Chapter 1

ThermoS26-04

1.1 The Euler Equation

Recall that internal energy and the entropy are homogenous of degree one:

$$\tilde{U}(\lambda S, \lambda V, \lambda \vec{N}) = \lambda \tilde{U}(S, V, \vec{N}), \qquad \lambda > 0, \tag{3.3}$$

where

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

Theorem 1.1.1. (3.1) *Let $\tilde{U}$ be the internal energy of an isolated system. Then*

$$\tilde{U} = TS - PV + \mu_1 N_1 + \cdots + \mu_r N_r. \tag{3.4}$$

Proof. Since $\tilde{U}$ is homogenous of degree one, differentiating (3.3) with respect to λ we obtain

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

Taking $\lambda = 1$ gives (3.4), as desired. /// $\square$

Remark: Equation (3.4) is known as Euler's Equation.

Definition 1.1.2. (3.2) A process path in state space Σ_S,

$$\Sigma_S \subseteq [0, \infty) \times [0, \infty) \times [0, \infty) \times \cdots \times [0, \infty),$$

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

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

A process path in Σ_U is defined similarly.

Thus, using the chain rule, we have

$$\frac{d}{d\gamma}\tilde{U}(\vec{Y}(\gamma)) = T\big(\vec{Y}(\gamma)\big)S'(\gamma) - P\big(\vec{Y}(\gamma)\big)V'(\gamma) + \sum_{i=1}^{r}\mu_i\big(\vec{Y}(\gamma)\big)N_i'(\gamma) \quad (3.5)$$

for a valid process path in state space.

Theorem 1.1.3. (3.3) *Suppose that $\vec{Y} : [0,1] \to \Sigma_S$ is a process path in state space Σ_S. Then*

$$0 = S(\gamma)\frac{dT_S(\vec{Y}(\gamma))}{d\gamma} - V(\gamma)\frac{dP_S(\vec{Y}(\gamma))}{d\gamma} + \sum_{i=1}^{r}N_i(\gamma)\frac{d\mu_S^i(\vec{Y}(\gamma))}{d\gamma}. \quad (3.6)$$

This equation is called the Gibbs-Duhem relation.

Proof. Begin with the Euler equation and differentiate with respect to the process parameter γ:

$$\begin{aligned} \frac{d\tilde{U}}{d\gamma}\big(\vec{Y}(\gamma)\big) &= \frac{dT}{d\gamma}\big(\vec{Y}(\gamma)\big)S(\gamma) + T\big(\vec{Y}(\gamma)\big)S'(\gamma) \\ &\quad - \frac{dP}{d\gamma}\big(\vec{Y}(\gamma)\big)V(\gamma) - P\big(\vec{Y}(\gamma)\big)V'(\gamma) \\ &\quad + \sum_{i=1}^{r}\left\{\frac{d\mu_i}{d\gamma}\big(\vec{Y}(\gamma)\big)N_i(\gamma) + \mu_i\big(\vec{Y}(\gamma)\big)N_i'(\gamma)\right\}. \end{aligned} \quad (3.7)$$

Substituting (3.5) into (3.7) yields (3.6). /// □