Unit 2: Classical Ensembles

In this unit we begin our discussion of statistical mechanics, the field which provides the link between microscopic mechanics and classical thermodynamics. After a very brief discussion of kinetic theory, which provides a microscopic characterization of the ideal gas, we consider the more modern ensemble theory of statistical mechanics, based on the ergodic hypothesis. We discuss the microcanonical, the canonical, and the grand canonical ensembles, as applied to systems obeying classical mechanics (in unit 3 we will apply these to quantum systems). We show how the partition functions, defined for these ensembles, allow us to compute the fundamental thermodynamic potentials such as entropy S, Helmholtz free energy A, and the grand potential Φ. We also briefly discuss the connection between ensemble theory and *Information Theory*.

Unit 2-1: Kinetic Theory of the Ideal Gas and the Maxwell Velocity Distribution

Some History

We can start with a brief history of the **Ideal Gas Law**, the pivotal topic behind the development of much of classical thermodynamics. The Ideal Gas Law, $pV = Nk_BT$, relates the pressure p of the gas to its volume V, number of particles N, and temperature T. The Boltzmann constant k_B is an empirically determined universal constant of nature (it has the same value for all gases).

1662 - Robert Boyle found that, when one holds temperature T constant and varies the pressure p or the volume V, then the product of pressure and volume always stays constant, $p_1V_1 = p_2V_2$.

1787 - Jacques Charles found that, when one holds pressure p constant and varies the temperature T or the volume V, then the ratio of volume to temperature always stays constant, $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$.

1809 - Joseph Louis Gay-Lussac found that, when one holds volume V constant and varies the pressure p or the temperature T, then the ratio of pressure to temperature always stays constant, $\dfrac{p_1}{T_1} = \dfrac{p_2}{T_2}$.

1811 $=$ Amedeo Avogadro found that, when one holds temperature T and pressure p constant, and varies the volume V or the number of particles N, then the ratio of volume to number of particles stays constant, $\dfrac{V_1}{N_1} = \dfrac{V_2}{N_2}$.

1824 - Nicolas Léonard Sadi Carnot proposed the Carnot cycle, giving the maximum thermodynamic efficiency for a heat engine operating between two fixed temperatures.

1834 - Benoît Paul Émile Clapeyron put these results together to formulate the Ideal Gas Law, $pV = Nk_BT$.

1854 - Rudolf Clausius developed the notion of entropy.

Much of classical thermodynamics was developed *before* it was widely understood that gases are comprised of microscopic particles undergoing random motion. But with this understanding came attempts to understand ideal gases on the basis of the mechanics of such particles. Some highlights in the history of this kinetic theory of the ideal gas are as follows.

~ 50 **BCE** - Titus Lucretius Carus wrote *On the Nature of Things*, advocating that nature is composed of indivisible objects termed *atoms*. Though the notion of atoms is older, going back at least to Democritus in ~ 400 BCE, Lucretius' work was rediscovered in the Middle Ages and prompted a revival of atomist philosophies.

1738 - Daniel Bernoulli showed that pressure can be related to the impact of particles hitting a wall, and that heat is related to the kinetic energy of particles. But this work was largely forgotten until around the 1850's.

1856 - August Kronig writes a paper with the basics of kinetic theory, proposing that gas molecules travel in straight lines until they collide with something. In contrast to similar earlier works (such as Bernoulli's) which were ignored, Kronig's paper is widely read.

1857 - Rudolf Clausius writes a paper on kinetic theory proposing that heat is energy distributed statistically among the gas particles.

1859 - James Clerk Maxwell presents his paper "Illustrations of the Dynamical Theory of Gases," developing a probablistic velocity distribution for the gas particles.

1905 - Albert Einstein develops a theory for the Brownian motion of small particles suspended in a liquid.

1906 - Marian Smoluchowski independently develops a theory of Brownian motion.

Kinetic Theory of the Ideal Gas

We know present a simple version of the kinetic theory of the ideal gas, and derive the Maxwell velocity distribution for particles in the gas.

In the kinetic theory one interprets the pressure (force/area) on the walls of the box containing the gas as due to the impact of randomly moving particles hitting the wall, which imparts momentum at a fixed rate to the wall, as they collide and bounce off.
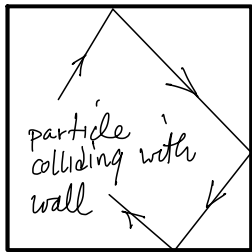
We will assume that the collisions of the particles with the wall are elastic, so when a particle hits the wall the component of its velocity normal to the wall reverses sign, and the component parallel to the wall remains the same. We can then write for the pressure,

$$p = \left\langle \frac{\Delta(mv_\perp)\, rate}{area} \right\rangle \tag{2.1.1}$$

where $\Delta(mv_\perp) = 2mv_\perp$ is the change in the normal component of momentum of a particle in a collision with the wall, $rate$ is the rate of collisions so that $\Delta(mv_\perp)\, rate$ is the total normal force exerted by collisions on the wall, and $area$ is the area of the wall. Here the angle brackets $\langle\ldots\rangle$ denote an average over time and over the particles in the gas.
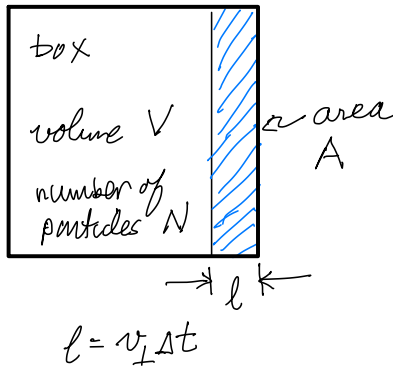
To compute the rate of collisions, we compute the number of collisions that will occur within a time period Δt. If a particle is traveling with a normal component of velocity of speed $v_\perp$, then it will hit the wall within the time Δt provided it is within a distance ℓ of the wall, where $\ell = v_\perp \Delta t$, and its velocity is in the direction approaching the wall. The number of particles within a distance ℓ of the wall is just the particle density times the volume of the box within distance ℓ of the wall, i.e. $(N/V)A\ell$, where N is the total number of particles in the box of volume V, and A is the area of the wall. Of these, on average half are moving towards the wall and half are moving away from the wall. So the number of particles that, on average, will hit the wall in time Δt is,

$$\# = \frac{1}{2}\frac{N}{V}A\ell = \frac{1}{2}\frac{N}{V}Av_\perp\Delta t \quad \text{and the rate of collisions is} \quad \frac{\#}{\Delta t} = \frac{1}{2}\frac{N}{V}Av_\perp \tag{2.1.2}$$

So the pressure is then,

$$p = \left\langle \frac{2mv_\perp}{A}\,\frac{1}{2}\frac{N}{V}Av_\perp \right\rangle = m\frac{N}{V}\langle v_\perp^2\rangle \tag{2.1.3}$$

Now if the gas is isotropic, we expect that the distribution of the component of velocity in any particular direction should be the same as in any other direction, so for a three dimensional box we have,

$$\langle v_\perp^2\rangle = \langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \frac{1}{3}\langle v_x^2 + v_y^2 + v_z^2\rangle = \frac{1}{3}\langle v^2\rangle \tag{2.1.4}$$

So finally we have for the pressure,

$$p = \frac{1}{3}m\frac{N}{V}\langle v^2 \rangle = \frac{2}{3}\frac{N}{V}\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{2}{3}\frac{N}{V}\langle \epsilon_{\text{kin}} \rangle \tag{2.1.5}$$

where ϵ_{kin} is the kinetic energy of a particle.

Comparing now to the ideal gas law, $pV = Nk_BT$, we conclude for the average kinetic energy of a particle in the gas,

$$\langle \epsilon_{\text{kin}} \rangle = \frac{3}{2}k_BT \tag{2.1.6}$$

So this simple kinetic picture tells us that the temperature of the gas is simply a measure of the average kinetic energy of the particles, $k_BT = (2/3)\langle \epsilon_{\text{kin}} \rangle$, and then also gives the ideal gas law $pV = Nk_BT$.

Maxwell Velocity Distribution (1859)

Let $f(\mathbf{v})$ be the probability density for a particle in a gas to have velocity $\mathbf{v}$. The probability density must be normalized,

$$\int d^3v\, f(\mathbf{v}) = 1 \tag{2.1.7}$$

We assume that in an isotropic gas, the probability densities for each component of velocity are statistically independent and identically distributed. The joint probability distribution of the components, $f(\mathbf{v}) = f(v_x, v_y, v_z)$, must then factor,

$$f(\mathbf{v}) = h(v_x)h(v_y)h(v_z) \tag{2.1.8}$$

where $h(v_\mu)$ is the probability density that the μ-th component of the velocity has value v_μ.

Also by the assumption of isotropy, we assume that the probability distribution $f(\mathbf{v})$ is independent of the direction of $\mathbf{v}$ and so a function only of the magnitude of $\mathbf{v}$, or equivalently of the magnitude squared, $v^2 = \mathbf{v} \cdot \mathbf{v}$,

$$f(\mathbf{v}) = g(v^2) \quad \text{so we have} \quad g(v_x^2 + v_y^2 + v_z^2) = h(v_x)h(v_y)h(v_z) \tag{2.1.9}$$

The only solution to the above equation is when $h(v_\mu)$ depends exponentially on its argument,

$$h(v_\mu) \propto C^{(v_\mu^2)} \quad \text{so that} \quad h(v_x)h(v_y)h(v_z) \propto C^{(v_x^2)}C^{(v_x^2)}C^{(v_x^2)} = C^{(v_x^2+v_y^2+v_z^2)} = C^{(v^2)} \tag{2.1.10}$$

where C is a constant. Since we can always write $C = e^{\ln C}$, then we can always write $C^{(v_\mu^2)}$ so that $h(v_\mu)$ has the form,

$$h(v_\mu) = Be^{-Av_\mu^2} \quad \text{with} \quad A, B > 0 \tag{2.1.11}$$

Here $B > 0$ since probability densities must be positive, while $A > 0$ is required so that the probability density can be normalized. The distribution $h(v_\mu)$ is thus a *Gaussian* probability distribution with variance $\sigma^2 = 1/2A$. From the normalization of a Gaussian distribution we have $B = 1/\sqrt{2\pi\sigma^2}$.

Note: a very good thing to remember is the form of the normalized Gaussian probability distribution:

$$h(v_\mu) = \frac{1}{\sqrt{2\pi\sigma^2}}e^{-v_\mu^2/2\sigma^2} \tag{2.1.12}$$

We therefore have,

$$f(\mathbf{v}) = h(v_x)h(v_y)h(v_z) = B^3 e^{-A(v_x^2+v_y^2+v_z^2)} = \frac{1}{(2\pi\sigma^2)^{3/2}}e^{-v^2/2\sigma^2} \tag{2.1.13}$$

The parameter σ^2 gives the variance of any component of the velocity,

$$\sigma^2 = \langle v_\mu^2 \rangle - \langle v_\mu \rangle^2 = \langle v_\mu^2 \rangle \quad \text{since by symmetry } \langle v_\mu \rangle = 0. \tag{2.1.14}$$

So then we have

$$\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\sigma^2 \tag{2.1.15}$$

and the average kinetic energy of a particle is

$$\langle \epsilon_{\text{kin}} \rangle = \frac{1}{2}m \langle v^2 \rangle = \frac{3}{2}m\sigma^2 \tag{2.1.16}$$

Compare to our result of Eq. (2.1.6) from kinetic theory, $\langle \epsilon_{\text{kin}} \rangle = \frac{3}{2}k_B T$, and we conclude,

$$\sigma^2 = \frac{k_B T}{m} \tag{2.1.17}$$

From Eq. (2.1.12) we thus get the probability distribution for velocity component v_μ,

$$h(v_\mu) = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-mv_\mu^2/(2k_B T)} \tag{2.1.18}$$

and for the probability distribution of the full velocity $\mathbf{v}$,

$$f(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\epsilon_{\text{kin}}/k_B T} \tag{2.1.19}$$

The $f(\mathbf{v})$ above is the *Maxwell velocity distribution*.

We see that $f(\mathbf{v})$ is proportional to the familiar *Boltzmann factor* $e^{-\epsilon_{\text{kin}}/k_B T}$. We will see a lot more of the Boltzmann factor!