# 11   Entropy Changes in a Rubber Band

## 11.1   Summary

The relation between work, temperature, and entropy is explored by testing the amount of work required to stretch a rubber band at different temperatuers.  The temperature is controlled using a very thermally stable water jacket around the rubber band, and the work is found using a strain gauge and data logger.

**Objectives**

1. To measure the change of entropy in a system and demonstrate the connection between work, energy, entropy and temperature.

2. To gain experience using data logging software to record measurements.

3. To demonstrate the connection between entropy and the relative amount of order or disorder in a system.

**Equipment**

A rubber band connected to a strain gauge and a transducer that measures extension of the rubber band.  The strain gauge is connected to the rubber band by a flexible steel strip.  The other end of the rubber band is connected via a stiff wire to the sleeve of a transducer.  This is a cylindrical device about 2 cm in diameter with a hollow axis along which a ferrite rod can slide.  The output voltage is sensitive to the position of the ferrite rod.  In the setup here, an aluminium sleeve has been fitted atop the transducer, and the rod attached to it.  The purpose of this is to enable a smooth, easily controllable motion.  The transducer output is fed to the other input channel of the data logger.  An electronics box with the setup contains an amplifier circuit for the strain gauge, a buffer circuit for the transducer, a feedback circuit for the temperature controller, and a digital display for the air and water temperature.  The rubber band is contained within a temperature-controlled water jacket.  There is a tap at the bottom of the jacket allowing you to drain out the hot water and replace it with cold, should it become necessary.

**Principal Data Taken**

1. Force on a rubber band measured with a strain gauge as a function of extension of the rubber band, at 5-6 temperatures ranging from room temperature to ∼95 °C. Data are logged onto a computer and recorded in a spreadsheet for calculation.

2. Associated calibration data to measure the performance of the strain gauge and transducer.

**Things to Watch Out For**

- There are several tricky aspects to this experiment, including the possibility of severe burns from the water in the thermal jacket. **Make sure the water in the jacket doesn't boil!**

- Both the strain gauge and transducer are nonlinear and need to be carefully calibrated. The contracting rubber band won't give the same results as the rubber band in extension. The flexible attachment of the rubber band to the strain gauge may lead to systematic errors.

## 11.2 Theoretical Background

The concept of entropy has always been a difficult one to communicate to students. This is not only due to the artificial feel of the well-known definition of entropy, but also to the lack of simple laboratory experiments for measuring entropy changes and for demonstrating its physical significance. In this experiment a rubber cord is stretched and relaxed to demonstrate the change in its entropy and other thermodynamic quantities. Rubber has been chosen because the changes in it are much larger than in most other materials (Treloar 1967). It is also particularly suited to demonstrating, at least qualitatively, the connection between entropy and disorder. The extension of rubber causes it to crystallise: that is, the tangled long-chain molecules of the unstretched rubber tend to form parallel, regular bundles. The disorder of the original situation is decreased by the extension, leading to a relatively large decrease in entropy (Mortlock 1972). This experiment does not prove the above theory of rubber behaviour but will give results that are consistent with the theory. It is important to appreciate that the total amount of entropy remains very difficult to quantify; you will only be able to measure changes in entropy.

The first law of thermodynamics states that the change in internal energy dU of any system is equal to the sum of the work dW done on the system and the heat dQ added to it:

$$dU = dQ + dW \qquad (11.1)$$

When a rubber band is stretched by the application of a force $f$, we may neglect the small change in volume and write

$$dW = f dl \qquad (11.2)$$

Since the process is a reversible one, we can express dQ in terms of the **entropy change** dS using the definition of entropy from Adkins (1967, p. 76):

$$dQ = T dS \qquad (11.3)$$

It is important to note that this definition is valid only for reversible processes. Substitution shows that the change in internal energy of the rubber cord due to extension d$l$ is

$$dU = TdS + fdl \qquad (11.4)$$

We can also calculate the expected change in entropy using the *Helmholtz Free Energy*, F, defined by Adkins (1967, p. 105) as:

$$F = U - TS \qquad (11.5)$$

**In your report:** Show from the definition of Helmholtz Free Energy, Equation 11.1, and Equation 11.4 that the *change* in F under expansion is

$$dF = fdl - SdT \qquad (11.6)$$

This equation can be manipulated to yield measurable quantities that can be related back to the change in entropy, dS. If we keep the temperature T constant and differentiate with respect to $l$, we find

$$\left(\frac{\partial F}{\partial l}\right)_T = f \qquad (11.7)$$

and if we differentiate with respect to T while holding $l$ constant, we obtain

$$\left(\frac{\partial F}{\partial T}\right)_l = -S \qquad (11.8)$$

Differentiating equations 11.7 and 11.8 again, with respect to the other variable, gives the following two relationships:

$$\left(\frac{\partial^2 F}{\partial T \partial l}\right) = \left(\frac{\partial f}{\partial T}\right)_l \qquad (11.9)$$

$$\left(\frac{\partial^2 F}{\partial l \partial T}\right) = -\left(\frac{\partial S}{\partial l}\right)_T \qquad (11.10)$$

The left hand sides of these two equations must be equivalent, so that

$$\left(\frac{\partial f}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T \qquad (11.11)$$

We can (indirectly) measure $(\partial f/\partial T)_l$ with our experimental apparatus, and the change in entropy per unit length of the stretched rubber band can then be obtained by integration. Note that this procedure does not enable us to measure the *total* entropy, only its change.

## 11.3   Procedure

1. Make sure that the water jacket is filled to about 1.5 cm from the top with cold water. Do not fill right to the top, as water expands on heating.

   During any refilling you probably will need to remove the wooden ring that supports the strain gauge assembly. Lift this ring off carefully because the cap on the air tube, the rubber cord and anything hanging from that will lift up too. Make sure the transducer sleeve is detached from everything above it before you lift the wooden ring.

2. Replace the strain gauge assembly and the old rubber band for some practice runs with the equipment. Re-attach the transducer sleeve. If a rubber band of the correct length (12 cm) is used, the transducer sleeve will be at the top of its travel when the rubber is relaxed. As the sleeve is pulled down, the rubber stretches and the strain gauge at the top responds to the increasing tension. The voltages fed into the "pico" data logger enable you to generate graphs of tension vs. extension using the computer.

   Check that the control box is plugged in to a mains voltage outlet and that the leads for the water heater element, the temperature transducer, the strain gauge and the displacement transducer are all connected between the correct sockets on the control box and the correct points of the apparatus.

3. First switch on the computer and the data logger. Then switch on the electronics control box. Make sure the "Set Temp" knob is turned down to the lowest possible reading. Double-click the "pico log" icon on the desktop.

4. You will need to adjust the channel settings to obtain useful results. Channels A and B are connected to the transducer and the strain gauge. Change one while keeping the other fixed to satisfy yourself what each channel measures.

5. It is good procedure to make a trial run or two before recording any data. This will allow you to set appropriate voltage range of data collection and to decide how many data points you wish to record for each run.

6. When you are satisfied, use the graph option in the software to view your results. You will be looking at a plot of voltage (probably the displacement voltage) vs. time. However, we would like to view the two voltages against each other. You can download the data to a spreadsheet and view a XY graph of the two voltages. Note that the graph will show a small amount of hysteresis (the relation between tension and displacement depends on history). This shows that the tension on the rubber band is different at a given displacement depending on whether the rubber band is being stretched or relaxed. The pragmatic way to deal with this difficulty is to record data only when the rubber band is being stretched. One way to approach the error estimates for this exercise is to repeat your practice runs a few times and look at the degree of repeatability in the results.

7. You are now in a position to prepare a fresh length of rubber band. Some rubber bands that have been cut so you can test a single length of rubber instead of a doubled loop may be ready on the bench. If not, cut a rubber band and form loops at the ends, so that the overall length is within a couple of millimetres of 12 cm (see Figure 11.1 for guidance). Fix the loops with a small stapler or superglue. Throw any broken rubber bands away.

8. Now you can make serious observations. Pull the transducer sleeve down just fast enough so that its one-way journey downward fully occupies the sampling time. Examine your XY graph. If there are no obvious problems, record the air temperature and **Save the**
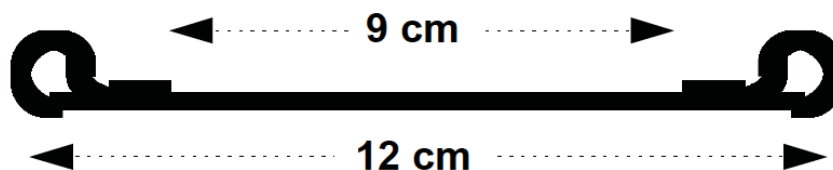
Figure 11.1: Detail of the single length of rubber band with looped ends for attachment to the transducer and strain gauge.

**data**.Give it a name that contains your name and the temperature information. This will make it easier to transfer your data to a USB for analysis later on.

9. Turn the water temperature controller up as necessary and repeat the previous step at temperature intervals of about 15 °C from room temperature up to about 95 °C without boiling the water. You do not need to open and set up a new file each time, but make sure to save your files with different names! If you decide that your measurements are unsatisfactory and you want to repeat them, you must empty the hot water from the jacket and replace it with cold (The hot water takes hours to cool down in the insulated jacket). Do not scald yourself!

10. Neither the strain gauge nor the displacement transducer has a perfectly linear output, so you will have to calibrate both devices in order to convert from voltage to force and displacement.

    **Displacement:** Unhook the transducer sleeve from the wire joining it to the rubber. Place objects of known size between the sleeve and the stop at the bottom of its travel. A set of spacer rods of known thickness has been provided. When each spacer is in position, note the voltage display. Of course, these marks indicate distances from the stop and not the displacement of the transducer; account for this in your calculations.

    Flexure of the steel strip causes an error in the measurements of rubber extension as the tension is increased. In your report, explain how this error arises, and whether or not it is serious.

    **Force:** To calibrate the strain gauge, remove the rubber band and the shorter stiff wire, and replace it with a long hooked wire that just protrudes from the bottom of the water jacket when the strain gauge assembly is back in position. A mass carrier, whose mass is 10 gm, and a set of 50 gm brass weights is available. The mass of the long, hooked wire is 6.4 ±0.2 gm. Add mass to the system and note the corresponding voltage changes. Make sure the range of voltages in your calibration is at least as great as the range you encountered during your data-taking observations.

## 11.4 Calculations

The following section assumes that you have a spreadsheet, curve fitting, and graphing program such as Excel or something similar available. Excel is available on the computers in the computer lab.

(i) Plot calibration curves for converting output voltages from the A and B channels of the

data logger to tension and extension values (confirm that you know which channel refers to which quantity!).

Create a graph of tension versus voltage, with voltage as the independent variable (i.e., on the x-axis). Fit a polynomial to your data points. In Excel, this is done by clicking on one of them and following the "Format Trendline" options. It is always good experimental practise to choose the lowest-order polynomial that obviously gives a good fit to the data; otherwise you risk "fitting the noise" and producing spurious, unphysical results. Check your fit quality by calculating an R-value for the fit. (In Excel, right-click on the Trendline and select the R-value). Record the calibration equation on your graph.

Repeat the preceding step using your linear transducer calibration data and the corresponding displacement voltages. Note however that you are interested in rubber extension, not transducer position. When the transducer is at its lowest position the rubber will be at maximum stretch, so you will need to modify your recorded transducer positions. Again fit a polynomial to the graph (and consider your units).

(ii) Plot a set of graphs of tension vs. extension, one for each temperature at which you took observations. Keep your raw voltages and error estimates to help you estimate the errors in your final results. Use the calibration equations from the previous step to convert your measured voltages to true extensions and forces, and plot the graph of tension vs. extension for each temperature.

Try fitting a polynomial to each curve. As usual, use the lowest-order polynomial that reproduces the overall shape of the curve. The danger in choosing a polynomial of arbitrarily high order (8, 12, 20 or higher?) is that you are simply matching a function to noisy data without capturing any real physical trend; use commonsense and computing power in equal measure.

An evaluation of the fit quality requires error estimates on each point. Make some estimate of the uncertainties in your measurements based on the circumstances of your experiment and calibration procedure and discuss these in your report.

(iii) What you have measured is tension vs. extension at constant temperature, for several different temperatures. Now you can manipulate this data to compare the tension vs. temperature at different lengths (recall from the Theoretical Background that this is the quantity related to entropy).

Start a new spreadsheet so you can start graphing tension $f$ vs. temperature T at constant extension $l$. Pick several values (at least 7) of $l$ for which you've obtained tension data, and use your polynomial fits from step (ii) to make plots of tension vs. temperature at your chosen fixed values of $l$. The graphs should look fairly linear; fit a straight line to each and record the fit equations.

In Excel, you might find that the following procedure works well: enter the $l$ values into Column A, starting from Row 2.. Each successive column will contain information for one of your temperatures (e.g., 20 °C in column B, 80 °C in column G, etc). Enter the appropriate fit equation for tension as a function of extension into each column, taking the extensions in column A as the argument of the functions. If you enter the temperatures into Row 1, you can then plot each row down against row 1 in order to make plots of tension vs. temperature.

(iv) You now have empirical determinations of $(\partial f/\partial T)_l$ for a range of $l$. Now recall Equation 11.11. Collect your values of extension $l$, and the corresponding values of dS/d$l$. Plot dS/d$l$ vs. $l$ and fit a polynomial to the data.

Now that you have a polynomial function describing dS/d*l* as a function of *l*, the relationship between S and *l* can be found by integration. Of course, there is the problem of the constant of integration. However, unless you have an amazingly detailed knowledge of energy levels throughout the Universe, you will never be able to arrive at an absolute value for that. Since what we?re interested in is the *change* in entropy, ΔS, you may as well set the integration constant to zero.

Calculate a set of values ΔS for chosen values of *l*. Use them to plot a graph of ΔS versus *l*. Since this graph represents the result of your experiment, you should plot it very carefully. Axes should be labelled and units given. A rigorous quantitative error analysis on ΔS may prove difficult to obtain, but you should make a reasoned attempt to estimate the uncertainties based on measurement errors and the various systematic effects you feel might be biasing your results.

(v) Are your results compatible with the theory of rubber crystallization proposed in the theoretical background to this exercise? Discuss.

(vi) Rubber heats up when it is stretched *adiabatically*. You may be able to demonstrate this by quickly stretching a rubber band and touching it to your lips. Can you detect a slight rise in its temperature as a result of the stretching? Use equations 11.1 and 11.4 *together with your results* to explain this phenomenon.

**References**
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Treloar, L.R.G. 1967, *The Physics of Rubber Elasticity*, (Clarendon Press: Oxford)
Adkins, C.J. 1968, *Equilibrium Thermodynamics*, (McGraw-Hill: London).