

Kinetic Theory of Gases

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Zeroth law of thermodynamics

Reversible and Irreversible processes

First law of Thermodynamics

Second law of Thermodynamics

Entropy

Thermodynamic Potential

Third Law of Thermodynamics

Phase diagram

# Kinetic Theory of Gases and Thermodynamics

**Bedanga Mohanty**

School of Physical Sciences  
NISER, Jatni, Orissa

Course on Kinetic Theory of Gases and Thermodynamics - P101

Suppose to be 12 lectures.

- Kinetic Theory of Gases

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- Kinetic Theory of Gases
- Principles of thermodynamics, thermodynamic state, extensive/intensive variables.

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- internal energy, Heat, work

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References:

- Thermodynamics, kinetic theory and statistical thermodynamics by Francis W. Sears, Gerhard L. Salinger
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About 5-7 Tutorials

One Quiz (10 Marks) and 2 Assignments (5 Marks)

End Semester Exam (40 Marks)

- Developed by Boltzmann, Maxwell and Clausius in later half of 19th Century

We discuss a simplified model, but it describes the basic ideas and experimental findings correctly.

## Assumptions

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- Collisions are **elastic**.
- Any interaction between the balls only occur during the collision (direct touch). For distances  $d > 2 r_0$  no interactions.

How does the interaction potential look like ?

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How does the interaction potential look like ?

When is the model called as **ideal gas** : if  $r_0 \ll \langle d \rangle$  - mean distance between the atoms. This implies: Atomic volume  $\ll$  Volume of the container  $V$ .

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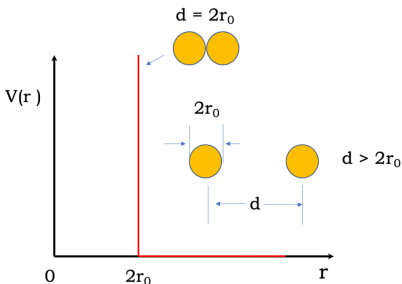
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## Model of Ideal Gas

How does the interaction potential look like ?

When is the model called as **ideal gas** : if  $r_0 \ll \langle d \rangle$  - mean distance between the atoms. This implies: Atomic volume  $\ll$  Volume of the container  $V$ .



- $V(r) = \infty$  for  $|r| \leq 2r_0$
- $V(r) = 0$  for  $|r| > 2r_0$

## Example

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Pressure 1 bar and temperature 300 K (room temperature)  $1 \text{ cm}^3$  of a gas  $\sim 3 \times 10^{19}$  molecules. The  $\langle d \rangle \sim 3 \text{ nm}$ .

For helium atom  $r_0 \sim 0.05 \text{ nm}$ .

$r_0/\langle d \rangle \sim 0.017 \ll 1$ .

Helium gas at 1 bar pressure and room temperature can be regarded as ideal gas.



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## Further Assumptions:

- Atoms treated as point mass

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## Further Assumptions:

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- Only take into account translational energy

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Let there be  $N$  molecules in a volume  $V$ . The number density  $n = N/V$ .

- Now consider only a part  $n_x$  of all molecules per  $cm^3$  in a cubical volume.

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- Each molecule has mass  $m$ .

# Basic equations

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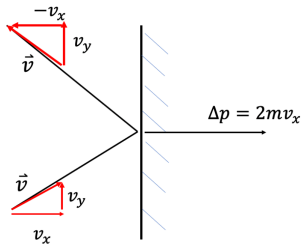
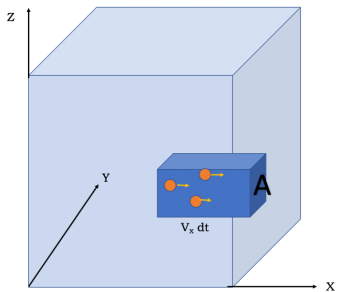
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- Number of molecules hitting the surface area  $A$  in the time interval  $\Delta t$  (inside the cuboid):  $Z = n_x v_x \Delta t A$ .

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- Number of molecules hitting the surface area  $A$  in the time interval  $\Delta t$  (inside the cuboid):  $Z = n_x v_x \Delta t A$ .
- The momentum transferred :  $\Delta p_x = 2 m v_x$  (elastic collisions).
- Force =  $\frac{\text{change in momentum}}{\text{time interval}} = Z \frac{\Delta p_x}{\Delta t} = 2 Z m v_x / \Delta t$ .

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- Pressure on the wall = Force / Area =  $2 m n_x v_x^2$ .
- Not all molecules will have the same velocity. The mean square value of velocities  $\langle v_x^2 \rangle = \overline{v_x^2} = \frac{1}{N} \int N(v_x) v_x^2 dv_x$
- $N(v_x)$  is the number of molecules in the volume  $V$  with velocity component  $v_x$  in the interval  $v_x$  to  $v_x + dv_x$ .

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- On the average 1/2 molecules move in the positive X-direction and the other 1/2 in negative X-direction.

## Basic equations

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Phase diagram

- Pressure exerted by all molecules in the X-direction on the wall in Y-Z plane:  $P = \frac{1}{2} n 2 m \overline{v_x^2} = n m \overline{v_x^2}$ .
- Under stationary condition, the velocities of the molecules are isotropically distributed. This means each direction has equal probability.
- Pressure of a gas is isotropic.
- Mean momentum transfer is same or equal in all directions:  $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3} \overline{v^2}$

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- The pressure,  $P = \frac{1}{3} n m \overline{v^2} = \frac{2}{3} n \frac{1}{2} m \overline{v^2} = \frac{2}{3} \overline{E_{kin}}$ .
- $\overline{E_{kin}} = \frac{1}{2} m \overline{v^2}$  is the mean kinetic energy per molecule.
- $PV = \frac{2}{3} N \frac{1}{2} m \overline{v^2}$

# Absolute temperature

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Phase diagram

- We have earlier studied that the product of  $PV$  depends on temperature - Boyle or Boyel-Mariotte's law.
- Look at  $PV = \frac{2}{3} N \frac{1}{2} m \overline{v^2}$  , This implies mean kinetic energy depends on temperature.

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- We have earlier studied that the product of  $PV$  depends on temperature - Boyle or Boyel-Mariotte's law.
- Look at  $PV = \frac{2}{3} N \frac{1}{2} m \overline{v^2}$  , This implies mean kinetic energy depends on temperature.
- We can then define absolute temperature as a quantity that is proportional to  $\overline{E_{kin}}$ .
- Temperature (in units of Kelvin) is defined through the relation:  $\frac{1}{2} m \overline{v^2} = \frac{3}{2} K T$ . Where  $K$  is the Boltzmann constant with the value  $1.38054 \times 10^{-23}$  Joule/K.
- Then we get  $PV = N K T$ , this is the generalisation of the Boyles law.



- Each molecule can move in 3-directions, X, Y, Z  $\Rightarrow$  **3 degrees of freedom** for translation.
- We had discussed  $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3} \overline{v^2}$
- We had discussed  $\frac{1}{2} m \overline{v^2} = \frac{3}{2} K T$ .
- Hence the mean kinetic energy of a molecule at temperature  $T$  is  $\overline{E_{kin}} = \frac{1}{2} K T$  per degrees of freedom.

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- We had discussed  $\frac{1}{2} m \overline{v^2} = \frac{3}{2} K T$ .
- Hence the mean kinetic energy of a molecule at temperature  $T$  is  $\overline{E_{kin}} = \frac{1}{2} K T$  per degrees of freedom.
- Law: In a gas that is kept sufficiently long at a constant temperature  $T$ , the energy of the atoms or molecules is uniformly distributed by collisions over all degrees of freedom. Therefore each molecule has on the average the energy  $\overline{E_{kin}} = f \left(\frac{1}{2}\right) K T$ ; where  $f$  is the number of degrees of freedom accessible to the molecules.

## Maxwell velocity distribution

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Students should closely look at the derivation of velocity distribution by Maxwell.

J. C. Maxwell, Illustrations of dynamical theory of gases. Part I. On the motions and collisions of perfectly elastic spheres. Reprinted in The Scientific Papers of James Clerk Maxwell, edited by W. D. Niven (Cambridge U.P., Cambridge, UK, 1890), Vol. I. pp. 377-391.

There is an interesting discussion as he himself called the reasoning – **May appear precarious.**

Also look at alternate ways of derivation by E. U. Condon - Physical Review 54 (1938) 937.

Tutorials # 1

## Maxwell velocity distribution

- Consider a molecule of mass  $m$  of ideal gas.  $E = E_{kin} + \epsilon^{int}$ ;  $E_{kin} = \frac{p^2}{2m}$ ,  $p =$  momentum and  $\epsilon^{int}$  is the internal energy (non-translational), could be rotational or vibrational etc.  $\epsilon^{int}$  does not depend on  $r$  and  $p$  and is a constant factor.
- The probability of finding a molecule with a position vector  $\vec{r}$  to  $\vec{r} + d\vec{r}$  and momentum  $\vec{p}$  to  $\vec{p} + d\vec{p}$  is :  $P(r, p)d^3rd^3p$ .
- $P(r, p)d^3rd^3p \propto \text{Exp}(-\frac{E_{kin}}{KT}) d^3rd^3p$ ; The first term is a Boltzmann factor and second part is Volume term.

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- Under similar considerations, the number of molecules between  $\vec{r}$  to  $\vec{r} + d\vec{r}$  and velocities  $\vec{v}$  to  $\vec{v} + d\vec{v}$  ( $\vec{v} = \vec{p}/m$ ) is:  
 $f(r, v)d^3rd^3v = C \text{Exp}(-\frac{mv^2}{2KT}) d^3rd^3v$ ;  $C$  is the constant of proportionality.
- $C$  can be determined from  $\int_r \int_v f(r, v)d^3rd^3v = N$  (total number of particles).

## Maxwell velocity distribution

- Using the previous equation and as all component of velocity are equally probable, we can write  $C V [\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \text{Exp}(-\frac{mv_z^2}{2KT}) dv_z ]^3 = N$
- $\int_{-\infty}^{\infty} \text{Exp}(-\frac{mv_z^2}{2KT}) dv_z = \sqrt{\frac{2KT}{m}} \int_{-\infty}^{\infty} \text{Exp}(-y^2) dy = \sqrt{\frac{2\pi KT}{m}}$ .
- So,  $C = \frac{N}{V} (\frac{m}{2\pi KT})^{3/2}$ .
- $f(r, v) d^3r d^3v = n (\frac{m}{2\pi KT})^{3/2} \text{Exp}(-\frac{mv^2}{2KT}) d^3r d^3v$
- $f$  is only function of velocity, if we assume distribution of molecular velocities are uniform in space. This is called the Maxwell - Boltzmann velocity probability distribution.

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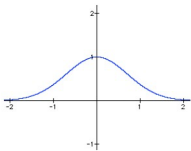
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- $f$  is only function of velocity, if we assume distribution of molecular velocities are uniform in space. This is called the Maxwell - Boltzmann velocity probability distribution.
- What is of interest is the number density  $n(v)dv$  of all molecules per unit volume with velocities between  $v$  and  $v + dv$ .
- $n(v)dv = f(v) 4\pi v^2 dv = n (\frac{m}{2\pi KT})^{3/2} 4\pi v^2 \text{Exp}(-\frac{mv^2}{2KT}) dv$  - Maxwell - Boltzmann velocity distribution.

# MB Distributions

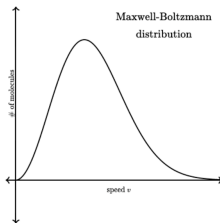
One is a symmetric distribution, Gaussian in Shape and extends to  $-\infty$  to  $\infty$ . The other is range  $v \geq 0$  (no negative value), asymmetric as there is a factor  $v^2$ .

$$f(u) = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT}$$



In the above formula  $u$  denotes one of the velocity components.

Note well: the MB distribution is strongly peaked around  $u = 0$ . The width of the distribution is related to the square root of the temperature.



Experiments: Usually flux density is measured,  $N = n(v) v$  - Number of particles reaching detector per unit time. Then the velocity distribution of flux density is  $N(v) = n v f(v)$  - now the dependence is  $v^3$  not  $v^2$ .



- Maximum of the distribution will give the most probable velocity  $v_p$ . Obtained by  $\frac{dn(v)}{dv} = 0$ . This will give  $v_p = \sqrt{\frac{2KT}{m}}$  - Tutorial #2
- Mean velocity  $\bar{v} = \int_0^\infty v f(v) dv = 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} \int_0^\infty v^3 \text{Exp}\left(-\frac{mv^2}{2KT}\right) dv = 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} \left(\frac{2KT}{m}\right)^2 \int_0^\infty y^3 e^{-y^2} dy = 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} \left(\frac{2KT}{m}\right)^2 \frac{1}{2}$  - Tutorial #3
- Mean velocity  $\bar{v} = \sqrt{\frac{8KT}{\pi m}}$
- Relation between  $v_p$  and  $\bar{v}$ :  $\bar{v} = \frac{2v_p}{\sqrt{\pi}} \Rightarrow \bar{v} > v_p$
- Mean square velocity  $\overline{v^2} = \int_0^\infty v^2 f(v) dv = \frac{3KT}{m}$  - Tutorial #4
- Mean energy per molecule :  $\frac{mv^2}{2} = \frac{3}{2}KT = fKT$ . This we have already discussed.

- Root mean square velocity:  $\sqrt{\overline{v^2}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3KT}{m}} = \sqrt{\frac{3}{2}} v_p$
- $v_p < \bar{v} < \sqrt{\langle v^2 \rangle}$
- Since all velocities can be expressed in terms of  $v_p$ ,
- $n(v)dv = n \frac{4v^2}{v_p^3 \sqrt{\pi}} \text{Exp}(-\frac{mv^2}{2KT}) dv = n \frac{4v^2}{v_p^3 \sqrt{\pi}} \text{Exp}(-\frac{v^2}{v_p^2}) dv$

# Properties

Kinetic Theory of Gases

Thermodynamics

State Variables

Zeroth law of thermodynamics

Reversible and Irreversible processes

First law of Thermodynamics

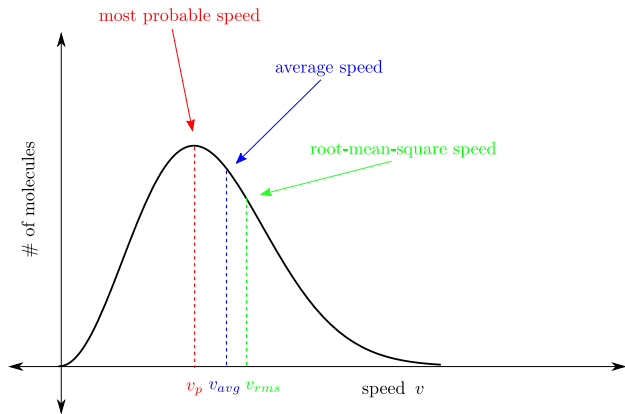
Second law of Thermodynamics

Entropy

Thermodynamic Potential

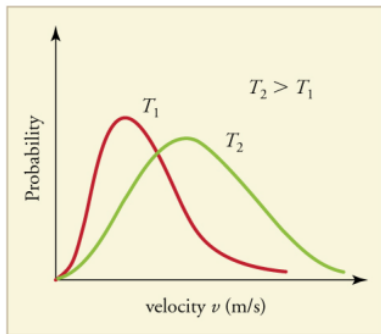
Third Law of Thermodynamics

Phase diagram



## Properties

Temperature dependence - strong dependence, if  $\frac{T_1}{T_2} = 1:4$ , the numerical values of  $\bar{v}$ ,  $v_p$  and  $\sqrt{v^2}$  change by factor 2 as they are proportional to square root of temperature.



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## Problem

Kinetic Theory of Gases

Thermodynamics

State Variables

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Second law of Thermodynamics

Entropy

Thermodynamic Potential

Third Law of Thermodynamics

Phase diagram

The density of nitrogen gas  $N_2$  at room temperature  $T = 300$  K at a pressure of 1 bar is  $\rho(N_2) = 1.2$  Kg/ $m^3$  and  $m(N_2) = 4.67 \times 10^{-26}$  kg.

Calculate :  $v_p$ ,  $\bar{v}$ ,  $\sqrt{\langle v^2 \rangle}$  and  $\overline{E_{kin}}$ .

$$v_p = \sqrt{\frac{2KT}{m}} = 422 \text{ m/sec}$$

$$\bar{v} = \frac{2v_p}{\sqrt{\pi}} = 476 \text{ m/sec}$$

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3KT}{m}} = 517 \text{ m/sec}$$

We see:  $v_p < \bar{v} < \sqrt{\langle v^2 \rangle}$

Mean kinetic energy of a molecule :  $\overline{E_{kin}} = \frac{3}{2}KT = 6.21 \times 10^{-21}$  J

Energy density =  $n \overline{E_{kin}} = 0.15$  J/ $cm^3$ .