Molecular dynamics, Monte Carlo dynamics
Time evolution of extended systems

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Paradigm: dense fluids

- Deterministic or random evolution
- Algorithms

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- Abstract dynamical systems
- Examples of chaotic maps
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Markov chains

- Markov chain on finite or countable set
- Detailed balance
- Monte Carlo in continuum

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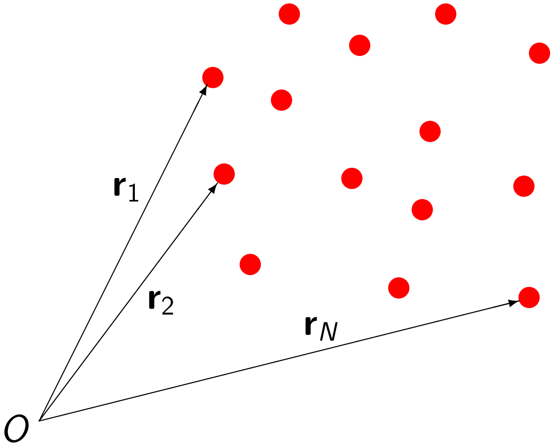

N particles in interaction:

differential equation

or

random walkers

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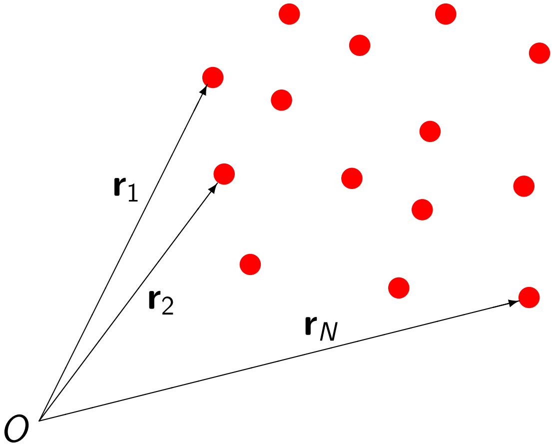

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$$\underline{\mathbf{r}}(t) = \big(\mathbf{r}_1(t), \mathbf{r}_2(t), \ldots, \mathbf{r}_N(t)\,\big) \in \mathbb{R}^{3N}$$

$$U(\underline{\mathbf{r}}) = \sum_{1 \le i < j \le N} u(|\mathbf{r}_i - \mathbf{r}_j|)$$

Molecular dynamics: differential equation

Newton's second law:

$$m\frac{d^2\underline{\mathbf{r}}}{dt^2} = -\underline{\nabla} U(\underline{\mathbf{r}})\,, \qquad t \in [0, T]$$

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$$\begin{aligned} \underline{\mathbf{r}}(0) &= \text{Initial configuration } (\textit{regular array}) \\ \frac{d\underline{\mathbf{r}}}{dt}(0) &= \text{Initial velocities } (3N \textit{ independent Gaussians}) \end{aligned}$$

Monte Carlo dynamics: random walkers

Each walker carries an independent Poisson clock: the time intervals between successive rings of each clock are iid exponential random variables. When a clock rings, the corresponding walker wakes up and attempts a blind move $\mathbf{r}_i \to \mathbf{r}_i + \delta$ where δ is an independent random vector uniformly distributed in a ball centred at the origin. This attempt would change the energy $U(\underline{\mathbf{r}})$ by an amount ΔU. If $\Delta U \leq 0$ the attempted move is accepted. Otherwise it is accepted with probability $\exp(-\Delta U)$ and rejected with probability $1 - \exp(-\Delta U)$. The walker falls asleep in the assigned position until the next ring of his clock.

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Game of werewolves

Initial condition: same as $\underline{\mathbf{r}}(0)$ for differential equation.

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- Time reversal

Algorithm for differential equation

Time step $\Delta t = h$, Taylor expansion:

$$\underline{\mathbf{r}}(t+h) = \underline{\mathbf{r}}(t) + h\,\underline{\mathbf{r}}'(t) + \frac{h^2}{2}\,\underline{\mathbf{r}}''(t) + \frac{h^3}{3!}\,\underline{\mathbf{r}}'''(t) + \mathcal{O}(h^4)$$

$$\underline{\mathbf{r}}(t-h) = \underline{\mathbf{r}}(t) - h\,\underline{\mathbf{r}}'(t) + \frac{h^2}{2}\,\underline{\mathbf{r}}''(t) - \frac{h^3}{3!}\,\underline{\mathbf{r}}'''(t) + \mathcal{O}(h^4)$$

$$\Longrightarrow$$

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Tomorrow = Today + (Today - Yesterday) + Acceleration

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Verlet algorithm:

$$\underline{\mathbf{r}}(t+h) = 2\underline{\mathbf{r}}(t) - \underline{\mathbf{r}}(t-h) - h^2\,\nabla U(\underline{\mathbf{r}}(t))$$

Two-step recursion relation, requires $\underline{\mathbf{r}}(0)$ and $\underline{\mathbf{r}}(h)$.

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Parallel dynamics !

Algorithm for random walkers

Poisson process of clock i : $(T_1^i, T_2^i, \dots T_n^i, \dots)$.

Law of large numbers $\Rightarrow$ $$\frac{T_1^i + T_2^i + \cdots + T_{[t]}^i}{t} \to 1 \quad \text{as} \quad t \nearrow \infty$$

Chronology of jumps up to time t:

$$\begin{array}{cc} t_1 & i_1 \\ t_2 & i_2 \\ \dots & \dots \\ t_{\text{nb.steps}} & i_{\text{nb.steps}} \end{array}$$

Law of large numbers $\Rightarrow$ $$\frac{\text{nb.steps}(t)}{t*N} \to 1 \quad \text{as} \quad t \nearrow \infty$$

Law of $\underline{\mathbf{r}}(t)$, given $\text{nb.steps}(t)$ and sequence of rings $i_1, i_2, \dots, i_{\text{nb.steps}}$, is independent of t. Use step number (discrete time) instead of t.

Sequence of rings iid uniform in $\{1, \dots, N\}$.

Random sequential dynamics

Molecular dynamics as dynamical system

First step: get first order differential equation. Let

$$y(t) = \begin{pmatrix} y_1(t) \\ y_2(t) \end{pmatrix} = \begin{pmatrix} \underline{\mathbf{r}}(t) \\ d\underline{\mathbf{r}}(t)/dt \end{pmatrix} \in \mathbb{R}^{6N}$$

$$\Longrightarrow \qquad \frac{dy}{dt} = \begin{pmatrix} y_2 \\ \\ -\frac{1}{m}\nabla U(y_1) \end{pmatrix}$$

Continuous time dynamical system:

$$\frac{dy}{dt} = \mathbf{F}(y)\,, \quad y \in \mathbb{R}^n \text{ or torus, } t \in \mathbb{R}_+ \text{ or } \mathbb{R}$$

Centred discretization scheme

$$y(t+h) = y(t) + hy'(t) + \frac{h^2}{2}y''(t) + \mathcal{O}(h^3)$$
$$y(t-h) = y(t) - hy'(t) + \frac{h^2}{2}y''(t) + \mathcal{O}(h^3)$$

$$y(t+h) = y(t-h) + 2hy'(t) + \mathcal{O}(h^3) = y(t-h) + 2h\mathbf{F}(y(t)) + \mathcal{O}(h^3)$$

$\Rightarrow$ two-step recursion.

Phase space and Liouville's theorem

Hamilton's equations of motion:
$(q_1, \dots q_s, p_1, \dots p_s) = (\underline{q}, \underline{p}) \in \mathbb{R}^{2s}$

$$\begin{aligned} \dot{q}_k &= \frac{\partial H}{\partial p_k} \\ \dot{p}_k &= -\frac{\partial H}{\partial q_k} \end{aligned}$$

State of system: probability measure $\rho(t, \underline{q}, \underline{p}) d\underline{q} d\underline{p}$.
Corresponding flux $\mathbf{J} = (\rho \underline{\dot{q}}, \rho \underline{\dot{p}})$. For any fixed $\Omega \subset \mathbb{R}^{2s}$,

$$\frac{d}{dt} \int_\Omega \rho d\underline{q} d\underline{p} = -\int_{\partial\Omega} \mathbf{J} \cdot \mathbf{n} \, dS = -\int_\Omega \nabla \cdot \mathbf{J} \, d\underline{q} d\underline{p} \quad \Longrightarrow$$

$$-\frac{\partial \rho}{\partial t} = \nabla \cdot \mathbf{J} = \sum_{k=1}^{s} \left(\frac{\partial \rho \dot{q}_k}{\partial q_k} + \frac{\partial \rho \dot{p}_k}{\partial p_k} \right) = \sum_{k=1}^{s} \left(\frac{\partial \rho}{\partial q_k} \dot{q}_k + \frac{\partial \rho}{\partial p_k} \dot{p}_k \right) \Rightarrow \frac{d\rho}{dt} = 0$$

Dynamical systems

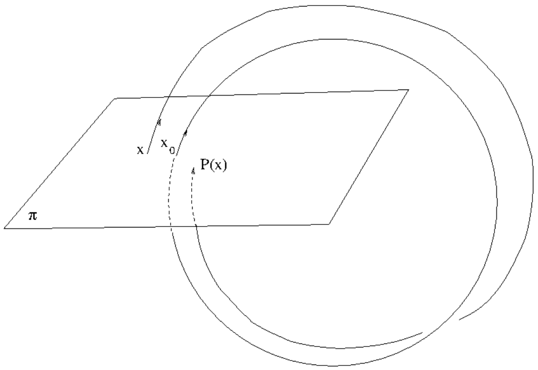
- Set of states Ω: words, $\mathbb{Z}$, $\mathbb{Z}/(n\mathbb{Z})$, $[0,1)$, $\mathbb{R}^{6N}\dots$
- Time evolution
  - Discrete time evolution: map $f:\Omega\to\Omega$
    $x_n \mapsto x_{n+1} = f(x_n)$.
    Orbit of x_0: $\{f^n(x_0)\}_{n\in\mathbb{Z}^+}$.
  - Continuous time semi-flow: family of maps $(\varphi_t)_{t\in\mathbb{R}^+}$

$$\varphi_t:\Omega\to\Omega,\quad \varphi_0 = I,\quad \varphi_s\circ\varphi_t = \varphi_{s+t}$$

    $x_t = \varphi_t(x_0)$. Orbit of x_0 : $(\varphi_t(x_0))_{t\in\mathbb{R}^+}$
  - Differential equation on manifold: vector field $\mathbf{F}$,

$$\frac{d\mathbf{x}}{dt} = \mathbf{F}(x)$$

Poincaré Map



Circle rotations: not chaotic

Circle $S^1 = [0, 1)$ with addition mod 1 and distance

$$d(x, y) = \min(|x - y|, 1 - |x - y|)$$

Rotation by angle $2\pi\alpha$:

$$R_\alpha x = x + \alpha \mod 1$$

preserves distance and Lebesgue measure.

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Rotation by angle $2\pi\alpha$:

$$R_\alpha x = x + \alpha \quad \mod 1$$

preserves distance and Lebesgue measure. Ergodicity:

$$\alpha = p/q \;\Rightarrow\; R_\alpha^q = \mathrm{Id} \;\Rightarrow\; \text{every orbit periodic}$$

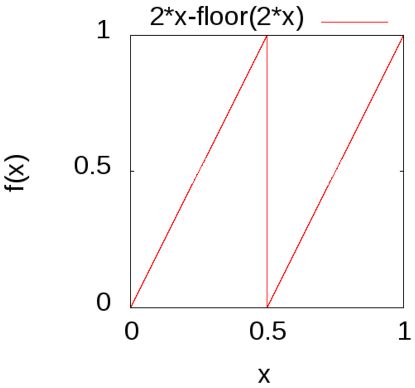
$$\alpha \notin \mathbb{Q} \;\Rightarrow\; R_\alpha^m \neq R_\alpha^n \;\forall m < n$$

$$\forall \varepsilon > 0 \;\exists m < n < 1/\varepsilon,\; d(R_\alpha^m, R_\alpha^n) < \varepsilon \quad \text{Pigeon-hole principle}$$

$\Rightarrow R_\alpha^{m-n}$ is rotation by angle $< \varepsilon \Rightarrow$ every positive semi-orbit is dense

$\Rightarrow$ no closed invariant subset other than $S^1, \emptyset \qquad \Rightarrow \quad R_\alpha$ ergodic

Doubling the angle I



$$\Omega = [0, 1)$$
$$x \mapsto f(x) = 2x \mod 1$$

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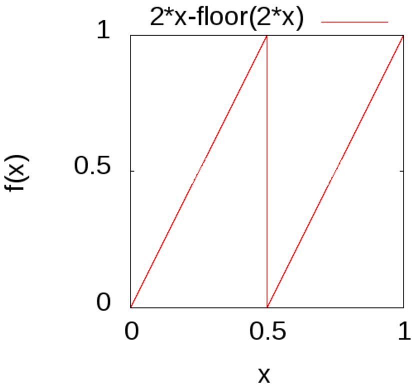

$\Omega = [0, 1)$
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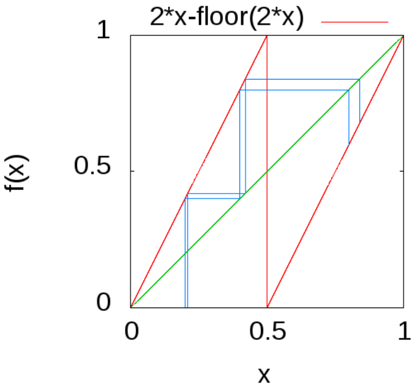
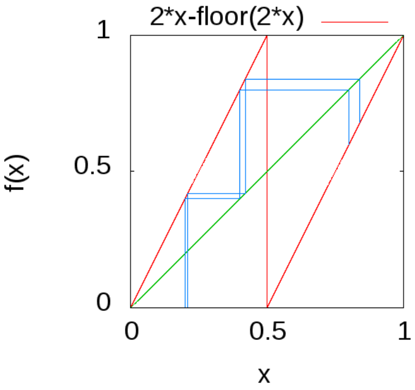
Not invertible,
not area preserving

Doubling the angle II



$$f^n(x+\varepsilon) - f^n(x) \mod 1 \;=\; 2^n\varepsilon \mod 1$$

Doubling the angle II



$$f^n(x+\varepsilon) - f^n(x) \mod 1 = 2^n \varepsilon \mod 1$$

Chaotic

Baker's transform

Aim: chaotic, area preserving, invertible. $\Omega = [0,1) \times [0,1) \subset \mathbb{R}^2$

$$\begin{pmatrix} x \\ y \end{pmatrix} \mapsto \begin{pmatrix} x' \\ y' \end{pmatrix} = \left(\begin{array}{c} 2x \quad \bmod 1 \\ \\ \begin{cases} \frac{y}{2} \text{ if } x < 0.5 \\ \\ \frac{y+1}{2} \text{ if } x \geq 0.5 \end{cases} \end{array} \right)$$

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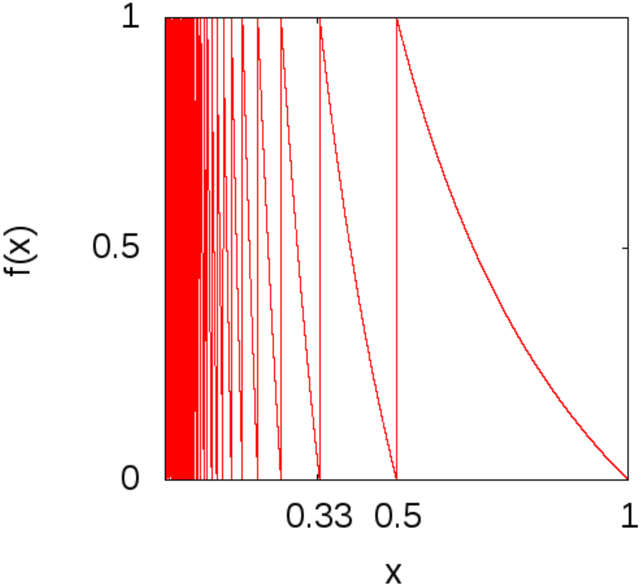
$$x < 0.5 \Leftrightarrow y' < 0.5$$

$$\begin{pmatrix} x' \\ y' \end{pmatrix} \mapsto \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} \begin{cases} \frac{x'}{2} \text{ if } y' < 0.5 \\ \frac{x'+1}{2} \text{ if } y' \geq 0.5 \end{cases} \\ 2y' \mod 1 \end{pmatrix}$$

Gauss transform



$$\begin{cases} 1/x - \lfloor 1/x \rfloor & \text{if} \quad x \in (0, 1] \end{cases}$$

Gauss transform: invariant measure

Let

$$\mu((a,b)) = (\log 2)^{-1} \int_a^b \frac{dx}{1+x} = (\log 2)^{-1} \log \frac{1+b}{1+a}$$

Then

$$\begin{aligned} \mu(f^{-1}((a,b))) &= \mu\left(\bigcup_{n=1}^{\infty} \left(\frac{1}{n+b}, \frac{1}{n+a}\right)\right) \\ &= \frac{1}{\log 2} \sum_{n=1}^{\infty} \log\left(\frac{n+a+1}{n+a} . \frac{n+b}{n+b+1}\right) = \mu((a,b)) \end{aligned}$$

Gauss transform: continued fraction

Idea:

$$x = \frac{1}{\left\lfloor \frac{1}{x} \right\rfloor + f(x)} = \frac{1}{\left\lfloor \frac{1}{x} \right\rfloor + \frac{1}{\left\lfloor \frac{1}{f(x)} \right\rfloor + f^2(x)}} = \dots$$

Let

$$a_i = \left\lfloor \frac{1}{f^{i-1}(x)} \right\rfloor, \qquad x = [a_1, a_2, \dots] = \frac{1}{a_1 + \frac{1}{a_2 + \dots}}$$

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Let

$$a_i = \left\lfloor \frac{1}{f^{i-1}(x)} \right\rfloor, \qquad x = [a_1, a_2, \dots] = \frac{1}{a_1 + \frac{1}{a_2 + \dots}}$$

$$f(x) \in \mathbb{Q} \Leftrightarrow x \in \mathbb{Q}$$

$$f^n(x) = 0 \;\Rightarrow\; f^{n-1}(x) \in \mathbb{Q} \;\Rightarrow\; \dots \;\Rightarrow\; x \in \mathbb{Q}$$

$$f(x) = [a_2, a_3, \dots]$$

Gauss transform on $[0, 1]$ is conjugate of shift on $(a_i)_{i=1}^{\omega}, \omega \in \mathbb{N} \cup \{\infty\}, a_i \in \mathbb{N}$

Dissipative dynamical systems

Pseudo-random number generators I

Circle rotations? Not chaotic!

In computer only integers modulo 2^{64}. For any $m \in \mathbb{Z}^+$, consider $\Omega = \mathbb{Z}/(m\mathbb{Z}) = \{0, 1, \ldots, m-1\}$

$$x_n \mapsto x_{n+1} = ax_n + c \quad \mod m$$

a=multiplier, c=increment, m=modulus, x_0=seed. Ex.:

$c = 1, m = 8, x_0 = 0$:

a=1 x =	0 1 2 3 4 5 6 7 0
2	0 1 3 7 7 7 7 7 7
3	0 1 4 5 0 1 4 5 0
4	0 1 5 5 5 5 5 5 5
5	0 1 6 7 4 5 2 3 0
6	0 1 7 3 3 3 3 3 3
7	0 1 0 1 0 1 0 1 0
8	0 1 1 1 1 1 1 1 1

Pseudo-random number generators II

```
n=69069*n+1013904243 ran=0.5d0+dble(n)*0.23283064d-9
```

$\mathtt{n} = 69069{*}\mathtt{n}{+}1013904243, \qquad \mathtt{ran} = 0.5\mathtt{d}0{+}\mathtt{dble}(\mathtt{n}){*}0.23283064\mathtt{d}{-}9$

```
n=n*2862933555777941757+1013904243
ran=0.5d0+dble(n)*dmul
```

$\mathtt{dmul} = 1.\mathtt{d}0/\mathtt{dble}(2 * (2_8 * *62 - 1) + 1)$

Generating more random variables: exponential, Gaussian...

- How to implement "jump accepted with probability $\exp(-(\Delta U)_+)$"?
- How to generate the attempted jumps with uniform distribution in a ball?
- How to generate the initial velocities with Gaussian distribution?

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Enough to generate random numbers ω uniformly in $[0,1[$:
If $\omega < \exp(-(\Delta U)_+)$, accept!
$\omega_1, \omega_2, \omega_3 \in U([0,1[)$. If $\omega_1^2 + \omega_2^2 + \omega_3^2 > 1$ try again!
Exponential random variable: $X = -\ln(1-\omega) \ \in \mathbb{R}_+$
Two Gaussians: $dx\, e^{-\frac{x^2}{2}}\, dy\, e^{-\frac{y^2}{2}} = d\theta d\frac{r^2}{2}\, e^{-\frac{r^2}{2}} =$ uniform $\times$ exponential

Random walk in $\mathbb{Z}$

$$X_0 = 0\,, \quad X_{t+1} = \begin{cases} X_t - 1 & \text{with probability } 1/2 \\ X_t + 1 & \text{with probability } 1/2 \end{cases}$$

$$\omega_t \in U([0,1[)\,, \quad X_{t+1} = X_t + 2\lfloor 2\omega_t \rfloor - 1$$

Markov chain:

$$X_{t+1} = f\left(X_t, \omega_t\right)$$

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$$X_{t+1} = f\left(X_t, \omega_t\right)$$

$$\underline{\mathbf{r}}_{t+1} = f(\underline{\mathbf{r}}_t, \omega_t)$$

Markov chain on finite or countable set $\Omega = \{a, b, \dots\}$

Stochastic matrix: $\{Q_{a\to b}\}_{a,b\in\Omega}, \; Q_{a\to b} \geq 0$

$$\forall a \in \Omega, \quad \sum_{b\in\Omega} Q_{a\to b} = 1 \qquad \text{(sub-stochastic if } \leq 1\text{)}$$

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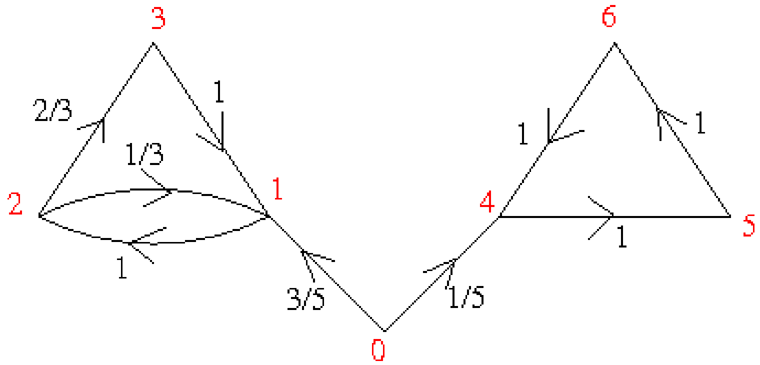
$$\mathbb{P}\left(X_{t+1} = b | X_t = a\right) = Q_{a\to b}$$

The stochastic matrix and the Markov chain are *irreducible* if
$\forall a, b \in \Omega$, $\exists n \in \mathbb{Z}_+$, $a_1, a_2, \dots, a_{n-1} \in \Omega$,

$$Q_{a\to a_1} Q_{a_1\to a_2} \dots Q_{a_{n-1}\to b} > 0$$

$$\Leftrightarrow \forall a, b \quad \exists n, \quad \left(Q^n\right)_{a\to b} > 0$$

Diagram for discrete time Markov chain I



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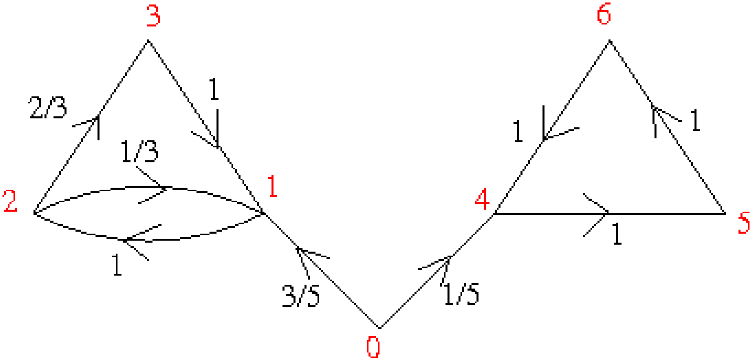

0 transient: $(Q^n)_{0\to 0} = 1/5^n$

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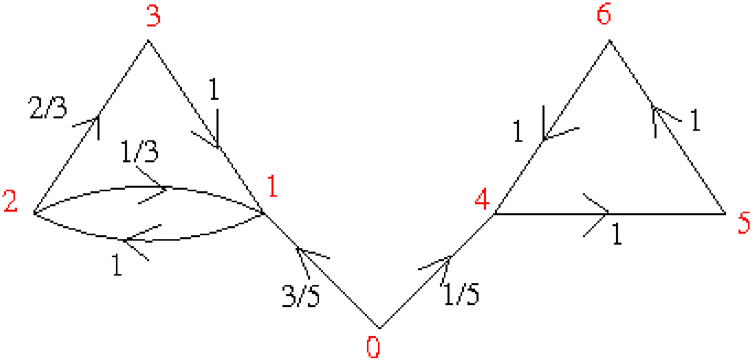
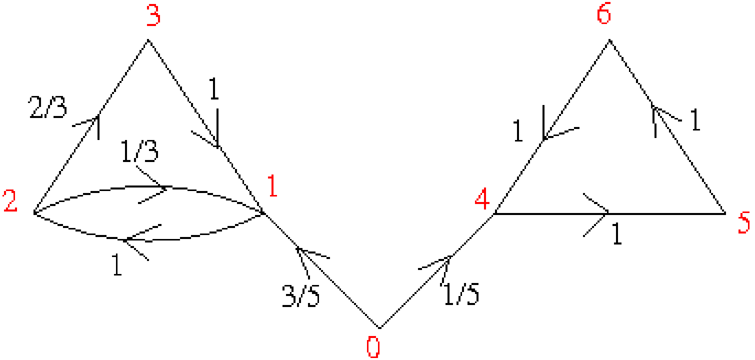


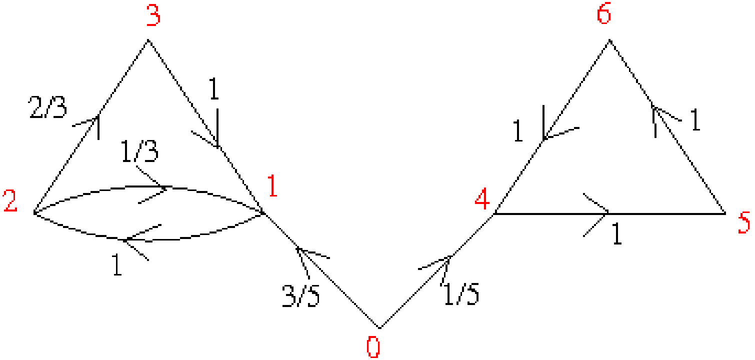
0 transient: $(Q^n)_{0\to 0} = 1/5^n$
4,5,6 periodic:
$(Q^{3n})_{0\to 4} = \frac{1}{5^3} + \frac{1}{5^6} + \cdots \to \frac{1}{5^3}\frac{1}{1-\frac{1}{5^3}} = \frac{1}{124}$
$(Q^{3n+1})_{0\to 4} = \frac{1}{5} + \frac{1}{5^4} + \cdots \to \frac{1}{5}\frac{1}{1-\frac{1}{5^3}} = \frac{25}{124}$
$(Q^{3n+2})_{0\to 4} = \frac{1}{5^2} + \frac{1}{5^5} + \cdots \to \frac{1}{5^2}\frac{1}{1-\frac{1}{5^3}} = \frac{5}{124}$

Diagram for discrete time Markov chain II



Assume $\exists\ p_i = \lim_{n \nearrow \infty} (Q^n)_{0 \to i},\ \ i = 1, 2, 3.$

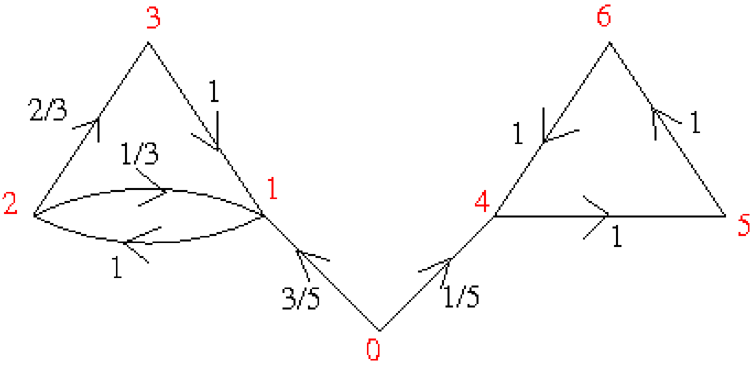
Diagram for discrete time Markov chain II



Assume $\exists\ p_i = \lim_{n\nearrow\infty}(Q^n)_{0\to i},\ \ i = 1, 2, 3.$

$$\begin{aligned} p_1 &= p_3 + p_2/3 \\ p_2 &= p_1 \\ p_3 &= p_2 * 2/3 \\ p_1 + p_2 + p_3 &= 3/4 \end{aligned}$$

Diagram for discrete time Markov chain II



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$$\begin{aligned} p_1 &= p_3 + p_2/3 \\ p_2 &= p_1 \\ p_3 &= p_2 * 2/3 \\ p_1 + p_2 + p_3 &= 3/4 \qquad \Rightarrow \quad p_1 = 9/32 \end{aligned}$$

Master equation

The initial condition may be a chosen configuration or a probability distribution $\{p_a(0)\}_{a\in\Omega}$. In any case let $\{p_a(t)\}_{a\in\Omega}$ denote the probability distribution of the Markov chain at time t:

$$p_a(t) = \mathbb{P}\left(X_t = a\right), \qquad a \in \Omega, \quad t \in \mathbb{Z}_+$$

Then

$$p_a(t+1) = \sum_{b\in\Omega} p_b(t) Q_{b\to a}$$

Invariant measures are left-eigenvectors of the matrix $Q_{a\to b}$ with eigenvalue 1.

Monte Carlo dynamics on finite or countable set

$$Q_{a\to b} = Q^{\mathrm{attempt}}_{a\to b}\,Q^{\mathrm{accept}}_{a\to b}, \qquad a \neq b$$

$Q^{\mathrm{attempt}}_{a\to b}$ symmetric sub-stochastic, $0 \leq Q^{\mathrm{accept}}_{a\to b} \leq 1$ $\forall a \neq b$.

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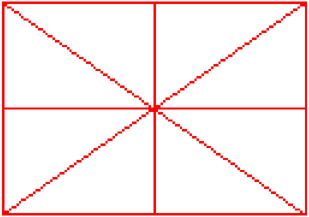
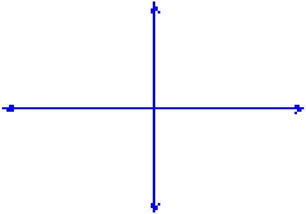
$$Q_{a\to a} = 1 - \sum_{b\neq a} Q_{a\to b}$$

Random walk on British flag





Ω ={vertices}={1,2,...,9}

$$Q^{\text{attempt}}_{a\to b} = \begin{cases} 1/4 & \text{if } a, b \text{ neighbours} \\ 0 & \text{otherwise} \end{cases}$$

$$Q^{\text{accept}}_{a\to b} = \begin{cases} 1 & \text{if } a, b \in \Omega \\ 0 & \text{otherwise} \end{cases}$$

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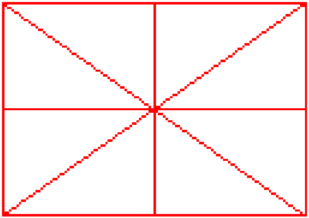 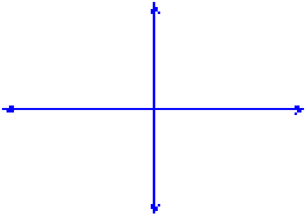

$\Omega = \{\text{vertices}\} = \{1, 2, \ldots, 9\}$

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$$Q^{\text{accept}}_{a\to b} = \begin{cases} 1 & \text{if } a, b \in \Omega \\ 0 & \text{otherwise} \end{cases} \qquad \Longrightarrow \qquad Q_{a\to a} \in \left\{0, \frac{1}{4}, \frac{1}{2}\right\}$$

Detailed balance

The dynamics defined by $\{Q_{a\to b}\}_{a,b\in\Omega}$ obeys the detailed balance condition with respect to a measure $\{p_a\}_{a\in\Omega}$ if and only if

$$p_b Q_{b\to a} = p_a Q_{a\to b} \quad \forall a, b \in \Omega$$

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Metropolis algorithm

Given $\{p_a\}_{a\in\Omega}$,

$$Q^{\text{accept}}_{a\to b} = \min\left\{\frac{p_b}{p_a}, 1\right\}, \qquad a, b \in \Omega,\ a \neq b$$

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Detailed balance with a Gibbs measure

$$p_a = \frac{e^{-E_a}}{Z}, \quad Z = \sum_{a \in \Omega} e^{-E_a}, \quad \frac{p_b}{p_a} = e^{-(E_b - E_a)}$$

Lattice gas

Finite volume $\Lambda \subset \mathbb{Z}^3$, configuration space $\Omega = \{0,1\}^\Lambda$, configuration $\underline{n} = \{n_i\}_{i\in\Lambda}$, occupation variable $n_i \in \{0,1\}$,

$$E(\underline{n}) = -\lambda \sum_{|i-j|=1} n_i n_j - \mu \sum_{i\in\Lambda} n_i$$

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Glauber dynamics:

$$Q^{\text{attempt}}_{\underline{n}\to\underline{n}'} = \begin{cases} \frac{1}{|\Lambda|} & \text{if } \underline{n}, \underline{n}' \text{ differ only at one site, } i \in \Lambda \\ 0 & \text{otherwise} \end{cases}$$

$$Q^{\text{accept}}_{\underline{n}\to\underline{n}'} = \min\left\{\frac{p(\underline{n}')}{p(\underline{n})}, 1\right\} = \min\left\{e^{(n_i'-n_i)(\lambda\sum_{j:|i-j|=1} n_j+\mu)}, 1\right\}$$

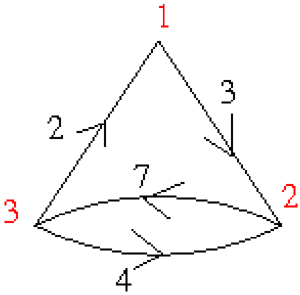
Kawasaki dynamics

Conserving particle number.

$$Q^{\text{attempt}}_{\underline{n}\to\underline{n}'} = \begin{cases} \frac{1}{|\Lambda|_{\text{bonds}}} & \text{if } \underline{n},\underline{n}' \text{ differ only at two neighboring sites,} \\ & \quad i,j\in\Lambda,\ n'_i = n_j,\ n'_j = n_i \\ 0 & \text{otherwise} \end{cases}$$

$$\begin{aligned} Q^{\text{accept}}_{\underline{n}\to\underline{n}'} &= \min\left\{\frac{p(\underline{n}')}{p(\underline{n})}, 1\right\} \\ &= \min\left\{\exp\left(\lambda(n'_i - n_i)\sum_{\substack{k\neq j\\ |k-i|=1}} n_k + \lambda(n'_j - n_j)\sum_{\substack{k\neq i\\ |k-j|=1}} n_k\right), 1\right\} \end{aligned}$$

Diagrams for a continuous time Markov chain $(X_t)_{t \geq 0}$



Exponential waiting times of density $\lambda e^{-\lambda t}$ w.r.t. to Lebesgue measure
$\lambda =$4, 7, 2, 3

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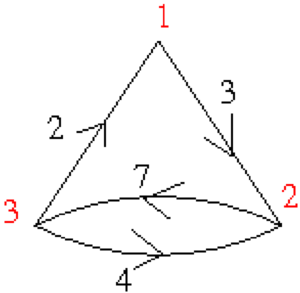

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Walker at 3. Waiting times T_1 for going to 1 and T_2 for going to 2.
Time spent in 3: $T = T_1 \wedge T_2$

$$\mathbb{P}(T > t) = \mathbb{P}(T_1 > t,\ T_2 > t) = 2\int_t^\infty dt_1 e^{-2t_1}\, 4\int_t^\infty dt_2 e^{-4t_2} = e^{-6t}$$

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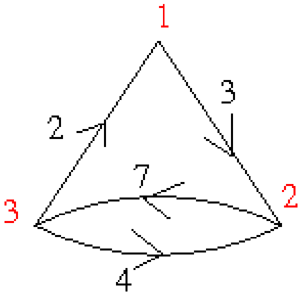

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$$\mathbb{P}(T_1 < T_2) = 2\int_0^\infty dt_1 e^{-2t_1}\, 4\int_{t_1}^\infty dt_2 e^{-4t_2} = 2\int_0^\infty dt_1 e^{-6t_1} = 1/3$$

Markov process in $\mathbb{R}^n$

$$\underline{\mathbf{r}}_{t+1} = f(\underline{\mathbf{r}}_t, \omega_t), \quad \{\omega_t\}_{t \in \mathbb{Z}_+} \text{independent sequence of r. v. in } \mathbb{R}^m$$

Law of $\underline{\mathbf{r}}_{t+1}$ given $\underline{\mathbf{r}}_t$?

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Law of $\underline{\mathbf{r}}_{t+1}$ given $\underline{\mathbf{r}}_t$? Ex.: random walk in $\mathbb{R}$

$$\omega_t \in U([0,1[)\,, \quad X_{t+1} = X_t + 2\omega_t - 1$$

$$\begin{aligned}
\mathbb{P}(X_{t+1} \in (y, y+dy) | X_t = x) &= \mathbb{P}\left(\omega_t \in \left(\frac{y-x+1}{2}, \frac{y+dy-x+1}{2}\right)\right) \\
&= \frac{dy}{2}\, 1_{|y-x|<1} \\
&= q(x \to y)dy
\end{aligned}$$

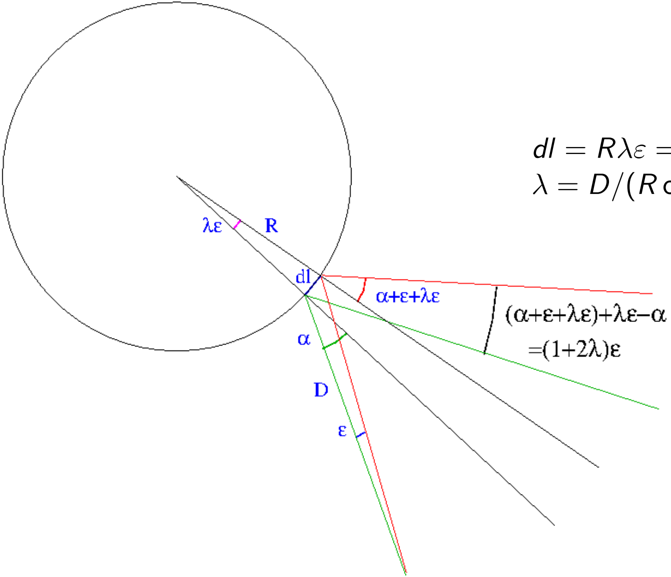
$$\mathbb{P}\left(\underline{\mathbf{r}}_{t+1} \in d^n r' \,\middle|\, \underline{\mathbf{r}}_t = \underline{\mathbf{r}}\right) = q(\underline{\mathbf{r}} \to \underline{\mathbf{r}}')d^n r', \; \int q(\underline{\mathbf{r}} \to \underline{\mathbf{r}}')d^n r' = 1$$

Master equation in $\mathbb{R}^n$

Initial condition $p^0(\underline{\mathbf{r}})$.

$$p^{t+1}(\underline{\mathbf{r}}') = \int d^n r \; p^t(\underline{\mathbf{r}})\, q(\underline{\mathbf{r}} \to \underline{\mathbf{r}}')$$

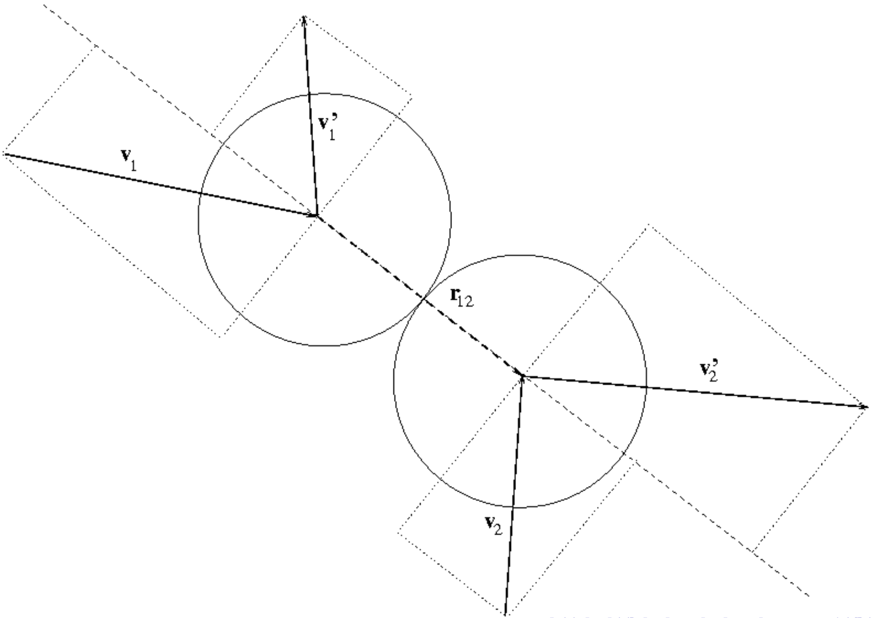
One ball convex billiard



$$dl = R\lambda\varepsilon = D\varepsilon/\cos\alpha$$
$$\lambda = D/(R\cos\alpha)$$

$\varepsilon \mapsto (1+2\lambda)\varepsilon \mapsto \cdots \mapsto (1+2\lambda)^n\varepsilon$. Chaos !

Hard spheres: conservation laws



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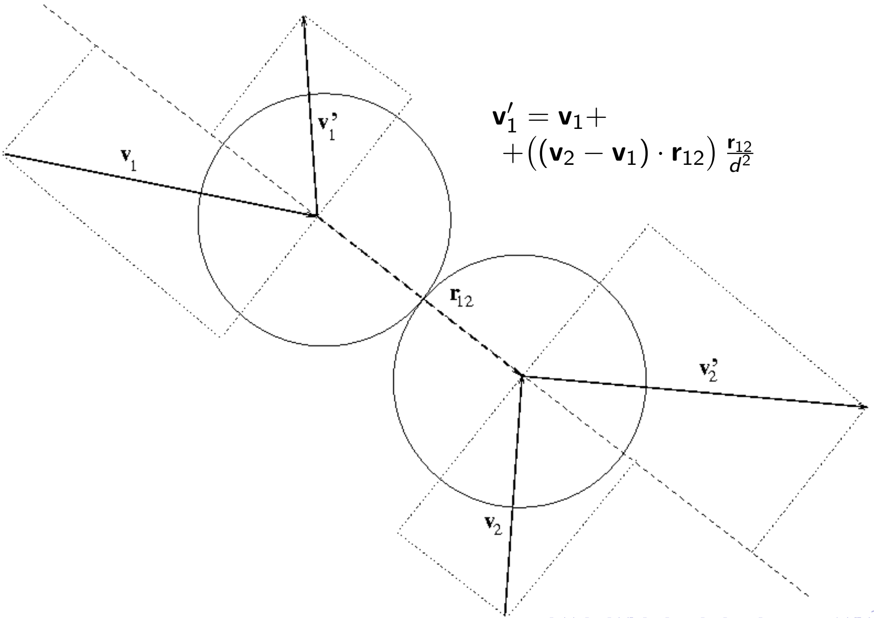

$$\mathbf{v}_1' = \mathbf{v}_1 + \\ + \big((\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{r}_{12} \big) \, \frac{\mathbf{r}_{12}}{d^2}$$

Hard spheres: collision times

Before collision, for $i, j = 1, \ldots, N$, with random initial velocities,

$$\mathbf{r}_i(t) \quad = \quad \mathbf{r}_i(0) + t\,\mathbf{v}_i\,, \quad \mathbf{r}_j(t) = \mathbf{r}_j(0) + t\,\mathbf{v}_j$$

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$$\begin{aligned} \mathbf{r}_i(t) &= \mathbf{r}_i(0) + t\,\mathbf{v}_i\,, \quad \mathbf{r}_j(t) = \mathbf{r}_j(0) + t\,\mathbf{v}_j \\ \mathbf{r}_{ij}(t) &= \mathbf{r}_i(t) - \mathbf{r}_j(t)\,, \quad \mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j \end{aligned}$$

$$0 = \mathbf{r}_{ij}(t)^2 - d^2$$

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\mathbf{r}_{ij}(t) &= \mathbf{r}_i(t) - \mathbf{r}_j(t)\,, \quad \mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j
\end{aligned}$$

$$\begin{aligned}
0 &= \mathbf{r}_{ij}(t)^2 - d^2 \\
&= \mathbf{v}_{ij}^2\,t^2 + 2\,\mathbf{r}_{ij}(0)\cdot\mathbf{v}_{ij}\,t + \mathbf{r}_{ij}(0)^2 - d^2
\end{aligned}$$

Collision at $t = t_{ij} > 0$ if $\Delta' > 0$ and $\mathbf{r}_{ij}(0)\cdot\mathbf{v}_{ij} < 0$.

Hard spheres: collision times

Before collision, for $i, j = 1, \ldots, N$, with random initial velocities,

$$\begin{aligned} \mathbf{r}_i(t) &= \mathbf{r}_i(0) + t\,\mathbf{v}_i\,, \quad \mathbf{r}_j(t) = \mathbf{r}_j(0) + t\,\mathbf{v}_j \\ \mathbf{r}_{ij}(t) &= \mathbf{r}_i(t) - \mathbf{r}_j(t)\,, \quad \mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j \end{aligned}$$

$$\begin{aligned} 0 &= \mathbf{r}_{ij}(t)^2 - d^2 \\ &= \mathbf{v}_{ij}^2\,t^2 + 2\,\mathbf{r}_{ij}(0)\cdot\mathbf{v}_{ij}\,t + \mathbf{r}_{ij}(0)^2 - d^2 \end{aligned}$$

Collision at $t = t_{ij} > 0$ if $\Delta' > 0$ and $\mathbf{r}_{ij}(0)\cdot\mathbf{v}_{ij} < 0$.
Otherwise set $t_{ij} = +\infty$.
Reflecting walls ($i = N+1$) or periodic boundary conditions (collision in neighboring boxes).

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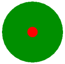
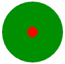
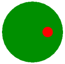
Reflecting walls ($i = N+1$) or periodic boundary conditions (collision in neighboring boxes).
$t_1 = \min\{t_{ij}\}$. Compute positions and velocities at $t = (t_1)_+$.
Iterate with t_1 as new initial time.

van der Waals interaction

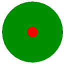


Atom $+q - q = 0$ no electric field outside atom

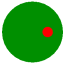
van der Waals interaction

	Atom $+q-q=0$	no electric field outside atom
	Atom in electric field $\vec{\mathcal{E}}$	Dipole $\vec{d}=q\vec{a}$, $\quad u=-\vec{d}\cdot\vec{\mathcal{E}}$, $\vec{d}=\alpha\vec{\mathcal{E}}$, $\quad \alpha=$polarizability Generated field $\sim \vec{d}/r^3$ at distance $r\nearrow\infty$ in direction $\vec{d}$

van der Waals interaction



Atom $+q-q=0$ — no electric field outside atom

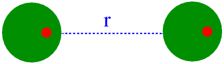


Atom in electric field $\vec{\mathcal{E}}$

Dipole $\vec{d} = q\vec{a}, \quad u = -\vec{d}\cdot\vec{\mathcal{E}},$

$\vec{d} = \alpha\vec{\mathcal{E}}, \quad \alpha =$polarizability

Generated field $\sim \vec{d}/r^3$ at distance $r \nearrow \infty$ in direction $\vec{d}$

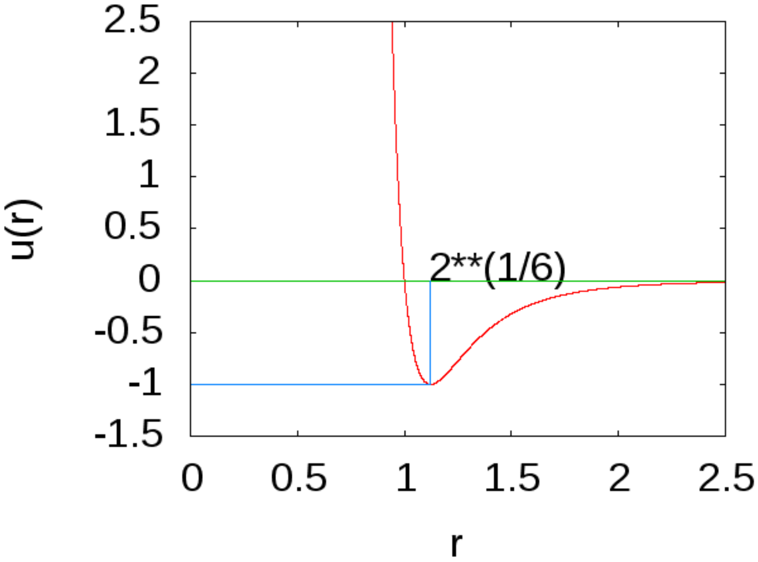


2 atoms at distance r

$\vec{d}_2 \sim \alpha\vec{d}_1/r^3, \quad u \sim -\alpha|\vec{d}_1|^2/r^6$

$\langle u\rangle \sim -\alpha\langle|\vec{d}_1|^2\rangle/r^6$

Lennard-Jones potential: $u(r) = 4(r^{-12} - r^{-6})$



$$u'(r) = -24(2r^{-13} - r^{-7}), \quad u'(2^{1/6}) = 0$$

```
program hard_spheres_mc
```

```
program hard_spheres_mc

integer i, j, k, t, tmax, p, n ;  parameter(p=3, n=p**3, tmax=20*n)
real r(1:3, 1:n), rt(1:3), rij2(1:n), u(1:4), diam, delta ;
parameter(diam=0.5, delta=0.1)
```

```
program hard_spheres_mc

integer i, j, k, t, tmax, p, n ;  parameter(p=3, n=p**3, tmax=20*n)
real r(1:3, 1:n), rt(1:3), rij2(1:n), u(1:4), diam, delta ;
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forall(k=1:3, i=1:n) r(k, i)=modulo((i-1)/p**(k-1), p)+0.5
```

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parameter(diam=0.5, delta=0.1)

forall(k=1:3, i=1:n) r(k, i)=modulo((i-1)/p**(k-1), p)+0.5

do t=1, tmax
call random_number(u) ;  i=int(n*u(1))+1
rt=r(:, i)+delta*(2*u(2:4)-1)
if ( (minval(rt)>diam/2).and.(maxval(rt)<p-diam/2)) then
forall(j=1:n, j/=i) rij2(j)=sum((rt-r(:, j))**2) ;  rij2(i)=2*diam**2
if (minval(rij2)>diam**2) then
r(:, i)=rt ;  write(6+i, *) r(:, i)
endif ;  endif
enddo
```

```
program hard_spheres_mc

integer i, j, k, t, tmax, p, n ;  parameter(p=3, n=p**3, tmax=20*n)
real r(1:3, 1:n), rt(1:3), rij2(1:n), u(1:4), diam, delta ;
parameter(diam=0.5, delta=0.1)

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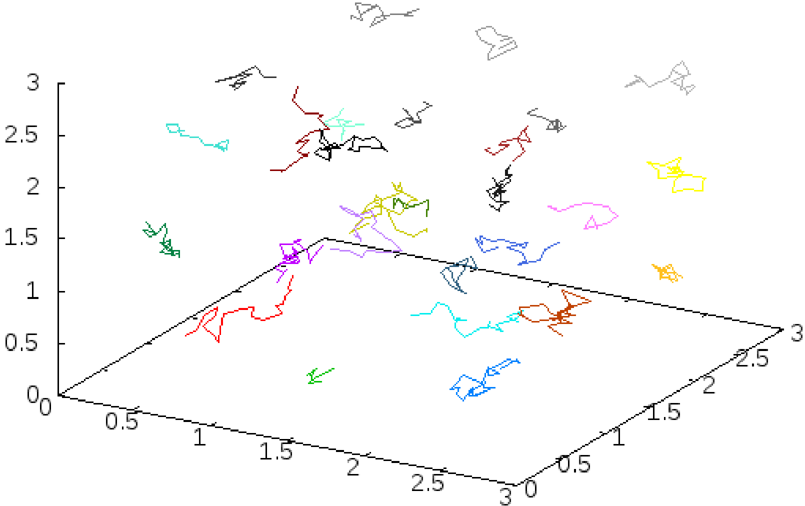
if ( (minval(rt)>diam/2).and.(maxval(rt)<p-diam/2)) then
forall(j=1:n, j/=i) rij2(j)=sum((rt-r(:, j))**2) ;  rij2(i)=2*diam**2
if (minval(rij2)>diam**2) then
r(:, i)=rt ;  write(6+i, *) r(:, i)
endif ;  endif
enddo

end
```

Hard spheres Monte Carlo



program mol_dyn

```
program mol_dyn
integer i, j, k, t, tmax, p, n ; parameter(p=5, n=p**3, tmax=11500)
real ri(1:3, 0:2, 1:n), rij(1:3, 1:n, 1:n), rij2(1:n, 1:n)
real Fij(1:3, 1:n, 1:n), Fi(1:3, 1:n), h2 ; parameter(h2=1e-3)
```

```
program mol_dyn
integer i, j, k, t, tmax, p, n ; parameter(p=5, n=p**3, tmax=11500)
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real Fij(1:3, 1:n, 1:n), Fi(1:3, 1:n), h2 ; parameter(h2=1e-3)

forall(k=1:3, i=1:n) ri(k, 0, i)=1.1*modulo((i-1)/p**(k-1), p)
ri(:,1,:)=ri(:,0,:) ; Fij=0
```

```
program mol_dyn
integer i, j, k, t, tmax, p, n ; parameter(p=5, n=p**3, tmax=11500)
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forall(k=1:3, i=1:n) ri(k, 0, i)=1.1*modulo((i-1)/p**(k-1), p)
ri(:,1,:)=ri(:,0,:) ; Fij=0

do t=1, tmax
   forall(i=1:n, j=1:n, i<j)
      rij(:, i, j)=ri(:, 1, i)-ri(:, 1, j) ; rij2(i, j)=sum(rij(:, i, j)**2)
      Fij(:, i, j)=rij(:, i, j)*(2*rij2(i, j)**(-7)-rij2(i, j)**(-4))
      Fij(:, j, i)=-Fij(:, i, j)
   end forall
   forall(k=1:3, i=1:n) Fi(k, i)=sum(Fij(k, i, :))
   ri(:, 2, :)=2*ri(:, 1, :)-ri(:, 0, :)+h2*Fi
   ri(:, 0, :)=ri(:, 1, :)
   ri(:, 1, :)=ri(:, 2, :)
   do i=1, n ; write(6+i, *) ri(:, 1, i) ; enddo
enddo
```

```
program mol_dyn
integer i, j, k, t, tmax, p, n ; parameter(p=5, n=p**3, tmax=11500)
real ri(1:3, 0:2, 1:n), rij(1:3, 1:n, 1:n), rij2(1:n, 1:n)
real Fij(1:3, 1:n, 1:n), Fi(1:3, 1:n), h2 ; parameter(h2=1e-3)

forall(k=1:3, i=1:n) ri(k, 0, i)=1.1*modulo((i-1)/p**(k-1), p)
ri(:,1,:)=ri(:,0,:) ; Fij=0

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   ri(:, 0, :)=ri(:, 1, :)
   ri(:, 1, :)=ri(:, 2, :)
   do i=1, n ; write(6+i, *) ri(:, 1, i) ; enddo
enddo
end
```

Gaussian initial velocities

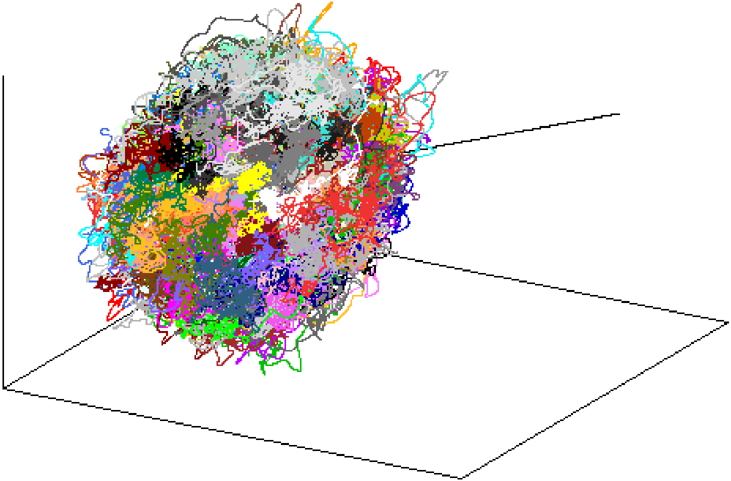
```
real x(1:3,1:n),y(1:3,1:n),pi,vi(1:3,1:n),v0
parameter(pi=2*asin(1.0),v0=0.005)
```

Gaussian initial velocities

```
real x(1:3,1:n),y(1:3,1:n),pi,vi(1:3,1:n),v0
parameter(pi=2*asin(1.0),v0=0.005)

call random_number(x); call random_number(y)
vi=v0*cos(2*pi*x)*sqrt(-2*log(1-y))
forall(k=1:3) vi(k,:)=vi(k,:)-sum(vi(k,:))/n
ri(:,1,:)=ri(:,0,:)+sqrt(h2)*vi(:,:)
```

Evaporation



Open Multi Processing

Explicit or implicit scheme

Fourier condition

CFL condition

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- P. Bergé, Y. Pomeau, C. Vidal: Order within Chaos. Wiley 1987.
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- P. Collet, F. Dunlop, T. Huillet: Critical wetting for a random line in long-range potential. J. Stat. Phys. 160, 1545-1622 (2015).
- F. M. Dunlop, P. A. Ferrari, L. R. G. Fontes: A dynamic one-dimensional interface interacting with a wall. J. Stat. Phys. 107, 705-727 (2002)