Fragile-to-strong crossover and non-monotonic breakdown of Stokes-Einstein relation

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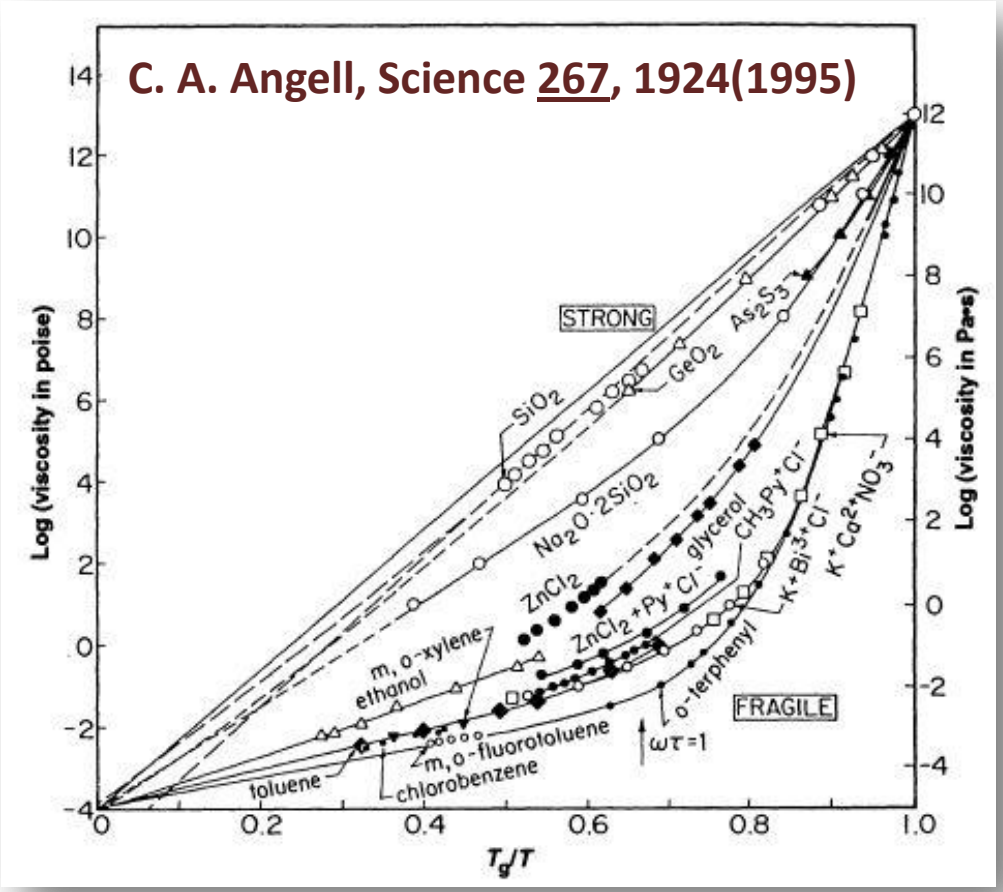
Outline

- Fragility of glass-forming liquids & the VFT equation
- Fragile-to-strong crossover(FSC)
  - Experimental observations
  - Theoretical scenario
  - A case of binary metallic glass-forming liquid
  - Is there a thermodynamic event underlying FSC?

Angell Plot, Fragility & Strong/Fragile classification



➡ Based on T dependence of Viscosity(η) or structural relaxation time (τ_α)

➡ Degree of deviation from Arrhenius behaviour gives a measure of fragility

➡ Steepness index 'm'

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

➡ Neither Experiments nor Computer Simulations can access the entire range $T_g < T < T_m$ for investigation of the dynamics.

Vogel-Fulcher-Tammann (VFT) equation & Fragility

$$\eta = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right)$$

➡ Normally, VFT eq. is utilized to extrapolate the temperature dependence of $\eta(\tau_\alpha)$ for $T_m \rightarrow T_g$

➡ Owing to the use of VFT, the concept of fragility remains limited.

$\Rightarrow$ fragility correctly describes the non-Arrhenian behavior over the entire temperature range of interest.
i.e. $T_m \rightarrow T_g$

➡ Many glass-forming liquids do not fall in the ambit of the "strong/fragile" classification scheme.

Fragile-to-Strong crossover: Experimental observations

- Analysis of experimental data of viscosity of variety of supercooled liquids display a fragile-to-strong crossover at T_x so that $T_g < T_x < T_m$

P. Taborek et al — 17 liquids
PRB 34, 1835 (1986)

F. Mallamace et al — 84 liquids
PNAS 107, 22457 (2010)

$$\eta = \eta_0 \left[\frac{T - T_x}{T_x} \right]^{-\theta}$$

Fragile-to-Strong crossover

➡ The FSC phenomenon is signified by:

⇒ Crossover of temperature dependence of the transport coefficients (D_s, η, τ_α) from non-Arrhenius to Arrhenius.

⇒ Stokes-Einstein(SE) to Fractional Stokes-Einstein(FSE) crossover

⇒ Non-monotonic decoupling of self-diffusion and structural relaxation

⇒ Possibility of polyamorphic(liquid-liquid) phase transition

A classic example of Supercooled Water

➡ F-S transition proposed.

- **Thermodynamic determination of fragility in liquids and a fragile-to-strong liquid transition in water**

  Kaori Ito*, Cornelius T. Moynihan† & C. Austen Angell‡

  Nature 398, 492 (1999).

→ F-S transition on cooling is intimately connected to the presence of a thermodynamic event in liquid water.

➡ Evidence from Experiments and Simulations

- **The violation of the Stokes–Einstein relation in supercooled water**

  Sow-Hsin Chen*†, Francesco Mallamace*‡, Chung-Yuan Mou§, Matteo Broccio*‡, Carmelo Corsaro‡, Antonio Faraone‡¶, and Li Liu*‖

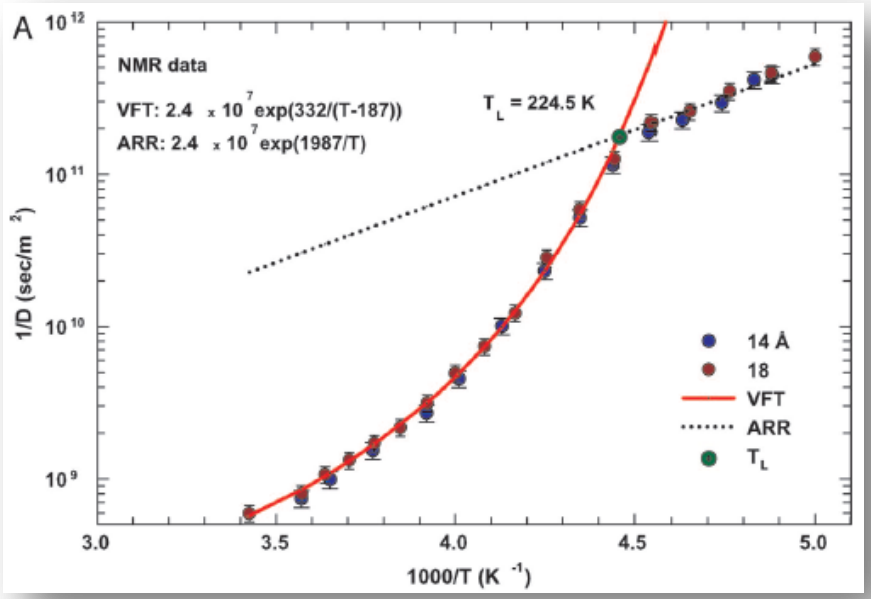
  PNAS 103, 12974 (2006).

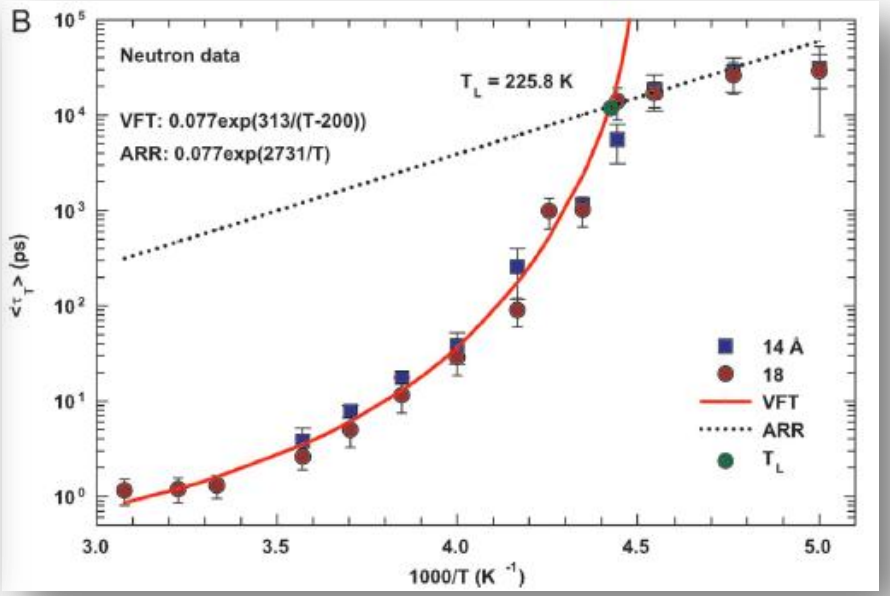
- **Appearance of a fractional Stokes–Einstein relation in water and a structural interpretation of its onset**

  Limei Xu[1,2], Francesco Mallamace[3]*, Zhenyu Yan[2], Francis W. Starr[4], Sergey V. Buldyrev[2,5] and H. Eugene Stanley[2]*

  Nature Phys. 5, 565 (2009).

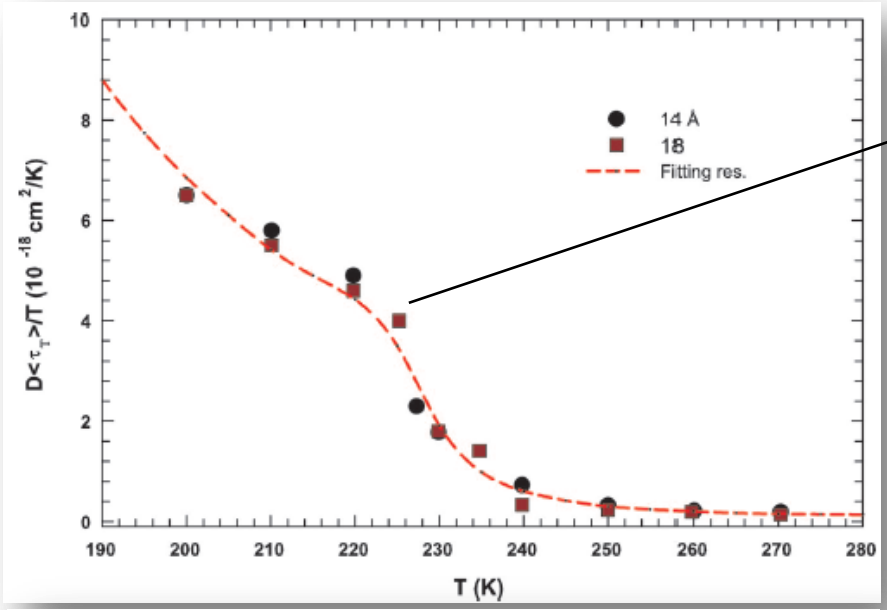
Supercooled Water: Non-Arrhenius to Arrhenius crossover





S. Chen et al. PNAS 103, 12974 (2006).

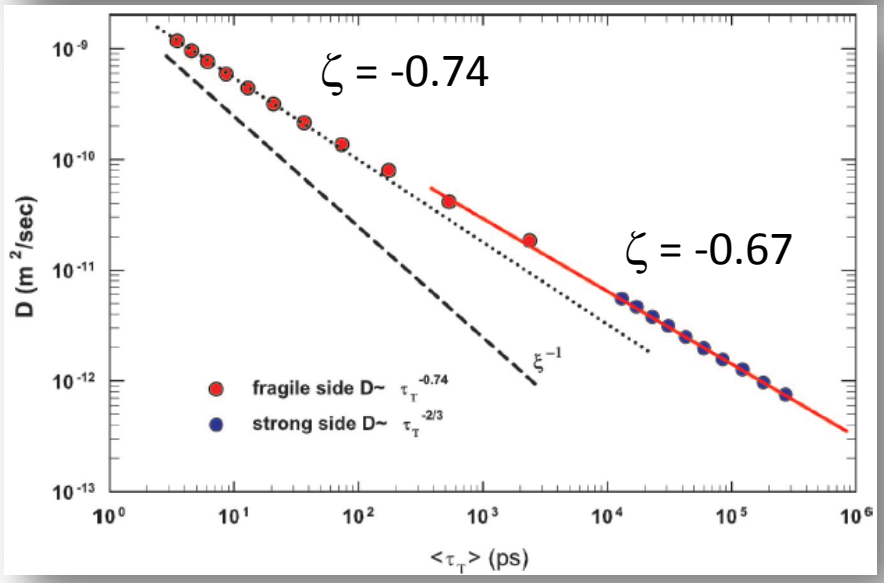
Supercooled Water: SE to FSE crossover



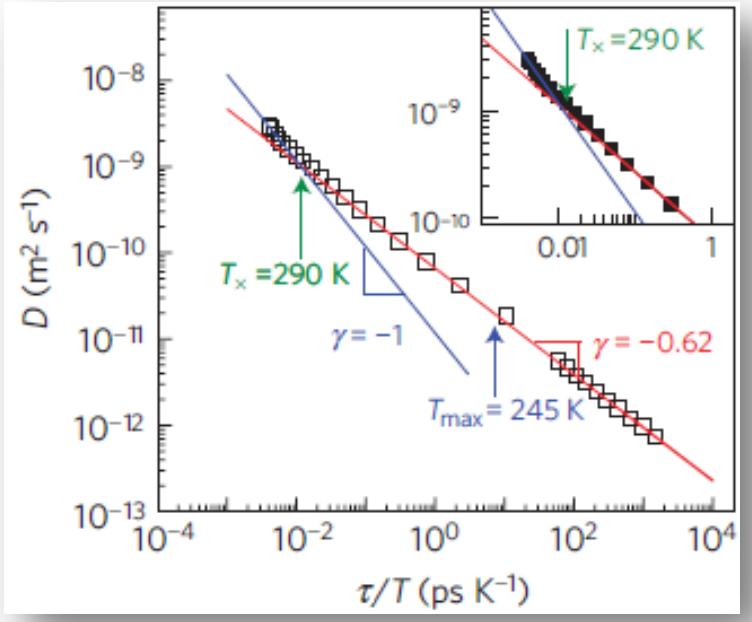
Non-monotonic decoupling

$$\frac{D\eta}{T} = const.$$

$$D: \ (\tau / T)^{-\zeta}$$

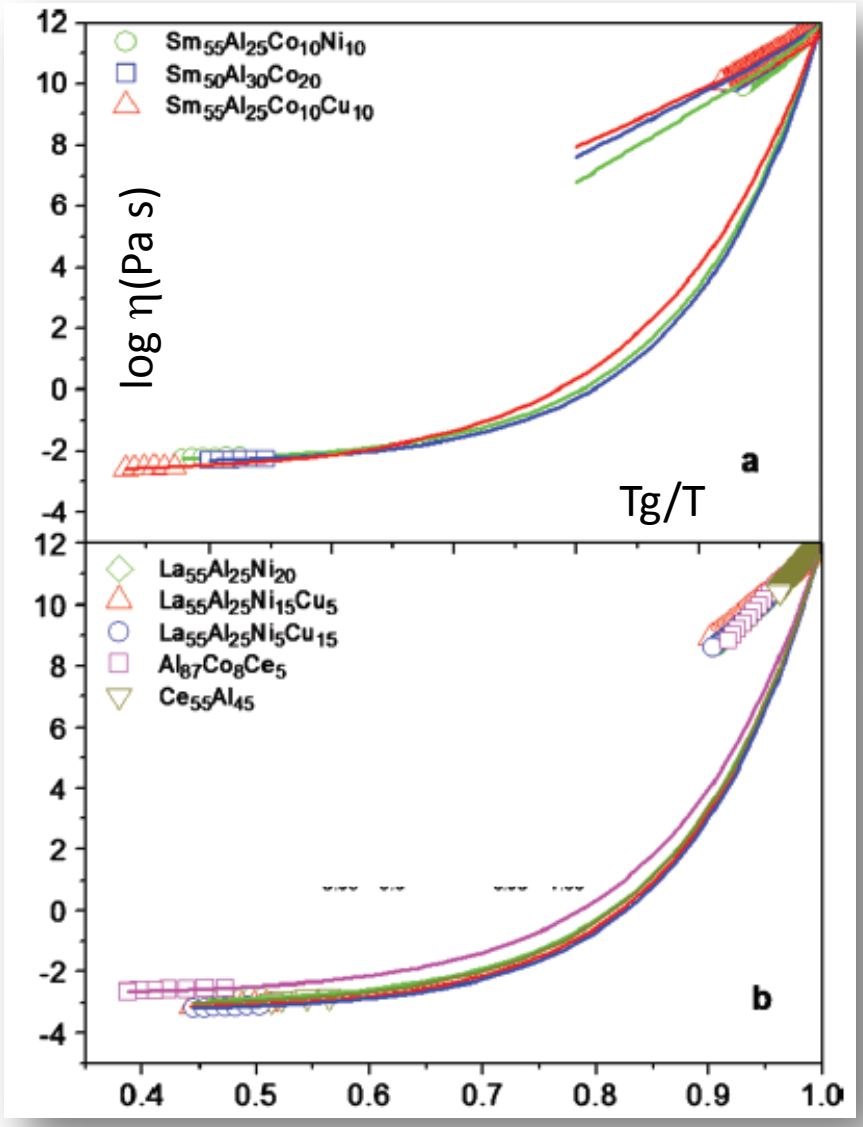


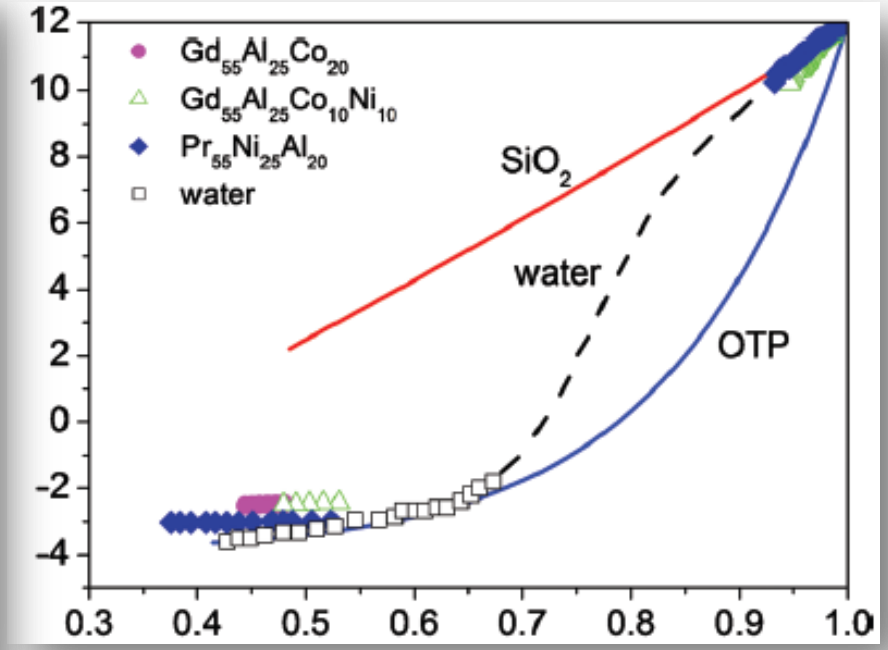
S. Chen et al. PNAS 103, 12974 (2006).



L. Xu et al. Nature Phys. 5, 565 (2009).

Metallic glass-forming liquids: Non-Arrhenius to Arrhenius crossover





C. Zhang et al J. Chem. Phys. 133, 14508 (2010)

FSC: Theoretical Scenario

➡ A possible scenario for FSC is predicted by the extended mode-coupling theory(MCT) for glass transition.
S-H Chong et al, J. Phys.: Condens. Matter 21, 504101 (2009).

⇒ Extended MCT predicts a dynamic crossover in the τ_α and D_s as a general implication of the structure of its equations of motion.

⇒ The crossover occurs near the critical temperature T_C of the idealized MCT.

⇒ It is attributed to the change in the diffusion process from that governed by "cage effect" to that dominated by "hopping" process.

⇒ The theory provides a possible explanation of the FSC observed in a variety of glass-forming systems in which the existence of the Widom line (as in case of water) is unlikely.

⇒ It also predicts that SE relation breaks down in different ways on the fragile and strong sides.

FSC: Theoretical Scenario

➡ A theory based on propagation of elastic waves.
K. Trachenko and V. V. Brazhkin, J. Phys.: Condens. Matter 21, 425104(2009).

$\Rightarrow$ Large-scale cage rearrangement due to the atomic jump induces a propagating high-frequency wave.

$\Rightarrow$ The wave propagates the volume expansion due to anharmonicity of the interaction potential.

$\Rightarrow$ The effect is to create a dynamic compressive stress which slows down relaxation of other events.

$\Rightarrow$ The range of propagation of these waves increases with liquid relaxation time.

$\Rightarrow$ It predicts a crossover from the VFT to a more Arrhenius-like relaxation at low temperature.

FSC: Theoretical Scenario

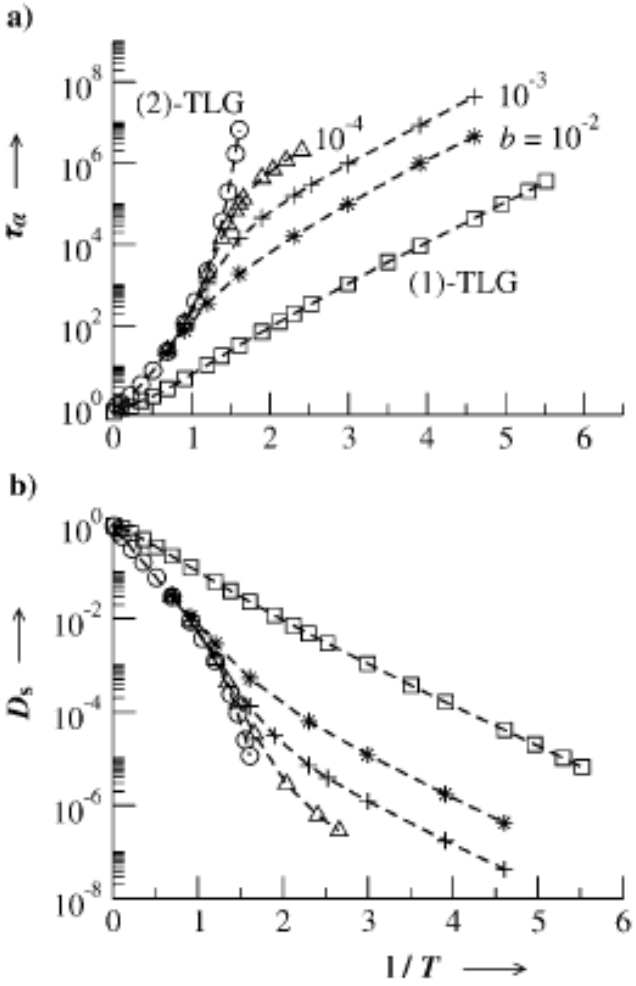
➡ FSC Crossover in a Kinetically Constrained Lattice Gas.
A. C. Pan, J. P. Garrahan and D. Chandler
Chem. Phys. Chem. 6, 1783 (2005).

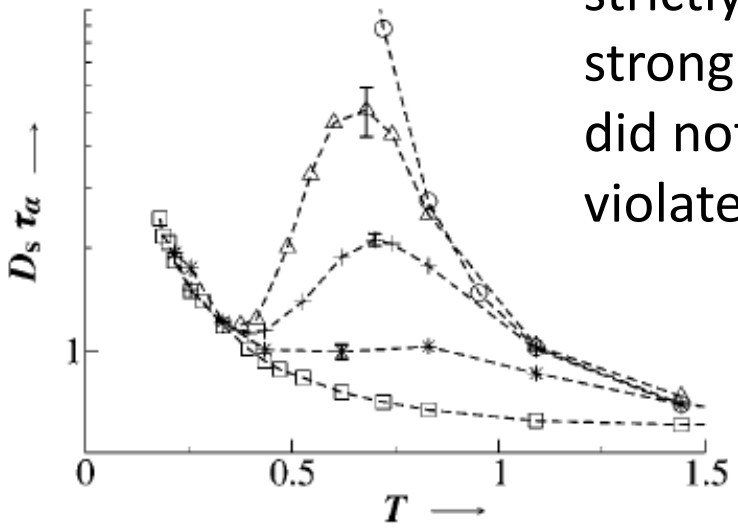
Triangular lattice gas model

➔ Non-monotonic decoupling of D_s and τ_α

➔ Systems with lower crossover temperatures(T_x) will exhibit a larger decoupling extremum during a FSC.

➔ The trend is only strictly true if strong glass formers did not themselves violate SE.





FSC : A case for binary bulk metallic glass-forming liquid $Cu_{64.5}Zr_{35.5}$

➡ Bulk glass-formation despite being simple(fragile) compared to multicomponent systems

➡ Bulk glass-formation is sensitive to composition.
Critical casting thickness : $Cu_{64}Zr_{36} \rightarrow$ 2mm
$Cu_{66}Zr_{34} \rightarrow$ 0.5 mm

D. Xu et al, Acta Mater. 52, 2621(2004).

➡ Key observations/findings of investigations on Structure, Dynamics & Thermodynamics in the supercooled region

$\Rightarrow$ Rapid evolution of short- and medium-range icosahedral ordering

$\Rightarrow$ Evolution of a network of interpenetrating icosahedra

$\Rightarrow$ Drastic slowdown of dynamics (super-Arrhenius increase in τ_α)

$\Rightarrow$ Faster increase in excess specific heat compared to strong system and a peak in C_p

➡ A debatable question is:
Can short and medium-range icosahedral ordering & its effect on dynamics explain good GFA ?

➡ FSC provides a possible explanation for good GFA

Is there an underlying thermodynamic event?

Classical MD investigations

➡ **System size :** Total No. of atoms = 10976

➡ **Interaction potential:** A semi-empirical Finnis-Sinclair type Embedded Atom Model(EAM)potential

M. I. Mendelev et al J. Appl. Phys. 102, 43501 (2007).

➡ **Simulation protocol**

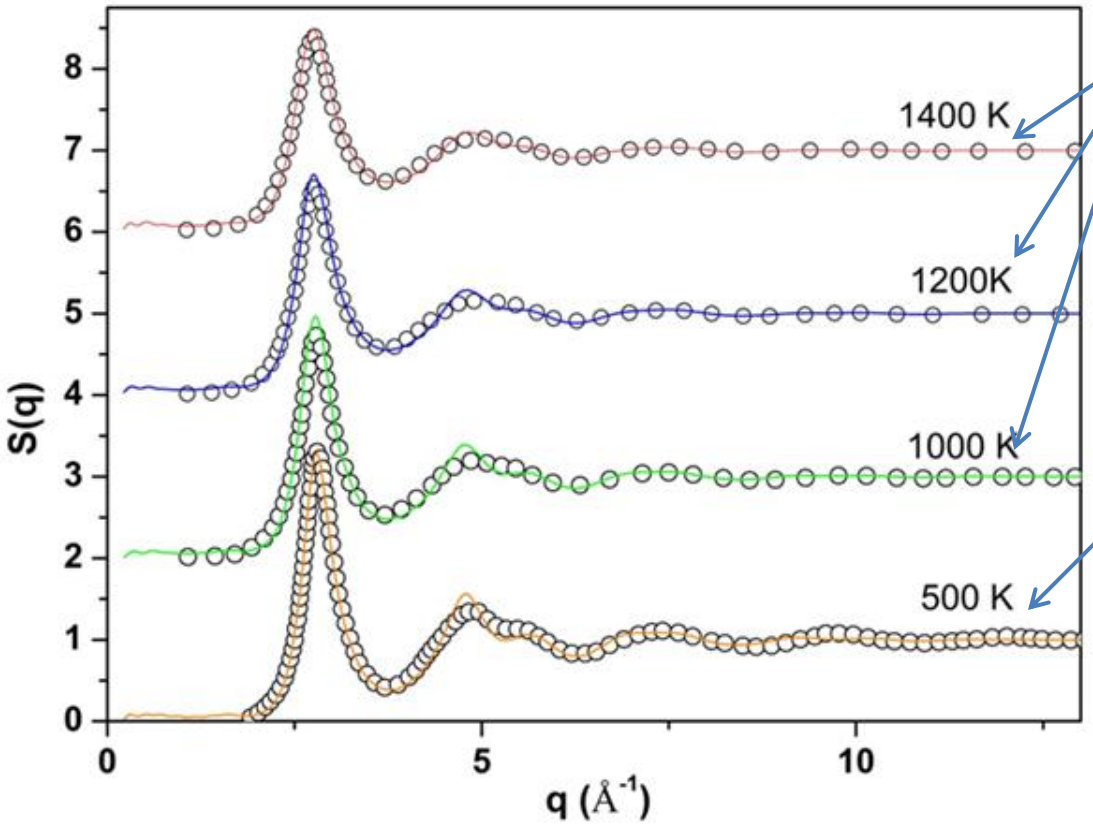
⇒ Generation of equilibrated & homogenized liquid alloy configuration at 2000 K.

⇒ Quench run : 2000 K to 300 K Cooling rate: 0.1 K/ps

⇒ Equilibration run: Configuration recorded were thoroughly equilibrated for simulation time upto 50 ns

➡ All simulations were performed at zero pressure in NPT ensemble using LAMMPS code.
Time step : 1 fs

Results: Total Static Structure Factor



High energy XRD data

V. Wessels et al

Phys. Rev. B 83, 94116 (2011).

Neutron scattering data

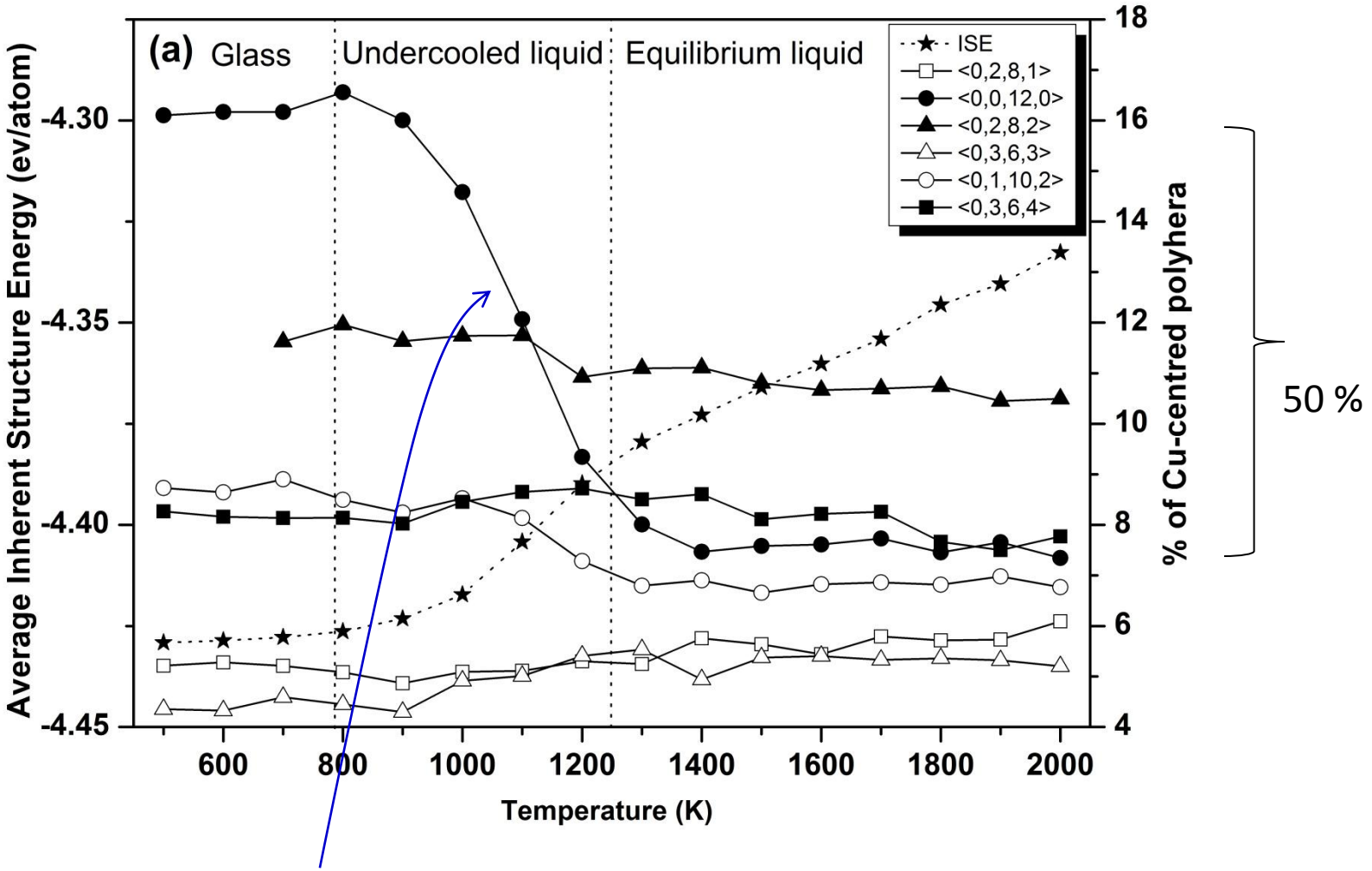
N. Mattern et al

J. Alloys Compd. 485, 163 (2009).

Solid lines represent our simulation results.

K. N. Lad, N. Jakse and A. Pasturel, J. Chem. Phys. 136, 104509(2012).

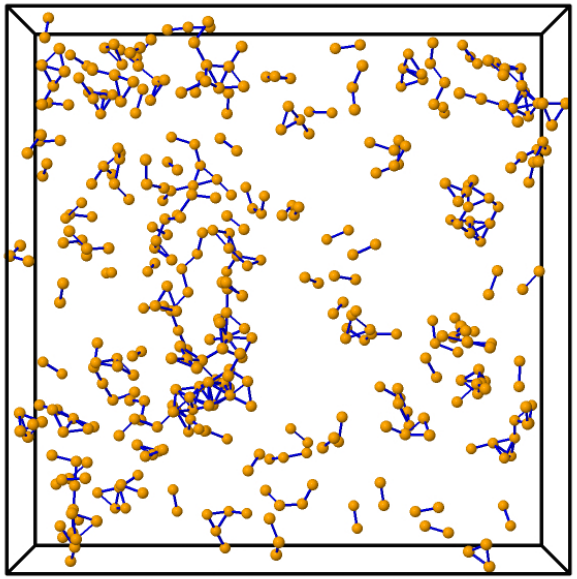
Temperature evolution of various Voronoi polyhedra types

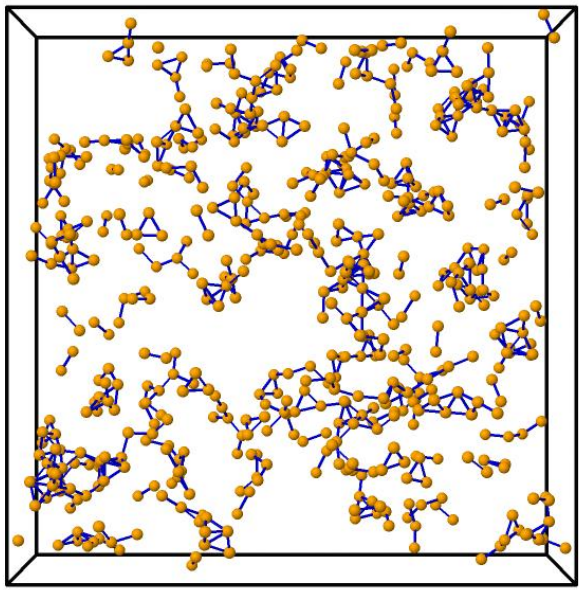


<0,012,0> shows rapid evolution

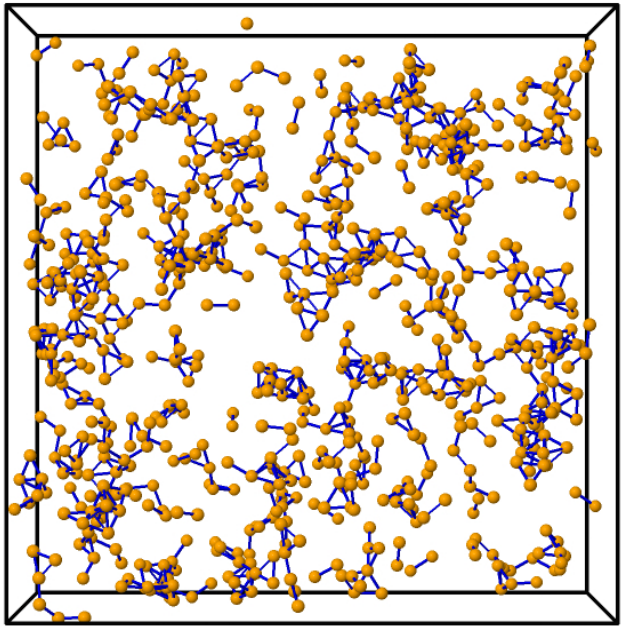
Snapshots of interconnected Icosahedral atoms

1300 K



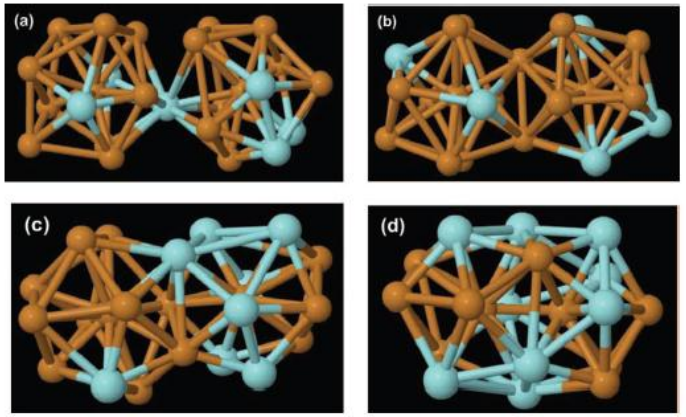


1200 K



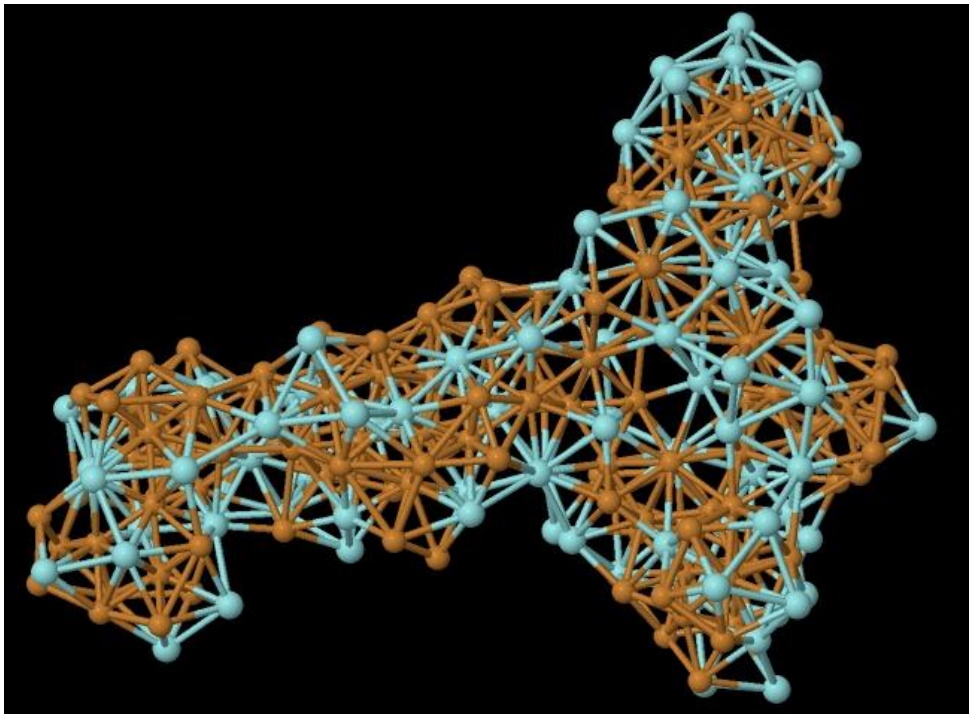
1000 K

Evolution of a network of interconnected Icosahedra and medium-range ordering

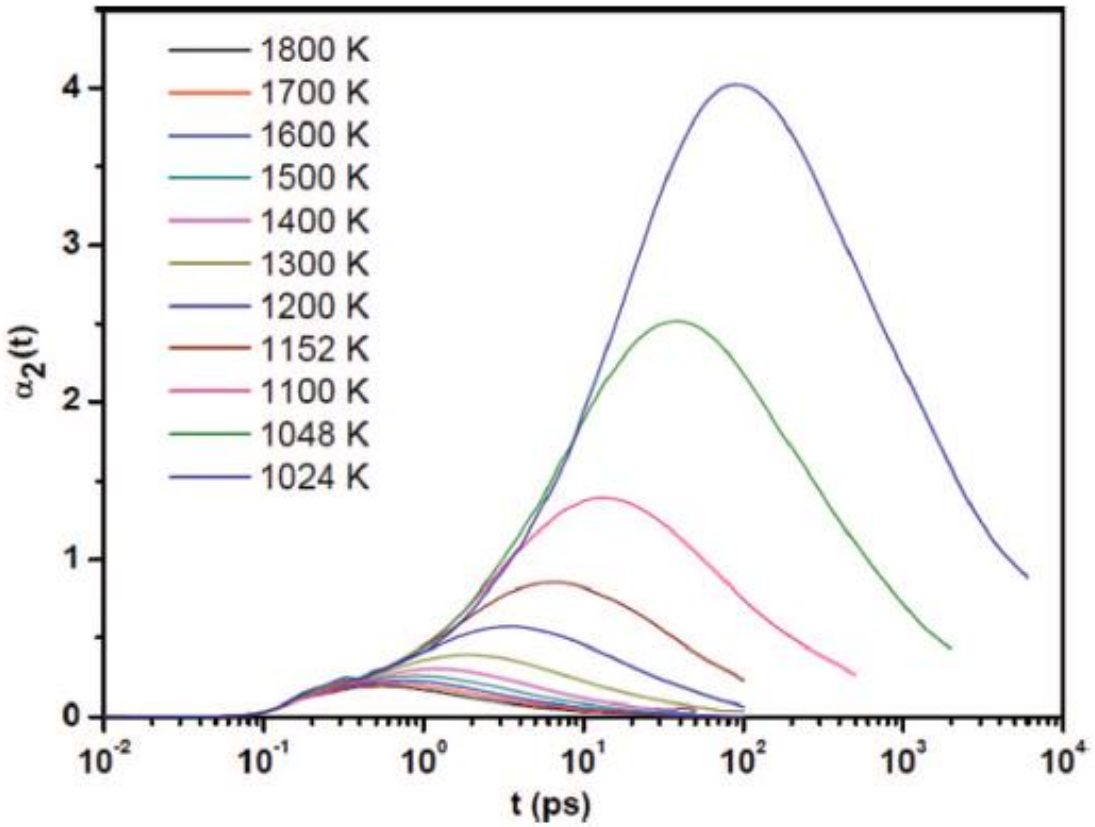


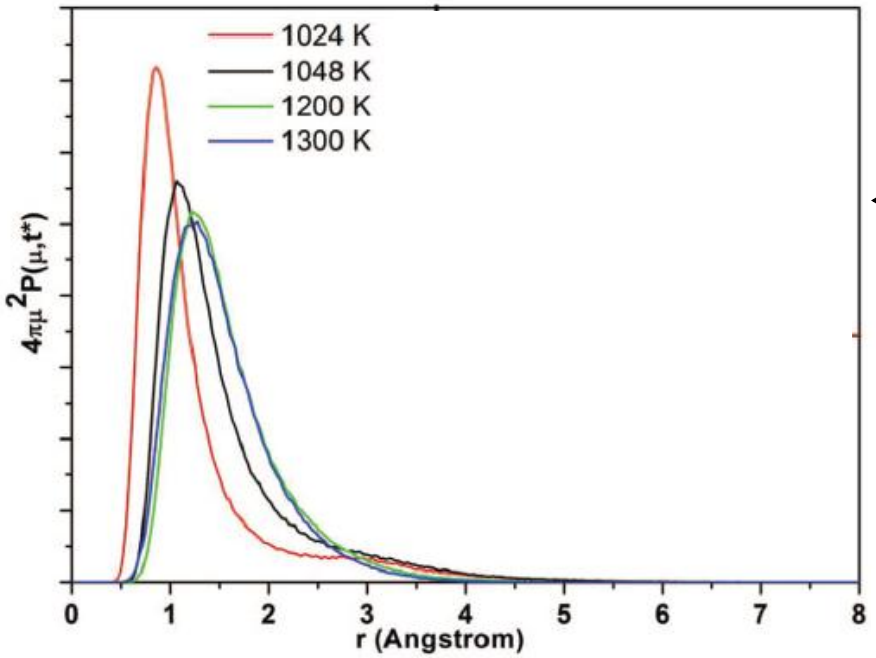
One of the longest chains of Interconnected icosahedra at 1000 K

The network contains 44 central Cu atoms with total 572 atoms and the typical length of the longest chains is ~2–3 nm.



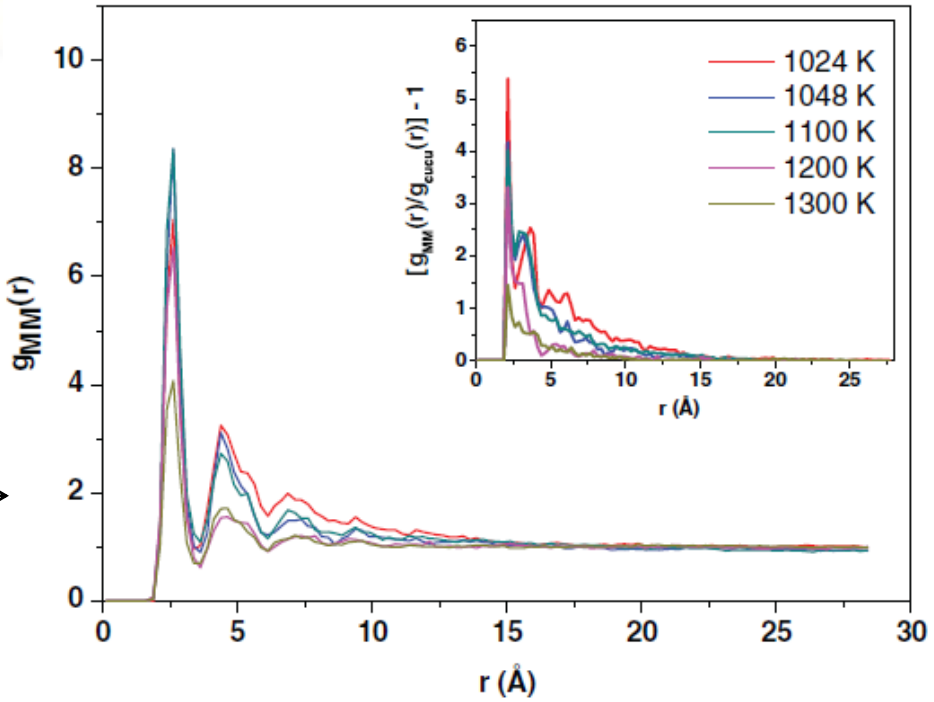
Non-Gaussian parameter and dynamic heterogeneity



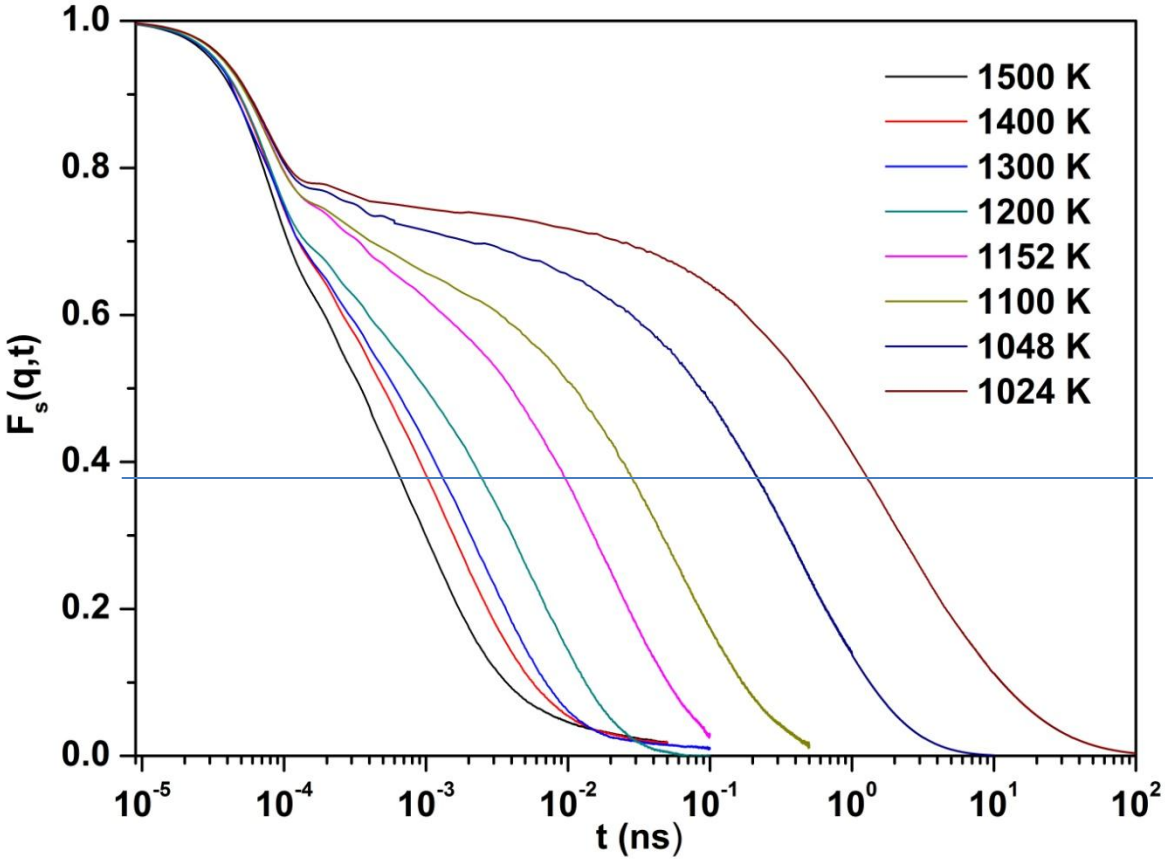


← Distribution of mobility of Cu atoms

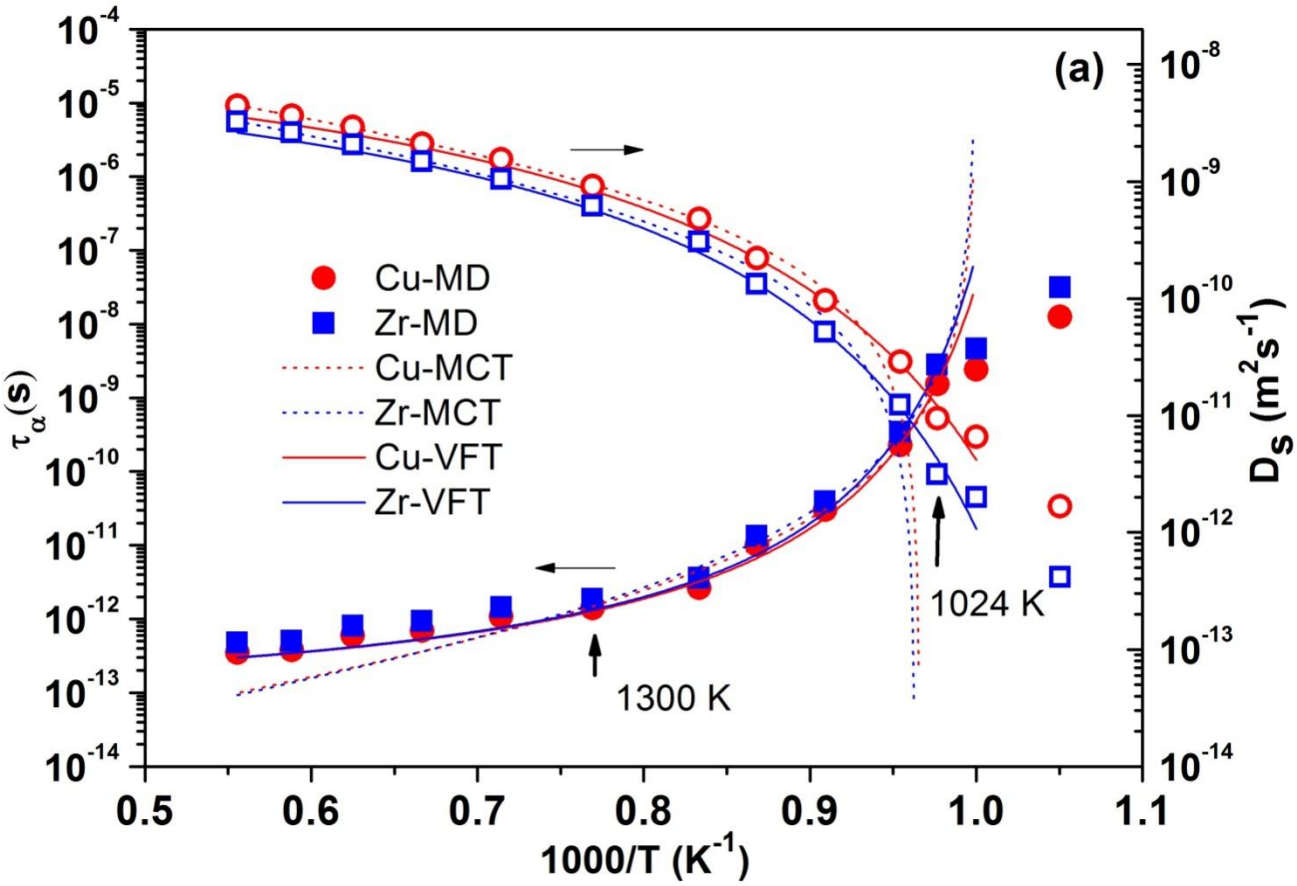
Dynamic correlation among
5% of most mobile Cu atoms →



Self-intermediate scattering function



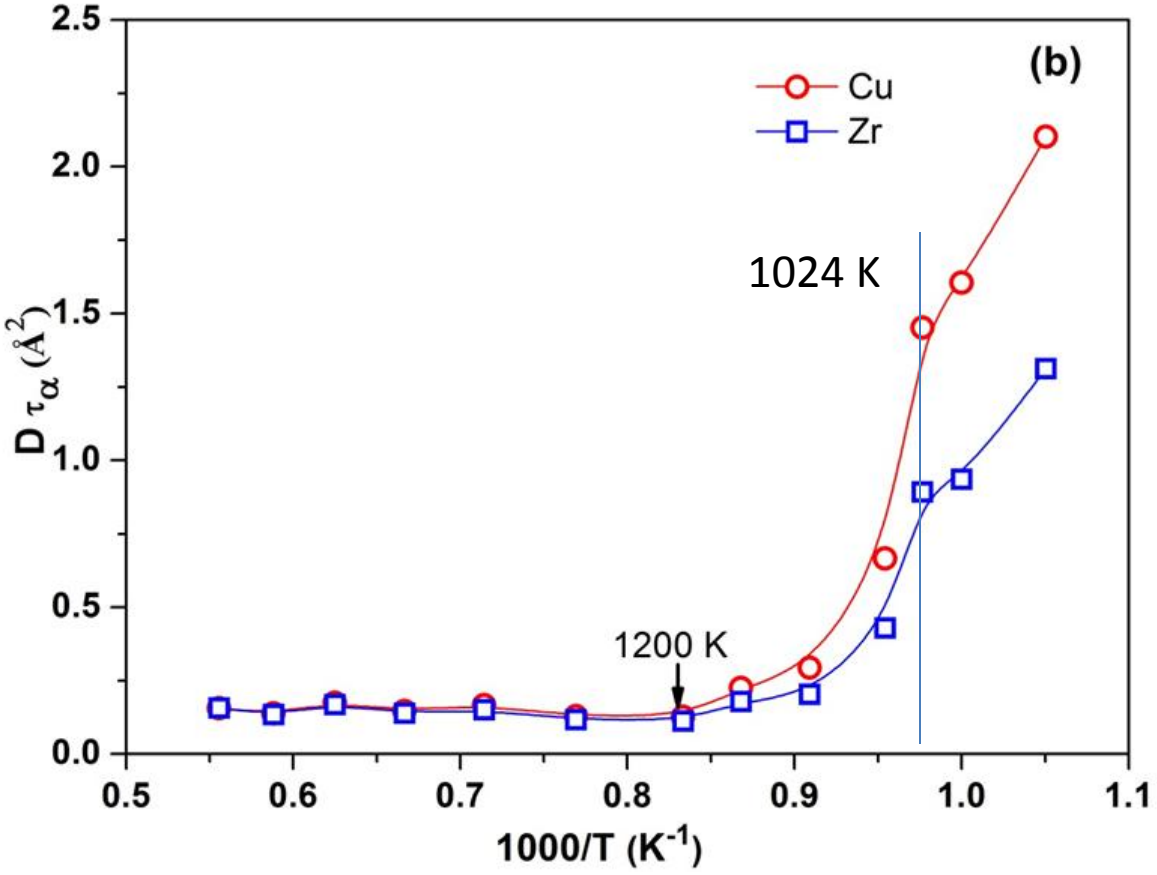
Temperature dependence of τ_α and D_s



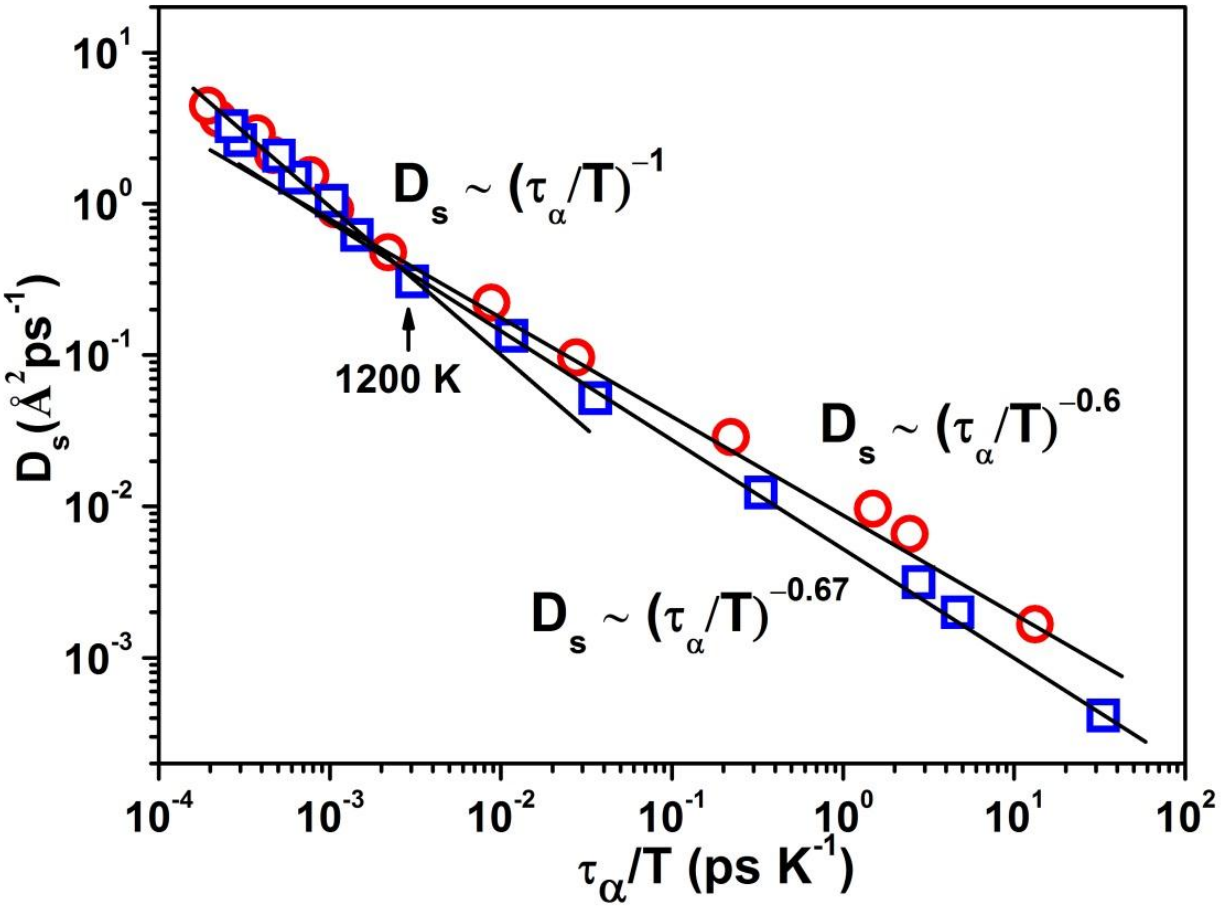
D = 5.4
T_0 = 702 K

D = 1.0
T_0 = 930 K

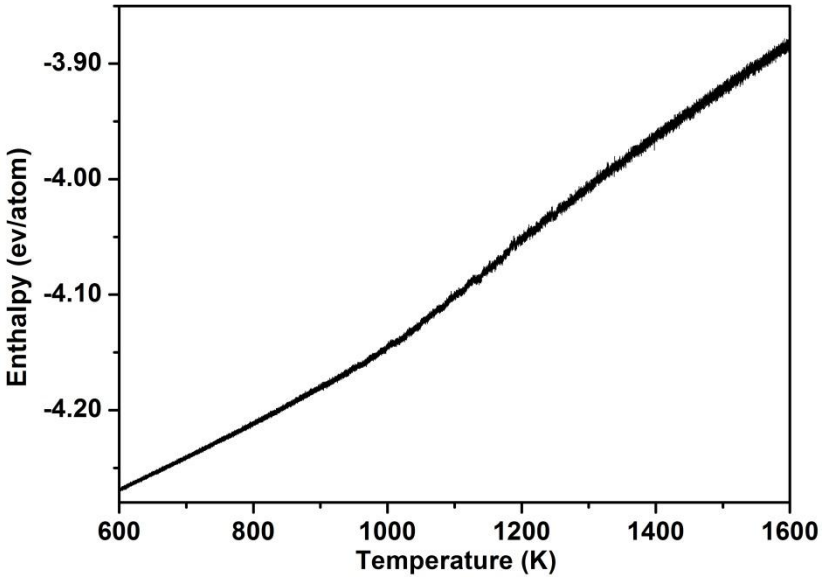
Non-monotonic decoupling of τ_α and D_s

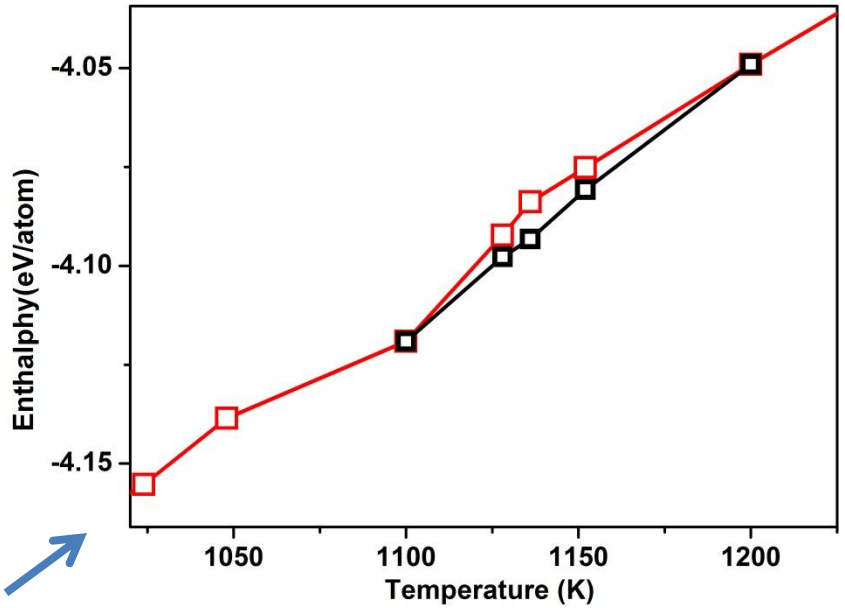


SE to FSE crossover



Observation of a weak first-order transition



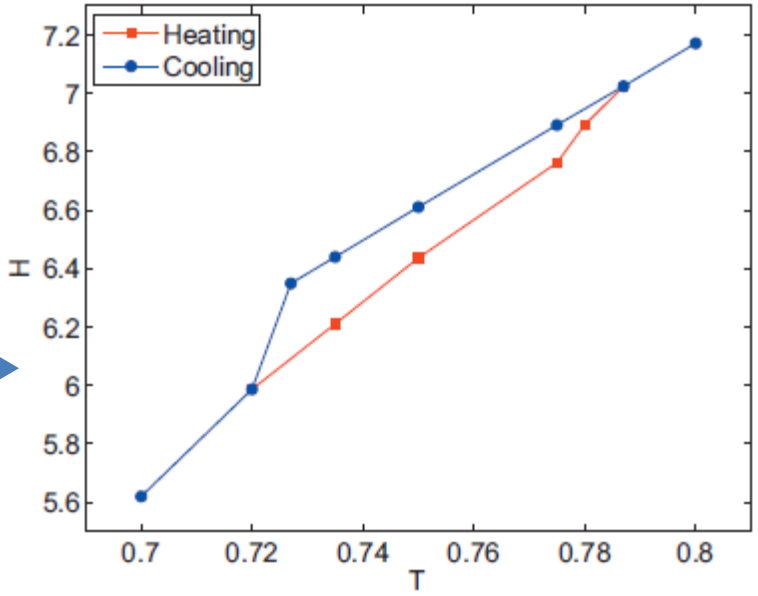


→A small but noticeable discontinuous drop in enthalpy.

→ Hysteresis behaviour along cooling and heating paths.

First-order LL transition in a model Monatomic metallic glass-former

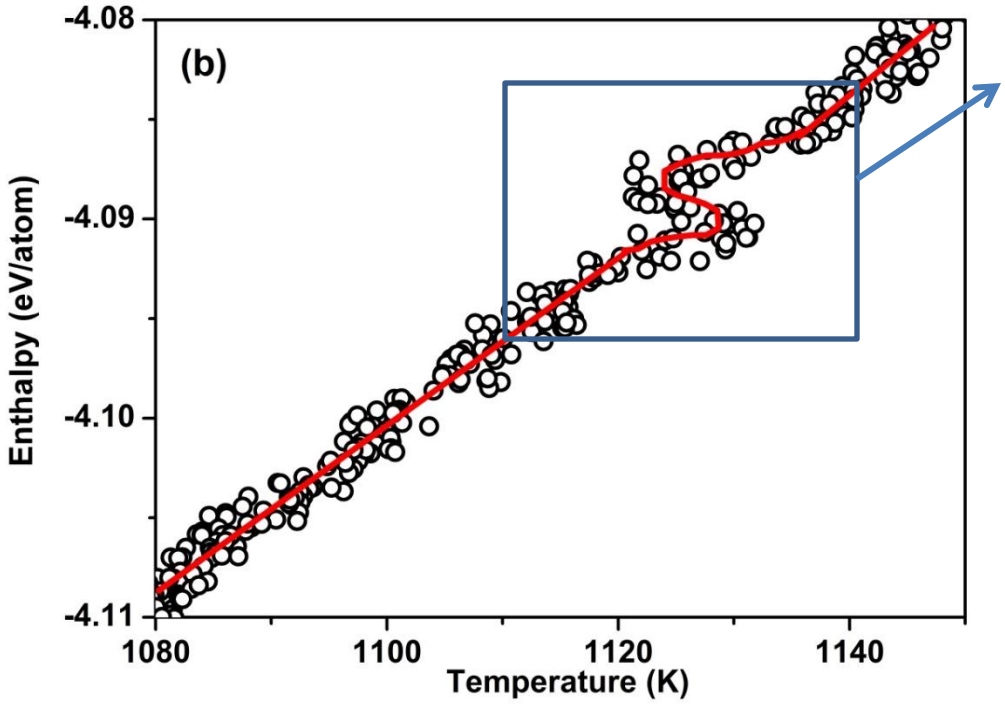
M. Elenius, T. Oppelstrup, and M. Dzugutov J. Chem. Phys. 133, 174502 (2010).



NPH run to confirm thermodynamic event

The effect of transition is not visible in static structure factor.

The enthalpy changes are relatively small.



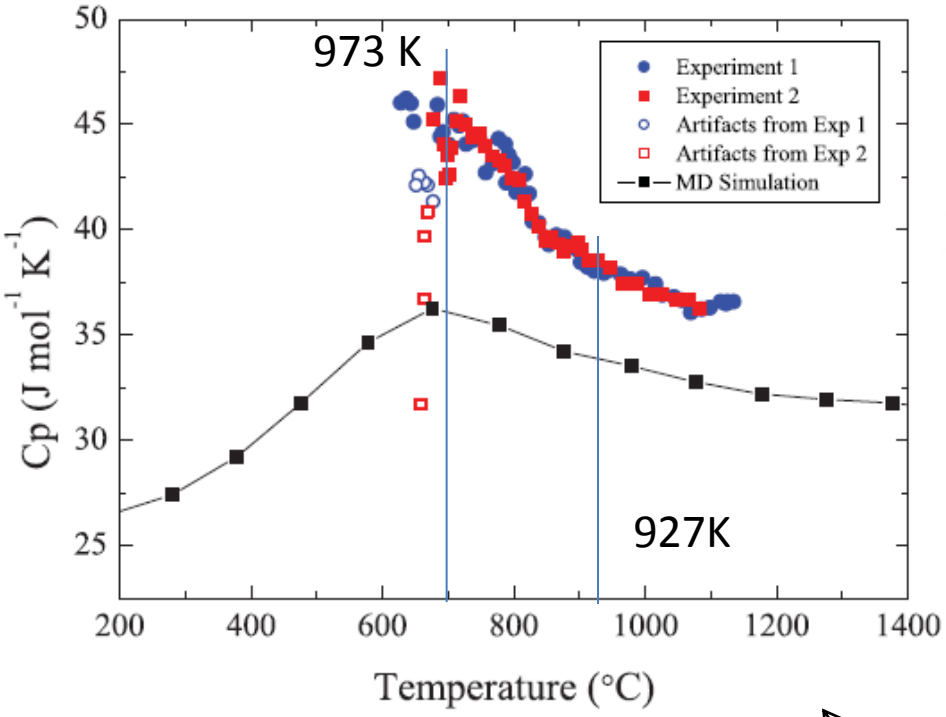
A non-monotonic change in H with T below 1140 K coincides with the discontinuous change in equilibrium enthalpies.

It clearly signifies a weak first-order phase transition.

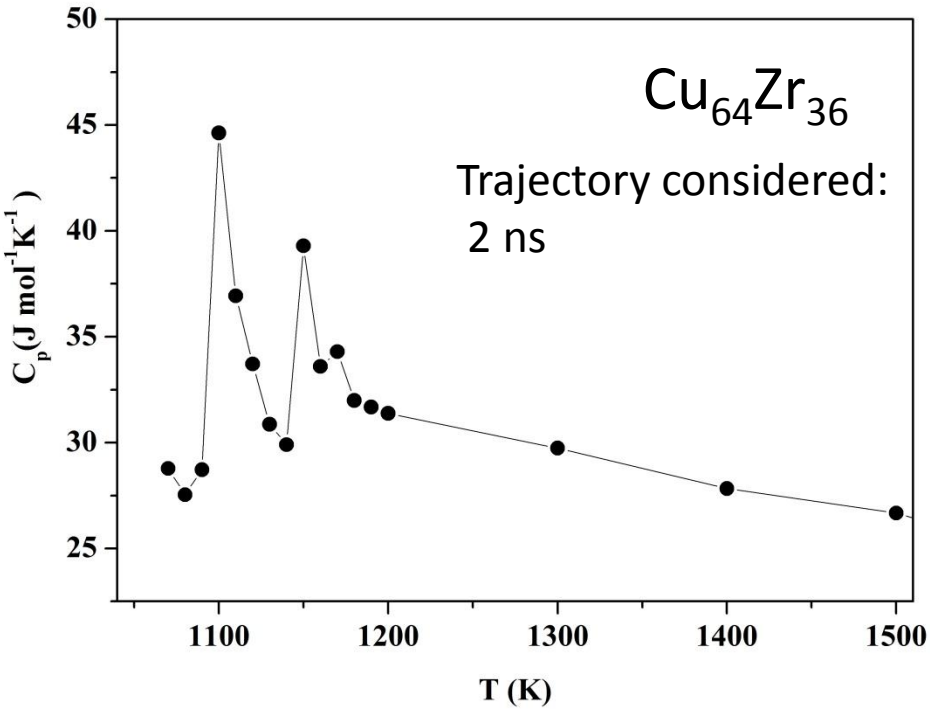
Specific heat peak

$$k_B T^2 C_p = \langle H^2 \rangle - \langle H \rangle^2$$

$Cu_{46}Zr_{54}$



MD results(unpublished)



Onset 75 °C below T_l

465 °C above T_g

V. Wessels et al
Phys. Rev. B **83**, 94116 (2011)
Phys. Rev. B **85**, 66102 (2012)

Attributed to rapid chemical & Topological ordering

Possibility of first as well as second order phase transition is ruled out.

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  (SIMAP Lab, Grenoble,France)