

Molecular Dynamics Simulation of Water by TIP5P

Motohiko Tanaka, PhD., Prof., Nagoya, Japan

Procedures of molecular dynamics simulation for water are written for the 5-point TIP5P method. Formerly, the shake/rattle method was used to show that ice state is not melted by microwaves – our theory discovery in J.Chem.Phys. 2007. Today instead, we use five-body water molecules with two hydrogens and two L1, L2 hydrogens of dummy sites. The fifth site of an oxygen site is used with Lennard-Jones potential $\Psi=A/r^{12} - B/r^6$. We regain similar results (values are different), due to the structure of six-membered ice !

- 1. “Classical Mechanics”, H. Goldstein, C. Poole, 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).*

Procedures of Water Molecules by 5-Body Method

- 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 at $\mathbf{r}_i = \mathbf{R}_j + A^{-1}\mathbf{s}_\alpha$ with three sites of $\alpha = x, y, z$, and 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 illustrates: translation (step 1), rotation (step 2-4), and adding the fields (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.M.Matsumoto, Okayama Univ).

1. Sum up five sites and advance, $\frac{d\mathbf{V}_j}{dt} = \frac{1}{m_j} \sum_{k=1}^5 \mathbf{F}_k$, $\frac{d\mathbf{R}_j}{dt} = \mathbf{V}_j$,
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. $\frac{d\mathbf{q}_j}{dt} = \frac{1}{2} Q(e_{j,0}, e_{j,1}, e_{j,2}, e_{j,3}) (\omega_{j,x}, \omega_{j,y}, \omega_{j,z}, 0)$
 $\dot{\mathbf{q}}_j$ of Q and $\boldsymbol{\omega}$ has four components in the Goldstein's book.

5. *Get a new rotational matrix $A_{ij}(e_0, e_1, e_2, e_3)$ written in the book p.205 for the next time step.*

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 $\Delta t = 0.025 - 0.05$, else the code is inaccurate or goes overflow.

Quaternions in Place of 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

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

$$\mathbf{A} = \begin{pmatrix} e_0^2 + e_1^2 - e_2^2 - e_3^2 & 2(e_1 e_2 + e_0 e_3) & 2(e_1 e_3 - e_0 e_2) \\ 2(e_1 e_2 - e_0 e_3) & e_0^2 - e_1^2 + e_2^2 - e_3^2 & 2(e_2 e_3 + e_0 e_1) \\ 2(e_1 e_3 + e_0 e_2) & 2(e_2 e_3 - e_0 e_1) & e_0^2 - e_1^2 - e_2^2 + e_3^2 \end{pmatrix}$$

Time derivative of
quaternions
e0,e1,e2,e3

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

The Lennard-Jones Potentials

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

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

for TIP4 :

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

for TIP5 – Ewald sum :

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

Some parameters are,

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

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

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.

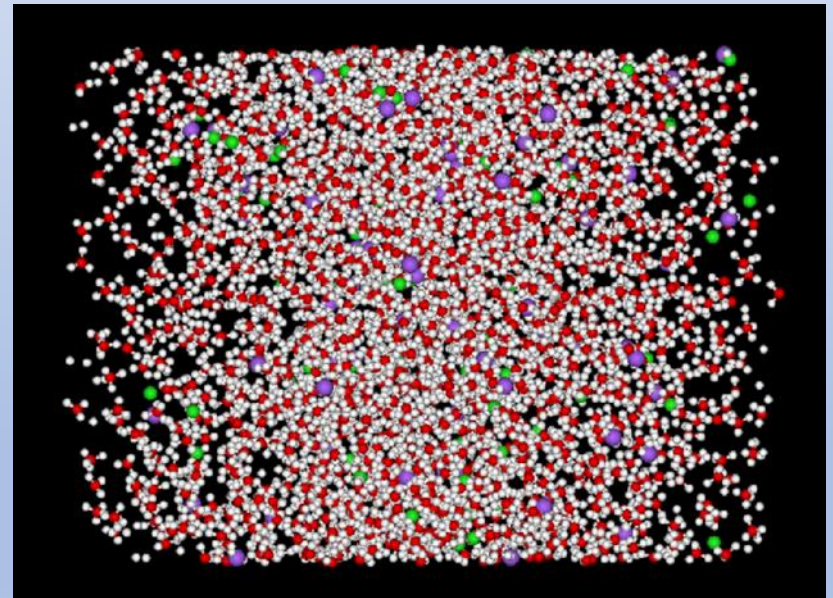
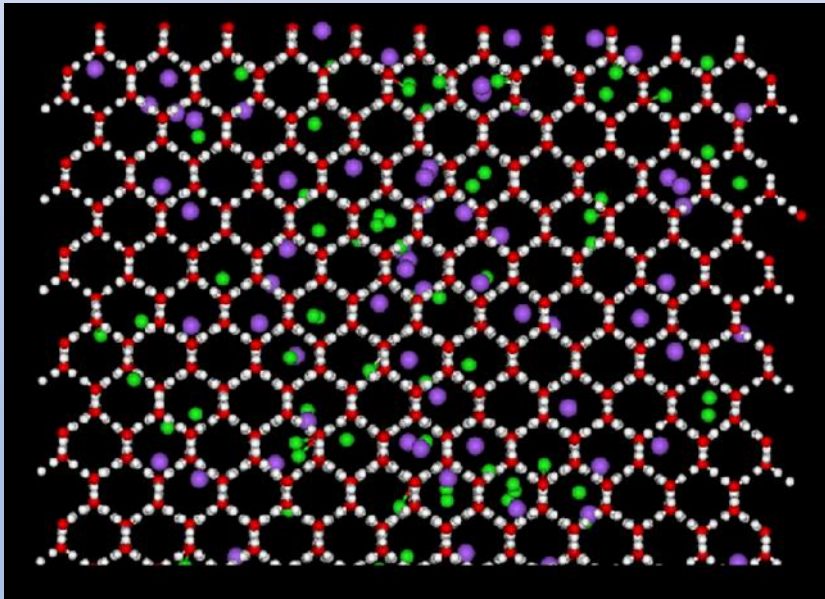
To get an initial state, we make the size of at least a 6x6x6 water cluster for numerical stability. Short-range and long-range Coulombic forces are best separated for interactions, and the short-range forces are made to be spatially dumped.

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 $E_x = E_0 \sin(\omega t)$ 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 5×10^{-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.

Check of quaternion: A_{ij} coefficient

$$\begin{aligned} A_{11} &= (-\xi^2 + \eta^2 - \zeta^2 + \chi^2) = -\sin^2 \frac{\theta}{2} \sin^2 \frac{\psi - \phi}{2} + \sin^2 \frac{\theta}{2} \cos^2 \frac{\psi - \phi}{2} \\ &\quad - \cos^2 \frac{\theta}{2} \sin^2 \frac{\psi + \phi}{2} + \cos^2 \frac{\theta}{2} \cos^2 \frac{\psi + \phi}{2}) \\ &= \sin^2 \frac{\theta}{2} (-\sin^2 \frac{\psi - \phi}{2} + \cos^2 \frac{\psi - \phi}{2}) - \cos^2 \frac{\theta}{2} (\sin^2 \frac{\psi + \phi}{2} - \cos^2 \frac{\psi + \phi}{2}) \\ &= \sin^2 \frac{\theta}{2} (2 \cos^2 \frac{\psi - \phi}{2} - 1) + \cos^2 \frac{\theta}{2} (\cos^2 \frac{\psi + \phi}{2} - 1) \\ &= \sin^2 \frac{\theta}{2} (1 + \cos(\psi - \phi) - 1) + \cos^2 \frac{\theta}{2} (1 + \cos(\psi + \phi) - 1) \\ &= \sin^2 \frac{\theta}{2} \cos(\psi - \phi) + \cos^2 \frac{\theta}{2} \cos(\psi + \phi) \\ &= \sin^2 \frac{\theta}{2} (\cos \psi \cos \phi + \sin \psi \sin \phi) + \cos^2 \frac{\theta}{2} (\cos \psi \cos \phi - \sin \psi \sin \phi) \\ &= \frac{1}{2} (1 - \cos \theta) (\cos \psi \cos \phi + \sin \psi \sin \phi) + \frac{1}{2} (1 + \cos \theta) (\cos \psi \cos \phi - \sin \psi \sin \phi) \\ &= \cos \psi \cos \phi - \cos \theta \sin \psi \sin \phi \end{aligned}$$

$$\begin{aligned}
A_{12} &= 2(\varsigma\chi - \xi\eta) = 2\left(\cos^2 \frac{\theta}{2} \sin \frac{\psi + \phi}{2} \cos \frac{\psi + \phi}{2} - \sin^2 \frac{\theta}{2} \sin \frac{\psi - \phi}{2} \cos \frac{\psi - \phi}{2}\right) \\
&= (1 + \cos \theta) \sin \frac{\psi + \phi}{2} \cos \frac{\psi + \phi}{2} - (1 - \cos \theta) \sin \frac{\psi - \phi}{2} \cos \frac{\psi - \phi}{2} \\
&= \sin \frac{\psi + \phi}{2} \cos \frac{\psi + \phi}{2} - \sin \frac{\psi - \phi}{2} \cos \frac{\psi - \phi}{2} + \cos \theta \left(\sin \frac{\psi + \phi}{2} \cos \frac{\psi + \phi}{2} \right. \\
&\quad \left. + \sin \frac{\psi - \phi}{2} \cos \frac{\psi - \phi}{2} \right) \\
&= \frac{1}{2} \sin\left(\frac{\psi + \phi}{2} + \frac{\psi + \phi}{2}\right) - \frac{1}{2} \sin\left(\frac{\psi - \phi}{2} + \frac{\psi - \phi}{2}\right) + \frac{1}{2} \cos \theta (\sin(\psi + \phi) \\
&\quad + \sin(\psi - \phi)) \\
&= \frac{1}{2} \sin(\psi + \phi) - \frac{1}{2} \sin(\psi - \phi) + \frac{1}{2} \cos \theta (\sin(\psi + \phi) - \frac{1}{2} \sin(\psi - \phi)) \\
&= \frac{1}{2} (\sin \psi \cos \phi + \cos \psi \sin \phi - \sin \psi \cos \phi + \cos \psi \sin \phi) + \frac{1}{2} \cos \theta (\text{same}) \\
&= \cos \psi \sin \phi + \cos \theta \sin \psi \cos \phi
\end{aligned}$$

$$\begin{aligned}
A_{13} &= 2(\eta\zeta + \xi\chi) = 2\left(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{\psi-\phi}{2}\sin\frac{\psi+\phi}{2}\right. \\
&\quad \left. + \sin\frac{\theta}{2}\cos\frac{\theta}{2}\sin\frac{\psi-\phi}{2}\cos\frac{\psi+\phi}{2}\right) \\
&= 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\left[\cos\frac{\psi-\phi}{2}\sin\frac{\psi+\phi}{2} + \sin\frac{\psi-\phi}{2}\cos\frac{\psi+\phi}{2}\right] \\
&= \sin\theta\left[\sin\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2} + \cos\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2}\right] \\
&= \sin\theta\left[\sin\left(\frac{\psi+\phi}{2} + \frac{\psi-\phi}{2}\right)\right] \\
&= \sin\theta\sin\psi
\end{aligned}$$

$$\begin{aligned}
A_{21} &= -2(\xi\eta + \zeta\chi) = -2\left(\sin^2 \frac{\theta}{2} \cos \frac{\psi - \phi}{2} \sin \frac{\psi - \phi}{2} \right. \\
&\quad \left. + \cos^2 \frac{\theta}{2} \sin \frac{\psi + \phi}{2} \cos \frac{\psi + \phi}{2} \right) \\
&= -(1 - \cos \theta) \cos \frac{\psi - \phi}{2} \sin \frac{\psi - \phi}{2} - (1 + \cos \theta) \sin \frac{\psi + \phi}{2} \cos \frac{\psi + \phi}{2} \\
&= -\frac{1}{2}(1 - \cos \theta) \sin(\psi - \phi) - \frac{1}{2}(1 + \cos \theta) \sin(\psi + \phi) \\
&= -\frac{1}{2}(\sin(\psi - \phi) + \sin(\psi + \phi)) + \frac{1}{2} \cos \theta (\sin(\psi - \phi) - \sin(\psi + \phi)) \\
&= -\frac{1}{2}(sc - cs + sc + cs) + \frac{1}{2} \cos \theta (sc - cs - sc - cs) \\
&= -\sin \psi \cos \phi - \cos \theta \cos \psi \sin \phi
\end{aligned}$$

$$\begin{aligned}
A_{22} &= \xi^2 - \eta^2 - \zeta^2 + \chi^2 \\
&= \sin^2 \frac{\theta}{2} \left(\sin^2 \frac{\psi - \phi}{2} - \cos^2 \frac{\psi - \phi}{2} \right) + \cos^2 \frac{\theta}{2} \left(-\sin^2 \frac{\psi + \phi}{2} + \cos^2 \frac{\psi + \phi}{2} \right) \\
&= \sin^2 \frac{\theta}{2} \left(1 - 2\cos^2 \frac{\psi - \phi}{2} \right) + \cos^2 \frac{\theta}{2} \left(2\cos^2 \frac{\psi + \phi}{2} - 1 \right) \\
&= -\sin^2 \frac{\theta}{2} \cos(\psi - \phi) + \cos^2 \frac{\theta}{2} \cos(\psi + \phi) \\
&= -\frac{1}{2}(1 - \cos \theta) \cos(\psi - \phi) + \frac{1}{2}(1 + \cos \theta) \cos(\psi + \phi) \\
&= \frac{1}{2}(-\cos(\psi - \phi) + \cos(\psi + \phi)) + \frac{1}{2}\cos \theta (\cos(\psi - \phi) + \cos(\psi + \phi)) \\
&= \frac{1}{2}(-cc - ss + cc - ss) + \frac{1}{2}\cos \theta (cc + ss + cc - ss) \\
&= -\sin \psi \sin \phi + \cos \theta \cos \psi \cos \phi
\end{aligned}$$

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

$$\begin{aligned}
A_{31} &= 2(\eta\zeta - \xi\chi) = 2\left(\sin\frac{\theta}{2}\cos\frac{\theta}{2}\sin\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2}\right. \\
&\quad \left.- \sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2}\right) \\
&= 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\left(\sin\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2} - \cos\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2}\right) \\
&= 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\sin\left(\frac{\psi+\phi}{2} - \frac{\psi-\phi}{2}\right) \\
&= \sin\theta\sin\phi
\end{aligned}$$

$$\begin{aligned}
A_{32} &= -2(\xi\zeta + \eta\chi) = -2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\left(\sin\frac{\psi+\phi}{2}\sin\frac{\psi-\phi}{2}\right. \\
&\quad \left.+ \cos\frac{\psi+\phi}{2}\cos\frac{\psi-\phi}{2}\right) \\
&= -\sin\theta\cos\left(\frac{\psi+\phi}{2} - \frac{\psi-\phi}{2}\right) \\
&= -\sin\theta\cos\phi
\end{aligned}$$

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