Math Diversion Problem 596: Use of Differential Forms in Thermodynamics, Part 1

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

1 Introduction

This is my first (and maybe last) article explaining and demonstrating the use of differential forms in thermodynamics. My source for this article is: "Beginner's guide to differential forms in thermodynamics," available on-line, by V. Tymchyshyn (2016).

The physical content of this paper centers on the equation:

$$dU = TdS - PdV\,. \tag{1}$$

According to some, this equation is the embodiment of the the laws of thermodynamics, yet it has no generally accepted identifying name. Copilot suggested calling it the 'Gibbs (Fundamental) Relation', others the 'Gibbs (Energy) Equation'. For this paper, I'll use the latter.

2 Very Basic Differential Forms

For our needs in this article, we need to know about 0-forms, 1-forms, and 2-forms. They have the following respective forms:

$$\alpha = \phi(x,y,z)\,, \tag{2a}$$

$$\beta = f(x,y,z)dx + g(x,y,z)dy + h(x,y,z)dz\,, \tag{2b}$$

$$\gamma = \mu(x,y,z)dx\wedge dy + \nu(x,y,z)dy\wedge dz + \omega(x,y,z)dz\wedge dx\,, \tag{2c}$$

where $\phi, f, g, h, \mu, \nu, \omega$ are all functions. Scalars are either numbers or functions.

► dx, dy, dz are gradients and hence vectors.

- ► $dx \wedge dy,\ dy \wedge dz,\ dz \wedge dx$ are bivectors (2-forms).

By the way, the symbol '$\wedge$' is called a 'wedge' or an outer product. Like the cross product of Gibbs' vector algebra, this product is antisymmetric on 1-forms. Thus,

$$dx_i \wedge dx_j = \begin{cases} -dx_j \wedge dx_i & \text{for } i \neq j \\ \quad 0 & \text{for } i = j \end{cases} . \tag{3}$$

So, don't be surprised if you see something like

$$dT \wedge dT = 0 \,. \tag{4}$$

The numbers 0,1,2, and higher numbers are referred to as the grades (degrees) of the forms. An equation of forms does not permit the mixing of grades. A scalar times a form does not change the grade of the form and it commutes with all forms.

Let A, B be any two forms of the same grade, then $A + B$ is also a form of the same grade.

The central operator on forms is the 'd'. For our work here,[1]

$$d^2 = 0 \,, \tag{5}$$

which means that for any form A,

$$d^2 A = 0 \,. \tag{6}$$

We can anticipate that the d^2 operator will be an easy way to generate equations.

We have four more properties to go.

First, for any number τ,

$$d\tau = \tau d \,, \tag{7}$$

or, 'd' commutes with numbers. However, 'd' does not generally commute with functions, far from it.

Second, 'd' is linear. Let A and B be any two forms of the same grade, then

$$d(A + B) = dA + dB \,. \tag{8}$$

Third, 'd' is a differential operator whose action on functions looks just like the differential of Newton. Let $\phi = \phi(x, y)$ be a scalar function of variables x, y, then,

$$d\phi = \frac{\partial \phi}{\partial x} dx + \frac{\partial \phi}{\partial y} dy \,. \tag{9}$$

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[1] There's deep water here, but I'll stay in the shallows. We will be working in spaces that have the topology of $\mathbb{R}^n$ on which to define forms. In such a space, $d^2 = 0$ is true for all forms of degree 1 and up. See Poincaré Lemma.

However, when we get to thermodynamics, we'll have to be a bit more fastidious and write

$$d\phi = \left(\frac{\partial \phi}{\partial x}\right)_y dx + \left(\frac{\partial \phi}{\partial y}\right)_x dy\,, \tag{10}$$

but we'll stay with unsubscripted partials for the time being.

Fourth, if $dA \neq 0$ and λ_1, λ_2 are scalars, then

$$\lambda_1 dA = \lambda_2 dA\,, \tag{11}$$

if and only if

$$\lambda_1 = \lambda_2\,. \tag{12}$$

The last fact we need to draw on—which is not within differential forms, per se—is that mixed partial derivatives commute with each other.[2]

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)\,, \tag{13}$$

or

$$\frac{\partial^2 f}{\partial x\,\partial y} = \frac{\partial^2 f}{\partial y\,\partial x}\,. \tag{14}$$

3 The Gibbs Relation

Now we apply these differential techniques to both sides of the Gibbs energy relation (1), to get

$$d(dU) = d(TdS) - d(PdV)\,, \tag{15a}$$

or

$$d^2U = dT \wedge dS - dP \wedge dV\,, \tag{15b}$$

or

$$0 = dT \wedge dS - dP \wedge dV\,, \tag{15c}$$

or even

$$dT \wedge dS = dP \wedge dV\,, \tag{15d}$$

which should look familiar to those who read the earlier papers I wrote on E. T. Jaynes's work on thermodynamics and jacobians.

If we're going to make contact with standard thermodynamics, we need to extract a scalar relationship from (15d). There are, in fact, many ways to do this. One way is to assume that T and P can be written as functions of S and V, thus,

$$T = T(S, V)\,, \tag{16a}$$

$$P = P(S, V)\,. \tag{16b}$$

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[2] See Clairaut's theorem for proof and restrictions that apply.

Then

$$dT = \left(\frac{\partial T}{\partial S}\right)_V dS + \left(\frac{\partial T}{\partial V}\right)_S dV\,, \tag{17a}$$

$$dP = \left(\frac{\partial P}{\partial S}\right)_V dS + \left(\frac{\partial P}{\partial V}\right)_S dV\,. \tag{17b}$$

So, notice what happens when we substitute (17a) into the LHS of (15d):

$$\left[\left(\frac{\partial T}{\partial S}\right)_V dS + \left(\frac{\partial T}{\partial V}\right)_S dV\right] \wedge dS = \left(\frac{\partial T}{\partial V}\right)_S \, dV \wedge dS\,. \tag{18}$$

And when we substitute (17b) into the RHS of (15d):

$$\left[\left(\frac{\partial P}{\partial S}\right)_V dS + \left(\frac{\partial P}{\partial V}\right)_S dV\right] \wedge dV = \left(\frac{\partial P}{\partial S}\right)_V \, dS \wedge dV = -\left(\frac{\partial P}{\partial S}\right)_V \, dV \wedge dS\,. \tag{19}$$

On substituting these two results into (15d), we have that

$$\left(\frac{\partial T}{\partial V}\right)_S \, dV \wedge dS = -\left(\frac{\partial P}{\partial S}\right)_V \, dV \wedge dS\,, \tag{20}$$

from which we conclude that

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

which is one of the Maxwell relations.

One last example.

Going back to (1) and dividing through by T and solving for dS, we have that

$$dS = \frac{dU}{T} + \frac{PdV}{T}\,. \tag{22}$$

After applying the differential across this, we get

$$0 = d\left(\frac{dU}{T}\right) + d\left(\frac{PdV}{T}\right)\,. \tag{23}$$

This can be rewritten as

$$-d\left(\frac{1}{T}\right) \wedge dU = d\left(\frac{P}{T}\right) \wedge dV\,, \tag{24}$$

or as

$$\left(\frac{dT}{T^2}\right) \wedge dU = \left[\left(\frac{dP}{T}\right) - \left(\frac{PdT}{T^2}\right)\right] \wedge dV\,. \tag{25}$$

But on simplification, this becomes

$$-dT \wedge dU = [T\,dP - PdT] \wedge dV = T\,dP \wedge dV - PdT \wedge dV\,. \tag{26}$$

We can get an interesting scalar result by assuming the following functionalities:

$$U = U(T, V)\,, \tag{27a}$$
$$P = P(T, V)\,. \tag{27b}$$

Then (26) becomes

$$dT \wedge \left[\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT\right] = T\left[\left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT\right] \wedge dV \\ - PdT \wedge dV\,. \tag{28}$$

We can first simplify this by distributing the wedge:

$$\left(\frac{\partial U}{\partial V}\right)_T dT \wedge dV = T\left(\frac{\partial P}{\partial T}\right)_V dT \wedge dV - P\,dT \wedge dV\,. \tag{29}$$

From this we can now easily extract the scalar relation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P\,. \tag{30}$$

4 Conclusion

The tendency for systems to find their minimal energy configuration is an organizing principle. The tendency of systems to maximize their disorder is a anti-organizing principle. Nature has told those two guys to somehow play nice together.