Chapter 1

ThermoS26-02

Remark 1.0.1. From this point forward, we will assume that all postulates hold.

Theorem 1.0.2 (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*

$$U^\alpha + U^\beta = U_o \tag{1.0.1}$$

and

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta). \tag{1.0.2}$$

Proof. Internal energy may be exchanged between systems α and β but cannot be exchanged with the outside world. Thus (1.0.1) must hold because of energy conservation. At equilibrium we must have

$$S(U^\alpha) = \tilde{S}^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + \tilde{S}^\beta(U_o - U^\alpha, V^\beta, \vec{N}^\beta) \tag{1.0.3}$$

and

$$\frac{\partial S}{\partial U^\alpha} = 0. \tag{1.0.4}$$

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

$$\begin{aligned}
0 &= \frac{\partial S}{\partial U^\alpha} = \frac{\partial S^\alpha}{\partial U^\alpha} + \frac{\partial S^\beta}{\partial U^\beta}\frac{\partial}{\partial U^\alpha}(U_o - U^\alpha) \\
&= [T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)]^{-1} + [T^\beta(U_o - U^\alpha, V^\beta, \vec{N}^\beta)]^{-1}(-1). \tag{1.0.5}
\end{aligned}$$

Thus,

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta) \tag{1.0.6}$$

with

$$U^\beta = U_o - U^\alpha. \tag{1.0.7}$$
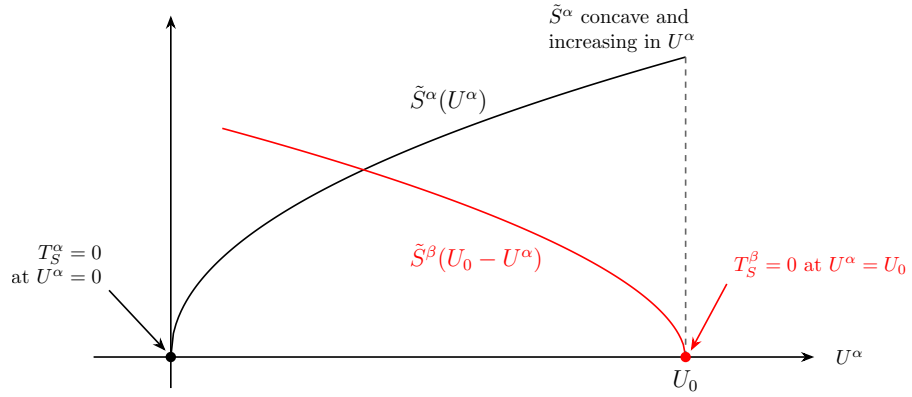
How do we know that solutions exist and are unique?

Figure 1.1: 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

$$J := S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + S^\beta(U^\beta, V^\beta, \vec{N}^\beta) + \lambda(U^\alpha + U^\beta - U_o). \tag{1.0.8}$$

Then, equilibrium is characterized by

$$0 = \frac{\partial J}{\partial U^\alpha} = [T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)]^{-1} + \lambda, \tag{1.0.9}$$

$$0 = \frac{\partial J}{\partial U^\beta} = [T^\beta(U^\beta, V^\beta, \vec{N}^\beta)]^{-1} + \lambda, \tag{1.0.10}$$

$$0 = \frac{\partial J}{\partial \lambda} = U^\alpha + U^\beta - U_o, \tag{1.0.11}$$

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

The Lagrange Multiplier technique can be visualized as follows:

Theorem 1.0.3 (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*
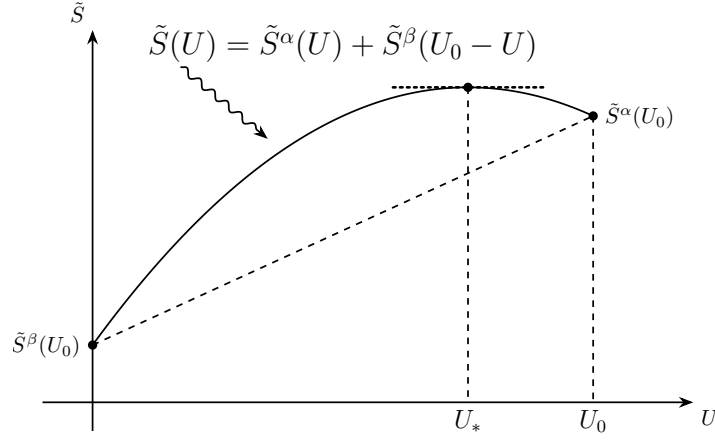
$$U^\alpha + U^\beta = U_o, \tag{1.0.12}$$

Figure 1.2: 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_*.

$$V^\alpha + V^\beta = V_o, \tag{1.0.13}$$

and

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad (\textit{thermal equilibrium}) \tag{1.0.14}$$

$$P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = P^\beta(U^\beta, V^\beta, \vec{N}^\beta). \quad (\textit{mechanical equilibrium}) \tag{1.0.15}$$

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

$$J := S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) + S^\beta(U^\beta, V^\beta, \vec{N}^\beta) + \lambda_u(U^\alpha + U^\beta - U_o) + \lambda_v(V^\alpha + V^\beta - V_o). \tag{1.0.16}$$

The conditions for equilibrium are

$$0 = \frac{\partial J}{\partial U^\alpha} = [T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)]^{-1} + \lambda_u, \tag{1.0.17}$$

$$0 = \frac{\partial J}{\partial U^\beta} = [T^\beta(U^\beta, V^\beta, \vec{N}^\beta)]^{-1} + \lambda_u, \tag{1.0.18}$$

$$0 = \frac{\partial J}{\partial V^\alpha} = \frac{P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)}{T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha)} + \lambda_v, \tag{1.0.19}$$

$$0 = \frac{\partial J}{\partial V^\beta} = \frac{P^\beta(U^\beta, V^\beta, \vec{N}^\beta)}{T^\beta(U^\beta, V^\beta, \vec{N}^\beta)} + \lambda_v, \tag{1.0.20}$$
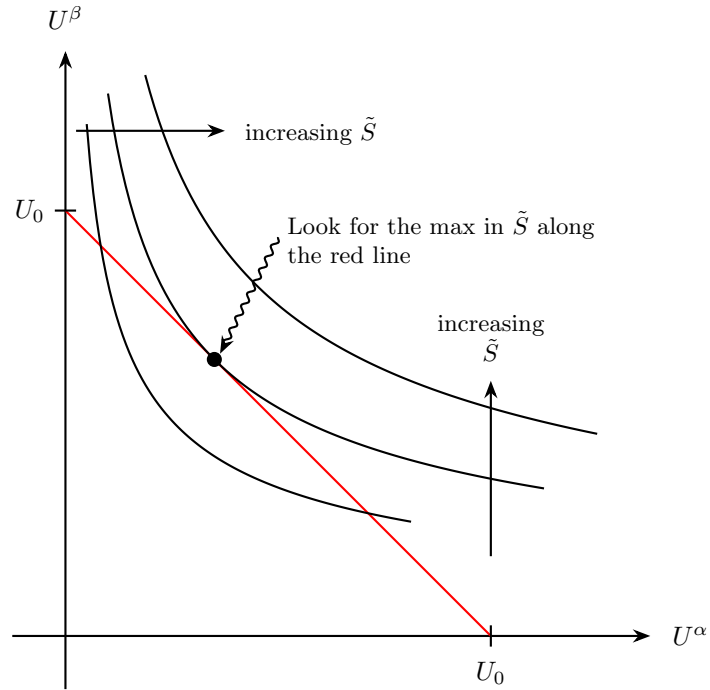
Figure 1.3: Lagrange multiplier visualization: finding the maximum in $\tilde{S}$ along the constraint $U^{\alpha} + U^{\beta} = U_o$ (red line). The contours show increasing $\tilde{S}$.

and

$$0 = \frac{\partial J}{\partial \lambda_u} = U^{\alpha} + U^{\beta} - U_o, \tag{1.0.21}$$

$$0 = \frac{\partial J}{\partial \lambda_v} = V^{\alpha} + V^{\beta} - V_o. \tag{1.0.22}$$

The result is clear. $\qquad\qquad\square$

Here, we have used the fact that

$$\frac{\partial \tilde{S}^{\alpha}}{\partial U^{\alpha}} = \frac{1}{T^{\alpha}}, \tag{1.0.23}$$

$$\frac{\partial S^{\alpha}}{\partial V^{\alpha}} = \frac{P^{\alpha}}{T^{\alpha}}, \tag{1.0.24}$$

$$\frac{\partial S^{\alpha}}{\partial N_i^{\alpha}} = -\frac{\mu_i^{\alpha}}{T^{\alpha}}. \tag{1.0.25}$$

As a short hand, we will write

$$d\tilde{U}^\alpha = T_u^\alpha dS^\alpha - P_u^\alpha dV^\alpha + \sum_{i=1}^r \mu_{u,i}^\alpha dN_i^\alpha \tag{1.0.26}$$

and

$$d\tilde{S}^\alpha = \frac{1}{T_s^\alpha} dU^\alpha + \frac{P_s^\alpha}{T_s^\alpha} dV^\alpha - \sum_{i=1}^r \frac{\mu_{s,i}^\alpha}{T_s^\alpha} dN_i^\alpha. \tag{1.0.27}$$

Using our abusive notations, we have

$$d\tilde{S}^\alpha = \frac{1}{T^\alpha} dU^\alpha + \frac{P^\alpha}{T^\alpha} dV^\alpha - \sum_{i=1}^r \frac{\mu_i^\alpha}{T^\alpha} dN_i^\alpha, \tag{1.0.28}$$

for example.

Theorem 1.0.4 (Full Equilibrium). *Suppose that a composite system is comprised of two otherwise isolated systems with no barrier between the systems. Suppose that*

$$S^\alpha = S^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) \tag{1.0.29}$$

and

$$S^\beta = S^\beta(U^\beta, V^\beta, \vec{N}^\beta) \tag{1.0.30}$$

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

$$U^\alpha + U^\beta = U_o, \tag{1.0.31}$$

$$V^\alpha + V^\beta = V_o, \tag{1.0.32}$$

$$N_i^\alpha + N_i^\beta = N_{o,i}, \tag{1.0.33}$$

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

$$T^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = T^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad (\textit{thermal equil.}) \tag{1.0.34}$$

$$P^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = P^\beta(U^\beta, V^\beta, \vec{N}^\beta), \quad (\textit{mech. equil.}) \tag{1.0.35}$$

$$\mu_i^\alpha(U^\alpha, V^\alpha, \vec{N}^\alpha) = \mu_i^\beta(U^\beta, V^\beta, \vec{N}^\beta). \quad (\textit{chem. equil.}) \tag{1.0.36}$$

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

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

$$+ \lambda_v(V^\alpha + V^\beta - V_o) + \sum_{i=1}^r \lambda_i(N_i^\alpha + N_i^\beta - N_{o,i}). \tag{1.0.37}$$

$\square$

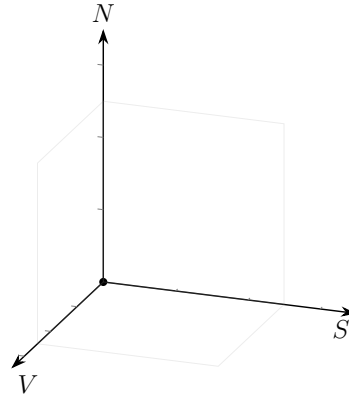## 1.1   Fundamental Relations and Equations of State

Figure 1.4: Coordinate system for state space with axes N (vertical), V (horizontal right), and S (downward).

Example 1.1.1. Suppose that, for an isolated unary fluid,

$$\tilde{U} = \left(\frac{v_0 e}{R^2}\right)\frac{S^3}{NV}, \quad \Sigma_s \subset [0, \infty)^3. \tag{1.1.1}$$

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

$$[U] = \text{Joules}. \tag{1.1.2}$$

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

$$[S] = \frac{\text{Joules}}{\text{degree Kelvin}} = \frac{J}{K}. \tag{1.1.3}$$

The units of volume, V, are

$$[V] = \text{meters}^3. \tag{1.1.4}$$

The units of N are

$$[N] = \text{moles}. \tag{1.1.5}$$

Of course, it is easy to see that

$$\tilde{S} = \left(\frac{NVUR^2}{v_0 e} \right)^{1/3}, \quad \Sigma_U = [0, \infty)^3. \tag{1.1.6}$$

An explicit function of the form

$$S = \tilde{S}(U, V, N) \tag{1.1.7}$$

is also called a **fundamental relation**.

In any case, the temperature which has units

$$[T] = \text{degrees Kelvin} = K, \tag{1.1.8}$$

is

$$T_U(S, V, N) = \frac{\partial \tilde{U}}{\partial S} = \frac{3 v_0 e}{R^2} \frac{S^2}{NV}. \tag{1.1.9}$$

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

Observe that

$$T_U(\lambda S, \lambda V, \lambda N) = T_U(S, V, N), \tag{1.1.10}$$

that is T_U is homogeneous of order 0.

This property is true of every equation of state.

Now,

$$\begin{aligned}
\left(\frac{\partial \tilde{S}}{\partial U} \right)^{-1} &= \left[\frac{1}{3} \left(\frac{NVUR^2}{v_0 e} \right)^{-2/3} \frac{NVR^2}{v_0 e} \right]^{-1} \\
&= \frac{3 v_0 e}{NVR^2} \left(\frac{NVUR^2}{v_0 e} \right)^{2/3} \\
&= \frac{3 v_0 e}{NVR^2} \tilde{S}(U, V, N)^2 \\
&= T_S(U, V, N). \tag{1.1.11}
\end{aligned}$$

Clearly

$$T_U \left(\tilde{S}(U, V, N), V, N \right) = T_S(U, V, N), \tag{1.1.12}$$

as claimed in Theorem (1.7).

The pressure satisfies the equation of state

$$\begin{aligned}
P_U(S, V, N) &= -\frac{\partial \tilde{U}}{\partial V} = -\frac{v_0 e}{R^2} \frac{S^3}{N} \left(-\frac{1}{V^2} \right) \\
&= \frac{v_0 e}{R^2} \frac{S^3}{NV^2}, \tag{1.1.13}
\end{aligned}$$

which is also homogeneous of order zero.

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

$$P_S(U, V, N) = P_U\left(\tilde{S}(U, V, N), V, N\right). \tag{1.1.14}$$

Finally, the chemical potential is

$$\mu_U(S, V, N) = \frac{\partial \tilde{U}}{\partial N} = -\frac{v_0 e}{R^2} \frac{S^3}{V N^2}, \tag{1.1.15}$$

which is clearly homogeneous of degree zero.

The reader can show that

$$\mu_S(U, V, N) = \mu_U\left(\tilde{S}(U, V, N), V, N\right). \tag{1.1.16}$$

1.2 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 1.2.1. *$\tilde{U}$ is homogeneous of degree one when written as*

$$\tilde{U} = \tilde{U}(S, V, \vec{N}). \tag{1.2.1}$$

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

$$T_U(\lambda S, \lambda V, \lambda \vec{N}) = T_U(S, V, \vec{N}) \tag{1.2.2}$$

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

$$S = \tilde{S}(U, V, \vec{N}), \tag{1.2.3}$$

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

$$\tilde{U}(S, V, \vec{N}) = \tilde{U}\left(\tilde{S}(U, V, \vec{N}), V, \vec{N}\right) = U, \quad \forall (S, V, \vec{N}) \in \Sigma_S. \tag{1.2.4}$$

Let $\lambda > 0$ be arbitrary; then (1.2.3) and (1.2.4) imply

$$\tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) = \tilde{U}\left(\lambda \widetilde{S}(U, V, \vec{N}), \lambda V, \lambda \vec{N}\right). \tag{1.2.5}$$

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

$$\lambda \tilde{S}(U, V, \vec{N}) = \tilde{S}(\lambda U, \lambda V, \lambda \vec{N}). \tag{1.2.6}$$

Also, recall that, generically,

$$\tilde{U}\left(\tilde{S}(\hat{U}, \hat{V}, \hat{N}), \hat{V}, \hat{N}\right) = \hat{U} \tag{1.2.7}$$

because of inverse relations. Combining (1.2.5)–(1.2.7) we have

$$\begin{aligned}
\tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) &= \tilde{U}\left(\tilde{S}(\lambda U, \lambda V, \lambda \vec{N}), \lambda V, \lambda \vec{N}\right) \\
&= \lambda U \\
&= \lambda \tilde{U}\left(\tilde{S}(U, V, \vec{N}), V, \vec{N}\right) \\
&= \lambda \tilde{U}(S, V, \vec{N}).
\end{aligned} \tag{1.2.8}$$

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

1.3   Path (Contour) Integrals

Definition 1.3.1 (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

$$\vec{Y}(a) = \vec{a} \quad \text{and} \quad \vec{Y}(b) = \vec{b}. \tag{1.3.1}$$

$\mathcal{D}$ 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

$$\vec{x}(t) = \vec{a}(1 - t) + \vec{b}t \in \mathcal{D} \tag{1.3.2}$$

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

Definition 1.3.2 (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

$$\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x} := \int_a^b \vec{F}(\vec{Y}(x)) \cdot \vec{Y}'(x) \, dx. \tag{1.3.3}$$

We will also use the notation

$$\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{Y}} F_1(\vec{x}) dx_1 + \cdots + F_n(\vec{x}) dx_n. \tag{1.3.4}$$

Definition 1.3.3 (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

$$\vec{Y}(a) = \vec{Y}(b). \tag{1.3.5}$$

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

$$\vec{Y}(c) \neq \vec{Y}(x) \quad \forall x \in [a, c) \cup (c, b]. \tag{1.3.6}$$

Theorem 1.3.4 (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*

$$\vec{x}(c) = \vec{Y}(a), \quad \vec{x}(d) = \vec{Y}(b), \tag{1.3.7}$$

and

$$Range(\vec{x}) = Range(\vec{Y}), \tag{1.3.8}$$

then

$$\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{x}} \vec{F}(\vec{x}) \cdot d\vec{x}. \tag{1.3.9}$$

This result guarantees that the path integrals are parametrically independent.

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

$$\int_c \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x}. \tag{1.3.10}$$

Definition 1.3.5 (Path Independence). Let $\mathcal{D} \subseteq \mathbb{R}^n$ be an open, simply connected set. Suppose that

$$\int_{\vec{Y}_1} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{Y}_2} \vec{F}(\vec{x}) \cdot d\vec{x} \tag{1.3.11}$$

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

$$\vec{Y}_1(a) = \vec{Y}_2(a) \quad \text{and} \quad \vec{Y}_1(b) = \vec{Y}_2(b). \tag{1.3.12}$$

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

$$\text{Range}(\vec{Y}_1) = \text{Range}(\vec{Y}_2). \tag{1.3.13}$$

Definition 1.3.6 (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

$$\vec{F}(\vec{x}) = \nabla f(\vec{x}), \quad \forall \vec{x} \in \mathcal{D}. \tag{1.3.14}$$

Theorem 1.3.7. *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*

$$\int_{\vec{Y}} \vec{F}(\vec{x}) \cdot d\vec{x} \tag{1.3.15}$$

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. ,

$$\vec{a} := \vec{Y}_1(a_1) = \vec{Y}_2(a_2), \quad \vec{Y}_1(b_1) = \vec{Y}_2(b_2) =: \vec{b}. \tag{1.3.16}$$

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

$$\frac{d}{dx} f(\vec{Y}_i(x)) = \nabla f(\vec{Y}_i(x)) \cdot \vec{Y}_i'(x)$$
$$= \vec{F}(\vec{Y}_i(x)) \cdot \vec{Y}_i'(x). \tag{1.3.17}$$

Thus,

$$\int_{\vec{Y}_1} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{a_1}^{b_1} \vec{F}(\vec{Y}_1(x)) \cdot \vec{Y}_1'(x)\, dx$$
$$= \int_{a_1}^{b_1} \frac{d}{dx} \left[f(\vec{Y}_1(x)) \right] dx$$
$$\overset{\text{FTC}}{=} f(\vec{b}) - f(\vec{a}), \tag{1.3.18}$$

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

We have the following well-known results.

Theorem 1.3.8. *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. *$\int_{\vec{\gamma}} \vec{F}(\vec{x})\, d\vec{x}$ is path independent*

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