Math Diversion Problem 641: Structured Differentiation in Thermodynamics

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> Life is either a daring adventure or nothing at all.
> — Helen Keller

> Thermodynamics is Nature's way of balancing
> entropy with enthalpy.
> — Rafael Jaramillo

The YouTube video is found at:

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Source: https://www.youtube.com/watch?v=2BJYXuZZK3c&list=
PLpi18tMShZSAQFNTb8Ji7EgCFP9lXbkOe&index=5
Title: Statistical Mechanics Notes for L. Susskind's
 Lecture Series (2013), Part 5
 Presenters: Susskind and then Patrick
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1 The Problem

In Part 5 of this vidue series, Prof. Susskind laid out a proof of a particular thermodynamic relation he needed. I found it interesting from the viewpoint of what it might look like if performed in SD.[1]

So, establish the relation

$$\frac{\partial \bar{E}}{\partial V}\Big|_S = \frac{\partial \bar{E}}{\partial V}\Big|_T - \frac{\partial \bar{E}}{\partial S}\Big|_V \frac{\partial S}{\partial V}\Big|_T , \tag{1}$$

where $\bar{E}$ is the average energy of a system. (This is a change in independent variable problem.)

[1]Structured Differentiation

2 The Solution according to my read-along class notes

To start this proof, we will take T and V as our two independent variables. We then derive two intuitive equations

$$d\bar{E} = \frac{\partial \bar{E}}{\partial V}\Big|_T dV + \frac{\partial \bar{E}}{\partial T}\Big|_V dT\,, \tag{2a}$$

$$dS = \frac{\partial S}{\partial V}\Big|_T dV + \frac{\partial S}{\partial T}\Big|_V dT\,. \tag{2b}$$

Soon, we will convert from V and T as our independent variables to V and S. But before we do that, let's convert $\frac{\partial \bar{E}}{\partial T}\Big|_V$. Now, we have assumed that we need only two independent variables, and one of them is V, which is being held constant in the presented partial derivative. Hence, that leaves only one variable left on which all the dependent variables are dependent. That means that their partial derivatives are necessarily just ordinary derivatives. In accordance with this fact, we can write

$$\begin{aligned}\frac{\partial \bar{E}}{\partial T}\Big|_V = \frac{d\bar{E}}{dT}\Big|_V &= \frac{d\bar{E}}{dS}\Big|_V \frac{dS}{dT}\Big|_V \\ &= \frac{\partial \bar{E}}{\partial S}\Big|_V \frac{\partial S}{\partial T}\Big|_V\,.\end{aligned} \tag{3}$$

Substituting this result into (2a), we get that

$$d\bar{E} = \frac{\partial \bar{E}}{\partial V}\Big|_T dV + \frac{\partial \bar{E}}{\partial S}\Big|_V \frac{\partial S}{\partial T}\Big|_V dT\,. \tag{4}$$

If we divide (2a) through by dV and take V and S as our new independent variables, we get that

$$\frac{\partial \bar{E}}{\partial V}\Big|_S = \frac{\partial \bar{E}}{\partial V}\Big|_T + \frac{\partial \bar{E}}{\partial S}\Big|_V \frac{\partial S}{\partial T}\Big|_V \frac{\partial T}{\partial V}\Big|_S\,. \tag{5}$$

To go from this last equation to get (1), we must take our thermodynamic process as isentropic, or of constant entropy (S = const), and we're down to just one independent variable V. Taking $dS = 0$ in (2b), we get

$$\frac{\partial S}{\partial V}\Big|_T dV + \frac{\partial S}{\partial T}\Big|_V dT = 0\,. \tag{6}$$

On dividing through by dV, we get

$$\frac{\partial S}{\partial V}\Big|_T + \frac{\partial S}{\partial T}\Big|_V \frac{\partial T}{\partial V}\Big|_S = 0\,, \tag{7}$$

which gives us

$$\frac{\partial S}{\partial T}\Big|_V \frac{\partial T}{\partial V}\Big|_S = -\frac{\partial S}{\partial V}\Big|_T\,. \tag{8}$$

Substituting this result into (5), gives us

$$\frac{\partial \bar{E}}{\partial V}\Big|_S = \frac{\partial \bar{E}}{\partial V}\Big|_T - \frac{\partial \bar{E}}{\partial S}\Big|_V \frac{\partial S}{\partial V}\Big|_T . \tag{9}$$

3 The Solution according to my SD formulation

For convenience we define the state vector

$$\psi = (\bar{E}, V, S, T)^t . \tag{10}$$

We start off with the two independent variables

$$\eta = (V, T)^t , \tag{11}$$

and switch to the two 'new' independent variables

$$\eta' = (V, S)^t . \tag{12}$$

Hence we have the functional dependencies mediated by a composite function

$$\psi'(\boldsymbol{\eta}') = \psi(\boldsymbol{\eta}(\boldsymbol{\eta}')) . \tag{13}$$

Differentiating this by $\boldsymbol{\eta}'$, we get

$$\frac{\partial \psi'}{\partial \boldsymbol{\eta}'} = \frac{\partial \psi}{\partial \boldsymbol{\eta}} \frac{\partial \boldsymbol{\eta}}{\partial \boldsymbol{\eta}'} , \tag{14}$$

which, in explicit matrix form, looks like this

$$\begin{bmatrix} \partial\bar{E}/\partial V & \partial\bar{E}/\partial S \\ \partial V/\partial V & \partial V/\partial S \\ \partial S/\partial V & \partial S/\partial S \\ \partial T/\partial V & \partial T/\partial S \end{bmatrix} = \begin{bmatrix} \partial\bar{E}/\partial V & \partial\bar{E}/\partial T \\ \partial V/\partial V & \partial V/\partial T \\ \partial S/\partial V & \partial S/\partial T \\ \partial T/\partial V & \partial T/\partial T \end{bmatrix} \begin{bmatrix} \partial V/\partial V & \partial V/\partial S \\ \partial T/\partial V & \partial T/\partial S \end{bmatrix} . \tag{15}$$

For the partials in the 4×2 matrix on the LHS, we have that

$$\partial V/\partial V = \partial S/\partial S = 1 \quad \text{and} \quad \partial V/\partial S = \partial S/\partial V = 0 . \tag{16}$$

For the partials in the 4×2 matrix on the RHS, we have that

$$\partial V/\partial V = \partial T/\partial T = 1 \quad \text{and} \quad \partial V/\partial T = \partial T/\partial V = 0 . \tag{17}$$

Lastly, for the partials in the 2×2 matrix (the Jacobian matrix), we have that

$$\partial V/\partial V = 1 \quad \text{and} \quad \partial V/\partial S = 0 . \tag{18}$$

Hence (15) simplifies to

$$\begin{bmatrix} \partial\bar{E}/\partial V & \partial\bar{E}/\partial S \\ 1 & 0 \\ 0 & 1 \\ \partial T/\partial V & \partial T/\partial S \end{bmatrix} = \begin{bmatrix} \partial\bar{E}/\partial V & \partial\bar{E}/\partial T \\ 1 & 0 \\ \partial S/\partial V & \partial S/\partial T \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ \partial T/\partial V & \partial T/\partial S \end{bmatrix} . \tag{19}$$

Now, there is a lot of useful information in this matrix equation! Once convenient way to extract this information is by taking the determinant of 2×2 submatrices.[2]

For starters, the *Jacobian matrix* is

$$\frac{\delta \boldsymbol{\eta}}{\delta \boldsymbol{\eta}'} = \begin{bmatrix} 1 & 0 \\ \partial T/\partial V & \partial T/\partial S \end{bmatrix} . \tag{20}$$

The determinant of this matrix (known as the *Jacobian*) is $\partial T/\partial S\big|_V$, and, naturally, this factor will appear in every computation when we extract by determinants.

There are $\binom{4}{2} = 6$ ways to form 2×2 matrix equations from (19). For instance, if we just extract on rows 2 and 3, we get

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ \partial S/\partial V & \partial S/\partial T \end{bmatrix} \begin{bmatrix} 1 & 0 \\ \partial T/\partial V & \partial T/\partial S \end{bmatrix} . \tag{21}$$

On taking the determinant across this equation, and remembering that the determinant of a product is the product of the determinants, we get

$$1 = \frac{\partial S}{\partial T}\bigg|_V \frac{\partial T}{\partial S}\bigg|_V . \tag{22}$$

This is a well-known identity in thermodynamics, referred to as *inversion* or *reciprocity*, or perhaps by even other names.

Now let's extract on rows 1 and 4, to get

$$\begin{bmatrix} \partial \bar{E}/\partial V & \partial \bar{E}/\partial S \\ \partial T/\partial V & \partial T/\partial S \end{bmatrix} = \begin{bmatrix} \partial \bar{E}/\partial V & \partial \bar{E}/\partial T \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ \partial T/\partial V & \partial T/\partial S \end{bmatrix} . \tag{23}$$

On taking determinants this we get

$$\frac{\partial \bar{E}}{\partial V}\bigg|_S \frac{\partial T}{\partial S}\bigg|_V - \frac{\partial \bar{E}}{\partial S}\bigg|_V \frac{\partial T}{\partial V}\bigg|_S = \frac{\partial \bar{E}}{\partial V}\bigg|_T \frac{\partial T}{\partial S}\bigg|_V . \tag{24}$$

This result already looks promising. Let's multiply through by the reciprical of $\frac{\partial T}{\partial S}\Big|_V = \frac{\partial S}{\partial T}\Big|_V$ to get

$$\frac{\partial \bar{E}}{\partial V}\bigg|_S - \frac{\partial \bar{E}}{\partial S}\bigg|_V \frac{\partial T}{\partial V}\bigg|_S \frac{\partial S}{\partial T}\bigg|_V = \frac{\partial \bar{E}}{\partial V}\bigg|_T . \tag{25}$$

Now, let's isolate $\frac{\partial \bar{E}}{\partial V}\Big|_S$:

$$\frac{\partial \bar{E}}{\partial V}\bigg|_S = \frac{\partial \bar{E}}{\partial S}\bigg|_V \frac{\partial T}{\partial V}\bigg|_S \frac{\partial S}{\partial T}\bigg|_V + \frac{\partial \bar{E}}{\partial V}\bigg|_T . \tag{26}$$

[2]The precise justification for this procedure is given in my many Structured Differentiation papers.

To our aid is another well-known identity called the *Triple-Product Rule*, given by[3]

$$\frac{\partial T}{\partial V}\Big|_S \frac{\partial S}{\partial T}\Big|_V \frac{\partial V}{\partial S}\Big|_T = -1\,. \tag{27}$$

By use of the reciprocal rule this becomes

$$\frac{\partial T}{\partial V}\Big|_S \frac{\partial S}{\partial T}\Big|_V = -\frac{\partial S}{\partial V}\Big|_T\,. \tag{28}$$

On substituting this into (26) and rearranging, we get

$$\frac{\partial \bar{E}}{\partial V}\Big|_S = \frac{\partial \bar{E}}{\partial V}\Big|_T - \frac{\partial \bar{E}}{\partial S}\Big|_V \frac{\partial S}{\partial V}\Big|_T\,, \tag{29}$$

which is what we were to prove.

By the way, the Triple Product Rule is extractable from (19) by taking determinants on rows 3 and 4.

I know that this proof is a bit long, but to its credit, it's clear, straightforward, free of unmotivated assumptions or unclear reasonings. In fact, the process used in the proof is completely familiar: We start with a change of dependent-vs-independent variables, which creates a composite functional relation in (13). Since we are looking for relationships among derivatives, we differentiate (13), using the chain rule to produce (14), which expands into the matrix version (15).

The next step is to simplify the components where possible. To do this, we need only keep in mind what are the independent variables for each matrix. To finish the problem, we merely choose one or more pairs of rows on which to extract information by determinants, adding in thermodynamics identities as needed.

Lastly, we did not need to concern ourselves if we needed to rely on the Zeroth Rule of Partial Differentiation in Thermodynamics. The reason for this is that all the differentiations were performed at one time in Equation (14), and not as a series of sequential steps.

Now, it's conceivable that by choosing fewer variables to stick into ψ in Equation (10), that one could produce the derived equations with fewer components to sort through. Almost always, I put **all** the relevant variables of the problem into ψ.

I will now propose the **First Principle of Structured Differentiation:**

> Let ψ be an ordered listing of all relevant thermodynamic variables to a given change-of-variable problem. Then, everything that can be

[3] There's nothing special about T, S, and V. You could use any three variables in it.

known about the first-partial derivatives of these variables is contained in the equation

$$\frac{\partial \psi'}{\partial \boldsymbol{\eta}'} = \frac{\partial \psi}{\partial \boldsymbol{\eta}} \frac{\partial \boldsymbol{\eta}}{\partial \boldsymbol{\eta}'}\,, \tag{30}$$

up to manipulations by thermodynamic identities.

Although I can't prove this principle, it certainly seems quite reasonable. And the problem I solved above it is a perfect example of how it all plays out.

Most of the problems I have solved of this type over many years have been quickly solved by the use of the method demonstrated above (using determinants), but it may actually be solved faster, in some cases, just to equate corresponding components. For example, on equating components from the LHS and RHS of (19) in position (1,1), we get that

$$\frac{\partial \bar{E}}{\partial V}\Big|_S = \frac{\partial \bar{E}}{\partial V}\Big|_T + \frac{\partial \bar{E}}{\partial T}\Big|_V \frac{\partial T}{\partial V}\Big|_S\,, \tag{31}$$

and from the (1,2) component, we get

$$\frac{\partial \bar{E}}{\partial S}\Big|_V = \frac{\partial \bar{E}}{\partial T}\Big|_V \frac{\partial T}{\partial S}\Big|_V\,, \tag{32}$$

and so on to completion, adding in thermodynamics identities as needed.

Note: in thermodynamics terminology, this last equation is variously referred to as 'adding in a variable' or 'the chain rule'.