Molecular Dynamics Simulation of Water by TIP5P Model

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Procedures of molecular dynamics simulation of water and ice are written for the five-point TIP5P model. Formerly, the shake/rattle method was used, showing the ice state not melted by microwaves – our theory discovery in J.Chem.Phys. 2007. Today, we use five-body water molecules with two hydrogens H1, H2 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 some different), due to the structure of six-membered water and 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 Five-Body 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 illustrates: translation (Step 1), rotation (Step 2–4), and adding the fields (Step 5–8).

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

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

   $for\ the\ translational\ motion.$

2. $\dfrac{d\mathbf{L}_j}{dt} = \sum_{k=1}^{5}\left(y_k F_k^z - z_k F_k^y,\quad z_k F_k^x - x_k F_k^z,\quad x_k F_k^y - y_k F_k^x\right)$

   $for\ the\ rotational\ motion: the\ sums\ are\ made\ over\ the\ five\ sites.$

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

(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 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

$$r = R + A^t r'''$$

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

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 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,

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

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

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

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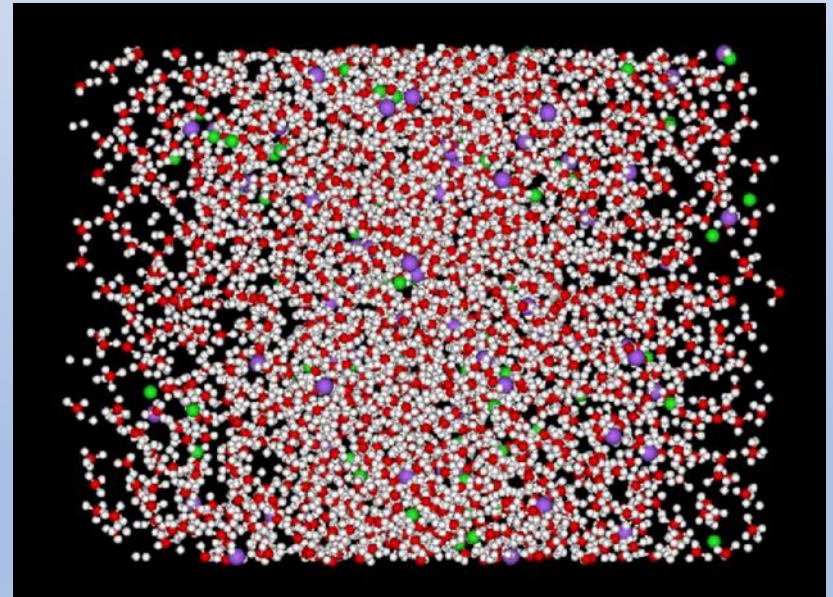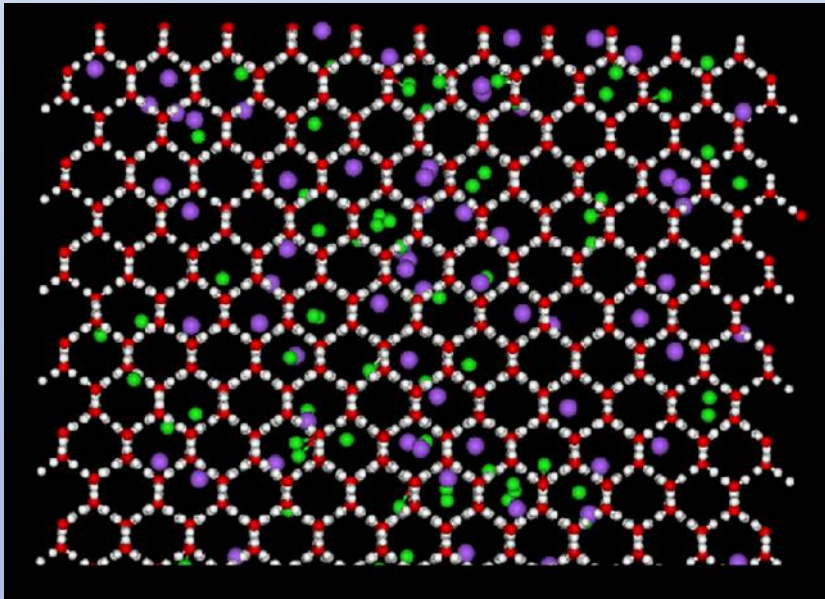
At start and the end of the dryrun of salt ions of t=0 - 3700. The dryrun without ions is continued afterward for 5 periods.

Check of quaternion: A_{ij} coefficients

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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