

Chapter 9: Kinetic Theory of Gases & Thermodynamics

Learning Outcomes

Molecular kinetic theory	1.	Define/State <ol style="list-style-type: none"> The assumptions of kinetic theory of gases. The principle of equipartition of energy Degrees of freedom
	2.	Describe/Explain: <ol style="list-style-type: none"> Root mean square (rms) speed of gas molecules, $v_{rms} = \sqrt{\langle v^2 \rangle}$ Translational kinetic energy of a molecule, $E_K = \frac{3}{2} \left(\frac{R}{N_A} \right) T = \frac{3}{2} kT$ Internal energy of gas
	3.	Solve problems related to: <ol style="list-style-type: none"> rms speed of gas molecules, $v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$ the equations, $PV = \frac{1}{3} Nmv_{rms}^2$; $P = \frac{1}{3} \rho v_{rms}^2$ Translational kinetic energy of a molecule, $E_K = \frac{3}{2} \left(\frac{R}{N_A} \right) T = \frac{3}{2} kT$ Internal energy, $U = \frac{1}{2} f N k T$
	4.	Identify number of degrees of freedom for monoatomic, diatomic and polyatomic gas molecules.
Thermodynamics	5.	Define/State: <ol style="list-style-type: none"> First Law of Thermodynamic, $\Delta U = Q - W$ Isothermal process Isochoric process Isobaric process Adiabatic process
	6.	Solve problems related to: <ol style="list-style-type: none"> First Law of Thermodynamics Isothermal process, $W = nRT \ln \left(\frac{V_f}{V_i} \right) = nRT \ln \left(\frac{p_i}{p_f} \right)$ Isobaric process, $W = \int P dV = P(V_f - V_i)$ Isochoric process, $W = \int P dV = 0$
	7.	Analyse $P - V$ graph for all the thermodynamic processes
	8.	Derive equation of work done in isothermal, isochoric and isobaric processes from $P - V$ graph.

Molecular Kinetic Theory

Kinetic Theory of Gases

Because atoms are very light, it is often useful to use the **atomic mass unit** for the masses of the atomic scale. The atomic mass unit is defined as $\frac{1}{12}$ of the mass of a carbon-12 atom. This atomic mass unit (a.m.u.) is related to the SI kilogram by

$$1u = 1.660539 \times 10^{-27} kg$$

Apart from that, in our daily lives, quite often we deal with a large number of atoms/molecules/particles. So rather than describing numerically by the number of particles, we often describe the number of atoms relative to the **Avogadro's Constant**,

$$N_A = 6.022 \times 10^{23} \text{ particle per mol.}$$

For example, instead of saying there are $5(10^{23})$ gas particles in a container, it is easier to say 0.83mol of gas particles in the container. These two new ways of quantifying the light-mass but large number particle systems leads to a very interesting result, that is **the mass per mole of any substance and the atomic (or molecular) mass unit has the same numerical value**. For example, the oxygen atom has a mass of 16u and therefore has a mass of $16g \text{ mol}^{-1}$.

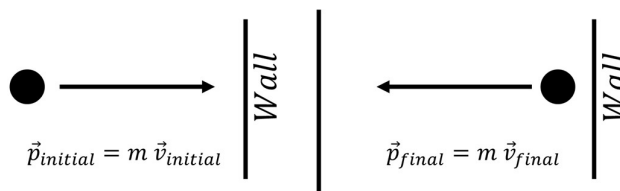
Macroscopically, the simplest model for gases is the **ideal gas law**, which states

$$pV = nRT = Nk_B T$$

where p is the pressure of the gas (in Pa), V is the volume of the gas (in m^3), n is the number of mole of the gas, T is the temperature in Kelvin of the gas, R is the gas constant ($J \text{ mol}^{-1} K^{-1}$) and k_B is the Boltzmann constant (defined as $k_B = \frac{R}{N_A}$).

Microscopically, though we want to start considering kinetic energies of the gas particles. Let us first lay down assumptions for our kinetic theory of gas. In one sentence, let us consider **gas to be composed of large numbers of non-null mass point-like particles that obeys Newton's laws of motion and interact elastically with each other where the average kinetic energy of the gas particles depends solely on the absolute temperature of the gas particle system**.

Consider gas particles in a cube container of side lengths L . We can think of the interaction between the gas particle and the container wall to be like that of a ball hitting a wall. We can determine the force exerted by the particle onto the container wall and then divide it by the area to determine the pressure.



We can see that the change in momentum is $\Delta \vec{p} = m(-v - (+v)) = -2mv$

. Considering the speed of the particle is v and the distance between walls of the container are L , the time between the collisions will simply be $t = \frac{2L}{v}$. The force exerted on the wall by the particle will then be

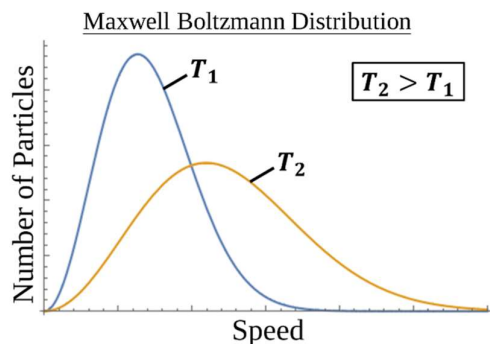
$$F = \frac{\Delta p}{t} = \frac{-2mv}{\left(\frac{2L}{v}\right)} = \frac{-mv^2}{L}$$

If there are N particles in the container, then the total force exerted on the container walls is

$$F = \frac{-Nm\overline{v^2}}{3L}$$

2 major changes happened - $\overline{v^2}$ has replaced v^2 and a factor of $\frac{1}{3}$ seemed to popped up. Here are the reasons:

- a. $\overline{v^2}$ has replaced v^2 because in a system of many particles, not all the particles will have the same speed. Their speed will follow the **Maxwell-Boltzmann distribution**.



So, to take that into account, we will use the **rms speed (v_{rms})** of the particle rather than the peak or average speed. This rms speed is defined by

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

- b. On the other hand, the factor of $\frac{1}{3}$ popped up because the particles can move in 3 dimensions. This means the velocities of the particles can happen in x, y or z axis. Considering the speeds are random, this would mean $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$, and since $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$, this would mean that

$$\overline{v^2} = 3\overline{v_x^2} \Rightarrow \overline{v_x^2} = \frac{\overline{v^2}}{3}$$

And thus the force can be written as

$$F = \frac{Nm v_{rms}^2}{3L}$$

We can now divide this force by the area

$$P = \frac{F}{L^2} = \frac{\left(\frac{Nm v_{rms}^2}{3L}\right)}{L^2} = \frac{Nm v_{rms}^2}{3L^3} = \frac{Nm v_{rms}^2}{3V}$$

Defining mass density as $\rho = \frac{Nm}{V}$,

$$P = \frac{Nm v_{rms}^2}{3V} \Rightarrow P = \frac{1}{3} \rho v_{rms}^2.$$

Rearranging the pressure – rms speed equation yields

$$PV = \left(\frac{2}{3}N\right) \left(\frac{1}{2} m v_{rms}^2\right) = \left(\frac{2}{3}N\right) (\bar{E}_{kinetic})$$

Comparing this to $pV = Nk_B T$ gives us an expression of the average kinetic energy as a function of the temperature,

$$Nk_B T = \left(\frac{2}{3}N\right) (\bar{E}_{kinetic}) \Rightarrow \bar{E}_{kinetic} = \frac{3}{2} k_B T \text{ (for a single particle)}$$

$$\text{Total Translational Kinetic Energy of } N \text{ gas molecules: } \Sigma E_{kinetic} = \frac{3}{2} N k_B T = \frac{3}{2} nRT$$

This result is significant because now we really do have a **kinetic** theory of gas, where the temperature of the gas is expressed in terms of the motion of the gas particles.

Kinetic & Internal Energy

Before talking about the classical principle equipartition of energy, we need to address what we mean when we say **degrees of freedom**. In the context of gas motion, degrees of freedom are the dynamical variables that contributes a squared term to the expression for the total particle energy. Classically, there two that we'd consider are

- a. translational kinetic energy,

$$K_{translational} = \frac{1}{2}mv^2$$

- b. Molecular rotational energy,

$$K_{rotational} = \frac{1}{2}I\omega^2$$

Though, in the quantum regime, we need to consider vibrational energy, in which the bonds between molecules may be treated as “springs” and that would add 2 more degrees of freedom.

The following table shows the cases and the number of degrees of freedom

Cases	Number of Degrees of Freedom
Monoatomic	3 (Only translational) $\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$
Diatomic*	5 (3 translational + 2 rotational) $\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}\omega(I_x^2 + I_y^2)$

*in the classical regime. Taking into consideration quantization of energy leads to consideration for vibrational energy.

Based on the idea of degrees of freedom, we can now extend our discussion to the classical theorem of energy equipartition which states **at equilibrium, each degree of freedom contributes $\frac{1}{2}k_B T$ of energy per molecule.**

That is to say, for N number of gas molecules of f degree of freedom, the total internal energy is

$$U = fN \frac{1}{2}k_B T = \frac{f}{2}nRT$$

Here what we mean by internal energy is simply the sum of all the kinetic energy of all the molecules accounted for in the systems. If we were to talk about translational kinetic energy, we mean kinetic energy associated with translation of the particle ($f = 3$). If we were to talk about the total kinetic energy, we are referring to the internal energy of the system, where the degree of freedom depends on the type of particle.

Thermodynamics

Thermodynamics is the study of heat and energy transformation. In this section, we discuss 3 things. Firstly, the 0th law of thermodynamics, which essentially provides us with the idea of **thermal equilibrium**. Secondly, we shall look at how the idea of adding (or taking out) energy to a system relates to the internal energy of the system, i.e. the 1st law of thermodynamics. Lastly, we shall consider the thermodynamical processes and lay foundations to understanding heat engines.

Zeroth law of Thermodynamics

The 0th law of thermodynamics focuses on the idea of a thermal equilibrium. If the temperature of system A is equal to system B, and that system B has a temperature equal to system C, then system C and A is said to be at **thermal equilibrium**.

$$T_A = T_B \text{ \& } T_B = T_C \Rightarrow T_A = T_C$$

In other words, two systems are to be in thermal equilibrium with each other if they have the same temperature. When two systems are in thermal equilibrium with each other, the net heat flow between them is essentially 0.

First Law of Thermodynamics

At this point, what we want to do is to relate the internal energy of the system with the external factors. By External factors, we mean whether we apply heat to the system, or take heat away from it or changing the geometry of the system (whether increasing it or decreasing it). Much like the conservation of energy, the sum total of the energy of an isolated system must be conserved. Therefore, when some heat ΔQ is added to the system and some work ΔW is added to the system, the change in internal energy ΔU can be calculate by

$$\Delta U = \Delta Q + \Delta W$$

Though some books may have a minus sign instead of a positive sign for the ΔW and the reason for that is that they have defined ΔW to be work done by the system.

Equation	Terms definition
$\Delta U = \Delta Q + \Delta W$	ΔW = work done onto the system
$\Delta U = \Delta Q - \Delta W$	ΔW = work done by the system

Thermodynamical Processes

Looking back at the first law of thermodynamics, we want to be able to do some calculations related to it. And thus, we shall quantitatively defined U , Q and W . By internal energy, we take the definition defined previously, that is internal energy of the gas depends on the temperature of the system,

$$\Delta U(\Delta T) = \frac{1}{2} f N k_B \Delta T = \frac{f}{2} n R \Delta T$$

By heat added, what we refer to is the heat transfer into or out of the system. This heat is defined by

$$\Delta Q = mc \Delta \theta$$

where m is the mass of the system, c is the heat capacity of the system and θ is the temperature of the system. By work done onto (or by) the system, we define it to be related to the change in volume of the system,

$$\Delta W = p \Delta V$$

In general, we want to consider 4 case studies on thermodynamical processes:

1. Isothermal

In isothermal expansion/compression, temperature of the system is kept constant, $\Delta T = 0$. Since the change in internal energy depends solely on change in temperature, this means that $\Delta U = 0$ and thus

$$\Delta U = 0 = \Delta Q + \Delta W \\ \Rightarrow \Delta Q = -\Delta W$$

In the isothermal case, pressure is not a constant, we can define pressure as a function of volume via the ideal gas law

$$p = \frac{nRT}{V}$$

And thus the work done is

$$W = \int_{V_i}^{V_f} p(V) dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{1}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right)$$

2. Isochoric / Isovolumetric

In the isochoric case, the volume of the gas is kept constant, $\Delta V = 0$ and thus

$$\Delta U = \Delta Q$$

3. Isobaric

In the isobaric expansion/compression cases, the pressure of the gas is kept constant, $\Delta p = 0$. This means that for the calculation of work done onto (or by) the system is simply

$$W = \int_{V_f}^{V_i} p dV = p \int_{V_f}^{V_i} dV = p(V_f - V_i)$$

4. Adiabatic

For the adiabatic process, what is kept constant is the heat transfer into and out of the system, $\Delta Q = 0$. This means that $\Delta U = \Delta W$. Since

$$\Delta U = \Delta W = \int_{T_i}^T nR dT$$

$$\Rightarrow W = \int_{T_i}^{T_f} \frac{f}{2} nR dT = \frac{f}{2} nR (T_f - T_i)$$

The p-V graph of each thermodynamical processes is shown in the diagram below.

