The Thermodynamic Properties of Elastomers: Equation of State and Molecular Structure

Objective
To determine the macroscopic thermodynamic equation of state of an elastomer, and relate it to its microscopic molecular properties.

Introduction
We are all familiar with the very useful properties of such objects as rubber bands, solid rubber balls, and tires. Materials such as these, which are capable of undergoing large reversible extensions and compressions, are called elastomers. An example of such a material is natural rubber, obtained from the plant *Hevea brasiliensis*. An elastomer has rather unusual physical properties; for example, an ordinary elastic band can be stretched up to 15 times its original length and then be restored to its original size. Although we might initially consider elastomers to be a solids, many have isothermal compressibilities comparable with that of liquids (e.g. toluene), about 10^{-4} atm^{-1} (compared with solids such as polystyrene or aluminum which have values of $\sim 10^{-6}$ atm^{-1}). Certain evidence suggests that an elastomer is a disordered "solid," i.e., a glass, that cannot flow as a result of internal, structural restrictions.

The reversible deformability of an elastomer is reminiscent of a gas. In fact the term *elastic* was first used by Robert Boyle (1660) in describing a gas, "There is a spring or elastical power in the air in which we live." In this experiment, you will encounter certain formal thermodynamic similarities between an elastomer and a gas.

One of the rather dramatic and anomalous properties of an elastomer is that once brought to an extended form, it *contracts* upon heating. This is in sharp contrast to the familiar response of expansion shown by other solids and liquids. This behavior, first reported by Gough (1805) and later studied in detail by Joule (1859), is called the Gough-Joule effect. Thermoelasticity is the basis of this experiment.

An understanding of the molecular properties and theoretical concepts that characterize elasticity was not fully developed until this century (1930s), when the foundations of polymer science were firmly established. The molecular requirements for elasticity are now rather well understood and can be described in terms of the most common (and historically most important) elastomer, natural rubber. This substance is a polymer having a molecular weight of about 350,000. The monomeric unit is isoprene, or 2-methylbutadiene
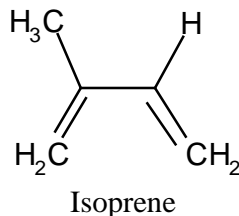
Isoprene

When polymerized, isoprene can form the cis-configured chain, which is *Hevea* rubber; in the trans configuration, the polymer, called gutta-percha, is crystalline at room temperature and thus not very elastic.
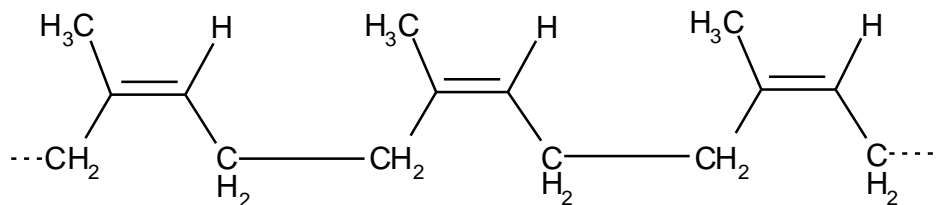
Hevea rubber

The elasticity of natural rubber is understood to be a consequence of three of its molecular properties: (1) The poly (isoprene) subunits can freely rotate, (2) forces between the polymer chains are weak (as in a liquid), and (3) the chains are linked together in a certain way at various points along the polymer. The latter property is especially important for reversible elasticity. It also eliminates the phenomenon called *creep* in which an elastomer, once deformed, will remember and "relax" back to the deformed shape. Property 3 is more specifically called *cross-linking*, and the phenomenon was first exploited by Charles Goodyear (1839) in a process he called vulcanization. Natural gum rubber is heated with sulfur (2 to 10%) and as a result, a number of cross-linking chains are imposed on the original polymer as shown in Figure 1, in which the black dots represent cross-linking sites.

In this type of cross-linking, which is essential to elastomers, the cross-links are bonded to a common point on the polymer backbone. A cross-linked elastomer thus resembles a fish net. The thermodynamic properties of an elastomer can be understood in terms of what happens to these cross-linked networks as the bulk material is stretched from its relaxed state.
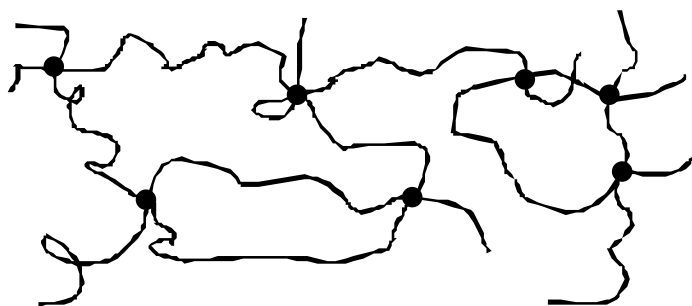

Figure 1. Schematic of a cross-linked polymer. The cross-links are joined at (or near) a common site.

THERMODYNAMICS OF ELASTICITY

Consider the consequence of subjecting an elastomer to an external force that causes it to undergo an extension (or a compression). The first law of thermodynamics may be written

$$dU = \text{\dj}q + \text{\dj}w, \tag{1}$$

where dU is the change in the elastomer's internal energy resulting from the absorption of heat, $\text{\dj}q$, and the dissipation of work, $\text{\dj}w$, on it by the external force. (The symbol $\text{\dj}$ indicates that heat and work are inexact differentials; their integrated values depend on the path of the process carried out.) If we assume that the deformation process is *reversible* (e.g., carried out very slowly), the heat flow can be expressed as

$$\text{\dj}q = TdS, \tag{2}$$

where T is the absolute temperature and dS is the entropy change, and thus

$$dU = T\,dS + dw \text{ (reversible process).} \tag{3}$$

In considering the reversible deformation of an elastomer, it is convenient to use the Helmholtz free energy, $A = U - T\,S$. For the deformation process, the infinitesimal isothermal change in A is

$$dA = dU - T\,dS. \tag{4}$$

Hence, in this case, $dA = dw$. The work done on the elastomer by the external force in this isothermal, reversible process is simply equal to the change in the Helmholtz free energy.

We must now consider the kind of work being done on the elastomer. In addition to the work associated with the expansion of the system against the atmosphere ($-P\,dV$, where P is the external pressure and dV is the change in volume accompanying elongation), work also arises from the application of a force to an elastomer. If its original length, L_0 is changed by an amount dL as a result of a force, f, the work done on the elastomer is

$$dw = f\,dL. \tag{5}$$

So if f is in the positive x-direction and dL is positive, the elastomer stretches, and thus work is done on the polymer. The total work done on the solid is thus

$$dw = f\,dL - PdV. \tag{6}$$

Because of the very small compressibility of elastomers (e.g., $\sim 10^{-4}$ atm^{-1}), $P\,dV$ is much smaller than $f\,dL$ under most circumstances (typically by a factor of 10^{-4}), and we can approximate the work as $f\,dL$. In more detailed treatments of elasticity, the $P\,dV$ term cannot be neglected.

Since from equation (5), $f = (dw/dL)_T$, and $dA = dw$, it follows that

$$f = \frac{\partial A}{\partial L}\bigg|_T \tag{7}$$

which means that the tensile force is equal to the (isothermal) change in the Helmholtz energy with respect to an infinitesimal change in elastomer length.

Differentiating equation (4) with respect to L (at constant T), we get

$$\frac{\partial A}{\partial L}\bigg|_T = \frac{\partial U}{\partial L}\bigg|_T - T\frac{\partial S}{\partial L}\bigg|_T \tag{8}$$

and combining this result with equation (7) gives

$$f = \frac{\partial U}{\partial L}\bigg|_T - T\frac{\partial S}{\partial L}\bigg|_T \tag{9}$$

It is desirable to express dA in terms of the infinitesimal (experimental) variables dL and dT. We can do this by taking the total differential of A,

$$dA = dU - T\, dS - S\, dT, \tag{10}$$

and inserting $dU = f\, dL + T\, dS$,

$$dA = f\, dL - S\, dT. \tag{11}$$

We now make use of the Maxwell relation for dA (A is a thermodynamic state function, hence dA is an exact differential),

$$\frac{\partial S}{\partial L}\bigg|_T = -\frac{\partial f}{\partial T}\bigg|_L. \tag{12}$$

This important result expresses the infinitesimal (isothermal) dependence of entropy on length in terms of an experimental quantity: the temperature dependence of the tension (at constant length).

Now, by substituting the left-hand side of (12) into equation (9), we can write the applied tensile force as

$$f = \frac{\partial U}{\partial L}\bigg|_T + T\frac{\partial f}{\partial T}\bigg|_L \tag{13}$$

Equations (9) and (13) are central to thermoelasticity. Equation (9) says that the force is composed of two components, one due to the change in the elastomer's internal energy as

a result of the elongation (or compression), and the other due to the entropy change accompanying the deformation. Because f and T are dependent and independent experimental variables, respectively, equation (13) allows us to obtain $(\partial U / \partial L)_T$ from a plot of f vs. T.

Comparison with Gases

It is very enlightening to compare the force acting on an elastomer with the pressure of a gas. Extending the length of an elastomer is analogous to compressing a gas (in both cases work is done on the system). If the work in equation (5) is replaced by $- P\, dV$, as is the case for a gas, the pressure can be expressed as

$$P = -\left(\frac{\partial U}{\partial V}\right)_T + T \left(\frac{\partial S}{\partial V}\right)_T .\tag{14}$$

Again we see two components to the pressure, one due to internal energy and the other due to the entropy. The internal energy term is small (zero for the ideal gas); thus if a gas is compressed, dV is negative, and the second term in equation (14) accounts for the pressure increase because dS is also negative for a compression.

The van der Waals equation of state, which expresses P as

$$P = -\frac{a}{V_m^2} + T \left(\frac{R}{V_m - b}\right) .\tag{15}$$

attempts to take intermolecular attractions into account through the constant a. Thus some of the thermal energy that is absorbed by a system undergoing an increase in temperature goes into overcoming these internal forces, and it is not all available to increase the kinetic energy. The significance of the two terms in the expressions for the force acting on the elastomer [see equations (9) and (13)], can be better appreciated by comparing equations (9), (14), and (15) in light of the foregoing discussion. The first term in the van der Waals equation is equal to $(\partial U / \partial V)_T$.

In analogy with the ideal gas, an *ideal elastomer* is defined as one for which $(\partial U / \partial L)_T$ is zero. It is to be noted that a certain amount of cross-linking is required for this kind of behavior. With either no cross-linking as in amorphous materials or an excessive amount as in hard rubber, this type of elasticity is nonexistent. There are a number of elastic polymers, particularly soft rubberlike substances, in which the energy is essentially independent of length, so any work done as a result of a change in length must be attributed to *entropy change alone*.

Stress vs. Strain and Temperature

We will now consider the relationship between the applied force, f, and the elastomer length, L. We will study this directly from isothermal stress-strain measurements $\{f(L)_T\}$,

as well as indirectly from measurements of the restoring force as a function of temperature carried out at various fixed elongations, i.e., $\{f(T)_L\}$. For the latter, the analogous experiment, if carried out on a gas, would be to measure the pressure as a function of temperature at fixed volume. The gas law pertaining to this $P(T)_V$ isometric is called Rudberg's law (1842). It is customary to refer to the applied force as a *stress* (dimensions, force per area) and to the deformation as a *strain*. It is also convenient to use a dimensionless quantity for the strain, s, namely,

$$s = \frac{L - L_0}{L_0} \ , \tag{16}$$

where L and L_0 are the stressed and unstressed lengths of the elastomer, respectively.

The stress, r, which is the force causing the elongation of the elastomer, f, divided by the cross-sectional area, a, of the elastomer, is usually determined on the basis of the unstressed elastomer's cross section, a_0 (when $L = L_0$, and taking $a = a_0$). This value is referred to as the *nominal stress*, as distinct from the actual stress.

If Hooke's law were obeyed by an elastomer, the stress would be linearly dependent on the strain, i.e.,

$$r = f / a = Y s, \tag{17}$$

where the constant, Y, is commonly known as Young's modulus. Equation (17) is found to be valid only for small extensions (that is, small for an elastomer but normal for other solids, i.e., ~ 1%). The fact that Hooke's law appears to be followed by many solids (including metals) but not by elastomers is a consequence of the very high deformation tolerated by an elastomer before its tensile limit, the point at which the material breaks, is reached, typically up to $s = 9$ (1000%).

One of the objectives of this experiment is to determine Young's modulus for the elastomer. Not surprisingly, Y for an elastomer is much smaller (typically several hundred times) than for other solids because it is, in fact, so "elastic."

The Origin of Thermoelasticity is Molecular Entropy

It is possible to relate such measureables as Y to theoretical models of elastomer structure and behavior. The molecular structure of soft vulcanized rubber is a network of flexible threadlike molecular strands that are in constant agitation because of their thermal energy. On stretching, these strands assume a partial alignment in the direction of stretch. The alignment represents diminished randomness and thus a decreased entropy. (Recall that entropy is a measure of the number of states accessible to the system: high randomness means there are many possible states that are accessible.) From Eq. (12), we see that $(\partial S / \partial L)_T < 0$, and thus $(\partial f / \partial T)_L > 0$. In other words, as the temperature of the rubber is increased, an increasing tension is required to maintain a given length, i.e., a

given extent of molecular-strand alignment. As the temperature is increased, the thermal motion tending to produce randomness of arrangement becomes intensified.

The degree of randomness, as measured by the entropy, S, can be directly calculated by counting the number of states (e.g. conformations), , accessible to the system. The precise relationship, $S = k_B \ln$, is the fundamental principle relating microscopic or molecular states to macroscopic thermodynamics, forming the basis of *statistical mechanics*.

A statistical mechanical treatment of rubber elasticity thus relies on a calculation of the entropy via the conformations accessible to the molecular chains. We present below the result of such a calculation, but defer the derivation to the upcoming dry lab. We simply note that molecular parameters, such as the average length of chain between crosslinks, can be anticipated to enter in the expression for entropy, which we will use to interpret our thermodynamic measurements.

Assuming that the polymer chains are freely jointed (see the structure for *Hevea* rubber), i.e., there is no barrier to rotations about the CH_2—CH_2 single bonds, and that, moreover, the distance between the termini of a given polymer chain is characterized by a random, or Gaussian, distribution, it is possible to derive an expression for the entropy. From this, the stress r can be related to the fractional elongation, $= L / L_0$:

$$ r = \frac{\rho RT}{zM}\left[\sigma - \frac{1}{\sigma^2}\right] = Y'\left[\sigma - \frac{1}{\sigma^2}\right] , \tag{18} $$

where ρ is the density of the (unstrained) polymer having a *monomer* molecular weight M, and z is the average number of monomer units between cross-links, R is the gas constant, and T is the absolute temperature. By comparing equations (17) and (18), we can see that the coefficient ($\rho RT/zM$) is an effective Young's modulus, Y', that can be obtained by plotting r vs. (- 1/ ^{2}). In this way, z can be determined, and an important characteristic of the elastomer can be obtained because z can be related to the more immediate (and practical) concept of the fraction of monomers that are cross-linked in the polymer, F_{cl}. If a polymer chain consisting of N monomer units contains n cross-links, the average number of monomer units between cross-link nodes is $z = N/n$, and the fraction of cross-links is $F_{cl} \sim n/N$. Typically, F_{cl} is a few percent; its value depends on the particular vulcanization process used.

Thermal Effects

It is interesting to consider the thermal effects of elastomer deformation. The phenomenon can be experienced by suddenly (i.e., quasi-adiabatically) stretching a rubber band or a balloon and then holding it to your lips (a sensitive temperature sensor). The rubber band will feel warmer relative to its initial state. Conversely, after the stretched elastomer is temperature equilibrated and then rapidly returned to its initial

length, it will feel cooler. The rapidity is necessary to minimize heat transfer from the rubber band to the surroundings and thus to keep the process nearly adiabatic. This process is thus analogous to the adiabatic compression and expansion of a gas. The formal expression for the temperature dependence of a reversible adiabatic (isentropic) deformation of an elastomer is $(\partial T / \partial L)_S$. This expression can be obtained from (12) by using the cyclic rule of partial derivatives, i.e.,

$$\frac{\partial T}{\partial L}\Big|_S = -\frac{\partial T}{\partial S}\Big|_L \frac{\partial S}{\partial L}\Big|_T = -\frac{(\partial S / \partial L)_T}{(\partial S / \partial T)_L} . \tag{19}$$

We can relate this expression to the tensile force, f, by using equations (12) and (13) and assuming that the rubber is "ideal" (i.e., that $(\partial U / \partial L)_T = 0$); thus

$$\frac{\partial S}{\partial L}\Big|_T = -\frac{f}{T} . \tag{20}$$

Further simplification results from identifying $(\partial S / \partial T)_L$ with the "constant-length" heat capacity, C_L:

$$C_L \quad T \frac{\partial S}{\partial T}\Big|_L .$$

Equation (19) now becomes

$$\frac{\partial T}{\partial L}\Big|_S = \frac{f}{C_L} . \tag{20}$$

The temperature change is determined from the integration of equation (20):

$$T = \int_{L_0}^{L} \frac{1}{C_L} f \, dL . \tag{21}$$

Assuming that C_L is independent of length and temperature (and that it is approximately equal to C_P of the elastomer—a more common physical constant), we have

$$T = \frac{1}{C_P} w , \tag{22}$$

in which w replaces $\int f \, dL$, and w is the work done on the elastomer in stretching it from L_0 to L. Qualitatively, we see that in stretching an elastomer, $w > 0$ and, hence, $T > 0$, the temperature rises. Conversely, in relaxing from the stretched state, $w < 0$, $T < 0$, and the elastomer cools. To use equation (22) quantitatively, we express C_P as the specific heat, c_P. For many elastomers c_P is 1.8 to 2.0J K^{-1} g^{-1}.

Procedure

The elastomer sample is a commercial rubber band made from a synthetic poly(isoprene). While similar to the natural product, it is free of some of the impurities present in *Hevea* rubber. The sample will have been "prestressed" to eliminate the hysteresis that is usually observed in the $f(T)_L$ plots of new samples. (With hysteresis present, heating and cooling will produce different, although reproducible, results. This is obviously unsatisfactory for determinations of an equation of state of a substance.) The prestressing is accomplished by keeping an elongated elastomer at the maximum temperature for some time and then slowly reducing the temperature.

The procedure is to measure the force as a function of elongation at various fixed temperatures: $\{ f(L)_T \}$. The elongations, L, will be set by fixed length wires, and so will be the same for the various temperatures. In this way, we can also generate $\{ f(T)_L \}$ curves. To be carried out successfully, this experiment (like so many others) requires much patience and attention to detail.

Force Sensor

To
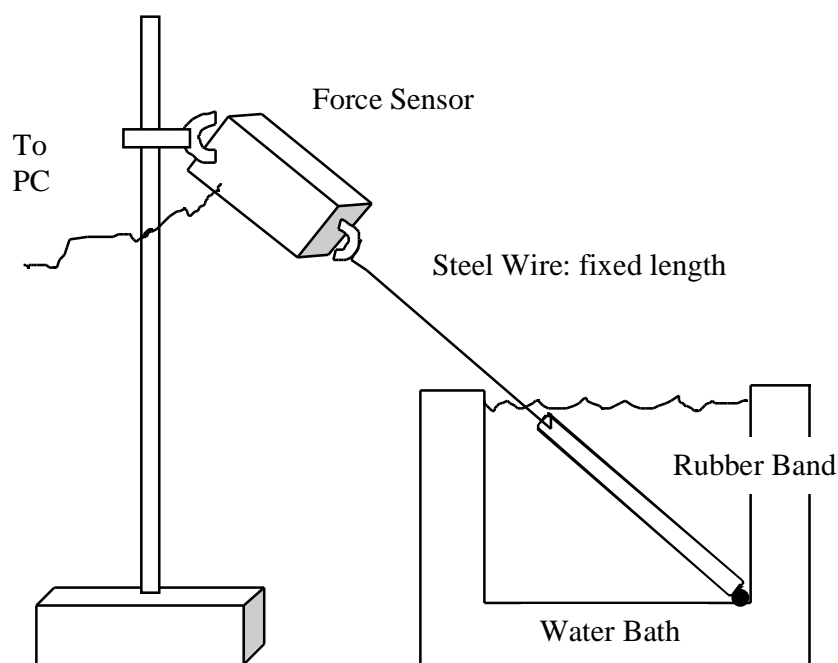PC

Steel Wire: fixed length

Rubber Band

Water Bath

Figure 2. Experimental setup for measuring force with varying temperature and elongation.

The apparatus is shown in Figure 2. The sample is attached at the bottom of the water tank, and is stretched diagonally out of the tank to keep as much of it under water as

possible. The other end of the rubber band is hooked onto a steel wire which connects it to the force meter, which sends its reading of the tension to the PC for data collection.

The temperature is controlled by setting the thermostat control on the front of the bath. The temperatures will range from hot to cold (55°C, 30°C, and 5°C), and equilibration can be speeded up with the addition of ice, which will be on hand. After each new desired temperature is reached, the rubber band needs about 15 minutes to "equilibrate" to the new settings. The elongation is varied by using the different pre-cut lengths of steel wire to hook the rubber band to the force sensor. This will save time since the lengths only need to be measured once at the start.

The tank should be initially set up to be at 55°C.

1. Verify that the force sensor is zeroed by removing the steel wire and checking that the PC reads zero tension.

2. Measure the length of the steel wires and record them in your notebook.

3. Starting with the longest wire, attach the wire to the force sensor and the rubber band as in Figure 2. The force sensor needs to be aligned with the steel wire in order to measure the full magnitude of the tension--you may need to slightly adjust the angle of the sensor. Measure the elongation, L, of the rubber band and record it in your notebook along with the displayed value of the tension.

4. From the previous measurement of the elongation, calculate the elongation the rubber band will have when the other pieces of wire are used instead. The maximum elongation should be about twice the unstretched length.

5. Now moving to the next longest wire, attach the wire, and record the tension and rubber band elongation. Repeat until you have measured using all the pieces of wire.

6. Remove the rubber band from the water, taking care not to leave it out of the water too long. Hold it flat, and measure the length of the unstretched rubber band, L_0. Measure the width of the rubber band, and finally measure the thickness of the rubber band. To get a more accurate thickness value, double up the rubber band so that you have at least 8 layers. Be careful not to compress the elastomer. Put the rubber band back in the tank, attached by the shortest wire (longest rubber band elongation).

7. You have now completed taking data for a range of elongations at one temperature. You should now check to see that your data is consistent with Eq. (18) before continuing. (See parts 2 and 3 in the Data Analysis section below.) However, to allow the rubber band time to equilibrate, set the thermostat down to 30°C, adding ice as necessary. Let the rubber band equilibrate to the new temperature while maximally stretched for at least 15 minutes.

8. Repeat steps 3, 5, and 6 at the new temperature until data acquisition is complete. (You don't need to remeasure the width and thickness.) Repeat at 5°C. Be sure to measure the unstretched elongation at each temperature.

Data Analysis

1. Convert all the tension readings, f, to nominal stress values, $r = f /(2\ a_0)$, using the unstressed cross section, a_0, of the sample to approximate the cross section, a. The factor of 2 appears because the tension is assumed to be divided evenly between the two lengths of rubber band forming the closed loop, each having equal cross section. Convert the elongations, L, to fractional elongation, $\sigma = L / L_0$.

2. For each temperature used, plot r^2 vs. ^{3}; see equation (18). You can use Excel on the laboratory computers. Fit a linear trendline through the data (select the data, and then choose "Add Trendline…" under the Chart menu), clicking the options "Display Equation on Chart" and "Display r-squared value on chart". R-squared values near 1 indicate a good fit. Obtain Y' from the slope of the plot.

3. From the extracted value of Y', determine a value for the fraction of cross-links, $1/z$, in the elastomer. Use a density of $\rho = 0.970$ g cm^{-3}. See equation (18) and the discussion thereafter. Does your result seem reasonable? To improve accuracy, plot Y' vs. T (in K) and obtain an estimate of the fraction of cross-links, $1/z$, in the elastomer.

4. Plot f vs T (in K) for each elongation, L. You should assume that these plots are linear. Using linear regression, determine the intercept (f, T=0) and the slope for each plot. Because of the very large extrapolation between the studied temperatures and 0 K, a considerable error in (f, 0) is inevitable. Determine these errors as well as those of the slopes.

5. From equation (13) determine the nonideal contribution, $(\partial U / \partial L)_T$, to the total force referenced to 30°C for each elongation. Tabulate these values. How large in magnitude is the nonideal contribution relative to the ideal contribution, $T(\partial f / \partial T)_L$, at 30°C?

Pre-lab Questions

1. Using the Maxwell relations and the thermodynamic equation of state, show that each of the terms in equations (14) and (15) is equivalent; i.e.,

$$-\left(\frac{\partial U}{\partial V}\right)_T = -\frac{a}{(V_m)^2} \quad \text{and} \quad T\left(\frac{\partial S}{\partial V}\right)_T = \frac{RT}{V_m - b}$$

for a van der Waals gas.

2. Young's modulus, defined by equation (17), is several hundred times smaller for an elastomer as compared with other solids. Why is this to be expected? Thus what would be the result of trying this experiment with a steel rod rather than a rubber band?

3. What do you expect for the graph of r^2 vs ^{3}, according to Equation (18) (multiply through by ^{2})?

3. Show that equation (14) follows from $dA = dU - T\,dS = -P\,dV - S\,dT$.

Further Readings

R. L. Anthony, R. H. Caston, and E. Guth, J. Phys. Chem., 46:826 (1942).
P. W. Atkins, Physical Chemistry, 5th ed., pp. A37-A38, W. H. Freeman (New York), 1994.
G. B. Kauffmann and R. B. Seymour, J. Chem. Educ., 67:422 (1990).
J. E. Mark, J. Chem. Educ., 58:898 (1981).
P. Meares, Polymers: Structure and Bulk Properties, chaps. 6-8, D. Van Nostrand (London), 1965.
J. H. Noggle, Physical Chemistry, 3d ed., pp. 157-163, HarperCollins (New York), 1996.
J. P. Queslel and J. E. Mark, J. Chem. Educ., 64:491 (1987).
F. Rodriguez, L.J. Mathias, J. Kroschivitz, and C. E. Carraher, J. Chem. Educ., 65:352 (1988).
M. Shen, W. F. Hall, and R. E. DeWames, Molecular Theories of Rubber-Like Elasticity and Polymer Viscoelasticity, in Reviews of Macromolecular Chemistry, G. B. Butler and K. F. O'Driscoll, eds. vol. 3, Marcel Dekker, Inc., New York, 1968.
L. R. G. Treloar, The Physics of Rubber Elasticity, Clarendon Press (Oxford), 1975.
L. R. G. Treloar, Introduction to Polymer Science, Wykeham Publications (London), 1974.
F. T. Wall, Chemical Thermodynamics, pp. 335-350, W. H. Freeman (San Francisco), 1974.
J. B. Byrne, J. Chem. Educ., 71:531 (1994).