Review of Example 1

$T = 1.5K$

$E = 2 \cdot 10^{-23} J$ — BF = .38 Prob = $\frac{.38}{1.38} = 28\%$

$E = 0$ — BF = 1 Prob = $\frac{1}{1.38} = 72\%$

continuing

(1B) → What if we have 100 atoms? How many in ground state? in Excited state?

schematic

for state E_1: $N_{ave} = N_{tot} \cdot \frac{BF_1}{BF_0 + BF_1 + BF_2 + \ldots}$

(1C) → What is average energy of the 100 atoms?

Weighted average

$E_{ave} = E_0 P(0) + E_1 P(1)$

=

=

(1D) → What if 2 states at $E = 2 \cdot 10^{-23} J$?

BF = 2 × .38 = .76 Prob $\frac{.76}{1.76} = 43\%$

BF = 1 $\frac{1}{1.76} = 57\%$

Relationship of handout to Phys 123 eqn

$\frac{dS}{dE} = \frac{1}{T}$ $\Delta S = \int \frac{dQ}{T}$

$dS = \frac{dE}{T}$ $dS = \frac{dQ}{T}$

$dQ = T dS$ → $\frac{1}{T}$ actually $= \frac{dS}{dQ}$.

1st Law $\Delta E_{int} = Q + W_{on}$

$\Delta E_{int} = \int T dS - \int P dV$

$dE = T dS - P dV$

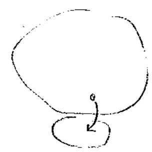
if $PdV \simeq 0$, then $dE = TdS$

$\frac{1}{T} = \frac{dS}{dE}$ as in handout

We've overlooked two things which need to be discussed now

① The first law is incomplete. Sometimes particles being added/subtracted cause a change of energy.

Example: gravitational potential energy



particle entering system gives up gravitational potential energy, leading to more thermal energy

Example: chemical potential energy

battery as pump to higher potential

system

There are other more subtle examples, but because of similarity to ②, the quantity used to characterize this is called the "chemical potential", μ.

μ = change in energy due to a change in N

First law: $dE_{int} = T\,dS + p\,dV + \mu\,dN$

still consider negligible

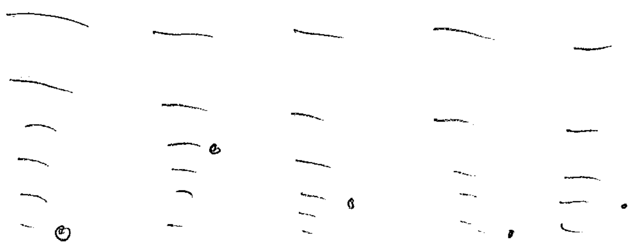
must account for

Result: instead of BF, use "Gibb's factor"

$$P_s \sim e^{-(E_s - \mu N_s)/kT}$$

(2) We've assumed systems are non interacting. I.e. their quantum states are independent

actual



etc

Drawn as

shortcut notation, not really saying atom 1 has 4 electrons in ground state.

(why can't ↗ be possible?

Pauli exclusion principle)

If single atom, or if interacting atoms, then may have to worry about ↑

When do we have to worry about interactions?

one way to estimate for electrons:

$$p = \frac{h}{\lambda} \leftarrow \text{de Broglie wavelength}$$

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$\rightarrow p = \sqrt{2mE}$$

$$\sqrt{2mE} = \frac{h}{\lambda}$$

$$\lambda = \frac{h}{\sqrt{2mE}}$$

KE from thermal effects: $E \sim kT$

$$\lambda = \frac{h}{\sqrt{2mkT}}$$

add factor of $\frac{1}{\sqrt{\pi}}$ for no apparent reason

$$l_Q = \frac{h}{\sqrt{2\pi mkT}} = \text{"quantum length"}$$

for electron at room T, $l_Q = 4.3$ nm

What is separation of atoms in solid? much smaller. Interactions!

How to handle interacting systems — states are states of combined system, not isolated atoms

Two types: Fermions — obey Pauli exclusion
ex: electrons, protons, neutrons

Bosons — don't obey Pauli exclusion
ex. photons, phonons

← focus on this state. what is N_{ave}?
("reservoir" = all other states)

$$N_{ave} = N_0 P(0) + N_1 P(1) + N_2 P(2) + \cdots$$

like E_{ave} equation

Fermions

can only have 0 or 1

$$N_{ave} = \cancel{0 \cdot P(0)} + 1\, P(1)$$

$$= \frac{1 \cdot e^{-(E-\mu)/kT}}{1 + e^{-(E-\mu)/kT}} \times \frac{e^{+(E-\mu)/kT}}{e^{+(E-\mu)/kT}}$$

$$\boxed{N_{ave} = \frac{1}{e^{(E-\mu)/kT} + 1}}$$

Fermi-Dirac distribution often: $f_{F\text{-}D}$

Note: this also just = probability of that state being occupied, since occupancy is either 0 or 1 (this case only!)

Bosons

can have any number

$$N_{ave} = 0\, P(0) + 1\, P(1) + 2\, P(2) + 3\, P(3) + \cdots$$

$$= 0 + \frac{1\, e^{-(E-\mu)/kT}}{1 + e^{-(E-\mu)/kT} + e^{-(2E-2\mu)/kT} + \cdots} + \frac{2\, e^{-(2E-2\mu)/kT}}{1 + e^{-(E-\mu)/kT} + e^{-(2E-2\mu)/kT} + \cdots} + \frac{3\, e^{-(3E-3\mu)/kT}}{\cdots}$$

Let $x = e^{-(E-\mu)/kT}$

$$N_{ave} = \frac{0 + x + 2x^2 + 3x^3 + \cdots}{1 + x + x^2 + x^3 + \cdots}$$

claim: that $= \dfrac{x}{1-x}$

proof: cross multiply

$$(1-x)\left(x+2x^2+3x^3+\dots\right) \overset{?}{=} x\left(1+x+x^2+x^3+\dots\right)$$

$$\begin{array}{l} x+2x^2+3x^3+\dots \\ \quad -x^2-2x^3-3x^4-\dots \\ \hline x+x^2+x^3+x^4+\dots \end{array}$$

✓ yes it's equal

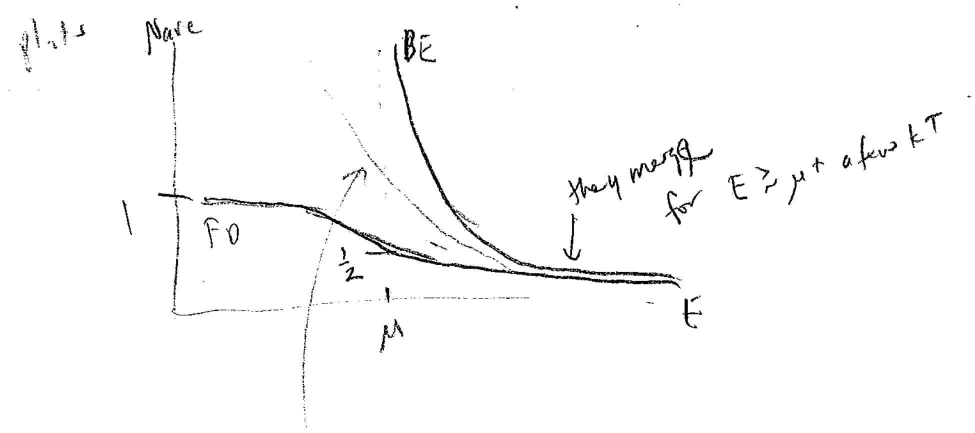
$$N_{ave} = \frac{e^{-(E-\mu)/kT}}{1-e^{-(E-\mu)/kT}} \times \frac{e^{+(\quad)}}{e^{+(\quad)}}$$

$$\boxed{N_{ave} = \frac{1}{e^{(E-\mu)/kT}-1}}$$

Bose-Einstein distribution — often: $f_{B\text{-}E}$

↑ small difference in sign ⟺ big difference in behavior

plots



Maxwell-Boltzmann. Turns out that even though we neglected μ in BF discussion, you can calculate μ (hard, see Schroeder pg 268) → $\mu = -kT \ln Z/N$

$$N_{ave} = N_{tot} \cdot \frac{BF(E)}{\sum \text{all } BFs}$$

$$= e^{-(E-\mu)/kT}$$

$N_{ave} = \dfrac{1}{e^{(E-\mu)/kT}}$

All 3 same when $E \gg \mu$, when $N_{ave} \ll 1$ "classical regime"