Lattice Dynamics

Normal Modes of a 1-D Monatomic Lattice

Consider a set of \( N \) identical ions of mass \( M \) distributed along a line at positions \( \mathbf{R} = na\hat{y} \) \((n = 1, 2, \ldots, N, \text{ and } a \text{ is the lattice constant})\). Let \( \mathbf{u}(\mathbf{R}) \) be the displacement from \( \mathbf{R} \) of the ion with equilibrium position \( \mathbf{R} \). For simplicity, we assume that only neighboring ions interact. One may thus write the harmonic potential energy as:

\[
U^{\text{harm}} = \frac{1}{2} K \sum_{n} [\mathbf{u}(na) - \mathbf{u}([n + 1]a)]^2, \tag{4.37}
\]

where \( K \) is the force constant. The equation of motions are then:

\[
\text{Hamilton's Equation:} \quad M \ddot{\mathbf{u}}(na) = - \frac{\partial U^{\text{harm}}}{\partial \mathbf{u}(na)} = -K[2\mathbf{u}(na) - \mathbf{u}([n - 1]a) - \mathbf{u}([n + 1]a)].
\]

(\text{where } n = 1, 2, \ldots, N) \tag{4.38}

To solve the set of \( N \) equations (4.38), the boundary conditions need to be specified. We choose the periodic boundary condition for mathematical convenience.

\[
\mathbf{u}([N + 1]a) = \mathbf{u}(a); \quad \mathbf{u}(0) = \mathbf{u}(Na).
\]
\[ u([N + n]a) = u(na) \quad (4.39) \]

We seek solutions to eqn. 4.38 of the form:

\[ u(na, t) \propto e^{i(kna - \omega t)}. \quad (4.40) \]

The periodic boundary condition requires that:

\[ e^{i(kNa)} = 1, \quad (4.41) \]

which gives:

\[ k = \frac{2\pi n}{a N}, \quad n \text{ an integer}. \quad (4.42) \]

If \( k \) is changed by \( \frac{2\pi}{a} \), the displacement \( u(na) \) (defined by (4.40)) remains the same. Consequently, only \( N \) values of \( k \) yield distinct solutions. Without loss of generality, we take them to lie between \(-\pi/a\) and \( \pi/a \). That is,

\[-\pi/a \leq k \leq +\pi/a\]

Substituting eqn. 4.40 in eqn. 4.38, we get:

\[-M\omega^2 e^{i(kna - \omega t)} = -K \left[ 2 - e^{-ika} - e^{ika} \right] e^{i(kna - \omega t)} = -2K(1 - \cos ka) e^{i(kna - \omega t)}, \quad (4.43)\]

For eqn. 4.43 to be valid, one must have

\[ \omega(k) = \sqrt{\frac{2K(1 - \cos ka)}{M}} = 2 \sqrt{\frac{K}{M}} |\sin \frac{1}{2}ka|, \quad (4.44) \]

\((\cos ka = 1 - 2\sin(ka/2))\)
This defines the dispersion relation $\omega = \omega(k)$. We ignore the negative branch of the solution for the following reason.

Consider the four solutions with $(k, \omega) = (\pm k_0, \pm \omega(k_0))$. The solutions with $(k, \omega) = (+k_0, +\omega(k_0))$ and $(k, \omega) = (-k_0, -\omega(k_0))$ are $e^{i(k_0x - \omega t)}$ and $e^{-i(k_0x - \omega t)}$, respectively. They have the same real parts and so are dependent solutions. Similarly, the solutions with $(k, \omega) = (+k_0, -\omega(k_0))$ and $(k, \omega) = (-k_0, +\omega(k_0))$ are dependent. From

Consider the two limits of $\omega(k)$ as given in eqn. (4.44),

(i) $k \ll \pi/a$

$$\omega = \left(a \sqrt{\frac{K}{M}} \right) |k|.$$  \hfill (4.46)

A linear relation as such is well known for ordinary sound waves, where the constant of proportionality gives the speed of sound, $c = \omega/k$.

(ii) $k \approx \pm \pi/a$

$$\omega = (4K/M)^{1/2}$$
$$v = d\omega/dk = 0$$

4.24 Normal Modes of a 1-D Lattice With a Basis

We consider a 1-D lattice where each primitive cell contains two identical ions with equilibrium positions $na$ and $na + d$. Without loss of generality, we further assume that $d$ is $\leq a/2$. Because $d < a$, the force between adjacent ions in the same primitive cell is stronger than that between adjacent ions in different primitive cells (whose separation is
(a – d) and ≥ d). Again, by assuming that only nearest neighbors interact, the harmonic potential energy can be written as:

\[
U_{\text{harm}} = \frac{K}{2} \sum_{n} [u_1(na) - u_2(na)]^2 + \frac{G}{2} \sum_{n} [u_2(na) - u_1([n + 1]a)]^2,
\]

where we have written \(u_1(na)\) for the displacement of the ion oscillating about site \(na\), and \(u_2(na)\) that about \(na + d\). In keeping with our choice that \(d \leq a/2\), we also assume \(G \leq K\). The equations of motion are:

\[
M\ddot{u}_1(na) = -\frac{\partial U_{\text{harm}}}{\partial u_1(na)} = -K[u_1(na) - u_2(na)] - G[u_1(na) - u_2([n - 1]a)],
\]

\[
M\ddot{u}_2(na) = -\frac{\partial U_{\text{harm}}}{\partial u_2(na)} = -K[u_2(na) - u_1(na)] - G[u_2(na) - u_1([n + 1]a)].
\]

We seek solutions to \(u_1(na)\) and \(u_2(na)\) of the form:

\[
u_1(na) = \varepsilon_1 e^{i(kna - \omega t)},
\]

\[
u_2(na) = \varepsilon_2 e^{i(kna - \omega t)}.
\]

where \(\varepsilon_1\) and \(\varepsilon_2\) are constants to be determined. Their ratio specifies the relative amplitude and phase of the vibration of the ions within each primitive cell. As before, we adopt the periodic boundary condition. This results in \(N\) non-equivalent values of \(k\) given by eqn. (4.42). Substituting eqn. (4.49) in eqn. (4.48), one obtains:
\[ [M \omega^2 - (K + G)] \epsilon_1 + (K + Ge^{-ika}) \epsilon_2 = 0, \]
\[ (K + Ge^{ika}) \epsilon_1 + [M \omega^2 - (K + G)] \epsilon_2 = 0. \quad (4.50) \]

This set of homogeneous equations has a solution only if the determinant of the coefficients vanishes:
\[ [M \omega^2 - (K + G)]^2 = |K + Ge^{-ika}|^2 = K^2 + G^2 + 2KG \cos ka. \quad (4.51) \]

Solving (4.51) for \( \omega \), and adopting only the positive solution, we find:
\[ \omega^2 = \frac{K + G}{M} \pm \frac{1}{M} \sqrt{K^2 + G^2 + 2KG \cos ka}, \quad (4.52) \]
with
\[ \frac{\epsilon_2}{\epsilon_1} = \mp \frac{K + Ge^{ika}}{|K + Ge^{ika}|}. \quad (4.53) \]

Given (4.52), there are two solutions for each of the \( N \) allowed values of \( k \). Each of the two solutions correspond to a different (positive) \( \omega \) (eqn. 4.52), and ratio of \( \epsilon_2/\epsilon_1 \) as given by eqn. (4.53). Altogether, there are \( 2N \) normal modes and so \( 2N \) degrees of freedom.

Among these degrees of freedom, \( N \) are attributable to the translational motion of individual primitive cell; the other \( N \) are due to relative motions between the two ions within each of the \( N \) cells.

Figure 4.4 shows a plot of the dispersion relation given by eqn. (4.52). Evidently, there are two branches (as opposed to one in the 1-D monatomic lattices). One of the branches (lower sign in (4.52)) resembles the \( \omega(k) \) of the monatomic case, with \( \omega(k) \) approaching zero linearly for small \( k \), and is known as the acoustic branch. The other branch (upper sign in (4.53)) has \( \omega = [2(K + G)/M]^{1/2} \) at \( k = 0 \), which decreases with increasing \( k \) and reaches \( [2K/M]^{1/2} \) at the zone edge. This branch is known as the optical branch because the long wavelength optical modes can interact with electromagnetic radiations, which are responsible for much of the optical behavior of the non-monatomic crystals. We examine the nature of the two branches by considering the two limits of \( k \).
Case 1 \( k \ll \pi/a \)

Here, \( \cos ka \approx 1 - (ka)^2/2 \), and to leading order in \( k \) the roots (eqn. (4.52)), corresponding to the upper (optical) and lower sign (acoustic), respectively, become:

\[
\omega = \sqrt{\frac{2(K + G)}{M} - O(ka)^2}
\]

\[
\omega = \sqrt{\frac{KG}{2M(K + G)}}(ka).
\]

(4.54)

At the same time, equation (4.53) reduces to:

\[
\epsilon_2 = \mp \epsilon_1
\]

(4.55)

The lower sign belongs to the acoustic mode, and describes a motion in which the two ions in a cell move in phase with one another. The upper sign belongs to the high-frequency optical mode, and describes a motion in which the motions of the two ions in a cell are \( 180^\circ \) out of phase. Figure 4.5 illustrates the ionic motions corresponding to these two modes.
Case 2 \( k = \pi/a \)

When \( k = \pi/a \), the roots corresponding to the upper (optical) and lower sign (acoustic) of eqn. (4.52) are, respectively:

\[
\omega = \sqrt{\frac{2K}{M}}, \quad \epsilon_1 = -\epsilon_2; \quad \omega = \sqrt{\frac{2G}{M}}, \quad \epsilon_1 = \epsilon_2.
\]

(4.56)

As Fig. 4.6 shows, in either the optical or acoustic modes, the motions in neighboring cells are 180° out of phase. Moreover, only one type of spring is stretched. Note that if the two spring constants were the same, there would be no gap between the two frequencies at \( k = \pi/a \).

The above results can be extended to 3-D lattices with a basis. For each of the \( N \) allowed wavevectors \( \mathbf{k} \) due to the periodic boundary condition (\( N \) is the total number of primitive cells in the solid), there are \( 3p \) normal modes, where \( p \) is the number of ions in the basis.
The frequencies \( \omega_s(k) \) \((s = 1, 2, 3, \ldots, 3p)\) are all functions of \( k \), possessing the periodicity of the reciprocal lattice.

Three of the \( 3p \) branches are acoustic, i.e., they describe vibrations with frequencies that vanish for small \( k \). The rest of the \( 3(p - 1) \) branches are optical. We can think of these modes as the generalizations to the crystalline case of the three translational and \( 3(p - 1) \) vibrational degrees of freedom of a \( p \)-atomic molecule.

According to the Dulong-Petit law for classical harmonic oscillators, the specific heat capacity of a solid with \( 3N \) degrees of freedom should be a constant, equal to \( \frac{3Nk}{V} \). But the observed heat capacity exhibits a strong temperature dependent. This calls for a different treatment for lattice vibrations.

### 4.3 Quantum Theory of the Harmonic Crystal

#### 4.31 Normal Modes and Phonons

In the above, the lattice vibration normal modes were solved classically. To treat the problem quantum mechanically, it amounts to converting the original Hamiltonian, which is

\[
H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} m \omega_k^2 \sum_{\{ij\}\{nm\}} (x_i - x_j)^2
\]

where \( m \) is the mass of each atom, and \( x_i \) and \( p_i \) are the position and momentum operators of the \( i^{th} \) atom, to

\[
H = \sum_{k,s} \left( \frac{\Pi_{k,s} \Pi_{-k,s}}{2m} + \frac{1}{2} m \omega_{k,s}^2 \right) (Q_{k,s}^2 Q_{-k,s}^2)
\]

by substituting \( x_i \) and \( p_i \) by the normal coordinates \( Q_{k,s} \) and its conjugate momentum \( \Pi_{k,s} \). Notice that \( Q \) and \( \Pi \) are labeled by both \( k \) and \( s \), with \( \omega_s(k) \) being given by the dispersion relation obtained previously by the classical approach. This allows us to treat the lattice vibrations as a set of \( 3Ns \) harmonic oscillators.

The solution to the Schrödinger equation for a harmonic oscillator, i.e., \((- \hbar^2 \nabla^2 / 2m + 1/2 \ m \omega^2 x^2) \Psi = E \Psi \), with angular frequency \( \omega_{k,s} \), gives:

\[
E_n = (1/2 + n) \hbar \omega_{k,s} \quad (n = 0, 1, \ldots, \infty)
\]

For a collection of independent harmonic oscillators, the eigen values of the Hamiltonian are:
\[ E = \sum_k \sum_s (1/2 + n_{k,s}) \hbar \omega_{k,s} = \sum_k \sum_s E_{k,s} \]  

(where \( n_{k,s} \) can be 0, 1, \ldots or \( \infty \))

At a finite temperature, we can find the average energy density of the system by performing a statistical averaging:

\[ u = \frac{1}{V} \sum_i E_i e^{-\beta E_i} \bigg/ \sum_i e^{-\beta E_i}, \quad \beta = 1/k_B T, \tag{4.76} \]

To evaluate \( u \), it is more convenient to derive it from the partition function:

\[ u = \frac{\partial f}{\partial \beta}, \tag{4.80} \]

\[ f = \frac{1}{V} \ln \left( \sum_i e^{-\beta E_i} \right), \tag{4.81} \]

\[ f = \frac{1}{V} \ln \left( \sum_{\{n_{i,s}\}} e^{-\beta \sum_i (n_{i,s} + 1/2) \hbar \omega_i (k)} \right) \tag{4.82} \]

It is not difficult to see that the sum enclosed in the bracket on the RHS of eqn. (4.82) is:

\[ \prod_{k,s} \left( e^{-\beta \hbar \omega_{k,s}/2} + e^{-3\beta \hbar \omega_{k,s}/2} + e^{-5\beta \hbar \omega_{k,s}/2} + \cdots \right). \tag{4.83} \]

The individual terms in this product is a convergent geometric series that can be summed to give:

\[ f = \frac{1}{V} \ln \prod_{k,s} \frac{e^{-\beta \hbar \omega_{k,s}/2}}{1 - e^{-\beta \hbar \omega_{k,s}/2}}. \tag{4.84} \]

Differentiate w.r.t. \( \beta \), we obtain the average thermal energy density (eqn. (4.80)):

\[ u = \frac{1}{V} \sum_{k,s} \hbar \omega_{s}(k) [n_s(k) + 1/2], \tag{4.85} \]

where

\[ n_s(k) = \frac{1}{e^{\beta \hbar \omega_s(k)} - 1}. \tag{4.86} \]

The value of \( n_s(k) \) given in eqn. (4.86) can be viewed as the mean excitation number of the normal mode \( k, s \) at temperature \( T \). In the phonon language, \( n_s(k) \) is the mean number of phonons of the type \( k, s \) present at thermal equilibrium at temperature \( T \). This allows the specific heat capacity to be determined:

\[ c_v = \frac{1}{V} \sum_{k,s} \frac{\partial}{\partial T} \frac{\hbar \omega_s(k)}{e^{\beta \hbar \omega_s(k)} - 1}, \tag{4.87} \]
4.32 High-Temperature Specific Heat \((k_B T >> \hbar \omega_s)\)

In this limit, \(x = \hbar \omega / k_B T\) is small and all the normal modes are in the highly excited states. With this, we have:

\[
\frac{1}{e^x - 1} = \frac{1}{x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \cdots} = \frac{1}{x} \left[ 1 - \frac{x}{2} + \frac{x^2}{12} + O(x^3) \right],
\]

\[x = \frac{\hbar \omega}{k_B T} \ll 1.\]  \hspace{1cm} (4.88)

Substituting eqn. 4.88 in eqn. 4.87 gives \(c_v = (1/V)\Sigma_k, s(1) = 3 N p / V\), which is just the classical Dulong-Petit law. Note that at temperatures high enough for the approximation in eqn. (4.88) to be valid, the anharmonic corrections may be considered to improve the Dulong-Petit law.

4.32 Low-Temperature Specific Heat \((k_B T << \hbar \omega_o\) where the linear \(\omega(k)\) relation starts to invalidate\)

By replacing \(\Sigma_k\) by \(1/(\Delta k)^3 \int d^3 k\), where \((\Delta k)^3 = (2\pi/L_1)(2\pi/L_2)(2\pi/L_3) = (2\pi)^3 / V\), one obtains

\[c_v = \frac{\hbar \omega(k) }{\partial T} \frac{\hbar \omega(k) }{e^{\hbar \omega(k) / k_B T} - 1},\]  \hspace{1cm} (4.89)

with the integral going over the first Brillouin zone, which would include all the distinct normal modes \(k\). For those modes with \(\hbar \omega(k) / k_B T \gg 1\), the average \(n_s(k) \approx \exp(-\hbar \omega(k) / k_B T)\) would be small and so make relatively little contribution to the integral. Modes as such include the optical modes and acoustic modes with sufficiently large \(k\). It is therefore justified to adopt the following simplifications: (1) We ignore all the optical modes in the sum over \(s\) since their frequencies are large for all \(k\). (2) We replace the dispersion relation \(\omega = \omega_s(k)\) by \(\omega_s(k) = c_s(k)k\). (3) We replace the integral over the first Brillouin zone by an integral over the entire \(k\)-space. This is allowable because the integrand is negligibly small except in the vicinity of \(k = 0\). Fig. 4.8 illustrates all these simplifications.
Fig. 4.8

The simplifications that can be made in evaluating the low-temperature specific heat of a harmonic crystal. (a) Typical normal-mode dispersion relations for a diatomic crystal along a particular direction in k-space (taken to be a direction of high enough symmetry for two of the acoustic and two of the optical branches to be degenerate). (b) The spectrum that replaces (a) in evaluating the integral (4.90). The acoustic branches are replaced by linear branches, extending over all k (i.e., the integral is extended from the first zone to all of k-space) and the optical branches are ignored. This is justified because frequencies large compared with $k_BT/\hbar$ (those parts of the dispersion curves in (a) and (b) above the horizontal dashed line) make negligible contributions to (4.90), and because the parts of the dispersion curves describing modes that do contribute (the parts below the horizontal dashed line) are identical in (a) and in (b).

These lead to
\[
  c_v = \frac{\partial}{\partial T} \sum_s \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\hbar c_s(\mathbf{k}) k}{e^{\hbar c_s(\mathbf{k})/k_BT} - 1},
\]  

(4.90)

We work in the spherical coordinate and write $dk = k^2 dk d\Omega$. We further employ the change of variables $x = \beta \hbar c_s(\mathbf{k}) k$. Eqn. 4.90 becomes:
\[
  c_v = \frac{\partial}{\partial T} \left( \frac{(k_B T)^4}{(\hbar c)^3} \frac{3}{2\pi^2} \int_0^\infty \frac{x^3}{e^x - 1} \right),
\]  

(4.91)

where $c$ is an average of the inverse third power of the small-k sound velocity of the three acoustic modes:
\[
  \frac{1}{c^3} = \frac{1}{3} \sum_s \int \frac{d\Omega}{4\pi} \frac{1}{c_s(\mathbf{k})^3}.
\]  

(4.92)

The definite integral of eqn. 4.91 can be evaluated:
\[
  \int_0^\infty \frac{x^3}{e^x - 1} = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} dx = 6 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15}.
\]  

(4.93)
\[ \chi = \beta \hbar C_s (\frac{\varepsilon}{\hbar}) k \]
\[ k = \chi / (\beta \hbar C_s (\frac{\varepsilon}{\hbar})) \]
\[ \sqrt[2]{dk} = \frac{1}{(\beta \hbar C_s (\frac{\varepsilon}{\hbar}))} \cdot \sqrt[2]{d\varepsilon} \]

\[ C_v = \frac{\partial}{\partial T} \sum_i \int_0^\infty \frac{x^2 dk d\varepsilon}{(2\pi)^3} \frac{\hbar C_s (\varepsilon) k}{e^{\frac{\hbar C_s (\varepsilon) k}{\kappa B T}} - 1} \]

\[ = \frac{\partial}{\partial T} \sum_i \int_0^\infty \int_0^\infty (2\pi)^3 \frac{x^2 d\varepsilon}{(\beta \hbar C_s (\frac{\varepsilon}{\hbar}))^3} \cdot \frac{1}{\beta} \cdot \frac{\varepsilon}{e^\frac{\varepsilon}{\kappa B T} - 1} \]

\[ = \frac{\partial}{\partial T} \frac{1}{(2\pi)^3} \cdot \frac{1}{\beta^2 \hbar^4} \left( \int_0^\infty d\varepsilon \frac{\varepsilon^3}{e^\varepsilon - 1} \right) \left( \frac{5}{8} \int_0^{\frac{\varepsilon_s}{2}} d\varepsilon \frac{1}{C_s (\varepsilon)} \right) \]

\[ = \frac{\partial}{\partial T} \frac{4 \pi}{(2\pi)^3} \cdot \frac{3}{\beta^2 \hbar^4} \left( \int_0^\infty d\varepsilon \frac{\varepsilon^3}{e^\varepsilon - 1} \right) \left( \frac{1}{8} \int_0^{\frac{\varepsilon_s}{2}} \frac{d\varepsilon}{C_s (\varepsilon)} \right) \]

\[ = \frac{\partial}{\partial T} \frac{3}{2\pi^2} \cdot \frac{1}{\hbar^2 C^3} \int_0^\infty d\varepsilon \frac{\varepsilon^3}{e^\varepsilon - 1} \]

\[ = \frac{\pi^2}{3} \frac{2}{\hbar^2 C^3} \]

\[ = \frac{\pi^2}{3} \frac{2}{\hbar^2 C^3} \]

Hence, the low temperature specific heat is:

\[ c_v \approx \frac{\partial}{\partial T} \frac{\pi^2}{10} \frac{(k_B T)^4}{(\hbar c)^3} = \frac{2\pi^2}{5} k_B \left( \frac{k_B T}{\hbar c} \right)^3 \]  \hspace{1cm} (4.94)
Eqn. 4.94 produces the $T^3$ dependence of lattice specific heat observed at low temperatures. However, for the derivation leading to eqn. 4.94 to hold, $k_B T / \hbar$ must lie well within the linear regime of the dispersion curve. This will require that $T$ be well below room temperature. However, $c_v(T)$ starts to deviate from the Dulong and Petit law as soon as $T$ drops below room temperature. Therefore, there is a wide range of intermediate temperatures where the specific heat remains unexplained.

### 4.34 Intermediate Temperature Specific Heat: The Models of Debye and Einstein

The earliest quantum theories of lattice specific heats were due to Debye and Einstein. Both of them did not use the general dispersion relation as those we derived above. Instead, they assumed much simplified ones. In particular, Debye assumed a linear dispersion relation for the whole $k$ range whereas Einstein assumed a constant frequency $\omega_E$. We shall discuss each of these two models below.

#### 4.34.1 The Debye Model

The Debye model replaces all (3p) branches of the vibrational spectra with the same linear dispersion relation:

$$\omega = ck.$$  (4.95)

In addition, the integration in eqn. 4.90 over the first Brillouin zone is replaced by an integral over a sphere of radius $k_D$, chosen to contain precisely $N$ allowed wavevectors, where $N = N_{cell} p$ is the number of ions in the crystal. Obviously,

$$(2\pi)^3 N / V = 4\pi k_D^3 / 3.$$  (4.96)

Hence,

$$n = k_D^3 / 6\pi^2.$$  (4.97)

With eqns. 4.95 and 4.97, we can re-write eqn. 4.90 as:

$$c_v = \frac{3h c}{\hbar^2 T^2} \frac{k_D}{2\pi^2} \int_0^{k_D} \frac{k^3 \, dk}{e^{\hbar c k / \hbar} - 1}. $$  (4.98)

We further define the Debye frequency, $\omega_D$:

$$\omega_D = ck_D,$$  (4.99)

and the Debye temperature, $\Theta_D$:

$$k_B \Theta_D = \hbar \omega_D = \hbar c k_D.$$  (4.100)

Note that the essential unknown of this model is the parameter $c$ in the presumed linear dispersion relation (4.95), which, through eqn. 4.100, can be related to the Debye temperature $\Theta_D$. Eqn. 4.96 shows that $k_D$ is essentially a measure of the interionic separation, and $\Theta_D$ is the temperature above which all the modes begin to be excited, and below which the modes begins to be frozen out.
To obtain the specific heat, we differentiate Eqn. 4.98 w.r.t. $T$. This gives

$$C_v = \frac{3}{2\pi^2} \int_0^{\beta D} \frac{k_B^3}{\beta C} \frac{\partial}{\partial T} e^\frac{\beta C}{k_B T}$$

Substitute $x = \frac{k_B T}{\beta D}$

$$\Rightarrow C_v = \frac{3}{2\pi^2} \left( \frac{k_B}{\beta C} \right)^2 \int_0^{\beta D} \frac{g_0}{k_B T^2} \frac{x^4 e^x dx}{(e^x - 1)^3}$$

From Eqn. 4.97, $k_D = (6\pi^2 n)^{1/3}$, one gets:

$$c_v = \frac{3}{2\pi^2} k_B \left( \frac{\beta D}{\beta C} \right)^3 \int_0^{\beta D} \frac{x^4 e^x dx}{(e^x - 1)^3}$$

(4.101)

At low $T$, the upper limit of the integral can be taken to be infinity, which gives the low-temperature limit of the specific heat:

$$c_v = \frac{12\pi^4}{5} n k_B \left( \frac{T}{\Theta_D} \right)^3 = 234 \left( \frac{T}{\Theta_D} \right)^3 n k_B.$$

(4.102)

One reasonable way to choose $\Theta_D$ is by making eqn. 4.102 agree with the observed specific heat at low temperatures. This ensures that the parameter $c$ in eqn. 4.95 is related to the acoustic speed from the actual phonon spectra. Table 4.1 quotes the values of $\Theta_D$ for some of the alkali halides determined by fitting the $T^3$ term in their low-temperature specific heats. The temperature dependence of $c_v$ in the entire temperature range can be obtained by evaluating eqn. 4.101. Fig. 4.9 displays a plot of $c_v$ so obtained vs. $T/\Theta_D$.

### Table 4.1
**Debye Temperatures for the Alkali Halide Crystals**

<table>
<thead>
<tr>
<th></th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
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<td>730</td>
<td>422</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Na</td>
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</tr>
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<td>K</td>
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<td>231</td>
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</tr>
<tr>
<td>Rb</td>
<td>---</td>
<td>165</td>
<td>131</td>
<td>103</td>
</tr>
</tbody>
</table>

*Given in degrees kelvin. All values were obtained by comparing the constant in the $T^3$ fit to the low-temperature specific heat to Eq. 4.102.
At temperatures much higher than $\Theta_D$, we may evaluate eqn. 4.101 by replacing the integrand with its limiting form for small $x$. It is easy to show that the result is consistent with the Dulong and Petit law. This is not surprising since it was built into the formula through the definition of $k_D$ that total number of normal modes is $3N$. Therefore, $\Theta_D$ can be regarded as the temperature separating the low-temperature regime wherein the quantum harmonic oscillator picture must be used for the lattice motions from the high-temperature regime wherein the classical harmonic oscillator picture is valid.

(Higher order BZs
- nth BZ is the region in reciprocal lattice space reached by crossing a minimum of n-1 BZ boundaries.)

4.34.2 The Einstein Model

In the Debye model of a crystal with a polyatomic basis, the optical branches of the spectrum are essentially represented by the high $k$ values of the same linear expression eqn. 4.95 whose low $k$ values give the acoustic branch (see Fig. 4.10a). An alternative scheme is to apply the Debye model only to the three acoustic branches of the spectrum,

Fig. 4.9
Specific heat in the Debye approximation

Fig. 4.10
Two different ways of approximating the acoustic and optical branches of a diatomic crystal (illustrated in 2-D along a line of symmetry). (a) The Debye approximation. The first two zones of the square lattice are replaced by a circle with the same total area, and the entire spectrum is replaced by a linear one within the circle. (b) Debye approximation for the acoustic branch and Einstein approximation for the optical branch. The first zone is replaced by a circle with the same area, the acoustic branch is replaced by a linear branch within the circle and the optical branch is replaced by a constant branch within the circle.
and approximate the optical branches by the Einstein approximation that assumes $\omega = \omega_E$, a constant (see Fig. 4.10b). In this model, the contribution from the acoustic branches to the specific heat will just be what 4.101 gives, but with $k_D$ determined by the total number of primitive cells (not by the total number of ions) in the crystal. Each optical branch, on the other hand, will contribute

$$\frac{n\hbar \omega_E}{e^{\hbar \omega_E/k_B T} - 1}$$

(4.103)

to the thermal energy density, $u$, where $n$ is the number of unit cells per unit volume. So if there are $p$ such branches, the total contribution to the specific heat due to the optical phonons will be given by:

$$C_v^{\text{optical}} = p nk_B \frac{(\hbar \omega_E/k_B T)^2 e^{\hbar \omega_E/k_B T}}{(e^{\hbar \omega_E/k_B T} - 1)^2}$$

(4.104)

From this equation, one can see that when $T$ is much higher than the Einstein temperature, $\Theta_E \equiv \hbar \omega_E/k_B$, each optical mode simply contributes $k_B/V$ to the specific heat, consistent with the law of Dulong and Petit. But when $T$ is much smaller than $\Theta_E$, the contribution of the optical mode falls exponentially with $1/T$ demonstrating the difficulty to thermally excite the optical modes at low temperatures. Fig. 4.11 compares the Debye and Einstein specific heats.

Fig. 4.11
A comparison of the Debye and Einstein approximations to the specific heat of an insulating crystal. $\Theta$ is either the Debye or the Einstein temperature, depending on which curve is being examined. Both curves are normalized to approach the Dulong and Petit value of 5.96 cal/mole-K at high temperatures. In fitting to a solid with an $m$-ion basis, the Einstein curve should be given $m$ times the weight of the Debye one.

In a metal, we expect both the electrons as well as the lattice contribute to the specific heat. We recall that the electronic specific heat is linear in $T$ (From eqn. 2.53, $c_v^e = (\pi^2 nk_B/2)(T/T_F)$). Since the lattice specific heat goes as $T^3$, we expect the electronic part to dominate at sufficiently low temperatures, but is eventually taken over by the lattice part as $T$ is increased. It is constructive to find out what this crossover temperature is. We take the ratio between the electronic specific heat from eqn. 2.53 and the low temperature Debye specific heat from eqn. 4.102, while allowing the electron density to be $Z$ times the density of the ions where $Z$ is the valence of the atoms composing the metal:

$$\frac{c_v^e}{c_v^\text{ph}} = \frac{5}{24\pi^2} Z \frac{\Theta_D^3}{T^2 T_F}$$

(4.105)
Thus the phonon contribution begins to dominate the electronic contribution at a temperature $T_0$ where

$$T_0 = 0.145 \left( \frac{Z \Theta_D}{T_F} \right)^{1/2} \Theta_D.$$  \hspace{1cm} (4.106)

Since the Debye temperature is $\sim 100$ K while the Fermi temperature is $\sim 100,000$ K, the temperature $T_0$ is typically or the order of 1 K.

### 4.35 Density of Normal Modes

To compute statistical averages for physical properties of a lattice such as the specific heat, one often encounters expressions of the form:

$$\frac{1}{V} \sum_k Q(\omega_d(k)) = \sum_q \int \frac{d\mathbf{k}}{(2\pi)^3} Q(\omega_d(k)).$$ \hspace{1cm} (4.107)

It is convenient to reduce the integral to one in the frequency domain. To do so, one needs to employ the **density of normal modes per unit volume**, $g(\omega)$, defined such that $g(\omega)d\omega$ gives the number of energy modes in the angular frequency range between $\omega$ and $\omega + d\omega$, divided by the volume of the crystal. In the language of phonons, the density of normal modes is also called the **phonon density of levels**.

With $g(\omega)$, the sum on the LHS of eqn. 4.107 can then be written as:

$$\int d\omega \ g(\omega)Q(\omega).$$ \hspace{1cm} (4.108)

**Example:** Find $g(\omega)$ for calculating the specific heat in the Debye or Einstein model.

**Solution**

$$Vg(\omega)d\omega = \text{Number of energy modes in the angular frequency range between } \omega \text{ and } \omega + d\omega$$

$$= \text{Number of energy modes in the } |k| \text{ range between } k \text{ and } k + dk, \text{ where } k = \frac{\omega}{c}.$$

$$= \sum_s \left[ \frac{V}{(2\pi)^3} \right] (4\pi k^2) dk, \text{ where } k = \frac{\omega}{c}$$

$$= \sum_s \left[ \frac{V}{(2\pi)^3} \right] (k^2 dk), \text{ where } k = \frac{\omega}{c}$$

$$= \sum_s \left[ \frac{V}{(2\pi^2 c^3)} \right] (\omega^2 d\omega)$$

Hence, $g(\omega) = \frac{\omega^2}{(2\pi^2 c^3)}$
Note that $g(\omega) = 0$ for $\omega > \omega_D = c k D$. The quadratic prediction does agree qualitatively with the actual behavior in the low temperature region. Also, the choice of $k_D$ guarantees that the area under the curve $g_D(\omega)$ will be the same as that under the correct $g(\omega)$. If the speed $c$ has been chosen according to eqn. 4.92, the agreement in the low temperature region will be exact.

In general, $\omega(k)$ is not isotropic. In that case, the angular frequency range between $\omega$ and $\omega + d\omega$ doesn’t correspond to the range of $|k|$ between $k$ and $k + dk$. Instead, it correspond to the elemental volume in k-space enclosed between the constant-$\omega$ surfaces with $\omega_s(k) = \omega$ and $\omega + d\omega$. This gives:

$$g(\omega)d\omega = \sum_s \int \frac{dS dk}{(2\pi)^3}, \quad (4.109)$$

where the integral is over the surface in k-space with $\omega_s(k) \equiv \omega$ and $dk_\perp$ is the perpendicular distance between the constant-$\omega$ surfaces at wavevector $k$. Since $d\omega = \nabla_k \omega(k) \cdot dk = |\nabla_k \omega(k)| dk_\perp$, we have:

$$g(\omega) = \sum_s \int \frac{dS}{(2\pi)^3} \frac{1}{|\nabla_k \omega(k)|}, \quad (4.110)$$

From the above, we can see that $g(\omega)d\omega$ is determined by two factors:

1. The surface area $S_k$ which is usually $\sim k^2$.
2. $d\omega/|\nabla_k \omega(k)|$, which is the width of the constant-energy surface in k-space.

When $|\nabla_k \omega(k)| = \text{group velocity} = 0$, $g(\omega)$ has singularities. These are called the van Hove singularities and occur at the BZ boundaries. That means energy levels at the BZ boundaries have the highest degeneracy, which usually facilitates scattering. A typical density of levels displaying these singularities is shown in Fig. 4.12.

![Fig. 4.12](image)

Phonon density of levels in aluminum, as deduced from neutron scattering data (Chapter 24). The highest curve is the full density of levels. Separate level densities for the three branches are also shown. (After R. Stedman, L. Almqvist, and G. Nilsson, *Phys. Rev.* 162, 549 (1967).)