Lecture 1.
Lattice vibrations, phonons and thermal properties of dielectrics.

Consider a periodic array of atoms (ions), which contains q units per elementary cell. The coordinate of an elementary cell is characterized by a vector $\mathbf{n}$ with integer components n_1,n_2 and n_3 which correspond to translations along the primitive vectors $\mathbf{a}_1$,$\mathbf{a}_2$ and $\mathbf{a}_3$ ($\mathbf{a}_1[\mathbf{a}_2\mathbf{a}_3] \neq 0$). The position $\mathbf{r}_{\mathbf{n}j}$ of the j-th atom in $\mathbf{n}$-th elementary cell is given by expression:

$$\mathbf{r}_{\mathbf{n}j} = \mathbf{R}_{\mathbf{n}j} + \mathbf{u}_{\mathbf{n}j} = \mathbf{a}_1 n_1 + \mathbf{a}_2 n_2 + \mathbf{a}_3 n_3 + \rho_j + \mathbf{u}_{\mathbf{n}j}. \qquad (1)$$

Here $\mathbf{R}_{\mathbf{n}j}$ is the equilibrium position of j-th atom in $\mathbf{n}$-th elementary cell, while ρ_j is its position in the cell at the origin. Vector $\mathbf{u}_{\mathbf{n}j}$ denotes a displacement of the atom $(\mathbf{n}, j)$ from its equilibrium position.

Vibration modes

Since the potential energy has an equilibrium at $\mathbf{r}_{\mathbf{n}j} = \mathbf{R}_{\mathbf{n}j}$, the classical Hamiltonian of the lattice as a function of momenta $\mathbf{p}_{\mathbf{n}j}$ and displacements $\mathbf{u}_{\mathbf{n}j}$ could be written as a power series in displacements:

$$H(\mathbf{p}_{\mathbf{n}j}, \mathbf{u}_{\mathbf{n}j}) = \sum_{\mathbf{n},j} \frac{\mathbf{p}_{\mathbf{n}j}^2}{2M_j} - \frac{1}{2} \sum \mathbf{n}\mathbf{n}'jj' A_{jj'}^{\alpha\ \beta}(\mathbf{n}-\mathbf{n}') u_{\mathbf{n}j}^{\alpha} u_{\mathbf{n}'j'}^{\beta} -$$
$$-\frac{1}{6} \sum B_{jj'j''}^{\alpha\ \beta\ \gamma}(\mathbf{n}-\mathbf{n}', \mathbf{n}-\mathbf{n}'') u_{\mathbf{n}j}^{\alpha} u_{\mathbf{n}'j'}^{\beta} u_{\mathbf{n}''j''}^{\gamma} - \dots \quad (2)$$

The system is invariant with respect to discrete translation along the Bravais lattice. Therefore, the force matrices $\hat{A}$, $\hat{B}$, etc depend not on $\mathbf{n}, \mathbf{n}'$ or $\mathbf{n}''$ themselves, but on their difference $\mathbf{n} - \mathbf{n}'$, $\mathbf{n}'' - \mathbf{n}'$, etc. The equation of motion follows from Eq (2):

$$\dot{p}_{\mathbf{n}j} = -\sum_{\mathbf{n}',j'} A_{jj'}^{\alpha\ \beta}(\mathbf{n}-\mathbf{n}')\ u_{\mathbf{n}'j'}^{\beta} - \frac{1}{2} \sum_{\mathbf{n}'\mathbf{n}''j'j''} B_{jj'j''}^{\alpha\ \beta\ \gamma}\ u_{\mathbf{n}'j'}^{\beta}\ u_{\mathbf{n}''j''}^{\gamma} - \quad (3)$$
$$M_j \dot{\mathbf{u}}_{\mathbf{n}j} = \mathbf{p}_{\mathbf{n}j}. \quad (4)$$

Since the translation of whole crystal along an arbitrary distance $\mathbf{d}$ ($u_{\mathbf{n}j}^{\alpha} \to u_{\mathbf{n}j}^{\alpha} + d^{\alpha}$) does not change its energy and generates no force, the force matrices $\hat{A}$, $\hat{B}$ obey the conditions:

$$\sum_{\mathbf{n}',j'} A_{jj'}^{\alpha\ \beta}(\mathbf{n}-\mathbf{n}') = 0, \quad (5)$$
$$\sum_{\mathbf{n}'\mathbf{n}''j'j''} B_{jj'j''}^{\alpha\beta\gamma}(\mathbf{n}'-\mathbf{n}, \mathbf{n}''-\mathbf{n}) = 0. \quad (6)$$

We forget for the time being about the higher powers of the displacements and restrict ourselves to harmonic approximation. A certain asymmetry of Eqs (3, 4) caused by inequality of the masses M_j could be removed by the substitution:

$$u^{\alpha}_{\mathbf{n}j}(t) = \frac{w^{\alpha}_{\mathbf{n}j}(t)}{\sqrt{M_j}}, \quad A^{\alpha\beta}_{jj'} = \sqrt{M_j M'_j}\, \mathcal{D}^{\alpha\beta}_{jj'}(\mathbf{n}' - \mathbf{n}), \tag{7}$$

which leads to the equations of motion of the form:

$$\ddot{w}^{\alpha}_{\mathbf{n}j}(t) = -\sum_{\mathbf{n}'j'} \mathcal{D}^{\alpha\beta}_{jj'}(\mathbf{n} - \mathbf{n}') w^{\beta}_{\mathbf{n}'j'}. \tag{8}$$

The Fourier transform of the real variable $w_{\mathbf{n}}(t)$

$$w_{\mathbf{n}j} = \sum_{\mathbf{k}} \left[w_j(\mathbf{k}) e^{-i\omega t + i\mathbf{k}\mathbf{r}_{\mathbf{n}}} + \bar{w}_j(\mathbf{k}) e^{i\omega t - i\mathbf{k}\mathbf{r}_{\mathbf{n}}} \right]; \quad w_j(\mathbf{k}) = \bar{w}_j(-\mathbf{k}) \tag{9}$$

leads to the equation of motion in the form of the eigenvalue problem for a $3q \times 3q$ matrix $\hat{\mathcal{D}}(\mathbf{k})$:

$$\omega^2 w^{\alpha}_j(\mathbf{k}) = \sum_{j'} \mathcal{D}^{\alpha\beta}_{jj'}(\mathbf{k}) w^{\beta}_{\mathbf{n}'j'}(\mathbf{k}). \tag{10}$$

The solution of this eigenvalue problem gives $3q$ branches of the vibration spectrum $\omega_s(\mathbf{k})$ with $3q$ eigenvectors $\mathbf{e}_j(\mathbf{k}, s)$ which obey ortho-normalization and completeness conditions:

$$\sum_j e^{\alpha}_j(\mathbf{k}, s) \bar{e}_j^{\,\alpha}(\mathbf{k}', s') = \delta_{ss'} \Delta(\mathbf{k} - \mathbf{k}'); \tag{11}$$

$$\sum_{\mathbf{k}s} e^{\alpha}_j(\mathbf{k}, s) \bar{e}_{j'}^{\,\beta}(\mathbf{k}, s) = \delta_{jj'} \delta^{\alpha\beta}. \tag{12}$$

Therefore, the displacement $\mathbf{u}_{\mathbf{n}j}$ can be expressed through the contributions of the eigenmodes of the crystal

$$\mathbf{u}_{\mathbf{n}j} = \frac{1}{\sqrt{M_j}} \sum_{\mathbf{k}\ s} \left[\mathcal{A}(\mathbf{k}s) \mathbf{e}_j(\mathbf{k}s) e^{-i\omega_s(\mathbf{k})t + i\mathbf{k}\mathbf{r}_{\mathbf{n}}} + \bar{\mathcal{A}}(\mathbf{k}s) \bar{\mathbf{e}}_j(\mathbf{k}s) e^{i\omega_s(\mathbf{k})t - i\mathbf{k}\mathbf{r}_{\mathbf{n}}} \right] \tag{13}$$

with partial complex amplitudes $\mathcal{A}(\mathbf{k}s)$.
For zero quasi-momentums $\mathbf{k} = 0$ Eq (10) takes the form:

$$\omega_s^2(\mathbf{k}=0)e_j^\alpha(\mathbf{k}=0,s) = \sum_{\mathbf{n}'j'} \frac{A_{jj'}^{\alpha\beta}(\mathbf{n}-\mathbf{n}')}{\sqrt{M_j M_j'}} e_j'^\beta(\mathbf{k}=0,s) \quad (14)$$

Multiplying Eq(14) by $\sqrt{M_j}$, summing over j and using Eq (5), we arrive at the condition:

$$\omega_s^2(\mathbf{k}=0)\sum_j \sqrt{M_j}\mathbf{e}_j(\mathbf{k}=0,s) = 0 \quad (15)$$

which clearly shows that either

$$\sum_j \sqrt{M_j}\mathbf{e}_j(\mathbf{k}=0,s) \neq 0$$

and then $\omega_s(\mathbf{k}) = 0$, or

$$\sum_j \sqrt{M_j}\mathbf{e}_j(\mathbf{k}=0,s) = 0$$

and, possibly, $\omega_s(\mathbf{k}) \neq 0$. This means that 3 branches of the lattice vibrations correspond to the displacement of the centre of mass of the elementary cell (acoustic modes) and their frequency vanishes as $\mathbf{k} \to 0$. In the rest of the vibration modes to the center of mass does not move (optic modes) and their frequencies do not vanish as $\mathbf{k} \to 0$.

Phonons

The momentum $\mathbf{p}_{\mathbf{n}j} = M_j \dot{u}_{\mathbf{n}j}$ can be expressed through the amplitudes $\mathcal{A}_s(\mathbf{k})$ as

$$\mathbf{p}_{\mathbf{n}j}(t) = -i\sum_{\mathbf{k}\ s} \sqrt{M_j}\,\omega_s(\mathbf{k})\left[\mathcal{A}(\mathbf{k}s)\mathbf{e}_j(\mathbf{k}s)e^{-i\omega_s(\mathbf{k})t+i\mathbf{k}\mathbf{r}_\mathbf{n}} - c.c.\right]. \quad (16)$$

Therefore, the Hamiltonian (2) can be rewritten in a diagonal form

$$H(\mathcal{A},\bar{\mathcal{A}}) = \sum_{\mathbf{k}\ s} \omega_s^2(\mathbf{k}) \left[\mathcal{A}(\mathbf{k}s)\bar{\mathcal{A}}(\mathbf{k}s) + \bar{\mathcal{A}}(\mathbf{k}s)\mathcal{A}(\mathbf{k}s)\right], \quad (17)$$

while the quantum commutation relations

$$[p^{\alpha}_{\mathbf{n}j}, u^{\beta}_{\mathbf{n}'j'}] = -i\hbar\delta(\mathbf{n}-\mathbf{n}')\delta_{j\ j'}\ \delta^{\alpha\beta} \quad (18)$$

take the form

$$[\mathcal{A}_s(\mathbf{k}), \mathcal{A}'_s(\mathbf{k}')] = [\bar{\mathcal{A}}_s(\mathbf{k}), \bar{\mathcal{A}}'_s(\mathbf{k}')] = 0; \quad (19)$$

$$[\mathcal{A}_s(\mathbf{k}), \bar{\mathcal{A}}'_s(\mathbf{k}')] = 2\hbar\omega_s(\mathbf{k})\Delta_{\mathbf{k}\mathbf{k}'}\delta_{s\ s'}. \quad (20)$$

Eqs (19,20) provoke the introduction the creation/annihilation operators

$$a^+_s(\mathbf{k}) = \sqrt{\frac{2\omega_s(\mathbf{k})}{\hbar}}\ \bar{\mathcal{A}}_s(\mathbf{k}), \quad a_s(\mathbf{k}) = \sqrt{\frac{2\omega_s(\mathbf{k})}{\hbar}}\ \mathcal{A}_s(\mathbf{k}), \quad (21)$$

$$[a^+_s(\mathbf{k}), a'^+_s(\mathbf{k}')] = [a_s(\mathbf{k}), a'_s(\mathbf{k}')] = 0,\ [a_s(\mathbf{k}), a'^+_s(\mathbf{k}')] = \Delta_{\mathbf{k}\mathbf{k}'}\delta_{ss'} \quad (22)$$

The displacement $\mathbf{u}_{\mathbf{n}j}$ can now be written as (we omit its dependence on time t):

$$\mathbf{u}_{\mathbf{n}j} = \sum_{\mathbf{k}\ s} \sqrt{\frac{\hbar}{2M_j\omega_s(\mathbf{k})}} \left[a_s(\mathbf{k})\mathbf{e}_j(\mathbf{k}s)e^{i\mathbf{k}\mathbf{r}_\mathbf{n}} + a^+_s(\mathbf{k})\bar{\mathbf{e}}_j(\mathbf{k}s)e^{-i\mathbf{k}\mathbf{r}_\mathbf{n}}\right], \quad (23)$$

while the Hamiltonian and its energy levels are:

$$H = \sum_{\mathbf{k}\ s} \frac{\hbar\omega_s(\mathbf{k})}{2} \left[a^+_s(\mathbf{k})a_s(\mathbf{k}) + a_s(\mathbf{k})a^+_s(\mathbf{k})\right], \quad (24)$$

$$E(\{n_s(\mathbf{k})\}) = \sum_{\mathbf{k}\ s} \frac{\hbar\omega_s(\mathbf{k})}{2}\left(2n_s(\mathbf{k})+1\right),\ n_s(\mathbf{k}) = a^+_s(\mathbf{k})a_s(\mathbf{k}) \quad (25)$$

Thermodynamics

The calculation of thermodynamic functions should begins with the partition function

$$Z = \sum_{\mathbf{k}s} \sum_{n_{\mathbf{k}s}=1}^{\infty} \exp\left[-\beta E(\{n\})\right] = \sum_{\mathbf{k}s} \frac{e^{-\beta\hbar\omega_s(\mathbf{k})/2}}{1 - e^{-\beta\hbar\omega_s(\mathbf{k})}}. \qquad (26)$$

The mean values of different quantum operators could be found by summation over occupation numbers $n_s(\mathbf{k})$. For instance, the mean occupation number is given by the Plank formula:

$$\langle n_s(\mathbf{k})\rangle = Z_{\mathbf{k}s}^{-1} \sum_{n=0} n \exp\left[-\beta\hbar\omega_s(\mathbf{k})\left(n + \frac{1}{2}\right)\right] = \frac{1}{\exp\left[\beta\hbar\omega_s(\mathbf{k})\right] - 1}. \qquad (27)$$

This shows that the chemical potential of phonons is equal to zero and, therefore, the grand-canonical thermodynamic potential Ω coincides with free energy

$$F(T) = -T \ln Z = \sum_{\mathbf{k}s} \left[\frac{\hbar\omega_s(\mathbf{k})}{2} + T \ln\left(1 - e^{-\beta\hbar\omega_s(\mathbf{k})}\right)\right], \qquad (28)$$

where the first term in the sum does not depend on temperature and stands for contribution of zero-point fluctuations, while the second one gives the contribution of thermal fluctuations. The entropy S and specific heat C_V are the first and the second derivative of free energy

$$C_V(T) = T\left(\frac{\partial S}{\partial T}\right) = \left(\frac{\partial}{\partial T} T \left(\frac{\partial F}{\partial T}\right)\right) = \sum_{\mathbf{k}s} \frac{\hbar^2\omega_s^2(\mathbf{k}) e^{\beta\hbar\omega_s(\mathbf{k})}}{T^2\left(e^{\beta\hbar\omega_s(\mathbf{k})} - 1\right)^2}. \qquad (29)$$

Using the phonon spectral density

$$g(\omega) = \sum_{\mathbf{k},s} \delta\left(\omega - \omega_s(\mathbf{k})\right), \tag{30}$$

we can rewrite Eq (29) in the form

$$C_V(T) = \int_0^{+\infty} d\omega\ g(\omega)\ \frac{\hbar^2\omega^2}{T^2\left(e^{\beta\hbar\omega} - 1\right)\left(1 - e^{-\beta\hbar\omega}\right)}. \tag{31}$$

Density of states is an additive value over partial contributions of different modes. At low frequencies $\omega \ll \langle\omega\rangle$, only three acoustic modes contribute to the density of states. Their frequencies $\omega(\mathbf{k})$ are linear with quasi-momentum $\mathbf{k}$, but sound velocities, strictly speaking, depend on its direction even for highly symmetric cubic crystals. If, nevertheless, to neglect this elastic anisotropy, the density of states takes the form

$$\begin{aligned} g(\omega)|_{\omega\to 0} &= \sum_{\mathbf{k},s} \delta\left(\omega - \omega_s(\mathbf{k})\right)_{\omega\to 0} = \int \frac{d\mathbf{k}}{(2\pi)^3}\left[\delta(\omega - c_l k) + 2\delta(\omega - c_t k)\right] = \\ &= \frac{3\omega^2}{2\pi^2}\left\{\frac{1}{3c_l^3} + \frac{2}{3c_t^3}\right\} = \frac{3\omega^2}{\omega_D^3 v_0}, \end{aligned} \tag{32}$$

where c_l and c_t are velocities of longitudinal and transverse sounds respectively, $\omega_D \sim \langle\omega\rangle$ is the so called Debye frequency and v_0 is the volume of the unit cell. The integral of the density of states over frequencies is equal to total number of modes per unit cell. This gives the sum-rule:

$$\int_0^{\infty} d\omega g(\omega) = \frac{3q}{v_0}. \tag{33}$$

Combination of Eq (31), Eq (32) and Eq (33) gives two asymptotes for specific heat:

$$C(T) = \frac{3}{v_0} \begin{cases} (T/\hbar\omega_D)^3, & T \ll \hbar\omega_D; \\ q - \frac{\hbar^2 \langle\omega^2\rangle}{36T^2}, & T \gg \hbar\omega_D \end{cases} \tag{34}$$

This presents the low-temperature Debye law $C \propto T^3$ and the high-temperature Dulong-Petit law of constant specific heat[1].

Thermal expansion

Thermal expansion occurs due to anharmonicity. It is easy to see that on a simple model of a diatomic molecule in which the nuclei move in the potential schematically represented in Fig. 1 as a function of distance R between the nuclei.

Near its minimum at $R = R_0$ the potential energy can be represented as

$$U(R) = U_0 + \frac{M\omega^2}{2}(R - R_0)^2 - \frac{\gamma}{6}(R - R_0)^3.^2 \tag{35}$$

In the framework of classical statistical mechanics, the mean distance of nuclei $R(T)$ is given by the following ratio:

$$R(T) = R_0 + \frac{\int dR(R - R_0)\exp[-\beta U(R)]}{\int dR \exp[-\beta U(R)]} \tag{36}$$

[1]Pay attention to small numerical coefficient at correction to high-temperature asymptote. This explains why the classical Dulong-Petit law is valid not only at $T \gg \hbar\omega_D$, but up to $T \geq \hbar\omega_D/7$.

[2]The sign of the coefficient γ in the cubic term in this formula ($\gamma > 0$) corresponds to convexity of the curve $U(R)$ at large R.

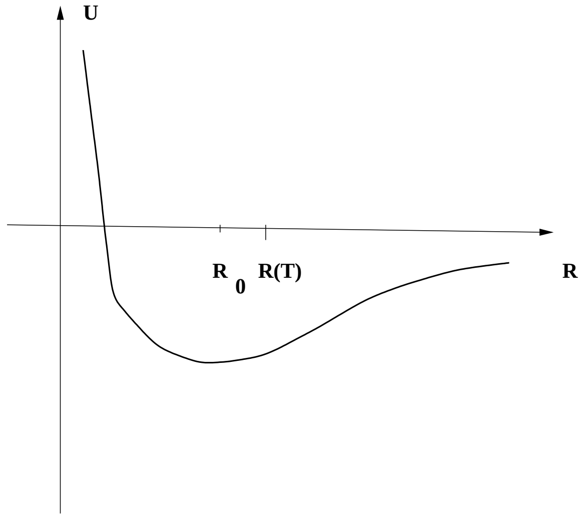

Figure 1: Potential energy of a diatomic molecule as a function of the distance R between the nuclei. It is seen that the average separation increases with increasing the temperature.

Expanding the exponentials in Eq (36) in cubic terms in oscillation amplitudes $R - R_0$, we arrive at the expression

$$R(T) = R_0 + \frac{\gamma}{6T}\langle (R - R_0)^4\rangle = R_0 + T\frac{\gamma}{2M^2\omega^4}, \qquad (37)$$

which couples the thermal expansion linear in temperature T to the sign of anharmonic constant ($\gamma > 1$).
Thermal expansion of crystals originates from the same basic source: the dependence of the free energy $F(T, V)$ and the Gibbs potential $\Phi(p, T)$ on both temperature and volume (pressure). For instance, at low temperature $T \ll \hbar\omega_D$

$$\Phi(p, T) = \Phi_0(T) - \frac{12T^4 V_0(p)}{v_0 \hbar^3 \omega_D^3}; \; V(T, p) = V_0(p) - \frac{12T^4 V_0}{\hbar^3}\frac{\partial}{\partial p}\left(\frac{1}{v_0 \omega_D^3}\right). \qquad (38)$$

At high temperature $T \geq \hbar\omega_D$

$$V(T,p) = V_0(p) - 3qTV_0\, \frac{d}{dp}\left(\frac{1}{v_0}\right). \tag{39}$$

Finally, the coefficient of thermal expansion α has the following asymptotes:

$$\alpha(T) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{d}{dp}\begin{cases} 12T^3(v_0\hbar^3\omega_D^3)^{-1}, & T \ll \hbar\omega_D; \\ v_0^{-1}, & T \geq \hbar\omega_D. \end{cases} \tag{40}$$

Equation (40) shows that the thermal expansion is the result of the dependence of the phonon frequencies on pressure and volume, i.e. it is the result of anharmonicity. At high temperature, the thermally expansion does not depend on temperature, while at low temperature it decreases as T^3 and vanishes at zero temperature. Therefore, the dependence of the coefficient of thermal expansion $\alpha(T)$ on temperature is very similar to that of the specific heat $C(T)$. If a single parameter $\Theta \sim \hbar\omega_D$ can be introduced as an energy scale in the temperature dependence of the Gibbs potential

$$\Phi(T,p) = \Phi_0(p) + \Theta(p) f\left(\frac{T}{\Theta(p)}\right), \tag{41}$$

then

$$\alpha(T) = -\frac{T}{V_0\Theta^2}\,\frac{d\Theta}{dp}\, f'', \quad C(T) = -\frac{T}{\Theta}\, f'', \tag{42}$$

and, finally

$$\frac{\alpha(T)}{C(T)} = -\frac{1}{V_0\Theta}\,\frac{d\Theta}{dp}\, f''. \tag{43}$$

Therefore, the temperature dependence of the ratio α/C can indicate whether the phonon system might be characterized by a single parameter of the dimension of energy.