Chapter 3 — Principle of Maximum Entropy

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1 Principle of Maximum Entropy

Classical thermodynamics is based on the study of macroscopic systems. To understand how a system evolves spontaneously, it is essential to introduce the notion of internal constraints and the principle of maximum entropy, which is the foundation of thermodynamic equilibrium.

1.1 Internal Constraints and the Principle of Maximum Entropy

1.1.1 Internal Constraints

An isolated thermodynamic system (which exchanges neither energy nor matter with the exterior) may be subject to internal constraints. These constraints are physical barriers or restrictions that prevent the system from spontaneously reaching its state of equilibrium.

- Example 1: A rigid and adiabatic wall separates a container into two compartments containing gases at different pressures or temperatures.
- Example 2: A chemical reaction blocked by an activation barrier.
- Example 3: A semi-permeable membrane that prevents the mixing of two solutes.

As long as these constraints exist, the system is blocked in a so-called metastable or non-equilibrium state. As soon as these constraints are removed (for example, by removing the wall or piercing a membrane), the system evolves irreversibly toward a new state of equilibrium.

1.1.2 Statement of the Principle of Maximum Entropy

The principle of maximum entropy (or the second principle of thermodynamics formulated for isolated systems) states that:

> **Principle of Maximum Entropy**
>
> The equilibrium state of an isolated system is the state for which the entropy S is maximal, taking into account the imposed internal constraints.

Mathematically, this translates into two conditions:

1. Equilibrium condition (extremum):

$$dS = 0 \qquad (1.1) \tag{1}$$

2. Stability condition (maximum):

$$d^2S < 0 \qquad (1.2) \tag{2}$$

If an internal constraint is removed, the system evolves so as to increase its entropy ($dS > 0$) until it reaches a new maximum. Entropy can never decrease for an isolated system: $\Delta S \geq 0$.

1.2 Thermodynamic Variables: Temperature, Pressure, Chemical Potential

To describe the state of a system, state variables are used. A distinction is made between extensive variables (proportional to the size of the system: U, V, N) and intensive variables (independent of size: T, P, μ).

In the entropic representation, entropy is a function of the extensive variables: $S = S(U, V, N_1, \ldots, N_k)$. Its total differential is written:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_j \neq i} dN_i \qquad (1.3) \qquad (3)$$

By analogy with classical thermodynamics, the intensive variables are defined as the partial derivatives of entropy:

$$\text{Temperature :} \quad \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \qquad (1.4)$$

$$\text{Pressure :} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \qquad (1.5)$$

$$\text{Chemical potential :} \quad -\frac{\mu_i}{T} = \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_j \neq i} \qquad (1.6)$$

Thus, the differential of entropy is written in the fundamental form:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_i \frac{\mu_i}{T} dN_i \qquad (1.7) \qquad (4)$$

By inverting this relation, we obtain the differential of the internal energy $U(S, V, N_i)$, which is the fundamental relation of thermodynamics:

$$dU = TdS - PdV + \sum_i \mu_i dN_i \qquad (1.8) \qquad (5)$$

1.3 Quasi-Static and Reversible Transformations

1.3.1 Quasi-Static Transformation

A transformation is said to be quasi-static if it is sufficiently slow that the system passes through a continuous succession of equilibrium states. At each instant, the intensive variables (T, P, μ) are defined and uniform throughout the entire system.

- A quasi-static transformation is a theoretical idealization.
- It can be represented by a continuous curve in a state diagram (e.g., $P - V$ diagram).

1.3.2 Reversible Transformation

A transformation is said to be reversible if it is quasi-static and if it generates no entropy creation. This means that the system and the external environment can be returned to their initial state without any modification of the universe.

- Condition: $\Delta S_{cre} = 0$, i.e., $dS = \delta Q_{cre}$
- A reversible transformation is an ideal limit. Every real transformation is irreversible (friction, viscosity, heat transfers under finite gradient, etc.).
- For an irreversible transformation, $\Delta S_{cre} > 0$.

1.4 Maximum Work and Thermal Machines

1.4.1 Maximum Work Theorem

The maximum work that a system can provide to the external environment between a given initial state and final state is obtained when the transformation is reversible. For a closed system in contact with a thermostat at T_0 and an atmosphere at P_0, the maximum extractable work (or exergy) is:

$$W_{max} = (U_i - U_f) - T_0(S_i - S_f) + P_0(V_i - V_f) \qquad (1.9) \tag{6}$$

Any irreversible transformation will provide work less than W_{max} (part of the energy is dissipated as heat).

1.4.2 Thermal Machines and the Carnot Cycle

A thermal machine is a device that converts heat into work by operating between a hot source (temperature T_c) and a cold source (temperature T_f).

The Carnot cycle is a theoretical reversible cycle composed of four transformations:

1. Isothermal expansion at T_c (absorption of heat Q_c).
2. Reversible adiabatic expansion (cooling from T_c to T_f).
3. Isothermal compression at T_f (rejection of heat Q_f).
4. Reversible adiabatic compression (heating from T_f to T_c).

The efficiency of a thermal machine is defined by:

$$\eta = \frac{W}{Q_c} = 1 - \frac{|Q_f|}{Q_c} \qquad (1.10) \tag{7}$$

For a reversible Carnot cycle, the efficiency is maximal and depends only on the temperatures of the sources:

$$\eta_{Carnot} = 1 - \frac{T_f}{T_c} \qquad (1.11) \tag{8}$$

Carnot's Theorem

No thermal machine operating between two given heat sources can have an efficiency greater than that of a Carnot machine operating reversibly between these same sources.

Table 1: Summary of key concepts of Chapter 3

Concept	**Essential idea**
Internal constraints	Restrictions preventing the system from reaching equilibrium.
Maximum entropy	Equilibrium state of an isolated system ($dS = 0$, $d^2S < 0$).
Intensive variables	Defined by the derivatives of S: $1/T$, P/T, $-\mu/T$.
Quasi-static transformation	Succession of equilibrium states, infinitely slow.
Reversible transformation	Quasi-static + no entropy creation.
Maximum work	Work obtained during a reversible transformation.
Carnot cycle	Ideal reversible cycle, maximum efficiency $\eta = 1 - T_f/T_c$.