Group Seminar (revised: August 1, 2017)[a)]

Artur Avkhadiev[1, b)]
Department of Physics, Brown University, Providence RI 02912, USA

(Dated: July 25, 2017)

This report consist of two parts:

1. A discussion of the constraint dynamics algorithm based on velocity Verlet numerical integration scheme, RATTLE .
2. A calculation of the kinetic energy of a freely-jointed polymer chain using the bond-vector representation in the CM frame of the molecule.

CONTENTS

I. RATTLE

A. General Problem Formulation

Generally, motion with (holonomic) constraints can be captured by the following two equations:

$$m_a \ddot{\mathbf{r}}_a = \mathbf{F}_a + \mathbf{G}_a \tag{I.1}$$

$$\mathbf{G}_a(t) = -\sum_{k=1}^{L} \lambda_k(t) \nabla_{\mathbf{r}_a} \sigma_k \left(t, \left\{ \mathbf{r}_a \mid 1 \leq a \leq N \right\} \right) \tag{I.2}$$

Where:

- a indexes N particles with masses m_a.
- k indexes L constraints σ_k.
- $\mathbf{F}_a$ is the total force on the particle a.
- σ_k depends only on time and particle positions $\mathbf{r}_a$; in particular, it does not depend on particle velocities (that is, the constraints are *holonomic*).
- $\mathbf{G}_a$ can be regarded as a "constraint force" on the particle at $\mathbf{r}_a$. Its Lagrange multiplier $\lambda_k(t)$, proportional to the magnitude of the "force", assumes the necessary units depending on the units of the corresponding constraint $\sigma_k(t)$.

B. Assumptions

RATTLE attempts to solve a specific case of the general problem posed above. It is a numerical integration of equations of motion for a molecule with N atoms, based on the velocity Verlet integration scheme. The only kind of constraint allowed is the constraint on an interatomic bond length: a bond between any two atoms a and b in the molecule may be required to have a constant length d_{ab}.

The last assumption fixes the form of constraints from equation I.1 and the contraint forces from equation I.2:

$$\begin{aligned}\sigma_{ab}(t) &= d_{ab}^2 - \left\|\mathbf{r}_{ab}(t)\right\|^2 \\ &= 0\end{aligned} \tag{I.3}$$

$$\begin{aligned}\mathbf{G}_a(t) &= -\sum_{(a,\,b)\in K} \lambda_{ab}(t)\nabla_{\mathbf{r}_a}\sigma_{ab}\left(t,\,\mathbf{r}_a,\,\mathbf{r}_b\right) \\ &= -2\sum_{(a,\,b)\in K} \lambda_{ab}(t)\mathbf{r}_{ab}(t)\end{aligned} \tag{I.4}$$

Where $\mathbf{r}_{ab}$ is the bond vector defined as

$$\mathbf{r}_{ab} = \mathbf{r}_a - \mathbf{r}_b \tag{I.5}$$

In equations I.3-I.4, we use unique atomic pairs $(a,\,b) \in K$ to label the constraints and the corresponding Lagrange multipliers λ_{ab}. All unique pairs corresponding to a constraint belong to a set K. For example, in a polymer molecule with N atoms, there can be at most $N-1$ constraints of the form $K = \left\{(a,\,a+1) \mid 1 \le a \le N-1\right\}$.

Note that if the only constraints of interest are those on bond lengths and bond angles, the above assumption is made without loss of generality: any constraint on two adjacent bonds connecting atom 1 with atom 2 and atom 2 with atom 3 is equivalent to a constraint on the length of the bond connecting atom 1 with atom 3.

C. Velocity Verlet

Given equations of motion:

$$m_a\ddot{\mathbf{r}}_a = \mathbf{F}_a \tag{I.6}$$

Velocity Verlet is a scheme for numerical integration of the above equations. Dropping the indices a labeling the particles, it comprises the following three equations:

$$\mathbf{v}\left(t+\frac{1}{2}\delta t\right) = \mathbf{v}(t) + \frac{1}{2}\delta t\frac{\mathbf{F}(t)}{m} \tag{I.7}$$

$$\mathbf{r}\left(t+\delta t\right) = \mathbf{r}(t) + \delta t\mathbf{v}\left(t+\frac{1}{2}\delta t\right) \tag{I.8}$$

$$\mathbf{v}\left(t+\delta t\right) = \mathbf{v}\left(t+\frac{1}{2}\delta t\right) + \frac{1}{2}\delta t\frac{\mathbf{F}\left(t+\delta t\right)}{m} \tag{I.9}$$

The scheme comprises two stages, separated by the force evaluation loop:

1.
   - Start with $\mathbf{r}(t)$, $\mathbf{v}(t)$, and $\mathbf{F}(t)$.
   - Calculate velocities at half timestep, $\mathbf{v}\left(t+\frac{1}{2}\delta t\right)$, according to equation I.7.
   - Using velocities at half timestep, $\mathbf{v}\left(t+\frac{1}{2}\delta t\right)$, calculate positions $\mathbf{r}\left(t+\delta t\right)$ according to equation I.8; store the values.
2. Using $\mathbf{r}\left(t+\delta t\right)$, calculate the forces $\mathbf{F}\left(t+\delta t\right)$; store the values.
   - Using velocities at half timestep, $\mathbf{v}\left(t+\frac{1}{2}\delta t\right)$, and forces $\mathbf{F}\left(t+\delta t\right)$, calculate velocities at full time step, $\mathbf{v}\left(t+\delta t\right)$, according to equation I.9; store the values.

This integration scheme stores positions, velocites and forces (or accelerations) at the same time, and minimizes the round-off error.

D. RATTLE : the gist

RATTLE is a numerical integration scheme based on velocity Verlet.

The difference between the equations of motion that ordinary velocity Verlet can integrate and the equations of motion that RATTLE can integrate is that the latter can contain constraint forces $\mathbf{G}_a$: forces that, at any point in time, act to keep the constrained bond lengths constant.

One can think of the total constraint force $\mathbf{G}_a$ on an atom a as a sum of constraint forces acting along the bonds that include the atom:

$$\mathbf{G}_a = \sum_b \mathbf{G}_{ab}$$

Where $\mathbf{G}_{ab}$ is a constraint force on atom a from atom b acting along the bond vector $\mathbf{r}_{ab}$ so as to

keep the bond length constant at any point in time. A constraint force equal in magnitude and opposite in direction is acting on atom b.

Let us have a molecule at time t, *with all the constraints satisfied*. That means, $\sigma_{ab}(t) = 0$ (and hence $\dot{\sigma}_{ab}(t) = 0$) for all unique atomic pairs $(a, b) \in K$ that are bound by a constraint on their bond length. Using the derived form of constraints in equation I.3, this means that

$$d_{ab}^2 - \left\|\mathbf{r}_{ab}(t)\right\|^2 = 0 \tag{I.10}$$

and

$$\mathbf{r}_{ab}(t) \cdot \mathbf{v}_{ab}(t) = 0 \tag{I.11}$$

Where $\mathbf{v}_{ab} = \mathbf{v}_a - \mathbf{v}_b$.

If the constraint forces are not present, we can integrate the equations of motion using ordinary velocity Verlet from t to $t+\delta t$, obtaining "unconstrained" positions and velocites $\mathbf{r}_a^{(0)}(t+\delta t)$ and $\mathbf{v}_a^{(0)}(t+\delta t)$. The resulting positions of atoms may violate the constraints: that is, equations I.10 and I.11 may not hold at time $t+\delta t$. However, assuming a reasonable timestep δt, the constraints should not be violated "too much": small corrective displacements $\delta\mathbf{r}_a(t+\delta t)$ and $\delta\mathbf{v}_a(t+\delta t)$ will yield positions and velocities that respect the constraints.

Since constraint forces on each atom are only acting along the bonds that include the atom, a corrective displacement is also a sum of displacements along the bonds:

$$\delta\mathbf{r}_a = \sum_b \delta\mathbf{r}_{ab}$$
$$\delta\mathbf{v}_a = \sum_b \delta\mathbf{v}_{ab}$$

Where $\delta\mathbf{r}_{ab} = \delta\mathbf{r}_a - \delta\mathbf{r}_b$ and $\delta\mathbf{v}_{ab} = \delta\mathbf{v}_a - \delta\mathbf{v}_b$.

After these corrective displacements are applied to the unconstrained positions $\mathbf{r}_a^{(0)}(t+\delta t)$ and velocities $\mathbf{v}_a^{(0)}(t+\delta t)$, the constraints at time $t+\delta t$ should be satisfied:

$$d_{ab}^2 - \left\|\mathbf{r}_{ab}^{(0)}(t+\delta t) + \delta\mathbf{r}_{ab}(t+\delta t)\right\|^2 = 0 \tag{I.12}$$

and

$$\mathbf{r}_{ab}(t+\delta t) \cdot \left(\mathbf{v}_{ab}^{(0)}(t+\delta t) + \delta\mathbf{v}_{ab}(t+\delta t)\right) = 0 \tag{I.13}$$

Where $\mathbf{r}_{ab}^{(0)} = \mathbf{r}_a^{(0)} - \mathbf{r}_b^{(0)}$ and $\mathbf{v}_{ab}^{(0)} = \mathbf{v}_a^{(0)} - \mathbf{v}_b^{(0)}$.

The gist of RATTLE is in *approximating* the corrective displacements $\delta\mathbf{r}_a(t+\delta t)$ and $\delta\mathbf{v}_a(t+\delta t)$ such that all constraints (and their derivatives) at time $t+\delta t$ are simultaneously satisfied to within the specified tolerance ξ.

If one thinks of velocity Verlet as a two-stage process, where the stages are separated by the force evaluation loop, then RATTLE is a four-stage process, where each velocity Verlet stage is followed by a corrective stage:

1. Follow stage I of velocity Verlet:
   - Start with corrected $\mathbf{r}(t)$, $\mathbf{v}(t)$ that respect the constraints, and $\mathbf{F}(t)$.
   - Obtain unconstrained $\mathbf{v}^{(0)}\left(t+\frac{1}{2}\delta t\right)$ and $\mathbf{r}^{(0)}(t+\delta t)$.
2. First corrective stage:
   - Calculate $\delta\mathbf{v}\left(t+\frac{1}{2}\delta t\right)$ and $\delta\mathbf{r}(t+\delta t)$.
   - Apply the corrections to the unconstrained values $\mathbf{v}^{(0)}\left(t+\frac{1}{2}\delta t\right)$ and $\mathbf{r}^{(0)}(t+\delta t)$, obtaining corrected $\mathbf{v}\left(t+\frac{1}{2}\delta t\right)$ and $\mathbf{r}(t+\delta t)$ that respect the constraints; store $\mathbf{r}(t+\delta t)$.
3. Using corrected positions $\mathbf{r}(t+\delta t)$, calculate the forces $\mathbf{F}(t+\delta t)$; store the values. Follow stage II of velocity Verlet:
   - Using corrected velocities at half timestep, $\mathbf{v}\left(t+\frac{1}{2}\delta t\right)$, and forces $\mathbf{F}(t+\delta t)$, calculate unconstrained velocities at full time step, $\mathbf{v}^{(0)}(t+\delta t)$
4. Second corrective stage:
   - Calculate $\delta\mathbf{v}(t+\delta t)$.
   - Apply the correction to $\mathbf{v}^{(0)}(t+\delta t)$, obtaining corrected $\mathbf{v}(t+\delta t)$; store the corrected values.

E. RATTLE Integration Scheme

How does the modified velocity Verlet integration scheme look like in RATTLE ? The difference between the two is in constraint forces. If we include the constraint forces $\mathbf{G}_a$ in equations I.7-I.9, we will obtain the new integration scheme:

$$\begin{aligned}\mathbf{v}\left(t+\frac{1}{2}\delta t\right) &= \mathbf{v}(t)+\frac{1}{2}\delta t\frac{\mathbf{F}(t)+\mathbf{G}(t)}{m}\\ &= \mathbf{v}^{(0)}\left(t+\frac{1}{2}\delta t\right)+\frac{1}{2}\delta t\frac{\mathbf{G}(t)}{m}\\ &= \mathbf{v}^{(0)}\left(t+\frac{1}{2}\delta t\right)+\delta\mathbf{v}\left(t+\frac{1}{2}\delta t\right)\end{aligned} \tag{I.14}$$

$$\begin{aligned}\mathbf{r}\left(t+\delta t\right) &= \mathbf{r}(t)+\delta t\mathbf{v}\left(t+\frac{1}{2}\delta t\right)\\ &= \mathbf{r}^{(0)}\left(t+\delta t\right)+\delta\mathbf{r}\left(t+\delta t\right)\end{aligned} \tag{I.15}$$

$$\begin{aligned}\mathbf{v}\left(t+\delta t\right) &= \mathbf{v}\left(t+\frac{1}{2}\delta t\right)+\frac{1}{2}\delta t\frac{\mathbf{F}\left(t+\delta t\right)}{m}\\ &\quad+\frac{1}{2}\delta t\frac{\mathbf{G}\left(t+\delta t\right)}{m}\\ &= \mathbf{v}^{(0)}\left(t+\delta t\right)+\frac{1}{2}\delta t\frac{\mathbf{G}\left(t+\delta t\right)}{m}\\ &= \mathbf{v}^{(0)}\left(t+\delta t\right)+\delta\mathbf{v}\left(t+\delta t\right)\end{aligned} \tag{I.16}$$

Where we have identified unconstrained velocity and position values, and defined the corrective displacements:

$$\delta\mathbf{v}_a\left(t+\frac{1}{2}\delta t\right) = \frac{1}{2}\delta t\frac{\mathbf{G}_a(t)}{m_a} \tag{I.17}$$

$$\delta\mathbf{r}_a\left(t+\delta t\right) = \delta t\delta\mathbf{v}_a\left(t+\frac{1}{2}\delta t\right) \tag{I.18}$$

$$\delta\mathbf{v}_a\left(t+\delta t\right) = \frac{\mathbf{G}_a\left(t+\delta t\right)}{m_a} \tag{I.19}$$

Since $\delta\mathbf{r}_a\left(t+\delta t\right)$ can be easily expressed via $\delta\mathbf{v}_a\left(t+\frac{1}{2}\delta t\right)$, we only need to concern ourselves with $\delta\mathbf{v}_a\left(t+\frac{1}{2}\delta t\right)$ and $\delta\mathbf{v}_a\left(t+\delta t\right)$. We can expand $\mathbf{G}_a$ as $\sum_b \mathbf{G}_{ab}$ where, in turn, each summand can be expressed via Lagrange multipliers and bond vectors using equation I.4, yielding:

$$\begin{aligned}\delta\mathbf{v}_a\left(t+\frac{1}{2}\delta t\right) &= \sum_{(a,\,b)\in K}\left(-\delta t\lambda_{ab}(t)\mathbf{r}_{ab}(t)\right)\\ &= \sum_{(a,\,b)\in K}\delta\mathbf{v}_{ab}\left(t+\frac{1}{2}\delta t\right)\\ \delta\mathbf{v}_a\left(t+\delta t\right) &= \sum_{(a,\,b)\in K}\left(-\delta t\lambda_{ab}\left(t+\delta t\right)\mathbf{r}_{ab}\left(t+\delta t\right)\right)\\ &= \sum_{(a,\,b)\in K}\delta\mathbf{v}_{ab}\left(t+\delta t\right)\end{aligned}$$

Where we defined $\delta\mathbf{v}_{ab}\left(t+\frac{1}{2}\delta t\right)$ and $\delta\mathbf{v}_{ab}\left(t+\delta t\right)$, and the definition of $\delta\mathbf{r}_{ab}\left(t+\delta t\right)$ follows from I.18:

$$\delta\mathbf{v}_{ab}\left(t+\frac{1}{2}\delta t\right) = -\delta t\lambda_{ab}(t)\mathbf{r}_{ab}(t) \tag{I.20}$$

$$\delta\mathbf{r}_{ab}\left(t+\delta t\right) = -\delta t^2\lambda_{ab}(t)\mathbf{r}_{ab}(t) \tag{I.21}$$

$$\delta\mathbf{v}_{ab}\left(t+\delta t\right) = -\delta t\lambda_{ab}\left(t+\delta t\right)\mathbf{r}_{ab}\left(t+\delta t\right) \tag{I.22}$$

Since we can find the bond vectors and know the timestep, the problem of calculating the corrective steps is reduced to finding the Lagrange multipliers at times t and $t+\delta t$.

F. Solving Constraints Approximately

In fact, if we are trying to solve the constraints to within a given tolerance — that is, if we are trying to satisfy the inequalities

$$\frac{\left|d_{ab}-\left\|\mathbf{r}_{ab}\left(t+\delta t\right)\right\|\right|}{d_{ab}} < \xi \tag{I.23}$$

and

$$\frac{\delta t\left|\hat{\mathbf{r}}_{ab}\left(t+\delta t\right)\cdot\mathbf{v}_{ab}\left(t+\delta t\right)\right|}{d_{ab}} < \xi \tag{I.24}$$

— then we do not need to the exact Largrange multipliers $\lambda_{ab}\left(t+\frac{1}{2}\delta t\right)$ and $\lambda_{ab}\left(t+\delta t\right)$: some approximations $\gamma_{ab}\left(t+\frac{1}{2}\delta t\right)$ and $\gamma_{ab}\left(t+\delta t\right)$ will suffice, as long as inequalities I.23 and I.24 are respected.

In particular, suppose the unconstrained positions $\mathbf{r}_a^{(0)}(t+\delta t)$ and velocities $\mathbf{v}_a^{(0)}(t+\delta t)$ satisfy the inequalities I.23-I.24: then, there is no need to correct them; in this case, even though the exact Lagrange multipliers λ_{ab} may be non-zero, we may take $\gamma_{ab}=0$, foregoing all corrections and completing the integration step.

Otherwise, at least one bond vector $\mathbf{r}_{ab}^{(0)}$ violates I.23 after the first stage of velocity Verlet (or at least one bond velocity $\mathbf{v}_{ab}^{(0)}$ violates I.24 after the second stage of velocity Verlet). In this case, we would need to compute the Lagrange multiplier approximation $\gamma_{ab}(t)$ (or $\gamma_{ab}(t+\delta t)$), and correct $\mathbf{r}_{ab}^{(0)}$ (or $\mathbf{v}_{ab}^{(0)}$).

However, if either of the atoms included in the corrected bond is also included in another bond, the constraint corresponding to that bond may now be destroyed beyond the specified tolerance. Then another correction is in order. What should we do?

G. Correcting Iteratively

One solution is to correct iteratively, until all constraints are satisfied simultaneously to within the specified tolerances ξ and ξ. Then, each of the two corrective stages is an iterative procedure; they are analogous, so let us only consider the first one, for the sake of brevity. Suppose we are iterating over all bond vectors $\mathbf{r}_{ab}^{(i)}(t+\delta t)$ at the ith step of the iterative procedure. Then:

1. If a given bond vector $\mathbf{r}_{ab}^{(i)}(t+\delta t)$ satisfies I.23, then $\gamma_{ab}^{(i)}(t)=0$, and thus
$$\mathbf{v}_{ab}^{(i+1)}\left(t+\frac{1}{2}\delta t\right)=\mathbf{v}_{ab}^{(i)}\left(t+\frac{1}{2}\delta t\right)$$
$$\mathbf{r}_{ab}^{(i+1)}(t+\delta t)=\mathbf{r}_{ab}^{(i)}((t+\delta t))$$

2. Otherwise, $\gamma_{ab}^{(i)}(t)$ needs to be calculated; once it is calculated, one can find the corrective displacements $\delta\mathbf{v}_{ab}^{(i)}\left(t+\frac{1}{2}\delta t\right)$ and $\delta\mathbf{r}_{ab}^{(i)}(t+\delta t)$ according to equations I.20 and I.21. Then
$$\mathbf{v}_{ab}^{(i+1)}\left(t+\frac{1}{2}\delta t\right)=\mathbf{v}_{ab}^{(i)}\left(t+\frac{1}{2}\delta t\right)+\delta\mathbf{v}_{ab}^{(i)}\left(t+\frac{1}{2}\delta t\right)$$
$$\mathbf{r}_{ab}^{(i+1)}(t+\delta t)=\mathbf{r}_{ab}^{(i)}(t+\delta t)+\delta\mathbf{r}_{ab}^{(i)}(t+\delta t)$$

3. If none of the bond vectors were moved at the ith step, then the corrective stage is complete: all bond vectors satisfy I.23 simulataneosly; otherwise, another iterative step is in order.
4. The procedure continues until I.23 is satisfied for all bond vectors at some step m, or the number of iterations exceeds the allotted maximum M.

For a discussion of convergence of the above procedure at either of the corrective stages, the original paper is a good place to start.

H. Calculating Corrections

How does one calculate $\gamma_{ab}(t)^{(i)}$ and $\gamma_{ab}(t+\delta t)^{(i)}$ in the first and in the second corrective procedure, respectively?

1. Calculating $\gamma_{ab}^{(i)}(t)$

Let us begin with $\gamma_{ab}^{(i)}(t)$. Suppose that at the ith correction step, a bond vector $\mathbf{r}_{ab}^{(i)}(t+\delta t)$ does not satisy I.23 — a correction is in order, so $\gamma_{ab}^{(i)}(t)$ needs to be calculated. This quantity is an approximation to $\lambda_{ab}^{(i)}(t)$. If we knew $\lambda_{ab}^{(i)}(t)$, we could calculate $\mathbf{r}_{ab}^{(i+1)}(t+\delta t)$ in such a way so as to satisfy the constraint exactly. That would mean:

$$\begin{aligned}
&d_{ab}^2-\left\|\mathbf{r}_{ab}^{(i+1)}(t+\delta t)\right\|^2\\
&\quad=d_{ab}^2-\left\|\mathbf{r}_{ab}^{(i+1)}(t+\delta t)\right\|^2\\
&\quad=d_{ab}^2-\left\|\mathbf{r}_{ab}^{(i)}(t+\delta t)+\delta\mathbf{r}_{ab}^{(i)}(t+\delta t)\right\|^2\\
&\quad=0
\end{aligned}$$

Where

$$\delta\mathbf{r}_{ab}^{(i)}(t+\delta t)=-\delta t^2\lambda_{ab}^{(i)}(t)\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\mathbf{r}_{ab}(t)$$

Expanding out, we obtain:

$$0 = \left(d_{ab}^2 - \left\|\mathbf{r}_{ab}^{(i)}\left(t+\delta t\right)\right\|^2\right) - 2\delta t^2 \lambda_{ab}^{(i)}(t)\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\left(\mathbf{r}_{ab}(t)\cdot\mathbf{r}_{ab}^{(i)}\left(t+\delta t\right)\right) + \left(\delta t^2 \lambda_{ab}^{(i)}(t)\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\right)^2 \left\|\mathbf{r}_{ab}(t)\right\|^2 \tag{I.25}$$

At this point, we will ignore the term quadratic in $\lambda_{ab}^{(i)}\left(t+\delta t\right)$, and solve the resulting linear equation. The solution to this equation will be our approximation of $\lambda_{ab}^{(i)}\left(t+\delta t\right)$: $\gamma_{ab}^{(i)}\left(t+\delta t\right)$. Thus,

$$\gamma_{ab}^{(i)}(t) = \frac{d_{ab}^2 - \left\|\mathbf{r}_{ab}^{(i)}\left(t+\delta t\right)\right\|^2}{2\delta t^2\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\left(\mathbf{r}_{ab}(t)\cdot\mathbf{r}_{ab}^{(i)}\left(t+\delta t\right)\right)} \tag{I.26}$$

Assumming a reasonable timestep, at no point in the iterative correction should the position vector $\mathbf{r}_{ab}^{(i)}\left(t+\delta t\right)$ turn away from $\mathbf{r}_{ab}(t)$ so much as to be perpendicular to it and yield $\mathbf{r}_{ab}(t)\cdot\mathbf{r}_{ab}^{(i)}\left(t+\delta t\right) = 0$. However, to avoid division by zero and ensure the algorithm is implemented correctly, it is a good practice to check during the correction stage that this inner product is not too small.

2. Calculating $\gamma_{ab}^{(i)}\left(t+\delta t\right)$

Now let us consider $\gamma_{ab}^{(i)}\left(t+\delta t\right)$. Suppose that at the ith correction step, a bond velocity $\mathbf{v}_{ab}^{(i)}\left(t+\delta t\right)$ does not satisy I.24 — a correction is in order, so $\gamma_{ab}^{(i)}\left(t+\delta t\right)$ needs to be calculated. This quantity is an approximation to $\lambda_{ab}^{(i)}\left(t+\delta t\right)$. If we knew $\lambda_{ab}^{(i)}\left(t+\delta t\right)$, we could calculate $\mathbf{v}_{ab}^{(i+1)}\left(t+\delta t\right)$ in such a way so as to satisfy the constraint exactly. That would mean:

$$\begin{aligned}&\mathbf{r}_{ab}\left(t+\delta t\right)\cdot\mathbf{v}_{ab}^{(i+1)}\left(t+\delta t\right)\\ &\quad= \mathbf{r}_{ab}\left(t+\delta t\right)\cdot\left(\mathbf{v}_{ab}^{(i)}\left(t+\delta t\right)+\delta\mathbf{v}_{ab}^{(i)}\left(t+\delta t\right)\right)\\ &\quad= 0\end{aligned}$$

Where

$$\begin{aligned}&\delta\mathbf{v}_{ab}^{(i)}\left(t+\delta t\right)\\ &\quad= -\delta t\lambda_{ab}^{(i)}\left(t+\delta t\right)\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\mathbf{r}_{ab}\left(t+\delta t\right)\end{aligned}$$

Expanding out, we obtain:

$$\begin{aligned}0 = &\left(\mathbf{r}_{ab}\left(t+\delta t\right)\cdot\mathbf{v}_{ab}^{(i)}\left(t+\delta t\right)\right)\\ &-\delta t\lambda_{ab}^{(i)}\left(t+\delta t\right)\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\left\|\mathbf{r}_{ab}\left(t+\delta t\right)\right\|^2\end{aligned} \tag{I.27}$$

Using I.27, we can calculate $\lambda_{ab}^{(i)}\left(t+\delta t\right)$:

$$\lambda_{ab}^{(i)}\left(t+\delta t\right) = \frac{\mathbf{r}_{ab}\left(t+\delta t\right)\cdot\mathbf{v}_{ab}^{(i)}\left(t+\delta t\right)}{\delta t\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\left\|\mathbf{r}_{ab}\left(t+\delta t\right)\right\|^2} \tag{I.28}$$

However, we actually do not know $\mathbf{r}_{ab}\left(t+\delta t\right)$ — we only know $\mathbf{r}_{ab}^{(m)}\left(t+\delta t\right)$, which is an approximation of $\mathbf{r}_{ab}\left(t+\delta t\right)$ that satisfies the constraint within the specified tolerance (here, m denotes the last iteration of the first correction stage). Therefore, what we find is an approximation of the Lagrange multiplier, $\gamma_{ab}^{(i)}\left(t+\delta t\right)$, equal to

$$\gamma_{ab}^{(i)}\left(t+\delta t\right) = \frac{\mathbf{r}_{ab}^{(m)}\left(t+\delta t\right)\cdot\mathbf{v}_{ab}^{(i)}\left(t+\delta t\right)}{\delta t\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\left\|\mathbf{r}_{ab}^{(m)}\left(t+\delta t\right)\right\|^2} \tag{I.29}$$

3. Approximating Corrective Displacements

Finally, we can write down the form of our approximations to corrections of bond vectors in I.20 - I.22 at any iteration i. They are:

$$\delta \mathbf{v}_{ab}^{(i)}\left(t+\frac{1}{2}\delta t\right)=\left\{\begin{array}{l}0,\\ -\left(\frac{\left(d_{ab}^2-\left\|\mathbf{r}_{ab}^{(i)}(t+\delta t)\right\|^2\right)\mathbf{r}_{ab}(t)}{2\delta t\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\left(\mathbf{r}_{ab}(t)\cdot\mathbf{r}_{ab}^{(i)}(t+\delta t)\right)}\right),\end{array}\quad\begin{array}{l}\frac{\left|d_{ab}^2-\left\|\mathbf{r}_{ab}^{(i)}(t+\delta t)\right\|^2\right|}{d_{ab}^2}<2\xi\\ \frac{\left|d_{ab}^2-\left\|\mathbf{r}_{ab}^{(i)}(t+\delta t)\right\|^2\right|}{d_{ab}^2}\geq 2\xi\end{array}\right\}=g_{ab}^{(i)}(t)\mathbf{r}_{ab}(t) \tag{I.30}$$

$$\delta \mathbf{r}_{ab}^{(i)}\left(t+\delta t\right)=\delta t\delta \mathbf{v}_{ab}^{(i)}\left(t+\frac{1}{2}\delta t\right)=\delta t g_{ab}^{(i)}(t)\mathbf{r}_{ab}(t) \tag{I.31}$$

$$\delta \mathbf{v}_{ab}^{(i)}\left(t+\delta t\right)=\left\{\begin{array}{l}0,\\ -\frac{\left(\mathbf{r}_{ab}^{(m)}(t+\delta t)\cdot\mathbf{v}_{ab}^{(i)}(t+\delta t)\right)\mathbf{r}_{ab}^{(m)}(t+\delta t)}{\left(\frac{1}{m_a}+\frac{1}{m_b}\right)\left\|\mathbf{r}_{ab}^{(m)}(t+\delta t)\right\|^2},\end{array}\quad\begin{array}{l}\frac{\delta t\left|\hat{\mathbf{r}}_{ab}(t+\delta t)\cdot\mathbf{v}_{ab}(t+\delta t)\right|}{d_{ab}}<\xi\\ \frac{\delta t\left|\hat{\mathbf{r}}_{ab}(t+\delta t)\cdot\mathbf{v}_{ab}(t+\delta t)\right|}{d_{ab}}\geq\xi\end{array}\right\}=g_{ab}^{(i)}\left(t+\delta t\right)\mathbf{r}_{ab}^{(m)}\left(t+\delta t\right) \tag{I.32}$$

Where we have defined the auxiliary quantities $g_{ab}^{(i)}(t)$ and $g_{ab}^{(i)}\left(t+\delta t\right)$. It is calculationally advantageous to operate with squares of vector norms, avoiding the expensive calculation of taking the square root; to this end, when defining $g_{ab}^{(i)}(t)$, we replaced the constraints I.23 with the first term of the Taylor expansion of the difference of squares of d_{ab} and $\left\|\mathbf{r}_{ab}^{(i)}\left(t+\delta t\right)\right\|$.

Having found the approximations I.30-I.32, we now know the form of iterative corrections to atomic positions and velocities:

$$\begin{aligned}\mathbf{v}_a^{(i+1)}\left(t+\frac{1}{2}\delta t\right)&=\mathbf{v}_a^{(i)}\left(t+\frac{1}{2}\delta t\right)\\&\quad+\sum_{(a,\,b)\in K}g_{ab}^{(i)}(t)\mathbf{r}_{ab}(t)\\ \mathbf{v}_b^{(i+1)}\left(t+\frac{1}{2}\delta t\right)&=\mathbf{v}_b^{(i)}\left(t+\frac{1}{2}\delta t\right)\\&\quad-\sum_{(a,\,b)\in K}g_{ab}^{(i)}(t)\mathbf{r}_{ab}(t)\end{aligned} \tag{I.33}$$

$$\begin{aligned}\mathbf{r}_a^{(i+1)}\left(t+\delta t\right)&=\mathbf{r}_a^{(i)}\left(t+\delta t\right)\\&\quad+\sum_{(a,\,b)\in K}\delta t g_{ab}^{(i)}(t)\mathbf{r}_{ab}(t)\\ \mathbf{r}_b^{(i+1)}\left(t+\delta t\right)&=\mathbf{r}_b^{(i)}\left(t+\delta t\right)\\&\quad-\sum_{(a,\,b)\in K}\delta t g_{ab}^{(i)}(t)\mathbf{r}_{ab}(t)\end{aligned} \tag{I.34}$$

$$\begin{aligned}\mathbf{v}_a^{(i+1)}\left(t+\delta t\right)&=\mathbf{v}_a^{(i)}\left(t+\delta t\right)\\&\quad+\sum_{(a,\,b)\in K}\delta t g_{ab}^{(i)}\left(t+\delta t\right)\mathbf{r}_{ab}\left(t+\delta t\right)\\ \mathbf{v}_b^{(i+1)}\left(t+\delta t\right)&=\mathbf{v}_b^{(i)}\left(t+\delta t\right)\\&\quad-\sum_{(a,\,b)\in K}\delta t g_{ab}^{(i)}\left(t+\delta t\right)\mathbf{r}_{ab}\left(t+\delta t\right)\end{aligned} \tag{I.35}$$

The summands on the right-hand sides of equations I.33-I.35 are not evaluated all at once: since at each iterative step we are looping over all the constraints one-by-one, $g_{ab}^{(i)}(t)$ and $g_{ab}^{(i)}\left(t+\delta t\right)$ are also evaluated one-by-one, in the same order as the corresponding constraints are considered. Even though the order in which the constraints are considered may affect the values of $g_{ab}^{(i)}(t)$ and $g_{ab}^{(i)}\left(t+\delta t\right)$, in the end all constraints are satisfied to within the specified tolerances simulataneously.

4. Implementation Details

Discussion Points:

- *It is not too hard to debug RATTLE* : if you missed an odd number of minus signs in calculating the approximations to constraint forces, your atoms in constrainted atomic pairs will be inexorably pushed away from each other.
- *Bookkeeping to avoid unnecessary work:* keeping track of all atoms that were moved in the last correction step $i-1$ or are being moved in the current step i. Implementation by Allen & Tildesley.
- *How does the tolerance parameter ξ affect quantities computed in the simulation*? See plots from the diatomic exercise. It is a molecular dynamics simulation of a single freely rotating diatomic with its center of mass at the origin. Atoms in the molecule have equal mass. The diatomic is initialiazed given two parameters $\left(\hat{\mathbf{\Omega}}, \dot{\hat{\mathbf{\Omega}}}\right)$ and allowed to rotate freely, subject to the constraint of the constant bond length.
- *How should the intramolecular potential be modified if the simulation is using RATTLE for numerical integration?*. How persisting interatomic interactions between pairs of constrained atoms affect numerical stability.

II. KINETIC ENERGY OF A FREELY-JOINTED POLYMER CHAIN

A. Setup

1. Kinetic Energy of a Classical System

Kinetic energy of a classical system can be conveniently written as:

$$K = \frac{1}{2} M_{\text{tot}} V_{\text{CM}}^2 + \sum_{a=0}^{N} m_a \frac{1}{2} (\mathbf{v}_a - \mathbf{V}_{\text{CM}})^2 \qquad \text{(II.1)}$$

Where we decompose the motion of the system into the motion of its center of mass and the relative motions about the center of mass. The former gives the first term in the equation above; the latter, the second term.

This equation is written in the space-fixed frame — $\mathbf{V}_{\text{CM}}$ is to be computed from atoms' velocities and masses.

Here, M_{tot} is the total mass of the system that consists of $N+1$ sites, indexed from 0 to N. In the case of a polymer molecule, each ath site corresponds to the ath atom in the chain, with mass m_a, position $\mathbf{r}_a$, and velocity $\mathbf{v}_a$.

2. Simplifying Assumptions

A few simplifying assumptions are in order. They will make the math (and subsequent simulation) more tractable; the essential dynamics of a polymer molecule will be preserved.

1. Our polymer molecule model is a rigid chain. All interatomic bonds in the molecule have a constant length.
2. All bonds in the polymer molecule have the same length, labeled d.
3. All atoms in the polymer molecule have the same mass, labeled m.

3. Representation

While the state of our polymer molecule model with $N+1$ atoms can be represented, at any moment in time, by m, d, and $6(N+1)$ position and velocity vectors of the constituent atoms (space-fixed frame), we would like to choose a different representation.

Note: if we know m, d, and the position and velocity vectors of center of mass, $\mathbf{R}_{\text{CM}}$ and $\mathbf{V}_{\text{CM}}$, then all the additional information we need to specify a unique state at any point in time can be captured by N *bond vectors* $\hat{\mathbf{\Omega}}_i$ and their time derivatives $\dot{\hat{\mathbf{\Omega}}}_i$.

We call a bond vector $\hat{\mathbf{\Omega}}_i$ the unit vector parallel to the bond between atoms $i-1$ and i in the polymer molecule. The vector points towards the atom with the larger index. It makes sense to use unit vectors, since the bonds in our model are constrained to a constant length d.

The bond vector $\hat{\mathbf{\Omega}}_i$ can be calculated as:

$$\hat{\mathbf{\Omega}}_i = \frac{\mathbf{r}_i - \mathbf{r}_{i-1}}{|\mathbf{r}_i - \mathbf{r}_{i-1}|} \qquad \text{(II.2)}$$

Because of the constraint on the bond length, we can write down the time derivative of the bond vector[2]:

$$\dot{\hat{\mathbf{\Omega}}} = \omega \times \hat{\mathbf{\Omega}} \tag{II.3}$$

Here, ω is the angular velocity vector of the corresponding bond, and each vector is written in the same space-fixed frame coorindates. $\dot{\hat{\mathbf{\Omega}}}_i$ is not necessarily a unit vector.

For a bond vector $\hat{\mathbf{\Omega}}_i$, its angular velocity vector ω_i can be calculated as

$$\omega_i = \frac{\mathbf{r}_{\text{bond CM}} \times \mathbf{v}_{\text{bond CM}}}{\|\mathbf{r}_{\text{bond CM}}\|^2} \tag{II.4}$$

B. Calculation

1. Kinetic Energy of the Center of Mass

Velocity of the Center of Mass

We will find $\mathbf{V}_{\text{CM}}$ as $\dot{\mathbf{R}}_{\text{CM}}$. The position vector of the center of mass can be found as

$$\begin{aligned}\mathbf{R}_{\text{CM}} &= \frac{\sum_{a=0}^{N} m_a \mathbf{r}_a}{\sum_{a=0}^{N} m_a} \\ &= \frac{1}{N+1}\left(\sum_{a=0}^{N} \mathbf{r}_a\right)\end{aligned} \tag{II.5}$$

Note: any atomic position vector in the polymer molecule $\mathbf{r}_i$, $i > 0$, can be found by following the bond vectors from the beginning of the chain:

$$\mathbf{r}_i = \mathbf{r}_0 + \sum_{j=1}^{i} d\hat{\mathbf{\Omega}}_j \tag{II.6}$$

Therefore, equation II.5 can be written as

$$\mathbf{R}_{\text{CM}} = \mathbf{r}_0 + \frac{d}{N+1}\sum_{i=1}^{N}(N+1-i)\hat{\mathbf{\Omega}}_i \tag{II.7}$$

Thus, velocity of the center of mass is given by

$$\mathbf{V}_{\text{CM}} = \mathbf{v}_0 + \frac{d}{N+1}\sum_{i=1}^{N}(N+1-i)\dot{\hat{\mathbf{\Omega}}}_i \tag{II.8}$$

This identitity will be userful when calculating internal kinetic energy.

2. Internal Kinetic Energy

We can now work out the second term of equation II.1. Using expression II.8 for the velocity of the center of mass and the time derivative of the expression II.6 for the position vector of the ith atom, we calculate the velocity of the ith atom relative to the center of mass:

$$\begin{aligned}\mathbf{v}_i - \mathbf{V}_{\text{CM}} &= \left(\mathbf{v}_0 + d\sum_{j=1}^{i}\dot{\hat{\mathbf{\Omega}}}_j\right) - \left(\mathbf{v}_0 + \frac{d}{N+1}\sum_{i=1}^{N}(N+1-i)\dot{\hat{\mathbf{\Omega}}}_i\right) \\ &= d\sum_{j=1}^{i}\dot{\hat{\mathbf{\Omega}}}_j - \frac{d}{N+1}\sum_{j=1}^{N}(N+1-j)\,\dot{\hat{\mathbf{\Omega}}}_j\end{aligned} \tag{II.9}$$

It is a calculation to show, using equation II.9, that the system's internal kinetic energy is equal to a quadratic form:

$$K_{\text{internal}} = \frac{1}{2}md^2 C_{ij}\left(\dot{\hat{\mathbf{\Omega}}}^i \cdot \dot{\hat{\mathbf{\Omega}}}^j\right) \tag{II.10}$$

Where:

$$C_{jk} = \frac{\min(j,\, k)(N+1) - jk}{N+1}$$

Thus, the internal kinetic energy of the system is given by:

$$K_{\text{internal}} = \frac{1}{2}md^2 C_{jk}\dot{\hat{\mathbf{\Omega}}}^j \cdot \dot{\hat{\mathbf{\Omega}}}^k \tag{II.11}$$

To summarize, one can calculate the total kinetic energy of a polymer molecule as $K(d,\, m,\, (\mathbf{r}_0, \mathbf{v}_0),\, \{(\hat{\mathbf{\Omega}}_i,\, \dot{\hat{\mathbf{\Omega}}}_i) \mid 1 \le i \le N\}$, where

$$\begin{aligned}K = &\frac{1}{2}(N+1)m\mathbf{V}_{\text{CM}}^2 \\ &+ \frac{1}{2}md^2 C_{ij}\left(\dot{\hat{\mathbf{\Omega}}}^i \cdot \dot{\hat{\mathbf{\Omega}}}^j\right)\end{aligned} \tag{II.12}$$

REFERENCES

[a]Professor Stratt, Vale Cofer-Shabica, Yan Zhao, Andrew Ton, Mansheej Paul, and Evan Coleman
[b]Electronic mail: artur_avkhadiev@brown.edu

[all]Computational chemistry list, ltd. CCL allen-tildesley-book. http://www.ccl.net/cca/software/SOURCES/FORTRAN/allen-tildesley-book/index.shtml. Accessed: 2017-06-13.
[2]Allen, M. P. and Tildesley, D. J. (1989). *Computer Simulation of Liquids*. Clarendon Press, New York, NY, USA.
[3]Andersen, H. C. (1983). Rattle: A velocity version of the shake algorithm for molecular dynamics calculations. *Journal of Computational Physics*, 52(1):24 – 34.
[4]Frenkel, D. and Smit, B. (2001). *Understanding Molecular Simulation*. Academic Press, Inc., Orlando, FL, USA, 2nd edition.
[5]Ryckaert, J.-P., Ciccotti, G., and Berendsen, H. J. (1977). Numerical integration of the cartesian equations of motion of a system with constraints: molecular dynamics of n-alkanes. *Journal of Computational Physics*, 23(3):327 – 341.

Appendices

A. INTERNAL KINETIC ENERGY CALCULATION

We start with the expression of for the velocity of the ith atom in the molecule relative to $\mathbf{V}_{\mathrm{CM}}$:

$$\begin{aligned}\mathbf{v}_i - \mathbf{V}_{\mathrm{CM}} &= \left(\mathbf{v}_0 + d\sum_{j=1}^{i}\dot{\hat{\mathbf{\Omega}}}_j\right) - \left(\mathbf{v}_0 + \frac{d}{N+1}\sum_{i=1}^{N}(N+1-i)\dot{\hat{\mathbf{\Omega}}}_i\right)\\ &= d\sum_{j=1}^{i}\dot{\hat{\mathbf{\Omega}}}_j - \frac{d}{N+1}\sum_{j=1}^{N}(N+1-j)\,\dot{\hat{\mathbf{\Omega}}}_j\end{aligned}$$

Squaring the expression and summing over all the atoms gives:

$$\sum_{i=0}^{N}(\mathbf{v}_i - \mathbf{V}_{\mathrm{CM}})^2 = d^2\sum_{i=0}^{N}\left(\left(\sum_{j=1}^{i}\dot{\hat{\mathbf{\Omega}}}_j\right)^2 + \left(\frac{1}{N+1}\right)^2 B_{jk}\dot{\hat{\mathbf{\Omega}}}^j\cdot\dot{\hat{\mathbf{\Omega}}}^k - \frac{2}{N+1}\left(A_j\dot{\hat{\mathbf{\Omega}}}^j\right)\left(\sum_{k=1}^{i}\dot{\hat{\mathbf{\Omega}}}_k\right)\right)$$

Where $A_j = (N+1-j)$ and $B_{jk} = (N+1-i)(N+1-j)$.

The first term in the expression, when summed over $N+1$ items, gives

$$\begin{aligned}d^2\sum_{i=0}^{N}\left(\sum_{j=1}^{i}\dot{\hat{\mathbf{\Omega}}}_j\right)^2 &= \sum_{i=0}^{N}d^2\left(\sum_{j=1}^{i}\dot{\hat{\mathbf{\Omega}}}_j\right)\left(\sum_{k=1}^{i}\dot{\hat{\mathbf{\Omega}}}_k\right)\\ &= d^2\sum_{j=1}^{N}\sum_{k=1}^{N}\left(N+1-\max(j,\,k)\right)\dot{\hat{\mathbf{\Omega}}}_j\cdot\dot{\hat{\mathbf{\Omega}}}_k\end{aligned}$$

The second term in the expression above does not have free indices, so summing over $N+1$ atoms simply gives $N+1$ identical terms.

Summing the third term in the expression above, we obtain

$$\begin{aligned}-d^2\frac{2}{N+1}\sum_{i=0}^{N}\left(A_j\dot{\hat{\mathbf{\Omega}}}^j\right)\left(\sum_{k=1}^{i}\dot{\hat{\mathbf{\Omega}}}_k\right) &= -d^2\frac{2}{N+1}\sum_{j=1}^{N}\sum_{k=1}^{N}(N+1-j)(N+1-k)\dot{\hat{\mathbf{\Omega}}}_j\cdot\dot{\hat{\mathbf{\Omega}}}_k\\ &= -d^2\frac{2}{N+1}B_{jk}\dot{\hat{\mathbf{\Omega}}}^j\cdot\dot{\hat{\mathbf{\Omega}}}^k\end{aligned}$$

Combining the three terms, we obtain:

$$\begin{aligned}
\sum_{i=0}^{N} \left(\mathbf{v}_i - \mathbf{V}_{\mathrm{CM}}\right)^2 &= d^2 \sum_{j=1}^{N}\sum_{k=1}^{N} \left(\left(N+1-\max(j,\,k)\right) \dot{\hat{\mathbf{\Omega}}}_j \cdot \dot{\hat{\mathbf{\Omega}}}_k + \frac{1}{N+1} B_{jk} \dot{\hat{\mathbf{\Omega}}}^j \cdot \dot{\hat{\mathbf{\Omega}}}^k - \frac{2}{N+1} B_{jk} \dot{\hat{\mathbf{\Omega}}}^j \cdot \dot{\hat{\mathbf{\Omega}}}^k \right) \\
&= d^2 \sum_{j=1}^{N}\sum_{k=1}^{N} \left(\left(N+1-\max(j,\,k) - \frac{(N+1-j)(N+1-k)}{N+1} \right) \dot{\hat{\mathbf{\Omega}}}^j \cdot \dot{\hat{\mathbf{\Omega}}}^k \right) \\
&= \frac{d^2}{N+1} \sum_{j=1}^{N}\sum_{k=1}^{N} \left(\left(\min(j,\,k)(N+1) - jk\right) \dot{\hat{\mathbf{\Omega}}}_j \cdot \dot{\hat{\mathbf{\Omega}}}_k \right) \\
&= d^2 \left(C_{jk} \dot{\hat{\mathbf{\Omega}}}^j \cdot \dot{\hat{\mathbf{\Omega}}}^k \right)
\end{aligned}$$

Where we defined a matrix C_{jk}:

$$C_{jk} = \frac{\min(j,\,k)(N+1) - jk}{N+1}$$

This yields an expression for the internal kinetic energy of the system:

$$K_{\mathrm{internal}} = \frac{1}{2} m d^2 C_{jk} \dot{\hat{\mathbf{\Omega}}}^j \cdot \dot{\hat{\mathbf{\Omega}}}^k$$