

Bruno H. Zimm on His 65th Birthday

Bruno Hasbrouck Zimm, one of the great universalists of the polymer world, turned 65 years old on October 31. Few workers in any field of modern physical science can point to achievements of comparable quality and importance in the three areas of theory, experimental design, and experimental measurement. And as to notoriety, who can match the "Zimm plot"? One suspects that if the 1948 paper where it was first demonstrated were to be listed as a reference at each mention of this manuever, Zimm's name would be close to the top of the Citation Index frequency list.

Bruno Zimm grew up in Woodstock, NY, on a mountainside, and the long lonely walks to school through the woods may have catalyzed his powers of sustained thought. He graduated from Columbia College in 1941 and stayed on at that University to take his doctorate in 1944 under Joseph E. Mayer, with a thesis on the vapor pressures of alkali halides and the lattice energies derived therefrom. As this was the time of World War II, Zimm had also to take part in some war-related research under the direction of Victor K. LaMer on light scattering by smokes. He and his fellow graduate student Paul Doty (also in the Mayer group and the LaMer project) were thus well prepared to understand the application of light scattering to polymer solutions when Debye's work became known in 1944, and through the pursuit of this interest with the encouragement and active collaboration of Herman Mark, both of them soon became polymer scientists. Zimm himself has given a more detailed personal account of this episode. Subsequently, Zimm's career has taken him to four principal locations: in 1944-1946 he was at the Polytechnic Institute of Brooklyn; from 1946 to 1952 at the University of California in Berkeley, where he attained the rank of Associate

Professor; from 1951 to 1960 at the General Electric Research Laboratory in Schenectady; and since 1960 at the University of California, San Diego, in La Jolla.

Roughly half of Zimm's published papers are theoretical, over 10% concern the design and development of new experimental methods and instruments, about 10% are review articles or chapters, and the remaining 30% report experimental measurements; there is also a solitary U.S. patent. For the first 10 or 15 years his favorite macromolecule was certainly polystyrene, but for the last quarter century the top position is overwhelmingly held by DNA. Although readers of this journal and of the Journal of Chemical Physics encounter him quite regularly, they must also consult Biopolymers and the Journal of Molecular Biology to appreciate the full range of his interest and mastery. The brief account that follows is unavoidably fragmentary and incomplete. Names of almost all coworkers have also been consistently suppressed, in order to avoid capricious and irresponsible distinctions.

Light scattering has from the start been one of Zimm's major interests. As already mentioned, he started as a collaborator of Mark and Doty; they published some of the first convincing experimental demonstrations of the Debye equations. During the same period, Zimm contributed to the molecular theory of scattering from dense fluids, starting a development that ultimately led at the hands of others to a complete correspondence between microscopic theory and the semimacroscopic fluctuation treatments of Einstein and Smoluchowski. He helped educate a generation in the fundamentals of the then novel technique by writing with Stein and Doty a masterly review. Moving to Berkeley, he built a new light scattering photometer that for years represented the state of the art.

With it he produced results of then unmatched accuracy on polystyrene solutions and contributed to the theory of their evaluation, including the famous plot.² Questions about absolute turbidities were also settled. Polymers were not all of the story, for there was also occasion for a careful study of light scattering by the binary liquid system perfluoro(methylcyclohexane)/carbon tetrachloride, which squashed his revered mentor's famous derby hat quite flat. Over the later years there have been several new instrumental contributions to scattering practice and many superb data on DNA.

Zimm has always been an incisive practitioner of equilibrium statistical mechanics. Already in the Brooklyn days he applied Mayer-type cluster theory to the two-chain problem of the osmotic second virial coefficient, initiating the era of two-parameter perturbation theory, which only later was applied to the single-chain problem and which is still of interest.⁴ His were the first extensive calculations of the dimensions of branched Gaussian macromolecules. The trend toward biophysical problems quickened during the 1950s, which witnessed the elegant helix-coil theories for polypeptides⁵ and polynucleotides.⁶ Treatments of polyelectrolytes followed, by both cluster and Monte Carlo Poisson-Boltzmann methods. Still more recently the collapse of a single chain, now experimentally realized for both polystyrene and DNA, has been discussed.7

Zimm's interest in nonequilibrium properties long appeared dormant until his famous dynamical theory for flexible chains⁸ burst upon the scene in 1956. This first practical treatment of a chain with strong hydrodynamic interactions among its parts, though now almost 30 years old, has still not been totally mined for useful applications and remains only a few percent short of quantitative validity. There can be no more impressive demonstration of any such allegation than Figures 9-11 of Ferry's book, showing accurate prediction of the viscoelastic behavior of dilute polystyrene solutions over 3 decades of frequency from knowledge only of molecular weight and steady-flow viscosity. The 1956 theory used a "preaveraged" form of the hydrodynamic interactions, and in recent years Zimm has used Monte Carlo methods to probe the effects produced on the steady-state transport coefficients by fluctuations from these preaverages. Perhaps inspired by his geneticist wife Georgianna, he has also not neglected the dynamics of DNA: there are theoretical studies of the effects of chain stiffness, of the rate of double-helix unwinding, 10 of nonlinear and entanglement influences on sedimentation, and of twisting and bending motions.¹¹ Most recently he has been involved in efforts to furnish a physically adequate theory for the biochemists' current everyday tool, gel electrophoresis.¹²

Experimental studies of DNA dynamics by the Zimm group have especially called forth the master's ingenuity in designing apparatus: a procession of instruments has evolved, to measure not only steady-flow Newtonian viscosity but also nonlinear behavior, creep relaxation, and stress relaxation.¹³ Specially suited to the time scale of giant chromosome-sized DNA molecules, the relaxation devices can yield accurate molecular weights up to tens of billions without requiring knowledge of absolute concentrations.

The honors that have come to Bruno Zimm in recognition of the above principal accomplishments include the following (partial list): Baekeland Award, North Jersey Section ACS, 1957; Membership in the National Academy of Sciences, 1958; Bingham Medal, Society of Rheology, 1960; High Polymer Physics Prize, APS, 1963; Fellow, American Academy of Arts and Sciences, 1969; National Academy of Sciences Award in the Chemical Sciences, 1981; Kirkwood Medal, New Haven Section ACS, 1982. He has served on advisory boards of many journals.

Bruno's avocations include sailing, hiking, and playing clarinet in chamber groups, such as those which form (almost) spontaneously at winter Gordon Polymer Conferences. He does not travel extensively, and we in the East are always happy when he is lured to New Hampshire by Gordon Conferences on Biopolymers or Polymer Physics.

It is tempting to fashion an imaginary scenario for Halloween 1920. As the various spirits hovered around the cradle of the new arrival, one endowed him with mathematical ability, another with superb physical insight, a third with manual skills and practical sense; and so on. Only one disgruntled witch pronounced a gift of a questionable kind: the boy would always remain much too modest for his unusual powers and accomplishments. But this was turned into perhaps the most admirable and certainly the most lovable of all of Bruno Zimm's gifts: he simply is unaware of his stature, and treats all creatures, anthropoid or not, always patiently and affectionately as no less than complete equals.

On the occasion of this milestone we record our affection, our praise for his many past accomplishments, our indebtedness for his contributions to our understanding of the physical-chemical world, and our firm expectations of many more good things to come.

References and Notes

- (1) Stockmayer, W. H.; Zimm, B. H. Annu. Rev. Phys. Chem. **1984**, *35*, 1.
- Zimm, B. H. J. Chem. Phys. 1948, 16, 1099.
- Zimm, B. H. J. Chem. Phys 1946, 14, 164.
- Muthukumar, M.; Nickel, B. G. J. Chem. Phys. 1984, 80, 5830.
- Zimm, B. H.; Bragg, J. K. J. Chem. Phys. 1959, 31, 526. Zimm, B. H. J. Chem. Phys. 1960, 33, 1349.
- Post, C. B.; Zimm, B. H. Biopolymers, 1982, 21, 2123.
- Zimm, B. H. J. Chem. Phys. 1956, 24, 269. Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980; p 197.
 (10) Longuet-Higgins, H. C.; Zimm, B. H. J. Mol. Biol. 1960, 2, 1.
 (11) Barkely, M. D.; Zimm, B. H. J. Chem. Phys. 1979, 70, 2991.

- (12) Lumpkin, O. J.; Zimm, B. H. Biopolymers 1982, 21, 2315. Troll, M. A.; Dill, K. A.; Zimm, B. H. Macromolecules 1980,

Walter H. Stockmayer

Department of Chemistry, Dartmouth College Hanover, New Hampshire 03755