

# Chapter 1

## ThermoS26-01

### Non-Equilibrium Thermodynamics

#### Course Plan

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

#### 1.1 Equilibrium Thermodynamics

**Definition 1.1.1** (Isolated System). An isolated system is a collection of matter that shares no information with the outside world.

**Postulate I:** There are particular states, called equilibrium states, of an isolated system that, macroscopically, are characterized by

- $U$ , the internal energy of the system,  $U \geq 0$ ,
- $V$ , the volume of the system,  $V \geq 0$ ,

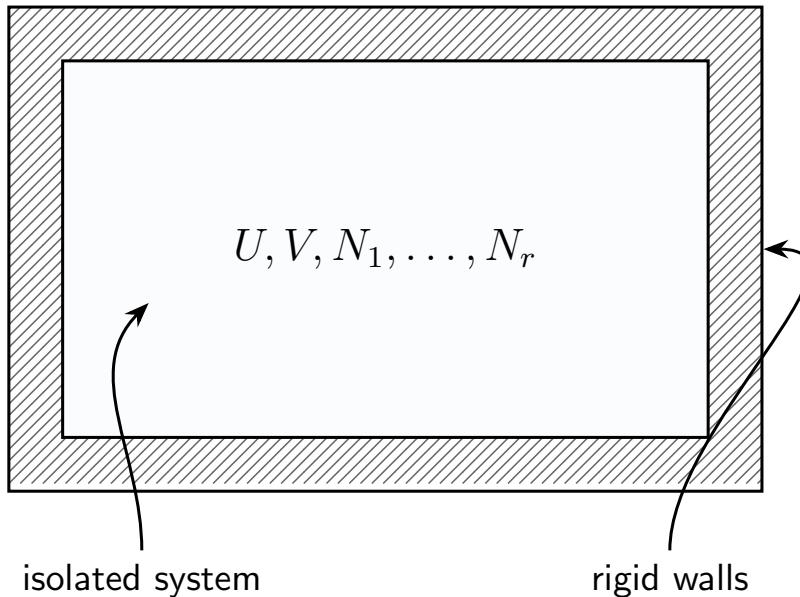


Figure 1.1: Isolated system with rigid walls. The system is characterized by internal energy  $U$ , volume  $V$ , and mole numbers  $N_1, \dots, N_r$ .

- $N_1, \dots, N_r$ , the mole numbers of the  $r$  chemical components of the system,  $N_i \geq 0$ .

The rigid walls that isolate the system from the rest of the universe allow no change in volume, no exchange of matter, and no exchange of energy.

**Definition 1.1.2** (Composite System). A composite system is the union of two isolated systems that can exchange volume, matter (chemical components) and/or energy; however, no volume, matter, or energy is exchanged with outside.

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.

A **diathermal piston** in a composite system is one which separates two otherwise isolated systems and allows for the exchange of energy and volume but not matter.

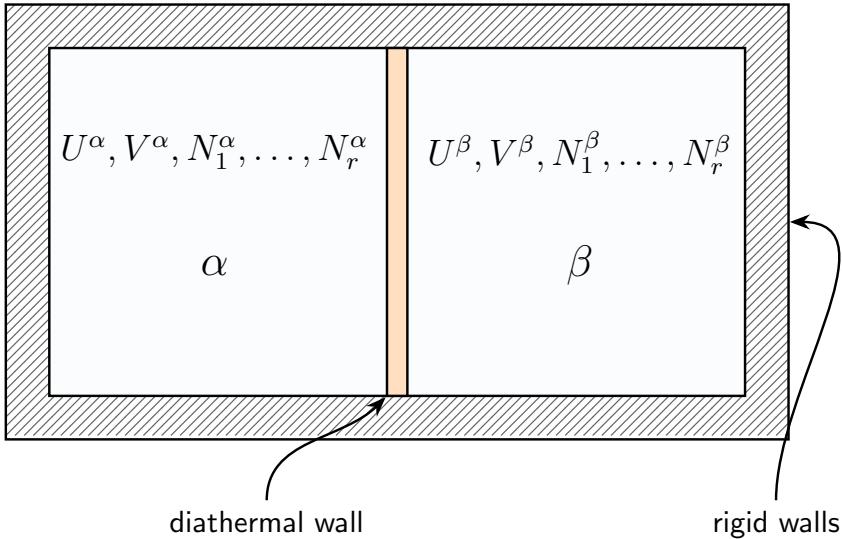


Figure 1.2: Composite system with diathermal wall separating subsystems  $\alpha$  and  $\beta$ .

**Postulate II:** There exists a function  $\tilde{S}$  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. ,

$$\tilde{S} = \tilde{S}(U, V, N_1, \dots, N_r). \quad (1.1.1)$$

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

$$\tilde{S} = \tilde{S}^\alpha + \tilde{S}^\beta = \tilde{S}^\alpha(U^\alpha, V^\alpha, N_1^\alpha, \dots, N_r^\alpha) + \tilde{S}^\beta(U^\beta, V^\beta, N_1^\beta, \dots, N_r^\beta). \quad (1.1.2)$$

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

$$\tilde{S}(\lambda U, \lambda V, \lambda N_1, \dots, \lambda N_r) = \lambda \tilde{S}(U, V, N_1, \dots, N_r) \quad (1.1.3)$$

for any  $\lambda > 0$ .

**Postulate III:** The entropy of an isolated system is a concave, twice continuously differentiable, non-negative function over its (convex) domain

$$\Sigma_u \subseteq [0, \infty)^{r+2} = \underbrace{[0, \infty)}_{(U)} \times \underbrace{[0, \infty)}_{(V)} \times \underbrace{[0, \infty)}_{(N_1)} \times \cdots \times \underbrace{[0, \infty)}_{(N_r)}. \quad (1.1.4)$$

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

$$\left( \frac{\partial \tilde{S}}{\partial U} \right)_{V, N_1, \dots, N_r} > 0, \quad \forall (U, V, \vec{N}) \in \Sigma_u^o, \quad (1.1.5)$$

where  $\Sigma_u^o$  is the interior of the set  $\Sigma_u$ .

**Theorem 1.1.3.** Suppose that Postulates I–III hold for an isolated system. Then, there is a function

$$\tilde{U} = \tilde{U}(S, V, N_1, \dots, N_r) \quad (1.1.6)$$

and a convex domain of definition

$$\Sigma_s \subseteq [0, \infty)^{r+2} = \underbrace{[0, \infty)}_{(S)} \times \underbrace{[0, \infty)}_{(V)} \times \underbrace{[0, \infty)}_{(N_1)} \times \cdots \times \underbrace{[0, \infty)}_{(N_r)} \quad (1.1.7)$$

that satisfies

$$\tilde{U}(\tilde{S}(U, V, \vec{N}), V, \vec{N}) = U, \quad \forall (U, V, \vec{N}) \in \Sigma_u \quad (1.1.8)$$

and

$$\tilde{S}(\tilde{U}(S, V, \vec{N}), V, \vec{N}) = S, \quad \forall (S, V, \vec{N}) \in \Sigma_s. \quad (1.1.9)$$

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

$$\left( \frac{\partial \tilde{U}}{\partial S} \right)_{V, N_1, \dots, N_r} > 0, \quad \forall (S, V, \vec{N}) \in \Sigma_s. \quad (1.1.10)$$

**Example 1.1.4.** Suppose that, for a unary material ( $r = 1$ ),

$$\tilde{S}(U, V, N) = \left( \frac{NVUR^2}{v_o \Theta} \right)^{1/3}, \quad \Sigma_u = [0, \infty)^3, \quad (1.1.11)$$

where  $R, v_o, \Theta > 0$  are constants. Consider the function

$$\tilde{U}(S, V, N) = \frac{S^3 v_o \Theta}{NVR^2}, \quad \Sigma_s = \underbrace{[0, \infty)}_{(S)} \times \underbrace{(0, \infty)}_{(V)} \times \underbrace{(0, \infty)}_{(N)}. \quad (1.1.12)$$

Then

$$\tilde{S}(\tilde{U}(S, V, N), V, N) = S, \quad \forall (S, V, N) \in \Sigma_s \quad (1.1.13)$$

and

$$\tilde{U}(\tilde{S}(U, V, N), V, N) = U, \quad \forall (U, V, N) \in \Sigma_u. \quad (1.1.14)$$

**Definition 1.1.5** (Temperature). Suppose that Postulates I–III hold. Then the temperature of an equilibrium isolated system is defined as

$$T_u(S, V, N_1, \dots, N_r) \equiv \left( \frac{\partial U}{\partial S} \right)_{V, N_1, \dots, N_r}. \quad (1.1.15)$$

**Postulate IV:** Equilibrium of a composite system is that state  $((U^\alpha, V^\alpha, \vec{N}^\alpha), (U^\beta, V^\beta, \vec{N}^\beta)) \in \Sigma^\alpha \times \Sigma^\beta$  such that

$$S = S^\alpha + S^\beta \quad (1.1.16)$$

is at its maximum possible value.

**Definition 1.1.6** (Pressure and Chemical Potential). The function

$$P_{\tilde{U}}(S, V, N_1, \dots, N_r) := - \left( \frac{\partial \tilde{U}}{\partial V} \right)_{S, N_1, \dots, N_r} \quad (1.1.17)$$

is called the pressure of a system. The function

$$\mu_{u,i}(S, V, N_1, \dots, N_r) := \left( \frac{\partial \tilde{U}}{\partial N_i} \right)_{S, V, N_j, j \neq i} \quad (1.1.18)$$

is called the  $i^{\text{th}}$  chemical potential.

**Theorem 1.1.7.** Let  $\tilde{S}$  and  $\tilde{U}$  be the entropy and internal energy functions of an isolated system. Then,

$$\frac{\partial \tilde{S}}{\partial U} = \frac{1}{T_s(U, V, \vec{N})}, \quad (1.1.19)$$

where

$$T_u(S, V, \vec{N}) = T_s(\tilde{U}(S, V, \vec{N}), V, \vec{N}) \quad (1.1.20)$$

and

$$T_s(U, V, \vec{N}) = T_u(\tilde{S}(U, V, \vec{N}), V, \vec{N}). \quad (1.1.21)$$

Furthermore,

$$\frac{\partial \tilde{S}}{\partial V} = \frac{P_s(U, V, \vec{N})}{T_s(U, V, \vec{N})}, \quad (1.1.22)$$

where

$$P_{\tilde{U}}(S, V, \vec{N}) = P_s(\tilde{U}(S, V, \vec{N}), V, \vec{N}), \quad (1.1.23)$$

and

$$P_s(U, V, \vec{N}) = P_u(\tilde{S}(U, V, \vec{N}), V, \vec{N}). \quad (1.1.24)$$

And, finally,

$$\frac{\partial \tilde{S}}{\partial N_j} = -\frac{\mu_{s,j}(U, V, \vec{N})}{T_s(U, V, \vec{N})}, \quad (1.1.25)$$

where

$$\mu_{u,j}(S, V, \vec{N}) = \mu_{s,j}(\tilde{U}(S, V, \vec{N}), V, \vec{N}) \quad (1.1.26)$$

and

$$\mu_{s,j}(U, V, \vec{N}) = \mu_{u,j}(\tilde{S}(U, V, \vec{N}), V, \vec{N}). \quad (1.1.27)$$

*Proof.* Proof Exercises.  $\square$

*Remark 1.1.8.* We will usually abuse notation and just write

$$T_u = T_s, \quad P_{\tilde{U}} = P_s, \quad \mu_{u,j} = \mu_{s,i}, \quad (1.1.28)$$

when the usage may be inferred from the context.

**Postulate V:** The entropy of an isolated system is zero when the temperature is zero; that is,

$$T_s(U, V, N_1, \dots, N_r) = 0 \implies \tilde{S}(U, V, N_1, \dots, N_r) = 0. \quad (1.1.29)$$

**Example 1.1.9.** Consider a unary ( $r = 1$ ) isolated system in equilibrium with the fundamental relation

$$\tilde{S}(U, V, N) = \left( \frac{NVUR^2}{v_o \Theta} \right)^{1/3}. \quad (1.1.30)$$

We can set

$$\Sigma_u = [0, \infty)^3. \quad (1.1.31)$$

$\tilde{S} = 0$  for all  $(U, V, N) \in \partial\Sigma_u$ , where

$$\partial\Sigma_u = \{(U, V, N) \in \Sigma_u \mid U = 0, \text{ or } V = 0, \text{ or } N = 0\}. \quad (1.1.32)$$

Recall,

$$\begin{aligned} T_s(U, V, N) &= \frac{3v_o \Theta}{NVU^2} \tilde{S}(U, V, N)^2 \\ &= \frac{3v_o \Theta}{NVU^2} \left( \frac{NVUR^2}{v_o \Theta} \right)^{2/3}. \end{aligned} \quad (1.1.33)$$

$T_s$  is not defined for all of  $\Sigma_u$ ! It is defined for all

$$(U, V, N) \in \text{dom}(T_s) \subset \Sigma_u. \quad (1.1.34)$$

Define

$$AZ := \{(U, V, N) \in \text{dom}(T_s) \mid T_s(U, V, N) = 0\}. \quad (1.1.35)$$

Then

$$AZ \subset \partial\Sigma_u. \quad (\text{Postulate V}) \quad (1.1.36)$$

I leave it as a homework exercise to determine  $\text{dom}(T_s)$  and  $AZ$ .