Chapter 1

ThermoS26-01

Non-Equilibrium Thermodynamics

Course Plan

1. Equilibrium Thermodynamics

2. Statistical Mechanics

3. Kinetic Theory of Gases

4. Conservation Laws in Continuous Systems

5. Entropy Production

6. Onsager's Principle

7. Applications

1.1 Equilibrium Thermodynamics

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

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

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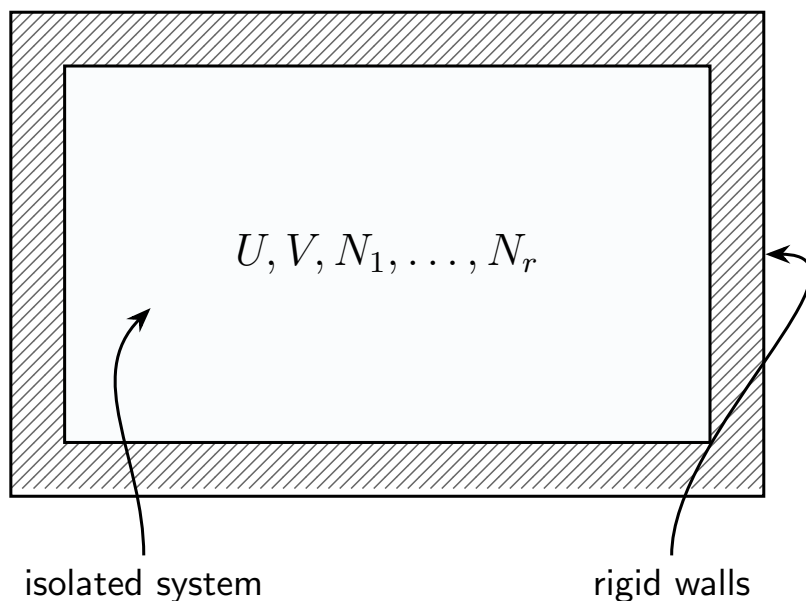
- V, the volume of the system, $V \geq 0$,

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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 efflux of matter, and no exchange of energy.

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

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

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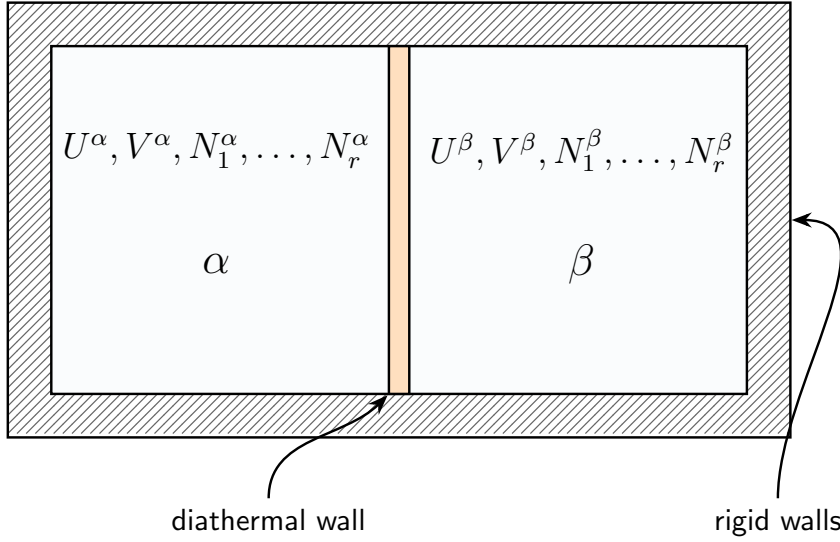
Figure 1.2: Composite system with diathermal wall separating subsystems α and β.

Postulate II: There exists a function $\tilde{S}$ for an isolated system called its entropy, defined for the system at equilibrium and depending on $U, V, N_1, \ldots, N_r$, 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, positive function over its (convex) domain

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

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

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

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

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

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

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

And, finally,

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

where

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

and

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

Proof. Proof Exercises.   □

Remark 1.1.8. We will usually abuse notation and just write

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

when the usage may be inferred from the context.

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

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

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

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

We can set

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

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

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

Recall,

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

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

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

Define

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

Then

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

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*

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

and

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

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

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

and

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

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

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

Thus,

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

with

$$U^\beta = U_o - U^\alpha. \qquad (1.1.43)$$
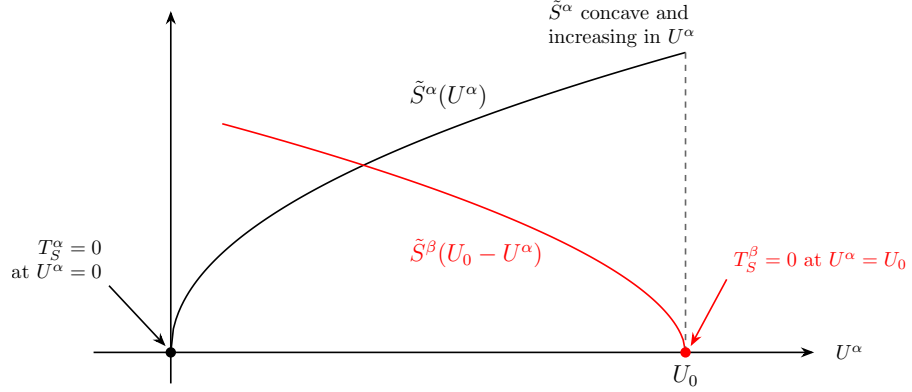
How do we know that solutions exist and are unique?

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

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

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

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. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ □

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*

$$U^\alpha + U^\beta = U_o, \qquad (1.1.48)$$
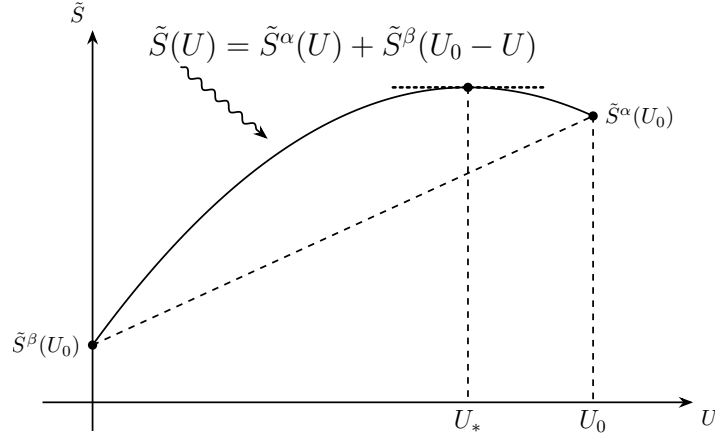
$$V^\alpha + V^\beta = V_o, \qquad (1.1.49)$$

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

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

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

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

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

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

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

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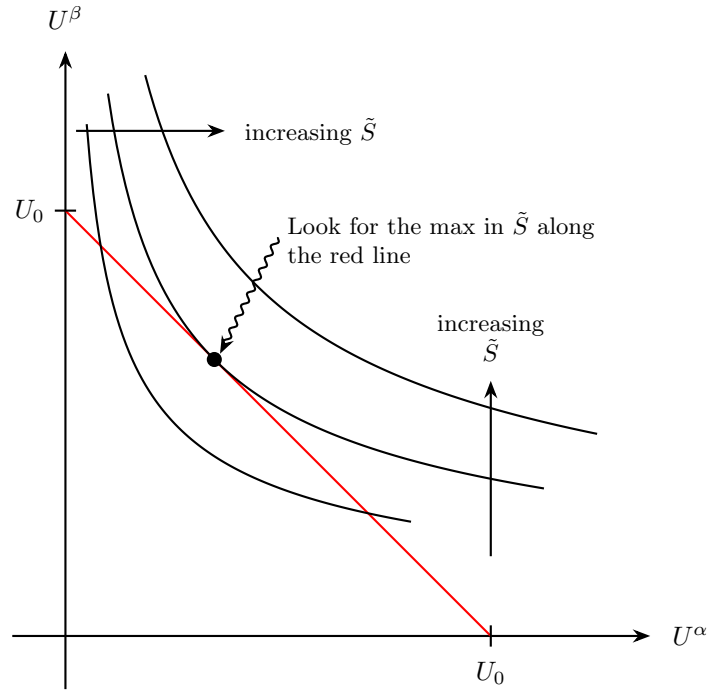
Figure 1.5: Lagrange multiplier visualization: finding the maximum in $\tilde{S}$ along the constraint $U^\alpha + U^\beta = U_o$ (red line). The contours show increasing $\tilde{S}$.

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. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\square$

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

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

and

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

Using our abusive notations, we have

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

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*

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

and

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

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

$$U^\alpha + U^\beta = U_o, \tag{1.1.67}$$

$$V^\alpha + V^\beta = V_o, \tag{1.1.68}$$

$$N_i^\alpha + N_i^\beta = N_{o,i}, \tag{1.1.69}$$

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

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

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

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

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

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

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

$\square$