

Scientific autobiography of Louis Brus

I am a member of the Sputnik generation, raised after WWII as the United States dramatically expanded science and technology in response to the Cold War, the molecular biology revolution initiated by Watson and Crick, and the microelectronics revolution. Great-grandfather Brus was a waiter born in France who immigrated to New York in 1868. My father was a businessman who worked his way through university during the Great Depression. I apparently inherited some abstract reasoning ability from my mother, who as a teacher had studied mathematics at the University of Missouri. In high school I had a talent for math and science, and also developed an affinity for tools and machines by working after school and on weekends in the local hardware store. We lived then in suburban Kansas City where I attended Shawnee Mission North High School in Johnson County, Kansas.

In 1961 I went to Rice University where I studied chemistry, physics and mathematics roughly equally. Zevi Salsburg taught a great course in physical chemistry. I also developed a love for history that has stayed with me to this day. Rice was a wonderful place, focused on the undergraduates and offering a rigorous, fundamental, yet broad education. In those days we took classes six days a week. I worked briefly in the lab of Ken Pitzer, and in the summer after graduation I worked in John Margrave's lab doing molecular spectroscopy.

I had gone to Rice on a US Navy scholarship, and was commissioned upon graduation. In my undergraduate summers I was Midshipman Brus, training in the Pacific and Mediterranean fleets. At Rice I loved science, but never really thought I had the native ability to earn a PhD or have a scientific career. After serving in the Navy I thought I would be a businessman like my father. Yet when the opportunity came as a senior to postpone my service and go to graduate school, I jumped at it. I remember thinking that quantum mechanics was so interesting that I would just like to spend some more time studying it before getting on with my life. As an undergraduate I had been more focused on physics, and did not think real chemistry, or chemical synthesis, was important. In retrospect this was a narrow view of reality and opportunity. In our nanocrystal work, synthesis has been the most creative and essential aspect, and the most difficult for me personally.

I went to Columbia University in the Chemical Physics program. My mentor was Richard Bersohn, who had trained as a theorist with van Vleck at Harvard. When I studied with Rich, he had experimental groups in biophysics, and in molecular kinetics and spectroscopy. I did a thesis on the gas phase reaction of excited Na atoms with halogen molecules. Rich had high standards, and was a deep and broad scientist of the old school. He did not closely direct me, yet we discussed all sorts of subjects. At Columbia I was exposed to outstanding faculty and visiting scientists of all types, and learned to approach scientific problems. As I worked on my thesis, the Vietnam War and civil protests in the US were coming to a head, and in the spring of 1968 Columbia was brought to its knees by massive war-related riots. The campus was closed for weeks, and the undergraduates were sent home, but somehow we continued our experimental work.

In the late 1960s my scientific community, the academic physical chemistry community, was focusing on the physics of molecules – structure, dynamics and reactions. The laser was just then first

used in research. We (and especially I) thought every good problem contained a Hamiltonian, and we more or less ignored thermodynamics and longer length scale, macroscopic phenomena. We knew nothing of semiconductors or other materials. Now, the discipline is very different: physical chemists are involved in nanoscience, new materials, and devices, as well as biophysics.

When I received my PhD in early 1969, I was assigned for active duty at the US Naval Research Laboratory in Washington DC. As a (supernumerary) scientific staff officer, I had no established responsibilities and over four years of active duty, I was more-or-less able to form my own collaborations and projects, and to publish research. With M. C. Lin, I worked on exothermic gas phase reactions producing product molecules with vibrational population inversions, for possible infrared chemical lasers. One year was spent doing surface science, and I systematically taught myself solid state physics from Kittel's textbook. This opened my eyes, as I saw how rich solid state phenomena could be. Solids involved the same electronic structure and spectroscopic problems that I had studied in molecules, now just applied to extended systems.

In late 1972 as my time as a Lieutenant in the Navy was coming to an end, Rich Bersohn recommended me to his friends in AT&T Bell Labs, Murray Hill, NJ. It was again a time of trouble in the US, with Nixon's resignation and a subsequent deep recession and surging inflation. Bell Labs had suspended hiring, but just then a brief window opened, and I joined the materials research division under Executive Director W. P. Slichter. A few months later recruiting shut down again, followed by a small layoff in the summer of 1974.

I was in Bell Labs 23 years. When I was hired, Bell Labs was at its apex: it was the best place to do physical science research anywhere, or so we thought. It was exhilarating and intimidating at the same time. How could I possibly do something on same level as all the famous scientists in Bell Labs? Throughout this time I was essentially free to form collaborations and define new projects. I was immersed in a culture of solid state physics, materials and microelectronics, which I slowly absorbed over the years. I did my own experiments in the lab, sometimes with a postdoc, and almost always with Bell Labs colleagues. I never wrote a research proposal or a budget: new ideas were discussed informally with management, and then we just went ahead. The managers, all the way up to Bell Labs President W. O. Baker, were themselves scientists of accomplishment. Looking back, it was a privileged opportunity and existence. Bell Labs was a wonderful yet narrow ivory tower. I could focus on difficult research, yet did not learn other skills valuable in the broader world.

I turned towards condensed phase research. With V. Bondybey I studied a very academic problem: the energy relaxation pathways of excited molecules trapped in solid rare gases at 4 K. This involved both the basic internal electronic and vibrational structure of molecules, and the solid state aspect of energy flow to the local environment. In time I searched for new research opportunities. I developed short pulse laser pump-probe resonance Raman spectroscopy, to study the structure of transient chemical species during solution phase organic photochemical reactions. Here I first came across the semiconductor colloid literature. Organic molecules can be oxidized or reduced when adsorbed on the surface of photoexcited semiconductor particles. Colloids of 5 nm particles have very

high solid/solution interface area in an optically homogeneous liquid medium, thus we used such colloids for transient Raman laser photochemistry.

In late 1982, we noticed that small 4 nm colloidal CdS nanocrystals had a band gap larger than the bulk value shown by larger nanocrystals. This size dependence was not an optical effect in Maxwell's equations; it had to be that the nanocrystal wavefunction itself was size dependent. A related effect, one dimensional quantum confinement in solid state GaAs/AlGaAs superlattices, had been explored a few years earlier. I modeled the three dimensional quantum confinement and electrostatics appropriate for nm-size nanocrystals. A nm-sized nanocrystal has discrete electronic states and in all essential aspects is a molecule.

The quantum size effect was just one aspect of the evolution of molecules into bulk semiconductors with increasing size. We realized this was (and is) an excellent research problem. It was basic research that was important as semiconductor microelectronics pushed down into the nm size regime. I put aside my photochemistry and short pulse laser spectroscopy interests, and began to concentrate on nanocrystals. To do excellent science you must have excellent samples, and we were frustrated with the poor quality and wide size distribution of colloidal nanocrystals. Colloid science had lain fallow since the early part of the twentieth century, and I personally knew very little real inorganic chemistry. Yet colloidal synthesis - bottom-up chemical synthesis - potentially had the great advantage of making a macroscopic nanocrystal product that could be used in devices and new materials. I learned to make smaller particles by precipitation reactions at low temperature in viscous organic solvents. In 1986, postdoc Paul Alivisatos and I apprenticed ourselves to the young organometallic chemist Mike Steigerwald to develop better synthetic methods. The three of us learned to use Lewis Bases to effectively solvate the nanocrystals. Most importantly, we learned to cap the particles with chemically bonded organic ligands, so that capped nanocrystals could be recovered as a pure dry product material. This program of nanocrystal synthesis, structural characterization, and laser spectroscopic excited state studies continued with postdoc Mounji Bawendi. Both Bawendi and Alivisatos took colloidal nanocrystal research into academic life, and the field grew as PhD students were trained.

Bell Labs deserves credit for supporting our small team before this area was recognized as important by the outside world. We had several years to systematically work out basic methods and ideas, and I could knock on the door of any scientist in Murray Hill or Holmdel to discuss new ideas and approaches. As I remember, it was Daniel Chemla in Holmdel who first called our nanocrystals "Quantum Dots". It was a special time and place, and an opportunity that does not come often.

After the invention of the transistor and the laser, Bell Labs shifted its focus from technology more towards basic science. Over time this had the effect of decoupling Bell Labs from the AT&T manufacturing arm Western Electric, and from AT&T itself. In the 1970s and 1980s there were few Bell Labs inventions that brought competitive advantage to AT&T. Moreover, when AT&T was broken up under the antitrust laws, Western Electric had operated in a monopoly fashion for so long that it could not effectively compete. These economic facts progressively diminished Bell labs, despite the best efforts of management to preserve the culture.

Over the past two centuries, curiosity-driven basic research has led, eventually and inexorably, to new technologies that have hugely improved our lives. Yet, discoveries and new knowledge are often unpredictable in their application. For example, we first thought that semiconductor nanocrystals would be used in transistors. Actually, nanocrystals were first used as luminescent tags in biological imaging. Basic research is best supported by society as a whole, and its natural home is in the universities. By its very nature, basic research tends to advance an entire industry, not one specific company.

I returned to Columbia, joining the chemistry faculty, and finding new opportunities and colleagues. My students and I explored the 2D phase diagram of nanocrystals on surfaces, looking at spinodal nucleation kinetics of condensed nanocrystal phases. We also studied the mechanism of the extraordinarily intense single molecule Raman signals which had been reported in aggregated silver colloids. In this work we used confocal microscope methods that Bell Labs colleagues E. Betzig, J. Trautman and T. D. Harris had invented for single molecule and single CdSe nanocrystal luminescence spectroscopy. By a comparison of STM images with Plasmon Rayleigh and Raman scattering images, we found that these intense Raman signals are generated by molecules adsorbed at the junctions between large Ag nanocrystals. Classical theory shows a strong localized electromagnetic hot spot is generated in the junction. There is still much new science to be done here involving the interaction of optically excited, ballistic electron-hole pairs in the Ag with adsorbed molecules. We also started a decade-long effort in single carbon nanotube optical spectroscopy. With colleague Tony Heinz, we discovered we could generate strong resonant Rayleigh spectra from single tubes. Rayleigh spectra could be used for tube identification without depending upon luminescence. Tony and I also discovered that the excited electronic states of semiconductor carbon nanotubes are deeply bound excitons. This result points towards strong direct electron-electron interaction, and multiple exciton generation, in nanotubes and graphene. We are just now exploring the consequences of this realization.

I am deeply honored to receive the inaugural Kavli Prize in Nanoscience, together with Sumio Iijima. Science has been a delight because I have worked with, and learned from, such outstanding mentors, colleagues and research students. In addition, teaching the basic ideas of science to Columbia undergraduates who ultimately go into all walks of life, has been rewarding.

Scientists struggle daily with their experiments, and tend to lose sight of the enormous collective progress of science and technology over the decades. Fred Kavli was born in 1927. Just consider how the world has changed since he was born, during one man's lifetime. Science has created a far better existence for mankind despite war, economic collapse and natural disaster. As Kavli said when a newspaper reporter asked why he supported basic research, "The future will be greater than we can ever imagine".