Chapter 1

Non-Equilibrium Thermodynamics

Math-Thermo
Chap 01
01/20/2026

1.1 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

1.2 Equilibrium Thermodynamics

Definition 1.2.1. (1.1) 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

$\quad\quad\quad\quad U,\quad$ the internal energy of the system, $\quad U > 0,$

$\quad\quad\quad\quad V,\quad$ the volume of the system, $\quad V > 0,$

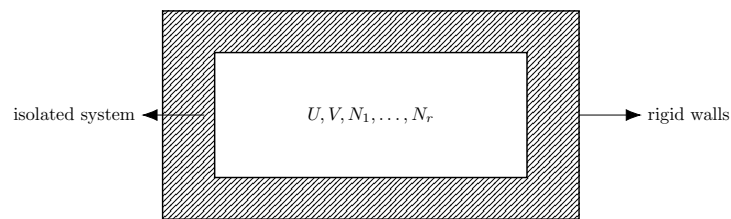$N_1, \ldots, N_r,\quad$ the mole numbers of the r chemical components of the system, $\quad N_i \geq 0.$

Figure 1.1: Isolated system with rigid walls.

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 1.2.2. (1.2) 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.
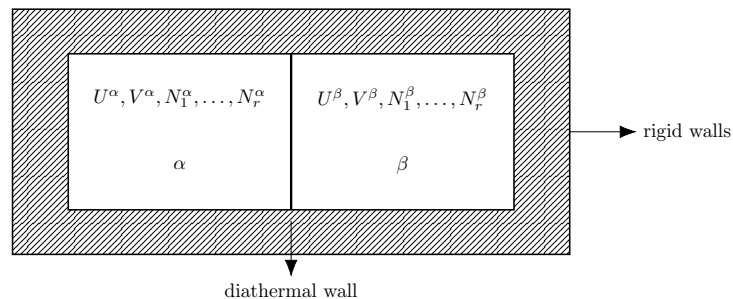

Figure 1.2: Composite system with a diathermal wall.

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

Postulate II. There exists a function $\tilde{S}$ for an isolated system called its entropy, defined for the system at equilibrium and dependent on $U, V, N_1, \ldots, N_r$, i.e.,

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

The entropy states 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.,

$$\tilde{S} = \tilde{S}^\alpha + \tilde{S}^\beta = \tilde{S}^\alpha(U^\alpha, V^\alpha, N_1^\alpha, \ldots, N_r^\alpha) + \tilde{S}^\beta(U^\beta, V^\beta, N_1^\beta, \ldots, N_r^\beta) \quad (1.1)$$

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

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

for any $\lambda > 0$.

Postulate III. The entropy of an isolated system is a concave, twice continuously differentiable, positive function over its (convex) domain,

$$\Sigma_0 \subseteq [0, \infty)^{r+2} = [0, \infty) \times [0, \infty) \times [0, \infty) \times \cdots \times [0, \infty)$$
$$(U) \quad (V) \quad (N_1) \quad \cdots \quad (N_r)$$

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

$$\left(\frac{\partial \tilde{S}}{\partial U} \right)_{V, N_1, \ldots, N_r} > 0, \quad \forall (U, V, \vec{N}) \in \Sigma_0.$$

Theorem 1.2.3. (1.3) *Suppose that Postulates I–III hold for an isolated system. Then, there is a function*

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

and a convex domain of definition

$$\Sigma_s \subseteq [0, \infty)^{r+2} = [0, \infty) \times [0, \infty) \times [0, \infty) \times \cdots \times [0, \infty)$$

$$(S) \quad (V) \quad (N_1) \quad \cdots \quad (N_r)$$

that satisfies

$$\tilde{U}(\tilde{S}(U, V, \vec{N}), V, \vec{N}) = U, \quad \forall (U, V, \vec{N}) \in \Sigma_0$$

and

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

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

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

Example 1.2.4. (1.4) Suppose that for a unary material ($r = 1$),

$$\tilde{S}(U, V, N) = \left(\frac{NVUR^2}{\nu_0 \Theta} \right)^{1/3}, \quad \Sigma_0 = [0, \infty)^3,$$

where R, ν_0, $\Theta > 0$ are constants. Consider the function,

$$\tilde{U}(S, V, N) = \frac{S^3 \nu_0 \Theta}{NVR^2}, \quad \Sigma_s = ?$$

Then

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

and

$$\tilde{U}(\tilde{S}(U, V, N), V, N) = U, \quad \forall (U, V, N) \in \Sigma_0.$$

Definition 1.2.5. (1.5) Suppose that Postulates I–III hold. Then the temperature of an equilibrium isolated system is defined as

$$T(U, S, N_1, \dots, N_r) \equiv \left(\frac{\partial \tilde{U}}{\partial S} \right)_{V, N_1, \dots, N_r}. \tag{1.2}$$

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

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

is at its maximum possible value.

Definition 1.2.6. (1.6) The functions

$$P_0(S, V, N_1, \ldots, N_r) := -\left(\frac{\partial \tilde{U}}{\partial V}\right)_{S, N_1, \ldots, N_r} \tag{1.3}$$

is called the pressure of a system. The function

$$\mu_{0,i}(S, V, N_1, \ldots, N_r) := \left(\frac{\partial \tilde{U}}{\partial N_i}\right)_{S, V, N_j, j \neq i} \tag{1.4}$$

is called the ith chemical potential.

Theorem 1.2.7. (1.7) *Let $\tilde{S}$ and $\tilde{U}$ be the entropy and internal energy functions of an isolated system. Then,*

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

where

$$T_0(S, V, \vec{N}) = T_s(\tilde{U}(S, V, \vec{N}), V, \vec{N})$$

and

$$T_s(U, V, \vec{N}) = T_0(\tilde{S}(U, V, \vec{N}), V, \vec{N}).$$

Furthermore,

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

where

$$P_0(S, V, \vec{N}) = P_s(\tilde{U}(S, V, \vec{N}), V, \vec{N}),$$

and

$$P_s(U, V, \vec{N}) = P_0(\tilde{S}(U, V, \vec{N}), V, \vec{N}).$$

And finally,

$$\frac{\partial \tilde{S}}{\partial N_i} = -\frac{\mu_{s,i}(U, V, \vec{N})}{T_s(U, V, \vec{N})}.$$

where

$$\mu_{0,i}(S, V, \vec{N}) = \mu_{s,i}(\tilde{U}(S, V, \vec{N}), V, \vec{N})$$

and

$$\mu_{s,i}(U, V, \vec{N}) = \mu_{0,i}(\tilde{S}(U, V, \vec{N}), V, \vec{N}).$$

Proof. Exercise !!!   □

Remark 1.2.8. We will usually abuse notation and just write

$$T_0 = T_s, \quad P_0 = P_s, \quad \mu_{0,i} = \mu_{s,i},$$

when the usage may inferred from the context.

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

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

Example 1.2.9. (1.8) Consider a unary $(r = 1)$ isolated system in equilibrium with the fundamental relation

$$\tilde{S}(U, V, N) = \left(\frac{NVUR^2}{\nu_0 \Theta} \right)^{1/3}.$$

We can set

$$\Sigma_0 = [0, \infty)^3.$$

$\tilde{S} = 0$ for all $(U, V, N) \in \partial \Sigma_0$, where

$$\partial \Sigma_0 = \{(U, V, N) \in \Sigma_0 : U = 0, \text{ or } V = 0, \text{ or } N = 0\}$$

Recall,

$$T_s(U, V, N) = \frac{3\nu_0 \Theta}{NVR^2} \breve{S}(U, V, N)$$

$$= \frac{3\nu_0 \Theta}{NVR^2} \left(\frac{NVUR^2}{\nu_0 \Theta} \right)^{1/3}.$$

T_s is not defined for all of Σ_0! It is defined for all

$$(U, V, N) \in \mathrm{dom}(T_s) \subset \Sigma_0$$

Define

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

Then

$$AZ \subset \partial \Sigma_0.$$

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

Remark 1.2.10. From this point forward, we will assume that all postulates hold.

Theorem 1.2.11. (1.9) *Suppose that in a composite system α and β are separated by a diathermal wall. Then, the equilibrium of the composite system may be characterized by*

$$U^\alpha + U^\beta = U_0 \tag{1.5}$$

and

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta). \tag{1.6}$$

Proof. Internal energy may be exchanged between systems α and β but cannot be exchanged with the outside world. Thus (1.5) must hold because of energy conservation. At equilibrium we must have

$$S(U^\alpha) = S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + S^\beta(U_0 - U^\alpha, V^\beta, \vec{N}^\beta)$$

and

$$\frac{\partial S}{\partial U^\alpha} = 0.$$

Note, all other variables besides U^α are fixed.

$$0 = \frac{\partial S^\alpha}{\partial U^\alpha} + \frac{\partial S^\beta}{\partial U^\beta} \frac{\partial}{\partial U^\alpha}(U_0 - U^\alpha)$$

$$= \left[T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)\right]^{-1} + \left[T^\beta(U_0 - U^\alpha, V^\beta, \vec{N}^\beta)\right]^{-1}(-1)$$

Thus,

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta)$$

with

$$U^\beta = U_0 - U^\alpha.$$

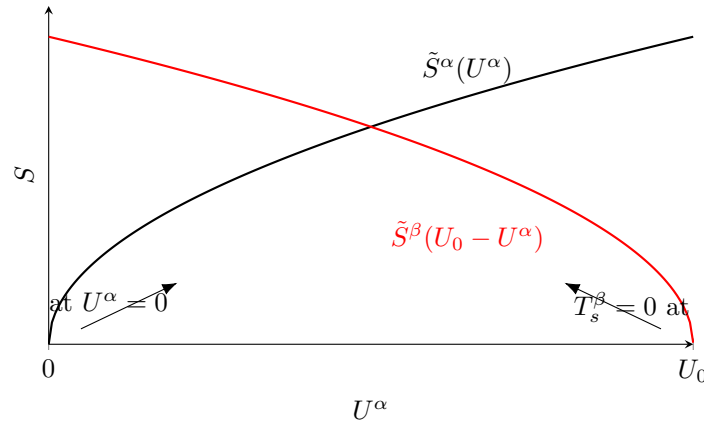How do we know that solutions exist and are unique?

Figure 1.3: Concave entropy curves $\tilde{S}^\alpha(U^\alpha)$ and $\tilde{S}^\beta(U_0 - U^\alpha)$.

This proof can also be carried out by using Lagrange multipliers. Set

$$J := S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + S^\beta(U^\beta, V^\beta, \vec{N}^\beta) + \lambda(U^\alpha + U^\beta - U_0)$$

Then, equilibrium is characterized by

$$0 = \frac{\partial J}{\partial U^\alpha} = \left[T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)\right]^{-1} + \lambda,$$

$$0 = \frac{\partial J}{\partial U^{\beta}} = \left[T^{\beta}(U^{\beta}, V^{\beta}, \vec{N}^{\beta}) \right]^{-1} + \lambda,$$

$$0 = \frac{\partial J}{\partial \lambda} = U^{\alpha} + U^{\beta} - U_0,$$

which yields the same result. /// $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ □
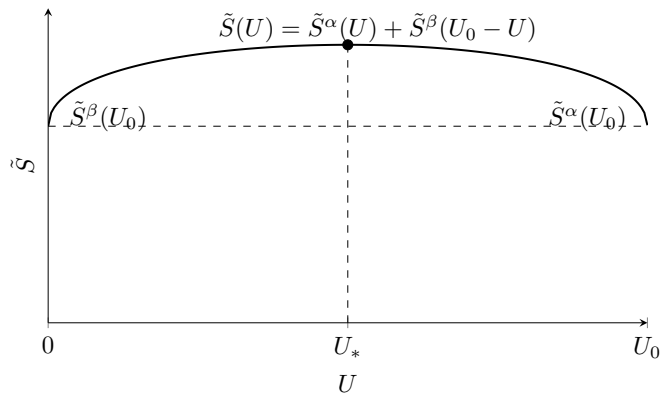

Figure 1.4: Graph of $\tilde{S}(U) = \tilde{S}^{\alpha}(U) + \tilde{S}^{\beta}(U_0 - U)$ with maximum at U_*.

The Lagrange Multiplier techniques can be visualized as follows:

Theorem 1.2.12. (1.9) *Suppose that in a composite system α and β are separated by a diathermal partition. Then, the equilibrium of the composite system may be characterized by*

$$U^{\alpha} + U^{\beta} = U_0, \tag{1.7}$$

$$V^{\alpha} + V^{\beta} = V_0, \tag{1.8}$$

and

$$T^{\alpha}(U^{\alpha}, V^{\alpha}, \vec{N}^{\alpha}) = T^{\beta}(U^{\beta}, V^{\beta}, \vec{N}^{\beta}), \quad \text{(thermal equil.)} \tag{1.9}$$

$$P^{\alpha}(U^{\alpha}, V^{\alpha}, \vec{N}^{\alpha}) = P^{\beta}(U^{\beta}, V^{\beta}, \vec{N}^{\beta}). \quad \text{(mechanical equil.)} \tag{1.10}$$
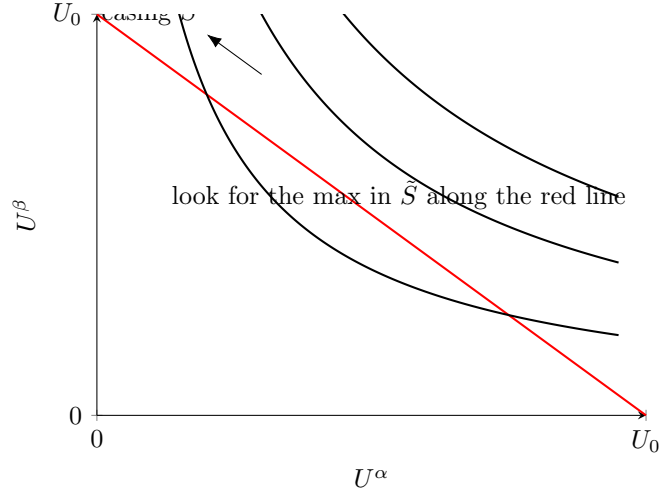
Figure 1.5: Contour lines of $\tilde{S}$ and the constraint line $U^\alpha + U^\beta = U_0$.

Proof. For this, we use the method of Lagrange multipliers. Note that $\vec{N}^\alpha$ and $\vec{N}^\beta$ are fixed. Define

$$J := S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + S^\beta(U^\beta, V^\beta, \vec{N}^\beta) + \lambda_u(U^\alpha + U^\beta - U_0) + \lambda_v(V^\alpha + V^\beta - V_0).$$

The conditions for equilibrium are

$$0 = \frac{\partial J}{\partial U^\alpha} = \left[T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) \right]^{-1} + \lambda_u,$$

$$0 = \frac{\partial J}{\partial U^\beta} = \left[T^\beta(U^\beta, V^\beta, \vec{N}^\beta) \right]^{-1} + \lambda_u,$$

$$0 = \frac{\partial J}{\partial V^\alpha} = -\frac{P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)}{T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)} + \lambda_v,$$

$$0 = \frac{\partial J}{\partial V^\beta} = -\frac{P^\beta(U^\beta, V^\beta, \vec{N}^\beta)}{T^\beta(U^\beta, V^\beta, \vec{N}^\beta)} + \lambda_v.$$

and

$$0 = \frac{\partial J}{\partial \lambda_u} = U^\alpha + U^\beta - U_0,$$

$$0 = \frac{\partial J}{\partial \lambda_v} = V^\alpha + V^\beta - V_0.$$

The result is clear. /// $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ □

Here, we have used the fact that

$$\frac{\partial S^\alpha}{\partial U^\alpha} = \frac{1}{T^\alpha}$$

$$\frac{\partial S^\alpha}{\partial V^\alpha} = \frac{P^\alpha}{T^\alpha}$$

and

$$\frac{\partial S^\alpha}{\partial N_i^\alpha} = -\frac{\mu_i^\alpha}{T^\alpha}.$$

As a short hand, we will write

$$dU^\alpha = T^\alpha \, dS^\alpha - P^\alpha \, dV^\alpha + \sum_{i=1}^r \mu_i^\alpha \, dN_i^\alpha$$

and

$$dS^\alpha = \frac{1}{T^\alpha} \, dU^\alpha + \frac{P^\alpha}{T^\alpha} \, dV^\alpha - \sum_{i=1}^r \frac{\mu_i^\alpha}{T^\alpha} \, dN_i^\alpha.$$

Using our abusive notation, we have

$$dS^\alpha = \frac{1}{T^\alpha} \, dU^\alpha + \frac{P^\alpha}{T^\alpha} \, dV^\alpha - \sum_{i=1}^r \frac{\mu_i^\alpha}{T^\alpha} \, dN_i^\alpha,$$

for example.

Theorem 1.2.13. (1.10) *Suppose that a composite system is comprised of two otherwise isolated systems with no barrier between the systems. Suppose that*

$$S^\alpha = S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)$$

and

$$S^\beta = S^\beta(U^\beta, V^\beta, \vec{N}^\beta)$$

are the fundamental entropy relations for two systems. Then the equilibrium state is defined by the relations

$$U^{\alpha} + U^{\beta} = U_0, \qquad (1.11)$$

$$V^{\alpha} + V^{\beta} = V_0, \qquad (1.12)$$

and

$$N_i^{\alpha} + N_i^{\beta} = N_{0,i} \qquad (1.13)$$

where $U_0, V_0, N_{0,i} > 0$, and

$$T^{\alpha}(U^{\alpha}, V^{\alpha}, \vec{N}^{\alpha}) = T^{\beta}(U^{\beta}, V^{\beta}, \vec{N}^{\beta}), \quad \textit{(thermal equil.)} \qquad (1.14)$$

$$P^{\alpha}(U^{\alpha}, V^{\alpha}, \vec{N}^{\alpha}) = P^{\beta}(U^{\beta}, V^{\beta}, \vec{N}^{\beta}), \quad \textit{(mech. equil.)} \qquad (1.15)$$

$$\mu_i^{\alpha}(U^{\alpha}, V^{\alpha}, \vec{N}^{\alpha}) = \mu_i^{\beta}(U^{\beta}, V^{\beta}, \vec{N}^{\beta}), \quad \textit{(chem. equil.)} \qquad (1.16)$$

Proof: The procedure is the same. One can use the method of Lagrange multipliers to do the calculations. In particular, define

$$J := S^{\alpha}(U^{\alpha}, V^{\alpha}, \vec{N}^{\alpha}) + S^{\beta}(U^{\beta}, V^{\beta}, \vec{N}^{\beta}) + \lambda_u(U^{\alpha} + U^{\beta} - U_0) + \lambda_v(V^{\alpha} + V^{\beta} - V_0) + \sum_{i=1}^{r} \lambda_i(N_i^{\alpha} + N_i^{\beta} - N_{0,i})$$

///