

# Chapter 5: Thermal Properties of Crystal Lattices

Debye

January 30, 2017

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In the previous chapter, we have shown that the motion of a harmonic crystal can be described by a set of decoupled harmonic oscillators.

$$H = \frac{1}{2} \sum_{\mathbf{k}, s} |\mathbf{P}_s(\mathbf{k})|^2 + \omega_s^2(\mathbf{k}) |\mathbf{Q}_s(\mathbf{k})|^2 \quad (1)$$

At a given temperature  $T$ , the occupancy of a given mode is

$$\langle n_s(\mathbf{k}) \rangle = \frac{1}{e^{\beta\omega_s(\mathbf{k})} - 1} \quad (2)$$

In this chapter, we will apply this information to calculate the thermodynamic properties of the ionic lattice, in addition to addressing questions regarding its long-range order in the presence of lattice vibrations (i.e. do phonons destroy the order). In order to evaluate the different formulas for these quantities, we will first discuss two matters of formal convenience.

## 1 Formalism

To evaluate some of these properties we can use the virial theorem and, integrals over the density of states.

### 1.1 The Virial Theorem

Consider the Hamiltonian for a quantum system  $H(\mathbf{x}, \mathbf{p})$ , where  $\mathbf{x}$  and  $\mathbf{p}$  are the canonically conjugate variables. Then the expectation value of any function of these canonically conjugate variables  $f(\mathbf{x}, \mathbf{p})$  in a stationary state (eigenstate) is constant in time. Consider

$$\begin{aligned} \frac{d}{dt} \langle \mathbf{x} \cdot \mathbf{p} \rangle &= \frac{i}{\hbar} \langle [H, \mathbf{x} \cdot \mathbf{p}] \rangle = \frac{i}{\hbar} \langle H\mathbf{x} \cdot \mathbf{p} - \mathbf{x} \cdot \mathbf{p}H \rangle \\ &= \frac{iE}{\hbar} \langle \mathbf{x} \cdot \mathbf{p} - \mathbf{x} \cdot \mathbf{p} \rangle = 0 \end{aligned} \quad (3)$$

where  $E$  is the eigenenergy of the stationary state. Let

$$H = \frac{p^2}{2m} + V(\mathbf{x}), \quad (4)$$

then

$$\begin{aligned}
0 &= \left\langle \left[ \frac{p^2}{2m} + V(\mathbf{x}), \mathbf{x} \cdot \mathbf{p} \right] \right\rangle \\
&= \left\langle \left[ \frac{p^2}{2m}, \mathbf{x} \cdot \mathbf{p} \right] + [V(\mathbf{x}), \mathbf{x} \cdot \mathbf{p}] \right\rangle \\
&= \left\langle \frac{1}{2m} [p^2, \mathbf{x}] \cdot \mathbf{p} + \mathbf{x} \cdot [V(\mathbf{x}), \mathbf{p}] \right\rangle
\end{aligned} \tag{5}$$

Then as  $[p^2, \mathbf{x}] = \mathbf{p} [p, \mathbf{x}] + [p, \mathbf{x}] \mathbf{p} = -2i\hbar \mathbf{p}$  and  $\mathbf{p} = -i\hbar \nabla_x$ ,

$$0 = \left\langle \frac{-i\hbar}{m} p^2 + i\hbar \mathbf{x} \cdot \nabla_x V(\mathbf{x}) \right\rangle \tag{6}$$

or, the Virial theorem:

$$2 \langle T \rangle = \langle \mathbf{x} \cdot \nabla_x V(\mathbf{x}) \rangle \tag{7}$$

Now, lets apply this to a harmonic oscillator where  $V = \frac{1}{2}m\omega^2 x^2$  and  $T = p^2/2m$ ,  $\langle H \rangle = \langle T \rangle + \langle V \rangle = \hbar\omega(n + \frac{1}{2})$  and . We get

$$\langle T \rangle = \langle V(\mathbf{x}) \rangle = \frac{1}{2} \hbar\omega(n + \frac{1}{2}) \tag{8}$$

Lets now apply this to find the RMS excursion of a lattice site in an elemental

lattice  $r = 1$

$$\begin{aligned}
\langle s^2 \rangle &= \frac{1}{N} \sum_{n,i} \langle s_{n,i}^2 \rangle \\
&= \frac{1}{N} \left\langle \sum_{n,i} \frac{1}{NM} \sum_{\mathbf{q},s,\mathbf{k},r} Q_s(\mathbf{q}) \epsilon_i^s(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_n} Q_r(\mathbf{k}) \epsilon_i^r(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}_n} \right\rangle \\
&= \frac{1}{N} \left\langle \sum_{n,i} \frac{1}{NM} \sum_{\mathbf{q},s,\mathbf{k},r} Q_s(\mathbf{q}) \epsilon_i^s(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_n} Q_r(-\mathbf{k}) \epsilon_i^r(-\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}_n} \right\rangle \\
&= \frac{1}{N} \left\langle \sum_{n,i} \frac{1}{NM} \sum_{\mathbf{q},s,\mathbf{k},r} Q_s(\mathbf{q}) \epsilon_i^s(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_n} Q_r^*(\mathbf{k}) \epsilon_i^{*r}(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}_n} \right\rangle \\
&= \frac{1}{NM} \sum_{\mathbf{q},s} \langle |Q_s(\mathbf{q})|^2 \rangle \\
&= \frac{1}{NM} \sum_{\mathbf{q},s} \frac{2}{\omega_s^2(\mathbf{q})} \left\langle \frac{1}{2} \omega_s^2(\mathbf{q}) |Q_s(\mathbf{q})|^2 \right\rangle \\
&= \frac{1}{NM} \sum_{\mathbf{q},s} \frac{2}{\omega_s^2(\mathbf{q})} \frac{1}{2} \hbar \omega_s(\mathbf{q}) \left( n_s(\mathbf{q}) + \frac{1}{2} \right) \\
\langle s^2 \rangle &= \frac{1}{NM} \sum_{\mathbf{q},s} \frac{\hbar}{\omega_s(\mathbf{q})} \left( n_s(\mathbf{q}) + \frac{1}{2} \right) \tag{9}
\end{aligned}$$

This integral, which must be finite in order for the system to have long-range order, is still difficult to perform. However, the integral may be written as a function of  $\omega_s(\mathbf{q})$  only.

$$\langle s^2 \rangle = \frac{1}{NM} \sum_{\mathbf{q},s} \frac{\hbar}{\omega_s(\mathbf{q})} \left( \frac{1}{e^{\beta\omega_s(\mathbf{q})} - 1} + \frac{1}{2} \right) \tag{10}$$

It would be convenient therefore, to introduce a density of phonon states

$$Z(\omega) = \frac{1}{N} \sum_{\mathbf{q},s} \delta(\omega - \omega_s(\mathbf{q})) \tag{11}$$

so that

$$\langle s^2 \rangle = \frac{\hbar}{M} \int d\omega Z(\omega) \frac{1}{\omega} \left( n(\omega) + \frac{1}{2} \right) \tag{12}$$

## 1.2 The Phonon Density of States

In addition to the calculation of  $\langle s^2 \rangle$ , the density of states  $Z(\omega)$  is also useful in the calculation of  $E = \langle H \rangle$ , the partition function, and the related thermodynamic properties

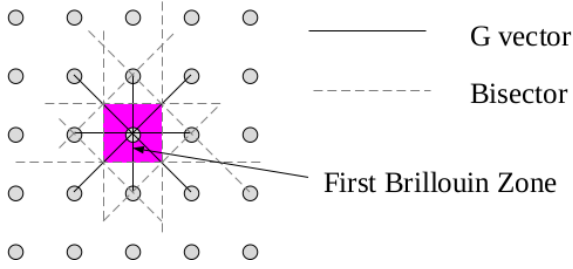


Figure 1: *First Brillouin zone of the square lattice*

lattice directions  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$ . Then, we want the Fourier representation to respect the periodic boundary conditions (pbc), so

$$e^{i\mathbf{q} \cdot (\mathbf{r} + N^{1/3}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3))} = e^{i\mathbf{q} \cdot \mathbf{r}} \quad (14)$$

This means that  $q_i = 2\pi m/N^{1/3}$ , where  $m$  is an integer, and  $i$  indicates one of the principle lattice directions. In addition, we only want unique values of  $q_i$ , so we will choose those within the first Brillouin zone, so that

$$\mathbf{G} \cdot \mathbf{q} \leq \frac{1}{2}G^2 \quad (15)$$

The size of this region is the same as that of a unit cell of the reciprocal lattice  $\mathbf{g}_1 \cdot (\mathbf{g}_2 \times \mathbf{g}_3)$ . Since there are  $N$  states in this region, the density of  $\mathbf{q}$  states is

$$\frac{N}{\mathbf{g}_1 \cdot (\mathbf{g}_2 \times \mathbf{g}_3)} = \frac{NV_c}{(2\pi)^3} = \frac{V}{(2\pi)^3} \quad (16)$$

where  $V_c$  is the volume of a Bravais lattice cell ( $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ ), and  $V$  is the lattice volume.

In order to calculate

$$Z(\omega) = \frac{1}{N} \sum_{\mathbf{q}, s} \delta(\omega - \omega_s(\mathbf{q})) \quad (13)$$

we must first better define the sum over  $\mathbf{q}$ . As we discussed last chapter for a 3-d cubic system, we will assume that we have a periodic finite lattice of  $N$  basis points, or  $N^{1/3}$  in each of the principle

Clearly as  $N \rightarrow \infty$  the density increases until a continuum of states is formed (all that we need here is that the spacing between  $\mathbf{q}$ -states be much smaller than any physically relevant value of  $\mathbf{q}$ ). The number of states in a frequency interval  $d\omega$  is then given by the volume of  $\mathbf{q}$ -space between the surfaces defined by  $\omega = \omega_s(\mathbf{q})$  and  $\omega = \omega_s(\mathbf{q}) + d\omega$  multiplied by  $V/(2\pi)^3$

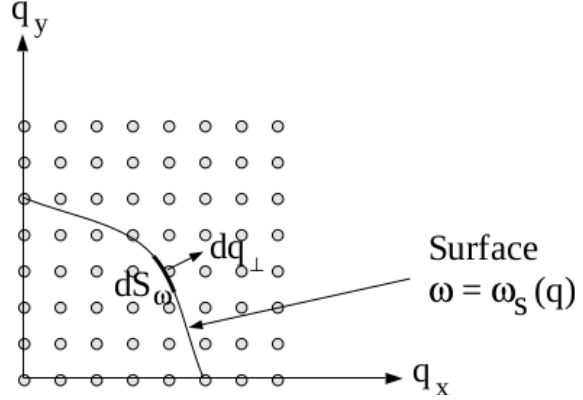


Figure 2: States in  $q$ -space.  $S_\omega$  is the surface of constant  $\omega = \omega_s(\mathbf{q})$ , so that

$$\begin{aligned} Z(\omega)d\omega &= \frac{V}{(2\pi)^3} \int_{\omega}^{\omega+d\omega} d^3q \\ &= \frac{V}{(2\pi)^3} d\omega \sum_s \int d^3q \delta(\omega - \omega_s(\mathbf{q})) \end{aligned} \quad (17) \quad d^3q = dS_\omega dq_\perp = \frac{dS_\omega d\omega}{\nabla_q \omega_s(\mathbf{q})}.$$

As shown in Fig. 2,  $d\omega = \nabla_q \omega_s(\mathbf{q}) dq_\perp$ , and

$$d^3q = dS_\omega dq_\perp = \frac{dS_\omega d\omega}{\nabla_q \omega_s(\mathbf{q})}, \quad (18)$$

where  $S_\omega$  is the surface in  $\mathbf{q}$ -space of constant  $\omega = \omega_s(\mathbf{q})$ . Then

$$Z(\omega)d\omega = \frac{V}{(2\pi)^3} d\omega \sum_s \int_{\omega=\omega_s(\mathbf{q})} \frac{dS_\omega}{\nabla_q \omega_s(\mathbf{q})} \quad (19)$$

Thus the density of states is high in regions where the dispersion is flat so that  $\nabla_q \omega_s(\mathbf{q})$  is small.

As an example, consider the 1-d Harmonic chain shown in Fig. 3. The phonon dispersion must be symmetric around  $q = 0$  and  $q = \pi/a$  due to the point group symmetries. In addition, there must be an acoustic mode as shown in Chapter 4. As a result, the dispersion is linear near  $q = 0$  and has a peak at the one boundary. Since the peak is flat there is a corresponding peak in the phonon DOS. In fact, any point within the Brillouin zone for which  $\nabla_q \omega(q) = 0$  (cusp, maxima, minima) will yield an integrable singularity in the DOS.

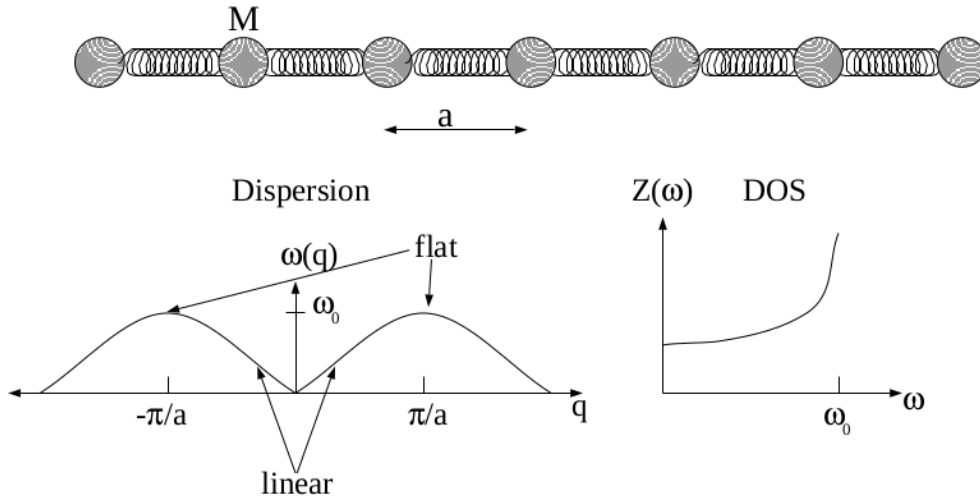


Figure 3: *Linear harmonic chain.* The dispersion  $\omega(q)$  is linear near  $q = 0$ , and flat near  $q = \pm\pi/a$ . Thus, the density of states (DOS) is flat near  $\omega = 0$  corresponding to the acoustic mode (for which  $\nabla_q\omega(q) = \text{constant}$ ), and divergent near  $\omega = \omega_0$  corresponding to the peak of the dispersion (where  $\nabla_q\omega(q) = 0$ )

## 2 Models of Lattice Dispersion

### 2.1 The Debye Model

For most thermodynamic properties, we are interested in the modes  $\hbar\omega(\mathbf{q}) \sim k_B T$  which are low frequency modes in general. From a very general set of (symmetry) constraints we have argued that all interacting lattices in which the total energy is invariant to an overall arbitrary rigid shift in the location of the lattice must have at least one acoustic mode, where for small  $\omega_s(\mathbf{q}) = c_s|\mathbf{q}|$ . Thus, for the thermodynamic properties of the lattice, we care predominantly about the limit  $\omega(\mathbf{q}) \rightarrow 0$ . This physics is rather accurately described by the Debye model.

In the Debye model, we will assume that all modes are acoustic (elastic), so that

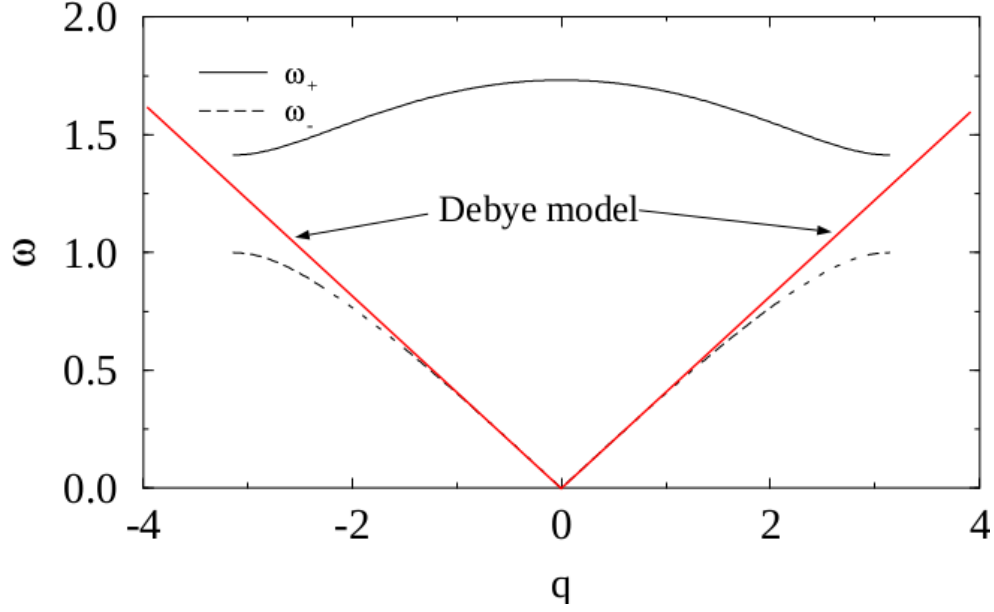


Figure 4: *Dispersion for the diatomic linear chain. In the Debye model, we replace the acoustic mode by a purely linear mode and ignore any optical modes.*

$\omega_s(\mathbf{q}) = c_s|\mathbf{q}|$  for all  $s$  and  $\mathbf{q}$ , then  $\nabla_{\mathbf{q}}\omega_s(\mathbf{q}) = c_s$  for all  $s$  and  $\mathbf{q}$ , and

$$\begin{aligned}
 Z(\omega) &= \frac{V}{(2\pi)^3} \sum_s \int \frac{dS_\omega}{\nabla_{\mathbf{q}}\omega_s(\mathbf{q})} \\
 &= \frac{V}{(2\pi)^3} \sum_s \int \frac{dS_\omega}{c_s}
 \end{aligned} \tag{20}$$

The surface integral may be evaluated, and yields a constant  $\int dS_\omega = S_s$  for each branch. Typically  $c_s$  is different for different modes. However, we will assume that the system is isotropic, so  $c_s = c$ . If the dispersion is isotropic, then the surface of constant  $\omega_s(\mathbf{q})$  is just a sphere, so the surface integral is trivial

$$S_s(\omega = \omega(\mathbf{q})) = \begin{cases} 2 & \text{for } d = 1 \\ 2\pi q = 2\pi\omega/c & \text{for } d = 2 \\ 4\pi q^2 = 4\pi\omega^2/c^2 & \text{for } d = 3 \end{cases} \tag{21}$$



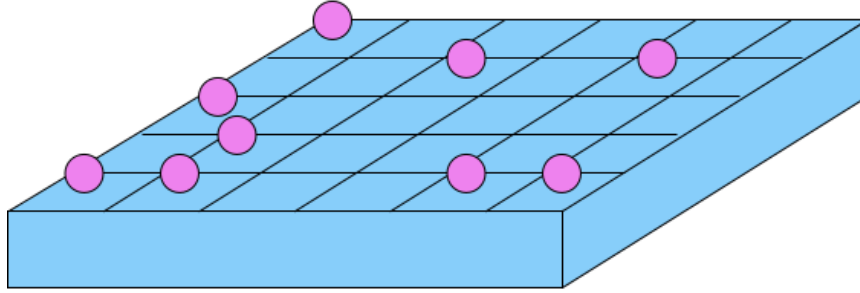


Figure 5: *Helium on a Vycor surface. Each He is attracted weakly to the surface by a van der Waals attraction and sits in a local minimum of the surface lattice potential.*

then since the number of modes =  $d$

$$Z(\omega) = \frac{V}{(2\pi)^3} \left\{ \begin{array}{l} 2/c \text{ for } d = 1 \\ 2\pi q = 4\pi\omega/c^2 \text{ for } d = 2 \\ 4\pi q^2 = 12\pi\omega^2/c^3 \text{ for } d = 3 \end{array} \right\} \quad 0 < \omega < \omega_D \quad (22)$$

Note that since the total number of states is finite, we have introduced a cutoff  $\omega_D$  on the frequency.

## 2.2 The Einstein Model

“Real” two dimensional systems, i.e., a monolayer of gas (He) deposited on an atomically perfect surface (Vycor), may be better described by an Einstein model where each atom oscillates with a frequency  $\omega_0$  and does not interact with its neighbors. The model is dispersionless  $\omega(\mathbf{q}) = \omega_0$ , and the DOS for this system is a delta function  $Z(\omega) = c\delta(\omega - \omega_0)$ . Note that it does not have an acoustic mode; however, this is not in violation of the discussion in the last chapter. Why?

## 3 Thermodynamics of Crystal Lattices

We are now in a situation to calculate many of the thermodynamic properties of crystal lattices. However before addressing such questions as the lattice energy free

energy and specific heat we should see if our model has long-range order... ie., is it consistent with our initial assumptions.

### 3.1 Mermin-Wagner Theory, Long-Range Order

For simplicity, we will work on an elemental lattice model. We may define long-ranged order (LRO) as a finite value of

$$\begin{aligned}\langle s^2 \rangle &= \frac{\hbar}{MN} \sum_{\mathbf{q},s} \frac{1}{\omega_s(\mathbf{q})} \left( \frac{1}{e^{\beta\omega_s(\mathbf{q})} - 1} + \frac{1}{2} \right) \\ &= \frac{\hbar}{2MN} \sum_{\mathbf{q},s} \frac{\sinh(\beta\omega_s(\mathbf{q})/2)}{\omega_s(\mathbf{q}) \cosh(\beta\omega_s(\mathbf{q})/2)}\end{aligned}\quad (23)$$

Since we expect all lattices to melt for some high temperature, we are interested only in the  $T \rightarrow 0$  limit. Given the factor of  $\frac{1}{\omega_s(\mathbf{q})}$  in the summand, we are most interested in acoustic modes since they are the ones which will cause a divergence.

$$\lim_{\beta \rightarrow \infty} \langle s^2 \rangle = \frac{\hbar}{2MN} \lim_{\beta \rightarrow \infty} \sum_{\mathbf{q},s} \frac{1}{\omega_s(\mathbf{q})} \left( \frac{1}{\beta\omega_s(\mathbf{q})} + \frac{1}{2} \right) \quad (24)$$

The low frequency modes are most important so a Debye model may be used

$$\lim_{\beta \rightarrow \infty} \langle s^2 \rangle \approx \frac{\hbar}{2MN} \int_0^{\omega_D} d\omega Z(\omega) \frac{1}{\omega} \left( \frac{1}{\beta\omega} + \frac{1}{2} \right), \quad (25)$$

where  $Z(\omega)$  is the same as was defined above in Eq. 22.

$$Z(\omega) = \frac{V}{(2\pi)^3} \left\{ \begin{array}{l} 2/c \text{ for } d = 1 \\ 2\pi q = 4\pi\omega/c^2 \text{ for } d = 2 \\ 4\pi q^2 = 12\pi\omega^2/c^3 \text{ for } d = 3 \end{array} \right\} \quad 0 < \omega < \omega_D \quad (26)$$

Thus in 3-d the DOS always cancels the  $1/\omega$  singularity but in two dimensions the singularity is only cancelled when  $T = 0$  ( $\beta = \infty$ ), and in one dimension  $\langle s^2 \rangle = \infty$  for all  $T$ . This is a specific case of the Mermin-Wagner Theorem. We should emphasize that the result  $\langle s^2 \rangle = \infty$  does not mean that our theory has failed. The harmonic approximation requires that the near-neighbor strains must be small, not the displacements.

$\langle s^2 \rangle$	$d = 1$	$d = 2$	$d = 3$
$T = 0$	$\infty$	finite	finite
$T \neq 0$	$\infty$	$\infty$	finite

Table 1:  $\langle s^2 \rangle$  for lattices of different dimension, assuming the presence of an acoustic mode.

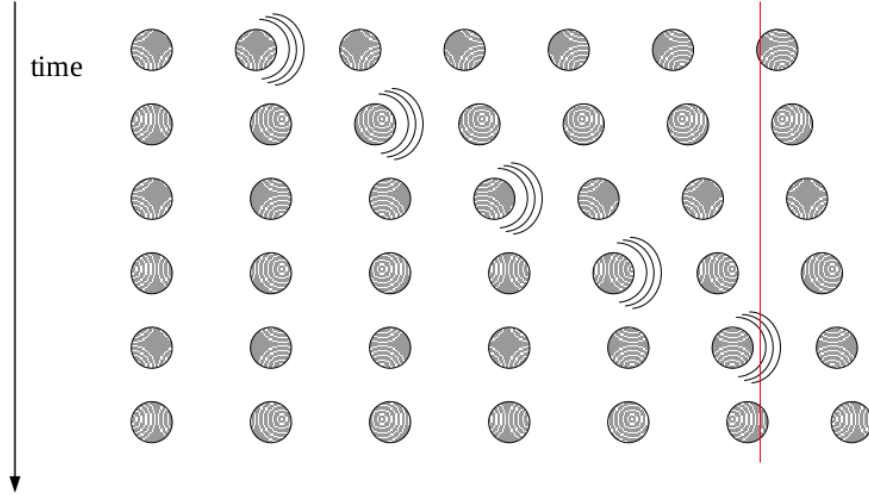


Figure 6: Random fluctuations of atoms in a 1-d lattice may accumulate to produce a very large displacements of the atoms.

Physically, it is easy to understand why one-dimensional systems do not have long range order, since as you go along the chain, the displacements of the atoms can accumulate to produce a very large rms displacement. In higher dimensional systems, the displacements in any direction are constrained by the neighbors in orthogonal directions. “Real” two dimensional systems, i.e., a monolayer of gas deposited on an atomically perfect surface, do have long-range order even at finite temperatures due to the surface potential (corrugation of the surface). These may be better described by an Einstein model where each atom oscillates with a frequency  $\omega_0$  and does not interact with its neighbors. The DOS for this system is a delta function as described

above. For such a DOS,  $\langle s^2 \rangle$  is always finite. You will explore this physics, in much more detail, in your homework.

## 3.2 Thermodynamics

We will assume that our system is in equilibrium with a heat bath at temperature  $T$ . This system is described by the canonical ensemble, and may be justified by dividing an infinite system into a finite number of smaller subsystems. Each subsystem is expected to interact weakly with the remaining system which also acts as the subsystems heat bath. The probability that any state in the subsystem is occupied is given by

$$P(\{n_s(\mathbf{k})\}) \propto e^{-\beta E(\{n_s(\mathbf{k})\})} \quad (27)$$

Thus the partition function is given by

$$\begin{aligned} \mathcal{Z} &= \sum_{\{n_s(\mathbf{k})\}} e^{-\beta E(\{n_s(\mathbf{k})\})} \\ &= \sum_{\{n_s(\mathbf{k})\}} e^{-\beta \sum_{\mathbf{k},s} \hbar\omega_s(\mathbf{k}) (n_s(\mathbf{k}) + \frac{1}{2})} \\ &= \prod_{s,\mathbf{k}} \mathcal{Z}_s(\mathbf{k}) \end{aligned} \quad (28)$$

where  $\mathcal{Z}_s(\mathbf{k})$  is the partition function for the mode  $s, \mathbf{k}$ ; i.e. the modes are independent and decouple.

$$\begin{aligned} \mathcal{Z}_s(\mathbf{k}) &= \sum_n e^{-\beta \hbar\omega_s(\mathbf{k}) (n + \frac{1}{2})} \\ &= e^{-\beta \hbar\omega_s(\mathbf{k})/2} \sum_n e^{-\beta \hbar\omega_s(\mathbf{k}) n} \\ &= \frac{e^{-\beta \hbar\omega_s(\mathbf{k})/2}}{1 - e^{-\beta \hbar\omega_s(\mathbf{k})}} \\ &= \frac{1}{2 \sinh(\beta \hbar\omega_s(\mathbf{k})/2)} \end{aligned} \quad (29)$$

The free energy is given by

$$\mathcal{F} = -k_B T \ln(\mathcal{Z}) = k_B T \sum_{\mathbf{k},s} \ln(2 \sinh(\beta \hbar\omega_s(\mathbf{k})/2)) \quad (30)$$

Since  $d\mathcal{E} = Td\mathcal{S} - PdV$  and  $d\mathcal{F} = Td\mathcal{S} - PdV - Td\mathcal{S} - \mathcal{S}dT$ , the entropy is

$$\mathcal{S} = - \left( \frac{\partial \mathcal{F}}{\partial T} \right)_V, \quad (31)$$

and system energy is then given by

$$\mathcal{E} = \mathcal{F} + T\mathcal{S} = \mathcal{F} - T \left( \frac{\partial \mathcal{F}}{\partial T} \right)_V \quad (32)$$

where constant volume  $V$  is guaranteed by the harmonic approximation (since  $\langle s \rangle = 0$ ).

$$\mathcal{E} = \sum_{\mathbf{k},s} \frac{1}{2} \hbar \omega_s(\mathbf{k}) \coth(\beta \omega_s(\mathbf{k})/2) \quad (33)$$

The specific heat is then given by

$$C = \left( \frac{d\mathcal{E}}{dT} \right)_V = k_B \sum_{\mathbf{k},s} (\beta \hbar \omega_s(\mathbf{k}))^2 \operatorname{csch}^2(\beta \omega_s(\mathbf{k})/2) \quad (34)$$

where  $\operatorname{csch}(x) = 1/\sinh(x)$

Consider the specific heat of our 3-dimensional Debye model.

$$\begin{aligned} C &= k_B \int_0^{\omega_D} d\omega \mathcal{Z}(\omega) (\beta \omega/2)^2 \operatorname{csch}^2(\beta \omega/2) \\ &= k_B \int_0^{\omega_D} d\omega \left( \frac{12V\pi\omega^2}{(2\pi c)^3} \right) (\beta \omega/2)^2 \operatorname{csch}^2(\beta \omega/2) \end{aligned} \quad (35)$$

Where the Debye frequency  $\omega_D$  is determined by the requirement that

$$3rN = \int_0^{\omega_D} d\omega \mathcal{Z}(\omega) = \int_0^{\omega_D} d\omega \left( \frac{12V\pi\omega^2}{(2\pi c)^3} \right), \quad (36)$$

or  $V/(2\pi c)^3 = 3rN/(4\omega_D^3)$ .

Clearly the integral for  $C$  is a mess, except in the high and low  $T$  limits. At high temperatures  $\beta \hbar \omega_D/2 \ll 1$ ,

$$C \approx k_B \int_0^{\omega_D} d\omega \mathcal{Z}(\omega) = 3Nr k_B \quad (37)$$

This is the well known classical result (equipartition theorem) which attributes  $(1/2)k_B$  of the specific heat to each quadratic degree of freedom. Here for each element of

the basis we have 6 quadratic degrees of freedom (three translational, and three momenta).

At low temperatures,  $\beta\hbar\omega/2 \gg 1$ ,

$$\operatorname{csch}^2(\beta\omega/2) \approx 2e^{-\beta\omega/2} \quad (38)$$

Thus, at low  $T$ , only the low frequency modes contribute, so the upper bound of integration may be extended to  $\infty$

$$C \approx 12\pi k_B \frac{3rN}{4\omega_D^2} \int_0^\infty d\omega \omega^2 \left( \frac{\beta\hbar\omega}{2} \right)^2 2e^{-\beta\omega_s(\mathbf{k})/2}. \quad (39)$$

If we make the change of variables  $x = \beta\hbar\omega/2$ , we get

$$C \approx \frac{9k_B r N \pi}{2} \left( \frac{1}{\omega_D \beta \hbar} \right)^3 \int_0^\infty dx x^4 e^{-x} \quad (40)$$

$$\approx \frac{9k_B r N \pi}{2} \left( \frac{1}{\omega_D \beta \hbar} \right)^3 24 \quad (41)$$

Then, if we identify the Debye temperature  $\theta_D = \hbar\omega_D/k_B$ , we get

$$C \approx 96\pi r N k_B \left( \frac{T}{\theta_D} \right)^3 \quad (42)$$

$C \propto T^3$  at low temperature is the characteristic signature of low-energy phonon excitations.

### 3.3 Thermal Expansion, the Gruneisen Parameter

Consider a cubic system of linear dimension  $L$ . If unconstrained, we expect that the volume of this system will change with temperature (generally expand with increasing  $T$ , but not always. cf. ice or Si). We define the coefficient of free expansion ( $P = 0$ ) as

$$\alpha_L = \frac{1}{L} \frac{dL}{dT} \quad \text{or} \quad \alpha_V = 3\alpha_L = \frac{1}{V} \frac{dV}{dT}. \quad (43)$$

Of course, this measurement only makes sense in equilibrium.

$$P = - \left( \frac{d\mathcal{F}}{dV} \right)_T = 0 \quad (44)$$

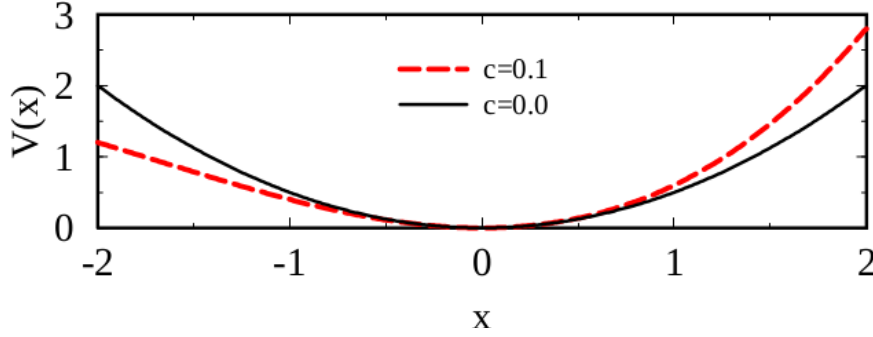


Figure 7: Plot of the potential  $V(x) = \frac{1}{2}m\omega^2 x^2 + cx^3$  when  $m = \omega = 1$  and  $c = 0.0, 0.1$ . The average position of a particle  $\langle x \rangle$  in the anharmonic potential,  $c = 0.1$ , will shift to the left as the energy (temperature) is increased; whereas, that in the harmonic potential,  $c = 0$ , is fixed  $\langle x \rangle = 0$ .

As mentioned earlier, since  $\langle s \rangle = 0$  in the harmonic approximation, a harmonic crystal does not expand when heated. Of course, real crystals do, so that lack of thermal expansion of a harmonic crystal can be considered a limitation of the harmonic theory. To address this limitation, we can make a quasiharmonic approximation. Consider a more general potential between the ions, of the form

$$V(x) = bx + cx^3 + \frac{1}{2}m\omega^2 x^2 \quad (45)$$

and let's see if any of these terms will produce a temperature dependent displacement. The last term is the usual harmonic term, which we have already shown does not produce a T-dependent  $\langle x \rangle$ . Also the first term does not have the desired effect! It corresponds to a temperature-independent shift in the oscillator, as can be seen by completing the square

$$\frac{1}{2}m\omega^2 x^2 + bx = \frac{1}{2} \left( x + \frac{b}{m\omega^2} \right)^2 - \frac{b^2}{2m\omega^2}. \quad (46)$$

Then  $\langle x \rangle = -\frac{b}{m\omega^2}$ , independent of the temperature; that is, assuming that  $b$  is temperature-independent. What we need is a temperature dependent coefficient  $b$ !

The cubic term has the desired effect. As can be seen in Fig 7, as the average energy (temperature) of a particle trapped in a cubic potential increases, the mean

position of the particle shifts. However, it also destroys the solubility of the model. To get around this, approximate the cubic term with a mean-field decomposition.

$$cx^3 \approx c\eta x \langle x^2 \rangle + c(1 - \eta)x^2 \langle x \rangle \quad (47)$$

and treat these two terms separately (the new parameter  $\eta$  is to be determined self-consistently, usually by minimizing the free energy with respect to  $\eta$ ). The first term yields the needed temperature dependent shift of  $\langle x \rangle$

$$\frac{1}{2}m\omega^2 x^2 + c\eta x \langle x^2 \rangle = \frac{1}{2}m\omega^2 \left( x + \frac{c\eta \langle x^2 \rangle}{m\omega^2} \right)^2 - \frac{c^2 \langle x^2 \rangle^2}{2m\omega^2} \quad (48)$$

so that  $\langle x \rangle = -\frac{c\eta \langle x^2 \rangle}{m\omega^2}$ . Clearly the renormalization of the equilibrium position of the harmonic oscillator will be temperature dependent. While the second term,  $(1 - \eta)x^2 \langle x \rangle$ , yields a shift in the frequency  $\omega \rightarrow \omega'$

$$\omega' = \omega \left( 1 + \frac{2(1 - \eta) \langle x \rangle}{m\omega^2} \right)^{\frac{1}{2}} \quad (49)$$

which is a function of the equilibrium position. Thus a mean-field description of the cubic term is consistent with the observed physics.

In what follows, we will approximate the effect of the anharmonic cubic term as a shift in the equilibrium position of the lattice (and hence the lattice potential) and a change of  $\omega$  to  $\omega'$ ; however, we imagine that the energy levels remain of the form

$$E_n = \hbar\omega' \langle x \rangle \left( n + \frac{1}{2} \right), \quad (50)$$

and that  $\langle x \rangle$  varies with temperature, consistent with the mean-field approximation just described.

To proceed, imagine the cube of cubic system to be made up of oscillators which are independent. Since the final result can be formulated as a sum over these independent modes, consider only one. In equilibrium, where  $P = -\left(\frac{d\mathcal{F}}{dV}\right)_T = 0$ , the free energy of one of the modes is

$$\mathcal{F} = \Phi + \frac{1}{2}\hbar\omega + k_B T \ln(1 - e^{-\beta\hbar\omega}) \quad (51)$$



and (following the notation of Ibach and Lüth), let the lattice potential

$$\Phi = \Phi_0 + \frac{1}{2}f(a - a_0)^2 + \dots \quad (52)$$

where  $f$  is the spring constant. Then

$$0 = P = \left( \frac{d\mathcal{F}}{da} \right)_T = f(a - a_0) + \frac{1}{\omega} \frac{\partial \omega}{\partial a} \left( \frac{1}{2} \hbar \omega - \frac{\hbar \omega}{1 - e^{-\beta \hbar \omega}} \right), \quad (53)$$

If we identify the last term in parenthesis as  $\epsilon(\omega, T)$ , and solve for  $a$ , then

$$a = a_0 - \frac{1}{\omega f} \epsilon(\omega, T) \frac{\partial \omega}{\partial a} \quad (54)$$

Since we now know  $a(T)$  for a single mode, we may calculate the linear expansion coefficient for this mode

$$\alpha_L = \frac{1}{a_0} \frac{da}{dT} = - \frac{1}{a_0^2 f} \frac{\partial \ln \omega}{\partial \ln a} \frac{\partial \epsilon(\omega, T)}{\partial T} \quad (55)$$

To generalize this to a solid let  $\alpha_L \rightarrow \alpha_V$  (as discussed above) and  $a_0^2 f \rightarrow V^2 \frac{dP}{dV} = V \kappa$  ( $\kappa$  is the bulk modulus) and sum over all modes the modes  $\mathbf{k}, s$

$$\alpha_V = \frac{1}{V} \frac{dV}{dT} = \frac{1}{\kappa V} \sum_{\mathbf{k}, s} - \frac{\partial \ln \omega_s(\mathbf{k})}{\partial \ln V} \frac{\partial \epsilon(\omega_s(\mathbf{k}), T)}{\partial T}. \quad (56)$$

Clearly (due to the factor of  $\frac{\partial \epsilon}{\partial T}$ ),  $\alpha_V$  will have a behavior similar to that of the specific heat ( $\alpha_V \sim T^3$  for low  $T$ , and  $\alpha_V = \text{constant}$  for high  $T$ ). In addition, for many lattices, the Gruneisen number

$$\gamma = \frac{\partial \ln \omega_s(\mathbf{k})}{\partial \ln V} \quad (57)$$

shows a weak dependence upon  $s, \mathbf{k}$ , and may be replaced by its average, called the Gruneisen parameter

$$\langle \gamma \rangle = \left\langle \frac{\partial \ln \omega_s(\mathbf{k})}{\partial \ln V} \right\rangle, \quad (58)$$

typically on the order of two.

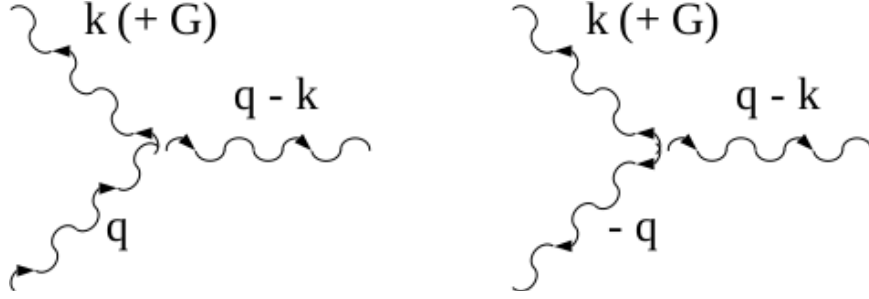


Figure 8: *Three-phonon processes resulting from cubic terms in the inter-ion potential. Six other three-phonon processes are possible.*

Before proceeding to the next section, I would like to reexamine the cubic term in a crystal where

$$\sum_l s_l^3 = \frac{1}{(2MN)^{3/2}} \sum_{l,\mathbf{k},\mathbf{q},\mathbf{p}} \frac{\hbar^{3/2}}{\sqrt{\omega(\mathbf{q})\omega(\mathbf{k})\omega(\mathbf{p})}} e^{i(\mathbf{p}+\mathbf{q}+\mathbf{k}-\mathbf{G})\cdot\mathbf{r}_l} \quad (59)$$

$$(a(\mathbf{k}) + a^\dagger(-\mathbf{k})) (a(\mathbf{p}) + a^\dagger(-\mathbf{p})) (a(\mathbf{q}) + a^\dagger(-\mathbf{q})) .$$

The sum over  $l$  yields a delta function  $\delta_{\mathbf{p}+\mathbf{q}+\mathbf{k},\mathbf{G}}$  (ie., crystal momentum conservation). Physically, these processes correspond to phonon decay in which a phonon can decompose into two others. As we shall see, such anharmonic processes are crucial to the calculation of the thermal conductivity,  $\kappa$ , of crystals.

### 3.4 Thermal Conductivity

Metals predominately carry heat with free electrons, and are considered to be good conductors. Insulators, which lack free electrons, predominantly carry heat with lattice vibrations – phonons. Nevertheless, some very hard insulating crystals have very high thermal conductivities - diamond C which is often highly temperature dependent. However, most insulators are not good thermal conductors. The square of the thermal conductivity also figures into the figure of merit for thermoelectrics[1]. This subsection will be devoted to understanding what makes stiff crystals like diamond such good conductors of heat.

material/T	273.2K	298.2K
C	26.2	23.2
Cu	4.03	4.01

Table 2: *The thermal conductivities of copper and diamond (CRC) ( in  $\mu\text{Ohm-cm}$ ).*

The thermal conductivity  $\kappa$  is measured by setting up a small steady thermal gradient across the material, then

$$Q = -\kappa \nabla T \quad (60)$$

where  $Q$  is the thermal current density; i.e., the energy times the density times the velocity. If the thermal current is in the x-direction, then

$$Q_x = \frac{1}{V} \sum_{\mathbf{q},s} \hbar \omega_s(\mathbf{q}) \langle n_s(\mathbf{q}) \rangle v_{sx}(\mathbf{q}) \quad (61)$$

where the group velocity is given by  $v_{sx}(\mathbf{q}) = \frac{\partial \omega_s(\mathbf{q})}{\partial q_x}$ . Since we assume  $\nabla T$  is small, we will only look at the linear response of the system where  $\langle n_s(\mathbf{q}) \rangle$  deviates little from its equilibrium value  $\langle n_s(\mathbf{q}) \rangle^0$ . Furthermore since  $\omega_s(\mathbf{q}) = \omega_s(-\mathbf{q})$ ,

$$v_{sx}(-\mathbf{q}) = \frac{\partial \omega_s(-\mathbf{q})}{\partial -q_x} = -v_{sx}(\mathbf{q}) \quad (62)$$

Thus as  $\langle n_s(-\mathbf{q}) \rangle^0 = \langle n_s(\mathbf{q}) \rangle^0$

$$Q_x^0 = \frac{1}{V} \sum_{\mathbf{q},s} \hbar \omega_s(\mathbf{q}) \langle n_s(\mathbf{q}) \rangle^0 v_{sx}(\mathbf{q}) = 0 \quad (63)$$

since the sum is over all  $\mathbf{q}$  in the B.Z. Thus if we expand

$$\langle n_s(\mathbf{q}) \rangle = \langle n_s(\mathbf{q}) \rangle^0 + \langle n_s(\mathbf{q}) \rangle^1 + \dots \quad (64)$$

we get

$$Q_x \approx \frac{1}{V} \sum_{\mathbf{q},s} \hbar \omega_s(\mathbf{q}) \langle n_s(\mathbf{q}) \rangle^1 v_{sx}(\mathbf{q}) \quad (65)$$

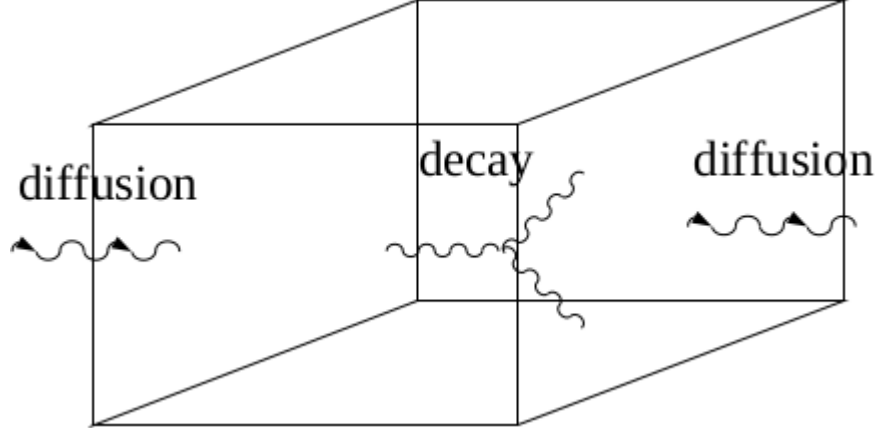


Figure 9: Change of phonon density within a trapezoidal region.  $\langle n_s(\mathbf{q}) \rangle$  can change either by phonon decay or by phonon diffusion into and out of the region.

since we presumably already know  $\omega_s(\mathbf{k})$ , the calculation of  $Q$  and hence  $\kappa$  reduces to the evaluation of the linear change in  $\langle n \rangle$ .

Within a region,  $\langle n \rangle$  can change in two ways. Either phonons can diffuse into the region, or they can decay through an anharmonic (cubic) term into other modes. so

$$\frac{d\langle n \rangle}{dt} = \left. \frac{\partial \langle n \rangle}{\partial t} \right|_{\text{diffusion}} + \left. \frac{\partial \langle n \rangle}{\partial t} \right|_{\text{decay}} \quad (66)$$

However  $\frac{d\langle n \rangle}{dt} = 0$  since we are in a steady state. The decay process is usually described by a relaxation time  $\tau$  (or a mean-free path  $l = v\tau$ )

$$\left. \frac{\partial \langle n \rangle}{\partial t} \right|_{\text{decay}} = -\frac{\langle n \rangle - \langle n \rangle^0}{\tau} \approx -\frac{\langle n \rangle^1}{\tau} \quad (67)$$

The diffusion part of  $\frac{d\langle n \rangle}{dt}$  is addressed pictorially in Fig. 10. Formally,

$$\begin{aligned} \left. \frac{\partial \langle n \rangle}{\partial t} \right|_{\text{diffusion}} &\approx \frac{\langle n(x - v_x \Delta t) \rangle - \langle n(x) \rangle}{\Delta t} \approx -\frac{\partial \langle n(x) \rangle}{\partial x} v_x \\ &\approx -v_x \frac{\partial \langle n(x) \rangle}{\partial T} \frac{\partial T}{\partial x} \approx -v_x \frac{\partial (\langle n(x) \rangle^0 + \langle n(x) \rangle^1)}{\partial T} \frac{\partial T}{\partial x} \end{aligned} \quad (68)$$

Keeping only the lowest order term,

$$\left. \frac{\partial \langle n \rangle}{\partial t} \right|_{\text{diffusion}} \approx -v_x \frac{\partial \langle n(x) \rangle^0}{\partial T} \frac{\partial T}{\partial x} \quad (69)$$

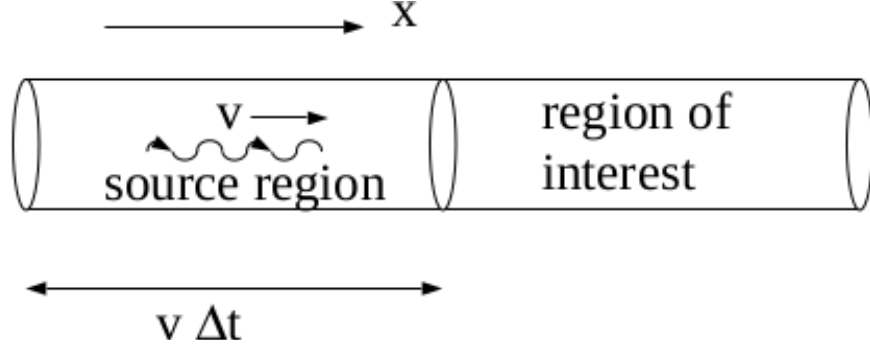


Figure 10: *Phonon diffusion.* In time  $\Delta t$ , all the phonons in the left, source region, will travel into the region of interest on the right, while those on the right region will all travel out in time  $\Delta t$ . Thus,  $\Delta n/\Delta t = (n_{left} - n_{right})/\Delta t$ .

Then as  $\frac{d\langle n \rangle}{dt} = 0$ ,

$$\left. \frac{\partial \langle n \rangle}{\partial t} \right|_{\text{diffusion}} = - \left. \frac{\partial \langle n \rangle}{\partial t} \right|_{\text{decay}} \quad (70)$$

or

$$\langle n \rangle^1 = -v_x \tau_s(\mathbf{q}) \frac{\partial \langle n(x) \rangle^0}{\partial T} \frac{\partial T}{\partial x}. \quad (71)$$

Thus

$$Q_x \approx -\frac{1}{V} \sum_{\mathbf{q},s} \hbar \omega_s(\mathbf{q}) v_{sx}^2(\mathbf{q}) \tau_s(\mathbf{q}) \frac{\partial \langle n(x) \rangle^0}{\partial T} \frac{\partial T}{\partial x}, \quad (72)$$

and since  $Q = -\kappa \nabla T$

$$\kappa \approx \frac{1}{V} \sum_{\mathbf{q},s} \hbar \omega_s(\mathbf{q}) v_{sx}^2(\mathbf{q}) \tau \frac{\partial \langle n(x) \rangle^0}{\partial T}. \quad (73)$$

From this relationship we can learn several things. First since  $\kappa \sim v_{sx}^2(\mathbf{q})$ , phonons near the zone boundary or optical modes with small  $\mathbf{v}_s(\mathbf{q}) = \nabla_{\mathbf{q}} \omega_s(\mathbf{q})$  contribute little to the thermal conductivity. Also, stiff materials, with very fast speed of the acoustic modes  $v_{sx}(\mathbf{q}) \approx c$  will have a large  $\kappa$ . Second, since  $\kappa \sim \tau_s(\mathbf{q})$ , and  $l_s(\mathbf{q}) = v_{sx}(\mathbf{q}) \tau_s(\mathbf{q})$ ,  $\kappa$  will be small for materials with short mean-free paths. The mean-free path is effected by defects, anharmonic Umklapp processes, etc. We will explore this effect, especially its temperature dependence, in more detail.

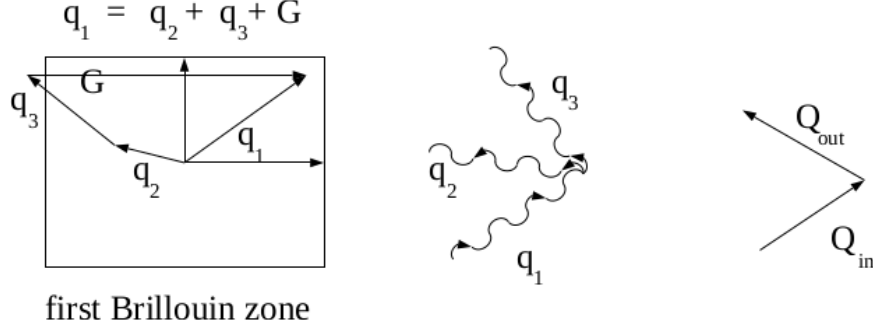


Figure 11: *Umklapp processes involve a reciprocal lattice vector  $\mathbf{G}$  in lattice momentum conservation. They are possible whenever  $q_1 > G/2$ , for some  $\mathbf{G}$ , and involve a virtual reversal of the momentum and heat carried by the phonons (far right).*

At low  $T$ , only low-energy, acoustic, modes can be excited (those with  $\hbar\omega_s(\mathbf{q}) \sim k_B T$ ). These modes have

$$v_s(q) = c_s \quad (74)$$

In addition, since the momentum of these modes  $q \ll G$ , we only have to worry about anharmonic processes which do not involve a reciprocal lattice vector  $\mathbf{G}$  in lattice momentum conservation. Consider one of the three-phonon anharmonic processes of phonon decay shown in Fig. 8 (with  $\mathbf{G} = 0$ ). For these processes  $Q \sim \hbar\omega c$  so the thermal current is not disturbed by anharmonic processes. Thus the anharmonic terms at low  $T$  do not affect the mean-free path, so the thermal resistivity (the inverse of the conductivity) is dominated by scattering from impurities in the bulk and surface imperfections at low temperatures.

At high  $T$  momentum conservation in an anharmonic process may involve a reciprocal lattice vector  $\mathbf{G}$  if the  $q_1$  of an excited mode is large enough and there exists a sufficiently small  $\mathbf{G}$  so that  $q_1 > G/2$  (c.f. Fig. 11). This is called an Umklapp process, and it involves a very large change in the heat current (almost a reversal). Thus the mean-free path  $l$  and  $\kappa$  are very much smaller for high temperatures where  $q_1$  can be larger than half the smallest  $\mathbf{G}$ .

So what about diamond? It is very hard and very stiff, so the sound velocities  $c_s$

are large, and so thermally excited modes for which  $k_B T \sim \hbar \omega \sim \hbar c q$  involve small  $\mathbf{q}_1$  for which Umklapp processes are irrelevant. Second  $\kappa \sim c^2$  which is large. Thus  $\kappa$  for diamond is huge!

## References

- [1] [https://en.wikipedia.org/wiki/Thermoelectric\\_materials](https://en.wikipedia.org/wiki/Thermoelectric_materials)