

# Constraint dynamics for diatomic molecules

Computational Statistical Physics, Exercise 9  
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## 1 Introduction

In this exercise the program from exercises 7 and 8 was extended with a new member function which implements constraint dynamics for diatomic molecules.

## 2 Theory

### 2.1 Langrange multipliers with verlet propagation

The Verlet scheme for propagating particles over discrete time steps reads:

$$x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \Delta^2 t \ddot{x}(t),$$

which is extended to include a constraint force which will guarantee the fulfillment of the constraint condition  $g = ||x_1(t + \Delta t) - x_2(t + \Delta t)||^2 - d^2 = 0$  :

$$x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \Delta^2 t (\ddot{x}(t) + Z_{1,2}).$$

### 2.2 Constraint force calculation

The force acting on a pair of atoms is proportional to the gradient of  $g$  :

$$Z_1 = \lambda/2 \nabla_1 g, \quad Z_2 = -\lambda/2 \nabla_1 g,$$

$\lambda$  being the langrange multiplier which has to be determined. We set  $x_{1,2}^! = 2x_{1,2}(t) - x_{1,2}(t - \Delta t) + \Delta^2 t \ddot{x}_{1,2}(t)$ , the theoretical new coordinates without constraint forces. The formula for the new coordinates then becomes  $(\nabla g = 2(x_1(t) - x_2(t)))$  :

$$x_{1,2}(t + \Delta t) = x_{1,2}^! \pm \Delta^2 t \frac{Z_1}{m} \tag{1}$$

$$= x_{1,2}^! \pm \Delta^2 t \frac{\lambda}{m} (x_1(t) - x_2(t)). \tag{2}$$

Plugging in this formula into the constraint condition yields an equation which can be solved for  $\lambda$  :

$$d^2 = ||x_1(t + \Delta t) - x_2(t + \Delta t)||^2 \tag{3}$$

$$d^2 = ||x_1^!(t + \Delta t) - x_2^!(t + \Delta t) + \Delta^2 t \frac{2\lambda}{m} (x_1(t) - x_2(t))||^2 \tag{4}$$

By basic algebra, this yields the following quadratic equation for  $\lambda$  :

$$\underbrace{\frac{4\Delta^4 t}{m^2} ||x_1 - x_2||^2}_{a} \lambda^2 + \underbrace{\frac{4\Delta^2 t}{m} \langle x_1^! - x_2^!, x_1 - x_2 \rangle}_{b} \lambda + \underbrace{||x_1^! - x_2^!||^2 - d^2}_{c} = 0$$

At a given time step,  $a, b, c$  can be computed and the equation above solved for  $\lambda$ . As soon as  $\lambda$  has been obtained, the coordinates of the next time step can be calculated using eq. (2).

### 3 Implementation details

The simulation code was extended in the following way:

- *diatomic\_constraint* in *space<P>* which is used instead of *global\_prop*
- *constraint\_verlet\_prop* and *coord\_next* in *point\_particle<numeric\_t>*
- *quad\_solver* in *modules.hpp*, an iterative solver for quadratic equations.

#### 3.1 Periodic boundary condition

The molecule is only shifted as a whole across a boundary and a shift is performed if the centre of mass overflows over a boundary.

#### 3.2 Initialization

Here the atoms were initially aligned in the same 2D grid from the previous exercise. Diatomic connections have a length of  $1\sigma$ .

## 4 Results

#### 4.1 Energy constancy

Figure 1 shows the evolution of the total energy with time. The simulation included 18 diatomic molecules over 6000 timesteps. The graph shows spurious peaks which coincide with the flickering in the movie. The reason for the flickering is that in certain situations a large part of the atoms overflow over the visible area, due to large constraint forces by a distance about the order of the space length. In the next time frame they return into the visible area. Making the time step smaller seems to postpone the problem. Redoing the simulation for the first third of the physical time by choosing a time step three times smaller, most of the spurious peaks in the physical time interval got eliminated.

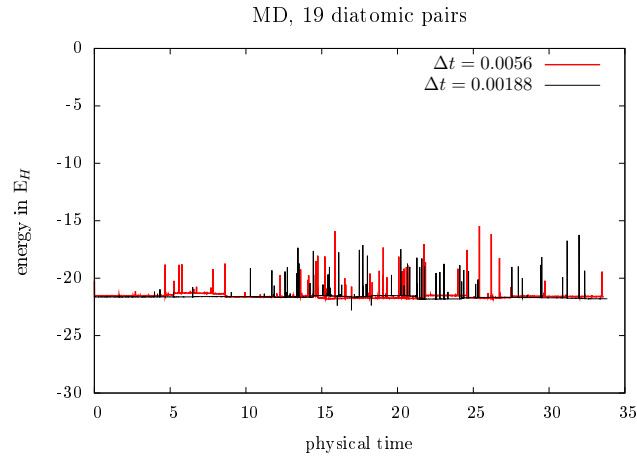


Figure 1: Evolution of system energy with time

#### 4.2 Movie

For generating a movie, the simulation was initialized with a 2D grid of 18 molecules. After every timestep a frame was output and later converted into an image with gnuplot and assembled to a video with mencoder.