Enhanced heating of salty water and ice under microwaves: Molecular dynamics study

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By molecular dynamics simulations, we have studied the enhanced heating process of salty ice and water by the electric field of applied microwaves at 2.5 GHz, and those in the range 2.5-10 GHz for the frequency dependence. We show that water molecules in salty ice are allowed to rotate in response to the microwave electric field to the extent comparable to those in pure water, because the molecules in salty ice are loosely tied by hydrogen bonds with adjacent molecules unlike the case of rigidly bonded pure ice. The weakening of hydrogen-bonded network of molecules in salty ice is mainly caused by the electrostatic effect of salt ions rather than the short-range geometrical (atom size) effect of salt ions since the presence of salt ions with small radii results in similar enhanced heating.

Keywords: microwave heating, salty ice, dipole rotation, electrostatic effects, molecular dynamics

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1. Introduction

Microwaves are frequently utilized as a highly efficient and less carbon-oxide releasing energy source for cooking or drying food, sintering metals and ceramics. It is known that dielectric materials including pure and salty water are heated efficiently by absorbing the electric field energy of microwaves [von Hippel 1954; Hobbs et al., 1966; Hasted, 1972; Buchner, 1999; Meissner and Wentz, 2004; Takei, 2007]. It is also known that metallic powders and magnetic materials such as magnetite and titanium oxides with oxygen defects TiO$_{2-x}$ ($x > 0$) are heated by the magnetic field of microwaves [Roy et al., 1999; Pellecandu et al. 2002; Sato et al. 2006; Suzuki et al. 2008; Tanaka et al., 2008].

In order to examine the mechanism of microwave heating of water and ice at the molecular level, we performed molecular dynamics simulations [Tanaka and Sato, 2007]. There we showed mechanistically that (i) rotational excitation of electric dipoles of water coupled with irreversible energy relaxation to the translational energy was responsible for the microwave heating of water, (ii) pure ice was not heated by microwaves because of strong hydrogen bonds between water molecules, (iii) the experimentally known enhanced heating of salt water by microwaves was due to acceleration of salt ions by the microwave electric field, which is usually termed as Joule heating. We numerically evaluated the time integrated Joule heating term of salt ions $E \cdot \mathbf{J}$ and the work associated with rotation of electric dipoles $E \cdot \mathbf{dP}/dt$ by summing up the contribution of all atoms or molecules, where $E$ is the electric field of microwaves, $\mathbf{J} = \sum_i q_i \mathbf{v}_i$ is the current carried by Na$^+$ and Cl$^-$ ions, and $\mathbf{P} = \sum_s \mathbf{d}_s$ is the sum of electric dipoles of all water molecules, with $q_i$ and $\mathbf{v}_i$ the charge and velocity of i-th atom, respectively, and $\mathbf{d}_s$ the electric dipole moment of s-th molecule. We obtained the relation $|E \cdot \mathbf{J}| \approx 2|E \cdot \mathbf{dP}/dt|$ for dilute saline solution of 1 mol% salinity and 10 GHz microwave [Tanaka and Sato, 2007].

We stated above that pure ice is not heated by microwaves. However, we have a daily experience of processing (melting) frozen food in microwave ovens. Our motivation of the present work is to examine the heating of salty ice as well as salty water by molecular dynamic simulation. In this paper we mainly use the microwaves with 2.5 GHz, except for 5-10 GHz microwaves for examining the frequency dependence of the heating.

2. Simulation Procedures

Ice and liquid water are characterized by a completely and partially ordered network of H$_2$O molecules, respectively, mediated by hydrogen bonds connecting adjacent two molecules [Matsumoto et al., 2002]. For this reason, we adopt an explicit water model with three point charges - the SPC/E water model [Toukan and Rahman, 1985; Berendsen et al., 1987]. A typical simulation run requires the computation time of a few days for roughly 3000 water molecules on our Opteron-based cluster machine (usually four processors are used per job). Although the model has reasonable electrostatic properties, for more accurate calculation of the energy absorption, the use of TIP4P-FQ model with polarization effect [English and MacElroy, 2003; English, 2006] may be preferred but with small number of water molecules due to large computation times.

We follow the same numerical procedures as those used previously [Tanaka and Sato 2007]. We start all the simulations with the crystal ice and relax it to the desired temperature before microwaves are applied. This is because molecules of initially random orientations take a very long time to arrive at the equilibrium with properly ordered hydrogen-bonded network. A water molecule of the SPC/E model in Fig.1 illustrates that three atoms form a rigid triangle H-O-H with partial charges $q (= 0.424e)$ and $-2q$ residing at the hydrogen and oxygen sites, respectively. The electrostatic forces are calculated for pairs of these atoms while the Lennard-Jones forces are calcu-
lateral only for the pairs of oxygen atoms. The equations of motion are

\[
m_i \frac{dv_i}{dt} = -\nabla \left( \sum_j \frac{q_i q_j}{r_{ij}} + 48 \varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} \right) + q_i E_{\text{mw}} \tag{1}
\]

\[
\frac{dr_i}{dt} = v_i \tag{2}
\]

where \( r_i \) and \( v_i \) are the position and velocity of \( i \)-th atom, respectively, and \( q_i \) is their mass charge, respectively, and \( r_{ij} = |r_i - r_j| \) is the distance between \( i \)-th and \( j \)-th atoms. The second term in the bracket on the right-hand side of Eq. (2) serves for two atoms not to overlap each other, where \( \sigma_{ij} \) is the sum of radii of two atoms and \( \varepsilon_{ij} \) is the Lennard-Jones energy. For water, \( \varepsilon_{\text{ww}} = 0.65 \text{ kJ/mol} \) and \( \sigma_{\text{ww}} = 0.317 \text{ nm} \). Salt ions are put randomly in space avoiding water molecules and are treated as isolated species with the charge \( q_{\text{Na}} = e \), the diameter \( 2\sigma_{\text{Na}} = 0.26 \text{ nm} \), and the Lennard-Jones energy \( \varepsilon_{\text{Na}} = 0.062 \text{ kJ/mol} \) for \( \text{Na}^+ \) and \( q_{\text{Cl}} = -e \), \( 2\sigma_{\text{Cl}} = 0.44 \text{ nm} \) and \( \varepsilon_{\text{Cl}} = 0.446 \text{ kJ/mol} \) for \( \text{Cl}^- \) [AMBER, 2008]; the hybrid rule

\[
\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}, \quad \sigma_{ij} = \sigma_i + \sigma_j \tag{3}
\]

is used when two species \( i \) and \( j \) are encountering. The diameter of \( \text{Cl}^- \) ion is comparable with the size of the network cell whose building blocks are six-membered water rings. The SHAKE and RATTLE algorithm [Andersen, 1983] is adopted in time integration of Eq. (1) and (2) to keep the rigid triangular shape of the molecule. The time step for integration is 1 fs.

Our simulation system consists of a cubic box of each side 4.2 nm that contains \((14)^3\) water molecules when salt is not added. The periodic boundary condition is imposed under the constant system volume. Thus, the Ewald sum for infinite number of periodic image charges is taken to correctly account for the electric field in which the particle-particle particle-mesh algorithm is adopted [Deserno and Holm, 1998]. The real space cutoff distance for both the electrostatic and Lennard-Jones forces is 1.0 nm, and 32 spatial grids are used for the Fourier-space calculation of the nonlocal electrostatic forces.

After an equilibration phase of 100 ps, a spatially homogeneous microwave electric field of the form \( \mathbf{E}_{\text{mw}}(t) = E_0 \sin \omega t \mathbf{x} \) is applied. The wave frequency \( f = \omega / 2 \pi \) is 2.5 GHz unless otherwise specified. To overcome the numerical noises in the simulation, the used wave amplitude is \( E_0 = 2.3 \times 10^6 \text{ V/cm} \) which is large but its associated energy with the electric dipole of a water molecule is less than the thermal energy at room temperature \( E_0 d / k_B T_{300K} \approx 0.4 \). This condition assures us the safe use of this electric field in our simulations, where \( d \approx 7.8 \times 10^{-30} \text{ Cm} \) is the dipole moment of the model water molecule.

3. Results and Discussion

The initial condition of the simulation is prepared by generating crystal ice of the \( I_h \) structure, and putting \( \text{Na}^+ \) and \( \text{Cl}^- \) ions of 1 mol% concentration (roughly 3 wt%) when salty ice or water is prepared. The \( I_h \) ice is isotropic in three directions whose physical properties are quite similar to those of the ordinary ice of the \( I_h \) structure [Eisenberg and Kauzman, 1969; Matsumoto et al., 2002]; we swap the O-H bonds of water molecules successively until an isotropic state has been reached. The initial structure is equilibrated for 100 ps at a given temperature, and then the microwave electric field of 2.5 GHz frequency is applied.

Figure 2 shows the time history of (a) the temperature (starting at 230 K) of the salty ice system, (b) time integrated value of the Joule heating and dipole heating terms, (c) the average velocity of \( \text{Na}^+ \) along the x
FIG. 3: The time history of the heating of salty water, (a) temperature of the whole system in Kelvin, (b) the Joule heating term of all salt (dotted) and that of Na ion (dashed), (c) the x-component velocity of Na ions, and (d) that of Cl ions with $v_0 = 10 \text{ m/s}$, $Q_0 = 10^{-9} \text{ J}$. The amplitude of the microwave electric field is shown by dotted lines in (c) and (d), where the electric field is turned on just after the equilibration phase at time 0 of the figure.

The heating of salty ice is compared with that of salty water in Fig. 3. Salty water with 1 mol% salinity is prepared in the same way as for salty ice, and is melted and equilibrated for 100 ps at 300 K. For the salty water, the heating rate increases with temperature above 350 K, as seen in Fig. 3(a) at which the slope of the curve becomes steeper. The velocity oscillations of Na and Cl ions in (c) and (d) also increase in time and are much larger than those for salty ice. The large oscillations at later times reveal de-trapping of salt ions from the cell of water network, which accelerates the heating due to the large amplitude of oscillations. A striking difference is found in the heating terms in panel (b): the Joule heating term much exceeds the dipole heating term, where the former is twice larger than the latter as shown previously [Tanaka and Sato, 2007]. It is interesting that Cl ions with heavier mass and larger radius respond more than Na ions to the microwave electric field. This implies that Cl ions are not stably contained in the cells of the hydrogen-bonded network of water molecules, which makes them more easily be de-trapped and move through the network.

As for reference, the heating of pure water against 2.5 GHz microwave is shown in Fig. 4. In this case, the excitation of dipole rotation is the only mechanism of energy absorption from the microwave. The heating rate of salty ice with 1 mol% salinity is comparable to that for pure water. The velocity oscillations are shown for (c) hydrogen atoms and (d) oxygen atoms, which are small compared with those in Fig. 3 and are out of phase with each other since the center of mass of water molecules is fixed because of the charge neutrality.

As pure ice is not heated by microwaves of the GHz band, the presence of salt in ice should be playing a decisive role in the heating (melting) process in the microwave electric field. We showed on the energy basis in Fig. 2 that not the Joule heating but the excitation of dipole rotation is responsible for the heating. Then it follows that electric dipoles of water molecules are allowed to rotate in salty ice, which occurs because of the local breaking of water network by salt ions. This is well recognized in Fig. 5 which shows the time history of the sum of the electric dipoles for (a) pure water and (b) salty ice.

For pure water, molecules begin rotational motions immediately with the microwave electric field. In the early phase when microwaves are applied to salty ice, the ro-
tational motion of the dipoles begins which is somewhat retarded and small compared to the case of pure water. This is completely different from the case of pure ice.

Figure 6 shows that the rigid network of ice is distorted quickly in the presence of salt ions even before microwave is applied, as seen in (b). Experimentally, anomalously high permittivity was reported for salty ice [Zhong et al., 1988]. Here, it is confirmed by numerical simulation at the molecular level that the high response of salty ice to microwaves is caused by the presence of salt ions in ice which weaken the hydrogen-bonded rigid network of water molecules.

The weakening of the hydrogen-bonded network of water molecules which occurs in salty ice is also confirmed by specially designed simulation: the diameter of charged salt ions is artificially reduced to 0.2 nm so that they nicely fit in the cell of the network. Even in such a condition, heating of salty ice does take place whose heating rate is almost three quarters that of the normal case. This proves that the weakening of the network in salty ice is caused mainly by the electrostatic effect of salt ions which is long-ranged, rather than the short-range geometrical effect.

4. Summary

By molecular dynamics simulation, we studied the heating process of salty ice, which we daily encounter when we melt frozen food in a microwave oven. We confirmed that the heating of salty ice is attributed to the weakening of the hydrogen-bonded network of water molecules in the presence of charged salt ions. In this process, the electrostatic effect was dominating over the short-range geometrical effect. The dependence of the heating rate on the microwave frequency was examined for salty ice and water, which again indicated that the internal structure of water molecules in salty ice is deformed. Thus, the water molecules in salty ice can rotate as freely as those in pure water under the microwave electric field.

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