Molecular Dynamics Simulation of Water by TIP5P Model

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Procedures of molecular dynamics simulation for water and ice are written in the five-point water TIP5P model. Before, the shake/rattle model was used to show the ice not melting by microwaves - theory discovery in JCP 2007. Today, five-body water molecules are used with two hydrogens H1, H2 and two dummy sites L1, L2. The fifth oxygen site is assigned as Lennard-Jones potential Psi= A/r^12 -B/r^6. One then gets the water TIP5P model by the six-membered water or ice crystals.

1. *"Classical Mechanics", H. Goldstein, C. Poolee, J. Safko, 3rd Edition, Pearson Education Inc., England, 2003.*

2. *"Microwave heating of water, ice and saline solution: Molecular dynamics study", M.Tanaka and M.Sato, J.Chem.Phys., 126, 034509 1-9 (2007).*

3. *"Water and hydrate by molecular dynamics TIP5P simulation", M. Tanaka, https://github.com/Mtanaka77/.*

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!************************************************* May, 2023 ****
!*                                                              *
!*   ## Molecular Dynamics of Water and Ice by TIP5P Code ##    *
!*     - Microwave heating, ice below T=273 K is not melted     *
!*                                                              *
!*   Author/Maintainer: Motohiko Tanaka, Ph.D., Nagoya, Japan   *
!*                                                              *
!*   Released by GPL-3.0 License, https://github.com/Mtanaka77/ *
!*   Copyright(C) 2006-2024. All rights reserved.               *
!*                                                              *
!*   Reference                                                  *
!*   1) M.Tanaka, J.Comput.Phys., vol. 79, 206 (1988).          *
!*   2) M.Tanaka, J.Comput.Phys., vol.107, 124 (1993).          *
!*   3) M.Tanaka, Comput.Phys.Comm., vol.87, 117 (1995).        *
!*   4) M.Tanaka and M.Sato, J.Chem.Phys,. 126, 034509 (2007).  *
!*   5) M.Tanaka, Comput.Phys.Comm., vol.241, 56 (2019).        *
!* ------------------------------------------------------------ *
!*                                                              *
!*   Files for this simulation                                  *
!*      @p3mtip5p code name (p3m + tip5p)                       *
!*          07a is a run name and sequential number (a,b,c...)  *
!*                                                              *
!*   1. @p3mtip5p07a.f03 : MD simulation code                   *
!*   2. param_tip5p_D07a.h : parameter file, physical constants *
!*   3. TIP507_config.start0 : parameter file, kstart=0         *
!*      or continuation TIP507_config.start1 : kstart=1 or 3    *
!*   4. Initial molecules (exyz and quaternion)                 *
!*      1cx666a.exyz/1cx666a.q for liquid water, 1cx666b.xyz in *
!*      230 K or mh3.exyz,mh3.q for methane hydrate.            *
!*      Refer to if_xyz1 or if_xyz2 parts in subroutine /init/. *
!*                                                              *
!*   Histories:                                                 *
!*     Translation and rotation of molecules                    *
!*      5-point hydrogen and oxygen pairs                       *
!*      prefactor (realteil) and pref_eps (Lennard-Jones)       *
!*      epslj_A,B for water, ep(i) for hybrid molecules.        *
!*                                                              *
!*     Fujitsu FX100 by Feb.2020, NEC-Aurora from July 2020.    *
!*                                                              *
!************************************** First code: 02/26/2005 ****
!*                                                              *
!*  1. >>> run's name is given by param_tip5p_D07a.h            *
!*                                                              *
!*  2. >>> Run parameters are given in TIP07_config.start0, or 1 *
!*       which is read by /read_conf/.                          *
!*                                                              *
!*  3. >>> Start, Restart and continue runs.                    *
!*                                                              *
!*   Physical units:                                            *
!*    t_unit= 0.0100d-12          ! 0.01 ps                     *
!*    a_unit= 1.0000d-08          ! 1 Ang                       *
!*    w_unit= 1.6605d-24*18.      ! H2O is the unit             *
!*    e_unit= 4.8033d-10          ! esu                         *
!*                                                              *
!*     ^  dv     t^2 e^2    qq'    12 t^2 eps   r0        1 r0  *
!*     m ---- = --------- ---- + ------- --- [(--)^12 - -(--)^6] *
!*        dt      ma^3     r^2     ma^2    r     r         2 r  *
```

Molecular dynamics simulation of water and ice molecules by TIP5P model

Type: Fortran 2003
Length 4000 lines

Main subroutines:
es3d_tip5, run_md, moldyn, realteil, forces_5, p3m_perform, perform_aliasing_sums, calculate_differential_operator, …, sinc, init

Post-processing routine & graphics:
data write/read by fort.11, fort.12, fort.08, fort.13, fort.18, fort.77.ps

Download from the site:
https://github.com/Mtanaka77/Water_and_Hydrate_by_Molecular_Dynamics_TIP5P_Simulation/

Procedures of Water and Ice Molecules by Five-Body TIP5P Model

A. *Five sites are oxygen*(O), *hydrogen* 1 *and* $2(H)$, *and hydrogen virtual* L *sites. They have*, $0, +0.241e$, *and* $-0.241e$ *charges, respectively. The* $L1$ *and* $L2$ *are called dummy sites.*

B. *Separate* $\mathbf{R}_j$, $\mathbf{V}_j$ *and* $\mathbf{r}_i$ *with* $j=1, N/5$, $i=1, N$ *for molecules, and* $\mathbf{r}_i = (x_i, y_i, z_i)$ *means for the three sites. The separation is done at the starting step only; once determined at* $t = 0$, *they become constant in time.*

C. *The half time step is first executed for a predictor step, and the full time step is made for advance of time.*

D. *Before the end of one step, the forces are calculated. The L sites are calculated by algebraic vector operation.*

E. *After correction of quaternions, go to the beginning of the cycle. The leap – frog method is used for the plasmas and waters.*

Each step: translation (Step 1), rotation (Step 2-4), adding the fields – three sites, Coulomb (Step 5-8).

0. *Read positions* $(x, y, z), i = 1, N$, *and quaternions from the file*, $'read(30)\, e0, e1, e2, e3',\ j = 1, N/5$ (*by Dr.Matsumoto, Okayama Univ*).

1. *Sum up five sites and advance*, $\dfrac{d\mathbf{V}_j}{dt} = \dfrac{1}{m_j}\sum_{k=1}^{5}\mathbf{F}_k, \quad \dfrac{d\mathbf{R}_j}{dt} = \mathbf{V}_j,$
   for the translational motion.

2. $$\frac{d\mathbf{L}_j}{dt} = \sum_{k=1}^{5}\left(y_k F_k^z - z_k F_k^y, \quad z_k F_k^x - x_k F_k^z, \quad x_k F_k^y - y_k F_k^x \right)$$
   for the rotational motion: the sums are made over the five sites.

3. $\omega_{j,\alpha} = (A_{\alpha 1} L_x + A_{\alpha 2} L_y + A_{\alpha 3} L_z) / Im_{j,\alpha}$, *the angular frequency for speices* $A_{\alpha\beta}$ *and inertia moments* $Im_{j,\alpha}$ *at* $\alpha = x, y, z$.

4. $$\frac{d\mathbf{q}_j}{dt} = \frac{\Delta t}{2}(-e_1\omega_x - e_2\omega_y - e_3\omega_z, e_0\omega_x - e_3\omega_y + e_2\omega_z,$$
$$e_3\omega_x + e_0\omega_y - e_1\omega_z, -e_2\omega_x + e_1\omega_y + e_0\omega_z).$$

(continued)

5. *Get a new rotational matrix* $A_{ij}(e_0, e_1, e_2, e_3)$ *of the next time step below.*

**The predictor and corrector method is used in timings of time steps of Steps* $2-5$.

6. $$\mathbf{r}_i = \mathbf{R}_j + \begin{pmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$ *at the three sites* $\mathbf{r}_i$ *and the position* $\mathbf{R}_j$.

The dummy sites are calculated by algebraic operation.

7. *Forces at Coulomb and LJ potentials are calculated using five sites.*

8. *Correction a normalization of quaternions is made at every* 10 *steps, and go to the next time step of Step* 1.

Note that a time step is important. It will be $\Delta t = 0.025$ *or less, else the code is inaccurate or goes overflow.*

Quaternions in place of three-dimensional angles

$$e_0 = \cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}$$

$$e_1 = \sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}$$

$$e_2 = \sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}$$

$$e_3 = \cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}$$

Classical Mechanics (3rd Edition)
H. Goldstein , C.P. Poole, J.Safko,
Pearson Education Inc., England 2003.

Only three of them are independent
to avoid a gimbal lock

Quaternion representation (4.47)

Rotation matrix

$$\boldsymbol{r} = \boldsymbol{R} + \mathbf{A}^t \boldsymbol{r}'''$$

$$\mathrm{A} = \begin{pmatrix} e_0^2+e_1^2-e_2^2-e_3^2 & 2(e_1e_2+e_0e_3) & 2(e_1e_3-e_0e_2) \\ 2(e_1e_2-e_0e_3) & e_0^2-e_1^2+e_2^2-e_3^2 & 2(e_2e_3+e_0e_1) \\ 2(e_1e_3+e_0e_2) & 2(e_2e_3-e_0e_1) & e_0^2-e_1^2-e_2^2+e_3^2 \end{pmatrix}$$

Time derivative of quaternions e0,e1,e2,e3

$$\begin{pmatrix} \dot{e}_0 \\ \dot{e}_1 \\ \dot{e}_2 \\ \dot{e}_3 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} -e_1 & -e_2 & -e_3 & e_0 \\ e_0 & -e_3 & e_2 & e_1 \\ e_3 & e_0 & -e_1 & e_2 \\ -e_2 & +e_1 & e_0 & e_3 \end{pmatrix}\begin{pmatrix} \omega_{x'} \\ \omega_{y'} \\ \omega_{z'} \\ 0 \end{pmatrix}$$

In Goldstein's book, these definitions are sign reversed in notations, minus or plus signs !

$$(e_0, e_1, e_2, e_3) \Leftrightarrow (\chi, \eta, \xi, \zeta)$$

Goldstein *Ueda (Japan)*

$$2\dot{\xi} = 2\left(\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}\right)'$$

$$= \dot{\theta}\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} + (\dot{\phi}-\dot{\psi})\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}$$

$$= (\omega_x\cos\psi - \omega_y\sin\psi)\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} + [(\omega_x\sin\psi + \omega_y\cos\psi)/\sin\theta$$

$$-\{\omega_z - (\omega_x\sin\psi + \omega_y\cos\psi)\frac{\cos\theta}{\sin\theta}\}]\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}$$

$$= \left\{ \begin{array}{l} \omega_x : \cos\psi\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} + \sin\psi(1+\cos\theta)/\sin\theta\times\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2} \\ \omega_y : -\sin\psi\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} + \cos\psi(1+\cos\theta)/\sin\theta\times\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2} \\ \omega_z : -\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2} = -\eta \quad \leftarrow \text{minus } -\eta \end{array} \right.$$

$$2\dot{\eta} = 2\left(\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}\right)'$$
$$= \dot{\theta}\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} - (\dot{\phi}-\dot{\psi})\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}$$
$$= (\omega_x\cos\psi - \omega_y\sin\psi)\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} \quad +[-(\omega_x\sin\psi + \omega_y\cos\psi)/\sin\theta$$
$$+[\omega_z - (\omega_x\sin\psi + \omega_y\cos\psi)\cos\theta)/\sin\theta]\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}$$

$$= \begin{cases} \omega_x : \cos\psi\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} - \sin\psi(1-\cos\theta)/\sin\theta \times \sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2} \\ \omega_y : -\sin\psi\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} - \cos\psi(1-\cos\theta)/\sin\theta \times \sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2} \\ \omega_z : \sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2} = \xi \quad \leftarrow \ \text{minus} - \xi \end{cases}$$

$$2\dot{\zeta} = 2\left(\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}\right)'$$

$$= -\dot{\theta}\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} + (\dot{\phi}+\dot{\psi})\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}$$

$$= -(\omega_x\cos\psi - \omega_y\sin\psi)\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} + [(\omega_x\sin\psi + \omega_y\cos\psi)/\sin\theta$$

$$+\omega_z - (\omega_x\sin\psi + \omega_y\cos\psi)\cos\theta/\sin\theta]\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}$$

$$= \begin{cases} \omega_{x:} : -\cos\psi\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} + \sin\psi(1+\cos\theta)/\sin\theta\times\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2} \\ \omega_{y:} : \sin\psi\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} + \cos\psi(1+\cos\theta)/\sin\theta\times\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2} \\ \omega_{z:} : \cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2} = \chi \end{cases}$$

$$2\dot{\chi} = 2\left(\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}\right)' = -\dot{\theta}\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} - (\dot{\phi}+\dot{\psi})\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}$$

$$= -(\omega_x\cos\psi - \omega_y\sin\psi)\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} + [-(\omega_x\cos\psi + \omega_y\sin\psi)] / \sin\theta$$

$$-(\omega_z - (\omega_x\cos\psi + \omega_y\sin\psi)\frac{\cos\theta}{\sin\theta})]\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}$$

$$= \begin{cases} \omega_x : -\cos\psi\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} - \cos\psi(1+\cos\theta)/\sin\theta\times\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2} \\ \omega_y : \sin\psi\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} - \sin\psi(1+\cos\theta)/\sin\theta\times\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2} \\ \omega_z : -\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2} \end{cases}$$

Check quaternions of A_{ij} coefficients

$$A_{11}=(-\xi^2+\eta^2-\zeta^2+\chi^2)=-\sin^2\frac{\theta}{2}\sin^2\frac{\psi-\phi}{2}+\sin^2\frac{\theta}{2}\cos^2\frac{\psi-\phi}{2}$$

$$-\cos^2\frac{\theta}{2}\sin^2\frac{\psi+\phi}{2}+\cos^2\frac{\theta}{2}\cos^2\frac{\psi+\phi}{2})$$

$$=\sin^2\frac{\theta}{2}(-\sin^2\frac{\psi-\phi}{2}+\cos^2\frac{\psi-\phi}{2})-\cos^2\frac{\theta}{2}(\sin^2\frac{\psi+\phi}{2}-\cos^2\frac{\psi+\phi}{2})$$

$$=\sin^2\frac{\theta}{2}(2\cos^2\frac{\psi-\phi}{2}-1)+\cos^2\frac{\theta}{2}(\cos^2\frac{\psi+\phi}{2}-1)$$

$$=\sin^2\frac{\theta}{2}(1+\cos(\psi-\phi)-1)+\cos^2\frac{\theta}{2}(1+\cos(\psi+\phi)-1)$$

$$=\sin^2\frac{\theta}{2}\cos(\psi-\phi)+\cos^2\frac{\theta}{2}\cos(\psi+\phi)$$

$$=\sin^2\frac{\theta}{2}(\cos\psi\cos\phi+\sin\psi\sin\phi)+\cos^2\frac{\theta}{2}(\cos\psi\cos\phi-\sin\psi\sin\phi)$$

$$=\frac{1}{2}(1-\cos\theta)(\cos\psi\cos\phi+\sin\psi\sin\phi)+\frac{1}{2}(1+\cos\theta)(\cos\psi\cos\phi-\sin\psi\sin\phi)$$

$$=\cos\psi\cos\phi-\cos\theta\sin\psi\sin\phi$$

$$A_{12} = 2(\varsigma\chi - \xi\eta) = 2(\cos^2\frac{\theta}{2}\sin\frac{\psi+\phi}{2}\cos\frac{\psi+\phi}{2} - \sin^2\frac{\theta}{2}\sin\frac{\psi-\phi}{2}\cos\frac{\psi-\phi}{2})$$

$$= (1+\cos\theta)\sin\frac{\psi+\phi}{2}\cos\frac{\psi+\phi}{2} - (1-\cos\theta)\sin\frac{\psi-\phi}{2}\cos\frac{\psi-\phi}{2}$$

$$= \sin\frac{\psi+\phi}{2}\cos\frac{\psi+\phi}{2} - \sin\frac{\psi-\phi}{2}\cos\frac{\psi-\phi}{2} + \cos\theta(\sin\frac{\psi+\phi}{2}\cos\frac{\psi+\phi}{2}$$

$$+ \sin\frac{\psi-\phi}{2}\cos\frac{\psi-\phi}{2})$$

$$= \frac{1}{2}\sin(\frac{\psi+\phi}{2} + \frac{\psi+\phi}{2}) - \frac{1}{2}\sin(\frac{\psi-\phi}{2} + \frac{\psi-\phi}{2}) + \frac{1}{2}\cos\theta(\sin(\psi+\phi)$$

$$+ \sin(\psi-\phi))$$

$$= \frac{1}{2}\sin(\psi+\phi) - \frac{1}{2}\sin(\psi-\phi) + \frac{1}{2}\cos\theta(\sin(\psi+\phi) - \frac{1}{2}\sin(\psi-\phi))$$

$$= \frac{1}{2}(\sin\psi\cos\phi + \cos\psi\sin\phi - \sin\psi\cos\phi + \cos\psi\sin\phi) + \frac{1}{2}\cos\theta(same)$$

$$= \cos\psi\sin\phi + \cos\theta\sin\psi\cos\phi$$

$$A_{13} = 2(\eta\zeta + \xi\chi) = 2(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{\psi-\phi}{2}\sin\frac{\psi+\phi}{2}$$

$$+\sin\frac{\theta}{2}\cos\frac{\theta}{2}\sin\frac{\psi-\phi}{2}\cos\frac{\psi+\phi}{2})$$

$$= 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}[\cos\frac{\psi-\phi}{2}\sin\frac{\psi+\phi}{2} + \sin\frac{\psi-\phi}{2}\cos\frac{\psi+\phi}{2}$$

$$= \sin\theta[\sin\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2} + \cos\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2}]$$

$$= \sin\theta[\sin(\frac{\psi+\phi}{2} + \frac{\psi-\phi}{2})]$$

$$= \sin\theta\sin\psi$$

$$A_{21} = -2(\xi\eta + \zeta\chi) = -2(\sin^2\frac{\theta}{2}\cos\frac{\psi-\phi}{2}\sin\frac{\psi-\phi}{2}$$

$$+\cos^2\frac{\theta}{2}\sin\frac{\psi+\phi}{2}\cos\frac{\psi+\phi}{2})$$

$$= -(1-\cos\theta)\cos\frac{\psi-\phi}{2}\sin\frac{\psi-\phi}{2} - (1+\cos\theta)\sin\frac{\psi+\phi}{2}\cos\frac{\psi+\phi}{2}$$

$$= -\frac{1}{2}(1-\cos\theta)\sin(\psi-\phi) - \frac{1}{2}(1+\cos\theta)\sin(\psi+\phi)$$

$$= -\frac{1}{2}(\sin(\psi-\phi)+\sin(\psi+\phi)) + \frac{1}{2}\cos\theta(\sin(\psi-\phi)-\sin(\psi+\phi))$$

$$= -\frac{1}{2}(sc - cs + sc + cs) + \frac{1}{2}\cos\theta(sc - cs - sc - cs)$$

$$= -\sin\psi\cos\phi - \cos\theta\cos\psi\sin\phi$$

$$A_{22} = \xi^2 - \eta^2 - \zeta^2 + \chi^2$$

$$= \sin^2\frac{\theta}{2}(\sin^2\frac{\psi-\phi}{2} - \cos^2\frac{\psi-\phi}{2}) + \cos^2\frac{\theta}{2}(-\sin^2\frac{\psi+\phi}{2} + \cos^2\frac{\psi+\phi}{2})$$

$$= \sin^2\frac{\theta}{2}(1 - 2\cos^2\frac{\psi-\phi}{2}) + \cos^2\frac{\theta}{2}(2\cos^2\frac{\psi+\phi}{2} - 1)$$

$$= -\sin^2\frac{\theta}{2}\cos(\psi-\phi)) + \cos^2\frac{\theta}{2}\cos(\psi+\phi)$$

$$= -\frac{1}{2}(1-\cos\theta)\cos(\psi-\phi) + \frac{1}{2}(1+\cos\theta)\cos(\psi+\phi)$$

$$= \frac{1}{2}(-\cos(\psi-\phi) + \cos(\psi+\phi)) + \frac{1}{2}\cos\theta(\cos(\psi-\phi) + \cos(\psi+\phi))$$

$$= \frac{1}{2}(-cc - ss + cc - ss) + \frac{1}{2}\cos\theta(cc + ss + cc - ss)$$

$$= -\sin\psi\sin\phi + \cos\theta\cos\psi\cos\phi$$

$$
\begin{aligned}
A_{23} &= 2(\eta\chi - \xi\zeta) = 2(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2} \\
&\quad - \sin\frac{\theta}{2}\cos\frac{\theta}{2}\sin\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2}) \\
&= 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}(\cos\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2} - \sin\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2}) \\
&= 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos(\frac{\psi+\phi}{2} + \frac{\psi-\phi}{2}) \\
&= \sin\theta\cos\psi
\end{aligned}
$$

$$A_{31} = 2(\eta\zeta - \xi\chi) = 2(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\sin\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2}$$

$$-\sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2})$$

$$= 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}(\sin\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2} - \cos\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2})$$

$$= 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\sin(\frac{\psi+\phi}{2} - \frac{\psi-\phi}{2})$$

$$= \sin\theta\sin\phi$$

$$A_{32} = -2(\xi\zeta + \eta\chi) = -2\sin\frac{\theta}{2}\cos\frac{\theta}{2}(\sin\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2}$$

$$+\cos\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2})$$

$$= -\sin\theta\cos(\frac{\psi+\phi}{2} - \frac{\psi-\phi}{2})$$

$$= -\sin\theta\cos\phi$$

$$
\begin{aligned}
A_{33} &= -\xi^2 - \eta^2 + \varsigma^2 + \chi^2 \\
&= -\sin^2\frac{\theta}{2}\left\{\sin^2(-) + \cos^2(-)\right\} + \cos^2\frac{\theta}{2}\left\{\sin^2(+) + \cos^2(+)\right\} \\
&= -\sin^2\frac{\theta}{2} + \cos^2\frac{\theta}{2} = \frac{1}{2}\left\{-(1-\cos\theta) + 1 + \cos\theta\right\} = \cos\theta \quad QED!
\end{aligned}
$$

The Lennard-Jones Potentials

With the Coulombic interactions, the 12-6 Lennard-Jones potential is adopted for the TIP4P and TIP5P cases:

$$\Phi(r) = A / r^{12} - B / r^{6}$$

$$for\ TIP4:$$

$$A = 4.17 \times 10^{-8} erg \bullet Ang^{12},\ B = 4.24 \times 10^{-11} erg \bullet Ang^{6}$$

$$for\ TIP5 - Ewald\ \ sum:$$

$$A = 3.85 \times 10^{-8} erg \bullet Ang^{12},\ B = 4.36 \times 10^{-11} erg \bullet Ang^{6}$$

Some parameters are,

$$r(OH) = 0.9572\,\mathrm{Ang},\ \Delta HOH\ = 104.52^{\circ}$$

$$r(OM) = 0.15\,\mathrm{Ang}\ \ for\ TIP4P\ only$$

The equipartition line of the virtual M site is on the plain that equally separates the HOH angle. The TIP5P cases are also available.

To Start a Run

To start a simulation of water cluster with the TIP5P code, the adjacent 4x4 hydrogen pairs are summed electrostatically, and oxygen pairs are coupled by TIP5P Lennard-Jones potentials.

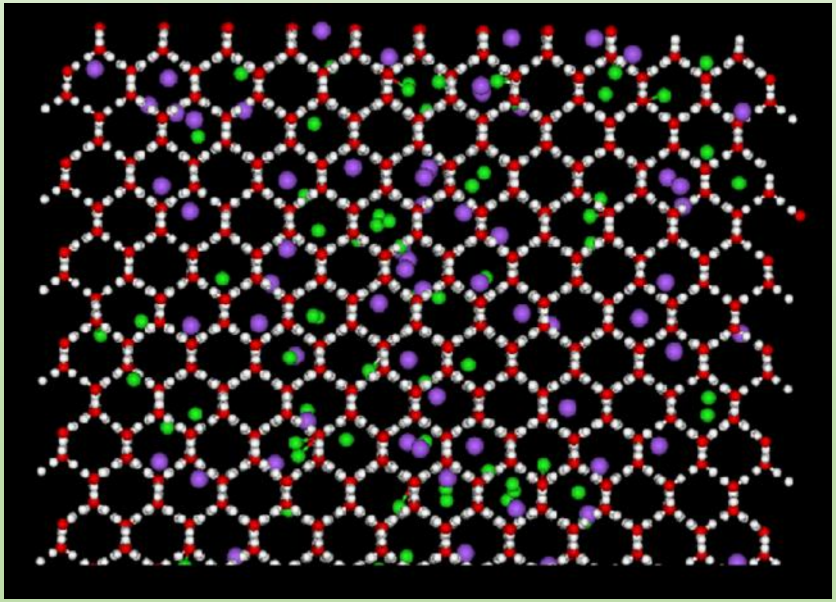
To get an initial state, we make the size of at least a 6x6x6 water cluster for numerical stability. Short-range and long-range Coulombic forces are best separated for interactions, and the short-range forces are made to be spatially dumped.

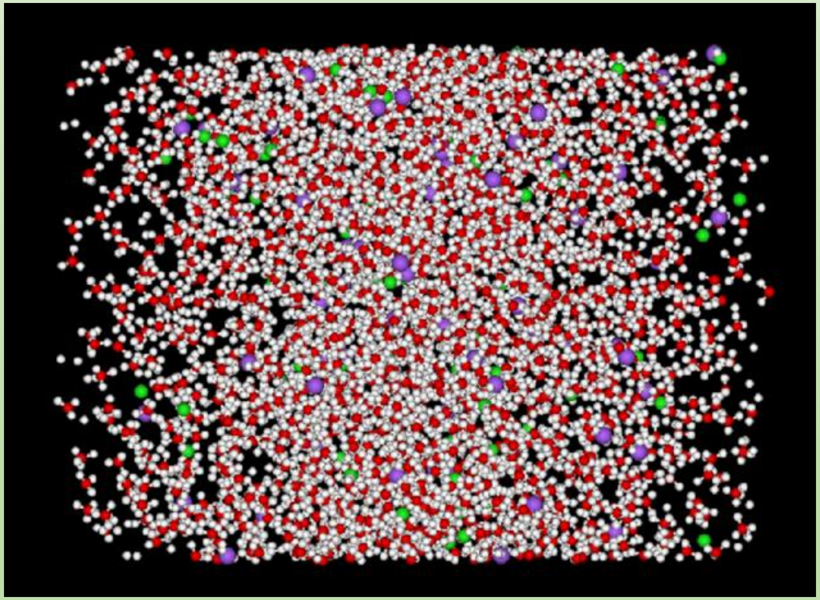
Around a given temperature, a dryrun is executed at least for 5 periods that is 10^(-9) seconds. The long dryrun is very important !!

*Then, we apply the electric field E_x= E_0 sin(omega*time) in the x-direction to excite the electric dipole interactions of water. For the moment, we give the electric field 10 GHz where the electric field E_0 and electric dipole p_0 are of the order of 5x10^(-3) eV.*

To Obtain the Initial Equilibrium for 298 K

We will use salt ions of Na(+) and Cl(-) initially as the dryrun to give random noises. The 6x6x6 water clusters have 64 Na(+) and 64 Cl(-) ions, and a run time is t=1,700. We can see random water clusters. Afterwards, the salt ions are gradually removed, and the dryrun is continued for 5 periods up to t=50,000.





At start and the end of the dryrun of salt ions of t=0 - 3700. The dryrun without ions is continued afterward for 5 periods.