MATHEMATICS and RHEOLOGY

Ronald S. Rivlin, Bingham Medalist for 1958, is chairman of the Division of Applied Mathematics at Brown University, Providence, R. I.

the 1958 Bingham Medal Address

By ***Ronald S. Rivlin***

The following article is based on an address presented at the Society of Rheology banquet in Philadelphia on November 5, 1958, by the recipient of the Society's Bingham Medal for 1958.

THE topic I shall discuss is mathematics and rheology and I shall, of course, concentrate on those aspects of mathematical rheology in which I have been interested. Many of you will no doubt recall that Sir Geoffrey Taylor chose a similar topic as the subject for his Presidential Address to the International Conference on Rheology held at Oxford in 1953. In it he advanced what seemed to me a rather pessimistic appraisal of the role of mathematics in rheology. I shall try to be more optimistic. Unfortunately, I was not able to attend the Oxford conference myself and merely read Sir Geoffrey's talk in the proceedings of the conference. I conjecture from its pessimistic note that Sir Geoffrey must have been talking before dinner. I like to think that if he had been talking after dinner, he too would have been more optimistic. In his preprandial pessimism he took the view that the mathematician must at best have the role of a handmaiden to the experimental rheologist, solving—or more often failing to solve—particular little problems that are posed. I would much rather regard his role as one of equal responsibility with the experimental rheologist for the advance of the subject—at times running ahead of the experimenter and determining the pattern of progress, at other times lagging behind.

So I shall, with your indulgence, spend a little time talking about one way in which a mathematical framework can be set up for describing the mechanics of classes of materials in which rheologists are interested. Specifically, I shall talk a little about the point of view underlying some recent developments in finite elasticity theory and shall then indicate how this same point of view can be extended and applied to rheologically more complicated systems.

I shall take as my starting point the position in finite elasticity theory at the beginning of the 20th century. Already in the course of the development of classical elasticity theory throughout the 19th century many results were obtained which did not involve the characteristic assumption of classical elasticity theory that the deformations are infinitesimally small. Consequently, by the beginning of the 20th century a framework already existed for a finite elasticity theory, in which no restrictions are imposed on the magnitudes of the elastic deformations. However, there were some missing links. It was realized that the physical properties of an elastic material can be characterized by a strain-energy function and that this cannot depend on the nine displacement gradients in a completely arbitrary fashion, but is restricted to a dependence through six strain components. These are, of course, not the classical strain components, but were perfectly well defined for the purpose at hand.

Furthermore, it was realized that if the material has some symmetry, the dependence of the strain energy on these strain components cannot be arbitrary. In particular, if the material is isotropic, the strain energy has to depend on only three functions of the strain—the so-called strain invariants. I might remark that Gerald Smith in a dissertation at Brown University worked out, a few years ago, the precise way in which the strain energy must depend on the strain components for each of the thirty-two classes of crystal symmetry. You will recall that Voigt, at the beginning of the century, discussed the analogous problem for infinitesimal deformations and found that for the thirty-two crystal classes, the dependence of the strain energy on the strain components must take one of nine different forms. Gerald Smith found that in the case of finite deformations, there are eleven possible forms for the thirty-two crystal classes.

Anyway, as I have already remarked, by the turn of the century it was fully realized that for an isotropic material the strain energy must involve the strain through the three strain invariants. It was also realized that if the form of this dependence is known for a particular material, stress-strain relations (or, as we should now say, constitutive equations), equations of equilibrium, etc., and indeed the whole formalism for a complete mechanics of the material can be derived. The open problem was the following—what form should be adopted for the strain-energy function? It is this matter which seems to have held up the development of finite elasticity theory during most of the first half of the 20th century.

One might have thought that there would have been a serious attempt to find the correct form for the strain-energy function from molecular considerations. But interest in elasticity theory in the early part of this century was primarily in its application to metals and hard crystals. Classical elasticity theory provided a satisfactory description of the behavior of such materials in the elastic range and, moreover, a satisfactory quantitative molecular basis even for classical elasticity theory did not exist. The course that was adopted by many workers was to postulate some form or other for the strain-energy function on grounds of simplicity and to proceed on that basis. Unfortunately, the views of different workers on what constituted the simplest possible form for the strain energy did not coincide. I reflect here on the remark made by Mephistopheles in Goethe's *Faust*, "For at the point where concepts fail, a timely word will be your bail." The word in this case is *simplest*. I hope, by the way, you will forgive the free and irreverent translation and my quoting the Devil for my own purposes.

Of course, even if there were a unique simplest form for the strain-energy function, which would result in a relatively tractable mathematical theory, this would not completely solve our problem—the particular material with which we are concerned might not be fortunate enough to have heard about this form. The "simplicity" argument I have cited reminds me of the story about the drunk who was painstakingly searching Times Square one night. When asked by a policeman what he was doing, he said that he was looking for his watch. The policeman asked him where he had lost it. "In Brooklyn" said the drunk. "Well, why are you looking for it on Times Square?" "It's lighter here than in Brooklyn," answered the drunk.

I can make these comments with the better grace in that my own entry into the field of finite elasticity was largely through this very road of alleged simplicity. It was only very recently that I appreciated that I might have stood on firmer ground. But more of that in due course.

A break with the notion of simplicity came with the publication by Murnaghan of his well-known paper in 1937. He considered the strain-energy function to be a function of the strain invariants and considered successive approximation to the strain-energy function when the deformations are small. He considered the classical form for the strain-energy function to be the first approximation—involving as it does two physical constants for the material, say Young's modulus and Poisson's ratio. He showed that the second approximation would involve five physical constants. Strictly, classical elasticity theory makes the assumption that both the extensions and rotations undergone by the material are small, while Murnaghan considered only the extensions to be small and allowed that the rotations might take any value. Mooney in 1940 advanced his well-known strain-energy function which is, in fact, the analog for incompressible materials of Murnaghan's strain energy for compressible materials.

My own interest in finite elasticity theory arose in a rather sticky fashion. In 1944, having spent the previous seven years working on problems related to electrical communications—television, telephony, and radar—I joined the British Rubber Producers' Research Association. I was asked to look into the adhesion mechanism involved in pressure-sensitive adhesive tapes, which employ rubberlike adhesives, such as Scotch Tape and Band-Aid. I rapidly came to the conclusion that the origin of their adhesive character lies in the fact that when such an adhesive tape is stripped off its adherend, more or less long filaments of the adhesive are drawn out before they detach themselves from the adherend and that it is the relatively large amount of work which has to be done in stretching these filaments that provides a measure of the adhesive quality of these tapes. It then occurred to me that it would be a good idea to calculate how much work would have to be done in stretching such filaments.

As soon as I tried to do this it became apparent that the basic theory on which any such calculation must depend did not exist.

However, Treloar had a year or two earlier given an expression for the strain-energy function for biaxial deformation of vulcanized rubber, which he had derived on the basis of the kinetic theory of rubberlike elasticity. When this is expressed in a more general context to render it applicable to inhomogeneous deformations, we obtain a mathematically simpler expression for the strain-energy function than any of the simple expressions used by workers earlier in the century. I called this the neo-Hookean form for the strain-energy function. It is a particular case of the Mooney form for the strain-energy function and provides a first approximation to the Mooney form if the extensions undergone by the material are sufficiently small, while the rotations may remain large. Using this form for the strain-energy function I was able to solve some simple problems concerning the forces necessary to produce simple extension, shear, or torsion. Now, even these simple calculations led to a result which seemed interesting. The forces which would have to be exerted on a block of material to produce in it a simple shear were not solely shearing forces, as would be predicted by classical elasticity theory, but also thrusts normal to the plane of shear. In the case of torsion, the forces which had to be exerted were not only a torque, but also a thrust distributed over the end of the rod in a parabolic fashion. Qualitatively this is the effect discovered experimentally by Poynting in about 1910 in rods of both metal and vulcanized rubber, but apparently largely forgotten in the intervening years.

Now, one of the features which makes the calculations particularly easy in the case of the neo-Hookean material is the simple form of the strain-energy function. Another is the incompressibility of the material. It occurred to me that taking advantage of the simplifications introduced by the incompressibility of the material the same problems could be solved without making any particular assumption about the form of the strain-energy function.

In this way it was possible to calculate the forces necessary to produce various simple types of deformation in an incompressible isotropic elastic material, such as vulcanized rubber, which undergoes large elastic deformations. In the expressions which are so obtained for the forces, the functional dependence of the strain energy on the strain invariants enters as an unknown, but may be found by comparing the analytical results with those of experiments, in which the forces necessary to produce an elastic deformation in a body of the material are measured. Such experiments were carried out for vulcanized rubbers by a number of collaborators—principally, Drs. Saunders, Thomas, Gent, and Mullins—and not only were they able to obtain the manner in which the strain energy depends on the strain invariants for vulcanized rubber compounds, but they were able to predict fairly accurately the results of various other types of experiment performed on the same material. I don't want to annoy you with the details of all of the experiments which were carried out. I should like to mention though that, in doing experiments on various vulcanized rubbers with various degrees of vulcanization, it was quite clear that the strain energy depended on the strain invariants essentially in the same way for all of them, the only differences being quantitative. Quite apart from its intrinsic interest, this is important for two reasons. First of all it opens up the whole question of the way in which the measured dependence of the strain energy on the strain invariants may be explained in terms of structure and indeed even suggests what are the particular structural elements involved. More generally it underlines the fact that even though we may construct a phenomenological theory of considerable generality—much too general one might think at first sight, to give any very specific answers—when we in fact apply it to a particular class of materials certain simplifications emerge.

The notions that have made possible the progress in finite elasticity theory that I have just described, also suggest ways of developing the mechanics of much more complicated materials. I remind you that the mathematical basis for finite elasticity theory rests on the assumption of the existence of a strain energy as a function of the displacement gradients. Then one makes use of the fact that a rotation of the whole physical system leaves this energy unaltered to show that it depends on the displacement gradients through the strain components. Finally, one introduces the further limitations which are imposed on the form that can be taken by the strain-energy function by the fact that the material is isotropic.

In the same way we can develop relations which describe the mechanical behavior of dissipative materials. All we have to know are the variables that enter into the determination of the stress components. Thus, if we are considering a fluid, the stress might depend on the velocity gradients. In that case we could limit the form of the relation between stress and velocity gradients by the consideration that it is independent of the angular velocity of the physical system and secondly that the fluid is isotropic. Alternatively, we might assume that the stress depends on the velocity gradients and acceleration gradients, in which case we can limit the expression for the stress by the consideration that it is independent of the angular velocity and angular acceleration of the physical system and is further limited by the isotropy of the material.

My own excursions into the mechanics of viscoelastic fluids had their origin in 1946, while I was visiting the United States for a year, in a conversation with Dr. Oliver Burke, who was at that time director of extramural research programs for the Office of the Rubber Reserve. During this conversation, I mentioned some experiments which had been carried out in England during the War by various people working in Professor Lander's laboratory at Imperial College on hydrocarbon gels of the type used as flame thrower fuels.

First of all Garner and Nissan made the observation that when a rod is rotated in a hydrocarbon gel, the liquid rises up the stirrer, while in an ordinary Newtonian fluid, there is a slight depression near the stirrer. Later, other very beautiful experimental demonstrations of essentially the same phenomenon were devised by Weissenberg and the phenomenon has been commonly

called the Weissenberg effect. Since paternity is a difficult thing to establish, I prefer to call it the normal stress effect.

When I described these effects to Dr. Burke, he suggested that during what remained of my stay in the United States I set up a program to examine these at the Mellon Institute under the auspices of the Office of the Rubber Reserve. I agreed to this and an apparatus was constructed at the Mellon Institute based essentially on one of Weissenberg's demonstrations. Concurrently, I started to worry about the origin of these effects and tried to work out a phenomenological theory for them. I want to spare you at this late stage a recapitulation of the way in which these ideas have developed. I think—although the detailed experimental verification of this is still lacking—that there are now two satisfactory phenomenological theories for describing the mechanical behavior of viscoelastic fluids and incidentally the normal stress effects. These two theories differ considerably in mathematical form, but can be shown to be substantially equivalent. In one of them, developed with Dr. Ericksen, it is assumed that the stress depends on the space gradients of velocity, acceleration, and of higher time derivatives of the velocity. Then, introducing the fact that the expression for the stress must be unaltered by superposition on the flow of a rigid body motion, and that the fluid is isotropic and incompressible, we can obtain the constitutive equations for an incompressible viscoelastic fluid. In the second theory, developed with Dr. A. E. Green, we take as our starting point the assumption that stress in an element of the fluid depends on the velocity gradients in that element at all instants up to the time of measurement—in other words that the fluid has memory of the velocity gradients in it at previous instants of time. Again, introducing the fact that the expression for the stress is unaltered by a rigid body motion of the fluid and introducing the restrictions imposed by isotropy one can obtain appropriate constitutive equations.

The constitutive equations obtained in either of these ways can be used as a basis for the analysis of simple normal stress effect type experiments and for predicting other interesting phenomena. In fact I think that the point has been reached where major progress will be experimental and much experimental work remains to be done.

It is perhaps worth mentioning, in conclusion, that the point of view adopted in developing the theories I have mentioned is a flexible one which can be applied to types of material other than those I have so far mentioned and indeed to branches of physics other than rheology, which involve nonlinear phenomena in continua. Indeed, a start has been made in this direction by Dr. R. Toupin, who has applied methods of this kind to discuss electrostrictive effects and in a recent dissertation by Mr. A. C. Pipkin, who has considered in addition electrical conduction in deformed materials, heat conduction, and indeed has developed to a considerable extent the general mathematical basis for handling such nonlinear theories in physics.