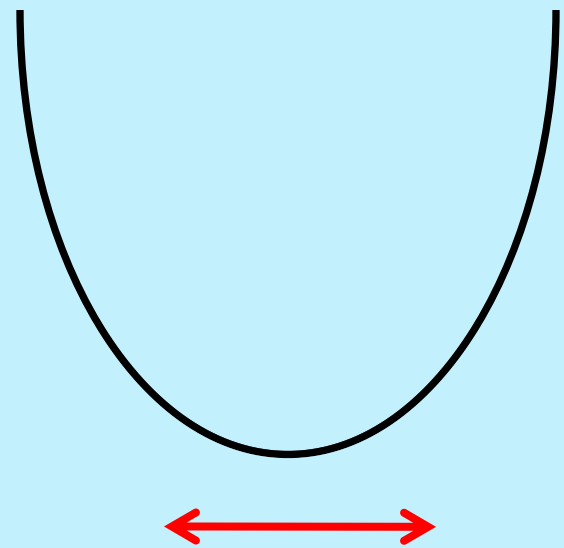
T. Egami, S. J. Poon, Z. Zhang and V. Keppens, *Phys. Rev. B* **76,** 024203 (2007).

Universal Minimum Local Strain

- Depth of the valley in the energy landscape.

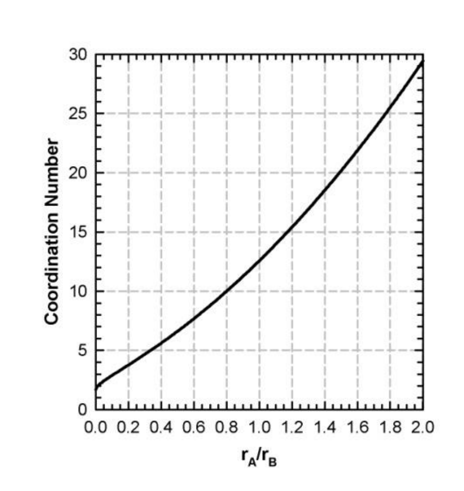
- If the strain is too large the local topology becomes unstable, and change.

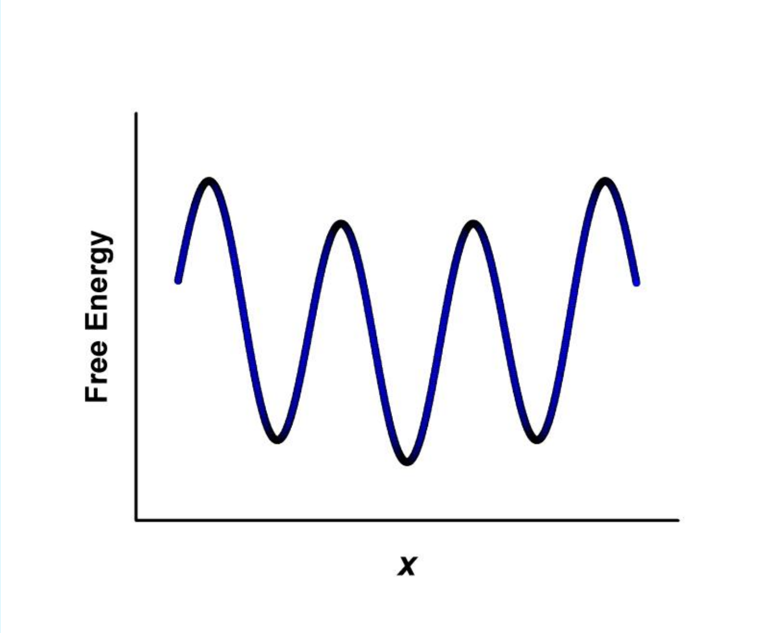




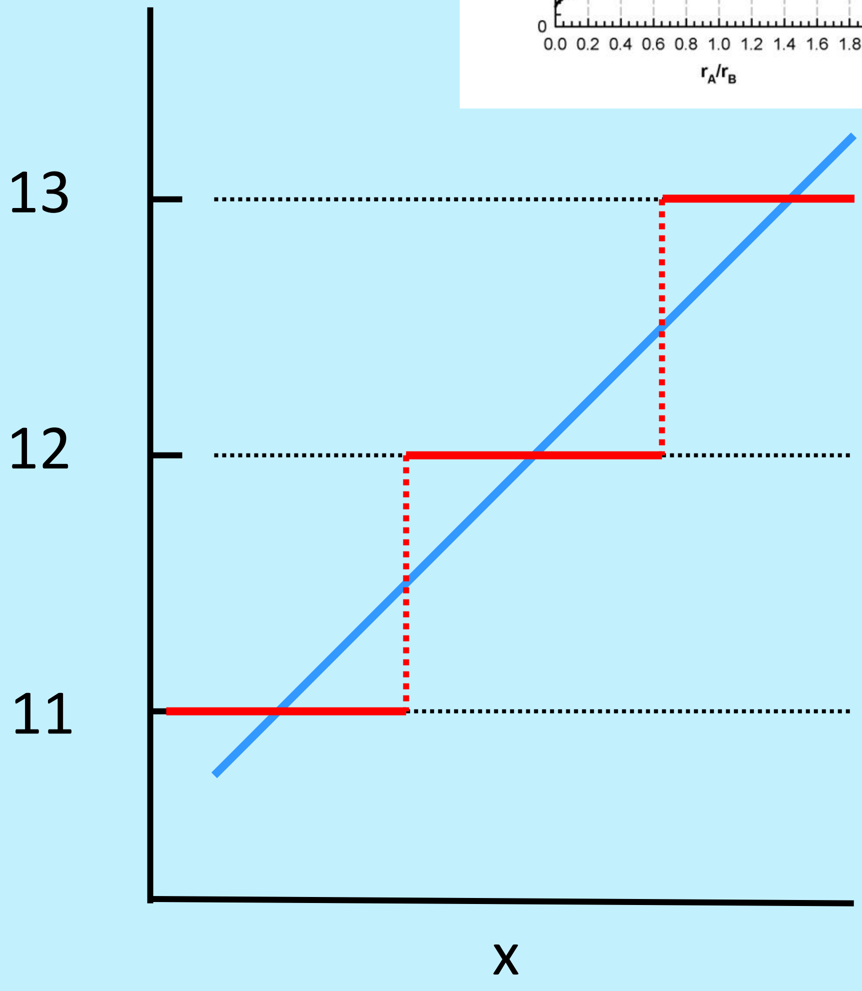
Local topological instability

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



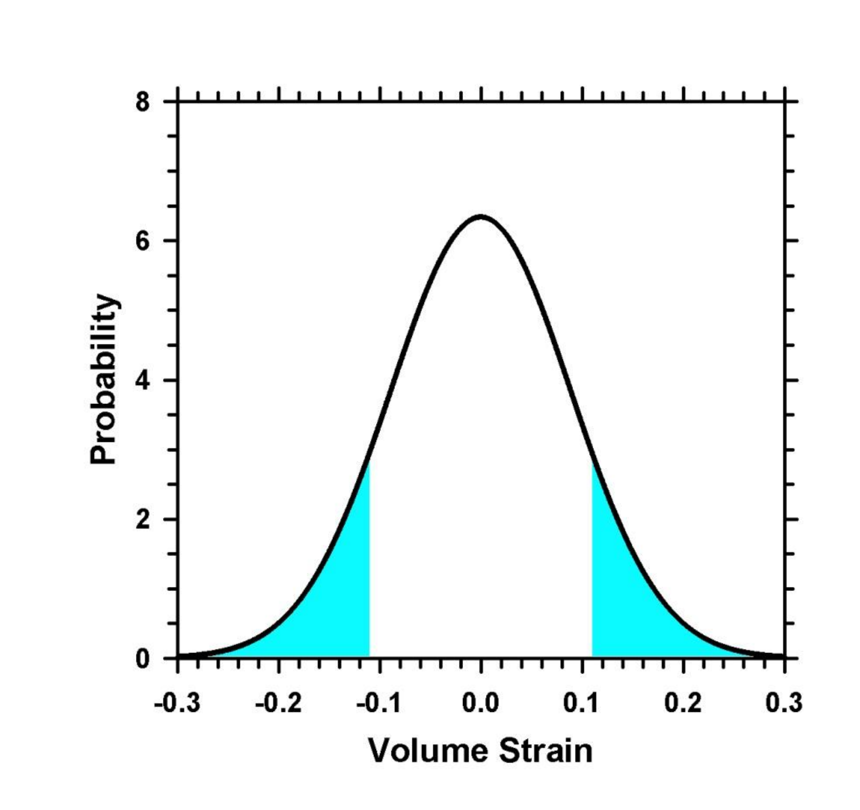


Local energy landscape



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.



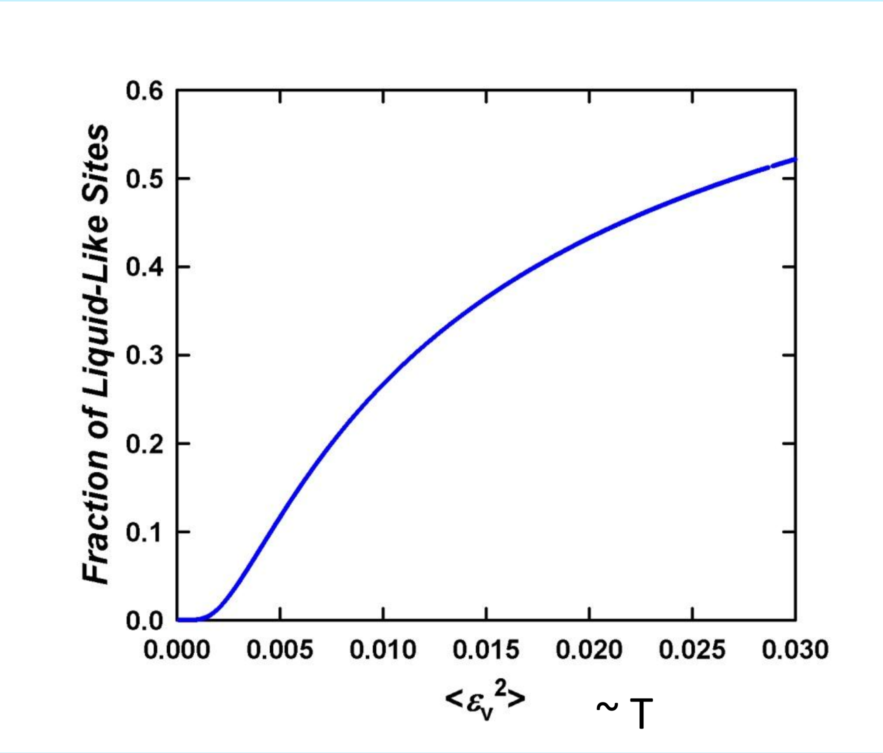
Free volume element

Percolation of the Liquid-like Sites

- Total fraction of the liquid-like sites:

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

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



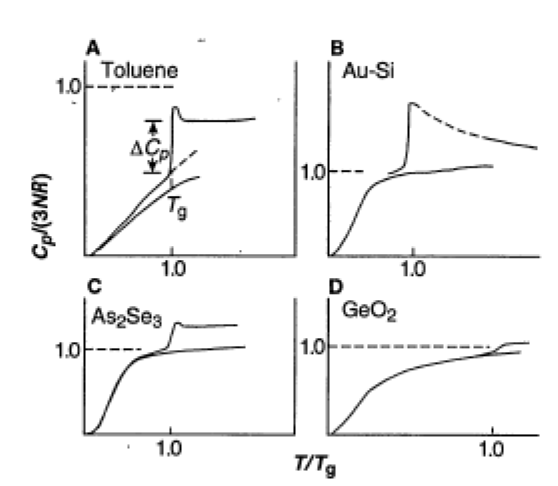
- For $\varepsilon_{v,T}$ = 0.095   0.003

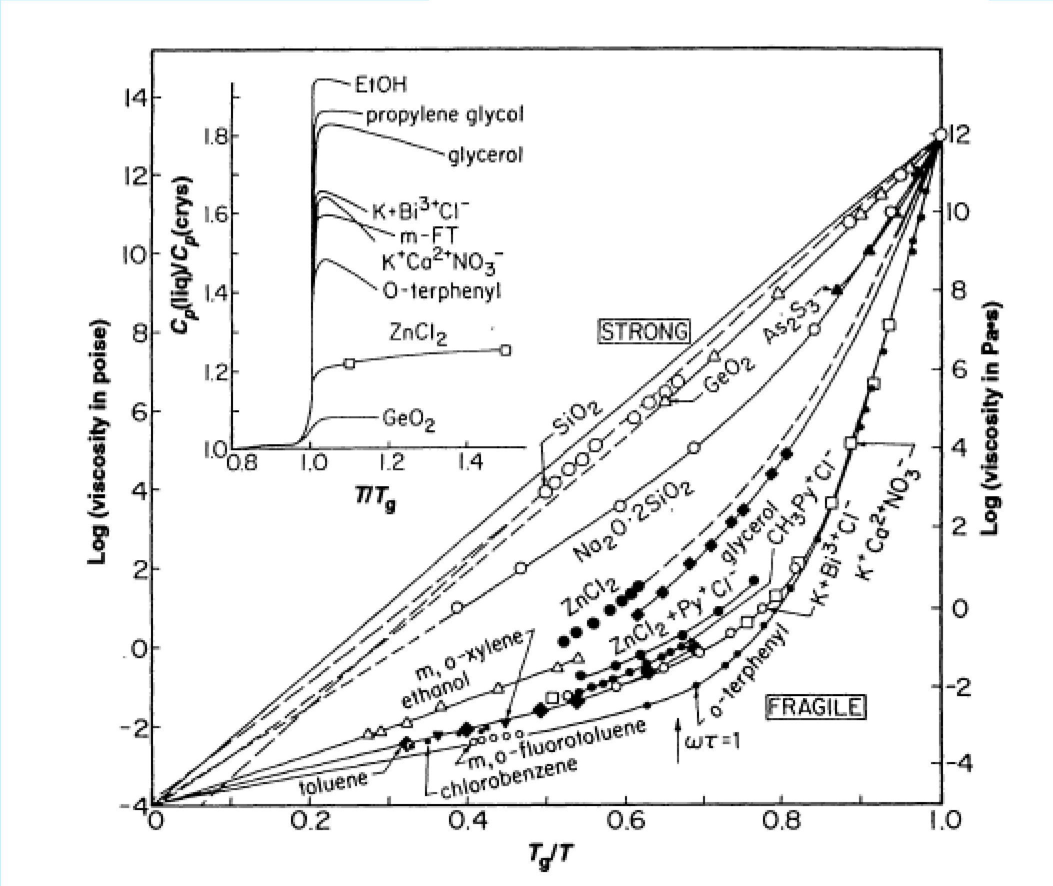
$$p(liq) = 0.243$$

- 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)

Jump in Specific Heat at T_g

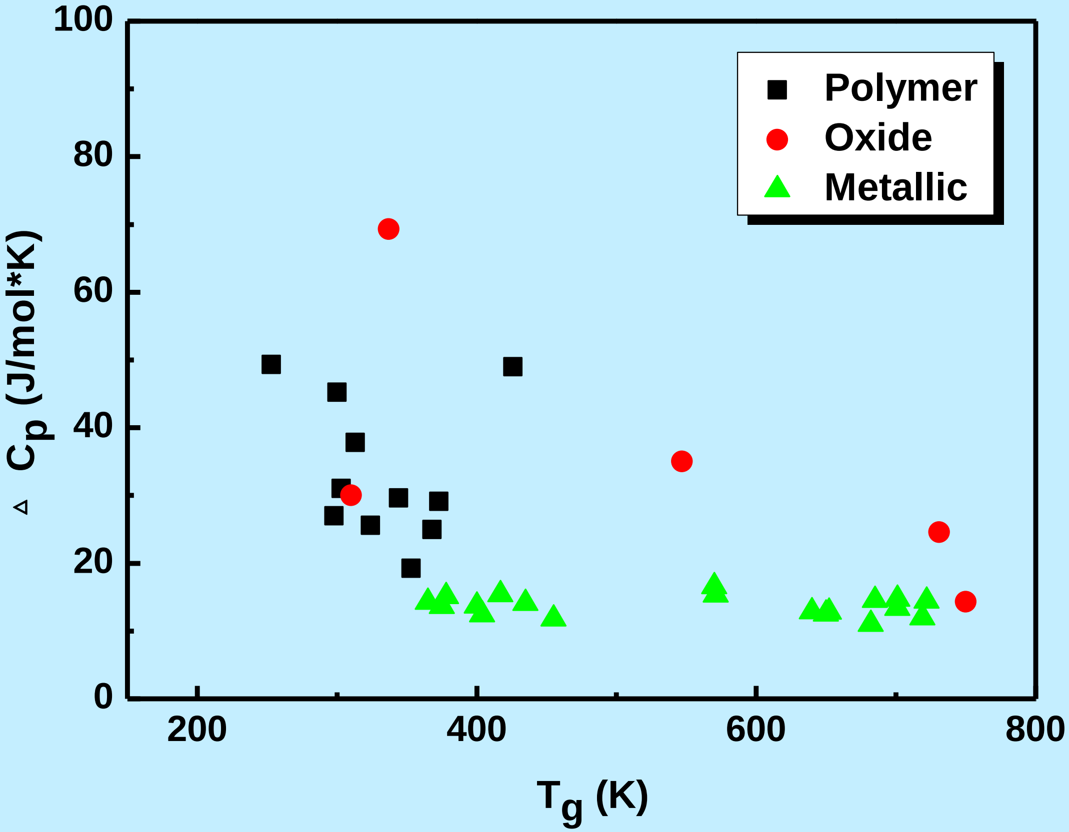
- All glasses show a jump in C_p at T_g.
- But the magnitude appears to vary widely.
- May be related to fragility.





A. C. Angell, *Science* **267,** 1924 (1995).

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



H. B. Ke, P. Wen, D. Q. Zhao and W. H. Wang, *Appl. Phys. Lett.* In press.

- Above T_g:

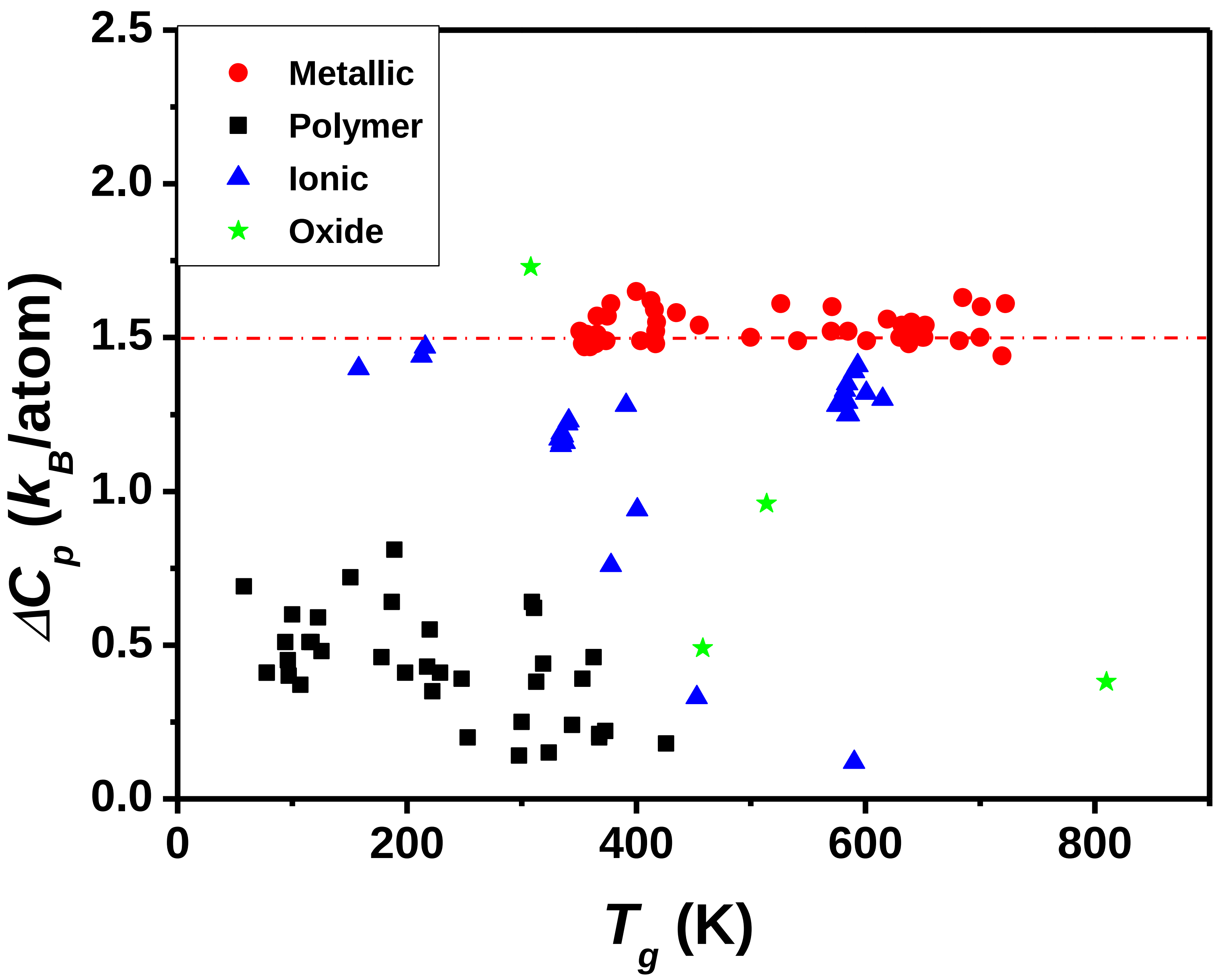
$$E_p = \frac{3}{2} k_B T$$

- Below T_g:

$$E_p = \frac{3}{2} k_B T_g$$

- Jump in C_p:

$$\Delta C_p = \frac{3}{2} k_B$$



Metallic
Polymer
Ionic
Oxide
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
ΔCp (kB/atom)
Tg (K)

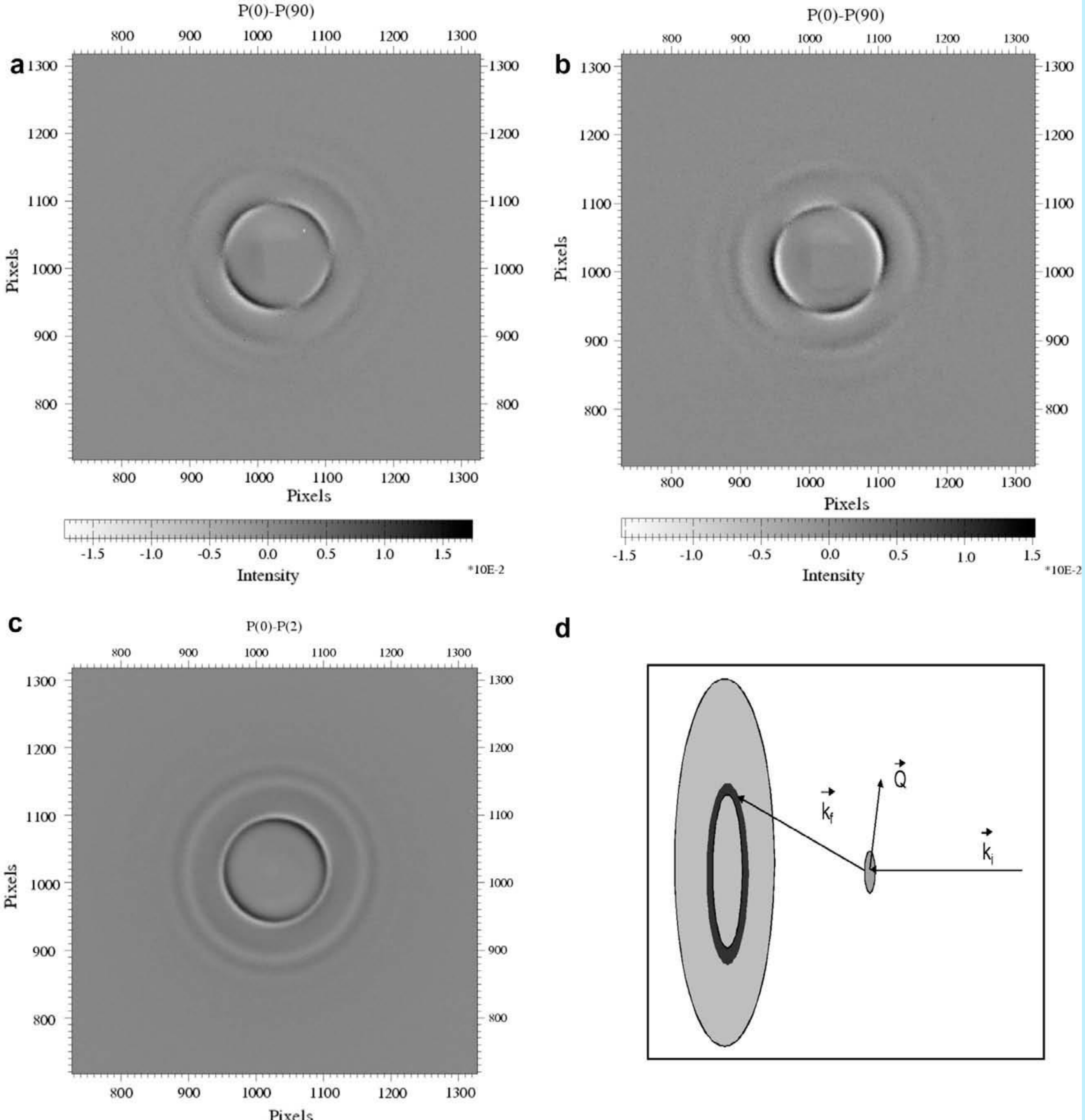
- For other glasses than metallic glasses:

$$\Delta C_p = \frac{3}{2}\frac{k_B}{n_d}$$

- For B_2O_3, n_d = 5/3; only oxygen atoms are active; light B atoms are dynamically slaved.

- B. Wunderlich, *J. Phys. Chem*. **64,** 1052 (1960).

$$\Delta C_p / beads = 2.70\, cal / mol.K = 1.38 k_B$$



a
P(0)-P(90)
Pixels
Pixels
Intensity
*10E-2
b
P(0)-P(90)
Pixels
Pixels
Intensity
*10E-2
c
P(0)-P(2)
Pixels
Pixels
d
Q
kf
ki

Analysis of the directional dependence of S(Q) and PDF(r) by expansion in terms of spherical harmonics

$$S(\vec{Q}) = \sum_{l,m} S_l^m(Q) Y_l^m(\vec{Q}/Q)$$

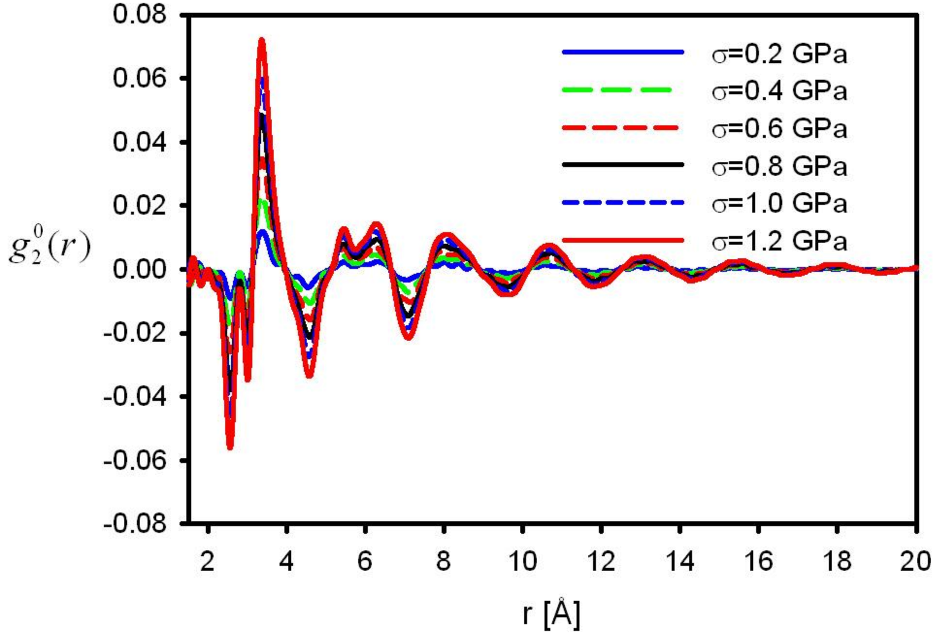
$$\rho(\vec{r}) = \sum_{l,m} \rho_l^m(r) Y_l^m(\vec{r}/r)$$

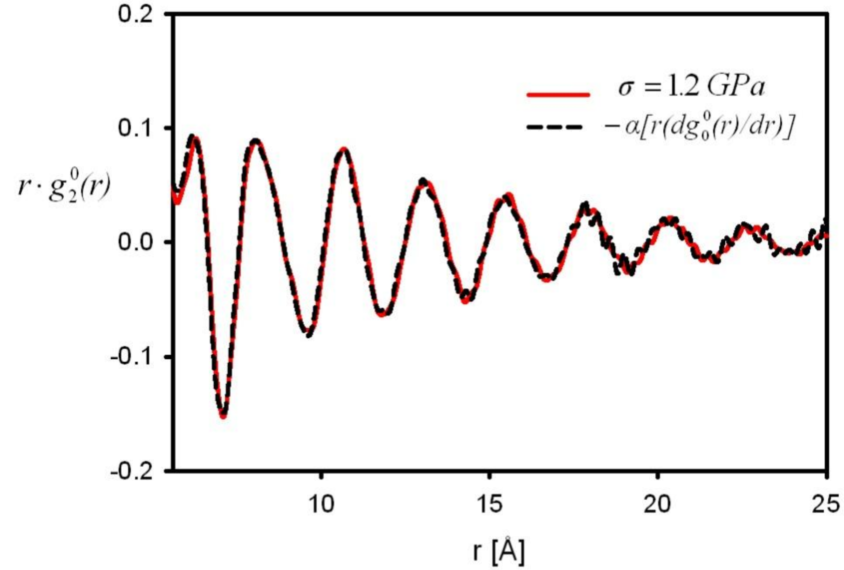
anisotropic PDF can be obtained by transformation

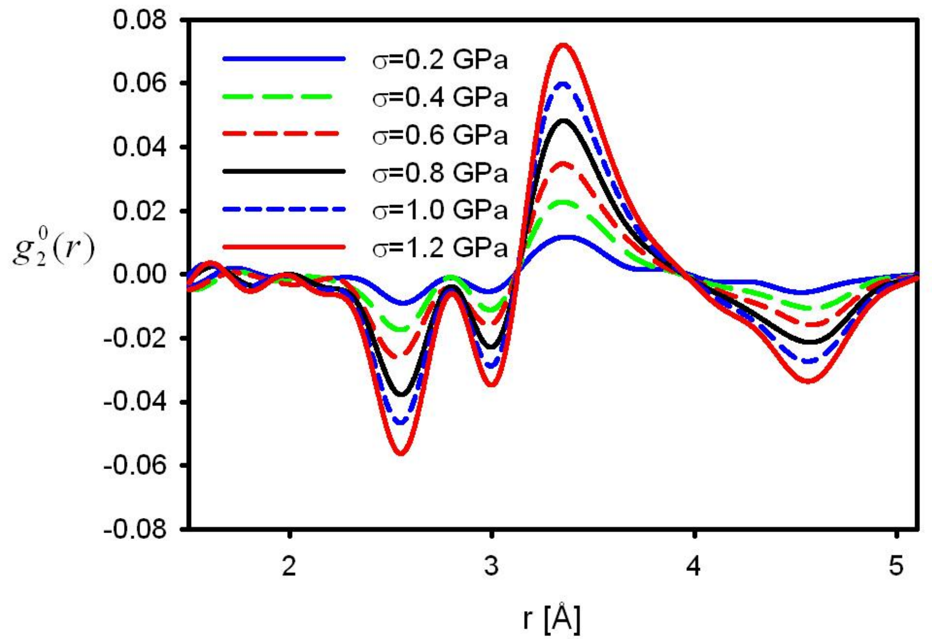
$$\rho_l^m(r) = \frac{(i)^l}{2\pi^2} \int S_l^m(Q) J_l(Qr) Q^2 dQ$$

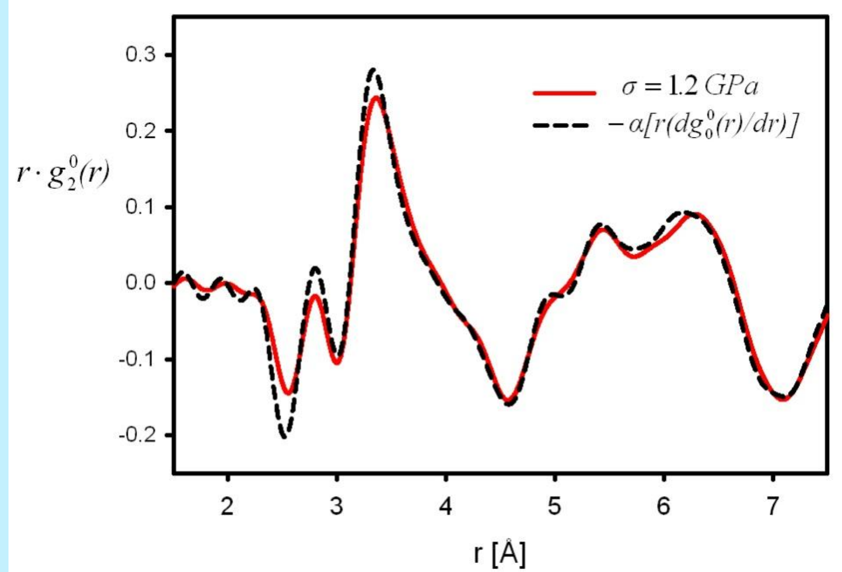
where J_l is the spherical Bessel function

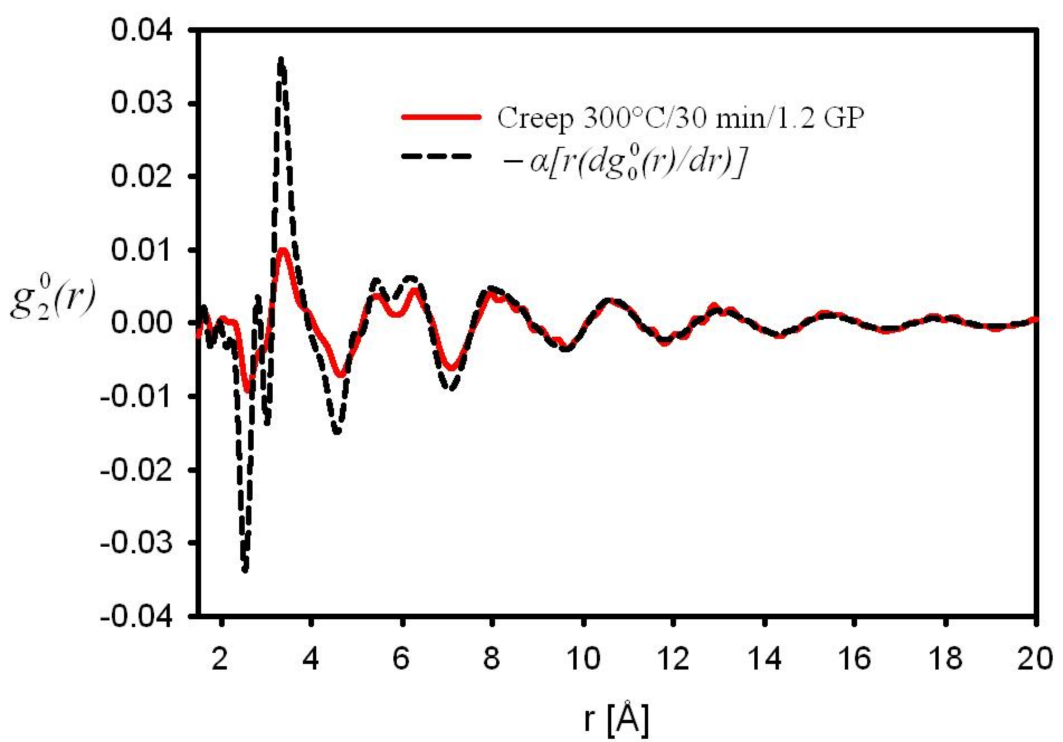
Y. Suzuki, J. Haimovich and T. Egami, *Phys. Rev. B* **35**, 2162 (1987)
W. Dmowski, T. Egami, J. Mater. Res, v 22, 412 (Feb 2007)


σ=0.2 GPa
σ=0.4 GPa
σ=0.6 GPa
σ=0.8 GPa
σ=1.0 GPa
σ=1.2 GPa
$g_2^0(r)$
r [Å]


$r \cdot g_2^0(r)$
$\sigma = 1.2\ GPa$
$-\alpha[r(dg_0^0(r)/dr)]$
r [Å]


σ=0.2 GPa
σ=0.4 GPa
σ=0.6 GPa
σ=0.8 GPa
σ=1.0 GPa
σ=1.2 GPa
$g_2^0(r)$
r [Å]


$r \cdot g_2^0(r)$
$\sigma = 1.2\ GPa$
$-\alpha[r(dg_0^0(r)/dr)]$
r [Å]

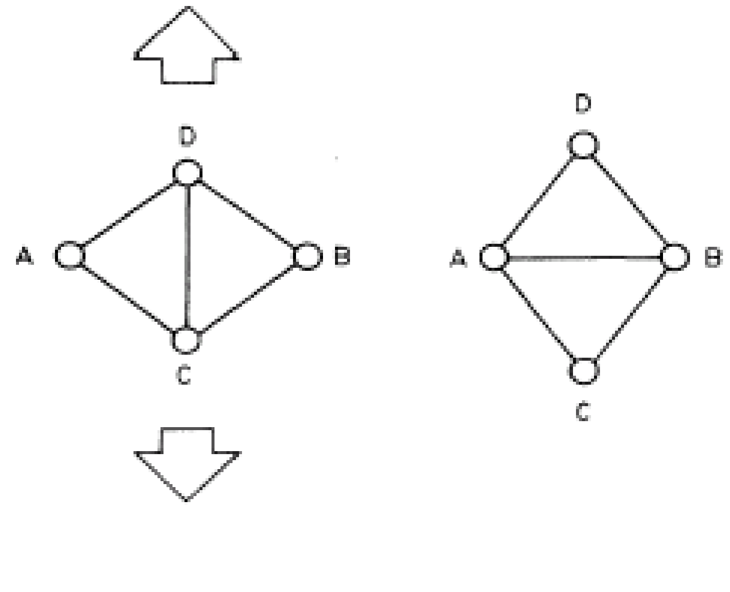

Creep 300°C/30 min/1.2 GP
$-\alpha[r(dg_0^0(r)/dr)]$
$g_2^0(r)$
0.04
0.03
0.02
0.01
0.00
-0.01
-0.02
-0.03
-0.04
2
4
6
8
10
12
14
16
18
20
r [Å]

Bond-Orientational Anisotropy

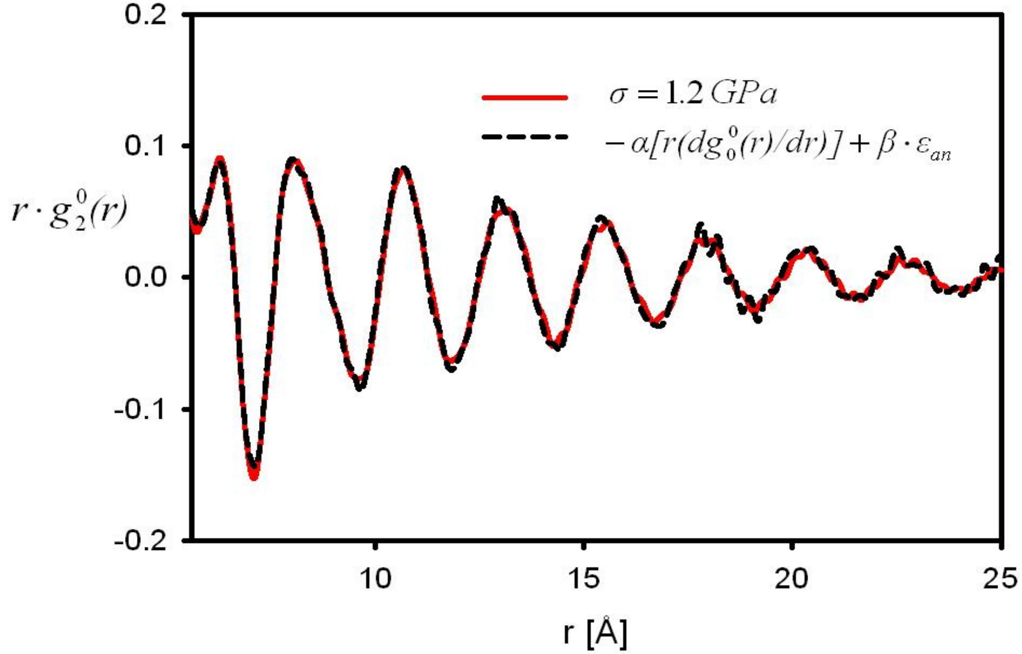
PHYSICAL REVIEW B VOLUME 35, NUMBER 5 15 FEBRUARY 1987-I

Bond-orientational anisotropy in metallic glasses observed by x-ray diffraction

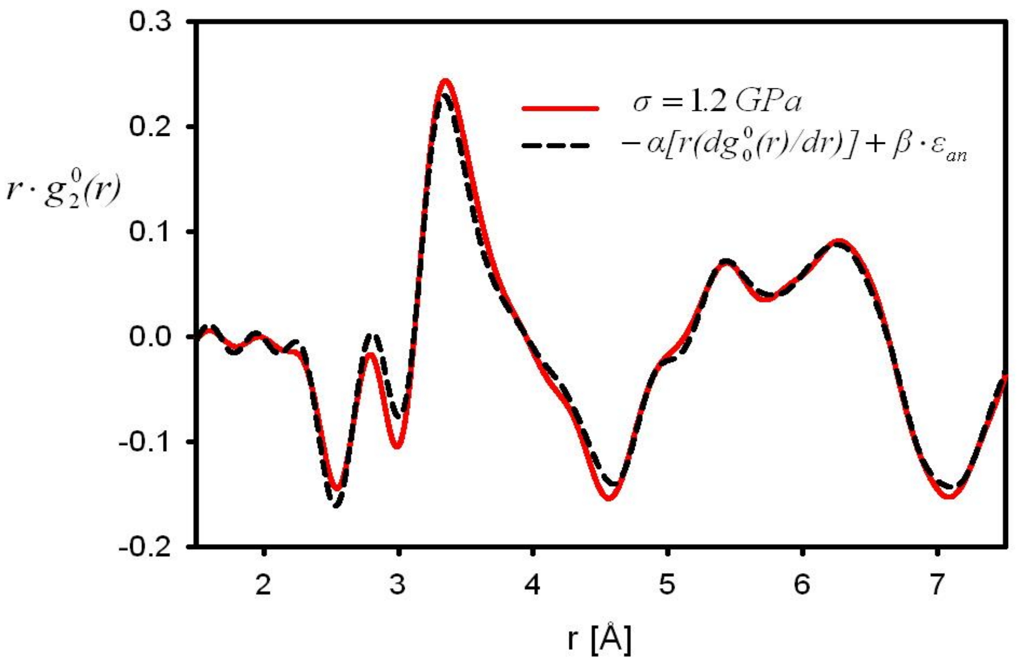
Y. Suzuki,[*] J. Haimovich,[†] and T. Egami



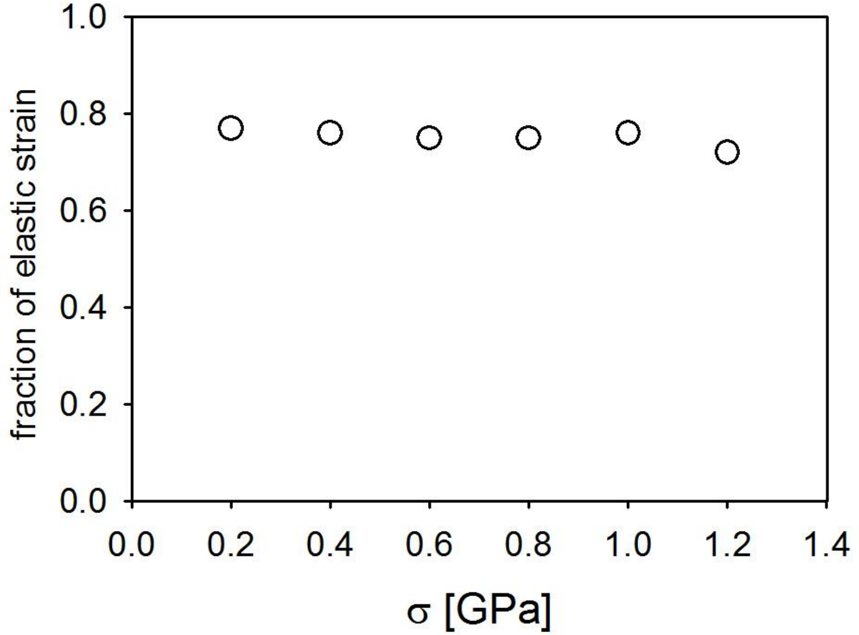
(a) (b)



0.2
0.1
0.0
-0.1
-0.2
$r \cdot g_2^0(r)$
$\sigma = 1.2\ GPa$
$-\alpha[r(dg_0^0(r)/dr)] + \beta \cdot \varepsilon_{an}$
10
15
20
25
r [Å]

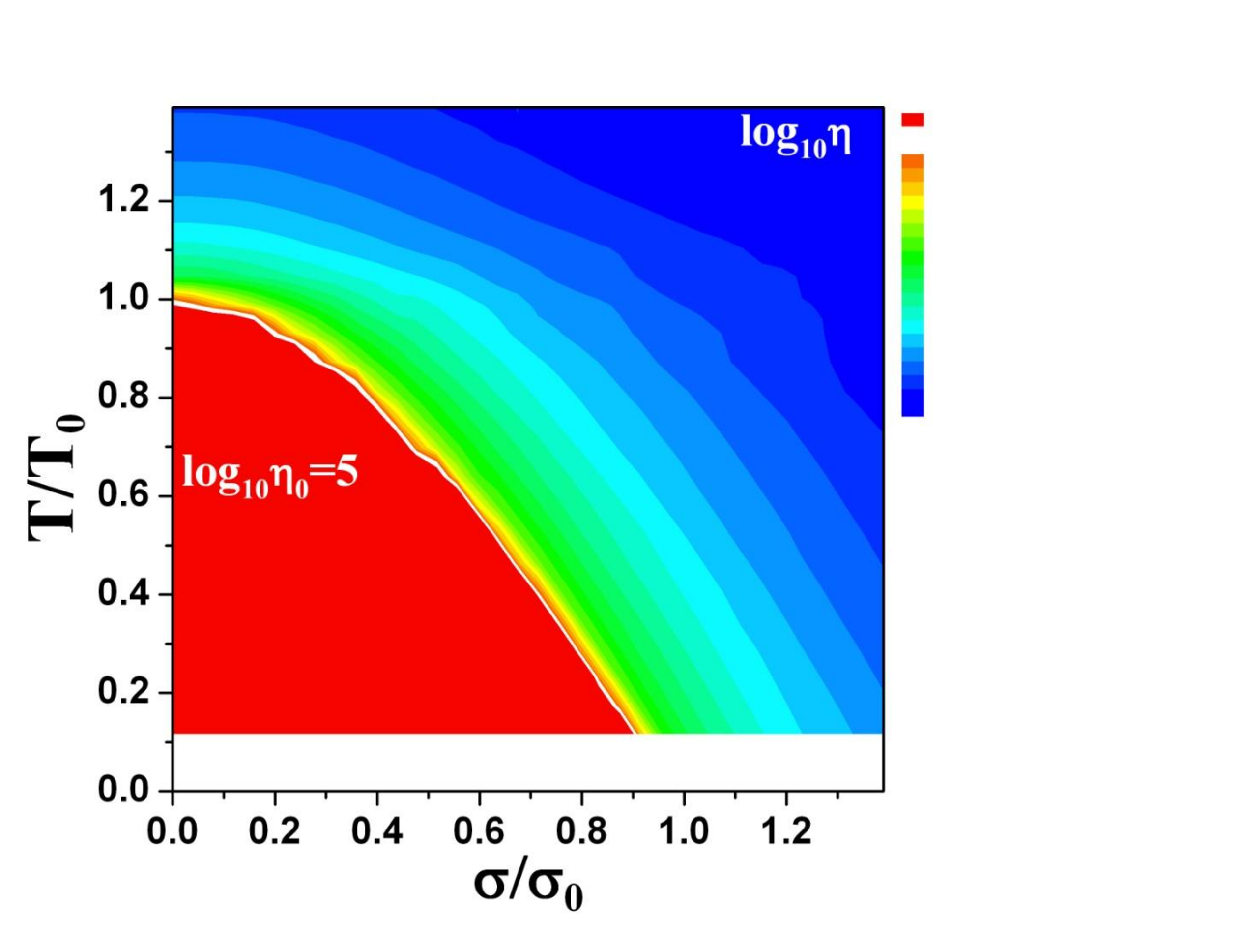


0.3
0.2
0.1
0.0
-0.1
-0.2
$r \cdot g_2^0(r)$
$\sigma = 1.2\ GPa$
$-\alpha[r(dg_0^0(r)/dr)] + \beta \cdot \varepsilon_{an}$
2
3
4
5
6
7
r [Å]



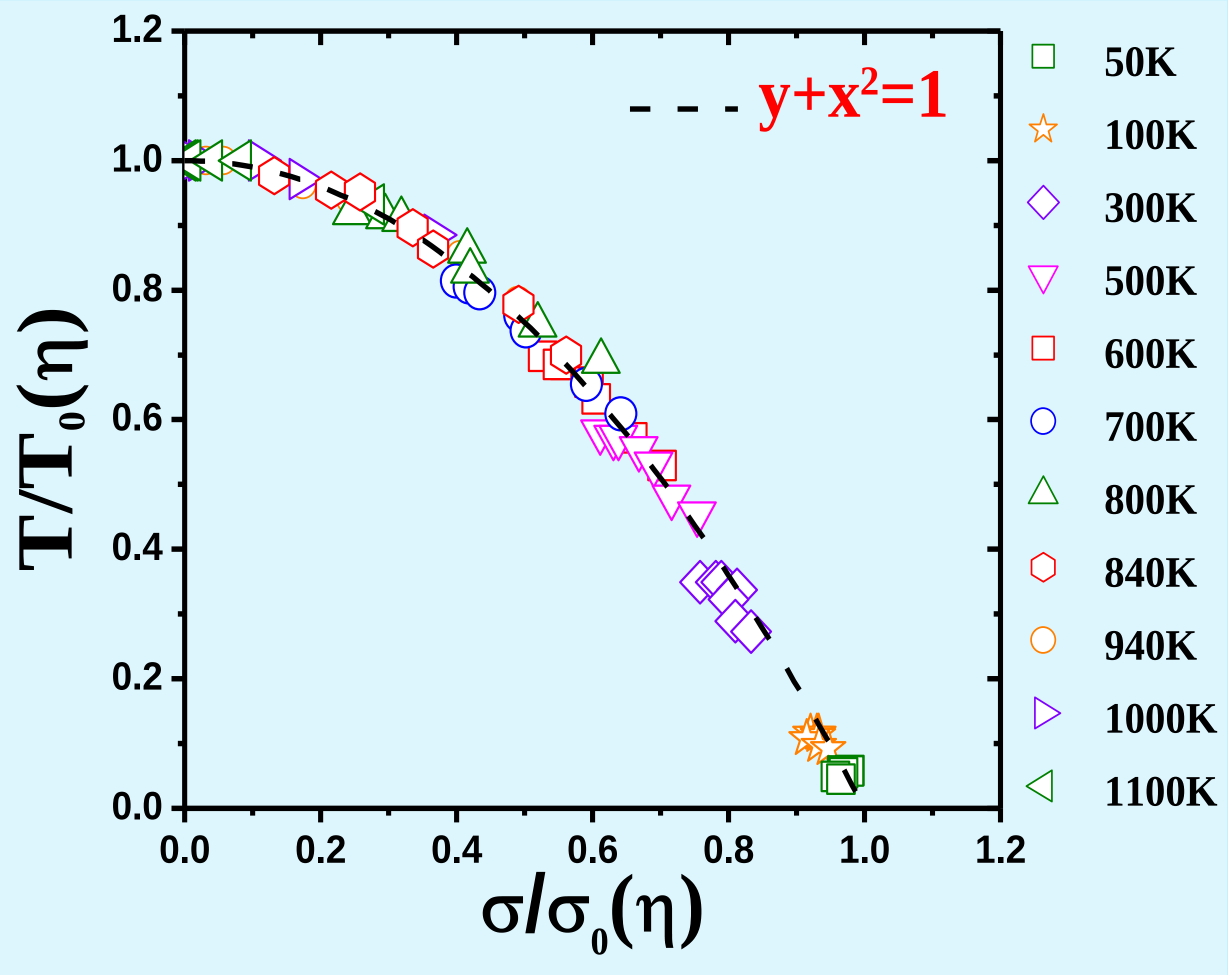
fraction of elastic strain
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
σ [GPa]

Equivalence of Temperature and Stress

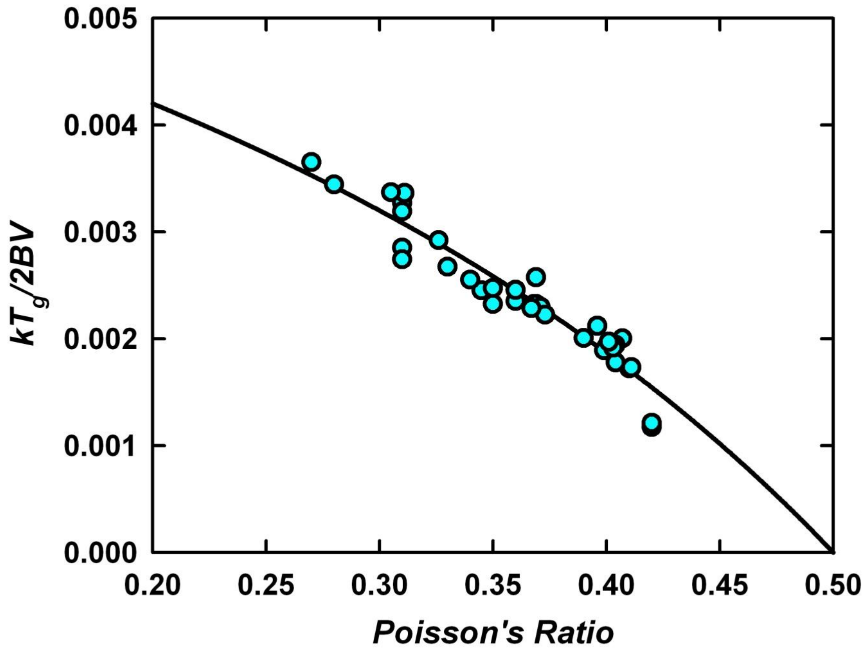


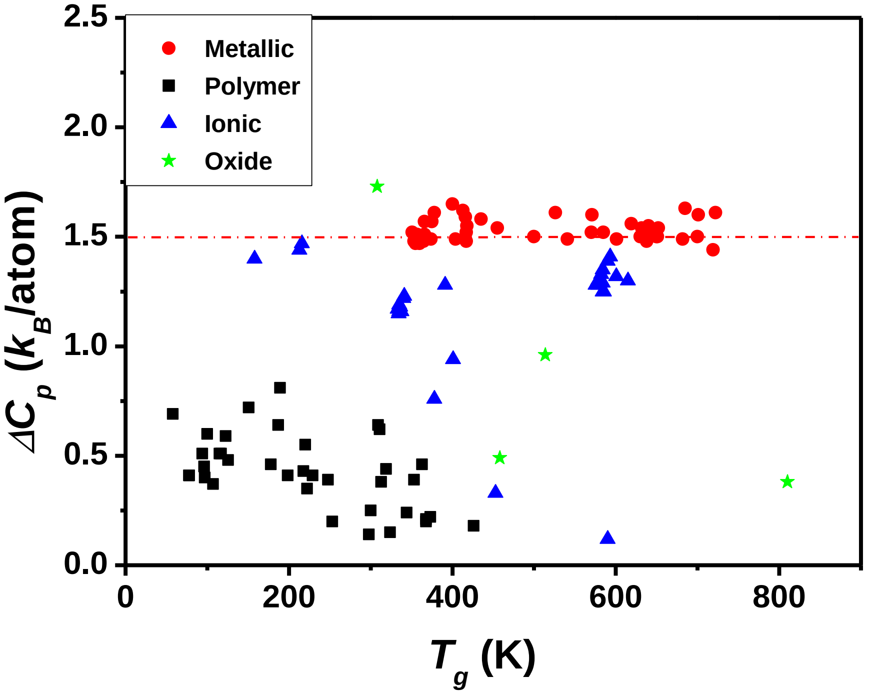
P. Guan, M.-W. Chen and T. Egami,

Phys. Rev. Lett., **104,** 205701 (2010).

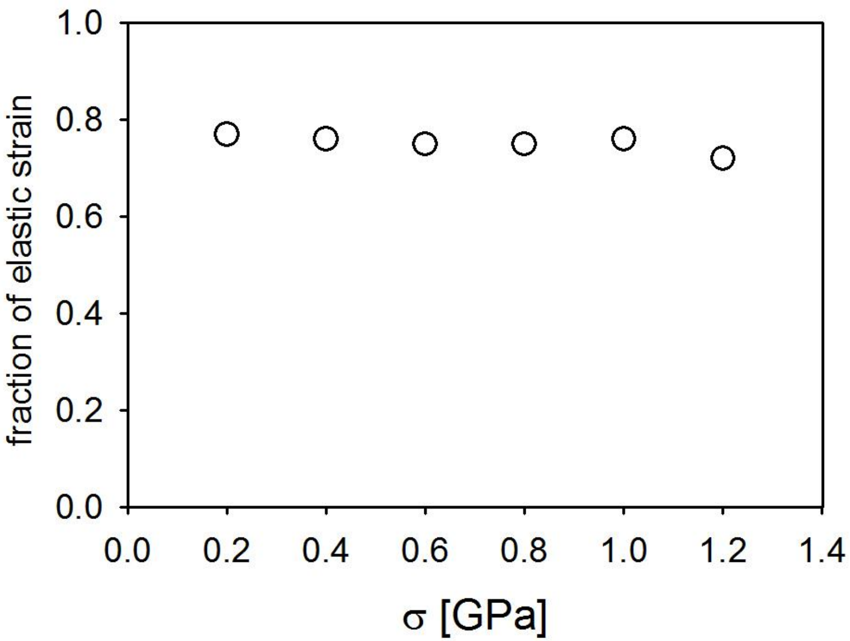


$$\frac{T}{T_0(\eta)} + \left(\frac{\sigma}{\sigma_0(\eta)}\right)^2 = 1$$





- Topological fluctuation theory explained:
  - T_g
  - ΔC_p
  - Fraction of defects.



Conclusions

- Atomic-level-stresses can explain
  - Atomic dynamics
  - Glass transition: T_g, ΔC_p
  - Anelastic behavior
- A good bases for statistical theories of glass and liquids.