Chapter 1

ThermoS26-06

1.1 Legendre Transforms and Thermodynamic Potentials

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

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

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

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

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

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

$$f^*(p) = x_p\, p - f(x_p), \tag{5.2}$$

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

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

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

$$f' : [0, \infty) \to \mathrm{Range}(f')$$

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

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

Since $f' : [0, \infty)$ is strictly increasing,
Fix $p \in \mathrm{Range}(f')$. 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 ξ_p between x and x_p.

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

□

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

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

Then,

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

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

Proof. Recall

$$f' : [0, \infty) \to \mathrm{Range}(f')$$

Then

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

Also, observe that $\frac{d}{dp}[f']^{-1} \in C(\mathrm{Range}(f'); \mathbb{R})$.
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 $p \in \mathrm{Range}(f')$. Since $f'' \in C([0, \infty))$ and $f''(x) > 0,\ \forall x \in [0, \infty)$,

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

□

Finally, we observe the following:

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

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

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

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

Furthermore

$$[f^*]^*(x) = f(x), \qquad \forall x \in [0,\infty). \tag{5.3}$$

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

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

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

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

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 $\tilde{S}$.

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

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

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

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

$$T_U(S_T(V, N), V, N) = T \tag{5.5}$$

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,

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

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,

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

Now,

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

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

$$\frac{\partial \tilde{F}}{\partial T} = -S_T. \tag{5.7}$$

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:*

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

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

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

Thus

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

and

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

Therefore,

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

Define

$$T_0 := \frac{2U_0}{3N_0 R}.$$

Then,

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