§7. Canonical Ensemble.

7.1 Gibbs Distribution

Now we are going consider systems with a fixed average energy (fixed meaning in equilibrium it is somehow maintained – and we can consistently measure the same value for it – e.g. gas in contact with walls at const temperature – I'll explain what this exactly means shortly). "Ensemble" refers to the realisations of the random variable E_α, i.e., many hypothetical systems with energies E_α, each occurring with probability p_α. To determine p_α, we must, according to the prescription we have adopted, maximise $S(p_1 \dots p_\Omega)$ subject to

$$\langle E_\alpha \rangle = \sum_\alpha p_\alpha E_\alpha = U.$$

By the method of Lagrange multipliers,

$$\boxed{\frac{S}{k_B}} - \lambda\left(\sum_\alpha p_\alpha - 1\right) - \beta\left(\sum_\alpha p_\alpha E_\alpha - U\right) \to \max$$

convenient

L. multipliers

$$\frac{S}{k_B} = -\sum_\alpha p_\alpha \ln p_\alpha$$

$$\underbrace{-\sum_\alpha dp_\alpha(\ln p_\alpha + 1) - \lambda\sum_\alpha dp_\alpha - \beta\sum_\alpha dp_\alpha E_\alpha}_{\boxed{-\sum_\alpha dp_\alpha(\ln p_\alpha + 1 + \lambda + \beta E_\alpha)}} - d\lambda\left(\sum_\alpha p_\alpha - 1\right) - d\beta\left(\sum_\alpha p_\alpha E_\alpha - U\right) = 0$$

Thus, $\ln p_\alpha = -1-\lambda-\beta E_\alpha \Rightarrow p_\alpha = e^{-\beta E_\alpha - 1 - \lambda}$

(normalisation) $\sum_\alpha p_\alpha - 1 = 0 \Rightarrow e^{-(1+\lambda)} \sum_\alpha e^{-\beta E_\alpha} = 1$

so we got λ: $e^{1+\lambda} = \boxed{Z(\beta) \equiv \sum_\alpha e^{-\beta E_\alpha}}$ ["Zustands-summe" in german, hence Z]

partition function

[illegible]

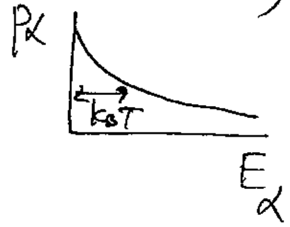
[illegible]

Boltzmann factor

$$\boxed{p_\alpha = \frac{1}{Z(\beta)} e^{-\beta E_\alpha}}$$ Gibbs distribution

and we define temperature via $\boxed{\beta \equiv \frac{1}{k_B T}}$ (width of the energy distr., like for Maxwell)

It is our other Lagrange multiplier, which must be calculated from



$$\sum_\alpha p_\alpha E_\alpha - U = 0,$$

or $U = \sum_\alpha p_\alpha E_\alpha = \frac{1}{Z(\beta)} \sum_\alpha E_\alpha e^{-\beta E_\alpha} = -\frac{\partial \ln Z}{\partial \beta}$

– really an implicit formula for T in terms of U – but we will soon see that what is often known and fixed is in fact T and U can be calculated from it.

[but for this, I will first have to explain (in a short while) how T is measured.]

L.8 ended here.

Note. More formal way of expressing this is as follows.

Consider 2 systems, one with micro states enumerated by α and energy levels $E_\alpha^{(1)}$

the other α' and $E_{\alpha'}^{(2)}$.

If these states are independent, then the microstates of the composite system are enumerated by pairs $\{\alpha, \alpha'\}$ and the corr. energy levels are

$$E_{\alpha\alpha'} = E_\alpha^{(1)} + E_{\alpha'}^{(2)}$$

So the partition function is

$$Z = \sum_{\alpha,\alpha'} e^{-\beta E_{\alpha\alpha'}} = \sum_{\alpha,\alpha'} e^{-\beta\left(E_\alpha^{(1)} + E_{\alpha'}^{(2)}\right)}$$

$$= \left(\sum_\alpha e^{-\beta E_\alpha^{(1)}}\right)\left(\sum_{\alpha'} e^{-\beta E_{\alpha'}^{(2)}}\right) = Z_1 Z_2$$

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln Z_1 Z_2}{\partial \beta} = -\frac{\partial \ln Z_1}{\partial \beta} - \frac{\partial \ln Z_2}{\partial \beta} = U_1 + U_2$$

$$S = \frac{U}{T} + k_B \ln Z = \frac{U_1 + U_2}{T} + k_B(\ln Z_1 + \ln Z_2) = S_1 + S_2$$

So, we now know how to calculate probabilities of any microstate of our system, provided we have computed its energy levels (from QM).

This allows us to compute any bulk quantities we wish, provided we can express them as averages – in terms of p_α's and E_α's.

What bulk quantities are we interested in?

7.2 Energy, entropy, volume

So far, we have encountered two bulk quantities:

- energy: $$\boxed{U = \sum_\alpha p_\alpha E_\alpha = -\frac{\partial \ln Z}{\partial \beta}}$$ (but remember that for now this is basically the def. of temperature and we will have to specify later how to measure T if this is to be useful as a formula for U)
- entropy: $$S = -k_B \sum_\alpha p_\alpha \ln p_\alpha =$$

$$= -k_B \sum_\alpha \frac{e^{-\beta E_\alpha}}{Z}\left(-\beta E_\alpha - \ln Z\right)$$

$$= k_B \beta \left(\sum_\alpha E_\alpha p_\alpha\right) + k_B \left(\sum_\alpha p_\alpha\right) \ln Z = k_B \beta U + k_B \ln Z$$

So $$\boxed{S = \frac{U}{T} + k_B \ln Z}$$

Both these quantities are additive [also known as extensive]: if the system is comprised of parts, (works for gases & fluids, but not solids)

$$U = \sum_{\text{parts}} U_{\text{part}}$$ (obvious with the QM proviso that parts should be indep., i.e. eigenstates of the whole are products of eigenstates of the parts and so energy levels are sums)

$$S = \sum_{\text{parts}} S_{\text{part}}$$ (by construction of the S function)

So they both depend just on the *volume* of the system and not on its *shape* because changing shape can be thought of as rearranging parts — additive quantities should not change (NB: we are assuming here that the system is not sitting in some coordinate-dependent external field, otherwise energy levels *will* depend on where various bits of the system are; *Example*: grav. field, Earth atmosphere — to be discussed later in the course)

Thus, another obviously interesting quantity is

- *volume* V.

7.3 Adiabatic processes and pressure

What happens when volume is changed?

Let us consider for now just deformations that occur very very slowly — then Quantum Mechanics teaches us that the set of microstates will remain the same, with the same probabilities p_α, but the energy levels E_α will change slowly as the volume is changed.

NB: system thermally isolated!

This is true for slow changes of any external parameter, not necessarily volume (see Binney's QM, §11.1).

Such processes are called *adiabatic* and they are *slow* in the sense explained above. Since p_α's do not change,

$$\boxed{S = \text{const}}$$ in adiabatic processes.

Sometimes "adiabatic" means that the process is *fast* — not a contradiction! Fast then means it is

→ but still slow enough for p_α = const

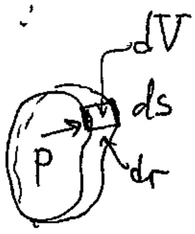
Fast enough for the system not to be able to come to any kind of new thermal equilibrium because it is in thermal contact with its surroundings. Formally we could just say that it is thermally isolated.

As V is changed in this way, the energy changes according to

$$dU_{ad.} = \left(\frac{\partial U}{\partial V}\right)_{p_1\cdots p_\Omega} dV = \sum_\alpha p_\alpha \left(\frac{\partial E_\alpha}{\partial V}\right)_{p_1\cdots p_\Omega} dV$$

But (slow) change of energy in an isolated system, due exclusively to change in its volume, can be related to work done <u>on</u> the system by whatever force is applied to effect the change (≡ <u>minus</u> work done <u>by</u> the system against that force; Newton's 3rd law):

$$d W_{ad} = dU_{ad} = -p\,dV \quad \Big(\equiv -\underset{\text{force}}{F}\,\underset{\text{area}}{dS}\,\underset{\text{distance}}{dr}\Big)$$



- So, we <u>define</u> <u>pressure</u>

$$\boxed{P = -\left(\frac{\partial U}{\partial V}\right)_{p_1\cdots p_\Omega} = -\sum_\alpha p_\alpha \left(\frac{\partial E_\alpha}{\partial V}\right)_{p_1\cdots p_\Omega}}$$

NB: In same way, we can introduce other external parameters (like V), change them adiabatically, and define analogs of pressure as a way of calculating work done during such a process — these quantities quantify the <u>response</u> of the system (in terms of change in energy) to change in the ext. paramet

E.g. Length of a string l → tension in the string

$$\tau = \left(\frac{\partial U}{\partial l}\right)_{p_1 \cdots p_\Omega} = \sum_\alpha p_\alpha \left(\frac{\partial E_\alpha}{\partial l}\right)_{p_1 \cdots p_\Omega}$$

(+ rather than − because more length ⇒ more tension, whereas more volume ⇒ less pressure
— this is just a convention of definitions!)

Magnetic field $\vec{B}$ → magnetisation $\vec{M}$

$$\vec{M} = -\left(\frac{\partial U}{\partial \vec{B}}\right)_{p_1 \cdots p_\Omega} = -\sum_\alpha p_\alpha \left(\frac{\partial E_\alpha}{\partial \vec{B}}\right)_{p_1 \cdots p_\Omega}$$

(energy lowest when more magnetisation, i.e. magnets align with $\vec{B}$)

We will study such systems later, but for now, let us concentrate on "pure" thermodynamical situations, where the only external parameter is volume of the system.

7.4 Fundamental eqn of thermodynamics

Let us consider a more general (not adiabatic) infinitesimal change in the state of the system, i.e. we will alow p_α's to change. We will still assume that this happens sufficiently slowly so at each step in the change the system has time to relax to equilibrium — quasistatic process. The difference with adiabatic process is that we are not assuming the system to be isolated (thermally) during it.

Then the entropy is <u>not</u> constant:

$$dS = -k_B \sum_\alpha \left(\ln p_\alpha \, dp_\alpha + \cancel{p_\alpha} \cdot \frac{1}{\cancel{p_\alpha}} dp_\alpha \right) =$$

$$= -k_B \sum_\alpha \ln p_\alpha \, dp_\alpha - k_B \, d \underbrace{\sum_\alpha p_\alpha}_{=0 \leftarrow \text{because } \sum_\alpha p_\alpha = 1}$$

$$= -k_B \sum_\alpha \left(-\beta E_\alpha - \ln Z \right) dp_\alpha =$$

$$= k_B \beta \left(\sum_\alpha E_\alpha \, dp_\alpha \right) + k_B \ln Z \cancel{\left(\sum_\alpha dp_\alpha \right)} \rightarrow 0 \text{ again}$$

Energy is not constant either:

$$dU = \sum_\alpha \left(E_\alpha \, dp_\alpha + p_\alpha \, dE_\alpha \right) = \qquad \leftarrow \text{change of } E_\alpha \text{ holding } p_\alpha\text{'s constant}$$

$$= \frac{dS}{\underbrace{k_B \beta}_{= 1/T \text{ by definition}}} + \underbrace{\sum_\alpha p_\alpha \left(\frac{\partial E_\alpha}{\partial V} \right)_{p_1 \dots p_\Omega}}_{= -p \text{ by definition! (pressure)}} dV + \text{similar terms if other ext. params. change too (ignore them for now)}$$

Thus, $\boxed{dU = T dS - p dV}$ <u>Fundamental equation of thermodynamics</u>

We have proved it by assuming a particular kind of process (quasistationarity). However, all quantities involved in this equation are <u>functions of state</u> – i.e. they depend on the state of the system and not on how it got there. Thus, the equation must hold in general.

7.5 Functions of State

An immediate consequence of this result is that energy is a function of two things: S and V

$$U = U(S,V)$$

and we can express

$$\boxed{p = -\left(\frac{\partial U}{\partial V}\right)_S} \quad \text{and} \quad \boxed{T = \left(\frac{\partial U}{\partial S}\right)_V}$$

This can in fact be treated as def. of temperature — a good one as we will see shortly

The difference with the def. on p.66 is that we have proved you just have to hold a macroscopic quantity, S, constant, not worry about all the p_α's (unmeasurable)

This means that also p and T are functions of S and V (can calculate them if we know $U(S,V)$), or, more generally, out of the set

$$U, S, V, p, T$$

only two are independent, the third can be expressed in terms of those two and the rest calculated from that. Which of these functions — or combinations thereof to use for describing the system depends on the specific situation one considers (you will study some specially convenient ones, called thermodynamic potentials, and relations between them, called Maxwell's relations later in the course).

Note: Unlike U, S, V, pressure and temperature are intensive (rather than extensive) quantities — i.e. they do not scale with size of system (indeed size cancels in the expressions above

L.9 ended here.