

Vibrations of Atoms. Phonons

Vibrations of atoms: General theory

We start with the general theory of vibrations of atoms that does not distinguish between molecules, amorphous solids, and crystals. As we discussed before, the adiabatic parameter (m_e is the electron mass, m_* is the typical mass of nuclei)

$$m_e/m_* \ll 1 \tag{1}$$

guarantees the following two facts. (i) The low-lying modes of the system can be viewed as the motion of nuclei in the effective potential $U(\{\mathbf{R}_n\})$ —with $\{\mathbf{R}_n\}$ the set of all the nuclei coordinates—consisting of the direct Coulomb repulsion of the ions and the groundstate energy of all the electrons in the potential of all the ions fixed at the positions $\{\mathbf{R}_n\}$. (ii) As long as the quantum numbers of the excitations are not very large, the excitations are nothing but harmonic modes. The latter circumstance is crucially important. In classical mechanics, the harmonicity of small-amplitude excitations about an equilibrium state is guaranteed by an appropriate smallness of the amplitude, or, equivalently, an appropriate smallness of the excitation energy. In quantum mechanics, the amplitudes of zero-point motion and low-lying excitations are *finite*, and, speaking generally, the motion is not supposed to be harmonic even for the lowest excited states.

The harmonicity of the motion guaranteed by the parameter (1) allows us to proceed classically, because the correspondence between classical and quantum harmonic oscillations is under perfect theoretical control. In fact, the purely quantum treatment is as simple as the classical one, and later on we will discuss it as well. The reason why we start with the classical picture is because it is very instructive to trace the connection to the general classical-mechanical theory of the normal modes.

The Lagrangian of the system reads

$$L = \sum_n \frac{m_n \dot{\mathbf{u}}_n^2}{2} - U(\{\mathbf{R}_n\}), \tag{2}$$

where m_n is the mass of the n -th atom, and \mathbf{u}_n is the displacement of the n -th atom from its equilibrium position $\mathbf{R}_n^{(0)}$: $\mathbf{R}_n = \mathbf{R}_n^{(0)} + \mathbf{u}_n$, so that $\dot{\mathbf{R}}_n = \dot{\mathbf{u}}_n$. To arrive at the normal modes we Taylor-expand the potential at

the point $\mathbf{R}_n^{(0)}$ up to the second-order terms ($i, i' = x, y, z$):

$$U(\{\mathbf{R}_n\}) = U(\{\mathbf{R}_n^{(0)}\}) + \sum_{ni} \left(\frac{\partial U}{\partial R_n^i} \right) u_n^i + \frac{1}{2} \sum_{nn'ii'} \left(\frac{\partial^2 U}{\partial R_n^i \partial R_{n'}^{i'}} \right) u_n^i u_{n'}^{i'} + \dots \quad (3)$$

The first term is a constant and thus is irrelevant for the equations of motion. The second term is identically zero since the equilibrium corresponds to an extremum of the potential. Hence, the leading term in the equations of motion at small enough displacements is the third term. Neglecting the higher-order terms, for the equations of motion we get

$$m_n \ddot{u}_n^i = - \sum_{n'i'} A_{nn'}^{ii'} u_{n'}^{i'}, \quad (4)$$

where

$$A_{nn'}^{ik} = \frac{1}{2} \left(\frac{\partial^2 U}{\partial R_n^i \partial R_{n'}^{i'}} + \frac{\partial^2 U}{\partial R_{n'}^{i'} \partial R_n^i} \right) \Big|_{\{\mathbf{R}_n\}=\{\mathbf{R}_n^{(0)}\}}. \quad (5)$$

At the formal level, we are dealing with a very simple mathematical problem, a system of linear homogeneous ordinary differential equations with constant coefficients. The linearity and homogeneity (i.e. absence of u -independent terms) of the equations allow one to construct the general solution as a linear combination of elementary ones. And the fact that the coefficients are time-independent means that the elementary solutions can be obtained by the exponential substitutions. Hence, we look for the elementary solutions—*the normal modes*—of the form (we look for a complex solution and then take the real or imaginary part)

$$\mathbf{u}_n(t) = \frac{\mathbf{v}_n}{\sqrt{m_n}} e^{-i\omega t}, \quad (6)$$

where \mathbf{v}_n is a certain constant vector (the square root of the mass in the denominator is for future convenience) and ω is the frequency of the mode (the minus sign is the matter of convention). Substituting (6) into (4) and dropping the global exponential factor, we arrive at a system of algebraic equations:

$$\omega^2 v_n^i = \sum_{n'i'} \tilde{A}_{nn'}^{ii'} v_{n'}^{i'}, \quad (7)$$

where

$$\tilde{A}_{nn'}^{ii'} = \frac{A_{nn'}^{ii'}}{\sqrt{m_n m_{n'}}}. \quad (8)$$

To clearly see the matrix structure of the system (7), introduce the composite subscripts $\alpha = (n, i)$ and $\beta = (n', i')$, and rewrite (7) as

$$\sum_{\beta} \tilde{A}_{\alpha\beta} v_{\beta} = \omega^2 v_{\alpha}. \quad (9)$$

Hence, the solutions are the eigenvectors of the matrix \tilde{A} and the frequencies are the square roots of corresponding eigenvalues. Hence, we are dealing with the standard linear algebra problem: The frequencies are given by the solution of the *characteristic equation*

$$\det(\tilde{A} - \omega^2 I) = 0, \quad (10)$$

where $I = \delta_{\alpha\beta} \equiv \delta_{nn'}\delta_{ii'}$ is the unity matrix. The matrix \tilde{A} is a Hermitian matrix—it is obviously real by construction and symmetric by (5) and (8)—and thus all its eigenvalues are real. Moreover, for a stable equilibrium point, that is a (local) minimum of U , there should be no negative eigenvalues. (There should be a few zero eigenvalues because of the global translational and rotational symmetry of the system.) The two different signs of ω correspond to one and the same physical solution in view of the necessity of taking the real (or imaginary) part of (6), after which changing the sign translates into the phase shift by π ; the former is redundant given an arbitrary phase of the complex amplitude \mathbf{v}_n .

Phonons

In a crystal, $n \rightarrow (\mathbf{n}, j)$, where \mathbf{n} labels the primitive cell corresponding to the translation of the basis by the vector $\mathbf{T}_{\mathbf{n}}$, and j is the label of the atom in a primitive cell; if there is only one atom in the primitive cell, j becomes redundant. Equation (4) now reads

$$m_j \ddot{u}_{\mathbf{n}j}^i = - \sum_{\mathbf{n}'j'i'} A_{jj'}^{ii'}(\mathbf{n} - \mathbf{n}') u_{\mathbf{n}'j'}^{i'}. \quad (11)$$

The two crucial properties of (11) as compared to generic Eq. (4) are the dependence of masses only on j , and the dependence of the constants A on \mathbf{n} and \mathbf{n}' in the form of difference. These properties are due to the crystal symmetry of the system.

With the crystal symmetry, and assuming for simplicity that the system is infinitely large, one can look for the elementary solutions in the form of the plane waves (as usual, we look for a complex solution and then take the

real or imaginary part)

$$\mathbf{u}_{\mathbf{n}j}(t) = \mathbf{u}_j(\mathbf{q}, t) e^{i\mathbf{q}\cdot\mathbf{R}_{\mathbf{n}j}^{(0)}} = \mathbf{u}_j(\mathbf{q}, 0) e^{i\mathbf{q}\cdot\mathbf{R}_{\mathbf{n}j}^{(0)} - i\omega(\mathbf{q})t}, \quad (12)$$

where, in accordance with the notation of the previous subsection, $\mathbf{R}_{\mathbf{n}j}^{(0)}$ stands for the equilibrium position of the j -th atom in the cell \mathbf{n} . The physical meaning of Eq. (12) is that its real (or imaginary) part represents a wave of displacements with the wavevector \mathbf{q} . By crystal symmetry,

$$\mathbf{R}_{\mathbf{n}j}^{(0)} = \mathbf{R}_{\mathbf{0}j}^{(0)} + \mathbf{T}_{\mathbf{n}}, \quad (13)$$

and absorbing the (otherwise redundant) exponential factor $e^{i\mathbf{q}\cdot\mathbf{R}_{\mathbf{0}j}^{(0)}}$ into the amplitude $\mathbf{u}_j(\mathbf{q}, 0)$:

$$\mathbf{u}_j(\mathbf{q}, 0) e^{i\mathbf{q}\cdot\mathbf{R}_{\mathbf{0}j}^{(0)}} \rightarrow \mathbf{u}_j(\mathbf{q}, 0), \quad (14)$$

we write (12) in the form

$$\mathbf{u}_{\mathbf{n}j}(t) = \mathbf{u}_j(\mathbf{q}, 0) e^{i\mathbf{q}\cdot\mathbf{T}_{\mathbf{n}} - i\omega(\mathbf{q})t}. \quad (15)$$

Now we substitute (15) into (11), perform time differentiation, and divide both parts by $e^{i\mathbf{q}\cdot\mathbf{T}_{\mathbf{n}} - i\omega(\mathbf{q})t}$. With $\mathbf{T}_{\mathbf{n}} - \mathbf{T}_{\mathbf{n}'} = \mathbf{T}_{\mathbf{n}-\mathbf{n}'}$ taken into account, we then get

$$-\omega^2(\mathbf{q}) m_j u_j^i(\mathbf{q}, 0) = -\sum_{j'i'} C_{jj'}^{ii'}(\mathbf{q}) u_{j'}^{i'}(\mathbf{q}, 0), \quad (16)$$

with

$$C_{jj'}^{ii'}(\mathbf{q}) = \sum_{\mathbf{n}'} A_{jj'}^{ii'}(\mathbf{n} - \mathbf{n}') e^{-i\mathbf{q}\cdot\mathbf{T}_{\mathbf{n}-\mathbf{n}'}} = \sum_{\mathbf{n}_1} A_{jj'}^{ii'}(\mathbf{n}_1) e^{-i\mathbf{q}\cdot\mathbf{T}_{\mathbf{n}_1}}. \quad (17)$$

(Note that the dependence on \mathbf{n} drops out due to the infinite system size.) We see that the infinite system of equations (12) decouples into *finite* systems of $d\nu_0$ equations (d is the dimensionality of the space and ν_0 is the number of atoms in the basis) for each individual wavevector \mathbf{q} . Each of the systems has exactly the same mathematical structure coinciding with that of the problem (4) of the previous subsection. Hence, we utilize the relations (6) through (10), replacing $n \rightarrow j$ and $A \rightarrow C$ (for a fixed wavevector \mathbf{q} playing the role of an external parameter). As a result, we get an elementary solution in the form of the running plane wave (the operation of taking the real part is performed after finding the complex solution)

$$\mathbf{u}_{\mathbf{n}j}(t) = \text{Re} \frac{\mathbf{v}_j(\mathbf{q})}{\sqrt{m_j}} e^{i\mathbf{q}\cdot\mathbf{T}_{\mathbf{n}} - i\omega(\mathbf{q})t}. \quad (18)$$

Each elementary mode (18) is referred to as a *phonon mode*. For a given wavevector \mathbf{q} , there are $d\nu_0$ linear independent elementary solutions given by the system of $d\nu_0$ equations [below $\alpha \equiv (i, j)$ and $\beta \equiv (i', j')$]

$$\sum_{\beta=1}^{d\nu_0} \tilde{C}_{\alpha\beta} v_{\beta} = \omega^2 v_{\alpha} \quad (\alpha = 1, 2, \dots, d\nu_0), \quad (19)$$

where

$$\tilde{C}_{jj'}^{ii'}(\mathbf{q}) = \frac{C_{jj'}^{ii'}(\mathbf{q})}{\sqrt{m_j m_{j'}}}. \quad (20)$$

The frequencies of the phonon modes (phonons) are found from the characteristic equation ($I \equiv \delta_{ii'} \delta_{jj'}$)

$$\det [\tilde{C}(\mathbf{q}) - \omega^2(\mathbf{q}) I] = 0. \quad (21)$$

Without loss of generality, we can require that $\omega \geq 0$ since, as we discussed it in the previous sub-section, changing the sign of ω becomes redundant after taking the real part of the solution.

The rank of the matrix \tilde{C} equals $d\nu_0$, so that there are $d\nu_0$ different *phonon branches*. For each of the branches, all distinctively different solutions are exhausted by \mathbf{q} 's lying within the first Brillouin zone. We can see that from the invariance of the matrix $C(\mathbf{q})$, Eq. (17), and then the solution (15), with respect to shifting \mathbf{q} by any vector \mathbf{G} of the reciprocal lattice. This, in particular, implies that $\omega(\mathbf{q})$ is periodic in the reciprocal (i.e., wavevector) space:

$$\omega(\mathbf{q} + \mathbf{G}) = \omega(\mathbf{q}). \quad (22)$$

Let us discuss some properties of the matrix \tilde{C} and their implications. Taking into account the general symmetries of the matrix A discussed in the previous sub-section—the matrix A is real and symmetric with respect to exchanging $(i, j, \mathbf{n}) \leftrightarrow (i', j', \mathbf{n}')$ —we check with (17) that the matrix C is Hermitian, and then from (20) see that \tilde{C} is Hermitian as well. Hence, ω^2 is real. (The fact that $\omega^2 \geq 0$ follows from mechanical stability of the system.) From (17) and the fact that the matrix A is real, we conclude that $C^*(\mathbf{q}) = C(-\mathbf{q})$; the same is then trivially true for \tilde{C} :

$$\tilde{C}^*(\mathbf{q}) = \tilde{C}(-\mathbf{q}). \quad (23)$$

Now complex-conjugating (21) and taking into account (23) along with the fact that $\omega(\mathbf{q})$ is real, we get

$$\det [\tilde{C}(-\mathbf{q}) - \omega^2(\mathbf{q}) I] = 0, \quad (24)$$

meaning that

$$\omega(-\mathbf{q}) = \omega(\mathbf{q}). \quad (25)$$

Combining Eqs. (25) and (22), we find

$$\omega(\mathbf{G}/2 + \mathbf{q}) = \omega(\mathbf{G}/2 - \mathbf{q}), \quad (26)$$

which in its turn implies

$$\left. \frac{\partial \omega}{\partial \mathbf{q}} \right|_{\mathbf{q}=\mathbf{G}/2} = 0, \quad (27)$$

meaning that, in the wavevector space, all the points $\mathbf{q} = \mathbf{G}/2$ are the points of extrema of the function $\omega(\mathbf{q})$. In accordance with the general theory of *wave packets*, the gradient $\partial\omega/\partial\mathbf{q}$ yields the so-called *group velocity*—the velocity of propagation of the wave packet with the wavevector \mathbf{q} . Equation (27) thus states that the group velocity for all the phonons with $\mathbf{q} = \mathbf{G}/2$ vanishes. And this is consistent with the fact that all the $\mathbf{q} = \mathbf{G}/2$ phonons have a common structure of a standing rather than running wave. The spatial pattern of the vibrational mode at $\mathbf{q} = \mathbf{G}/2$ becomes clear from the observation that

$$e^{i\mathbf{G}\cdot\mathbf{T}_n/2} = \exp(i\pi \times \text{integer}) = \pm 1, \quad (28)$$

meaning that the Bravais lattice splits into two rigid sub-lattices performing counter-phase oscillations.

In the previous subsection we mentioned that continuous-space rotational and translational symmetries of the finite-size atomic systems (molecules) imply that there are corresponding modes with zero frequencies. The rotational symmetry is irrelevant to the spectrum of phonons because the solution (18) does not capture a global rotation of the system.¹ In the context of phonons, it is only the continuous translation of all the atoms by the same vector \mathbf{e}_0 that is captured by the solution (18). In this case $\mathbf{q} = 0$, $\omega = 0$, because $\mathbf{u}_{n_j}(t) \equiv \mathbf{e}_0$. Given that there are d linear independent choices of the vector \mathbf{e}_0 , there should be d phonon branches such that $\lim_{q \rightarrow 0} \omega(\mathbf{q}) = 0$. These branches are called acoustic branches. The dispersion $\omega(\mathbf{q})$ of the acoustic branches is linear at sufficiently small q . This is readily seen by Taylor expanding $\omega^2(\mathbf{q})$ —the eigenvalues of the matrix $\tilde{C}(\mathbf{q})$ are normally analytic functions of \mathbf{q} —up to the second order [the linear terms vanish in accordance with (25)] :

$$\omega^2(\mathbf{q}) \rightarrow \sum_{ik} \gamma_{ik} q_i q_k \quad \text{at} \quad q \rightarrow 0. \quad (29)$$

¹For a rotation, the amplitude of the displacement grows linearly with the distance from the rotation center.

Here q_i and q_k are components of the vector \mathbf{q} , and γ_{ik} is a real and, without loss of generality, symmetric² matrix. The phonons of the acoustic branches at low enough wavevectors corresponding to the linear dispersion are called acoustic phonons. They are nothing but the elastic sound waves. As we see from Eq. (29), the sound velocity in a generic crystal depends on the direction of the wavevector:

$$v_{\text{sound}}(\mathbf{q}/q) = \sqrt{\sum_{ik} \gamma_{ik} q_i q_k / q^2}. \quad (30)$$

Born–von Karman boundary condition. Lattice Fourier transform

Sometimes it is very convenient to work with a finite rather than infinite system. In particular, this is important in statistics. If we are interested in the thermodynamic properties of a macroscopic system, particular boundary conditions do not change the final answer. That is why it makes perfect sense to select the simplest possible boundary conditions, namely the conditions under which there are no boundaries at all. We mean the periodic (a.k.a. Born–von Karman) boundary conditions. Let $Q_{\mathbf{n}}$ be some quantity defined in a crystal, \mathbf{n} labeling the cell corresponding to the translation vector $\mathbf{T}_{\mathbf{n}}$. The quantity can be either vector or scalar, and it can also depend on the number of atoms in the primitive cell. For example, it can be the i -th component of the vector of displacement of the j -th atom (in the cell \mathbf{n}). For our purposes, all the super- and subscripts different from \mathbf{n} are not important, and we suppress them. Formally, we pretend that our crystal is infinite. The actual finiteness of the system—by which we mean the finite number of degrees of freedom—is enforced by the Born–von Karman boundary conditions. To formulate these conditions, we pick up some primitive set of translations vectors $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, select three “macroscopic” integers, N_1, N_2 , and N_3 , defining the desired linear sizes of the system in each of the three directions, and require that all the functions $Q_{\mathbf{n}} \equiv Q(\mathbf{T}_{\mathbf{n}})$ be periodic with respect to the “macroscopic” translations, $\vec{\mathcal{T}}$,

$$Q(\mathbf{T}_{\mathbf{n}} + \vec{\mathcal{T}}) = Q(\mathbf{T}_{\mathbf{n}}), \quad (31)$$

defined as

$$\vec{\mathcal{T}} \equiv \vec{\mathcal{T}}_1 = l_1 N_1 \mathbf{a}_1 + l_2 N_2 \mathbf{a}_2 + l_3 N_3 \mathbf{a}_3, \quad (32)$$

²Since it can always be symmetrized.

where l_i ($i = 1, 2, 3$) are integers. All the vectors \vec{T} form a translation group \mathcal{G}_T , with a primitive set $(N_1\mathbf{a}_1, N_2\mathbf{a}_2, N_3\mathbf{a}_3)$. The group \mathcal{G}_T is a subgroup of \mathcal{G}_T , because for any vector \vec{T}_1 we have $\vec{T}_1 = \mathbf{T}_n$, where $\mathbf{n} = (l_1N_1, l_2N_2, l_3N_3)$. With respect to the periodic structure generated by the translations \vec{T}_1 , our physical system plays the role of a (macroscopically large) unit cell.

The periodicity of the problem allows one to employ the Fourier transform technique. We already know that the Fourier transform should be based on the plane waves with the reciprocal-lattice wavevectors. This lattice corresponds to the group \mathcal{G}_q (reciprocal to \mathcal{G}_T) consisting of the following vectors

$$\mathbf{q} \equiv \mathbf{q}_m = \frac{m_1\mathbf{b}_1}{N_1} + \frac{m_2\mathbf{b}_2}{N_2} + \frac{m_3\mathbf{b}_3}{N_3}, \quad (33)$$

where $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ is the primitive set reciprocal to $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ [$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$] and m_i ($i = 1, 2, 3$) are integers. Indeed, if the set $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ is reciprocal to $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, then the set $(\mathbf{b}_1/N_1, \mathbf{b}_2/N_2, \mathbf{b}_3/N_3)$ is reciprocal to $(N_1\mathbf{a}_1, N_2\mathbf{a}_2, N_3\mathbf{a}_3)$. [Note that the group \mathcal{G}_G is a subgroup of \mathcal{G}_q .]

An important feature of the Fourier transform that comes from the *discreteness* of Q_n —the fact that we are dealing with the set of $N = N_1N_2N_3$ numbers rather than a function of continuous coordinate—is the *finite number* N of independent Fourier harmonics $F_m \equiv F(\mathbf{q}_m)$. The resulting Fourier transform has the following form

$$Q_n = \frac{1}{\sqrt{N}} \sum_{\mathbf{m}}^{BZ} e^{i\mathbf{q}_m \cdot \mathbf{T}_n} F_m, \quad (34)$$

$$F_m = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}}^{(\text{system})} e^{-i\mathbf{q}_m \cdot \mathbf{T}_n} Q_n. \quad (35)$$

Here the summation over \mathbf{m} and \mathbf{n} is over distinctively different N values of F_m and Q_n , respectively. The symbol BZ here is understood in a broader context: It can be just the first Brillouin zone, as well as *any* primitive cell of the reciprocal lattice. For example,

$$\sum_{\mathbf{m}}^{BZ} (\dots) = \sum_{m_1=0}^{N_1-1} \sum_{m_2=0}^{N_2-1} \sum_{m_3=0}^{N_3-1} (\dots), \quad (36)$$

$$\sum_{\mathbf{n}}^{(\text{system})} (\dots) = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} (\dots). \quad (37)$$

In general, it is seen that the sum over \mathbf{n} does not change if for a given $\mathbf{n} = \mathbf{n}_0$ we replace $\mathbf{T}_{\mathbf{n}_0} \rightarrow \mathbf{T}_{\mathbf{n}_0} + \vec{T}$. For any $\mathbf{m} = \mathbf{m}_0$ we can replace $\mathbf{q}_{\mathbf{m}_0} \rightarrow \mathbf{q}_{\mathbf{m}_0} + \mathbf{G}$: the exponentials and $F_{\mathbf{m}_0}$ will remain the same. Hence, the summation over \mathbf{m} can be done within either the first Brillouin zone of the lattice \mathcal{G}_G , or any other primitive cell of \mathcal{G}_G (containing N distinctively different Fourier coefficients $F_{\mathbf{m}}$). Note that apart from the sign of the exponents, which is the matter of convention, there is a perfect symmetry between the quantities $Q_{\mathbf{n}}$ and the Fourier transforms $F_{\mathbf{m}}$. To further emphasize the symmetry, we note that the exponentials actually depend only on \mathbf{n} , \mathbf{m} , and the three numbers N_i (note also factorization of the exponential):

$$e^{i\mathbf{q}_{\mathbf{m}} \cdot \mathbf{T}_{\mathbf{n}}} = e^{i\frac{2\pi m_1 n_1}{N_1}} e^{i\frac{2\pi m_2 n_2}{N_2}} e^{i\frac{2\pi m_3 n_3}{N_3}}. \quad (38)$$

The type and period of the Bravais lattice play no role for the Fourier transform!

To prove the Fourier transform (34)-(35) we have to demonstrate that (35) implies (34), and vice versa. The poof is based on the following two relations (both being essentially the same relation, up to summing in the direct or reciprocal space):

$$\sum_{\mathbf{n}}^{(\text{system})} e^{\pm i\mathbf{q}_{\mathbf{m}} \cdot \mathbf{T}_{\mathbf{n}}} = \begin{cases} N, & \mathbf{q}_{\mathbf{m}} = \mathbf{G}, \\ 0, & \text{otherwise,} \end{cases} \quad (39)$$

$$\sum_{\mathbf{m}}^{BZ} e^{\pm i\mathbf{q}_{\mathbf{m}} \cdot \mathbf{T}_{\mathbf{n}}} = \begin{cases} N, & \mathbf{T}_{\mathbf{n}} = \vec{T}, \\ 0, & \text{otherwise.} \end{cases} \quad (40)$$

The upper lines in these equalities are trivial, so we only need to show that the sum (39) is zero for $\mathbf{q}_{\mathbf{m}} \neq \mathbf{G}$, and the sum (40) is zero for $\mathbf{T}_{\mathbf{n}} \neq \vec{T}$. Using (37) and (38), we reduce the sum to a product of three geometric series:

$$\sum_{\mathbf{n}}^{(\text{system})} e^{\pm i\mathbf{q}_{\mathbf{m}} \cdot \mathbf{T}_{\mathbf{n}}} = \left(\sum_{n_1=0}^{N_1-1} e^{\pm i\frac{2\pi m_1 n_1}{N_1}} \right) \left(\sum_{n_2=0}^{N_2-1} e^{\pm i\frac{2\pi m_2 n_2}{N_2}} \right) \left(\sum_{n_3=0}^{N_3-1} e^{\pm i\frac{2\pi m_3 n_3}{N_3}} \right).$$

We then have ($j = 1, 2, 3$)

$$\sum_{n_j=0}^{N_j-1} e^{\pm i\frac{2\pi m_j n_j}{N_j}} = \begin{cases} N_j, & m_j/N_j = \text{integer,} \\ (1 - e^{\pm i2\pi m_j}) / (1 - e^{\pm i2\pi m_j/N_j}) = 0, & \text{otherwise,} \end{cases}$$

which proves (39). Analogously, using (36) and (38), we prove (40). To show that (35) implies (34), we multiply both sides of (35) by $(1/\sqrt{N})e^{i\mathbf{q}_{\mathbf{m}} \cdot \mathbf{T}_{\mathbf{n}_0}}$

and sum over \mathbf{m} , with taking into account (40):

$$\frac{1}{\sqrt{N}} \sum_{\mathbf{m}}^{BZ} e^{i\mathbf{q}\mathbf{m}\cdot\mathbf{T}_{\mathbf{n}_0}} F_{\mathbf{m}} = \frac{1}{N} \sum_{\mathbf{n}}^{(\text{system})} Q_{\mathbf{n}} \sum_{\mathbf{m}}^{BZ} e^{i\mathbf{q}\mathbf{m}\cdot(\mathbf{T}_{\mathbf{n}_0}-\mathbf{T}_{\mathbf{n}})} = Q_{\mathbf{n}_0}.$$

Here we also take into account that within the system there is only one cell \mathbf{n} satisfying the condition $\mathbf{T}_{\mathbf{n}} = \mathbf{T}_{\mathbf{n}_0} + \vec{\mathcal{T}}$, namely $\mathbf{n} = \mathbf{n}_0$. Given the symmetry between (34) and (35), and between (39) and (40), the proof that (34) implies (35) is essentially the same.

Thermodynamics of phonons

General relations for harmonic modes

In the harmonic approximation³ phonons are non-interacting harmonic oscillators. For thermodynamic purposes, it is convenient to set $\hbar = 1, k_B = 1$ and measure phonon frequency in Kelvins. The typical frequency of phonons (corresponding to the wavevectors on the order of the inverse lattice period) is ~ 300 K. This means that at the temperatures significantly less than the room temperature the quantization of phonons is crucial and we are dealing with the thermodynamics of an ensemble of non-interacting *quantum* harmonic oscillators described by the Hamiltonian:

$$H_{\text{ph}} = \sum_{\nu\mathbf{q}} \varepsilon_{\nu\mathbf{q}} \left(b_{\nu\mathbf{q}}^\dagger b_{\nu\mathbf{q}} + 1/2 \right), \quad (41)$$

where $\nu = 1, 2, \dots, \nu_0$ enumerates the phonon branches, \mathbf{q} is the phonon wavevector, $\varepsilon_{\nu\mathbf{q}} = \omega_{\nu}(\mathbf{q})$ is the quantum of energy (we remind that $\hbar = 1$) of the mode (ν, \mathbf{q}) —we call it the *energy of the phonon*, because quantum-mechanically the phonon (ν, \mathbf{q}) is understood as the excitation quantum of the mode (ν, \mathbf{q}) . The operators $b_{\nu\mathbf{q}}^\dagger$ and $b_{\nu\mathbf{q}}$ are the creation and annihilation operators of the phonon, so that $\hat{n}_{\nu\mathbf{q}} = b_{\nu\mathbf{q}}^\dagger b_{\nu\mathbf{q}}$ is the operator⁴ of the total number of phonons of the mode (ν, \mathbf{q}) . It is convenient to split the phonon Hamiltonian into the groundstate term,⁵

$$E_0^{(\text{ph})} = (1/2) \sum_{\nu\mathbf{q}} \varepsilon_{\nu\mathbf{q}}, \quad (42)$$

³The harmonic approximation—the accuracy of which is controlled by the adiabaticity parameter (1)—corresponds to replacing actual interparticle interactions with pairwise harmonic potentials with the distance-independent spring constants $A_{jj'}^{ii'}(\mathbf{n} - \mathbf{n}')$.

⁴For thermodynamic purposes, we only care about the eigenvalues of the Hamiltonian (41), that is only about the eigenvalues $n_{\nu\mathbf{q}} = 0, 1, 2, \dots$ of the operators $\hat{n}_{\nu\mathbf{q}}$.

⁵Physically, this term is due to the zero-point fluctuations of nuclei.

and the sum of single-mode Hamiltonians:

$$H_{\text{ph}} = E_0^{(\text{ph})} + \sum_{\nu\mathbf{q}} H_{\nu\mathbf{q}}, \quad H_{\nu\mathbf{q}} = \varepsilon_{\nu\mathbf{q}} \hat{n}_{\nu\mathbf{q}}. \quad (43)$$

The groundstate term is just a constant that should be added to the total groundstate energy of the crystal found at fixed positions of the nuclei. The thermodynamic role of the groundstate energy is trivial; we thus omit this term from now on.

The standard statistico-mechanical protocol of evaluating thermodynamic functions of a quantum system is based on the two general relations between the free energy, F , partition function, Z , and the statistical operator, $e^{-H/T}$:

$$F = -T \ln Z, \quad Z = \text{Tr} e^{-H/T}. \quad (44)$$

Since our Hamiltonian is a sum of Hamiltonians of independent subsystems—each phonon mode (ν, \mathbf{q}) is a harmonic oscillator decoupled from the rest of the world—the partition function factorizes into the product of partition functions for each individual mode:

$$Z = \prod_{\nu\mathbf{q}} Z_{\nu\mathbf{q}}, \quad (45)$$

$$Z_{\nu\mathbf{q}} = \text{Tr} e^{-H_{\nu\mathbf{q}}/T} = \sum_{n=0}^{\infty} e^{-\varepsilon_{\nu\mathbf{q}} n/T} = \frac{1}{1 - e^{-\varepsilon_{\nu\mathbf{q}}/T}}. \quad (46)$$

We thus get the following expression for the free energy

$$F = T \sum_{\nu\mathbf{q}} \ln \left(1 - e^{-\varepsilon_{\nu\mathbf{q}}/T} \right). \quad (47)$$

In fact, our treatment is generic for *any* system that can be viewed as a set of independent harmonic oscillators, up to replacing (if necessary) the composite subscript (ν, \mathbf{q}) with the one relevant to the particular system. For example, for the theory of equilibrium electro-magnetic field (normally referred to as the theory of black body radiation) the wavevector \mathbf{q} would be the wavevector of a photon, while $\nu = 1, 2$ would label the polarization of the photon, and $\varepsilon_{\nu\mathbf{q}} = cq$, with c the speed of light, would be the photon dispersion (note that with $\hbar = 1$ the wavevector \mathbf{q} is equal to the momentum). The difference between phonons and photons is only in (i) the number of branches and (ii) the form of the function $\varepsilon_{\nu\mathbf{q}}$. (The latter includes the domain of $\varepsilon_{\nu\mathbf{q}}$, which, in the case of phonons, is limited to the first Brillouin

zone for the vector \mathbf{q} .) Moreover, with minor modifications the theory applies to a gas of non-interacting bosonic particles with conservation of their total number.⁶

The universality of the treatment becomes especially transparent when one introduces the spectral density function,

$$D(\varepsilon) = \sum_{\nu\mathbf{q}} \delta(\varepsilon - \varepsilon_{\nu\mathbf{q}}), \quad (48)$$

and writes the expression for the free energy in the form

$$F = T \int d\varepsilon D(\varepsilon) \ln \left(1 - e^{-\varepsilon/T} \right). \quad (49)$$

This procedure is naturally combined with replacing the summation in (48) with integration—see below—in which case the function $D(\varepsilon)$ becomes a regular function, apart from special singular points, the so-called Van Hove singularities, associated with points of extrema of the function $\varepsilon_{\nu\mathbf{q}}$.

In Eq. (49), all the information about the system specific properties is encoded in the temperature independent function $D(\varepsilon)$ while the bosonic nature of the system comes from the universal temperature dependent factor $\ln \left(1 - e^{-\varepsilon/T} \right)$. The problem thus splits into two separate parts: (i) calculation—and/or exploring important limiting cases—of the function $D(\varepsilon)$ and (ii) proceeding with Eq. (49) to get the other thermodynamic quantities. The part (ii) can be done in general form—without explicitly calculating $D(\varepsilon)$ —on the basis of general thermodynamic relations. Indeed,

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = \int d\varepsilon D(\varepsilon) \left[\frac{\varepsilon/T}{e^{\varepsilon/T} - 1} - \ln \left(1 - e^{-\varepsilon/T} \right) \right], \quad (50)$$

$$E = F + TS = \int \frac{d\varepsilon D(\varepsilon) \varepsilon}{e^{\varepsilon/T} - 1}, \quad (51)$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V = \int d\varepsilon D(\varepsilon) \frac{(\varepsilon/T)^2 e^{\varepsilon/T}}{(e^{\varepsilon/T} - 1)^2}. \quad (52)$$

The expression for the energy has a very transparent form:

$$E = \int d\varepsilon D(\varepsilon) \varepsilon n_\varepsilon, \quad (53)$$

⁶Accounting for the conservation of the total number of bosons amounts to shifting the energy $\varepsilon_{\nu\mathbf{q}} \rightarrow \varepsilon_{\nu\mathbf{q}} - \mu$ by the chemical potential μ , the value of which is then adjusted to get the desired total number of particles. An important circumstance to remember is that in this case one also has to replace the free energy in the l.h.s. of Eq. (47) with the grand canonical potential.

where

$$n_\varepsilon = \frac{1}{e^{\varepsilon/T} - 1} \quad (54)$$

is known to be the thermodynamic average for the occupation number of the bosonic mode with the energy ε . Similarly, for the total number of bosons we have

$$N_{\text{bosons}} = \int d\varepsilon D(\varepsilon) n_\varepsilon. \quad (55)$$

For both photons and phonons this number depends on temperature, vanishing at $T \rightarrow 0$ and diverging at $T \rightarrow \infty$.

Summation in the wavevector space. Dimensionless wavevector

For a macroscopic crystal, the summation in the wavevector space is replaced by an integration. Indeed, the vector $\mathbf{q} \equiv \mathbf{q}_{\mathbf{m}}$, Eq. (33) changes by a macroscopically small amount when the components of the integer vector \mathbf{m} change by unity. Hence, with the macroscopic accuracy we can replace summation over \mathbf{m} with the integration (below $d^3m \equiv dm_1 dm_2 dm_3$):

$$\sum_{\mathbf{q}} (\dots) \equiv \sum_{\mathbf{m}} (\dots) \approx \int_{BZ} d^3m (\dots). \quad (56)$$

The integration over d^3m can then be replaced with the (more convenient) integration over d^3q :

$$\int_{BZ} d^3m (\dots) = \int_{BZ} d^3q |J| (\dots), \quad (57)$$

where

$$J = \frac{\mathcal{D}(m_1, m_2, m_3)}{\mathcal{D}(q_x, q_y, q_z)} \quad (58)$$

is the Jacobian of the transformation of variables $\mathbf{m} \rightarrow \mathbf{q}$. To evaluate J , we observe that its inverse is straightforwardly found from Eq. (33):

$$J^{-1} = \frac{\mathcal{D}(q_x, q_y, q_z)}{\mathcal{D}(m_1, m_2, m_3)} = \begin{vmatrix} \frac{\partial q_x}{\partial m_1} & \frac{\partial q_y}{\partial m_1} & \frac{\partial q_z}{\partial m_1} \\ \frac{\partial q_x}{\partial m_2} & \frac{\partial q_y}{\partial m_2} & \frac{\partial q_z}{\partial m_2} \\ \frac{\partial q_x}{\partial m_3} & \frac{\partial q_y}{\partial m_3} & \frac{\partial q_z}{\partial m_3} \end{vmatrix} = \begin{vmatrix} b_{1x}/N_1 & b_{1y}/N_1 & b_{1z}/N_1 \\ b_{2x}/N_2 & b_{2y}/N_2 & b_{2z}/N_2 \\ b_{3x}/N_3 & b_{3y}/N_3 & b_{3z}/N_3 \end{vmatrix}.$$

We see that, up to the sign, J^{-1} equals to the ratio of the volume of the primitive cell of the reciprocal lattice, $V_c^{(\text{rcpr})}$, and the total number of cells:

$$|J|^{-1} = V_c^{(\text{rcpr})}/N, \quad V_c^{(\text{rcpr})} = |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|. \quad (59)$$

Recalling that $V_c^{(\text{rcpr})}$ is related to the volume of the primitive cell of the direct lattice by $V_c^{(\text{rcpr})} = (2\pi)^3/V_c$ (see the Reciprocal Lattice section), we arrive at the universal (independent of the lattice type) relation:

$$\sum_{\mathbf{q}} (\dots) \rightarrow \frac{V}{(2\pi)^3} \int_{BZ} d^3q (\dots), \quad (60)$$

where $V = NV_c$ is the volume of the crystal. Apart from confining the integration to the first Brillouin zone, the form of (60) is identical to the integration over wavevectors in the continuous space. Normally, this similarity is very instructive, especially when one deals with the limit of low energies and, correspondingly, small q 's. Nevertheless, there are cases when the similarity is deceptive. Those are the cases when the thermodynamic role of the system volume goes beyond being a trivial macroscopic factor scaling the total amount of matter. We are talking of the response of the crystal to changing the volume at fixed amount of matter, implying fixed number of the cells. Here it is important to realize that the dependence of the function (we omit ν for brevity)

$$D(\varepsilon) = \frac{V}{(2\pi)^3} \int_{BZ} d^3q \delta(\varepsilon - \varepsilon_{\mathbf{q}})$$

on the volume comes also from the volume dependence of $\varepsilon_{\mathbf{q}}$. Moreover, the two dependencies exactly cancel each other in a harmonic crystal!

Indeed, since, by the definition of the harmonic crystal, the spring constants $A_{jj'}^{ii'}(\mathbf{n})$ are distance independent, the dependence of the constants $C_{jj'}^{ii'}(\mathbf{q})$ on lattice periods is exclusively due to the fact that for a fixed \mathbf{m} the value of the vector $\mathbf{q} = \mathbf{q}_{\mathbf{m}}$ depends on the lattice period. The coefficient $C_{jj'}^{ii'}(\mathbf{q}_{\mathbf{m}})$ remains the same for a given \mathbf{m} irrespectively of changing the lattice period:

$$C_{jj'}^{ii'}(\mathbf{q}_{\mathbf{m}}) = \sum_{\mathbf{n}} A_{jj'}^{ii'}(\mathbf{n}) e^{-i\mathbf{q}_{\mathbf{m}} \cdot \mathbf{T}_{\mathbf{n}}} = \sum_{\mathbf{n}} A_{jj'}^{ii'}(\mathbf{n}) e^{-i\mathbf{g}_{\mathbf{m}} \cdot \mathbf{n}},$$

where

$$\mathbf{g}_{\mathbf{m}} = 2\pi \left(\frac{m_1}{N_1}, \frac{m_2}{N_2}, \frac{m_3}{N_3} \right) \quad (61)$$

is a *dimensionless wavevector* living in the space associated with the lattice reciprocal to the simple cubic lattice formed by the integer vectors \mathbf{n} . (Note that the first Brillouine zone of this space is a cube with the side 2π .) We see that that the dependence on the lattice periods drops out if we use \mathbf{g} as a parameter:

$$C_{jj'}^{ii'}(\mathbf{g}) = \sum_{\mathbf{n}} A_{jj'}^{ii'}(\mathbf{n}) e^{-i\mathbf{g} \cdot \mathbf{n}}.$$

Therefore, the frequencies, if expressed as functions of \mathbf{g} , are also volume-independent. Finally, replacing the summation over the wavevector \mathbf{g} with integration,

$$dm_1 = (N_1/2\pi)dg_1, \quad dm_2 = (N_2/2\pi)dg_2, \quad dm_3 = (N_3/2\pi)dg_3,$$

we find that

$$\sum_{\mathbf{q}} (\dots) \rightarrow \frac{N}{(2\pi)^3} \int_{BZ} d^3g (\dots), \quad (62)$$

where

$$\int_{BZ} d^3g (\dots) \equiv \int_{-\pi}^{\pi} dg_1 \int_{-\pi}^{\pi} dg_2 \int_{-\pi}^{\pi} dg_3 (\dots). \quad (63)$$

With Eq. (62) we have

$$D(\varepsilon) = \frac{N}{(2\pi)^3} \sum_{\nu} \int_{BZ} d^3g \delta(\varepsilon - \varepsilon_{\nu}(\mathbf{g})),$$

$$E_0^{(\text{ph})} = \frac{N}{16\pi^3} \sum_{\nu} \int_{BZ} d^3g \varepsilon_{\nu}(\mathbf{g}),$$

and, recalling that $\varepsilon(\mathbf{g})$ does not depend on the lattice periods, conclude that $D(\varepsilon)$ and the energy $E_0^{(\text{ph})}$ (of the zero-point motion of phonons) do not depend on the volume (more generally, any linear size) of the crystal. There are crucial thermodynamic implications of this fact. The phonon contribution to pressure is absent:

$$P^{(\text{ph})} = - \left(\frac{\partial F^{(\text{ph})}}{\partial V} \right)_T = 0.$$

Correspondingly, there is no thermal expansion in a harmonic crystal.

Quantum theory of phonons

We start with the harmonic Hamiltonian

$$H = \sum_{\alpha} \frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha, \beta} A_{\alpha\beta} u_{\alpha} u_{\beta}. \quad (64)$$

Here $\{u_{\alpha}\}$ is the set of scalar coordinates (displacements); the structure of the subscript α is not important at this point; $p_{\alpha} = -i\partial/\partial u_{\alpha}$ is the

momentum operator ($\hbar = 1$), m_α is the mass, and the matrix $A_{\alpha\beta}$ is real and symmetric.⁷

First, we get rid of masses by performing a simple canonical transformation [re-scaling of the coordinates and momenta]:

$$u_\alpha = \frac{\tilde{u}_\alpha}{\sqrt{m_\alpha}}, \quad p_\alpha = \sqrt{m_\alpha} \tilde{p}_\alpha. \quad (65)$$

$$H = \frac{1}{2} \sum_\alpha \tilde{p}_\alpha^2 + \frac{1}{2} \sum_{\alpha,\beta} \tilde{A}_{\alpha\beta} \tilde{u}_\alpha \tilde{u}_\beta, \quad (66)$$

with

$$\tilde{A}_{\alpha\beta} = \frac{A_{\alpha\beta}}{\sqrt{m_\alpha m_\beta}}. \quad (67)$$

Below we omit tildes for brevity.

Consider the set $\{e_\alpha^{(s)}\}$ of eigenvectors of the matrix $A_{\alpha\beta}$ (here s is the label of the eigenvector):

$$\sum_\beta A_{\alpha\beta} e_\beta^{(s)} = \lambda^{(s)} e_\alpha^{(s)}. \quad (68)$$

Since our matrix is Hermitian all its eigenvalues $\lambda^{(s)}$ are real. Moreover, they have to be non-negative—otherwise the system is unstable—and we can write them as

$$\lambda^{(s)} = \omega_s^2 \quad (\omega_s \geq 0). \quad (69)$$

We then require that (i) the set of vectors $\{e_\alpha^{(s)}\}$ is orthonormal and (ii) all the vectors are real; this can be always achieved for a real Hermitian matrix. As a result, we have the following properties

$$\sum_\alpha e_\alpha^{(s_1)} e_\alpha^{(s_2)} = \delta_{s_1 s_2}, \quad \sum_s e_\alpha^{(s)} e_\beta^{(s)} = \delta_{\alpha\beta}. \quad (70)$$

Then we perform a canonical transformation to the new coordinates, $\{X_s\}$, and momenta, $\{P_s\}$:

$$u_\alpha = \sum_s e_\alpha^{(s)} X_s, \quad p_\alpha = \sum_s e_\alpha^{(s)} P_s, \quad (71)$$

the inverse transformation being

$$X_s = \sum_\alpha e_\alpha^{(s)} u_\alpha, \quad P_s = \sum_\alpha e_\alpha^{(s)} p_\alpha. \quad (72)$$

⁷If the matrix $A_{\alpha\beta}$ is not symmetric, we can safely symmetrize it by $A_{\alpha\beta} \rightarrow (A_{\alpha\beta} + A_{\beta\alpha})/2$.

The properties (70) guarantee that the new operators satisfy the canonical commutation relations:

$$[X_{s_1}, P_{s_2}] = i\delta_{s_1 s_2}, \quad [X_{s_1}, X_{s_2}] = 0, \quad [P_{s_1}, P_{s_2}] = 0. \quad (73)$$

Substituting (72) into the Hamiltonian and using (68)-(70), we arrive at the system of independent quantum harmonic oscillators

$$H = \frac{1}{2} \sum_s (P_s^2 + \omega_s^2 X_s^2). \quad (74)$$

The Hamiltonian (74) is readily written in the standard form

$$H = \sum_s \omega_s (b_s^\dagger b_s + 1/2), \quad (75)$$

with the annihilation and creation operators

$$b_s = \frac{\omega_s X_s + iP_s}{\sqrt{2\omega_s}}, \quad b_s^\dagger = \frac{\omega_s X_s - iP_s}{\sqrt{2\omega_s}}, \quad (76)$$

in terms of which

$$X_s = \frac{b_s + b_s^\dagger}{\sqrt{2\omega_s}}, \quad P_s = i\sqrt{\frac{\omega_s}{2}} (b_s^\dagger - b_s). \quad (77)$$

It is important that Eqs. (76) and (73) imply the commutation relations

$$[b_{s_1}, b_{s_2}^\dagger] = \delta_{s_1 s_2}, \quad [b_{s_1}, b_{s_2}] = 0. \quad (78)$$

In accordance with (65), (72), and (77), the expression for the original coordinates in terms of the creation and annihilation operators reads

$$u_\alpha = \frac{1}{\sqrt{2m_\alpha}} \sum_s e_\alpha^{(s)} \frac{b_s + b_s^\dagger}{\sqrt{\omega_s}}. \quad (79)$$

In the context of phonons (and other problems) it is normally more convenient to use the eigenvectors $e_\alpha^{(s)}$ in the form of the plane waves rather than sines/cosines. A minor issue arises then with the fact that the plane waves are essentially complex, while our treatment so far was implying that the eigenvectors are real. An important circumstance that allows us to generalize our treatment to the complex eigenvectors is that if $|e_s\rangle = e_\alpha^{(s)}$ is a complex eigenvector of a real Hermitian matrix, then its complex conjugate, $|e_s^*\rangle = [e_\alpha^{(s)}]^*$, has to be a *different* complex eigenvector, $|e_s^*\rangle \equiv |e_{s'}\rangle$, with the

same eigenvalue, meaning that the real and imaginary parts—respectively, $|e_{s1}\rangle$ and $|e_{s2}\rangle$ —of the vector $|e_s\rangle$ are two real eigenvectors with the same eigenvalue. We have

$$|e_s\rangle = \frac{|e_{s1}\rangle + i|e_{s2}\rangle}{\sqrt{2}}, \quad |e_{s'}\rangle = \frac{|e_{s1}\rangle - i|e_{s2}\rangle}{\sqrt{2}}, \quad (80)$$

$$|e_{s1}\rangle = \frac{|e_s\rangle + |e_{s'}\rangle}{\sqrt{2}}, \quad |e_{s2}\rangle = \frac{|e_s\rangle - |e_{s'}\rangle}{i\sqrt{2}}. \quad (81)$$

Then, considering our original expression (79) in terms of the real vectors, where we have

$$|e_{s1}\rangle (b_{s1} + b_{s1}^\dagger) + |e_{s2}\rangle (b_{s2} + b_{s2}^\dagger), \quad (82)$$

we observe that if we introduce new annihilation operators by the canonical transformation

$$b_s = \frac{b_{s1} - ib_{s2}}{\sqrt{2}}, \quad b_{s'} = \frac{b_{s1} + ib_{s2}}{\sqrt{2}}, \quad (83)$$

implying

$$b_{s1} = \frac{b_s + b_{s'}}{\sqrt{2}}, \quad b_{s2} = \frac{b_{s'} - b_s}{i\sqrt{2}}, \quad (84)$$

then the expression (82) becomes

$$|e_s\rangle b_s + |e_{s'}\rangle b_s^\dagger + |e_{s'}\rangle b_{s'} + |e_s\rangle b_{s'}^\dagger \equiv |e_s\rangle b_s + |e_s^*\rangle b_s^\dagger + |e_{s'}\rangle b_{s'} + |e_{s'}^*\rangle b_{s'}^\dagger.$$

This brings us to the generalization of (79) in the form

$$u_\alpha = \frac{1}{\sqrt{2m_\alpha}} \sum_s \frac{e_\alpha^{(s)} b_s + [e_\alpha^{(s)}]^* b_s^\dagger}{\sqrt{\omega_s}}. \quad (85)$$

Now we have to adjust the above theory to phonons. We recall that the structure of the displacement subscript is $\alpha \equiv (\mathbf{n}, j, i)$, where the integer vector \mathbf{n} labels the cells, j labels the atoms in the basis, $i = x, y, z$ labels components of the displacement vector. The structure of the phonon subscript is $s \equiv (\mathbf{g}, \nu)$, where \mathbf{g} is the dimensionless wavevector⁸ and ν is the branch subscript. Correspondingly, Eq. (85) now reads

$$\mathbf{u}_{\mathbf{n}j} = \frac{1}{\sqrt{2Nm_j}} \sum_{\nu\mathbf{g}} \frac{\mathbf{v}_{j\nu}(\mathbf{g}) e^{i\mathbf{g}\cdot\mathbf{n}} b_{\nu\mathbf{g}} + \mathbf{v}_{j\nu}^*(\mathbf{g}) e^{-i\mathbf{g}\cdot\mathbf{n}} b_{\nu\mathbf{g}}^\dagger}{\sqrt{\omega_\nu(\mathbf{g})}}, \quad (86)$$

⁸Working with \mathbf{g} rather than with \mathbf{q} renders expressions more compact.

where $\mathbf{v}_{j\nu}(\mathbf{g})$ and $\omega_\nu(\mathbf{g})$ are found by solving the eigenvector/eigenvalue problem (19):

$$\sum_{i'j'} \tilde{C}_{jj'}^{ii'}(\mathbf{g}) v_{j'\nu}^{i'}(\mathbf{g}) = \omega_\nu^2(\mathbf{g}) v_{j\nu}^i(\mathbf{g}). \quad (87)$$

By writing the square root of N in the denominator of (86) we fix the normalization⁹ of the vectors $\mathbf{v}_{j\nu}(\mathbf{g})$:

$$\sum_{ij} \left(v_{j\nu_1}^i(\mathbf{g}) \right)^* v_{j\nu_2}^i(\mathbf{g}) = \delta_{\nu_1\nu_2}.$$

Thermal and zero-point fluctuations of atomic positions

The expectation values of the displacements are zero, $\langle \mathbf{u}_{\mathbf{n}j} \rangle = 0$, because the equilibrium statistics of non-interacting harmonic oscillators imply $\langle b_{\nu\mathbf{g}} \rangle = \langle b_{\nu\mathbf{g}}^\dagger \rangle = 0$. But the displacements do fluctuate.

The fluctuations of atomic positions can be characterized by the variances of the displacement vectors, $\langle \mathbf{u}_{\mathbf{n}j}^2 \rangle$. To evaluate this quantity, we take into account that

$$\langle b_{s1} b_{s2} \rangle = \langle b_{s1}^\dagger b_{s2}^\dagger \rangle = 0, \quad \langle b_{s1}^\dagger b_{s2} \rangle = \langle b_{s1}^\dagger b_{s1} \rangle \delta_{s1s2} \equiv \langle n_{s1} \rangle \delta_{s1s2}. \quad (88)$$

Then, for the dispersion of the i -th component of $\mathbf{u}_{\mathbf{n}j}$ we get

$$\begin{aligned} \langle (u_{\mathbf{n}j}^i)^2 \rangle &= \frac{1}{Nm_j} \sum_{\nu\mathbf{g}} |v_{j\nu}^i(\mathbf{g})|^2 \frac{\bar{n}_{\nu\mathbf{g}} + 1/2}{\omega_\nu(\mathbf{g})} \\ &= \frac{1}{m_j} \sum_{\nu} \int_{BZ} \frac{d^d g}{(2\pi)^d} |v_{j\nu}^i(\mathbf{g})|^2 \frac{\bar{n}_{\nu\mathbf{g}} + 1/2}{\omega_\nu(\mathbf{g})}. \end{aligned} \quad (89)$$

Here

$$\bar{n}_{\nu\mathbf{g}} \equiv \langle n_{\nu\mathbf{g}} \rangle = \frac{1}{e^{\omega_\nu(\mathbf{g})/T} - 1} \quad (90)$$

is the average phonon occupation number for the mode (ν, \mathbf{g}) .

A remarkable fact is that the dispersion (89) *diverges* at finite temperatures in the dimensions $d \leq 2$, and in $d = 1$ it diverges even in the ground state! As is easily seen, the divergence is due to the acoustic modes. Indeed, at small enough g , the frequency of the acoustic mode behaves as

$$\omega_\nu(\mathbf{g}) \sim g \quad (\text{acoustic mode at } g \rightarrow 0).$$

⁹Note that in the quantum case, as opposed to the classical one, the normalization of the eigenvectors of the normal modes is not arbitrary.

At any finite temperature, we also have

$$\bar{n}_{\nu\mathbf{g}} \approx \frac{T}{\omega_{\nu}(\mathbf{g})} \sim \frac{T}{g} \quad (\text{acoustic mode at } g \rightarrow 0, \omega_{\nu}(\mathbf{g}) \ll T).$$

We thus deal with the following long-wave divergence of the dispersion

$$\langle (u_{\mathbf{n}j}^i)^2 \rangle \sim [\text{non-singular part}] + T \int_0^{\text{cutoff}} \frac{dg}{g^{3-d}} \rightarrow \infty \quad (d \leq 2, T > 0),$$

$$\langle (u_{\mathbf{n}j}^i)^2 \rangle \sim [\text{non-singular part}] + \int_0^{\text{cutoff}} \frac{dg}{g} \rightarrow \infty \quad (d = 1, T = 0).$$

These divergencies imply that:

- (i) There is no qualitative difference between solid and liquid in 1D.
- (ii) In 2D at finite T, there are no crystals in the sense of the definition based on spatially periodic profiles of density and other observables.¹⁰

Under the conditions of divergence of the variance of the displacements, we need to resort to a more delicate characteristic of fluctuations. Namely, the variance of the distance between two atoms (of the same sort j , for the sake of simplicity of the expressions):

$$\langle (\mathbf{R}_{\mathbf{n}1j} - \mathbf{R}_{\mathbf{n}2j})^2 \rangle = \left(\mathbf{R}_{\mathbf{n}1j}^{(0)} - \mathbf{R}_{\mathbf{n}2j}^{(0)} \right)^2 + \langle (\mathbf{u}_{\mathbf{n}1j} - \mathbf{u}_{\mathbf{n}2j})^2 \rangle.$$

Here we get

$$\langle (u_{\mathbf{n}1j}^i - u_{\mathbf{n}2j}^i)^2 \rangle = \frac{1}{m_j} \sum_{\nu} \int_{BZ} \frac{d^d g}{(2\pi)^d} \left| e^{i\mathbf{g} \cdot (\mathbf{n}_1 - \mathbf{n}_2)} - 1 \right|^2 |v_{j\nu}^i(\mathbf{g})|^2 \frac{\bar{n}_{\nu\mathbf{g}} + 1/2}{\omega_{\nu}(\mathbf{g})}. \quad (91)$$

This expression is not divergent because

$$|e^{i\mathbf{g} \cdot (\mathbf{n}_1 - \mathbf{n}_2)} - 1|^2 \rightarrow |\mathbf{g} \cdot (\mathbf{n}_1 - \mathbf{n}_2)|^2 \quad \text{at} \quad |\mathbf{g} \cdot (\mathbf{n}_1 - \mathbf{n}_2)| \ll 1.$$

At $|\mathbf{n}_1 - \mathbf{n}_2| \sim 1$ the behavior of the r.h.s. of (91) is essentially the same in all dimensions, showing that the problem with divergences in low dimensions does not affect the fluctuations of the relative positions of the atoms at the microscopic scales.¹¹ Clearly, considering (91) as a function of $|\mathbf{n}_1 - \mathbf{n}_2|$, we

¹⁰In 2D at $T > 0$, one defines the solid as a state with *topological* order meaning the existence of cells labeled with an integer vector \mathbf{n} . Such a state features shear rigidity and thus is distinctively different from liquid.

¹¹And this is why we can speak of the topological order in 2D.

get the divergent behavior at $|\mathbf{n}_1 - \mathbf{n}_2| \rightarrow \infty$ in all the cases where $\langle (u_{\mathbf{n}j}^i)^2 \rangle$ diverges. In those cases, an important quantity is the correlation radius r_c defined as $r_c \sim |\mathbf{T}_{\mathbf{n}_c}|$, where

$$\sqrt{\langle (u_{\mathbf{n}_c j}^i - u_{0j}^i)^2 \rangle} \sim a,$$

with a the period of the lattice. The correlation radius is the distance at which the crystal order is destroyed. In the context of the Bragg diffraction, $1/r_c$ yields the typical width of the Bragg peaks in 1D and 2D ($T > 0$). Note that the Bragg peaks *do not* broaden in 3D; they get only weaker with increasing temperature.—See the next section.

Debye–Waller factor

The effective Hamiltonian of interaction of a neutron with nuclei of a crystal reads¹²

$$U_{\text{int}} = \sum_{\mathbf{n}j} f_j \delta(\mathbf{r} - \mathbf{R}_{\mathbf{n}j}), \quad (92)$$

where f_j is the effective interaction constant for the j -th atom of the basis, \mathbf{r} is the coordinate of the neutron,

$$\mathbf{R}_{\mathbf{n}j} = \mathbf{T}_{\mathbf{n}} + \mathbf{R}_j^{(0)} + \mathbf{u}_{\mathbf{n}j} \quad (93)$$

is the coordinate of the j -th atom in the \mathbf{n} -th cell, $\mathbf{R}_j^{(0)}$ is the position of the j -th atom in the cell $\mathbf{n} = 0$. The matrix element $M_{\mathbf{k}\mathbf{k}'}$ for the elastic scattering of the neutron with momentum \mathbf{k} into the state with momentum \mathbf{k}' is ($\mathbf{q} = \mathbf{k}' - \mathbf{k}$)

$$M_{\mathbf{k}\mathbf{k}'} = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \langle \text{crystal} | \sum_{\mathbf{n}j} f_j \delta(\mathbf{r} - \mathbf{R}_{\mathbf{n}j}) | \text{crystal} \rangle. \quad (94)$$

Here $|\text{crystal}\rangle$ is a representative state of the system.¹³ The integration over \mathbf{r} removes the delta-functions, provided the integration is done before

¹²The small parameter controlling the accuracy of this effective description is the ratio of the typical size of the nucleus to the de Broglie wavelength of the neutron.

¹³In view of the macroscopicity of the system, instead of averaging the final answer for the scattering probability over the Gibbs distribution we simply take one representative state of the system. For such a state, the quantum-mechanical expectation value of a typical operator is equal to the thermodynamical average of this operator: $\langle \text{crystal} | (\dots) | \text{crystal} \rangle = \langle (\dots) \rangle$.

(and inside) the averaging:

$$M_{\mathbf{k}\mathbf{k}'} = \sum_{\mathbf{n}j} f_j \langle e^{-i\mathbf{q}\cdot\mathbf{R}_{\mathbf{n}j}} \rangle. \quad (95)$$

With (93) we then have

$$M_{\mathbf{k}\mathbf{k}'} = \sum_{\mathbf{n}j} f_j e^{-i\mathbf{q}\cdot\mathbf{T}_{\mathbf{n}}} e^{-i\mathbf{q}\cdot\mathbf{R}_j^{(0)}} \langle e^{-i\mathbf{q}\cdot\mathbf{u}_{\mathbf{n}j}} \rangle. \quad (96)$$

All the relevant information about thermal fluctuations of the atomic positions is encoded in the average

$$F_j^{\text{DW}}(\mathbf{q}) = \langle e^{-i\mathbf{q}\cdot\mathbf{u}_{\mathbf{n}j}} \rangle \equiv \langle e^{-i\mathbf{q}\cdot\mathbf{u}_j} \rangle, \quad (97)$$

known as the *Debye–Waller factor*. Because of translation invariance, it depends only on j . The expression for $M_{\mathbf{k}\mathbf{k}'}$ acquires the form of the standard Bragg sum

$$M_{\mathbf{k}\mathbf{k}'} = S(\mathbf{q}) \sum_{\mathbf{n}} e^{-i\mathbf{q}\cdot\mathbf{T}_{\mathbf{n}}},$$

with the amplitude (structure factor) given by

$$S(\mathbf{q}) = \sum_j f_j F_j^{\text{DW}}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_j^{(0)}}.$$

Hence, the role of thermal fluctuations reduces to renormalizing the effective coupling constants f_j by corresponding Debye–Waller factors:

$$f_j \rightarrow f_j F_j^{\text{DW}}(\mathbf{q}).$$

Calculating Debye–Waller factors and other averages: Wick’s theorem

How do we calculate the Debye–Waller factors? We rely on the general theorem of quantum statistics—the so-called Wick’s theorem—dealing with averaging of quantities that are linear combinations of creation and annihilation operators,

$$A = \alpha_1 b_1^{(\pm)} + \alpha_2 b_2^{(\pm)} + \alpha_3 b_3^{(\pm)} + \dots, \quad (98)$$

over the Gibbs distribution (or just the ground state) of independent harmonic oscillators, or, equivalently, bosonic modes. In the expression (98),

α_j 's are constant coefficients, while $b_j^{(+)} \equiv b_j^\dagger$ and $b_j^{(-)} \equiv b_j$. The Wick's theorem states that (i) the average of a product of an odd number of type-(98) operators is zero (m is integer),

$$\langle A_1 A_2 \cdots A_{2m+1} \rangle = 0,$$

and (ii) the average of a product of an even number of type-(98) operators decomposes into the sum of products of pairwise averages by the following rule

$$\begin{aligned} \langle A_1 A_2 \cdots A_{2m} \rangle &= \langle A_1 A_2 \rangle \langle A_3 A_4 \rangle \cdots \langle A_{2m-1} A_{2m} \rangle + \\ &+ \text{all similar terms with alternative pairings.} \end{aligned}$$

For example,

$$\langle A_1 A_2 A_3 A_4 \rangle = \langle A_1 A_2 \rangle \langle A_3 A_4 \rangle + \langle A_1 A_3 \rangle \langle A_2 A_4 \rangle + \langle A_1 A_4 \rangle \langle A_2 A_3 \rangle.$$

The pairwise averages are readily calculated by the rules (88), Eq. (89) serving as a typical example. Hence, the Wick's theorem solves the problem of evaluating the averages of polynomials of type-(98) operators.

The Wick's theorem implies the following elegant formula for a type-(98) operator:

$$\langle e^A \rangle = e^{\langle A^2 \rangle / 2}. \quad (99)$$

To see that, expand both the l.h.s and the r.h.s. into the Taylor series and observe that, within each order of expansion, the r.h.s. corresponds to the Wick's theorem applied to the l.h.s.

Equation (99) immediately solves the problem of evaluating the Debye-Waller factor, reducing it to the previously obtained result (89):

$$F_j^{\text{DW}}(\mathbf{q}) = \langle e^{-i\mathbf{q}\cdot\mathbf{u}_j} \rangle = \exp \left[-\frac{q^2}{2} \left\langle \left(u_j^{(\mathbf{q})} \right)^2 \right\rangle \right]. \quad (100)$$

Here $u_j^{(\mathbf{q})}$ is the component of the vector \mathbf{u}_j along the direction \mathbf{q}/q .

Debye-Waller factor and the Mössbauer effect

If a nucleus of a free atom emits/absorbs a gamma ray, it experiences a recoil due to the conservation laws. As a result, the resonant frequencies in the emission and absorption processes are slightly different from each other.

Even this slight mismatch proves to be fatal for applications in which tiny shifts of the resonant gamma radiation are used to extract the information about the environment of a given atom. A remarkable fact, however, is that in a 3D crystal there is a finite probability to emit/absorb a gamma ray purely elastically—i.e. without emitting or absorbing phonons. This is the so-called Mössbauer effect.

Consider the Mössbauer effect in the emission process. The effective interaction Hamiltonian reads (we do not care about the coupling constant)

$$H_{\text{int}} \propto \sum_{\mathbf{k}, \lambda} e^{i\mathbf{k} \cdot \mathbf{u}_0} f_{\mathbf{k}, \lambda}^\dagger a_0 + \text{H.c.}, \quad (101)$$

where $f_{\mathbf{k}, \lambda}^\dagger$ creates a photon with the wavevector \mathbf{k} and polarization λ , a_0 annihilates the excited state of the nucleus, and \mathbf{u}_0 is the operator of displacement of the excited nucleus. With the Hamiltonian (101) we see that the matrix element for the recoilless Mössbauer emission is proportional to the Debye–Waller factor

$$\langle e^{i\mathbf{k} \cdot \mathbf{u}_0} \rangle = \exp \left[-\frac{k^2}{2} \left\langle \left(u_0^{(\mathbf{k})} \right)^2 \right\rangle \right].$$

The fact that the Debye-Waller factor gets progressively lower with increasing temperature should not be interpreted as if the lifetime of the excited nuclei increases. This simply means that while the fraction of recoilless events gets smaller, the fraction of the processes accompanied by absorption/emission of phonons increases. In this respect very instructive is the following relation.

$$\sum_{f \neq i} \left| \langle f | e^{i\mathbf{k} \cdot \mathbf{u}_0} | i \rangle \right|^2 = 1 - \left| \langle i | e^{i\mathbf{k} \cdot \mathbf{u}_0} | i \rangle \right|^2. \quad (102)$$

Here $|i\rangle$ and $|f\rangle$ are, respectively, the initial and final states of phonon subsystem, so that the l.h.s. is the sum of squares of matrix elements for all *inelastic* processes (note $f \neq i$), while the Debye-Waller factor in the r.h.s. characterizes the rate of elastic processes. The proof of (102) is simple. By the completeness relation

$$\sum_f |f\rangle \langle f| = 1$$

we can write

$$\sum_f e^{-i\mathbf{k} \cdot \mathbf{u}_0} |f\rangle \langle f| e^{i\mathbf{k} \cdot \mathbf{u}_0} = e^{-i\mathbf{k} \cdot \mathbf{u}_0} e^{i\mathbf{k} \cdot \mathbf{u}_0} = 1.$$

Hence

$$1 = \sum_f \langle i | e^{-i\mathbf{k}\cdot\mathbf{u}_0} | f \rangle \langle f | e^{i\mathbf{k}\cdot\mathbf{u}_0} | i \rangle = \sum_{f \neq i} \langle i | e^{-i\mathbf{k}\cdot\mathbf{u}_0} | f \rangle \langle f | e^{i\mathbf{k}\cdot\mathbf{u}_0} | i \rangle + \\ + \langle i | e^{-i\mathbf{k}\cdot\mathbf{u}_0} | i \rangle \langle i | e^{i\mathbf{k}\cdot\mathbf{u}_0} | i \rangle = \sum_{f \neq i} \left| \langle f | e^{i\mathbf{k}\cdot\mathbf{u}_0} | i \rangle \right|^2 + \left| \langle i | e^{i\mathbf{k}\cdot\mathbf{u}_0} | i \rangle \right|^2 .$$