POLYMER PHYSICS

From Suspensions to Nanocomposites and Beyond

Edited by

LESZEK A. UTRACKI
National Research Council Canada
Boucherville, Quebec, Canada

ALEXANDER M. JAMIESON
Case Western Reserve University
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PREFACE

This book is dedicated to the memory of Professor Robert Simha. To celebrate his ninety-fifth birthday on August 4, 2007, and recognizing his decades-long collaboration and support, the Industrial Materials Institute of the National Research Council Canada (NRCC/IMI) decided to organize the *Simha Symposium on Polymer Physics*. Robert Simha has been part of the NRCC/IMI research activities as a visitor, resident scientist, research collaborator, and speaker. In 1981 he inaugurated the first of a long series of IMI symposia on polymer blends, composites, foams, and nanocomposites. It was during these meetings that he presented his new works, which helped the Institute's technological developments. He has been a friend, advisor, coauthor of many publications, and an inspiration.

When organizing the symposium we contacted colleagues, ex-students, and collaborators of Professor Simha residing on three continents. The response was overwhelming. Realizing the scientific importance of the occasion, we proposed that John Wiley & Sons publish a book which would provide a window into Simha's research activities in several domains of polymer physics. The plan for the book was accepted in February 2007, well ahead of the October symposium. Robert Simha was the leading speaker at that meeting as well as coauthor of two book chapters, the last completed a day before his unexpected death on June 5, 2008. Thus, the book offers a perspective onto his scientific life from the earliest publications in 1936 to the final article and chapters in 2010. The introductory chapter in the book provides a brief biography of Professor Simha.

The book is not a compilation of research articles but, rather, a survey of seven decades of Simha's scientific activities. Its four parts reflect the evolution of his interests from the hydrodynamics of liquids and suspensions to statistical thermodynamics and their extension to positron annihilation lifetime spectroscopy and the physical

properties of polymeric nanocomposites. Each chapter focuses on a specific topic, providing background information, reviewing the topical literature, and presenting the most recent developments, often the authors' own contributions.

One area of Robert Simha's activity that is missing here is work on the kinetics and statistics of chemical reactions such as polymerization, copolymerization, depolymerization, degradation, and sequencing of biomacromolecules (e.g., proteins, polynucleotides, DNA). The decision to omit this topic was based, on the one hand, on its "chemical" character, and on the other, on the vastness of these topics, which would essentially require an additional volume.

Simha's 1935 Ph.D. dissertation (*Contribution to Colloid Hydrodynamics*) provided a base for extending Albert Einstein's theory on the viscosity of dilute spherical particle suspensions to higher concentrations and to particles of different shape and character, including the polymer random coil configuration. It is worth recalling that only after the Faraday Society meeting on September 28, 1935 did the flexible macromolecular nature begin to gain recognition and the theory of polymer solution flow provided a vital supportive element. Thus, Part I starts with Jamieson and Simha's chapter tracing the evolution of the Newtonian viscosity concept from the 1930s to the present. An interesting closure to it is provided in Chapter 3, by Nakajima and Nishi, who discuss the rheology of individual macromolecules. Thus, during one lifespan, science not only identified the molecular character of the polymeric chains, but developed means of measuring the viscoelastic properties of individual macromolecules.

The remaining three chapters of Part I cover various aspects of the polymer physics of the liquid state, including the dynamics and practical application of solution flow properties for drag reduction. In Chapter 4, Robertson and Simha discuss volume relaxation during physical aging based on the lattice–hole model. It is significant that the derivation is cast in the form of the Schrödinger equation since "we know how to solve it" (Robert Simha Symposium lecture, October 2007). In a sense, the chapter returns Simha to the theoretical physics of 1930s and the already recognized "relationship between classical statistics with quantum mechanics in the Schrödinger formulation."

Since the late 1930s Simha had been interested in the statistical thermodynamics of liquids, but his first publications on the topic appeared 20 years later. In 1958 he accepted a faculty position at the University of Southern California, where he begun detailed studies of the thermodynamics of molten, glassy, and semicrystalline polymers. These studies eventually led in 1969 to the seminal paper with Thomas Somcynsky, which provided a basis for worldwide research activities during the following 40 years. Accordingly, Part II is dedicated to thermodynamics. Chapter 6, by Moulinié and Utracki, outlines the evolution of the equation of state, the crystallization of the Simha–Somcynsky (S-S) ideas about the liquid structure, and the formulation of their theory. The chapter also summarizes the wide applications of S-S theory to liquid, glasses, and solids, to neat and multicomponent polymeric systems, to systems under thermodynamic equilibrium, and to dynamic ones. The other three chapters of Part II present specific applications of the theory to liquid crystals (Chapter 7, by Abe and Furuya), to surface properties (Chapter 8, by Kammer and Kressler), and physical aging (Chapter 9, by Cowie and Arrighi).

Since the 1960s position annihilation lifetime spectroscopy (PALS) has been used to measure free-volume cell size and/or its content in liquids or solids. The three chapters of Part III discuss correlations between the PALS experimental values and those computed from the S-S theory. Chapter 10, by Consolati and Quasso, considers free volume in amorphous polymers; Chapter 11, by Dlubek, its distribution from PALS; and Chapter 12, by Jamieson et al., the free volume in heterogeneous polymer systems. These "state of the art" texts offer intriguing observations on the structure of polymeric systems and its variation with independent variables. In all cases, good correlation has been found between the free-volume quantity measured by PALS and its variability computed from the S-S equation of state.

The final section Part IV is concerned with physical properties of polymeric nanocomposites (PNCs). Two types of nanoparticles, leading to two different characters and applicabilities of PNC, are discussed: layered silicates (with natural or synthetic clays), used in structural-type PNCs and the others used in functional PNCs. Sender et al. in Chapter 13 describe the performance of PNCs with acicular ferroelectric particles producing PNCs with good electroactive (dc conductivity) and mechanical properties. In Chapter 15, Nicolais and Carotenuto focus on metal clusters in polymeric matrices, which combine optical transparency with magnetism, luminescence, Ultraviolet–visible absorption, thermochromism, and so on.

The S-S mean-field theory is relatively simple, well rooted in the ideas developed by Lennard-Jones, Prigogine, Eyring, and others. Owing to the simplicity of the basic assumptions and the mean-field character, Robert Simha tried continuously to find limits of its applicability. In the 1990s, PNCs with exfoliated clay platelets became of industrial interest. The reinforcing effect of a miniscule quantity of these nanoparticles is surprisingly large. The explanation was found in the multiplying effects of the adsorption and solidification of the organic phase on the high-energy clay surface. The solidification significantly affects the free-volume content with corresponding changes in the PNC physical properties. Starting in the year 2000, a series of articles explored the applicability of S-S theory for improved understanding of PNC physics in the molten, glassy and semicrystalline phases. This work is summarized by Utracki in Chapter 14 (pressure–temperature–volume behavior) and by Utracki et al. in Chapter 16 (rheology). It was gratifying to see that the S-S theory offers a unique insight into the structure and performance of these complex systems. For example, one may calculate the binary thermodynamic interaction parameters, predict the temperature and pressure effects of free volume, and thus deduce their influence on flow or physical properties in the solid state. There is a direct relationship between the hole fraction/free volume and liquid flow.

Science is in incessant evolution; it grows with more precise theories and better instrumentation. The thermodynamic theories of polymers and polymeric systems move toward atomistic considerations for isomeric species modeled mathematically by molecular dynamics or Monte Carlo methods. At the same time good mean-field theories remain valid and useful—they must be remembered not only for the historical evolution of human knowledge, but also for the very practical reason of applicability, usefulness, and as tools for the understanding of material behavior.

We trust that in addition to providing a lasting record of Robert Simha's contribution to polymer science, the book will encourage readers to study his original articles. As his publications demonstrate (see Appendix B), he has been a brilliant, active, and dedicated theoretical physicist who has had a lasting impact on the science and engineering of polymers and plastics. He demonstrated clearly the importance of fundamental research both for technology and for the economy.

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ROBERT SIMHA: A LIFE WITH POLYMERS

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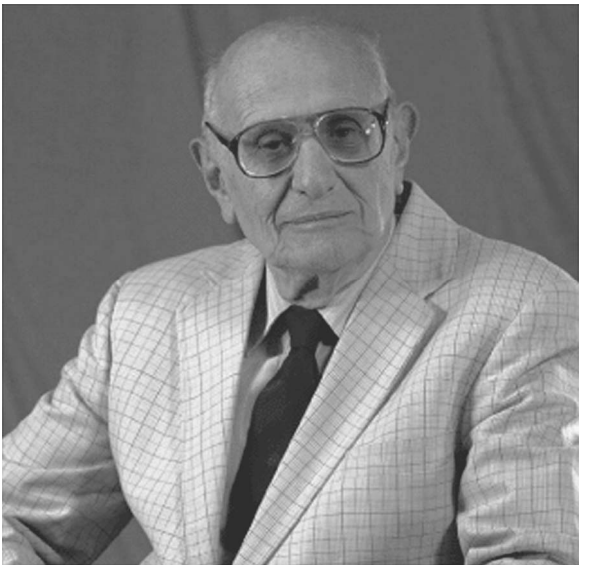

Robert Simha

Polymer Physics: From Suspensions to Nanocomposites and Beyond, Edited by Leszek A. Utracki and Alexander M. Jamieson

Introduction

To have contributed creatively to the theoretical foundations of polymer science for more than 70 years is a rare achievement. Good health and longevity are required, yes, but there must be a love of science that holds interest and excitement long after most have retired and laid down their pens. Health and longevity are a gift from his parents, but dedication to science has to arise from a milieu where early accomplishment and success drew Robert deeply into the arcane world of polymer physics.

Vienna, 1912–1938

Robert Simha was born August 4, 1912, to Marco and Mathilda Simha during the last years of Franz Joseph's reign in Vienna, Austria. He would have been 2 at the time of the assassination of the heir Franz Ferdinand and the outbreak of World War I: too young to have memories of the disruption in the world order, but young enough to have been born into a world where German was still the language of science and technology.

Vienna was then the music capital of the world and the melodies of the Strausses and the symphonies of Mahler and Bruckner mingled with those of Brahms, Mozart, and Beethoven. Young Robert studied the violin and, for a time, thought he wanted to be a professional violinist. However, in the Realgymnasium, his interests were strongly drawn to math and physics, yet both Latin and music left indelible imprints. His discussions could be sprinkled with Latin phrases, and conversations could be interrupted when from his antique radio—always tuned to classical music—arose the strains of a particularly poignant piece.

The early twentieth century was an exhilarating period for physics. Einstein's doctoral thesis had provided the first theoretical description of the viscosity of particulate dispersions [Einstein, 1906] and of Brownian motion [Einstein, 1905]. He had rocked the foundations of physics with his groundbreaking publications on relativity in 1905 and 1916. The fundamental principles of quantum mechanics were being elucidated by Planck, Bohr, Schrödinger, Heisenberg, and Pauli. As a good student, intrigued by the knowledge that physical phenomena could be modeled by mathematical formulas, Robert was drawn to study physics.

After graduation from the Realgymnasium, Robert spent one semester at Vienna's Polytechnic School (now called Technical University), transferring then to the University of Vienna, from which he graduated with the a Ph.D. degree after seven additional semesters [Simha, 1935]. At that time, there were no bachelor's or master's degree programs in physics at the university. Theoretical physics was a subspecialty in the philosophy department: thus, in addition to examinations for his competency in physics and mathematics, Robert had to pass exams in philosophy given by Professors Schlink and Reiniger.[†] As shown in Figure 1, on February 18, 1935, Robert Simha

[†]We thank Dr. Pohl for his retrieval and review of the records of R. Simha's youth and education.

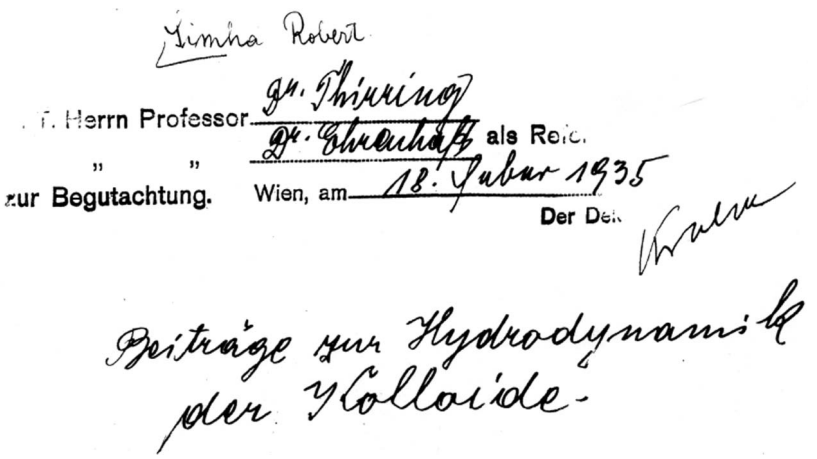

FIGURE 1 First page of Robert Simha's Ph.D. thesis at the University of Vienna, dated February 18, 1935.

presented his thesis, entitled "Beiträge zur Hydrodynamik der Kolloide" (Contribution to Colloid Hydrodynamics), and at the age of 23 he received a Ph.D. in theoretical physics.

Robert's dissertation advisers were both good friends of Albert Einstein: Hans Thirring, whose Lense–Thirring equation had provided a method for testing Einstein's special theory of relativity, and Felix Ehrenhaft, who had provided support for Einstein's theory of Brownian motion by making observations of the movement of silver particles in air (which brought him the Lieben Prize of the Vienna Academy of Sciences). For his postdoctoral research topic Robert approached Thirring, chair of the Institute for Theoretical Physics, who directed him to Herman Mark in the First Chemical Laboratory of the University of Vienna.

In 1932, Herman Mark [Mark, 1981] accepted the position of the late Dr. R. Wegscheider at his alma mater, the University of Vienna, as professor of chemistry and director of the First Chemical Laboratory. Mark received his doctorate in organic chemistry (on the synthesis and characterization of the pentaphenyl ethyl free radical) with Wilhelm Schlenk in 1922, and then moved to work with Fritz Haber in the Kaiser Wilhelm Institute of Fiber Chemistry in Berlin to carry out x-ray crystallographic studies. In 1926 he was invited to join IG Farbenindustrie in Ludwigshafen as assistant director of an interdisciplinary research laboratory for high-molecular weight compounds. There his work on polymers became internationally known. He might have stayed there, but the Nazis assumed power in Germany and Mark was advised to find a position in a friendlier place. Upon accepting the position at the First Chemical Laboratory in Vienna, he quickly set up a dynamic interdisciplinary program on three themes: polymerization kinetics, rubber elasticity, and polymer solution viscosity [Eirich, 1992].

This led to studies in polymerization kinetics, determination of molecular weights and the fractionation of polymers. Since the long, flexible polymer molecule could adopt many different conformations, Mark believed description of its physical properties might be amenable to treatment with the statistical methods of physics. He therefore consulted the famous Viennese theoretical physicist, Hans Thirring, chair of the Institute for Theoretical Physics, for assistance. Thirring "loaned" him his senior assistant, Eugene Guth, who had just returned to the Department of Physics in 1932 after studies with Wolfgang Pauli in Zurich and Werner Heisenberg in Leipzig. In the First Chemical Laboratory, Guth began working with Mark on developing a theoretical explanation for rubber elasticity and with Friedrich Roland Eirich on the viscosity of solutions and suspensions.

Mark had empirically modified Staudinger's equation describing the relationship between molecular weight and viscosity, and with Guth had extensively reviewed prior work on the viscosity of polymer solutions [Guth and Mark, 1933]. They were well acquainted with Einstein and his theoretical analysis of the viscosity of a suspension of hard spherical particles and Jeffery's extension to ellipsoids [Jeffry, 1923]. Frederick (Fred) Eirich, a talented experimentalist who obtained his doctorate in colloid chemistry working with Rudolf Wegscheider and Wolfgang Pauli, Sr., had recently become an assistant to Mark and had assumed responsibility for the experimental exploration of the rheology of suspensions and polymer solutions [Simha, 2006]. Robert, still attached to the Institute of Theoretical Physics, was assigned to work with Guth and Eirich, concentrating on the theoretical aspects.

Robert focused on two problems: extension of Einstein's theory to higher concentrations and then to nonspherical particles. "Armed with the tools provided by Lamb's hydrodynamic bible, Einstein's famous doctoral dissertation and a lengthy review by Guth and Mark, I started out." After an unsatisfactory beginning and a Black Sea vacation [Simha, 1999], he successfully extended the treatment of viscosity, η, to higher concentrations by including binary hydrodynamic interactions:

$$\eta = \eta_o \left(1 + \frac{5}{2}\phi + \frac{109}{14}\phi^2\right)$$

where η_o is the solvent viscosity and ϕ is the volume fraction of the suspended particles [Guth and Simha, 1936; Simha, 1936]. This early theoretical prediction extended applicability of Einstein's equation to $\phi \leq 0.15$, providing excellent agreement with the experimental results for suspensions of spherical particles.

Subsequently, Robert collaborated with Fred Eirich on analysis of the experimental data of rigid versus swollen and porous spheres, the latter being a model for flexible coils [Eirich and Simha, 1937a, b]. The passing of Eirich's father necessitated that his son take over running the Eirich publishing house, specializing in theater. The office was located in one of Vienna's concert halls. As Eirich was preparing for the position of docent (only a docent had the right to present lectures at the university), Robert and Fred met in the theater on evenings when there were no performances, to discuss hydrodynamic matters and to practice trial lectures for Fred's habilitation. This connection with the arts provided Robert with fringe benefits in the form of

free theater and concert tickets [Simha, 2006]. The studies culminated in Eirich's promotion from assistant to docent, and the first publication for both authors in an English journal (*Journal of Chemical Physics*) [Eirich and Simha, 1939].

With Fred, there were also Sunday walks in the woods after going over manuscripts, there were ski outings (without manuscripts), and there was an attempt at studying insect physiology. They went into mosquito-infested areas and studied the interaction of the insects and various potential repellants formulated by Eirich [Simha, 2006]; no publications resulted.

During the three productive years of a postdoctoral stay in Mark's Laboratory, Robert extended Einstein's equation (originally derived for linear stress gradient) to parabolic Poiseuille flow. There were "excursions" with Eirich into kinetic theory and viscosity of gaseous paraffins, as well as viscosity, surface tension, and heat of vaporization correlations of chain molecular fluids. The latter made use of the recently formulated transition-state theory of Eyring, Polanyi, and Wigner.

New York–Washington, 1938–1958

Robert's work in Vienna was completed with a paper on diffusion written with Herman Mark [Mark and Simha, 1937]. In 1938, with the German annexation of Austria, Nazi policies were enforced. That resulted in a tremendous outmigration of people of the "wrong" politics or of Jewish ancestry. Robert lost his close collaborators, as the First Chemistry Laboratory was decimated. Guth left for the United States in 1937, Mark fled to Canada, and Eirich sold the family publishing house and left for a teaching position at Cambridge University, only to be deported to Australia with the outbreak of war in 1940. As luck would have it, Herman Mark had been commissioned to write a review chapter on catalysis for the *Handbuch der Katalyse* and took Robert as coauthor [Simha and Mark, 1941]. Happily, on completion of the article, Robert was paid a handsome fee by Springer-Verlag, enough to buy a second-class passage by ship from Boulogne to New York to take up his new position as a postdoctoral fellow with Professor Victor LaMer at Columbia.

At Columbia University Robert continued work on modeling the viscosity of particulate suspensions, specifically attacking the problem of particle shape and the ensuing orientation effects [Simha, 1940]. The solution in the low shear limit, where Brownian motion randomizes the particle orientation, was a source of particular pleasure because, as he wrote, "the final strategy came to mind in the course of food shopping. More importantly it led to an invitation to come to Yale by future Nobel prizewinner Professor Lars Onsager (I declined because my future wife, Genevieve Cowleigh, was then a student in New York), and it led to my first presentation at an ACS meeting, and the occasion for meeting Maurice Huggins" [Simha, 1999]. His publication on the influence of Brownian movement was particularly significant in that it is applicable to molecular-scale particles such as proteins and other rigid macromolecules, and thus stimulated interest in the laboratory of J. L. Oncley at Yale, where experimental studies of protein structure were being pursued. During the same American Chemical Society meeting, Robert was highly gratified to hear a presentation by Oncley, in which the Simha–Einstein equations were used to interpret

viscometric data on protein solutions. Subsequently, with Mehl and Oncley, Robert coauthored a paper about the molecular shape of proteins deduced from the viscosity measurements [Mehl et al., 1940].

In 1940, Herman Mark was invited to become an adjunct professor at the Polytechnic Institute of Brooklyn, a position funded largely by DuPont. There he established the first academic professorship in polymer science and soon assembled a team of excellent collaborators, one of whom was Robert. In Brooklyn at Mark's suggestion, Robert took up a new topic, the degradation of polymers [Mark and Simha, 1940]. Robert had maintained contact with Elliot Montroll, also a postdoc at Columbia, and together they produced a general solution for random scission of macromolecules, valid at all chain lengths and having intramolecular position-dependent rate constants [Montroll and Simha, 1940]. The ensuing results, known as the Simha–Montroll theory, remain today the basis for interpreting the time evolution of the molecular-weight distribution of polymer chains in polymer degradation experiments.

Robert's growing reputation led to his first faculty position in 1942, as assistant professor in the Department of Chemistry of Howard University in Washington, DC. There, with a colleague in the Physics Department, Herman Branson, he investigated the statistics of copolymerization reactions, predicting the bivariate product distribution (i.e., with respect to masses and copolymer composition) [Simha and Branson, 1944]. Subsequently, Walter Stockmayer simplified their result, replacing summations with integrals and factorials with Stirling's approximation, in a paper that still finds widespread practical applications [Stockmayer, 1945]. An interesting caveat to Robert's paper with Branson is that, in an appendix, it presents the first derivation of the van Laar heat of mixing term for a copolymer in a solvent, expressed in terms of the copolymer composition and the monomer–monomer interaction energies. This paper is often referenced because it is the first rigorous derivation of the bivariate distribution and it is the first derivation of the copolymer heat of mixing.

In 1944, while at Howard, Robert was invited to present a course covering the kinetic and equilibrium aspects of polymer science in the graduate evening school of the National Bureau of Standards [NBS; now the National Institute of Science and Technology (NIST)]. In its broad coverage of the various topics it was one of the earliest courses offered in the United States, following only Mark's course in Brooklyn. In the audience, among others, there were ranking members of the Division of Organic and Fibrous Materials. The result was an invitation in 1945 to join the Bureau as a Consultant and Coordinator of Polymer Research. When Robert negotiated his contract, he stipulated that he did not want a paid vacation. Instead, he wanted the freedom to take time when he felt he needed it. He said "when stuck deep in a problem," he wanted the freedom to travel, to visit colleagues, to clear the mind, and to open new channels of thought.

At the NBS, in addition to his polymer activities, he was also part of a large effort for the preparation and characterization of hydrocarbons within a molecular-weight range of 170 to 351, which comprised normal paraffins, cycloparaffins, aromatics, and fused ring compounds. The characterization included the pressure and temperature variation of density, viscosity, refractive index, and so on [Schliesser et al., 1956].

The pressure range for these measurements was from atmospheric to 1 GPa, limited to lower values to avoid solidification. The temperature ranged from 37.8 to 135°C. These data were used by Robert and his associates during the next four decades [Utracki, 1983; Simha and Yahsi, 1995]. At NBS, Robert with S. G. Weissberg undertook extensive measurements of the concentration, molar mass, and solvent dependence of viscosity that led to derivation of quantitative expressions and formed a basis for future developments [Rothman et al., 1950; Weissberg and Simha, 1947; Weissberg et al., 1951]. Robert also collaborated closely with Leo Wall (a student of Rice and Herzfeld in free-radical chemistry and kinetics), who, working with a mass spectroscopist, Sam Madorsky, was carrying out quantitative pyrolytic studies of polymer degradation. Thus, the six years that Robert spent at NBS were very productive, enjoyable, and provided the foundation for future developments.

The reaction mechanism for polymer degradation proposed by Simha while at NBS involves initiation, propagation, transfer, and termination steps [Simha and Wall, 1952]. There were three experimental quantities: the monomer content in the volatiles, the molar mass decrease with conversion, and the rate that could be determined. A potentially complicated spectrum of rate parameters was simplified by allowing for single initiation, propagation, termination, and chain transfer constants. Depending on the relative values of these constants and the initial chain lengths, it was possible to account for the experimental behavior, varying from random scission in linear polymethylene to an unzipping process with high monomer recovery in poly(methyl methacrylate) or α -methyl styrene. The relationship between the three experimental quantities was established.

In 1951 Robert returned to New York to a position in the Department of Chemical Engineering at New York University (NYU). He taught a new graduate course on transport processes that proved very successful. New endeavors with old friends were undertaken. First, collaboration with Harry L. Frisch and Fred Eirich, now both at Brooklyn Polytechnic, led to development and refinement of a statistical mechanical model of the adsorption of flexible macromolecules on surfaces [Simha et al., 1953], still widely cited as a seminal paper in the theory of polymer adsorption isotherms. Since the early days of seminars in Mark's Vienna Laboratory, Robert had been interested in the statistical thermodynamics of the liquid state, and the success and failures of a particular version, the Lennard-Jones and Devonshire cell theory. The essential assumption is a reference unit executing thermal motions subject to interactions with surroundings defined by the mean positions of lattice sites. This model had been generalized by Prigogine and co-workers from the original spherical to chain molecular fluids and their solutions and mixtures. Robert recognized the necessity to develop a theoretical equation of state to derive contributions as an expression of environmental changes. Stuart Hadden, a doctoral student with Robert, demonstrated that the cell theory could quite accurately describe *PVT* data for linear and branched paraffins [Simha and Hadden, 1956, 1957]. This work had far-reaching consequences, in that it presaged major explorations into the properties of the molten polymer state. In addition, Robert revisited the issue of extending the viscosity theory of particle suspensions to higher concentrations, by developing a widely cited hydrodynamic cell model, based on a unit cell consisting of a single particle surrounded

by a spherical volume of suspending fluid, chosen to give the desired solid volume fraction [Simha, 1952]. The expression derived for the relative viscosity over the full range of concentration had two theoretical parameters, the intrinsic viscosity and the maximum packing volume fraction, which could be measured independently. With their experimental values, the theoretical expression was proved valid for numerous suspensions of not necessarily spherical monodispersed particles [Utracki, 1988]. Moreover, a start was made, with a graduate student, Jacques Zakin, on adapting hard-sphere theory to develop a corresponding-states principle for the viscosity of concentrated solutions of flexible coils [Simha and Zakin, 1960, 1962].

Los Angeles, 1958–1968

In 1958, Robert followed a call from the University of Southern California's Department of Chemistry. Although there was an old red brick pharmacology and chemistry building, the inorganic, physical, and polymer chemists were housed in two-story World War II wooden army barracks. When the fire department threatened to close the buildings down because of a lack of fire escapes, Anton Burg (a prominent inorganic chemist and former Olympic high jumper) opened the second-floor window and jumped out, walked around, and greeted the stunned fire marshal with: "See, fire escapes are not necessary!" The buildings had no air conditioning, except the ground floor—during the summer it was possible to pour buckets of water on the "permeable" wooden floor to cool the labs by setting the doors ajar.

Robert's office was on the first floor, where his radio played classical music continuously. When radio station KPFK initiated a classical music quiz, Robert was consistently the first to call in the name of the music. Soon he was banned from calling in with the answer. As a result, when the music for a quiz started playing, Robert would rush out of his office to find someone to call in the title (years later the events were repeated at CWRU in Cleveland!).

During his stay at the University of Southern California (USC) Robert reached a peak of involvement in professional affairs. He was elected president of the Polymer Group of the Southern California Section and held memorable monthly meetings in the elegant faculty club, with prominent invited speakers as well as distinguished Polymer Group members (Maurice Huggins, Roger Porter, Geoff Holden, Nick Tschoegl, to name a few). During summer breaks it was time for special lectures given by, among others, the Nobel prize winners Peter Debye and Linus Pauling. During these years Robert was also active in the Winter Gordon Conferences held in lovely Santa Barbara, first as a member of the organizing committee, and then, in the winter of 1962–1963, as the meeting chairman.

Robert was recognized as a fine, albeit unpredictable teacher, and his lectures, particularly on fluid dynamics, were memorable. With his customary disregard for historical sequencing of events, he generally began his lectures by discussing the most recent research paper in the field, then following with derivations from memory of the basic theoretical relations on which the paper was based. This certainly caught the attention of certain students, and in later years served as a model for their own teachings.

Scientifically, this was also a busy period for Robert Simha. Unexpectedly, his work on polymer degradation found application in space [Simha, 1961]. In 1961 he was joined by Leszek Utracki, with whom he continued the work started at NYU with Jack Zakin on the corresponding-states principle for polymer solutions. This was followed by extensive experimental studies on the effect of concentration, molar mass, chain stiffness, temperature, and solvent quality, including chain mobility, in the sub-theta region evidenced by viscosity and nuclear magnetic resonance. Remarkably, the corresponding-states relationships were found to apply over a wide range of concentrations, extending to the vicinity of the melt. This collaboration continued for 47 years, resulting in many publications on solution viscosity, free-volume effects on flows, *PVT*, and the dynamic behavior of polymer blends, composites, foams, and nanocomposites [Utracki and Simha, 1963, 2004].

In tandem with the work on solution viscosity, during this time, Robert, with a graduate student, A. J. Havlik, and a visiting professor, V. S. Nanda (University of Delhi), continued to develop the cell theory of Ilya Prigogine and others to describe the thermodynamics of polymeric fluids. Subsequently, with Nanda and a postdoctoral associate, Thomas Somcynsky, the concept of disorder was introduced by incorporating lattice vacancies (holes). The resulting Simha–Somcynsky cell–hole theory was found to give good agreement with experiment (e.g., describing the zero-pressure isobar of liquid argon over the entire temperature range). The cell–hole statistical thermodynamic theory is unique, not only in offering a precise description of liquid behavior, but also by the explicit incorporation of the free-volume parameter, which in turn could be used for the interpretation of equilibrium as well as nonequilibrium behavior of liquids and glasses. It suffices to note that the seminal paper [Simha and Somcynsky, 1969] has received the highest number of citations, is still widely quoted, and the theory has continued to evolve, as discussed below.

Although one might imagine that at USC Simha's interests were focused solely on solution viscosity and statistical thermodynamics, he found time to be involved in such diverse topics as computation of DNA sequences (with Jovan Moacanin from the Jet Propulsion Laboratory), in glass transition phenomena and thermal expansion of polymers (with Moacanin and Ray Boyer of the Dow Chemical Co.), observation of multiple subglass transitions in polymers (with a research associate, Robert Haldon), and thermal degradation (another collaboration with Leo Wall from NBS).

Cleveland, 1968–2008

In October 1966, Robert and Gen left for a nine-month visiting professorship at the Weizmann Institute of Science. There Robert began a collaboration with A. Silberberg on the kinetics of cooperative processes in macromolecular structures [Silberberg and Simha, 1968]. The next five months of his sabbatical Robert spent in Europe, with Ron Koningsveld at DSM in the Netherlands and Colin Price in Manchester. The Simhas sailed from Southampton to New York on the *Queen Elisabeth*, arriving in the United States on January 24, 1968 and two days later arriving in Cleveland in their new Volvo. Robert detested the invariably sunny weather and smog in Los Angeles,

and the seasonal changes in Cleveland were more to his taste. In 1968, Robert became a professor in the Department of Macromolecular Science and Engineering at Case Western Reserve University, where for 40 years he maintained a continuous record of outstanding publications. Astonishingly, 92 of Robert's 298 scientific publications (i.e., 30%) were published after his mandatory so-called "retirement" in 1983—the list includes two coauthored chapters in this book, written in 2007, his ninety-fifth year!

The kinetics of cooperative processes in macromolecular structures, synthetic or biological, was developed further with his student R. H. Lacombe [Simha and Lacombe, 1971]. The authors also examined cooperative equilibria in copolymer systems of specified sequence structures. This implied solutions of the classical Ising problem for linear lattices. It had already been treated by the methods of statistical mechanics for homogeneous chains and, most recently, for copolymers. Lacombe and Simha showed how these problems could be dealt with advantageously by the method of detailed balancing of opposing rates [Lacombe and Simha, 1973, 1974]. The results were examined for a spectrum of linear structures, chain lengths, and sequential distributions, such as he had computed, for example, with Jack Zimmermann for polypeptides [Zimmerman et al., 1968].

During this phase of his career, Robert's focus was on polymer thermodynamics. With Roe and Nanda he developed new corresponding states theory based on a cell model and Einstein's Gruneisen parameter. This theory found general application at temperatures below 80 K, for all 11 polymers tested, and later its elements were incorporated into an equation of state for crystalline polymers [Simha et al., 1972]. Robert also tested the applicability of his cell–hole Simha–Somcynsky (S-S) theory, applying it to progressively more complex polymeric systems and subjecting it to more demanding experimental tests. Anh Quach, his first student at Case, built a pressure dilatometer and carried out extensive *PVT* studies of various polymers, to test the theory quantitatively [Quach and Simha, 1971]. Subsequently, exhaustive tests of the theory against *PVT* data in both the molten and vitreous states were carried out by a succession of students (Phil Wilson, Shirley Lee, Jim Berg, Olagoke Olabisi, and Jim Roe). With John McKinney, Robert extended the S-S theory to nonequilibrium polymeric systems, such as glasses [McKinney and Simha, 1974, 1976, 1977]. Other important theoretical developments were, with Raj Jain, an extension of single-component S-S treatment to binary mixtures [Jain and Simha, 1984] and, with Eric Nies and co-workers, an introduction of nonrandomness in the hole distribution by Xie et al. [1992]. Still other ventures included the application of the theory, with John Curro and Richard Robertson, to predict physical aging of glassy polymers [Robertson et al., 1984] and, with John McGervey, Alex Jamieson, and others, to direct tests of the theoretical free-volume function using positron annihilation lifetime spectroscopy [Kobayashi et al., 1989; Yu et al., 1994; Higuchi et al., 1995].

At Case, Robert was not only a leader in groundbreaking research but also instituted a new course in polymer physics which was very popular with students, several of whom relate how much they enjoyed his classroom demonstration of a random walk! Robert's office radio was again tuned continuously to the local radio station, WCLV, and, as in Los Angeles, he dominated the station's daily music quiz to the

extent that they finally instituted a "Simha Rule": Winners were excluded from the competition until six weeks had elapsed (nowadays, they select a caller at random). Robert continued to be a cherished member of the faculty, enlivening the social events with his wry sense of humor and remaining a valuable intellectual resource to students and colleagues [Crenshaw et al., 2007].

The Simha Symposium on Polymer Physics, honoring his ninety-fifth birthday, was organized by the Industrial Materials Institute of the National Research Council Canada and held October 17–19, 2007. There he presented his latest work with Richard Robertson, on volume relaxation during physical aging in glassy polymers in response to changes in temperature and pressure. The problem was discussed on the basis of the S-S cell-hole theory, comprising an excess free-volume quantity. The physical aging processes are coupled to local free-volume states through two Fokker–Planck Kolmogorov probability functions, which may be transformed into Schrödinger-type relations. The derivation well described the classical Kovacs up-and-down temperature jump experiments in polymer glasses. During the three-day meeting, Robert was a lively participant, asking questions and discussing ideas. As it came out, it was to be his last lecture and his last conference. On June 5, 2008, after more than 70 years of dedicated efforts, a great voice was silenced.

Remembering Robert

Robert Simha was one of the pioneers of polymer science. He has left his imprint throughout the field in his theoretical work, his unique insight into polymer physics, his advice, and his friendship. His ideas will live on and his work will provide a foundation for the next generations of polymer scientists, but his warmth and friendship are sorely missed by all who knew him.

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