III.3. The Kinetic Theory of Ideal Gases

The first glimpse at the origin of thermodynamic laws is already provided by the very simple ***microscopic model of an ideal gas of non-interacting*, *structure-less particles*** (atoms or molecules) ***moving randomly inside a container and colliding elastically with its walls***. This model already provides an understanding of the structure of the most important gas law, the ideal-gas *EOS*, if the motion of the gas particles is in fact random.

Consider first a single gas particle of mass m and initial momentum $\vec{p}_i$ in a rectangular container with rigid walls, shown on the left in cross-sectional view. Let a coordinate system $\{x,y,z\}$ be aligned with the edges of the container. This geometry facilitates the following calculation but does not restrict the generality of the conclusions.

The particle under consideration will eventually collide with one of the container walls, e.g., the one on the right, which is assumed to be parallel to the *y-z* plane. The collision with the rigid wall is assumed to be ***elastic***, i.e., essentially ***no energy is lost*** by the particle. This would be exactly true only, if the mass (***M***M_{Wall}) of the wall were infinitely large, such that a collision with a gas particle would impart very little energy, namely

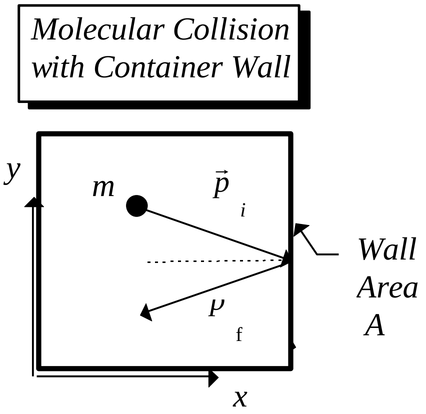

Figure III-8: Reflection

$$\Delta E_{Wall} = \frac{q^2}{2M_{Wall}} \approx 0 \qquad \text{(III.64)}$$

for any ***momentum q transferred*** to the wall. For the present discussion, it is assumed for simplicity that the wall is at rest, i.e., that the mass ***M_{Wall}*** of the wall is very large compared to the mass *m* of a gas particle ***(M_{Wall} π m)***. Then, the particle is reflected almost perfectly from the wall, that is, its momentum components parallel to the wall, p_y and p_z, are not changed in the collision, but the component perpendicular to it, p_x, is reversed in direction, i.e., it changes its sign but not its magnitude $|\, p_x \,|$:

$$\underset{before}{\vec{p}_i = \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix}} \qquad \text{☑} \qquad \underset{after}{\vec{p}_f = \begin{pmatrix} -p_x \\ p_y \\ p_z \end{pmatrix}} \tag{III.65}$$

Since in every collision, there is ***conservation of linear momenta***, i.e., the sum of all momenta remains constant, the wall must have received the difference in the momenta of the particle before and after the collision. This must be true, even though the mass of the wall is assumed to be very large. This momentum transfer to the wall is equal to

$$\vec{q} = \vec{p}_i - \vec{p}_f = \begin{pmatrix} 2p_x \\ 0 \\ 0 \end{pmatrix} \tag{III.66}$$

This means that the container wall experiences a "kick" in the $x>0$ direction. This kick can be viewed as a ***force ΔF_x, acting on the wall during the short time Δt*** of the collision. Because of Equ. III.66, the relation between momentum transfer and force is given by

$$\Delta F_x \bullet \Delta t = q_x = 2p_x \tag{III.67}$$

ΔF_x is the force that the container wall “feels” during the time ***Δt*,** from the ***effect of a single particle*** colliding with it.

However, there may be many particles in the gas container, some of which collide with the wall on the right, some collide with one of the other walls. The question is: ***How many particles collide with the wall during the same (small) time interval Δt?*** - The answer is simple and can be obtained by counting the number of particles in a "collision layer" (shaded in Fig. III-9) in front of the container wall. If a particle has a velocity component in positive x direction, i.e., $u_x = p_x/m > 0$, the particle moves to the right and will eventually hit the right wall, those with $u_x < 0$ will hit the wall on the left. If, by assumption, the ***motion of the gas particles is truly random***, 1/2 of the particles will have $u_x < 0$, the other 1/2 will have $u_x > 0$. If there are N particles in the container, then $N/2$ will *eventually* collide with the wall in question, ***given enough time Δt***.

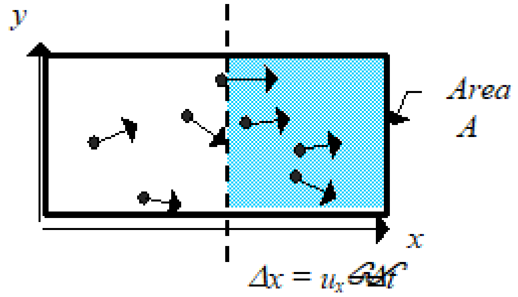

Figure III-9:Collision Layer

However, only those particles that are close enough to the wall will actually ***hit it during Δt***. Only those that are ***closer than $\Delta x = u_x \bullet \Delta t$ and have $u_x > 0$*** will do so. This implies that ***all particles in the volume $\Delta V = A \bullet u_x \bullet \Delta t$ with $u_x > 0$ will impinge on the wall***. With a ***particle density of $\rho = N/V$***, one calculates that

$$\Delta N_+ = (1/2)\rho \cdot \Delta V = (1/2) N \cdot A \cdot u_x \cdot \Delta t / V \qquad \text{(III.68)}$$

particles impinge on the wall within the time interval Δt, each transferring a momentum $q_x = 2p_x$ to the wall. The total momentum transfer during Δt is then given by

$$\Delta F_x \cdot \Delta t = \Delta N_+ \cdot (2p_x) = N \cdot A \cdot m u_x^2 \cdot \Delta t / V \qquad \text{(III.69)}$$

Therefore, the pressure on the wall, defined as ***force*** ΔF_x ***per area A***, can be written as

$$p = \Delta F_x / A = N \cdot m u_x^2 / V \qquad \text{(III.70)}$$

or

$$p \cdot V = N \cdot m\overline{u_x^2} \qquad \text{(III.71)}$$

Realizing that the particles may not all have the same velocity, the quantity u_x^2 ***has been replaced*** in Equ. III.71 ***by the average,*** $\overline{u_x^2}$ **,** ***over the entire particle ensemble***.

A similar calculation can be done for any other wall, taking into consideration also the other independent components, u_y and u_z, of the gas particles. If, as assumed, the motion is truly random, then there is no reason, why the average of the velocity u_x in x direction, *or its square,* should be any different from those in other directions. Therefore, it is justified to take

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = (1/3)\overline{u^2} \qquad \text{(III.72)}$$

where the ***speed*** of the particles is defined as

$$u = |\vec{u}| = \sqrt{u^2} = \sqrt{u_x^2 + u_y^2 + u_z^2} \qquad \text{(III.73)}$$

Then, Equ. III.71 can be transformed into

$$p\cdot V = N\cdot(1/3)m\overline{u^2} \qquad \text{(III.74)}$$

which is now independent of any coordinate system adopted.

Since the kinetic energy of a gas particle is equal to $\varepsilon = (1/2)mu^2$ relation III.74 can be rewritten as

$$\boxed{p\cdot V = N\cdot(2/3)\bar{\varepsilon}} \qquad \text{(III.75)}$$

Equ. III.75 makes good sense, because it relates (something like) the ***total energy content*** ***pV*** **[=** ***(force/area) area distance*****]** ***of*** the gas to a product of average energy per particle**,** $\bar{\varepsilon}$, and the number of particles, *N*, in the gas volume. Since *V* and, hence, the product ***pV***, are extensive observables, it must be that $\boldsymbol{pV \propto N^1}$ and no other power of *N* must appear. In other words, the average ***specific (per particle) kinetic energy*** $\bar{\varepsilon}$ is seen to determine the magnitude of the total ***energy content*** per particle, *pV/N*, as is plausible. This ***average specific energy*** $\bar{\varepsilon}$ ***naturally depends <u>only</u> on the heat content of the gas, which is determined by the temperature T***. What remains to be explained is the factor (2/3) in Equ. III.75. The present phenomenological treatment does not explain this factor, it only provides the structure of the *EOS*. However, comparing <u>Equs. III.60b</u> and 75, one derives an expression for the ***average kinetic energy of the gas particles***:

$$\boxed{\bar{\varepsilon} = \frac{3}{2} \cdot k_B T} \qquad \text{(III.76)}$$

Furthermore, since the motion of the particles along any of the *x*, *y*, and *z* ***"degrees of freedom"*** is independent, the average total energy is equal to the sum of the average energies associated with the individual degrees of freedom,

$$\boxed{\bar{\varepsilon}_x = \bar{\varepsilon}_y = \bar{\varepsilon}_z = \frac{1}{2} k_B T}$$

One concludes the validity of an ***Equipartition_Law*** (III.77)

In thermal equilibrium, each degree of freedom has an average energy given by the amount (1/2)$k_B T$. (III.78)

This Equipartition Law (Equ. III.78) has been made plausible here only for the kinetic energies of gas particles. However, it is derived more rigorously in the theory of statistical mechanics. This ***Equipartition Law is valid for essentially all degrees of freedom of practical interest.*** This is a very useful result, because it allows one immediately to estimate a number of quantities related to the average energy per degree of freedom, for an arbitrary system at thermal equilibrium. It also helps to understand the ***relation between the concepts of temperature and internal energy*** of a system.

For ideal gases at equilibrium, including mixtures of different types *i*, the ***Equipartition Law implies that all particles have the same average kinetic energies***, $\overline{\varepsilon(i)}$, which are dependent only on the common temperature *T* but independent of their masses m_i. From this statement, one concludes immediately that the ***velocities must scale inversely with the masses*** of these particles. Considering, for simplicity, only two different particle types and only the *x* degree of freedom and the associated velocities $u_x(i)$, Equ. III.77 can be used to calculate this scaling:

$$\overline{\varepsilon_x(1)} = \frac{m_1}{2}\overline{u_x^2(1)} = \frac{1}{2}k_B T = \overline{\varepsilon_x(2)} = \frac{m_2}{2}\overline{u_x^2(2)} \qquad \text{(III.79)}$$

Therefore, one derives

$$\overline{u_x^2(2)} \Big/ \overline{u_x^2(1)} = m_1 / m_2 \qquad \text{(III.80)}$$

Heavier particles in the equilibrium gas mixture move more slowly than the lighter particles in the mixture.

Obviously, the same arguments can be made for the other degrees of freedom *y* and *z*, saying that the ***mean-square velocities*** $\overline{u^2(i)}$ scale inversely proportionally with the masses m_i of the particles, i.e., $\overline{u^2(i)} \propto m_i^{-1}$. As will be shown later on, the ***mean velocities*** $\overline{u(i)}$ differ only by a constant numerical factor from the ***root-mean-square velocities*** $\sqrt{\overline{u^2(i)}}$. Hence,

$$\overline{u(i)} \propto m_i^{-1/2} \qquad \text{(III.81)}$$

In thermal equilibrium with other gas particles, heavier particles move more slowly than the lighter ones.

This latter principle has important applications for the decomposition of mixtures, e.g., the industrial ***separation of isotopes*** of a gas, or the ***differential permeability of membranes*** in biology and medicine. Here, one uses the scaling of the velocities with the inverse mass to deplete a gas mixture of the more mobile, lighter particles.

The method uses a gas container with small holes or pores through which particles can escape (effuse) from the container for further processing. The principle is illustrated in the sketch showing a container with two gas particle types $i = 1,2$. The derivation of the rates of effusion of the particles through the hole in the container is simple, following Equ. III.68 with the average x velocities of the particles given by $\overline{u_x(i)}$: The number of particles $\Delta N_+(i)$ escaping through the hole of area A per unit time Δt is given by

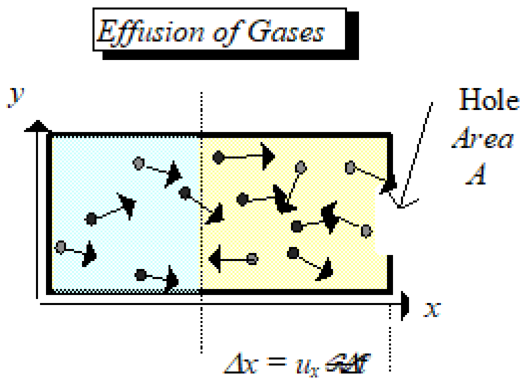

Figure III-10

$$\Delta N_+(i) = (1/2)\rho_i \cdot \Delta V = (1/2)N(i) \cdot A \cdot \bar{u}_x(i) \cdot \Delta t / V \quad \text{(III.82)}$$

where $\rho_i = N(i)/V$ is the ***(partial) particle density*** of component i. This is different from the partial ***mass density defined as***

$$\rho_m(i) = m_i \bullet \rho_i. \qquad \text{(III.83)}$$

The effusion rates are then seen to be proportional to the partial densities and to the inverse of the square-root of the particle masses:

$$R_{eff}\left(i\right)=\frac{\Delta N_{+}\left(i\right)}{\Delta t}\propto\rho_i\cdot\overline{u}_x\left(i\right)\propto\frac{\rho_i}{\sqrt{m_i}}\qquad\text{(III.84)}$$

The masses of the particles in an "ideal" gas, defined by the Equation of state (EOS), are the only properties that distinguish them thermodynamically from each other. This observation relates to the fact that the energies, and not the momenta or velocities, are characterized by the same characteristic value $\overline{\varepsilon}_i=\left(1/2\right)k_BT$ per degree of freedom (i). Hence, in thermal equilibrium, the ***energies are "equilibrated"***. Yet, the simple but important EOS, relating the macroscopic state variables *p, V,* and *T* to each other, comes about from the ***momentum transfer*** to a wall, from the particles reflected from it. In the derivation of the EOS, an assumption was made of the ***random distribution of the velocity directions***. Given the deterministic laws of mechanical motion, it is not obvious, how such a random distribution may develop on its own, in an interaction-free ideal gas. In fact, this is the result of multiple interactions between the gas particles, ***chaotic molecular scattering***. Such scattering processes will be considered next.