Thermodynamics and Statistical Mechanics Lecture 4

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29Jan20

Example of Independent Spins

$$S(E) = -kN\left(\frac{1}{2} + \frac{E}{BN}\right)\ln\left(\frac{\frac{1}{2}+\frac{E}{BN}}{\frac{1}{2}-\frac{E}{BN}}\right)$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{-k}{N}\ln\left(\frac{\frac{1}{2}+\frac{E}{BN}}{\frac{1}{2}-\frac{E}{BN}}\right)$$

Our entropy can be defined as

$$S(E) = k\ln(\Omega(E))$$

And our temperature can then be found using

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

We can define a new quality, Specific Heat, to gain a little bit more information about our system and make calculating other quantities easier.

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{\partial E}{\partial S}\frac{\partial S}{\partial T}$$

$$\frac{\partial S}{\partial T} = \frac{\partial S}{\partial E}\frac{\partial E}{\partial T} = \frac{C_V}{T}$$

$$S(T_2) - S(T_1) = \Delta S = \int_{T_1}^{T_2}\frac{\partial S}{\partial T}dT = \int_{T_1}^{T_2}\frac{C_V}{T}dT$$

Specific Heat of a Spin System

It turns out it is a lot more difficult to calculate the specific heat of a solid. Not only is there the spin to take into account, but there are extra degrees of freedom within the lattice structure such as phonons, or lattice vibrations. We're only going to look into the specific heat attributed to just the spin degrees of freedom and ignore the others for now. Our energy can be represented by

$$E(T) = \frac{BN}{2}\frac{e^{\frac{-B}{kT}} - 1}{e^{\frac{-B}{kT}} + 1}$$

$$C_V = \frac{\partial E}{\partial T} = \frac{B}{kT} = \frac{1}{1 + \cosh\left(\frac{B}{kT}\right)}$$

When our temperature is low $kT << B$, the specific heat behaves like

$$C_v = \frac{2B}{kT^2}e^{\frac{-B}{kT}}$$

When our temperature is high $kT >> B$, the specific heat behaves like

$$C_v = \frac{B}{2kT^2}$$

Harmonic Quantum Oscillators

We will take a brief look at a system of N quantum harmonic oscillators. Their energy can be represented by

$$E_n = \bar{h}\omega(n + \frac{1}{2})$$

With N of these oscillators, our total energy will be

$$E = \bar{h}\omega(\sum_{i=1}^{N} n_i) + \frac{N\bar{h}\omega}{2}$$

We can define q to make calculations more simple.

$$q = \sum_{i=1}^{N}$$

Now, how many ways are there t partition q objects among N compartments? We can use a trick to solve this. If we laid the objects in a line, we would have one more compartments than we have partitions.

$$\text{number of objects} = N - 1 + q$$

or written differently

$$\begin{bmatrix} N-1+q \\ N-1 \end{bmatrix} \Rightarrow \Omega(q) = \frac{(N-1+q)!}{(N-1)!q!} \tag{1}$$

Mechanical Equilibrium

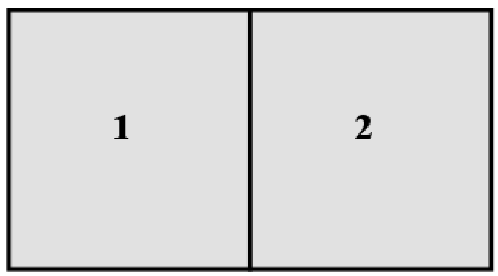

Figure 1

We will now consider a system like figure 1. The border between the two subsystems can move, so, although the total volume stays the same, the subsystem volumes are allowed to vary. The total volume and energy are fixed in this system, but each subsystem's volume and energy can vary.

$$V_- = V_1 - V_2$$
$$E_- = E_1 - E_2$$

$$0 = \frac{\partial S}{\partial V_-} = \frac{\partial S_1}{\partial V_-} + \frac{\partial S_2}{\partial V_-} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}$$

Pressure can then be defined by

$$p = T\left(\frac{\partial S}{\partial V}\right)_E$$

We can take a look at entropy as a function of energy and volume $S(E, V)$. This gives us

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV = \frac{1}{T}dE + \frac{p}{T}dV$$

With some rearranging, we can find energy as a function of entropy and volume.

$$dE = TdS - pdV$$

The first term on the right hand side is heat, and the second term on the right hand side is work.