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Combining Quantum Chemistry with Mechanistic Simulations to Determine Liquid Properties

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Abstract. Theoretical chemistry is used to answer questions of everyday life.

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Further details of his research interests are to be found at http://www.chemie.unibas.ch/PC/Huber/huber.html.

Watch the *Basilisk* spitting the water into the basin (*Fig. 1*). Why is that water *liquid* and not solid? Why is its viscosity so much lower than that of honey? You might be asked such questions by children, grandparents, or indeed anybody who is interested in nature. Do you have a ready answer? Specialists will have even more questions: what is its energy content, its heat capacity, its compressibility, its thermal expansion coefficient, its heat conductivity, its diffusion coefficient, its density, or its liquid structure? They might not restrict themselves to bulk properties, but ask: what is the chemical shift of a proton, or what is the vibrational frequency of the O–H bond?

Why is it that chemists often have difficulties to answer such questions? We surely agree that the answer lies in the microscopic structure of the matter. We can readily imagine a water molecule. That is how we explain reactions at the blackboard – by drawing structures of molecules and declaring which groups of atoms come and leave, hence forming new molecules. The difference in the above questions, though, is that we are not dealing with single molecules but with ensembles of molecules, and that the origin of the bulk properties is more to be found in the interactions between molecules than in the internal 'life' of molecules. In the case of chemical shifts or intramolecular vibrational frequencies, the situation is again different in that the ensemble modifies the molecular property, which one usually refers to as a *solvent effect*.

These are the questions we try to answer in our research by combining quantum chemistry with simulations. We discuss now three groups of properties: bulk

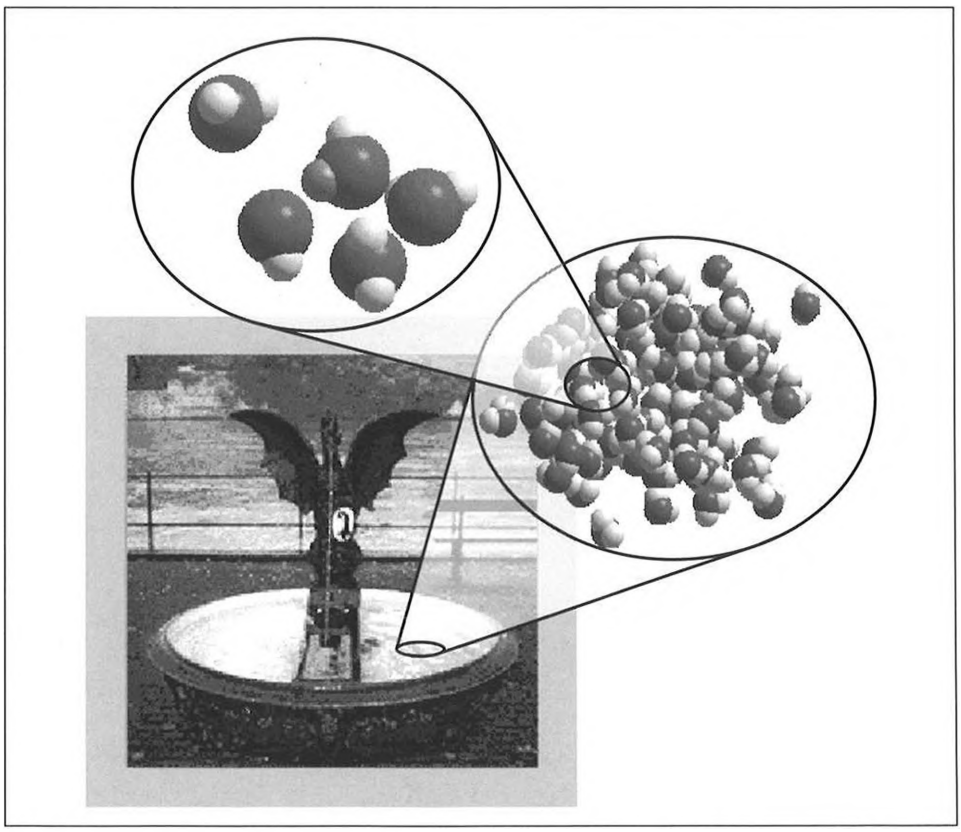

Fig. 1. *Water from the* Basilisk *in Basel*

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properties of a liquid as a whole, static properties in a liquid, and dynamic molecular or nuclear properties in a liquid.

Bulk properties, such as enthalpy, pressure, and heat capacities, are calculated by obtaining pair-wise intermolecular potentials from quantum-chemical *ab initio* calculations and applying them in molecular-dynamics simulations. To begin with, we restricted ourselves to much simpler liquids than water (which forms hydrogen-bonds leading to quantum phenomena like 'intermolecular vibrations' and tunneling of the proton) which is probably one of the most complicated liquids. We have dealt up to now with rare gases (neon and argon) and carbon dioxide. The potential in the former case is a one-dimensional function. Ten to fifteen energy calculations are enough to fit an accurate potential. However, for carbon dioxide, the potential is a four-dimensional surface (if we keep the monomers rigid as a further approximation) and that means typically 250 *ab initio* calculations to make a fit. The analytical (multi-dimensional) potential function is then implemented in the simulation program and used to obtain the forces at each time-step in order to integrate the *Newtonian* equations of motion. For readers who are not familiar with this technique, there is a more detailed explanation, complete with some small movies, available on the internet (http://www.chemie.unibas.ch/PC/Huber/bulk1.html). The main errors in such simulations are: *i*) limited accuracy in the quantum-chemical calculation of the potential, *ii*) the assumption that pair-potentials are additive (*i.e.*, neglecting many-body non-additive interactions, where bodies are molecules), and *iii*) the assumption that classical mechanics is valid for the translational movement of the atoms or molecules. There is not yet much known about the influence of these approximations, and the main goal of our work in recent years has been to contribute to the knowledge in this field [1]. *Fig. 2* shows the melting curve of neon to give an idea about the accuracy which can be obtained.

Static nuclear or molecular properties, such as a nuclear quadrupole coupling constant, a chemical shift in NMR, or a vibrational frequency in infrared spectroscopy, are calculated in a general microscopic scheme. First, an intermolecular potential is calculated or taken from the literature and applied in molecular-dynamics simulations. From time to time, during such a simulation, a snap-shot is taken of the molecular coordinates in the liquid. To calculate the proton shift, for example, a proton is randomly selected, and a molecular cluster around this proton is cut out (see *Fig. 1*). This cluster is treated like a 'super-molecule' in a quantum-chemical calculation to obtain the shift. Such shift calculations are standard today for single molecules, and there is no principle difference in the quantum-chemical calculation between a single molecule or a cluster. Whereas the single molecule calculation yields the shift corresponding to the gas phase, the cluster corresponds to a typical liquid surrounding. Repeating the procedure for many clusters and averaging yields the liquid value. The difference is what is usually called the solvent effect. So far, our group has used this approach to calculate chemical shifts [2] and quadrupole couplings in water [3]. We have obtained solvent effects for protons in liquid water at ambient conditions of between –2.8 and –3.4 ppm (for different potentials from literature) compared to an experimental value of –4.3 ppm. For ^{17}O, the values were between –36.8 and –46.6 ppm compared to an experimental value of –36.1 ppm. For the quadrupole couplings of deuterium, the agreement with experiments was nearly perfect; whereas for ^{17}O only about 66% of the experimental solvent effect was found.

Dynamic nuclear or molecular properties, like an NMR relaxation time T_1, cannot be obtained in the above way as this approach is purely static and the simulation is only used to get cluster configurations. To calculate T_1 due to a quadrupolar relaxation, for example, we would need to know the quadrupole coupling at each nucleus at every time-step of the simulation. Typically, several tens of thousands of time-steps are performed in a simulation, and to calculate the coupling by a quantum-chemical calculation in each step would not be feasible. Hence, we make an additional approximation by assuming pair-wise additivity for this *coupling* as is done for the *potential*. Then, we only have to calculate a quadrupole-coupling curve (for atoms) or a multidimensional surface (for molecules) before the simulation and to implement it in the simulation program. At each step, the coupling can then be obtained by a few algebraic manipulations. We have calculated the relaxation time of liquid and supercritical neon at high densities and obtained a fair agreement with experiments [4]. However, a perfect agreement has not yet been possible, as the relaxation time is extremely sensitive to the potential as well as the quadrupole-coupling curve. Presently, we are working on the coupling constants and quadrupolar relaxation in a mixture of water and DMSO, a much more complex system. Experimentalists have found a very strange behaviour which needs to be confirmed or disproved in an independent way.

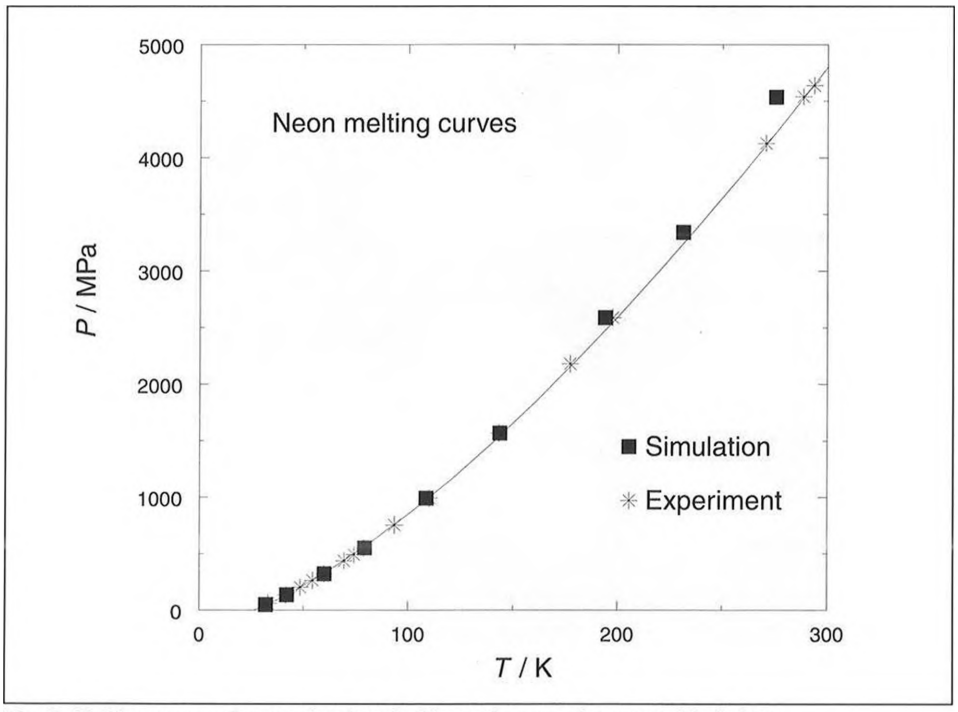

Fig. 2. *Melting curve of neon simulated without the use of any empirical data*

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