models by simple modifications of the equations. The MeOH model which employs the united atom approach for the methyl group is a good example. The SETTLE can be applied to a four-point water model like TIP4P[5] which has the fourth point with a certain charge and no mass if the force acting on the fourth point is distributed onto the other three points with masses in a reasonable manner.

Since SHAKE or RATTLE are widely employed in existing MD programs, SETTLE seems to be straightforward to implement in those programs, as we have done for the SPASMS package. Furthermore, this method is suitable for vector and parallel machines since it is not iterative and therefore the computation time spent is constant. Mertz et al. used a matrix inversion method for SHAKE in their study on vector and parallel algorithms for MD simulations.[7] Their approach, however, could not avoid the use of an iterative method, resulting in a decline of the speed-up ratio due to load imbalance while successful behaviors were attained for other parts of the MD calculation. Better results upon parallelization may be expected for water molecule constraints using SETTLE.

CONCLUSION

In this article we described an algorithm for satisfying constraints of the rigid water model and discussed its performance using the simulation package SPASMS. The main and subsidiary advantages of the method introduced here are:

1. SETTLE is quite accurate. The constraints are fulfilled exactly at each step of integration. This feature is ideal for the TIP3P and SPC water models, which have been parameterized using rigid geometries.
   - 1′. One need not worry about the choice of the tolerance value for rigid water, although reasonable numbers to be used with the conventional RATTLE are presented here.
2. SETTLE is fast. With respect to scalar machines, it is at least three to seven times faster than RATTLE. If used with reasonable tolerances mentioned above, the speed-up factor amounts to seven to nine. On vector machines, significant improvement of performance has been obtained, up to a factor of 98 over RATTLE.
   - 2′. SETTLE is also suitable for parallelization of the code because it is not iterative.
3. SETTLE can be easily implemented in standard MD packages. Since this algorithm is still based on Cartesian coordinates, it is straightforwardly incorporated into those packages in place of SHAKE or RATTLE on rigid water models.

Copies of FORTRAN subroutines SETTLE are available on request.

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APPENDIX A: DETAILS OF POSITION RESETTING OF SETTLE

Let us denote the coordinates of point A in $X'Y'Z'$ coordinate system by primes, i.e., $A' = (s, t, u)$ or $A = (X'_A, Y'_A, Z'_A)$. As is shown in Figure 2a, the coordinates of $\Delta a_0 b_0 c_0$ are given by

$$a'_0 = (0, r_a, 0)$$
$$b'_0 = (-r_c, -r_b, 0)$$
$$c'_0 = (r_c, -r_b, 0) \qquad \text{(A1)}$$

where r_a, r_b, and $r_c > 0$.

$\Delta a_1 b_1 c_1$ is obtained by the rotation ψ ($-\pi/2 \le \psi \le \pi/2$) about Y' axis as illustrated in Figure 2b:

$$a'_1 = a'_0 = (0, r_a, 0)$$
$$b'_1 = (-r_c \cos\psi, -r_b, r_c \sin\psi)$$
$$c'_1 = (r_c \cos\psi, -r_b, -r_c \sin\psi) \qquad \text{(A2)}$$

As indicated in Fig. 2c. ϕ ($-\pi < \phi \le \pi$) gives a rotation of $\Delta a_1 b_1 c_1$ around X' into $\Delta a_2 b_2 c_2$

$$a'_2 = (0, r_c \cos\phi, r_c \sin\phi) = (X'_{a_2}, Y'_{a_2}, Z'_{a_2})$$
$$b'_2 = (-r_c \cos\psi, -r_b \cos\phi - r_c \sin\psi \sin\phi, -r_b \sin\phi + r_c \sin\psi \cos\phi) = (X'_{b_2}, Y'_{b_2}, Z'_{b_2})$$
$$c'_2 = (r_c \cos\psi, -r_b \cos\phi + r_c \sin\psi \sin\phi, -r_b \sin\phi - r_c \sin\psi \cos\phi = (X'_{c_2}, Y'_{c_2}, Z'_{c_2}) \qquad \text{(A3)}$$

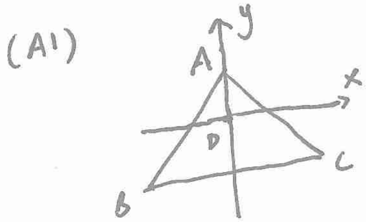
$\Delta a_3 b_3 c_3$ is produced by the rotation θ ($-\pi < \theta \le \pi$) about Z' axis as shown in Figure 2d. Although the coordinates of $\Delta a_3 b_3 c_3$ might be expressed in the similar way as eq. (A3), the expression is rather complicated. In addition, θ could be determined separately from ψ and ϕ. Therefore we write the coordinates of $\Delta a_3 b_3 c_3$ based on those of $\Delta a_2 b_2 c_2$

$$a'_3 = (X'_{a_2} \cos\theta - Y'_{a_2} \sin\theta, X'_{a_2} \sin\theta + Y'_{a_2} \cos\theta, Z'_{a_2}) = (X'_{a_3}, Y'_{a_3}, Z'_{a_3})$$
$$b'_3 = (X'_{b_2} \cos\theta - Y'_{b_2} \sin\theta, X'_{b_2} \sin\theta + Y'_{b_2} \cos\theta, Z'_{b_2}) = (X'_{b_3}, Y'_{b_3}, Z'_{b_3})$$
$$c'_3 = (X'_{c_2} \cos\theta - Y'_{c_2} \sin\theta, X'_{c_2} \sin\theta + Y'_{c_2} \cos\theta, Z'_{c_2}) = (X'_{c_3}, Y'_{c_3}, Z'_{c_3}) \qquad \text{(A4)}$$

The Z' coordinates do not change after the rotation of θ and the Z' coordinates of $\Delta A_1 B_1 C_1$ are the same as those of $\Delta A_3 B_3 C_3$, as discussed in the explanation of the algorithm. Those relations as well as $\Delta A_3 B_3 C_3 \equiv \Delta a_3 b_3 c_3$ leads to

$$Z'_{A_1} = Z'_{A_3} = Z'_{a_3} = Z'_{a_2} = r_a \sin\phi \qquad \text{(A5)}$$

(A1)



If $m_b \neq m_c$, or $|AB| \neq |AC|$,
B and C are not symmetric.

$m_a \vec{DA} + m_b \vec{DB} + m_c \vec{DC} = \vec{0}$

$\Rightarrow D = \dfrac{m_a A + m_b B + m_c C}{m_A + m_B + m_C}$

To Get ∠DAB and ∠DAC.

$\cos A = \dfrac{AB^2 + AC^2 - BC^2}{2AB\,AC}$

$\sin A > 0$.

$A(0,0)$, $B(l_b, 0)$

C: $l_c(\cos A, \sin A)$

$D = \dfrac{\sum m_i i}{\sum m_i}$

$\Rightarrow$ cos DAB and cos DAC

$\Rightarrow$ sin DAB and sin DAC

$\Rightarrow$ y_a, x_b, x_c, y_b, y_c

(A2)

$$R_x(\phi) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos & -\sin \\ 0 & \sin & \cos \end{pmatrix}$$

$$R_y(\psi) = \begin{pmatrix} \cos & 0 & \sin \\ 0 & 1 & 0 \\ -\sin & 0 & \cos \end{pmatrix}$$

$$R_z(\theta) = \begin{pmatrix} \cos & -\sin & 0 \\ \sin & \cos & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$\psi \in [-\frac{\pi}{2}, \frac{\pi}{2}]$

$\phi \in (-\pi, \pi]$

$\theta \in (-\pi, \pi]$

$a_0 = \begin{pmatrix} 0 \\ y_a \\ 0 \end{pmatrix}$ $b_0 = \begin{pmatrix} x_b \\ y_b \\ 0 \end{pmatrix}$ $c_0 = \begin{pmatrix} x_c \\ y_c \\ 0 \end{pmatrix}$

$a_1 = R_y(\psi) a_0 = a_0$

$a_2 = R_x(\phi) a_1 = \begin{pmatrix} 0 \\ y_a \cos\phi \\ y_a \sin\phi \end{pmatrix}$

$b_1 = R_y(\psi) b_0 = \begin{pmatrix} x_b \cos\psi \\ y_b \\ -x_b \sin\psi \end{pmatrix}$

$b_2 = R_x(\phi) b_1 = \begin{pmatrix} x_b \cos\psi \\ y_b \cos\phi + x_b \sin\phi \sin\psi \\ y_b \sin\phi - x_b \cos\phi \sin\psi \end{pmatrix}$

$x_b = x'_{b_0}$ $y'_{b_0} = y_b$

$x_c = x'_{c_0}$ $y'_{c_0} = y_c$

$$Z'_{B_1} = Z'_{B_3} = Z'_{b_3} = Z'_{b_2} = -r_b \sin\phi + r_c \sin\psi \cos\phi \qquad \text{(A6)}$$

$$Z'_{C_1} = Z'_{C_3} = Z'_{c_3} = Z'_{c_2} = -r_b \sin\phi - r_c \sin\psi \cos\phi \qquad \text{(A7)}$$

Equation (A5) gives

$$\sin\phi = \frac{Z'_{A_1}}{r_a} \qquad \text{(A8)}$$

where $|Z'_A| \leq r_a$. This is almost always true because $|Z'_A| \ll r_a$ in the practical MD simulations.* Adding eq. (A6) and eq. (A7), we also obtain the alternative expression

$$\sin\phi = \frac{Z'_{B_1} + Z'_{C_1}}{2r_b}$$

which is shown to be identical to eq. (A8) by a simple transformation. Subtracting eq. (A7) from eq. (A6), we find

$$2r_c \sin\psi \cos\phi = Z'_{B_1} - Z'_{C_1}$$

If $\cos\phi \neq 0$ (as is the case in general MD simulations)

$$\sin\psi = \frac{Z'_{B_1} - Z'_{C_1}}{2r_c \cos\phi} \qquad \text{(A9)}$$

(A9)

$$\sin\psi = \frac{(Z'_{B_1} - Z'_{C_1}) - (Y'_{b_0} - Y'_{c_0})\sin\phi}{(X'_{c_0} - X'_{b_0})\cos\phi}$$

where $|Z'_{B_1} - Z'_{C_1}| < 2r_c|\cos\phi|$. By use of the basic relation of $\sin^2\omega + \cos^2\omega = 1$, we obtain

$$\cos\phi = \sqrt{1 - \sin^2\phi}, \qquad \cos\psi = \sqrt{1 - \sin^2\psi} \qquad \text{(A10)}$$

where the positive sign of the square root is chosen for $\cos\phi$. Substituting eqs. (A8), (A9), and (A10) into eq. (A3), coordinates of $\Delta a_2 b_2 c_2$ are calculated.† Since the time consuming calculation of sine and cosine functions are not performed, this approach is fast as well as accurate.

In the next step θ can be calculated analytically by using the condition that constraint forces directed along the bond of $\Delta A_0B_0C_0$ are of equal magnitudes and opposite orientations as expressed in eq. (4) (Fig. 1b). Suppose $\Delta A_3B_3C_3$ is determined; then the displacement vectors are given by

$$\delta\mathbf{r}_A = \overline{A_1A_3},\ \delta\mathbf{r}_B = \overline{B_1B_3},\ \delta\mathbf{r}_C = \overline{C_1C_3} \qquad \text{(A11)}$$

According to eq. (4) the displacement vectors are given by

$$\delta\mathbf{r}_A = \frac{(\delta t)^2}{2m_a}(\mathbf{g}_{A_0B_0} + \mathbf{g}_{A_0C_0}) = \frac{(\delta t)^2}{2m_a}(\lambda_{AB}\overline{A_0B_0} + \lambda_{AC}\overline{A_0C_0})$$

$$\delta\mathbf{r}_B = \frac{(\delta t)^2}{2m_b}(\mathbf{g}_{B_0C_0} + \mathbf{g}_{B_0A_0}) = \frac{(\delta t)^2}{2m_b}(\lambda_{BC}\overline{B_0C_0} + \lambda_{BA}\overline{B_0A_0})$$

$$\delta\mathbf{r}_C = \frac{(\delta t)^2}{2m_c}(\mathbf{g}_{C_0A_0} + \mathbf{g}_{C_0B_0}) = \frac{(\delta t)^2}{2m_c}(\lambda_{CA}\overline{C_0A_0} + \lambda_{CB}\overline{C_0B_0}) \qquad \text{(A12)}$$

(A13-2)

$$\begin{pmatrix} X'_{B_0C_0} & X'_{B_0A_0} \\ Y'_{B_0C_0} & Y'_{B_0A_0} \end{pmatrix}\begin{pmatrix} \lambda_{BC} \\ \lambda_{BA} \end{pmatrix} = m_b\begin{pmatrix} X'_{B_1B_3} \\ Y'_{B_1B_3} \end{pmatrix}$$

$$\lambda_{BC} = \frac{|\ \ |}{|\ \ |} = \frac{C_1}{D_1}$$

(A13-3)

$$\begin{pmatrix} X'_{C_0A_0} & X'_{C_0B_0} \\ Y'_{C_0A_0} & Y'_{C_0B_0} \end{pmatrix}\begin{pmatrix} \lambda_{CA} \\ \lambda_{CB} \end{pmatrix} = m_c\begin{pmatrix} X'_{C_1C_3} \\ Y'_{C_1C_3} \end{pmatrix}$$

$$\lambda_{CB} = \frac{|\ \ |}{|\ \ |} = \frac{C_2}{D_2}$$

Substituting eq. (A11) into (A12), we obtain the following expressions

$$\frac{2m_a}{(\delta t)^2}\overline{A_1A_3} = \lambda_{AB}\overline{A_0B_0} + \lambda_{AC}\overline{A_0C_0}$$

$$\frac{2m_b}{(\delta t)^2}\overline{B_1B_3} = \lambda_{BC}\overline{B_0C_0} + \lambda_{BA}\overline{B_0A_0}$$

$$\frac{2m_c}{(\delta t)^2}\overline{C_1C_3} = \lambda_{CA}\overline{C_0A_0} + \lambda_{CB}\overline{C_0B_0} \qquad \text{(A13)}$$

okay.

Since $\overline{A_0B_0}$, $\overline{B_0C_0}$ and $\overline{C_0A_0}$ are not parallel to each other, λ_{ij} in eq. (A13) are uniquely defined. In the case of λ_{BC} and λ_{CB}, they can be written as

$$\lambda_{BC} = \frac{X'_{B_1B_3}Y'_{B_0A_0} - X'_{B_0A_0}Y'_{B_1B_3}}{X'_{B_0C_0}Y'_{B_0A_0} - X'_{B_0A_0}Y'_{B_0C_0}}$$

$$(-\lambda_{CB}) = \frac{X'_{C_1C_3}Y'_{C_0A_0} - X'_{C_0A_0}Y'_{C_1C_3}}{X'_{B_0C_0}Y'_{C_0A_0} - X'_{C_0A_0}Y'_{B_0C_0}}$$

← missed a (−) sign

denominators are the same.

Since λ_{BC} should be equal to λ_{CB}, we obtain

$$m_b \cdot \frac{(X'_{B_3} - X'_{B_1})(Y'_{A_0} - Y'_{B_0}) - (X'_{A_0} - X'_{B_0})(Y'_{B_3} - Y'_{B_1})}{(X'_{C_0} - X'_{B_0})(Y'_{A_0} - Y'_{B_0}) - (X'_{A_0} - X'_{B_0})(Y'_{C_0} - Y'_{B_0})}$$
$$= \frac{(X'_{C_3} - X'_{C_1})(Y'_{A_0} - Y'_{C_0}) - (X'_{A_0} - X'_{C_0})(Y'_{C_3} - Y'_{C_1})}{(X'_{C_0} - X'_{B_0})(Y'_{A_0} - Y'_{C_0}) - (X'_{A_0} - X'_{C_0})(Y'_{C_0} - Y'_{B_0})} \ (-m_c)$$

After the rearrangement

$$m_b(X'_{B_3} - X'_{B_1})(Y'_{B_0} - Y'_{A_0}) + m_c(X'_{C_3} - X'_{C_1})(Y'_{C_0} - Y'_{A_0})$$
$$= m_b(Y'_{B_3} - Y'_{B_1})(X'_{B_0} - X'_{A_0}) + m_c(Y'_{C_3} - Y'_{C_1})(X'_{C_0} - X'_{A_0})$$

← okay, if $m_b = m_c$

Substitutions of eq. (A4) and $X'_{c_2} = X'_{b_2}$ into the above relation gives

$$[X'_{b_2}(X'_{B_0} - X'_{C_0}) + (Y'_{B_0} - Y'_{A_0})Y'_{b_2} + (Y'_{C_0} - Y'_{A_0})Y'_{c_2}]\sin\theta$$
$$+ [X'_{b_2}(Y'_{C_0} - Y'_{B_0}) + (X'_{B_0} - X'_{A_0})Y'_{b_2} + (X'_{C_0} - X'_{A_0})Y'_{c_2}]\cos\theta$$
$$= (X'_{B_0} - X'_{A_0})Y'_{B_1} - X'_{B_1}(Y'_{B_0} - X'_{A_0})$$
$$+ (X'_{C_0} - X'_{A_0})Y'_{C_1} - X'_{C_1}(Y'_{C_0} - Y'_{A_0}) \qquad \text{(A14)}$$

(A14) Typo. $Y'_{B_0} - Y'_{A_0}$

okay if $m_b = m_c$

The other relations of $\lambda_{AB} = \lambda_{BA}$ and $\lambda_{CA} = \lambda_{AC}$ provide the more complicated equations. Since these equations are equivalent to eq. (A14), we develop the discussion of only eq. (A14). Defining

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*In the typical simulations with a time step of 1 to 2 fs at 300 K, the maximum values of ψ and ϕ are about 7°. They are small enough to guarantee $\cos\phi > 0$, $\cos\psi > 0$, $|Z'_A| \ll r_a$ and $|Z'_{B_1} - Z'_{C_1}| \ll 2r_c|\cos\phi|$. In the case of a longer step size of 5 fs and a higher temperature of 1500 K, maximum values are about 38°. Still, they are small enough to satisfy $\cos\phi > 0$, $\cos\psi > 0$, $|Z'_A| \ll r_a$ and $|Z'_{B_1} - Z'_{C_1}| \ll 2r_c|\cos\phi|$.

†Because of the numerical error in the calculation of $\cos\psi$, the coordinates of hydrogens (b_2 and c_2) might be adjusted to obtain the canonical geometry of the triangle.

$\alpha = m_1(Y'_{b2} \cdot Y'_{\overrightarrow{A_0B_0}} + X'_{b2} \cdot X'_{\overrightarrow{A_0B_0}})$
$+ m_2(Y'_{c2} \cdot Y'_{\overrightarrow{A_0C_0}} + X'_{c2} X'_{\overrightarrow{A_0C_0}})$

$\beta = m_1(Y'_{b2} X'_{\overrightarrow{A_0B_0}} - X'_{b2} Y'_{\overrightarrow{A_0B_0}})$
$+ m_2(Y'_{c2} X'_{\overrightarrow{A_0C_0}} - X'_{c2} Y'_{\overrightarrow{A_0C_0}})$

$\gamma = m_1(Y'_{b1} X'_{\overrightarrow{A_0B_0}} - X'_{b1} Y'_{\overrightarrow{A_0B_0}})$
$+ m_2(Y'_{c1} X'_{\overrightarrow{A_0C_0}} - X'_{c1} Y'_{\overrightarrow{A_0C_0}})$

$$\alpha = X'_{b_2}(X'_{B_0} - X'_{C_0}) + (Y'_{B_0} - Y'_{A_0})Y'_{b_2} + (Y'_{C_0} - Y'_{A_0})Y'_{c_2}$$

$$\beta = X'_{b_2}(Y'_{C_0} - Y'_{B_0}) + (X'_{B_0} - X'_{A_0})Y'_{b_2} + (X'_{C_0} - X'_{A_0})Y'_{c_2}$$

$$\gamma = (X'_{B_0} - X'_{A_0})Y'_{B_1} - X'_{B_1}(Y'_{B_0} - Y'_{A_0}) + (X'_{C_0} - X'_{A_0})Y'_{C_1} - X'_{C_1}(Y'_{C_0} - Y'_{A_0})$$

we can write eq. (A14) as

$$\alpha \sin\theta + \beta\cos\theta = \gamma \qquad \text{(A15)}$$

This is transformed into

$$\sqrt{\alpha^2 + \beta^2}\sin(\theta + \varepsilon) = \gamma, \qquad \tan\varepsilon = \frac{\beta}{\alpha}$$

The solution of the above trigonometric equation is given by*

$$\theta = \sin^{-1}\frac{\gamma}{\sqrt{\alpha^2 + \beta^2}} - \tan^{-1}\frac{\beta}{\alpha} \qquad \text{(A16)}$$

On the other hand, applying $\sin^2\theta + \cos^2\theta = 1$, eq. (A15) is expressed as

$$(\alpha^2 + \beta^2)\sin^2\theta - 2\alpha\gamma\sin\theta + \gamma^2 - \beta^2 = 0$$

The solution of this quadratic equation is given by the root's rule

$$\sin\theta = \frac{\alpha\gamma - \beta\sqrt{\alpha^2 + \beta^2 - \gamma^2}}{\alpha^2 + \beta^2} \qquad \text{(A17)}$$

where the sign of the square root is chosen so that eq. (A15) is satisfied. From either eq. (A16) or (A17), $\sin\theta$ and then $\cos\theta$ can be calculated while the latter might be preferable due to avoiding the calculations of trigonometric functions. Finally, the coordinates of $\Delta A_3B_3C_3$ are calculated by substitutions of $\sin\theta$ and $\cos\theta$ with the numbers obtained above into eq. (A4).

For velocity verlet, δV due to the positional constraints:

$\delta V = \frac{\delta r}{\delta t} = \frac{r_3 - r_1}{\delta t}$ (positional)

Similar to RATTLE

APPENDIX B: DETAILS OF VELOCITY RESETTING OF SETTLE

Equation (8) can be written as

$$\delta t(m_a + m_b)\cdot\tau_{AB} + \delta t\cdot m_a\cos B\cdot\tau_{BC} + \delta t\cdot m_b\cos A\cdot\tau_{CA} = 2m_am_bv^0_{AB}$$

$$\delta t\cdot m_c\cos B\cdot\tau_{AB} + \delta t(m_b + m_c)\cdot\tau_{BC} + \delta t\cdot m_b\cos C\cdot\tau_{CA} = 2m_bm_cv^0_{BC}$$

$$\delta t\cdot m_c\cos A\cdot\tau_{AB} + \delta t\cdot m_a\cos C\cdot\tau_{BC} + \delta t(m_c + m_a)\cdot\tau_{CA} = 2m_cm_av^0_{CA} \qquad \text{(B1)}$$

where $v^0_{AB} = \mathbf{e}_{AB}\cdot\mathbf{v}^0_{AB}$, $v^0_{BC} = \mathbf{e}_{BC}\cdot\mathbf{v}^0_{BC}$, and $v^0_{CA} = \mathbf{e}_{CA}\cdot\mathbf{v}^0_{CA}$ are the components of relative velocities along the bonds. The solution of the above simultaneous linear equations is given by

$$\tau_{AB} = m_a\{v^0_{AB}[2(m_a + m_b) - m_a\cos^2 C] + v^0_{BC}[m_b\cos C\cos A - (m_a + m_b)\cos B] + v^0_{CA}(m_a\cos B\cos C - 2m_b\cos A)\}/d$$

$$\tau_{BC} = \{v^0_{BC}[(m_a + m_b)^2 - m_b^2\cos^2 A] + v^0_{CA}m_a[m_b\cos A\cos B - (m_a + m_b)\cos C] + v^0_{AB}m_a[m_b\cos C\cos A - (m_a + m_b)\cos B]\}/d$$

$$\tau_{CA} = m_a\{v^0_{CA}[2(m_a + m_b) - m_a\cos^2 B] + v^0_{AB}(m_a\cos B\cos C - 2m_b\cos A) + v^0_{BC}[m_b\cos A\cos B - (m_a + m_b)\cos C]\}/d$$

$$d = \delta t\{2(m_a + m_b)^2 + 2m_am_b\cos A\cos B\cos C - 2m_b^2\cos^2 A - m_a(m_a + m_b)\times(\cos^2 B + \cos^2 C)\}/2m_b \qquad \text{(B2)}$$

This equation (B2) only assumed $m_b = m_c$.

based on the Cramer's rule

$$\tau_i = \frac{D_i}{D}$$

where D is the system determinant and D_i is the determinant obtained on replacing the respective coefficients of ith column $[\delta t(m_a + m_b), \delta t m_c\cos B \ldots]$ of D by $2m_am_bv^0_{AB}$, $2m_bm_cv^0_{BC}$ .... Substituting thus calculated τ_{AB}, τ_{BC}, and τ_{CA} into eq. (7), we get the constrained velocities, $\mathbf{v}_A$, $\mathbf{v}_B$, and $\mathbf{v}_C$.

This δV has contribution to the virial tensor.

Similar to RATTLE2.

(A17) $\alpha \sim 1 \sim 2$

$\beta \sim (-\varepsilon \sim +\varepsilon)$

$\gamma \sim (-\varepsilon \sim +\varepsilon)$

Since $\theta \sim (-\varepsilon \sim +\varepsilon)$, $\sin\theta$ can be $(-\varepsilon \sim +\varepsilon)$, but $\cos\theta$ is always positive. so

$\cos\theta = \frac{\beta\gamma \pm \alpha\sqrt{\alpha^2 + \beta^2 - \gamma^2}}{\alpha^2 + \beta^2}$

$\Rightarrow$ only $\cos\theta = \frac{\beta\gamma + \alpha\sqrt{\alpha^2 + \beta^2 - \gamma^2}}{\alpha^2 + \beta^2} > !$

which is equivalent to (A17)

References

1. W.F. Van Gunsteren and H.J.C. Berendsen, *Angew. Chem. Int. Ed. Engl.*, **29**, 992 (1990); D.L. Beveridge and F.M. DiCapura, *Annu. Rev. Biophys. Biophys. Chem.*, **18**, 431 (1989).
2. W.L. Jorgensen and M. Briggs, *J. Am. Chem. Soc.*, **111**, 4190 (1989); T.P. Straatsma and H.J.C. Berendsen, *J. Chem. Phys.*, **89**, 5879 (1988).
3. C.L. Brooks and J.J. McDonald, *J. Am. Chem. Soc.*, **113**, 2295 (1991); S. Ha, J. Geo, B. Tidor, J.W. Brady, and M. Karplus, *J. Am. Chem. Soc.*, **113**, 1553 (1991).
4. D.M. Ferguson and P.A. Kollman, *Antisense Res. Dev.*, **1**, 243 (1991); D.A. Pearlman and P.A. Kollman, *Biopolymers*, **29**, 1193 (1990).
5. W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, R.W. Impey, and M.L. Klein, *J. Chem. Phys.*, **79**, 926 (1983).
6. H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, and J. Hermans, *Intermolecular Forces*, B. Pullman, Ed., Reidel, Dordrecht, The Netherlands, 1981, pp 331–342.
7. J.E. Mertz, D.J. Tobias, C.L. Brooks III, and U.C. Singh, *J. Comp. Chem.*, **12**, 1270 (1991).
8. A. Rahman and F.H. Stillinger, *J. Chem. Phys.*, **55**, 3336 (1971).
9. D.J. Evans and S. Murad, *Mol. Phys.*, **34**, 327 (1977).
10. J.P. Ryckaert, G. Ciccotti, and H.J.C. Berendsen, *J. Comp. Phys.*, **23**, 327 (1977).
11. H. Andersen, *J. Comp. Phys.*, **52**, 24 (1983).
12. L. Verlet, *Phys. Rev.*, **159**, 98 (1967).

*In the typical simulations with a time step of 1 to 2 fs at 300 K, the maximum value of θ is about 1°. In the case of a longer step size of 5 fs and a higher temperature of 1500 K, the maximum value is about 9°. These values are small enough to satisfy $-1/2\pi < \theta < 1/2\pi$ or $\sin\theta \ll 1$.