Computational Statistical Mechanics and Molecular Dynamics

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1 Classical, Deterministic Motion

We wish to simulate the classical Newtonian model equation of motion:

$$m\ddot{r} \;=\; f \tag{1}$$

where m is the mass of an object with coordinate r, and f is the force acting on the object. Assuming that the trajectory $r(t)$ is smooth, we can write the following Taylor expansions

$$r(t_n+dt) \;=\; r(t_n)+dt\,v(t_n)+\frac{dt^2}{2}\,a(t_n)+\frac{dt^3}{6}\,\dot{a}(t_n)+\frac{dt^4}{24}\,\ddot{a}(t_n)+\cdots \tag{2}$$

$$r(t_n-dt) \;=\; r(t_n)-dt\,v(t_n)+\frac{dt^2}{2}\,a(t_n)-\frac{dt^3}{6}\,\dot{a}(t_n)+\frac{dt^4}{24}\,\ddot{a}(t_n)-\cdots \tag{3}$$

where discrete time is given by $t_n=t_0+n\,dt$, with n being an integer counter of time steps of size dt. We immediately get the two following second order (in dt) central difference approximations to the velocity, $v=\dot{r}$, and acceleration, $a=\dot{v}=\ddot{r}$, by subtracting and adding the two expansions:

$$v(t_n) \;=\; \frac{r(t_n+dt)-r(t_n-dt)}{2\,dt}-\frac{dt^2}{6}\,\dot{a}(t_n)-\cdots \tag{4}$$

$$a(t_n) \;=\; \frac{r(t_n+dt)-2r(t_n)+r(t_n-dt)}{dt^2}-\frac{dt^2}{12}\,\ddot{a}(t_n)-\cdots \tag{5}$$

We now denote the discrete-time , position, velocity, and force variables by $r^n\approx r(t_n)$, $v^n\approx v(t_n)$, $f^n\approx m\,a(t_n)$, such that

$$v^n \;=\; \frac{r^{n+1}-r^{n-1}}{2\,dt} \tag{6}$$

$$f^n \;=\; m\frac{r^{n+1}-2r^n+r^{n-1}}{dt^2} \tag{7}$$

where Eq. (7) can also be written

$$r^{n+1} \;=\; 2r^n-r^{n-1}+\frac{dt^2}{m}f^n \tag{8}$$

This equation is the Størmer-Verlet equation that is a second order (higher if $f(t,r)$), discrete-time version of Newton's equation of motion Eq. (1). Thus, if r^n and r^{n-1} are known, we know $f^n=f(t_n,r^n)$, and then we can find r^{n+1} at the new time t_{n+1}. Notice that Eq. (8) is time reversible, since dt appears only to even power. This implies conservation properties.

1.1 Analysis of the Trajectory

Since f^n is generally a nonlinear function, we cannot analyze either Eq. (1) or Eq. (8) in general. However, we can analyze the dynamics for linear systems. We therefore assume that f represents a Hooke's spring, $f = -\kappa r$, where $\kappa \geq 0$ is a linear spring constant.

Inserting the Hooke's force into Eq. (1) yields the exact, continuous-time solution

$$\ddot{r} = -\Omega_0^2 r \quad \Rightarrow \tag{9}$$

$$r(t_n) = (r^0 + i\frac{v^0}{\Omega_0}) \exp(\pm i\,\Omega_0 dt\, n) \tag{10}$$

where we have written $t_n = n\,dt$, and where $r(t_0) = r^0 + i\,\Omega_0^{-1}v^0$ is the initial condition.

Inserting Hooke's law into Eq. (8) yields the discrete-time Verlet equation

$$r^{n+1} = 2r^n(1 - \frac{\Omega_0^2 dt^2}{2}) - r^{n-1} \tag{11}$$

which has the exact solution $r^n = (r^0 + i\frac{v^0}{\Omega_V})\Lambda_\pm^n$, where $\Lambda_\pm$ are the roots of the characteristic polynomial from Eq. (11)

$$\Lambda_\pm = 1 - \frac{\Omega_0^2 dt}{2} \pm i\,\Omega_0 dt\sqrt{1 - \frac{\Omega_0^2 dt^2}{4}} \tag{12}$$

We notice that $|\Lambda_\pm| = 1$ for as long as $\Omega_0 dt \leq 2$. For $\Omega_0 dt > 2$ we have that $-1 < \Lambda_+$ and $\Lambda_- < -1$, the latter implying an unstable trajectory. Thus, the discrete-time solution is a stable harmonic oscillator for $\Omega_0 dt \leq 2$, which is the stability range of the time step. Within the stability range, we can write

$$\Lambda_\pm = \exp(\pm i\,\Omega_V dt) \quad \Rightarrow \tag{13}$$

$$r^n = (r^0 + i\frac{v^0}{\Omega_V}) \exp(\pm i\,\Omega_V dt\, n) \tag{14}$$

where Ω_V is the discrete-time frequency given by

$$\cos\Omega_V dt = 1 - \frac{\Omega_0^2 dt^2}{2} \tag{15}$$

$$\sin\Omega_V dt = \Omega_0 dt\sqrt{1 - \frac{\Omega_0^2 dt^2}{4}} \tag{16}$$

These expressions show that $\Omega_V > \Omega_0$, $\Omega_V \to \Omega_0$ for $\Omega_0 dt \to 0$ (with an error $\propto (\Omega_0 dt)^2$), and $\Omega_V \to \Omega_0\frac{\pi}{2}$ for $\Omega_0 dt \to 2$. Thus, the discrete-time harmonic oscillator has an elevated frequency, which increases with the reduced time step $\Omega_0 dt$.

1.2 The behavior of the velocity variable

The discrete-time on-site velocity was found in Eq. (6). We can evaluate the quality of this variable by using the harmonic oscillator results from the trajectory above:

$$v^n = \frac{r^{n+1}-r^{n-1}}{2\,dt} = (r^0+i\frac{v^0}{\Omega_V})\frac{\exp(\pm i\,\Omega_V dt(n+1))-\exp(\pm i\,\Omega_V dt(n-1))}{2\,dt} \tag{17}$$

$$= (r^0+i\frac{v^0}{\Omega_V})\exp(\pm i\,\Omega_V dt\,n)\frac{\exp(\pm i\,\Omega_V dt)-\exp(\mp i\,\Omega_V dt)}{2\,dt} \tag{18}$$

$$= \pm\,r^n\,i\,\Omega_V\,\frac{\sin\Omega_V dt}{\Omega_V dt} \tag{19}$$

Thus, we see that the velocity is correctly orthogonalized to the trajectory, but it is depressed by the last factor, which approaches zero when $\Omega_V dt\to\pi$ or, equivalently, $\Omega_0 dt\to 2$.

We may define another discrete-time velocity, also central difference:

$$u^{n+\frac{1}{2}} = \frac{r^{n+1}-r^n}{dt} \tag{20}$$

This half-step velocity yields the harmonic oscillator result

$$u^{n+\frac{1}{2}} = \frac{r^{n+1}-r^n}{dt} = (r^0+i\frac{v^0}{\Omega_V})\frac{\exp(\pm i\,\Omega_V dt(n+1))-\exp(\pm i\,\Omega_V dt\,n)}{dt} \tag{21}$$

$$= (r^0+i\frac{v^0}{\Omega_V})\exp(\pm i\,\Omega_V dt\,(n+\frac{1}{2}))\frac{\exp(\pm i\,\frac{\Omega_V dt}{2})-\exp(\mp i\,\frac{\Omega_V dt}{2})}{dt} \tag{22}$$

$$= \pm\,r^{n+\frac{1}{2}}\,i\,\Omega_V\,\frac{\sin\frac{\Omega_V dt}{2}}{\frac{\Omega_V dt}{2}} \tag{23}$$

This velocity still have problems with the amplitude, but considerably less problems than the on-site velocity v^n shown above. For example, at the stability limit, $u^{n+\frac{1}{2}}$ is depressed only by a factor of $\frac{2}{\pi}$. The downside to the half-step velocity is that it is an approximation at the half-step, which is slighly out of step with the associated trajectory r^n.

1.3 Integrated formulations of the Verlet method

We can rewrite the second order Størmer-Verlet second order difference equation Eq. (8) by combining it with the velocity variables.

For the on-site velocity Eq. (6), we can insert r^{n-1} from Eq. (6) into Eq. (8) and obtain the truncated Taylor expansion

$$r^{n+1} = r^n+dt\,v^n+\frac{dt^2}{2m}f^n \tag{24}$$

The corresponding velocity equation is found by writing the velocity and inserting Eq. (24) twice

$$v^{n+1} = \frac{r^{n+2}-r^n}{2\,dt} = \frac{r^{n+1}+dt\,v^{n+1}+\frac{dt^2}{2m}f^{n+1}-r^n}{2\,dt} \tag{25}$$

$$
\begin{aligned}
&= \frac{r^n + dt\,v^n + \frac{dt^2}{2m}f^n + dt\,v^{n+1} + \frac{dt^2}{2m}f^{n+1} - r^n}{2\,dt} && (26)\\
&= v^n + \frac{dt^2}{2m}(f^n + f^{n+1}) && (27)
\end{aligned}
$$

The two equations Eqs. (24) and (27) constitute the Velocity-explicit Verlet method.

For the half-step velocity Eq. (20), we can rewrite Eq. (8)

$$
\begin{aligned}
\frac{r^{n+1} - r^n}{dt} &= \frac{r^n - r^{n-1}}{dt} + \frac{dt}{m}f^n && (28)\\
u^{n+\frac{1}{2}} &= u^{n-\frac{1}{2}} + \frac{dt}{m}f^n && (29)
\end{aligned}
$$

and the corresponding trajectory is given by the definition of the half-step velocity

$$
r^{n+1} = r^n + dt\,u^{n+\frac{1}{2}} \qquad (30)
$$

The two equations Eqs. (30) and (29) constitute the Leap-Frog Verlet method.

The combination of all methods, Størmer-Verlet, velocity-explitit, and leap-frog, we can write the following

$$
\begin{aligned}
u^{n+\frac{1}{2}} &= v^n + \frac{dt}{2m}f^n && (31)\\
r^{n+1} &= r^n + dt\,u^{n+\frac{1}{2}} && (32)\\
v^{n+1} &= u^{n+\frac{1}{2}} + \frac{dt}{2m}f^{n+1} && (33)
\end{aligned}
$$

It is easy to validate that these three equations are precisely the same trajectory and velocities described above.