

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

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

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

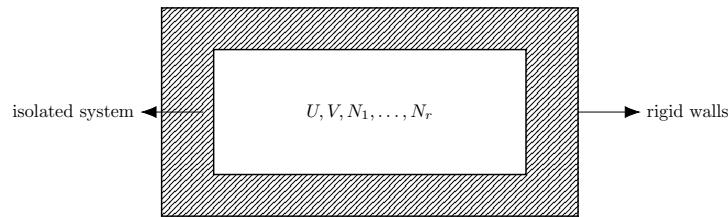


Figure 1.1: Isolated system with rigid walls.

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.

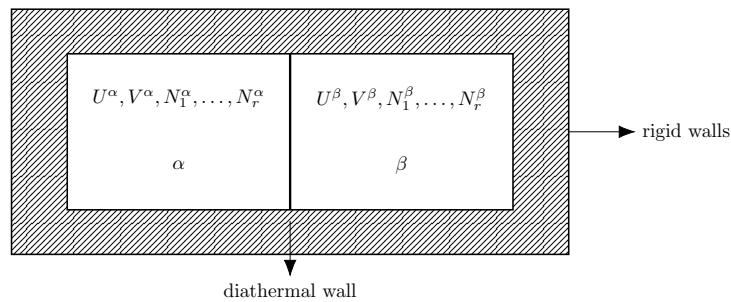


Figure 1.2: Composite system with a diathermal wall.

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, \dots, N_r , i.e.,

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

The entropy states 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.,

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

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 $\lambda > 0$.

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

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

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

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

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

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

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 $R, \nu_0, \Theta > 0$ are constants. Consider the function,

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

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

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

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

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

is called the pressure of a system. The function

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

is called the i^{th} 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,

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

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,

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

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

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

Define

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

Then

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

(Postulate V)

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

$$U^\alpha + U^\beta = U_0 \quad (1.5)$$

and

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

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.

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

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

Thus,

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

with

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

How do we know that solutions exist and are unique?

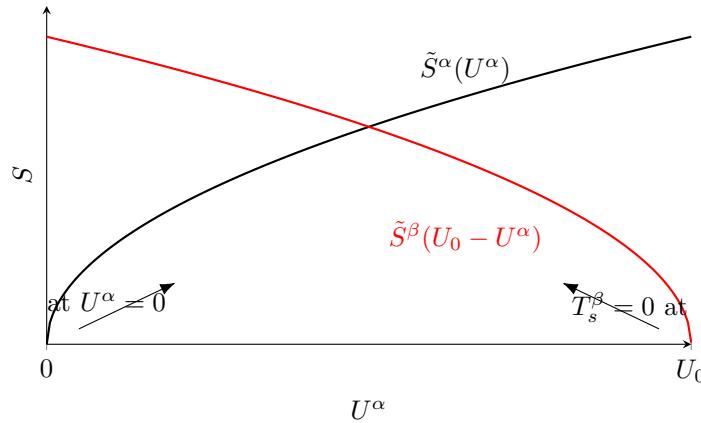


Figure 1.3: Concave entropy curves $\tilde{S}^\alpha(U^\alpha)$ and $\tilde{S}^\beta(U_0 - U^\alpha)$.

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

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

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

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

which yields the same result. ///
□

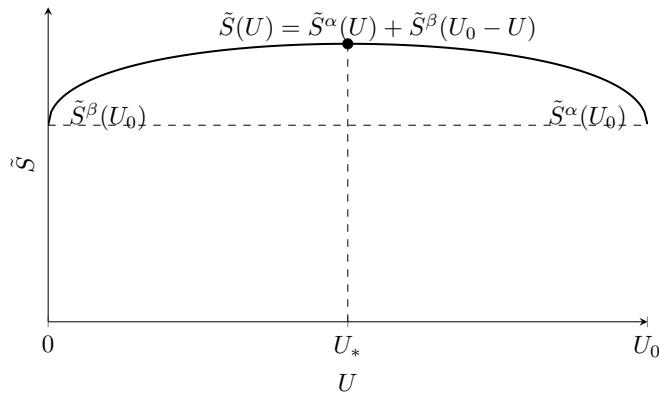


Figure 1.4: Graph of $\tilde{S}(U) = \tilde{S}^\alpha(U) + \tilde{S}^\beta(U_0 - U)$ with maximum at U_* .

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

$$U^\alpha + U^\beta = U_0, \quad (1.7)$$

$$V^\alpha + V^\beta = V_0, \quad (1.8)$$

and

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

$$P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = P^\beta(U^\beta, V^\beta, \vec{N}^\beta). \quad (\text{mechanical equil.}) \quad (1.10)$$

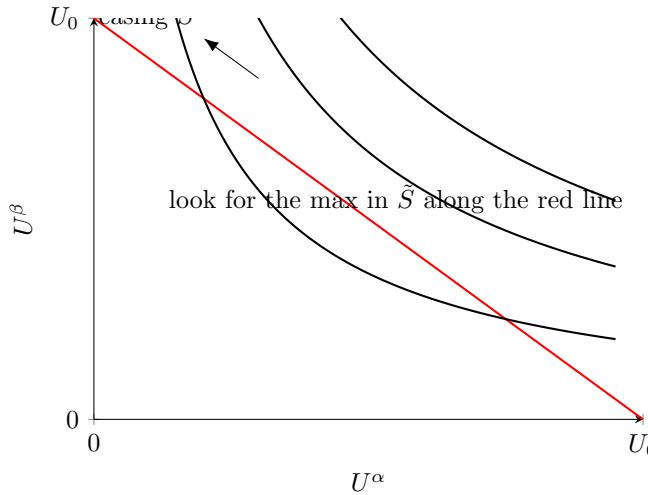


Figure 1.5: Contour lines of \tilde{S} and the constraint line $U^\alpha + U^\beta = U_0$.

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

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

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

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

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

The result is clear. ///

□

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

$$U^\alpha + U^\beta = U_0, \quad (1.11)$$

$$V^\alpha + V^\beta = V_0, \quad (1.12)$$

and

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

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

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

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

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

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

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

///

Chapter 2

Math Thermo

Math Thermo
Class 02
01/22/2026

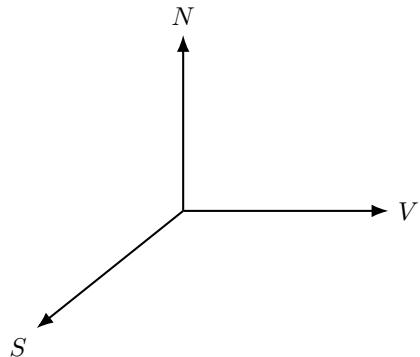


Figure 2.1: Coordinate axes labeled N , V , and S .

Example 2.0.1. (2.1) Suppose that, for an isolated unary fluid

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

A explicit expression of the form $\tilde{U} = \tilde{U}(S, V, N)$ is called a fundamental relation. Here v_0 , θ and R are positive constants. The units of U and \tilde{U} are

$$[U] = \text{Joules.}$$

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

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

The units of volume, V , are

$$[V] = \text{meters}^3.$$

The units of N are

$$[N] = \text{moles}.$$

Of course, it is easy to see that

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

An explicit function of the form

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

is also called a fundamental relation.

In any case, the temperature which has units

$$[T] = \text{degrees Kelvin} = K,$$

is

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

This expression is called an equation of state.

Observe that

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

that is T_U is homogeneous of order 0. This property is true of every equation of state.

Now,

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

$$= T_S(U, V, N),$$

Clearly

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

as claimed in Theorem (1.7).

The pressure satisfies the equation of state

$$\begin{aligned} P_S(S, V, N) &= -\frac{v_0 \theta}{R^2} \frac{S^3}{N} \frac{1}{V^2} \\ &= \frac{v_0 \theta}{R^2} \frac{S^3}{NV^2}, \end{aligned}$$

which is also homogeneous of order zero. We leave it as an exercise for the reader to show that

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

Finally, the chemical potential is

$$\mu_S(S, V, N) = -\frac{v_0 \theta}{R^2} \frac{S^3}{VN^2},$$

which is clearly homogeneous of degree zero. The reader can show that

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

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

Theorem 2.0.2. (2.2) \tilde{U} is homogeneous of degree one when written as

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

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. I mean:

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

for any $\lambda > 0$, and similarly for P and μ_{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

$$S = \tilde{S}(U, V, \vec{N}), \quad (2.1)$$

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

$$\tilde{U}(S, V, \vec{N}) = \tilde{U}(\tilde{S}(U, V, \vec{N}), V, \vec{N}), \quad \forall (S, V, \vec{N}) \in \Sigma_S. \quad (2.2)$$

Let $\lambda > 0$ be arbitrary; then (2.1) and (2.2) imply

$$\tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) = \tilde{U}(\lambda \tilde{S}(U, V, \vec{N}), \lambda V, \lambda \vec{N}) \quad (2.3)$$

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

$$\lambda \tilde{S}(U, V, \vec{N}) = \tilde{S}(\lambda U, \lambda V, \lambda \vec{N}) \quad (2.4)$$

Also, recall that, generically,

$$\tilde{U}(\tilde{S}(U, V, \vec{N}), V, \vec{N}) = U \quad (2.5)$$

because of inverse relations. Combining (2.3) – (2.5) we have

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

□

2.1 Path (Contour) Integrals

Definition 2.1.1. (2.4) Suppose that $D \subset \mathbb{R}^n$ is open. A function $\vec{\gamma} : [a, b] \rightarrow D$ is called a path (or contour) iff $\vec{\gamma}$ is continuous and piecewise smooth. The domain D is called path-connected iff for any two distinct points $\vec{a}, \vec{b} \in D$ there is a path $\vec{\gamma} : [a, b] \rightarrow D$ such that $\vec{\gamma}(a) = \vec{a}$ and $\vec{\gamma}(b) = \vec{b}$.

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

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

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

Definition 2.1.2. (2.5) Let $\vec{F} : D \rightarrow \mathbb{R}^n$ be a C^1 function, i.e., $\vec{F} \in C^1(D; \mathbb{R}^n)$. Let $\vec{\gamma} : [a, b] \rightarrow D$ be a path in D which is assumed to be simple-connected. Then the path integral $\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}$ is defined via

$$\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x} := \int_a^b \vec{F}(\vec{\gamma}(\tau)) \cdot \vec{\gamma}'(\tau) d\tau. \quad (2.6)$$

We will also use the notation

$$\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{\gamma}} F_1(\vec{x}) dx_1 + \cdots + F_n(\vec{x}) dx_n$$

Definition 2.1.3. (2.6) Let $D \subset \mathbb{R}^n$ be a simply connected open set. A path $\vec{\gamma} : [a, b] \rightarrow D$ is called closed iff

$$\vec{\gamma}(a) = \vec{\gamma}(b).$$

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

$$\vec{\gamma}(c) \neq \vec{\gamma}(\tau), \quad \tau \in [a, c) \cup (c, b]$$

Theorem 2.1.4. (2.7) Let $D \subset \mathbb{R}^n$ be an open, simply-connected set. Assume $\vec{\gamma} : [a, b] \rightarrow D$ is a simple path. If $\vec{x} : [c, d] \rightarrow D$ is a path in D , with the property that

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

and

$$\text{Range}(\vec{x}) = \text{Range}(\vec{\gamma}),$$

then

$$\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{x}} \vec{F}(\vec{x}) \cdot d\vec{x}.$$

This result guarantees that the path integrals are parametrization independent. If $C = \text{Range}(\vec{\gamma}) = \text{Range}(\vec{x})$, then we write

$$\int_C \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}.$$

Definition 2.1.5. (2.7) Let $D \subset \mathbb{R}^n$ be an open, simply connected set. Suppose that

$$\int_{\vec{\gamma}_1} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{\gamma}_2} \vec{F}(\vec{x}) \cdot d\vec{x}$$

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

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

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

$$\text{Range}(\vec{\gamma}_1) = \text{Range}(\vec{\gamma}_2).$$

Definition 2.1.6. (2.8) Let D be an open set and $\vec{F} \in C^1(D; \mathbb{R}^n)$. We say that \vec{F} is conservative iff there is a function $f \in C^1(D; \mathbb{R})$ such that

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

Theorem 2.1.7. (2.9) Let D be an open simply connected set in \mathbb{R}^n . If $\vec{F} \in C^1(D; \mathbb{R}^n)$ is conservative, then the integral

$$\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}$$

is path-independent.

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

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

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

$$\begin{aligned} \frac{d}{d\tau} f(\vec{\gamma}_i(\tau)) &= \nabla f(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}'_i(\tau) \\ &= \vec{F}(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}'_i(\tau). \end{aligned}$$

Thus,

$$\begin{aligned} \int_{\vec{\gamma}_i} \vec{F}(\vec{x}) \cdot d\vec{x} &= \int_{a_i}^{b_i} \vec{F}(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}'_i(\tau) d\tau \\ &= \int_{a_i}^{b_i} \frac{d}{d\tau} f(\vec{\gamma}_i(\tau)) d\tau \\ &= f(\vec{b}) - f(\vec{a}), \end{aligned}$$

for $i = 1, 2$. □

We have the following well-known results.

Theorem 2.1.8. (2.10) Let $D \subset \mathbb{R}^n$ be a simply-connected set and suppose that $\vec{F} \in C^1(D; \mathbb{R}^n)$. The following are equivalent

1. \vec{F} is conservative
2. $\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}$ is path independent
3. $\oint_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x} = 0$ for any closed path.

Recall, we write, as a shorthand

$$d\tilde{U} = T_U dS - P_U dV + \sum_{i=1}^r \mu_{U_i} dN_i.$$

This has the form

$$F_1 dx_1 + F_2 dx_2 + \cdots + F_n dx_n = \vec{F} \cdot d\vec{x}$$

where $F_1 = T_U$, $F_2 = -P_U$, ... We say that $\vec{F} \cdot d\vec{x}$ is an exact differential if \vec{F} is conservative.

Clearly

$$d\tilde{U} = \nabla \tilde{U} \cdot d\vec{\sigma} \quad (\vec{\sigma} \in \Sigma_s)$$

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

$$\int_{\vec{\gamma}} d\tilde{U} = \int_{\vec{\gamma}} \nabla \tilde{U} \cdot d\vec{\sigma}$$

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

$$\vec{\gamma}(a) = \vec{\sigma}_a, \quad \vec{\gamma}(b) = \vec{\sigma}_b,$$

then

$$\int_{\vec{\gamma}} d\tilde{U} = \int_{\vec{\gamma}} \nabla \tilde{U} \cdot d\vec{\sigma} = \tilde{U}(\vec{\sigma}_b) - \tilde{U}(\vec{\sigma}_a).$$

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

The same is true for

$$d\tilde{S} = \frac{1}{T_s} dU + \frac{P_s}{T_s} dV - \sum_{i=1}^r \frac{\mu_{S_i}}{T_s} dN_i,$$

that is

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

is an exact differential.

Chapter 3

ThermoS26-03

Math Thermo
class 03
01/27/2025

3.1 Heat Flow

Let us examine the approach to thermal equilibrium using a diathermal wall. Suppose the substance is binary $r = 1$. 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 $\gamma = 0$ initial state $\gamma = 1$

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

equilibrium state

We require that

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

The entropy is at a max at equilibrium.

Suppose that, as indicated by the figure above,

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

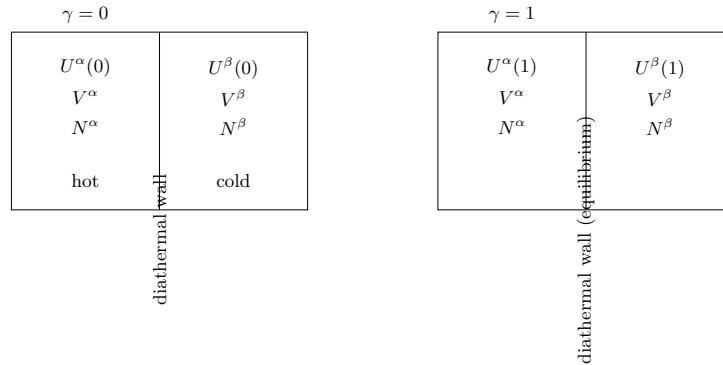


Figure 3.1: Subsystems α and β separated by a diathermal wall, with hot and cold initial states and equilibrium at $\gamma = 1$.

We know that when equilibrium is attained

$$T^\alpha(U^\alpha(1), V^\alpha, N^\alpha) = T^\beta(U^\beta(1), V^\beta, N^\beta)$$

We will show that

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

and

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

To see this compute

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

where

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

We know that

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

We know that

$$\tilde{T}_s^\alpha(0) > \tilde{T}_s^\beta(0)$$

and

$$\tilde{T}_s^\alpha(1) = \tilde{T}_s^\beta(0)$$

Set

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

We know that

$$R(0) < 0 \quad \text{and} \quad R(1) = 0$$

Thus

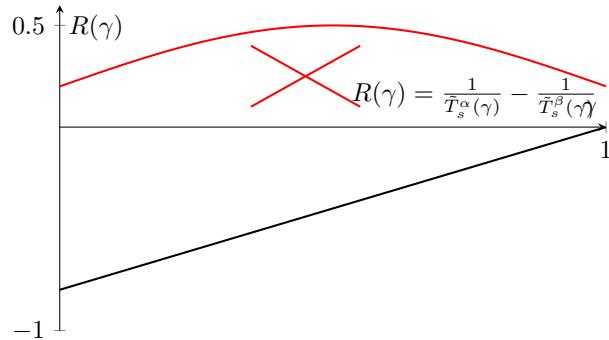


Figure 3.2: $R(\gamma)$ versus γ , with the invalid red curve crossed out.

The red curve 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 equation (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

Case (1) $U^\alpha(0) > U^\alpha(1)$

or Case (2) $U^\alpha(0) \leq U^\alpha(1)$.

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

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

Then

$$\text{Case (1)} \Rightarrow C^\alpha < 0$$

$$\text{Case (2)} \Rightarrow C^\alpha \geq 0$$

The integral in (3.2) is

$$0 \leq \tilde{S}(1) - \tilde{S}(2) = C^\alpha \int_0^1 R(\gamma) d\gamma$$

$$< 0$$

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 $T^\alpha(0) > T^\beta(0)$ net energy flows from subsystem α to subsystem β .

$$\gamma = 0 \quad \gamma = 1$$

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

3.2 The Euler Equation

Recall that internal energy and the entropy are homogeneous of degree one.

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

where

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

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 homogeneous of degree one differentiating equation (3.1) with respect to λ we obtain

$$T(\lambda S, \lambda V, \lambda \tilde{\mathbf{N}})S - P(\lambda S, \lambda V, \lambda \tilde{\mathbf{N}})V + \sum_{j=1}^r \mu_j(\lambda S, \lambda V, \lambda \tilde{\mathbf{N}})N_j = \tilde{U}(S, V, \tilde{\mathbf{N}})$$

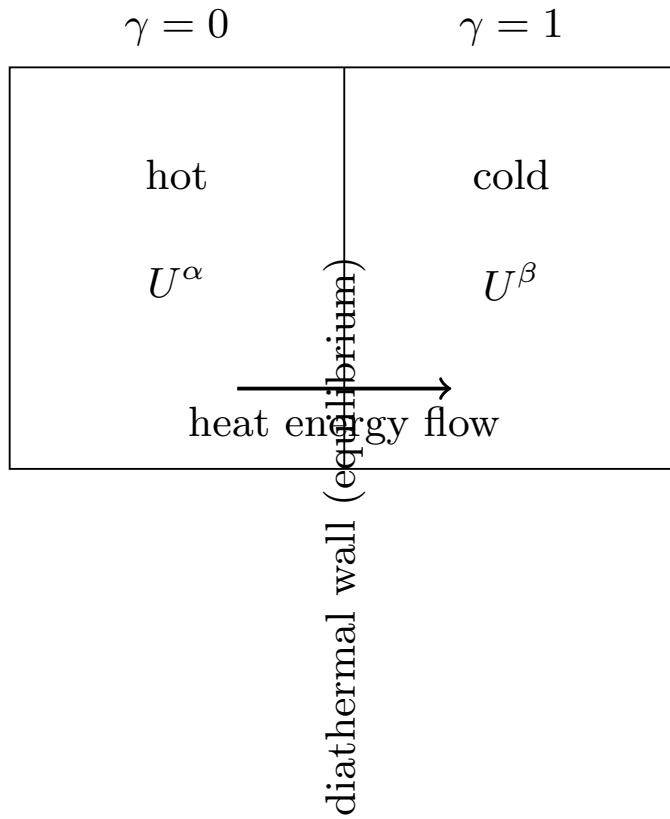


Figure 3.3: Heat energy flow from subsystem α to subsystem β .

Taking $\lambda = 1$, we get

$$\tilde{U}(S, V, \tilde{\mathbf{N}}) = T(S, V, \tilde{\mathbf{N}})S - P(S, V, \tilde{\mathbf{N}})V + \sum_{j=1}^r \mu_j(S, V, \tilde{\mathbf{N}})N_j,$$

as desired. // /

□

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

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

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

$(S) \quad (V) \quad (N_1) \cdots (N_r)$
 is a continuous, piecewise differentiable function $\vec{\xi} : [0, 1] \rightarrow \Sigma_S$, defined by

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

A process path in Σ_U is defined similarly.

Thus, we have, using the chain rule,

$$\frac{d}{d\gamma} \tilde{U}(\vec{\xi}(\gamma)) = T(\vec{\xi}(\gamma))S'(\gamma) - P(\vec{\xi}(\gamma))V'(\gamma) + \sum_{j=1}^r \mu_j(\vec{\xi}(\gamma))N'_j(\gamma) \quad (3.5)$$

for a valid process path in state space.

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

$$0 = S(\gamma) \frac{dT}{d\gamma}(\vec{\xi}(\gamma)) - V(\gamma) \frac{dP}{d\gamma}(\vec{\xi}(\gamma)) + \sum_{j=1}^r N_j(\gamma) \frac{d\mu_j}{d\gamma}(\vec{\xi}(\gamma)). \quad (3.6)$$

This equation is called the Gibbs-Duhem relation.

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

$$\begin{aligned} \frac{d\tilde{U}}{d\gamma}(\vec{\xi}(\gamma)) &= \frac{dT}{d\gamma}(\vec{\xi}(\gamma))S(\gamma) + T(\vec{\xi}(\gamma))S'(\gamma) \\ &\quad - \frac{dP}{d\gamma}(\vec{\xi}(\gamma))V(\gamma) - P(\vec{\xi}(\gamma))V'(\gamma) \\ &\quad + \sum_{j=1}^r \left\{ \frac{d\mu_j}{d\gamma}(\vec{\xi}(\gamma))N_j(\gamma) + \mu_j(\vec{\xi}(\gamma))N'_j(\gamma) \right\} \end{aligned} \quad (3.7)$$

Subtracting (3.5) from (3.7), we get (3.6). // /

Example 3.2.4. (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 homogeneous of degree one. Let us check that. Suppose $\lambda > 0$. Then

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

Recall that

$$\begin{aligned}T &= \frac{1}{\partial \tilde{S}/\partial U} = \left(AU^{-3/4}V^{1/2}N^{1/4} \right)^{-1} \\ &= \frac{U^{3/4}}{AV^{1/2}N^{1/4}}\end{aligned}$$

which is homogeneous degree zero.

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

so

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

Finally,

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

Example 3.2.5. (3.5) Suppose that the fundamental relation is

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

Recall that

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

The same as above.

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

Finally,

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

Let us establish the Euler Equation with respect to entropy.

Theorem 3.2.6. (3.5) Let \tilde{S} be the internal energy of an isolated system. Then

$$\tilde{S} = \frac{1}{T_s}U + \frac{P_s}{T_s}V - \sum_{j=1}^r \frac{\mu_{s,j}}{T_s}N_j, \quad (3.8)$$

where

$$T_s = T_s(U, V, \tilde{\mathbf{N}}),$$

$$P_s = P_s(U, V, \tilde{\mathbf{N}}),$$

$$\mu_{s,j} = \mu_{s,j}(U, V, \tilde{\mathbf{N}}),$$

and

$$\frac{1}{T_s} = \frac{\partial \tilde{S}}{\partial U}, \quad \frac{P_s}{T_s} = \frac{\partial \tilde{S}}{\partial V}, \quad \frac{\mu_{s,j}}{T_s} = \frac{\partial \tilde{S}}{\partial N_j}.$$

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

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

Taking the derivative with respect to λ , we have

$$\frac{1}{T_s(\lambda U, \lambda V, \lambda \tilde{\mathbf{N}})}U + \frac{P_s(\lambda U, \lambda V, \lambda \tilde{\mathbf{N}})}{T_s(\lambda U, \lambda V, \lambda \tilde{\mathbf{N}})}V + \sum_{j=1}^r \frac{\mu_{s,j}(\lambda U, \lambda V, \lambda \tilde{\mathbf{N}})}{T_s(\lambda U, \lambda V, \lambda \tilde{\mathbf{N}})}N_j = \tilde{S}(U, V, \tilde{\mathbf{N}})$$

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

The Gibbs-Duhem equation is similarly derived.

Theorem 3.2.7. (3.6) Suppose that $\vec{\xi}: [0, 1] \rightarrow \Sigma_U$ is a process path. Then

$$\begin{aligned} 0 &= \frac{dT_s}{d\gamma}(\vec{\xi}(\gamma))\tilde{S}(\vec{\xi}(\gamma)) - \frac{dP_s}{d\gamma}(\vec{\xi}(\gamma))V(\gamma) \\ &\quad - \sum_{j=1}^r \frac{d\mu_{s,j}}{d\gamma}(\vec{\xi}(\gamma))N_j(\gamma). \end{aligned} \quad (3.9)$$

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

Proof. Using (3.8), we have

$$\begin{aligned} T_s(\vec{\xi}(\gamma))\tilde{S}(\vec{\xi}(\gamma)) &= U(\gamma) + P_s(\vec{\xi}(\gamma))V(\gamma) \\ &\quad - \sum_{j=1}^r \mu_{s,j}(\vec{\xi}(\gamma))N_j(\gamma). \end{aligned}$$

Taking the γ -derivative of the last equation we have

$$\begin{aligned}
 & \frac{dT_s}{d\gamma}(\vec{\xi}(\gamma))\tilde{S}(\vec{\xi}(\gamma))T_s(\vec{\xi}(\gamma))\frac{d\tilde{S}}{d\gamma}(\vec{\xi}(\gamma)) \\
 &= U'(\gamma) \\
 &+ \frac{dP_s}{d\gamma}(\vec{\xi}(\gamma))V(\gamma) + P_s(\vec{\xi}(\gamma))V'(\gamma) \\
 &- \sum_{j=1}^r \left\{ \frac{d\mu_{s,j}}{d\gamma}(\vec{\xi}(\gamma))N_j(\gamma) \right. \\
 &\quad \left. + \mu_{s,j}(\vec{\xi}(\gamma)) \right. \\
 &\quad \left. N'_j(\gamma) \right\} \tag{3.10}
 \end{aligned}$$

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

$$\begin{aligned}
 \frac{d\tilde{S}}{d\gamma}(\vec{\xi}(\gamma)) &= \frac{1}{T_s(\vec{\xi}(\gamma))}U'(\gamma) \\
 &+ \frac{P_s(\vec{\xi}(\gamma))}{T_s(\vec{\xi}(\gamma))}V'(\gamma) \\
 &- \sum_{j=1}^r \frac{\mu_{s,j}(\vec{\xi}(\gamma))}{T_s(\vec{\xi}(\gamma))}N'_j(\gamma).
 \end{aligned}$$

□

Equivalently,

$$\begin{aligned}
 T_s(\vec{\xi}(\gamma))\frac{d\tilde{S}}{d\gamma}(\vec{\xi}(\gamma)) &= U'(\gamma) + P_s(\vec{\xi}(\gamma))V'(\gamma) \\
 &- \sum_{j=1}^r \mu_{s,j}(\vec{\xi}(\gamma))N'_j(\gamma) \tag{3.11}
 \end{aligned}$$

Subtracting (3.11) from (3.10) we get

$$\begin{aligned}
 \frac{dT_s}{d\gamma}(\vec{\xi}(\gamma))\tilde{S}(\vec{\xi}(\gamma)) &= \frac{dP_s}{d\gamma}(\vec{\xi}(\gamma))V(\gamma) \\
 &- \sum_{j=1}^r \frac{d\mu_{s,j}}{d\gamma}(\vec{\xi}(\gamma))N_j(\gamma).
 \end{aligned}$$

which is the desired result. //

Remark: Compare (3.6) and (3.9):

(3.6)

$$0 = S(\gamma) \frac{dT}{d\gamma}(\vec{\xi}(\gamma)) - V(\gamma) \frac{dP}{d\gamma}(\vec{\xi}(\gamma)) + \sum_{j=1}^r N_j(\gamma) \frac{d\mu_j}{d\gamma}(\vec{\xi}(\gamma)),$$

(3.9)

$$0 = \frac{dT_s}{d\gamma}(\vec{\xi}(\gamma)) \tilde{S}(\vec{\xi}(\gamma)) - \frac{dP_s}{d\gamma}(\vec{\xi}(\gamma)) V(\gamma) - \sum_{j=1}^r \frac{d\mu_{s,j}}{d\gamma}(\vec{\xi}(\gamma)) N_j(\gamma),$$

These are essentially the same expressions!

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