David Chandler

1944-2017

BIOGRAPHICAL

A Biographical Memoir by Hans C. Andersen, Arup K. Chakraborty, and John D. Weeks

©2019 National Academy of Sciences. Any opinions expressed in this memoir are those of the authors and do not necessarily reflect the views of the National Academy of Sciences.





NATIONAL ACADEMY OF SCIENCES

October 15, 1944–April 18, 2017 Elected to the NAS, 1995

David Chandler was born on October 15, 1944, in New York City. His father, Herbert S. Chandler, was the youngest of seven children in an Austrian Jewish immigrant family. Herbert was an autodidact and self-made businessman. He was blacklisted for association with the worker's rights movement in the 1930s, and he credited this with compelling him to build his own businesses. While blacklisted, Herbert spent countless hours at the New York Public Library studying art and befriending artists. He had a great interest in graphic arts, and he instilled in David a profound love of prints, particularly political art of the modernist era, which David carried with him through his life. Herbert's influence also instilled in David a strong moral compass and an inexorable drive to succeed. Herbert founded H. S. Chandler & Co. a successful tool and dye company. This, and later business ventures, allowed him to provide a comfortable material and cultural life for



By Hans C. Andersen, Arup K. Chakraborty, and John D. Weeks

his children growing up in the prosperous suburb of Great Neck on Long Island. David's mother, Sylvia, was one of four children in a middle class Russian Jewish immigrant family. She and her sisters were all college graduates. Sylvia too had sophisticated tastes in the arts and expressed a keen desire for her children to excel academically.

But young David was not an academic star; indeed, he had great difficulty learning to read and exhibited several traits associated with dyslexia. Initially he focused his creative energy and self-esteem on the athletic and cultural activities that the Great Neck area provided him. He showed early athletic ability in basketball and baseball. In summer camp he was introduced to swimming, tennis, and sailing, activities that he pursued with skill and enthusiasm the rest of his life. Tennis fit in with his desire to excel in a quantifiable way, and he relished the competition with bigger and stronger players, many of whom he managed to beat through superior strategy and sheer determination.

Music was another area where his creativity could shine, and, led by an excellent teacher, he developed a great love for the piano, mastering both classical and jazz pieces and playing in a local dance band.

Despite poor grades in high school, he scored well enough on the College Board exams to be admitted in 1962 to Stevens Institute of Technology in Hoboken, New Jersey. His time at Stevens proved pivotal to his future development as a scientist. Inspired by excellent teachers in chemistry and physics, David became interested in fundamental questions in the physical sciences and began to work hard on his studies for the first time. Somewhat to his surprise, he discovered his latent talents and he excelled in chemistry, physics, and mathematics. Following the advice and encouragement of his physics teacher, Jack Fajans, he applied for admission to MIT and was accepted as a second-year student in the fall of 1963.

Undergraduate studies

At MIT, David was a chemistry major. He took almost enough physics to get a physics degree as well as a chemistry degree. He took a thermodynamics course taught by Professor Irwin Oppenheim. (The graduate teaching assistant in the course was Hans Andersen, one of the authors of this memoir.) For his senior thesis, David chose to work under the direction of Oppenheim. The research led to an award from the MIT chemistry department for the best undergraduate thesis in the department that year, as well as a publication in the *Journal of Chemical Education*.¹ In his senior year, he married Elaine Ackles, an MIT undergraduate student who went on to become an accomplished physicist in her own right, eventually serving as program manager in the Dynamics of Metals Program at Lawrence Livermore National Laboratory and then as Deputy Director of the HELIOS Solar Energy Research Center at Lawrence Berkeley National Laboratory.

David's marriage was more than a mere love connection. It was the launch of a life-long scientific collaboration. Elaine served as a scientific muse—daily they debated science and worked through strategies for approaching diverse scientific problems. Still finding reading and writing to be highly challenging at MIT, David credited Elaine with teaching him procedures for writing clear scientific papers that he used throughout his career, enabling him to publish prolifically.

Graduate work at Harvard

In 1966, David entered Harvard as a graduate student in the chemistry department. His adviser, Roy Gordon, gave him a great deal of freedom and independence. In his

3 -

graduate research, he collaborated with Hans Andersen, who at that time was a Junior Fellow at Harvard. The result of the work was the "mode expansion," a theory for the equilibrium properties of simple liquids and electrolyte solutions.² While David was at Harvard, Elaine finished her bachelor and master's degrees in physics and gave birth to their two daughters, Phoebe and Cynthia.

Postdoctoral research at UC San Diego

In September 1969, Chandler and several other new postdocs (including John Weeks, one of the authors of this memoir) joined the group of Kurt Shuler at the new campus of the University of California, San Diego. UC San Diego provided an exciting scientific environment in statistical and quantum physics, with distinguished faculty members like Joe Mayer, Bruno Zimm, and Walter Kohn readily available for discussions. Shuler gave his strong group lots of freedom in their choice of research topics. This suited Chandler especially well. He and John Weeks often went to meetings in the Mayer group and spent most of their time in increasingly animated discussions about theories for the structure and thermodynamics of dense atomic liquids at equilibrium. Indeed, such was the volume and duration of their discourse that the other postdocs successfully petitioned Shuler to move Chandler and Weeks from the shared postdoc space to a smaller and more soundproofed room far down the hall.

Thermodynamic perturbation theories of dense atomic liquids developed by Zwanzig, Barker, Henderson, and others, were based on a separation of the interatomic pair potential into two parts, u_0 and u_1 . The u_0 part was either a hard sphere potential or a continuous but highly repulsive short ranged potential, and this part is used to define a reference system. The free energy difference between the full LJ fluid and the reference system is expressed as an infinite series in powers of u_1/k_BT . The first order term ignores all effects of the u_1 tail on the fluid structure.

Chandler and Weeks tried to relate such theories to the simple physical picture used by Ben Widom to explain the success of the van der Waals equation for dense atomic liquids near the triple point.³ Hans Andersen had just joined the Chemistry faculty at Stanford and in several visits to UC San Diego, which initially focused on the mode expansion, he became an active participant in the discussions. Widom had argued that the many longer-range attractive forces exerted on an atom by the other atoms in a uniform simple liquid nearly cancel one another in typical configurations. The average particle arrangements (i.e., the liquid structure) should then primarily be determined by the harshly repulsive short ranged interactions in the potential.



Chandler, Weeks, and Andersen in a relaxed mood at the 1973 Gordon Conference on the Chemistry and Physics of Liquids, after a talk by Andersen discussing their theory. Chandler had a special affinity for the biannual Liquids conference and attended every meeting from 1967 until 2015 when illness prevented him. When combined with the general perturbation expansion, this suggests that especially accurate results for the total free energy for atomic liquids could be found from first order perturbation theory but *only* if the potential is separated in such a way that *the perturbation* u_1 *contains all and only the (nearly canceling) weak longer ranged forces*. All the rapidly varying repulsive core forces in the full potential are then generated by the u_0 component, and these forces primarily determine the structure of the liquid at high density.

Calculations by Weeks, Chandler, and Andersen (WCA)⁴ using this forcebased separation were indeed much more accurate than those from earlier approaches in which the chosen u₁ contained some strong short-ranged

forces as well as the longer ranged forces. The zeroth order radial distribution function that takes into account only the repulsive force reference potential u₀ was found to be remarkably accurate in representing the structure of the LJ liquid, as were the first order thermodynamic properties. The same insight proved useful in understanding many nonpolar molecular liquids that have similar forces.⁵

University of Illinois

Structure of Polyatomic Fluids: RISM and the PC Theory

In 1970, Chandler joined the Chemistry faculty at the University of Illinois at Urbana-Champaign. He and his students Lawrence Lowden and C. S. Hsu developed a novel theory for molecular correlation functions, describing the molecular shape as an arrangement of overlapping hard spheres representing molecular core regions. They generalized arguments that led to the accurate Percus-Yevick (PY) theory for pair correlation functions in hard sphere fluids⁶ and fluid mixtures to arrive at expressions for intermolecular site-site pair correlation functions for liquid nitrogen⁷ and acetonitrile.⁸ Their *reference interaction site model* (RISM) theory was technically difficult and required

additional approximations beyond those made by PY, but their results were physically plausible and usually gave good qualitative agreement with experiment and subsequent molecular simulations. RISM ideas gained wide acceptance for many molecular liquids. The extension of the RISM method to polymers was developed by Chandler's former student, Schweitzer, and Curro.⁹

But water, the most important liquid, presented a host of new and difficult challenges because of strong short-ranged attractive hydrogen bond interactions that play a key role in determining the network structure of the liquid. But Chandler was undaunted. In 1977, he and his student Lawrence Pratt¹⁰ developed a microscopic theory for the structural and thermodynamic properties of an infinitely dilute solution of hydrophobic solutes in water, focusing first on atomic solutes, and then extending those ideas to molecular solutes such as ethane and other n-alkanes.

A key physical idea in the PC theory was that correlations and fluctuations determined from the experimental water oxygen correlation function can give information about the energetics of cavity formation needed to describe the hydration of small solutes that repel water molecules, and that more general cavity distribution functions can describe solvation properties of apolar RISM-type molecular solutes. Initially, this idea was met with considerable skepticism because hydrogen bond correlations are only implicitly accounted for, but more recent work based on Gaussian fluctuation theory has confirmed and extended the validity of this basic insight.¹¹

Detailed predictions of the PC theory are mostly of historical interest now, since it is difficult to quantitatively assess errors introduced by the use of experimental data and RISM-based approximations. That said, it was conceptually very important—representing the first plausible microscopic theory to discuss both hydrophobic hydration and association. Many of the physical ideas PC introduced have played a key role in modern approaches using realistic molecular models of water and better approximations for solute-solvent and solute-solute correlations as will be discussed later.

Isomerization and Chemical Reaction Rates (1978–1980)

In 1978, Chandler published a paper¹² about unimolecular isomerization dynamics in liquids. This paper clarified and extended the classical statistical mechanical relationships between chemical reaction rate constants, which describe nonequilibrium behavior, and equilibrium time correlation functions. For unimolecular chemical reactions in a condensed phase whose kinetics can be described by a macroscopic first order rate law, this paper derived and justified a microscopic formula for the rate constant that expresses

it as the product of a transition state theory rate constant and a transmission coefficient. Moreover, this work clarified the meaning of transition state theory and the physical reasons for deviation of the actual rate constant from the predictions of transition state theory.

The evaluation of the rate constant using this approach focuses on a time correlation function that is called the "reactive flux." The algorithm for calculating this function requires molecular dynamics simulations that are constrained to start near the transition state for the chemical reaction and that extend forward in time only for times much smaller than the inverse of the rate constant. With Bruce Berne, John Montgomery, Stephen Holmgren, and Robert Rosenberg,¹³ Chandler performed the first calculations of first order chemical rate constants in condensed phases using the reaction flux method.



David and Elaine Chandler sailing on Squam Lake. Chandler loved the New Hampshire Lake area and water sports almost as much as water theory. He and his family spent most of their summers in New Hampshire, first in rental cottages, before they bought their own property near Squam Lake, complete with his sailboat "Fanny" above and a tennis court.

This work not only enabled the use of simulations to calculate chemical reaction rates but also clarified the theoretical understanding of how the chemical reaction of a molecule in a condensed phase can be influenced by the surrounding molecules. One decade later Chandler extended these results to situations in which the microscopic dynamics is quantum mechanical. Two decades later, he returned to the problem of chemical reaction dynamics and made yet another important advance, transition path sampling, which similarly had implications for computer simulations and theoretical understanding. These will be discussed below.

Quantum Processes in Liquids (1980-2000)

Nonperturbative approximations. In 1980, in an important paper published with Peter Wolynes,¹⁴ Chandler started an extended research program on quantum processes in liquids. The papers focused on an earlier observation of Richard Feynman that the



Chandler at Illinois discussing the calculation of quantum properties using discretized path integral methods.

equilibrium canonical partition function of a quantum mechanical system can be expressed in terms of Feynman path integrals, and if such a path integral is discretized, the result is equivalent to an equilibrium canonical partition function of a *classical* mechanical system with more degrees of freedom.¹⁵ Roughly speaking, the classical system has one ring polymer for each of the quantum mechanical atomic particles.

The new observation of Chandler and Wolynes was that analytic methods developed by Chandler and coworkers (see above) to calculate the structure of classical polyatomic fluids could be applied to the evaluation of discretized path integrals, thereby providing ways of generating nonperturbative approximations for the quantum properties of macroscopic systems. Chandler applied this approach to the theory of electronic polarization in liquids¹⁶ and the theory of excess electrons in liquids.¹⁷

Electron transfer in liquids. Chandler also used discretized path integral methods to perform classical Monte Carlo simulations of systems in which a single quantum mechanical electron interacts with a classical liquid. With Michiel Sprik and Michael Klein, he developed an algorithm that improved the efficiency of calculations of this type.¹⁸

In subsequent research, which also included Robert Kuharski, Joel Bader, and Roger Impey, they developed a realistic model for aqueous ferrous-ferric electron transfer in water that could be studied by discretized path integral Monte Carlo methods.¹⁹ In so doing, they extended classical statistical mechanical techniques into the study of electron transfer reactions in liquids. This simple, carefully constructed model had enough of the right physics built in so that two of the results calculated for this model were in remarkably good agreement with experiment.

As discussed in the original papers, this work is confirmation of the hypothesis that this ferrous-ferric electron transfer system is well described by a spin-boson model, in which a two-state system is linearly coupled to a harmonic bath. This model underlies the classic

Marcus theory of electron transfer,²⁰ and several of the predictions of Marcus theory were found to hold in this model. Rudy Marcus mentioned this in his Nobel Lecture.

Pennsylvania and Berkeley

In 1983, Chandler accepted a long-standing offer from the chemistry department at the University of Pennsylvania. While at Pennsylvania, Chandler took time to document his unique approaches to teaching and understanding statistical mechanics, resulting in his textbook, *Introduction to Modern Statistical Mechanics* (Oxford University Press, USA, 1987).

Chandler's approach to science and teaching was often unorthodox, reflecting the way learning disabilities impacted how he pictured and understood new ideas. He created detailed lecture notes, incorporating visual cues, to convey information both to himself and his students. He decided to make it his mission to create a textbook that could concisely and affordably offer his alternative view on science. His resulting "little green book" is appreciated by students and specialists alike for its novelty and pedagogy and is considered a must-read text in the field. The chapters on phase transitions, renormalization group, and non-equilibrium theory describe the central concepts clearly without recourse to advanced mathematics.

In 1986, Chandler moved to the chemistry department at the University of California, Berkeley, where he would, despite his professional success, wonder at events that allowed a child who was so vastly underestimated to grow to work alongside colleagues he considered the best scientists in the world. His insecurities and sheer determination to conquer his own learning challenges drove him to push himself, his students, his peers, and his family to constantly do better and take on increasingly challenging work. Rest was unimaginable in his work ethic; problems were best tackled from their most complex roots; no success was grand enough if questions still remained to be solved. Often viewed as irreverent by elders in his field, he courageously pushed the scientific community to embrace change quickly. At Berkeley, Chandler formed unfaltering loyalty to his most respected colleagues, whom he respected first and foremost for their dedication to scientific discovery.

In 1995, Chandler was elected to the National Academy of Sciences and the American Academy of Arts and Sciences. In 1996, he was diagnosed with advanced, aggressive prostate cancer like that which had caused his father to die at a young age. He underwent surgery and radiation treatment, which slowed the progress of the disease. In 1998, he

underwent surgery for heart disease, and in 2000, the cancer started to grow again. For the subsequent seventeen years, he endured treatments that sapped his energy and made it difficult to lead a normal life for extended periods of time. But characteristically, he was undeterred. Chandler viewed his time after diagnosis of cancer as providing him a second life, during which he carried out research that he regarded as his most significant, some of which is described below.

Ensembles of trajectories and transition path sampling (1998–2013)

Between 1998 and 2002, Chandler and several students and coworkers²¹ constructed a nontrivial and useful generalization of the basic statistical mechanical idea of an equilibrium ensemble. The work was motivated by the desire to formulate a theoretical description of nonequilibrium experiments in which chemical reactions and structural rearrangements take place in a material system. During such an experiment, the phase point of an experimental system moves along an unknown trajectory in phase space. The set of all possible trajectories can be regarded as a "trajectory space." It is then useful to consider the trajectory for a material system as a random variable and to construct probability distributions of trajectories in this trajectory space. The result is an "ensemble of trajectories."

The Chandler group showed how to define and make reasonable postulates about the probability distribution of trajectories in trajectory space that correspond to particular chemical or structural reactions. Moreover, they developed practical algorithms for sampling trajectories from such distributions using generalizations of the Monte Carlo methods commonly used to sample from a canonical probability distribution of mechanical states in configuration space. These methods are referred to as "transition path sampling." An important feature of this formalism is that the transition state (or states) for a reaction need not be characterized in advance in order to calculate the rate constant of the reaction. Moreover, the trajectories that are required to calculate the rate constant can be much shorter than the macroscopic chemical relaxation time for the reaction. Transition path sampling has been applied to calculate the rates of many kinetic processes.²²

Dynamic facilitation theory and the glass transition (2002–2016)

Many liquid substances, if cooled well below their freezing point, will become noncrystalline solids (glasses) in a phenomenon called the glass transition. As a liquid is cooled toward this transition and then through it, its viscosity becomes larger, deviating from the usual Stokes-Einstein relation, and structural relaxation of the liquid become much

slower, typically by more than 10 orders of magnitude. The structural relaxation also exhibits dynamic heterogeneity in which molecules in some regions of the liquid change their positions much faster than in other regions a few nanometers away. There appear to be two different modes of structural relaxation in glass-forming liquids, leading to the categorization of some liquids as "strong" glass formers and some as "fragile" glass formers. Several theories of the glass transition have been proposed, but there is no general consensus about which of these theories are correct and which provides the most useful way of understanding the phenomenon.

In 2002, Chandler and Juan Garrahan began a research program that led to what has been called the dynamical facilitation theory of the glass transition. The basic idea of the theory is that at very low temperatures, the relaxation of a supercooled liquid toward equilibrium consists of local structural changes that are facilitated by local positive fluctuations in the energy density. They demonstrated that certain members of a class of simple kinetic lattice models,²³ now called kinetically constrained models (KCMs), exhibit the same behaviors as those exhibited by supercooled liquids (as described above) Their work started with the study of such KCMs.^{24, 25, 26} For models of fragile glass formers, they derived a corresponding states principle that well describes experimental data for 58 glass-forming liquids.²⁷

A collaboration of Chandler and Garrahan with Aaron Keys, Lester Hedges, and Sharon Glotzer,²⁸ studied the behavior of molecular dynamics models of five different two-component atomic liquids at supercooled temperatures. They identified excitations in these liquids that played the same role as the structural excitations that facilitate relaxation in the KCMs. The overall similarity of the dynamics in the lattice models and the atomic liquids was striking, and the temperature-dependent structural relaxation times for the atomic liquids agreed well with the corresponding states principle mentioned above. These and other results suggest that the dynamic facilitation theory, or an extension of it, has the possibility of becoming the long-sought basis for understanding the glass transition.

Length scale dependence of hydrophobic interactions and hydrophobic assembly (1998–2015)

A major limitation of the Pratt-Chandler theory of hydrophobicity arose from its use of the experimental oxygen-oxygen correlation function in liquid water to estimate the probability of forming larger cavities that could accommodate the repulsive cores of solutes. While appropriate for the small noble gas solutes originally considered by PC,

11 –

this picture of small Gaussian fluctuations must fail for sufficiently large solutes or near a hard wall. In such situations, hydrogen bonds involving water molecules near the solute must be broken.

The Weeks group in the mid-1990s had begun development of a systematic approach called Local Molecular Field (LMF) theory that accurately accounted for the effects of unbalanced attractive forces on the structure of a LJ fluid near repulsive core solutes of varying size.²⁹ Chandler and his student Ka Lum realized that similar ideas might apply to hydrophobic solvation in water, and Chandler set up a sabbatical visit by Weeks to



Chandler in his Berkeley office discussing aspects of hydrophobic solvation.

Berkeley in the autumn of 1998. Lum, Chandler, and Weeks (LCW) developed an LMF-based mean field theory that predicted a transition in the interface structure of water around hydrophobic solutes as a function of the solute core size.³⁰ Bulk-like hydrogen bonds with reduced fluctuations can be maintained around small solutes, but some hydrogen bonds must be broken around a large solute, leading to the formation of a fluctuating interface, whose position depends sensitively on the attractive force balance. The semi-empirical LCW theory used the liquid-vapor surface tension of water as input and predicted that the crossover occurs for core sizes on a nanometer length scale. The solvation free energy naturally scales linearly with solute volume for smaller solutes but is predicted to scale linearly with solute area after interface formation.

Large primarily hydrophobic regions with a high concentration of small apolar units can also arise from conformational changes in biopolymers and can similarly induce local interface formation. LCW argued that this process could play a key role in generating the large driving forces needed to stabilize protein assemblies and protein folding. Chandler and coworkers developed this idea much further in later work,³¹ and he viewed this connection between hydrophobic interactions, interface formation on larger length scales, and hydrophobic assembly as one of his most important research accomplishments.

Impact on future generations

Chandler had a deep and broad impact on younger generations of scientists. This impact extends far beyond his former students and postdocs, many of whom hold positions at outstanding institutions throughout the world.

One illustration of Chandler's impact on younger scientists is provided by his influence during the development of the Crooks Fluctuation Theorems³² and their precursor, the Jarzynski Equality.³³ This development, one of the most important advances in nonequilibrium theory in nearly a century, took place in the late 1990s, at the same time Chandler and his students were creating transition path sampling (TPS) as discussed above. There are historical and intellectual links between these developments.

Prior to the publication of his now-famous equality, Chris Jarzynski and Chandler corresponded about Jarzynski's new result. Chandler was skeptical but found the correspondence intriguing, enough so that he invited Jarzynski to give a Chandler-group seminar at Berkeley. Those seminars were famously interactive, with much give and take between the speakers and the audience. Jarzynski's presentation at that forum went over very well, though Chandler remained concerned that this new equality described special cases only and could not be generalized.

In the aftermath, one of Chandler's students, Gavin Crooks, began studying the preprint that Jarzynski left behind. As a member of the Chandler group during that time, Crooks had been extensively exposed to the idea of trajectories as fundamental objects, and that exposure, as Crooks recently reminded one of us,³⁴ was the key to his thinking about Jarzynski's result in terms of the relative probabilities of forward and reverse trajectories. That thinking led Crooks to what is now known as the Crooks Fluctuation Theorem. The Jarzynski Equality is a corollary to the theorem. These two results are deep and significant consequences of classical statistical mechanics that apply far from equilibrium on microscopic time and length scales. On seeing Crooks' work, Chandler understood his prior concerns were completely resolved; moreover, he was witnessing a fundamental advance in science. But unlike many senior scientists, he encouraged his protégé to publish his theorem on his own. It was also Chandler who introduced his Berkeley colleague, Carlos Bustamante, to these ideas, resulting in experimental tests³⁵ and uses of the Jarzynski Equality and the Crooks Fluctuation Theorem. This history illustrates Chandler's generous, motivational, and behind-the-scenes activities furthering science and the professional reputations of worthy young scientists.

The second illustration is developments in immunology made over the past two decades by one of us (AKC). As is well known and noted above, Chandler's scientific work has been characterized by a combination of computer simulations and deep analytical theory, the latter necessary for rigor and often key to what makes the simulations possible and meaningful. Furthermore, typically, Chandler's insights have sparked new experiments. AKC's studies in immunology and virology using statistical mechanical approaches, and its impact on experimental and clinical investigations could not have happened without adopting Chandler's style of research. He learned this style by watching Chandler work and teach when he was a junior faculty member at Berkeley. Chandler made this sort of impact on many younger scientists. At a 2014 symposium at MIT in honor of his seventieth birthday, nearly every one of the twenty-four speakers reiterated that their emulation of Chandler's style was a key to their success.

In 2000, Chandler started a series of meetings focused on statistical mechanics that take place every January in Berkeley. These so called "Mini Stat Mech" meetings continue today as one of the key gatherings of scientists in the field.

Finally, no testament to Chandler's impact on younger scientists can be complete without mentioning his impact on his daughters, Phoebe and Cynthia. Chandler provided his children with much inspiration to believe that, like him, they could accomplish anything they set their minds to do, as long as they were brave, competitive, and determined. They joke that he provided them much freedom to dream up unorthodox careers, following their passions, as long as they were "the best" at whatever they did. Phoebe went on to become a middle school math and science teacher before transitioning to becoming an automotive technician and shop owner of an all-female, green garage. Cynthia followed Chandler's tradition of irreverence and challenging institutionalized modes of thinking by becoming a civil and human rights activist attorney, challenging the human cost of mass imprisonment. They both cherish his influence.

In 2017, Chandler died of prostate cancer in his home after a short period of hospice care. He lived his life with passion and intensity. Science was a major passion. His family and his friendships were extremely important to him, and he was devoted to both. His tennis was very competitive and not merely recreational. He fought prostate cancer for two decades with his intelligence and his determination, while making very significant contributions to the field of statistical mechanics.

His one regret was not finishing papers and research he had started. His confidence in the talents of his students and colleagues allowed him peace, knowing his work would be completed and improved upon.

Chandler's intensity, brilliance, and courage will be missed. His friends, students, and co-workers have endowed an annual "Chandler Lecture" at Berkeley to celebrate his memory.

ACKNOWLEDGMENTS

We are grateful to the Chandler family, Phillip Geissler, Juan Garrahan, and Gavin Crooks for their comments, insights and assistance in writing this memoir.

NOTES

- 1. Chandler, D., and I. Oppenheim. 1966. Some comments on the third and second laws of thermodynamics. *Journal of Chemical Education* 43:525–533.
- Andersen, H. C., and D. Chandler. 1970. Mode Expansion in Equilibrium Statistical Mechanics. I. General Theory and Application to the Classical Electron Gas. *J. Chem. Phys.* 53:547–554; Chandler, D., and H. C. Andersen. 1971. Mode Expansion in Equilibrium Statistical Mechanics. II. A Rapidly Convergent Theory of Ionic Solutions. *J. Chem. Phys.* 54:26–33.
- 3. Widom, B. 1967. Intermolecular forces and the nature of the liquid state. *Science* 157:375–382.
- 4. Weeks, J. D., D. Chandler, and H. C. Andersen. 1971. Role of repulsive forces in determining the equilibrium structure of simple liquids. *J. Chem. Phys.* 54:5237–5247.
- Chandler, D., J. D. Weeks, and H. C. Andersen. 1983. Van der Waals picture of liquids, solids, and phase transformations. *Science* 220:787–794.
- 6. Stell, G. 1963. The Percus–Yevick equation for the radial distribution function of a fluid. *Physica* 29:517–354.
- 7. Lowden L. J., and D. Chandler. 1973. Solution of a new integral equation for pair correlation functions in molecular liquids. *J. Chem. Phys.* 59:6587–6595.
- Hsu, C., and D. Chandler. 1978. RISM calculation of the structure of liquid acetonitrile. *Mol. Phys.* 36:215–224.
- 9. Schweizer, K., and J. Curro. 1987. Integral–equation theory of the structure of polymer melts. *Phys. Rev. Lett.* 58:246–249.
- 10. Pratt, L. R., and D. Chandler. 1977. Theory of the hydrophobic effect. J. Chem. Phys. 67:3683–3704.
- 11. Hummer, G., S. Garde, A. Garcia, A. Pohorille, and L. Pratt. 1996. An information theory model of hydrophobic interactions. *Proc. Natl. Acad. Sci. USA*. 93:8951–8955.
- 12. Chandler, D. 1978. Statistical mechanics of isomerization dynamics in liquids and the transition state approximation. *J. Chem. Phys.* 68:2959–2970.
- Montgomery, J. A., S. L. Holmgren, and D. Chandler. 1980. Stochastic molecular dynamics study of trans gauche isomerization processes in simple chain molecules. *J. Chem. Phys.* 73:3688–3694; Rosenberg, R. O., Berne, B. J., and D. Chandler. 1980. Isomerization dynamics in liquids by molecular dynamics. *Chem. Phys. Lett.* 75:162–168.

- 14. Chandler, D., and P. G. Wolynes. 1981. Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids. *J. Chem. Phys.* 74:4078–4095.
- 15. Feynman, R. P. and A. R. Hibbs. 1965. *Quantum Mechanics and Path Integrals*. New York: McGraw–Hill.
- Thompson, M. J., K. S. Schweizer, and D. Chandler. 1982. Quantum theory of polarization in liquids: Exact solution of the mean spherical and related approximations. *J. Chem. Phys.* 76:1128–1135; Chandler, D. 1984. Quantum theory of solvation. *J. Phys. Chem.* 88:3400–3407.
- 17. Chandler, D., Y. Singh, and D. M. Richardson. 1984. Excess electrons in simple fluids. I. General equilibrium theory for classical hard sphere solvents. *J. Chem. Phys.* 81:1975–1982 and later work.
- Sprik, M., M. L. Klein, and D. Chandler. 1985. Staging: A sampling technique for the Monte Carlo evaluation of path integrals. *Phys. Rev. B* 31:4234–4244.
- Kuharski, R. A., J. S. Bader, Chandler, D., Sprik, M., Klein, M. L., and R. W. Impey. 1988. Molecular model for aqueous Ferrous–Ferric electron transfer. J. Chem. Phys. 89:3248–3257.
- Marcus, R. A. 1964. Chemical and electrochemical electron-transfer theory. *Annual Review of Physical Chemistry* 15:155–196.
- 21. These included P. G. Bolhuis, G. Crooks, F. Csajka, C. Dellago, and P. L. Geissler.
- Bolhuis, P. G., D. Chandler, C. Dellago, and P. L. Geissler. 2002. Transition Path Sampling: Throwing Ropes Over Rough Mountain Passes in the Dark. *Annual Review of Physical Chemistry* 53:291–318.
- Fredrickson, G. H., and H. C. Andersen. 1985. Facilitated kinetic Ising models and the glass transition. J. Chem. Phys. 83:5822–5831.
- Garrahan, J. P., and D. Chandler, 2003. Coarse grained microscopic model for glass formers, *Proc. Natl Acad. Sci. U.S.A.* 100:9710–9714.
- 25. Garrahan, J. P., and D. Chandler. 2002. Geometrical explanation and scaling of dynamical heterogeneities in glass forming systems. *Phys. Rev. Lett.* 89:035704.
- Jung, Y., J. P. Garrahan, and D. Chandler. 2003. Excitation lines and the breakdown of Stokes–Einstein relations in super–cooled liquids. *Phys. Rev. E* 69:061205.
- 27. Elmatad, Y. S., D. Chandler, and J. P. Garrahan. 2009. Corresponding States of Structural Glass Formers. *J. Phys. Chem. B* 113:5563–5567.
- Keys, A. S., L. O. Hedges, J. P. Garrahan, S. C. Glotzer, and D. Chandler. 2011. Excitations are localized and relaxation is hierarchical in glass–forming liquids. *Phys. Rev. X* 1:021013–021015.

- Weeks, J. D., K. Katsov, and K. Vollmayr. 1998. Roles of repulsive and attractive forces in determining the structure of nonuniform liquids: generalized mean field theory. *Phys. Rev. Lett.* 81:4400–4403.
- 30. Lum, K., D. Chandler, and J. D. Weeks. 1999. Hydrophobicity at small and large length scales. *J. Phys. Chem. B* 103:4570–4577.
- 31. Chandler, D. 2005. Interfaces and the driving force of hydrophobic assembly. *Nature* 437:640–647.
- 32. Crooks, G. E. 1999. Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences. *Phys. Rev. E* 60:2721–2726.
- Jarzynski, C. 1997. Nonequilibrium equality for free energy differences. *Phys. Rev. Lett.* 78:2690–2693.
- 34. Gavin Crooks, private communication to AKC.
- Collin, D., F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco, Jr., and C. Bustamante. 2005. Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies. *Nature* 437:231–234.

SELECTED BIBLIOGRAPHY

- 1970 With H. C. Andersen. Mode expansion in equilibrium statistical mechanics. I. general theory and application to the classical electron gas. J. Chem. Phys. 53:547–554.
- 1971 With J. D. Weeks and H. C. Andersen. Role of repulsive forces in determining the equilibrium structure of simple liquids. *J. Chem. Phys.* 54:5237–5247.
- 1972 With H. C. Andersen. Optimized cluster expansions for classical fluids. II. Theory of molecular liquids. J. Chem. Phys. 57:1930–1937.
- 1976 With C. S. Hsu and L. J. Lowden. Applications of the RISM equation to diatomic fluids: the liquids nitrogen, oxygen and bromine. *Chemical Physics* 14:213–228.
- 1977 With L. R. Pratt. Theory of the hydrophobic effect. J. Chem. Phys. 67:3683–3704.
- 1978 Statistical mechanics of isomerization dynamics in liquids and the transition state approximation. J. Chem. Phys. 68:2959–2970.
- 1980 With R. O. Rosenberg and B. J. Berne. Isomerization dynamics in liquids by molecular dynamics. *Chem. Phys. Lett.* 75:162–168.
- 1981 With P. G. Wolynes. Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids. *J. Chem. Phys.* 74:4078–4095.
- 1983 With J. D. Weeks and H. C. Andersen. Van der Waals picture of liquids, solids, and phase transformations. *Science* 220:787–794.
- 1985 With M. Sprik and M. L. Klein. Staging: A sampling technique for the Monte Carlo evaluation of path integrals. *Phys. Rev. B* 31:4234–4244.
- 1988 With R. A. Kuharski, J. S. Bader, M. Sprik, M. L. Klein, and R. W. Impey. Molecular model for aqueous Ferrous-Ferric electron transfer. *J. Chem. Phys.* 89:3248–3257.
- 1989 With G. A. Voth and W. H. Miller. Rigorous formulation of quantum transition-state theory and its dynamical corrections. *J. Chem. Phys.* 91:7749–7760.
- 1993 Gaussian field model of fluids with an application to polymeric fluids. *Phys. Rev. E* 8:2898–2905.
- 1998 With C. Dellago, P. Bolhuis, and F. Csajka. Transition path sampling and the calculation of rate constants. *J. Chem. Phys.* 108:1964–1977.

19 —

- 1999 With K. Lum and J. D. Weeks. Hydrophobicity at small and large length scales. *J. Phys. Chem. B* 103:4570–4577.
- 2001 With P. L. Geissler, C. Dellago, J. Hutter and M. Parrinello. Autoionization in liquid water. *Science* 291:2121–2124.
- 2002 With P. G. Bolhuis, C. Dellago and P. L. Geissler. Transition path sampling: Throwing ropes over rough mountain passes, in the dark. *Annual Review of Physical Chemistry* 53:291–318.
- 2002 With J. P. Garrahan. Geometrical explanation and scaling of dynamical heterogeneities in glass forming systems. *Phys. Rev. Lett.* 89:035704.
- 2003 With J. P. Garrahan. Coarse grained microscopic model for glass formers. Proc. Natl.Acad. Sci. U.S.A. 100:9710–9714.
- 2005 Interfaces and the driving force of hydrophobic assembly. Nature 437:640-647.
- 2006 With M. F. Hagan. Dynamic pathways for viral capsid assembly. *Biophysical J.* 91:42–54.
- 2010 With A. P. Willard. Instantaneous Liquid Interfaces. J. Phys. Chem. B 114:1954–1958.
- 2011 With A. S. Keys, L. O. Hedges, J. P. Garrahan, and S. C. Glotzer. Excitations are localized and relaxation is hierarchical in glass-forming liquids. *Phys. Rev. X* 1:021013.
- 2014 With D. T. Limmer. Theory of amorphous ices. *Proc. Natl. Acad. Sci. U.S.A.* 111:9413-9418.
- 2016 With S. Katira, K. K. Mandadapu, S. Vaikuntanathan, and B. Smit. Pre-transition effects mediate forces of assembly between transmembrane proteins. *eLife* 5:e13150.

Published since 1877, *Biographical Memoirs* are brief biographies of deceased National Academy of Sciences members, written by those who knew them or their work. These biographies provide personal and scholarly views of America's most distinguished researchers and a biographical history of U.S. science. *Biographical Memoirs* are freely available online at www.nasonline.org/memoirs.