

Legendre Transforms

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1 Introduction

In thermodynamics, we encode the information of a system within equations of state that completely specify the energy of a system. However, we have encountered some parameters that would be difficult to measure in a lab, such as entropy. Fortunately we can transform the equations such that the system changes with respect to a different, more measurable variable.

2 Theory

The Legendre transform allows us to replace the variable x with the derivative df/dx without losing the information in the original equation. We make use of the derivative

$$m(x) = f'(x) = \frac{df}{dx} \quad (1)$$

In order to not lose any information, we have to reconstruct the equation of the line tangent to the point where we have evaluated the derivative. Otherwise we would have information that could be paired with an infinite number of functions that looked the same but were shifted vertically from the one we want.

Our goal is to find $g(m)$ such that we replace the information in $\{x, f(x)\}$ with $\{m, g(m)\}$. We consider the tangent line that passes through some point $(x_0, f(x_0))$, with slope m and intercept b at $x = 0$. Thinking of the general equation of a line $y = mx + b$, we can rearrange the equation for b so that

$$b = y - mx \quad (2)$$

and then replace the quantities with the analogous ones in terms of $g(m)$, $f(x)$ and $m(x)$. At an arbitrary point x , this function is given by

$$g(m(x)) = f(x) - xf'(x) = f(x) - xm \quad (3)$$

Since we want to have an equation of g just in terms of m , we take the differential of the equation (just like some of our favorite thermodynamics equations, no? Stay tuned.)

$$dg = df - m dx - x dm \quad (4)$$

When we look at the equation of the line above, we see that $dy = df(x) = m dx$, so we replace the df in the equation and get the result

$$dg = -x dm \quad (5)$$

And we have achieved what we set out to! We have an equation that only depends on m that preserved all the information we started with.

3 Application

When we apply this to problems in thermodynamics, we transform the equations of state to get a more approachable set of variables that we can measure. For example, we can transform the energy to the Helmholtz Free energy. Starting with the differential form of the energy and the free energy:

$$dE = TdS - PdV + \mu dN \quad (6)$$

We suppose that volume and number of particles are fixed in this case, which allows us to easily follow the single variable case of the Legendre transform. We have to be careful in thermodynamics, so we use partials with constants.

In the case of the first equation, S is the independent variable. We want to take the derivative with respect to this variable to find our equivalent "slope".

$$m(s) = \frac{\partial E}{\partial S}_{V,N} = T \quad (7)$$

Our objective is to find the function g that is a function of the derivative of S m instead of S . Since we are looking for the equation of a tangent line to the original energy equation, we can think back to the equation of a line $y = mx + b$.

$$E(S) = \frac{\partial E}{\partial S}_{V,N} S + g(m(S)) \quad (8)$$

If we rearrange this equation to isolate $g(m(S))$, we get

$$g(m(S)) = E - TS \quad (9)$$

remembering that $\frac{\partial E}{\partial S}_{V,N}$ is equal to T . We call $g(m(S))$ F , for our Helmholtz free energy.

If we do the transform again, we would get the original energy equation back out, which lets us know that all the original information has been preserved in our new equation. Take a look at the differential form of the Helmholtz free energy:

$$dF = -SdT - PdV + \mu dN \quad (10)$$

Here we see that all the variable quantities are quite easily measurable, whereas before one of the variable quantities was entropy, which is extremely difficult to measure in a laboratory. We can also perform Legendre transforms focusing on other variables like pressure and volume to obtain different quantities, as seen in the cycle below:

$$\begin{array}{ccc}
 U(S, V) & \leftarrow PV \rightarrow & H(S, P) \\
 \uparrow & & \uparrow \\
 TS & & TS \\
 \downarrow & & \downarrow \\
 F(T, V) & \leftarrow PV \rightarrow & G(T, P)
 \end{array}$$

Here we see that from one complete equation of state, we can obtain other equations of state that are more approachable for measurements, as well as tell us about the energy of a system under different kinds of constraints, such as constant temperature or constant volume.