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Topics for today:

(1) how to express thermodynamic variables S, P, μ, etc. in terms of the partition f^Δ Schroeder 6.5

(2) thermodynamic potentials like H, F, G that reach minimum when system is in equilibrium with reservoir with certain properties, the thermodynamic identities for such potentials Schroeder Sections 5.1 and 5.2

(3) the partition function for a many-particle system, cases of distinguishable, indistinguishable §6.6

(4) <u>application to the ideal gas</u> ← valuable application: how to calculate all macroscopic features of an equil ideal gas in terms of internal quantum properties (vibrational, rotational, and electronic states). §6.7

Note: no more kinetics through rest of course. :)

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Outline of argument: we will show that there is a thermodynamic potential $F(T,V,N)$ called the "Helmholtz free energy F" that has the property that F evolves to a minimum value for a system reaching equilibrium with a reservoir whose temperature is constant with value T, and whose volume is constant with value V

$$\boxed{F(T,V,N) = U - TS}$$

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

We will then show that $Z = \sum_s e^{-\beta \epsilon_s}$ is related to F by:

$$\boxed{F = -kT\ln Z}$$

$Z = e^{-\beta F}$
analogous to
$\Omega = e^{S/k}$

From thermodynamic identity for F, which we can find as follows

$$dF = d(U - TS) = dU - d(TS) = dU - TdS - SdT$$

$$= \left[TdS - PdV + \mu dN\right] - TdS - SdT$$

$$\boxed{dF = -S\underset{\uparrow}{dT} - P\underset{\uparrow}{dV} + \mu \underset{\uparrow}{dN}}$$

$F = F(T,V,N)$

notice how dependent variables appear as differential

Then:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -\left(\frac{\partial}{\partial T}\right)_{V,N}\left[-kT\ln Z\right] = \frac{\partial}{\partial T}\left[kT\ln Z\right]$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}; \quad \mu = -kT\left(\frac{\partial \ln Z}{\partial N}\right)_{T,V}$$

$$U = \underset{\text{known}}{\underset{\uparrow}{F}} + T\underset{\text{known}}{\underset{\uparrow}{S}}$$

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Discover thermodynamic potentials by integrating by parts

From $F = U - TS$, we can discover thermodynamic identity, but what if we want to discover potential corresponding to particular experimental variables of interest, say (T, P, N) or (T, P, μ) or (T, V, μ), etc? Can do this by a kind of integration by parts.

For example, let's say we find it convenient or desirable to manipulate the experimental variables T, P, and N. We can discover potential $G = G(T, P, N)$ like this, starting from identity for dU:

$$dU = TdS - PdV + \mu dN$$

$$= \left[d(TS) - SdT\right] - \left[d(PV) - VdP\right] + \mu dN$$

or

$$d(\underbrace{U - TS - PV}_{= G}) = -S\underset{\uparrow}{dT} + V\underset{\uparrow}{dP} + \mu \underset{\uparrow}{dN}$$

must be f^n that depends on T, P, N!

we have discovered the <u>Gibbs free energy</u>

$$G(T, P, N) = U - TS - PV = F - PV$$

G widely used in chemistry and biology and engineering since easy to let experiment equilibrate with atmosphere with constant P, constant T.

Why Does $F = -kT \ln Z$?

See Schroeder p. 248. Argument is subtle and clever, you do not need to know it for quizzes or final exam but should see it once (perhaps exactly once).

Observe that, for constant volume V and constant number of particles N, $F = F(T,V,N) = F(T)$ satisfies a first-order ordinary differential equation (abbreviated o.d.e. or ode and pronounced "oh" "dee" "ee").

$$dF = -S\,dT - P\,dV + \mu\,dN \quad \text{and} \quad F = U - TS$$

implies

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

where we assume $U = U(T)$ is known fn, say from heat capacity measurements at constant volume, $U = \int C_V(T)\,dT$.

We also know an initial condition for this ode by looking at $T=0$:

$$F(T=0) = \lim_{T\to 0} U - TS = \lim_{T\to 0} U = U(0) = U_0$$

Let's define

$$\tilde{F} = -kT \ln Z \qquad Z = \sum_s e^{-\beta U_s}$$

I claim

$$\frac{\partial \tilde{F}}{\partial T} = \frac{\tilde{F} - U}{T} \quad \text{and} \quad \tilde{F}\Big|_{T=0} = U_0$$

So $\tilde{F} = -kT\ln Z$ satisfies the same ode and goes through same initial data $(T=0, U_0)$ as F which implies $F = \tilde{F} = -kT\ln Z$ by existence-uniqueness theorem for "nice" odes.

To complete argument, observe that

$$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{V,N} = \left(\frac{\partial}{\partial T}\right)_{V,N}\left[-kT\ln Z\right]$$

$$= -k\ln Z - kT\frac{\partial \ln Z}{\partial T}$$

$$= -k\ln Z - kT\cdot\left(\frac{\partial\beta}{\partial T}\right)\frac{\partial \ln Z}{\partial \beta} \qquad U = \langle E\rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$= -k\ln Z - kT\left[-\frac{1}{kT^2}\right](-U)$$

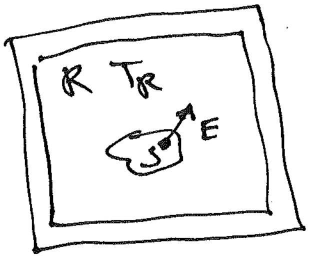
$$\boxed{\frac{\partial \tilde{F}}{\partial T} = +\frac{\tilde{F}}{T} - \frac{U}{T} = \frac{\tilde{F} - U}{T}} \qquad \text{same ode}$$

$$\lim_{T\to 0}\tilde{F} = \lim_{T\to 0} -kT\ln Z = \lim_{T\to 0} -kT\ln\left[e^{-\beta U_0} + \underbrace{e^{-\beta U_1} + e^{-\beta U_2} + \cdots}_{\text{all tiny compared to first term as } T\to 0}\right]$$

$$\simeq \lim_{T\to 0} -kT\ln\left[e^{-\beta U_0}\right]$$

$$= U_0 \checkmark$$

Why is free energy $F = U - TS$ a thermodynamic potential that reaches minimum value when system is in equilibrium?



$$\frac{dF}{dt} < 0 \quad \text{and} \quad \frac{dF}{dt} = 0 \text{ in equilibrium}$$

nonequil

Assume system in thermal contact with reservoir of constant temp T is not in equilibrium. If system and reservoir are isolated, of time, But entropy must increase over short interval of time

$$\Delta S_{total} = \Delta S + \Delta S_R$$

R subscript = reservoir
no subscript = system
N = const, V = const

From thermodynamic identity for reservoir

$$dU_R = T_R dS_R - \underbrace{P_R dV_R}_{=0} + \underbrace{\mu_R dN_R}_{=0}$$

$$= T_R dS_R$$

so $\Delta S_R \approx \frac{\Delta U_R}{T_R} = -\frac{\Delta U}{T_R}$ ⇐ key trick, use conservation of energy to express ΔS_R in terms of system parameters.

$$\Delta S_{total} = \Delta S + \Delta S_R = \Delta S - \frac{\Delta U}{T_R} = -\frac{(\Delta U - T_R \Delta S)}{T_R}$$

$$\boxed{\Delta S_{total} = -\frac{\Delta F}{T_R}} \qquad \boxed{F = U - T_R S}$$

not quite the system F since T_R appears

$$\frac{d\Delta S_{total}}{dt} > 0 \Rightarrow \frac{d\Delta F}{dt} < 0 \Rightarrow$$ ΔF ~~increases~~ decreases until equil. attained

Partition Function For Composite Systems

Section 6.6 of Schroeder

So far, have conceptually thought of system as distinct physical object compared to reservoir, e.g. balloon that can exchange energy and volume with atmosphere, or surface of crystal that can exchange energy and molecules with surrounding gas. But in many cases, and especially for examples we will soon discuss like ideal gas, electron gas, photon gas, the reservoir consists of the same particles as the system of interest.

In this case, we can compute the partition function Z for all the particles, the entire system, using two simple formulas:

$$Z_{system} = Z_1 \cdot Z_2 \cdots Z_N$$

N weakly interacting <u>distinguishable</u> particles

$$Z_{system} = \frac{1}{N!} Z_1^N$$

N <u>identical</u> weakly interacting particles

<u>"Weakly interacting"</u> means that the energy of several particles is the sum of the energies of each separate particle, the presence of one particle does not affect the energy of the other particles. This is good approximation for low-density high-T gas, particles are far from one another and so don't affect each other. Remarkably, this is true for electrons in metal.

Discuss examples of two particles to see how this works.

Case 1: two distinguishable weakly interacting particles

$$E_s = E_1(s) + E_2(s) \quad \text{energy additive if weakly interacting}$$
$$= E_1(s_1) + E_2(s_2)$$

state s of two particles requires identifying states s_1, s_2 of each particle. Partition f

Partition f^n becomes

$$Z = \sum_s e^{-\beta E_s} = \sum_s e^{-\beta[E_1(s)+E_2(s)]}$$
$$= \sum_{s_1, s_2} e^{-\beta E_1(s_1)} e^{-\beta E_2(s_2)}$$

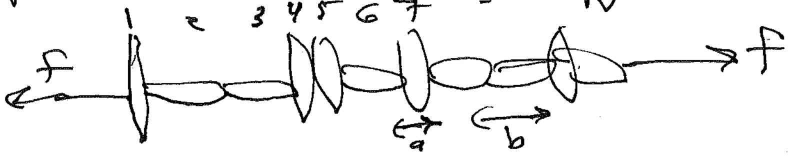
But if particles are distinguishable, each state (s_1, s_2) are distinct and we can write

$$Z = \sum_{s_1, s_2} e^{-\beta E_1(s_1)} e^{-\beta E_2(s_2)} = \sum_{s_1} e^{-\beta E_1(s_1)} \left(\sum_{s_2} e^{-\beta E_2(s_2)} \right)$$
$$= \left(\sum_{s_1} e^{-\beta E_1} \right) \left(\sum_{s_2} e^{-\beta E(s_2)} \right)$$
$$= Z_1 Z_2$$

Can easily generalize to N particles that are weakly interacting and distinguishable, $Z_N = Z_{\text{system}} = Z_1 Z_2 \cdots Z_N = \prod_1^N Z_i$

$$\langle \varepsilon \rangle = -\frac{\partial \ln Z_N}{\partial \beta} \quad \text{etc.}$$

Example of weakly-interacting distinguishable particles: keratin molecule under tension



Assume molecule that consists of beads that have elliptical shape, each bead can have two orientations, parallel to axis with length b, or perpendicular to axis with length $a < b$. Assume that molecule is under tension f at each end, and molecule has energy ϵ_a when perpendicular to axis, energy ϵ_b when parallel. Then can assume (and it is roughly correct) that beads are weakly interacting, state of one bead does not affect another. Also assume beads are distinguishable, they are big enough to be spatially localized and identifiable. Then

$$Z_N = Z_1 Z_2 \cdots Z_N$$

$$= Z_1^N$$

$$= \left[e^{-\beta(\epsilon_a - fa)} + e^{-\beta(\epsilon_b - fb)} \right]^N$$

Average length of molecule as function of temperature T, tension f given by:

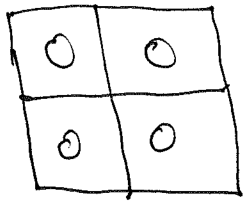
$$\langle L \rangle = N \langle \ell \rangle = N \left[\left(\frac{e^{-\beta(\epsilon_a - fa)}}{Z_1} \right) \cdot a + \left(\frac{e^{-\beta(\epsilon_b - fb)}}{Z_1} \right) b \right]$$

$$\boxed{\langle L \rangle = \frac{N \cdot kT}{Z_1} \frac{\partial Z_1}{\partial f} = kTN \frac{\partial \ln Z_1}{\partial f} = kTN \frac{\partial \ln Z_N}{\partial f}}$$

as $T \to 0$, if $f = 0$, $\epsilon_a > \epsilon_b$, $\langle \ell \rangle \to b$

$T \to \infty$, if $f = 0$, $\epsilon_a > \epsilon_b$, $\langle \ell \rangle \to \frac{a+b}{2}$

Second example of weakly-interacting distinguishable particles: egg-carton model of adsorption.



Assume surface has N binding sites and that atom can bond to surface with energy $\epsilon<0$ from surrounding gas. If sites are independent,

$$Z_{\text{total}} = Z_1 \cdot Z_2 \cdots Z_N = Z_1^N$$

$$= \left(e^{-\beta[0]} + e^{-\beta\epsilon}\right)^N \qquad \epsilon<0$$

$$\langle E\rangle = -\frac{\partial \ln Z_{\text{total}}}{\partial\beta} = -N\frac{\partial \ln Z_1}{\partial\beta} = -N\frac{1}{e^{-\beta 0}+e^{-\beta\epsilon}}\left[-\epsilon e^{-\beta\epsilon}\right]$$

$$= N\epsilon\cdot\frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}} = N\epsilon\frac{1}{e^{\beta\epsilon}+1}$$

$$\langle n\rangle = \text{average number of adatoms on surface} = \frac{\langle E\rangle}{\epsilon} = \frac{N}{e^{\beta\epsilon}+1}$$

$$\lim_{T\to 0}\langle n\rangle = N \qquad \lim_{T\to\infty}\langle n\rangle = \frac{N}{2}$$

Can calculate chemical potential of surface from:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{A,T} = +\frac{\partial}{\partial N}\left[-kT\ln Z_N\right] = -kT\frac{\partial}{\partial N}\left[N\ln Z_1\right]$$

$$\boxed{\mu = -kT\left[\ln Z_1\right] = -kT\ln\left[1+e^{-\beta\epsilon}\right]}$$

Can equate this μ to μ of surrounding gas to get equilibrium condition