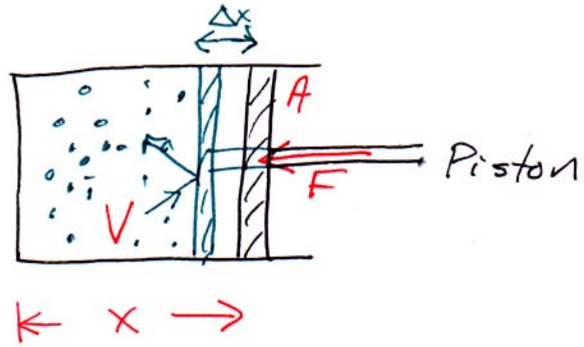
Rework, introduce $\rho(p_x)$!

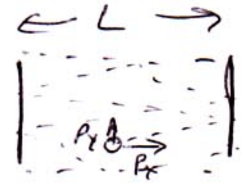
Kinetic Theory of Gases



- Pressure $P = F/A$
- Work done on gas

$$dW = F(-dx) = -PA\,dx = -P\,dV$$

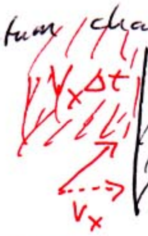
Decrease volume, increase energy & pressure inside



- Ideal gas (no collisions)
- Perfect reflections

Time between collisions $\Delta t = \frac{2mL}{p_x}$

Momentum change $= \Delta p = 2p_x$



$\bar{F} = \frac{\Delta p}{\Delta t} = \frac{p_x^2}{mL}$

$N_{atoms} = nV$

$\rho(p_x)$ $\quad F = \frac{nV}{mL}\int \rho(p_x)\,p_x^2\,dx = \frac{n\langle p_x^2\rangle A}{m}$

$P = F/A = \frac{n\langle p_x^2\rangle}{m}$

Simplifications:

- Individual collisions of atoms inside balance P, F

(Liquids, solids – many atoms at once mushing...)

- Perfect reflections

$$(p_x, p_y, p_z) \Rightarrow (-p_x, p_y, p_z)$$

- ~~Assume all atoms have same p_x~~

Density $n = N/V$, time Δt

Particle within $V_x \Delta t$ hits in next Δt; $\# = n V_x A \Delta t$

contributes force $F = 2p_x$

$\rightarrow$ Force during $\Delta t = (n \underbrace{V_x}_{p_x/m} A \Delta t)(2p_x)$

$$PA = 2nA\,p_x^2/m$$

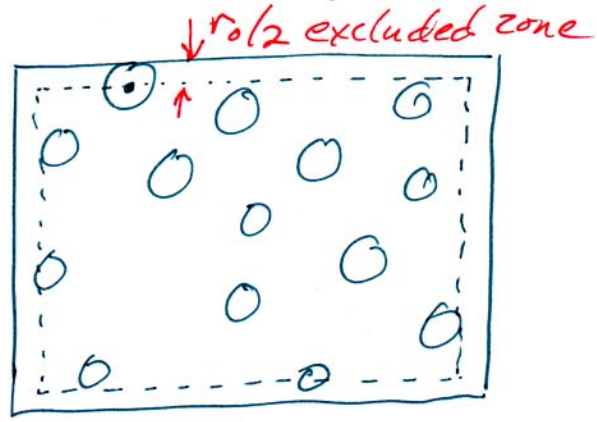
- Average over $p_x > 0$

$$P = n\langle p_x^2\rangle/m = \frac{2}{3} n \left\langle \frac{p^2}{2m} \right\rangle = \frac{2}{3} U/V$$

$$\frac{\langle p_x^2\rangle}{m} = \frac{\langle p_y^2\rangle}{m} = \frac{\langle p_z^2\rangle}{m} = \frac{1}{3}\langle p^2/m\rangle = \frac{2}{3}\left\langle \frac{p^2}{2m}\right\rangle = \frac{2}{3}(K.E.)$$

Seems like a trick: don't ever need distribution $\rho(\vec{p})$, only average energy. Often, we want whole probability distribution... What is $\rho(\vec{p})$?

What is $\rho(\vec{r})$, probability density in space?



Simplification: Hard spheres, radius r_0, rigid box $L \times L \times L$

$$\rho(\vec{r}) = \frac{1}{(L-r_0)^3} = \frac{1}{V}$$ constant away from the sides of the box, for a dilute gas

What is $\rho(\vec{R})$ for N atoms?

$\vec{\mathbb{R}}$ = 3N-dimensional vector in Position Space

$\rho(\vec{\mathbb{R}})$ = constant inside box for ideal gas $r_0 \to 0$.
$= [V^N/N!]^{-1}$ (if indistinguishable)

Basis of Statistical Mechanics: In equilibrium, all possible configurations of positions and momenta occur with equal probability.

"Possible" = Consistent with energy conservation

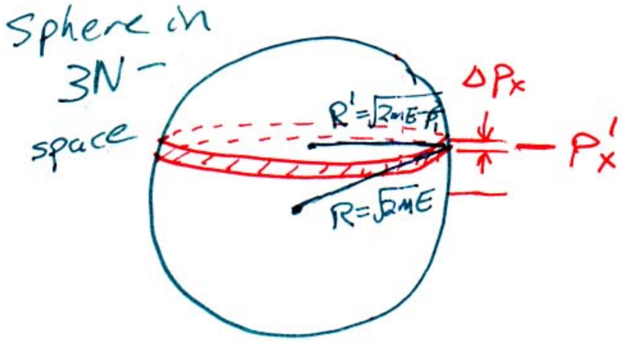
Feynman (using Maxwell's flawed? argument) shows that binary collisions smear out the momentum distribution... I'm going to just assume it.

What is $\rho(\vec{\mathbb{P}})$, for $\vec{\mathbb{P}} = (\vec{p}^{\,1}, \vec{p}^{\,2}, \ldots, \vec{p}^{\,N})$ 3N-vector? in Momentum Space.

$$E = \sum_{n=1}^{N} \frac{\vec{\mathbf{P}}^{n\,2}}{2m} = \frac{1}{2m}\vec{\mathbb{P}}^{2} \quad \text{is conserved}$$

$\rho(\vec{\mathbb{P}})$ = constant on sphere of radius $\sqrt{2mE}$ in 3N dimensions. {Mathematicians: 3N-1 sphere}

What is $\rho(p_x^1)$, the probability atom 1 has p_x^1?



$$\rho(P_1^x)\Delta p = \frac{\text{Area of "circle" disk}}{\text{Area of Sphere}}$$

Area of Sphere Radius R in Dimension D $= \underbrace{\begin{pmatrix}\pi\text{'s,} \\ \text{const}\end{pmatrix}}_{\text{Not crucial here}} R^{D-1}$

Area of "Circle" $= (\pi\text{'s})\, R'^{\,D-2} \underbrace{/\cos\theta}_{\text{Not crucial either}}$

$R = \sqrt{2mE}$

$R' = \sqrt{2m\left(E - \frac{p_x^{1\,2}}{2m}\right)}$

$D = 3N$

$$\rho(p_x') = \left(\frac{\pi\text{'s}}{\cos\theta}\right) \frac{(2mE - p_x^2)^{\frac{3N-1}{2}}}{(2mE)^{3N/2}}$$

$$= \left(\frac{\pi\text{'s}\sqrt{2mE}}{(2mE - p_x^2)\cos\theta}\right)\left(1 - \frac{p_x^2}{2mE}\right)^{3N/2}$$

$B = 3N/2$

$$\lim_{B\to\infty}\left(1-\frac{a}{B}\right)^B = e^{-a}. \quad N \approx 10^{23}. \qquad \frac{a}{3N/2} = \frac{p_x^2}{2mE}$$

$$a = \frac{p_x^2}{2m}\left(\frac{3N}{2E}\right)$$

$$\rho(p_x) = (\ldots)\, e^{-\frac{p_x^2}{2m}\left(\frac{3N}{2E}\right)}$$

arbitrary scaling: Boltzmann's constant

We define $T = \frac{1}{k_B}\left(\cancel{\frac{3N}{2E}}\ 2E/3N\right)$,
for ideal gas.

$$\rho(p_x) = \frac{1}{\sqrt{2\pi m k T}} e^{-\frac{p_x^2}{2mkT}} \qquad \sigma^2 = mkT = \langle p_x^2 \rangle$$

Normalization $\frac{1}{\sqrt{2\pi}\,\sigma} = \frac{1}{\sqrt{2\pi m k T}}$

$$\langle \text{Kinetic Energy in } p_x' \rangle = \frac{\langle p_x^2 \rangle}{2m} = \frac{k_B T}{2}$$

ignoring quantum mechanics!

Equipartition Theorem: In a classical gas, each component of the velocity will have kinetic energy average $\frac{1}{2}kT$. [Also holds for positions if $V(\vec{r})$ is harmonic.]

- Most of the surface area of a large-dimension sphere is very close to the equator!

- Pressure $P = n \frac{\langle P_x^2 \rangle}{m} = n k_B T = \frac{N}{V} k_B T$

$$\boxed{PV = \underbrace{N k_B}_{} T}$$ Ideal Gas Law

~~also~~ known as R if N in moles

K_B = Boltzmann's Constant

- Two kinds of atoms?
  - → surface area of ellipsoid
  - → still $\frac{1}{2} k_B T$ energy per velocity component

- Probability $\sim e^{-(\text{Kinetic Energy})/kT}$

First example of a Boltzmann distribution - very powerful!

- Temperature is the $\overset{\text{entropy}}{\underline{\text{cost}}}$ of stealing energy from the rest of the world
  - Like pressure is energy cost for stealing volume
  - "Rest of the World" often called <u>heat</u> <u>bath</u>

What currency is being paid?

- Call $\Omega(E-K)$ = Volume of "circle" in $(3N-1)$ dimensions of radius $\sqrt{2M(E-K)}$ $\quad K = \frac{P^2}{2m}$ = Kinetic Energy

"$\mathcal{E}$", "available" energy for rest

$$\boxed{\frac{1}{T} = k_B \frac{d \log \Omega}{d\mathcal{E}} = \frac{dS}{d\mathcal{E}}}$$

$S = k_B \log \Omega$ = <u>Entropy</u>

What Currency is being Paid for stealing this energy? ENTROPY!

- Probability of having particle momentum $\frac{P^2}{2m}$

  = Volume of "circle" (3N-2 sphere) of radius $\sqrt{2M\mathcal{E}}$ with $\mathcal{E} = E_{tot} - \frac{P^2}{2m}$ "available" energy

Define $\Omega_{\mathbb{P}}(\mathcal{E})$ = Volume of "Circle"

$$= (2m\mathcal{E})^{\frac{3N-\cancel{2}}{2}} = e^{\frac{3N}{2}\log(2m\mathcal{E})}$$

unimportant

Define $S_{\mathbb{P}}(\mathcal{E}) = k_B \log \Omega_{\mathbb{P}}(\mathcal{E})$ "Momentum-Space Entropy"

$$= \frac{3}{2} N k_B \log(2m\mathcal{E})$$

Entropy cost for stealing energy

$$\frac{\partial S_{\mathbb{P}}}{\partial \mathcal{E}} = \frac{3}{2} N k_B \left(\frac{1}{\mathcal{E}}\right) = \frac{3Nk_B}{2\mathcal{E}} = \frac{1}{T}$$

Statistical Mechanics Definition of Temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial \mathcal{E}}\right)\Big|_V$$

$$\text{Entropy} = k_B \log \Omega(\mathcal{E}) = k_B \log \left\{ \begin{array}{c} \text{Volume in Phase Space} \\ \text{at Energy } \mathcal{E} \\ \text{-or-} \\ \text{Number of Configurations} \end{array} \right\}$$