

Natural and Artificial Rubber: the Elasticity of Long-chain Molecules

By Prof. H. Mark, University of Vienna

INTRODUCTION

THE elasticity of rubber and related substances is not of the same kind as the elasticity of steel or glass, but seems more to possess the nature of the elasticity of gases. This may appear strange, because we are accustomed to regard rubber as a solid body, but as a matter of fact technical men have since long realized this peculiar relationship. Hence they nearly always use rubber or rubber-like material in conjunction with air, when they try to produce a high elastic combination as a ball, a tube, a tyre, etc., but they never combine soft rubber with metals or other solid bodies. Only hard rubber is used in this field. Our technical experience so far can be summarized thus: soft rubber is best used in conjunction with gases, hard rubber with solid bodies.

It may be very surprising that recent research work in the field of high molecular substances has shown, indeed, that the elasticity of soft rubber is based on exactly the same fundamental effect as the elasticity of gases, while on the other hand the elastic properties of hard rubber are closely related to those of metals or other solid bodies.

We have well-founded ideas on the elastic behaviour of normal crystals, and we know that the single atoms or ions oscillate around equilibrium positions, which are shifted when we extend the crystal elastically. The energy which enters in this way in the lattice represents the elastic energy of the sample; this is the cause of the experimentally observed fact that a normal crystal cools during rapid extension and heats during rapid relaxation. On the other hand, soft rubber heats during rapid extension and cools down when it is rapidly relaxed, while hard rubber shows the same behaviour as normal solid crystals.

All these facts show that we have to look for quite a different mechanism when we want to explain the high reversible elasticity of soft rubber and a number of analogous substances, which are grouped together under the title 'synthetic rubber', but may be built up from substances chemically quite different. Searching for such a new explanation, we have first to note that all bodies with characteristic rubber-like elasticity have one common property, namely, they are built up of long chain-like molecules, every one of which consists of some hundred members and every one of which shows a remarkable internal flexibility. Substances built up of long thread-like molecules, so-called main-valence chains, play an important

part in the constitution of organized matter. There are rubber, proteins, cellulose, chitin, starch, etc. Synthetic products of the same molecular type are the well-known high polymeric substances such as polystyrene, buna, duprene, sowpren, thiokol, perdurene, etc. Always, when the long chains are flexible, as is the case with rubber, proteins, buna, duprene, thiokol, sulphur, etc., we get typical rubber-like elasticity, while in the case of more or less stiff chains—cellulose, chitin, polystyrene—we get plastic materials, which may be used technically as artificial resins.

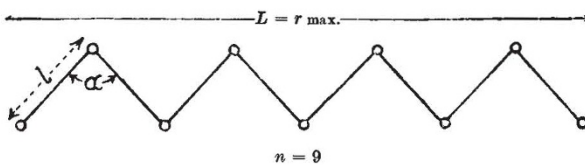
We have therefore to put the question: What particular properties have long flexible chain-like molecules?

BEHAVIOUR OF A SINGLE CHAIN-MOLECULE

Starting from very simple assumptions, we study an isolated chain-molecule of the type



n being a number between 100 and 10,000. We are quite aware that our results must be preliminary, because rubber does not consist of one single chain of this type, but contains many such chains substituted with methyl groups and linked together by secondary valences.



Bragg's experiments show that the length of every carbon linkage is 1.45 Å. and stereochemistry teaches us that the angle between two valencies is 109° , and that, around every linkage, free or nearly free rotation has to be assumed. When we stretch the molecule we get a chain of the length

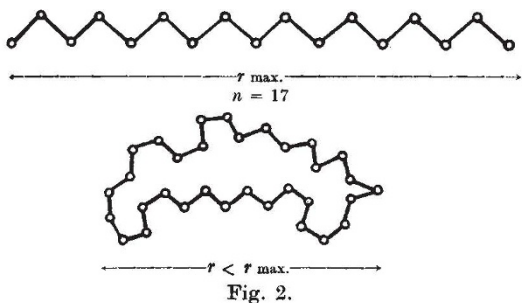
$$L = (n - 1) \cdot l \sin \frac{\alpha}{2} = r_{\max.}$$

the shape of which is shown in Fig. 1. The distance between the first and the last atom of the chain represents the maximum possible distance which can be produced between these two atoms, and can be realized only in the way represented by Fig. 1.

But when we prescribe for the distance between the first and last C-atom another value r such that

$$r < r_{\max.},$$

it is easily seen that we can obtain this distance in many different ways. According to the flexibility of the chain, we are free to fold it together in different ways, so that the distance between the ends is just r . To every given r belongs a certain number of possibilities, realizing this value in geometrically different ways. This reminds us rather closely of the Boltzmann statistics of an ideal gas, where we also have to enumerate the possibilities of microscopic realization for one given macroscopic state. In our case the macroscopic state is the fixed distance r between the chain-ends, and the different possibilities or aspects are afforded by the different shapes of the chain, all of which give the same distance between the ends (compare Fig. 2).



These considerations invite us to assume that a chain-like molecule, being in thermodynamical equilibrium with its surrounding—getting from all directions at random thermal impulses—will by itself always appear in that state which has the greatest number of aspects. This means nothing else but the application of Boltzmann's ideas to the case of a single chain-like molecule. When we have the extended chain and allow it to be in free contact with its surroundings, it will try to increase its number of possible states, that is, to reach a higher statistical probability. This is certainly not the extended state, because that has the realization number *one*. It will be another state, in which the ends of the chain are nearer together than in the case shown in Fig. 1. That means nothing else but that the extended chain will contract by itself, as an ideal gas expands by itself, because the number of aspects increases with increasing volume of the gas. On the other hand, when we want to extend the contracted chain, we have to bring it in a less probable state. According to the general laws of thermodynamics, this is only possible if one puts work into the system, and this work is used to extend the elastic chain.

It is seen, therefore, that the contraction of an extended piece of rubber is not due to the action of

molecular forces but to the thermal movement of the single members in the different chain molecules which build up the sample. Exactly in the same way, the pressure which an ideal gas exerts on its wall is not due to forces but to the thermal movement of the single molecules. It is very significant that in both cases thermodynamics requires that with increasing temperature the effect should increase. In fact, it has long been well known that the pressure of an ideal gas is proportional to the absolute temperature, and it was a very important observation made independently by K. H. Meyer, to whom we owe the new development on this field, and L. S. Ornstein that the elasticity of rubber also increases with the temperature.

It is not very difficult to put all this in formulae, which was done by E. Guth some years ago. To every prescribed distance r between the ends of the chain belongs a certain number of realization possibilities. It can be calculated by the laws of probability. One finds the probability, W , that a chain with n members each of the length l , combined together by a valence angle α , should give a distance r between its first and last atom is given by :

$$W(n, l, \alpha, r)r^2 dr = \sqrt{\frac{6}{\pi}} \cdot \frac{3}{n^2 l^2 l_\alpha^2} \cdot \exp\left(-\frac{3r^2}{2nl_\alpha^2}\right) r^2 dr.$$

$$l_\alpha^2 = l^2 \frac{1 + \cos \alpha}{1 - \cos \alpha} \quad (1)$$

When we regard this as the statistical probability function of our system, we may define the *entropy of a single chain* by the well-known Boltzmann expression,

$$S = k \log W, \quad (2)$$

and can derive from the entropy all properties of the substance. It is well known that in the theory of ideal gases the pressure can be calculated from the entropy by the formula

$$p = +\left(\frac{\partial S}{\partial V}\right)_T \cdot T.$$

When we put in this equation the entropy of an ideal gas, we get the fundamental equation of state

$$pV = RT.$$

In very close analogy to this we can put for our chain molecule the relation

$$\sigma = -\left(\frac{\partial S}{\partial \delta l}\right)_T \cdot T$$

$$\sigma = \text{tension or stress.} \quad (3)$$

$$\delta l = \text{extension.}$$

Taking (2) for S and (1) for W , we get the equation of state for our system. In this way we obtain :

$$\sigma = kT \frac{3}{nl^2} \cdot \frac{1 - \cos \alpha}{1 + \cos \alpha} \cdot \delta l, \quad (4)$$

which is nothing else than a theoretical expression for the *extension curve* of a single flexible molecular chain in thermodynamical equilibrium with its surroundings.

APPLICATION OF THE THEORY

It is interesting to note that experiment is in very fair agreement with these ideas. We have already mentioned the experiments of K. H. Meyer and L. S. Ornstein, which show the fundamental fact that the elasticity of rubber increases with increasing temperature. Other measurements due to L. Hock and to P. A. Thiessen show that the thermo-elastic properties of rubber do not at all contradict the ideas of statistical elasticity. The relation (4) contains the number n of the chain-members, which is closely connected with its molecular weight. In fact, W. Kuhn, to whom we owe very interesting calculations on this field, was able to derive the average molecular weight of rubber starting from its modulus of elasticity. He got values between 20,000 and 100,000, in very satisfactory agreement with other methods earlier applied. Another consequence is that the specific heat of stretched rubber measured at constant length must be different from the specific heat measured at constant tension. This also has been proved experimentally, and supports the ideas put forward in this article.

To get real quantitative agreement between experiment and theory it is necessary to improve our model in two directions:

(1) We have to consider that a macroscopic piece of rubber consists of *many* long-chain molecules connected together by van der Waals' forces. This means that the molecules are not independent of one another, but have the property of hindering each other during the extension.

(2) It is not necessary that the rotation around the single carbon linkages in one chain should be

really free. There can be some steric hindrance, which allows only a certain amount of free rotation.

Both improvements are on the same lines by which one proceeds from the equation of state of an ideal gas to the van der Waals' equation.

Our second point is identical with the van der Waals' volume correction, while the first one brings into consideration the forces between the different molecules. From the theory of gases we know that at high pressures and low temperatures during the compression of a gas a new phase, namely a liquid phase, arises, and that in this region an equilibrium between two phases plays an important part in the behaviour of the system. In very close analogy it has been found that rubber also shows at high tensions and low temperatures a new phase, namely, the small rubber crystals, which were detected by J. R. Katz and afterwards were investigated by many other workers. Under these conditions, again, an equilibrium between liquid and solid rubber determines the behaviour of the system. This equilibrium was carefully investigated by G. v. Susich and by P. A. Thiessen and his collaborators. In gases the condensation process is subject to the Clausius-Clapeyron equation, and it is very easy to derive from the formulæ mentioned above a relation which corresponds exactly to the Clausius-Clapeyron equation and which seems to be in very good agreement with the experimental facts found by L. Hock, G. v. Susich, P. A. Thiessen and others.

There is no question that a lot of experimental and theoretical work has still to be done before we shall be able to survey the whole field of elastic extensibility of high-molecular substances, but we seem to be on the right path, and many other properties, such as the viscosity of high-molecular solutions and the dielectric behaviour of long-chain dipoles, will be elucidated by such studies.

Science, Logic and Philosophy*

By Dr. Harold Jeffreys, F.R.S.

MUCH in current discussion of scientific method turns on the ancient problem of idealism versus realism. As I understand it, an idealist holds that he is inventing a universe for himself as he goes along, while a realist holds that there is a "universe existing independently of our thought and our examination of it"—to use the words of Prof. Dingle—and that what we are doing in science is to find out something about this universe.

* Based on a lecture given at the University of Leeds on January 31.

Realism has been severely criticized, and some forms of it not too severely. Nevertheless, I do not believe that anybody is an idealist. If an idealist regards the world as a mere mental construct of his own, so are other people, being part of that world. Hence if an idealist argues with other people he must think that he is arguing with his own mental constructs, and all discussion should be futile for him. So far as my observation goes, people that call themselves idealists are at