

## Virtual Issue in Memory of David Chandler

We mourn the loss of David Chandler, who passed away on April 18, 2017. Early in his career David established himself as a standard-bearer of statistical mechanics, demonstrating over and over again its power to reveal the essential workings of complex molecular systems. His extensive accomplishments in applying its principles, advancing its physical underpinnings, and innovating methods of analysis and computer simulation address a range of molecular phenomena that mark the modern frontiers of physical chemistry—from the glass transition to biomolecular assembly, from electron transfer in solution to the hydrophobic effect, from the microscopic dynamics of acid–base chemistry to the collective dynamics of water at electrodes. David's work invigorated research in these diverse areas, injecting many key ideas and techniques, and held it to exacting standards that were both treasured and feared.

The magnitude of David's scientific achievements is clear from the influence of his research—papers cited thousands of times (some of which appeared in *J. Phys. Chem.* and are referenced below) decade after decade—evidence of the creativity, longevity, and impact of his work. These achievements were of course recognized by his peers. David, among his many accolades, was both a member of the National Academy of Sciences and a Foreign Member of the Royal Society. Such objective measures surely indicate David's significance and distinction, but they do not alone paint an accurate portrait of a man whose life was inseparable from his science.

Early in his life David was perceived as having no talent for academics. He was keen on music (an accomplished pianist) and excelled in sport, playing tennis at a very high standard. Only during his first year at university did he find the calling of science, subsequently excelling in both chemistry and physics.

As an undergraduate David met Hans Andersen, and as a postdoc, John Weeks. Together they produced WCA theory, which soon became the standard theory of the liquid state. Beyond the enormous success of this early work, the bond that formed between them stands out, of which David remarked in his 2005 autobiography (*J. Phys. Chem. B* **2005**, *109*, 6459–6464): “The ties I made [with them] 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.” This quote highlights how David saw science and humanity intertwined, and the way in which he cultivated the ties of friendship with his close collaborators. Conversely, bonds of friendship and family nourished David's scientific life. Most notably, his wife Elaine served throughout his career as a critical collaborator and consultant, pushing him to communicate clearly, to reason carefully, and to employ the most sophisticated mathematical and computational tools available. His reputation as an unrivaled expert in these very skills testifies to the depth of Elaine's influence.

A constant in David's work was the search for connections between problems in diverse areas of science and the use of statistical mechanics as the conceptual and methodological framework with which to address them. This synthetic

approach is a signature of the school of thought he built at Berkeley, whose basic perspective is articulated in his “little green book”, *Introduction to Modern Statistical Mechanics*. This academic best seller became the standard introductory text in statistical mechanics for a generation of physical scientists. By all accounts, David was an outstanding teacher, both in writing and in front of a class.

A second notable effort toward creating a community of thought was establishing the *Berkeley Mini StatMech Meeting*. These yearly meetings are unique in style, covering broad topics in chemistry, physics, biology, and beyond, with statistical mechanics as a common theme. They aim to bring down the barriers between disciplines, and have been instrumental in fostering a sense of common purpose among those who adhere to the way David thought about science.

Adding to his legacy is the number of David's trainees who now occupy faculty positions across the world. David, for the authors of this piece, was in turn a mentor, a colleague, and a close friend. We are part of a large group of scientists who have been profoundly influenced by our interactions with him, an international group that includes many scientists of distinction, and many who are on their way to being so. We believe we speak on behalf of them all in expressing our debt of gratitude to David for the impact he had in our lives both as a scientist and as a friend.

The papers in this [Virtual Issue](#) exemplify David's accomplishments in a few of the primary areas of his scholarship. The thrust of these efforts is summarized below. Implicit in our summaries are important contributions from David's co-workers, invariably enabled by his unique and dedicated mentorship.

### ■ HYDROPHOBICITY

David's early work with John Weeks and Hans Andersen established a basic understanding of microscopic structure in the liquid state that has guided decades of research in the field. Their theory delineated quantitatively the roles of excluded volume and slowly varying attractions in simple liquids like argon, modernizing the classic picture put forth by van der Waals and setting the stage for explorations of structure and thermodynamics in more complicated systems of broader interest, such as liquid water. Developing a comparably powerful theory for the hydrophobic effect was a career-long goal for David, one that he ultimately achieved by synthesizing methods and concepts from the statistical mechanics of linear response and phase equilibrium. His landmark *J. Phys. Chem.* paper with Lum and Weeks<sup>1</sup> provides the framework of this LCW theory, emphasizing distinct mechanisms of hydrophobe solvation on small (a few Å) and large (>1 nm) length scales. Papers 2–7 elaborate its implications for solvation scenarios that involve hydrophobes ranging from small methane-like molecules to extended hydrophobic surfaces and phase boundaries.

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The hydrophobic entities of greatest modern interest are constituents of biological molecules, e.g., nonpolar amino acid side-chains and phospholipids' greasy tail groups. Their typical size lies precisely at the crossover length scale identified by LCW theory. Implications for biomolecular solubility, structure, and assembly are profound and far-reaching.<sup>8–11</sup>

## ■ RARE EVENTS

The low rates of chemical reactions, relative to frequencies of basic molecular motion, drew David's interest throughout his career. In very small systems this slowness arises transparently from the topography of potential energy surfaces. Indeed, the conventional chemist's perspective on kinetics focuses narrowly on saddle points of such surfaces. Complex systems of modern interest, however, navigate diverse pathways from reactants to products, and their dynamical bottlenecks occur in a high-dimensional phase space that cannot be directly visualized or exhaustively surveyed. David's key recognition is that slowness in this case is best understood as a feature not of standard configurational ensembles, but instead of ensembles comprising trajectories. The separation of time scales intrinsic to barrier crossing begets a *rareness* in this trajectory space—from the distribution of short equilibrium trajectories, only a tiny fraction exhibit reactivity. From this perspective he invented methods for sampling and quantifying reactive dynamics that revolutionized theoretical work on chemical kinetics.

David's first key contribution to the study of such rare but important events was to formulate an efficient and exact numerical method for determining corrections to traditional transition state theory. Leveraging time scale separation, this "reactive flux" procedure requires only the propagation of very short trajectories from a transition state in order to quantify effects of transient barrier recrossing.<sup>12,13</sup> While powerful and widely employed, this approach rests upon foreknowledge of the transition state, a knowledge that is often the most challenging and interesting target of kinetic studies. Overcoming the reliance on *a priori* mechanistic understanding required invention of a new theoretical and computational framework for the statistical dynamics of barrier crossing. The resulting method of transition path sampling (TPS) opened doors to studying kinetic processes that were previously approachable only through dangerously uncontrolled approximations. As an important milestone, paper 14 presented the first application of TPS to chemical dynamics in the liquid state. Papers 15 and 16 illustrate its great versatility, elucidating complex and collective dynamical mechanisms of phase change.

## ■ ELECTRON TRANSFER

David's interests in solvation and rare events intersected in a series of contributions to electron transfer theory that illuminated the molecular details underpinning successful phenomenological treatments. This area clearly demonstrated David's ability to see connections between seemingly disparate theoretical works and translate those connections into deep physical insight. In particular, this work established two principles that continue to guide researchers' perspectives on the topic. The first was that quantum theory of solvation is isomorphic with the classical theory of solvation with additional fluctuating degrees of freedom.<sup>17</sup> While this perspective has its roots in Feynman's path integral formulation of quantum mechanics, David shaped it into an elegant and practical way to solve otherwise intractable computational challenges. This

quantum–classical isomorphism allowed one to use the full arsenal of classical statistical mechanics to study solvated electrons and their motions.<sup>18–20</sup> The second principle was that fluctuations within the liquid state, as the sum of many weakly correlated components, ought to be Gaussian distributed. This principle simultaneously informed the theory of dielectrics and the theory of the hydrophobic effect, and, when it broke down, signaled the emergence of collective phenomena. Gaussian fluctuations are a built-in assumption to Marcus' theory of electron transfer, one whose reliability David was able to discern and expand upon with Marcus for simple solvents.<sup>21</sup> With others David later illustrated the consequences of collective fluctuations at extended interfaces for similar electrochemical processes.<sup>22,23</sup>

## ■ GLASS TRANSITION

It would have seemed natural, after elucidating the behavior of simple liquids, for David to focus on the glass transition—the generic slowing down and dynamical arrest observed in liquids supercooled below their melting temperature—but it was only three decades after WCA that he turned his attention to this area. In the early 2000s the dominant theoretical perspectives were based on sophisticated mean-field approximations, but novel local probe experiments (and computer simulations) had revealed that relaxation in glass formers displayed strong spatial fluctuations, a phenomenon termed dynamical heterogeneity. This indicated that glassy dynamics was fluctuation dominated in a manner that could not be anticipated from thermodynamic considerations alone. The first step was to realize that this behavior could be explained due to the presence of effective constraints in the dynamics—as captured by models first conceived in the 1980s by Hans Andersen and co-workers. This in turn allowed the development of what is known as the *dynamic facilitation* (DF) theory of the glass transition. The key insight is that the complexity in glassy systems lies in the statistics of the trajectories of the dynamics—rather than in their static structure—echoing a theme from his work on rare events.

Of this body of work, two significant papers appeared in *J. Phys. Chem. B*. A prediction of the DF approach is that the characteristic super-Arrhenius growth of the relaxation time or the viscosity of supercooled liquids goes as the exponential of a parabola of the inverse temperature. This "parabolic law" contrasts with the traditional Vogel–Fulcher–Tamman law in that there is no finite temperature (and unobservable) singularity. Paper 23 confirmed the validity of the parabolic law by showing it can account in a universal manner for all the available experimental data (paper 24 did the same for existing numerical simulations), convincingly demonstrating the applicability of DF theory.

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## Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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