THE JOURNAL OF PHYSICAL CHEMISTRY B

Special Issue Preface

pubs.acs.org/JPCB

A Scientific Memoir

I was born four days before the correct structural model for deoxyribose nucleic acid appeared in print.[1] It was the atomic age, an age of anxiety. As a child, I learned the Russians might drop atomic bombs on us. The movies showed that as a result radioactive mutated monsters would be released. My first distinct memory was a radio broadcast that announced the Russians had launched a satellite into outer space. There was a dog in it, and it was flying over our country. In the movies, the scientists formed teams to work together to save us from atomic disasters. I therefore knew I had to become a scientist when I grew up. But what kind of scientist? Many accidents of birth and development as well as just plain accidents determined this.

My mother and father had very different personalities and world views. I now see how both my imitation of them and rebellion against them shaped me intellectually. My mother was a Christian Scientist from a Danish-Swiss family, and my father was a chemical engineer whose parents both came from Russia. By saying my mother was a Christian Scientist, I do not mean my mother was a scientist who went to church but rather that she had been brought up in the religion called Christian Science, which is orthodox neither in its Christianity nor in its science. Although she was not the strictest follower of its injunctions, the Christian Science way of thinking permeated her life. She was optimistic, trusting, and extremely generous, sometimes to a fault in my father's view. Her optimism was based on the Christian Science doctrine (borrowed from Plato) that the physical world is an illusion. Death and disease are illusory, and the "real" world is much better than it appears and is eternal. According to this belief, if you think clearly enough, you will see through the fog of appearance just as Christ did, and never die. Strictly following these ideas implies you do not need medical doctors and do not need vaccinations or medications. My mother compromised: I would be taken to the doctor but only when very sick, and I would get vaccinations as required to get into school. Because of an ancient rule, presumably from colonial times, I later had to get vaccinated against smallpox in order to go to Harvard. This did not make me a fan of Cotton Mather FRS. I can tell you smallpox vaccinations make you feel quite sick, which is very uncomfortable even if it is an illusion. My mother's metaphysical world view might not seem the most auspicious for raising a natural scientist, but growing up with this abstract philosophy made it easier for me to swallow quantum mechanics and its Copenhagen interpretation later on.

My father was not at all metaphysical but a realist engineer. He carried out pilot scale manufacturing research at a plant that made cement from the byproducts of making steel in the Gary, Indiana mills. His work involved huge machines like hundred-foot-long rotating kilns. It also involved atomic thinking and deadly X-rays just like in science fiction. He showed me once an X-ray diffraction picture of cement that had been made in the kiln. He also programmed computers to optimize cement compositions. To compute in the early 1960s, he would write out longhand instructions on special forms. These instructions would be mailed to corporate headquarters in Pittsburgh, Pennsylvania where they were put on punch cards and run through the computers and the results were returned (in less than a week!) by post.

At home, my dad was even more of a practical man than at work. He thought paying someone to fix something was immoral. He therefore spent most weekends disassembling and reassembling our cars and prowling junkyards for replacement parts. I, of course, had to help. I hated going out in the cold and lying on my back under the car even though a helping hand was always needed. Our television also always needed repair. Every other week, we would test the vacuum tubes to see precisely which ones had burned out and needed to be replaced. I, of course, had to learn to do this. These attempts by my father to educate me in practicalities apparently backfired, since I am now a theorist and refuse to fix things around the house.

The best way to escape helping my dad was to go to the basement. Downstairs there was an extensive collection of back issues of *Popular Science* along with some books from the 1930s and 1940s that my father had purchased when he was younger. I loved reading these, especially the heroic tales about chemists in books like *This Chemical Age*.[2] I was impressed by the story of Baekeland getting rich by first negotiating with Eastman about licensing his photographic patents and later starting his own plastics company. Two adventures were inspired by these readings. First, I decided to earn money for my third grade class by making and selling homemade glue, beginning my fascination with polymers. *Popular Science* told me that glue could be made out of curdled milk. Somehow I persuaded my mother to try out this scheme. We bought gallons and gallons of milk that I curdled with vinegar. My attempt to separate the curds from the whey pretty much failed, so the milk continued to ferment. The terrible smell eventually convinced us that no glue or money would be forthcoming, so we abandoned the project. *This Chemical Age* also explained how artificial vanilla was made from cloves. The process involved heating clove extract with alkali under pressure. I decided to do this in the kitchen. I mixed some cloves with rubbing alcohol, added baking soda, and put this concoction in a test tube. I was careful. I knew heating something under pressure could be dangerous. Therefore, I wrapped the sealed test tube in aluminum foil before heating it on the stove. Even when it started to "bump" furiously, I kept on heating it. Eventually, the test tube blew up into fragments too small to find. I convinced myself the room smelled like vanilla, but my mother was very angry. Thankfully, no one was blinded.

My reading and experiments grew a bit more sophisticated. At the library, I discovered Isaac Asimov. Although remembered nowadays more for his fictional Three Laws of Robotics, Asimov, a trained biochemist, was a brilliant writer of science fact and wrote hundreds of books. I learned the most from his collections that reprinted brief articles he wrote as columns in the monthly *Fantasy and Science Fiction*.[3] Each few page essay was usually pretty much self-contained, raised an interesting point, and often involved a simple calculation that underlined the main idea. I still

Special Issue: Peter G. Wolynes Festschrift

Published: October 24, 2013

   dx.doi.org/10.1021/jp407073n | *J. Phys. Chem. B* 2013, 117, 12672−12675

consider this style the ideal one for a scientific paper. I also learned about DNA from these essays and later did a science fair project on it in fifth grade. My first foray into structural biology did pay off (I won a prize at the fair), but my recollection of the structural model I built out of styrofoam Christmas ornaments is now that it was all wrong, apart from satisfying Chargaff's rules. I also gathered from Asimov that organic chemistry was the secret of life, and I started to study that subject more intensely and got my dad to buy me apparatus and chemicals from a science supply store, which happened to be near one of the junkyards. I am sure that nowadays it would be assumed we were making meth, considering all the ether, benzene, etc., that we bought. The good news is that there were no more explosions, luckily!

I also came across and bought a few books on modern physics and physical chemistry. These made a lasting impact on my science. The first was Reichenbach's *The Philosophy of Space and Time*.[4] I pored over this book which was a philosopher's introduction to relativity. I got the notion that you really have to think hard about what experiments really tell you. Perhaps I was overenthusiastic, but I really bought the idea that science is not just about things blowing up or making money and was about seeing the world in a deeper way. This notion was reinforced when I later bought Persico's *Quantum Mechanics*[5] ($1.50 hardbound), but the great book for me was Denbigh's *Principles of Chemical Equilibrium*,[6] which I bought at the book store of Chicago's Museum of Science and Industry. I read, reread, and read over and over again this book. My copy long ago completely fell apart. Two things got to me: entropy and rates. The second law was so confusing. I knew from Asimov it meant the end of the universe (actually that is not true[7]), but what was entropy? The statistical meaning of the second law made some sense, but I had to go over and over it to try to comprehend. Was the world really random? After covering equilibrium through the whole book, the very last chapter was about kinetics. This chapter really bothered me. I got it that chemicals had to change (they blew up, right?), but what is change? When does a molecule stop being one thing and become another? Aristotle would have been pleased with my confusion. Finally, what is a transition state and can I put it in a bottle? Would not the bottle explode? As it has turned out, most of my career has been spent trying to make sense of these questions, so reading this book made a big impact on me.

What about school? Did I learn anything there? Well, yes, a few things. First, I had learned to read and do arithmetic there in the early grades. I could not have read the books downstairs without this start. Second, I learned, but more slowly, how not to bother the teachers when I asked my questions. I learned to be more polite than was natural for me. In later years, these skills became useful in attending seminars. On the other hand, because of my slowness in learning these things, I did get sent to the principal's office quite often and (mild) corporal punishment still was practiced even in the eighth grade. A few teachers (the math teachers who were not coaches) were very encouraging and eventually got me to take courses at the local campus of Indiana University. I dropped out of school and enrolled as a chemistry major in the university. Organic chemistry was still my career goal, but I was taking a lot of math courses and the math professors wanted me to major in math. In the end, I took more advanced math and physics than I did chemistry. Two aspects of the organic lab changed my trajectory. The stuff we did in the lab was quite simple compared to what I had already been doing in the basement. Thus, it could have been boring. Fortunately, the instructor, Professor Hered, allowed us to write lab reports in a strange way—the introduction could be about anything related to the experiment. Therefore, my lab reports were quite theoretical; the distillation experiment's introduction was about the phase equilibria involved, and the introduction to the report on S_N1 reactions tried to rationalize the effects using quantum mechanics. The second impetus from the university lab experience was less positive. For one of the experiments (esterification), we needed to use glacial acetic acid and sulfuric acid which were both stored in a hood. When I was getting my acetic acid, I noticed something odd—my legs had suddenly gotten very warm. I looked down and I was standing in a puddle of concentrated sulfuric acid, which had been stored in a gallon container. One of my lab mates had simply picked up the bottle which then spontaneously shattered because it had been sitting next to a hot plate in the hood. She was seriously burned because she had gotten the biggest part of the spill. I was luckier, but it was a very troubling incident.

The theory of nucleophilic attack became a kind of hobby for me. I thought I could use transition state theory and polymer chain statistics to model the steric effects in S_N2 reactions using computers. When I tried to explain this idea to Prof. Hered, he said this was beyond him but that there were real theoreticians at the main Indiana campus at Bloomington who could help me. My parents drove me on the three hour trip down to Bloomington where I met Don MacQuarrie and a new assistant professor, Robert Roberts. Explaining my ideas to MacQuarrrie was difficult, and he seemed very critical. I was crying on the way home. I later learned that he was actually somewhat impressed, and he and Roberts suggested that I transfer to Bloomington to complete my studies. My year in Bloomington was a real college experience. I learned to play pinochle and Risk and stay up late; no alcohol though, I was too young and it would destroy brain cells. My research project now on S_N2 reactions did not get very far, but I started to learn how to do real research. Roberts was an excellent mentor and let me work on the project like a graduate student. MacQuarrie tried to get me interested in biological problems—the brain actually. I told Roberts I did not want to do this because it was not chemistry. He set me straight—what do you care what a problem is called? You should do it if it is interesting. This was a small piece of important, transformative advice, but nevertheless I did not work on biology at the time.

I came across a great book in Bloomington, a lecture note volume on the Many Body Problem by David Pines.[8] It contained an eye-opening idea for me that the basic equations were not everything but that new concepts could emerge at a higher level, for example, the idea of "quasi-particles" in which the elementary objects are modified by interaction with their environment but somehow maintain their identity. It seemed to me like there might be a possibility of developing many body thinking in chemistry, so that chemistry could be understood as well as computed.

With a bachelor's degree, I was now formally ready to go to graduate school. There were some constraints. My parents were worried about me living far from family. One option would be the University of Chicago, near home, but my grandmother lived in Cambridge, Massachusetts, so Harvard and MIT were possibilities too. I am not sure I made the best choice, but Harvard was it.

Harvard really was the "big leagues". I was intimidated already at the welcoming party where I encountered other entering students. While I had taken real analysis and complex variables as an undergrad, one fellow student had studied topology, and at Princeton! In the Chemical Physics Ph.D. program, we had to take essentially the same courses as Physics graduate students the first year. Although I thought quantum would be easy (it was), graduate electromagnetism worried me. I had not taken E&M as an undergrad and there were about ten assigned texts, ranging from the standard Jackson[9] to Born and Wolf's *Optics*,[10] both relevant volumes of Landau−Lifschitz,[11] and finally to two books by the lecturer himself, Nicolaas Bloembergen.[12] I did fine but only because the fear that Bloembergen evoked motivated me to work hard. Although Bloembergen is known as an experimentalist, I learned a lot about how to do theory professionally from this class. Twenty years later, I was shocked to find Bloembergen (now a Nobelist) was not actually the austere figure he portrayed in class. At the Garden Party of an NAS meeting, he was charming and garrulous, nearly as chummy as a politician.

While nowadays students start research by picking an advisor and getting immersed in an ongoing research project, at Harvard then, things were different. I gathered you were supposed to find a thesis problem first and then get some advice from a faculty member about how to do it. (At any rate, I thought that was how it worked.) Although theory students had advisors, they were only lightly advised. My official advisor was Roy Gordon. The theoretical chemistry students were housed in a separate building from the faculty. This was a frame building called "The Morton Stanley Prince Psychological House" or "Prince House" for short. Timothy Leary, the infamous Harvard psychology professor, was housed there in the 1960s, and the suspicion was that latent quantities of the psychedelic drugs with which he experimented might have some effects on the current occupants. Certainly, a lot of creative theorists spent time there—Bill Miller, Eric Heller, Bill Reinhardt, and Arieh Warshel to name a few. There was a strong group in Prince House when I arrived that included Iwao Ohmine, Zan Luthey, Peter Rossky, Klaus Schulten, Attila Szabo, and Andy McCammon. We learned a lot from each other and started our own seminar series in the basement that the faculty would occasionally attend.

I had trouble finding a thesis project that would work. I was intrigued by critical phenomena and the puzzle of nonclassical exponents, but this was being solved elsewhere just at this time using the ideas of Widom, Kadanoff, Fisher, and Wilson. Hydrodynamics fascinated me as an example of an emergent, many body concept. The theoretical framework of this emergence was threatened by the discovery of "long time tails" in the computer simulations of Alder and Wainwright.[13] An explanation was provided by the mode coupling theories, but these were not rigorous. I thought I could do something about that. I could, but it was only a little step. I showed rigorously that mode coupling theories overestimated the effect,[14] so hydrodynamics was safe. This was a boring result. Still, the theory led to my first paper which is probably my only mathematically rigorous paper! To finish my thesis, I went searching for more advice—all the way to MIT. There, John Ross gave me some excellent advice. He said the paper on rigorous mode coupling showed I could do something but that I should remember that, just because a problem is hard and could be solved, that does not mean that it is important or worth solving; I should (and would) pick future projects better. I also started to talk with John Deutch from MIT who was spending time at Harvard. He liked my ideas about trying to understand the origin of the boundary conditions of hydrodynamics. This study was to form the bulk of my thesis. A few months later, John offered me a postdoc, since I wanted to stay in Cambridge for personal reasons. He was distressed, however, when my rigorous paper appeared in *Physical Review*.[14] I had mockingly named my office in Prince House "The Center for Correlation Function Research". This was a long while before everyone in academia had a center, as has become the norm today. I used this address in the byline of the article in *Physical Review*. When the article came out, John was furious. He said, "Science is serious. Science is War. There is no room for humor in Science." He went on to explain there were powerful people in Science who had no sense of humor, Herb Gutowsky, for example. He said if Gutowsky saw this paper I would never get a job at Illinois. I later learned that Herb had enough of a sense of humor, apparently, to overlook my lapse of decorum.

As soon as I arrived at MIT, John informed me that Harvard had called and they were asking me to apply to go back, now on the Faculty. He advised against it, but I did not listen. My time on the Faculty at Harvard was stressful, but nevertheless, I got a good start on my program of finding new many body concepts for chemistry. My work with Jim Skinner on trying to understand environmental friction effects on rates in condensed phases resurrected Kramers' old ideas which had been largely forgotten by physical chemists. This work got a lot of attention, and as a result, to my relief, several places, including Illinois, offered me tenured positions three years after I had returned to Harvard. Despite (or because of) its reputation for seriousness, I accepted a job at Illinois. This turned out to be a great decision. The traditions of excellence in chemistry and physics were well-established there, yet there was a sense that no one could rest on their laurels—John Bardeen in the physics department had been twice recognized by the Nobel Committee but pointed out that two times one-third was still just two-thirds. I started to interact with Hans Frauenfelder and Harry Drickamer who became wonderful mentors. I still needed a lot of education, and they were patient.

My science was able to flourish at Illinois, but my most important discovery at Illinois was Kathleen Bucher. Although it took some work for me to convince her, she was persuaded to marry me and she has been with me in all the adventures that were to follow, always a staunch supporter but when needed a sensible critic too.

I have too many stories to tell you about my later scientific escapades at Illinois, UCSD, and Rice. Getting out of the laboratory has minimized the explosions, except when I teach freshmen. I have been able to follow Roberts' advice and not worry about what my research is called. The only downside of that has been the need to attend a large number of faculty meetings in multiple departments. I have been able to work on thermodynamics, rates, randomness, quantum phenomena, glasses, proteins, and even cells and genes but not yet the brain. Some useful concepts in many body chemistry like funnels and rugged energy landscapes have been developed through these studies. All of my work has in itself been a many body phenomenon in which I play the role only of a quasi-particle. My list of publications proves how much I have learned with collaborators. I have tried to learn from my co-workers and competitors, alike. They all deserve my thanks.

Peter G. Wolynes

REFERENCES

(1) Watson, J. D.; Crick, F. H. C. A Structure for Deoxyribose Nucleic Acid. *Nature* **1953**, *171*, 737−738.

(2) Haynes, W. T. *This Chemical Age: The Miracle of Man-Made Materials*; Alfred A. Knopf: New York, 1942.

(3) See, for example: Asimov, I. *Only a Trillion*; Abelard-Schuman: New York, 1957. Protein folders will enjoy the essay "Hemoglobin and the Universe", while quantum mechanicians will enjoy the essay on thiotimoline.

(4) Reichenbach, H. *The Philosophy of Space and Time*; Dover Publications: 1957.
(5) Persico, E. *Fundamentals of Quantum Mechanics*; Prentice-Hall: New York, 1950.
(6) Denbigh, K. G. *Principles of Chemical Equilibrium*; Cambridge University Press: 1957.
(7) Tolman, R. C. *Relativity, Thermodynamics, and Cosmology*; Clarendon Press: Oxford, U.K., 1934. Dyson, F. Time without End: Physics and Biology in an Open Universe. *Rev. Mod. Phys.* **1979**, *51*, 447−460.
(8) Pines, D. *The Many-Body Problem (Frontiers in Physics: Lecture Note and Reprint Series A, VI.)*; W.A. Benjamin: 1961.
(9) Jackson, J. D. *Classical Electrodynamics*; John Wiley & Sons: New York, 1962.
(10) Born, M.; Wolf, E. *Principles of Optics*; Permagon Press: London, 1959.
(11) Landau, L. D.; Lifschitz, M. E. *The Classical Theory of Fields*; Pergamon Press: Oxford, U.K., 1962. Landau, L. D.; Lifschitz, M. E. *Electrodynamics of Continuous Media*; Pergamon Press: Oxford, U.K., 1960.
(12) Bloembergen, N. *Nuclear Magnetic Relaxation*; W.A. Benjamin: New York, 1961. Bloembergen, N. *Nonlinear Optics*; W.A. Benjamin: New York, 1965.
(13) Alder, B. J.; Wainwright, T. E. Decay of Velocity Autocorrelation Function. *Phys. Rev. A* **1970**, *1*, 18−21.
(14) Wolynes, P. G. Bounds for Convective Contributions to Transport Coefficients. *Phys. Rev. A* **1975**, *11*, 1700−1705.

dx.doi.org/10.1021/jp407073n | *J. Phys. Chem. B* 2013, 117, 12672−12675