

VIETNAM JAPAN UNIVERSITY
MASTER PROGRAM IN NANO TECHNOLOGY

NANOMECHANICS

INTRODUCTION ON MOLECULAR DYNAMICS SIMULATION

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Lecture outline

❖ **Introduction**

What is Molecular Dynamics, history of Molecular Dynamics,...

❖ **Equations of motion**

Newton's equations of motion, Lagrangian equations of motion,...

❖ **Integration algorithms**

Verlet algorithm, predictor-corrector algorithm,...

❖ **Interatomic potentials**

Lennard-Jones potential, EAM potential, Tersoff potential,...

❖ **Temperature and pressure controls**

Nosé-Hoover thermostat, Andersen thermostat, barostat,...

❖ **Acceleration techniques on simulation**

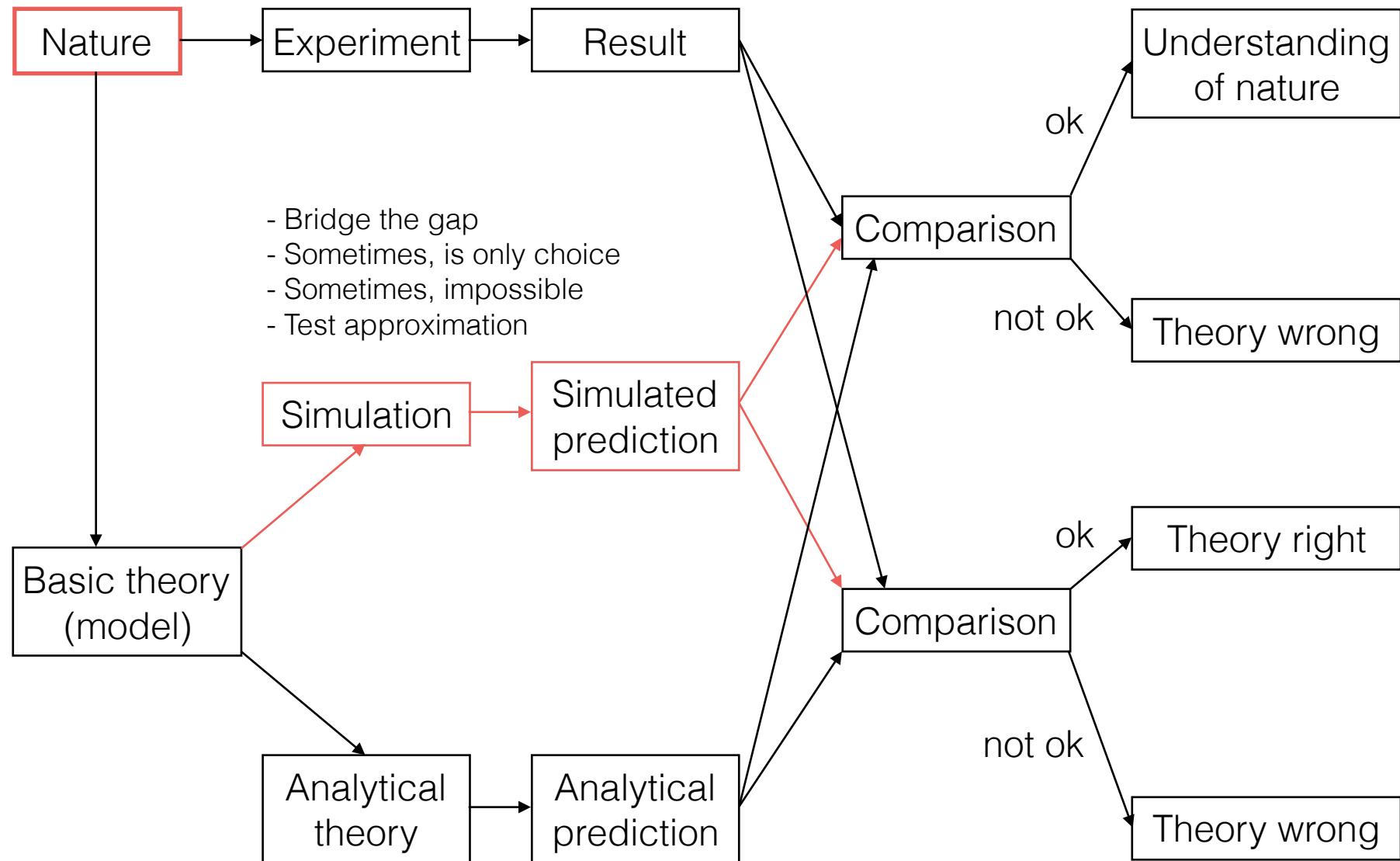
Potential cutoff, book-keeping, linked-cell,...

❖ **Molecular dynamics simulation examples**

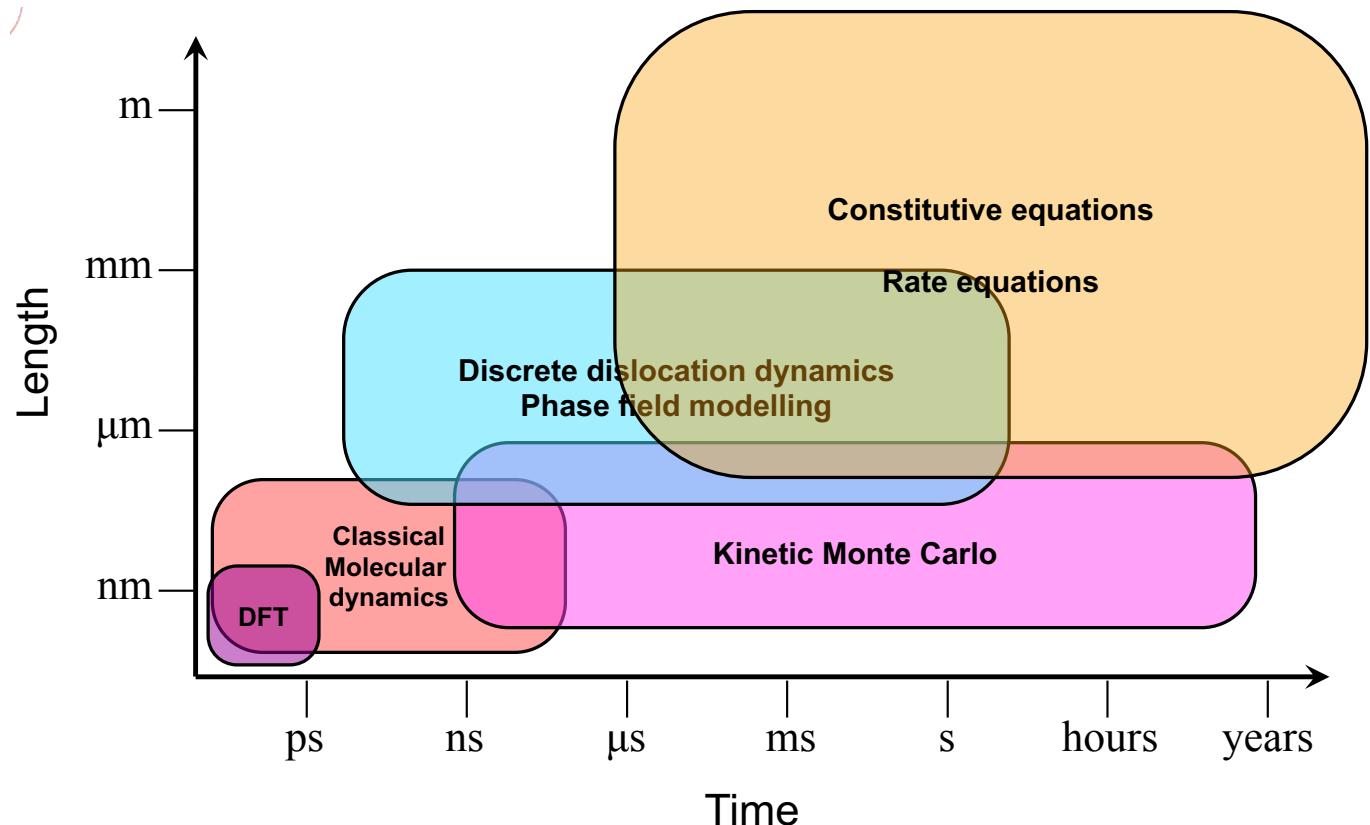
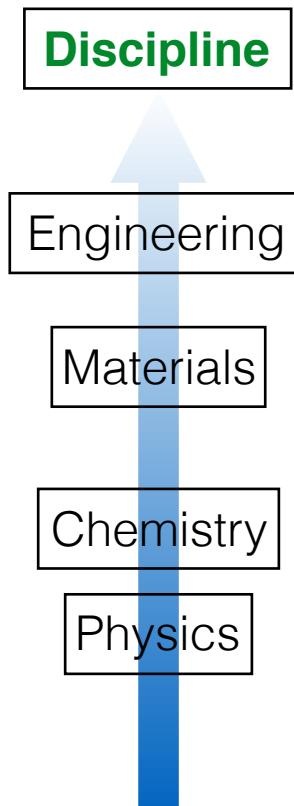
Introduction to LAMMPS, simulation techniques, LAMMPS examples,...

Introduction

Computer simulation in physics



Multi-scale modeling hierarchy



Macro-scale

- Time: $> 1\text{s}$
- Length: $> 1\mu\text{m}$
- Phase field models, FEM,...

Meso-scale

- Time: $\sim 10^{-8} \div 10^{-2}\text{s}$
- Length: $\sim 10 \div 1000\text{nm}$
- DPD, coarse-graining, kinetic Monte Carlo,...

Nano-scale

- Time: $\sim 10^{-15} \div 10^{-9}\text{s}$
- Length: $0.1 \div 10\text{nm}$
- Molecular dynamics, Monte Carlo,...

Subatomic scale

- Electronic structures
- Ab initio, Quantum Monte Carlo,...

What is Molecular Dynamics?

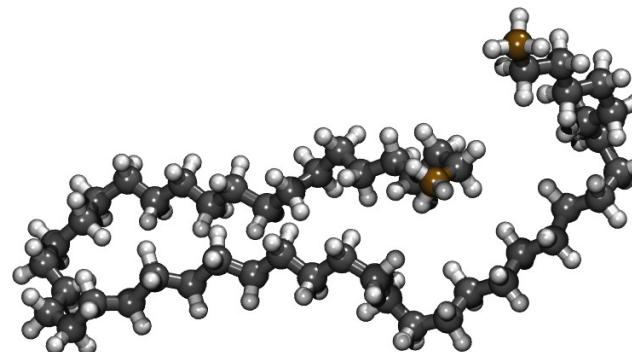
❖ Molecular Dynamics (MD)

Computer simulation technique to predict the time evolution of an atom under a force contributed by other atoms based on classical or quantum mechanics (numerically solve the N-body problem)

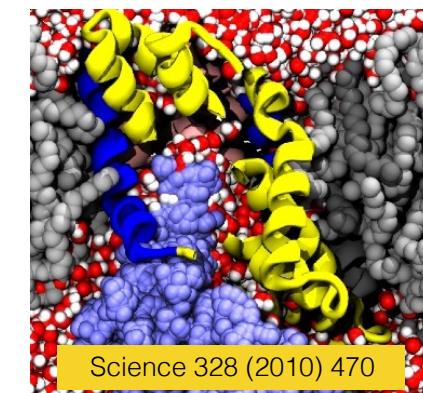
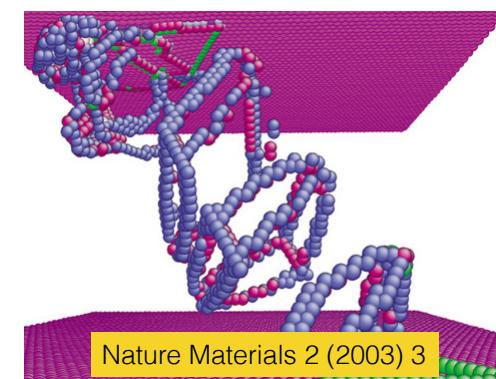
Deterministic method: state of the system at any future time can be predicted from its current state

❖ What can we do with Molecular Dynamics?

- Atomic systems
- Metals
- Bead-spring polymers
- Organic molecules
- Granular systems
- Hybrid systems
- ...



http://www.moltemplate.org/visual_examples.html



History of Molecular Dynamics

❖ 1950s: Alder and Wainwright

“Phase Transition for a Hard Sphere System”

B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* 27 (1957) 1208

“Studies in Molecular Dynamics. I. General Method”

B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* 31 (1959) 459

Hard sphere

Defined simply as impenetrable spheres that cannot overlap in space



Berni Julian Alder

❖ 1964: Rahman

“Correlations in the Motion of Atoms in Liquid Argon”

A. Rahman, *Phys. Rev. A* 136 (1964) 405



R. Car and M. Parrinello

❖ 1974: Rahman and Stillinger

“Improved simulation of liquid water by molecular dynamics”

F. H. Stillinger and A. Rahman, *J. Chem. Phys.* 60 (1974) 1545

❖ 1985: Car and Parrinello

“Unified Approach for Molecular Dynamics and Density-Functional Theory”

R. Car and M. Parrinello, *Phys. Rev. Lett.* 55 (1985) 2471

Molecular Dynamics categories

$$H = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i < j} \frac{e^2}{|r_i - r_j|} - \sum_{I,i} \frac{Z_I e^2}{|R_I - r_i|} + \sum_{i < j} \frac{Z_I Z_J e^2}{|R_I - R_J|}$$

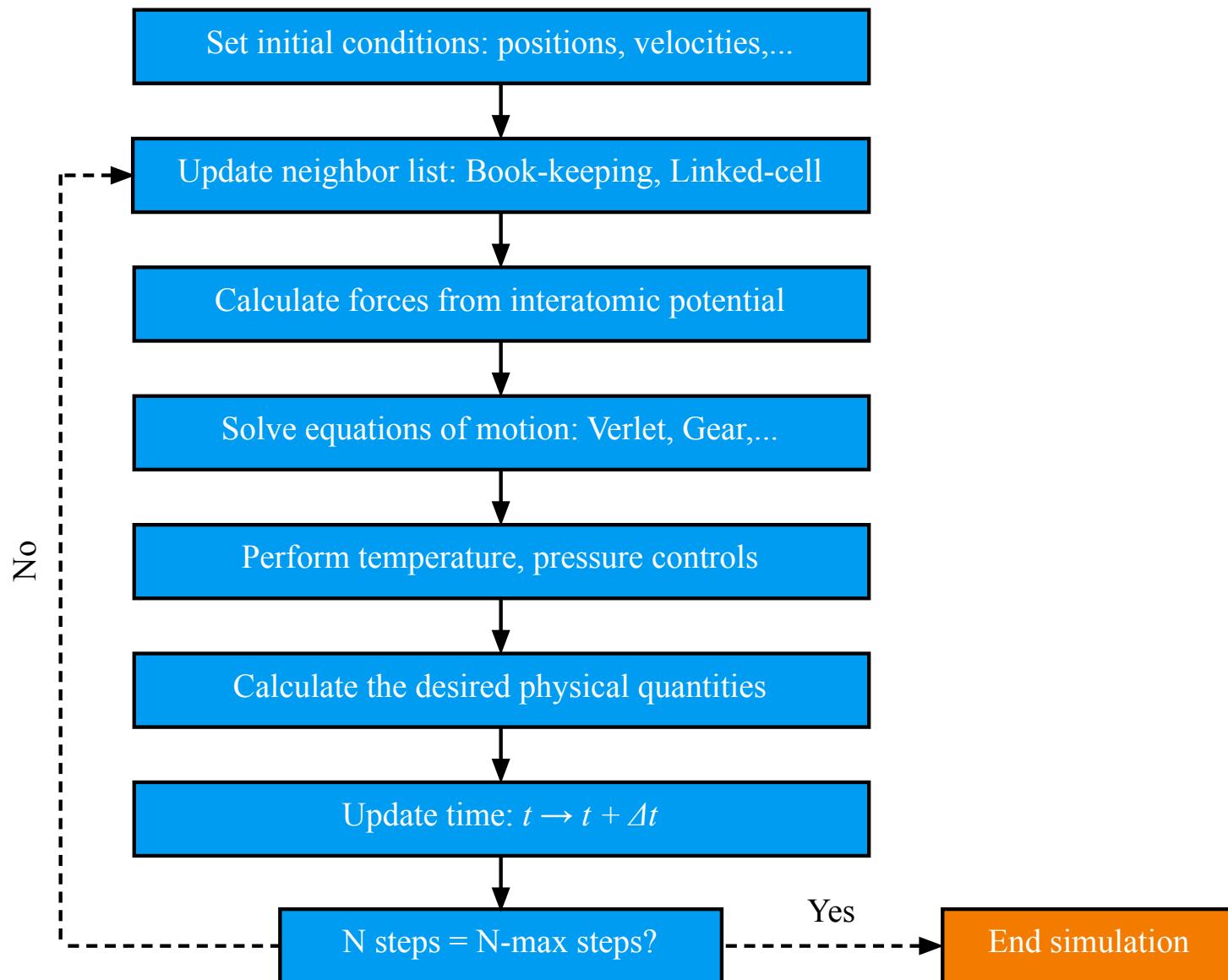
❖ Classical Molecular Dynamics

- Nuclei and electrons are not explicitly treated
- Atoms are treated as classical objects and ruled classical mechanics laws
- Simulation of systems: many thousand or millions particles
- Biology, materials science,...

❖ Quantum Molecular Dynamics

- Quantum mechanical effects of electrons (and nuclei)
- More accurate and improvement over classical method
- Simulation of systems: few hundreds of particles (due to computer resource)
- Covalently bonded, metallic systems, reactions of surfaces,...

Molecular Dynamics algorithm

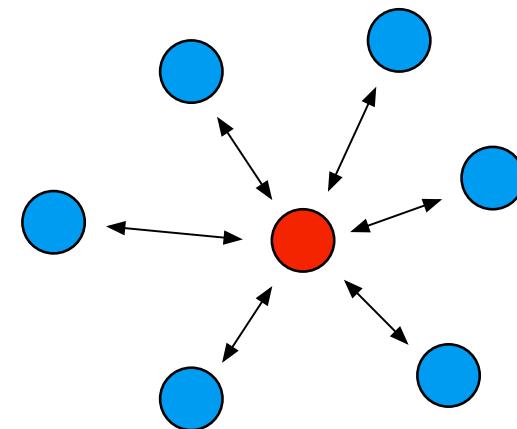


Equations of Motion

Newton's equations of motion

Newton's second law:

$$F_i = m_i a_i = m_i \frac{dv_i}{dt} = m_i \frac{d^2 r_i}{dt^2}$$



Force = Derivative of the interacting potential:

$$F_i = -\nabla_i U(r_1, r_2, \dots, r_N) = -\frac{\partial U}{\partial r_i}$$

Equations of motion (EoM):

$$\frac{d^2 r_i}{dt^2} = -\frac{1}{m_i} \frac{\partial U}{\partial r_i}$$

MD simulation = solve equations of motion

N-body: $3N$ second-order differential equations

Given interacting potential, one can find the trajectories of the particles for an interval time frame, the velocities of the particles and other physical quantities

Equations of motion are time-reversible

From Lagrangian formulation

Lagrangian:

$$L(q, \dot{q}) = K(\dot{q}) - U(q)$$

\dot{q} time derivatives of q

Generalized coordinates and momenta:

$$q = (q_1, q_2, \dots, q_N)$$

$$p = (p_1, p_2, \dots, p_N)$$

Euler-Lagrange equation:

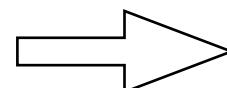
$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0$$

Advantage: can treat the simulated system in any coordinate

N-body: $3N$ second-order differential equations

Kinetic energy in Cartesian coordinates:

$$K = \sum_i \frac{m_i v_i^2}{2} = \sum_i \frac{m_i \dot{r}_i^2}{2}$$



$$\frac{d^2 r_i}{dt^2} = -\frac{1}{m_i} \frac{\partial U}{\partial r_i}$$

From Hamiltonian formulation

Hamiltonian:

$$H(q, p) = K(p) + U(q)$$

Generalized coordinates and momenta:

$$q = (q_1, q_2, \dots, q_N)$$

$$p = (p_1, p_2, \dots, p_N)$$

Equations of motion:

$$\frac{\partial p_i}{\partial t} = -\frac{\partial H}{\partial q_i}$$

$$\frac{\partial q_i}{\partial t} = \frac{\partial H}{\partial p_i}$$

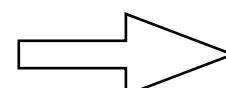
Advantage: can treat the simulated system in any coordinate

N-body: $6N$ first-order differential equations

For Cartesian coordinates:

$$\frac{\partial p_i}{\partial t} = -\frac{\partial U}{\partial r_i}$$

$$\frac{\partial r_i}{\partial t} = \frac{\partial K}{\partial p_i}$$



$$\frac{d^2 r_i}{dt^2} = -\frac{1}{m_i} \frac{\partial U}{\partial r_i}$$

Integration Algorithm

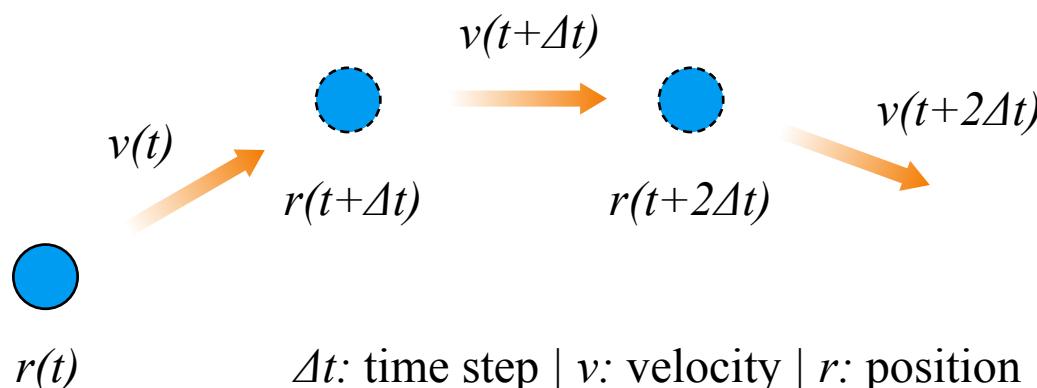
Criteria for a good integrator

❖ Criteria for integrator

- Conserves energy and momentum, and is time-reversible
- Be able to approximate true trajectory
- Allow a long time-step for integration
- Be computationally efficient: easy to implement, take up little memory, fast,...

❖ Numerical schemes

- Based on Finite Difference Method (time is discretized on a finite grid)
- Euler method, Verlet method, Beeman method, Gear method,...



Position & velocity expansions

Velocity:

$$v(t + \Delta t) = v(t) + \frac{dv(t)}{dt} \Delta t + \frac{1}{2!} \frac{d^2 v(t)}{dt^2} (\Delta t)^2 + O[(\Delta t)^3]$$

Position:

$$r(t + \Delta t) = r(t) + v(t) \Delta t + \frac{1}{2!} \frac{dv(t)}{dt} (\Delta t)^2 + O[(\Delta t)^3]$$

❖ Computation errors

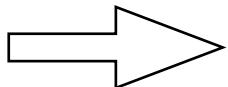
- Truncation errors: related to the accuracy of the finite difference method with respect to the true solution. These are intrinsic to the integration algorithm.
- Round-off errors: related to errors associated to a particular implementation of the integration algorithm such as the number of digits used in computer floating point arithmetics.

The Verlet algorithm

Forward and backward time-steps of position:

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2!} \frac{dv(t)}{dt} (\Delta t)^2 + \frac{1}{3!} \frac{d^2v(t)}{dt^2} (\Delta t)^3 + O[(\Delta t)^4]$$

$$r(t - \Delta t) = r(t) - v(t)\Delta t + \frac{1}{2!} \frac{dv(t)}{dt} (\Delta t)^2 - \frac{1}{3!} \frac{d^2v(t)}{dt^2} (\Delta t)^3 + O[(\Delta t)^4]$$


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

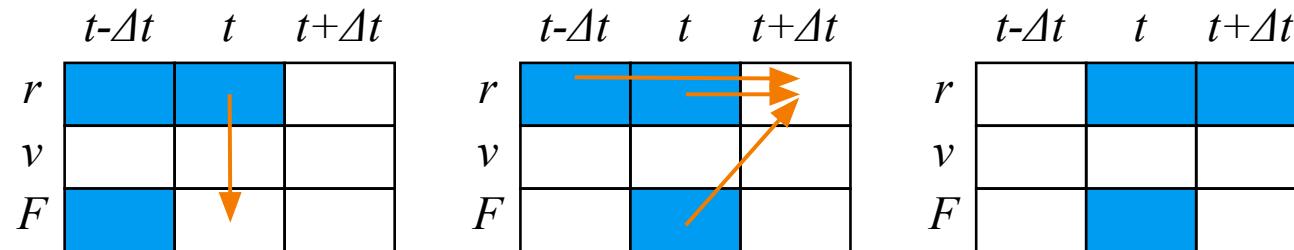
Estimation of velocity:

$$v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t}$$

Acceleration:

$$a(t) = \frac{dv(t)}{dt} = \frac{F(t)}{m}$$

The Verlet algorithm



❖ Implementation

- Given current position and the position at the end of previous step
- Compute force at the current position
- Compute new position from the present and previous positions, and the present force
- Advance to next time step and repeat (1) → (3)

❖ Advantages and drawbacks

- Simple to implement; time-reversible; no drift in energy
- Fluctuates heavily; not self-starting; velocities & positions are inaccurate

The leap-frog Verlet algorithm

Start with half-step velocity:

$$v(t + \frac{1}{2}\Delta t) = v(t - \frac{1}{2}\Delta t) + a(t)\Delta t$$

Acceleration:

$$a(t) = \frac{dv(t)}{dt} = \frac{F(t)}{m}$$

Then calculate position at full-step:

$$r(t + \Delta t) = r(t) + v(t + \frac{1}{2}\Delta t)\Delta t$$

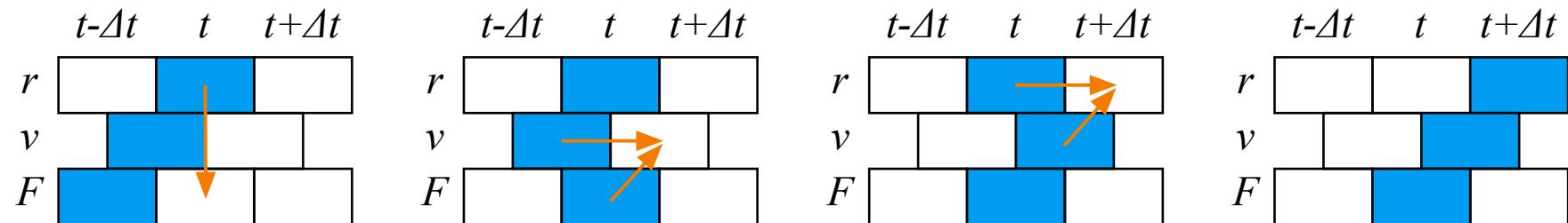
Velocities are at different times than positions

Leap-frog: velocities leap over positions then the positions, in turn, leap over the velocities

Estimation of velocity at full-step:

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

The leap-frog Verlet algorithm



❖ Implementation

- Given current position and the velocity at the last half-step
- Compute force at the current position
- Compute new velocity at next half-step
- Compute new position from the present positions and next half-step velocity
- Advance to next time step and repeat (1) → (4)

❖ Advantages and drawbacks

- Simple to implement; time-reversible; explicitly velocities; reduce num. error
- Fluctuates; positions & velocities are asynchronous; more expensive than Verlet

The velocity Verlet algorithm

Position:

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

Acceleration:

$$a(t) = \frac{dv(t)}{dt} = \frac{F(t)}{m}$$

Velocity at half-step:

$$v(t + \frac{1}{2}\Delta t) = v(t) + \frac{1}{2}a(t)\Delta t$$

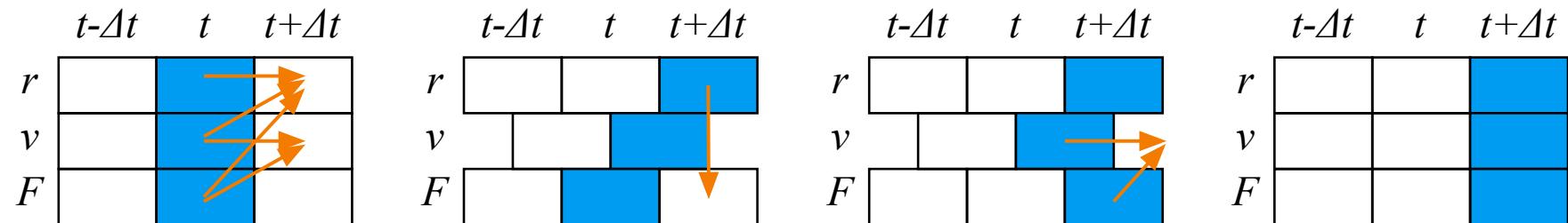
Acceleration at next step:

$$a(t + \Delta t) = \frac{F(t + \Delta t)}{m}$$

Velocity at full-step:

$$v(t + \Delta t) = v(t + \frac{1}{2}\Delta t) + \frac{1}{2}a(t + \Delta t)\Delta t$$

The velocity Verlet algorithm



❖ Implementation

- Given current position, velocity and force
- Compute new position from the present position, velocity and force
- Compute new velocity at the next half-step from the present velocity and force
- Compute force at the new position
- Compute new velocity at full step
- Advance to next time step and repeat (1) → (5)

❖ Advantages and drawbacks

- Simple to implement; time-reversible; velocity synchrony; reasonably accurate
- Fluctuates heavily in total energy; cost in time and memory than leap-frog Verlet

Predictor-corrector algorithm

Predict position and their time derivatives at next time step:

$$\tilde{q}(t + \Delta t) = Gq(t)$$

$q(t)$ has $p+1$ components

→ p -order Gear

Predictor: Pascal's upper-triangular matrix

$$G = \begin{pmatrix} 1 & 1 & 1 & 1 & \dots \\ 0 & 1 & 2 & 3 & \dots \\ 0 & 0 & 1 & 3 & \dots \\ 0 & 0 & 0 & 1 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Coordinates & their time derivatives:

$$q(t) = \begin{pmatrix} r(t) \\ (dr(t)/dt)\Delta t \\ (d^2r(t)/dt^2)(\Delta t)^2 / 2! \\ (d^3r(t)/dt^3)(\Delta t)^3 / 3! \\ \vdots \end{pmatrix}$$

Predictor-corrector algorithm

Notations for original and predicted vectors:

$$r^{(n)} = \frac{1}{n!} \frac{d^n r}{dt^n} (\Delta t)^n \quad \tilde{r}^{(n)} = \frac{1}{n!} \frac{d^n \tilde{r}}{dt^n} (\Delta t)^n$$

The fifth-order predictor (Gear5):

$$\begin{pmatrix} \tilde{r}^{(0)}(t + \Delta t) \\ \tilde{r}^{(1)}(t + \Delta t) \\ \tilde{r}^{(2)}(t + \Delta t) \\ \tilde{r}^{(3)}(t + \Delta t) \\ \tilde{r}^{(4)}(t + \Delta t) \\ \tilde{r}^{(5)}(t + \Delta t) \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 1 & 2 & 3 & 4 & 5 \\ 0 & 0 & 1 & 3 & 6 & 10 \\ 0 & 0 & 0 & 1 & 4 & 10 \\ 0 & 0 & 0 & 0 & 1 & 5 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} r^{(0)}(t) \\ r^{(1)}(t) \\ r^{(2)}(t) \\ r^{(3)}(t) \\ r^{(4)}(t) \\ r^{(5)}(t) \end{pmatrix}$$

Predictor-corrector algorithm

Difference in acceleration (error signal):

$$\Delta a(t + \Delta t) = \frac{\tilde{F}(t + \Delta t)}{m} - \frac{d^2 \tilde{r}(t + \Delta t)}{dt^2}$$

Positions and their time derivatives are corrected:

$$q(t + \Delta t) = \tilde{q}(t + \Delta t) + \frac{1}{2} c \Delta a(t + \Delta t) (\Delta t)^2$$

$$q(t + \Delta t) = \tilde{q}(t + \Delta t) + \dots$$

$$c(\Delta t)^2 \times \frac{1}{2} \left[\frac{\tilde{F}(t + \Delta t)}{m} - \frac{d^2 \tilde{r}(t + \Delta t)}{dt^2} \right]$$

Correction vector:

$$c = \begin{pmatrix} 3/20 \\ 251/360 \\ 1 \\ 11/18 \\ 1/6 \\ 1/60 \end{pmatrix}$$

Predictor-corrector algorithm

❖ Implementation

- Given current position and its time derivatives up to chosen order
- Compute the predicted coordinates at the next step from the current coordinates and predictor matrix
- Compute force at the next step from the predicted coordinates above
- Compute the error signal and the corrected coordinates with the use of corrector vector
- Advance to next time step and repeat (1) → (4)

❖ Advantages and drawbacks

- Small energy fluctuation; more advanced than Verlet for small time-step
- Not time-reversible (large drift in energy); requires more computational resources

Newer algorithm: Theoretically well-motivated, reversible, ~Gear4 accuracy

“Symplectic reversible integrators: Predictor–corrector methods”

G. J. Martyna and M. E. Tuckerman, J. Chem. Phys. 102 (1995) 8071

So which one to use?

"How accurate a simulation has to be in order to provide reliable statistical results is still a matter of debate. The purpose is never to produce reliable trajectories. Whatever accuracy the forces and the algorithms have, significant deviations from the exact solution will inevitably occur.

Also in the real physical world individual trajectories have no meaning: in a quantum mechanical sense they do not exist and even classically they become unpredictable in the long run due to the non-isolated character of any real system. So what counts are statistical averages.

It seems that very little systematic evaluation of algorithm has been done with this in mind. We have the impression that a noise as high as 10% of the kinetic energy fluctuation is still acceptable, although the accuracy of fluctuations may not be sufficient to obtain thermodynamic data from them.

*With such a level of inaccuracy **the Verlet or leap-frog algorithm is always to be preferred.***

*H. J. C. Berendsen and W. F. van Gunsteren
in Molecular-Dynamics Simulations of Statistical-Mechanical Systems
Enrico Fermi Summer School, Varenna, Italy, 1986, pp 43-65*

Interatomic Potentials

Interatomic potentials

Interatomic potentials are key components of molecular dynamics simulation because forces are derived from potentials. Realistic outcomes from the molecular dynamics simulation requires accurate potentials:

$$F_i = -\nabla_i U(r_1, r_2, \dots, r_N)$$

Classical: does not include any electronic degrees of freedom explicitly, all the electronic effects are incorporated into the potentials

Can be expanded in terms of a many-body components:

$$U(r_1, r_2, \dots, r_N) = \sum_i U_1(r_i) + \sum_{i,j>i} U_2(r_i, r_j) + \sum_{i,j>i, k>j} U_3(r_i, r_j, r_k) + \dots$$

pair potential

three-body potential

one-body term and it is only meaningful if the atoms are placed in an external field

Lennard-Jones potential

Pair-wise potential, proposed in 1924 by Lennard-Jones, for studying systems with weak, pair-wise interactions:

$$U_{LJ}(r) = \varepsilon_0 \left[\left(\frac{r_0}{r} \right)^m - \frac{m}{n} \left(\frac{r_0}{r} \right)^n \right]$$

Repulsive part

Attractive part

$(m,n) = (12,6)$ Rare gases

$(m,n) = (8,4)$ Metallic

r_0 Equilibrium bond distance

ε_0 Equilibrium bond energy

Standard form: $(m,n) = (12,6)$

Attractive: motivated by van der Waals interactions

Repulsive: no clear theoretical reason, $12 = 2 \times 6 \rightarrow$ make calculations easier

Simple pair-wise, properties are well known (phase behaviour etc.), still frequently used in soft matter simulations and testing of theories of statistical physics

Lennard-Jones potential

Alternative form:

$$U_{LJ}(r) = 4\epsilon_0 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

$$r_0 = 2^{1/6} \sigma \approx 1.122\sigma$$

Characteristic scales:

ϵ_0 Energy

σ Length

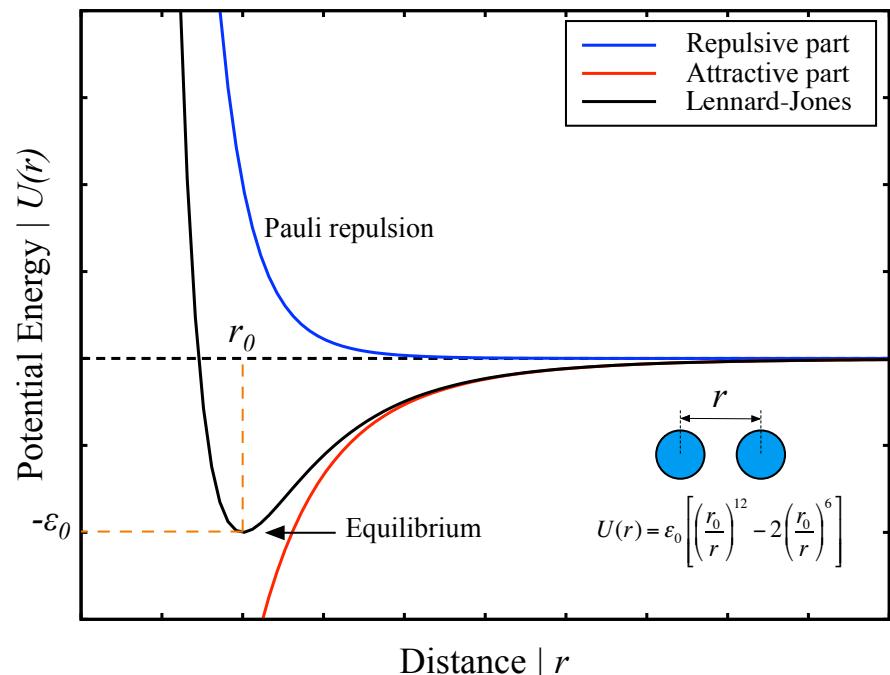
m Mass

→ time:

$$\tau = \sigma \sqrt{\frac{m}{\epsilon}}$$

Long-range interaction:

$$U_{CL}(r) = \frac{Q_1 Q_2}{4\pi\epsilon r}$$



Buckingham potential

Pair potential, proposed by Buckingham, describes the short-range interaction of two atoms that are not directly bonded:

$$U_{BK}(r) = Ae^{-Br} - \frac{C}{r^6}$$

Coulomb-Buckingham: extension of the Buckingham potential for application to ionic systems

$$U_{CB}(r) = Ae^{-Br} - \frac{C}{r^6} + \frac{Q_1 Q_2}{4\pi\epsilon r}$$

Buckingham potential “turns over” as atomic distance becomes small:

→ is problematic when dealing with a structure with very short interatomic distances, as the nuclei that cross the turn-over distance will become strongly and unphysically bound to one another at a distance close to zero.

Embedded atom method potential

Many-body potential, proposed by Daw and Baskes for metallic systems and based on the ideas of effective medium theory (real material is replaced by “jellium” = homogeneous electron gas + positive background nuclei density):

$$E = \frac{1}{2} \sum_{i \neq j} \varphi_{ij}(r_{ij}) + \sum_i F_i(\bar{\rho}_i)$$

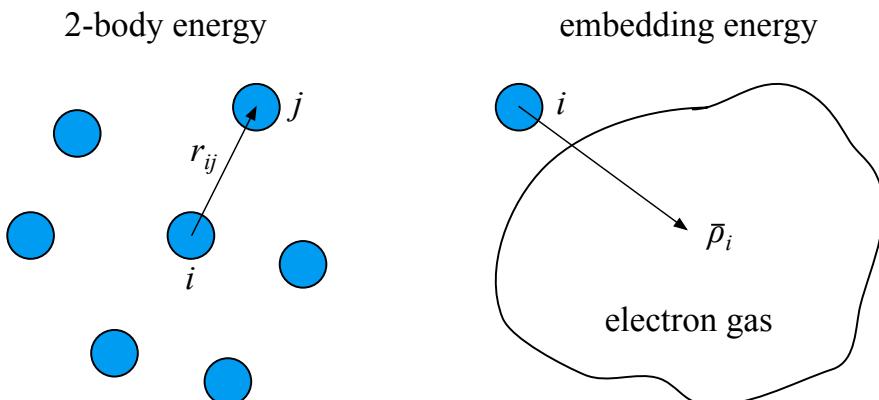
$F_i(\bar{\rho}_i)$ Embedding energy
 $\varphi_{ij}(r_{ij})$ Pair energy

Electron density: linear superposition of contribution of neighbor atoms

$$\bar{\rho}_i = \sum_{i \neq j} \rho_j(r_{ij})$$

$\rho_j(r_{ij})$ Individual charge

Central-force characteristic:
Depend on the interatomic distances only and not on bond angles → challenging for systems with covalent effects



Embedded atom method potential

❖ Potential forms

- Usually determined empirically by fitting to various bulk properties. For the metals, the functions are determined by fitting to bulk lattice constant, sublimation energy, elastic constants and vacancy formation energy.
- For energetic processes: add the universal ZBL repulsive potential (by Ziegler, Biersack and Littmark) at some short interatomic separation.

❖ Some limitations

- There are many available potential forms and parametrizations for any typical metal. Some might have better properties when describing, e.g., point defects, while others might provide a better description for diffusivity.
- While it is possible to construct potentials for the simulation of metal alloys, the potential formalism makes it quite tricky to include non-metallic elements, e.g. C, N, O,...
- Non-equilibrium simulations are based on the assumption that the equilibrium parametrization of the potential can adequately describe processes far away from equilibrium (electron density).

Modified embedded atom method potential

Many-body potential, proposed by Baskes for metallic + covalent systems:

$$E = \frac{1}{2} \sum_{i \neq j} \varphi_{ij}(r_{ij}) + \sum_i F_i(\bar{\rho}_i)$$

$F_i(\bar{\rho}_i)$ Embedding energy
 $\varphi_{ij}(r_{ij})$ Pair energy

Electron density: linear superposition of contribution of neighbor atoms and include angular-dependent contributions

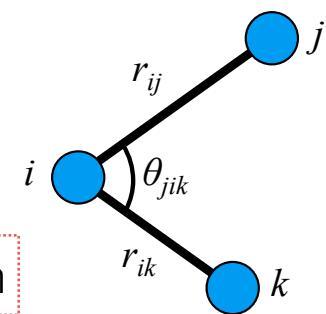
$$\bar{\rho}_i = \sum_{i \neq j} \rho_j(r_{ij}) + \sum_{j,k \neq i} \left[a_j^1 a_k^1 \cos \theta_{jik} - a_j^2 a_k^2 (1 - 3 \cos^2 \theta_{jik}) \right] \rho_j(r_{ij}) \rho_k(r_{ik})$$

A simplified version that employs cubic splines:

$$\bar{\rho}_i = \sum_{i \neq j} \rho_j(r_{ij}) + \frac{1}{2} \sum_{j,k \neq i} f_{ij}(r_{ij}) f_{ik}(r_{ik}) g_i(\cos \theta_{jik})$$

radial function

angular function



Angular dependent potential

Many-body potential, suggested by Mishin based on the embedded atom method potential model (initially, for investigation of the Fe-Ni system):

$$E = \frac{1}{2} \sum_{i \neq j} \varphi_{ij}(r_{ij}) + \sum_i F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{i,\alpha} (\mu_i^\alpha)^2 + \frac{1}{2} \sum_{i,\alpha,\beta} (\lambda_i^{\alpha\beta})^2 - \frac{1}{6} \sum_i v_i^2$$

Non-central components of bonding:

dipole and quadrupole distortions

$$\mu_i^\alpha = \sum_{j \neq i} u_{ij}(r_{ij}) r_{ij}^\alpha$$

$$\lambda_i^{\alpha\beta} = \sum_{j \neq i} w_{ij}(r_{ij}) r_{ij}^\alpha r_{ij}^\beta$$

$$v_i = \sum_\alpha \lambda_i^{\alpha\alpha}$$

pair-wise function

In modified embedded atom method, angular-dependent interactions also introduced through dipole, quadrupole and higher-order multipoles. However, in modified embedded atom method, they constitute a part of the tensor electron density whereas in the angular-dependent potential they contribute directly to the total energy.

Stillinger-Weber potential

Two-body + three-body potential, introduced by Stillinger and Weber for modeling semiconductors:

$$E = \sum_{i,j>i} U_2(r_i, r_j) + \sum_{i,j>i, k>j} U_3(r_i, r_j, r_k)$$

Single-particle potential normally describes the wall and external forces to which the system is subject therefore it is absent

Two-body part:

- Similar to Lennard-Jones potential
- Smoothly terminates at the cutoff distance

$$U_2(r) = \begin{cases} \varepsilon A \left(\frac{B}{r^p} - \frac{1}{r^q} \right) e^{(r-a)^{-1}}, & r \leq a \\ 0, & r > a \end{cases} \quad A, B, q, p, a \quad \text{Positive}$$

Stillinger-Weber potential

Three-body part:

$$U_3(r_i, r_j, r_k) = h_{jik} + h_{ijk} + h_{ikj}$$

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \varepsilon \lambda e^{\gamma(r_{ij}-a)^{-1} + \gamma(r_{ik}-a)^{-1}} \left(\cos \theta_{jik} + \frac{1}{3} \right)^2 \quad \lambda, \gamma > 0$$

The original intention of this potential is to describe the bonding in silicon. That means the potential should predict the diamond-like tetrahedral structure with bond angle of 109.47° as the most stable atomic configuration.

Advantage: Fairly realistic description of crystalline silicon.

Disadvantages:

- Cannot predict the right energies of the non-tetrahedral polytypes found under pressure (due to built-in tetrahedral bias); the coordination of the liquid is too low; surface structures are not correct.
- Transferability problems: it is difficult to use the potential under conditions different from those it was designed for.

Tersoff potential

Developed by Tersoff, based on the concept of bond order: the strength of a bond between two atoms is not constant, but depends on the local environment.

$$E = \frac{1}{2} \sum_{i \neq j} f_c(r_{ij}) [f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$

cutoff function

$$f_R(r_{ij}) = A e^{-\lambda_1 r_{ij}} \quad \text{Repulsive pair}$$
$$f_A(r_{ij}) = -B e^{-\lambda_2 r_{ij}} \quad \text{Attractive pair}$$

Bond-order term which includes three-body interactions and angularity:

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-\frac{1}{2n}}$$
$$\zeta_{ij} = \sum_{k \neq i, j} f_c(r_{ik}) g(\theta_{jik}) e^{\lambda_3^m (r_{ij} - r_{ik})^m}$$

coordination function

angular function

$$g(\theta_{jik}) = \gamma_{ijk} \left(1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta_{jik})^2} \right)$$

h minimum; c strength of the angular effect

d determines how sharp the dependence on angle is

Tersoff potential

Cutoff function:

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} \leq R \\ \frac{1}{2} + \frac{1}{2} \cos\left(\frac{\pi(r_{ij} - R)}{S - R}\right), & R < r_{ij} \leq S \\ 0, & r_{ij} > S \end{cases}$$

cutoff distance

chosen so as to include the first-neighbor shell only for several selected high-symmetry bulk structure

$A, B, \lambda_1, \lambda_2, n, \beta$ used for two-body interactions

$m, \gamma, \lambda_3, c, d, h$ used for three-body interactions

R, S both two-body and three-body interactions

Tersoff potential

Correction 1: original form does not always reproduce correctly the elastic constants and melting point

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} \leq R \\ \frac{1}{2} + \frac{9}{16} \cos\left(\frac{\pi(r_{ij} - R)}{S - R}\right) - \frac{1}{16} \cos\left(\frac{3\pi(r_{ij} - R)}{S - R}\right), & R < r_{ij} \leq S \\ 0, & r_{ij} > S \end{cases}$$

Correction 2: increase the flexibility of the potential

$$g(\theta) = c_1 + g_0(\theta)g_a(\theta)$$

$$g_0(\theta) = \frac{c_2(h - \cos\theta)^2}{c_3 + (h - \cos\theta)^2}$$

$$g_a(\theta) = 1 + c_4 e^{-c_5(h - \cos\theta)^2}$$

Tersoff potential

Correction 3: for simulations of high-energy events (sputtering simulations,...)

$$\tilde{U}_{ij} = f(r_{ij})U_{ij} + (1 - f(r_{ij}))U_{ij}^{ZBL}$$

Fermi-like function used to smoothly join the ZBL with the Tersoff parts

ZBL universal screening function

$$U_{ij} = f_c(r_{ij}) [f_R(r_{ij}) + b_{ij}f_A(r_{ij})]$$
$$f(r) = \frac{1}{1 + e^{-b_f(r-r_f)}}$$

$$U_{ij}^{ZBL} = \frac{1}{4\pi\epsilon_0} \frac{Z_1 Z_2 e^2}{r_{ij}} \phi\left(\frac{r_{ij}}{a}\right)$$

$$a = \frac{0.8854a_0}{Z_i^{0.23} + Z_j^{0.23}}$$
$$\phi(x) = 0.1818e^{-3.2x} + 0.5099e^{-0.9423x} + ...$$
$$+ 0.2802e^{-0.4029x} + 0.02817e^{-0.2016x}$$

Tersoff potential

- The potentials contain quite few number of functional forms as compared to EAM, MEAM and ADP.
- Typically, 12 parameters are required for Tersoff binary system, while for MEAM and ADP, we need from 13 to 16 parameters are needed.
- Because of the disparate characteristic of H and C, Brenner found that the Tersoff form could not be satisfactorily fitted to hydrocarbon systems. By somewhat generalizing the bond-order function, a new and improved potential (called Tersoff-Brenner potential) could be obtained.
- However, the Tersoff (and Tersoff-Brenner) form cannot correctly choose between certain structural arrangements and it does not accurately model the so-called “ π -bond” in hydrocarbons. These are limitations in the transferability of the model because it was, in essence, designed to model certain structural arrangements at the expense of others.

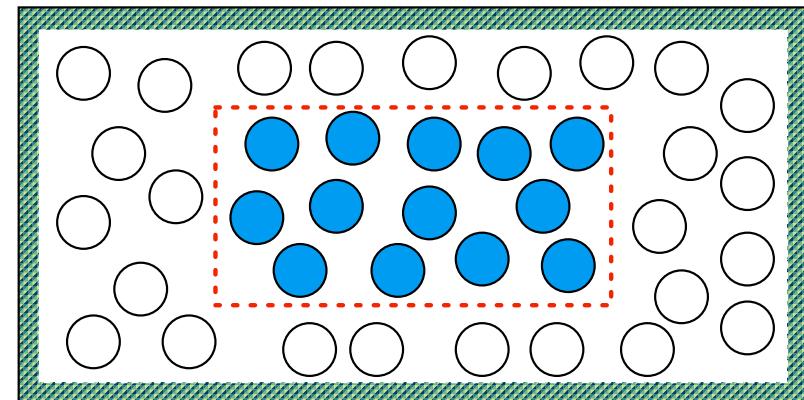
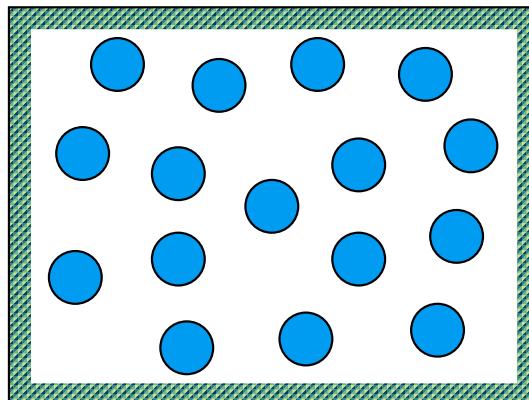
Temperature and Pressure Controls

Molecular Dynamics ensembles

- Molecular dynamics simulations: The microscopic quantities are produced
- Microscopic properties: Particles' positions, and momenta
- Experiments: The macroscopic quantities are usually explored
- Macroscopic properties: Temperature, Pressure, and Number of particles
- Link between 2 levels: Statistical mechanics
- Positions and momenta: can be considered as coordinates in a multi-dimensional space called phase space
- A single point in phase space describes a microscopic state of the system. A collection of points in phase space satisfying the conditions of a particular thermodynamic state is called an ensemble.

Molecular Dynamics ensembles

- Common ensembles in statistical physics are: NVE (microcanonical), NVT (canonical), NPT (isothermal-isobaric) and μ VT (grand canonical)

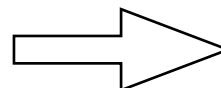


- The first three are often used in Molecular Dynamics simulations (the last one is used, for example, in Monte Carlo simulations).
- Without external controls, Molecular Dynamics should generate a microcanonical ensemble. However, numerical errors and force fluctuations cause fluctuations in energy (and possible drifts as well).
- Temperature and pressure are quantities that are typically constant in experiments. Thus, it is natural to take these as the control variables for simulations of small atomistic systems.

Temperature in Molecular Dynamics

The equipartition theorem states that the average kinetic energy per particle (with 3 degrees of freedom) is related to temperature as:

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}k_B T$$



$$T = \frac{1}{3(N-1)k_B} \sum_i m_i v_i^2$$

N-particle system, Zero or fixed total momentum

This is different from the true temperature because the kinetic energy fluctuates in time. For such reason, it is called “instantaneous temperature”.

NVT and NPT, under the thermal equilibrium condition, the relative variance of the temperature is:

$$\frac{\sigma_T^2}{\langle T \rangle^2} = \frac{\langle T^2 \rangle - \langle T \rangle^2}{\langle T \rangle^2} = \frac{2}{3N}$$

Temperature controls

Velocity rescaling:

$$v_i^0(t) = \lambda v_i(t)$$

One of the simplest ways to control the temperature. When we want the system temperature to reach a desired temperature from the current temperature.

Rescaling factor:

$$\lambda = \sqrt{\frac{T_0}{T}}$$

The kinetic energy will remain constant in time, with zero fluctuations. The rescaling procedure totally suppresses any possible fluctuation in the temperature of the system, and hence, it does not provide the correct statistical ensemble as expected from relative variance of the temperature.

Temperature controls

Berendsen thermostat: based on some velocity rescaling, however the rescaling is “softer” as compared to the original velocity rescaling method by assigning a time scale for the updating of the velocities.

$$\frac{d^2 r_i}{dt^2} = -\frac{1}{m_i} \frac{\partial U}{\partial r_i} + \gamma \left(\frac{T_0}{T} - 1 \right) \frac{dr_i}{dt}$$

A frictional term is added to the equations of motion to describe the weak-coupling to the heat bath.

Rescaling factor:

$$\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T} - 1 \right)}$$

Note:

$\tau_T = \Delta t$ Back to original velocity rescaling

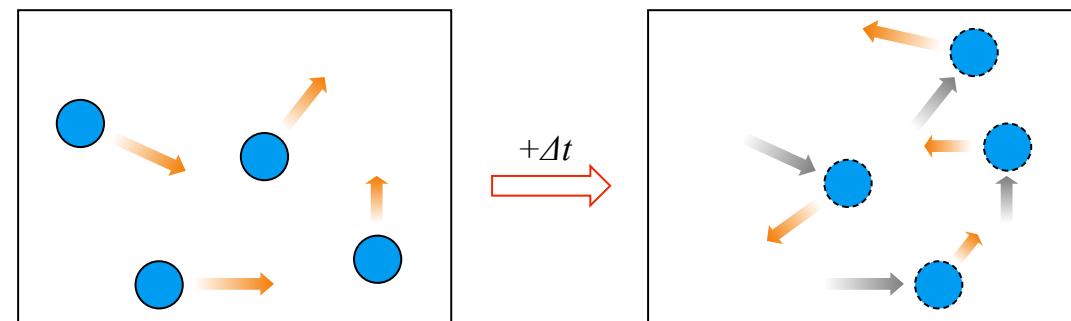
$\tau_T \rightarrow \infty$ No rescaling

Temperature controls

Andersen thermostat: some particles undergo random “collisions” with external degrees of freedom. The velocities of these particles are changed randomly based on a Maxwell-Boltzmann distribution:

$$P(v) = \left(\frac{m}{2\pi k_B T_0} \right)^{1/2} e^{-\frac{mv^2}{2k_B T_0}}$$

This can be thought as coupling all the atoms in the system to an imaginary external heat bath that imposes the desired temperature.



The stochastic collision procedure in simulation is not necessary to be done every time-step but rather by adopting a collision frequency.

Due to the perturbation of velocities, i.e., generating discontinuous velocity trajectories, the method messes up the natural dynamics of the system

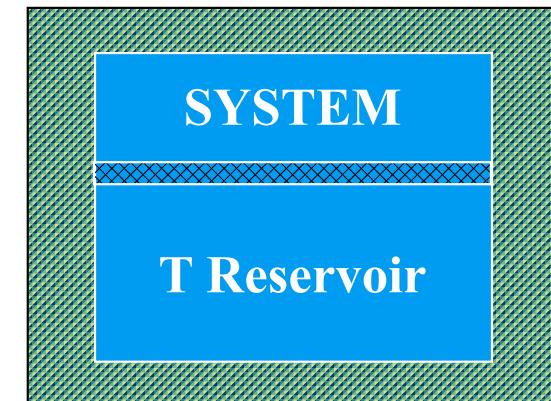
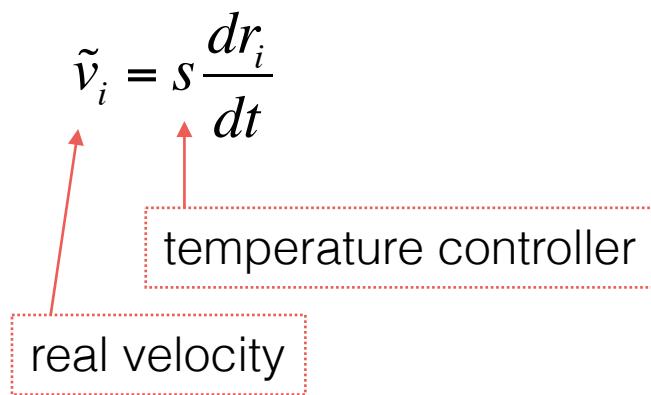
Temperature controls

Nosé-Hoover thermostat: extend the Lagrangian of the system in a way that it contains additional, artificial coordinates and velocities (Due to this, it is called the extended-system method):

Add additional degrees of freedom to the system which are the “position”, the conjugate “momentum” and effective “mass”:

$$p_s = Q\dot{s}$$

The interaction between the physical system and the heat bath is expressed via the scaling of the velocities:



Temperature controls

Nosé-Hoover thermostat (continue...):

The Lagrangian of the extended system:

$$L_{\text{Nosé}} = \frac{1}{2} \sum_i m_i s^2 \left(\frac{dr_i}{dt} \right)^2 - U(r) + \frac{Q}{2} \dot{s}^2 - (N_f + 1) k_B T_0 \ln s$$

Third and forth terms are the kinetic and potential energies associated with additional “position” variable. Logarithmic dependence of the potential is essential for producing the canonical ensemble.

Equations of motion:

$$\frac{d^2 r_i}{dt^2} = -\frac{1}{m_i s^2} \frac{\partial U}{\partial r_i} - \frac{2\dot{s}}{s} \frac{dr_i}{dt} \quad \frac{d^2 s}{dt^2} = \frac{1}{Q} \sum_i m_i s \left(\frac{dr_i}{dt} \right)^2 - \frac{(N_f + 1) k_B T_0}{Q s}$$

Note: while the atomic coordinates are identical in both systems the timescale in the virtual system is stretched.

Temperature controls

Nosé-Hoover thermostat (continue...):

The use of an extended system with a stretched timescale is not very intuitive and rather impractical. Therefore, the equations of motion can be reformulated in terms of real system variables:

$$\tilde{s} = s, \quad \tilde{r}_i = r_i, \quad \tilde{p}_i = p_i / s, \quad \tilde{t} = \int_0^t \frac{dt}{s}$$

$$\zeta = p_s / Q = \dot{s} \quad \tilde{\xi} = \xi = \dot{\tilde{s}} / \tilde{s}$$

thermodynamic friction coefficient (simplified by Hoover)

Equations of motion:

$$\frac{d^2\tilde{r}_i}{d\tilde{t}^2} = -\frac{1}{m_i} \frac{\partial U}{\partial \tilde{r}_i} - \tilde{\xi} \frac{d\tilde{r}_i}{d\tilde{t}} \quad \frac{d\tilde{\xi}}{d\tilde{t}} = \frac{1}{Q} \sum_i m_i \left(\frac{d\tilde{r}_i}{d\tilde{t}} \right)^2 - \frac{N_f k_B T_0}{Q}$$

Temperature controls

Nosé-Hoover thermostat (continue...):

$$T = \frac{1}{3(N-1)k_B} \sum_i m_i v_i^2 \quad \longrightarrow \quad \frac{d\tilde{\xi}}{d\tilde{t}} = \frac{N_f k_B T}{Q} \left(1 - \frac{T_0}{T} \right)$$

In Nosé-Hoover thermostat, the energy of the physical system fluctuates, however, the energy of the system plus the heat bath is conserved.

Hamiltonian:

$$H_{\text{Nosé-Hoover}} = \frac{1}{2} \sum_i m_i \left(\frac{d\tilde{r}_i}{d\tilde{t}} \right)^2 + U(\tilde{r}) + \frac{Q}{2} \tilde{\xi}^2 + N_f k_B T_0 \ln s$$

Note: care must be taken in the choice of the fictitious mass. Too large values of (loose coupling) may cause a poor temperature control. Too small values (tight coupling) may cause high-frequency temperature oscillations leading to the same effect.

Pressure in Molecular Dynamics

From the general formulation of the equipartition theorem:

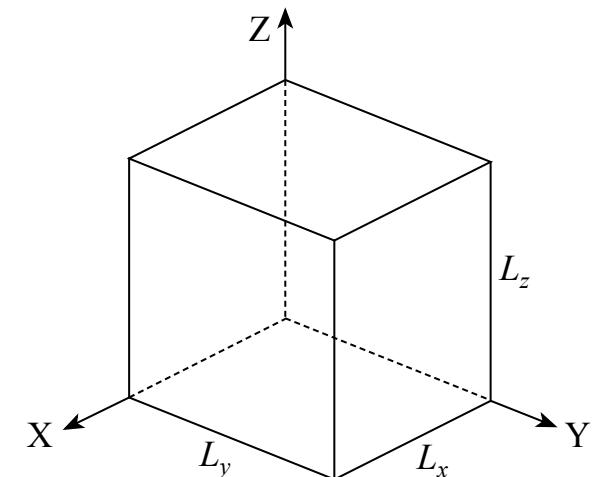
$$\left\langle p_k \frac{\partial H}{\partial p_k} \right\rangle = \left\langle q_k \frac{\partial H}{\partial q_k} \right\rangle = k_B T$$

Using the equations of Hamiltonian mechanics:

$$\left\langle p_k \frac{\partial H}{\partial p_k} \right\rangle = \left\langle q_k \frac{\partial H}{\partial q_k} \right\rangle = k_B T$$

Hence:

$$\left\langle \mathbf{r}_i \cdot \mathbf{F}_i^{TOT} \right\rangle = \left\langle x_i \frac{dp_i^x}{dt} \right\rangle + \left\langle y_i \frac{dp_i^y}{dt} \right\rangle + \left\langle z_i \frac{dp_i^z}{dt} \right\rangle = -3k_B T$$



Pressure in Molecular Dynamics

Sum over all particles:

$$\left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i^{TOT} \right\rangle = -3Nk_B T$$

Decomposed total force into internal and external forces:

$$\mathbf{F}_i^{TOT} = \mathbf{F}_i + \mathbf{F}_i^{EXT}$$

$$\left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i^{EXT} \right\rangle = L_x(-PL_yL_z) + L_y(-PL_xL_z) + L_z(-PL_xL_y) = -3PV$$

Therefore:

$$-3Nk_B T = \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle - 3PV \quad \Rightarrow \quad PV = Nk_B T + \frac{1}{3} \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle$$

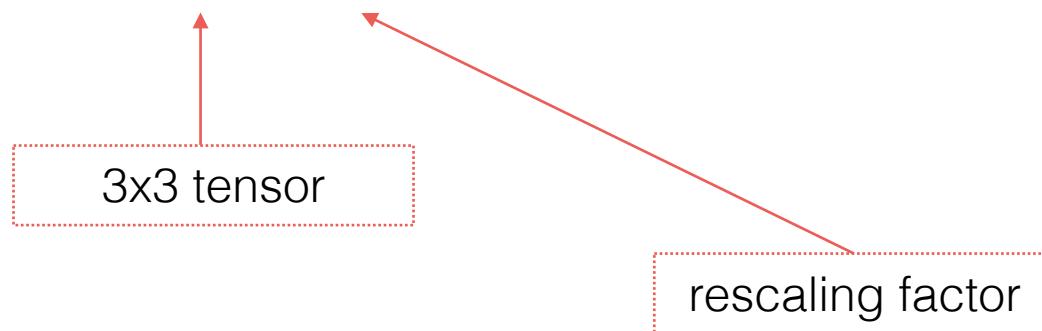
“instantaneous pressure”

Pressure controls

Volume rescaling:

One of the simplest ways to control the pressure. The instantaneous pressure is made to equal to the desired pressure by rescaling the simulation cell dimensions as well as all components of the atom positions.

$$h_{\alpha\beta}^0 = h_{\alpha\beta} [1 - \varepsilon (P_0 - P(t))] \quad h = (a, b, c)$$



Note: If the simulated system has a fixed boundary, the pressure can not be controlled. Thus, pressure control methods are always accompanied by the changes of the boundary conditions. The pressure will be decreased if the simulation cel is enlarged and vice versa.

Pressure controls

Berendsen barostat: the idea is very similar to that of Berendsen thermostat.

$$\frac{dP(t)}{dt} = \frac{P^0 - P(t)}{\tau_P}$$

relaxation time constant

the larger relaxation time constant, the weaker the coupling with “pressure bath”

In the isotropic implementation, scale factors for simulation cell volume and coordinates:

$$\eta(t) = 1 - \frac{\Delta t}{\tau_P} \gamma (P^0 - P(t)) \quad \eta'(t) = \eta(t)^{1/3}$$

isothermal compressibility

The extension to anisotropic cell variations is straightforward by applying the scale factors differently for different dimensions.

Pressure controls

Andersen barostat: an extended system method, involves coupling the system to a fictitious “pressure bath” using an extended Lagrangian and introducing new degrees of freedom.

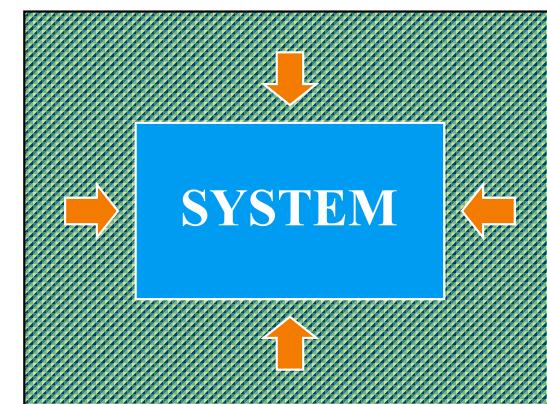
This coupling mimics the action of a piston on a real system. Here the piston is not of the usual cylindrical type that expands or contracts the system along only one direction; instead, this fictitious piston can cause an isotropic expansion or contraction on the system.

Relation between real and scaled coordinates:

$$s_i = \frac{r_i}{V^{1/3}}$$

For simplicity, shape is restricted to be cubic.

New constant parameter called “mass” of the imaginary piston is introduced to control the volume of the simulation cell



Pressure controls

Andersen barostat (continue...):

The Lagrangian of the extended system:

$$L_{\text{Andersen}} = \frac{1}{2} \sum_i m_i V^{2/3} \left(\frac{ds_i}{dt} \right)^2 - U(V^{1/3} s) + \frac{Q}{2} \dot{V}^2 - P^0 V$$

Volume of the simulation cell itself is taken as a fictitious dynamical variable just like the “position” variable in the Nosé-Hoover thermostat.

Equations of motion:

$$\frac{d^2 s_i}{dt^2} = -\frac{1}{m_i V^{1/3}} \frac{\partial U}{\partial r_i} - \frac{2}{3} \frac{\dot{V}}{V} \frac{ds_i}{dt}$$

$$\frac{d^2 V}{dt^2} = \frac{1}{Q} \frac{1}{3V} \sum_i \left(m_i V^{2/3} \left(\frac{ds_i}{dt} \right)^2 - V^{1/3} s_i \frac{\partial U}{\partial r_i} \right) - \frac{P^0}{Q}$$

Pressure controls

Andersen barostat (continue...):

Define a correspondence for the momenta between the scaled system and the original system:

$$p_i = \pi_i / V^{1/3}$$

$$\pi_i = \frac{\partial L_{\text{Andersen}}}{\partial \dot{s}_i} = m_i V^{2/3} \dot{s}_i$$

momentum conjugated to scaled coordinate

Equations of motion:

$$\frac{dr_i}{dt} = \frac{p_i}{m_i} + \frac{1}{3V} \dot{V} r_i$$

$$\frac{dp_i}{dt} = -\frac{\partial U}{\partial r_i} - \frac{1}{3V} \dot{V} p_i$$

$$\frac{d^2V}{dt^2} = \frac{1}{Q} \frac{1}{3V} \sum_i \left(\frac{p_i^2}{m_i} - r_i \frac{\partial U}{\partial r_i} \right) - \frac{P^0}{Q}$$

Pressure controls

Andersen barostat (continue...):

$$PV = Nk_B T + \frac{1}{3} \left\langle \sum_i r_i \cdot F_i \right\rangle \quad \longrightarrow \quad \frac{d^2V}{dt^2} = \frac{P(t) - P^0}{Q}$$

That means, the cell motion is triggered by the deviation of the internal pressure from the external pressure

For the choice of the fictitious “mass” of the piston: A low “mass” will result in rapid box size oscillations, which are not damped very efficiently by the motions of the molecules. While a large “mass” will give rise to a slow adjustment of the volume, i.e., the pressure.

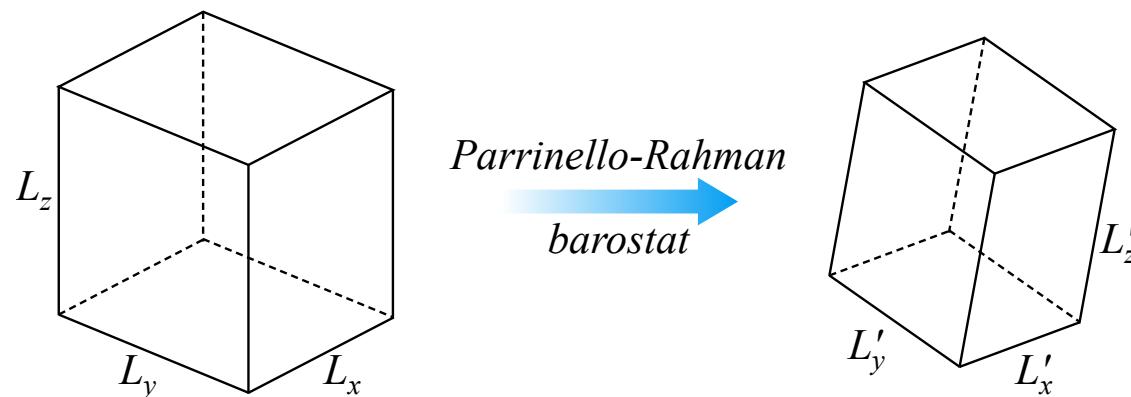
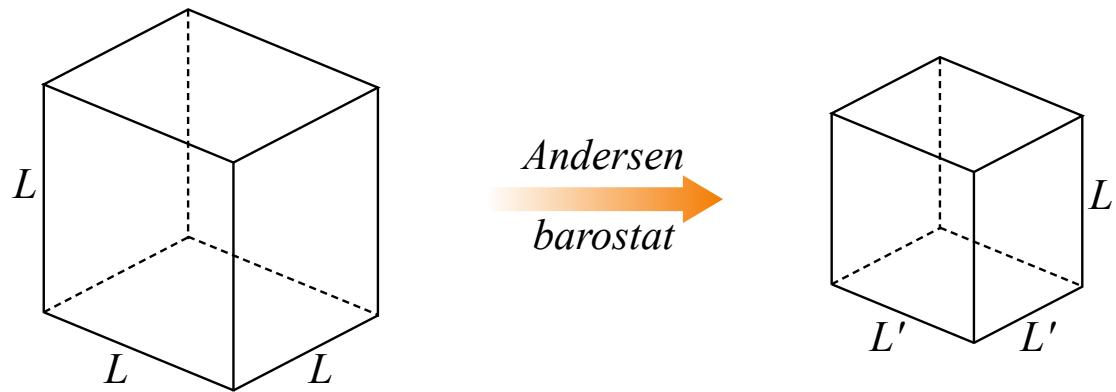
In the limit:

$$Q \rightarrow \infty \qquad dV / dt = 0$$

The equations of motion become equivalent to the dynamical equations for normal molecular dynamics

Pressure controls

A more advanced method to control the pressure is found by Parrinello and Rahman. In this method, a variable simulation cell shape is allowed. Basically, the box vectors are set to follow an equation of motion, and the equations of motion of the particles are also changed as in the Nosé-Hoover thermostat.



Acceleration Techniques on Simulation

Potential cutoff

To reduce the calculation cost, the potential functions are usually designed to have a cutoff radius. Which is the maximum atomic distance to the central atom in which the surrounding atoms affect on the central atom.

- Long-range interaction: Ewald summation scheme
- Short-range interaction:
 - Potential (or force) should remain minimally perturbed by modifying function at small distances
 - Modified potential (or force) must remain a smooth function. This requirement is crucial because any violation may result in catastrophic instability of the integration of equation of motions due to sudden variation of forces
 - Because energy is conserved in standard molecular dynamics simulations (NVE ensemble), modification of potentials should not lead to noticeable energy drift.
- Potential modification methods:
 - Simple truncation
 - Truncation and shift
 - Switching using cutoff functions

Potential cutoff

Simple truncation:

$$U^{\text{mod}}(r) = \begin{cases} U(r), & r \leq r_c \\ 0, & r > r_c \end{cases}$$

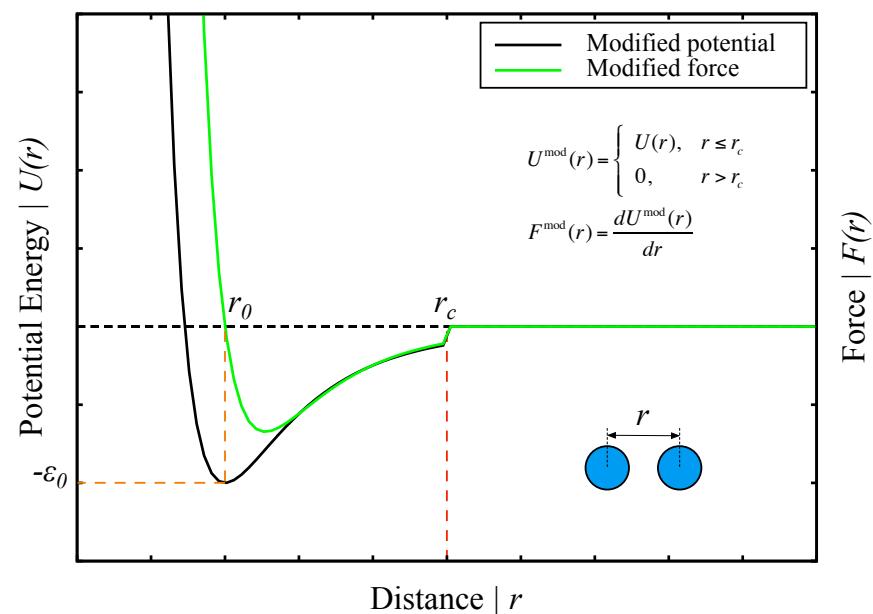
Discontinuity in the potential

→ Infinite force at cutoff distance

If the potential function is already close to zero at the cutoff distance, the numerical error associated with the truncation is small and might be acceptable.

Lennard-Jones potential:

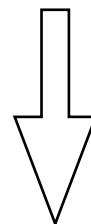
$$r_c \geq 2.5\sigma$$



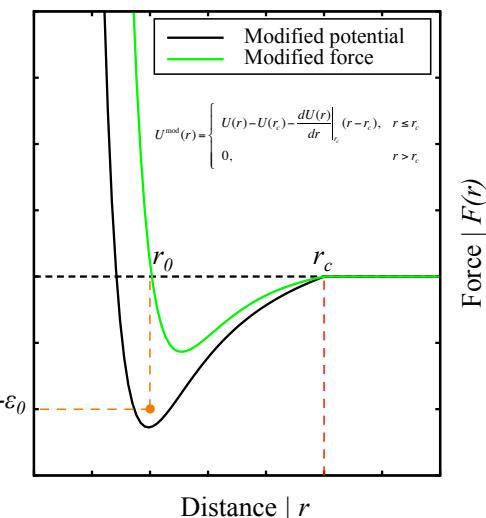
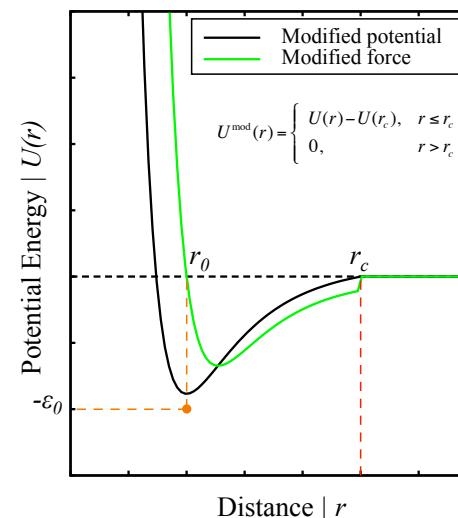
Potential cutoff

Truncation and shift:

$$U^{\text{mod}}(r) = \begin{cases} U(r) - U(r_c), & r \leq r_c \\ 0, & r > r_c \end{cases}$$



Discontinuity in the potential is smeared out but force still has discontinuity.



$$U^{\text{mod}}(r) = \begin{cases} U(r) - U(r_c) - \frac{dU(r)}{dr} \Big|_{r_c} (r - r_c), & r \leq r_c \\ 0, & r > r_c \end{cases}$$

Potential cutoff

Switching:

$$U^{\text{mod}}(r) = g(r)U(r)$$

$$g(r)|_{r_s} = 1$$

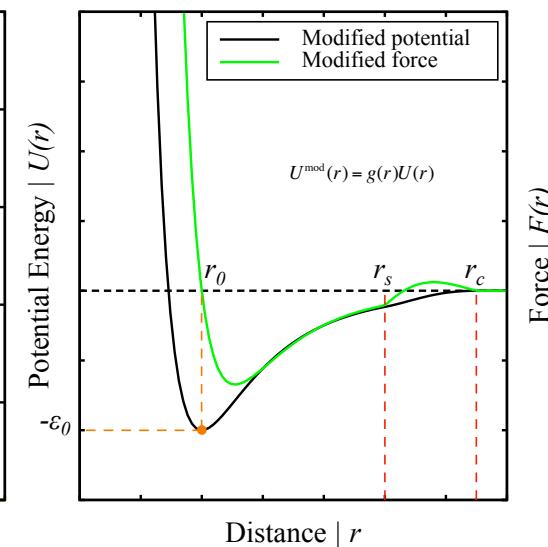
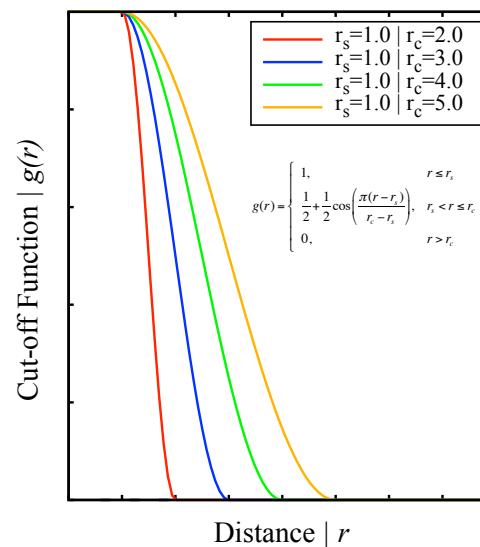
$$\left. \frac{dg(r)}{dr} \right|_{r_s} = \left. \frac{d^2g(r)}{dr^2} \right|_{r_s} = 0$$

$$g(r)|_{r_c} = 0$$

$$\left. \frac{dg(r)}{dr} \right|_{r_c} = \left. \frac{d^2g(r)}{dr^2} \right|_{r_c} = 0$$

Tersoff potential:

$$g(r) = \begin{cases} 1, & r \leq r_s \\ \frac{1}{2} + \frac{1}{2} \cos\left(\frac{\pi(r - r_s)}{r_c - r_s}\right), & r_s < r \leq r_c \\ 0, & r > r_c \end{cases}$$



Book-keeping method

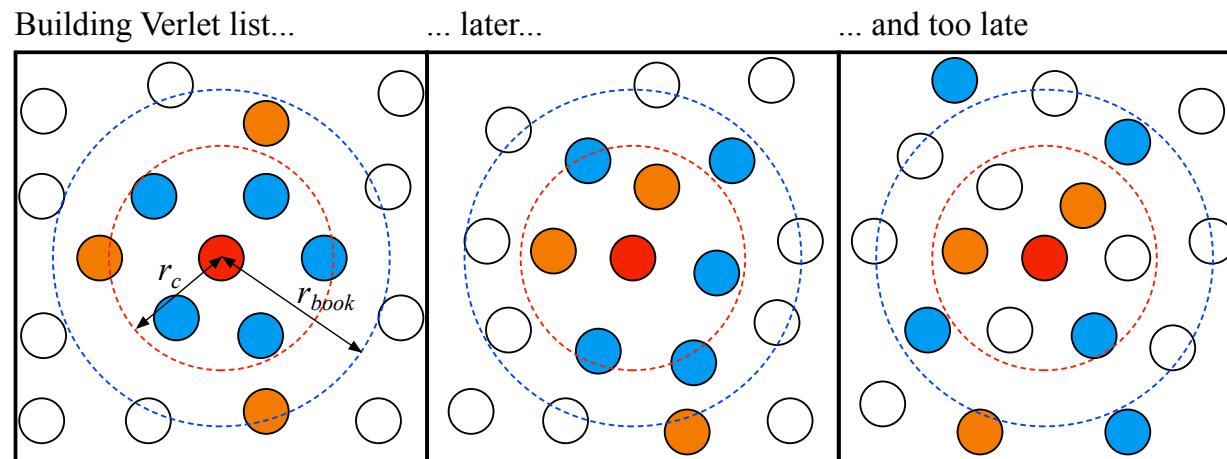
Each atom has the list (book-keeping list or Verlet list) of its neighboring atoms which reside within the cutoff sphere of radius:

$$r_{book} = r_c + r_{margin}$$

Safety zone or skin distance

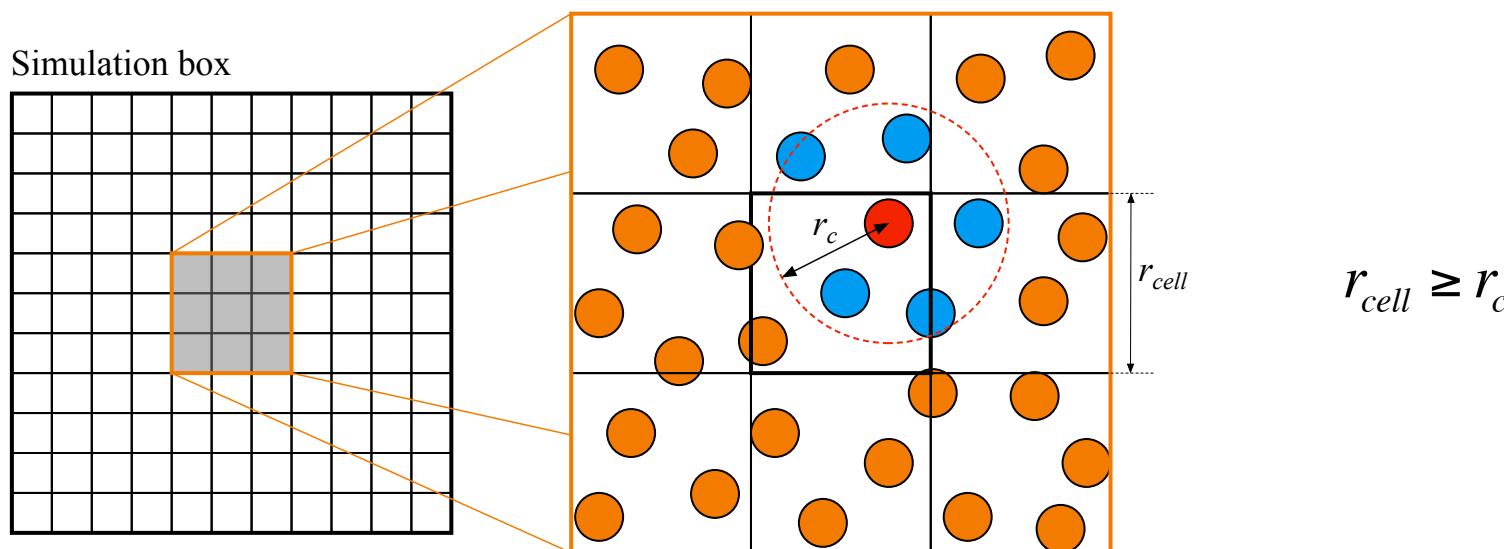
List is regularly updated after a certain number of time-steps. Cutoff radius should be long enough for atoms outside of the list which has crossed the safety zone not to come into the interaction range until next update.

$$r_{book} = r_c + N_{book} \Delta t v_{max}$$



Linked-cell method

The cell lists are generated by dividing the simulated system into cubic cells of the size larger than the cutoff distance. For each cell, the list of atoms which belong to a given cell is created.



In the simulation, the calculation of interactions for an atom in a given cell is restricted only to the current cell and its neighboring cells.

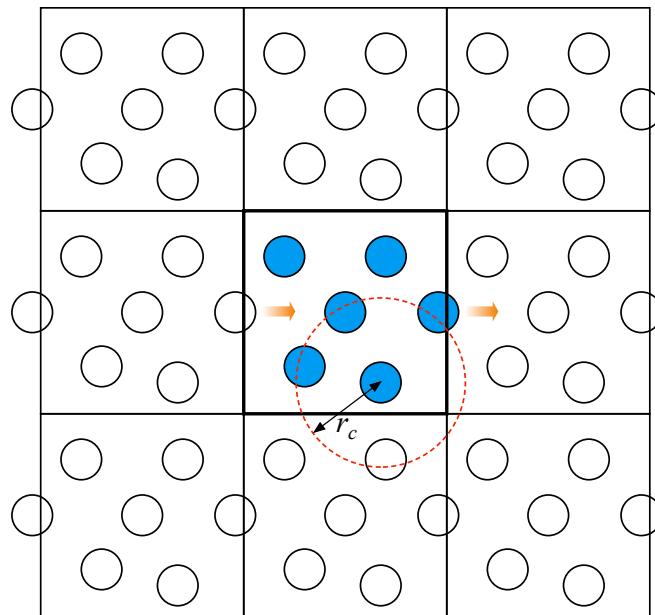
Book-keeping method: Good for small systems (less than 1000 particles)

Linked-cell method: For large systems

Periodic boundary conditions

In order to overcome length scale problem, it is essential to choose boundary conditions that mimic the presence of an infinite bulk surrounding system.

All atoms are confined in a box (primitive cell), and then replicate the box, together with the atoms in the box, identically in three directions.



$$E_{tot} = \frac{1}{2} \sum_{l,m,n} \sum_{i,j} U(|r_{ij} + la + mb + nc|)$$

An atom leaving the box to the right via one boundary can be identified with an atom entering the box from the left at the opposite boundary. A given atom will interact with all other atoms not only in cell but also in all other replicated cells.