# Representations of Partial Derivatives in Thermodynamics

John R. Thompson*, Corinne A. Manogue†,
David J. Roundy†, Donald B. Mountcastle*

*Department of Physics and Astronomy, University of Maine, 5709 Bennett Hall, Orono, ME, 04469
†Department of Physics, Oregon State University, Weniger Hall 301, Corvallis, OR 97331

**Abstract.** One of the mathematical objects that students become familiar with in thermodynamics, often for the first time, is the partial derivative of a multivariable function. The symbolic representation of a partial derivative and related quantities present difficulties for students in both mathematical and physical contexts, most notably what it means to keep one or more variables fixed while taking the derivative with respect to a different variable. Material properties are themselves written as partial derivatives of various state functions (e.g., compressibility is a partial derivative of volume with respect to pressure). Research in courses at the University of Maine and Oregon State University yields findings related to the many ways that partial derivatives can be represented and interpreted in thermodynamics. Research has informed curricular development that elicits many of the difficulties using different representations (e.g., geometric) and different contexts (e.g., connecting partial derivatives to specific experiments).

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## INTRODUCTION

In this paper, we will describe preliminary results from a collaboration between the Paradigm in Physics group at Oregon State University and the Physics Education Research Laboratory at the University of Maine to develop and assess curricular materials designed to help address student understanding of the mathematics used in thermodynamics, particularly the mathematics of partial derivatives and differentials. The Energy and Entropy course at Oregon State University (OSU) is one of the Paradigms in Physics courses developed as part of a comprehensive reform of the upper division [1,2]. A signature of Paradigms courses is extensive use of student-centered activities, lab activities, and a particular emphasis on connecting the mathematics to the physics, especially connecting the way mathematics is taught in mathematics courses to the way it is used in physics. During the winter and spring quarters, the Paradigms include a “Preface” or “Interlude” week, which feature student experiences with relevant math methods immediately before the related physics courses. Multiple representations are presented and students develop fluency through a variety of activities [3].

Beyond their mathematics core courses, where have our students seen partial derivatives prior to their first upper division thermodynamics courses? At the University of Maine, students have seen this content in E&M and math methods. At OSU, this material is touched on briefly in the two paradigms on electrostatics and magnetostatics, but always in the context of derivatives with respect to *x*, *y*, and *z*.

In thermodynamics, the ubiquity of multivariable functions to represent the state and properties of an equilibrium system lead to the use of multivariable differential calculus to describe any changes to the system based on changes in the equilibrium state. Understanding the mathematical formalism of multivariable differential calculus is thus integral to the analysis of thermodynamic processes.

There are several facets of partial differentiation and total differentials that are necessary to understand to properly connect the mathematical formalism to the physical scenario. The distinction between the derivative of a single-variable function and that of a multivariable function is important, especially knowing that all other independent variables are held fixed in a partial derivative. Recognition of the empirical significance of a thermodynamic partial derivative is central to a functional understanding of the role of partial derivatives in thermodynamics. Understanding what the terms in a total differential represent, *e.g.*, that the coefficients of the differentials of the independent variables are themselves partial derivatives, is important to make connections between different state variables in a physical scenario.

Several different representations are used to describe partial derivatives. The first is symbolic: the mathematical expression for the partial derivative in question. Second, emphasis is placed on the derivative as experiment. The course instructor at OSU (DR) has developed a “Name the experiment” activity for which students must describe the experiment corresponding to a particular partial derivative [4]. A third representation connects a partial derivative with its graphical equivalent. This is used in particular to help students think about second-order partials, especially mixed second-order partials. The primary activity for this representation is based on one developed by researchers at the University of Maine [5].

## NAME THE EXPERIMENT

One representational problem that students have when they come to thermodynamics is that the need to specify the quantities held constant (the little subscripts after a partial derivative) is not clear to them.

$$\left(\frac{\partial V}{\partial p}\right)_{S,N}$$

Previously, students have always been able to simply say “everything else is held constant”, which is possible so long as there is a clear distinction between dependent and independent variables, as is the case in electrostatics where physical quantities such as the charge density or the electrostatic potential are function of the spatial variables. Thermodynamics introduces a whole slew of variables, of which a wide variety of different subsets may be chosen as independent. Students initially resist explicitly mentioning which variables are held constant, as they feel that this is redundant.

In order to help students to understand what we mean in physics by a partial derivative, we have introduced a series of activities [4] in which students work in groups to describe physical experiments that would be needed to measure particular thermodynamic derivatives. Doing this reinforces the idea that a thermodynamic partial derivative describes a physically measurable quantity, which is independent of how we choose to write our functions (e.g. writing $U = 3/2\,kT$ rather than as a function of $S$ and $V$ —as we encourage students to think of it—doesn’t affect the value of $\left(\partial U/\partial V\right)_S$ with $S$ constant). These activities also serve to reinforce the definitions of thermodynamic quantities in terms of measurable quantities. In particular, pressure and entropy are quantities that we feel students learn to understand better experimentally through these activities.

We begin with very simple derivatives corresponding to experiments involving changing one of $\left(p,V,T\right)$ and measuring another while holding the third fixed. This gives students a first chance to recognize that they need to come up with an approach to keep the constant quantity fixed. We move on to trickier derivatives involving entropy, which forces students to grapple with the question of how to measure a change in entropy or how to keep it fixed. The latter is simple (insulation), but the former requires that they grapple with the thermodynamic definition of entropy change as an integral of heat over temperature. Finally, when we discuss Maxwell relations, we have a third name-the-experiment activity in which students work out *two* experiments to measure the same derivative, in which it is usually obvious that one experiment will be significantly easier than the other, thus demonstrating a use for Maxwell relations (if they can imagine that they would want to know the derivative in the first place).

## MATHEMATICAL RELATIONSHIPS VS. PHYSICAL LAWS

The next two representations of differentials are both symbolic, and may not easily be recognized as two separate representations. The first is referred to as the “math” version, which lays out the expression for a total differential in the general form, while the second, “physics” version replaces the partial derivatives with the appropriate physical quantity. Instruction emphasizes the two different representations as distinct, which is a useful pedagogical tool to explicit connect math and physics in this context. Research on student learning suggests that students may have difficulties connecting the coefficients of the physics version of a total differential to the partial derivatives that their math equivalent represents [6].

$$dU = \left(\frac{\partial U}{\partial S}\right)_L dS + \left(\frac{\partial U}{\partial L}\right)_S dL$$

$$dU = T\,dS + \tau\,dL$$

Encouraging students to distinguish the “math” differential relationship from the “physics” one is part of a common strategy in the Paradigms—sense-making about which equations are true because of general mathematical relationships, which are true because of physical laws, and which are true only for specific physical examples [7].

## CHAIN RULE

Computationally, knowing how and when to apply the chain and product rules when taking derivatives of expressions containing multivariable functions is a necessary skill to work through problems successfully.

At OSU, we have found it useful to use a representation, which we call a derivative tree [8], a standard mnemonic tool, common in many vector calculus texts [9], for keeping track of nested multivariable functions.

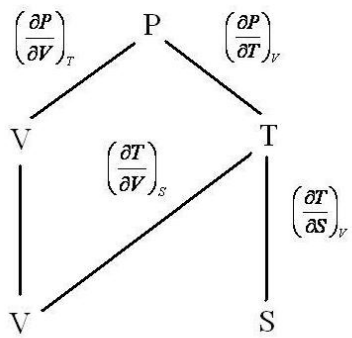


**FIGURE 1.** Derivative tree for the pressure $P$ thought of first as a function of volume $V$ and temperature $T$ and then as a function of volume and entropy $S$.

This diagram corresponds to the chain rule:

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

$$dP = \left(\left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_S\right) dV + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V dS$$

The different levels in the diagram are particularly helpful to keep track of which variables are held constant in their partial derivatives. OSU students use this representation spontaneously on homework and exams.

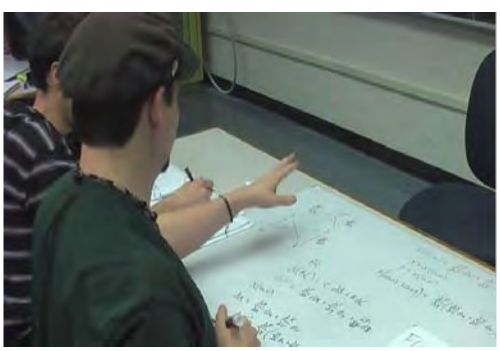

**FIGURE 2.** Students working with a derivative tree in class.

## MAXWELL RELATIONS

Second-order partial derivatives occur frequently in thermodynamics; the most common type is the mixed second-order partial derivative, for which each derivative is with respect to a different independent variable. For a two-variable function that satisfies requirements for continuity of both the function and its first partial derivatives, these mixed second-order partial derivatives are equal; this is known as Clairaut's Theorem. The Maxwell relations, important relationships between second-order mixed partial derivatives of "thermodynamic potentials" (different energy functions), allow for inferences about changes in system properties such as entropy by measuring other changes in the system.

## ACTIVITY ON GRAPHICAL INTERPRETATION OF PARTIALS

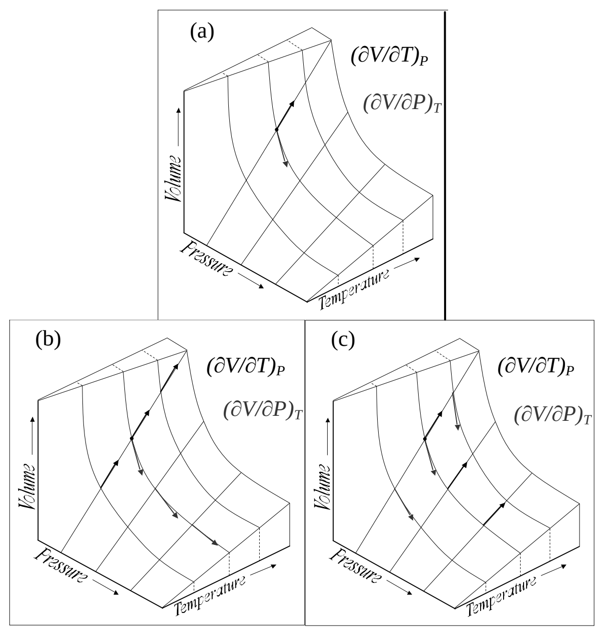


**FIGURE 3.** *P-V-T* diagrams for an ideal gas showing (a) first partial derivatives, (b) full second-order partials, and (c) mixed second-order partials of volume.

One activity incorporated in the course has students graphically interpreting various partial derivatives, both first- and second-order. The activity is an excerpt from a small-group, guided-inquiry activity (i.e., a tutorial) that was developed at the University of Maine, based on an instructional sequence used (by DBM) in the thermodynamics course there [5]. The tutorial attempts to answer the questions: what does it mean graphically (physically) for the mixed second partials of a function to be equal, and yet not equal to zero? In particular, what does the equality of mixed second partials tell us about the state function of volume? As mentioned above, the tutorial is a response to the findings of Bucy *et al*. that students misinterpret the meaning of "holding a variable constant" during partial differentiation, considering the fixed variable to remain constant after differentiation rather than being fixed only during the process [6].

Classroom video from this activity at OSU shows students having problems in the tutorial that demonstrate that they are having to wrestle with the geometric and physical meaning of many of the derivatives: Some confuse a curve on the graph of $V$ (T) for a given $P$ with the partial derivative of $V$ for constant (fixed) $P$ (i.e. the confuse the curve with its first derivative). Some have trouble coordinating a 3-d plot of the function with a plot (provided) of the cross-sections of the function. Many have trouble understanding the geometric meaning of the second derivative—how are the slopes changing? And most of the class is stumped on a question that has negative slopes which become shallower. They have trouble seeing that as an "increasing" slope.

## OVERALL ASSESSMENT

In the Energy and Entropy paradigm and the preceding Interlude (developed in the last couple of years), students were assessed on their functional understanding of partial derivatives and differentials, using a combination of questions developed earlier (by JRT and colleagues at the University of Maine) and asked in both physics [10,5] and analogous mathematics contexts [11], as well as questions developed specifically for the paradigm. In general, many of the successes and difficulties identified earlier were confirmed in the OSU students. We find that students at the beginning of the Interlude have less facility with partial derivatives and total differentials than in a traditional curriculum (e.g., at the University of Maine), and have many of the difficulties identified in earlier research. They also seem to be equally skilled at making the empirical connection from a partial derivative, based on the "name the experiment" results. However, our preliminary results suggest that by the end of the paradigm, OSU students make strong gains in their skills and facility, with most of the class recognizing the connections between the math and the physics easily.

This apparent success is attributed to the deliberate effort to make explicit pedagogical connections between the math and the physics, including making students aware of the differences in notation, convention, etc. between the disciplines in this area. The multiple representations used serve to bridge the disciplinary distinctions, and it seems like students in the paradigms courses have gained a greater appreciation for the role of mathematics in the physics.

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