Math Thermo
class 02
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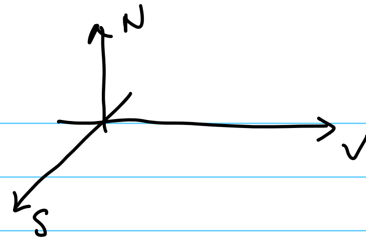

<u>Example</u> (2.1): Suppose that, for an isolated unary fluid

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

A explicit expression of the form $U = \tilde{U}(S,V,N)$ is called a <u>fundamental relation</u>.

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

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

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

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

This expression is called an <u>equation of state</u>.

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,

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

$$= \frac{3 v_0 \theta}{NVR^2}\left(\frac{NVUR^2}{v_0\,\theta}\right)^{2/3}$$

$$= \frac{3 v_0 \theta}{NVR^2}\, \tilde{S}(U,V,N)$$

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

Clearly

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

as claimed in Theorem (1.7).

The pressure satisfies the equation of state

$$P_U(S,V,N) = -\frac{v_0\,\theta}{R^2}\,\frac{S^3}{N}\,\frac{-1}{V^2}$$

$$= \frac{v_0\,\theta}{R^2}\,\frac{S^3}{NV^2},$$

which is also homogeneous of order zero.

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

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

Finally, the chemical potential is

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

which is clearly homogeneous of degree zero.

The reader can show that

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

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

<u>Theorem (2.2)</u>: $\tilde{U}$ 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, meaning

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

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

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

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

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

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

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

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

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

Also, recall that, generically,

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

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

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

Path (Contour) Integrals

Defn (2.4): Suppose that $D \subseteq \mathbb{R}^n$ is open. A function $\vec{\gamma}:[a,b] \to D$ is called a <u>path</u> (or <u>contour</u>) iff $\vec{\gamma}$ is continuous and piecewise smooth. D is called <u>path-connected</u> iff for every two distinct points $\vec{a},\vec{b} \in D$ there is path $\vec{\gamma}:[a,b] \to D$ such that

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

D is called simply-connected iff it is (1) path connected and (2) 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 (2.5): Let $\vec{F}: D \to \mathbb{R}^n$ be a C^1 function, i.e., $\vec{F} \in C^1(D; \mathbb{R}^n)$. Let $\vec{\gamma}: [a,b] \to D$ path in D, which is assumed to be simply connected. Then the path integral $\int_{\vec{\gamma}} \vec{F}(\vec{x}) \cdot d\vec{x}$ is defined via

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

We will also use the notation

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

Defn (2.6): Let $D \subseteq \mathbb{R}^n$ be a simply connected open set. A path $\vec{\gamma}: [a,b] \to D$ 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 $c \in (a,b)$

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

<u>Theorem</u> (2.7): Let $D \subseteq \mathbb{R}^n$ be an open, simply-connected set. Assume $\vec{\gamma}:[a,b] \to D$ is a path. If $\vec{\chi}:[c,d] \to D$ is a path in D, with the property that

$$\vec{\chi}(c) = \vec{\gamma}(a), \qquad \vec{\chi}(d) = \vec{\gamma}(b),$$

and

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

then

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

This result guarantees that the path integrals are parametrization independent.

If $C = \text{Range}(\vec{\gamma}) = \text{Range}(\vec{\chi})$, then we write

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

<u>Dfn</u> (2.7): Let $D \subseteq \mathbb{R}^n$ 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 $\vec{\gamma}_1 : [a,b] \to D$, $\gamma_2 : [c,d] \to D$ 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 <u>path independent</u>. Note that we are <u>not</u> assuming that

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

<u>Defn</u> (2.8): Let D be an open set and $\vec{F} \in C^1(D; \mathbb{R}^n)$. We say that $\vec{F}$ is <u>conservative</u> iff there is a function $f \in C^2(D; \mathbb{R})$ such that

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

<u>Theorem</u> (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.

<u>Proof</u>: Let $\vec{\gamma}_1 : [a_1, b_1] \to D$ and $\vec{\gamma}_2 : [a_2, b_2] \to D$ be paths in D with the same end points, i.e.,

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

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

$$\frac{d}{d\tau} f(\vec{\gamma}_i(\tau)) = \nabla f(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}_i'(\tau)$$

$$= \vec{F}(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}_i'(\tau)$$

Thus,

$$\int_{\vec{\gamma}_i} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_{a_i}^{b_i} \vec{F}(\vec{\gamma}_i(\tau)) \cdot \vec{\gamma}_i'(\tau)\, dt$$

$$= \int_{a_i}^{b_i} \frac{d}{d\tau}\left[f(\vec{\gamma}_i(\tau))\right] d\tau$$

$$\overset{FTC}{=} f(\vec{b}) - f(\vec{a}),$$

for $i = 1, 2$.

We have the following well-known results.

<u>Theorem</u> (2.10): Let $D \subseteq \mathbb{R}^n$ 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) $\int_{\vec{\gamma}} \vec{F}(\vec{x})\, d\vec{x}$ is path independent

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

Recall, we wrote, as a short hand

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

This has the form

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

where

$$F_1 = T_U, \quad F_2 = -P_U, \quad \ldots$$

We say that $\vec{F} \cdot d\vec{x}$ is an <u>exact differential</u> if $\vec{F}$ is conservative.

Clearly
$$d\tilde{U} = \nabla\tilde{U} \cdot d\vec{\sigma} \qquad (\vec{\sigma} \in \Sigma_s)$$
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 $\vec{\gamma} : [a,b] \to \Sigma_s$ 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
$$d\tilde{S} = \nabla\tilde{S} \cdot d\vec{\sigma} \qquad (\vec{\sigma} \in \Sigma_v)$$
is an exact differential.