

Statistical Thermodynamics

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” Put a cool quote here or your lame ”

-Thomas Brosnan

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1 Concepts and Terminology

1.1 System macrostate

- Properties at large scale of the system when we know constraining thermodynamic parameters such as P, V and T .

1.2 Quantum microstate

- Each quantum state is a separate and distinct microstate of the system.

1.3 Weakly coupled systems

- We assume weakly coupled systems. These are isolated systems such that the total macro-parameters E, V, N , are constant. Weak coupling implies that the energy levels of a single particle are effectively unchanged by particle interactions, but the interaction is sufficiently large to allow energy exchange. This means that at equilibrium the system must have a common temperature.

This assumption makes the quantum mechanics involved easier, as coupled systems in quantum mechanics can be quite complex where as simple systems like a gas of H_2 can be solved analytically (eigenvalues of vibration, rotation and translation).

1.4 Locality

- Localised particles are particles that are restricted to a certain place like a lattice for example. This way each particle of the lattice is *distinguishable*, i.e. it can be told apart from the other particles in the gas due to its position. If particles in a system are non-localised they are *indistinguishable*.

1.5 Bosons and Fermions

- In the case of indistinguishable particles we have two cases. Consider a two state system with two single particle states (orbitals) a and b and a wave function Ψ describing the system. We assume (weakly coupled systems) that the particles are non-interacting so that we can write the wavefunction as a product of the two states:

$$\Psi(1, 2) = \psi_a(1)\psi_b(2) \quad \text{or} \quad \Psi(2, 1) = \psi_a(1)\psi_b(2) \quad (1.1)$$

Where here there are two possibilities for the states as the particles are indistinguishable. Quantum mechanics tells us that the wavefunction must be a linear combination of all the (equally likely thus same amplitude) possible states, so we write:

$$\Psi(1, 2) \propto \psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1) \quad (1.2)$$

The \pm here indicates the two possibilities with respect to particle exchange. If we swap two particles and the system is symmetric (i.e. we get a $+$) then these particles are *Bosons*. And we can have any number of them in a single state, as if the states $a = b$ 1.2 is not 0.

However if we swap two particles and the system is anti-symmetric (now we get a $-$ sign) then the particles are *Fermions* and we can only have one fermion per state, as 1.2 is 0 if $a = b$. This is the Pauli exclusion principle.

1.6 Probability of microstates

- The probability of finding the system in a microstate l is given by the number of times the system was found in that microstate $n(l)$ divided by the total number of states $\sum_l n(l) = r$:

$$P(l) = \frac{n(l)}{r} \quad (1.3)$$

Note that this means $\sum_l P(l) = 1$. This probability allows us to calculate average values of quantities. The average value of a quantity $\langle A \rangle$, is given by:

$$\langle A \rangle = \sum_l A(l)P(l) = \frac{1}{r} \sum_l A(l)n(l) \quad (1.4)$$

- To realize this property, observations must be on a time scale that is long in comparison with the time for the system to randomize (come to equilibrium), known as the *relaxation time*.

1.7 Ensemble average

- An ensemble average or thermal average is the average over a large number of replicas of the entire system. A replica realizes one microstate of the system and it is the collection of replicas we call an ensemble.

The ensemble can also be used to determine $P(l)$, and is postulated to be equivalent to the time sampling of a single system. This is essentially assuming the system is constantly jumping from state to state, essentially randomly. This assumption that these two averages, over time and over all possible states is known as the *ergodic hypothesis*.

1.8 Fundamental assumption of statistical thermodynamics

- A system in thermal equilibrium is equally likely to be in any of the microstates accessible to it.
- This is the assumption of equal *a priori probabilities*.

2 Entropy and Temperature

2.1 Physics Principle

- Using the postulate we had earlier of a priori probabilities, we can say that since the system is equally likely to be any state then and assuming our system moves randomly from one microstate to the next, then it is far more likely for the system, when not in equilibrium to evolve towards a state with higher number of microstates Ω as there are just more of them. The system has more ways of arriving at those scenarios than the ones with smaller Ω .

Another way of seeing that the most probable macrostate is indeed the one realised by the maximum number of microstates is because this is where the system spends most its time, as it is far more likely to jump to a state with large Ω . This is what we meant by the ergodic hypothesis. This essentially coincides with the definition of equilibrium, the system spends most its time where there are a lot of states.

In the next section Cross uses a specific spin system example to introduce entropy but we don't need to do that we can keep it more general as Manuela did in the Statistical Physics I modal. The following few sections are taken from my note from that class.

2.2 Combined system

- Consider an isolated system split, by a partition into two subsystems, 1 and 2 (with out loss of generality we can say that the system 1 is larger than 2). The systems have there own thermodynamic variables E_1, V_1, N_1 and E_2, V_2, N_2 , respectively. The system is in equilibrium. At some point we allow energy exchange between the two systems. The two systems can now be considered one, described by the quantities E, V and N , where $E = E_1 + E_2$. The number of microstates for this system is now:

$$\Omega(E_1, E_2, V, N) = \Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_2) \quad (2.1)$$

This is because fundamentally Ω tells us how many different configurations of the system there are that result in the same energy, but system 1 and 2 are independent so naturally, the amount of different configurations is the product of the number of configurations of each subsystem.

2.2.1 Entropy

- Now we return to our two systems that have just been allowed to exchange energy. We want to know how E_1 and consequently $E_2 = E - E_1$, change as the system moves to a new equilibrium position. We know that we have to maximise the number of microstates $\Omega = \Omega_1\Omega_2$, so if E_1^* and $E_2^* = E - E_1^*$ are the values of the energy's at equilibrium. Then taking the derivative of $\Omega = \Omega_1\Omega_2$ with respect to E_1 , we must have that:

$$\Omega_2 \frac{\partial \Omega_1}{\partial E_1} \Big|_{E_1=E_1^*} + \Omega_1 \frac{\partial E_2}{\partial E_1} \frac{\partial \Omega_2}{\partial E_2} \Big|_{E_2=E_2^*} = 0 \quad (2.2)$$

Now $\frac{\partial E_2}{\partial E_1} = -1$ as $E_2 = E - E_1$, so we can divide this equation by $\Omega_1\Omega_2$ to get:

$$\begin{aligned} \frac{1}{\Omega_1} \frac{\partial \Omega_1}{\partial E_1} \Big|_{E_1=E_1^*} - \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial E_2} \Big|_{E_2=E_2^*} &= 0 \\ \Rightarrow \frac{\partial \ln(\Omega_1)}{\partial E_1} \Big|_{E_1=E_1^*} &= \frac{\partial \ln(\Omega_2)}{\partial E_2} \Big|_{E_2=E_2^*} \end{aligned} \quad (2.3)$$

- We can now introduce the quantity $\beta = \frac{\partial \ln(\Omega)}{\partial E} \Big|_{E=E_1^*+E_2^*}$, So that the above equation 2.3 can be written as $\beta_1 = \beta_2$. We know that in thermodynamics equilibrium between two systems is reached

when their temperatures are the same $T_1 = T_2$. Naively we might say $\beta \propto T$, but if we remember that temperature is defined as $T \equiv \frac{\partial E}{\partial S}$, then looking at the definition of β , it makes much more sense to write $\beta \propto \frac{1}{T}$ as now at equilibrium:

$$\boxed{\frac{\partial S}{\partial E} = \frac{1}{T} \propto \beta = \frac{\partial \ln(\Omega)}{\partial E}} \quad (2.4)$$

From the left most and right most expressions we can get an expression for entropy! If we denote the constant of proportionality between β and T as $1/k$, i.e. $\beta = \frac{1}{kT}$, Then entropy can be written as:

$$\boxed{S = k \ln(\Omega)} \quad (2.5)$$

This expression makes sense as if adding two systems together results in the number of microstates being the product of the original two systems Ω 's, then the natural way to turn this into entropy would be a function that separates products into sums, as entropy of two systems add together, its an extensive variable. The most suitable function for this task is naturally the logarithm. The constant of proportionality here k , is Boltzmann's constant.

