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NOTE

Direct Application of SHAKE to the Velocity Verlet Algorithm*

Since their introduction in 1977 [1], constraint algorithms have been developed for many of the numerical integration schemes used in molecular dynamics (MD) simulations. Among these are SHAKE [1] and RATTLE [2], which represent the use of constraints in the Verlet and velocity Verlet algorithms. A number of other implementations for performing free energy calculations [3, 4] and for studying constant pressure-constant temperature MD [5] have been devised.

The purpose of this note is to propose an alternative to RATTLE for applying constraints to the velocity Verlet algorithm. As described by Andersen [2], the RATTLE algorithm requires two calculations of the constraint forces, one for updating the positions and one for updating the velocities. This is somewhat surprising given that SHAKE contains only one calculation of the constraint forces. Because of the ease with which the velocity Verlet algorithm can be converted to the standard Verlet algorithm, one would intuitively expect that a constraint procedure could be constructed for the velocity Verlet algorithm which requires only one evaluation of the constraint forces; this is shown in the following.

Suppose the total forces, $\mathbf{f}_i(t)$, and velocities, $\mathbf{v}_i(t)$, acting on the ith particle at time t are known. Both the force due to the interatomic potentials, $\mathbf{f}_i'(t)$, and the force due to the constraints, $\mathbf{g}_i(t)$, are included in $\mathbf{f}_i(t)$ so that

$$\mathbf{f}_i(t) = \mathbf{f}_i'(t) + \mathbf{g}_i(t). \tag{1}$$

The first two steps in the velocity Verlet algorithm consists of calculating the coordinates $\mathbf{r}_i$ at time $t+\delta t$ and the velocities at time $t+\frac{1}{2}\delta t$,

$$\mathbf{r}_i(t+\delta t) = \mathbf{r}_i(t) + \delta t\, \mathbf{v}_i(t) + \frac{(\delta t)^2}{2m_i}\mathbf{f}_i(t), \tag{2}$$

$$\mathbf{v}_i\left(t+\frac{1}{2}\delta t\right) = \mathbf{v}_i(t) + \frac{\delta t}{2m_i}\mathbf{f}_i(t). \tag{3}$$

The $\mathbf{f}_i(t)$ already include the correct constraint forces so that the $\mathbf{r}_i(t+\delta t)$ satisfy the constraints. These are usually of the form

$$d_{ij}^2 - r_{ij}^2 = 0. \tag{4}$$

The problem now arises when one tries to complete the final step in the velocity Verlet algorithm and calculate $\mathbf{v}_i(t+\delta t)$ via

$$\mathbf{v}_i(t+\delta t) = \mathbf{v}_i\left(t+\frac{1}{2}\delta t\right) + \frac{\delta t}{2m_i}\mathbf{f}_i(t+\delta t). \tag{5}$$

The $\mathbf{f}_i'(t+\delta t)$ can be calculated since they only depend on the atomic coordinates and the $\mathbf{r}_i(t+\delta t)$ are already known. Computing the $\mathbf{g}_i(t+\delta t)$ requires that the $\mathbf{r}_i(t+2\delta t)$ satisfy the constraint equations. This creates an apparent difficulty, because in order to calculate $\mathbf{r}_i(t+2\delta t)$ the $\mathbf{v}_i(t+\delta t)$ are needed; they in turn depend on $\mathbf{f}_i(t+\delta t)$. Andersen's solution is to make use of the constraint equations

$$\mathbf{r}_{ij}\cdot\mathbf{v}_{ij} = 0, \tag{6}$$

which can be obtained by differentiating Eq. (4) with respect to time. Imposing the constraints from Eq. (6) allows the calculation of the constraint forces $\mathbf{g}_i^V$, which in turn allows the calculation of the velocites at $t+\delta t$. However, in the next step a new set of constraint forces, $\mathbf{g}_i^R$, must be computed so that the $\mathbf{r}_i(t+2\delta t)$ satisfy the original constraints from Eq. (4).

The main point of this paper is that it is possible to calculate the constraint forces $\mathbf{g}_i(t+\delta t)$ directly. By rewriting $\mathbf{v}_i(t+\delta t)$ using Eq. (5), the coordinates at time $t+2\delta t$ can be written as

$$\mathbf{r}_i(t+2\delta t) = \mathbf{r}_i(t+\delta t) + \delta t\, \mathbf{v}_i\left(t+\frac{1}{2}\delta t\right) + \frac{(\delta t)^2}{m_i}\mathbf{f}_i'(t+\delta t) + \frac{(\delta t)^2}{m_i}\mathbf{g}_i(t+\delta t). \tag{7}$$

Note that most of the terms on the right-hand side of Eq. (7) are known at time $t+\delta t$. The $\mathbf{r}_i(t+\delta t)$ and

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$\mathbf{v}_i(t+\frac{1}{2}\delta t)$ have already been calculated. The $\mathbf{f}_i'(t+\delta t)$ can also be computed since they depend only on the $\mathbf{r}_i(t+\delta t)$. Define the quantities

$$\mathbf{r}_i'(t+2\delta t)=\mathbf{r}_i(t+\delta t)+\delta t\,\mathbf{v}_i\left(t+\frac{1}{2}\delta t\right)+\frac{(\delta t)^2}{m_i}\mathbf{f}_i'(t+\delta t);$$

then

$$\mathbf{r}_i(t+2\delta t)=\mathbf{r}_i'(t+2\delta t)+\frac{(\delta t)^2}{m_i}\mathbf{g}_i(t+\delta t). \tag{8}$$

Equation (8) has exactly the same form as those encountered in the SHAKE algorithm. After Eq. (8) has been inserted into Eq. (4) the $\mathbf{g}_i(t+\delta t)$ can be found by using an iterative scheme almost identical to SHAKE. This algorithm is described briefly.

For a system that contains only bond length constraints of the type in Eq. (4) the force acting on the ith atom can be written as

$$\mathbf{g}_i(t+\delta t)=\sum_k \lambda_{ik}\mathbf{r}_{ik}(t+\delta t). \tag{9}$$

The summation over k is over all atoms that are constrained to atom i and $\mathbf{r}_{ik}$ is the separation vector between the i and the k atoms. The parameters λ_{ik} satisfy the relation $\lambda_{ik}=\lambda_{ki}$. If there are L distinct constraints then there are L distinct λ_{ik}'s and the problem is well posed.

Suppose a set of approximations to the λ_{ij}, labeled λ_{ij}^A, exist. Approximate values for the constraint forces, $\mathbf{g}_i^A(t+\delta t)$, can be obtained from Eq. (9). Equation (2) can then be used to obtain approximate values for the coordinates, $\mathbf{r}_i^A(t+2\delta t)$, at time $t+2\delta t$. The λ_{ij}^A can be improved by picking a particular pair, ij, and writing

$$\mathbf{r}_i(t+2\delta t)=\mathbf{r}_i^A(t+2\delta t)+\delta\lambda_{ij}\frac{(\delta t)^2}{m_i}\mathbf{r}_{ij}(t+\delta t),$$

$$\mathbf{r}_j(t+2\delta t)=\mathbf{r}_j^A(t+2\delta t)-\delta\lambda_{ij}\frac{(\delta t)^2}{m_j}\mathbf{r}_{ij}(t+\delta t).$$

The quantity $\delta\lambda_{ij}$ is an estimate of the difference between λ_{ij}^A and the true λ_{ij}. The contributions from all other constraint forces not involving the ij pair are neglected. Using these expressions in the constraint equation (4) and retaining terms only to order $\mathcal{O}((\delta t)^2)$ give

$$d_{ij}^2-|\mathbf{r}_{ij}^A(t+2\delta t)|^2=2(\delta t)^2\left(\frac{1}{m_i}+\frac{1}{m_j}\right)\delta\lambda_{ij}\mathbf{r}_{ij}^A(t+2\delta t)\cdot\mathbf{r}_{ij}(t+\delta t)+\mathcal{O}((\delta t)^4). \tag{10}$$

This is solved for $\delta\lambda_{ij}$ and the result used to improve $\mathbf{r}_i^A(t+2\delta t)$ and $\mathbf{r}_j^A(t+2\delta t)$. The calculation is repeated for another pair, jk, until the list of constraints is exhausted. This procedure is iterated until all bonds satisfy the constraint equations to some previously specified accuracy.

The only real difference between this algorithm and SHAKE is that the definition of $\mathbf{r}_i'(t+2\delta t)$ in Eq. (8) is different. It is also necessary to update the $\mathbf{v}_i(t+\delta t)$ as the $\delta\lambda_{ij}$ are calculated. Because of the similarity between this algorithm and SHAKE, it should have similar convergence and stability properties. This algorithm has been implemented on several rigid water models and gives constant energy trajectories.

For completeness it is shown that the errors in this algorithm are of the same order as those in the original velocity Verlet algorithm. Following Ryckaert *et al.* [1], note that the exact constraint forces have the form

$$\mathbf{g}_i(t+\delta t)=\sum_k \Lambda_{ik}(t+\delta t)\,\mathbf{r}_{ik}(t+\delta t).$$

If $\mathbf{r}_i(t+2\delta t)$ is expanded to all orders in δt about the point $\mathbf{r}_i(t+\delta t)$ then the $\mathcal{O}((\delta t)^3)$ and higher terms will contain time derivatives of $\mathbf{f}_i'$ and $\mathbf{g}_i$. For the velocity Verlet algorithm this expansion is truncated at $\mathcal{O}((\delta t)^2)$. Substituting the Taylor expansion of $\mathbf{r}_i(t+2\delta t)$ into the constraint equations and retaining only terms of $\mathcal{O}((\delta t)^2)$ give

$$d_{ij}^2-|\mathbf{r}_{ij}(t+2\delta t)|2=\mathcal{O}((\delta t)^3).$$

Replacing the $\Lambda_{ij}(t+2\delta t)$ by the λ_{ij} means that the constraint equations are satisfied exactly. This gives the equations

$$\begin{aligned}d_{ij}^2-|\mathbf{r}_{ij}'(t+2\delta t)|^2&-2\frac{(\delta t)^2}{m_i}\sum_k \Lambda_{ik}(t+\delta t)\,\mathbf{r}_{ik}(t+\delta t)\cdot\mathbf{r}_{ij}'(t+2\delta t)\\&+2\frac{(\delta t)^2}{m_j}\sum_l \Lambda_{jl}(t+\delta t)\,\mathbf{r}_{jl}(t+\delta t)\cdot\mathbf{r}_{ij}'(t+2\delta t)\\&=\mathcal{O}((\delta t)^3),\end{aligned}$$

$$\begin{aligned}d_{ij}^2-|\mathbf{r}_{ij}'(t+2\delta t)|^2&-2\frac{(\delta t)^2}{m_i}\sum_k \lambda_{ik}\mathbf{r}_{ik}(t+\delta t)\cdot\mathbf{r}_{ij}'(t+2\delta t)\\&+2\frac{(\delta t)^2}{m_j}\sum_l \lambda_{jl}\mathbf{r}_{jl}(t+\delta t)\cdot\mathbf{r}_{ij}'(t+2\delta t)\\&=\mathcal{O}((\delta t)^4).\end{aligned}$$

Subtracting these equations from each other results in

$$-2\frac{(\delta t)^2}{m_i}\sum_k (\Lambda_{ik}(t+\delta t)-\lambda_{ik})\,\mathbf{r}_{jk}(t+\delta t)\cdot\mathbf{r}'_{ij}(t+2\delta t)$$

$$+2\frac{(\delta t)^2}{m_j}\sum_l (\Lambda_{jl}(t+\delta t)-\lambda_{jl})\,\mathbf{r}_{jl}(t+\delta t)\cdot\mathbf{r}'_{ij}(t+2\delta t)$$

$$=\mathcal{O}((\delta t)^3).$$

It follows that

$$\Lambda_{ij}(t+\delta t)-\lambda_{ij}=\mathcal{O}(\delta t).$$

These contribute errors of $\mathcal{O}((\delta t)^3)$ to the $\mathbf{r}_i(t+2\delta t)$, which is the same as the error inherent in the velocity Verlet algorithm.

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