

STATISTICAL MECHANICS IN QUANTUM THEORY: COUNTING STATES

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.22.

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

$$E = \frac{(n\pi\hbar)^2}{2ma^2} \quad (1)$$

The total energy of a collection of particles is then

$$E_{tot} = \frac{\pi^2\hbar^2}{2ma^2} \sum_{j=1}^N n_j^2 \quad (2)$$

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 $j = 1 \dots m$, where m is the number of different energies in the set of particles, then the number of distinct states is

$$S = \frac{N!}{n_1!n_2! \dots n_m!} \quad (3)$$

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

$$\psi_{(11,11,11)}(x_1, x_2, x_3) = \psi_{11}(x_1) \psi_{11}(x_2) \psi_{11}(x_3) \quad (4)$$

$$\psi_{(17,5,7)}(x_1, x_2, x_3) = \psi_{17}(x_1) \psi_5(x_2) \psi_7(x_3) \quad (5)$$

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

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

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):

$$\begin{aligned} \sqrt{6}\psi_{(5,7,17)}(x_1, x_2, x_3) &= \psi_5(x_1) \psi_7(x_2) \psi_{17}(x_3) + \psi_7(x_1) \psi_{17}(x_2) \psi_5(x_3) + \psi_{17}(x_1) \psi_5(x_2) \psi_7(x_3) \\ &\quad (7) \\ &\quad - \psi_7(x_1) \psi_5(x_2) \psi_{17}(x_3) - \psi_5(x_1) \psi_{17}(x_2) \psi_7(x_3) - \psi_{17}(x_1) \psi_7(x_2) \psi_5(x_3) \end{aligned}$$

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

$$\psi_{(11,11,11)}(x_1, x_2, x_3) = \psi_{11}(x_1) \psi_{11}(x_2) \psi_{11}(x_3) \quad (8)$$

$$\sqrt{3}\psi_{(1,1,19)}(x_1, x_2, x_3) = \psi_1(x_1) \psi_1(x_2) \psi_{19}(x_3) + \psi_1(x_1) \psi_{19}(x_2) \psi_1(x_3) + \psi_{19}(x_1) \psi_1(x_2) \psi_1(x_3) \quad (9)$$

$$\begin{aligned} \sqrt{6}\psi_{(5,7,17)}(x_1, x_2, x_3) &= \psi_5(x_1) \psi_7(x_2) \psi_{17}(x_3) + \psi_7(x_1) \psi_{17}(x_2) \psi_5(x_3) + \psi_{17}(x_1) \psi_5(x_2) \psi_7(x_3) \\ &\quad (10) \\ &\quad + \psi_7(x_1) \psi_5(x_2) \psi_{17}(x_3) + \psi_5(x_1) \psi_{17}(x_2) \psi_7(x_3) + \psi_{17}(x_1) \psi_7(x_2) \psi_5(x_3) \end{aligned}$$

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