

THE LEGENDRE TRANSFORM AND TWO-DIMENSIONAL THERMODYNAMICS

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ABSTRACT. The mathematics of thermodynamics provides an important application of the Legendre transform and techniques of partial differentiation. This succinct account highlights the mathematically sophisticated notion of state space and brings out the symmetry of the theory. The standard examples of the ideal gas law and the ideal van der Waals fluid are worked out in detail.

1. INTRODUCTION

1.1. **My motivation.** In designing an advanced calculus course, it is important to think about what parts of the vast amount of material will actually be of use to students in later courses, especially courses outside of the mathematics department. In 2007, I made such a study, with the help of Dr. Janet Rankin of MIT's Teaching and Learning Laboratory. What emerged was that for the majority of students, comfort with manipulating functions of several variables was more important than "vector calculus." Thermodynamics forms important and widespread application of these techniques, and a key method in that subject is the Legendre transform. (Another instance of the Legendre transform is the relationship between Lagrangian and Hamiltonian mechanics.)

Motivated by this discovery, I looked for succinct and mathematically sensible accounts of elementary thermodynamics. Finding none, I wrote some notes for myself, and they form the basis of this paper. I hope that mathematics instructors find it useful as background for designing courses that emphasizes this aspect of advanced calculus. Most students in a calculus class will not have seen this material in its thermodynamical context, so use of this as an example has to be accompanied by an assurance that it will occur if they go on to take a serious course in thermodynamics.

Conversely, I hope that a clear and unambiguous mathematical presentation may be of use to physicists, chemists, or materials scientists tasked with teaching thermodynamics.

1.2. State space. In addition to demonstrating the utility of manipulations of functions of several variables, thermodynamics involves a key concept that can be greatly clarified by a mathematical perspective: namely, the notion of the “state space.” This should be thought of as a geometrical object, a “manifold” (to use the term in a loose sense), one that exists without coordinates or parametrization. “State variables” provide parametrizations of it, but should not be considered intrinsic to the state space itself. The subtlety of thermodynamics is that various different sets of state variables are relevant to different applications; but the state space itself remains the same. The range of a set of state variables has to be regarded as distinct from the state space itself.

Mathematically inclined instructors often complain about the use of the symbol $f(x)$ for a function, rather than merely f . As with many aspects of basic undergraduate mathematics, this usage can instead be celebrated as conveying a deep mathematical idea, embodied in the notion of state space and state parameters. The state space D may have a function defined on it that one chooses to regard as a coordinate; say $x : D \rightarrow \mathbb{R}$. Given some function of interest on D , we may attempt to write it in terms of the coordinate x , that is, as $f \circ x : D \rightarrow \mathbb{R}$. (This is more likely to be successful if D is “one-dimensional.”) It’s not unreasonable to write that composite as $f(x)$, giving real significance to this expression as a function.

This symbolic convention suggests that we use the symbol x for the coordinate on the target of $x : D \rightarrow \mathbb{R}$. Overloading notation in this way is a cause of confusion, but it is so common that one should encourage students to get used to it.

In the language of thermodynamics, x is a state parameter and f is a potential or energy function. A thermodynamic system can be described by specifying values of state variables. It seeks equilibrium, which is identified as minimizing some potential.

1.3. The Legendre transform. If f is convex, the value of x (if there is one) for which $f'(x) = p$ (for a real number p) is determined by p . This entitles us to think of p as a new coordinate on D , a new state parameter. The question then arises: How is the composite $f(x)$ expressed in terms of this new state parameter p ? It turns out that a choice leading to a pleasingly symmetrical theory is to define a new potential g by the equation (and I choose the sign preferred in the thermodynamics literature)

$$g(p) = f(x) - xp.$$

Once again, this equation has a dual meaning. One can regard it as an equality of functions on the state space D . But we also have a copy of \mathbb{R}^2 with coordinates x, p (which I'll denote by \mathbb{R}_{xp}^2), and this is an equality of functions on it (or on a subspace of it). So f and g are now both functions of both x and p , but f depends only on x and g depends only on p .

With this perspective in mind, we may apply the theory of partial differentiation:

$$\left(\frac{\partial f}{\partial x}\right)_p = p, \quad \left(\frac{\partial g}{\partial p}\right)_x = -x$$

Putting the matter more symmetrically, we may say that the “Legendre package” is this (in dimension one): A domain D with two real-valued functions defined on it, x and p . Two smooth real-valued functions f and g , defined on an interval containing the values of x and p respectively, are said to be *Legendre conjugates* of each other if (as functions on D)

$$f(x) - g(p) = xp$$

and so

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

To make this work out one assumes either that f is convex, $f''(x) > 0$ – so that $f'(x)$ is an increasing function, and its inverse function $-g'(p)$ is increasing as well, and so g is concave, $g''(p) < 0$ – or that g is convex, in which case f is concave.

The utility of the Legendre transform in thermodynamics is as follows. First, some state parameters are quite easy to measure – temperature and volume, for example – while others are not directly measurable – entropy, for example. In the presence of an energy function, the Legendre transform allows you relate measurable state variables to ones that are not directly measurable, with no loss of information. These latter are often the natural variables of the energy whose extrema specify equilibrium states of interest.

In thermodynamics the state space is typically more than one-dimensional; so one has several independent state parameters. 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.

1.4. Outline. After running through the various state variables and potentials occurring in two-dimensional thermodynamics, we recall the

Maxwell and Gibbs-Helmholtz equations, and point out the extremely simple model for this system given by “quadratic thermodynamics.” We then consider the mathematics of two somewhat more realistic models, the ideal gas law and the ideal van der Waals fluid. As with any mathematical model, the assumptions underlying either of these models break down if parameters pass some threshold; there are phase changes. For all of this a basic reference is Callen [1].

I make no attempt whatsoever to illuminate the physical significance of the various state variables and potentials discussed here. The account is intentionally quite telegraphic. The basic story is of course well-known, but I believe that the symmetry of this pattern of functions has not been brought out sufficiently elsewhere, and I do not know a place where either the mathematically illuminating example of quadratic thermodynamics occurs, nor where explicit fundamental relations for the two standard examples can be found.

I am indebted to Janet Rankin for the survey work we did long ago, as well as many informative and enjoyable conversations about the mathematics of thermodynamics, and for her help in improving the utility of this paper.

2. STATE PARAMETERS AND POTENTIALS IN TWO DIMENSIONS

One pair of state parameters that is close to our common experience is given by temperature T and volume V . The relevant form of energy is the “Helmholtz free energy,” or “Helmholtz potential,” $F = F(T, V)$. This function is also written $A(T, V)$ in the literature. So F denotes both a function on the state space D and a function on the (T, V) plane.

The Helmholtz potential is arranged so that:

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

We will accept a notational confusion that is universal in this field. The state parameters T and V are functions on the state space D . As such they define together a function $D \rightarrow \mathbb{R}^2$. But we will also use these symbols to denote the two coordinates on \mathbb{R}^2 . This lets us make sense of expressions like $(\partial F / \partial T)_V$, and regard them as new functions on the state space D .

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 that 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 equally well 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 P 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:

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

Identities in (2) and (3) imply 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 that minimizes enthalpy H . This is the same state as the state that minimizes the internal energy U for fixed volume V .

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

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

Identities in (4) and (1) imply 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).

3. 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.

3.1. Total differentials. 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:

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

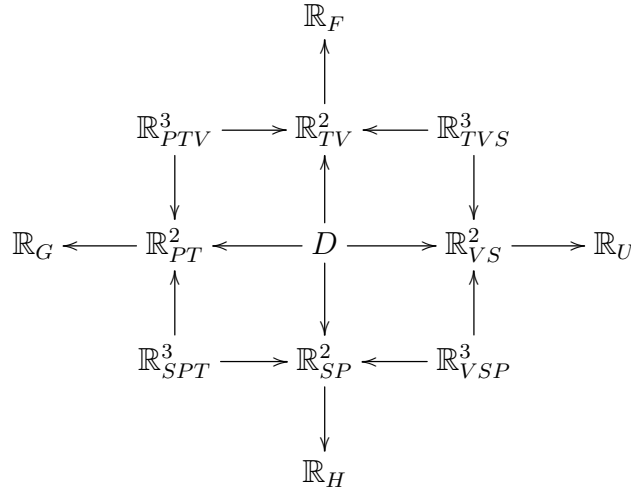
$$dH = T dS + V dP$$

together with the relations

$$U(S, V) - F(T, V) = ST = H(S, P) - G(T, P)$$

$$G(T, P) - F(T, V) = PV = H(S, P) - U(S, V).$$

3.2. Graphic. The state space is a two-dimensional domain D . It comes equipped with four functions on it, T , V , S , and P , called *state parameters*, and four potential functions or energy functionals, F , U , G , and H . The potentials come expressed naturally as functions of pairs of state parameters. They are all related to each other via various maps:



3.3. Quadratic thermodynamics. With

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

we find

$$S = T \quad , \quad U(S, V) = \frac{S^2}{2} + \frac{V^2}{2}$$

$$P = -V \quad , \quad G(T, P) = -\frac{T^2}{2} - \frac{P^2}{2}$$

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

4. MAXWELL AND GIBBS-HELMHOLTZ

4.1. **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.

4.2. **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:

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

5. 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. In standard treatments, a third state variable is present, the molarity N , and $r = RN$ where R is a universal constant. A relation among system parameters, such as this, is an “equation of state.”

This equation of state 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

$$U = a + c_V T$$

for some constant a . Together 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 $T > 0$, a natural assumption from the physical perspective.) 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

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

6. 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. 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

$$U = c_V T - \frac{a}{V}.$$

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

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

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

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

The solution is

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

for a constant k . Thus

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

and

$$S - S_0 = r \ln(V - V_0) + c_V \ln T$$

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

$$T = \frac{e^{(S-S_0)/c_V}}{(V - V_0)^{r/c_V}}.$$

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

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

7. HIGHER DIMENSIONAL THERMODYNAMICS

Suppose that the state space D has dimension n . For example, we may add the quantity of material involved (in moles, for example) as a state variable, to get a 3-dimensional theory. The standard form of the ideal gas law

$$PV = RNT$$

is naturally an equation of state of a 3-dimensional thermodynamic system; the molarity N is just another state variable, and R is a universal constant. If there are several species of matter involved, the dimensionality goes up accordingly.

Given a choice of n state parameters coordinatizing the state space and a potential expressed as a 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.

REFERENCES

- [1] Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, Second edition, Wiley, 1991.

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