Math Thermo
class # 04
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## The Euler Equation

Recall that internal energy and the entropy are homogeneous of degree one.

(4.1) $$\tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) = \lambda \tilde{U}(S, V, \vec{N}), \quad \lambda > 0,$$

where

$$\vec{N} = \begin{bmatrix} N_1 \\ N_2 \\ \vdots \\ N_r \end{bmatrix}.$$

Theorem (4.1): Let $\tilde{U}$ be the internal energy of an isolated system. Then

(4.2) $$\tilde{U} = TS - PV + \mu_1 N_1 + \cdots + \mu_r N_r$$

Proof: Since $\tilde{U}$ is homogeneous of degree one differentiating equation (4.1) with respect to $\lambda$

we obtain

$$T(\lambda S, \lambda V, \lambda \vec{N})\, S - P(\lambda S, \lambda V, \lambda \vec{N})\, V + \sum_{j=1}^{r} \mu_j(\lambda S, \lambda V, \lambda \vec{N})\, N_j = \tilde{U}(S, V, \vec{N}).$$

Taking $\lambda = 1$, we get

$$\tilde{U}(S,V,\vec{N}) = T(S,V,\vec{N})S - P(S,V,\vec{N})V + \sum_{j=1}^{r} \mu_j(S,V,\vec{N})N_j,$$

as desired. ///

Remark: Equation (4.1) is known as <u>Euler's Equation</u>, and in some books it is called the <u>integrated form</u> of the internal energy.

<u>Defn</u> (4.2): A <u>process path</u> in state space $\Sigma_S$,

$$\Sigma_S \subseteq \underbrace{[0,\infty)}_{(S)} \times \underbrace{[0,\infty)}_{(V)} \times \underbrace{[0,\infty)}_{(N_1)} \times \cdots \times \underbrace{[0,\infty)}_{(N_r)}$$

is a continuous, piecewise differentiable function $\vec{\gamma} : [0,1] \to \Sigma_S$, defined by

$$\vec{\gamma}(\tau) = \begin{bmatrix} S(\tau) \\ V(\tau) \\ N_1(\tau) \\ \vdots \\ N_r(\tau) \end{bmatrix}.$$

A process path in $\Sigma_U$ is defined similarly.

Thus, we have, using the chain rule,

(4.3)
$$\frac{d}{d\tau}\tilde{U}(\vec{\gamma}(\tau)) = T(\vec{\gamma}(\tau))\, S'(\tau) - P(\vec{\gamma}(\tau))\, V'(\tau) + \sum_{j=1}^{r} \mu_j(\vec{\gamma}(\tau))\, N_j'(\tau)$$

for a valid process path in state space.

Theorem (4.3): Suppose that $\vec{\gamma} : [0,1] \to \Sigma_S$ is a process path in state space $\Sigma_S$. Then,

(4.4)
$$0 = S(\tau)\frac{dT_0}{d\tau}(\vec{\gamma}(t)) - V(\tau)\frac{dP_0}{d\tau}(\vec{\gamma}(\tau)) + \sum_{j=1}^{r} N_j(\tau)\frac{d\mu_{0,j}}{d\tau}(\vec{\gamma}(\tau)).$$

This equation is called the Gibbs–Duhem relation.

Proof: Begin with the Euler equation and differentiate with respect to the process parameter $\tau$:

(4.5)
$$\frac{d\tilde{U}}{d\tau}(\vec{\gamma}(\tau)) = \frac{dT}{d\tau}(\vec{\gamma}(\tau))\, S(\tau) + T(\vec{\gamma}(\tau))\, S'(\tau) - \frac{dP}{d\tau}(\vec{\gamma}(\tau))\, V(\tau) - P(\vec{\gamma}(\tau))\, V'(\tau) + \sum_{j=1}^{r}\left\{ \frac{d\mu_j}{d\tau}(\vec{\gamma}(\tau))\, N_j(\tau) + \mu_j(\vec{\gamma}(\tau))\, N_j'(\tau) \right\}$$

Subtracting (4.5) from (4.3), we get (4.4). ///

Example (4.4): Suppose that the fundamental relation for a material is given by

$$\tilde{S} = 4AU^{1/4}V^{1/2}N^{1/4} + BN, \quad \Sigma_U = [[0,\infty)]^3.$$

where $A, B > 0$ are constants. This function must be homogeneous of degree one. Let us check that. Suppose $\lambda > 0$. Then

$$\tilde{S}(\lambda U, \lambda V, \lambda N) = 4A\lambda U^{1/4}V^{1/2}N^{1/4} + B\lambda N$$

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

Recall that

$$T = \frac{1}{\frac{\partial \tilde{S}}{\partial U}} = \left(A U^{-3/4} V^{1/2} N^{1/4}\right)^{-1}$$

$$= \frac{U^{3/4}}{AV^{1/2}N^{1/4}},$$

which is homogeneous degree zero.

$$\frac{P}{T} = \frac{\partial \tilde{S}}{\partial V}$$

So

$$P = T\frac{\partial \tilde{S}}{\partial V}$$

$$= \frac{U^{3/4}}{AV^{1/2}N^{1/4}}\left(\frac{2A\,U^{1/4}N^{1/4}}{V^{1/2}}\right)$$

$$= \frac{2U}{V}$$

Finally,

$$\mu = -T\frac{\partial \tilde{S}}{\partial N}$$

$$= \frac{-U^{3/4}}{AV^{1/2}N^{1/4}}\left(\frac{AU^{1/4}V^{1/2}}{N^{3/4}} + B\right)$$

$$= -\frac{U}{N} - \frac{BU^{3/4}}{AV^{1/2}N^{1/4}}. \quad ///$$

Example (4.5): Suppose that the fundamental relation is

$$\tilde{U} = \left(\frac{S-BN}{4AV^{1/2}N^{1/4}}\right)^4$$

Recall that

$$T = \frac{\partial \tilde{U}}{\partial S}$$

$$= 4\left(\frac{S-BN}{4AV^{1/2}N^{1/4}}\right)^3 \frac{1}{4AV^{1/2}N^{1/4}}$$

$$= \frac{\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}},$$

The same as above.

$$P = -\frac{\partial \tilde{U}}{\partial V}$$

$$= -4\left(\frac{S-BN}{4AV^{1/2}N^{1/4}}\right)^3\left(\frac{S-BN}{4A\,N^{1/4}}\right)\left(-\frac{1}{2}\right)\frac{1}{V^{3/2}}$$

$$= 2\left(\frac{S-BN}{4AV^{1/2}N^{1/4}}\right)^4 \frac{1}{V}$$

$$= \frac{2\tilde{U}}{V}.$$

Finally,

$$\mu = \frac{\partial \tilde{U}}{\partial N}$$

$$= 4\left(\frac{S-BN}{4AV^{1/2}N^{1/4}}\right)^3 \frac{1}{4AV^{1/2}} \frac{N^{1/4}(-B)-(S-BN)\frac{1}{4}N^{-3/4}}{N^{1/2}}$$

$$= 4\left(\frac{S-BN}{4AV^{1/2}N^{1/4}}\right)^3 \frac{1}{4AV^{1/2}} \frac{N^{1/4}(-B)-(S-BN)\frac{1}{4}N^{-3/4}}{N^{1/2}}$$

$$= 4\tilde{U}^{3/4} \cdot \frac{N^{1/4}}{4AV^{1/2}N^{1/2}} \cdot \left(-B - \frac{S-BN}{4N}\right)$$

$$= \frac{-B\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} - \frac{\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} \cdot \frac{(S-BN)}{4N}$$

$$= \frac{-B\tilde{U}^{3/4}}{AV^{1/2}N^{1/4}} - \frac{\tilde{U}}{N}. \quad ///$$

Let us establish the Euler Equation with respect to entropy.

<u>Theorem</u> (4.6): Let $\tilde{S}$ be the internal energy of an isolated system. Then

(4.6) $$\tilde{S} = \frac{1}{T_s}U + \frac{P_s}{T_s}V - \sum_{j=1}^{r} \frac{\mu_{s,j}}{T_s} N_j ,$$

where

$$T_s = T_s(U, V, \vec{N}),$$

$$P_s = P_s(U, V, \vec{N}),$$

$$\mu_{s,j} = \mu_{s,j}(U, V, N),$$

and

$$\frac{1}{T_s} = \frac{\partial \tilde{S}}{\partial U}, \quad \frac{P_s}{T_s} = \frac{\partial \tilde{S}}{\partial V}, \quad \frac{\mu_{s,j}}{T_s} = \frac{\partial \tilde{S}}{\partial N_j} .$$

<u>Proof</u>: We again use the fact that $\tilde{S}$ is homogeneous of degree one. For any $\lambda > 0$,

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

Taking the derivative with respect to $\lambda$, we have

$$\frac{1}{T_s(\lambda U, \lambda V, \lambda \vec{N})} U + \frac{P_s(\lambda U, \lambda V, \lambda \vec{N})}{T_s(\lambda U, \lambda V, \lambda \vec{N})} V$$

$$+ \sum_{j=1}^{r} \frac{\mu_{s,j}(\lambda U, \lambda V, \lambda \vec{N})}{T_s(\lambda U, \lambda V, \lambda \vec{N})} N_j = \tilde{S}(U, V, \vec{N})$$

Setting $\lambda = 1$ gives the desired result. ///

The Gibbs–Duhem equation is similarly derived.

**Theorem (4.7):** Suppose that $\vec{\gamma} : [0,1] \to \Sigma_0$ is a process path. Then

(4.7)
$$0 = \frac{dT_s}{d\tau}(\vec{\gamma}(\tau))\,\tilde{S}(\vec{\gamma}(\tau)) - \frac{dP_s}{d\tau}(\vec{\gamma}(\tau))\,V(\tau) + \sum_{j=1}^{r} \frac{d\mu_{s,j}}{d\tau}(\vec{\gamma}(\tau))\,N_j(\tau).$$

This equation is called the Gibbs–Duhem relation in the entropy form.

*Proof:* Using (4.6), we have

$$T_s(\vec{\gamma}(\tau))\,\tilde{S}(\vec{\gamma}(\tau)) = U(\tau) + P_s(\vec{\gamma}(\tau))\,V(\tau) - \sum_{j=1}^{r} \mu_{s,j}(\vec{\gamma}(\tau))\,N_j(\tau).$$

Taking the $\tau$-derivative of the last equation we have

(4.8)
$$\frac{dT_s}{d\tau}(\vec{\gamma}(\tau))\,\tilde{S}(\vec{\gamma}(\tau)) + T_s(\vec{\gamma}(\tau))\,\frac{d\tilde{S}}{dt}(\vec{\gamma}(t)) = U'(\tau) + \frac{dP_s}{d\tau}(\vec{\gamma}(\tau))\,V(\tau) + P_s(\vec{\gamma}(t))\,V'(\tau) - \sum_{j=1}^{r} \left\{ \frac{d\mu_{s,j}}{d\tau}(\vec{\gamma}(\tau))\,N_j(\tau) + \mu_{s,j}(\vec{\gamma}(\tau))\,N_j'(\tau) \right\}$$

Taking the $\tau$ derivative of $\tilde{S}(\vec{\gamma}(\tau))$ we have

$$\frac{d\tilde{S}}{d\tau}(\vec{\gamma}(t)) = \frac{1}{T_s(\vec{\gamma}(t))}\,U'(\tau) + \frac{P_s(\vec{\gamma}(\tau))}{T_s(\vec{\gamma}(\tau))}\,V'(\tau)$$

$$- \sum_{j=1}^{r} \frac{\mu_{s,j}(\vec{\gamma}(\tau)) N_j'(\tau)}{T_s(\vec{\gamma}(\tau))} .$$

Equivalently,

(4.9)
$$T_s(\vec{\gamma}(\tau)) \frac{dS}{d\tau}(\vec{\gamma}(t)) = U'(\tau) + P_s(\vec{\gamma}(\tau)) V'(\tau) - \sum_{j=1}^{r} \mu_{s,j}(\vec{\gamma}(\tau)) N_j'(\tau)$$

Subtracting (4.9) from (4.8) we get

$$\frac{dT_s}{d\tau}(\vec{\gamma}(\tau)) \tilde{S}(\vec{\gamma}(\tau)) = \frac{dP_s}{d\tau}(\vec{\gamma}(\tau)) V(\tau) - \sum_{j=1}^{r} \frac{d\mu_{s,j}}{d\tau}(\vec{\gamma}(\tau)) N_j(\tau),$$

which is the desired result. ///

Remark: Compare (4.4) and (4.7):

(4.4)
$$0 = S(\tau) \frac{dT_U}{d\tau}(\vec{\gamma}(t)) - V(\tau) \frac{dP_U}{d\tau}(\vec{\gamma}(\tau)) + \sum_{j=1}^{r} N_j(\tau) \frac{d\mu_{U,j}}{d\tau}(\vec{\gamma}(\tau)),$$

(4.7)
$$0 = \frac{dT_s}{d\tau}(\vec{\gamma}(\tau)) \tilde{S}(\vec{\gamma}(\tau)) - \frac{dP_s}{d\tau}(\vec{\gamma}(\tau)) V(\tau) + \sum_{j=1}^{r} \frac{d\mu_{s,j}}{d\tau}(\vec{\gamma}(\tau)) N_j(\tau).$$

These are essentially the same expressions!