

Mathematical Thermodynamics Course Notes: Theory and Applications

Course Notes¹

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¹Transcribed from handwritten lecture notes

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Listings

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, $V \geq 0$,

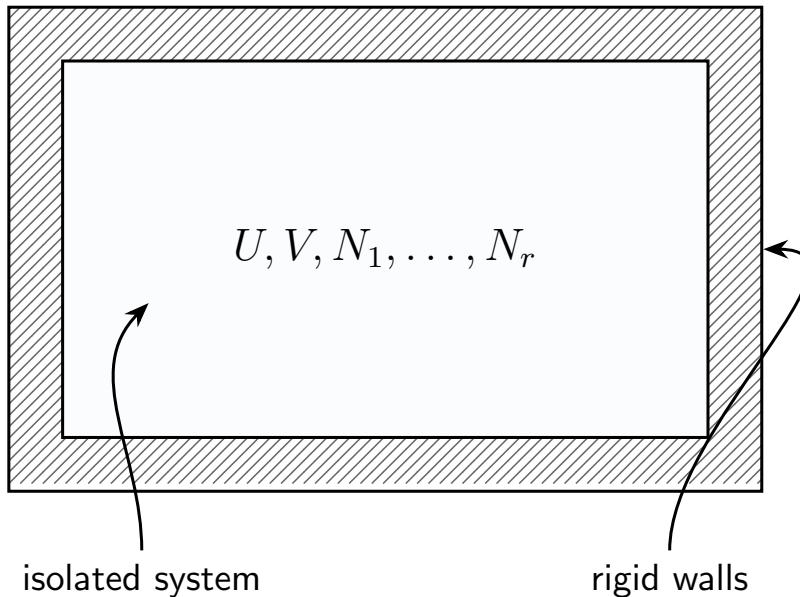


Figure 1.1: Isolated system with rigid walls. The system is characterized by internal energy U , volume V , and mole numbers N_1, \dots, N_r .

- 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 efflux 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.

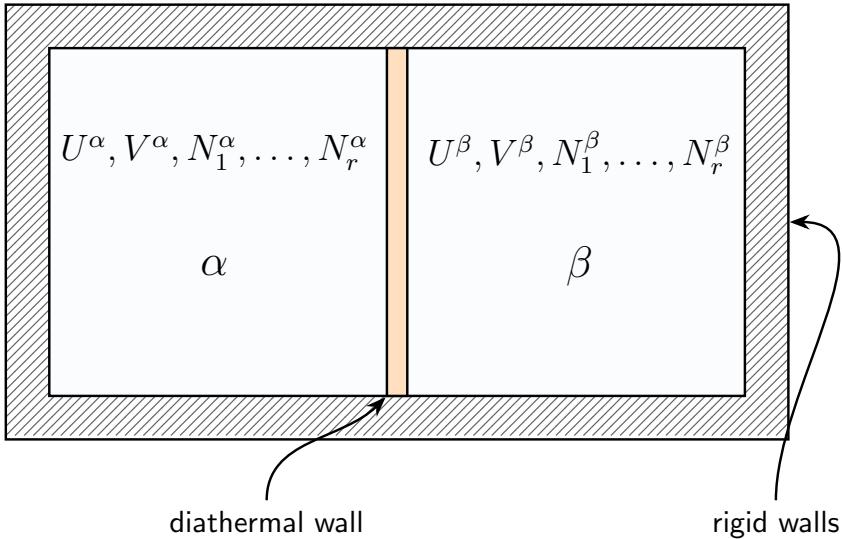


Figure 1.2: Composite system with diathermal wall separating subsystems α and β .

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}^α and \tilde{S}^β , 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, positive 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,

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

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

$$\tilde{U}(S, V, N) = \frac{S^3 v_o \Theta}{NVR^2}, \quad \Sigma_s = ? \quad (1.1.12)$$

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^{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 Σ_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 .

Remark 1.1.10. From this point forward, we will assume that all postulates hold.

Theorem 1.1.11 (Thermal Equilibrium). *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*

$$U^\alpha + U^\beta = U_o \quad (1.1.37)$$

and

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta). \quad (1.1.38)$$

Proof. Internal energy may be exchanged between systems α and β but cannot be exchanged with the outside world. Thus (1.1.37) must hold because of energy conservation. At equilibrium we must have

$$S(U^\alpha) = \tilde{S}^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + \tilde{S}^\beta(U_o - U^\alpha, V^\beta, \vec{N}^\beta) \quad (1.1.39)$$

and

$$\frac{\partial S}{\partial U^\alpha} = 0. \quad (1.1.40)$$

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

$$\begin{aligned} 0 &= \frac{\partial S}{\partial U^\alpha} = \frac{\partial S^\alpha}{\partial U^\alpha} + \frac{\partial S^\beta}{\partial U^\beta} \frac{\partial}{\partial U^\alpha}(U_o - U^\alpha) \\ &= [T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)]^{-1} + [T^\beta(U_o - U^\alpha, V^\beta, \vec{N}^\beta)]^{-1}(-1). \end{aligned} \quad (1.1.41)$$

Thus,

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta) \quad (1.1.42)$$

with

$$U^\beta = U_o - U^\alpha. \quad (1.1.43)$$

How do we know that solutions exist and are unique?

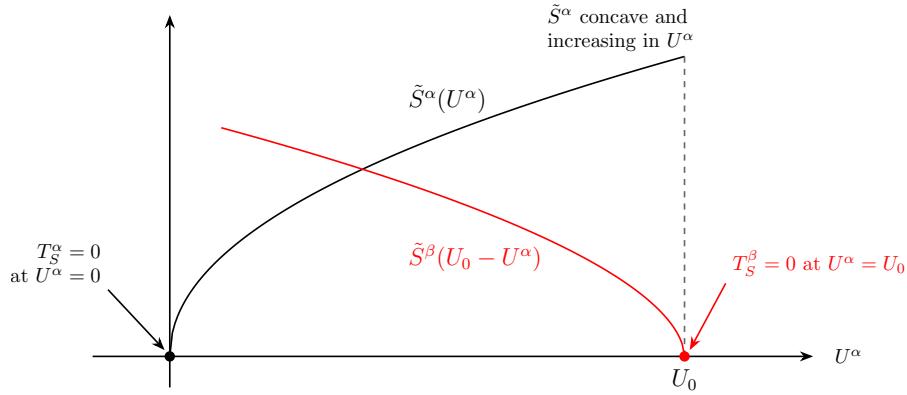


Figure 1.3: Entropy functions vs U^α for subsystems α and β . The curves show $\tilde{S}^\alpha(U^\alpha)$ (convex, increasing) and $\tilde{S}^\beta(U_o - U^\alpha)$ (decreasing). The temperature conditions at the boundaries are indicated.

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

$$J := S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + S^\beta(U^\beta, V^\beta, \vec{N}^\beta) + \lambda(U^\alpha + U^\beta - U_o). \quad (1.1.44)$$

Then, equilibrium is characterized by

$$0 = \frac{\partial J}{\partial U^\alpha} = [T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)]^{-1} + \lambda, \quad (1.1.45)$$

$$0 = \frac{\partial J}{\partial U^\beta} = [T^\beta(U^\beta, V^\beta, \vec{N}^\beta)]^{-1} + \lambda, \quad (1.1.46)$$

$$0 = \frac{\partial J}{\partial \lambda} = U^\alpha + U^\beta - U_o, \quad (1.1.47)$$

which yields the same result. \square

The Lagrange Multiplier technique can be visualized as follows:

Theorem 1.1.12 (Thermal and Mechanical Equilibrium). *Suppose that in a composite system α and β are separated by a diathermal piston. Then, the equilibrium of the composite system may be characterized by*

$$U^\alpha + U^\beta = U_o, \quad (1.1.48)$$

$$V^\alpha + V^\beta = V_o, \quad (1.1.49)$$

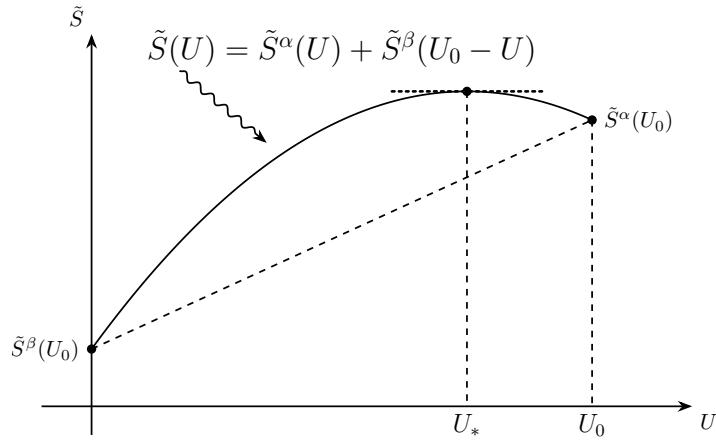


Figure 1.4: Total entropy $\tilde{S}(U^\alpha) = \tilde{S}^\alpha(U^\alpha) + \tilde{S}^\beta(U_o - U^\alpha)$ vs U^α . The concave function achieves its maximum at U_* .

and

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad (\text{thermal equil.}) \quad (1.1.50)$$

$$P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = P^\beta(U^\beta, V^\beta, \vec{N}^\beta). \quad (\text{mechanical equil.}) \quad (1.1.51)$$

Proof. For this let us use the method of Lagrange multipliers. Note that \vec{N}^α and \vec{N}^β are fixed. Define

$$J := S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + S^\beta(U^\beta, V^\beta, \vec{N}^\beta) + \lambda_u(U^\alpha + U^\beta - U_o) + \lambda_v(V^\alpha + V^\beta - V_o). \quad (1.1.52)$$

The conditions for equilibrium are

$$0 = \frac{\partial J}{\partial U^\alpha} = [T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)]^{-1} + \lambda_u, \quad (1.1.53)$$

$$0 = \frac{\partial J}{\partial U^\beta} = [T^\beta(U^\beta, V^\beta, \vec{N}^\beta)]^{-1} + \lambda_u, \quad (1.1.54)$$

$$0 = \frac{\partial J}{\partial V^\alpha} = \frac{P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)}{T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)} + \lambda_v, \quad (1.1.55)$$

$$0 = \frac{\partial J}{\partial V^\beta} = \frac{P^\beta(U^\beta, V^\beta, \vec{N}^\beta)}{T^\beta(U^\beta, V^\beta, \vec{N}^\beta)} + \lambda_v, \quad (1.1.56)$$

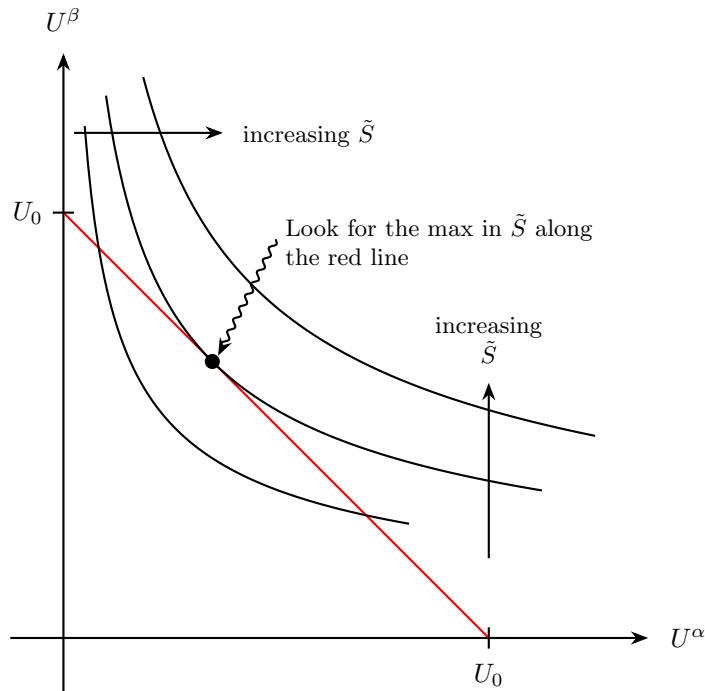


Figure 1.5: Lagrange multiplier visualization: finding the maximum in \tilde{S} along the constraint $U^\alpha + U^\beta = U_o$ (red line). The contours show increasing \tilde{S} .

and

$$0 = \frac{\partial J}{\partial \lambda_u} = U^\alpha + U^\beta - U_o, \quad (1.1.57)$$

$$0 = \frac{\partial J}{\partial \lambda_v} = V^\alpha + V^\beta - V_o. \quad (1.1.58)$$

The result is clear. \square

Here, we have used the fact that

$$\frac{\partial \tilde{S}^\alpha}{\partial U^\alpha} = \frac{1}{T^\alpha}, \quad (1.1.59)$$

$$\frac{\partial S^\alpha}{\partial V^\alpha} = \frac{P^\alpha}{T^\alpha}, \quad (1.1.60)$$

$$\frac{\partial S^\alpha}{\partial N_i^\alpha} = -\frac{\mu_i^\alpha}{T^\alpha}. \quad (1.1.61)$$

As a short hand, we will write

$$d\tilde{U}^\alpha = T_u^\alpha dS^\alpha - P_u^\alpha dV^\alpha + \sum_{i=1}^r \mu_{u,i}^\alpha dN_i^\alpha \quad (1.1.62)$$

and

$$d\tilde{S}^\alpha = \frac{1}{T_s^\alpha} dU^\alpha + \frac{P_s^\alpha}{T_s^\alpha} dV^\alpha - \sum_{i=1}^r \frac{\mu_{s,i}^\alpha}{T_s^\alpha} dN_i^\alpha. \quad (1.1.63)$$

Using our abusive notations, we have

$$d\tilde{S}^\alpha = \frac{1}{T^\alpha} dU^\alpha + \frac{P^\alpha}{T^\alpha} dV^\alpha - \sum_{i=1}^r \frac{\mu_i^\alpha}{T^\alpha} dN_i^\alpha, \quad (1.1.64)$$

for example.

Theorem 1.1.13 (Full Equilibrium). *Suppose that a composite system is comprised of two otherwise isolated systems with no barrier between the systems. Suppose that*

$$S^\alpha = S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) \quad (1.1.65)$$

and

$$S^\beta = S^\beta(U^\beta, V^\beta, \vec{N}^\beta) \quad (1.1.66)$$

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

$$U^\alpha + U^\beta = U_o, \quad (1.1.67)$$

$$V^\alpha + V^\beta = V_o, \quad (1.1.68)$$

$$N_i^\alpha + N_i^\beta = N_{o,i}, \quad (1.1.69)$$

where $U_o, V_o, N_{o,i} > 0$, and

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad (\text{thermal equil.}) \quad (1.1.70)$$

$$P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = P^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad (\text{mech. equil.}) \quad (1.1.71)$$

$$\mu_i^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = \mu_i^\beta(U^\beta, V^\beta, \vec{N}^\beta). \quad (\text{chem. equil.}) \quad (1.1.72)$$

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

$$\begin{aligned} J := & S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + S^\beta(U^\beta, V^\beta, \vec{N}^\beta) + \lambda_u(U^\alpha + U^\beta - U_o) \\ & + \lambda_v(V^\alpha + V^\beta - V_o) + \sum_{i=1}^r \lambda_i(N_i^\alpha + N_i^\beta - N_{o,i}). \end{aligned} \quad (1.1.73)$$

□

Chapter 2

ThermoS26-02

2.1 Fundamental Relations and Equations of State

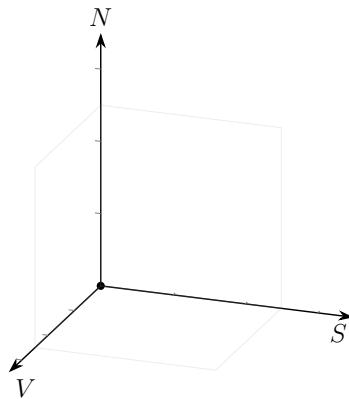


Figure 2.1: Coordinate system for state space with axes N (vertical), V (horizontal right), and S (downward).

Example 2.1.1. Suppose that, for an isolated unary fluid,

$$\tilde{U} = \left(\frac{v_0 e}{R^2} \right) \frac{S^3}{NV}, \quad \Sigma_s \subset [0, \infty)^3. \quad (2.1.1)$$

An explicit expression of the form $\tilde{U} = \tilde{U}(S, V, N)$ is called a **fundamental relation**.

Here v_0 , e , and R are positive constants.

The units of U and \tilde{U} are

$$[U] = \text{Joules}. \quad (2.1.2)$$

The units of entropy, S and \tilde{S} , are

$$[S] = \frac{\text{Joules}}{\text{degree Kelvin}} = \frac{J}{K}. \quad (2.1.3)$$

The units of volume, V , are

$$[V] = \text{meters}^3. \quad (2.1.4)$$

The units of N are

$$[N] = \text{moles}. \quad (2.1.5)$$

Of course, it is easy to see that

$$\tilde{S} = \left(\frac{NVUR^2}{v_0 e} \right)^{1/3}, \quad \Sigma_U = [0, \infty)^3. \quad (2.1.6)$$

An explicit function of the form

$$S = \tilde{S}(U, V, N) \quad (2.1.7)$$

is also called a **fundamental relation**.

In any case, the temperature which has units

$$[T] = \text{degrees Kelvin} = K, \quad (2.1.8)$$

is

$$T_U(S, V, N) = \frac{\partial \tilde{U}}{\partial S} = \frac{3v_0 e}{R^2} \frac{S^2}{NV}. \quad (2.1.9)$$

This expression is called an **equation of state**.

Observe that

$$T_U(\lambda S, \lambda V, \lambda N) = T_U(S, V, N), \quad (2.1.10)$$

that is T_U is homogeneous of order 0.

This property is true of every equation of state.

Now,

$$\begin{aligned} \left(\frac{\partial \tilde{S}}{\partial U} \right)^{-1} &= \left[\frac{1}{3} \left(\frac{NVUR^2}{v_0 e} \right)^{-2/3} \frac{NVR^2}{v_0 e} \right]^{-1} \\ &= \frac{3v_0 e}{NVR^2} \left(\frac{NVUR^2}{v_0 e} \right)^{2/3} \\ &= \frac{3v_0 e}{NVR^2} \tilde{S}(U, V, N)^2 \\ &= T_S(U, V, N). \end{aligned} \quad (2.1.11)$$

Clearly

$$T_U(\tilde{S}(U, V, N), V, N) = T_S(U, V, N), \quad (2.1.12)$$

as claimed in Theorem (1.7).

The pressure satisfies the equation of state

$$\begin{aligned} P_U(S, V, N) &= -\frac{\partial \tilde{U}}{\partial V} = -\frac{v_0 e}{R^2} \frac{S^3}{N} \left(-\frac{1}{V^2} \right) \\ &= \frac{v_0 e}{R^2} \frac{S^3}{NV^2}, \end{aligned} \quad (2.1.13)$$

which is also homogeneous of order zero.

We leave it as an exercise for the reader to show that

$$P_S(U, V, N) = P_U(\tilde{S}(U, V, N), V, N). \quad (2.1.14)$$

Finally, the chemical potential is

$$\mu_U(S, V, N) = \frac{\partial \tilde{U}}{\partial N} = -\frac{v_0 e}{R^2} \frac{S^3}{VN^2}, \quad (2.1.15)$$

which is clearly homogeneous of degree zero.

The reader can show that

$$\mu_S(U, V, N) = \mu_U(\tilde{S}(U, V, N), V, N). \quad (2.1.16)$$

2.2 Homogeneity of the Fundamental Relations

Recall, we have assumed with Postulate II that \tilde{S} is homogeneous of degree one. We also must have the following, as suggested by the example.

Theorem 2.2.1. \tilde{U} is homogeneous of degree one when written as

$$\tilde{U} = \tilde{U}(S, V, \vec{N}). \quad (2.2.1)$$

Further, $T_U(S, V, \vec{N})$, $P_U(S, V, \vec{N})$, and $\mu_{U;i}(S, V, \vec{N})$, the equations of state, are homogeneous of degree zero, meaning

$$T_U(\lambda S, \lambda V, \lambda \vec{N}) = T_U(S, V, \vec{N}) \quad (2.2.2)$$

for any $\lambda > 0$, and similarly for P_U and $\mu_{U;i}$; $i = 1, \dots, r$.

Likewise $T_S(U, V, \vec{N})$, $P_S(U, V, \vec{N})$, and $\mu_{S;i}(U, V, \vec{N})$ are homogeneous of degree zero.

Proof. Fix $V \in [0, \infty)$ and $\vec{N} \in [0, \infty)^r$. \tilde{S} is a monotonically increasing function of $U \in [0, \infty)$. For each $S \in [0, \infty)$ there exists a unique $U \in [0, \infty)$ such that

$$S = \tilde{S}(U, V, \vec{N}), \quad (2.2.3)$$

where we assume, for simplicity, that $\Sigma_U = [0, \infty)^{r+2}$. Then,

$$\tilde{U}(S, V, \vec{N}) = \tilde{U}\left(\tilde{S}(U, V, \vec{N}), V, \vec{N}\right) = U, \quad \forall(S, V, \vec{N}) \in \Sigma_S. \quad (2.2.4)$$

Let $\lambda > 0$ be arbitrary; then (2.2.3) and (2.2.4) imply

$$\tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) = \tilde{U}\left(\lambda \tilde{S}(U, V, \vec{N}), \lambda V, \lambda \vec{N}\right). \quad (2.2.5)$$

Since \tilde{S} is homogeneous of degree 1, it follows that

$$\lambda \tilde{S}(U, V, \vec{N}) = \tilde{S}(\lambda U, \lambda V, \lambda \vec{N}). \quad (2.2.6)$$

Also, recall that, generically,

$$\tilde{U}(\tilde{S}(\hat{U}, \hat{V}, \hat{\vec{N}}), \hat{V}, \hat{\vec{N}}) = \hat{U} \quad (2.2.7)$$

because of inverse relations. Combining (2.2.5)–(2.2.7) we have

$$\begin{aligned} \tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) &= \tilde{U}\left(\tilde{S}(\lambda U, \lambda V, \lambda \vec{N}), \lambda V, \lambda \vec{N}\right) \\ &= \lambda U \\ &= \lambda \tilde{U}\left(\tilde{S}(U, V, \vec{N}), V, \vec{N}\right) \\ &= \lambda \tilde{U}(S, V, \vec{N}). \end{aligned} \quad (2.2.8)$$

This completes the proof. \square

2.3 Path (Contour) Integrals

Definition 2.3.1 (Path, Path-connected, Simply-connected, Convex). Suppose that $\mathcal{D} \subseteq \mathbb{R}^n$ is open. A function $\vec{Y} : [a, b] \rightarrow \mathcal{D}$ is called a **path** (or **contour**) iff \vec{Y} is continuous and piecewise smooth. \mathcal{D} is called **path-connected** iff for every two distinct points $\vec{a}, \vec{b} \in \mathcal{D}$ there is a path $\vec{Y} : [0, 1] \rightarrow \mathcal{D}$ such that

$$\vec{Y}(a) = \vec{a} \quad \text{and} \quad \vec{Y}(b) = \vec{b}. \quad (2.3.1)$$

\mathcal{D} is called **simply-connected** iff it is (1) path connected and (2) paths can be continuously deformed to a point, i.e., there are no holes. \mathcal{D} is called **convex** iff: for every pair $\vec{a}, \vec{b} \in \mathcal{D}$, the point

$$\vec{x}(t) = \vec{a}(1-t) + \vec{b}t \in \mathcal{D} \quad (2.3.2)$$

for all $t \in [0, 1]$.

Definition 2.3.2 (Path Integral). Let $\vec{F} : \mathcal{D} \rightarrow \mathbb{R}^n$ be a C^1 function, i.e., $\vec{F} \in C^1(\mathcal{D}; \mathbb{R}^n)$. Let $\vec{Y} : [a, b] \rightarrow \mathcal{D}$ be a path in \mathcal{D} , which is assumed to be simply connected. Then the path integral $\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x}$ is defined via

$$\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x} := \int_a^b \vec{F}(\vec{Y}(x)) \cdot \vec{Y}'(x) dx. \quad (2.3.3)$$

We will also use the notation

$$\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{Y}} F_1(\vec{x}) dx_1 + \cdots + F_n(\vec{x}) dx_n. \quad (2.3.4)$$

Definition 2.3.3 (Closed Path, Simple Path). Let $\mathcal{D} \subseteq \mathbb{R}^n$ be a simply connected open set. A path $\vec{Y} : [a, b] \rightarrow \mathcal{D}$ is called **closed** iff

$$\vec{Y}(a) = \vec{Y}(b). \quad (2.3.5)$$

A closed path is called **simple** iff it does not intersect itself except at $t = a$ and $t = b$, i.e., for every $c \in (a, b)$

$$\vec{Y}(c) \neq \vec{Y}(x) \quad \forall x \in [a, c) \cup (c, b]. \quad (2.3.6)$$

Theorem 2.3.4 (Parametric Independence). Let $\mathcal{D} \subseteq \mathbb{R}^n$ be an open, simply-connected set. Assume $\vec{Y} : [a, b] \rightarrow \mathcal{D}$ is a path. If $\vec{x} : [c, d] \rightarrow \mathcal{D}$ is a path in \mathcal{D} , with the property that

$$\vec{x}(c) = \vec{Y}(a), \quad \vec{x}(d) = \vec{Y}(b), \quad (2.3.7)$$

and

$$\text{Range}(\vec{x}) = \text{Range}(\vec{Y}), \quad (2.3.8)$$

then

$$\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{x}} \vec{F}(\vec{x}) \cdot d\vec{x}. \quad (2.3.9)$$

This result guarantees that the path integrals are parametrically independent.

If $c = \text{Range}(\vec{Y}) = \text{Range}(\vec{x})$, then we write

$$\int_c \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x}. \quad (2.3.10)$$

Definition 2.3.5 (Path Independence). Let $\mathcal{D} \subseteq \mathbb{R}^n$ be an open, simply connected set. Suppose that

$$\int_{\vec{Y}_1} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{Y}_2} \vec{F}(\vec{x}) \cdot d\vec{x} \quad (2.3.11)$$

for any two paths $\vec{Y}_1 : [a, b] \rightarrow \mathcal{D}$, $\vec{Y}_2 : [a, b] \rightarrow \mathcal{D}$ with

$$\vec{Y}_1(a) = \vec{Y}_2(a) \quad \text{and} \quad \vec{Y}_1(b) = \vec{Y}_2(b). \quad (2.3.12)$$

Then we say that the integral is **path independent**. Note that we are not assuming that

$$\text{Range}(\vec{Y}_1) = \text{Range}(\vec{Y}_2). \quad (2.3.13)$$

Definition 2.3.6 (Conservative Vector Field). Let \mathcal{D} be an open set and $\vec{F} \in C^1(\mathcal{D}; \mathbb{R}^n)$. We say that \vec{F} is **conservative** iff there is a function $f \in C^1(\mathcal{D}; \mathbb{R})$ such that

$$\vec{F}(\vec{x}) = \nabla f(\vec{x}), \quad \forall \vec{x} \in \mathcal{D}. \quad (2.3.14)$$

Theorem 2.3.7. Let \mathcal{D} be an open simply connected set in \mathbb{R}^n . If $\vec{F} \in C^1(\mathcal{D}; \mathbb{R}^n)$ is conservative, then the integral

$$\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x} \quad (2.3.15)$$

is path-independent.

Proof. Let $\vec{Y}_1 : [a_1, b_1] \rightarrow \mathcal{D}$ and $\vec{Y}_2 : [a_2, b_2] \rightarrow \mathcal{D}$ be paths in \mathcal{D} with the same end points, i.e. ,

$$\vec{a} := \vec{Y}_1(a_1) = \vec{Y}_2(a_2), \quad \vec{Y}_1(b_1) = \vec{Y}_2(b_2) =: \vec{b}. \quad (2.3.16)$$

By the chain rule, for $i = 1, 2$,

$$\begin{aligned} \frac{d}{dx} f(\vec{Y}_i(x)) &= \nabla f(\vec{Y}_i(x)) \cdot \vec{Y}'_i(x) \\ &= \vec{F}(\vec{Y}_i(x)) \cdot \vec{Y}'_i(x). \end{aligned} \quad (2.3.17)$$

Thus,

$$\begin{aligned} \int_{\vec{Y}_1} \vec{F}(\vec{x}) \cdot d\vec{x} &= \int_{a_1}^{b_1} \vec{F}(\vec{Y}_1(x)) \cdot \vec{Y}'_1(x) dx \\ &= \int_{a_1}^{b_1} \frac{d}{dx} \left[f(\vec{Y}_1(x)) \right] dx \\ &\stackrel{\text{FTC}}{=} f(b) - f(a), \end{aligned} \quad (2.3.18)$$

for $i = 1, 2$. This completes the proof. \square

We have the following well-known results.

Theorem 2.3.8. Let $\mathcal{D} \subseteq \mathbb{R}^n$ be a simply-connected set and suppose that $\vec{F} \in C^1(\mathcal{D}; \mathbb{R}^n)$. The following are equivalent:

1. \vec{F} is conservative
2. $\int_Y \vec{F}(\vec{x}) d\vec{x}$ is path independent
3. $\oint_Y \vec{F}(\vec{x}) d\vec{x} = 0$ for any closed path.

2.4 Exact Differentials in Thermodynamics

Recall, we wrote, as a shorthand,

$$d\tilde{U} = T_U dS - P_U dV + \sum_{i=1}^r \mu_{U,i} dN_i. \quad (2.4.1)$$

This has the form

$$F_1 dx_1 + F_2 dx_2 + \cdots + F_n dx_n = \vec{F} \cdot d\vec{x}, \quad (2.4.2)$$

where

$$F_1 = T_U, \quad F_2 = -P_U, \quad \dots \quad (2.4.3)$$

We say that $\vec{F} \cdot d\vec{x}$ is an **exact differential** iff \vec{F} is conservative.

Clearly

$$d\tilde{U} = \nabla \tilde{U} \cdot d\vec{r} \quad (\vec{r} \in \Sigma_S) \quad (2.4.4)$$

is an exact differential, because $\nabla \tilde{U}$ is conservative, trivially. Thus, the integral

$$\int_Y d\tilde{U} = \int_Y \nabla \tilde{U} \cdot d\vec{r} \quad (2.4.5)$$

is path independent. If $\vec{Y} : [a, b] \rightarrow \Sigma_S$ is the path in question, with

$$\vec{Y}(a) = \vec{r}_a, \quad \vec{Y}(b) = \vec{r}_b, \quad (2.4.6)$$

then

$$\int_{\vec{Y}} d\tilde{U} = \int_{\vec{Y}} \nabla \tilde{U} \cdot d\vec{r} = \tilde{U}(\vec{r}_b) - \tilde{U}(\vec{r}_a). \quad (2.4.7)$$

We can use any path we want in state space Σ_S .

The same is true for

$$d\tilde{S} = \frac{1}{T_S} dU + \frac{P_S}{T_S} dV - \sum_{i=1}^r \frac{\mu_{S;i}}{T_S} dN_i, \quad (2.4.8)$$

that is

$$d\tilde{S} = \nabla \tilde{S} \cdot d\vec{r} \quad (\vec{r} \in \Sigma_U) \quad (2.4.9)$$

is an exact differential.

Chapter 3

ThermoS26-03

3.1 Heat Flow

We examine the approach to thermal equilibrium using a diathermal wall. Suppose the substance is unary, $r = 1$. It must be that the variables

$$V^\alpha, V^\beta, N^\alpha, N^\beta$$

are fixed, but energy can be exchanged in the process. Suppose the variable γ parameterizes the process.

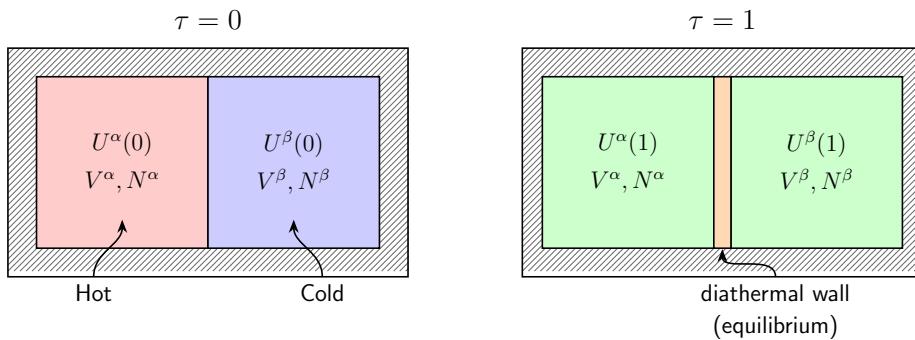


Figure 3.1: Initial and equilibrium configurations for $\gamma = 0$ and $\gamma = 1$. At $\gamma = 0$ the insulating wall is replaced with a diathermal wall; left hot subsystem has $U^\alpha(0)$, V^α, N^α and right cold subsystem has $U^\beta(0)$, V^β, N^β . At $\gamma = 1$ a diathermal wall separates subsystems with $U^\alpha(1)$, V^α, N^α and $U^\beta(1)$, V^β, N^β in equilibrium.

The initial and equilibrium states satisfy

$$\begin{aligned} S(0) &= \tilde{S}^\alpha(U^\alpha(0), V^\alpha, N^\alpha) + \tilde{S}^\beta(U^\beta(0), V^\beta, N^\beta) \\ &\leq \tilde{S}^\alpha(U^\alpha(1), V^\alpha, N^\alpha) + \tilde{S}^\beta(U^\beta(1), V^\beta, N^\beta) = S(1). \end{aligned}$$

We require that

$$U^\alpha(\gamma) + U^\beta(\gamma) = U_0.$$

The entropy is at a maximum at equilibrium. Suppose that, as indicated by Figure 3.1,

$$\tilde{T}^\alpha(U^\alpha(0), V^\alpha, N^\alpha) > \tilde{T}^\beta(U^\beta(0), V^\beta, N^\beta)$$

while at equilibrium

$$\tilde{T}^\alpha(U^\alpha(1), V^\alpha, N^\alpha) = \tilde{T}^\beta(U^\beta(1), V^\beta, N^\beta).$$

We will show that

$$U^\alpha(0) > U^\alpha(1) \quad (\text{energy is lost in } \alpha)$$

and

$$U^\beta(0) < U^\beta(1) \quad (\text{energy is gain in } \beta).$$

To see this, compute

$$\begin{aligned} \frac{dS}{d\gamma} &= \frac{\partial \tilde{S}^\alpha}{\partial U^\alpha} \frac{\partial U^\alpha}{\partial \gamma} + \frac{\partial \tilde{S}^\beta}{\partial U^\beta} \frac{\partial U^\beta}{\partial \gamma} \\ &= \frac{1}{\tilde{T}_S^\alpha(\gamma)} \frac{\partial U^\alpha}{\partial \gamma} + \frac{1}{\tilde{T}_S^\beta(\gamma)} \frac{\partial U^\beta}{\partial \gamma} \\ &= \left(\frac{1}{\tilde{T}_S^\alpha(\gamma)} - \frac{1}{\tilde{T}_S^\beta(\gamma)} \right) \frac{\partial U^\alpha}{\partial \gamma}, \end{aligned} \tag{3.1}$$

where

$$\tilde{T}_S^q(\gamma) := T_S^q(U^q(\gamma)), \quad q = \alpha, \beta.$$

We know that

$$S(0) \leq \tilde{S}(1).$$

We also know that

$$\tilde{T}_S^\alpha(0) > \tilde{T}_S^\beta(0) \quad \text{and} \quad \tilde{T}_S^\alpha(1) = \tilde{T}_S^\beta(1).$$

Set

$$R(\gamma) := \frac{1}{\tilde{T}^\alpha(\gamma)} - \frac{1}{\tilde{T}^\beta(\gamma)}, \quad 0 \leq \gamma \leq 1.$$

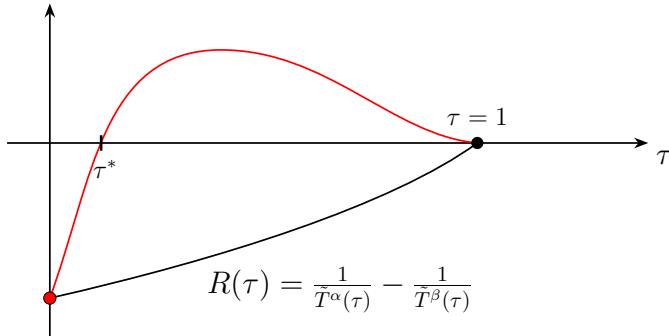


Figure 3.2: Plot of $R(\gamma)$ on $[0, 1]$. The red curve is impossible; if it occurred, equilibrium would be reached earlier at $\gamma = \gamma^*$. The valid curve remains negative with $R(1) = 0$.

We know that $R(0) < 0$ and $R(1) = 0$.

The red curve in Figure 3.2 is not possible; if it were, equilibrium would be reached earlier at $\gamma = \gamma^*$. Thus

$$R(\gamma) < 0 \quad \forall \gamma \in [0, 1].$$

Integrating (3.1), we get

$$0 \leq \tilde{S}(1) - \tilde{S}(0) = \int_0^1 R(\gamma) \frac{dU^\alpha}{d\gamma} d\gamma. \quad (3.2)$$

For $U^\alpha(\gamma)$ we have two options:

$$\text{Case (1)} \quad U^\alpha(0) > U^\alpha(1), \quad \text{Case (2)} \quad U^\alpha(0) \leq U^\alpha(1).$$

We are free to pick a parameterization however we want. Let us take a simple linear path

$$\frac{dU^\alpha}{d\gamma} = U^\alpha(1) - U^\alpha(0) =: C^\alpha.$$

Then Case (1) implies $C^\alpha < 0$, while Case (2) implies $C^\alpha \geq 0$. The integral in (3.2) is

$$0 \leq \tilde{S}(1) - \tilde{S}(0) = C^\alpha \int_0^1 R(\gamma) d\gamma.$$

Therefore the only possible choice is Case (1). Thus

$$U^\alpha(0) > U^\alpha(1) \quad (U^\beta(0) < U^\beta(1)).$$

This is consistent with our intuition about temperature. If $\tilde{T}^\alpha(0) > \tilde{T}^\beta(0)$ heat energy flows from subsystem α to subsystem β .

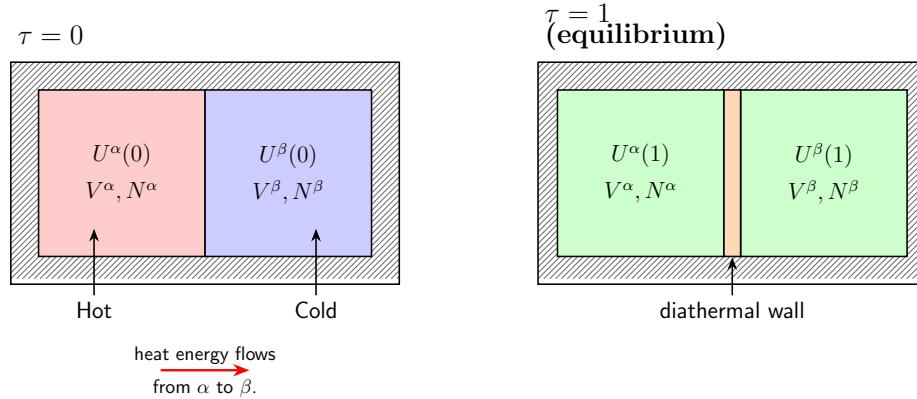


Figure 3.3: Energy transfer for $\gamma = 0$ (hot to cold through replaced wall) and $\gamma = 1$ (equilibrium with diathermal wall) showing flow from subsystem α to subsystem β .

Heat Transfer Principle: Heat energy always flows from hotter to colder system. This is equivalent to the second law of thermodynamics.

3.2 The Euler Equation

Recall that internal energy and the entropy are homogenous of degree one:

$$\tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) = \lambda \tilde{U}(S, V, \vec{N}), \quad \lambda > 0, \quad (3.3)$$

where

$$\vec{N} = \begin{bmatrix} N_1 \\ N_2 \\ \vdots \\ N_r \end{bmatrix}.$$

Theorem 3.2.1. (3.1) Let \tilde{U} be the internal energy of an isolated system. Then

$$\tilde{U} = TS - PV + \mu_1 N_1 + \cdots + \mu_r N_r. \quad (3.4)$$

Proof. Since \tilde{U} is homogenous of degree one, differentiating (3.3) with respect to λ we obtain

$$T(\lambda S, \lambda V, \lambda \vec{N}) S - P(\lambda S, \lambda V, \lambda \vec{N}) V + \sum_{i=1}^r \mu_i(\lambda S, \lambda V, \lambda \vec{N}) N_i = \tilde{U}(S, V, \vec{N}).$$

Taking $\lambda = 1$ gives (3.4), as desired. \square

Remark: Equation (3.4) is known as Euler's Equation.

Definition 3.2.2. (3.2) A process path in state space Σ_S ,

$$\Sigma_S \subseteq [0, \infty) \times [0, \infty) \times [0, \infty) \times \cdots \times [0, \infty),$$

is a continuous, piecewise differentiable function $\vec{Y} : [0, 1] \rightarrow \Sigma_S$, defined by

$$\vec{Y}(\gamma) = \begin{bmatrix} S(\gamma) \\ V(\gamma) \\ N_1(\gamma) \\ \vdots \\ N_r(\gamma) \end{bmatrix}.$$

A process path in Σ_U is defined similarly.

Thus, using the chain rule, we have

$$\frac{d}{d\gamma} \tilde{U}(\vec{Y}(\gamma)) = T(\vec{Y}(\gamma)) S'(\gamma) - P(\vec{Y}(\gamma)) V'(\gamma) + \sum_{i=1}^r \mu_i(\vec{Y}(\gamma)) N'_i(\gamma) \quad (3.5)$$

for a valid process path in state space.

Theorem 3.2.3. (3.3) Suppose that $\vec{Y} : [0, 1] \rightarrow \Sigma_S$ is a process path in state space Σ_S . Then

$$0 = S(\gamma) \frac{dT_S(\vec{Y}(\gamma))}{d\gamma} - V(\gamma) \frac{dP_S(\vec{Y}(\gamma))}{d\gamma} + \sum_{i=1}^r N_i(\gamma) \frac{d\mu_S^i(\vec{Y}(\gamma))}{d\gamma}. \quad (3.6)$$

This equation is called the Gibbs-Duhem relation.

Proof. Begin with the Euler equation and differentiate with respect to the process parameter γ :

$$\begin{aligned} \frac{d\tilde{U}}{d\gamma}(\vec{Y}(\gamma)) &= \frac{dT}{d\gamma}(\vec{Y}(\gamma)) S(\gamma) + T(\vec{Y}(\gamma)) S'(\gamma) \\ &\quad - \frac{dP}{d\gamma}(\vec{Y}(\gamma)) V(\gamma) - P(\vec{Y}(\gamma)) V'(\gamma) \\ &\quad + \sum_{i=1}^r \left\{ \frac{d\mu_i}{d\gamma}(\vec{Y}(\gamma)) N_i(\gamma) + \mu_i(\vec{Y}(\gamma)) N'_i(\gamma) \right\}. \end{aligned} \quad (3.7)$$

Substituting (3.5) into (3.7) yields (3.6). /// \square

3.3 Examples

Example 3.3.1. (3.4) Suppose that the fundamental relation for a material is given by

$$\tilde{S} = 4AU^{1/4}V^{1/2}N^{1/4} + BN, \quad \Sigma_U = [0, \infty)^3,$$

where $A, B > 0$ are constants. This function must be homogenous of degree one. Suppose $\lambda > 0$. Then

$$\tilde{S}(\lambda U, \lambda V, \lambda N) = 4A\lambda U^{1/4}\lambda V^{1/2}\lambda N^{1/4} + B\lambda N = \lambda \tilde{S}(U, V, N).///$$

Recall that

$$T = \frac{1}{\frac{\partial \tilde{S}}{\partial U}} = \left(A U^{-3/4} V^{1/2} N^{1/4} \right)^{-1} = \frac{U^{3/4}}{AV^{1/2}N^{1/4}},$$

which is homogenous degree zero.

$$\frac{P}{T} = \frac{\partial \tilde{S}}{\partial V}$$

so

$$P = T \frac{\partial \tilde{S}}{\partial V} = \frac{U^{3/4}}{AV^{1/2}N^{1/4}} \left(\frac{2AU^{1/4}N^{1/4}}{V^{1/2}} \right) = \frac{2U}{V}.$$

Finally,

$$\mu = -T \frac{\partial \tilde{S}}{\partial N} = -\frac{U^{3/4}}{AV^{1/2}N^{1/4}} \left(\frac{AU^{1/4}V^{1/2}}{N^{3/4}} + B \right) = -\frac{U}{N} - \frac{BU^{3/4}}{AV^{1/2}N^{1/4}}.///$$

Example 3.3.2. (3.5) Suppose that the fundamental relation is

$$\tilde{U} = \left(\frac{S - BN}{4AV^{1/2}N^{1/4}} \right)^4.$$

Recall that

$$T = \frac{\partial \tilde{U}}{\partial S} = 4 \left(\frac{S - BN}{4AV^{1/2}N^{1/4}} \right)^3 \frac{1}{4AV^{1/2}N^{1/4}} = \frac{\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}},$$

the same as above.

$$P = -\frac{\partial \tilde{U}}{\partial V} = -4 \left(\frac{S - BN}{4AV^{1/2}N^{1/4}} \right)^3 \left(\frac{S - BN}{4AN^{1/4}} \right) \left(-\frac{1}{2} \right) \frac{1}{V^{3/2}}$$

so

$$= 2 \left(\frac{S - BN}{4AV^{1/2}N^{1/4}} \right)^4 \frac{1}{V} = \frac{2\tilde{U}}{V}.$$

Finally,

$$\begin{aligned} \mu &= \frac{\partial \tilde{U}}{\partial N} = 4 \left(\frac{S - BN}{4AV^{1/2}N^{1/4}} \right)^3 \frac{1}{4AV^{1/2}} \frac{N^{1/4}(-B) - (S - BN)\frac{1}{4}N^{-3/4}}{N^{1/2}} \\ &= 4 \left(\frac{S - BN}{4AV^{1/2}N^{1/4}} \right)^3 \frac{1}{4AV^{1/2}} \frac{N^{1/4}(-B) - (S - BN)\frac{1}{4}N^{-3/4}}{N^{1/2}} \\ &= 4\tilde{U}^{3/4} \frac{N^{1/4}}{4AV^{1/2}N^{1/2}} \cdot \left(-B - \frac{S - BN}{4N} \right) \\ &= -\frac{B\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} - \frac{\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} \frac{(S - BN)}{4N} = -\frac{B\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} - \frac{\tilde{U}}{N}. // \end{aligned}$$

3.4 Euler Equation with Respect to Entropy

Theorem 3.4.1. (3.5) Let \tilde{S} be the internal energy of an isolated system. Then

$$\tilde{S} = \frac{1}{T_S}U + \frac{P_S}{T_S}V - \sum_{i=1}^r \frac{\mu_{S,i}}{T_S}N_i, \quad (3.8)$$

where

$$T_S = T_S(U, V, \vec{N}), \quad P_S = P_S(U, V, \vec{N}), \quad \mu_{S,i} = \mu_{S,i}(U, V, \vec{N}),$$

and

$$\frac{1}{T_S} = \frac{\partial \tilde{S}}{\partial U}, \quad \frac{P_S}{T_S} = \frac{\partial \tilde{S}}{\partial V}, \quad \frac{\mu_{S,i}}{T_S} = \frac{\partial \tilde{S}}{\partial N_i}.$$

Proof. We again use the fact that \tilde{S} is homogenous of degree one. For any $\lambda > 0$,

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

Taking the derivative with respect to λ , we have

$$\frac{U}{T_S(\lambda U, \lambda V, \lambda \vec{N})} + \frac{P_S(\lambda U, \lambda V, \lambda \vec{N})}{T_S(\lambda U, \lambda V, \lambda \vec{N})}V + \sum_{j=1}^r \frac{\mu_{S,j}(\lambda U, \lambda V, \lambda \vec{N})}{T_S(\lambda U, \lambda V, \lambda \vec{N})}N_j = \tilde{S}(U, V, \vec{N}),$$

and setting $\lambda = 1$ gives the desired result. // /

□

3.5 Gibbs-Duhem Relation in the Entropy Form

The Gibbs-Duhem equation is similarly derived.

Theorem 3.5.1. (3.6) Suppose that $\vec{Y} : [0, 1] \rightarrow \Sigma_U$ is a process path. Then

$$0 = \frac{dT_S}{d\gamma}(\vec{Y}(\gamma)) \tilde{S}(\vec{Y}(\gamma)) - \frac{dP_S}{d\gamma}(\vec{Y}(\gamma))V(\gamma) + \sum_{j=1}^r \frac{d\mu_{S,j}^i}{d\gamma}(\vec{Y}(\gamma))N_j(\gamma). \quad (3.9)$$

This equation is called the Gibbs-Duhem relation in the entropy form.

Proof. Using (3.8), we have

$$T_S(\vec{Y}(\gamma)) \tilde{S}(\vec{Y}(\gamma)) = U(\gamma) + P_S(\vec{Y}(\gamma))V(\gamma) - \sum_{j=1}^r \mu_{S,j}(\vec{Y}(\gamma))N_j(\gamma).$$

Taking the γ -derivative of the last equation, we have

$$\begin{aligned} \frac{dT_S}{d\gamma}(\vec{Y}(\gamma)) \tilde{S}(\vec{Y}(\gamma)) + T_S(\vec{Y}(\gamma)) \frac{d\tilde{S}}{d\gamma}(\vec{Y}(\gamma)) &= U'(\gamma) + \frac{dP_S}{d\gamma}(\vec{Y}(\gamma))V(\gamma) + P_S(\vec{Y}(\gamma))V'(\gamma) \\ &\quad - \sum_{j=1}^r \left\{ \frac{d\mu_{S,j}}{d\gamma}(\vec{Y}(\gamma))N_j(\gamma) + \mu_{S,j}(\vec{Y}(\gamma))N'_j(\gamma) \right\}. \end{aligned} \quad (3.10)$$

Taking the γ -derivative of $\tilde{S}(\vec{Y}(\gamma))$ we have

$$\frac{d\tilde{S}}{d\gamma}(\vec{Y}(\gamma)) = \frac{1}{T_S(\vec{Y}(\gamma))}U'(\gamma) + \frac{P_S(\vec{Y}(\gamma))}{T_S(\vec{Y}(\gamma))}V'(\gamma) - \sum_{j=1}^r \frac{\mu_{S,j}(\vec{Y}(\gamma))}{T_S(\vec{Y}(\gamma))}N'_j(\gamma). \quad (3.11)$$

Substituting (3.11) into (3.10) yields (3.9). // / □

Remark: Compare (3.6) and (3.9):

$$\begin{aligned} 0 &= S(\gamma) \frac{dT_S(\vec{Y}(\gamma))}{d\gamma} - V(\gamma) \frac{dP_S(\vec{Y}(\gamma))}{d\gamma} + \sum_{i=1}^r N_i(\gamma) \frac{d\mu_{S,i}^i(\vec{Y}(\gamma))}{d\gamma}, \\ 0 &= \frac{dT_S}{d\gamma}(\vec{Y}(\gamma)) \tilde{S}(\vec{Y}(\gamma)) - \frac{dP_S}{d\gamma}(\vec{Y}(\gamma))V(\gamma) + \sum_{j=1}^r \frac{d\mu_{S,j}^i}{d\gamma}(\vec{Y}(\gamma))N_j(\gamma), \end{aligned}$$

These are essentially the same expression!

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