Applications of the canonical distribution

Ex 2. Molecule in an ideal gas

Monatomic gas at temp T, vol V.

molecule : system

reservoir : rest of the gas

$$E = \frac{1}{2} m v^2 = \frac{\vec{p}^{\,2}}{2m}$$

molecule has position between $\vec{r}$ & $\vec{r} + d\vec{r}$

momentum between $\vec{p}$ & $\vec{p} + d\vec{p}$

volume of phase space corresponding to this

$$d^3\vec{r}\, d^3\vec{p} \equiv dx\, dy\, dz\, dp_x\, dp_y\, dp_z$$

$$\underbrace{\underbrace{P(\vec{r}, \vec{p})}_{\text{Prob. density}}\, d^3\vec{r}\, d^3\vec{p}}_{\text{prob. that molecule be found in this range}} \propto \left(\frac{d^3\vec{r}\, d^3\vec{p}}{h_0^3}\right) e^{-\frac{\beta p^2}{2m}}$$

prob. that molecule be found in this range

Prob. density.

$P(\vec{p})\, d^3\vec{p} \longrightarrow$ Prob that molecule has momentum between $\vec{p}$ & $\vec{p} + d\vec{p}$ (irrespective of location)

$P'(\vec{v})\, d^3\vec{v} \longrightarrow$ ... velocity between $\vec{v}$ & $\vec{v} + d\vec{v}$

$P'(\vec{v})\, d^3\vec{v} \Rightarrow$ integrate over all values of position

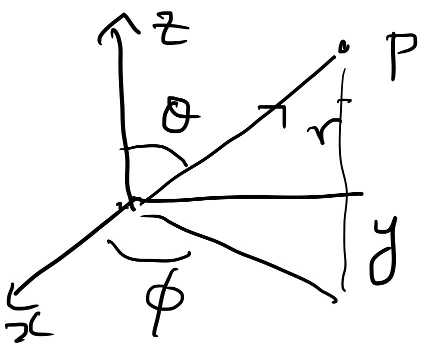
$$\iint \underbrace{d^3\vec{r}} = V$$

$$\boxed{P'(\vec{v})\, d^3\vec{v} = \underbrace{C}_{V \text{ factor}}\, e^{-\frac{\beta m v^2}{2}}\, d^3\vec{v}} \longrightarrow \text{Maxwell's velocity distribution}$$

Speed distribution $\longrightarrow$ irrespective of direction

molecules has speed between v & $v + dv$

$$\underline{P(v)\,dv} = C \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} e^{-\beta m v^2/2}\, v^2\, dv\, \sin\theta\, d\theta\, d\phi$$



$$d^3\vec{r} = r^2 \underbrace{dr \sin\theta\, d\theta\, d\phi}_{dx\,dy\,dz}$$

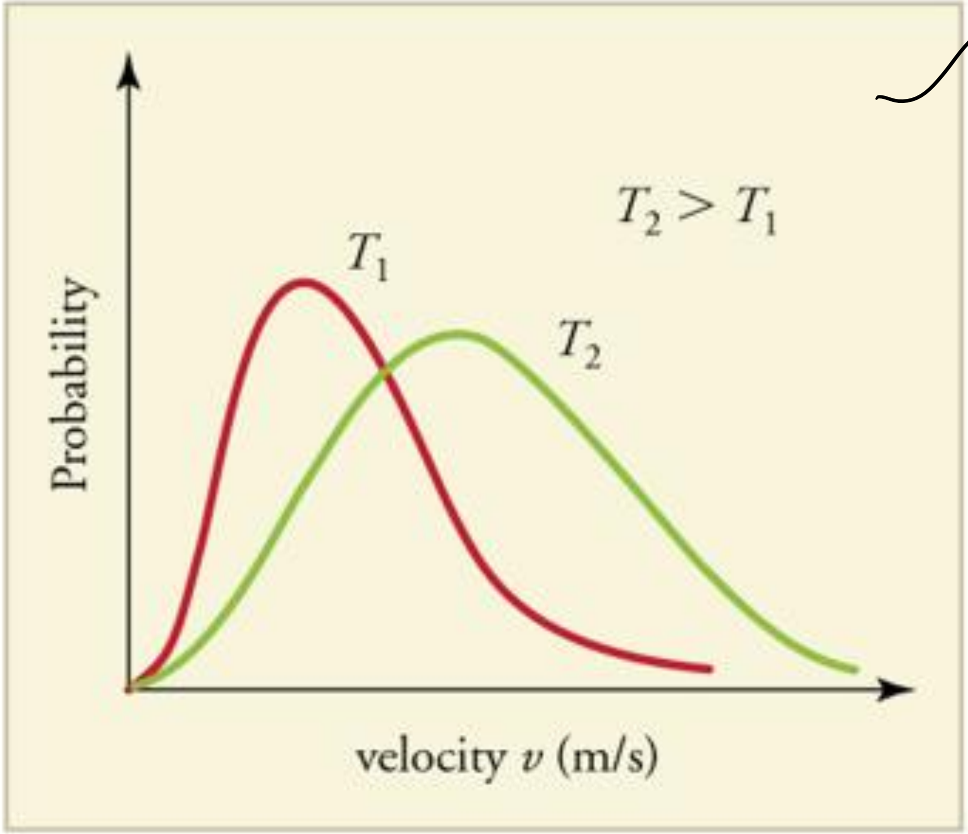
$\downarrow$

$$d^3\vec{v} = v^2 dv \sin\theta\, d\theta\, d\phi$$

$$\int \sin\theta\, d\theta\, d\phi = 4\pi$$

$$C' = 4\pi C$$

$$\boxed{P(v)\,dv = C'\, e^{-\beta m v^2/2}\, v^2\, dv}$$ speed dist.



$$e^{-\beta \frac{mv^2}{2}} v^2$$

$$e^{-\frac{mv^2}{2kT}} v^2$$

Example 3 : Thermal excitation of atoms.

Hydrogen atom in the sun, $T = 5800\,K$.

$P(s_2)$; prob that the atom is in $n=2$ state (first excited state)

$P(s_1)$: prob. . . . . . . is in $n=1$ state ground state.

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{-(E_2-E_1)/kT}$$

$$\Delta E = 10.2 \text{ eV}$$

$$kT = (8.62 \times 10^{-5} \text{ eV/k})(5800 \text{ k})$$

$$= 0.5 \text{ eV}.$$

$$\frac{P(s_2)}{P(s_1)} = e^{-20.4} \simeq 1.4 \times 10^{-9}$$

} 1.4 atoms in a billion will be in an excited state.

$n=1 \longrightarrow$ only 1 state with E_1

$n=2 \longrightarrow$ has 4 states with E_2.

Total # of atoms in $n=2$ state $\sim 1.4 \times 4 \times 10^{-9}$

~ 5.6.

Atoms in atm of sun absorb sunlight on way to earth

→ induces transition to excited states.

1st excited 656 nm, 486 nm, 434 nm → Balmer series

$n=2$.

→ solar spectrum these appear as dark lines

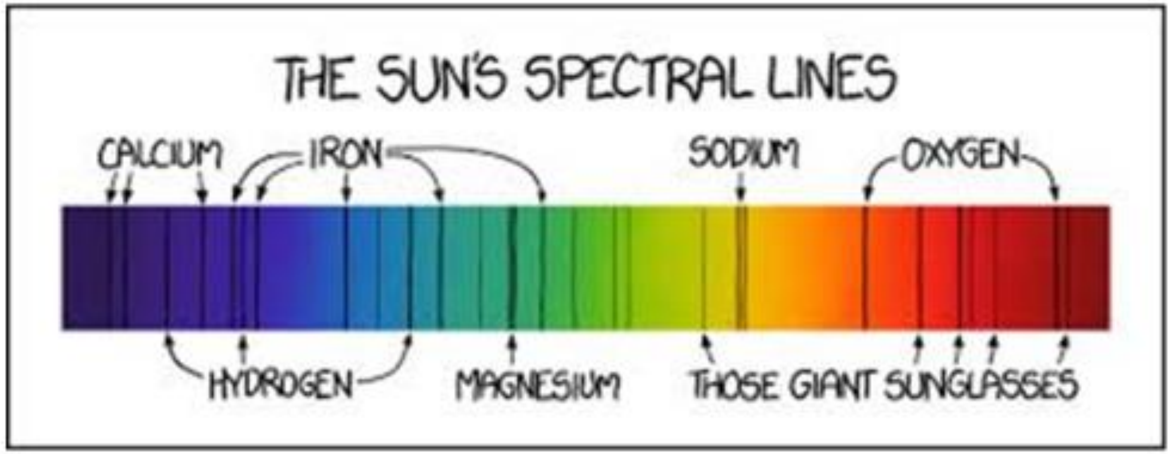
Absorption bands. also have (Fe, Mg, Na, Ca) etc.

Weird thing: all the other wavelengths that are absorbed by atoms start out in states $< 3\,eV$ from ground state.

→ these lines ought to be more prominent.

- Fact is Balmer lines are quite prominent among others.

$\Longrightarrow$ H is <u>much</u> more abundant in the sun than other atoms!!


THE SUN'S SPECTRAL LINES
CALCIUM
IRON
SODIUM
OXYGEN
HYDROGEN
MAGNESIUM
THOSE GIANT SUNGLASSES

Calculation of mean values in a canonical ensemble

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}.$$

$$\text{Mean energy} = \bar{E} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}.$$

sums are over all accessible states

Can be expressed in a much more compact form using the <u>partition function</u>

$$Z = \sum_r e^{-\beta E_r}.$$

$$\sum_r E_r e^{-\beta E_r} = -\frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r} = -\frac{\partial Z}{\partial \beta}.$$

$$\boxed{\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}} \qquad \boxed{\bar{E} = -\frac{\partial}{\partial \beta} \ln Z}$$

Dispersion

$$\overline{(\Delta E)^2} = \overline{E^2} - (\overline{E})^2 .$$

$$\overline{E^2} = \frac{\sum E_r^2 e^{-\beta E_r}}{\sum e^{-\beta E_r}} .$$

$$= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} .$$

$$\overline{E}^2 = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2$$

$$\overline{E^2} = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

$$= -\frac{\partial \overline{E}}{\partial \beta} + (\overline{E})^2 .$$

$$\overline{(\Delta E)^2} = \overline{E^2} - (\overline{E})^2$$

$$\boxed{\overline{(\Delta E)^2} = -\frac{\partial \overline{E}}{\partial \beta} = -\frac{\partial^2}{\partial \beta^2} \ln Z} > 0$$

$$-\frac{\partial \overline{E}}{\partial \beta} \geqslant 0$$

$$\frac{\partial \overline{E}}{\partial T} \geqslant 0 .$$