

Chapter 1

Math Thermo

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Class 02
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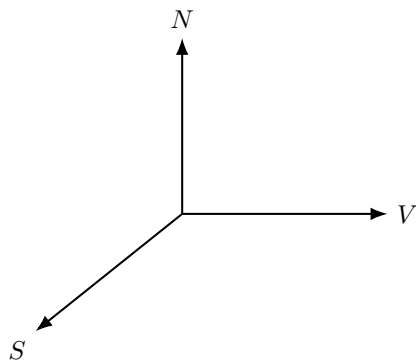


Figure 1.1: Coordinate axes labeled N , V , and S .

Example 1.0.1. (2.1) Suppose that, for an isolated unary fluid

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

A explicit expression of the form $\tilde{U} = \tilde{U}(S, V, N)$ is called a fundamental relation. Here v_0 , θ and R are positive constants. The units of U and \tilde{U} are

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

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

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

The units of volume, V , are

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

The units of N are

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

Of course, it is easy to see that

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

An explicit function of the form

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

is also called a fundamental relation.

In any case, the temperature which has units

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

is

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

This expression is called an equation of state.

Observe that

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

that is T_U is homogeneous of order 0. This property is true of every equation of state.

Now,

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

$$= T_S(U, V, N),$$

Clearly

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

as claimed in Theorem (1.7).

The pressure satisfies the equation of state

$$\begin{aligned} P_S(S, V, N) &= -\frac{v_0 \theta}{R^2} \frac{S^3}{N} \frac{1}{V^2} \\ &= \frac{v_0 \theta}{R^2} \frac{S^3}{NV^2}, \end{aligned}$$

which is also homogeneous of order zero. We leave it as an exercise for the reader to show that

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

Finally, the chemical potential is

$$\mu_S(S, V, N) = -\frac{v_0 \theta}{R^2} \frac{S^3}{VN^2},$$

which is clearly homogeneous of degree zero. The reader can show that

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

Recall we have assumed with the Postulate II that \tilde{S} is homogeneous of degree one. We also must have the following, as suggested by the example.

Theorem 1.0.2. (2.2) \tilde{U} is homogeneous of degree one when written as

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

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. I mean:

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

for any $\lambda > 0$, and similarly for P and μ_{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

$$S = \tilde{S}(U, V, \vec{N}), \quad (2.1)$$

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

$$\tilde{U}(S, V, \vec{N}) = \tilde{U}(\tilde{S}(U, V, \vec{N}), V, \vec{N}), \quad \forall (S, V, \vec{N}) \in \Sigma_S. \quad (2.2)$$

Let $\lambda > 0$ be arbitrary; then (2.1) and (2.2) imply

$$\tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) = \tilde{U}(\lambda \tilde{S}(U, V, \vec{N}), \lambda V, \lambda \vec{N}) \quad (2.3)$$

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

$$\lambda \tilde{S}(U, V, \vec{N}) = \tilde{S}(\lambda U, \lambda V, \lambda \vec{N}) \quad (2.4)$$

Also, recall that, generically,

$$\tilde{U}(\tilde{S}(U, V, \vec{N}), V, \vec{N}) = U \quad (2.5)$$

because of inverse relations. Combining (2.3) – (2.5) we have

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

□

1.1 Path (Contour) Integrals

Definition 1.1.1. (2.4) Suppose that $D \subset \mathbb{R}^n$ is open. A function $\vec{\gamma} : [a, b] \rightarrow D$ is called a path (or contour) iff $\vec{\gamma}$ is continuous and piecewise smooth. The domain D is called path-connected iff for any two distinct points $\vec{a}, \vec{b} \in D$ there is a path $\vec{\gamma} : [a, b] \rightarrow D$ such that $\vec{\gamma}(a) = \vec{a}$ and $\vec{\gamma}(b) = \vec{b}$.

D is called simply-connected iff it is (1) path-connected and (2) a path can be continuously deformed to a point, i.e., there are no holes. D is called convex iff for every pair $\vec{a}, \vec{b} \in D$ the point

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

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

Definition 1.1.2. (2.5) Let $\vec{F} : D \rightarrow \mathbb{R}^n$ be a C^1 function, i.e., $\vec{F} \in C^1(D; \mathbb{R}^n)$. Let $\vec{\gamma} : [a, b] \rightarrow D$ be a path in D which is assumed to be simple-connected. Then the path integral $\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}$ is defined via

$$\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x} := \int_a^b \vec{F}(\vec{\gamma}(\tau)) \cdot \vec{\gamma}'(\tau) d\tau. \quad (2.6)$$

We will also use the notation

$$\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{\gamma}} F_1(\vec{x}) dx_1 + \cdots + F_n(\vec{x}) dx_n$$

Definition 1.1.3. (2.6) Let $D \subset \mathbb{R}^n$ be a simply connected open set. A path $\vec{\gamma} : [a, b] \rightarrow D$ is called closed iff

$$\vec{\gamma}(a) = \vec{\gamma}(b).$$

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

$$\vec{\gamma}(c) \neq \vec{\gamma}(\tau), \quad \tau \in [a, c) \cup (c, b]$$

Theorem 1.1.4. (2.7) Let $D \subset \mathbb{R}^n$ be an open, simply- connected set. Assume $\vec{\gamma} : [a, b] \rightarrow D$ is a simple path. If $\vec{x} : [c, d] \rightarrow D$ is a path in D , with the property that

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

and

$$\text{Range}(\vec{x}) = \text{Range}(\vec{\gamma}),$$

then

$$\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{x}} \vec{F}(\vec{x}) \cdot d\vec{x}.$$

This result guarantees that the path integrals are parametrization independent. If $C = \text{Range}(\vec{\gamma}) = \text{Range}(\vec{x})$, then we write

$$\int_C \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}.$$

Definition 1.1.5. (2.7) Let $D \subset \mathbb{R}^n$ be an open, simply connected set. Suppose that

$$\int_{\vec{\gamma}_1} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{\vec{\gamma}_2} \vec{F}(\vec{x}) \cdot d\vec{x}$$

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

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

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

$$\text{Range}(\vec{\gamma}_1) = \text{Range}(\vec{\gamma}_2).$$

Definition 1.1.6. (2.8) Let D be an open set and $\vec{F} \in C^1(D; \mathbb{R}^n)$. We say that \vec{F} is conservative iff there is a function $f \in C^1(D; \mathbb{R})$ such that

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

Theorem 1.1.7. (2.9) Let D be an open simply connected set in \mathbb{R}^n . If $\vec{F} \in C^1(D; \mathbb{R}^n)$ is conservative, then the integral

$$\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}$$

is path-independent.

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

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

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

$$\begin{aligned} \frac{d}{d\tau} f(\vec{\gamma}_i(\tau)) &= \nabla f(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}_i'(\tau) \\ &= \vec{F}(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}_i'(\tau). \end{aligned}$$

Thus,

$$\begin{aligned} \int_{\vec{\gamma}_i} \vec{F}(\vec{x}) \cdot d\vec{x} &= \int_{a_i}^{b_i} \vec{F}(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}_i'(\tau) d\tau \\ &= \int_{a_i}^{b_i} \frac{d}{d\tau} f(\vec{\gamma}_i(\tau)) d\tau \\ &= f(\vec{b}) - f(\vec{a}), \end{aligned}$$

for $i = 1, 2$. □

We have the following well-known results.

Theorem 1.1.8. (2.10) *Let $D \subset \mathbb{R}^n$ be a simply- connected set and suppose that $\vec{F} \in C^1(D; \mathbb{R}^n)$. The following are equivalent*

1. \vec{F} is conservative
2. $\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}$ is path independent
3. $\oint_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x} = 0$ for any closed path.

Recall, we write, as a shorthand

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

This has the form

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

where $F_1 = T_U$, $F_2 = -P_U$, \dots . We say that $\vec{F} \cdot d\vec{x}$ is an exact differential if \vec{F} is conservative.

Clearly

$$d\tilde{U} = \nabla \tilde{U} \cdot d\vec{\sigma} \quad (\vec{\sigma} \in \Sigma_s)$$

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

$$\int_{\vec{\gamma}} d\tilde{U} = \int_{\vec{\gamma}} \nabla \tilde{U} \cdot d\vec{\sigma}$$

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

$$\vec{\gamma}(a) = \vec{\sigma}_a, \quad \vec{\gamma}(b) = \vec{\sigma}_b,$$

then

$$\int_{\vec{\gamma}} d\tilde{U} = \int_{\vec{\gamma}} \nabla \tilde{U} \cdot d\vec{\sigma} = \tilde{U}(\vec{\sigma}_b) - \tilde{U}(\vec{\sigma}_a).$$

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

The same is true for

$$d\tilde{S} = \frac{1}{T_s} dU + \frac{P_s}{T_s} dV - \sum_{i=1}^r \frac{\mu_{S_i}}{T_s} dN_i,$$

that is

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

is an exact differential.