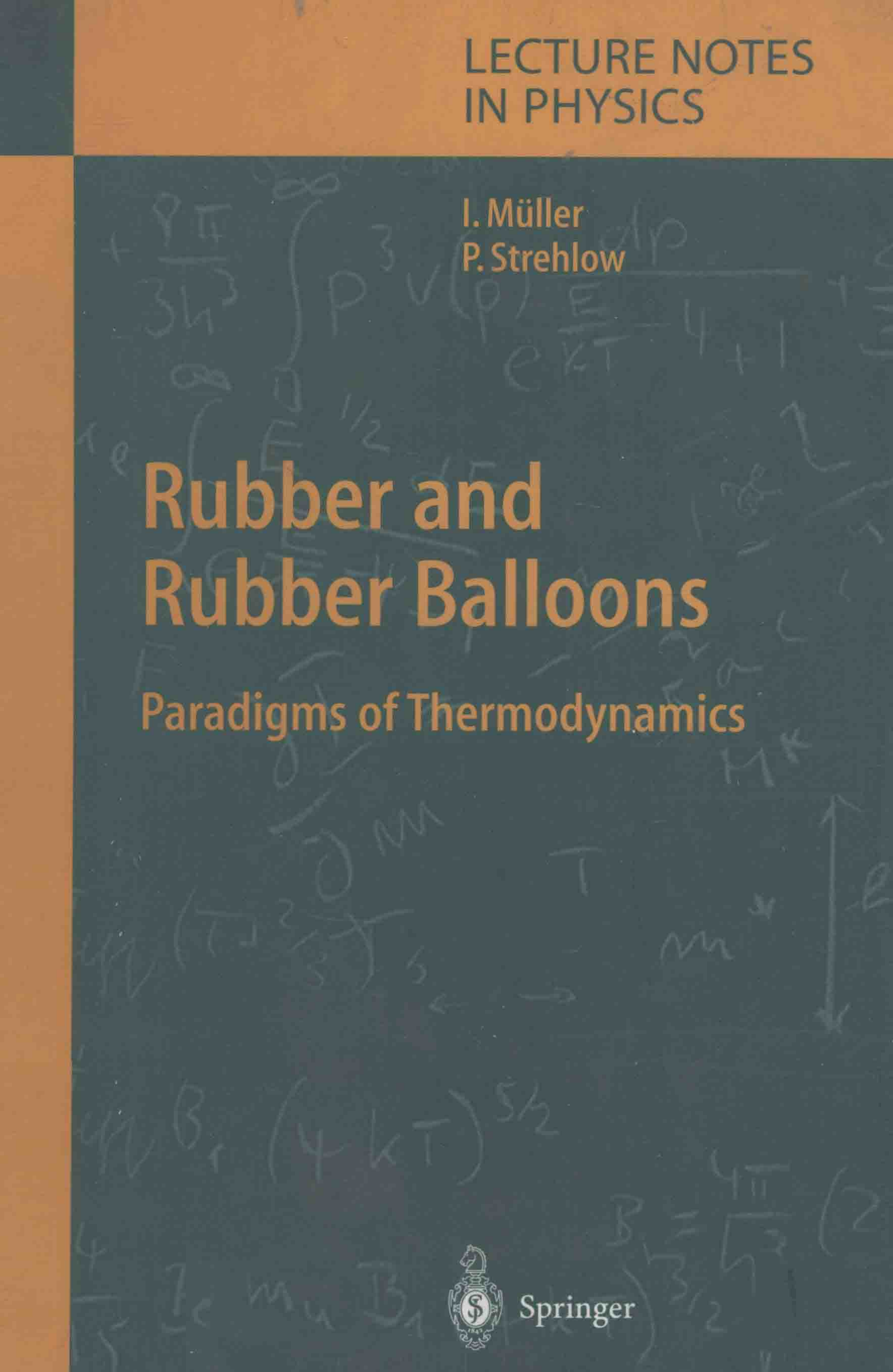

LECTURE NOTES
IN PHYSICS

I. Müller
P. Strehlow

Rubber and Rubber Balloons

Paradigms of Thermodynamics

Springer

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Contents

1 Stability of Two Rubber Balloons

Rubber balloons, that usually adorn children's parties, can also enchant the scientist. Indeed, there is much more than fun and games to be had with balloons; they form a suitable subject for mathematical studies and an interesting paradigm of methods of modeling in physics and chemistry.

First of all, balloons consist of rubber, a remarkably unique elastic material with an extreme extensibility – superior to that of all other solids – and perfectly resilient. In a sense to be explained later the closest relatives of rubber amongst natural materials are the ideal gases, like air. Both, rubber and gas, are the only examples of entropic materials.

In order to catch the reader's attention and raise his curiosity for the rich properties of rubber and rubber balloons, we perform the experiment shown in Fig. 1.1. Two balloons inflated to the same size are fixed to the ends of a connecting pipe, cf. Fig. 1.1_{top}. However, that situation proves to be unstable when the tap is opened; air flows from one balloon to the other one until the *stable* equilibrium is reached, which is demonstrated in the bottom part of Fig. 1.1, where one balloon is small and the other one is large. The initial symmetry of the arrangement has been broken spontaneously.

From this we must *not*, however, conclude that a small balloon always inflates the large one with which it can exchange air. The stability depends on the amount of filling and the process shown in Fig. 1.1 will only occur for intermediate fillings. Indeed, with either more air or less air in the two balloons, the larger one inflates the smaller one until a symmetric equilibrium situation is attained and both are equal in size, see Figs. 1.2 and 1.3. We shall study that phenomenon in due time and understand it completely as a question of stability.

The early research relevant to balloons does not concern balloons at all but droplets, bubbles and, in particular, soap bubbles. Rubber balloons were unknown before the 1820's, when Michael Faraday glued one together – or so they say. To be sure balloons are different from bubbles but there is some similarity; certainly both enclose air in a spherical membrane. Therefore it is somewhat pertinent to balloon-research that, 200 years ago, Young and Laplace related the pressure difference $[p] = p - p_0$ between the inside and the outside of a soap bubble to the radius r. Their result is now known as the Young-Laplace formula and it reads

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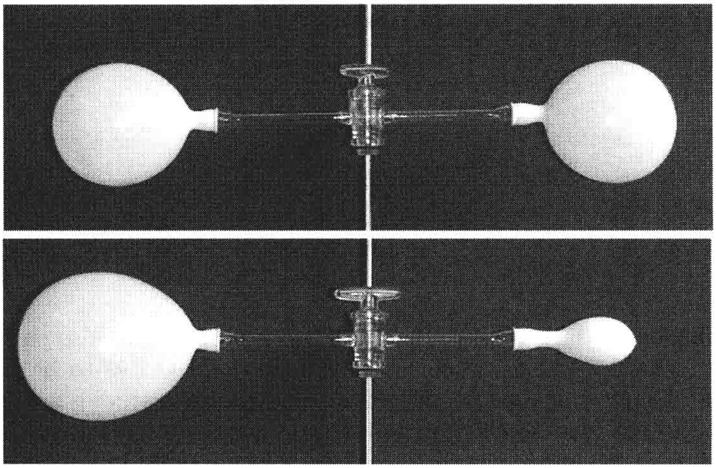

Fig. 1.1. Symmetry breaking. The initial equilibrium is unstable. Top: Tap closed. Bottom: Tap open

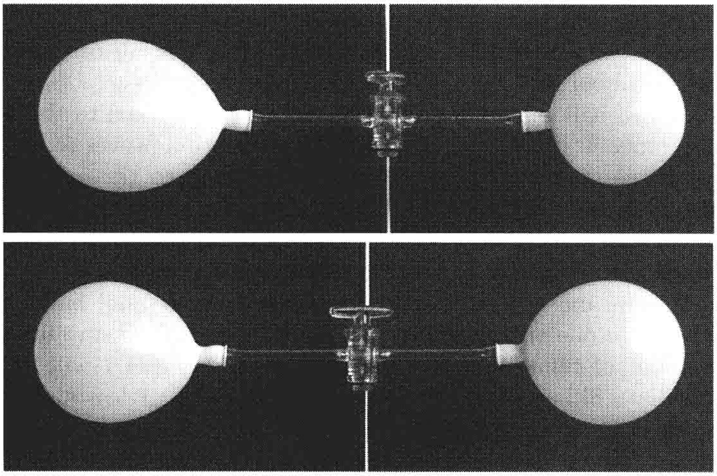

Fig. 1.2. Large filling: An initially asymmetric situation (top) becomes a symmetric equilibrium upon opening the tap

$$[p] = \frac{4\sigma}{r}. \tag{1.1}$$

The coefficient σ is called surface energy or also surface tension.[1]

In later times, when the close relation between work and energy became common knowledge, the equation (1.1) was derived as follows: For an increase $\mathrm{d}r$ of the bubble radius, the surfaces – inner and outer surface – increase

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[1] For literature and literary references we refer the reader to Chap. 12.

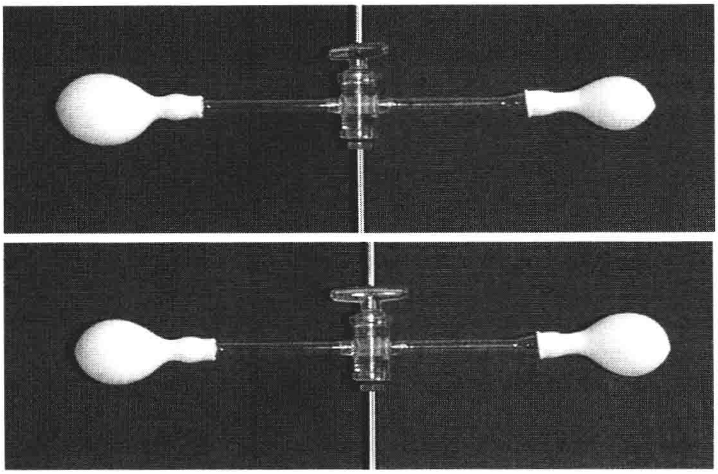

Fig. 1.3. Small filling: Same process as in Fig. 1.2: A symmetric equilibrium situation will evolve from an asymmetric situation when the balloons can exchange air

by $\mathrm{d}A = 2 \cdot 8\pi r \mathrm{d}r$. That expansion of surface requires a certain amount of work which we assume to be proportional to $\mathrm{d}A$. Let us say that the work is equal to $\sigma \mathrm{d}A$, where σ is a factor of proportionality, possibly dependent on the extant r. The work is done by the pressure difference $[p]$ which inflates the volume $V = \frac{4\pi}{3} r^3$ by $\mathrm{d}V = 4\pi r^2 \mathrm{d}r$ so that the work equals $[p]\mathrm{d}V$. Thus we have

$$[p]\mathrm{d}V = \sigma \mathrm{d}A, \qquad \text{and hence} \qquad [p] = \frac{4\sigma}{r}. \tag{1.2}$$

So what about stability? Let us concentrate on Fig. 1.2_{bottom} and test the stability of that situation in which p is equal in both ballons. In a thought experiment we squeeze the right balloon (say), thereby decreasing its radius and making air move to the left balloon, which will therefore grow. If in that process the pressure in the squeezed balloon decreases and the pressure in the inflated one increases, the air will move back as soon as the squeezing stops; the initial situation will be reestablished and therefore it is a stable situation. Thus stability requires that $\frac{\mathrm{d}[p]}{\mathrm{d}r} > 0$ holds. If $\frac{\mathrm{d}[p]}{\mathrm{d}r}$ were smaller than zero, the imposed shift would not heal itself, but become worse and thus expose the initial state as unstable.

Actually, the thought experiment does not require an active experimenter to do the squeezing. Indeed, even if the balloons are initially exactly alike, the inevitable thermal fluctuations of pressure will be enough to test their stability.

The unstable situation can remind us of the predicament of Buridan's ass who should starve – according to the scholastic philosopher – in the middle of two equal bales of hay. Of course it does not starve, because the tiniest fluctuation of its head will make one or the other bale more attractive spontaneously.

By (1.1) the stability condition $\frac{\mathrm{d}[p]}{\mathrm{d}r} > 0$ may be written in the form

$$-\frac{4\sigma}{r^2} + \frac{4}{r}\frac{\mathrm{d}\sigma}{\mathrm{d}r} > 0, \quad \text{hence} \quad \frac{\mathrm{d}\sigma}{\mathrm{d}r} > \frac{\sigma}{r}. \tag{1.3}$$

A stability argument like this was first given by Gibbs and it implies that σ must depend on r, since the experiments of Figs. 1.2 and 1.3 have shown that there are stable equilibria between balloons of equal size. To be sure we do not expect the inequality (1.3) to hold for all values of r, since we have seen in Fig. 1.1 that two balloons with equal pressures and equal radii may also be unstable.

The question is *how* the surface tension σ depends on r, and that question will be answered in the next two chapters which deal with the Kinetic Theory of Rubber (Chap. 2) and with Non-linear Elasticity (Chap. 3). Those two theories are masterpieces of materials' science in their own right, far outreaching their applicability to rubber balloons. Therefore, in presenting these theories, we do a little more than we must for the purpose of explaining balloons; we thus hope to be able to share some exciting results of thermodynamics, statistical mechanics and continuum mechanics with the reader.

Of course, we need not rely upon theory; there is always experiment and, indeed, it is quite easy to measure the pressure difference $[p]$ across the balloon membrane as a function of its radius r. Figure 1.4_{left} shows a suitable manometer: We attach a fully inflated balloon to its inlet and let the air drain out slowly through a small opening in the connecting pipe. We monitor the

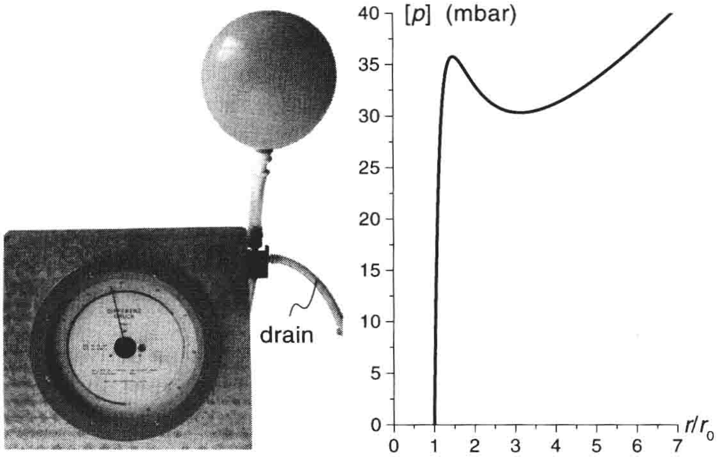

Fig. 1.4. Left: A manometer to measure the graph $[p]$ vs. $\frac{r}{r_0}$. Right: The pressure-radius characteristic of the balloon

size of the balloon, and the pressure indicated by the pointer on the manometer scale. Thus we obtain a graph $[p]$ versus $\frac{r}{r_0}$, where r_0 is the radius of the non-inflated balloon. Such a graph is shown in Fig. 1.4_{right}.

Inspection of Fig. 1.4 shows that there are two ascending branches of the pressure-radius characteristic of the balloon, one for large radii the other for small ones. On those branches we expect stable equilibria for interconnected balloons of the same size according to the above-described thought experiment. And indeed, in Figs. 1.2 and 1.3 we have seen stable equilibria establish themselves between two large balloons and two small ones. By the same token the initially unstable situation of Fig. 1.1 occurs in balloons of intermediate size and we must conclude that their radii correspond to the descending branch on the characteristic of Fig. 1.4.

The reader who is interested in balloons only – and not in rubber as such – should take a good look at the pressure-radius graph of Fig. 1.4_{right} and at (3.24) which represents that graph analytically. He is then prepared to study the Chaps. 5 through 8 which are the ones that deal with balloons.

2 Kinetic Theory of Rubber

2.1 Rubber Elasticity is "Entropy Induced"

We start by considering an elastic bar of any solid material, be it steel, aluminium, wood – or rubber. The bar is fixed to the bottom at one end and a tensile load P_λ is applied to the other end slowly, or as we say, *quasistatically.* This means that the deformation of the bar caused by the tensile load P_λ is homogeneous and that the load itself is always equilibrated by the retractive elastic force $\bar{P}_\lambda$ of the bar. Accelerations are negligible and so is the kinetic energy of the bar and the dissipation, or entropy production. The undistorted length of the bar is L_λ^0 and the deformed length under the load P_λ – or $\bar{P}_\lambda$ – is L_λ, see Fig. 2.1. The temperature is equal to T everywhere in the bar and at all times.

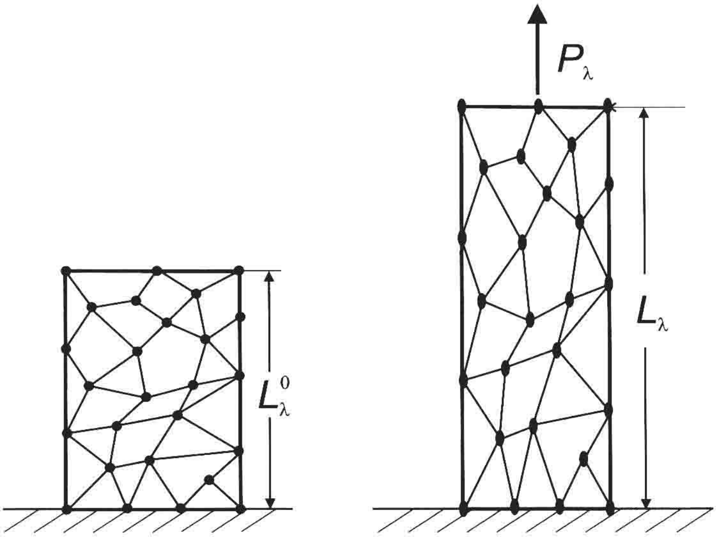

Fig. 2.1. An elastic bar in the undistorted state (left) and deformed by the load P_λ (right)

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Under quasistatically applied loads the first and second laws of thermodynamics read

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \dot{Q} + \dot{W} \qquad \text{and} \qquad \frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\dot{Q}}{T}. \tag{2.1}$$

U and S are the internal energy and entropy respectively and $\dot{W}$ is the working, or power, of the load, i.e.

$$\dot{W} = P_\lambda \frac{\mathrm{d}L_\lambda}{\mathrm{d}t} \qquad \text{or here} \qquad \dot{W} = \bar{P}_\lambda \frac{\mathrm{d}L_\lambda}{\mathrm{d}t}. \tag{2.2}$$

$\dot{Q}$ is the heating needed to maintain the constant temperature T. Both equations (2.1) represent somewhat mutilated forms of the laws of thermodynamics. Thus the first law, or energy balance, has no kinetic energy term because the process is quasistatic. For the same reason the second law, or entropy balance, is an equality rather than an inequality. Indeed, the entropy production vanishes in a quasistatic or reversible process.

Later, in Chap. 3 we shall have to consider rapid, irreversible processes and that will force us to give the complete form of the thermodynamic laws. Also we shall then have to make a distinction between the applied load P_λ, and the elastic force $\bar{P}_\lambda$.

Elimination of $\dot{Q}$ and $\dot{W}$ between (2.1) and (2.2) provides the Gibbs equation for S

$$T\mathrm{d}S = \mathrm{d}U - \bar{P}_\lambda \mathrm{d}L_\lambda, \tag{2.3}$$

or, equivalently, for the free energy $F = U - TS$

$$\mathrm{d}(U - TS) = -S\mathrm{d}T + \bar{P}_\lambda \mathrm{d}L_\lambda. \tag{2.4}$$

The elastic force $\bar{P}_\lambda$ and the internal energy U depend on L_λ and T and so does S, by (2.3). The functions $\bar{P}_\lambda(L_\lambda, T)$ and $U(L_\lambda, T)$ are called thermal and caloric equations of state, respectively, and their specific form is characteristic for a material. The two equations of state are not independent, because (2.4) implies

$$\bar{P}_\lambda = \frac{\partial U}{\partial L_\lambda} - T\frac{\partial S}{\partial L_\lambda} \quad \text{and} \quad \frac{\partial S}{\partial L_\lambda} = -\frac{\partial \bar{P}_\lambda}{\partial T}, \quad \text{hence} \quad \frac{\partial U}{\partial L_\lambda} = \bar{P}_\lambda - T\frac{\partial \bar{P}_\lambda}{\partial T}. \tag{2.5}$$

Equation $(2.5)_2$ results as an integrability condition for the free energy F, cf. (2.4), while $(2.5)_1$ allows us to split the elastic force $\bar{P}_\lambda$ into

- an energetic part $\frac{\partial U}{\partial L_\lambda}$ and
- an entropic part $-T\frac{\partial S}{\partial L_\lambda}$. (2.6)

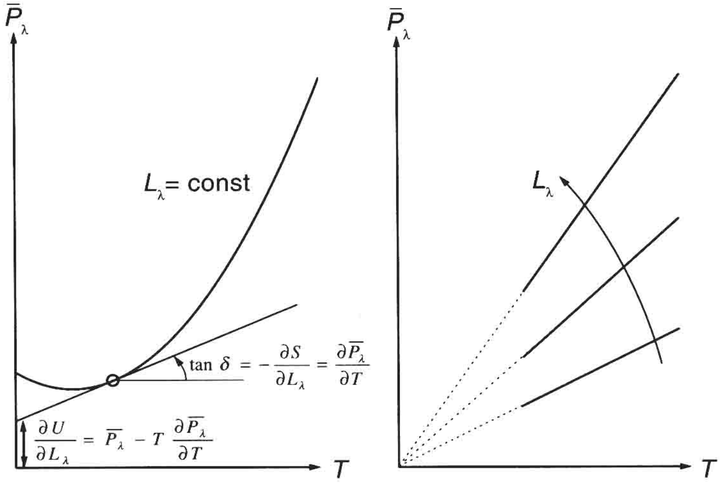

Fig. 2.2. Left: Measured load-temperature graph of a bar of an arbitrary material (schematic). Right: Measured load-temperature graphs of rubber for different constant values of L_λ

Thus we recognize that part of the elastic force is due to a change of energy with length and part is due to a change of entropy.

It is possible to identify the two parts of $\bar{P}_\lambda$ – the energetic and entropic ones – for every L_λ and T from a simple experiment: For different temperatures, we measure the load $\bar{P}_\lambda$ needed to maintain a fixed length L_λ and we plot $\bar{P}_\lambda(L_\lambda, T)$. Let Fig. 2.2_{left} represent such a measured plot for one L_λ. At one point of that curve the slope $\frac{\partial \bar{P}_\lambda}{\partial T}$ determines the entropic part of $\bar{P}_\lambda$ – to within the factor T – because, by $(2.5)_2$, that slope equals $-\frac{\partial S}{\partial L_\lambda}$. Also, the ordinate intercept of the tangent in that point determines the energetic part, because, by $(2.5)_3$, we have $\frac{\partial U}{\partial L_\lambda} = \bar{P}_\lambda - T\frac{\partial \bar{P}_\lambda}{\partial T}$.

When we perform this experiment for rubber, we obtain straight lines as those shown in Fig. 2.2_{right} and, upon extrapolation of these lines down to absolute zero temperature, we see that the ordinate intercept is equal to zero. Accordingly the internal energy U of rubber is independent of L_λ, or we may say that the energy has nothing to do with the elastic force of rubber. That force is *entropy-induced.* Indeed, for rubber $(2.5)_1$ reduces to

$$\bar{P}_\lambda = -T\frac{\partial S}{\partial L_\lambda}. \tag{2.7}$$

Rubber is not the only material with entropy-induced elasticity. Ideal gases have the same property. Let us consider:

The framework of quasistatic or reversible thermodynamics is equally valid for any fluid and for the elastic bar in uniaxial tension considered heretofore. In particular, the first and second laws have the forms (2.1) and the only difference