Math Diversion Problem 455: Partial Derivatives Using SD

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Thermodynamics is the study of the laws which govern
transformations of matter and energy during
physical and chemical changes.
— S. M. Blinder[1]

1 Introduction

This is my second paper on an article by S. M. Blinder. I shall be using the techniques of structured differentiation to perform and explain what Blinder has done in the next section of his article.

Let's begin with a simple example of things to come. Consider the made-up equation

$$x = y^2 z - (z-3)^3 y\,. \tag{1}$$

This can be rewritten as

$$x - y^2 z + (z-3)^3 y = 0\,. \tag{2}$$

Now let's regard the LHS of this as a function F of variables x, y, z, i.e.,

$$F(x,y,z) = x - y^2 z + (z-3)^3 y\,. \tag{3}$$

As stated above, $F(x,y,z)$ has three degrees of freedom. But if we then accept that (2) places a constraint on F, we get

$$F(x,y,z) = 0\,, \tag{4}$$

and then our degrees of freedom have dropped from 3 to 2. By the Implicit Function Theorem, we can choose to regard one of these variants as a function of the other two.[2] In particular, let's assume that

$$z = z(x,y)\,. \tag{5}$$

[1]Found in "Mathematical Methods in Elementary Thermodynamics," S. M. Blinder, J. of Chem. Ed., Vol. 43, No. 2, 1966, pp 85–88.

[2]A variant of a function is a variable on which the function is explicitly dependent.

If we like, (4) can be rewritten as

$$F(x, y, z(x, y)) = 0\,. \tag{6}$$

Now, say we wish to solve for $\dfrac{\partial z}{\partial x}$ without going to the effort of solving (1) for z first. In first-year calculus, we learn to do this under the name of 'implicit differentiation', but I prefer not to use that term in SD, as it clashes with the notion of implicit differentiation in SD. In any case, we'll do it now by an 'advanced calculus' method. The total derivative of (6) by x is

$$\frac{\delta F}{\delta x} = 0\,, \tag{7}$$

which expands to

$$\frac{\partial F}{\partial x} + \frac{\partial F}{\partial z}\frac{\partial z}{\partial x} = 0\,. \tag{8}$$

Now we just solve for $\dfrac{\partial z}{\partial x}$:

$$\frac{\partial z}{\partial x} = -\frac{\dfrac{\partial F}{\partial x}}{\dfrac{\partial F}{\partial z}}\,. \tag{9}$$

You may have noticed that I did not subscript the derivatives in (9). I didn't because in SD a partial derivative is always explicit anyway. However, this is a luxury we have in this case because we are stuck in a system with fixed basis of independent variables, x, y. But what happens if we change the set of independent variables to something else? In that case, it would be better to indicate with subscripts what we had kept constant. Regarding (9) that looks like

$$\left(\frac{\partial z}{\partial x}\right)_y = -\frac{\left(\dfrac{\partial F}{\partial x}\right)_y}{\left(\dfrac{\partial F}{\partial z}\right)_y}\,, \tag{10}$$

which amounts to declaring that y was being treated as an independent variable. But we could go one step further in removing ambiguity by stating the obvious, as follows

$$\left(\frac{\partial z}{\partial x}\right)_y = -\frac{\left(\dfrac{\partial F}{\partial x}\right)_{y,z}}{\left(\dfrac{\partial F}{\partial z}\right)_{y,x}}\,, \tag{11}$$

It's as if we're stepping back from F defined in (6) to F defined in (4). So, by subscripting we have removed the possible ambiguity of what we mean by a 'partial' derivative.

Okay, so in this paper I'm reviewing partial derivatives applied to thermodynamics. Why does this come up here as so important? Well, because in the science of thermodynamics one is just as concerned with derivatives (rates of change) as in any other science. But one's first attempt at solving for a derivative may find itself in terms of variables that are not so easy to measure in the laboratory. For example, how would one measure the energy or entropy of a substance? The variables that are easy to measure are volume V, temperature T, and pressure P.

The game is to find a transformation on the independent variables so that the variables that characterize the system are easy to measure. So, if you have a partial derivative in one basis, you have to retain the legacy subscripting to retain the information of what variables are held constant under a change in basis of independent variables. We won't need to deal with a change in the basis in this paper, but I have already uploaded such problems to this forum in the recent past and I expect to upload many more before this series on SD used for thermodynamic is over.

2 Dieterici's Equation of State

The Dieterici Equation of State for a real (as opposed to ideal) gas takes the form

$$P(V-b)e^{a/RTV} = RT\,, \tag{12}$$

where a, b are constants that characterize the gas, and R is the 'ideal gas constant'. Now, suppose that the derivative we're really interested in is $\left(\dfrac{\partial V}{\partial T}\right)_P$. How should we obtain this derivative? One fine way would be to differentiate (12) implicitly by T, holding P constant. But let's do it the other way that we just saw demonstrated.

Let

$$F(P,V,T) = P(V-b)e^{a/RTV} - RT = 0\,. \tag{13}$$

This constraint on F allows us to write[3]

$$F(P,V(P,T),T) = 0\,. \tag{14}$$

After taking the total derivative of this by T and then algebraically solving for $\left(\dfrac{\partial V}{\partial T}\right)_P$, we get

$$\left(\frac{\partial V}{\partial T}\right)_P = -\frac{\left(\dfrac{\partial F}{\partial T}\right)_{V,P}}{\left(\dfrac{\partial F}{\partial V}\right)_{T,P}}\,. \tag{15}$$

[3]Here, I'm ignoring the subtleties of the Implicit Function Theorem.

Now, we'll calculate the derivatives in the numerator and denominator.

$$\left(\frac{\partial F}{\partial T}\right)_{V,P} = -\frac{P(V-b)a}{RT^2V}\,e^{a/RTV} - R\,, \tag{16}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,P} = P\left[1 - \frac{a(V-b)}{RTV^2}\right]e^{a/RTV}\,. \tag{17}$$

Fortunately, we can use (12) to eliminate the exponential factor in both of these expressions, which will simplify both of them considerably. Thus, on substituting these simplified expressions into (18), we have that

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R + \dfrac{a}{TV}}{\dfrac{RT}{V-b} - \dfrac{a}{V^2}}\,. \tag{18}$$

For an outside reference, see

https://math.stackexchange.com/questions/2441387/dietericis-equation