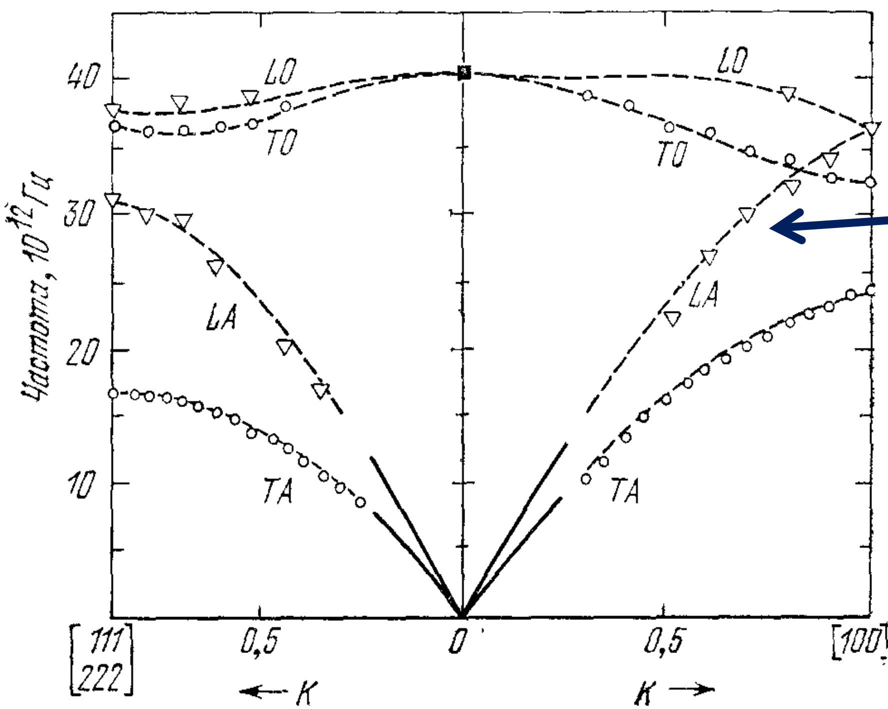
Phonon contribution to the total energy

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

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

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 $\omega(\mathbf{k})$ may consist of several branches α.

The phase volume $\int V d^3k/(2\pi)^3$ 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 $E = \int d\omega\, \mathscr{D}(\omega) \langle n(\omega, T) \rangle \hbar\omega.$

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

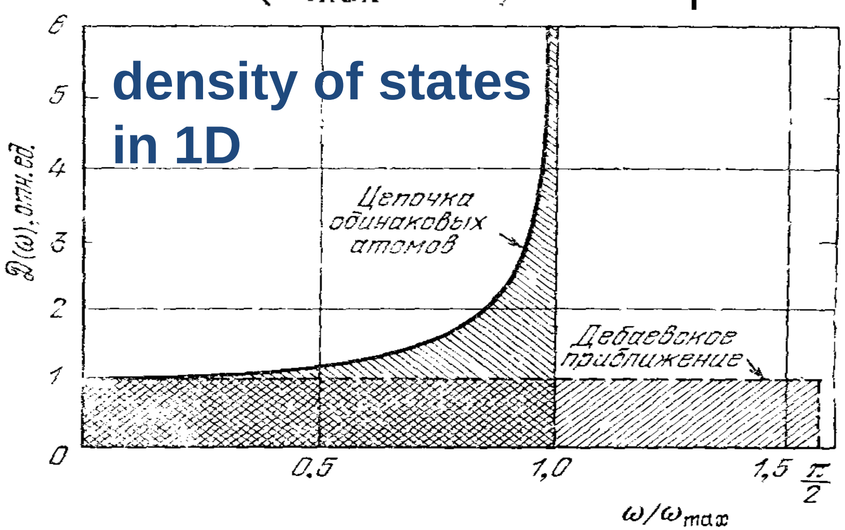
In 1D case $\mathscr{D}(\omega)\, d\omega = \frac{L}{\pi} \frac{dK}{d\omega} d\omega = \frac{L}{\pi} \frac{d\omega}{d\omega/dK}$.

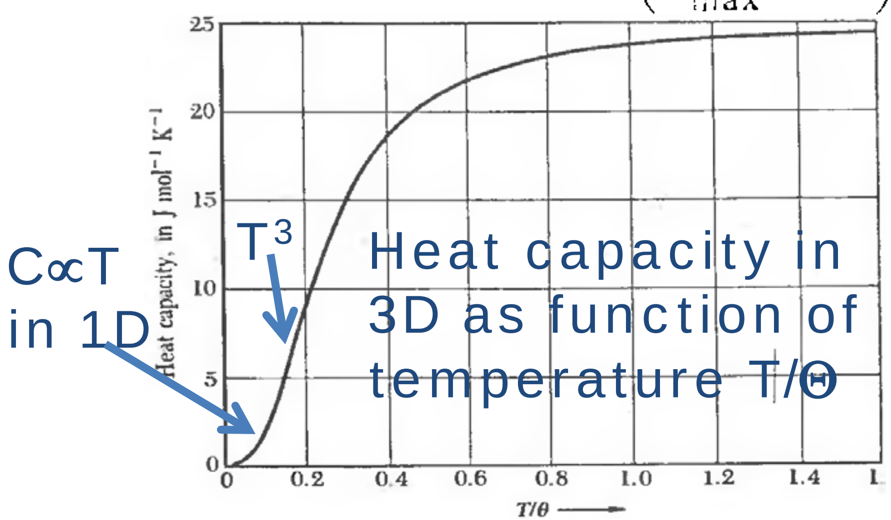
1. In Debye approximation $\omega(K) = vK$, and $\mathscr{D}(\omega) = \frac{L}{\pi v}$ при $\omega \leqslant \frac{v\pi}{a}$

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)

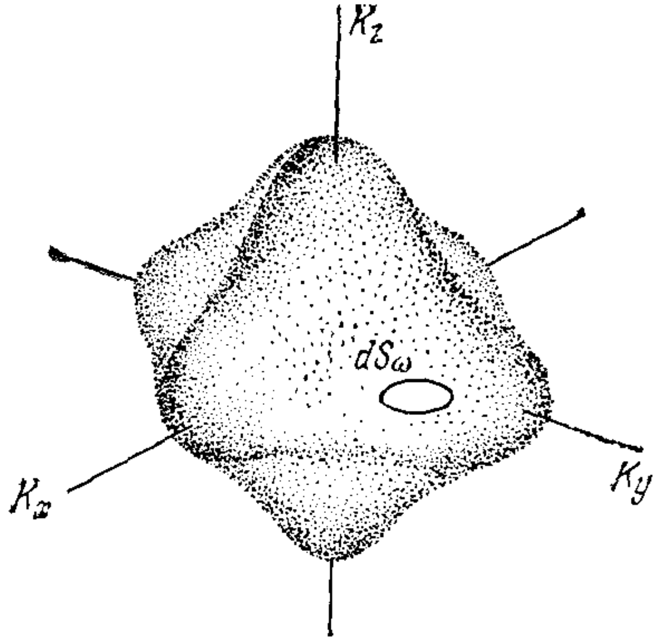


Рис. 6.10а. Элементарная площадка dS_ω на поверхности постоянной частоты в $\boldsymbol{K}$-пространстве. Объем слоя между двумя поверхностями постоянной частоты ω и $\omega + d\omega$ равен $\int dS_\omega\, d\omega/(\mathrm{grad}_K \omega)$.

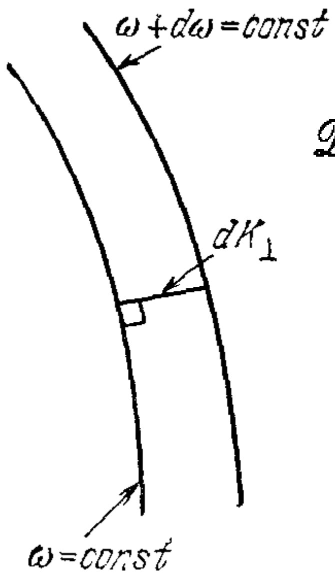


Рис. 6.10б. Величина $dK_\perp$ есть расстояние между поверхностями постоянных частот ω и $\omega + d\omega$, взятое вдоль нормали к ним.

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

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

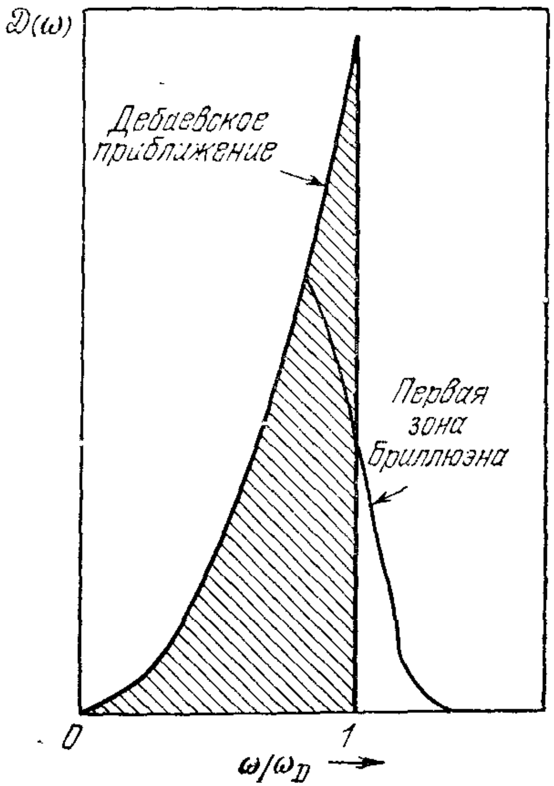
$$|\nabla_K \omega|\, dK_\perp = d\omega$$

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

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

$$\mathscr{D}(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{v_g} \propto \omega^2$$

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

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

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

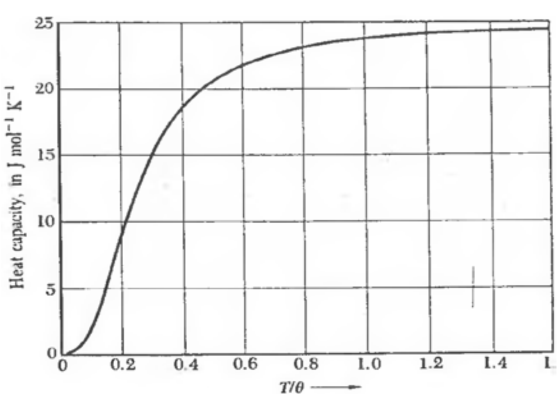
The Debye (cut off) frequency $\omega_D^3 = \dfrac{6\pi^2 v^3 N}{V}$

The thermal energy is given by

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

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

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



Van Hove singularity in the density of states

Density of states $\mathscr{D}(\omega) = \left(\frac{L}{2\pi}\right)^3 \int \frac{dS_\omega}{v_g}$ where group velocity $v_g = |\nabla_K \omega|,$

The integrand has a singularity (singularity) where the group velocity vanishes, i.e., where the dependence of frequency ω on the wave vector K has a local flat section. Points in K-space for which this occurs are called critical points. A critical point can correspond to the maximum, minimum, or saddle point.

Near the critical point $\omega(q) = \omega_c + a_1 q_1^2 + a_2 q_2^2 + a_3 q_3^2 + \ \ldots$

a) Maximum case. Let us assume for simplicity that the local surface of constant frequency has the shape of a sphere. Then $\omega(q) = \omega_c - aq^2.$

For the volume of a sphere of radius q in the Fourier space we have: $\Omega = \frac{4\pi}{3} q^3 = \frac{4\pi}{3} \left(\frac{\omega_c - \omega}{a}\right)^{3/2}.$

Then for the density of states near ω_c we have (for $\omega < \omega_c$) $\mathscr{D}(\omega) = \left(\frac{L}{2\pi}\right)^3 \left|\frac{d\Omega}{d\omega}\right| = \left(\frac{L}{2\pi}\right)^3 \frac{2\pi}{a^{3/2}} (\omega_c - \omega)^{1/2},$

and for ($\omega > \omega_c$) $\mathscr{D}(\omega) = 0.$

Van Hove singularity in the density of states