GENERAL PHYSICS PH1110

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2. THERMODYNAMICS

2.1 KINETIC THEORY AND LAWS OF DISTRIBUTION

1. Starting points

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- **States of matter**

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$$\boxed{N_A = 6.02214 \times 10^{23}\,\mathrm{mol}^{-1}}$$

2. THERMODYNAMICS

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- Here, $N = nN_A$ is the total number of particles in the gas.

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A gas which obeys the equation of state, $pV = nRT$, for all pressures, volumes and temperatures is called an **ideal gas**.

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  - The gas pressure cannot be explained if the gas is continuous.

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5. The particles mostly move in straight lines at constant velocities. The collision time is negligible compared with the time between collisions.

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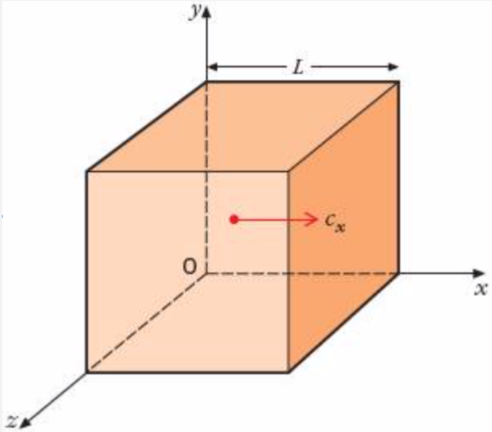

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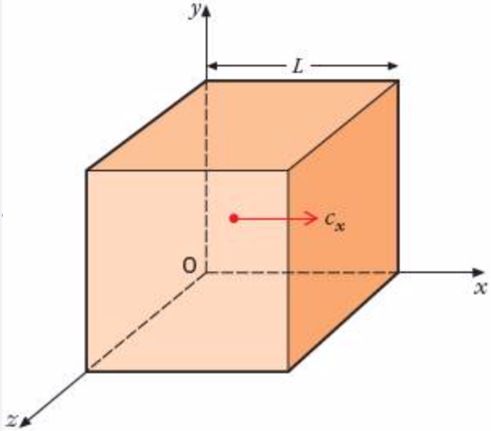

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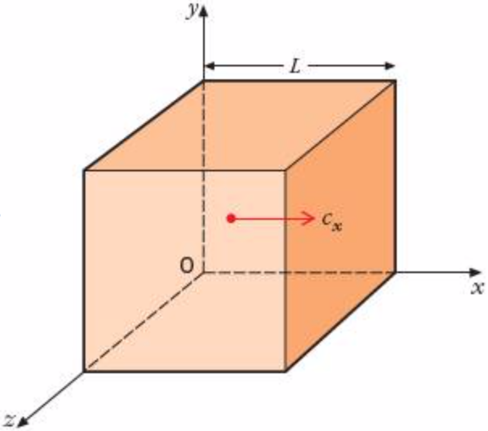

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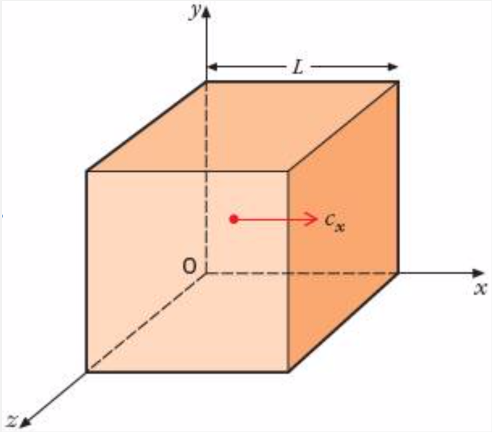

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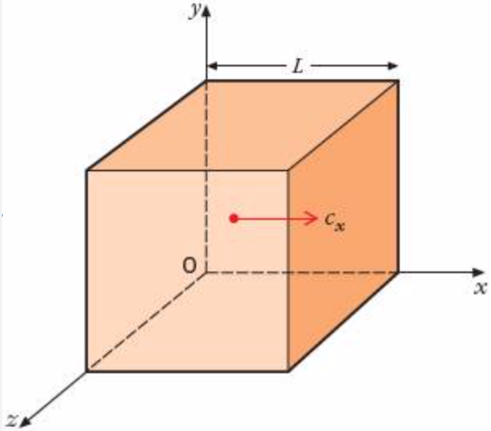

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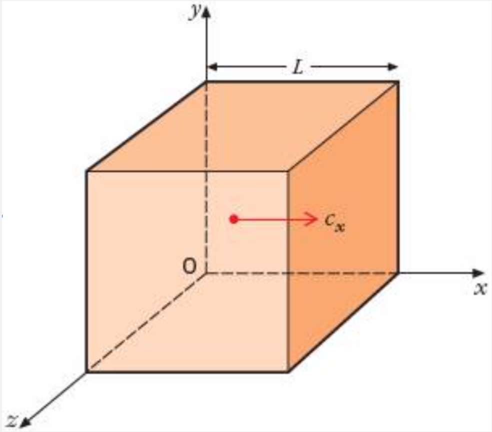

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- Finally:

3. Kinetic theory of gases

- Therefore, $pV = Nm\left\langle c_x^2 \right\rangle.$
- Because the number of particles is very large and the motion of the particles is random $\rightarrow \left\langle c_x^2 \right\rangle = \left\langle c_y^2 \right\rangle = \left\langle c_z^2 \right\rangle.$
- Since $c^2 = c_x^2 + c_y^2 + c_z^2 \rightarrow \left\langle c^2 \right\rangle = \left\langle c_x^2 \right\rangle + \left\langle c_y^2 \right\rangle + \left\langle c_z^2 \right\rangle = 3\left\langle c_x^2 \right\rangle.$
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Remember that, in this relation, m is the molecular mass and $\left\langle c^2 \right\rangle$ is the **mean-square speed** of the molecules.

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♣ **Average kinetic energy and thermodynamic temperature**

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3. Kinetic theory of gases

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3. Kinetic theory of gases

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3. Kinetic theory of gases

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In thermal equilibrium, the average energy is shared equally to every degree of freedom.

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3. Kinetic theory of gases

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- **Root-mean-square speed**

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  - Normally: $c_{\text{r.m.s.}} \approx 1.1 \times \langle c \rangle$.

3. Kinetic theory of gases

- **Internal energy**

3. Kinetic theory of gases

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Internal energy of a thermodynamic system

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$$\boxed{U = \sum E_{\mathrm{k}} + \sum E_{\mathrm{p}}} \qquad \begin{cases} E_{\mathrm{k}} \rightarrow \text{random motions of molecules} \\ E_{\mathrm{p}} \rightarrow \text{interactions between molecules} \end{cases}$$

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3. Kinetic theory of gases

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  - Here, μ is the molar mass and m is the mass of the system.

3. Kinetic theory of gases

1 The speed of seven molecules in a gas are numerically equal to 2, 4, 6, 8, 10, 12, and 14 units. Find the numerical values of

(a) the mean speed $\langle c \rangle$,

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(a) the mean speed $\langle c \rangle$, [8.0 units]

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3. Kinetic theory of gases

2 Find the total kinetic energy of molecules in one mole of ideal gas at standard temperature (273 K).

Take $R = 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

3 The mass of a nitrogen molecule is 4.6×10^{-26} kg. Find the root-mean-square speed of molecules in nitrogen gas at 27 °C.

Take $k_{\mathrm{B}} = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$.

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$$c_{\mathrm{r.m.s.}} = \sqrt{\frac{3k_\mathrm{B}T}{m}} = \sqrt{\frac{3\times 1.38\times 10^{-23}\times 300}{4.6\times 10^{-26}}} = 520\,\mathrm{m\,s^{-1}}$$

2. THERMODYNAMICS

2.1 KINETIC THEORY AND LAWS OF DISTRIBUTION

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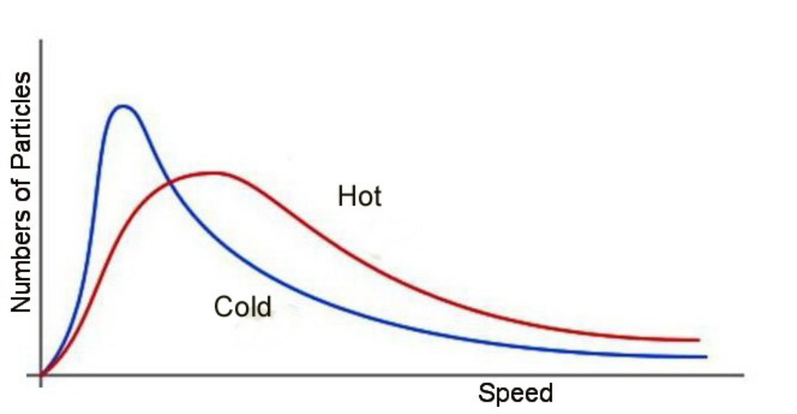

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- The function $F(c)$ is called the **distribution function** of the molecules with speed.

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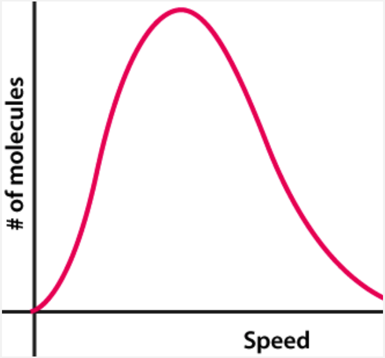

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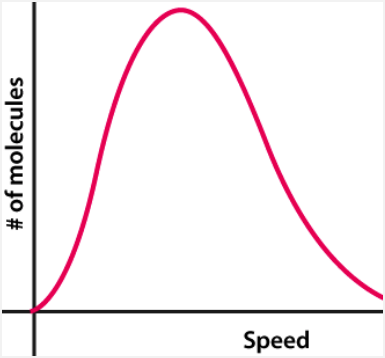

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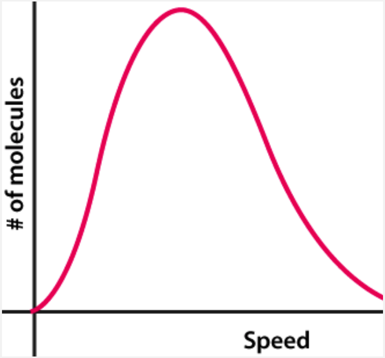

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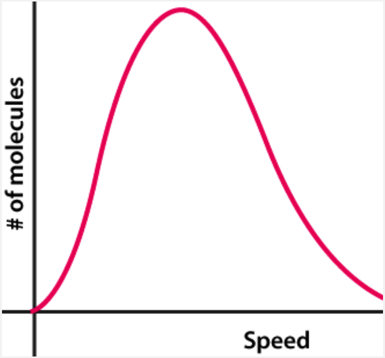

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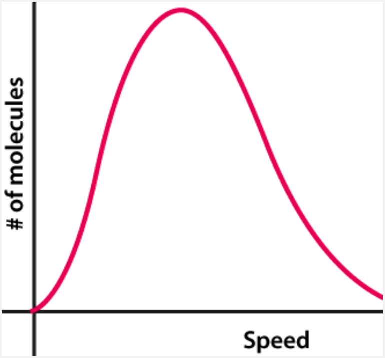

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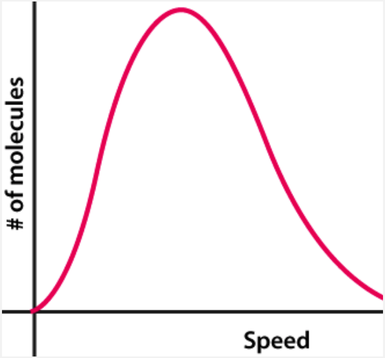

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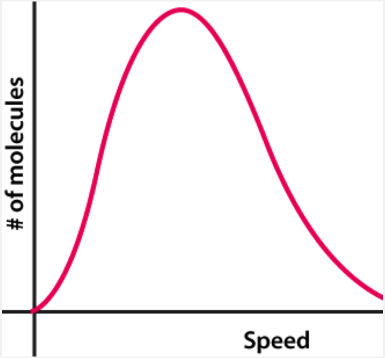
A and α are positive constants.



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$$\langle f \rangle = \sum f(c_i) p_i \quad \rightarrow \quad \langle f \rangle = \int f(c) \mathrm{d}p = \int f(c) \frac{\mathrm{d}N}{N}$$

$$\boxed{\langle f \rangle = \int_0^\infty f(c) F(c) \mathrm{d}c}$$

4. Maxwell distribution

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$$\langle E_\mathrm{k}\rangle = \frac{1}{2}m\left\langle c^2\right\rangle = \frac{3}{2}k_\mathrm{B}T \quad \rightarrow \quad \frac{1}{2}m\frac{3}{\alpha} = \frac{3}{2}k_\mathrm{B}T$$

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$$\boxed{F(c) = \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} 4\pi c^2 \exp\left(-\frac{mc^2}{2k_\mathrm{B}T}\right)}$$

4. Maxwell distribution

♣ **Typical speeds**

4. Maxwell distribution

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$$c_{\mathrm{r.m.s.}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}} = \sqrt{\frac{3RT}{\mu}}$$

- **Most probable speed** (at which $F(c)$ is maximum):

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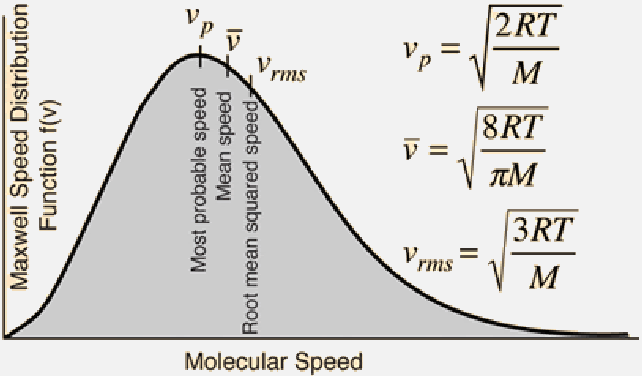
4. Maxwell distribution

♣ Typical speeds

$$f(v) = 4\pi \left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$



$$v_p = \sqrt{\frac{2RT}{M}}$$

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

2. THERMODYNAMICS

2.1 KINETIC THEORY AND LAWS OF DISTRIBUTION

5. Boltzmann distribution

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- **Atmospheric pressure**

5. Boltzmann distribution

♣ Atmospheric pressure

- Suppose that the gas in the uniform gravitational field of the Earth is an ideal gas.

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- For a small amount (mass $\mathrm{d}M$ and volume $\mathrm{d}V$) of gas at z:

5. Boltzmann distribution

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$$p\mathrm{d}V = \frac{\mathrm{d}M}{\mu}RT$$

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$$\frac{\mathrm{d}p}{p} = -\frac{\mu g}{RT}\mathrm{d}z$$

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Here, p_0 is the pressure at $z = 0$.

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- Let n be the molecular density (number of molecules per unit volume):

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- This is called the **Boltzmann distribution**, the distribution of particles in term of potential energy.