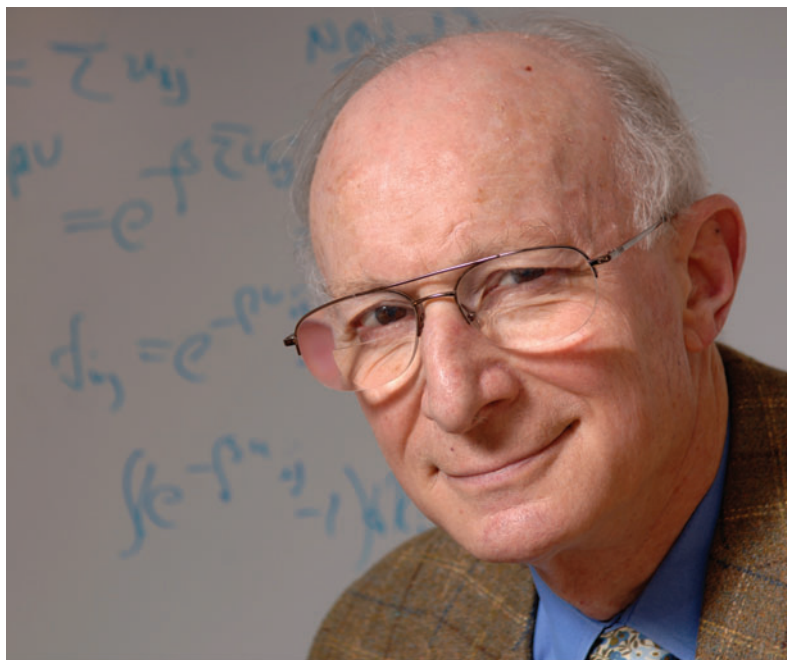




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A Fortunate Life in Physical Chemistry

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Abstract

This article contains a very personal account of my evolution as a physical chemist/chemical physicist, with commentary on some of the influences on that evolution and summary accounts of research accomplishments in four of the subject areas that have engaged my attention, ranging from isolated molecules to condensed matter.

PREAMBLE

I suppose it is a consequence of working in a field for more than 50 years, in the “no good deed goes unpunished” category, to be asked to write about one’s experiences. Nevertheless I was surprised, and pleased, to be invited by the *ARPC* Editorial Committee to write about my evolution as a physical chemist. After I accepted that invitation I began to wonder how to start, and what to include. Having no prior experience with autobiographical writing, I examined how my predecessors had handled describing themselves. I could find no uniform pattern. What follows, then, is an abbreviated account of my activities in various parts of physical chemistry. Owing to space limitations, I have had to be selective, so I describe only four of the many subjects that have engaged my attention. I have tried to identify the excellent students, postdoctoral research associates, and colleagues who contributed to these research efforts, and I apologize for any omissions, as well as for not reporting the efforts of all those who have worked with me on other research problems.

IN THE BEGINNING

I was born in New York City in 1932, at the beginning of the Depression, and I lived there until departing to start graduate school. The population of the Bronx, where I lived, grew rapidly after World War I, when the combination of limited space in Manhattan and the construction of subway lines led to the migration of many recent immigrant families to new neighborhoods. Almost all the cohort of my childhood acquaintances, like me, consisted of first-generation Americans. As I think about my personal evolution, I see how it was greatly influenced by the social, political, and economic circumstances of the Depression era and World War II and by the high quality of the New York City public education system during that period. The economic climate of the 1930s created immense financial hardship for millions of people. Employment was difficult to find, and many families shared living space to pare expenses; until I was five my parents and I, my grandparents, and my uncle lived in a two-bedroom apartment. The difficulty in finding professional positions caused the diversion of many talented people from their original fields into other work. My father was one such individual; he was an engineer who, after losing his position, could not find employment that utilized his professional education until the start of World War II.

With such economic conditions, individuals sought positions of any sort that had stability. Among the few such positions was that of public school teacher. The New York City public school system benefited from this diversion of talent, and throughout my lower school and high school education, I had teachers with exceptional talents. At the pinnacle of the New York City public school system of that time was a subset of high schools that accepted students from anywhere in the city, with entry determined by examination. The Bronx High School of Science, which I attended, attracted a stellar student body. Together, those students, the faculty, and the broad and well-defined program of studies provided a rigorous education in a scintillating intellectual atmosphere with a strong emphasis on individual worth and independence.

The school was housed in a run-down and crowded building; no matter, we thrived on the interactions in school and after school in activities such as the chemistry club and the mathematics team. There were no sports teams to distract us from academic pursuits.

My first exposure to research occurred in my junior year in high school, when I worked in Dr. Michael Levine's laboratory at Montefiore Hospital. He was a student of T.H. Morgan. Largely because of anti-Semitism in the interwar period, he was unable to find a university position and became a high school teacher. Throughout that high school teaching career, he maintained as active a research program as he could, and when he retired at the end of World War II, he acquired a grant from the Damon Runyon Cancer Fund and space at Montefiore Hospital to carry out in vitro culture studies of the differentiation of plant tissue, in particular the regeneration of healthy tissue from crown gall tissue. He believed that young people should be given the opportunity to practice science, and he invited, one at a time, high school students to work in his laboratory. At first I learned the laboratory lore by having responsibility for various chores, such as sterilizing media and growing bacterial cultures. Soon, however, Levine designed a problem suited to my level of knowledge, namely, a study of the influence of aminopterin, vitamin K, and folic acid on cell division in the onion root. At the time each of these substances was under consideration for the treatment of cancer, and the theme of the study was the determination of their influence on the rate and character of cell division in a rapidly growing tissue, for which the onion root was the test vehicle. It was an exhilarating experience for a 16 year old to be given only general directions, the independence to execute the experiments with only minor supervision, and the responsibility for analyzing the results. The results were the content of the first scientific paper that carried my name (1). I learned a great deal from that experience about the ways of science, and because of it I have always welcomed having a high school student work in my laboratory.

I stopped working at Montefiore Hospital when I entered Brooklyn College in the fall of 1949. There I met and was greatly influenced by two exceptional teachers. Donald Wright taught an accelerated first year chemistry—qualitative analysis course, Chemistry 2.5, that was restricted to 25 students with admission by examination; it covered three semesters work in two, yet it was much deeper than the standard course. Wright was not a brilliant lecturer, but his choice of material and presentation communicated to me a sense of grand themes in chemistry. More than a teacher, he became a friend and provided valuable help when I had a medical problem. The other of these teachers, arguably even more important to me, was Melba Phillips. She was an extraordinary woman: intelligent, sophisticated, and socially aware. Her physics courses were characterized by an elegance of presentation coupled with deep insights. I am convinced that it was from her that I learned what taste in science means and how to identify fundamental problems. We became lifelong friends, a relationship that had particular importance when she was fired by Brooklyn College in 1952 for refusing to testify to the House Un-American Activities (McCarthy) committee.

Toward the end of my freshman year I met Marian Coopersmith at a Chemistry Society picnic. We hit it off immediately, became a pair, and were married June 1, 1952, just days before graduating from Brooklyn College. In September 1952 we both

entered the graduate program in Chemistry at Harvard (Marian was officially enrolled at Radcliffe), me with a National Science Foundation predoctoral fellowship and Marian as a quarter-time teaching fellow. But before that enrollment, just two weeks after we were married, a medical crisis had to be addressed. The war in Korea was still in progress, and I was summoned for a preinduction physical examination. That examination revealed a largish spot in my lung, which was diagnosed as tuberculosis, which led the Army to classify me 4F; if that diagnosis held up, we would have to abandon our plans for graduate school. At this point Donald Wright stepped in and arranged for me to take part in a trial of new antituberculosis medications (isoniazid and streptomycin) at the Grace Clinic in Brooklyn. Fortunately, by the end of the summer no evidence for tuberculosis could be found, and Marian and I were allowed to proceed as originally planned. We had a wonderful, mutually supportive and loving marriage for 42 years; it was terminated by her untimely death at age 63 from brain cancer.

HARVARD

I received a good and broad undergraduate education at Brooklyn College, and its intellectual environment determined what I knew about the academic world at the time of my graduation. With a focus on undergraduate education, only a nominal night-school master's degree program, and heavy teaching loads, the faculty at Brooklyn College carried out little research. The scale of research activity and the breadth of the intellectual environment at Harvard opened new worlds for me. Two aspects of that intellectual atmosphere are worthy of further comment. Unlike Brooklyn College, which fired Melba Phillips for refusing to testify to the House Un-American Activities Committee, Harvard actively supported the academic freedom of the faculty during the difficult period when that committee was wreaking havoc. Enrollment at Harvard also brought me into contact with eminent scientists such as John Edsall, who took principled stands against arbitrary federal actions despite the personal cost, and others such as E. Bright Wilson, George Kistiakowsky, and Paul Doty, who believed that public service was an important part of their responsibilities. The manner in which these individuals conducted themselves greatly influenced the evolution of my attitude concerning the balance between personal research and responsibility to the public and to the several nested institutions to which I belong.

The graduate program in chemistry had only a few required courses because great emphasis was placed on having students start research early in their careers. I liked the kinds of problems studied in Doty's laboratory, and I joined his group in February 1953. It was, for me, a fortunate choice of research advisor: Doty had a discriminating and individual approach to working with each student that balanced *laissez-faire* with specific suggestions and guidance. He encouraged my interactions with other faculty and my interest in both theory and experiment. The experimental part of my thesis research dealt with the helix-to-coil transition (denaturation) of DNA and with the attempt to separate the two strands of this molecule (2). I did not succeed in providing evidence that the strands could be separated; this was accomplished later in Doty's laboratory, and that finding laid the foundations for all of recombinant

DNA chemistry and technology. The interpretation of my experimental results was based on what I believe was the first, admittedly crude, model of the DNA helix-coil transition, worked out in collaboration with Akiyoshi Wada (3, 4). The larger part of the theoretical work reported in my thesis was the product of a collaboration with Frank Harris, then an instructor in chemistry. The goal of the research was to develop a model of polyelectrolytes that included chain connectivity and flexibility in the description of the response of the molecule to charging. The theory we developed included, albeit with some crude approximations, the effects of these characteristic features on the expansion of the molecule as a function of charging and counter-ion binding and the dependence of polyampholyte behavior on chain composition and monomer arrangement (described in 5). A few years later the two parts of my thesis research were bridged in a study, with Bruno Zimm, of the helix-coil transition in charged polypeptides (6).

Every individual's education has an unsatisfactory episode that attentive faculty can turn into a learning experience. At the beginning of my second year in graduate school, Bill Moffitt organized a physical chemistry graduate-student colloquium series with the purpose of giving each student an opportunity to learn how to organize material and speak to an interested but diverse audience. The talk I gave was on irreversible thermodynamics. I flew around speaking rapidly and writing equations on the blackboard rapidly, equally rapidly losing the audience. When the talk ended, there was a sea of glassy eyes in the audience. After a few moments of silence, E.B. Wilson commented, "Young man, next time do it in one-dimension, and come see me tomorrow." When I met with Wilson he gave me a gentle but firm lecture on the purpose of a talk, how to choose the level of presentation and examples, and how to bring the audience along with you, advice that strongly influenced my career. Although I was not his student, he cared about all the students.

Shortly before receiving my Ph.D. in June 1955, I was elected a Junior Fellow of the Society of Fellows; the three-year appointment started July 1. The 24 Junior Fellows had interests distributed across all fields. My cohort of eight included Marshall Cohen (philosophy), George Field (astrophysics), Kurt Gottfried (nuclear physics), Andrew Meyerriecks (ornithology), Peter Ray (biology), and Neil Smelser (sociology); overlapping earlier cohorts included, among others, Donald Hall (poetry), John Hollander (English), George Kateb (political philosophy), Marvin Minsky (artificial intelligence), Henry Rosovsky (history), and Edward O. Wilson (evolutionary biology). Interaction between Junior Fellows was stimulated at weekly dinners (with Senior Fellows) and lunches (without Senior Fellows) at which there were diverse lively conversations: Babe Ruth's prowess as a home run hitter, the history of revolution, recent poetry, and new developments in science. These contacts whetted my appetite to try new research directions.

I had become friendly with Bill Klemperer, then an instructor, and we jointly decided to test the Rittner (ionic) model of binding in alkali halide molecules by studying their infrared spectra in the vapor phase. Although the technology of the time was primitive by current standards, we were able to examine the spectra of a large number of alkali halides at high temperature. Because of the congestion in these spectra, the vibrational frequencies had to be extracted from the calculated

superposition of many rovibrational transitions, making use of the properties of the band heads. The overall data set provided frequencies for many more molecules than had been available previously and made possible a good test of the Rittner model of binding in alkali halide molecules (7, 8).

I had read many of the papers dealing with the theory of liquids written by J.G. Kirkwood and by J.E. Mayer; the subject fascinated me. I was determined to spend the second year of my Junior Fellow tenure at Yale working with Kirkwood. Marian finished the experimental work for her Ph.D. at the end of the summer in 1956, and we moved to New Haven in September 1956. I believe I have the unique distinction of being the only individual to have been supported by Harvard to carry out research at Yale!

YALE

In 1956, the physical chemistry research portfolio at Yale was quite different from that at Harvard; there were no research programs in gas-phase spectroscopy, quantum chemistry, or gas-phase kinetics. Instead, there were research programs in statistical mechanics and the experimental study of solutions of all kinds; these differences considerably broadened my education and my interests.

I came to Yale interested in studying transport in liquids, a field in which Kirkwood was a pioneer. In 1946 he published a seminal paper (9) that introduced an approach to constructing equations for the time dependences of the singlet, pair, and higher-order distribution functions in a liquid based on a generalization of ideas from Brownian motion. The assumption was that one could define a fundamental dynamical event with the property that successive such events could be considered independent. In the dilute gas the fundamental event is a binary collision, but it is more complex in a dense fluid. The way the assumption was applied involved, first, deriving from the N -body Liouville equation the exact equations of motion for the singlet, pair, and higher-order distribution functions and, second, time averaging those equations over the duration of the fundamental dynamical event. The coupled hierarchy of kinetic equations so obtained was presumed to describe irreversible processes in the system. However, the time smoothing operation does not generate irreversibility in a formal mathematical sense; it is the additional assumption that the fundamental dynamical event is independent of preceding and succeeding such events that generates the irreversibility. This approach is now recognized to be inadequate. However, in 1956 it was the only approach that permitted the study, albeit approximate, of transport in the liquid phase.

Kirkwood suggested two problems to me: the systematic derivation of the Enskog equation for a dense hard sphere fluid (10) and the development of a theory of transport in Lennard-Jones-type liquids based on the evaluation of the exact equations for the heat flux and stress tensor using an expansion of the time-dependent pair interaction and the assumption of local equilibrium in pair space (11). Both these projects led to ideas and insights that were valuable in later research.

I found working with Kirkwood to be rewarding. Kirkwood and I had a regularly scheduled weekly meeting at which my research progress and a variety of other “topics

of the day” were discussed. During one of these meetings I witnessed an event at which I still marvel. Shortly after I arrived in Kirkwood’s office that day, there was a knock on the door, and Lars Onsager came into the room. He stood silent for a few moments, possibly as long as two minutes, then asked Kirkwood if he could be on the Ph.D. oral examination committee of a certain student. Kirkwood examined his date book and said yes. Onsager replied, “Good. I particularly wanted you for this examination because you know more quantum mechanics than anyone else in the department.” Kirkwood replied, “No, Lars, you do.” And then, as if playing a tennis game, Onsager and Kirkwood exchanged successive statements, with variations, about who knew more. After two or three of these exchanges, Onsager straightened up, smiled, and said, “But you know more about valence bond theory,” and turned and left.

In early 1957 Kirkwood learned of faculty openings at several universities and urged me to consider applying for these positions. He also suggested that I give careful consideration to a position at Bell Labs because the opportunities and environment there rivaled or exceeded those at the best universities. Just before I left for Yale, E.B. Wilson had talked to me about my future. He put forward the view that faculty openings at first-rank research universities were so rare that if one became available I should apply, and if offered the position I should resign from the Society of Fellows early to accept it. Kirkwood offered the same advice. When I discussed where to apply with my wife, she reminded me that Bob Gomer had urged me, during a visit to Harvard in 1956, to write to him at the University of Chicago when I was ready to look for a faculty position. Following her suggestion, I wrote to Gomer. I received a quick response along with an invitation for an interview, and only a few weeks after the interview was offered an assistant professorship. I have never looked back.

A young reader of this commentary will likely be surprised by my description of the speed with which the interview and appointment processes were carried out, and perhaps even more surprised that, unlike current common appointment procedure, I was not asked to describe a research program or a likely source for funding, or propose a startup research package. The interview process I experienced did not include delivering a talk; it consisted of conversing with a large number of chemistry and physics faculty about diverse problems in several different fields with questions that probed how I thought about finding problems to study, how I might approach solving such problems, and what I regarded to be fundamental issues. I fear that the current common procedure for interviewing potential new faculty has so many hurdles that it can screen out a truly original and somewhat quirky candidate whose different approach may be the key to a great advance.

CHICAGO

Just as my undergraduate experience at Brooklyn College formed my first view of an academic institution, my graduate and postdoctoral experiences at Harvard and Yale formed my first view of a research university. The chemistry faculties at both Harvard and Yale at that time were rather sharply divided between tenured and untenured individuals, there was little intellectual collaboration between the younger and older faculty, the participation of the untenured faculty in department business

was severely limited, and the rate of promotion from untenured to tenured ranks was extremely low. I expected Chicago to have the same characteristics but found that its sociology was entirely different. I was welcomed as an, albeit inexperienced, equal by even the most senior faculty (Joe Mayer, Harold Urey, Clyde Hutchison, Henry Taube, and others), and the faculty solicited and listened to my opinions on various matters. The senior faculty promoted the attitude that new appointees were expected to do great things, that they had the responsibility to help make that happen, and that provided an individual's scholarship was of appropriate quality, promotion to tenure was to be expected. Because of the structure of the Research Institutes, mixing with faculty from different fields was (and is) facile, and interdisciplinary research was (and is) promoted. Throughout my entire tenure in Chicago, my research has benefited from quick and easy access to colleagues in many disciplines, from early exposure to new approaches in their fields, and from frequent serendipitous hallway meetings and exchanges. In addition to the personal enjoyment generated by those contacts, the spirited exchange of ideas has led to joint research and publications.

It is one of the joys of university life that it is possible to quickly change the direction of one's research to exploit new developments, or as one's interests evolve. I have taken advantage of that flexibility to work in many fields of physical chemistry, often simultaneously on apparently diverse and unconnected problems. For presentation in this article, I have chosen to focus attention on four subject areas, ranging from isolated molecules to condensed matter.

TRANSPORT IN LIQUIDS

The first research I carried out in Chicago concerned the transport properties of simple liquids; as did later programs, it involved simultaneous experimental and theoretical studies.

In 1957 there were few reported measurements of the transport coefficients of a simple liquid such as Ar, yet such data were needed to test the extant theoretical treatments of diffusion, thermal conductivity, and viscosity. Although I had never before made measurements under cryogenic conditions, I was encouraged to undertake the experiments, and was given technical advice, by Lothar Meyer. Three brave students undertook the tasks of building the necessary equipment and making these measurements, as a function of temperature and pressure. Jamshid Nagizadeh (12) studied self-diffusion in liquid Ar, Kr, Xe, and CH₄, and Lynn Ikenberry (13) and Bright Lowry (14) determined the thermal conductivities and the shear viscosities, respectively, of the same liquids. As part of my extended collaboration with Meyer, about the same time Ted Davis carried out studies of the mobilities of electrons and ions in liquid He (15) and of positive and negative ions in liquid Ar, Kr, and Xe (16), and somewhat later Harold Schnyders and James Jahnke studied excess electron mobility in liquid Ar and Kr in which the electrons are nearly free particles (17, 18). The latter were the first experimental studies of nearly free electrons in simple liquids.

In parallel with these experiments, we carried out theoretical studies of transport in simple liquids. The generalized Brownian motion approach to transport theory introduced by Kirkwood had several deficiencies. Among these were the use of time

smoothing to isolate an independent dynamical event, the assumption that the motion of a molecule with the same mass as its neighbors could be described in a fashion similar to the Brownian motion of a colloid in a liquid, and the lack of differentiation between the dynamics associated with short-ranged repulsion between molecules and that associated with weaker longer-ranged attraction between molecules. I thought that the last of these deficiencies was the most important to address and that its improvement would reduce the difficulties attending the use of Brownian dynamics for molecules with equal mass. The idea I had was to treat a strongly repulsive short-ranged interaction between molecules as a short-lived binary collision in the weak longer-ranged attractive field generated by the surrounding molecules. The physical picture is that fluctuations in the attractive potential destroy velocity correlations generated in the binary collision and render successive binary encounters independent. With this representation, and neglecting the repulsive-attractive cross-correlation term in the force-force autocorrelation function, Alan Allnatt and I worked out the kinetic equations for the singlet and pair distribution functions (19, 20) and solved those equations for the several transport coefficients. Later rederivations of these kinetic equations eliminated the use of time smoothing (21, 22), and subsequent work by Davis (23) included the repulsive-attractive cross-correlation term in the force-force autocorrelation function.

The transport coefficients predicted using this theory were in modestly good agreement with experimental data (24). Two obvious sources for the discrepancies were the use of imperfect pair potentials and the failure of the assumptions concerning the underlying molecular dynamics. That the former was important is suggested by a recent reexamination of the calculation of transport coefficients for a dense fluid that uses the same conceptual structure as the modified Kirkwood approach described above in a renormalized representation (25); for temperatures that exceed the attractive well depth, there is very good agreement over a wide density range with the transport coefficients obtained from simulations of a Lennard-Jones fluid. That the latter was important became evident when computer simulation data showed that the treatment of motion in the attractive part of the potential was inadequate in that it did not account for the negative (collision rebound) part of the velocity autocorrelation function, and the theory also did not account for the long time tail attributable to the generation of vortices. Bruce Berne and Jean-Pierre Boon (26) showed that improvement of the approximation for the time dependence of the force-force autocorrelation function, by replacing the Brownian motion delta function in time dependence with an exponential decay in time that builds in a memory function for the dynamics, captures the essential features of the velocity autocorrelation function in the collision rebound region.

The theory of excess electron mobility in simple liquids can be based on an understanding of the scattering of a single electron from an assembly of atoms, which requires knowledge of the electron-atom interaction. It was the development of pseudopotential theory, and collaboration with Morrell Cohen, that made calculation of that interaction feasible (27). The electron-He pseudopotential is found to be strong and repulsive, leading to localization of the excess electron in a cavity and low mobility. The electron-Rg (Rg = Ar, Kr, Xe) pseudopotential is found to be weak and

attractive, leading to delocalization of the excess electron in a conduction band and high mobility.

ELECTRONIC STATES OF MOLECULAR CRYSTALS AND LIQUIDS

I spent the academic year 1960–1961 at the Department of Theoretical Chemistry at Cambridge University. I no longer recall how, but during that year I learned of a conjecture that exciton-exciton annihilation contributes to the photoconductivity of a molecular crystal. The then-existing theory of excitons in molecular crystals of, say, aromatic molecules was based on the assumption that the electron density of an electronic excited state of a molecule in the crystal does not overlap neighboring molecules (the Frenkel exciton limit). However, because of the translational symmetry of the crystal, the electronic excitation cannot be permanently localized at one crystal site. The interaction that generates the exciton bandwidth was taken to be transition dipole–transition dipole coupling without any further reference to the electronic structure of the molecule. This approach cannot address the legitimacy of the conjecture concerning exciton-exciton interactions. It also cannot address other issues, for example, describing the properties of triplet excitons.

Improving the theory of electronic excitations of a molecular crystal appealed to me, and when I returned to Chicago in the fall of 1961, I asked a new postdoctoral research associate, Sang-il Choi, to calculate the rate of exciton-exciton annihilation for a model system. He did so for a hypothetical lattice of hydrogen atoms (28); when scaled to approximate the characteristics of a crystal of aromatic molecules, the results of the calculation gave an ionization rate close to the rather uncertain rate estimated from experiments, but that was much less important than the demonstration of the plausibility of the physical process and the use of the full electronic structure of the atom in the analysis. A later calculation of the rate of exciton-exciton annihilation in crystalline anthracene (29) using π -electron wave functions, also carried out by Choi, accounted for all the observed features of the annihilation process.

In early 1962 Joshua Jortner joined me as a postdoctoral research associate. His depth of knowledge and breadth of interests made him an immediate equal and full colleague; his intensity and energy, and the contributions of an exceptional cadre of students, greatly advanced aggressive attacks on several different problems. Foremost among those problems was the study of a wide variety of properties associated with the electronic states of molecular crystals. In only a few years the work of Choi and Jortner, and the dissertation research of Joseph Katz, Martin Vala, Robert Silbey, and William Greer, generated analyses of the singlet and triplet exciton band structures of crystalline benzene, naphthalene, and anthracene and of isotactic polystyrene and polyvinyl naphthalene (30–37). The latter calculations are, to my knowledge, the first studies of electronic band structure and hole and electron mobility in polymeric systems. The former calculations included accurate predictions of the then-known Davydov splittings of the singlet exciton states and the first predictions of the then-unknown Davydov splittings of the triplet exciton states of these species, later verified experimentally, and predictions of hole and electron mobilities in these systems.

Although now more than 40 years old, the results obtained have not been superseded, and recent experimental data for hole mobility in anthracene testify to their accuracy.

The description of crystal excitations with Frenkel exciton states is a limiting case that is appropriate when the excited molecule electron density distribution does not overlap near neighbor molecules. In the other limit, more typical of atomic crystals, the excited electron density distribution overlaps many shells of neighboring atoms, so the appropriate description of crystal excitations is with pseudohydrogenic Wannier excitons. Obviously, some crystals have excitations with electron density distributions that fall between these limiting cases. Steve Webber studied two cases of this type: the exciton states of crystalline Ne (38) and the spectral shift associated with deep impurity states of Ar in crystalline Ne (39). In these cases the lowest atomic excitation has an electron density distribution that strongly overlaps only the nearest neighbors; hence it is not so diffuse that treating the medium surrounding an atom as a dielectric continuum appears plausible. Webber's calculations provided a rationale for the remarkable and puzzling observation that, notwithstanding the unfavorable extent of the electron density overlap with neighbors, a pseudohydrogenic Hamiltonian with dielectric screening of the Coulomb interaction does provide a good description of the excited crystal states of Ar, Kr, and Xe. Specifically, the calculations showed that this model becomes accurate when the ratio of the sizes of the lowest hydrogenic excited-state wave function and the Wannier function defining the localized wave function is large, which occurs in the rare-gas crystals because the conduction-band states have nearly free-electron character.

Stimulated by experimental studies of the vibrational excited states of crystalline HCl, Jortner and I developed the formalism for describing cooperative two particle excitations (40), the simultaneous creation of, say, $v = 1$ molecular vibrations at two sites by excitation of the molecular $v = 0 \rightarrow v = 2$ transition; David Chock (41) later generalized this theory to the case when there is more than one molecule per unit cell.

The delocalization of excitation that characterizes exciton states depends on the translational symmetry of a crystal. It then appears senseless to ask if exciton states can exist in a liquid. Yet a liquid does have translational symmetry on a length scale that is large compared to a molecular diameter but small compared to the wavelength of visible light, and the transition dipole–transition dipole coupling that determines the exciton band width and dispersion relation is long ranged. In a conversation on this question that grew more excited as it progressed, Jortner and I realized that if the scattering of the electron by the neighboring atoms or molecules in the liquid was weak enough that a trajectory closes, it can support a bound excited state, and there could be Wannier exciton states in a liquid (42). Estimates of the electron-scattering length in liquid Ar derived from studies of excess electron mobility led us to predict that such states do exist, and the prediction was subsequently confirmed for several rare-gas liquids. When Gregoire Nicolis came to Chicago as a postdoctoral research associate, I asked him to determine if Frenkel excitons with transition dipole–transition dipole coupling can exist in a liquid. He developed an elegant theory of classical polarization waves in a liquid (43) and a specific representation of the exciton band structure of the liquid. The theory was later extended to describe the electronic states of simple liquid

mixtures (44) and nonresonant broadening of impurity spectra in simple liquids (45). With these results as inspiration, Sighart Fischer (46) developed a quantum theory of exciton dynamics in a simple liquid.

FROM RADIATIONLESS TRANSITIONS TO QUANTUM CONTROL

For several years Jortner and I mused about radiationless transitions in isolated molecules, but we could not translate our thoughts and our understanding into a satisfactory theoretical description. The breakthrough came with the development of the Bixon-Jortner model (47), which provided a framework for calculating the rates of radiationless transitions. At the time the Bixon-Jortner theory was published, there were few experimental reports of the rates of radiationless transitions in isolated molecules, and none with vibrational state resolution. To test the theory Ken Spears (48) carried out a systematic study of the rates of radiationless decay from a large number of vibrational levels of the $^1B_{2u}$ electronic state of isolated benzene molecules and showed that the decay rate depends on the character of the initial state, not just its energy as was widely believed to be the case for large molecules. At the same time, and in collaboration with Karl Freed, Bill Gelbart (49) extended the theoretical analysis of the dependence of the decay rate on the character and energy of the prepared state, providing support for the possibility of mode-selective dynamics within a dense manifold of states. Follow-up studies of the rates of radiationless decay from different initial vibronic levels of other aromatic molecules generated extensive evidence for mode-sensitive excited-state evolution (50–57). These results led to new research programs, specifically, the study of collision-induced selective vibrational relaxation of electronically excited molecules (58–66) and the study of the state-selective predissociation of van der Waals molecules (67–71). Concurrently, there were theoretical studies of energy flow among vibrations in polyatomic molecules and of different approaches to unimolecular reaction rate theory (72–79). In turn, these studies led to the examination of the role of deterministic classical-mechanical chaos in unimolecular reactions (80–92), of quantum chaos and its relevance to chemical reactions (93–98), and development of the theory of optical control of molecular dynamics (99–118).

We took the first step in extending the Bixon-Jortner model to the description of unimolecular reactions with Ian McLaughlin (72), who developed a formal analysis of the time evolution of an excited molecule that has a dense manifold of states separating the initial state and the product state and no direct coupling between the initial and product states; the intermediate manifold was taken to have uniform energy spacing and uniform coupling to the initial state and the product state. When Kenneth Kay came to work with me, I asked him to reexamine the problem, and he was able to evaluate the formal expressions for the rate for an important limiting case (77); the results showed that the assumed uniform energy spacing of the intermediate manifold and its constant coupling to the prepared state and the product state led to the coherent flow of excitation amplitude and nonsequential decay. Then Eric Heller (78) showed that replacing the constant couplings with random couplings changes the nonsequential decay to a sequential time dependence that obeys the

phenomenological rate equations. Later work by (Muthu) Muthukumar (79) further extended the theory and showed how a nonrandom distribution of coupling matrix elements influences the time evolution of the excited molecule. Taken together, these results further convinced me that it should be possible, under some conditions, to control the evolution of the molecular excitation.

The Bixon-Jortner model also stimulated other branches of the theory of unimolecular reaction rates. Frank Novak (119, 120) worked out the influence of rotational motion on intersystem crossing in small and large isolated polyatomic molecules, which was used to explain the (lack of) rotational state dependence of the predissociation of ClO_2 found by Steve Michielsen (121). Gelbart developed a formal theory of photoinduced molecular rearrangements, paying particular attention to the case of internal rotation in *cis-trans* isomerization (73, 74). Man Him Hui (51) successfully used the latter theory to analyze the results of an experimental study of the initial state dependence of the competition between energy transfer and *cis-trans* isomerization in styrene- d_1 . Other studies of initial state-dependent rates of single-collision-induced energy transfer (58–66) and of the predissociation of van der Waals molecules (67–71) further supported the view that mode-selective evolution can prevail even when the density of states is fairly large.

In the early 1970s I became aware of the work on deterministic chaos in classical systems. I was stimulated by those works to begin investigations of the relevance to determination of the rate of a unimolecular reaction of classical deterministic chaos and quantum chaos. The line of study associated with classical deterministic chaos involved a number of students and postdoctoral associates: Pierre Gaspard (86, 87) made a detailed analysis of scattering from a classically chaotic repeller and later used similar ideas to examine aspects of unimolecular reaction rate theory (89), David Oxtoby (81) used the onset of overlapping nonlinear resonances to characterize intramolecular energy exchange, Ronnie Kosloff (82) developed a local criterion for the onset of chaos using the transverse curvature along a path on the potential energy surface, and Stephen Gray (83–85) and Meishan Zhao (89, 90) developed an approximate but systematic theory of unimolecular reactions using the separatrix in phase space as the transition state and other new findings in nonlinear mechanics. The line of study associated with quantum chaos started with Sture Nordhom's (93) development of a possible analog of classical KAM (Kolmogorov-Arnold-Moser) behavior in the quantum description of evolution in model systems, the proof by Kosloff (95) that the quantum Kolmogorov entropy of a bounded system is zero (hence no chaos) even though the corresponding classical system does exhibit deterministic chaos, Gaspard's (96, 97) semiclassical and full quantum analyses of scattering from a chaotic repeller, and Gaspard and Nakamura's (98) analysis of the use of level repulsion to characterize quantum chaos. In the course of these studies, several different ways to represent the dynamics of a unimolecular reaction were developed (94), always with a focus on understanding when the statistical picture of RRKM (Rice-Ramsperger-Kassel-Marcus) theory broke down and selective evolution of the excited molecule could be generated.

The goal of achieving control of molecular evolution with laser excitation was frustrated for many years, in part by physical processes such as rapid intramolecular energy redistribution and in part by inappropriate a priori selection of the control

path. The breakthrough in understanding how to control the evolution of a molecule came, almost simultaneously, with the exploitation of wave packet dynamics (99) and excitation path interference (100, 101). Given the purpose of this article, I discuss only the former because it was developed in Chicago. David Tannor (99, 101–103) showed that if a reaction branches to form different products on, for example, the ground-state potential energy surface, transfer of amplitude from that surface to an excited-state potential energy surface and then, after a specified time delay, back to the ground-state surface can be used to control the selection of products. This procedure exploits the fact that the wave packet created on the excited-state surface is not, in general, stationary with respect to the Hamiltonian for that surface, so it evolves by translation and by the dephasing of its components, and a second suitably timed pulse can dump some of the amplitude from the excited state into a selected reaction channel on the ground-state surface beyond any barrier obstructing product formation. The search for optimal pump and dump pulse shapes was formulated as a variational problem within the framework of perturbation theory.

In principle, finding a method for guiding the evolution of a quantum system by coupling it to an external field is an inverse problem: Given the initial and target states and the quantum mechanical equations of motion, one can calculate the guiding field that is required. The physical basis for the calculation of the optimal control field is easily grasped. The pump-dump procedure generates a large concentration of a particular reaction product only if most of the wave packet amplitude on the excited-state potential energy surface is simply and compactly distributed over that product exit channel on the ground-state potential energy surface. That is not the typical case; the evolution of the wave packet on the excited-state surface usually generates a complicated distribution of amplitude. The target state yield is maximized if the amplitude, frequency, and phase of the applied field are varied continuously as the excited- and ground-state wave packets move about, with their variations selected to optimize the transfer of population into the exit channel via the minimization of amplitude cancellation. Kosloff (104) first realized numerically this optimal pulse-shaping scheme and then (with Gaspard, Tersigni, and Tannor) reformulated it as a variational calculation of the spectral content and temporal shape of the field; the mathematical structure of the theory is the same as the optimal control formalism developed slightly earlier, and from a different point of view, by Rabitz (105). Later work by Hui Tang (106) developed a more general formalism.

The set of very good control pulse shapes is unexpectedly rich, so a control field associated with a specified Hamiltonian and target state is not hard to find, but the calculations are tedious, and they provide no clues to the underlying dynamics. It is usual to address both problems by adopting a model Hamiltonian for the system that has fewer degrees of freedom than the real molecule studied (107). Suhail Shah (108) studied the consequences of that reduction and showed, disappointingly, that it leads to a field quite different from that calculated keeping all degrees of freedom of the molecule; hence any such reduction must be viewed critically.

The control of population transfer between states in a molecule is also possible using rapid adiabatic passage techniques (101). Taking this point of view, Mark Kobra (109) developed an extended STIRAP (stimulated Raman adiabatic passage) method

that controls branching to two different reaction products; later work by Jiangbin Gong (110–114) showed that there is an extensive range of situations in which one can use adiabatic transfer to control molecular evolution.

Of course, the greater part of chemistry is carried out in solution. Because of the central role of interference effects in all the control methodologies, at first sight it appears to be futile to seek to control the quantum dynamics of a molecule in the liquid phase wherein frequent interactions are known to generate rapid dephasing. However, studies of vibrational relaxation in the liquid state show that, in the absence of strong specific interactions such as hydrogen bonding, population relaxation occurs on the time scale of tens of picoseconds, whereas phase relaxation occurs on the time scale of picoseconds, implying the existence of a time window for the application of short shaped pulses that can control population transfer between selected states of a solute molecule. Moreover, there are several experimental demonstrations of the active control of molecular dynamics in solution. I asked Mustafa Demirplak to determine if, in the presence of energy-level fluctuations generated by the solvent, transfer of population in a solute molecule can be achieved with a STIRAP process. Because electronic dephasing occurs on the femtosecond time scale, the objective was to control molecular dynamics within the manifold of vibrational states on the ground electronic state. Demirplak (115–118) showed that there can be efficient population transfer, and control of a product branching ratio, under specified conditions for the ratio of the Rabi frequency to the frequency of energy-level fluctuations. Gong (110, 111) later showed that adiabatic population transfer in a liquid remains robust even when decaying states are involved. He also showed that exploitation of transitions to/from a decaying state can enhance selectivity of population transfer.

THE LIQUID METAL–VAPOR INTERFACE

One of the classic problems of mid-twentieth-century condensed matter physics was the lack of understanding of the electrical conductivity of liquid metals. The theory of crystalline metals makes extensive use of lattice symmetry to characterize the delocalization of the valence electrons and, consequently, the electronic band structure. The delocalized electrons are treated as free particles with an effective mass that depends on the band structure, and the conductivity is limited by the interaction between the electrons and the lattice vibrations, which leads to a finite electron mean free path that is typically many lattice spacings. The lack of translational order in a liquid suggests that its electrical conductivity should be much smaller than that of the parent crystal, but it usually differs by only approximately a factor of two. At the beginning of the 1960s, John Ziman (122) started the modern theory of electronic properties of liquid metals. I first learned of this theory during my 1960–1961 stay in Cambridge. When Guy Wilson came to Chicago as a Commonwealth Fellow in 1963, we began experimental studies of the electronic properties of liquid metals; the principal tool was the measurement of the reflection spectrum. The first liquid metals studied were Hg, In, and Bi, over the range of 2–20 eV (123); measurements of the reflectivity of liquid Hg were extended to the infrared by James Boiani (124), then to the far infrared by Aaron Bloch (125). To interpret a reflection spectrum, one usually makes a Kramers-Kronig

transformation of the data and extracts the real and imaginary parts of the dielectric function; these can then be compared with the values determined from ellipsometric measurements carried out on the same interface. In turn, one can use the real and imaginary parts of the dielectric function to test a model of the optical conductivity in the liquid-vapor interface. At that time there was not believed to be any difference between the bulk conductivity and the conductivities in the liquid-vapor and liquid-solid interfaces. When it is assumed that the liquid metal is homogeneous up to a mathematical plane that defines the liquid-X interface, there is a discrepancy between the dielectric functions of liquid Hg calculated from reflection data and from ellipsometric data. Bloch and I (125) proposed that the discrepancy provided evidence for an inhomogeneous distribution of optical conductivity in the liquid-X interface and showed that a simple model based on this interpretation could fit the available data. Howard Lemberg and Daniel Guidotti (126) then developed the theory of surface plasmon dispersion in an inhomogeneous liquid-X interface, and Guidotti (127) carried out experimental studies of the surface plasmon dispersion relation for liquid Hg in contact with alkali halide windows; the experimental results were best fit with a model inhomogeneous liquid-X interface such as that inferred from the comparison of reflectance and ellipsometric data. Although this result hints at an underlying structural inhomogeneity in the liquid-X interface, the wavelengths used in all the experiments are too large to yield any direct information about that structure.

The suggestion that the liquid metal-vapor interface has an inhomogeneous ion core-density distribution was not widely accepted despite the observation that it must be the case. That is, because the valence electrons in the metal are delocalized and the valence electrons in the atoms or molecules that constitute the vapor are localized, there must be a dramatic change in electronic structure and electron distribution across the transition region between the liquid and vapor, and by the Hellman-Feynman theorem, there must be an associated change in the ion-ion interaction and the ion core distribution. Clearly, to get the relevant structural information, we needed both theoretical and experimental advances.

The theoretical advances came in two stages. First, John Allen (128) showed that the nuclear density profile in a jellium-vacuum interface, depending on the bulk electron density, can be a nonmonotonic function of distance along the normal. Although this result is interesting, the jellium model neglects the most important contributor to the liquid structure, namely the nonzero volume of the ion core. The real breakthrough in understanding occurred when Mark D'Evelyn (129, 130) developed a self-consistent scheme to simulate the liquid metal-vapor interface. The formalism underlying the simulation was based on density functional theory; it utilized a pseudopotential representation of the ion core-electron interaction and the Kohn-Sham equation for calculating the electron density distribution. The rearrangement of electron density that follows nuclear motion and the consequent change in the effective interaction of ion cores mediated by the density distribution of the electrons were the input to a self-consistent Monte Carlo calculation of the ion core-density distribution. These simulations predicted that the liquid-vapor interface of a metal is layered, with decaying amplitudes of the layer densities, for three to four atomic diameters into the bulk liquid.

The experimental advance came with the use of the angular dependence of X-ray reflectivity to probe the inhomogeneous density distribution along the normal to the surface on the atomic length scale and grazing incidence X-ray diffraction with total external reflection of X rays to determine the in-plane pair distribution function. We carried out our first X-ray reflectivity studies with a conventional X-ray tube and home-built spectrometer. Bo Ching Lu's measurements (131), started and finished prior to D'Evelyn's simulations, clearly showed that the liquid-vapor interface of Hg was diffuse with a width that could be qualitatively accounted for by Allen's jellium model. Douglas Sluis (132), with the benefit of the results of D'Evelyn's simulations, showed that his later measurements of the X-ray reflectivity from the liquid-vapor interface of Cs were better fit with a stratified interfacial density distribution than with a monotone density distribution. In both experiments the X-ray intensity available from the tube source greatly limited the range of momentum transfer that could be probed, so the fits of the results to models, particularly for the case of a stratified interface, were more suggestive than definitive.

With an improved version of the simulation method, developed by Jonathan Harris and Jan Gryko (133), the density distributions along the normal to the interface and the pair correlation functions parallel to the interface were computed for liquid metals with different valences and different electron densities, and for several alloys (134–145); the results of these more advanced calculations in every case showed that the liquid metal–vapor interface is stratified. And a theoretical study (146) of the electrical conductivity in a stratified liquid metal–vapor interface confirmed the general conclusions reached from the optical experiments mentioned above. The predictions that the atomic distribution parallel to the interface is liquid-like and that the solute in a binary alloy segregates in the interface as a complete monolayer were verified by experiments carried out by a wonderful group of students and postdoctoral research associates using synchrotron X-ray sources (147–151).

Despite the apparent convergence of prediction and observation, the notion that the liquid metal–vapor interface is stratified along the normal was still not widely accepted. Acceptance of the theoretical predictions finally came after Pershan and coworkers (152) published the results of measurements of the reflectivity of the liquid-vapor interface of Ga. The density profile extracted from these measurements is well described by the results of calculations (136).

In the work described above, theoretical predictions preceded experimental measurements. More recently, the reverse situation has occurred. Experimental studies by Bin Yang, Dongxu Li, and Zhengquing Huang (144, 145) led to the discovery that some solutes (e.g., Pb and Tl in Ga) can form a crystalline monolayer in the liquid-vapor interface, a finding that was not anticipated by theory but that the results of simulation studies do reproduce (153); the study of ternary alloys revealed differential surface segregation of the two solutes to an unexpected extent (154–156), not anticipated but correctly accounted for by simulations (153). And experimental studies by Huisman and van der Veen (157) have been interpreted to show that contact between liquid Ga and the 111 surface of crystalline diamond induces dimer formation in the liquid, another finding that was not anticipated by theory. In this case too, after the fact, and with reinterpretation of the role of dimers bonded to the diamond

surface, the results of simulation studies of that system (158) are in agreement with the experimental findings.

EPILOGUE

In this article I present an idiosyncratic and very personal view of my career in physical chemistry, describing some of the subjects that fascinated me but omitting many others (water, theory of freezing, monolayers on liquids, confined colloid systems, and more). As to the science, one of the messages I hope to transmit is that there is much to be gained from a joint experimental and theoretical attack on a problem and from receptiveness to and modification of ideas from other fields. As to personal satisfaction, the message I hope to transmit is that I have been fortunate to be able to combine my avocation and vocation, I have worked with supportive and interactive colleagues at an institution that places the highest value on intellectual inquiry, and I have collaborated with numerous exceptional students and postdoctoral research associates, many of whom have become lifelong friends. What may not have come through adequately in my commentary is the pleasure of doing science, the continuous rejuvenation and challenge afforded by working with students and postdoctoral fellows, the satisfaction associated with solving a problem, and the frustration with failure to find a solution. All my research has been curiosity driven, and often orthogonal to strategic initiatives put forward by funding agencies. Perhaps the greatest long-term impact of the research will be derived from applications developed by others for specific purposes, but I remain confident that fundamental understanding of phenomena and properties is an important contribution to our intellectual heritage, irrespective of the immediacy of practical usage. That I have had the opportunity to do what I have described above has contributed to a fortunate life in physical chemistry.

DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

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I have tried to cite the many contributions of my collaborators in the discussions of the subjects discussed, and I apologize for any omissions. As mentioned above, space limitations have made it impossible for me to describe other subjects that have engaged me and to cite my coworkers in those studies. I am profoundly grateful to all my coworkers, whether mentioned or not.

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