

# **NSSC II Exercise 2**

## **Molecular Dynamics**

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# 1 Questions on Molecular Dynamics

(a) *Describe a suitable and consistent system of units for molecular dynamics, and specifically the units of length, mass, velocity, energy and time.*

The *Hartree* system of atomic units is used in molecular dynamics. Atomic units are tailored to the demands of systems on atomic scale. They can be transferred to the SI unit system. The environment is derived from the properties of an electron in a hydrogen atom.

All units in the atomic system of units are derived from the pre-defined following four basic units

- $\hbar \simeq 1.054571817 \times 10^{-34} Js$  ... reduced plack constant, atomic unit of action
- $e \simeq 1.602176634 \times 10^{-19} C$  ... elementary charge, atomic unit of charge
- $a_0 \simeq 5.29177210903 \times 10^{-11} m$  ... *Bohr* radius, atomic unit of length,  $1\text{\AA}$
- $m_e \simeq 9.1093837015 \times 10^{-31} kg$  ... electron mass, atomic unit of mass

Other important derived units are:

- $E_h = \frac{\hbar^2}{m_e a_0^2}$  ... Energy
- $t = \frac{\hbar}{E_h}$  ... time
- $v = \frac{a_0 E_h}{\hbar}$  ... velocity

(b) *Explain the advantages of automatic differentiation as a method to calculate forces.* Computing Forces requires the derivative of the potential Energy with respect to spatial coordinates. The computation

$$m_L \frac{d^2 x_L^{(\alpha)}}{dt^2} = - \frac{\partial E_{Pot}}{\partial x_L^{(\alpha)}}, \text{ with } \alpha \in \{x, y, z\}$$

is done at every time step. The problem at hand requires us to compute the same derivative repeatedly for different coordinates and time steps. The two classical differentiation approaches have disadvantages compared to the concept of automatic differentiation. Symbolic differentiation leads to inefficient code and redundant calculations. Numerical differentiation may induce round off errors which accumulates to a significant error if

number of time steps  $\gg 1$ .

Automatic differentiation is different in a way that it exploits the fact that a derivative can be split up regarding to the chain rule. A derivative then becomes a product of inner derivatives with respect to variables, depending on its underlying variable. The computer does not see this underlying variable and just computes the "simple" partial derivatives with respect to the dummy variables. This is done using a trick. While evaluating the function, the derivatives are computed simultaneously with respect to each inner variable. This means that while the potential energy  $E_{Pot}$  is computed, the forces  $F = m_e \frac{\partial E_{Pot}}{\partial x}$  come as a byproduct. Automatic differentiation of the forces adds a constant factor to the computational cost of evaluating the energies.

$$\begin{aligned} y &= f(g(h(x))) = f(g(h(w_0))) = f(g(w_1)) = f(w_2) = w_3 \\ w_0 &= x \\ w_1 &= h(w_0) \\ w_2 &= g(w_1) \\ w_3 &= f(w_2) = y \end{aligned}$$

$$\frac{dy}{dx} = \frac{dy}{dw_2} \frac{dw_2}{dw_1} \frac{dw_1}{dx} = \frac{df(w_2)}{dw_2} \frac{dg(w_1)}{dw_1} \frac{dh(w_0)}{dx}$$

(source: [wikipedia.org/wiki/Automatic\\_differentiation](https://wikipedia.org/wiki/Automatic_differentiation))

(c) When the potential energy of a system is described using the Morse model, how does the number of calculations per time step scale with the number of particles? Why?

The potential energy in our system is described by

$$E_{Pot}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_M) = \sum_{i=1}^{M-1} \sum_{j=i+1}^M V_{Morse}(|\mathbf{x}_i - \mathbf{x}_j|)$$

with the morse totential

$$V_{Morse}(|\mathbf{x}_i - \mathbf{x}_j|) = V_{Morse}(r) = D_e[e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}]$$

Building the sums over all  $V_{Morse}$  with respect to the number of particles  $M$  quadratic leads to an increase in atom pairs for every added particle at  $\mathbf{x}_i$ . The number of atomic pairs  $N_P$ , with respect to the number of particles  $N$  scales according to

$$N_P = \frac{N(N-1)}{2}$$

This is due to the way the morse potential is constructed. By definition of an interatomic pair-potential, every particle added to the system interacts with every other particle in the system.

(d) *Describe a strategy to make that number of calculations proportional to the number of particles.* The naive approach described in (c) leads to a quadratic increase of computations per calculations for every added particle to the system. This computational increase per particle can be trimmed down to a constant factor  $c$ . This is done by introducing a so called cutoff radius  $r_{cutoff}$  in the calculation of the interatomic potential. Introducing  $r_{cutoff}$  is justified because contribution of particles to  $E_{Pot}$  rapidly converges to zero for increasing interatomic distances.

A truncated potential needs to be differentiable on the whole domain to give meaningful expressions of interatomic forces. The potential is then modified in a way that we introduce another variable, the so called switching radius  $r_{switch}$ , with  $r_{switch} < r_{cutoff}$ . Between  $r_{switch}$  and  $r_{cutoff}$  a continuously differentiable smoothing function is applied. A simple smoothing function:

$$f(t) = \begin{cases} e^{-\frac{1}{t}}, & \text{if } t > 0 \\ 0, & \text{otherwise} \end{cases}$$
$$t = \frac{r^2 - r_{switch}^2}{r_{cutoff}^2 - r_{switch}^2}$$