

# Mathematical Thermodynamics Course Notes: Theory and Applications

Course Notes<sup>1</sup>

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<sup>1</sup>Transcribed from handwritten lecture notes



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# Chapter 1

## Non-Equilibrium Thermodynamics

### 1.1 Course Plan

This course covers the following topics:

1. Equilibrium Thermodynamics
2. Statistical Mechanics
3. Kinetic Theory of Gases
4. Conservation Laws in Continuous Systems
5. Entropy Production
6. Onsager's Principle
7. Applications

### 1.2 Equilibrium Thermodynamics

#### 1.2.1 Isolated Systems and Equilibrium States

**Definition 1.2.1** (Isolated System). An **isolated system** is a collection of matter that shares no information with the outside world.

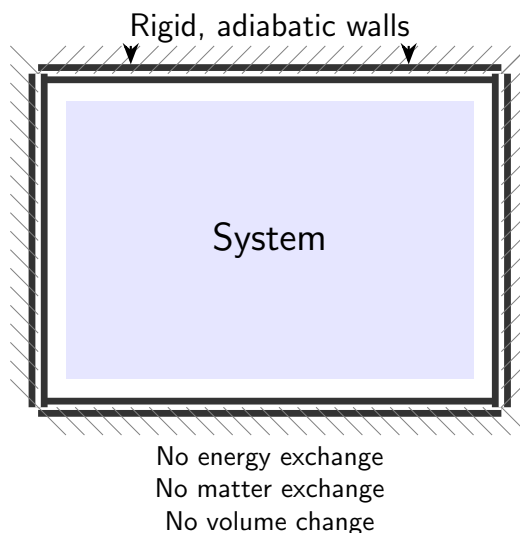


Figure 1.1: Isolated system with rigid, adiabatic walls. The system boundary prevents exchange of energy, matter, and volume with the surroundings.

*Remark 1.2.2.* The rigid walls that isolate the system from the rest of the universe allow no change in volume nor exchange of matter, and no exchange of energy.

[Equilibrium States] There are particular states, called **equilibrium states** of an isolated system that, macroscopically, are characterized by:

- $U$ , the internal energy of the system,  $U > 0$ ,
- $V$ , the volume of the system,  $V \gg 0$ ,
- $N_1, \dots, N_r$ , the mole numbers of the  $r$  chemical components of the system,  $N_i > 0$ .

### 1.2.2 Composite Systems

**Definition 1.2.3** (Composite System). A **composite system** is the union of two isolated systems (chemical components) that can exchange volume, matter (chemical components) and/or energy, however no volume, matter, or energy is exchanged with the outside.

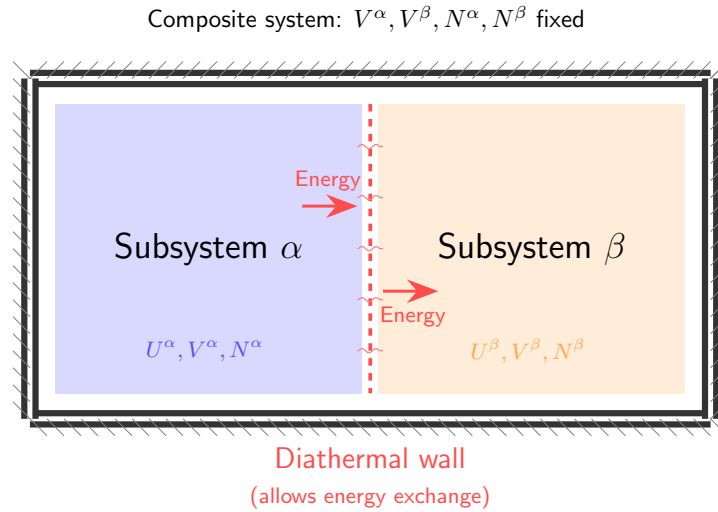


Figure 1.2: Composite system with diathermal wall separating subsystems  $\alpha$  and  $\beta$ . The diathermal wall allows energy exchange but prevents matter and volume exchange between subsystems.

**Definition 1.2.4** (Diathermal Wall). A **diathermal wall** in a composite system is one which separates two otherwise isolated systems and allows for the exchange of energy, but not matter or volume.

### 1.2.3 The Entropy Postulates

[Existence of Entropy] There exists a function  $S$  for an isolated system called its **entropy**, defined for the system at equilibrium and depending on  $(U, V, N_1, \dots, N_r)$ , i.e.

$$\tilde{S} = \tilde{S}(U, V, N_1, \dots, N_r).$$

The entropy for a composite system is the sum of the entropy functions,  $\tilde{S}^\alpha$  and  $\tilde{S}^\beta$ , for the respective subsystems, i.e.

$$\tilde{S} = \tilde{S}^\alpha + \tilde{S}^\beta = \tilde{S}^\alpha(U^\alpha, V^\alpha, \tilde{N}^\alpha) + \tilde{S}^\beta(U^\beta, V^\beta, \tilde{N}^\beta).$$

The entropy of an isolated system is **homogeneous of degree 1**, meaning:

$$\tilde{S}(\lambda U, \lambda V, \lambda N_1, \dots, \lambda N_r) = \lambda \tilde{S}(U, V, N_1, \dots, N_r)$$

for any  $\lambda > 0$ .

[Properties of Entropy] The entropy of an isolated system is a **concave, twice continuously differentiable, positive function** over its (convex) domain:

$$\Sigma_U \subseteq \underbrace{[0, \infty)}_{(U)} \times \underbrace{[0, \infty)}_{(V)} \times \underbrace{[0, \infty)}_{(N_1)} \times \cdots \times \underbrace{[0, \infty)}_{(N_r)}.$$

The entropy is a **monotonically increasing function** of  $U$ . In particular:

$$\left( \frac{\partial \tilde{S}}{\partial U} \right)_{V, N_1, \dots, N_r} > 0, \quad \forall (U, V, N) \in \Sigma_U.$$

### 1.2.4 Fundamental Relation in the Energy Representation

**Theorem 1.2.5** (Energy Representation). *Suppose that Postulates 1–3 hold for an isolated system. Then, there is a function:*

$$\tilde{U} = \tilde{U}(S, V, N_1, \dots, N_r)$$

and a convex domain of definition:

$$\Sigma_S \subseteq \underbrace{[0, \infty)}_{(S)} \times \underbrace{[0, \infty)}_{(V)} \times \underbrace{[0, \infty)}_{(N_1)} \times \cdots \times \underbrace{[0, \infty)}_{(N_r)}$$

that satisfies:

$$(i) \quad \tilde{U}(\tilde{S}(U, V, N), V, N) = U, \quad \forall (U, V, N) \in \Sigma_U$$

$$(ii) \quad \tilde{S}(\tilde{U}(S, V, N), V, N) = S, \quad \forall (S, V, N) \in \Sigma_S$$

Moreover,  $\tilde{U}$  is a **twice continuously differentiable convex function** with the property:

$$\left( \frac{\partial \tilde{U}}{\partial S} \right)_{V, N_1, \dots, N_r} > 0, \quad \forall (S, V, N) \in \Sigma_S.$$

**Example 1.2.6** (Unary Material). For a unary material ( $r = 1$ ), consider the function:

$$\tilde{S}(U, V, N) = \left( \frac{NVUR^2}{v_0\theta} \right)^{1/3}, \quad \Sigma_V = [0, \infty]^3$$

where  $R, v_0, \theta > 0$  are constants.

The corresponding energy representation is:

$$\tilde{U}(S, V, N) = \frac{S^3 v_0 \theta}{NV R^2}.$$

### 1.2.5 Temperature

**Definition 1.2.7** (Temperature). The **temperature** of an equilibrium isolated system is defined as:

$$T_0(S, V, N_1, \dots, N_r) \equiv \left( \frac{\partial \tilde{U}}{\partial S} \right)_{V, N_1, \dots, N_r} = \left( \left( \frac{\partial \tilde{S}}{\partial U} \right)_{V, N_1, \dots, N_r} \right)^{-1}.$$

### 1.2.6 Equilibrium Condition

[Maximum Entropy Principle] Equilibrium of a composite system is a state where subsystems are in equilibrium such that:

$$S = S^\alpha + S^\beta$$

is at its maximum possible value.

*Remark 1.2.8.* This postulate forms the basis for deriving equilibrium conditions in composite systems. Further mathematical derivations and proofs will follow in subsequent lectures.

## 1.3 Notes for Future Lectures

The material presented here establishes the foundational postulates of equilibrium thermodynamics. Future lectures will explore:

- Derivation of equilibrium conditions from the maximum entropy principle
- Thermodynamic potentials and Legendre transforms
- Maxwell relations and thermodynamic identities
- Connection to statistical mechanics
- Applications to specific systems

