

# ***Molecular Dynamics Simulations of Water and Hydrate Molecules by TIP5P Code***

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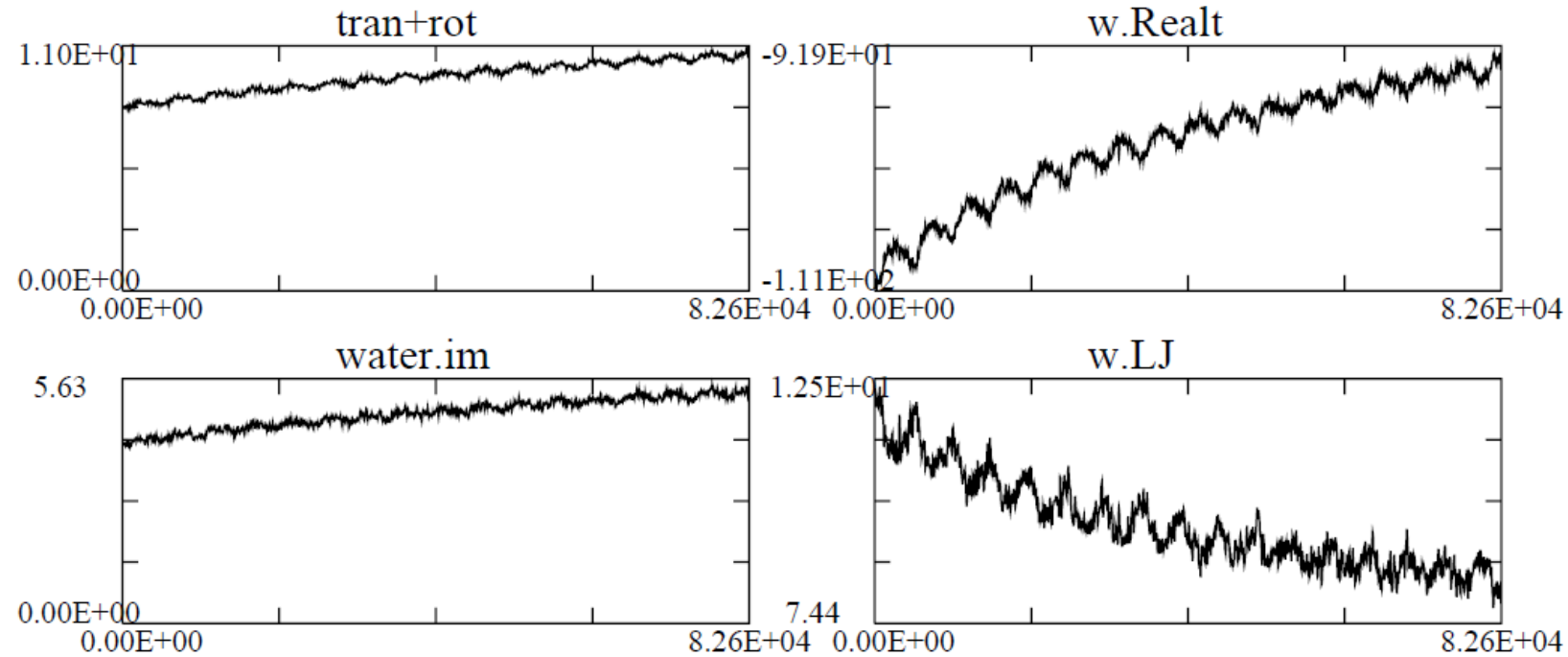
# Dielectric constant of water and ice

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).

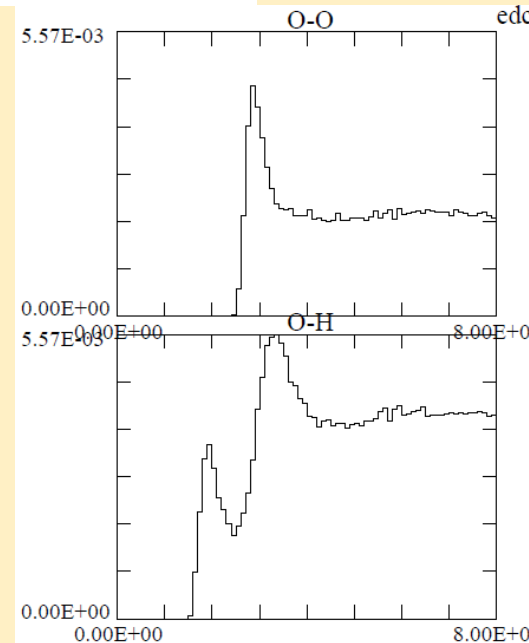
Water	T (K), Dielectric constant of liquid
273 K	88 $\leftarrow 298$ K, $\epsilon = 80$
373 K	56
473 K	35

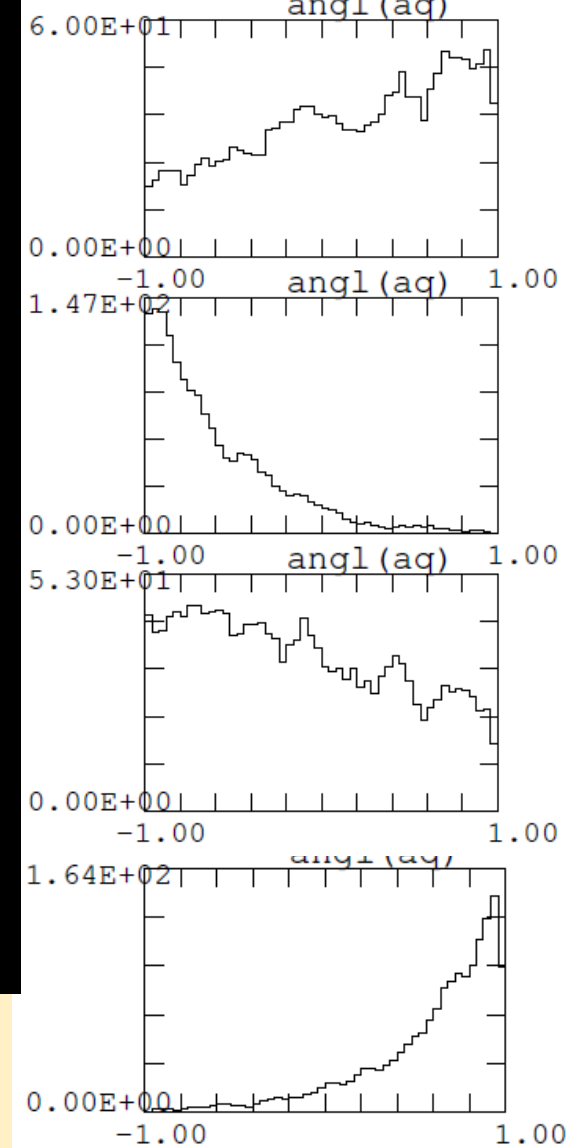
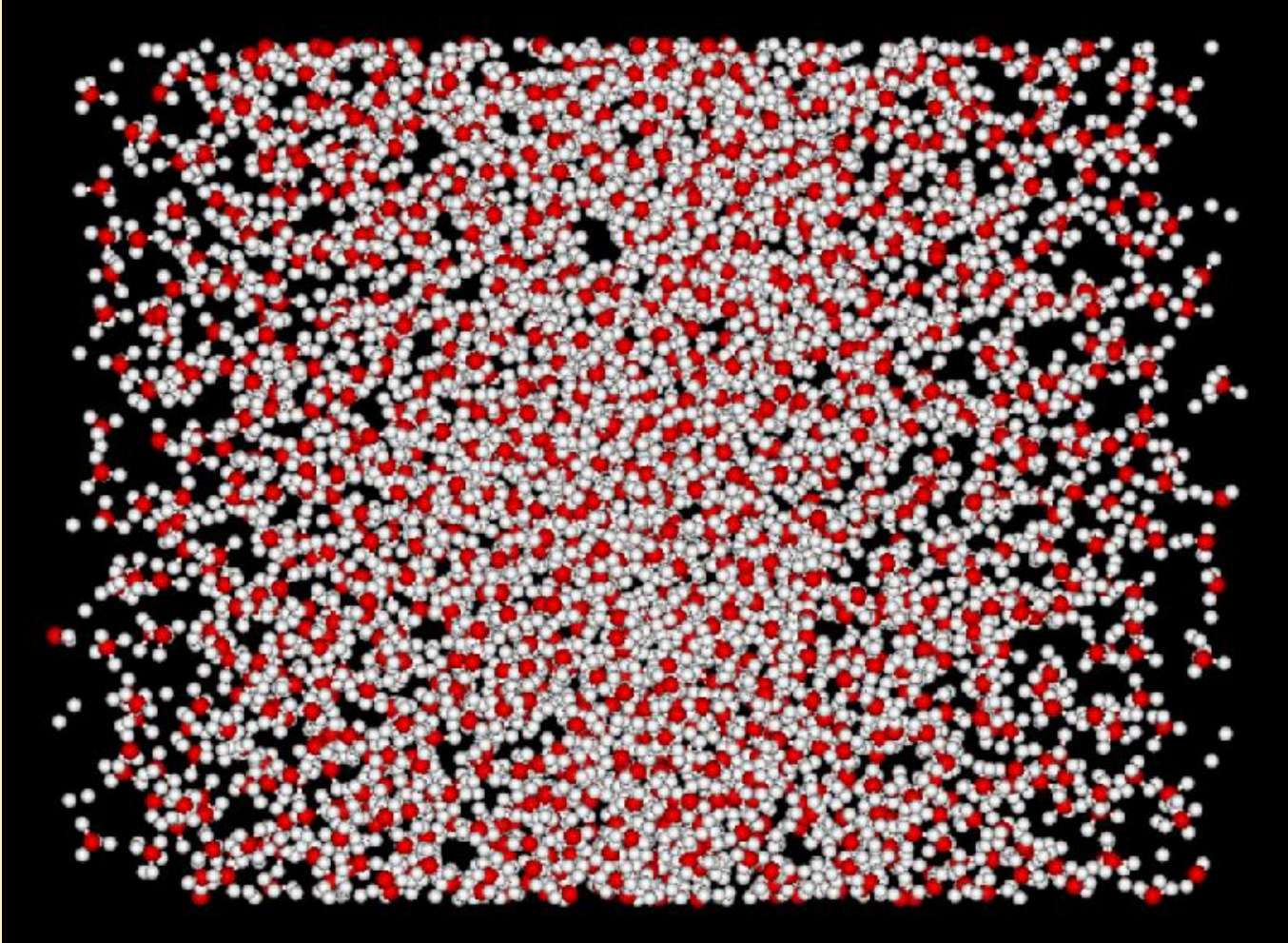
Ice I, T (K), Dielectric constant	
273 K	91.5
262.3 K	95.0
252.2 K	97.4
241 K	100
228.4 K	104 ← 230 K, $\epsilon = 104$
216.3 K	114

# 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.

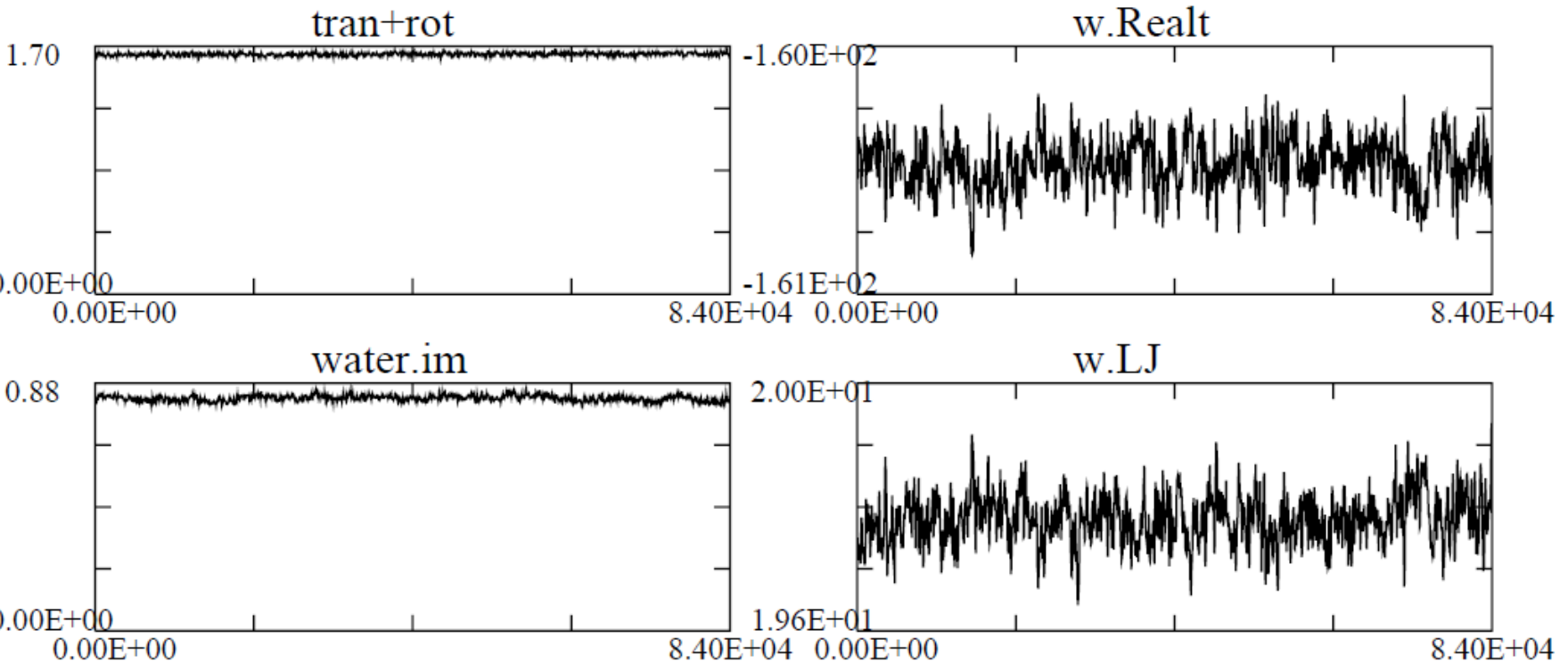




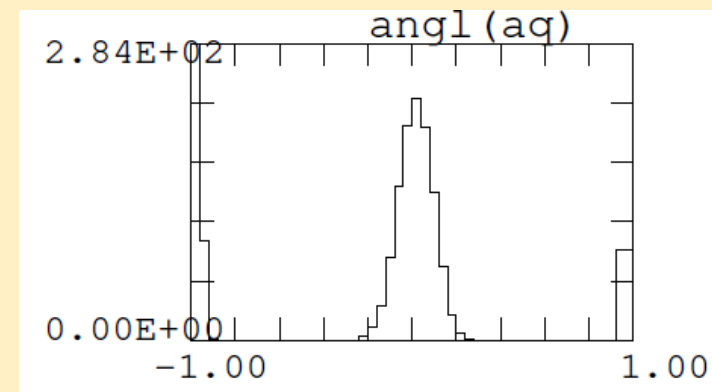
Water molecules starting 298 K.

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,

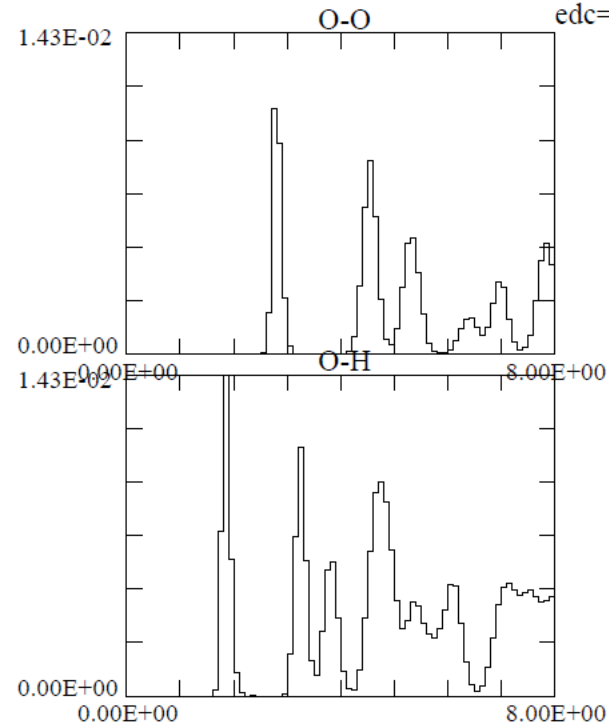
## *Simulation starting at ice 230 K, NVE*



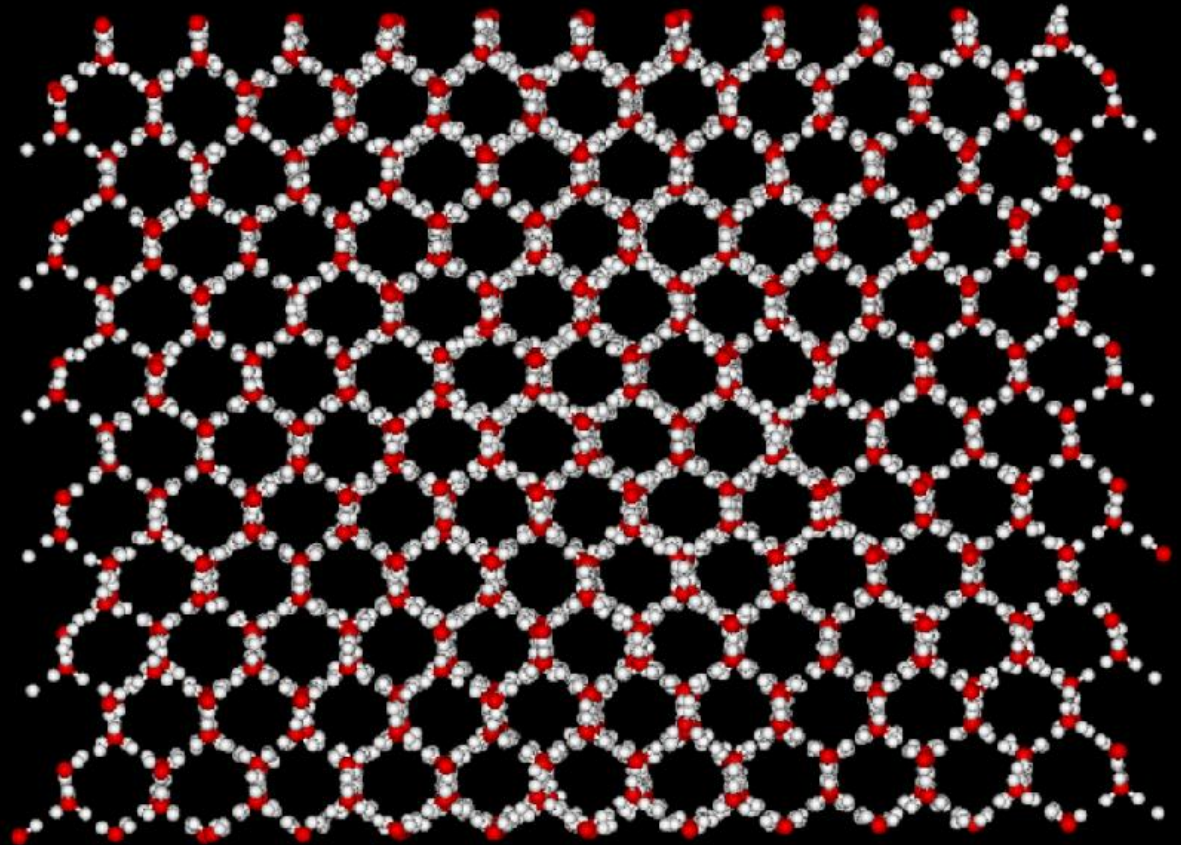
At temperature 230 K of 1728 water molecules, AC electric field 10 GHz in the x-direction with intensity  $E_0 = 5 \times 10^6$  V/cm. Left: a) total kinetic energy, b) rotational energy only, c) Coulombic energy, d) Lennard-Jones energy, at the time of  $t=84,000$ . Right: cosine distribution of water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





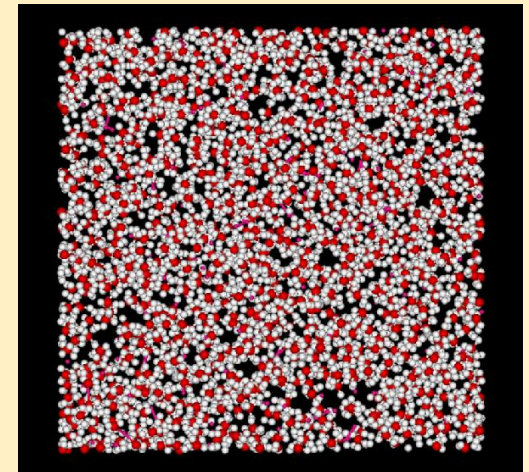
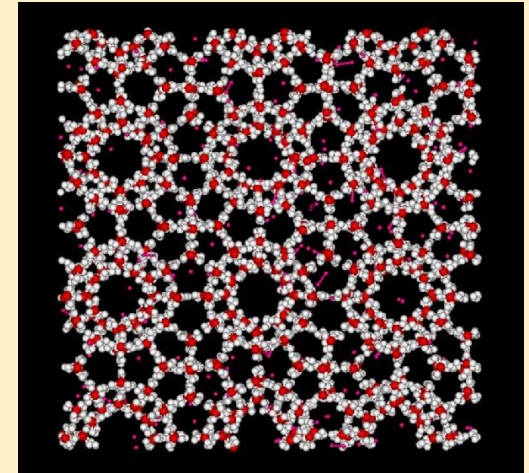
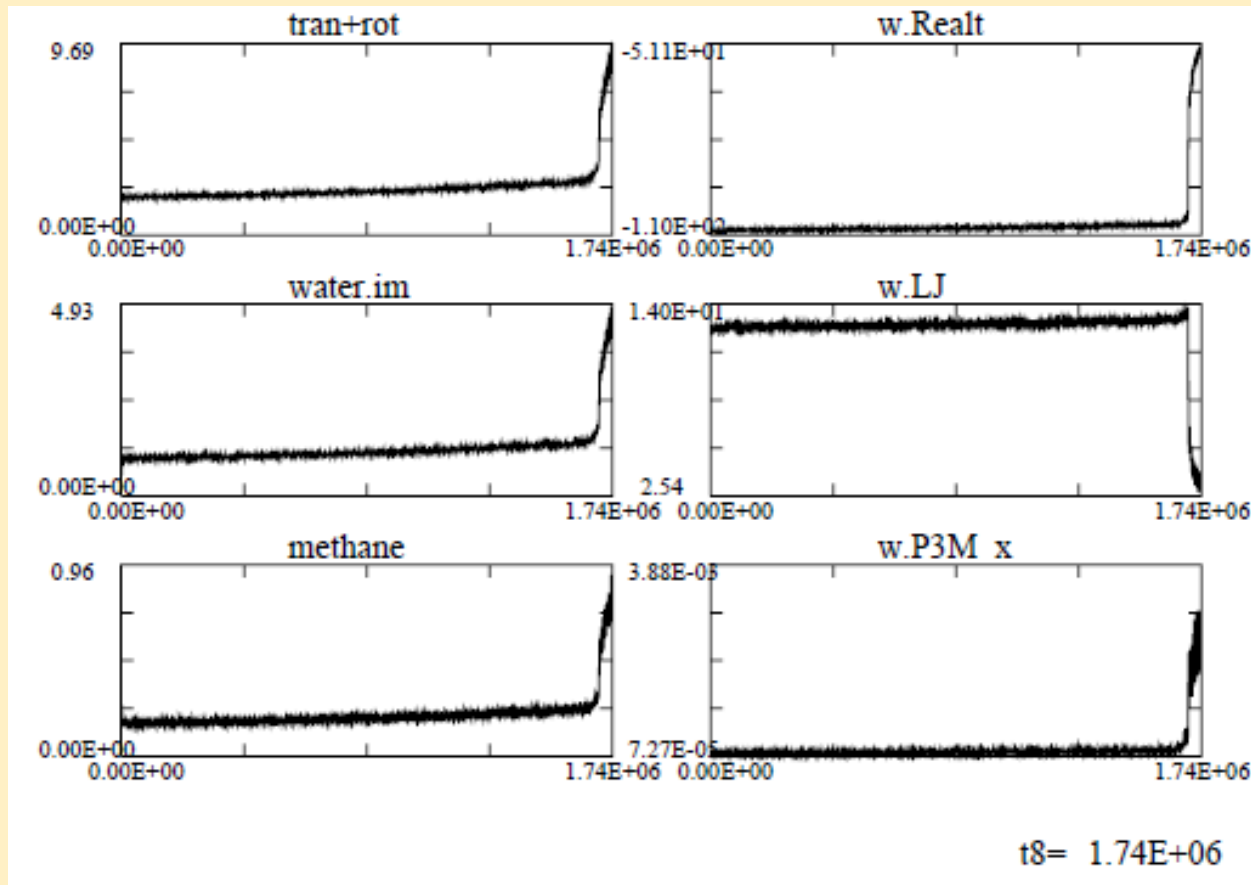


Time  $t=80,000$  of the temperature 230 K.  
Left: a) Pair distribution functions of O-O atoms  
b) O-H atoms for  $R=0-8$  Angstrom. Peaks are well separated at this temperature.  
Right: Scatter plot of water molecules where ice is frozen by 6-membered water clusters.



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

Microwaves at 10 GHz are excited for methane hydrate at  $T > 273\text{ K}$  by the TIP5P-Ewald code. The collapse of molecules is shown here.



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

# 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