

Stress Relaxation With Finite Strain

Soon after World War II, the development and use of synthetic polymers, such as rubber and plastics, burgeoned. The rapidly expanding uses of these materials demanded a better understanding of their fundamental properties, especially their mechanical properties. At that time engineers were more accustomed to dealing with materials such as metals, which behaved very differently under stress than did polymers. When a reasonable load is placed on a metal, it will bend or deform by an amount uniquely determined by its elastic properties. Sustaining the load for a longer period of time does not produce any further elastic deformation. For synthetic rubbers or polymers, such uniquely determined deformation cannot be assumed to occur. Inevitably, and often dramatically, the deformation corresponding to a given load will change as time progresses. Such behavior is called *time-dependent*.

It was necessary, then, to learn how to deal with time-dependent properties in these new materials, to discover which properties were controlling and controllable, to learn how to measure such properties, and to understand how to handle them in engineering design. What was needed was a rather ambitious undertaking, namely the construction of a fully three-dimensional theory that obeyed the laws of thermodynamics and

that went beyond the assumption commonly known as linearity. The paper *Stress Relaxation with Finite Strain* [1], published in 1962 by Bernstein, Kearsley, and Zapas, was a major milestone in meeting this challenge.

By *linearity* we mean the following: If you double the load, you double the displacements involved in the corresponding deformation. More generally, a model is said to be linear if, when one multiplies a load by any factor, all displacements are multiplied by the same factor. In theoretical models, it is more convenient to deal with relative displacements called strains. Essentially, a strain is a change in a length divided by a reference length. For linearly elastic models, the strain is simply proportional to the stress that produces it. For nonlinear models, such simple and unique proportionality does not occur. That was the fundamental problem for models of synthetic rubber and polymers.

In early work, Herbert Leaderman in the Rubber Section at NBS attempted to adapt his very successful linear models to the new materials. He did this by trying various nonlinear strain measures, with which he reformulated his models. But such stratagems proved to be simply perturbations, or slight variations, on the theme of linear models, and offered only very limited insights into the effects of nonlinearity.



Fig. 1. Louis Zapas, Elliot Kearsley, and Barry Bernstein, ca. 1991.

Beginning in 1962, a fresh attack was made on this problem in the Rheology Section of the Mechanics Division of NBS by a team composed of physicist Elliot A. Kearsley and chemical engineer Louis J. Zapas of the Rheology Section, together with mathematician Barry Bernstein of the Mathematical Physics Section in the Mathematics Division. By allowing for very wide variations in characteristic times and characteristic temperatures, this group observed what appeared to be striking qualitative similarities in the nonlinear viscoelastic behavior of widely different materials. With respect to certain characteristic quantities, the qualitative behaviors of polymeric materials ordinarily treated as solids and of materials ordinarily treated as liquids seemed indistinguishable. Motivated by this observation, the NBS team constructed a phenomenological model of nonlinear viscoelasticity within the following limitations:

- (1) It is inherently nonlinear, not a perturbation of linear viscoelasticity.
- (2) It is consistent with all the geometric and thermodynamic constraints appropriate to the mechanics of a material deforming in three-dimensional space.
- (3) It models the known qualitative characteristics of viscoelastic materials.
- (4) It is based on a generalized micromechanics of viscoelastic materials, but is not tied to the details of any particular material.

This effort resulted in a model representing a material whose responses in shear arise from a time-dependent potential bearing the dimensions of entropy. Furthermore, this potential depends not simply on the current value of deformation, but rather on the whole past-time history of the deformation. In other words, to compute its value at a given time, one needs to know the history of the deformation as a function of time. In producing elastic effects, this potential plays the role of an elastic strain-energy function. It induces an elastic stress in a current configuration derived from a weighted sum of partial stresses arising from the deformations of past configurations to the current configuration. As the current configuration evolves, each particular past configuration recedes in time, and the weight of its contribution to the current stress recedes accordingly, resulting in viscous energy loss.

In addition, the notion of the “material clock” was incorporated. Consider a temperature-sensitive clock that runs faster at higher temperatures than at lower temperatures. Suppose that what determines how long ago in the past a particular event occurred is, to the

material, effectively the time interval on that temperature-sensitive clock rather than the time interval on the temperature-insensitive laboratory clock. Such a conceptual clock, with its rate adjusted appropriately for the material with respect to the laboratory clock, is what one means by a material clock.

The first public presentation of this work occurred at the annual meeting of the Society of Rheology in 1962. At that time, a version of the model suitable for use under isothermal conditions was presented in a series of three talks. This presentation was followed by a summary of the model published as a paper in the 1963 transactions of the Society [1]. Subsequently, a more complete version including thermodynamic considerations was published in the *NBS Journal of Research* in 1964 [2].

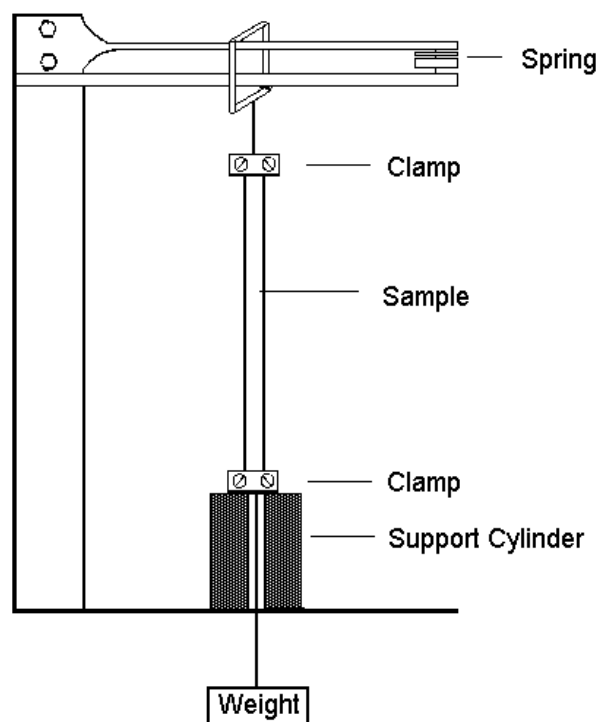


Fig. 2. Schematic of a stress-relaxation apparatus. The rigid support cylinder determines the ratio of final to initial length (extension ratio) of the sample while the displacement of the spring measures the force on the sample.

For the next few years, attention to this model was pursued only at NBS and a few other laboratories where experimental studies were conducted to establish the successes and limitations of the model for treating the mechanics of polymeric materials. However, by 1970, inherent difficulties in alternative competing models led researchers to turn in greater numbers to the NBS

model. The authors had called the model “a perfect elastic fluid” by analogy to the concept of a perfect gas. However, as the number of citations to the 1963 article began to climb, the model became widely known as “the BKZ fluid” or, on occasion, as “the K-BKZ fluid.” During the next decade, the use of the BKZ fluid became ubiquitous among rheologists. By 1988 the BKZ model was so well established in rheological circles that the Society of Rheology, at its annual meeting, held a session entitled “25 Years of the BKZ Theory” to mark the 25th anniversary of its initial publication and to review the subsequent developments. The BKZ model is now expounded in most texts on mechanical properties of materials and is commonly taught in courses for students of polymer science and of chemical and mechanical engineering.

According to the BKZ model, the response of a material to any deformation history can be calculated from measured behavior in stress-relaxation. This is a very convenient property for calculation. Furthermore, the limitations of the BKZ model have been well established. Despite some failings, it has been shown to afford an excellent representation of the mechanical behavior of most polymeric materials in most situations. Consequently, versions of the BKZ model are widely used in finite-element calculations; in designing injection molding and blow molding processes; in film

stretching and extrusion processes; and in designing systems for processing and handling materials with complex rheology. Such processes occur, for example, in the fabrication of plastic objects, in packaging, in food processing, and in the mixing of paints and other coatings. Modifications and ornamentation of the model are still being proposed and tested to overcome the known failings, and the end is not in sight. On the occasion of the 25th anniversary of the publication of the BKZ paper, R. I. Tanner opined in a presentation [3], “I believe that we will continue to use the (BKZ) theory, . . . I do not think that the theory will fade away rapidly since it is the optimal type of single-integral equation”

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Bibliography

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