The Kinetic Theory of Gases

The description of the macroscopic state of a gas can be related to simple averages of microscopic quantities such as the mass and speed of the molecules in the gas. From the point of view of kinetic theory, a gas consists of a large number of molecules making elastic collisions with each other and with the walls of the container. In the absence of external forces (gravity may be neglected as it leads only to a slight increase of pressure at the bottom of the container), there is no preferred position for a molecule in the container and no preferred direction of its velocity vector.

The Pressure Exerted by a Gas:

We consider a rectangular container of volume V containing N molecules, each of mass m moving with a speed v. Let us calculate the force exerted by the molecules on the right wall of area A (Figure 18-9 of Tipler). The molecules hitting this wall in a time interval $\triangle t$ are those which are within distance $v_x \triangle t$ of the wall. This number of molecules is

$$\text{Molecules that hit the wall in } \triangle t = \frac{1}{2} \frac{N}{V} v_x \triangle t \, A$$

where the factor $1/2$ comes because, on the average, only half the molecules move to the right. The magnitude of the total change of momentum $\triangle p$ of these molecules during the time interval $\triangle t$ is

$$\triangle p = (2m\, v_x) \left(\frac{1}{2} \frac{N}{V} v_x \triangle t\, A \right) = \frac{N}{V} m\, v_x^2 \triangle t\, A$$

The force exerted on the wall is $\triangle p / \triangle t$. The pressure is the force divided by the area:

$$P = \frac{F}{A} = \frac{1}{A} \frac{\triangle p}{\triangle t} = \frac{N}{V} m\, v_x^2 \quad \text{or} \quad P\, V = N\, m\, v_x^2 \ .$$

To allow for the fact that the molecules in the container have different speeds, we replace v_x^2 with its average $(v_x^2)_{\rm av}$. Using the average for the kinetic energy, we have

$$P\, V = N\, k\, T = 2N\, (m\, v_x^2/2)_{\rm av} \ .$$

The Molecular Interpretation of Temperature: Dividing the number of molecules out, we have

$$(m\, v_x^2/2)_{\rm av} = k\, T \,/\, 2 \ .$$

Using $(v^2)_{\rm av} = (v_x^2)_{\rm av} + (v_y^2)_{\rm av} + (v_z^2)_{\rm av} = 3\, (v_x^2)_{\rm av}$ we have

$$K_{\rm av} = \left(\frac{1}{2} m\, v^2 \right)_{\rm av} = \frac{3}{2} k\, T \ .$$

The last equation relates the average translational kinetic energy of the molecules to the absolute temperature. We can use this result to estimate the order of magnitude of the speeds of the molecules of the gas:

$$\left(v^2\right)_{\mathrm{av}} = \frac{3kT}{m} = \frac{3RT}{M}$$

where $M = N_A\, m$ is the molar mass. The root mean square (rms) speed becomes:

$$v_{\mathrm{rms}} = \sqrt{v^2_{\mathrm{av}}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}\ .$$

This is similar to the equation for the speed of sound in a gas $v_{\mathrm{sound}} = \sqrt{\gamma RT/M}$. This is not surprising since pressure fluctuations are propagated by collisions between molecules.

Examples at $300\,$K:

$$v_{\mathrm{rms}}(O_2) = 483\,\mathrm{m/s}\,, \qquad v_{\mathrm{rms}}(H_2) = 1.93\,\mathrm{km/s}\ .$$

For H_2 the order of magnitude is such that the escape velocity of earth is slightly exceeded, while Jupiter retains H_2 easily.

The Equipartition Theorem

Degrees of freedom are associated with the kinetic energy of translations, rotation, vibration and the potential energy of vibrations. A result from classical statistical mechanics is the equipartition theorem, which states:

When a substance is in equilibrium, there is an average energy of $kT/2$ per molecule or $RT/2$ per mole associated with each degree of freedom.

The Mean Free Path

Despite the high average speed of the molecules in a gas, the transmission of odor is relatively slow. The reason are collisions of the molecules with one another. If we have one type of molecule and regard it as a little sphere of diameter d, the average time τ between collisions may be calculated:

$$\tau = \frac{1}{\sqrt{2}\, v_{\rm av}\, n_v\, \pi\, d^2} \ .$$

Here $v_{\rm av}$ is the average speed of a molecule and $n_v = N/V$ is the number of molecules per unit volume. The average distance traveled by the molecule between collisions is called the mean free path: $\lambda = v_{\rm av}\, \tau$.

The Maxwell-Boltzmann Distribution

Not all molecules in the gas are at the average speed. We would like to calculate the distribution of speeds. Familiar examples of distributions are the grades distribution in a class of students or the distribution of the heights of a (large) number of people.

The Maxwell-Boltzmann speed distribution of molecules in a gas is

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k\,T}\right)^{3/2} v^2 \exp\left(-\frac{m\,v^2}{2k\,T}\right) \; .$$

This function is a probability density which fulfills

$$\int_0^\infty dv\, f(v) = 1 \; .$$

The average of the velocity squared is then a standard integral:

$$(v^2)_{\rm av} = \int_0^\infty dv\, v^2\, f(v) = \frac{3k\,T}{m} \; .$$

This is our familiar result, which gives the rms velocity $v_{\rm rms} = \sqrt{3kT/m}$. Note that the rms velocity is not the most likely velocity, which is given by the velocity $v_{\rm max}$ for which the probability density takes its maximum. A short calculation gives $v_{\rm max} = \sqrt{2k\,T/m}$.

With decreasing temperature $f(v)$ gets narrower peaked around its maximum values $f(v_{\rm max})$. This is depicted in figure 18-14b of Tipler.

The Energy Distribution:

The Maxwell-Boltzmann speed distribution yields the distribution of kinetic energies. For $E = mv^2/2$ we get

$$dE = m\,v\,dv$$

and we can write

$$\begin{aligned} f(v)\,dv &= \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k\,T}\right)^{3/2} v^2 \exp\left(-\frac{m\,v^2}{2k\,T}\right) dv \\ &= \frac{2}{\sqrt{\pi}} \left(\frac{1}{k\,T}\right)^{3/2} \sqrt{\frac{m\,v^2}{2}} \exp\left(-\frac{m\,v^2}{2k\,T}\right) m\,v\,dv \\ &= \frac{2}{\sqrt{\pi}} \left(\frac{1}{k\,T}\right)^{3/2} \sqrt{E} \exp\left(-\frac{E}{k\,T}\right) dE \\ &= f_{\rm energy}(E)\,dE \end{aligned}$$

where

$$f_{\mathrm{energy}}(E) = \frac{2}{\sqrt{\pi}} \left(\frac{1}{k\,T}\right)^{3/2} \sqrt{E}\ \exp\left(-\frac{E}{k\,T}\right)$$

is the Maxwell-Boltzmann energy distribution. In the language of statistical physics the factor

$$\frac{2}{\sqrt{\pi}} \left(\frac{1}{k\,T}\right)^{3/2} \sqrt{E}$$

is called the density of states, seen to be proportional to $\sqrt{E}$, and the factor

$$\exp\left(-\frac{E}{k\,T}\right)$$

is called the Boltzmann factor.

Heat and the First Law of Thermodynamics (Chapter 19)

In the 1840s James Joule showed that heat is a form of energy, and energy is conserved.

Heat Capacity and Specific Heat

When heat energy flows into a substance, the temperature of the substance rises unless the substance undergoes a phase transition, which are treated later. The amount of heat energy Q needed to raise the temperature of a substance by a small amount is proportional to the temperature change and to the mass of the substance:

$$Q = C \triangle T = m\, c \triangle T$$

where C is called heat capacity and c specific heat. The heat capacity is energy needed per one degree temperature change, and the specific heat is the heat capacity per unit mass:

$$c = \frac{C}{m}\,.$$

The molar specific heat c' is defined by

$$c' = \frac{C}{n}$$

where n is the number of moles.

The calorie (cal) is the historical unit of heat energy, originally defined as the amount of energy needed to raise the temperature of one gram water by one degree, more precisely from 20°C to 21°C, but in the range from 0°C to 100°C the variations are less than 1%. In the same way one one defines the kcal using one kilogram of water. Nowadays the calorie is defined in terms of the SI energy unit:

$$1\,\mathrm{cal} = 4.184\,\mathrm{J}\ .$$

Another customary unit of heat is the British thermal unit (BTU), which was originally defined as the amount of energy needed to raise the temperature of one pound of water by on Fahrenheit. The BTU is related to the calorie and joule by

$$1\,\mathrm{BTU} = 252\,\mathrm{cal} = 1.054\,\mathrm{kJ}\ .$$

The original definition of the calorie implies that the specific heat of water is

$$c_{\mathrm{water}} = 1\,\mathrm{cal/g}\cdot\mathrm{K} = 1\,\mathrm{kcal/kg}\cdot\mathrm{K}\ .$$

Table 19-1 of Tipler lists the specific heats of some solids and liquids.

Calorimetry:

The specific heat of an object is conveniently measured by heating the object to some temperature, placing it in an thermally insulated water bath of known mass and temperature, and measuring the final equilibrium temperature. This procedure is called calorimetry, and the insulated water container is called calorimeter.

Change of Phase and Latent Heat

When heat is added to ice at $0°$C, the temperature of the ice does not change, instead it melts. This is an example of a phase change. Common type of phase changes include:

1. Fusion (liquid to solid)
2. Melting (solid to liquid)
3. Vaporization (liquid to vapor or gas)
4. Condensation (vapor or gas to liquid)
5. Sublimation (solid to vapor or gas, e.g., for dry ice)
6. Various forms of crystallization

The fact that the temperature remains constant during a phase change has to do with the potential energy of the molecules. For instance, the molecules in a liquid are close together and exert attractive forces on each other, while the molecules in a gas are far apart. Vaporization achieves the corresponding increase in potential energy.

The heat energy pre unit mass required for a change of phase is called the latent heat L:

$$Q = m\,L\ .$$

The latent heat for melting is called latent heat of fusion. Example: For water at a pressure of 1 atm the latent heat of fusion is $L_f = 79.7$ kcal/kg$=333.5$ kJ/kg and the latent heat of vaporization is $L_v = 540$ kcal/kg$=$ 2.26 MJ/kg. Table 19-2 of Tipler compiles the latent heats of fusion and vaporization for various substances.