



Photo by Huafeng Xu

Autobiography of Bruce J. Berne

“You can take the boy out of Brooklyn but you cannot take Brooklyn out of the boy”. I was born in the Flatbush section of Brooklyn, New York in 1940, was educated in its public schools from grade school through college, played stickball and touch-football in its streets, and spent numerous afternoons at Ebbets Field, watching the Brooklyn Dodgers and my boyhood heroes, Duke Snider, Jackie Robinson, and Gil Hodges, play ball. Brooklyn was a great place to grow up in those days. Step out of your apartment building and there were hordes of kids to play with. One could find pickup games, take the trolley, bus, or subway to other sections of the borough, or at an early age even travel to Manhattan to visit museums, movies, or, later, theater with friends without depending on parents for transportation. Growing up in this way, I became independent and self-reliant at an early age.

During my childhood, my family would spend the entire summer living in a farmhouse on a working dairy farm in Livingston Manor in the Catskill Mountains region of New York State. I worked on the farm milking cows, collecting chicken eggs, helping with other chores, and hunting woodchucks with a 22-caliber rifle. I probably acquired my love for the outdoors from my early days on the farm. I look back with great fondness on my childhood in Brooklyn and in the “mountains”.

Brooklyn’s public schools were excellent in those days, but as a student, until my last year in high school, I was not. I attended grade school at PS 181, junior high at Walt Whitman, high School at Erasmus Hall, and college at Brooklyn College, one of the colleges in what later was to become the City University. Erasmus Hall High School was a distinguished school. At that time, it often triumphed over Stuyvesant and the Bronx High School of Science in winning more Westinghouse Science Scholarships than those elite schools. I was accepted at Stuyvesant, but when I found out that it was a boy’s school, I refused to go there. At that time, the notion of traveling every morning on the subway to a school with no girls was absurd. So I went to Erasmus and have never regretted it.

Erasmus Hall is the second oldest public high school in the country (Boston Latin is the oldest). It had its start as a private school in the 18th century. Erasmus is the alma matter to several generations of my family. Other distinguished alumni were Barbara McClintock, a Nobel Laureate in Biology, Morrison (Mickey) Spilane, Bernard Malamud, Jeff Chandler, Barbara Stanwyck, Beverley Sills, Eli Wallach, John Forsythe, Neil Diamond, Sid Luckman, Lainie Kazan, Samuel Lefrak, Arthur Sackler, Barbara Streisand, and Bobby Fisher (who dropped out).

My career as a student at Erasmus was somewhat checkered. I ignored subjects that I was not interested in. I had to attend summer school after failing the French Regents examination. However, I did remarkably well in chemistry and mathematics. From early childhood, I was deeply interested in science. A cousin gave me a chemistry set for my seventh or eighth birthday, but my mother warned me not to play with it because it was too “dangerous.” It was hidden away, but the “danger” was alluring, and I soon found it and had to play with it. I was hooked, and by the time I was thirteen, I had assembled a rather advanced laboratory in my bedroom. In those days, a youngster could buy glassware and dangerous chemicals that today would never be sold to minors. I was able to do experiments that were pyrotechnic and explosive. This interest in chemistry continued throughout high school but took second place to my hyperactive social life. Despite my interest in science and mathematics, I did poorly in high school during my sophomore and junior years.

In the summer of my junior year, I and some of my friends from Erasmus worked as counselors at Camp Sussex, a camp for disadvantaged children in Sussex, New Jersey. Almost all of the other counselors went to private schools such as Horace Mann, Fieldstone, and Dalton and came from very privileged homes. These kids, especially the girls, were fascinated with the Brooklynites, and we formed friendships that lasted through the next few years. My exposure to this entirely different lifestyle opened my eyes. I became a “serious” student. When

I returned to Erasmus for my senior year, my grades improved dramatically, and I started thinking seriously about going to college. In my senior year, under the influence of a charismatic English teacher, I started to read the great literary classics, which marked the beginning of my intellectual transformation. Unfortunately, my overall grades were unimpressive. My family could not afford the cost of a college education, and in any case, my grades were such that I would have trouble getting into a desirable school. Fortunately the colleges run by the city of New York were quite good. I applied to Brooklyn College, but my grades fell far below their requirements. The city administered a three hour exam, which was equivalent to the SATs with one difference: one could not prepare for this exam. The grade on this exam, combined according to some formula with one's high school average, determined success or failure. Failure meant that you would go to evening school instead. I took the exam and to my amazement was admitted to Brooklyn College. During orientation week, a guidance counselor told me that I received the second highest grade in the city on this special exam and yet was admitted "by the skin of my teeth". At that time, Brooklyn College cost \$8 per semester plus lab fees and books. I had to work during that period in order to pay for food, transportation, and recreation, but I continued to live at home, which was approximately 2 miles from the campus.

The Brooklyn College curriculum was then modeled after the Contemporary Civilization Program of Columbia College, and some of the professors in the social sciences and humanities were excellent. John Hope Franklin, Hannah Arendt, and Hans Morgenthau, among others, were on the Brooklyn faculty at that time. I was a chemistry major and math minor. The science faculty was not stellar, but the mathematics faculty was good. I was accepted into an experimental program that allowed me to finish all of the required chemistry courses for a major very quickly, and thus, I was able to explore other interests such as the study of classical Greek, philology, and literature. After completing all of the requirements for a major in chemistry, I took a reading course in statistical mechanics, a subject that was then not in the chemistry curriculum. Bob Silbey, now Dean of Sciences at MIT, was one of the four students enrolled. We read a chapter a week in the textbook by Mayer and Mayer, a very difficult book, and each week one of us would have the responsibility of trying to explain the subject matter to the others. The next semester we followed the same route in a reading course in quantum mechanics. Success in understanding statistical and quantum mechanics, without any help from a professor, made a major impact on my early development as a scientist. It helped to shape my decision to become a theorist. Bob and I taught each other the material and probably learned more effectively than we would have in a lecture class. This experience instilled in me self-confidence and independence, which played a large role in my success in graduate school.

The course in statistical mechanics led to a lifelong friendship with the Silbeys. Bob and I knew each other from our days as students in Walt Whitman Junior High and Erasmus Hall High, but became friends while students enrolled in statistical mechanics. I had started dating Naomi Maizel since the beginning of my sophomore year. We spent many good times with Bob and Susan Sorkin. Naomi and I married the summer after we graduated from Brooklyn College in 1961 and Bob and Susan married one year later. This summer we will celebrate our fortieth wedding anniversary with our wonderful sons David and Michael.

During the summer of my junior year, I worked in a research laboratory at Pennsylvania State University determining the

crystal structures of high-temperature phosphides using X-ray crystallography. The next summer I worked in a program for talented undergraduate science students at the Brookhaven National Laboratories and did research on solvent extraction of radioactive nuclides. The joy in learning theory in my statistical mechanics course the preceding year, the boredom of the repetitious experiments in these two laboratories, and a frightening accident in the lab at Brookhaven which exposed me to nitrobenzene vapor all led me to decide to pursue a career in theory.

Choosing a graduate school was not difficult. Our departmental advisor urged us to go to the University of Chicago where Stuart Rice, an alumnus of Brooklyn College, was a professor. Chicago looked like a great place for theory. Joseph Mayer, the author of our statistical mechanics textbook, was also a professor there. The other major theory departments at that time were Yale and the University of Wisconsin. Neither Harvard nor Berkeley then had full time theorists. Naomi and I chose Chicago; she to pursue a Ph.D. in psychology, and I, in theoretical chemistry. We were very happy to hear that Bob Silbey also decided to go to Chicago and would later be joined there by Susan.

I have fond memories of our graduate school years, although the first year was grueling. Aside from a heavy course load, a first year physical chemistry student was required to take a three hour comprehensive examination on all aspects of physical chemistry and to take an oral examination in which he or she defended an original research proposal. It was recommended that each student immediately start thinking about the original research proposal, as its preparation would take a great deal of time. The faculty was not permitted to suggest a topic or to coach the students. This was a very serious and threatening task for most students fresh out of undergraduate schools, especially if they had not already done undergraduate research in physical chemistry. We were all very worried about this part of the exam. Being an avid reader of *Scientific American*, I had recently read an article about the Mossbauer Effect and thought that it could be used to measure diffusion coefficients. After trying to read Frauenfelder's book on the Mossbauer effect, I realized that the little bit of statistical mechanics and quantum mechanics that I had learned was insufficient for dealing with the theory of the Mossbauer effect. So, for my first month at Chicago, I struggled to read papers on time correlation functions, linear response theory, and the theory of thermal neutron scattering. This was very rough going. There were no textbooks on these subjects. After much work, things started falling into place. I must have read over one hundred papers, and I finally started to understand how to apply theory to this problem. Months of pain and pleasure paid off, despite the emotional angst connected with this project. When the time came, I did very well on the oral exam. The written exam was a trivial task by comparison. In retrospect, preparation for the oral exam was the most intense and rewarding educational experience of my academic career. It transformed me from being a student to being an active research scientist. I was able to read complex theoretical papers and to think in an independent and original way about problems on the cutting edge of the field I ultimately chose: the theory of dynamic processes in condensed media.

I looked at several research groups at Chicago; I chose to work with Stuart Rice and was very pleased to be accepted into his group. The next fall I settled into the Rice group which consisted of approximately twenty members. Joshua Jortner was a post doc in the group, and he later became an assistant professor in the department. Kazuo Hiroike was also in the

group at that time, and he is well-known for his papers on topological reduction in summing diagrammatic series. Later Bob Silbey and John Lekner joined the group and, still later, Leon Glass and John Weeks. During my last year, I became very friendly with Jean-Pierre Boon from Brussels, who was a new postdoc in the Rice group. From time to time, Bob Harris, Rice's first Ph.D. student, would visit and would tell me about many-body theory. Chicago was a great place for theory. Joseph Mayer had already left for San Diego, but Ryogo Kubo was a visiting professor as was Ilya Prigogine.

Stuart Rice gave me a three-page list of possible research projects, and I chose to work on a problem in the kinetic theory of liquids. The problem was a carry-over from Bob Harris's dissertation on determining the coefficient of thermal diffusion in liquid mixtures. In retrospect, this was a horrible problem. To solve the integro-differential equations required a great deal of hairy algebra involving the evaluation of 4×4 determinants each of whose elements were long and complex algebraic expressions. Using large index cards for each of the elements, arranged on the floor of my office, I would rearrange the cards, multiply the expressions. Every time I did the calculations I got a different answer. Today, of course, one would use MAPLE or MATHEMATICA, but in 1962, this was a frightful task. Moreover, I started to doubt the validity of the so-called Rice–Allnatt equations. I proved that for the one component liquid, the corresponding RA equation, a Fredholm equation, a solution did not exist according to the theorems in Courant and Hilbert. Yet Rice and Allnatt found a solution using perturbation theory. After much work, I derived the correct equation, proved solutions rigorously existed for this equation, and solved the new equation by perturbation theory. Lo and behold, I got the same solution as that found by Rice and Allnatt when they solved the equation that had no solution. Somewhat disillusioned, I gave up my quest to solve the original problem; instead, I did some work on the kinetic theory of fused salts and then asked to move on to another problem.

My real break in graduate school came when, during the spring of 1964, Annesur Rahman sent Stuart Rice a preprint of his ground-breaking paper on the molecular dynamics simulation of the structure and dynamics of liquid argon. Stuart put this on my desk and then went out of town on a trip. Because of my extensive readings about time correlation functions in preparation for my oral exam during my first year, I was primed for this paper. In addition, during the preceding year, I had spent time studying Zwanzig's Boulder lecture on projection operator methods. When I saw Rahman's graph of the velocity autocorrelation function, I was immediately able to explain the result on the basis of the memory function equation. For simplicity, I approximated the memory function as an exponential function of time and solved the Volterra equation for this. By adjusting the two parameters to give the measured self-diffusion coefficient and the measured mean square force, I was able to approximate the Rahman result in which the correlation function decayed nonexponentially, with a negative region arising from the coherent backscattering of the atoms in their liquid cages. This became the last chapter of my thesis, submitted during the summer of 1964, and the beginning of my efforts in memory function modeling of condensed matter dynamics. I decided not to publish this work in a journal until I had a chance to mull the results over, and it was not until I was well into my postdoctoral year in Brussels that I got around to publishing this work. By that time Jean-Pierre Boon working with Stuart had extended my work to angular momentum correlation functions. We decided to combine these efforts in a joint paper,

which came out in 1966. I sent Annesur Rahman my results within a few weeks of reading his preprint, and he invited me to visit him at Argonne National Laboratories. He showed me his latest results and was impressed with what I had done. We soon became good friends, and I regard him along with Robert Zwanzig as one of the major influences on my scientific career.

The Gordon conference on liquids during the summer had a profound effect on me. It was a time when people were arguing about the nature of phase transitions, and it was an exciting period in statistical mechanics. The meaning of new laser light scattering experiments were being debated. Such luminaries as Peter Debye, Lars Onsager, and Joel Hildebrand were in attendance. Michael Fisher reported on his high temperature expansions. Ben Widom talked about scaling laws. As is the custom at Gordon conferences, one can choose any empty seat at dinner. An older man sat down next to me. During dinner he told stories about the young Lars Onsager. This older gentleman turned out to be Peter Debye. I, a mere twenty-three years old, was absolutely star struck. What an exciting meeting! I also met Frank Stillinger, Gene Helfand, and Harry Frisch—then of Bell Laboratories—at that meeting. I was so inspired by this Gordon conference that I returned to Chicago to complete my degree in three years.

Two important things happened during my last year at Chicago: I got an academic job and I received a NATO postdoctoral fellowship to spend a postdoctoral year in Brussels. In December of 1963, Stuart Rice recommended me for a job at Columbia University. At age twenty-three, after only two and a half years of graduate school, with no previous experience with academic interviews, I interviewed at Columbia during Christmas recess and was offered the position of assistant professor soon after. I was offered no start-up package. Unlike today, theorists were thought to require only pencils and yellow pads, and for that, I received a small research allotment. Before starting at Columbia, I had to complete my dissertation, which I did during the summer of 1964, and to spend a year doing postdoctoral research.

During the spring quarter of 1964 at Chicago, I attended lectures given by Ilya Prigogine. He had a very large group in Belgium working on the theory of irreversible processes, and many people suggested that this was a great place to spend a postdoctoral year. I applied for and received a NATO postdoctoral fellowship and received an offer from Prigogine to join his group. Because I completed my Ph.D. in the summer of 1964 and my wife had some more data to collect for her Ph.D. dissertation in psychology, I spent the fall quarter in Chicago working on an idea that sprung from my work on time correlation functions. The idea was to derive a Langevin equation with memory for particles moving in liquids using projection operators. I made fair progress on this and was able to derive what is now known as the generalized Langevin equation, but I decided that much more had to be done. In February of 1965, Naomi and I made a stormy North Atlantic crossing on an ocean liner to Europe and I joined the Prigogine group at the Université Libre de Bruxelles. Many North Americans chose to work in the Prigogine group at that time. My stay overlapped with those of Roy Gordon, Gerald Manning, Henry Glyde, and Stuart Rice. I shared an office with Manning and spent considerable time talking about science with Gordon and Rice. In addition, I had very fruitful interactions with Pierre Resibois and Gregoire Nicolis, both members of the group. In retrospect, I could not have made a better choice of a postdoctoral venue. The food, wine, and beer were excellent, we lived very well on the NATO stipend, and we were able to

make frequent trips to Paris, London, and to the Côte d'Azur, the last for relief from the daily rain in Brussels. I worked very hard on several problems including the generalized Langevin work that I initiated in Chicago, wrote a joint paper with Rice and Boon on velocity and angular velocity correlation functions using projection operators and memory functions, and started some work on vibrational relaxation in liquids. I did not publish much while in Brussels, but I learned a great deal and after a gestation period, some of the work initiated there was incorporated in later work.

In January 1966, we made another stormy crossing back to the U.S., and I started working at Columbia. When I arrived, the chairman, Cheves Walling, asked me what I would be doing during the summer since Columbia would not pay my summer salary! Because I had not yet applied for a grant, he suggested that I find an outside job. Because my wife had to put the finishing touches on her dissertation, that summer we returned to the University of Chicago. I spent the summer writing up my work on the derivation and properties of the generalized Langevin equation, work that I believed would make my reputation. I showed the manuscript around, and Jean-Pierre Boon mentioned a very recent paper by Mori covering the same topic. When I read Mori's paper, a paper that covered considerably more ground than my manuscript, I was distraught. It took a long time to get over the disappointment of being scooped on such an important piece of work, and of course, I never submitted my paper for publication. To be sure of employment for the next summer, I called Harry Frisch and Frank Stillinger, and they were instrumental in getting me a job at the Bell Telephone Laboratories in Murray Hill, New Jersey.

When I started my job at Columbia, I learned that Martin Karplus, the colleague partly responsible for my getting the offer from Columbia, was leaving for Harvard. This news was very troubling at first, but it ultimately played to my advantage. The computer center was designed around Martin, who used roughly one-third of the facility. At that time, the Center was funded from overhead on government grants so that users did not have to pay for computer time as a direct charge on their grants. Computer use was essentially "free" to the users. Soon after I arrived, the chairman of the department asked me if I could use Martin's computer time. My immediate reaction was that as an analytical theorist I had no use for it. At that time, I was teaching the advanced statistical mechanics course. George Harp, a student in that course who had been working for my colleague Jack Miller, asked me if I could suggest a computational dissertation in statistical mechanics, as he loved the material in the course and was also a former systems programmer for Boeing. The offer of copious amounts of computer time, the appearance of a student wanting to do a computational project, and my keen appreciation of Rahman's molecular dynamics work on atomic liquids with realistic force fields all led me to suggest to George Harp that we should extend molecular dynamics to molecular liquids such as liquid N_2 and CO. Nobody had yet extended the methodology to handle molecules, and this was a great opportunity to get into this exciting field. He agreed, and in the spring semester of 1966, we embarked on this project. We were given the evening shift on the computer. Because operators were unionized, but no operators were available for the evening shift, George had to become a member of the union. He stayed up many evenings operating the computer once the code was put into production. This work represents the first "molecular" molecular dynamics simulation, and the first results were published in a 1968 paper and a 1969 paper incorporating memory function modeling, but most of

the results appeared in our *Advances in Chemical Physics* article in 1970. This work launched my lifelong interest in the development of new methods and force fields for computer simulation. Writing our review of molecular dynamics for the *Annual Review of Physical Chemistry* in 1971 was a simple task, as I was familiar with almost every paper written on the subject until then. Now, literally thousands of papers each year use these techniques.

In the early 1970s, Frank Stillinger asked me if we could collaborate on applying molecular dynamics to a model force field for water that he and Ben-Naim had been developing. I calculated that each time step would require between five to eight minutes and that this project would usurp all of my computer time for some time to come. In one of the great mistakes of my scientific career, I decided that the computer time would be better used on the problems I had already planned. Frank then asked Aneesur Rahman, and, as the saying goes, the rest is history.

In retrospect, my research interests have fallen into several broad but interrelated areas: memory function modeling of dynamics processes in liquids; dynamic light scattering; all aspects of computer simulation, including molecular dynamics, stochastic molecular dynamics, and Monte Carlo; force fields for polyatomic molecules, including polarizability; the structure and dynamics in quantum disordered systems; chemical reaction dynamics; and recently protein folding and dynamics.

My interest in light scattering started when my colleague Richard Bersohn showed me a theoretical paper by Robert Pecora, his former doctoral student, showing how inelastic laser light scattering could be used to measure diffusion coefficients in polymer solutions. I thought that inelastic light scattering could in principle be used to determine rate constants of fast chemical reactions. This interest was furthered by my collaboration with Bob Pecora. A nostalgic Brooklynite, Pecora would visit his family every year and during this time would visit Columbia. It became a tradition to write papers together when he visited. On one occasion we worked out the whole theory for depolarized dynamic light scattering from a reacting system of anisotropic molecules in one day and had the whole paper written within another day. We worked so well together that we decided to write a book on dynamic light scattering. This project took several years of on and off work, and in 1976, the book was published. During this period, I collaborated with Dale Shaefer at IBM's Watson Laboratories. Shaefer observed an unexpected background in the light scattered from a very dilute colloid dispersion, which he thought an artifact, but no matter what he did, it would not go away. For days, I sat and watched the oscilloscope, until while away for a weekend, things suddenly fell into place, and I was able to derive a theory that explained all of the observations—the first theory for number fluctuation spectroscopy. My interest in light scattering finally waned, partly because of its lack of specificity in addressing chemical reactions, and by the time the book appeared, I decided not to continue working in this field.

My fascination with molecular dynamics has never abated. In the early 1970s, I wanted to simulate nematic liquid crystals. Given limitations on memory, mass storage, and speed of existing computers, it was not feasible to study all-atom models. To reduce the computational cost of such simulations, my colleague Phil Pechukas and I invented the overlap model potential in 1972, which modeled the interaction between ellipsoidal molecules and gave the potential as a function of intermolecular distance and relative orientations. Jack Gay and I modified this potential in 1981, making it much more realistic.

This modified potential became known as the Gay–Berne potential and has been widely adapted to the modeling of liquid crystals and also is now used in predicting protein folding. My student Joe Kushick and I used the original Berne–Pechukas potential to simulate a model nematic liquid crystal in work published in 1975, probably the first simulation of a liquid crystal with a realistic potential. Given the computers of that time, one could only simulate small systems. If the axial ratio of the molecule were large, as in liquid crystals, the orientational relaxation would be so slow that enormously long simulations would be required to obtain statistically meaningful correlation functions. Nevertheless, once more robust computers became available, others, using the Gay–Berne potential, made great strides in achieving the goal that we set for ourselves in 1972. We continued to use the Gay–Berne potential; in 1993, Cao and I used it to model polarizable ellipsoids with embedded Drude dispersion oscillators and to calculate the optical birefringence of liquid crystals as a function of the order parameter. In 1995, Wallqvist and I also used it to study the hydrophobic interaction between oblate ellipsoids.

In 1974, I was invited to give a talk on molecular dynamics at the Gordon conference on dielectrics, but I had never done any theoretical work on dielectrics. Fortunately, I thought of a problem that was worth solving. This resulted in an analytical theory of dielectric relaxation in model polar fluids in which the individual dipoles undergo translational and rotational diffusion and the molecules are coupled through the dipole–dipole interaction. The bath was treated as a dielectric continuum, but it also could contain an electrolyte. I solved the linearized Smoluchowski equation coupled to the Poisson–Boltzmann equation for this system and showed that the total electric polarization decayed on two time scales, a fast time scale and a slow time scale. These two time scales turned out to be the transverse and longitudinal dielectric relaxation times introduced by Fröhlich. This was the first quasimolecular theory of this effect. I am proud of this work even though it is not well-known. This was the only time in my life when an invitation to a meeting led me to produce interesting new science.

During the second half of the 1970s, my research moved toward the mainstream of chemistry. In 1977, my student Collin Pangali, postdoc Mikkilineni Rao, and I began a series of Monte Carlo and molecular dynamics simulations of the hydrophobic interaction. In 1976, David Chandler and Lawrence Pratt presented a simple semiempirical theory of the hydrophobicity of small solutes in water. Chandler was spending his sabbatical year with us at Columbia in 1977. We decided to test the Pratt–Chandler theory by simulating the hydrophobic hydration of inert gas atoms as well as the potential of mean force (pmf) between two atoms in water. This was the first such simulation of the potential of mean force between hydrophobes in water. We constructed this pmf by one of the first, if not the first, weighted histogram methods and showed that solvent-separated pairs of hydrophobes were more probable than contact pairs, in agreement with the Pratt–Chandler theory. Thus, small hydrophobic particles did not conform to the conventional view of hydrophobicity, which predicted that contact pairing is more probable. We went on to perform the first determination of the effect of hydrophobicity on the folding of chain hydrocarbons by studying the dihedral distribution of *n*-butane and its associated potential of mean force. Unfortunately, the computer power in those days made it very difficult to obtain good statistics. An important byproduct of our work on hydrophobicity was our invention of the Force–Bias Monte Carlo method in

1978, which accelerated the sampling of the configuration space of aqueous solutions. In 1997, Steve Rick and I simulated the pmf of two methane molecules in polarizable water and showed that making the water polarizable does not change the hydrophobic interaction between the methanes. In 1995, Anders Wallqvist and I simulated the pmf between two parallel oblate ellipsoids in water and showed that as the stacked plates were brought together there was a drying transition in which all of the water was ejected from the space between the two plates. I believe that this work has played an important role in stimulating subsequent work by Chandler and Weeks on the drying transition.

Fruitful collaboration with David Chandler began during his sabbatical year at Columbia in 1977. He was then working on the projection operator theory of chemical reactions in which he derived a reactive-flux formula for calculating rate constants, a cause for many productive discussions with Pechukas and I. This led to my collaborations with Chandler using molecular dynamics to calculate the reactive flux for liquid state chemical reactions involving activated barrier crossing. This approach requiring sampling of initial transition state configurations avoids the more direct method of waiting for molecules to become activated. With John Montgomery, a former student of mine, we first applied the reactive flux method to a reaction involving a double well “molecule” colliding with a bath through BGK collisions and observed the analogue of the Kramers turnover in the rate constant as a function of collision rate. Our work led Jiri Jonas to measure, by NMR, the boat to chair interconversion of cyclohexane in various solvents as a function of pressure. He observed the Kramers turnover at unexpectedly high pressures. Jonas’ experiment still remains one of the very few observations of the turnover in liquids. Although our paper stimulated Jonas’ experiments, we were perplexed by his results—more about that later. The Chandler–Berne collaboration continued when my student Robert Rosenberg simulated the rate constant for gauche–trans isomerization of *n*-butane in liquid CCl₄. This was the first simulation of a realistic reaction in a liquid and showed that the Kramers theory could not explain the result.

My interest in the theory of reaction dynamics in different environments, ranging from isolated molecules to gases, clusters, and liquids, has continued throughout my career. In 1980, my student Nelson De Leon and I initiated a study of reactions in systems with two degrees of freedom to better understand reactions in isolated molecules and to explore the role of Hamiltonian chaos in reaction dynamics. Building on this work, in 1986, my students Straub and Borkovec and I coupled the De Leon–Berne “molecule” to a bath and showed how the rate constant depends on collision rate (or friction). At very low collision rates, the “molecule” had time for intramolecular energy equipartitioning so that the RRK theory applied and the reaction appeared to be two-dimensional, whereas at higher collision rates, the “molecule” lost its energy to the bath before it had time to equipartition and the reaction appeared to be one-dimensional. In 1986, Straub and I wrote an important paper clarifying the primary processes involved in this energy diffusion limit. The breakdown of equipartitioning at intermediate collision rates had the unexpected consequence that the Kramers turnover should occur at a much higher pressure than would be expected on the basis of the RRK theory. This realization led us to suggest this as an explanation for why Jonas observed the Kramers turnover for cyclohexane at such a high pressure, an explanation later confirmed by Chandler’s simulations of cyclohexane.

We became interested in chemical reaction dynamics in clusters as a function of cluster size, especially to determine at what size the cluster dynamics began to resemble liquid-state dynamics. Francois Amar and I studied the photodissociation reaction of Br₂ in argon clusters, work that had a large influence on the cluster community. We observed the “cage effect” with much less than a monolayer of coverage and studied the mechanism for dissociation as a function of cluster size. My interest in clusters continued and focused on Coulomb explosions, quantum effects on the structure of small clusters of water, electron attachment to xenon clusters, and, more recently, the hydration of anions in polarizable water clusters.

Borkovec, Straub, and I began a series of interesting studies of reaction dynamics which marked the beginning of an important avenue of research in the mid 1980s. We simulated the stochastic dynamics of a particle undergoing Langevin dynamics with colored noise in a double well potential. This work showed that when the memory friction had a lifetime that increased with viscosity there would be very strong deviations from the Grote–Hynes theory of reaction dynamics in non-Markovian systems. This work prompted Pollak, Grabert, and Hänggi to derive the so-called PGH theory of the Kramers turnover, an important theoretical development of rate theory. In our early work on reactions, the reactive flux was calculated, but for systems with very small reaction rates, this method would be inaccurate. Straub and I invented an absorbing boundary condition approximation that enabled us to compute the rate constant in these formerly inaccessible regimes. This method permitted us to study reactions in the very weak coupling regime where energy diffusion is rate determining and where the non-RRKM effects could be observed. The formulation of the absorbing boundary method then led to a very interesting analytical calculation of the rate for nonadiabatic barrier crossing as a function of friction constant. My interest in reaction rates has continued into the 1990s. With postdocs Eran Rabani and Eunji Sim and with student Goran Krilov, we have used Bayesian methods to analytically continue imaginary time flux–flux correlation functions, computed using path integral techniques, to real times, using maximum entropy techniques, and thus were able to determine rate constants for barrier crossing in quantum systems.

In 1978, when I gave a talk at IBM’s laboratories in San Jose, John Barker gave me a preprint in which he used the Feynman path integral to determine the average energy and density matrix of a particle in a one-dimensional box. I was intrigued by this work, and to gain familiarity with this approach, my postdoc Rao and I used path integral Monte Carlo to simulate harmonic oscillators. We found that the error bars on the average energy grew larger as the Trotter number was increased, a mystifying result. Finally in 1981, we devised the now widely adopted virial energy estimator that circumvented this problem and allows one to calculate accurate internal energies. Thus began more than a decade of work using path integrals to simulate structure and dynamics in quantum systems. In various combinations, my students and postdocs—Bruskin, Thirumalai, Hall, Hua, Herman, Wallqvist, Coker, Martyna, Krilov, Sim, and Rabani—participated in this endeavor. We introduced the numerical matrix multiplication method for determining quantum thermal and dynamic properties in one and two-dimensional systems. Throughout the 1980s, we made several simulations of the excess electron in water, helium, and xenon. For example, in 1993, my student Zhihua Liu and I showed that in liquid ethane the excess electron would be self-trapped, whereas in liquid methane, it would be

in an extended state, an experimental result that had perplexed the radiation chemistry community.

Since 1989, I have been very interested in devising methods to handle the multiple time scale problem in molecular dynamics. My students Mark Tuckerman and Glenn Martyna and I, using the Trotter factorization of the classical propagator, devised the r-RESPA algorithm, which has been widely adopted and is now used in many molecular dynamics packages. We also designed a very efficient molecular dynamics method for sampling path integrals that is equivalent to the Ceperley staging algorithm. My group has devised very efficient algorithms for treating systems with long range electrostatic forces and multiple time scales by combining r-RESPA with the fast multipole method (FMM/r-RESPA; done with Zhou), combining r-RESPA with the particle–particle–particle mesh method (P3ME/r-RESPA; done with Zhou, Harder, and Xu). These methods are particularly useful for simulating complex systems like protein solutions, in which I have become increasingly interested in recent years.

One of my major interests during the last eight years has been the study of polarizable systems. I was intrigued by early electronegativity equalization models, and in 1994, and with student Steven Stuart and postdoc Steven Rick, I introduced a dynamic fluctuating charge model of water, which allowed for polarizability through intramolecular charge transfer. We used an extended Lagrangian method to solve for the rapid charge equilibration with changes in the nuclear configuration. When applied to water, this model required only 10% more computation time than fixed charge models and, moreover, gave very good static and dynamic dielectric constants and better transport coefficients than fixed charge models. Dipole polarization models in contrast require between two and three times as much computation time. In collaboration with my colleague Richard Friesner, my student Harry Stern and I have now devised promising hybrid polarizable models for water, amino acids, peptides, and amides that may well give chemical accuracy in contrast to fixed charge models. We plan to use these models to study protein dynamics.

I hope that the foregoing is prologue.

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One learns to be a parent from one’s own parents. One learns to be graduate supervisor from one’s own dissertation supervisor. I hope that I have learned well from my supervisor, Stuart Rice. He was always generous and optimistic, and he gave me free reign in solving problems. I have always treated my students as full-fledged collaborators with whom I have enjoyed the give and take of argument, and I have always delighted in their success. This has been one of the most rewarding aspects of being a professor.

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