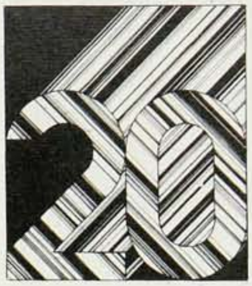

TWENTY YEARS OF PHYSICS

# RHEOLOGY

By ROBERT S. MARVIN

IN ITS PAST two decades rheology has been mainly concerned with development of models that represent the mechanical behavior of various types of materials, measurements required to test such models and evaluate the functions they predict, and theories required to relate models and measurements. The results are important not only for their academic significance but also for industrial processes like extrusion.

The traditional definition of rheology—the study of the deformation and flow of matter—is not particularly helpful in distinguishing between rheology and other branches of physics such as fluid dynamics, polymer physics and solid-state physics. In this article we shall adopt a somewhat more specific and limiting definition: the study of the properties of matter that determine its response to mechanical force. We still must draw an arbitrary dividing line between rheology and polymer physics because so many rheological studies during the past 20 years have been made on polymers. These studies have been closely related to a number of important developments relating properties to structure. But here we will stress the phenomenological aspects, leaving those dealing with molecular structure to polymer physics.

The author has been first a chemist and then a physicist at the National Bureau of Standards where he went in 1949 after getting his PhD at Wisconsin. His bachelor's and master's degrees are from the U. of Minnesota. He is a former Society of Rheology president.

### *Linear theories*

The period 1947 to 1952 was primarily devoted to developing the concepts of linear viscoëlastic behavior, developing measurements and showing that such measurements represent fundamental material properties. By the end of this very active period, it had been conclusively demonstrated that, for many materials within reasonable ranges of deformations and deformation rates, an adequate description of mechanical properties consisted of the specification of two functions (of either time or frequency) that are exactly analogous to the shear and bulk moduli of classical elasticity. Relations between the various representations of these functions that can be measured directly (the creep function, the response to a constant force; the stress relaxation function, the response to a constant deformation; and the dynamic modulus or compliance, the response to a sinusoidal force or deformation) can be obtained from the Laplace transform. But since the experimental measurements never cover the complete range of time or frequency and seldom even a major part of the significant range, a good deal of activity centered on various approximations to the exact mathematical relationships. The other major development during this period was the demonstration that the influence of temperature on these viscoëlastic functions could be expressed quite accurately in terms of its effect on (steady-flow) viscosity. There have been further developments of measurement techniques and additional approximation techniques since 1952, but the main focus of activity in the linear region is now more along lines classed here as polymer physics.

This theory of linear viscoëlasticity, or anelasticity as those concerned primarily with metals would call it, is the limiting form (for small deformations or velocities) of a more general nonlinear constitutive equation. But a proper nonlinear theory must be based on a three-dimensional description of materials, rather than the essentially one-dimensional linear formulation in terms of shear and bulk moduli.

### *Nonlinear theories*

Such formulations were achieved during a period roughly from 1947 to 1962, and once the linear theory was in satisfactory shape, these later developments have been of primary interest to most rheologists. A general formulation of finite elasticity was achieved first in terms of a strain-energy function that could be evaluated by appropriate measurements if isotropy and incompressibility were assumed. Nonlinear viscoëlastic behavior proved more difficult to represent. We can describe the formulation that was achieved as involving a time-dependent energy or free energy with a memory of past configurations that fades monotonically in time. It is based on a minimum number of assumptions, some essentially geometric. One physical assumption is that stress is determined by the history of the deformation gradient. It reduces to the appropriate linear form if motions have been slow enough in the recent past.

These developments provided a solid basis for specific constitutive equations. The period since 1962 has been notable for the development of such equations and the discovery of conditions (special classes of flow and limiting cases) under which the general functionals reduce to functions—in both these cases yielding expressions that can be evaluated experimentally—and the accompanying experimental efforts towards evaluating and checking such expressions. In addition some real progress has been made towards development of a nonlinear thermodynamics that must be a part of any complete description.

These developments are beginning to influence the attack on many complex industrial problems connected with extrusion and the like, just as earlier work on linear viscoëlasticity has had a pronounced influence on the resolution of many problems concerned with the processing of complex materials. Formulations now available are limited in at least two ways. First, they assume that only the first gradient of deformation need be considered, thus ruling out any influence of gradients of rotation, an a-priori assumption that has never been adequately checked. Second, all theories developed to the point permitting experimental evaluation assume incompressibility. The justification for this assumption, speaking somewhat loosely in linear terms, is that for systems usually employed in the study of nonlinear phenomena the shear moduli are very much less than the bulk moduli. This justification is recognized as a shortcoming of all such theories, but experiments suggesting how a better description could be included are only being initiated now.

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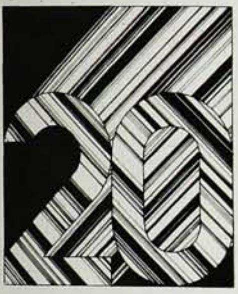

## TWENTY YEARS OF PHYSICS

# SOLID STATE

By JOHN M. ZIMAN

THE LAST TWO DECADES may well have been the era of solid-state physics. Certainly it has growed and growed; absolutely, of course, like all science and all physics, but also relatively to other fields. I guess it now occupies almost 40% of the family bed, instead of about 15% at the end of World War II. With its leading American and British exponents at the head of the National Academy of Sciences and in the Cavendish Chair, even the disciples of Rutherford are being forced to acknowledge its existence!

Excuse the impudence of trying to sum up such a vast amount of human activity. Intellectual history is notoriously difficult and always false. "No names: no pack drill" is a safe principle—and not inappropriate to a discipline that is not yet entirely dominated by the "star" system. Solid-state physics is too diversified, in subject matter, technique and scientific motivation, to be ruled by too few big names or to be corrupted by the lure of too many Nobel prizes. Let me write, instead, about trends and fashions, movements and achievements even though these only exist in the minds of tens of thousands of research workers and in the words and symbols of a hundred thousand papers.

### *A golden heritage*

Surprisingly our era was not a period of rampant ideological revolution. Most of the basic concepts of the modern theory were already invented by 1945. The foundations of lattice dynamics (that is, *phonons*), of *electronic band structure*, of electron dynamics in crystals (for example, *holes* in filled valence bands) and of *spin waves* had been well laid in the 1930's as an immediate consequence of the discovery of quantum mechanics. It was already established practice to use *group theory* wherever possible; *many-body* effects associated with the electron–electron coulomb interaction were recognized; the *Ising model* for order–disorder phenomena was familiar; the analysis of imperfect crystallinity in terms of relatively well defined and stable entities called *dislocations* was already well understood by those who could understand that sort of thing.

Has our generation invented new concepts to match the power of these? I can think of only two really big and revolutionary ideas that have been both invented and come to fruition in our time. The first would be the *quasiparticle* concept. The "true" particles of any solid—atomic nuclei and electrons—are always interacting so forcibly that one would think that they must always merge their individuality with the crowd. Sometimes this process is so, as in lattice waves and plasma oscillations; but the solid often behaves as if it were merely an assembly of nearly independent entities with dynamical and electrical properties akin to those of ordinary particles. Something like this was divined by the pioneers, who treated metals very successfully as if full of free electrons. Many-body theory, leaning heavily on the methods of quantum field theory, has shown how to derive, justify and make quantitative this fruitful fudge.

The notion of a *pseudopotential* is not so deep but has also proved extraordinarily useful. The problem was to decouple the electrons from the fields of the ions of the crystal lattice; out of the strong must come weakness. The discovery that the algebra used in calculating electronic band structure could be rearranged to give results that did not depend very much

John Ziman earned his PhD at Oxford, was a fellow at Kings College, Cambridge, and since 1964 has been professor of theoretical physics at Bristol University. Besides his work in solid state, he frequently writes on science, education and academic politics. He is a Fellow of the Royal Society.