VERLET DYNAMICS

It is an approximate dynamics that preserves the TIME-REVERSAL INVARIANCE of the Newton dynamics.

$$r(t+\Delta t) = r(t) + \frac{dr}{dt}(t)\,\Delta t + \frac{1}{2}\frac{d^2r}{dt^2}(t)\,\Delta t^2 + \frac{1}{6}\frac{d^3r}{dt^3}(t)\,\Delta t^3 + \dots$$

$\boxed{\text{Taylor expansion}}$

ⓐ $$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}\frac{1}{m}F(r(t))\,\Delta t^2 + \frac{1}{6}b(t)\,\Delta t^3$$

We require time-reversal invariance. if we change $\Delta t \to -\Delta t$

ⓑ $$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{1}{2m}F(r(t))\,\Delta t^2 - \frac{1}{6}b(t)\,\Delta t^3$$

WE REQUIRE THE VALIDITY OF ⓐ AND ⓑ

FIRST SCHEME: POSITION VERLET

We use the sum of ⓐ and ⓑ

$$r(t+\Delta t) + r(t-\Delta t) = 2r(t) + \frac{1}{m}F(r(t))\,\Delta t^2 + O(\Delta t^4)$$

$$r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \frac{1}{m}F(r(t))\,\Delta t^2 + O(\Delta t^4)$$

We have thus a recursive scheme that allows the computation of the evolution with errors of order Δt^4.

The velocity can be computed using ⓐ − ⓑ

ⓐ − ⓑ ⇒

$$r(t+\Delta t) - r(t-\Delta t) = 2v(t)\Delta t + \frac{1}{3} b(t)\Delta t^3$$

$$v(t) = \frac{1}{2\Delta t}\left(r(t+\Delta t) - r(t-\Delta t)\right) + O(\Delta t^2)$$

THE ALGORITHM:

- STARTING DATA : $r(t=0) = r_0$ $\quad v(t=0) = v_0$
- COMPUTE $r(\Delta t) = r(t=0) + v(t=0)\Delta t + \frac{1}{2m} F(r(0))\Delta t^2$
  the position at time $t = \Delta t$.
- start a recursive procedure using

$$r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \frac{1}{m} F(r(t))\Delta t^2$$

If the velocity is needed, compute it as

$$v(t) = \frac{1}{2\Delta t}\left[r(t+\Delta t) - r(t-\Delta t)\right]$$

SECOND SCHEME: VELOCITY VERLET

b $\quad r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{1}{2m} F(t)\Delta t^2 + O(\Delta t^3)$

$F(t)$ short-hand for $F(r(t))$

change $t' = t - \Delta t$

$$r(t') = r(t'+\Delta t) - v(t'+\Delta t)\Delta t + \frac{1}{2m} F(t'+\Delta t)\Delta t^2$$

b' $\quad r(t) = r(t+\Delta t) - v(t+\Delta t)\Delta t + \frac{1}{2m} F(t'+\Delta t)\Delta t^2$

Now we consider a + b'

$$r(t+\Delta t) + r(t) = r(t) + r(t+\Delta t) + v(t)\Delta t - v(t+\Delta t)\Delta t + \frac{1}{2m} F(t)\Delta t^2 + \frac{1}{2m} F(t+\Delta t)\Delta t^2$$

$$0 = v(t) - v(t+\Delta t) + \frac{1}{2m}\left(F(t) + F(t+\Delta t)\right)\Delta t$$

$$v(t+\Delta t) = v(t) + \frac{1}{2m}\left(F(t) + F(t+\Delta t)\right)\Delta t$$

The algorithm is based on

$$\begin{cases} r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{1}{2m} F(t)\Delta t^2 & \text{(A)} \\ v(t+\Delta t) = v(t) + \frac{1}{2m}\left(F(t) + F(t+\Delta t)\right)\Delta t & \text{(B)} \end{cases}$$

A SINGLE STEP IN THE VELOCITY VERLET

Given $r(t)$, $v(t)$, $F(t) = F(r(t))$

compute $r(t+\Delta t)$ using A

Compute $F(t+\Delta t) = F(r(t+\Delta t))$

Compute $v(t+\Delta t)$ ~~using~~ B

iterate

Velocity verlet is the algorithm that we will consider in the theoretical analysis

It describes the evolution in phase space

$$(r(t), p(t) = mv(t)) \longrightarrow (r(t+\Delta t), p(t+\Delta t))$$

Reduced units

$$U = \epsilon f(r/\sigma) \qquad \vec{F} = -\nabla U$$

$$= -\frac{\vec{r}}{r}\frac{\partial U}{\partial r} = -\frac{\epsilon}{\sigma}\frac{\vec{r}}{r} f'\left(\frac{r}{\sigma}\right)$$

We define $\vec{x} = \frac{\vec{r}}{\sigma}$ (adimensional)

$$\hat{x} = \frac{\vec{x}}{x} = \frac{\vec{r}}{r} \qquad \vec{F} = -\frac{\epsilon}{\sigma}\hat{x} f'(x)$$

adimensional force $\vec{F}_{ad} = \hat{x} f'(x)$ $\qquad = +\frac{\epsilon}{\sigma}\vec{F}_{ad}$

In terms of the adimensional $\vec{r}/\sigma$, $\vec{F}_{ad}$ the position Verlet evolution is

$$\vec{x}(t+\Delta t) = \frac{\vec{r}(t+\Delta t)}{\sigma} = 2\vec{x}(t) - \vec{x}(t-\Delta t) + \frac{1}{m}\frac{\epsilon}{\sigma^2}\vec{F}_{ad}\Delta t^2$$

Dimensionally $\frac{\epsilon}{m\sigma^2} = \frac{[M L^2 T^{-2}]}{[M L^2]} = [T^{-2}]$

We define an adimensional time $\tau = \sqrt{\frac{\epsilon}{m\sigma^2}}\, t$ so that

$$\boxed{\vec{x}(t+\Delta t) = 2\vec{x}(t) - x(t-\Delta t) + \vec{F}_{ad}\Delta\tau^2}$$

This is the expression that is used in practice $[m, \sigma, \epsilon = 1]$

For the velocity

$$\vec{v}_{ad} = \sqrt{\frac{m}{\epsilon}}\, \vec{v}$$

Velocity Verlet in adimensional units

$$x(t+\Delta t) = x(t) + v_{ad}(t)\Delta\tau + \frac{1}{2} F_{ad}(t)\Delta\tau^2$$

$$v_{ad}(t+\Delta t) = v_{ad}(t) + \frac{1}{2}\left(F_{ad}(t) + F_{ad}(t+\Delta t)\right)\Delta\tau$$

In practice: set $\epsilon = \sigma = m = 1$ and reintroduce units in the final results

OBSERVATION: if $U(x) = Ax^p$ (these potentials are irrelevant in practice) there is no intrinsic energy scale. One fixes the scale on the basis of the problem [fix ϵ and σ so that $x(t=0)$, $v_{ad}(t=0)$ are of order 1]

TYPICAL TIME SCALES IN M.D.

For typical atomic systems

$$\epsilon \sim eV = 1.6 \cdot 10^{-19}\ J$$

$$\sigma \sim nm = 10^{-9}\ m$$

$$\text{massa} \sim 10^{-26}\ Kg \qquad (\text{hydrogen} = 1.7 \cdot 10^{-27}\ Kg)$$

Typical time scale $\sim \sqrt{\frac{m\sigma^2}{\epsilon}} \sim 10^{-13}\, s$

Therefore $\Delta t \ll 10^{-13}\, s$

Typically Δt is of the order of $10^{-15} - 10^{-14}$.
It is thus clear that MD can investigate dynamic phenomena on scales of at most, 10-100 ps.

COMPUTATION OF TEMPERATURE IN THE MD SIMULATIONS

For a monoatomic system (the only one we consider)

$$\sum_{i=1}^{N} \left\langle \frac{1}{2} m v_i^2 \right\rangle = \frac{3}{2} NkT \qquad N \equiv \text{number of particles}$$

This relation can be easily proved in the canonical ensemble $\left[K = \sum_{i=1}^{N} \frac{1}{2} m v_i^2 \right]$

$$\langle K \rangle = \frac{\int \frac{dp\,dq}{h^{3N} N!} e^{-\beta H} (K)}{\int \frac{dp\,dq}{h^{3N} N!} e^{-\beta H}} = \frac{\frac{1}{h^{3N} N!} \int dp\, K e^{-\beta K} \int dq\, e^{-\beta U}}{\frac{1}{h^{3N} N!} \int dp\, e^{-\beta K} \int dq\, e^{-\beta U}}$$

$$= -\frac{\partial}{\partial \beta} \ln \int d\overset{3N}{p}\, e^{-\beta K} = -\frac{\partial}{\partial \beta} \ln \left[\int_{-\infty}^{+\infty} dp\, e^{-\beta p^2/2m} \right]^{3N}$$

$$= -\frac{\partial}{\partial \beta} \left\{ 3N \ln \left(\frac{2m\pi}{\beta} \right)^{1/2} \right\} = \frac{3N}{2} \frac{1}{\beta} = \frac{3NkT}{2}$$

The temperature is a fluctuating variable in MD simulations.