Addressing Student Difficulties with Statistical Mechanics: The Boltzmann Factor

Trevor I. Smith*, John R. Thompson*,† and Donald B. Mountcastle*

*Department of Physics & Astronomy, University of Maine, Orono, ME 04469
†Maine Center for Research in STEM Education, University of Maine, Orono, ME 04469

Abstract. As part of research into student understanding of topics related to thermodynamics and statistical mechanics at the upper division, we have identified student difficulties in applying concepts related to the Boltzmann factor and the canonical partition function. With this in mind, we have developed a guided-inquiry worksheet activity (tutorial) designed to help students develop a better understanding of where the Boltzmann factor comes from and why it is useful. The tutorial guides students through the derivation of both the Boltzmann factor and the canonical partition function. Preliminary results suggest that students who participated in the tutorial had a higher success rate on assessment items than students who had only received lecture instruction on the topic. We present results that motivate the need for this tutorial, the outline of the derivation used, and results from implementations of the tutorial.

Keywords: Statistical Mechanics, Thermal Physics, Boltzmann Factor, Physics Education Research
PACS: 01.30.Cc, 01.40.Fk, 01.40.G-, 05.20.-y

INTRODUCTION

As part of a larger project on the learning and teaching of thermal physics at the upper division, we have identified several specific student difficulties in relevant courses. One area of focus is the Boltzmann factor and the canonical partition function. The Boltzmann factor (BF) is proportional to the probability that a system in thermal equilibrium is in a particular energy state:

$$P(\Psi_j) \propto e^{-E_j/kT}, \qquad (1)$$

where Ψ_j denotes the energy eigenstate with eigenvalue E_j. The canonical partition function (Z) is the result of the normalization constraint that the sum of $P(\Psi_j)$ over all j must be unity:

$$P(\Psi_j) = \frac{e^{-E_j/kT}}{Z} \rightarrow Z = \sum_i e^{-E_i/kT}. \qquad (2)$$

The BF and Z may be used to determine many thermodynamic quantities of a system at fixed temperature, including internal energy, Helmholtz free energy, entropy, and heat capacity. As such they are considered cornerstones of statistical mechanics.

Studies show that guided-inquiry worksheet activities (tutorials) are effective supplements to traditional lecture-based instruction in introductory physics courses (e.g. ref. 1), and that they may be beneficial to upper-division students as well.[2] With this in mind we have developed a Boltzmann factor tutorial (BFT) that guides students through the characteristic derivation of the BF in order to promote a deeper understanding of its origin than is typically gained from lectures alone. We expect that this deeper understanding will result in an improved ability to appropriately apply the BF to relevant physical scenarios. In the following sections we discuss some specific difficulties seen in student understanding of the BF and Z. We then summarize the pedagogical approach used within the BFT. We conclude by presenting some preliminary results and implications for future research.

STUDENT RECOGNITION OF THE USE OF THE BOLTZMANN FACTOR

One desired result of teaching students about the BF is that they will recognize applicable situations and use it to make claims about probabilities. The probability ratios question (PRQ, shown in Figure 1) probes their ability to do this. The correct solution to the PRQ requires students to recognize two pieces of information:

- The probability of the particle being in each state will be proportional to the BF for that state
- The energy difference between the states for each ratio is the same ($\Delta E = 0.05eV$)

The first item implies that each ratio of probabilities will be an exponential function of the energy difference between the two states. The second item reveals that both pairs of ratios in the PRQ are equal.

Starting in 2005, the PRQ was given to students in the Statistical Mechanics course (PHY463) at the University of Maine (UMaine) after they had completed all lecture instruction on the BF and Z. PHY463 is a semester-long

Consider a particle (Particle A) in a system with three evenly spaced energy levels, as seen in the figure at right. The probability that Particle A is in the n^{th} energy level is $P_A(n)$.

$n=3$	———	$0.10eV$
$n=2$	———	$0.05eV$
$n=1$	———	$0.00eV$

A. Is the ratio of the probabilities $\frac{P_A(3)}{P_A(2)}$ *greater than*, *less than*, or *equal to* the ratio of the probabilities $\frac{P_A(2)}{P_A(1)}$? Please explain your reasoning.

B. Consider a second single particle, Particle B, that can also only be in three states. The energies of the three states of each system are listed in the table at right. Both systems are in equilibrium with a reservoir at temperature T.

n	Particle A	Particle B
1	$0.00eV$	$-0.05eV$
2	$+0.05eV$	$0.00eV$
3	$+0.10eV$	$+0.05eV$

Is the ratio of the probabilities $\frac{P_B(3)}{P_B(2)}$ for Particle B *greater than*, *less than*, or *equal to* the ratio of the probabilities $\frac{P_A(3)}{P_A(2)}$ for Particle A? Please explain your reasoning.

FIGURE 1. Probability ratios question (PRQ).

course dedicated to statistical mechanics offered every spring. The majority of students in PHY463 are senior physics majors, many of whom have taken a semester-long classical thermodynamics course offered in the fall. The class population usually includes between 6 and 12 students each semester and includes physics graduate students as well as some undergraduates majoring in related fields (mathematics, chemistry, etc.). Figure 2 shows the response frequencies for the entire 5-year data corpus. It should be noted that some incorrect responses were not accompanied by thorough or consistent reasoning, and that some students were inconsistent between parts A and B of the PRQ.

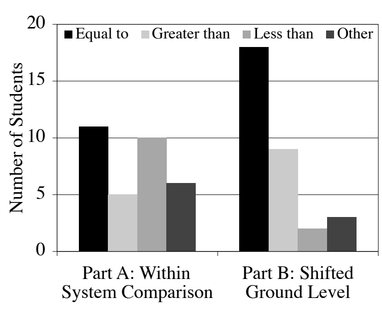

FIGURE 2. Response frequencies for the probability ratios question after lecture instruction. $N = 32$.

Considering Figure 1 and Figure 2, we can see that the most common incorrect response for both parts of the PRQ is the idea that, $\frac{P(0.10eV)}{P(0.05eV)} < \frac{P(0.05eV)}{P(0.00eV)}$ ("less than" for part A and "greater than" for part B). These answers are considered consistent since the second and third energy

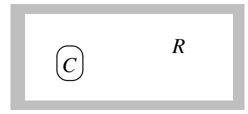

FIGURE 3. An isolated container of an ideal gas is separated into a small system (C) and a large reservoir (R). The label "C" is used to avoid confusion with entropy.

levels in system B have the same numerical values as the first and second energy levels in system A. One student justified this response for part A stating that, "...the most probable state...is the one with the lowest energy; hence $P_A(1) > P_A(2) > P_A(3)$," and indicated that, $\frac{P_A(3)}{P_A(2)} < \frac{P_A(2)}{P_A(1)}$. This could be seen as an application of the *Numerator Principle*, with which students compare fractions based solely on the relative magnitudes of their numerators.[3] Figure 2 also shows us that students are more likely to answer part B correctly (which discusses an effective shift in the ground state energy of a system) than part A (comparing two different sets of probabilities for states within the same system). Another student articulated this very clearly in stating that, "...it does not matter what the 'baseline' is, just the amount of energy added."

STUDENT APPRECIATION OF THE ORIGIN OF THE BOLTZMANN FACTOR

During tutorial development one author (TIS) conducted individual interviews with 4 students after classroom instruction to determine their familiarity with the BF, its applications, and its origin. The interview consisted of asking students to complete the second half of a preliminary version of the BFT. Students worked individually, and the interviewer solicited explanations for their work and gave assistance when required. Two interview participants had participated in the first half of the BFT during class, and the other two had not seen the first half. One student (Joel, who had seen part of the first half of the BFT in class) was very familiar with the applications of the BF and seemed to be just as familiar with its origin. During his interview Joel was presented with a scenario in which a container of ideal gas is divided into relatively small and large sections (shown in Figure 3). The system of interest (C) is said to be in thermal equilibrium with the reservoir (R). Since the multiplicities of C and R are so different ($\omega_C \ll \omega_R$) a toy model is proposed in which $\omega_{tot} = \omega_C \cdot \omega_R = \omega_R$, and the energy of C can only take on a handful of discrete values, $E_C \in \{E_j\} = \{E_1, E_2, ...\}$ (see Table 1). Joel was given the table of multiplicities and asked to determine which macrostate (defined by E_C) is most probable and which is least probable. The desired solution is that the macrostate in which R has the largest number of microstates (multiplicity) would be the most probable (E_4 below) since all microstates are equally likely.

TABLE 1. Values of energy and multiplicity given to students during the interview and the tutorial (see Figure 3).

E_C	ω_C	E_R	ω_R
E_1	1	$E_{tot} - E_1$	3×10^{18}
E_2	1	$E_{tot} - E_2$	5×10^{19}
E_3	1	$E_{tot} - E_3$	4×10^{17}
E_4	1	$E_{tot} - E_4$	1×10^{20}
E_5	1	$E_{tot} - E_5$	7×10^{18}

Rather than reasoning about multiplicities, Joel wanted to use the BF even though no information had been given about the relative energy values. The interviewer asked Joel to show where the BF came from before applying it to this situation, at which point Joel quoted the textbook derivation of the BF practically verbatim. The final portion of Baierlein's mathematical derivation is as follows, [4, p. 92]

$$P(\Psi_j) = \text{const} \times \begin{pmatrix} \text{multiplicity of reservoir} \\ \text{when it has energy } E_{tot} - E_j \end{pmatrix} \quad (3)$$

$$P(\Psi_j) = \text{const} \times \exp\left[\frac{1}{k} S_R(E_{tot} - E_j)\right] \quad (4)$$

$$P(\Psi_j) = (\text{new constant}) \times \exp\left(-E_j/kT\right). \quad (5)$$

When asked how the multiplicity of the reservoir relates to the BF, however, Joel was at a loss. Without explicit help from the interviewer, Joel could not make the connection between the multiplicity of the reservoir and the decaying exponential function of energy that he had (implicitly) written to be proportional to one another. Furthermore, Joel could not relate the physical example used in the text (a "bit of cerium magnesium nitrate...in good thermal contact with a relatively large copper disc"[4, p. 91]) to the ideal gas example used during the interview. Joel's failure to make these connections suggests an incomplete understanding of the physical reasoning used to derive the BF even after memorizing the textbook derivation.

Joel was also unique in that he was the only student interviewed who could spontaneously generate a Taylor series expansion of entropy as a function of energy as it relates to the given physical scenario, the necessary step to go from Eq. 4 to Eq. 5. Unfortunately the interviewer did not question Joel further as to his understanding of the Taylor series. Another 2 students were able to generate the appropriate expansion when given a generic mathematical expression for a Taylor series, but the final student (of 4) was unable to make any connections between the generic Taylor expansion and the physical scenario without explicit instruction from the interviewer. These results indicate that student understanding of the motivation for a Taylor series expansion (a crucial part of the derivation of the BF) cannot be taken for granted. In contrast, results from a supplement to the PRQ pretest in two years showed that 9 out of 16 students were able to correctly interpret a Taylor series expansion of a function given its graph.

OVERVIEW OF TUTORIAL

Given students' apparent inabilities to properly use the BF or to meaningfully articulate its origin, we created a tutorial to guide students through the derivation of the BF and encourage deep connections between the physical quantities involved. The derivation chosen for use in the BFT is found in many widely used textbooks including the one used at UMaine.[4, 5][1] The BFT begins by asking students to consider an isolated container of an ideal gas. They are guided to recognize that the container will have a fixed internal energy (E_{tot}) and multiplicity (ω_{tot}), and that all microstates are equally probable.

Once the properties of the isolated container (microcanonical ensemble) have been established, the students are told that the container is actually divided into the sections shown in Figure 3 and asked to compare the values of the intensive and extensive properties of C to those of R. Using the toy model described above ($\omega_C = 1$) the students determine which value of E_C is most probable and which is least probable, leading them to the proportionality between probability and the multiplicity of the reservoir ($P(\Psi_j) \propto \omega_R(\Psi_j)$).

The final section of the BFT is the derivation of the BF itself. Using a Taylor series expansion of $S_R(E_R)$ about E_{tot}, one obtains S_R as a linear function of E_C:

$$S_R(E_R) = S_R(E_{tot}) - \left.\frac{\partial S_R}{\partial E_R}\right|_{E_{tot}} E_C + \ldots \approx S_{tot} - \frac{E_C}{T}, \quad (6)$$

where $\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$ from the first law of thermodynamics. Then, using the relationship between entropy and multiplicity ($S = k\ln(\omega)$), ω_R may be written as a decaying exponential of the energy of C (the BF):

$$\omega_R = e^{S_R/k} \approx e^{S_{tot}/k - E_C/kT} \rightarrow \omega_R \propto e^{-E_C/kT}. \quad (7)$$

Students have now found that $P(\Psi_j) \propto \omega_R(\Psi_j)$ and that $\omega_R(\Psi_j) \propto e^{-E_j/kT}$, leading to the proportionality in Eq. 1. Finally, they are asked to normalize the probability, thus deriving Z (see Eq. 2).

To ensure that students could complete the Taylor series portion of the derivation we developed a homework

[1] Notably, Schroeder's derivation differs from these other texts.[6]

assignment to be completed by the students and brought to class for tutorial. This assignment asks the students to write the Taylor series expansion of $S(E)$ about the fixed value E_0. During the BFT the students are asked to relate the generic physical variables in this assignment to those relevant to the physical scenario in question.

IMPLEMENTATION AND RESULTS

The BFT was administered in PHY463 after all lecture instruction on the BF in two consecutive years. Students were given one 50-minute class period to complete the BFT. The course instructor and one TA were available during the tutorial session. No course credit is offered for the tutorial itself, but the course grade includes an in-class participation aspect. Data from both implementations of the BFT indicate that students benefit from going through the tutorial whether or not they knew how to use the BF on the PRQ after lecture instruction alone.

The PRQ or an analogous question was given on a course examination after each implementation of the BFT. From these two years we have 15 sets of matched data: 6 undergraduate physics majors and 4 graduate students in physics who participated in the BFT, and 5 undergraduates who did not come to class the day of the BFT. Additionally, 5 undergraduate students who participated in the BFT did not complete the pre-tutorial assessment. Table 2 shows how many of each of these groups answered correctly with correct reasoning both before and after tutorial instruction. While these findings are not conclusive, we are encouraged that the BFT helps students recognize the utility of the BF and how to apply it properly.

TABLE 2. Number correct on pre- and post- tutorial assessments. Percentages shown in parentheses.

	N	Pre-tutorial	Post-tutorial
BFT	6	1 (17%)	5 (83%)
BFT No Pre	5	n/a	5 (100%)
Grad BFT	4	3 (75%)	4 (100%)
No BFT	5	2 (40%)	3 (60%)

In order to check that students were engaging in discussions about the physical concepts and phenomena in the derivation, the tutorial sessions were videotaped. The video data show that the tutorial in fact promotes these conversations and suggest that students are gaining an appreciation for where the BF comes from as a result. It is unclear at present the specific benefits that result from understanding the derivation of an equation in terms of abilities to use the equation, and we are in the process of developing assessment questions to determine the lasting effects of the appreciation students may gain from the BFT.

SUMMARY AND IMPLICATIONS FOR FUTURE WORK

We have shown that students' written responses to a question requiring the use of the Boltzmann factor do not indicate mastery of the topic after lecture instruction alone. We have shown that students who learn the derivation of the BF from the textbook may not have a thorough understanding of the mathematical implications of and physical reasoning behind this derivation (especially the physical motivation for using a Taylor series expansion). Moreover, we see that students benefit from our tutorial, gaining an increased ability to use the BF in quantitative scenarios (as shown on the course examination). Video data suggest that students may also gain an appreciation for the origin of the BF, and we are developing assessment items to determine the effects of understanding this origin.

We have begun implementing the BFT in different institutions to gather data from a more diverse population. We have also begun conducting interviews to assess student understanding of the relationship between the BF and the density of states function. Preliminary results suggest that a thorough understanding of the origin of the BF is required to fully appreciate this relationship. These interviews will also determine how well students truly understand the derivation they worked through during the tutorial session.

ACKNOWLEDGMENTS

We gratefully acknowledge the contributions of Brandon Bucy, Warren Christensen, and Evan Pollock to the various stages of this project. We thank the rest of the UMaine Physics Education Research Laboratory for feedback on several preliminary versions of the tutorial. We also thank our three reviewers for helpful comments on the structure and content of this paper.

REFERENCES

1. N. D. Finkelstein and S. J. Pollock, *Phys. Rev. ST Phys. Educ. Res.* **1**, 010101 (2005).
2. S. V. Chasteen and S. J. Pollock, *AIP Conf. Proc.* **1064**, 91–94 (2008).
3. J. P. Smith, *Cognition & Instruction* **13**, 3–50 (1995).
4. R. Baierlein, *Thermal Physics*, Cambridge University Press, Cambridge, UK, 1999, pp. 91–93.
5. F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill, Inc., Boston, MA, 1965, pp. 202–204.
6. D. V. Schroeder, *An Introduction to Thermal Physics*, Addison-Wesley, San Francisco, CA, 2000, pp. 220–225.