Homework 10 out Tuesday night, due week later

Quiz 6 may be canceled if I run tight on time

Begin Chapter 7: "Quantum statistics"

Outline of logic

(1) generalize Boltzmann factor to systems that can exchange energy and particles with reservoir constant T, μ

$$e^{-\beta E_s} \rightarrow e^{-\beta(E_s - \mu N_s)}$$

(2) relate grand partition fn $\mathcal{Z} = \sum_s e^{-\beta(E_s - \mu N_s)}$ to thermodynamics

$$\mathcal{Z} \neq \Phi = F - \mu N = U - TS - \mu N = -kT \ln \mathcal{Z}$$

(3) Apply Gibb's factor to dense, cold quantum systems of identical, weakly interacting particles for which approximation $Z_N \simeq \frac{1}{N!} Z_1^N$ does not hold. New insight is to calculate the occupation number $\bar{n}(\epsilon)$ = average number of particles in quantum level with energy ϵ.

Then calculate:

$$\langle U \rangle = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(n_x, n_y, n_z)\, \bar{n}[\epsilon(n_x, n_y, n_z)]$$

$$\langle P \rangle = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

$$\langle B \rangle = \text{bulk modulus} = -V\left(\frac{\partial P}{\partial V}\right)_T$$

$$C = \frac{\partial \langle U \rangle}{\partial T}$$

magnetization $\langle M \rangle$, spectrum $\mathcal{D}(\epsilon)$ for electrons, photons, etc.

New result and perhaps a surprise: results depend on deep symmetry of quantum particles, whether they are fermions with half-integer spin, or bosons, with integer spin

fermions: electrons, protons, neutrons, He^3 nucleus, He^3 atom, ... $\bar{n}_{FD}(\epsilon) = \dfrac{1}{e^{\beta(\epsilon-\mu)}+1}$

bosons photons, He^4, gravitons, phonons $n_{BE}(\epsilon) = \dfrac{1}{e^{\beta(\epsilon-\mu)}-1}$

classical particles $n_{Boltzmann}(\epsilon) = \dfrac{N e^{-\beta\epsilon}}{Z}$

Gibbs factor $e^{-\beta(E-\mu N)}$ for systems that can exchange energy and particles with a reservoir

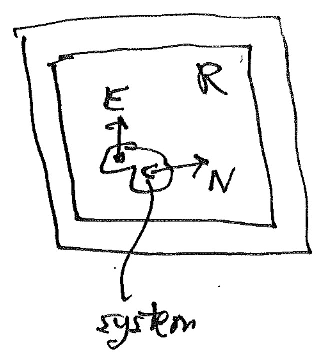
Will not give derivation in class, but see my notes; recommend learning my argument over Schroeder's

Key conclusion: probability P_s to observe system in particular state s with energy E_s and number of particles N_s given by

$$P_s = \frac{e^{-\beta[E_s - \mu N_s]}}{\mathcal{Z}}$$

$\mathcal{Z}$ = grand partition function = Gibbs ~~part~~ sum

$$= \sum_s e^{-\beta[E_s - \mu N_s]}$$



Here system is in equilibrium with reservoir with constant temperature T and constant chemical potential μ

$E + E_R$ = constant
$N + N_R$ = constant

As before: calculate averages

$$\langle X_s \rangle = \sum_s X_s \cdot P_s = \sum_s X_s \cdot \frac{e^{-\beta(E_s - \mu N_s)}}{\mathcal{Z}}$$

$$= \frac{\int X(\vec{q})\, e^{-\beta(E(\vec{q}) - \mu N(\vec{q}))}\, d\vec{q}}{\int e^{-\beta(E(\vec{q}) - \mu N(\vec{q}))}\, d\vec{q}}$$

$\vec{q} = x_1, x_2, x_3, p_1, p_2, p_3$ or similar continuous variables

Derivation of Gibbs factor

If system and reservoir form isolated system, probability to observe system in particular state s is equal to number of equally likely accessible microstates over total number of microstates.

$$P_s = \frac{\text{"\# accessible states when system has energy } E_s\text{, particles } N_s\text{"}}{\text{total number of microstates}}$$

so

$$P_s \propto \Omega_{total}(N_s, E_s) = \underset{\substack{\uparrow \\ \text{proportionality constant}}}{c}\,\Omega_R(N-N_s, E-E_s)$$

since, for particular state s, multiplicity of system $=1$

As before:
$$\begin{aligned}
P_s &= c\,\Omega_R(N-N_s, E-E_s) \\
&= c\exp\left[\frac{1}{k} S_R(N-N_s, E-E_s)\right] \qquad \text{since } S_R = k\ln\Omega_R \\
&\simeq c\exp\left[\frac{1}{k}\left(S_R(N,E) + \frac{\partial S_R}{\partial N}(N)\times(-N_s) + \frac{\partial S_R}{\partial E}(N)\times(-E_s) \right.\right. \\
&\qquad \left.\left. + \text{"higher order terms in } -N_s, -E_s\text{"}\right)\right] \\
&= \underbrace{c\, e^{\frac{S_R(N,E)}{k}}}_{\tilde{c}} \cdot e^{-\beta[E_s - \mu N_s]}.
\end{aligned}$$

$$\sum_s P_s = 1 \Rightarrow c = \frac{1}{Z} \qquad Z = \sum_s e^{-\beta(E_s - \mu N_s)} \qquad \text{QED}$$

If there are multiple kinds of particles, generalization is

$$P_s = \frac{e^{-\beta[E_s - \mu_A N_{As} - \mu_B N_{Bs}]}}{Z}$$

$$Z = \sum_s \exp\left[-\beta\left(E_s - \mu_A N_{A,s} - \mu_B N_{B,s}\right)\right]$$

Partition function machinery for Gibbs factor

For $Z = \sum e^{-\beta E_s}$, saw $\langle E \rangle = \sum E_s P_s = \sum E_s e^{-\beta E_s}/Z$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

This relation does not hold for Gibbs factor

$$-\frac{\partial Z}{\partial \beta} = \sum_s (E_s - \mu N_s) \frac{e^{-\beta(E_s - \mu N_s)}}{Z} \neq \sum_s E_s \frac{e^{-\beta(E_s - \mu N_s)}}{Z}$$

$$= \langle E \rangle - \mu \langle N \rangle \qquad \neq \langle E \rangle$$

But we have new parameter we can differentiate with respect to

$$\frac{\partial Z}{\partial \mu} = \sum_s \beta N_s e^{-\beta(E_s - \mu N_s)} = \beta \langle N \rangle$$

so $$\langle N \rangle = \frac{kT}{Z}\frac{\partial Z}{\partial \mu} = kT \frac{\partial \ln Z}{\partial \mu}$$

Conclude: $$\langle E \rangle = \mu \bar{N} - \frac{1}{Z}\frac{\partial Z}{\partial \beta}$$ or

$$\boxed{\langle E \rangle = \mu k T \frac{\partial \ln Z}{\partial \mu} - \frac{\partial \ln Z}{\partial \beta}}$$

From this, we can compute $C = \frac{d\langle E \rangle}{\partial T}$, heat capacity

Relating The Gibbs Sum To Thermodynamics

If $F =$ Helmholtz free energy $= -kT\ln Z$

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

What potential might correspond to $-kT\ln \mathcal{Z}$?

Hint is result: $\langle N \rangle = kT \dfrac{\partial \ln \mathcal{Z}}{\partial \mu} = \dfrac{\partial [\;]}{\partial \mu}$

Can we find potential that has property that $\dfrac{\partial X}{\partial \mu} = N$ and X reduces to F when $\mu = 0$ (no particle exchange)?

$$dF = -S\,dT - P\,dV + \mu\,dN = -S\,dT - P\,dV + d(\mu N) - N\,d\mu$$

$$d(F - \mu N) = -S\,dT - P\,dV - N\,d\mu$$

So let's define $\boxed{\Phi = F - \mu N = U - TS - \mu N}$ grand potential function or grand free energy

and guess $\boxed{\Phi = -kT\ln \mathcal{Z}}$

Can prove this as before by showing that Φ, $-kT\ln\mathcal{Z}$ satisfy same 1st-order ode, go through same initial data for $\mu = 0$, $\dfrac{\partial \Phi}{\partial \mu} = -N$

from $d\Phi = -S\,dT - P\,dV - N\,d\mu$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} \qquad P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} \qquad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

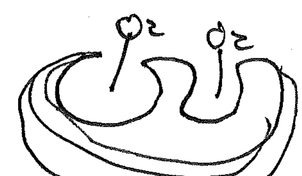
$$U = \Phi + TS + \mu N$$

~~exercise: try~~

$$C = dU/dT$$

Example 1 of 3: Hemoglobin and O_2 transport

Problem 7.2 on p. 260 of Schroeder



hemoglobin

Hemoglobin complicated 4-unit protein that
has special features for transporting O_2 through blood,
To illustrate application of Gibbs factor, assume simplified model
for which hemoglobin has two binding sites, each of
which can be empty or have one O_2 bound so four possible
states in general. Assume no O_2 is $\epsilon = 0$, one O_2 in either site
is $\epsilon_1 = -0.55\,\mathrm{eV}$, and two O_2 bound has $\epsilon_2 = -1.3\,\mathrm{eV}$: two
O_2 are bound more deeply by $-0.2\,\mathrm{eV}$ compared to two separate O_2,
example of "cooperative binding".

Strategy with Chapter 7 problems is to write out particle number N_s
as well as energy E_s for all possible states:

d_s = degeneracy

n_s	ϵ_s	d_s	
0	0	1	
1	ϵ_1	2	$\sqcup\ \sqcup O_2 \sqcup$ or $\sqcup O_2 \sqcup\ \sqcup$
2	ϵ_2	1	

so
$$\mathcal{Z} = \sum_s e^{-\beta(E_s - \mu N_s)} = \sum_n d_n\, e^{-\beta(E_n - \mu N_n)}$$

$$\boxed{\mathcal{Z} = 1 + 2e^{-\beta(\epsilon_1 - \mu)} + e^{-\beta(\epsilon_2 - 2\mu)}}$$

hemoglobin example continued:

$$\langle N \rangle = \sum_s n_s P_s = 0 \cdot P_0 + 1 \cdot P_1 + 2 \cdot P_2$$
$$= 1\left(\frac{2e^{-\beta(\epsilon_1-\mu)}}{Z}\right) + 2\left(\frac{e^{-\beta(\epsilon_2-2\mu)}}{Z}\right)$$

$\langle \bar{n} \rangle$ = occupancy = fraction of occupied sites

$$= \frac{\bar{N}}{\text{total \# of sites}} = \frac{\langle N \rangle}{2} = \frac{e^{-\beta(\epsilon_1-\mu)} + e^{-\beta(\epsilon_2-2\mu)}}{1 + 2e^{-\beta(\epsilon_1-\mu)} + e^{-\beta(\epsilon_2-2\mu)}}$$

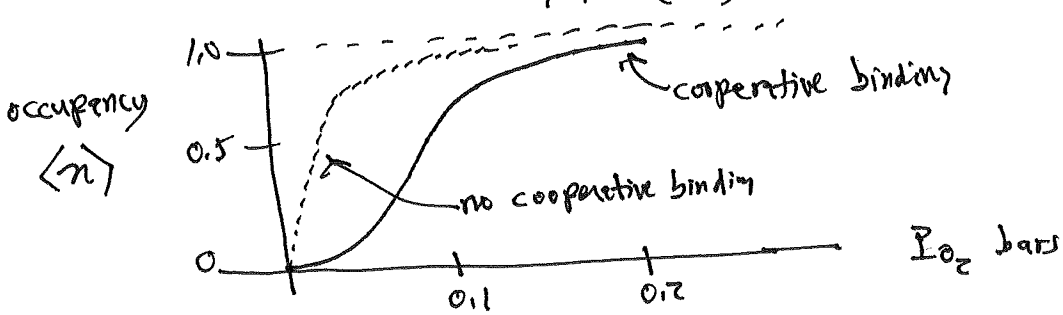
Can express occupancy in terms of O_2 pressure in reservoir (air person breathes) via formula we derived for chemical potential of ideal gas:

$$\mu = kT \ln\left[\frac{P}{P_0}\right] \Rightarrow e^{\mu\beta} = \frac{P}{P_0}$$

$$P_0 = \frac{kT Z_{int} e^{\epsilon/kT}}{V_Q}$$

Let's define $\delta = 2\epsilon_1 - \epsilon_2 = +2eV$

then
$$\text{occupancy} = \frac{P/P_0 + e^{\beta\delta}(P/P_0)^2}{1 + 2(P/P_0) + e^{\beta\delta}(P/P_0)^2}$$



occupancy $\simeq$ 100% near lungs for which $P_{O_2} = 0.2$ bars

cooperative binding makes it easier to release O_2 as pressure O_2 drops, further from lungs. Apply ideas to

Schroeder discusses in text example of CO poisoning

one site, can bind O_2 or CO or nothing, 3 states

$\overset{CO}{N}$	$\overset{O_2}{N_s}$	E_s	d_s
0	0	0	1
0	1	ϵ_1	1
1	0	ϵ_2	1

$\epsilon_1 = -0.7\,eV$

$\epsilon_2 = -0.85\,eV$

$\mu_{CO} = -0.72\,eV$

$\mu_{O_2} = -0.60\,eV$

$$\mathcal{Z} = 1 + \underbrace{e^{-(\epsilon_1-\mu_1)\beta}}_{O_2} + \underbrace{e^{-(\epsilon_2-\mu_2)\beta}}_{CO}$$

in absence of CO, $\quad P_{O_2} = \dfrac{e^{-\beta(\epsilon_1-\mu_{O_2})}}{1+e^{-\beta(\epsilon_1-\mu_{O_2})}} \simeq 98\%$

in presence of CO $\quad P_{O_2} = \dfrac{e^{-\beta(\epsilon_1-\mu_{O_2})}}{1+e^{-\beta(\epsilon_1-\mu_{O_2})}+e^{-\beta(\epsilon_2-\mu_{CO})}} \simeq 25\%$

So CO prevents O_2 from binding, causes suffocation even though lungs are fine.

Supplementary calculation: chemical potential

μ_{O_2} in atmosphere at room temp and sea level

Problem 6.48b, page 255 Schroeder

$$P_{O_2} = 0.2\ P_{atm} \simeq 0.2 \cdot 10^5 \text{ pascals}$$

$$T \simeq 300\,K$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln\left[\frac{V/N}{V_Q} Z_{int}\right]$$

$$Z_{int} \simeq Z_{electronic} \times Z_{rotation}$$

$$\simeq 3 \times \frac{kT}{2\epsilon}$$

$\epsilon = 2 \cdot 10^{-4}\,eV$ for O_2

can ignore vibrations, degrees of freedom freeze out at room temp for O_2

high T approx to $\sum_j (2j+1) e^{-j(j+1)\epsilon}$

Factor $\frac{1}{2}$ because O_2 symmetric

$$V_Q = \left[\frac{h}{(2\pi m kT)^{1/2}}\right]^3$$

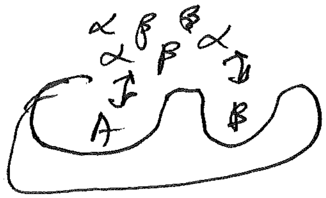
$$\cong \left[\frac{7 \cdot 10^{-34}\ J\cdot s}{\left(2 \cdot 3 \cdot (2 \cdot 10^{-27}\,kg) \cdot (1.4 \cdot 10^{-23})\, 300\right)^{1/2}}\right]^3 \simeq 10^{-32}\,m^3$$

$$\frac{V/N}{V_Q} \simeq 10^7$$

$$V/N = \frac{kT}{P_{O_2}} \simeq 2 \cdot 10^{-25}\,m^3 \gg V_Q$$

$$\mu_{O_2} = -k(300) \cdot \ln\left[10^7 \cdot 200\right]$$

$$\simeq -0.6\,eV.$$



Problem for you to try:

A certain biological molecule has ~~single~~ two binding sites A and B, each of which can be empty or hold one molecule. Site A can bind single molecule of type α with binding energy $\epsilon_{A,\alpha}$, or bind single molecule of type β with energy $\epsilon_{A,\beta}$, or not bind anything with energy $\epsilon = 0$. Site B, independently of site A, can bind an α molecule with energy $\epsilon_{B,\alpha}$, or bind a β molecule with energy $\epsilon_{B,\beta}$, or nothing with energy 0. The molecule is in equilibrium with a reservoir of α and β molecules whose chemical potentials are respectively μ_α and μ_β, the ~~se~~ reservoir has temperature T.

In terms of $\epsilon_{A,\alpha}$, $\epsilon_{A,\beta}$, $\epsilon_{B,\alpha}$, $\epsilon_{B,\beta}$, μ_α, μ_β and T, what is probability for molecule to have one α molecule and one β molecule bound to it? How does $P_{\alpha,\beta}$ vary with the partial pressures of α and of β molecules?

Example 2: mammalian olfaction

Challenging, important, and unsolved example of these ideas is to olfaction: how do animals identify objects in the world by smell?

mice have ≈ 1,200 distinct kinds of odor receptors
humans used to have ~900, now have ≈ 300

each receptor binds ~~to~~ most odorants, ~~at least~~ with varying affinity
all odorants bind to receptors to some degree

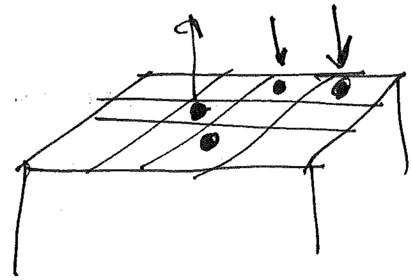
olfactory ~~cell~~ neuron receptor fires digital pulses (action potentials) to degree receptor is bound, i.e.

neuronal firing rate = f(occupancy on given receptor)

Why are 1,200 receptors needed to discriminate, identify odors?
How do brain "read out" chemical sensor array.
Hard problems: identifying "object" mixtures like coffee, rose, steak
identifying weak mixtures in presence of strong mixture

show Katz movie: mice can smell immunohisto compatibility,
humans can not (have lost vomeronasal passage)

Example 3: more careful derivation of surface adsorption, Langmuir isotherm



Assume surface is like egg-carton with fixed independent binding sites for adatom of given kind

(1) molecules bind to surface with binding energy $-\epsilon < 0$ where $\epsilon > 0$

(2) molecules stick to single site, are not mobile

Just-like hemoglobin, make table of possible states with distinct energies

$\#N_A$	E_A	d_A
0	0	1
1	$-\epsilon$	$\binom{N_S}{1} = N_S$
2	-2ϵ	$\binom{N_S}{2} = \frac{N_S(N_S-1)}{2}$
⋮		
N_S	$-N_S\epsilon$	$\binom{N_S}{N_S} = 1$

$$\mathcal{Z} = \sum_s e^{-\beta(E_s - \mu N_s)} = \sum_n e^{-\beta(E_n - \mu N_n)} \times d_n$$

$$= 1 + \binom{N_S}{1} e^{-\beta(-\epsilon-\mu)} + \binom{N_S}{2} e^{-\beta(-2\epsilon-2\mu)} + \cdots + \binom{N_S}{N_S} e^{\beta(N_S\epsilon + N_S\mu)}$$

$$= \left(1 + e^{\beta(\epsilon+\mu)}\right)^{N_S}$$ by binomial theorem $(a+b)^n = a^n + \binom{n}{1} a^{n-1} b + \binom{n}{2} a^{n-2} b^2 + \ldots$

$$= \mathcal{Z}_1^N,$$ if sites are independent!

What is average # of adatoms?

$$\langle N \rangle = kT \frac{\partial \ln Z}{\partial \mu}$$

$$= kT \frac{\partial}{\partial \mu}\left[N_s \ln\left(1 + e^{\beta(\epsilon+\mu)}\right)\right]$$

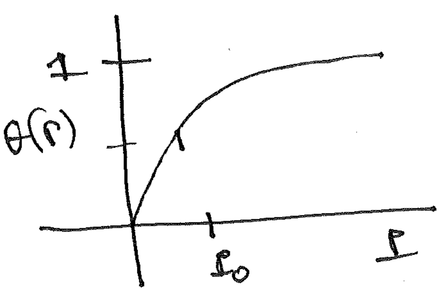
$$= N_s kT \cdot \frac{1}{1 + e^{\beta(\epsilon+\mu)}} \times e^{\beta(\epsilon+\mu)} \times \beta$$

$$\boxed{\langle N \rangle = \frac{N_s}{1 + e^{-\beta(\epsilon+\mu)}}}$$

$$\theta = \text{surface coverage} = \frac{\langle N \rangle}{N_s} = \frac{1}{1 + e^{-\beta\epsilon} e^{-\beta\mu}} = \frac{1}{1 + e^{-\beta\epsilon}\left[\frac{P_0}{P}\right]}$$

$$\Rightarrow \boxed{\theta = \frac{P}{P + \tilde{P}_0}} \qquad \tilde{P}_0 = e^{-\beta\epsilon} P_0 = \frac{V_Q e^{-\beta\epsilon}}{kT Z_{int}} = \frac{C}{Z_{el}} T^{-7/2} e^{-\beta\epsilon}$$

Now we have included binding energy ϵ into the analysis.



Langmuir a favorite scientist of mine:

- lightbulbs with Ar
- speed of fly before stroboscopes
- cloud seeding (with controversial result)
- plasma physics
- surface physics