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Partial derivatives as a new representation in thermodynamics

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Role of partial derivatives in thermodynamics

Thermodynamics utilizes

- Multivariable functions, *e.g.*, $U = U(S, V, N\ldots)$
- Equations of state (functions), *e.g.*,

$$v = V/N = kT/P; \qquad f\,(P, V, N, T) = 0$$

Thermodynamic processes require changes in state functions
⇒ exact differentials and partial derivatives, *e.g.:*

$$dU = TdS - PdV + \mu dN$$

$$P = -\,(\partial U/\,\partial V)_{S,N}$$

Issues regarding student understanding of partial derivatives

- Understand the distinction between total derivative (i.e., of one-variable function) and partial derivatives
- Recognize empirical implications of (first-order) partial derivative
- Understand total differentials (of multivariable functions)
- Apply chain rule and product rule when appropriate
- Recognize significance of *second-order* partial derivatives – especially *mixed* second partials

Thompson, Bucy, Mountcastle, *2005 PERC Proc.*, AIP Conf Proc **818**, 77-80 (2006).
Bucy, Thompson, Mountcastle, *2006 PERC Proc.,* AIP Conf. Proc. **883**, 157-160 (2007).

Student understanding of partial derivatives

- Students can recognize what a first partial derivative is and does, for the most part *
  - understand the distinction between total and partial derivatives
  - state empirical meaning of partial derivative
- What about *second-order* partial derivatives – especially *mixed* second partials?
  - derivatives of material properties
  - the Maxwell relations

J.R. Thompson, B.R. Bucy, D.B. Mountcastle, *2005 PERC Proc.*, AIP Conf Proc **818**, 77-80 (2006).
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Paradigms in Physics: Energy and Entropy

- Student-centered
  - Small WhiteBoard Questions
  - Large WhiteBoard Questions
  - Kinesthetic Activities
- Lab activities
  - rubber band lab
- Interlude: "Just-in-Time Math"
  - week before OR day before physics instruction
  - Bridging math and physics

Paradigms in Physics: Energy and Entropy

- Activities in E&E
  - New Interlude activities
    - Partial derivatives: piece of UMaine tutorial*
    - Differentials
      - physics formula vs. math expression
      - derivative tree
    - Legendre Transforms
  - "Name the experiment!"
  - Model system: rubber band (vs. ideal gas)

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*B.R. Bucy, J.R. Thompson, D.B. Mountcastle, *2006 PERC Proc.,* AIP Conf. Proc. **883**, 157-160 (2007).
B.R. Bucy, Ph.D. dissertation, U.Maine, 2007.

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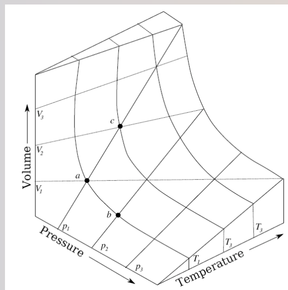
Representations used

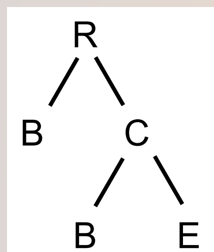
Partial derivatives

- symbolic $\left(\frac{\partial S}{\partial p}\right)_T$
- graphical

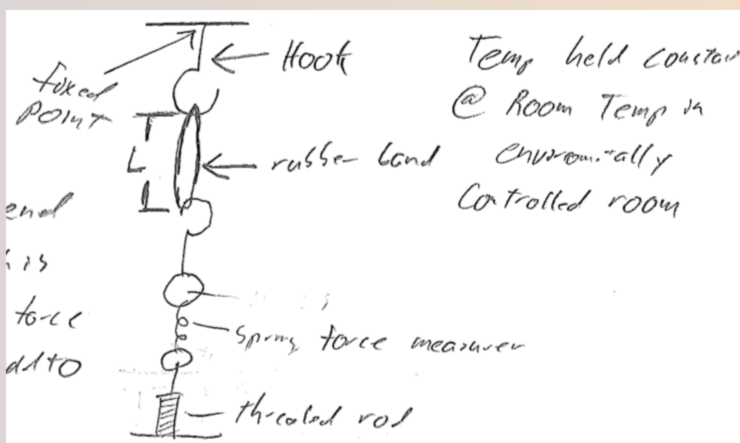


- "derivative tree"

R(B,C) ; C(B,E)



- as experiment



Differentials

- symbolic: math

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

- symbolic: physics

$$dU = TdS + \tau dL$$

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Questions: total differentials and partial derivatives

Math version

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.

Physics version

The Gibbs Free Energy, G, is a function of the independent variables T and P,
i.e., it can be written as $G(T,P)$.
The total differential of G can be written as $dG = -SdT + VdP$.
Interpret the above equation in order to determine an expression for the entropy, S.

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Mixed second partial derivatives questions

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

$$\alpha = -\frac{1}{Z}\frac{\partial Z}{\partial x} \qquad \beta = \frac{1}{Z}\frac{\partial Z}{\partial y}$$

Show that in general

$$\left(\frac{\partial \beta}{\partial P}\right)_T + \left(\frac{\partial \kappa}{\partial T}\right)_P = 0\,.$$

Show that in general

$$\frac{\partial \alpha}{\partial y} + \frac{\partial \beta}{\partial x} = 0.$$

Bucy, Thompson, Mountcastle, *2006 PERC Proc.*, AIP Conf. Proc. **883**, 157-160 (2007).

Christensen and Thompson, in *Proc. 13th Ann. Conf. on Research in Undergraduate Mathematics Education* (2010).

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"Name the experiment!" question

Question 1 Describe an experiment that would measure

$$\left(\frac{\partial \tau}{\partial L}\right)_T$$

where τ is the tension in a rubber band, L is its length, and T is its temperature. Be explicit about how you would perform the measurement, and draw a sketch of your apparatus.

- Early in class: just physical description of experiment
- By end of term: partial that needs Maxwell relation to get experiment

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Differentials in physics: previous research on student ideas

M. Artigue, J. Menigaux, & L. Viennot, *Eur. J. Phys.* **11,** 262-267 (1990)

- Parallel conceptions among introductory students in both disciplines:
  - a mathematical object or function (linear approximation)
  - a small part of a physical quantity
- Students see the idea of “differential as a linear approximation” as an excuse for loose reasoning

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Partial derivatives and exact differentials

At Maine: Asked immediately before instruction on the Maxwell relations

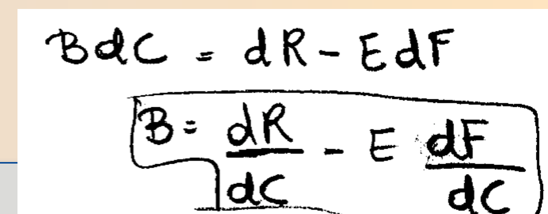
R is a function of the independent variables *C* and *F*, that is $R = R(C,F)$.
The total differential of *R* can be written as

$$dR = BdC + EdF.$$

a. Interpret the above equation in order to determine an expression for *B*.

desired response: $B = (\partial R/ \partial C)_F$

- Omission of requirement of constant *F*
- Found *algebraic* solution for *B*



Some students treated differential expressions algebraically

Students do not recognize the physical significance of the differentials and the relevance of the context

Total differentials questions: math version

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*.

PRETEST	Energy and Entropy N=15 (N_{class}=1)	Thermo (Ithaca) N=4 (N_{class}=1)	Physical Thermo. N=7 (N_{class}=1)
Correct (differential soln)	**1 (7%)**	**0 (0%)**	**5 (72%)**
Algebraic soln	***4 (27%)***	***2 (50%)***	***2 (28%)***

$BdC = dR - EdF$

$$B = \frac{dR}{dC} - E\frac{dF}{dC}$$

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Total differentials questions: physics version

The Gibbs Free Energy, *G,* is a function of the independent variables *T* and *P*,

i.e., it can be written as *G(T,P)*.

The total differential of *G* can be written as $dG = -SdT + VdP$.

Interpret the above equation in order to determine an expression for the entropy, *S*.

Energy and Entropy	Pretest N=37 (N_{class}=2)	Post-test N=40 (N_{class}=2)
Correct (differential soln)	**0 (0%)**	**33 (83%)**
Algebraic soln (only or with diff)	***29 (78%)***	***5 (13%)***

$$S = -\frac{dG - VdP}{dT}$$

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β–κ question: *Calculus III* issues

$$\left(\frac{\partial \beta}{\partial P}\right)_T + \left(\frac{\partial \kappa}{\partial T}\right)_P = 0$$

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

"If β and κ 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."

$$\frac{\partial}{\partial P}\left(\left(\frac{\partial V}{\partial T}\right)_P\right)_T$$ compared with $$\frac{\partial^2 V}{\partial P\,\partial T}$$

"hold variable constant" = "make the variable a constant"

constant ≠ fixed

Mixed second partials question: Results

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Show that in general

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

Student Pretest Responses	Energy and Entropy $N=15$ ($N_{\text{class}}=1$)	Physical Thermodynamics $N=26$ ($N_{\text{class}}=4$)
Mixed 2nd Partials Equal	**1 *(7%)***	**14 (54%)**
Each Equals Zero	***4 (27%)***	***9 (35%)***

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Mixed second partials question: Results

$$\alpha = -\frac{1}{Z}\frac{\partial Z}{\partial x}$$

$$\beta = \frac{1}{Z}\frac{\partial Z}{\partial y}$$

Show that in general

$$\frac{\partial \alpha}{\partial y} + \frac{\partial \beta}{\partial x} = 0.$$

Student Responses	Energy and Entropy N=52 (N_{class}=3)	Calculus III (UMaine) N=64
Mixed 2nd Partials Equal	**19 (37%)**	**14 (22%)**
Each Equals Zero	***9 (17%)***	***25 (39%)***
Calculus 1 issues (product/chain)	**33 (63%)**	

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name the experiment results

Question 1 Describe an experiment that would measure

$$\left(\frac{\partial \tau}{\partial L}\right)_T$$

where τ is the tension in a rubber band, L is its length, and T is its temperature. Be explicit about how you would perform the measurement, and draw a sketch of your apparatus.

- Early in class: just physical description of experiment
- By end of term: partial that needs Maxwell relation to get experiment
  (i.e., would need to measure *S* otherwise)