

### §13. First-Principle Molecular Dynamics Study of Heating by Tera-Hertz Waves

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

Tera-hertz waves are widely used to heat dielectric materials including plasma and water. When we started our studies of the heating of dielectric and magnetic materials by microwaves in the beginning of 21st century, there had been experimental evidences of material heating by microwaves [1]. But no one knew exactly how the microwave energy is transferred to those materials. Concerning the heating of liquid water by microwaves (2.5GHz), there were numerous experimental data which one vaguely interpreted as being due to induced rotation of H<sub>2</sub>O molecules. Enhanced heating of salty water and inability of heating pure ice by microwaves were not explained.

In order to study the properties of liquid, polymer and crystalline materials, we have adopted two types of molecular dynamics (MD) simulations, (i) classical MD based on Newton equations of motion, and (ii) quantum mechanical MD which is based on a reduced set of quantum mechanical equations. In the former, we simulated heating of water by microwaves using the well-established SPC/E model water, and the heating mechanisms of liquid water, ice and salty water were clarified [2]. But, in general, all the force field must be prescribed, which is not always obvious.

On the other hand, nice things of quantum mechanical MD is that the force on each atom is determined in a self-consistent fashion following the calculated electron (cloud) distribution. However, the Schroedinger equation is applicable only to the system involving a small number of atoms and electrons due to the vast degrees of freedom of quantum numbers and the necessity of anti-symmetrization of wavefunctions. Thus, to handle many body problems in quantum mechanics, a reduced set of equations was derived for the ground-state electrons based on the density functional theory (DFT) [3].

The DFT method solves the Kohn-Sham (KS) equation for the electrons involved in the model system. Using  $\varphi_i(r,t)$  which is the density functional that represents electron density distribution, we have

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

The subscript-i stands for the i-th atom - *not* a quantum number, unlike the Schroedinger equation.

Electron density is given by  $n(r,t) = \sum_i^{occ} |\varphi_i(r,t)|^2$

Figure 1 shows the simulated molecular system irradiated by tera-hertz waves [4]. The time history of kinetic energy of all atoms is shown as temperature in Fig.2 (top). It increases linearly in time after the wave application. Its component corresponding to the guiding-center translational motion is shown in Fig.2 (middle), which stays nearly the same up to t=17ps unlike for the case of microwaves. Instead, the molecules make intense atomic vibrations of O and H atoms. In the DFT simulation, the electron energy (Kohn-Sham energy), which is the sum of Coulombic and exchange-correlation energies, increase in time as seen in Fig.2 (bottom). The increase is due to overlapping of electron clouds because of atomic stretching and bending vibration.



Fig.1 DFT simulated molecular system.

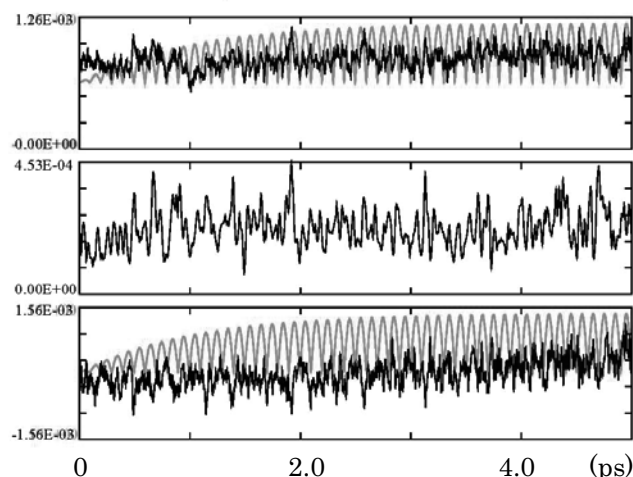


Fig.2 Kinetic, guiding-center, K-s (electron) energies.

1. R. Roy, D. Agrawal, et al., "Full sintering of powdered-metal bodies in a microwave field", *Nature (London)* vol.399, p. 668 (1999).
2. M. Tanaka and M. Sato, "Microwave heating of water, ice and saline solution: Molecular dynamics study", *J. Chem. Phys.* vol.126, 034509, 2007.
3. The SIESTA project, <http://www.icmab.es/siesta/>.
4. M. Tanaka, H. Kono, K. Maruyama, and Y. Zempo, "Theoretical studies of microwave heating of dielectric liquid and magnetic crystal by classical and quantum mechanical molecular dynamics simulations", p.185-188, *Microwave and RF Power Applications* (ed. J.Tao, Cepadues Publ., France, 2011).