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The rubber elastic state

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1.1 Introduction

1.1.1 Basic concepts

The elastic properties of rubber-like materials are so strikingly unusual that it is essential to begin by defining rubber-like elasticity, and then to discuss what types of materials can exhibit it. Accordingly, this type of elasticity may be operationally defined as very large deformability with essentially complete recoverability. In order for a material to exhibit this type of elasticity, three molecular requirements must be met: (i) the material must consist of polymeric chains, (ii) the chains must have a high degree of flexibility and mobility, and (iii) the chains must be joined into a network structure [1–5].

The first requirement arises from the fact that the molecules in a rubber or elastomeric material must be able to alter their arrangements and extensions in space dramatically in response to an imposed stress, and only a long-chain molecule has the required very large number of spatial arrangements of very different extensions. This versatility is illustrated in Fig. 1.1 [3], which depicts a two-dimensional projection of a random spatial arrangement of a relatively short polyethylene chain in the amorphous state. The spatial configuration shown was computer generated, in as realistic a manner as possible. The correct bond lengths and bond angles were employed, as was the known preference for *trans* rotational states about the skeletal bonds in any n-alkane molecule. A final feature taken into account is the fact that rotational states are interdependent; what one rotational skeletal bond does depends on what the adjoining skeletal bonds are doing [6–8]. One important feature of this typical configuration is the relatively high spatial extension of some parts of the chain. This is due to the preference for the *trans* conformation, as has already been mentioned, which is essentially a planar zig-zag and thus of high extension. The

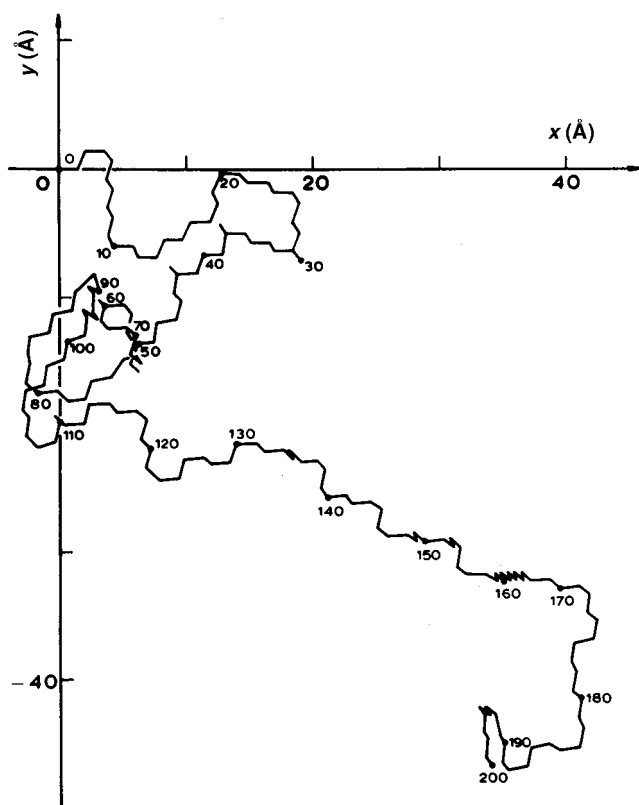


Fig. 1.1. A two-dimensional projection of an n-alkane chain having 200 skeletal bonds [3]. The end-to-end vector starts at the origin of the coordinate system and ends at carbon atom number 200.

second important feature is the fact that, in spite of these preferences, many sections of the chain are quite compact. Thus, the overall chain extension (measured in terms of the end-to-end separation) is quite small. Even for such a short chain, the extension could be increased approximately four-fold by simple rotations about skeletal bonds, without any need for distortions of bond angles or increases in bond lengths.

The second characteristic required for rubber-like elasticity specifies that the different spatial arrangements be *accessible*, i.e. changes in these arrangements should not be hindered by constraints such as might result from inherent rigidity of the chains, extensive chain crystallization, or the very high viscosity characteristic of the glassy state [1, 2, 9].

The last characteristic cited is required in order to obtain the elastomeric recoverability. It is obtained by joining together or “cross-linking” pairs of segments, approximately one out of a hundred, thereby preventing stretched polymer chains

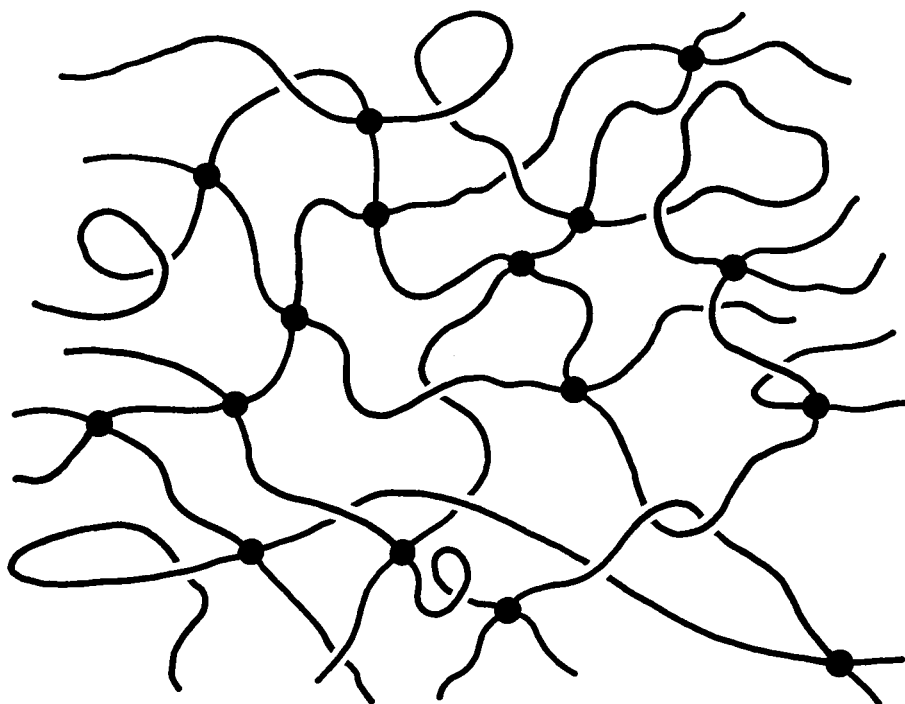


Fig. 1.2. A sketch of an elastomeric network, with the cross-links represented by dots [3].

from irreversibly sliding by one another. The network structure thus obtained is illustrated in Fig. 1.2 [9], in which the cross-links may be either chemical bonds (as would occur in sulfur-vulcanized natural rubber) or physical aggregates, for example the small crystallites in a partially crystalline polymer or the glassy domains in a multiphase block copolymer [3]. Additional information on the cross-linking of chains is given in Section 1.1.6.

1.1.2 The origin of the elastic retractive force

The molecular origin of the elastic force f exhibited by a deformed elastomeric network can be elucidated through thermoelastic experiments, which involve the temperature dependence of either the force at constant length L or the length at constant force [1, 3]. Consider first a thin metal strip stretched with a weight W to a point short of that giving permanent deformation, as is shown in Fig. 1.3 [3]. An increase in temperature (at constant force) would increase the length of the stretched strip in what would be considered the “usual” behavior. Exactly the opposite, a *shrinkage*, is observed in the case of a stretched elastomer! For purposes

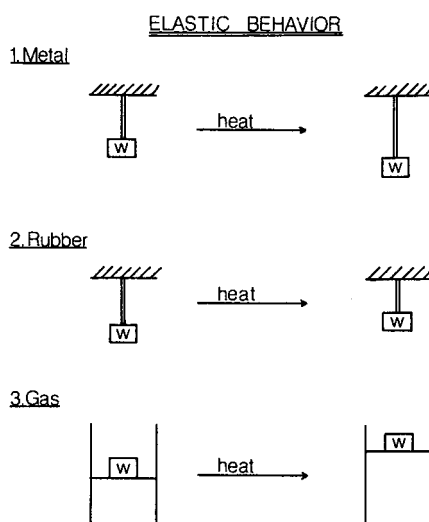


Fig. 1.3. Results of thermoelastic experiments carried out on a typical metal, rubber, and gas [3].

of comparison, the result observed for a gas at constant pressure is included in Fig. 1.3. Raising its temperature would of course cause an increase in volume V , as exemplified by the ideal-gas law.

The explanation for these observations is given in Fig. 1.4 [3]. The primary effect of stretching the metal is the increase ΔE in energy caused by changing the separation d between the metal atoms. The stretched strip retracts to its original length upon removal of the force since this is associated with a decrease in energy. Similarly, heating the strip at constant force causes the usual expansion arising from an increase in oscillations about the minimum in the asymmetric potential-energy curve. In the case of the elastomer, however, the major effect of the deformation is the stretching out of the network chains, which substantially reduces their entropy [1–3]. Thus, the retractive force arises primarily from the tendency of the system to increase its entropy toward the (maximum) value it had in the undeformed state. An increase in temperature increases the magnitude of the chaotic molecular motions of the chains and thus increases the tendency toward this more random state. As a result, there is a decrease in length at constant force, or an increase in force at constant length. This is strikingly similar to the behavior of a compressed gas, in which the extent of deformation is given by the reciprocal volume $1/V$. The pressure of the gas is also largely entropically derived, with an increase in deformation (i.e. an increase in $1/V$) also corresponding to a decrease in entropy. Heating the gas increases the driving force toward the state of maximum entropy (infinite volume or zero deformation). Thus, increasing the temperature

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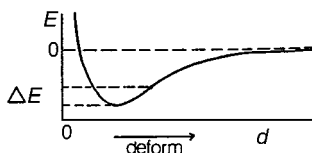
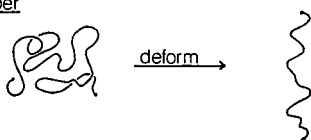
ORIGINS OF ELASTICITY1. Metal2. Rubber3. Gas

Fig. 1.4. Sketches explaining the observations described in Fig. 1.3 in terms of the molecular origin of the elastic force or pressure [3].

increases the volume at constant pressure, or increases the pressure at constant volume.

This surprising analogy between a gas and an elastomer (which is a condensed phase) carries over into the expressions for the work dw of deformation. In the case of a gas, dw is of course $-p dV$. For an elastomer, however, this pressure–volume term is generally essentially negligible. For example, network elongation is known to take place at very nearly constant volume [1, 3]. The corresponding work term now becomes $+fdL$, where the difference in sign is due to the fact that positive dw corresponds not to a decrease in volume of a gas but to an increase in length of an elastomer. Adiabatically stretching an elastomer increases its temperature in the same way that adiabatically compressing a gas (for example in a diesel engine) will increase its temperature. Similarly, an elastomer cools on adiabatic retraction, just as a compressed gas cools during the corresponding expansion. The basic point here is the fact that the retractive force of an elastomer and the pressure of a gas are both primarily entropically derived and, as a result, the thermodynamic and molecular descriptions of these otherwise dissimilar systems are very closely related.

1.1.3 Some historical high points

The simplest of the thermoelastic experiments described above were first carried out many years ago, by J. Gough, back in 1805 [1, 2, 9, 10]. Gough was a clergyman,

who also practiced botany, but had to do it through his sense of touch since he was blind. This is presumably the reason some of his experiments involved sensing the increase in temperature of a rubber strip rapidly stretched while it was in contact with his lips. Particularly important in this regard was the discovery of vulcanization or curing of rubber into network structures by C. Goodyear and N. Hayward in 1839; it permitted the preparation of samples that could be investigated in this regard with much greater reliability. Specifically, the availability of such cross-linked samples led to the more quantitative experiments carried out by J. P. Joule, in 1859. This was, in fact, only a few years after the entropy had been introduced as a concept in thermodynamics in general! Another important experimental fact relevant to the development of these molecular ideas was the fact that deformations of rubber-like materials generally occurred essentially at constant volume, so long as crystallization was not induced [1]. (In this sense, the deformation of an elastomer and that of a gas are very different.)

A molecular interpretation of the fact that rubber-like elasticity is primarily entropic in origin had to await H. Staudinger's much more recent demonstration, in the 1920s, that polymers were covalently bonded molecules, rather than being some type of association complex best studied by the colloid chemists [1]. In 1932, W. Kuhn used this observed constancy in volume to point out that the changes in entropy must therefore involve changes in orientations or spatial configurations of the network chains. These basic qualitative ideas are shown in the sketch in Fig. 1.5 [9], where the arrows represent some typical end-to-end vectors of the network chains.

Later in the 1930s, W. Kuhn, E. Guth, and H. Mark first began to develop quantitative theories based on this idea that the network chains undergo configurational changes, by rotations of skeletal bonds, in response to an imposed stress [1, 2]. More rigorous theories began with the development of the "phantom-network" theory by H. M. James and E. Guth in 1941, and the "affine-model" theory by F. T. Wall, and by P. J. Flory and J. Rehner Jr in 1942 and 1943.

These theories, and some of their modern-day refinements, are described in the following sections.

1.1.4 Basic postulates

There are several important postulates that have been used in the development of the molecular theories of rubber-like elasticity [9].

The first is that, although intermolecular interactions are certainly present in elastomeric materials, they are independent of chain configuration and are therefore also independent of deformation. In effect, the assumption is that rubber-like elasticity is entirely of *intramolecular* origin.

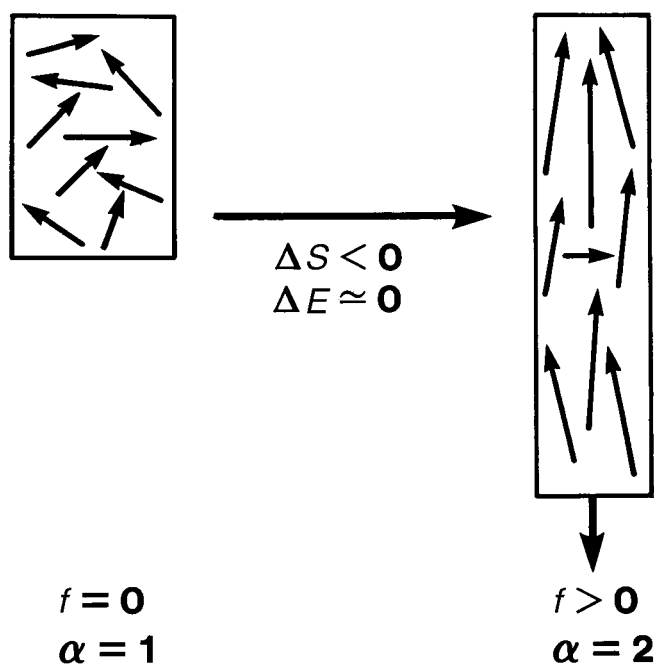


Fig. 1.5. A sketch showing changes in length and orientation of network end-to-end vectors upon elongation of a network [9]. Note that vectors lying approximately perpendicular to the direction of stretching (i.e. horizontally) become *compressed*.

The second postulate states that the free energy of the network is separable into two parts, a liquid-like part and an elastic part, with the former not depending on deformation. This permits the elasticity to be treated independently of other properties characteristic of solids and liquids in general.

In some of the theories it is further assumed that the deformation is affine, i.e. that the network chains move in a simple linear fashion with the macroscopic deformation. Most theories invoke a Gaussian distribution. Non-Gaussian theories have, however, been developed for network chains that are unusually short or stretched close to the limits of their extensibility [2].

1.1.5 Some rubber-like materials

Since high flexibility and mobility are required for rubber-like elasticity, elastomers generally do not contain groups such as ring structures and bulky side chains [2, 9]. These characteristics are evidenced by the low glass-transition temperatures T_g exhibited by these materials. (The structural features of a polymeric chain conducive to low values of T_g are discussed by K. L. Ngai in Chapter 2.) These polymers also tend to have low melting points, if any, but some do undergo crystallization upon being

subjected to sufficiently large deformations. Examples of typical elastomers include natural rubber and butyl rubber (which do undergo strain-induced crystallization), and poly(dimethylsiloxane) (PDMS), poly(ethyl acrylate), styrene–butadiene copolymer, and ethylene–propylene copolymer (which generally do not). The crystallization of polymers in general is discussed by L. Mandelkern in Chapter 4.

Some polymers are not elastomeric under normal conditions but can be made so by raising the temperature or adding a diluent (“plasticizer”). Polyethylene is in this category because of its high degree of crystallinity. Polystyrene, poly(vinyl chloride), and the biopolymer elastin are also of this type, but because of their relatively high glass-transition temperatures [9].

A final class of polymers is inherently non-elastomeric. Examples are polymeric sulfur, because its chains are too unstable, poly(*p*-phenylene), because its chains are too rigid, and thermosetting resins because their chains are too short [9].

There is currently much interest in designing network chains of controlled stiffness. The primary aim here is to increase the melting point of an elastomer such as PDMS so that it undergoes strain-induced crystallization. This crystallization is the origin of the superb mechanical properties of natural rubber, and it results from the reinforcing effects of the crystallites. One way of stiffening elastomeric chains such as PDMS is to put a *meta*- or *para*-phenylene group in the backbone, in an attempt to increase the melting point by bringing about a decrease in the entropy of fusion [9, 11].

Also of interest are fluorosiloxane elastomers. Placing fluorine atoms into siloxane repeat units can be useful for increasing the solvent resistance, thermal stability, and surface-active properties of a polysiloxane [12–14].

One example of another interesting elastomeric material is a new hydrogenated nitrile rubber with good oil resistance and a wide service-temperature range [15]. Another is a type of “*baroplastic*” elastomer, which parallels *thermoplastic* elastomers in that an increase in pressure instead of the usual increase in temperature gives the desired softening required for processing [16].

1.1.6 Preparation of networks

One of the simplest ways to introduce the cross-links required for rubber-like elasticity is to carry out a copolymerization in which one of the comonomers has a functionality ϕ of three or higher [9, 17]. This method, however, has been used primarily to prepare materials so heavily cross-linked that they are in the category of relatively hard thermosets rather than elastomeric materials [18].

A sufficiently stable network structure can also be obtained by physical aggregation of some of the chain segments onto filler particles, by formation of microcrystallites, by condensation of ionic side chains onto metal ions, by chelation of ligand

side chains to metal ions, and by microphase separation of glassy or crystalline end blocks in a triblock copolymer [9]. The main advantage of these materials is the fact that the cross-links are generally only temporary, which means that such materials frequently exhibit reprocessability. This temporary nature of the cross-linking can, of course, also be a disadvantage since the materials are rubber-like only so long as the aggregates are not broken up by high temperatures, the presence of diluents or plasticizers, etc.

1.1.7 Gelation

The formation of network structures necessary for rubber-like elasticity has been studied extensively by a number of groups [19–21]. One approach is to carry out random end linking of functionally terminated precursor chains with a multifunctional reagent, and then to examine the sol fraction with regard to amounts and types of molecules present, and the gel fraction with regard to its structure and mechanical properties. One of the systems most studied in this regard [20] involves chains of PDMS having end groups X that are either hydroxyl or vinyl groups, with the corresponding Y groups on the end-linking agents then being OR alkoxy groups in an organosilicate, or H atoms in a multifunctional silane [22].

In a study of this type, the Monte Carlo method was used to simulate these reactions and thus generate information on the vinyl–silane end linking of PDMS [23, 24]. The simulations gave a very good account of the extent of reaction at the gelation points, but overestimated the maximum extent attainable. The discrepancy may be due to experimental difficulties in taking a reaction close to completion within a highly viscous, entangled medium.

1.1.8 Structures of networks

Before commenting further on such experiments, however, it is useful to digress briefly to establish the relationship among the three most widely used measures of the cross-link density. The first involves the number (or number of moles) of network chains ν , with a network chain defined as one that extends from one cross-link to another. This quantity is usually expressed as the chain density ν/V , where V is the volume of the (unswollen) network [1]. A second measure, directly proportional to it, is the density μ/V of cross-links. The relationship between the number of cross-links μ and the number of chains ν must obviously depend on the cross-link functionality. The two most important types of networks in this regard are the tetrafunctional ($\phi = 4$), almost invariably obtained upon joining two segments from different chains, and the trifunctional, obtained, for example, on forming a polyurethane network by end-linking hydroxyl-terminated chains

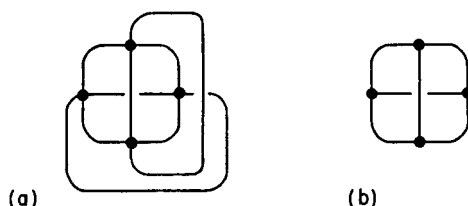


Fig. 1.6. Sketches of some simple, perfect networks having (a) tetrafunctional and (b) trifunctional cross-links (both of which are indicated by the dots) [25]. (Reproduced with permission; copyright 1982, *Rubber Chem. Technol.*)

with a triisocyanate. The relationship between μ and ν is illustrated in Fig. 1.6 [25], which consists of sketches of two simple, perfect network structures, the first tetrafunctional and the second trifunctional. They are simple in the sense of having small enough values of μ and ν for them to be easily counted, and perfect in the sense of not having any dangling ends or elastically ineffective loops (chains with both ends attached to the same cross-link). As can be seen, the tetrafunctional network yields $\mu/\nu = 4/8$ or $1/2$, and the trifunctional one $4/6$ or $2/3$.

In general, for a perfect ϕ -functional network the number $\phi\mu$ of cross-link attachment points equals the number 2ν of chain ends, thus giving the simple relationship $\mu = (2/\phi)\nu$ [1]. Another (inverse) measure of the cross-link density is the molecular weight M_c between cross-links. This is simply the density (ρ , in g cm^{-3}) divided by the number of moles of chains (ν/V , in mol cm^{-3}): $M_c = \rho/(\nu/V)$ [1]. A related structural quantity that is important in the more modern theories is the cycle rank ξ , which denotes the number of chains that have to be cut in order to reduce the network to a tree with no closed cycles at all. It is given by $\xi = (1 - 2/\phi)\nu$ [9].

1.2 Theory

1.2.1 Phenomenological

The phenomenological approach to rubber-like elasticity is based on continuum mechanics and symmetry arguments rather than on molecular concepts [2, 17, 26, 27]. It attempts to fit stress-strain data with a minimum number of parameters, which are then used to predict other mechanical properties of the same material. Its best-known result is the Mooney–Rivlin equation, which states that the modulus of an elastomer should vary linearly with reciprocal elongation [2].

1.2.2 The affine model

This theory, like any other molecular theory of rubber-like elasticity, is based on a chain-distribution function, which gives the probability of any end-to-end