Chapter 1

ThermoS26-02

1.1 Fundamental Relations and Equations of State

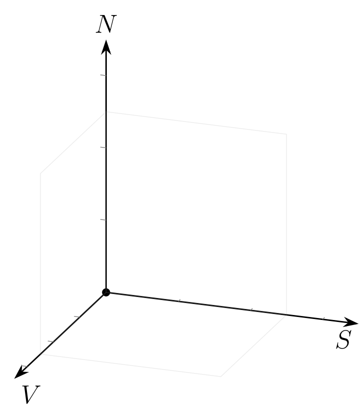

Figure 1.1: Coordinate system for state space with axes N (vertical), V (horizontal right), and S (downward).

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

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

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,

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

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

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

which is also homogeneous of order zero.

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

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

Finally, the chemical potential is

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

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

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

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. □

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 $i = 1, 2$,

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

Thus,

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

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

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

1.4 Exact Differentials in Thermodynamics

Recall, we wrote, as a shorthand,

$$d\tilde{U} = T_U dS - P_U dV + \sum_{i=1}^{r} \mu_{U;i} dN_i. \qquad (1.4.1)$$

This has the form

$$F_1 dx_1 + F_2 dx_2 + \cdots + F_n dx_n = \vec{F} \cdot d\vec{x}, \qquad (1.4.2)$$

where

$$F_1 = T_U, \quad F_2 = -P_U, \quad \ldots \qquad (1.4.3)$$

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

Clearly

$$d\tilde{U} = \nabla\tilde{U} \cdot d\vec{r} \quad (\vec{r} \in \Sigma_S) \qquad (1.4.4)$$

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

$$\int_{\vec{Y}} d\tilde{U} = \int_{\vec{Y}} \nabla\tilde{U} \cdot d\vec{r} \qquad (1.4.5)$$

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

$$\vec{Y}(a) = \vec{r}_a, \quad \vec{Y}(b) = \vec{r}_b, \tag{1.4.6}$$

then

$$\int_{\vec{Y}} d\tilde{U} = \int_{\vec{Y}} \nabla\tilde{U} \cdot d\vec{r} = \tilde{U}(\vec{r}_b) - \tilde{U}(\vec{r}_a). \tag{1.4.7}$$

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

The same is true for

$$d\tilde{S} = \frac{1}{T_S} dU + \frac{P_S}{T_S} dV - \sum_{i=1}^{r} \frac{\mu_{S;i}}{T_S} dN_i, \tag{1.4.8}$$

that is

$$d\tilde{S} = \nabla\tilde{S} \cdot d\vec{r} \quad (\vec{r} \in \Sigma_U) \tag{1.4.9}$$

is an exact differential.