Preface

Ions are fascinating chemical species. They are ubiquitous in nature and play a fundamental role in many essential ecological, biochemical, physiological and technological processes. Under the conditions of pressure and temperature prevailing on earth, ions would probably not play such an important role if their presence was not associated with that of large amounts of water. In the absence of water and at room temperature and ambient pressure, the long-ranged and extremely strong Coulombic interactions existing between oppositely-charged ions promote their aggregation into solid salts (exceptionally ionic liquids). The magnitude of these interactions is such that gas-phase ions are essentially non-existing species at equilibrium. Yet, in polar solvents (prominently water), dielectric screening of these direct Coulombic interactions by the dipolar solvent molecules represents an almost equally strong opposing force that permits, in synergy with entropic effects, the existence of solvated ions as dissociated entities. The properties of ions in solution crucially depend on the nature and magnitude of these solvation forces, and their experimental and theoretical characterization is thus an essential step towards the understanding of ionic properties. The key quantity accounting for the magnitude of ion-solvent interactions, in the simplest context of an individual ion at infinite dilution in a given solvent, is the corresponding *single-ion solvation free energy*. Knowledge of the pressure and temperature dependence of this property also gives access to all other derivative thermodynamic solvation parameters, *e.g.* single-ion solvation enthalpy, entropy, volume, heat capacity, compressibility or expansivity, as well as corresponding partial molar variables in solution. However, this fundamental quantity can be defined in two distinct ways.

The *real* single-ion solvation free energy corresponds to the reversible work associated with the hypothetical process of transferring the ion from the gas phase to the solution environment. Although this process is hypothetical in the sense that it cannot be carried out directly in an experiment involving a single ion, the corresponding free energy can still be deduced from the results

of appropriate electrochemical and spectroscopic measurements. However, the real solvation free energy encompasses two physically very distinct contributions: a *bulk* contribution, arising from the interaction of the ion with the surrounding solvent molecules, and a *surface* contribution, arising from the electric potential jump upon entering the solvent. In contrast, the *intrinsic* single-ion solvation free energy only accounts for the bulk component. This free energy is in principle of greater theoretical value compared to the corresponding real quantity, because it does not intermingle surface and bulk effects. Unfortunately, the intrinsic solvation free energy cannot be determined on the sole basis of experimental data. Its evaluation requires the introduction of some *extra-thermodynamic assumption*, namely an apparently reasonable but not strictly provable postulate concerning the physics of the bulk solvation process or of the solvent surface properties. Note that the above issues only affect *single-ion* solvation parameters. The need to distinguish between real and intrinsic quantities disappears when corresponding sums over overall neutral sets of ions (salts) are considered instead. These sums are readily available by means of thermodynamic cycles relying on an appropriate combination of calorimetric, electrochemical or spectroscopic measurements.

The problem of the experimental or theoretical evaluation of intrinsic single-ion solvation free energies, as well as of corresponding derivative thermodynamic solvation parameters, has represented a challenge to the physical chemistry community for more than one century, and cannot be claimed to have found a satisfactory solution even nowadays.

From the *experimental* point of view, the problem amounts to determining *conventional* (relative, *e.g.* taking the proton as a reference ion) or *real* single-ion solvation free energies, both accessible experimentally, along with either of three solvent-dependent quantities: the *air-liquid interfacial potential χ_{svt} of the pure solvent*, the *intrinsic absolute potential $\mathcal{V}_{H,svt}$ of the reference hydrogen electrode in this solvent*, or the *intrinsic solvation free energy $\mathcal{G}_{H,svt}$ of the proton in this solvent*. Similarly, the pressure or temperature derivatives of these quantities, along with corresponding conventional or real single-ion solvation parameters, would give access to all other intrinsic derivative thermodynamic solvation properties. However, due to the constraints imposed by the electroneutrality of macroscopic matter at equilibrium and by the unavoidable presence of polarization effects at interfaces, these three quantities are experimentally *elusive*, *i.e.* neither of them can be evaluated without the help of some extra-thermodynamic assumption. Unfortunately, considering the case of water at atmospheric pressure and room temperature, the use of different experimental approaches along with distinct (apparently equally reasonable) assumptions leads to a very large uncertainty range on the order of $0.5 - 1.0$ V (potentials) or $50 - 100$ kJ·mol^{-1} (free energy) in the estimated values for the above elusive quantities.

From the *theoretical* point of view, three main approaches have been employed to evaluate intrinsic single-ion solvation free energies, as well as corresponding derivative thermodynamic solvation parameters: continuum-electro-

statics calculations, classical atomistic simulations, and quantum-mechanical computations (calculations or simulations).

On the low-resolution end, *continuum-electrostatics calculations* (Born model and modified versions thereof) typically represent the ion as a rigid non-polarizable sphere and the solvent as a continuous (structureless) medium characterized by an infinite extent and a linear dielectric response. These approaches have a long history and the merit of providing a simple (often analytical) and qualitatively correct framework for intuitive reasoning, as well as a solid baseline for the discussion of more complex effects. However, their major shortcomings are to neglect the microscopic structure of the solvent molecules and the specific details of ion-solvent interactions, and to rely on the ill-defined concept of an ionic radius. As a result, these methods fail, even after application of various corrections, to provide a quantitative description of ionic solvation.

In the middle-resolution range, *classical atomistic simulations* represent the ion in solution as a system of classical point particles (atoms) interacting according to an empirically designed and calibrated potential energy function (force field). These methods have been applied both to the direct calculation of intrinsic single-ion solvation free energies and to the evaluation of the air-liquid interfacial potential of pure solvents. They should in principle be more accurate than continuum-electrostatics approaches, by accounting for the microscopic structure of the solvent molecules. However, in contrast to the latter methods, the averaging over solvent configurations must be carried out explicitly and the considered system is now of finite extent (*e.g.* liquid droplet or periodic computational box). The first difference does not represent a serious problem in the context of ionic solvation. Given the computational resources available at present, the sampling of a statistically representative number of configurations can easily be achieved, and simulations are able to provide a direct and accurate connection between molecular and thermodynamic properties *via* statistical mechanics. However, the second difference introduces serious methodological issues regarding the choice of boundary conditions, the approximate treatment of electrostatic interactions, and the evaluation of electrostatic potentials based on the sampled configurations. These issues have, up to recently, prevented the obtension of consistent results from atomistic simulations. Fortunately, the situation has changed in the past few years with the realization that the corresponding errors could be corrected *ex post*, so as to achieve methodological independence in the simulation results (*i.e.* consistent results across various choices regarding the three above issues). This achievement, which takes the atomistic approach to the same level of consistency as the Born model, opens new perspectives for the reliable application of atomistic simulation techniques to the investigation of problems related to ionic solvation. Still, the outcome of these calculations remains affected by three major sources of error: the mean-field treatment of electronic polarizability (in most calculations), the approximate representation of van der Waals interactions (functional form and combination rules)

and the dependence of the results on the ion-solvent van der Waals interaction parameters. The latter parameters can be viewed as representing the atomistic analog of the ionic radius used in continuum-electrostatics calculations, and their calibration involves a similar ambiguity. Nevertheless, it is possible that the results of atomistic simulations concerning a large spectrum of ionic properties, including but extending beyond single-ion solvation free energies, provides in the near future a reliable approach for the accurate evaluation of the above elusive quantities. The corresponding extra-thermodynamic assumption will be termed in this book the *atomistic-consistency assumption*.

Finally, on the high-resolution end, *quantum-mechanical computations* represent the ion in solution as a many-particle system characterized by a wave-function obeying the Schrödinger equation, given a Hamiltonian encompassing Coulombic interactions between all the elementary particles involved. These methods have also been applied both to the direct calculation of intrinsic single ion solvation free energies and to the evaluation of the air-liquid interfacial potential of the pure solvent. They have a bright future and the potential to definitely settle the problem by providing the framework for formulating what will be referred to as the *ultimate extra-thermodynamic assumption*. As first-principles (at least in principle) approaches, they promise to enable the calculation of the three above elusive quantities based on the most accurate physical model available nowadays, and without relying on the specification of ambiguous quantities such as ionic radii or ion-solvent van der Waals interaction parameters. This calculation nevertheless relies on the acceptance of a definition for partitioning the charge density (nuclei and electrons) into bulk and surface components. That such a definition is required can be viewed as the ultimate cause for the need of extra-thermodynamic assumptions in the determination of the three elusive quantities. Unfortunately, these approaches have the major shortcoming of being computationally expensive. This high computational cost results in practice nowadays in severe restrictions concerning the system size, configuration sampling, basis-set size and treatment of electron correlation. It may be reduced by interfacing a quantum-mechanical treatment of the ion and its first solvation shells with a classical atomistic or/and continuum-electrostatics approach for the surrounding bulk solvent. However, even in this case, the computation of single-ion solvation free energies represents a considerable challenge, and the necessary approximations may still for a while compromise the gain in accuracy expected from a more fundamental treatment of the problem.

The purpose of this book is to provide the reader with: (*i*) a clear picture of the concepts, definitions and difficulties underlying the problem of evaluating single-ion solvation free energies, as well as corresponding derivative thermodynamic parameters, *via* experiment or theory; (*ii*) an overview of the various experimental approaches employed to date; (*iii*) a discussion of the various theoretical approaches employed to date, with a particular focus on classical atomistic simulations; (*iv*) an extensive and consistent compilation of experimental data regarding ionic solvation, in the restricted context of alkali

and halide hydration. As a compact account (experimental and theoretical issues, physical concepts, methods, results, data and literature) of a relatively complex field with both a very long history and a significant share of subsisting ambiguities and controversies, it is the hope of the authors that this book will provide the reader with a useful and solid basis for further investigations in the area. Towards this goal, a particular attention has been paid throughout this text to: (i) the clarity and consistency of the employed terminology and mathematical notation, including the introduction of new terms, acronyms or symbols, whenever necessary; (ii) the critical examination of the physics underlying key concepts, semantic, terminological and symbolic ambiguity representing here also an important source of complexity, inconsistencies and mistakes in the field; (iii) the consistent application of a clearly defined thermodynamic standard-state convention, alternative standards representing another important source of confusion and errors; (iv) the extensive citation of relevant literature sources, including over 2300 references spanning more than 100 years of research; (v) the establishment of appropriate connections between experimental and theoretical research, encompassing both historical and front-edge components.

Since the presented material was initially planned for a review article rather than for a book (see below), the text is intended for a linear rather than modular reading. However, readers who are primarily concerned with experimental or theoretical aspects, respectively, might decide to focus on Chapters 2 and 5 or on Chapters 3 and 6, respectively, in first priority, Chapter 4 providing common background information. Readers who are exclusively interested in an experimental data compilation concerning alkali, halide and proton hydration properties (including estimates for the three above elusive quantities) will find their happiness in Chapter 5, and in particular in Section 5.19, where recommended values are provided based on an extensive account and analysis of the available literature.

One thing should be stated once (and never mentioned again): we never really intended to write this book, we rather let ourselves be "sucked" into this task. As many (good and bad) things in life, all started "accidentally", when we were asked in February 2007 by the editors of the *Proceedings of the Royal Society of Chemistry* (RSC) to write a review about the theoretical calculation of ionic solvation properties. In March 2009, the planned date for the manuscript delivery, the "review" was already 400 (double-spaced) pages long, and there was no way it could be published as a single (even long) article. Thus, we asked RSC if they would consider publishing it as a book instead, which they kindly agreed to do. With this sort of birth, it is no surprise that the book turned into a (multi-)recidivist in terms of broken deadlines. Yet, almost two years (and quite some work) later, the book was ready to be published in the present state. In addition to the initially planned theory overview, it also included a significant experimental component. In fact, the simultaneous discussion of experiment and theory appears to be essential in this area, considering that the two aspects are so intimately intertwined.

Writing a scientific book of this kind is a massive effort, and the authors would like to express their deep gratitude to a number of persons for their help and support, before and during the writing process. The theoretical part of this text concerning classical atomistic simulations relies largely on the recent achievement of calculating methodology-independent single-ion solvation free energies. This success is a result from the remarkable scientific work of (in chronological order) Nathan Baker, Wolfgang Weber, Christine Peter, Michael Bergdorf and Mika Kastenholz (in addition to the authors' own contributions). A wealth of information concerning this theoretical part has also been gathered from insightful discussions with (in chronological order) Wilfred van Gunsteren, Alan Mark, Paul Smith, Andrew Torda, Brock Luty, Andy McCammon, Adrian Elcock, Gerhard Hummer, Herman Berendsen, Thomas Hofer, Nico van der Vegt, Benoit Roux, Joost van de Vondele and Chris Oostenbrink. The authors are also very grateful to Wilfred van Gunsteren, head of the group for Informatikgestützte Chemie (IGC) at ETHZ, for being both a leading and inspiring scientist in the area of molecular simulation, as well as the laureate of the Golden Tricycle Award 2009. Thanks to Wilfred, the IGC group is at the same time a highly stimulating and a socially extremely pleasant (family-like) working environment. This wonderful atmosphere was and is also the fact of all past and present IGC group members (including Jolande, Prisca, Daniela, Ana and Carmen), but they are too numerous to be thanked here individually. A special mention, still, for the subgroup of "Phil's angels", Cristina Pereira, Lovorka Perić-Hassler, Halvor Hansen, Bruno Horta and Monika Laner. Many thanks also go to Peter Chen, Markus Reiher, Beat Meier and Wilfred van Gunsteren for being the very first readers of (an early version of) this book, and for their insightful feedback on these pages. The editorial team at RSC also deserves our acknowledgments for their kindness and professionalism. First Graham Webb and Robert Eagling, for their patience with our never-to-appear review article. Then Janet Freshwater, Alice Toby-Brant and Katrina Harding for their support in designing the soon-to-appear book.

Maria Reif would like to dedicate this book to her parents. She is thankful to all the people who showed continuous and motivating interest in the progress of the book. She thanks Cristina, Lovorka, Halvor and Bruno for the unforgettable time in IGC. She would also like to express her gratitude to the MMS group of Chris Oostenbrink at BOKU University Vienna, where she was during the finalization of the manuscript, for the very nice and helpful atmosphere.

Philippe Hünenberger would like to dedicate this book to his four spiritual fathers (for one, also biological) in the various areas of Natural Sciences, Léopold Hünenberger (Gymnase de Chamblandes, Lausanne) for Chemistry, Marco Nicollerat (Gymnase du Belvédère, Lausanne) for Mathematics, Christian Gruber (EPFL) for Physics, and Wilfred van Gunsteren (ETHZ) for Computational Chemistry. This book is dedicated as well to his "little" family, Valérie, Achille and Gaspard. Without them, even the best science would

have no sense, and life would be dangerously imbalanced towards the intrinsic rather than the real side. Gratitude also extends to his "larger" family (Léo, Gisèle, Fabien, Anne-Catherine, Babette, Germain, Suzanne, Marie-Line, Martine and Brigitte, and their own families), and to his friends of always (Marc-Aurèle, Sylvie, Zoltan & Agnès, Xavier & Judith, Roberto & Thereza, Wolfgang & Jelka, Nicolas & Sylvie, Eric, Vincent & Karin, Chantal & Catherine, François & Gabrielle, Franca & Jens, Daniel & Karin, Kathia & Dieter, Karin & Sarah, Jozi and Zrinka, and their own families) for their love, care and steady support in life.

And, when they are at it, the two authors of this book would also like to express their gratitude to each other for what has been a beautiful and inspiring four-years scientific collaboration, often as thrilling as a detective investigation on a particularly intricate case, and sometimes as frustrating as a crazy race through an endless maze.

Last but not least, the authors would like to thank Ana Nedić-Eigenmann for designing the cover picture of this book and providing the funny ion drawings appearing at the end of each chapter. These drawings are meant to summarize the reader's (expected) state of mind after reading the preceding text, and as an invitation to turn the page. With a wink. Just like the one on the next page...
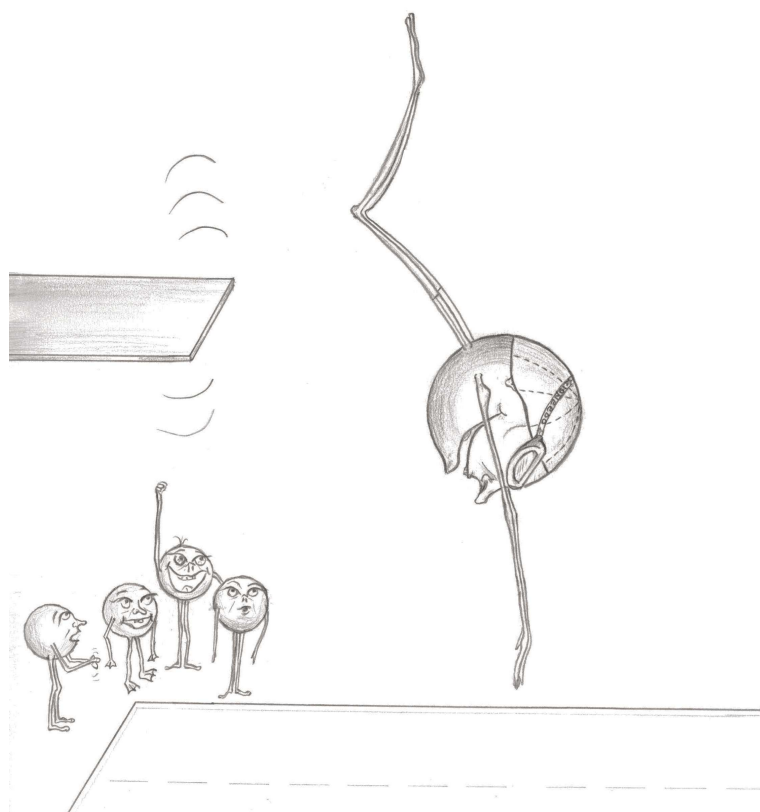
A single ion has decided to jump from the gas-phase into a swimming pool of pure liquid. It is eager to experience solvation! This ion is also about to discover a fundamental and painful fact of nature: it is impossible to reach the bulk of a liquid without crossing its surface.