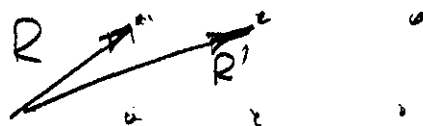Phonons, thermal properties   1

Elasticity of a classical harmonic lattice

Consider a lattice of atoms, that interact with a
pair potential $V(r-r')$.

The total energy is

$$E_{int} = \frac{1}{2} \sum_{RR'} V(R-R')$$

If atoms are displaced then the energy is

$$E_{int} = \frac{1}{2} \sum_{R,R'} V(R-R' + u(R) - u(R')) =$$

$$= E_0 + \frac{1}{2} \sum_{R,R'} \frac{\partial V}{\partial R_\lambda} \left[u_\lambda(R) - u_\lambda(R') \right] +$$

$$+ \frac{1}{4} \sum_{R,R'} \frac{\partial^2 V(R-R')}{\partial R_\alpha \partial R_\beta} \left[u_\alpha(R) - u_\alpha(R') \right]\left[u_\beta(R) - u_\beta(R') \right]$$

Since initial positions $(u=0)$ were equilibrium
positions the linear in $u(R)$ term vanishes

As a result we obtain

$$\delta E_{int} = \frac{1}{4} \sum_{R,R',\alpha\beta} \Phi_{\alpha\beta}(R-R')[u_\alpha(R)-u_\alpha(R')][u_\beta(R)-u_\beta(R')]$$

with $\Phi_{\alpha\beta}(R) = \dfrac{\partial^2 V}{\partial R_\alpha \partial R_\beta}$

Expanding $u_\alpha(R) = u_\alpha(R') + \dfrac{\partial u_\alpha}{\partial R_\beta}(R-R')_\beta$ and

shifting $R - R' \rightarrow R$ we can rewrite

$$\delta E_{int} = \frac{N}{4} \sum_R \Phi_{\alpha\beta}(R) R_\gamma R_\delta \frac{\partial u_\alpha}{\partial R_\gamma} \frac{\partial u_\beta}{\partial R_\delta},$$

where N is the total number of atoms.

Since the energy does not change under

rotation we can replace

$$\frac{\partial u_\alpha}{\partial R_\beta} = \underbrace{\frac{1}{2}\left(\frac{\partial u_\alpha}{\partial R_\beta} + \frac{\partial u_\beta}{\partial R_\alpha}\right)}_{u_{\alpha\beta}} + \underbrace{\frac{1}{2}\left(\frac{\partial u_\alpha}{\partial R_\beta} - \frac{\partial u_\beta}{\partial R_\alpha}\right)}_{=0}$$

Then

$$\delta E_{int} = \frac{N}{4} \sum_R \Phi_{\alpha\beta} R_\gamma R_\delta u_{\alpha\gamma} u_{\beta\delta}$$

To write it in symmetrized form let us

interchange indices $\alpha \leftrightarrow \gamma$, $\beta \leftrightarrow \delta$

and add

$$\delta E_{int} = \frac{N}{16} \sum_R \left[\Phi_{\alpha\beta} R_\gamma R_\delta u_{\alpha\gamma} u_{\beta\delta} + \Phi_{\gamma\beta} R_\alpha R_\delta u_{\delta\alpha} u_{\beta\delta} + \right.$$

$$\left. + \Phi_{\alpha\delta} R_\gamma R_\beta u_{\alpha\gamma} u_{\delta\beta} + \Phi_{\gamma\delta} R_\alpha R_\beta u_{\gamma\alpha} u_{\delta\beta} \right]$$

Since $u_{\alpha\beta}$ is symmetric tensor, $u_{\alpha\beta} = u_{\beta\alpha}$
all the products $u_\smile u_\smile$ are the same, thus

$$\delta E_{int} = \frac{N}{16} \sum_R \left[\Phi_{\alpha\beta} R_\gamma R_\delta + \Phi_{\gamma\beta} R_\alpha R_\delta + \Phi_{\alpha\delta} R_\gamma R_\beta + \right.$$

$$\left. + \Phi_{\gamma\delta} R_\alpha R_\beta \right] u_{\alpha\gamma} u_{\beta\delta}$$

Elastic tensor is defined as

$$\delta E_{el} = \frac{1}{2} \int dV \, \lambda_{\alpha\beta\gamma\delta} \, u_{\alpha\beta} \, u_{\gamma\delta} \quad \Rightarrow$$

$$\lambda_{\alpha\beta\gamma\delta} = \frac{1}{8 V_0} \sum_R \left[\Phi_{\alpha\gamma}(R) R_\beta R_\delta + \Phi_{\beta\gamma}(R) R_\alpha R_\delta + \right.$$

$$\left. + \Phi_{\alpha\delta}(R) R_\gamma R_\beta + \Phi_{\beta\delta}(R) R_\alpha R_\gamma \right]$$

where V_0 is the unit cell volume $V = N V_0$
For an isotropic crystal

$$\lambda_{\alpha\beta\gamma\delta} = \frac{\lambda}{2} \delta_{\alpha\beta}\delta_{\gamma\delta} + \mu\left(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\beta\gamma}\delta_{\alpha\delta} \right)$$

and $\delta E_{el} = \int dV \left[\frac{\lambda}{2}(u_{\alpha\alpha})^2 + \mu(u_{\alpha\beta})^2 \right]$

Longitudinal and transverse sound

Equation of motion is obtained from

$$\rho \frac{\partial^2 u_\alpha}{\partial t^2} = \frac{\delta E_{el}}{\delta u_\alpha} = \mu \frac{\partial^2}{\partial x_\beta^2} u_\alpha + (\lambda + \mu) \frac{\partial}{\partial x_\alpha} \frac{\partial u_\beta}{\partial x_\beta}$$

$$\rho \ddot{\vec{u}} = \mu \nabla^2 \vec{u} + (\mu + \lambda) \, grad \, div \, \vec{u}$$

There are two kind of waves $\vec{u} = \vec{u}_\ell + \vec{u}_t$

longitudinal $rot \, \vec{u}_\ell = 0$ and transverse $div \, \vec{u}_t = 0$

For longitudinal waves we can rewrite

$$\nabla^2 \vec{u} = grad \, div \, \vec{u} - \underbrace{rot \, rot \, \vec{u}}_{=0} = grad \, div \, u_\ell =>$$

$$\rho \ddot{u}_t = (2\mu + \lambda) \nabla^2 u_t = C_\ell \nabla^2 u_\ell =>$$

longitudinal sound velocity $C_\ell = \sqrt{\frac{2\mu + \lambda}{\rho}}$

For transverse waves $div \, \vec{u} = 0$ and

$$\rho \ddot{u}_t = \mu u \nabla^2 u_t =>$$

$$C_t = \sqrt{\frac{\mu}{\rho}}$$

For monochromatic plane wave

$$\vec{u} = Re \, \vec{A}_k \, e^{i\kappa x - i\omega t} \qquad \text{and dispersion law}$$

Longitudinal $\vec{A}_k \parallel \vec{k}$, $\omega_\ell = C_\ell k$

Transverse $\vec{A}_k \perp \vec{k}$, $\omega_t = C_s k$

There is one longitudinal and two transverse modes

Lattice specific heat

Planck distribution formula

What is the average number of phonons with frequency ω_k?

The probability to find n phonon state is given by

$$P(n) = \frac{e^{-\beta E(n)}}{\sum_{n=0,1,\infty} e^{-\beta E(n)}}$$

where $E(n) = \left(n + \frac{1}{2}\right)\hbar\omega$

Then $\langle n \rangle = \sum_n n\, P(n) = \dfrac{\sum_n n\, e^{-\beta\hbar\omega(n+\frac{1}{2})}}{\sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})}}$

The sum in the denominator is

$$Z = \sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})} = e^{-\frac{\beta\omega\hbar}{2}} \sum_n \left(e^{-\beta\hbar\omega}\right)^n =$$

$$= \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}}$$

Thus $\langle n_\omega \rangle = (1 - e^{-\beta\hbar\omega}) \sum_n n \, e^{-\beta\hbar\omega n} =$

$$= -(1 - e^{-\beta\hbar\omega}) \frac{\partial}{\partial\hbar\omega} \sum_n (e^{-\beta\hbar\omega})^n =$$

$$= -(1 - e^{-\beta\hbar\omega}) \frac{\partial}{\partial\hbar\omega} \cdot \frac{1}{1 - e^{-\beta\hbar\omega}} =$$

$$= \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \boxed{\frac{1}{e^{\beta\hbar\omega} - 1}}$$

This is the Planck distribution formula.

One can get it directly using Bose statistics of phonons: $\langle n_\omega \rangle = \dfrac{1}{e^{\varepsilon_\omega - \mu} + 1}$

The density of phonons is not fixed. It is determined by minimisation of the free energy $\frac{\partial F}{\partial N} = 0$. But $\frac{\partial F}{\partial N} = \mu \Rightarrow$

$\mu = 0$ and we obtain the Planck distribution from the Bose distribution

Specific heat

The internal energy density is given by

$$E = \sum_K \hbar \omega_K \left(\langle n_K \rangle + \frac{1}{2} \right) =$$

$$= \sum_K \frac{\hbar \omega_K}{2} + \sum_K \frac{\hbar \omega_K}{e^{\hbar \omega_K \beta} - 1}$$

Taking derivative over temperature we obtain

$$C_V = \frac{1}{V} \frac{\partial E}{\partial T} = \frac{1}{V} \sum_K \frac{\partial}{\partial T} \frac{\hbar \omega_K}{e^{\beta \hbar \omega_K} - 1}$$

High temperature specific heat

For temperature higher than the maximal phonon frequency we can expand

$$\frac{1}{e^{\beta \hbar \omega} - 1} = \frac{1}{\beta \hbar \omega + \frac{(\beta \hbar \omega)^2}{2} + \dots} = \frac{1}{\beta \hbar \omega} \left[1 - \frac{\beta \hbar \omega}{2} + \frac{(\beta \hbar \omega)^2}{12} + \dots \right]$$

$$\approx \frac{T}{\hbar \omega}$$

Then $C_v = \frac{1}{V} \sum_K \frac{\partial}{\partial T} \hbar \omega \frac{T}{\hbar \omega} + \dots = \frac{1}{V} \sum_K 1$

The total number of modes is 3 times the number of atoms and we obtain the classical law of Dulong and Petit. $C_v = 3n$

Low temperature specific heat

For crystal of finite size L $K = \frac{2\pi}{L} n$ and replacing sum by the integral over Brillouin zone we obtain

$$C_v = \frac{\partial}{\partial T} \sum_S \int \frac{d^3 k}{(2\pi)^3} \frac{\hbar \omega_s(k)}{e^{\hbar \omega_s \beta} - 1}$$

For low temperatures main contribution comes from three acoustic phonon modes

$$\omega_s = C_s k$$

$$C_v = \frac{\partial}{\partial T} \sum_s \int \frac{\kappa^2 d\kappa \, d\Omega}{(2\pi)^3} \frac{\hbar \, C_s \kappa}{e^{\frac{\hbar C_s \kappa}{T}} - 1}$$

introducing $\frac{\hbar C_s \kappa}{T} = X$ we can rewrite

$$C_v = \frac{\partial}{\partial T} \frac{T^4}{\hbar^3} \sum_s \frac{d\Omega}{C_s^3(\kappa)} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

Here we extended the κ integration from the Brillouin zone to the whole κ-space since the integral is quickly convergent

Then

$$C_v = \frac{T^3}{\hbar^3} \sum_s \frac{d\Omega}{C_s^3(\kappa)} \frac{1}{2\pi^3} \int_0^\infty \frac{x^3}{e^x - 1} dx =$$

$$= \left(\frac{T}{\hbar \bar{c}}\right)^3 \frac{6}{\pi^2} \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

We introduced effective sound velocity

$$\bar{c}^{-3} = \frac{1}{3} \sum_s \int \frac{d\Omega}{4\pi \, C_s(\kappa)^3}$$

For isotropic solid $\frac{3}{\bar{c}^3} = \frac{2}{c_t^2} + \frac{1}{c^2}$

The integral can be evaluated by rewriting

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} dx = 6 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15}$$

Finally for low temperatures

$$C_V = \frac{2\pi^2}{5} \left(\frac{T}{\hbar \bar{c}} \right)^3$$

Thus the phonon specific heat is $\propto T^3$ at low temperatures. This is the main contribution for insulators.

For metals we have additional electronic contribution γT that dominates at lowest temperatures. Since $\gamma \simeq m^* p_F \sim m^2 v_s$

then lattice contribution becomes important for $T^2 > m^2 v_F \bar{c}^3 \Rightarrow T > \varepsilon_F \left(\frac{\bar{c}}{v_F} \right)^{3/2}$

For typical metal $\frac{\bar{c}}{v_F} \sim \sqrt{\frac{m}{M}} << 1$ and Lattice contribution becomes important already at rather low temperatures $\sim 10\,K$

Black body radiation

The calculation that we performed is almost identical to the theory of black body radiation. The only difference is replacing the sound velocity by the speed of light and additional factor $\frac{2}{3}$ since there are only transverse photons but no longitudinal.

The corresponding internal energy is given by the Stefan-Boltzmann law

$$E = \frac{\pi^2}{15} \frac{T^4}{(\hbar c)^3}$$

Quite often one uses the <u>Debye</u> interpolation scheme. In this model we replace all spectrum by the single mode $\omega = ck$.

In addition the integration over the Brillouin zone is replaced the sphere of radius k_D. which has the same volume as the Brillouin zone

$$\frac{4\pi}{3} k_D^3 = (2\pi)^3 \frac{N}{V} \implies n = \frac{k_D^3}{6\pi^2}$$

The maximal wave vector k_D defines the Debye frequency $\omega_D = ck_D$ and the Debye temperature $\Theta_D = \hbar\omega_D$. Then specific heat can be presented as

$$C_v = 9n \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x \, dx}{(e^x - 1)^2}$$

Typical values of Θ_D are $\sim 10^2 - 10^3 \, K$

Contribution of the optical phonons is often discussed in the framework of the Einstein model. In this approximation one replaces the optical branch by the single frequency ω_E and again considers spherical Brillouin zone. Each mode contributes

$$\frac{n \hbar \omega_E}{e^{\hbar \omega_E / T} - 1}$$

and the specific heat is

$$C_v^{opt.} = 3N \left(\frac{\hbar \omega_E}{T}\right)^2 \frac{e^{\frac{\hbar \omega_E}{T}}}{\left(e^{\frac{\hbar \omega_E}{T}} - 1\right)^2}$$

Phonon density of states

In the same way as for electrons, for general dispersion law we can replace

$$\int \frac{d^3 k}{(2\pi)^3} = \int d\omega \, g(\omega) \quad \text{with the}$$

phonon density of states

$$g(\omega) = \sum_s \int \frac{dS}{(2\pi)^3} \frac{1}{\left|\frac{\partial \omega_s(k)}{\partial k}\right|}$$

Since ω_s has extrema in the Brillouin zone it produces Van Hove singularities $g(\omega) \propto \sqrt{|\omega - \omega_0|}$

Anharmonicity and thermal expansion

Interaction between the atoms is not always quadratic. Cubic terms lead to the thermal expansion. We can describe it consider the phonon gas but with frequencies that depend on volume

$$\frac{\Delta \omega_s}{\omega_s} = - \gamma \frac{\Delta V}{V} \quad , \quad \gamma \text{ is Grüneisen parameter}$$

The total free energy can be written as

$$F = \frac{1}{2} K \left(\frac{\Delta V}{V} \right)^2 + T \sum_{K,S} \ln \left(2 \sinh \frac{\hbar \omega_s}{2T} \right)$$

here $K = \lambda + \frac{2}{3} \mu$ -compressibility modulus, and the second term is phonon contribution to free energy. Taking derivative over ΔV we obtain

$$K \frac{\Delta V}{V} = \sum_{K,S} \gamma \, \hbar \omega_{K,S} \coth \frac{\hbar \omega_s}{2T} = \gamma E(T)$$

where $E(T)$ is internal energy from page 7.

Taking derivative we obtain

$$\alpha = \frac{1}{V}\frac{dV}{dT} = \frac{\gamma}{K} C_V$$

Thus at low temperatures thermal expansion is proportional to T^3

In general one different modes have different density dependence and one should replace γ by the weighted average

$$\gamma = \frac{\sum_{ks}\gamma_{ks} C_{vs}(\kappa)}{\sum_{ks} C_{vs}(\kappa)}$$

where C_{vs} is the contribution to the K,S mode to the specific heat