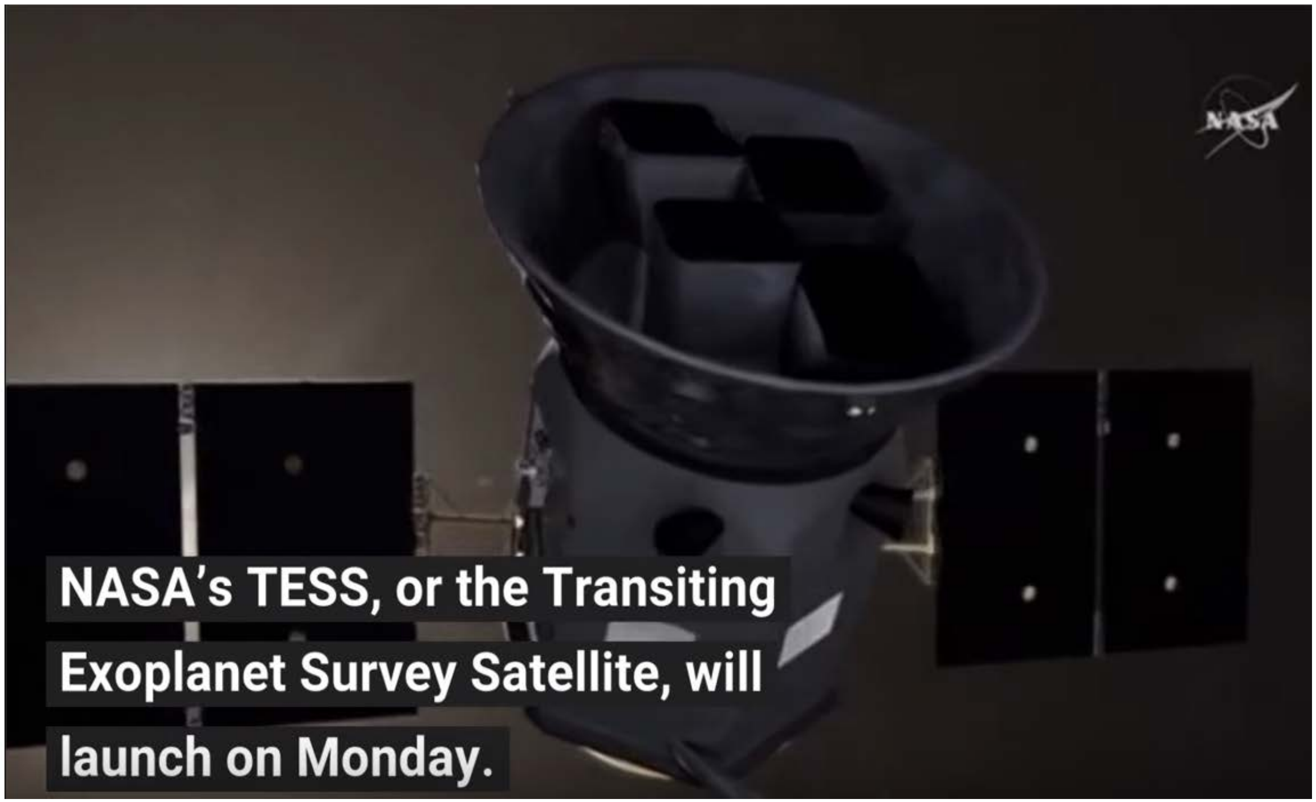
Thermal Physics

Lecture 3 – Heat, Specific Heat, First Law of Thermodynamics

Textbook reference: 18.4-18.6



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This lecture...

- Equipartition of energy
- Degrees of freedom
- Mean free path of a gas molecule
- Distribution of molecular speeds

Textbook sections 19.3, 19.5, 19.6, 19.8

Last lecture

$$PV = nRT$$

$$PV = Nk_BT$$

Assumptions of kinetic theory of gasses.

$$\Rightarrow T = \frac{2}{3k_B}(\frac{1}{2}m_0\overline{v^2}) \quad v_{rms} = \sqrt{\frac{3k_BT}{m}}$$

$$PV = \frac{2}{3} N \left(\frac{1}{2} m_0 \overline{v^2}\right)$$

$$PV = N k_B T$$

$$\Rightarrow T = \frac{2}{3k_B} \left(\frac{1}{2} m_0 \overline{v^2}\right)$$

Definition of temperature for a gas

What is this rms nonsense anyway?

$$v_{rms} = \sqrt{\overline{v^2}}$$

Find the rms velocity of:

-1ŷ, 2ŷ, 4ŷ, -3ŷ

$$v_{rms} = \sqrt{\frac{1+4+16+9}{4}}$$

$$= 2.74$$

Question

The rms speed of an oxygen molecule (O_2) in a container of oxygen gas is 625 m/s. What is the temperature of the gas?

$V_{rms} = 625\, m/s \quad m_0 = \dfrac{32 \times 10^{-3}}{6.022 \times 10^{23}} = 5.31 \times 10^{-26}$

$$T = \frac{2}{3k_B}\left(\frac{1}{2} m_0 \bar{v}^2\right)$$

$$= \frac{2}{3 \times 1.381 \times 10^{-23}} \times \frac{1}{2} \times 5.31 \times 10^{-26} \times 625^2$$

$$= 501\, K$$

Equipartition of energy...

- Kinetic theory says: $$T = \frac{2}{3k_\mathrm{B}}\left(\frac{1}{2}m_0\overline{v^2}\right)$$
- Let's go back into derivation:

$$\frac{3}{2}k_\mathrm{B}T = \frac{1}{2}m_0\overline{v^2} = \frac{1}{2}m_0\left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right)$$

  - But there are many many molecules, and they are just as likely to move in the x, y or z direction. We assumed:

$$\Rightarrow \frac{1}{2}m_0\overline{v_x^2} = \frac{1}{2}m_0\overline{v_y^2} = \frac{1}{2}m_0\overline{v_z^2} = \frac{1}{2}k_\mathrm{B}T$$

  - Each direction of motion stores on average the **same amount of energy → equipartition**.

Equipartition>Degrees of freedom…

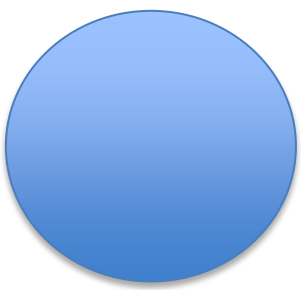
- Every type of molecule has a certain number of **degrees of freedom** f, which are independent ways in which the molecule can store energy.
  - **Equipartition of energy** means each degree of freedom of a molecule stores, on average, an energy:

$$E(\text{per d.o.f.}) = \frac{1}{2}k_{\mathrm{B}}T$$

- What degrees of freedom are there?
  - Depends on the type of molecule.

Monatomic (1 atom)

eg. He



f = 3

Energy = $\frac{3}{2}k_B T$

- Can move in the x, y, z direction: can have KE in each of these directions (translational)
- Classically: can rotate and have rotational KE but very little as

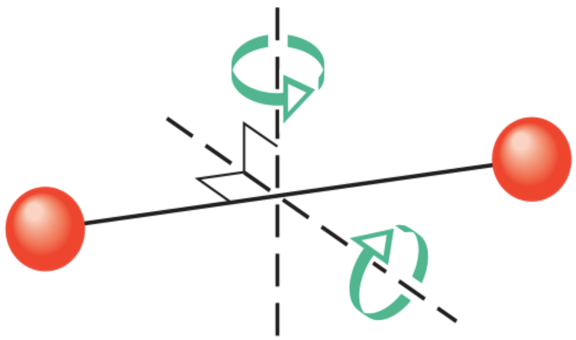
$$I = \frac{2}{5}MR^2$$

the mass is concentrated in the nucleus (~10^{-15}m)

Diatomic molecules…

- For example, O_2.

- Degrees of freedom:
  - It has **translational motion** in the x, y, and z directions → 3 degrees of freedom
  - Can **rotate** about 2 axes → 2 degrees of freedom
  - Can vibrate too at T > 10000 K (would add 2 extra d.o.f. for KE and PE; ignored at room temperature)

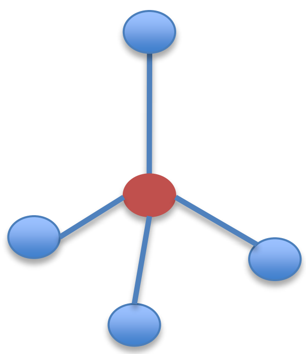


Average total kinetic energy per diatomic molecule at room temperature

$$E = \frac{5}{2} k_{\mathrm{B}} T$$

Polyatomic (many atoms)

eg. Methane
CH_4



- Can move in the x, y, z direction: can have KE in each of these directions (translational)
- Classically: can rotate about 3 axes
- Can vibrate in multiple ways
- Total d.o.f. up to 15!

Note: We will come back to this later but below ~100K molecule does not rotate. Below ~ 1000K molecule does not vibrate

A crystal

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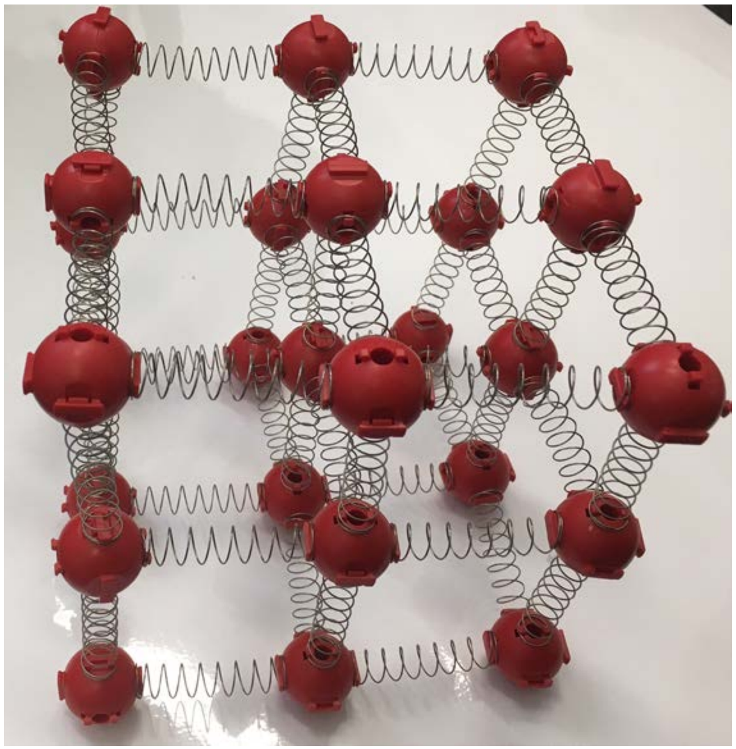

Consider the atom in the middle.

- How many translational f?
- How many rotational f?
- How many vibrational f?

Theorem of Equipartition of energy

Each degree of freedom contributes $\frac{1}{2}k_B T$ to the energy of a system, where possible degrees of freedom are those associated with translation, rotation, and vibration of molecules.

Total energy of a gas = $\frac{1}{2} f N k_B T$

Monatomic gas: $E_{int} = \frac{3}{2} N k_B T$

Question

Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas, but container B has twice the volume of container A.

(i) What is the average translational kinetic energy per molecule in container B?

(ii) Describe the internal energy of the gas in container B.

(a) Twice that of container A

(b) The same as that of container A

(c) Half that of container A

(d) Impossible to determine

(iii) And (iv) What if the gasses are of different types?

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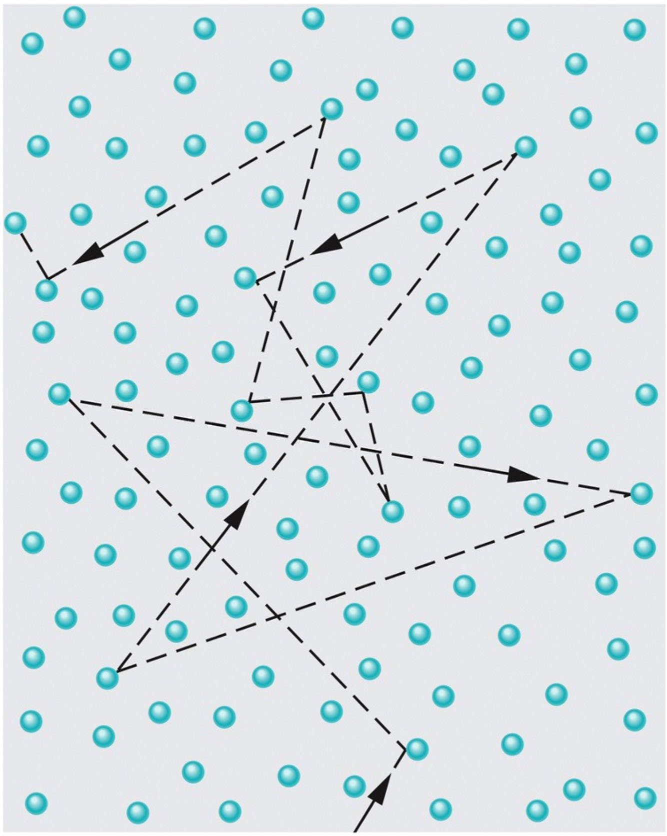
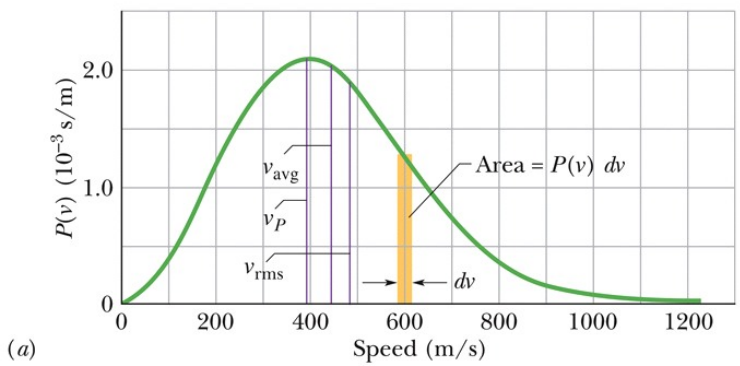
Mean Free Path

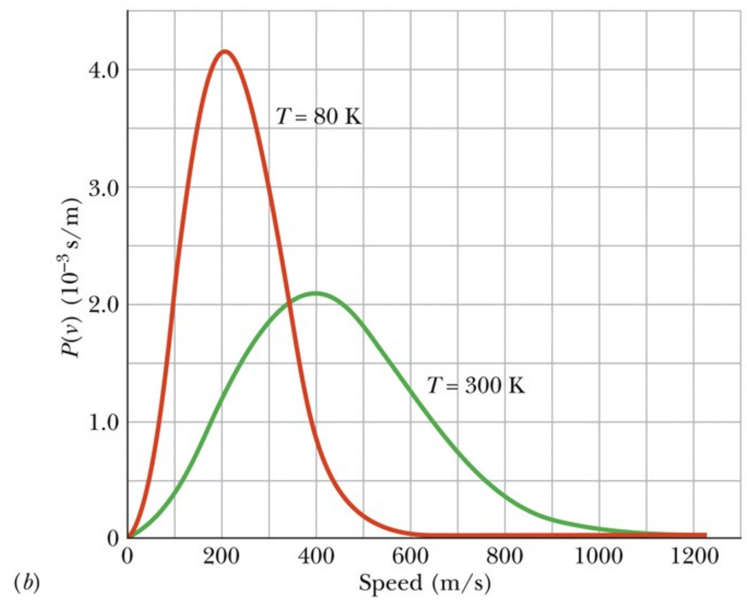
This is average distance traversed between collisions.

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V}$$



The distribution of Molecular speeds





$$P(v) = 4\pi(\frac{M}{2\pi RT})^{3/2}v^2e^{-Mv^2/2RT}$$

The distribution of Molecular speeds

$$v_{avg} = \int_0^\infty vP(v)dv = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{rms} = \sqrt{(v^2)_{avg}}$$

$$(v^2)_{avg} = \int_0^\infty v^2 P(v)dv = \frac{3RT}{M}$$

$$v_P \rightarrow dP/dv = 0 \rightarrow v_P = \sqrt{\frac{2RT}{M}}$$

Question

In oxygen (molar mass M = 0.0320 kg/mol) at room temperature (300 K), what fraction of molecules have speeds in the interval 599 to 601 m/s?

Question

A 2.00 mol sample of oxygen gas is confined to a 5.00 L vessel at a pressure of 8.00 atm. Find the average translational kinetic energy of the oxygen molecules under these conditions.

Question

(a) How many atoms of helium gas fill a spherical balloon of diameter 30.0 cm at 20.0 ^{o} C and 1.00 atm?

(b) What is the average kinetic energy of the helium atoms?

(c) What is the rms speed of the helium atoms?