Heat capacity and thermal conductivity in glasses

interpretation in terms of two level systems in glasses; analysis at “low” and “high” temperatures

July 1, 2021

Glass vs crystal

- Glass is a non-crystalline, often transparent amorphous solid or simpler a disordered system. The perfect symmetry of the lattice is broken.
- The amorphous solids are formed when the solidification process is very fast (The atoms don't have time to dispose in a regular structure).

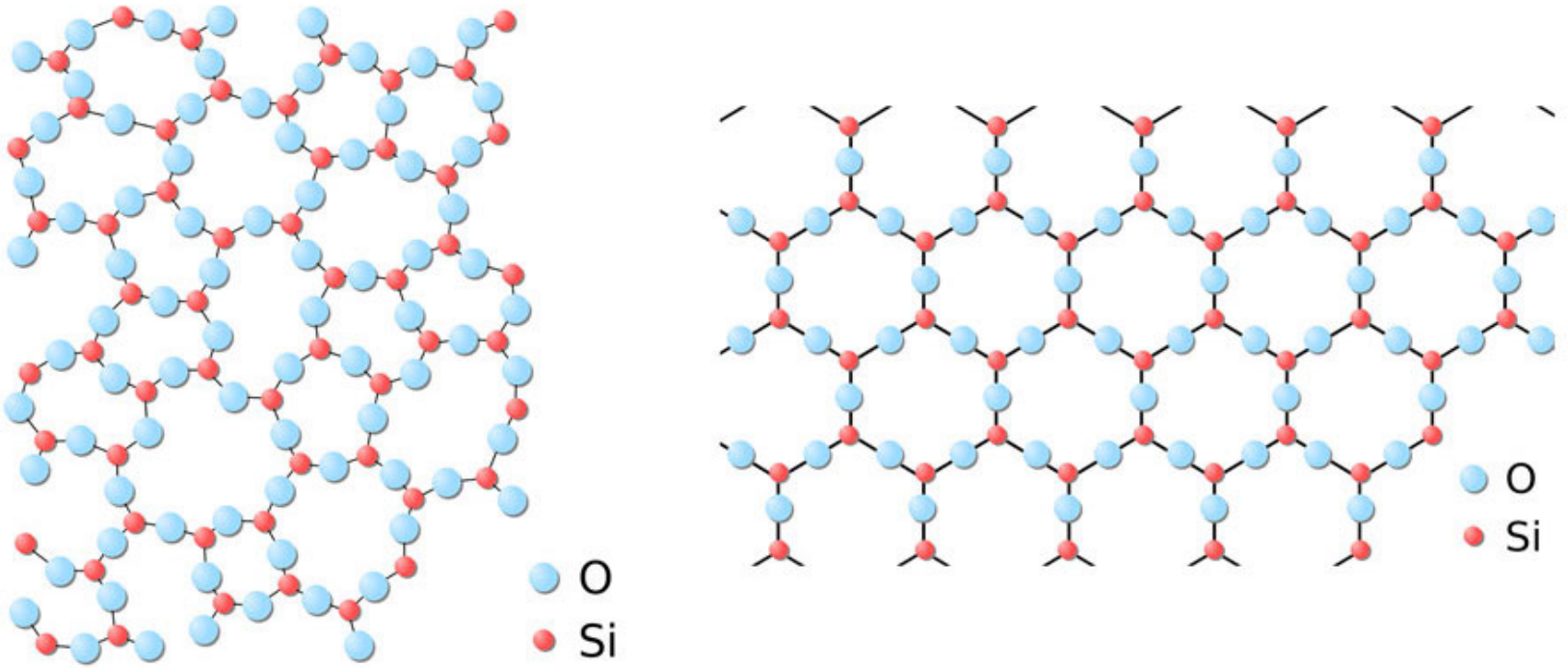
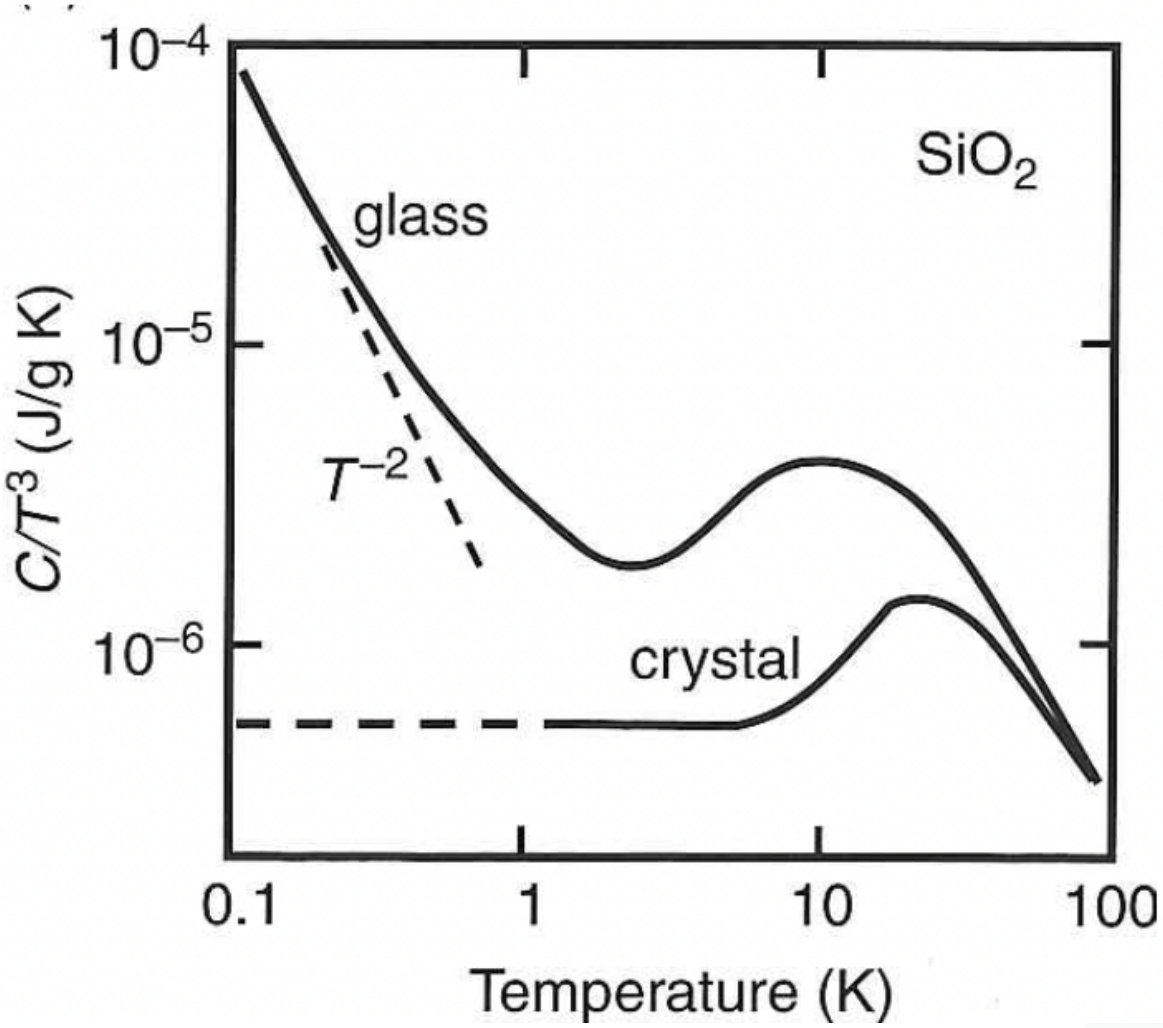


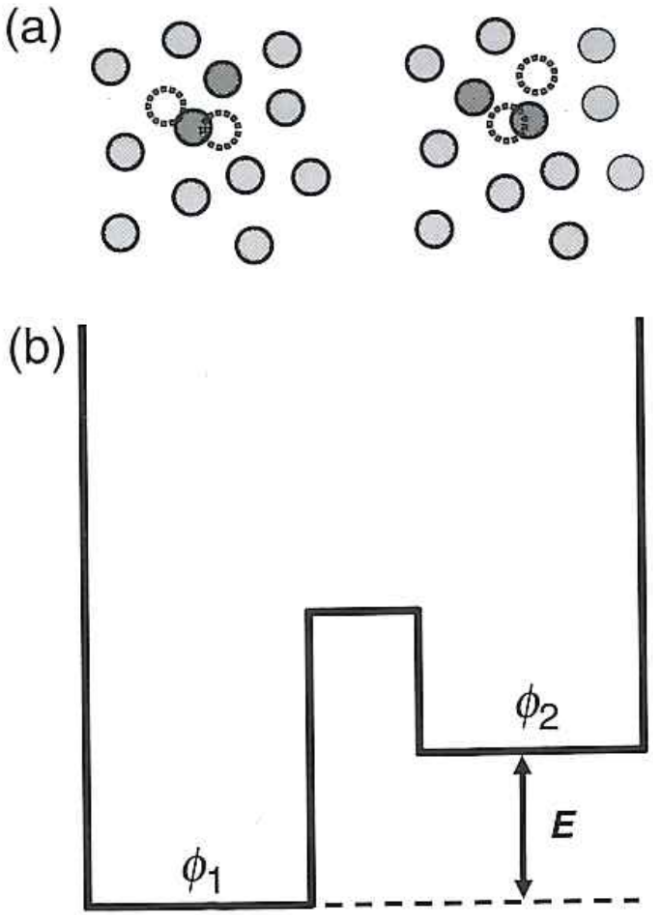
Figure 1: Difference in the structure of amorphous solids (glasses) and crystals

Heat capacity

- At low temperatures, the low-energy excitations responsible for the heat capacity are long-wavelength phonons.
- The scattering of phonons by disorder is efficient for phonons with wavelength comparable to or shorter than the distance between defects. Phonons with wavelength longer than this are seeing an effective homogeneous medium, and are relatively little affected by the disorder.
- At $T \to 0$ the heat capacity is dominated by long wavelength phonons we would expect it to show the same behaviour for a glass as for a crystal. This is indeed the case if the temperature is relatively high. However, at $T \to 0$ the behaviour is different, with $C \propto T$. The reason for this is the presence of additional low-energy excitations which can be excited at low temperatures, and therefore give increased heat capacity.

Heat capacity: Glass vs crystal





- The possible configurations for a single spot in a glass can be modelled using a quantum mechanical 2 level system.
- In a glass there will be many places where one or a group of atoms can exist in two different positions or configurations. Hence, we limit defect of the solid to choose only 2 possible configurations with two different energies. The energies of these configurations will be very close, and the atoms can quantum tunnel between the two configurations.
- An amorphous solids can be modelled also using a n level system.

Heat capacity

- we can look at it as an ensemble of two level systems. The average energy for a 2 level system is given from statistical mechanics:

$$\langle E \rangle = \frac{1}{\mathcal{Z}} \sum_{i=1,2} E_i e^{\beta E_i}$$

where $\beta = \frac{1}{k_B T}$ and $\mathcal{Z}$ is the canonical partition function of the TLS, i.e the sum of all the Boltzmann weight for the allowed energies.

- One can set the lowest energy state as the zero of energy, so $E_1 = 0$ and as a consequence $E_2 = E$. This setting yields to an average energy for a TLS equal to:

$$\langle E \rangle = \frac{E}{1 + e^{\beta E}} \tag{1}$$

each of these TLS contributes to the heat capacity of the glass in the following way:

$$C_{TLS} = \left. \frac{\partial \langle E \rangle}{\partial T} \right|_V = k_B (\beta E)^2 \frac{e^{\beta E}}{(e^{\beta E} + 1)^2}$$

Heat capacity

- However, to calculate the total heat capacity another important ingredient is needed: the density of states of these TLS. This quantity indicates the number of TLS with energy between E and $E + dE$.
- We assume as the simplest choice that $g_{TLS}(E) = N_{TLS}$ is a constant.
- In the light of the above, the total heat capacity is given by:

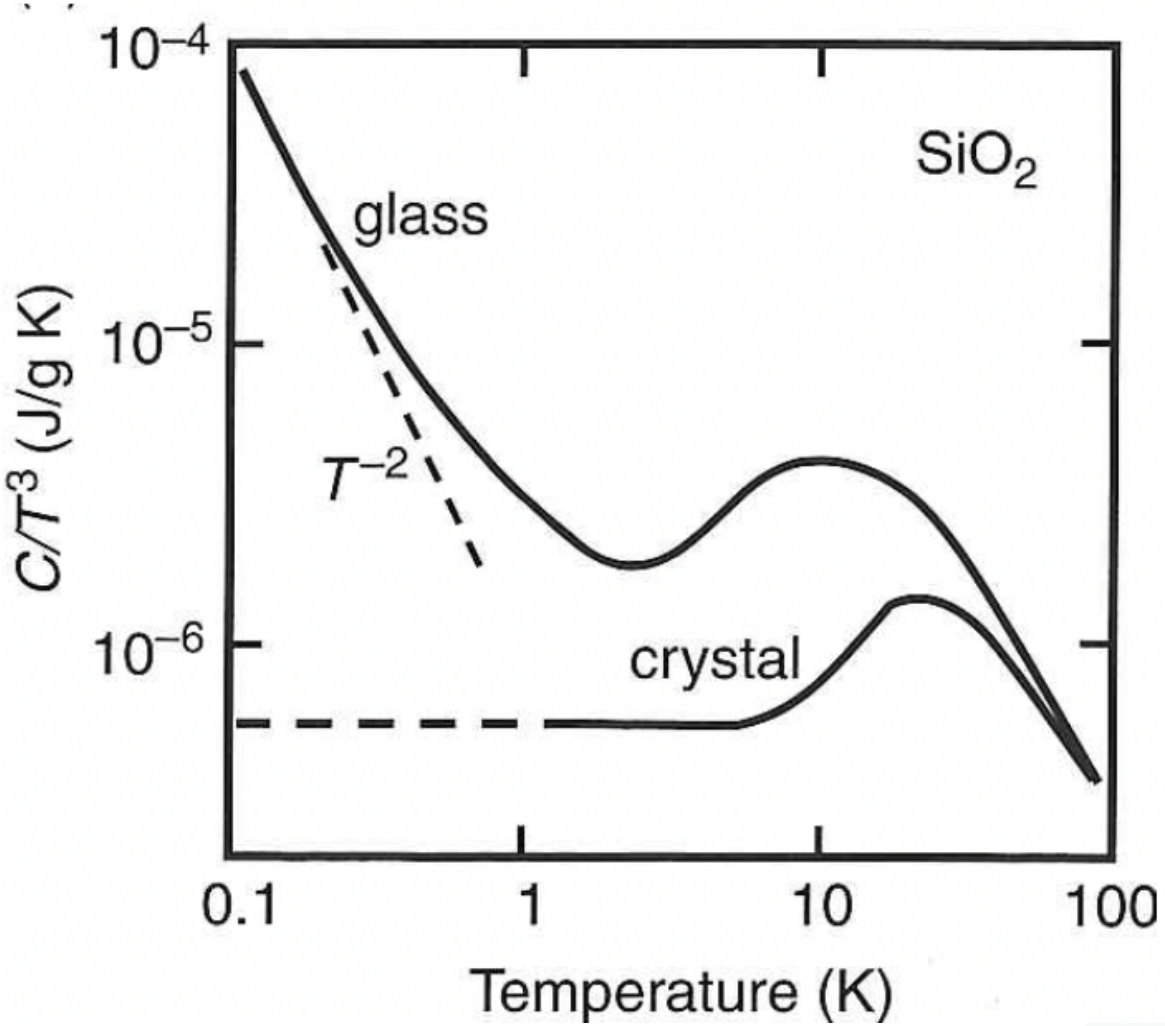
$$C = \int_0^{+\infty} DOS_{TLS}(E) C_{TLS} dE$$

- Assuming the DOS constant we obtain:

$$\begin{aligned} C &= N_{TLS} k_B \int_0^{\infty} \left(\frac{E}{k_B T} \right)^2 \frac{e^{E/k_B T} dE}{\left(e^{E/k_B T} + 1 \right)^2} \\ &= N_{TLS} k_B^2 T \int_0^{\infty} \frac{x^2 e^x dx}{(e^x + 1)^2} \\ &= \frac{\pi^2}{6} N_{TLS} k_B^2 T \propto T \end{aligned}$$

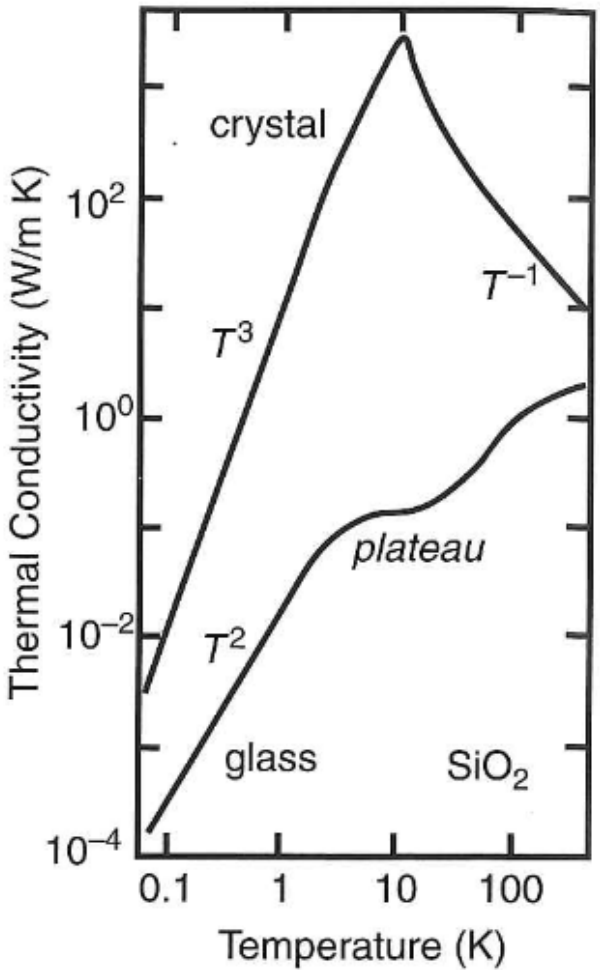
Heat capacity: Glass vs crystal

- We see that the TLS model can explain the temperature dependence of the heat capacity observed in experiments.



Thermal current and thermal conductivity in glasses

- We are interested in the thermal current
$$j = -\kappa \nabla T$$
and in the thermal conductivity
$$\kappa = \frac{1}{3} C v \Lambda$$
where C is the specific heat, v is the sound velocity and Λ is the mean free path
- Each phonon with velocity v and energy E contributes vE to the current. If the change in temperature with respect to x is slow
$$j = \frac{n}{2} v_x [E[T(x-\Lambda)] - E[T(x+\Lambda)]] \approx -n v_x \frac{\partial E}{\partial T} \frac{\partial T}{\partial x} \Lambda$$
Thus it follows :
$$\kappa = \frac{1}{3} C v \Lambda = \frac{1}{3} C \tau v^2$$



- We see that a crystal shows the expected behaviour, as described above. The glass has $\kappa \propto T^2$ at low temperature, a temperature independent plateau at intermediate temperatures, and approaches the value of the crystal at high temperatures.
- The plateau in the thermal conductivity was interpreted as an effect of phonon localization. This happens when at relatively high temperature only the impurities scatters the phonons. Thus, if we increase more the temperature also the atoms will start scattering, reaching the crystal behaviour.

Thermal conductivity

The thermal conductivity of one phonon is

$$\kappa = \frac{1}{3} v\, C \Lambda$$

so that the thermal conductivity of the whole system is

$$\kappa = \frac{v}{3} \int_0^{\omega_D} C(\omega, T) \Lambda(\omega) d\omega$$

where

$$C(\omega, T) = 3k \frac{g(\omega)}{V} \frac{(\hbar\omega/kT)^2 e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT} + 1\right)^2}$$

is the heat capacity contribution of the systems at frequency ω

$$\Lambda = \Lambda(\omega) = v\, \tau(\omega)$$

The relaxation time τ can be derived by considering the rate of change in the number of phonons given the transition probabilities from one state to the other of the TLS

$$\frac{dn(E)}{dt} = -N_{TLS} B(E) (p_1 - p_2) n(E)$$

Thermal conductivity

This leads to an expression for the relaxation time

$$\frac{1}{\tau} = N_{TLS} B(E) \tanh \frac{E}{2kT}$$

which leads to a more correct expression for the thermal conductivity

$$\kappa = \frac{k^3 T^2}{2\hbar^3 N_{TLS} A v} \propto T^2$$