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. 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).

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 $\mathbf{R}_i$, $\mathbf{V}_i$ and $\mathbf{r}_k$ with $i = 1 - N$ for molecules, and $\mathbf{s}_{i,k} = (x_{i,k}, y_{i,k}, z_{i,k})$ means for the five sites $k = 1 - 5$.
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 $\mathbf{r}_{i,k} = \mathbf{R}_i + A^{-1}\mathbf{s}_k$ with three sites of $k = 1 - 3$, and the L sites are also calculated by algebraic 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 is: translation (step 1), rotation (step 2–4), and adding the fields (step 5–8).

0. *Read quaternions from the file,* '$read(30)\,e0, e1, e2, e3$'
   $(by\ Dr.M.Matsumoto, Okayama\ University)$.

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

2. $$\frac{d\mathbf{L}_i}{dt} = \sum_k \left(y_{i,k}F_{i,k}^{z} - z_{i,k}F_{i,k}^{y}, \quad z_{i,k}F_{i,k}^{x} - x_{i,k}F_{i,k}^{z}, \quad x_{i,k}F_{i,k}^{y} - y_{i,k}F_{i,k}^{x} \right)$$
   for the rotational motion: the sums are made over the five sites.

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

4. $$\frac{d\mathbf{q}_i}{dt} = \frac{1}{2}Q(e_{i,0}, e_{i,1}, e_{i,2}, e_{i,3})\left(\omega_{i,x}, \quad \omega_{i,y}, \quad \omega_{i,z}, \quad 0\right)$$
   $\dot{\mathbf{q}}_i$ *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. $$\mathbf{r}_{i,k} = \mathbf{R}_i + \begin{pmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{pmatrix} \begin{pmatrix} x_{i,k} \\ y_{i,k} \\ z_{i,k} \end{pmatrix}$$ *at the three sites* $\mathbf{r}_{i,k}$ *and the position* $\mathbf{R}_i$*. 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: Goldstein's book

$$e_0 = \cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}$$
$$e_1 = \sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}$$
$$e_2 = \sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}$$
$$e_3 = \cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}$$

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

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

The Lennard-Jones Potentials

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

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

$$\text{for } TIP4:$$

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

$$\text{for } TIP5 - Ewald\ sum:$$

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

Some parameters are,

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

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

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

Check of quaternion: A_{ij} coefficient

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$A_{33} = -\xi^2 - \eta^2 + \varsigma^2 + \chi^2$$

$$= -\sin^2\frac{\theta}{2}\left\{\sin^2(-) + \cos^2(-)\right\} + \cos^2\frac{\theta}{2}\left\{\sin^2(+) + \cos^2(+)\right\}$$

$$= -\sin^2\frac{\theta}{2} + \cos^2\frac{\theta}{2} = \frac{1}{2}\left\{-(1-\cos\theta) + 1 + \cos\theta\right\} = \cos\theta \quad QED!$$