Statistical Physics

Basic Problem:
Suppose I have N particles which are distributed into a set of energy states such that the total energy of the particles is fixed to be E_{tot}:

(1) $\sum_{states} n_s = N$

(2) $\sum_{states} n_s E_s = E_{tot}$

Question: What is the equilibrium distribution of particles, or what is the particle density f(E)?

Solution: The problem is solved by assuming that every specific configuration satisfying equations (1) and (2) above is equally probable.

The function f(E) is then found by averaging over all configurations. We shall show this procedure in a simple example.
In deciding what represents a unique, specific configuration, we classify the particles into three categories (where we limit ourselves to identical particles):

(1) Identical and distinguishable: such as a set of billiard balls, each with a different color or number.
$\rightarrow$ Maxwell-Boltzmann (MB) distribution

(2) Identical, indistinguishable fermions: in this case, a particular energy state cannot be occupied by more than one particle because of the Pauli Exclusion Principle.
$\rightarrow$ Fermi-Dirac (FD) distribution

(3) Identical, indistinguishable bosons
$\rightarrow$ Bose-Einstein (BE) distribution

One can show that:

(1) $f_{MB} = A\, e^{-E/kT}$

(2) $$f_{FD} = \frac{1}{C\, e^{E/kT} + 1} \equiv \frac{1}{e^{(E-E_f)/kT} + 1}$$

(3) $$f_{BE} = \frac{1}{B\, e^{E/kT} - 1}$$

Where A, B, and C are all normalization constants. Commonly $C \equiv e^{-E_f/kT}$, where E_f = "Fermi Energy" and where T= temperature and k=1.381 × 10^{-23} J/K = Boltzmann's constant.

Note: If certain energy states are degenerate, so that g(E) states have all the same energy, then the particle density is n(E) = g(E) f(E).

The proof for (1) – (3) above is beyond the scope of this course, but we can make the ideas clear with a simple example.

Simple Example:

A) Let's take the case of identical, distinguishable particles

We assume we have 4 such particles (labeled A,B,C,D) that can be placed in 5 energy states:
with $E_1 = 1$
$E_2 = 2$
$E_3 = 3$ arbitrary energy units
$E_4 = 4$
$E_5 = 5$

Such that $E_A + E_B + E_C + E_D = E_{tot} = 8$

What is the probability of finding particles in each energy level? Or, what is the average number of particles in each energy level?
To solve this problem, let's distribute the particles into the energy levels such that $E_{tot} = 8$. There are 5 configurations of doing this. The number of different combinations for each configuration can be worked out in tabular form, or using standard methods from permutation:

Configurations with $E_{tot} = 8$

Configuration index (Macrostates)	E_1	E_2	E_3	E_4	E_5	Number of different combinations for distinguishable particles (Microstates)	boson	fermion with spin
1								
2								
3								
4								
5								

Note: for configuration 1 we can place A or B or C or D into level $E_1 \Rightarrow$ 4 possibilities
For each of these we can place any of the remaining 3 particles into level E_3. The remainder then go into level E_2. So total number of different possibilities = 4 x 3 = 12

for configuration 2 the total number of different possibilities is 4! / 2! 1! 1! = 12

for configuration 3 the number of distinct pairs that can be placed into level E_1 is 6 since we don't distinguish AB from BA, for example. So in level E_1 we can have

AB AC AD BC BD CD

Once the content of level E_1 is fixed for 3, the content of level E_3 is not adjustable.

We obtain the average number of particles in each level as follows:

$$n1 = \frac{\sum (\text{occupancy})(\#\text{ of combinations})}{\sum (\#\text{ of combinations})}$$

where the sum Σ is over the different configurations.

$$n1 = \frac{1(12)+2(12)+2(6)+3(4)+0(1)}{12+12+6+4+1} = \frac{60}{35} = 1.714$$

Similarly

$$n2 = \frac{\_(12)+\_(12)+\_(6)+\_(4)+\_(1)}{35} = \frac{40}{35} = 1.143$$

And

$$n3 = \frac{1(12)+2(6)}{35} = \frac{24}{35} = 0.686$$

$$n4 = \frac{1(12)}{35} = \frac{12}{35} = 0.343$$

$$n5 = \frac{1(4)}{35} = \frac{4}{35} = 0.114$$

Note: $\Sigma n_i =$ 1.714
1.143
0.686
0.343
<u>0.114</u>
= 4.000 (!) as required

Let's see what the Maxwell-Boltzmann distribution would have predicted:

$$n_i = A\, e^{-E_i/kT}$$

The exponential gives an average energy of $\bar{E}$= kT.

$$\overline{E} = \frac{\text{total energy}}{\#\text{ of particles}} = \frac{8}{4} = 2$$

The normalization constant A is determined from $\Sigma n_i = 4 = A \Sigma e^{-E_i/kT}$ where E_1=1, E_2 = 2, etc.

4 = $A\,[e^{-1/2} + e^{-1} + e^{-3/2} + e^{-2} + e^{-5/2}] = A\,[0.606 + 0.368 + 0.223 + 0.135 + 0.082] = A\,[1.414]$
A=2.829

E	Explicit Calculation	Maxwell-Boltzmann $n_i = 2.289\, e^{-E_i/2}$
1	1.714	1.714
2	1.143	1.041
3	0.686	0.631
4	0.343	0.382
5	0.114	0.232

These numbers come out pretty close!

B) Let's continue with this simple example:
Suppose the particles are identical, indistinguishable bosons. In this case the table on page 2 is still valid except that each of the five configurations can only be counted once, since the particles are no longer distinguishable.

Therefore:
$n_1 = 8/5 = 1.600$
$n_2 = 7/5 = 1.400$
$n_3 = 3/5 = 0.600$
$n_4 = 1/5 = 0.200$
$n_5 = 1/5 = \underline{0.200}$
Total $= 4.000$ as expected

To compare with the Bose-Einstein distribution:

$$n_i = \frac{1}{Be^{E_i/kT} - 1}$$

would require solving for kT and B using

$$4 = \sum n_i = \sum_{i=1}^{5} \frac{1}{B\,e^{E_i/kT} - 1}$$

$$8 = E_{tot} = \sum_{i=1}^{5} \frac{E_i}{B\,e^{E_i/kT} - 1}$$

This can be done only by numerical (trial + error) methods, and we skip it!

C) What about identical, indistinguishable fermions ?

If only one fermion could be put into each level, none of the configurations would be valid on page 2. Let's assume each particle carries a spin index which can be up or down so that two particles can be put into each level. In this case configurations 1 – 3 on page 1 are valid, but 4 – 5 are not. So:

Therefore:
$n_1 = 5/3 = 1.667$
$n_2 = 3/3 = 1.000$
$n_3 = 3/3 = 1.000$
$n_4 = 1/3 = 0.333$
$n_5 = 0/3 = \underline{0.000}$
Total $= 4.000$ as expected

Comparison with Fermi-Dirac statistics would require solving

$$4 = \sum n_i = \sum_{i=1}^{5} \frac{1}{C\,e^{E_i/kT} + 1}$$

$$8 = E_{tot} = \sum_{i=1}^{5} \frac{E_i}{C\,e^{E_i/kT} + 1}$$

We skip it