Thermodynamics of Rubber Elasticity

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In spite of the fact that Lord Kelvin presented a thermodynamic study of elasticity as long ago as 1857, this chapter is missing in most current thermodynamics textbooks. The reference to elastic systems is often made in either a section, comments, or problems. Thus, the formulation of thermodynamic principles is usually presented for p–V systems, and students are led to the conclusion that thermodynamics only describes simple fluids, instead of a wide variety of physical systems.

Background

Most materials, when stressed, exhibit a limited elastic region where the material regains its original dimensions if the stress is removed. As the resulting strain is related to the extent of movements of atoms from their equilibrium conditions, substances such as crystalline solids and amorphous glasses have elastic limits rarely exceeding 1% because atomic adjustments are localized. The elastic properties of elastomers, however, are truly exceptional. Elastomers are polymeric materials, natural or synthetic, that can undergo large deformations without breaking owing to the ability of their constituent polymeric chains to rotate about the chain bonds (*1*).

By far the most widely studied elastomer is natural rubber, which is obtained from the coagulation of latex from some tropical trees, mainly from the species *Hevea brasiliensis*. An interesting overview of the history of natural rubber has been presented by Kauffman and Seymour (*2*). In 1839, Charles Goodyear invented the process known as vulcanization, which produces a tridimensional network of polymer chains interlinked by sulfur compounds. These links avoid the flow or sliding of chains when a stress is applied, and therefore the elastic properties of vulcanized rubber depend on the degree of linkage. This paper describes only the thermodynamic properties of vulcanized rubber.

In the next section, the choice of stress (τ), length (L), and temperature (T) as state variables is justified, and a simple equation of state is presented. Rubberlike elasticity is described as an entropic effect, similar to the pressure of an ideal gas. It is shown, however, that rubber is not an ideal elastomer (because it verifies only approximately the generalized Joule's law), and this is related to the small but non-negligible energy changes in stretching. Then, the thermoelastic properties of rubber, in particular the thermal expansion at constant stress and the change in the stress with temperature at constant length, are studied. The thermoelastic inversion is also con-

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sidered and the experimental observations are easily rationalized. Finally, the entropy of rubber is evaluated as the sum of two terms, one being a function of temperature and the other a function of length, which permits the evaluation of temperature changes in adiabatic stretching processes.

State Variables and Equation of State

A solid surface is said to be under uniform stress if there is a force acting on the surface whose magnitude is proportional to the surface area. The force, as a vector quantity, may be oriented in any direction with respect to the surface. This study is restricted to forces applied perpendicular to the surface.

The force per unit area acting on a solid surface of arbitrary orientation can be evaluated from three (Cartesian) normal stress components τ_{xx}, τ_{yy}, and τ_{zz}; the components have two subindexes because stress is a second-rank tensor. When the three normal stress components take the same value, $\tau_{xx} = \tau_{yy} = \tau_{zz} = -p$; the solid is said to be under pressure p, and this implies that the stress is the same in every direction. A solid under uniaxial stress, for example along the z direction, has normal stress components $\tau_{xx} = \tau_{yy} = -p$, $\tau_{zz} = \tau - p$, which implies that pressure acts to compress every surface, whereas a tensile stress τ tries to stretch the solid along the z direction. (Note that pressure is not defined here as the mean normal stress.)

The (intensive) thermodynamic state of an isotropic elastic solid is determined by the stress components and the temperature. Hence, at constant mass and composition, all the dependent variables of state (the volume V, the length L along the z direction, the internal energy U, the entropy S, etc.) can be expressed as functions of p, τ and T. Most of the published work (at academic level) on the thermodynamics of elastic systems assumes that stress τ and temperature T are the independent variables of state. This is equivalent to assuming that volume V is constant, and renders unnecessary any reference to p. The resulting thermodynamic equations are the same as for the conventional p–V systems except that p and V are substituted by $-\tau$ and L. This convenient approximation is justified from the fact that upon elongation the cross-sectional area of an elastomer diminishes by such an amount that the volume V remains nearly constant.

Although convenient, this assumption can result in error and misunderstanding when the equations are applied to cases where the assumption is not valid. It is more precise and less misleading to note the constant volume assumption by using V as a subscript on the partial derivatives for which the assumption is made. However, it is also true that consideration of both pressure–volume and stress–length terms in the expression of thermodynamic work makes such a rigorous study more obscure to the students and the relatively simple physical concepts behind rubberlike elasticity might become buried under mathematical expressions with three independent variables (e.g. p, τ, and T). The aim of our contribution is to present a simple yet correct approach that could be included in elementary textbooks. We therefore restrict most of the equations to the case of constant volume, as it is done in the textbooks that include rubber elasticity (*3*, *4*). More rigorous studies including volume changes have been presented in scientific journals (*5*, *6*). Some of the basic ideas that explain the need to make a clear difference between processes at constant volume and processes at constant pressure are included in the Appendix.

While some thermodynamic relations in rubberlike elasticity can be deduced without introducing any particular equation of state (*7*), most of the results obtained in the following sections depend on the equation of state accepted to describe the behavior of rubber. This equation cannot be deduced from thermodynamics because no hypothesis on the structure of matter can be made in any rigorous thermodynamic study. However, the rubberlike elasticity can also be studied using the methods of statistical mechanics. The different microscopic Gaussian models so far available (*8*–*14*), are based on a few common ideas and lead to similar results (*15*). In particular, for small and moderate strains, the equation of state of an isotropic rubber band of length L at temperature T under stress τ (in Newtons) is

$$\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] \qquad (1)$$

at constant volume, where k is a constant that depends on the composition and geometry of the sample considered and L_0 is the length in the absence of applied stress, which depends only on temperature at ordinary pressures (*16*). In deriving eq 1 it is assumed that the strain of the rubber sample takes place at constant volume (*8*–*14*). However, it is sometimes preferable to keep the volume dependence in the stress–strain equations, especially for detailed comparison with the results of statistical theories.

Rubber Is Not an Ideal Elastomer

According to the first and second laws of thermodynamics, the deformation of an elastic system (at constant volume) involves changes in both internal energy and entropy which are related by

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = \tau + T\left(\frac{\partial S}{\partial L}\right)_{T,V} \qquad (2)$$

The derivative $(\partial U/\partial L)_{T,V}$ vanishes for ideal elastic systems (*17*–*20*), which, in the case of rubberlike materials, means that the polymer chains can rotate freely and its internal energy U does not change with conformation—similar to the case of an ideal gas, where the absence of molecular forces implies that its internal energy does not change with volume.

The use of eq 1 and the Maxwell relation, $(\partial S/\partial L)_{T,V} = -(\partial \tau/\partial T)_{L,V}$, yields

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = kT^2\lambda_0\left[\frac{L}{L_0} + 2\left(\frac{L_0}{L}\right)^2\right] \qquad (3)$$

where

$$\lambda_0 = \frac{1}{L_0}\frac{\mathrm{d}L_0}{\mathrm{d}T} \qquad (4)$$

is the coefficient of linear expansion of rubber under zero stress; note that L_0 is considered to be a function of tem-

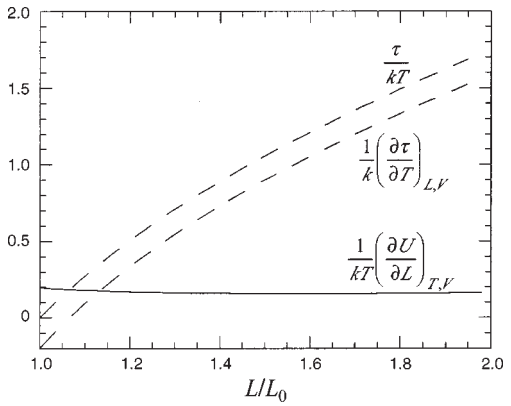

Figure 1. The variation of the internal energy (——) of rubber and its contributions with strain at 25 °C according to eq 2 (– – –).

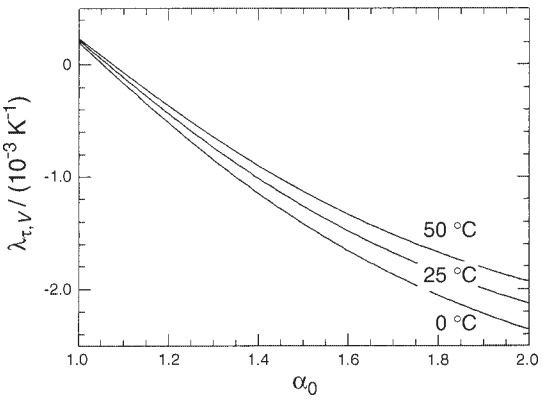

Figure 2. The coefficient of linear expansion of rubber $\lambda_{\tau,V}$ as a function of strain $\alpha_0 \equiv L/L_0(T_0)$ at temperatures 0, 25, and 50 °C.

perature only, which is valid at ordinary pressures (*16*). The value of this coefficient is $\lambda_0 = 2.2 \times 10^{-4}$ K^{-1} (*21*) and remains approximately constant with temperature at ordinary temperatures (*16*). The derivative $(\partial U/\partial L)_{T,V}$ at 25 °C has been represented in Figure 1 over a range of low to moderate strains for a rubber band with $k = 4.86 \times 10^{-3}$ N K^{-1} (*22*). The value of this derivative is certainly small when compared to either of the two terms in the r.h.s. of eq 2. In other words, the energetic contribution to the stress τ is much smaller than the entropic contribution, at least for isothermal processes, and it can be stated that rubber obeys the generalized Joule's law, $(\partial U/\partial L)_{T,V} = 0$, to a high degree of accuracy when the strain is small or moderate. These conclusions are in good agreement with experimental observations (*23*) and have led some authors to describe rubber as an ideal system (*3*, *16*, *24–26*).

Note finally that, according to eq 2, the equation of state of an ideal elastomer at constant V is

$$\tau f(L) = T \tag{5}$$

where $f(L)$ is an arbitrary function of L. Equation 5, in contrast to eq 1, requires that L_0 does not change with temperature and therefore $\lambda_0 = 0$ for an ideal elastomer.

Thermoelastic Inversion

The behavior of rubber in response to temperature changes is rather complex. Whereas most materials exhibit a positive coefficient of linear expansion, that of elastomers changes from positive to negative values with increasing strain. Making use of eq 1, the coefficient of linear expansion at constant tensile stress and volume takes the form

$$\lambda_{\tau,V} \equiv \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\tau,V} = \lambda_0 - \frac{1}{T}\frac{[L/L_0(T)]^3 - 1}{[L/L_0(T)]^3 + 2} \tag{6}$$

where the variation of L_0 with T

$$L_0(T) = L_0(T_0)\exp[\lambda_0(T - T_0)] \tag{7}$$

follows from the integration of eq 4. The term λ_0 in the r.h.s. of eq 6 accounts for the normal liquidlike thermal expansion, and the second term describes the thermoelastic behavior of the entropic restoring forces of the polymer chains.

The coefficient $\lambda_{\tau,V}$ at different temperatures is represented in Figure 2 as a function of $\alpha_0 \equiv L/L_0(T_0)$, which represents the strain of rubber related to its natural length at a reference temperature $T_0 = 298.15$ K. All curves show a sign reversal of $\lambda_{\tau,V}$ when $\alpha_0 \approx 1.1$, which is in agreement with experimental observations (*23*). This means that the coefficient of linear expansion of rubber becomes negative when $\alpha_0 > 1.1$, and therefore the rubber band contracts when temperature increases (*27*, *28*). In contrast, the coefficient of linear expansion of rubber is positive under very low stress ($\alpha_0 < 1.1$), and the usual (liquidlike) increase in length with temperature is observed. This change in the sign of $\lambda_{\tau,V}$ is known as thermoelastic inversion and the corresponding temperature is known as the inversion temperature T_i. The condition $\lambda_{\tau,V} = 0$ and eqs 6 and 7 yield the following relation between α_0 and T_i:

$$\alpha_0^3 = \frac{1 + 2\lambda_0 T_i}{1 - \lambda_0 T_i}\exp[3\lambda_0(T_i - T_0)] \tag{8}$$

For example, an inversion temperature $T_i = T_0 = 298.15$ K requires $\alpha_0 = 1.067$. Note that an ideal elastomer does not show thermoelastic inversion because $\lambda_0 = 0$ and $\lambda_{\tau,V}$ is always negative.

Another aspect of the thermoelastic behavior of a rubber band is the change in τ with T at constant L, and therefore constant strain α_0 (*19*, *29*). By using eqs 1 and 7, the derivative $(\partial\tau/\partial T)_{L,V}$ can be evaluated as

$$\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = -kT\lambda_{\tau,V}\left\{\alpha_0 \exp[-\lambda_0(T - T_0)] + \frac{2}{\alpha_0^2}\exp[2\lambda_0(T - T_0)]\right\} \tag{9}$$

In Figure 3, the stress τ has been represented against T for different values of α_0. It is observed that the slope of these lines decreases with α_0 and becomes negative when the strain is of the order of 10% ($\alpha_0 \approx 1.1$) (*16*). Evidently, this phenomenon is closely related to the inversion in Figure 2, since the change in the slope of the curves in Figure 3 occurs when $(\partial\tau/\partial T)_{L,V} = -L\lambda_{\tau,V}(\partial\tau/\partial L)_{T,V} = 0$; that is, when $T = T_i$.

Temperature Changes in Adiabatic Stretching

The entropy S of a rubber band at constant volume can be evaluated, by using eq 1 and Maxwell's relation $(\partial S/\partial L)_{T,V} = -(\partial \tau/\partial T)_{L,V}$, as

$$S(T,L) = S_0(T) + \int_{L_0}^{L} \left(\frac{\partial S}{\partial L}\right)_{T,V} \mathrm{d}L = S_0(T) - kL_0\left[\frac{L^2}{2L_0^2} + \frac{L_0}{L} - \frac{3}{2} - \lambda_0 T\left(\frac{L^2}{2L_0^2} - \frac{2L_0}{L} + \frac{3}{2}\right)\right] \quad (10)$$

where $S_0(T) = S(T,L_0)$ denotes the entropy in the absence of stress. Figure 4 represents the entropy of rubber ($\lambda_0 = 2.2 \times 10^{-4}$ K^{-1}) at 25 °C and that of an ideal elastomer ($\lambda_0 = 0$) under the same conditions. In the case of small strains and for the ideal elastomer, the entropy reduces to

$$S \approx S_0 - \frac{3}{2}kL_0\left(\frac{L}{L_0} - 1\right)^2 \quad (11)$$

which has also been represented in Figure 4.

The decrease of S with L at constant T and V has some interesting implications for the changes observed in temperature when the length of the rubber band is varied under adiabatic (and constant volume) conditions. By using the Maxwell relation $(\partial T/\partial L)_{S,V} = (\partial \tau/\partial S)_{L,V}$, the derivative $(\partial T/\partial L)_{S,V}$ can be written as

$$\left(\frac{\partial T}{\partial L}\right)_{S,V} = \frac{T}{C_{L,V}}\left(\frac{\partial \tau}{\partial T}\right)_{L,V} \quad (12)$$

where $C_{L,V}$ is the heat capacity at constant length. Since T and $C_{L,V}$ are positive, the sign of $(\partial T/\partial L)_{S,V}$ is equal to that of $(\partial \tau/\partial T)_{L,V}$, which is positive when $\alpha_0 > 1.1$ (Fig. 3). Thus, eq 12 implies that rubber band warms up when its length is suddenly increased with $\alpha_0 > 1.1$ (*30*, *31*). The temperature change in this irreversible adiabatic process can be evaluated by considering a reversible process between the same initial and final states, denoted by 0 and 2, respectively. Since the entropy is a function of state, the entropy change is also zero in the reversible process. Such a reversible process can be thought of as an isothermal reversible process $0 \rightarrow 1$ (at the reference temperature T_0) followed by a reversible process $1 \rightarrow 2$ at constant length (i.e., constant α_0). The entropy change $\Delta S_{0\rightarrow 1}$ can be obtained from eq 10 as

$$\Delta S_{0\rightarrow 1} = -kL_0\left[\frac{\alpha_0^2}{2} + \frac{1}{\alpha_0} - \frac{3}{2} - \lambda_0 T_0\left(\frac{\alpha_0^2}{2} - \frac{2}{\alpha_0} + \frac{3}{2}\right)\right] \quad (13)$$

and the entropy change $\Delta S_{1\rightarrow 2}$ is simply given by

$$\Delta S_{1\rightarrow 2} = C_{L,V}\ln\left(\frac{T}{T_0}\right) \quad (14)$$

Since $\Delta S_{0\rightarrow 1} + \Delta S_{1\rightarrow 2} = 0$,

$$\ln\left(\frac{T}{T_0}\right) = \frac{kL_0}{C_{L,V}}\left[\frac{\alpha_0^2}{2} + \frac{1}{\alpha_0} - \frac{3}{2} - \lambda_0 T_0\left(\frac{\alpha_0^2}{2} - \frac{2}{\alpha_0} + \frac{3}{2}\right)\right] \quad (15)$$

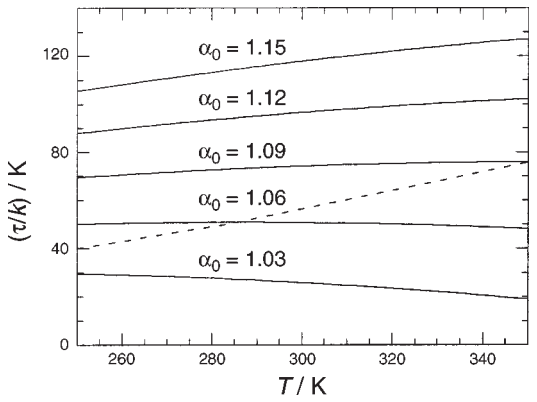

Figure 3. The variation of stress with temperature under constant α_0. The dashed line represents the inversion curve, which results from joining the maxima of the continuous lines.

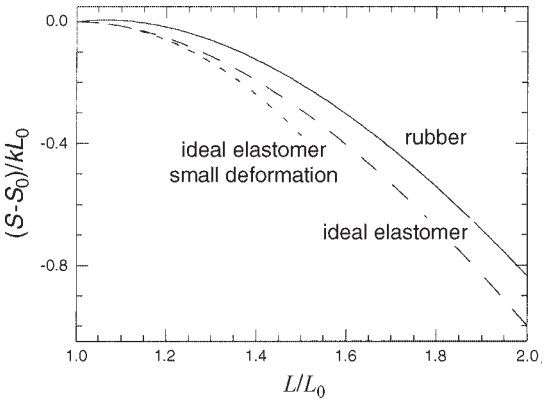

Figure 4. Entropy vs strain for (——) a rubber band with $\lambda_0 = 2.2 \times 10^{-4}$ K^{-1}, (– – –) an ideal elastomer, and (- - -) an ideal elastomer in the approximation of small strains given by eq 11. All curves correspond to 25 °C.

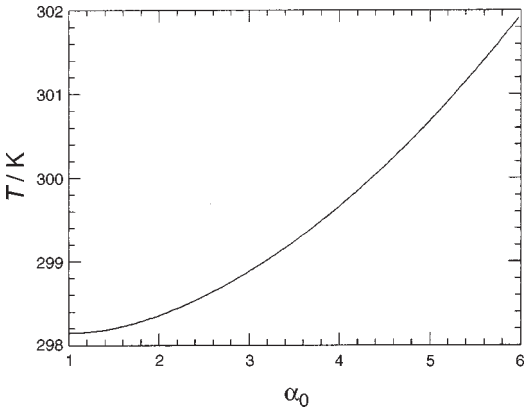

Figure 5. Temperature of the rubber band for an adiabatic stretching process. The following values were used: $T_0 = 298.15$ K, $\lambda_0 = 2.2 \times 10^{-4}$ K^{-1}, and $C_{L,V}/kL_0 \approx 1220$.

which has been represented in Figure 5. The value of $C_{L,V}/kL_0$ has been estimated as $3\rho c_p T_0/E_0 \approx 1220$, where ρ is the rubber density, c_p is the specific heat at constant pressure, and E_0 is the isothermal Young's modulus when $\alpha_0 = 1$ (*21*). It is observed that the temperature of the rubber band increases only a few tenths of a kelvin when its length is doubled from the value L_0, but the temperature increase can reach 4 K for a 500% extension. The temperature increase observed experimentally for a 500% extension varies between 5 and 10 K (*18*). The warming felt by placing a rubber band in contact with the lips (which are very sensitive to temperature changes) and stretching it suddenly with both hands. If the initial length is suddenly recovered, the rubber band is observed to cool down. This and some other experiences related to thermoelastic inversion were described by John Gough as early as 1802. Although he used natural rubber, his experiments showed, at least qualitatively, most of the thermodynamic properties of rubber (*32*).

Conclusions

A thermodynamic study of a rubber band at constant volume under uniaxial stress has been presented on the basis of its equation of state. The study is rather thorough and includes the most representative characteristics of rubberlike elasticity, and the agreement between theoretical results and experimental observations is remarkable. The material is suitable for undergraduates taking thermodynamics courses for physics, chemistry, materials science, or engineering degrees, and is expected to contribute to filling the gap found in most thermodynamics textbooks.

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Appendix

While making thermoelastic measurements, it is very difficult to maintain a constant volume. Experiments at constant pressure are much easier, but the elongation of the rubber sample due to the application of a tensile stress is then accompanied by a volume increase. Although this volume increase is very small, the effect is connected with a significant change in internal energy. Therefore it is mandatory to consider both the pressure–volume and the stress–length contributions to the thermodynamic work, and to write the fundamental equation for the internal energy as

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \tau\mathrm{d}L \tag{A1}$$

When T, L, and V are chosen as independent variables describing the system, the change in internal energy can also be specified as

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{L,V}\mathrm{d}T + \left(\frac{\partial U}{\partial L}\right)_{T,V}\mathrm{d}L + \left(\frac{\partial U}{\partial V}\right)_{T,L}\mathrm{d}V \tag{A2}$$

and a standard thermodynamic manipulation leads to

$$\left(\frac{\partial U}{\partial L}\right)_{T,p} = \left(\frac{\partial U}{\partial L}\right)_{T,V} + \left(\frac{\partial U}{\partial V}\right)_{L,T}\left(\frac{\partial V}{\partial L}\right)_{T,p} \tag{A3}$$

Having already pointed out that $(\partial V/\partial L)_{T,p}$ is very small for rubber, it is important to note that $(\partial U/\partial V)_{L,T}$ is of the order of 0.4 GPa, and hence the last term in eq A3 is appreciable (*5*, *6*, *16*).

The coefficient of linear expansion and the heat capacity also depend on the measurement conditions. It can be easily shown that the differences between their values at constant pressure and at constant volume are given by

$$\lambda_{\tau,p} = \lambda_{\tau,V} + \frac{1}{L}\left(\frac{\partial L}{\partial V}\right)_{T,\tau}\left(\frac{\partial V}{\partial T}\right)_{\tau,p} \tag{A4}$$

$$C_{L,p} = C_{L,V} + T\left(\frac{\partial S}{\partial V}\right)_{T,L}\left(\frac{\partial V}{\partial T}\right)_{L,p} \tag{A5}$$

In conclusion, the subtle differences between derivatives taken at constant pressure or constant volume are not trivial, and eqs A3–A5 are of decisive practical importance for experimental work. However, rubber elasticity is an important topic, as Kelvin and Gibbs realized, and this complication should not prevent us from incorporating it into the teaching of elementary thermodynamics.