Contents

List of Figures

List of Tables

Chapter 3

Deformations of Crystals

3.1 Elasticity

3.1.1 Stress and strain tensors

An elastic medium is described by a local deformation field $u(r)$, corresponding to the elastic displacement of the solid at r. The *strain tensor* is defined by the dimensionless expression

$$\varepsilon_{ij}(r) = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \quad . \tag{3.1}$$

Note that $\varepsilon = \varepsilon^{\mathsf{T}}$ is a symmetric tensor by definition. Similarly, the *stress tensor* $\sigma_{ij}(r)$ is defined by

$$dF_i(r) = -\sigma_{ij}(r)\, n_j\, d\Sigma \quad , \tag{3.2}$$

where $dF(r)$ is the differential force on a surface element $d\Sigma$ whose normal is the vector $\hat{n}$. Angular momentum conservation requires that the stress tensor also be symmetric[1]. The stress and strain tensors are related by the rank four *elastic modulus tensor*, *viz.*

$$\sigma_{ij}(r) = C_{ijkl}\, \varepsilon_{kl}(r) = \frac{\delta f}{\delta \varepsilon_{ij}(r)} \quad , \tag{3.3}$$

where the second equality is a statement of thermal equilibrium akin to $p = -\partial F/\partial V$. Here,

$$f(r) = f_0 + \tfrac{1}{2}\, C_{ijkl}\, \varepsilon_{ij}(r)\, \varepsilon_{kl}(r) + \mathcal{O}(\varepsilon^3) \tag{3.4}$$

---

[1]Integrate the differential torque $dN = r \times dF$ over the entire body. Integrating by parts, one obtains a surface term and a volume term. The volume torque density is $-\epsilon_{ijk}\,\sigma_{jk}$, which must vanish, thereby entailing the symmetry $\sigma = \sigma^{\mathsf{T}}$.

is the local free energy density. Since ε is a dimensionless tensor, the elastic moduli have dimensions of energy density, typically expressed in cgs units as $\mathrm{dyn/cm^2}$. For an *isotropic* material, the only $\mathsf{O}(3)$ invariant terms in the free energy to order ε^2 are proportional to either $(\mathsf{Tr}\ \varepsilon)^2$ or to $\mathsf{Tr}(\varepsilon^2)$. Thus,

$$f = f_0 + \tfrac{1}{2}\lambda\,(\mathsf{Tr}\ \varepsilon)^2 + \mu\ \mathsf{Tr}\,(\varepsilon^2) \quad . \tag{3.5}$$

The parameters λ and μ are called the *Lamé coefficients*[2]. For isotropic elastic materials, then,

$$\sigma_{ij} = \frac{\partial f}{\partial \varepsilon_{ij}} = \lambda\ \mathsf{Tr}\ \varepsilon\,\delta_{ij} + 2\mu\,\varepsilon_{ij} \quad . \tag{3.6}$$

In the literature, one often meets up with the quantity $K \equiv \lambda + \tfrac{2}{3}\mu$, in which case the free energy density becomes

$$f = f_0 + \tfrac{1}{2}K\,(\mathsf{Tr}\ \varepsilon)^2 + \mu\ \mathsf{Tr}\left(\varepsilon - \tfrac{1}{3}\ \mathsf{Tr}\ \varepsilon\right)^2 \tag{3.7}$$

The reason is that the tensor $\widetilde{\varepsilon} \equiv \varepsilon - \tfrac{1}{3}(\mathsf{Tr}\ \varepsilon)\cdot\mathbf{1}$ is traceless, and therefore the constant K tells us about *bulk deformations* while μ tells us about *shear deformations*. One then requires $K > 0$ and $\mu > 0$ for thermodynamic stability. We then may write, for isotropic materials,

$$\begin{aligned}
\sigma &= K\,(\mathsf{Tr}\ \varepsilon)\cdot\mathbf{1} + 2\mu\,\widetilde{\varepsilon} \\
\varepsilon &= \frac{1}{9K}\,(\mathsf{Tr}\ \sigma)\cdot\mathbf{1} + \frac{1}{2\mu}\,\widetilde{\sigma} \quad ,
\end{aligned} \tag{3.8}$$

with $\widetilde{\sigma} \equiv \sigma - \tfrac{1}{3}(\mathsf{Tr}\ \sigma)\cdot\mathbf{1}$ the traceless part of the stress tensor[3].

If one solves for the homogeneous deformation[4] of a rod of circular cross section, the only nonzero element of the stress tensor is $\sigma_{zz} = p$, where p is the pressure on either of the circular faces of the rod. One then finds that $\varepsilon_{xx} = \varepsilon_{yy} = \left(\tfrac{1}{9K} - \tfrac{1}{6\mu}\right)p$ and $\varepsilon_{zz} = \left(\tfrac{1}{9K} + \tfrac{1}{3\mu}\right)p$ are the only nonzero elements of the strain tensor. Thus,

$$Y \equiv \frac{\sigma_{zz}}{\varepsilon_{zz}} = \frac{9K\mu}{3K + \mu} \quad , \qquad \beta \equiv -\frac{\varepsilon_{xx}}{\varepsilon_{zz}} = \frac{3K - 2\mu}{2(3K + \mu)} \quad . \tag{3.9}$$

The quantity Y is called the *Young's modulus*, and must be positive. The quantity β is the *Poisson ratio* β and satisfies $\beta \in \left[-1, \tfrac{3}{2}\right]$. A material like tungsten carbide has a very large Young's modulus of $Y = 53.4 \times 10^{11}\ \mathrm{dyn/cm^2}$ at STP, which means that you have to pull like hell in order to get it to stretch a little. Normally, when you stretch a material, it narrows in the transverse directions, which corresponds to a positive Poisson ratio. Materials for which $\beta < 0$ are called *auxetics*. When stretched, an auxetic becomes thicker in the directions perpendicular to the applied force. Examples include various porous foams and artificial macrostructures.

---

[2]If you were wondering why we've suddenly switched to roman indices C_{ijkl} instead of Greek $C_{\alpha\beta\mu\nu}$, it is to obviate any confusion with the Lamé parameter μ.

[3]In d space dimensions, one has $K = \lambda + 2d^{-1}\mu$ and $\widetilde{m} = m - d^{-1}\ \mathsf{Tr}\ m$ is the traceless part of any matrix m.

[4]In a homogeneous deformation, the strain and stress tensors are constant throughout the body.

$(\alpha\beta):$	(11)	(22)	(33)	(23)	(31)	(12)
$a:$	1	2	3	4	5	6

Table 3.1: Abbreviation for symmetric compound indices $(\alpha\beta)$.

3.1.2 Elasticity and symmetry

Since

$$C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij} \quad , \tag{3.10}$$

we may use the composite index notation in Tab. 3.1 to write the rank four tensor $C_{ijkl} \equiv C_{ab} = C_{ba}$ as a symmetric 6×6 matrix, with 21 independent elements before accounting for symmetry considerations. The linear stress-strain relation is then given by

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ 2\varepsilon_4 \\ 2\varepsilon_5 \\ 2\varepsilon_6 \end{pmatrix} \quad . \tag{3.11}$$

Since the elastic tensor is rank four, it is symmetric under inversion.

And now, let the symmetry commence!

- For triclinic crystals with point group C_1 or C_i, there are no symmetries to apply to C_{ab}, hence there are 21 independent elastic moduli. However, one can always rotate axes, and given the freedom to choose three Euler angles, this means we can always choose axes in such a way that three of the 21 moduli vanish, leaving 18. Again, this requires a nongeneric choice of axes.

- For monoclinic crystals, there is symmetry under $z \to -z$, and as in the example of the piezoelectric tensor $d_{\mu\nu\lambda}$, we have that C_{ijkl} vanishes if the index $3(z)$ appears an odd number of times, which means, in composite index notation,

$$C_{14} = C_{15} = C_{24} = C_{25} = C_{34} = C_{35} = C_{46} = C_{56} = 0 \quad , \tag{3.12}$$

leaving 13 independent elastic moduli for point groups C_2, C_s, and C_{2h}. The 6×6 matrix

C_{ab} thus takes the form

$$
C_{ab}^{\text{MONO}} =
\begin{pmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\
C_{12} & C_{22} & C_{23} & 0 & 0 & C_{26} \\
C_{13} & C_{23} & C_{33} & 0 & 0 & C_{36} \\
0 & 0 & 0 & C_{44} & C_{45} & 0 \\
0 & 0 & 0 & C_{45} & C_{55} & 0 \\
C_{16} & C_{26} & C_{36} & 0 & 0 & C_{66}
\end{pmatrix} .
\tag{3.13}
$$

- For orthorhombic crystals, $x \to -x$ and $y \to -y$ are each symmetries. Adding $z \to -z$ in the case of D_{2h} doesn't buy us any new restrictions since C is symmetric under inversion. We then have $C_{ab} = 0$ whenever $a \in \{1,2,3\}$ and $b \in \{4,5,6\}$. The general form of C_{ab} is then

$$
C_{ab}^{\text{ORTHO}} =
\begin{pmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{pmatrix} .
\tag{3.14}
$$

- For the tetragonal system, we can rotate (x, y, z) to $(-y, x, z)$. For the lower symmetry point groups among this system, namely C_4, S_4, and C_{4h}, the most general form is

$$
C_{ab}^{\text{TET}}[C_4, S_4, C_{4h}] =
\begin{pmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\
C_{12} & C_{11} & C_{13} & 0 & 0 & -C_{16} \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
C_{16} & -C_{16} & 0 & 0 & 0 & C_{66}
\end{pmatrix} ,
\tag{3.15}
$$

which has seven independent moduli. For the higher symmetry tetragonal point groups D_4, C_{4v}, D_{2d}, and D_{4h}, we have $C_{16} = 0$ because of the twofold axes which send (x, y, z) into $(x, -y, -z)$ and $(-x, y, -z)$, and there are only six independent moduli.

- For the trigonal point groups, our lives are again complicated by the C_3 rotations. One convenient way to deal with this is to define $\xi \equiv x + iy$ and $\bar{\xi} \equiv x - iy$, with

$$
\begin{aligned}
\varepsilon_{\xi\xi} &= \xi_i \, \xi_j \, \varepsilon_{ij} = \varepsilon_{xx} - \varepsilon_{yy} + 2i \, \varepsilon_{xy} \\
\varepsilon_{\xi\bar{\xi}} &= \xi_i \, \bar{\xi}_j \, \varepsilon_{ij} = \varepsilon_{xx} + \varepsilon_{xy} \\
\varepsilon_{z\xi} &= \xi_i \, \varepsilon_{zi} = \varepsilon_{zx} + i \, \varepsilon_{zy} \\
\varepsilon_{z\bar{\xi}} &= \bar{\xi}_i \, \varepsilon_{zi} = \varepsilon_{zx} - i \, \varepsilon_{zy} \quad ,
\end{aligned}
\tag{3.16}
$$

where $\xi_i = \partial_i \xi$ where $x_1 = x$ and $x_2 = y$, and $\bar{\xi}_i = \partial_i \bar{\xi}$. A C_3 rotation then takes $\xi \to e^{2\pi i/3} \, \xi$ and $\bar{\xi} \to e^{-2\pi i/3} \, \bar{\xi}$. The only allowed elements of C_{ijkl} are

$$
C_{zzzz} \quad , \quad C_{zz\xi\bar{\xi}} \quad , \quad C_{\xi\xi\bar{\xi}\bar{\xi}} \quad , \quad C_{\xi\bar{\xi}\xi\bar{\xi}} \quad , \quad C_{z\xi z\bar{\xi}} \quad , \quad C_{z\xi\xi\xi} \quad , \quad C_{z\bar{\xi}\bar{\xi}\bar{\xi}} \quad ,
\tag{3.17}
$$

and their corresponding elements obtained by permuting $C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij}$. The first five of these are real, and the last two are complex conjugates: $C_{z\bar{\xi}\bar{\xi}\bar{\xi}} = C^*_{z\xi\xi\xi}$. So there are seven independent elastic moduli for the point groups C_3 and S_6. Note the general rule that we must have either no complex indices, one ξ and one $\bar{\xi}$ index, two each of ξ and $\bar{\xi}$, three ξ, or three $\bar{\xi}$. All other coefficients vanish by C_3 symmetry. We may now construct the elastic free energy density,

$$f = f_0 + \tfrac{1}{2}C_{zzzz}\,\varepsilon^2_{zz} + C_{\xi\xi\bar{\xi}\bar{\xi}}\,\varepsilon_{\xi\xi}\,\varepsilon_{\bar{\xi}\bar{\xi}} + 2\,C_{\xi\bar{\xi}\xi\bar{\xi}}\,\varepsilon^2_{\xi\bar{\xi}} + 2\,C_{zz\xi\bar{\xi}}\,\varepsilon_{zz}\,\varepsilon_{\xi\bar{\xi}}$$
$$+ 4\,C_{z\xi z\bar{\xi}}\,\varepsilon_{z\xi}\,\varepsilon_{z\bar{\xi}} + 2\,C_{z\xi\xi\xi}\,\varepsilon_{z\bar{\xi}}\,\varepsilon_{\xi\xi} + 2\,C_{z\bar{\xi}\bar{\xi}\bar{\xi}}\,\varepsilon_{z\bar{\xi}}\,\varepsilon_{\bar{\xi}\bar{\xi}} \quad .$$

$$(3.18)$$

Note the coefficient of four in front of the $C_{z\xi z\bar{\xi}}$ term, which arises from summing over the eight equal contributions,

$$\tfrac{1}{2}\big(C_{z\xi z\bar{\xi}} + C_{z\xi\bar{\xi}z} + C_{\xi zz\bar{\xi}} + C_{\xi z\bar{\xi}z} + C_{z\bar{\xi}z\xi} + C_{z\bar{\xi}\xi z} + C_{\bar{\xi}zz\xi} + C_{\bar{\xi}z\xi z}\big)\,\varepsilon_{z\xi}\,\varepsilon_{z\bar{\xi}} = 4\,C_{z\xi z\bar{\xi}}\,\varepsilon_{z\xi}\,\varepsilon_{z\bar{\xi}} \quad . \quad (3.19)$$

From the free energy, one can identify the coefficients of $\varepsilon_a\,\varepsilon_b$, where a and b are composite indices, and thereby determine the general form for C_{ab}, which is

$$C^{\text{TRIG}}_{ab}[C_3, S_6] = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & -C_{25} & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & C_{25} & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & C_{25} \\ -C_{25} & C_{25} & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & C_{25} & C_{14} & \tfrac{1}{2}(C_{11} - C_{12}) \end{pmatrix} \quad , \quad (3.20)$$

Adding in reflections or twofold axes, as we have in the higher symmetry groups in this system, *i.e.* D_3, C_{3v}, and D_{3d} allows for $\xi \leftrightarrow \bar{\xi}$, in which case $C_{z\xi\xi\xi} = C_{z\bar{\xi}\bar{\xi}\bar{\xi}}$, reducing the number of independent moduli to six, with $C_{25} = 0$.

- For all seven hexagonal system point groups, we have $C_{z\xi\xi\xi} = C_{z\bar{\xi}\bar{\xi}\bar{\xi}} = 0$, because C_6 rotations take ξ to $\xi\,e^{i\pi/3}$, hence $C_{z\xi\xi\xi}$ to $-C_{z\xi\xi\xi}$. C_{3h} and D_{3h} don't contain this element, but do contain the mirror reflection $z \to -z$, hence in all cases the elastic tensor resembles that for the trigonal case, but with $C_{14} = C_{25} = 0$. Hence there are five independent moduli, with

$$C^{\text{HEX}}_{ab} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \tfrac{1}{2}(C_{11} - C_{12}) \end{pmatrix} \quad , \quad (3.21)$$

- For the cubic system (five point groups), the only independent elements are C_{xxxx}, C_{xxyy},

C_{xyxy}, and their symmetry-related counterparts such as C_{zzzz}, C_{yzyz}, etc. Thus,

$$
C_{ab}^{\text{CUB}} = \begin{pmatrix}
C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44}
\end{pmatrix} , \tag{3.22}
$$

- For an isotropic material, $C_{11} = C_{22} + 2C_{44}$. The Lamé parameters are $\lambda = C_{12}$ and $\mu = C_{44}$.

3.2 Phonons in Crystals

Crystalline solids support propagating waves called *phonons*, which are quantized vibrations of the lattice. Recall that the quantum mechanical Hamiltonian for a harmonic oscillator, $\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2$, may be written as $\hat{H} = \hbar\omega_0 \left(a^\dagger a + \frac{1}{2}\right)$, where a and $a^\dagger$ are 'ladder operators' satisfying commutation relations $\left[a, a^\dagger\right] = 1$.

3.2.1 One-dimensional chain

Consider the linear chain of masses and springs depicted in fig. 3.1. We assume that our system consists of N mass points on a large ring of circumference L. In equilibrium, the masses are spaced evenly by a distance $b = L/N$. That is, $x_n^0 = nb$ is the equilibrium position of particle n. We define $u_n = x_n - x_n^0$ to be the difference between the position of mass n and The Hamiltonian is then

$$
\begin{aligned}
\hat{H} &= \sum_n \left[\frac{p_n^2}{2m} + \tfrac{1}{2}\kappa \left(x_{n+1} - x_n - a\right)^2 \right] \\
&= \sum_n \left[\frac{p_n^2}{2m} + \tfrac{1}{2}\kappa \left(u_{n+1} - u_n\right)^2 \right] + \tfrac{1}{2}N\kappa(b-a)^2 ,
\end{aligned} \tag{3.23}
$$

where a is the unstretched length of each spring, m is the mass of each mass point, κ is the force constant of each spring, and N is the total number of mass points. If $b \neq a$ the springs are under tension in equilibrium, but as we see this only leads to an additive constant in the Hamiltonian, and hence does not enter the equations of motion.

The classical equations of motion are

$$\dot{u}_n = \frac{\partial \hat{H}}{\partial p_n} = \frac{p_n}{m} \tag{3.24}$$

$$\dot{p}_n = -\frac{\partial \hat{H}}{\partial u_n} = \kappa \left(u_{n+1} + u_{n-1} - 2u_n \right) . \tag{3.25}$$

Taking the time derivative of the first equation and substituting into the second yields

$$\ddot{u}_n = \frac{\kappa}{m} \left(u_{n+1} + u_{n-1} - 2u_n \right) . \tag{3.26}$$

We now write

$$u_n = \frac{1}{\sqrt{N}} \sum_k \tilde{u}_k \, e^{ikna} , \tag{3.27}$$

where periodicity $u_{N+n} = u_n$ requires that the k values are quantized so that $e^{ikNa} = 1$, i.e. $k = 2\pi j / Na$ where $j \in \{0, 1, \ldots, N-1\}$. The inverse of this discrete Fourier transform is

$$\tilde{u}_k = \frac{1}{\sqrt{N}} \sum_n u_n \, e^{-ikna} . \tag{3.28}$$

Note that $\tilde{u}_k$ is in general complex, but that $\tilde{u}_k^* = \tilde{u}_{-k}$. In terms of the $\tilde{u}_k$, the equations of motion take the form

$$\ddot{\tilde{u}}_k = -\frac{2\kappa}{m} \left(1 - \cos(ka) \right) \tilde{u}_k \equiv -\omega_k^2 \, \tilde{u}_k . \tag{3.29}$$

Thus, each $\tilde{u}_k$ is a normal mode, and the normal mode frequencies are

$$\omega_k = 2 \sqrt{\frac{\kappa}{m}} \left| \sin \left(\tfrac{1}{2}ka \right) \right| . \tag{3.30}$$

The density of states for this band of phonon excitations is

$$\begin{aligned}
g(\varepsilon) &= \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \, \delta(\varepsilon - \hbar\omega_k) \\
&= \frac{2}{\pi a} \left(J^2 - \varepsilon^2 \right)^{-1/2} \Theta(\varepsilon) \, \Theta(J - \varepsilon) ,
\end{aligned} \tag{3.31}$$

where $J = 2\hbar\sqrt{\kappa/m}$ is the phonon bandwidth. The step functions require $0 \le \varepsilon \le J$; outside this range there are no phonon energy levels and the density of states accordingly vanishes.

The entire theory can be quantized, taking $\left[p_n , u_{n'} \right] = -i\hbar \delta_{nn'}$. We then define

$$p_n = \frac{1}{\sqrt{N}} \sum_k \tilde{p}_k \, e^{ikna} \qquad , \qquad \tilde{p}_k = \frac{1}{\sqrt{N}} \sum_n p_n \, e^{-ikna} , \tag{3.32}$$
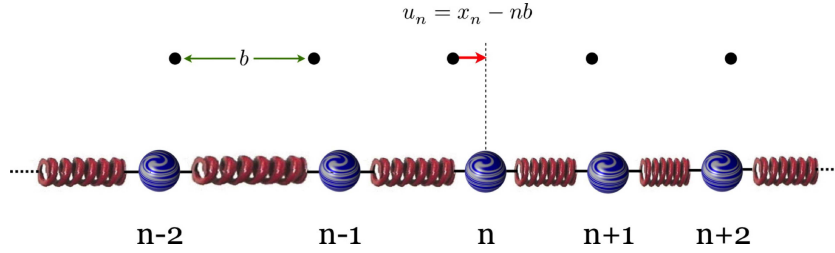
$$u_n = x_n - nb$$

Figure 3.1: A linear chain of masses and springs. The black circles represent the equilibrium positions of the masses. The displacement of mass n relative to its equilibrium value is u_n.

in which case $\left[\tilde{p}_k , \tilde{u}_{k'}\right] = -i\hbar\delta_{kk'}$. Note that $\tilde{u}_k^\dagger = \tilde{u}_{-k}$ and $\tilde{p}_k^\dagger = \tilde{p}_{-k}$. We then define the ladder operator

$$a_k = \left(\frac{1}{2m\hbar\omega_k}\right)^{1/2} \tilde{p}_k - i\left(\frac{m\omega_k}{2\hbar}\right)^{1/2} \tilde{u}_k \tag{3.33}$$

and its Hermitean conjugate $a_k^\dagger$, in terms of which the Hamiltonian is

$$\hat{H} = \sum_k \hbar\omega_k \left(a_k^\dagger a_k + \tfrac{1}{2}\right) , \tag{3.34}$$

which is a sum over independent harmonic oscillator modes. Note that the sum over k is restricted to an interval of width 2π, e.g. $k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$, which is the *first Brillouin zone* for the one-dimensional chain structure. The state at wavevector $k + \frac{2\pi}{a}$ is identical to that at k, as we see from eqn. 3.28.

3.2.2   General theory of lattice vibrations

Consider next the vibrations of a general crystalline lattice in d space dimensions with an r component basis. We define $\boldsymbol{R}$ to be a Bravais lattice vector, *i.e.* a label for a unit cell, and $\boldsymbol{u}_i(\boldsymbol{R})$ to be the displacement of the ith basis ion in the $\boldsymbol{R}$ unit cell. The Hamiltonian is

$$H = \sum_{\boldsymbol{R},i} \frac{\boldsymbol{p}_i^2(\boldsymbol{R})}{2m_i} + \frac{1}{2}\sum_{\boldsymbol{R},\boldsymbol{R}'}\sum_{i,j}\sum_{\alpha,\beta} u_i^\alpha(\boldsymbol{R})\,\Phi_{ij}^{\alpha\beta}(\boldsymbol{R} - \boldsymbol{R}')\,u_j^\beta(\boldsymbol{R}') + \mathcal{O}(u^3) \quad , \tag{3.35}$$

where

$$\Phi_{ij}^{\alpha\beta}(\boldsymbol{R} - \boldsymbol{R}') = \frac{\partial^2 U}{\partial u_i^\alpha(\boldsymbol{R})\,\partial u_j^\beta(\boldsymbol{R}')} \quad . \tag{3.36}$$

Remember that the indices i and j run over the set $\{1, \ldots, r\}$, where r is the number of basis vectors, while α and β are Cartesian vector indices taken from $\{1, 2, \ldots, d\}$, where d is the dimension of space.

In the case of molecules, the dynamical matrix is of rank dN. For a molecule with no point group symmetries, this is the dimension of the eigenvalue problem to be solved. In crystals,

by contrast, we may take advantage of translational invariance to reduce the dimension of the eigenvalue problem to dr, *i.e.* to the number of degrees of freedom within a unit cell. This is so even in the case of a triclinic system with no symmetries (*i.e.* point group C_1). Each vibrational state is labeled by a wavevector $\boldsymbol{k}$, and at certain high symmetry points $\boldsymbol{k}$ in the Brillouin zone, crystallographic point group symmetries may be used to group these dr states into multiplets transforming according to point group IRREPs.

Upon Fourier transform,

$$u_i^\alpha(\boldsymbol{R}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \hat{u}_i^\alpha(\boldsymbol{k})\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_i}$$
$$p_i^\alpha(\boldsymbol{R}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \hat{p}_i^\alpha(\boldsymbol{k})\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_i} \quad, \tag{3.37}$$

where the sum is over all $\boldsymbol{k}$ within the first Brillouin zone. The Fourier space dynamical matrix is then

$$\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} \Phi_{ij}^{\alpha\beta}(\boldsymbol{R})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{\delta}_i}\, e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_j} \quad. \tag{3.38}$$

The Hamiltonian, to quadratic order, takes the form

$$H = \sum_{\boldsymbol{k},i} \frac{\hat{p}_i^\alpha(\boldsymbol{k})\, \hat{p}_i^\alpha(-\boldsymbol{k})}{2m_i} + \frac{1}{2} \sum_{\boldsymbol{k}} \sum_{i,j} \sum_{\alpha,\beta} \hat{u}_i^\alpha(-\boldsymbol{k})\, \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})\, \hat{u}_j^\beta(\boldsymbol{k}) \quad, \tag{3.39}$$

Note that $\hat{u}_i^\alpha(-\boldsymbol{k}) = \left[\hat{u}_i^\alpha(\boldsymbol{k})\right]^*$ because the displacements $u_i^\alpha(\boldsymbol{R})$ are real; a corresponding relation holds for the momenta. Note also the Poisson bracket relation in crystal momentum space becomes

$$\left\{u_i^\alpha(\boldsymbol{R}),\, p_j^\beta(\boldsymbol{R}')\right\}_{\text{PB}} = \delta_{\boldsymbol{R}\boldsymbol{R}'}\, \delta_{ij}\, \delta_{\alpha\beta} \quad\Rightarrow\quad \left\{\hat{u}_i^\alpha(\boldsymbol{k}),\, \hat{p}_j^\beta(\boldsymbol{k}')\right\}_{\text{PB}} = \delta_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{0}}^{\text{P}}\, \delta_{ij}\, \delta_{\alpha\beta} \quad, \tag{3.40}$$

where $\delta_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{0}}^{\text{P}} = \sum_{\boldsymbol{G}} \delta_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{G}}$ requires $\boldsymbol{k}+\boldsymbol{k}' = \boldsymbol{0}$ modulo any reciprocal lattice vector. Note also that

$$\Phi_{ij}^{\alpha\beta}(\boldsymbol{R}) = \Phi_{ji}^{\beta\alpha}(-\boldsymbol{R}) \quad\Rightarrow\quad \hat{\Phi}_{ji}^{\beta\alpha}(\boldsymbol{k}) = \hat{\Phi}_{ij}^{\alpha\beta}(-\boldsymbol{k}) = \left[\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})\right]^* \quad. \tag{3.41}$$

Thus, for each crystal momentum $\boldsymbol{k}$, the dynamical matrix $\hat{\Phi}_{ji}^{\beta\alpha}(\boldsymbol{k})$ is Hermitian, where we take $(i\alpha)$ and $(j\beta)$ as composite indices. We now have the eigensystem

$$\sum_{\beta,j} \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})\, \hat{e}_{j\lambda}^\beta(\boldsymbol{k}) = m_i\, \omega_\lambda^2(\boldsymbol{k})\, \hat{e}_{i\lambda}^\alpha(\boldsymbol{k}) \tag{3.42}$$

where $\lambda \in \{1,\ldots,rd\}$ indexes the normal modes, and $S_{i\alpha,\lambda}(\boldsymbol{k}) \equiv \hat{e}_{i\lambda}^\alpha(\boldsymbol{k}) \equiv m_i^{-1/2} U_{i\alpha,\lambda}(\boldsymbol{k})$ diagonalizes the dynamical matrix, with $U_{i\alpha,\lambda}(\boldsymbol{k})$ unitary. We may now write the completeness relation,

$$\sum_{\lambda=1}^{dr} \hat{e}_{i\lambda}^{\alpha*}(\boldsymbol{k})\, \hat{e}_{j\lambda}^\beta(\boldsymbol{k}) = \frac{1}{m_i}\, \delta_{ij}\, \delta_{\alpha\beta} \tag{3.43}$$
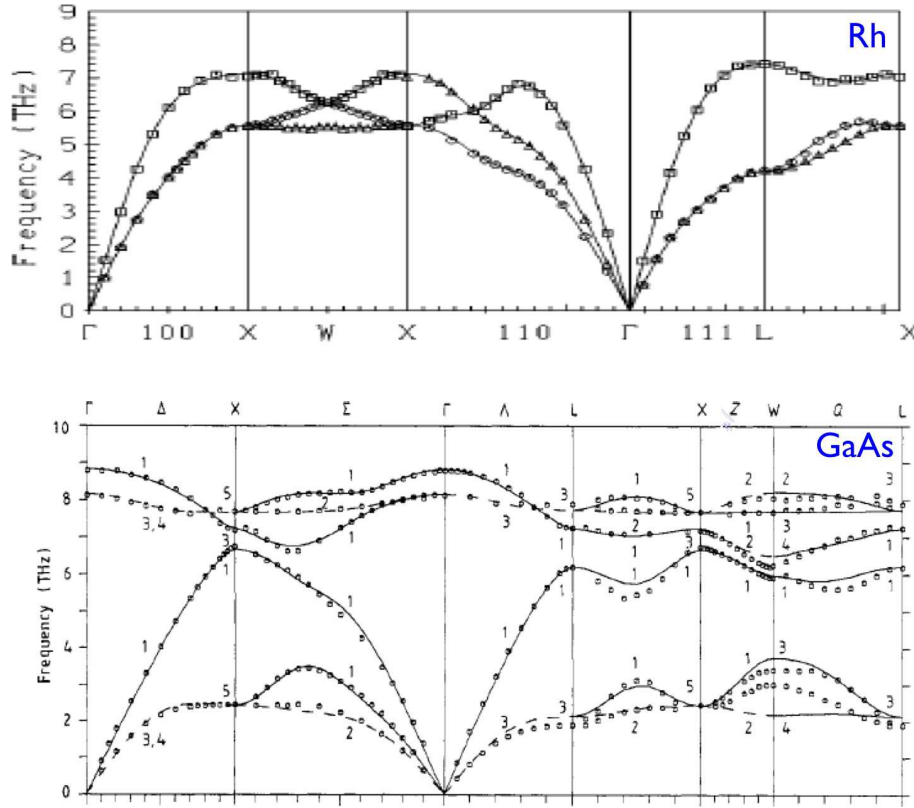
Figure 3.2: Upper panel: phonon spectrum in fcc elemental rhodium (Rh) at $T = 297\,\text{K}$ measured by high precision inelastic neutron scattering (INS) by A. Eichler *et al.*, *Phys. Rev. B* **57**, 324 (1998). Note the three acoustic branches and no optical branches, corresponding to $d = 3$ and $r = 1$. Lower panel: phonon spectrum in gallium arsenide (GaAs) at $T = 12\,\text{K}$, comparing theoretical lattice-dynamical calculations with INS results of D. Strauch and B. Dorner, *J. Phys.: Condens. Matter* **2**, 1457 (1990). Note the three acoustic branches and three optical branches, corresponding to $d = 3$ and $r = 2$. The Greek letters along the x-axis indicate points of high symmetry in the Brillouin zone.

and the orthogonality relation,

$$\sum_{i=1}^{r}\sum_{\alpha=1}^{d} m_i\, \hat{\text{e}}_{i\lambda}^{\alpha*}(\boldsymbol{k})\, \hat{\text{e}}_{i\lambda'}^{\alpha}(\boldsymbol{k}) = \delta_{\lambda\lambda'} \quad , \tag{3.44}$$

which are the completeness and orthogonality relations, respectively. Since $\hat{\text{e}}_{i\lambda}^{\alpha*}(-\boldsymbol{k})$ and $\hat{\text{e}}_{i\lambda}^{\alpha}(\boldsymbol{k})$ obey the same equation, we have that $\omega_\lambda(-\boldsymbol{k}) = \omega_\lambda(\boldsymbol{k})$. If the phonon eigenmode $|\,\boldsymbol{k}, \lambda\,\rangle$ is nondegenerate, we may choose $\hat{\text{e}}_{i\lambda}^{\alpha}(-\boldsymbol{k}) = \hat{\text{e}}_{i\lambda}^{\alpha*}(\boldsymbol{k})$. Else at best we can conclude $\hat{\text{e}}_{i\lambda}^{\alpha}(-\boldsymbol{k}) = \hat{\text{e}}_{i\lambda'}^{\alpha*}(\boldsymbol{k})\, e^{i\eta}$ where $|\,\boldsymbol{k}, \lambda'\,\rangle$ is another state from the degenerate manifold of phonon states at this wavevector, and $e^{i\eta}$ is a phase.

Expressing $\hat{u}_i^\alpha(\boldsymbol{k})$ and $\hat{p}_i^\alpha(\boldsymbol{k})$ in terms of the normal modes, we write

$$\hat{u}_i^\alpha(\boldsymbol{k}) = \sum_{\lambda=1}^{dr} \hat{e}_{i\lambda}^\alpha(\boldsymbol{k}) \, \hat{q}_\lambda(\boldsymbol{k}) \qquad , \qquad \hat{p}_i^\alpha(\boldsymbol{k}) = m_i \sum_{\lambda=1}^{dr} \hat{e}_{i\lambda}^{\alpha*}(-\boldsymbol{k}) \, \hat{\pi}_\lambda(\boldsymbol{k}) \tag{3.45}$$

where $\left\{ \hat{q}_\lambda(\boldsymbol{k}), \hat{\pi}_{\lambda'}(\boldsymbol{k}) \right\}_{\text{PB}} = \delta_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{0}} \, \delta_{\lambda\lambda'}$. This entails

$$\hat{q}_\lambda(\boldsymbol{k}) = \sum_{i=1}^{r} \sum_{\alpha=1}^{d} m_i \, \hat{e}_{i\lambda}^{\alpha*}(\boldsymbol{k}) \, \hat{u}_i^\alpha(\boldsymbol{k}) \qquad , \qquad \hat{\pi}_\lambda(\boldsymbol{k}) = \sum_{i=1}^{r} \sum_{\alpha=1}^{d} \hat{e}_{i\lambda}^\alpha(-\boldsymbol{k}) \, \hat{p}_i^\alpha(\boldsymbol{k}) \quad . \tag{3.46}$$

The phonon Hamiltonian now takes the diagonalized form

$$H = \sum_{\boldsymbol{k}} \sum_{\lambda=1}^{rd} \left\{ \tfrac{1}{2} \, \hat{\pi}_\lambda(-\boldsymbol{k}) \, \hat{\pi}_\lambda(\boldsymbol{k}) + \tfrac{1}{2} \, \omega_\lambda^2(\boldsymbol{k}) \, \hat{q}_\lambda(-\boldsymbol{k}) \, \hat{q}_\lambda(\boldsymbol{k}) \right\} \quad , \tag{3.47}$$

with $\left\{ \hat{q}_\lambda(\boldsymbol{k}) , \hat{\pi}_{\lambda'}(\boldsymbol{k}') \right\}_{\text{PB}} = \delta_{\lambda\lambda'} \, \delta_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{0}}^{\text{P}}$. To quantize, promote the Poisson brackets to commutators: $\left\{ A, B \right\}_{\text{PB}} \to -i\hbar^{-1} \left[A, B \right]$. Then define the ladder operators,

$$A_\lambda(\boldsymbol{k}) = \left(\frac{\omega_\lambda(\boldsymbol{k})}{2\hbar} \right)^{1/2} \hat{q}_\lambda(\boldsymbol{k}) + i \left(\frac{1}{2\hbar\omega_\lambda(\boldsymbol{k})} \right)^{1/2} \hat{\pi}_\lambda(\boldsymbol{k}) \quad , \tag{3.48}$$

which satisfy $\left[A_\lambda(\boldsymbol{k}) , A_{\lambda'}^\dagger(\boldsymbol{k}') \right] = \delta_{\boldsymbol{k}\boldsymbol{k}'}^{\text{P}} \, \delta_{\lambda\lambda'}$. The quantum phonon Hamiltonian is then

$$\hat{H} = \sum_{\boldsymbol{k}} \sum_{\lambda=1}^{rd} \hbar\omega_\lambda(\boldsymbol{k}) \left(A_\lambda^\dagger(\boldsymbol{k}) \, A_\lambda(\boldsymbol{k}) + \tfrac{1}{2} \right) \quad . \tag{3.49}$$

Of the dr phonon branches, d are *acoustic*, and behave as $\omega_a(\boldsymbol{k}) = c(\hat{\boldsymbol{k}}) \, k$ as $\boldsymbol{k} \to 0$, which is the Γ point in the Brillouin zone. These gapless phonons are the Goldstone bosons of the spontaneously broken translational symmetry which gave rise to the crystalline phase. To each broken generator of translation, there corresponds a Goldstone mode. The remaining $d(r-1)$ modes are called *optical phonons*. Whereas for acoustic modes, all the ions in a given unit cell are moving in phase, for optical modes they are moving out of phase. Hence optical modes are always finite frequency modes. Fig. 3.2 shows the phonon spectra in elemental rhodium (space group $Fm\overline{3}m$, point group O_h), and in gallium arsenide (space group $F\overline{4}3m$, point group T_d). Since Rh forms an fcc Bravais lattice, there are no optical phonon modes. GaAs forms a zincblende structure, *i.e.* two interpenetrating fcc lattices, one for the gallium, the other for the arsenic. Thus $r = 2$ and we expect three acoustic and three optical branches of phonons.

Nota bene : One may choose to define the Fourier transforms above taking the additional phases for the basis elements to all be unity, *viz.*

$$u_i^\alpha(\boldsymbol{R}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \hat{u}_i^\alpha(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \quad , \quad p_i^\alpha(\boldsymbol{R}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \hat{p}_i^\alpha(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \quad , \quad \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} \Phi_{ij}^{\alpha\beta}(\boldsymbol{R}) \, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \quad . \tag{3.50}$$

All the equations starting with Eqn. 3.39 remain the same. Setting the basis phases to unity amounts to a choice of *gauge*. It is somewhat simpler in certain contexts, but it may obscure essential space group symmetries. On the other hand, it should also be noted that the Fourier transforms $\hat{u}_i^\alpha(\boldsymbol{k})$, $\hat{p}_i^\alpha(\boldsymbol{k})$, and $\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})$ are not periodic in the Brillouin zone, but instead satisfy generalized periodic boundary conditions,

$$
\begin{aligned}
\hat{u}_i^\alpha(\boldsymbol{K}+\boldsymbol{k}) &= e^{-i\boldsymbol{K}\cdot\boldsymbol{\delta}_i}\,\hat{u}_i^\alpha(\boldsymbol{k}) \\
\hat{p}_i^\alpha(\boldsymbol{K}+\boldsymbol{k}) &= e^{-i\boldsymbol{K}\cdot\boldsymbol{\delta}_i}\,\hat{p}_i^\alpha(\boldsymbol{k}) \\
\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{K}+\boldsymbol{k}) &= e^{-i\boldsymbol{K}\cdot(\boldsymbol{\delta}_i-\boldsymbol{\delta}_j)}\,\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k}) \quad,
\end{aligned}
\tag{3.51}
$$

where $\boldsymbol{K} \in \hat{\mathcal{L}}$ is any reciprocal lattice vector.

3.2.3   Translation and rotation invariance

The potential energy $U\big(\{u_i^\alpha(\boldsymbol{R})\}\big)$ must remain invariant under the operations

$$
\begin{aligned}
u_i^\alpha(\boldsymbol{R}) &\to u_i^\alpha(\boldsymbol{R}) + d^\alpha \\
u_i^\alpha(\boldsymbol{R}) &\to u_i^\alpha(\boldsymbol{R}) + \epsilon_{\alpha\mu\nu}\left(R^\mu + \delta_i^\mu - \delta_j^\mu\right) d^\nu
\end{aligned}
\tag{3.52}
$$

for an infinitesimal vector $\boldsymbol{d}$. The first equation represents a uniform translation of all lattice sites by $\boldsymbol{d}$. The second represents an infinitesimal rotation about the jth basis ion in the $\boldsymbol{R} = 0$ unit cell. We are free to choose any j.

Writing $U(u + \Delta u) = U(u)$, we must have that the linear terms in Δu vanish, hence

$$
\sum_{\boldsymbol{R},i} \Phi_{ij}^{\alpha\beta}(\boldsymbol{R}) = \sum_i \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{0}) = 0
$$

$$
\epsilon_{\alpha\mu\nu}\sum_{\boldsymbol{R},i}(R^\mu + \delta_i^\mu - \delta_j^\mu)\,\Phi_{ij}^{\nu\beta}(\boldsymbol{R}) = i\,\epsilon_{\alpha\mu\nu}\sum_i \frac{\partial\hat{\Phi}_{ij}^{\nu\beta}(\boldsymbol{k})}{\partial k^\mu}\bigg|_{\boldsymbol{k}=0} = 0 \quad.
\tag{3.53}
$$

Note that (α, β, j) are free indices in both equations. The first of these equations says that any vector d^β is an eigenvector of the dynamical matrix at $\boldsymbol{k} = 0$, with zero eigenvalue. Thus, at $\boldsymbol{k} = 0$, there is a three-dimensional space of zero energy modes. These are the Goldstone modes associated with the three broken generators of translation in the crystal.

3.2.4   Phonons in an fcc lattice

When the crystal is a Bravais lattice, there are no basis indices, and the dynamical matrix becomes

$$
\hat{\Phi}^{\alpha\beta}(\boldsymbol{k}) = {\sum_{\boldsymbol{R}}}'(1 - \cos\boldsymbol{k}\cdot\boldsymbol{R})\,\frac{\partial^2 v(\boldsymbol{R})}{\partial R^\alpha\,\partial R^\beta} \quad,
\tag{3.54}
$$

where $v(r)$ is the inter-ionic potential, and the prime on the sum indicates that $\boldsymbol{R} = 0$ is to be excluded. For central potentials $v(\boldsymbol{R}) = v(R)$,

$$\frac{\partial^2 v(\boldsymbol{R})}{\partial R^\alpha \, \partial R^\beta} = \left(\delta^{\alpha\beta} - \hat{R}^\alpha \, \hat{R}^\beta\right) \frac{v'(R)}{R} + \hat{R}^\alpha \, \hat{R}^\beta \, v''(R) \quad . \tag{3.55}$$

For simplicity, we assume $v(R)$ is negligible beyond the first neighbor. On the fcc lattice, there are twelve first neighbors, lying at $\boldsymbol{\Delta} = \frac{1}{2}a\,(\pm\hat{y} \pm \hat{z})$, $\boldsymbol{\Delta} = \frac{1}{2}a\,(\pm\hat{x} \pm \hat{z})$, and $\boldsymbol{\Delta} = \frac{1}{2}a\,(\pm\hat{x} \pm \hat{y})$. Here a is the side length of the underlying simple cubic lattice, so the fcc lattice constant is $a/\sqrt{2}$. We define

$$A = \frac{\sqrt{2}}{a} \, v'\left(a/\sqrt{2}\right) \quad , \quad B = v''\left(a/\sqrt{2}\right) \quad . \tag{3.56}$$

Along (100), we have $\boldsymbol{k} = k\hat{x}$ and

$$\hat{\Phi}^{\alpha\beta}(\boldsymbol{k}) = 4\sin^2(\tfrac{1}{4}ka) \begin{pmatrix} 2A + 2B & 0 & 0 \\ 0 & 3A + B & 0 \\ 0 & 0 & 3A + B \end{pmatrix} \quad , \tag{3.57}$$

which is already diagonal. Thus, the eigenvectors lie along the cubic axes and

$$\omega_{\mathrm{L}} = 2\sqrt{\tfrac{2(A+B)}{m}} \, \big|\sin(ka/4)\big| \quad , \quad \omega_{\mathrm{T1}} = \omega_{\mathrm{T2}} = 2\sqrt{\tfrac{3A+B}{m}} \, \big|\sin(ka/4)\big| \quad . \tag{3.58}$$

Along (111), we have $\boldsymbol{k} = \frac{1}{\sqrt{3}} k \, (\hat{x} + \hat{y} + \hat{z})$. One finds

$$\hat{\Phi}^{\alpha\beta}(\boldsymbol{k}) = 4\sin^2\left(ka/\sqrt{12}\right) \begin{pmatrix} 4A + 2B & B - A & B - A \\ B - A & 4A + 2B & B - A \\ B - A & B - A & 4A + 2B \end{pmatrix} \quad . \tag{3.59}$$

$$\omega_{\mathrm{L}} = 2\sqrt{\tfrac{A+2B}{m}} \, \big|\sin\left(ka/\sqrt{12}\right)\big| \quad , \quad \omega_{\mathrm{T1}} = \omega_{\mathrm{T2}} = 2\sqrt{\tfrac{5A+B}{2m}} \, \big|\sin\left(ka/\sqrt{12}\right)\big| \quad . \tag{3.60}$$

3.2.5 Phonons in the hcp structure

The HCP structure is represented as an underlying simple hexagonal lattice with a two-element basis:

$$\boldsymbol{a}_1 = a\,\hat{x} \quad , \quad \boldsymbol{a}_2 = \tfrac{1}{2}a\,\hat{x} + \tfrac{\sqrt{3}}{2}a\,\hat{y} \quad , \quad \boldsymbol{a}_3 = \sqrt{\tfrac{8}{3}}\,a\,\hat{z} \, . \tag{3.61}$$

Bravais lattice sites are of the form $\boldsymbol{R} = l\boldsymbol{a}_1 + m\boldsymbol{a}_2 + n\boldsymbol{a}_3$. The A sublattice occupies the sites $\{\boldsymbol{R}\}$, while the B sublattice occupies the sites $\{\boldsymbol{R} + \boldsymbol{\delta}\}$, where

$$\boldsymbol{\delta} = \tfrac{1}{2}a\,\hat{x} + \tfrac{1}{2\sqrt{3}}\,a\,\hat{y} + \sqrt{\tfrac{2}{3}}\,a\,\hat{z} \, . \tag{3.62}$$

The nearest neighbor separation is $|\boldsymbol{a}_1| = |\boldsymbol{a}_2| = |\boldsymbol{\delta}| = a$. Note that $\boldsymbol{R}$ can be used to label the unit cells, *i.e.* each unit cell is labeled by the coordinates of its constituent A sublattice site.

Classical energy

The classical energy for the system is the potential energy of the fixed lattice, given by

$$\frac{U_0}{N} = \sum_{\boldsymbol{R}} \left[v(\boldsymbol{R}) \left(1 - \delta_{\boldsymbol{R},0} \right) + v(\boldsymbol{R} + \boldsymbol{\delta}) \right] , \tag{3.63}$$

where $v(\boldsymbol{r})$ is the interatomic potential.

Dynamical matrix

When phonon fluctuations are included, the positions of the A and B sublattice sites are written

$$\begin{aligned}
\boldsymbol{R} &\longrightarrow \boldsymbol{R} + \boldsymbol{u}_{\mathsf{A}}(\boldsymbol{R}) \\
\boldsymbol{R} + \boldsymbol{\delta} &\longrightarrow \boldsymbol{R} + \boldsymbol{\delta} + \boldsymbol{u}_{\mathsf{B}}(\boldsymbol{R}) .
\end{aligned} \tag{3.64}$$

Then the potential energy is

$$\begin{aligned}
U = U_0 &+ \sum_{\boldsymbol{R}} \left(\boldsymbol{u}_{\mathsf{A}}(\boldsymbol{R}) \cdot \boldsymbol{F}_{\mathsf{A}}(\boldsymbol{R}) + \boldsymbol{u}_{\mathsf{B}}(\boldsymbol{R}) \cdot \boldsymbol{F}_{\mathsf{B}}(\boldsymbol{R}) \right) \\
&+ \tfrac{1}{2} \sum_{\boldsymbol{R},\boldsymbol{R}'} \sum_{j,j'} \sum_{\alpha,\alpha'} \Phi_{jj'}^{\alpha\alpha'}(\boldsymbol{R} - \boldsymbol{R}') \, u_j^{\alpha}(\boldsymbol{R}) \, u_{j'}^{\alpha'}(\boldsymbol{R}') + \mathcal{O}(u^3) ,
\end{aligned} \tag{3.65}$$

where

$$\Phi_{jj'}^{\alpha\alpha'}(\boldsymbol{R} - \boldsymbol{R}') = \frac{\partial^2 U}{\partial u_j^{\alpha}(\boldsymbol{R}) \, \partial u_{j'}^{\alpha'}(\boldsymbol{R}')} . \tag{3.66}$$

Here $\{\alpha, \alpha'\}$ are spatial indices (x, y, z), and $\{j, j'\}$ are sublattice indices (A, B).

It is convenient to Fourier transform, with

$$\begin{aligned}
u_{\mathsf{A}}^{\alpha}(\boldsymbol{R}) &= \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \hat{u}_{\mathsf{A}}^{\alpha}(\boldsymbol{k}) \, e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \\
u_{\mathsf{B}}^{\alpha}(\boldsymbol{R}) &= \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \hat{u}_{\mathsf{B}}^{\alpha}(\boldsymbol{k}) \, e^{i\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{\delta})} ,
\end{aligned} \tag{3.67}$$

where N is the total number of unit cells. Then

$$U = U_0 + \sum_{\boldsymbol{k}} \sum_{j} \hat{\boldsymbol{u}}_j(\boldsymbol{k}) \cdot \hat{\boldsymbol{F}}_j(-\boldsymbol{k}) + \tfrac{1}{2} \sum_{\boldsymbol{k}} \sum_{j,j'} \sum_{\alpha,\alpha'} \hat{\Phi}_{jj'}^{\alpha\alpha'}(\boldsymbol{k}) \, \hat{u}_j^{\alpha}(\boldsymbol{k}) \, \hat{u}_{j'}^{\alpha'}(-\boldsymbol{k}) + \mathcal{O}(u^3) , \tag{3.68}$$

where the dynamical matrix is

$$\hat{\Phi}_{jj'}^{\alpha\alpha'}(\boldsymbol{k}) = \begin{pmatrix} \hat{\Phi}_{11}^{\alpha\alpha'}(\boldsymbol{k}) & \hat{\Phi}_{12}^{\alpha\alpha'}(\boldsymbol{k}) \\ \hat{\Phi}_{21}^{\alpha\alpha'}(\boldsymbol{k}) & \hat{\Phi}_{22}^{\alpha\alpha'}(\boldsymbol{k}) \end{pmatrix} . \tag{3.69}$$
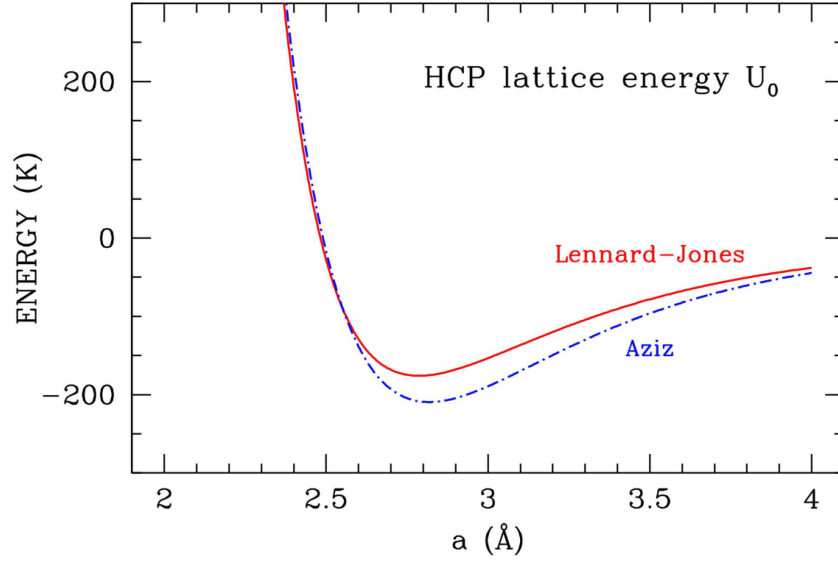
Figure 3.3: Classical lattice energy for hcp ^{4}He as a function of nearest neighbor separation a for the Lennard-Jones potential (red) and the Aziz potential (blue).

where

$$
\hat{\Phi}_{11}^{\alpha\beta}(\boldsymbol{k}) = {\sum_{\boldsymbol{R}}}'(1 - \cos\boldsymbol{k}\cdot\boldsymbol{R}) \frac{\partial^2 v(\boldsymbol{R})}{\partial R^\alpha\,\partial R^\beta} + \sum_{\boldsymbol{R}} \partial_\alpha\partial_\beta\, v(\boldsymbol{R}+\boldsymbol{\delta})
$$

$$
\hat{\Phi}_{12}^{\alpha\beta}(\boldsymbol{k}) = -\sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{\delta})} \frac{\partial^2 v(\boldsymbol{R}+\boldsymbol{\delta})}{\partial R^\alpha\,\partial R^\beta}
$$

(3.70)

Note that $\hat{\Phi}_{21}^{\alpha\beta}(\boldsymbol{k}) = \left[\hat{\Phi}_{12}^{\alpha\beta}(\boldsymbol{k})\right]^*$. Note also that if $v(\boldsymbol{R}) = v(R)$ is a central potential, then

$$
\frac{\partial^2 v(R)}{\partial R^\alpha\,\partial R^\beta} = \left(\delta^{\alpha\beta} - \hat{R}^\alpha\hat{R}^\beta\right)\frac{v'(R)}{R} + \hat{R}^\alpha\hat{R}^\beta\,v''(R)\,,
$$

(3.71)

where $\hat{R}^\alpha = R^\alpha/|\boldsymbol{R}|$.

Lennard-Jones potential

The Lennard-Jones potential is given by

$$
v(r) = 4\varepsilon_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]
$$

(3.72)

where

$$
\varepsilon_0 = 10.22\,\mathrm{K} \qquad , \qquad \sigma = 2.556\,\text{Å}\,.
$$

(3.73)
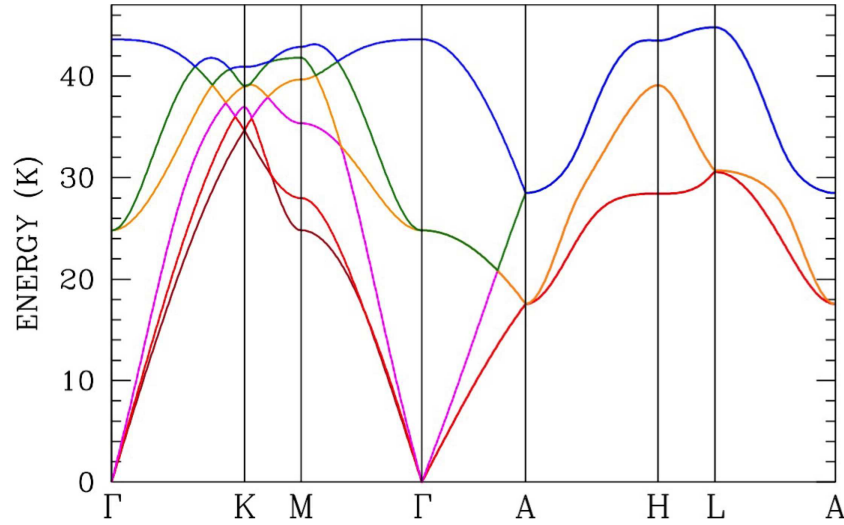
Figure 3.4: Phonon dispersions along high-symmetry directions in the Brillouin zone for hcp ^{4}He at molar volume $v_0 = 12\,\mathrm{cm}^3/\mathrm{mol}$, using the Lennard-Jones potential.

Aziz potential

The Aziz potential is given by

$$v(r) = \varepsilon_0 \left\{ A\,e^{-\alpha r/b} - \left[C_6 \left(\frac{b}{r} \right)^6 + C_8 \left(\frac{b}{r} \right)^8 + C_{10} \left(\frac{b}{r} \right)^{10} \right] F(r) \right\} , \qquad (3.74)$$

where

$$F(r) = \begin{cases} e^{-\left(\frac{Db}{r} - 1 \right)^2} & \text{if } r \leq Db \\ 1 & \text{if } r > Db \, , \end{cases} \qquad (3.75)$$

with

$$\varepsilon = 10.8\,\mathrm{K} \quad , \quad b = 2.9763\,\mathrm{\AA} \quad , \quad A = 5.448504 \times 10^5 \quad , \quad \alpha = 13.353384 \qquad (3.76)$$

and

$$C_6 = 1.37732412 \quad , \quad C_8 = 0.4253785 \quad , \quad C_{10} = 0.171800 \quad , \quad D = 1.231314 \, . \qquad (3.77)$$

The mass of the helium-4 atom is $m = 6.65 \times 10^{-24}\,\mathrm{g}$.

3.2.6 Phonon density of states

For a crystalline lattice with an r-element basis, there are then $d \cdot r$ phonon modes for each wavevector $\boldsymbol{k}$ lying in the first Brillouin zone. If we impose periodic boundary conditions, then the $\boldsymbol{k}$ points within the first Brillouin zone are themselves quantized, as in the $d = 1$ case where

we found $k = 2\pi n/N$. There are N distinct $\boldsymbol{k}$ points in the first Brillouin zone – one for every direct lattice site. The total number of modes is than $d \cdot r \cdot N$, which is the total number of translational degrees of freedom in our system: rN total atoms (N unit cells each with an r atom basis) each free to vibrate in d dimensions. Of the $d \cdot r$ branches of phonon excitations, d of them will be *acoustic modes* whose frequency vanishes as $\boldsymbol{k} \to 0$. The remaining $d(r-1)$ branches are *optical modes* and oscillate at finite frequencies. Basically, in an acoustic mode, for $\boldsymbol{k}$ close to the (Brillouin) zone center $\boldsymbol{k} = 0$, all the atoms in each unit cell move together in the same direction at any moment of time. In an optical mode, the different basis atoms move in different directions.

There is no number conservation law for phonons – they may be freely created or destroyed in anharmonic processes, where two photons with wavevectors $\boldsymbol{k}$ and $\boldsymbol{q}$ can combine into a single phonon with wavevector $\boldsymbol{k} + \boldsymbol{q}$, and *vice versa*. Therefore the chemical potential for phonons is $\mu = 0$. We define the density of states $g_s(\omega)$ for the sth phonon mode as

$$g_s(\omega) = \frac{1}{N} \sum_{\boldsymbol{k}} \delta(\omega - \omega_s(\boldsymbol{k})) = \Omega \int_{\hat{\Omega}} \frac{d^d k}{(2\pi)^d} \delta(\omega - \omega_s(\boldsymbol{k})) \, , \tag{3.78}$$

where N is the number of unit cells, Ω is the unit cell volume of the direct lattice, and the $\boldsymbol{k}$ sum and integral are over the first Brillouin zone only. Note that ω here has dimensions of frequency. The functions $g_a(\omega)$ is normalized to unity:

$$\int_0^{\infty} d\omega \, g_s(\omega) = 1 \, . \tag{3.79}$$

The total phonon density of states per unit cell is given by[5] $g(\omega) = \sum_{s=1}^{dr} g_s(\omega)$.

The grand potential for the phonon gas is

$$\Omega(T, V) = -k_{\mathrm{B}} T \ln \prod_{\boldsymbol{k}, s} \sum_{n_a(\boldsymbol{k})=0}^{\infty} e^{-\beta \hbar \omega_s(\boldsymbol{k}) \left(n_s(\boldsymbol{k}) + \frac{1}{2}\right)}$$

$$= k_{\mathrm{B}} T \sum_{\boldsymbol{k}, s} \ln \left[2 \sinh \left(\frac{\hbar \omega_s(\boldsymbol{k})}{2 k_{\mathrm{B}} T}\right)\right] = N k_{\mathrm{B}} T \int_0^{\infty} d\omega \, g(\omega) \ln \left[2 \sinh \left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right)\right] \, . \tag{3.80}$$

Note that $V = N \mathcal{V}_0$ since there are N unit cells, each of volume $\mathcal{V}_0$. The entropy is given by $S = -\left(\frac{\partial \Omega}{\partial T}\right)_V$ and thus the heat capacity is

$$C_V = -T \frac{\partial^2 \Omega}{\partial T^2} = N k_{\mathrm{B}} \int_0^{\infty} d\omega \, g(\omega) \left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right)^2 \operatorname{csch}^2 \left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right) \tag{3.81}$$

---

[5]Note the dimensions of $g(\omega)$ are $(\text{frequency})^{-1}$. By contrast, the dimensions of $g(\varepsilon)$ are $(\text{energy})^{-1} \cdot (\text{volume})^{-1}$. The difference lies in the a factor of $\mathcal{V}_0 \cdot \hbar$, where $\mathcal{V}_0$ is the unit cell volume.
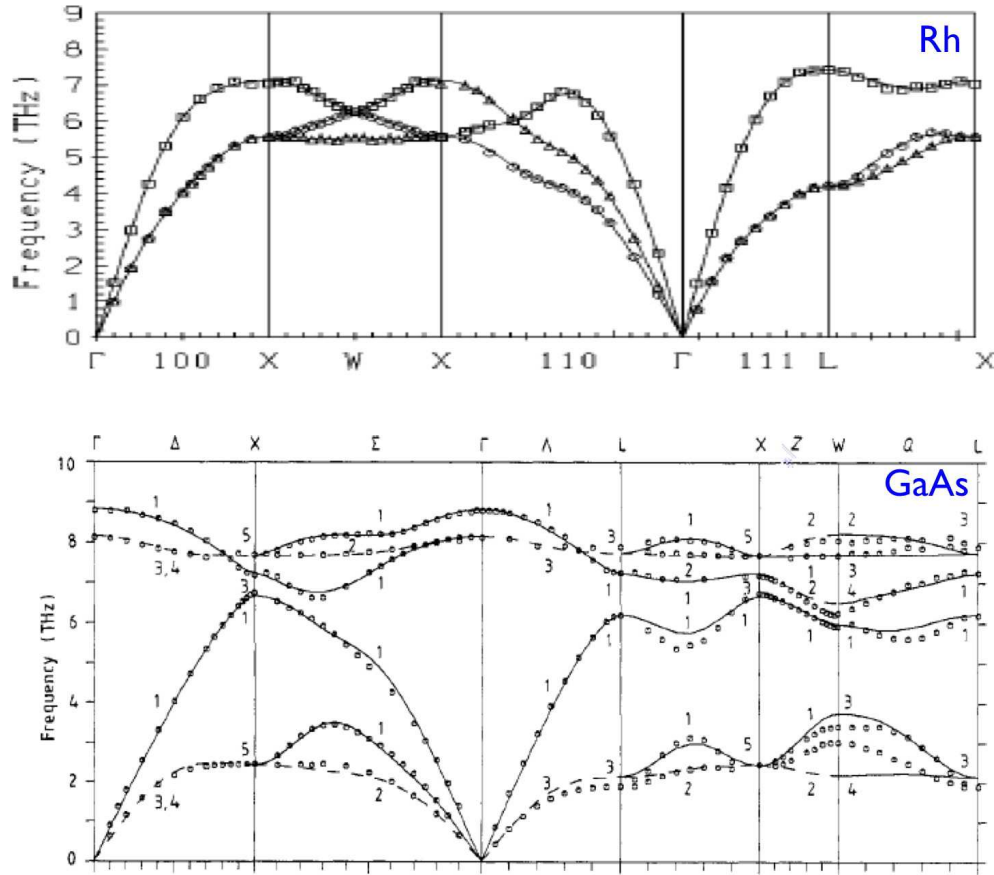
Figure 3.5: Upper panel: phonon spectrum in elemental rhodium (Rh) at $T = 297\,\mathrm{K}$ measured by high precision inelastic neutron scattering (INS) by A. Eichler *et al.*, *Phys. Rev. B* **57**, 324 (1998). Note the three acoustic branches and no optical branches, corresponding to $d = 3$ and $r = 1$. Lower panel: phonon spectrum in gallium arsenide (GaAs) at $T = 12\,\mathrm{K}$, comparing theoretical lattice-dynamical calculations with INS results of D. Strauch and B. Dorner, *J. Phys.: Condens. Matter* **2**, 1457 (1990). Note the three acoustic branches and three optical branches, corresponding to $d = 3$ and $r = 2$. The Greek letters along the x-axis indicate points of high symmetry in the Brillouin zone.

Note that as $T \to \infty$ we have $\mathrm{csch}\!\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right) \to \frac{2k_{\mathrm{B}}T}{\hbar\omega}$, and therefore

$$\lim_{T \to \infty} C_V(T) = N k_{\mathrm{B}} \int\limits_{0}^{\infty} d\omega\, g(\omega) = r d N k_{\mathrm{B}}\,. \tag{3.82}$$

This is the classical Dulong-Petit limit of $\frac{1}{2}k_{\mathrm{B}}$ per quadratic degree of freedom; there are rN atoms moving in d dimensions, hence $d \cdot rN$ positions and an equal number of momenta, resulting in a high temperature limit of $C_V = r d N k_{\mathrm{B}}$.

3.2.7 Einstein and Debye models

HIstorically, two models of lattice vibrations have received wide attention. First is the so-called *Einstein model*, in which there is no dispersion to the individual phonon modes. We approximate $g_a(\omega) \approx \delta(\omega - \omega_a)$, in which case

$$C_V(T) = N k_{\mathrm{B}} \sum_s \left(\frac{\hbar \omega_s}{2 k_{\mathrm{B}} T} \right)^2 \mathrm{csch}^2 \left(\frac{\hbar \omega_s}{2 k_{\mathrm{B}} T} \right) . \tag{3.83}$$

At low temperatures, the contribution from each branch vanishes exponentially, because $\mathrm{csch}^2 \left(\frac{\hbar \omega_s}{2 k_{\mathrm{B}} T} \right) \simeq 4 \, e^{-\hbar \omega_s / k_{\mathrm{B}} T} \to 0$. Real solids don't behave this way.

A more realistic model. due to Debye, accounts for the low-lying acoustic phonon branches. Since the acoustic phonon dispersion vanishes linearly with $|k|$ as $k \to 0$, there is no temperature at which the acoustic phonons 'freeze out' exponentially, as in the case of Einstein phonons. Indeed, the Einstein model is appropriate in describing the $d(r-1)$ optical phonon branches, though it fails miserably for the acoustic branches.

In the vicinity of the zone center $k = 0$ (also called Γ in crystallographic notation) the d acoustic modes obey a linear dispersion, with $\omega_s(k) = c_s(\hat{k}) \, k$. This results in an acoustic phonon density of states in $d = 3$ dimensions of

$$\begin{aligned}
\tilde{g}(\omega) &= \frac{\mathcal{V}_0 \, \omega^2}{2 \pi^2} \sum_s \int \frac{d\hat{k}}{4 \pi} \frac{1}{c_s^3(k)} \, \Theta(\omega_{\mathrm{D}} - \omega) \\
&= \frac{3 \mathcal{V}_0}{2 \pi^2 \bar{c}^3} \, \omega^2 \, \Theta(\omega_{\mathrm{D}} - \omega) ,
\end{aligned} \tag{3.84}$$

where $\bar{c}$ is an average acoustic phonon velocity (*i.e.* speed of sound) defined by

$$\frac{3}{\bar{c}^3} = \sum_s \int \frac{d\hat{k}}{4 \pi} \frac{1}{c_s^3(k)} \tag{3.85}$$

and ω_{D} is a cutoff known as the *Debye frequency*. The cutoff is necessary because the phonon branch does not extend forever, but only to the boundaries of the Brillouin zone. Thus, ω_{D} should roughly be equal to the energy of a zone boundary phonon. Alternatively, we can define ω_{D} by the normalization condition

$$\int_0^\infty d\omega \, \tilde{g}(\omega) = 3 \quad \Longrightarrow \quad \omega_{\mathrm{D}} = (6 \pi^2 / \mathcal{V}_0)^{1/3} \, \bar{c} . \tag{3.86}$$

This allows us to write $\tilde{g}(\omega) = \left(9 \omega^2 / \omega_{\mathrm{D}}^3 \right) \Theta(\omega_{\mathrm{D}} - \omega)$.

The specific heat due to the acoustic phonons is then

$$C_V(T) = \frac{9Nk_{\mathrm{B}}}{\omega_{\mathrm{D}}^3} \int\limits_0^{\omega_{\mathrm{D}}} d\omega\, \omega^2 \left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)^2 \mathrm{csch}^2\!\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)$$

$$= 9Nk_{\mathrm{B}} \left(\frac{2T}{\Theta_{\mathrm{D}}}\right)^3 \phi\big(\Theta_{\mathrm{D}}/2T\big)\ , \tag{3.87}$$

where $\Theta_{\mathrm{D}} = \hbar\omega_{\mathrm{D}}/k_{\mathrm{B}}$ is the *Debye temperature* and

$$\phi(x) = \int\limits_0^x dt\, t^4\, \mathrm{csch}^2 t = \begin{cases} \frac{1}{3}x^3 & x \to 0 \\[2mm] \frac{\pi^4}{30} & x \to \infty\ . \end{cases} \tag{3.88}$$

Therefore,

$$C_V(T) = \begin{cases} \frac{12\pi^4}{5}\, Nk_{\mathrm{B}} \left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3 & T \ll \Theta_{\mathrm{D}} \\[4mm] 3Nk_{\mathrm{B}} & T \gg \Theta_{\mathrm{D}}\ . \end{cases} \tag{3.89}$$

Thus, the heat capacity due to acoustic phonons obeys the Dulong-Petit rule in that $C_V(T \to \infty) = 3Nk_{\mathrm{B}}$, corresponding to the three acoustic degrees of freedom per unit cell. The remaining contribution of $3(r-1)Nk_{\mathrm{B}}$ to the high temperature heat capacity comes from the optical modes not considered in the Debye model. The low temperature T^3 behavior of the heat capacity of crystalline solids is a generic feature, and its detailed description is a triumph of the Debye model.

3.2.8   Phenomenological theory of melting

Atomic fluctuations in a crystal

For the one-dimensional chain, eqn. 3.33 gives

$$\tilde{u}_k = i \left(\frac{\hbar}{2m\omega_k}\right)^{1/2} \big(a_k - a^\dagger_{-k}\big)\ . \tag{3.90}$$

Therefore the RMS fluctuations at each site are given by

$$\langle u_n^2 \rangle = \frac{1}{N} \sum_k \langle \tilde{u}_k\, \tilde{u}_{-k} \rangle = \frac{1}{N} \sum_k \frac{\hbar}{m\omega_k} \big(n(k) + \tfrac{1}{2}\big)\ , \tag{3.91}$$

where $n(k,T) = \big[\exp(\hbar\omega_k/k_{\mathrm{B}}T) - 1\big]^{-1}$ is the Bose occupancy function.

Element	Ag	Al	Au	C	Cd	Cr	Cu	Fe	Mn
Θ_{D} (K)	227	433	162	2250	210	606	347	477	409
T_{melt} (K)	962	660	1064	3500	321	1857	1083	1535	1245
Element	Ni	Pb	Pt	Si	Sn	Ta	Ti	W	Zn
Θ_{D} (K)	477	105	237	645	199	246	420	383	329
T_{melt} (K)	1453	327	1772	1410	232	2996	1660	3410	420

Table 3.2: Debye temperatures (at $T = 0$) and melting points for some common elements (carbon is assumed to be diamond and not graphite). (*Source: the internet!*)

Let us now generalize this expression to the case of a d-dimensional solid. The appropriate expression for the RMS position fluctuations of the ith basis atom in each unit cell is

$$\langle u_l^2(\boldsymbol{R}) \rangle = \frac{1}{N} \sum_{\boldsymbol{k}} \sum_{s=1}^{dr} \frac{\hbar}{\mathcal{M}_{ls}(\boldsymbol{k})\, \omega_s(\boldsymbol{k})} \left(n_s(\boldsymbol{k}) + \tfrac{1}{2} \right) . \tag{3.92}$$

Here we sum over all wavevectors $\boldsymbol{k}$ in the first Brilliouin zone, and over all normal modes a. There are dr normal modes per unit cell *i.e.* d branches of the phonon dispersion $\omega_s(\boldsymbol{k})$. (For the one-dimensional chain with $d = 1$ and $r = 1$ there was only one such branch to consider). Note also the quantity $M_{is}(\boldsymbol{k})$, which has units of mass and is defined in terms of the polarization vectors $\mathrm{e}_{ls}^{\alpha}(\boldsymbol{k})$ as

$$\frac{1}{\mathcal{M}_{ls}(\boldsymbol{k})} = \sum_{\mu=1}^{d} \left| \mathrm{e}_{ls}^{\mu}(\boldsymbol{k}) \right|^2 . \tag{3.93}$$

The dimensions of the polarization vector are $[\mathrm{mass}]^{-1/2}$, since the generalized orthonormality condition on the normal modes is

$$\sum_{l,\mu} M_l \, \mathrm{e}_{ls}^{\mu\,*}(\boldsymbol{k}) \, \mathrm{e}_{ls'}^{\mu}(\boldsymbol{k}) = \delta_{ss'} , \tag{3.94}$$

where M_i is the mass of the atom of species i within the unit cell ($i \in \{1, \ldots, r\}$). For our purposes we can replace $\mathcal{M}_{is}(\boldsymbol{k})$ by an appropriately averaged quantity which we call $\mathcal{M}_i$; this 'effective mass' is then independent of the mode index a as well as the wavevector $\boldsymbol{k}$. We may then write

$$\langle u_l^2 \rangle \approx \int_0^{\infty} d\omega \, g(\omega) \, \frac{\hbar}{\mathcal{M}_l\, \omega} \cdot \left\{ \frac{1}{e^{\hbar\omega/k_{\mathrm{B}}T} - 1} + \frac{1}{2} \right\} , \tag{3.95}$$

where we have dropped the site label $\boldsymbol{R}$ since translational invariance guarantees that the fluctuations are the same from one unit cell to the next. Note that the fluctuations $\langle u_i^2 \rangle$ can be divided into a temperature-dependent part $\langle u_i^2 \rangle_{\mathrm{th}}$ and a temperature-independent quantum

contribution $\langle u_i^2 \rangle_{\mathrm{qu}}$, where

$$\langle u_l^2 \rangle_{\mathrm{th}} = \frac{\hbar}{\mathcal{M}_l} \int\limits_0^\infty d\omega \, \frac{g(\omega)}{\omega} \cdot \frac{1}{e^{\hbar\omega/k_{\mathrm{B}}T} - 1}$$

$$\langle u_l^2 \rangle_{\mathrm{qu}} = \frac{\hbar}{2\mathcal{M}_l} \int\limits_0^\infty d\omega \, \frac{g(\omega)}{\omega} \, .$$

(3.96)

Let's evaluate these contributions within the Debye model, where we replace $g(\omega)$ by

$$\bar{g}(\omega) = \frac{d^2 \, \omega^{d-1}}{\omega_{\mathrm{D}}^d} \, \Theta(\omega_{\mathrm{D}} - \omega) \, .$$

(3.97)

We then find

$$\langle u_l^2 \rangle_{\mathrm{th}} = \frac{d^2 \hbar}{\mathcal{M}_l \, \omega_{\mathrm{D}}} \left(\frac{k_{\mathrm{B}}T}{\hbar\omega_{\mathrm{D}}} \right)^{d-1} F_d(\hbar\omega_{\mathrm{D}}/k_{\mathrm{B}}T)$$

$$\langle u_l^2 \rangle_{\mathrm{qu}} = \frac{d^2}{d-1} \cdot \frac{\hbar}{2\mathcal{M}_l \, \omega_{\mathrm{D}}} \, ,$$

(3.98)

where

$$F_d(x) = \int\limits_0^x dy \, \frac{y^{d-2}}{e^y - 1} = \begin{cases} \frac{x^{d-2}}{d-2} & x \to 0 \\ \\ \zeta(d-1) & x \to \infty \end{cases} \, .$$

(3.99)

We can now extract from these expressions several important conclusions:

1) The $T = 0$ contribution to the the fluctuations, $\langle u_l^2 \rangle_{\mathrm{qu}}$, diverges in $d = 1$ dimensions. *Therefore there are no one-dimensional quantum solids.*

2) The thermal contribution to the fluctuations, $\langle u_l^2 \rangle_{\mathrm{th}}$, diverges for any $T > 0$ whenever $d \leq 2$. This is because the integrand of $F_d(x)$ goes as y^{d-3} as $y \to 0$. *Therefore, there are no two-dimensional classical solids.*

3) Both the above conclusions are valid in the thermodynamic limit. Finite size imposes a cutoff on the frequency integrals, because there is a smallest wavevector $k_{\mathrm{min}} \sim 2\pi/L$, where L is the (finite) linear dimension of the system. This leads to a low frequency cutoff $\omega_{\mathrm{min}} = 2\pi\bar{c}/L$, where $\bar{c}$ is the appropriately averaged acoustic phonon velocity from eqn. 3.85, which mitigates any divergences.

Lindemann melting criterion

An old phenomenological theory of melting due to Lindemann says that a crystalline solid melts when the RMS fluctuations in the atomic positions exceeds a certain fraction η of the lattice constant a. We therefore define the ratios

$$
\begin{aligned}
x_{l,\mathrm{th}}^2 &\equiv \frac{\langle\, \boldsymbol{u}_l^2\,\rangle_{\mathrm{th}}}{a^2} = d^2 \cdot \left(\frac{\hbar^2}{\mathcal{M}_l\, a^2\, k_{\mathrm{B}}}\right) \cdot \frac{T^{d-1}}{\Theta_{\mathrm{D}}^d} \cdot F(\Theta_{\mathrm{D}}/T) \\
x_{l,\mathrm{qu}}^2 &\equiv \frac{\langle\, \boldsymbol{u}_l^2\,\rangle_{\mathrm{qu}}}{a^2} = \frac{d^2}{2(d-1)} \cdot \left(\frac{\hbar^2}{\mathcal{M}_l\, a^2\, k_{\mathrm{B}}}\right) \cdot \frac{1}{\Theta_{\mathrm{D}}} \quad ,
\end{aligned}
\tag{3.100}
$$

with $x_l = \sqrt{x_{l,\mathrm{th}}^2 + x_{l,\mathrm{qu}}^2} = \sqrt{\langle\, \boldsymbol{u}_l^2\,\rangle}\big/a$.

Let's now work through an example of a three-dimensional solid. We'll assume a single element basis ($r = 1$). We have that

$$
\frac{9\hbar^2/4k_{\mathrm{B}}}{1\ \mathrm{amu}\ \mathring{\mathrm{A}}^2} = 109\ \mathrm{K} \ .
\tag{3.101}
$$

According to table 3.2, the melting temperature always exceeds the Debye temperature, and often by a great amount. We therefore assume $T \gg \Theta_{\mathrm{D}}$, which puts us in the small x limit of $F_d(x)$. We then find

$$
x_{\mathrm{qu}}^2 = \frac{\Theta^\star}{\Theta_{\mathrm{D}}} \quad , \qquad x_{\mathrm{th}}^2 = \frac{\Theta^\star}{\Theta_{\mathrm{D}}} \cdot \frac{4T}{\Theta_{\mathrm{D}}} \quad , \qquad x = \sqrt{\left(1 + \frac{4T}{\Theta_{\mathrm{D}}}\right)\frac{\Theta^\star}{\Theta_{\mathrm{D}}}} \ .
\tag{3.102}
$$

where

$$
\Theta^* = \frac{109\ \mathrm{K}}{M[\mathrm{amu}] \cdot \left(a[\mathring{\mathrm{A}}]\right)^2} \ .
\tag{3.103}
$$

The total position fluctuation is of course the sum $x_l^2 = x_{l,\mathrm{th}}^2 + x_{l,\mathrm{qu}}^2$. Consider for example the case of copper, with $M = 56\ \mathrm{amu}$ and $a = 2.87\ \mathring{\mathrm{A}}$. The Debye temperature is $\Theta_{\mathrm{D}} = 347\ \mathrm{K}$. From this we find $x_{\mathrm{qu}} = 0.026$, which says that at $T = 0$ the RMS fluctuations of the atomic positions are not quite three percent of the lattice spacing (*i.e.* the distance between neighboring copper atoms). At room temperature, $T = 293\ \mathrm{K}$, one finds $x_{\mathrm{th}} = 0.048$, which is about twice as large as the quantum contribution. How big are the atomic position fluctuations at the melting point? According to our table, $T_{\mathrm{melt}} = 1083\ \mathrm{K}$ for copper, and from our formulae we obtain $x_{\mathrm{melt}} = 0.096$. The *Lindemann criterion* says that solids melt when $x(T) \approx 0.1$.

We were very lucky to hit the magic number $x_{\mathrm{melt}} = 0.1$ with copper. Let's try another example. Lead has $M = 208\ \mathrm{amu}$ and $a = 4.95\ \mathring{\mathrm{A}}$. The Debye temperature is $\Theta_{\mathrm{D}} = 105\ \mathrm{K}$ ('soft phonons'), and the melting point is $T_{\mathrm{melt}} = 327\ \mathrm{K}$. From these data we obtain $x(T = 0) = 0.014$, $x(293\ \mathrm{K}) = 0.050$ and $x(T = 327\ \mathrm{K}) = 0.053$. Same ballpark.

We can turn the analysis around and predict a melting temperature based on the Lindemann criterion $x(T_{\mathrm{melt}}) = \eta$, where $\eta \approx 0.1$. We obtain

$$T_{\mathrm{L}} = \left(\frac{\eta^2 \, \Theta_{\mathrm{D}}}{\Theta^\star} - 1 \right) \cdot \frac{\Theta_{\mathrm{D}}}{4} \ . \tag{3.104}$$

We call T_{L} the *Lindemann temperature*. Most treatments of the Lindemann criterion ignore the quantum correction, which gives the -1 contribution inside the above parentheses. But if we are more careful and include it, we see that it may be possible to have $T_{\mathrm{L}} < 0$. This occurs for any crystal where $\Theta_{\mathrm{D}} < \Theta^\star/\eta^2$.

Consider for example the case of ^{4}He, which at atmospheric pressure condenses into a liquid at $T_{\mathrm{c}} = 4.2\,\mathrm{K}$ and remains in the liquid state down to absolute zero. At $p = 1\,\mathrm{atm}$, it never solidifies! Why? The number density of liquid ^{4}He at $p = 1\,\mathrm{atm}$ and $T = 0\,\mathrm{K}$ is $2.2 \times 10^{22}\,\mathrm{cm}^{-3}$. Let's say the Helium atoms want to form a crystalline lattice. We don't know *a priori* what the lattice structure will be, so let's for the sake of simplicity assume a simple cubic lattice. From the number density we obtain a lattice spacing of $a = 3.57\,\text{Å}$. OK now what do we take for the Debye temperature? Theoretically this should depend on the microscopic force constants which enter the small oscillations problem (*i.e.* the spring constants between pairs of helium atoms in equilibrium). We'll use the expression we derived for the Debye frequency, $\omega_{\mathrm{D}} = (6\pi^2/\mathcal{V}_0)^{1/3}\bar{c}$, where $\mathcal{V}_0$ is the unit cell volume. We'll take $\bar{c} = 238\,\mathrm{m/s}$, which is the speed of sound in liquid helium at $T = 0$. This gives $\Theta_{\mathrm{D}} = 19.8\,\mathrm{K}$. We find $\Theta^\star = 2.13\,\mathrm{K}$, and if we take $\eta = 0.1$ this gives $\Theta^\star/\eta^2 = 213\,\mathrm{K}$, which significantly exceeds Θ_{D}. Thus, the solid should melt because the RMS fluctuations in the atomic positions at absolute zero are huge: $x_{\mathrm{qu}} = (\Theta^\star/\Theta_{\mathrm{D}})^{1/2} = 0.33$. By applying pressure, one can get ^{4}He to crystallize above $p_{\mathrm{c}} = 25\,\mathrm{atm}$ (at absolute zero). Under pressure, the unit cell volume $\mathcal{V}_0$ decreases and the phonon velocity $\bar{c}$ increases, so the Debye temperature itself increases.

It is important to recognize that the Lindemann criterion does not provide us with a theory of melting *per se*. Rather it provides us with a heuristic which allows us to predict roughly when a solid should melt.

3.2.9   Goldstone bosons

The vanishing of the acoustic phonon dispersion at $\boldsymbol{k} = 0$ is a consequence of *Goldstone's theorem* which says that associated with every *broken generator* of a *continuous symmetry* there is an associated bosonic gapless excitation (*i.e.* one whose frequency ω vanishes in the long wavelength limit). In the case of phonons, the 'broken generators' are the symmetries under spatial translation in the x, y, and z directions. The crystal selects a particular location for its center-of-mass, which breaks this symmetry. There are, accordingly, three gapless acoustic phonons.

Magnetic materials support another branch of elementary excitations known as spin waves, or *magnons*. In *isotropic* magnets, there is a global symmetry associated with rotations in internal

spin space, described by the group $SU(2)$. If the system spontaneously magnetizes, meaning there is long-ranged ferromagnetic order ($\uparrow\uparrow\uparrow \cdots$), or long-ranged antiferromagnetic order ($\uparrow\downarrow\uparrow\downarrow \cdots$), then global spin rotation symmetry is broken. Typically a particular direction is chosen for the magnetic moment (or staggered moment, in the case of an antiferromagnet). Symmetry under rotations about this axis is then preserved, but rotations which do not preserve the selected axis are 'broken'. In the most straightforward case, that of the antiferromagnet, there are two such rotations for $SU(2)$, and concomitantly two gapless magnon branches, with linearly vanishing dispersions $\omega_a(\boldsymbol{k})$. The situation is more subtle in the case of ferromagnets, because the total magnetization is conserved by the dynamics (unlike the total staggered magnetization in the case of antiferromagnets). Another wrinkle arises if there are long-ranged interactions present.

For our purposes, we can safely ignore the deep physical reasons underlying the gaplessness of Goldstone bosons and simply posit a gapless dispersion relation of the form $\omega(\boldsymbol{k}) = A\,|\boldsymbol{k}|^\sigma$. The density of states for this excitation branch is then

$$g(\omega) = \mathcal{C}\,\omega^{\frac{d}{\sigma}-1}\,\Theta(\omega_{\mathrm{c}} - \omega)\,, \tag{3.105}$$

where $\mathcal{C}$ is a constant and ω_{c} is the cutoff, which is the bandwidth for this excitation branch.[6] Normalizing the density of states for this branch results in the identification $\omega_{\mathrm{c}} = (d/\sigma\mathcal{C})^{\sigma/d}$.

The heat capacity is then found to be

$$
C_V = Nk_{\mathrm{B}}\,\mathcal{C}\int\limits_0^{\omega_{\mathrm{c}}} d\omega\,\omega^{\frac{d}{\sigma}-1}\left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)^2 \mathrm{csch}^2\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)
$$

$$
= \frac{d}{\sigma}\,Nk_{\mathrm{B}}\left(\frac{2T}{\Theta}\right)^{d/\sigma}\phi(\Theta/2T)\,, \tag{3.106}
$$

where $\Theta = \hbar\omega_{\mathrm{c}}/k_{\mathrm{B}}$ and

$$
\phi(x) = \int\limits_0^x dt\,t^{\frac{d}{\sigma}+1}\,\mathrm{csch}^2 t =
\begin{cases}
\dfrac{\sigma}{d}\,x^{d/\sigma} & x \to 0 \\[2ex]
2^{-d/\sigma}\,\Gamma\!\left(2+\tfrac{d}{\sigma}\right)\zeta\!\left(2+\tfrac{d}{\sigma}\right) & x \to \infty\,,
\end{cases} \tag{3.107}
$$

which is a generalization of our earlier results. Once again, we recover Dulong-Petit for $k_{\mathrm{B}}T \gg \hbar\omega_{\mathrm{c}}$, with $C_V(T \gg \hbar\omega_{\mathrm{c}}/k_{\mathrm{B}}) = Nk_{\mathrm{B}}$.

In an isotropic ferromagnet, *i.e.* a ferromagnetic material where there is full SU(2) symmetry in internal 'spin' space, the magnons have a k^2 dispersion. Thus, a bulk three-dimensional isotropic ferromagnet will exhibit a heat capacity due to spin waves which behaves as $T^{3/2}$ at low temperatures. For sufficiently low temperatures this will overwhelm the phonon contribution, which behaves as T^3.

---

[6]If $\omega(\boldsymbol{k}) = Ak^\sigma$, then $\mathcal{C} = 2^{1-d}\,\pi^{-\frac{d}{2}}\,\sigma^{-1}\,A^{-\frac{d}{\sigma}}\,\mathrm{g}\,\big/\,\Gamma(d/2)\,.$

3.2.10   Elasticity theory redux : Bravais lattices

In a Bravais lattice, we have $\hat{\Phi}^{\alpha\beta}(\boldsymbol{0}) = 0$ from translational invariance. The potential energy may then be written in the form

$$U = U_0 - \frac{1}{4} \sum_{\boldsymbol{R},\boldsymbol{R}'} \sum_{\alpha,\beta} \left[u^\alpha(\boldsymbol{R}) - u^\alpha(\boldsymbol{R}') \right] \Phi^{\alpha\beta}(\boldsymbol{R} - \boldsymbol{R}') \left[u^\beta(\boldsymbol{R}) - u^\beta(\boldsymbol{R}') \right] \quad . \tag{3.108}$$

We now assume a very long wavelength disturbance, and write

$$u^\alpha(\boldsymbol{R}) - u^\alpha(\boldsymbol{R}') = (R^\mu - R'^\mu) \left. \frac{\partial u^\alpha}{\partial x^\mu} \right|_{\boldsymbol{R}} + \ldots \quad . \tag{3.109}$$

Thus,

$$U = U_0 - \frac{1}{4} \sum_{\boldsymbol{R},\boldsymbol{R}'} \sum_{\alpha,\beta} \sum_{\mu,\nu} \left. \frac{\partial u^\alpha}{\partial x^\mu} \right|_{\boldsymbol{R}} \left. \frac{\partial u^\beta}{\partial x^\nu} \right|_{\boldsymbol{R}} (R^\mu - R'^\mu)(R^\nu - R'^\nu) \Phi^{\alpha\beta}(\boldsymbol{R} - \boldsymbol{R}') \quad . \tag{3.110}$$

We may symmetrize with respect to Cartesian indices[7] to obtain the elastic tensor

$$C_{\alpha\beta\mu\nu} \equiv -\frac{1}{8\Omega} \sum_{\boldsymbol{R}} \left(R^\mu R^\nu \, \Phi^{\alpha\beta}(\boldsymbol{R}) + R^\mu R^\beta \, \Phi^{\alpha\nu}(\boldsymbol{R}) + R^\alpha R^\nu \, \Phi^{\mu\beta}(\boldsymbol{R}) + R^\alpha R^\beta \, \Phi^{\mu\nu}(\boldsymbol{R}) \right) \quad . \tag{3.111}$$

Note that

$$C_{\alpha\beta\mu\nu} = C_{\beta\alpha\mu\nu} = C_{\alpha\beta\nu\mu} = C_{\mu\nu\alpha\beta} \quad , \tag{3.112}$$

where Ω is the Wigner-Seitz cell volume.

Elasticity in solids

Recall from §3.1.2 that we may regard the rank four tensor $C_{\alpha\beta\mu\nu}$ as a symmetric 6×6 matrix C_{ab}, where we replace $(\alpha\beta) \to a$ and $(\mu\nu) \to b$ according to the scheme from Tab. 3.1. In cubic crystals, for example, we have

$$\begin{aligned} C_{11} &= C_{xxxx} = C_{yyyy} = C_{zzzz} \\ C_{12} &= C_{xxyy} = C_{xxzz} = C_{yyzz} \\ C_{44} &= C_{xyxy} = C_{xzxz} = C_{yzyz} \quad . \end{aligned} \tag{3.113}$$

Typical values of C_{ab} in solids are on the order of gigapascals, *i.e.* 10^9 Pa:

---

[7]Symmetrization is valid because the antisymmetric combination $\left(\frac{\partial u^\alpha}{\partial x^\beta} - \frac{\partial u^\beta}{\partial x^\alpha} \right)$ corresponds to a rotation.

element	C_{11}	C_{12}	C_{44}
^{4}He	0.031	0.028	0.022
Cu	16	8	12
Al	108	62	28.3
Pb	48.8	41.4	14.8
C (diamond)	1040	170	550

Table 3.3: Elastic moduli for various solids (in GPa).

The *bulk modulus* of a solid is defined as $\mathcal{B} = V\,\partial^2 F/\partial V^2$. We consider a uniform dilation, which is described by $\boldsymbol{R} \to (1+\zeta)\boldsymbol{R}$ at each lattice site. Thus the displacement field is $\boldsymbol{u}(\boldsymbol{r}) = \zeta\boldsymbol{r}$. This leads to a volume change of $\delta V = 3\zeta V$, hence $\zeta = \delta V/3V$. The strain tensor is $\varepsilon_{\alpha\beta} = \zeta\,\delta_{\alpha\beta}$, hence

$$\delta F = \frac{(\delta V)^2}{18V} \sum_{\alpha,\beta} C_{\alpha\alpha\beta\beta} = \tfrac{1}{9} \sum_{a,b=1}^{3} C_{ab} \quad . \tag{3.114}$$

Thus, for cubic materials, $\mathcal{B} = \tfrac{1}{3}C_{11} + \tfrac{2}{3}C_{12}$.

Elastic waves

The Lagrangian of an elastic medium is be written as

$$L = \int d^d r\, \mathcal{L} = \int d^d r\, \left\{ \tfrac{1}{2}\rho \left(\frac{\partial u^\alpha}{\partial t}\right)^2 - \tfrac{1}{2} C_{\alpha\beta\mu\nu} \frac{\partial u^\alpha}{\partial x^\beta} \frac{\partial u^\mu}{\partial x^\nu} \right\} \quad , \tag{3.115}$$

where ρ is the overall mass density of the crystal, *i.e.* $\rho = m/\Omega$. The Euler-Lagrange equations of motion are then

$$\begin{aligned}
0 &= \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial(\partial_t u^\alpha)} + \frac{\partial}{\partial x^\beta} \frac{\partial \mathcal{L}}{\partial(\partial_\beta u^\alpha)} \\
&= \rho\, \frac{\partial^2 u^\alpha}{\partial t^2} - C_{\alpha\beta\mu\nu} \frac{\partial^2 u^\nu}{\partial x^\beta\,\partial x^\mu} \quad .
\end{aligned} \tag{3.116}$$

The solutions are *elastic waves*, with $\boldsymbol{u}(\boldsymbol{x},t) = \hat{\mathbf{e}}(\boldsymbol{k})\,e^{i(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)}$ where

$$\rho\omega^2\,\mathrm{e}^\alpha(\boldsymbol{k}) = C_{\alpha\beta\mu\nu}\,k^\beta\,k^\mu\,\mathrm{e}^\nu(\boldsymbol{k}) \quad . \tag{3.117}$$

Thus, the dispersion is $\omega_a(\boldsymbol{k}) = c_a(\hat{\boldsymbol{k}})\,k$, where

$$\det\left[\rho\,c^2(\hat{\boldsymbol{k}})\,\delta_{\alpha\nu} - C_{\alpha\beta\mu\nu}\,\hat{k}^\beta\,\hat{k}^\mu\right] = 0 \tag{3.118}$$

is the equation to be solved for the speeds of sound $c_a(\hat{\boldsymbol{k}})$ in each elastic wave branch a.

For isotropic solids, $C_{12} \equiv \lambda$, $C_{44} \equiv \mu$, and $C_{11} = C_{12} + 2C_{14} = \lambda + 2\mu$, where λ and μ are the Lamé coefficients. The free energy density is discussed in §3.1 and is given by

$$f = \tfrac{1}{2}\lambda \left(\partial_i u_i\right)^2 + \tfrac{1}{2}\mu \left(\partial_i u_j\right)\left(\partial_i u_j\right) + \tfrac{1}{2}\mu \left(\partial_i u_j\right)\left(\partial_j u_i\right) \quad , \tag{3.119}$$

which results in the Euler-Lagrange equations of motion

$$\rho\,\ddot{\boldsymbol{u}} = (\lambda + \mu)\,\boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{u}) + \mu\,\nabla^2 \boldsymbol{u} \quad . \tag{3.120}$$

Writing $\boldsymbol{u}(\boldsymbol{r},t) = u_0\,\hat{\mathrm{e}}(\boldsymbol{k})\,e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}$, where $\hat{\mathrm{e}}$ is a polarization unit vector, we obtain a longitudinal mode when $\hat{\mathrm{e}}(\boldsymbol{k}) \cdot \hat{\boldsymbol{k}} = 1$ with $\omega_{\mathrm{L}}(\boldsymbol{k}) = c_{\mathrm{L}}\,|\boldsymbol{k}|$ and $c_{\mathrm{L}} = \sqrt{(\lambda + 2\mu)/\rho}$, and two transverse modes when $\hat{\mathrm{e}}(\boldsymbol{k}) \cdot \hat{\boldsymbol{k}} = 0$ with $\omega_{\mathrm{T}}(\boldsymbol{k}) = c_{\mathrm{T}}\,|\boldsymbol{k}|$ and $c_{\mathrm{T}} = \sqrt{\mu/\rho}$.

In cubic crystals, there are three independent elastic moduli, C_{11}, C_{12}, and C_{14}. We then have

$$\rho\, c^2(\hat{\boldsymbol{k}})\,\mathrm{e}^x = \left[C_{11}\,\hat{k}_x^2 + C_{44}\big(\hat{k}_y^2 + \hat{k}_z^2\big)\right]\hat{\mathrm{e}}^x + (C_{12} + C_{44})\big(\hat{k}_x\,\hat{k}_y\,\hat{\mathrm{e}}^y + \hat{k}_x\,\hat{k}_z\,\hat{\mathrm{e}}^z\big)$$

$$\rho\, c^2(\hat{\boldsymbol{k}})\,\mathrm{e}^y = \left[C_{11}\,\hat{k}_y^2 + C_{44}\big(\hat{k}_x^2 + \hat{k}_z^2\big)\right]\hat{\mathrm{e}}^y + (C_{12} + C_{44})\big(\hat{k}_x\,\hat{k}_y\,\hat{\mathrm{e}}^x + \hat{k}_y\,\hat{k}_z\,\hat{\mathrm{e}}^z\big) \tag{3.121}$$

$$\rho\, c^2(\hat{\boldsymbol{k}})\,\mathrm{e}^z = \left[C_{11}\,\hat{k}_z^2 + C_{44}\big(\hat{k}_x^2 + \hat{k}_y^2\big)\right]\hat{\mathrm{e}}^z + (C_{12} + C_{44})\big(\hat{k}_x\,\hat{k}_z\,\hat{\mathrm{e}}^x + \hat{k}_y\,\hat{k}_z\,\hat{\mathrm{e}}^y\big) \quad .$$

This still yields a cubic equation, but it can be simplified by looking along a high symmetry direction in the Brillouin zone.

Along the (100) direction $\boldsymbol{k} = k\,\hat{\boldsymbol{x}}$, we have

$$\hat{\mathrm{e}}_{\mathrm{L}} = \hat{\boldsymbol{x}} \qquad\qquad\qquad c_{\mathrm{L}} = \sqrt{C_{11}/\rho} \tag{3.122}$$

$$\hat{\mathrm{e}}_{\mathrm{T1}} = \hat{\boldsymbol{y}} \qquad\qquad\qquad c_{\mathrm{T1}} = \sqrt{C_{44}/\rho} \tag{3.123}$$

$$\hat{\mathrm{e}}_{\mathrm{T2}} = \hat{\boldsymbol{z}} \qquad\qquad\qquad c_{\mathrm{T2}} = \sqrt{C_{44}/\rho} \quad . \tag{3.124}$$

Along the (110) direction, we have $\boldsymbol{k} = \frac{1}{\sqrt{2}}\,k\,(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})$. In this case

$$\hat{\mathrm{e}}_{\mathrm{L}} = \tfrac{1}{\sqrt{2}}\big(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}\big) \qquad\qquad c_{\mathrm{L}} = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3\rho} \tag{3.125}$$

$$\hat{\mathrm{e}}_{\mathrm{T1}} = \tfrac{1}{\sqrt{2}}\big(\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}}\big) \qquad\qquad c_{\mathrm{T1}} = \sqrt{(C_{11} - C_{12})/2\rho} \tag{3.126}$$

$$\hat{\mathrm{e}}_{\mathrm{T2}} = \hat{\boldsymbol{z}} \qquad\qquad\qquad\quad c_{\mathrm{T2}} = \sqrt{C_{44}/\rho} \quad . \tag{3.127}$$

Along the (111) direction, we have $\boldsymbol{k} = \frac{1}{\sqrt{3}}\,k\,(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$. In this case

$$\hat{\mathrm{e}}_{\mathrm{L}} = \tfrac{1}{\sqrt{3}}\big(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}\big) \qquad\qquad c_{\mathrm{L}} = \sqrt{(C_{11} + C_{12} + 2C_{44})/2\rho} \tag{3.128}$$

$$\hat{\mathrm{e}}_{\mathrm{T1}} = \tfrac{1}{\sqrt{6}}\big(2\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}\big) \qquad\quad c_{\mathrm{T1}} = \sqrt{(C_{11} - C_{12})/3\rho} \tag{3.129}$$

$$\hat{\mathrm{e}}_{\mathrm{T2}} = \tfrac{1}{\sqrt{2}}\big(\hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}\big) \qquad\qquad\quad c_{\mathrm{T2}} = \sqrt{(C_{11} - C_{12})/3\rho} \quad . \tag{3.130}$$

3.2.11 Elasticity theory in cases with bases

The derivation of the elastic tensor $C_{\alpha\beta\mu\nu}$ is significantly complicated by the presence of a basis. Sadly, translational invariance if of no direct avail because

$$U \neq U_0 - \frac{1}{4} \sum_{\boldsymbol{R},\boldsymbol{R}'} \sum_{\alpha,\beta} \sum_{i,j} \left[u_i^\alpha(\boldsymbol{R}) - u_i^\alpha(\boldsymbol{R}') \right] \Phi_{ij}^{\alpha\beta}(\boldsymbol{R} - \boldsymbol{R}') \left[u_j^\beta(\boldsymbol{R}) - u_j^\beta(\boldsymbol{R}') \right] \quad . \tag{3.131}$$

The student should understand why the above relation is not an equality.

Rather than work with the energy, we will work with the eigenvalue equation 3.42,

$$\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k}) \, \hat{e}_{j\lambda}^\beta(\boldsymbol{k}) = m_i \, \omega_\lambda^2(\boldsymbol{k}) \, \hat{e}_{i\lambda}^\alpha(\boldsymbol{k}) \quad ,$$

and expand in powers of $\boldsymbol{k}$. Accordingly, we write

$$\hat{e}_{i\lambda}^\alpha(\boldsymbol{k}) = d_i^\alpha + k^\sigma f_{i\sigma}^\alpha + \tfrac{1}{2} k^\sigma k^\tau g_{i\sigma\tau}^\beta + \mathcal{O}(k^3)$$

$$\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k}) = \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{0}) + k^\mu \left. \frac{\partial \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu} \right|_{\boldsymbol{0}} + \tfrac{1}{2} k^\mu k^\nu \left. \frac{\partial^2 \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu \, \partial k^\nu} \right|_{\boldsymbol{0}} + \mathcal{O}(k^3) \quad . \tag{3.132}$$

We retain the basis index i on d_i^α *even though it is independent of i* because we will use it to make clear certain necessary sums on the basis index within the Einstein convention. We then have

$$m_i \, \omega^2 \left\{ d_i^\alpha + k^\sigma f_{i\sigma}^\alpha + \dots \right\} = \tag{3.133}$$

$$\left\{ \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{0}) + k^\mu \left. \frac{\partial \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu} \right|_{\boldsymbol{0}} + \tfrac{1}{2} k^\mu k^\nu \left. \frac{\partial^2 \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu \, \partial k^\nu} \right|_{\boldsymbol{0}} + \dots \right\} \left\{ d_j^\beta + k^\tau f_{j\tau}^\beta + \dots \right\} \quad ,$$

where there is no implied sum on i on the LHS. We now work order by order in $\boldsymbol{k}$. To start, note that $\omega^2(\boldsymbol{k}) = c^2(\hat{\boldsymbol{k}}) \, k^2$ is already second order. On the RHS, we have $\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{0}) \, d_j^\beta = 0$ to zeroth order in k. At first order, we must have

$$\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{0}) \, f_{j\sigma}^\beta + \left. \frac{\partial \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\sigma} \right|_{\boldsymbol{0}} d_j^\beta = 0 \quad , \tag{3.134}$$

and defining the matrix inverse $\hat{\Upsilon}_{li}^{\gamma\alpha}(\boldsymbol{k})$ by the relation

$$\hat{\Upsilon}_{li}^{\gamma\alpha}(\boldsymbol{k}) \, \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k}) = \delta^{\gamma\beta} \, \delta_{lj} \quad , \tag{3.135}$$

we have

$$f_{l\sigma}^\gamma = -\hat{\Upsilon}_{li}^{\gamma\alpha}(\boldsymbol{0}) \left. \frac{\partial \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\sigma} \right|_{\boldsymbol{0}} d_j^\beta \tag{3.136}$$

Finally, we obtain the eigenvalue equation for the elastic waves,

$$m_i \, \omega^2 \, d_i^\alpha = \left[\frac{1}{2} \left. \frac{\partial^2 \hat{\Phi}_{il}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu \, \partial k^\nu} \right|_{\boldsymbol{0}} - \left. \frac{\partial \hat{\Phi}_{ij}^{\alpha\sigma}(\boldsymbol{k})}{\partial k^\mu} \right|_{\boldsymbol{0}} \hat{\Upsilon}_{jm}^{\sigma\gamma}(\boldsymbol{0}) \left. \frac{\partial \hat{\Phi}_{ml}^{\gamma\beta}(\boldsymbol{k})}{\partial k^\nu} \right|_{\boldsymbol{0}} \right] k^\mu \, k^\nu \, d_l^\beta \quad . \tag{3.137}$$

Remember that d_i^α is independent of the basis index i. We have dropped the mode index λ here for notational convenience. Note that the quadratic coefficient $g_{i\sigma\tau}^\beta$ never entered our calculation because it leads to an inhomogeneous term in the eigenvalue equation, and therefore must be dropped. We do not report here the explicit form for the elastic tensor, which may be derived from the above eigenvalue equation.

3.3   Neutron diffraction

3.3.1   Inelastic differential scattering cross-section

Elastic X-ray scattering yields a measure of the static structure factor of a crystal,

$$S(\boldsymbol{q}) = \frac{1}{N} \sum_{\boldsymbol{R},\boldsymbol{R}'} \sum_{i,j} e^{i\boldsymbol{q}\cdot(\boldsymbol{R}'+\boldsymbol{\delta}_j - \boldsymbol{R}-\boldsymbol{\delta}_i)} \quad . \tag{3.138}$$

The wavevector transfer is $\boldsymbol{q} = \boldsymbol{k}_f - \boldsymbol{k}_i$. Now consider an inelastic process between states

$$| \Psi_i \rangle \equiv \big| \boldsymbol{k}_i \, , \, \{n_s^i(\boldsymbol{k})\} \big\rangle \to \big| \boldsymbol{k}_f \, , \, \{n_s^f(\boldsymbol{k})\} \big\rangle \equiv | \Psi_f \rangle \quad . \tag{3.139}$$

The initial and final energies are given by

$$\begin{aligned}
E_i &= \frac{\hbar^2 \boldsymbol{k}_i^2}{2m_{\mathsf{n}}} + \sum_{\boldsymbol{k},s} \hbar\omega_s(\boldsymbol{k}) \left(n_s^i(\boldsymbol{k}) + \tfrac{1}{2} \right) \\
E_f &= \frac{\hbar^2 \boldsymbol{k}_i^2}{2m_{\mathsf{n}}} + \sum_{\boldsymbol{k},s} \hbar\omega_s(\boldsymbol{k}) \left(n_s^f(\boldsymbol{k}) + \tfrac{1}{2} \right) \quad .
\end{aligned} \tag{3.140}$$

Energy conservation requires $E_f = E_i$, and we define the energy transfer to the lattice to be

$$\hbar\omega \equiv \frac{\hbar^2}{2m_{\mathsf{n}}} \left(\boldsymbol{k}_i^2 - \boldsymbol{k}_f^2 \right) = \sum_{\boldsymbol{k},s} \hbar\omega_s(\boldsymbol{k}) \left(n_s^f(\boldsymbol{k}) - n_s^i(\boldsymbol{k}) \right) \equiv \mathcal{E}_f - \mathcal{E}_i \quad , \tag{3.141}$$

where $\mathcal{E} = \sum_{\boldsymbol{k},s} \hbar\omega_s(\boldsymbol{k}) \left(n_s(\boldsymbol{k}) + \tfrac{1}{2} \right)$ is the energy of the lattice vibrations.

The scattering rate from $| \Psi_i \rangle$ to $| \Psi_f \rangle$ is given by Fermi's Golden Rule, *viz.*

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} \left| \langle f | V | i \rangle \right|^2 \delta(E_f - E_i) \quad , \tag{3.142}$$

from which we derive the differential scattering cross section

$$\frac{\partial^2 \sigma}{\partial\Omega \, \partial\omega} = \frac{\hbar}{4\pi v_i} \sum_{i,f} P_i \, \Gamma_{i\to f} \, g(k_f) \quad , \tag{3.143}$$

where P_i is the Boltzmann weight for the lattice state $|\,i\,\rangle = |\,\{n^i_s(\mathbf{k})\}\,\rangle$, and where $g(k_f)$ is the density of states,

$$g(k_f) = \int \frac{d^3k}{(2\pi)^3} \, \delta\left(\frac{\hbar^2 \mathbf{k}^2}{2m_{\mathsf{n}}} - \frac{\hbar^2 \mathbf{k}_f^2}{2m_{\mathsf{n}}}\right) = \frac{m_{\mathsf{n}} k_f}{2\pi^2 \hbar^2} \quad . \tag{3.144}$$

Thus,

$$\frac{\partial^2 \sigma}{\partial\Omega\,\partial\omega} = \frac{m_{\mathsf{n}}^2 \, k_i}{4\pi^2 \hbar^3 \, k_f} \sum_{i,f} P_i \, \big|\langle\, \mathbf{k}_f, f \,|\, V \,|\, \mathbf{k}_i, i\,\rangle\big|^2 \delta(E_f - E_i) \quad . \tag{3.145}$$

We may approximate the potential $V(\mathbf{r})$ as

$$V(\mathbf{r}) = \sum_{\mathbf{R},l} \frac{2\pi a_l \hbar^2}{m_{\mathsf{n}}} \, \delta\big(\mathbf{r} - \mathbf{R} - \boldsymbol{\delta}_l - \mathbf{u}_l(\mathbf{R})\big) \quad , \tag{3.146}$$

where a_l is the effective s-wave scattering length for ions of species l. The matrix element is thus

$$\langle\, \mathbf{k}_f, f \,|\, V \,|\, \mathbf{k}_i, i\,\rangle = \big\langle\, f \,\big|\, \sum_{\mathbf{R},l} \frac{2\pi \hbar^2 a_l}{m_{\mathsf{n}}} \, e^{-i\mathbf{q}\cdot(\mathbf{R}+\boldsymbol{\delta}_l)} \, e^{-i\mathbf{q}\cdot\mathbf{u}_l(\mathbf{R})} \,\big|\, i \,\big\rangle \quad , \tag{3.147}$$

which is an approximation of the more correct form

$$V(\mathbf{r}) = \sum_{\mathbf{R},l} v_l\big(\mathbf{r} - \mathbf{R} - \boldsymbol{\delta}_l - \mathbf{u}_l(\mathbf{R})\big)$$

$$\langle\, \mathbf{k}_f \,|\, V \,|\, \mathbf{k}_i \,\rangle = \sum_{\mathbf{R},l} \hat{v}(\mathbf{q}) \, e^{-i\mathbf{q}\cdot(\mathbf{R}+\boldsymbol{\delta}_l)} \, e^{-i\mathbf{q}\cdot\mathbf{u}_l(\mathbf{R})} \quad . \tag{3.148}$$

We now have

$$\frac{\partial^2 \sigma}{\partial\Omega\,\partial\omega} = \frac{\hbar k_f}{k_i} \sum_{\mathbf{R},\mathbf{R}'} \sum_{l,l'} a_l \, a_{l'}^* \, e^{i\mathbf{q}\cdot(\mathbf{R}'-\mathbf{R}+\boldsymbol{\delta}_{l'}-\boldsymbol{\delta}_l)} \sum_{i,f} P_i \, \langle\, i \,|\, e^{i\mathbf{q}\cdot\mathbf{u}_{l'}(\mathbf{R}')} \,|\, f \,\rangle \, \langle\, f \,|\, e^{-i\mathbf{q}\cdot\mathbf{u}_l(\mathbf{R})} \,|\, i \,\rangle \, \delta(\hbar\omega+\mathcal{E}_i-\mathcal{E}_f) \quad . \tag{3.149}$$

Writing

$$\delta(\hbar\omega + \mathcal{E}_i - \mathcal{E}_f) = \int\limits_0^\infty \frac{dt}{2\pi\hbar} \, e^{i\omega t} \, e^{i(\mathcal{E}_i - \mathcal{E}_f)t/\hbar} \quad , \tag{3.150}$$

we have,

$$\frac{\partial^2 \sigma}{\partial\Omega\,\partial\omega} = N \frac{k_f}{k_i} \sum_{l,l'} a_l \, a_{l'}^* \, e^{i\mathbf{q}\cdot(\boldsymbol{\delta}_{l'}-\boldsymbol{\delta}_l)} \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} \int\limits_{-\infty}^\infty \frac{dt}{2\pi} \, e^{i\omega t} \, \big\langle e^{-i\mathbf{q}\cdot\mathbf{u}_l(\mathbf{R},t)} \, e^{+i\mathbf{q}\cdot\mathbf{u}_{l'}(\mathbf{0},0)} \big\rangle_T \quad , \tag{3.151}$$

where $\langle\mathcal{O}\rangle_T = \sum_i P_i \langle\, i \,|\, \mathcal{O} \,|\, i\,\rangle$ is the thermodynamic average. We define the *dynamic structure factor* (dsf),

$$S_{ll'}(\mathbf{q}, \omega) = \int\limits_{-\infty}^\infty \frac{dt}{2\pi} \, e^{i\omega t} \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} \big\langle e^{-i\mathbf{q}\cdot\mathbf{u}_l(\mathbf{R},t)} \, e^{+i\mathbf{q}\cdot\mathbf{u}_{l'}(\mathbf{0},0)} \big\rangle_T \quad . \tag{3.152}$$

3.3.2   Evaluation of $S_{ll'}(q, \omega)$

To evaluate the dsf, it is convenient to express the displacements $u_a(R, t)$ in terms of the ladder operators, *viz.*

$$u_l^\alpha(R, t) = \frac{1}{\sqrt{N}} \sum_{k,s} \left(\frac{\hbar}{2\omega_s(k)}\right)^{1/2} \mathrm{e}_{ls}^\alpha(k)\, e^{ik \cdot R} \left(A_s(k)\, e^{-i\omega_s(k)\, t} + A_s^\dagger(-k)\, e^{+i\omega_s(k)\, t}\right) \quad . \qquad (3.153)$$

Thus,

$$iq \cdot u_l(R, t) = \sum_{k,s} \left(X_{k,s} A_{k,s} - X_{k,s}^* A_{k,s}^\dagger\right)$$

$$iq \cdot u_{l'}(0, 0) = \sum_{k,s} \left(Y_{k,s} A_{k,s} - Y_{k,s}^* A_{k,s}^\dagger\right) \quad , \qquad (3.154)$$

where

$$X_{k,s} = \frac{i}{\sqrt{N}} \left(\frac{\hbar}{2\omega_s(k)}\right)^{1/2} q \cdot \mathbf{e}_{ls}(k)\, e^{ik \cdot R}\, e^{-i\omega_s(k)\, t}$$

$$Y_{k,s} = \frac{i}{\sqrt{N}} \left(\frac{\hbar}{2\omega_s(k)}\right)^{1/2} q \cdot \mathbf{e}_{l's}(k) \quad . \qquad (3.155)$$

Thus, we may write

$$\left\langle e^{-iq \cdot u_l(R,t)}\, e^{+iq \cdot u_{l'}(0,0)} \right\rangle_T = \prod_{k,s} \left\langle \exp\left(X_{k,s}^* A_{k,s}^\dagger - X_{k,s} A_{k,s}\right) \exp\left(Y_{k,s} A_{k,s} - Y_{k,s}^* A_{k,s}^\dagger\right) \right\rangle \quad , \qquad (3.156)$$

where we have invoked the fact that $\left[A_{k,s}, A_{k',s'}^\dagger\right] = \delta_{kk'}\, \delta_{ss'}$. To evaluate this expression, we appeal to the Baker-Campbell-Hausdorff equality,

$$e^A\, e^B = e^{A+B}\, e^{\frac{1}{2}[A,B]} \quad , \qquad (3.157)$$

valid when both A and B commute with their commutator $[A, B]$. We may then write, for each (k, s) pair,

$$\exp\left(X_{k,s}^* A_{k,s}^\dagger - X_{k,s} A_{k,s}\right) \exp\left(Y_{k,s} A_{k,s} - Y_{k,s}^* A_{k,s}^\dagger\right) = \qquad (3.158)$$

$$\exp\left[\tfrac{1}{2}\left(X_{k,s} Y_{k,s}^* - X_{k,s}^* Y_{k,s}\right)\right] \exp\left(Z_{k,s} A_{k,s} - Z_{k,s}^* A_{k,s}^\dagger\right) \quad ,$$

where $Z_{k,s} = Y_{k,s} - X_{k,s}$. Now consider a single harmonic oscillator with Hamiltonian $H = \hbar\omega\left(a^\dagger a + \tfrac{1}{2}\right)$ and define $g(x, y) = \langle e^{xa}\, e^{ya^\dagger}\rangle_T$. Then from the cyclic property of the trace, we

have[8]

$$
\begin{aligned}
g(x,y) &\equiv \left\langle e^{xa}\, e^{ya^\dagger}\right\rangle_T \\
&= Z^{-1}\, \mathsf{Tr}\left(e^{-\beta H} e^{xa}\, e^{ya^\dagger}\right) \\
&= Z^{-1}\, e^{xy}\, \mathsf{Tr}\left(e^{-\beta H} e^{ya^\dagger} e^{xa}\right) \\
&= Z^{-1}\, e^{xy}\, \mathsf{Tr}\left(e^{-\beta H} e^{\beta H} e^{xa} e^{-\beta H} e^{ya^\dagger}\right) \\
&= Z^{-1}\, e^{xy}\, \mathsf{Tr}\left(e^{-\beta H} e^{x\exp(-\beta\hbar\omega)\, a} e^{ya^\dagger}\right) \\
&= e^{xy}\, g\!\left(x\exp(-\beta\hbar\omega), y\right) \\
&= e^{xy}\, e^{x\exp(-\beta\hbar\omega)\, y}\, g\!\left(x\exp(-2\beta\hbar\omega), y\right) \\
&= \exp\!\left(\sum_{n=0}^{\infty} xy\, e^{-n\beta\hbar\omega}\right) g(0,y) \\
&= \exp\!\left(\frac{xy}{1-\exp(-\beta\hbar\omega)}\right) \quad,
\end{aligned}
\tag{3.159}
$$

since $g(0,y) = \left\langle e^{ya^\dagger}\right\rangle_T = 1$. We therefore find

$$
\begin{aligned}
\left\langle \exp\!\left(Z_{\boldsymbol{k},s} A_{\boldsymbol{k},s} - Z^*_{\boldsymbol{k},s} A^\dagger_{\boldsymbol{k},s}\right)\right\rangle &= \exp\!\left(\tfrac{1}{2} Z^*_{\boldsymbol{k},s} Z_{\boldsymbol{k},s}\right) \left\langle e^{Z_{\boldsymbol{k},s} A_{\boldsymbol{k},s}}\, e^{-Z^*_{\boldsymbol{k},s} A^\dagger_{\boldsymbol{k},s}}\right\rangle \\
&= \exp\!\left(-\left(n_{\boldsymbol{k},s} + \tfrac{1}{2}\right) Z^*_{\boldsymbol{k},s} Z_{\boldsymbol{k},s}\right) \quad,
\end{aligned}
\tag{3.160}
$$

where

$$
n_{\boldsymbol{k},s} = \frac{1}{e^{\beta\hbar\omega_s(\boldsymbol{k})} - 1}
\tag{3.161}
$$

is the Bose function. Finally, we have

$$
\begin{aligned}
\left\langle e^{-i\boldsymbol{q}\cdot\boldsymbol{u}_l(\boldsymbol{R},t)}\, e^{+i\boldsymbol{q}\cdot\boldsymbol{u}_{l'}(\boldsymbol{0},0)}\right\rangle_T &= \exp\left\{-\sum_{\boldsymbol{k},s}\left(|X_{\boldsymbol{k},s}|^2 + |Y_{\boldsymbol{k},s}|^2\right)\left(n_s(\boldsymbol{k}) + \tfrac{1}{2}\right)\right\} \\
&\times \exp\left\{\sum_{\boldsymbol{k},s}\left[X_{\boldsymbol{k},s} Y^*_{\boldsymbol{k},s}\left(n_s(\boldsymbol{k}) + 1\right) + X^*_{\boldsymbol{k},s} Y_{\boldsymbol{k},s}\, n_s(\boldsymbol{k})\right]\right\} \quad.
\end{aligned}
\tag{3.162}
$$

3.3.3 Dynamic structure factor for Bravais lattices

For the case of Bravais lattices, we have $r = 1$ and

$$
S(\boldsymbol{q},\omega) = e^{-2W(\boldsymbol{q})}\int_{-\infty}^{\infty}\frac{dt}{2\pi}\sum_{\boldsymbol{R}} e^{-i\boldsymbol{q}\cdot\boldsymbol{R}}\, e^{i\omega t}\, e^{\Gamma(\boldsymbol{q},\boldsymbol{R},t)} \quad,
\tag{3.163}
$$

---

[8]See N. D. Mermin, *J. Math. Phys.* **7**, 1038 (1966).

where

$$W(\boldsymbol{q}) = \tfrac{1}{2}\Omega\int\limits_{\hat{\Omega}} \frac{d^d k}{(2\pi)^d} \sum_{s=1}^{d} \hbar\omega_s^{-1}(\boldsymbol{k}) \left|\boldsymbol{q}\cdot\mathbf{e}_s(\boldsymbol{k})\right|^2 \mathrm{ctnh}\left(\frac{\hbar\omega_s(\boldsymbol{k})}{2k_\mathrm{B}T}\right) \tag{3.164}$$

and

$$\Gamma(\boldsymbol{q},\boldsymbol{R},t) = \tfrac{1}{2}\Omega\int\limits_{\hat{\Omega}} \frac{d^d k}{(2\pi)^d} \sum_{s=1}^{d} \frac{\hbar}{\omega_s(\boldsymbol{k})} \left|\boldsymbol{q}\cdot\mathbf{e}_s(\boldsymbol{k})\right|^2 \left\{ \left(n_s(\boldsymbol{k})+1\right)e^{i\boldsymbol{k}\cdot\boldsymbol{R}}e^{-i\omega_s(\boldsymbol{k})\,t} + n_s(\boldsymbol{k})\,e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\,e^{i\omega_s(\boldsymbol{k})\,t} \right\} \quad . \tag{3.165}$$

Expanding $e^{\Gamma} = 1 + \Gamma + \tfrac{1}{2}\Gamma^2 + \ldots$ in a power series, we have

$$S(\boldsymbol{q},\omega) = e^{-2W(\boldsymbol{q})}\left\{ \overbrace{\hat{\Omega}\,\delta(\omega)\sum_{\boldsymbol{G}}\delta(\boldsymbol{q}-\boldsymbol{G})}^{\text{zero phonons}} + \tfrac{1}{2}\int\limits_{\hat{\Omega}}\frac{d^d k}{(2\pi)^d}\sum_{s=1}^{d}\frac{\hbar}{\omega_s(\boldsymbol{k})}\left|\boldsymbol{q}\cdot\mathbf{e}_s(\boldsymbol{k})\right|^2 \times \right. \tag{3.166}$$

$$\left. \left[\overbrace{n_s(\boldsymbol{k})\,\delta\big(\omega+\omega_s(\boldsymbol{k})\big)\sum_{\boldsymbol{G}}\delta(\boldsymbol{q}+\boldsymbol{k}-\boldsymbol{G})}^{\text{single phonon absorption}} + \overbrace{\left(n_s(\boldsymbol{k})+1\right)\delta\big(\omega-\omega_s(\boldsymbol{k})\big)\sum_{\boldsymbol{G}}\delta(\boldsymbol{q}-\boldsymbol{k}-\boldsymbol{G})}^{\text{single phonon emission}} \right] + \ldots \right\} \quad .$$

Here we have labeled the terms corresponding to zero phonon processes, in which the entire lattice recoils elastically, and single phonon absorption and emission processes. The ellipses contain terms corresponding to multiphonon processes. The fact that processes in which a phonon is created (emitted) are proportional to $n_s(\boldsymbol{k})+1$, while processes in which a phonon is destroyed (absorbed) are proportional to $n_s(\boldsymbol{k})$ is a consequence of detailed balance. Satisfying the Dirac delta functions for the single phonon processes, we may write

$$S(\boldsymbol{q},\omega) = e^{-2W(\boldsymbol{q})}\left\{ \overbrace{\hat{\Omega}\,\delta(\omega)\sum_{\boldsymbol{G}}\delta(\boldsymbol{q}-\boldsymbol{G})}^{\text{zero phonons}} + \sum_{s=1}^{d}\frac{\hbar}{2\omega_s(\boldsymbol{q})}\left|\boldsymbol{q}\cdot\mathbf{e}_s(\boldsymbol{q})\right|^2\left[\overbrace{n_s(\boldsymbol{q})\,\delta\big(\omega+\omega_s(\boldsymbol{q})\big)}^{\text{single phonon absorption}} \right. \right.$$

$$\left. \left. + \overbrace{\left(n_s(\boldsymbol{q})+1\right)\delta\big(\omega-\omega_s(\boldsymbol{k})\big)}^{\text{single phonon emission}} \right] + \ldots \right\} \quad . \tag{3.167}$$

3.3.4   Debye-Waller Factor

The term $e^{-2W(\boldsymbol{q})}$ is called the Debye-Waller factor. Note that

$$2W(\boldsymbol{q}) = \big\langle \left(\boldsymbol{q}\cdot\boldsymbol{u}(\boldsymbol{R})\right)^2 \big\rangle_T = \Omega\int\limits_{\hat{\Omega}}\frac{d^d k}{(2\pi)^d}\sum_{s=1}^{d}\frac{\hbar}{\omega_s(\boldsymbol{k})}\left|\boldsymbol{q}\cdot\mathbf{e}_s(\boldsymbol{k})\right|^2\,\mathrm{ctnh}\left(\frac{\hbar\omega_s(\boldsymbol{k})}{2k_\mathrm{B}T}\right) \quad . \tag{3.168}$$

We may approximate the angular integral

$$\int \frac{d\hat{\boldsymbol{k}}}{4\pi} \, \big|\boldsymbol{q} \cdot \mathbf{e}_s(\boldsymbol{k})\big|^2 \approx \tfrac{1}{3}\boldsymbol{q}^2 \big|\hat{\boldsymbol{q}} \cdot \mathbf{e}_s(\boldsymbol{k})\big|^2 = \frac{\boldsymbol{q}^2}{3M} \quad , \tag{3.169}$$

where M is the ionic mass. We then obtain

$$2W(\boldsymbol{q}) \approx \frac{\boldsymbol{q}^2}{3M} \int\limits_0^\infty d\omega \, g(\omega) \, \frac{\hbar}{2\omega} \, \mathrm{ctnh}\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right) \quad , \tag{3.170}$$

where $g(\omega)$ is the total phonon density of states. Within the Debye model in $d = 3$ dimensions,

$$g_{\mathsf{Debye}}(\omega) = \frac{9\omega^2}{\omega_{\mathsf{D}}^2} \, \Theta(\omega_{\mathsf{D}} - \omega) \quad , \tag{3.171}$$

For $k_{\mathrm{B}}T \ll \hbar\omega_{\mathsf{D}}$, we find

$$2W(\boldsymbol{q}) = \frac{3\hbar\boldsymbol{q}^2}{4M\omega_{\mathsf{D}}}\left\{1 + \frac{2\pi^2}{3}\left(\frac{k_{\mathrm{B}}T}{\hbar\omega_{\mathsf{D}}}\right)^2 + \dots\right\} \quad , \tag{3.172}$$

while for $k_{\mathrm{B}}T \gg \hbar\omega_{\mathsf{D}}$ we obtain

$$2W(\boldsymbol{q}) = \frac{3\hbar\boldsymbol{q}^2}{M\omega_{\mathsf{D}}} \cdot \frac{k_{\mathrm{B}}T}{\hbar\omega_{\mathsf{D}}} \quad . \tag{3.173}$$

We see that $W(\boldsymbol{q})$ increases linearly with T, and that as $T \to 0$ it approaches a constant, given by $W_{T=0}(\boldsymbol{q}) = 3\hbar\boldsymbol{q}^2/8M\omega_{\mathsf{D}}$. The $\boldsymbol{q}$-dependence has the effect of reducing the intensity of large $|\boldsymbol{q}|$ processes relative to small $|\boldsymbol{q}|$ processes. One noteworthy feature is that finite temperature fluctuations *do not* smooth out the Bragg peaks in $\sum_{\boldsymbol{G}} \delta(\boldsymbol{q} - \boldsymbol{G})$. Rather, the Bragg peaks at each reciprocal lattice vector $\boldsymbol{G}$ are simply reduced in intensity by the Debye-Waller factor $e^{-2W(\boldsymbol{G})}$. Note that $W(\boldsymbol{q})$ does not vanish at $T = 0$, due to *quantum fluctuations* of the ionic positions. In a one-dimensional lattice, these fluctuations are strong enough to melt the lattice and destroy long-ranged positional order.

3.3.5   The Mössbauer effect

Suppose a stationary ion (or atom) of mass M radiates and decays from an excited state with energy $E = E_1$ to its ground state at $E = E_0$. A photon of energy $\varepsilon = h\nu$ and momentum $p = h\nu/c$ is emitted in the process. This results in a recoil of the ion with energy $R = (h\nu/c)^2/2m$. Thus, energy conservation requires

$$E_1 = E_0 + h\nu + R \quad \Rightarrow \quad h\nu = \Delta E - \frac{(h\nu)^2}{2Mc^2} \simeq \Delta E - \frac{(\Delta E)^2}{2Mc^2} \quad , \tag{3.174}$$

where $\Delta E = E_1 - E_0$, assuming $Mc^2 \gg \Delta E$. In ^{57}Fe, for example, we have $\Delta E = 14.4\,\mathrm{keV}$ and $Mc^2 = 53.3\,\mathrm{GeV}$, and the recoil energy is $R \approx 1.96\,\mathrm{meV}$. If the photon is reabsorbed by another ^{57}Fe nucleus in its ground state, then the energy change is

$$\Delta E' = \Delta E - \frac{(h\nu)^2}{2Mc^2} \simeq \Delta E - \frac{(\Delta E)^2}{Mc^2} \quad , \tag{3.175}$$

and we have $\Delta E - \Delta E' = 2R = 3.91\,\mathrm{meV}$. This is small, but still much greater than the natural linewidth of the transition, which is $\Gamma = 4.6 \times 10^{-9}\,\mathrm{eV}$. So the resonant absorption should never happen. Except that it is indeed observed, as first shown by Mössbauer in 1958 in an experiment for which he won the Nobel Prize in Physics in 1961[9]. The reason is that in a crystal there are zero phonon processes in which the entire lattice recoils, hence $R = (h\nu)^2/2NMc^2$, where N is the number of unit cells of the crystal, which is thermodynamically large, *i.e.* $R = 0$ for all intents and purposes. In addition, by using a moving source, the Doppler shift may be used to probe the structure of the absorption line. The Doppler shifted frequency is

$$\omega' = \frac{\omega - \boldsymbol{v} \cdot \boldsymbol{k}}{\sqrt{1 - \frac{v^2}{c^2}}} = \omega - \boldsymbol{v} \cdot \boldsymbol{k} + \mathcal{O}(v^2/c^2) \quad . \tag{3.176}$$

If we take $\boldsymbol{v} \parallel \boldsymbol{k}$ then we have $\delta\omega = vk$ and $\hbar\,\delta\omega = (v/c) \cdot \hbar ck \approx (v/c)\Delta E$. Setting $\hbar\,\delta\omega = \Gamma$, we obtain $v = 0.01\,\mathrm{cm/s}$ – a very small velocity compared with c indeed! Since the Debye-Waller factor involves the ratio $\hbar\boldsymbol{q}^2/2M\omega_{\mathrm{D}} = (h\nu)^2/2Mc^2\hbar\omega_{\mathrm{D}}$, where the Debye energy $\hbar\omega_{\mathrm{D}}$ is on the order of millivolts, only low energy atomic γ-transitions yield observable Mössbauer effects.

---

[9]Mössbauer used a ^{191}Os source and a ^{191}Ir absorber.