§12. The First-Principle DFT Molecular Dynamics Simulations of Liquid Water

Tanaka, M. (Chubu Univ.), Zempo, Y. (Hohsei Univ.), Yamashiro, M. (Nihon Univ.)

Previously we studied the microwave heating of various states of water using classical molecular dynamics simulation. Our results were: (i) the heating of liquid water is due to excitation of small-angle rotation of water molecules by the electric field (E-field) of microwaves [1]. (ii) Addition of even small amount of salt (NaCl) enhances the heating because salt ions directly absorb microwave energy on top of water dipoles. (iii) Pure crystalline ice is not heated because of the rigid hydrogen bond network. (iv) Salty ice is heated and melted because of local destruction of the network by charged salt ions [2].

We are now performing the molecular dynamics simulation based on quantum mechanics in which we have to deal with the system of many electrons. For such system, the Schroedinger equation is not tractable because of vast degrees of freedom of quantum numbers and the necessity of anti-symmetrization of wavefunctions. The method to go around this difficulty is to solve the Kohn-Sham (KS) equation for the electrons involved in the model system, which is given by

$$i\frac{\partial}{\partial t}\varphi_i(r,t) = \left[-\frac{\nabla^2}{2} + v_{KS}(r,t)\right]\varphi_i(r,t).$$

Here $\varphi_i(r,t)$ is the density functional that represents electron density distribution, and the subscript-i stands for the i-th atom (this is *not* a quantum number). The Kohn-Sham potential term appearing in the righthand-side of above equation is given by

$$v_{KS}(r,t) = v_{ext}(r,t) + \int d^3 r' \frac{n(r,t)}{|r-r'|} + v_{xc}(r,t)$$

where v_{ext} is the potential of an external field, v_{xc} is the exchange-correlation potential. The functional φ_i is related to the electron density by the summation over atom indices

$$n(r,t) = \sum_i^{occ} |\varphi_i(r,t)|^2$$

The KS equation is equivalent to the Schroedinger equation when all electrons reside in the ground state.

We use the density functional theory (DFT) molecular dynamics simulation code SIESTA [3] which uses the atomic orbital basis set, thus enabling more efficient simulations of isolated molecular systems like liquid than the planewave basis code. The model water consists of 16x4x4 H_2O molecules with periodic boundary conditions as shown in Fig.1(top). The system is equilibrated at a given temperature 300K before the microwave electric field is applied along the long axis. The water molecules form the network of six-membered rings virtually connected by hydrogen bonds. In this model, the hydrogen and oxygen atoms of each molecule are not rigidly bound but vibrate with each other. Such vibrations occur in a petahertz range.

After the microwave electric field of 1 THz frequency is applied, atoms of the H_2O molecule start bond-stretching and bond-angle vibrations. The molecules undergo rotational motion, but the guiding center positions remain nearly unchanged as seen by comparing Fig.1(top) and Fig.1(bottom). This is due to constraint by hydrogen-bonded network of H_2O even in the liquid water. The kinetic energy of atoms increases linearly in time after the microwave application. Its component corresponding to the guiding-center translational motion stays nearly the same as seen in Fig.1.
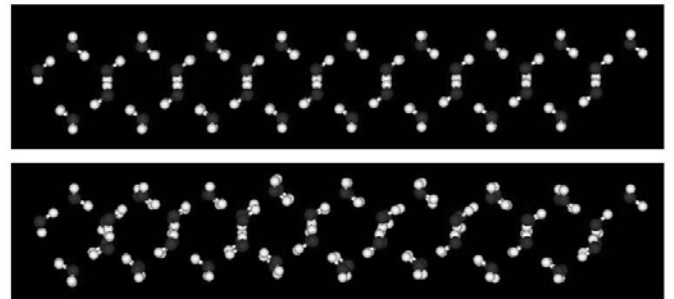

Fig1. The DFT molecular dynamics simulation of liquid water starting at room temperature. An equilibrated state before microwave application (top). We can see small-angle rotation of water molecules during the microwave application (bottom).

1. M. Tanaka and M. Sato, "Microwave heating of water, ice and saline solution: Molecular dynamics study", J. Chem. Phys. vol.126, 034509, 2007.
2. M. Tanaka and M. Sato, "Mechanism of enhanced heating of salty water and iceunder microwaves", J. Microwave Power Electromagnetic Energy, vol.42, p. 62, 2008.
3. The SIESTA project, http://www.icmab.es/siesta/.