

Preface

Michel Mandel 65

Michel Mandel has never been one to shy away from those problems in physical chemistry many would consider particularly tenacious and sometimes even downright unresolvable. Throughout his scientific career he has consistently devoted his none too considerable energy to elucidating complex fields of research many investigators have merely dared to touch. With avid interests ranging from statistical physics to biophysical chemistry, from pure theory to intricate experimental technique, Mandel has played an active role in breaking down the awkward historical barriers between physics and chemistry, both worldwide and in The Netherlands.

Mandel studied chemistry at the Université Libre in Brussels. After specializing in physical chemistry in his thesis work under the guidance of Professor L. de Brouckère, he received his Ph.D. degree in 1955. He became an associate professor at the University of Leiden in 1958 and was appointed full professor of physical chemistry in 1961. He has never severed his roots for he has been a visiting professor at the Université Libre since that same year.

Michel Mandel is well known for his energetic personality as is evidenced in his keenness for heated discussion, so it is not surprising that he has enjoyed intense relationships with many scientists abroad. He was a visiting professor at the Weizmann Institute, the University of Trieste and the University of Leuven. His idiosyncratic blend of persistently seeking scientific truth and ardour for thorough experimentation has also engendered cordial relations with many Japanese scientists culminating in an extended visit to Japan in 1980 which was sponsored by the Japanese Society for Progress in Science. Closer to home Mandel was recognized for his varied contributions to the fields of dielectrics and polyelectrolytes when

he received an honorary degree from the University of Uppsala in 1985. He has also been active in the politics of science, having been a lively member of the IUPAC Macromolecular Division.

The title of Mandel's thesis reads: "Propriétés diélectriques de solutions aqueuses d'électrolytes forts." It already alludes to his two major lifelong passions: the dielectric properties of complex fluids and the physical chemistry of polyelectrolytes. A large portion of what we know and understand in both disciplines is in no small measure due to his thorough investigations. I shall attempt to summarize several highlights in Mandel's career within the context of these two lines of research.

Early on, Mandel already displayed an aptitude for both physics and chemistry, for both theory and experiment. In particular, he was intrigued by the dielectrics of all kinds of fluids: liquids and gases, electrolytes, solutions of polymers and polyelectrolytes. On the experimental side he began to tackle a very hard problem of an applied nature: the precise measurement of the permittivity of conducting fluids (the subject of his thesis). But Mandel wasn't satisfied with measurement for its own sake, he wanted to address another notoriously difficult task: how does one glean molecular information from the macroscopic permittivity. This inclination led him to write a classic paper with Mazur on the statistical mechanics of electrical polarization.

By 1960 Mandel was well prepared for a major effort to comprehend the dielectric properties of polyelectrolytes. In the fifties the field of polyelectrolytes had been emerging rapidly thanks to the pioneering insight of Fuoss, Katchalsky and Lifson. It had become abundantly clear that polyelectrolytes possessed their own peculiarities setting them apart from both simple electrolytes and polymers. So it was quite logical for a novel

expert in the dielectrics of conducting fluids to turn to this waxing discipline. In a renowned paper published in 1961 Mandel attributed the gigantic dielectric increment of polyelectrolytes to the polarization of “condensed” counterions along the polyion contour. This idea made a great deal more sense than the competing theories of the Maxwell–Wagner type. At the same time the new insight warranted a comprehensive investigation of the permittivity as a function of a variety of polyelectrolyte variables which was carried out by Mandel and Jennard on polymethacrylic acid and polyvinylamine. They found definitive evidence for the existence of at least two dispersion regions, the one of lower frequency being in reasonable accord with Mandel’s theory.

By then Mandel had become permanently enamored of polyelectrolytes in their own right. In several key studies Leyte and Mandel gave a quantitative interpretation of the titration curve of polymethacrylic acid in terms of a conformational transition between two states. Mandel’s interest in ion binding led to their study of the polyion’s complexation with bivalent ions. Later on he developed a remarkably simple empiricism for the titration of weak polyacids not undergoing conformational transitions.

The second dispersion region at higher frequencies had remained a nagging, elusive riddle, so in the seventies Mandel renewed his attack on it in an exhaustive study with Van der Touw. They took on three major experimental hurdles with a much improved and more sensitive version of a Schering type bridge developed by Mandel early in his career: (1) the almost insignificant phase angle of conducting fluids below 1 MHz; (2) the awkward polarization at the surface of the electrodes; (3) the inevitable nonideality of the plane condenser. Using in addition a Boonton bridge that had been adapted for conducting liquids at Mandel’s lab, they were able to measure with some confidence the permittivity of polyelectrolyte solutions between 10 kHz and 100 MHz. Rodlike Alfalfa Mosaic virus gave one dispersion, flexible polyelectrolytes like polystyrene sulfonate and polyacrylic acid gave two. Hence, in an often cited paper they explained the second dispersion in terms of a local length scale determined by potential barriers along the chainlike contour.

Even though this view is nowadays often contested, their analysis established beyond doubt that dielectric studies at higher frequencies probe polyion structure.

Van Beek and Mandel used the same bridges to investigate simple electrolytes. They were the first to demonstrate unequivocally the peculiar dependence of the static permittivity on the concentration. At low concentrations the permittivity increased with the ionic strength in complete agreement with the classic Debye–Falkenhagen theory. By contrast, at high concentrations the permittivity decreased which was an enigma. As it turned out Mandel was one of the rare scientists with whom Onsager was willing to communicate so Mandel sent him the results. Onsager’s startling reply was that he had already developed unpublished ideas on so-called kinetic depolarization conjecturing the anomaly! (This was to become the famous Hubbard–Onsager theory).

During the period that I worked at Mandel’s laboratory (in the late seventies and early eighties) one of his prime concerns was the configurational statistics of polyelectrolytes. He launched a methodical investigation of the (possible) scaling relations for semidilute polyelectrolytes employing osmometry, static and dynamic light scattering, electric birefringence and yet more sensitive dielectric equipment. This is currently still a turbulent field of activity.

Mandel has always been acutely aware of the implications of new developments in physical chemistry for the characterization of biopolymers. This is of course reflected in his long editorship of *Biophysical Chemistry*. Dozens of his papers deal with macromolecules of biological origin; several of these careful studies are quoted often.

Michel Mandel’s approach to science is, I think, best qualified by the connotation “skeptical” in the philosophical sense. It explains his long-term ambitions and his determination to uncover facts no matter how long it takes.

Fortunately for us, Mandel’s retirement doesn’t mean physical chemistry has lost its lustre for he is still active as ever, ready to embark on new tough problems, quick to point out the merits and shortcomings of some wild idea or experiment.