Chapter 1

ThermoS26-03

Math Thermo
class 03
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1.1 Heat Flow

Let us examine the approach to thermal equilibrium using a diathermal wall. Suppose the substance is binary $r = 1$. 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 $\gamma = 0$ $\gamma = 1$
initial state

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

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

equilibrium state

We require that

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

The entropy is at a max at equilibrium.

Suppose that, as indicated by the figure above,

$$T^\alpha(U^\alpha(0), V^\alpha, N^\alpha) > T^\beta(U^\beta(0), V^\beta, N^\beta)$$

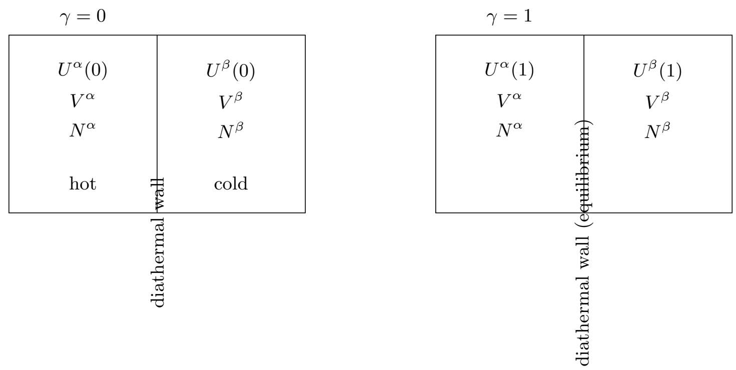

Figure 1.1: Subsystems α and β separated by a diathermal wall, with hot and cold initial states and equilibrium at $\gamma = 1$.

We know that when equilibrium is attained

$$T^\alpha(U^\alpha(1), V^\alpha, N^\alpha) = T^\beta(U^\beta(1), V^\beta, N^\beta)$$

We will show that

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

and

$$U^\beta(0) < U^\beta(1) \quad \text{(energy is gained in } \beta)$$

To see this compute

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

where

$$\tilde{T}_s^q(\gamma) := T_s^q(U^q(\gamma)), \quad q = \alpha, \beta.$$

We know that

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

We know that

$$\tilde{T}_s^{\alpha}(0) > \tilde{T}_s^{\beta}(0)$$

and

$$\tilde{T}_s^{\alpha}(1) = \tilde{T}_s^{\beta}(0)$$

Set

$$R(\gamma) := \frac{1}{\tilde{T}_s^{\alpha}(\gamma)} - \frac{1}{\tilde{T}_s^{\beta}(\gamma)} \quad 0 \le \gamma \le 1$$

We know that

$$R(0) < 0 \quad \text{and} \quad R(1) = 0$$

Thus

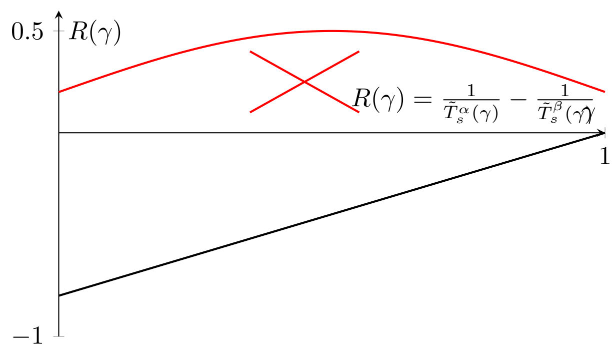

Figure 1.2: $R(\gamma)$ versus γ, with the invalid red curve crossed out.

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

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

Integrating equation (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

Case (1) $\quad U^{\alpha}(0) > U^{\alpha}(1)$

or 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

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

Then
Case (1) $\Rightarrow C^\alpha < 0$
Case (2) $\Rightarrow C^\alpha \geq 0$
The integral in (3.2) is

$$0 \leq \tilde{S}(1) - \tilde{S}(2) = C^\alpha \int_0^1 R(\gamma)\, d\gamma$$

< 0
Therefore, the only possible choice is Case (1). Thus

$$U^\alpha(0) > U^\alpha(1) \quad (U^\beta(0) < U^\beta(1))$$

This is consistent with our intuition about temperature. If $T^\alpha(0) > T^\beta(0)$ net energy flows from subsystem α to subsystem β.
$\gamma = 0$ $\gamma = 1$
Heat Transfer Principle: heat energy always flows from hotter to colder systems. This is equivalent to the second law of thermodynamics.

1.2 The Euler Equation

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

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

where

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

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 homogeneous of degree one differentiating equation (3.1) with respect to λ we obtain

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

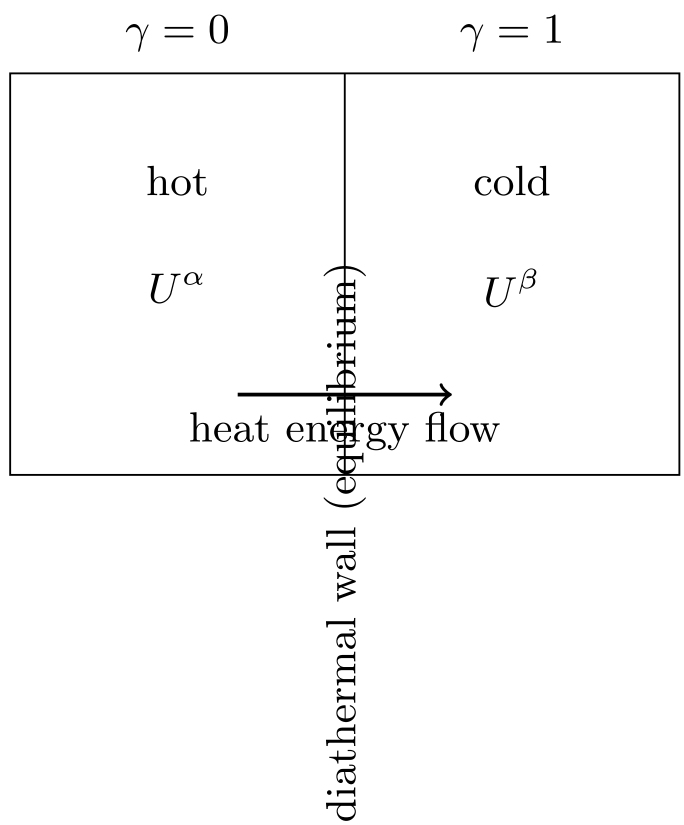

Figure 1.3: Heat energy flow from subsystem α to subsystem β.

Taking $\lambda = 1$, we get

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

as desired. /// $\square$

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

Definition 1.2.2. (3.2) A process path in state space Σ_S,

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

$(S) \quad (V) \quad (N_1) \ \cdots \ (N_r)$

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

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

A process path in Σ_U is defined similarly.

Thus, we have, using the chain rule,

$$\frac{d}{d\gamma}\tilde{U}(\vec{\xi}(\gamma)) = T(\vec{\xi}(\gamma))S'(\gamma) - P(\vec{\xi}(\gamma))V'(\gamma) + \sum_{j=1}^{r} \mu_j(\vec{\xi}(\gamma))N_j'(\gamma) \tag{3.5}$$

for a valid process path in state space.

Theorem 1.2.3. (3.3) *Suppose that $\vec{\xi} : [0,1] \to \Sigma_S$ is a process path in state space Σ_S. Then*

$$\begin{aligned} 0 = S(\gamma)\frac{dT}{d\gamma}(\vec{\xi}(\gamma)) - V(\gamma)\frac{dP}{d\gamma}(\vec{\xi}(\gamma)) \\ + \sum_{j=1}^{r} N_j(\gamma)\frac{d\mu_j}{d\gamma}(\vec{\xi}(\gamma)). \end{aligned} \tag{3.6}$$

This equation is called the Gibbs-Duhem relation.

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

$$\begin{aligned} \frac{d\tilde{U}}{d\gamma}(\vec{\xi}(\gamma)) = {} & \frac{dT}{d\gamma}(\vec{\xi}(\gamma))S(\gamma) + T(\vec{\xi}(\gamma))S'(\gamma) \\ & - \frac{dP}{d\gamma}(\vec{\xi}(\gamma))V(\gamma) - P(\vec{\xi}(\gamma))V'(\gamma) \\ & + \sum_{j=1}^{r}\left\{\frac{d\mu_j}{d\gamma}(\vec{\xi}(\gamma))N_j(\gamma) + \mu_j(\vec{\xi}(\gamma))N_j'(\gamma)\right\} \end{aligned} \tag{3.7}$$

Subtracting (3.5) from (3.7), we get (3.6). /// □

Example 1.2.4. (3.4) 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

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

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

Recall that

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

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

which is homogeneous degree zero.

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

so

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

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

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

Finally,

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

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

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

Example 1.2.5. (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.

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

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

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

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

Finally,

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

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

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

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

Let us establish the Euler Equation with respect to entropy.

Theorem 1.2.6. (3.5) *Let $\tilde{S}$ be the internal energy of an isolated system. Then*

$$\tilde{S} = \frac{1}{T_s}U + \frac{P_s}{T_s}V - \sum_{j=1}^{r} \frac{\mu_{s,j}}{T_s}N_j, \tag{3.8}$$

where

$$T_s = T_s(U, V, \tilde{\mathbf{N}}),$$
$$P_s = P_s(U, V, \tilde{\mathbf{N}}),$$
$$\mu_{s,j} = \mu_{s,j}(U, V, \tilde{\mathbf{N}}),$$

and

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

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

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

Taking the derivative with respect to λ, we have

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

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

The Gibbs-Duhem equation is similarly derived.

Theorem 1.2.7. (3.6) *Suppose that $\vec{\xi} : [0, 1] \to \Sigma_U$ is a process path. Then*

$$\begin{aligned} 0 = {} & \frac{dT_s}{d\gamma}(\vec{\xi}(\gamma))\tilde{S}(\vec{\xi}(\gamma)) - \frac{dP_s}{d\gamma}(\vec{\xi}(\gamma))V(\gamma) \\ & - \sum_{j=1}^{r} \frac{d\mu_{s,j}}{d\gamma}(\vec{\xi}(\gamma))N_j(\gamma). \end{aligned} \tag{3.9}$$

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

Proof. Using (3.8), we have

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

Taking the γ-derivative of the last equation we have

$$\begin{aligned}\frac{dT_s}{d\gamma}(\vec{\xi}(\gamma))\tilde{S}(\vec{\xi}(\gamma))T_s(\vec{\xi}(\gamma))\frac{d\tilde{S}}{d\gamma}(\vec{\xi}(\gamma)) \\ &= U'(\gamma) \\ &\quad + \frac{dP_s}{d\gamma}(\vec{\xi}(\gamma))V(\gamma) + P_s(\vec{\xi}(\gamma))V'(\gamma) \\ &\quad - \sum_{j=1}^{r}\Big\{\frac{d\mu_{s,j}}{d\gamma}(\vec{\xi}(\gamma))N_j(\gamma) \\ &\qquad + \mu_{s,j}(\vec{\xi}(\gamma)) \\ &\qquad N_j'(\gamma)\Big\}\end{aligned} \tag{3.10}$$

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

$$\begin{aligned}\frac{d\tilde{S}}{d\gamma}(\vec{\xi}(\gamma)) &= \frac{1}{T_s(\vec{\xi}(\gamma))}U'(\gamma) \\ &\quad + \frac{P_s(\vec{\xi}(\gamma))}{T_s(\vec{\xi}(\gamma))}V'(\gamma) \\ &\quad - \sum_{j=1}^{r}\frac{\mu_{s,j}(\vec{\xi}(\gamma))}{T_s(\vec{\xi}(\gamma))}N_j'(\gamma).\end{aligned}$$

□

Equivalently,

$$\begin{aligned}T_s(\vec{\xi}(\gamma))\frac{d\tilde{S}}{d\gamma}(\vec{\xi}(\gamma)) &= U'(\gamma) + P_s(\vec{\xi}(\gamma))V'(\gamma) \\ &\quad - \sum_{j=1}^{r}\mu_{s,j}(\vec{\xi}(\gamma))N_j'(\gamma)\end{aligned} \tag{3.11}$$

Subtracting (3.11) from (3.10) we get

$$\begin{aligned}\frac{dT_s}{d\gamma}(\vec{\xi}(\gamma))\tilde{S}(\vec{\xi}(\gamma)) &= \frac{dP_s}{d\gamma}(\vec{\xi}(\gamma))V(\gamma) \\ &\quad - \sum_{j=1}^{r}\frac{d\mu_{s,j}}{d\gamma}(\vec{\xi}(\gamma))N_j(\gamma).\end{aligned}$$

which is the desired result. ///

Remark: Compare (3.6) and (3.9):
(3.6)

$$0 = S(\gamma)\frac{dT}{d\gamma}(\vec{\xi}(\gamma)) - V(\gamma)\frac{dP}{d\gamma}(\vec{\xi}(\gamma)) + \sum_{j=1}^{r} N_j(\gamma)\frac{d\mu_j}{d\gamma}(\vec{\xi}(\gamma)),$$

(3.9)

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

These are essentially the same expressions!