

# The Debye Model of Lattice Heat Capacity

The Debye model of lattice heat capacity is more involved than the relatively simple Einstein model, but it does keep the same basic idea: the internal energy depends on the energy per phonon ( $\epsilon = \hbar\Omega$ ) times the average number of phonons (Planck distribution:  $n_{\text{avg}} = 1/[e^{\hbar\Omega/kT} - 1]$ ) times the number of modes. **It is in the number of modes that the difference between the two models occurs.**

In the Einstein model, we simply assumed that each mode was the same (same frequency,  $\Omega$ ), and that the number of modes was equal to the number of atoms in the lattice.

**In the Debye model, we assume that each mode has its own  $\mathbf{K}$**  (that is, has its own  $\lambda$ ). Since  $\Omega$  is related to  $\mathbf{K}$  (by the dispersion relation), **each mode has a different  $\Omega$ .**

## 1. Number of modes

In the Debye model we **assume that the normal modes consist of STANDING WAVES**. If we have travelling waves, they will carry energy through the material; if they contain the heat energy (that will not move) they need to be standing waves. Standing waves are waves that do travel but go back and forth and interfere with each other to create standing waves.

Recall that Newton's Second Law gave us atoms that oscillate: [here  $x = sa$  where  $s$  is an integer and  $a$  the lattice spacing]

$$u_s = u_0 e^{i\Omega t} e^{iKsa};$$

and if we use the form  $\sin(Ksa)$  for  $e^{iKsa}$  [both indicate oscillations]:

$$u_s = u_0 e^{i\Omega t} \sin(Ksa).$$

We now apply the boundary conditions on our solution: to have standing waves both ends of the wave must be tied down, that is, we must have  $u_0 = 0$  and  $u_N = 0$ . This means that we need to use the sine function rather than the cosine function [since  $\sin(0) = 0$ ,  $\cos(0) = 1$ ], and further:

$$K_{\#}L = \#\pi, \quad \text{where } L = \text{full length of solid and } \# \text{ is any integer.}$$

For a one-dimensional model,  $L = Na$ , where  $N$  is the number of atoms. Therefore, our condition for a standing wave gives:

$$K_{\#} = \#\pi/L = \#\pi/Na.$$

Since the maximum  $K$  is  $K_{\text{max}} = \pi/a$ , [recall that any  $K > G$  gives the same oscillation as  $K \pm G$  as shown in Problem 9] the maximum number is  $\#_{\text{max}} = N$ . Hence there are  $N$  modes if we have  $N$  atoms (just as Einstein assumed).

## 2a. Density of states - standing waves

The density of states (or density of modes) is simply the number of modes per range of  $K$  values:

$$\text{Density of modes} = D(K) = N/K_{\text{max}} = N/(\pi/a) = Na/\pi = L/\pi.$$

Hence the number of modes in a range  $dK$  is  $D(K) dK = (L/\pi) dK$ . However, since the energy per phonon and the Planck distribution ( $n_{\text{avg}}$ ) are in terms of  $\Omega$  instead of  $K$ , it would be useful to find the density of states in terms of  $\Omega$  instead of  $K$ . If we add up all the states, we should get the total number of states which is  $N$ :

$$\int_0^{K_{\text{max}}} D(K) dK = N = \int_0^{\Omega_{\text{max}}} D(\Omega) d\Omega, \quad \text{where } \Omega_{\text{max}} = K_{\text{max}} v_{\text{phase}}. \quad [\text{Recall that } v_{\text{phase}} = \Omega/K, \text{ so } \Omega = K v_{\text{phase}}.]$$

We note that  $dK/d\Omega = 1/(d\Omega/dK)$ .

$$D(\Omega) d\Omega = D(K) dK = D(K) dK (d\Omega/dK) = D(K) (dK/d\Omega) d\Omega,$$

and with  $D(K) = L/\pi$  and  $dK/d\Omega = 1/(d\Omega/dK)$  we get:  $D(\Omega) d\Omega = (L/\pi) d\Omega / (d\Omega/dK)$ .

Recall that  $v_{\text{group}} = d\Omega/dK$ , so  $D(\Omega) d\Omega = (L/\pi v_{\text{group}}) d\Omega$ .

This is for 1-D. While  $K$  can be extended to 3-D by making  $K$  a vector,  $\Omega$  is a scalar.

## 2b. Density of states - periodic travelling waves

Another way (which will be easier to extend to three dimensions) of getting the modes is to assume that we have **periodic travelling waves** such that the wave repeats over a distance,  $L$ :

$$\mathbf{K}_{\#}L = \pm\#(2\pi), \text{ and since } L=Na: \mathbf{K}_{\#} = \pm\#2\pi/Na \text{ (where } \# \text{ is an integer).}$$

Again,  $\mathbf{K}$  is limited to the first Brillouin zone since  $\mathbf{K}' = \mathbf{K} + \mathbf{G}$  gives the same oscillation pattern for the atoms:

$$\mathbf{K}_{\max} = \pi/a, \text{ so } \mathbf{K}_{\max} = \#_{\max} 2\pi/Na = \pi/a, \text{ so } \#_{\max} = N/2.$$

But the fact that we have a  $\pm$  sign gives us  $N$  modes. To get the density of states:

$$D(\mathbf{K}) = \Delta\#/\Delta\mathbf{K} = N/(\pi/a - (-\pi/a)) = N/(2\pi/a) = Na/2\pi = L/2\pi.$$

For three dimensions:  $D(\mathbf{K}) = (L_x/2\pi)(L_y/2\pi)(L_z/2\pi)$ , so

$$D(\mathbf{K}) dK_x dK_y dK_z = (L/2\pi)^3 dK_x dK_y dK_z.$$

Since the total number of nodes still should be  $N_x N_y N_z = N_{\text{total}}$ , we have, with  $a_x = a_y = a_z$ :

$$N = \int_{-\pi/a}^{+\pi/a} \int_{-\pi/a}^{+\pi/a} \int_{-\pi/a}^{+\pi/a} (L/2\pi)^3 dK_x dK_y dK_z.$$

This is in rectangular form. We can also put this in spherical form, (in analogy with  $dx dy dz = dV = dr r d\theta r(\sin\theta)d\phi$ ),

and with spherical symmetry,  $dx dy dz = 4\pi r^2 dr$ , so  $dK_x dK_y dK_z = 4\pi K^2 dK$ , and

$$N = \int_0^{K_{\max}} (L/2\pi)^3 4\pi K^2 dK = (L/2\pi)^3 4\pi K_{\max}^3 / 3,$$

or  $N = (L^3/6\pi^2) K_{\max}^3$ , and so  $\mathbf{K}_D \equiv \mathbf{K}_{\max} = (6\pi^2 N/V)^{1/3}$ , where  $(L^3 = V)$ ;

in terms of  $\Omega$  (since  $\Omega/K = v_{\text{phase}}$ , so  $K = \Omega/v_{\text{phase}}$ , and  $d\Omega/dK = v_{\text{group}}$ , so  $dK = d\Omega/v_{\text{group}}$ ):

$$N = \int_0^{\Omega_{\max}} (L/2\pi)^3 4\pi (\Omega/v_{\text{phase}})^2 (d\Omega/v_{\text{group}}), \text{ and integrating we get:}$$

$$N = (V/6\pi^2) \Omega_{\max}^3 / (v_{\text{phase}}^2 v_{\text{group}}). \text{ Now we assume } \mathbf{v}_{\text{group}} = \mathbf{v}_{\text{phase}} = \mathbf{v}.$$

Rearranging:  $\mathbf{\Omega}_D \equiv \mathbf{\Omega}_{\max} = [6\pi^2 v^3 N/V]^{1/3}$ .

Also,  $\mathbf{D}(\mathbf{\Omega}) \equiv dN/d\Omega = 3\Omega^2(V/6\pi^2 v^3) = \mathbf{V}\Omega^2/2\pi^2 v^3$ .

## 3. Internal energy of a lattice:

$$U(T) = (\text{energy/phonon}) (\text{average number of phonons/mode}) (\text{number of modes})$$

but since each mode has a different energy (different frequency), we must integrate:

$$U(T) = \int_0^{\Omega_D} (\hbar\Omega) (1/[e^{\hbar\Omega/kT} - 1]) D(\Omega) d\Omega,$$

or using the results of part 2-b above:  $D(\Omega) = dN/d\Omega = V\Omega^2/2\pi^2 v^3$ :

$$U(T) = \int_0^{\Omega_D} (\hbar\Omega) (1/[e^{\hbar\Omega/kT} - 1]) (V\Omega^2/2\pi^2 v^3) d\Omega.$$

We should get this contribution to  $U$  for each (of three) polarizations. If we **assume that the phase velocity is independent of polarization**, then:

$$U(T) = (3V\hbar/2\pi^2 v^3) \int_0^{\Omega_D} \{ \Omega^3 / [e^{\hbar\Omega/kT} - 1] \} d\Omega.$$

We now have two ways to go. We can try to get a nicer expression for  $U(T)$ , or we can now take the derivative of  $U$  with respect to  $T$  to get an expression for  $C_V$ . Each way has advantages and disadvantages, so we will do both ways.

#### 4. Getting a nicer form for U(T) for use in C:

To get the integral into more standard form, let  $x = \hbar\Omega/k_B T$  (note: x is dimensionless), so  $\Omega = k_B T x / \hbar$ ,  $\Omega_D = (k_B T / \hbar) x_D$  and  $d\Omega = (k_B T / \hbar) dx$ :

$$U(T) = (3V\hbar/2\pi^2v^3) (k_B T / \hbar)^4 \int_0^{x_D} \{x^3 / [e^x - 1]\} dx .$$

Now let  $\Theta \equiv \hbar\Omega_D/k_B$  ( $\Theta$  has units of T and is called the **Debye Temperature**), where from 2-b above  $\Omega_D = (6\pi^2v^3N/V)^{1/3}$ . Also, if we multiply the coefficient out front of the integral by  $3N/3N$ :

$$3N(3V\hbar/[3N\cdot 2\pi^2v^3]) = 9N\hbar(V/N6\pi^2v^3) = 9N\hbar/\Omega_D^3; \text{ and } x_D = \hbar\Omega_D/k_B T = \Theta/T:$$

$$U(T) = (9N\hbar/\Omega_D^3) (k_B T / \hbar)^4 \int_0^{\Theta/T} x^3 / [e^x - 1] dx , \text{ or (with } \Theta = \hbar\Omega_D/k_B):$$

$$U(T) = 9Nk_B T (T/\Theta)^3 \int_0^{\Theta/T} x^3 / [e^x - 1] dx .$$

This is the "nicer" form for U(T). It has usefulness in finding U(T) and  $C_V$  **for small T**, since for small T (compared to  $\Theta$ ): as  $T \rightarrow 0$ ,  $(\Theta/T) \rightarrow \infty$ , and hence the limits of the integral become 0 to  $\infty$ , and this integral,  $\int_0^\infty x^3 / [e^x - 1] dx$  can then be integrated (although not easily). What we do is expand the denominator in a Taylor series:

$$1/[e^x - 1] = e^{-x} / [1 - e^{-x}] = e^{-x} \{1 + e^{-x} + e^{-2x} + e^{-3x} + \dots\} = \sum_{s=1}^\infty e^{-sx} .$$

$$\int_0^\infty x^3 \sum_{s=1}^\infty e^{-sx} dx = 6 \sum_{s=1}^\infty (1/s^4) = \pi^4/15$$

where we have integrated by parts three times to get rid of the  $x^3$  term plus one last integration (hence the  $1/s^4$  terms), and have used a series identity to get the final numerical result.

*Problem 17 asks you to demonstrate [not necessarily prove] that this works out numerically.*

Therefore, **for small T** ( $T \ll \Theta$ ):

$$U(T) \approx 9N\pi^4 k_B T^4 / 15\Theta^3 \text{ and}$$

$$C = dU/dT \approx 36N\pi^4 k_B T^3 / 15\Theta^3 \approx 234Nk_B (T/\Theta)^3 ,$$

which **does go as T<sup>3</sup>** as it does in the experiments. Recall now what  $\Theta$  was:

$$\Theta \equiv \hbar\Omega_D/k_B \text{ (}\Theta \text{ has units of T), where from 2-b above}$$

$$\Omega_D = (6\pi^2v^3N/V)^{1/3} .$$

Therefore,

$$\Theta = \hbar(6\pi^2v^3N/V)^{1/3} / k_B ,$$

which depends on the number density and the velocity (group = phase) of oscillations in the material (speed of sound in the material). For example,  $\Theta = 428$  K for Aluminum and 343 K for Copper.

In the low temperature limit, the probability of exciting high  $\Omega$  would be extremely low (from the Boltzmann distribution:  $P(E) = Ae^{-E/kT}$  with  $E = \hbar\Omega$ ). Therefore the optical branch will not be appreciably excited at low temperatures, and the Debye approximation of  $v_{\text{phase}} \approx \text{constant} \approx v_{\text{group}}$  should hold very well (as it appears to do experimentally!).

*You should be able to do homework problem 18 now.*

## 5. Working to get C directly from U(T) in section 3:

$$U(T) = (3V\hbar/2\pi^2v^3) \int_0^{\Omega_D} \{ \Omega^3 / [e^{\hbar\Omega/kT} - 1] \} d\Omega \quad \text{from section 3;}$$

now recall that  $d[1/f(x)]/dx = [-1/f(x)^2][df(x)/dx]$ , and  $d(e^{a/x})/dx = (-a/x^2)e^{a/x}$ , so

$$C = dU(T)/dT = (3V\hbar/2\pi^2v^3) \int_0^{\Omega_D} \{ \Omega^3 / [e^{\hbar\Omega/kT} - 1]^2 \} (-e^{\hbar\Omega/kT})(-\hbar\Omega/k_B T^2) d\Omega$$

$$\text{or } C = (3V\hbar^2/2\pi^2v^3k_B T^2) \int_0^{\Omega_D} \{ \Omega^4 e^{\hbar\Omega/kT} / [e^{\hbar\Omega/kT} - 1]^2 \} d\Omega .$$

Again, we will let  $x = \hbar\Omega/k_B T$  (note: x is dimensionless), so

$\Omega = k_B T x / \hbar$ ,  $\Omega_D = (k_B T / \hbar) x_D$  and  $d\Omega = (k_B T / \hbar) dx$ , and C becomes:

$$C = (3V\hbar^2/2\pi^2v^3k_B T^2)(k_B T / \hbar)^5 \int_0^{x_D} \{ x^4 e^x / [e^x - 1]^2 \} dx .$$

Again, multiply through by  $3N/3N$  and let  $\Theta \equiv \hbar\Omega_D/k_B$  as we did above:

$$C = 9Nk_B(V/6\pi^2v^3)(k_B T / \hbar)^3 \int_0^{\Theta/T} x^4 e^x / [e^x - 1]^2 dx$$

and we recognize that  $(6\pi^2v^3N/V) = \Omega_D^3$ , (again assuming  $v_p \approx v_g = v$ ), and again letting  $\Theta = \hbar\Omega_D/k_B$ , we get:  $C = 9Nk_B(T/\Theta)^3 \int_0^{\Theta/T} x^4 e^x / (e^x - 1)^2 dx$ .

This form is most useful for looking at what happens at **large T (that is,  $T \gg \Theta$ )**: in this case, the limits of the integral extend over only a small distance from the origin, and therefore x is always small. This allows us to approximate the  $e^x$  in a Taylor series:  $e^x \approx 1$  in the numerator, but  $e^x \approx 1 + x$  in the denominator since we don't want 0 there:

$$C = 9Nk_B(T/\Theta)^3 \int_0^{\Theta/T} x^4 (1) / [(1+x) - 1]^2 dx = 9Nk_B(T/\Theta)^3 \int_0^{\Theta/T} x^4 / x^2 dx$$

$$C = 9Nk_B(T/\Theta)^3 (1/3)(\Theta/T)^3 = 3Nk_B = 3nR \quad (\text{n is the number of moles}),$$

which matches the results of experiments in the high T limit.

Why does this result work? If we consider the high T limit, all modes are active, and the energy is about evenly distributed throughout the modes (low energy modes have low  $\Omega$  but that means they also have high  $n_{\text{avg}}$ ). Therefore both the Einstein and the Debye result agree with experiment, because in both we have N modes all with about the same average energy.

*You should be able to do homework problem #19 now.*

## 6. Numerical example

For copper, atomic mass = 63 grams/mole;  $\Theta = 343$  K; experimental heat capacity at room temp  
 $= .385$  J/gm- $C^\circ$ .

For high temperatures, theoretical  $C = 3nR = 3(1 \text{ mole}/63 \text{ grams}) * 8.3 \text{ J/mole-K} = .395$  J/gm- $C^\circ$ .