Student (Mis)application of Partial Differentiation to Material Properties

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Abstract. Students in upper-level undergraduate thermodynamics courses were asked about the relationship between the complementary partial derivatives of the isothermal compressibility and the thermal expansivity of a substance. Both these material properties can be expressed with first partial derivatives of the system volume. Several of the responses implied difficulty with the notion of variables held fixed in a partial derivative. Specifically, when asked to find the partial derivative of one of these quantities with respect to a variable that was initially held fixed, a common response was that this (mixed second) partial derivative must be zero. We have previously reported other related difficulties in the context of the Maxwell relations, indicating persistent confusion applying partial differentiation to state functions. We present results from student homework and examination questions and briefly discuss an instructional strategy to address these issues.

Keywords: Thermal physics, mathematics, partial differentiation, material properties, thermal expansivity, isothermal compressibility, Maxwell relations, upper-level, physics education research.
PACS: 01.40.-d, 01.40.Fk, 05.70.Ce, 65.40.De, 65.40.Gr.

INTRODUCTION

At the University of Maine (UMaine), we are currently engaged in a research project 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. However, a growing body of research presents clear evidence that university students display a number of difficulties in learning many introductory and advanced thermal physics concepts [1-5].

Mathematics is a primary representation that can be used to articulate relationships among variables in physics. Mathematical facility allows a fuller understanding of empirical results, while more robust mathematical ability allows for the extension of physical concepts beyond a basic 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. We have recently shown that thermal physics students have difficulties with regard to these mathematics concepts in addition to the above mentioned difficulties with physics concepts [5]. We have designed and administered questions to students in an upper-level thermodynamics course in the context of exploring the relationship between the physical properties of the thermal expansivity *(β)* and the isothermal compressibility *(κ)* of a system. These questions probe student understanding of the mathematics that underlie these physical properties, particularly multivariable calculus and partial differentiation.

We present results from a survey of two semesters of UMaine's *Physical Thermodynamics* course, taught in Fall 2004 and 2005 (by DBM). This course deals primarily with classical thermodynamics, covering the first 11 chapters of Carter's textbook [6] 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 processes 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 fourteen students taking the courses: two juniors, eleven seniors, and one physics grad student; eleven physics majors, one math major, and one marine sciences major. All students had completed the prerequisite third semester of calculus, which includes multivariable differential calculus. All students but one had additionally completed one or more courses in ordinary and partial differential equations.

INSTRUMENT AND RESULTS

We focus here on student responses to a written question dealing with the relation between complementary partial derivatives of the isothermal compressibility and the thermal expansivity of a substance. The *"β–κ"* question was administered to students twice during the semester: as part of a homework assignment after instruction on state functions and partial derivatives, and again after the homework was graded with instructor comments and returned with an answer key, in a slightly modified form as part of a graded examination (Figure 1).

(a) Show that in general $\left(\frac{\partial \beta}{\partial P}\right)_T + \left(\frac{\partial \kappa}{\partial T}\right)_P = 0.$

(b) With the usual definitions of isothermal compressibility *(κ)* and thermal expansivity *(β)*, for any substance where both are continuous, show how these two derivatives are related:

$$\left(\frac{\partial \kappa}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial \beta}{\partial P}\right)_T .$$

FIGURE 1. "*β-κ* question" asked to students on (a) homework and (b) a midterm examination. Based on Problem 2-9 in Carter's text [6].

The thermal expansivity of a thermodynamic system is related to the partial derivative of the system volume with respect to temperature at a fixed pressure: $\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. The isothermal compressibility is related to the partial derivative of the system volume with respect to pressure at a fixed temperature: $\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. Physically, β describes the response of the system volume to a change in temperature while κ describes the response of the system volume to a change in pressure. By convention, the negative sign is included in the definition of κ recognizing that the volume of a system always decreases with increased pressure. Division by volume makes the properties of β and κ *intensive*, that is, a material property of a substance, independent of the sample size.

In order to answer the question, students must first take the requested derivatives of β and κ. Application of the product rule and the chain rule results in the following expressions:

$$\left(\frac{\partial \beta}{\partial P}\right)_T = -\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \frac{1}{V}\frac{\partial^2 V}{\partial P \partial T} \qquad (1)$$

$$\left(\frac{\partial \kappa}{\partial T}\right)_P = \frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V}\frac{\partial^2 V}{\partial T \partial P} \qquad (2)$$

It is easy to see that the first terms in equations (1) and (2) are exact opposites, containing products of first partials, while the second terms contain complementary mixed second partials – one taken with respect to pressure then temperature, the other vice-versa. It turns out that for any function for which the second partial derivatives are defined and continuous, the mixed second partials are identical, regardless of the order of differentiation. This relationship is known as Clairaut's Theorem, or as "the equality of mixed second partials." Applying Clairaut's Theorem in this case allows one to see that the complementary second partial derivatives of β and κ are identically opposite.[1]

TABLE 1. Student responses to *β-κ* question.

Category of Student Response (Non-exclusive)	# Student Responses on Homework (N = 14)	# Student Responses on Exam (N = 11)
Correct	6	5
Calculus I problems	7	3
Calculus III problems	6	5

Student performance on this question is presented in Table 1. Slightly less than half of the students answered the question correctly, both on the homework assignment and on the exam. This poor performance is somewhat surprising, given that the exam question was nearly identical to the homework question, which had been graded and returned to students along with a detailed answer key depicting the solution.

Several noteworthy aspects of student reasoning were observed. A sizeable proportion of the students displayed one or more difficulties with the process of differentiation in their responses, referred to as *Calculus I problems* in Table 1. Several students had

[1] There is a more elegant way to solve this problem; simply by recognizing that $-\kappa$ and β are the coefficients of the total differential of the logarithm of the system volume. Thus, by Clairaut's theorem, their complementary partials must be equal.

difficulties in applying the product rule in their differentiation. A common approach in student strategy was to simply factor the $1/V$ term out of the derivatives of both β and κ, as if volume were not a function of either pressure or temperature. A related problem involved incorrect or missing differentiation of either the $1/V$ term or of the partial derivative terms themselves.

Other students had specific difficulties in applying of the chain rule. When differentiating the $1/V$ term with respect to pressure or temperature, some students simply wrote down $-1/V^2$, neglecting to further differentiate V with respect to P or T. Consequently, the first terms in equations (1) and (2) were not identical opposites in these students' derivations.

Fully half of the students made one or more of these mistakes on the homework assignment. This inability to correctly differentiate a relatively simple expression calls into question many of the skills that most physics professors assume their incoming upper-level students possess. It is important to note, however, that this homework assignment was only the second assignment of ten total. Fewer students made one of these mistakes on the exam, which occurred after the homework and several weeks later in the semester. While these problems were much more prevalent on the homework question than on the exam, these responses are still troubling in terms of prerequisite knowledge and skills that students are expected to bring into an upper level physics course.

Another specific flaw in student reasoning was observed, labeled *Calculus III problems* in Table 1. This type of response indicated a higher order mathematical difficulty than simple differentiation problems, namely the role of fixed variables in partial differentiation. Consider this typical student response: "If κ and β are defined as such, then $\left(\frac{\partial \beta}{\partial P}\right)_T = \left(\frac{\partial \kappa}{\partial T}\right)_P = 0$ since P has already been held constant for β and T has already been held constant for κ." The student is saying that, since the variable T has been held constant in the first derivative of volume within the definition of κ, then any subsequent differentiation with respect to that variable will yield zero as simply the derivative of a constant. This specific difficulty was as prevalent in student responses as correct answers, and a few otherwise correct answers relied on this reasoning to arrive at the correct result on the homework problem.

Such responses seem to indicate confusion between the terms "constant" and "fixed;" one implying a permanent constraint and the other a temporary one. Typical treatments of partial differentiation tend to be less than precise when introducing the terminology, often giving the verbal definition of $\left(\frac{\partial z}{\partial x}\right)_y$ as the partial derivative of z with respect to x *at constant y*, rather than specifically stating that the subscript variable is to be *fixed at a particular value only during the differentiation*. This casual use of terminology can be confusing to students. The notation itself could also be confusing, as few disciplines other than thermal physics make explicit reference to those variables being held fixed, i.e. $\frac{\partial}{\partial P}\left(\left(\frac{\partial V}{\partial T}\right)_P\right)_T$ compared with $\frac{\partial^2 V}{\partial P \partial T}$.

DISCUSSION

It seems that students' desire to set the mixed second partials identically equal to zero is a persistent and strongly held difficulty. Approximately the same proportion of students held these ideas on the exam question as had them in their homework assignment, despite receiving an answer key and a brief explanation by the instructor. Additionally, based on classroom observation data, students in the 2004 course were noticeably animated about this question when their exams were handed back to them. Several of them expressed disbelief that the mixed second partial could be anything but zero due to the variable being held constant.

We believe, however, that this tendency arises chiefly from mathematical errors, and not from any student ideas about the physics. In order to explicate this claim, a brief digression into the graphical interpretation of Clairaut's Theorem is illustrative. Just what does it mean 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?

The first partials tell us how the function varies along one axis, i.e., the tangent slope. Further differentiation by the complementary variable tells us how *that slope* changes with respect to an orthogonal independent variable. This rate of change of the two orthogonal tangent slopes (in the limit) must therefore be equal by Clairaut's Theorem. In the case of an ideal gas (Figure 2(a)), both slopes decrease at the same rate as pressure and temperature increase.

For a function with zero mixed second partials, as in Figure 2(b), there would be no change in the slope along either axis as we move along the other axis. Such a situation is even less interesting than the ideal gas, and is constrained quite artificially. That constraint need not be as severe as the tilted plane shown in Figure 2(b), but must be limited along one of the independent axes such that all slopes with respect to that variable can change along that variable axis, but must be constant (parallel tangents) at all locations while moving along the orthogonal axis.

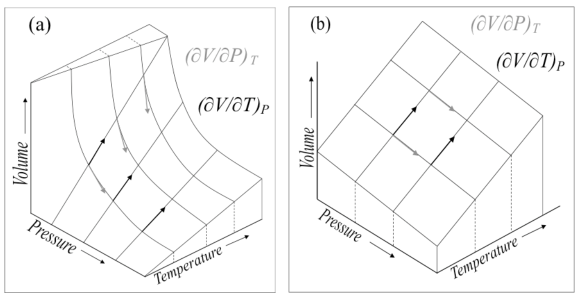

FIGURE 2. *P-V-T* diagram for (a) an ideal gas, and (b) a substance with zero mixed second partials of volume.

Thinking about the physical situation should help students in realizing that the situation is unlikely at best. Consequently, we have developed a question designed to see if students are aware of the physical implications of forcing the derivatives of β and κ to be zero: "The thermal expansivity of mercury is 37.5 K^{-1} at 1 atm and a given temperature. Do you expect the expansivity to increase, decrease, or remain the same if the sample pressure were 1000 atm instead at the same temperature? Please explain your reasoning." This question, along with the graphical reasoning depicted above, will be incorporated into a tutorial designed to improve student understanding of mixed second partials. We expect that students should then be able to use this mathematical reasoning to verify any physical intuitions about changes in these material properties.

Comparison with the Maxwell Relations

We have documented related difficulties with mixed second partials used in the Maxwell relations, which are applications of Clairaut's Theorem to the so-called thermodynamic potentials (e.g., *U, H, F, G*) [5]. In particular, students seemed to have difficulties with the physical interpretations of the equated partials. Even those students who could derive the Maxwell relations often lacked any ability to apply them in a physical context, or even to interpret their meaning.

In contrast to the results in the β–κ question, *no* students indicated that the partial derivatives generating the Maxwell relations were identically equal to zero. This suggests that students may not consider the mathematical significance of the Maxwell relations, i.e., that they are mixed second partial derivatives. We believe two factors support this idea. First, the Maxwell relations are typically used as relationships between first partials of various thermodynamic functions, e.g., entropy, volume, pressure, temperature, rather than as second partials of the thermodynamic potentials, while β and κ are defined using first partials of volume, so that their derivatives clearly include second partials. That is, for the Maxwell relations, students are interpreting the functions as *variables* rather than *coefficients* (of a total differential), allowing a nonzero mixed differentiation. Second, it may be that students consider β and κ as physical constants rather than functions, leading to derivative values of zero.

Summary

In particular, we see evidence 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.

Our results also suggest that students do not see the Maxwell relations as relating mixed second partial derivatives, implying a disconnect between the mathematical and physical meanings of these relations.

The results presented here, in conjunction with prior work, indicate that students often enter upper-level physics courses lacking the necessary (and assumed) prerequisite mathematics knowledge and/or the ability to apply it productively in a physical context. Students avoid using physical reasoning to verify their mathematical results. Taken as a whole, these results point to difficulties among advanced students in incorporating mathematics and physics into a coherent framework.

We are currently developing curricular materials aimed at addressing some of these issues in the context of state functions and material properties.

ACKNOWLEDGMENT

Supported in part by NSF Grant PHY-0406764.

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