STATISTICAL MECHANICS IN QUANTUM THEORY: MOST PROBABLE STATE FOR FERMIONS

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.28.

We've seen how to derive the number of particles in each energy state when the overall system is in its most probable state. The result for distinguishable particles is

$$n_j = d_j e^{-\alpha-\beta E_j} \tag{1}$$

where E_j is the energy of state j, d_j is the degeneracy of that energy state, and α and $\beta = 1/k_B T$ are values that depend ultimately on the number of particles N and the temperature T. These last two parameters are usually replaced by the values ϵ and μ where

$$\mu \equiv -\alpha k_B T \tag{2}$$

is called the *chemical potential*. The parameter ϵ is numerically equal to E_j, but now refers to a single substate with that energy, rather than all the d_j substates with that energy. Since all states with a given energy are equally probable, the number of particles in each substate with energy E_j is n_j/d_j. We then get the formula

$$\begin{aligned} n(\epsilon) &= \frac{n_j}{d_j} && (3)\\ &= e^{-(\epsilon-\mu)/k_B T} && (4) \end{aligned}$$

The chemical potential μ must be defined so that the total number of particles works out to N, which means:

$$\int_0^\infty d(\epsilon)\, n(\epsilon)\, d\epsilon = N \tag{5}$$

where $d(\epsilon)$ is the degeneracy of energy ϵ.

We can do similar calculations for fermions. For fermions the total number of states is

$$S_f\left(\{n_j\}\right)=\prod_{j=1}^{m}\binom{d_j}{n_j} \tag{6}$$

Taking the log of this and using Lagrange multipliers to add in the constraints, we get the function

$$\begin{aligned} G &= \ln S_f+\alpha\left(N-\sum_{j=1}^{\infty}n_j\right)+\beta\left(E-\sum_{j=1}^{\infty}n_jE_j\right) && (7)\\ &= \sum_{j=1}^{\infty}\left[\ln d_j!-\ln n_j!-\ln\left(d_j-n_j\right)!-\alpha n_j-\beta n_jE_j\right]+\alpha N+\beta E && (8)\end{aligned}$$

If we assume the degeneracy of level j is much larger than the number of particles in that level (which isn't always true, but will be for most macroscopic situations), then we can use Stirling's approximation again to get

$$G\approx\sum_{j=1}^{\infty}\left[\ln d_j!-n_j\ln n_j+n_j-\left(d_j-n_j\right)\ln\left(d_j-n_j\right)+n_j-d_j-\alpha n_j-\beta n_jE_j\right]+\alpha N+\beta E \tag{9}$$

We can now take the derivative to get n_j:

$$\begin{aligned} \frac{\partial G}{\partial n_j} &= -\ln n_j+\ln\left(d_j-n_j\right)-\alpha-\beta E_j=0 && (10)\\ n_j &= \left(d_j-n_j\right)e^{-\alpha-\beta E_j} && (11)\\ n_j &= \frac{d_je^{-\alpha-\beta E_j}}{1+e^{-\alpha-\beta E_j}} && (12)\\ &= \frac{d_j}{1+e^{\alpha+\beta E_j}} && (13)\end{aligned}$$

At this stage, we can try to find α and β by evaluating the total number of particles and the total energy for a particular potential, such as the infinite square well. Using the same technique as before, we get

$$\begin{aligned} N &= \int_0^{\infty}\frac{d(k)}{1+e^{\alpha+\beta E_j}}dk && (14)\\ &= \frac{V}{2\pi^2}\int_0^{\infty}\frac{k^2}{1+e^{\alpha+\hbar^2k^2\beta/2m}}dk && (15)\end{aligned}$$

This integral does not appear to have a closed form, even if we try to find some special functions. If we use the same definitions for α and β as before, we get

$$N = \frac{V}{2\pi^2} \int_0^\infty \frac{k^2}{1 + e^{\left(\hbar^2 k^2/2m - \mu\right)/k_B T}} dk \tag{16}$$

This of course doesn't help us do the integral, but we can investigate the properties at absolute zero ($T = 0$). In that case, the exponential in the denominator of the integrand becomes a step function, with a value of 0 if $k < \sqrt{2m\mu}/\hbar$ and infinity otherwise. Thus the integrand is non-zero only for $k < \sqrt{2m\mu}/\hbar$, so at $T = 0$:

$$\begin{aligned} N &= \frac{V}{2\pi^2} \int_0^{\sqrt{2m\mu}/\hbar} k^2 dk & (17) \\ &= \frac{V}{2\pi^2} \frac{(2m\mu)^{3/2}}{3\hbar^3} & (18) \end{aligned}$$

For electrons, the total number is actually twice this amount, since there is a degeneracy of 2 spin states for every energy state that hasn't been considered up to now. So in this case, we have

$$N_e = \frac{V}{\pi^2} \frac{(2m\mu)^{3/2}}{3\hbar^3} \tag{19}$$

The maximum energy at $T = 0$ occurs when $k_{max} = \sqrt{2m\mu}/\hbar$ or

$$\mu = \frac{\hbar^2 k_{max}^2}{2m} \tag{20}$$

In terms of the particle number

$$\mu = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \tag{21}$$

At absolute zero, all particles are in their ground state, so this maximum energy should be the same as the Fermi energy. Comparing this with the formula we got earlier, we see they do in fact match:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(3\pi^2 \rho\right)^{2/3} = \frac{\hbar^2}{2m} \left(3\pi^2 N q\right)^{2/3} V^{-2/3} \tag{22}$$

We can work out the total energy at $T = 0$ in a similar way:

$$E_{tot} = 2\times\frac{V}{2\pi^2}\frac{\hbar^2}{2m}\int_0^{\sqrt{2m\mu}/\hbar}k^4dk \tag{23}$$

$$= \frac{2\sqrt{2}Vm^{3/2}\mu^{5/2}}{5\pi^2\hbar^3} \tag{24}$$

$$= \frac{\hbar^2\left(6\pi^2N\right)^{5/3}}{10\pi^2m}V^{-2/3} \tag{25}$$

This also agrees with the earlier result.

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