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CONDENSED MATTER PHYSICS

Obituary

Karl Heinzinger and computer modelling of water and aqueous solutions

Photography courtesy of Dr. Monika Weidmann

This brief essay commemorates Karl Heinzinger, one of the pioneers in the field of computer modelling of fluid systems, particularly of water and aqueous electrolyte solutions in the bulk phase and near interfaces. Karl Heinzinger died peacefully on January 14, 2023, after a short illness. We express our deepest condolences to his family, colleagues, and friends.

Karl Heinzinger was born on December 25, 1930, in Klein-Auheim, Landkreis Offenbach, Hessen, Germany. In 1951 he started to study physics at the University of Frankfurt/Main and in 1957 received the diploma (Diplom Physiker) from the Institute of Applied Physics. His research career began as a PhD student under the guidance of Alfred Klemm at the Max-Planck Institute for Chemistry in Mainz. In 1961 he received his doctorate from the University of Mainz. He then spent two years, 1962 to 1964, as a Postdoctoral Research Associate at the Chemistry Department of the Brookhaven National Laboratory, Upton, N.Y., USA. In 1964 he came back to Germany and was appointed to head the Physical Chemistry group at the Max-Planck Institute for Chemistry (Otto-Hahn-lnstitut) in Mainz.

The first scientific projects of Karl Heinzinger were concerned with the heat capacity of ortho- and para-hydrogen at very low temperatures. Experimental research on isotope effects in water and aqueous solutions, but also in crystal hydrates, was prevailing during the early stages of his scientific career.

Starting in 1973, Karl Heinzinger and his group turned their attention to the emerging methods of computer modelling, focusing on water and aqueous electrolyte solutions. This activity mainly aimed at investigating the properties that could not easily, or not at all, be obtained experimentally and were thus little known by researchers at that time. The structures of the hydration shells of cations and anions and their impact on the dynamic properties of the electrolytes were for the first time investigated in some detail. In 1983, in collaboration with Philippe Bopp and Gábor Jancsó, Karl Heinzinger suggested a non-rigid

water model — the Bopp-Jancsó-Heinzinger or BJH model of water [1], which was used to investigate the shifts in the vibrational frequencies of the water molecules in the solutions. Even though quite specialized and computationally demanding, the model became rather popular in the physical-chemistry community interested in water and electrolytes as well as, more generally, in computer modelling of aqueous media in various (more applied) fields of scientific knowledge (at this time, there are almost 500 citations according to ISI Web of Knowledge). Studies based on this model have for the first time highlighted the significant changes in the internal structure of the water molecules that belong to the hydration shell of the cations Ca^{2+} and Mg^{2+} due to the interaction with these ions [2].

This type of research was soon extended in Heinzinger's group to include other solutions such as the aqueous solution of methyl alcohol [3], metal-ammonia solutions [4] and then mercury-electrolyte and platinum-electrolyte interfaces [5] as well as water in zeolites [6] and the combination of analytical theory and computer simulation [7], among some other systems. A significant feature of such studies carried out under Heinzinger's supervision is, from early on, the combination of computer simulation techniques with quantum-mechanical calculations of the solute-solvent interaction potentials, constructing in this way potential models that would allow systematic studies (or 'computer experiments') at various ionic concentrations, temperatures, and densities (pressures), often in tight collaboration with experimental groups. Besides basic science, Karl Heinzinger thus became interested in various practical aspects, including geological, related to the study of aqueous electrolytes at high pressures and temperatures. He summarized his work in a number of review articles on different aspects of computer simulations of electrolyte solutions and also became a coauthor of an application-oriented textbook on molecular dynamics [8] written in German.

In 1991 the journal Zeitschrift für Naturforschung, where most of Heinzinger's early works were published, made a special issue [Z. Naturforsch., 46a (1-2)] in honor of Karl Heinzinger's sixtieth anniversary. The range of topics of the work published was impressive, showing in many ways the interplay between experiment, theory and computer simulations in the study of electrolyte solutions and liquids in general and in many related areas.

Karl Heinzinger retired in 1996 (but remained active for quite some time afterward). On the occasion of his retirement there was a meeting, attended by many of his closest collaborators, colleagues, and students. The photo is taken in front of the old Max Planck-Institute in Mainz. During his entire career

Karl Heinzinger sought to establish and maintain scientific contacts and collaborations with scientists from around the world. He initiated the very first exchange agreement between the Deutsche Forschungsgemeinschaft (DFG) and the Hungarian Academy of Science (MTA), which allowed many scientists from this county to come to Mainz for longer or shorter visits. Through these visitors he exerted quite some influence on physical chemistry research in this country. This influence was also exerted through the European and Japanese Molecular Liquids Groups (EMLG/JMLG), of which he was one of the oldest and keenest members.

In Ukraine Karl Heinziger closely collaborated with researchers from the Bogolyubov Institute for

Theoretical Physics (Kyiv) and the Institute for Condensed Matter Physics (Lviv) both belong to the National Academy of Sciences of Ukraine. In 2015 Karl Heinzinger was conferred the title of Doctor Honoris Causa of the Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine for pioneering studies in the field of electrolyte solutions by means of molecular dynamics.

This mix of Hungarians, Ukrainians and many other, senior and junior, visitors (from China, Japan, Poland, Russia, Thailand, USA) created a unique atmosphere in the research group, which is fondly recalled by everybody who had the privilege to be a member. Not only were several successful scientific collaborations spawned among the alumni, but many lifelong friendships also arose in that time. Having created and maintained such a friendly, and yet stringent working atmosphere is not the least of Karl Heinzinger's merits. He was always willing to listen and discuss, and his advice was always sympathetic. His scientific honesty and integrity were exemplary; he thus became the scientific mentor for many of us.

Besides his commitment to science and research, Karl Heinzinger was also socially engaged. For many years he was the head of the Mainz section of Technisches Hilfswerk (THW), the federal civil protection organization of Germany. In this capacity he was posted several times to Africa to help after natural disasters.

Finally, we would like to summarize some of the most important messages left to us by Karl.

- ✓ When well founded and carefully used, computer simulations will help to understand, describe, and predict the properties of condensed phases which cannot be studied in experiments.
- ✓ Scientific rigor says, be careful, and do not get carried away by wishful thinking.
- ✓ Know the limits! Even though, drastically simplified models can be useful and will yield insight, e.g., the flexible water model in conjunction with classical mechanics to study the influence of cations like Ca^{2+}, Mg^{2+} on the intramolecular structure and dynamics of the water molecule.
- ✓ Combine, when possible, computer simulations with quantum mechanical calculations.

As a consequence of the breathtaking evolution of the field of computer simulations and its expansion into almost every field of science, many of these early studies may seem to be less important nowadays. However, many of the essential lessons learned on water and its properties remain. We will always remember Karl Heinzinger for his ceaseless efforts to focus our views on science in a friendly yet determined manner, very much in the spirit of William of Ockham's razor and the probably incorrectly attributed to Albert Einstein phrase "Simplify as much as possible, but not more than that!"

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