I believe that nobody who has a reasonably reliable sense for the experimental test of a theory will be able to contemplate these results without becoming convinced of the mighty logical power of the quantum theory.

W. Nernst, Z. fur Elektrochem. 17, p.265 (1911).

Chapter 10

Lattice Heat Capacity

10.1 Heat Capacity of Solids

The Dulong-Petit (1819) “rule” for molar heat capacities of crystalline matter \( c_v \), predicts the constant value

\[
c_v = \frac{3}{2} N_A k_B \quad (10.1)
\]

\[
= 24.94 \text{ J/mole}, \quad (10.2)
\]

where \( N_A \) is Avagadro’s number. Although the Dulong-Petit rule, which assumes solids to be dense, classical, ideal gases [see Eq.8.29] is in amazingly good agreement with the high temperature (\( \sim 300K^\circ \)) molar heat capacities of many solids, it fails to account for the observed rapid fall in \( c_v \) at low temperature. An especially large effect in diamond caught Einstein’s (1907) attention and with extraordinary insight he applied Plank’s “quanta” to an oscillator model of an atomic lattice to predict a universal decline in \( c_v \) as \( T \to 0K^\circ \). Several years later, when low temperature molar heat capacities could be accurately measured, they were indeed found to behave in approximate agreement with Einstein’s prediction.\(^1\) It was this result that ultimately succeeded in making the case for quantum theory and the need to radically reform physics to accommodate it.

\(^1\) \( c_v \) in metals has an additional very low temperature contribution from conduction electrons which, of course, Einstein could not account for.
10.1.1 Einstein’s Model

Einstein’s model assumes a solid composed of $N$ atoms, each of mass $M$, bound to equilibrium sites within a unit cell by simple harmonic forces. The potential energy of each atom is

$$V(R_\alpha) = \frac{1}{2} M \omega_0^2 \delta R_\alpha \cdot \delta R_\alpha$$  \hspace{1cm} (10.3)$$

with a classical equation of motion

$$\delta \ddot{R}_\alpha + \omega_0^2 \delta R_\alpha = 0$$  \hspace{1cm} (10.4)$$

where $\delta R_\alpha = R_\alpha - R_{\alpha,0}$ is the displacement vector of the $\alpha^{th}$ ion from its origin $R_{\alpha,0}$. Einstein’s independent oscillator model ignores any interactions between ions so there is only a single mode with oscillator frequency $\omega_0$. From a modern perspective Einstein’s intuitive harmonic assumption is correct, since atoms in a solid are bound by a total potential energy $V(R)$ consisting of:

1. A short range repulsive component arising from the screened coulomb interaction between positively charged ion cores

$$V_{\alpha,\beta} \approx \frac{e^2}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta \exp^{-\gamma |R_\alpha - R_\beta|}}{|R_\alpha - R_\beta|},$$  \hspace{1cm} (10.5)$$

2. A long range attractive component arising from quantum mechanical electron-electron correlations and ion-electron interactions.

The two potential energy components are shown in Figure 10.1 together with their sum, $V(R)$, which has a nearly harmonic minimum near $R_0$.

10.1.2 Einstein in $1-D$

Einstein’s landmark calculation of the heat capacity of a crystal lattice – the first application of a quantum theory to solids – is based on an independent oscillator

\footnote{With increasing displacement from $R_0$ departures from pure harmonicity (anharmonicity) become important with significant physical consequences.}
Figure 10.1: Long dashed line is the screened (short-range) coulomb repulsion between ion cores. Short dashed line is the effective ion-ion attraction due to quantum mechanical electron correlations and ion-electron interactions. Solid line, $V(r)$, is the sum of the two contributions, displaying a nearly harmonic potential minimum at $R_0$.

Model. In its simplest form, consider a one-dimensional lattice with the $\alpha^{th}$ independent oscillator having the potential

$$V(R_\alpha) = \frac{1}{2} M \omega_0^2 \delta R_\alpha^2$$

and quantum energy levels

$$E(n_\alpha) = \hbar \omega_0 \left(n_\alpha + \frac{1}{2}\right)$$

where $\alpha = 1, 2, \cdots N$ and $\omega_0$ is the natural oscillator frequency. For the 1-$D$ oscillator the quantum number $n_\alpha = 0, 1, 2, \cdots \infty$. 
With all $N$ atoms contributing, the macroscopic eigen-energies are

$$E(n) = \frac{N\hbar\omega_0}{2} + \hbar\omega_0 \sum_{\alpha=1}^{N} n_{\alpha}$$

(10.8)

$$= \frac{N\hbar\omega_0}{2} + \hbar\omega_0 n$$

(10.9)

with

$$\sum_{\alpha=1}^{N} n_{\alpha} = n$$

(10.10)

Figure 10.2: Cartoon array of 1-D Einstein harmonic oscillator potentials showing the equally spaced energy levels of Eq.10.7.

10.1.2.1 Partition Function for 1−D Einstein Model

Initially, in the spirit of Boltzmann we emphasize the role of “degeneracy” and reproduce results from Chapter 6 [see Eqs. ?? and ??] where the partition function was written

$$Z = \sum_{n=0}^{\infty} \frac{(N-1+n)!}{(N-1)!n!} e^{\beta\hbar\omega_0 \left( \frac{N}{2} + n \right)}$$

(10.11)

$$= e^{-\frac{N\beta\hbar\omega_0}{2}} \sum_{n=0}^{\infty} \frac{(N-1+n)!}{(N-1)!n!} e^{-n\beta\hbar\omega_0}.$$ 

(10.12)

The result of this sum is not entirely obvious, but with a little fancy mathematics using the $\Gamma$− function integral representation for the factorial

$$\Gamma(n) = (n-1)! = \int_{0}^{\infty} dt t^{n-1} e^{-t}$$

(10.13)
we can make the replacement

\[(N + n - 1)! = \int_0^\infty dt t^{N+n-1}e^{-t}\] (10.14)

so the partition function becomes

\[Z = e^{-\frac{N\beta h\omega_0}{2}} \int_0^\infty dt t^{N-1}e^{-t} \sum_{n=0}^\infty \frac{1}{n!} t^n e^{-n\beta h\omega_0}.\] (10.15)

Now summing over \(n\) (to get an exponential) and then integrating over \(t\) (again using the \(\Gamma\) function)

\[Z = \frac{e^{\frac{N\beta h\omega_0}{2}}}{(e^{\beta h\omega_0} - 1)^N}.\] (10.16)

Evaluation of this 1\(-D\) partition function is not difficult, but it is not extensible to higher dimensionality or to more physically interesting models.

**10.1.3 Quasi-particles and the 1\(-D\) Oscillator**

A more useful route is through the occupation number (phonon quasi-particle) method of Appendix D.

Using Eq.10.9 for the eigen-energies, the 1\(-D\) oscillator partition function is

\[Z = \exp\left[-\beta \left(\frac{N\hbar\omega_0}{2} + \hbar\omega_0 \sum_{\alpha=1}^N n_\alpha\right)\right]\] (10.17)

\[= e^{-\beta N\hbar\omega_0/2} \sum_{n_1=0}^\infty \sum_{n_2=0}^\infty \ldots \sum_{n_N=0}^\infty \exp\left[-\beta \hbar\omega_0 \sum_{\alpha=1}^N n_\alpha\right],\] (10.18)

where the sum over states is equivalent to the sum over all phonon quasi-particle occupation numbers \(n_\alpha\). Explicitly summing over \(\alpha\) we get a product of \(N\) identical geometrical series

\[Z = e^{-\frac{\beta N\hbar\omega_0}{2}} \left(\sum_{n_1=0}^\infty \exp[-\beta \hbar\omega_0 n_1]\right) \left(\sum_{n_2=0}^\infty \exp[-\beta \hbar\omega_0 n_2]\right) \ldots \left(\sum_{n_N=0}^\infty \exp[-\beta \hbar\omega_0 n_N]\right)\] (10.19)
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or

\[ Z = e^{-\beta N \hbar \omega_0 / 2} \left( \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_0 n} \right)^N \]  \hspace{1cm} (10.20)

which is summed to give

\[ Z = \frac{e^{\beta N \hbar \omega_0 / 2}}{\left( e^{\beta \hbar \omega_0} - 1 \right)^N} \]  \hspace{1cm} (10.21)

the same result as in Eq.10.16.

10.1.4 The 3-D Einstein Model

The 3-D Einstein partition function although approaching a realistic model, still falls short of what is physical observed. [See the Debye model discussion later in the chapter.] It uses the same method as above, except that the coordinate components \( x, y, z \), of the \( \alpha^{th} \) independent oscillator displacements are taken into account. The 3-D oscillator model has the eigen-energies

\[ E(n_{\alpha,x}, n_{\alpha,y}, n_{\alpha,z}) = \hbar \omega_0 (n_{\alpha,x} + n_{\alpha,y} + n_{\alpha,z} + 3/2) \]  \hspace{1cm} (10.22)

where again \( \alpha = 1, 2, 3, \ldots N \), \( n_{\alpha,x}, n_{\alpha,y}, n_{\alpha,z} = 0, 1, 2, \ldots, \infty \) and \( \omega_0 \) is the oscillator frequency. The \( N \) oscillator lattice has the eigen-energies

\[ E_{x,y,z} = \frac{3N \hbar \omega_0}{2} + \hbar \omega_0 \sum_{\alpha=1}^{N} (n_{\alpha,x} + n_{\alpha,y} + n_{\alpha,z}) \]  \hspace{1cm} (10.23)

10.1.4.1 Partition Function for the 3-D Einstein Model

Using the result of Eq.10.23 the partition function is written

\[ Z = e^{\frac{3N \beta \hbar \omega_0}{2}} \sum_{n_{1,x}=0}^{\infty} \sum_{n_{1,y}=0}^{\infty} \ldots \sum_{n_{N,z}=0}^{\infty} \exp \left\{ -\beta \left[ \hbar \omega_0 \sum_{\alpha=1}^{N} (n_{\alpha,x} + n_{\alpha,y} + n_{\alpha,z}) \right] \right\} \]  \hspace{1cm} (10.24)
10.1. HEAT CAPACITY OF SOLIDS

The sum is managed, as in section 10.1.3, by first explicitly taking the sum over \( \alpha \) in the exponential. Then, because the three coordinate sum sets \((n_{\alpha,x}, n_{\alpha,y}, n_{\alpha,z})\) are identical, what remains is

\[
Z = e^{-\frac{3\beta N\hbar\omega_0}{2}} \left( \sum_{n_1=0}^{\infty} \exp[-\beta\hbar\omega_0 n_1] \right)^3 \left( \sum_{n_2=0}^{\infty} \exp[-\beta\hbar\omega_0 n_2] \right)^3 \cdots \left( \sum_{n_N=0}^{\infty} \exp[-\beta\hbar\omega_0 n_N] \right)^3.
\]

(10.25)

Finally,

\[
Z = e^{-\frac{3N\beta\hbar\omega_0}{2}} \left( \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_0 n} \right)^{3N},
\]

(10.26)

where the remaining sum gives

\[
Z = \left[ e^{-\frac{\beta\hbar\omega_0}{2}} \left( \frac{1}{1 - e^{-\beta\hbar\omega_0}} \right) \right]^{3N}.
\]

(10.27)

10.1.4.2 Thermodynamics of the 3-\( D \) Einstein Model

Following the steps from previous chapters, the internal energy is

\[
\mathcal{U} = -\frac{\partial}{\partial\beta} \ln Z = 3N\hbar\omega_0 \left[ \frac{1}{2} + \langle n \rangle \right]
\]

(10.29)

where\(^3\)

\[
\langle n \rangle = \frac{1}{(e^{\beta\hbar\omega_0} - 1)}.
\]

(10.30)

\(^3\)\( (n) \) is called a Bose-Einstein “function” or, for the case of phonons, the average Bose-Einstein quasi-particle occupation number.

There is a distinction between the Bose-Einstein function for real, massive, boson particles, e.g. \( He^4 \) [see Chapter 17], and boson quasi-particles, e.g. phonons and photons, which are merely energy excitations.
Einstein’s constant volume heat capacity is therefore
\[ C_N = \left( \frac{\partial U}{\partial T} \right)_N \]
\[ = -k_B \beta^2 \left( \frac{\partial U}{\partial \beta} \right)_N \]
\[ = 3Nk_B \frac{(\beta \hbar \omega_0)^2 e^{\beta \hbar \omega_0}}{(e^{\beta \hbar \omega_0} - 1)^2} \]  \hspace{1cm} (10.31)

It is conventional to replace the harmonic force \( \omega_0 \) with an Einstein temperature \( \theta_E \)
\[ k_B \theta_E = \hbar \omega_0. \]  \hspace{1cm} (10.32)

Then
\[ C_N = 3Nk_B \frac{(\theta_E/T)^2 e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \]  \hspace{1cm} (10.33)

which can characterize specific materials by fitting to experimental data.

![Graph](image)

Figure 10.3: 3 - D Einstein model heat capacity \( \frac{C_N}{3Nk_B} \) vs. \( \frac{T}{\theta_E} \). Note the sharp exponential drop as \( T \to 0 \)

In the low temperature limit Eq.10.33 becomes
\[ \lim_{T \to 0} C_N \to 3Nk_B (\theta_E/T)^2 e^{-\theta_E/T} \]  \hspace{1cm} (10.34)
as shown in Figure 10.3. Sadly, this steep exponential decline is never observed. What is universally observed is $C \sim T^3$.

Einstein was aware that a single oscillator frequency model was bound to be inadequate and he did try to improve upon it, without success. His primary objective, however, was to apply quantum theory and show that it explained several poorly understood phenomena. This he achieved.

At high temperature the Einstein result is $\lim_{T \to \infty} C_N = 3Nk_B$, in accord with Dulong-Petit.

## 10.2 Debye Model

The effect of atom-atom interactions were added to Einstein’s theory by Debye. Their consequence is to introduce dispersion into the oscillator frequencies, which is precisely the correction Einstein sought but never achieved.

As a result of atom-atom interactions:

1. Translational (crystal) symmetry is introduced, with a new wave vector quantum number $k$, sometimes called crystal momentum, with

$$k_j = \frac{2\pi}{N_j a_j} \nu_j \quad j = x, y, z,$$

where $a_j$ is the $j^{th}$ crystal direction lattice spacing, $N_j$ the number of atoms in the $j^{th}$ crystal direction and where $\nu_j = 1, 2, 3 \ldots N_j$.

2. As shown in Figure 10.4, rather than a single lattice frequency $\omega_0$ there is now a range of frequencies which Debye assumed varied linearly with $|k|$:

$$\omega = \omega(k)$$

$$= c_s |k|$$

where $c_s$ is an average speed of sound in the crystal.

---


5In solid state physics it is conventional to choose $-\frac{N}{2} < \nu \leq \frac{N}{2}$ which, in this example, would define a 1-D Brillouin Zone.

6One might say that the atom-atom interactions have lifted the degeneracy among single atom oscillator frequencies.

7This turns out to be an approximation that accurately replicates the small $|k|$ behavior of lattice vibrations in 3-D crystals.
3. The infinitely sharp Einstein “phonon” density of states

\[ D_E(\omega) = N\delta(\omega - \omega_0) \]  

becomes, in the Debye model,\(^8\)

\[ D_D(\omega) = \frac{V\omega^2}{2\pi^2 c_s^3} \]  

4. Since in a finite crystal the quantum number \( k \) is bounded, the range of Debye’s oscillator frequencies is also bounded, i.e.

\[ 0 \leq \omega < \Omega_D. \]  

so that

\[ \int_0^\infty d\omega D_E(\omega) = \int_0^{\Omega_D} d\omega D_D(\omega), \]  

i.e. the total number of modes is the same in both models.

Whereas the Einstein internal energy \( U_E \) is [see Eq.10.29]

\[ U_E = 3\hbar \int_0^\infty \omega \, d\omega \, \{ N\delta(\omega - \omega_0) \} \left[ \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right] \]  

\[ = 3N\omega_0 \left[ \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_0} - 1} \right] \]  

the changes introduced by Debye give instead the internal energy \( U_D \)

\[ U_D = 3\hbar \int_0^{\Omega_D} \omega \, d\omega \left\{ \frac{V}{2\pi^2 c_s^3} \right\} \left[ \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right] \]  

\[ = \frac{3V}{2\pi^3 c_s^3 \beta^4} \int_0^{\beta\hbar\Omega_D} dx \, x^3 \left( \frac{1}{2} + \frac{1}{e^x - 1} \right) \]  

\(^8\)See Appendix E.
10.2. DEBYE MODEL

Figure 10.4: Mode dependent frequencies. The solid curve represents an approximate result for a real lattice. The dashed line represents Debye’s linear approximation. The slope of the dashed line is the average speed of sound in the crystal. The horizontal dashed grey line at $\omega = \omega_0$ represents the dispersion of an Einstein lattice model.

10.2.0.3 Thermodynamics of the Debye Lattice

At high temperature, $\beta \hbar \Omega_D << 1$, the integral in Eq.10.45 can be approximated by expanding $e^x \approx 1 + x$. Then using Eq.10.41 the Debye internal energy is

$$\lim_{T \to \infty} U_D = \frac{V}{2\pi^2} \left( \frac{\Omega_D}{c_s} \right)^3 k_B T$$

$$= 3Nk_B T$$
a result also consistent with the Dulong-Petit rule.

At low temperature, $\beta\hbar\Omega_D >> 1$, the internal energy integral can be approximated as

$$\lim_{T \to 0} U_D \to \frac{3V}{2\pi^3 \hbar^3 c_s^3 \beta^4} \int_0^\infty dx x^3 \left( \frac{1}{2} + \frac{1}{e^x - 1} \right)$$

(10.48)

from which follows the low temperature heat capacity

$$\lim_{T \to 0} C_V \to \frac{6k_B^4}{\pi^2 \hbar^3 c_s^3} \times \frac{\pi^4}{15} T^3$$

(10.49)

$$= Nk_B \left( \frac{12\pi^4}{5} \right) \times \left( \frac{T}{\Theta_D} \right)^3.$$ 

(10.50)

where

$$\hbar\Omega_D = k_B\Theta_D$$

(10.51)

with $\Theta_D$ the Debye temperature.

The $T^3$ low temperature heat capacity is almost universally observed in solids. Examples of Debye temperatures are given in Figure 10.5.
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<th>Substance</th>
<th>Debye Temperature $\Theta_D$</th>
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<tr>
<td>Cadmium</td>
<td>209 K</td>
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</tr>
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<td>Zinc</td>
<td>327 K</td>
</tr>
</tbody>
</table>

Figure 10.5: Debye temperatures $\Theta_D$ in solids. Charles Kittel, Introduction to Solid State Physics, 7th Ed., Wiley, (1996).