Lecture 7
CH-4114
Molecular Simulation

"Everything that living things do can be understood in terms of the jigglings and wigglings of atoms."

- Richard P. Feynman

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Approach-2: Gaussian random number generator algorithm

Box-Muller Transform

The Definition of the Algorithm

We can therefore identify an algorithm that maps the values drawn from a uniform distribution into those of a normal distribution. The algorithm that we describe here is the Box-Muller transform. **This algorithm is the simplest one to implement in practice**, and it performs well for the pseudorandom generation of normally-distributed numbers.

The algorithm is very simple. We first start with two random samples of equal length, u_1 and u_2, drawn from the uniform distribution $U(0, 1)$. Then, we generate from them two normally-distributed random variables z_1 and z_2. Their values are:

- $z_1 = \sqrt{-2\ln(u_1)}\cos(2\pi u_2)$
- $z_2 = \sqrt{-2\ln(u_1)}\sin(2\pi u_2)$

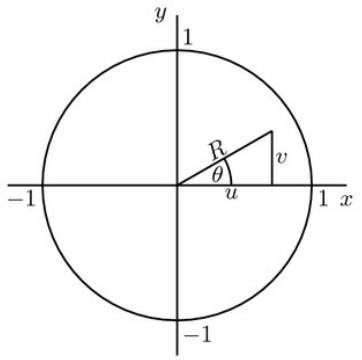
Geometric Interpretation

Suppose U_1 and U_2 are independent samples chosen from the uniform distribution on the unit interval $(0, 1)$. Let

$$Z_0 = R\cos(\Theta) = \sqrt{-2\ln U_1}\cos(2\pi U_2)$$

and

$$Z_1 = R\sin(\Theta) = \sqrt{-2\ln U_1}\sin(2\pi U_2).$$



$$R^2 = u^2 + v^2$$
$$\cos\theta = \frac{u}{R}$$
$$\sin\theta = \frac{v}{R}$$

Then Z_0 and Z_1 are independent random variables with a standard normal distribution.

The derivation[5] is based on a property of a two-dimensional Cartesian system, where X and Y coordinates are described by two independent and normally distributed random variables, the random variables for R^2 and Θ (shown above) in the corresponding polar coordinates are also independent and can be expressed as

$$R^2 = -2\cdot\ln U_1$$

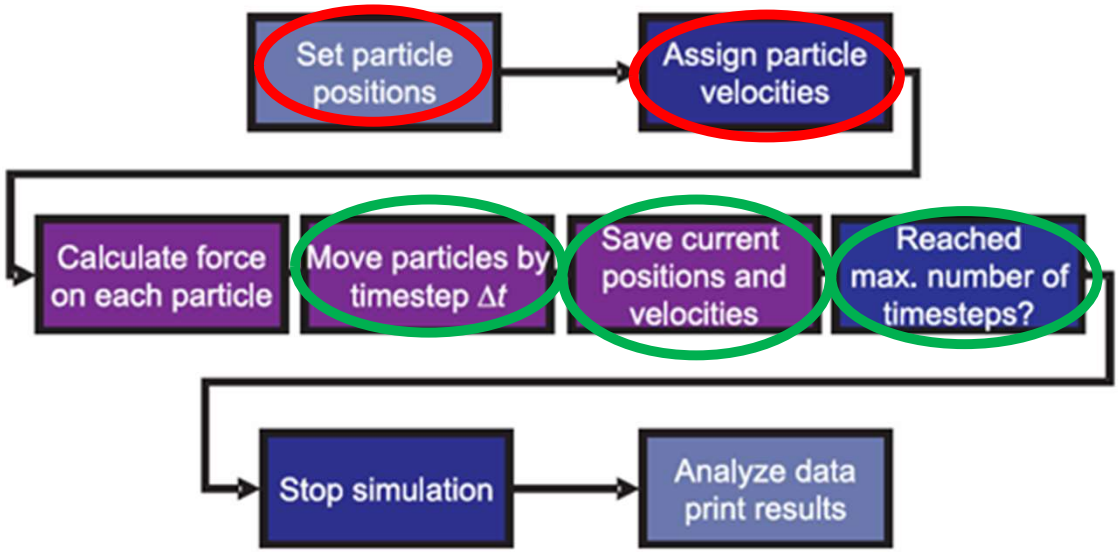
and

$$\Theta = 2\pi U_2.$$

Because R^2 is the square of the norm of the standard bivariate normal variable (X, Y), it has the

Summary: Atomistic simulation – numerical approach “molecular dynamics – MD”

- Atomistic model; requires atomistic microstructure and atomic position at beginning
- Step through time by integration scheme
- Repeated force calculation of atomic forces
- Explicit notion of chemical bonds – captured in interatomic potential



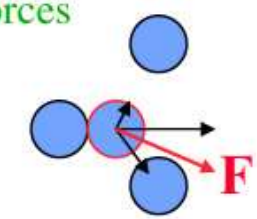
Integration Algorithms: To Move particle by certain timestep

Equations of motion in cartesian coordinates

$$\frac{d\mathbf{r}_j}{dt} = \frac{\mathbf{p}_j}{m}$$
$$\frac{d\mathbf{p}_j}{dt} = \mathbf{F}_j$$

$\mathbf{r} = (r_x, r_y)$
$\mathbf{p} = (p_x, p_y)$
} 2-dimensional space (for example)

$$\mathbf{F}_j = \sum_{\substack{i=1 \\ i \neq j}}^{N} \mathbf{F}_{ij}$$ pairwise additive forces



Desirable features of an integrator

- *minimal need to compute forces (a very expensive calculation)*
- *good stability for large time steps*
- *good accuracy*
- *conserves energy and momentum*
- *time-reversible*
- *area-preserving (symplectic)*

} More on these later

Solving the equations: What we want

To solve those equations: Discretize in time (n steps), Δt time step:

$$r_i(t_0) \rightarrow r_i(t_0 + \Delta t) \rightarrow r_i(t_0 + 2\Delta t) \rightarrow r_i(t_0 + 3\Delta t) \rightarrow \ldots \rightarrow r_i(t_0 + n\Delta t)$$

Solving the equations

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Recall: Taylor expansion of function f around point a

$$f(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \ldots + \frac{f^{(n)}(a)}{n!}(x-a)^n + \ldots.$$

Solving the Equation

To solve those equations: Discretize in time (n steps), Δt time step:

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Taylor series expansion $r_i(t)$ around $a = t_0$ $\quad x = t_0 + \Delta t$

$$x - a = t_0 + \Delta t - t_0 = \Delta t$$

Solving the equations

To solve those equations: Discretize in time (n steps), Δt time step:

$$r_i(t_0) \rightarrow r_i(t_0+\Delta t) \rightarrow r_i(t_0+2\Delta t) \rightarrow r_i(t_0+3\Delta t) \rightarrow \ldots \rightarrow r_i(t_0+n\Delta t)$$

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Taylor series expansion $r_i(t)$ around $a = t_0$ $x = t_0 + \Delta t$

$$x - a = t_0 + \Delta t - t_0 = \Delta t$$

$$r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

Taylor expansion of $r_i(t)$

$$r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

$$r_i(t_0-\Delta t) = r_i(t_0) - v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

Time reversibility of Phase Space Vector is Possible

(Using Liouville Operator and Propagator of Classical Statistical Mechanics)

$$a = t_0 \qquad x = t_0 + \Delta t \qquad x - a = t_0 + \Delta t - t_0 = \Delta t$$

$$a = t_0 \qquad x = t_0 - \Delta t \qquad x - a = t_0 - \Delta t - t_0 = -\Delta t$$

Review of Hamiltonian Dynamics and Operators in Classical Mechanics

For a classical system, specifying the instantaneous positions and momenta of all the particles constituting the system can specify the microstate at any time t. For N particles there are $3N$ coordinates $q_1, q_2 \ldots q_{3N}$ and $3N$ conjugate momenta $p_1, p_2 \ldots p_{3N}$. The equations of motion are *first order* differential equations

$$\dot{q}_i = \frac{\partial H(q_i, p_i)}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H(q_i, p_i)}{\partial q_i}$$

Let us consider a simple one-particle system in one dimension with a Hamiltonian

$$H = \frac{p^2}{2m} + U(x)$$

The equations of motion are

$$\dot{q} = \frac{p}{m} \qquad \dot{p} = -\frac{dU}{dx} = F(x)$$

Now Liouville's theorem says that any phase space function A(x, p) evolves as

$$\frac{dA}{dt}=\{A,H\}$$

where the the {A, H} is the Poisson bracket given by

$$\{A,H\}=\frac{\partial H}{\partial p}\frac{\partial A}{\partial x}-\frac{\partial H}{\partial x}\frac{\partial A}{\partial p}$$

The evolution equation gives back Hamilton's equation of motion: To see that take A(x,p) =x. Then

$$\frac{dx}{dt}=\dot{x}=\{x,H\}$$

$$\{x,H\}=\frac{p}{m}\frac{\partial x}{\partial x}-\frac{dU}{dx}\frac{\partial x}{\partial p}=\frac{p}{m}$$

So we have $\dot{x}=p/m$ **Since** $\frac{\partial x}{\partial p}=0$

Similarly if we take A(x,p) = p

$$\frac{dp}{dt} = \dot{p} = \{p, H\}$$

$$\{p, H\} = \frac{p}{m}\frac{\partial p}{\partial x} - \frac{dU}{dx}\frac{\partial p}{\partial p} = -\frac{dU}{dx} = F(x)$$

So we have $\dot{p} = F(x)$

As expected evolution equation gives back Hamilton's equation of motion

Now define a two-dimensional phase space vector Γ=(x,p). Hamilton's equation of motion for this Γ is

$$\frac{d\Gamma}{dt} = \{\Gamma, H\}$$

Now we define Liouville operator L such that $iL\Gamma = \{\Gamma, H\}$

iL can be expressed as differential operator using Hamilton's equation

$$
\begin{aligned}
iL &= \frac{\partial H}{\partial p}\frac{\partial}{\partial x} - \frac{\partial H}{\partial x}\frac{\partial}{\partial p} \\
&= \frac{p}{m}\frac{\partial}{\partial x} - \frac{dU}{dx}\frac{\partial}{\partial p} \\
&= \frac{p}{m}\frac{\partial}{\partial x} - F(x)\frac{\partial}{\partial p} \\
&= \dot{x}\frac{\partial}{\partial x} + \dot{p}\frac{\partial}{\partial p}
\end{aligned}
$$

The equation of motion in operator form is given by

$$\frac{d\Gamma}{dt} = iL\Gamma$$

which can be solved to give

$$\Gamma(t) = e^{iLt}\Gamma(0)$$

The operator exp(*iLt*) is called the classical propagator and the presence of *i* gives a nice analogy with the QM propagator exp(-iHt/ħ)

Properties of Liouville Operator and propagator

It is Hermitian: $L^{\dagger} = L$

The propagator $U(t) \equiv exp(iLt)$ is a unitary operator

$$U^{\dagger}(t)U(t) = I$$

The unitarity of the propagator implies time reversal symmetry in the equations of motion. If the system is propagated forward in time up to a time t and then the clock is allowed to run backwards for a time $-t$, the system will evolve according to the same equations of motion but the direction of the velocities will be reversed, so that the system will simply return to its initial condition.

$$U(-t) = exp(-iLt)$$

Coming Back to

Taylor expansion of $r_i(t)$

$$r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

$$+\left[\, r_i(t_0-\Delta t) = r_i(t_0) - v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots \,\right]$$

$$\downarrow$$

$$r_i(t_0-\Delta t) + r_i(t_0+\Delta t) = 2r_i(t_0) - v_i(t_0)\Delta t + v_i(t_0)\Delta t + a_i(t_0)\Delta t^2 + \ldots$$

Taylor expansion of $r_i(t)$

$$r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

$$+\left[\; r_i(t_0-\Delta t) = r_i(t_0) - v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots \;\right]$$

$$\downarrow$$

$$r_i(t_0-\Delta t) + r_i(t_0+\Delta t) = 2r_i(t_0) \cancel{- v_i(t_0)\Delta t + v_i(t_0)\Delta t} + a_i(t_0)\Delta t^2 + \ldots$$

$$\downarrow$$

$$r_i(t_0+\Delta t) = 2r_i(t_0) - r_i(t_0-\Delta t) + a_i(t_0)\Delta t^2 + \ldots$$

Taylor expansion of $r_i(t)$

$$r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

$$+ \left[r_i(t_0-\Delta t) = r_i(t_0) - v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots \right]$$

$$r_i(t_0-\Delta t) + r_i(t_0+\Delta t) = 2r_i(t_0) - \cancel{v_i(t_0)\Delta t + v_i(t_0)\Delta t} + a_i(t_0)\Delta t^2 + \ldots$$

$$r_i(t_0+\Delta t) = \underbrace{2r_i(t_0)}_{\text{Positions at } t_0} - \underbrace{r_i(t_0-\Delta t)}_{\text{Positions at } t_0-\Delta t} + \underbrace{a_i(t_0)}_{\text{Accelerations at } t_0}\Delta t^2 + \ldots$$

Verlet Algorithm

$$r_i(t_0 + \Delta t) = \underbrace{2r_i(t_0)}_{\text{Positions at } t_0} - \underbrace{r_i(t_0 - \Delta t)}_{\text{Positions at } t_0\text{-}\Delta t} + \underbrace{a_i(t_0)}_{\text{Accelerations at } t_0}\Delta t^2 + \ldots$$

How to obtain accelerations?

$$f_i = ma_i$$

$$a_i = f_i / m$$

Need forces on atoms!

Verlet central difference method

or

Verlet Algorithm

$$r_i(t_0 + \Delta t) = 2r_i(t_0) - r_i(t_0 - \Delta t) + f_i(t_0)/m\Delta t^2 + \ldots$$

Positions at t_0

Positions at t_0-Δt

Forces at t_0

Verlet Algorithm 2. Flow diagram