The Micro/Macro

Connection

Readings: Chapter 18

Gas: Molecular Collisions

Gas consists of a vast number of molecules

 $N_A = 6.02 \times 10^{23} mol^{-1}$

Collisions between molecules – elastic – conservation of energy and momentum

The total kinetic energy of all molecules is conserved

The molecules move freely between the collision

We can define the average distance between the collisions – mean free path:

$$\lambda = \frac{1}{4\sqrt{2}\pi \left(N/V \right) r^2}$$





Gas: Molecular Collisions: mean free path

Mean free path:

$$\lambda = \frac{1}{4\sqrt{2}\pi \left(N/V \right) r^2}$$

- N the number of molecules in the gas
- V volume of the gas
- r radius of the molecule

It does not depend on the velocity of the molecules (on the temperature of the gas).

It is approximately the average distance between the molecules in the gas.

Typical values of mean free path:

 $\lambda \sim 100 nm = 10^{-7} m$





Gas: Collisions with the Wall: Presure

During the collision of the molecule with the wall the momentum of the molecule is changed - there is a force acting on the molecule from the wall.

The same force (with the opposite direction) should act on the wall from the molecule.

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$$p = \frac{1}{3} \frac{N}{V} m v_{rms}^{2}$$

$$v_{rms}^{2} = \left\langle v^{2} \right\rangle_{average over all molecules} = \frac{\sum_{i-sum over all molecules}^{i} v_{i}^{2}}{N}$$

Gas: average velocity



$$K_{gas} = N \frac{m v_{rms}^2}{2}$$

Gas: Kinetic Energy

$$K_{gas} = N \frac{m v_{rms}^2}{2}$$

$$p = \frac{1}{3} \frac{N}{V} m v_{rms}^2$$

Ideal Gas:
$$pV = nRT = Nk_BT$$

$$pV = \frac{1}{3}Nmv_{rms}^{2} = Nk_{B}T$$

$$\frac{1}{3}mv_{rms}^{2} = k_{B}T \qquad \frac{1}{2}mv_{rms}^{2} = \frac{3}{2}k_{B}T \qquad v_{rms} = \sqrt{\frac{3k_{B}T}{m}}$$

$$K_{gas} = N\frac{mv_{rms}^{2}}{2} = \frac{3}{2}Nk_{B}T = \frac{3}{2}nRT$$

n - number of moles

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$$K_{gas} = N \frac{m v_{rms}^2}{2} = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

Monatomic gas:

Thermal energy is the kinetic energy of the molecules

$$E_{th} = K_{gas} = \frac{3}{2}nRT = nC_V T$$

$$C_V = \frac{3}{2}R$$

Coefficient **3** is because there three possible motion modes – along x, y, and z – directions

EQUIPARTITION THEOREM: each energy mode has energy $\frac{1}{2}k_B T$

Energy (motion) modes are called degrees of freedom.

For monatomic gas – 3 degrees of freedom

$$K_{gas} = N \frac{m v_{rms}^2}{2} = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

Diatomic molecules

Possible motion:

-motion of a molecule as a whole (translation) along x, y, and z – directions - 3 degrees of freedom

- rotation about y and z- axis - 2 degrees of freedom

(no rotation about x-axis)

- vibration along x-axis – 2 degrees of freedom





Diatomic molecules

- **3 translational degrees of freedom**
- 2 rotation degrees of freedom
- 2 vibration degrees of freedom

Each degree of freedom has $\frac{1}{2}k_{B}T$ energy Then if there are μ degrees of freedom then the thermal energy of the gas is

$$E_{th} = \frac{\mu}{2} N k_B T = \frac{\mu}{2} n R T$$

$$C_V = \frac{\mu}{2}R$$

$C_V = \frac{\mu}{2}R$

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Diatomic molecules

- **3 translational degrees of freedom**
- 2 rotation degrees of freedom
- 2 vibration degrees of freedom

Each degree of freedom of diatomic gas will open at different temperature



$$C_V = \frac{\mu}{2}R$$

Solid (or molecules with three atoms)

6 degrees of freedom

$$C_V = \frac{6}{2}R = 3R$$

The Second Law of Thermodynamics

Reversible and Irreversible Processes

Reversible process: If we change the direction of velocities of particles then they will go backward: both types of motion is possible



Reversible and Irreversible Processes

Irreversible process: Heat transfer from hot to cold



Diffusion of molecules of gas



The molecules will never return to the initial position

Reversible and Irreversible Processes



During this process we have only collision between the particles – the collision between the particles is the reversible process. Let us change the direction of velocities of all molecules at moment of time D.

Will they return back to the initial state /? Yes.

Does it mean that the molecules can return to the initial state *I* from the state D? No. To return to state *I* the molecules should have specific positions and specific velocities. The probability to have such state is very very low. 15

Second Law of Thermodynamics

1. When two systems at different temperatures interact, heat energy is transferred spontaneously from the hotter to the colder system, never from the colder to the hotter.

1. The entropy of an isolated system never decreases. The entropy either increased, until the system reaches equilibrium, or if the system began in equilibrium, stays the same.

The entropy is the probability of realization of a given macroscopic state.

