Chapter 2

Thermodynamics basics

2.1 Thermodynamic systems and variables

For the classification of the division between a "system" and its "surroundings" we distinguish between isolated, closed and open systems:

	exchange of		
	matter	energy	
isolated	-no-	-no-	System, Bath
closed	-no-	-yes-	$\delta A = - p\,\mathrm{d}V$ work, δQ
open	-yes-	-yes-	Matter, δA, δQ

A macroscopic system comes with thermodynamic variables which can be classified as either *extensive* or *intensive*.

- **Extensive** quantities are proportional to the amount of matter present.

- **Intensive** quantities are independent of the amount of matter present.

Intensive quantities	Extensive quantities
Pressure P	Volume V
Temperature T (in Kelvin)	Mass m
θ (in Celsius)	Internal energy U
	Entropy S
	molar quantity n
Magnetic Field $\mathcal{H}$	Magnetization M

2.1.1   Thermodynamic limit and state

Thermodynamic states are states of matter defined in the *thermodynamic limit*.

- **TD Limit:** A material body consisting of N atoms in a volume V approaches the thermodynamic limit when

$$N \to \infty, \qquad V \to \infty, \qquad \frac{N}{V} = \text{const.}$$

  The limit has to be taken separately for each phase when a separation into phases of low/high densities occurs.

- **TD state:** A thermodynamic state is in specified (in the thermodynamic limit) by a number of either extensive or intensive thermodynamic variables, which are usually the pressure P, the volume V and the temperature T.

  For magnetic systems we consider in addition the magnetization M or the magnetic field H.

2.2   Temperature

In the description of a thermodynamic state we understand the meaning of most of the observable, since we know them either from mechanics (P, V, ρ, ...) or electrodynamics ($\mathcal{H}$, M, ...).

The *temperature* is on the other side a concept needing a precise definition. Relating it only to the feeling of "cold" and "warm" would be too subjective.

There are several ways to define the temperature, which appears in the context of statistical mechanics as a Lagrange parameter. In the context of thermodynamics we *postulate* the existence of the temperature.

Zeroth Law of thermodynamics:

1 - Each macroscopic system has a *temperature T*. This is an *intensive* quantity and, in an *isolated system*, it has everywhere the same value.

2 - Since T is defined via a *number*, it is a *scalar* quantity.

3 - For two thermodynamic systems A and B, which are in equilibrium within themselves, it is always possible to say that

$$T_A > T_B \quad \text{or} \quad T_A < T_B \quad \text{or} \quad T_A = T_B \quad \text{(axioms of ordering)}.$$

4 - For thermodynamic systems A, B, and C it holds that, if $T_A > T_B$ and $T_B > T_C$, then $T_A > T_C$.

5 - If the systems A and B are in *thermal contact*, while the joint system $A \cup B$ is isolated, then, in equilibrium, $T_A = T_B = T_{A \cup B}$.

6 - Consider two separate thermodynamic systems A and B, with $T_A < T_B$. After putting them in contact, the temperature of the system $A \cup B$ will be $T_A < T_{A \cup B} < T_B$.

Thermometer: any physical property of a system that behaves *monotonically* with T can be used to construct a *thermometer* to measure temperature T. For instance, Hg (volume), gas thermometer (pressure), resistance thermometer (electrical resistance).

2.2.1 Thermal equilibrium and transformations

Thermal equilibrium: from our experience we know that a macroscopic system generally relaxes to a stationary state after a short time. This stationary state is called a state of *thermal equilibrium*.

Equation of state. If a system is in thermal equilibrium, the thermodynamic variables are not independent of one another, but constrained by the so-called *equation of state* of the form:

$$f(P, V, T) = 0 , \tag{2.1}$$

where f is a characteristic function of the system under study.

> *Example*: the equation of state of a classical ideal gas (a real gas in the limit of low density and high temperature) is
>
> $$f(P, V, T) = PV - Nk_B T ,$$
>
> where T is the *ideal gas temperature* measured in Kelvin (K), and $k_B = 1.381 \times 10^{-16}$ erg/K is the Boltzmann constant.

The equation of state (2.1) leaves two independent variables out of the original three.

Geometrical representation. The equation of state (2.1) can be represented by a *surface* in the state space spanned by P, V, and T. All equilibrium states must be on this surface. f is a continuous, differentiable function, except at some special points.
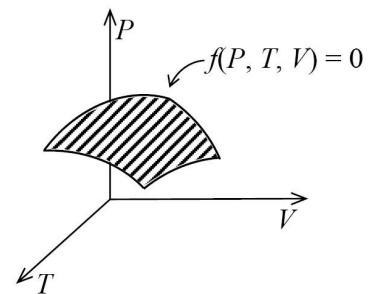
Thermodynamic transformation. A change in the external conditions changes the equilibrium state of the system. This transformation of the equilibrium state is called a *thermodynamic transformation or process*. For instance, application of external pressure causes the volume of the body to decrease. Thermodynamic transformations are classified as

1 - **quasi-static:** The transformation proceeds sufficiently slowly so that the system can be considered to remain in equilibrium;

2 - **reversible:** The system retraces the transformation backwards when the external change is reversed; for example, slow compression of a gas is a reversible thermodynamic transformation;

3 - **irreversible:** An irreversible transformation cannot be retraced by reversing the external conditions. Such a transformation cannot be represented by a path in the equation-of-state space. An example of an irreversible transformation is mixing of two gases by removing the separation wall
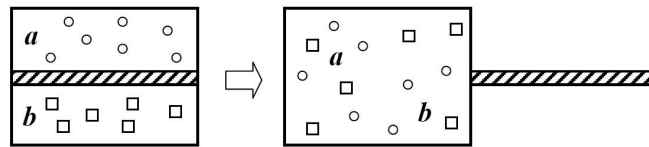
A reversible transformation is characterized in state space by infinitesimal paths on the surface defined by the equation of state (2.1). The transformation becomes irreversible once the path leave the equation-of-state surface.