Lecture 31 Highlights

Quantum statistical mechanics, continued…

We found the statistical weight *W* of the arrangement (n_1, n_2, n_3, n_4, …n_s, …):

$$W(n_1, n_2, ..., n_s, ...) = \prod_{s=1}^{\infty} P_s ,$$

for three different types of statistics. This weight is proportional to the probability of finding this particular distribution of occupation numbers.

1) Distinguishable classical particles $W_{Dist}(n_1, n_2, ..., n_s, ...) = N! \prod_{s=1}^{\infty} \frac{g_s^{n_s}}{n_s!}$ (1)
2) Indistinguishable identical Fermions

   $W_{Fermions}(n_1, n_2, ..., n_s, ...) = \prod_{s=1}^{\infty} \frac{g_s!}{n_s!(g_s - n_s)!}$ (2)
3) Indistinguishable identical Bosons $W_{Bosons}(n_1, n_2, ..., n_s, ...) = \prod_{s=1}^{\infty} \frac{(n_s + g_s - 1)!}{n_s!(g_s - 1)!}$ (3)

The next step is to maximize $W(n_1, n_2, ..., n_s, ...)$ by varying all of the occupation numbers, subject to the number and total energy constraints: $\sum_{i=1}^{\infty} n_i = N$ and $\sum_{i=1}^{\infty} n_i E_i = E$.

We will include the constraints using the method of Lagrange multipliers. This method allows one to perform a constrained maximization. We will form a new function to maximize, namely;

$$G(n_1, n_2, ..., n_s, ..., \alpha, \beta) = W(n_1, n_2, ..., n_s, ...) + \alpha\left(N - \sum_{i=1}^{\infty} n_i\right) + \beta\left(E - \sum_{i=1}^{\infty} n_i E_i\right)$$

To maximize this function we must enforce these conditions:

$$\frac{\partial G}{\partial n_s} = 0 \ \forall s \text{ and } \frac{\partial G}{\partial \alpha} = \frac{\partial G}{\partial \beta} = 0 .$$

The form of *G* already satisfies the last two conditions.

Because of the products appearing in Eqs. (1)-(3), it is easier to maximize the logarithm of *W*. This will yield the same result since *W* and *lnW* have maxima at the same values of their arguments. The newly defined *G* for distinguishable particles now is:

$$G_{Dist}(n_1, n_2, ..., n_s, ..., \alpha, \beta) = \ln\left(N! \prod_{s=1}^{\infty} \frac{g_s^{n_s}}{n_s!}\right) + \alpha\left(N - \sum_{i=1}^{\infty} n_i\right) + \beta\left(E - \sum_{i=1}^{\infty} n_i E_i\right)$$

$$= \ln N! + \sum_{s=1}^{\infty}\left(n_s \ln g_s - \ln n_s!\right) + \alpha\left(N - \sum_{i=1}^{\infty} n_i\right) + \beta\left(E - \sum_{i=1}^{\infty} n_i E_i\right)$$

To take the derivative of *G* with respect to n_s we must now decide what to do with the logarithm of $n_s!$. One approach is to employ Stirling's approximation: $\ln x! \cong x \ln x - x$, good for $x >> 1$. With this approximation, G_{Dist} becomes:

$$G_{Dist}(n_1, n_2, ..., n_s, ..., \alpha, \beta) \cong \ln N! + \sum_{s=1}^{\infty}\left(n_s \ln g_s - n_s \ln n_s + n_s\right) + \alpha\left(N - \sum_{i=1}^{\infty} n_i\right) + \beta\left(E - \sum_{i=1}^{\infty} n_i E_i\right)$$

Taking the derivative of G with respect to some particular n_s (called n_t in the lecture) and setting it equal to zero (to find the maximum), yields;

$$n_s = g_s e^{-(\alpha + \beta E_s)} \quad \text{Distinguishable particles}$$

For the other cases one gets

$$n_s = \frac{g_s}{e^{+(\alpha + \beta E_s)} + 1} \quad \text{Identical Fermions}$$

$$n_s = \frac{g_s}{e^{+(\alpha + \beta E_s)} - 1} \quad \text{Identical Bosons}$$

What are the Lagrange multipliers α and β? They are determined by the number and energy constraints $\sum_{i=1}^{\infty} n_i = N$ and $\sum_{i=1}^{\infty} n_i E_i = E$. . The challenge is to determine the energies and degeneracies of all of the single-particle states of the system - this is the hardest part of quantum statistical mechanics. Calculating the total energy of an ideal gas, which is a relatively easy case, Griffiths (pp. 239-240) finds that $\beta = 1/k_B T$, where T is the absolute temperature of the gas. The other parameter α is re-defined in terms of the chemical potential μ as $\alpha \equiv -\mu\beta$. The chemical potential is a measure of how much energy is required to change the particle number of the system from N to $N+1$. The three distribution functions can now be written as:

$$n_s = g_s e^{-(E_s - \mu)/k_B T} \quad \text{Distinguishable particles}$$

$$n_s = \frac{g_s}{e^{+(E_s - \mu)/k_B T} + 1} \quad \text{Identical Fermions}$$

$$n_s = \frac{g_s}{e^{+(E_s - \mu)/k_B T} - 1} \quad \text{Identical Bosons}$$