Lecture 3.
Displacement type phase transitions.

Due to a large ratio $M/m \gg 1$ of the mass of a nucleus to that of an electron, the amplitude of lattice vibrations is relatively small and the harmonic approximation is valid (see Introduction). This allows to view the thermal excitations of a dielectric crystal as a nearly ideal gas of phonons. Weak anharmonicity plays a crucial role in the phonon kinetics because this is the only way for relaxation of total energy, momentum and the occupation numbers of phonons. It also plays its role in thermodynamics, if the approximation of non-interacting phonons does not describe the phenomenon of interest. We have seen an example of that, treating the thermal expansion. Another good example is provided by the structural phase transitions. Since this phenomenon occurs fairly often, we consider it in details.

The Lagrangian of soft optical phonons and dielectric constant.

Let us consider a crystal with a centre of symmetry and an optical mode which is characterized by an optical displacement $x_{\mathbf{n}}$ ($\mathbf{n}$ is the coordinate of an elementary cell). Then

$$Z = \int_{x_{\mathbf{n}}(0)=x_{\mathbf{n}}(\beta)} \mathcal{D}x_{\mathbf{n}} \exp\left\{-\int_0^\beta d\tau \mathcal{L}\left[\{x(\tau)\}, \left\{\frac{\partial x}{\partial \tau}\right\}\right]\right\}; \quad (1)$$

$$\mathcal{L} = \frac{1}{2}\sum_{\mathbf{n}}\left[\frac{\dot{x}_{\mathbf{n}}^2}{2} + \frac{\mu x_{\mathbf{n}}^2}{2} + \frac{\gamma x_{\mathbf{n}}^4}{4}\right] + \sum_{\mathbf{n},\mathbf{n}'} V(\mathbf{n}-\mathbf{n}')(x_{\mathbf{n}} - x_{\mathbf{n}'})^2. \quad (2)$$

The Lagrangian $\mathcal{L}$ contains the kinetic and potential energy with an anharmonic on-site potential and the interaction $V(\mathbf{n}-\mathbf{n}') > 0$ of displacements $x_{\mathbf{n}}$ and $x_{\mathbf{n}'}$, which makes the energy larger if $x_{\mathbf{n}} \neq x_{\mathbf{n}'}$. Taking the Fourier transform

$$x_{\mathbf{n}}(\tau) = T\sum_{\mathbf{q},\omega_n} x_{\mathbf{q}}(\omega_n) e^{i\mathbf{q}\mathbf{r}_{\mathbf{n}} - i\omega_n \tau},$$

we can rewrite the partition function in the following form:

$$Z = \int \prod_{\omega_n,\mathbf{q}} dx_{\mathbf{q}}(\omega_n) \exp\left\{-\frac{1}{2T}\sum_{\omega_n,\mathbf{q}}[\omega_n^2 + \omega^2(\mathbf{q})]|x_{\mathbf{q}}(\omega_n)|^2\right\}\cdot$$

$$\exp\left\{-\frac{\gamma}{4T}\sum_{n_i,\mathbf{q}_i} x_{\mathbf{q}_1}(\omega_{n_1}) x_{\mathbf{q}_2}(\omega_{n_2}) x_{\mathbf{q}_3}(\omega_{n_3}) x_{\mathbf{q}_4}(\omega_{n_4}) \delta_{n_1+n_2+n_3+n_4} \delta_{\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4}\right.$$

$$\omega^2(\mathbf{q}) = \mu + s^2 q^2$$

The Green's function of optical phonons, $G(\omega_n, \mathbf{q})$, is, literally, the mean square of displacements.

$$G(\omega_n, \mathbf{q}) = \langle |x(\mathbf{q}, \omega_n)|^2 \rangle = \frac{T}{\omega_n^2 + \mu + s^2\mathbf{q}^2 + \Sigma(\omega_n, \mathbf{q})} = [G_0^{-1} + \Sigma]^{-1}, \tag{4}$$

where

$$G_0(\omega_n, \mathbf{q}) = \frac{T}{\omega_n^2 + \mu + s^2\mathbf{q}^2} \tag{5}$$

is the bare Green's function, calculated neglecting the anharmonicity ($\gamma = 0$), and $\Sigma(\omega_n, \mathbf{q})$ is the self-energy part which arises due to anharmonicity. In the case of displacement x_i corresponding to the finite dipole momentum $d_i = zx_i$, where z is an effective charge of the ions, the dielectric constant $\epsilon(\omega, \mathbf{q})$ and dielectric susceptibility $\chi(\omega, \mathbf{q})$ are connected with the retarded Green's function $G^R(\omega, \mathbf{q})$:

$$\epsilon\ (\omega, \mathbf{q}) = 1 + 4\pi\chi\ (\omega, \mathbf{q}), \qquad \chi(\omega, \mathbf{q}) = \frac{z^2}{v_0}\, G^R(\omega, \mathbf{q}). \tag{6}$$

The analytic continuation of the Green's function to $\omega_n \to i\omega + \delta$, from positive Matsubara frequencies to the imaginary axis, determines the spectrum of the optical phonons through the equation:

$$\omega^2(\mathbf{q}) = \mu + s^2\mathbf{q}^2 + \mathbf{\Sigma}^R(\omega, \mathbf{q}). \tag{7}$$

If μ is of the order of the square of the Debye frequency ω_D^2 and the anharmonicity γ is small, Eqs (7) and (6) describe a conventional dielectric with optical phonons and a dielectric function which weakly depends on temperature. If, by accident, the optical phonons turn out to be soft ($\mu \ll \omega_D^2$), then the corrections due to anharmonicity to both the Green's function and spectrum are large, which means that our dielectric has a strong temperature dependence of its dielectric properties and optical phonons with the temperature-dependent frequency of its excitations. The most dramatic situation occurs if $\mu < 0$, $|\mu| \ll \omega_D^2$. The negative sign of the square of the phonon frequency at $\mathbf{q} = 0$ means that the lattice is unstable at zero temperature with respect to spontaneous breaking of the inversion symmetry. At zero temperature, the crystal develops a spontaneous uniform displacement $\langle x \rangle$, which leads to the formation of a spontaneous polarization $\mathbf{P} = z v_0^{-1} \langle x \rangle$. Therefore, it is the ferroelectric phase. If μ is large, the crystal remains in the ferroelectric phase until melting. If μ is small, the temperature-dependent correction to $\mathbf{\Sigma}$ may give a positive contribution, which may compensate, at high enough temperature, the negative contribution of μ. This means that, at high enough temperature, the instability of the lattice disappears and the crystal restores its para-electric properties with zero spontaneous polarization, i.e. $\mathbf{P} = 0$. We will see that this transition is accompanied by an anomaly in dielectric susceptibility and the formation of a soft phonon mode with temperature-dependent frequency.

In what follows, it is not very important at which temperature T_c the transition occurs. This is why we choose the simplest and most typical case of $T_c \geq \hbar\omega_D$. Under this condition all Matsubara frequencies $\omega_n = 2\pi n T$ are too large, except for ω_0, and, therefore, the variables of integration $x(\omega_n)$ in Eq (3) could be neglected for all $n \neq 0$. The remaining partition function corresponds to that of classical statistical mechanics:

$$Z = \int \prod_{\mathbf{q}} dx_{\mathbf{q}} \exp\left\{ -\frac{1}{2T} \sum_{\mathbf{q}} \frac{\mu + s^2 q^2}{2} \; |x_{\mathbf{q}}|^2 \right\} \cdot$$
$$\cdot \exp\left\{ -\frac{\gamma}{4T} \sum_{\mathbf{q}_i} x_{\mathbf{q}_1} \; x_{\mathbf{q}_2} \; x_{\mathbf{q}_3} \; x_{\mathbf{q}_4} \delta_{\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4} \right\}. \qquad (8)$$

The static correlation function $G(\mathbf{q}, T)$ is

$$G(\mathbf{q}, T) = \langle |x_{\mathbf{q}}|^2 \rangle = \frac{T}{\omega^2(\mathbf{q}, T)}, \qquad \omega^2(\mathbf{q}, T) = \mu + s^2 q^2 + \Sigma(\mathbf{q}, T), \qquad (9)$$

which shows that the soft optical phonons have the temperature dependent frequency $\omega(0, T)$ at zero quasi-momentum $\mathbf{q} = 0$. This temperature dependence arises from the self-energy part Σ, which, in the leading order in anharmonicity γ (the diagram a in Fig1 a.), does not depend on the momentum $\mathbf{q}$ and has the following form:

$$\Sigma(T) = \frac{\gamma T}{v_0} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{\mu + \Sigma + s^2 q^2}. \qquad (10)$$

The integral on the right-hand side of Eq(10) is determined mostly by large values of the momentum $\mathbf{q}$ and, therefore,

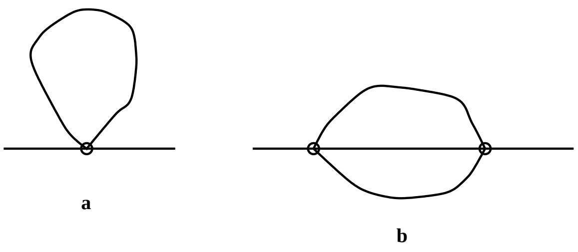

Figure 1: Diagrams for phonon self-energy

weakly depends on the vicinity to the transition $\mu+\Sigma$. Neglecting this dependence, we arrive at the, so-called, Curie-Weiss law for susceptibility and linear dependence of the square of the frequency $\omega^2(0)$ on temperature T:

$$\chi(T) = \frac{C}{T - T_c}; \quad \omega^2(0,T) = A(T - T_c); \quad C = \frac{sv_0}{\gamma},\ T_c = \frac{\mu}{\gamma},\ A = \gamma. \tag{11}$$

Thermodynamics of non-symmetric phase. Landau theory of type II phase transitions.

At low temperatures $T < T_c$, the symmetric phase becomes unstable and a spontaneous displacement $\langle x_{\mathbf{n}} \rangle \equiv \eta$ develops. This spontaneous displacement plays the role of the order parameter and measures the degree of deviation from the symmetric phase. In order to develop the thermodynamics in the presence of the symmetry breaking, let us separate this static displacement η from thermal fluctuation $\tilde{x}_{\mathbf{n}}$:

$$x_{\mathbf{n}} = \eta + \tilde{x}_{\mathbf{q}}; \qquad x_{\mathbf{q}} = \eta\delta(\mathbf{q}) + \tilde{x}_{\mathbf{q}}$$

and substitute it into Eq (8). As a result, the free energy $F(T,\eta) = -T\ln Z$ consists of an η independent part and a power expansion in η:

$$F(\eta,T) = F_0(T) + \frac{1}{2\chi_0(T)}\eta^2 + \frac{\gamma}{4}\eta^4, \qquad \chi(T) = \frac{C}{T - T_c}. \tag{12}$$

Equation (12)[1] is an example of the Landau expansion,

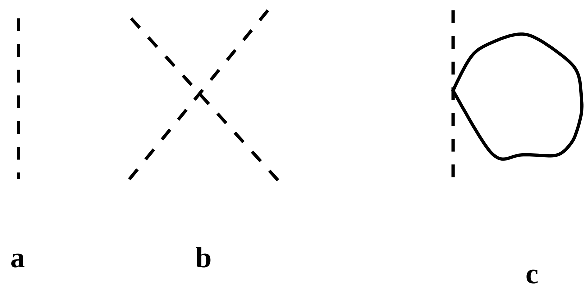

Figure 2: Diagrams for Free energy of the phase with broken symmetry

typical of all type II phase transitions. At $T > T_c$, the free energy F has a minimum at $\eta = 0$ and, therefore, the symmetry is not broken. At $T < T_c$, the free energy has a maximum at $\eta = 0$. This means that there are two minima, $\eta(T) = \pm\sqrt{\gamma(T_c - T)/C}$, corresponding to spontaneously broken symmetry. The order parameter grows continuously when the temperature goes down (second order phase transition). At equilibrium, the free energy is given by the expression:

$$F(T) = F_0(T) + \frac{T - T_c}{2C}\eta^2(T) + \frac{\gamma}{4}\eta^4(T), \qquad \left(\frac{\partial F}{\partial \eta}\right)_{\eta=\eta(T)} = 0, \tag{13}$$

and, at its minimum, the dielectric susceptibility follows the modified Curie-Weiss law and the square of the frequency $\omega^2(0,T)$ is, again, linear in T:

$$\chi(T) = \frac{C}{2(T_c - T)}; \quad \omega^2(0,T) = 2A(T_c - T). \tag{14}$$

[1]The expansion (12) can be obtained as the sum of contributions of the diagrams, presented in Fig 2, in which the dashed lines correspond to η.

Critical phenomena

The previous analysis is based on the lowest order of perturbation theory and the assumption that all integrals over quasi-momenta are determined by their large values and do not depend on the vicinity of transition $T-T_c$ or $\mu+\Sigma$. The usage of the lowest order contribution seems to be justifiable by the small value of anharmonicity γ. Nevertheless, very close to the transition ($T \to T_c$) both assumptions fail. Indeed, the expression (10) for the self-energy part can be rewritten as:

$$\Sigma(T) = \frac{\gamma T}{v_0} \int \frac{d\mathbf{q}}{(2\pi)^3} \left\{ \frac{1}{s^2q^2} + \left[\frac{1}{\mu + \Sigma + s^2q^2} - \frac{1}{s^2q^2} \right] \right\} =$$

$$= \Sigma_0 - (\mu + \Sigma) \int \frac{d\mathbf{q}}{s^2q^2(s^2q^2 + \mu + \Sigma)} = \Sigma_0 - g\sqrt{\Sigma_0(\mu + \Sigma)} \quad (15)$$

where $g \propto \gamma$ is the dimensionless coupling constant of the theory As a result, the square of the frequency $\omega^2(0,T)$, for example, has the following temperature dependence:

$$\omega^2(0,T) = A(T - T_c) \left[1 - g \sqrt{\frac{T}{T - T_c}} \right]. \quad (16)$$

It is clearly seen from Eq (16) that the result (11) is valid, if the coupling constant is small ($g \ll 1$) and the temperature is not very close to the critical temperature. The corrections in the mutual interaction of soft modes for small wave vectors form a power series in $g\sqrt{T_C/(T-T_c)}$[2], which cannot be truncated for the vicinity to the transition. The

[2]This inverse square root dependence is characteristic of the dimension $d = 3$. For $d = 4$ the correction consists of $g \log(T - T_c)$ and for $d = 5$ the relevant integral converges. It is usually said that $d = 4$ is "the upper critical dimension"

account for this mutual interaction (critical phenomena) changes the temperature dependences, and all thermodynamic functions near the transition have power-law dependence:

$$C(T) \propto (T - T_c)^{-\alpha}; \qquad \chi(T) \propto (T - T_c)^{-1-\gamma} \quad 0 < \alpha < 1, \quad 0 < \gamma < 1.$$

The discussion of the scaling theory of critical phenomena goes beyond the scope of these lectures. So, we stop here.