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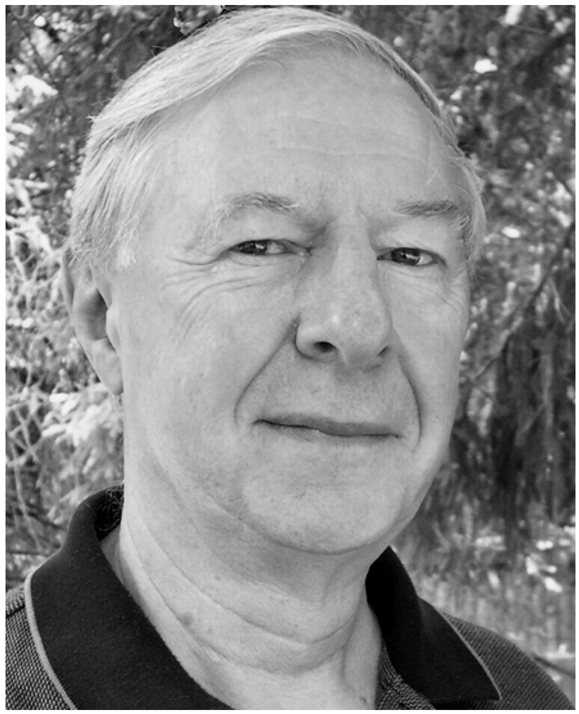

Frank H. Stillinger, Theoretical Chemist: A Tribute

Frank Stillinger is one of the major figures of contemporary theoretical chemistry. In the course of a career spanning 45 years, he has produced a body of work whose quality, depth, breadth, and importance admit few parallels in this field. The major themes of Frank's research have been the molecular theory of water and aqueous solutions, structure and relaxation processes in supercooled liquids and glasses, the physical chemistry of liquid and solid interfaces, the theory of phase transitions, the statistical geometry of hard particle packings, and molecular quantum theory.

Underlying his vast scientific output is a mastery of theoretical techniques and a truly visionary appreciation for the power of molecular-based computer simulation, which Frank has used, with admirable consistency, to extract deep physical insight from every problem he has tackled. What follows is a brief synopsis of some of the highlights of Frank's scientific output, grouped by topic.

Water and Aqueous Solutions

Frank's pioneering molecular dynamics studies of water, with Aneesur Rahman [54, 65, 66, 72, 100][‡] had an extraordinary impact (1045 citations to date for [66], 692 for [54]), because they showed, for the first time, how water's liquid-phase anomalies could be obtained from relatively simple potentials. Almost thirty years after its publication, the Rahman and Stillinger paper on sound propagation in liquid water [68] remains one of the classic examples of the discovery of a new phenomenon by computer simulation. In this case, the phenomenon was "fast sound", the search for a full understanding of which constitutes an active area of research. Frank's 1973 paper on the structure and statistical mechanics of aqueous solutions

[‡] Numbers in brackets correspond to the publications listed in the enclosed bibliography.

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of nonpolar solutes ([63], with 250 citations) laid the foundation of modern theories of hydrophobic hydration.

Glasses and Supercooled Liquids

The glass transition is one of the most active areas of research in condensed matter theory. Frank has been one of the major intellectual driving forces in this field. Building on prescient arguments by Martin Goldstein (*J. Chem. Phys.* **1969**, *51*, 3728), Frank formulated the "inherent structure" or "energy landscape" theory of liquids and glasses [122] (with Tom Weber; 511 citations). This statistical mechanical formalism, in which equilibrium configurations are mapped onto local potential energy minima, is one of the most widely used tools in the analysis of glass formation phenomena. Frank's powerful theoretical superstructure underlies a major body of work by leading international researchers on topics as diverse as landscape-based approaches to protein folding, investigations of cluster stability, and computational studies of the glass transition. He has used the inherent structure formalism to obtain deep and important theoretical results, such as the impossibility of an ideal glass transition in molecular liquids [170] (147 citations) and the exponential multiplicity of local minima in energy landscapes [240]. His many computational applications of the inherent structure formalism include the demonstration, with Srikanth Sastry and one of us, of the relationship between dynamics and the manner in which a system samples its energy landscape [234] (263 citations), and the application of energy minimization to relaxation dynamics in liquids [135] (307 citations), melting and freezing phenomena [110, 152], and the calculation of mechanical properties of glasses [255, 266].

Particle Packings

Frank's many contributions in the area of particle packings include the formulation with Edmund DiMarzio of a fundamental theory of the hard-disk phase transition [19]; the development of the widely used Lubachevsky−Stillinger algorithm for the simulation of hard-particle packings [186]; the identification, with Tom Truskett and ourselves, of a structural precursor to freezing in hard-sphere and hard-disk systems [236]; the development, with one of us, of systematic procedures for the generation and classification of jammed hard-particle packings [260], for controlling short-range order in particle packings [265], and for the efficient generation of dense polydisperse packings [267]; and the demonstration with Aleksandar Donev and one of us that disordered hard ellipsoid systems pack as densely as the densest crystal hard sphere packings [278].

Fluid Interfaces and Clusters

Frank's 1965 paper on the vapor/liquid interface in the critical region with Frank Buff and Ronald Lovett [25] (428 citations) introduced the capillary wave theory of fluid interfaces. His 1963 paper on physical clusters [13] (133 citations) has been highly influential in the framing rigorous statistical mechanical approaches to nucleation phenomena.

Electrolytes

In 1968, Frank and Ronald Lovett wrote three important papers on the statistical mechanics of concentrated electrolytes [37, 38, 42]. This work contains a fundamental new and exact result, the so-called "Stillinger−Lovett second moment condition" on the radial distribution of ion densities [42] (237 citations).

Miscellaneous

Space limitations make it impossible to do full justice to Frank Stillinger's output. Although the above comments mention some of the highlights, numerous other contributions deserve mention. These include a classic 1986 paper with Tom Weber [150], which introduced the widely used Stillinger−Weber potential for the computer simulation of silicon; this is his most cited work, with 1373 "hits" to date. Additional notable accomplishments include Frank's insightful analysis of the rotation−translation paradox of nucleation theory [36]; his theoretical and computational studies, many in collaboration with his wife, Dorothea Stillinger, of Gaussian core fluids [22, 41, 85, 101, 102, 110, 115, 116, 120, 133, 228]; his numerous contributions to theoretical and computational quantum chemistry [3, 30, 47, 71, 78, 90, 104, 143, 171, 190, 250]; the development of the tiling model of the glass transition with Tom Weber, Glenn Fredrickson, and Jonathan Harris [160, 162, 166, 179, 180]; a plausible interpretation of the breakdown of the Stokes−Einstein relation in supercooled liquids [206]; and the introduction, with Tom Truskett, Chris Roberts, and one of us, of the notion of the equation of state of an energy landscape [243]. With Melissa Feeney and one of us, Frank recently introduced the first statistical mechanical model of inverse melting [271]. This refers to the unusual but experimentally observed phenomenon whereby a liquid freezes upon being heated, with implications in materials science and possibly biology [272].

Reviews

Last, but by no means least, we want to mention several important reviews that Frank has written. The clarity and elegance of his writing, together with his encyclopedic knowledge of the subject matter, make these much-cited articles as valuable to the specialist as they are to those venturing into these topics for the first time. Examples include his articles on water [105] (475 citations), and on supercooled liquids and the glass transition ([217], with 395 citations; [254], with 209 citations).

The bulk of Frank Stillinger's distinguished career was spent at Bell Laboratories, where he was a member of the technical staff from 1959 until 2000. He headed Bell Laboratory's Chemical Physics Research Department between 1976 and 1978, and was a member of Agere Systems' technical staff between 2000 and 2001. For the past eight years, Frank has been associated with Princeton University, through Visiting Research Collaborator appointments with the Princeton Materials Institute and the Chemistry Department, where he is now a Senior Scientist. During this period, both of us have been privileged to collaborate with him on a wide variety of scientific topics. Several of our respective graduate students have benefited greatly from Frank's involvement in their research projects.

The distinguishing characteristics of Frank Stillinger's work are technical mastery, clarity of thought, and elegance of expression in the service of physical insight and fundamental understanding. Recognition of Frank's numerous accomplishments includes election to the National Academy of Sciences (1984) and receipt of the ACS Hildebrand (1986) and Debye (1992) awards, the APS Langmuir Prize (1989), and the Onsager Medal (2002). This volume, for which we are privileged to serve as guest editors, honors Frank Stillinger's outstanding scientific output on the happy occasion of his 70th birthday.

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