Statistical Mechanics primer for Solid State.

Chapter 5 start with a derivation of the heat capacity which is based on statistical mechanics. As some of you have not taken statistical mechanics yet here some background.

If you assume a set of identical harmonic oscillators in thermal equilibrium, the ratio of the number of oscillators in the (n+1)th quantum state to the number of oscillators in the nth quantum state is given by the following expression:

$$\frac{N_{n+1}}{N_n} = e^{-\frac{\hbar\omega}{\tau}}$$ [1]

Note that for a harmonic oscillator the energy between the nth and (n+1)th state is $\hbar\omega$. The τ is the fundamental temperature and is equal to:

$$\tau = k_B T$$ [2]

Where T is the temperature in Kelvin and k_B is the Boltzman constant equal to 1.38E-23 $m^2 kgs^{-2} K^{-1}$. In the following text I will explain the origin of equation [1].

In statistical mechanics we define the fundamental temperature in terms of entropy. So let us first have a look at entropy. The entropy is a measure of the number of specific ways in which a thermodynamic system may be arranged. It is measure of disorder. For example consider a system consisting of 5 harmonic oscillators. In chapter 4 we saw that the energy of a harmonic oscillator is given by its quantum number (see equation 27). If ε_i the energy of the ith harmonic oscillator and n_i is the quantum number of the ith harmonic oscillator then, the energy of the ith harmonic oscillator is given by:

$$\varepsilon_i = \left(n_i + \frac{1}{2}\right)\hbar\omega$$ [3]

The total energy of the system of five harmonic oscillators is given by:

$$U = \sum_{i=1}^{5} \varepsilon_i = \sum_{i=1}^{5}\left(n_i + \frac{1}{2}\right)\hbar\omega$$ [4]

Now assume that the total energy of the system is $4.5\hbar\omega$. There are different ways that this energy can be divided over the five harmonic oscillators. The table below shows the different ways.

Oscillator 1	Oscillator 2	Oscillator 3	Oscillator 4	Oscillator 5
$0.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$	$2.5\hbar\omega$
$0.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$	$2.5\hbar\omega$	$0.5\hbar\omega$
$0.5\hbar\omega$	$0.5\hbar\omega$	$2.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$
$0.5\hbar\omega$	$2.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$
$2.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$	$0.5\hbar\omega$

$1.5\,\hbar\omega$	$1.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$
$1.5\,\hbar\omega$	$0.5\,\hbar\omega$	$1.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$
$1.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$	$1.5\,\hbar\omega$	$0.5\,\hbar\omega$
$1.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$	$1.5\,\hbar\omega$
$0.5\,\hbar\omega$	$1.5\,\hbar\omega$	$1.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$
$0.5\,\hbar\omega$	$1.5\,\hbar\omega$	$0.5\,\hbar\omega$	$1.5\,\hbar\omega$	$0.5\,\hbar\omega$
$0.5\,\hbar\omega$	$1.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$	$1.5\,\hbar\omega$
$0.5\,\hbar\omega$	$0.5\,\hbar\omega$	$1.5\,\hbar\omega$	$1.5\,\hbar\omega$	$0.5\,\hbar\omega$
$0.5\,\hbar\omega$	$0.5\,\hbar\omega$	$0.5\,\hbar\omega$	$1.5\,\hbar\omega$	$1.5\,\hbar\omega$

Each of those configurations are referred to as a microstate or a quantum state. The fundamental assumption of thermal physics is that a closed system is <u>equally likely to be in any of the quantum state</u>. So the probability to find the oscillator 2 in the ground state is 9/14 as nine of the microstates listed in the table above have $\varepsilon_2 = 0.5\,\hbar\omega$. The probability to find the same oscillator in $1.5\,\hbar\omega$ is proportional to 4/14 as 4 of the 14 microstates in the table show $\varepsilon_2 = 1.5\,\hbar\omega$. The number of different microstates that result in the 2nd oscillator to have a certain energy $\varepsilon_2 = U$, is called the multiplicity of that macro-state, i.e. $g(\varepsilon_2 = U)$. Note that the macro-state considered here is "oscillator 2 has and energy U". As the multiplicity of a macro-state can be very large one defines a new quantity called the entropy σ:

$$\sigma\!\left(\varepsilon_2 = U\right) = \ln\!\left(\left[g(\,\varepsilon_2 = U)\right]\right) \qquad [5]$$

The equation indicates that both the entropy and the multiplicity are a function of the energy of oscillator 2. So the natural log of the multiplicity of a macro-state is the entropy. The macro-state with the largest entropy is normally the most likely macro-state. It is clear that it is not very likely that oscillator 2 has an energy of $2.5\,\hbar\omega$ as only one microstate corresponds to that. If one increases the total energy of above given system to $12.5\,\hbar\omega$, the number of microstates increases significantly. The multiplicity of the macro-state for which oscillator 2 has $10.5\,\hbar\omega$ units of energy and the other oscillators have each $0.5\,\hbar\omega$ is still one though. So the probability that all this extra energy goes to oscillator 2 is very unlikely. The most likely energy of oscillator 2, i.e. the most likely macro-state, is the macro-state that has the largest multiplicity, i.e. the macro-state with the largest multiplicity, i.e. largest entropy.

If you bring two systems A and B in contact with each other, energy will flow from the system with the highest temperature (A) to the system with the lowest temperature (B). This transfer of energy is driven by an increase of the total entropy of the system. The total entropy of the system is the sum of the entropy of the separate systems. So as long as $\left(\dfrac{\partial \sigma}{\partial U}\right)_A$ is smaller than $\left(\dfrac{\partial \sigma}{\partial U}\right)_B$ a flow of energy from A to B will result in an increase in total entropy. A small slope means a high temperature. Therefore the fundamental temperature is often defined as the reciprocal value of the slope of the energy-entropy graph, i.e.

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N \qquad [6]$$

We can now explain equation [1] using multiplicities or entropy. Assume the total system to consists of S and a reservoir R and that both R and S are in thermal equilibrium with each other. Furthermore assume that the total system, i.e. R+S has an energy of U_o. We can express the ratio of the number of oscillators in the (n+1)th quantum state to the number of oscillators in the nth quantum state of system S in terms of probabilities ($P_S(\varepsilon_n)$ is the probability that an oscillator has an energy ε_n) or multiplicities (g_s(en) is the multiplicity of the macro-state S has an energy ε_n):

$$\frac{N_{n+1}}{N_n} = \frac{P_S(\varepsilon_{n+1})}{P_S(\varepsilon_n)} = \frac{g_S(\varepsilon_{n+1})g_R(U_o - \varepsilon_{n+1})}{g_S(\varepsilon_n)g_R(U_o - \varepsilon_n)} \qquad [7]$$

Where $g_s(\varepsilon_{n+1})$ is the multiplicity of S and $g_R(U_0-\varepsilon_{n+1})$ is the multiplicity of the reservoir R when S has an energy ε_2. Note that the multiplicity of the total system, i.e. S+R, is equal to the product of the multiplicity of S and the multiplicity of R. Also note that if we assume that S has only one oscillator then $g_s(\varepsilon_{n+1})$ and $g_s(\varepsilon_n)$ are both 1, so [7] turns into:

$$\frac{N_{n+1}}{N_n} = \frac{g_R(U_o - \varepsilon_{n+1})}{g_R(U_o - \varepsilon_n)} \qquad [8]$$

We can write [8] in terms of entropy using equation [5]

$$\frac{N_{n+1}}{N_n} = \frac{g_R(U_o - \varepsilon_{n+1})}{g_R(U_o - \varepsilon_n)} = \frac{e^{\sigma_R(U_o - \varepsilon_{n+1})}}{e^{\sigma_R(U_o - \varepsilon_n)}} = e^{\sigma_R(U_o - \varepsilon_{n+1}) - \sigma_R(U_o - \varepsilon_n)} = e^{\Delta \sigma_R} \qquad [9]$$

We can do a Taylor approximation on $\Delta \sigma$, i.e.

$$\sigma_R(U_o - \varepsilon_{n+1}) - \sigma_R(U_o - \varepsilon_n) = \sigma_R(U_o) - \varepsilon_{n+1}\left(\frac{\partial \sigma_R}{\partial U}\right)_V + ... - \sigma_R(U_o) + \varepsilon_n\left(\frac{\partial \sigma_R}{\partial U}\right)_V - ..... \qquad [10]$$

We can now use the definition of temperature, i.e. equation [6] to simplify equation [10]:

$$\Delta \sigma_R = -\frac{(\varepsilon_{n+1} - \varepsilon_n)}{\tau} \qquad [11]$$

Or now equation [9] can be written as:

$$\frac{N_{n+1}}{N_n} = e^{-\frac{\varepsilon_{n+1} - \varepsilon_n}{\tau}} \qquad [12]$$

As for a harmonic oscillator $\varepsilon_{n+1} - \varepsilon_n = \hbar\omega$ we can write [12] as:

$$\frac{N_{n+1}}{N_n} = \frac{P_S(\varepsilon_{n+1})}{P_S(\varepsilon_n)} = e^{-\frac{\varepsilon_{n+1}-\varepsilon_n}{\tau}} = e^{-\frac{\hbar\omega}{\tau}} \qquad [13]$$

Which is equation [1]. This equation gives the ratio between the number of oscillators in the (n+1)th quantum state to the number of oscillators in the nth quantum state.

Notice that we can rewrite equation [13] to:

$$\frac{P(\varepsilon_n)}{e^{-\frac{\varepsilon_n}{\tau}}} = \frac{P(\varepsilon_{n+1})}{e^{-\frac{\varepsilon_{n+1}}{\tau}}} \qquad [14]$$

The left only depends on ε_n and is independent of ε_{n+1} and the right only depends on ε_{n+1} and is independent of ε_n. Since they are both equal to each other both the left and the right are independent of both ε_n and ε_{n+1} and equal to a constant. If we call this constant 1/Z we can rewrite equation [14] as:

$$\frac{P(\varepsilon_n)}{e^{-\frac{\varepsilon_n}{\tau}}} = \frac{1}{Z} \Leftrightarrow P(\varepsilon_n) = \frac{e^{-\frac{\varepsilon_n}{\tau}}}{Z} \qquad [15]$$

This is often referred to as the most important equation of statistical mechanics. The term is the numerator is the Boltzmann factor for a state with energy ε_n, and the term in the denominator is the partition function. Z depends on the temperature and the energy levels of the available states of the system. It is a measure for the number of accessible states. We can derive an expression for Z by realizing that the sum of all probabilities should be 1, i.e.

$$\sum_{i=1}^{\infty} P(\varepsilon_i) = 1 = \sum_{i=1}^{\infty} \frac{e^{-\frac{\varepsilon_i}{\tau}}}{Z} = \frac{1}{Z}\sum_{i=1}^{\infty} e^{-\frac{\varepsilon_i}{\tau}} \Leftrightarrow Z = \sum_{i=1}^{\infty} e^{-\frac{\varepsilon_i}{\tau}} \qquad [16]$$

Now we can use equation [15] and [16] to find the fraction of the total number of oscillators in the nth quantum state, i.e.

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{e^{-n\hbar\omega/\tau}}{\sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau}} \qquad [17]$$

Or this fraction is equal to the Boltzmann factor of the nth state divided by the partition function. And of course the average excitation quantum number becomes a weighted average, i.e.

$$\langle n \rangle = \frac{\sum_{s=0}^{\infty} s e^{-s\hbar\omega/\tau}}{\sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau}} \qquad [18]$$