Nonequilibrium Theromdynamics:
From an Applied Mathematical Perspective

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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, $V \geq 0$,
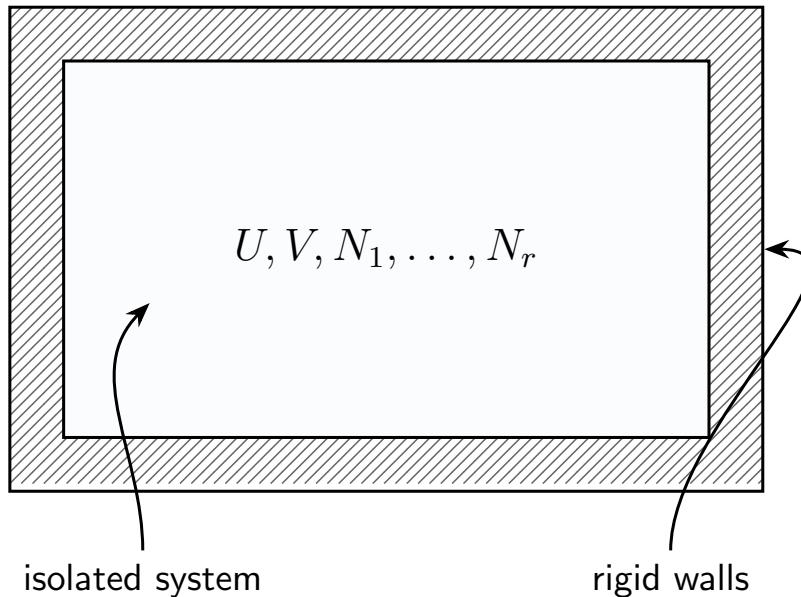
Figure 1.1: Isolated system with rigid walls. The system is characterized by internal energy U, volume V, and mole numbers $N_1, \ldots, N_r$.

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

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

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

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

A **diathermal piston** in a composite system is one which separates two otherwise isolated systems and allows for the exchange of energy and volume but not matter.
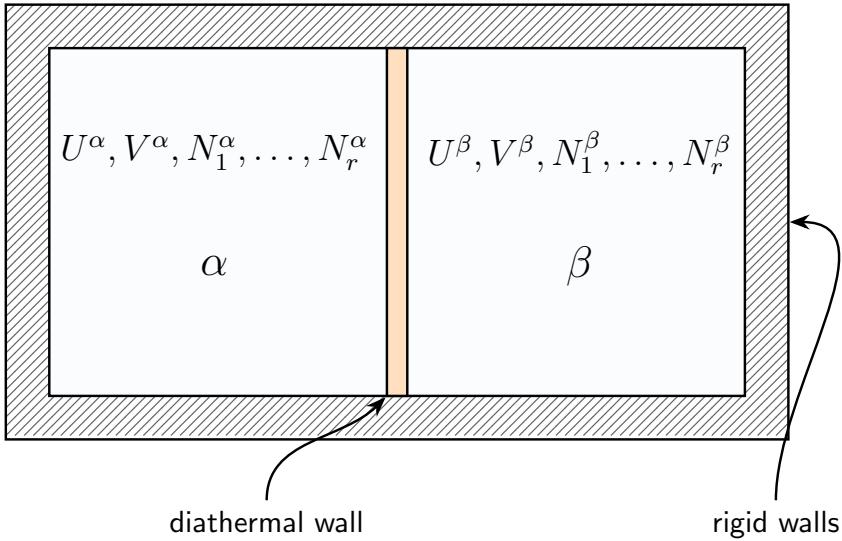
Figure 1.2: Composite system with diathermal wall separating subsystems α and β.

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

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

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

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

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

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

for any $\lambda > 0$.

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

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

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

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

where Σ_u^o is the interior of the set Σ_u.

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

$$\tilde{U} = \tilde{U}(S, V, N_1, \ldots, N_r) \tag{1.1.6}$$

and a convex domain of definition

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

that satisfies

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

and

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

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

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

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

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

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

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

Then

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

and

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

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

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

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

$$S = S^\alpha + S^\beta \tag{1.1.16}$$

is at its maximum possible value.

Definition 1.1.6 (Pressure and Chemical Potential). The function

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

is called the pressure of a system. The function

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

is called the ith chemical potential.

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

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

where

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

and

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

Furthermore,

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

where

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

and

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

And, finally,

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

where

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

and

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

Proof. Proof Exercises. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\square$

Remark 1.1.8. We will usually abuse notation and just write

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

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,

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

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

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

We can set

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

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

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

Recall,

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

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

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

Define

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

Then

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

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*

$$U^\alpha + U^\beta = U_o \tag{1.1.37}$$

and

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

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

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

and

$$\frac{\partial S}{\partial U^\alpha} = 0. \tag{1.1.40}$$

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

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

Thus,

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

with

$$U^\beta = U_o - U^\alpha. \tag{1.1.43}$$
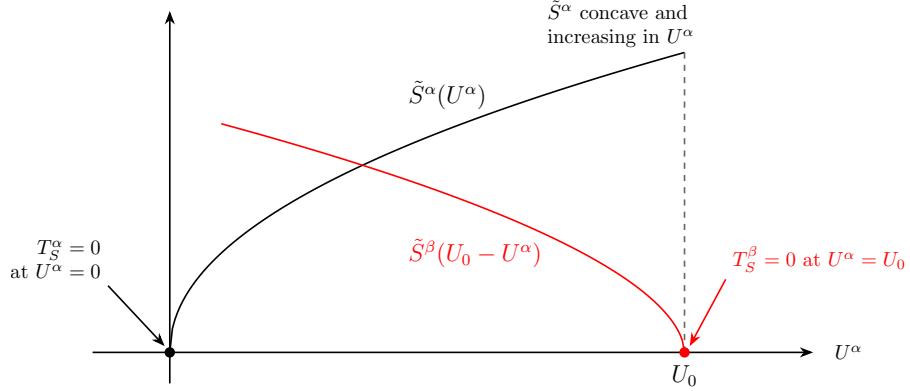
Figure 1.3: Entropy functions vs U^α for subsystems α and β. The curves show $\tilde{S}^\alpha(U^\alpha)$ (convex, increasing) and $\tilde{S}^\beta(U_o - U^\alpha)$ (decreasing). The temperature conditions at the boundaries are indicated.

How do we know that solutions exist and are unique?

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

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

Then, equilibrium is characterized by

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

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

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

which yields the same result. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\square$

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*

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

$$V^\alpha + V^\beta = V_o, \qquad (1.1.49)$$
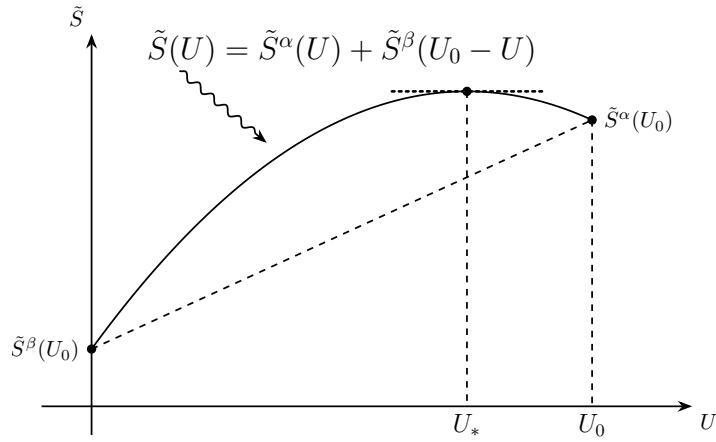
$$\tilde{S}(U) = \tilde{S}^\alpha(U) + \tilde{S}^\beta(U_0 - U)$$

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

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad (\textit{thermal equilibrium}) \qquad (1.1.50)$$

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

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

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

The conditions for equilibrium are

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

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

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

$$0 = \frac{\partial J}{\partial V^\beta} = \frac{P^\beta(U^\beta, V^\beta, \vec{N}^\beta)}{T^\beta(U^\beta, V^\beta, \vec{N}^\beta)} + \lambda_v, \tag{1.1.56}$$
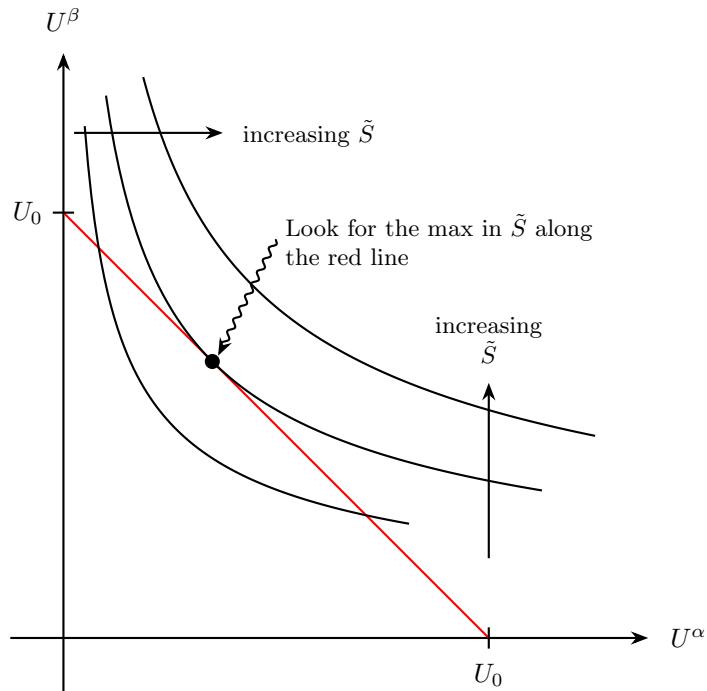
Figure 1.5: Lagrange multiplier visualization: finding the maximum in $\tilde{S}$ along the constraint $U^\alpha + U^\beta = U_o$ (red line). The contours show increasing $\tilde{S}$.

and

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

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

The result is clear.   □

Here, we have used the fact that

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

$$\frac{\partial S^\alpha}{\partial V^\alpha} = \frac{P^\alpha}{T^\alpha}, \tag{1.1.60}$$

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

As a short hand, we will write

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

and

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

Using our abusive notations, we have

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

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*

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

and

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

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

$$U^\alpha + U^\beta = U_o, \qquad (1.1.67)$$
$$V^\alpha + V^\beta = V_o, \qquad (1.1.68)$$
$$N_i^\alpha + N_i^\beta = N_{o,i}, \qquad (1.1.69)$$

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

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad \text{(thermal equil.)} \qquad (1.1.70)$$
$$P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = P^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad \text{(mech. equil.)} \qquad (1.1.71)$$
$$\mu_i^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = \mu_i^\beta(U^\beta, V^\beta, \vec{N}^\beta). \quad \text{(chem. equil.)} \qquad (1.1.72)$$

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

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

$$+ \lambda_v(V^\alpha + V^\beta - V_o) + \sum_{i=1}^{r} \lambda_i(N_i^\alpha + N_i^\beta - N_{o,i}). \quad (1.1.73)$$

$\square$

Chapter 2

ThermoS26-02

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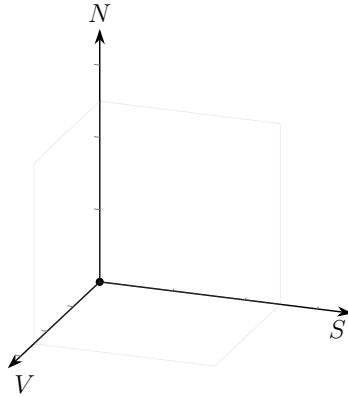
Figure 2.1: Coordinate system for state space with axes N (vertical), V (horizontal right), and S (downward).

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

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

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

$$[U] = \text{Joules}. \tag{2.1.2}$$

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

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

The units of volume, V, are

$$[V] = \text{meters}^3. \tag{2.1.4}$$

The units of N are

$$[N] = \text{moles}. \tag{2.1.5}$$

Of course, it is easy to see that

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

An explicit function of the form

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

is also called a **fundamental relation**.

In any case, the temperature which has units

$$[T] = \text{degrees Kelvin} = K, \tag{2.1.8}$$

is

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

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

Observe that

$$T_U(\lambda S, \lambda V, \lambda N) = T_U(S, V, N), \tag{2.1.10}$$

that is T_U is homogeneous of order 0.

This property is true of every equation of state.

Now,

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

Clearly

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

as claimed in Theorem (1.7).

The pressure satisfies the equation of state

$$P_U(S, V, N) = -\frac{\partial \tilde{U}}{\partial V} = -\frac{v_0 e}{R^2}\frac{S^3}{N}\left(-\frac{1}{V^2}\right)$$

$$= \frac{v_0 e}{R^2}\frac{S^3}{NV^2}, \qquad (2.1.13)$$

which is also homogeneous of order zero.

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

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

Finally, the chemical potential is

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

which is clearly homogeneous of degree zero.

The reader can show that

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

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*

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

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

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

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

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

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

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

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

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

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

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

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

Also, recall that, generically,

$$\tilde{U}\left(\tilde{S}(\hat{U}, \hat{V}, \hat{N}), \hat{V}, \hat{N}\right) = \hat{U} \tag{2.2.7}$$

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

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

This completes the proof. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\square$

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 $\vec{Y} : [a, b] \to \mathcal{D}$ 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 $\vec{Y} : [0, 1] \to \mathcal{D}$ such that

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

$\mathcal{D}$ 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

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

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

Definition 2.3.2 (Path Integral). Let $\vec{F} : \mathcal{D} \to \mathbb{R}^n$ be a C^1 function, i.e. , $\vec{F} \in C^1(\mathcal{D}; \mathbb{R}^n)$. Let $\vec{Y} : [a, b] \to \mathcal{D}$ 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

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

We will also use the notation

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

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

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

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

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

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

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

and

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

then

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

This result guarantees that the path integrals are parametrically independent.

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

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

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

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

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

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

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

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

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

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

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*

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

is path-independent.

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

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

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

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

Thus,

$$\int_{\vec{Y}_1} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{a_1}^{b_1} \vec{F}(\vec{Y}_1(x)) \cdot \vec{Y}_1'(x) \, dx$$

$$= \int_{a_1}^{b_1} \frac{d}{dx}\left[f(\vec{Y}_1(x)) \right] dx$$

$$\overset{\text{FTC}}{=} f(\vec{b}) - f(\vec{a}), \tag{2.3.18}$$

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. $\int_{\vec{Y}} \vec{F}(\vec{x}) \, d\vec{x}$ *is path independent*

3. $\oint_{\vec{Y}} \vec{F}(\vec{x}) \, d\vec{x} = 0$ *for any closed path.*

2.4   Exact Differentials in Thermodynamics

Recall, we wrote, as a shorthand,

$$d\tilde{U} = T_U dS - P_U dV + \sum_{i=1}^{r} \mu_{U;i} dN_i. \tag{2.4.1}$$

This has the form

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

where

$$F_1 = T_U, \quad F_2 = -P_U, \quad \ldots \tag{2.4.3}$$

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

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

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

$$\int_{\vec{Y}} d\tilde{U} = \int_{\vec{Y}} \nabla\tilde{U} \cdot d\vec{r} \tag{2.4.5}$$

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

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

then

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

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

The same is true for

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

that is

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

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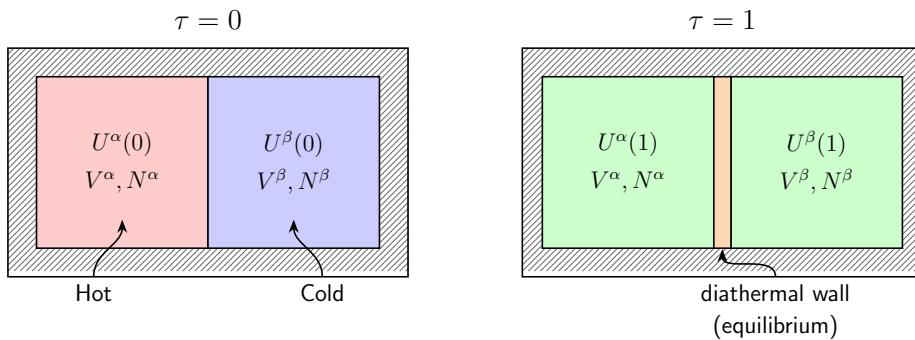
Figure 3.1: Initial and equilibrium configurations for $\gamma = 0$ and $\gamma = 1$. At $\gamma = 0$ the insulating wall is replaced with a diathermal wall; left hot subsystem has $U^\alpha(0)$, V^α, N^α and right cold subsystem has $U^\beta(0)$, V^β, N^β. At $\gamma = 1$ a diathermal wall separates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

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

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,

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

while at equilibrium

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

We will show that

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

and

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

To see this, compute

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

where

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

We know that

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

We also know that

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

Set

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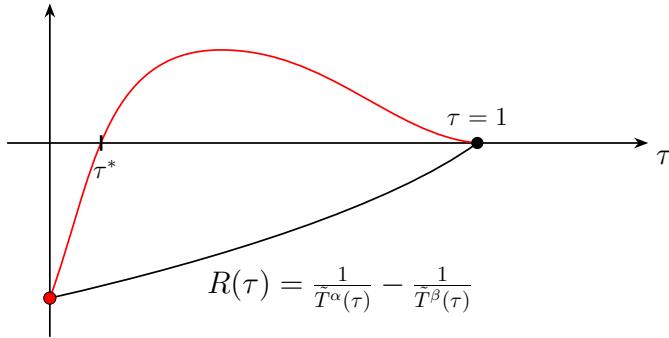
Figure 3.2: Plot of $R(\gamma)$ on $[0,1]$. The red curve is impossible; if it occurred, equilibrium would be reached earlier at $\gamma = \gamma^*$. The valid curve remains negative with $R(1) = 0$.

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

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

Integrating (3.1), we get

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

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

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

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

$$U^\alpha(0) > U^\alpha(1) \qquad \left(U^\beta(0) < U^\beta(1)\right).$$

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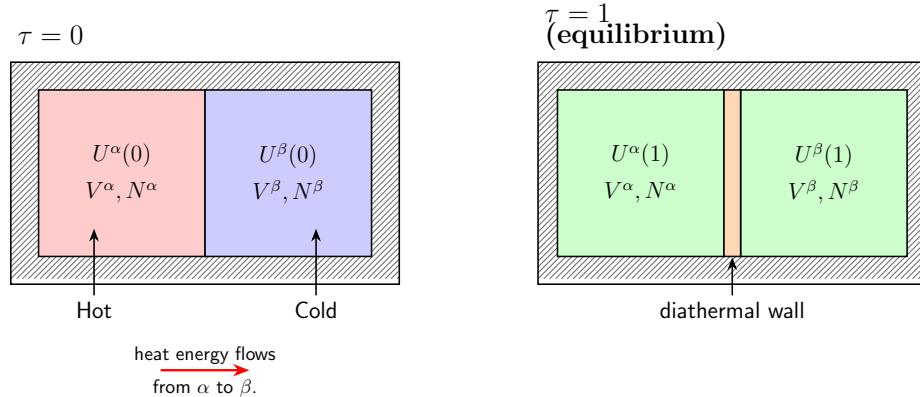
Figure 3.3: Energy transfer for $\gamma = 0$ (hot to cold through replaced wall) and $\gamma = 1$ (equilibrium with diathermal wall) showing flow from subsystem α to subsystem β.

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:

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

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*

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

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. /// $\qquad\square$

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 $\vec{Y} : [0, 1] \to \Sigma_S$, 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

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

for a valid process path in state space.

Theorem 3.2.3. (3.3) *Suppose that $\vec{Y} : [0, 1] \to \Sigma_S$ 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:

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

Substituting (3.5) into (3.7) yields (3.6). ///   □

3.3   Examples

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

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

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

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

Finally,

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

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,

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

$$= 4\left(\frac{S - BN}{4AV^{1/2}N^{1/4}}\right)^3 \frac{1}{4AV^{1/2}} \frac{N^{1/4}(-B) - (S - BN)\frac{1}{4}N^{-3/4}}{N^{1/2}}$$

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

$$= -\frac{B\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} - \frac{\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} \frac{(S - BN)}{4N} = -\frac{B\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} - \frac{\tilde{U}}{N}.///$$

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*

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

where

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

and

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

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 $\vec{Y} : [0, 1] \to \Sigma_U$ is a process path. Then*

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

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

Proof. Using (3.8), we have

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

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

$$\frac{dT_S}{d\gamma}\left(\vec{Y}(\gamma)\right)\tilde{S}\left(\vec{Y}(\gamma)\right) + T_S\left(\vec{Y}(\gamma)\right)\frac{d\tilde{S}}{d\gamma}\left(\vec{Y}(\gamma)\right) = U'(\gamma) + \frac{dP_S}{d\gamma}\left(\vec{Y}(\gamma)\right)V(\gamma) + P_S\left(\vec{Y}(\gamma)\right)V'(\gamma)$$

$$- \sum_{j=1}^{r}\left\{\frac{d\mu_{S,j}}{d\gamma}\left(\vec{Y}(\gamma)\right)N_j(\gamma) + \mu_{S,j}\left(\vec{Y}(\gamma)\right)N_j'(\gamma)\right\}.$$

$$(3.10)$$

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

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

$$(3.11)$$

Substituting (3.11) into (3.10) yields (3.9). /// $\qquad\qquad\square$

   Remark: Compare (3.6) and (3.9):

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

$$0 = \frac{dT_S}{d\gamma}\left(\vec{Y}(\gamma)\right)\tilde{S}\left(\vec{Y}(\gamma)\right) - \frac{dP_S}{d\gamma}\left(\vec{Y}(\gamma)\right)V(\gamma) + \sum_{j=1}^{r}\frac{d\mu_S^j}{d\gamma}\left(\vec{Y}(\gamma)\right)N_j(\gamma),$$

These are essentially the same expression!

Chapter 4

ThermoS26-04

Math Thermo
Class #04
01/29/2026

Suppose that $\tilde{S}$ is the fundamental entropy relation for an isolated system containing a unary ($r = 1$) material.

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

Suppose that $N > 0$ is fixed. Define

$$u := \frac{U}{N}, \qquad \text{the molar energy,}$$

$$v := \frac{V}{N}, \qquad \text{the molar volume.}$$

Then, since, for any $\lambda > 0$,

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

it follows that

$$\frac{1}{N} \tilde{S}(U, V, N) = \tilde{S}\left(\frac{U}{N}, \frac{V}{N}, \frac{N}{N}\right) = \tilde{S}(u, v, 1).$$

Now, define the molar entropy relation

$$\tilde{s} = \tilde{s}(u, v) := \tilde{S}(u, v, 1).$$

It then follows that

$$\tilde{S}(U, V, N) = N\tilde{s}(u, v).$$

Likewise, if we define

$$s = \frac{S}{N} \qquad v = \frac{V}{N}$$

and

$$\tilde{u} = \tilde{u}(s, v) := \tilde{U}(s, v, 1),$$

then it follows that

$$\tilde{U}(S, V, N) = N\tilde{u}(s, v).$$

Example 4.0.1. (4.1) Suppose that

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

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

$$\tilde{s}(u, v) = \tilde{S}(u, v, 1) = \left(\frac{vuR^2}{v_0 \theta} \right)^{1/3}.$$

$$N\tilde{s}(u, v) = \left(\frac{N^3 vuR^2}{v_0 \theta} \right)^{1/3} = \left(\frac{NVUR^2}{v_0 \theta} \right)^{1/3} = \tilde{S}(U, V, N).$$

$\tilde{U}$ and $\tilde{S}$ are homogeneous of degree one (also called extensive variables).
T, P, μ on the other hand are homogeneous of degree zero (also called intensive variables).

Recall that, for all $\lambda > 0$,

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

Thus,

$$T_U(S, V, N) = T_U(s, v, 1).$$

We could, of course, give a new symbol for $T_U(s, v, 1)$, for example

$$t_U(s, v) := T_U(s, v, 1) \dots$$

4.1   Molar Euler and Gibbs–Duhem Equation

For a unary material ($r = 1$), recall

$$\tilde{U}(S, V, N) = T_U(S, V, N)S - P_U(S, V, N)V + \mu_U(S, V, N)N$$

Suppose $N > 0$ is fixed. Then,

$$\frac{1}{N}\tilde{U}(S, V, N) = T_U(S, V, N)\frac{S}{N} - P_U(S, V, N)\frac{V}{N} + \mu_U(S, V, N)$$

or, equivalently,

$$\tilde{u}(s, v) = T_U(s, v)s - P_U(s, v)v + \mu_U(s, v). \tag{4.1}$$

This is the molar version of Euler's equation. How do we get the Gibbs–Duhem equation?

Let $\vec{z}(\gamma) = (s(\gamma), v(\gamma))$ be a path in molar state space. Then

$$\frac{d}{d\gamma}\tilde{u}(\vec{z}(\gamma)) = \frac{\partial \tilde{u}}{\partial s}(\vec{z}(\gamma))\, s'(\gamma) + \frac{\partial \tilde{u}}{\partial v}(\vec{z}(\gamma))\, v'(\gamma).$$

But
exercise

$$\frac{\partial \tilde{u}}{\partial s}(\vec{z}(\gamma)) = T_U(s(\gamma), v(\gamma))$$

and

$$\frac{\partial \tilde{u}}{\partial v}(\vec{z}(\gamma)) = -P_U(s(\gamma), v(\gamma)).$$

Thus, the combined First and Second laws are

$$\frac{d}{d\gamma}\tilde{u}(\vec{z}(\gamma)) = T_U(\vec{z}(\gamma))s'(\gamma) - P_U(\vec{z}(\gamma))v'(\gamma). \tag{4.2}$$

On the other hand, differentiate the molar Euler relation (4.1), we have

$$\frac{d}{d\gamma}\tilde{u}(\vec{z}(\gamma)) = \frac{d}{d\gamma}T_U(\vec{z}(\gamma))s(\gamma) + T_U(\vec{z}(\gamma))s'(\gamma) \tag{4.1.1}$$

$$- \frac{d}{d\gamma}P_U(\vec{z}(\gamma))v(\gamma) - P_U(\vec{z}(\gamma))v'(\gamma) \tag{4.1.2}$$

$$+ \frac{d}{d\gamma}\mu_U(\vec{z}(\gamma)). \tag{4.3}$$

Therefore, the molar Gibbs–Duhem equation is

$$0 = \frac{d}{d\gamma}T_U(\vec{z}(\gamma))s(\gamma) - \frac{d}{d\gamma}P_U(\vec{z}(\gamma))v(\gamma) + \frac{d}{d\gamma}\mu_U(\vec{z}(\gamma)). \qquad (4.4)$$

The molar entropy form of the Euler and Gibbs– Duhem equations are (as one would expect)

$$\tilde{s}(u, v) = \frac{1}{T_S(u, v)}u + \frac{P_S(u, v)}{T_S(u, v)}v - \frac{\mu_S(u, v)}{T_S(u, v)}. \qquad (4.6)$$

and

$$0 = \frac{d}{d\gamma}\left(\frac{1}{T_S(\vec{z}(\gamma))}\right)u(\gamma) + \frac{d}{d\gamma}\left(\frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))}\right)v(\gamma) - \frac{d}{d\gamma}\left(\frac{\mu_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))}\right). \qquad (4.7)$$

The molar representation of the First and Second laws is

$$\frac{d}{d\gamma}\tilde{s}(\vec{z}(\gamma)) = \frac{1}{T_S(\vec{z}(\gamma))}u'(\gamma) + \frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))}v'(\gamma). \qquad (4.8)$$

where $\vec{z}(\gamma) = (u(\gamma), v(\gamma))$ is a process path in molar state space.

4.2   Examples

Let's look at a couple of examples.

Example 4.2.1. (4.2) Suppose that

$$P = \frac{2U}{V}$$

$$T = \left(\frac{AU^{3/2}}{VN^{1/2}}\right)^{1/2}$$

(homog. deg. zero)

We should be able to recover the fundamental relation using these two equations of state. Observe that

$$\frac{1}{T_S} = A^{-1/2}u^{-3/4}v^{1/2}$$

$$\frac{P_S}{T_S} = 2A^{-1/2}u^{1/4}v^{-1/2}$$

Using the molar 1st and 2nd laws (4.8)

$$\frac{d}{d\gamma}\tilde{s}(\vec{z}(\gamma)) = \frac{1}{T_S(\vec{z}(\gamma))}u'(\gamma) + \frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))}v'(\gamma)$$
$$= A^{-1/2}\left(u(\gamma)^{-3/4}v(\gamma)^{1/2}u'(\gamma) + 2u(\gamma)^{1/4}v(\gamma)^{-1/2}v'(\gamma)\right)$$
$$= 4A^{-1/2}\frac{d}{d\gamma}\left((u(\gamma))^{1/4}(v(\gamma))^{1/2}\right).$$

Therefore,

$$\tilde{s}(\gamma) = 4A^{-1/2}(u(\gamma))^{1/4}(v(\gamma))^{1/2} + s_0.$$

Equivalently,

$$\tilde{S}(\gamma) = 4A^{-1/2}U^{1/4}V^{1/2}N^{1/4} + Ns_0.$$

here s_0 is a positive constant. ///

Let's try an alternative method.

Example 4.2.2. (4.3) Same problem as above. This time we will use the Gibbs–Duhem equation (4.7) as the starting point:

$$\frac{d}{d\gamma}\left(\frac{\mu_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))}\right) = \frac{d}{d\gamma}\left(\frac{1}{T_S(\vec{z}(\gamma))}\right)u(\gamma) + \frac{d}{d\gamma}\left(\frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))}\right)v(\gamma)$$

$$= A^{-1/2}\frac{d}{d\gamma}\left((u(\gamma))^{-3/4}(v(\gamma))^{1/2}\right)u(\gamma)$$

$$+ A^{-1/2}\frac{d}{d\gamma}\left(2(u(\gamma))^{1/4}(v(\gamma))^{-1/2}\right)$$

$$v(\gamma)$$

$$= A^{-1/2}\left(-\frac{3}{4}(u(\gamma))^{-3/4}(v(\gamma))^{1/2}u'(\gamma)\right.$$

$$\left.+(u(\gamma))^{1/4}\frac{1}{2}(v(\gamma))^{-1/2}v'(\gamma)\right)$$

$$+ A^{-1/2}\left(\frac{1}{2}(u(\gamma))^{-3/4}(v(\gamma))^{1/2}u'(\gamma)\right.$$

$$\left.-2(u(\gamma))^{1/4}\frac{1}{2}(v(\gamma))^{-1/2}v'(\gamma)\right)$$

$$= A^{-1/2}\left(-\frac{1}{4}(u(\gamma))^{-3/4}(v(\gamma))^{1/2}u'(\gamma)\right.$$

$$\left.-\frac{1}{2}(u(\gamma))^{1/4}(v(\gamma))^{-1/2}v'(\gamma)\right)$$

$$= -A^{-1/2}\frac{d}{d\gamma}\left((u(\gamma))^{1/4}(v(\gamma))^{1/2}\right).$$

Thus,

$$\frac{\mu_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))} = -A^{-1/2}(u(\gamma))^{1/4}(v(\gamma))^{1/2} - s_0.$$

or

$$\frac{\mu_S(u,v)}{T_S(u,v)} = -A^{-1/2}u^{1/4}v^{1/2} - s_0.$$

Using Euler's equation (4.6), we have

$$\tilde{s}(u,v) = \frac{1}{T_S(u,v)}u + \frac{P_S(u,v)}{T_S(u,v)}v - \frac{\mu_S(u,v)}{T_S(u,v)}$$

$$= A^{-1/2}u^{1/4}v^{1/2} + 2A^{-1/2}u^{1/4}v^{1/2} + A^{-1/2}u^{1/4}v^{1/2} + s_0$$

$$= 4A^{-1/2}u^{1/4}v^{1/2} + s_0,$$

which is the same as before.

Using 2 equations of state, we can recover the 3rd and then utilizing Euler's equation we get the fundamental relation. ///

Example 4.2.3. (4.4) Ideal Gas law

$$PV = NRT$$

$$U = \frac{3}{2}NRT$$

With these two equations of state we can find the fundamental relations. Observe that

$$\frac{1}{T_S} = \frac{3R}{2u} \qquad \frac{P_S}{T_S} = \frac{R}{v}.$$

This suggests that we again use the entropy equation (in molar form). The Gibbs–Duhem equation is

$$\frac{d}{d\gamma}\left(\frac{\mu_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))}\right) = \frac{d}{d\gamma}\left(\frac{1}{T_S(\vec{z}(\gamma))}\right)u(\gamma) + \frac{d}{d\gamma}\left(\frac{P_S(\vec{z}(\gamma))}{T_S(\vec{z}(\gamma))}\right)v(\gamma)$$

$$= \frac{3R}{2}\frac{d}{d\gamma}\left(\frac{1}{u(\gamma)}\right)u(\gamma) + R\frac{d}{d\gamma}\left(\frac{1}{v(\gamma)}\right)v(\gamma)$$

$$= -\frac{3R}{2}\frac{u'(\gamma)}{u(\gamma)} - R\frac{v'(\gamma)}{v(\gamma)}.$$

Integrating, we have

$$\frac{\mu_S(u(\gamma), v(\gamma))}{T_S(u(\gamma), v(\gamma))} - \frac{\mu_0}{T_0} = -\frac{3R}{2}\ln\left(\frac{u(\gamma)}{u_0}\right) - R\ln\left(\frac{v(\gamma)}{v_0}\right),$$

where

$$\frac{\mu_0}{T_0} := \frac{\mu_S(u_0, v_0)}{T_S(u_0, v_0)}.$$

Using the molar Euler equation, we have

$$\tilde{s}(u, v) = \frac{1}{T_S(u, v)}u + \frac{P_S(u, v)}{T_S(u, v)}v - \frac{\mu_S(u, v)}{T_S(u, v)}$$

$$= \frac{3R}{2} + R + \frac{3R}{2}\ln\left(\frac{u}{u_0}\right) + R\ln\left(\frac{v}{v_0}\right) - \frac{\mu_0}{T_0}$$

$$= s_0 + R\ln\left(\left(\frac{u}{u_0}\right)^{3/2}\left(\frac{v}{v_0}\right)\right).$$

Thus,

$$\tilde{S}(U, V, N) = N s_0 + N R \ln\left(\left(\frac{U}{U_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right),$$

where

$$U = uN, \; V = vN,$$

$$U_0 = u_0 N_0, \; V_0 = v_0 N_0,$$

and

$$s_0 = \frac{5}{2} R - \frac{\mu_0}{T_0}. ///$$

Chapter 5

ThermoS26-05

Math Thermo
Class #05
02/03/2026

5.1 Legendre Transforms and Thermodynamic Potentials

Definition 5.1.1. (5.1) Suppose that $f : [a, b] \to \mathbb{R}$ is continuous. For every $p \in [c, d]$, define

$$f^*(p) := \sup_{x \in [a,b]} \{xp - f(x)\} \tag{5.1}$$

The function $f^* : [c, d] \to \mathbb{R}$ is called the Legendre transform of f.

Theorem 5.1.2. (5.2) *Suppose that $f \in C^2([0, \infty); \mathbb{R})$ with*

$$f''(x) > 0, \qquad \forall x \in [0, \infty).$$

Then, for all $p \in \text{Range}(f')$,

$$f^*(p) = x_p\, p - f(x_p), \tag{5.2}$$

where $x_p \in [0, \infty)$ is the unique solution to

$$f'(x_p) = p.$$

Proof. let $p \in \text{Range}(f')$.

$$f' : [0, \infty) \to \text{Range}(f')$$

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For every $p \in \mathrm{Range}(f')$ $\exists! \ x_p \in [0, \infty)$ and that,

$$f'(x_p) = p.$$

Since $f' : [0, \infty)$ is strictly increasing,
Fix $p \in \mathrm{Range}(f')$. By Taylor's Theorem,

$$f(x) = f(x_p) + p(x - x_p) + \frac{1}{2} f''(\xi_p)(x - x_p)^2$$

for some ξ_p between x and x_p.

$$\sup_{0 \leq x < \infty} \{x \cdot p - f(x)\} = \sup_{0 \leq x < \infty} \{x_p \cdot p - f(x_p) - \tfrac{1}{2} f''(\xi_p)(x - x_p)^2\}$$

$$= x_p \cdot p - f(x_p).///$$

$\square$

Theorem 5.1.3. (5.3) *Suppose that* $f \in C^2([0, \infty); \mathbb{R})$ *with*

$$f''(x) > 0, \qquad \forall x \in [0, \infty).$$

Then,
$$[f^*]'(p) = [f']^{-1}(p), \qquad [f^*]''(p) > 0,$$

for all $p \in \mathrm{Range}(f')$.

Proof. Recall
$$f' : [0, \infty) \rightarrow \mathrm{Range}(f')$$

Then
$$f'\big([f']^{-1}(p)\big) = p, \qquad \forall \ p \in \mathrm{Range}(f').$$

Also, observe that $\frac{d}{dp}[f']^{-1} \in C(\mathrm{Range}(f'); \mathbb{R})$.
Now,

$$\frac{d}{dp}[f^*(p)] = \frac{d}{dp}\{x_p \cdot p - f(x_p)\} = \frac{d}{dp}\{[f']^{-1}(p) \cdot p - f([f']^{-1}(p))\}$$

$$= p \cdot \frac{d}{dp}[f']^{-1}(p) + [f']^{-1}(p) - \frac{df}{dx}([f']^{-1}(p)) \cdot \frac{d}{dp}[f']^{-1}(p)$$

$$= [f']^{-1}(p).$$

Now that this is established, we have

$$\frac{d^2}{dp^2}[f^*(p)] = \frac{d}{dp}[f']^{-1}(p)$$

for all $p \in \text{Range}(f')$. Since $f'' \in C([0, \infty))$ and $f''(x) > 0$, $\forall x \in [0, \infty)$,

$$\frac{d}{dp}[f']^{-1}(p) > 0, \qquad \forall p \in \text{Range}(f').///$$

$\square$

Finally, we observe the following:

Theorem 5.1.4. (5.4) *Suppose that $f \in C^2([0, \infty); \mathbb{R})$ with*

$$f''(x) > 0, \qquad \forall x \in [0, \infty).$$

Then $f^* \in C^2(\text{Range}(f'); \mathbb{R})$ with

$$[f^*]''(p) > 0, \qquad \forall p \in \text{Range}(f')$$

Furthermore
$$[f^*]^*(x) = f(x), \qquad \forall x \in [0, \infty). \tag{5.3}$$

In other words, the Legendre transform is involutive and in fact an isomorphism.

Proof. It follows that, for all $x \in [0, \infty)$,

$$[f^*]^*(x) = x\, p_x - f^*(p_x),$$

where $p_x \in \text{Range}(f')$ is the unique solution to

$$f^{*\prime}(p_x) = x.$$

Recall
$$f^*(p_x) = p_x \cdot x_{p_x} - f(x_{p_x}),$$

where $x_{p_x} \in [0, \infty)$ is the unique solution to

$$f'(x_{p_x}) = p_x.$$

Of course, by uniqueness,
$$x_{p_x} = x.$$

So,
$$[f^*]^*(x) = x \cdot p_x - \{p_x \cdot x_{p_x} - f(x_{p_x})\} = f(x).///$$

$\square$

Why is the Legendre transform useful in Thermodynamics?

This transform allows us to introduce new thermodynamics coordinates/-variables.

Recall

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

or

$$d\tilde{U} = T\, dS - p\, dV + \mu\, dN$$

The latter means

$$T = \frac{\partial \tilde{U}}{\partial S} \quad p = -\frac{\partial \tilde{U}}{\partial V} \quad \mu = \frac{\partial \tilde{U}}{\partial N}$$

in short hand

Extensive Quantity	Conjugate Variable	Variable
$\tilde{U}$	$T, -p, \mu$	S, V, N
$\tilde{S}$	$\frac{1}{T}, \frac{p}{T}, -\frac{\mu}{T}$	U, V, N

Table 5.1: Conjugate variables for $\tilde{U}$ and $\tilde{S}$.

Definition 5.1.5. (5.5) Suppose that all of the Thermodynamic Postulates hold. Assume that the material in question is unary ($r = 1$). Define

$$\tilde{F}(T, V, N) = \tilde{U}(S_T, V, N) - T S_T \tag{5.4}$$

where $S_T = S_T(V, N)$ is the unique solution of the equation

$$T_U(S_T(V, N), V, N) = T \tag{5.5}$$

for fixed values of N and V.

$\tilde{F}$ is called the Helmholtz free energy.

Formally, we have

$$\begin{aligned} d\tilde{F} &= d\tilde{U} - S\, dT - T\, dS \\ &= T\, dS - p\, dV + \mu\, dN - S\, dT - T\, dS \\ &= -S\, dT - p\, dV + \mu\, dN. \end{aligned}$$

Extensive Quantity	Conjugate Variable	Variable
$\tilde{U}$	$T, -p, \mu$	S, V, N
$\tilde{F}$	$-S, -p, \mu$	T, V, N

Table 5.2: Conjugate variables for $\tilde{U}$ and $\tilde{F}$.

Example 5.1.6. (5.6) Suppose that

$$\tilde{S}(U, V, N) = \left(\frac{NVUR^2}{v_0\theta}\right)^{1/3}.$$

It follows that

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

The temperature function is

$$T_U(S, V, N) = \frac{3S^2 v_0\theta}{NVR^2}.$$

Or

$$\frac{1}{T_S(U, V, N)} = \frac{1}{3}\left(\frac{NVUR^2}{v_0\theta}\right)^{-2/3}\frac{NVR^2}{v_0\theta} = \frac{1}{3}\left(\frac{NVR^2}{v_0\theta}\right)^{1/3}U^{-2/3}.$$

Thus

$$T_S(U, V, N) = 3\left(\frac{v_0\theta}{NVR^2}\right)^{1/3}U^{2/3}.$$

Recall that

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

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

By definition

$$\tilde{F}(T, V, N) = \tilde{U}(S_T, V, N) - TS_T$$

where

$$T_U(S_T(V, N), V, N) = T.$$

For our example,

$$T_U(S, V, N) = \frac{3S^2 v_0\theta}{NVR^2}.$$

Hence,

$$S_T = \sqrt{\frac{TNVR^2}{3v_0\theta}}.$$

Thus,

$$\tilde{F}(T, V, N) = \tilde{U}\left(\sqrt{\frac{TNVR^2}{3v_0\theta}}, V, N\right) - T\sqrt{\frac{TNVR^2}{3v_0\theta}}$$

$$= \left(\frac{TNVR^2}{3v_0\theta}\right)^{3/2} \frac{v_0\theta}{NVR^2} - T\sqrt{\frac{TNVR^2}{3v_0\theta}}.$$

But

$$\tilde{U}(S_T, V, N) = \frac{S_T^3 v_0\theta}{NVR^2} = \left(\frac{TNVR^2}{3v_0\theta}\right)^{3/2} \frac{v_0\theta}{NVR^2}$$

so that

$$\tilde{F}(T, N, V) = \frac{1}{3}T^{3/2}\frac{1}{\sqrt{3}}\sqrt{\frac{NVR^2}{v_0\theta}} - \frac{T^{3/2}}{\sqrt{3}}\sqrt{\frac{NVR^2}{v_0\theta}}.$$

Finally,

$$\tilde{F}(T, N, V) = -\frac{2T^{3/2}}{3}\sqrt{\frac{NVR^2}{3v_0\theta}}. \tag{5.6}$$

Now,

$$\frac{\partial \tilde{F}}{\partial T} = -\frac{2}{3}\frac{3}{2}\sqrt{T}\sqrt{\frac{NVR^2}{3v_0\theta}}.$$

But

$$T_U(S, V, N) = \frac{3S^2 v_0\theta}{NVR^2}$$

Thus,

$$\sqrt{T} = \sqrt{\frac{3v_0\theta}{NVR^2}}S_T$$

and

$$\frac{\partial \tilde{F}}{\partial T} = -S_T. \tag{5.7}$$

Theorem 5.1.7. (5.7) *Suppose that all of the Thermodynamic Postulates hold. Assume that the material in question is unary ($r = 1$). The following procedure is equivalent means for finding the Helmholtz free energy:*

$$\tilde{F}(T, V, N) = U_T - T\tilde{S}(U_T, V, N) \tag{5.8}$$

where $U_T = U_T(V, N)$ is the unique solution of the equation

$$T_S(U_T(V, N), V, N) = T$$

for fixed values of N and V.
Proof: Exercise ///

Example 5.1.8. (5.8) Let us use the second version to calculate the free energy for the monatomic ideal gas. Recall,

$$\tilde{S}(U, V, N) = Ns_0 + NR \ln \left(\left(\frac{U}{U_0} \right)^{3/2} \left(\frac{V}{V_0} \right) \left(\frac{N}{N_0} \right)^{-5/2} \right),$$

where s_0, R, U_0, V_0, N_0 are positive constants.
Then

$$\frac{\partial \tilde{S}}{\partial U} = \frac{NR}{\left(\frac{U}{U_0} \right)^{3/2}} \cdot \frac{3}{2} \left(\frac{U}{U_0} \right)^{1/2} \frac{1}{U_0}$$

$$= \frac{3NR}{2U_0} \cdot \frac{U_0}{U} = \frac{3NR}{2U}$$

Thus

$$T_S(U, V, N) = \frac{2}{3} \frac{U}{NR}$$

and

$$U_T = \frac{3NRT}{2}$$

Therefore,

$$\tilde{F}(T, V, N) = \frac{3NRT}{2} - TNs_0$$
$$- NRT \ln \left(\left(\frac{3NRT}{2U_0} \right)^{3/2} \left(\frac{V}{V_0} \right) \left(\frac{N}{N_0} \right)^{-5/2} \right)$$

Define

$$T_0 := \frac{2U_0}{3N_0 R}.$$

Then,

$$\tilde{F}(T, V, N) = \frac{3NRT}{2} - TNs_0 - NRT \ln \left(\left(\frac{T}{T_0} \right)^{3/2} \left(\frac{V}{V_0} \right) \left(\frac{N}{N_0} \right)^{-1} \right) \quad (5.9)$$
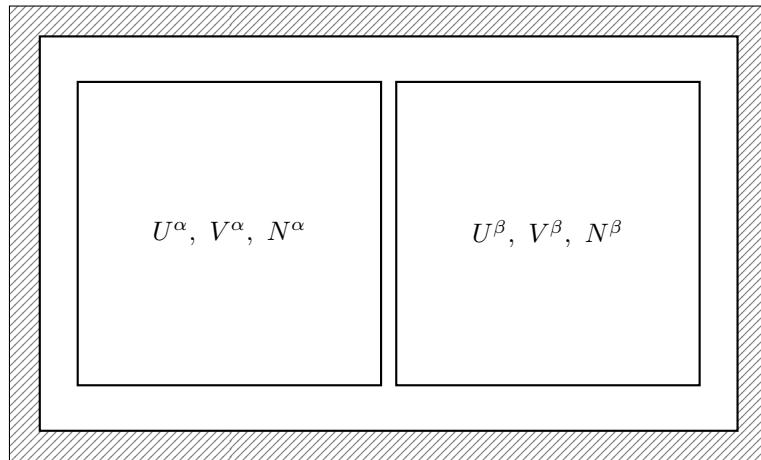
Figure 5.1: Two isolated systems initially separated by insulating walls.

5.2   Equilibrium with a heat Bath

Consider two isolated systems that are initially isolated from each other.

Now, let us remove the isolating walls so that energy, volume, and mass may be exchanged.

The entropy will attain its maximum at equilibrium and

$$T^\alpha = T^\beta$$

$$P^\alpha = P^\beta$$

$$\mu_i^\alpha = \mu_i^\beta, \qquad i = 1, \dots, r.$$

How can we characterize equilibrium?

Now, suppose that instead of isolating from the universe, our composite system is put into contact with a heat bath.

Definition 5.2.1. (5.9) A heat bath is an otherwise- isolated thermodynamic system that is so large that, when it exchanges a finite amount of energy with an otherwise-isolated, composite system, its temperature, pressure, and chemical potential changes are so small as to be negligible.

Similarly, we have

heat-pressure bath: finite exchanges of energy and volume lead to negligible changes in T, P, and μ in baths.
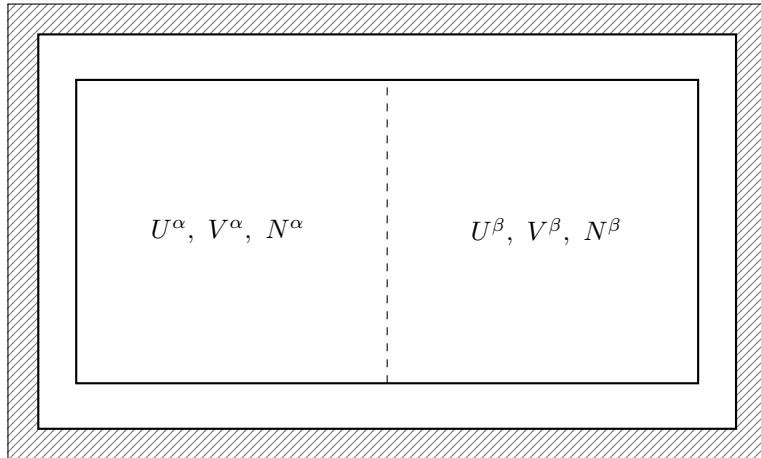
Figure 5.2: Isolating wall removed so energy, volume, and mass can be exchanged.

A heat-pressure-chemical bath is defined analogously.

Let us consider a picture for the case of the heat bath.

Let us recall the "integrated form" of the entropy function.

$$\tilde{S}^B = \tilde{S}^B(U^B, V^B, N^B) = \frac{1}{T^0}U^B + \frac{P^0}{T^0}V^B - \frac{\mu^0}{T^0} \cdot N^B$$

where

$$T^0 = T^0(U^0, V^0, N^0)$$

et cetera. We will write

$$S^{tot} = \tilde{S}^B + \tilde{S}^\alpha + \tilde{S}^\beta$$

$$= \tilde{S}^B + \tilde{S}^{\alpha+\beta}$$

Now, our system will not exchange volume or mass with the bath, only energy, because we will replace the horizontal isolations wall with a diathermal wall.

We know that, at equilibrium

$$T^\alpha = T^\beta = T^B = T_0.$$

Recall the deviations of T^B from T_0 at equilibrium is assumed negligible.

The heat bath is
significantly larger
$U^B, V^B, \vec{N}^B$

$\left(T^B = T_0, \ P^B = P_0, \ \tilde{\mu}^B = \tilde{\mu}_0\right)$

$U^\alpha, V^\alpha, \vec{N}^\alpha$ $U^\beta, V^\beta, \vec{N}^\beta$
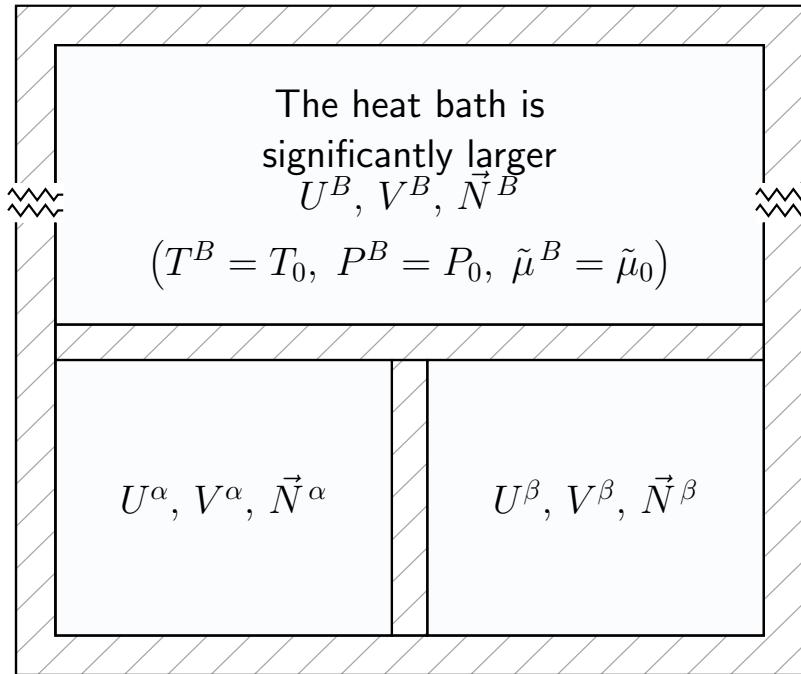
Figure 5.3: Composite system in contact with a heat bath.

System α and β can exchange energy. System α and β can exchange volume and mass with each other but not with the bath.

Thus,

$$S^{tot,eq} = \max_C \{\tilde{S}^B + \tilde{S}^{\alpha+\beta}\}$$

Now

$$\tilde{S}^B = \frac{1}{T_0}U^B + \frac{P_0}{T_0}V^B - \frac{\mu_0}{T_0} \cdot N^B$$

The changes in T^B, P^B, μ^B from T_0, P_0, μ_0 is negligible because the bath is so large.

Writing

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

$$\tilde{S}^B = -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + \frac{U_0}{T_0} + C_1$$
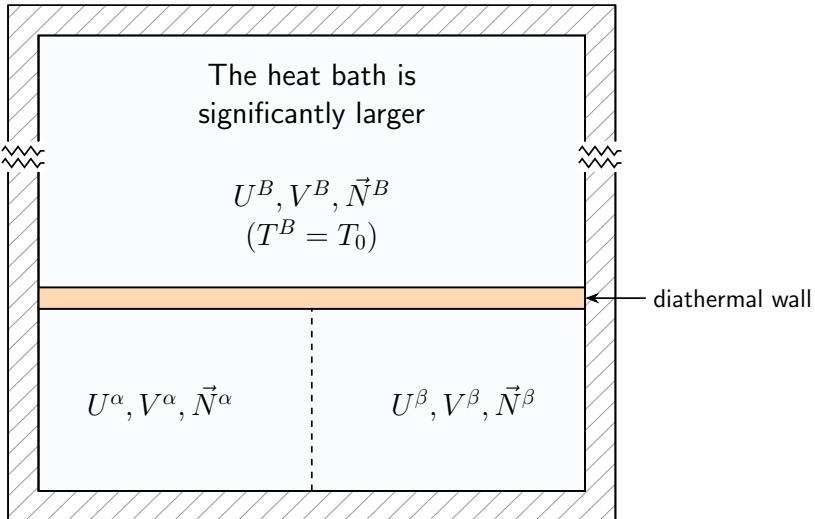
Figure 5.4: Diathermal wall configuration: only energy exchange with the bath.

$$= -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + C_2$$

Thus,

$$
\begin{aligned}
S^{tot,eq} &= \max_C \left\{ -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + C_2 + \tilde{S}^{\alpha+\beta} \right\} \\
&= C_2 + \max_C \left\{ -\frac{U^\alpha + U^\beta}{T_0} + \tilde{S}^\alpha + \tilde{S}^\beta \right\} \\
&= C_2 + \max_C \left\{ -\frac{F^\alpha + F^\beta}{T_0} \right\} \\
&= C_2 - \frac{1}{T_0} \min_C \left\{ F^\alpha(T_0, V^\alpha, N^\alpha) + F^\beta(T_0, V^\beta, N^\beta) \right\}
\end{aligned}
$$

Postulate VI: Consider a compound, otherwise- isolated thermodynamic system in contact with an otherwise-isolated heat bath at temperature T_0. Equilibrium of the compound system is the state satisfying the isothermal condition

$$T^\alpha = T^\beta = T_0$$

which minimizes

$$F^\alpha(T_0, V^\alpha, N^\alpha) + F^\beta(T_0, V^\beta, N^\beta)$$

subject to the constraints

$$V^\alpha + V^\beta = V_0, \qquad \text{(volume conservation)}$$

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

Remark: Since the system $\alpha + \beta$ exchanges energy with the heat bath, energy is not conserved in $\alpha + \beta$.

Energy is conserved in the system $B + \alpha + \beta$.

Chapter 6

ThermoS26-06

Math Thermo
Class #06
02/05/2026

6.1 Maxwell's Common Tangent Construction

Here we will review a situation for which the Helmholtz potential is important.

Consider a unary material, two phase system, for example liquid and solid iron.

We will assume the β phase is the high- density phase (a solid perhaps) and the α phase is the low-density phase (a liquid perhaps).

Both phases are in contact with a heat bath at temperature T_0.

Here the densities ρ^α and ρ^β play the roles of the numbers of moles, N^α and N^β.

We will assume, for simplicity, that parameters vary in only one spatial dimension, z.

Suppose the cross-section area of the container is A. Then

$$V^\alpha = Az_I$$

$$V^\beta = A(L - z_I)$$

$$V^\alpha + V^\beta = A \cdot L = V_0 \qquad \text{(total volume constant)}$$

Now,

$$N^\alpha = V^\alpha \rho^\alpha$$

$$N^\beta = V^\beta \rho^\beta$$
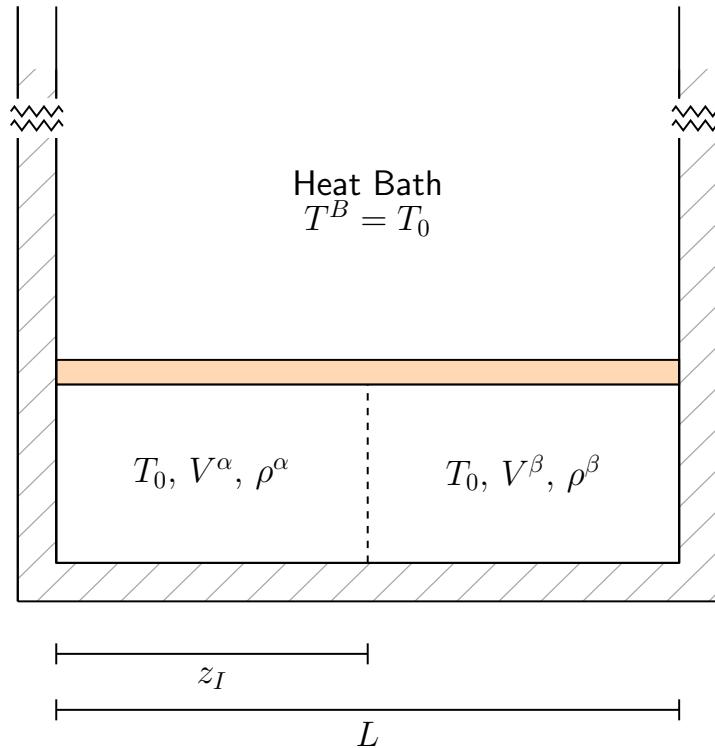
Figure 6.1: Two-phase system in contact with a heat bath, with interface at z_I.

Here
$$[\rho^*] = \text{moles/unit vol}$$

$$N_0 = N^\alpha + N^\beta \qquad \text{(total mole number const)}$$
$$= V^\alpha \rho^\alpha + V^\beta \rho^\beta$$
$$= A z_I \rho^\alpha + A(L - z_I)\rho^\beta$$

It will be convenient to introduce
$$\rho_0 = \frac{N_0}{V_0} = \frac{N_0}{L \cdot A}.$$

Hence,
$$\boxed{\rho_0 \cdot L = z_I \rho^\alpha + (L - z_I)\rho^\beta} \tag{5.1}$$

We will assume that the total free energy can be expressed as

$$F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) = V^\alpha f^\alpha(\rho^\alpha) + V^\beta f^\beta(\rho^\beta)$$

The variables f^α and f^β are called free energy densities. We can eliminate the volume variable using constraint:

$$F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) = V^\alpha f^\alpha(\rho^\alpha) + V^\beta f^\beta(\rho^\beta)$$

$$= A z_I f^\alpha(\rho^\alpha) + A(L - z_I) f^\beta(\rho^\beta)$$

Using the mass constraint (5.1), we have

$$z_I = \frac{L(\rho_0 - \rho^\beta)}{\rho^\alpha - \rho^\beta}$$

or, equivalently,

$$\boxed{z_I = \frac{L(\rho^\beta - \rho_0)}{\rho^\beta - \rho^\alpha}} \tag{5.2}$$

Similarly, we have

$$\boxed{L - z_I = \frac{L(\rho_0 - \rho^\alpha)}{\rho^\beta - \rho^\alpha}} \tag{5.3}$$

Thus,

$$F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) = L \cdot A \cdot \tilde{F}(\rho^\alpha, \rho^\beta),$$

where

$$\tilde{F}(\rho^\alpha, \rho^\beta) = \frac{\rho^\beta - \rho_0}{\rho^\beta - \rho^\alpha} f^\alpha(\rho^\alpha) + \frac{\rho_0 - \rho^\alpha}{\rho^\beta - \rho^\alpha} f^\beta(\rho^\beta).$$
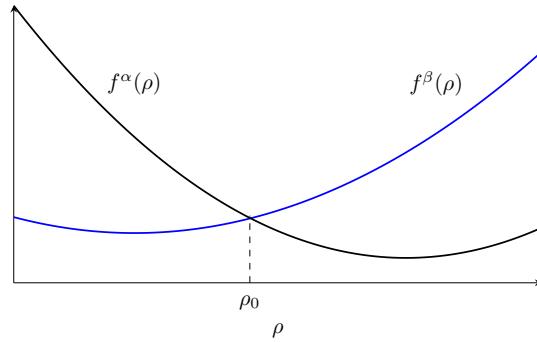
Recall the setting is isothermal $T^\alpha = T^\beta = T_0$. So equilibrium is characterized by a minimum in the free energy. Thus, we seek a minimizing of $\tilde{F}$.

The setting is as follows:
We want ρ^α and ρ^β that minimize $\tilde{F}$.

$$0 = \frac{\partial \tilde{F}}{\partial \rho^\alpha}(\rho^\alpha, \rho^\beta)$$

$$0 = \frac{\partial \tilde{F}}{\partial \rho^\beta}(\rho^\alpha, \rho^\beta)$$

Figure 6.2: Free energy densities $f^\alpha(\rho)$ and $f^\beta(\rho)$ versus ρ.

Now,

$$\frac{\partial \tilde{F}}{\partial \rho^\alpha} = \frac{\rho^\beta - \rho_0}{(\rho^\beta - \rho^\alpha)^2} f^\alpha(\rho^\alpha) + \frac{\rho^\beta - \rho_0}{\rho^\beta - \rho^\alpha} f^{\alpha'}(\rho^\alpha)$$

$$+ \frac{\rho_0 - \rho^\beta}{(\rho^\beta - \rho^\alpha)^2} f^\beta(\rho^\beta)$$

$$= \frac{\rho^\beta - \rho_0}{\rho^\beta - \rho^\alpha} \left\{ \frac{f^\alpha(\rho^\alpha) - f^\beta(\rho^\beta)}{\rho^\beta - \rho^\alpha} + f^{\alpha'}(\rho^\alpha) \right\}$$

and

$$\frac{\partial \tilde{F}}{\partial \rho^\beta} = \frac{\rho_0 - \rho^\alpha}{(\rho^\beta - \rho^\alpha)^2} f^\alpha(\rho^\alpha) - \frac{\rho_0 - \rho^\alpha}{(\rho^\beta - \rho^\alpha)^2} f^\beta(\rho^\beta) + \frac{\rho_0 - \rho^\alpha}{\rho^\beta - \rho^\alpha} f^{\beta'}(\rho^\beta)$$

$$= \frac{\rho_0 - \rho^\alpha}{\rho^\beta - \rho^\alpha} \left\{ \frac{f^\alpha(\rho^\alpha) - f^\beta(\rho^\beta)}{\rho^\beta - \rho^\alpha} + f^{\beta'}(\rho^\beta) \right\}$$

Thus, the minimizers must satisfy

$$\boxed{\frac{f^\beta(\rho^\beta) - f^\alpha(\rho^\alpha)}{\rho^\beta - \rho^\alpha} = f^{\alpha'}(\rho^\alpha)} \tag{5.4}$$

and

$$\boxed{\frac{f^\beta(\rho^\beta) - f^\alpha(\rho^\alpha)}{\rho^\beta - \rho^\alpha} = f^{\beta'}(\rho^\beta)} \tag{5.5}$$

Graphically, these solutions represent the following scenario:
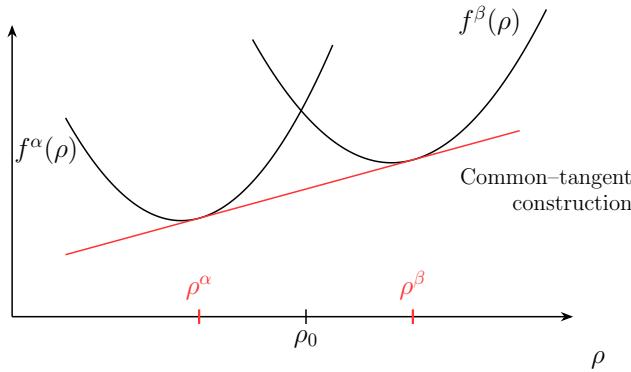
Figure 6.3: Common tangent construction for f^α and f^β.

For everything to make sense, we require that average density

$$\rho^\alpha < \rho_0 < \rho^\beta$$

(low density phase)   (high density phase)

What happens if, say,

$$\rho^\alpha < \rho^\beta < \rho_0,$$

that is, the average is higher than the density of the high-density phase, ρ^β?

Recall,

$$z_l = \frac{L(\rho^\beta - \rho_0)}{\rho^\beta - \rho^\alpha}.$$

If $\rho^\alpha < \rho^\beta < \rho_0$, it follows that

$$z_l < 0,$$

which is unphysical.

On the other hand if $\rho_0 < \rho^\alpha < \rho^\beta$ then

$$z_l > L,$$

which is unphysical.

But if

$$\rho^\alpha < \rho_0 < \rho^\beta$$

it follows that z_l is fully determined and

$$0 < z_l < L,$$

as desired.

By the way we can redefine the chemical potential such that

$$\mu^\alpha = \frac{\partial f^\alpha}{\partial \rho^\alpha}$$

$$\mu^\beta = \frac{\partial f^\beta}{\partial \rho^\beta}$$

So that equilibrium occurs when

$$\mu^\alpha = \mu^\beta.$$

6.2   Unary Isothermal Phase Diagrams (at constant volume)

let us consider the following phase diagram
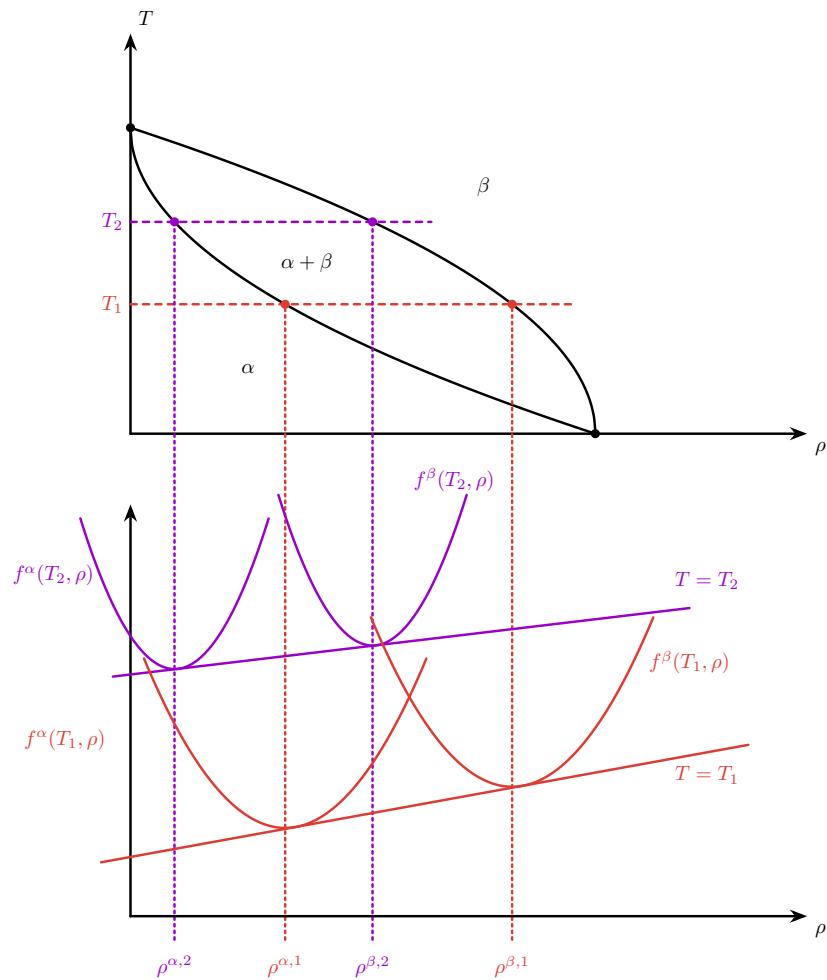
Figure 6.4: Unary isothermal phase diagram and corresponding free-energy curves.

Bibliography

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