Lecture 8

Physics 404

Now we will try to understand the role of temperature in the thermodynamic properties of real systems. Consider a system S in thermal contact with a much larger reservoir R, all at a constant temperature τ and total energy U_0. The system and reservoir exchange energy, but not particles. What is the probability that any given state "s" of the system is occupied in thermal equilibrium?

If we specify the exact quantum state of the system (labeled by "s", which is a list of quantum numbers), with energy ε_s, then the multiplicity of the entire system+reservoir is given by the multiplicity of the reservoir alone: $g_{Total} = g_R(U_0 - \varepsilon_s) \times 1$, since specifying the precise state of the system means that it has a multiplicity of exactly 1. Utilizing the Fundamental Assumption of statistical mechanics applied to the system+reservoir, this says that the relative likelihood of the system to be in state "1" (of energy ε_1) versus state "2" (of energy ε_2) is simply the ratio of the number of ways that the reservoir can have energy $U_0 - \varepsilon_1$ versus energy $U_0 - \varepsilon_2$, or in other words: $\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{g_R(U_0 - \varepsilon_1)}{g_R(U_0 - \varepsilon_2)}$. By writing the multiplicity in terms of the entropy (as $g = e^{\sigma}$), and doing a Taylor expansion for $\sigma_R(U)$ about U_0, we found $\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{e^{-\varepsilon_1/\tau}}{e^{-\varepsilon_2/\tau}}$, which is independent of the details of the reservoir. The factors of $e^{-\varepsilon_s/\tau}$ are called Boltzmann factors.

Define the Partition function (*Zustandssumme* in German) as $Z = \sum_{\text{All States "s"}} e^{-\varepsilon_s/\tau}$, where the sum is NOT over all energy levels ε_s, but over every single quantum state with a unique set of quantum numbers "s". With this, we can calculate the probability of occupation of each energy level as $P(\varepsilon_s) = \frac{e^{-\varepsilon_s/\tau}}{Z}$. This probability is normalized since $\sum_{\text{All States "s"}} P(\varepsilon_s) = \frac{Z}{Z} = 1$, and it also reproduces the result above for $\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{e^{-\varepsilon_1/\tau}}{e^{-\varepsilon_2/\tau}}$. With this probability of occupation we can now calculate all of the macroscopic thermodynamic properties of a system in thermal contact with a reservoir as a thermal average or ensemble average of the associated microscopic quantity.

To illustrate how the partition function can be used to calculate thermodynamic quantities, we calculated the ensemble average or thermal average of the energy as $U = \langle \varepsilon_s \rangle = \sum_{\text{All States "s"}} \varepsilon_s P(\varepsilon_s) = \frac{1}{Z} \sum_{\text{All States "s"}} \varepsilon_s e^{-\varepsilon_s/\tau} = \tau^2 \frac{\partial \log(Z)}{\partial \tau}$. The last step comes after manipulating the series and exploiting its dependence on τ. Later on we will identify the logarithm of Z as the Helmholtz free energy (up to a factor of $-\tau$). Many other thermodynamic quantities can be calculated more or less directly from Z. Note that Z has its origins in the quantum mechanical solution that forms the basis for the particle states.

We did the example of a 2-state spin system in class, calculating the partition function *Z* and energy *U*.

Finally we considered how pressure is related to the energy states of a system. By considering the quantum particle-in-a-box problem in three dimensions, we found that the eigen-energies are given by $E_{n_x,n_y,n_z} = \frac{\left(n_x^2 + n_y^2 + n_z^2\right)\pi^2\hbar^2}{2mL^2}$, where the particle has mass *m*, is confined to a cube of side length *L*, and the three quantum numbers are arbitrary positive integers. This shows that the eigen-energies are inversely proportional to the volume of the system to the 2/3 power. If we take a single particle in a box and apply hydrostatic pressure (equal normal force applied to each wall of the box), then this result says that the energy of the particle goes up as we compress the box volume. By the work-energy theorem we know that this increase in energy of the particle comes from work that we do in applying a force through a distance. By equating the work and increase in energy, we came up with an expression for the pressure applied to produce the change in energy of the particle in state "s": $p_s = -\frac{d\varepsilon_s}{dV}$. Performing a thermal average for a many particle system yields the total macroscopic pressure p: $p = -\frac{\partial U}{\partial V}\Big|_\sigma$, where it is assumed that the compression is performed iso-statically slowly, and the number of states in the system is kept fixed (hence constant multiplicity *g* and entropy σ).