

Molecular Dynamics Simulations of Water and Hydrate Molecules by TIP5P Code

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Dielectric constant of water and ice

Water dielectric constant in temperature. It changes slowly for less than 273 K, and after phase transition it becomes rapidly for > 273 K. (Eyring et al., PNAS, 1966).

Water T (K), Dielectric constant of liquid

273 K 88 $\leftarrow 298$ K, $\epsilon = 80$

373 K 56

473 K 35

Ice I, T (K), Dielectric constant

273 K 91.5

262.3 K 95.0

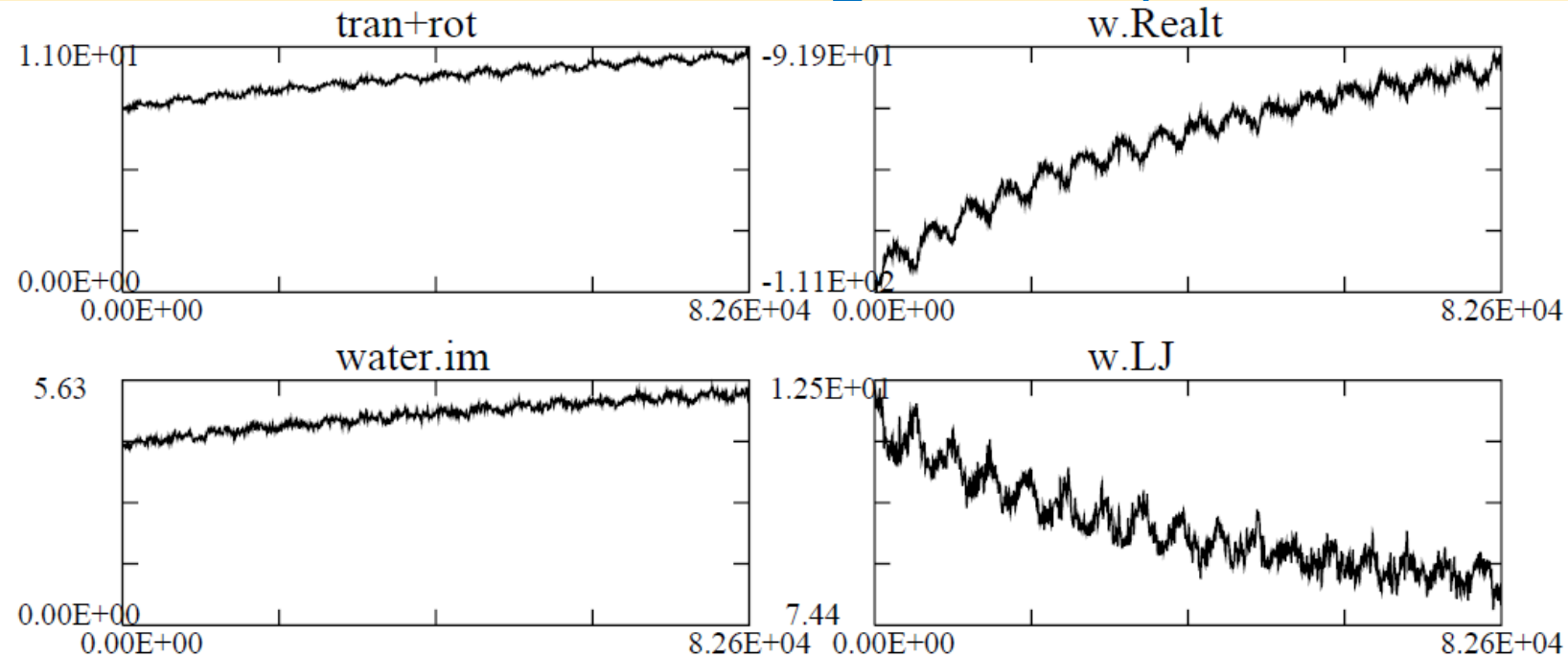
252.2 K 97.4

241 K 100

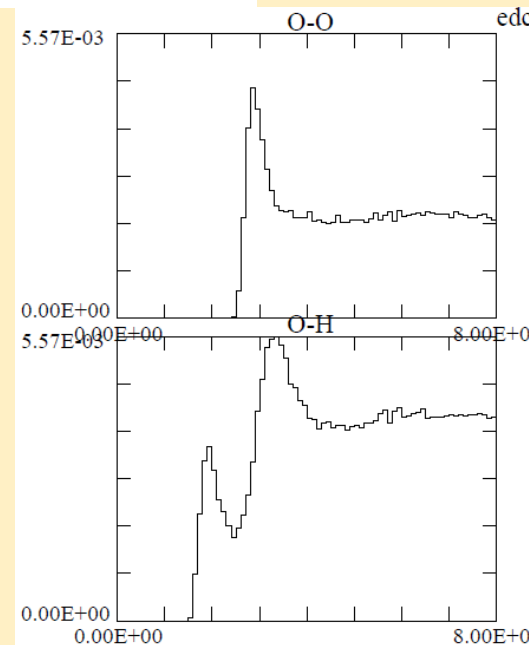
228.4 K 104 $\leftarrow 230$ K, $\epsilon = 104$

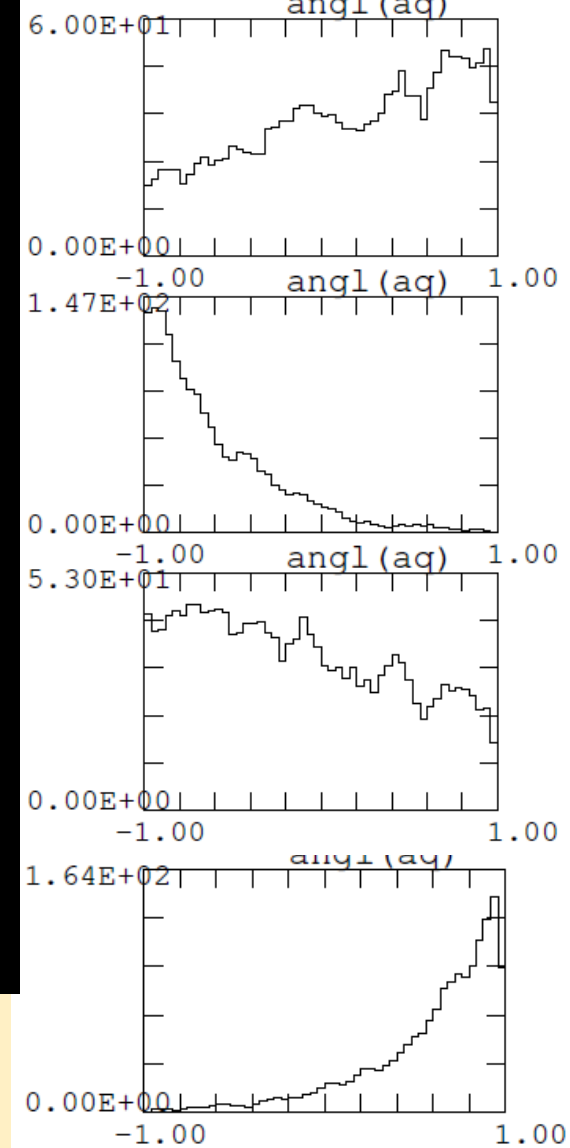
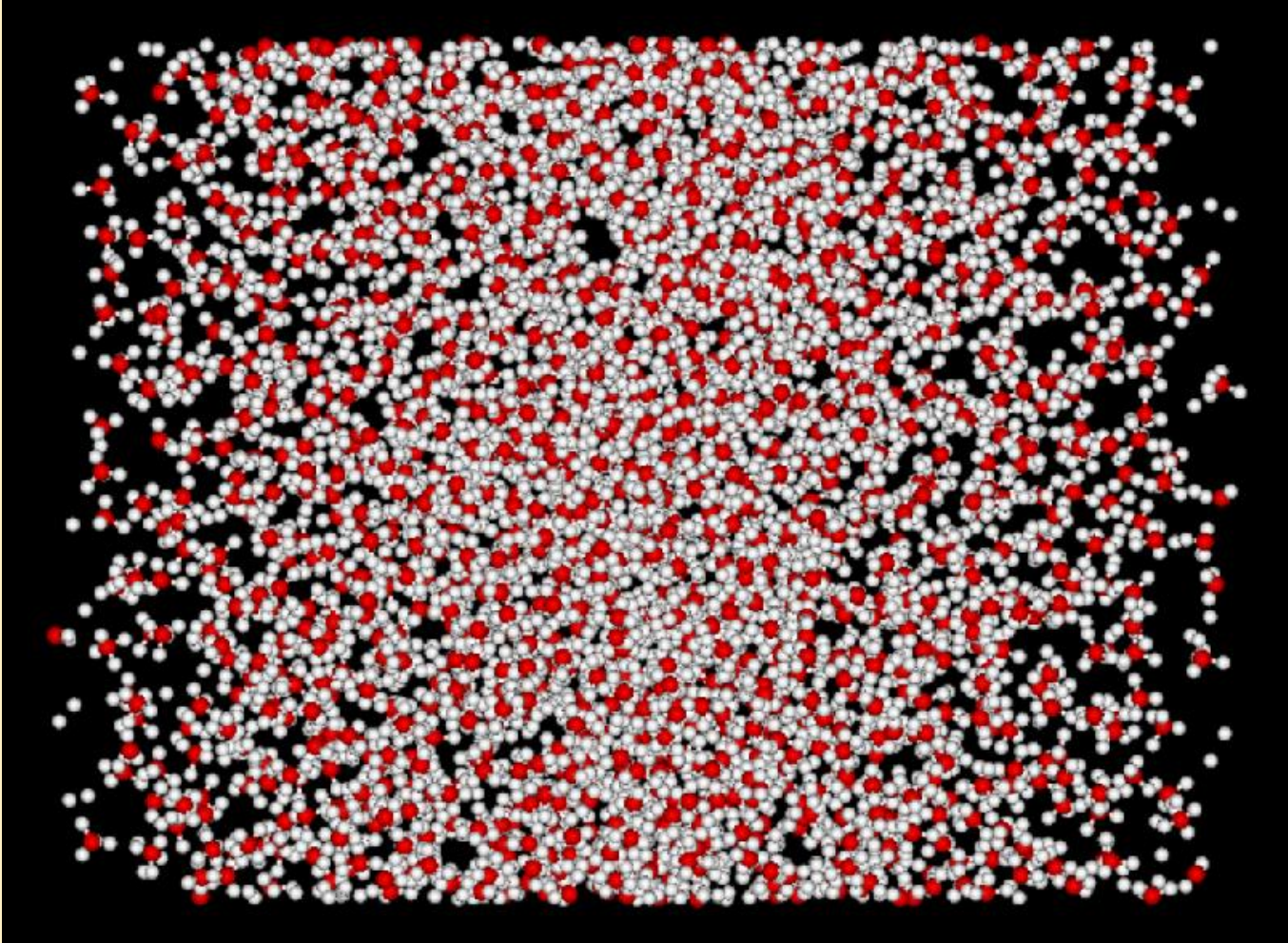
216.3 K 114

Simulation water starting at 298 K, NVE



The time $t=82,600$ starting from 298 K with 1728 water molecules, imposed electric field 10 GHz in x-direction with $E_0 = 5 \times 10^6$ V/cm and NV run (by 8.3 periods). Left: a) Total kinetic energy, b) rotational energy only, c) Coulombic energy, Lennard-Jones energy. The final temperature is about 405 K. Right: Pair distribution functions of a) O-O atoms, b) O-H atoms in $R=0-8$ Angstrom. O and H atoms are thus mixed showing heavy water interactions. Compare with the frozen ice of 230 K.

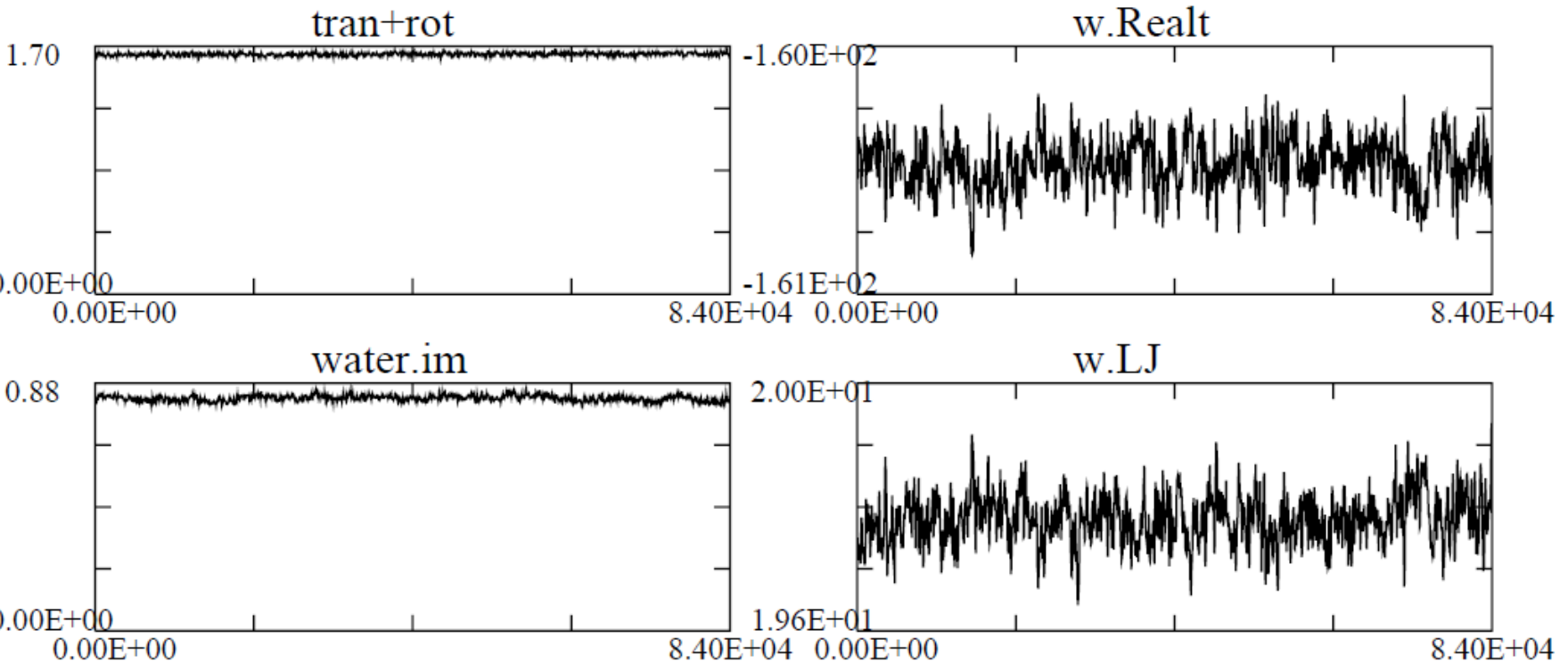




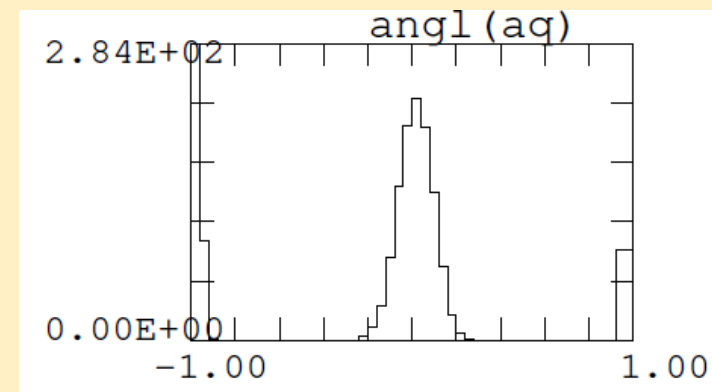
Water molecules starting 298 K.

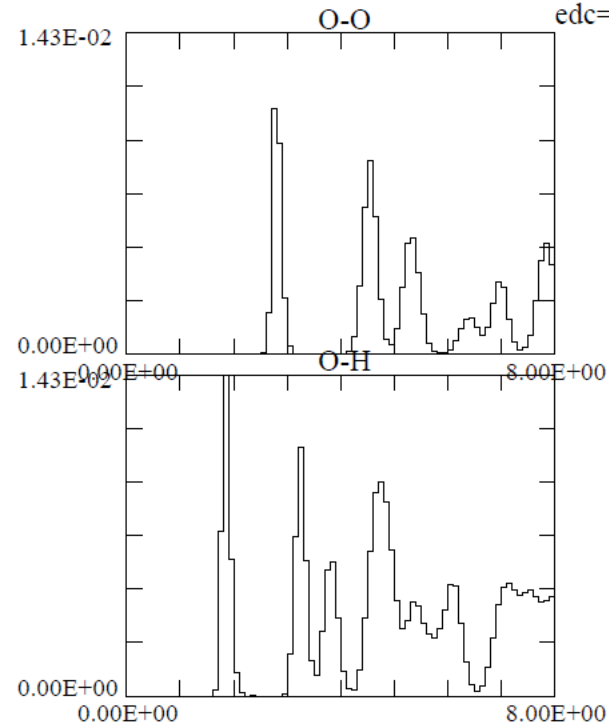
Left: Scatter plot of water at $t=80,000$, b) x-directional cosine distribution for the cross bins of $(-1.0, 1.0)$ at $t=72,500$ to $80,000$. Due to phase lag of molecules compared to imposed electric field, water is largely heated,

Simulation starting at ice 230 K, NVE

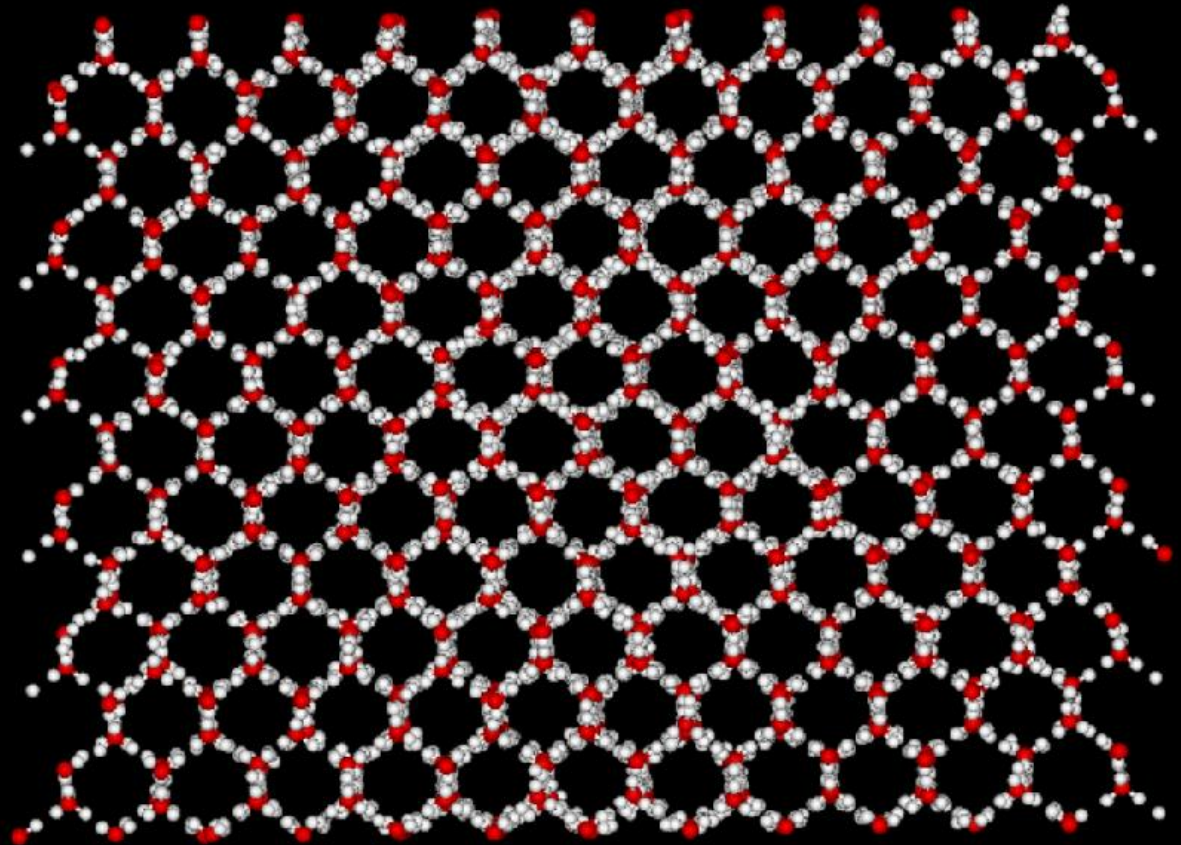


At temperature 230 K of 1728 water molecules, AC electric field 10 GHz in the x-direction with intensity $E_0 = 5 \times 10^6$ V/cm. Left: a) total kinetic energy, b) rotational energy only, c) Coulombic energy, d) Lennard-Jones energy, at the time of $t=84,000$. Right: cosine distribution of water in Bins $(-1,1)$ of the x-direction. No oscillations are really found at the imposed electric field.



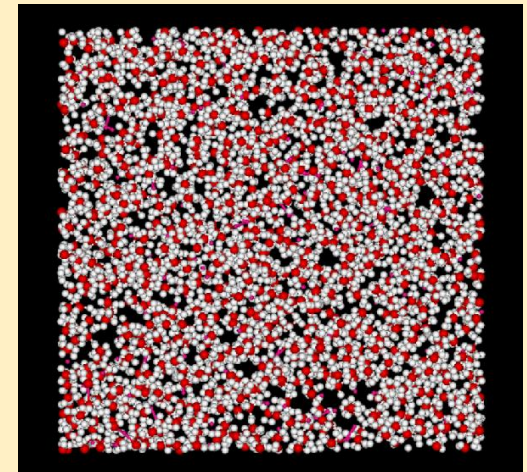
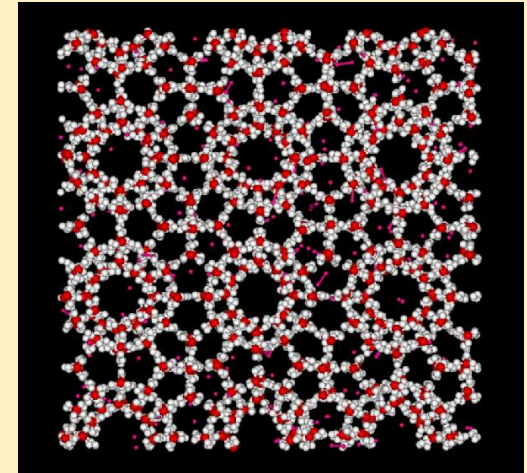
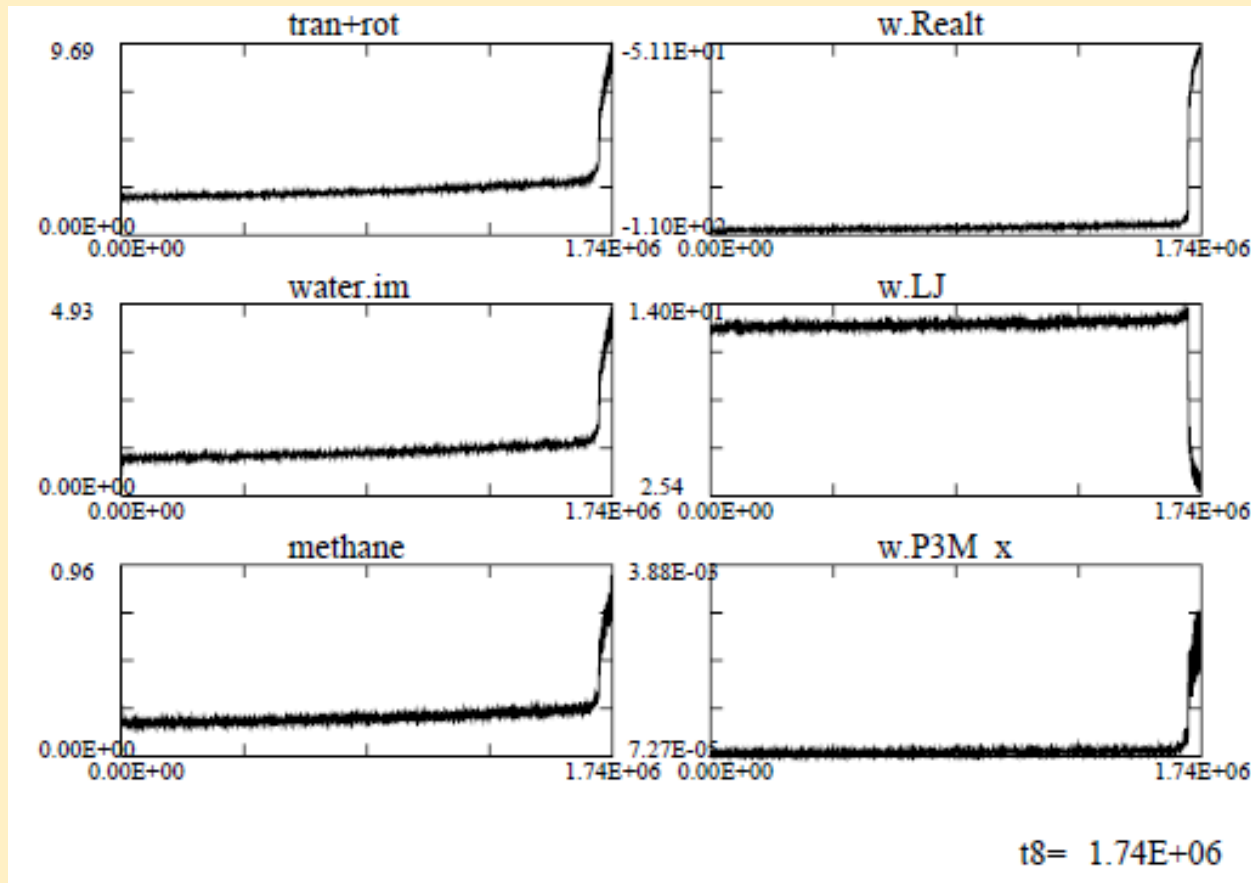


Time $t=80,000$ of the temperature 230 K.
Right: Scatter plot of water molecules where ice is frozen by 6-membered water clusters.

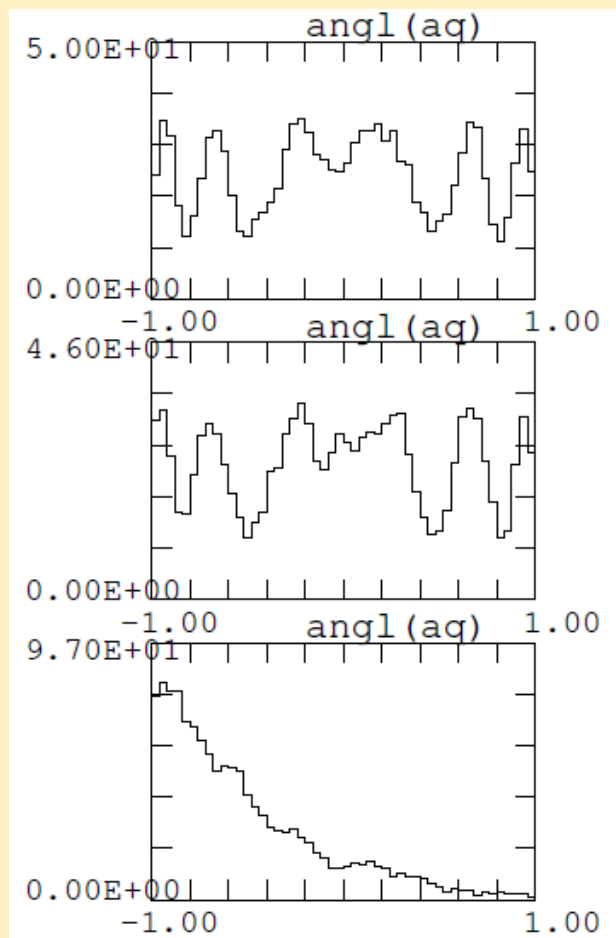


Methane Hydrate at $T > 273\text{ K}$

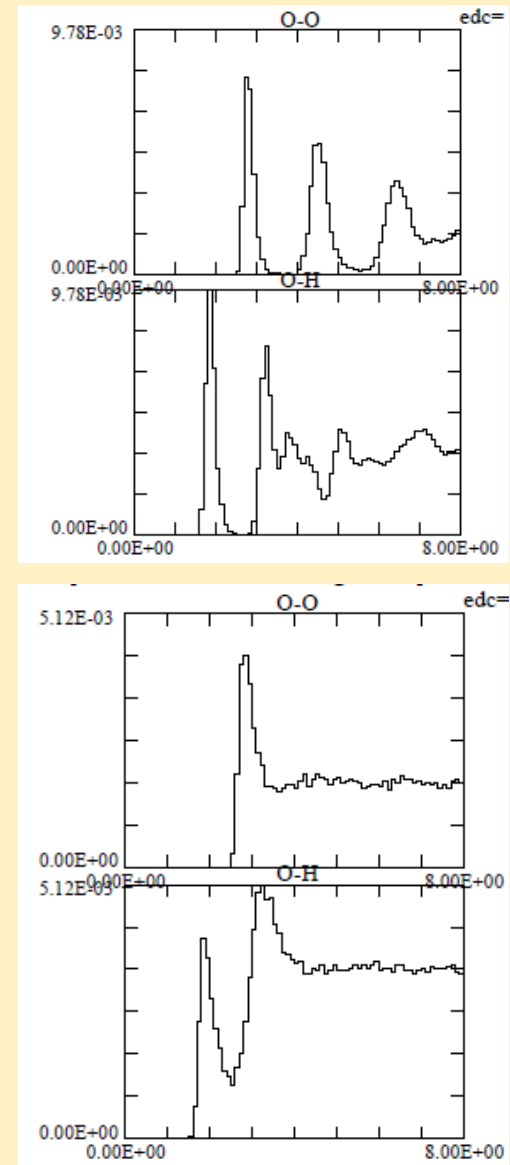
Microwaves at 10 GHz are excited for methane hydrate at $T > 273\text{ K}$ by the TIP5P-Ewald code. The collapse of molecules is seen at $t = 1,700,000$.



Energy of water and methane, and that of Coulombic and LJ potentials (top), and scatter plots at the times of $t = 1.70 \times 10^6$ and after sudden collapse at $t = 1.74 \times 10^6$ (right).



Distribution of cosine's in the x direction at the times of $t=1,500,000$ to $t=1,700,000$, where it undergoes the explosive collapse of methane hydrate at that time.



Pair distribution functions of O-O and O-H atoms at the time $t=1,600,000$ (top) and $1,700,000$ (bottom).

References

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3. ”Microwave heating of water, ice and saline solution: Molecular dynamics study”, M.Tanaka and M.Sato, J.Chem.Phys., 126, 034509 1-9 (2007).
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5. “Microwave heating and collapse of methane hydrate by molecular dynamics simulations, M. Tanaka, M. Sato, and S. Nakatani, arXiv.1909.01024, Cornell University, 2019, USA