

Statistical Physics

Permutations and Combinations

${}^n P_r = \frac{n!}{(n-r)!}$ gives the number of ways n objects can fit in r boxes if each object is identifiable and the order is important.

${}^n C_r = \frac{n!}{r!(n-r)!}$ gives the number of ways n objects can fit in r boxes if the objects are not identifiable or the order doesn't matter.

Stirling's Approximation, I've already used this for Stats

Stirling's Approximation lets us deal with factorials in equations,

$\ln N! \approx N \ln N - N$, For large N

What are degeneracies? (check this explanation)

Sometimes there are different states that occupy the same energy. The number of different states occupying one energy is called the degeneracy.

For example;

If we group electrons by energy we have a set of states with different energies

$n_1, n_2, n_3 \dots$, but each state is made up of two electrons (one spin up and one spin down) therefore the number of degeneracies is two and $g_j = 2$

Counting Particles

I find this very confusing but it is very important. First of all, the number of possible arrangements of anything is given the greek letter omega, Ω .

REAL PARTICLES ARE ALMOST ALWAYS INDISTINGUISHABLE

1. Distinguishable objects without boxes

If you have N objects how many ways can you arrange them if order matters?

$$\Omega = N!$$

2. Distinguishable objects in boxes

If you have N objects how many different ways can you sort them into r boxes with n_j particles in each box, the order of the particles in one box doesn't matter, the particles are distinguishable?

Obviously the numbers of particles in all the boxes must add up to the total number of particles, N .

$$N = \sum_{j=0}^r n_j$$

The number of different arrangements of particles for this setup is

$$\Omega = N! \frac{1}{n_0! \times n_1! \times n_2! \times \dots \times n_r!} = N! \frac{1}{\prod_j n_j!}$$

when we consider degeneracies we have to multiply by the number of degeneracies for each box so

$$\Omega = N! \prod_j \left(\frac{g_j^{n_j}}{n_j!} \right)$$

I agree with this but can't explain why the degeneracy factor is $g_j^{n_j}$.

3. Indistinguishable objects in boxes (think of electrons in energy levels)

We find that if the particles are indistinguishable the number of microstates is reduced.

$$\Omega = \prod_j \left(\frac{g_j^{n_j}}{n_j!} \right)$$

Boltzmann Entropy

$$S = k_B \ln \Omega$$

I doubt it's very important but in one problem sheet we have to calculate the entropy from the Helmholtz Free Energy. This is a pretty simple thing to do in thermodynamics and gives

$$S = - \left(\frac{\partial F}{\partial T} \right)_V$$

The partition function Z

$$Z = \sum_j e^{\beta \epsilon_j} \text{ for a system without degeneracies } (g_j = 1)$$

$$Z = \sum_j g_j e^{\beta \epsilon_j} \text{ for a system with degeneracies}$$

What is the partition function?

I've defined the partition function mathematically but what does it mean? It is not

a purely mathematical tool like α just to scale the distribution, it is a more subtle and powerful parameter.

The particles in a distribution are split up into energy boxes in the same ratios as the partition function is split up.

SURELY THERE ARE BETTER WAYS TO EXPLAIN THIS???

The Boltzmann Distribution (describes distinguishable, weakly interacting particles)

If we know the temperature of a system and the number of particles in it the Boltzmann distribution tells us how many particles will have a given energy.

$$n_j = g_j e^{\alpha + \beta \epsilon_j} \quad \text{where} \quad \beta = \frac{-1}{k_B T}$$

Alpha is the same for all energy levels and is simply a normalisation factor so that the Boltzmann distribution describes the correct number of particles. In fact we can rewrite the constant alpha in terms of N and Z $\alpha = N / Z$

The best form of the Boltzmann equation is thus

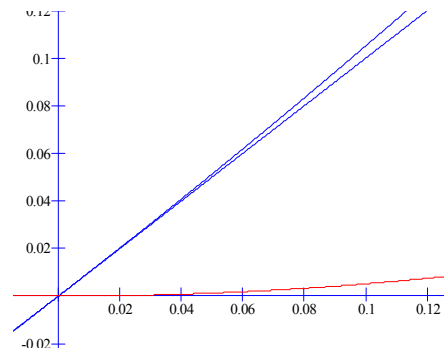
$$n_j = \frac{N}{Z} g_j e^{\beta \epsilon_j}$$

Crazy Approximations

It's in one of the problem sheets, it kind of works. Actually I like it.

$$e^x - 1 = x \quad \text{for} \quad x \ll 1$$

the two blue lines are $y = e^x$ and $y = x$, the red line is the difference



Helmholtz Free energy

The Helmholtz Free Energy tells us the maximum work that can be done by a gas without it changing temperature.

From Thermodynamics we can remember that the Free Energy (F) is defined as, $F = U - TS$

For distinguishable particles in statistical physics it is given by

$$F = -N k_B T \ln Z$$

This link between thermodynamics and statistical physics means this equation is sometimes called the Bridge Equation.

For indistinguishable particles this equation is slightly different,

$$F = k_B T \ln \left(\frac{Z^N}{N!} \right)$$

Dealing with Product Signs

The product sign \prod could be a real pain to deal with mathematically.

$$\prod_j n_j = n_0 \times n_1 \times n_2 \times \dots$$

But it's not actually impossible as long as we deal with logs,

$$\ln \prod_j n_j = \ln (n_0 \times n_1 \times n_2 \times \dots) = \ln n_0 + \ln n_1 + \ln n_2 + \dots = \sum_j \ln n_j$$

along with Stirling's Approximation,

$$\ln \prod_j n_j! = \sum_j \ln n_j! = \sum_j n_j \ln n_j - n_j$$

Chemical Potential

Chemical Potential is dealt with much more completely in the Electrons in Solids course. It is defined as the Gibbs Free Energy per particle,

$$\mu = G / N$$

We can express all the three following distributions in terms of chemical potential by making the substitution

$$\mu = \alpha k_B T$$

The Pauli exclusion Principle

You are absolutely joking? You don't know about the principle? Get out of town. Okay..... the PEP says that no two fermions can occupy the same energy level. Simple as that. You can't have two electrons at the same energy level around an atom, just can't have it, won't happen, nope. You kind of can because a spin

up and a spin down electron can occupy the same energy state but they're degeneracies within an energy level, that's why we define degeneracies. If there wasn't a reason we wouldn't have defined degeneracies would we? Well actually there are other reasons for degeneracies but this is definitely one of the, and it's a great reason.....

EiS uses PEP a lot w.r.t the Fermi Level (FE) of a metal, check it out, IMHO and FYO, I'm LMAO that you're still reading this, LOL.

The Three Distributions,

In the ancient times there were three distributions on the face of the Earth. Each its own land, each its own lifestyle. The Fermi-Dirac distribution dealt with collections of fermions and the laws stated that no two fermions could share the same plot of land. The Bose-Einstein distribution dealt with collections of Bosons which could share plots of land. The mysterious Maxwell-Boltzmann Distribution dealt with dilute gasses of fermions and bosons. Here there was so much space that no-one could see another persons plot of land so they didn't even need to consider sharing it or whether they were fermions or bosons.

M-B =	distinguishable classical particles, do not obey the Pauli exclusion Principle,
F-D =	indistinguishable particles that obey the Pauli exclusion Principle,
B-E =	indistinguishable particles that do obey the Pauli exclusion Principle,

Number of Microstates in these distributions

Maxwell Boltzmann, this is shown in the counting section earlier

$$\Omega_{MB} = \prod_j \left(\frac{g_j^{n_j}}{n_j!} \right)$$

Fermi Dirac

$$\Omega_{FD} = \prod_k \frac{g_k!}{N_k!(g_k - N_k)!}$$

The energy levels are split into bundles so they are more manageable. Each bundle contains g_k members and N_k is the population of the k^{th} bundle

Bose Einstein

$$\Omega_{BE} = \prod_k \frac{(N_k + g_k)!}{N_k! g_k!}$$

Deriving the Distribution Functions from the Number of Macrostates

We get the number of macrostates from the condition imposed on the particles (PEP and distinguishability). From the number of macrostates we can calculate the much more useful Distribution function, In order to do this we follow four main steps

1. Take \ln of both sides to find $\ln \Omega$
2. Remove factorials using Stirling's Approximation
3. Differentiate with respect to N_k
4. Use the method of Lagrange multipliers to find the most probable distribution,

$$\frac{\partial}{\partial N_k} \left(\ln \Omega + \alpha \sum_k N_k + \beta \sum_k N_k \epsilon_k \right) = 0$$

Distribution Functions

$$f_{FD}(\epsilon) = \frac{n_k}{g_k} = \frac{1}{e^{(-\alpha - \beta\epsilon)} + 1} = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$

$$f_{BE}(\epsilon) = \frac{n_k}{g_k} = \frac{1}{e^{(-\alpha - \beta\epsilon)} - 1} = \frac{1}{e^{(\epsilon - \mu)/k_B T} - 1}$$

$$f_{MB}(\epsilon) = e^{(\alpha + \beta\epsilon)} = e^{(\mu - \epsilon)/k_B T}$$

Note that sometimes we have to times these distributions by g_ϵ which is the number of degeneracies at a given energy level.

Method of Lagrange Multipliers

Yeah well it's difficult. Haven't done it yet, probably never will. That's the thing though isn't it. Life's a bitch and then you marry one.

Reduction of Quantum Distributions to the Maxwell-Boltzmann distribution (HELP! HELP! HELP!)

Both of these distributions tend towards to the classical Maxwell-Boltzmann

distribution when energy states are sparsely populated; at low pressure and/or high temperature.

Density of States

Basically in an atom the energy levels are quantised but they aren't spread out evenly. Dealing with the positions of the energy levels is a pain in the arse but if we have loads and loads of energy levels we can just deal with the density of the energy levels and integrate rather than deal with each energy level and sum them up. In order to do this we need define how the density of energy states changes with energy. This is called the density of states and depends on the number of dimensions of the problem. In EiS we write the density of states as $D(\epsilon)$, in Statistical Physics we write as the number of degeneracies at a given point (which makes sense) $g(\epsilon)$. Remember we've assumed there are so many energy levels we can hardly distinguish them and thus we can integrate them instead of adding them up. This means the degeneracies aren't integer numbers like we might expect; they are more like weighting degeneracies and this part of the subject is really hard to write down but not actually impossible to do.

Number of Particles and Internal Energy

The number of particles is quite simple, just add up all the particles

$$N = \sum_j n_j$$

The internal energy is also quite simple, add up each particles times that particles energy

$$U = \sum_j n_j \epsilon_j$$

The more difficult bit is if you don't know each particles energy. Thankfully the number of particles at a given energy is given by the product of the distribution function at that energy and the density of states (or the degeneracy) at that energy,

$$U = \sum_j g_j f_j \epsilon_j$$

It really needs to be noted that for systems with smalls numbers of energy levels or small numbers of particles or small number of anything we have to be careful with these approximations. The distributions functions and the density of states are all averages over large numbers. They are statistical ideals and need to be used carefully. As long as we are careful we can use the continuum

approximation. This says that the sums are so small they might as well be integrals.

Another Little Mathematical Trick

Sometimes when you deal with very very very small numbers calculaters aren't that much use, this little trick can very useful.

$$e^N \approx 1 + N \quad \text{when } N \ll 1$$

This comes from the Maclaurin Series expansion of e^x

$$e^x = 1 + x + x^2 + x^3 + x^4 + \dots \quad \text{taken to first order}$$

The rule can also be expressed as

$$\ln\left(1 + \frac{1}{N}\right) \approx \frac{1}{N}, \quad \text{valid for very large } N \text{ (ie } 1/N \text{ is very large)}$$

OR

$$\ln(1 + N) \approx N, \quad \text{valid for very small } N$$

Check up on the Lagrange Multiplier method for finding the most likely arrangement, it sounds sexy as...