Irrevrsible Monte Carlo methods for particle simulations

algorithms for thermodynamic simulation

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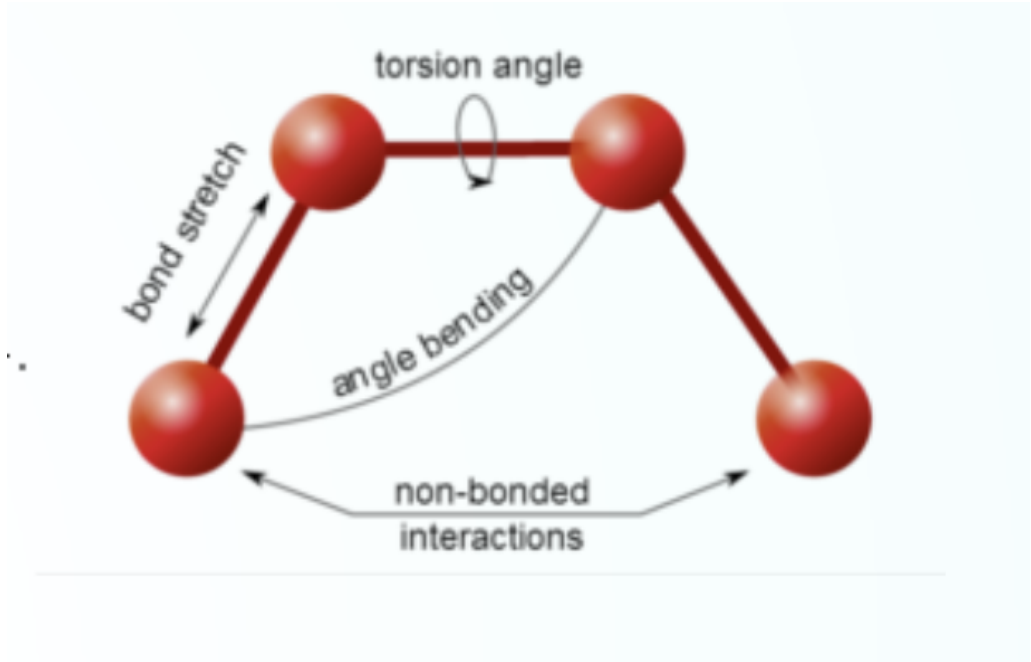
Particle simulation in molecular physics

Why particles? What Particles?

- To a "reasonable" approximation atoms behave like classical particles, with known interaction energies
- The basis of much materials science, engineering, hydrodynamics, biophysics...
- The particles move according to Newtons laws



Interactions

- Short range pairs: Lennard-Jones $V(r) = 1/r^{12} - 1/r^6$
- Short range, triplets: $V(\theta) = -\cos(\theta)$
- Long range pairs, electrostatics: $V(r) = 1/r$
- Parameterisations are rather crude
- AMBER, CHARMM
- Validated over limit ranges of conditions – temperature, pressure, chemical composition

- Evaluation tactics very different according to kind of interaction

Example of electrostatics

Full double loop to evaluate electrostatic interactions is too slow:

$$U = \sum_{i<j} \frac{q_i q_j}{4\pi r_{ij}}$$

Prefer to solve the Poisson equation:

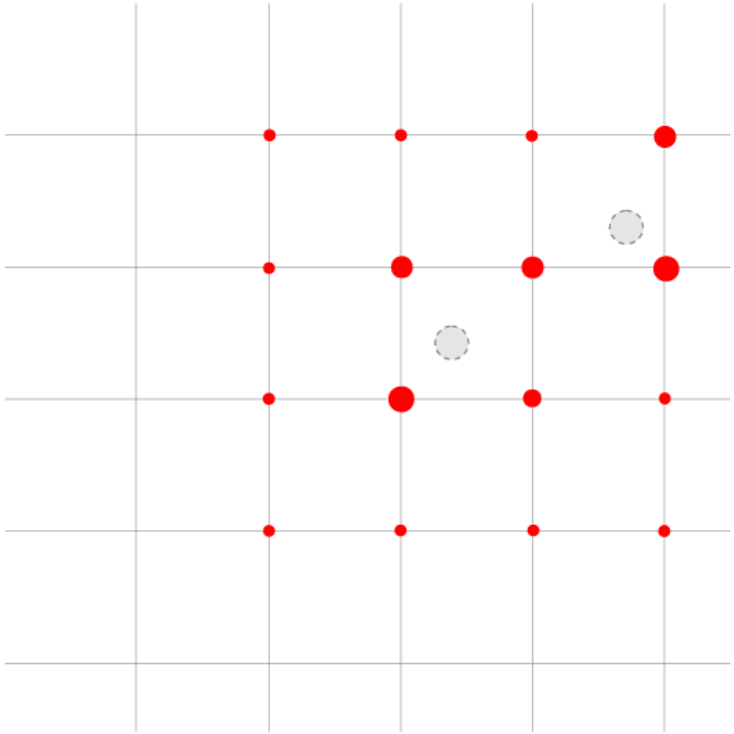
$$\nabla^2 \phi = -\rho \qquad U = \frac{\phi \rho}{2}$$

Poisson equation is easy to solve by Fourier analysis (FFT) if charges are on a uniform grid.

However, we have charges moving in a continuum.

Charge interpolation

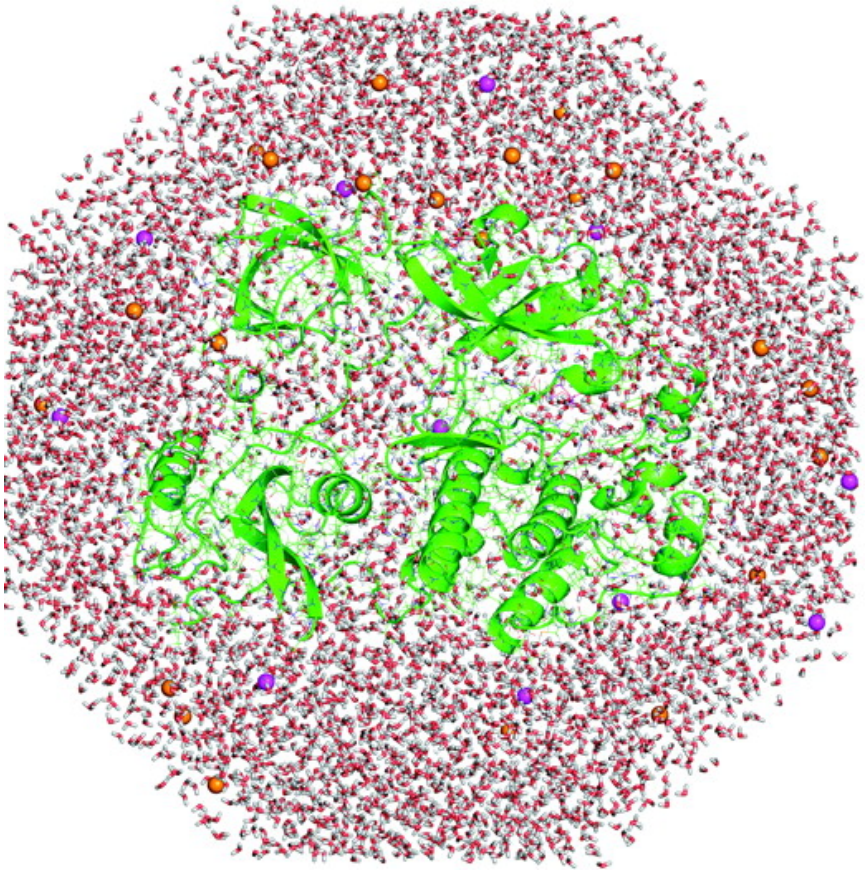
Use a smoothing/convolution function to send point charges to a lattice:
Spline/ Gaussian



Solve Poisson equation with FFT
Push back forces from grid to particles
Working codes push 1 charge to several hundred sites, to minimize lattice artefacts

Examples

Protein in Water



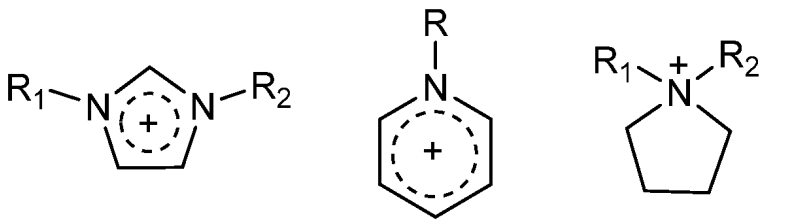
50,000 particles

Notice large number of spectator water particles [with at least 3 charges]

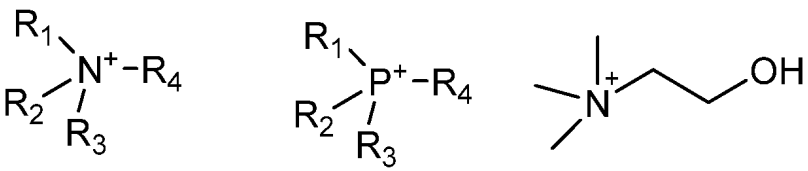
Examples

Ionic liquids

Cations

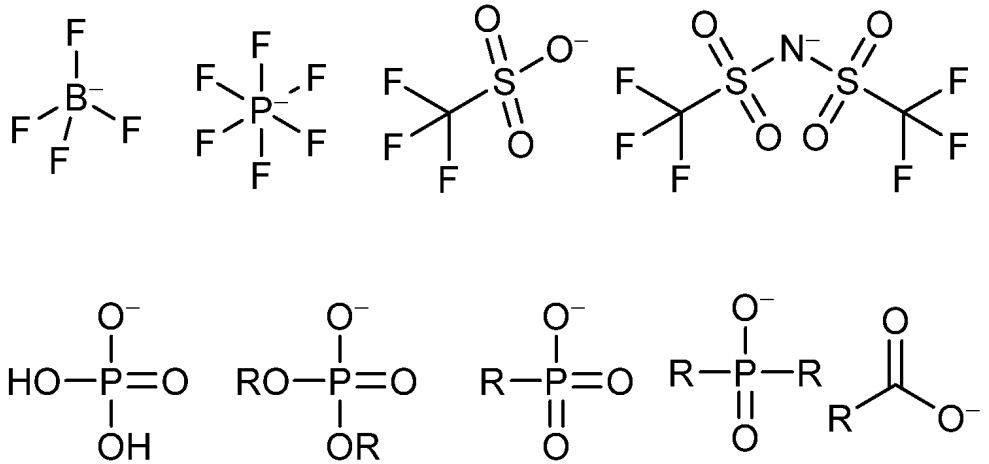


$R, R_1, R_2 = C_nH_{2n+1}$, n = 1-18



$R_1, R_2, R_3, R_4 = C_nH_{2n+1}$, n = 1-18

Anions



- again every link is represented by bending/stretching/twisting interaction potentials
- Used in green chemistry as solvents
- Batteries

Time scales

- Molecular dynamics time steps: $1\,fs$
- Water rotation time: $1\,ps$
- Sampling time for a sodium atom near a charged surface $1\,ns$
- Interesting biological time scales $1\,\mu s - 1\,ms$

Very large numbers of time steps, each time step 1000's of operations per particle, above all due to electrostatics

Simplified models in physics

- Some features of materials are very insensitive to the exact details of the potentials
- Details of phase transitions Ice-Water-Steam less so
- Can use much simplified models : billiard balls/hard disks to learn much about the global properties without putting in every detailed interaction
- Thermodynamics [states] does not require knowledge of dynamics so we can replace MD by other dynamical system implementing balance

Particle simulation with ECMC

Replacing Classical Monte Carlo and Molecular Dynamics

Can one find algorithms that better equilibrate for thermodynamic simulation? Two obvious criteria:

- Autocorrelation of energy/density. I take a system close to equilibrium, how long do typical fluctuations take to equilibrate.
- Mixing times – worst case – includes nucleation from "wrong" phase: eg supercooled water, stable for days at

Breaking detailed balance – keeping balance

Major algorithms today 1

- Metropolis Monte Carlo
- Make a random update to system – displace particle
- Accept or reject based on energy change
  - large individual steps
  - slow diffusive explorations of space
  - exact sampling, this is nice!

Major algorithms today 2

- Time step driven molecular dynamics
- Integrate Newton's equation of motion given the forces
  - propagative modes – density fluctuations relax quickly
  - small steps for stability – slow stepping – shift in thermodynamic properties
  - multiple time-step MD for long-ranged interactions.

Introduce methods that have the potential of : large steps, propagation, exact sampling with particle systems

Why are simulations slow: Hydrodynamics in simple fluids

MD: Slow modes in large systems are hydrodynamic: linked to conservation laws/broken symmetry

- Mass
- momentum
- energy

Gives rise to

- sound: $\omega = \pm cq$
- heat: $\omega = Dq^2$
- vorticity (transverse): $\omega = D'q^2$

Modes with dynamic exponent $z = 1$ and $z = 2$: $\tau \sim L^z$

Molecular dynamics "inherits" these hydrodynamics modes, perhaps modified by thermostats
Also problems of barrier crossing, large configurations space eg Proteins.

Monte Carlo modes

MC: single locally conserved quantity: density, $\omega = D'' q^2$ for $\langle \rho(r,t)\rho(0,0)\rangle$
Most large scale simulations use MD and not MC

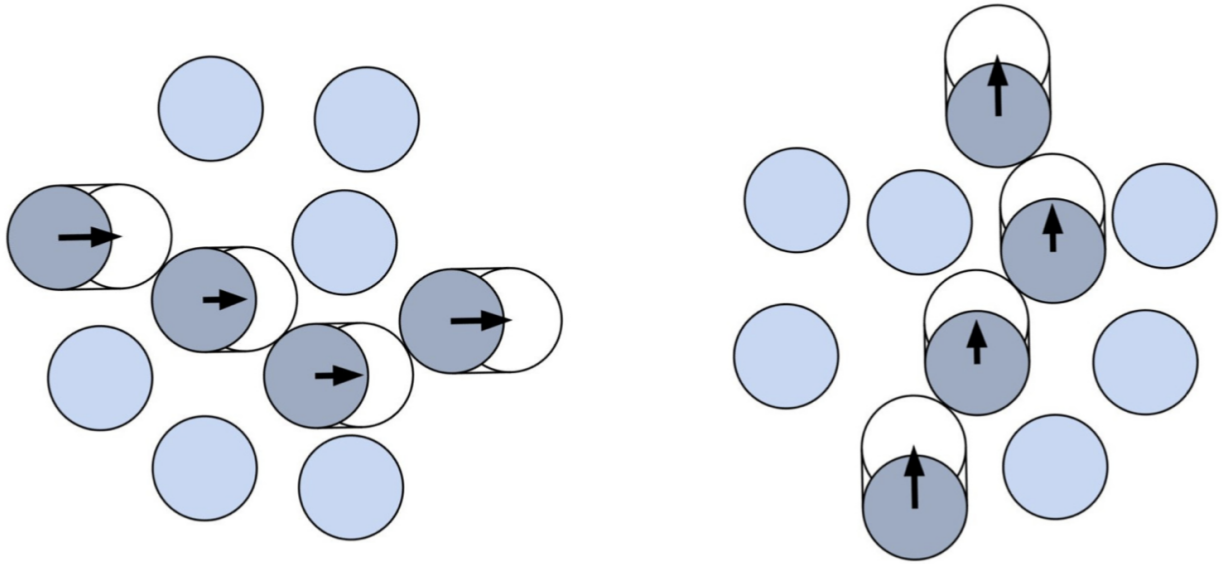
- MC difficult with electrostatics eg $O(N)$ algorithms rather than $O(N^2)$
- Density is faster in MD due to sound waves, historically very important in short simulations

Hydrodynamic theories of liquid crystals, multicomponent systems have other slow modes that may be important

Event Chain MC Algorithms

Event Chain algorithm: lift rather than reject

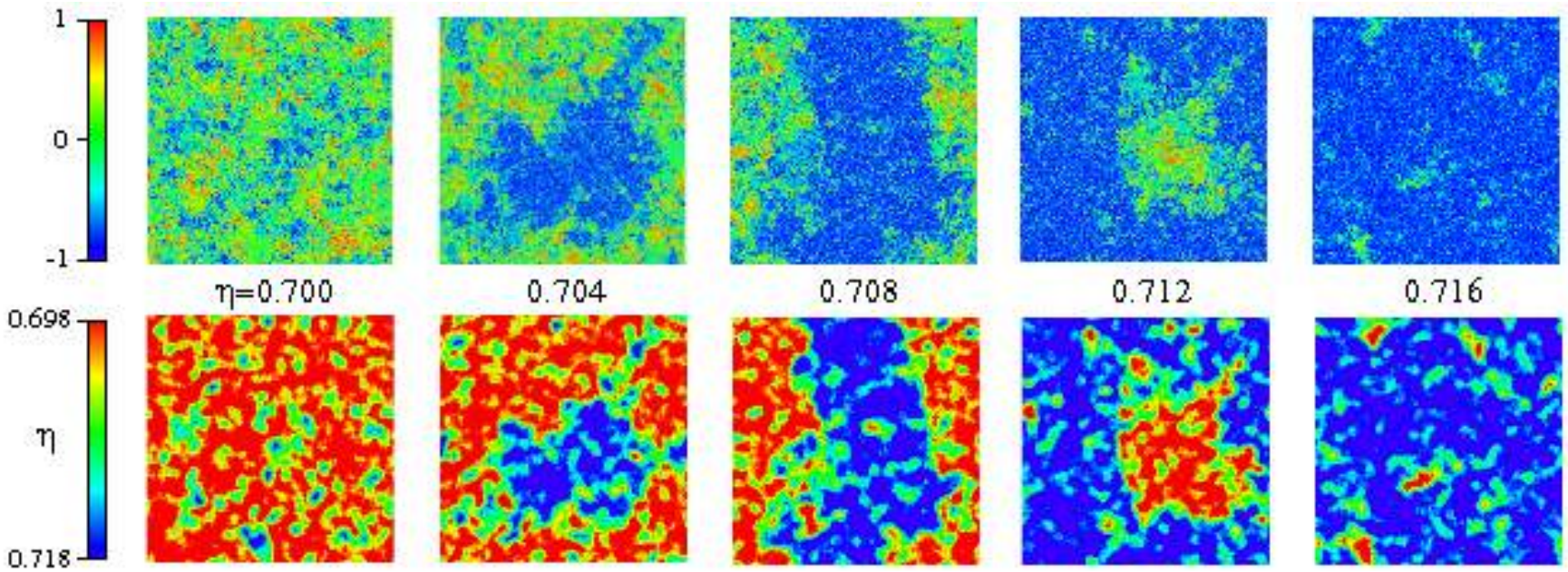
Choose a starting particle: the ACTIVE particle
Transfer motion on a collision EVENT, a LIFTING



- Rejection free
- For hard spheres (Bernard, Krauth, Hexatic-solid transition, 2011)
- Balance, Not detailed balance : no back moves, no rejection

Hexatic fluids in 2d

Coexistence:



- Weakly first order liquid-hexatic transition
- Second order hexatic-solid

Unachieved with classic methods, $N = 10^6$

Irreversible MC for general potentials

Event chain with general potentials

How to generalize the hard sphere algorithm with potentials?

- Rejection does not uniquely identify a collision
- If we interact with two other particles and reject a move who is responsible?
- Who is the target for the next particle in motion?

Identifying the collision partner with general potentials

Manon Michel, 2013

An alternative to the standard choice: $\Delta E = e_a + e_b$
Factorized Metropolis: $p(e_a, e_b) = \min(1, e^{-\beta e_a}) \times \min(1, e^{-\beta e_b})$

sign	foward	back	ratio
$++$	$e^{-\beta e_a}.e^{-\beta e_b}$	1	$e^{-\beta(e_a+e_b)}$
$+-$	$e^{-\beta e_a}.1$	$1.\ e^{+\beta e_b}$	$e^{-\beta(e_a+e_b)}$

Advantages:

- Each factor can be considered as a statistically independent event, or collision
- We can now identify a specific particle which has triggered the collision
- Transfer activity to new collision partner

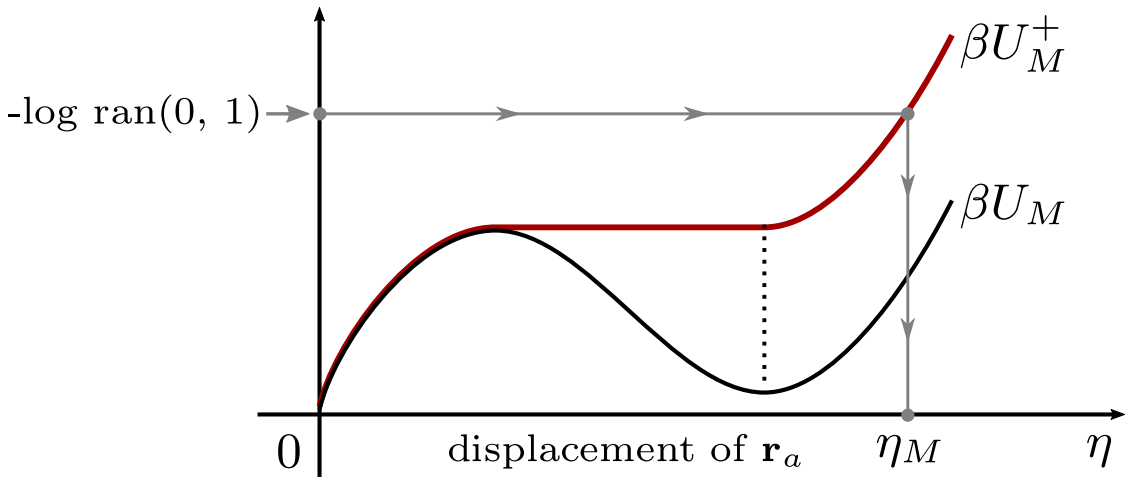
Multibody : Harland, Michel... 2017.

Full collision rule

- Split the potential into disjoint terms
- Choose active particle
- Calculate possible candidate event from each contribution to the potential
- Select the first event among those calculated
- Transfer motion to new particle
- Continue moving in same direction until total path length achieved
- Change direction of propagation after generating long trajectory

Identify first collision

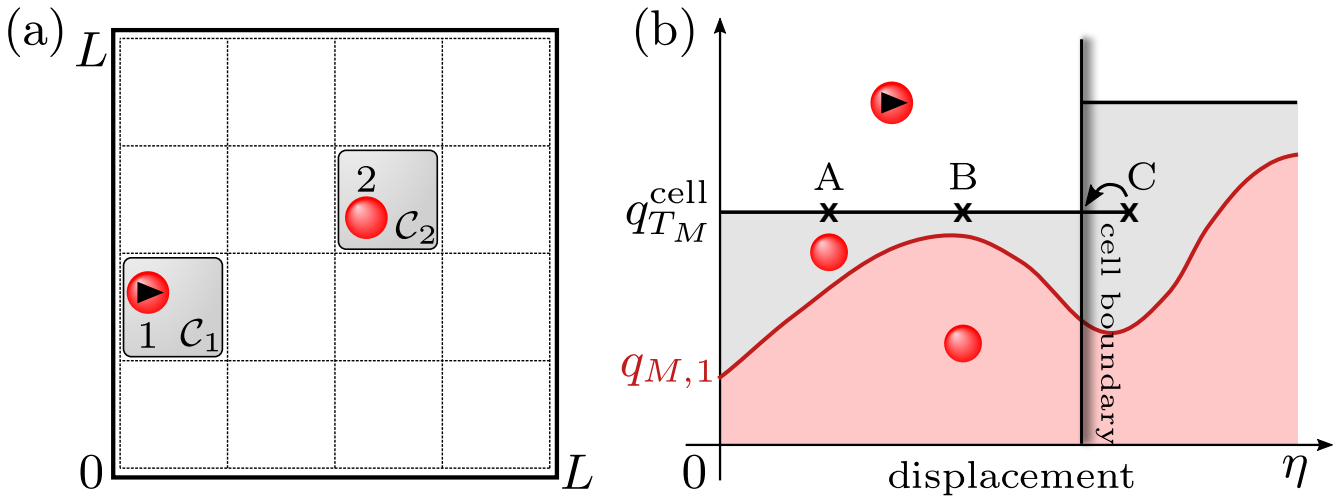
We want to go as far as possible and identify the first collision
Infinitesimal formulation: $p(\mathit{reject}) = [1 - \min(1, e^{-\beta\epsilon(dE/dx)})] = \beta\epsilon \left[\frac{dE}{dx}\right]^+$



- Find collision by inverting the potential curve (cf E. A. J. F. Peters and G. de With, 2012)

Long-ranged interactions with event chains

Many possibilities for increasing efficiency with long-ranged potentials:
Dipole-Dipole rate $\frac{1}{r^3}$: Total rate $\int d^3r \, \frac{1}{r^3} \sim \ln L$



- Efficiently manage rare long distance collisions by a bounded rate, before looking more carefully. Kapfer, Krauth, 2016
- Perfect multiscale algorithms, with no time-stepping errors, stability problems, only logarithmic slowdown with system size.

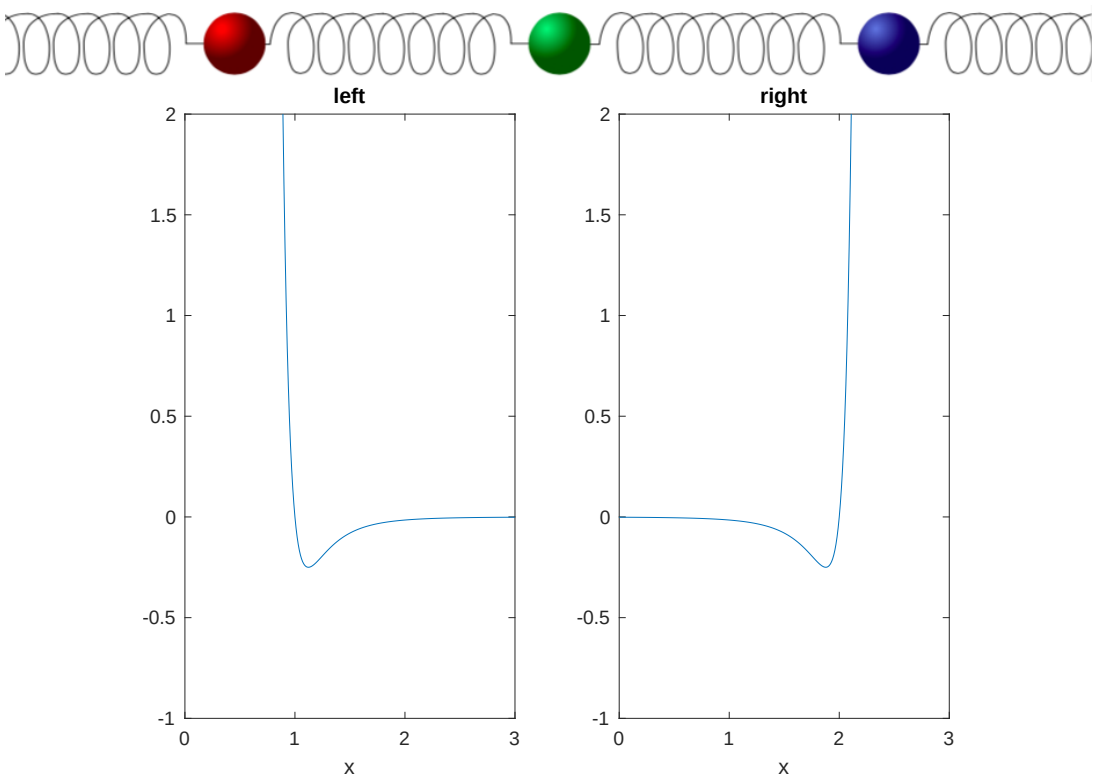
Relaxation dynamics in 1 and 2 dimensions

Back to model systems

What is the equivalent of the hydrodynamic description of fluids?

- Characterise large scale dynamics and possible optimisations
- Detailed dynamics in one and two dimension

Lennard-Jones chains

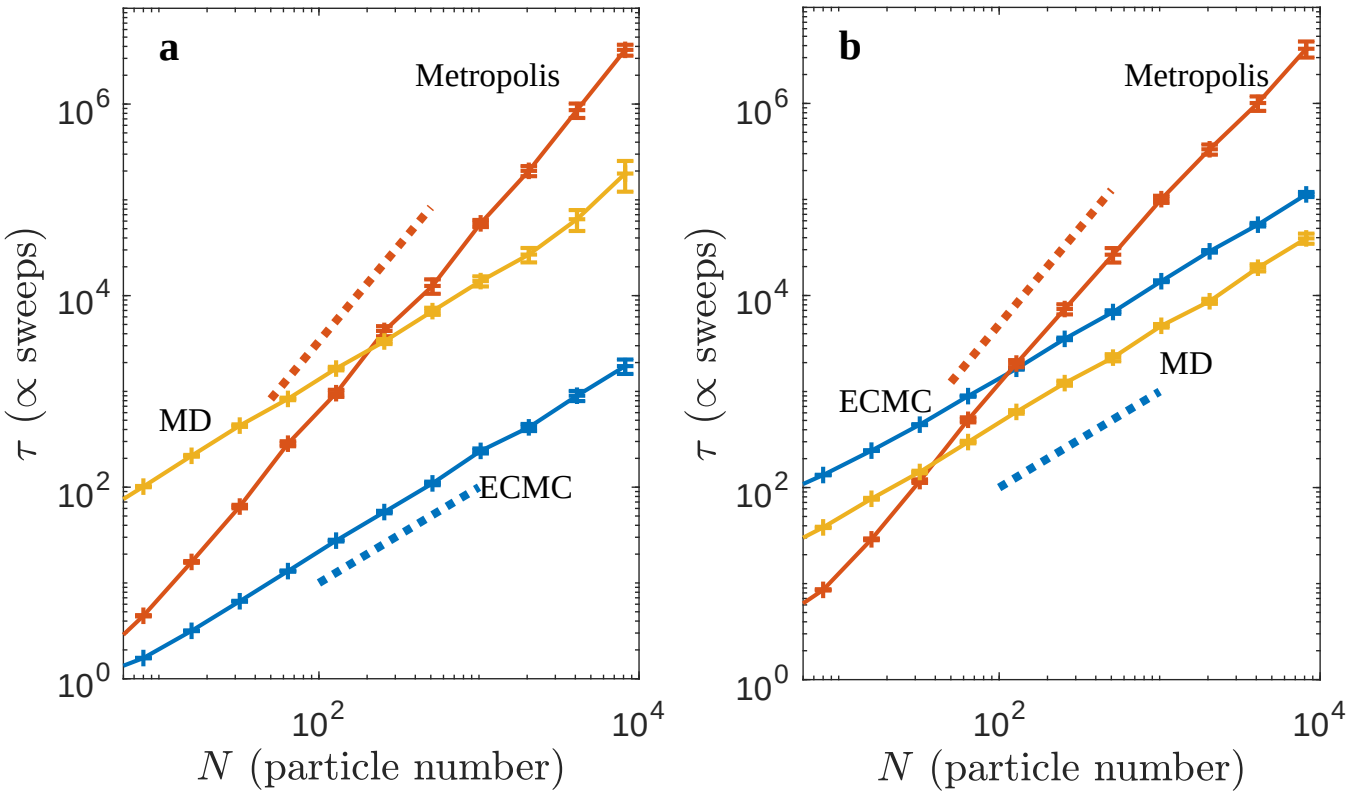


- Remember: events when potential is increasing
- Lifting can go left and right, even if particle motion is uni-directional

Lennard-Jones chains

Relaxation time of $\langle \rho(t,q)\rho(0,-q)\rangle$

Autocorrelation time in sweeps: $cpu \sim N^{z+1}$



- See dynamic exponent $z = 2$ for metropolis, $z = 1$ for MD and event chain.
- High and low temperatures: it works sometimes...

Harmonic model

Low temperature LJ is harmonic, so why is it slow?
Compressed/stretched harmonic chain:

$$u_{i,i+1} \sim (x_{i+1} - x_i - \ell).^2$$

But:

$$\sum_i u_{i,i+1} = \sum_i (\Delta x_{i+1} - \Delta x_i)^2 + \text{const}$$

since

$$\sum_i (x_{i+1} - x_i) = L$$

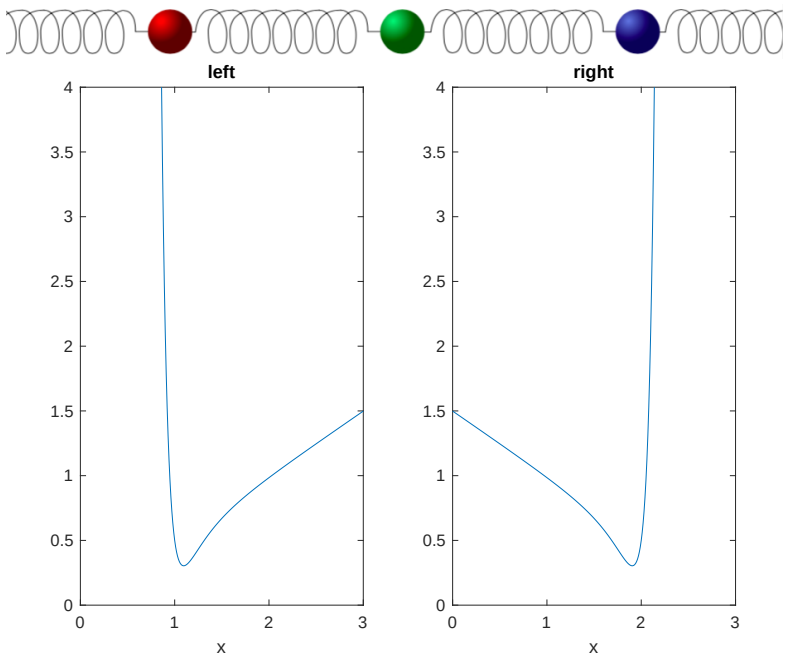
The lower temperature dynamics is dominated by the the cross term

$$\ell(x_{i+1} - x_i)$$

Large "spurious" collision rates

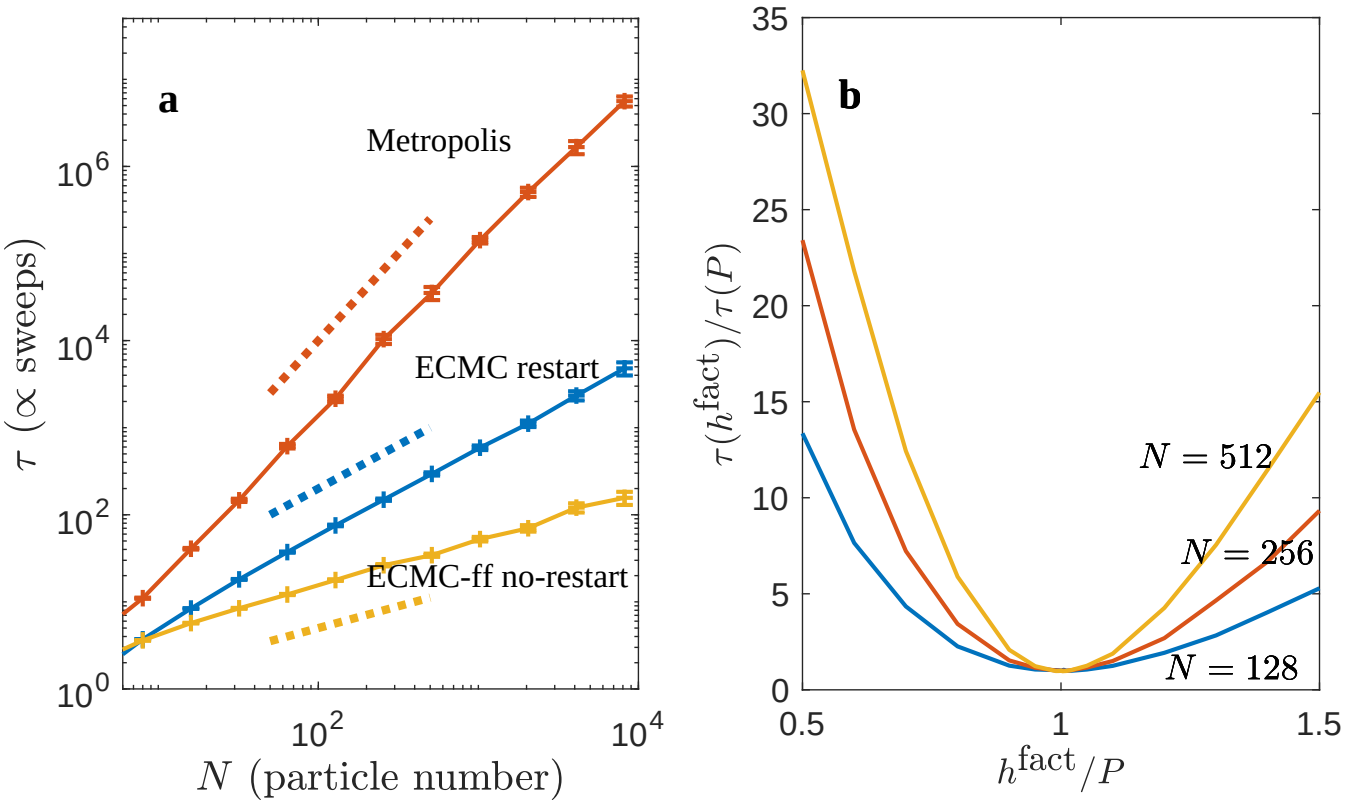
Factor field

- Add in a constant to the energy: $\Delta U = -h \sum (x_{i+1} - x_i) = -hL$
- Does not change thermodynamics, how does changes dynamics
- Choose the special value $h = P$
- "Obvious" thermodynamic generalisation of the force between two particles



Autocorrelation times

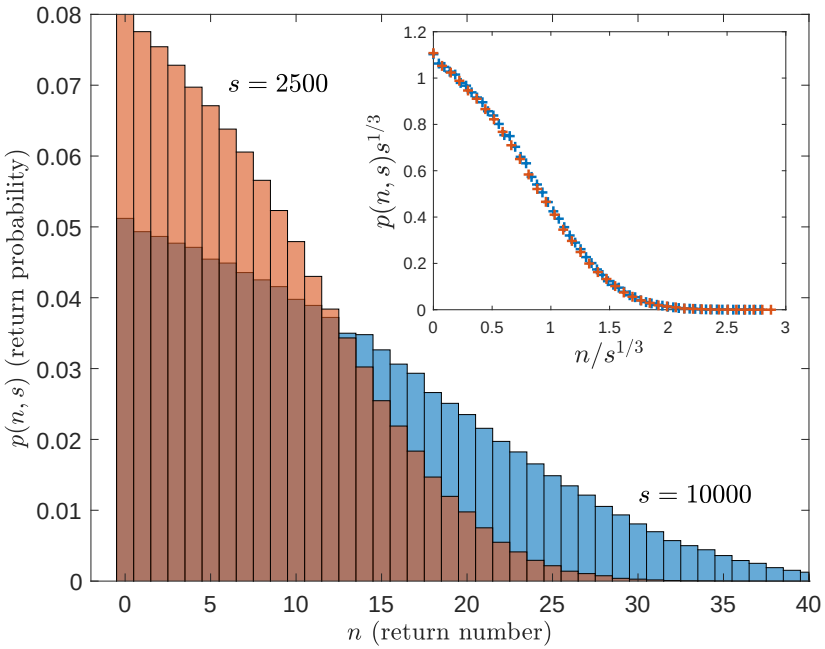
Low temperature LJ: the bad case



Super-fast relaxation: $z = 1/2$, hard-rods and LJ.

Return probability and hyperdiffusion

term How does the activity move with time?
Activity jumps back and forwards, how often does it return to the origin?



The position of the activity as a function of time is "hyperdiffusive"
$r^2 \sim t^{4/3}$
Number of returns to origin: distribution scales as $t^{1/3}$

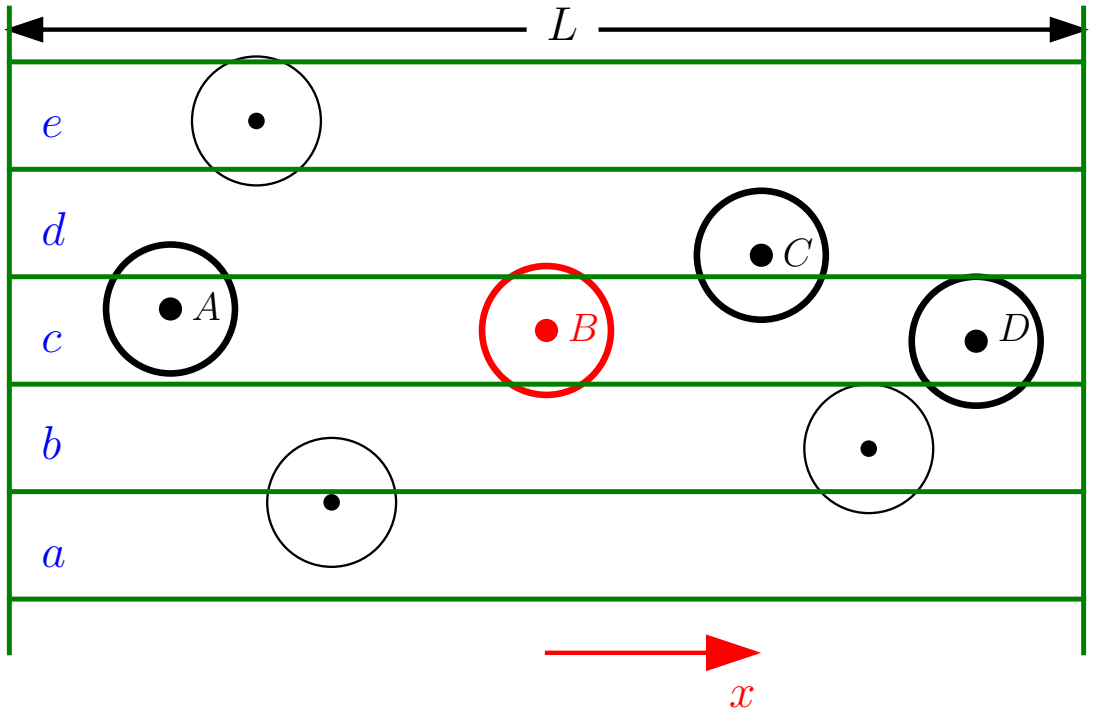
1d Conclusions

- Introducing a factor field accelerates the dynamics
- $z = 1/2$, better than Molecular dynamics
- Interesting stochastic process with $r^2 \sim t^{4/3}$

What is the origin of this stochastic process?
What is the continuum theory?

Up to two (or more) dimensions, hard spheres

How to add factor-field in two dimensions:
Lanes

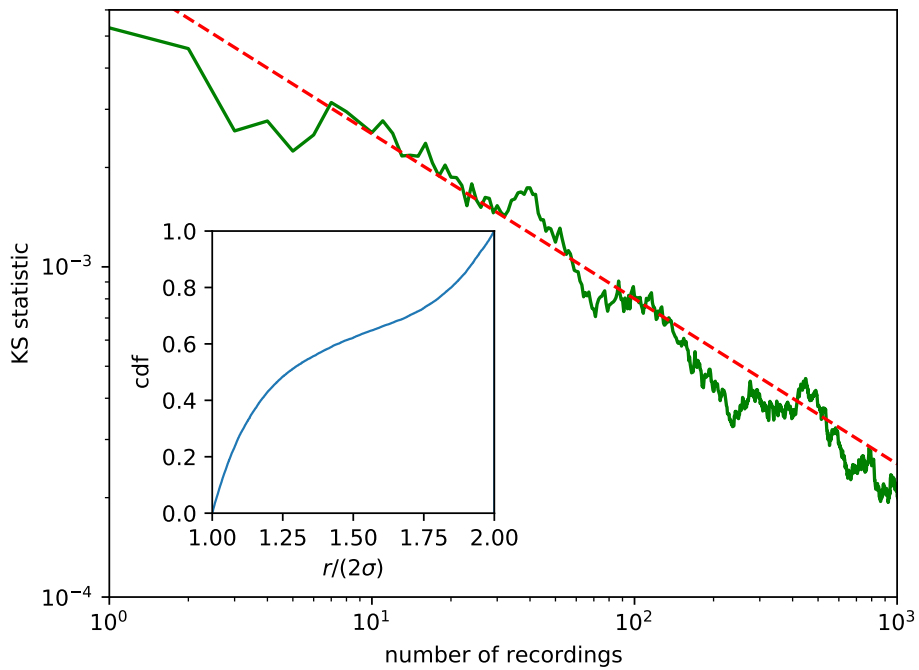


- Link up A-B-D with factor field
- Activity changes lanes with B-C collision

Two-dimensional hard sphere fluid

Testing for correctness: Kolmogorov-Smirnov test for

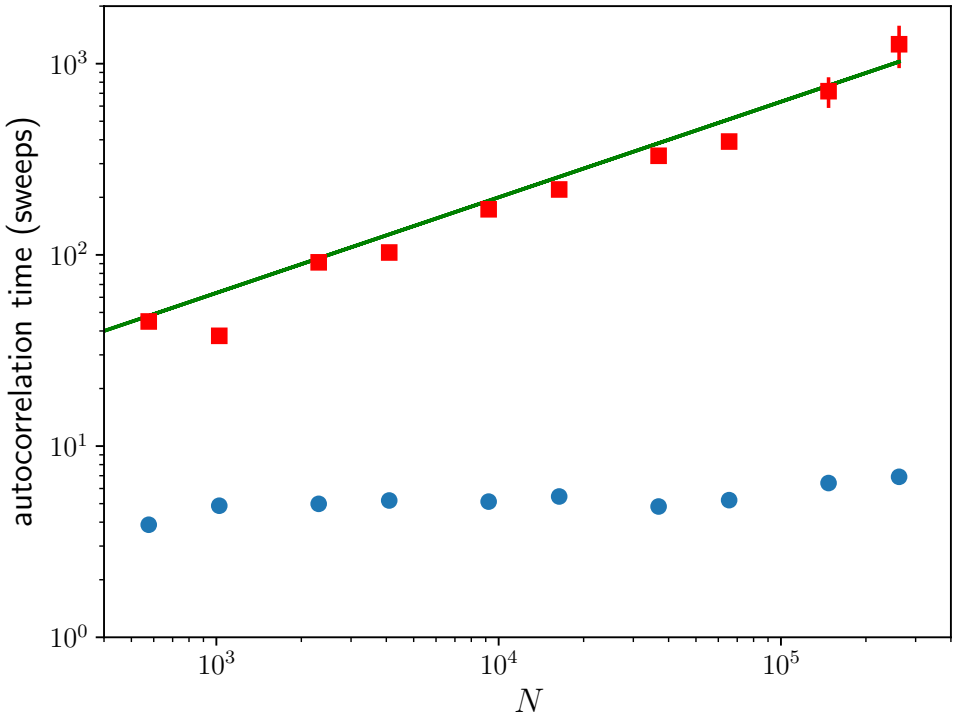
$$\int_1^r g(r) \quad 1 < r/(2\sigma) < 2$$



Compare simulations for two formulations, $\Delta(\mathrm{cdf}) \sim 1/\sqrt{n}$, n number of recordings. N=4096, 1000 recordings

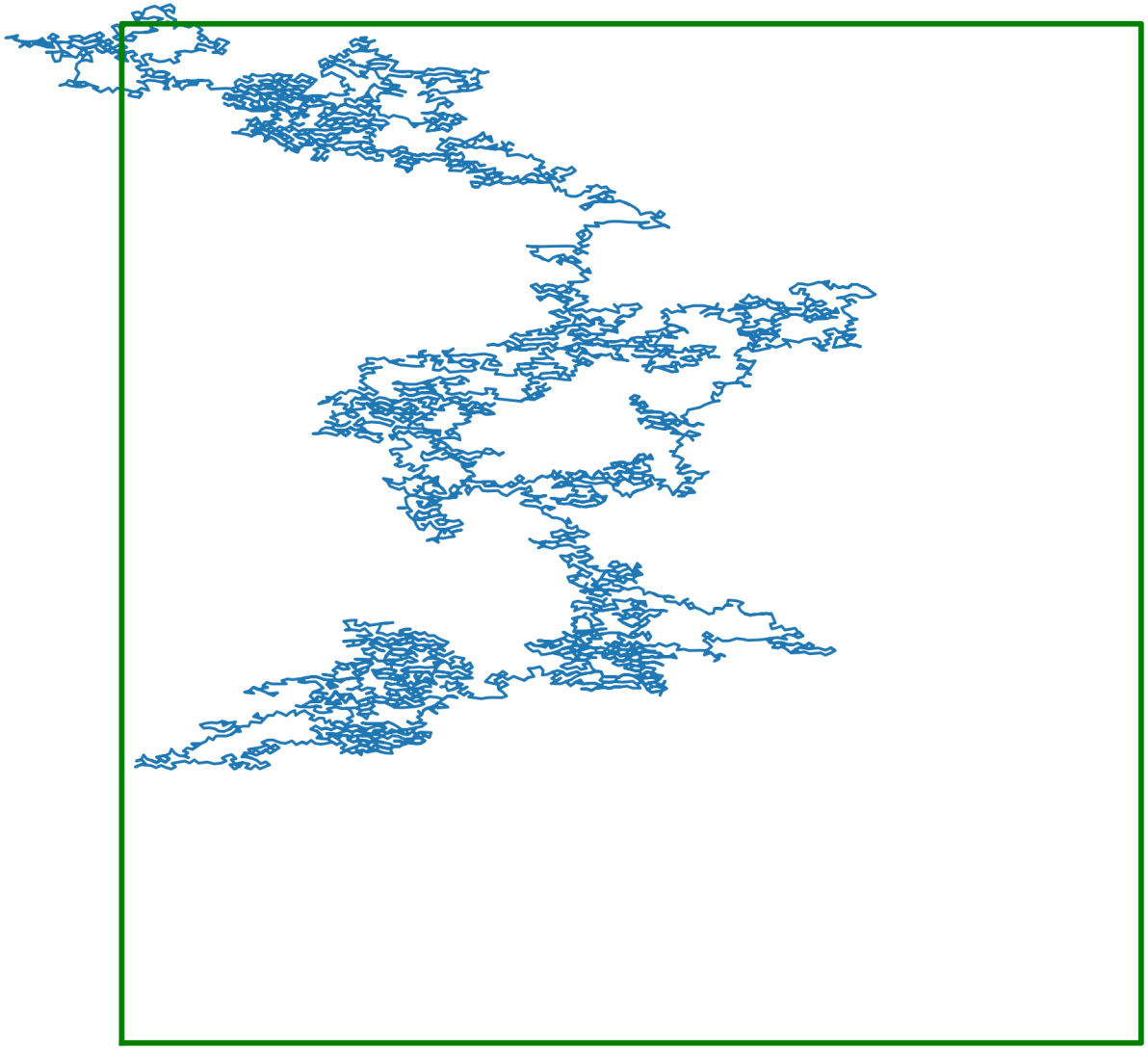
Two-dimensional hard sphere fluid

Autocorrelation of $\rho(q)\rho(-q)$ volume fraction $\eta = .67$. Fluid, hexatic transition at $\eta = 0.7$



- Red: Krauth/Bernard
- Blue: Factor field (log?)
- Line $z = 1$

Trajectories of activity



Evolution modes in a single trajectory

Perform a long simulation and measure

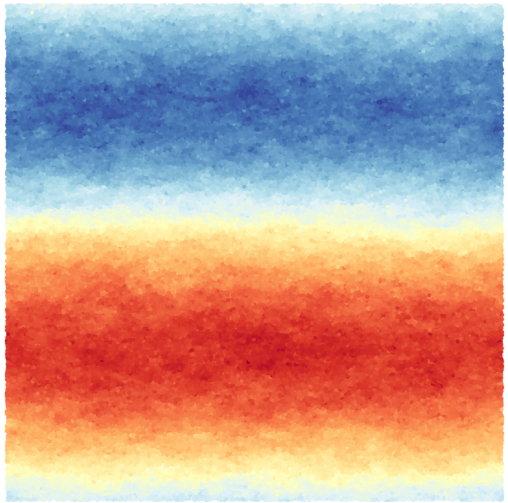
$$\bar{x}_i = \frac{1}{m}\sum_{s=1}^{m} x_i(t) \tag{1}$$

And correlation matrix

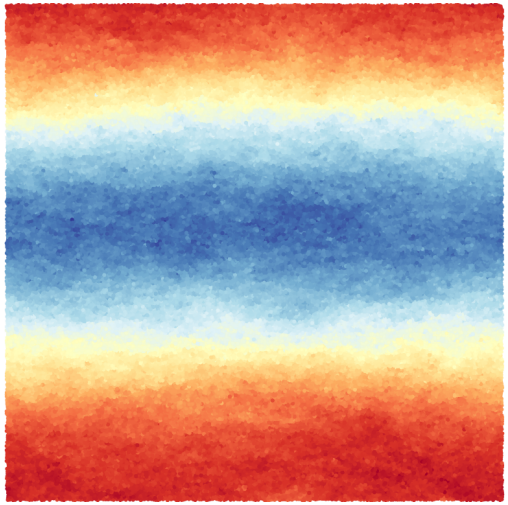
$$D_{jl} = \frac{1}{m}\sum_{s=1}^{m}(x_i(t) - \bar{x}_i)(x_j(t) - \bar{x}_j) \tag{2}$$

Diagonalize (Lanczos) to find the dominate modes in the dynamics

Modes



(a)



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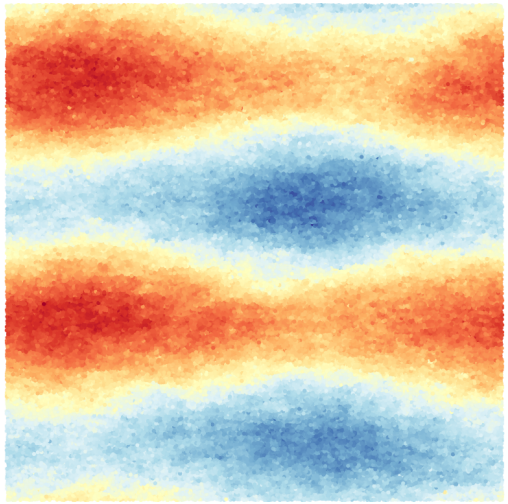

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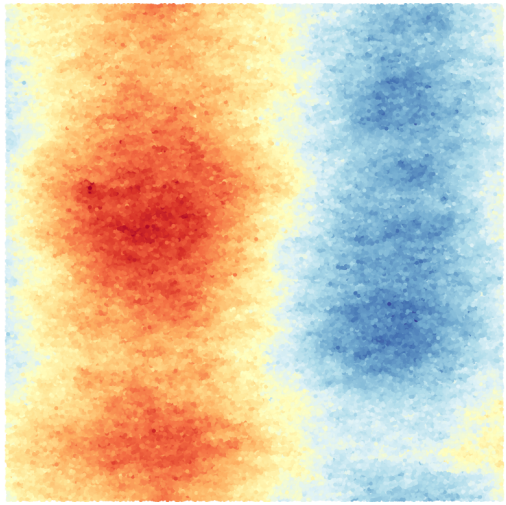

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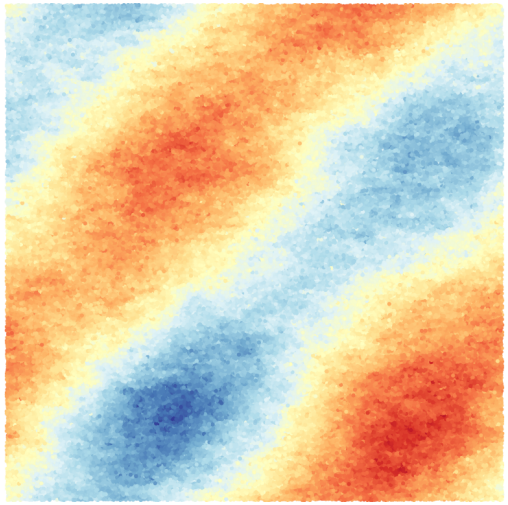

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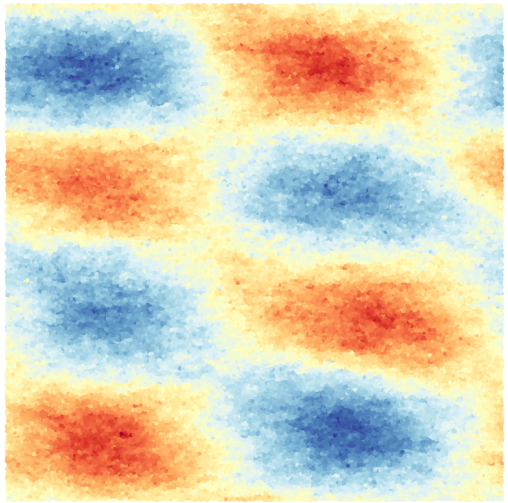


(f)

Mode dynamics

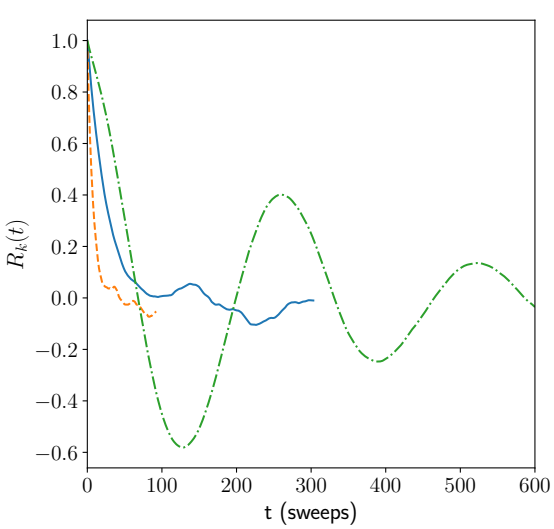
Define:

$$(a_k(t) = x(t) \cdot v_k$$

Measure autocorrelation functions

$$R_k(t) = \langle a_k(0)\, a_k(t) \rangle$$

- Bernard/Krauth long trajectories – longitudinal oscillations
- Bernard/Krauth short trajectories – slow transverse relaxation
- all modes at same speed, $O(1)$ sweeps



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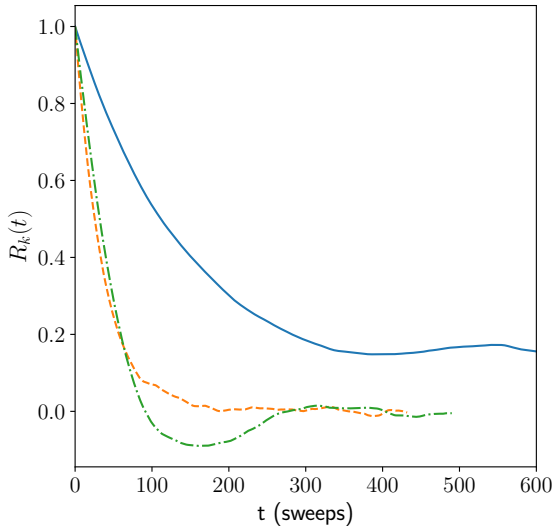

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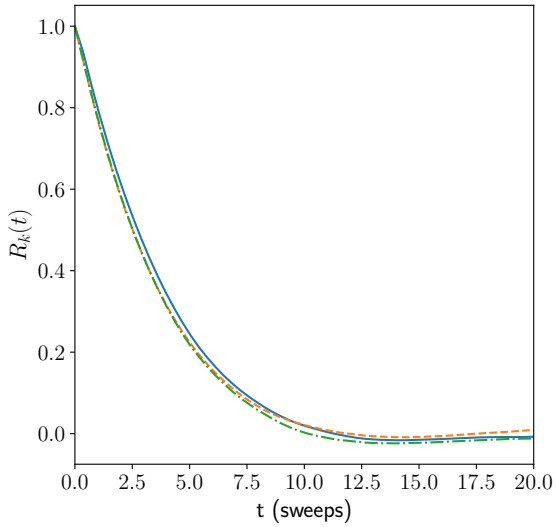

(i)

Conclusions

Conclusions+questions

- Event driven framework for thermodynamic simulation
- between MC and MD
- Factor-fields lead to further acceleration
- Future: multi-walker [Parallelization]
- Soft-matter simulation with general potentials

- Some things work with factor fields: density equilibration
- Some things don't...

What are the "hydrodynamic" equations of this kind of algorithm?

References

- Event-chain Monte Carlo with factor fields: Ze Lei, Werner Krauth, and A. C. Maggs, Phys. Rev. E 99, 043301 (2019).
- All-atom computations with irreversible Markov chains , Michael F. Faulkner, Liang Qin, A. C. Maggs, and Werner Krauth, J. Chem. Phys. 149, 064113 (2018).
- Multithreaded event-chain Monte Carlo with local times, Botao Li, Synge Todo, A.C. Maggs Werner Krauth, Computer Physics Communications 261, (2020)
- 2D factor field out this week