Molecular Dynamics Simulations of Water and Hydrate Molecules by TIP5P Code

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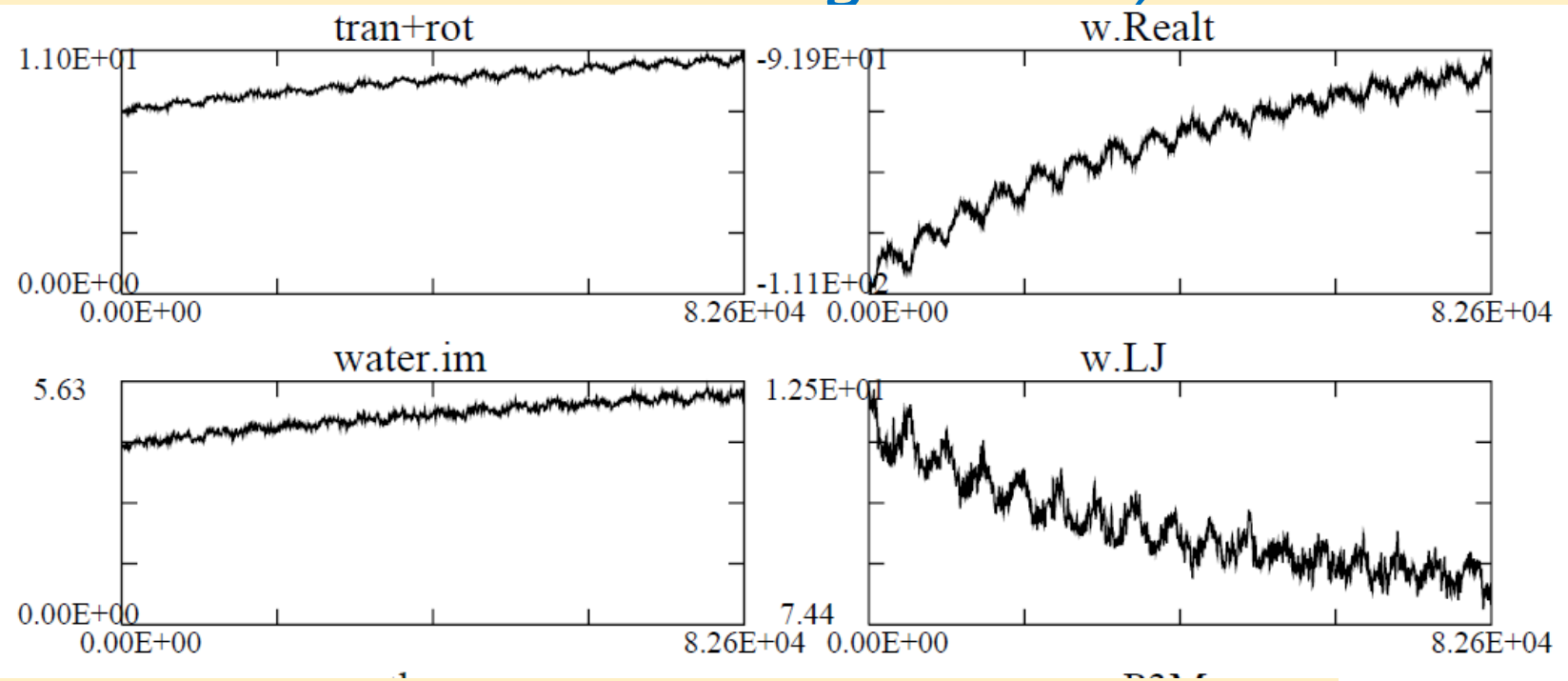
Dielectric constant of water and ice

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).

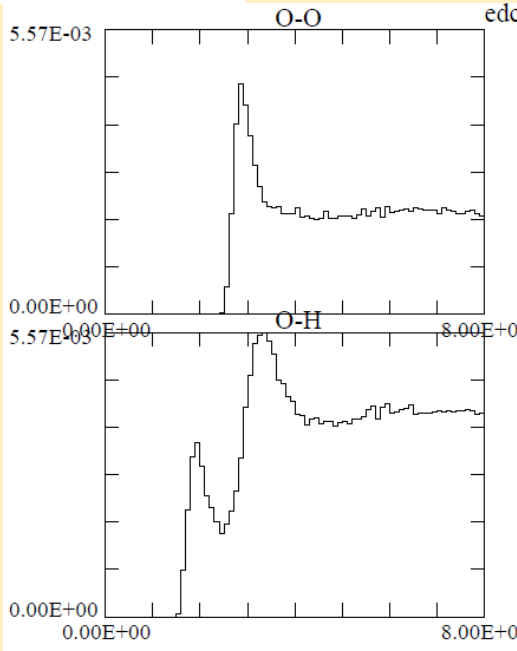
Water T (K)	Dielectric constant of liquid
273 K	88 <– 298 K, $\varepsilon = 80$
373 K	56
473 K	35

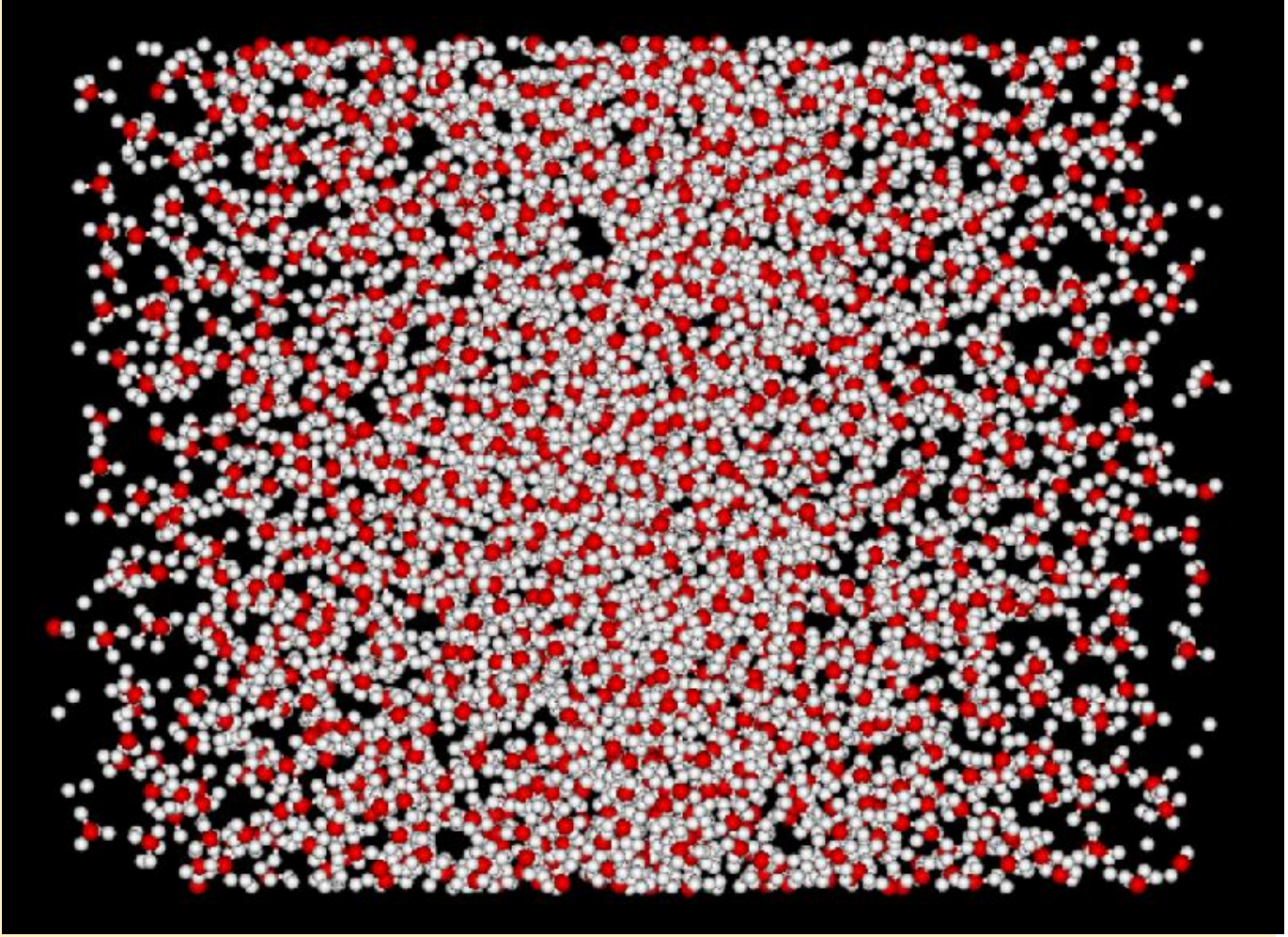
Ice I, T (K)	Dielectric constant
273 K	91.5
262.3 K	95.0
252.2 K	97.4
241 K	100
228.4 K	104 <– 230 K, $\varepsilon = 104$
216.3 K	114

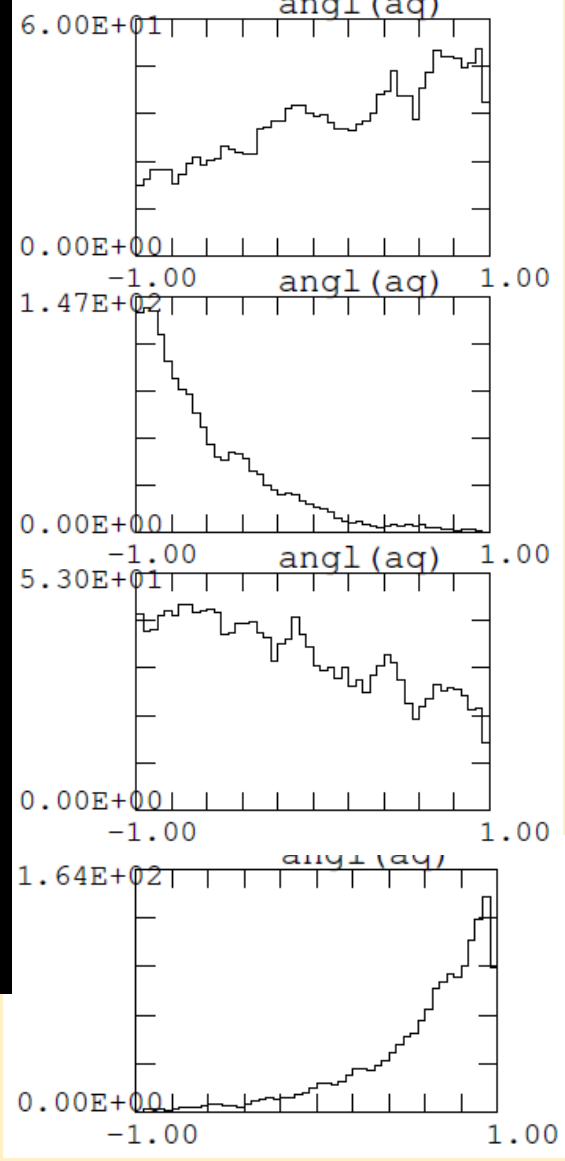
Simulation water starting at 298 K, NVE



The time t=82,600 starting from 298 K with 1728 water molecules, imposed electric field 10 GHz in x-direction with E_0= 5x10^6 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.

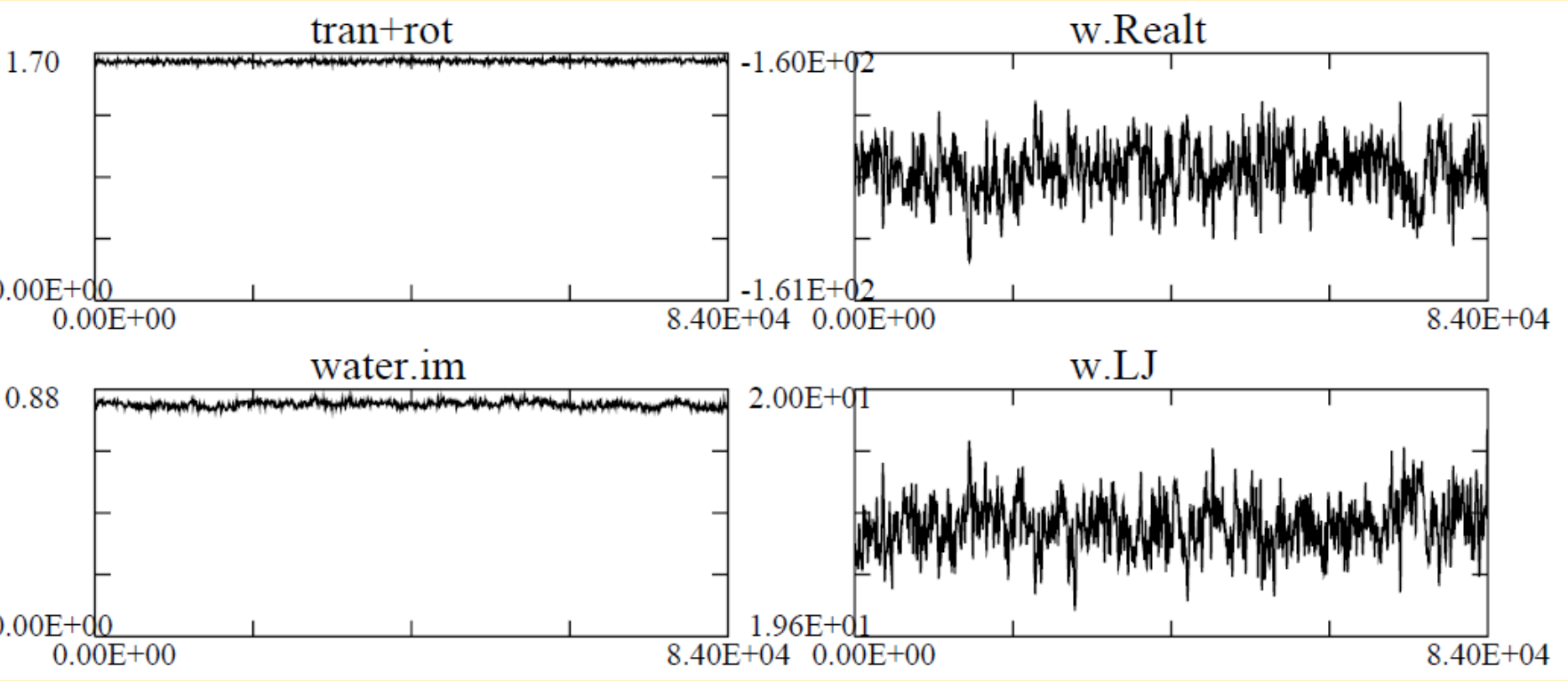




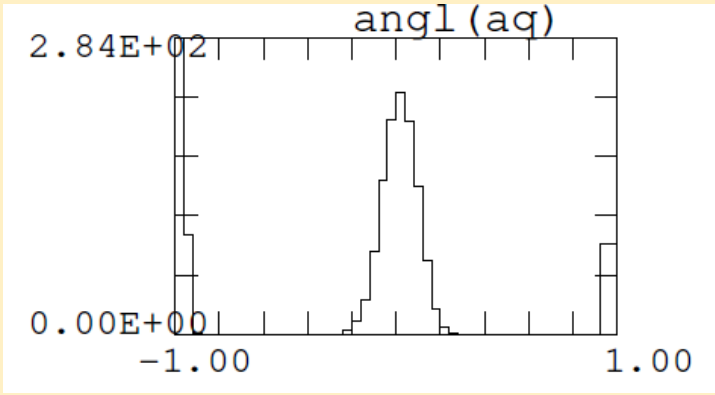


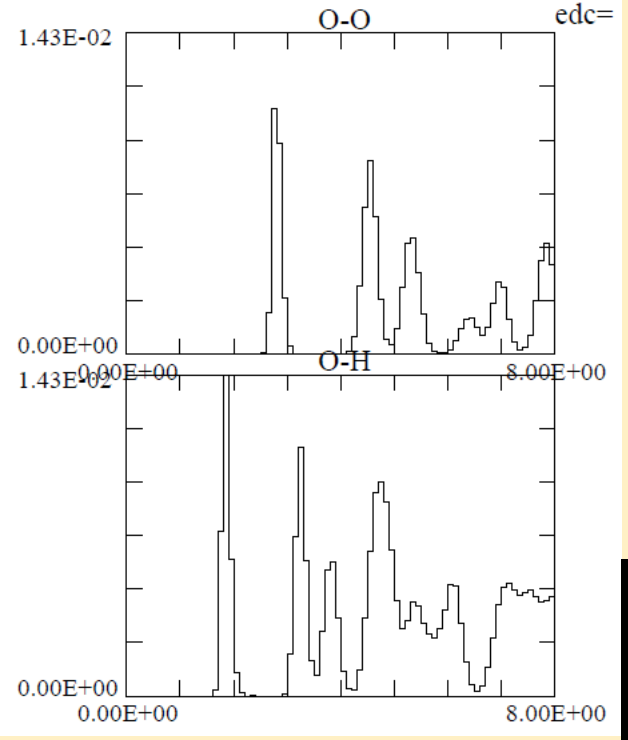
Water molecules starting 298 K.
Left: Scatter plot of water at t=80,000, b) x−directional cosine distribution for the cross bins of (−1.0,1.0) at t=72,500 to 80,000. Due to phase lag of molecules compared to imposed electric field, water is largely heated,

Simulation starting at ice 230 K, NVE

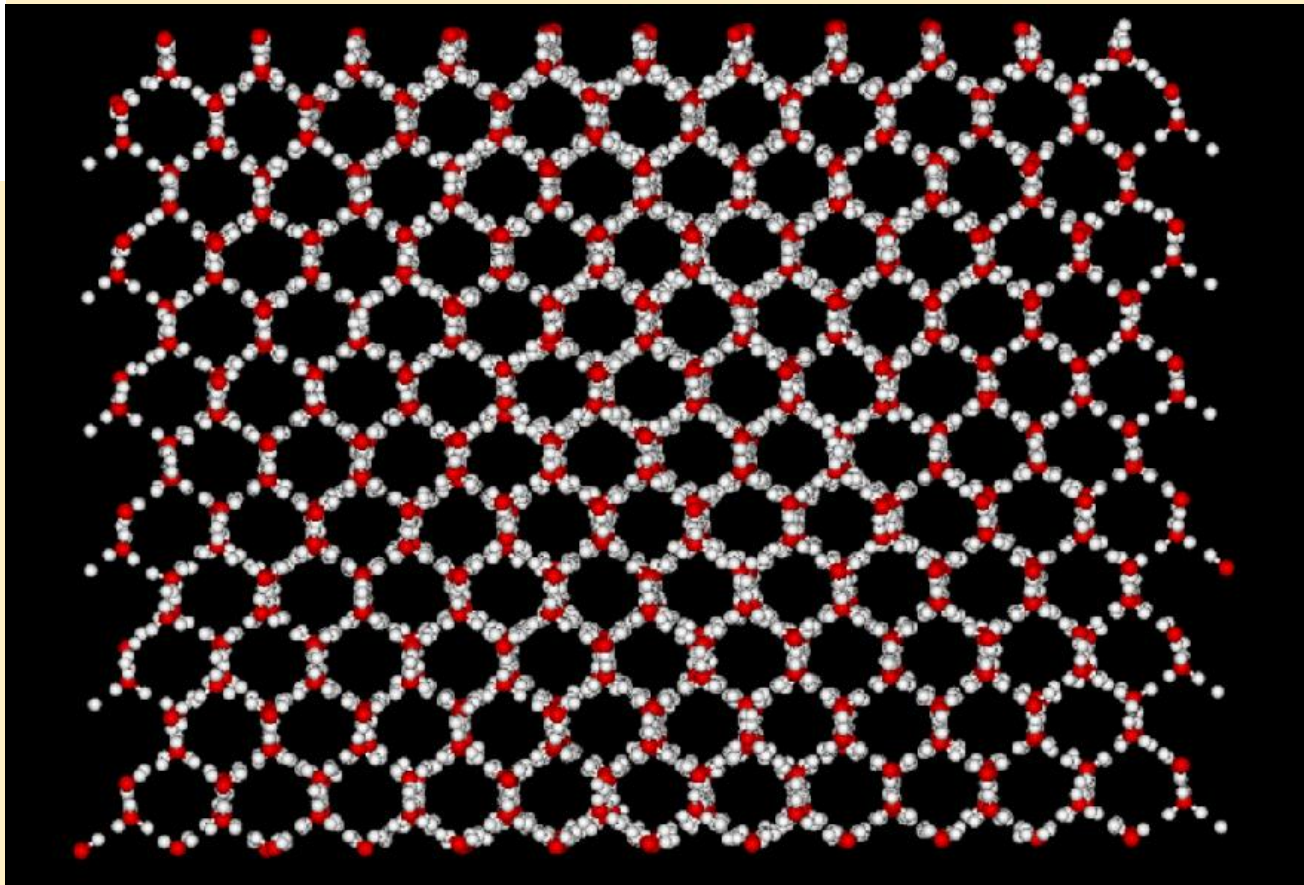


At temperature 230 K of 1728 water molecules, AC electric field 10 GHz in the x-direction with intensity E_0= 5x10^6 V/cm. Left: a) total kinetic energy, b) rotational energy only, c) Coulombic energy, d) Lennard-Jones energy, at the time of t=84,000. Right: cosine distribution of water in Bins (-1,1) of the x-direction. No oscillations are really found at the imposed electric field.



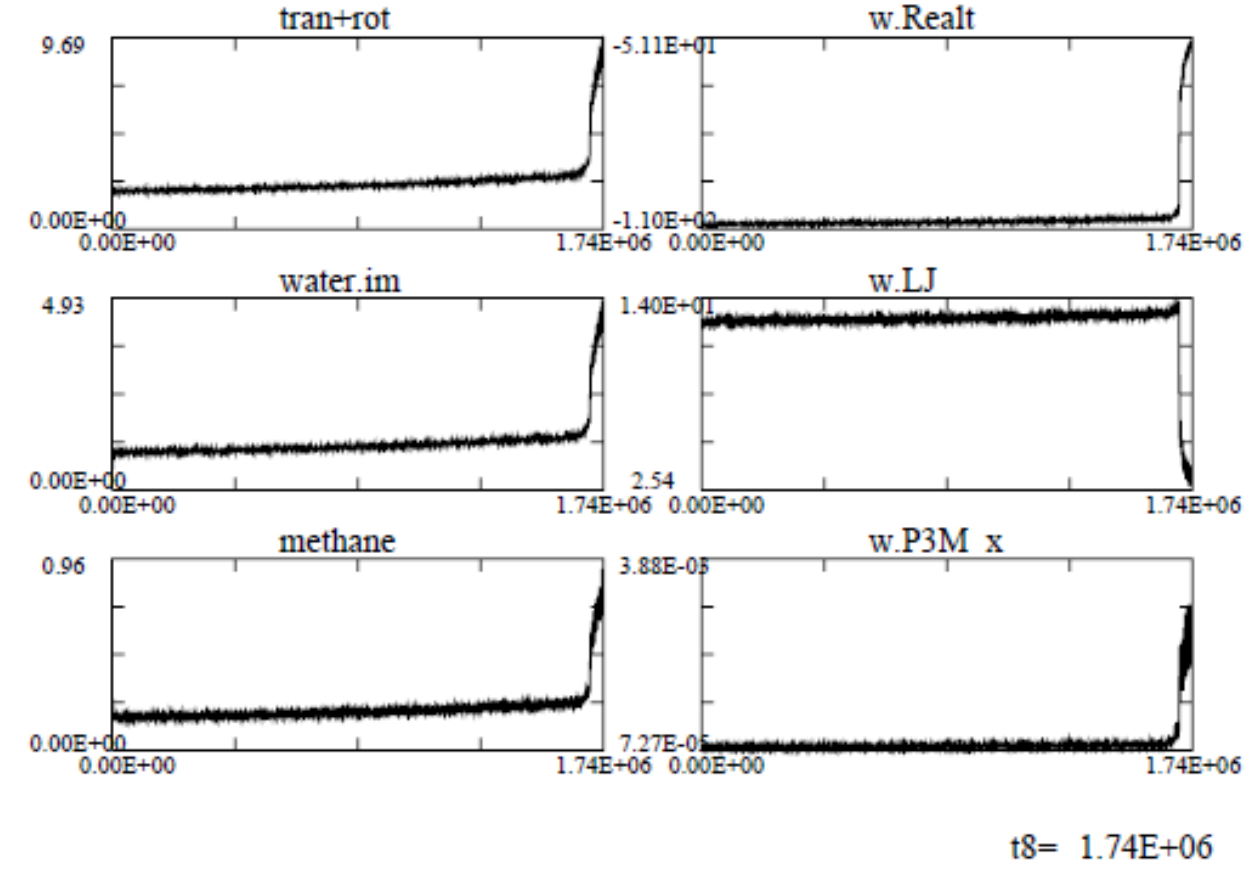


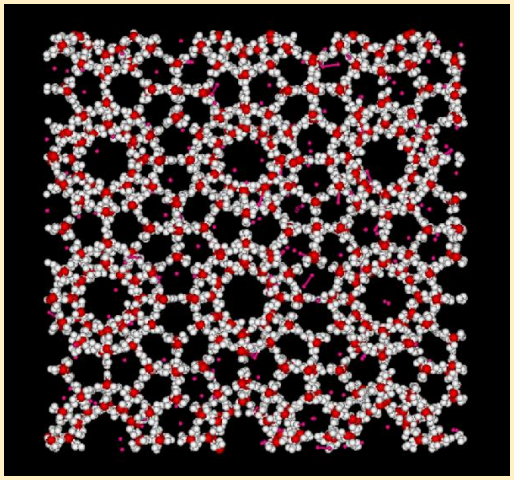
Time t=80,000 of the temperature 230 K.
Left: a) Pair distribution functions of O–O atoms b) O–H atoms for R=0–8 Angstrom. Peaks are well separated at this temperature.
Right: Scatter plot of water molecules where ice is frozen by 6–membered water clusters.

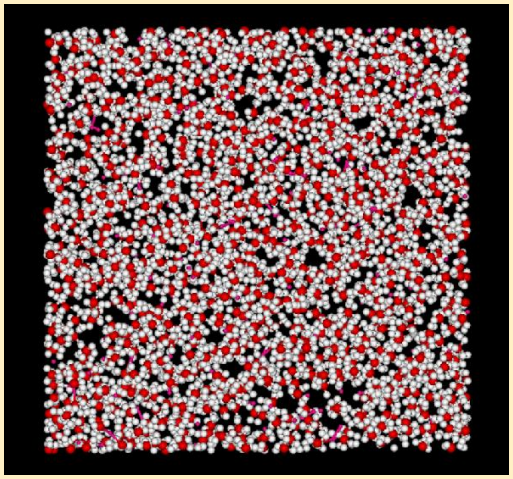


Methane Hydrate at T > 273 K

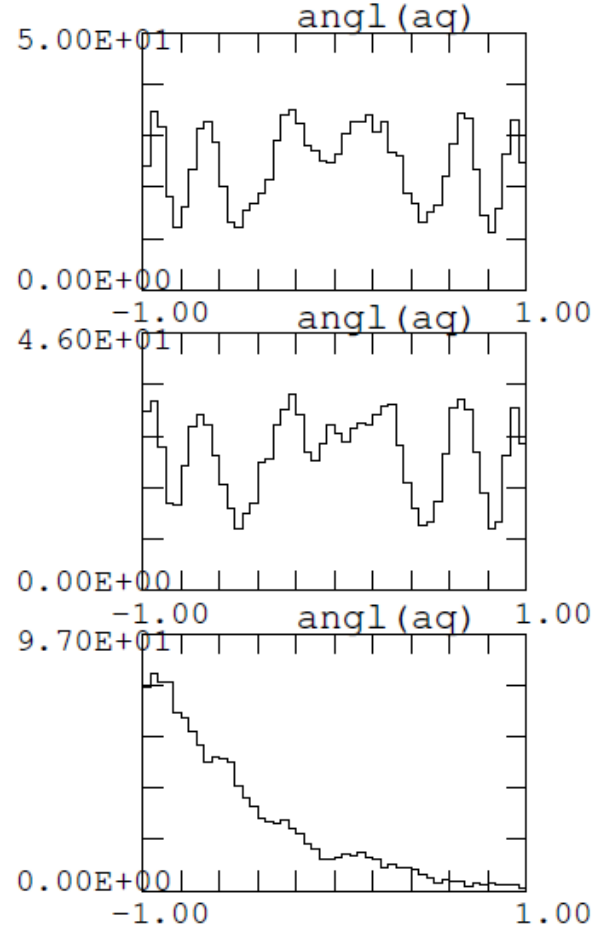
Microwaves at 10 GHz are excited for methane hydrate at T>273 K by the TIP5P-Ewald code. The collapse of molecules is seen at t=1,700,000..



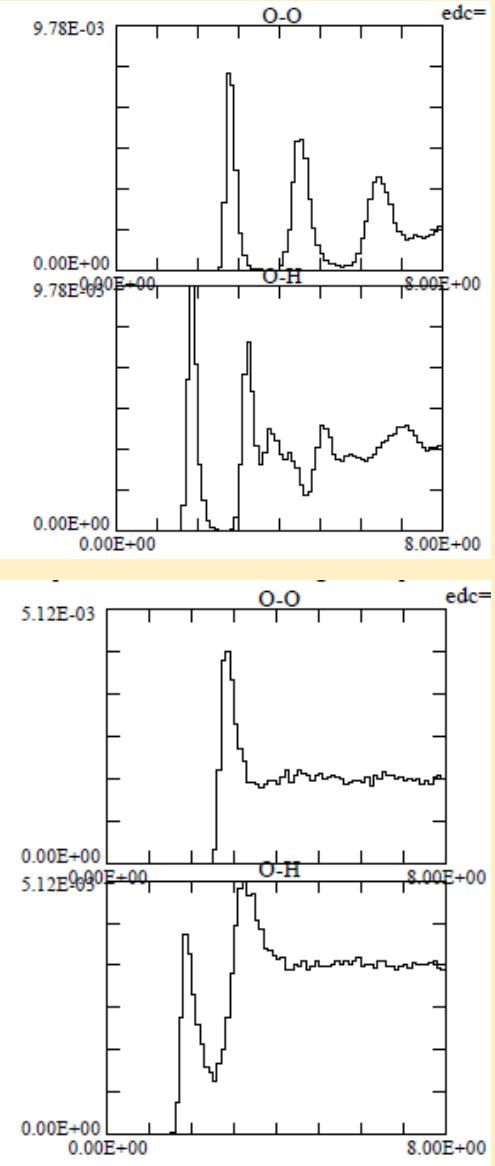




Energy of water and methane, and that of Coulombic and LJ potentials (top), and scatter plots at the times of t= 1.70 x 10^6 and after sudden collapse at t=1.74 x 10^6 (right).



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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4. “Microwave heating of water and ice by TIP5P code”, M. Tanaka, https://github.com/Mtanaka77/ (May 2023).
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