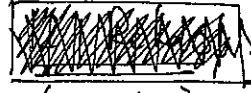


PART III. FURTHER STAT. MECHANICS.

§12. Grand Canonical Ensemble.

12.1 Ensembles Redux



We start by recalling the basic construction of statistical mechanics.

usually defined as just some subvolume of the world (sometimes changeable - e.g. pistons)

Our primary object of interest was "a system" - a large collection of particles and/or degrees of freedom, which we characterised by its full (hypothetically known from QM) set of possible collective microstates (i.e. full wave function) labeled  $\alpha$  and each having an associated energy  $E_\alpha$  and probability  $p_\alpha$ .

While the microstates  $\alpha$  and their energies were <sup>the</sup> subject of QM, finding their probabilities was the task of SM and we formulated the general principle that  $p_\alpha$  must be found by maximising Gibbs entropy

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

subject to whatever constraints we wished to impose on the system. It is these constraints that decided which "ensemble" we were using.

["ensemble" meant that formally we were thinking of a very large number of macroscopically identical systems  $\Pi$  meaning constraints are the same ( $U, T, V, \dots$ )

and probabilities referred to the likelihood of finding any given one in a given microstate. [Note that another interpretation would be to think of the evolution of one system over a long period of time covering the phase space - then the probabilities ~~refer to the~~ measure what microstates the system spends most time in. The statement of time avg's = ensemble avg's is mathematically nontrivial and is known as "ergodic hypothesis", or ergodic theorem in the cases when it can be proven].

We have encountered two ensembles:

1) Microcanonical (S11) Completely isolated system, no contact with the world. So fixed energy  $E_\alpha = E$  for all available  $\alpha$  and also fixed particle #  $N$ .

$$\frac{S}{k_B} - \lambda \left( \sum_{\alpha} p_{\alpha} - 1 \right) \rightarrow \max \quad \Leftrightarrow \quad \boxed{p_{\alpha} = \frac{1}{\Omega}} \quad \text{equal prob.}$$

$\uparrow$  Lagrange multiplier       $\uparrow$  normalisation of probabilities       $\uparrow$  # of microstates (with energy  $E$ )

2) Canonical (S7) A system that had a fixed volume and fixed # of particles, but ~~was not~~ could exchange energy with the world (reservoir, heat bath) in such a way that only its avg energy  $U = \langle E \rangle$  was fixed.

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

fixed avg. energy.

associated  
Lagrange multiplier.

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

Gibbs  
(Boltzmann)

This was technically speaking  
simply to be found from

$$\sum_{\alpha} p_{\alpha} E_{\alpha} = U$$

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}}$$

but it turned out that  $\beta = \frac{1}{k_B T}$  had a profound  
meaning, directly related to our intuitive understanding  
of hot and cold (temperature) and directly  
measurable, so in fact the constraint of fixed  
average energy was much better expressed as the  
constraint of fixed temperature. (\*)

[The key reason this was possible was that

$T = \left( \frac{\partial U}{\partial S} \right)_{V, N}$  could be proved to equalize  
between all parts of a system  
in equilibrium.

Once this <sup>setup</sup> ~~was~~ was in place, we also introduced  
pressure (or other things like magnetisation, tension  
etc. for non-PV systems) and were then able to  
spin off thermodynamics and also calculate  
various useful quantities like  $C_V$ .

(\*) Let me give you a ~~slightly~~ slightly different derivation than I did in MT (useful to have variation):

Helmholtz free energy by definition was

$$F = -k_B T \ln Z = U - TS$$

Ex. Prove these two are equiv. for Gibbs distr.

Then  $Z = e^{-\beta F}$

and  $p_\alpha = e^{\beta(F - E_\alpha)}$  a cute and compact form.

Take the differential of both sides of

$$\sum_\alpha p_\alpha = 1$$

$$\sum_\alpha p_\alpha [(F - E_\alpha) d\beta + \beta (dF - dE_\alpha)] = 0$$

$$(F - U) d\beta + \beta dF - \beta \sum_\alpha p_\alpha dE_\alpha = 0$$

$-TS \cdot \left(-\frac{dT}{k_B T^2}\right) = \frac{SdT}{k_B T}$        $-PdV$

So  $SdT + dF + pdV = 0$

$dF = -SdT - pdV$   
 $dU = TdS - pdV$

and so on to whatever thermodynamical relations you desire.

Note that for the microcanonical ensemble, it was also possible to introduce temperature:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N} \quad \text{and prove all the same things about it, then set up thermodynamics.}$$

The difference between the two ensembles was the difference between precise energy and its mean value (well, and also the practical or even conceptual impossibility to have a completely closed system) However, in quantitative terms, this difference was extremely small for a system containing a large # of particles: in one of the HWs we proved

$$\frac{\langle \Delta E^2 \rangle}{U^2} = \frac{C_V k_B T^2}{U^2} \propto \frac{1}{N} \quad \left[ \begin{array}{l} \text{because } C_V \text{ and } U \\ \text{were ext. quantities} \end{array} \right]$$

Note further that the microcanonical distribution could be considered a particular case of canonical:

indeed if all  $E_\alpha = E$ , then

$$P_\alpha = \frac{e^{-\beta E_\alpha}}{Z} = \frac{e^{-\beta E}}{Z} = \frac{1}{\Omega}$$

$$Z = \sum_{\alpha} e^{-\beta E_\alpha} = \Omega e^{-\beta E}$$

12.2 Variable # of particles

All through those considerations, we treated our # of particles as a constant. i.e., our system had a ~~closed~~ wall, which might (canonical) or might not (microc.) have been permeable to energy and which was allowed to shrink or expand under work, but always contained within it a fixed  $N$ .

We are now going to make a further generalisation: let the system (defined as some subvolume of the world) to be able to exchange particles with the world, so only the average # of particles will be fixed.

This will also help deal with situations where  $N$  is fixed, but it is useful to allow it not to be, to facilitate counting (Fermi, Bose)

This allowance for a variable # of particles will also enable us to deal with situations when

- system contains same matter but in different phases, which can exchange particles (vapour, water, ice...)
- it contains different substances, which may chemically react with each, ~~give rise to new~~ particles of the reactants giving rise to new particles of reaction products [similarly ionization/recombination, pair production/annihilation etc.]
- it doesn't conserve particles at all (radiation)

~~So~~ microstates are now characterised also by the # of particles in them:

$$\alpha \leftrightarrow E_\alpha, N_\alpha \quad \text{and} \quad \sum_\alpha P_\alpha N_\alpha = \langle N_\alpha \rangle \equiv \bar{N}$$

is fixed.

We know the routine: maximise S with fixed U and N

$$\frac{S}{k_B} - \lambda \left( \sum_{\alpha} p_{\alpha} - 1 \right) - \beta \left( \sum_{\alpha} p_{\alpha} E_{\alpha} - U \right) + \beta \mu \left( \sum_{\alpha} p_{\alpha} N_{\alpha} - \bar{N} \right) \rightarrow \max$$

$$- \sum_{\alpha} p_{\alpha} \ln p_{\alpha}$$

$$- (1 + \ln p_{\alpha}) - \lambda - \beta E_{\alpha} + \beta \mu N_{\alpha} = 0$$

I choose my lagrange multipliers to be  $-\beta\mu$ ,  $\mu$  as yet devoid of physical meaning

$$p_{\alpha} = \frac{e^{-\beta(E_{\alpha} - \mu N_{\alpha})}}{\mathcal{Z}(\beta, \mu)}$$

Grand canonical distribution

$$\mathcal{Z}(\beta, \mu) = \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu N_{\alpha})}$$

Grand partition function

and, as usual, the lagrange multipliers  $\beta$  and  $\mu$  are determined from

$$\sum_{\alpha} p_{\alpha} E_{\alpha} = U$$

$$\sum_{\alpha} N_{\alpha} p_{\alpha} = \bar{N}$$

$$\beta = \frac{1}{k_B T}$$

$$\mu = \mu(U, V, \bar{N})$$

as a function of  $U, V, \bar{N}$

chemical potential

$$U = - \left( \frac{\partial \ln \mathcal{Z}}{\partial \beta} \right)_{\mu} + \mu \bar{N}$$

(has physical - and, indeed, chemical, meaning, to be elucidated shortly)

$$\bar{N} = \frac{1}{\beta} \left( \frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)_{\beta}$$

Note that the canonical distribution is a particular case of this: if all  $N_\alpha = N$  (fixed # of particles),

$$p_\alpha = \frac{e^{-\beta E_\alpha} e^{\beta \mu N}}{\mathcal{Z}} = \frac{e^{-\beta E_\alpha}}{\mathcal{Z}} \quad \leftarrow \text{canonical.}$$

where  $\mathcal{Z} = e^{-\beta \mu N} \sum_\alpha e^{-\beta (E_\alpha - \mu N)} = \sum_\alpha e^{-\beta E_\alpha}$  ex.

$$\mathcal{Z} = \underbrace{(e^{\beta \mu})^N}_{\substack{\uparrow \text{grand} \\ \uparrow \text{"fugacity"}}} \underbrace{\mathcal{Z}(\beta)}_{\uparrow \text{simple}}$$

This will be useful in our calculation of stat. mech. of quantum gases.

12.3 Thermodynamics <sup>of open systems</sup> ~~of open systems~~  
and the meaning of chemical potential

Let's follow the old and tried procedure:

~~Introduce~~ 1) Introduce ~~the~~  
~~grand~~ grand (canonical) potential  $\Phi$

$$\boxed{\Phi = -k_B T \ln \mathcal{Z}} \quad (\text{analog of Helmholtz free energy in the can. formalism})$$

Then  $\mathcal{Z} = e^{-\beta \Phi}$  and  $\boxed{p_\alpha = e^{\beta (\Phi - E_\alpha + \mu N_\alpha)}}$  cf. p. 102a

$$\begin{aligned} S &= -k_B \sum_\alpha p_\alpha \ln p_\alpha = -k_B \sum_\alpha p_\alpha \beta (\Phi - E_\alpha + \mu N_\alpha) = \\ &= -\frac{1}{T} (\Phi - U + \mu \bar{N}) \end{aligned}$$

or  $\Phi = U - TS - \mu \bar{N} = F - \mu \bar{N}$  Helmholtz free energy.



Now  $\sum_{\alpha} p_{\alpha} = 1$  differentiate both sides:

$$\sum_{\alpha} p_{\alpha} \left[ (\Phi - E_{\alpha} + \mu N_{\alpha}) d\beta + \beta (d\Phi - dE_{\alpha} + N_{\alpha} d\mu) \right] = 0$$

$$\underbrace{(\Phi - U + \mu \bar{N})}_{(-TS)} \left( -\frac{dT}{k_B T^2} \right) + \beta (d\Phi + p dV + \bar{N} d\mu) = 0$$

note that  $dN_{\alpha} = 0$  because we are considering quasi-st. changes, #'s of particles in quantum states do not change.

So, we get

$$SdT + d\Phi + p dV + \bar{N} d\mu = 0$$

$$\boxed{d\Phi = -SdT - p dV - \bar{N} d\mu}$$

$$\hookrightarrow \text{so } S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V, \mu} \quad p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T, \mu} \quad \bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T, V}$$

since  $\Phi = U - TS - \mu \bar{N}$ ,

but,  $d\Phi = dU - TdS - SdT - \mu d\bar{N} - \bar{N} d\mu$

equation of state

$$\text{so, } \boxed{dU = TdS - p dV + \mu d\bar{N}}$$

fundamental eqn of thermodynamics, generalised to variable  $N$ .

Ex. Do a similar derivation for canonical case.

$$\boxed{\mu = \left(\frac{\partial U}{\partial \bar{N}}\right)_{S, V} = -T \left(\frac{\partial S}{\partial \bar{N}}\right)_{U, V}}$$

$\mu$  measures how much energy changes if particles are added/subtracted

change in entropy as particles added/sub-trd.

Lecture ended here.

~~scribbles~~

From the last formula, we can derive the property of  $\mu$  that clarifies its ~~physical~~ role in thermodynamics.

Consider two systems in contact, otherwise isolated:

$$U_1 + U_2 = \text{const}$$

$$N_1 + N_2 = \text{const} \quad (\text{assume their vols don't change})$$

$$S = S_1(U_1, N_1) + S_2(U_2, N_2) \rightarrow \text{max}$$

$$dS = \left(\frac{\partial S_1}{\partial U_1}\right)_{V, N} dU_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{U, V} dN_1 +$$

$$+ \left(\frac{\partial S_2}{\partial U_2}\right)_{V, N} dU_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U, V} dN_2 =$$

$$= \underbrace{\left[ \left(\frac{\partial S_1}{\partial U_1}\right)_{V, N} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V, N} \right]}_{\substack{\text{"} \\ \frac{1}{T_1} - \frac{1}{T_2}}} dU_1 + \underbrace{\left[ \left(\frac{\partial S_1}{\partial N_1}\right)_{U, V} - \left(\frac{\partial S_2}{\partial N_2}\right)_{U, V} \right]}_{\substack{\text{" see p.107} \\ \frac{\mu_2 - \mu_1}{T}}} dN_1 = 0$$

$$\frac{1}{T_1} - \frac{1}{T_2}$$

$\Downarrow$

$$T_1 = T_2 = T$$

(or  $dU_1 > 0$  if  $T_1 < T_2$   
heat flows from hot to cold)

// see p.107

$$\frac{\mu_2 - \mu_1}{T}$$

$\Uparrow T$

$\Downarrow$

$$\mu_2 = \mu_1$$

(or  $dN_1 > 0$  if  $\mu_2 > \mu_1$   
So particles flow from larger to smaller  $\mu$ )

Thus, equality of  $\mu$  across the system is the condition for (~~chemical~~ particle) equilibrium.

$\mu$  to # of particles is basically what temperature is to energy or pressure to volume.

One example of this will be the requirement that ~~in a~~ a multi-phase system in equilibrium would organise so that  $\mu$  is the same across the phase boundary (see derivation of the Clapeyron-Clausius equation in a few lectures).

12.5 Chemical Potential and the Gibbs Function

Recall that  $\Phi = F - \mu \bar{N} \Rightarrow d\Phi = dF - \mu d\bar{N} - \bar{N} d\mu$   
Therefore (see p.107)

$dF = -SdT - PdV + \mu d\bar{N} \Rightarrow \mu = \left( \frac{\partial F}{\partial \bar{N}} \right)_{V,T}$

Finally,  $G = F + PV$   
"Gibbs function"

$dG = dF + PdV + VdP$

$dG = -SdT + VdP + \mu d\bar{N} \Rightarrow \mu = \left( \frac{\partial G}{\partial \bar{N}} \right)_{P,T}$

this will be very useful for systems with fixed # of particles.

But we can do better than this if we recall that we require  $S, U$  and  $V$  to be extensive functions

[This means that if  $S = S(U, V, \bar{N})$ , then

$$S = \bar{N} f\left(\frac{U}{\bar{N}}, \frac{V}{\bar{N}}\right)$$

some function

Similarly,  $F = F(V, T, \bar{N})$  and so

$$F = \bar{N} f\left(\frac{V}{\bar{N}}, T\right)$$

some other function

temperature is not extensive

Finally,  $G = G(P, T, \bar{N})$  and so

$$G = \bar{N} f(P, T)$$

yet another function

both pressure and temp. are not extensive.

Therefore  $\mu = \left(\frac{\partial G}{\partial \bar{N}}\right)_{P, T} = f(P, T) = \frac{G}{\bar{N}}$  ]

Thus,  $\mu = \frac{G}{\bar{N}}$  chemical potential is Gibbs function per particle! NB:  $\mu$  is an intensive quantity

This immediately implies

$$\Phi = F - \mu \bar{N} = F - G = -PV$$

nice and simple

and implies that knowing  $\Phi$  immediately gives us the equation of state.

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-110a-

⇒ A slightly different proof:

$$G = G(P, T, \bar{N})$$

Change  $\bar{N}$  by factor of  $\lambda$ . Then, since  $G$  is an extensive quantity, it must also change by the same factor. So

$$G(P, T, \lambda \bar{N}) = \lambda G(P, T, \bar{N})$$

↑  
intensive, so they don't care about  $\lambda$ .

Differentiate this wrt  $\lambda$ , then set  $\lambda=1$ :

$$\underbrace{\left(\frac{\partial G}{\partial \bar{N}}\right)_{P, T}}_{\mu} \cdot \bar{N} = G$$

$$\text{So } G = \mu \bar{N}$$

This is generalised to many species on p. 112

Note. Since  $\mu$  is intensive, it will be a function of  $P$  and  $T$ , not  $\bar{N}$ :

$$\mu(P, T, \lambda \bar{N}) = \mu(P, T, \bar{N}) \Rightarrow \text{indep. of } \bar{N}.$$

~~scribble~~  
~~scribble~~

→ Note. So the condition of equilibrium,  $\mu_1(P, T) = \mu_2(P, T)$  (p. 108) can, for example, define the phase boundary  $P = P(T)$  (this will be covered in just a few lectures).

12.6 Chemical Potential of a Classical Ideal Gas.

As has been our custom, let us test our formalism on our favorite special case: the ideal gas.

The set of microstates now is (cf. §10, p.84)

$\alpha = \{ \vec{p}_1 \}$	1 particle	} of course, we don't really care about cases with small $N$ , but they won't hurt.
$\{ \vec{p}_1, \vec{p}_2 \}$	2 particles	
$\{ \vec{p}_1, \vec{p}_2, \vec{p}_3 \}$	3 particles	
...		
$\{ \vec{p}_1, \vec{p}_2, \dots, \vec{p}_N \}$	$N$ particles	

and within each  $N$ , particles are indistinguishable. If we continue neglecting quantum correlations (not long now before we relax this assumption!) this will lead to compensating factors  $N!$  in our calculation of the partition function.

Calculate the grand partition function [cf. pp. 84, 89]

$$\begin{aligned}
 \mathcal{Z} &= \sum_{\alpha} e^{-\beta E_{\alpha} + \beta \mu N_{\alpha}} = \sum_{\alpha} e^{-\beta E_{\alpha} + \beta \mu N} \quad \swarrow \text{energies of individual particles} \\
 &= \sum_N e^{\beta \mu N} \sum_{\{ \vec{p}_1, \dots, \vec{p}_N \}} e^{-\beta (E_{\vec{p}_1} + \dots + E_{\vec{p}_N})} \cdot \frac{1}{N!} \quad \swarrow \text{indistinguishability correction} \\
 &= \sum_N e^{\beta \mu N} \frac{Z_1^N}{N!} = \sum_N \frac{(Z_1 e^{\beta \mu})^N}{N!} = e^{Z_1 e^{\beta \mu}} \quad \swarrow \text{single-particle partition function}
 \end{aligned}$$

From p. 105, we are supposed to find  $\mu$  from the condition that  $\langle N \rangle = \bar{N}$ , or

$$\bar{N} = \frac{1}{\beta} \left( \frac{\partial \ln Z}{\partial \mu} \right)_{\beta} = Z_1 e^{\beta \mu} \Rightarrow \boxed{\mu = -k_B T \ln \frac{Z_1}{\bar{N}}}$$

Note that if we take a monatomic gas, with no other degrees of freedom but translational, then (p. 86)

$$Z_1 = \frac{V}{\lambda_{th}^3}, \quad \lambda_{th} = \frac{h}{\sqrt{m k_B T}}$$

and so  $\boxed{\mu = k_B T \ln(n \lambda_{th}^3)}$ ,  $n = \frac{\bar{N}}{V}$   $\otimes$  (p. 110d)

Ex. (you can check that this exactly coincides with  $\frac{G}{N}$  for the ideal gas, calculated ~~there~~ from the canonical formalism).

From the results above,  $e^{\beta \mu} = \frac{\bar{N}}{Z_1}$  and so we get a set of remarkably simple formulae:

$$Z = e^{\bar{N}} \quad \text{grand partition function for ideal gas}$$

$$\Phi = -k_B T \bar{N} \quad \text{grand potential}$$

$$= -k_B T Z_1 e^{\beta \mu} \quad \text{more convenient form if we want to differentiate at const } \mu$$

Equation of state (p. 107):

$$p = - \left( \frac{\partial \Phi}{\partial V} \right)_{T, \mu} = k_B T \left( \frac{\partial \bar{N}}{\partial V} \right)_{T, \mu} = n k_B T \quad \text{as it should be}$$

and so  $\underline{\Phi = -n k_B T V = -PV}$  (see p. 110)

~~This also allows us to write  $\mu$  in terms of its natural variables  $P, T$ :  $n = P/k_B T$ , so~~

~~[Scribbled out text]~~

(\*)

$$\mu = \underbrace{-k_B T \ln \frac{k_B T}{\lambda_{th}^3}}_{\text{function of temperature only}} + \underbrace{k_B T \ln p}_{\text{pressure dependence}}$$

Finally, free energy

$$\begin{aligned} F &= \Phi + \mu \bar{N} = -k_B T \bar{N} + \bar{N} \left( -k_B T \ln \frac{Z_1}{\bar{N}} \right) = \\ &= -k_B T \bar{N} \left( 1 + \ln \frac{Z_1}{\bar{N}} \right) = \\ &= -k_B T \bar{N} \left[ 1 - \ln (n \lambda_{th}^3) \right] \text{ same as on p. 90.} \end{aligned}$$

So all the old formulae with fixed  $N$  generalise directly by replacing  $N$  with  $\bar{N}$  and adding the  $\mu dN$  terms to differentials in the right places.

All this might look like not a lot of gain for all the pain, but it will become very useful once we start considering multi-species systems.