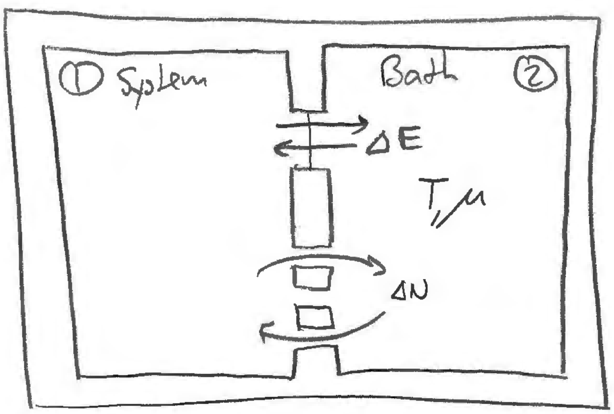
In a QM statistical system, this is the question that drives us:

What is the ground state and Excited state ($T>0$) occupation of a large number of Quantum particles?

First, let's introduce the <u>GRAND CANONICAL ENSEMBLE</u>

Grand Canonical Ensemble

Consider an equilibrium system which can exchange energy and particles with a heat bath (A second subsystem)



The probability density that the system will be in a state s is

$$\rho(s) \propto \Omega_2(E-E_s, N-N_s)$$
$$\propto \Omega_1(E_s, N_s)$$

Since

$$E = E_{bath} + E_s \Rightarrow E_{Bath} = E - E_s$$
$$N = N_{Bath} + N_s \Rightarrow N_{Bath} = E - N_s$$

This is completely analogous to the 2 subsystem model we used previously.

Recall

$$S = k_B \log \Omega \Rightarrow \Omega = e^{S/k_B}$$

Hence

$$\rho(s) \propto \Omega_2(E-E_s, N-N_s)$$
$$= \exp\left[S_2(E-E_s, N-N_s)/k_B\right]$$

Now, recall we showed

ΔS_1 ΔS_2

$$\Delta S = \left[\left(\frac{\partial S_1}{\partial E_1}\right)_{V,N} - \left(\frac{\partial S_2}{\partial E_2}\right)_{V,N}\right]\Delta E$$
$$+ \left[\left(\frac{\partial S_1}{\partial V_1}\right)_{E,N} - \left(\frac{\partial S_2}{\partial V_2}\right)_{E,N}\right]\Delta V$$
$$+ \left[\left(\frac{\partial S_1}{\partial N_1}\right)_{E,V} - \left(\frac{\partial S_2}{\partial N_2}\right)_{E,V}\right]\Delta N$$

Let's plug this into $\rho(s)$:

$$\rho(s) \propto \Omega_2(E-E_s, N-N_s)$$
$$= \exp\left[\left(-E_s\frac{\partial S_2}{\partial E_2} - N_s\frac{\partial S_2}{\partial N_2}\right)/k_B\right]$$

Recall

$$-\frac{\mu}{T} = \frac{\partial S}{\partial N}$$
$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

So

$$\rho(s) \propto \exp\left[-\frac{E_s}{k_B T} + \frac{N_s \mu}{k_B T}\right] = \exp\left[-(E_s - \mu N_s)/k_B T\right]$$

From thermo,

$$dE = TdS - PdV + \mu dN$$

we see that $\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$ is the energy change needed to add an additional particle adiabatically, and keep the N+1 particle system in equilibrium.

At low temp, a system will fill with particles until the energy needed to jam in another particle reaches μ.

Now, we need a normalization factor:

$$\mathcal{Z} = \sum_n \exp\left[-(E_n - \mu N_n)/k_B T\right]$$

So that

$$\rho(s_i) = \frac{\exp\left[-(E_i - \mu N_i)/k_B T\right]}{\mathcal{Z}} = \frac{\exp\left[-(E_i - \mu N_i)/k_B T\right]}{\sum_n \exp\left[-(E_n - \mu N_n)/k_B T\right]}$$

Now, what do we do with this?

It turns out that $\mathcal{Z}$, in this context called the Grand Partition Function, is not just a normalization factor... it is incredibly useful in its own right. We can extract most of the useful information about any system once you know $\mathcal{Z}$.

Lets define another function $\Phi(T,V,\mu)$, called the Grand Free Energy:

$$\Phi(T,V,\mu) = -k_B T \ln \mathcal{Z}$$

You can show that this is

$$\Phi(T,V,\mu) = \langle E \rangle - TS - \mu N$$

(This is a Legendre Transform of $E(S,V,N)$... essentially we're just changing variables)

Most quantities of interest can be calculated from Φ, which in turn is determined by $\mathcal{Z}$.

For example, to calculate the expected number of particles in a system, $\langle N \rangle$:

$$\langle N \rangle = \sum_m N_m \rho(N_m)$$

$$= \frac{\sum_m N_m e^{-(E_m - \mu N_m)/k_B T}}{\sum_m e^{-(E_m - \mu N_m)/k_B T}}$$

Notice that

$$N_m e^{\mu N_m / k_B T} = k_B T \frac{\partial e^{\mu N / k_B T}}{\partial \mu}$$

So

$$\sum_m N_m e^{\mu N_m / k_B T} = k_B T \sum_m \frac{\partial}{\partial \mu} e^{\mu N_m / k_B T}$$

$$= \frac{\partial}{\partial \mu}\left[k_B T \sum_m e^{\mu N_m / k_B T} \right]$$

$$= \frac{\partial}{\partial \mu}\left(k_B T \cdot Z \right)$$

Now notice that

$$\frac{\partial}{\partial \mu} \ln Z = \frac{1}{Z} \frac{\partial Z}{\partial \mu}$$

Such that

$$\langle N \rangle = \frac{\sum N_m e^{-(E_m - \mu N_m)/k_B T}}{\sum_m e^{-(E_m - \mu N_m)/k_B T}} = \frac{1}{Z} \cdot \frac{\partial}{\partial \mu}\left(k_B T Z \right)$$

$$= \frac{\partial}{\partial \mu}\left(\overbrace{k_B T \ln Z}^{= -\Phi} \right)$$

$$\boxed{\langle N \rangle = -\frac{\partial \Phi}{\partial \mu}}$$

For the problem of finding the occupation of quantum energy levels very easy!

Also, this is a general strategy: ① Find the partition function

② Take an appropriate derivative to calculate expectation values!