

Microscopic Reversibility

Microscopic reversibility is concerned with the behaviour of matter at the molecular level. To understand this concept clearly, it is first necessary to distinguish between the microscopic and macroscopic descriptions of a thermodynamic system.

Microscopic and Macroscopic View

Consider a glass of water. It contains an enormous number of water molecules. These molecules are continuously moving, colliding with one another and changing their directions and speeds.

The study of the behaviour of individual molecules is called the **microscopic description**.

In the microscopic description, quantities such as the position, velocity and momentum of individual molecules are considered.

In an experiment, however, it is not usually possible or necessary to follow every molecule separately. Instead, we observe the whole system and measure quantities such as temperature, pressure, volume, density and concentration. This is called the **macroscopic description**.

Thus, the distinction can be stated simply:

Microscopic description: behaviour of individual molecules.

Macroscopic description: overall measurable behaviour of the system.

Example of Heat Flow

Consider a metal rod whose one end is maintained at a high temperature and the other end at a lower temperature.

At the macroscopic level, we observe that heat flows from the hot end towards the cold end:

Hot end $\rightarrow$ Cold end

This observation can be described using temperature and heat flux without considering the motion of individual molecules.

At the microscopic level, the atoms and electrons inside the material are continuously moving and interacting. Their individual motions are not all in the same direction. Some particles may move towards the hot region and others towards the cold region.

The combined effect of the enormous number of microscopic motions produces the macroscopic heat flow observed experimentally.

Meaning of Microscopic Reversibility

Consider the motion of a particle having velocity $\mathbf{V}$. If its direction of motion is reversed, its velocity becomes

$$\mathbf{v} \rightarrow -\mathbf{v}$$

and its momentum changes as

$$\mathbf{p} \rightarrow -\mathbf{p}.$$

The corresponding reversal of time is represented by

$$t \rightarrow -t.$$

For ordinary molecular motion, the fundamental equations of mechanics retain their form under this reversal, provided there is no external influence that breaks time-reversal symmetry.

Therefore, if a particular sequence of molecular motions is physically possible, the corresponding sequence obtained by reversing the molecular motions is also possible in principle.

This property of the microscopic laws is known as **microscopic reversibility**.

Microscopic Reversibility and Macroscopic Irreversibility

The importance of microscopic reversibility becomes clearer when an irreversible process is considered.

Suppose heat is flowing through a rod from a region of higher temperature to a region of lower temperature. At the macroscopic level, the process has a definite direction:

High temperature $\rightarrow$ Low temperature

The reverse macroscopic process would be spontaneous heat flow from the colder region to the hotter region. Such a process is not observed under the same conditions.

This does not mean that the microscopic laws have become irreversible. The individual molecules continue to obey the laws of mechanics.

The difference arises because a macroscopic system contains an extremely large number of molecules. Thermodynamic properties such as temperature and heat flux represent the collective or average behaviour of these molecules.

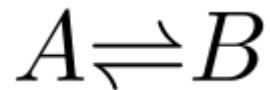
The reverse macroscopic behaviour would require an extraordinarily improbable coordinated motion

of a very large number of molecules. Consequently, although the reverse motion is not prohibited by the microscopic equations, it is practically never observed for a macroscopic system.

Microscopic Reversibility at Equilibrium

Microscopic reversibility is also important for understanding equilibrium. A system at equilibrium is not microscopically inactive. Molecules continue to move, collide and exchange energy.

Consider two possible molecular states:



Molecular transitions can occur in both directions. At equilibrium, the average rate of the forward transition is equal to the average rate of the reverse transition:

$$\text{Rate}(A \rightarrow B) = \text{Rate}(B \rightarrow A)$$

As a result, there is no net macroscopic change, even though microscopic events continue to occur.

This condition is known as **detailed balance**.

Relation with Irreversible Processes

When a system is away from equilibrium, there are gradients of thermodynamic quantities such as temperature or chemical potential. These gradients produce macroscopic fluxes.

For example, a temperature gradient produces heat flow:

$$\nabla T \neq 0$$

and the resulting heat flux can be represented by $\mathbf{J}_q$.

Similarly, a chemical-potential gradient can produce matter transport.

The macroscopic flux is therefore the collective result of molecular motion. Although individual molecular movements occur in different directions, their statistical average gives the observable transport process.

This provides the connection between molecular dynamics and the macroscopic description used in non-equilibrium thermodynamics.

Significance of Microscopic Reversibility

Microscopic reversibility provides a fundamental connection between the laws governing individual molecules and the behaviour observed for macroscopic systems.

It helps explain why:

- molecules can obey time-reversible microscopic laws,
- macroscopic systems can nevertheless show irreversible behaviour,
- equilibrium can contain continuous molecular motion without producing a net macroscopic change, and
- thermodynamic transport phenomena can be understood in terms of the collective behaviour of molecules.

Therefore, microscopic reversibility should be understood primarily as a property of the **microscopic laws of motion**, while macroscopic irreversibility describes the observable behaviour of a very large collection of molecules.