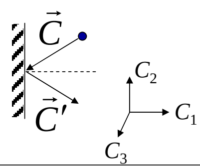
Pressure, Temperature and Energy

- Begin by using simple models to find relations between *p*, *T* and *E* due to random molecular (translational) motions
- Consider region filled with molecules having no avg. motion, at equilibrium, containing a wall
- Start with molecule moving with (random) velocity $\vec{C}$ colliding with wall
  - elastic and smooth surface (specular reflection)



$$\vec{C}_1 = -\vec{C}_1'$$
$$\vec{C}_2 = \vec{C}_2'$$

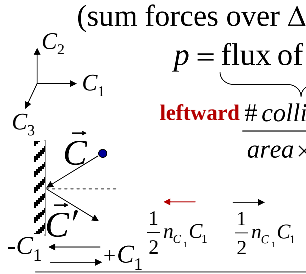
⇒molec. momentum changes
⇒force exerted (on wall)
= pressure force

Gas Kinetic Pressure

- So from mechanical viewpoint (Newton's Law, *F*=d(*mu*)/d*t*), pressure (normal stress) results from change of momentum of molecules (e.g., momentum transfer to wall)

forcer per collision → $\dfrac{F}{A} = \dfrac{\Delta\left(m\vec{C}\right)/\Delta t}{A}$

- To get pressure, need to consider all collisions with wall (sum forces over Δ*t*)



$$p = \underbrace{\text{flux of molec}}\times\underbrace{\text{normal force per collision}}$$

leftward $\dfrac{\#\,collisions}{area \times time} = \dfrac{1}{2} n_{C_1} C_1$ $\qquad = 2mC_1$

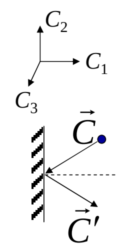
$$= mn_{C_1} C_1^2$$

n_{C_1} = concen. of molecules with speed C_1

Gas Kinetic Pressure

- To get total pressure, need to sum over all molecules (or all speeds) $p = \sum_{C_1} m n_{C_1} C_1^2 = m \sum_{C_1} n_{C_1} C_1^2$
- Define average squared speed

$$\overline{C_1^2} \equiv \frac{\sum_{C_1} n_{C_1} C_1^2}{\sum_{C_1} n_{C_1}} \qquad \Rightarrow p = mn\overline{C_1^2}$$



- At equilibrium, p should be same in all directions
  - shouldn't depend on orientation of wall
  - so should write in terms of C

$$\overline{C^2} \equiv \overline{C_1^2} + \overline{C_2^2} + \overline{C_3^2}$$

At equil. $\overline{C_1^2} = \overline{C_2^2} = \overline{C_3^2}$

$$\overline{C^2} = 3\overline{C_1^2}$$

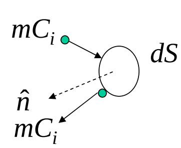
$$p = \frac{1}{3} mn\overline{C^2}$$

in transl. equil.

Gas Kinetic Pressure

- We defined pressure as normal force on wall
  - but we know pressure is defined whether a wall is present or not $\displaystyle \frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_U$
- So we can instead interpret p as total (rightward + leftward) one-way flux of normal momentum across an arbitrary plane in space

$$p = \frac{1}{3} mn\overline{C^2}$$



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Kinetic Energy and Temperature

- Consider kinetic energy of molecules
  - restricting consideration to translational motion

$$E_{tr} = 1/2\underbrace{(Vnm)}_{\text{total mass}}\overline{C^2}$$

$$p = \frac{1}{3}nm\overline{C^2}$$

$$E_{tr} = 1/2\,V\,3p \quad \Rightarrow pV = \frac{2}{3}E_{tr}$$

N = # moles

- Compare to TPG state relation $pV = N\overline{R}T$

$$\Rightarrow E_{tr} = \frac{3}{2}N\overline{R}T$$

$k=\overline{R}/\mathcal{N}_{Av}$ ***Boltzmann's Constant***

on per molec. basis $\frac{E_{tr}}{N} = \frac{3}{2}kT$ **on per mass basis** $e_{tr} = \frac{3}{2}RT$

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Kinetic Energy and Temperature

- (Translational) temperature is a measure of (kinetic) energy $T = \frac{2}{3}\frac{E_{tr}}{N\overline{R}}$
- Specific heat $de = c_v dT$

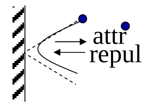
$$\Rightarrow c_{v,tr}/R = 3/2$$

$$\Rightarrow \gamma = \frac{c_{p,tr}}{c_{v,tr}} = \frac{5}{3}$$

- ***Specific heat associated w/ random translational energy***
- ***Agrees with Stat. Thermo.***

Intermolecular Force Correction

- In previous “derivation”, we ignored molecular interactions/“collisions” effects to straight line motion before molecule hits wall (or before molecule crosses our arbitrary plane)
  - attractive force
    $\Rightarrow$ less mom. xfer to wall (across plane
  - repulsive force
    $\Rightarrow$ more mom. xfer



- Correction factor: can show $p = nkT\left(1 \overset{\text{repul}}{\underset{\text{attr}}{\pm}} a\,\underbrace{n\overset{\text{sphere of influence}}{d}{}^3}_{\text{\# other molec. in sphere}}\right)$
  - for hard sphere $p = nkT\left(1 + \dfrac{2\pi}{3} nd^3\right)$

$nd^3 << 1$ for P.G.

Random Kinetic Energy

- Look at $\overline{C^2}$
  - from previous, random (transl.) KE = thermal energy

$$\frac{1}{2} m\overline{C^2} = \frac{3}{2} kT \quad \Rightarrow \sqrt{\overline{C^2}} = \sqrt{\frac{3kT}{m}}$$

  - speed of sound $a = \sqrt{\gamma RT} = \sqrt{\gamma \dfrac{k}{m} T}$

$$\frac{E_{tr}}{N} = \frac{3}{2} kT \qquad \frac{\sqrt{\overline{C^2}}}{a} \sim \sqrt{\frac{3}{\gamma}} \sim O(1)$$

why?

- Note: E_{tr} only function of T, not mass of particle

At fixed T, how does C compare for light vs. heavy particles?