Classical force fields for water from density functional theory based molecular dynamics simulations and force matching algorithm

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Water is one of the most abundant substances and is essential for all life on Earth. Therefore, it has been the subject of numerous studies but, despite all this effort, water clusters and condensed phases are still not fully understood. The main way to achieve this aim is represented by *ab initio* molecular dynamics (MD), particularly in the Car-Parrinello (CP) implementation[1]. Density functional theory (DFT) is the method often employed to simulate this kind of system. Despite advances in this so called first principle simulations field, only system size from few tens up to one hundred molecules are now approachable.

In this scenario, classical force fields (FFs) still play an important role. Basic ingredients of this kind of pairwise potentials are repulsive-dispersive (*i.e.,* Lennard-Jones potential) and Coulombian interactions. Polarization effects and flexible geometry of the water molecules can be also included. Several models are developed in the last decades[2] and are continuously object of refinement, in order to reproduce majority of physical properties of water (density, heat of vaporization, radial distribution function, critical parameters and so on).

The parametrization approaches could be gathered into two classes: fit of experimental properties or fit of *ab initio* potential energy surface. A recently proposed method, that belongs to the latter class, is the so called *force matching algorithm*[3]. It is based on a least-squares fitting of the potentials to force data obtained from reference calculations at a higher level of description. This approach has been used successfully in the development of new families of FFs[4].

In this contribution we present the results of the force matching application. The least-squares fitting is performed on both *ab initio* forces and molecular dipoles. Reference data were obtained from a 15 ps CP simulation of 96 water molecules with DFT level of theory. The teperature was set to 330 K and the density was held fixed to 0.997 g cm^{-3}. Standard periodic boundary were applied. Wannier centers[5] were computed along the simulation to calculate molecular dipole moments.

The force matching algorithm led to parameterize new classical FFs in which polarization is taken into account explicitly by using polarizable point dipoles method and damping functions[6]. Structural and dynamical properties have been computed for the water models here presented and these properties show a good agreement with the *ab initio* ones.
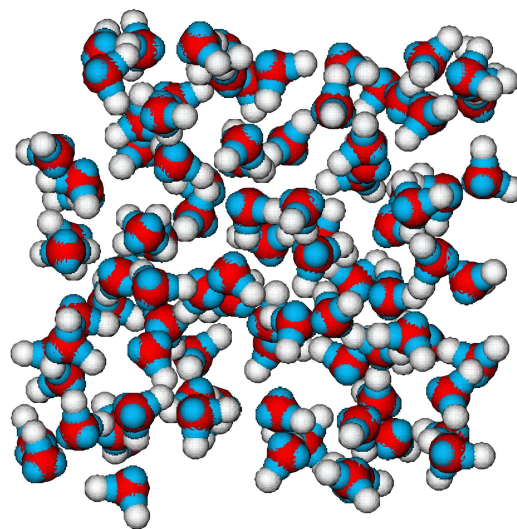

FIG. 1. Snapshot of a typical MD configuration taken from the CP dynamics. H atoms are in white, O atoms in red and Wannier centers are in cyan.

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