Lecture 8 — Anharmonic effects in crystals.

1 Introduction

Most of the effects related to lattice dynamics that you have so far encountered in this course and in previous courses — lattice specific heat, Debye-Waller factors, thermal diffuse scattering etc., could be very well interpreted in terms of the harmonic theory of the crystal lattice. Indeed, deviation from the harmonic expression for the Debye-Waller factors ($W \propto q^2$) are only really significant at high temperatures, and so is the anharmonic correction to the expression for the phonon specific heat. In this lecture, we will focus our attention on two effects that can be observed at all temperatures, and that can only be explained within the dynamical theory of the crystal lattice by invoking anharmonic terms in the lattice energy.

Anharmonic terms lead to a lattice potential energy of the form:

$$U = U^{eq} + \sum_{n=2}^{\infty} \frac{1}{n!} \sum_{\mathbf{R}_1 \ldots \mathbf{R}_n} D^{(n)}_{\mu_1 \ldots \mu_n} \left(\mathbf{R}_1 \ldots \mathbf{R}_n \right) u_{\mu_1}(\mathbf{R}_1) \ldots u_{\mu_n}(\mathbf{R}_n) \tag{1}$$

where the term with $n = 2$ is the familiar harmonic term. It is customary to retain terms up to $n = 4$, mainly because the cubic term is unbound from below. In many cases, however, stopping the series at $n = 3$ in the small-displacements limit still yields sensible results.

It may come as a surprise to learn that the ubiquitous phenomenon of **thermal expansion** cannot be explained within the harmonic theory of the crystal lattice. The reason, as we shall see, is that the *pressure of a gas of harmonic phonons is temperature-independent*, since the phonon frequency does not depend on the amplitude of the oscillations. However, by introducing an anharmonic term, the phonon gas acquires a finite temperature-dependent pressure, which is ultimately responsible for the thermal expansion of the crystal.

Another physical effect that requires phonon anharmonicity as a key ingredient is **thermal conductivity**. In a perfect crystal of an insulators, **harmonic phonons would never be scattered**, so such a crystal would have infinite thermal conductivity at all temperatures. Scattering of phonons from lattice imperfections would produce a finite thermal conductivity, but with a completely wrong temperature dependence. The only way to explain the data is to admit that **phonons can be scattered by other phonons**, and this can only occur by abandoning the harmonic approximation.

As we shall see, only certain phonon-phonon scattering processes, known as **umklapp processes**

can affect the thermal conductivity. This stems from the fact that **real momentum and crystal momentum are separately conserved quantities**. For the phonon gas in an insulator (or by the phonon and electron gasses in a metal), crystal momentum is conserved to within $\hbar$ times a RL vector. However, **the phonon gas can exchange total momentum with the center-of-mass momentum of the crystal** (and with particles, such as neutrons, that are scattered in and out of the crystal). **Umklapp processes**, for which the total momentum of the interacting phonons is not conserved, are the only ones capable to affect the conduction of heat.

As an introduction to the subject of anharmonicity, we will review the important issue of real momentum and crystal momentum conservation. Our treatment will follow that of Ashcroft and Mermin, Appendix M [1], but we will use some of the results and notation from the previous lectures. Thermal expansion and thermal conductivity of insulators are also discussed in details in Ashcroft and Mermin, Chapter 25 [1].

2 Real momentum and crystal momentum conservation

2.1 Symmetry considerations

In the previous lectures, we have seen that all the translation operators act on normal modes as:

$$t\left[u(\boldsymbol{R}_i)\right] = e^{-i\boldsymbol{k}\cdot\boldsymbol{t}}[u(\boldsymbol{R}_i)] \tag{2}$$

where t is a symmetry translation and the $u(\boldsymbol{R}_i)$ will, in general, be complex modes. Eq. 2 will in general be true also for **wavefunctions**, as they also represent a linear space, provided that the system as a whole has translational symmetry. We can therefore introduce the quantum mechanical operator $T_{\mathbf{R}}$ (R being a real lattice vector), and we can always find a complete set of wavefunctions so that

$$T_{\mathbf{R}}\psi = e^{\boldsymbol{K}\cdot\boldsymbol{R}}\psi \tag{3}$$

The capital $\boldsymbol{K}$ in eq. 3 is deliberate, as we shall see shortly. Note that $T_{\mathbf{R}}$ is not Hermitian (it has complex eigenvalues).

The next step is to look at the symmetry of the Hamiltonian. When we say that "the system possesses translational symmetry" we may mean two things: that the Hamiltonian containing coordinates shifted by R is the same operator as the original Hamiltonian or that if ψ_i is an eigenstate of H, $T_{\mathbf{R}}\psi_i$ is also an eigenstate with the same eigenvalue. We can convince ourselves

that in fact these two statements are identical, provided that we define the "shifted" Hamiltonian as:

$$H(\mathbf{r} + \mathbf{R}) = T_{\mathbf{R}} H T_{\mathbf{R}}^{-1} = T_{\mathbf{R}} H T_{-\mathbf{R}} \tag{4}$$

The translational symmetry condition is thus expressed with the statement that H commutes with T_R for all symmetry translations:

$$T_{\mathbf{R}} H(\mathbf{r}) T_{-\mathbf{R}} = H(\mathbf{r}) \tag{5}$$

Since H commutes with $T_{\mathbf{R}}$, we can always find a set of common eigenvectors for both operators so that

$$T_{\mathbf{R}} \psi_i = e^{i\boldsymbol{K}\cdot\boldsymbol{R}} \psi_i \tag{6}$$

holds with ψ_i being eigenvectors of the Hamiltonian.

It is obvious that if ψ_i is a single-particle Block state, $\boldsymbol{K}$ is the same thing as Bloch wavevector $\mathbf{k}$ we have previously introduced. It is also quite clear that if ψ_i describes a set of n Bloch-state non-interacting bosons or fermions

$$\boldsymbol{K} = \sum_i \mathbf{k}_i \tag{7}$$

where the $\mathbf{k}_i$ are the individual Bloch wavevectors of each particle. We can therefore call $\hbar\boldsymbol{K}$ the **total crystal momentum**. This is because we can write explicitly the n-particle wavefunction as a *symmetrised* or *antisymmetrised* **product** of 1-particle wavefunctions. It can be shown that eq. 7 represents a completely general result, which is valid even in the interacting case (non-separable wavefunction) and, in particular, in the case of **anharmonic lattice vibrations**, where the phonon number is not a constant of the motion. In fact, one can prove the general equation:

$$T_{\mathbf{R}} a_{\mathbf{k},j}^\dagger T_{-\mathbf{R}} = e^{i\mathbf{k}\cdot\mathbf{R}} a_{\mathbf{k},j}^\dagger \tag{8}$$

from which one can prove straightforwardly by induction

$$T_{\mathbf{R}} \prod_{i,j} a_{\mathbf{k}_i,j}^\dagger |0> = e^{i(\sum_i \mathbf{k}_i)\cdot\mathbf{R}} \prod_{i,j} a_{\mathbf{k}_i,j}^\dagger |0> \tag{9}$$

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We can also write

$$T_{\mathbf{R}} = e^{i\frac{1}{\hbar}\hat{\mathcal{K}}\cdot\mathbf{R}} \tag{10}$$

where $\hat{\mathcal{K}}$ is the **total crystal momentum operator** (we have use the hat to indicate that it is an operator), the definition of which should now be obvious when applied to a generic n-particle state or linear combination thereof.

2.2 Conservation of the total crystal momentum

2.2.1 Non-interacting particles

As we have just seen, if translational symmetry is present, the Hamiltonian commutes with the translation operator $e^{i\hat{\mathcal{K}}\cdot\mathbf{R}}$ for a given set of particles, e.g., electrons and phonons. This means that $e^{i\mathbf{K}\cdot\mathbf{R}}$ **is a constant of the motion** — if it has a definite value in the initial state, it must have the same value subsequently. Also, since this is true for all lattice translations $\mathbf{R}$, it must be true that:

$$\mathbf{K}_i = \mathbf{K}_f + \hbar\boldsymbol{\tau} \tag{11}$$

where $\boldsymbol{\tau}$ is a **Reciprocal Lattice Vector**. in other words

> **Crystal momentum is conserved to within $\hbar$ times a RL vector.**

If more than one set of Bloch non-interacting particles is present, this statement is true for each set individually, as the operators $\hat{\mathcal{K}}$ for each set all commute with the Hamiltonian.

2.2.2 Interacting Bloch particles

If an interaction term between different particles is present in the Hamiltonian, the crystal momenta of each set of particles will not, in general, be conserved, but **the total crystal momentum for all particles will be conserved to within $\hbar$ times a RL vector**. This is because the interaction term will in have the form:

$$\sum_{i,n} w\left(\mathbf{r}_i - \mathbf{R}_n - \mathbf{u}(\mathbf{R}_n)\right) \tag{12}$$

where the $\mathbf{r}_i$'s are the coordinates of the particles (e.g., electrons) and $\mathbf{R}_n + \mathbf{u}(\mathbf{R}_n)$ is the position of the nucleus at the lattice node n. This term is clearly invariant, for example by:

$$
\begin{aligned}
\mathbf{r}_i &\rightarrow \mathbf{r}_i + \mathbf{a}_1 \\
\mathbf{u}(\mathbf{R}_n) &\rightarrow \mathbf{u}(\mathbf{R}_{n-1})
\end{aligned}
\tag{13}
$$

We may stop for a second and ponder the significance of eq. 13 — particularly the second line, which indicates the crystal symmetry translation by one lattice unit. The consequence of this is:

> **For interacting Bloch particles, the sum of the crystal momenta is conserved to within $\hbar$ times a RL vector.**

2.2.3 Interaction with external particles

In absorption, emission and scattering experiments, there will be one or more particles which will, in their initial state, final state or both, travel far away from the crystal, so that the interaction terms with the crystal will be negligible. In these states, the operator $\hat{\mathcal{K}}$ for these particles will be nothing other than the **total real momentum**. Therefore, we can conclude that

> **For a system of Bloch particles interacting with themselves and with "external" particles, the sum of the crystal momenta of the Block particles and the real momenta of the external particles is conserved to within $\hbar$ times a RL vector.**

2.3 Normal and umklapp processes

As we have seen, the total crystal momentum (plus the real momenta of the external particles) is in general conserved to within $\hbar$ times a RL vector. One implication is that **we can always define *each* of the crystal momenta within the first Brillouin zone** (by contrast, the real momenta have an absolute significace to within an overall factor accounting from the centre-of-mass velocity). Once we have done this we can define:

> *Normal* **processes are the ones for which the crystal momentum conservation holds exactly, i.e., the additional RL vector is zero.**
> *Umklapp* **processes are the ones for which the crystal momentum conservation holds to within a *finite* RL vector times $\hbar$.**

2.4 Conservation of the total *real* momentum and energy

As we anticipated, the total *real* momentum of the crystal plus all the external particles is conserved, in the absence of external forces. This conservation arises from a *different* invariance, this time infinitesimal — the invariance by translation of all the coordinates by an arbitrary vector $\mathbf{r}$:

$$
\begin{aligned}
\mathbf{r}_i &\rightarrow \mathbf{r}_i + \mathbf{r} \\
\mathbf{R}_n &\rightarrow \mathbf{R}_n + \mathbf{r} \\
\mathbf{u}(\mathbf{R}_n) &\rightarrow \mathbf{u}(\mathbf{R}_n + \mathbf{r})
\end{aligned}
\tag{14}
$$

Again, it is important to recognise the difference between eq. 13 and eq. 14 even when $\mathbf{r} = \mathbf{R}$ (a real lattice vector). It is not difficult to see that this difference amounts to **a translation of the center of mass of the crystal by** $\mathbf{R}$. Two important consequences of this are (we skip the detailed demonstrations):

> *Normal processes conserve real momentum.* **In an *umklapp* process, the additive term** $\hbar\tau$ **corresponds to real momentum transferred to the center of mass of the crystal.**

An interesting implication arises when one considers the possibility of selecting different unit cells (i.e., different Brillouin zones) in certain crystal systems (triclinic, monoclinic). The possibility arises that a process that is classified as normal in one setting may be umklapp in the other. This amounts to a different repartition of the total momentum between the phonon system and the center of mass, and is of no physical consequence, as expected.

2.4.1 Energy conservation

As we have seen, in umklapp processes *real* momentum is transferred to the crystal as a whole. However, because of the large mass of the crystal, **real momentum transfer to the whole crystal implies essentially no energy transfer**. In other words,

> **Total energy is conserved in both normal and umklapp processes.**

3 Thermal expansion

Let us know examine the phenomenon of thermal expansion, and show that it is related in a fundamental way to the anharmonicity of the lattice interaction potential. Let us recall the important

thermodynamic expression for the pressure:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{15}$$

where F is the Helmholtz free energy given by

$$F = U - TS \tag{16}$$

When applied to a solid, eq. 15 states that the **equilibrium state for a solid (e.g., at ambient pressure) is reached when the external pressure exactly balances the volume derivative of the free energy at a given temperature.**

The Helmholtz free energy of an insulator has two contributions:

- The equilibrium energy U_0 of the crystal lattice, i.e., the energy of the "springs" in their equilibrium positions. By definition, $P_0 = \frac{\partial U_0}{\partial V}$ is *temperature independent*:

$$\frac{\partial P_0}{\partial T} = \frac{\partial^2 U_0}{\partial V \partial T} = 0 \tag{17}$$

- The energy and entropy term for the **phonon system**. The volume derivative of this part of the Helmholtz free energy can be considered to be the **pressure of the phonon gas P_{ph}**.

The calculation os P_{ph} in the general case (including anharmonicity) is not difficult but is rather lengthy, and is reported in Appendix I. Here, we will assume the result as given and proceed with the derivation of the **linear thermal expansion coefficient**:

$$\alpha = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{3V}\frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} \tag{18}$$

Eq. 18 is obtained by recognising that T, P and V are linked by the **equation of state**

$$f(T, P, V) = 0 \tag{19}$$

taking the *total* derivatives with respect to each variable and solving the resulting determinant equation.

Using the definition of the **bulk modulus** (inverse compressibility):

$$B = -V \left(\partial P / \partial V \right)_T \tag{20}$$

eq. 18 becomes:

$$\alpha = \frac{1}{3B} \left(\frac{\partial P}{\partial T} \right)_V = \frac{1}{3B} \left(\frac{\partial P_{ph}}{\partial T} \right)_V \tag{21}$$

where we have used eq. 17.

We now write the phonon gas pressure:

$$P_{ph} = -\frac{\partial}{\partial V} \left[\frac{1}{2} \sum_{\boldsymbol{k},s} \hbar \omega_s(\boldsymbol{k}) \right] + \sum_{\boldsymbol{k},s} \left(-\hbar \frac{\partial \omega_s(\boldsymbol{k})}{\partial V} \right) \frac{1}{e^{\beta \hbar \omega_s(\boldsymbol{k})} - 1} \tag{22}$$

The first term is the volume derivative of the zero-point energy; it is **temperature independent** and can be ignored for the calculation of the thermal expansion coefficient. The second term depends on temperature through the phonon population $n_s(\mathbf{k}) = (exp(\beta \hbar \omega_s(\boldsymbol{k})) - 1)^{-1}$, but **is non-zero only if at least some the phonon frequencies depend on volume.** Note that **if all the phonon frequencies are volume-independent, there is an exact cancellation between energy en entropy terms, so that only the zero-point energy survives**.

In analogy with case of the single oscillator, we can conclude that:

> **If the lattice potential is harmonic, the phonon frequencies are volume-independent, and the thermal expansion coefficient is zero at all temperatures.**

From here onward, we follow closely the treatment by Ashcroft and Mermin. In order to describe the experimental data, it is therefore necessary to go beyond the harmonic approximation. We can write

$$\alpha = \frac{1}{3B} \sum_{\boldsymbol{k},s} \left(-\frac{\partial \hbar \omega_s(\boldsymbol{k})}{\partial V} \right) \frac{\partial}{\partial T} n_s(\mathbf{k}) \tag{23}$$

Remembering the expression for the specific heat:

$$c_V = \sum_{\boldsymbol{k},s} \frac{\hbar \omega_s(\boldsymbol{k})}{V} \frac{\partial}{\partial T} n_s(\mathbf{k}) \tag{24}$$

it is natural to define the **contribution to individual phonon modes to the specific heat**:

$$c_{vs}(\boldsymbol{k}) = \frac{\hbar\omega_s(\boldsymbol{k})}{V}\frac{\partial}{\partial T}n_s(\mathbf{k}) \tag{25}$$

the so-called **partial Grüneisen parameter** — related to the anharmonicity of individual phonons:

$$\gamma_{\boldsymbol{k}s} = -\frac{V}{\omega_s(\boldsymbol{k})}\frac{\partial\omega_s(\boldsymbol{k})}{\partial V} = -\frac{\partial(\ln\omega_s(\boldsymbol{k}))}{\partial(\ln V)} \tag{26}$$

and the **overall Grüneisen parameter**

$$\gamma = \frac{\sum_{\boldsymbol{k},s} c_{vs}(\boldsymbol{k})\gamma_{\boldsymbol{k}s}}{\sum_{\boldsymbol{k},s} c_{vs}(\boldsymbol{k})} \tag{27}$$

With these definitions, the thermal expansion coefficient is written as

$$\alpha = \frac{\gamma c_v}{3B} \tag{28}$$

 Note that γ **is dimensionless, and for typical materials is** *positive* **(springs become stiffer as the volume is reduced) and is usually of the order of unity, although it can be much larger and sometimes** *negative* **in special cases**.

3.1   Example 1: the Debye model

In most material, thermal expansion at low temperatures is dominated by the anharmonicity of the acoustic phonons. We can therefore calculate the thermal expansion coefficient using the Debye model.

In the Debye model, all the phonon frequencies scale linearly with the Debye frequency:

$$\omega(\boldsymbol{k}) = \omega_D\frac{k}{(6\pi^2 n)^{1/3}} \tag{29}$$

where n is the number of unit cell per unit volume. Therefore

$$\gamma_D = -\frac{\partial(\ln \omega_D)}{\partial(\ln V)} \tag{30}$$

and

$$\gamma = \gamma_D \frac{c_{vD}}{c_v} \tag{31}$$

where we recall the expression for the Debye specific heat

$$c_{vD} = 9nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2} \tag{32}$$

3.2 Example 2: the Einstein model

For some materials, the thermal expansion is certain temperature ranges is dominated by the anharmonicity of a single optical branch. This may occur near phase transitions, where part of the optical branch goes soft, or in particular geometries admitting the so-called "rigid unit modes" — anomalously soft and anharmonic optical phonons. In this, case, one can employ the Einstein model with:

$$\gamma_E = -\frac{\partial(\ln \omega_E)}{\partial(\ln V)} \tag{33}$$

and the Einstein specific heat for a *single* branch:

$$c_{vE} = \sum_{\boldsymbol{k},s} c_{vE}(\mathbf{k}) = nk_B \frac{x^2 e^x}{(e^x - 1)^2} \tag{34}$$

where $x = \Theta_E/T$. Therefore

$$\boxed{\gamma = \gamma_E \frac{c_{vE}}{c_v}} \tag{35}$$

Debye and Einstein models can be combined to give a better description of the thermal expansion in all temperature ranges.

3.3 Thermal expansion in metals

The previous derivation of the thermal expansion coefficient only strictly applied to insulators, since it only took into account the pressure of the phonon gas. It is natural to extend this to metals by including the pressure of the electron gas. It is an elementary result of the Sommerfeld theory of metals that:

$$
\begin{aligned}
P_{el} &= \frac{2}{3}\frac{U_{el}}{V} \\
\left(\frac{\partial P_{el}}{\partial T}\right)_V &= \frac{2}{3}c_v^{el}
\end{aligned}
\tag{36}
$$

The complete expression of the linear thermal expansion coefficient is therefore

$$\boxed{\alpha = \frac{1}{3B}\left(\gamma c_v^{ph} + \frac{2}{3}c_v^{el}\right)} \tag{37}$$

In assessing the relative importance of the two terms, it is important to remember that typically $\gamma \approx 1$ and that, in the Debye model:

$$\boxed{\frac{c_v^{el}}{c_v^{ph}} = \frac{5}{24\pi^2}Z\frac{\Theta_D^3}{T^2 T_F}} \tag{38}$$

where Z is the nominal valence of the metal. When evaluated numerically, eq. 38 leads to the conclusion that the pressure of the electron gas contributes significantly to the thermal expansion only below $\sim 10K$. The main difference in the thermal expansion of insulators and metals is therefore in the low-temperature behaviour: $\propto T^3$ for insulators, $\propto T$ for metals.

4 Lattice thermal conductivity

In this section, we will consider in some detail the phenomenon of thermal conductivity in insulators. As we shall see, the experimental data can only be explained by considering phonon-phonon scattering, and assuming that umklapp processes alone contribute to the thermal mean free path. Before discussing the specific subject of phonon thermal conductivity, we will provide a short introduction to the elementary theory of thermal transport, with an emphasis on the comparison between different transport phenomena. Although far from being numerically accurate, these considerations provide good order-of-magnitude assessments and a good way to "think about" these problems. A complete treatment of transport phenomena (with an emphasis on metals) in the semiclassical approximation is given in Ashcroft and Mermin [1] chapter 13.

4.1 An elementary guide to thermal transport theory

All transport phenomena (mass transport, charge transport, spin transport, heat transport) have in common some important features: they are **non-equilibrium, steady state phenomena**, and they are characterised by a **quantity that is being transported**, say Q, and a **transport speed** v. One defines a **current** as $j = (Q/V)v$ were V is the volume. For example, for charge transport the transported quantity is electric charge, so $Q/V = -en_e$ and the transport speed is the drift velocity $v_d = -eE\tau/m^*$, so that $j_e = e^2 n_e \tau/m^* E$. The conductivity (in this case, the electrical conductivity) is the ratio of the current and the "driving parameter" (E in this case). For thermal transport, the transported quantity is heat (or entropy) and the velocity is that of the particles that transport the entropy. However, as we said right at the beginning, transport is essentially a non-equilibrium phenomenon: whereas an electron retain its charge after a collision, **a particle releases its entropy when it reaches thermal equilibrium through collisions** (not all collisions are capable of this, as we shall see).
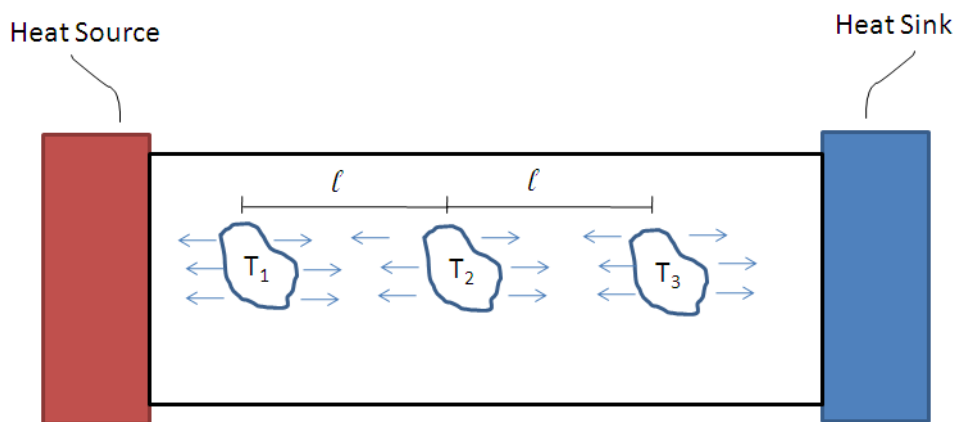

Figure 1: Schematic representation of thermal transport.

Let us look at the scheme shown in fig. 1 (for complete rigour, we consider 3 domains in a somewhat pedestrian argument; typical phonon mean free paths at RT are a few tens of nm). The entropy per unit volume at each point is given by:

$$s = \int_0^T dT \frac{c_v}{T} \tag{39}$$

The entropy balance at the mid position T_2 is given by the entropy flowing *in* the domain and released therein minus that flowing *out*:

$$
\begin{aligned}
\Delta s_{in} &= \frac{1}{2}(s_1 + s_3) \\
\Delta s_{out} &= s_2 \\
\Delta s_{tot} &= \frac{1}{2}\frac{c_v}{T}(T_1 - T_3) = \frac{c_v}{T} \mathit{l} \nabla T
\end{aligned}
\tag{40}
$$

where l is the mean free path. The transported quantity is the heat transfer per unit volume

$$\frac{Q}{V} = c_v \mathit{l} \nabla T \tag{41}$$

while the relevant velocity is the average 1-dimensional speed in the x direction — $v/3$. Note that we have made the approximation that the average velocities do not depend on temperature, which is about (but not exactly) correct for both phonons and electrons (but, of course, would be very wrong for bosons with a mass). Our discussion is summarised in tab. 1

Table 1: Various parameters relevant to thermal and electrical transport.

Transport	Transported quantity	Velocity	Current	Conductivity
Electrical	$-en_e$	$-eE\tau/m^*$	$e^2 n_e \tau/m^* E$	$\sigma = e^2 n_e \tau/m^*$
Phonon Thermal	$c_v^{ph} \mathit{l} \nabla T$	$c/3$	$\frac{1}{3}c_v^{ph} \mathit{l} c \nabla T$	$\kappa^{ph} = \frac{1}{3}c_v^{ph} \mathit{l} c$
Electron Thermal	$c_v^{el} \mathit{l} \nabla T$	$v_F/3$	$\frac{1}{3}c_v^{el} \mathit{l} v_F \nabla T$	$\kappa^{el} = \frac{1}{3}c_v^{el} \mathit{l} v_F$

The mean free path l and the relaxation time τ in eq 1 have in general a complex temperature dependence, making exact theory of transport a very difficult problem. However, we can write:

$$\mathit{l} = (n_s \Sigma)^{-1} \tag{42}$$

Where n_s is the density of scatterers and Σ is the scattering cross section; this simply shifts the problem to determining the temperature (or energy) dependence of the cross section.

Note that, in the free electron model

$$c_v^{el} = n_e k_B \frac{\pi^2}{2} \left(\frac{k_B T}{\mathcal{E}_F} \right) = n_e k_B \pi^2 \left(\frac{k_B T}{m^* v_F^2} \right) \tag{43}$$

and $\ell = v_F \tau$, so the electronic thermal conductivity becomes:

$$\kappa^{el} = \frac{n_e \tau}{m^*} \frac{\pi^2}{3} k_B^2 T \tag{44}$$

whence the famous **Wiedemann-Franz law**:

$$\kappa^{el} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T \sigma \tag{45}$$

In other words, the ratio between electrical and electronic thermal conductivities does not depend on any materials-specific parameter, and should be the same (within the employed approximations) for all materials.

4.2 Thermal conductivity due to phonons

Keeping in mind the result we obtain for the phonon thermal conductivity in tab. 1, it should now be easy to predict the temperature dependence of the thermal conductivity due to phonons (i.e., in insulating materials) within the framework of the harmonic model. In a perfect crystal, harmonic phonons would propagate without hinderance as free particles; furthermore, in an insulator, we have removed the possibility for them to scatter off electrons. We would therefore conclude that phonons can only be scattered by **crystal imperfections**, i.e., defects and, ultimately, the surfaces of the crystal themselves. Note that, in both cases, **real momentum is transferred between the phonons and the crystal as a whole**. These collisions are therefore efficient in thermalising the phonon energy distribution and therefore in transferring entropy. On this basis, taking Σ as a constant, we can as a first approximation write $\ell \propto 1/n_d$ with n_d being the defect density. If n_d is very small, ℓ is eventually limited by the crystal size. In either case, **the harmonic approximation predicts that the phonon thermal conductivity should be proportional to the phonon specific heat**, that is, $\propto T^3$ at least up to temperatures where the optical phonons become important. In most materials, the relation $\kappa^{ph} \propto T^3$ should therefore hold in a wide domain up to a significant fraction of the Debye temperature.

The experimental situation is, however, rather different. The relation $\kappa^{ph} \propto T^3$ is indeed obeyed at very low temperatures (typically to $\sim 10K$), but **the lattice thermal conductivity drops rather abruptly above this temperature**. This is exemplified in fig. 2.
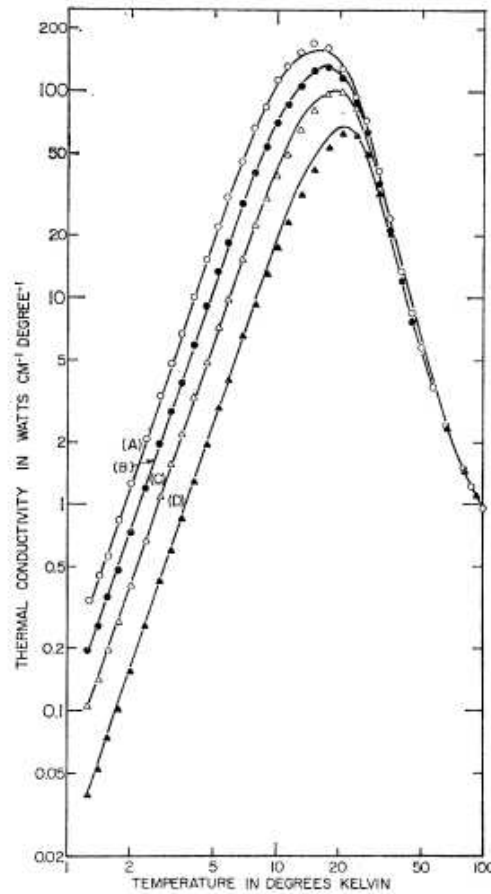

Figure 2: Thermal conductivity of isotopically pure LiF. The different curves at low temperatures correspond to different crystal sizes: (A) 7.25 mm, (B) 4.00 mm (C) 2.14 mm and (D) 1.06 mm. The figure is the same as in Ashcroft and Mermin, an is reproduced from P.D. Thacher, Phys. Rev. **156**, 957 (1967).

The crystals employed in the Thacher experiment (fig. 2) where very pure, so that the scattering from defects was negligible. Therefore, at low temperatures, we can clearly see the effect of crystal size, which determines the mean free path ℓ. In assessing the data, we have to acknowledge that, above $\sim 10K$ something starts scattering the phonons more than the crystal boundaries, and this can be nothing other than other phonons.

However, **we cannot simply assume that the mean free path is inversely proportional to the total density of phonons**, as it would seem logical. It is easy to see that this would give a completely wrong temperature dependence. In fact, in the Debye model, the low-temperature phonon density scales like T^3 (like the specific heat), so we would get $\ell^{ph} = const$. **We should therefore expect the thermal conductivity to have a "plateau" at the point where the phonon**

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mean free path becomes smaller than the crystal size. One way to reproduce the data is to introduce a **low-energy cutoff** for the phonons that contribute to reducing the mean free path. Phonons below this energy cut-off will be ineffective. This amounts to introduce a "density of effective phonons" (effective in reducing the mean free path). The total and "effective" phonon densities in the Debye model are:

$$
\begin{aligned}
n^{ph} &= 3n\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} dx\frac{x^2}{e^x-1} \\
n_{eff}^{ph} &= 3n\left(\frac{T}{\Theta_D}\right)^3 \int_{\Theta_C/T}^{\Theta_D/T} dx\frac{x^2}{e^x-1}
\end{aligned}
$$

(46)

where Θ_C is the cut-off temperature, and, as we shall see, is a significant fraction of room temperature. At low temperatures, $x \gg 1$ and we can ignore the additive term -1 in the denominator and (left as an exercise) we obtain

$$
n_{eff}^{ph} \propto e^{-\Theta_C/T}\left(\Theta_C/T+1\right)^2 \approx e^{-\Theta_C/T}\left(\Theta_C/T\right)^2
$$

(47)

In other words

> **With the introduction of a cut-off frequency, the number of "effective" phonons grows exponentially with temperature in the relevant low-temperature range.**

With the correct parameters, it is easy to see that the functional form in eq. 47, combined "in parallel" with the constant mean free path from defects or boundaries, will produce the observed peak in the thermal conductivity. In fact, the data in fig. 2 are fitted *quantitatively* with slightly more complex but analogous expression.

We still have to justify the introduction of the low-energy cut-off. Before doing that, let us take a brief look at the high-temperature thermal conductivity.

4.2.1 High-temperature phonon thermal conductivity

At high temperatures, the total number of phonons becomes $\propto T$, while the specific heat saturates (Dulong-Petit law). Therefore, one can easily predict that

> **At high temperatures, the thermal conductivity should decrease as $1/T$.**

This is in fact confirmed by experimental data. in fact, $\kappa^{ph} \propto 1/T^x$ where x is usually between one and two. The discrepancy is an indication that **not all phonons are equally effective in reducing the mean free path for entropy transfer.**

4.2.2 Umklapp processes and low-energy cut-off

The results of the previous section, and the last general statement in particular, can be understood by the fact that

> **Only unklapp processes can bring about the release of entropy and the attainment of thermal equilibrium.**

This can be simply understood by looking again at the diagram in fig. 1. Phonons that transfer entropy from T_1 to T_2 will carry a net crystal momentum, whereas phonons in thermal equilibrium will have $\sum_i \mathbf{k}_i = 0$

> **Since normal processes conserve crystal momentum exactly, they can never restore a thermal equilibrium configuration of crystal momenta.**

The low-energy cut-off arises naturally from the fact that only unklapp processes can reduce the mean free path. In fact, simple kinematics accounting for the simultaneous energy and crystal momentum conservation (the latter to within a non-zero RL vector) imposes that

> **The crystal momentum of *all* the phonons involved in an umklapp process must be a significant fraction of a non-zero reciprocal lattice vector. This means also that their energy must be a significant fraction of the Debye energy.**

This will be seen better in the following section.

4.2.3 Anharmonicity and phonon "collision" processes

in order to understand the kinematics of normal and umklapp processes, it is useful to think of them as phonon "collisions". The justification for this is not complex but goes beyond the scope of this lecture (for more detail, see Ashcroft and Mermin [1], especially Appendices L,M and O. In essence, one writes a perturbative anharmonic Hamiltonian in terms of the phonon raising and lowering operators.

- The harmonic part only contains the phonon counting operators $a_s^\dagger(\mathbf{k})a_s(\mathbf{k})$, which is read as the distruction of a single phonon of branch s and momentum $\mathbf{k}$ followed by the creation
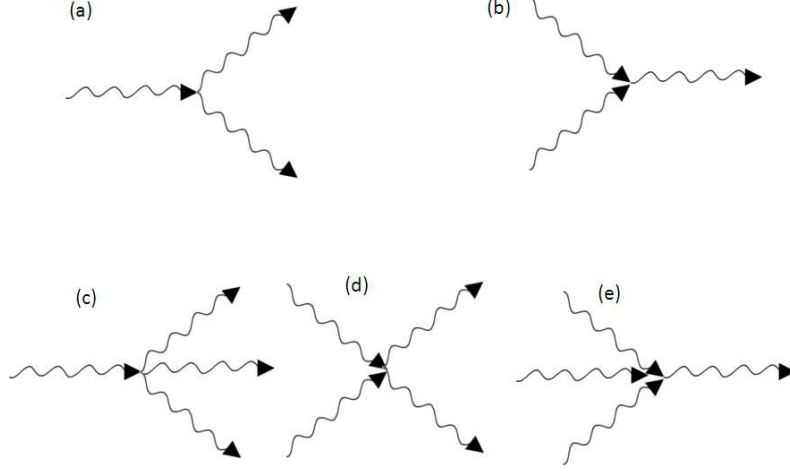
Figure 3: Multi-phonon processes enabled by cubic — (a) and (b)— and quartic —(c), (d) and (f) — terms in the Hamiltonian.

of the *same* phonon.

- The cubic term contains terms of the type $a^\dagger_{s_1}(\mathbf{k}_1)a^\dagger_{s_2}(\mathbf{k}_2)a_{s_3}(\mathbf{k}_3)$ (process (a) in fig. 3) and $a^\dagger_{s_1}(\mathbf{k}_1)a_{s_2}(\mathbf{k}_2)a_{s_3}(\mathbf{k}_3)$, where the three crystal momenta are bound by conservation of energy and momentum — for instance for (a):

$$
\begin{aligned}
\mathbf{k}_1 &= \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{K} \\
\omega_{s_1}(\mathbf{k}_1) &= \omega_{s_2}(\mathbf{k}_2) + \omega_{s_3}(\mathbf{k}_3)
\end{aligned}
\tag{48}
$$

- The quartic term contains terms of the type $a^\dagger_{s_1}(\mathbf{k}_1)a^\dagger_{s_2}(\mathbf{k}_2)a^\dagger_{s_3}(\mathbf{k}_3)a_{s_4}(\mathbf{k}_4)$ (process (c)), etc., where a conservation law similar to eq. 48 holds for the four crystal momenta.

It is important to understand that the conservation laws as in eq. 48 (particularly for the cubic term) are very restrictive, and, for acoustic phonons, only allow processes near the zone boundary .

For example, in 1 dimension and with a linear dispersion $\omega = ck$, the only allowed cubic (a) process would be

$$
\begin{aligned}
k_1 &= K/2 \\
k_2 &= k_3 = -K/4
\end{aligned}
\tag{49}
$$

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for which the incoming phonon is exactly at the zone boundary. The deviation from linear dispersion and the higher dimensionality lift this strict condition, but 3-phonon acoustic collisions remain restricted to the outer part of the Brillouin zone. Four-phonon collisions are less restricted, but are also less likely (at least at low temperatures), and still carry a low-energy cut-off.

References

[1] Neil W. Ashcroft and N. David Mermin, *Solid State Physics*, HRW International Editions, CBS Publishing Asia Ltd (1976)

5 Appendix I: The pressure of the phonon gas

Our starting point for the calculation of the pressure of the phonon gas is the Helmholtz free energy, defined as:

$$F = U - TS \tag{50}$$

We recall that F is the appropriate thermodynamic potential to calculate quantities at constant volume and temperature. Remembering that

$$
\begin{aligned}
dU &= -PdV + TdS \\
\left(\frac{\partial S}{\partial T}\right)_V &= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \\
dF &= -PdV - SdT \\
P &= -\left(\frac{\partial F}{\partial V}\right)_T
\end{aligned}
\tag{51}
$$

we can write the following expression for the pressure of the phonon gas:

$$P = -\frac{\partial}{\partial V}\left[U - T\int_0^T \frac{dT'}{T'}\frac{\partial}{\partial T'}U(T',V)\right] \tag{52}$$

where the integral term of eq. 52 is the *entropy*, (second line of eq. 51). The *energy* of the phonon gas is ($\beta = 1/k_B T$):

$$U = \frac{1}{2} \sum_{\boldsymbol{k},s} \hbar\omega_s(\boldsymbol{k}) + \sum_{\boldsymbol{k},s} \frac{\hbar\omega_s(\boldsymbol{k})}{e^{\beta\hbar\omega_s(\boldsymbol{k})} - 1} = U_0 + \tilde{U}(T) \tag{53}$$

where we have separated out the zero point energy, which does not depend on temperature and does not therefore contribute to the integral in eq. 52. We now focus on the integral term:

$$I = T \int_0^T \frac{dT'}{T'} \frac{\partial}{\partial T'} \tilde{U}(T') \tag{54}$$

To solve it, we introduce the variable x as:

$$x = \beta\hbar\omega_s(\boldsymbol{k}) \tag{55}$$

whence

$$
\begin{aligned}
\frac{dT'}{T'} &= -\frac{dx'}{x'} \\
\frac{\partial}{\partial T'} &= -\frac{k_B}{\hbar\omega_s(\boldsymbol{k})} x'^2 \frac{\partial}{\partial x'}
\end{aligned}
\tag{56}
$$

leading to

$$I = x \int_\infty^x dx' x' \frac{\partial}{\partial x'} \tilde{U}(x') \tag{57}$$

We can integrate by parts the limit at ∞ (T=0) yields zero because we removed the zero-point energy from $\tilde{U}$):

$$I = \tilde{U}(x) - \frac{1}{x} \int_\infty^x dx' \tilde{U}(x') = \tilde{U}(x) - \frac{1}{\beta} \int_\infty^x dx' \frac{1}{e^x - 1} \tag{58}$$

By writing

$$\frac{\partial}{\partial V} = \beta\hbar \frac{\partial\omega_s(\boldsymbol{k})}{\partial V} \frac{\partial}{\partial x} \tag{59}$$

we find

$$\frac{\partial I}{\partial V} = \frac{\partial \tilde{U}(x)}{\partial V} - \hbar \frac{\partial \omega_s(\boldsymbol{k})}{\partial V} \frac{\partial}{\partial x} \int_\infty^x dx' \frac{1}{e^x - 1} = \frac{\partial \tilde{U}(x)}{\partial V} - \hbar \frac{\partial \omega_s(\boldsymbol{k})}{\partial V} \frac{1}{e^x - 1} \qquad (60)$$

We can now reconstruct eq. 52:

$$P = -\frac{\partial}{\partial V} \left[U - T \int_0^T \frac{dT'}{T'} \frac{\partial}{\partial T'} U(T', V) \right] = -\frac{\partial U_0}{\partial V} - \hbar \frac{\partial \omega_s(\boldsymbol{k})}{\partial V} \frac{1}{e^x - 1} \qquad (61)$$

or also

$$P = -\frac{\partial}{\partial V} \left[\frac{1}{2} \sum_{\boldsymbol{k},s} \hbar \omega_s(\boldsymbol{k}) \right] + \sum_{\boldsymbol{k},s} \left(-\hbar \frac{\partial \omega_s(\boldsymbol{k})}{\partial V} \right) \frac{1}{e^{\beta \hbar \omega_s(\boldsymbol{k})} - 1} \qquad (62)$$