

'Recent developments in both experimental and computational techniques are leading to a greater understanding of the liquid state at the microscopic molecular level. The following three articles, in describing some of these advances, extend and update the coverage of activities in the area of liquids that was presented in the Liquids Special Issue, EPN 30/3.'

## Reactive liquids from first principles

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Modelling and computer simulation have played a vital role in our understanding of liquids. The use of numerical methods has enabled us to characterize and quantify the finite temperature fluctuations which stabilize the liquid phase and distinguish it from the solid state. Dynamical disorder is also the decisive factor that makes liquids a suitable medium for chemical reactions. Diffusive and reorientational motion gives solvent

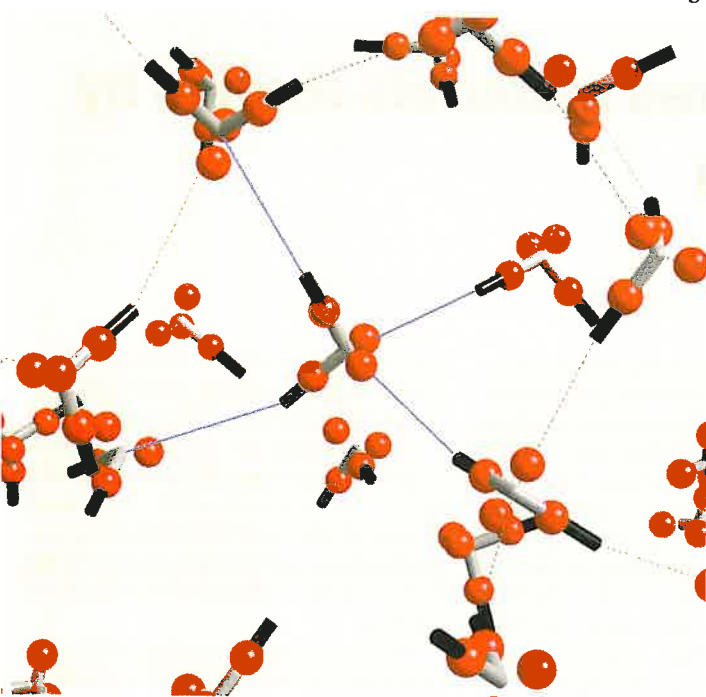
molecules the freedom to make way for solvated reactive species allowing them to assume the often highly specific configurations required for a successful reactive encounter. Polar solvents have the further crucial function of assisting in the separation of charged products. An all important example of a polar solvent is, of course, water. What is unique for this most famous among solvents is the ability of water molecules to form strong hydrogen bonds to

ionic or polar solutes and at same time maintain hydrogen bonding to fellow water molecules in the surrounding solvent. Multiple hydrogen bonding is the explanation why water is capable of stabilizing ionic species that hardly exist anywhere else. However, the tendency of water to directly participate in a reaction, either as reactant or catalyst, makes aqueous reactions complex and difficult to control. This is the reason that water, in fact, is one of the less popular solvents in organic chemistry laboratories. Living organisms, on the

other hand, have learned to exploit these properties and water is the preferred solvent in biochemistry.

Computer modelling has already made essential contributions to unravelling the complexity of aqueous solutions. In particular it has helped us rationalizing the activity of biomolecules. Numerical simulation is certain to play a similar role in the study of reactive solutions, such as water at non-neutral pH. However, owing to the lack of reliable force fields, aqueous chemistry has eluded treatment by atomistic modelling so far. This situation is rapidly changing now as a result of advances in *ab initio* Molecular Dynamics (MD) methods. This new technique in computational chemistry combines the Density Functional Theory (DFT) approach to electronic structure calculation with simulation of finite temperature dynamics, thus avoiding parametrized force fields altogether.

A first priority in the application to liquids was verifying that the accuracy of DFT is adequate to describe the comparatively weak intermolecular interactions determining the physics and chemistry of these systems. For aprotic solvents, dominated by VanderWaals forces, the technical difficulties have not been fully resolved yet. For hydrogen bonded liquids, on the other hand, a class of electronic energy functionals developed by chemists specifically for the application to molecules, such as BLYP, was found to be able to stabilize liquid conditions at ambient temperature yielding structural and dynamical properties in excellent agreement with experiment[1, 2]. Using this approach Silvestrelli and Parrinello determined the effective molecular dipole moment in liquid water[2]. The value they obtained is 3.1D, almost the double of the 1.85D in vacuum. This result is a good illustration of how *ab initio* MD can be used to obtain data that cannot be directly deduced from experiment. Also from a more technical point of view this computation represents a major step forward. It required overcoming the difficulty of identifying molecular entities in the collective extended DFT electronic ground state which makes no such distinctions. Thus, by using a localization



Snapshot of an *ab initio* MD simulation of liquid water. The H<sub>2</sub>O geometry is indicated by wire frames with black for H and gray for O atoms. The blue lines are hydrogen bonds. The red balls are a representation of the instantaneous (adiabatic) electronic ground state. They are the centres of localized (Wannier) wavefunctions[3] with an occupation of two electrons per site. Each molecular frame has four of these centres attached to it, corresponding to the valence states of that particular molecule. This representation was employed by Silvestrelli and Parrinello[2] to compute the molecular dipole moment in the liquid(3.1D).

scheme[3] Silvestrelli and coworkers succeeded in recovering the molecular description of the liquid.

The encouraging results for pure water gave the green light for a series of *ab initio* MD applications to simple acidic and basic solutions. A milestone here was the detailed examination of the excess proton in water by Tuckerman et al.[4] which contributed to resolving the old controversy about the role of the  $\text{H}_5\text{O}_2^+$  (Zundel) and  $\text{H}_9\text{O}_4^+$  (Eigen) cation. When these ions are viewed embedded in the hydrogen bonded network of the surrounding liquid, they turn out to be two phases of the same fluctuating complex. The simulation showed that the dynamical rearrangements in the pattern of hydrogen bonds driving the interconversion of these two structures are also the key to the explanation of the structural (Grotthuss) diffusion of the solvated proton. Subsequent investigations of two prototypical strong aqueous acids, sulphuric and hydrochloric acid (Laasonen et al.) are extensions of the excess proton work and confirmed that DFT estimates for the pH of these solutions are in the correct range of values. Recent path-in-

tegral *ab initio* MD calculations by Marx et al., addressing the role of proton quantum effects, have validated and refined this picture[5]. Weak acids pose more of a technical problem, because of the highly activated nature of proton release. A first attempt to a determination of the pK of water resulted in a value of 13 (Trout et al.).

*Ab initio* MD is ready to be employed in investigations of reaction mechanisms in aqueous solution. Examples of studies that have been recently completed, or are currently under way, concern acid catalyzed addition of water to a carbonyl group (Meijer et al.), ligand substitution of a cisplatin complex (Carloni et al.) and the conformation of peroxyxynitrous acid (Docchio et al.). In all of these cases the *ab initio* MD clearly exposed the concerted nature of the processes in aqueous chemistry. Looking ahead, an important task for the near future will be the quantitative characterization of reactivity in water and other protic solvents. In particular the first principle computation of pK, redox potentials, activation energies and, ultimately, reaction rates is a major challenge. A

further topic which is already the subject of intensive ongoing research is the development of methods for the evaluation of the response functions determining optical and NMR spectra of liquids with as a first result a fully DFT based computation of the infrared absorption spectrum of liquid water[6]. *Ab initio* molecular dynamics may very well be the only way to deal with the level of complexity prevailing in liquids in which the electronic states are strongly coupled to thermal disorder.

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