

# Chapter 1

## ThermoS26-05

Math Thermo  
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### 1.1 Legendre Transforms and Thermodynamic Potentials

**Definition 1.1.1.** (5.1) Suppose that  $f : [a, b] \rightarrow \mathbb{R}$  is continuous. For every  $p \in [c, d]$ , define

$$f^*(p) := \sup_{x \in [a, b]} \{xp - f(x)\} \quad (5.1)$$

The function  $f^* : [c, d] \rightarrow \mathbb{R}$  is called the Legendre transform of  $f$ .

**Theorem 1.1.2.** (5.2) Suppose that  $f \in C^2([0, \infty); \mathbb{R})$  with

$$f''(x) > 0, \quad \forall x \in [0, \infty).$$

Then, for all  $p \in \text{Range}(f')$ ,

$$f^*(p) = x_p p - f(x_p), \quad (5.2)$$

where  $x_p \in [0, \infty)$  is the unique solution to

$$f'(x_p) = p.$$

*Proof.* let  $p \in \text{Range}(f')$ .

$$f' : [0, \infty) \rightarrow \text{Range}(f')$$

For every  $p \in \text{Range}(f') \exists! x_p \in [0, \infty)$  and that,

$$f'(x_p) = p.$$

Since  $f' : [0, \infty)$  is strictly increasing,  
Fix  $p \in \text{Range}(f')$ . By Taylor's Theorem,

$$f(x) = f(x_p) + p(x - x_p) + \frac{1}{2}f''(\xi_p)(x - x_p)^2$$

for some  $\xi_p$  between  $x$  and  $x_p$ .

$$\begin{aligned} \sup_{0 \leq x < \infty} \{x \cdot p - f(x)\} &= \sup_{0 \leq x < \infty} \{x_p \cdot p - f(x_p) - \frac{1}{2}f''(\xi_p)(x - x_p)^2\} \\ &= x_p \cdot p - f(x_p). \end{aligned}$$

□

**Theorem 1.1.3.** (5.3) Suppose that  $f \in C^2([0, \infty); \mathbb{R})$  with

$$f''(x) > 0, \quad \forall x \in [0, \infty).$$

Then,

$$[f^*]'(p) = [f']^{-1}(p), \quad [f^*]''(p) > 0,$$

for all  $p \in \text{Range}(f')$ .

*Proof.* Recall

$$f' : [0, \infty) \rightarrow \text{Range}(f')$$

Then

$$f'([f']^{-1}(p)) = p, \quad \forall p \in \text{Range}(f').$$

Also, observe that  $\frac{d}{dp}[f']^{-1} \in C(\text{Range}(f'); \mathbb{R})$ .

Now,

$$\begin{aligned} \frac{d}{dp}[f^*(p)] &= \frac{d}{dp}\{x_p \cdot p - f(x_p)\} = \frac{d}{dp}\{[f']^{-1}(p) \cdot p - f([f']^{-1}(p))\} \\ &= p \cdot \frac{d}{dp}[f']^{-1}(p) + [f']^{-1}(p) - \frac{df}{dx}([f']^{-1}(p)) \cdot \frac{d}{dp}[f']^{-1}(p) \\ &= [f']^{-1}(p). \end{aligned}$$

Now that this is established, we have

$$\frac{d^2}{dp^2}[f^*(p)] = \frac{d}{dp}[f']^{-1}(p)$$

for all  $p \in \text{Range}(f')$ . Since  $f'' \in C([0, \infty))$  and  $f''(x) > 0$ ,  $\forall x \in [0, \infty)$ ,

$$\frac{d}{dp}[f']^{-1}(p) > 0, \quad \forall p \in \text{Range}(f').///$$

□

Finally, we observe the following:

**Theorem 1.1.4.** (5.4) Suppose that  $f \in C^2([0, \infty); \mathbb{R})$  with

$$f''(x) > 0, \quad \forall x \in [0, \infty).$$

Then  $f^* \in C^2(\text{Range}(f'); \mathbb{R})$  with

$$[f^*]''(p) > 0, \quad \forall p \in \text{Range}(f')$$

Furthermore

$$[f^*]^*(x) = f(x), \quad \forall x \in [0, \infty). \quad (5.3)$$

In other words, the Legendre transform is involutive and in fact an isomorphism.

*Proof.* It follows that, for all  $x \in [0, \infty)$ ,

$$[f^*]^*(x) = x p_x - f^*(p_x),$$

where  $p_x \in \text{Range}(f')$  is the unique solution to

$$f^{*'}(p_x) = x.$$

Recall

$$f^*(p_x) = p_x \cdot x_{p_x} - f(x_{p_x}),$$

where  $x_{p_x} \in [0, \infty)$  is the unique solution to

$$f'(x_{p_x}) = p_x.$$

Of course, by uniqueness,

$$x_{p_x} = x.$$

So,

$$[f^*]^*(x) = x \cdot p_x - \{p_x \cdot x_{p_x} - f(x_{p_x})\} = f(x).///$$

□

Why is the Legendre transform useful in Thermodynamics?

This transform allows us to introduce new thermodynamics coordinates/-variables.

Recall

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

or

$$d\tilde{U} = T dS - p dV + \mu dN$$

The latter means

$$T = \frac{\partial \tilde{U}}{\partial S} \quad p = -\frac{\partial \tilde{U}}{\partial V} \quad \mu = \frac{\partial \tilde{U}}{\partial N}$$

in short hand

Extensive Quantity	Conjugate Variable	Variable
$\tilde{U}$	$T, -p, \mu$	$S, V, N$
$\tilde{S}$	$\frac{1}{T}, \frac{p}{T}, -\frac{\mu}{T}$	$U, V, N$

Table 1.1: Conjugate variables for  $\tilde{U}$  and  $\tilde{S}$ .

**Definition 1.1.5.** (5.5) Suppose that all of the Thermodynamic Postulates hold. Assume that the material in question is unary ( $r = 1$ ). Define

$$\tilde{F}(T, V, N) = \tilde{U}(S_T, V, N) - TS_T \quad (5.4)$$

where  $S_T = S_T(V, N)$  is the unique solution of the equation

$$T_U(S_T(V, N), V, N) = T \quad (5.5)$$

for fixed values of  $N$  and  $V$ .

$\tilde{F}$  is called the Helmholtz free energy.

Formally, we have

$$\begin{aligned} d\tilde{F} &= d\tilde{U} - S dT - T dS \\ &= T dS - p dV + \mu dN - S dT - T dS \\ &= -S dT - p dV + \mu dN. \end{aligned}$$

Extensive Quantity	Conjugate Variable	Variable
$\tilde{U}$	$T, -p, \mu$	$S, V, N$
$\tilde{F}$	$-S, -p, \mu$	$T, V, N$

Table 1.2: Conjugate variables for  $\tilde{U}$  and  $\tilde{F}$ .

**Example 1.1.6.** (5.6) Suppose that

$$\tilde{S}(U, V, N) = \left( \frac{NVUR^2}{v_0\theta} \right)^{1/3}.$$

It follows that

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

The temperature function is

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

Or

$$\frac{1}{T_S(U, V, N)} = \frac{1}{3} \left( \frac{NVUR^2}{v_0\theta} \right)^{-2/3} \frac{NVR^2}{v_0\theta} = \frac{1}{3} \left( \frac{NVR^2}{v_0\theta} \right)^{1/3} U^{-2/3}.$$

Thus

$$T_S(U, V, N) = 3 \left( \frac{v_0\theta}{NVR^2} \right)^{1/3} U^{2/3}.$$

Recall that

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

$$T_S(U, V, \vec{N}) = T_U(\tilde{S}(U, V, \vec{N}), V, \vec{N}).$$

By definition

$$\tilde{F}(T, V, N) = \tilde{U}(S_T, V, N) - TS_T$$

where

$$T_U(S_T(V, N), V, N) = T.$$

For our example,

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

Hence,

$$S_T = \sqrt{\frac{TNVR^2}{3v_0\theta}}.$$

Thus,

$$\begin{aligned}\tilde{F}(T, V, N) &= \tilde{U}\left(\sqrt{\frac{TNVR^2}{3v_0\theta}}, V, N\right) - T\sqrt{\frac{TNVR^2}{3v_0\theta}} \\ &= \left(\frac{TNVR^2}{3v_0\theta}\right)^{3/2} \frac{v_0\theta}{NVR^2} - T\sqrt{\frac{TNVR^2}{3v_0\theta}}.\end{aligned}$$

But

$$\tilde{U}(S_T, V, N) = \frac{S_T^3 v_0\theta}{NVR^2} = \left(\frac{TNVR^2}{3v_0\theta}\right)^{3/2} \frac{v_0\theta}{NVR^2}$$

so that

$$\tilde{F}(T, N, V) = \frac{1}{3}T^{3/2} \frac{1}{\sqrt{3}} \sqrt{\frac{NVR^2}{v_0\theta}} - \frac{T^{3/2}}{\sqrt{3}} \sqrt{\frac{NVR^2}{v_0\theta}}.$$

Finally,

$$\tilde{F}(T, N, V) = -\frac{2T^{3/2}}{3} \sqrt{\frac{NVR^2}{3v_0\theta}}. \quad (5.6)$$

Now,

$$\frac{\partial \tilde{F}}{\partial T} = -\frac{2}{3} \sqrt{T} \sqrt{\frac{NVR^2}{3v_0\theta}}.$$

But

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

Thus,

$$\sqrt{T} = \sqrt{\frac{3v_0\theta}{NVR^2}} S_T$$

and

$$\frac{\partial \tilde{F}}{\partial T} = -S_T. \quad (5.7)$$

**Theorem 1.1.7.** (5.7) Suppose that all of the Thermodynamic Postulates hold. Assume that the material in question is unary ( $r = 1$ ). The following procedure is equivalent means for finding the Helmholtz free energy:

$$\tilde{F}(T, V, N) = U_T - T\tilde{S}(U_T, V, N) \quad (5.8)$$

where  $U_T = U_T(V, N)$  is the unique solution of the equation

$$T_S(U_T(V, N), V, N) = T$$

for fixed values of  $N$  and  $V$ .

Proof: Exercise ///

**Example 1.1.8.** (5.8) Let us use the second version to calculate the free energy for the monatomic ideal gas. Recall,

$$\tilde{S}(U, V, N) = Ns_0 + NR \ln \left( \left( \frac{U}{U_0} \right)^{3/2} \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-5/2} \right),$$

where  $s_0, R, U_0, V_0, N_0$  are positive constants.

Then

$$\begin{aligned} \frac{\partial \tilde{S}}{\partial U} &= \frac{NR}{\left( \frac{U}{U_0} \right)^{3/2}} \cdot \frac{3}{2} \left( \frac{U}{U_0} \right)^{1/2} \frac{1}{U_0} \\ &= \frac{3NR}{2U_0} \cdot \frac{U_0}{U} = \frac{3NR}{2U} \end{aligned}$$

Thus

$$T_S(U, V, N) = \frac{2}{3} \frac{U}{NR}$$

and

$$U_T = \frac{3NRT}{2}$$

Therefore,

$$\begin{aligned} \tilde{F}(T, V, N) &= \frac{3NRT}{2} - TNs_0 \\ &\quad - NRT \ln \left( \left( \frac{3NRT}{2U_0} \right)^{3/2} \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-5/2} \right) \end{aligned}$$

Define

$$T_0 := \frac{2U_0}{3N_0R}.$$

Then,

$$\tilde{F}(T, V, N) = \frac{3NRT}{2} - TNs_0 - NRT \ln \left( \left( \frac{T}{T_0} \right)^{3/2} \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-1} \right) \quad (5.9)$$

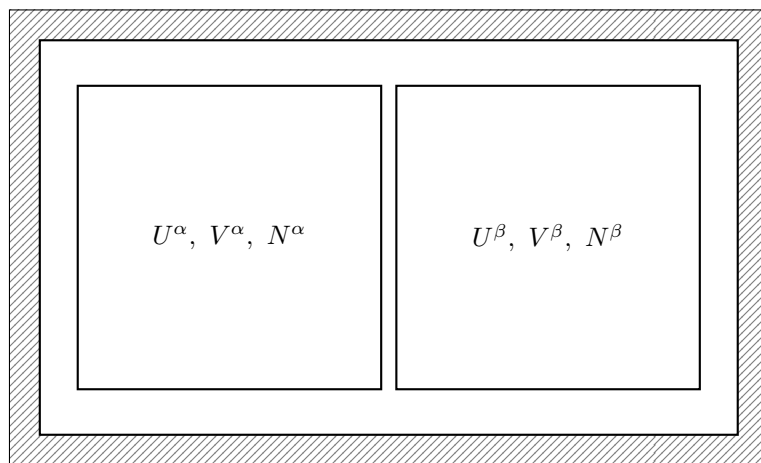


Figure 1.1: Two isolated systems initially separated by insulating walls.

## 1.2 Equilibrium with a heat Bath

Consider two isolated systems that are initially isolated from each other.

Now, let us remove the isolating walls so that energy, volume, and mass may be exchanged.

The entropy will attain its maximum at equilibrium and

$$\begin{aligned} T^\alpha &= T^\beta \\ P^\alpha &= P^\beta \\ \mu_i^\alpha &= \mu_i^\beta, \quad i = 1, \dots, r. \end{aligned}$$

How can we characterize equilibrium?

Now, suppose that instead of isolating from the universe, our composite system is put into contact with a heat bath.

**Definition 1.2.1.** (5.9) A heat bath is an otherwise- isolated thermodynamic system that is so large that, when it exchanges a finite amount of energy with an otherwise-isolated, composite system, its temperature, pressure, and chemical potential changes are so small as to be negligible.

Similarly, we have

heat-pressure bath: finite exchanges of energy and volume lead to negligible changes in  $T$ ,  $P$ , and  $\mu$  in baths.



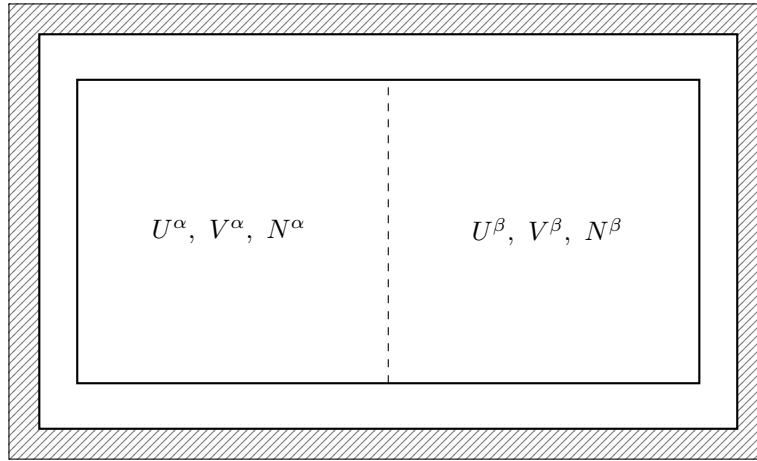


Figure 1.2: Isolating wall removed so energy, volume, and mass can be exchanged.

A heat-pressure-chemical bath is defined analogously.

Let us consider a picture for the case of the heat bath.

Let us recall the "integrated form" of the entropy function.

$$\tilde{S}^B = \tilde{S}^B(U^B, V^B, N^B) = \frac{1}{T^0} U^B + \frac{P^0}{T^0} V^B - \frac{\mu^0}{T^0} \cdot N^B$$

where

$$T^0 = T^0(U^0, V^0, N^0)$$

et cetera. We will write

$$\begin{aligned} S^{tot} &= \tilde{S}^B + \tilde{S}^\alpha + \tilde{S}^\beta \\ &= \tilde{S}^B + \tilde{S}^{\alpha+\beta} \end{aligned}$$

Now, our system will not exchange volume or mass with the bath, only energy, because we will replace the horizontal isolations wall with a diathermal wall.

We know that, at equilibrium

$$T^\alpha = T^\beta = T^B = T_0.$$

Recall the deviations of  $T^B$  from  $T_0$  at equilibrium is assumed negligible.

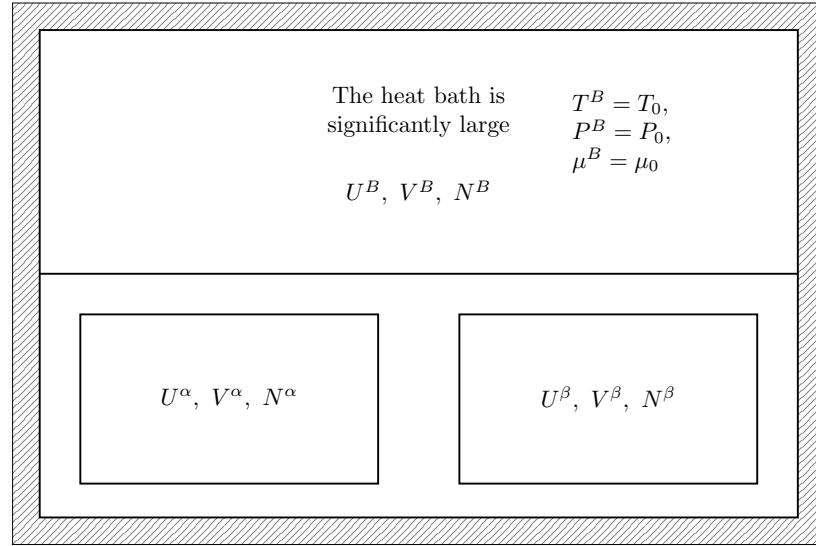


Figure 1.3: Composite system in contact with a heat bath.

System  $\alpha$  and  $\beta$  can exchange energy. System  $\alpha$  and  $\beta$  can exchange volume and mass with each other but not with the bath.

Thus,

$$S^{tot,eq} = \max_C \{ \tilde{S}^B + \tilde{S}^{\alpha+\beta} \}$$

Now

$$\tilde{S}^B = \frac{1}{T_0} U^B + \frac{P_0}{T_0} V^B - \frac{\mu_0}{T_0} \cdot N^B$$

The changes in  $T^B$ ,  $P^B$ ,  $\mu^B$  from  $T_0$ ,  $P_0$ ,  $\mu_0$  is negligible because the bath is so large.

Writing

$$U^B = U_0 - U^\alpha - U^\beta$$

$$\tilde{S}^B = -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + \frac{U_0}{T_0} + C_1$$

$$= -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + C_2$$

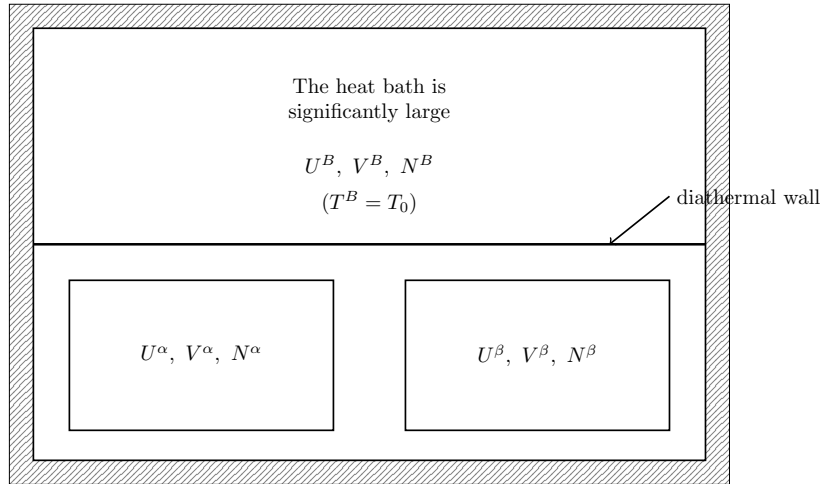


Figure 1.4: Diathermal wall configuration: only energy exchange with the bath.

Thus,

$$\begin{aligned}
 S^{tot,eq} &= \max_C \left\{ -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + C_2 + \tilde{S}^{\alpha+\beta} \right\} \\
 &= C_2 + \max_C \left\{ -\frac{U^\alpha + U^\beta}{T_0} + \tilde{S}^\alpha + \tilde{S}^\beta \right\} \\
 &= C_2 + \max_C \left\{ -\frac{F^\alpha + F^\beta}{T_0} \right\} \\
 &= C_2 - \frac{1}{T_0} \min_C \{ F^\alpha(T_0, V^\alpha, N^\alpha) + F^\beta(T_0, V^\beta, N^\beta) \}
 \end{aligned}$$

Postulate VI: Consider a compound, otherwise- isolated thermodynamic system in contact with an otherwise-isolated heat bath at temperature  $T_0$ . Equilibrium of the compound system is the state satisfying the isothermal condition

$$T^\alpha = T^\beta = T_0$$

which minimizes

$$F^\alpha(T_0, V^\alpha, N^\alpha) + F^\beta(T_0, V^\beta, N^\beta)$$

subject to the constraints

$$V^\alpha + V^\beta = V_0, \quad (\text{volume conservation})$$

$$N_i^\alpha + N_i^\beta = N_{i,0}, \quad (\text{mass conservation})$$

Remark: Since the system  $\alpha + \beta$  exchanges energy with the heat bath, energy is not conserved in  $\alpha + \beta$ .

Energy is conserved in the system  $B + \alpha + \beta$ .