

Contribution of Phonons to Specific Heat

The energy of lattice vibrations is quantized (phonons). **Phonons** are thermally excited $\rightarrow$ thermal phonons. The energy can be calculated based on the harmonic oscillator model.

$E_n = (n + \frac{1}{2})\hbar\omega$ with $n=0,1,2,3,\dots$. Total energy has to sum up over N oscillators. The question how many oscillators are excited and how large is the mean energy of all oscillators needs to calculate the mean $n \rightarrow \langle n \rangle$. After calculation one obtains the mean thermal equilibrium

occupancy of a certain state n as function of the thermal energy kT : $\langle n \rangle = \frac{1}{\exp(\frac{\hbar\omega}{kT}) - 1}$

which is **Bose-Einstein** distribution, valid for all quanta with an integer spin. Therefore the

total energy of excited phonons is given by $E = \sum_q (\langle n \rangle + \frac{1}{2})\hbar\omega(q)$. (*)

The question what is the **density of states (DOS)** of excited energy levels per unit volume for a system with propagating waves within a crystal of size $L^3=(Na)^3$

is $\Delta\omega(q) = (L/2\pi)^3 = \text{const.}$. The sum of spectral number densities $S_j(\omega)$ over all the

branches j within the phonon dispersion $\int_0^{\omega_{\max}} S(\omega)d\omega = \sum_{j=1}^{3p} \int_0^{\omega_{\max}} S_j(\omega)d\omega = 3pN$ depends on

the number of atoms per cell p and number unit cells N . in 3D space the spectral density of

states $S_j(\omega)$ is given by $S_j(\omega) = (\frac{L}{2\pi})^3 \iint \frac{dF}{|grad_q \omega|}$ where dF is an area element with $\omega(q) =$

const. and $grad_q \omega$ the derivative $d\omega/dq$ in 3D. In general case, the last formula has no analytic solution. Therefore two models exit:

A: **Einstein model**, where the optical branch is approximated by a constant

$S_j(\omega) = \begin{cases} 0 & \omega \neq \omega_E \\ 3pN & \omega = \omega_E \end{cases}$ where ω_E is the Einstein frequency.

B: **Debye model**, where the acoustic branches are approximated by $\omega=v_s q$ with $v_s=\text{const.}$ as

the sound velocity up to a certain $q_{\max}$. Here $S_j(\omega) = \frac{3N}{\omega_D} \omega^2$ for $\omega < \omega_D$, with ω_D being the

Debye frequency given by: $\omega_D = \left(\frac{3Nv_s^3}{(L/2\pi)^2 4\pi} \right)^{1/3}$.

Both approximations are helpful to calculate the **specific heat contribution of phonons**. Here one needs to calculate the temperature dependent part of the equ.(*) which is:

$$c_v = \left(\frac{\partial E}{\partial T} \right)_{V=\text{const}} = k \int_0^{\omega_{\max}} d\omega S(\omega) \left(\frac{\hbar\omega}{kT} \right)^2 \frac{\exp(\frac{\hbar\omega}{kT})}{(\exp(\frac{\hbar\omega}{kT}) - 1)^2}.$$

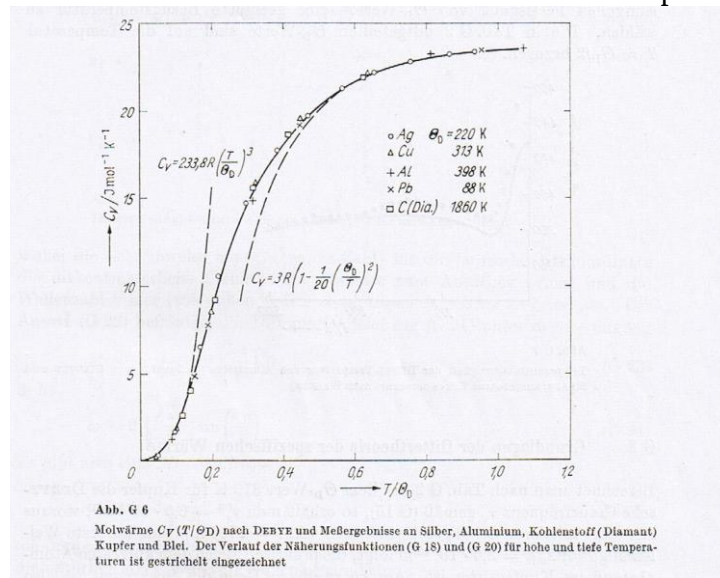
Using Einstein model for $S(\omega)$ one gets $c_v = 3k$ for the case of high T, i.e. $\hbar\omega \ll kT$, as expected by Dulong-Petit law. but a wrong result for low temperatures. However, the artificial temperature which equals the Einstein frequency is named Einstein – Temperature T_E

Alternatively the Debye model provides the correct relation for the low T case:

$$c_v = 3Nk \left(\frac{T^3}{\Theta_D^3} \right) \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad \text{where } \Theta_D \text{ is the Debye temperature (Temperature where all}$$

possible phonon modes are excited) and $x_D = \Theta_D/T$. $\int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$ is the **Debye integral** which cannot be solved analytical (data are tabulated or calculated numerical) The Debye model provides the correct proportionality $c_v \approx T^3$ as expected from experiment but Debye model fails for high temperatures.

In summary, there is no close solution to calculate the contribution of phonons to specific heat



Phonon contribution to thermal conductivity

Heat transport depends on T- gradient dT/dx : $J = -\lambda \frac{dT}{dx}$ where λ is the coefficient of

thermal conductance $\lambda = \frac{1}{3} C_v \langle v \rangle \ell$. with $\langle v \rangle$ as mean particle velocity and ℓ is mean

path way between two particle collisions. Considering Phonons as “particles, the transport process can be understood in similar way as known from in kinetic gas theory. In this picture thermal conductivity will increase proportional to T^3 for low temperature considering increasing population of phonon modes but will decrease proportional to T^{-1} for high temperature due to the increase number of collisions. The latter, **the phonon-phonon interaction**, can be described by elastic collisions considering conservation of phonon energies and phonon momentum.

$$\begin{aligned} \hbar\omega_1 + \hbar\omega_2 &= \hbar\omega_3 \\ \hbar q_1 + \hbar q_2 &= \hbar q_3 \end{aligned}$$

Collisions taking place within the 1.BZ are **normal processes**, processes with final $q > \pi/2a$ gives rise to Peierls-**Umklapp-processes**, reflecting the final momentum back into the 1. BZ.