Molecular Dynamics

Molecular Dynamics

The Basis:

$$F_i = m_i a_i$$

$$i = 1, 2, \ldots, N$$

N-body problem. Can only be solved numerically

(except in very special cases)

How?

$$X(t+\Delta t) = X(t) + \dot{X}(t)\Delta t + \frac{1}{2!}\ddot{X}(t)\Delta t^2 + \frac{1}{3!}\dddot{X}(t)\Delta t^3 + \ldots$$

...at least, in principle.

Naive approach: truncate Taylor expansion.

$$X(t+\Delta t) \approx X(t) + \dot{X}(t)\Delta t + \frac{1}{2!}\ddot{X}(t)\Delta t^2$$

ABSOLUTELY FORBIDDEN!

The naive “forward Euler” algorithm

- is not time reversible
- does not conserve volume in phase space
- suffers from energy drift

Better approach: “Verlet” algorithm

$$X(t+\Delta t) = X(t) + \dot{X}(t)\Delta t + \frac{1}{2!}\ddot{X}(t)\Delta t^2 + \frac{1}{3!}\dddot{X}(t)\Delta t^3 + \frac{1}{4!}\ddot{\dddot{X}}(t)\Delta t^4 + \ldots$$

$$X(t-\Delta t) = X(t) - \dot{X}(t)\Delta t + \frac{1}{2!}\ddot{X}(t)\Delta t^2 - \frac{1}{3!}\dddot{X}(t)\Delta t^3 + \frac{1}{4!}\ddot{\dddot{X}}(t)\Delta t^4 + \ldots$$

+

$$X(t+\Delta t) + X(t-\Delta t) = 2X(t) + \ddot{X}(t)\Delta t^2 + O(\Delta t^4)$$

or

$$\boxed{X(t+\Delta t) \approx 2X(t) - X(t-\Delta t) + \ddot{X}(t)\Delta t^2}$$

Verlet algorithm

Verlet algorithm

- is time reversible
- does conserve volume in phase space
- (is “symplectic”)
- does not suffer from energy drift

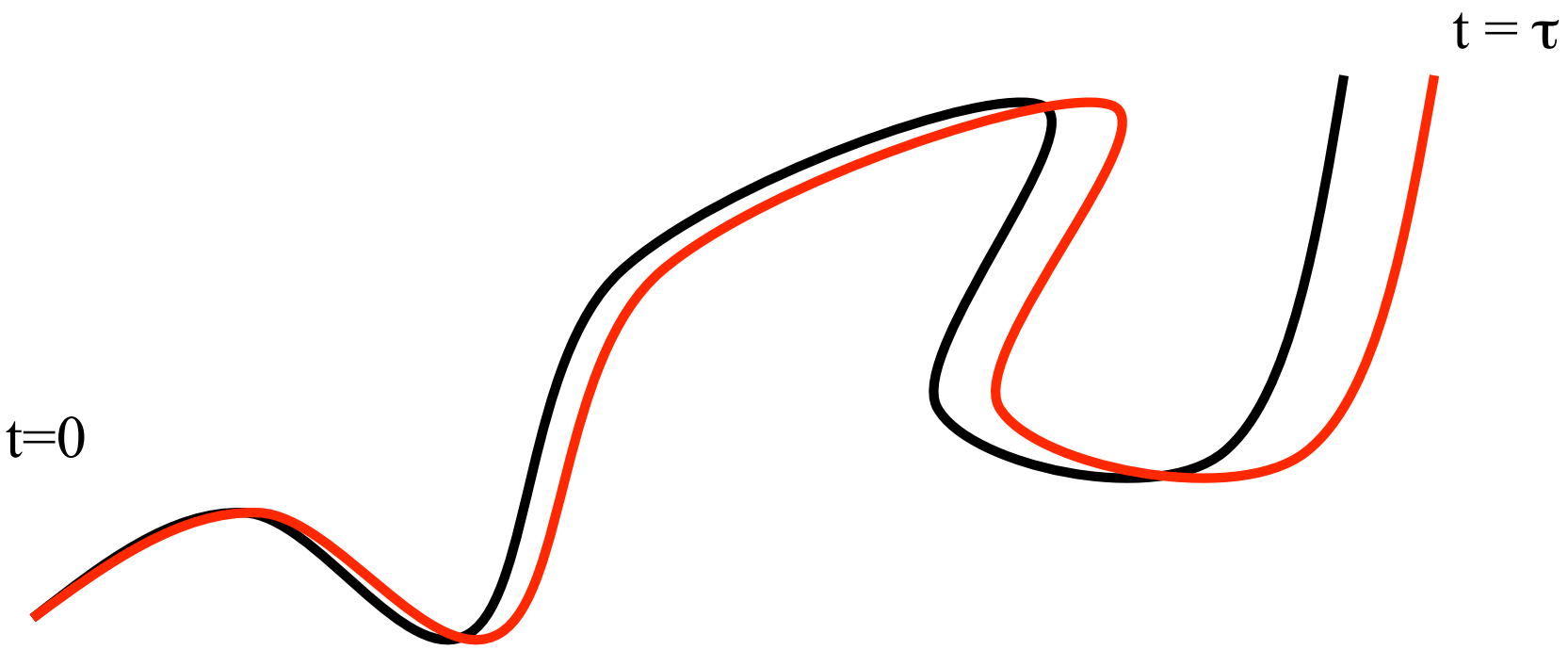
...but is it a good algorithm?

i.e. does it predict the time evolution of the system correctly???

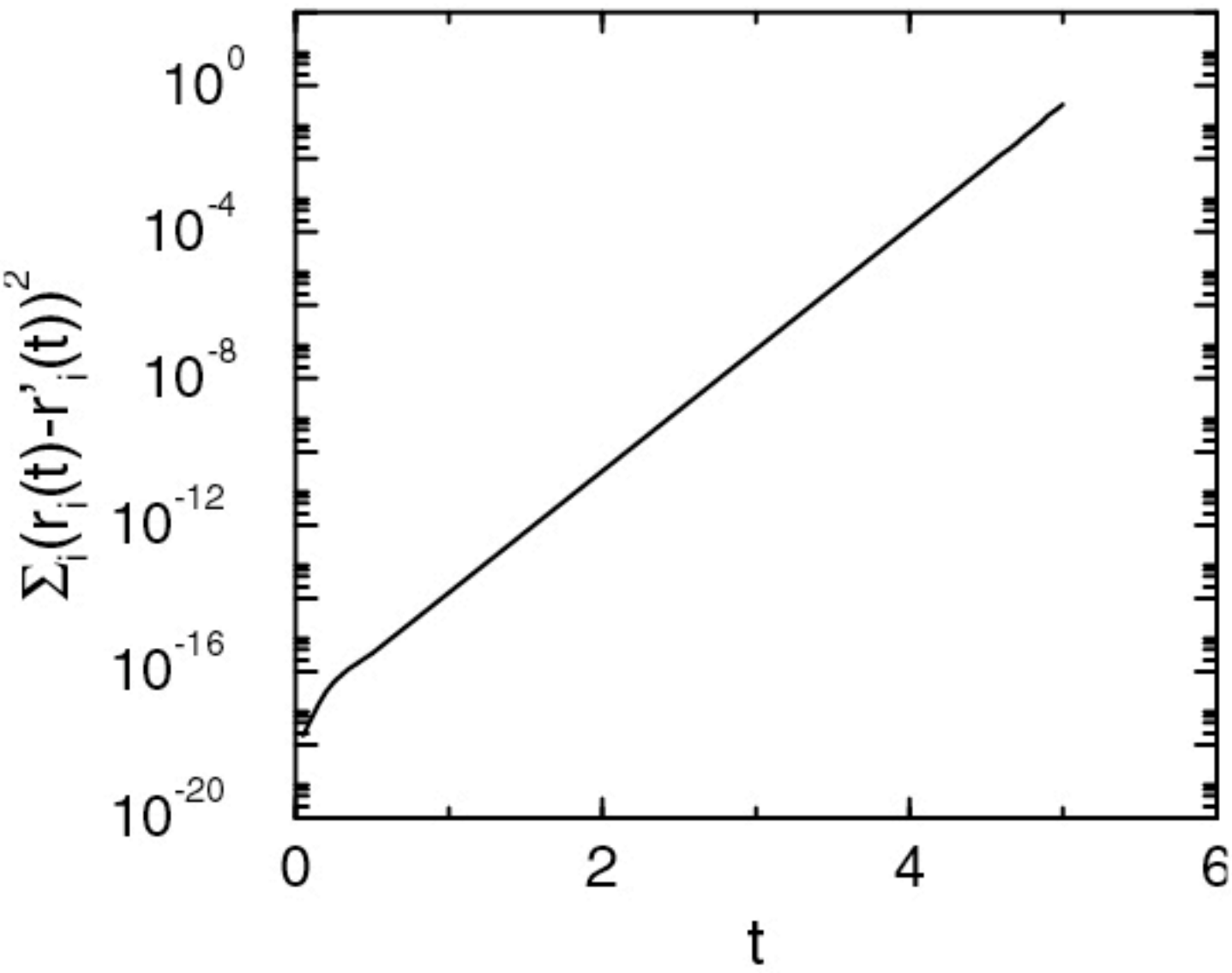
Dynamics of “well-behaved” classical many-body system is chaotic.

Consequence:

Trajectories that differ very slightly in their initial conditions DIVERGE EXPONENTIALLY (“Lyapunov instability”)



The Lyapunov disaster in action...



Any small error in the numerical integration of the equations of motion, will blow up exponentially....

always...

...and for any algorithm!!

SO:

Why should anyone believe Molecular Dynamics simulations ???

Answers:

1. In fact, one should not...

exit Molecular Dynamics...

Answers:

1. In fact, one should not...
2. Good MD algorithms (e.g. Verlet) can also be considered as good Monte Carlo algorithms – they therefore yield reliable **STATIC** properties ("Hybrid Monte Carlo")

What is the point of simulating dynamics, if we cannot trust the resulting time-evolution???

Answers:

1. In fact, one should not...
2. Good MD algorithms (e.g. Verlet) can also be considered as good Monte Carlo algorithms – they therefore yield reliable **STATIC** properties ("Hybrid Monte Carlo")
3. All is well (probably), because of...

The Shadow Theorem....

For any realistic many-body system, the shadow theorem is merely a hypothesis.

It states that (my words):

Good algorithms generate numerical trajectories that are “close to” a REAL trajectory of the many-body system.

Question:

Does the Verlet algorithm indeed generate “shadow” trajectories?

Take a different look at the problem.

Do not discretize NEWTON's equation of motion...

...but discretize the ACTION

Intermezzo:

Classical mechanics – the Lagrangian approach.

Newton: $\mathbf{F_i} = m_i \ddot{\mathbf{r}}_i$

Lagrange:

Consider a system that is at a point $\mathbf{r_0}$ at time t=0 and at point $\mathbf{r_t}$ at time t=t, then:

The system follows a trajectory r(t) such that:

"Action"

$$S \equiv \int_0^t dt' \mathcal{L}(\mathbf{r}(t))$$ is an extremum.

"Lagrangian"

Where the Lagrangian is defined as:

$$\mathcal{L}(\mathbf{r}(t)) = T_{kinetic} - U_{pot}(\mathbf{r})$$

For example, if we use cartesian coordinates:

$$\mathcal{L}(\mathbf{r}(t)) = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{\mathbf{r}}_i^2 - U(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$$

What does this mean?

Consider the “true” path **R**(t), with **R**(0)=$\mathbf{r}_0$ andR(t)=$\mathbf{r}_t$.

Now, consider a path close to the true path:

$$\mathbf{r}(t') = \mathbf{R}(t') + \delta\mathbf{r}(t')$$

Then the action **S** is an extremum if

$$\frac{\delta S}{\delta \mathbf{r}(t')} = 0 \quad , (\forall t')$$

(what does this equation mean??)

$$S_{continuous} = \int_{t_0}^{t_1} dt\, L(t)$$

Discretized version

$$S_{discrete} = \Delta t \sum_{i=0}^{i_{max}} L(t_i)$$

$$L(t_i) = T(t_i) - U(t_i)$$

e.g. for one coordinate in one dimension

$$L(t_i)\Delta t = \frac{1}{2} m\Delta t \frac{(X_{i+1} - X_i)^2}{\Delta t^2} - U(X_i)\Delta t$$

and hence the discretized action is

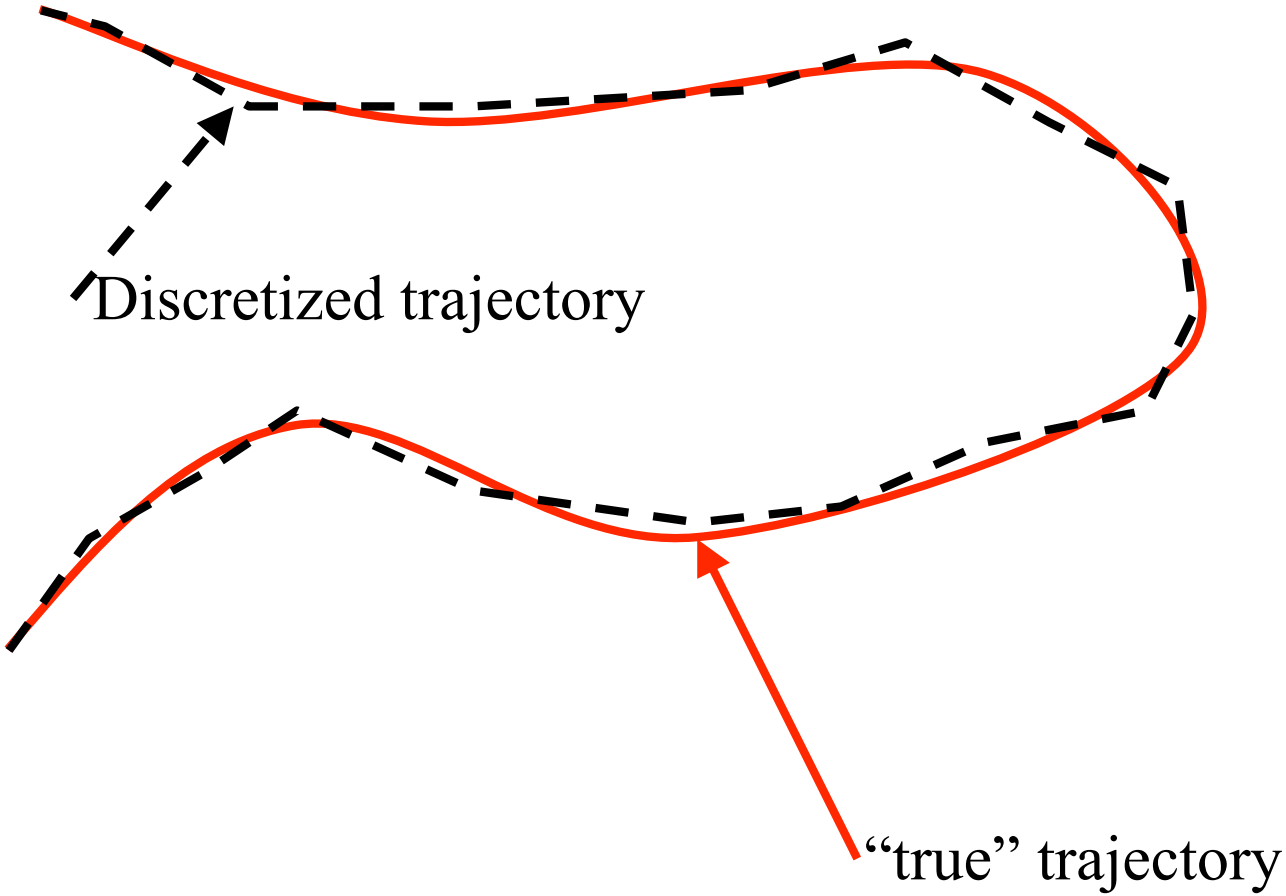
$$S_{discrete} = \sum_{i=1}^{i_{max}} \left(\frac{m(X_{i+1} - X_i)^2}{2\Delta t} - U(X_i)\Delta t \right)$$

Now do the standard thing:

Find the extremum for small variations in the path, i.e. for small variations in all X_i.

$$\frac{\partial S_{discrete}}{\partial X_i} = 0 \qquad (\forall i)$$

This will generate a discretized trajectory that starts at time t_0 at X_0 , and ends at time t_1 at X_1.



$$\frac{\partial S_{discrete}}{\partial X_i} = \frac{\partial}{\partial X_i} \sum_{i=1}^{i_{max}} \left(\frac{m(X_{i+1} - X_i)^2}{2\Delta t} - U(X_i)\Delta t \right)$$

$$\frac{\partial S_{discrete}}{\partial X_i} = \frac{-m(X_{i+1} - X_i) + m(X_i - X_{i-1})}{\Delta t} - \Delta t \frac{\partial U(X_i)}{\partial X_i}$$

And hence:

$$0 = \frac{m}{\Delta t} \left(2X_i - X_{i+1} - X_{i-1} - \frac{\Delta t^2}{m} \frac{\partial U(X_i)}{\partial X_i} \right)$$

$$0 = \left(2X_i - X_{i+1} - X_{i-1} - \frac{\Delta t^2}{m} \frac{\partial U(X_i)}{\partial X_i} \right)$$

REWRITE AS:

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

VERLET!!!

The Verlet algorithm generates trajectory that satisfies the boundary conditions of a REAL trajectory – both at the beginning and at the endpoint.

Hence, if we are interested in statistical information about the dynamics (e.g. time-correlation functions, transport coefficients, power spectra...)

...then a “good” MD algorithm (e.g. Verlet) is fine.

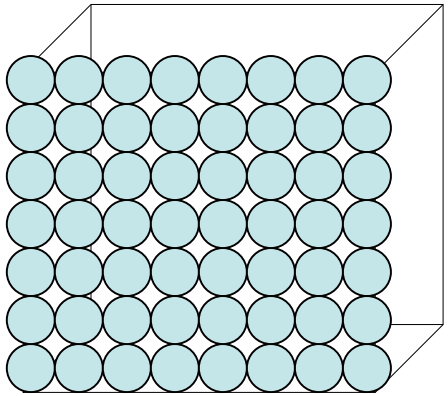
However...

But Professor Verlet! You said that your calculations showed that the asteroid would MISS the earth!!!

Not at all!
I just said that that would be close to a POSSIBLE scenario!!!

Practical issues:

1. Boundary conditions
2. Reduced units
3. Time-saving devices

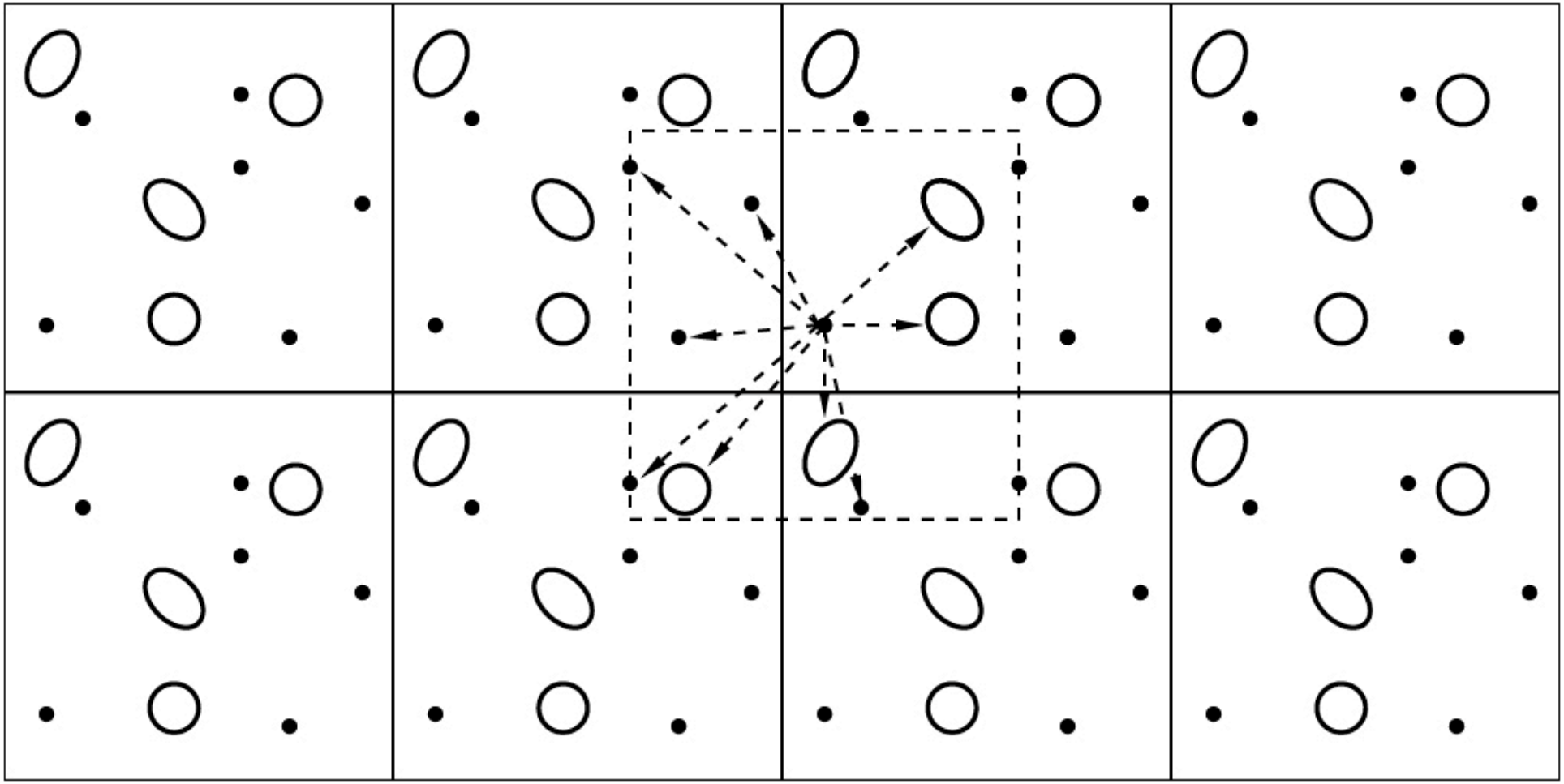


In small systems, boundary effects are always large.

1000 atoms in a simple cubic crystal – 488 boundary atoms.

1000000 atoms in a simple cubic crystal – still 6% boundary atoms…

“Solution” : Periodic boundary conditions



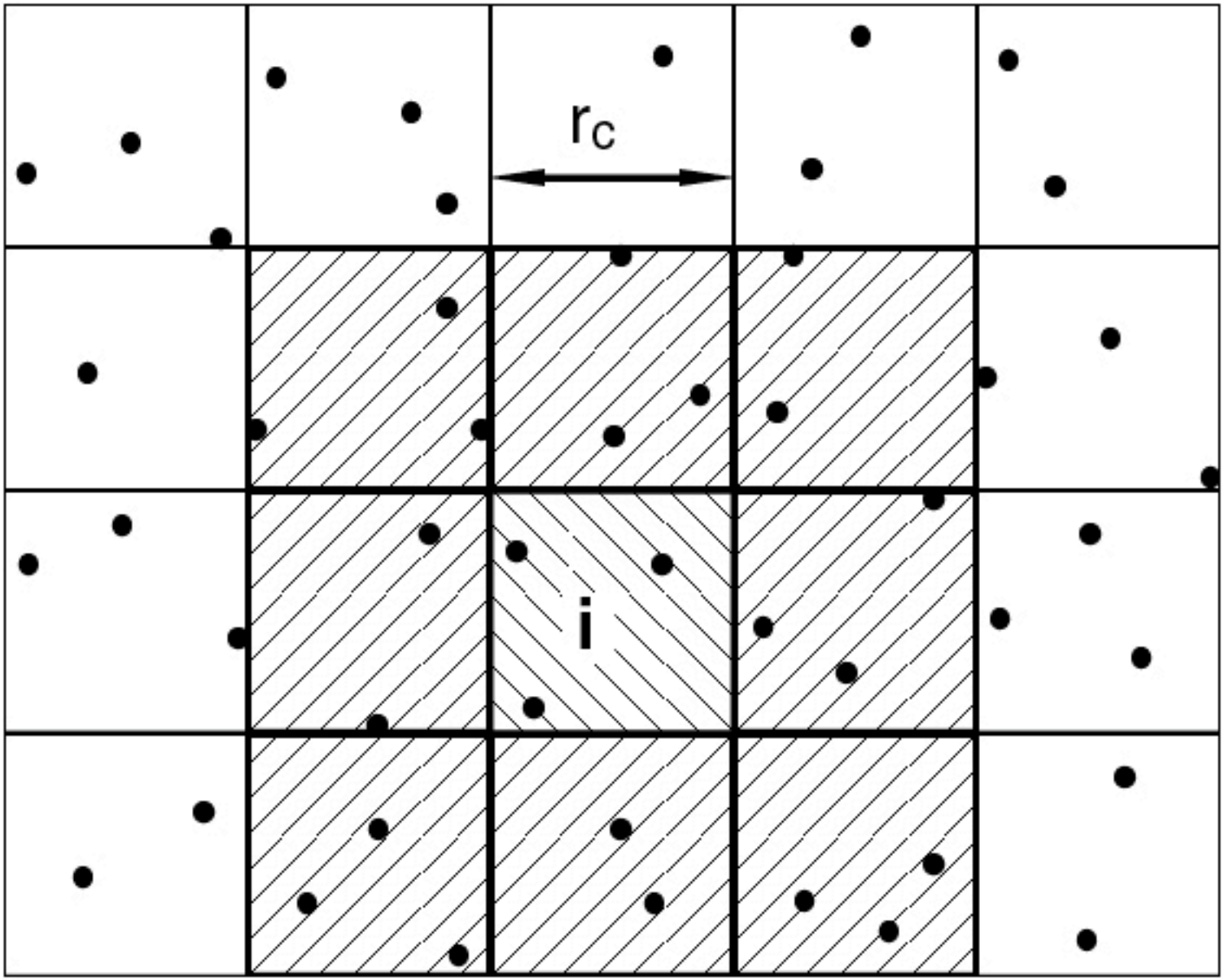
The most time-consuming part of any simulation is the evaulation of all the interactions between the molecules.

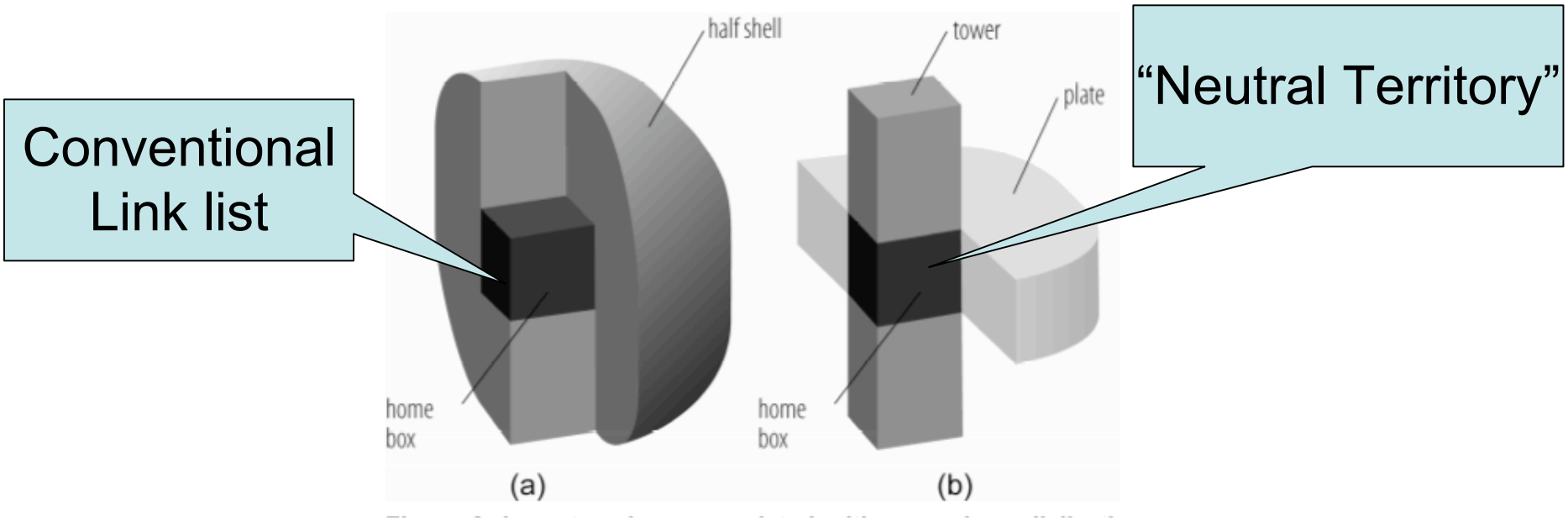
In general: $N(N-1)/2 = O(N^2)$

But often, intermolecular forces have a short range:

Therefore, we do not have to consider interactions with far-away atoms…

Link list





New decomposition : "Neutral Territory" method

(Bowers, Dror & Shaw: J. Chem. Phys, 124: 184109 (2006)).

The **black** box maps onto one processor.

Each processor handles interaction between all particles i that are within the *xy* coordinates of the box and with its *z*-range, with all particles j that are within the *z* coordinates of the box and within its *xy* range.

NOTE:

Long-ranged forces require special techniques.

1. Coulomb interaction (1/r in 3D)
2. Dipolar interaction ($1/r^3$ in 3D)

…and, in a different context:

1. Interactions through elastic stresses (1/r in 3D)
2. Hydrodynamic interactions (1/r in 3D)
3. …

Beyond Newtonian dynamics:

1. Langevin dynamics
2. Brownian dynamics
3. Stokesian dynamics
4. Dissipative particle dynamics
5. Stochastic rotation dynamics
6. Etc. etc.

Reduced units

Example: Particles with mass **m** and pair potential:

$$v(r) = \epsilon f(r/\sigma)$$

Unit of length: σ

Unit of energy: ε

Unit of time: $\sigma\sqrt{m/\epsilon}$

Why ?

Saving time.

These algorithms are often used to simulate molecular motion in a viscous medium, without solving the equations of motion for the solvent particles.

Friction force

Conservative force

First, consider mo with friction alone:

$$m\dot{\vec{v}} = -\gamma\vec{v}(t') - \nabla U \ ,$$

After a short while, all particles will stop moving, due to the friction..

"random" force

Better:

$$m\dot{\vec{v}} = -\gamma\vec{v}(t') - \nabla U + \vec{\zeta}(t) \ ,$$

There is a relation between the correlation function of the random force and the friction coefficient:

$$< \zeta_x(0)\zeta_x(t) >= 2kT\gamma\delta(t)$$

The derivation is straightforward, but beyond the scope of this lecture. The KEY point is that the friction force and the random force ARE RELATED.

$$m\dot{\vec{v}}(t) = -\int_0^t k(t-t')\vec{v}(t') + \vec{\zeta}(t) \qquad < \vec{v}(0).\vec{\zeta}(t) >= 0 \quad \forall t.$$

Generalizsed Langevin Equation

Laplace transform

$$m < \vec{v}(0).\dot{\vec{v}}(t) >= -\int_0^t k(t-t') < \vec{v}(0)\vec{v}(t') >$$

$$m(sV(s) - < v(0)^2 >) = -K(s)V(s) + \frac{}{s + K(s)/m}$$

Derivation

$$m\dot{\vec{v}}(0) = \vec{\zeta}(0)$$

$$m^2 < \dot{\vec{v}}(0).\dot{\vec{v}}(t) >= -$$

$$-m^2\left(s^2V(s) - s < v(0$$

$$-m^2\left(s^2V(s) + sV(s$$

$$-m < v(0)^2 >)$$

$$-(sV(s) - < v(0)^2 >)K(s) + Z(s)$$

$$-m < v(0)^2 >)K(s) + Z(s)$$

$$Z(s) = 0 \quad Z(s) = m < v(0)^2 > K(s)$$

$$k(t) = 2\gamma\delta(t)$$

$$\dot{\vec{v}}(t) = -\gamma\vec{v}(t') + \vec{\zeta}(t)$$

Fluctuation-Dissipation

$$< \vec{\zeta}(0).\vec{\zeta}(t) >= m < v(0)^2 > 2\gamma\delta(t) = 6kT\gamma\delta(t)$$

Limiting case of Langevin dynamics:

No inertial effects (m=0)

$$m\dot{\vec{v}} = -\gamma\vec{v}(t') - \nabla U + \vec{\zeta}(t) \ ,$$

Becomes:

$$0 = -\gamma\vec{v}(t') - \nabla U + \vec{\zeta}(t) \ ,$$

“Brownian Dynamics”

(But still the friction force and the random force are related)

What is missing in Langevin dynamics and Brownian dynamics?

1. Momentum conservation
2. Hydrodynamics

(1 implies 2).

Is this serious?

Not always: it depends on the time scales.

Momentum “diffuses” away in a time L^2/ν. After that time, a “Brownian” picture is OK.

However: hydrodynamics makes that the friction constant depends on the positions of all particles (and so do the random forces…).

Momentum conserving, coarse-grained schemes:

Dissipative particle dynamics

Stochastic Rotation Dynamics

Lattice-Boltzmann simulations

These schemes represent the solvent explicitly (i.e. as particles), but in a highly simplified way.


Happy Diwali
Thank You !