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Tribute to Lawrence R. Pratt

I first met Lawrence Pratt my first year of graduate school at the University of Delaware. My advisor, Mike Paulaitis, had used Lawrence's work on the hydrophobic effect as a primer for the work my group mate, Shekhar Garde, and I would work on over our Ph.Ds. Mike invited Lawrence to give a departmental seminar that spring, and afterwards he met with our group to discuss his broad range of scientific interests. I felt like I was drinking from a fire hydrant trying to take in the conversation that went on for many hours. A takeaway I had from that meeting concerned Lawrence's exciting work with Andrew Pohorille using scaled particle theory to discriminate between nonpolar solute solvation in aqueous and organic solvents. Those ideas followed me throughout my graduate studies, and for years I played around with advancing the theory from microscopic to macroscopic nonpolar surfaces. Following my postdoc with Lawrence at Los Alamos, this questioning ultimately resulted in a paper in Reviews of Modern Physics in 2006 on the applications of scaled particle theory to describe hydrophobic hydration. I am forever thankful that Lawrence inspired me to pursue this research, and I take great pleasure honoring him by helping organize this special issue celebrating his career.

Henry S. Ashbaugh

My initial introduction to Lawrence Pratt was through his research papers on ion hydration. Through Hank Ashbaugh and Shekhar Garde I found the opportunity to pursue my postdoctoral studies with Lawrence. My earliest memories of my postdoc were coming to work and finding his review with Mike Paulaitis on my desk: thus began my studies on the quasi chemical organization of the potential distribution theorem. I fondly remember the many lunch meetings with Lawrence, Hank, and our Los Alamos colleagues when many of our new ideas were fleshed out. Lawrence almost always left his office door ajar, signaling he was always on hand to discuss ideas, and although we are now in different places, he has always remained available to engage in discussions and share his perspectives. As a mentor, Lawrence always used a light touch, which was crucial in helping us grow scientifically and develop our ideas. In working with my own students, I have followed his lead in encouraging students to be a bit "actively irresponsible." Thank you Lawrence for being a wonderful mentor and colleague!

Dilipkumar Asthagiri

During the latter stages of my graduate student work at the University of Chicago, I applied for several postdoctoral positions, one of which was at Los Alamos with Jimmie Doll. I met Lawrence during my interview there, on a day when the lab was "shut down" due to a major snowstorm. It was the best decision of my career to choose the postdoc with Jimmie, which also led to many interactions with Lawrence. There began my initiation into the deeper world of path integrals and statistical mechanics. Many of the discussions occurred during long lunches at various locations in Los Alamos. I had the great fortune to learn first-hand, on a daily basis, from Doll and Pratt. Several years later, after settling into my position at Cincinnati, I wrote up some notes on deriving the traditional solution phase activity coefficients in physical chemistry texts from the Widom potential distribution theorem. I emailed Lawrence and said, "do you think this might be of interest for a Journal of Chemical Education article?" He replied, "maybe we should set our sights higher." This inquiry ultimately culminated in our book with Mike Paulaitis: The Potential Distribution Theorem and Models of Molecular Solutions. Thank you Lawrence for setting the bar so high for so long!

Thomas L. Beck

I was lucky to join Lawrence's Los Alamos group as a postdoc just after he articulated quasi-chemical theory. Thus, I was among the first to explore the meanings of the terms and how to evaluate them. Our first overview, ultimately my statistical mechanics bible, appeared in the proceedings of a conference organized by Lawrence and Gerhard Hummer. I remember our excitement as we discovered something new about the theory and hydration of each ion. (See our recent review in Annual Reviews of Physical Chemistry.) Lawrence imparted memorable wisdom during my postdoc. Fresh from thesis studies made extra challenging by four small children, I was glad to learn that a successful

scientific career can go hand-in-hand with "a life." For Lawrence, that meant discussing mathematical ideas with his daughter Jane, who now teaches at Georgia State. Lawrence emphasized generosity in authorship and citation as every person and publication may influence your thinking. Our initial paper on lithium ion hydration, with Gerhard, Joel Kress, Rich Martin, and Tony Redondo, illustrates that policy in action as I had visited with nearly everyone in our department during those studies. Lawrence also stressed that words matter, something I already believed, owing to undergraduate studies at Columbia. Still, there are principles and applications. Whereas, in extending the theory to proteins, I was inclined to phrases like "phase-activated" and "quasi-liquid," requiring 15-minute explanations, Lawrence crystallized how we set the boundaries between inner and outer solvation environments in three words: "no split shell." Thank you, Lawrence, for all the wisdom and for the great pleasure of working with you.

Susan B. Rempe

Lawrence Pratt's career following completion of his Ph.D. at the University of Illinois Urbana Champaign has taken him from Harvard University, to the University of California, Berkeley, and Los Alamos National Laboratory. Most recently, he joined the faculty of the Department of Chemical and Biomolecular Engineering at Tulane University in 2008. Over his career Lawrence has been a leader in theoretical physical chemistry, making influential contributions to a number of areas including the theory of the hydrophobic effect, the development of transition path sampling, contributions to orbital free density functional theory, and the theory of liquids and solutions. Below we highlight some of Lawrence's major contributions, although this discussion is an incomplete account of his wide ranging research interests.

Lawrence is probably best known for his contributions to our understanding of the hydrophobic effect. As Lawrence would summarize his rationale for studying this phenomena: Many of the molecules of life are held together by the insolubility of nonpolar groups in water; so if we want to understand life we better understand the hydrophobic effect. Lawrence's initiation into this field of research was his paper with his advisor David Chandler "Theory of the Hydrophobic Effect" appearing in the *Journal of Chemical Physics* in 1977. Pratt/Chandler theory was one of the first theories to incorporate the then recently acquired scattering structures of liquid water, obtained by Narten and Levy, into an integral equation description of nonpolar species hydration. Prior to this, most theories of the hydrophobic effect invoked *ad hoc* accountings of hydrogen bonding, enhanced water structuring, and/or empirical parameterizations in their theoretical development; although Frank Stillinger's contributions are a notable exception. Beyond the poor solubility of hydrophobic species in water, Pratt/Chandler theory made explicit predictions of the water mediated forces between nonpolar groups which drive self-assembly processes. These theoretical predictions, in turn, spurred numerous molecular simulation inquiries into the understanding the potential-of-mean force between simple gases in water. As the use of molecular simulations expanded through the 80's and 90's, Lawrence and his collaborators expanded their research to: bridge molecular and macroscopic descriptions of the hydrophobic effect utilizing scaled-particle theory; incorporate the impact of solvent density fluctuations into the description of solute

hydration through information theory; and piece apart the role of water on driving nonpolar gases together in solution and its curious dependence on temperature. A key conclusion from Lawrence's work on information theory is that many of the surprising temperature dependent phenomena associated with the hydrophobic effect (*e.g.*, solubility minima, large positive heat capacity increment, isotope effects) can be linked directly to the unique equation-of-state properties of water, like the observation of a temperature of maximum density, that are distinct from nearly all other liquids. This stands in opposition to explanations that invoke water forming clathrate-like structures about nonpolar moieties, which pervades biochemistry text book descriptions of the origin of the hydrophobic effect but whose scientific import are still an area of debate.

While still at Berkeley, Lawrence laid down pioneering groundwork for another area of intense current interest, namely "orbital-free density functional theory". The famous Hohenberg-Kohn theorems produced a fundamental link between the electron density and the ground-state energy in many-body electronic structure theory. While the atomic orbitals in Kohn-Sham Density Functional Theory provided a useful route to accurately computing the kinetic energy portion of the total energy, those orbitals are not in principle necessary. Very early work by Thomas and Fermi produced an approximate statistical model of the atom that involved the electron density directly but had serious physical shortcomings (such as infinite density at the nucleus and no chemical binding). Over the following decades several researchers, including Norman March and Julian Schwinger, developed more accurate but still flawed models. The Harris/Pratt paper of 1985 thus made a major conceptual step forward by providing an exact theoretical solution to the problem. By combining an inverse Laplace transform representation of the ground state electron density matrix with path integral methods, a high-dimensional integral equation was derived. Further work by Pratt, Hoffman, and Harris developed an Optimized Thomas-Fermi theory that removed the unphysical behavior of the density near the nucleus. A follow-up paper exploited analogies with the renormalization group by introducing length scales via a Fourier representation of the paths. That development benefitted from related work called "partial averaging" developed by Jimmie Doll and coworkers for improving sampling in finite temperature path integral simulations of liquids.

Over the past 20 years, Lawrence has focused considerable effort in the development of the quasi-chemical (QC) theory of liquids and molecular solutions. The QC approach explicitly rests on realizing that the potential distribution theorem in fact defines a local partition function. This partition function can be rearranged in terms of cluster integrals involving only the solvent, cluster integrals involving the solute plus the solvent, and a long-range contribution part that is once again in the form of the potential distribution theorem, but now for a solute whose strong-interactions with the solvent have been removed. In this sense, the QC approach is philosophically akin to a renormalization transformation. The appellation quasi-chemical derives from the fact that the cluster integrals are nothing but chemical equilibrium constants. The final form of the QC approach is then an exact expression, indeed a tautology akin to the Ornstein-Zernike equation, for the excess chemical potential of the solute in terms of local hydrophobic, local hydrophilic, and long-range contributions. To quote Lawrence, the QC form is "All of known physics and all of unknown physics."

The QC approach has another interpretation, one as a way to regularize the statistical problem of computing the excess chemical potential from the known solute-

solvent binding energy distribution. This interpretation has proven very productive in enabling calculation of free energies in a variety of challenging problems including in: all-electron DFT calculations broadly, without the need to introduce arbitrary charge states; hydration of ions and water, in all-electron, polarizable, and non-polarizable models; and in modeling the hydration of proteins, without the need to resort to any approximations. All these aspects continue to be vigorously pursued and investigated.

Lawrence is widely recognized as a leader in the statistical thermodynamics of liquids, routinely asked to deliver invited lectures at international meetings, and writes authoritative reviews and accounts of the areas of inquiry he is presently investigating. Lawrence's achievements were recognized by Tulane University when he was installed as the Herman and George R. Brown Chair of Chemical and Biomolecular Engineering in 2008. More recently, he was awarded the 2018 Joel Henry Hildebrand Award by the American Chemical Society for his contributions to understanding the chemistry and physics of liquids. A perhaps more lasting tribute to Lawrence's contributions to the field, however, are the junior investigators who collaborated with him over the years that have gone on to academic and national laboratory positions including: Gerhard Hummer (Max Planck, Frankfurt), Shekhar Garde (RPI), Stephen Paddision (U. Tennessee), Maria Gomez (Mt. Holyoake), Randall LaViollete (DOE), Gary Hoffman (Elizabethtown), Susan Rempe (Sandia), Tom Beck (U. Cincinnati), Dilip Asthagiri (Rice), and Hank Ashbaugh (Tulane).

Each of us has been driven by Lawrence's enthusiasm and curiosity to better understand the molecular nature of liquids and the puzzles surrounding this significant phase of matter. His intelligence and mental acuity have shaped and pushed our own studies to a higher level. Indeed, none of us would be the researchers we are today if it were not for his influence on our careers. It is a great honor for the four of us to serve as Guest Editors for this special issue of the *Journal of Physical Chemistry B* dedicated to our mutual friend and collaborator, Lawrence Pratt.

Henry S. Ashbaugh
Tulane University

Dilipkumar Asthagiri
Rice University

Thomas L. Beck
University of Cincinnati

Susan B. Rempe
Sandia National Laboratories