

# ThermoS26-02 - Proofreading Document

Lecture Notes

January 19, 2026



# Chapter 1

## ThermoS26-02

### 1.1 Fundamental Relations and Equations of State

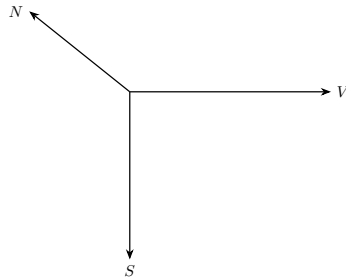


Figure 1.1: Coordinate system for state space with axes  $N$  (vertical),  $V$  (horizontal right), and  $S$  (downward).

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

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

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

$$[U] = \text{Joules}. \quad (1.1.2)$$

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

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

The units of volume,  $V$ , are

$$[V] = \text{meters}^3. \quad (1.1.4)$$

The units of  $N$  are

$$[N] = \text{moles}. \quad (1.1.5)$$

Of course, it is easy to see that

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

An explicit function of the form

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

is also called a **fundamental relation**.

In any case, the temperature which has units

$$[T] = \text{degrees Kelvin} = K, \quad (1.1.8)$$

is

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

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

Observe that

$$T_U(\lambda S, \lambda V, \lambda N) = T_U(S, V, N), \quad (1.1.10)$$

that is  $T_U$  is homogeneous of order 0.

This property is true of every equation of state.

Now,

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

Clearly

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

as claimed in Theorem (1.7).

The pressure satisfies the equation of state

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

which is also homogeneous of order zero.

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

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

Finally, the chemical potential is

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

which is clearly homogeneous of degree zero.

The reader can show that

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

## 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*

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

*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*

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

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

*Likewise  $T_S(U, V, \vec{N})$ ,  $P_S(U, V, \vec{N})$ , and  $\mu_{S;i}(U, V, \vec{N})$  are homogeneous of degree zero.*

*Proof.* Fix  $V \in [0, \infty)$  and  $\vec{N} \in [0, \infty)^r$ .  $\tilde{S}$  is a monotonically increasing function of  $U \in [0, \infty)$ . For each  $S \in [0, \infty)$  there exists a unique  $U \in [0, \infty)$  such that

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

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

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

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

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

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

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

Also, recall that, generically,

$$\tilde{U}(\tilde{S}(\hat{U}, \hat{V}, \hat{N}), \hat{V}, \hat{N}) = \hat{U} \quad (1.2.7)$$

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

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

This completes the proof.  $\square$

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

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

$\mathcal{D}$  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

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

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

**Definition 1.3.2** (Path Integral). Let  $\vec{F} : \mathcal{D} \rightarrow \mathbb{R}^n$  be a  $C^1$  function, i.e. ,  $\vec{F} \in C^1(\mathcal{D}; \mathbb{R}^n)$ . Let  $\vec{Y} : [a, b] \rightarrow \mathcal{D}$  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

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

We will also use the notation

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

**Definition 1.3.3** (Closed Path, Simple Path). Let  $\mathcal{D} \subseteq \mathbb{R}^n$  be a simply connected open set. A path  $\vec{Y} : [a, b] \rightarrow \mathcal{D}$  is called **closed** iff

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

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

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

**Theorem 1.3.4** (Parametric Independence). Let  $\mathcal{D} \subseteq \mathbb{R}^n$  be an open, simply-connected set. Assume  $\vec{Y} : [a, b] \rightarrow \mathcal{D}$  is a path. If  $\vec{x} : [c, d] \rightarrow \mathcal{D}$  is a path in  $\mathcal{D}$ , with the property that

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

and

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

then

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

This result guarantees that the path integrals are parametrically independent.

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

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

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

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

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

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

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

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

**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

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

**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

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

is path-independent.

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

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

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

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



Thus,

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

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

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.

## 1.4 Exact Differentials in Thermodynamics

Recall, we wrote, as a shorthand,

$$d\tilde{U} = T_U dS - P_U dV + \sum_{i=1}^r \mu_{U,i} dN_i. \tag{1.4.1}$$

This has the form

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

where

$$F_1 = T_U, \quad F_2 = -P_U, \quad \dots \tag{1.4.3}$$

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

Clearly

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

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

$$\int_{\vec{\gamma}} d\tilde{U} = \int_{\vec{\gamma}} \nabla \tilde{U} \cdot d\vec{r} \tag{1.4.5}$$

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

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

then

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

We can use any path we want in state space  $\Sigma_S$ .

The same is true for

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

that is

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

is an exact differential.