1 Langevin Equation

The Langevin Equation for the i-th particle is:

$$m_i \ddot{\vec{x}}_i = \vec{F}(\vec{x}_i(t)) - \gamma_i m_i \dot{\vec{x}}_i + \vec{R}_i \tag{1}$$

where $\vec{F}(\vec{x}_i(t)) = \vec{F}_i$ is the interaction force, γ_i is the collision frequency and $\vec{R}_i$ represents a random force which is related to the mass m_i, the Temperature T and the collision frequency γ_i by:

$$\langle \vec{R}_i(t)\vec{R}_j(t')\rangle = 2m_l k_B T \gamma_l \delta_{i,j}\delta(t - t') \tag{2}$$

and

$$\langle \vec{R}_i(t)\rangle = 0 \tag{3}$$

This force can be calculated using a Gaussian distribution

$$\rho(\vec{R}_i) = \frac{1}{\sqrt{4\pi\gamma_i m_i k_B T}} \cdot e^{\frac{-\vec{R}_i^2}{4\gamma_i m_i k_B T}} \tag{4}$$

or using

$$\vec{R}_i(t) = \sqrt{2k_B T \gamma_i m_i}\eta(t) \tag{5}$$

where $\eta(t) = \dot{W}(t)$ is a white-noise ($W(t)$ being a Wiener process). In order to solve the differential equation one needs to integrate the equation of motion. A second-order integrator for Langevin equations was found by Eric Vanden-Eijnden and Giovanni Ciccotti [1] and is a generalizaton of the BBK integrator. The algorithm reduces to the velocity-Verlet algorithm when $\gamma_i = 0$.

2 Derivation of the integrator

Written componentenwise as a coupled stochastic differential equation (1) becomes

$$\begin{cases} dx_i(t) = v_i(t)dt \\ dv_i(t) = (m_i^{-1}F_i(x(t)) - \gamma_i v_i(t))dt + \sqrt{2k_B T\gamma_i m_i^{-1}}dW_i(t) \end{cases} \tag{6}$$

It's more convenient to rewrite the equation to

$$\begin{cases} dx_i(t) = v_i(t)dt \\ dv_i(t) = (f_i(x(t)) - \gamma_i v_i(t))dt + \sigma_i dW_i(t) \end{cases} \tag{7}$$

where $f_i = m_i^{-1}F_i(x)$ and $\sigma_i = \sqrt{2k_B T\gamma_i m_i^{-1}}$. Written as a system of integal equations (integrated with respect to ds from t to $t + \Delta t$) in vectorial notation (the index i is dropped for clarity)

$$\begin{cases} \vec{x}(t + \Delta t) = \vec{x}(t) + \int_t^{t+\Delta t} \vec{v}(s)ds \\ \vec{v}(t + \Delta t) = \vec{v}(t) + \int_t^{t+\Delta t} \vec{f}(\vec{x}(s))ds - \gamma \int_t^{t+\Delta t} \vec{v}(s)ds + \sigma(\vec{W}(t + \Delta t) - \vec{W}(\Delta t)) \end{cases} \tag{8}$$

For $\vec{v}(s)$ under the integral one can use:

$$\vec{v}(s) = \vec{v}(t) + \int_t^s \vec{f}(\vec{x}(u))du - \gamma \int_t^s \vec{v}(u)du + \sigma(\vec{W}(s) - \vec{W}(t)) \tag{9}$$

...

Finally the integrator becomes:

$$
\begin{cases}
\vec{v}^{(n+1/2)} = \vec{v}^{(n)} + \dfrac{1}{2}\Delta t \vec{f}(\vec{x}^{(n)}) - \dfrac{1}{2}\Delta t \gamma \vec{v}^{(n)} + \dfrac{1}{2}\sqrt{\Delta t}\sigma \vec{\xi}^{(n)} \\
\qquad\quad - \dfrac{1}{8}\Delta t^2 \gamma(\vec{f}(\vec{x}^{(n)}) - \gamma \vec{v}^{(n)}) - \dfrac{1}{4}\Delta t^{3/2}\gamma\sigma\left(\dfrac{1}{2}\vec{\xi}^{(n)} + \dfrac{1}{\sqrt{3}}\vec{\eta}^{(n)}\right) \\
\vec{x}^{(n)} = \vec{x}^{(n)} + \Delta t \vec{v}^{(n+1/2)} + \Delta t^{3/2}\sigma \dfrac{1}{\sqrt{12}}\vec{\eta}^{(n)} \\
\vec{v}^{(n+1)} = \vec{v}^{(n+1/2)} + \dfrac{1}{2}\Delta t \vec{f}(\vec{x}^{(n+1)}) - \dfrac{1}{2}\Delta t \gamma \vec{v}^{(n+1/2)} + \dfrac{1}{2}\sqrt{\Delta t}\sigma \vec{\xi}^{(n)} \\
\qquad\quad - \dfrac{1}{8}\Delta t^2 \gamma(\vec{f}(\vec{x}^{(n+1)}) - \gamma \vec{v}^{(n+1/2)}) - \dfrac{1}{4}\Delta t^{3/2}\gamma\sigma\left(\dfrac{1}{2}\vec{\xi}^{(n)} + \dfrac{1}{\sqrt{3}}\vec{\eta}^{(n)}\right)
\end{cases}
\tag{10}
$$

where $(\vec{\xi}^{(n)}, \vec{\eta}^{(n)})$ are independent Gaussian variables with mean zero and covariance

$$
\langle \xi_i^{(n)} \xi_j^{(n)} \rangle = \langle \eta_i^{(n)} \eta_j^{(n)} \rangle = \delta_{i,j} \qquad \langle \xi_i^{(n)} \eta_j^{(n)} \rangle = 0
\tag{11}
$$

3 Reduced Units

As molecular dynamics actions take place on a small time- and spacescale it's convenient to change the unit system to the system of reduced units (MD units). Following changes are made

$$
\tilde{r} \rightarrow r\sigma
\tag{12}
$$

$$
\tilde{E} \rightarrow E\epsilon
\tag{13}
$$

$$
\tilde{m} \rightarrow m m_a
\tag{14}
$$

where σ and ϵ are paramter of the Lennard-Jones potential (ϵ governs the strength of the interaction and σ defines a length scale, both just numbers) and m_a is the atomic mass. In order to derive the factor for the conversion factor of time one can use the fact that for example the formula for the kinetic energy shouldn't change under unit system transformations. This leeds to

$$
\tilde{t} \rightarrow t\sqrt{\frac{m_a \sigma^2}{\epsilon}}
\tag{15}
$$

By setting $k_B = 1$ the MD unit of temperature is now also defined. The following table contains the most used quantities, as well as values for argon:

Physical quantity	Unit	Value for Ar
Length	σ	$3.4 \cdot 10^{-10}\ m$
Energy	ϵ	$1.65 \cdot 10^{-25}\ J$
Mass	m	$6.69 \cdot 10^{-26}\ kg$
Time	$\sigma(m/\epsilon)^{1/2}$	$2.17 \cdot 10^{-12}\ s$
Velocity	$(\epsilon/m)^{1/2}$	$1.57 \cdot 10^2\ m/s$
Force	ϵ/σ	$4.85 \cdot 10^{-12}\ N$
Pressure	ϵ/σ^3	$4.20 \cdot 10^7\ Nm^{-2}$
Temperature	ϵ/k_B	$120\ K$

Table 1: Conversation factors for MD units and specific values for argon

4 Check implementation for a simple potential

In order to check the implementation one can use a potential of the form

$$V(x) = \frac{1}{2}kx^2 \tag{16}$$

If $\gamma = 0$, the Langevin Equation reduces to a simple harmonic oscillator where the probability density for position can be derived in the following way:

4.1 Probability density for position for the harmonic oscillator

A particle moving with velocity $v(t)$ spends the time dt in a small region of space dx via

$$dt = \frac{dx}{v(t)} \tag{17}$$

For a periodic motion with period τ, the probability of finding the particle in this region is the ration of the time spent to the total time for one traversal $\tau/2$ is

$$P(x)dx = \text{Probability}[(x, x + dx)] = \frac{dt}{\tau/2} = \frac{2}{\tau}\frac{dx}{v(t)} \tag{18}$$

Since the kinetic energy is $T = \frac{mv^2}{2}$, we can rewrite the equation to

$$P(x) = \frac{2}{\tau}\sqrt{\frac{m}{2T}} = \frac{2}{\tau}\sqrt{\frac{m}{2(E - V(x))}} \tag{19}$$

For the harmonic oscillator we have $V(x) = \frac{1}{2}kx^2$ and $\tau = 2\pi\sqrt{\frac{m}{k}}$. The total energy is conserved and therefore one can use the initial conditions x_0 and v_0 to calculate the energy. This leads to

$$P(x) = \frac{1}{\pi}\sqrt{\frac{k}{2E - kx^2}} \tag{20}$$

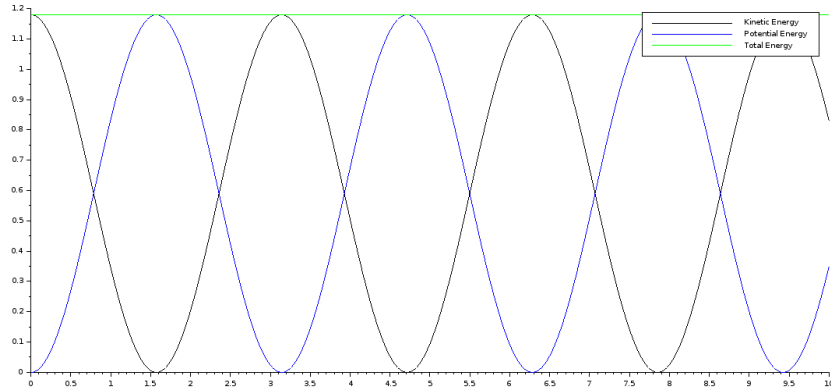After implementation one can check if the total energy is conserved. In 1 it can be seen that this is the case.

Figure 1: Kinetic-, Potential and total energy as a function of time

Another possibility to check the implementation is to plot $P(x)$.

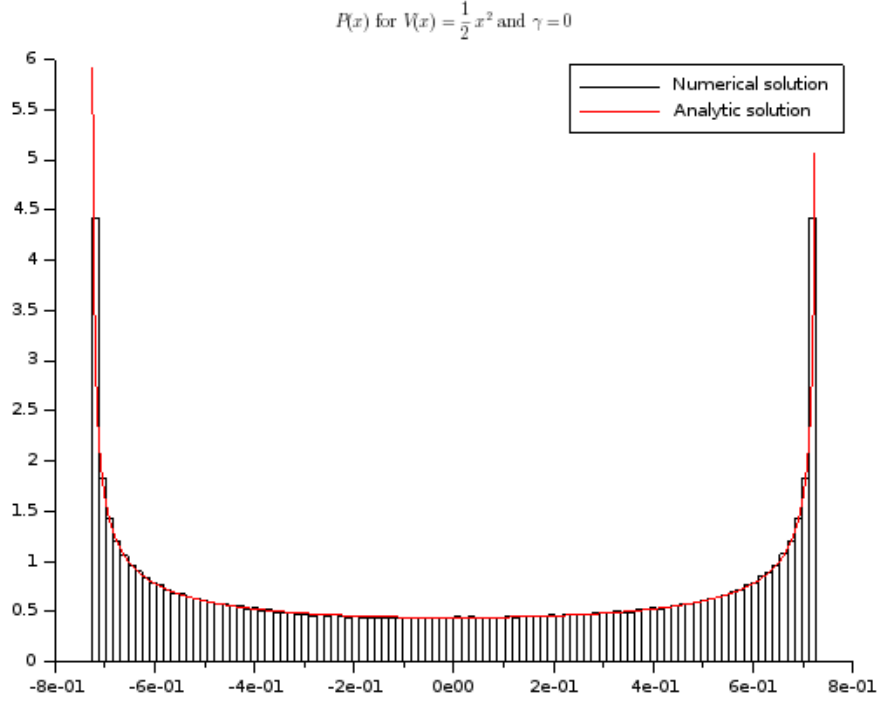$P(x)$ for $V(x) = \frac{1}{2}x^2$ and $\gamma = 0$

Figure 2: $P(x)$ for $g = 0$

In the cases where $\gamma \neq 0$ the probability density changes.

4.2 Probability density for the Langevin Equation and the harmonic oscillator

Equation 7 can be rewriten as Fokker-Planck equation. In this case the corresponding equation is known as the Klein-Kramers equation

$$\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial x} = \frac{\partial}{\partial v}\left(\gamma v - f(x) + \sigma^2 \frac{\partial}{\partial v}\right)P \tag{21}$$

The steady state $\left(\frac{\partial P_s}{\partial t} = 0\right)$ is given by a Boltzmann distribution:

$$P_s(x,v) = ce^{\frac{-U(x)}{k_B T}} e^{\frac{-mv^2}{2k_B T}} \tag{22}$$

The normalization condition leeds to $c = \frac{\sqrt{km}}{2\pi k_B T}$ and therefore

$$P_s(x,v) = \frac{\sqrt{km}}{2\pi k_B T} e^{\frac{-U(x)}{k_B T}} e^{\frac{-mv^2}{2k_B T}} \tag{23}$$

In the case of $V(x) = \frac{1}{2}kx^2$ the expression becomes

$$P_s(x,v) = \frac{\sqrt{km}}{2\pi k_B T} e^{\frac{-kx^2}{2k_B T}} e^{\frac{-mv^2}{2k_B T}} \tag{24}$$

4

References

[1] Giovanni Ciccotti Eric Vanden-Eijnden. Second-order integrators for langevin equations with holonomic constraints. *Chemical Physics Letters*, 429, 2006.