Math Diversion Problem 509: Use of Jacobians in Thermodynamics (E.T. Jaynes), Part 3

P. Reany

April 11, 2025

> When I give this talk to a physics audience, I
> remove the quotes from my 'Theorem'.
> — Brian Greene

1 Introduction

This is my third article explaining and demonstrating the revisions that physicist E.T. Jaynes[1] long ago proposed to the scientific community regarding how thermodynamics should be presented mathematically, especially with regard to partial derivatives and jacobians. I think it's probably necessary for the reader to have read and understood the first two papers in this series to understand this paper.

Warning: I shall be using the techniques of structured differentiation (SD) throughout my explanations (where it should apply), to perform and explain what Jaynes has done in this section of his article. Some knowledge of calculus and matrices is assumed on the part of the reader throughout this series.

Note: The paper on SD immediately preceding this one contains some results necessary to understand a section of this paper. But, in theory, you could just take those results at face value and you'd still get something out of it.

Last time we established the identities found at the top of page 4, namely,

$$[AB] = -[BA], \qquad [AA] = 0\,, \tag{1a}$$

$$[A \pm B, C] = [AC] \pm [BC]\,, \tag{1b}$$

$$[AB, C] = [AC]B + A[BC]\,. \tag{1c}$$

---

[1] Found in: "Use of Jacobians in Thermodynamics," available from on-line notes at https://bayes.wustl.edu/etj/thermo/stat.mech.2.pdf

The point of this article is bring the discussion beyond Eq. (2a). from page 4:

$$[AB]dC + [BC]dA + [CA]dB = 0\,, \tag{2a}$$

$$[A[B,C]] + [B[C,A]] + [C[A,B]] = 0\,, \tag{2b}$$

$$[AB][CX] + [BC][AX] + [CA][BX] = 0\,. \tag{2c}$$

Then Jaynes presented the ‘theorem’: If

$$dA = bdB + cdC\,. \tag{3}$$

then for all X,

$$[AX] = b[BX] + c[CX]\,. \tag{4}$$

2 Recap

Last time we got as far as Eq. (2a), which is Jaynes’s Eq. (2-9). For now, I will skip over (2b) and (2c) for a later time (hopefully).

3 Continuing the discussion

We’ll begin by proving Jaynes’s theorem. I don’t know why Jaynes put this theorem in quotes. Technically it is a theorem, but Jaynes seemed embarrassed to label something he would consider so trivial as such.

Theorem: Given

$$dA = bdB + cdC\,, \tag{5}$$

then for all X, show that

$$[AX] = b[BX] + c[CX]\,. \tag{6}$$

Proof: I’m going to interpret dA, dB, dC as actual differentials in the traditional physics sense. Then, dividing (5) through by dx, we get[2]

$$\frac{\partial A}{\partial x} = b\frac{\partial B}{\partial x} + c\frac{\partial C}{\partial x}\,. \tag{7}$$

Next, we multiply this through by $\dfrac{\partial X}{\partial y}$:

$$\frac{\partial A}{\partial x}\frac{\partial X}{\partial y} = b\frac{\partial B}{\partial x}\frac{\partial X}{\partial y} + c\frac{\partial C}{\partial x}\frac{\partial X}{\partial y}\,. \tag{8}$$

Now, in this last equation we interchange x and y, to get

$$\frac{\partial A}{\partial y}\frac{\partial X}{\partial x} = b\frac{\partial B}{\partial y}\frac{\partial X}{\partial x} + c\frac{\partial C}{\partial y}\frac{\partial X}{\partial x}\,. \tag{9}$$

---

[2] Since we’re in thermodynamics, these should be converted to partials.

Next, we subtract (9) from (8):

$$\frac{\partial A}{\partial x}\frac{\partial X}{\partial y}-\frac{\partial A}{\partial y}\frac{\partial X}{\partial x}=b\left[\frac{\partial B}{\partial x}\frac{\partial X}{\partial y}-\frac{\partial B}{\partial y}\frac{\partial X}{\partial x}\right]+c\left[\frac{\partial C}{\partial x}\frac{\partial X}{\partial y}-\frac{\partial C}{\partial y}\frac{\partial X}{\partial x}\right]. \tag{10}$$

On converting this to Jaynes's shorthand, we get

$$[AX]=b[BX]+c[CX]\,, \tag{11}$$

which completes the proof.

Now, as for Jaynes's Eq. (2-14), I think I'll leave it as an exercise, since it is somewhat easy for real.

4 The Maxwell Relations (p.5)

In parallel to (5) and (6), Jaynes gives us

$$dU=T\,dS-P\,dV\,, \tag{12}$$

and

$$[UX]=T[SX]-P[VX]\,, \tag{13}$$

which is one of the four equation in (2-16). Jaynes then moved back to Eq. (2-14), namely

$$\left(\frac{\partial A}{\partial B}\right)_C=\frac{[AC]}{[BC]}=\frac{[CA]}{[CB]}\,. \tag{14}$$

He then claimed that, in view of (2-14), the Maxwell relations can be reduced to his equation (2-18),

$$[TS]=[PV]\,, \tag{15}$$

and I'm still working on this connection.

Anyway, I took up his implied challenge to prove it, so I chose

$$x=V\,,\qquad y=T\,. \tag{16}$$

First, let's expand (15):

$$\frac{\partial T}{\partial x}\frac{\partial S}{\partial y}-\frac{\partial S}{\partial x}\frac{\partial T}{\partial y}=\frac{\partial P}{\partial x}\frac{\partial V}{\partial y}-\frac{\partial V}{\partial x}\frac{\partial P}{\partial y}\,, \tag{17}$$

where x and y are dummy variables. And now we substitute in from (16):

$$\left(\frac{\partial T}{\partial V}\right)_T\left(\frac{\partial S}{\partial T}\right)_V-\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial T}{\partial T}\right)_V=\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_V-\left(\frac{\partial V}{\partial V}\right)_T\left(\frac{\partial P}{\partial T}\right)_V. \tag{18}$$

We have some special factors to consider. For a couple of them,

$$\left(\frac{\partial T}{\partial V}\right)_T=\left(\frac{\partial V}{\partial T}\right)_V=0\,. \tag{19}$$

For a couple more,

$$\left(\frac{\partial T}{\partial T}\right)_V = \left(\frac{\partial V}{\partial V}\right)_T = 1\,. \tag{20}$$

Thus, (18) reduces to

$$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V\,. \tag{21}$$

Dropping the minus signs, this equation becomes (2-17c)—one of the Maxwell relations.