Chapter 1

ThermoS26-03

1.1 Heat Flow

We examine the approach to thermal equilibrium using a diathermal wall. Suppose the substance is unary, $r = 1$. It must be that the variables

$$V^{\alpha},\ V^{\beta},\ N^{\alpha},\ N^{\beta}$$

are fixed, but energy can be exchanged in the process. Suppose the variable γ parameterizes the process.

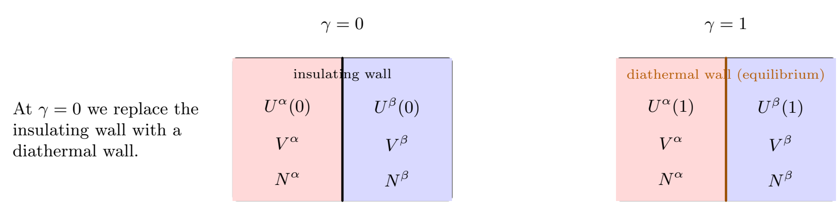

Figure 1.1: Initial and equilibrium configurations for $\gamma = 0$ and $\gamma = 1$. At $\gamma = 0$ the insulating wall is replaced with a diathermal wall; left hot subsystem has $U^{\alpha}(0)$, V^{α}, N^{α} and right cold subsystem has $U^{\beta}(0)$, V^{β}, N^{β}. At $\gamma = 1$ a diathermal wall separates subsystems with $U^{\alpha}(1)$, V^{α}, N^{α} and $U^{\beta}(1)$, V^{β}, N^{β} in equilibrium.

The initial and equilibrium states satisfy

$$S(0) = \tilde{S}^{\alpha}\big(U^{\alpha}(0), V^{\alpha}, N^{\alpha}\big) + \tilde{S}^{\beta}\big(U^{\beta}(0), V^{\beta}, N^{\beta}\big) \leq \tilde{S}^{\alpha}\big(U^{\alpha}(1), V^{\alpha}, N^{\alpha}\big) + \tilde{S}^{\beta}\big(U^{\beta}(1), V^{\beta}, N^{\beta}\big) = S(1).$$

We require that

$$U^{\alpha}(\gamma) + U^{\beta}(\gamma) = U_0.$$

The entropy is at a maximum at equilibrium. Suppose that, as indicated by Figure 1.1,

$$\tilde{T}^{\alpha}\big(U^{\alpha}(0), V^{\alpha}, N^{\alpha}\big) > \tilde{T}^{\beta}\big(U^{\beta}(0), V^{\beta}, N^{\beta}\big)$$

while at equilibrium

$$\tilde{T}^{\alpha}\big(U^{\alpha}(1), V^{\alpha}, N^{\alpha}\big) = \tilde{T}^{\beta}\big(U^{\beta}(1), V^{\beta}, N^{\beta}\big).$$

We will show that

$$U^{\alpha}(0) > U^{\alpha}(1) \qquad \text{(energy is lost in } \alpha\text{)}$$

and

$$U^{\beta}(0) < U^{\beta}(1) \qquad \text{(energy is gain in } \beta\text{)}.$$

To see this, compute

$$\begin{aligned} \frac{dS}{d\gamma} &= \frac{\partial \tilde{S}^{\alpha}}{\partial U^{\alpha}} \frac{\partial U^{\alpha}}{\partial \gamma} + \frac{\partial \tilde{S}^{\beta}}{\partial U^{\beta}} \frac{\partial U^{\beta}}{\partial \gamma} \\ &= \frac{1}{\tilde{T}^{\alpha}_{S}(\gamma)} \frac{\partial U^{\alpha}}{\partial \gamma} + \frac{1}{\tilde{T}^{\beta}_{S}(\gamma)} \frac{\partial U^{\beta}}{\partial \gamma} \\ &= \left(\frac{1}{\tilde{T}^{\alpha}_{S}(\gamma)} - \frac{1}{\tilde{T}^{\beta}_{S}(\gamma)} \right) \frac{\partial U^{\alpha}}{\partial \gamma}, \end{aligned} \tag{3.1}$$

where

$$\tilde{T}^{q}_{S}(\gamma) := T^{q}_{S}\big(U^{q}(\gamma)\big), \qquad q = \alpha, \beta.$$

We know that

$$S(0) \leq \tilde{S}(1).$$

We also know that

$$\tilde{T}^{\alpha}_{S}(0) > \tilde{T}^{\beta}_{S}(0) \qquad \text{and} \qquad \tilde{T}^{\alpha}_{S}(1) = \tilde{T}^{\beta}_{S}(1).$$

Set

$$R(\gamma) := \frac{1}{\tilde{T}^{\alpha}(\gamma)} - \frac{1}{\tilde{T}^{\beta}(\gamma)}, \qquad 0 \leq \gamma \leq 1.$$

We know that $R(0) < 0$ and $R(1) = 0$.

The red curve in Figure 1.2 is not possible; if it were, equilibrium would be reached earlier at $\gamma = \gamma^*$. Thus

$$R(\gamma) < 0 \qquad \forall\, \gamma \in [0, 1).$$

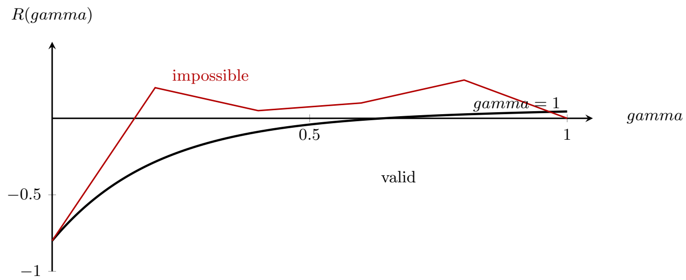

Figure 1.2: Plot of $R(\gamma)$ on $[0,1]$. The red curve is impossible; if it occurred, equilibrium would be reached earlier at $\gamma = \gamma^*$. The valid curve remains negative with $R(1) = 0$.

Integrating (3.1), we get

$$0 \le \tilde{S}(1) - \tilde{S}(0) = \int_0^1 R(\gamma) \frac{dU^\alpha}{d\gamma}\, d\gamma. \tag{3.2}$$

For $U^\alpha(\gamma)$ we have two options:

$$\text{Case (1)} \quad U^\alpha(0) > U^\alpha(1), \qquad \text{Case (2)} \quad U^\alpha(0) \le U^\alpha(1).$$

We are free to pick a parameterization however we want. Let us take a simple linear path

$$\frac{dU^\alpha}{d\gamma} = U^\alpha(1) - U^\alpha(0) =: C^\alpha.$$

Then Case (1) implies $C^\alpha < 0$, while Case (2) implies $C^\alpha \ge 0$. The integral in (3.2) is

$$0 \le \tilde{S}(1) - \tilde{S}(0) = C^\alpha \int_0^1 R(\gamma)\, d\gamma.$$

Therefore the only possible choice is Case (1). Thus

$$U^\alpha(0) > U^\alpha(1) \qquad \big(U^\beta(0) < U^\beta(1)\big).$$

This is consistent with our intuition about temperature. If $\tilde{T}^\alpha(0) > \tilde{T}^\beta(0)$ heat energy flows from subsystem α to subsystem β.

Heat Transfer Principle: Heat energy always flows from hotter to colder system. This is equivalent to the second law of thermodynamics.

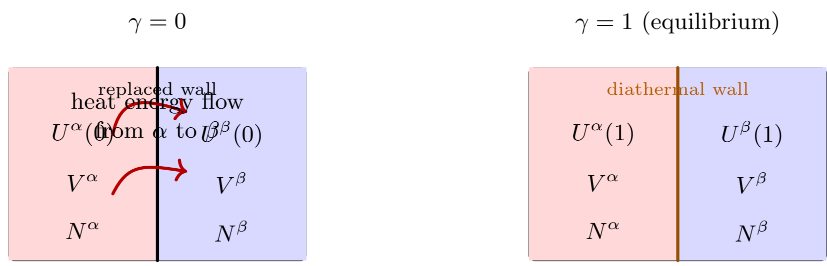

Figure 1.3: Energy transfer for $\gamma = 0$ (hot to cold through replaced wall) and $\gamma = 1$ (equilibrium with diathermal wall) showing flow from subsystem α to subsystem β.

1.2 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 1.2.1. (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. /// □

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

Definition 1.2.2. (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

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

for a valid process path in state space.

Theorem 1.2.3. (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:

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

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

1.3 Examples

Example 1.3.1. (3.4) Suppose that the fundamental relation for a material is given by

$$\tilde{S} = 4A\,U^{1/4}V^{1/2}N^{1/4} + BN, \qquad \Sigma_U = [0,\infty)^3,$$

where $A, B > 0$ are constants. This function must be homogenous of degree one. Suppose $\lambda > 0$. Then

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

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 homogenous 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,

$$\mu = -T\,\frac{\partial \tilde{S}}{\partial N} = -\frac{U^{3/4}}{AV^{1/2}N^{1/4}}\left(\frac{A\,U^{1/4}V^{1/2}}{N^{3/4}} + B\right) = -\frac{U}{N} - \frac{BU^{3/4}}{AV^{1/2}N^{1/4}}.///$$

Example 1.3.2. (3.5) 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.

$$P = -\frac{\partial \tilde{U}}{\partial V} = -4\left(\frac{S - BN}{4AV^{1/2}N^{1/4}}\right)^3 \left(\frac{S - BN}{4AN^{1/4}}\right)\left(-\frac{1}{2}\right)\frac{1}{V^{3/2}}$$

so

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

Finally,

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

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

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

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

1.4 Euler Equation with Respect to Entropy

Theorem 1.4.1. (3.5) *Let $\tilde{S}$ be the internal energy of an isolated system. Then*

$$\tilde{S} = \frac{1}{T_S}U + \frac{P_S}{T_S}V - \sum_{i=1}^{r} \frac{\mu_{S,i}}{T_S} N_i, \tag{3.8}$$

where

$$T_S = T_S(U, V, \vec{N}), \qquad P_S = P_S(U, V, \vec{N}), \qquad \mu_{S,i} = \mu_{S,i}(U, V, \vec{N}),$$

and

$$\frac{1}{T_S} = \frac{\partial \tilde{S}}{\partial U}, \qquad \frac{P_S}{T_S} = \frac{\partial \tilde{S}}{\partial V}, \qquad \frac{\mu_{S,i}}{T_S} = \frac{\partial \tilde{S}}{\partial N_i}.$$

Proof. We again use the fact that $\tilde{S}$ is homogenous 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 λ, we have

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

and setting $\lambda = 1$ gives the desired result. /// $\square$

1.5 Gibbs-Duhem Relation in the Entropy Form

The Gibbs-Duhem equation is similarly derived.

Theorem 1.5.1. (3.6) *Suppose that $\vec{Y} : [0, 1] \to \Sigma_U$ is a process path. Then*

$$0 = \frac{dT_S}{d\gamma}(\vec{Y}(\gamma))\, \tilde{S}(\vec{Y}(\gamma)) - \frac{dP_S}{d\gamma}(\vec{Y}(\gamma))V(\gamma) + \sum_{j=1}^{r} \frac{d\mu_S^j}{d\gamma}(\vec{Y}(\gamma))\, N_j(\gamma). \tag{3.9}$$

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

Proof. Using (3.8), we have

$$T_S\big(\vec{Y}(\gamma)\big)\,\tilde{S}\big(\vec{Y}(\gamma)\big) = U(\gamma) + P_S\big(\vec{Y}(\gamma)\big)V(\gamma) - \sum_{j=1}^{r} \mu_{S,j}\big(\vec{Y}(\gamma)\big)N_j(\gamma).$$

Taking the γ-derivative of the last equation, we have

$$\begin{aligned}\frac{dT_S}{d\gamma}\big(\vec{Y}(\gamma)\big)\,\tilde{S}\big(\vec{Y}(\gamma)\big) + T_S\big(\vec{Y}(\gamma)\big)\frac{d\tilde{S}}{d\gamma}\big(\vec{Y}(\gamma)\big) &= U'(\gamma) + \frac{dP_S}{d\gamma}\big(\vec{Y}(\gamma)\big)V(\gamma) + P_S\big(\vec{Y}(\gamma)\big)V'(\gamma)\\ &\quad - \sum_{j=1}^{r}\left\{\frac{d\mu_{S,j}}{d\gamma}\big(\vec{Y}(\gamma)\big)N_j(\gamma) + \mu_{S,j}\big(\vec{Y}(\gamma)\big)N_j'(\gamma)\right\}.\end{aligned} \tag{3.10}$$

Taking the γ-derivative of $\tilde{S}\big(\vec{Y}(\gamma)\big)$ we have

$$\frac{d\tilde{S}}{d\gamma}\big(\vec{Y}(\gamma)\big) = \frac{1}{T_S(\vec{Y}(\gamma))}U'(\gamma) + \frac{P_S(\vec{Y}(\gamma))}{T_S(\vec{Y}(\gamma))}V'(\gamma) - \sum_{j=1}^{r}\frac{\mu_{S,j}(\vec{Y}(\gamma))}{T_S(\vec{Y}(\gamma))}N_j'(\gamma). \tag{3.11}$$

Substituting (3.11) into (3.10) yields (3.9). /// □

Remark: Compare (3.6) and (3.9):

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

$$0 = \frac{dT_S}{d\gamma}\big(\vec{Y}(\gamma)\big)\,\tilde{S}\big(\vec{Y}(\gamma)\big) - \frac{dP_S}{d\gamma}\big(\vec{Y}(\gamma)\big)V(\gamma) + \sum_{j=1}^{r}\frac{d\mu_S^j}{d\gamma}\big(\vec{Y}(\gamma)\big)N_j(\gamma),$$

These are essentially the same expression!