STATISTICAL MECHANICS IN QUANTUM THEORY: COUNTING STATES

In statistical mechanics the central assumption is that all states with a given energy are equally probable, if the system is in thermal equilibrium, which means that it is not exchanging energy with its surroundings. This is quite a hefty assumption, but it does seem to be borne out by observations.

In classical physics, the allowed energy levels for a collection of particles form a continuous set, so there are infinitely many possible states. In quantum mechanics, the number of allowed states is restricted by the potential so is usually finite.

As a simple example, suppose we have \( N \) (noninteracting) particles in a one-dimensional infinite square well of width \( a \). The allowed energies for each particle are

\[
E = \frac{(n\pi\hbar)^2}{2ma^2}
\]  

(1)

The total energy of a collection of particles is then

\[
E_{\text{tot}} = \frac{\pi^2\hbar^2}{2ma^2} \sum_{j=1}^{N} n_j^2
\]  

(2)

The sum must therefore be an integer which is the sum of squares of \( N \) individual integers. If we have 3 particles, one possible total is 363, which allows the following combinations of 3 integers: (11,11,11), (5,13,13), (1,1,19), (5,7,17). The number of states with each configuration depends on the type of particle: distinguishable, fermion or boson.

Consider first \( N \) distinguishable particles. If \( n_j \) of these particles have energy \( E_j \) for \( j = 1 \ldots m \), where \( m \) is the number of different energies in the set of particles, then the number of distinct states is

\[
S = \frac{N!}{n_1!n_2!\ldots n_m!}
\]  

(3)
This is a multinomial coefficient (a generalization of the binomial coefficient). In the example of 3 particles above, this means that we have 1 possible state with configuration (11,11,11), 3 each with (5,13,13) and (1,1,19), and 6 with (5,7,17). The wave function in each case is just the product of the individual wave functions for each particle. Thus

$$\psi_{(11,11,11)}(x_1, x_2, x_3) = \psi_{11}(x_1) \psi_{11}(x_2) \psi_{11}(x_3)$$  \hspace{1cm} (4)

$$\psi_{(17,5,7)}(x_1, x_2, x_3) = \psi_{17}(x_1) \psi_{5}(x_2) \psi_{7}(x_3)$$  \hspace{1cm} (5)

and so on. Here, each individual wave function is the standard infinite square well wave function:

$$\psi_n(x_j) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x_j}{a}$$  \hspace{1cm} (6)

For fermions, we must have a completely antisymmetric wave function which means (assuming all particles have the same spin) that each particle’s energy state must be different, so only a (5,7,17) state is possible. The fermion wave function is the completely antisymmetric combination of the 6 possible states which can be generated by finding the even and odd permutations and adding the former and subtracting the latter (or using a Slater determinant):

$$\sqrt{6}\psi_{(5,7,17)}(x_1, x_2, x_3) = \psi_{5}(x_1) \psi_{7}(x_2) \psi_{17}(x_3) + \psi_{7}(x_1) \psi_{17}(x_2) \psi_{5}(x_3) + \psi_{17}(x_1) \psi_{5}(x_2) \psi_{7}(x_3)$$

$$\hspace{1cm} - \psi_{7}(x_1) \psi_{5}(x_2) \psi_{17}(x_3) - \psi_{5}(x_1) \psi_{17}(x_2) \psi_{7}(x_3) - \psi_{17}(x_1) \psi_{7}(x_2) \psi_{5}(x_3)$$  \hspace{1cm} (7)

For bosons, we must have a completely symmetric wave function, so all energy configurations are possible. We can have:

$$\psi_{(11,11,11)}(x_1, x_2, x_3) = \psi_{11}(x_1) \psi_{11}(x_2) \psi_{11}(x_3)$$  \hspace{1cm} (8)

$$\sqrt{3}\psi_{(1,1,19)}(x_1, x_2, x_3) = \psi_{1}(x_1) \psi_{1}(x_2) \psi_{19}(x_3) + \psi_{1}(x_1) \psi_{19}(x_2) \psi_{1}(x_3) + \psi_{19}(x_1) \psi_{1}(x_2) \psi_{1}(x_3)$$  \hspace{1cm} (9)

$$\sqrt{6}\psi_{(5,7,17)}(x_1, x_2, x_3) = \psi_{5}(x_1) \psi_{7}(x_2) \psi_{17}(x_3) + \psi_{7}(x_1) \psi_{17}(x_2) \psi_{5}(x_3) + \psi_{17}(x_1) \psi_{5}(x_2) \psi_{7}(x_3)$$

$$\hspace{1cm} + \psi_{7}(x_1) \psi_{5}(x_2) \psi_{17}(x_3) + \psi_{5}(x_1) \psi_{17}(x_2) \psi_{7}(x_3) + \psi_{17}(x_1) \psi_{7}(x_2) \psi_{5}(x_3)$$  \hspace{1cm} (10)

Pingbacks

Pingback: Statistical mechanics in quantum theory: energy probabilities
Pingback: Statistical mechanics in quantum theory: counting states, general case
Pingback: Statistical mechanics in quantum theory: most probable state