Thermodynamics Fundamental Equation of a "Non-Ideal" Rubber Band from Experiments

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Ⓢ Supporting Information

ABSTRACT: In this paper, we describe laboratory and classroom exercises designed to obtain the *fundamental* equation of a rubber band by combining experiments and theory. The procedure shows students how classical thermodynamics formalism can help to obtain empirical equations of state by constraining and guiding in the construction of the physical models for the system under investigation. It also serves as an "experimental" link to statistical thermodynamics models for a rubber band, which is taught to students in more advanced courses. The rubber band system also serves as an example of a "non-ideal" thermodynamics system to introduce a van der Waals-like equation in a context different from gases.

Classroom   Laboratory

KEYWORDS: *Upper-Division Undergraduate, Physical Chemistry, Hands-On Learning/Manipulatives, Thermodynamics, Inquiry-Based/Discovery Learning, Laboratory Instruction*
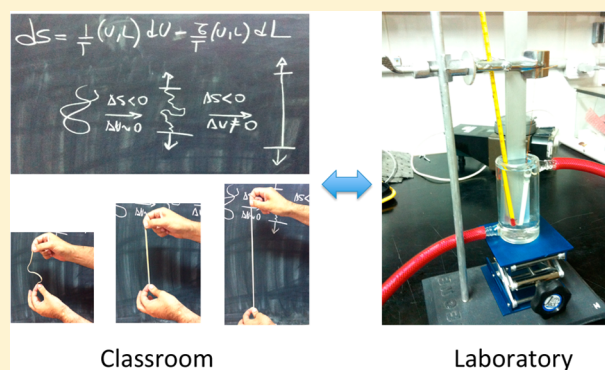
■ INTRODUCTION

When introducing students to thermodynamics in first courses, we emphasize that the subject is of general applicability: the laws of thermodynamics apply to all physical systems. However, the number of simple, interesting, affordable experiments for students is small.[1] Here, we propose an experiment designed to obtain the equations of state of a rubber band and, from them, the fundamental relation of the system using classical (macroscopic) thermodynamics formalism. Although there are many different versions of demonstrative practices of rubber elasticity,[1−10] they use old experimental setups or deal just with the fact that the force (or tension) on a rubber band increases with temperature, a behavior which is opposite to most materials. The generality of these experimental practices is focused on experimental validation of equations of state derived from statistical thermodynamics theory,[2,6] which cannot be explained rigorously in introductory courses of classical thermodynamics. Additionally, most of the literature about rubber bands in the context of undergraduate classroom and laboratory deals with "ideal" rubber bands, meaning that the internal energy does not depend on the extension, which is usually not the case.

Both the experiment and the analysis procedure that we propose here was devised the other way around; they were designed to obtain from experiments the equations of state and to demand from students a good laboratory practice and a rigorous knowledge of the underlying classical thermodynamics principles and relations. Instead of giving students the

equations to be contrasted with the experiments, we ask them to find out the equations of state from their experimental results. This work is a consequence of an effort to coordinate the contents of two courses, Thermodynamics and Statistical Thermodynamics, and was used in our department to evaluate students' experimental skills and knowledge of classical thermodynamics formalism as a final examination. This guided-inquiry experiment could be used in an advanced physical chemistry or thermodynamics laboratory.

■ THEORETICAL BACKGROUND

Fundamental Relation of a Thermodynamics System

Historically, Clausius defined the change in entropy for an infinitesimal process as $dS = (dQ_{quasi}/T)$, with dQ_{quasi} being the heat exchanged in a quasistatic path from the initial to the final state and T the absolute temperature. By combining this definition with the first thermodynamic principle for a closed system, also stated mathematically for the first time by Clausius, $dU = dQ + dW$ (with U being the internal energy), and assuming by now than only pressure−volume (PV) work (quasistatic) can be done, $dW = -PdV$, it follows

$$dU = TdS - PdV \qquad (1)$$

Written in this way, U can be viewed as some function of the extensive independent variables S and V, $U(S,V)$; then, its differential will be

$$dU = \left.\frac{\partial U}{\partial S}\right|_V dS + \left.\frac{\partial U}{\partial V}\right|_S dV \qquad (2)$$

By comparing eqs 1 and 2, we can define T as the partial derivative of $U(S,V)$ with respect to the entropy: $T = (\partial U/\partial S)|_V$ and, in the same way, $-P = (\partial U/\partial V)|_S$. Because the partial derivatives of any function are also functions of the same variables, then $T(S,V)$ and $P(S,V)$ give the relations between T and P with the independent variables S and V.

It is neither common nor convenient to have S as independent variable. Let us then rewrite eq 1 as

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \qquad (3)$$

Now, we can say that S, in eq 3, is a function of the independent variables U and V, $S(U,V)$.

When the differential form is written as in eq 1, we say that it is in the *energy representation,* meaning that U is the dependent variable; when written as eq 3, we say that it is in the *entropic representation,* meaning that S is now the dependent variable.

We can identify in eq 3 the partial derivatives as $(\partial S/\partial U)|_V = (1/T)$ and $(\partial S/\partial V)|_U = (P/T)$; again, this partial derivatives are also functions of the same independent variables as S: U and V, and we express that by writing $\frac{1}{T}(U, V)$ and $\frac{P}{T}(U, V)$. We write these functions in that way (and not as $T(U,V)$ and $P(T,U,V)$) to emphasize that the fundamental relation is in *entropic representation.*

Because the second principle of thermodynamics is expressed in terms of the maximum of the entropy,[11] then we assume (postulate) that for any thermodynamics system there is a fundamental relation $S(U,X_i)$, *the entropy,* which is a function of all extensive parameters X_i relevant to describe it correctly. That is, *we postulate the existence of the integral of* eq 3 *for each* thermodynamic system, and then we generalize the treatment to all systems by including in $S(U,X_i)$ all the relevant extensive parameters needed to describe those systems. The second principle states that this function $S(U,X_i)$ should be a maximum at equilibrium ($dS = 0$, $d^2S < 0$).

Differential Form of the Fundamental Relation for Rubber Bands

For a rubber band, the relevant extensive parameters are U, V, N, and L, N being the mole number (the number of polymer molecules within the rubber band divided by the Avogadro's number) and L the length of the rubber band. Then, the fundamental relation $S(U,X_i)$, in the absence of any external field, can be expressed as a function $S = S(U,V,N,L)$.

The differential of $S(U,X_i)$ for the rubber band system is then

$$dS = \left(\frac{\partial S}{\partial U}\right)dU + \left(\frac{\partial S}{\partial V}\right)dV + \left(\frac{\partial S}{\partial N}\right)dN + \left(\frac{\partial S}{\partial L}\right)dL \qquad (4)$$

All the partial derivatives on the previous equation are also functions of the same extensive parameters. If we explicitly know the function $S(U,X_i)$, we can obtain all the partial derivatives as functions of the extensive parameter; we will call those relations equations of states (ref 11, ch. 2). All the terms on the right-hand side of eq 4 have units of entropy (energy/temperature); the partial derivative in the last term has the

units of force divided by temperature, and we indentify that term with the force.[11] The equations of state so defined are

$$\left(\frac{\partial S}{\partial U}\right)_{V,N,L} = \frac{1}{T} = f(U, V, N, L) \qquad (5)$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N,L} = \frac{P}{T} = f(U, V, N, L) \qquad (6)$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V,L} = -\frac{\mu}{T} = f(U, V, N, L) \qquad (7)$$

$$\left(\frac{\partial S}{\partial L}\right)_{V,N,L} = -\frac{\tau}{T} = f(U, V, N, L) \qquad (8)$$

Here, μ is the chemical potential and τ is the tensile force. If the whole set of equations of state is known, the fundamental relation can be obtained by means of the Euler relation,[11] or by integration of the differential form, eq 4.

Differential Form for a Rubber Band at Constant *V* and *N*

Let us now consider a piece of rubber band of a relaxed length L_0 ($\tau = 0$). For this system, the number of moles is constant (no polymer molecule enters or leaves the rubber band). The volume V can be considered, in a first approximation, also constant, even if the band is stretched. This means that, within limits, the band changes the length and the cross section in such a way that the total volume is constant (for a discussion about the assumption of constant V see ref 6). Then, we can eliminate the two terms involving changes on N and V on eq 4, and the fundamental relation for our rubber band becomes a function of only two extensive parameters: U and L

$$dS = \frac{1}{T}(U, L)dU - \frac{\tau}{T}(U, L)dL$$

at constant N and V \qquad (9)

So, if we want the fundamental relation $S(U,L)$, we need to work out the two equations of state $\frac{1}{T}(U, L)$ and $\frac{\tau}{T}(U, L)$; from them, the fundamental relation can be recovered by integration of eq 9.

■ EXPERIMENTAL PROCEDURE

This laboratory exercise was used as a final examination for second year students of physics, but is appropriate for upper-level students in physical chemistry or thermodynamics. The instructors present the main problem: *experimentally obtain the equations of state of a rubber band.* The students, in groups of two or three, conduct a literature search and propose an experiment to obtain a solution to the given problem. After a review with the instructor, students build the setup and perform the experiment.

A scheme of one of the experimental setups designed by students is shown in Figure 1. The details are included in the Supporting Information. For this particular experiment, students used an ordinary rubber band attached from both ends; one of them, to a force transducer which can be moved to the left, allowing changes in the length of the rubber band, and the other, to a fixed position. With an electric resistor wrapped around a quartz tube, students were able to heat the rubber band, which passed through the center of the tube. With a ruler, a force transducer, and a thermometer (or a thermocouple), the
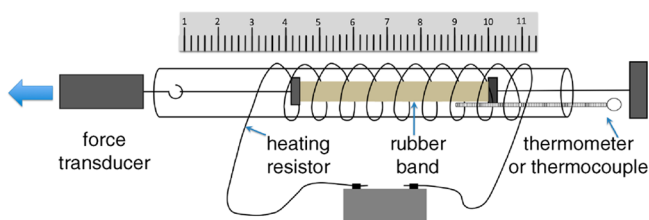
Figure 1. Scheme of the experimental setup.

length, the force, and the temperature were measured simultaneously.

Once they have obtained their experimental results, they have to work out the equations of state, in an inquiry-guided process, and from them the "fundamental relation" using the formalism they have learned (see next section).

Finally, they write up their results and discussion following the format of a research paper. They also present the work in a seminar using PowerPoint (or similar) and answer questions from the instructor and other students. The students need six to eight 3-h laboratory periods to design the experimental setup, carry out the experiment, and obtain the equations working at the lab, at the library, or on computers at home or at the University.

■ HAZARDS

Be careful with the heating setup. Students used here a resistor, which is potentially dangerous. Other experimental setups avoiding the use of a resistor are proposed in the Supporting Information and in references.

■ RESULTS AND DISCUSSION

Phenomenological Equation of State from Experiments

Typical results obtained with the setup of Figure 1 are shown in Figures 2 and 3.

From Figure 2, students found that τ is a nonlinear function of L, Hooke's law is not fulfilled and, then, it is not a perfect elastic body. The rubber band used in this particular experiment
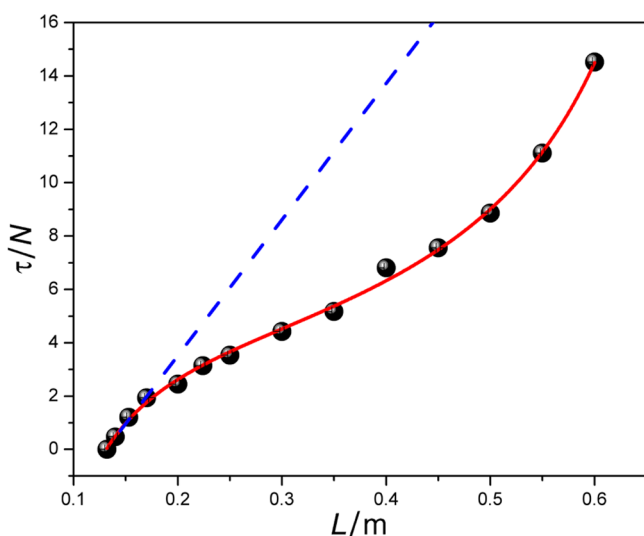

Figure 2. Force as a function of L at constant $T = 300$ K ($L_0 = 13.2$ cm). The line corresponds to the fitting with eq 12. The errors are smaller than the size of the points. The dashed line correspond to Hooke's law (linear elastic).
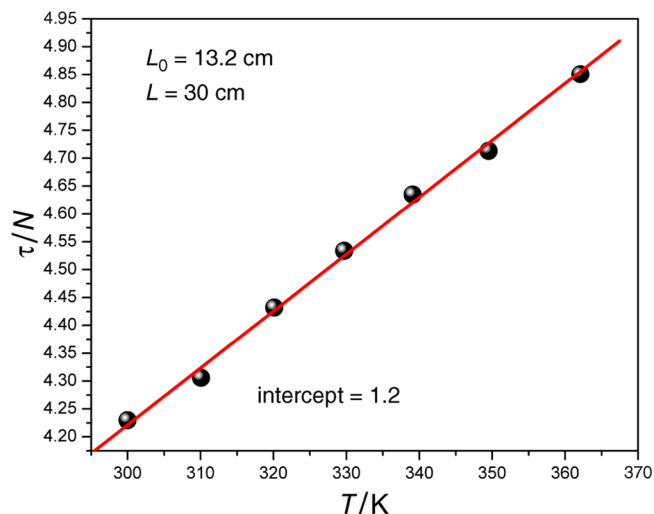

Figure 3. Force as a function of T at constant $L = 0.3$ m. The error bars are smaller than the size of the points.

had a length of $L_0 = 13.2 \pm 0.2$ cm at 300 K in the absence of any applied force and was forced to the rupture point, which happened at about $L \sim 78$ cm.

In the classroom, we had shown students the similarities between "ideal" rubber bands and ideal gases,[12,13] and it was clear to them that the behavior observed in this rubber sample was not ideal, in the sense that U depends also on L (for an ideal rubber band, U is only a function of T, as for ideal gases, see Figure 3 and eq 16 below). Because the form of the τ vs L curve (Figure 2), which resembles those of P vs V isotherms for van der Waals gases, they proposed a van der Waals-like equation for the their rubber band

$$\tau = \frac{BT}{L_M - L} + \frac{D}{L^2} \tag{10}$$

where D and B are empirical constants, and L_M is the maximum length attainable for the rubber band before the rupture point. This is the equivalent, for the rubber band, to the constant "b", the excluded volume in the van der Waals equation for gases. How to interpret this constant was a matter of discussion with students. The constant D is a global interaction parameter (attractive) among the polymer chains within the rubber band (like the constant "a" in gases); however, the L^{-2} dependence in eq 10 is not so easily justified heuristically as it is the v^{-2} dependence in the van der Waals equation for gases. Then, we make clear to students that this equation is simply phenomenological. In fact, a van der Waals-like equation was applied to rubber bands,[14,15] but L in eq 10 should be replaced by $\lambda = (L/L_0) + (L_0/L)^2$, and the justification for this equation comes from statistical thermodynamics. A comparison between the equation of state of an "ideal" rubber band and the van der Waals equation is also presented in ref 1 in the context of undergraduate laboratory practices.

Even though eq 10 is a phenomenological equation not rigorously justified from theory, it is perfect for our purposes because it allows the use of the thermodynamics formalism to find out a *consistent relation*, from the thermodynamics point of view, for the other equation of state, as it will be shown in the next section.

The experimental points in Figure 2 were fitted with eq 10 given, $D = (-0.131 \pm 0.002)$ J·m; $L_M = (0.77 \pm 0.01)$ m, and $B = (8.8 \pm 0.3) \ 10^{-3}$ J·K^{-1}. The result of fitting the experimental

points with eq 10 is shown as a line in Figure 2. Now students have the first of the equations of state, see eq 9, in the entropic representation with all the numerical constants

$$\frac{\tau}{T} = \frac{B}{L_M - L} + \frac{D}{L^2}\frac{1}{T} \tag{11}$$

Second Equation of State from Thermodynamics Formalism

From the thermodynamics formalism, the cross derivatives of the fundamental relation in entropic representation, have to be equal

$$\frac{\partial}{\partial U}\left(\frac{\partial S}{\partial L}\right) = \frac{\partial}{\partial U}\left(-\frac{\tau}{T}\right) = \frac{\partial}{\partial L}\left(\frac{\partial S}{\partial U}\right) = \frac{\partial}{\partial L}\left(\frac{1}{T}\right) \tag{12}$$

and, from eq 11 and 12 and considering that $1/T$ (entropic representation) is a function of U and L

$$\frac{\partial}{\partial U}\left(-\frac{\tau}{T}\right) = -\frac{D}{L^2}\frac{\partial}{\partial U}\left(\frac{1}{T}\right)$$

$$-\frac{D}{L^2}\frac{\partial}{\partial U}\left(\frac{1}{T}\right) = \frac{\partial}{\partial L}\left(\frac{1}{T}\right) \Rightarrow$$

$$\frac{\partial}{\partial U}\left(\frac{1}{T}\right) = \frac{\partial}{\partial(D/L)}\left(\frac{1}{T}\right) \tag{13}$$

then, the function $1/T$ must depend on the variables (D/L) and U in such a way that the two derivatives, $\frac{\partial}{\partial(D/L)}\left(\frac{1}{T}\right)$ and $\frac{\partial}{\partial U}\left(\frac{1}{T}\right)$ are equal. Students could propose any function of those variables that obey eq 13. Maybe, the simplest way to accomplish this is by making the function to depend on the sum $(D/L + U)$ (we had mentioned this to students in the classroom in relation to van der Waals fluids), and remembering the "thermal" equation of state for an ideal gas in entropic representation, $1/T = (cNR)/U$, commonly written $U = cNRT$, and again by analogy, they arrived to the following expression for the second equation of state of their rubber band

$$\frac{1}{T}(U, L) = \frac{cNR}{U + D/L} \tag{14}$$

In order to be rigorous with the thermodynamics formalism, eq 11 should be a function of U and L only (see eq 9); then, we introduced eq 14 into 11 to obtain

$$\frac{\tau}{T}(U, L) = \frac{B}{L_M - L} + \frac{D}{L^2}\frac{cNR}{(U + D/L)} \tag{15}$$

Equations 14 and 15 are all students need to integrate eq 9 and recover the fundamental relation in entropic representation $S(U,L)$, for their rubber band (see Supporting Information).

Experimental Validation of Eq 14

Before integrating eq 9 to recover the fundamental relation, students had to evaluate experimentally the second equation of state, eq 14, which was obtained by combining thermodynamics formalism, an empirical equation of state and the use of the similarities with gases. Again, they needed to work with the formalism; because the volume was supposed to be constant, it was more convenient to use the Helmholtz representation, A, where the fundamental relation is expressed as a function of T, V and L: $A(T,V,L)$ and is given by (see Supporting Information)

$$A = U - TS$$

$$\left.\frac{\partial A}{\partial L}\right|_T = \left.\frac{\partial U}{\partial L}\right|_T - T\left.\frac{\partial S}{\partial L}\right|_T$$

$$\tau = \frac{D}{L^2} + T\left.\frac{\partial \tau}{\partial T}\right|_L \tag{16}$$

where eq 14 and the Maxwell relation, $(\partial S/\partial L)|_T = (\partial \tau/\partial T)|_L$ were used (see Supporting Information).

Figure 3 shows the experimental results for the force measured as a function of T at constant L ($L = 30$ cm). The force varies linearly with the absolute temperature, as in eq 16. The intercept is not zero, meaning that the derivative $(\partial U/\partial L)|_T \neq 0$; then, U is function of L (a nonideal rubber band). The experimental value of the intercept (Figure 3) ∼1.2 N is quite close to the value of D/L^2 (∼1.4 N), obtained by fitting the experimental points in Figure 2 using eq 10.

Fundamental Relation for the Rubber Band

Now we return to the fundamental equation for the rubber band, which is obtained by integration of expression 9 using eq 14 and 15 to yield (see Supporting Information)

$$S = S_0 + NR\ln[(U + D/L)^c(L_M - L)] \tag{17}$$

where S_0 is the entropy in the absence of stress and we used, for convenience, $B = NR$ (see Supporting Information).

Force Is Zero When $L = L_0$

At this stage, we pointed out to students that, in eq 9, the force τ should be zero when L equals L_0 because they had not realized that fact; then

$$D = -\frac{BTL_0^2}{L_M - L_0} \tag{18}$$

which, when introduced in eq 10 gives

$$\frac{\tau}{T} = B\left[\frac{1}{L_M - L} - \frac{L_0^2}{(L_M - L_0)L^2}\right] \tag{19}$$

Replacing the measured values of both $L_0 = 0.13$ m (measured at 300 K) and $L_M = 0.78$ m (rupture point) in eq 19, and using $B = (8.8 \pm 0.3)\ 10^{-3}$ J·K^{-1}, the experimental points are very well reproduced being the curve indistinguishable from the line shown in Figure 2.

Of course, eq 19 could be introduced at an early stage in place of eq 10.

Constant c in Eq 14 and Other Thermodynamics Information from the Fundamental Relation

At this point, we asked students to identify the unknown constant c in eq 14 and to propose a way to estimate its value. If they were aware (and they had to be) of the formal definition of the heat capacity, at constant L

$$C_L = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_L = cR \tag{20}$$

C_L could then be measured or estimated by calorimetric experiments (see the Supporting Information).

Finally, because eq 17 contains in principle all the thermodynamics information for our system, students could explore its consequences; for example, they could calculate the linear expansion coefficient, $\alpha_L = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)$ and search for a way to measure it in the laboratory, or they could compute the

change in temperature produced by stretching the rubber[16] in a reversible process and then compare it with the value measured in a rapid stretching of the same rubber;[17] this will lead to the discussion of irreversible processes.

This fundamental relation empirically obtained can also be used to analyze a heat engine that makes use of rubber bands[18,19] as a working agent. It can also be used to discuss the stability conditions derived from $d^2S < 0$ and phase transitions.[20]

It should be noted that the fundamental equation obtained does not fulfill the third principle (for eq 17, $S \neq 0$ when $T \rightarrow 0$), and therefore, it is not a "real" fundamental relation. This happens also for the fundamental equation of an ideal gas[11] obtained from the equations of state (see Supporting Information). This fact can be used to illustrate the limits that theories often have, and the importance of being aware of them when applying the theory on systems beyond the limits imposed on the development of those theories (in our case, $L_0 < L < L_M$, limited T range and constant volume).

■ SUMMARY

We present an experimental and analytical procedure to obtain the *fundamental* equation of a rubber band. Contrary to the common practice of giving students the equations of state to be contrasted with the experiments, we asked them to work out those equations. By combining experiments and the thermodynamics formalism, students were able, in an inquiry-guided process, to work out an empirical fundamental relation for their rubber bands. The consequences of this equation, that in principle contains all the imaginable thermodynamics information for that system (under restrictions stated above), can be explored in the classroom and it can help to develop the theory in introductory thermodynamics courses. In our case, the present work is a consequence of an effort to integrate and coordinate the contents of two courses: *Thermodynamics* and *Statistical Thermodynamics*. The fundamental relation obtained from the experiment and classical thermodynamics formalism can be used in the subsequent Statistical Thermodynamics course as a starting point to introduce the Gaussian model.[6,21]

One interesting consequence of this work with rubber bands was an emergent discussion about the meaning of the constant D on eq 12 and the foundations of the van der Waals equation of state.[22]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

A detailed description of the experimental setup and some other information is included. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Halpern, A.; McBane, G. *Experimental Physical Chemistry: A Laboratory TextBook*, 3rd ed.; W. H. Freeman Inc.: New York, 2006.

(2) Nash, L. Entropy and Rubbery Elasticity. *J. Chem. Educ.* **1979**, *58* (6), 363−368.

(3) Mark, J. E. Rubber Elasticity. *J. Chem. Educ.* **1981**, *58* (11), 898−903.

(4) Bader, M. Rubber Elasticity—A Physical Chemistry Experiment. *J. Chem. Educ.* **1981**, *58* (3), 285.

(5) Sabarino, G.; Fisch, R. A general physics laboratory investigation of the thermodynamics of a rubber band. *Am. J. Phys.* **1991**, *59* (2), 141−145.

(6) Pellicer, J.; Manzanares, J. A.; Zúiga, J.; Utrillas, P.; Fernández, J. Thermodynamics of Rubber Elasticity. *J. Chem. Educ.* **2001**, *78* (2), 263−267.

(7) Byrne, J. P. Rubber elasticity: A simple Method for Measurement of Thermodynamic Properties. *J. Chem. Educ.* **1994**, *71* (6), 531−533.

(8) Mitschele, J. Elasticity to Measure Thermodynamic Properties. *J. Chem. Educ.* **1997**, *74*, 368.

(9) Hirsch, W. Rubber Bands, Free Energy, and Le Châtelier's Principle. *J. Chem. Educ.* **2002**, *79* (2), 200A.

(10) Dole, M. Lecture Table Experimental Demonstration of Entropy. *J. Chem. Educ.* **1977**, *54* (12), 754−755.

(11) Callen, H. B. *Thermodynamics and an Introduction to Thermostatics*, 2nd ed.; John Wiley & Sons: Ney York, 1985.

(12) Smith, B. Using Rubber-Elastic Material-Ideal Gas Analogies To Teach Introductory Thermodynamics. Past I: Equations of State. *J. Chem. Educ.* **2002**, *79* (12), 1444−1452.

(13) Smith, B. Using Rubber-Elastic Material-Ideal Gas Analogies To Teach Introductory Thermodynamics. Past II: The Law of Thermodynamics. *J. Chem. Educ.* **2002**, *79* (12), 1453−1461.

(14) Kilian, H.-G; Enderle; Unseld, K. The use of the van der Waals model to elucidate universal aspects of structure-property relationships in simply extended dry and swollen rubbers. *Colloid Polym. Sci.* **1986**, *264*, 866−876.

(15) Kilian, H.-G; Vilgis, Th. Fundamentals aspects of rubber-elasticity in real networks. *Colloid Polym. Sci.* **1984**, *262*, 15−21.

(16) King, A. L. Note in Memory of John Gough. *Am. J. Phys.* **1953**, *21*, 231−232.

(17) Gedde, U. W. *Polymer Physics*; Chapman and Hall: London, 1995.

(18) Cox, E.G. A Heat Engine run by rubber. *J. Chem. Educ.* **1954**, *31*, 307.

(19) See the rubber band machine working: Micolich, A. *The Rubber Band Heat Engine*. http://www.youtube.com/watch?v=dBXL93984cQ (accessed Aug 2014).

(20) Mau, M.; McIver, J. W., Jr. Alternative Approach to Phase Transitions in the van der Waals Fluid. *J. Chem. Educ.* **1986**, *63*, 880−882.

(21) Treloar, L. R. G. The elasticity and related properties of rubbers. *Rep. Prog. Phys.* **1973**, *36*, 755−826.

(22) Swinbourne, E. S. The van der Waals Gas Equation. *J. Chem. Educ.* **1955**, *32*, 366−369.