PHY101: Introduction to Physics I

Monsoon Semester 2023

Lecture 31

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Previous Lecture

Monoatomic gas
Involvement of temperature

This Lecture

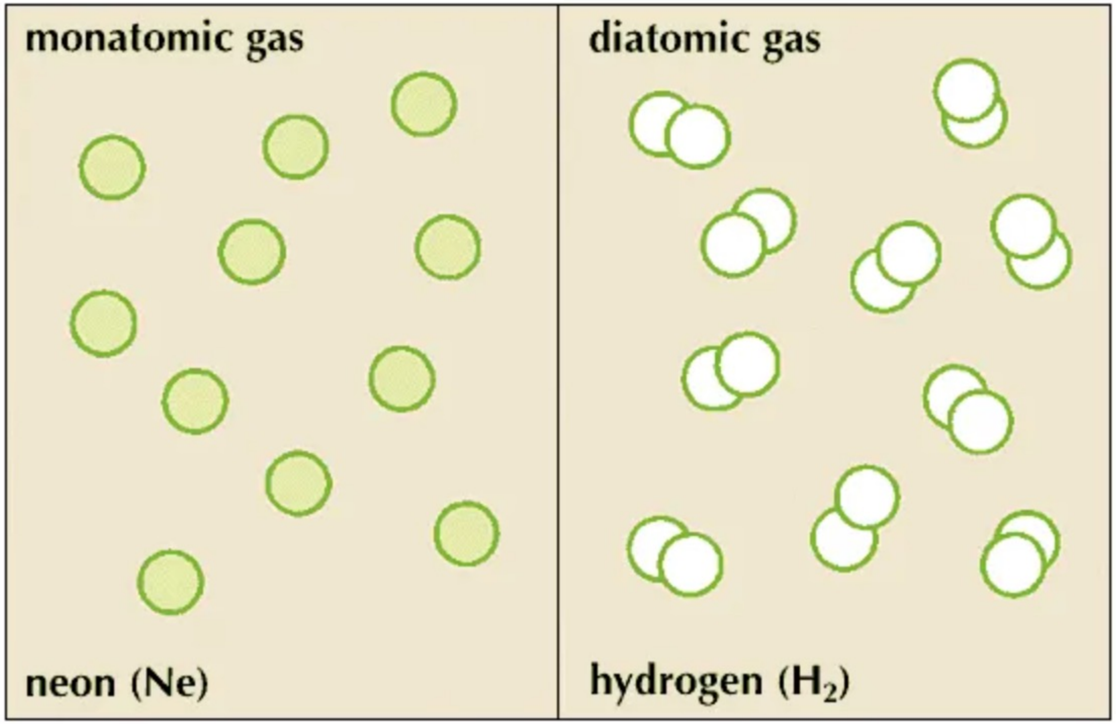
Diatomic gas system

Energy associated with degrees of freedom

Equipartition theorem

Diatomic gas and its dynamics

Example



Molecules of neon, a monatomic gas, have only one atom.
Molecules of diatomic gases, such as hydrogen, have two atoms.

Rotational and vibrational motion

https://en.m.wikipedia.org

Total kinetic energy of a diatomic gas molecule

DIATOMIC MOLECULE

- Consider now a gas containing a diatomic molecule. The diatomic molecule consists of atoms A and B. The molecule has a center of mass motion as well as the internal motion (rotation, vibration).
- If $\vec{v}_A$ and $\vec{v}_B$ are the corresponding velocities and the gas is at temperature T, then

$$\left\langle \frac{1}{2} m_A v_A^2 \right\rangle = \frac{3}{2} kT = \left\langle \frac{1}{2} m_B v_B^2 \right\rangle .$$

- Thus the total kinetic energy of A+B (the molecule)=$3kT$

  (*Here* $k \equiv k_B$, *the Boltzmann constant*)

Kinetic energy of the center of mass

- Now consider the Center of Mass (COM) of the molecule,
- The velocity of the COM is $\vec{V}_{CM} = \frac{m_A\vec{v}_A + m_B\vec{v}_B}{m_A + m_B}$.
- Therefore, $V_{CM}^2 = \vec{V}_{CM} \cdot \vec{V}_{CM}$

$$= \left(\frac{m_A\vec{v}_A + m_B\vec{v}_B}{m_A + m_B}\right) \cdot \left(\frac{m_A\vec{v}_A + m_B\vec{v}_B}{m_A + m_B}\right)$$

$$= \frac{1}{M^2}\left(m_A^2 v_A^2 + m_B^2 v_B^2 + 2m_A m_B \vec{v}_A \cdot \vec{v}_B\right)$$

- where $M = m_A + m_B$

$$\Rightarrow \frac{1}{2}MV_{CM}^2 = \frac{1}{M}\left(\frac{1}{2}m_A^2 v_A^2 + \frac{1}{2}m_B^2 v_B^2 + m_A m_B \vec{v}_A \cdot \vec{v}_B\right)$$

Average kinetic energy of the center of mass

Take average,

$$\left\langle \frac{1}{2} M V_{CM}^2 \right\rangle = \frac{1}{M}\left(m_A \left\langle \frac{1}{2} m_A v_A^2 \right\rangle + m_B \left\langle \frac{1}{2} m_B v_B^2 \right\rangle + m_A m_B \langle \vec{v}_A \cdot \vec{v}_B \rangle \right)$$

Now, as already seen, for individual motions of A and B,

$$\left\langle \frac{1}{2} m_A v_A^2 \right\rangle = \frac{3}{2} kT = \left\langle \frac{1}{2} m_B v_B^2 \right\rangle .$$

Thus,

$$\left\langle \frac{1}{2} M V_{CM}^2 \right\rangle = \frac{1}{M}\left((m_A + m_B) \frac{3}{2} kT + m_A m_B \langle \vec{v}_A \cdot \vec{v}_B \rangle \right)$$

$$\Rightarrow \left\langle \frac{1}{2} M V_{CM}^2 \right\rangle = \frac{3}{2} k_B T + \frac{m_A m_B}{m_A + m_B} \langle \vec{v}_A \cdot \vec{v}_B \rangle$$

Assumptions valid for monoatomic gases and diatomic gases

- If A and B were part of independent gases we could have intuitively set $\langle \vec{v}_A \cdot \vec{v}_B \rangle = 0$, as we did earlier. However, in this case we must analyze this term as A and B are bound as a molecule.

- Even in this case, for the relative velocity $\vec{w} = \vec{v}_A - \vec{v}_B$, we can safely assume that

$$\left\langle \vec{w} \cdot \vec{V}_{CM} \right\rangle = 0$$

$$\Rightarrow \left\langle (\vec{v}_A - \vec{v}_B) \cdot \left(\frac{m_A \vec{v}_A + m_A \vec{v}_A}{m_A + m_B} \right) \right\rangle = 0$$

$$\Rightarrow \langle (\vec{v}_A - \vec{v}_B) \cdot (m_A \vec{v}_A + m_B \vec{v}_B) \rangle = 0$$

Final form of the average kinetic energy of the center of mass

$$\Rightarrow \langle m_A\vec{v}_A\cdot\vec{v}_A + m_B\vec{v}_A\cdot\vec{v}_B - m_A\vec{v}_B\cdot\vec{v}_A - m_B\vec{v}_B\cdot\vec{v}_B\rangle = 0$$

$$\Rightarrow \langle m_1v_1^2 - m_2v_2^2 + (m_2-m_1)\vec{v}_1\cdot\vec{v}_2\rangle = 0$$

$$\Rightarrow \langle m_1v_1^2\rangle - \langle m_2v_2^2\rangle + (m_2-m_1)\langle\vec{v}_1\cdot\vec{v}_2\rangle = 0$$

Now, $\left\langle\frac{1}{2}m_1v_1^2\right\rangle = \left\langle\frac{1}{2}m_2v_2^2\right\rangle$, thus

[A, B and 1, 2 in the subscripts represents the same quantity]

$$(m_2-m_1)\langle\vec{v}_1\cdot\vec{v}_2\rangle = 0$$

$$\Rightarrow \langle\vec{v}_1\cdot\vec{v}_2\rangle = 0$$

So this relation holds in this case also. Therefore,

$$\left\langle\frac{1}{2}MV_{CM}^2\right\rangle = \frac{3}{2}kT$$

Thus kinetic energy associated with the center of mass motion is $\frac{3}{2}kT$.

Average kinetic energy of the internal motion of the molecule

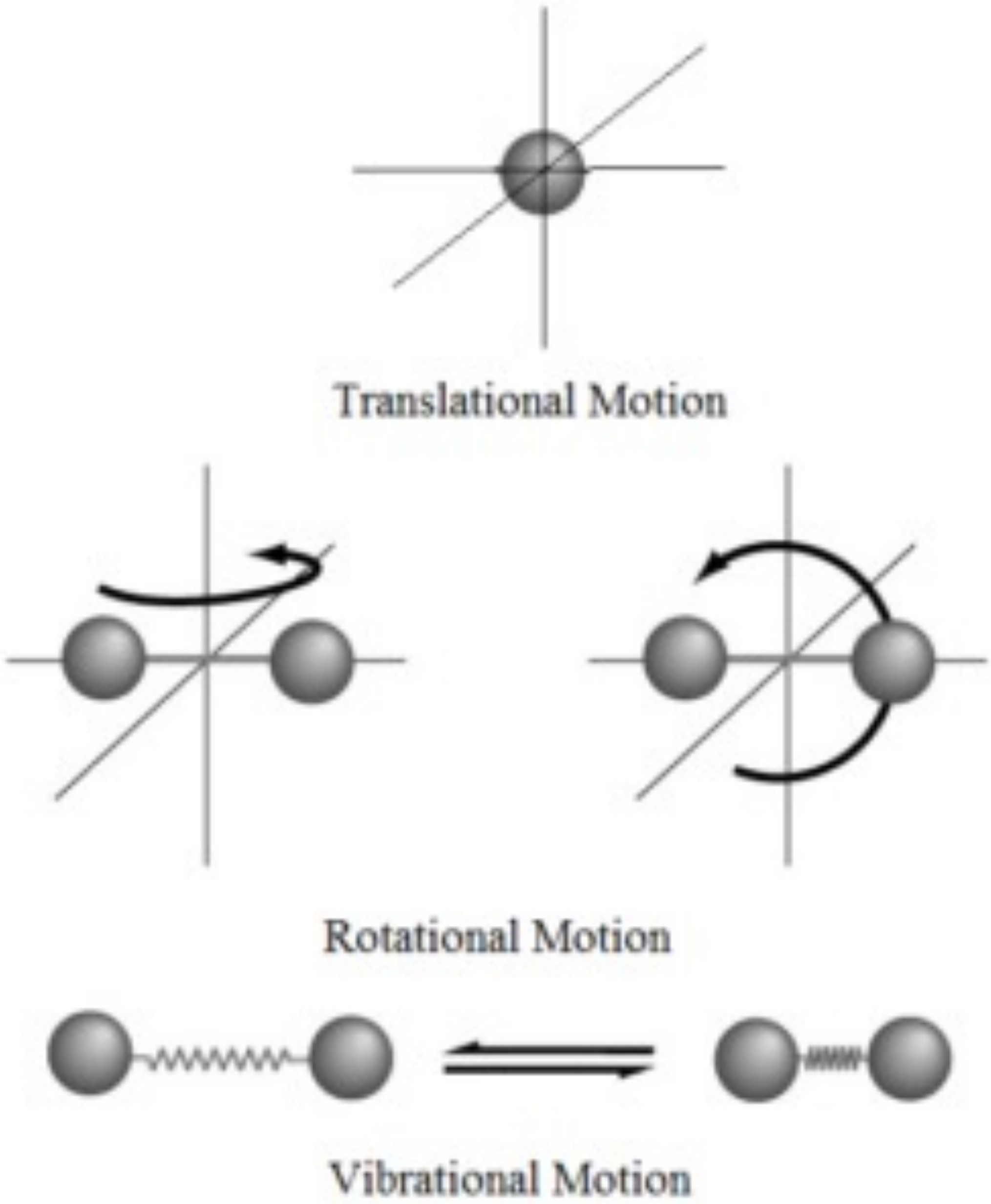
- Total average kinetic energy of the molecule $= 3kT$.

- Average kinetic energy of center of mass $= \frac{3}{2}kT$

(*The bodily motion of the entire molecule, regarded as a single particle of mass* $M = m_1 + m_2$)

- Therefore, the average kinetic energy associated with the internal motion of the molecule (rotation+vibration)= $3kT - \frac{3}{2}kT = \frac{3}{2}kT$

Degrees of freedom: motion of the diatomic molecule



Energy associated with each type of motion

Consider for example a diatomic molecule.

The total average kinetic energy has to be $2 \times \frac{3kT}{2} = 3kT$.

This has contribution:

- $\frac{3kT}{2}$ *from the center of mass motion.*
- $2 \times \frac{kT}{2}$ *from rotational degrees of freedom.*

  (There are two axes of rotation)
- $\frac{kT}{2}$ *from vibrational degree of freedom.*

Energies associated with polyatomic molecule

Recall the relation

$$PV = (\gamma - 1)U = NkT$$

For a gas with monatomic molecules, $\gamma = 5/3$. In this case the internal energy $U = 3NkT/2$ is entire due to kinetic energy.

However, for polyatomic molecules the contribution to U comes from the total average kinetic energy and potential energy associated with the bound atoms in the molecule.

Total energy: Kinetic + Potential

At low energies the vibration of the molecule can be very well be modeled by a harmonic potential. In this case we know that the average kinetic and potential energies are same.

Thus potential energy associated with vibration= $\frac{kT}{2}$.

Therefore total internal energy of the gas,

$$U = N\left(3kT + \frac{kT}{2}\right) = \frac{7NkT}{2}.$$

Thus $(\gamma - 1)U = (\gamma - 1)\frac{7NkT}{2} = NkT$, giving $\boldsymbol{\gamma = 9/7}$.

In absence of energy contribution from vibrational motion

- However, usually the vibrational degree of freedom is not excited (for example at the room temperature: *Quantum mechanical reason*), and then the total contribution to the total internal energy is $U = \frac{5NkT}{2}$, which gives $\gamma = \frac{7}{5} = 1.4$

- *The terrestrial air is primarily made up of diatomic gases (~78% nitrogen (N_2) and ~21% oxygen (O_2)) and at standard conditions it can be considered to be an ideal gas. The above value of 1.4 is highly consistent with the measured values 1.403, 1.400,1.401 at 0°C, 20°C, 100°C respectively.*

EQUIPARTITION THEOREM

If there are f degrees of freedom, then each of them has an associated contribution $\frac{kT}{2}$ to the internal energy.

Thus,

$U = N\,\frac{f\,kT}{2}$, and thus $(\gamma - 1)U = (\gamma - 1)\frac{fNkT}{2} = NkT$

gives

$$\gamma = 1 + 2/f.$$

Problem set for practice

- **Reference book: Fundamentals of Physics, 5th Edition, (Chapter 20, problem 20-4)**
- **Reference book: Physics for Scientists and Engineers, 9th Edition (Chapter 21, problem 21-1, 21-2, 21-3, 21-4)**

What is average translational kinetic energy of the oxygen and nitrogen molecule at room temperature?

Hints: Average translational kinetic energy depends only on the temperature and not on the nature of molecule.
Thus, using the following relationship the answer is **0.039 eV**

$$E = \frac{3kT}{2}$$