Meaningful timescales from Monte Carlo simulations of molecular systems: the case of hard disks

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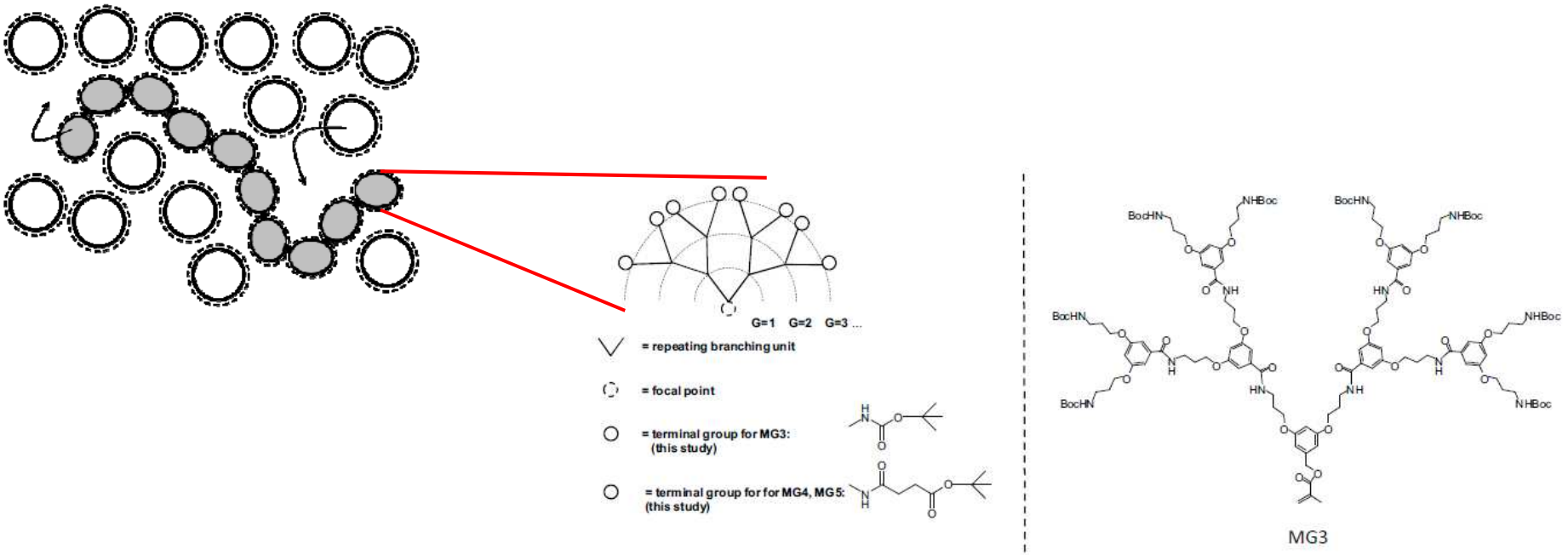
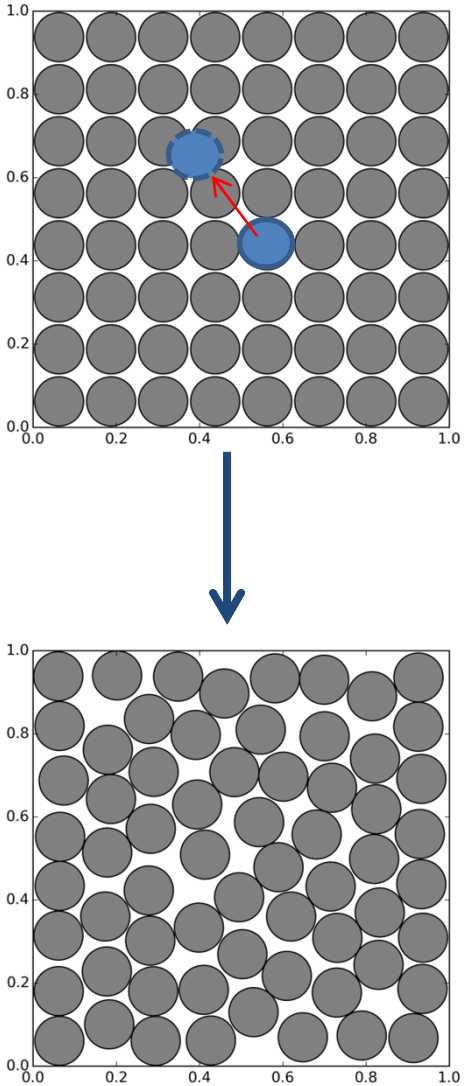
Meaningful timescales from Monte Carlo simulations of ~~molecular~~ particle systems: the case of hard disks



Costa and Storti, *Journal of Polymer Science*, 2010, 48, 529
Costa et al., *Macromolecular Reaction Engineering*, 2012, 6, 24

Costa et al, *Macromolecular Rapid Comm*, 2008, 29, 1609
Costa et al., *Macromolecules*, 2011, 44, 4038

Introduction: molecular simulations



Given initial positions, $\boldsymbol{r}_i$, and velocities, $\boldsymbol{v}_i$, at time t_0

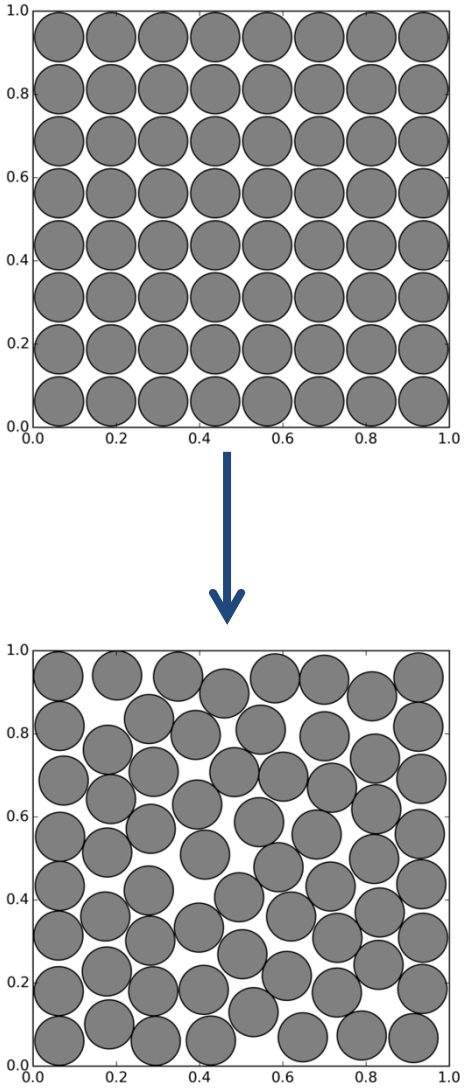
- Molecular dynamics
  - Newtonian trajectories
- $\boldsymbol{r}_i$ and $\boldsymbol{v}_i$ at any time t
  - Static properties
  - Dynamics

- Metropolis Monte Carlo
  - Stochastic (unphysical) trajectories
- $\boldsymbol{r}_i$ at "MC time"
  - Easier to implement
  - Fast convergence to Eq.
  - Static properties
  - no dynamics, no velocities

MC = no time!

Bal and Neyts, *Journal of Chemical Physics*, 2014, 141, 204104
Baumgartner, *Journal of Chemical Physics*, 1980, 72, 871
Landau and Binder, *A guide to MC simulations in Stat. Phys.*, 2015

Introduction: molecular simulations



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- Molecular dynamics
  - Newtonian trajectories
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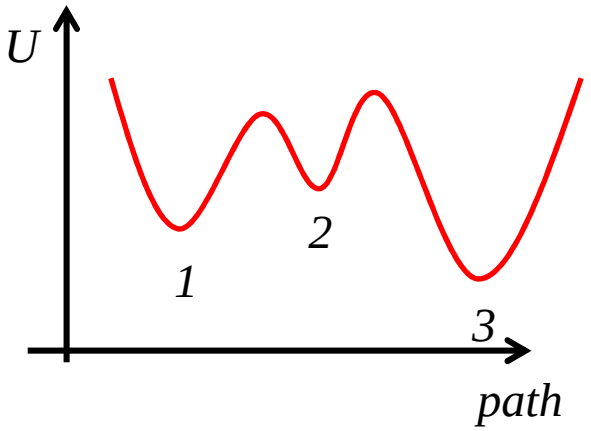
  - Dynamics

- Kinetic Monte Carlo

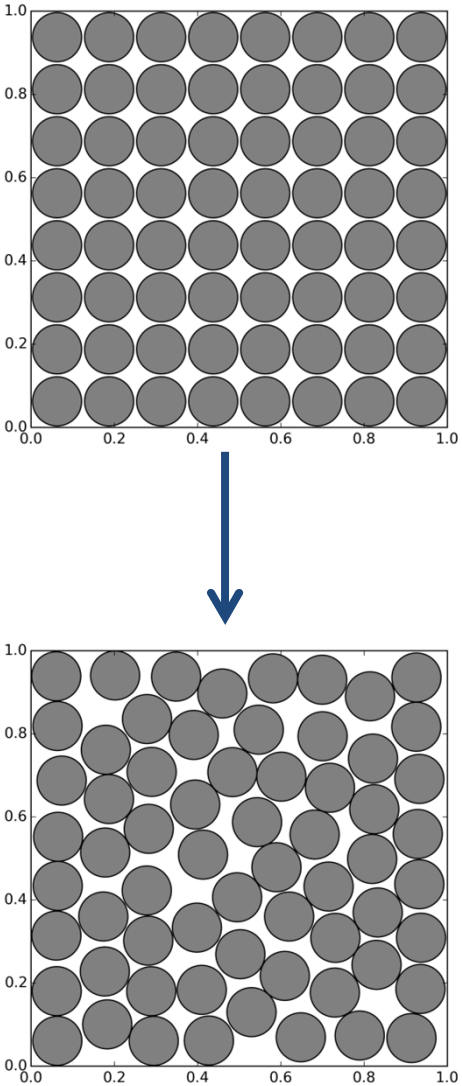


$$\frac{\partial P(t,i)}{\partial t} = \sum_j a_{ji} P(t,j) - \sum_j a_{ij} P(t,i)$$

$$\tau = \frac{1}{\sum a} \ln\left(\frac{1}{\zeta}\right)$$

Fichthorn and Weinberg, *Journal of Chemical Physics*, 1991, 95, 1090
Voter in Radiation Effects in Solids, Springer, 2005
Henkelman and Jonsson, *The Journal of Chemical Physics*, 2001, 115, 9657.

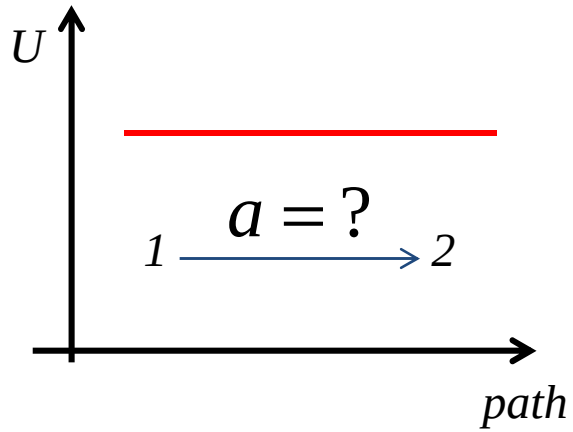
Introduction: molecular simulations



Given initial positions, $\boldsymbol{r}_i$, and velocities, $\boldsymbol{v}_i$, at time t_0

- Molecular dynamics
  - Newtonian trajectories
- $\boldsymbol{r}_i$ and $\boldsymbol{v}_i$ at any time t
  - Static properties
  - Dynamics

- Kinetic Monte Carlo
  - Needs discrete $N^{\#}$ of states

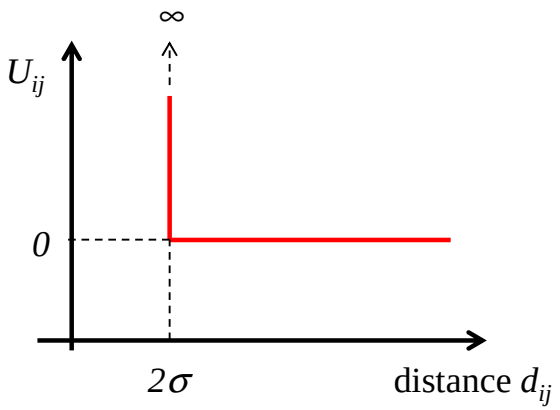


MD, or MMC → no time!
Is it necessarily true?

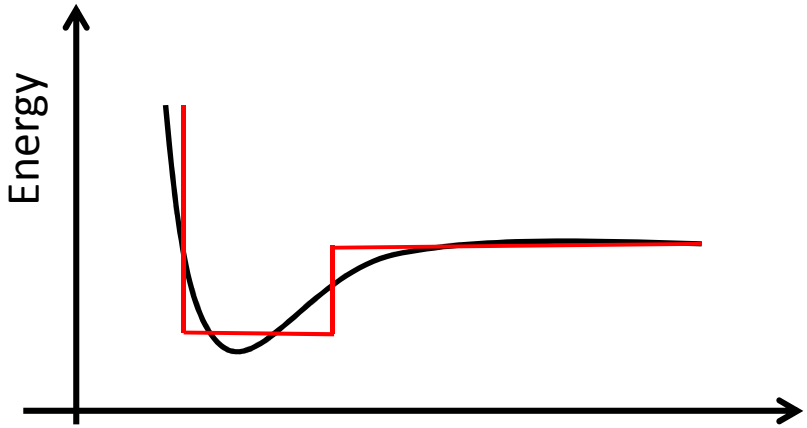
Bernard and Krauth, *Physical Review Letters*, 2011, 107, 155704.

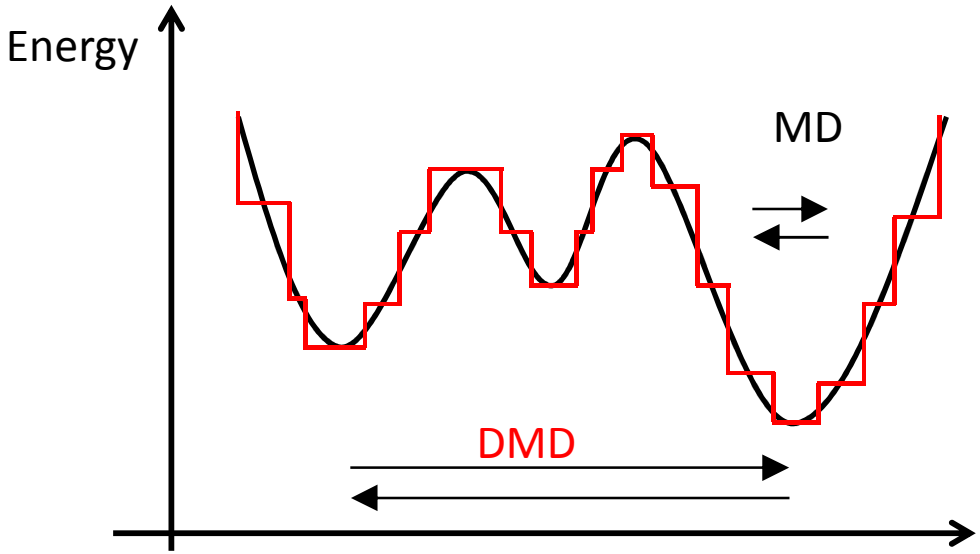
This work

- Question: can one construct a MC algorithm providing the «correct» dynamics of a molecular system, e.g., which includes a physically ***meaningful timescale***?



- Easy to generalize to «soft» potentials



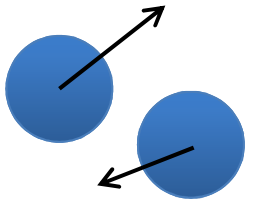


Proctor et al., *WIREs Computational Molecular Science*, 2011, 1, 80 (DMD)

Back to basics

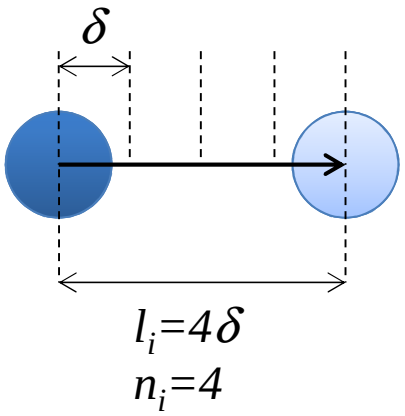
- Equation of motion for non interacting disks (no collisions)
  - displacement of disk i : l_i
  - velocity of disk i : v_i

$$\frac{dl_i}{dt} = v_i$$



- Let us define a unit of displacement δ
  - displacement: $n_i = l_i/\delta$
  - *velocity:* $a_i = v_i/\delta$

$$\frac{dn_i}{dt} = a_i$$



- **By discretizing the space, the equations of motion can be written equivalently in terms of numbers n_i of steps δ**

Motion ≈ Chemical reaction network

- Describes the motion of hard disks

$$\frac{dn_i}{dt} = a_i$$

- Describes the dynamics of a chemical reaction network (*N* species) with external source type reactions

$$\begin{cases} \varnothing \xrightarrow{a_1} n_1 \\ \varnothing \xrightarrow{a_2} n_2 \\ \dots \\ \varnothing \xrightarrow{a_n} n_N \end{cases}$$

- Probability evolution given by the Chemical Master Equation:

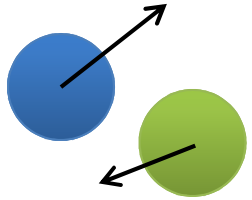
$$\frac{\partial P(t, n_1, \dots, n_N)}{\partial t} = \sum_i a_i \left[P(t, n_1, \dots, n_i - 1, \dots, n_N) - P(t, n_1, \dots, n_i, \dots, n_N) \right]$$

- **Solution of the CME: Stochastic Simulation Algorithm = Kinetic Monte Carlo**
  - propensities (transition probabilities) $a_i = v_i/\delta$
  - time step $\langle \tau \rangle = 1/\sum a_i = \delta/\sum v_i$

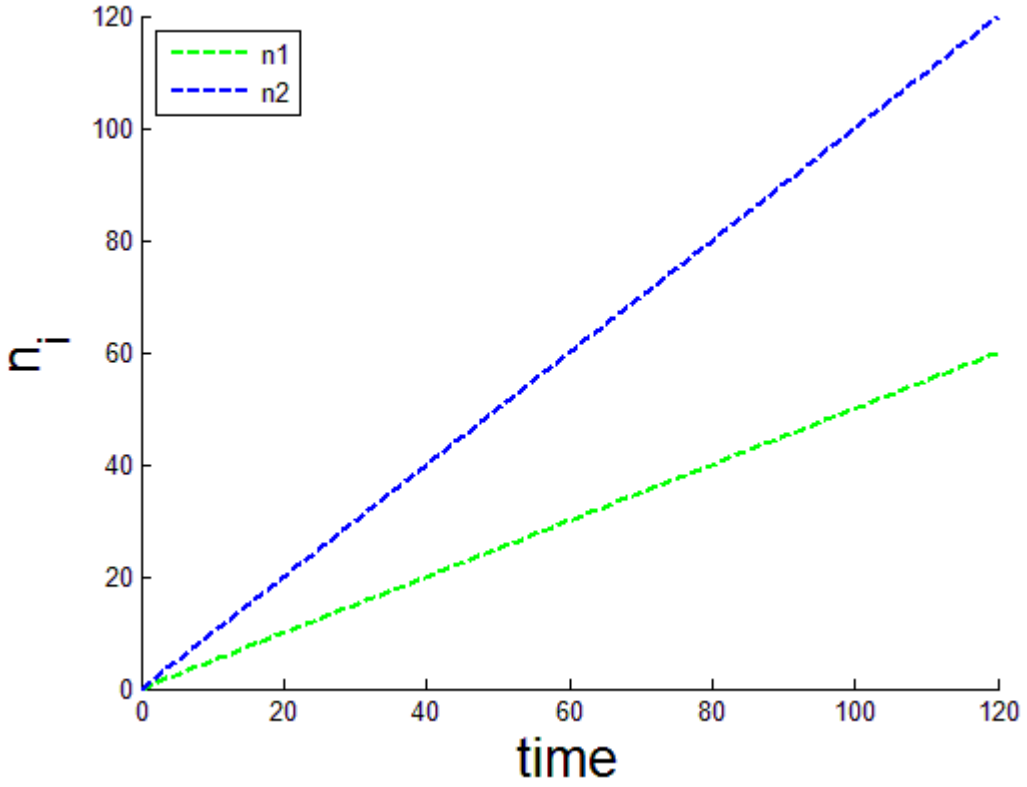
Gillespie, *Journal of Computational Physics*, 1976, 22, 403

An example

- Two non interacting disks: deterministic approach

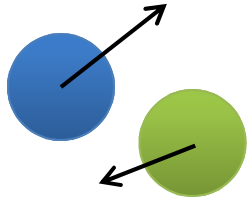


$$\begin{cases} \dfrac{dl_1}{dt} = v_1 = 5 \\ \dfrac{dl_2}{dt} = v_2 = 10 \end{cases} \Rightarrow \begin{cases} \dfrac{dn_1}{dt} = a_1 \\ \dfrac{dn_2}{dt} = a_2 \end{cases}$$



An example

- SSA-Algorithm



$$\begin{cases} \dfrac{dn_1}{dt} = a_1 \\ \dfrac{dn_2}{dt} = a_2 \end{cases}$$

while $t<t_{end}$

draw a random numbers r_1

propensities $a_i \longleftarrow v_i/\delta$

sample the disk μ to be displaced with probability = a_i

$$\sum_{i=1}^{\mu-1} a_i < r_1 \sum_{i=1}^{N} a_i \leq \sum_{i=i}^{\mu} a_i$$

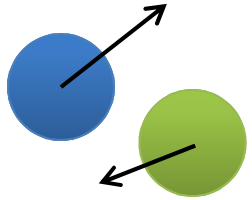
update: $n_\mu \longleftarrow n_\mu + 1$

time step = $\tau = \left(\sum_{i=1}^{N} a_i \right)^{-1}$

$t \longleftarrow t + \tau$

An example

- SSA-Algorithm



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An example

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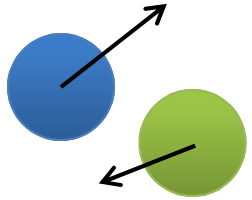

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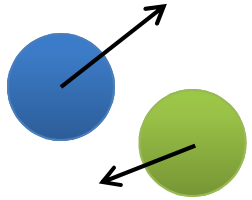
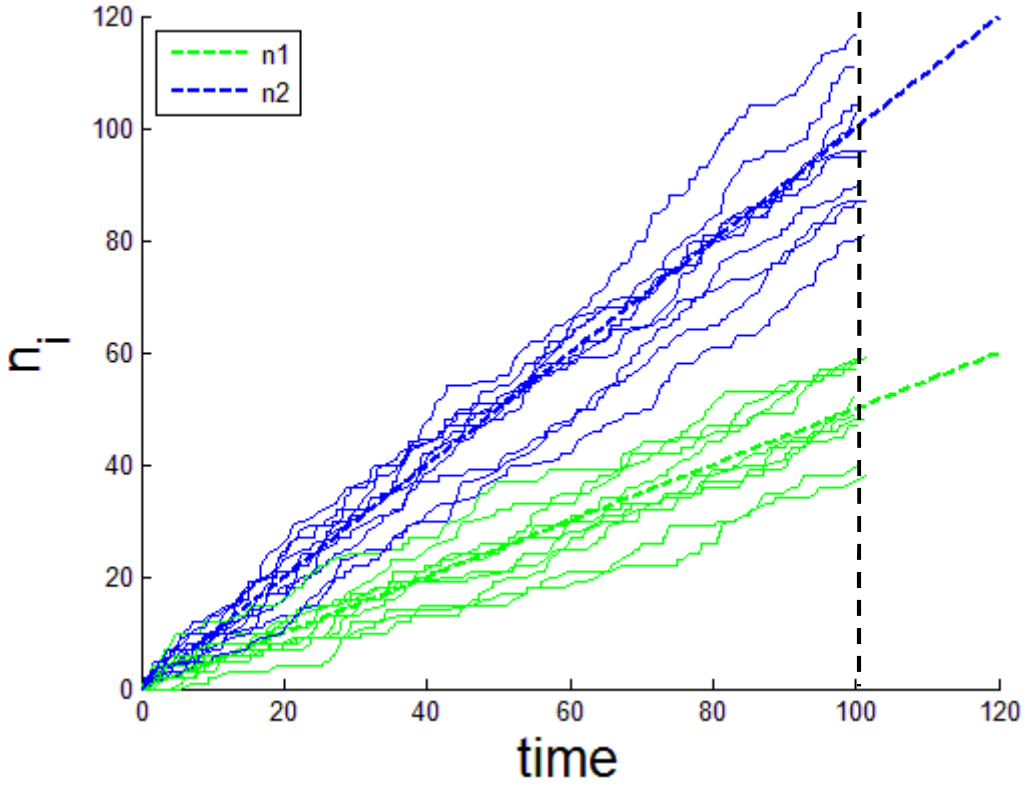
An example

- Distance traveled by disk i:

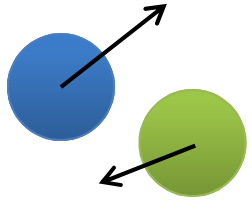
$$\langle l_i(t^*)\rangle = \delta \langle n_i(t^*)\rangle$$

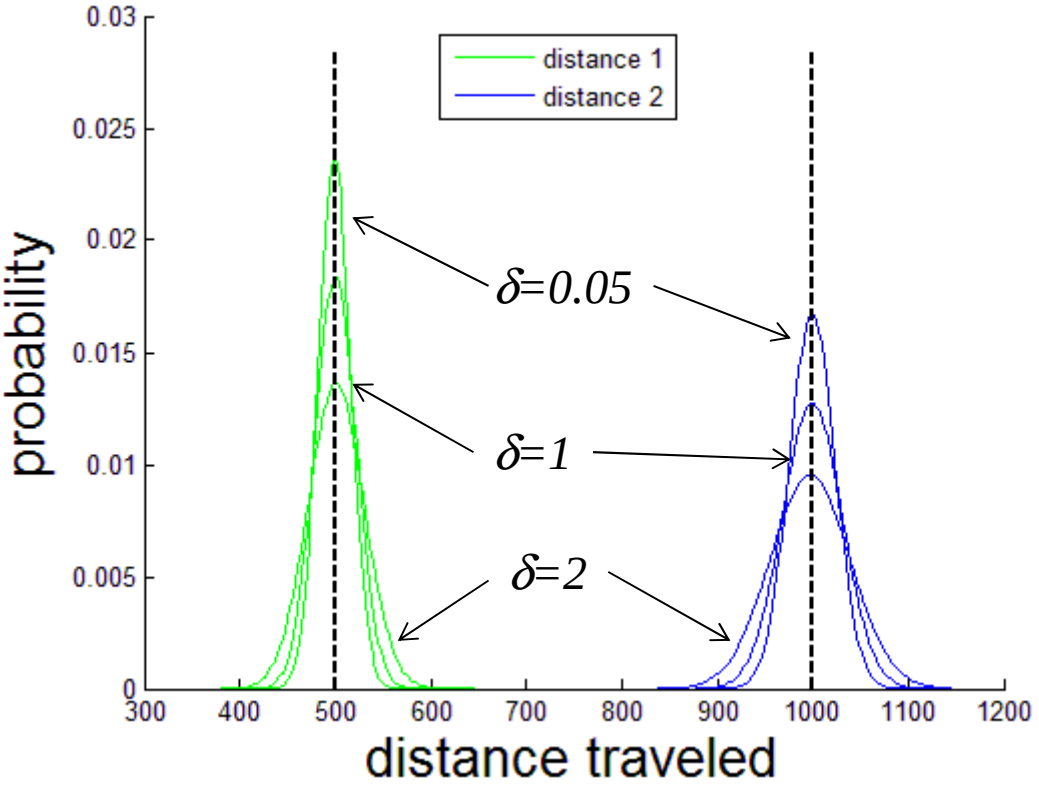




An example

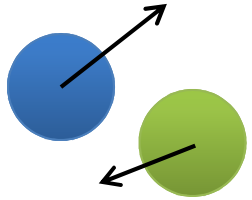
- Distribution probability for $l_i(t^*) = \delta n_i(t^*)$

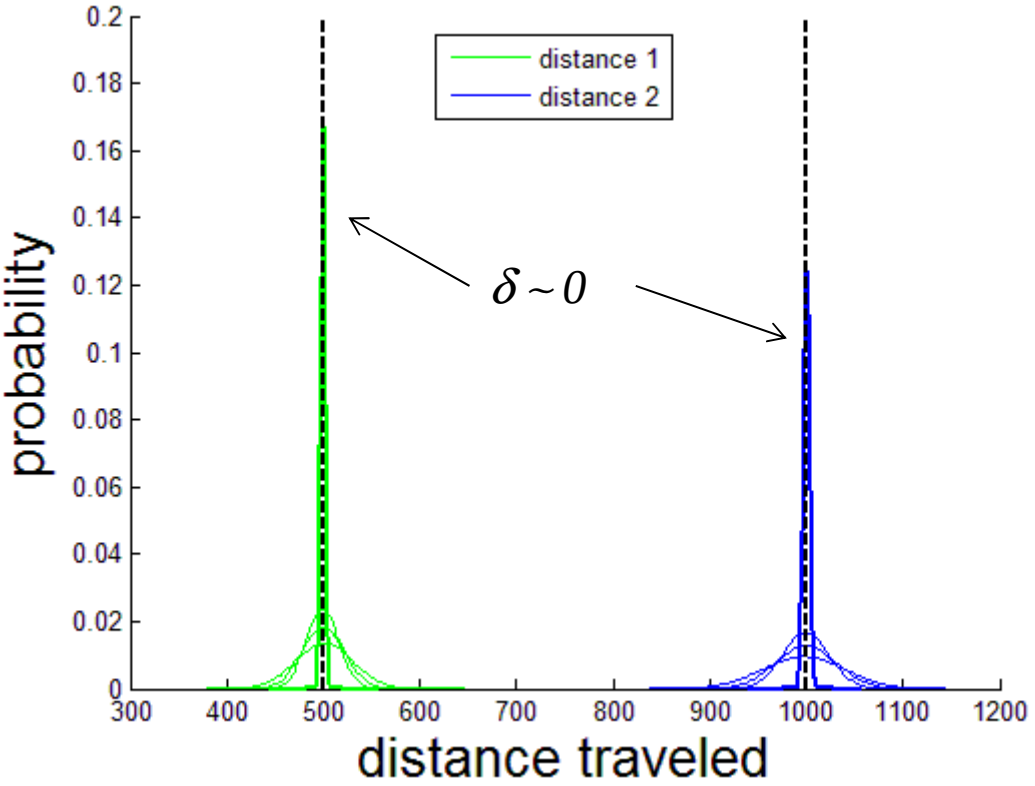




An example

- for $\delta \longrightarrow 0$
  - $l_i\,(t^*)$ converges to the deterministic solution





In short:

- A MCMC algorithm can be constructed as a KMC with:
  - propensities $\sim v_i$
  - particle displacements parallel to their velocities

  - established a link between MC time step τ and physical time
  - convergence to deterministic dynamics as $\delta \longrightarrow 0$

- Stochastic counterpart of MD: Monte Carlo Molecular Dynamics (MCMD)

- What is missing?
  - Avoiding the space discretization (fixed δ)
  - Taking collision events into account

MCMD Algorithm

while $t<t_{end}$

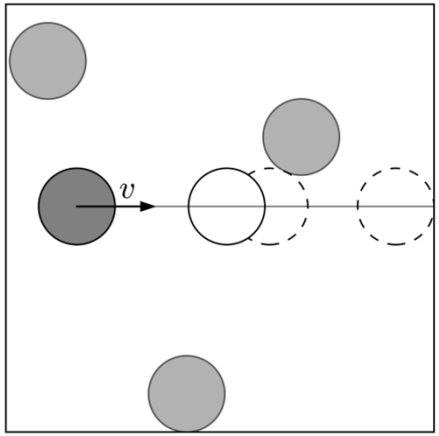
draw two random numbers r_1, r_2

step size $\longleftarrow$ $r_1\delta$

Propensities a_i $\longleftarrow$ $v_i/r_1\delta$

sample the disk μ to be displaced $\longleftarrow$ $\sum_{i=1}^{\mu-1} a_i < r_2 \sum_{i=1}^{N} a_i \leq \sum_{i=i}^{\mu} a_i$

Sampling



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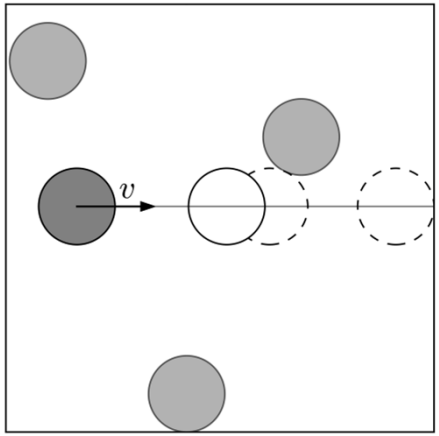
if $r_1\delta<min(\delta_{wall}, \delta_{pair})$ there are no collisions

$$x_\mu \leftarrow x_\mu + r_1\delta v_{\mu x}/v_\mu$$
$$y_\mu \leftarrow y_\mu + r_1\delta v_{\mu y}/v_\mu$$

$$\tau = \left(\sum_{i=1}^{N} a_i\right)^{-1}$$

$\longleftarrow$

Displacement



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else there is a collision

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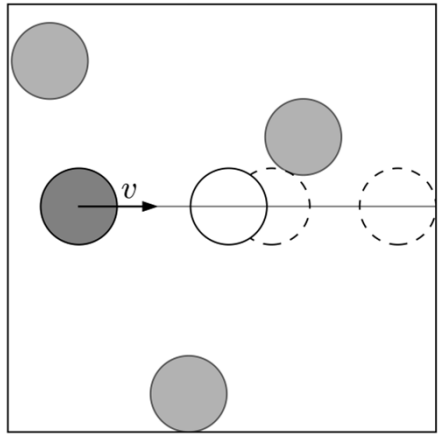
$$\tau = \min\left(\delta_{wall}, \delta_{pair}\right) \left(\sum_{i=1}^{N} v_i \right)^{-1}$$

update the velocities to post-collision values

$t \longleftarrow t + \tau$

"Kill" the Markov Chain



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update the velocities to post-collision values

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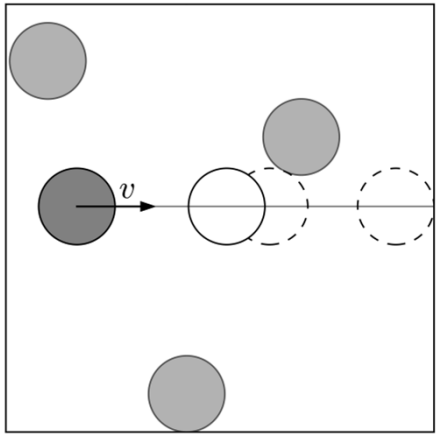
Time advance



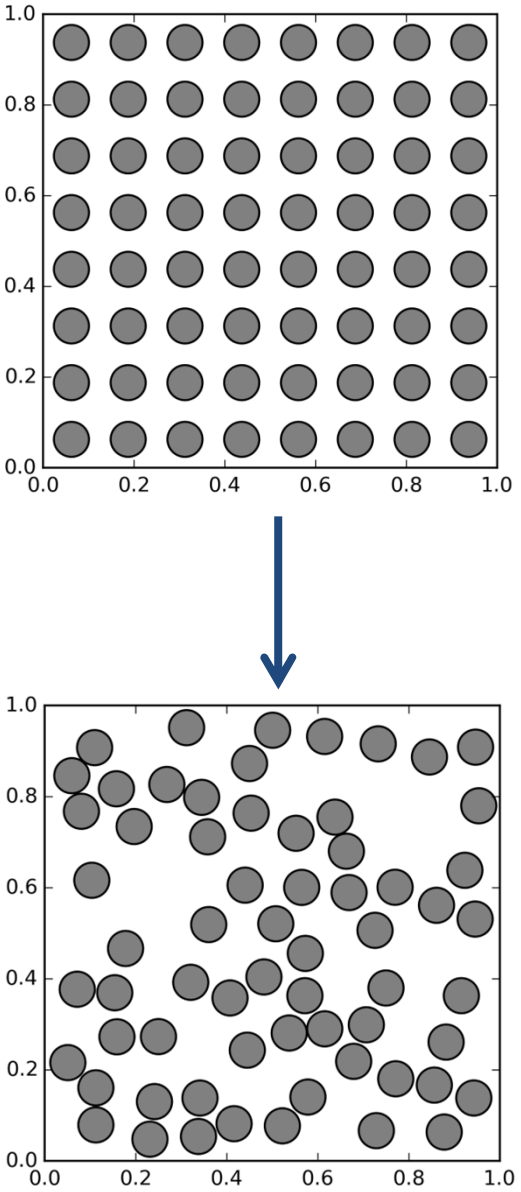
Simulations

- Microcanonical ensemble (NVE)

- N = 64 in a rigid square box (m = 1)
- density η = 0.3 (liquid)
- $E_k/N = 10^{-4}$

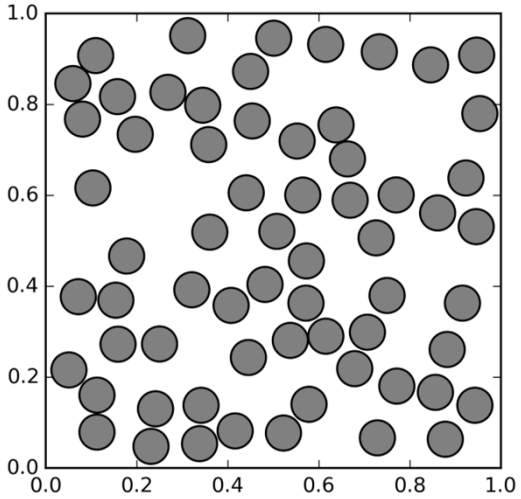
- Compare runs with MD and MCMD
- Each run starts from
  - square lattice (**non-equilibrium**)
  - velocities sampled from uniform distr. (**non-eq.**)

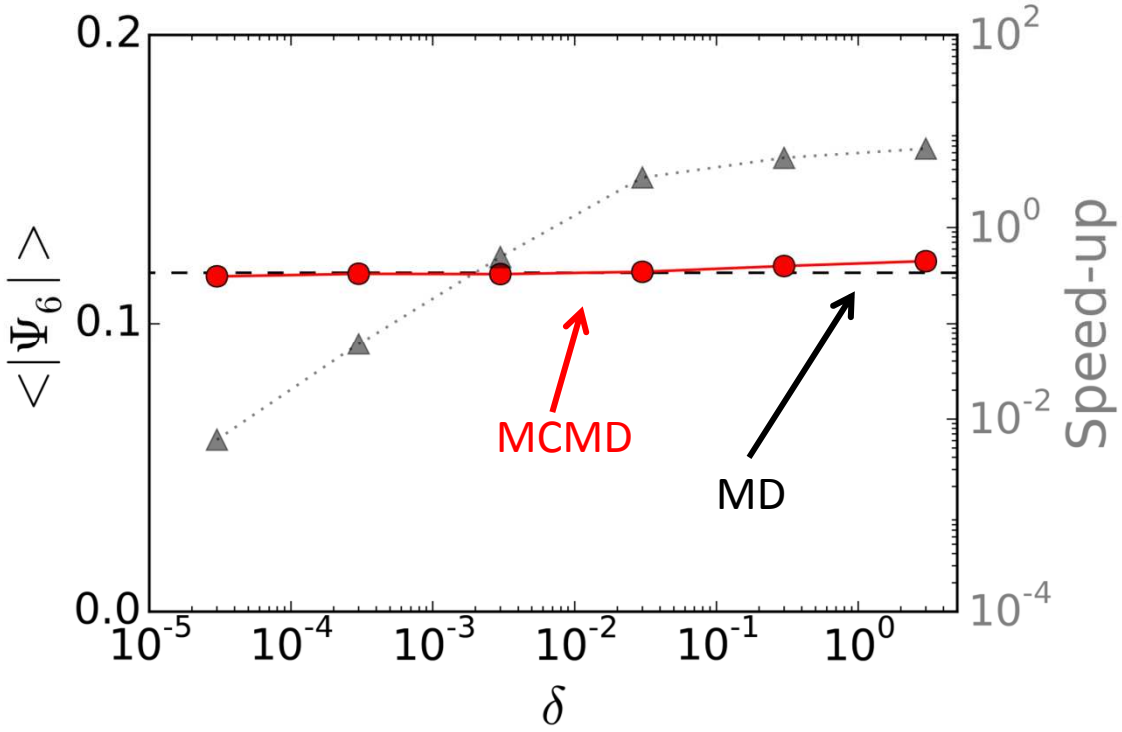
- Equilibration > 200 τ_R
- Sampling every $\Delta t = 1$ for > 1000 τ_R



Validation vs. MD: Static properties

- Mean value of <|Ψ_6|>
- Speed-up



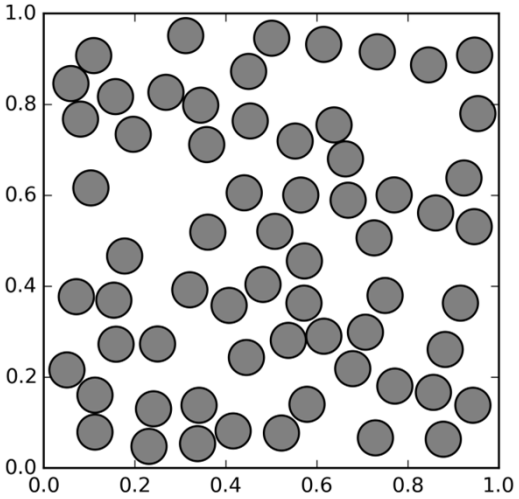


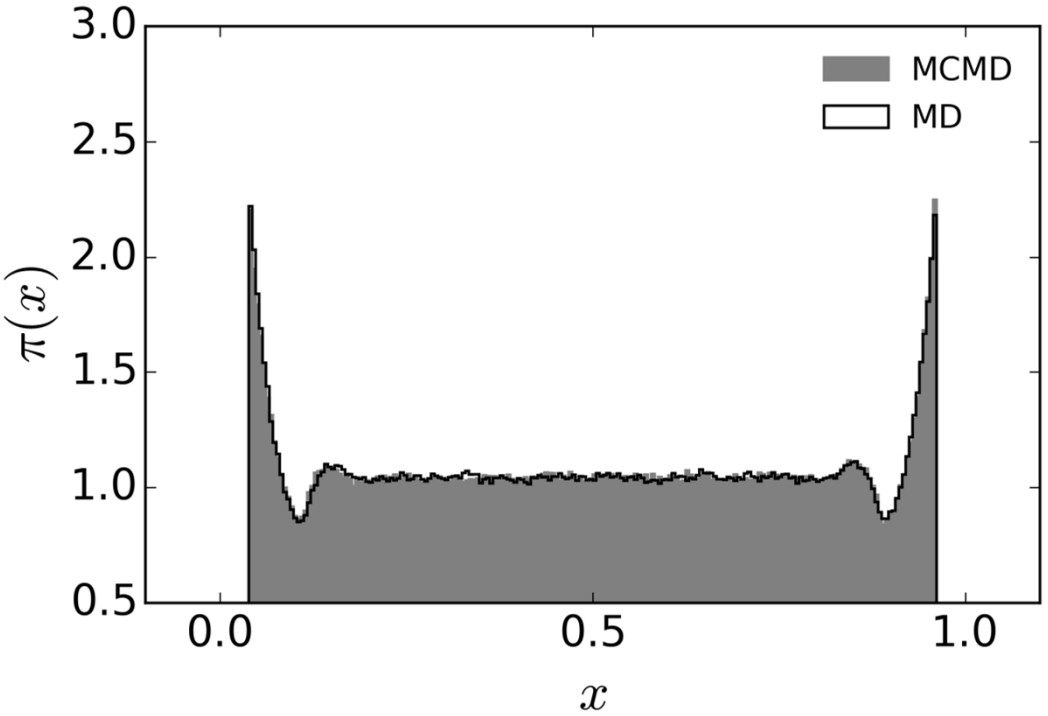
$$\psi_{6,j} = \frac{1}{N_{br,j}} \sum_{l=1}^{N_{br,j}} e^{\left(6i\phi_{jl}\right)}$$

$$|\Psi_6| = \left| \frac{1}{N} \sum_{j=1}^{N} \psi_{6,j} \right|$$

Validation vs. MD: Static properties

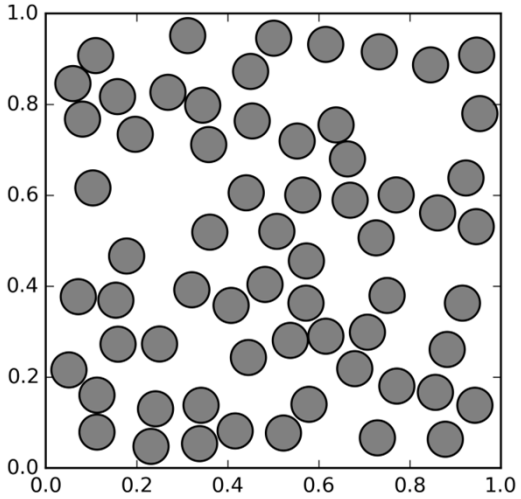
- Position probability distributions
  - Excluded volume (depletion interactions)
  - Non-uniform distribution
  - (δ= 10^{-3}, 1 run for > 35000 τ_R)

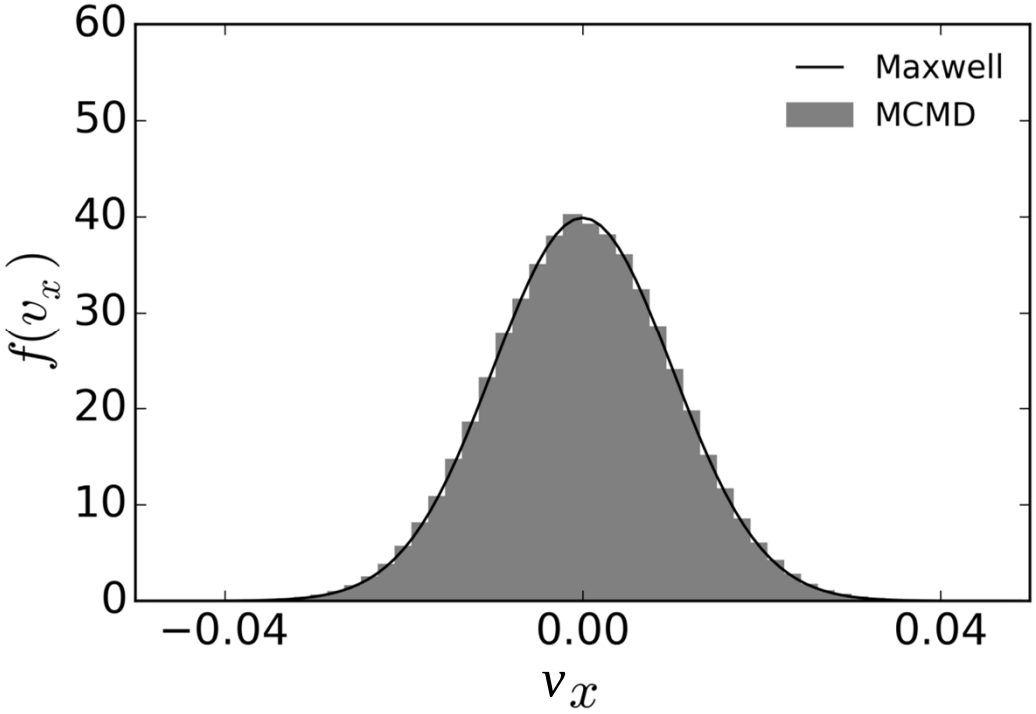




Validation vs. MD: Static properties

- Velocity distribution
  - Matches Maxwell distribution
  - Not accessible from standard MC (req. independent sampling)



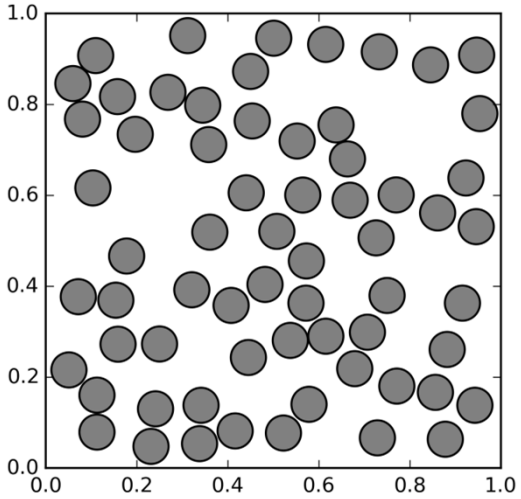


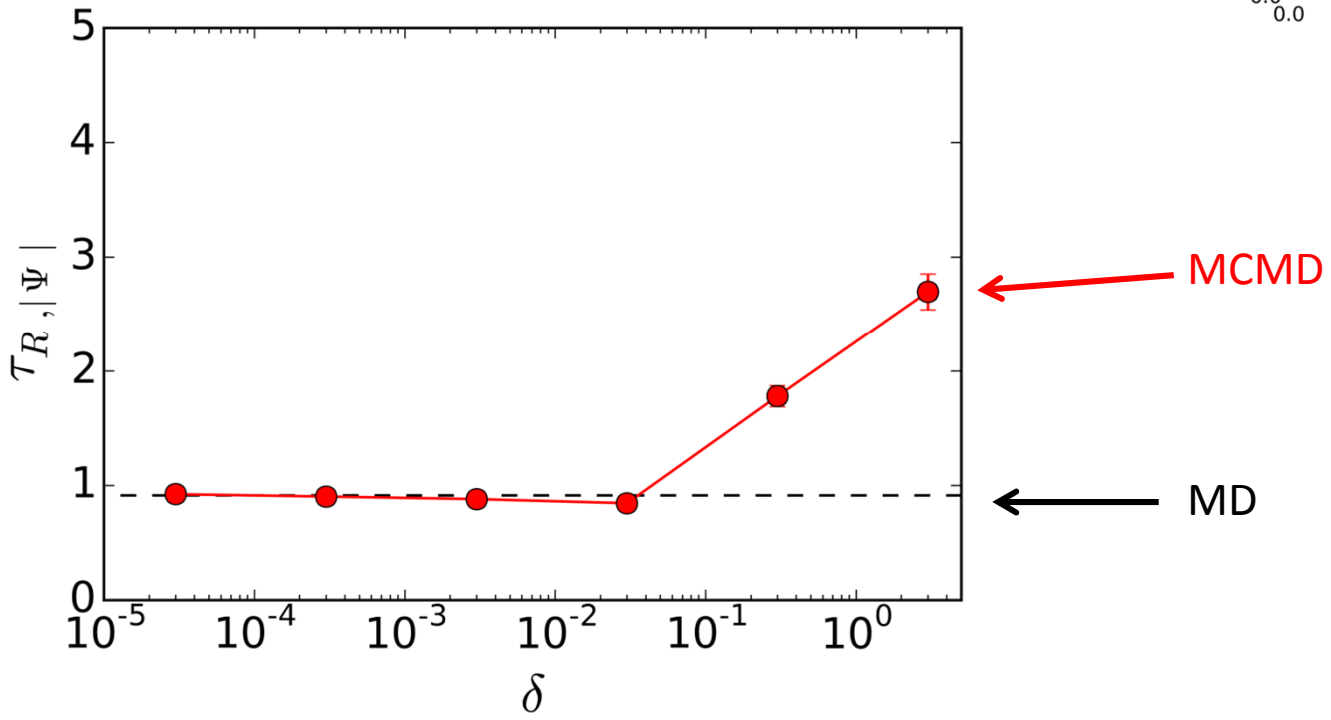
Validation vs. MD: Dynamics

- Relaxation time of order parameter

$$C_{\Psi_6}(t) = \frac{\left\langle \left|\Psi_6(t_0)\right|\left|\Psi_6(t_0+t)\right| \right\rangle - \left\langle \left|\Psi_6\right| \right\rangle^2}{\left\langle \left|\Psi_6\right|^2 \right\rangle - \left\langle \left|\Psi_6\right| \right\rangle^2}$$

$$C_{\Psi_6}(\tau_R) = \frac{1}{e}$$



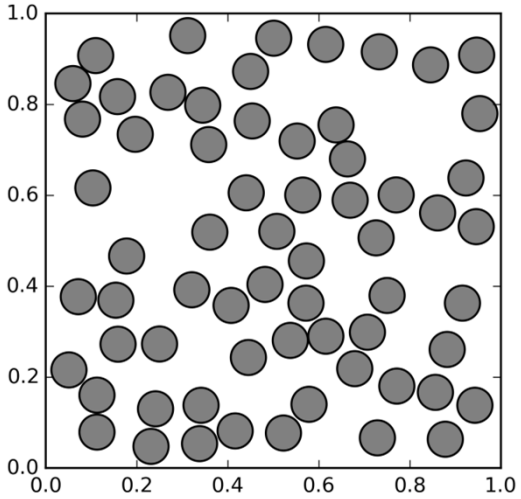


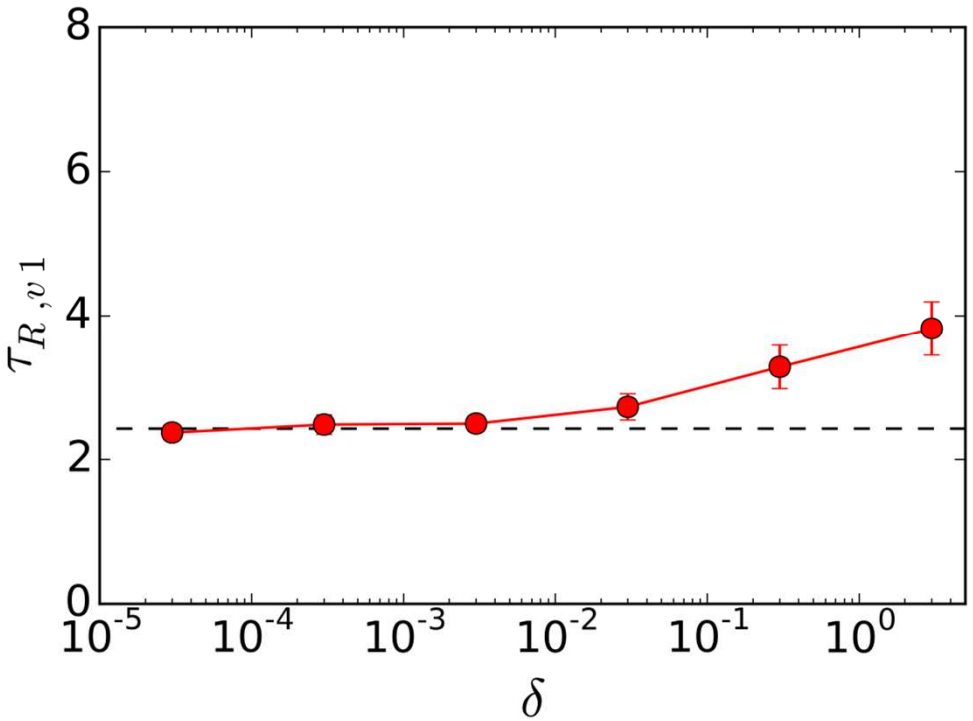
Validation vs. MD: Dynamics

- Relaxation time of disk-1 velocity

$$C_{v_1}(t) = \frac{\langle v_1(t_0)\, v_1(t_0+t)\rangle}{\langle v_1^{\,2}\rangle}$$

$$C_{v_1}(\tau_R) = \frac{1}{e}$$





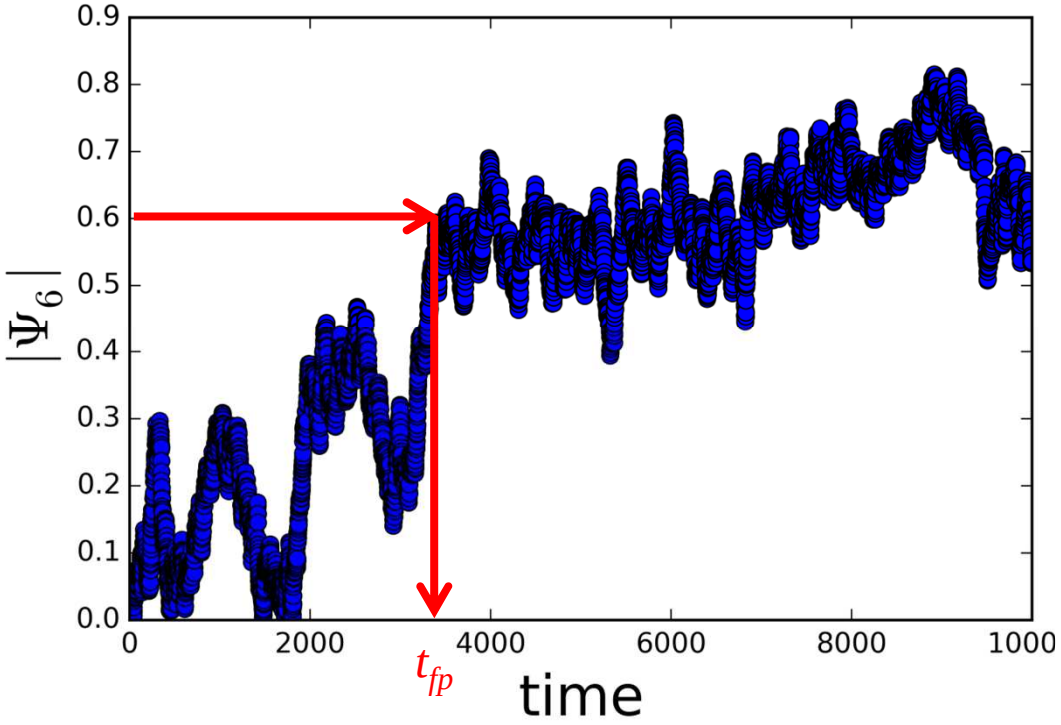
MCMD

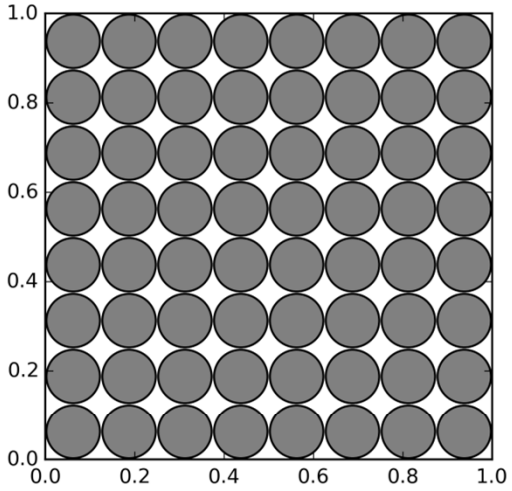
MD

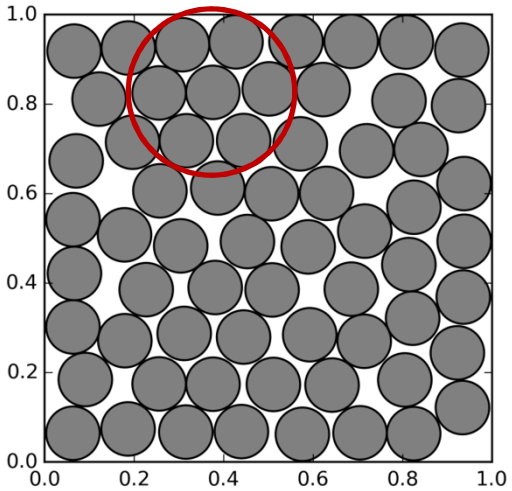
Validation: Non Equilibrium Dynamics

- $N = 64$
- density $\eta = 0.72$ (region of sol-liq transition)
- $E_k/N = 10^{-5}$

- A First-Passage time Problem

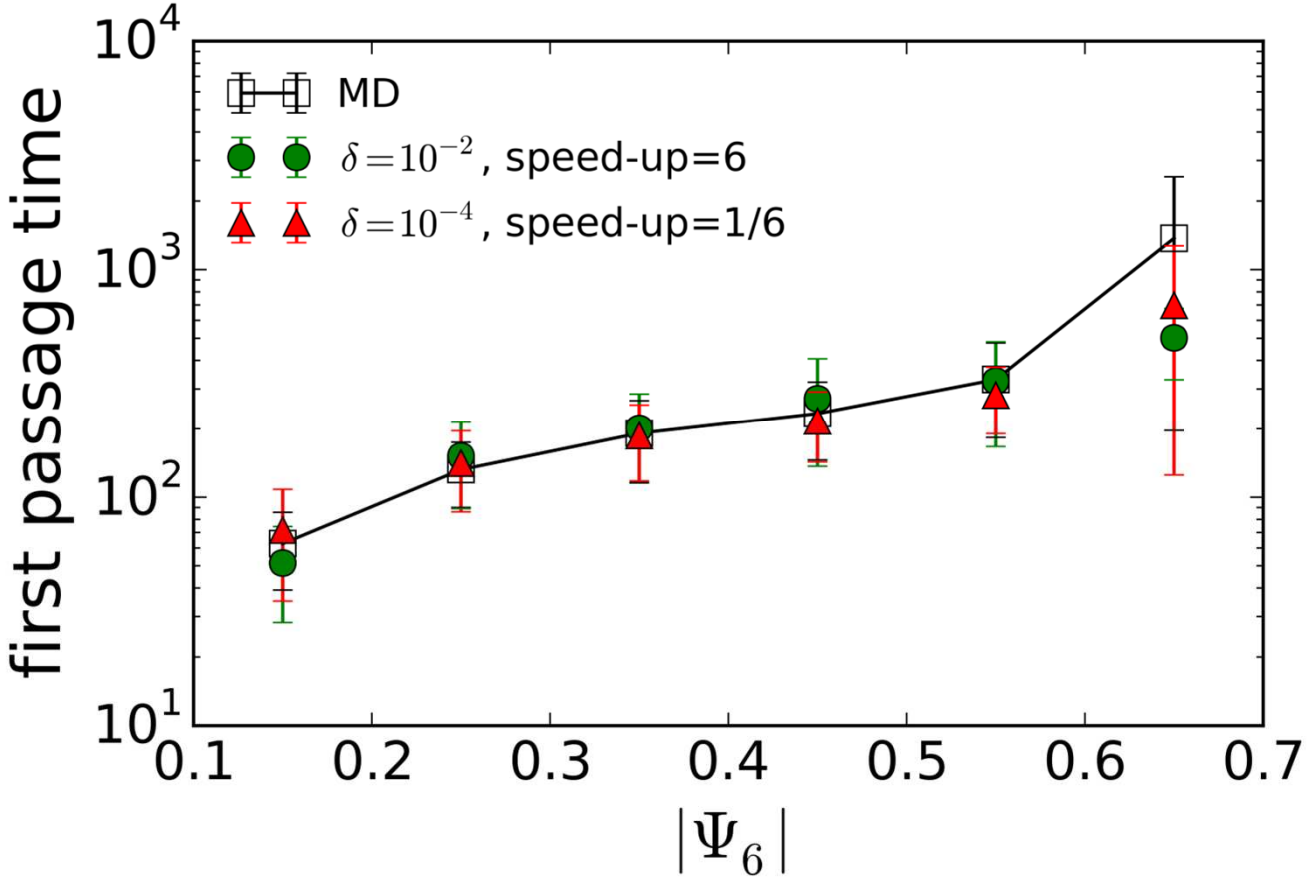






Validation: Non Equilibrium Dynamics

- First passage time



- Good agreement with MD (at comparable computational time)

Summary

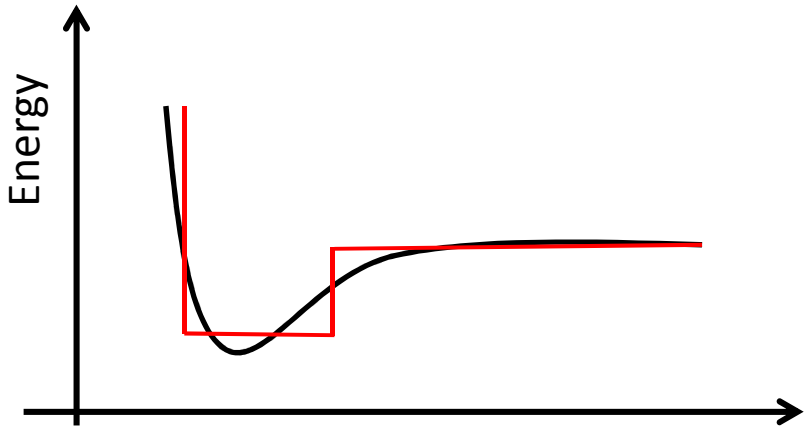
- For hard-core interactions:
  - Atom sampling proportional to ***v*** and displacement parallel to ***v***

  - (*Rejection free*) MC algorithm with meaningful timescales
  - Access to velocity distribution (*as output*)
  - The algorithm is as simple as a basic MC, but is «velocity driven»

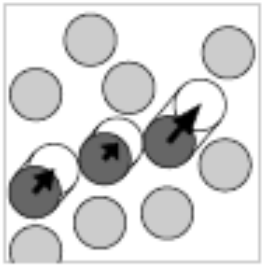
Costa, *Journal of computational physics*, accepted; ArXiv: 1603.07015

Summary

- Future work:
  - validation at larger number of particles (pbc)
  - «soft» potentials

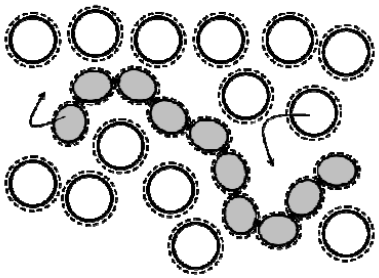


  - «*event chain*» with $\langle \tau \rangle = 1/\sum a_i$



Bernard et al, *Phys. Rev. E*, 80, 2009

  - polymers



Acknowledgments: Prof. W. Krauth and his team at ENS for efficient code snippets