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Supporting Information

Picosecond Melting of Ice by an Infrared Laser Pulse - A Simulation Study

Carl Caleman and David van der Spoel*
Department of Cell and Molecular Biology, Biomedical Centre
Box 596, Uppsala University, SE-75124 Uppsala, Sweden
*corresponing author, email: spoel@xray.bmc.uu.se

1   Electric field under periodic boundary conditions

Under the influence of an external electric field the molecules will order themselves such that the simulation box will get a net dipole moment. The effective electric field experienced in the simulation therefore consists of the applied electric field and the induced electric field from the dipoles in all the surrounding simulation boxes.

$$\boldsymbol{E}_{\text{eff}} = \boldsymbol{E}_0 + \boldsymbol{E}_{\text{dp}} \tag{1}$$

The field from the electric dipoles,

$$\boldsymbol{E}_{\text{dp}} = \frac{\boldsymbol{p}}{4\pi\varepsilon_0} \sum_{\theta,r} \frac{2\cos^2\theta - \sin^2\theta}{r^3} \tag{2}$$

(where $\boldsymbol{p}$ is the total dipole of the simulation box, r the distance to the dipole and θ the angle between the direction of dipole at the dipole and the point where the electric field is calculated) will direct itself opposite the applied electric field, due to the periodic boundary conditions. To study surface effects we have, in addition to the starting structure presented in the paper, also simulated an ice-sheet consisting of the water molecules possitioned at the same positions as in the
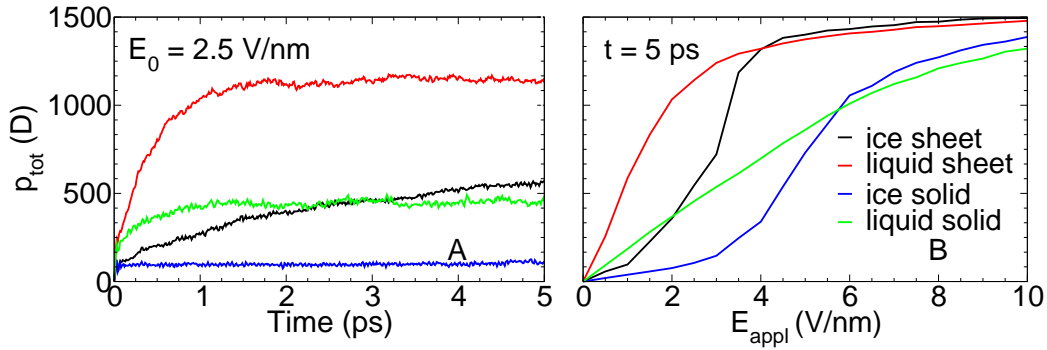
Figure 1: A: The total dipole moment in a constant electric field ($\mathbf{E_0} = 2.5$ V/nm) as a function of time. In water the dipole moment reaches a maximum after a few picoseconds. This is not the case in the ice sheet (2d), due to the fact that it takes time to melt. B: The total dipole moment in a constant electric field after 5 ps as a function of the applied electric field. At field strength below $\mathbf{E_0} = 2.5$ V/nm, the dipole moment in water is linearly dependent on the applied field. In ice this is not as clear, since it melts more at higher field strengths.

bulk case but with the (X) axis extended by a factor of three. We will refer to the different systems as "3d" and "2d" models, respectively. The 2d model allows us to investigate whether melting kinetics is affected by the presence of a surface. In a constant electric field the total dipole of the system is linearly dependent of the electric field for low field strengths (Fig. 1). Introducing α as the effective polarizability of the box, the dipole moment can be expressed as:

$$\boldsymbol{p} = \alpha \boldsymbol{E}_0. \tag{3}$$

The effective electric field can then be written as:

$$\boldsymbol{E}_{\text{eff}} = \boldsymbol{E}_0\Big(1 + \frac{\alpha}{4\pi\varepsilon_0} \sum_{\theta,r} \frac{2\cos^2\theta - \sin^2\theta}{r^3}\Big). \tag{4}$$

As shown in the paper (Paper, Fig. 1B) the dipole moment in a solid ice crystal (3d), in the direction of the applied electric field of the system will not surpass 80 Debye in a field oscillating with a frequency of 100 THz ($\lambda = 3.00~\mu$m). Using this result and Eq. 2 the maximum $\boldsymbol{E}_{\text{dp}}$ can be determined to be less than 0.08 V/nm, i.e. significantly lower than the applied electric field of 0.5-2.5 V/nm. In a constant electric field where the dipoles would have time to fully respond to the applied external field, $\boldsymbol{E}_{\text{dp}}$ can not be neglected in a simulation box with

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periodic boundary in three directions. For a 2d system with periodic boundary conditions $\boldsymbol{E}_{\mathrm{dp}} > \boldsymbol{E}_0$ for $\boldsymbol{E}_0 = 2.5$ V/nm (using Eq. 3 and Eq. 2), since $\alpha = 112 \times 10^{-9}$ (m Debye)/V (Fig. 1B). The dipole moment of the 3d ice solid aligns somewhat with the external field (Paper, Fig.1B). Although the dipole moment in the absence of a field is almost zero in the liquid and ice, a complete alignment with the field would yield a system dipole of around 450 Debye and 110 Debye respectively (Fig. 1A).

2 Absorption spectrum for the flexible TIP4P water model

The peak in the absorption spectrum is at $\lambda = 3.00$ μm (Fig. 2). At $\lambda = 3.00$ μm 10 kJ/mol is absorbed versus only 4 kJ/mol at $\lambda = 2.85$ μm. In liquid water there are two main vibrational absorption peaks around 3.0 μm .(1) The so called symmetric stretch, where the hydrogens oscillate away from the oxygen simultaneously, absorbs at 3.05 μm, and the asymmetric stretch, where the hydrogens are oscillating such that one is always moving towards the oxygen, at 2.87 μm.(2) The absorption intensities of the two oscillations mentioned are related as 87:100 (1), where the asymmetric is the dominant. In ice these absorptions are red shifted.(3; 4) Comparing the intensity of the absorbed energy (I_{abs}) and the integrated intensity of the applied field (I_{appl}) we find that roughly $I_{\mathrm{abs}}^2 \sim I_{\mathrm{appl}}^2$, as expected. The simulated absorption spectra agree well with experimental spectra for water and ice (5; 6; 7), which is expected since the water model was developed to do so. At the broad peak around 3.0 μm there is no significant difference between the three directions of the external electric field (Fig. 2).

The two columns of spectra, for the 3d and the 2d structures, are almost identical, indicating that as far as absorption concerns there are no or very little surface effects in our system. The same conclusion can be drawn by comparing the melt time for the 2d and the 3d (not shown) - there is no, or very little difference in the melting process between the two set ups. For a system under the influence of a constant electric field there are indeed surface effects at picosecond time scale (Fig. 1A).
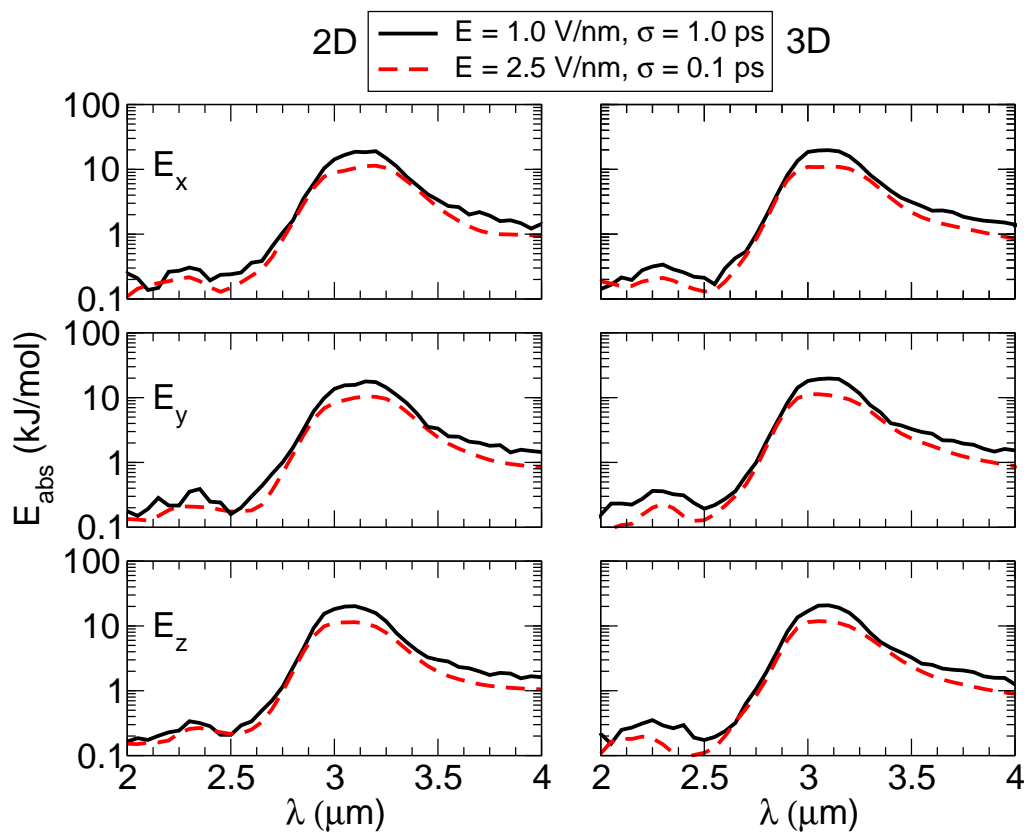
Figure 2: Energy absorbed by the crystal (computed as the difference in the total energy of the system at t = 0 ps and at t = 20 ps) as a function of wavelength, for two different laser intensities and pulse lengths. On the left, results for the 2d ice sheet, on the right for the solid 3d crystal. In the first row the electric field vector is pointing along the x-axis, the second row along the y-axis and the last row along the z-axis. The absorption peak seen at 3.00 μm is due to the stretching (asymmetric and symmetric) and the bending overtone (at 2.94 μm in liquid water (8)) of the liquid water. No significant difference between the three different directions of the electric field vector is observed.

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