Math Diversion Problem 488: Jacobians in Thermodynamics, Part 1

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> There is general agreement that a procedure for deriving relations among the thermodynamic derivatives without resorting to the Bridgman tables is highly desirable. The use of Jacobians makes for directness and speed.
> — Benjamin Carroll [1]

> I'll tell ya, that's a million dollar idea right there. Just sell the [muffin] tops!
> — Elaine (*Seinfeld*)

1 Introduction

This is my first paper on an article by Benjamin Carroll. I shall not be using the techniques of structured differentiation (SD) to perform and explain what Carroll has done in this section of his article.[2] If I did use SD, the only difference would be that I'd assiduously treat an expression like

$$\frac{\partial(W,X)}{\partial(Y,Z)} \tag{1}$$

as a matrix (the jacobian matrix), and the 'jacobian' derived from it as

$$\det\left[\frac{\partial(W,X)}{\partial(Y,Z)}\right]. \tag{2}$$

However, in conventional thermodynamics, an expression like (1) is a determinant already.

[1] Found in: "On the Use of Jacobians in Thermodynamics," Benjamin Carroll, J. of Chem. Ed., Vol. 42, No. 4, 1965, pp 218–221.

[2] This statement is true so far as the main body of this article is concerned. However, I do explain one important equation, namely (15), using SD in an appendix.

The point of this article is to prove a lemma that Carroll will use to conclude the Joule-Thompson expansion equation

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right], \tag{3}$$

but the derivation for (3) is for the next article.

2 The Lemma

Carroll shows us the four basic differentials in E, H, A, and G (what he refers to as 'secondary variables'), though we will only need the first one, that being

$$dE = T\,dS - P\,dV\,, \tag{4}$$

but I will rewrite this in the form preferred by physicists,[3] as

$$dU = T\,dS - P\,dV\,. \tag{5}$$

Carroll's first goal is to obtain the enigmatic relation

$$J(T,S) = J(P,V)\,, \tag{6}$$

of which he explained neither what it means nor how he derived it. Fortunately, he has left us some clues. Carroll gave this relation the equation number 5. Then, on page 219, in the first paragraph of Step 3, he referenced it as useful to produce the relation

$$\frac{\partial(T,S)}{\partial(T,P)} = \frac{\partial(P,V)}{\partial(T,P)}\,. \tag{7}$$

Confused? So was I at first.[4] But after I checked references to the Maxwell relations (such as in Wikipedia), I concluded that it goes as follows:

Since U in (5) is a state function, a loop integral around a small loop will be zero, that is,

$$\oint dU = 0\,. \tag{8}$$

And since all the variables in (5) are state functions, we can write

$$0 = \oint T\,dS - \oint P\,dV\,. \tag{9}$$

Now, we can use Green's theorem in the plane to convert these loop integrals into area integrals.

$$0 = \int dT\,dS - \int dP\,dV\,, \tag{10}$$

[3] Apparently even to this day, E is preferred over U to represent the energy among engineers.

[4] We will soon discover that (7) follows trivially from (6).

where the area is integrated over the area enclosed by the loop.[5]

Next, we can transform the differential area $dT\,dS$ into $dP\,dV$ by use of an appropriate jacobian, as follows:

$$0 = \int \frac{\partial(T,S)}{\partial(P,V)}\, dP\,dV - \int dP\,dV\,. \tag{11}$$

This takes the alternative form:

$$0 = \int \left[\frac{\partial(T,S)}{\partial(P,V)} - 1\right] dP\,dV\,. \tag{12}$$

And from this, we conclude that

$$\frac{\partial(T,S)}{\partial(P,V)} = 1\,. \tag{13}$$

Let's not be tempted to forget that this last equation will not hold for an arbitrary choice of thermodynamic variables. Typically, thermodynamic jacobians are not identically equal to a constant. That this last one is, reflects the physical content in Eq. (5), from which it was derived.

Okay, so all that's left for me to do in this article is to show how (13) relates to (6).

Let W, X, Y, Z be arbitrary differentiable variables. Now consider the 'jacobian':

$$\frac{\partial(W,X)}{\partial(Y,Z)}\,, \tag{14}$$

under some unspecified choice of independent variables, which are two in number. Now, let's make a change in the independent variables to the formal variables x, y, then

$$\frac{\partial(W,X)}{\partial(Y,Z)} = \frac{\partial(W,X)/\partial(x,y)}{\partial(Y,Z)/\partial(x,y)}\,. \tag{15}$$

Note that the change in coordinates performed in this last equation has no physical content. But now we're going to change that by setting

$$\frac{\partial(W,X)}{\partial(Y,Z)} = 1\,. \tag{16}$$

Then

$$\frac{\partial(W,X)/\partial(x,y)}{\partial(Y,Z)/\partial(x,y)} = 1\,, \tag{17}$$

where we remember that the LHS of this is the quotient of two determinants, which are scalars, hence, we can write

$$\frac{\partial(W,X)}{\partial(x,y)} = \frac{\partial(Y,Z)}{\partial(x,y)}\,. \tag{18}$$

[5]See the Appendix for a little write up on Green's theorem in the plane.

So, three decades before *Seinfeld*, Carroll invented or (further propagated) the 'Top of the Muffin to you' by throwing away the arbitrary differential 'stumps' $\partial(x, y)$ and leaving just the 'tops'

$$\partial(W, X) = \partial(Y, Z)\,, \tag{19}$$

or a bit less confusing but still enigmatic,

$$J(W, X) = J(Y, Z)\,. \tag{20}$$

Or, if my analysis is correct, this notation is no longer mysterious, yet it still seems to be to be idiosyncratic.

So, in all this mess, what is the lemma part? I'd say that it's Eq. (13). Thus, the 'muffin top equation' is (6) and is repeated here,

$$J(T, S) = J(P, V)\,, \tag{21}$$

but this so-called 'equation' is just a stand-in (or shorthand) for

$$\frac{\partial(T, S)}{\partial(x, y)} = \frac{\partial(P, V)}{\partial(x, y)}\,, \tag{22}$$

where x, y are intentionally unspecified — which seems to be the whole point of it. But if we make a specific choice for x, y, say T, P, we have that

$$\frac{\partial(T, S)}{\partial(T, P)} = \frac{\partial(P, V)}{\partial(T, P)}\,, \tag{23}$$

which is a restatement of (7).

The uptake of this is that the muffin 'tops', as presented in (21), can be arbitrarily attached to the muffin 'stumps' as represented by the denominators in (22), and might make for some interesting muffin eating.

3 Appendix 1: Green's theorem in the plane

Let ∂A be a simply-connected, smooth loop in the xy-plane, bounding the area A. Further, let L, M be differentiable functions on the plane. Then Green's theorem in the plane can be written as

$$\oint_{\partial A} (L\,dx + M\,dy) = \iint_A \left(\frac{\partial M}{\partial x} - \frac{\partial L}{\partial y} \right) dx\,dy\,. \tag{24}$$

Depending on how we choose L and M, we could do a lot with this general equation, but for our immediate purposes, let $L = 0$ and $M = x$, to produce,

$$\oint_{\partial A} x\,dy = \iint_A dx\,dy\,, \tag{25}$$

or, expressed a bit more simply,

$$\oint x\,dy = \iint dx\,dy\,. \tag{26}$$

4 Appendix 2: Explaining Eq. (15) in SD

Let $\mathbf{W} = (W, X)$, $\mathbf{U} = (Y, Z)$, and $\mathbf{x} = (x, y)$. Then, in more or less physics notation, we can write:

$$\mathbf{W}(\mathbf{x}) = \mathbf{W}(\mathbf{U}(\mathbf{x}))\,. \tag{27}$$

Now, on taking the total derivative of this by $\mathbf{x}$ we get,

$$\frac{\delta \mathbf{W}}{\delta \mathbf{x}} = \frac{\delta \mathbf{W}}{\delta \mathbf{U}} \frac{\delta \mathbf{U}}{\delta \mathbf{x}}\,, \tag{28}$$

and we recognize this as an application of the chain rule. Now, because of the restricted way that functional dependencies are defined in (27), it's generally safe to demote total derivatives to partial derivatives, yielding,

$$\frac{\partial \mathbf{W}}{\partial \mathbf{x}} = \frac{\partial \mathbf{W}}{\partial \mathbf{U}} \frac{\partial \mathbf{U}}{\partial \mathbf{x}}\,. \tag{29}$$

Next, we just take the determinant across this equation, leaving us with

$$\det\left[\frac{\partial \mathbf{W}}{\partial \mathbf{x}}\right] = \det\left[\frac{\partial \mathbf{W}}{\partial \mathbf{U}}\right] \det\left[\frac{\partial \mathbf{U}}{\partial \mathbf{x}}\right]\,, \tag{30}$$

or more simply as

$$\left|\frac{\partial \mathbf{W}}{\partial \mathbf{x}}\right| = \left|\frac{\partial \mathbf{W}}{\partial \mathbf{U}}\right| \left|\frac{\partial \mathbf{U}}{\partial \mathbf{x}}\right|\,. \tag{31}$$

On dividing through by $\left|\frac{\partial \mathbf{U}}{\partial \mathbf{x}}\right|$ and then flipping sides, we get

$$\left|\frac{\partial \mathbf{W}}{\partial \mathbf{U}}\right| = \left|\frac{\partial \mathbf{W}}{\partial \mathbf{x}}\right| \Big/ \left|\frac{\partial \mathbf{U}}{\partial \mathbf{x}}\right| = \frac{|\partial \mathbf{W}/\partial \mathbf{x}|}{|\partial \mathbf{U}/\partial \mathbf{x}|}\,. \tag{32}$$

Then, on putting in the components, we have that

$$\left|\frac{\partial(W, X)}{\partial(Y, Z)}\right| = \frac{|\partial(W, X)/\partial(x, y)|}{|\partial(Y, Z)/\partial(x, y)|}\,. \tag{33}$$

And the convention form of this last equation is the same as (15).

This derivation illustrates the need to use both matrix equations and their determinants. We can't make both of them 'clean', i.e., having the fewer symbols. One of them has to be messy to distinguish them. For example, I chose the determinant bars in (31) to distinguish that scalar equation from the matrix equation (29). And this is the simple explanation why SD convention uses the determinant bars in (33), even though standard convention does not.