

# Editorial for PCCP Themed Issue: “Frontiers in Molecular Simulation of Solvated Ions, Molecules and Interfaces”

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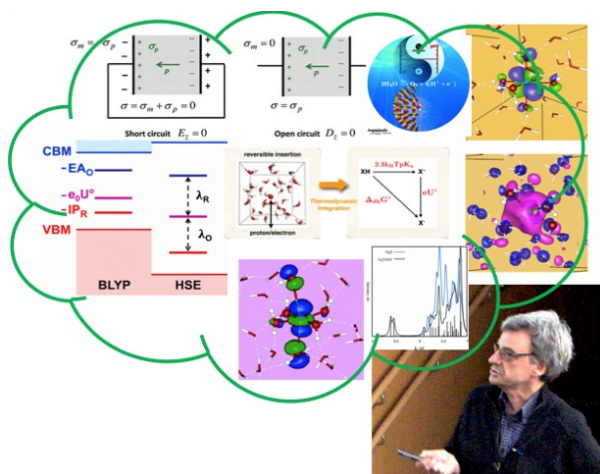
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This special issue provides a timely snapshot of the current state-of-the-art in the molecular simulation of solvated ions, molecules and interfaces and honours the pioneering and inspiring contributions of Prof Michiel Sprik in this now established field of Computational Physical Chemistry. The last thirty years have witnessed tremendous progress in our understanding of a wide range of physicochemical phenomena in the condensed phase. With the marriage of electronic structure theory and statistical mechanics to what is nowadays known as *ab-initio molecular dynamics*, it has become possible to break through the limitations of classical molecular dynamics and simulate liquids, ionic solvation, chemical reactions, solvated interfaces, heterogeneous and homogeneous catalysis, aqueous interfaces and nowadays even electrochemistry in a most rigorous way, from first principles theories. The field has come a long way from the seminal work of Car and Parrinello in the mid eighties and the path towards the current state-of-the-art was a long and winding road, offering both plenty of pitfalls and unexpected surprises. It was here that Sprik has made numerous essential contributions, provided leadership and foresight for a generation of students and postdocs and restlessly explored new ideas often stirring the ship in uncharted waters.

The papers of this special issue can be roughly divided in four topics, ionic and interfacial solvation, enhanced sampling techniques, condensed phase spectroscopy and computational electrochemistry including electron and proton transfer reactions. Sprik was indeed a pioneer on all these topics. He was one of the first to develop and apply path integral Monte Carlo calculations to study electron solvation in polar solvents including liquid ammonia<sup>1</sup> and liquid water.<sup>2</sup> Through the use of a “Staging” algorithm<sup>3</sup> to sample the quantum paths of the electron, the number of beads could be increased from hundreds to thousands as deemed necessary for excess electrons - quite a feat for 1980s high performance computing! Nowadays path-integral simulations for nuclear motion are so efficient (and computers so powerful) that they can be routinely carried out in combination with density functional-based electronic structure theory, as shown in the present contribution by Wang *et al.* who report on the impact of ions on nuclear quantum effects in liquid water by analysing quantum kinetic energy and isotope fractionation ratios (DOI: 10.1039/C9CP06483D). The development of classical force field models including many-body polarisation was another one of Sprik’s early highlights.<sup>4,5</sup> He estimated that the effective dipole moment of a water molecule in liquid water is 2.85 Debye,<sup>4</sup> not far off from what *ab-initio* MD predicts nowadays. In this issue Wang *et al.* review the *responsible* use of Lennard-Jones potentials and report on a class of finite-ranged potentials that can be made to be Lennard-Jones-like or colloidal-like (DOI: 10.1039/C9CP05445F).

Sprik’s experience with solvated electrons should also prove immensely useful for studies of electron transfer reactions. Not long after the seminal contributions of Warshel and Newton in the early to mid-eighties, Kuharski *et al.*, equipped with Sprik’s pseudopotentials for quantal excess electrons, investigated the prototypical electron self-exchange reaction between ferrous and ferric ions in aqueous solution offering

a detailed atomistic picture of Marcus' continuum treatment.<sup>6</sup> Until today this reaction serves as a testing ground for non-adiabatic reaction dynamics including theories on nuclear tunneling in the condensed phase. In this issue Fang *et al.* apply their Golden-rule quantum transition-state theory to show that the nuclear quantum enhancement factor is significantly lower than previous estimates based on Wolynes theory and they argue that the latter breaks down for this solvated system (DOI: 10.1039/C9CP06841D). Less is known about electron transfer in non-polar media - in his contribution Matyushov predicts small but finite reorganisation energies due to molecular polarisability, breakdown of the fluctuation-dissipation theorem and a non-Arrhenius kinetic rate law (DOI: 10.1039/C9CP06166E). Electron transfer also plays a major role in the solid state, in particular in oxide materials for energy applications.<sup>7</sup> Ahart *et al.* characterise electron and hole polarons in the photoanode material hematite ( $\text{Fe}_2\text{O}_3$ , DOI: 10.1039/C9CP06482F) and Behara *et al.* present a new implementation of periodic density functional theory for calculation of electronic couplings with applications to  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{BiVO}_4$  (DOI:10.1039/C9CP05133C).

Sprik has also made important early contributions to the simulation of heterogeneous systems, in particular electrode-solvent interfaces. Initially, these efforts were motivated by the desire to interpret scanning tunneling microscopy experiments at an atomistic detail. Together with Siepmann, he proposed an ingenious scheme to simulate the electrode in the experimentally relevant constant-potential rather than constant-charge ensemble by treating the charge of each electrode atom as an additional degree of freedom that adapts in response to the instantaneous electrolyte configurations.<sup>8</sup> In this issue Scalfi *et al.* revisit the statistical mechanics of the constant-potential ensemble and derive a fluctuation-dissipation relation for the differential capacitance as a sum of two contributions, the thermal charge fluctuations between Born-Oppenheimer and constant-potential ensemble and the differential capacitance of the empty capacitor (DOI:10.1039/C9CP06285H). Zhang *et al.* investigate the water dynamics at electrified graphene interfaces presenting a perspective on their jump model (DOI: 10.1039/D0CP00359J).

With the advent of Car-Parrinello molecular dynamics it became possible to treat both the solute and the solvent at the same density functional theory level of detail. This was a major advance compared to the quantum chemists' continuum solvation models that dominated the field until then because for the first time one could study reactions where the solvent is not merely a spectator but indeed the feature participant, e.g. autodissociation of and proton transport in liquid water. Sprik hardly ever forgot to remind us about the appealing features of an all-QM treatment, and in fact he and Sulpizi went so far to even treat a fully solvated protein (rubredoxin) at all-DFT level for the purpose of calculating reorganisation energy.<sup>9</sup> Returning to the early days of *ab-initio* water, Sprik contributed to many of the truly pioneering papers on this topic<sup>10-12</sup> paying attention to the performance of the density functional used<sup>13-15</sup> and addressing the delocalization error for solvated odd-electron systems, i.e. radicals.<sup>16</sup>

Some twenty years later *ab-initio* ionic solvation has not lost any attraction. In this issue *ab-initio* molecular dynamics is used to assess the (a)symmetry of the local hydrogen bond network of liquid water (*Elgabarty et al.* (DOI: 10.1039/C9CP06960G), the properties of supercritical water in terms of structural dynamics and electronic polarisation effects (*Schienbein et al.* DOI: 10.1039/C9CP05610F), the hydration structure of sodium and potassium ions using the strongly constrained and appropriately normed (SCAN) functional and the random phase approximation (*Duignan et al.* DOI: 10.1039/C9CP06161D), the aqueous solution structure of the chloride ion using hybrid functionals and SCAN (*DelloStritto et al.* DOI: 10.1039/C9CP06821J) and the solvation of carbon dioxide, bicarbonate and carbonate ions under deep Earth conditions (*Dettoni et al.* DOI: 10.1039/C9CP06904F). Artificial intelligence methods are now also becoming an increasingly important tool for reactive solvation dynamics - in their contribution *Shao et al.* use a high dimensional neural network, based on DFT calculations, to investigate temperature effects on the ionic conductivity in concentrated alkaline electrolyte solutions (DOI: 10.1039/C9CP06479F).

*Ab-initio* MD has also had a major impact on our understanding of solvation structure, surface potential and surface tension at the air-liquid interface. In this issue *Eggimann et al.* report on how temperature affects the spatial distribution of electrolyte mixtures at the aqueous liquid-vapour interface (DOI: 10.1039/C9CP06729A), and *Zhang and Sprik and Creazzo et al.* go even a step further and investigate electrified air-water interfaces. *Zhang and Sprik* report on their electromechanics and show, by interpreting *ab-initio* MD results with a phenomenological model, how surface potential and surface tension are related to one another (DOI: 10.1039/C9CP06901A). *Creazzo et al.* find that at moderate electric field strengths the proton conductivity at the electrified airwater interface is enhanced by a factor of two compared to bulk water, whereas for high field strengths the conductivities are similar (DOI: 10.1039/C9CP06970D).

One of the major drawbacks of *ab-initio* MD used to be and arguably still is the limited time scale accessible, typically on the order of pico- to nano-seconds depending on the computational demands set by the exchange correlation functional and the system size used. This falls many orders of magnitude short of the millisecond or longer time scales of typical rare events, e.g. chemical reactions. To address this problem, *Sprik and Ciccotti* developed constrained molecular dynamics for calculation of free energy profiles, also termed potential of mean force, by imposing a mechanical constraint on a general reaction coordinate during the molecular dynamics run.<sup>17</sup> They showed that the mean force can be directly obtained from the average force on the constraint (Lagrange multiplier) and a geometric correction term, both readily available from the simulation. The theory was successfully applied to the autoionisation of liquid water owing to a clever choice of the reaction coordinate, the coordination number,<sup>18-20</sup> as well as to several other chemical reactions.

Recently, *Ciccotti* and co-workers employed constrained molecular dynamics for the simulation of sys-

tems involving adiabatically separated dynamical variables, e.g. the shell model for electronic polarisation, to enforce a vanishing force on the fast variables. Here, Bonella *et al.* further extend this methodology to first principles molecular dynamics (DOI: 10.1039/D0CP00163E) and Kronberg *et al.* applies constrained MD to investigate the Volmer-Heyrovsky mechanism of hydrogen evolution on a nitrogen doped carbon nanotube (DOI: 10.1039/C9CP06474E). Schwermann *et al.* present a novel technique to compute free energy profiles for exciton transfer by restraining the Wannier-Centres of the electron hole-pair along a suitable reaction coordinate (DOI: 10.1039/C9CP06419B), in analogy to umbrella sampling, and Tavernelli investigates correlation effects and the role of swapping frequency for parallel tempering (DOI: 10.1039/C9CP06772H).

With the implementation of time-dependent density functional theory in plane wave codes, one could for the first time study the impact of the finite temperature fluctuations of a DFT solvent on excitation spectra. Sprik made several early contributions on this topic<sup>21</sup> studying charge-transfer and intramolecular electronic excitations in aqueous molecules<sup>22</sup> and transition metal ions.<sup>23</sup> He also led the way in using *ab-initio* MD to calculate the vibrational spectroscopy of solvated molecules,<sup>24</sup> and later contributed to sum frequency generation spectroscopy at interfaces.<sup>25,26</sup> In this issue Blasius *et al.* look at vibrational circular dichroism, infrared, and possible mechanisms in dry and moist ionic liquids (DOI: 10.1039/C9CP06798A), Marzari *et al.* present a first principles operando XANES approach with application to iridium oxide (DOI: 10.1039/C9CP06726D) and Bold *et al.* benchmark long-range corrected DFT and DFTB functionals for the calculation of electronic excitation energies in retinal and light harvesting proteins (DOI: 10.1039/C9CP05753F).

At the turn of the millennium Sprik opened a new avenue for *ab-initio* molecular dynamics: *ab-initio* redox chemistry, which should later become *ab-initio* electrochemistry. Initially, he, together with Tavernelli and Vuilleumier, derived an elegant expression for the redox potential within a semi-grand canonical ensemble formulation.<sup>27</sup> The algorithm required one to carry out *ab-initio* molecular dynamics on a composite potential energy surface (PES) made up of the PESs for the oxidised and reduced states with dynamical weights determined by how the instantaneous vertical ionisation potential compares to the (fixed) electrochemical potential. While elegant, the method suffered from severe sampling problems<sup>28</sup> and was later replaced by a robust *ab-initio* thermodynamic integration approach,<sup>29</sup> following partially successful previous attempts to enforce redox reactions via constrained MD.<sup>30,31</sup> *Ab-initio* thermodynamic integration gave redox potentials in reasonably good agreement with experiment (with the accuracy mostly limited by the density functional used) and provided a rigorous way to calculate kinetic parameters as well such as reorganisation and activation free energy. Moreover it was a powerful tool to assess some of the crucial assumptions of Marcus theory, most prominently the paradigm of equal curvature free energy parabolas.<sup>29,32,33</sup> In the contribution of Reeves *et al.* such *ab-initio* simulations clearly show that the free energy profiles for biredox ionic species (that are of interest for capacitative energy storage) fall outside the Marcus regime and are more

suitably described by a 2-Gaussian state model (DOI: 10.1039/C9CP06658F). Critical to these simulations is the accurate calculation of vertical ionisation energies and in the contribution of Toth *et al.* a QM:QM fragmentation scheme is suggested as an alternative to all-QM calculations (DOI: 10.1039/C9CP06154A).

The success of *ab-initio* thermodynamic integration for redox reactions prompted Sprik, Sulpizi and Cheng to develop a similar technique for *ab-initio* molecular dynamics calculation of acidity constants. The slight but important difference was that now one had to deal with the statistical mechanics of removing and inserting a proton and one had to relate the computed *ab-initio* insertion/removal energies to equilibrium constants or pKa values.<sup>34–36</sup> The methodology was applied successfully to estimation of pKa’s of acidic groups in aqueous solution<sup>35–37</sup> and at inorganic surfaces.<sup>36,38,39</sup> Essential to these approaches are accurate vertical (de)protonation energies and Rudorff *et al.* present in their contribution a rapid quantum alchemical approach for their estimation (DOI: 10.1039/C9CP06471K). Proton transport also plays a crucial role in other condensed phase systems including solids, solid electrolytes and surfactants. In this issue Dreßler *et al.* use *ab-initio* molecular dynamics to investigate the temperature effect of anion reorientation on proton mobility in a family of solid acids (DOI: 10.1039/C9CP06473G). Using an alternative, multi-scale reactive molecular dynamics approach Li *et al.* explore the dynamics of proton transport in reverse micelles (DOI: 10.1039/D0CP00378F).

The *ab-initio* MD methodologies developed for redox and deprotonation free energies culminated in Sprik’s computational hydrogen electrode, realised by simultaneously inserting/removing an electron *and* a proton to/from the simulation box. This computational trick allowed him to align electronic energy levels and band edges of solvated molecules and inorganic surfaces, respectively, with respect to the experimental redox scale.<sup>38,40,41</sup> Distinct from Norskov’s approach, the resultant free energies for proton-coupled oxidation/reduction (or (de)hydrogenation) reactions were obtained from finite-temperature molecular dynamics treating the surface and the solvent at the DFT-level. Moreover, proton-coupled oxidation/reduction could now be understood in terms of the separate free energy contributions for oxidation and proton transfer.<sup>41,42</sup>

*Ab-initio* electrochemistry and the simulation of electrochemically relevant interfaces is now a burgeoning field drawing in an increasing number of computational chemists. In his Perspective Article, Leung explains DFT methods and challenges for the modelling of solid-solid interfaces in batteries (DOI: 10.1039/C9CP06485K), Lautar *et al.* review concepts and tools for the modelling of interfacial electrochemistry (DOI: 10.1039/C9CP06684E), Hanselman *et al.* investigates the thermodynamics of the formation of surface PtO<sub>2</sub> stripes on Pt(111) (DOI: 10.1039/C9CP05107D), Sakong *et al.* reports on water structures on a Pt(111) electrode at various electrochemical conditions (DOI: 10.1039/C9CP06584A), Grosjean *et al.* report on the spontaneous liquid water dissociation on hybridised boron nitride and graphene atomic layers (DOI: 10.1039/C9CP06765E), Juarez *et al.* characterise the interactions of ions across carbon nanotubes

(DOI: 10.1039/C9CP04463A), Ntim *et al.* assess the role of image charges in an ionic liquid confined between metallic interfaces (DOI: 10.1039/D0CP00409J) and Baba *et al.* look at interfacial Li-ion transport in battery materials (DOI: 10.1039/C9CP06608J). The related field of electrocatalysis is also represented in this issue with Kumar *et al.* reporting an exhaustive list of reaction paths for reduction of CO<sub>2</sub> on a  $\alpha$ -hematite (0001) surface (DOI: 10.1039/C9CP06453B), Wen *et al.* investigating site-dependent reactivity of Pt single atoms on TiO<sub>2</sub> (101) (DOI: 10.1039/C9CP05097C) and Puthenkalathil *et al.* uncovering the mechanism of biomimetic hydrogen fuel production (DOI: 10.1039/C9CP06770A).

More recently, Sprik drew inspiration from the work of Stengel, Spaldin, and Vanderbilt,<sup>43</sup> and extended their finite-field method to a finite-temperature variant for molecular dynamics simulation at constant electric displacement ( $D$ ) or macroscopic field ( $E$ ).<sup>44–49</sup> The formalism was applied to the calculations of the dielectric constant of liquid water,<sup>44</sup> the modelling of charged insulator/electrolyte interfaces for recovery of the correct charge compensation at the interface<sup>45,47</sup> and to the calculation of ionic conductivities in bulk electrolyte solutions.<sup>49</sup>

In summary, this issue provides an impressive collection of papers on the current state-of-the-art of molecular simulation of condensed phase systems, ranging from classical, to *ab-initio* to *ab-initio* path integral molecular dynamics and covering latest progress and insights on ionic solvation in the bulk, at solid-liquid and vapour-liquid interfaces, on enhanced sampling techniques, *ab-initio* spectroscopy and electrochemistry. It shows how *ab-initio* statistical mechanics techniques have matured to become an essential tool for the atomistic understanding, interpretation and prediction of thermodynamic and kinetic properties of solvated systems. It also attests to the wide-ranging influence that Michiel Sprik has had on the scientific community in computational physics and chemistry.

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