Lattice Heat Capacity, the Planck Distribution, and the Einstein Model

1. Review: Heat capacity, C, is the measure of how much heat (energy) it takes to raise the temperature of the object a certain amount.   In MKS units, it is measured in Joules/Kelvin.

To take out the dependence on the size of the object, we can specify a heat capacity per mass or a heat capacity per mole.

There are basically two heat capacities: one is when we add heat and watch the temperature rise while we hold the volume constant, C_V, and one where we hold the pressure constant, C_P.   For a gas, this makes a significant difference since as you heat a gas its pressure goes up and it tends to expand.   If the gas is allowed to expand, it will do work on the surrounding gas (or container or piston).   This work will take some of the heat energy out of the system and not be available to raise the temperature.   If the gas is not allowed to expand, then there will be no work done (recall work is force thru a distance), and so all of the heat added will go to raising the temperature.   Hence for a gas, $C_P > C_V$.   As you can see, the most direct measure of the heat capacity will then be the C_V since all of the heat will go into raising the temperature.

Since a solid expands very little when heated (unlike a gas), there is essentially very little difference between C_V and C_P.   Experimentally it is easier to measure C_P than C_V, but we can say that for our purposes, $C_P \approx C_V = C$.

2. Experimental facts:
At room T, $C \approx 3Nk_B$, where N is the number of atoms in the crystal and k_B is Boltzmann's constant. Recall that the gas constant, R, is defined in terms of Boltzmann's constant: $R = N_{A*}k_B$, where N_A is Avagadro's number.   Thus the **molar** heat capacity, $C_{molar} \approx 3Nk_B / n$ where n is the number of moles, and $n = N/N_A$, so $C_{molar} \approx 3N_Ak_B = 3R$.
At low T, $C \alpha T^3$ for insulators,   and $C \alpha T$ for metals.
At low T, magnetic ordering affects C.

3. Internal Energy:
The heat that goes into a solid to raise its temperature shows up as **"internal" energy**.   We will designate this internal energy as **U**.   For a solid this shows up as vibrational energy (phonons).   If we can determine how U is related to T, then we can calculate C_V since $C_V \equiv (\partial U/\partial T)_V$.

In calculating U, we recognize that we need to consider the following: (1) what is the average energy of each phonon; (2) what is the average quantum number (number of phonons) existing at any T for each type (mode) of vibration; and (3) how many different types (modes) of vibration are there.

4. Energy of a phonon: [Here we will use Ω as the frequency of the phonon.]
From the quantum theory, we know that for a harmonic oscillator, $E_{HO} = (n+\frac{1}{2})\hbar\Omega$.   Since we are interested only in how the internal energy **changes** with Temperature, we can disregard the ½.   Hence we can see that **each phonon should have an energy of $\hbar\Omega$.**

5. Average number of phonons of energy $\varepsilon=\hbar\Omega$ at temperature, T: (Planck distribution)
5a) Definition of average:
To find an average, we simply take the sum of the values and divide by the number of values.   Or we can take the sum of the values multiplied by their probability (and divide by the total probability which should be one).

5b) Probability of have n phonons of energy $\varepsilon=\hbar\Omega$ at a temperature, T: (Boltzmann distribution)
From probability theory we get that **the probability of having a certain amount of something** [here number of phonons] **depends on how much of that something** [total energy] **there is and how many ways it can be divided** [distributing the total energy among the total number of modes].   **Assuming that each piece** (each phonon)

has an equal probability of belonging to any of the objects [modes], the probability of having a certain number, n, of pieces [phonons] falls off exponentially with n.   This is the Boltzmann probability distribution. For a more detailed example, see the one page section on the Boltzmann distribution.   The result is that the probability of having an energy, $E=n\varepsilon$, [here $\varepsilon=\hbar\Omega$ is the energy of one phonon] is:

$$P(E) \;=\; A\,e^{-E/kT} \;=\; A\,e^{-n\varepsilon/kT}\;, \qquad \textbf{(Boltzmann distribution)}$$

where k is Boltzmann's constant, T is the Temperature in Kelvins, and A is some amplitude such that the sum of all the probabilities is 1.

5c)   Average number of phonons of energy $\varepsilon=\hbar\Omega$ at temperature, T: (Planck distribution)
From the basic definition of average, we have   (where the k in the exponent is k_B):

$$E_{avg} \;=\; n_{avg}\varepsilon \;=\; \left[\,{}_n\Sigma\,(n\varepsilon)\,A\,e^{-n\varepsilon/kT}\right] / \left[\,{}_n\Sigma\,A\,e^{-n\varepsilon/kT}\right]\;;$$

we can divide through by ε, and we can divide out the A to get an expression for n_{avg}:

$$n_{avg} \;=\; \left[\,{}_n\Sigma\,n\,e^{-n\varepsilon/kT}\right] / \left[\,{}_n\Sigma\,e^{-n\varepsilon/kT}\right]\;.$$

Here we **become tricky**.   Note that the numerator is the derivative with respect to $\varepsilon/k_B T$ of the denominator. Recall that if we integrate dx/x we get the ln function.   So if we differentiate the ln function, we get dx/x. From these facts:

$$-k_B T\,\partial\{\ln[\Sigma e^{-n\varepsilon/kT}]\}/\partial\varepsilon \;=\; \left[\,{}_n\Sigma\,n\,e^{-n\varepsilon/kT}\right] / \left[\,{}_n\Sigma\,e^{-n\varepsilon/kT}\right]\;,\ \text{so}$$

$$n_{avg} \;=\; -k_B T\,\partial\{\ln[\Sigma e^{-n\varepsilon/kT}]\}/\partial\varepsilon\;.$$

Having experience with doing the Taylor series expansions forward, we can sometimes recognize an expansion as belonging to some function and effectively do the Taylor series expansion backwards:

$$ {}_n\Sigma\,e^{-n\varepsilon/kT} \;=\; 1 + e^{-\varepsilon/kT} + e^{-2\varepsilon/kT} + e^{-3\varepsilon/kT} + \ldots \;=\; 1/[1 - e^{-\varepsilon/kT}]\;.$$

Therefore, we can put this together to get [using $\ln(1/x) = -\ln(x)$]:

$$n_{avg} \;=\; -k_B T\,\partial\{\ln[1/(1 - e^{-\varepsilon/kT})]\}/\partial\varepsilon \;=\; +k_B T\,\partial\{\ln[1 - e^{-\varepsilon/kT}]\}/\partial\varepsilon$$

and now performing the differentiation:

$$n_{avg} \;=\; k_B T\,\{1/[1 - e^{-\varepsilon/kT}]\}*\{0 - (-1/k_B T)\,e^{-\varepsilon/kT}\} \;=\; e^{-\varepsilon/kT}/[1 - e^{-\varepsilon/kT}]$$

and multiplying through by $e^{+\varepsilon/kT}$:

$$n_{avg} \;=\; 1/[e^{+\varepsilon/kT} - 1]\;. \qquad \underline{\textbf{(Planck distribution)}}$$

where n_{avg} is the average number (of phonons) that have energy, ε, at temperature, T.   Recall that for phonons, $\varepsilon=\hbar\Omega$.

You should be able to do homework problem #16 now.

Note that for $\varepsilon \ll k_B T$ we get $n_{avg} \approx 1/[(1 + \varepsilon/k_B T) - 1] = k_B T/\varepsilon$,   plenty of energy compared to size of energy piece, so probability of exciting a photon is high, so all of thermal energy goes into phonons, $k_B T = n_{avg}\varepsilon$;

and   that for $\varepsilon \gg k_B T$ we get $n_{avg} \approx 1/e^{+\varepsilon/kT} = e^{-\varepsilon/kT}$,   energy of one photon is high compared to available thermal energy, so probability reduces to that of the Boltzmann Distribution – becomes exponentially small.

6. **Different models for heat capacity** use different ways of determining the types (modes) of oscillation. We will consider two models: the Einstein model and the Debye model.   In each model we use the idea that internal energy, U, depends on three things:

     (1) the energy of a phonon   [$\varepsilon = \hbar\Omega = hf$ where $f = \Omega/2\pi)$],
     (2) the average number of phonons with $\varepsilon = \hbar\Omega$ [$n_{avg} = 1/(e^{\varepsilon/kT} - 1)$], (Planck Distribution), and
     (3) the types (modes) of oscillations (which will be different for - and in fact distinguishes - the Einstein and Debye models).

     We consider the Einstein model below, and the Debye model in the next section.

7. **The Einstein model**   (a simple, rough model)

7a) Setting up the model:

In this model we **assume that there is only one Ω** (not different Ω's for different K's).   This is approximately what occurs for the optical branch of the dispersion relation, but is way off for the acoustical branch.   We also assume that since there are N atoms in the crystal, there will be N modes of oscillation (one for each atom).   This model amounts to assuming that the heat energy is stored in the crystal simply as the oscillating energy of N independent atoms:

$$U \;=\; N\, n_{avg}\, \hbar\Omega \;=\; N\hbar\Omega/[e^{\hbar\Omega/kT} - 1]\,,$$

where U is the internal energy, N is the number of atoms in the crystal, n_{avg} is the Planck distribution function which is the average number of phonons excited at temperature, T, and $\hbar\Omega = hf$ is the energy of each phonon.

7b) Getting the heat capacity relation:

     To get the heat capacity from this model, we simply apply the definition:

$$C_V \;\equiv\; (\partial U/\partial T)_V \;=\; \partial\,[N\hbar\Omega/(e^{\hbar\Omega/kT} - 1)]/\partial T\,, \text{ so}$$

$$C_V \;=\; (N\hbar\Omega)(-\hbar\Omega/k_B T^2)(-1)\,e^{\hbar\Omega/kT}/[e^{\hbar\Omega/kT} - 1]^2 \quad\text{, or}$$

$$\mathbf{C_V \;=\; [Nk_B(\hbar\Omega/k_B T)^2\, e^{\hbar\Omega/kT}]/[e^{\hbar\Omega/kT} - 1]^2}\,.$$

7c) Seeing how well this model's predictions agree with experiment:

To see if this behaves properly, let's look at two limiting cases:

     7c-1) what happens **for large T**:

for $\hbar\Omega/k_B T \ll 1$,   using Taylor series approximations: $e^{\hbar\Omega/kT} \approx 1 + \hbar\Omega/kT$,   (and neglecting the small $\hbar\Omega/kT$ in the numerator but keeping it in the denominator since the 1 cancels out)   so

$$C_V \;\approx\; Nk_B(\hbar\Omega/k_B T)^2\,(1)/[\hbar\Omega/k_B T]^2 \;=\; Nk_B \quad\text{or}\quad C_{molar} = R \;\;(\text{when } N = N_A);$$

for 3 dimensions this would become for the molar heat capacity: **$C_{molar} \approx 3R$**, which agrees with experiment!

     7c-2) what happens **for small T**:

for $\hbar\Omega/k_B T$ large, we can ignore the minus 1 in the denominator (which essentially uses the Boltzmann distribution instead of the Planck):

$$C_V \;\approx\; (Nk_B\,(\hbar\Omega/k_B T)^2\, e^{-\hbar\Omega/kT}\,, \quad\text{so}\quad \mathbf{C_V \to 0}\;\; \mathbf{as\; T \to 0}\,, \text{ since the dying exponential term will "win" over}$$

the power law (T^{-2}), **but NOT as T^3**, which is what experiment gives us.

7d) Conclusions:

The Einstein model gives rather good results considering how rough the initial assumptions were.   It gives the correct result in the high T limit, and only fails in the low T limit in **the way** C_V approaches zero.