

Autobiography of David Chandler

Early Years and Background

I was born the younger of my parents' two children, on October 15, 1944, at Brooklyn Jewish Hospital, in New York. Except for two years when I was five and six years old, I spent my formative years in Great Neck, a north shore Long Island suburb of New York City, where I benefited from material comforts, excellent schools, and abundant opportunities for cultural and recreational activities.

My father, Herbert S. Chandler, was trained as a toolmaker. He became a labor union leader in the 1930s, and then, near the end of the Great Depression, created H. S. Chandler & Co, a tool and dye firm that developed and held a valuable patent during World War II. Later, after surviving a heart attack in 1948, he sold the company and began another career as the East coast sales representative for a few small midwestern manufacturing firms. My father was the youngest of seven children in a poor Austrian Jewish immigrant family. His father died when my father was six years old. The oldest brother, Willy, supported the family, first on what seemed to be substantial earnings as a prizefighter and then on meager earnings as a janitor. The aftermath of prizefighting left Willy with life-long injuries that made most employment impossible. My father, like his older brother, was an excellent athlete and a local hero. He played semi-pro baseball. His older brother would not permit him to become a prizefighter.

My mother, Sylvia, was the second youngest in a middle-class Russian Jewish immigrant family with four children. She had a college degree and sophisticated tastes in clothing, art, and literature. Around the time she met my father in the late 1930s, she worked as a comparison shopper and then as a buyer for Macy's Department Store. My mother always enjoyed shopping. She also had very high expectations for my father, my sister, and me.

As a young boy, I was not a good student. My sister Elsie was our family's good student. I spent my time with music and athletics. My first entrée into music was playing drums. My mother convinced me that I would be a better drummer if I would also learn to play the piano, and piano became one of my great loves. I had a wonderful teacher that would reward me with a small lesson in jazz for every classical piece I would master. My repertoire of jazz became sufficiently broad that I could perform as the pianist in a dance band. This band—the "Blue Notes"—played at functions throughout Long Island. Later in college, I used my piano-playing skills to introduce myself to young women, showing up at women's dormitories throughout the Boston area, playing the piano. One woman, later to be my wife Elaine, found these performances annoying, but even she, my toughest critic, would eventually succumb.

I loved almost all sports. For a child, I was a good baseball and basketball player. But by my middle teens, my small size had become a handicap that I could not surmount to my satisfaction. Trying to be "best" was important to me, so I decided to focus on tennis, believing that small size was not a significant handicap in tennis. The Australian tennis stars of that era, Ken Roswall and Rod Laver, were both small men, about my size. I was a good competitor, not a star, but good enough to obtain high rankings in collegiate tennis and a notable

mention in a later United States Tennis Association listing. What I lacked in power I could often compensate for with determination. Until my 40s, when injuries and then cancer would limit my playing, tennis would be one of my greatest sources of enjoyment.

College and Graduate School

I began my college education in the fall of 1962 at Stevens Institute of Technology, a small college in Hoboken, New Jersey. During the previous summer, I worked on an assembly line at Grumman Aircraft Corporation in Bethpage, Long Island. This experience motivated me to avoid that sort of work in the future. I began studying hard at school, something I had never done before. Applying myself turned into a revelation. For the first time, intellectual activity was rewarding. I excelled in chemistry, physics, and mathematics, and I had an inspiring chemistry instructor, an Indian chemist named Manhas. My physics teacher, Jack Fajans, was excellent too. Fajans suggested that I consider moving to MIT where my studies could be even more rewarding. I followed Fajans' advice, and my application to transfer was accepted. Some 30 years later, Jack Fajans' son Joel became one of my colleagues, a professor of physics at Berkeley.

In the fall of 1963, I moved to Cambridge, Massachusetts, and began my three undergraduate years at MIT. I soon caught sight of Elaine Ackles. She was a freshman, sitting on a bench in one of the MIT buildings, talking to another freshman that happened to live in the dormitory across the hall from me. I noticed that Elaine was very attractive. We dated that year in college, but Elaine found me not charming, and the friendship did not last. Two years later, in the 1965–1966 academic year, we encountered one another again, and this time we fell deeply in love. I had finally grown up. We married that spring, and we have remained together ever since. We raised two daughters, Phoebe and Cynthia, and we are now grandparents.

I attempted to major in both chemistry and physics. In my sophomore year, my inept laboratory skill—mainly impatience—led to a frightening explosion while I was carrying out an organic chemistry synthesis. I sought advice from my chemistry advisor, Dietmar Seyferth, but he was too busy to meet with me, so I went instead to my physics instructor, Nathaniel Frank. Frank was in the twilight of his career. He had taught many outstanding MIT students, Richard Feynman among them, and he had served as the Physics Department Chair in the late 1940s. He had plenty of time to talk with me, and following his advice, I took a hefty amount of physics and mathematics. This put me on the track to becoming a theoretician.

In my junior year, I took a thermodynamics course from Irwin Oppenheim, and Hans Andersen was my teaching assistant. I was enormously impressed with Irwin and with Hans. I spent many extra hours studying thermodynamics, and I often pestered Hans for advice on the topic. I wanted to do whatever Hans was doing, and Hans was one of Irwin's graduate students, so I asked Irwin if doing undergraduate research under his guidance was possible. Irwin said yes, and that is how I became a statistical mechanician.

I graduated from MIT in June 1966 majoring in chemistry. I was one laboratory course short of satisfying my earlier plan to

major in both chemistry and physics. The many hours each week spent playing college tennis were partly to blame. I received an award from the MIT Chemistry Department signifying that the faculty judged my performance in undergraduate research to be better than that of all others in my class. Elaine likes to keep the notice of that award together with one of my junior high school report cards. The juxtaposition is breathtaking.

I entered graduate school in chemical physics at Harvard in the fall of 1966, and I joined Roy Gordon's research group. Roy's first three years on the Harvard faculty coincided with my years as a graduate student. Roy was extraordinarily productive, publishing in almost every issue of the *Journal of Chemical Physics*. He was pioneering the use of time-correlation functions to interpret spectral line shapes. Students were impressed and called him "Flash Gordon." The Harvard faculty was impressed too. Roy was promoted to full professor after three years as an assistant professor, when he was 29 years old. Since Roy was very busy, he let me work on my own. This was not an uncommon practice for excellent theory students at Harvard during that period.

Elaine gave birth to both Phoebe and Cynthia during my graduate school years. Looking back, it is difficult to recall how we packed in so much into so little time. I obtained my Ph.D. in chemical physics, Elaine obtained a bachelor's degree and then a master's degrees in physics, I played tournament tennis during one spring and summer season, and we parented two baby girls.

In my graduate research, I collaborated with Hans Andersen. Hans had moved to Harvard where he was a Junior Fellow. One afternoon, I described some vague ideas to Hans about using collective coordinates as a basis for treating the statistical mechanics of fluids. Hans suggested how to make the ideas concrete with a type of cluster series that became known as the "mode expansion." This expansion proved reasonably useful for treating effects of long-ranged intermolecular interactions. My Ph.D. thesis was entitled "The mode expansion, a new method in statistical mechanics." Hans and I applied the mode expansion to treat the equilibrium properties of electrolyte solutions and simple liquids.

WCA Theory

In the fall of 1969, I began postdoctoral work in Kurt Shuler's research group at UCSD in La Jolla, California. John Weeks began his postdoctoral study with Shuler at the same time. While working on a research topic that Kurt Shuler suggested, I continued to think about different scientific problems on my own. One was the structure of simple liquids, which was a particularly timely topic in 1969–1970. A few years earlier, Anees Rahman had introduced the molecular dynamics technique for simulating simple liquids, and in 1968, Loup Verlet followed up on Rahman's work, publishing a remarkable paper presenting detailed molecular dynamics results for the structure factor of the Lennard-Jones liquid. Verlet had shown that this structure factor was very close to that of an empirically chosen hard sphere fluid. Verlet did not have a theory for the coincidence. The result by itself, however, was important because it showed that the van der Waals picture of the liquid state might be quantitatively accurate. A year earlier, Ben Widom had described how this picture should result from the tendency for attractive intermolecular forces to cancel in a dense fluid, the near cancellation due to packing constraints imposed by repulsive intermolecular forces.

John Weeks and I often talked about these papers by Verlet and by Widom. We believed it should be possible to derive the

formal connection between fluids with repulsive forces and the hard sphere fluid. Such a derivation would provide a quantitative understanding of how repulsive intermolecular forces in a dense fluid screen the effects of attractive forces. It would also provide a quantitative theory of real liquids in terms of properties of the hard sphere fluid. John Barker and Douglas Henderson had created a theory with the same motivation, but in fact, the structure predicted by Barker and Henderson's hard sphere model was far from that of the Lennard-Jones fluid. It thus seemed unsatisfactory to us. We proposed an alternative two-step approach. Step one separated the pair potential between atoms into a purely repulsive-force part and a purely attractive-force part. This unique decomposition is usually called the WCA (i.e., Weeks, Chandler, and Andersen) separation. Step two was a mean field argument that connected the compressibility of the hard sphere fluid to that of the WCA repulsive force system.

John and I described this second step to Hans Andersen, and Hans quickly demonstrated that our physical argument could be justified in terms of a systematic perturbation theory, the so-called "blip function" expansion. The final result of this and subsequent analysis is the WCA theory. During the summer of 1970, John and I published a preliminary account of this work in *Physical Review Letters*, and with Hans, we submitted what would become our primary paper to the *Journal of Chemical Physics*. While it is now a well-accepted work,¹ cited thousands of times, it was initially rejected for publication. Fortunately, the editor of the *Journal of Chemical Physics*, Willard Stout, was open-minded and exerted editorial judgment. Sensing that our work did have merit, he provided ample opportunity for us to make the case. It would take a year to settle it.

In the meantime, Elaine and I moved with our little girls from La Jolla, California, to Urbana-Champaign, Illinois, in August 1970. There, I began my first academic appointment as an assistant professor of chemistry at the University of Illinois, Urbana-Champaign. Six months earlier, I had interviewed for assistant professor positions at several universities, Illinois among them. The position at Illinois was particularly attractive to me, mainly because Bill Flygare was working there. Willis H. ("Bill") Flygare was an energetic and brilliant physical chemist, and I found it impossible to resist his efforts to recruit me. Bill became my mentor and my most meaningful friend in Illinois.

Throughout the fall and winter of 1970 and 1971, John, Hans, and I argued with referees about our submission to the *Journal of Chemical Physics*. I felt embattled and expressed my frustrations openly. I was developing an aggressive and combative reputation. My Illinois colleagues Rudy Marcus and Bill Flygare were beginning to worry about me, and I could sense their concern. Relief finally came in the spring of 1971, nearly a year after the paper had been submitted. At the IUPAP StatPhys meeting in Chicago, Loup Verlet chose to give his plenary lecture on the WCA theory. Verlet told the audience of several hundred scientists that he had received a preprint of the WCA paper and that he found its ideas intriguing, so much so that he set about to test the ideas with computer simulation in all ways he could imagine. The results of his tests, Verlet reported, demonstrated to his satisfaction that WCA theory is correct and superior to the Barker–Henderson theory. A few weeks later, the *Journal of Chemical Physics* accepted the WCA paper. Two years later, Hans was invited to give a principal lecture at the 1973 Gordon Research Conference on Liquids. WCA had become the standard equilibrium theory of the liquid state.

Decades later, I still remember the emotions felt during that period: the elation in discovering something true and important and the aggravation in not having this discovery initially

accepted. The ties I made to John Weeks and Hans Andersen during this time are everlasting. They are my brothers in science and in spirit. We have faithfully supported one another for more than three decades.

Illinois

While arguing with referees that first year in Illinois, I was also learning to be a professor. I was initially assigned to teach graduate thermodynamics and statistical mechanics. Preparing my lectures, problem sets, and so forth, I was careful and complete. Nevertheless, I was not a good teacher. I was overly demanding and impatient, and the students did not like me. It took two or more years before I acquired sufficient self-confidence that I could properly engage students. With my initial difficulties behind me, I believe I have been a consistently excellent and appreciated teacher. I have often prepared detailed notes for students to read. A significantly pruned version of such notes became my textbook *Introduction to Modern Statistical Mechanics*.

My father died of prostate cancer in the spring of 1973. During the last year of his life, my father was very uncomfortable but always happy to see me. I made several trips to New York during that last year, often facilitated by a standing invitation from Bruce Berne to visit him and his colleagues at Columbia University. On each occasion, my father would give me a fine etching or lithograph. Over the previous 20 years, my father had time and resources to act on his love of art, becoming a noted collector of graphic arts. He owned several Rembrandts and Whistlers and also excellent examples of 20th century art, including works by Picasso and Matisse. One piece he gave to me in 1973, the Whistler etching "Street at Saverne," remains one of Elaine's favorites from my father's collection.

My father was very proud of my successes at MIT and Harvard and proud too of my young scientific career. During his last year of life, he and I would talk at length about my work. I would try to explain some of its scientific content, and my father seemed able to relate to it. I also described the conflicts involved in finding acceptance of my work. Having watched me on the tennis court, my father was concerned about my temper. He was correct in believing that a bad temper is not helpful in scientific issues. (It was never helpful in tennis either!) My combative style—competitive and emotionally committed—has produced enemies, and I regret and am sometimes embarrassed by these conflicts. Over the years, this aspect of my personality has softened, and my temper is now rarely provoked.

Following up on WCA theory, Hans Andersen and I created the reference interaction site model (RISM) to treat the packing of oddly shaped particles as a model to interpret the structures of molecular liquids.² My Illinois students and I worked out the predictions of the model in numerous applications.³ In so doing, we provided the first understanding of molecular correlations in polyatomic fluids. Subsequent computer simulation work and experimental measurements verified many of the predictions of the model. In current times, the most important uses of the model are in interpreting the pair correlations of polymer melts, a development due largely to my former student Kenneth Schweizer.

The underlying approximation in the RISM equation is the assumption that density fields obey Gaussian statistics. Fluctuations in atomic and molecular fluids are constrained by excluded volume forces. The RISM equation captures effects of excluded volume constraints approximately through a choice of metric for Gaussian density fluctuations. This choice of metric makes

the RISM equation nonlinear. While nonlinear, the underlying physical picture is that of small-amplitude fluctuations in a homogeneous fluid. It took me 20 years to understand this fact.⁴

In all of this work, and that which followed, my most significant insights have been gained from geometry. Analysis is important too, but that is not my strength. The few tools of analysis that I have exploited in my research were mainly learned from Hans Andersen and from Elaine. An example of the latter occurred one weekend in 1973. I was struggling to understand why my first numerical calculations aimed at solving the RISM equation were not converging. Possibly, I thought, the solutions possessed singularities that were absent in the basis functions used to approximate the solution, but how is the existence of singularities demonstrated without first knowing the solutions? I was unable to answer the question. I described the problem to Elaine, and she quickly demonstrated how successive differentiations of the RISM equation laid bare all the important singularities.

Armed with this technique, I was able to create an efficient numerical algorithm to solve the RISM equation. I asked Elaine to coauthor the first paper announcing these solutions, but she declined saying she had done nothing worthy of a publication. Later, my postdoctoral student, Branka Ladanyi, and I extended Elaine's approach to show that the singularities in the RISM equation are rigorous features of molecular pair correlation functions.⁵ In fact, these singularities control the most significant qualitative aspects of molecular pair correlation functions. In my textbook *Introduction to Modern Statistical Mechanics*, I describe these qualitative features from a geometrical perspective rather than analysis. Once knowing the answer, I am always most comfortable expressing my understanding with geometry.

When our youngest daughter, Cindy, began elementary school in Urbana, Elaine returned to her graduate studies of physics. She was "wonder woman," doing full time work as a wife and mom, plus being a successful graduate student. Some graduate students did not know what to make of her, this "older" married woman in their midst. Emotionally, she was much more mature than her fellow students. Yet she looked young, so much so that she was sometimes questioned about her age when purchasing alcohol. In addition, she was very beautiful. This was not the typical physics student! Elaine did her Ph.D. research under the guidance of Gordon Baym. Together, they worked out the hydrodynamic theory of rotating superfluids.

Through my years at Illinois, I maintained a small research group, with typically two or three graduate students and one or two postdoctoral students. Lawrence Pratt was one of the best of those students. He and I worked out a rigorous statistical mechanical treatment of chemical equilibrium in liquids,⁶ and we also developed our theory of hydrophobic effects to describe the solvation of small oily species in water.⁷ In 1978, I derived an exact statistical mechanical procedure for computing rate constants for rare events, such as the rates of transitions or interconversions between long-lived molecular species.⁸ Bruce Berne and Phil Pechukas helped and motivated me in this work, done during my 1977–1978 year of leave from Illinois at Columbia University. The procedure I derived, the "reactive flux" method, is useful when the mechanism—the transition state surface—is already known. Charles Bennett independently developed this method. Bruce Berne and I collaborated in using it to carry out the first computer simulations of chemical dynamics in liquids.⁹

I was promoted to Associate Professor with tenure in 1975 and to Professor in 1978. During this period, the University of Illinois had an extraordinary program in physical chemistry,

perhaps the best in the world. Harry Drickamer, Bill Flygare, Herb Gutowsky, Jiri Jonas, and Rudy Marcus, all National Academy members with numerous additional accolades, were among its stellar and active faculty. In 1978, however, Rudy Marcus resigned to take a professorship at Cal Tech, and Bill Flygare learned that he was dying of amyotrophic lateral sclerosis (often called “Lou Gehrig’s disease”). Bill would eventually pass away in the spring of 1981. Various recruiting efforts were made to shore up the program from these devastating losses, but nearly all were unsuccessful. The exception was the recruitment of Peter Wolynes, at the time a third year assistant professor at Harvard. I was convinced that Peter was brilliant, and I pushed hard for his recruitment.

Peter’s arrival in Urbana in 1980 had a stimulating effect on me. We talked often, and soon a collaboration began. Peter convinced me to begin using Feynman path integrals to treat quantum phenomena, and together we worked out several facets of the isomorphism between quantum theory and classical polymer theory.¹⁰ These connections allowed us to exploit techniques that I had been using earlier to describe classical chemical equilibria in liquids and structures of chain molecules in liquids. The approach we were taking together was exciting and caught the attention of theorists around world. In the midst of it all, however, Peter and I became uncomfortable with each other, and our scientific styles and attitudes drifted apart.

Pennsylvania and Then Berkeley

In the summer of 1983, I resigned from Illinois and accepted a long-standing offer from the University of Pennsylvania. Robin Hochstrasser was the person who attracted me most to Penn. A brilliant physical chemist, he pioneered much of time-resolved spectroscopy and trained numerous successful graduate and postdoctoral students, including one Nobelist. During my nearly three years at Penn, I interacted closely with Robin virtually every day. I am proud to know him and to have worked with him, and I am grateful for the friendship and sage advice he has provided for more than two decades.

I built a new research group at Penn, one that was much larger than I had had at Illinois, and I produced most of my work on the behavior of electrons in liquids. Some of these studies were done in a fruitful collaboration with Michael Klein during the time when Mike was working in Canada. This collaboration was the start of interactions between Mike and the University of Pennsylvania that eventually led Mike to join its faculty. Also during this time, I wrote the final draft of the “little green book,” *Introduction to Modern Statistical Mechanics*.

In the spring of 1985, C. Bradley Moore, then Chair of Chemistry at Berkeley, called me to say that his Department had voted unanimously to offer me a faculty position. Berkeley had shown interest in me as long ago as 1975, but a job for me had never before materialized. I told Robin Hochstrasser about the phone call. He expressed happiness that I had this new career opportunity and sadness that I might be leaving Penn. Negotiations with Berkeley proceeded smoothly, and on my 41st birthday, October 15, 1985, I wrote to Brad Moore accepting the offer to begin working at Berkeley on January 1, 1986. A year later, Elaine acquired a rewarding and long-term professional post at Lawrence Livermore Laboratory. She rose through its ranks, eventually developing and administrating basic research on the physics of materials for Science Based Stockpile Stewardship.

Our oldest daughter, Phoebe, began college at Rutgers University in the fall of 1985, when the family was still in Pennsylvania. She continued on at Rutgers, playing college

tennis, majoring in geography, and graduating in 1989. Following that, she spent two years on the East coast before moving to California in the fall of 1991. Most recently, she has been a partner in a small import company, bringing fancy foods from France, Spain, and elsewhere to the Bay area. Cindy entered Berkeley High School in the fall of 1986 and then UC Berkeley in January 1987. She graduated with honors, majoring in rhetoric, in 1991 and left California in the fall of 1991, first to study criminology at Cambridge University and then to study law at Harvard. In 1992, she obtained a master’s degree with honors from Cambridge; in 1993, she married David “Bud” Sperman, a Californian she first met as an undergraduate at Berkeley; and in 1995, she obtained a law degree from Harvard, also with honors. At that point, Cindy and Bud returned to California, where Cindy created the Oakland law practice known as Justice Now. The firm is dedicated to representing poor women in prison.

My research at Berkeley before 1996 was largely derivative of my earlier work. I worked on the topics of energy flow in liquid-phase chemical reactions, solvated electrons, and electron-transfer processes. My research group remained at the size I established at Penn—about 8 to 10 students. Perhaps my most influential work during that era was done with my colleague Bill Miller and our joint postdoctoral student Greg Voth. We developed a way to think about quantum effects on thermal rate constants by employing the concept of a quantum centroid. In later work, Greg has done many interesting things extending this approach to molecular dynamics.

During that same period, I interacted well with my colleagues, and I was active in Departmental leadership, including service as Chair of the Department Planning Committee for two years. I am particularly proud of the role I played in this capacity in recruiting Graham Fleming to Berkeley. I also led the Department in revamping the undergraduate physical chemistry syllabus and taught large classes of undergraduate physical chemistry and huge classes of general chemistry. In my graduate-level courses, I introduced the Department (and the University) to the modern subject of statistical mechanics.

I also played much tennis, being admitted into the Berkeley Tennis Club in short time. I was pleased by this “early” admission and often said that it was more important to me than election to the National Academy of Sciences. I spent hours each week at the Berkeley Tennis Club. Sometimes, I would compete in United States Tennis Association sponsored seniors’ tennis tournaments, occasionally winning a few matches in these events. My tennis was sometimes interrupted by chronic shoulder pain. But excepting those interruptions, I was energetic and active at play as well as at work.

In April 1995, I was elected to the National Academy of Sciences and also to the American Academy of Arts and Sciences. When I told my mother of the news, she responded that my father would have been very proud and that she would tell him about it in her dreams. My mother, who passed away in year 2000, often expressed concern over whether I was successful. On that day in 1995, however, I was pleased by her response, believing that now her concerns were abated. A day later she called back to remind me that my distant cousin, Richard Klausner, had been elected seven years earlier. I corrected her, saying that Rick had been elected just two years before, in 1993. She retorted that Rick is five years younger than me.

1996 and After

In 1996, I was diagnosed with advanced prostate cancer. Surgery and subsequent radiation quieted the disease tempo-

rarily, but it recurred in 2000. In 1998, yet another health crisis required four stents to be inserted into my coronary arteries. During this time, while battling cancer and heart disease, I believe I have carried out my most significant contributions to science. Perhaps this rejuvenation in creativity is somehow tied to my response to illness. Whatever the case, it would have been impossible without Elaine's continued support and without the luck of having an outstanding research group, the best I ever assembled. I believe these people helped save my life.

Ka Lum began working with me in 1994. She was the valedictorian of her graduating class at Berkeley. I suggested that she work on the hydrophobic effect—the tendency of oil and water to segregate. The effect is believed to play a central role in the formation of biological structures because the microscopic segregation of oily and aqueous components is a most common facet of lipid and protein assemblies. At the point when Ka began working with me, the Pratt–Chandler theory was the most successful theory describing the hydration of oily species. But this theory applies to hydrophobicity only at small length scales, and it does not predict large length scale phase separation of oil and water. As such, it misses the physics of robust self-assembly. I told Ka that she should try to find this missing element.

Ka spent the first two years of her graduate career learning about statistical mechanics of phase transitions and becoming expert in applying techniques of statistical physics to liquids and solvation. She tried various ideas for solving the problem I had posed, but nothing pointed toward an answer. In the midst of this activity, in the fall of 1996, when I was undergoing my first round of cancer treatments, Phill Geissler arrived at Berkeley to begin his graduate studies. A few months later, Christoph Dellago and then Peter Bolhuis arrived to be postdoctoral students in my research group. Christoph had just completed his physics Ph.D. in Vienna with Harold Posch, and Peter had done similarly in Amsterdam working with Daan Frenkel. Their presence at Berkeley would have an uplifting effect on Ka and on me.

When Phill Geissler entered Berkeley, I was unimpressed with his knowledge of mathematics and physics, and I was reluctant to take him into my group. I warned Phill that it would be difficult to catch up with other entering students. Phill more than caught up. By the start of his second year, Phill was clearly the star theoretician of his class. At the same time, he and Ka were sitting in on brainstorming sessions that I carried on with Christoph and Peter. In the early aftermath of my cancer treatments, I had only enough energy to work 2 hours each day, which I did in my group's offices, talking science with Peter and Christoph. These rewarding and delightful discussions planted the seeds for a way of doing computer simulations from the perspective of a statistical mechanics of trajectories. Peter and Christoph were as they remain: brilliant, friendly, and committed to science. Each day, the discussions led to scientific progress, and each day I felt stronger and increasingly grateful that these people had come to work with me.

Inspired by these interactions, Ka became bold and original in her own thinking. Specifically, she saw a way to piece together a few seemingly disparate but important ideas. A few years earlier, I had shown that Pratt–Chandler theory was based upon a form of Gaussian statistics for density fluctuations, and Lawrence Pratt and co-workers at Los Alamos National Laboratory demonstrated with computer simulation in 1996 that water density fluctuations at small length scales are indeed almost exactly Gaussian. Meanwhile, John Weeks had developed a view

of interfacial structure based upon the concept of an unbalancing potential. Ka came to appreciate that while maintaining a consistent Gaussian theory at small length scales she could use John's unbalancing potential to capture large length scale hydrophobic hydration. Frank Stillinger had described the large length scale regime many years earlier. Ka's melding of the small and large length scale regimes resulted in the Lum–Chandler–Weeks (LCW) theory of hydrophobicity.¹¹ According to this theory, the driving force for hydrophobic assembly results from the formation of a soft interface, akin to a liquid–vapor interface, that is nucleated by an extended hydrophobic surface. While basic predictions of this theory remain controversial, reports of experiments from various groups around the world have begun to appear in support of the theory.¹²

While Ka was making her advances, Peter and Christoph were developing methods to sample trajectory space. A decade earlier, Lawrence Pratt had written an intriguing paper suggesting how a Monte Carlo sampling of chains of states might be used to find transition states. Several groups had picked up on this idea, but nothing done up to that point was entirely satisfactory. In particular, physical trajectories obey time reversal symmetry and detailed balance, but the chains of states considered in these early works did not obey these properties. As such, the earlier chains-of-states sampling could not coincide with sampling trajectory space. Peter and Christoph appreciated that consistency with trajectory space was crucial, and they began developing methods for adhering to it. They invented ways of taking random walk steps in trajectory space and then accepting or rejecting those steps in accord with whatever rules specified the ensemble of trajectories of interest. The body of techniques created in this way is called “transition path sampling.”¹³

One afternoon, while viewing some of the first trajectories harvested with this sampling, I wondered what governed the reversible work to change an ensemble of trajectories. This thought quickly led us to understand that time correlation functions were, in effect, Boltzmann's factors for such work, and from that point, we appreciated that the entire technology of equilibrium statistical mechanics and free-energy calculations could be transposed onto the nonequilibrium statistical mechanics of trajectories. This breakthrough established a generalization of the second law of thermodynamics applicable for computing properties of systems driven arbitrarily far from equilibrium. It is especially useful for sampling rare but important dynamical processes in complex systems without prior knowledge of transition states or mechanisms.

Conceptions of statistical mechanics of trajectories have a distinguished history. One such view provided Lars Onsager with the perspective from which his celebrated reciprocal relations were derived. More recently, these conceptions provided the basis for field theories of classical dynamics, starting with Martin–Siggia–Rose theory. My group's approach is distinguished by being the first to show how it applies in computer simulation and the first to establish its rigor in conditions arbitrarily far from equilibrium. An outgrowth of this development is the work of my student, Gavin Crooks, in deriving the famous Jarzynski equality and a more general fluctuation theorem. A further outgrowth is an understanding of glassy dynamics based upon the geometry of trajectory space that I have helped Juan Garrahan develop.¹⁴

In what I see as a most impressive application of transition path sampling, Phill Geissler, Christoph, and I combined forces with Michele Parrinello and his group to unravel the mechanism of autoionization in water, the fundamental kinetic step of pH.¹⁵ The mechanism of water dissociation thus revealed shows an

intricate interplay between very large but short-lived electric field fluctuations and the breaking of hydrogen bond chains. It remains for experimentalists to observe this interplay directly, and experimentalists have indeed been motivated to try.¹⁶

Research groups throughout the world are adopting transition path sampling in different contexts, including studies of solvated biomolecules, nucleation theory, signal transduction, and aging of metastable systems. Special workshops have been held to discuss and disseminate this technique. At one of these meetings, held in Paris in September 2003, I sat in the audience and thought how pleased I am to hear a community of scientists discussing an approach to science my students and I have created. This pleasure, the pride in my students, and the joy of discovery are feelings that enrich my life, a life I am so very fortunate to have. I have mentioned only a few of my students on these pages. Many others have worked productively and closely with me, and some have worked productively but independently, not unlike my behavior in Roy Gordon's and Kurt Shuler's groups. I am forever grateful for having known them all. I am grateful too for being honored with this Festschrift by so many of my students, friends, and colleagues.

David Chandler

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