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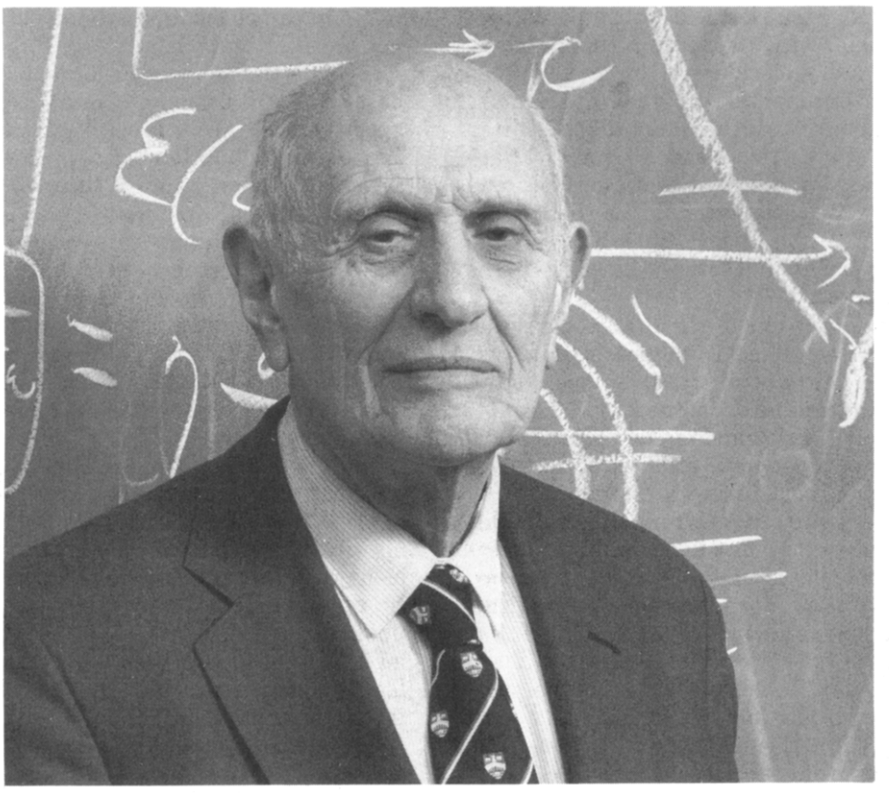

Robert Simha on His 80th Birthday

Robert Simha has strongly influenced the directions taken by polymer theorists during the past 60 years, having been the first to formulate tractable mathematical descriptions of many important problems ranging from solution hydrodynamics, kinetics and statistics of polymer reactions, to the equilibrium and relaxational behavior of polymeric solids. A characteristic feature of Simha's approach is a frequent dialogue between experiment and theory to arrive at a solution which successfully describes the essential phenomenological details of the question addressed. During this, his 80th year, Simha maintains an energetic commitment to his scientific interests with a vigor and productivity which many of us, his more youthful colleagues, are hard-pressed to match. Indeed, since he became Professor Emeritus at Case Western Reserve University, the only change in Robert's activities which we have observed is that he works even harder and travels more!

Simha's contributions to polymer physics began with theoretical studies leading to the Ph.D. degree in Physics at the University of Vienna in 1935. For his dissertation project, Simha chose a topic suggested by Herman Mark, at that time Professor of Physical Chemistry, namely, the extension of Einstein's theory of the viscosity of colloidal suspensions in two directions.[1,2] One accounted for concentration effects by a consideration of hydrodynamic interactions; a second, developed thereafter at Columbia University, generalized the analysis to nonspherical (ellipsoidal) particles. The latter results became the basis for evaluation of the size and shape of native protein molecules from Newtonian viscosity data. These issues continue to challenge hydrodynamics theorists to the present time. Simha's expressions, while approximate, have proven to be remarkably accurate, in light of subsequent more complete treatments of the rotary Brownian forces. Later in his career at the University of Southern California, he embarked on extensive experimental studies on polymer solution viscosity to explore the dependence on concentration, molar mass, temperature, and solvent quality, including sub-Θ temperatures. This work, with L. A. Utracki and others, was coupled to a scaling analysis based on a corresponding states principle.[3] Remarkably, the ensuing relations are found to apply over a wide range of concentrations extending to the vicinity of the melt. These observations remain a valuable guide in the continuing search for a molecular description which encompasses moderate and elevated concentrations.

Simha's pioneering efforts on viscosity theory at the University of Vienna took place in a politically turbulent atmosphere culminating in the annexation of Austria by Germany in 1938. This event prompted an exodus of prominent scientists to the U.S.A., including Simha himself, who accepted a postdoctoral position at Columbia University. The next 17 years, marked by a series of

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professional appointments at various institutions including Brooklyn Polytechnic Institute, Howard University, the National Bureau of Standards, and New York University, were a period of prolific activity during which Simha and various collaborators tackled a diverse range of problems. Theoretical studies were initiated in the kinetics and statistics of macromolecular reactions. Of particular note are the pioneering studies of degradation reactions as step processes and of free-radical-induced chain depolymerization, which culminated in the development, with L. A. Wall, of a unifying theory,[4] sufficiently robust to interpret a wide range of behavior with respect to monomer yield, overall reaction rate, and molecular weight change. This work inspired an experimental program by Simha's colleagues at the National Bureau of Standards on selected polymer structures. While this classical analytical approach has recently been replaced by more powerful Monte Carlo treatments of chain scission, Simha's theory successfully accounts for certain correlations between different types of measurements and between kinetic patterns and molecular structure.

Also, in 1944, Simha was one of the first to develop a statistical analysis of free-radical copolymerization.[5] Of additional interest, in the appendix to this paper, is the earliest derivation of the expression for the Flory–Huggins–van Laar interaction energy of a random copolymer. Some years later, the theory of copolymerization led to a concern with biological macromolecules in several directions. With J. M. Zimmerman, sequence analyses for polynucleotides were undertaken, necessarily based on limited experimental information available at that time. Moreover, kinetic models of polynucleotide replication were studied.[6] Later, with A. Silberberg, and, independently, R. H. Lacombe, the kinetics of cooperative processes on linear lattices, as exemplified by helix–coil transitions in polymers, was investigated by combined analytical and computer methodology.[7,8] Another important problem, first stated and analyzed in this period by Simha in collaboration with H. L. Frisch and F. R. Eirich, was a configurational analysis of the adsorption isotherm of a single polymer coil on a surface.[9] This endeavor served as the starting point for first-generation descriptions including those of A. Silberberg, C. A. J. Hoeve, and R. J. Roe, which subsequently led to second-generation theories such as that of J. M. H. M. Scheutjens and G. J. Fleer. Of additional note, in a paper published in 1948, is an attempt to compute the expansion of the radius of gyration of a flexible-chain molecule due to the excluded-volume effect.[10] This partially successful effort was soon supplanted by Flory's classical paper in 1949 in which the famous limiting exponent of $^3/_5$ in the radius–molecular weight relation was derived.

In 1958, Simha moved to the University of Southern California. There, inspired by Prigogine's cell theory of chain molecular liquids, Simha was one of the first theorists to attempt a statistical mechanical equation of state for polymeric liquids. In 1969, this endeavor culminated in the formulation with T. Somcynsky of a powerful lattice model description.[11] Experimental studies by Simha and co-workers[12] and calculations by R. K. Jain at Case Western Reserve University, together with independent observations by colleagues such as P. Zoller, J. M. G. Cowie, and E. Nies, suggest that the Simha–Somcynsky (SS) theory is arguably the most successful of its kind in describing phenomena associated with thermal expansivity of bulk polymers, including UCST and LCST behavior of solutions and mixtures.[13] A unique feature of the SS formalism is a "structural disorder" or "free volume" function whose behavior is determined in the melt by minimization of the configurational free energy. Extension to the nonequilibrium glassy state is possible by utilizing P–V–T data on glasses of well-specified formation histories and yields a history-dependent disorder function which can be used, for example, as a basis for predictions of thermoelastic properties, among others.[14]

Recently, Simha, collaborating with J. G. Curro and R. E. Robertson, has shown that the SS theory can rationalize a variety of kinetic phenomena in glasses, e.g., the volume response in respect to simple and multiple temperature and pressure jumps.[15] Furthermore, connections can be made, via the structure function, between the physical aging behavior of bulk volume and mechanical properties (stress relaxation or creep compliance). A current enthusiasm of Simha is to explore whether spectroscopic probes sensitive to structure (in particular, positron annihilation lifetime measurements) can be interpreted in terms of the theoretical equation of state.[16] A related theme, inspired by a collaboration with R. F. Boyer which led to the discovery of certain quite general connections between glass transition temperature T_g and the change in thermal expansivity at T_g,[17] was a series of experimental studies which established dilatometry as an important low-frequency (thus high-resolution) tool for the analysis of sub-glass mechanical relaxations in amorphous and semicrystalline polymers.[18]

Simha's accomplishments have been acknowledged by a number of awards and honors from scientific societies and institutions in the U.S. and abroad.

Robert shows, to this day, the Viennese passion for classical music which plays continuously on his office radio as he works. Indeed, a technical discussion may have to be temporarily delayed if the strains of a particularly poignant air are heard. Also, Robert was at one time such a frequent winner of the daily radio musical contest that, legend has it, the local classical station introduced what friends refer to as the "Simha Rule": winners are excluded from the competition until a period of 6 weeks has elapsed. We are fortunate that Robert Simha can continue to make valuable contributions to our understanding of physical phenomena of polymers, especially in view of his occasionally-voiced whimsy to embark on a new degree program in literature or music. We wish him many future years of good health to enjoy his intellectual pursuits.

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Alex M. Jamieson
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

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