Math Diversion Problem 614: Use of Differential Forms in Thermodynamics, Part 2

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> Many students find that thermodynamics, although mathematically almost trivial, is nevertheless one of the most difficult subjects in their program. A large part of the blame for this lies in the extremely cumbersome partial derivative notation.
> — E.T. Jaynes

1 Introduction

This is my second (and maybe last) article explaining and demonstrating the use of differential forms in thermodynamics.

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Source:  https://johncarlosbaez.wordpress.com/2012/01/19/
     classical-mechanics-versus-thermodynamics-part-1/
Title: Classical Mechanics versus Thermodynamics (Part 1)
Presenter: John Baez
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John Baez is an interesting educator. He is a mathematical physicist, and from my research on him, I report that he is currently professor of mathematics at UC Riverside. He educates through articles and books, and teaches by video on many subjects, especially on category theory and quantum mechanics. Among his many books is *Gauge Fields, Knots and Gravity*, which he co-authored with Javier Muniain. He has apparently read and agreed with much of what physicist E. T. Jaynes held to.

2 Similarity of classical mechanics to thermodynamics

I'm only going to skim quickly through this section because I want to emphasize the parts of the article that deal with differential forms. The main point is the similarity between the Hamilton equations and the Maxwell relations: The former being

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}\,, \tag{1a}$$

$$\frac{dq}{dt} = -\frac{\partial H}{\partial pq}\,,\,, \tag{1b}$$

and the latter being

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V\,, \tag{2a}$$

$$\left.\frac{\partial S}{\partial V}\right|_T = -\left.\frac{\partial P}{\partial T}\right|_V\,, \tag{2b}$$

which are the first and second Maxwell relations.

The interested reader can examine this section for other results in the Maxwell relations and in the introduction of Helmholtz's free energy A.

3 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:

$$\alpha = \phi(x,y,z)\,, \tag{3a}$$

$$\beta = f(x,y,z)dx + g(x,y,z)dy + h(x,y,z)dz\,, \tag{3b}$$

$$\gamma = \mu(x,y,z)dx \wedge dy + \nu(x,y,z)dy \wedge dz + \omega(x,y,z)dz \wedge dx\,, \tag{3c}$$

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,

$$dx_i \wedge dx_j = \begin{cases} -dx_j \wedge dx_i & \text{for } i \neq j \\ 0 & \text{for } i = j \end{cases}\,. \tag{4}$$

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

$$dT \wedge dT = 0\,. \tag{5}$$

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]

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

which means that for any form A,

$$d^2 A = 0\,. \tag{7}$$

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,

$$d\tau = \tau d\,, \tag{8}$$

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

$$d(A+B) = dA + dB\,. \tag{9}$$

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,

$$d\phi = \frac{\partial \phi}{\partial x} dx + \frac{\partial \phi}{\partial y} dy\,. \tag{10}$$

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

$$d\phi = \left(\frac{\partial \phi}{\partial x}\right)_y dx + \left(\frac{\partial \phi}{\partial y}\right)_x dy\,, \tag{11}$$

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

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

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

if and only if

$$\lambda_1 = \lambda_2\,. \tag{13}$$

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]

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)\,, \tag{14}$$

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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.

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

or

$$\frac{\partial^2 f}{\partial x\,\partial y} = \frac{\partial^2 f}{\partial y\,\partial x}\,. \tag{15}$$

4 Poincaré Lemma for R^n

> **Every closed differential form defined on R^n (which is a simply connected manifold) is also exact.**

Definition: A differential form α is said to be **closed** if

$$d\alpha = 0\,. \tag{16}$$

Definition: A differential form α is said to be **exact** if there exists a differential form β such that

$$\alpha = d\beta\,. \tag{17}$$

Now, because of the fact that

$$d^2 = 0\,, \tag{18}$$

if we apply the d operator on (17), we get that

$$d\alpha = d^2\beta = 0\,. \tag{19}$$

And we conclude from this that every exact form is also closed. But does it work the other way around? Is it true that every closed form is also exact? The answer is No. But it's not our purpose here to go over the proof of the general Poincaré Lemma. For our purposes, it's sufficient that the lemma is true for R^2.

So then what's the significance of the Poincaré Lemma for R^2? It's significance lies in the fact that it's an **existence theorem**. In other words, if α is a form defined on R^2 and (16) is true, then there exists a β such that (17) is true. This is what Baez refers to as 'pulling a rabbit out of a hat'.

5 The Long-Awaited Application

Suppose we have a differential form defined as

$$dS = pdq - Hdt\,. \tag{20}$$

Then, because of (18), we can write down

$$\begin{aligned} 0 &= d(pdq - Hdt) \\ &= dp \wedge dq - dH \wedge dt \\ &= -dq \wedge dp - dH \wedge dt \\ &= d(-qdp - Hdt)\,. \end{aligned} \tag{21}$$

So, since

$$d(-qdp - Hdt) = 0\,, \tag{22}$$

then there exists a function X such that

$$dX = -qdp - Hdt\,, \tag{23}$$

where

$$X = S - pq\,. \tag{24}$$

This is easy to prove from the information above.

Such is the value of existence theorems!