

Lectures on Statistical Physics (A1)

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PART IV : APPLICATIONS OF STATISTICAL MECHANICS

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PART V : OPEN SYSTEMS & QUANTUM GASES.

§14. Grand Canonical Ensemble.

So you now know what to do if you are interested in a system whose quantum microstates you know and the probabilities for it being in any of these microstates you have to guess based on (the expectation of) the knowledge of some measurable mean properties of the system.

So far this measurable property has always been mean energy — and the resulting canonical stat's characterized a system in contact with a heat bath at some fixed temperature.

You might have noticed that there were some other properties of the system that we treated as being fixed exactly rather than in the mean : V volume, N # of particles — these were not constraints but "external parameters". They did not need to be measured, they were ~~unmeasurable~~ just there (a box of definite volume, with impenetrable walls...)

Mathematically speaking, our microstates and their energies depended parametrically on V and N :

$$E_\alpha = E_\alpha(V, N) \quad (1)$$

14.1 Variable Number of Particles

There are good reasons to treat N as a measurable mean quantity rather than a fixed parameter.

This will allow us to treat systems that are not entirely closed and so can exchange particles with other systems. For example:

- inhomogeneous systems in some external potential, where parts of the system can be thought of exchanging particles with other parts where the external field has a different value (gravity, rotation, electric field, ...)
- multiphase systems, where different phases can exchange particles (vapour, water, ice...)
- systems containing different substances that can react with each other and turn into each other: chemical reactions, partially ionized systems, pair production (annihilation etc.)
- systems where the # of particles is not fixed at all (e.g. radiation)
- situations where N is really fixed but, for the purposes of counting microstates, it is convenient to formally allow it to vary (Fermi, Bose statistics for quantum gases).

So, for each microstate, we now have

$$\alpha \leftrightarrow E_\alpha, N_\alpha$$

\uparrow \uparrow
 energy # of particles

and we will have two constraints:

$$\sum_{\alpha} p_{\alpha} E_{\alpha} = U \quad \text{mean energy} \quad (2)$$

$$\sum_{\alpha} p_{\alpha} N_{\alpha} = \bar{N} \quad \text{mean \# of particles} \quad (3)$$

(which we can measure; this is equivalent to measuring mean density: $n = \frac{\bar{N}}{V}$)

We know the routine:

maximize entropy

\uparrow
 volume is still a fixed external parameter!

$$-\sum_{\alpha} p_{\alpha} \ln p_{\alpha} - \lambda (\sum_{\alpha} p_{\alpha} - 1) - \beta (\sum_{\alpha} E_{\alpha} p_{\alpha} - U) + \beta \mu (\sum_{\alpha} N_{\alpha} p_{\alpha} - \bar{N}) \rightarrow \max$$

\Downarrow

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

\uparrow
 Lagrange multiplier, factor of $-\beta$ introduced to accommodate future conventional notation

\Downarrow

$$p_{\alpha} = \frac{e^{-\beta(E_{\alpha} - \mu N_{\alpha})}}{\mathcal{Z}(\beta, \mu)} \quad (4)$$

μ is as yet w/o clear physical meaning.

grand canonical distribution, normalised by the grand canonical partition function:

$$\mathcal{Z}(\beta, \mu) = \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu N_{\alpha})} \quad (5)$$

It remains to calculate β and μ from (2) & (3):

• Since

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z} \sum_{\alpha} (-E_{\alpha} + \mu N_{\alpha}) e^{-\beta(E_{\alpha} - \mu N_{\alpha})} =$$

$$= \sum_{\alpha} (-E_{\alpha} + \mu N_{\alpha}) p_{\alpha} = -U + \mu \bar{N}, \text{ so}$$

$$\boxed{U = -\frac{\partial \ln Z}{\partial \beta} + \mu \bar{N}} \quad (6) \quad \beta \equiv \frac{1}{k_B T} \text{ as before}$$

T temperature (tbl.)

• Since

$$\frac{\partial \ln Z}{\partial \mu} = \frac{1}{Z} \sum_{\alpha} \beta N_{\alpha} e^{-\beta(E_{\alpha} - \mu N_{\alpha})} = \beta \bar{N}, \text{ so}$$

$$\boxed{\bar{N} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu}} \quad (7) \quad \mu \text{ is "chemical potential"}$$

(to be endowed with physical meaning later)

Eqs. (6) & (7) determine β and μ as functions of U, \bar{N} (and V and any other external parameters)

Note: The canonical distribution can be recovered as a special case: suppose for all α , $N_{\alpha} = N$ (fixed # of particles). Then

$$p_{\alpha} = \frac{e^{-\beta E_{\alpha}} e^{\beta \mu N}}{Z} = \frac{e^{-\beta E_{\alpha}}}{Z} \leftarrow \text{canonical stats!}$$

$$\text{where } Z = e^{-\beta \mu N} Z = e^{-\beta \mu N} \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu N)} = \sum_{\alpha} e^{-\beta E_{\alpha}} \quad (8)$$

$$\text{and } Z = (e^{\beta \mu})^N Z(\beta)$$

\uparrow ground \uparrow "fugacity" \uparrow regular

14.2 Thermodynamics and the meaning of chemical potential

We now generalise the argument from §9.2:

$$S_G = -\sum_{\alpha} p_{\alpha} \ln p_{\alpha} = -\sum_{\alpha} p_{\alpha} \left[-\beta(E_{\alpha} - \mu N_{\alpha}) - \ln \mathcal{Z} \right]$$

$$= \beta(U - \mu \bar{N}) + \ln \mathcal{Z} \quad (9)$$

$$dS_G = \beta(dU - \cancel{d\mu} \bar{N} - \mu d\bar{N}) + (U - \mu \bar{N}) d\beta + \frac{d\mathcal{Z}}{\mathcal{Z}}$$

$$= \beta(dU - \mu d\bar{N})$$

$$- \beta \sum_{\alpha} p_{\alpha} dE_{\alpha}$$

$$\sum_{\alpha} p_{\alpha} \frac{\partial E_{\alpha}}{\partial V} dV = -P dV$$

Thus,

$$dS_G = \beta(dU + P dV - \mu d\bar{N}) \quad (10)$$

" dQ_{rev} because we want to keep the

correspondence between S_G and the thermodynamic entropy (and between β and $1/k_B T$). This implies the physical interpretation of μ : $-\mu$ is the amount, per particle, of heat in a reversible process where U and V stay the same and \bar{N} changes.

$$\frac{1}{\mathcal{Z}} \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu N_{\alpha})} \left[-\beta dE_{\alpha} + \beta N_{\alpha} d\mu - (E_{\alpha} - \mu N_{\alpha}) d\beta \right]$$

$$= -\beta \sum_{\alpha} p_{\alpha} dE_{\alpha} + \beta \bar{N} d\mu - (U - \mu \bar{N}) d\beta$$

(NB: $dN_{\alpha} = 0$ because we are considering changes due to external parameters changing: $dE_{\alpha} = \frac{\partial E_{\alpha}}{\partial V} dV$ which do not alter the # of particles in any given microstate)

So, $S_G = \frac{1}{k_B} S$, $\beta = \frac{1}{k_B T}$ and then

$$T dS = dU + P dV - \mu d\bar{N}$$

$$\text{or } \boxed{dU = T dS - P dV + \mu d\bar{N}} \quad (11)$$

Fundamental eqn of thermodynamics for open systems.

So another interpretation of μ is energy per particle at const S, V if particles are added or subtracted

$$\mu = \left(\frac{\partial U}{\partial \bar{N}} \right)_{S, V} = -T \left(\frac{\partial S}{\partial \bar{N}} \right)_{U, V} \quad (12)$$

To complete our new thermodynamics, let's generalise the notion of free energy:

$$\boxed{\Phi = -k_B T \ln \mathcal{Z} = U - TS - \mu \bar{N} = F - \mu \bar{N}} \quad (13)$$

↑
eq. (9)

grand (canonical) potential.

$$d\Phi = dU - T dS - S dT - \mu d\bar{N} - \bar{N} d\mu \stackrel{\text{eq. (11)}}{=} -S dT - P dV - \bar{N} d\mu \quad (14)$$

$$\text{So, } \boxed{\begin{aligned} P &= - \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu} \\ \bar{N} &= - \left(\frac{\partial \Phi}{\partial \mu} \right)_{T, V} \\ S &= - \left(\frac{\partial \Phi}{\partial T} \right)_{V, \mu} \end{aligned}} \quad \begin{aligned} &\text{equation of state} \\ &[\text{but see eq. (33) p. 158 -} \\ &\text{a great simplification!}] \\ &\Rightarrow U = \Phi + TS + \mu \bar{N} \end{aligned} \quad (15)$$

thermodynamics

Again, we have found that all we ~~have~~ need to do is calculate $\mathcal{Z}(\beta, \mu)$, which incorporates all the microphysics relevant to the thermodynamical description of an open system, then Φ , then take derivatives - and we know everything we care about!

So what will be the practical role of μ in all this? Eq. (11) suggests that $-\mu$ to \bar{N} is what P is to V and $-T$ to S , i.e. it regulates equilibrium.

14.3 Particle Equilibrium

Just as we did in §10.2, consider 2 systems in thermal and particle contact, so

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

$$\bar{N} = \bar{N}_1 + \bar{N}_2 = \text{const}$$

(assume volumes do not change)

$$S = S_1 + S_2 \rightarrow \text{max, subject to}$$

$$dS = \left(\frac{\partial S_1}{\partial U_1} \right)_{\bar{N}_1, V_1} dU_1 + \left(\frac{\partial S_1}{\partial \bar{N}_1} \right)_{U_1, V_1} d\bar{N}_1$$

$$+ \left(\frac{\partial S_2}{\partial U_2} \right)_{\bar{N}_2, V_2} dU_2 + \left(\frac{\partial S_2}{\partial \bar{N}_2} \right)_{U_2, V_2} d\bar{N}_2$$

\parallel \parallel
 $-dU_1$ $-d\bar{N}_1$

$$= \left[\left(\frac{\partial S_1}{\partial U_1} \right)_{\bar{N}_1, V_1} - \left(\frac{\partial S_2}{\partial U_2} \right)_{\bar{N}_2, V_2} \right] dU_1 + \left[\left(\frac{\partial S_1}{\partial \bar{N}_1} \right)_{U_1, V_1} - \left(\frac{\partial S_2}{\partial \bar{N}_2} \right)_{U_2, V_2} \right] d\bar{N}_1 = 0 \quad (16)$$

$$\frac{1}{T_1} - \frac{1}{T_2} = 0 \Rightarrow T_1 = T_2 = T$$

thermal equilibrium

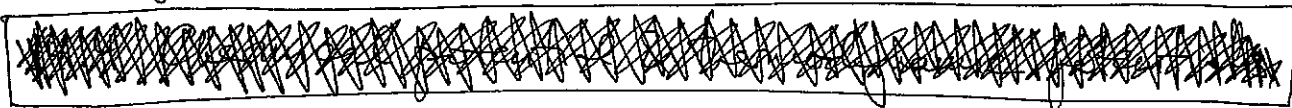
$$\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1} = 0$$

$$\mu_1 = \mu_2$$

[$dU_1 > 0$ if $T_1 < T_2$ heat flows from hot to cold]

Thus, $\mu = \text{const}$ across the system in particle equilibrium
 and eq. (16) also implies that $\Delta \bar{N}_1 > 0$ if $\mu_2 > \mu_1$,
 i.e. particles flow from larger to smaller μ .

So it appears that if we learn how to calculate μ ,
 we could predict equilibrium states: how many
 particles, on average, there will be in each part of
 our system. Lectwell ends here.



14.4 Chemical Potential of a Classical Ideal Gas

So, let's learn how to calculate μ for our favorite
 special case: ideal gas.

What are the microstates?

The same as before, except now we can have an
 arbitrary # of particles, so we may say

$$\alpha = (\alpha_N, N) \quad [\text{i.e. } (\alpha_1, 1), (\alpha_2, 2), \dots]$$

microstates of ideal gas of N particles:

$\alpha_N = \{n_1, \dots, n_i, \dots\}$, $\sum_i n_i = N$ where i are
 microstates of a single particles and n_i their
 occupation #'s

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

$$= \sum_N e^{\beta \mu N} \underset{\uparrow}{Z}_N \approx \sum_N e^{\beta \mu N} \frac{Z_1^N}{N!}$$

regular partition function for
 N particles

neglecting
 quantum
 correlations

[p. 107 eq (19)]

$$= \sum_N \frac{(e^{\beta\mu} z_1)^N}{N!} = e^{z_1 e^{\beta\mu}}$$

Thus, for ^{classical} ideal gas, $Z = e^{z_1 e^{\beta\mu}}$ (17)

and, from eq. (7),

$$\bar{N} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = z_1 e^{\beta\mu} \Rightarrow \mu = -k_B T \ln \frac{z_1}{\bar{N}} \quad (18)$$

Now recall that

$$z_1 = \frac{V}{\lambda_{th}^3} \cdot z_1^{(internal)}, \quad \lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}} \quad (19)$$

z_1 for monatomic gas z_1 for whatever internal degrees of freedom molecules have, e.g., for diatomic gas, $z_1^{(internal)} = z_1^{(rot)} \cdot z_1^{(vib)}$

So, $\mu = k_B T \ln \frac{n \lambda_{th}^3}{z_1^{(internal)}} \quad (20) \quad (n = \frac{\bar{N}}{V} \text{ density})$

Also, from eq. (17) & (7),

$$Z = e^{\bar{N}} \quad (21)$$

$$\Phi = -k_B T \ln Z = -k_B T \bar{N} = -k_B T z_1 e^{\mu/k_B T}$$

$$F = \Phi + \mu \bar{N} = -k_B T \bar{N} \left(1 - \ln \frac{n \lambda_{th}^3}{z_1^{(internal)}} \right) \quad (22)$$

Thus, ~~thermodynamic~~ all unchanged cf. eq. (22) on p 108.

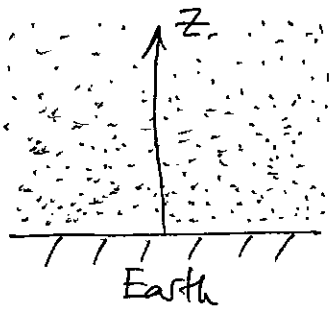
from the canonical result except n is now $\frac{\bar{N}}{V}$, not $\frac{N}{V}$.

All previous results survive, including eq. of state, expressions for energy, entropy, heat capacity etc., with $N \rightarrow \bar{N}$.

14.5 Equilibria of inhomogeneous systems

Let us now learn how to calculate the equilibrium states of a class of systems embedded in some external field that depends, say, on the spatial coordinate via some potential $\varphi(\vec{r})$.

To be specific, consider an ideal gas in gravitational field (atmosphere), so $\varphi = \varphi(z) = mgz$



If this system is in equilibrium, we know that both T and μ must be the same everywhere in it

(think of subdividing the atmosphere into thin layers of const z and asking for them all to be equilibrated with each other).

So $T(z) = \text{const}$ ("isothermal atmosphere" - not a great model, but will do for now)

and $\mu(z) = \text{const}$

From eq. (18), $\mu = -k_B T \ln \frac{Z_1}{N}$

The single-particle energy levels are the same as before plus potential energy per particle, $m\varphi = mgz$, so

$$Z_1 = \underbrace{Z_1^{(g=0)}}_{\substack{\uparrow \\ \text{partition fun w/o gravity}}} \cdot e^{-\beta mgz}$$

$$\hookrightarrow \mu = \underbrace{\mu^{(g=0)}}_{\substack{\uparrow \\ \text{ch. potential w/o gravity}}} + mgz \tag{23}$$

From eq. (18), $\mu (g=0) = -k_B T \ln \frac{Z_1}{N} = k_B T \ln \frac{n \lambda_{th}^3}{Z_1^{(internal)}}$

So,

$$k_B T \ln \left(n \frac{\lambda_{th}^3}{Z_1^{(internal)}} \right) + mgz = \text{const} \quad \text{- condition of particle equilibrium.}$$

↑
function of T only \Rightarrow independent of z
and $T(z) = \text{const}$

Therefore, $n(z) = n(0) e^{-mgz/k_B T}$ Boltzmann distribution

↑
density at $z=0$ (24)

The obvious generalization is

$$n(\vec{r}) \propto e^{-W(\vec{r})/k_B T} \quad (25)$$

↑
potential energy per particle at location \vec{r}

} (of course it must be assumed that $W(\vec{r})$ varies at distances long enough for quantum uncertainty about particle positions not to matter)

Remark. An interesting and useful lesson from eq. (23): if we know the single-particle behaviour for some system and wish to adjust these results for the same system but with energy levels drifted by W , all we need to do is replace $\mu \rightarrow \mu + W$ everywhere (this is useful, e.g., for treatment of magnetization).

This makes sense: μ is ^{the} energetic cost of adding a particle to the system [see p.151, eq. (11-12)].

14.6. Chemical Potential and Thermodynamic Potentials

Finally, let us derive a few important general results about the relationship between μ and other thermodynamic quantities.

Recall (p. 151) that

$$d\Phi = -SdT - PdV - \bar{N}d\mu \quad [\text{eq. (14)}]$$

and $\Phi = F - \mu\bar{N}$ [eq. (13)] $\Rightarrow d\Phi = dF - \mu d\bar{N} - \bar{N}d\mu$

$$\Downarrow$$

$dF = -SdT - PdV + \mu d\bar{N}$

(26)

$$\Downarrow$$

$$\mu = \left(\frac{\partial F}{\partial \bar{N}} \right)_{T, V} \quad \text{handy for systems with controllable } T, V \quad (27)$$

Also $G = F + PV$ by definition, so

$$dG = dF + PdV + VdP$$

$dG = -SdT + VdP + \mu d\bar{N}$

(28)

$$\Downarrow$$

$$\mu = \left(\frac{\partial G}{\partial \bar{N}} \right)_{T, P} \quad (29)$$

This expression leads to a remarkable further simplification. From (28),

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

\uparrow
extensive
(= U - TS + PV)

\uparrow
intensive

\uparrow
extensive

If we change \bar{N} by some factor λ , G must change by the same factor, while P, T don't care:

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

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

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

|| from (29) \Rightarrow $\mu = \frac{G}{\bar{N}}$ (30)

Thus, μ is simply Gibbs free energy per particle!

Ex. Calculate $G = U - TS + PV$ for the ideal gas and compare the outcome with eq. (19)

Eq. (30) shows that μ is an intensive quantity (well, this was obvious before) and so

$$\forall \lambda, \mu(P, T, \lambda \bar{N}) = \mu(P, T, \bar{N}) \Rightarrow \mu = \mu(P, T)$$

independent of \bar{N}

Indeed, for ideal gas, eq. (19):

$$\mu = k_B T \ln \left(n \frac{\lambda^3}{h^3} \right) = k_B T \ln p \quad - \quad k_B T \ln \frac{k_B T}{\lambda^3 h^3} \quad (31)$$

↑
pressure dependence
function of T only

Finally, from (30),

$$\boxed{\Phi = F - \mu \bar{N} = F - G = -PV} \quad (32)$$

checks out for ideal gas, see eq. (21)

nice and simple and implies that knowing $\Phi(T, \mu, V)$ immediately gives the equation of state! (no need to differentiate as in eq. (15)!) $\Phi = -\frac{\Phi}{V}$ (33)