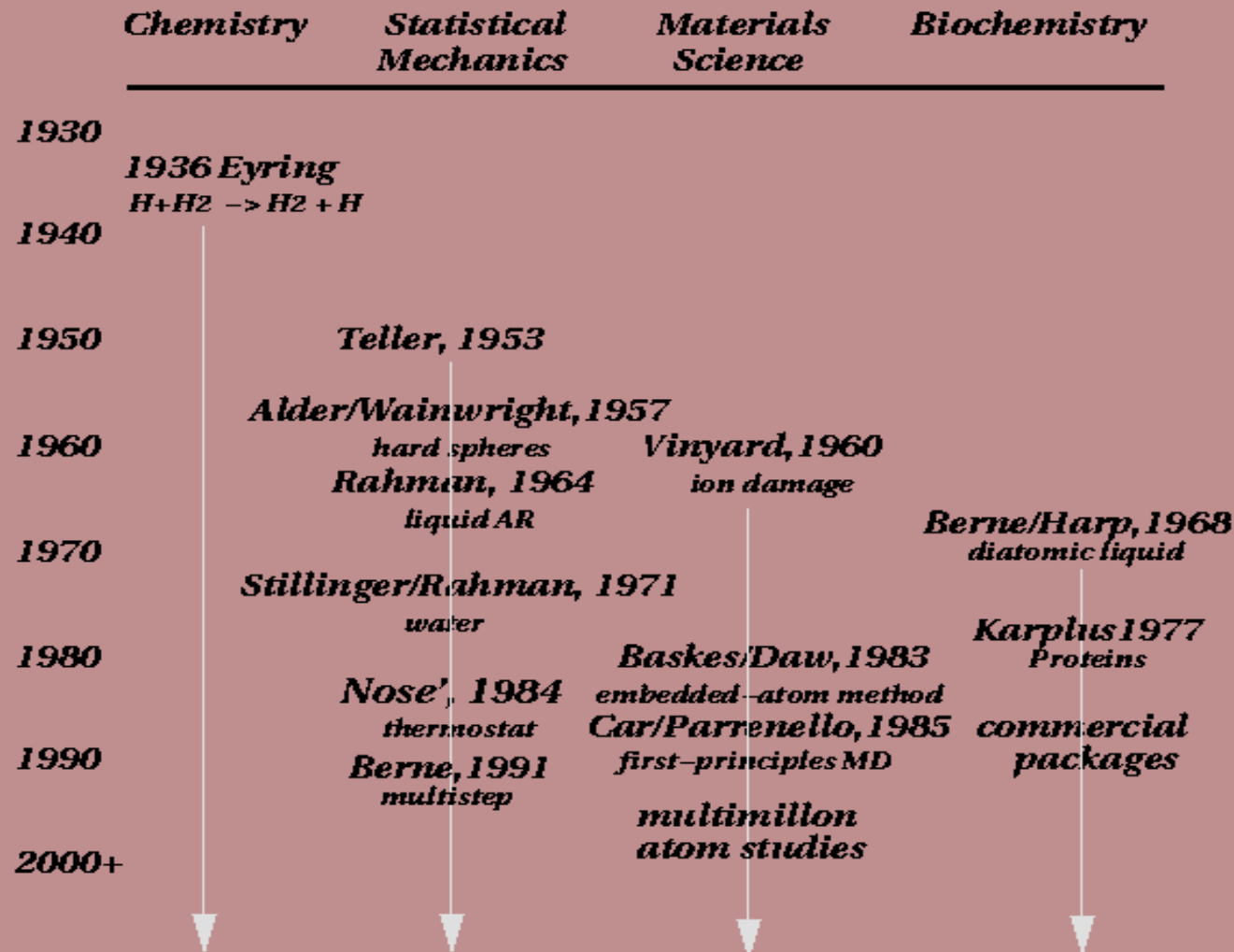# Molecular Dynamics

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Historical Perspective on Molecular Dynamics Simulations

Chemistry	Statistical Mechanics	Materials Science	Biochemistry
1930			
1936 Eyring $H+H2 \rightarrow H2 + H$			
1940			
1950	**Teller, 1953**		
Alder/Wainwright, 1957 hard spheres		**Vinyard, 1960** ion damage	
1960 **Rahman, 1964** liquid AR			
1970			**Berne/Harp, 1968** diatomic liquid
Stillinger/Rahman, 1971 water			
1980		**Baskes/Daw, 1983** embedded–atom method	**Karplus 1977** Proteins
Nose', 1984 thermostat			
1990 **Berne, 1991** multistep	**Car/Parrenello, 1985** first–principles MD	**commercial packages**	
2000+		**multimillon atom studies**	

2

MD: History

Phase Transition for a Hard Sphere System

B. J. ALDER AND T. E. WAINWRIGHT

University of California Radiation Laboratory, Livermore, California

(Received August 12, 1957)

Studies in Molecular Dynamics. I. General Method*

B. J. ALDER AND T. E. WAINWRIGHT

Lawrence Radiation Laboratory, University of California, Livermore, California

(Received February 19, 1959)

A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles. The study of this many-body problem is carried out by an electronic computer which solves numerically the simultaneous equations of motion. The limitations of this numerical scheme are enumerated and the important steps in making the program efficient on the computers are indicated. The applicability of this method to the solution of many problems in both equilibrium and nonequilibrium statistical mechanics is discussed.

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MD: History

## Correlations in the Motion of Atoms in Liquid Argon*

A. RAHMAN

Argonne National Laboratory, Argonne, Illinois

(Received 6 May 1964)

A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4°K and a density of 1.374 g cm^{-3}. The pair-correlation function and the constant of self-diffusion are found to agree well with experiment; the latter is 15% lower than the experimental value. The spectrum of the velocity autocorrelation function shows a broad maximum in the frequency region $\omega = 0.25(k_B T/\hbar)$. The shape of the Van Hove function $G_s(r,t)$ attains a maximum departure from a Gaussian at about $t = 3.0 \times 10^{-12}$ sec and becomes a Gaussian again at about 10^{-11} sec. The Van Hove function $G_d(r,t)$ has been compared with the convolution approximation of Vineyard, showing that this approximation gives a too rapid decay of $G_d(r,t)$ with time. A delayed-convolution approximation has been suggested which gives a better fit with $G_d(r,t)$; this delayed convolution makes $G_d(r,t)$ decay as t^4 at short times and as t at long times.

MD: History
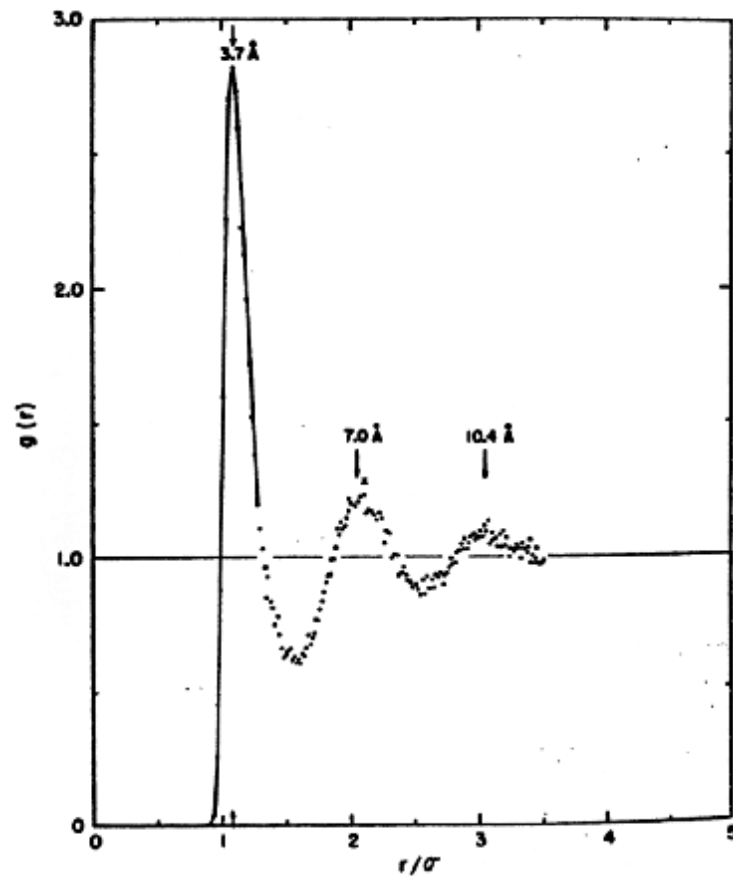
864 particles
Time / Step ~ 45s
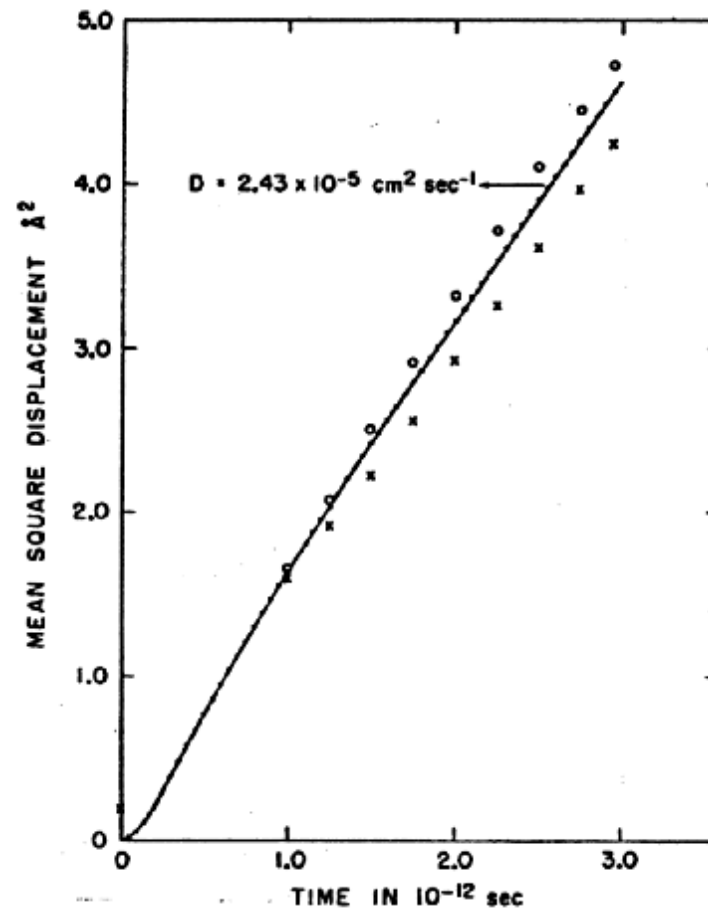
Production run ~20000 steps @ 10 days !   5

MD: How

```
program MD

call init
t=0
do while (t.lt.tmax)
    call force(f,en)
    call integrate(f,en)
    t=t+delt
    call sample
enddo
stop
end
```

$$m_i \ddot{\vec{r}}_i = \vec{F}_i$$

$$\vec{F}_i = -\nabla_{r_i} U(\vec{r}_i)$$

$$\vec{r}(t+dt) = \vec{r}(t) + dt\vec{v}(t) + (1/2)dt^2\vec{a}(t) + \mathbf{L}$$

$$\vec{r}(t-dt) = \vec{r}(t) - dt\vec{v}(t) + (1/2)dt^2\vec{a}(t) - \mathbf{L}$$

$$\vec{r}(t+dt) \approx 2\vec{r}(t) - \vec{r}(t-dt) + dt^2\vec{a}(t)$$

Verlet Algorithm

Leap-Frog Algorithm

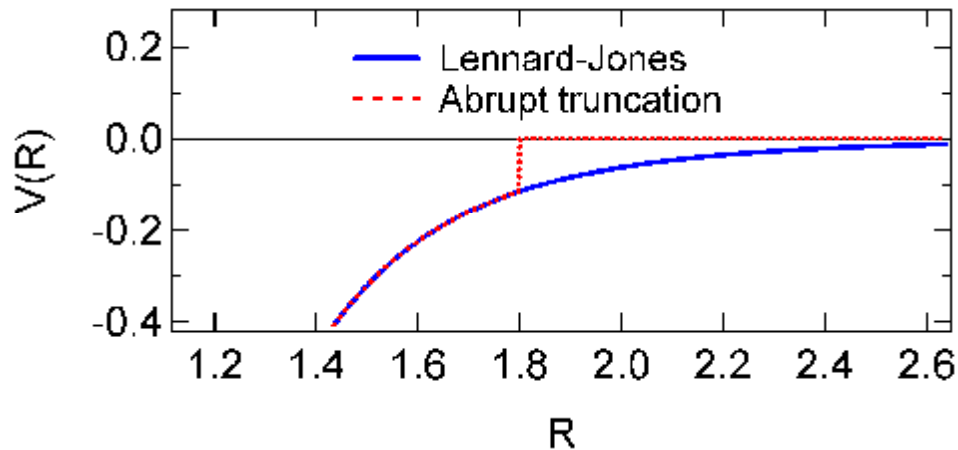*Velocity Verlet Algorithm*

......

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MD: Init and Force

Ø **Initialization**

- **Total momentum should be zero (no external forces)**
- **Temperature rescaling to desired temperature**
- **Particles start on a lattice**

Ø **Force calculations**

- **Periodic boundary conditions**
- **Order N^2 algorithm**
- **Order N: neighbor lists, linked cell**
- **Truncation and shift of the potential**

MD: Force

$$U_{NB} = \sum_{i,j} w_{ij} S(r_{ij}) e_{ij} \left[\left(\frac{R_{ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{ij}}{r_{ij}} \right)^6 \right] + \sum_{i,j} w_{ij} S(r_{ij}) \frac{q_i q_j}{4 p e_0 e r_{ij}}$$

w_{ij} : weights *(0< w_{ij} <1). Can be used to exclude bonded terms, or to scale some interactions (usually 1-4).*

$S(r)$: cut-off function.

$$S(r) = \begin{cases} 1 & r < b \\ 0 & r \geq b \end{cases}$$

MD: Force

- **Approximate distant interactions by assuming uniform distribution beyond cutoff: g(r) = 1 r > r$_{cut}$**
- **Corrections to thermodynamic properties**
  - **Internal energy**   *Expression for Lennard-Jones model*

$$U_{lrc} = \frac{N}{2}r\int_{r_{cut}}^{\infty} u(r)4\pi r^2 dr \qquad U_{lrc}^{LJ} = \frac{8}{9}\pi N \rho s^3 e\left[\left(\frac{s}{r_c}\right)^9 - 3\left(\frac{s}{r_c}\right)^3\right]$$

  - **Virial**

$$P_{lrc} = \frac{1}{6}r^2\int_{r_{cut}}^{\infty} r\frac{du}{dr}4\pi r^2 dr \qquad P_{lrc}^{LJ} = \frac{32}{9}\pi r^2 s^3 e\left[\left(\frac{s}{r_c}\right)^9 - \frac{3}{2}\left(\frac{s}{r_c}\right)^3\right]$$

  - **Chemical potential**

$$m_{lrc} = r\int_{r_{cut}}^{\infty} u(r)4\pi r^2 dr = 2\frac{U_{lrc}}{N}$$

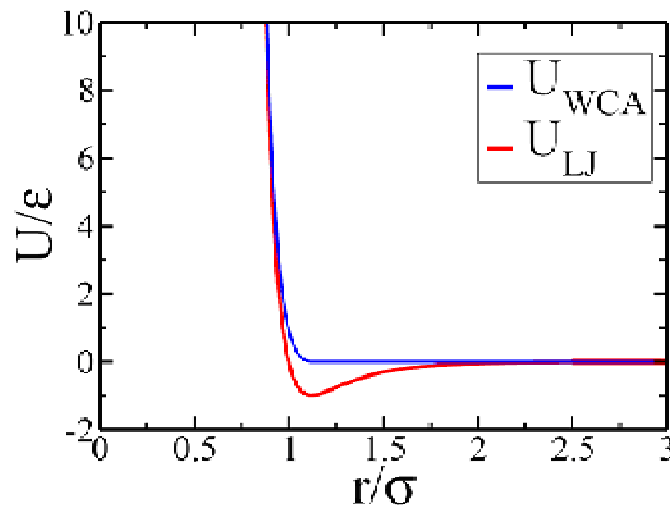*For r$_c$/σ = 2.5, these are about 5-10% of the total values*

MD: Force
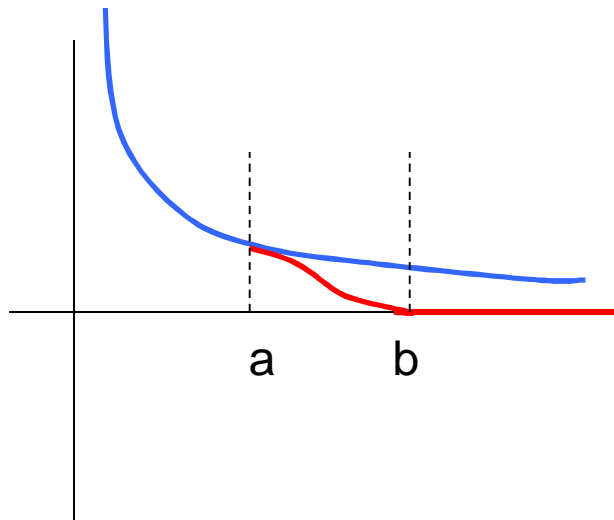
$$S(r) = \begin{cases} 1 & r < a \\ 1 + y(r)^2[2y(r) - 3] & a \le r \le b \\ 0 & r > b \end{cases}$$
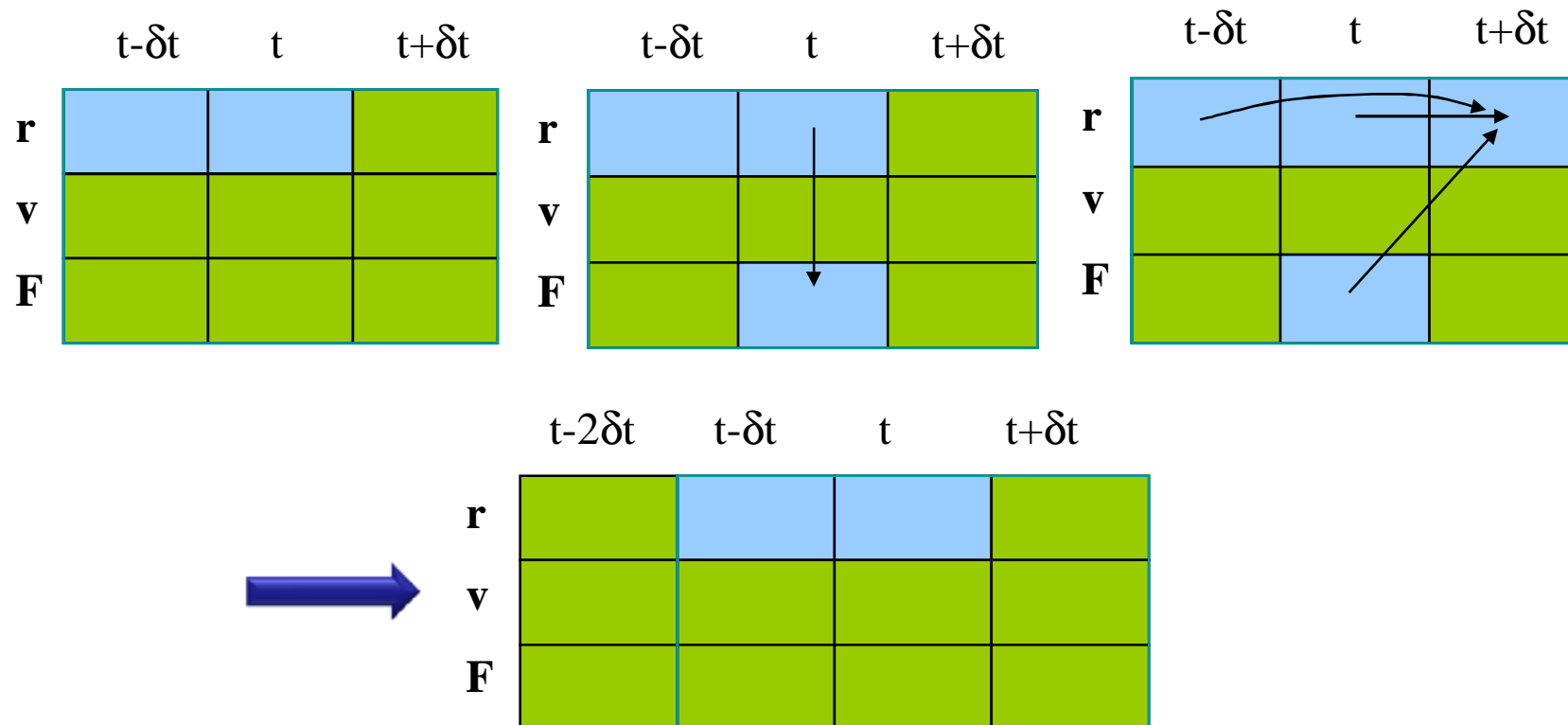
with $\quad y(r) = \dfrac{r^2 - a^2}{b^2 - a^2}$

$$U_{LJ}(r) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right] - 4\varepsilon\left[\left(\dfrac{\sigma}{r_c}\right)^{12} - \left(\dfrac{\sigma}{r_c}\right)^{6}\right] & r < r_c \\ 0 & r > r_c \end{cases}$$

MD: Integrate

Verlet Algorithm

$$\vec{r}(t+dt) \approx 2\vec{r}(t) - \vec{r}(t-dt) + dt^2\vec{a}(t)$$

Verlet Algorithm

- **Obtaining the velocities**
  - *not evaluated during normal course of algorithm*
  - *needed to compute some properties, e.g.* temperature

  finite difference:

  $$\mathbf{v}(t) = \frac{1}{2dt}\left[\mathbf{r}(t+dt) - \mathbf{r}(t-dt)\right] + O(dt^2)$$

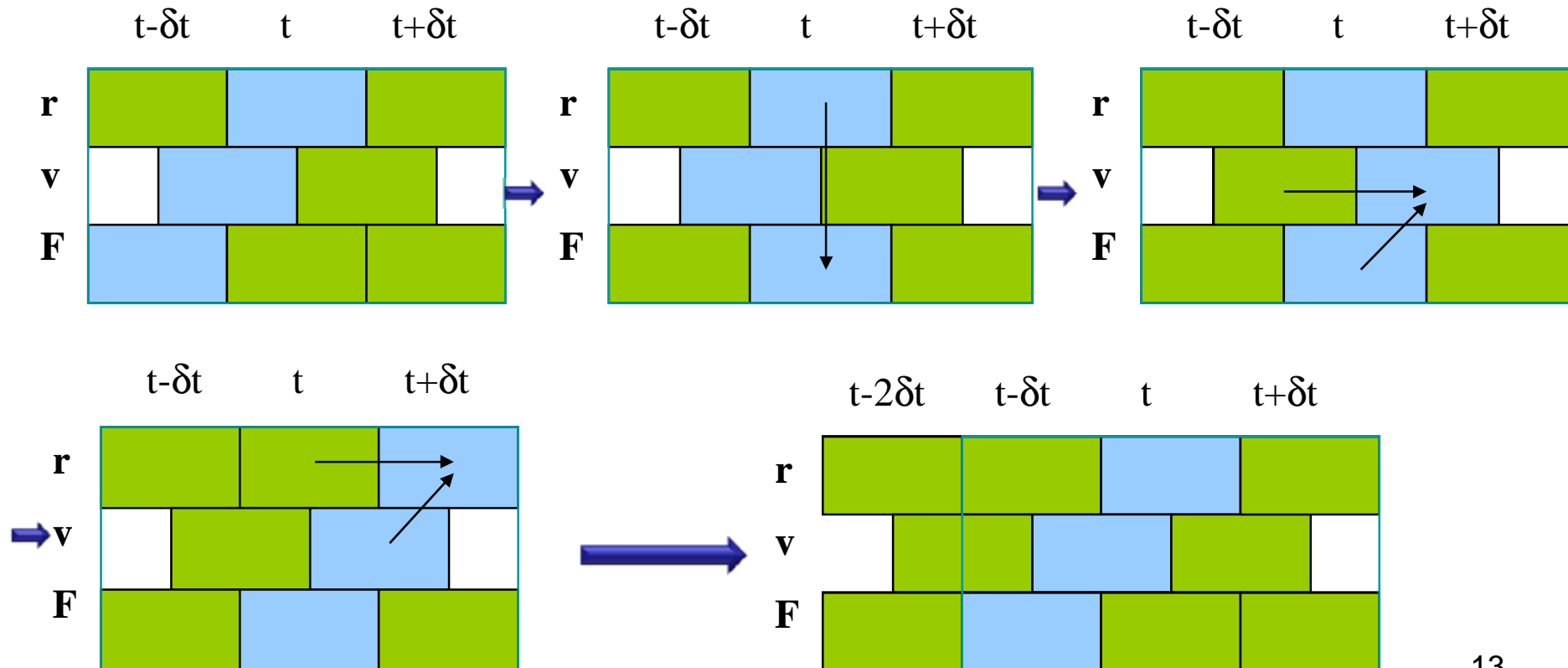- **Numerical imprecision of adding large/small numbers:**

$$\underbrace{\mathbf{r}(t+dt) - \mathbf{r}(t)}_{} = \underbrace{\mathbf{r}(t)}_{O(\delta t^0)} - \underbrace{\mathbf{r}(t-dt)}_{O(\delta t^0)} + \underbrace{\frac{1}{m}\mathbf{F}(t)dt^2}_{O(\delta t^2)}$$

$O(\delta t^1) \qquad O(\delta t^1)$

>>>>An improvement: half-step Verlet or *leapfrog* algorithm.

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Leapfrog Algorithm

$$\mathbf{r}(t+dt) = \mathbf{r}(t) + \mathbf{v}(t+\tfrac{1}{2}dt)dt$$

$$\mathbf{v}(t+\tfrac{1}{2}dt) = \mathbf{v}(t-\tfrac{1}{2}dt) + \tfrac{1}{m}\mathbf{F}(t)dt$$

Leapfrog Algorithm

$$\mathbf{r}(t+dt) = \mathbf{r}(t) + \mathbf{v}(t+\tfrac{1}{2}dt)dt$$

$$\mathbf{r}(t+dt) = \mathbf{r}(t) + \left[\mathbf{v}(t-\tfrac{1}{2}dt) + \tfrac{1}{m}\mathbf{F}(t)dt\right]dt$$

$$\mathbf{v}(t+\tfrac{1}{2}dt) = \mathbf{v}(t-\tfrac{1}{2}dt) + \tfrac{1}{m}\mathbf{F}(t)dt$$

Velocity at half time-step

$$\mathbf{r}(t) = \mathbf{r}(t-dt) + \mathbf{v}(t-\tfrac{1}{2}dt)dt$$

$$\mathbf{r}(t+dt) = \mathbf{r}(t) + \left[\left(\mathbf{r}(t) - \mathbf{r}(t-dt)\right) + \tfrac{1}{m}\mathbf{F}(t)dt^2\right] \qquad \text{(Verlet algorithm)}$$

Verlet and leapfrog algorithms are equal, they are extremely stable.

Obtain the current velocity by interpolation:
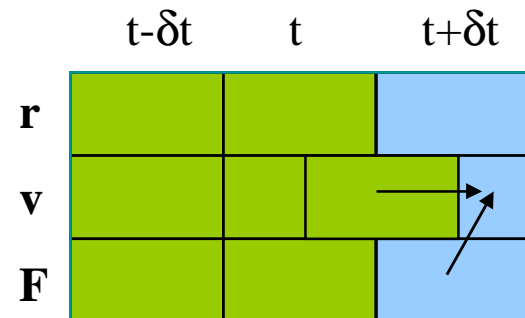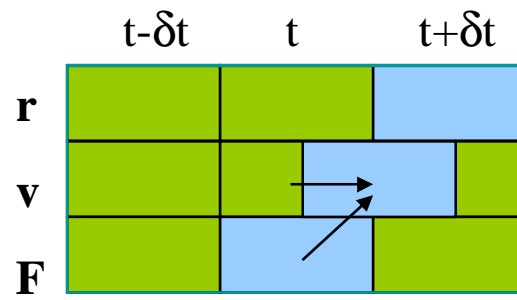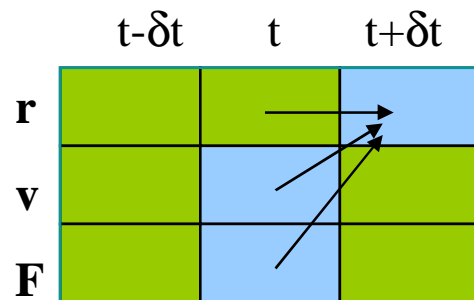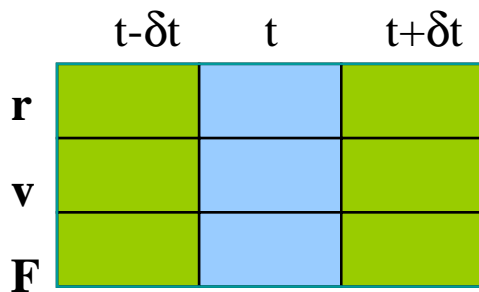
$$\mathbf{v}(t) = \frac{1}{2}\left[\mathbf{v}(t+\tfrac{1}{2}dt) + \mathbf{v}(t-\tfrac{1}{2}dt)\right]$$

Velocity-Verlet Algorithm

$$\mathbf{r}(t+dt) = \mathbf{r}(t) + \mathbf{v}(t)dt + \frac{1}{2m}\mathbf{F}(t)dt^2$$

$$\mathbf{v}(t+dt) = \mathbf{v}(t) + \frac{1}{2m}\big[\mathbf{F}(t) + \mathbf{F}(t+dt)\big]dt$$
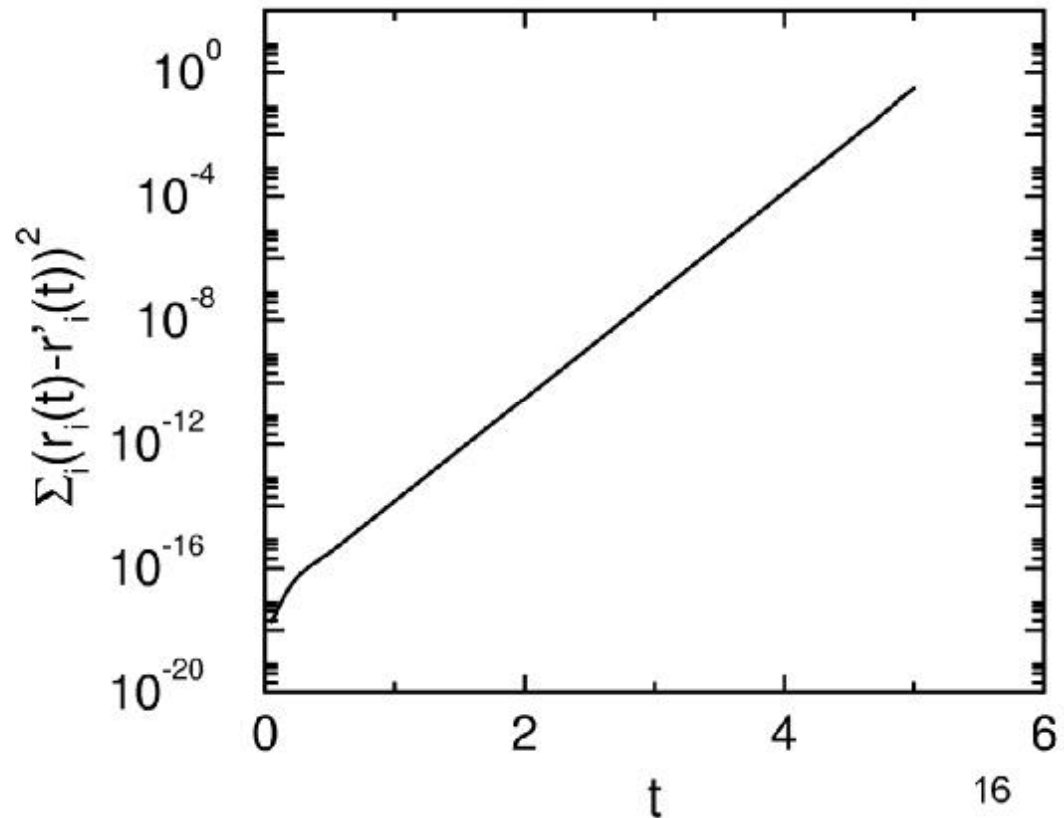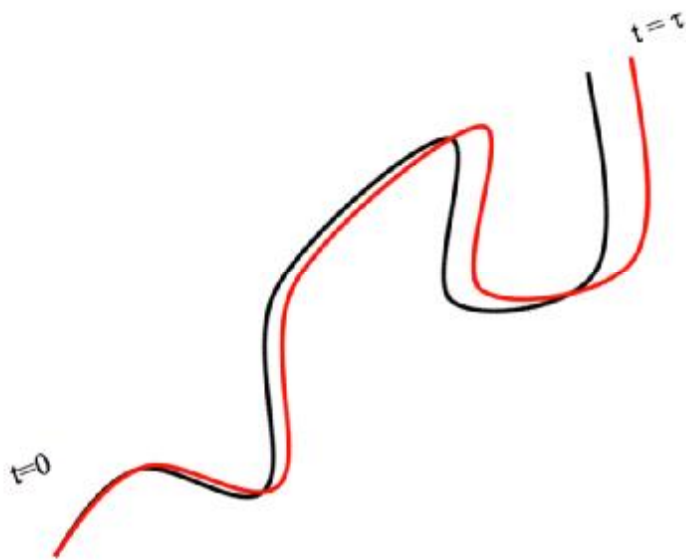

15
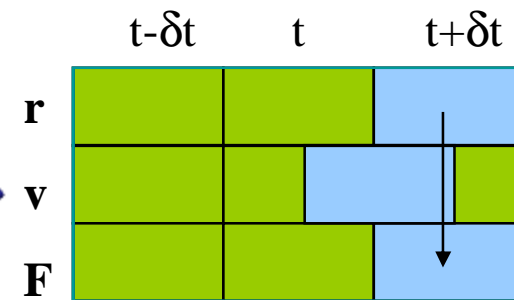
Lyaponov Instability

$$\left(\mathbf{r}^N(0), \mathbf{p}^N(0)\right)$$

$$\left(\mathbf{r}^N(0), \mathbf{p}_1(0), \mathbf{L}, \mathbf{p}_i(0) + e, \mathbf{p}_j(0) - e\mathbf{L}, \mathbf{p}_N(0)\right)$$

$$\varepsilon = 10^{-10}$$

Choosing Correct Timestep

- The choice of time step is crucial: too short and phase space is sampled inefficiently, too long and the energy will fluctuate wildly and the simulation may become catastrophically unstable.

- The instabilities are caused by the motion of atoms being extrapolated into regions where the potential energy is prohibitively high (e.g. atoms overlapping).

- For flexible molecules, the time step should be an order of magnitude less than the period of the fastest motion (usually bond stretching: C—H around 10 fs so use 1 fs).

Long Range Interaction

- **Coulombic interactions must be treated specially**
  - **very long range**
  - **1/r form does not die off as quickly as volume grows**

$$\int_{r_c}^{\infty} \frac{1}{r} 4p\, r^2 dr = \infty$$

  - **finite only because + and – contributions cancel**
- **Methods**
  - **Ewald sum**
  - **Treat surroundings as dielectric continuum (reaction field)**
  - **Multipole expansion**

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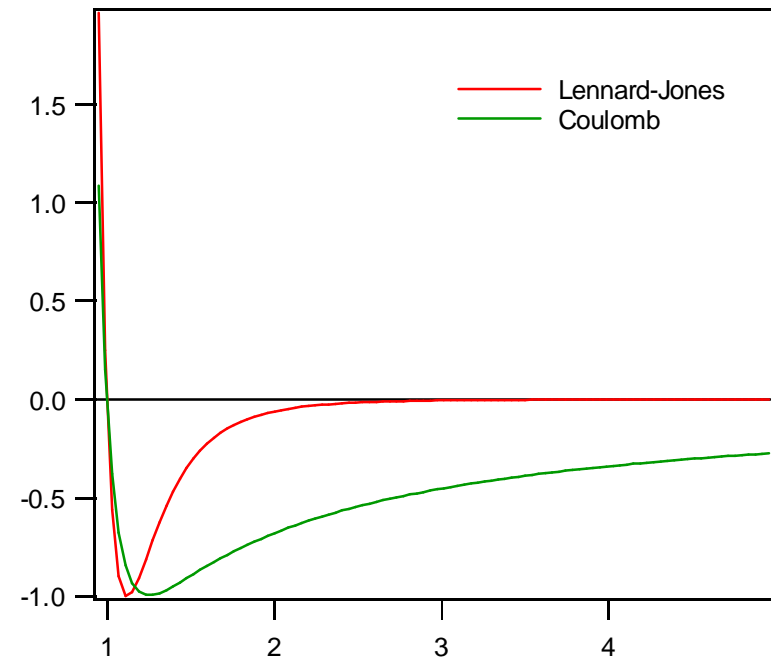
Long Range Interaction

Recall: electrostatics

- **Force between charges** $\mathbf{F} = \dfrac{q_1 q_2}{r^2}\hat{\mathbf{r}}$
- **In terms of electric field** $\quad \mathbf{F}(\mathbf{r}) = q_1 \mathbf{E}(\mathbf{r})$
- **Static electric field satisfies**

  $\nabla \cdot \mathbf{E}(\mathbf{r}) = 4pr(\mathbf{r})$
- **Charge density** $r(\mathbf{r})$
    - for point charge q_2: $\quad r(\mathbf{r}) = q_2 d(\mathbf{r})$
- **Electrostatic potential**
    - **E can be written** $\quad \mathbf{E}(\mathbf{r}) = -\nabla f(\mathbf{r})$
    - **potential energy of charge q_1 at r, relative to position at infinity**

      $u(\mathbf{r}) = q_1 f(\mathbf{r})$
- **Poisson's equation**
    - $\nabla^2 f(\mathbf{r}) = -4pr(\mathbf{r})$

Long Range Interaction

Ewald sum method: for charges in PBC. The system must be neutral.

$$\Delta f_j(\mathbf{r}) = f_j^p(\mathbf{r}) - f_j^G(\mathbf{r})$$

$$r(\mathbf{r}) = \sum_{\substack{\mathbf{n}, \text{image} \\ \text{vectors}}} \sum_{j \text{ in } \mathbf{n}} q_j d(\mathbf{r})$$

$$= \sum_{\mathbf{n}} \sum_j q_j d\left(\left|\mathbf{r} - (\mathbf{r}_j + \mathbf{n}L)\right|\right)$$

Converge fast enough in reciprocal space

$$= \frac{q_j}{|\mathbf{r} - \mathbf{r}_j|} - \frac{q_j}{|\mathbf{r} - \mathbf{r}_j|} erf\left(\sqrt{a}|\mathbf{r} - \mathbf{r}_j|\right)$$

$$= \frac{q_j}{|\mathbf{r} - \mathbf{r}_j|} erfc\left(\sqrt{a}|\mathbf{r} - \mathbf{r}_j|\right)$$

$$r(\mathbf{r}) = \sum_{\mathbf{n}} \sum_j q_j (a/p)^{3/2} \exp\left[-a\left|\mathbf{r} - (\mathbf{r}_j + \mathbf{n}L)\right|^2\right]$$

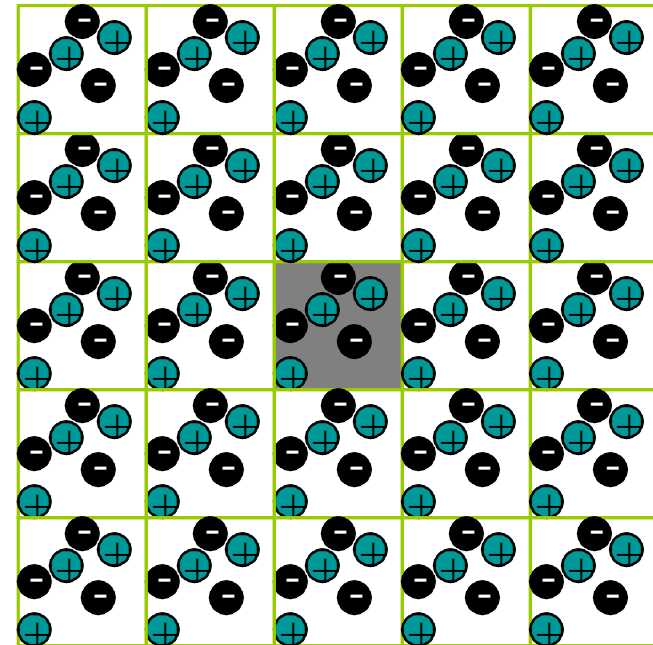*Converge fast enough in real space*

Ewald方法的主要策略

Long Range Interaction

We need to calculate the interaction energy of each charge in the central volume with all images of the other charges

$$U_q = \frac{1}{2} \sum_{\substack{\text{charge } i \\ \text{in central} \\ \text{volume}}} q_i f(\mathbf{r}_i)$$

The charge density creating the potential is

$$r(\mathbf{r}) = \sum_{\substack{\mathbf{n},\text{image } j \text{ in } \mathbf{n} \\ \text{vectors}}} \sum q_j d(\mathbf{r})$$

$$= \sum_{\mathbf{n}} \sum_{j} q_j d\left(\left|\mathbf{r} - (\mathbf{r}_j + \mathbf{n}L)\right|\right)$$

Long Range Interaction

Compute field instead by smearing all the charges

$$r(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{j} q_j (a/p)^{3/2} \exp\left[-a\left|\mathbf{r} - (\mathbf{r}_j + \mathbf{n}L)\right|^2\right]$$

Smeared charged density, not the original one

include $\mathbf{n} = 0$

Large α takes ρ back to δ function

The choice of α is important

We then can obtain the electrostatic potential via Poisson's equation

$$\nabla^2 f(\mathbf{r}) = -4pr(\mathbf{r})$$

To do this, we consider the Fourier transform of the charge density

$$r(\mathbf{k}) = \frac{1}{V} \int_V d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, r(\mathbf{r})$$

$$= \frac{1}{V} \sum_{j} q_j e^{-i\mathbf{k}\cdot\mathbf{r}_j} e^{-k^2/4a}$$

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Long Range Interaction

Use Poisson's equation for electrostatic potential

$$f(\mathbf{k}) = -\frac{4p}{k^2}\, r(\mathbf{k})$$

Invert transform to recover real-space potential

$$f(\mathbf{r}) = \sum_{k \neq 0} f(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$= \frac{1}{V} \sum_{k \neq 0} \sum_j \frac{4p\, q_j}{k^2} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_j)} e^{-k^2/4a}$$

The electrostatic energy can now be obtained

$$U_q = \tfrac{1}{2} \sum_i q_i f(\mathbf{r}_i)$$

$$= \tfrac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{4pV}{k^2} e^{-k^2/4a} \sum_{i,j} \frac{q_i q_j}{V^2} e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}$$

$$= \tfrac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{4pV}{k^2} e^{-k^2/4a} \left| r(\mathbf{k}) \right|^2 \qquad r(\mathbf{k}) = \frac{1}{V} \sum_j q_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}$$
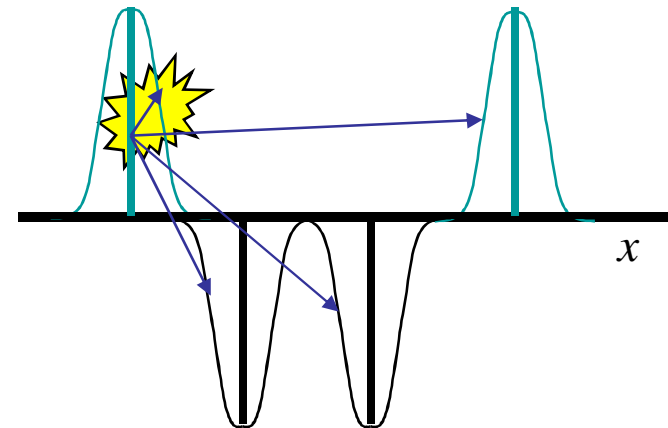
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Long Range Interaction

Two corrections are needed: self interaction and correct for smearing

1, Self Interaction

All point charges interact with the smeared electrostatic field to yield the potential energy
- **This means that the point charge interacts with its own smeared representation**
- **We need to subtract this**

x

Long Range Interaction

1, Self Interaction

Poisson's equation for the electrostatic potential due to a *single* smeared charge

$$\nabla^2 f(\mathbf{r}) = -4pr(\mathbf{r}) \longleftarrow \quad r(\mathbf{r}) = q_j(a/p)^{3/2}\exp\left[-a\left|\mathbf{r}-\mathbf{r}_j\right|^2\right]$$

The solution is

$$f(r) = \frac{q_j}{r} erf\left(\sqrt{a}\, r\right)$$

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt.$$

当电荷与自身弥散电场作用时，也即r=0时，上式为：

$$f(0) = 2q_j(a/p)^{1/2}$$

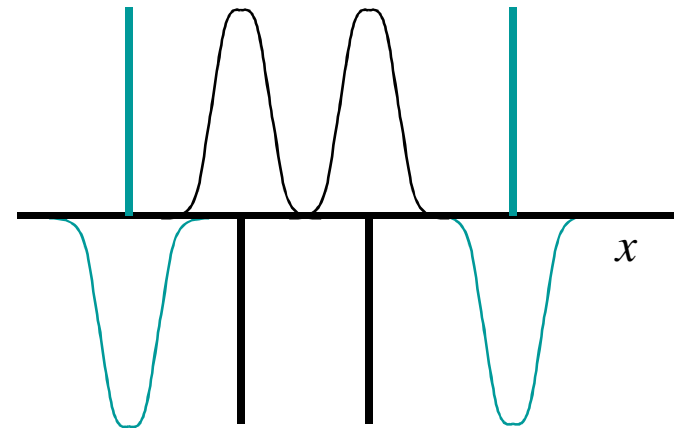$$U_{self} = \tfrac{1}{2}\sum_j q_j f(0)$$

$$= \left(\frac{a}{p}\right)^{1/2}\sum_j q_j^2$$

为常数，可从
总能量中减去

Long Range Interaction

2, Smearing Correction

$$\Delta f_j(\mathbf{r}) = f_j^p(\mathbf{r}) - f_j^G(\mathbf{r})$$

$$= \frac{q_j}{|\mathbf{r}-\mathbf{r}_j|} - \frac{q_j}{|\mathbf{r}-\mathbf{r}_j|} erf\left(\sqrt{a}\,|\mathbf{r}-\mathbf{r}_j|\right)$$

$$= \frac{q_j}{|\mathbf{r}-\mathbf{r}_j|} erfc\left(\sqrt{a}\,|\mathbf{r}-\mathbf{r}_j|\right)$$

This field is short ranged for large a (narrow Gaussians)
can view as point charges surrounded by shielding
countercharge distribution

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Long Range Interaction

2, Smearing Correction

usually α is chosen so that sum converges within central image

$$\Delta U = \frac{1}{2}\sum_{\mathbf{n}}\sum_{i \neq j} q_i \Delta f_j(r_{ij})$$

$$= \frac{1}{2}\sum_{\mathbf{n}}\sum_{i \neq j} \frac{q_i q_j}{r_{ij}} erfc\left(\sqrt{a}\, r_{ij}\right)$$
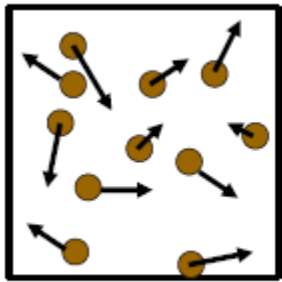
Total Coulomb energy

$$U_c = U_q(a) - U_{self}(a) + \Delta U(a)$$

> **Basic form requires an O(N²) calculation**
> - **efficiency can be introduced to reduce to O(N³/²)**
> - **can be extended to sum point dipoles**

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MD in other ensembles

Temperature in MD simulations:

$$E_k = \frac{3}{2} N k_B T$$

$$E_k = \sum_i \frac{1}{2} m v_i^2$$

$$\longrightarrow \quad \frac{3}{2} N k_B T = \sum_i \frac{1}{2} m v_i^2$$

Equipartition theorem

- T defined by the <u>ensemble average of kinetic energies</u> of all particles
  - $\rightarrow$ impossible to fix T exactly at a set value during the simulation
  - $\rightarrow$ temperature can be kept constant only as an average
  - $\rightarrow$ fluctuations will always occur

MD in other ensembles

Methods to control temperature:

1. Scaling velocities
   - simple velocity scaling (isokinetic thermostat)
   - Berendsen thermostat
2. Adding stochastic forces and/or velocities
   - Andersen thermostat
   - Langevin thermostat
3. Using "extended Lagrangian" formalisms (extended system methods)
   - Nosé-Hoover thermostat

MD in other ensembles

Velocity scaling: velocities of all particles multiplied at each step by a factor λ

$$\lambda = \sqrt{T/T_i}$$

T – target temperature

T_i **– instantaneous temperature after ith step**

- severely influenced the dynamics

- does not generate correct canonical ensemble

- cannot be used for production runs

-OK for initialization phase (fast warming up or cooling down)

MD in other ensembles

Berendsen thermostat

$$\lambda = \left[1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T} - 1 \right) \right]^{1/2}$$

t_T – user defined time constant
- determines the degree of rescaling of the velocities
- describes the strength of the coupling of the system to a hypothetical heat bath (the larger , the weaker the coupling)

- pushes a system towards a desired temperature as opposed to enforcing it
- the larger t_T, the longer it takes to achieve the desired temperature after an instantaneous change of T_0
- does not strictly follow the canonical ensemble
- in practice the deviation from canonical is usually small

MD in other ensembles

Andersen thermostat

Every particle can collide with the Andersen demon

After collision the particle is given a new velocity

$$p(\mathbf{p}) = \frac{1}{\left(2pmk_BT\right)^{3/2}} \exp\left(-\frac{\mathbf{p}^2}{2mk_BT}\right)$$ Maxwell-Boltzmann distribution
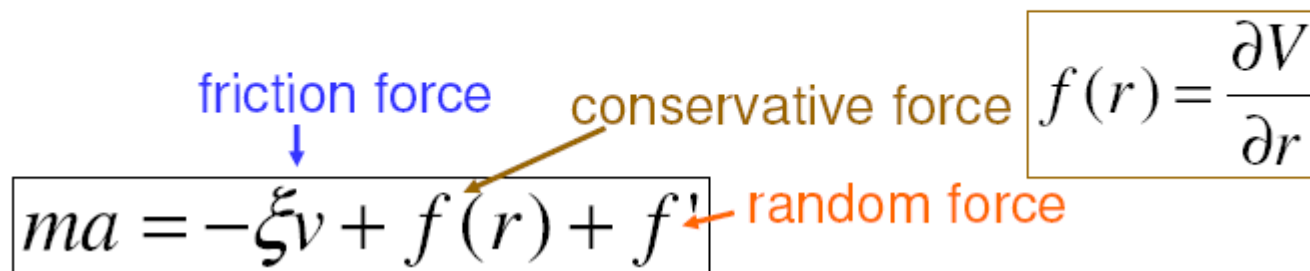
Collision frequency ν describes strength of coupling
- Probability of collision over time dt is ν dt
- Poisson process governs collisions $P(t;\boldsymbol{n}) = \boldsymbol{n}e^{-nt}$

泊松分布描述单位时间内随机事件发生的次数

MD in other ensembles

Langevin thermostat

- Langevin equation of motion

friction force   conservative force $f(r) = \dfrac{\partial V}{\partial r}$

$$ma = -\xi v + f(r) + f'$$ random force

- at each time step all particles receive a random force and have their velocities lowered using a constant friction (friction constant $\xi > 0$)

MD in other ensembles

Nosè thermostat

- **introduce a new degree of freedom, s, representing reservoir**
- **associate kinetic and potential energy with s**

$$L_{Nose} = \sum_{i=1}^{N} \frac{m_i (s \dot{\mathbf{r}}_i)^2}{2} - U(\mathbf{r}^N) + \frac{Q}{2} \dot{s}^2 - gkT \ln s \qquad \textbf{Lagrangian = K-U}$$

$$\mathbf{p}_i \equiv \frac{\partial L}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i$$

effective mass

$$p_s \equiv \frac{\partial L}{\partial \dot{s}} = Q \dot{s}$$

$$H_{Nose} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2 m_i s^2} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + gkT \ln s \qquad \textbf{Hamiltonian = K+U}$$

$$\boxed{p'=p/s} \qquad = \sum_{i=1}^{N} \frac{\mathbf{p'}_i^2}{2 m_i} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + gkT \ln s = H_{Nose}(\mathbf{p'}, \mathbf{r}) + \frac{p_s^2}{2Q} + gkT \ln s$$

MD in other ensembles

$$Q_{Nose} = \frac{1}{N!} \int dp_s \int dp^N \int dr^N \int ds \, d(H_{Nose} - E)$$

$$= \frac{1}{N!} \int dp_s \int dp'^N \int dr^N \int ds \, s^{3N} d\left(H(p',r) + \frac{p_s^2}{2Q} + \frac{g}{b}\ln s - E\right)$$

$$d(h(s)) = \frac{d(s - s_0)}{h'(s)}$$

$$d\left(H(p',r) + \frac{p_s^2}{2Q} + \frac{g}{b}\ln s - E\right) \Bigg\}$$

$$h'(s) = \frac{g}{b}\frac{1}{s}$$

$$s_0 = \exp\left\{\frac{b}{g}\left[E - H(p',r) - \frac{p_s^2}{2Q}\right]\right\}$$

$$\frac{bs}{g} d\left(s - e^{\frac{b}{g}\left[E - H(p',r) - \frac{p_s^2}{2Q}\right]}\right)$$

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MD in other ensembles

$$Q_{Nose} = \frac{1}{N!} \int dp_s \int dp'^N \int dr^N \int ds s^{3N} d(H(p',r) + \frac{p_s^2}{2Q} + \frac{g}{b} \ln s - E)$$

$$= \frac{1}{N!} \int dp_s \int dp'^N \int dr^N \int ds \frac{b}{g} s^{3N+1} d\left(s - e^{\frac{b}{g}\left[E-H(p',r)-\frac{p_s^2}{2Q}\right]} \right)$$

$$= \frac{1}{N!} \int dp_s \int dp'^N \int dr^N \frac{b}{g} e^{(3N+1)\frac{b}{g}\left[E-H(p',r)-\frac{p_s^2}{2Q}\right]}$$

积分掉p_s，剩下的就是原来坐标体系的配分函数。

$$Q_{Nose} = \frac{C}{N!} \int dp'^N \int dr^N e^{-(3N+1)\frac{b}{g}H(p',r)}$$

若g=3N+1，上式表明以p'，r为坐标的体系满足正则系综。

MD in other ensembles

Hamiltonian

$$H_{\text{Nose}} = \sum_{i=1}^{N} \frac{p_i^2}{2ms^2} + \frac{p_s^2}{2Q} + U\left(r^N\right) + \frac{g}{\beta}\ln s$$

Equations of motion:

$$\frac{dr_i}{dt} = \frac{\partial H_{\text{Nose}}}{\partial p_i} = \frac{p_i}{ms^2} \qquad \frac{dp_i}{dt} = -\frac{\partial H_{\text{Nose}}}{\partial r_i} = -\frac{\partial U\left(r^N\right)}{\partial r_i}$$

$$\frac{ds}{dt} = \frac{\partial H_{\text{Nose}}}{\partial p_s} = \frac{p_s}{Q} \qquad \frac{dp_s}{dt} = -\frac{\partial H_{\text{Nose}}}{\partial s} = \frac{1}{s}\left(\sum \frac{p_i^2}{ms^2} - \frac{g}{\beta}\right)$$

since s varies during the simulation, each "true" time step is of varying length

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MD in other ensembles

Nosé-Hoover Thermostat

Advantageous to work with non-fluctuating time step

- Real-variables equation of motion

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{sp_s}{Q}\mathbf{p}_i$$

$$\frac{\dot{s}}{s} = \frac{sp_s}{Q}$$

$$\frac{\partial(sp_s/Q)}{\partial t} = \frac{1}{Q}\left(\sum_{i=1}^{N}\frac{p_i}{m_i} - gkT\right)$$

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - x\mathbf{p}_i$$

$$\frac{\dot{s}}{s} = x$$

$$\dot{x} = \frac{1}{Q}\left(\sum_{i=1}^{N}\frac{p_i}{m_i} - gkT\right)$$

(redundant; s is not present in other equations)

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MD in other ensembles

Reminder: Kinetic temperature vs. configurational temperature

$$k_B T = \frac{1}{3N} \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m}$$

The standard canonical ensemble "equipartition" result

我们一般只控制动量定义
的温度。

$$k_B T = \frac{|\nabla_{\mathbf{r}} U|^2}{\nabla_{\mathbf{r}}^2 U}$$

$$= \frac{\displaystyle\sum_{i=1}^{N} \mathbf{F}_i^2}{-\displaystyle\sum_{i=1}^{N} \left(\frac{\partial F_{ix}}{\partial r_{ix}} + \frac{\partial F_{iy}}{\partial r_{iy}} + \frac{\partial F_{iz}}{\partial r_{iz}} \right)}$$

事实上也可以定义构型空
间的温度。

体系达到平衡的标志是二者相等。这提供了一个检测
体系状态的重要手段。