

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: 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:

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

Here v_{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: $\lambda = v_{\text{av}} \tau$.

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

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

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:

$$(v^2)_{\text{av}} = \int_0^{\infty} dv v^2 f(v) = \frac{3kT}{m} .$$

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

With **decreasing temperature** $f(v)$ gets narrower peaked around its maximum values $f(v_{\text{max}})$. This is depicted in figure 17-16 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

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

where

$$f_{\text{energy}}(E) = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT} \right)^{3/2} \sqrt{E} \exp \left(-\frac{E}{kT} \right)$$

is the Maxwell-Boltzmann energy distribution.

In the language of statistical physics the factor

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

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

$$\exp\left(-\frac{E}{kT}\right)$$

is called the **Boltzmann factor**.

Heat Capacity and Specific Heat (Chapter 19)

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:

$$Q = C \Delta T = m c \Delta T$$

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 defines the kcal using one kilogram of water. Nowadays the calorie is defined in terms of the SI energy unit:

$$1 \text{ cal} = 4.184 \text{ J} .$$

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 one Fahrenheit. The BTU is related to the calorie and joule by

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

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

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

Table 18-1 of Tipler-Mosca 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 per 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 $L_f = 79.7 \text{ kcal/kg} = 333.5 \text{ kJ/kg}$ and the latent heat of vaporization is $L_v = 540 \text{ kcal/kg} = 2.26 \text{ MJ/kg}$. Table 19-2 of Tipler compiles the latent heats of fusion and vaporization for various substances.

The First Law of Thermodynamics

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

This is simply energy conservation. Joule was the first to demonstrate the conversion of mechanical work into heat. His apparatus is shown in figure 18-2 of Tipler-Mosca.

It is customary to write W for the work done by the system on its surroundings, for example if a gas expands against a piston. The heat Q is taken positive when it is put into the system. Using these conventions and denoting the **internal energy** of the system by U , the first law of thermodynamics reads

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

The Internal Energy of an Ideal Gas

We have already seen that the kinetic energy K of the molecules of an ideal gas is related to the absolute temperature T by $K = 3nRT/2$, where n is the number of moles of a gas and R is the universal gas constant. If the internal energy of a gas is just the translational kinetic energy, then

$$U = K = \frac{3}{2}nRT .$$

If the molecules have other types of energy in addition to the translational energy, such as rotation, the internal energy will be larger, adding $nRT/2$ for every additional degree of freedom according to the equipartition theorem. Again, the internal energy depends only on the temperature, and not on the volume or the pressure:

$$U = U(T) \quad \text{for the ideal gas.}$$

Joule verified this by finding no temperature decrease in the **free expansion experiment** of figure 18-5 of Tipler-Mosca. Precision measurements show a small temperature decrease due to slightly non-ideal behavior of real gases.

Work and the PV Diagram for a Gas

In many types of engines work is done by a gas expanding against a movable piston. Examples are steam and gasoline engines.

Quasi-static Processes:

Figure 18-6 of Tipler-Mosca shows an ideal gas confined in a container with a tightly fitting piston, assumed to be frictionless. We move the piston slowly in small steps, so that equilibrium holds after each step. Such a process is called **quasi-static**. Let A be the area of the piston. If the piston moves a small distance x , the work done by the gas on the piston is

$$dW = F dx = P A dx = P dV$$

where $dV = A dx$ is the increase in the volume of the gas.

PV Diagrams:

We can represent the states of a gas on a diagram P versus V . Figure 18-7 of Tipler-Mosca shows a PV diagram with a horizontal line representing states which all have the same value of P . Such a process is called an **isobaric expansion**. The work done by the gas is equal to the area under the P versus V curve:

$$W = \int P dV .$$

Figure 18-8 of Tipler-Mosca shows three different paths on a PV diagram for a gas that is **initially** in the state (P_1, V_1, T) and **finally** in the state (P_2, V_2, T) . As the initial and final temperatures agree $P_1 V_1 = P_2 V_2 = n R T$ holds (ideal gas).

Figure 18-8a: The gas is heated at constant pressure and then cooled at constant volume. The **work** done is $P_1 (V_2 - V_1)$.

Figure 18-8b: The gas is cooled at constant volume and then heated at constant pressure. The **work** done is $P_2 (V_2 - V_1)$. Clearly,

$$P_2 (V_2 - V_1) < P_1 (V_2 - V_1) .$$

Figure 18-8c: Path C represents an **isothermal expansion**, meaning that the temperature remains constant. We calculate the work done using $P = nRT/V$:

$$dW_{\text{isothermal}} = P dV = \frac{nRT}{V} dV ,$$

$$W_{\text{isothermal}} = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \left(\frac{V_2}{V_1} \right) .$$

We see that the amount of **work done** by the gas is different for each process illustrated.

Since $U_2 = U_1$ for all these states, the net amount of **heat added** must also be different for each of the processes.

This illustrates that the work done and the heat added depend on how the system moves from one state to another, whereas the change in the **internal energy** does not.