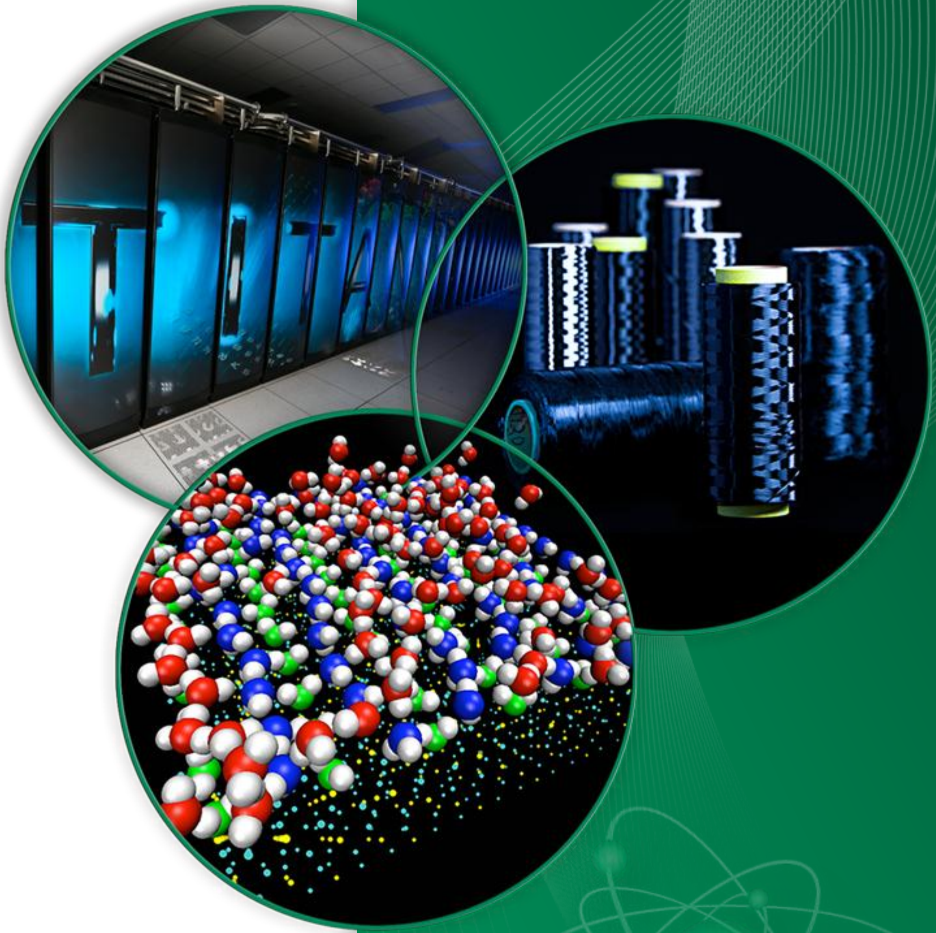
Angell Symposium, Jan. 6, 2014

Angell Dynamics of Liquids



T. Egami

Joint Institute for Neutron Sciences, Department of Materials Science and Engineering, Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996 USA

and Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

Work supported by the Department of Energy, Office of Basic Energy Sciences, Materials Science and Engineering Division

JINS Joint Institute for Neutron Sciences

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE U.S. DEPARTMENT OF ENERGY

Collaborators

T. Iwashita	University of Tennessee
V. Levashov	University of Tennessee
D. M. Nicholson	Oak Ridge National Laboratory
J. S. Langer	UC Santa Barbara
K. F. Kelton	Washington University

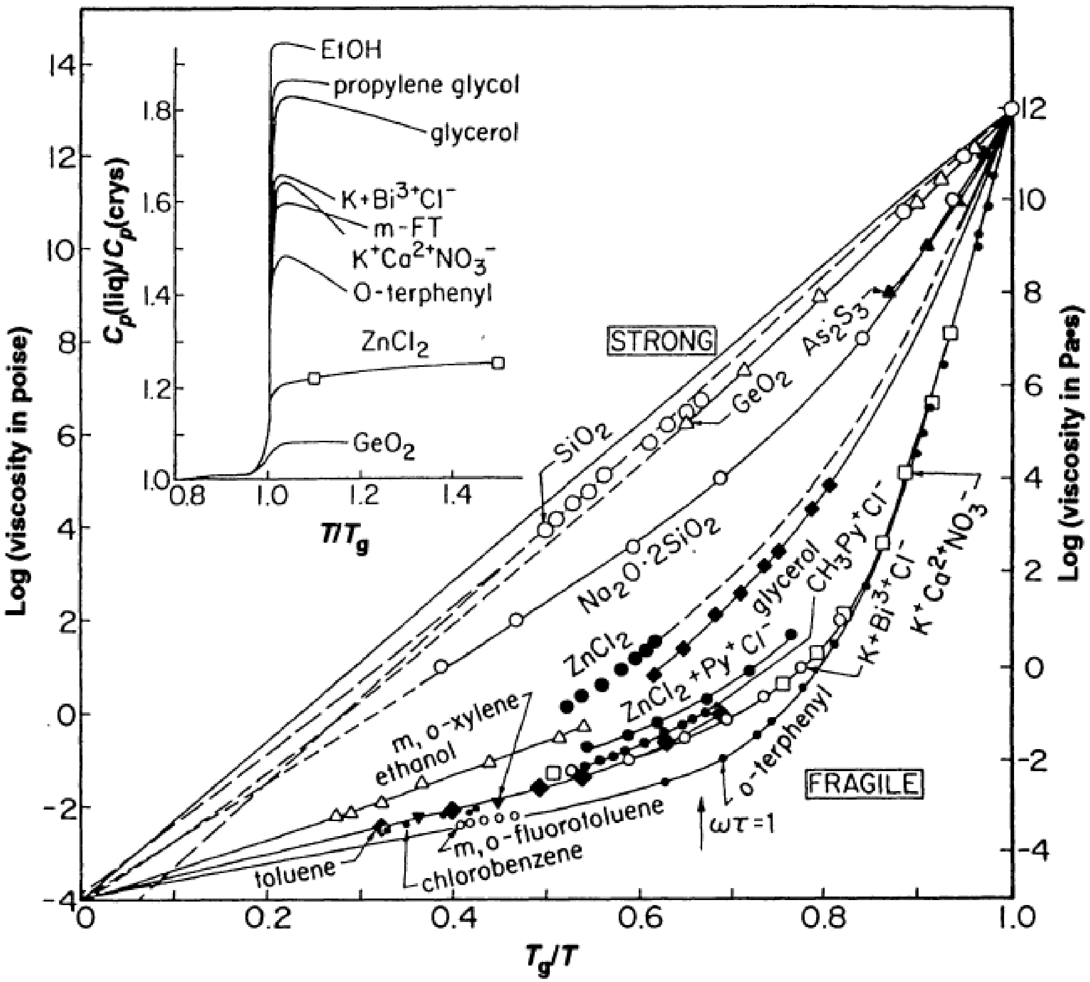
Main Points

[Q1] Convergence at high temperature

[Q2] Nature of the crossover phenomenon

[Q3] What does the fragility represent ?

High Temperature Behavior



C. A. Angell, *Science* **267,** 1927 (1995)

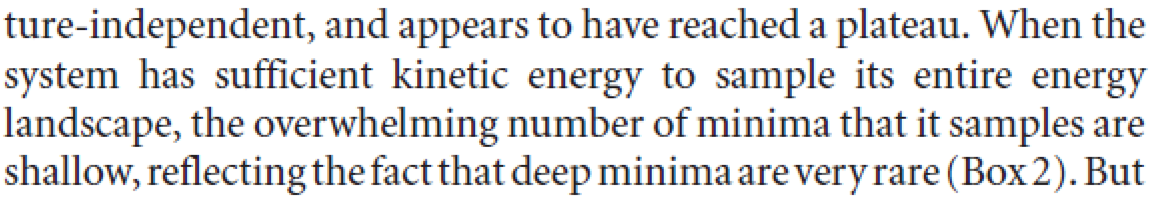
- Convergence at T_g by definition.
- [Q1] Why do the curves converge at $T \to \infty$?
- For gas $\eta \to \infty$ as $T \to \infty$.
- [Q2] The origin of the “knee” (crossover).

Liquids at High Temperatures

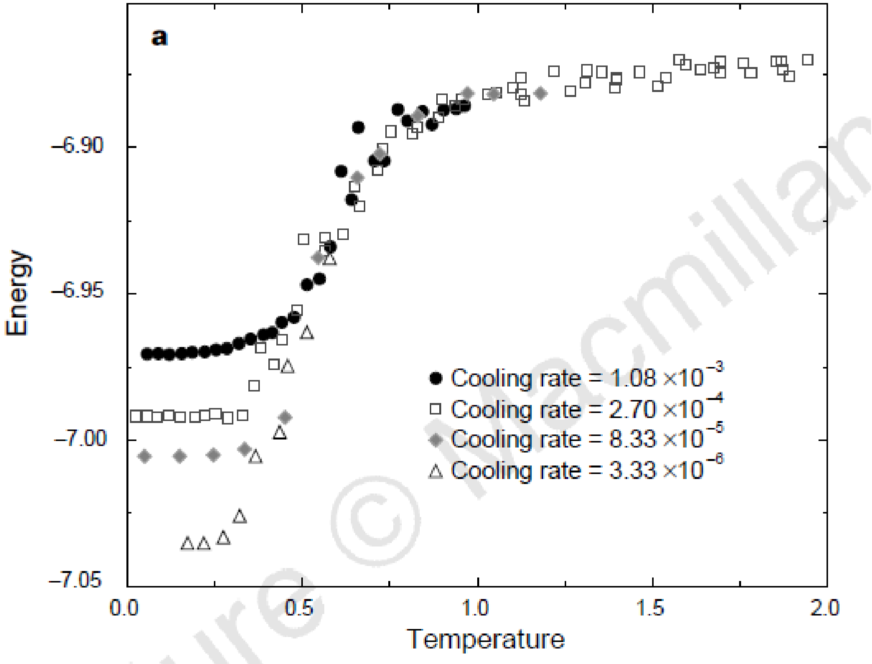
Supercooled liquids
and the glass transition

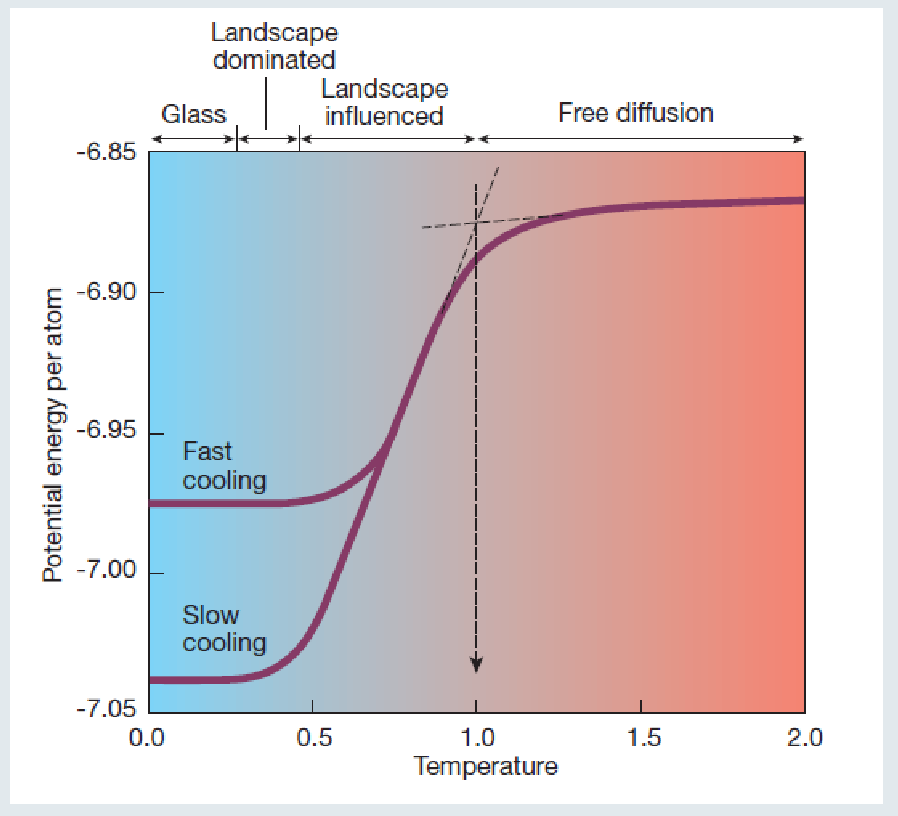
Pablo G. Debenedetti* & Frank H. Stillinger†‡

NATURE | VOL 410 | 8 MARCH 2001 |



ture-independent, and appears to have reached a plateau. When the system has sufficient kinetic energy to sample its entire energy landscape, the overwhelming number of minima that it samples are shallow, reflecting the fact that deep minima are very rare (Box 2). But

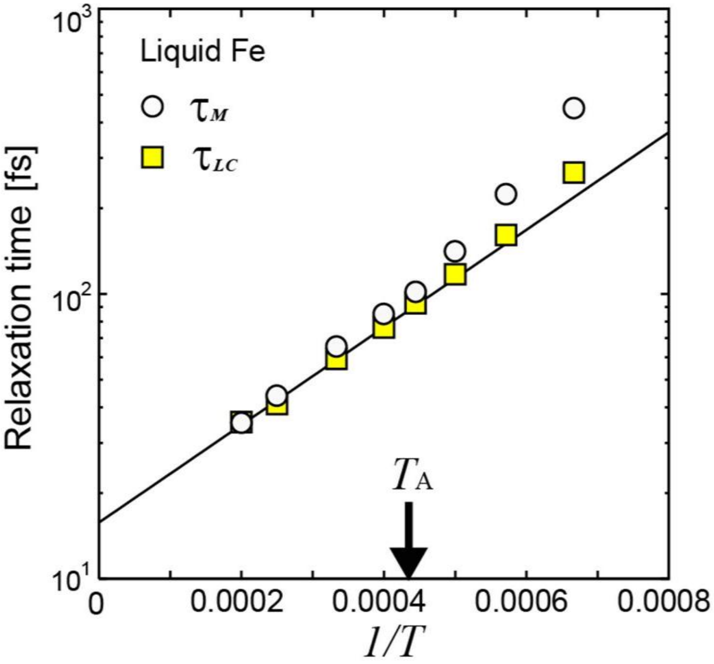


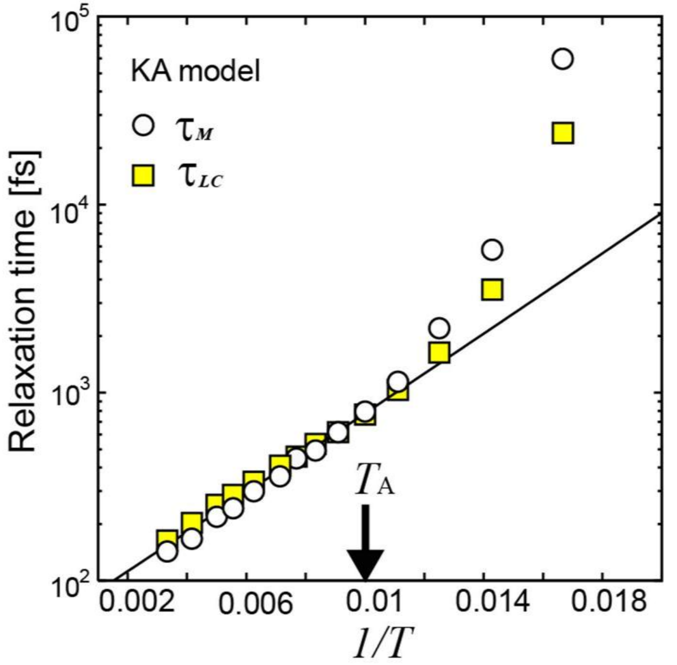


S. Sastry, P. Debenedetti, F. H. Stillinger, *Nature* **393**, 554 (1998)

Molecular Dynamics Simulation

- Different systems
  - Pairwise potential (Fe, modified Johnson potential)
  - Binary L-J (Kob-Andersen model)
  - EAM (Zr-Cu, Zr-Cu-Al)
  - Ab initio (Zr-Cu, VASP)
- Viscosity η by Kubo-Green equation, and Maxwell relaxation time by $\tau_M = \eta/G_\infty$.
- Change in the local coordination, τ_{LC}.
- We found that $\tau_M = \tau_{LC}$ at $T > T_A$.


Liquid Fe
○ τ_M
🟨 τ_{LC}
T_A
Relaxation time [fs]
10^1
10^2
10^3
0
0.0002
0.0004
0.0006
0.0008
1/T


KA model
○ τ_M
🟨 τ_{LC}
T_A
Relaxation time [fs]
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10^3
10^4
10^5
0.002
0.006
0.01
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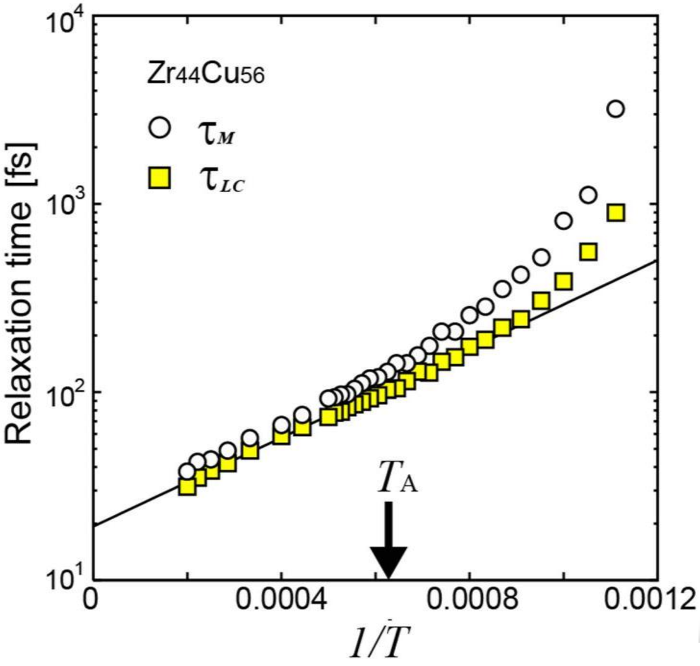
0.018
1/T


Zr44Cu56
○ τ_M
🟨 τ_{LC}
T_A
Relaxation time [fs]
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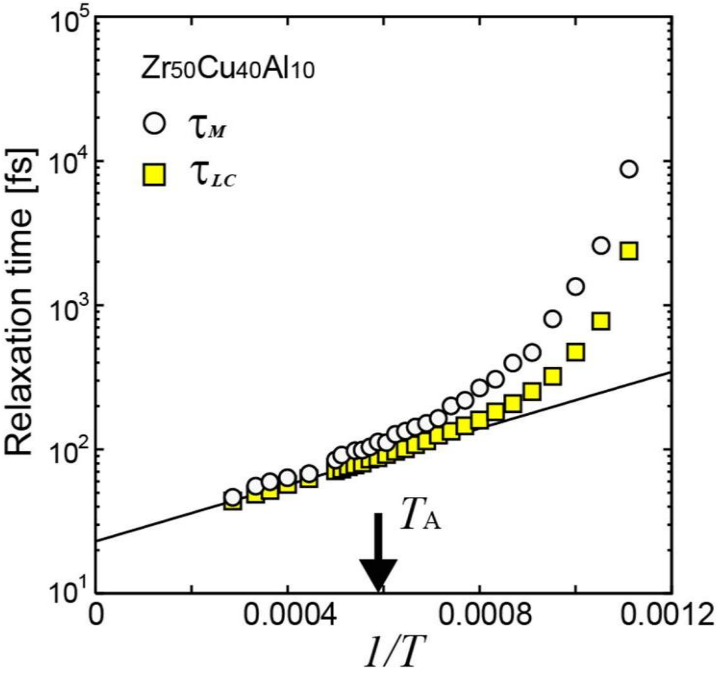
10^2
10^3
10^4
0
0.0004
0.0008
0.0012
1/T


Zr50Cu40Al10
○ τ_M
🟨 τ_{LC}
T_A
Relaxation time [fs]
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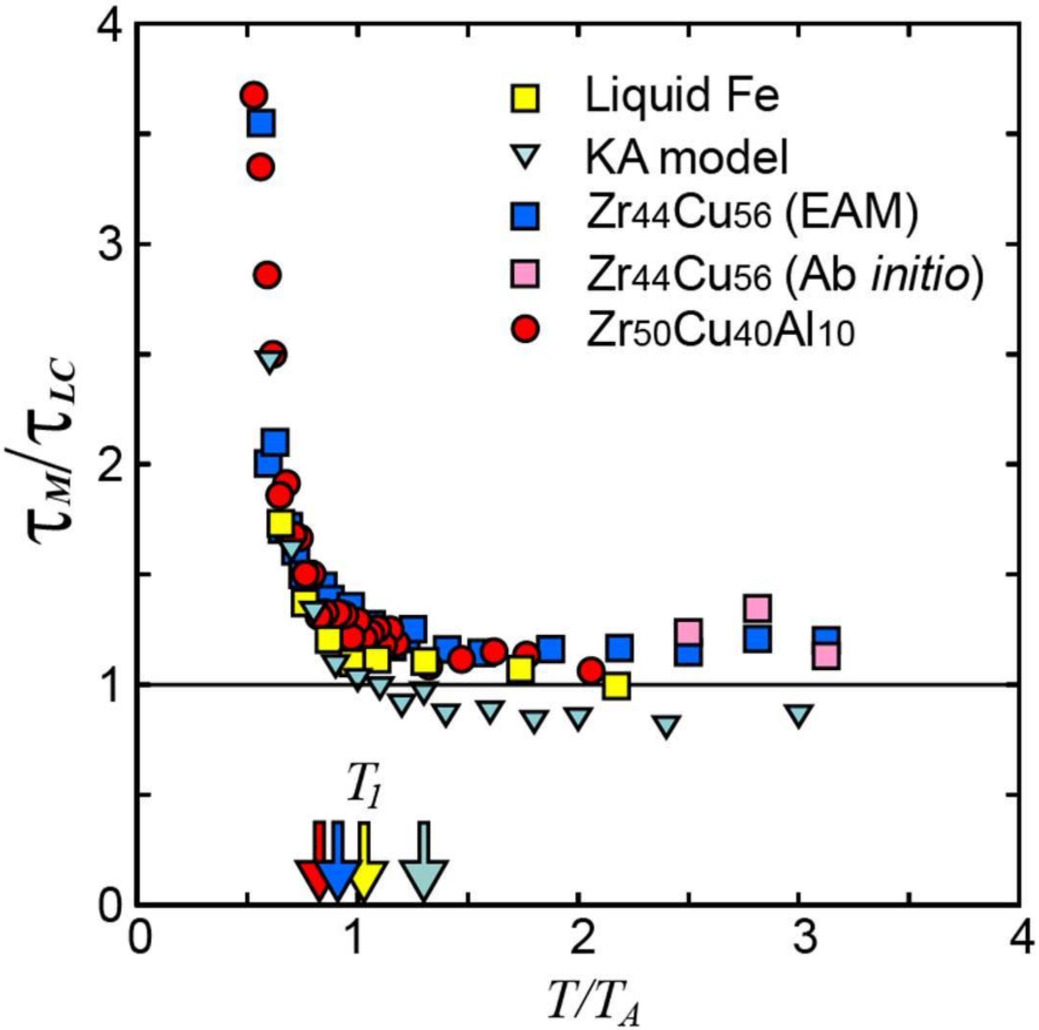
10^2
10^3
10^4
10^5
0
0.0004
0.0008
0.0012
1/T

Universal Relationship



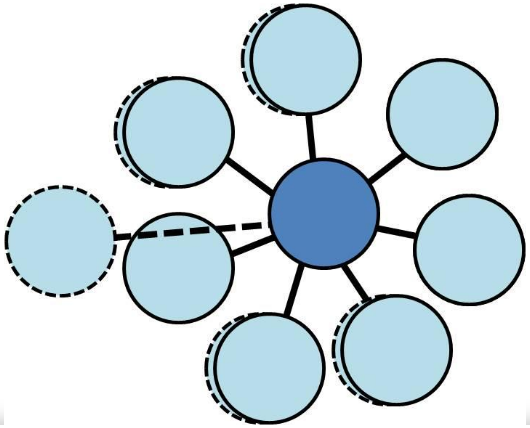
$$\tau_M = \tau_{LC}$$

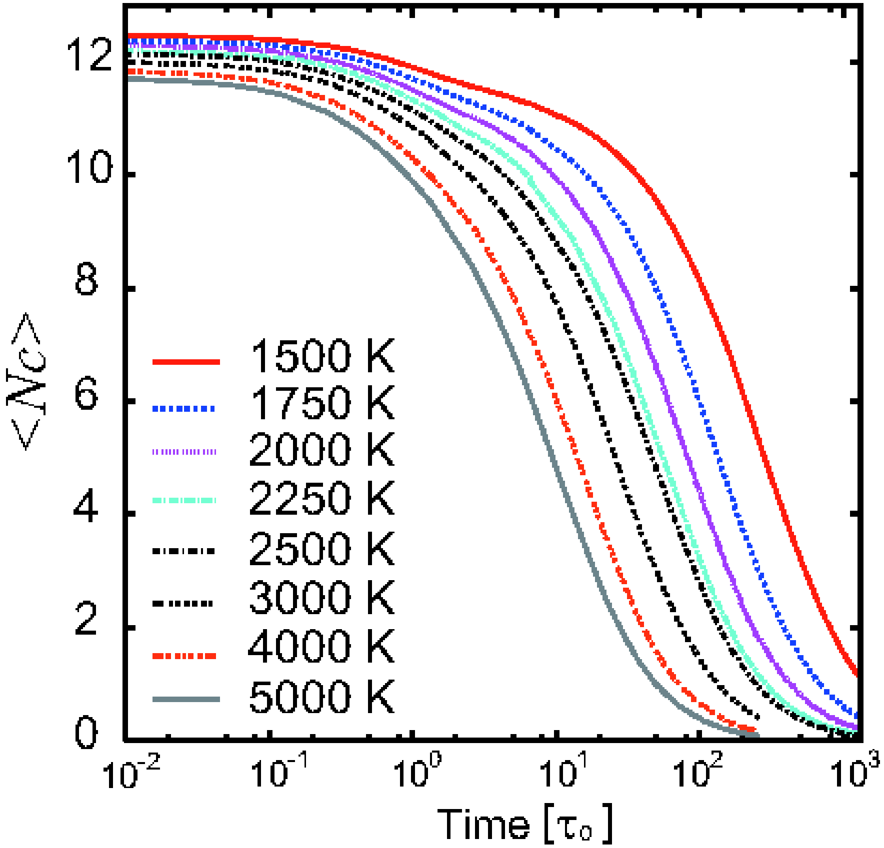
- **Fe: Johnson potential**
- **KA: Kob-Andersen potential ($Ni_{80}P_{20}$)**
- **$Cu_{56}Zr_{44}$: EAM**
- **$Zr_{50}Cu_{40}Al_{10}$: EAM**
- **$Cu_{56}Zr_{44}$: DFT-MD**

T. Iwashita, D. M. Nicholson and T. Egami, *Phys. Rev. Lett.*, **110,** 205504 (2013)

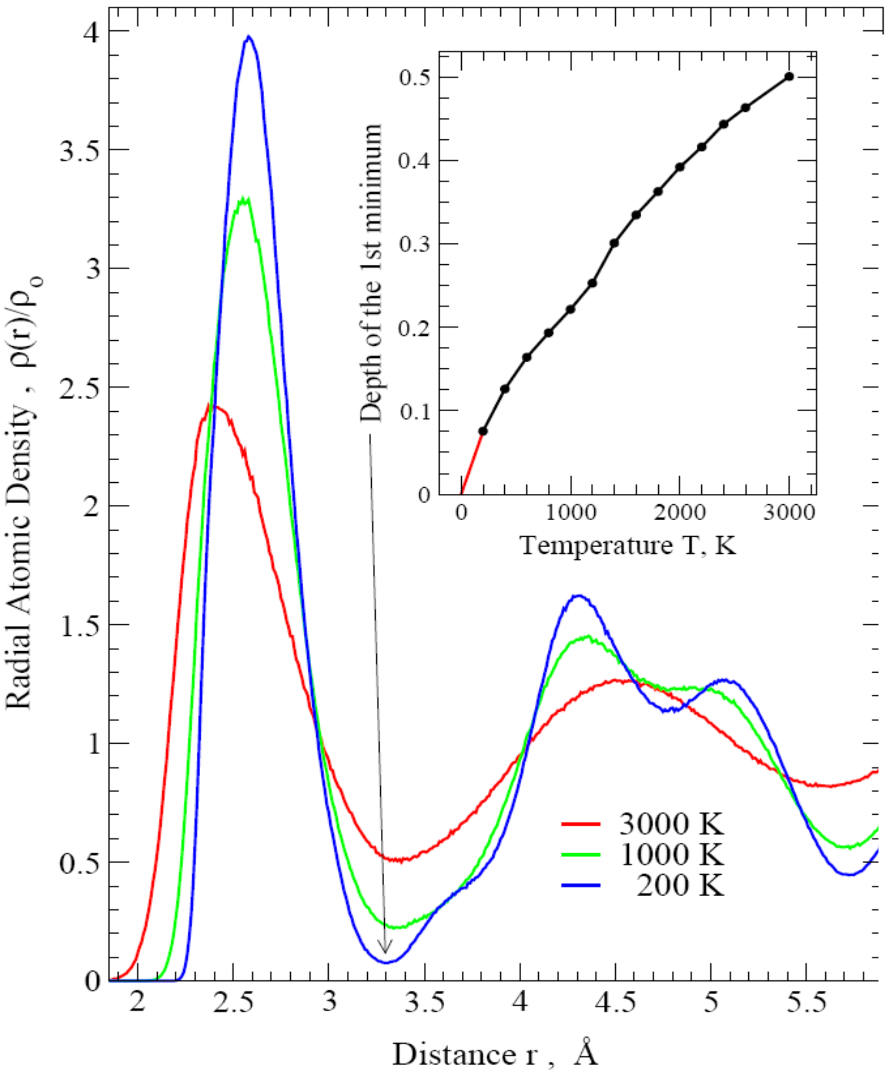
Local Configurational Excitation (LCE)

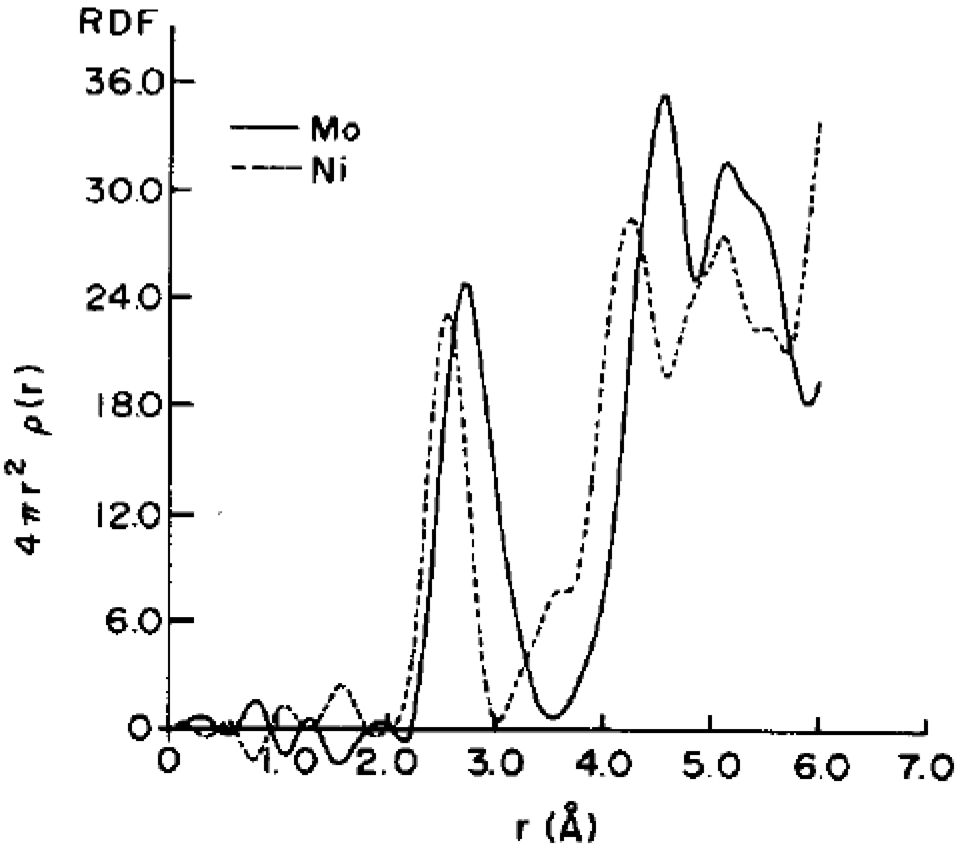
- **Local topology of atomic connectivity is changed by gaining or losing a nearest neighbor (topological excitation).**
- **τ_{LC} is defined as the time to lose (or gain) ONE neighbor.**



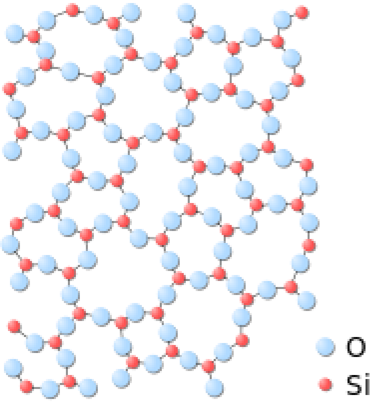


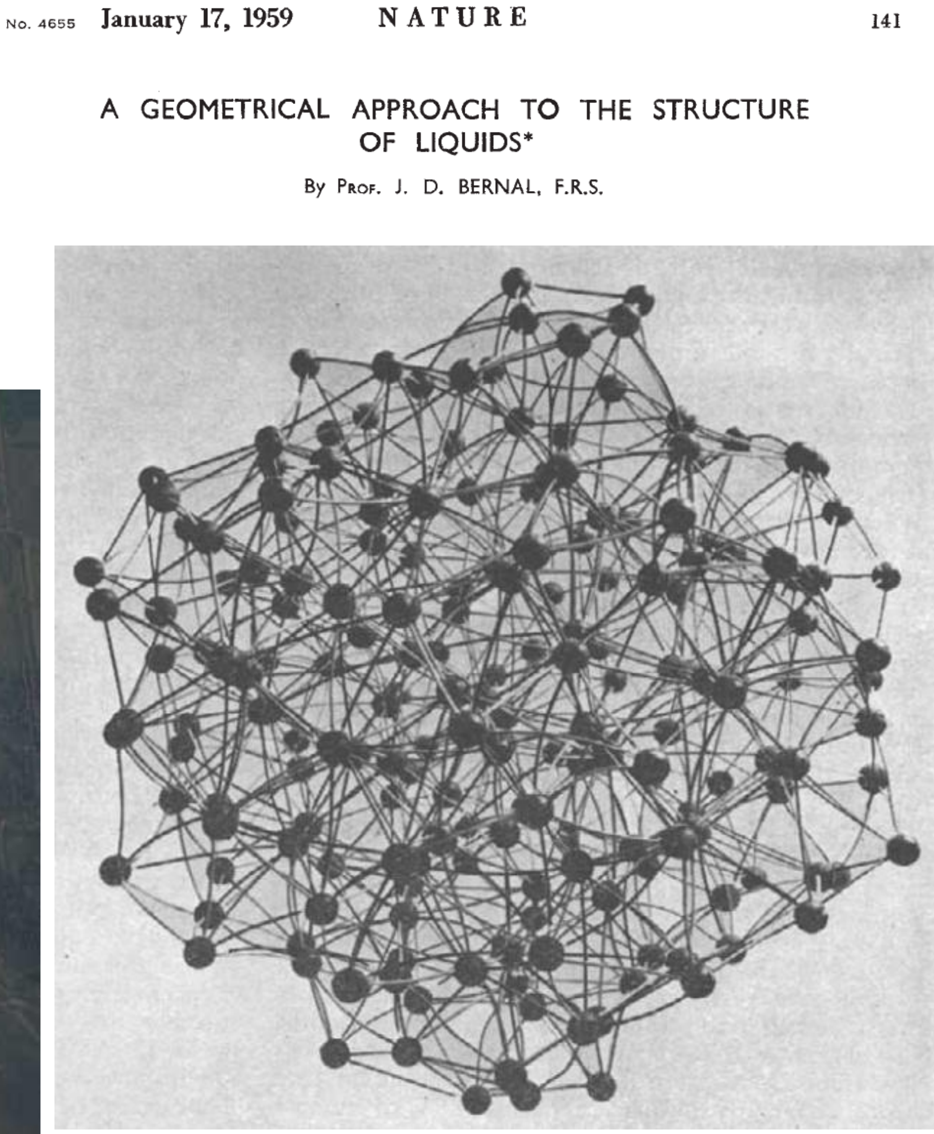
Definition of Nearest Neighbor





Continuous Random Network



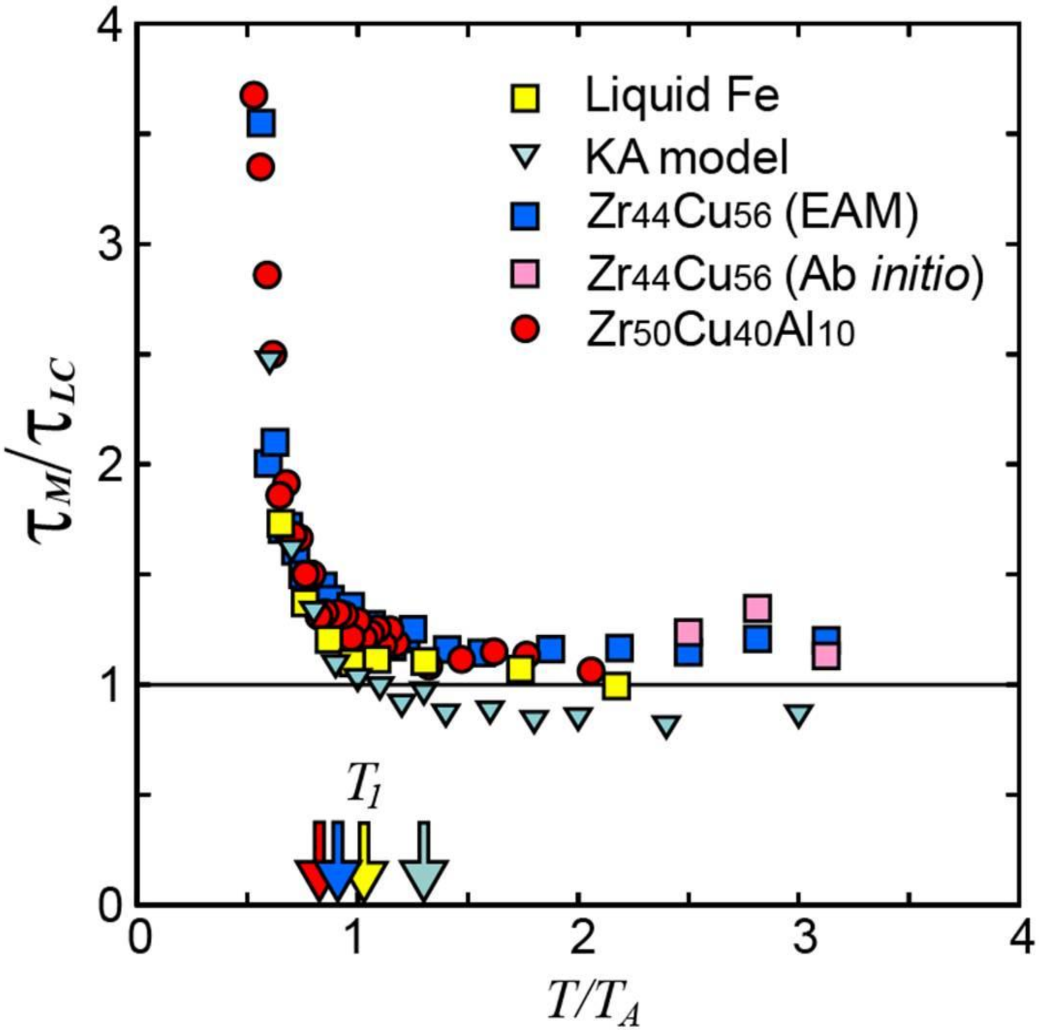


No. 4655 **January 17, 1959** **NATURE** 141

A GEOMETRICAL APPROACH TO THE STRUCTURE OF LIQUIDS*

By PROF. J. D. BERNAL, F.R.S.

Universal Relationship



$$\tau_M = \tau_{LC}$$

- **Fe: Johnson potential**
- **KA: Kob-Andersen potential ($Ni_{80}P_{20}$)**
- **$Cu_{56}Zr_{44}$: EAM**
- **$Zr_{50}Cu_{40}Al_{10}$: EAM**
- **$Cu_{56}Zr_{44}$: DFT-MD**

T. Iwashita, D. M. Nicholson and T. Egami, *Phys. Rev. Lett.*, **110,** 205504 (2013)

Maxwell Relaxation Time

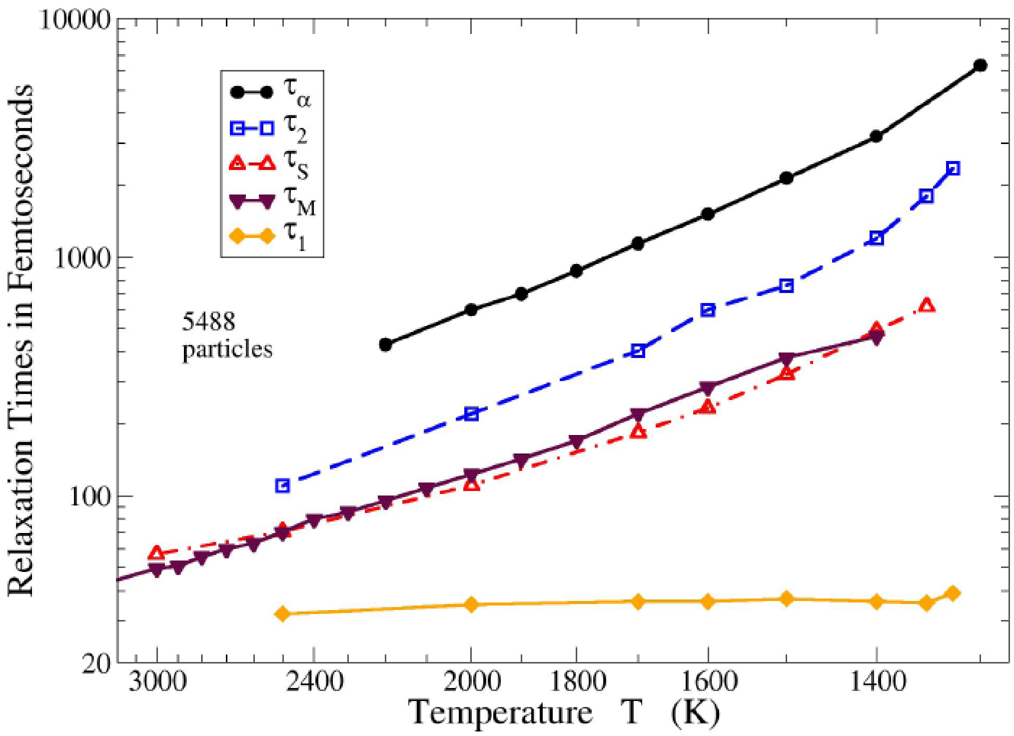
$$\tau_M = \frac{\eta}{G_\infty}$$

- **Fluctuation-dissipation theorem:**

$$\eta = \frac{V}{kT}\int_0^\infty \left\langle \sigma^{xy}(0)\sigma^{xy}(t) \right\rangle dt$$

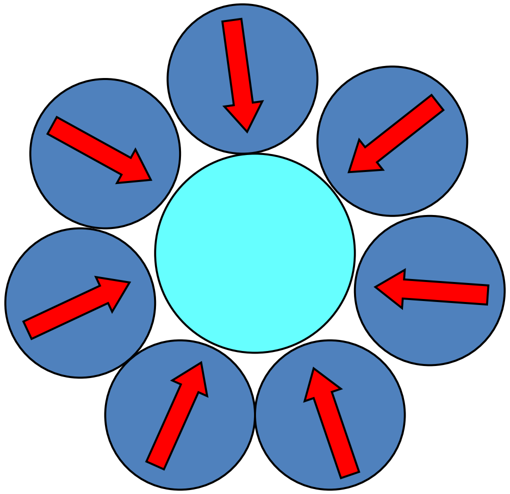
$$G_\infty = \frac{V}{kT}\left\langle \left(\sigma^{xy}(0)\right)^2 \right\rangle$$

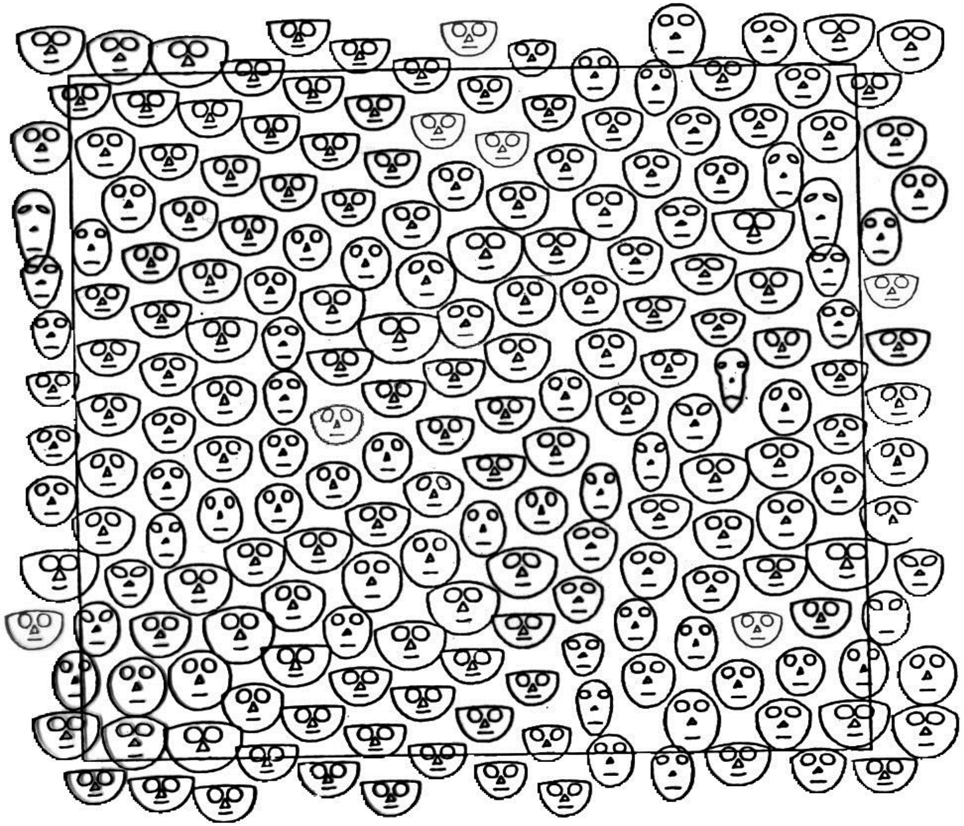
$$\tau_M = \int_0^\infty \frac{\left\langle \sigma^{xy}(0)\sigma^{xy}(t) \right\rangle}{\left\langle \left(\sigma^{xy}(0)\right)^2 \right\rangle} dt$$



Atomic Level Stresses and Strains

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



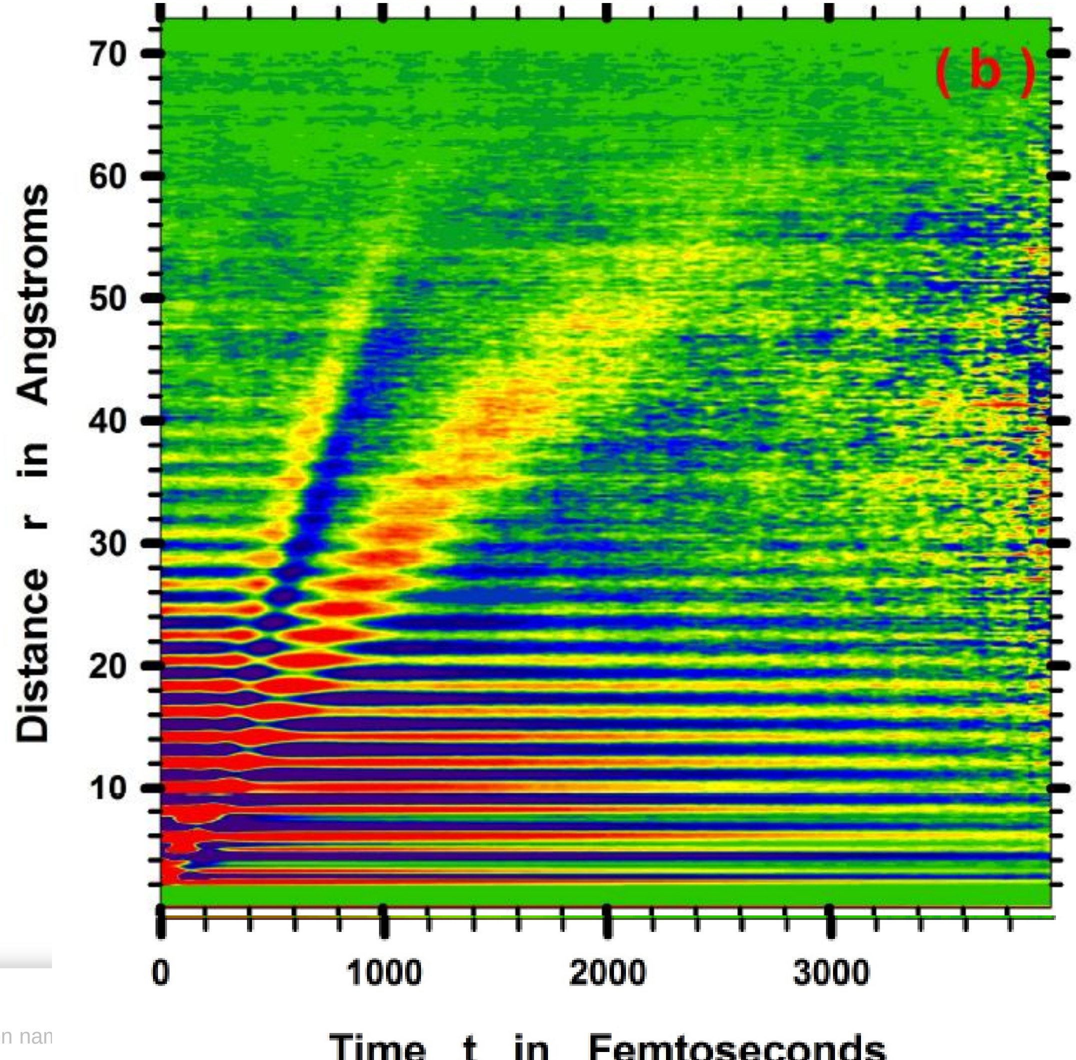


T. Egami, K. Maeda and V. Vitek,
Phil. Mag. **A41**, 883 (1980).

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

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

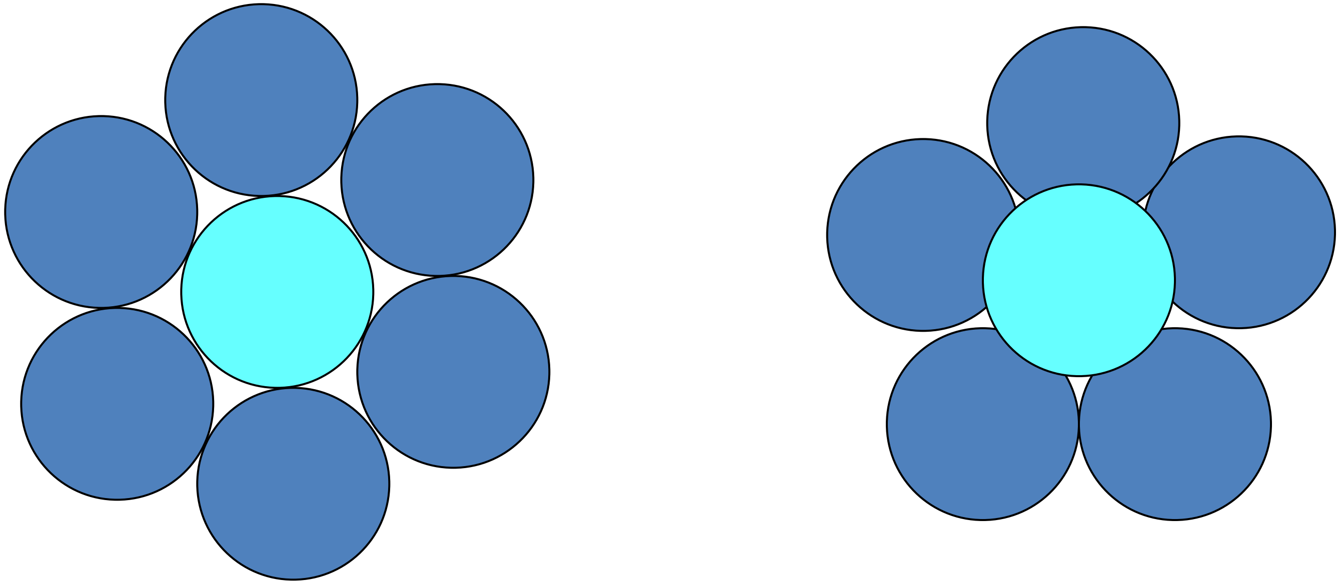
$$\Sigma(r,t)=\iint\left\langle\sigma^{xy}(\mathbf{r}',0)\sigma^{xy}(\mathbf{r}'',t)\right\rangle\delta\left(r-\left|\mathbf{r}'-\mathbf{r}''\right|\right)d\mathbf{r}'d\mathbf{r}''$$



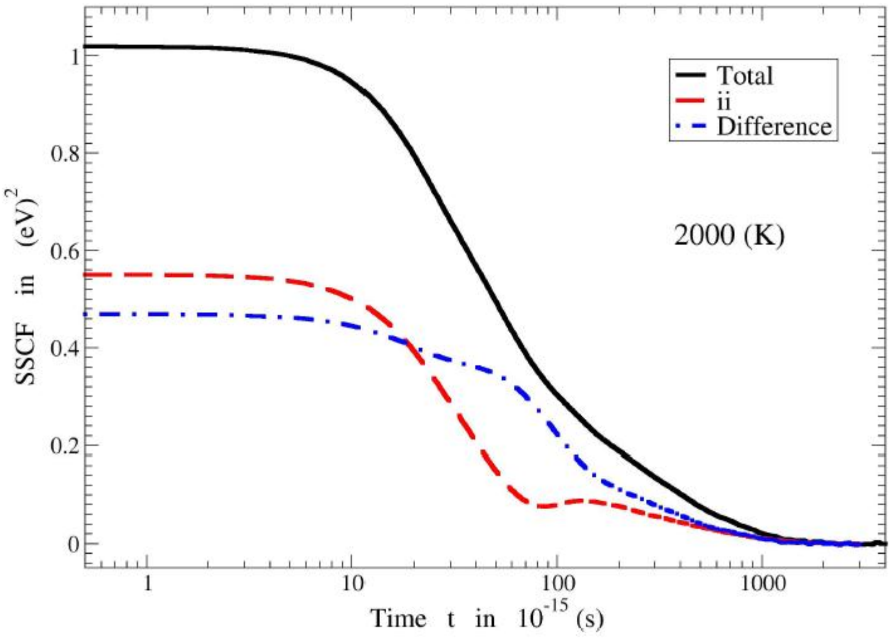
V. A. Levashov, J. R. Morris and T. Egami, *Phys. Rev. Lett.* **106,** 115703 (2011)

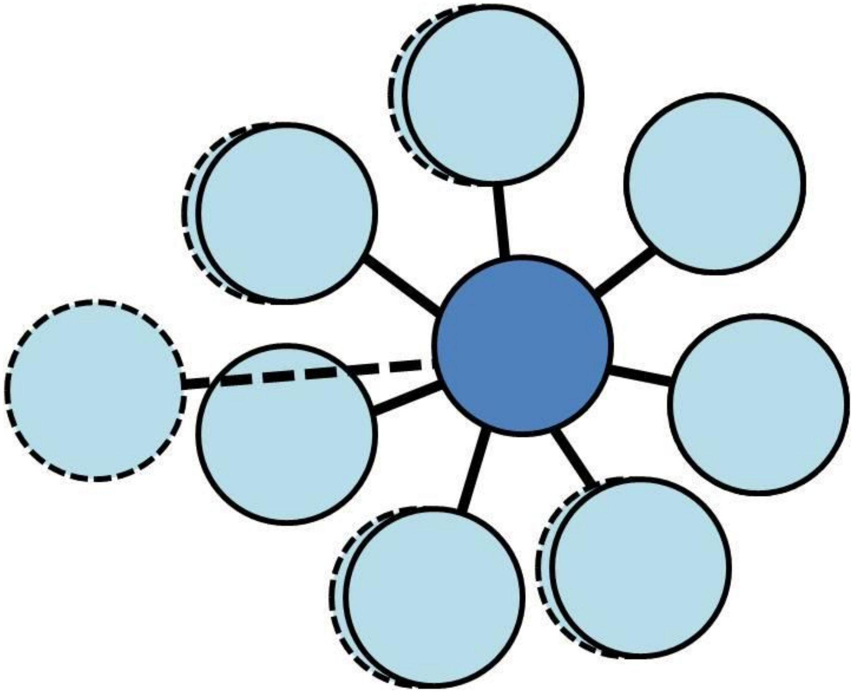
Origin of the Atomic-Level Stresses

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



Lifetime of Local Stress



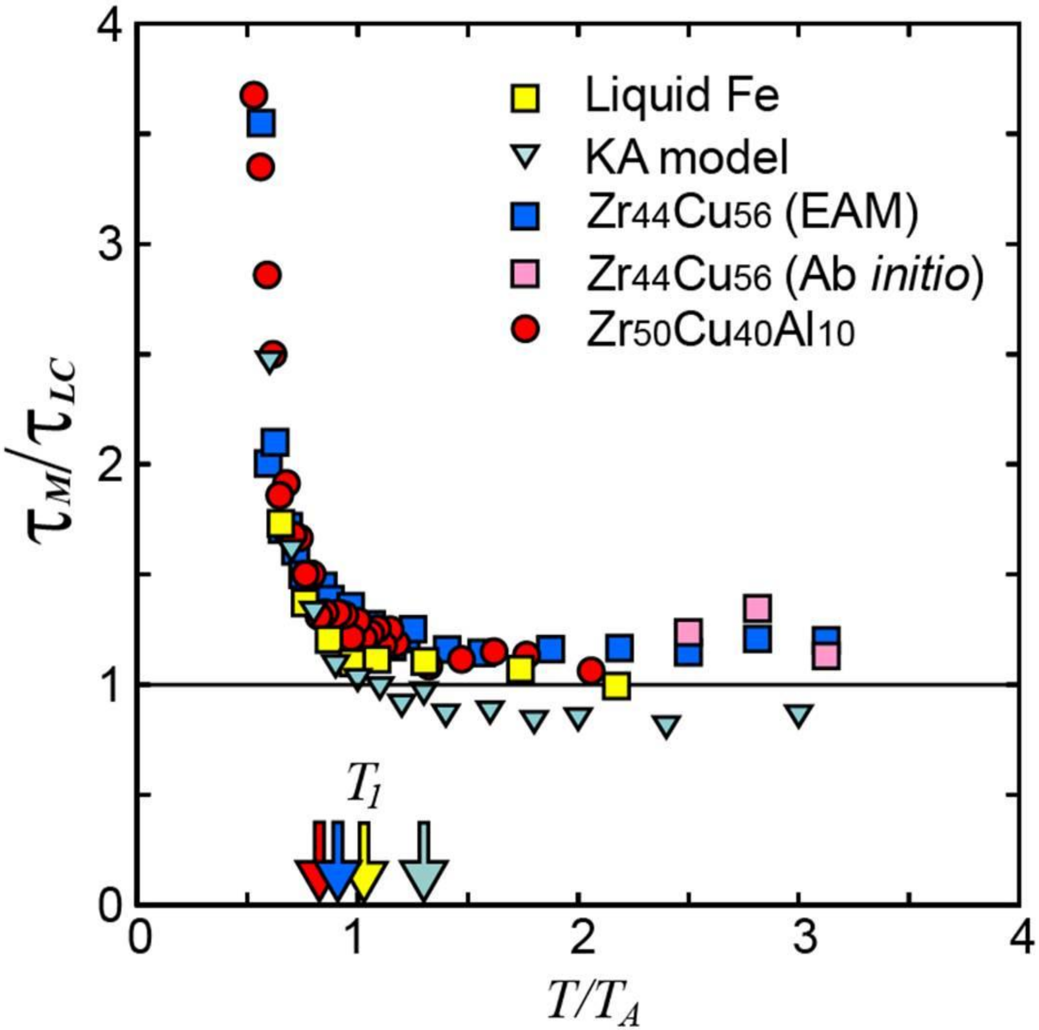


- **Losing one nearest neighbor is enough to change the local stress state.**

$$\tau_M = \int_0^\infty \frac{\left\langle \sigma^{xy}(0)\sigma^{xy}(t)\right\rangle}{\left\langle \left(\sigma^{xy}(0)\right)^2\right\rangle} dt$$

V. A. Levashov, J. R. Morris and T. Egami, *J. Chem. Phys.* **138,** 044507 (2013)

Universal Relationship



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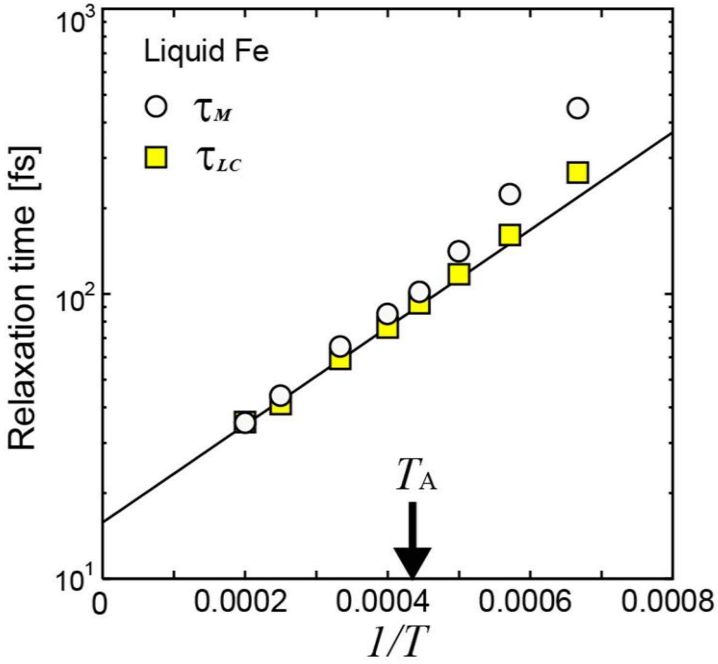
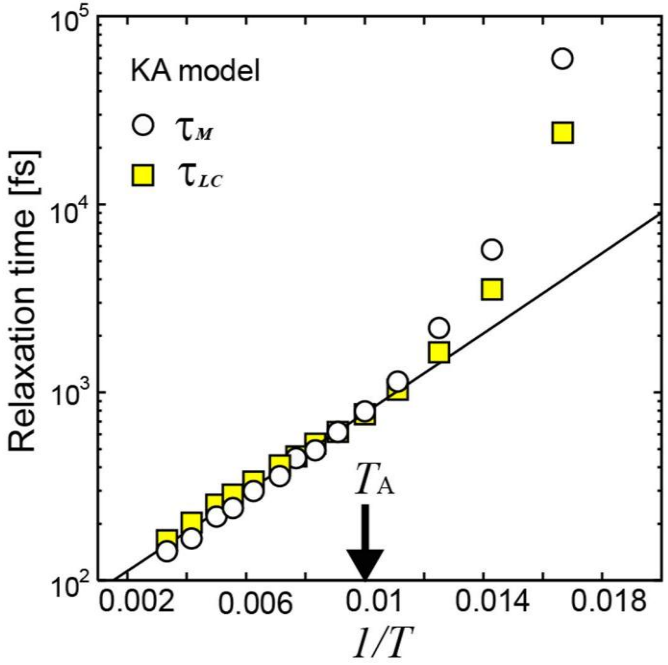
T. Iwashita, D. M. Nicholson and T. Egami, *Phys. Rev. Lett.*, **110,** 205504 (2013)

Q1


Liquid Fe
○ τ_M
■ τ_{LC}
Relaxation time [fs]
10^3
10^2
10^1
T_A
0
0.0002
0.0004
0.0006
0.0008
1/T


KA model
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10^5
10^4
10^3
10^2
T_A
0.002
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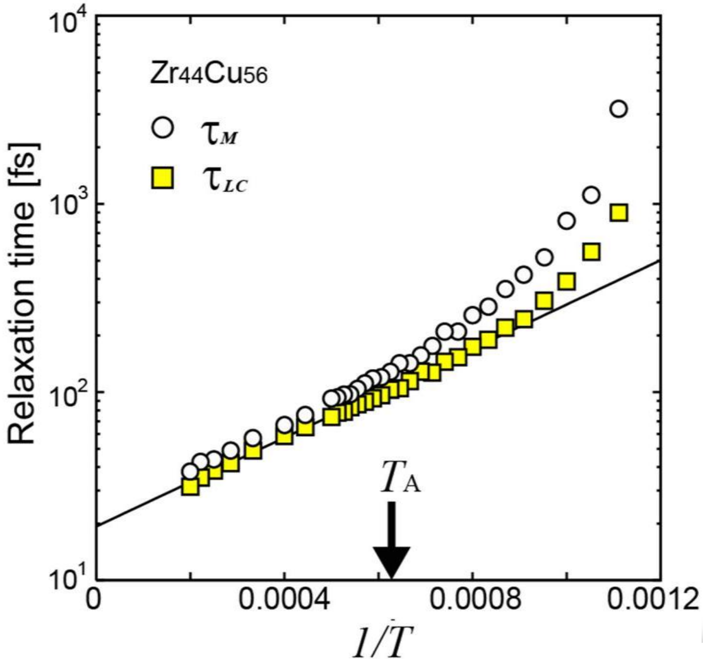
1/T


Zr44Cu56
○ τ_M
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Relaxation time [fs]
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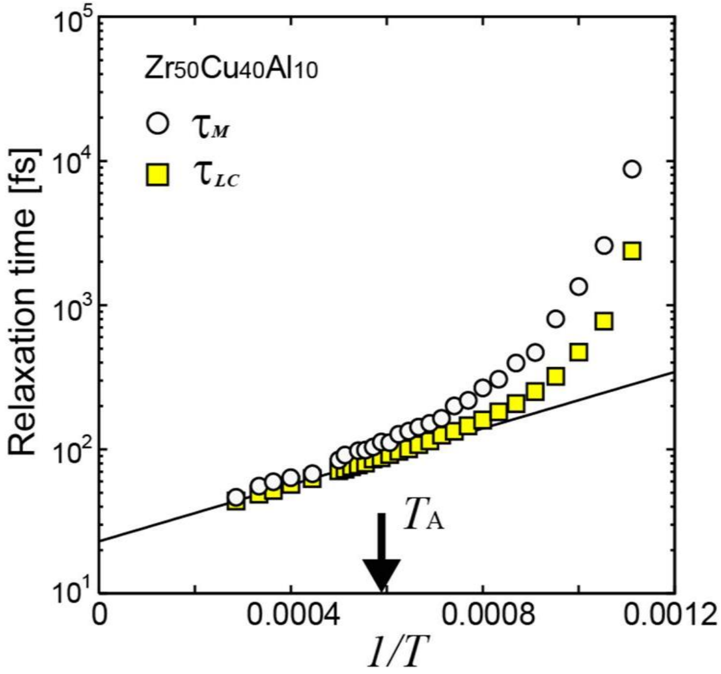

Zr50Cu40Al10
○ τ_M
■ τ_{LC}
Relaxation time [fs]
10^5
10^4
10^3
10^2
10^1
T_A
0
0.0004
0.0008
0.0012
1/T

[Q1] High Temperature Limit

$$\tau(T) = \tau(\infty)\exp\left(\frac{E_a}{kT}\right)$$

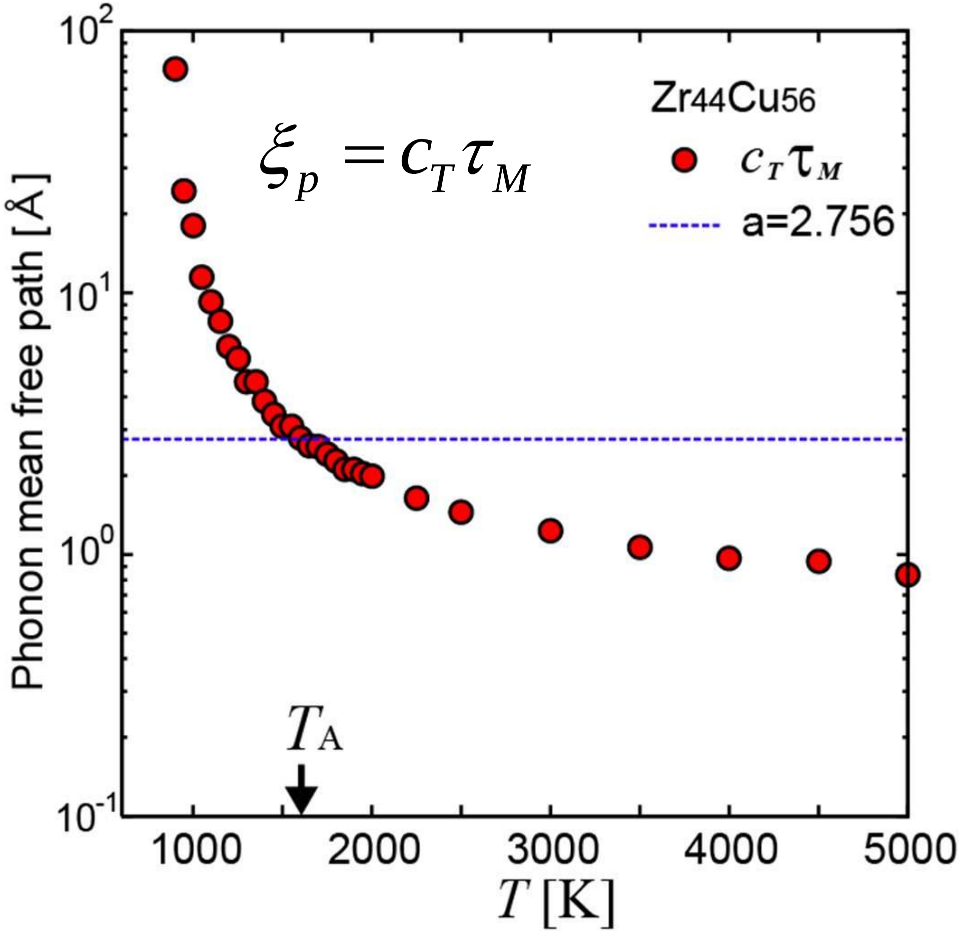
- $\eta_\infty \approx 10^{-4}$ poise, thus $\tau_\infty \approx 10$ fs.
- τ_∞ cannot be the Debye frequency because it is too short ($\tau_D \sim 100$ fs or longer) and phonons are dead at high temperatures.
- [Q1] We find $h/\tau(\infty) \approx E_a$. Thus τ_∞ represents the bond energy, which is similar to all liquids within an order of magnitude. This explains the convergence.

[Q2] Crossover Temperature

- **At T_1,** $a = c_T \tau_{LC}$

- **Above T_1 LCE cannot talk to each other.**

- **Below T_1 LCEs interact, and shield each other.**



- **Phonon localization (Ioffe-Regel) at T_A.**

Configurational Excitation

- Local configurational excitation (LCE) is the *elementary excitation* in high temperature liquid.
- At $T > T_A$ the dynamics is so fast that atoms cannot communicate each other. Thus the physics is local, and the mean-field approximation is valid.
- Below T_A LCE's interact by screening each other. Thus excitations become more collective.
- We can describe low temperature behavior in terms of LCE's.

Anankeon

- Ananke, Greek Goddess of force, constraint and destiny
- Brings order in disorder.

Jean Bellissard,
Georgia Tech, Atlanta, GA

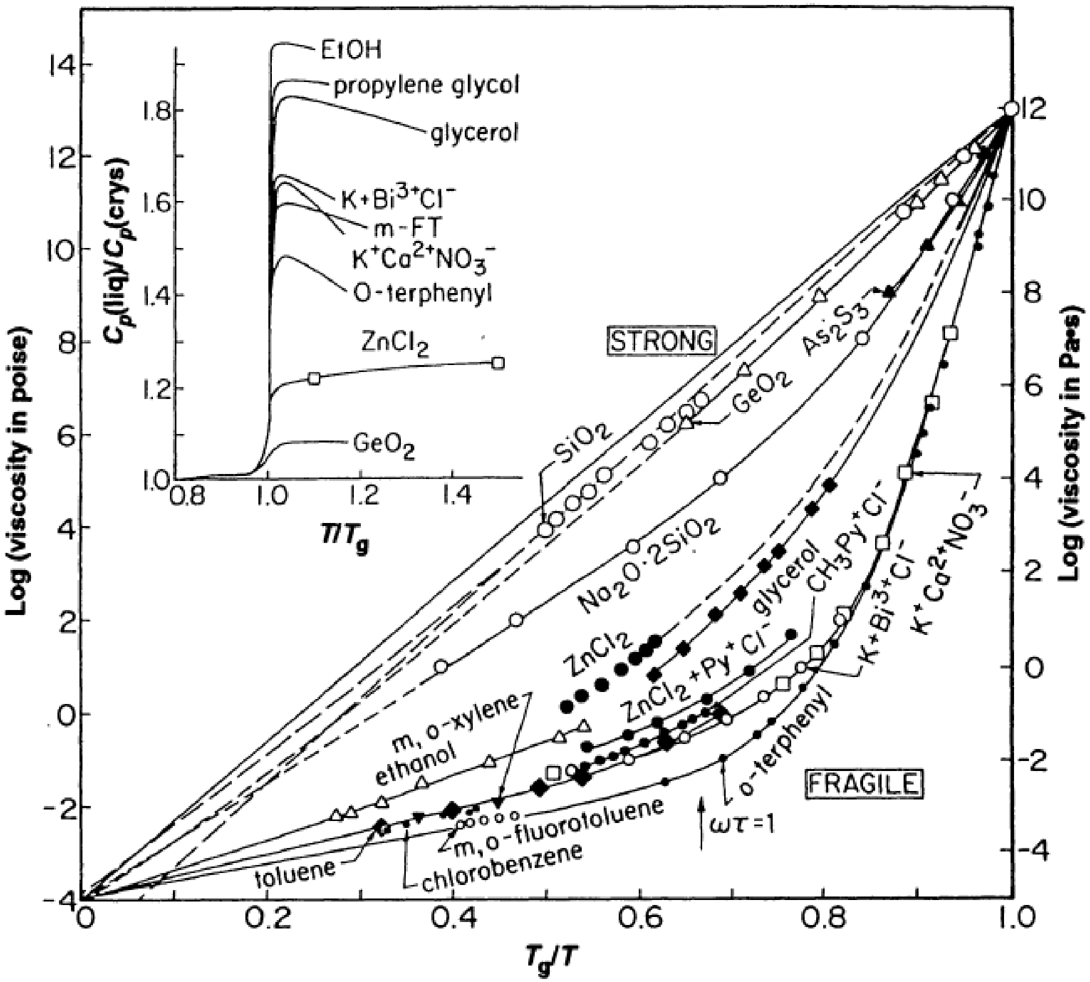
[Q3] Fragility

$$m = \left.\frac{d\log\eta(T)}{d\left(T_g/T\right)}\right|_{T_g}$$

$$n = \left.\frac{d\log\eta(T)}{d\left(T_g/T\right)}\right|_{\infty}$$

$$\frac{\log\eta\left(T_g\right)-\log\eta\left(T_A\right)}{m} = 1-\frac{T_g}{T_A}$$

$$\frac{\log\eta\left(T_A\right)-\log\eta(\infty)}{n} = \frac{T_g}{T_A}$$



$$n = 0.434 \frac{E_a}{k_B T_g}$$

$$\frac{GV}{2}\left(\varepsilon_s^0\right)^2 \sim E_a$$

$$n = 0.217 \frac{GV}{k_B T_g}\left(\varepsilon_s^0\right)^2$$

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

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

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

$$n = C_F K_\alpha \frac{G}{B}$$

$$C_F = 0.108\left(\frac{\varepsilon_v^0}{\varepsilon_v^{T,crit}}\right)^2$$

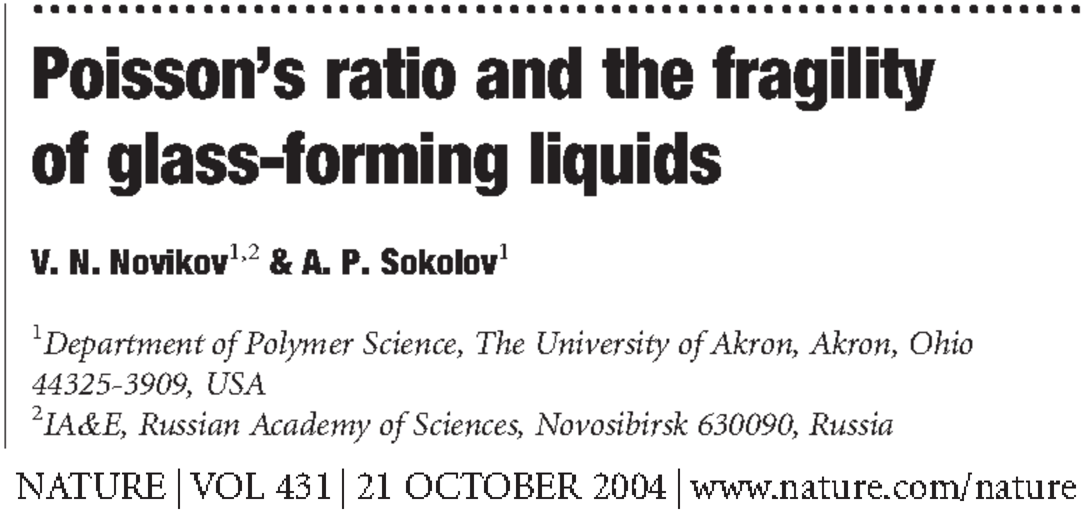
$$x = \frac{G}{B} = \frac{3(1-2\nu)}{2(1+\nu)},$$

$$\nu = \frac{3-2x}{2(3+x)}$$

$$n = C_F \frac{3+4x}{4}$$

$$\frac{n_0}{n} = 1 - \frac{17-n_0}{m}$$

$$m = C_1\left(\frac{B}{G} + C_2\right) \qquad C_1 = \frac{3(17-n_0)}{4}, \quad C_2 = \frac{4}{3}$$

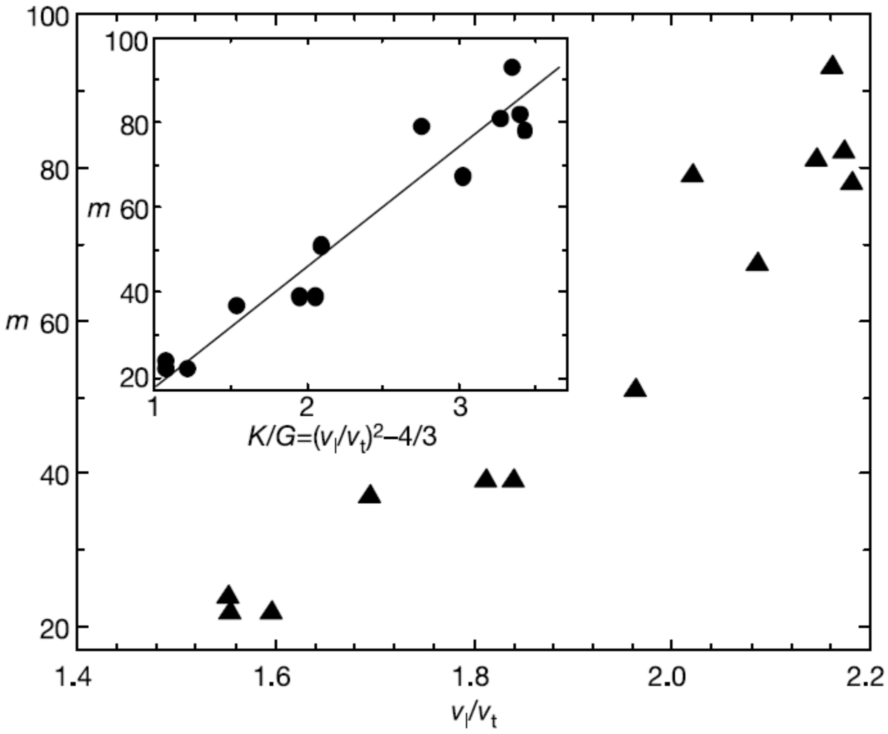


Poisson's ratio and the fragility of glass-forming liquids

V. N. Novikov[1,2] & A. P. Sokolov[1]

[1]*Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, USA*
[2]*IA&E, Russian Academy of Sciences, Novosibirsk 630090, Russia*

NATURE | VOL 431 | 21 OCTOBER 2004 | www.nature.com/nature



$$m = C_1\left(\frac{B}{G} + C_2\right)$$

Source	C_1	C_2
Novikov/Sokolov	29	-0.41
Liquid Fe model	11.6	1.33

Materials Transactions, Vol. 46, No. 12 (2005) pp. 2915 to 2919
Special Issue on Materials Science of Bulk Metallic Glasses
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Is There a Link between Melt Fragility and Elastic Properties of Metallic Glasses?

Livio Battezzati

Dipartimento di Chimica IFM e Centro di Eccellenza NIS, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

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Philosophical Magazine,
Vol. 86, No. 11, 11 April 2006, 1567–1579

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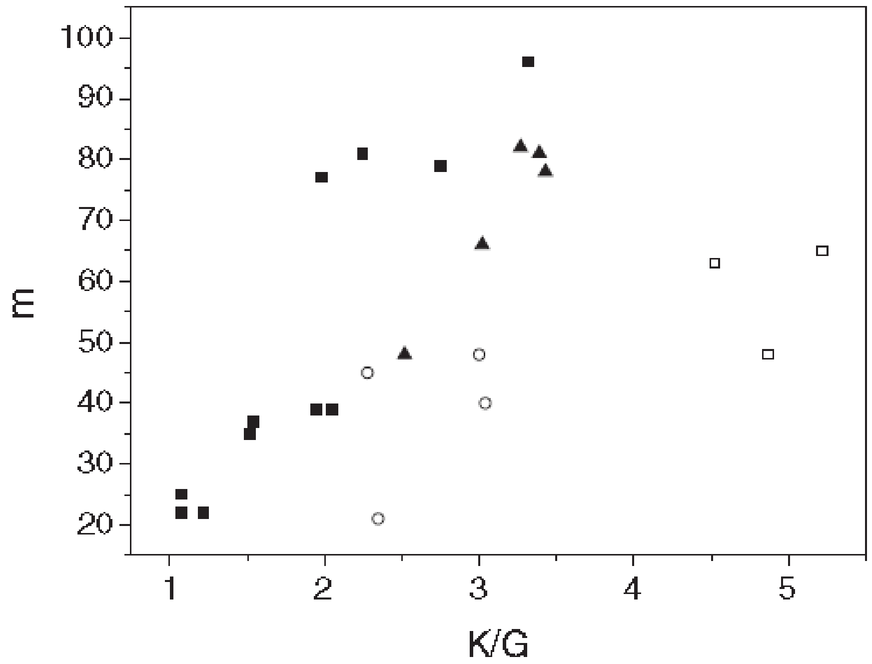
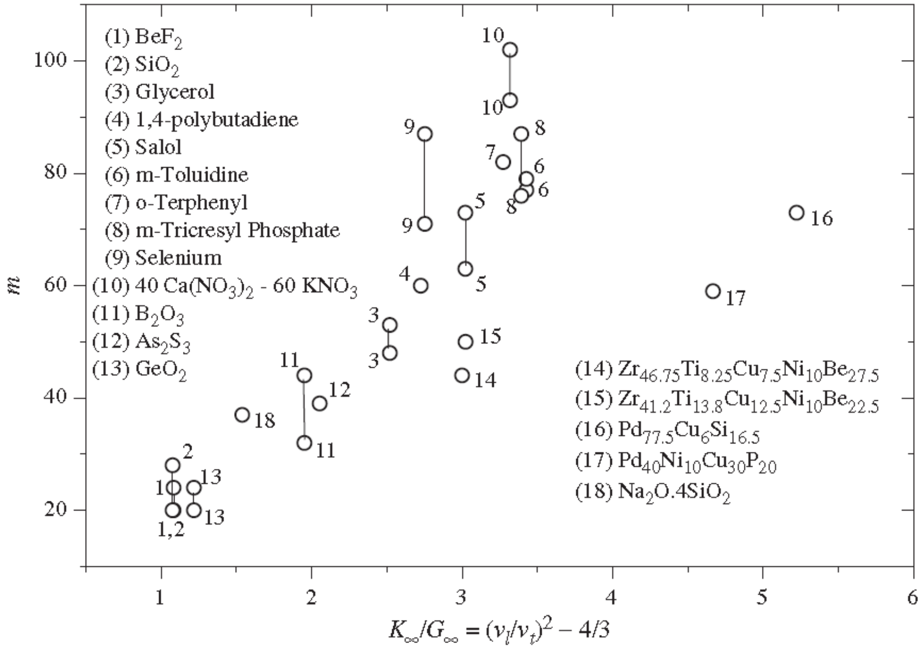
On Poisson's ratio of glass and liquid vitrification characteristics

G. P. JOHARI*

Department of Materials Science and Engineering, McMaster University,
Hamilton, Ontario L8S 4L7, Canada





PHYSICAL REVIEW E 71, 061501 (2005)

Correlation of fragility of supercooled liquids with elastic properties of glasses

V. N. Novikov,[1,2] Y. Ding,[1] and A. P. Sokolov[1,*]

Results for Metallic Glasses

Source	C_1	C_2
Ref. 18 (Novikov)	29	-0.41
Liquid Fe model	11.6	1.33
Ref. 21 (Battezzati)	7	2
Ref. 22 (Novikov)	7	3
Refs. 23, 24 (Johari)	10	1.9

What does the dependence on G/B mean?

$$m = C_1\left(\frac{B}{G} + C_2\right)$$

$$E_c \sim N_C E_B + E_{cv}$$

$$E_c = \beta VB = \frac{N_C GV}{2}\left(\varepsilon_s^0\right)^2 + E_{cv}$$

$$x = \frac{G}{B} = \frac{2\beta\gamma}{N_C\left(\varepsilon_s^0\right)^2}, \quad \gamma = \frac{E_c - E_{cv}}{E_c}$$

- **Covalency: $\gamma = 1$ for totally covalent solid.**
- **Coordination number: Openness of the structure and covalency.**

Conclusions

- The elementary excitation in a liquid (Anankeon) is an excitation to change the local topology of atomic connectivity (LCE), and is responsible for viscosity.
- Conspicuous features of the Angell plot can be explained in terms of LCE.
- The concept of random network is valid even for metallic liquids and glasses.
- The inclusive vision of Austen led to the recognition of the universal importance of topological excitation in liquids and glasses.