CC/NUMBER 27 JULY 2, 1979

This Week's Citation Classic

Zimm B H. Dynamics of polymer molecules in dilute solution: viscoelasticity, flow birefringence and dielectric loss. J. Chem. Phys. 24:269-78, 1956. [General Electric Research Laboratory, Schenectady, NY]

The equations of motion of a model of chain molecule а diffus-ina viscous fluid in а under the in-fluence of external forces are solved exactly. Hydrodynamic interaction between parts of the chain is included in approximate form. The evolution with time of macroscopic observables is then calculated. [The SCI® indicates that this paper has been cited over 600 times since 1961.]

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> > April 20, 1978

"I got into this field in 1949 when C.T. O'Konski and I found that the relaxation of electrically induced birefringence was a very sensitive tool for studying the size and structure of rigid macromole-cules, notably tobacco mosaic virus particles, in solution. I was seized with the desire to extend relaxation methods to my main in-terest, flexible chain polymers. Beginning in late 1951, I spent some time reading the older literature on the theory of orienta-tional relaxation of rigid molecules by Brownian motion, and at-tempted to transfer these ideas to the much more complicated case of flexible molecules. There were already several approaches to this in the

literature, but the theories gave one no confidence that they could produce reliable quantita-tive results. Therefore I worked for some time to put together a simple-minded but quantitatively reasonable theory based on an elasticdumbbell model (two beads connected by a spring with a vibra-tion damper). I had just finished doing this when P.E. Rouse's impor-tant 1953 paper appeared in the Journal of Chemical Physics.¹ I found this paper very impressive, but failed to understand it fully on first reading; I thought that Rouse had considered only the internal motions of the polymer chain and had ignored the rotations of the molecule with respect to external axes. Fortunately, I wrote to Rouse about this, and he quickly straightened out my error.

"I then abandoned my dumbbell model and tried to extend Rouse's calculation by including hydrody-namic interaction between the parts of the chain, which was the main omission in his otherwise ex-cellent theory. At first I simply did numerical calculations in chains with a small number of segments, i.e., four or five. I was pleasantly surprised to find that the equations of motion of these small molecules, even with hydrodynam-ic interaction, were exactly soluble by a normal-coordinate transfor-mation. I was thus encouraged (in the summer of 1954) to try to con-struct a formal theory. The paper herein cited was the result "

^{1.} Rouse P E. A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. J. Chem. Phys. 21:1272-80, 1953.