Frequency-dependent specific heat of supercooled liquids and glasses

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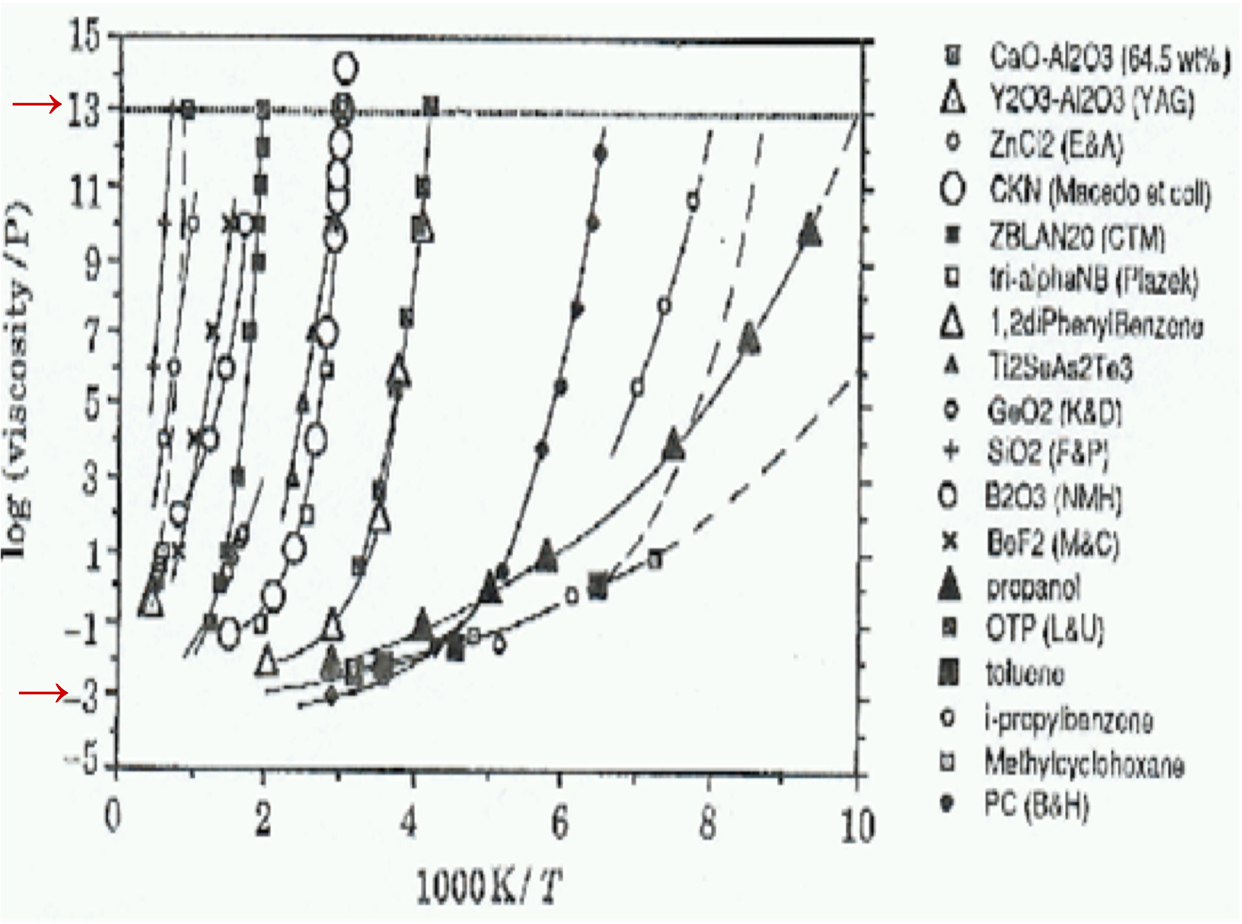
Erlangen, 12-05-2019
School Thermodynamics of Glasses

glassforming liquids: shear viscosity

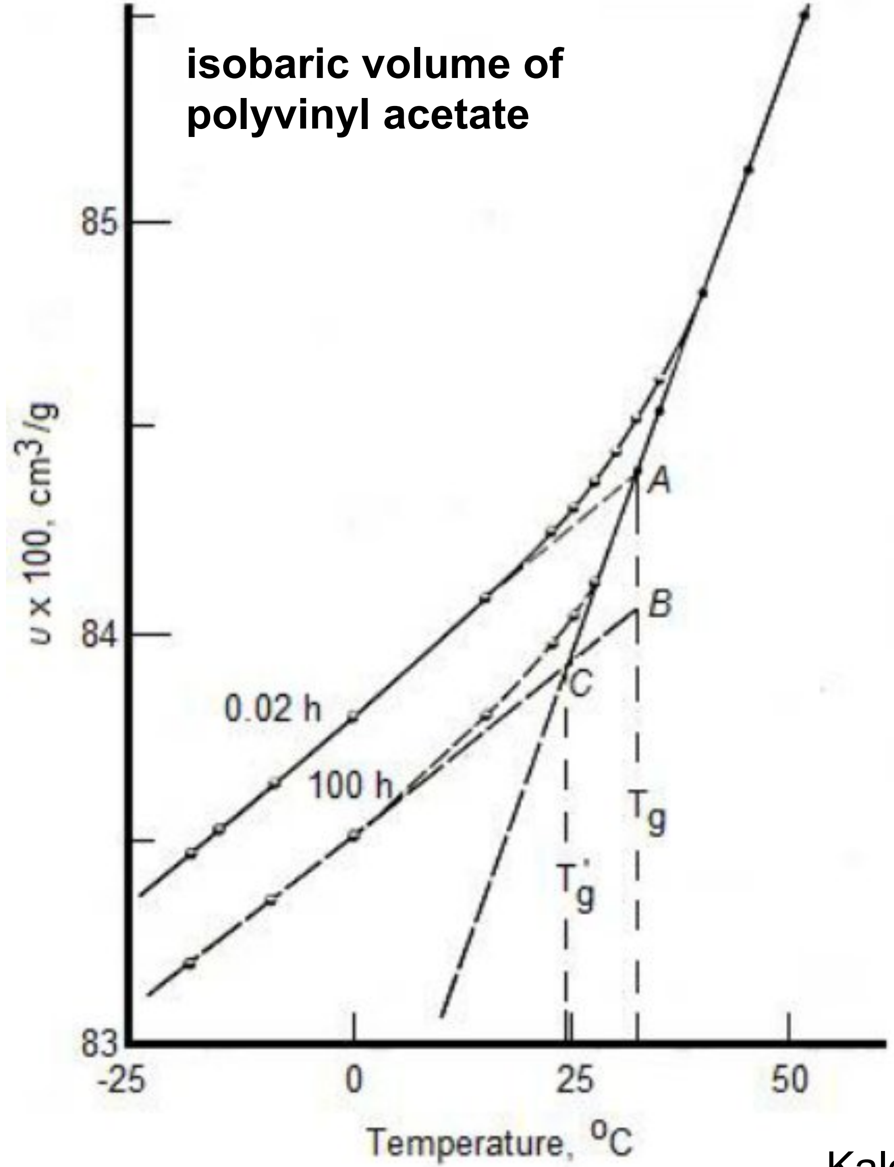


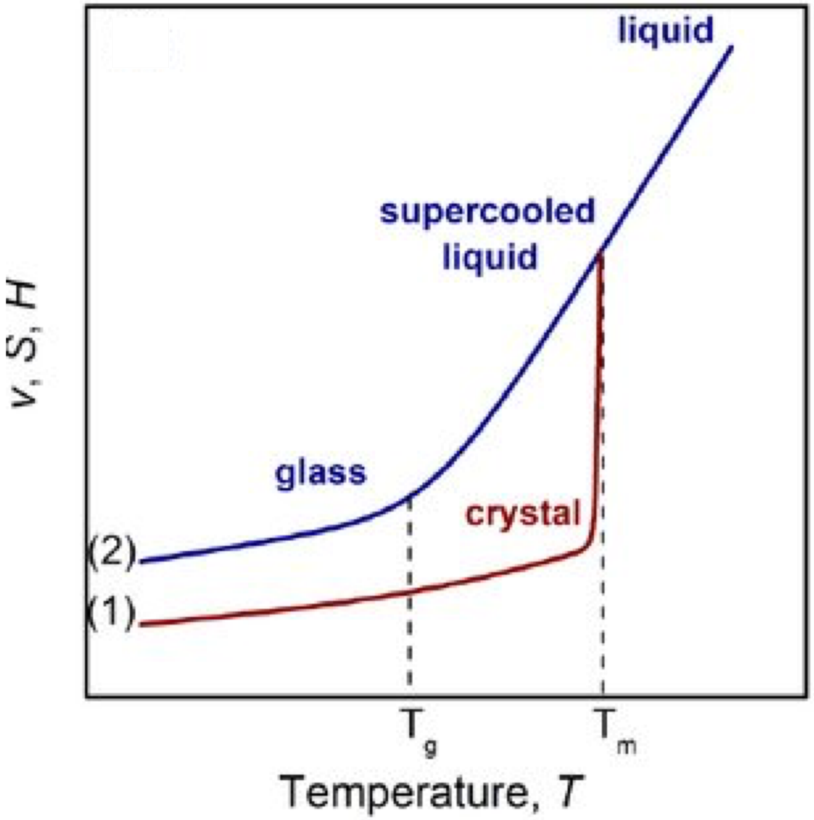
10^{13} Poise →

10^{-3} Poise →

- drastic increase change of dynamics, only small changes in structure
- relation between structural relaxation and thermodynamics?

glass transition: thermodynamic quantities


isobaric volume of polyvinyl acetate



behavior of 2nd derivatives of thermodynamic potentials?

Kalogeras, Lobland, *J. Mater. Edu.* **34**, 69 (2012).

specific heat

- specific heat at constant volume in canonical ensemble:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial \langle \mathcal{H} \rangle_{\text{can}}}{\partial T} = \frac{1}{k_{\text{B}} T^2}\left(\langle \mathcal{H}^2 \rangle_{\text{can}} - \langle \mathcal{H} \rangle_{\text{can}}^2\right)$$

- *H*: Hamilton function of the system

- canonical average:

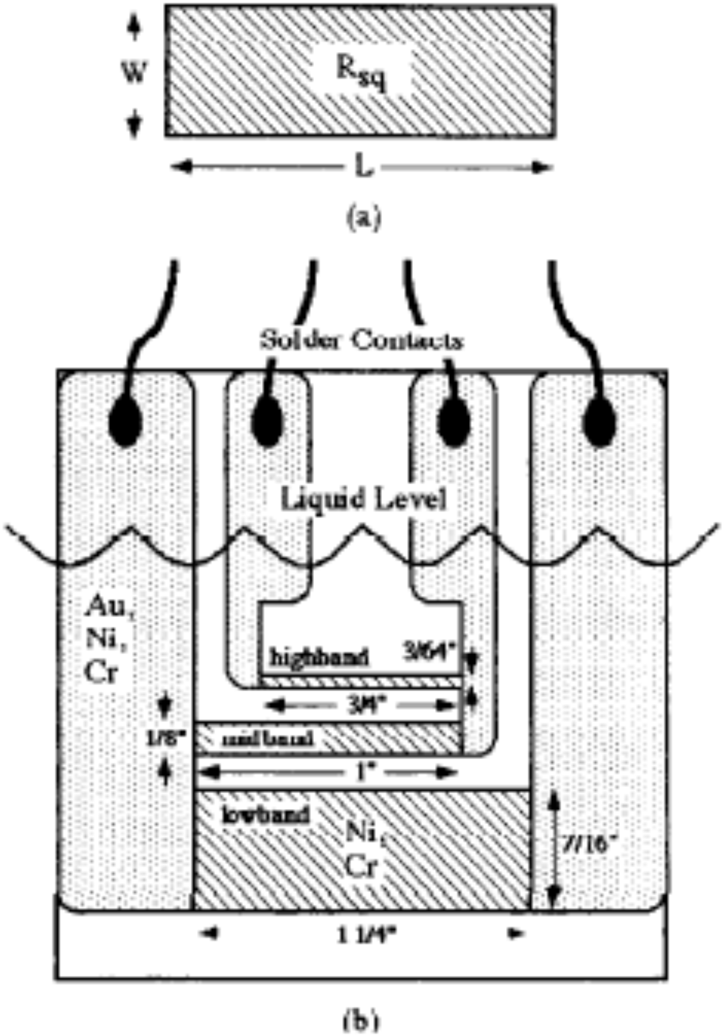
$$\langle \ldots \rangle_{\text{can}} = \frac{1}{Z_{can}} \int \ldots \, e^{-\beta \mathcal{H}} \, d\Gamma \;\; \text{with} \;\; Z_{\text{can}} = \int e^{-\beta \mathcal{H}} \, d\Gamma \;\; \text{and} \;\; \beta = \frac{1}{k_{\text{B}} T}$$

- Z_{can}: canonical partition function

- at constant pressure *P* in isobaric-isothermal ensemble:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \quad \text{with} \;\; H: \; \text{enthalpy}$$

specific heat spectroscopy



- system coupled to a frequency-dependent heat bath
- frequency range of 6 decades
- heat diffusion equation

$$i\omega c_p(\omega)T(x,\omega) = \kappa(\omega)\frac{\partial^2 T(x,\omega)}{\partial x^2}$$

$c_p(\omega)$: specific heat

$\kappa(\omega)$: thermal conductivity

N. O. Birge, S. R. Nagel, *Rev. Sci. Instrum.* **58**, 1464 (1987); N. O. Birge, P. K. Dixon, N. Menon, *Thermochimica Acta* **304/305**, 51 (1997).

frequency-dependent specific heat

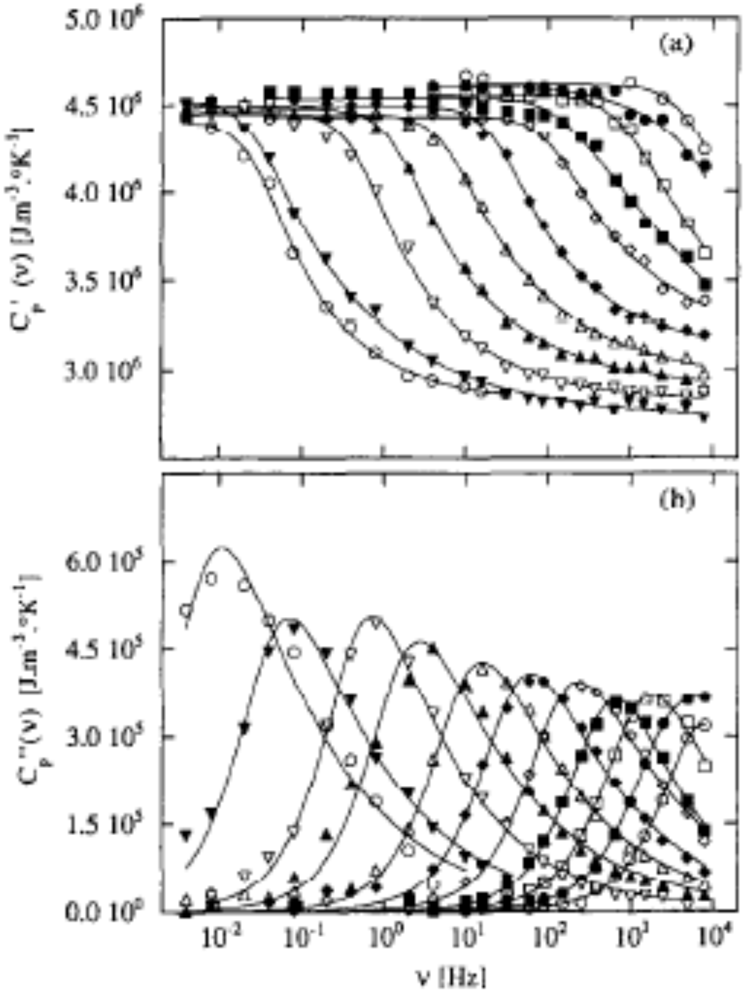


Fig. 6. Real and imaginary parts of $c_p(\nu)$ plotted against $\log_{10}[\nu(Hz)]$ for 11 temperatures from 176.5 to 201 K for the supercooled liquid di-*n*-butylphthalate [12]. The crossover in (a) and the peak in (b) move to lower frequency and become wider at lower *T*. The lines are fits by a Davidson–Cole form [39].

- real part of frequency-dependent specific heat

$$c'_P(\nu)$$

- imaginary part of frequency-dependent specific heat

$$c''_P(\nu)$$

- what can one learn from these data?

N. Menon, *J. Chem. Phys.* **105**, 5246 (1995).

outline

(1) Molecular Dynamics simulation of silica (SiO_2)

(2) specific heat of glasses

- harmonic approximation, vibrational density of states
- Boson peak

(3) frequency-dependent specific heat in undercooled melts

- real and imaginary part
- thermal diffusivity

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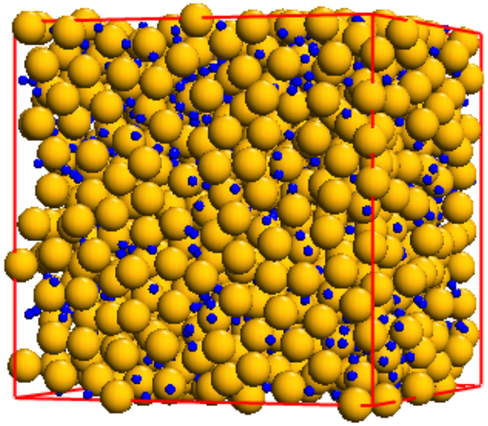
Molecular Dynamics simulation

- classical system of *N* particles at positions $\{\vec{r}_i\},\ i = 1,\ldots,N$

$$m_i \ddot{\vec{r}}_i = -\frac{\partial U_{\text{pot}}}{\partial \vec{r}_i} = \vec{F}_i$$



- U_{pot} : potential function

- simplest case: pairwise additive interaction between point particles

$$U_{\text{pot}} = \sum_{i=1}^{N-1} \sum_{j>i}^{N} u(r_{ij}) \qquad r_{ij} = \vec{r}_i - \vec{r}_j$$

- solution of equations of motion yield trajectories of the particles, i.e. positions and velocities of all the particles as a function of time

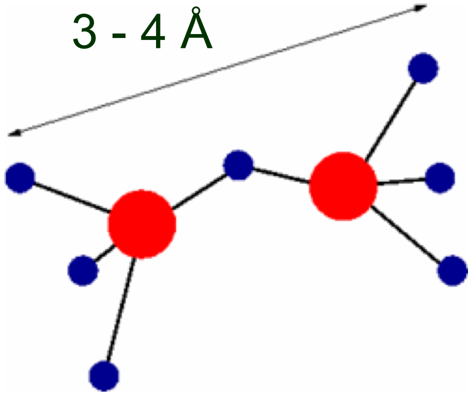
simulation details: SiO_2

- BKS potential for silica:

$$u_{\alpha\beta}(r) = \frac{q_\alpha q_\beta e^2}{4\pi\varepsilon r} + A_{\alpha\beta}\exp(-B_{\alpha\beta} r) - \frac{C_{\alpha\beta}}{r^6}$$

$$\alpha\beta = \text{SiSi, SiO, OO}$$

- parameters $A_{\alpha\beta}$, $B_{\alpha\beta}$, $C_{\alpha\beta}$ in van Beest, Kramer, van Santen, *Phys. Rev. Lett.* **64**, 1955 (1990).
- $N = 336 – 8064$, simulations at constant density $\rho = 2.36$ g/cm^3
- undercooled melt 6100 K ≥ T ≥ 2750 K; glass at 300 K (obtained by runs from 2750 K with a cooling rate of 10^{12} K/s
- tetrahedral network structure



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specific heat for harmonic solid

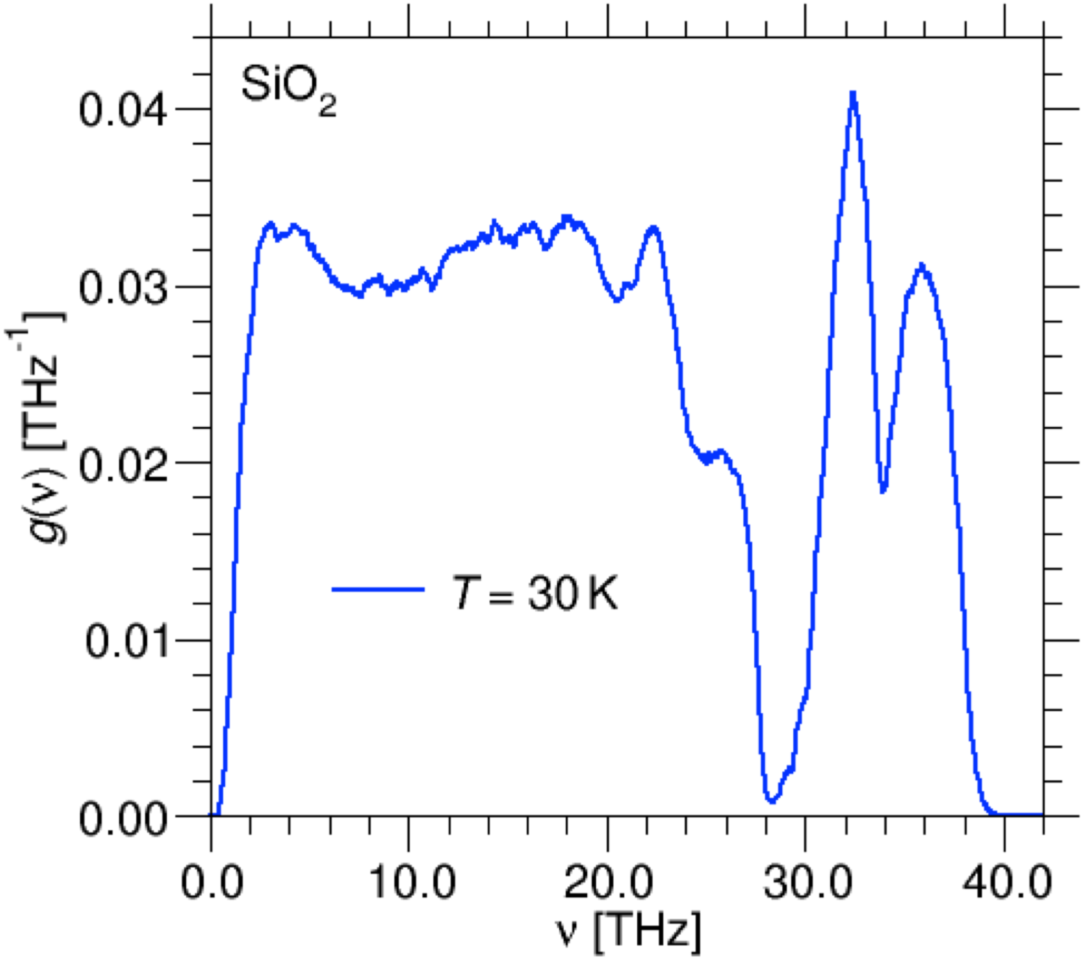
- in harmonic approximation: $$C_V = \frac{h^2}{k_B T^2}\int_0^\infty \frac{\nu^2 \exp(\beta h\nu)}{\left(\exp(\beta h\nu)-1\right)^2} g(\nu)\,d\nu$$
- classical limit: Dulong-Petit law: $C_V = 3N_A k_B$
- *g*(v): vibrational density of states (VDOS), with v the frequency
- VDOS can be obtained from velocity autocorrelation function (VACF):

$$g(\nu) = \frac{1}{Nk_B T}\sum_{j=1}^{N}\int_{-\infty}^{\infty} dt\ m_j \exp(i2\pi\nu t)\left\langle \vec{v}_j(t)\cdot\vec{v}_j(0)\right\rangle$$

- low temperatures: Debye theory

$$g_D(\nu) = \frac{3\nu^2}{\nu_D^3} \quad \text{with} \quad \nu_D = \left(\frac{9N}{4\pi V}\right)^{1/3}\left(\frac{2}{c_T^3}+\frac{1}{c_L^3}\right)^{-1/3} \quad \Rightarrow \quad C_V(T) \propto T^3$$

vibrational density of states (VDOS)



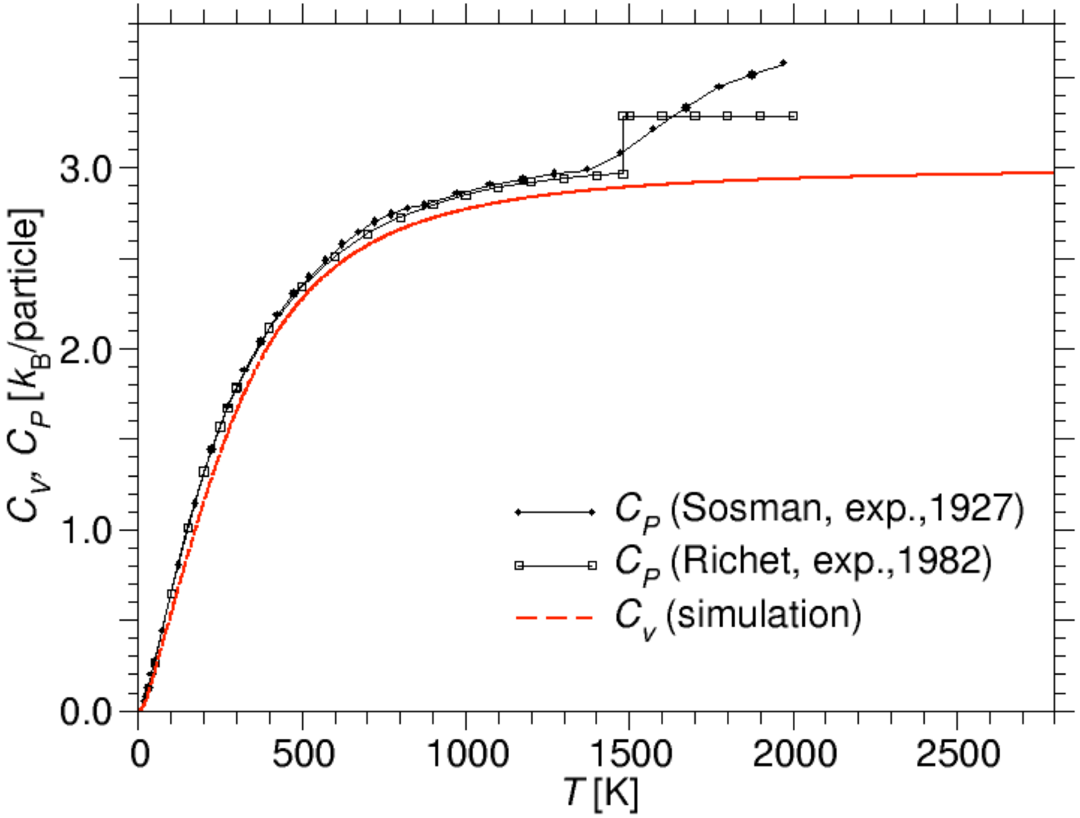
g(v) for BKS silica:

- purely classical calculation
- v >30 THz: stretching modes in single SiO$_4$ unit
- intermediate frequency band not in good agreement with ab initio calculations

J. Horbach, W. Kob, K. Binder, *J. Phys. Chem. B* **103**, 4104 (1999); P. Scheidler, W. Kob, A. Latz, J. Horbach, K. Binder, *Phys. Rev. B* **63**, 104204 (2001).

comparison to experiment

$$C_V = \frac{h^2}{k_B T^2} \int_0^\infty \frac{\nu^2 \exp(\beta h \nu)}{\left(\exp(\beta h \nu) - 1\right)^2} g(\nu) d\nu$$

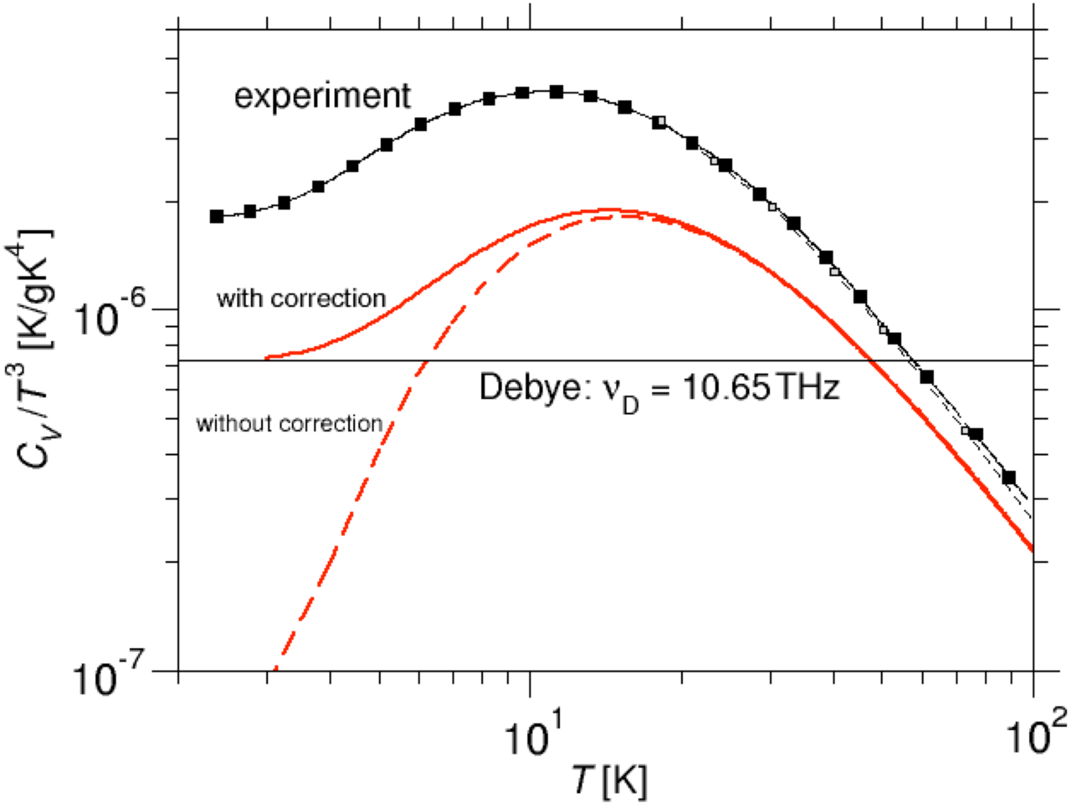


- good agreement between simulation and experiment below T_g
- deviations to the experiment for $T > T_g$ mainly due to structural relaxation (and anharmonicities)
- behavior at low temperatures: $T < 50$ K

J. Horbach, W. Kob, K. Binder, *J. Phys. Chem. B* **103**, 4104 (1999).

low temperatures: Boson peak

$$g_D(\nu) = \frac{3\nu^2}{\nu_D^3} \quad \text{with} \quad \nu_D = \left(\frac{9N}{4\pi V}\right)^{1/3} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3}\right)^{-1/3} \quad \Rightarrow \quad C_V(T) \propto T^3$$



- correction: add $g_D(\nu)$ to measured g(ν) for ν ≤ 0.73 THz

$$c_L = 6161\,\text{m/s}$$

$$c_T = 3915\ \text{m/s}$$

$$\Rightarrow \nu_D = 10.65\ \text{THz}$$

J. Horbach, W. Kob, K. Binder, *J. Phys. Chem. B* **103**, 4104 (1999).

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q-dependent temperature fluctuation

- microscopic temperature of a particle:

$$\theta(\vec{p}_i) = \frac{1}{3k_\mathrm{B}m}\vec{p}_i^{\,2} \quad \text{with} \quad \vec{p}_i: \ \text{momentum of particle i}$$

- microscopic temperature field density:

$$T(\vec{r},t) = \sum_{i=1}^{N}\theta(\vec{p}_i)\delta(\vec{r}-\vec{r}_i(t)), \ \text{FT:} \ T_q(t) = \sum_{i=1}^{N}\theta(\vec{p}_i)\exp(i\vec{q}\cdot\vec{r}_i)$$

- temperature fluctuation in Fourier space:

$$\delta T_q(t) = T_q(t) - T\rho_q(t)$$

central quantity: ACF of kinetic energy

- static correlation function independent of q:

$$S^c_{TT} = \left\langle \delta T^*_q(0)\delta T_q(0) \right\rangle = \frac{2}{3} N T^2$$

- time-dependent autocorrelation function (ACF):

$$\Phi_{TT}(q,t) = \left\langle \delta T^*_q(t)\delta T_q(0) \right\rangle$$

$$q \to 0: \;\; \Phi_{TT}(t) = \left\langle \delta T^*_0(t)\delta T_0(0) \right\rangle$$

- normalized ACF of kinetic energy:

$$K(t) = \frac{\Phi_{TT}(t)}{S^c_{TT}}$$

→ $K(t)$ related in harmonic approximation to VACF

→ Laplace transform of $K(t)$ related to frequency-dependent specific heat

→ $\Phi_{TT}(q,t)$ related to thermal conductivity

relation between ACF of kinetic energy vs. VACF

- VACF weighted with mass *m*:

$$J(t) = m\left\langle \vec{v}(t) \cdot \vec{v}(0) \right\rangle$$

- in harmonic approximation the following relation between ACF of the kinetic energy, *K*(*t*), and *J*(*t*) holds:

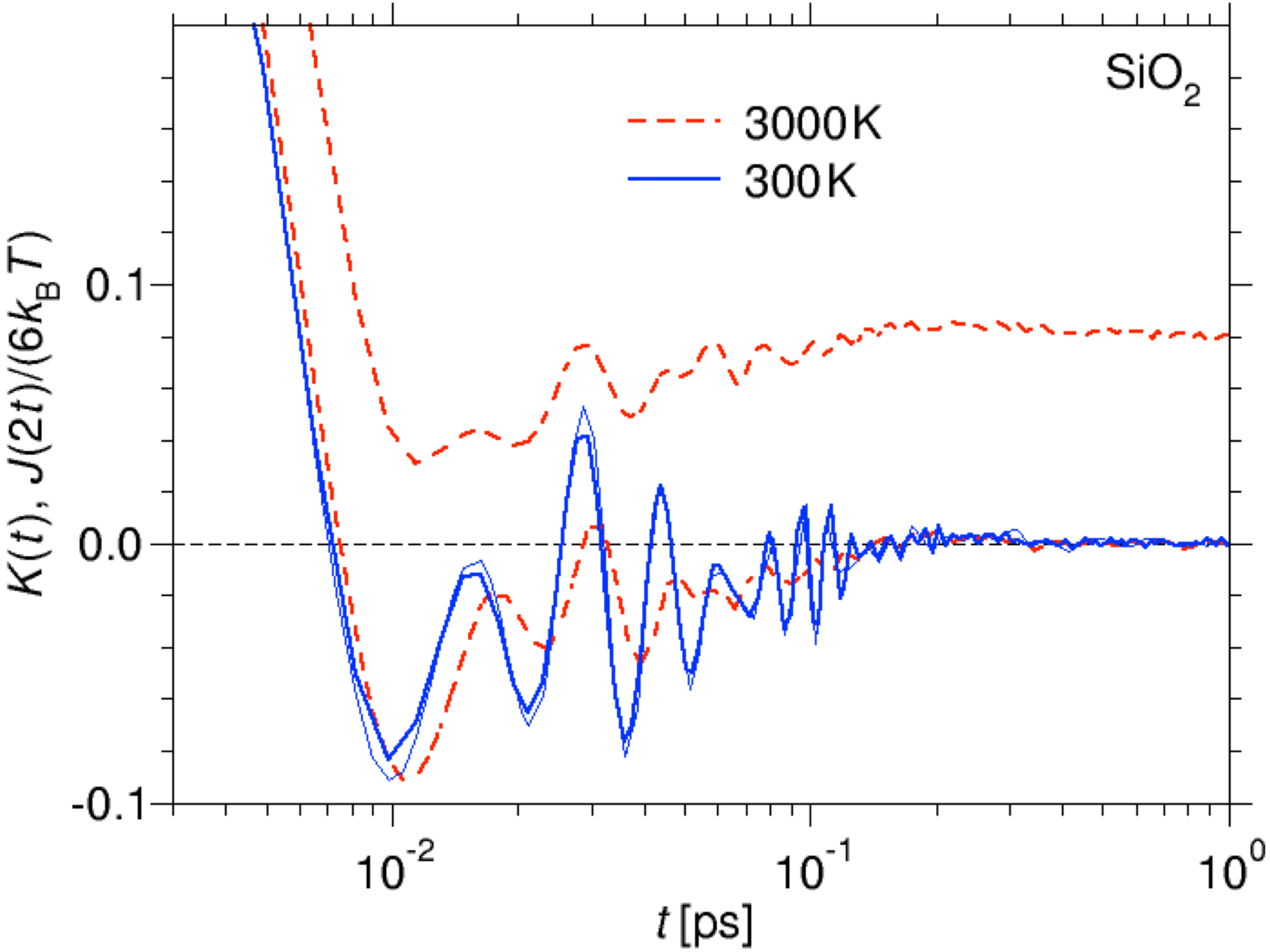
$$K(t) = \frac{J(2t)}{6k_{\mathrm{B}}T}$$

- this implies a relation between *K*(ω) and VDOS, *g*(ω):

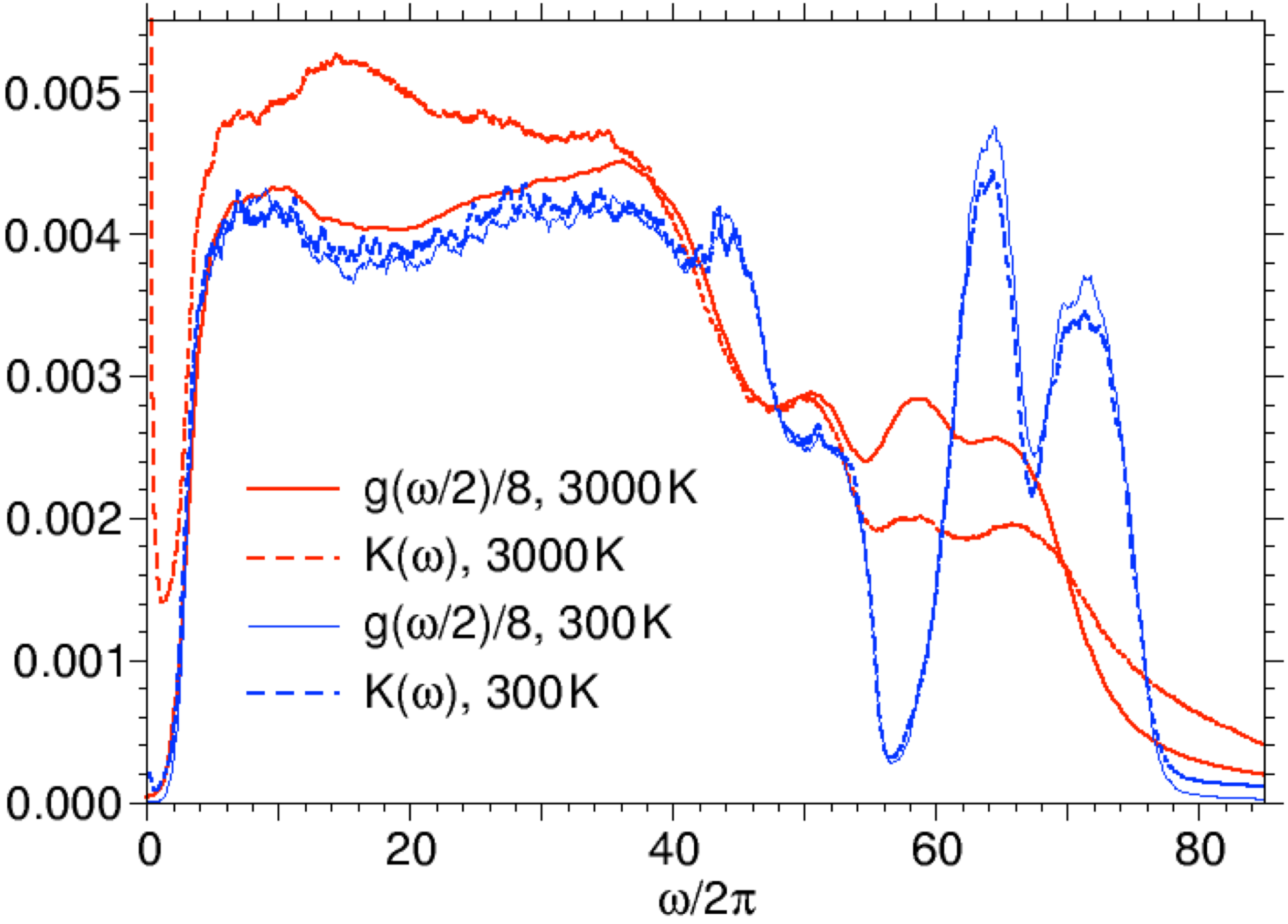
$$K(t) = \frac{J(2t)}{6k_{\mathrm{B}}T} \quad \text{and} \quad \widehat{K}(\omega) = \frac{1}{8}g(\omega/2)$$

- consistent with simulation?

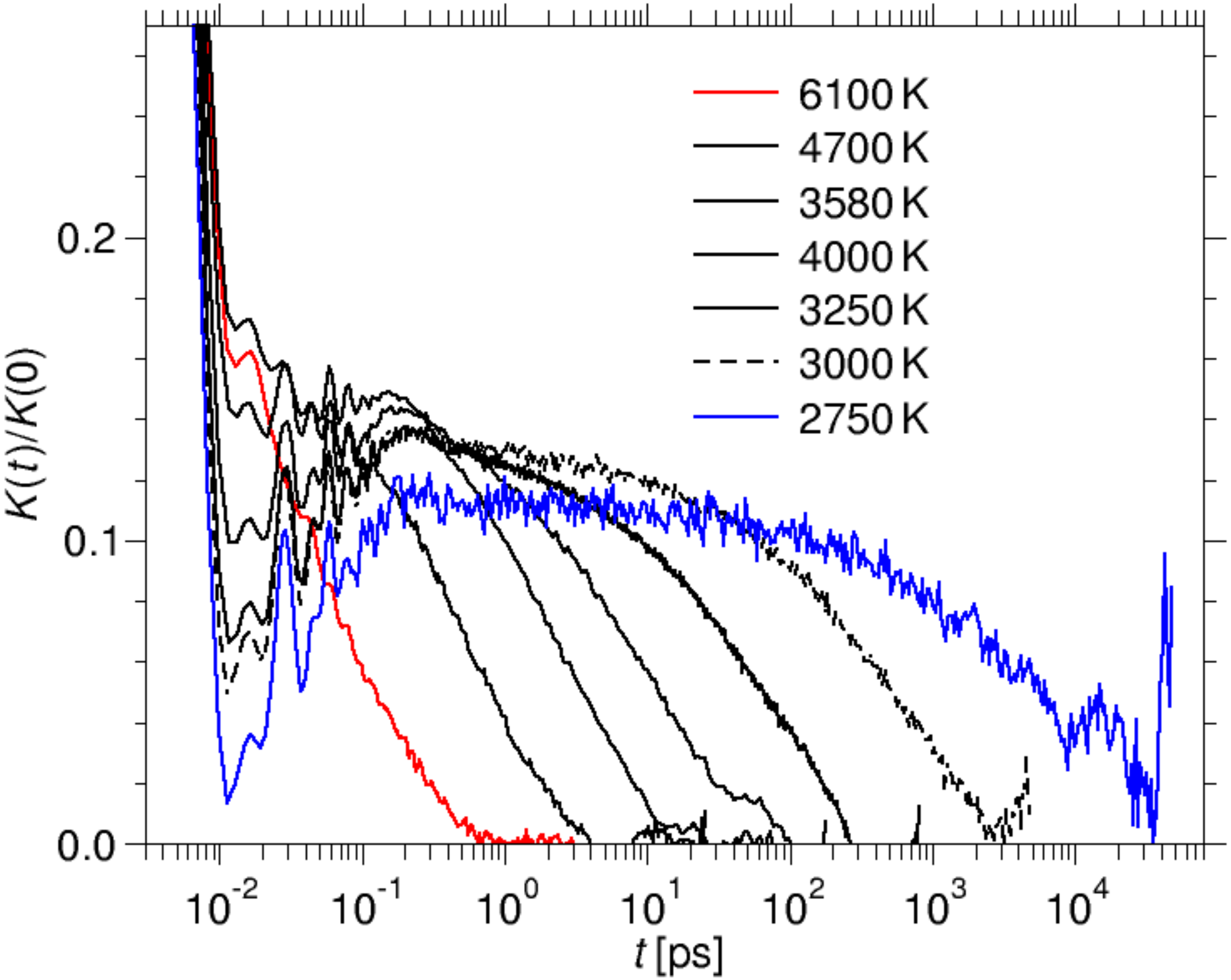
ACF of kinetic energy vs. VACF: harmonic approximation



ACF of kinetic energy vs. VDOS: harmonic approximation?



ACF of kinetic energy at high temperature



→ two-step decay indicates structural relaxation, relation to specific heat?

frequency-dependent specific heat

- static specific heat per particle in canonical ensemble:

$$c_V = \frac{1}{Nk_B T^2}\left(\left\langle \mathcal{H}^2 \right\rangle_{\text{can}} - \left\langle \mathcal{H} \right\rangle_{\text{can}}^2\right)$$

- microcanonical ensemble: $c_V = \dfrac{3k_B/2}{1 - K(0)}$

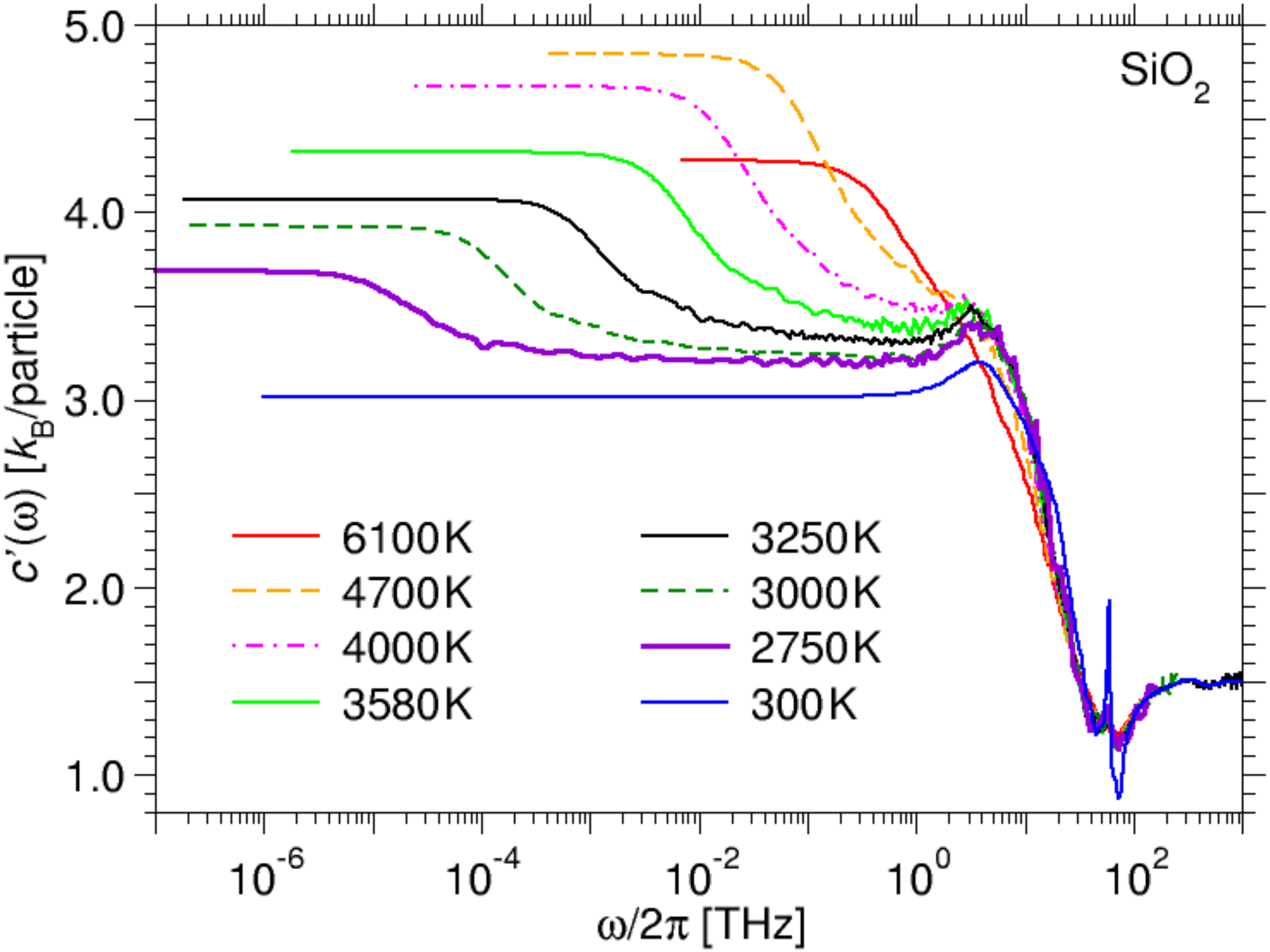
- generalization to frequency-dependent specific heat:

$$c_V(z) = \frac{3k_B/2}{1 - K(0) - z\ \mathrm{LT}[K(t)](z)}$$

$\mathrm{LT}[K(t)](z)$: Laplace transform of $K(t)$

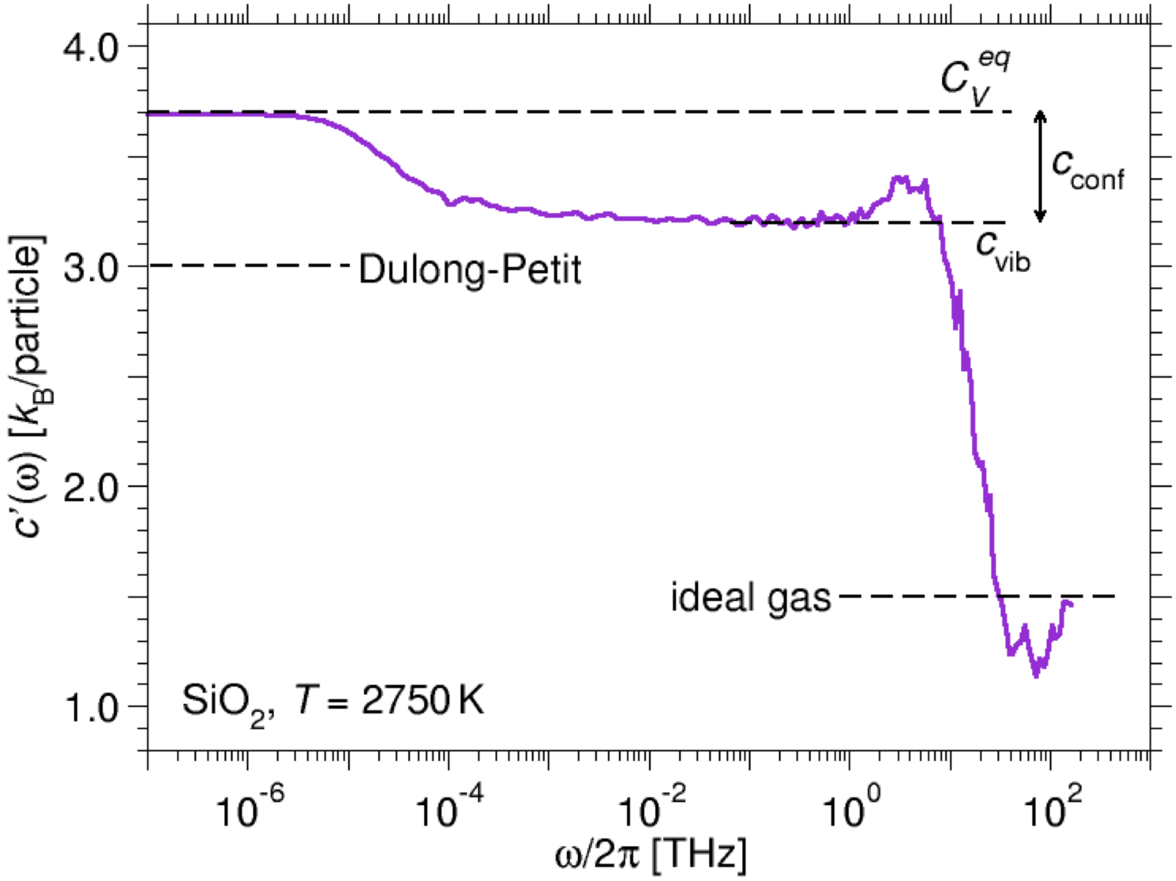
- Fourier transform: $z = i\omega$ $\quad c_V(\omega) = c'(\omega) + ic''(\omega)$

real part of frequency-dependent specific heat



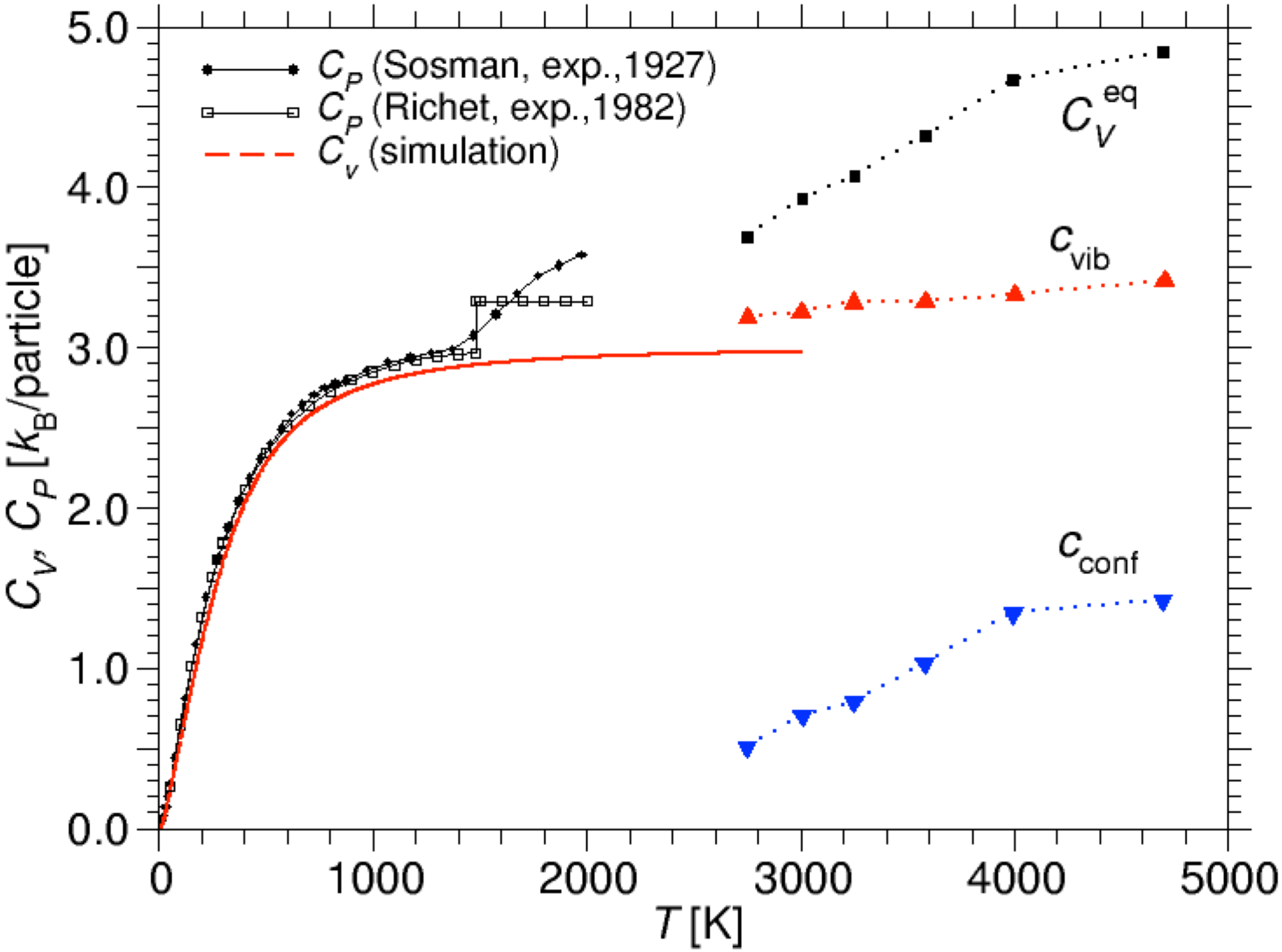
- static specific heat at low ω: with decreasing *T* this regime shifts to lower frequencies

configurational specific heat

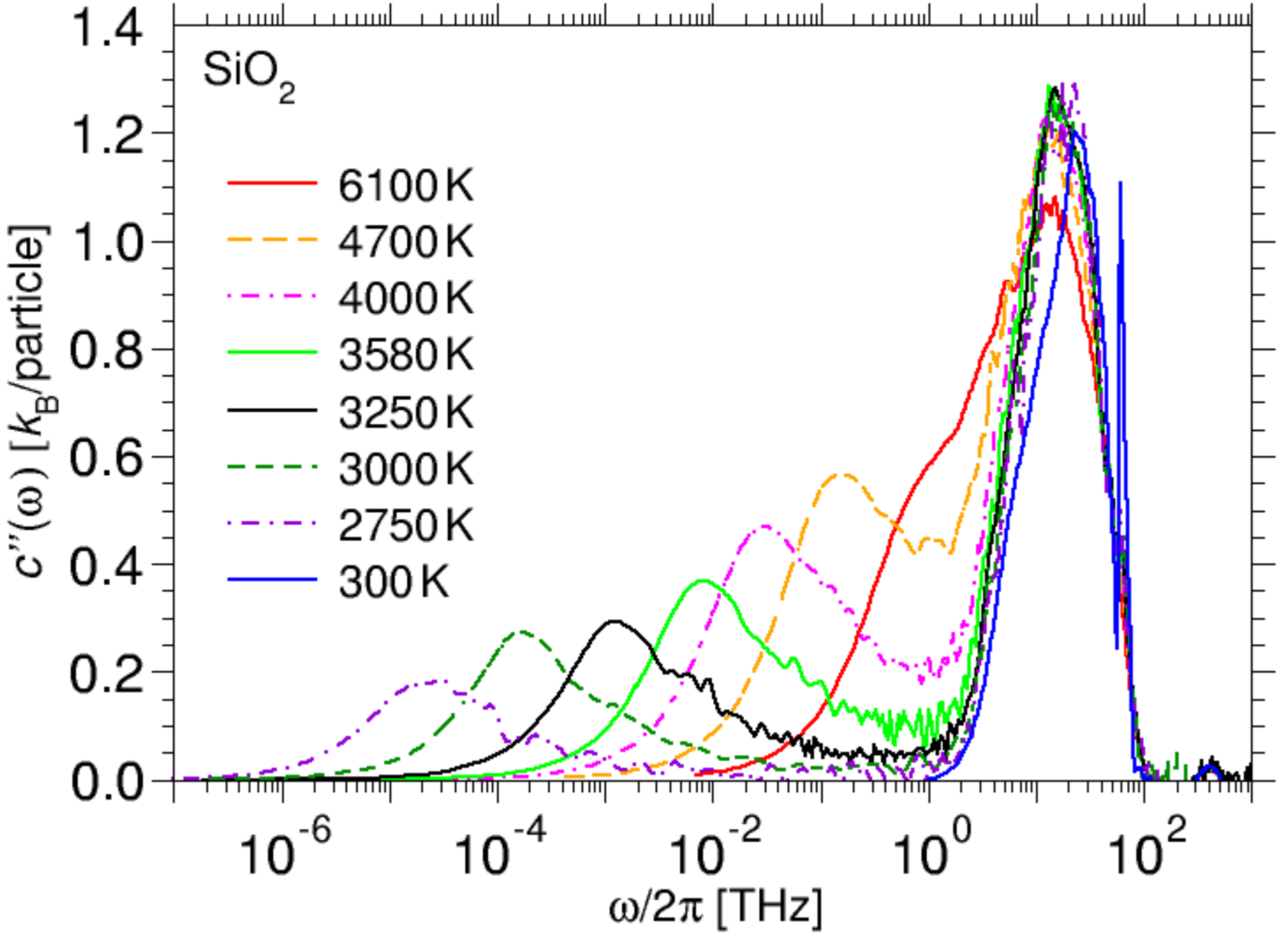


- define “configurational“ specific heat $c_{\rm conf}$: $c_{\rm conf} = c_V^{\rm eq} - c_{\rm vib}$
- vibrational part $c_{\rm vib}$ remains below the glass transition temperature

specific heat: comparison to experiment II

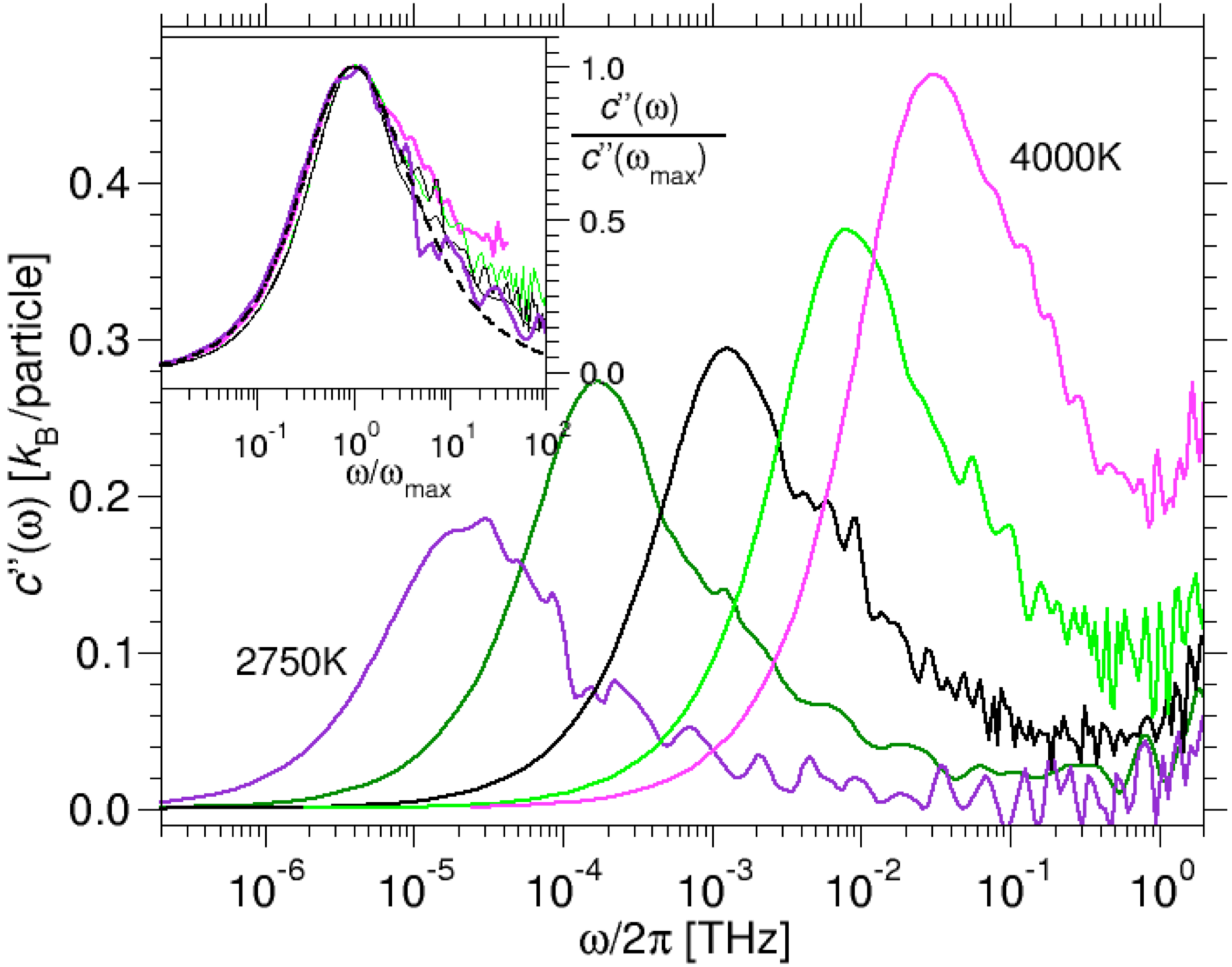


imaginary part of frequency-dependent specific heat



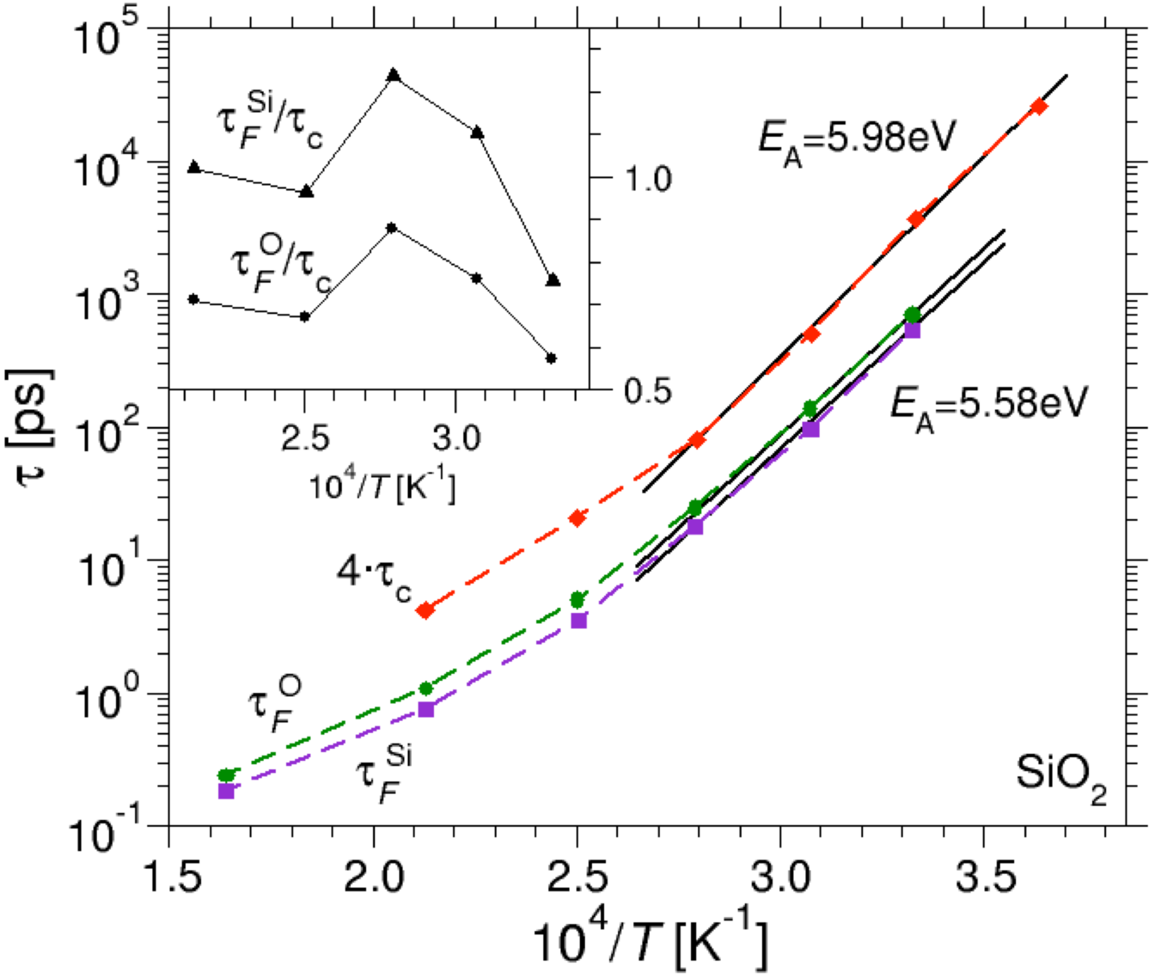
- spectrum with α peak at low frquencies and microscopic peak around 10 THz

the α relaxation



- define α relaxation time: $\tau_c = 1/\omega_{\max}$

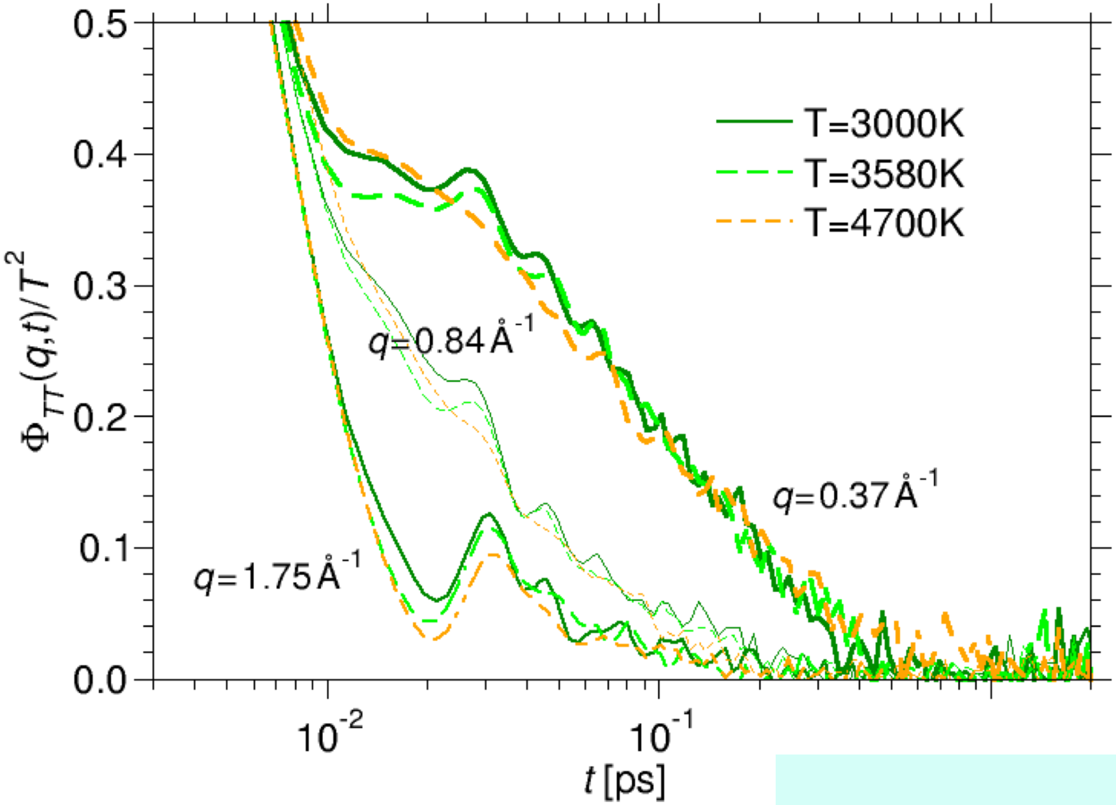
α relaxation times



- relaxation times τ_F obtained from incoherent intermediate scattering functions for Si and O

autocorrelation function of *q*-dependent temperature

$$\Phi_{TT}(q,t) = \left\langle \delta T_q^*(t)\,\delta T_q(0) \right\rangle$$



T dependence weak: no coupling to structural relaxation

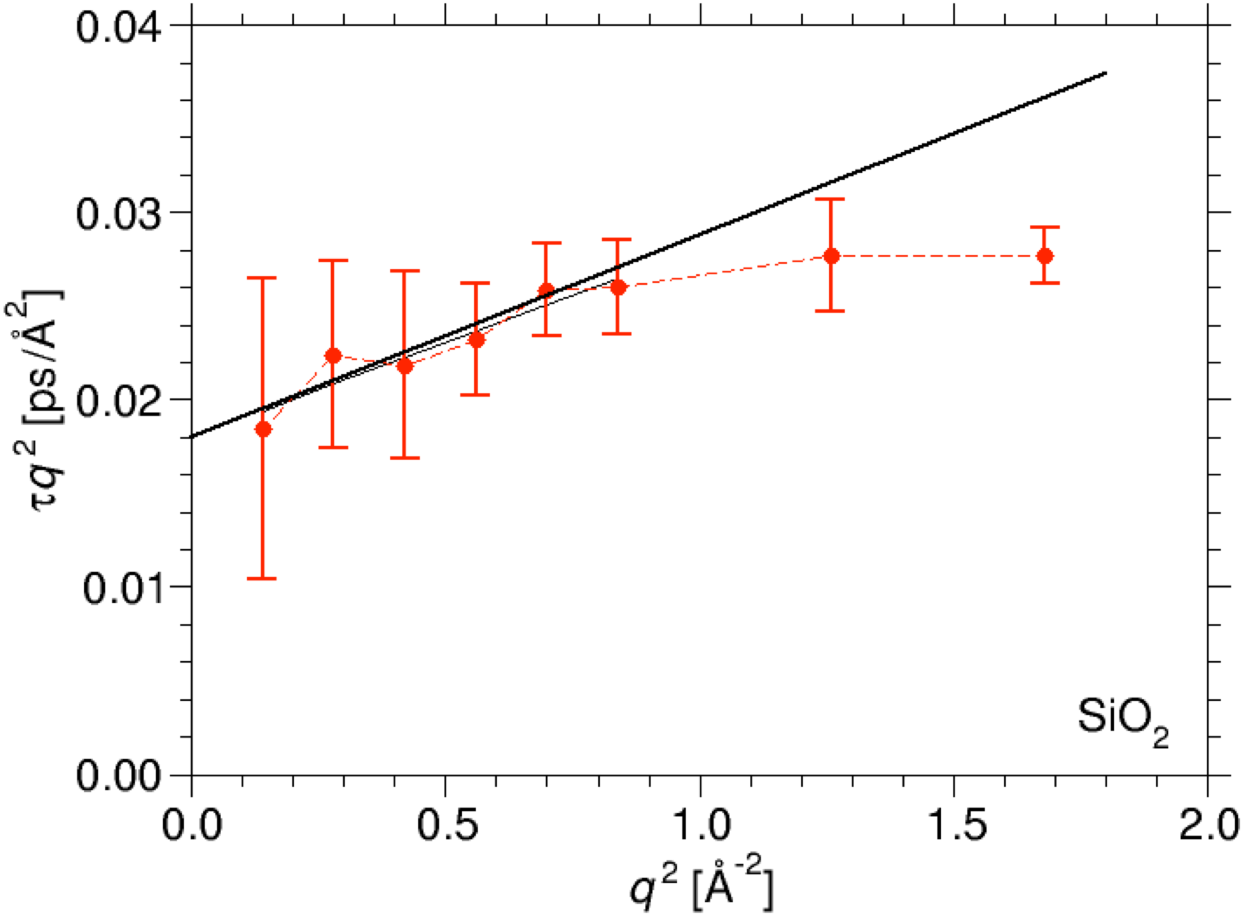
$$\Phi_{TT}(q,t) \propto T^2$$

exponential decay at long times:

$$\Phi_{TT}(q,t) \propto \exp(-t/\tau_q) \quad \text{with } \tau_q = \frac{1}{D_T q^2} + c$$

$$D_T = \frac{\kappa}{n c_P^{\mathrm{eq}}} \quad \text{thermal diffusivity}$$

thermal conductivity



- thermal conductivity from fit: $\kappa = 2.4\ \mathrm{W/(Km)}$

summary

computer simulation of SiO_2 melts and glasses:

- low temperatures: c_V in harmonic approximation using $g(\omega)$ from classical MD simulation
- frequency-dependent specific heat allows to determine the contribution of the configurational degrees of freedom to the static specific heat
- from $\Phi_{TT}(q,t)$ one can extract the thermal conductivity

G. S. Grest, S. R. Nagel, J. Phys. Chem. **91**, 4916 (1987);
W. Götze, A. Latz, J. Phys.: Condens. Matter **1**, 4169 (1989);
J. K. Nielsen, Phys. Rev. E **60**, 471 (1999);
J. Horbach, W. Kob, K. Binder, *J. Phys. Chem. B* **103**, 4104 (1999);
P. Scheidler, W. Kob, A. Latz, J. Horbach, K. Binder, *Phys. Rev. B* **63**, 104204 (2001).

acknowledgement

- Kurt Binder (Univ. Mainz)
- Walter Kob (Univ. Montpellier II)
- Arnulf Latz (Univ. Ulm)
- Peter Scheidler