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Glass Transition Studied by Molecular Dynamics Simulations

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Glasses are nonequilibrium states

History dependence

$$U \neq U(T, P)$$

but

$$U = U(T, P, \{history\})$$

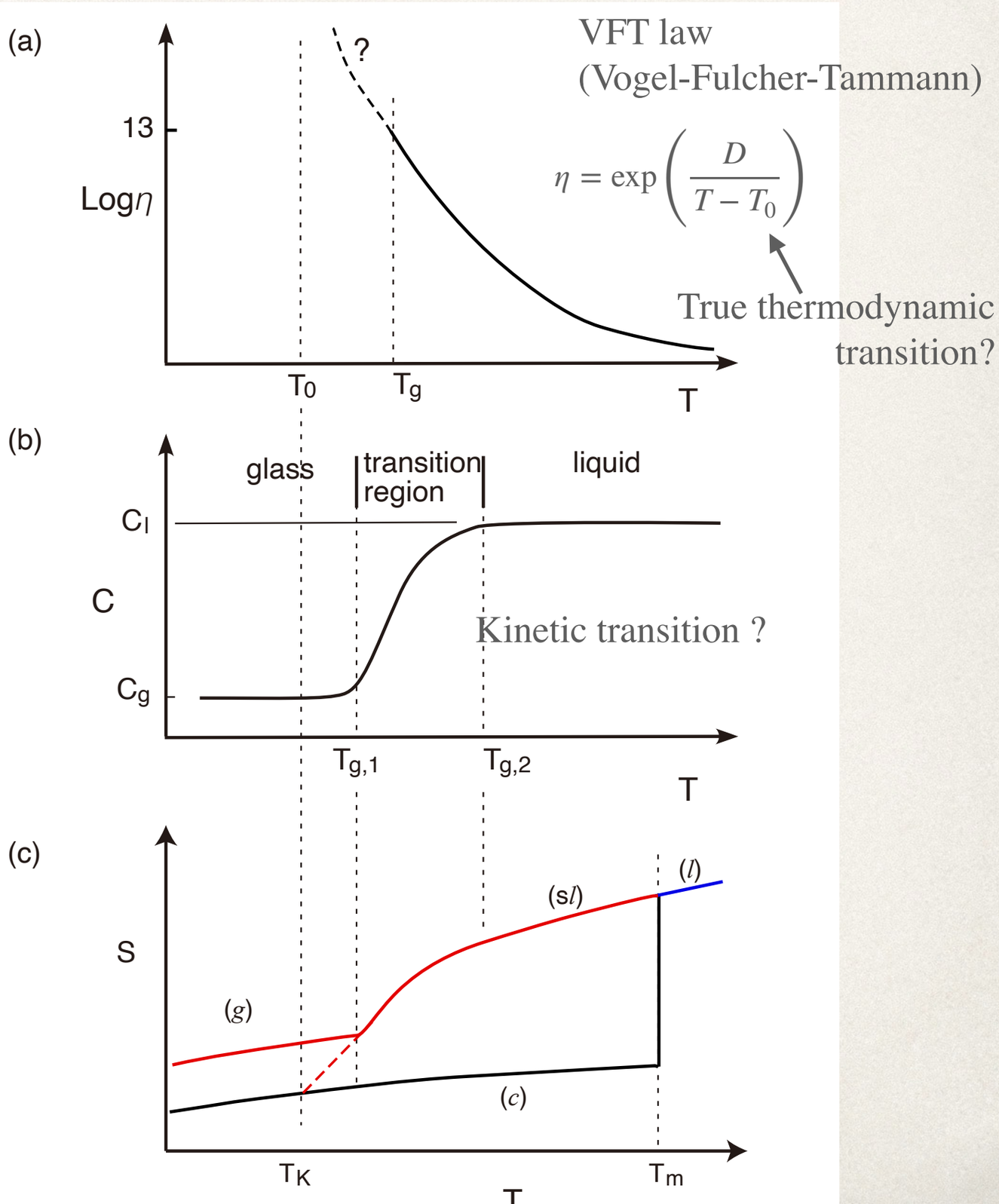
- Memory effect
- Aging phenomena
- Rejuvenation

in DFT

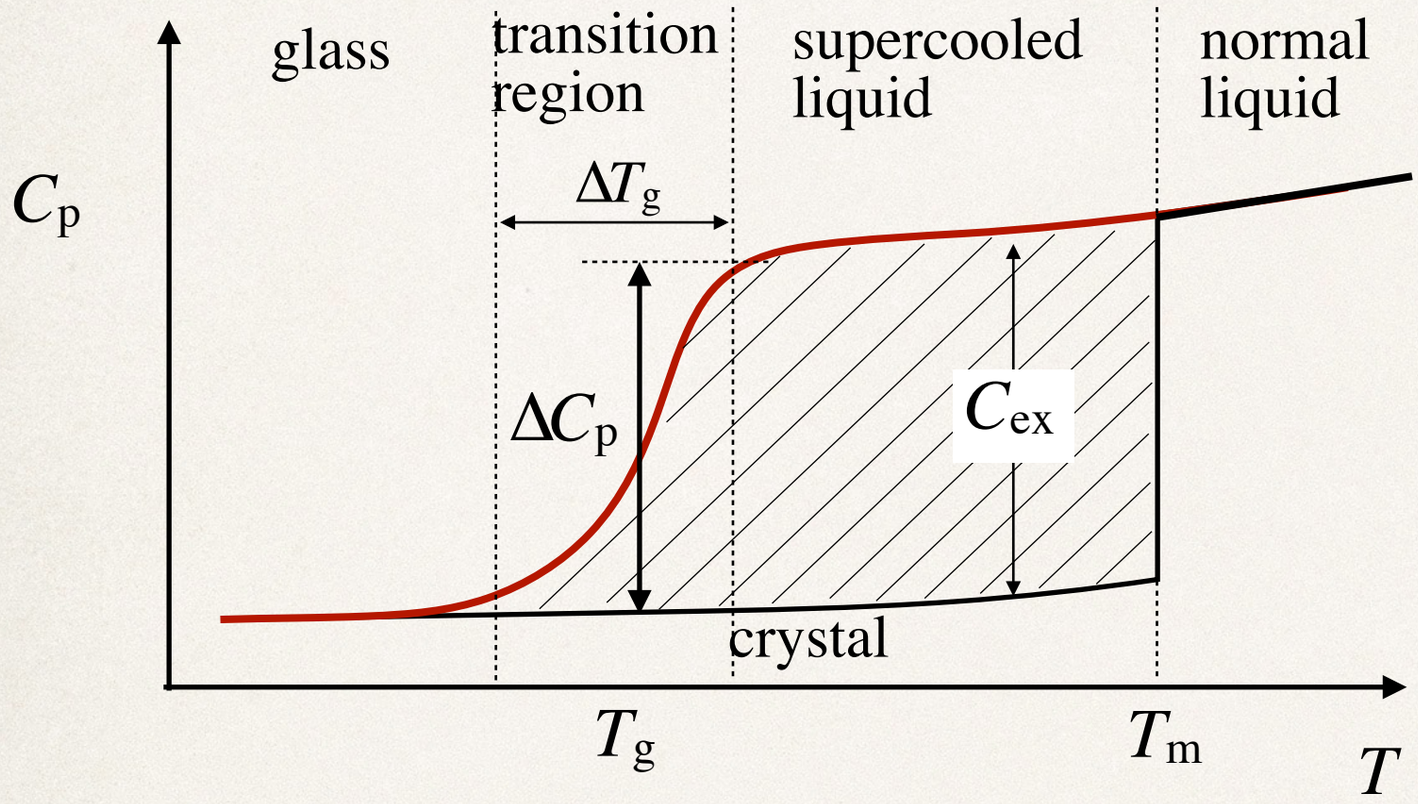
$$U = \bar{E}(T, P, \{\bar{\mathbf{R}}_j\})$$

K.S, J. Phys. Commun. **4**, 085015 (2020)

J. Phys. Commun. **5**, 015004 (2021)



Nature of Glass Transition



Absence of latent heat L

no first-order transition

Jump at T_g

$$\Delta C_p = C_p^{(l)} - C_p^{(g)}$$

Excess specific heat

$$C_{ex} = C_p^{(l)} - C_p^{(c)}$$

Π : Prigogine-Defay (PD) ratio $\qquad \Pi = \dfrac{\Delta C_p \Delta\kappa}{TV(\Delta\alpha)^2} > 1$

$\Pi = 1$ for the second-order transition

ΔC_p Kinetic origin?

Difficulties in calculating ΔC_{p}

1. Lack of standard theory of specific heat for liquid

$$\Delta C_p = C_p^{(l)} - C_p^{(g)}$$

2. Hysteresis of *C*-*T* curve in glass transition

3. Large separation in the timescale
between glass transition and MD simulations

Glass transition time	simulation time of FP-MD
> 1 min	10 ps

Theory of specific heat

C_v: Classical limit

$\frac{3}{2}$ gas

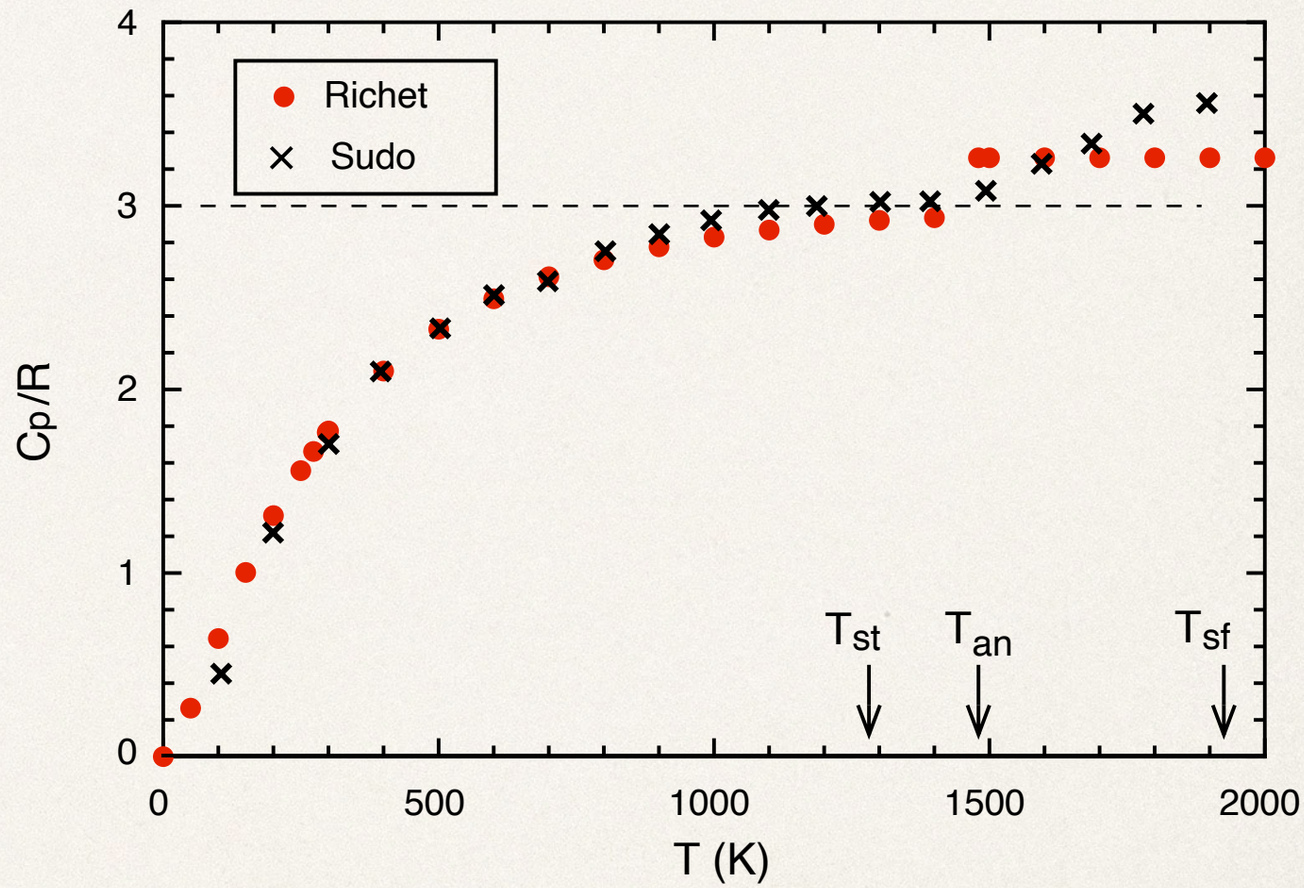
? liquid

3 solid

in k_B

per atom

Specific heat of silica glass (experiment)



P. Richet, et al., Geochim. Cosmochim. Acta **46** 2639 (1982)

H. Sudo, *Practical Manual for Amorphous Siliceous Materials*, ed H. Kawazoe (Tokyo: REALIZE, 1999), p. 83.

First-principles calculation of specific heat

Specific heat $C_x = \left(\frac{\partial U}{\partial T}\right)_X$

Microscopic energy

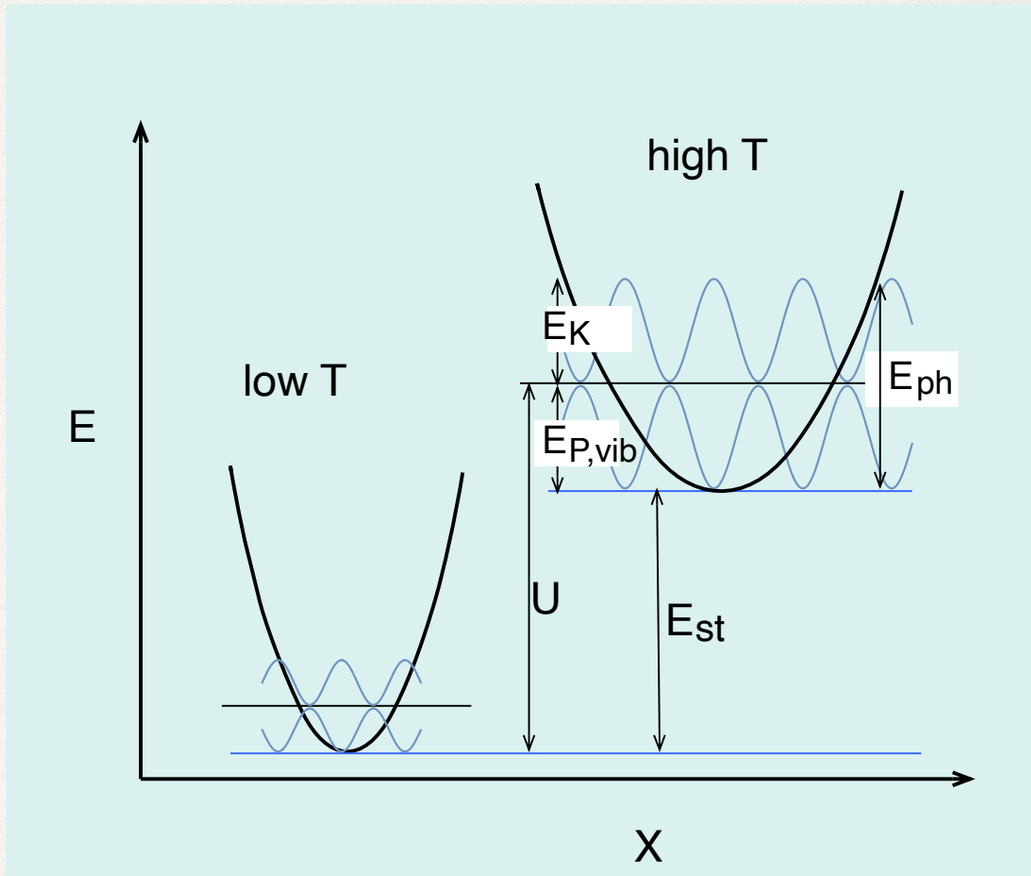
$$E_{\mathrm{tot}}(t) = E_{\mathrm{GS}}(\{\mathbf{R}_j(t)\}) + \frac{1}{2}\sum_j M_j v_j(t)^2$$

in thermodynamic equilibrium

Internal energy

$$U = \overline{E_{\mathrm{tot}}(t)} = \overline{E_{\mathrm{GS}}(\{\mathbf{R}_j(t)\})} + \frac{1}{2}\sum_j \overline{M_j v_j(t)^2}$$

$\frac{3}{2}k_{\mathrm{B}}T$



in adiabatic MD

For solids, Harmonic approx.

$$\mathbf{R}_j(t) = \bar{\mathbf{R}}_j + \mathbf{u}_j(t)$$

$$E_{\mathrm{st}}(\{\bar{\mathbf{R}}_j\}) + E_{\mathrm{ph}}(T) + E_{\mathrm{te}}(V)$$

structural part (configurational) | phonon | thermal expansion

$$C_{\mathrm{p}} = C_{\mathrm{st}} + C_{\mathrm{ph}} + C_{\mathrm{te}}$$

Phonon contribution to specific heat

For solids

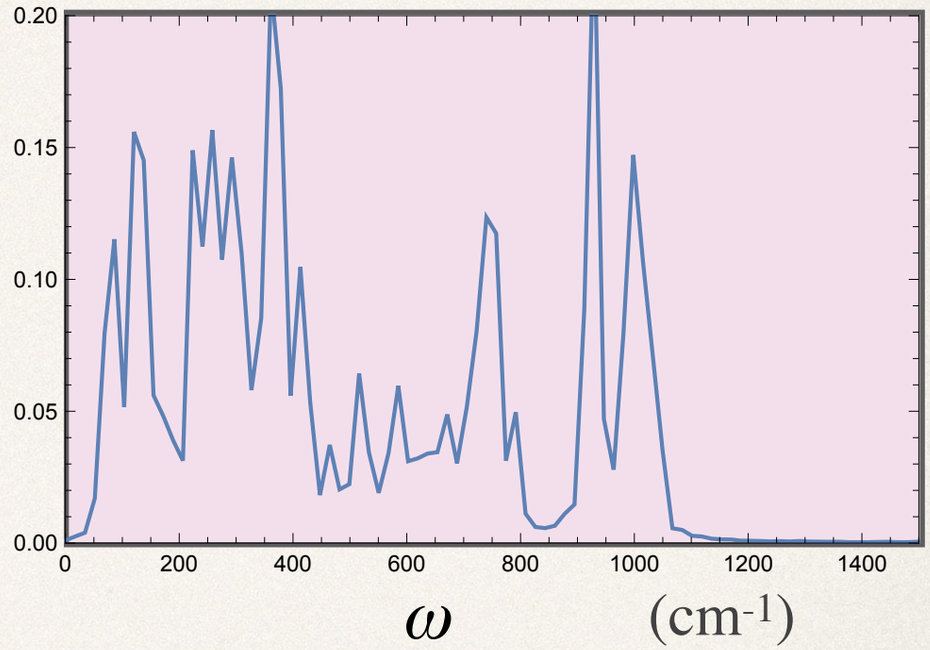
$$E_{\mathrm{ph}} = \sum_k \left(\bar{n}_k + \frac{1}{2} \right) \hbar\omega_k$$

$$C_{\mathrm{ph}}(T) = k_{\mathrm{B}} \int \left(\frac{\hbar\omega}{k_{\mathrm{B}}T} \right)^2 \frac{e^{\hbar\omega/k_{\mathrm{B}}T}}{(e^{\hbar\omega/k_{\mathrm{B}}T} - 1)^2} g(\omega) d\omega$$

$$C_p = C_{\mathrm{st}} + C_{\mathrm{ph}} + C_{\mathrm{te}}$$

- C_{st}: structural part
- C_{ph}: phonon
- C_{te}: thermal expansion

Phonon DOS of quartz



For liquids

Is the phonon-picture realistic for liquids? ⟶ No!

$$U = \overline{E_{\mathrm{tot}}(t)}$$

Effect of energy dissipation

⟶ Need of adiabatic MD simulation

Problem for liquids

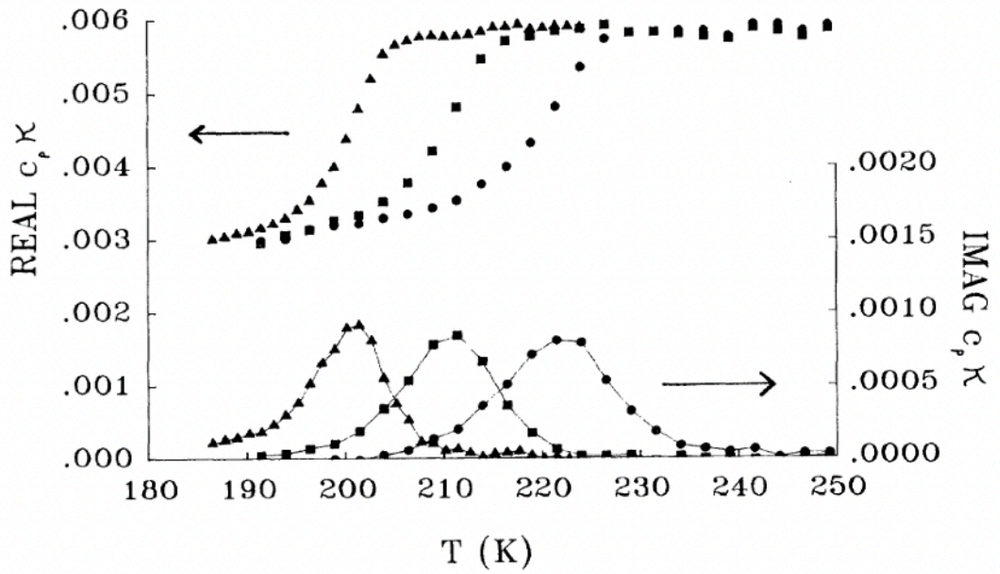
No eigenstates

$$Z = \sum_i e^{-\beta \epsilon_i}$$

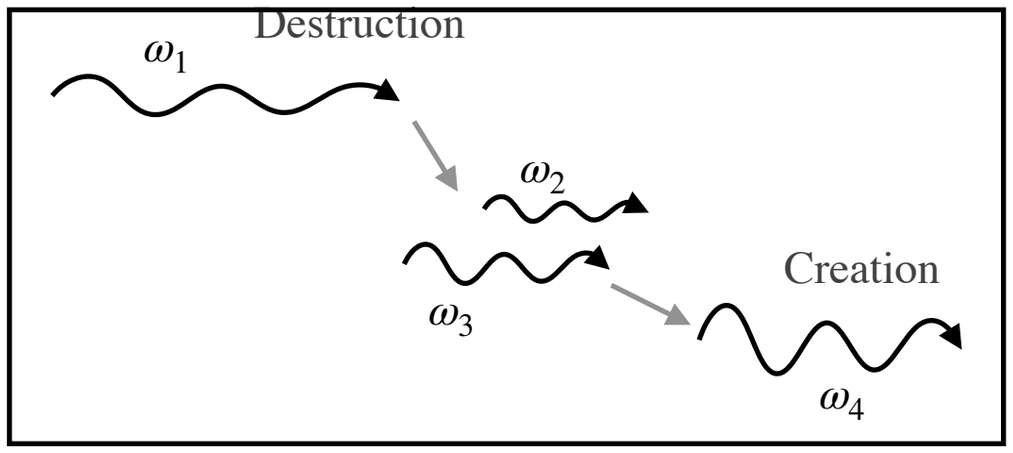
Energy dissipation determines C

Relaxation processes

$$dU(\omega) = C(\omega) dT(\omega)$$



N. O. Birge and S. R. Nagel, Phys. Rev. Lett. **54**, 2674 (1985).



$$C(\omega) = \frac{C_0}{1 - i\omega\tau_s} \longrightarrow$$

Energy dissipation

Relaxation

Adiabatic MD simulations automatically take the energy dissipation process into account.

$$T_{\text{ini}} \xrightarrow{\text{Relaxation}} T$$

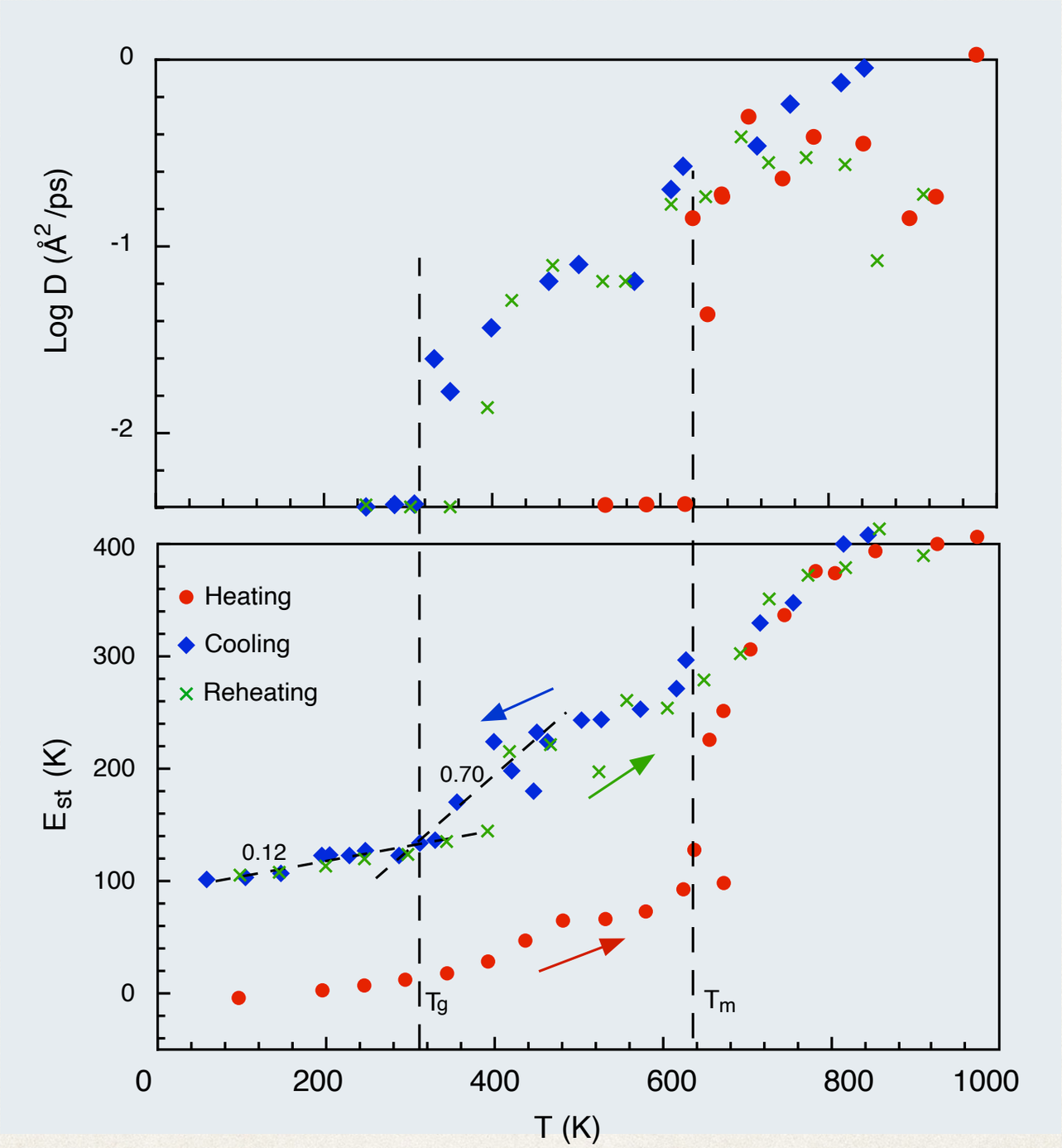
U=const

Equilibrium

Glass Transition of Glycerol

Diffusion constant

Structural energy



Exp.

$T_g = 185$ K

$\Delta C_p = 0.70\ R$

$$\Delta C_{st} = 0.58\ R$$

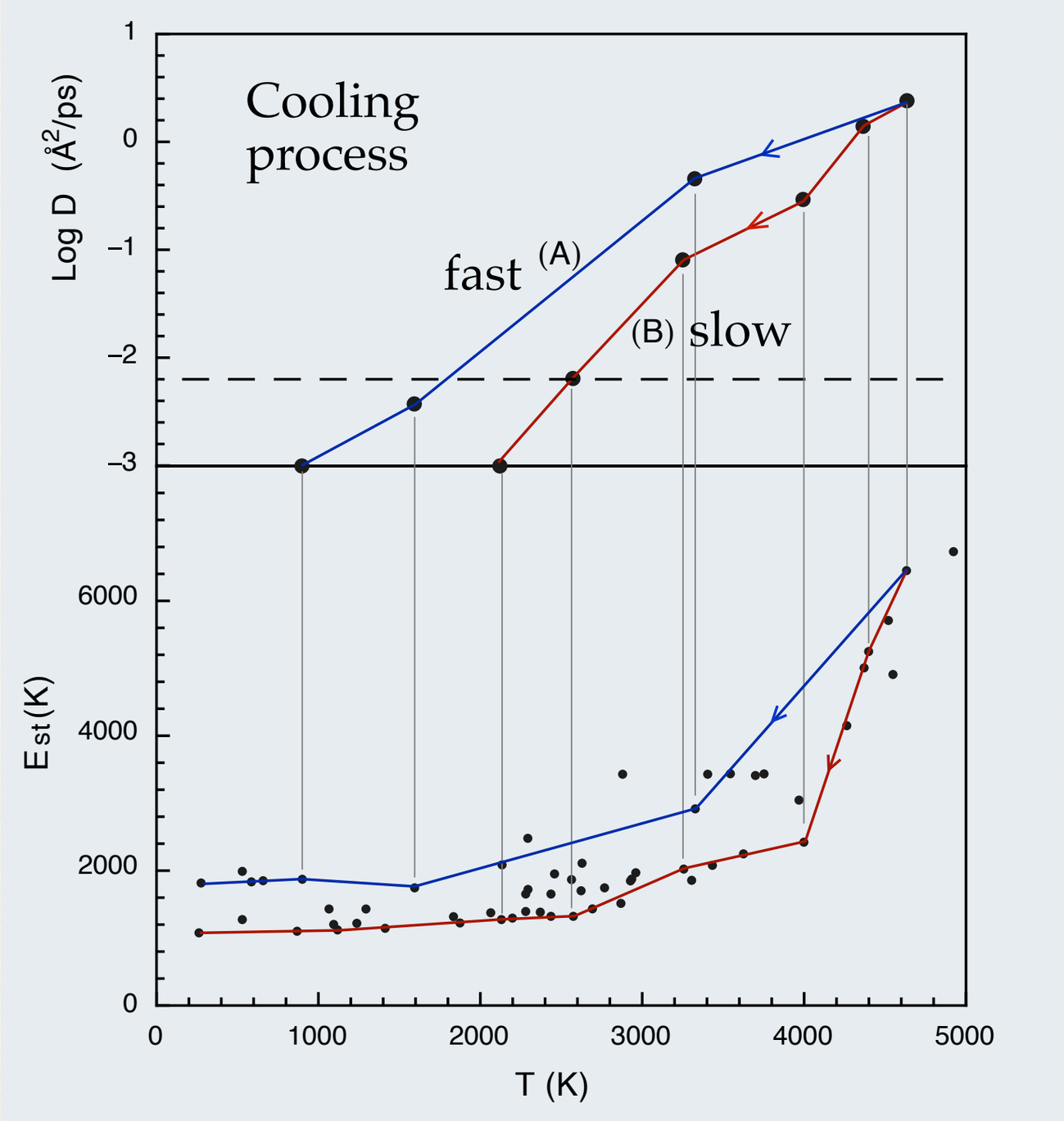
$$\approx \Delta C_p^{(exp)}$$

K. Shirai, K. Watanabe, and H. Momida, J. Phys.: Condens. Matters **34**, 375902 (2022)

Glass Transition of Silica

Diffusion constant

Structural energy



Exp.

$T_g = 1480$ K

$\Delta C_p = 0.32\ R$

$\Delta C_{st} = 0.5\ R$

K. Shirai, *et al*., J. Phys.: CM **35** 505401 (2023)

Nature of Glass Transition

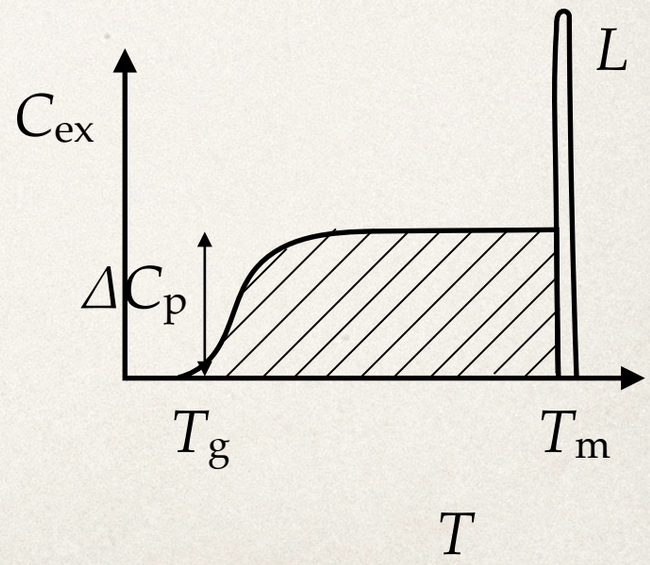
$$\Delta C_p \approx \Delta C_{\mathrm{st}}$$

For Silica glass

more than 99% of ΔC_p comes from ΔC_{st}

Almost all the part ΔC_p is determined by the structural change.

$$\Delta C_p (T_m - T_g) \approx L$$



essentially the structural transition

but the randomness breaks the latent heat into the excess specific heat.

Interpretation of Prigogine-Defay ratio

$$\Pi = \frac{\Delta C_p \Delta\kappa}{TV(\Delta\alpha)^2}$$

$$C_{\text{te}} = \frac{TV}{\kappa}\alpha^2$$

$$\frac{\Delta\kappa}{\kappa} = \frac{\Delta\alpha}{\alpha}$$

$$\Pi = \frac{\Delta C_p}{\Delta C_{\text{te}}} = \frac{\text{(Change in the total energy)}}{\text{(Part of isotropic volume change)}}$$

$\Pi > 1$

There are more than one order parameters

N_{at} $\{\bar{\mathbf{R}}_j\}$

$$\Delta C_p = \Delta C_{\text{st}} + \Delta C_{\text{ph}} + \Delta C_{\text{te}}$$

$\Pi > 1$ ⟶ Structural transition

Summary

	Present results	Traditional view
Glass state	Equilibrium state $U = U(T, V, \{\bar{\mathbf{R}}_j\})$	Nonequilibrium state $U \neq U(T, V)$
ΔC_p	Thermodynamically well-defined quantity mostly determined by ΔE_{st} $\Pi > 1$	Kinetic parameter? due to order parameters
Glass transition	Structural transition	Kinetic transition

The present view for glass

The traditional view

Glass has hysteresis.

→ NEQ

Experimental fact

All solids have hysteresis.

Present theory ↓

$$U = U(T, \{\bar{\mathbf{R}}_j\})$$

All the static states of a solid are equilibrium states

frozen glass

within the time scale in which the solid maintains its current structure.

Applications

- General theory of state variables → arXiv:1812.08977
- Thermodynamic method for glass → J. Phys. Commun. **4**, 085015 (2020) **5**, 015004 (2021)
- Activation energy of GT → J. Phys. Commun. **5** 095013 (2021)
- FP-MD simulation of specific heat jump → J. Phys.: CM **34** 375902 (2022)
- FP-MD study on the Prigogine-Defay ratio → J. Phys.: CM **35** 505401 (2023)
- The third law → arXiv:2207.11421

History-dependent properties

Nonequilibrium!

$U \neq U(T, P)$

but

$U = U(T, P, \{history\})$

- Memory effect

  The Kovacs effect

- Aging phenomena

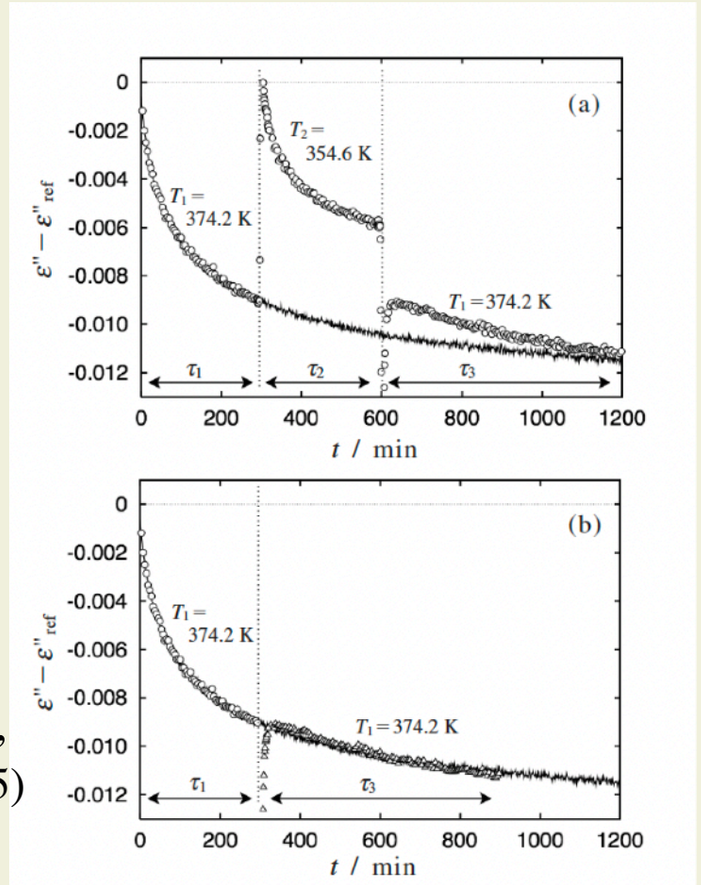
- Rejuvenation

in DFT

$$U = \bar{E}(T, P, \{\bar{\mathbf{R}}_j\})$$

K.S, J. Phys. Commun. **4**, 085015 (2020)
J. Phys. Commun. **5**, 015004 (2021)

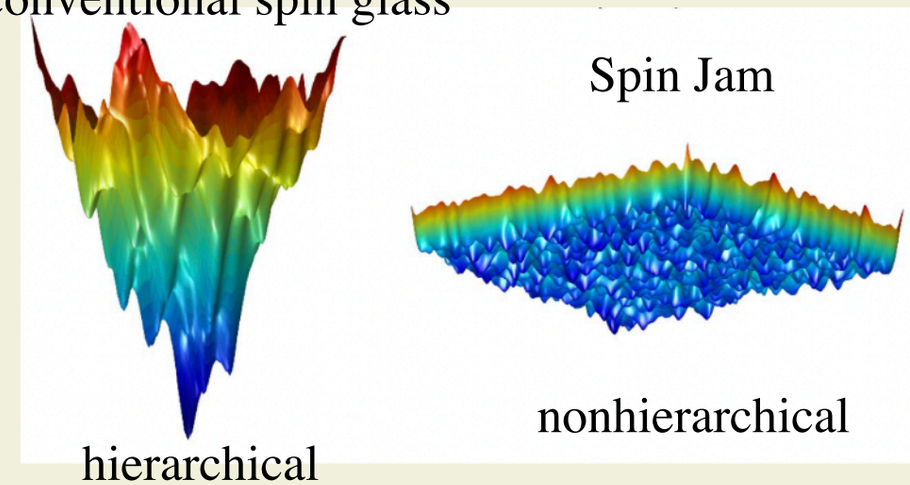
Memory and rejuvenation in polymethyl methacrylate



K. Fukao and A. Sakamoto,
Phys. Rev. E **71**, 041803 (2005)

Energy landscape of spin glass

Conventional spin glass



A. M. Samarakoon, *et al*., Proc. Natl. Acad. Sci. U.S.A. **113** 11806 (2016)