

# Exploring the thermodynamics of a rubber band

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We describe an upper-division experiment in thermal physics where students measure the tension of a rubber band as a function of temperature and length, and use a Maxwell relation to find the change in internal energy and entropy for an isothermal stretch. This allows students to experimentally check the predictions of the entropic spring model for elastomers and observe that the entropy does indeed decrease as a rubber band is stretched.

## I. INTRODUCTION

Rubber bands provide an appealing subject for a thermal physics laboratory experiment. In contrast to most solids and liquids, which respond weakly to small changes in temperature, rubber's tension noticeably increases with increasing temperature. This Gough-Joule effect—which is contrary to student expectations—is a standard example in courses in statistical mechanics. Combined with low cost and familiarity to students, these factors make the lowly rubber band an almost ideal material for a thermal physics experiment.

Numerous laboratories and classroom demonstrations address how the tension of rubber bands increases with temperature,<sup>1–6</sup> or to measure mechanical properties of rubber bands at room temperature.<sup>7,8</sup> However, few of these experiments involve carefully measuring a rubber band's equation of state. The majority of the experiments that demonstrate the surprising dependence of tension on temperature make a purely qualitative demonstration in which the temperature is changed, but not measured.<sup>2–5</sup> Savarino and Fisch describe a laboratory experiment that involves measuring the tension in a rubber band as a function of temperature and extension, using a space heater to change the temperature of the rubber band.<sup>6</sup> Their experiment is used to teach data analysis methods by using multiple approaches to extract the parameters in an equation of state for the rubber band; however, there is no thermodynamic analysis of the resulting values, nor do they address the applicability of the equation of state. In this paper, we introduce a rubber band experiment that uses Maxwell relations to measure changes in entropy and internal energy.

## II. THEORETICAL BACKGROUND

The thermodynamic identity for a rubber band is

$$dU = TdS + \tau dL, \quad (1)$$

where  $T$  is the temperature,  $\tau$  is the tension,  $U$  is the internal energy of the rubber band,  $S$  is its entropy, and  $L$  is its length. This relation follows naturally from the

First Law of Thermodynamics, combined with the definition of work as the dot product of force and displacement. We could use the differential relation given in Eq. (1), but since we are working at constant  $T$ , the Helmholtz free energy  $F$  provides a more useful starting point

$$dF = \tau dL - SdT. \quad (2)$$

The corresponding Maxwell relation

$$-\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial \tau}{\partial T}\right)_L, \quad (3)$$

tells us that we can determine how entropy changes with length at fixed temperature by measuring how the tension changes with temperature at fixed length. At the same time, measurement of the tension reveals how the free energy varies with isothermal changes in length

$$\tau = \left(\frac{\partial F}{\partial L}\right)_T. \quad (4)$$

Thus, measurements of  $\tau$  and  $(\partial\tau/\partial T)_L$ , as a function of length, allow us to find  $\Delta F$ ,  $\Delta S$ , and ultimately  $\Delta U$  by integration.

## III. EXPERIMENTAL ARRANGEMENT

Figure 1 shows a photo and a schematic of the experimental setup. Students stretch a rubber band from a hook in a stopper at the bottom of a glass tube to a chain connected to a force meter at the top of the tube. This setup allows the rubber band to be completely submerged when the tube is filled with water. It also allows students to quickly alter the length of the rubber band by changing which link of the chain is hooked onto the force meter.

During the experiment, students adjust the temperature by pouring water into the tube. They then measure tension as a function of rubber band length for different water temperatures. By emptying the water out of the top of the tube, students can efficiently replace the water and change the temperature using water prepared by mixing boiling water, room-temperature water, and ice.

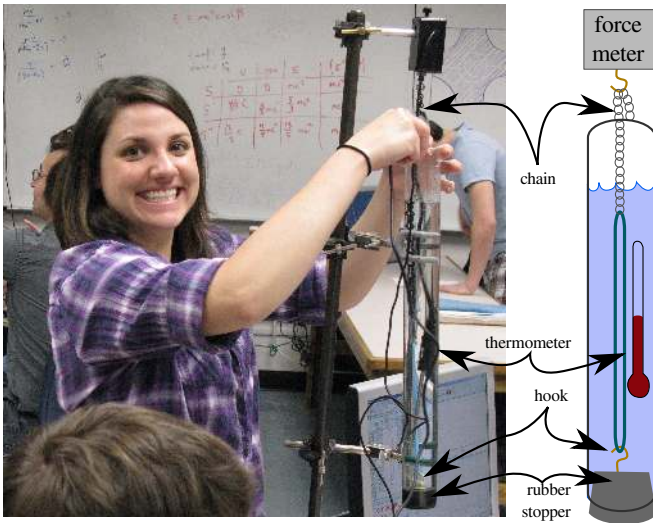


FIG. 1: A photograph and schematic of the experimental apparatus.

Once the water is added to the system, the temperature is monitored with an electronic thermometer while students make their measurements; several measurements can be made for different lengths before the temperature has dropped (or risen) by as much as  $1^\circ\text{C}$ .

Unfortunately, deviations from ideal elastic behavior present a major challenge. Ideally, a rubber band should return to its original state when released. However, rubber deviates from elastic behavior in two ways. First, rubber bands only slowly return to their original state after being released, leading to hysteresis in tension measurements—a different tension is measured when a rubber band is stretched to a given length than when it is stretched further and relaxed to the same length. The second deviation is due to plasticity—if a rubber band remains stretched for too long, it never returns to its original length. Avoiding very high tensions (greater than about  $6\text{ N}$ ) and maintaining a relaxed state between tension measurements (e.g. while changing the temperature) reduces plastic behavior.

#### IV. ANALYSIS

As shown in Fig. 2, students plot tension versus length for a few different temperatures. The data in this figure was taken starting at the shortest length ( $24.5\text{ cm}$ ), moving to the longest length ( $38.8\text{ cm}$ ), and returning again to the shortest length. Solid lines show the tension as the rubber band is stretched and dashed lines show the tension as it is subsequently relaxed. The close proximity of the measured curves shows that the variation of the tension due to temperature ( $\sim 0.2\text{ N}$ ) is small compared with its variation with length ( $\sim 2\text{ N}$ ). Figure 2 also shows that the tension increases with increasing temperature, contrary to student expectations.

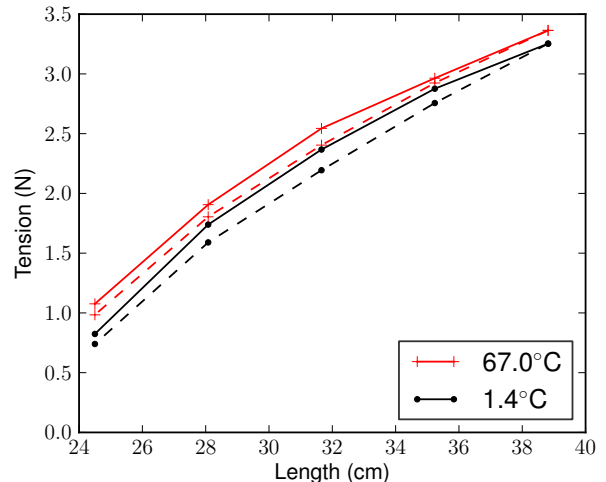


FIG. 2: (color online) Tension versus length at the highest and lowest temperatures measured. The solid lines are the tension as the rubber band is stretched and the dashed lines are the tension as it relaxes. The difference between the two curves is due to hysteresis.

The hysteretic behavior of the rubber band is easily visible in Fig. 2. The tension during stretching is  $\sim 0.1\text{ N}$  greater than the tension relaxing (at the maximum length there is no hysteresis because this point was only measured once). Although this change in tension is less than 10% of the measured value, it is comparable to the change in tension due to temperature. By measuring the tension for the same sequence of lengths—and in the same order—students can achieve reproducible results that distinguish between the effects of temperature and hysteresis.

Using the same data, students next plot tension versus temperature for each of the measured lengths, as shown in Fig. 3. The trend of increasing tension with increasing temperature is again evident. Because we plot all temperatures and lengths that were measured in this plot, it is apparent that experimental uncertainties in tension are significant. Some of these uncertainties come from hysteretic effects, which can be seen by comparing the solid and dashed lines, which correspond respectively to tensions measured while stretching and relaxing the rubber band.

Because most errors are due to rate-dependent hysteretic and plastic effects—which tend to be systematic, rather than statistical—error analysis is challenging in this experiment. These effects depend on the time the rubber band spends at each length before the tension measurement is taken, which is challenging to control. The thermal equilibrium tension should be measured after waiting for the tension to stabilize after changing the length. However, the tension takes a long time to fully stabilize—too long for the experiment to be completed in a few hours—and waiting for this to happen would

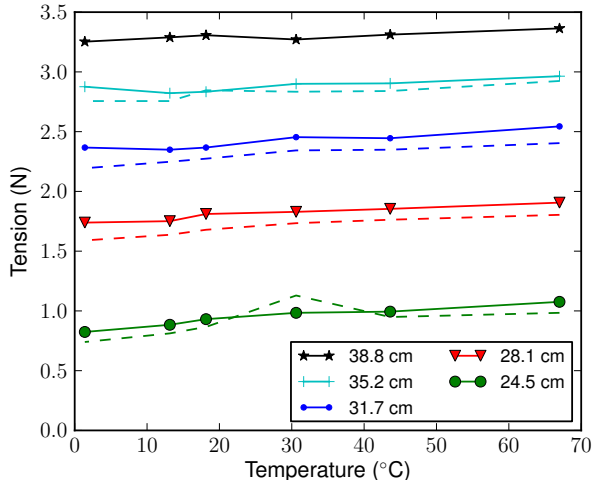


FIG. 3: (color online) Tension versus temperature for each measured length. As in Fig. 2, the solid lines represent measurements taken with increasing length, while dashed lines correspond to decreasing length.

Potential Change (J)	
$T\Delta S$	-0.09
$\Delta F$	0.22
$\Delta U$	0.13

TABLE I: Results for changes in thermodynamic potentials found by integrating the curves in Figs. 2 and 4. This data corresponds to an isothermal stretch of 14 cm at 30 °C.

allow the rubber band to plastically deform. Therefore, instead of waiting for the tension to completely stabilize, we merely wait for it to stop changing rapidly. This leads to hysteresis in our measurements, and errors due to the human choice of how long is long enough to wait while making each measurement. We avoid taking temperature measurements in monotonic order so as to avoid any confusion between temperature dependence and the effect of plasticity.

Students complete their analysis by calculating the change in internal energy, free energy, and entropy for an isothermal stretch of their rubber band at a specific temperature of their choosing. They first numerically integrate the tension with respect to length to get the work done on the rubber band, which is the change in Helmholtz free energy when their rubber band is isothermally stretched

$$\Delta F|_T = \int \tau dL. \quad (5)$$

Next, students use the slope of each curve in Fig. 3 and the Maxwell relation (3) to find  $(\partial S/\partial L)_T$  as a function of length (see Fig. 4). In principle, this derivative will depend on temperature, but as can be seen from the linearity of the curves in Fig. 3, it is essentially constant

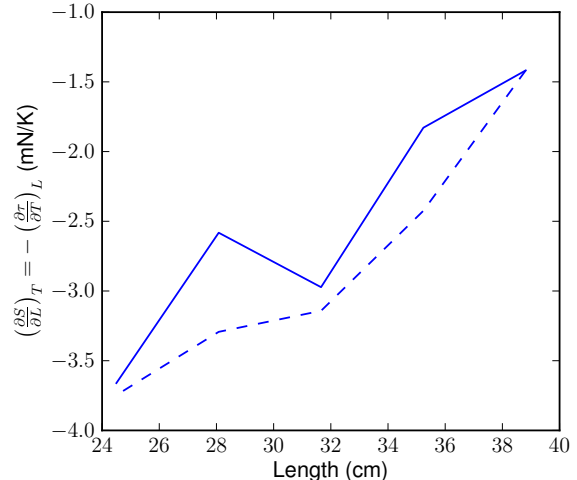


FIG. 4:  $(\partial S/\partial L)_T$  versus length, as extracted from the slopes found from Fig. 3. The solid and dashed lines respectively correspond to slopes taken from the data as the rubber band is stretched and relaxed.

over the range of temperatures studied. Once students have created Fig. 4, they can numerically integrate with respect to length to find the entropy change for their isothermal stretch

$$\Delta S|_T = \int \left( \frac{\partial S}{\partial L} \right)_T dL. \quad (6)$$

Combining this change in entropy with the change in free energy found earlier and the definition of the Helmholtz free energy  $F = U - TS$ , students find the change in internal energy for the isothermal stretch. Table I gives the results for the (student) data shown in this paper.

Finally, we ask students to compare the change in internal energy  $\Delta U$  during their isothermal stretch with the amount of energy transferred to the surroundings by heating, given by  $-T\Delta S$ . This is an interesting comparison because in the entropic spring model the internal energy will not change as the material is stretched, while in an ordinary material the heat is negligible when compared with the change in internal energy as it is stretched. Thus a comparison of these two quantities provides a measure of the applicability of the entropic spring model. Real rubber bands lie somewhere between these two extremes, and students typically find that the values of  $\Delta U$  and  $-T\Delta S$  are comparable, indicating that it would be inappropriate to neglect either term in a quantitative model.

## V. STUDENT DIFFICULTIES

Students find a few steps in the analysis challenging, and these aspects of the analysis provide useful and important learning experiences that are not present elsewhere in our curriculum. The first challenge is that students are forced to deal with data in multiple dimensions:

tension is measured as a function of both length and temperature and must be plotted as a function of each variable. This poses a purely computational difficulty, but also serves to highlight the multidimensional nature of thermodynamics, which causes particular challenges in the context of partial derivatives.<sup>9,10</sup> Our students typically overcome this difficulty without the assistance of specifically targeted instruction.

The second challenge that students face is to find a derivative numerically from noisy experimental measurements of tension as a function of temperature. Some students select a small value of  $\Delta T$  to perform a finite difference derivative, a natural inclination given the mathematical definition of a derivative. But such a procedure can cause problems when there is noise in the data. One way we address this problem is by asking students to plot the entire curve so they get a sense of the big picture. In this experiment, the data is essentially linear, which makes it easy to perform a curve fit to find the slope. Alternatively, some students perform a finite difference calculation using two widely separated temperatures to reduce the effects of noise. Dealing with such an approach requires little beyond having students plot the curves before trying to find the slope.

Finally, most of our students struggle when required to numerically integrate their experimental measurements. Before we started providing specific hints, we found that many students would attempt to perform an analytic integral and would find themselves stymied by the lack of a functional form. We now spend a few minutes in class talking about what an integral really is—a summation—and explaining that students will need to perform a numerical integration.

We assign the analysis portion of this experiment in place of a homework assignment so that students can work at their own pace on this challenging assignment. Although the students struggle on this assignment, they are able to find help during office hours and by working together. Alternatively, the analysis could be done as an in-class activity, which would help address some of these difficulties. Doing the analysis in class, however, would likely require that all students use the same software to perform the analysis, and could impose a prohibitive time constraint.

## VI. CONCLUSIONS

In our experience, rubber bands provide a useful system for thermodynamic study. The Gough-Joule effect

is a classic demonstration of entropy in action having an effect that is surprising to students, and the entropic spring model is a standard example in statistical mechanics. We describe an experiment that connects this simplified model with real rubber bands, in which students make measurements that not only demonstrate the qualitative prediction that tension increases with temperature, but also demonstrate the dependence of internal energy on tension—in contrast to the simplistic entropic spring model. Moreover, by using a Maxwell relation to measure entropy we drive home to students that entropy is a real, measurable state variable. The analysis moreover highlights the connection between Helmholtz free energy, internal energy, and entropy, and provides students with a concrete application in which the Helmholtz free energy is useful.

This experiment is practical because temperature strongly influences the mechanical properties of rubber bands. Unfortunately, a related (and less desirable) property of rubber bands is their hysteretic behavior, which makes the experiment challenging while at the same time demonstrating to students the need for careful data acquisition. This experiment also provides an opportunity to discuss the concept of thermal equilibrium in a context that is far more tangible than two abstracted systems in thermal contact. In our experience, the difficulties of working with rubber bands are well balanced by the advantages, both in the behavior that can be observed as well as in the student experience of applying thermodynamics to an everyday object.

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