NQEAIMD – IEF Final Report
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The aim of this project was to develop and apply computer simulation techniques to model the quantum nature of both the electrons and light nuclei at the same time. Density functional theory (DFT) provides a framework that is both reasonably accurate and computationally affordable to solve the quantum mechanical electronic structure problem for condensed-phase systems. Path integral molecular dynamics (PIMD) provides a convenient and systematically convergent approach to deal with deviations from Newtonian behaviour of nuclei, which can be very significant at room temperature and below for hydrogen and other light atoms. For example, it is straightforward to show using experimental data for light, heavy, and tritiated water that the heat capacity of $H_2O(l)$ would be 50% higher, and its pH would be 8.5, if protons behaved as classical particles.

Unfortunately, DFT is affordable but still expensive, and PIMD typically requires one to simulate several tens of replicas of the physical system, leading – in the case of room-temperature water – to an overhead of a factor of 30 or more relative to classical molecular dynamics. This has meant that, so far, PIMD and DFT have only been used together very rarely, despite the fact that nuclear quantum effects (NQEs, e.g. zero-point energy, tunnelling, large deviations from the classical Maxwell-Boltzmann distribution) can have a similar or larger impact on the accuracy of simulations than the approximations that are made in the solution of the electronic structure problem by DFT.

The broad objective of this project was to make PIMD simulations more affordable, so that NQEs could be combined more easily with DFT simulations. The fundamental idea was to apply a colored-noise, Generalized Langevin Equation (GLE) thermostat – which had already been shown to be capable of *approximately* modelling NQEs within a classical molecular dynamics framework – to a PIMD simulation with a small number of replicas, in order to accelerate convergence and reduce the computational cost of including NQEs *accurately*. Having established this methodology, we aimed to demonstrate its potential by studying the impact of NQEs on the properties of water, and then to apply it to more complex problems with relevance to energy storage and production, collaborating closely with experimental groups.

The Fellowship had to be interrupted after 15 months, because on November 1st 2013 Dr. Ceriotti moved to École Polytéchnique Fédérale de Lausanne to take a position as a tenure-track assistant professor. Despite the early termination, the main objectives of the Fellowship were completely fulfilled. We have developed PI+GLE, a hybrid technique that combines PIMD with GLE thermostatting, and reduces the computational cost of a fully-converged simulation by a factor of 5 or more [1]. We have also shown that a competing way to reduce the number of path integral replicas – by using a higher-order discretisation of the imaginary time path – will inevitably be less efficient than PI+GLE for large-scale simulations [2]. PI+GLE was further improved into the PIGLET method [4], which gives more rapid convergence of the quantum kinetic energy and can straightforwardly be used to estimate the
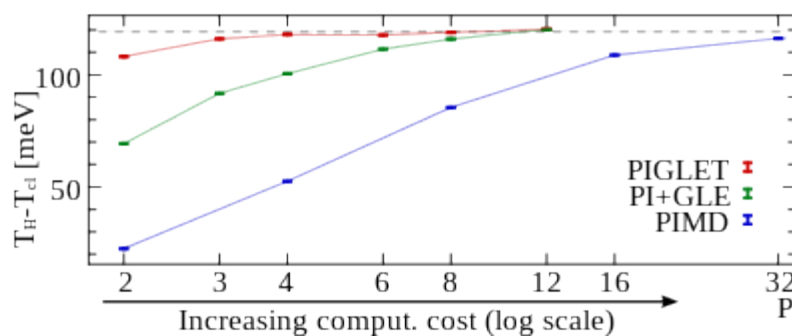

Figure 1: The quantum component of the kinetic energy of a hydrogen atom in liquid water, as a function of the number of PIMD replicas. Conventional PIMD is compared with PI+GLE [1] and PIGLET [4].

particle momentum distribution in a way that makes it possible to compare the results of simulations and those of Deep Inelastic Neutron Scattering (DINS) experiments [4,5].

We have benchmarked PIGLET for the archetypical case of room-temperature liquid water, demonstrating that convergence can be achieved with as few as 4-6 path integral replicas (Figure 1), [3,4] whereas at least 32 would be needed when using conventional PIMD. This made it possible to achieve considerable insight into the quantum behaviour of liquid water: we could corroborate experiments that for the first time measured directly the competition of quantum effects on hydrogen kinetic energy in water [8], and demonstrate the profound (and quite unexpected) influence of the quantum nature of the proton on hydrogen bond fluctuations in neat, room-temperature water [10]. We are now exploiting this saving to study the role of NQEs in more complex problems, including aqueous solutions, interfaces, and confined water. National and international collaborations have been established for these studies with X. Chen at Boston University [6], T. Markland at Stanford [7], C. Andreani and R. Senesi at Rome-Tor Vergata [8], A. Seel at the Rutherford-Appleton Laboratory [5] and D. Donadio at MPI Mainz.
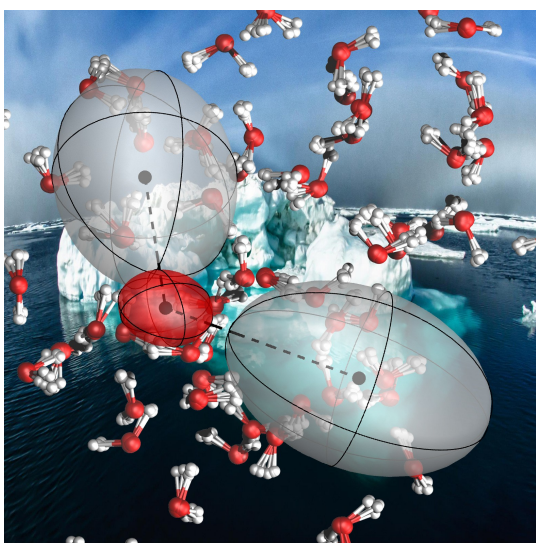

Figure 2: A representation of the particle momentum distribution in liquid water [8] - Background image used with permission of the NOAA's National Ocean Service

PIGLET has the potential for making the inclusion of NQEs in ab initio molecular dynamics routine. It is often the case, however, that the adoption of new methodological developments is slowed down by the considerable effort that is necessary to implement them into existing electronic structure codes. To eliminate this obstacle, we have developed i-PI, a Python interface designed to use electronic structure codes as the back-end to solve the electronic structure problem, obtaining the Born-Oppenheimer energy and forces that are then used to propagate PIMD or PIGLET dynamics. Interfacing i-PI to an existing code requires minimal effort, and we have already developed appropriate patches for many software packages, such as CP2K, CPMD, FHI-AIMS, quantum-Espresso, LAMMPS. We are using i-PI for our current projects, and have released it as an open source code, accompanied by a publication in Computer Physics Communications [10]. Considering that one of the objectives of our proposal was implementing PI+GLE techniques in *one* electronic-structure code, having released a piece of code that makes it possible to use colored-noise and path integral techniques in *any* atomistic simulation code is a significant improvement over our initial target.

We believe that PIGLET will have a significant impact on the simulation community, particularly after the release of i-PI has made it easier for external groups to have access to this technique. As is becoming increasingly evident, an accurate treatment of NQEs is necessary to achieve quantitative precision in atomistic simulations of materials and chemicals that contain hydrogen or other light atoms. These include materials for hydrogen storage, lithium batteries, fuel cells, water, as well as many enzymes and biologically-relevant molecules. Making these simulations more affordable will help in achieving the level of accuracy and predictive power that is needed to fulfil the promise of computer-aided materials design, that is the main aim of strategic research lines such as the materials genome project in the US.

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