Statistical Mechanics, Kinetic Theory Ideal Gas

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Statistical Mechanics and Thermodynamics

- Thermodynamics Old & Fundamental
  - Understanding of Heat (I.e. Steam) Engines
  - Part of Physics Einstein held inviolate
  - Relevant to Energy Crisis of Today

- Statistical Mechanics is Modern Justification
  - Based on mechanics: Energy, Work, Momentum
  - Ideal Gas model gives observed thermodynamics

- Bridging Ideas

  Temperature (at Equilibrium) is Average Energy

  Equipartition - as simple/democratic as possible

Temperature and Equilibrium

- Temperature is Energy per Degree of Freedom
  - More on this later (Equipartition)

- Heat flows from hotter to colder object

  Until temperatures are equal

  Faster if better thermal contact

  Even flows at negligible Δt (for reversible process)

- The Unit of Temperature is the Kelvin

  Absolute zero (no energy) is at 0.0 K

  Ice melts at 273.15 Kelvin (0.0 C)

  Fahrenheit scale is arbitrary

State Variables of System

- State Variables - Definition

  Measurable Static Properties

  Fully Characterize System (if constituents known)

  e.g. Determine Internal Energy, compressibility

  Related by Equation of State

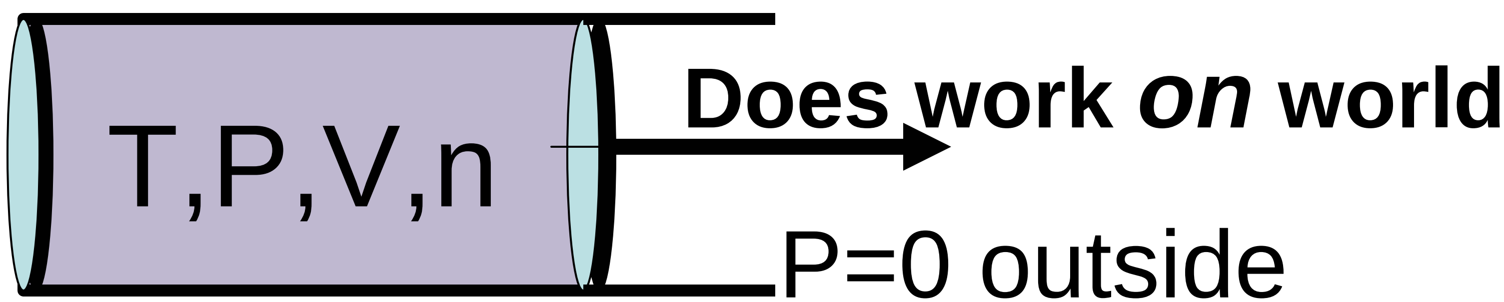
- State Variables: Measurable Static Properties
  - Temperature - measure with thermometer
  - Volume (size of container or of liquid in it)
  - Pressure (use pressure gauge)
  - Quantity: Mass or Moles or Number of Molecules
    - Of each constituent or phase (e.g. water and ice)

Equation of State

- A condition that the system must obey
  - Relationship among state variables
- Example: Perfect Gas Law
  - Found in 18th Century Experimentally
  - $pV = NkT = nRT$
  - K is Boltzmann's Constant 1.38×10^{-23} J/K
  - R is *gas constant* 8.315 J/mole/K
- Another Eq. Of State is van der Waals Eq.
  - You don't have to know this.

PV = n R T = N k T

- P is the Absolute pressure
  - Measured from Vacuum = 0
  - Gauge Pressure = Vacuum - Atmospheric
  - Atmospheric = 14.7 lbs/sq in = 10^5 N/m
- V is the volume of the system in m^3
  - often the system is in cylinder with piston
  - Force on the piston does work on world



$PV = n R T = N k T$
chemists vs physicists

- Mole View (more Chemical) = nRT
  - R is *gas constant* 8.315 J/mole/K

- Molecular View (physicists) = NkT
  - N is number of molecules in system
  - K is Boltzmann's Constant 1.38×10^{-23} J/K

Using PV=nRT

- Recognize: it relates state variables of a gas

- Typical Problems
  - Lift of hot air balloon
  - Pressure change in heated can of tomato soup
  - Often part of work integral

Heat and Work are Processes

- Processes accompany/cause state changes
  - Work **along particular path** to state B from A
  - Heat added along path to B from A

- Processes are **not state variables**
  - Processes change the state!
  - But Eq. Of State generally obeyed

Ideal Gas Law Derivation: Assumptions

- Gas molecules are hard spheres without internal structure
- Molecules move randomly
- All collisions are elastic
- Collisions with the wall are elastic and instantaneous

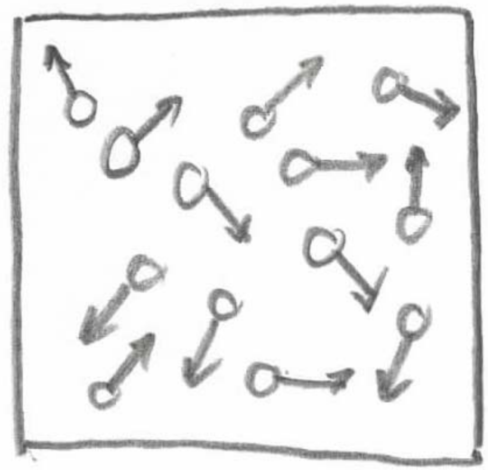
Gas Properties

- N number of atoms in volume
- n_m moles in volume
- m is atomic mass ($^{12}C = 12$)
- mass density $\rho = \frac{m_T}{V} = \frac{nm}{V} = \frac{n_m N_A m}{V}$
- Avogadro's Number $N_A = 6.02 \times 10^{23} molecules \cdot mole^{-1}$

Motion of Molecules

- Assume all molecules have the same velocity (we will drop this latter)

- The velocity distribution is isotropic

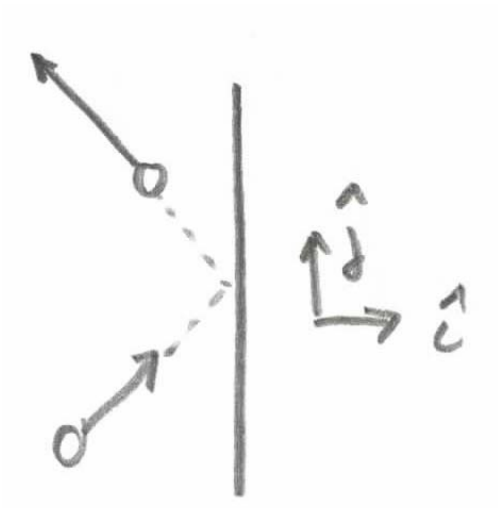


Collision with Wall

- Change of momentum

$$\hat{\mathbf{i}} : \Delta p_x = -mv_{x,f} - mv_{x,0}$$

$$\hat{\mathbf{j}} : \Delta p_y = mv_{y,f} - mv_{y,0}$$



- Elastic collision

$$v_{y,f} = v_{y,0}$$

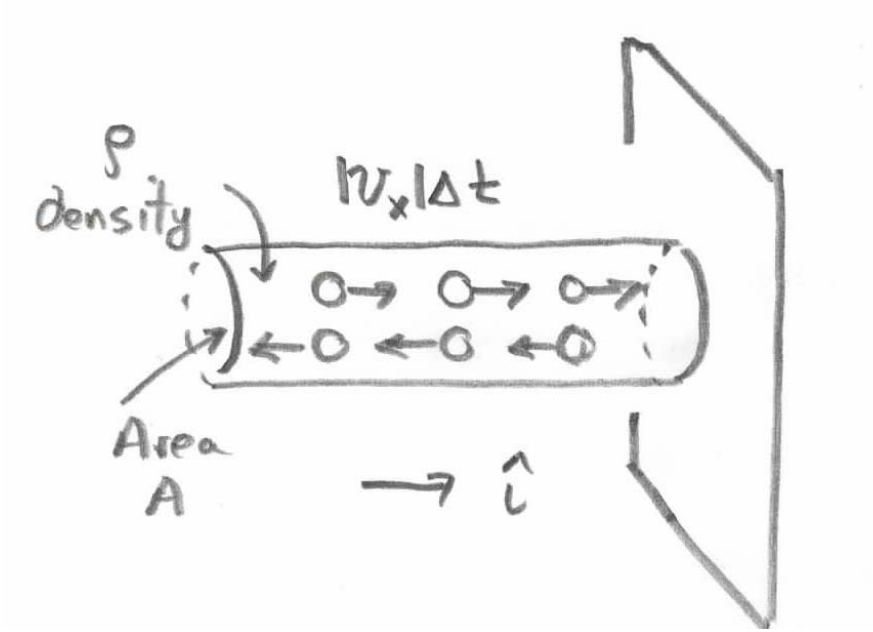
$$v_x \equiv v_{x,f} = v_{x,0}$$

- Conclusion

$$\hat{\mathbf{i}} : \Delta p_x = -2mv_x$$

Momentum Flow Tube

- Consider a tube of cross sectional area A and length $v_x \Delta t$



- In time Δt half the molecules in tube hit wall

- Mass enclosed that hit wall $$\Delta m = \frac{\rho}{2} Volume = \frac{\rho}{2} A v_x \Delta t$$

Pressure on the wall

- Newton's Second Law

$$\vec{\mathbf{F}}_{wall,gas} = \frac{\Delta\vec{\mathbf{p}}}{\Delta t} = \frac{-2\Delta m v_x}{\Delta t}\hat{\mathbf{i}} = -\frac{2\rho A v_x{}^2 \Delta t}{2\Delta t}\hat{\mathbf{i}} = -\rho A v_x{}^2\hat{\mathbf{i}}$$

- Third Law $\vec{\mathbf{F}}_{gas,wall} = -\vec{\mathbf{F}}_{wall,gas} = \rho A v_x{}^2\hat{\mathbf{i}}$

- Pressure $P_{pressure} = \dfrac{\left|\vec{\mathbf{F}}\right|_{gas,wall}}{A} = \rho v_x{}^2$

Average velocity

- Replace the square of the velocity with the average of the square of the velocity

$$\left(v_x^{\ 2}\right)_{ave}$$

- random motions imply

$$\left(v^2\right)_{ave} = \left(v_x^{\ 2}\right)_{ave} + \left(v_y^{\ 2}\right)_{ave} + \left(v_z^{\ 2}\right)_{ave} = 3\left(v_x^{\ 2}\right)_{ave}$$

- Pressure

$$P_{pressure} = \frac{1}{3}\rho\left(v^2\right)_{ave} = \frac{2}{3}\frac{n_m N_A}{V}\frac{1}{2}m\left(v^2\right)_{ave}$$

Degrees of Freedom in Motion

- Three types of degrees of freedom for molecule

1. Translational
2. Rotational
3. Vibrational

- Ideal gas Assumption: only 3 translational degrees of freedom are present for molecule with no internal structure

Equipartition theorem: Kinetic energy and temperature

- Equipartition of Energy Theorem

$$\frac{1}{2}m(v^2)_{ave} = \frac{(\#\text{degrees of freedom})}{2}kT = \frac{3}{2}kT$$

- Boltzmann Constant $k = 1.38 \times 10^{-23}\, J \cdot K^{-1}$

- Average kinetic of gas molecule defines kinetic temperature

Ideal Gas Law

- Pressure

$$p_{pressure} = \frac{2}{3}\frac{n_m N_A}{V}\frac{1}{2}m\left(v^2\right)_{ave} = \frac{2}{3}\frac{n_m N_A}{V}\frac{3}{2}kT = \frac{n_m N_A}{V}kT$$

- Avogadro's Number $N_A = 6.022 \times 10^{23}\, molecules \cdot mole^{-1}$

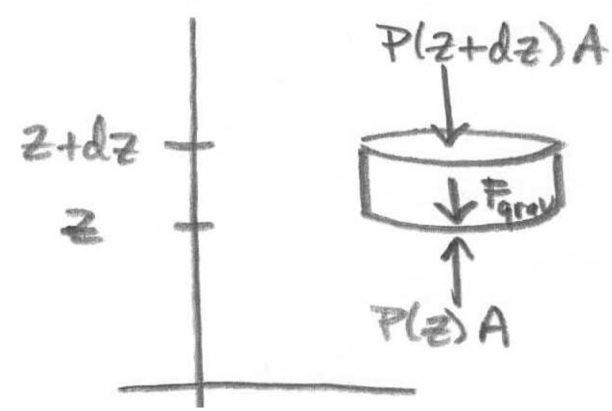
- Gas Constant $R = N_A k = 8.31\, J \cdot mole^{-1} \cdot K^{-1}$

- Ideal Gas Law $pV = n_m RT$

Ideal Gas Atmosphere

- Equation of State $PV = n_m RT$

- Let M_{molar} be the molar mass.



- Mass Density $\rho = \dfrac{n_m M_{molar}}{V} = \dfrac{M_{molar}}{RT} P$

- Newton's Second Law

$$A\big(P(z) - P(z + \Delta z)\big) - \rho g A \Delta z = 0$$

Isothermal Atmosphere

- Pressure Equation

$$\frac{P(z+\Delta z)-P(z)}{\Delta z}=\rho g$$

- Differential equation

$$\frac{dP}{dz}=-\rho g=-\frac{M_{molar}g}{RT}P$$

- Integration

$$\int_{P_0}^{P(z)}\frac{dp}{p}=-\int_{z=0}^{z}\frac{M_{molar}g}{RT}dz'$$

- Solution

$$ln\left(\frac{P(z)}{P_0}\right)=-\frac{M_{molar}g}{RT}z$$

- Exponentiate

$$P(z)=P_0\exp\left(-\frac{M_{molar}g}{RT}z\right)$$