

Legendre transform in two-dimensional thermodynamics

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The Legendre transform is a useful device for producing new state functions from old ones. In thermodynamics, it is usual to employ a slight variant, differing by a sign from the usual Legendre transform. So the package is

$$f(x) - g(p) = xp \quad , \quad x = -g'(p) \quad , \quad p = f'(x) .$$

The second and third relations imply the first one up to a constant, and the first one fixes the constant. One says that $f(x)$ is the Legendre conjugate of $g(p)$, and x is the Legendre conjugate of p . To make this work out one assumes that $g''(p) < 0$ —so that $-g'(p)$ is an increasing function, and its inverse function $f'(x)$ is increasing as well, and so $f''(x) > 0$ —or that $g''(p) > 0$, in which case $f''(x) < 0$.

In thermodynamics one often has more than one independent variable. In this case, one can form the Legendre transform with respect to one variable at a time, holding the others fixed. A beautiful, complex, symmetrical pattern of potentials and new state functions arises. This is of interest independent of the apparatus of thermodynamics, but we will use the notation and names arising there.

The conceptual framework is this: There is a space D of possible states of a thermodynamic system. It admits various coordinate systems. In the two-dimensional case, the coordinates consist of a pair of real-valued functions or “state parameters”; that is, a function $D \rightarrow \mathbb{R}^2$. Then on \mathbb{R}^2 there is defined a “potential function” that determines the thermodynamic properties of the system.

One pair of state parameters that is close to our common experience is given by temperature T and volume V . The relevant potential is the “Helmholtz free energy,” or “Helmholtz potential,” $F = F(T, V)$. This function is also written $A(T, V)$ in the literature. The Helmholtz potential is arranged so that:

If the system is constrained to have a fixed temperature T , it selects the state which minimizes the Helmholtz free energy F .

We assume that

$$\left(\frac{\partial^2 F}{\partial T^2} \right)_V < 0 \quad , \quad \left(\frac{\partial^2 F}{\partial V^2} \right)_T > 0 .$$

Let's start with T , holding V constant. The Legendre transform package is then

$$(1) \quad U(S, V) - F(T, V) = ST, \quad S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad T = \left(\frac{\partial U}{\partial S} \right)_V.$$

The quantity S is the “entropy” of the system, and U is the “internal energy.” The internal energy is the Legendre conjugate of Helmholtz free energy obtained by replacing temperature with entropy as an independent variable, keeping V constant.

We claim that

$$(2) \quad \left(\frac{\partial F}{\partial V} \right)_T = \left(\frac{\partial U}{\partial V} \right)_S.$$

This follows from the Legendre relation: differentiate with respect to V , holding both S and T fixed.

Therefore, the condition of minimizing F for fixed T is equivalent to the condition of minimizing U for fixed S , so:

If a system is constrained to have fixed entropy S , it selects the state which minimizes the internal energy U .

We find that

$$\left(\frac{\partial^2 U}{\partial S^2} \right)_V > 0 \quad , \quad \left(\frac{\partial^2 U}{\partial V^2} \right)_S > 0.$$

We can also swap V for a new variable, P , keeping T constant:

$$(3) \quad G(T, P) - F(T, V) = PV, \quad P = - \left(\frac{\partial F}{\partial V} \right)_T, \quad V = \left(\frac{\partial G}{\partial P} \right)_T.$$

P is “pressure,” and G is the “Gibbs free energy” or “Gibbs potential.”

Differentiating (3) with respect to T , holding both V and T constant, gives us

$$(4) \quad \left(\frac{\partial F}{\partial T} \right)_V = \left(\frac{\partial G}{\partial T} \right)_P.$$

We find that

$$\left(\frac{\partial^2 G}{\partial T^2} \right)_P < 0 \quad , \quad \left(\frac{\partial^2 G}{\partial P^2} \right)_T < 0.$$

Then we can, if we want, take U and swap V for a new variable, keeping S constant:

$$(5) \quad H(S, \bar{P}) - U(S, V) = \bar{P}V, \quad \bar{P} = - \left(\frac{\partial U}{\partial V} \right)_S, \quad V = \left(\frac{\partial H}{\partial \bar{P}} \right)_S.$$

The identity (2) implies that $\bar{P} = P$. This new potential $H(S, P)$ is the “enthalpy” of the system.

We get a third claim, as well:

$$(6) \quad \left(\frac{\partial U}{\partial S} \right)_V = \left(\frac{\partial H}{\partial S} \right)_P.$$

We find that

$$\left(\frac{\partial^2 H}{\partial S^2} \right)_P > 0 \quad , \quad \left(\frac{\partial^2 H}{\partial P^2} \right)_S < 0.$$

A system subject to fixed pressure P selects the state which minimizes enthalpy H . This is the same state as that which minimizes the internal energy U for fixed volume V .

Or we could take G and swap T for a new variable, keeping P constant:

$$(7) \quad \bar{H}(\bar{S}, P) - G(T, P) = \bar{S}T \quad , \quad \bar{S} = - \left(\frac{\partial G}{\partial T} \right)_P \quad , \quad T = \left(\frac{\partial \bar{H}}{\partial \bar{S}} \right)_P.$$

The identity (4) implies that $\bar{S} = S$. Then

$$\bar{H} = ST + G = ST + PV + F = PV + U = H$$

Combining the formulas for T in (1) and (7) confirms (6). Differentiating (7) with respect to P gives the identity

$$(8) \quad \left(\frac{\partial G}{\partial P} \right)_T = \left(\frac{\partial H}{\partial P} \right)_S$$

which we already know by combining the formulas for V in (3) and (5).

Summary: Application of the Legendre transform takes a parametrization of the state space by two variables and a potential function of those two variables, and produces two other parameters and three other potentials. The result is that each of the parameters has two expressions as a partial derivative of a potential.

The relationships between the four potentials and the four state parameters can be summarized by the following formulas for the total differentials of the various potentials:

$$\begin{aligned} dF &= -S dT - P dV \\ dG &= -S dT + V dP \\ dU &= T dS - P dV \\ dH &= T dS + V dP \end{aligned}$$

together with the relations

$$\begin{aligned} U(S, V) - F(T, V) &= ST = H(S, P) - G(T, P) \\ G(T, P) - F(T, V) &= PV = H(S, P) - U(S, V). \end{aligned}$$

Maxwell's relations: Using (1), commutativity of partial derivatives, and (3),

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial}{\partial V}\bigg|_T \left(-\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T}\bigg|_V \left(-\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

Similarly, using other pairs of odd numbered equations gives us the other equations in:

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\ \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial S}{\partial P}\right)_T & \left(\frac{\partial V}{\partial S}\right)_P &= \left(\frac{\partial T}{\partial P}\right)_S. \end{aligned}$$

These merely express the fact that the differentials of the potentials are closed.

Gibbs-Helmholtz equations: Calculate

$$\left(\frac{\partial(FT^{-1})}{\partial T}\right)_V = \left(\frac{\partial F}{\partial T}\right)_V T^{-1} - FT^{-2} = ST^{-1} - FT^{-2} = -UT^{-2}$$

so that

$$(9) \quad U = -T^2 \left(\frac{\partial(F/T)}{\partial T}\right)_V.$$

Exactly similar calculations lead to seven other identities:

$$\begin{aligned} F &= -P^2 \left(\frac{\partial(G/P)}{\partial P}\right)_T & F &= -S^2 \left(\frac{\partial(U/S)}{\partial S}\right)_V \\ G &= -S^2 \left(\frac{\partial(H/S)}{\partial S}\right)_P & G &= -V^2 \left(\frac{\partial(F/V)}{\partial V}\right)_T \\ H &= -V^2 \left(\frac{\partial(U/V)}{\partial V}\right)_S & H &= -T^2 \left(\frac{\partial(G/T)}{\partial T}\right)_P \\ U &= -T^2 \left(\frac{\partial(F/T)}{\partial T}\right)_V & U &= -P^2 \left(\frac{\partial(H/P)}{\partial P}\right)_S \end{aligned}$$

Quadratic thermodynamics: With

$$F(T, V) = -\frac{T^2}{2} + \frac{V^2}{2}$$

we find

$$\begin{aligned} S = T \quad , \quad U(S, V) &= \frac{S^2}{2} + \frac{V^2}{2} \\ P = -V \quad , \quad G(T, P) &= -\frac{T^2}{2} - \frac{P^2}{2} \end{aligned}$$

$$H(S, P) = \frac{S^2}{2} - \frac{P^2}{2}$$

The “ideal gas law”: A “fundamental relation” is an explicit formula for one of the potentials in terms of its natural variables.

Usually one gives much less information than that. For example, the “ideal gas law” (Clapeyron, 1834) is the relation

$$PV = RT$$

where R is constant. A relation among system parameters, such as this, is an “equation of state.”

This implies that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}.$$

From $dU = T dS - P dV$ we find, using one of Maxwell’s relations,

$$(10) \quad \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

so in an ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{R}{V} - P = P - P = 0.$$

This relation is known as “Joule’s law,” and (10) shows that it is equivalent to the relation

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T}.$$

Under the hypothesis only of Joule’s law,

$$P = T f'(V)$$

for some function $f(V)$. Now

$$T f'(V) = P = - \left(\frac{\partial F}{\partial V}\right)_T$$

integrates to

$$F(T, V) = g(T) - T f(V)$$

for some function $g(T)$. Then

$$S = - \left(\frac{\partial F}{\partial T}\right)_V = f(V) - g'(T)$$

and U depends only on T :

$$(11) \quad U(S, V) = ST + F(T, V) = g(T) - T g'(T).$$

Conversely, it is clear that if U depends only on T , then $\left(\frac{\partial U}{\partial V}\right)_T = 0$, so Joule's law is equivalent to U depending only on T .

Another relevant condition is the assumption that the "heat capacity at constant volume,"

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V$$

is constant. The conjunction of this condition with Joule's law is equivalent to requiring

$$U = a + c_V T$$

They give $g(T) = a + bT - c_V T \ln T$ for some a, b . We take this moment to normalize the potentials, by choosing U so that $a = 0$.

Then

$$F(T, V) = (c_V - S)T \quad , \quad T = \left(\frac{\partial U}{\partial S}\right)_V \quad , \quad S = -\left(\frac{\partial F}{\partial T}\right)_V .$$

We can solve $T = \left(\frac{\partial c_V T}{\partial S}\right)_V$ to get

$$T = e^{(S/c_V) - k(V)}$$

for some function $k(V)$. (We've taken the liberty of forcing $T > 0$.) We now have a pretty explicit fundamental relation, depending on the function $k(V)$:

$$U(S, V) = c_V e^{(S/c_V) - k(V)} .$$

Also,

$$S = c_V (\ln T + k(V))$$

so

$$F(T, V) = c_V T (1 - \ln T - k(V))$$

and incidentally we have computed the two functions of interest earlier:

$$g(T) = c_V T (1 - \ln T) \quad , \quad f(V) = c_V k(V) .$$

So

$$P = T f'(V) = c_V T k'(V) .$$

If the ideal gas law holds and c_V is constant, then this equation implies

$$\frac{R}{c_V} \frac{1}{V} = k'(V)$$

so

$$k(V) = c_V^{-1} (S_0 + R \ln V)$$

for a constant S_0 . Then

$$T = V^{-R/c_V} e^{(S - S_0)/c_V} \quad , \quad S - S_0 = c_V \ln T + R \ln V$$

and we get explicit fundamental relations:

$$U(S, V) = c_V V^{-R/c_V} e^{(S-S_0)/c_V}$$

$$F(T, V) = c_V T(1 - \ln T) - T(S_0 + R \ln V)$$

depending upon the parameters R , c_V , and S_0 .

As long as V and c_V are positive, the condition

$$\left(\frac{\partial^2 U}{\partial S^2} \right)_V > 0$$

holds. If R is also positive then also

$$\left(\frac{\partial^2 U}{\partial V^2} \right)_S > 0.$$

The “ideal van der Waals fluid”: The van der Waals ansatz (1873) modifies the ideal gas law, and its companion assumption that c_V is constant, to accommodate interaction between particles in the fluid. Reference: Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistics*. The ideal gas law gets replaced by the equation of state

$$P = \frac{RT}{V - V_0} - \frac{a}{V^2}$$

and the hypothesis that $U = c_V T$ with c_V constant gets replaced by

$$U = cRT - \frac{a}{V}.$$

We can integrate

$$\left(\frac{\partial F}{\partial V} \right)_T = -P = -\frac{RT}{V - V_0} + \frac{a}{V^2}$$

to

$$F(T, V) = -RT \ln(V - V_0) - \frac{a}{V} + f(T)$$

for some function $f(T)$. Then

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = R \ln(V - V_0) - f'(T)$$

so

$$F = U - ST = cRT - \frac{a}{V} - ST = cRT - \frac{a}{V} - RT \ln(V - V_0) + T f'(T).$$

Comparing these two expressions for F gives a differential equation for $f(T)$:

$$T f'(T) = f(T) - cRT.$$

The solution is

$$f(T) = kT - cRT \ln T$$

for a constant k . Thus

$$F(T, V) = -RT \ln(V - V_0) - \frac{a}{V} - cRT \ln T + kT$$

and

$$S - S_0 = R \ln(V - V_0) + cR \ln T$$

where we write $S_0 = cR - k$. Solving for T :

$$T = \frac{e^{(S-S_0)/cR}}{(V - V_0)^{1/c}}.$$

Plugging this into the hypothesized form for U gives the fundamental relation

$$U(S, V) = cR \frac{e^{(S-S_0)/cR}}{(V - V_0)^{1/c}} - \frac{a}{V}.$$

Higher dimensional thermodynamics. Suppose that the state space D has dimension n . Given a choice of n state parameters coordinatizing it and a potential function of them, we can swap each one out for a Legendre conjugate variable while holding others constant. Here “the others” can be Legendre conjugates of the originals; you’ll get the same result. So there is a bigger family of $2n$ state parameters – the original n , and their Legendre conjugates. There are 2^n potential functions, one for each set of choices between a state parameter and its conjugate.

Note that when $n = 1$, the Legendre conjugate of $g(p)$ is $f(-x)$ and the Legendre conjugate of p is $-x$: so (up to these signs) you get two potentials, namely $f(x)$ and $g(p)$. In general it’s probably better to revert to the mathematician’s signless version of the Legendre transform here.