THE FLOW

THE PRESENT widespread use of polymer plastics has made necessary the study of the mechanical properties of these substances and thus has focussed the interest of the engineer and the physicist once again upon the general problem of the flow properties of solid materials. This is a classical problem; over a period of nearly 100 years it has repeatedly made headlines in physics. The empirical foundations were laid by men whose names mark the development of classical physics —Maxwell, Hopkinson, Kohlrausch. Boltzmann and Wiechert developed a phenomenological, e.g. descriptive, theory which is still unsurpassed. The great Italian mathematician V. Volterra recognized the mathematical implications of this theory and therefrom established the theory of the integral equation that carries his name. The applied physicists and engineers joined forces, bringing with them the tools of modern technology and extending the field of experimental research to a point undreamed of some years ago. And now the theorists of modern physics begin to see a way in which the observed macroscopical behavior of matter may be explained in detail by a satisfactory molecular theory. But in spite of all this combined effort the problem is far from being completely solved.

A problem that in itself is of a rather particular kind seldom remains for so long a time in the front line of scientific interest. When this happens there must be something about it which definitely sets it apart from the great majority of related problems. In the present case one clearly discerns two outstanding features: (1) the time scale of flow phenomena is completely different from that of ordinary laboratory observations; and (2) the behavior of the flowing system depends not only on the conditions prevailing at a given moment of observation, but on the entire history of the system. This situation hardly fits into the pattern of theory which is current in other fields of physics.

THE BEHAVIOR of solid materials under stress can be studied in many different ways. A fundamental method of observation to which frequent reference will be made in the following is the simple stretching experiment. A rod of the material to be studied is firmly suspended at one end and a weight attached at the other end. The deformation, here mainly an elongation of the rod, is observed for different values and at different times after the application of the weight. The results of this experiment lead to a classification of solid substances into elastic, viscous, and viscoelastic materials.

Elasticity. A material is perfectly elastic when the application of the weight produces a deformation which is directly proportional to the value of the weight, remains constant so long as the weight is kept the same, and disappears immediately upon its removal (Fig. 1a). Such an effect can be characterized by a single constant of material, the modulus of elasticity, which is the relation between the force and the deformation for a sample of standard dimensions. Hardened steel and objects constituted of it approach this ideal picture as nearly as is possible. The spring has become the prototype of the perfectly elastic element.

Viscosity. In a perfectly viscous medium the sudden application of an external force does not at once produce a deformation. A deformation reveals itself only when the load is kept constant for a while. It increases at a linear rate as time goes on, the rate of growth being proportional to the value of the load. Upon removal of the load, however, the deformation does not recede but remains at its ultimate value (Fig. 1b). A single constant is still sufficient for the description of this effect; it is the relation between the force and the rate of deformation or velocity of flow for the standard sample and is called the coefficient of viscosity. Only liquids are ideal viscous substances. A mechanism exhibiting perfect viscous behavior is the dashpot, which is simply an oil-filled cylinder in which a piston moves. Between the piston and the wall there is provided some escape for the oil to flow through, and when the piston is loaded it begins to move, pressing the oil out of the escape. In its movement the piston meets with a viscous resistance which is strictly proportional to its velocity, but not with a reaction force trying to reestablish its initial position. Therefore when unloaded (abstraction being made of its own weight) it stops just where it is left at that moment.

Viscoelasticity. Although a body may show superposed viscous and elastic behavior under certain circumstances, this is not identical with viscoelastic behavior as understood here. A truly viscoelastic body will not suffer any instantaneous deformation upon application of a load; it will, however, become deformed when the load is kept constant, the rate of deformation becoming smaller and smaller as time goes on and eventually reaching an ultimate value. Upon removal of the load the deformation decreases in exactly the

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OF SOLIDS

By B. Gross

same way as it had increased before, and after a sufficiently long time the body will have regained its initial undisturbed shape (see Fig. 1c). Another characteristic of viscoelastic behavior is stress relaxation; this will be discussed below. The amplitudes of deformation are still proportional to the imposed forces and therefore the phenomena are linear. But a single constant is now insufficient for an adequate description; instead, a time function must be introduced which will give the deformation of a standard specimen under unit stress. The progressive deformation is called creep and the time function is the creep function. Its special shape and significance will be discussed later. Suffice it to say here that together with the modulus of elasticity and the coefficient of viscosity it will prove sufficient for the formal theory of the linear viscoelastic body under the most general conditions. The viscoelastic effect contains aspects of elasticity and viscosity together — elasticity because all deformations are reversible, viscosity because deformations occur not instantaneously but with some delay. It seems that in the case of rubber this picture is very nearly approached.

Complex viscoelastic behavior. Most real bodies behave in a more complex form. Thus, loading produces an instantaneous deformation which under a constantly applied load goes on increasing with a slope that eventually tends to a final value different from zero. Unloading gives an instantaneous contraction followed by a further gradual recovery, but even after a very long time a finite "plastic" deformation may remain. It is easy to see how such a behavior can be obtained as a superposition of the idealized cases mentioned above (See Fig. 1d).

Relaxation. Instead of constant load one may alternatively have constant deformation. Think for instance of a rubber strip which after having been stretched is kept at constant length. Subsequently not the deformation is measured, but the force necessary to maintain the strip in a stretched condition. In a perfectly elastic body the force would remain constant; in a viscoelastic body it decreases with time from its initial rather high value to a final quite low one, because the material slowly yields to the applied stress. The grip which holds the outstretched rubber can be relaxed, which is termed stress relaxation.

Energy loss. A purely elastic system like a spring can be, and frequently is, used for energy storage. The mechanical energy spent in the process of deformation is converted into elastic energy and stored in the elastically deformed body. It can be recovered entirely when the system is released. A truly viscous system cannot be used for any sort of energy storage, because heat — frictional heat — is produced. Thus the energy consumed for the deformation is completely lost. A viscoelastic system (and for the sake of simplicity consider a perfect system, not the complex one) can again be used for energy storage, but lacks the 100% efficiency of the elastic system, because some heat is produced in creep, and the corresponding amount of mechanical energy is irreparably lost. There exists a type of energy loss which is entirely due to the viscoelastic mechanism. This is particularly important in applications where alternating stresses or deformations appear. Consider, for instance, the transmission of sound through a rubber sheet in which each volume element of the sheet is compressed and extended a great number of times per second. In each cycle of compression and extension some heat is produced. The corresponding energy is extracted from the travelling

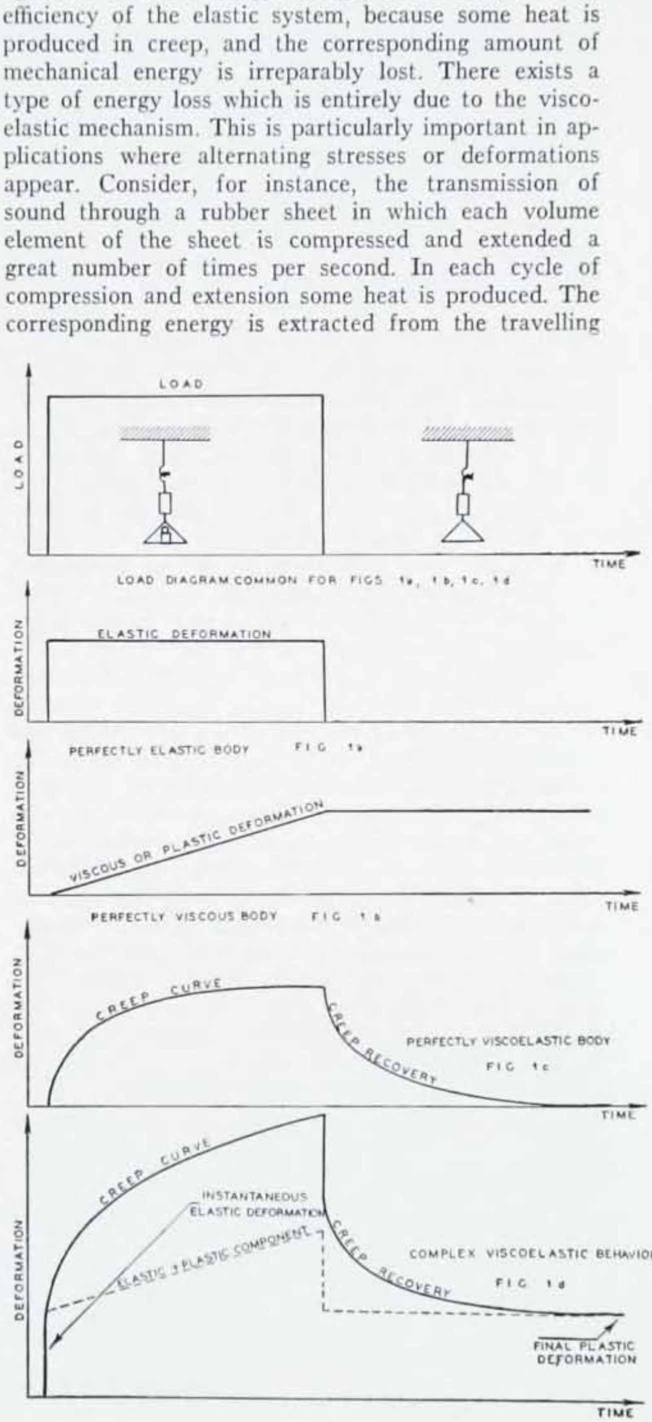
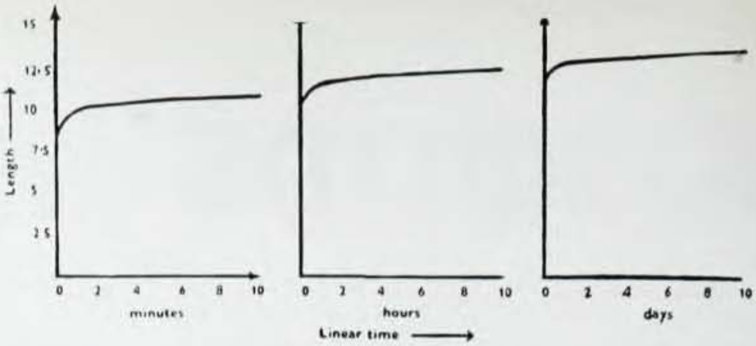


Fig. 2



sound wave which therefore suffers an energy loss and consequently damping. Another example of the energy loss associated with creep is given by the heating of the rubber tires of fast moving vehicles. The tires continually experience periodic deformations; during each rotation of the tire a certain amount of heat is produced and, if low grade material were to be used, this heat, together with that resulting from friction with the ground, could be sufficient to bring about a dangerous rise of the temperature of the tire.

THE TIME SCALE.* Let us now fix our attention more closely upon the shape of the creep curve and the problem of its measurement. As an example, consider an elementary process of observation which consists in measuring periodically, say from minute to minute, the distance between two fixed points on a suspended and loaded rod. Suppose that the rod consists of a viscoelastic material that does not suffer plastic deformations. The result of such an observation invariably would be a considerable increase in length during the first minutes, so much so that the first measurement is rather difficult and it is hard to say exactly what the length of the rod might be immediately after loading. But as time goes on the movement becomes slower and slower and the displacements smaller and smaller. And after a certain time the rod apparently will have ceased to creep (Fig. 2a). However, if a more refined method of observation is employed — if the amplification of the measuring microscope or the length of the levers in the testing apparatus is increased — it will again be possible to discern the creep of the rod. But even refined methods of observation have their limitations and the differences between subsequent measurements will again become minute. Then the observer will perhaps find it expedient to increase the interval between one measurement and the following one from minutes to hours, and from hours to days or perhaps weeks (Figs. 2b and 2c). But eventually even the patience of a physicist may come to an end, and rather than concede that this has happened, some observers have in the past concluded that ultimately the creeping rod has come to rest, the period assigned to it thus depending rather more on the character of the observer than on the characteristics of the rod.

However, the way in which the results of Fig. 2 have been plotted, together with the previous reference to a continuous increase of the intervals between measurements, suggests another type of interpretation. Curves of similar aspect are obtained when successively greater units of time are chosen. Actually the time-scales of the three plots are different. 1 cm is respectively equivalent to 4 minutes, 4 hours, and 4 days. Or, conversely, 1 minute corresponds successively to 2.5 mm, 1/24 mm, and 1/576 mm. Thus the time scale of the last plot is contracted with regard to that of the preceding one by a factor of 24 and with regard to the first one by a factor of 1440. But time is not discontinuous. Generalization from the discontinuous to the continuous case leads to the introduction of a uniformly contracting time scale. Experiments point to a logarithmic scale. Plotted on such a scale, the increase in length of the rod is approximately linear over a wide interval (Fig. 3) so that events reaching from microseconds to years can now be packed into a single plot. The success of this new representation convinces us that the creeping rod has a time scale of its own, one that is contracting, not linear like that of the phenomena with which we are accustomed to deal in daily life.

Short times and high frequencies. Even with the introduction of the new time scale not all problems are resolved. One of the unsolved problems is the measurement of the creep function for very short time intervals. How does this function behave near zero time? What is the deformation of the rod immediately after loading (admitting for a moment the possibility of the rod being loaded instantaneously). The answer to these questions is important because on it will depend the value to be assigned to the instantaneous elastic modulus. Zero time of the ordinary linear scale corresponds to minus infinite on the logarithmic scale (cf. Fig. 3). Therefore this scale does not lend itself readily to extrapolation into the region of the very short times, and an entirely new method of measurement has to be devised. A solution has been found in the application of alternating stress by the transmission of waves within the specimen. Nowadays, sound and ultrasonic waves are easily produced over a wide range of frequencies. An alternative technique is the transmission of detonation waves set up by an explosion produced at one end of the sample. The wave pattern and the intensity of the transmitted wave are observed throughout the sample, from which the creep function can be calculated by rigorous mathematical methods. Since the period of an oscillation varies inversely with frequency, short times are translated into high frequencies. An oscillation which has a frequency of one hundred-thousand cycles per second has a period of one-hundred-thousandth of

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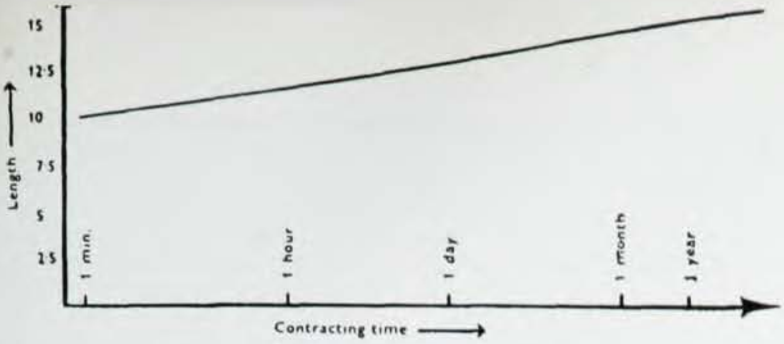

Fig. 3

a second and will yield a point of the creep curve belonging to approximately the same time. To obtain other points along this curve, other frequencies must be used. In this way the difficult problem of measuring deformations at very short times has been reduced to the much simpler one of measuring amplitudes of standing waves and high frequencies.

Temperature and time. Another puzzle is the behavior of the creep curve for very long times. Some conclusions may be reached by extrapolation, but the conscientious physicist, even if not shunning this method, wants to see his predictions confirmed by direct observation. Since even a very patient observer will hardly wish to waste some years of his life for the purpose of getting some more points of the creep curve, possibly to find only that the new points perpetuate the trend of the curve defined by the old ones, he will perhaps try to discover the means for speeding up the creep process. This is indeed possible by the application of heat, because creep proceeds faster at a higher temperature. Thus, when the rod is loaded at a sufficiently high temperature, it may reach within hours a state of deformation which at room temperature it would perhaps not reach in a saeculum. Mathematical methods have been developed which show for a given temperature increase its worth in time and allow one to join together creep curves obtained at different temperatures. It is in this way that more precise information has now been gained about the final equilibrium state of the creeping rod. The same method has also been applied to the study of the short-time sector of the creep curve. Here the process of creep must be slowed down; this is done by cooling of the rod to a sufficiently low temperature, thus decelerating the phenomenon.

The results of these different methods, represented in the contracting time scale, give at least in some cases a rather complete picture of the entire creep curve. It has been found that this curve extends over an interval of time covering not less than 14 decades.

MEMORY. It was stated that the experiments with sound waves and oscillations could be interpreted in terms of the creep function. This statement tacitly implies the assumption that even under rather complicated conditions of stress and strain one single time function is sufficient for the theory. This is by no means self-evident. Consider again the simple loading experiment, but suppose that after a while the load is increased to twice its original value. Can the ensuing deformation of the rod be predicted? Experiment has shown that the answer is affirmative. It has been found, for example, that an increase of the load from 5 to 10 kg after the load of 5 kg had remained applied for some time, gives rise to a creep effect of exactly the same shape as that which started at zero time when the load had been increased from zero to 5 kg. Independent of this "belated" creep the original creep still goes on all the time as if nothing else had happened. Therefore after the second loading two creep effects are proceeding simultaneously — the original one, already slowed down in view of the time elapsed since it had started, and the "secondary" one starting afresh later and therefore prevailing. Neither of the two effects seems to mind the presence of the other. The total deformation at any time is given as the sum of both. This behavior is not dependent upon a particular type of load or upon the time of application of the load. Quite generally, the same loading — and the term "loading" is here used in the transitive sense of the word, meaning "the same act of applying a load" — always produces the same effect irrespective of the time of its occurrence or the state of the system at this time. Any creep or recovery effect, once started, proceeds at its own rate quite oblivious to whatever else may happen to the specimen. The deformation at a given moment therefore depends not only on the load applied at that moment, but also on what the sample has been through before. It seems as if the sample remembers what has been done to it in the past — faintly if the previous treatment lies a long time back and vividly if the event is recent. In a quantitative way this "memory" finds its expression in a time function which is a measure of the gradual disappearance of the creep effect; it has been called "memory" function. The curve of creep recovery (which is an image of the creep function) does this service. The superposition of the deformations associated with successive mechanical usage finds its quantitative expression in a very general mathematical theorem, the "principle of superposition", which is valid for linear systems and constitutes the foundation of an important class of theories of mathematical physics.

An experiment was devised may years ago that shows in a very impressive manner the superposition of effects caused by successive deformations. A firmly suspended metal or plastic wire is twisted first in one direction for a long time and then in the other direction for a short time. Immediately after release the deflection will be in the direction of the last twisting, but it decreases rapidly. Presently a reversal occurs, and the wire begins to turn in the other direction corresponding to the first twisting — the memory of the recent short-term handling has been obliterated by that of the more remote but longer lasting and therefore more impressive one. The behavior of the specimen in this experiment could be predicted correctly with the help of the memory function.

THE MODEL. To review the foregoing conclusions: The behavior of the linear viscoelastic body under any type of stress or deformation can be formally accounted for in terms of the memory function and two constants, provided the history of the body is known. An analogous situation may be commonplace for a psychoanalyst who understands the reactions of the objects of his studies only in terms of their past, but it is not commonplace for the physicist. Within the framework of classical physics of continuous media, the state of a system is always sufficiently defined by a set of initial and boundary conditions. Once these data are given, the general laws of dynamics provide the means for calculating the evolution of the system from its initial state under any specified external conditions, and in particular under the action of a unit force. One can do without a knowledge of the system's history, because its present condition is fully known; one does not need an empirically determined memory function, because the behavior for unit force (which corresponds to the memory function) follows from theory itself. One must conclude that the formal creep theory is insufficient. The macroscopical stress and deformation data do not precisely define the state of the system and therefore do not constitute sufficient premises for the theory. The heuristical principle of superposition is not a legitimate substitute for the fundamental laws of mechanics or thermodynamics. But it would be an injustice to put all the blame on the formal theory. In reality the task of this theory is not that of the classical theory. In the present case the fundamental parameters of the system are not observables but must be inferred from observation. The viscoelastic body is like a carefully closed box which contains a very complicated mechanism. One knows the forces acting on the box and the way it reacts to them. One can predict what the box will do from a certain moment on, once one knows what it has done up to this moment. But what one really wants is to open the box and find out what the complicated mechanism in the box looks like. The additional knowledge would permit formulation of a satisfactory theory. The right way to execute this program is to study the problem from the point of view of the modern theory of solids. However, the objects one is dealing with are very complex ones, multicrystalline metals with lattice defects, high polymers with complicated molecular structures, the rigorous mathematical treatment of which is uninviting. An alternative procedure might be to attempt to construct a model consisting of known classical elements in the hope that in this way the behavior of the complex viscoelastic system can be duplicated.

It was recognized at an early stage that complex models can be constructed with springs and dashpots which behave like a viscoelastic body. Several arrangements were studied and it has been found that the simplest forms which at least qualitatively exhibit this behavior are those represented in Fig. 4. Once the arrangement of the elements of a model is given, the form of the memory function can be calculated. The two models depicted above will give an exponential function. Comparison with experiment, however, shows that the memory function rarely takes this simple shape. The next step is to assemble a multiplicity of the elements shown in Fig. 4. In some cases a few of them may be sufficient for a representation of the memory function within a limited interval of time. But a really satisfactory representation is obtained only when an infinite number of elements is assumed to exist with parameters distributed over an enormous range of values. Each element can be labeled by a characteristic time constant, the relaxation time of that particular element. The distribution of the relaxation times is inferred from the experimentally determined memory function and adjusted so that the theoretical and the experimental curves coincide everywhere. Thus a mechanical model is constructed that behaves exactly like the complex creeping system. The concepts of classical mechanics can be applied; when the deformations of the springs and dashpots at a given moment are known, the subsequent behavior can be calculated.

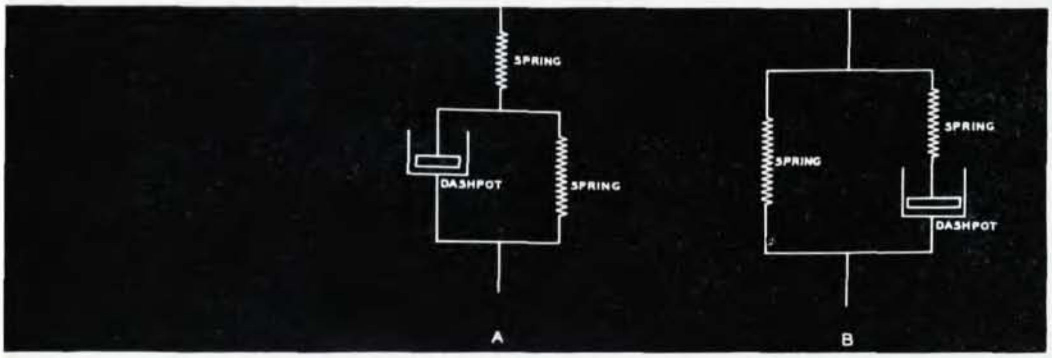

Fig. 4

The models have done a great service in visualizing the very complicated behavior of the viscoelastic body and relating it to that of well-known mechanical elements. But what is their physical significance? Using again the analogy of the box, one may wonder whether one has not by chance taken out what was in the box and substituted something completely different.

It is true that a certain danger lies in the exaggerated application of the concept of a mechanical model. On the other hand it has its definite value. Nobody will, or at least should, pretend that the springs and dashpots actually do exist. Instead they must be taken figuratively — they serve in a general way for elementary phenomena which obey linear differential equations and can be characterized by relaxation times. The determination of the relaxation time distribution then indicates the way in which these elements are grouped together. Therefore information is derived about the constitution of the complex body. Once understood in this way, there remains the final task of discovering the nature of the elementary process and of associating it with a physically significant entity. This means that while so far the theory has been phenomenological and therefore rather general, now specialization becomes necessary. The composition of the body (whether it is crystalline or amorphous) and its constitution (single crystal or polycrystalline) will have to be considered. Briefly, we now have to do what we have avoided so far, we must leave the domain of descriptive theories and enter that of the interpretative ones.

WHEN TRYING TO DEVELOP the interpretative theory one must search for a complete set of fundamental parameters. The deformation of the loaded system never depends on the load alone. Temperature, chemical composition and physical constitution, degree of order of the lattice in the case of a metal or of the molecular arrangement in the case of a polymer, are among the factors which play a role.

Temperature fluctuations. The temperature effect provides perhaps the best example of the manner in which such factors can cause delayed deformation. It is well known that a rise in temperature of a metallic specimen always causes expansion. But the converse is true also. When the specimen is suddenly stretched it suffers a sudden reduction in temperature. Heat will then flow into it from its surroundings until temperature equilibrium is reached again. Therefore, sudden stretching is followed by a period of gradual temperature increase. Consequently the specimen will undergo a subsequent further increase in length (creep). Besides temperature exchange with the surroundings, temperature fluctuation can occur within the specimen itself and will give the same result. This happens in a metallic body which is not a chemical compound, but is instead a mixture of two or more elements in solid solution. The stretching will differently affect each of the separate constituents and will therefore produce internal temperature fluctuations. Internal conduction of heat will equalize the temperature. The attainment of equilibrium conditions is accompanied by further dimensional changes.

Lattice deformations. A similar effect is related to modifications of the atomic lattices of metals. In the absence of external stress the atoms in the lattice are distributed isotropically and the lattice points are occupied by the different atoms in an established order. Application of stress sometimes induces nonisotropic distribution in which some of the atoms prefer certain well-defined directions, or it changes the order of the atoms in the lattice. In either case a new equilibrium will be reached. Usually any change in the lattice occurs parallel with a macroscopic deformation. Approach to equilibrium is not instantaneous but delayed, and one is therefore again confronted with creep and relaxation effects.

Heterogeneity of composition or structure. Sometimes an apparently uniform metallic solution actually consists of a mixture of two phases, one perfectly elastic and the other perfectly viscous. Within each phase, fluctuations of the elastic modulus and the coefficient of viscosity exist, caused by differences in the size and shape of the metallic grains which make up a polycrystalline metal. Here the elements of the two phases correspond to the springs and dashpots of the model and similarly give rise to relaxation effects.

The presence of two different phases is not an indispensable prerequisite. An effect of heterogeneity is already caused by the existence of distinct grains in a metallic body. Each grain represents a single crystal and may respond to stress as a perfectly elastic medium. But, besides deformations, relative movements of grains are observed, one grain slipping over adjacent ones. The movement along grain boundaries is opposed by frictional forces governed by the laws of viscous motion and the grain boundaries therefore play the role of the viscous phase of the foregoing example.

Molecular structure. In amorphous materials, particularly high polymers, the structure of the molecules interferes. The molecules frequently form long chains which normally are contracted and interwoven, forming a complicated and disordered pattern. Under load they become uncoiled and untangled, tending to constitute a pattern of a higher degree of order. But they will spring back into their initial disordered state upon release of the load. The thermal movement interferes with the orientation and disorientation of the molecules and ultimately causes delay in the expansion and contraction of the specimen.

A detailed description of the different mechanisms which have been mentioned here and of many others which are known to exercise some influence on the behavior of solid materials would presuppose a detailed knowledge of the theory of the solid state. It would furthermore have to account for nonlinear phenomena, for fatigue, and for fracture. This would go far beyond the scope of the present article which will have achieved its purpose if it has explained why the study of the flow of solids has attracted so many scientists from so many different branches of science.