Kinetic theory of gases (also developed by James Maxwell)

By mid 1800 people knew from experiments on gas

- Boyle's law \((T=\text{const.} \rightarrow PV=PV_0)\)
- Charles' law \((P=\text{const.} \rightarrow V\propto T)\)
- Gay-Lussac's law \((V=\text{const.} \rightarrow P\propto T)\)
- Avogadro's law \((P, T=\text{const.} \rightarrow V\propto N)\)

\[ P = \frac{kT}{V} \quad \text{ideal gas law} \]

Microscopic model:

Assume \(N\) molecules in a box of volume \(V=L^3\).

Velocity of the molecule is \(V\).

Total energy of the system is

\[ U = N \frac{m}{2} \left< \sum_{i=1}^{N} \mathbf{v}_i^2 \right> = N \frac{m}{2} \left( \left< \mathbf{v}_x^2 \right> + \left< \mathbf{v}_y^2 \right> + \left< \mathbf{v}_z^2 \right> \right) \]

\[ = \frac{3}{2} Nm \left< \mathbf{v}_x^2 \right> \]

\[ \equiv N E_k \quad \text{mean kinetic energy per molecule.} \]

Pressure on the wall = Force/area

\[ P = \frac{F}{A} = \frac{\Delta P/\Delta t}{L^2} = \frac{1}{L^2} \cdot N \left< \frac{1}{2} m \mathbf{v}_x^2 \right> = \frac{N \, m \, \left< \mathbf{v}_x^2 \right>}{V} = \frac{N \, m \, \left< \mathbf{v}_x^2 \right>}{L} = \frac{N \, m \, \left< \mathbf{v}_x^2 \right>}{V^2} = \frac{3}{2} \frac{N E_k}{V^2} \]

Compare with \(P = n \, k \, T\) \(\Rightarrow E_k = \frac{3}{2} kT\), \(\Rightarrow \frac{3}{2} \left< \mathbf{v}_x^2 \right> = \frac{3}{2} m \, \left< \mathbf{v}_x^2 \right> = \frac{3}{2} m \, \left< \mathbf{v}_y^2 \right> = \frac{3}{2} m \, \left< \mathbf{v}_z^2 \right> = \frac{5}{2} \, k \, T\)

\[ \Rightarrow U = N \times kT \]

Equipartition theorem: In equilibrium, each degree of freedom has a mean energy \(\frac{1}{2} kT\).
Atomic gas: $E_k = \frac{3}{2} kT$ (translational energy) $\Rightarrow$ rms velocity $\sqrt{\langle \nu^2 \rangle} = \sqrt{\frac{3kT}{m}}$

molecular gas: $E_k = \frac{3}{2} kT + KT + \text{vibrational + electronic + nuclear}$...

at room temperature.

$\Rightarrow U = NTkT \quad \gamma = \frac{3}{2} \text{ (molecules), } \frac{5}{2} \text{ (regular molecules)}$

What's the probability distribution $P(v_x, v_y, v_z)$. $\int P(v) \, d^3v = 1$ ?

Statistical mechanics: probability $P(E)$ of a particle with energy $E$ is

$$P(E) = \frac{1}{Z} e^{-E/kT}, \text{ where } Z \text{ is the normalization constant } \sum_{E} \frac{1}{Z} e^{-E/kT} = 1 \Rightarrow Z = \frac{1}{e} e^{-E/kT}.$$ 

Maxwell's approach: Probability $P(v_x, v_y, v_z)$ should be independent in all directions

$$P(v) = p(v_x) p(v_y) p(v_z) \quad v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

$$\partial_{v_x} P(v) = p'(v) \frac{dv}{dv_x} = p(v_x) \frac{v_x}{v} = p(v_x) p(v_y) p(v_z)$$

$$\Rightarrow \frac{p'}{p} = \frac{n}{v_x} \text{ constant } \Rightarrow \frac{dp}{p} = c \, v \, dv \quad \frac{dv}{p} = c \, v_x \, dv_x$$

$$\Rightarrow P(v) = c_1 e^{-c v^2} \quad p(v_x) = c_2 e^{-c v_x^2}$$

$$\Rightarrow P(v) = c_1 e^{-\beta v^2} = c_1 e^{-\beta v_x^2} e^{-\beta v_y^2} e^{-\beta v_z^2}$$

Using $\int P(v) \, dv = 1$ and $\langle \frac{1}{2} m \nu^2 \rangle = \frac{3}{2} kT$. We get

$$P(v_x, v_y, v_z) = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\beta \frac{m}{2} (v_x^2 + v_y^2 + v_z^2)}, \quad \beta = \frac{1}{kT}$$
Thermodynamics was developed to understand and improve heat engines: Internal combustion engines (ICE), refrigeration.

We will use engines to illustrate how engines do work.
Thermodynamical processes:

1. Isochoric process \((V = \text{const})\)

- Isochoric specific heat \(C_v\)
- Heat transfer: \(dQ = C_v \Delta T\)

\[
dQ = dU = d[N\gamma kT] \Rightarrow C_v = \frac{1}{M} \frac{dU}{dT} = \frac{\gamma k}{m}
\]

2. Isobaric process \((P = \text{const})\)

- Isobaric specific heat \(C_p\)
- Heat transfer: \(dQ = dU - PdV\)

\[
dU = dQ - Fdx = dQ - PdV
\]

\[
isobaric \ specific \ heat \ C_p = \frac{1}{M} \frac{dQ}{dT} = \frac{1}{M} \left( \frac{dU}{dT} + P \frac{dV}{dT} \right) \Rightarrow \frac{dV}{dT} |_{p=\text{const}} = \frac{Nk}{P}
\]

\[
= \frac{N}{M} \gamma k + \frac{N}{M} k = \frac{N}{M} (\gamma + 1) k = \frac{\gamma + 1}{\gamma} C_v
\]

3. Adiabatic process (no heat exchange, isolated system)

- Adiabatic process: \(dU = \gamma Nk \Delta T\)

\[
dU = -PdV = \gamma Nk \Delta T = \gamma Nk d(PV)
\]

\[
\Rightarrow PdV + \gamma PdV + \gamma Vdp = 0
\]

\[
\Rightarrow (\gamma + 1)pdV + \gamma Vdp = 0 \Rightarrow \frac{\gamma + 1}{\gamma} Vdp = 0 \Rightarrow PV^{\frac{\gamma + 1}{\gamma}} = \text{const}
\]

4. Isothermal process \((T = \text{const})\) \(\Rightarrow PV = C, \ U = C\)

\[
\Rightarrow dU = dQ - PdV = 0 \Rightarrow dQ = PdV
\]
Carnot Cycle: The most efficient process we know for a heat engine.

System absorbs heat from $T_H$, does work, and cools down by $T_c$.

Step 1: Isothermal expansion ($T = T_H$, $V_a \rightarrow V_b$)

\[ \Delta U = \Delta Q - P \Delta V = 0. \quad \Delta Q = P \Delta V = \int_A^B P \, dV \]

Absorb energy from heat source and do work by expanding.

Step 2: Adiabatic expansion ($T_H \rightarrow T_c$, $\Delta Q = 0$)

Cool down the system and do some more work.

Step 3: Isothermal contraction ($T = T_H$, $V_c \rightarrow V_d$)

Contract and dump excess heat to cold reservoir.

Step 4: Adiabatic contraction ($T_c \rightarrow T_H$, $\Delta Q = 0$)

More contraction and heat system back to $T_H$. 
Energy absorbed from the hot source at $T_H$

$$\Delta Q = P_A V = \int_A^B P \, dV = \int_A^B \frac{NKT_H}{V} \, dV = NKT_H \ln \frac{V_B}{V_A}$$

Energy released into the cold source at $T_C$

$$\Delta Q = P_A V = \int_C^D P \, dV = \int_C^D \frac{NKT_C}{V} \, dV = NKT_C \ln \frac{V_D}{V_C}$$

During steps 2 and 4, no heat exchange we only need to evaluate work $\int P \, dV$

Step 2: Work done $= \int_B^C P \, dV = P_B V_B \int_B^C V^{-\alpha} \, dV = P_B V_B^{\alpha-1} \frac{1}{\alpha-1} (V_c^{\alpha} - V_B^{\alpha})$

Step 4: Work done $= P_A V_A^{\alpha-1} (V_a^{\alpha-1} - V_D^{\alpha-1})$

Total work done by the system:

$$ABCD \text{ area } = \int_A^B + \int_B^C + \int_C^D + \int_D^A P \, dV$$

$$= NK \left( T_H \ln \frac{V_B}{V_A} + T_C \ln \frac{V_D}{V_C} \right) + NKT_H \frac{1}{\alpha-1} \left[ \left( \frac{V_B}{V_C} \right)^{\alpha-1} - 1 + 1 - \left( \frac{V_B}{V_C} \right)^{\alpha-1} \right]$$

Step 1: $P_A V_A = P_B V_B$  Step 1: $P_B V_B^{\alpha} = P_C V_C^{\alpha}$  $\Rightarrow \frac{V_B}{V_C} = \frac{P_B}{P_C}$  $\frac{V_B}{V_C} = \frac{P_B}{P_C}$  $\frac{V_B}{V_C} = \frac{V_B}{V_C}$

Step 3: $P_C V_C = P_B V_B$  Step 4: $P_D V_D^{\alpha} = P_A V_A^{\alpha}$  $\Rightarrow V_A / V_D = V_B / V_C$

Step 2 and 4 do zero network: $\int_B^C + \int_D^A P \, dV = 0$.

$\Rightarrow ABCD \text{ area } = NK (T_H - T_C) \ln \frac{V_B}{V_A}$

Cannot cycle efficiency $= \frac{\text{work}}{\text{energy needed}} = \frac{NK(T_H - T_C) \ln \frac{V_B}{V_A}}{NK T_H \ln \frac{V_B}{V_A}} = 1 - \frac{T_C}{T_H}$