Specific heat (definition)

and its relation to the temperature derivative of total internal energy

Change of the heat Q consists of the change of total energy + the work done:

$$\frac{dQ}{dt} = \frac{dE}{dt} + P\frac{dV}{dt} \quad , \quad \frac{dE}{dt} = T\frac{dS}{dt} - P\frac{dV}{dt} \quad , \quad dQ/dt = T\, dS/dt.$$

Hence, the specific heat C=dQ/dT is

$$C_v = T(\partial S/\partial T)_V,$$
$$C_p = T(\partial S/\partial T)_P.$$

The energy differential $dE = T\,dS - P\,dV \;\Rightarrow\; C_v = (\partial E/\partial T)_V.$

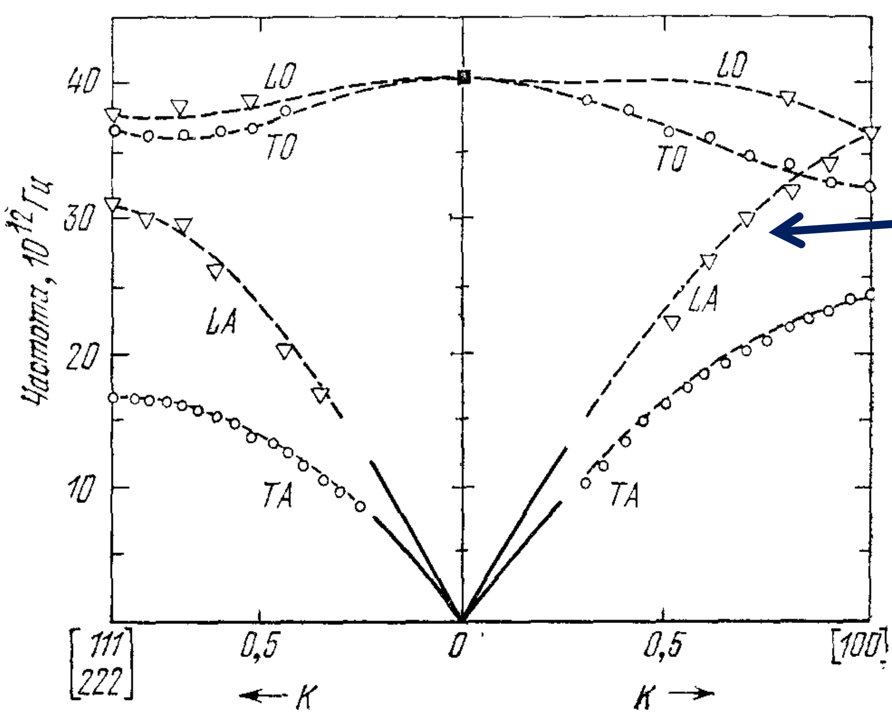
Phonon contribution to the total energy

The energy of all excitations (phonons) is given by the sum over all quantum states, which are numbered by the wave vector $k=p/\hbar$:

$$E_{ph}(T)=\sum_{k,\alpha}\varepsilon_{\alpha}(k)n_{k}(\varepsilon)=\sum_{\alpha}\int\frac{Vd^{3}k}{(2\pi)^{3}}\varepsilon_{\alpha}(k)n_{k}(\varepsilon_{\alpha})$$

The filling number n_k of the quantum states of phonons is given by Bose-Einstein distribution function:

$$n_{k}(\varepsilon)=\frac{1}{\exp([\varepsilon(k)-\mu]/k_{B}T)-1}$$



The phonon dispersion $\omega(k)$ may consist of several branches α.

The phase volume $\int Vd^{3}k/(2\pi)^{3}$ gives the number of quantum states.

Specific heat (heat capacity of unit mass) $C_v = (\partial E/\partial T)_V$

Heat capacity and density of phonon sates in 1D

Energy of phonon gas $E = \sum_K \langle n_K \rangle \hbar\omega_K$, or $E = \int d\omega\, \mathscr{D}(\omega) \langle n(\omega, T) \rangle \hbar\omega.$

$$\langle n \rangle = \frac{1}{\exp(\hbar\omega/\tau) - 1}$$

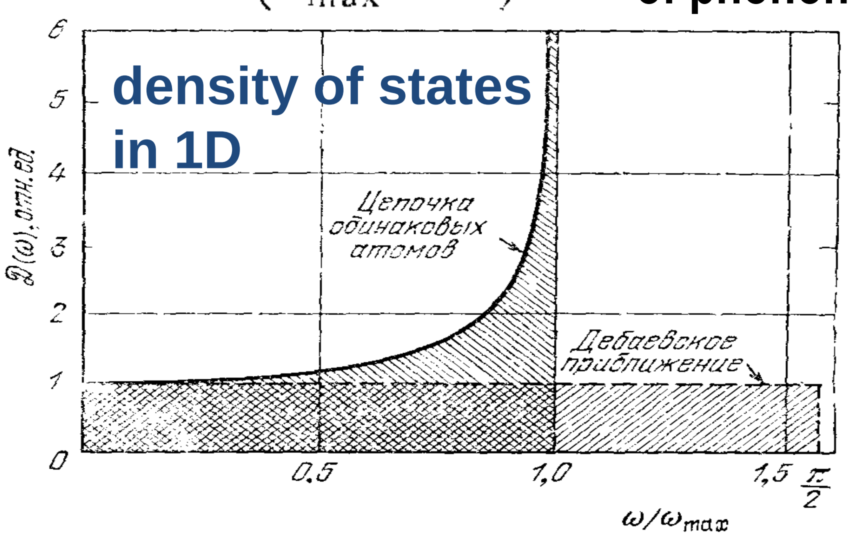
In 1D case $\mathscr{D}(\omega)\, d\omega = \frac{L}{\pi} \frac{dK}{d\omega} d\omega = \frac{L}{\pi} \frac{d\omega}{d\omega/dK}$.

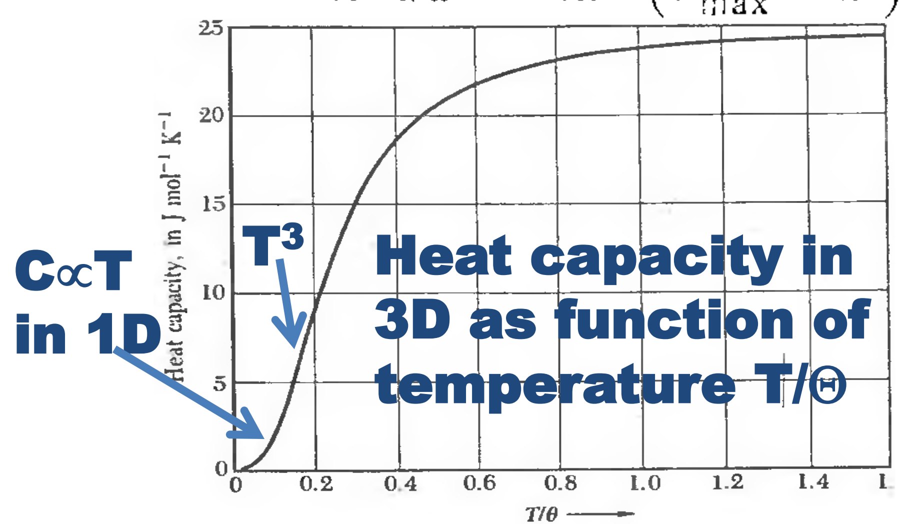
1. In Debye approximation $\omega(K) = vK$, and $\mathscr{D}(\omega) = \frac{L}{\pi v}$ при $\omega \leqslant \frac{v\pi}{a}$

2. In the Einstein model $\mathscr{D}(\omega) = N\delta(\omega - \omega_E)$,

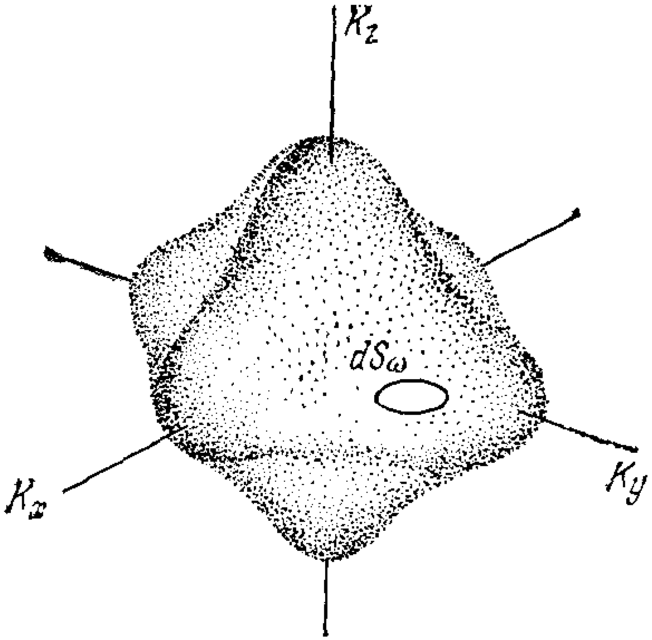
3. For 1D chain of atoms $\omega = \omega_{max} \left| \sin \frac{1}{2} Ka \right|$, $K = \frac{2}{a} \arcsin \frac{\omega}{\omega_{max}}$,

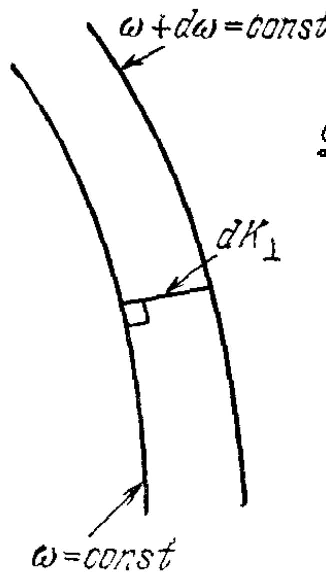
$\frac{dK}{d\omega} = \frac{2}{a} \frac{1}{(\omega_{max}^2 - \omega^2)^{1/2}}$ and the density of phonon states $\mathscr{D}(\omega) = \frac{L}{\pi} \frac{dK}{d\omega} = \frac{2L}{\pi a} \frac{1}{(\omega_{max}^2 - \omega^2)^{1/2}}$





Density of phonon states in 3D (general case)





$$\mathscr{D}(\omega)\,d\omega=\left(\frac{L}{2\pi}\right)^3\int\limits_{\text{shell}} d^3K.$$

$$\int\limits_{\text{shell}} d^3K=\int dS_\omega\,dK_\perp.$$

$$|\nabla_K\omega|\,dK_\perp=d\omega$$

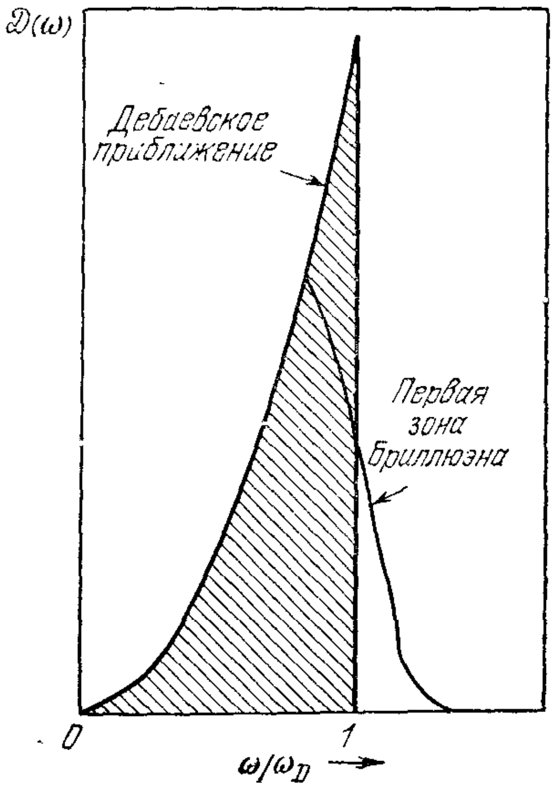
Рис. 6.10а. Элементарная площадка dS_ω на поверхности постоянной частоты в $\boldsymbol{K}$-пространстве. Объем слоя между двумя поверхностями постоянной частоты ω и $\omega+d\omega$ равен $\int dS_\omega\,d\omega/(\mathrm{grad}_K\omega)$.

Рис. 6.10б. Величина $dK_\perp$ есть расстояние между поверхностями постоянных частот ω и $\omega+d\omega$, взятое вдоль нормали к ним.

$$dS_\omega\,dK_\perp=dS_\omega\frac{d\omega}{|\nabla_K\omega|}=dS_\omega\frac{d\omega}{v_g},$$ где $v_g=|\nabla_K\omega|$ — величина групповой скорости фонона.

$$\mathscr{D}(\omega)\,d\omega=\left(\frac{L}{2\pi}\right)^3\int\frac{dS_\omega}{v_g}\,d\omega. \quad\Rightarrow\quad \mathscr{D}(\omega)=\frac{V}{(2\pi)^3}\int\frac{dS_\omega}{v_g}\propto\omega^2$$

Density of phonon states in 3D Debye model



In Debye model [linear ω (k)] the number of phonon states with energy less than ω in a volume V=L[3] is

$$N = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{3} K^3 = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi\omega^3}{3v^3} = \frac{V\omega^3}{6\pi^2 v^3}.$$

$$\mathscr{D}(\omega) = \frac{dN}{d\omega} = \frac{V\omega^2}{2\pi^2 v^3}$$

The Debye (cut off) frequency $\omega_D^3 = \dfrac{6\pi^2 v^3 N}{V}$

The thermal energy is given by

$$U = \int d\omega\, D(\omega)\langle n(\omega)\rangle\hbar\omega = \int_0^{\omega_D} d\omega \left(\frac{V\omega^2}{2\pi^2 v^3}\right)\left(\frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}\right)$$

$$U = \frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} = \frac{3Vk_B^4 T^4}{2\pi^2 v^3 \hbar^3}\int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

$$C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2}\int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2} = 9Nk_B\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$