Electrokinetics: it's in their genes

Work carried out in the Soviet Union 30 years ago by the father-and-son team of Stanislav and Andrei Dukhin now has implications in nanotechnology and microfluidics.

Because they don't delve into the fundamental theories of electrokinetics very often, few analytical chemists instantly recognize the names of Stanislav Dukhin and his son Andrei. Some may vaguely recollect seeing a dimensionless number, the Dukhin number (Du), in research papers, but that's about it. But analytical chemists freely take advantage of electroosmosis (the electrokinetic flow around stationary surfaces) and electrophoresis (the electrokinetic motion of freely suspended particles), for which the Dukhins helped lay down the theoretical foundations.

In their research, the two men focused on the behavior of colloidal systems which, upon cursory examination, seem to have a tenuous connection to microfluidics and nanotechnology. But Juan Santiago of Stanford University says, "Stanislav Dukhin's seminal work is of extreme importance. He developed a wide range of theories and principles which are directly relevant to microfluidics today." And his son's contributions are equally important: "Andrei's work is extremely relevant to micro- and nanofluidic systems, as it provides a fundamental framework for a wide range of phenomena," states Santiago. The ability to explain electrokinetics seems to be ingrained in the Dukhin genes.

Meet the Dukhins

Stanislav and Andrei Dukhin began their scientific careers under the grip of the Communist government in the Soviet Union. The elder Dukhin was born in Kharkov (Ukraine) but moved the family to Kiev, then the scientific, technological, and industrial center of the region.

In the 1950s, there was a burning need in the Soviet Union to develop theories to predict and support experimental observations in colloidal science. Colloidal science was critical for the nation's economic growth because it had implications for a wide range of applications: coal mining, crude oil extraction, water purification, and civil engineering. After training under Iliy M. Lifshits at Kharkov University, Stanislav climbed the ranks of the Ukrainian Academy of Sciences and was drawn to colloidal science by none other than Boris Derjaguin.

COURTESY OF ANDREI DUKHIN

An informal photo of Stanislav Dukhin (right) and Hans Lyklema in Yugoslavia in 1986. About this time, Lyklema informed Dukhin that he was going to name the dimensionless surface excess conductivity number after him.

Derjaguin—known as the "Russian Langmuir" (after Irving Langmuir, the famous American physical chemist)—worked on the stability of colloids and thin films of liquids. His name is now enshrined in the DLVO theory. (The acronym comes from the names of its contributors: Derjaguin, Landau, Verwey, and Overbeek.)

"Derjaguin had an interest in electrokinetics," recalls the senior Dukhin. Derjaguin's contribution to DLVO theory was the idea that particles remain stable in suspension and don't aggregate because of the repulsive forces between them; the repulsive forces depend on the electric surface charge of particles. But at that time, there was no way to calculate the surface charge. Derjaguin was curious about electrokinetics because it was a way to measure the surface charges and ζ-potentials of particles. Derjaguin's urging led the elder Dukhin to work on the polarization effects of particles undergoing electrokinetic motion.

Stanislav established one of the first research groups that studied theoretical colloidal science. He says, "I arranged to have a very strong team of young theoretical physicists and guided this team in the creation of the theoretical background for colloidal science." That group eventually grew into a department in the Ukrainian Academy of Sciences. The group's research developed theories that allowed experimental data to be interpreted. The investigators, for instance, came up with a theory to link properties of particles with speed of particle motion in electric fields. In the course of his research, Stanislav discovered the phenomenon of "electroosmosis of the second kind" and coined the term.

The work he did during this time also earned the honor of having an IUPAC unit named after him, the Du. Hans Lyklema at Wageningen University (The Netherlands) named the dimensionless surface excess conductivity number after the elder Dukhin in one of his books (*Fundamentals of Interface and Colloid Science, Volume II: Solid-Liquid Interfaces*, p 3.208, Academic Press: New York, 1995). The Dukhin number pops up in hundreds of research papers to describe the ratio between a particle's surface conductivity and the bulk electric conductivity of the surrounding fluid; this ratio is then multiplied by the particle's size.

Although the parameter had surfaced in earlier works—it was first described by

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Jacob J. Bikerman when he was at the Research Laboratory of Glass Fibres (*Trans. Faraday Soc.* **1940**, *36*, 154–160)—Lyklema attributed the parameter to Stanislav Dukhin because Dukhin had explicitly described it in his analyses of electrokinetic phenomena. (During his studies, Dukhin called this ratio "Rel" to emphasize the number's relevance in interpreting a large number of electrokinetic phenomena for which surface conduction had to be taken into account.)

In 1974, two of Stanislav's books on electrokinetics, *Electrokinetic Phenomena*, written with Derjaguin, and *Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes*, coauthored with Vladimir Shilov, were translated into English and published by Wiley & Sons. The books received international recognition, and Stanislav was deluged with invitations to various countries. "But I was not a Communist, and I was forbidden to visit other countries," he says. "I could not enjoy this international success."

Not everyone issuing the invitations was easily daunted by the Soviet Union's Communist government. Several Dutch researchers got creative. "I heard this story as a young boy," says Andrei. "They arranged an invitation through The Netherlands' department of foreign affairs. When this high-level invitation came, the Soviet government couldn't decline it anymore." For the first time, Stanislav was allowed to visit a Western country. When the Soviet Union collapsed, he started to travel all over the world.

But the books also caused trouble for the elder Dukhin. *Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes* was smuggled out of the Soviet Union to Israel, where it was translated and reprinted without Dukhin's permission or knowledge. "The Communist government accused my father and his editor of sending knowledge from the Soviet Union to Western countries without their permission," says the younger Dukhin. Fortunately, he says, his father was saved by a group of leading Ukrainian scientists who backed him up in the conflict.

Andrei was inspired by his father and luckily demonstrated a special aptitude for mathematics and science. He went to a school that specialized in training children gifted in the sciences and mathematics and, as a schoolboy, won a number of competitions in those areas.

He soon followed his father in studying electrokinetics. "I was majoring in theoretical nuclear physics at the University of Kiev. I realized that work in this field could only be done as a member of a large group," in which an individual's initiative and contributions were irrelevant, says Andrei. "Theoretical work in colloid science offers much more personal freedom in conducting research—that's what I had learned from my father's experience."

Andrei recalls some of the peculiarities of being a Soviet researcher. Although he and his co-workers published in the mainstream Russian scientific journals, practically all of their papers were translated in the U.S. for publication. "The American government was purchasing copyrights from scientists who published in these scientific journals," he states. "When they published it in English, they paid us some small amount of money. For us, at that time, it was a huge amount of money that we actually received in dollars."

But the translations happened only in the late phase of the Soviet Union's existence, and many of the old papers in the Russian literature remain hidden from Western researchers. Andrei, however, is an avid contributor to Wikipedia, and he suggests that newcomers to the field of colloidal and interface science delve into the appropriate entries to get more information about DLVO theory, electrokinetics, and electroacoustic phenomena.

Crossing borders

The Dukhins' entry into the U.S. involved a coincidence of meeting the right person at the right time. In the 1980s, Philip Goetz, who had founded Pen Kem, Inc., was focusing on dielectric spectroscopy. He needed to ask an expert in the field a few questions, so he contacted Stanislav. They arranged to meet in Germany, "and at the same time, I met his son Andrei," recalls Goetz.

Goetz and the younger Dukhin met a few more times at conferences, so Goetz extended an invitation to Andrei to visit him if he ever made it to the U.S. Dukhin eventually took a short-term teaching position at McGill University (Canada), and when that drew to a close in the early 1990s, he asked Goetz if he could take up the offer to visit. On that visit, "we realized we had a lot of things in common," says Goetz. "So I suggested he stay! He never went home, and we've been working together ever since."

The timing couldn't have been better. It was 1991, and the Soviet Union was falling apart. "There was concern in the U.S. that the dispersion of Russian scientists would create trouble," says Andrei. "So Senator Ted Kennedy introduced a special program to grant green cards to outstanding Russian scientists and encourage them to come to the U.S. I was the third person in this program. My father was in the first 10."

Within two months of submitting the paperwork, the younger Dukhin got his green card. "I want to express my personal gratitude to Senator Kennedy because he provided the opportunity for us to be here and to the American government's initiative," he says.

Peer review draws back the Iron Curtain

In the 1980s, the younger Dukhin worked with Vladimir Murtsovkin on a line of research that, in the early 21st century, caught the attention of researchers interested in electrokinetic phenomena in microfluidics and nanofluidics. In their work, Dukhin and Murtsovkin described the flow field a particle generates around itself on the micrometer and submicrometer scale and how this flow field affects a particle's interactions with its neighbors.

"The hope was that it was something that could be seen and affect the macroscopic scale of colloids. I don't think they were imagining that those flows [were] for anything in a microfluidic device," says Martin Bazant of the Massachusetts Institute of Technology. "Now, we use those flows for mixing or pumping fluids on the micron scale."

The Dukhins credit Bazant for unearthing their work and introducing it to the modern Western scientific literature. In the late 1990s, Bazant and his colleague, Todd Squires, now at the University of California Santa Barbara, were thinking about nonlinear electroosmotic flows around electrodes with ac voltages. They submitted a paper to the *Journal of Fluid Mechanics*, and although the paper got good reviews, one reviewer pointed out that some of the phenomena they described were already published in the Russian scientific literature (that reviewer later revealed himself to be Stanislav Dukhin). Sure enough, when Bazant and Squires dug through the literature, they came across the work Dukhin and Murtsovkin had done in the 1980s.

"I found that working in classical fields like electrokinetics, it's hard to find anything that people have not considered at some point in the past. But things get forgotten if they don't have an immediate impact or application," says Bazant. "I did spend several years giving talks about the work all around the world, hoping that somebody would say that it reminded them of some work somebody else had done. But that didn't happen."

So when the reviewer of the paper pointed him toward the work by Dukhin and Murstovskin, Bazant felt reassured. He says, "When you find a reference or discover someone else has found something similar in the past, it builds confidence."

Bazant does state that there are some important differences between Dukhin and Murstovkin's work and what researchers like him are trying to do today. "I give them a lot of credit for being first. But on the other hand, the kinds of problems people were considering up to that time and during that time in electrokinetics were very different. At that time, there was no ability to microfabricate anisotropic particles or special geometries at the microscale. Even if you could design them, there was really no way to observe what was going on at that scale," he says. "What you cared about was macroscopic behavior of colloids."

The Dukhins say they are occasionally startled by where their papers are cited. For instance, they were surprised when Bazant went back after the review and dug up their body of work from the Russian literature and cited it in his papers (see, for example, *J. Fluid Mech.* **2004**, *509*, 217–252). "From time to time, we get some surprising applications and references," says the younger Dukhin. "For instance, when you search for 'Dukhin number', some papers come up where we don't have any clue or knowledge of these scientific groups."

But the Dukhins say, upon reflection, that it's not surprising that their work in the Soviet Union has bearing on modern research endeavors. "Many people come to nanotechnology not knowing anything about colloidal science. They think they will synthesize small particles, put them in a liquid, and be fine and done with it," says Andrei. "They don't realize that preventing these small particles from aggregating is an enormous problem."

Colloidal scientists have grappled with the problem for decades. Along the way, they have developed a body of literature full of theories and experiments that suggest ways for stabilizing these systems.

Keeping busy

Stanislav worked for 10 years at the New Jersey Institute of Technology as a research professor and also collaborated with a company called Novaflux. Although he has now retired from his academic position, he continues to consult for Novaflux, where he is helping to come up with a system for cleaning narrow tubes, such as in medical endoscopes.

Goetz and Andrei initially worked at Pen Kem, where the focus was on optical methods to characterize the charge on colloidal particles. They soon realized that the methods were pretty limiting. For instance, the techniques didn't work with concentrated, opaque samples. So "we developed an acoustic spectroscopy technique which allows us to work with very concentrated systems," says Goetz. The men founded Dispersion Technology, Inc., to market the technology. "This technique has been very useful for many types of systems, whether it be a ceramic, slurry, paint, pharmaceutical preparation, or food product. All these things can be handled directly, as is, without dilution," explains Goetz.

The younger Dukhin is active with the company that he and Goetz now run, and he continues to publish in the scientific literature and travel the world giving talks. Intrigued by the research that is called "microfluidics" these days, he has been attending sessions at conferences like the Pittsburgh Conference (Pittcon) to learn more about the field. Although some aspects of the research endeavors seem novel and cutting-edge to him, Andrei says, "If you define microfluidics as the motion of liquid on small dimensions, well, then I have been involved in this field for almost 40 years."

—Rajendrani Mukhopadhyay