Introduction to Thermal Physics


• Postulates of Atomic Theory

  ○ Matter is composed of atoms.

    This postulate used to be known as the Atomic Hypothesis until the beginning of the XXth century, when the experimental basis for the existence of atoms was established (by measuring Avogadro’s Number).

  ○ Atoms are in a constant state of motion.

    This postulate associates the concept of an absolute temperature scale with the average kinetic energy of atoms in matter. “Absolute zero” is, therefore, defined as the temperature at which all atoms in matter are at rest and, since the total kinetic energy of a collection of atoms (and its average) cannot ever be negative, it is impossible to talk about negative Kelvin temperatures.

  ○ When atoms get sufficiently close to each other, they begin to experience an attractive force.

    This postulate implies that atoms can be used to build molecules and, therefore, it forms the basis of chemistry.

  ○ When atoms get too close, they experience a repulsive force.

    This postulate implies that the density of matter must remain finite.

• Temperature

  Two temperature scales are used in this course. The Celsius scale (denoted °C) is based on the freezing and boiling points of water: 0 °C and 100 °C, respectively. The second scale is known as the Kelvin scale (denoted K), or absolute scale, with conversion formulas

  \[ T(K) = T(°C) + 273.15 \text{ K} \quad \text{or} \quad T(°C) = T(K) - 273.15 \text{ °C}. \]

  Hence, 0 K (absolute zero) = −273.15 °C and 0 °C = 273.15 K. Note that \( \Delta T(K) = \Delta T(°C) \) and, by convention, temperature changes are expressed on the Celsius scale.
• **Zeroth Law of Thermodynamics**

As indicated by the second postulate of Atomic Theory, the absolute temperature scale is proportional to the average kinetic energy of atoms in matter. This means that the atoms of an object with a low temperature will have a lower average kinetic energy than the atoms of another object with a high temperature.

When two objects (1 and 2) at different temperatures \( T_1 < T_2 \) are placed in thermal contact (i.e., when heat can be transfered from the hot object to the cold object), the two objects will eventually reach thermal equilibrium at temperature \( T_f \) (with \( T_1 < T_f < T_2 \)).

○ **Zeroth Law of Thermodynamics**

If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

We will see in Chapter 19 that the final temperature \( T_f \) is determined by the respective heat capacities \( C_1 \) and \( C_2 \) of the two objects (measured in units of \( J \cdot^o C^{-1} \)) as

\[
T_f = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}.
\]

As expected, if the two objects have identical heat capacities, \( C_1 = C_2 \), the final temperature \( T_f = (T_1 + T_2)/2 \) is exactly in the middle of the temperature range.

• **Thermal Expansion**

In general, the second and third postulates of Atomic Theory imply that, as the temperature of an object is increased, its atoms acquire greater kinetic energy (on average). Consequently, the atoms typically move farther away, which leads to the object exhibiting thermal expansion along each of its dimensions.

For *linear* thermal expansion, we find that an object with an original length \( L_0 \) expands to a length \( L_0 + \Delta L \) under a temperature change \( \Delta T \). A simple analysis shows that the length increase \( \Delta L \) must itself be proportional to the original length \( L_0 \) and the temperature change \( \Delta T \). Hence, the linear thermal expansion law is

\[
\Delta L = \alpha L_0 \Delta T,
\]

where the proportionality constant \( \alpha \) is known as the coefficient of linear expansion (measured in units of \(^o C^{-1}\)). Note that, in general, \( \Delta L \) has the same sign as \( \Delta T \) and \( \alpha \) typically shows only a small temperature dependence.
Typical values for $\alpha$ (at 20 °C) for solids range from $0.4 \times 10^{-6} \, ^\circ C^{-1}$ for quartz (which makes it quite stable as a resonant oscillating crystal) to $12 \times 10^{-6} \, ^\circ C^{-1}$ for steel and concrete and $25 \times 10^{-6} \, ^\circ C^{-1}$ for aluminum. For example, a 10 m steel rod experiences a length increase of

$$\Delta L = 12 \times 10^{-6} \, ^\circ C^{-1} \times 20 ^\circ C \times 10 \text{ m} = 2.4 \times 10^{-3} \text{ m} = 2.4 \text{ mm}$$

when subjected to a temperature increase of 20 °C.

The volume thermal expansion law $\Delta V = \beta V_0 \Delta T$, where $\beta$ is the coefficient of volume expansion; for most solids, we find $\beta \simeq 3 \alpha$ and, in general, we find $\beta_{\text{solid}} \ll \beta_{\text{liquid}} \ll \beta_{\text{gas}}$.\(^1\) Volume thermal expansion for liquids forms the basis for most thermometers. For example, a liquid-filled glass thermometer with a liquid column of initial volume $V_0$ shows a relative change $\Delta V/V_0 = \beta \Delta T$ in the volume of the liquid column as a result of the temperature change $\Delta T$; the increase in liquid volume is amplified by requiring the liquid to flow into a very thin cylindrical column from a spherical chamber.

- **Gas Laws & Ideal Gas Law**

  For the remainder of these Notes, we focus our attention on the gas phase of matter. A gas is characterized by four variables: the volume $V$ of the gas (measured in m$^3$ or L = $10^{-3}$ m$^3$ = 10$^3$ cm$^3$), the pressure $P$ of the gas (measured in Pa = N/m$^2$ or atm = $101 \times 10^3$ Pa), its temperature $T$ (measured in K), and the number of moles $n$ of gas particles (measured in mol).

  - **Boyle’s Law:** $P_1 V_1 = P_2 V_2$ for constant $(n, T)$
  - **Charles’ Law:** $V_1/T_1 = V_2/T_2$ for constant $(n, P)$
  - **Gay-Lussac’s Law:** $P_1/T_1 = P_2/T_2$ for constant $(n, V)$

  These laws are approximate laws and hold only if the molar density $n/V$ and pressure $P$ are not too large and the gas temperature is not too close to condensation.

  We now combine these three gas laws to obtain the Ideal Gas Law

  $$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} = R = 8.315 \text{ J/(mol} \cdot \text{K)} \quad \text{or} \quad PV = n RT,$$

  where $R$ denotes the universal gas constant. For example, when a bubble rises in a liquid, its volume increases by $\Delta V$, the pressure of the gas trapped inside the bubble decreases by

\(^1\)An important exception to the volume thermal expansion law is provided by water, which actually expands as its temperature goes from 4 °C to 0 °C.
\(\Delta P\), and its temperature increases by \(\Delta T\). Since the number of moles \(n_0\) stays constant (i.e., assuming that the bubble rises fast enough), the ideal gas law implies that

\[
\frac{P_0 V_0}{T_0} = \frac{(P_0 - \Delta P) (V_0 + \Delta V)}{(T_0 + \Delta T)} \quad \rightarrow \quad \frac{\Delta P}{P_0} = \frac{(\Delta V/V_0) - (\Delta T/T_0)}{(\Delta V/V_0) + 1},
\]

where \((P_0, V_0, n_0, T_0)\) describes the initial state of the bubble.

- **Avogadro’s Hypothesis**

  Equal volumes of gas at the same pressure and temperature contain equal numbers of gas particles.

  The number of gas particles in one mole of gas is defined as Avogadro’s Number

  \[N_A = 6.02 \times 10^{23} \text{ particles} \cdot \text{mol}^{-1} .\]

  The number \(N\) of gas particles in \(n\) moles of gas is, therefore, defined as \(N = n N_A\) and the Ideal Gas Law can be re-expressed as

  \[PV = nRT = N \left( \frac{R}{N_A} \right)T = NkT ,\]

  where \(k\) is Boltzmann’s constant:

  \[k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K} .\]