Mercedes Benz Potential

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1 Introduction

The Mercedes Benz (MB) potential was first introduced in 1970 [1] as a simple model for a system of molecules such as water. In the MB model, each body has three arms originating at its center of mass as illustrated in Figure 1.1. These arms makes the particle anisotropic and one must therefore introduce rigid body terms in the equations of motion to account for the particles' rotational dynamics.

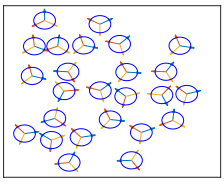

Figure 1.1: Illustration of 25 Mercedes Benz particles in a periodic box

In the original paper, both three and four arm variants were considered, but we shall only consider three arms in this tutorial. Moreover, we will restrict to planar motion of the bodies. The interaction between the arms can be thought of as forming a hydrogen bond, which corresponds to alignment of the arms of neighboring bodies. Depending on the choice of the parameters it is possible for the particles to form either double bonds or single bonds, as illustrated in 1.2. We will use this model to simulate water, so the parameters are chosen such that the likelihood of observing a double bond is low.

First some notation. Consider the pair potential between two particles, say particles i and j, and label their arms as shown in Figure 1.3 and let the particles be separated by a distance

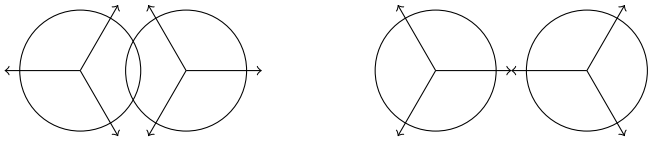

Figure 1.2: The two different types of bonds that can be formed in simulations using the MB potential.

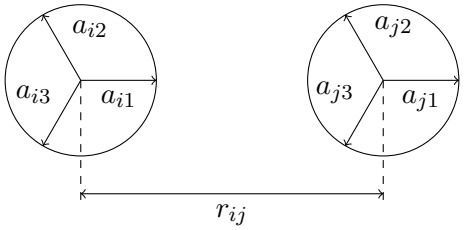

Figure 1.3: At left is particle i and on the right is particle j, the two separated by a distance r_{ij}. The arms on both particles are labelled in ascending order counter-clockwise.

of r_{ij}. Each particle's orientation, w.r.t an Eulerian frame of reference, is described by an orthogonal rotation tensor $Q_i, Q_j \in \mathrm{SO}(2)$. Also let the orthogonal rotation matrix $R(\alpha) \in \mathrm{SO}(2)$ be

$$R(\alpha) = \begin{pmatrix} \cos(\alpha) & -\sin(\alpha) \\ \sin(\alpha) & \cos(\alpha) \end{pmatrix}. \tag{1.1}$$

We establish the convention that a counter-clockwise rotation of an orthogonal matrix, say $Q \in \mathrm{SO}(2)$ is a function $\mathscr{R} : \mathbb{R}^{2\times 2} \to \mathbb{R}^{2\times 2}$,

$$\mathscr{R}(Q) = QR^T. \tag{1.2}$$

In addition, for any vector $v \in \mathbb{R}^2$ define the change of variables from the Lagrangian to Eulerian frame of reference by a function $\mathscr{O} : \mathbb{R}^2 \to \mathbb{R}^2$,

$$\mathscr{O}(v) = Q^T v. \tag{1.3}$$

Now, introduce the MB pair potential as,

$$V(x_i, x_j, Q_i, Q_j) = 4\varepsilon_{LJ}\left(\left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{6}\right) \tag{1.4}$$

$$+ \varepsilon_{HB} G(r_{ij} - r_{HB}) \sum_{k,l=1}^{3} G(\left(Q_i^T a_{ik}\right)^T u_{ij} - 1) G(\left(Q_i^T a_{ik}\right)^T u_{ij} + 1) \tag{1.5}$$

$$= V_{LJ}(x_i, x_j) + V_{HB}(x_i, x_j, Q_i, Q_j). \tag{1.6}$$

Here, the vectors a_{ik}, refer to the k^{th} arm of the i^{th} particle and u_{ij} is the unit vector in the direction $i \to j$ of the separation $r_{ij} = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2}$, i.e

$$u_{ij} = \frac{1}{r_{ij}} \begin{pmatrix} x_j - x_i \\ y_j - y_i \end{pmatrix}. \tag{1.7}$$

G is taken to be an unnormalized Gaussian,

$$G(x) = \exp\left(-\frac{x^2}{2\sigma_{HB}}\right). \tag{1.8}$$

Together with the two additional parameters r_{HB} and ε_{HB} this defines all the terms in (1.5), $V(x,Q) = \sum_{i \neq j} V_{ij}$. The total translational force on the system is,

$$F = -\nabla_x \left(\sum_{i=1}^{N} \sum_{j \neq i}^{N} V(x_i, x_j, Q_i, Q_j) \right). \tag{1.9}$$

Note: it is useful to introduce the following quantities for the purpose of implementation,

$$h_{ik} = \left(Q_i^T a_{ik}\right)^T u_{ij}, \tag{1.10}$$

$$h_{jl} = \left(Q_j^T a_{jl}\right)^T u_{ij}. \tag{1.11}$$

Newton's third law can be used in calculating the forces:

```
for(unsigned i=0;i<N;i++)
        for(unsigned j=i;j<N;j++)
        {
                // solve for force due to particle j acting on particle i, f_ij

                // force on particle i
                f_i += f_ij

                // force on particle j
                f_j -= f_ij
        }
```

The algorithm that we will use for the rigid body motion is the the DLM (Dullweber-Leimkuhler-McLachlan) algorithm [2]. We introduce the torque on body i:

$$\tau_i = -\mathrm{rot}\left(Q_i^T \frac{dV_{HB}}{dQ_i}\right), \tag{1.12}$$

where τ_i is the torque on particle i and the rot function is defined for a scalar s and matrix A as,

$$s = \mathrm{skew}^{-1}\left(A - A^T\right) = \mathrm{rot}(A) \tag{1.13}$$

where,

$$\mathrm{skew}(s) = \begin{pmatrix} 0 & s \\ -s & 0 \end{pmatrix}, \tag{1.14}$$

2 THE DLM ALGORITHM

A 2D version of the DLM algorithm [2] can be implemented as,

$$p_{n+1/2} = p_n + \frac{h}{2} f_n \qquad \pi_{n+1/2} = \pi_n + \frac{h}{2}\tau_n \tag{2.1}$$

$$q_{n+1} = q_n + \frac{h}{m} p_{n+1/2} \qquad Q_{n+1} = Q_n R^T\left(\frac{h}{I}\pi_{n+1/2}\right) \tag{2.2}$$

$$\text{Force/Torque solve} \tag{2.3}$$

$$p_{n+1} = p_{n+1/2} + \frac{h}{2} f_{n+1} \qquad \pi_{n+1} = \pi_n + \frac{h}{2}\tau_{n+1} \tag{2.4}$$

$$\tag{2.5}$$

This algorithm can be used to sample the microcanonical ensemble NVE. To exclude the possibility of double bonds forming, we use the following parameters [3],

$$\begin{aligned} m &= 1 \\ r_{HB} &= 1 \\ \epsilon_{HB} &= -1 \\ \epsilon_{LJ} &= 0.1 \\ \sigma_{HB} &= 0.085 \\ \sigma_{LJ} &= 0.7 \\ I &= 0.001126 \end{aligned} \tag{2.6}$$

Exercise: Implement the above algorithm for 25 Mercedes Benz particles in a periodic box of size $10x10$ **at temperature** $k_B T = 0.16$ **and timestep** $\Delta t = 0.5 \times 10^{-3}$**.**

Things to consider:

1. Check that the algorithm is working by plotting the energy at each timestep. Decreasing (or increasing) the timestep by a factor of 2 should dramatically lower (respectively, increase) the fluctuations around the expected value.

2. Plot the radial distribution for $r_{ij} < 4.0$, it should have a clear peak at $r_{ij} = 1.0$.

3. Introduce the BAOAB [4, p. 271] method to integrate the translational degrees of freedom.

4. Is this method ergodic? The BAOAB method is designed to sample the NVT (canonical) ensemble, but here we have coupled it with the rotational degree of freedom indirectly, i.e. only through the potential. How would one go about examining the ergodic properties of a method like this using simulation? [Note: this could be complicated, even to do numerically!]

5. Assuming a discretization scheme for Langevin dynamics is ergodic, it nonetheless introduces an effective *bias* with respect to the target probability distribution. Estimate the bias as a function of the stepsize for BAOAB applied to the MB potential (by coupling

to translational dofs) by computing an observable (e.g. the mean potential energy) for decreasing stepsizes, averaging several runs to obtain a reliable value each time. You should see a progression toward a well defined limit for small stepsize. Taking this as a reference value, compute the error in the observable as a function of stepsize and graph this in a log-log scale. The slope of the error graph in log-log scale should reveal the order of accuracy of the method (for computing observable averages). (why?) What is the order of accuracy of the BAOAB/DLM method for observables?

6. To be able to scale the experiments we must introduce a much more efficient algorithm, one such algorithm is the cell method given in Chapter 3 of [5]. Implement this scheme and rerun the tests with 400 particles and verify that the results are consistent with the first part.

7. To further improve the efficiency of the algorithm one could consider using simple OpenMP commands to exploit multi-thredding capabilities.

8. Implement the NHL piston method [4, p. 381] to perform experiments in an NPT ensemble.

9. Verify that there are two different crystal structures, check [3] for details.

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