Hail Euler and Farewell: Rotational Motion in the Laboratory Frame[1].

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Abstract

In this paper we consider the treatment of rotational motion in molecular dynamics simulation and re-examine the Euler approach. It is shown that, for numerical integration, it is not necessary to couch the problem in terms of the principal reference frame in which the moment of inertia tensor is diagonal. From these considerations a new algorithm is developed which is solved entirely in the laboratory reference frame and avoids the pitfalls associated with applying Euler's method in numerical simulations.

Introduction

In molecular dynamics the numerical integration schemes for integrating the rotational motion of a rigid body (in our case a rigid molecule), are conventionally discussed in terms of Euler's rotational equations of motion [1]. In these equations it is assumed that, at a given instant, the rotation is described in a frame of reference in which the moment of inertia tensor is diagonal. This instantaneous frame of reference is known as the principal frame. In the principal frame the relationship between the applied torque and the rate of change of angular velocity is particularly simple and allows a simple numerical integration of the angular velocity. However, because the body rotates, it is necessary for the principal frame to rotate also, in order to ensure that the moment of inertia tensor remains diagonal.

Thus a numerical solution of Euler's equations needs to be supplemented by a prescription for updating the principal frame as the simulation proceeds. While such a prescription can be easily obtained [2], it is well known that there are disadvantages to the scheme, due to the real possibility of the equations becoming indeterminate for certain angles of orientation. This was discussed in detail by Evans and Murad [3] some years ago and led to the introduction of quaternions, with singularity free equations of motion, into the methodology of molecular dynamics. There is however another approach, and that is to relinquish the concept of the principal frame of reference altogether and tackle the problem

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directly in the laboratory frame. It turns out that this approach has advantages for a numerical integration scheme. Firstly however we must re-examine the mathematical treatment of rotational motion as it is conventionally presented.

The Equations of Motion for Rigid Molecules

A molecule in the context of this treatment is a rigid assembly of point masses (atoms) of mass m_i, where $i=1,…,n$. From this simple definition a number of important molecular properties are obtained:

$$M=\sum_{i=1}^{n} m_i \qquad (a) \qquad \vec{R}=M^{-1}\sum_{i=1}^{n} m_i \vec{r}_i \qquad (b)$$

$$\tag{1}$$

$$\vec{d}_i=\vec{r}_i-\vec{R} \qquad (c) \qquad I^{\alpha\beta}=\sum_{i=1}^{n} m_i\left(d_i^2\delta_{\alpha\beta}-d_i^\alpha d_i^\beta\right) \qquad (d)$$

In which M is the molecular mass, $\vec{R}$ the centre-of-mass, $\vec{d}_i$ the location of an atom with respect to the centre-of-mass and I is the moment of inertia tensor.

The velocity and angular momentum associated with these variables are:

$$\vec{V}=M^{-1}\sum_{i=1}^{n} m_i \vec{v}_i \qquad (a)$$

$$\vec{J}=\sum_{i=1}^{n} m_i\left(\vec{d}_i\times\vec{v}_i\right) \qquad (b) \tag{2}$$

$$\omega^\alpha=\left(I^{-1}\right)^{\alpha\beta} J^\beta \qquad (c)$$

Where $\vec{V}$ is the molecular (translational) velocity, $\vec{J}$ is the angular momentum and $\vec{\omega}$ is the angular velocity, while $\vec{v}_i$ is the velocity of an individual atom in the laboratory frame. (Note the use of the Einstein convention regarding tensor indices in equation (2c) here, and elsewhere in this paper.)

The dynamics of each molecule are driven by the molecular force $\vec{F}$ and torque $\vec{T}$:

$$\vec{F}=\sum_{i=1}^{n} \vec{f}_i \qquad (a) \qquad \vec{T}=\sum_{i=1}^{n} \vec{d}_i\times\vec{f}_i \qquad (b) \tag{3}$$

In which the atomic forces $\vec{f}_i$ are the vector sums of atom-atom forces acting between molecules.

It is important to note that in these definitions, moment of inertia, angular momentum, torque and angular velocity are defined with respect to the molecular centre-of-mass. It should also be noted that all have been defined with respect to the laboratory frame of reference, which means any inertial frame that happens to be convenient.

The equations of motion for each molecule (again in the laboratory frame) are well known:

$$\frac{d}{dt}\vec{V}=M^{-1}\vec{F} \qquad (a) \qquad\qquad \frac{d}{dt}\vec{J}=\vec{T} \qquad (b) \qquad\qquad (4)$$

The first of these is the standard Newtonian equation for translational motion, while the second embodies the rotational motion of the molecule. Following Euler this equation may be cast into the principal frame where it takes the familiar form know as Euler's equations [1] but here we take an alternative approach. Equation (4b) can be expanded into:

$$\vec{T}=\frac{d}{dt}\left(I^{\alpha\beta}\omega^{\beta}\right)=I^{\alpha\beta}\dot{\omega}^{\beta}+\dot{I}^{\alpha\beta}\omega^{\beta} \qquad\qquad (5)$$

Where the time derivative of the moment of inertia tensor can be obtained from equation (1d) as:

$$\dot{I}^{\alpha\beta}=-\sum_{i=1}^{n}m_{i}\left(\dot{d}_{i}^{\alpha}d_{i}^{\beta}+d_{i}^{\alpha}\dot{d}_{i}^{\beta}\right) \qquad\qquad (6)$$

We now recognise that

$$\dot{\vec{d}}_{i}=\vec{\omega}\times\vec{d}_{i} \qquad\qquad \text{or} \qquad\qquad \dot{d}_{i}^{\alpha}=\epsilon_{\alpha\beta\gamma}\omega^{\beta}d_{i}^{\gamma} \qquad\qquad (7)$$

in which the Levi-Civita tensor $\epsilon_{\alpha\beta\gamma}$ is 1 for an *even* permutation of indices, -1 for a odd permutation and zero if any index is repeated. Substitution of (7) into (6) provides the following result:

$$\dot{I}^{\alpha\beta}=\epsilon_{\alpha\lambda\mu}\omega^{\lambda}I^{\mu\beta}+\epsilon_{\beta\rho\sigma}\omega^{\rho}I^{\sigma\alpha} \qquad\qquad (8)$$

If equation (5) is rearranged we obtain:

$$\dot{\vec{\omega}}=I^{-1}\left(\vec{T}-\dot{I}\vec{\omega}\right) \qquad\qquad (9)$$

Equation (9) forms the basis for an integration of the angular velocity. We may therefore outline a possible numerical scheme for integrating the equations of motion for rigid molecules:

Scheme 1:

1. At time step t_n $\quad \{M, \vec{R}^n, \vec{V}^n, \vec{d}_i^n, \boldsymbol{I}^n, \vec{J}^n, \vec{F}^n, \vec{T}^n\}$ are known.

2. For each molecule:

   3. Update: $\quad \vec{V}^{n+1/2} \leftarrow \vec{V}^n + \dfrac{\Delta t}{2M} \vec{F}^n$.

   4. Update: $\quad \vec{J}^{n+1/2} \leftarrow \vec{J}^n + \dfrac{\Delta t}{2} \vec{T}^n$.

   5. Update: $\quad \vec{R}^{n+1} \leftarrow \vec{R}^n + \Delta t \, \vec{V}^{n+1/2}$.

   6. Calculate: $\quad \vec{\omega}^n = (\boldsymbol{I}^n)^{-1} \vec{J}^n$.

   7. Calculate: $\quad \dot{\boldsymbol{I}} \equiv \dot{I}^{\alpha\beta} = \epsilon_{\alpha\lambda\mu} \omega^\lambda I^{\mu\beta} + \epsilon_{\beta\rho\sigma} \omega^\rho I^{\sigma\alpha}$.

   8. Calculate $\quad \dot{\vec{\omega}}^n = (\boldsymbol{I}^n)^{-1} (\vec{T}^n - \dot{\boldsymbol{I}}^n \vec{\omega}^n)$.

   9. Update: $\quad \vec{\omega}^{n+1/2} \leftarrow \vec{\omega}^n + \Delta t \, \dot{\vec{\omega}}^n$.

   10. Update: $\quad \vec{d}_i^{n+1} \leftarrow \vec{d}_i^n + \Delta t \, \vec{\omega}^{n+1/2} \times \vec{d}_i^n, \quad \forall \vec{d}_i^n$.

   11. Calculate: $\vec{F}^{n+1}$ and $\vec{T}^{n+1}$ using $\vec{R}^{n+1}$ and $\{\vec{d}_i^{n+1}\}$.

   12. Update: $\quad \vec{V}^{n+1} \leftarrow \vec{V}^{n+1/2} + \dfrac{\Delta t}{2M} \vec{F}^{n+1}$.

   13. Update: $\quad \vec{J}^{n+1} \leftarrow \vec{J}^{n+1/2} + \dfrac{\Delta t}{2} \vec{T}^{n+1}$.

14. End For

Scheme 1 is based on the velocity Verlet algorithm [2]. The scheme is remarkably simple, but experienced molecular dynamicists will notice a serious weakness at step 10. This step is meant to compute the change in the orientation of the vector $\vec{d}_i$ as a result of the rotation generated by vector $\vec{\omega}^{n+1/2}$. However in this form it does not conserve the normalisation of $\vec{d}_i$ and consequently cannot maintain the structural integrity of the molecule during the rotation. Fortunately the geometric interpretation of this operation affords a reliable alternative prescription.

In Figure 1 we provide a geometric interpretation of the action of an angular velocity vector $\vec{\omega}$ on a typical displacement vector $\vec{d}$. Under this operation the tip of vector $\vec{d}$ traces out an arc of the circle shown. The plane of the circle is perpendicular to the vector $\vec{\omega}$. The radius of the circle is represented by the vector $\vec{u}$ which is given by:
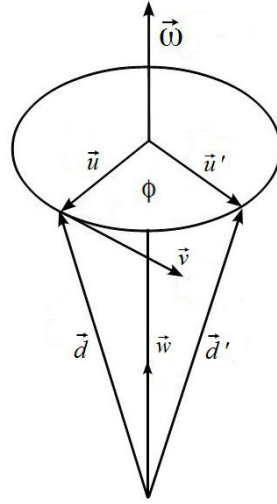
Figure 1

$$\vec{u} = \vec{d} - \vec{w} \qquad (9)$$

where

$$\vec{w} = \left(\frac{\vec{\omega} \cdot \vec{d}}{\omega^2} \right) \vec{\omega} \qquad (10)$$

is the projection of $\vec{d}$ in the direction of $\vec{\omega}$. From equation (7) we also have the velocity vector $\vec{v}$ defined as

$$\vec{v} = \vec{\omega} \times \vec{d} . \qquad (11)$$

Taking $\vec{u}$, $\vec{v}$ and $\vec{w}$ together we have a set of mutually orthogonal vectors.

In a time step Δt, the vector $\vec{u}$ is turned through an angle ϕ in the plane of the circle to become vector $\vec{u}'$. The angle ϕ is given by

$$\phi = \Delta t \omega = \Delta t \left(\frac{v}{u} \right) \qquad (12)$$

where ω, u and v are the magnitudes of vectors $\vec{\omega}, \vec{u}$ and $\vec{v}$ respectively. It is easy to show that

$$\vec{u}' = \cos(\phi) \vec{u} + \Delta t \frac{\sin(\phi)}{\phi} \vec{v} \qquad (13)$$

and from this we can obtain vector $\vec{d}'$, which is given by

$$\vec{d}\,' = \vec{w} + \vec{u}\,'. \tag{14}$$

Vector $\vec{d}\,'$ is the updated position of vector $\vec{d}$ after the time step has been completed. This is the required result.

A scheme for replacing step 10 of Scheme 1 is presented below.

Scheme 2:

1. Calculate: $\phi = \Delta t\, \omega^{n+1/2}$.

2. For each atom i in molecule:

3. Calculate: $\vec{w} = \left(\dfrac{\vec{\omega}^{\,n+1/2} \cdot \vec{d}_i^{\,n}}{|\vec{\omega}^{\,n+1/2}|^2} \right) \vec{\omega}^{\,n+1/2}$

4. Calculate: $\vec{u} = \vec{d}_i^{\,n} - \vec{w}$

5. Calculate: $\vec{v} = \vec{\omega}^{\,n+1/2} \times \vec{d}_i^{\,n}$.

6. Update: $\vec{d}_i^{\,n+1} \leftarrow \vec{w} + \cos(\phi)\vec{u} + \Delta t\, \dfrac{\sin(\phi)}{\phi}\vec{v}$.

7. End For

There is one further improvement that can be made. Step 6 of *Scheme 2* contains the ratio $\sin(\phi)/\phi$, which tends to 1 as $\phi \to 0$. To ensure this occurs cleanly, when ϕ is small $(\phi < 10^{-2})$ the ratio should be replaced by the expansion

$$\frac{\sin(\phi)}{\phi} = 1 - \frac{\phi^2}{6}\left(1 - \frac{\phi^2}{20}\left(1 - \frac{\phi^2}{42}\right)\right), \tag{15}$$

which has an error better than 3 parts in 10^{-22} and is accurate enough to preserve the length of $\vec{d}_i^{\,n+1}$ as it rotates.

Application

The proposed algorithm has been implemented in Fortran [4] and run on a set of model systems (all of which are defined in Lennard-Jones reduced units, and all pair interactions with $\varepsilon = 1$ and $\sigma = 1$ shifted to zero force at the cut off):

1. Case 1: 27 tetrahedral clusters of Lennard-Jones sites, with intramolecular site-site distance 1.2642, site masses $0.5, 1.5, 0.75, 1.25$, cluster density $\rho^* = 0.175$, temperature $T^* = 1.5$ and time step $\Delta t = 0.001$.
2. Case 2: *pseudo*-ammonia; 27 molecules, with H atoms at 3 vertices of a tetrahedron and the N atom at the tetrahedron

centre. Site masses 1.0 (N), 0.1 (H), N-H distance 0.7404, molecular density $\rho^*=0.2$, temperature $T^*=1.0$ and time step $\Delta t=0.001$.

3. Case 3: *pseudo*-water; 27 molecules, with H atoms at 2 vertices of a tetrahedron and the O atom at the tetrahedron centre, plus an additional L-J site bisecting O-H bonds at distance 0.1644 from oxygen, O-H bond length $.7119$, site masses 1.0 (O), 0.1 (H), 0.0 (additional site),molecular density $\rho^*=0.225$, temperature $T^*=1.25$ and time step $\Delta t=0.001$.

4. Case 4: As Case 1, with time step $\Delta t=0.0005$.
5. Case 5: As Case 2, with time step $\Delta t=0.0005$.
6. Case 6: As Case 3, with time step $\Delta t=0.0005$.

In each case a simulation of 1 million time steps was conducted, with the first 10,000 time steps reserved for equilibration. The average energy and drift over 990,000 time steps was obtained. The results are presented in Table 1.

Case	<Energy>	Total Drift	Drift per Δt
1	-1.7269×10^2	1.43×10^{-3}	1.45×10^{-9}
2	-2.8175×10^2	1.13×10^{-1}	1.14×10^{-7}
3	-4.5250×10^2	2.08	2.11×10^{-6}
4	-1.7521×10^2	7.33×10^{-4}	7.41×10^{-10}
5	-2.9530×10^2	5.86×10^{-3}	5.92×10^{-9}
6	-4.5611×10^2	1.74×10^{-1}	1.76×10^{-7}

Table 1

The total drift presented in Table 1 was obtained from the slope of the Energy *versus* Time plot fitted by least squares and multiplied by $990,000\,\Delta t$.

Cases 1, 2 and 3 represent molecular structures with decreasing moments of inertia, so it is anticipated that the algorithm will show greater drift progressing from 1 to 3. This is clearly seen in Table 1, The drift in Cases 1 and 2 is arguably negligible, but the result for Case 3 would not normally be acceptable. The particularly poor result obtained reflects, no doubt, the very low moment of inertia of this molecule. Nevertheless, reducing the time step by half (Case 6), improves the result significantly. The equivalent reduction in time step applied in Case 4 and Case 5 reduces the drift here also. For many applications the results obtained with the shorter time step would be quite acceptable.

Conclusion

The main conclusion to be drawn form this note is that casting the rotational equations of motion into a principal frame of reference is unnecessary if a numerical integration scheme is required. Solving the motion in the laboratory frame does not require recourse to quaternions as there are no difficulties with particular molecular orientations; the equations are singularity free. Finally, to this author at least, the method has an appealing directness that leans more on physical than mathematical intuition, which will be an advantage for others also.

References

[1] H. Goldstein, *Classical Mechanics*, Addison Wesley (1980).

[2] M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press (1980)

[3] D.J. Evans amd S. Murad, Molec. Phys. **34** (1977) 327.

[4] A copy of the test program ***revo.f*** is available from the author on request.