Kinetic Theory of Gases

- Pressure \( P = \frac{F}{A} \)
- Work done on gas \( dW = F(-dx) = -PA \, dx = -P \, dV \)

Decrease volume, increase energy & pressure inside

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 \( n = \frac{N}{V} \), time \( \Delta t \)
Particle within \( V \Delta t \) hits in next \( \Delta t \); \( \# = nV_xA\Delta t \)

- Force \( F = 2P_x \)
- Force during \( \Delta t = (nV_xA\Delta t)(2P_x) \)
  \( PA = 2nA \frac{P_x^2}{m} \)

- Average over \( P_x > 0 \)

\[
P = \left\langle \frac{P_x^2}{m} \right\rangle = \frac{2}{3} n \left\langle \frac{P_x^2}{2m} \right\rangle = \frac{2}{3} \frac{U}{N}
\]

\[
\left\langle \frac{P_x^2}{m} \right\rangle = \left\langle \frac{P_y^2}{m} \right\rangle = \left\langle \frac{P_z^2}{m} \right\rangle = \frac{1}{3} \left\langle \frac{P_m^2}{m} \right\rangle = \frac{2}{3} \left\langle \frac{P_m^2}{2m} \right\rangle = \frac{2}{3} (\text{K.E.})
\]
Seems like a trick: don't ever need distribution \( p(\vec{v}) \), only average energy. Often, we want whole probability distribution... What is \( p(\vec{v}) \)?

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

Simplification! Hard spheres, radius \( r_0 \), rigid box \( L \times L \times L \)

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

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

\[
\vec{R} = 3N\text{-dimensional vector in Position Space}
\]

\[
\rho(\vec{R}) = \text{constant inside box for ideal gas } r_0 \to 0,
\]

\[
= \frac{V^n}{N!} \text{ (if indistinguishable)}
\]

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 \( \rho(\vec{P}) \), for \( \vec{P} = (\vec{P}_1, \vec{P}_2, \ldots, \vec{P}_N) \) 3N-vector?

\[
E = \frac{1}{2m} \sum_{n=1}^{N} \vec{P}_{n}^2 \quad \text{in Momentum Space},
\]

is conserved.

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

What is \( \rho(\vec{P}_x) \), the probability atom 1 has \( \vec{P}_x \)?

Sphere in 3N-1 space

\[
\text{Area of "circle" disk} = \frac{\text{Area of Sphere}}{\text{Area of Sphere}}
\]

Area of Sphere = \( (\pi \text{'}s) R^{D-1} \)

Radius \( R \) in Dimension \( D \)

Not crucial here

\( R = \sqrt{2mE} \)

\( R' = \sqrt{2m(E - \frac{P_x^2}{2m})} \)

\( D = 3N \)

Area of "Circle"

\( = (\pi \text{'}s) R^{D-2} / \cos \theta \)

Not crucial either
\[ p(x') = \left( \frac{\pi^1 S}{\cos \theta} \right) \frac{(2mE - px^2)^{3N/2}}{(2mE)^{3N/2}} \]

\[ = \left( \frac{\pi^1 S \cdot 2mE}{2mE - px^2 \cos \theta} \right) \left( 1 - \frac{px^2}{2mE} \right)^{3N/2} \]

\[ \lim_{B \to \infty} \left( 1 - \frac{a}{B} \right)^B = e^{-a} \quad N \approx 10^{23} \quad \frac{a}{3N/2} = \frac{px^2}{2mE} \quad a = \frac{px^2}{2m} \left( \frac{3N}{2E} \right) \]

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

\[ p(x) = \left( \cdots \right) e^{-\frac{px^2}{2m}} \left( \frac{3N}{2E} \right) \]

\[ \text{Normalization} \quad \frac{1}{\sqrt{2\pi m kT}} = \frac{1}{\sqrt{2\pi m kT}} \]

\[ \langle \text{Kinetic Energy in } p_x \rangle = \frac{\langle p_x^2 \rangle}{2m} = \frac{KT}{2} \]

\[ \sigma^2 = m kT = \langle p_x^2 \rangle \]

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 \( V(r) \) is harmonic.]
Most of the surface area of a large-dimension sphere is very close to the equator.

Pressure \( P = n \frac{\langle p^2 \rangle}{m} = n k_B T = \frac{N}{V} k_B T \)

\[ PV = N k_B T \]  
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 \( \sim e^{-\frac{(\text{Kinetic Energy})}{k_B T}} \)

First example of a Boltzmann distribution - very powerful!

Entropy

Temperature is the cost of stealing energy from the rest of the world

- Like pressure is energy cost for stealing volume
- "Rest of the World" often called heat bath

What currency is being paid?

Volume of "circle" in \( (3N-1) \) dimensions of radius \( \sqrt{2M(E-K)} \)

\( K = \frac{P^2}{2m} = \text{Kinetic Energy} \)

\( E \), "available" energy for rest

\[ S = k_B \log \mathcal{S} = \text{Entropy} \]
What Currency is being Paid for stealing this energy? **ENTROPY!**

- Probability of having particle momentum $\frac{P^2}{2m} = \text{Volume of "circle" (3N-2 sphere) of radius } \sqrt{2mE}$ with $E = E_{\text{tot}} - \frac{P^2}{2m} \text{ "available" energy}$

Define $S_P(\varepsilon) = \text{Volume of "Circle"}$

$$= (2mE)^{\frac{3N-2}{2}} = e^{\frac{3N}{2}\log(2mE)}$$

Unimportant

Define $S_P^E = k_B \log S_P(\varepsilon) \text{ "Momentum-Space Entropy"}$

$$= \frac{3}{2} N k_B \log(2mE)$$

Entropy cost for stealing energy

$$\frac{\partial S_P}{\partial \varepsilon} = \frac{3}{2} N k_B \left( \frac{1}{\varepsilon} \right) = \frac{3Nk_B}{2\varepsilon} = \frac{1}{T}$$

Statistical Mechanics Definition of Temperature:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial \varepsilon} \right)_v$$

Entropy $= k_B \log S_P(\varepsilon) = k_B \log \{ \text{Volume in Phase Space} \}$

or

$\{ \text{Number of Configurations} \}$