Assessing Student Understanding of Partial Derivatives in Thermodynamics

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Abstract. We are engaged in a research project to study teaching and learning in upper-level thermal physics courses. We have begun to explore student functional understanding of mathematical concepts when applied in thermal physics contexts. We report here preliminary findings associated with partial differentiation and the Maxwell relations, which equate mixed second partial derivatives of various state functions. Our results suggest that students are often unable to apply the appropriate mathematical concepts and operations to the physical situations encountered in the course, despite having taken the prerequisite mathematics courses.

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INTRODUCTION

At the University of Maine (UMaine), we are currently engaged in a collaborative research project with colleagues at Iowa State University to explore student understanding of thermal physics concepts for the purposes of improving instruction. Research on student learning of thermal physics concepts in university physics courses, particularly beyond the introductory level, is rare. There is clear evidence that university students display a number of difficulties in learning many introductory thermal physics concepts, including difficulties with heat, temperature, the Ideal Gas Law and the First and Second Laws of Thermodynamics [1-8].

Mathematics is a primary representation to articulate relationships among variables in physics. Mathematical facility allows a fuller understanding of empirical results, while more robust mathematical ability allows for extension of the concepts beyond a qualitative comprehension. As the physics becomes more advanced, so does the prerequisite mathematics. In thermal physics, there are topics that require specific mathematical concepts for a complete understanding of the physics.

As part of our investigation into student understanding of thermal physics concepts, we designed and administered questions that probe the connections between physics and mathematics in an upper-level thermodynamics course. We are interested in the correlation between student understanding of the mathematical formalism related to first- and second-order partial derivatives and their appreciation of the physical significance of these derivatives.

We present results from an exploratory survey of UMaine's *Physical Thermodynamics* course, taught in Fall 2004 (by DBM). This course deals primarily with classical thermodynamics, covering the first 11 chapters of Carter's textbook [9] along with supplemental material. A separate statistical mechanics course is offered in the spring semester.

Instruction included lecture, class discussions, and demonstrations; homework assignments included standard problems and instructor-designed conceptual questions. The instructor emphasized explicit connections between physical situations and relevant mathematical models to a greater extent than is common in typical textbooks. The homework was graded and returned with comments, and a detailed answer key was supplied to students. Data were obtained from the eight students taking the course: two juniors and six seniors; seven physics majors and one marine sciences major. All students had completed the prerequisite third semester of calculus, which includes multivariable differential calculus. Two students had also completed the first semester of a two-semester *Partial Differential Equations* (PDE) course; one of those two had also completed the second PDE course. Both students received grades of A or B in these courses. (A third student took PDE I

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concurrently, receiving an A.) We focus here on student responses to written questions dealing with partial derivatives and with the Maxwell relations.

INSTRUMENTS AND RESULTS

Questions that dealt with mathematical concepts using both abstract symbols and meaningful thermal physics variables were administered to students throughout the semester. Below we describe one set of questions and results.

Day One: Definition of Partial Derivative

On the first day of class, students were asked to define a partial derivative, and to "include a clear distinction between *(dz/dx)* and $(\partial z/\partial x)_y$."

All students gave a reasonable definition of a partial derivative, *e.g.*, "the derivative of a function… with respect to only one of its variables." Most students used the term *derivative* in their definitions, as above. Only three actually specified a distinction between *dz/dx* and $(\partial z/\partial x)_y$; likewise, only four specifically stated that the remaining variables must be held constant in a partial differentiation. The student who had taken one PDE course was part of both of these groups; the student who had taken both PDE courses was not part of either.

Only one student response implied recognition of the meaning of a derivative: "$\partial z/\partial x$: the change in *z* along *x* as all other dimensions are held constant."

Pretest: Mixed Second Partial Derivatives and Maxwell Relations

Shortly before introducing the Maxwell relations (but after starting instruction on the so-called "thermodynamic potentials," about two-thirds of the way through the course), students completed a pretest on both math and physics related to the Maxwell relations. The first question was asked in a purely mathematical context, and the second dealt with thermodynamic quantities. The questions are shown in Fig. 1.

In question 1, students were told that *R* was a function of two independent variables, and were given the total differential. In part (a) we wanted to see whether students recognized that *B* was the partial derivative of *R* with respect to *C while holding F constant, i.e.*, $B = \left(\frac{\partial R}{\partial C}\right)_F$. Part (b) gave a relationship between the partial derivatives of the two coefficients, and asked about the conditionality of this relationship. These two partial derivatives of the coefficients are, in fact, the two "mixed second partials" of the original function *R*, that is, the second derivatives taken with respect to each variable in sequence, but in reversed order. For example, in part (b) the expression on the left can also be written as either $\left(\frac{\partial}{\partial F}\left(\frac{\partial R}{\partial C}\right)_F\right)_C$ or $\left(\frac{\partial^2 R}{\partial F \partial C}\right)$, while that on the right is $\left(\frac{\partial}{\partial C}\left(\frac{\partial R}{\partial F}\right)_C\right)_F$ or $\left(\frac{\partial^2 R}{\partial C \partial F}\right)$. For any function for which the second partial derivatives are defined and continuous, these two expressions are identical. This relationship is known as Clairaut's Theorem, or as "the equality of mixed second partials," and are the basis for the Maxwell relations.

1. *R* is a function of the independent variables *C* and *F*, that is *R = R(C,F)*. The total differential of *R* can be written as
$$dR = BdC + EdF.$$
a. Interpret the above equation in order to determine an expression for *B*.
b. Is the following statement *sometimes true*, *always true*, or *always false*? Please explain your reasoning.
$$\left(\frac{\partial B}{\partial F}\right)_C = \left(\frac{\partial E}{\partial C}\right)_F$$

2. *G* is the Gibbs Function. The total differential of *G* can be written as
$$dG = -SdT + VdP$$
where *S* is the entropy, *T* is the temperature, *V* is the volume, and *P* is the pressure. In a certain experiment, it is found that
$$\left(\frac{\partial V}{\partial T}\right)_P = 4.6\times10^{-6} m^3/K.$$
a. Is this a reasonable result? Please explain your reasoning.
b. From this data, is it possible to determine $\left(\frac{\partial S}{\partial P}\right)_T$?
If so, explain how, and give a value.
If not, explain what additional information you would need to do so.

FIGURE 1. Pretest questions on mixed second partial derivatives and Maxwell relations.

In question 1(a), five students stated that *B* was the partial derivative of *R* with respect to *C*, although three of these students did not specify that *F* should be held constant. Four of these five students also answered question 1(b) correctly, including the PDE students. Two of these four students stated that the expression was *sometimes* true, with the condition "iff *dR* is exact" or "if we are dealing with state functions"; these qualified responses were counted as correct for our purposes, since it was stated in the question that *R* is a function of *C* and *F*. The other two students who gave correct responses explicitly differentiated *R* in each sequence to show that the expressions were identical. Two other students solved for *B* algebraically, rather than treating the equation as differential.

Question 2 defines the Gibbs function $G(T,P)$ and provides the total differential. In question 2(a), students were asked to consider whether a numerical value for the partial derivative of volume with respect to temperature at constant pressure, $(\partial V/\partial T)_P$ is reasonable. Two reasonable attributes of this value are noteworthy: (i) it is positive, meaning that the substance expands with increased temperature; (ii) it is dimensionally consistent with the derivative.

Five students explicitly – and only – mentioned the physical relationship between the volume and the temperature: if the temperature increases the volume increases. One student assessed only the units; two commented specifically about the rather small magnitude with no further elaboration.

In question 2(b) students were asked whether it is possible to determine another partial derivative, $(\partial S/\partial P)_T$, from this data, and to explain their reasoning. The partial derivative in question 2(b) is the Maxwell relation counterpart of the derivative given earlier in question 2; thus their numerical values are of equal magnitude but opposite sign. It is important to recognize that a *direct* measurement of this quantity is experimentally impossible, and thus a relationship to another, empirically obtainable quantity is necessary.

Only two students gave a completely correct response to question 2(b); a third equated the two values, simply neglecting the negative sign in the first term of the total differential. These three students were also part of the four who answered question 1 correctly, and were all PDE students. Two students incorrectly specified that the value could be determined if dG were set to zero. These were the same two students who gave algebraic solutions to question 1; it is reasonable to interpret these responses as algebraically motivated also. Two students explicitly stated that they did not know how to answer the question.

Final Exam: Expansion of a Thin Film

On the final exam a question was given that dealt with the expansion of an elastic thin film (see Fig. 2). This was one of six questions from which students had to complete four, with the option of a fifth for extra credit. All seven students taking the final exam attempted this question; two worked it as extra credit.

Students had prior experience in the course with problems similar to that in Fig. 2, both as in-class examples and as assigned homework. Two homework problems of this nature asked students to derive Maxwell relations, one for a wire under tension (a one-dimensional analog of the final exam question) and one for a rechargeable battery. Follow-up questions were discussed in class.

We focus here on parts (c) and (d) of the problem. The exam included reference tables with numerical values for relevant material properties (*e.g.*, the thermal expansivities and the bulk modulus) of several materials, including aluminum.

A correct response to part (c) demonstrates an understanding of the mathematical procedure for obtaining Maxwell relations from the differentials of thermodynamic potentials; a correct procedure on (d) shows an understanding of the physical significance of those Maxwell relations. There are, admittedly, some assumptions that have to be made in part (d) (*e.g.*, the relationship between the linear, area, and volume expansivity) which make it difficult. For this paper, we are not as interested in students' ability to successfully complete these problems as we are in their ability to recognize a successful strategy to arrive at a solution.

> Write an expression showing how to determine the work necessary to expand (stretch) an elastic thin film.
>
> a) Show how the surface tension is related to the internal energy, and to the Helmholtz function of the film. *Briefly* explain *one* of these relations in words.
>
> b) Deduce expressions for the differentials of the internal energy, the enthalpy, the Helmholtz function, and the Gibbs function appropriate for this system (the film).
>
> c) Deduce four different Maxwell relations describing such a film.
>
> d) Calculate the change in entropy of a 1.5 *m* x 2.5 *m* rectangular sheet of aluminum foil when the surface tension is increased at constant temperature from 1 *N/m* to 800 *N/m*.
>
> e) If possible, calculate the change in area for the process in (d). If not possible, explain what additional information you need to do so.

FIGURE 2. Final exam question on expansion of a thin film and corresponding Maxwell relations.

Part (c) in general did not give much trouble to students. Two students produced incorrect relations, that were, however, consistent with incorrect expressions for the potentials asked for in (b). Only two students had serious difficulty with this part. However, on part (d), only two students recognized that the solution required the use of one of their Maxwell relations from part (c); only one of these students chose the correct Maxwell relation, but then was confused as to how to proceed. Two students, for whom this problem was voluntary, stopped answering the question after part (c), apparently due to similar confusion.

DISCUSSION

There are several findings in the data presented above that merit discussion. We discuss the successes and the difficulties observed, and then summarize the common features of each set.

Successes

In general, students were able to discuss the mathematical distinction between a partial and a total derivative. They were also able to perform the calculus necessary to solve a problem, albeit not without errors (some calculus errors were occasionally observed). Most students either explicitly mentioned or implied that other variables need to be held constant when dealing with partial derivatives, even if they did not consistently acknowledge this in their responses.

Students also seemed to recognize that, given a partial derivative that contains well-understood physical variables *(e.g., V, T, P),* the mathematical expression represents "the change in physical variable *X* as a result of a change in physical variable *Y*."

Finally, most students extracted Maxwell relations from a given set of thermodynamic potentials without much difficulty, *after* instruction.

Difficulties

We note three specific difficulties in the data. First, a small subset of students treated differential expressions algebraically. This difficulty was seen well over halfway through the course, after the students had worked extensively with exact differentials, the coefficients of which either are related to or are partial derivatives of state functions. This might imply that these students did not recognize the physical significance of the differentials, treating them merely as algebraic equations. These are the only students in this course who received grades below A in all three introductory calculus courses.

Second, many students at this level were still unable to take a description of a physical process and produce a partial derivative that represents that process mathematically, that is, translate from a verbal description to a mathematical expression, even after instruction. The reverse, *i.e.,* stating the physical equivalent of a given partial derivative, is one of the successes described above.

Third, many students had difficulty recognizing when a physical situation calls for the use of a Maxwell relation, and even fewer were able to select the appropriate Maxwell relation.

Summary

All of the successes delineated above have a common feature: a largely algorithmic, rather than conceptual, understanding. For example, construction of a verbal description of a partial derivative requires merely inserting the relevant physical variables in place of the mathematical symbols.

The difficulties seemed to arise when students were required to extend their mathematical understanding beyond familiar algorithmic contexts, resulting in inappropriate applications, despite relevant experience in class and on homework assignments. Based on our final exam results, students learn to extract Maxwell relations from thermodynamic potentials. Several mnemonics for Maxwell relations exist, attesting to the algorithmic nature of this procedure. However, despite the ability to produce them, we see little recognition among students of the utility of the Maxwell relations, even after significant instructional emphasis.

More students could interpret the physical meaning of a partial derivative in context than could write the appropriate partial derivative describing a particular process. Our results suggest that making connections between physics and mathematics, even at the advanced undergraduate level, is not trivial for most students. In addition, failure to make these connections in both directions may prevent a full understanding of the relevant physical phenomena, at least in thermodynamics.

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