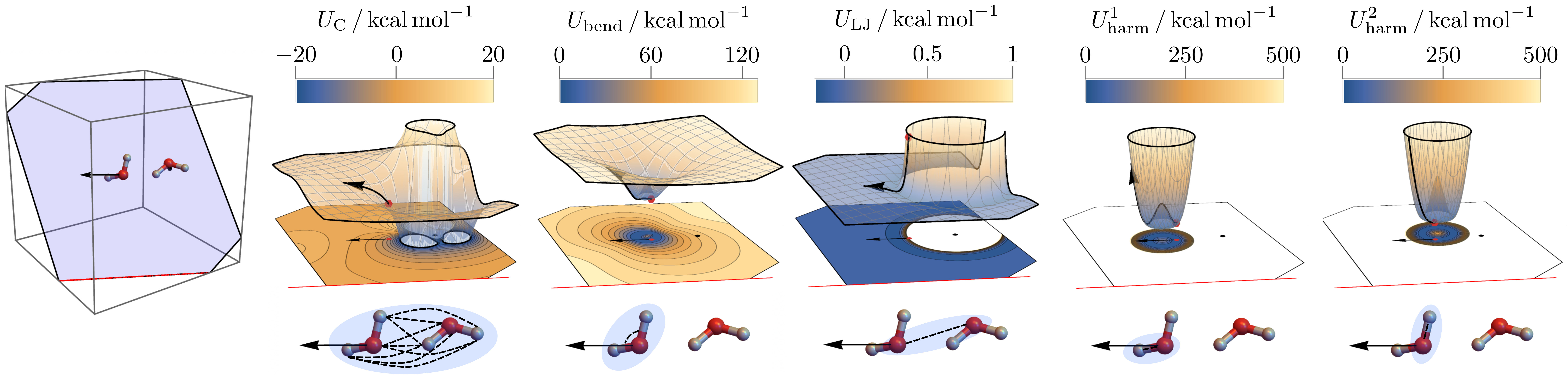
Bringing the Power of Monte Carlo methods to Long-Range-Interacting Molecular Systems

Philipp Höllmer (AG Monien)

09. November 2022, Journal Club on Condensed Matter Theory, University of Bonn

Collaborators: N. Noirault (ENS Paris), B. Li (ENS Paris), A. C. Maggs (ESPCI Paris), W. Krauth (ENS Paris)



Physikalisches Institut

UNIVERSITÄT BONN

LPENS LABORATOIRE DE PHYSIQUE DE L'ÉCOLE NORMALE SUPÉRIEURE

ENS | PSL

ESPCI PARIS

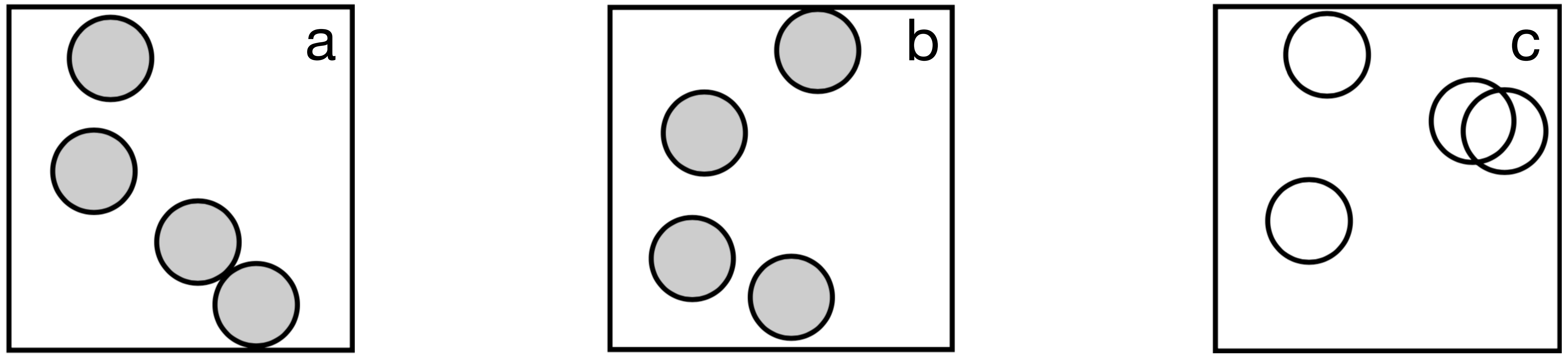
EDUCATION SCIENCE INNOVATION

Structure

1. Non-Reversible Event-Chain Monte Carlo (ECMC) for the Hard-Disk Model.
2. Generalization of ECMC to Molecular Systems.
3. ECMC Variants and Simulation Results.

Hard-Disk Model

- Probability density of configuration $c = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$: $\pi(c) \propto \begin{cases} 1 & \text{if } c \text{ legal,} \\ 0 & \text{otherwise} . \end{cases}$



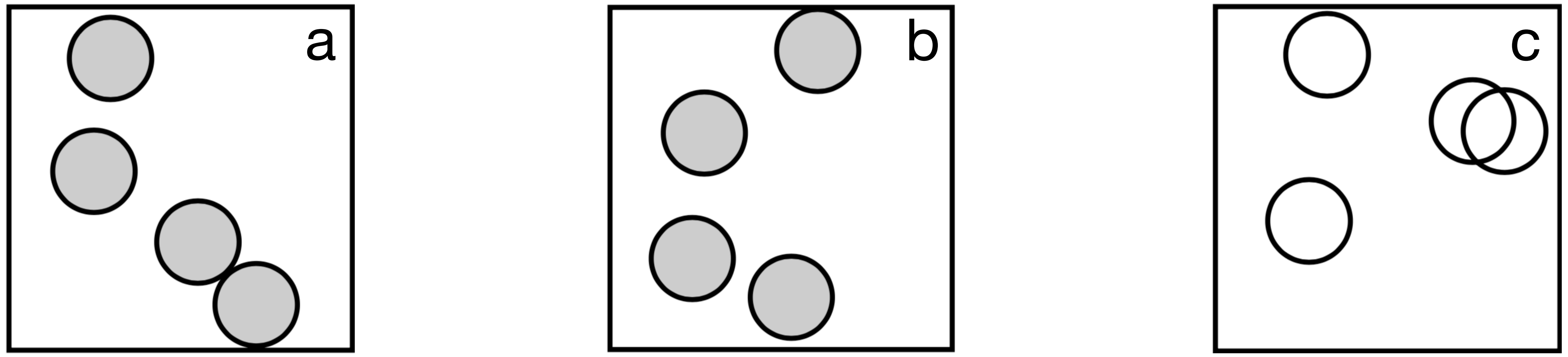
$\pi(a) = \pi(b) \propto 1$

$\pi(c) = 0$

W. Krauth, *Statistical Mechanics: Algorithms and Computations* (Oxford University Press, 2006)

Hard-Disk Model

- Probability density of configuration $c = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$: $\pi(c) \propto \begin{cases} 1 & \text{if } c \text{ legal,} \\ 0 & \text{otherwise.} \end{cases}$

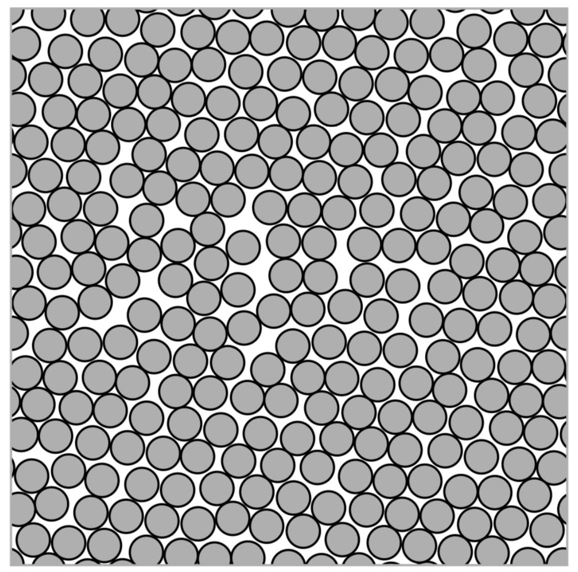


$$\pi(a) = \pi(b) \propto 1$$

$$\pi(c) = 0$$

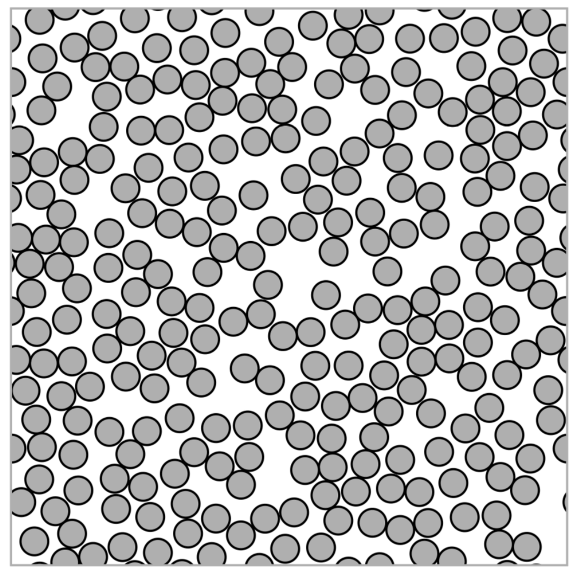
W. Krauth, *Statistical Mechanics: Algorithms and Computations* (Oxford University Press, 2006)

- Hard-disk model has a phase transition when hard-disk density is changed:



Solid

Precise melting scenario?



Fluid

E. Bernard, *Algorithms and applications of the Monte Carlo method: Two-dimensional melting and perfect sampling* (PhD thesis, 2011)

Markov-Chain Monte Carlo (MCMC)

- Idea: Change configuration from c to c' with transition probability $p(c \to c')$.

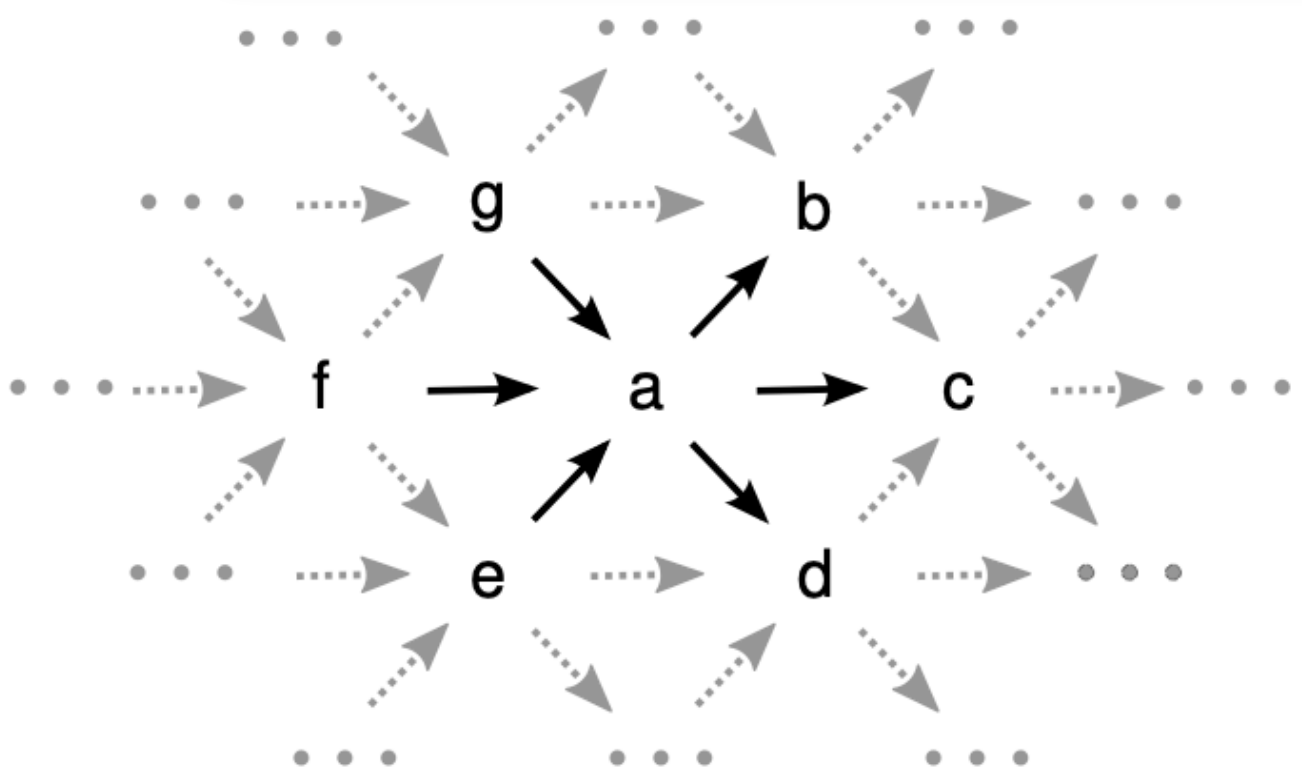
  $\to$ Only converges to probability distribution π if:

$$\sum_{c'} \pi(c')\, p(c' \to c) = \pi(c) \quad \text{(global balance)}$$

- **Reversible** Markov chains obey global balance by satisfying a weaker condition:

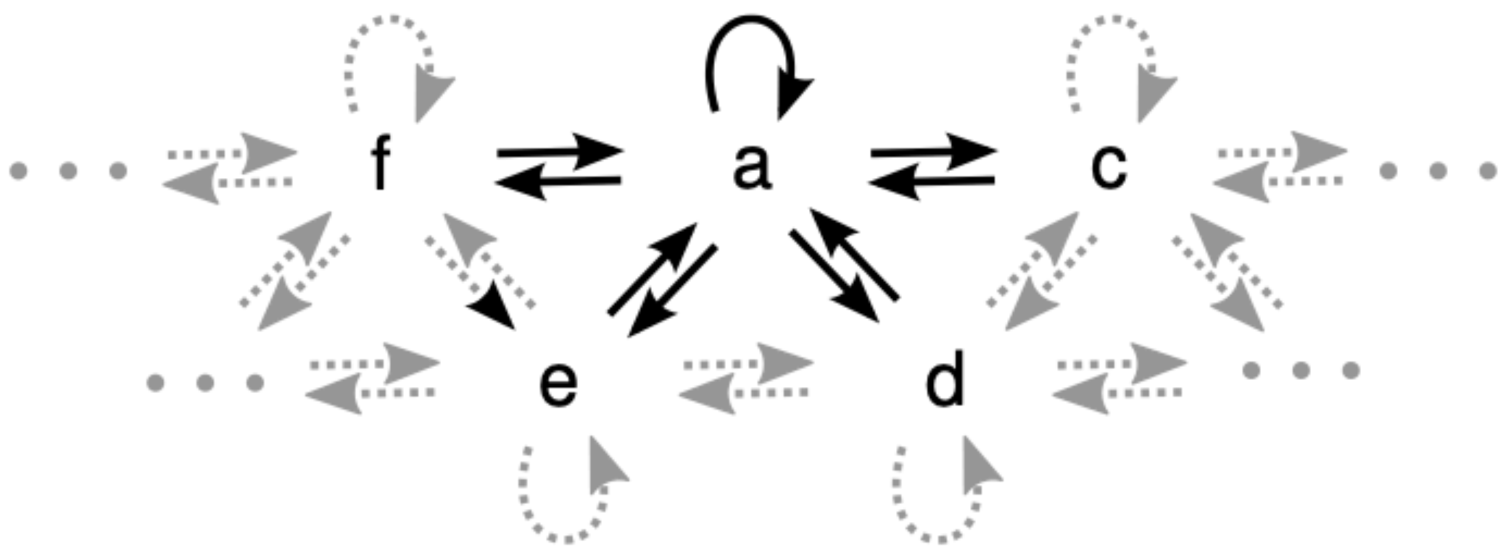
$$\pi(c')\, p(c' \to c) = \pi(c)\, p(c \to c') \quad \text{(detailed balance)}$$

Global:



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Detailed:



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

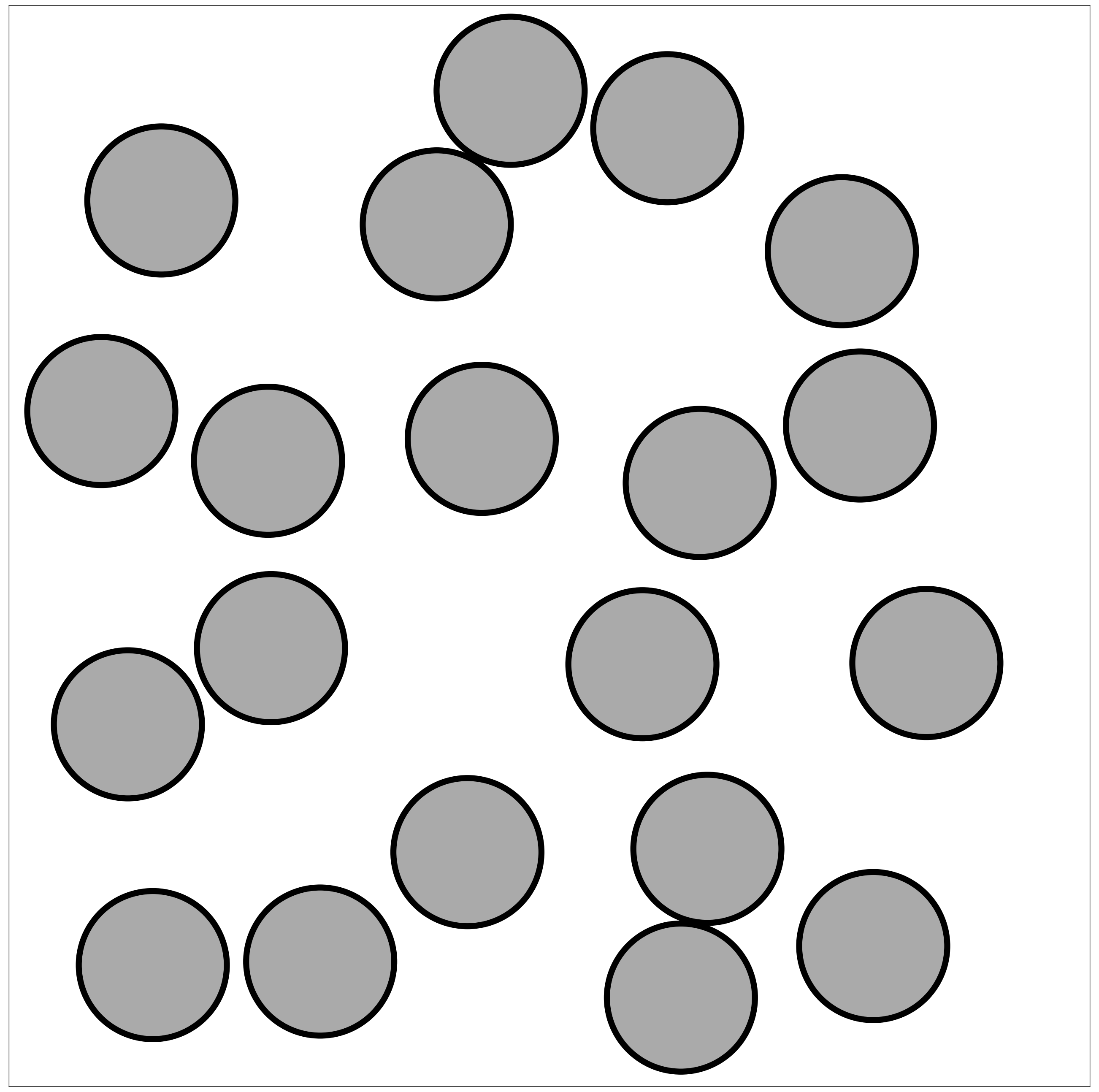
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

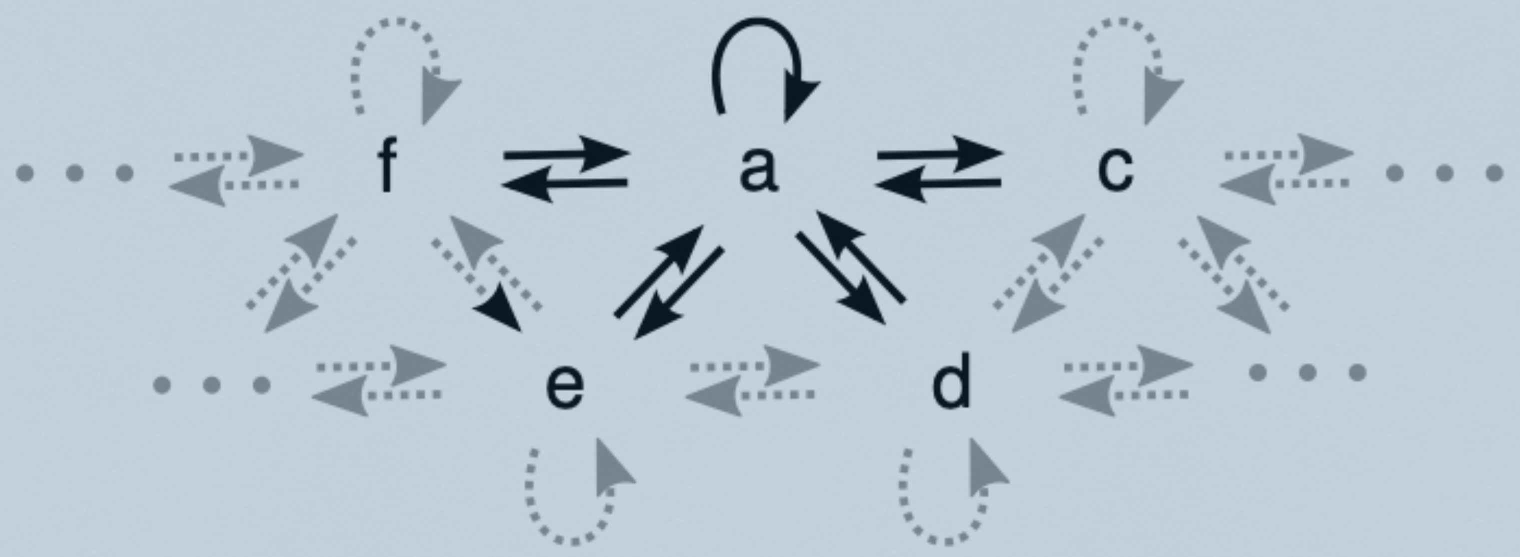
$$\mathbf{r}_i = (x_i, y_i) \to \mathbf{r}_i' = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \mathrm{ran}(-\delta, \delta), \Delta_y \leftarrow \mathrm{ran}(-\delta, \delta) \,.$$

2. Accept proposed configuration c' if no overlap is introduced (or more generally with probability $p(c \to c') = \min[1, \pi(c')/\pi(c)]$).



Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

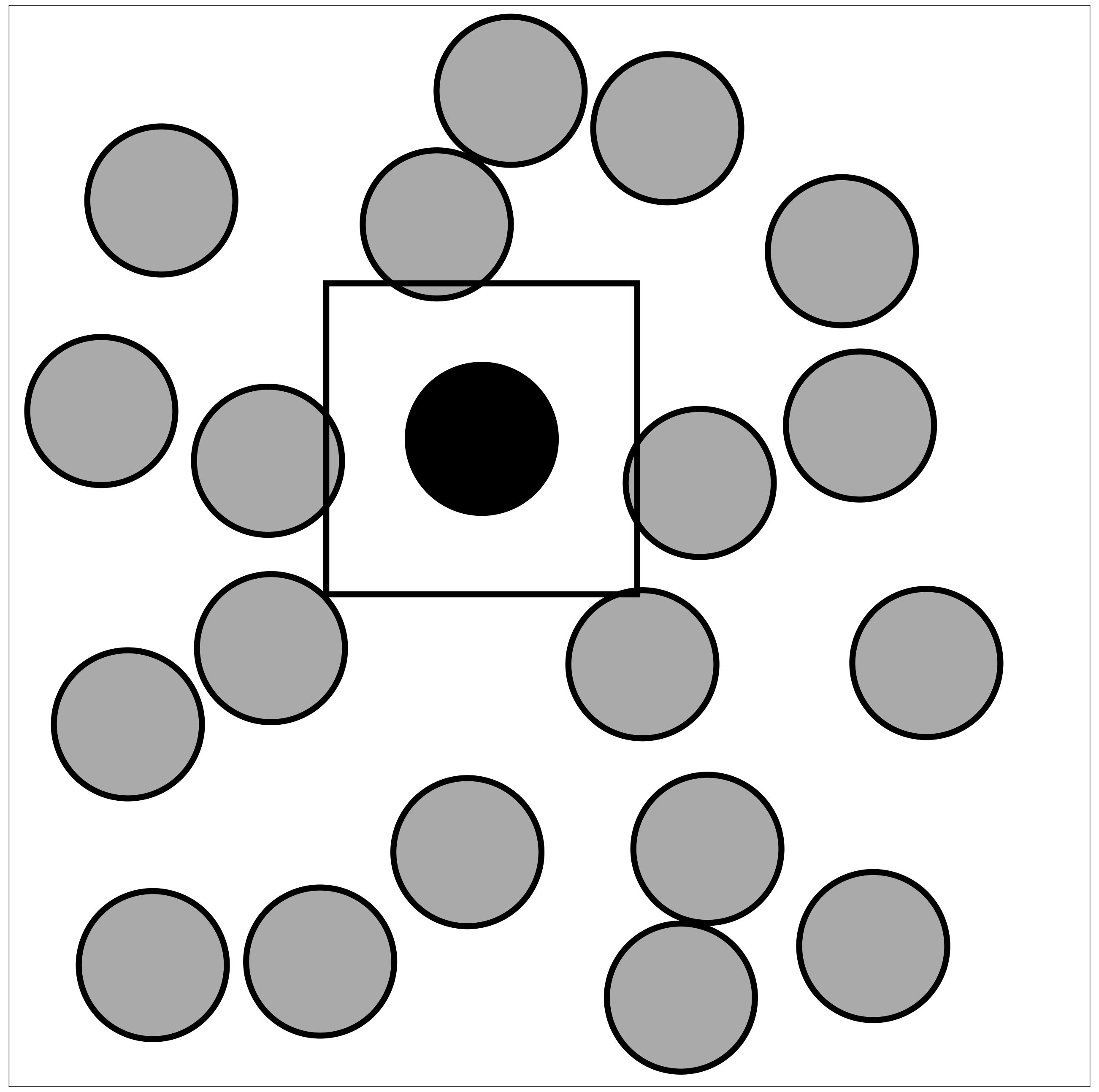
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

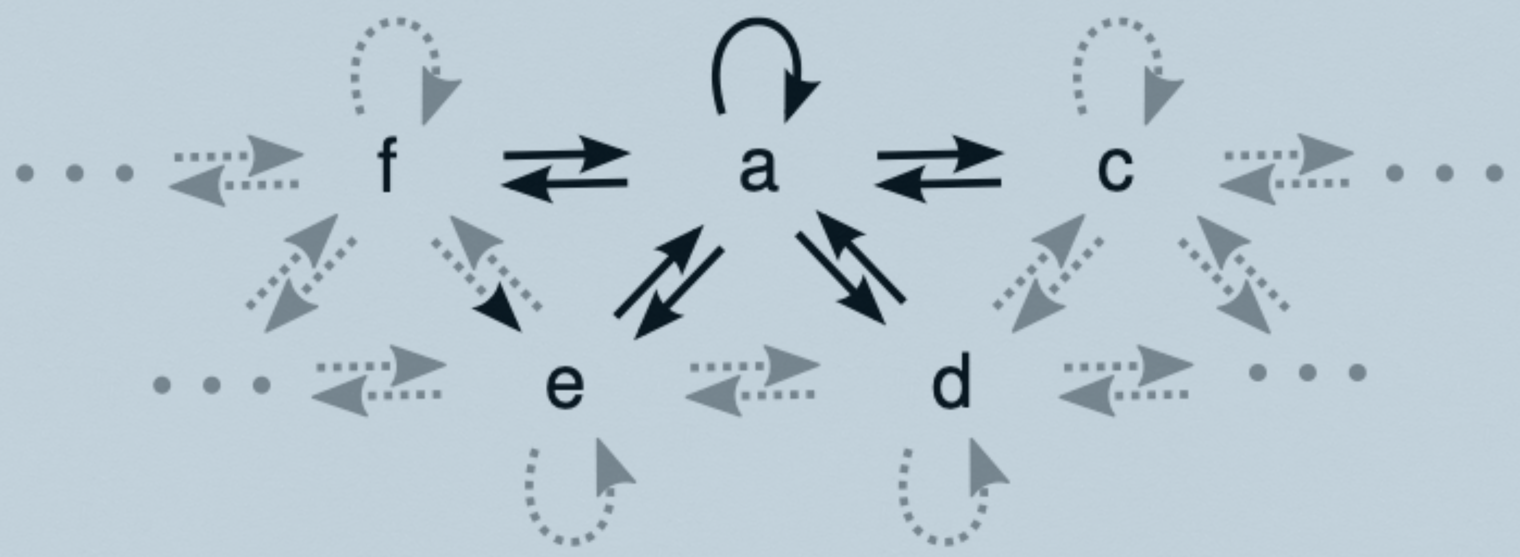
$$\mathbf{r}_i = (x_i, y_i) \to \mathbf{r}_i' = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \mathrm{ran}(-\delta, \delta), \Delta_y \leftarrow \mathrm{ran}(-\delta, \delta)\,.$$

2. Accept proposed configuration c' if no overlap is introduced
(or more generally with probability $p(c \to c') = \min[1, \pi(c')/\pi(c)]$).



Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

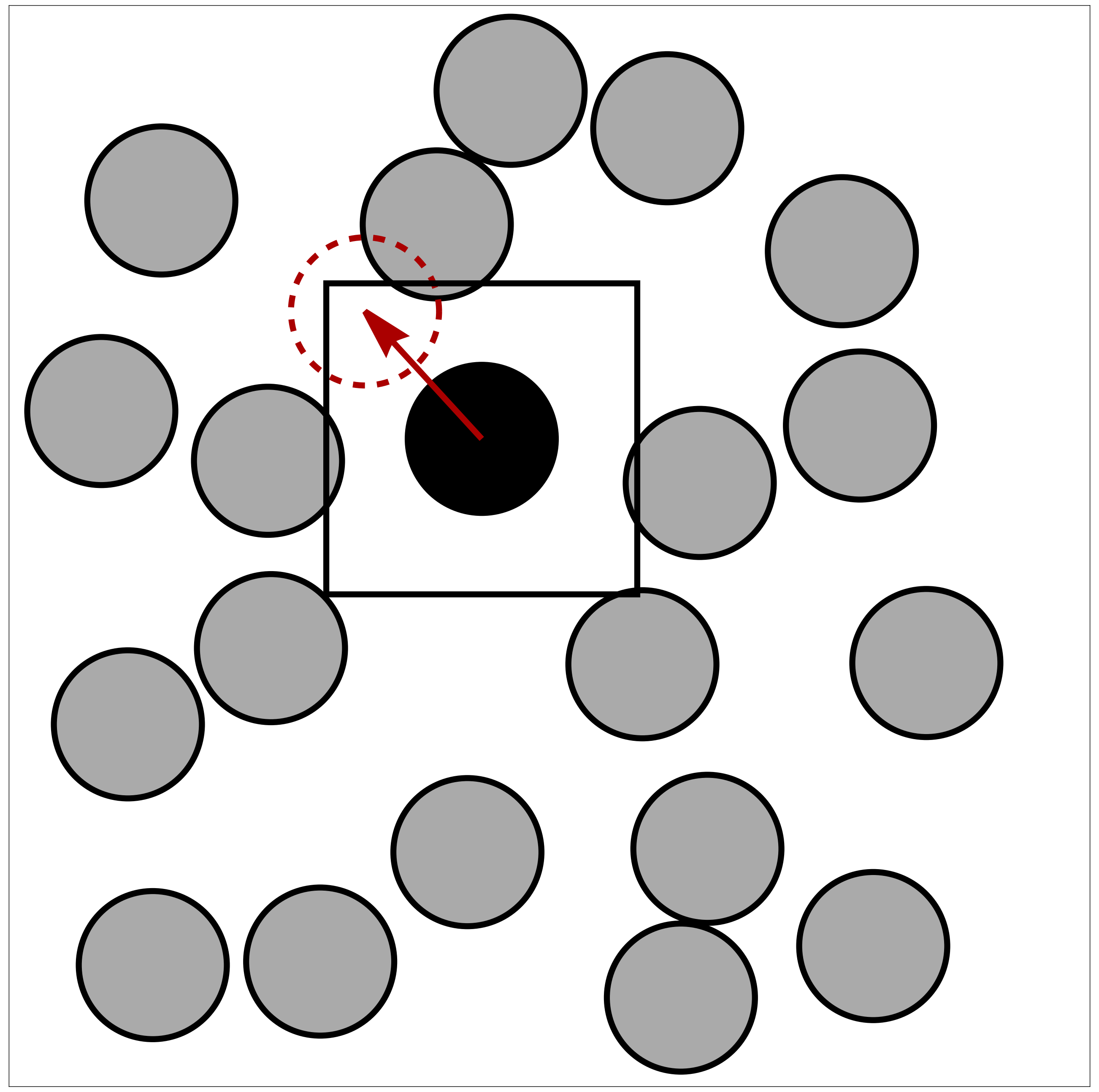
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

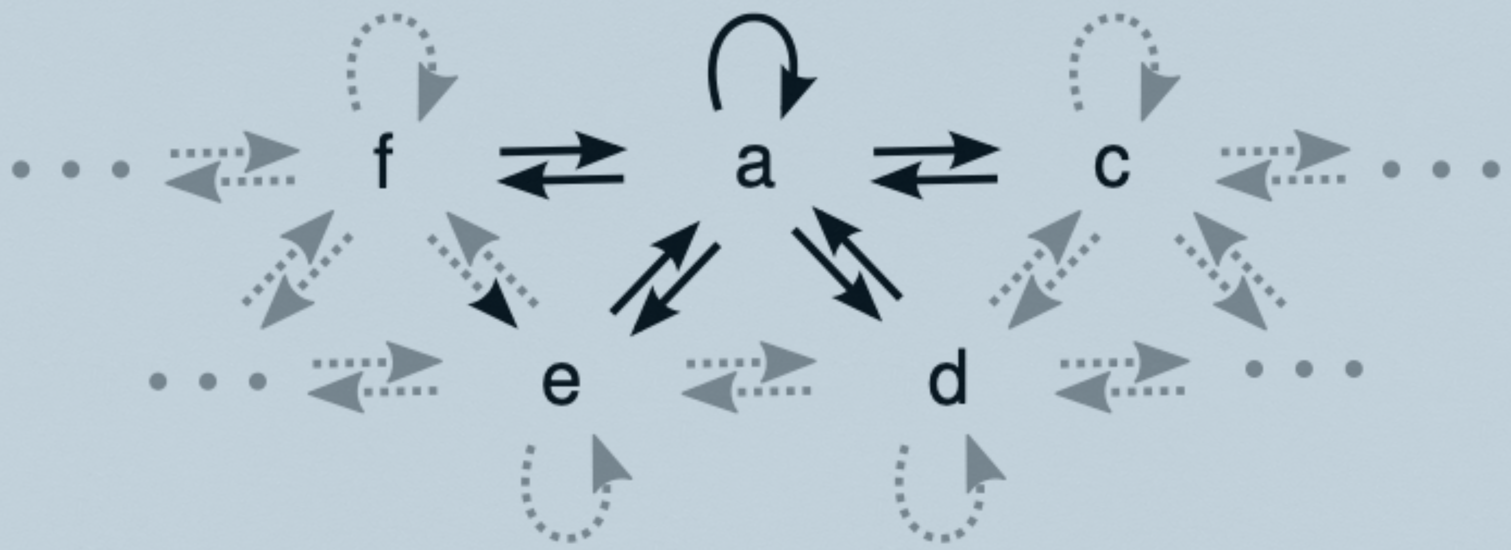
$$\mathbf{r}_i = (x_i, y_i) \rightarrow \mathbf{r}_i' = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \mathrm{ran}(-\delta, \delta), \Delta_y \leftarrow \mathrm{ran}(-\delta, \delta) \,.$$

2. Accept proposed configuration c' if no overlap is introduced
(or more generally with probability $p(c \rightarrow c') = \min[1, \pi(c')/\pi(c)]$).



Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

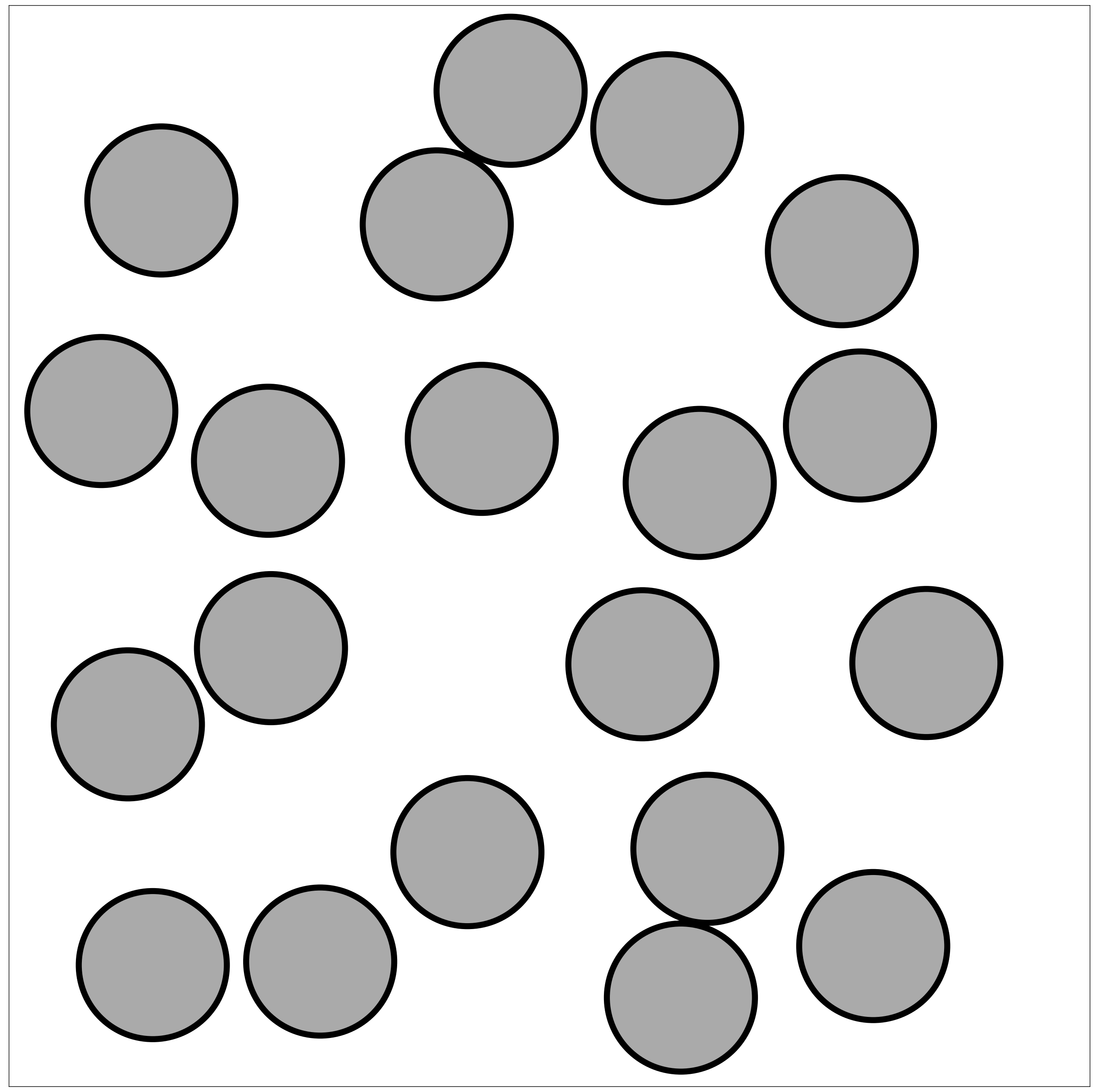
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

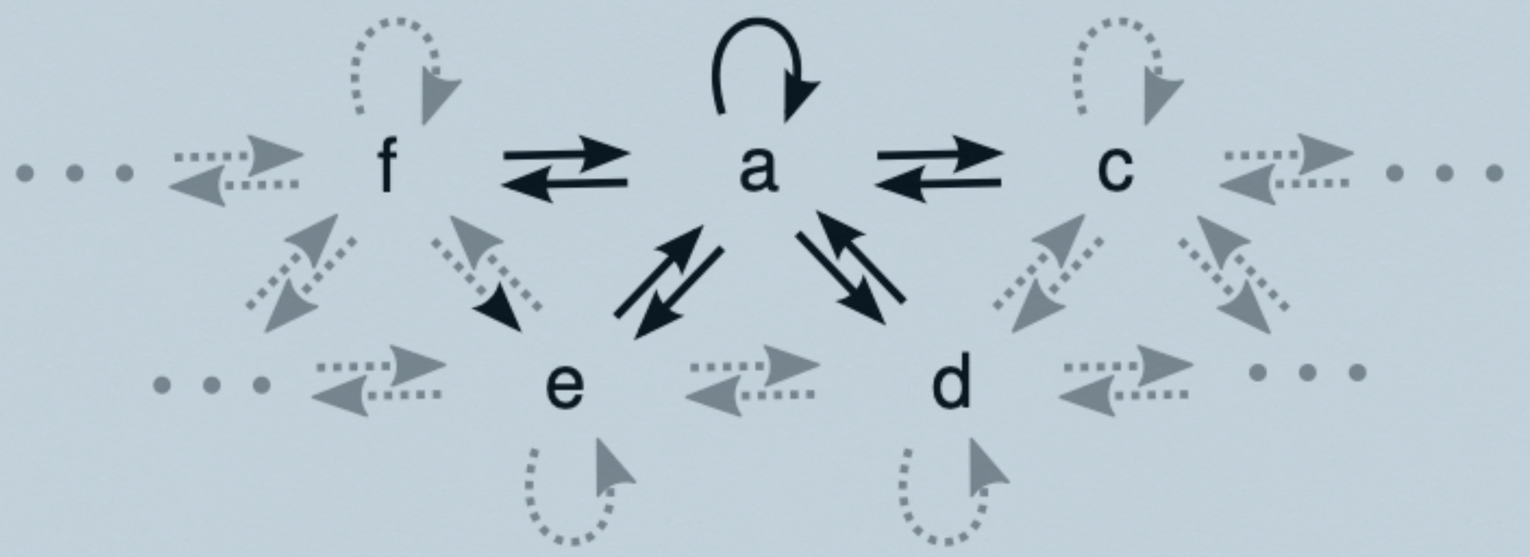
$$\mathbf{r}_i = (x_i, y_i) \to \mathbf{r}_i' = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \mathrm{ran}(-\delta, \delta), \Delta_y \leftarrow \mathrm{ran}(-\delta, \delta)\,.$$

2. Accept proposed configuration c' if no overlap is introduced
(or more generally with probability $p(c \to c') = \min[1, \pi(c')/\pi(c)]$).



Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

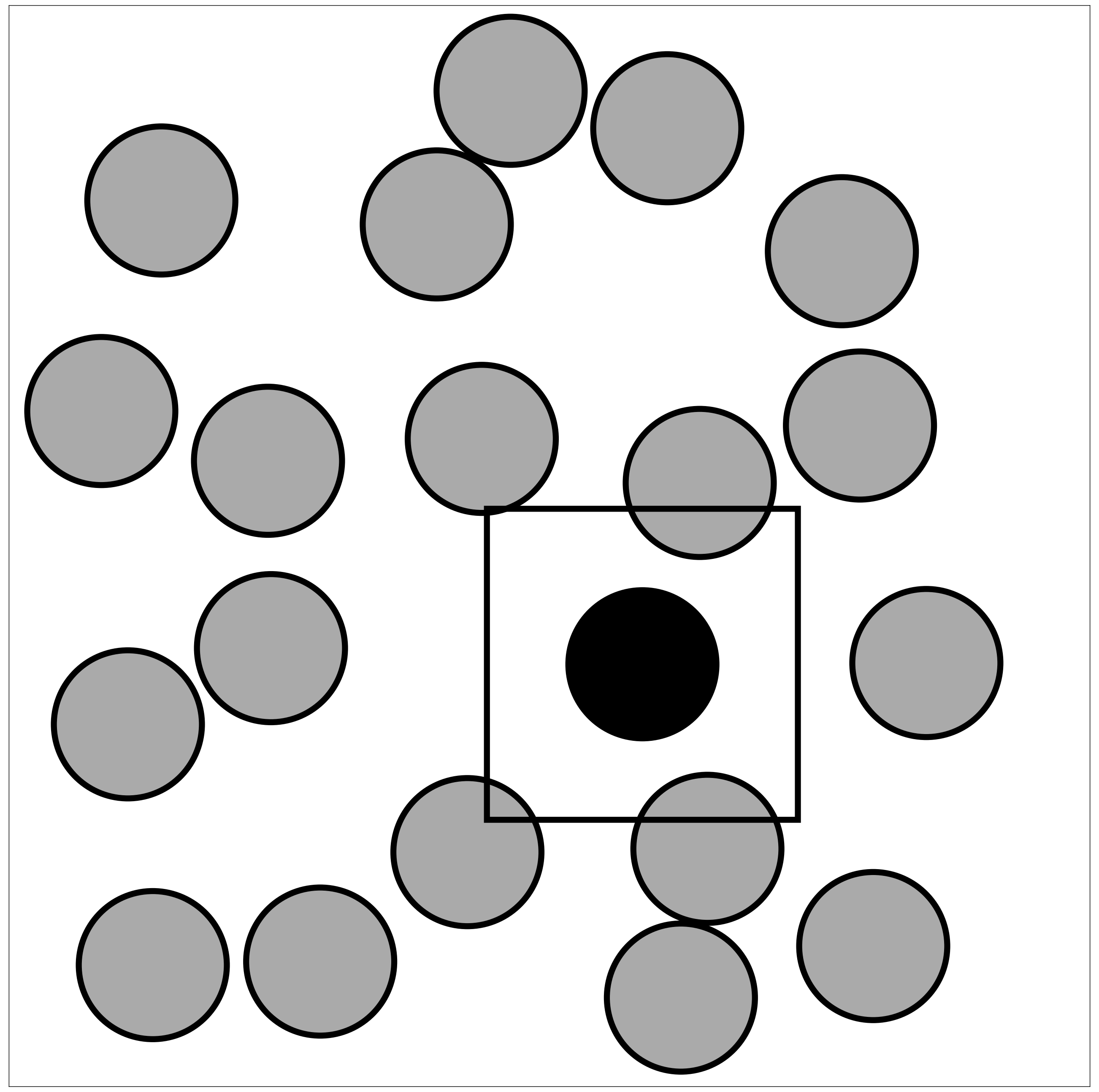
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

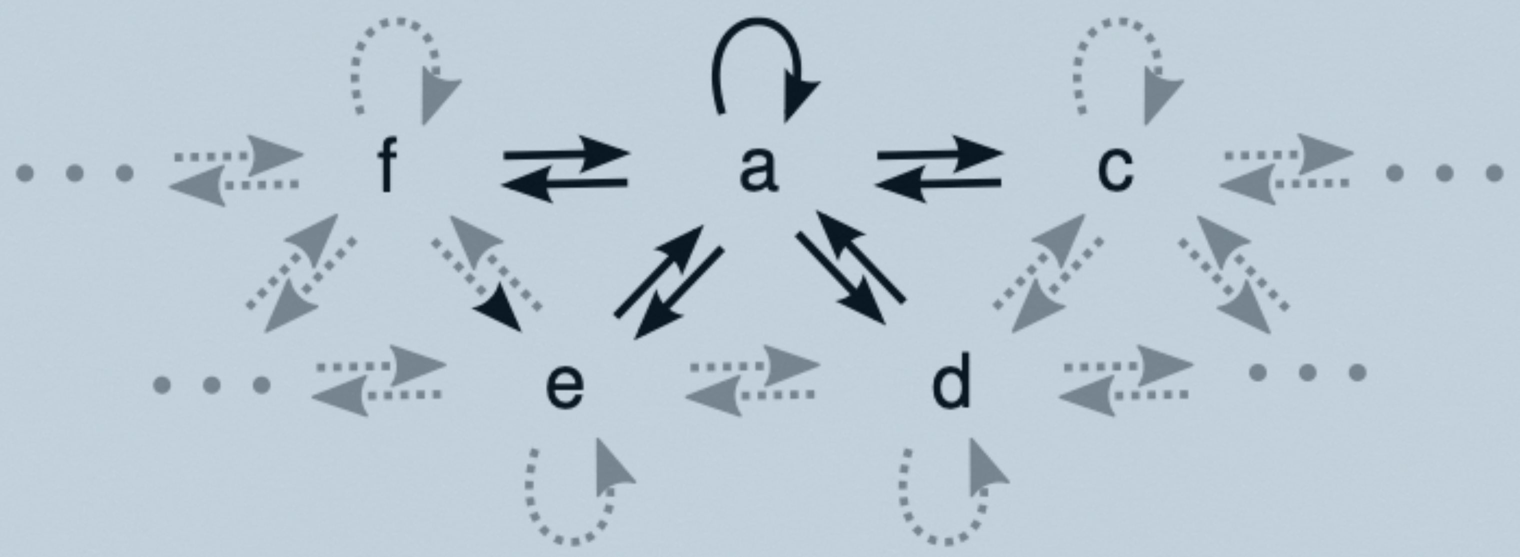
$$\mathbf{r}_i = (x_i, y_i) \rightarrow \mathbf{r}_i' = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \mathrm{ran}(-\delta, \delta), \Delta_y \leftarrow \mathrm{ran}(-\delta, \delta)\,.$$

2. Accept proposed configuration c' if no overlap is introduced
(or more generally with probability $p(c \rightarrow c') = \min[1, \pi(c')/\pi(c)]$).



Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

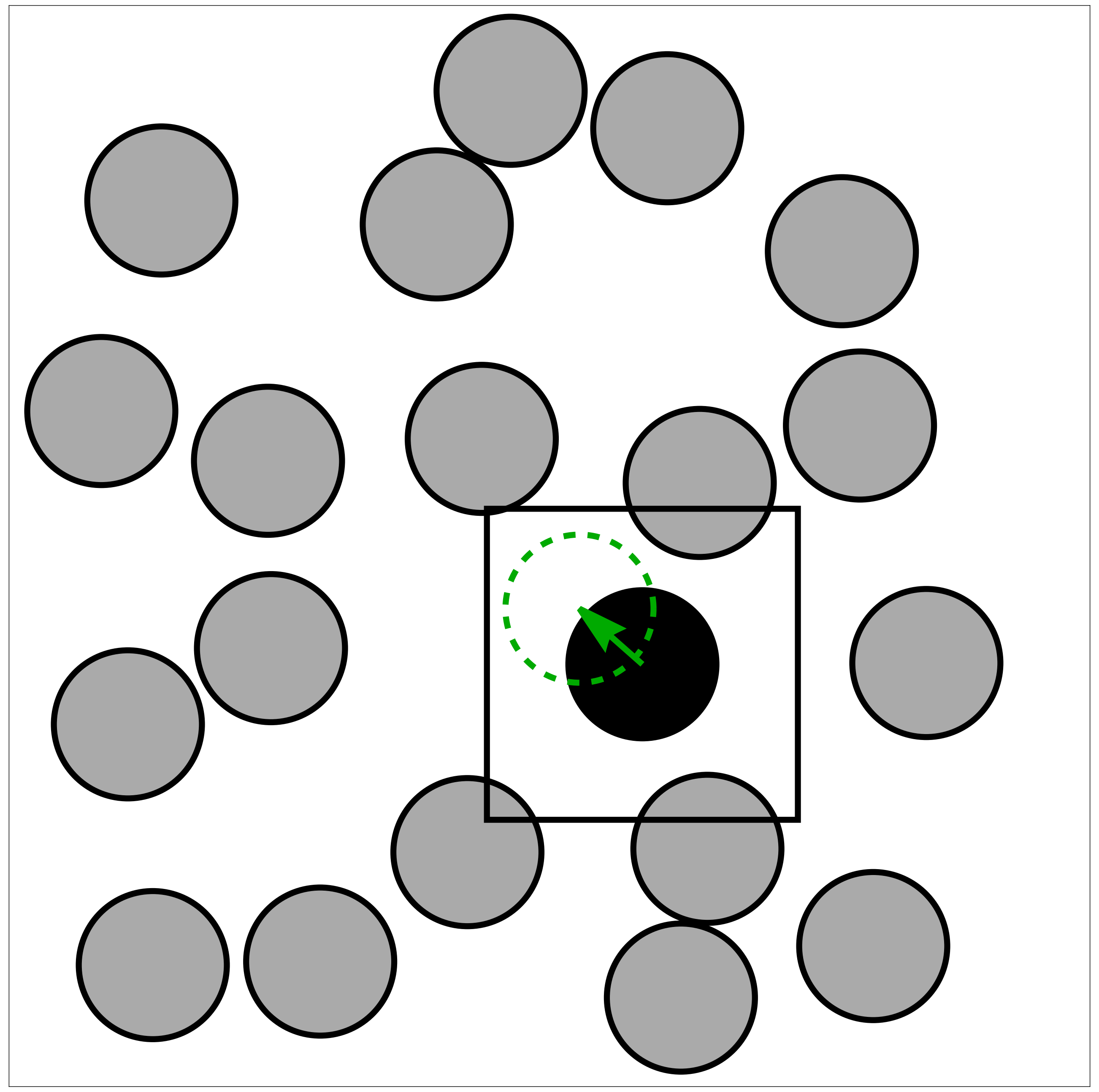
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

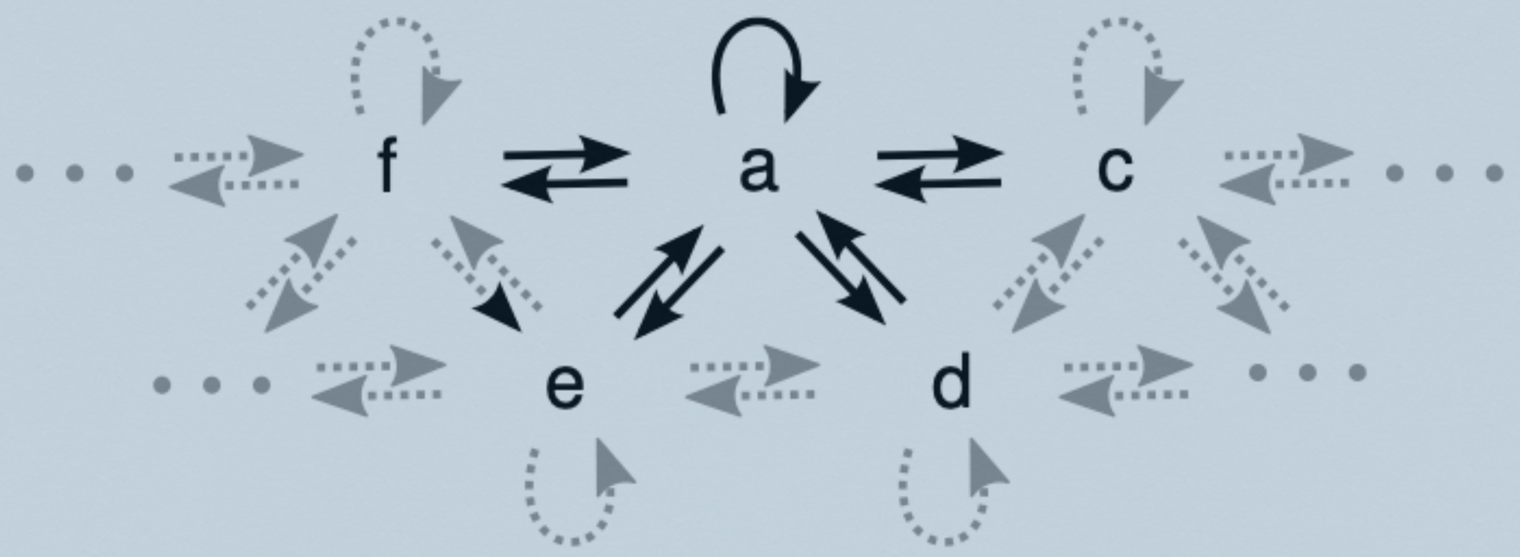
$$\mathbf{r}_i = (x_i, y_i) \to \mathbf{r}_i' = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \mathrm{ran}(-\delta, \delta), \Delta_y \leftarrow \mathrm{ran}(-\delta, \delta)\,.$$

2. Accept proposed configuration c' if no overlap is introduced
(or more generally with probability $p(c \to c') = \min[1, \pi(c')/\pi(c)]$).



Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

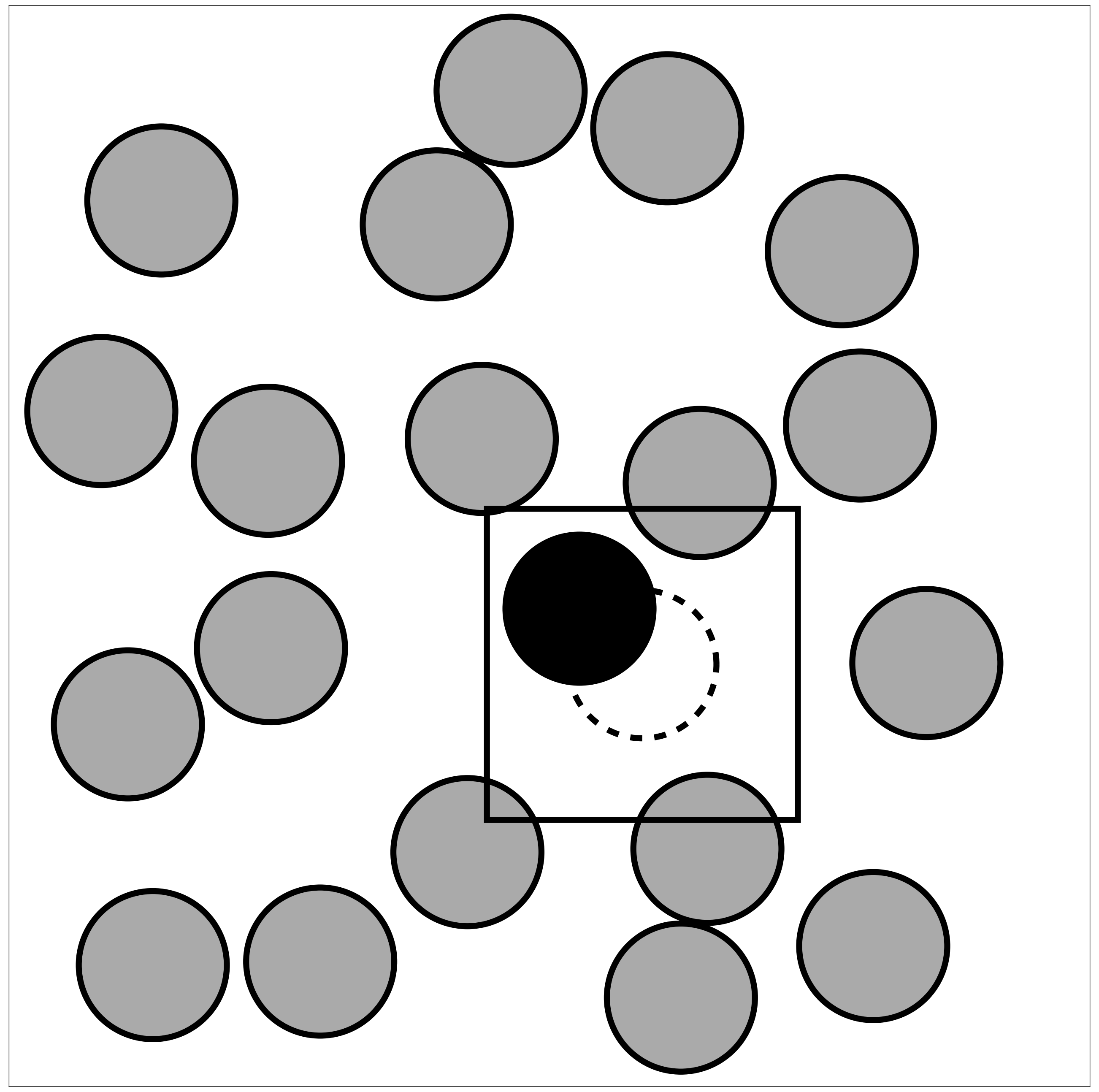
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

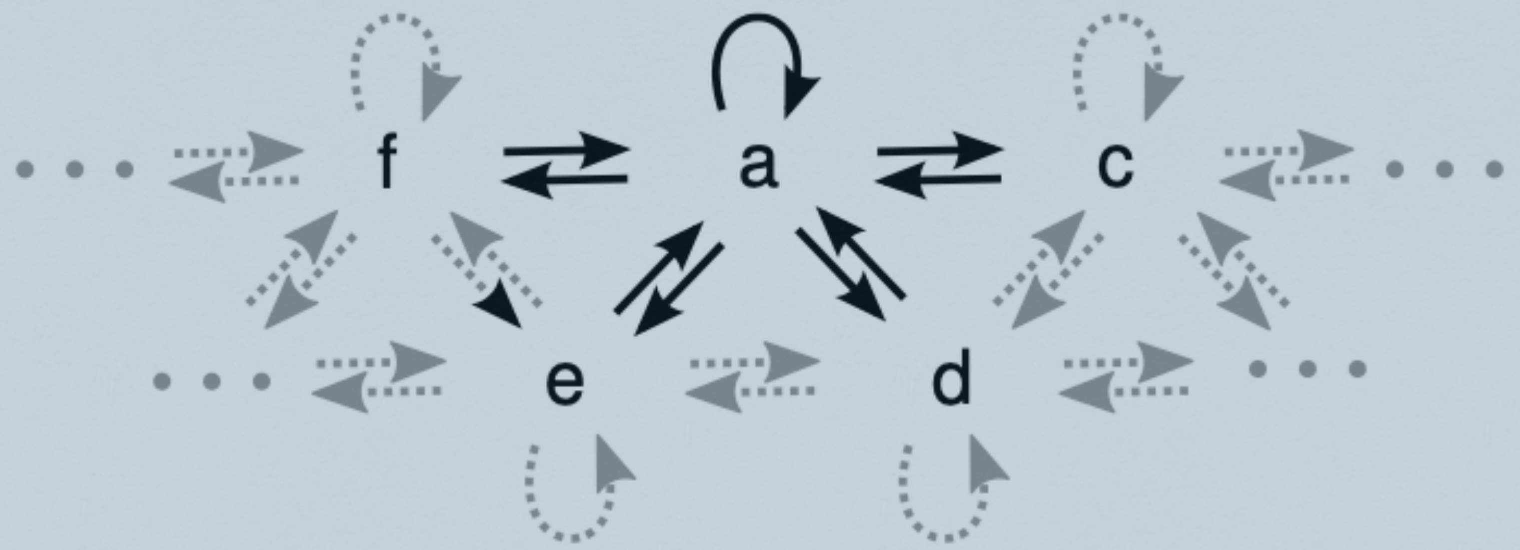
$$\mathbf{r}_i = (x_i, y_i) \to \mathbf{r}'_i = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \text{ran}(-\delta, \delta), \Delta_y \leftarrow \text{ran}(-\delta, \delta)\,.$$

2. Accept proposed configuration c' if no overlap is introduced (or more generally with probability $p(c \to c') = \min[1, \pi(c')/\pi(c)]$).



Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

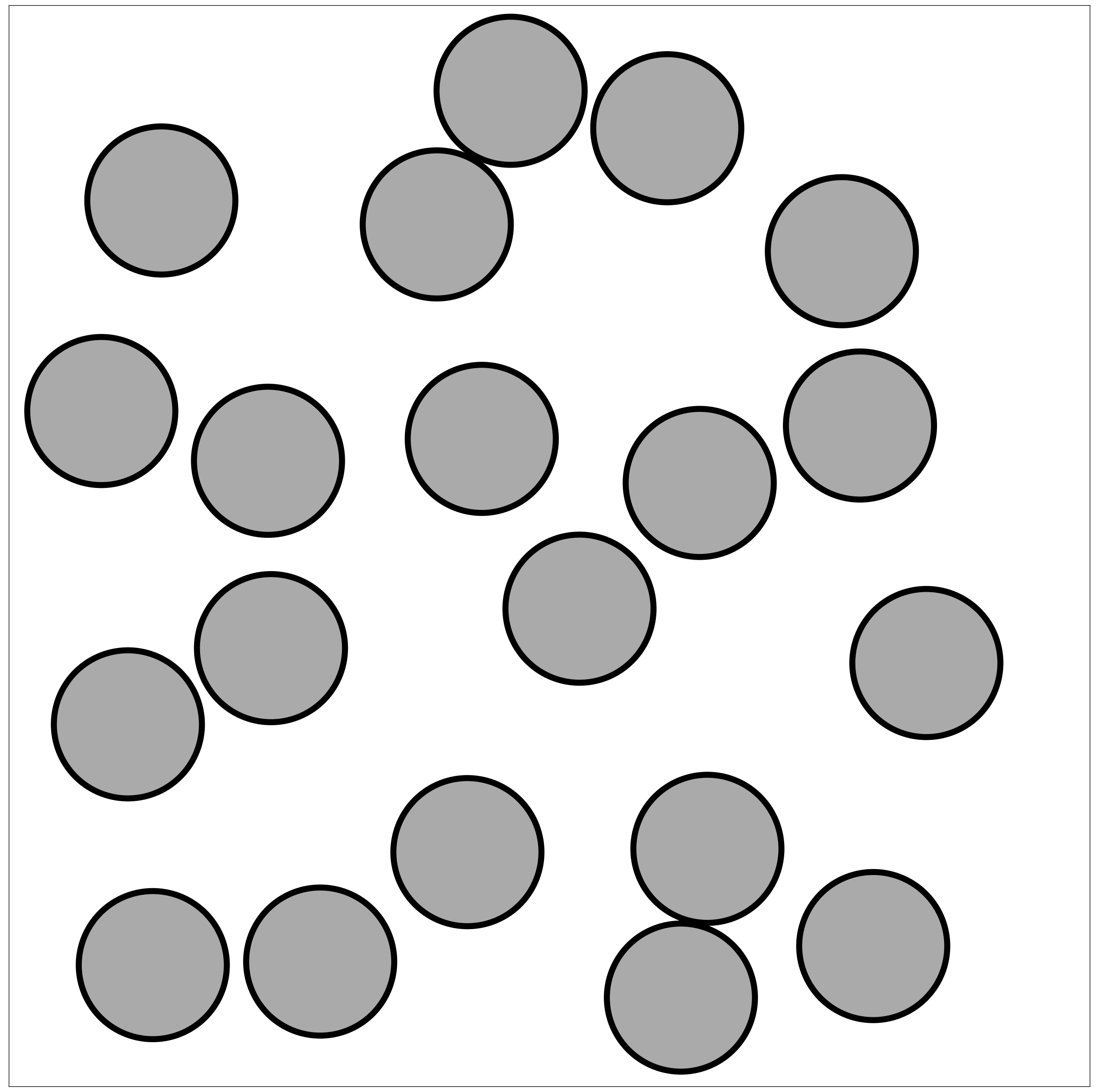
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

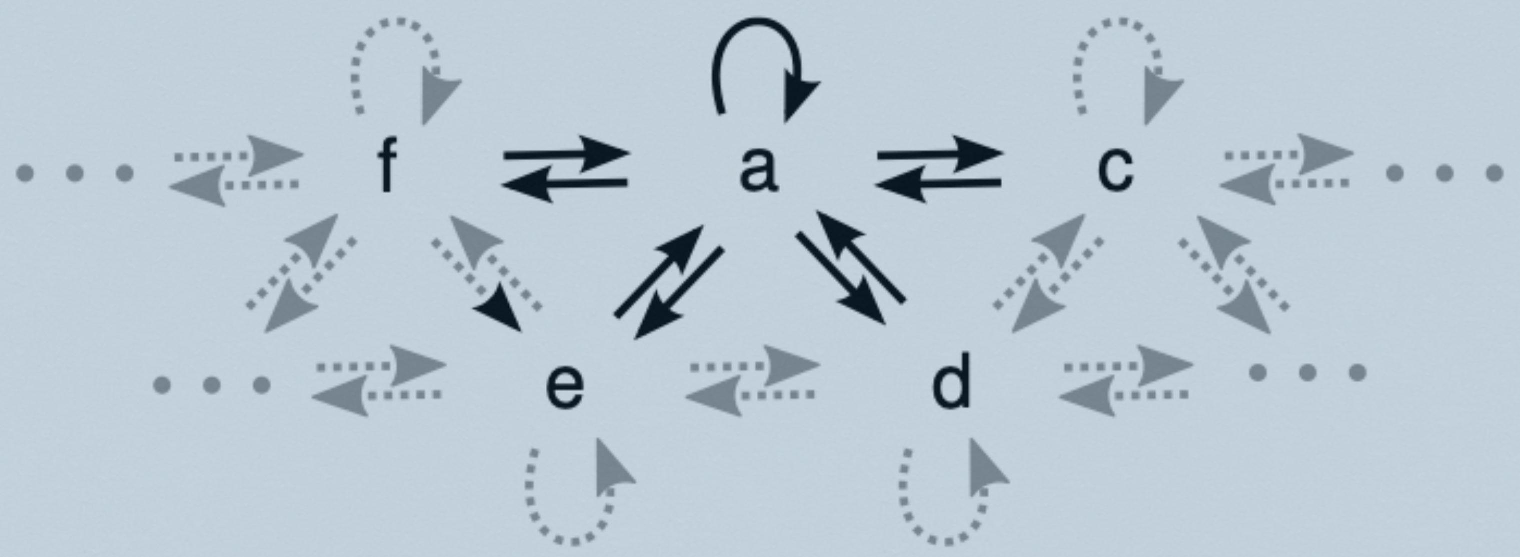
$$\mathbf{r}_i = (x_i, y_i) \to \mathbf{r}_i' = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \mathrm{ran}(-\delta, \delta), \Delta_y \leftarrow \mathrm{ran}(-\delta, \delta)\,.$$

2. Accept proposed configuration c' if no overlap is introduced (or more generally with probability $p(c \to c') = \min[1, \pi(c')/\pi(c)]$).



Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

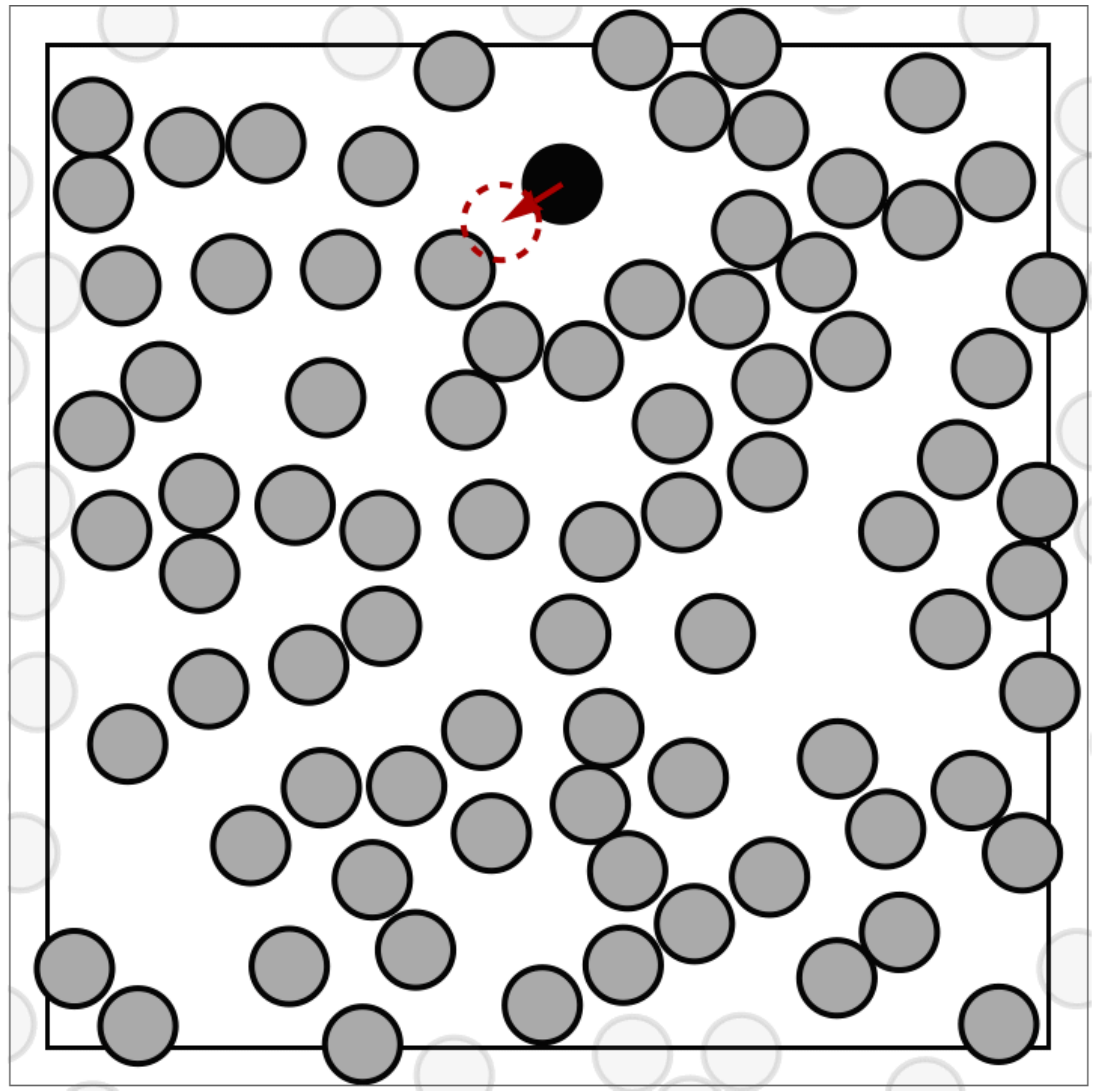
Reversible Metropolis Algorithm

1. Choose random disk i and propose random displacement in square around $\mathbf{r}_i$:

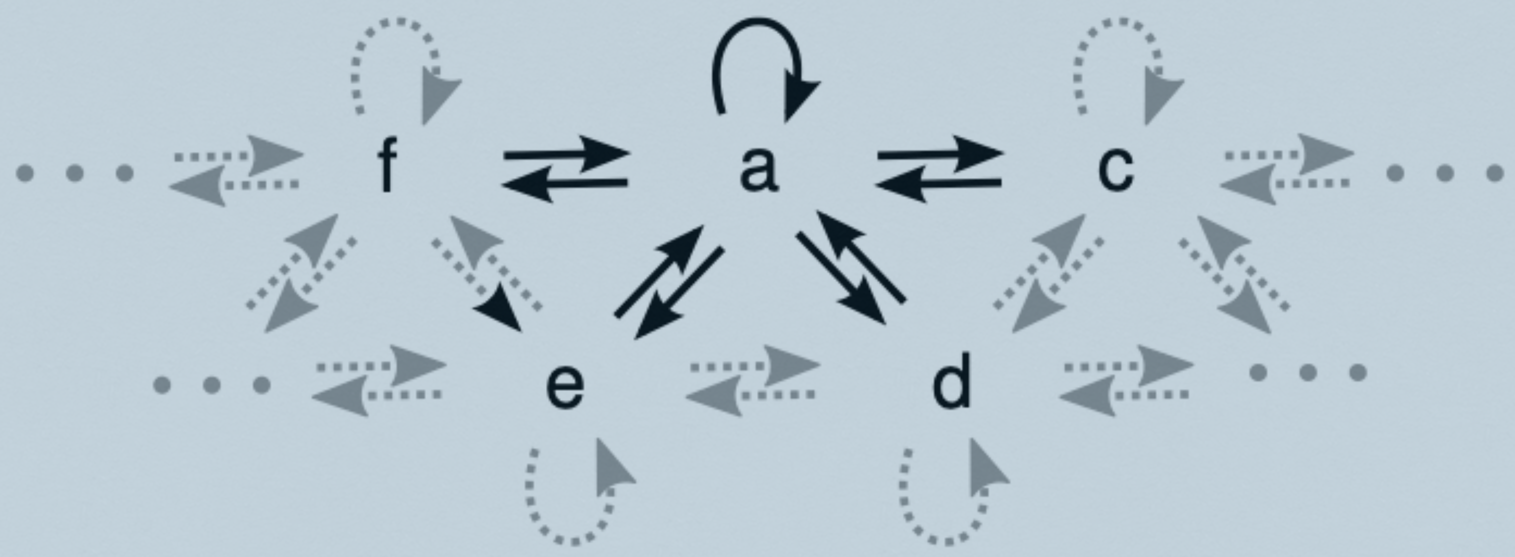
$$\mathbf{r}_i = (x_i, y_i) \to \mathbf{r}_i' = (x_i + \Delta_x, y_i + \Delta_y),$$

$$\Delta_x \leftarrow \mathrm{ran}(-\delta, \delta), \Delta_y \leftarrow \mathrm{ran}(-\delta, \delta)\,.$$

2. Accept proposed configuration c' if no overlap is introduced
   (or more generally with probability $p(c \to c') = \min[1, \pi(c')/\pi(c)]$).



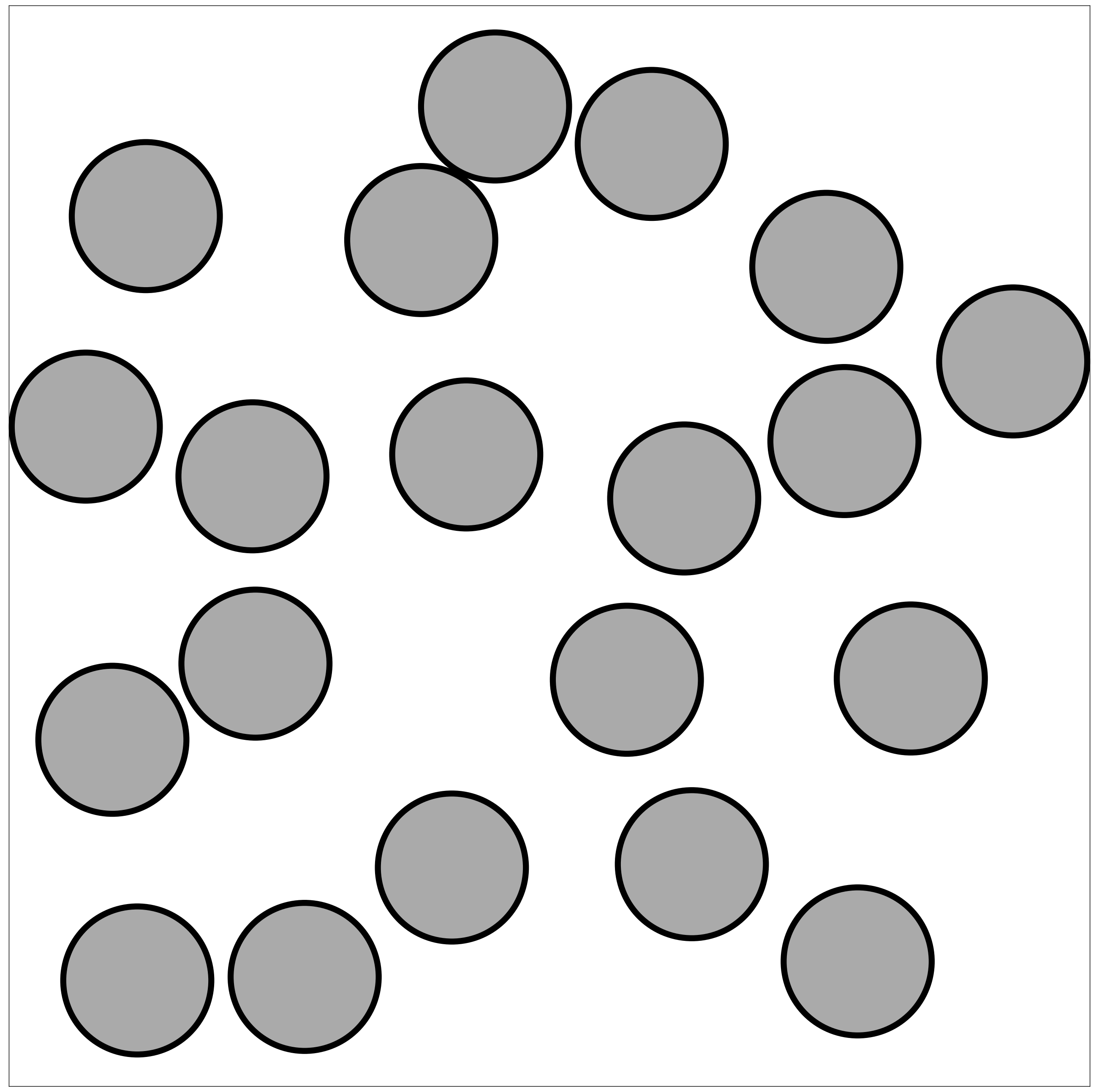
Obeys detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1, 0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.

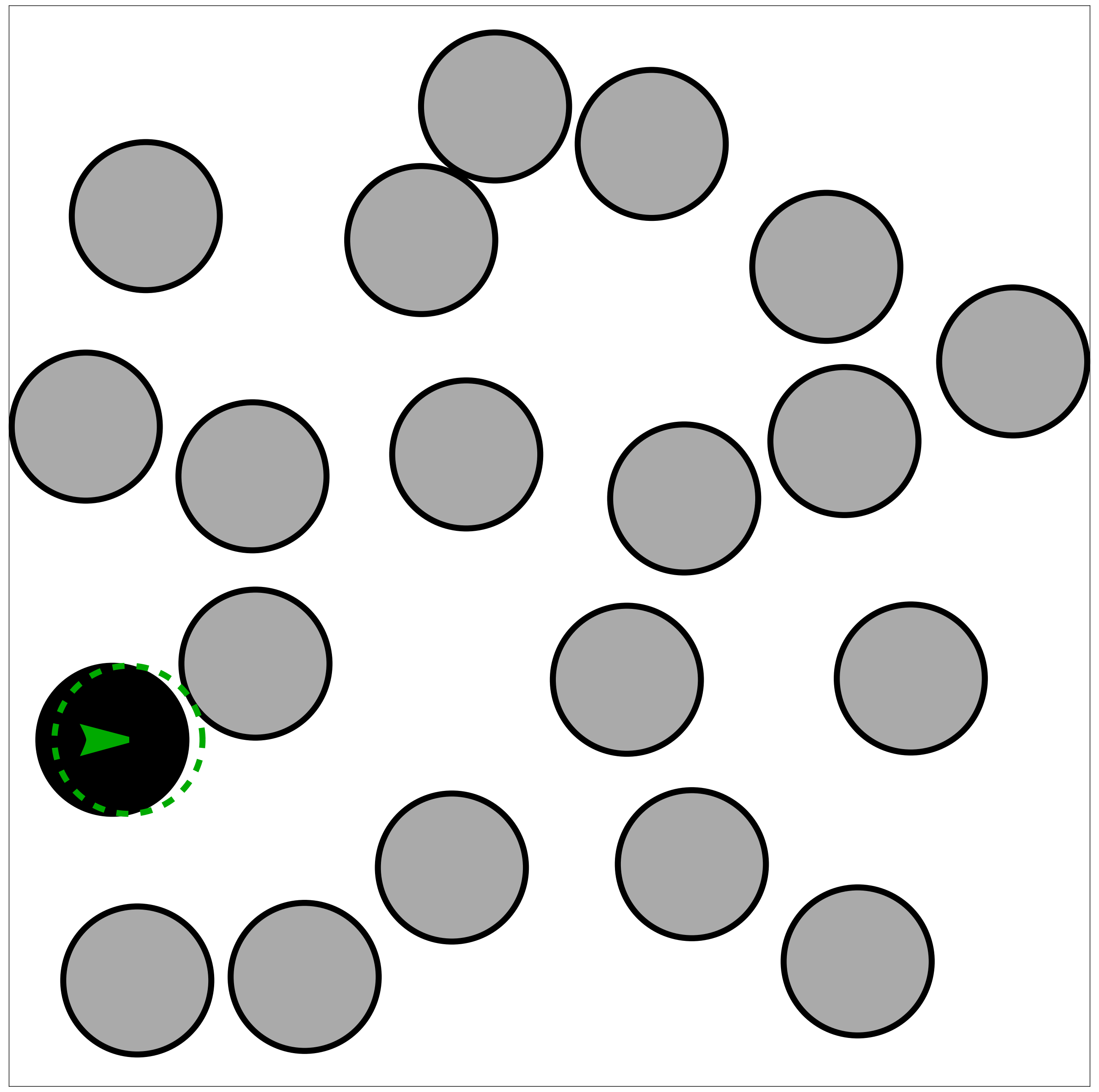


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1,0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.

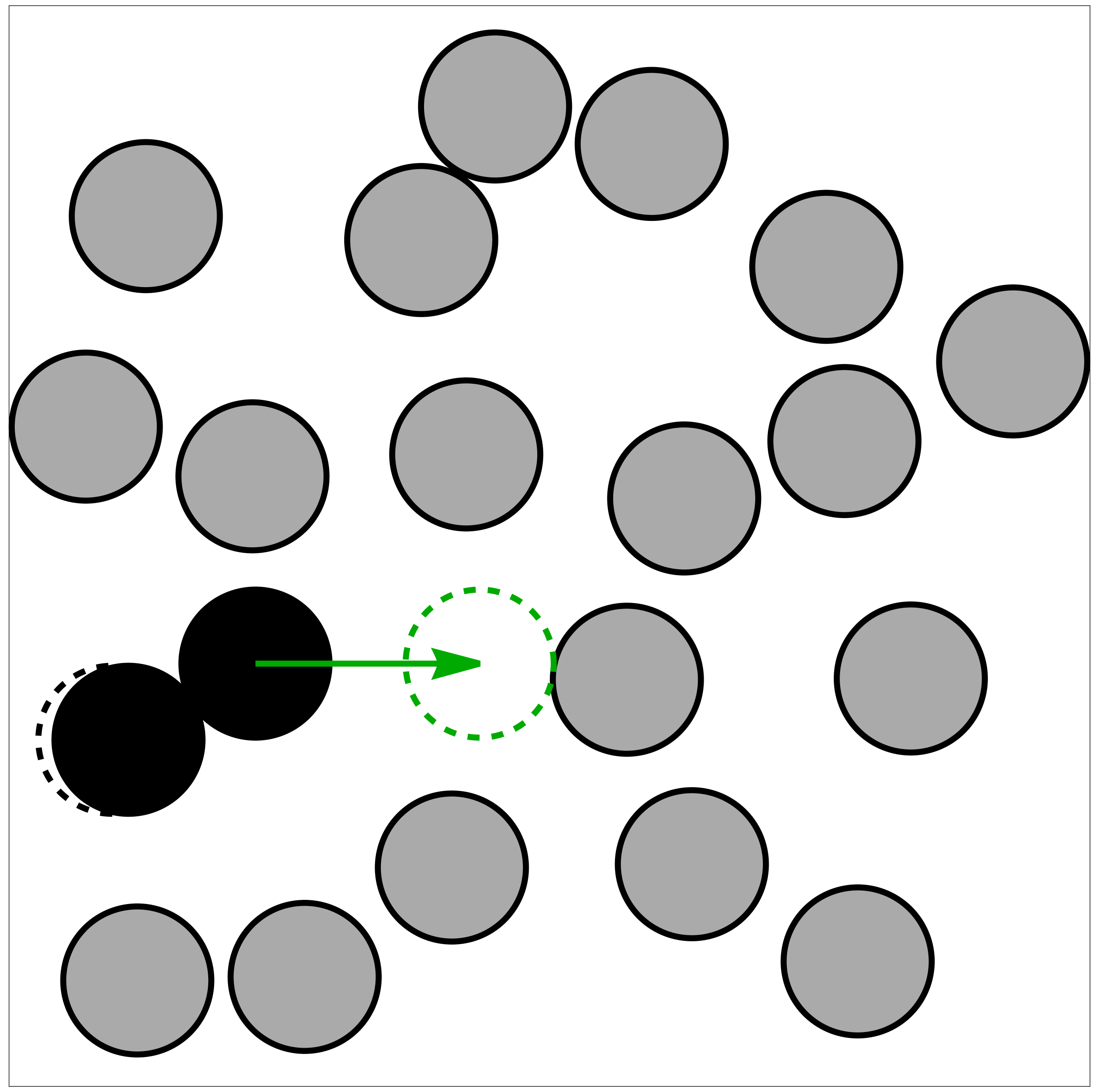


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1,0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.

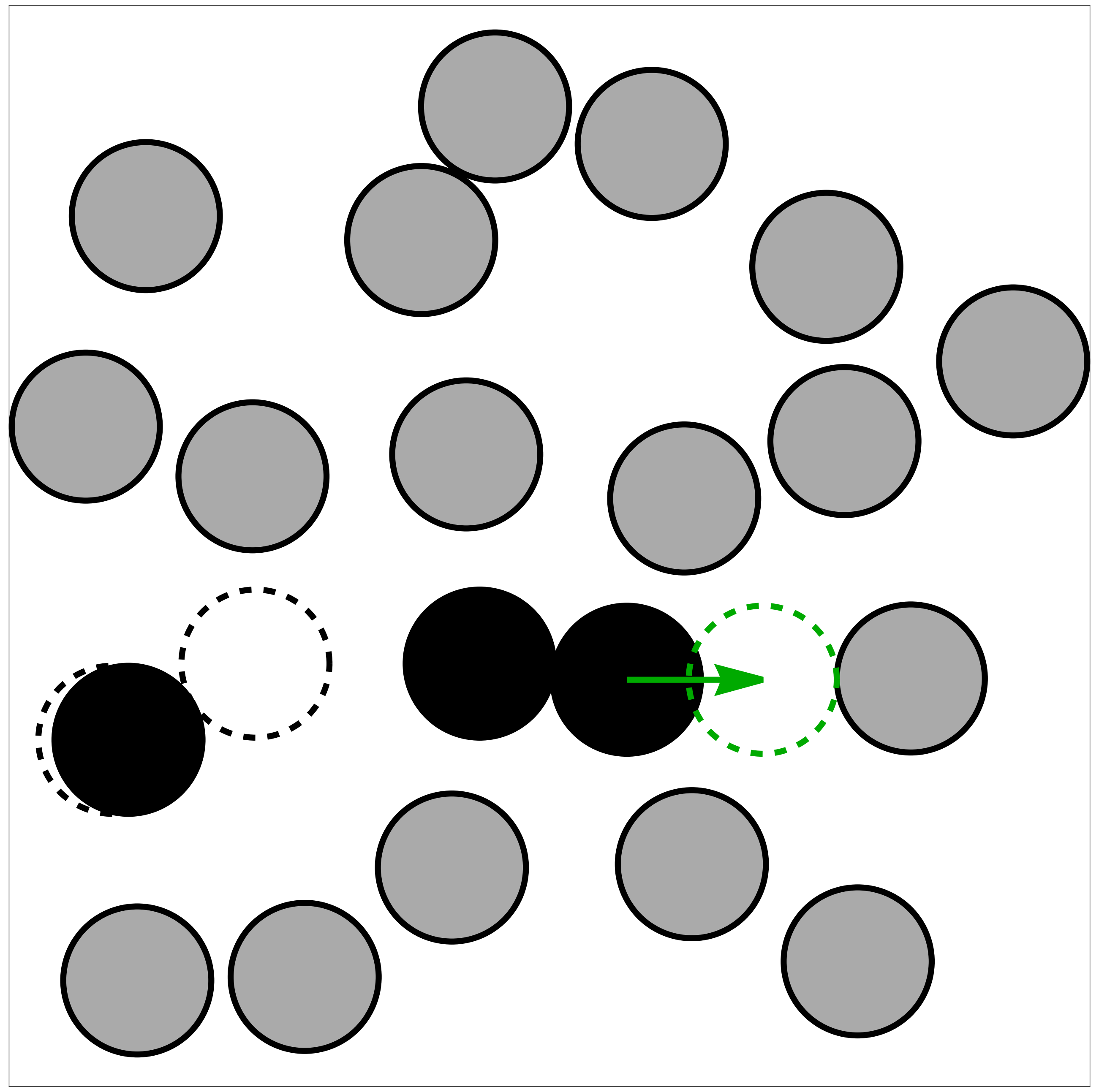


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes “active” with velocity $\mathbf{v} = (1, 0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.

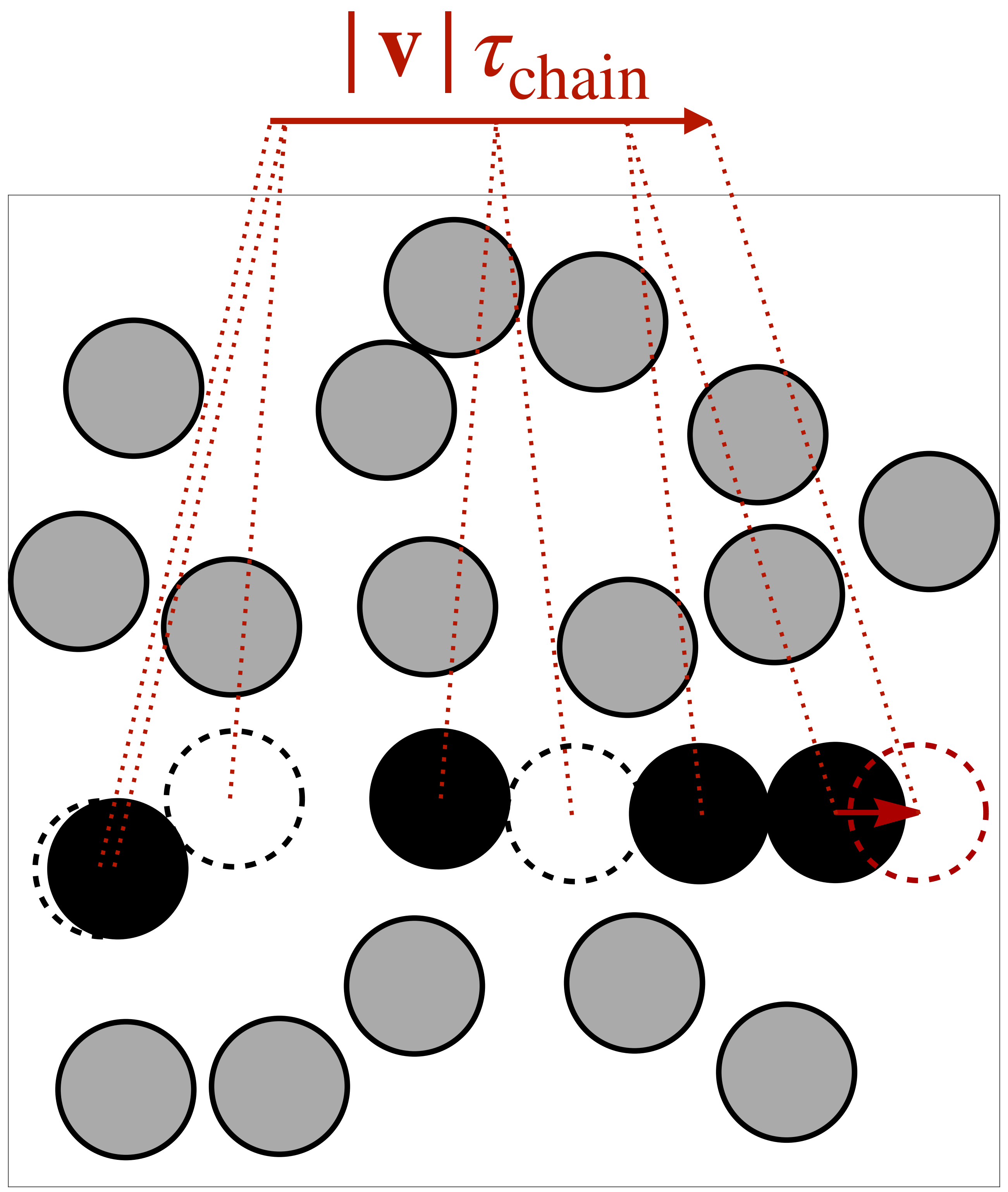


Breaks detailed balance.

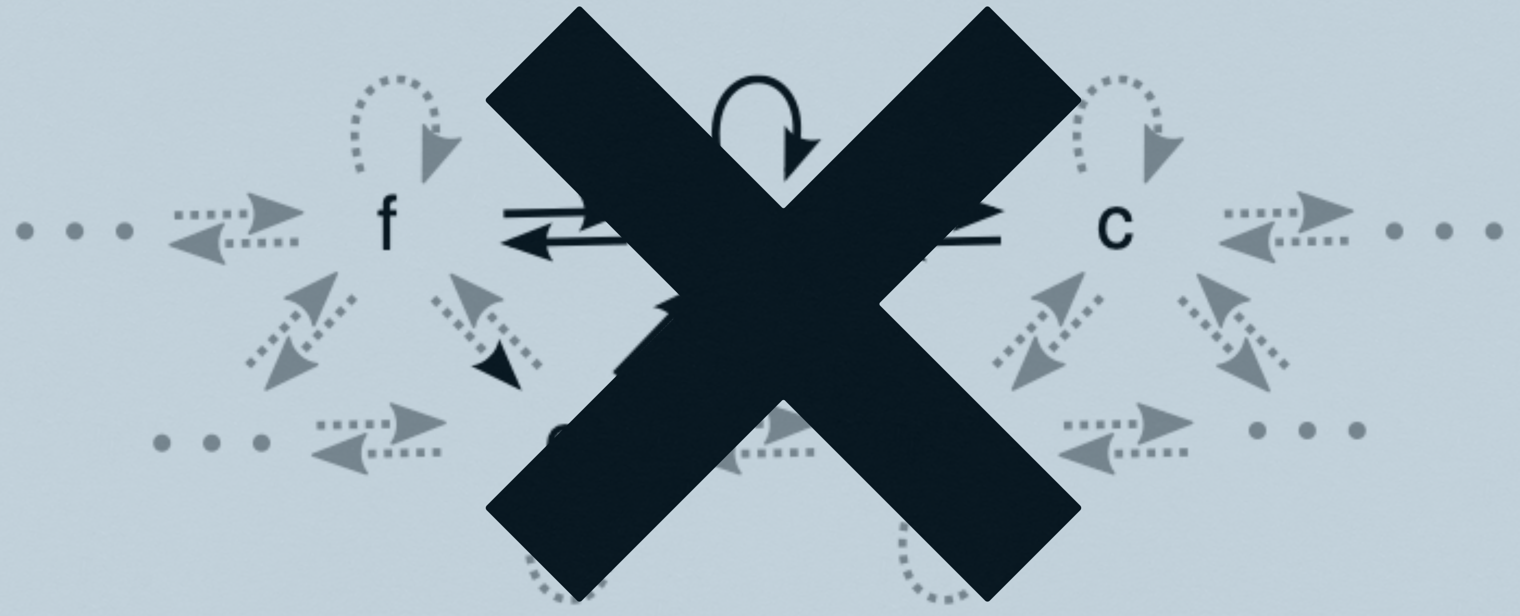
Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes “active” with velocity $\mathbf{v} = (1, 0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.



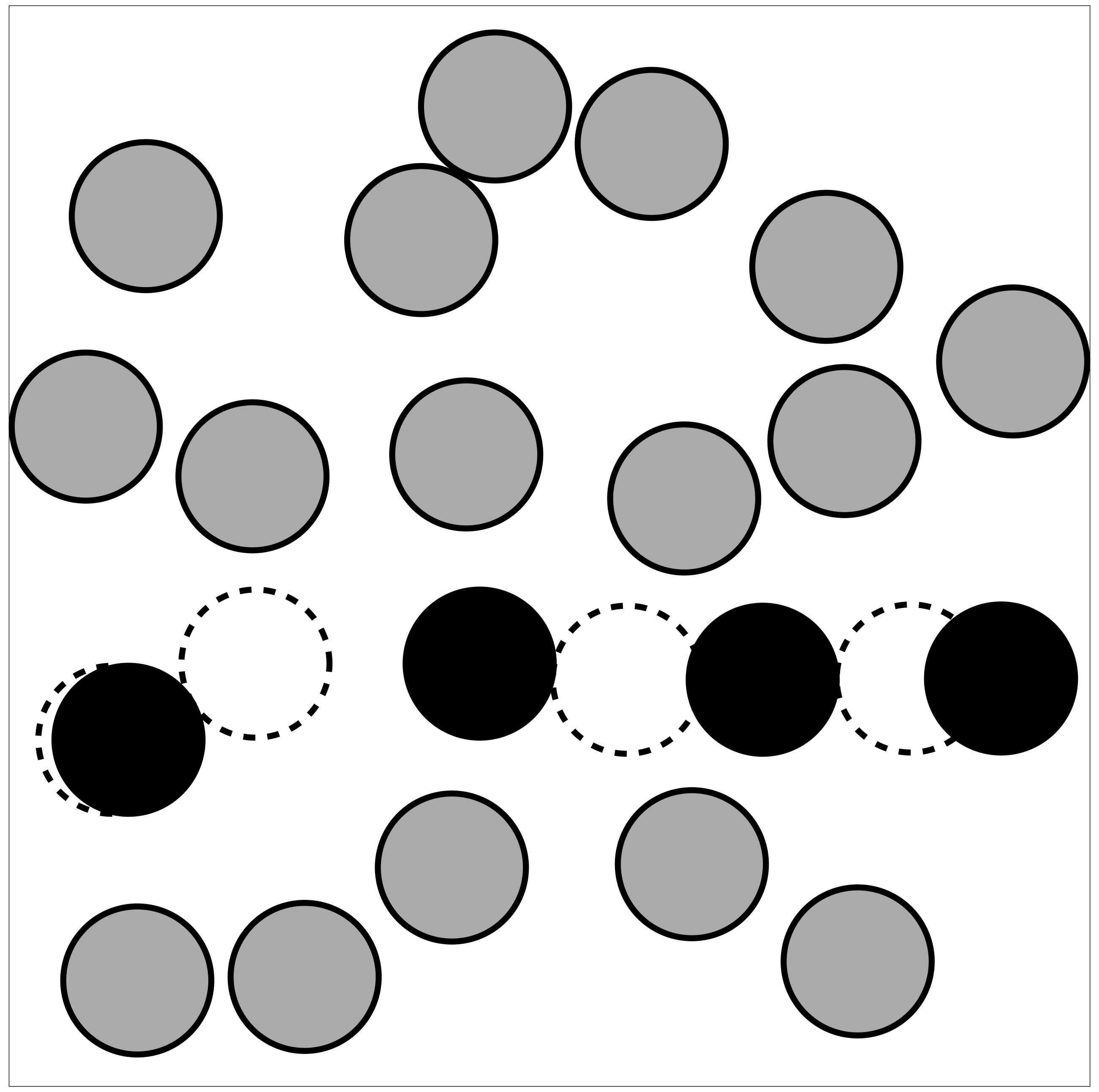
Breaks detailed balance.



Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1,0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.

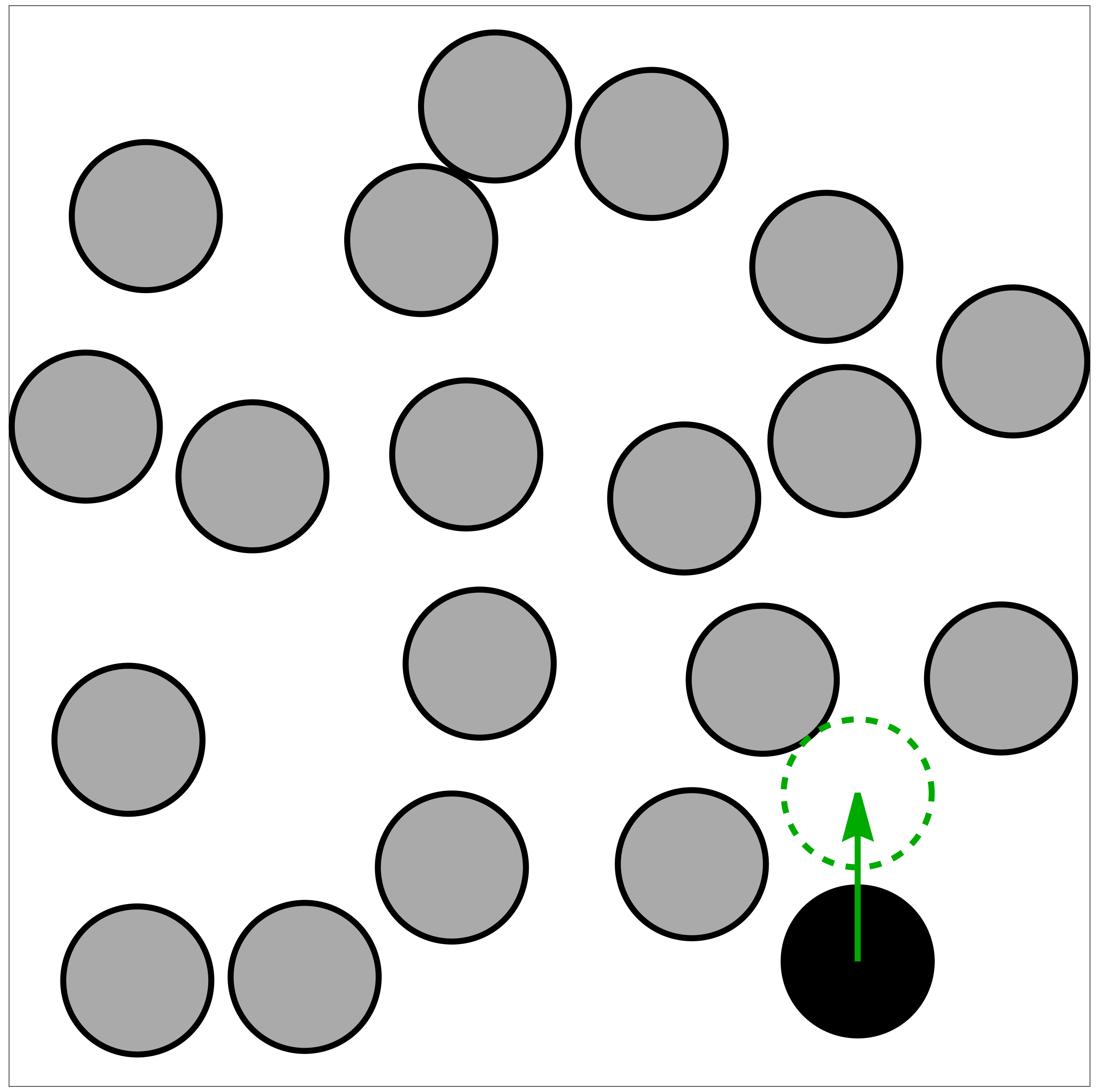


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes “active” with velocity $\mathbf{v} = (1,0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.
5. Change velocity to $\mathbf{v} = (0,1)^T$ and repeat.

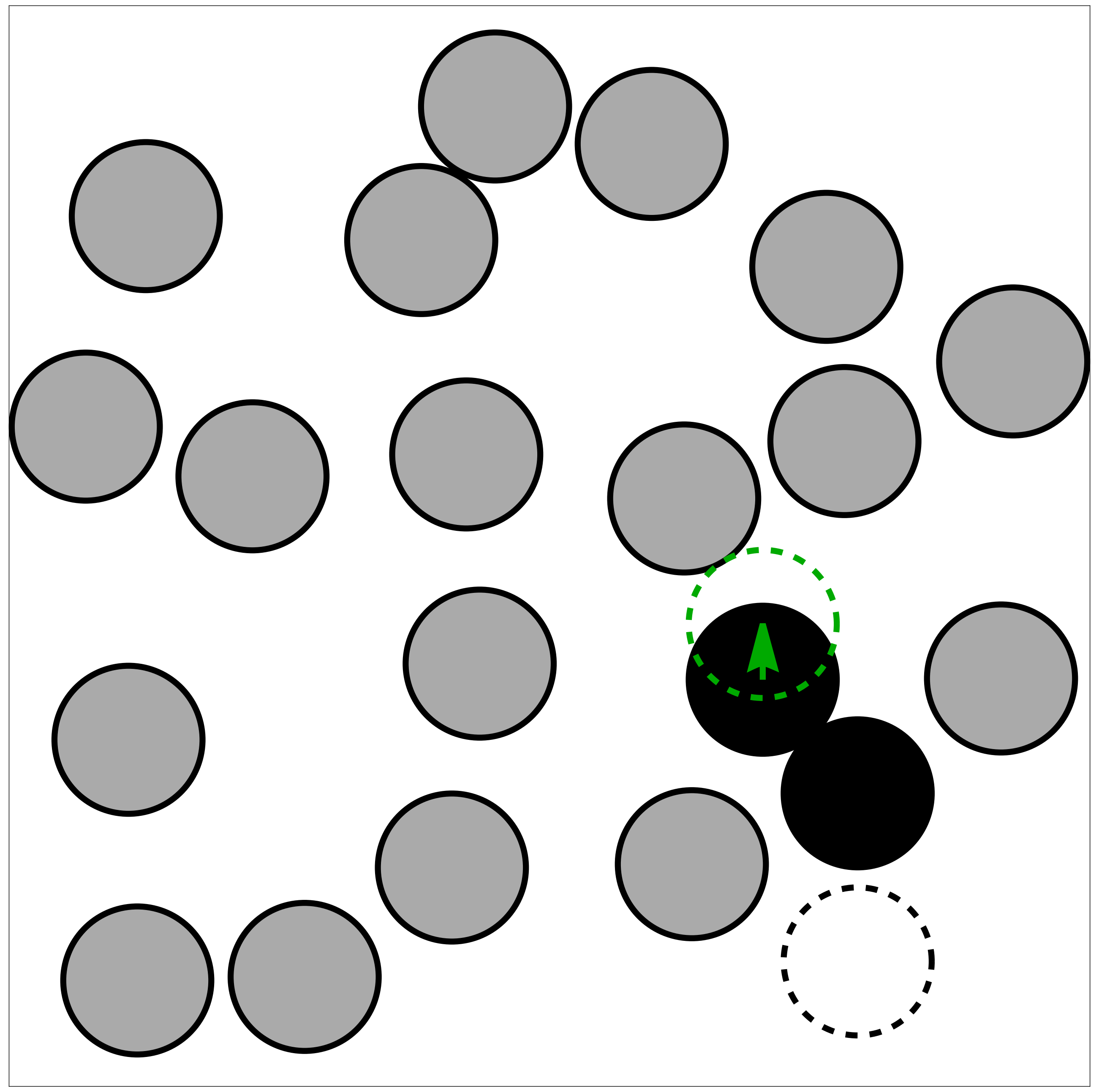


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1,0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.
5. Change velocity to $\mathbf{v} = (0,1)^T$ and repeat.

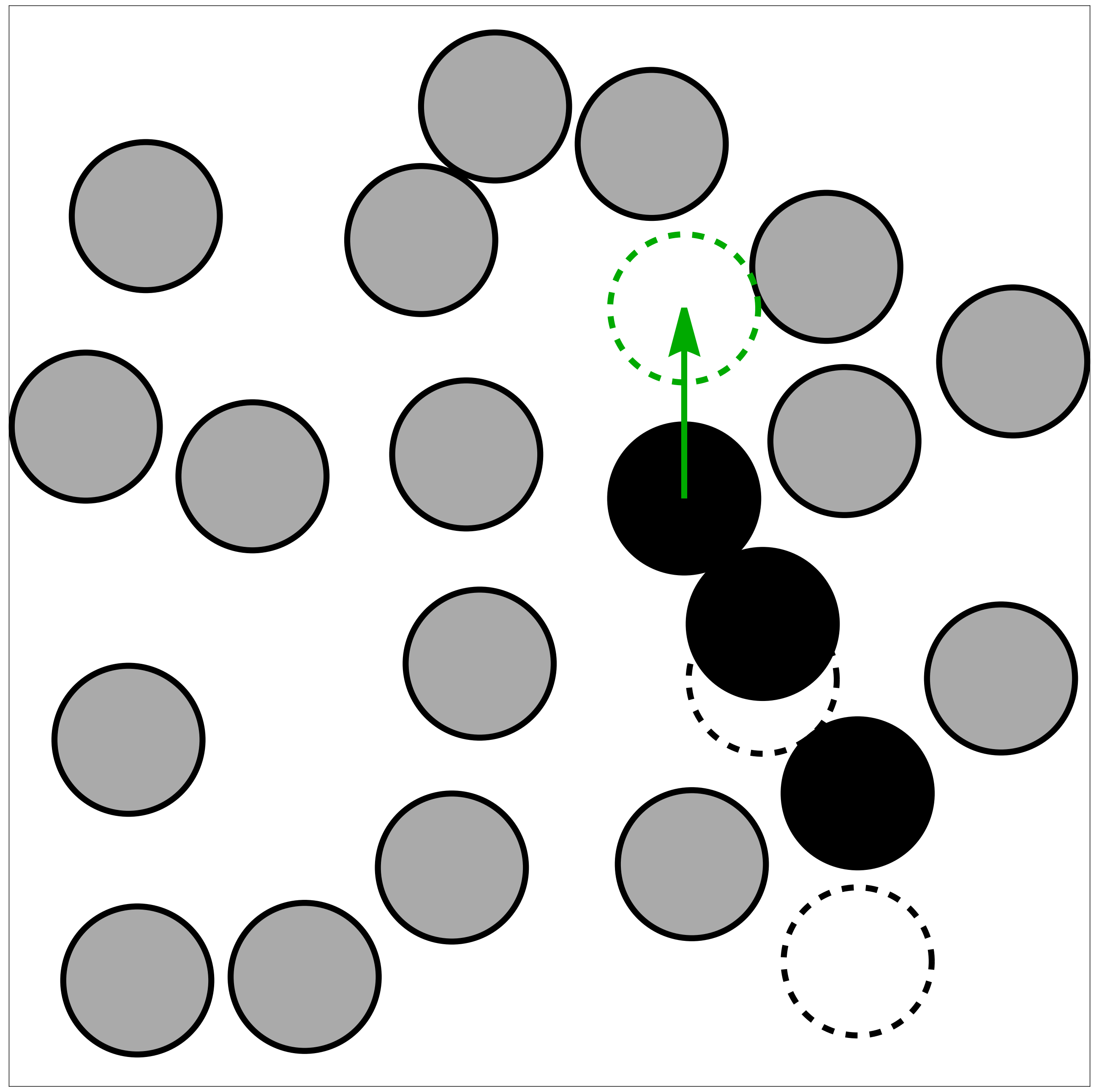


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1, 0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.
5. Change velocity to $\mathbf{v} = (0,1)^T$ and repeat.

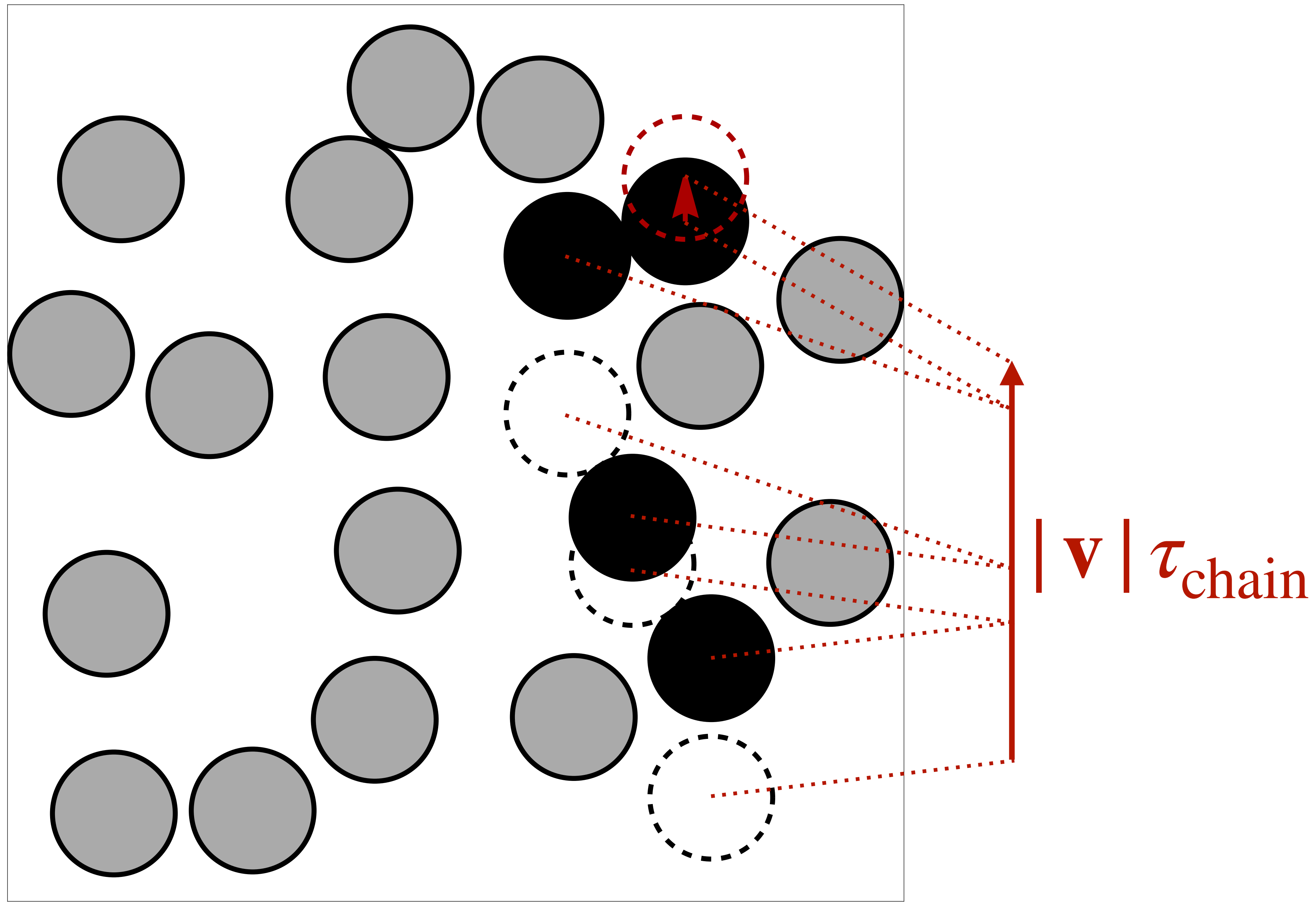


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1, 0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.
5. Change velocity to $\mathbf{v} = (0,1)^T$ and repeat.

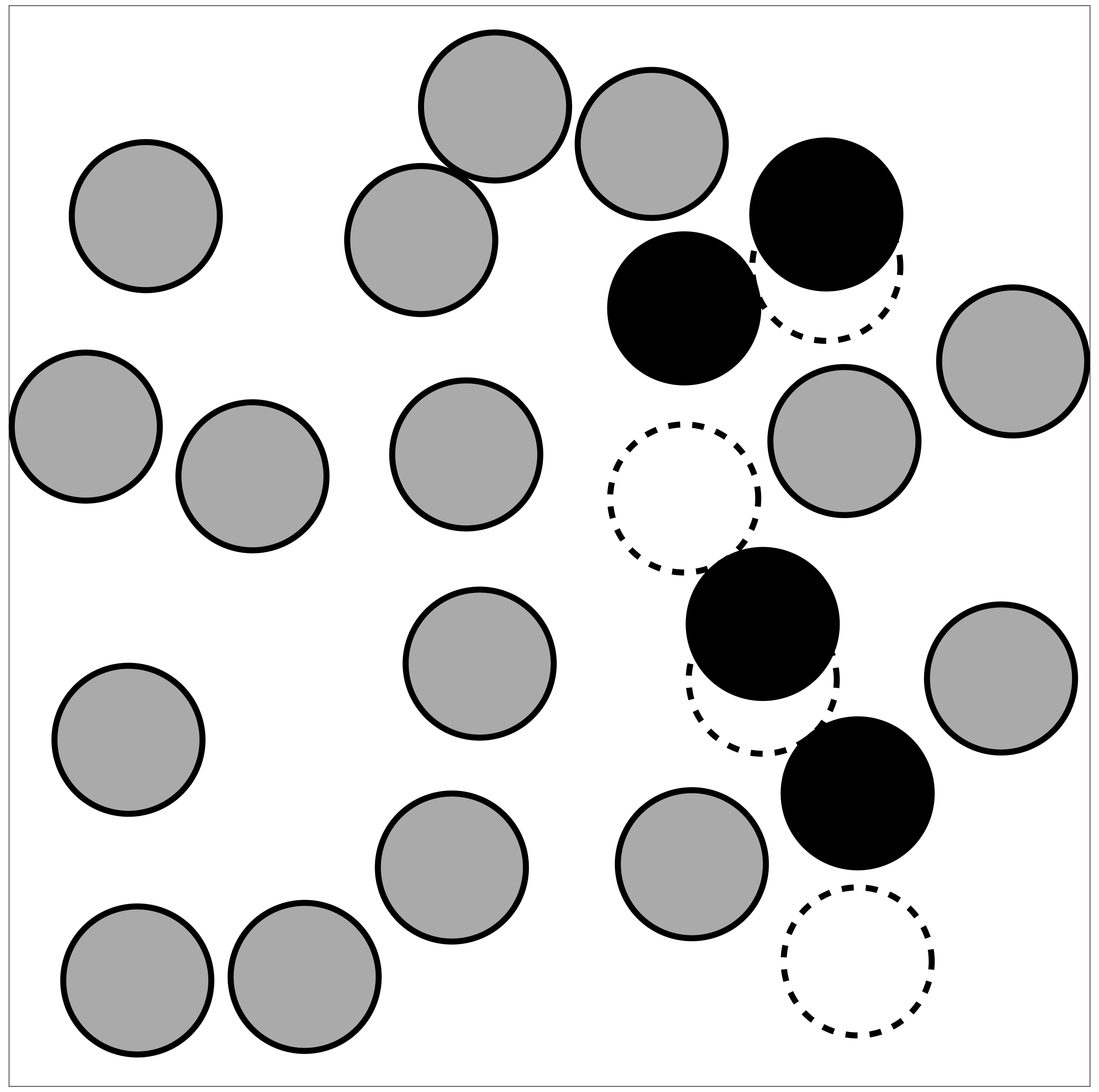


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1, 0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.
5. Change velocity to $\mathbf{v} = (0,1)^T$ and repeat.

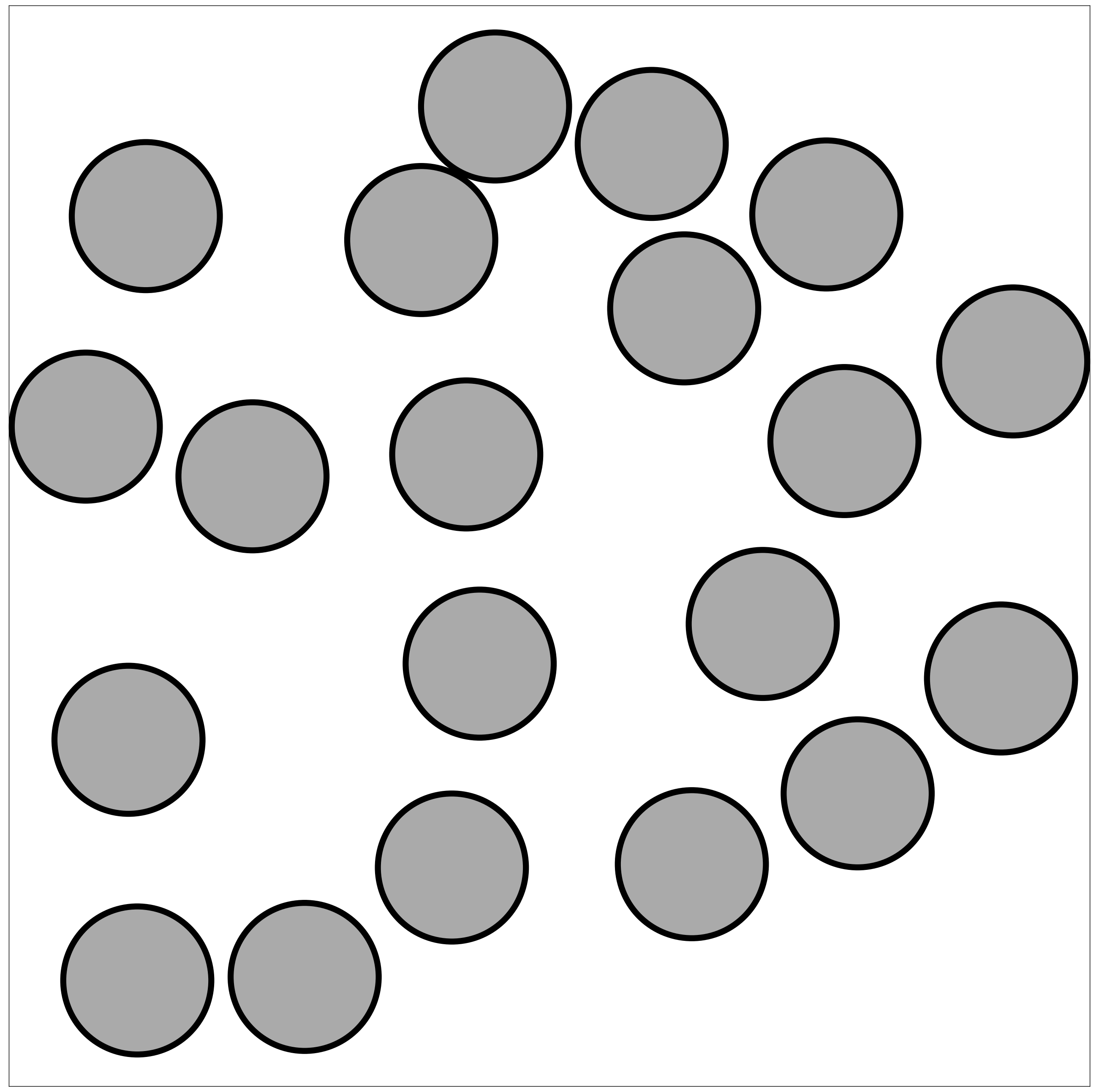


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes “active” with velocity $\mathbf{v} = (1,0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.
5. Change velocity to $\mathbf{v} = (0,1)^T$ and repeat.

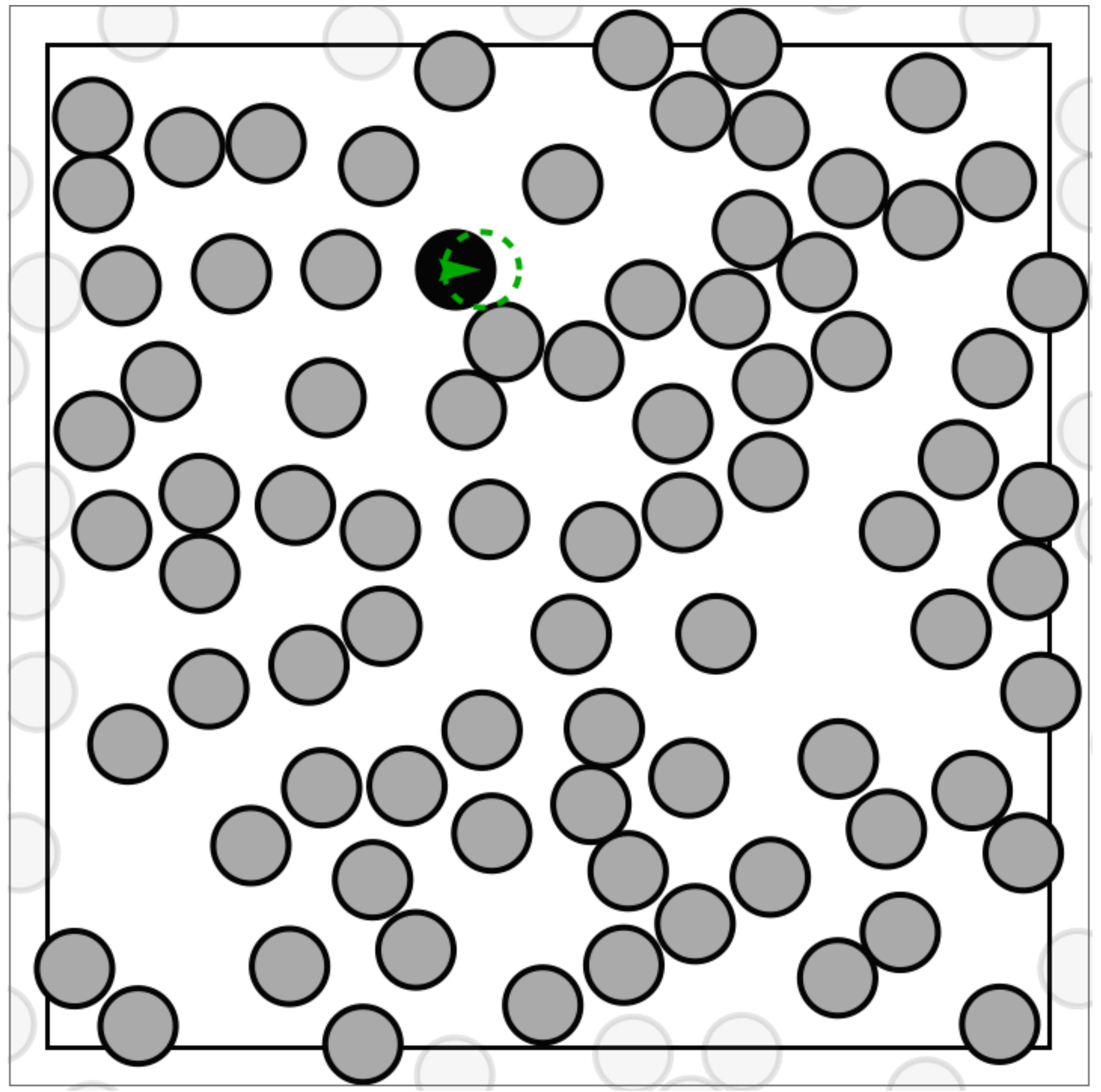


Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

Straight Event-Chain Monte Carlo (ECMC)

1. Choose random disk i which becomes "active" with velocity $\mathbf{v} = (1, 0)^T$.
2. Move i with $\mathbf{v}$ until collision with another disk t .
3. Transfer velocity $\mathbf{v}$ from disk i to disk t.
4. Repeat steps 2. and 3. for chain time τ_{chain}.
5. Change velocity to $\mathbf{v} = (0,1)^T$ and repeat.



Breaks detailed balance.

Michel et al., J. Chem. Phys. **140**, 054116 (2014)

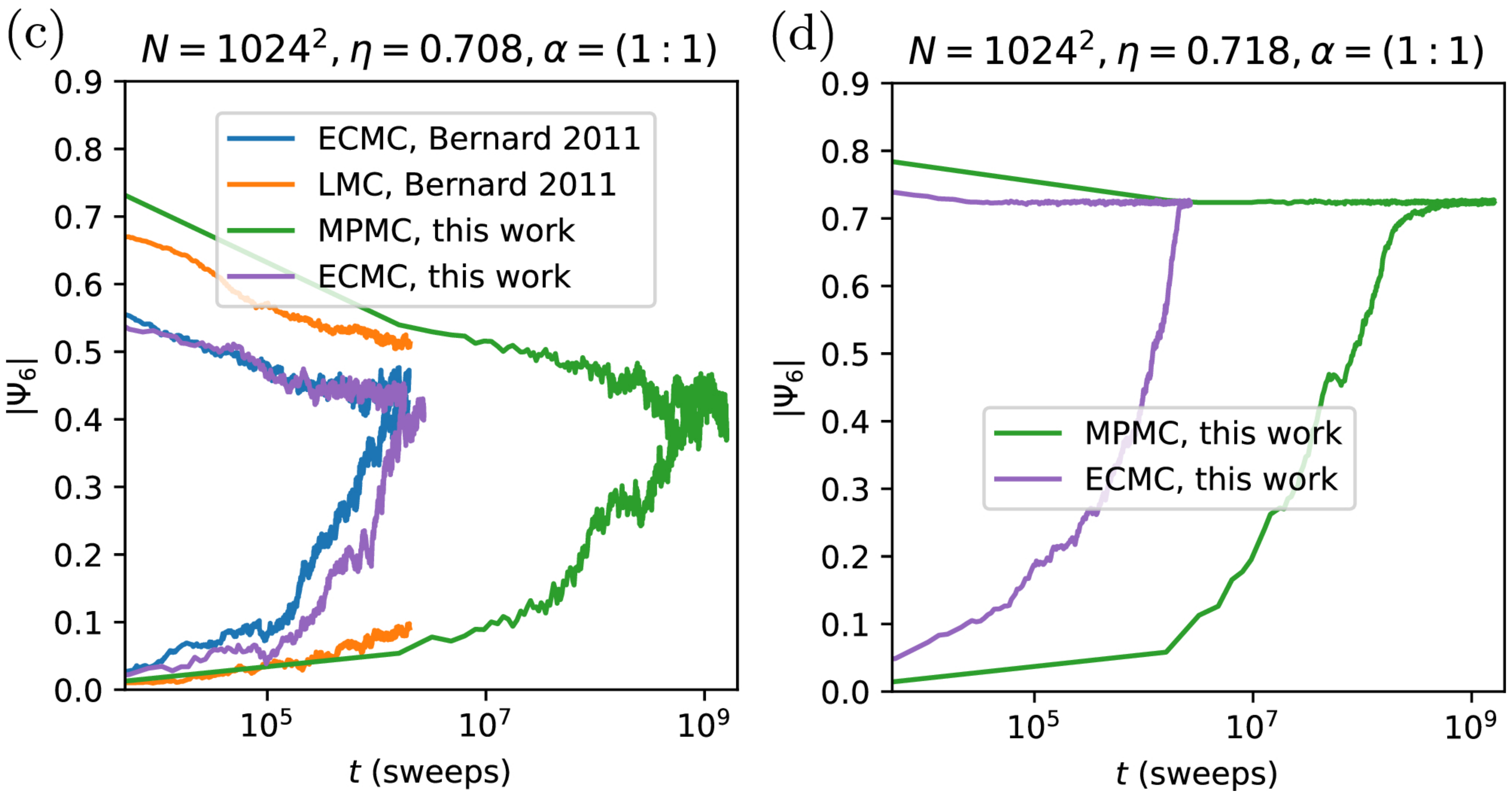
Phase Transition in the Hard-Disk Model

- For hard-disk model at high densities: Non-reversible straight ECMC about three orders of magnitude faster than reversible Metropolis algorithm (LMC).

Global orientational order parameter $|\Psi_6|$.

Fluid-hexatic coexistence.

Hexatic phase.

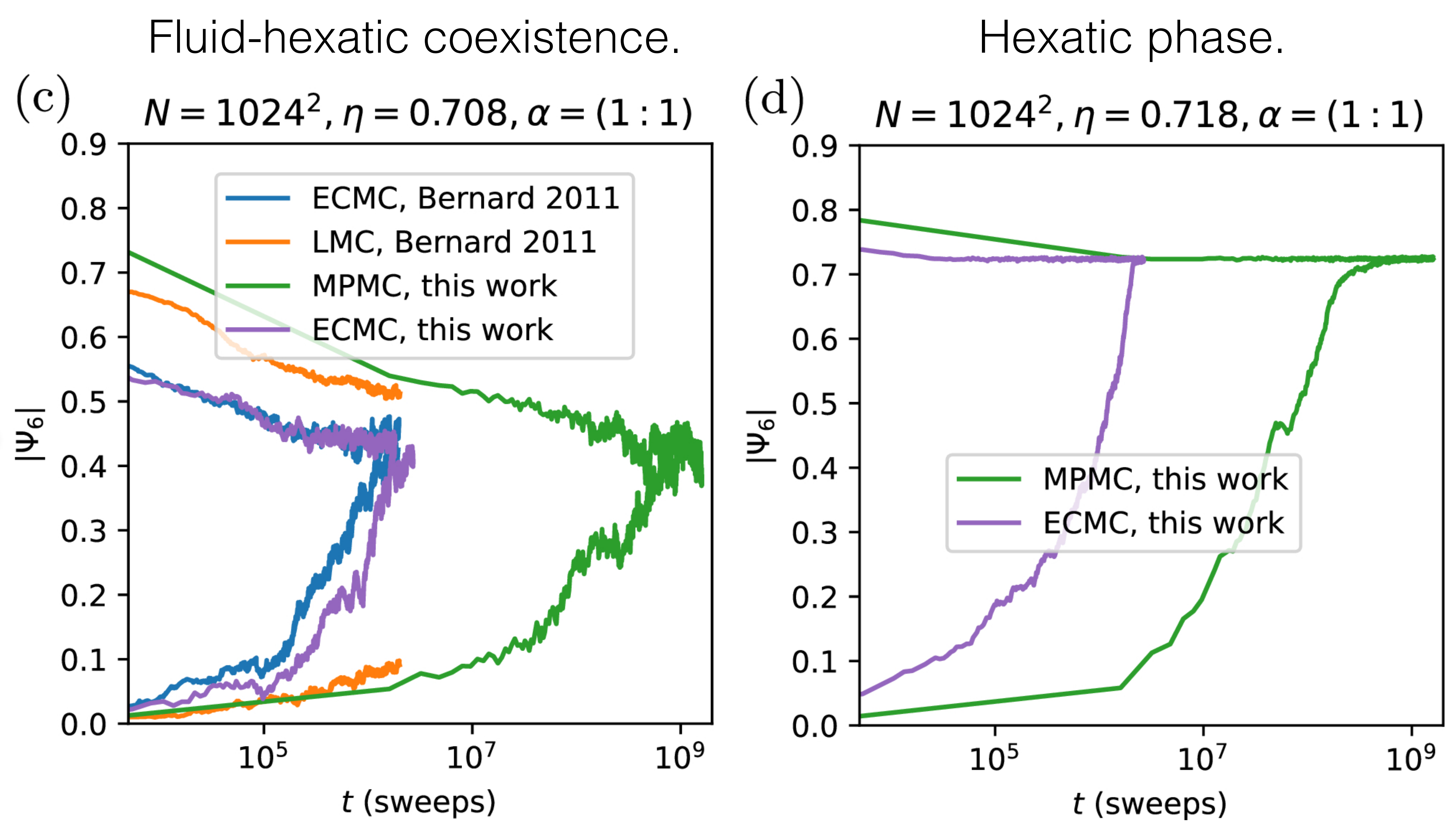


Li, Nishikawa, **PH**, Carillo, Maggs, and Krauth, arXiv:2207.07715 (2022, manuscript submitted for publication)

Phase Transition in the Hard-Disk Model

- For hard-disk model at high densities: Non-reversible straight ECMC about three orders of magnitude faster than reversible Metropolis algorithm (LMC).

Global orientational order parameter $|\Psi_6|$.



Li, Nishikawa, **PH**, Carillo, Maggs, and Krauth, arXiv:2207.07715 (2022, manuscript submitted for publication)

- Required (single-core) CPU time for coalescence:

ECMC: $\sim$ 1 week. $\Leftrightarrow$ LMC: $\sim$ 10 years.

Phase Transition in the Hard-Disk Model

PRL **107,** 155704 (2011) PHYSICAL REVIEW LETTERS week ending 7 OCTOBER 2011

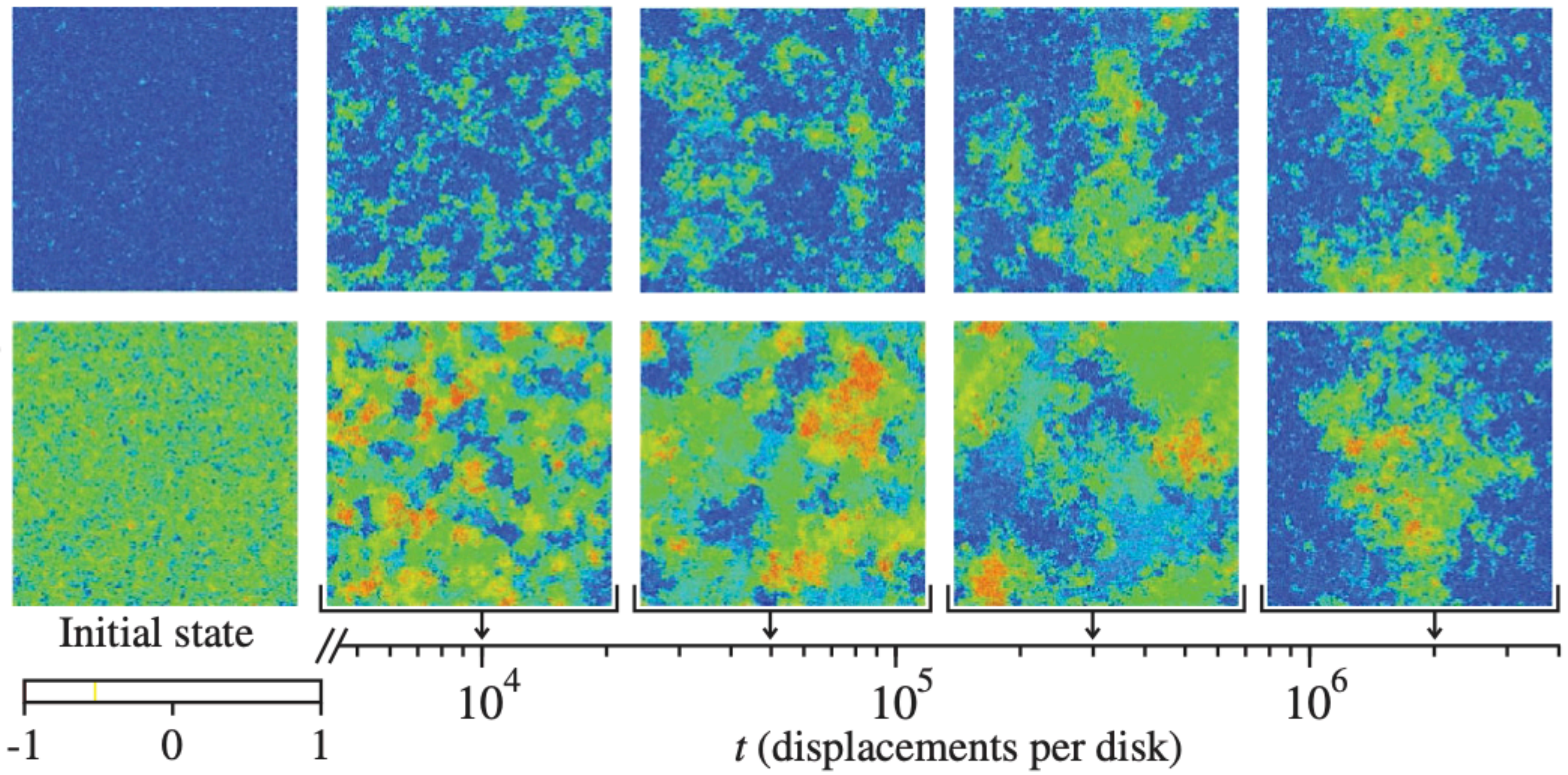
Two-Step Melting in Two Dimensions: First-Order Liquid-Hexatic Transition

Etienne P. Bernard* and Werner Krauth†

Laboratoire de Physique Statistique Ecole Normale Supérieure, UPMC, CNRS 24 rue Lhomond, 75231 Paris Cedex 05, France

(Received 6 July 2011; published 7 October 2011)

Melting in two spatial dimensions, as realized in thin films or at interfaces, represents one of the most fascinating phase transitions in nature, but it remains poorly understood. Even for the fundamental hard-disk model, the melting mechanism has not been agreed upon after 50 years of studies. A recent Monte Carlo algorithm allows us to thermalize systems large enough to access the thermodynamic regime. We show that melting in hard disks proceeds in two steps with a liquid phase, a hexatic phase, and a solid. The hexatic-solid transition is continuous while, surprisingly, the liquid-hexatic transition is of first order. This melting scenario solves one of the fundamental statistical-physics models, which is at the root of a large body of theoretical, computational, and experimental research.



Molecular Simulations

Molecular Dynamics (MD)	MCMC
• Physical time evolution based on Newton's equations of motion. • Discretizes time (and possibly space).	• Unphysical time evolution only restricted by global-balance condition. • Directly samples Boltzmann distribution.

Molecular Simulations

Molecular Dynamics (MD)	MCMC
• Physical time evolution based on Newton's equations of motion. • Discretizes time (and possibly space).	• Unphysical time evolution only restricted by global-balance condition. • Directly samples Boltzmann distribution.

- MD is predominantly used for long-range-interacting N-body molecular systems.

MD	**Reversible** MCMC
• Superior computational complexity per MD time step: $\mathcal{O}(N \log N)$. • Superior (Newtonian) exploration of configuration space.	• Inferior computational complexity per MCMC sweep: $\mathcal{O}(N^{3/2})$. • Inferior (diffusive) exploration of configuration space.

Molecular Simulations

Molecular Dynamics (MD)	MCMC
• Physical time evolution based on Newton's equations of motion. • Discretizes time (and possibly space).	• Unphysical time evolution only restricted by global-balance condition. • Directly samples Boltzmann distribution.

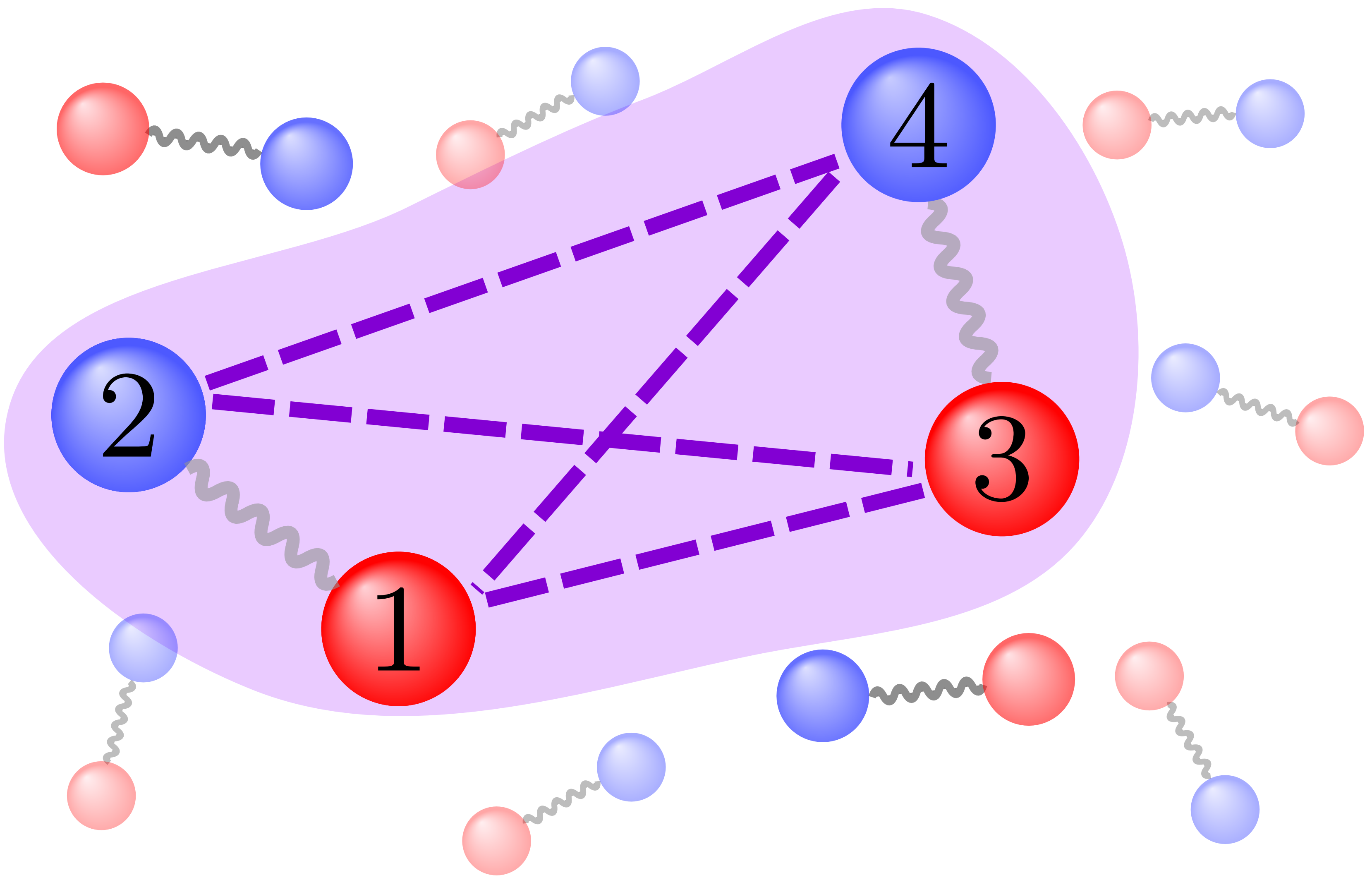
- MD is predominantly used for long-range-interacting N-body molecular systems.

MD	**Reversible** MCMC
• Superior computational complexity per MD time step: $\mathcal{O}(N \log N)$. • Superior (Newtonian) exploration of configuration space.	• Inferior computational complexity per MCMC sweep: $\mathcal{O}(N^{3/2})$. • Inferior (diffusive) exploration of configuration space.

Both disadvantages are overcome by non-reversible ECMC.

Generalization of ECMC

- ECMC constructs a **non-reversible rejection-free continuous-time Markov chain**.
- Conceived for systems described by continuous variables.
  → Here: N point-like atoms with positions $\{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$, $\mathbf{r}_i \in \mathbb{R}^d$.
- Exploits translational symmetry of interaction potentials in molecular systems.



Faulkner et al., J. Chem. Phys. **149**, 064113 (2018)

Generalization of ECMC

- ECMC constructs a **non-reversible rejection-free continuous-time Markov chain**.
- Conceived for systems described by continuous variables.
  $\rightarrow$ Here: N point-like atoms with positions $\{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$, $\mathbf{r}_i \in \mathbb{R}^d$.
- Exploits translational symmetry of interaction potentials in molecular systems.

- ECMC relies on three concepts:

1. **Factorized Metropolis filter** accepts/rejects proposed configurations.
2. **Lifting framework** proposes new configurations and solves rejections.
3. **Event-driven implementation**.

Factorized Metropolis Filter

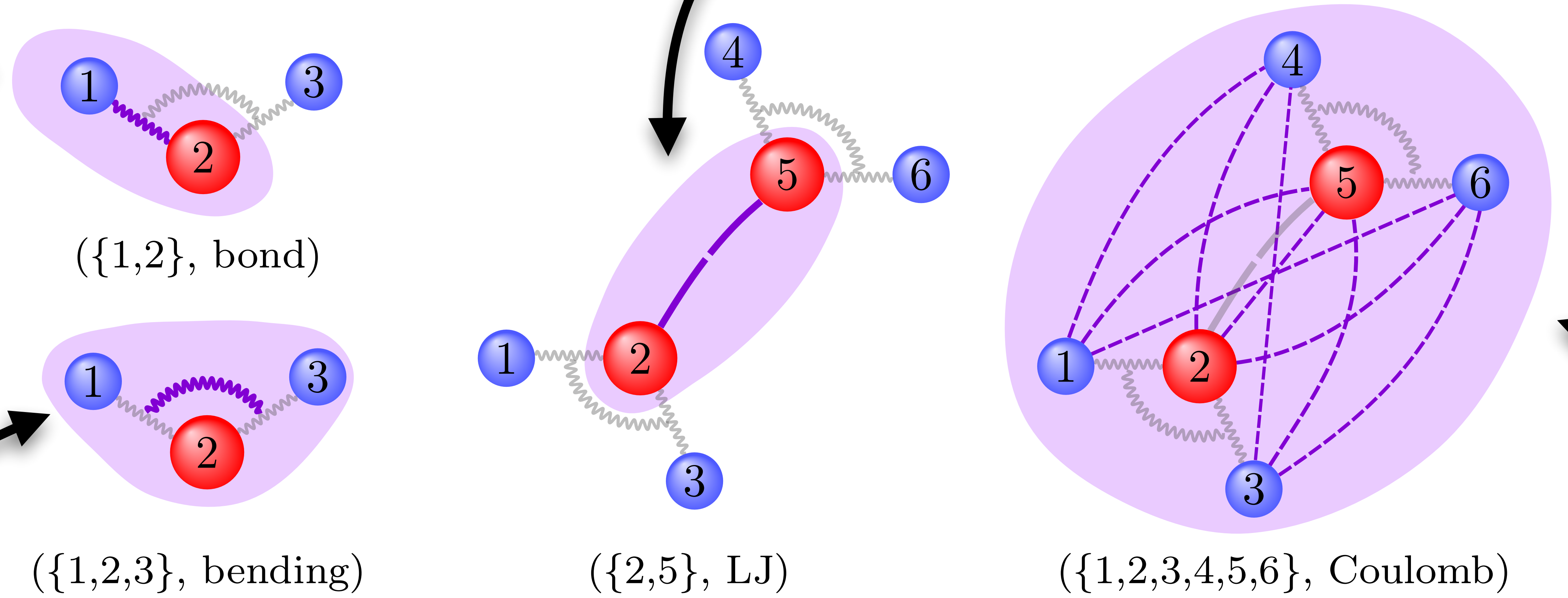
- Decompose total potential U into sum over factor potentials U_M of factors M:

$$U(c = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}) = \sum_M U_M(c_M = \{\mathbf{r}_i : i \in M\}) \longrightarrow \pi_B(c) = \frac{1}{Z} \prod_M \mathrm{e}^{-\beta U_M(c_M)}$$

- SPC/Fw water model:

$$U_{(\{1,2\},\,\mathrm{bond})}(\mathbf{r}_{12}) = \frac{1}{2} k_b \left(|\mathbf{r}_{12}| - r_0 \right)^2$$

$$U_{(\{2,5\},\,\mathrm{LJ})}(\mathbf{r}_{25}) = k_{\mathrm{LJ}} \left[\left(\frac{\sigma}{|\mathbf{r}_{25}|} \right)^{12} - \left(\frac{\sigma}{|\mathbf{r}_{25}|} \right)^{6} \right]$$



$$U_{(\{1,2,3\},\,\mathrm{bending})}(\phi_{\{1,2,3\}}) = \frac{1}{2} k_a \left(\phi_{\{1,2,3\}} - \phi_0 \right)^2$$

$$U_{(\{1,2,3,4,5,6\},\,\mathrm{Coulomb})}(\mathbf{r}_1, \dots, \mathbf{r}_6) = \sum_{i=1}^{3} \sum_{j=4}^{6} U_C(\mathbf{r}_{ij})$$

Faulkner et al., J. Chem. Phys. **149**, 064113 (2018)

Factorized Metropolis Filter

- Decompose total potential U into sum over factor potentials U_M of factors M:

$$U(c = \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}) = \sum_M U_M(c_M = \{\mathbf{r}_i : i \in M\}) \longrightarrow \pi_B(c) = \frac{1}{Z} \prod_M \mathrm{e}^{-\beta U_M(c_M)}$$

- Replace original Metropolis filter that accepts a change of configuration $c \to c'$:

$$\underbrace{A^{\mathrm{Met}}(c \to c') = \min\left[1, \prod_M \mathrm{e}^{-\beta \Delta U_M(c_M \to c'_M)}\right]}_{\text{Original Metropolis filter.}} \longrightarrow \underbrace{A^{\mathrm{Fact}}(c \to c') = \prod_M \min\left[1, \mathrm{e}^{-\beta \Delta U_M(c_M \to c'_M)}\right]}_{\text{Factorized Metropolis filter.}}$$

- Formulates **consensus principle,** new configuration is accepted from all factors **independently**:

$$\boxed{X^{\mathrm{Fact}}(c \to c')} = \bigwedge_M X_M(c_M \to c'_M) \qquad \boxed{X_M(c_M \to c'_M)} = \begin{cases} \text{True} & \text{if } \mathrm{ran}_M(0,1) < \mathrm{e}^{-\beta \Delta U_M(c_M \to c'_M)} \\ \text{False} & \text{otherwise} \end{cases}$$

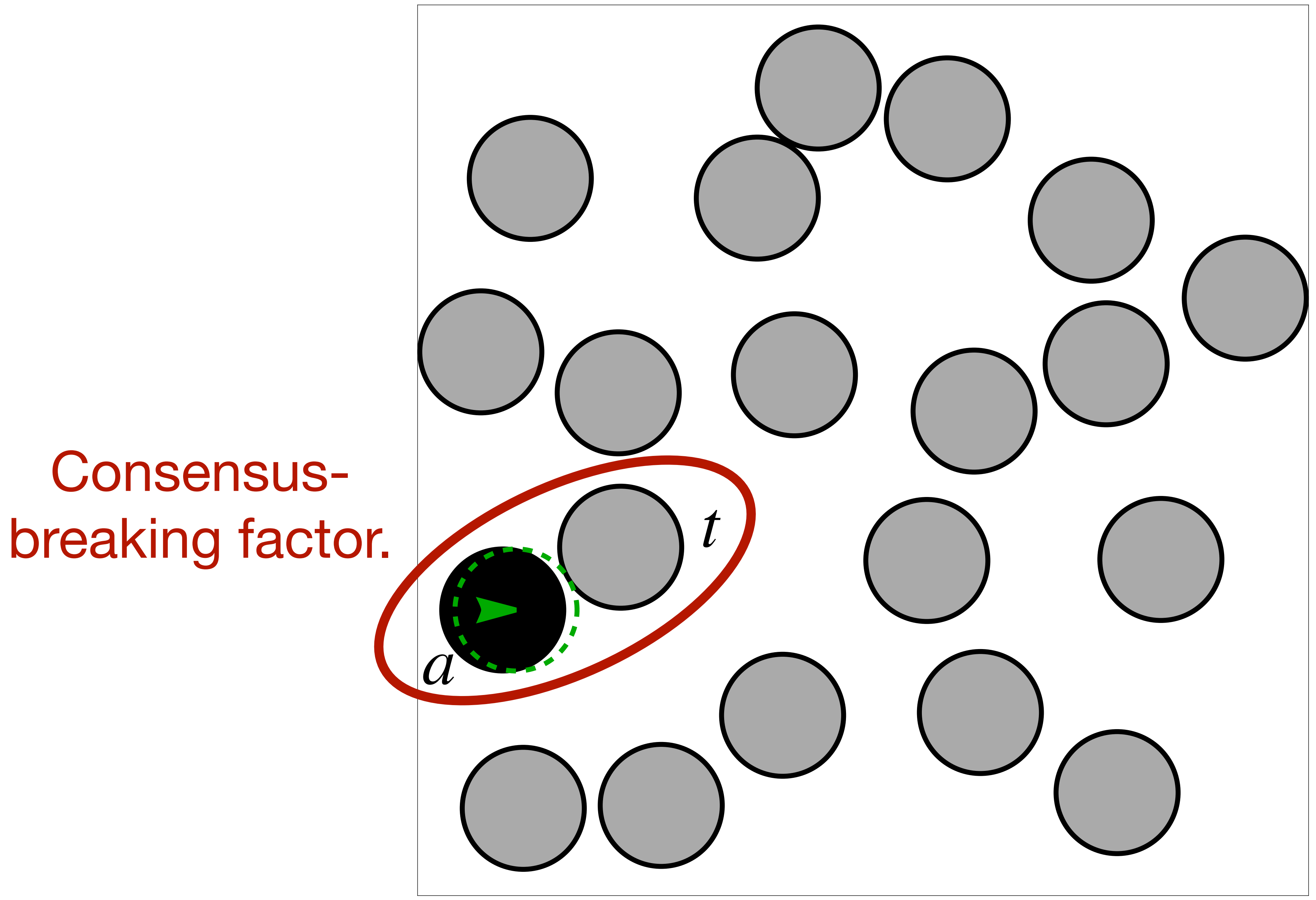
Whether the new configuration is accepted by all factors

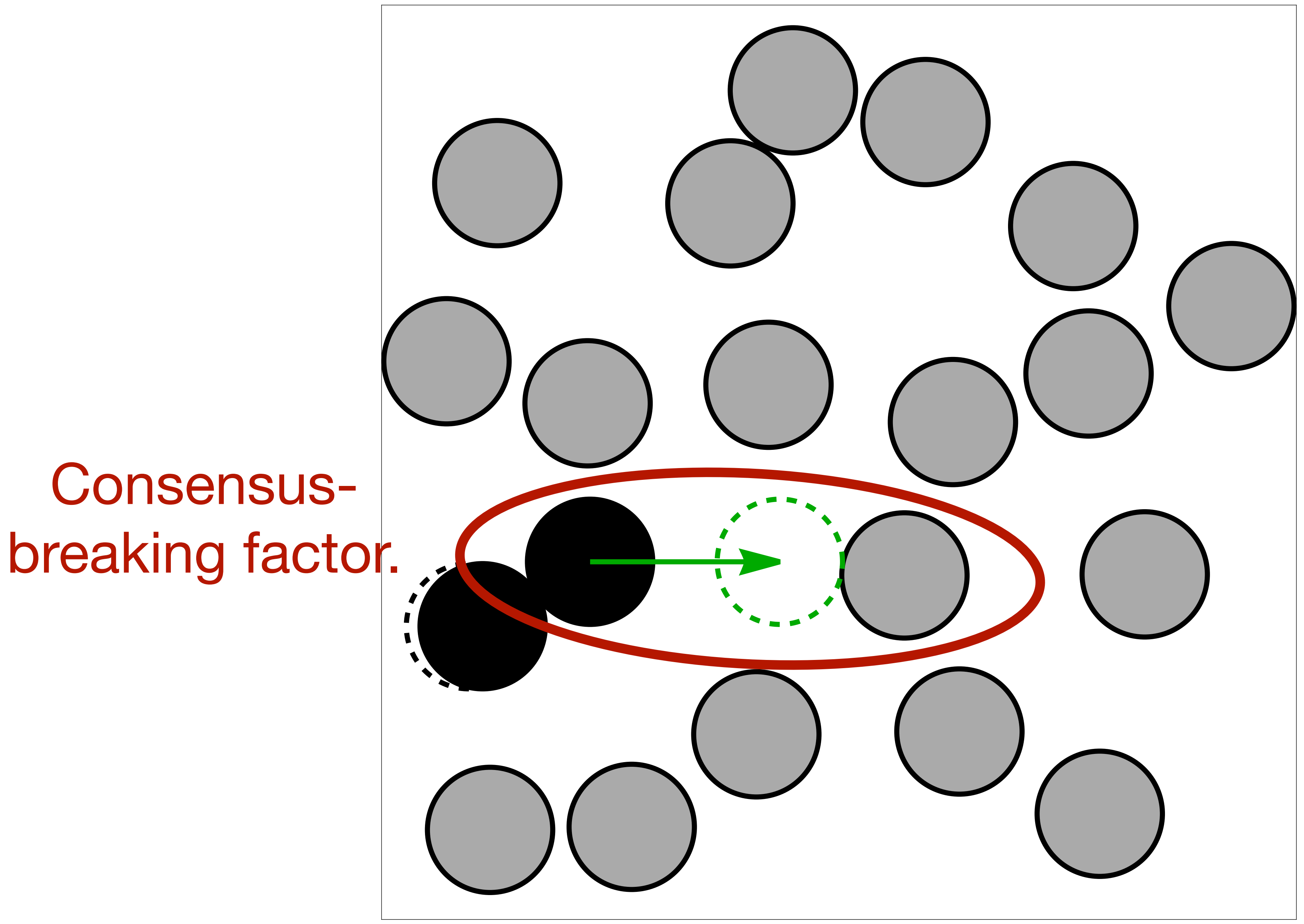
Whether the new configuration is accepted by factor M

Lifting Framework

- Lift configuration $c \rightarrow (c, \mathbf{v}, a)$ to include active atom a and its velocity $\mathbf{v}$.
- Atom a moves with $\mathbf{v}$ until a factor breaks consensus.
- If a translationally symmetric pair potential between a and t breaks consensus:

  $\rightarrow$ Change active atom from a to t in a lifting move.





Event-Driven Implementation

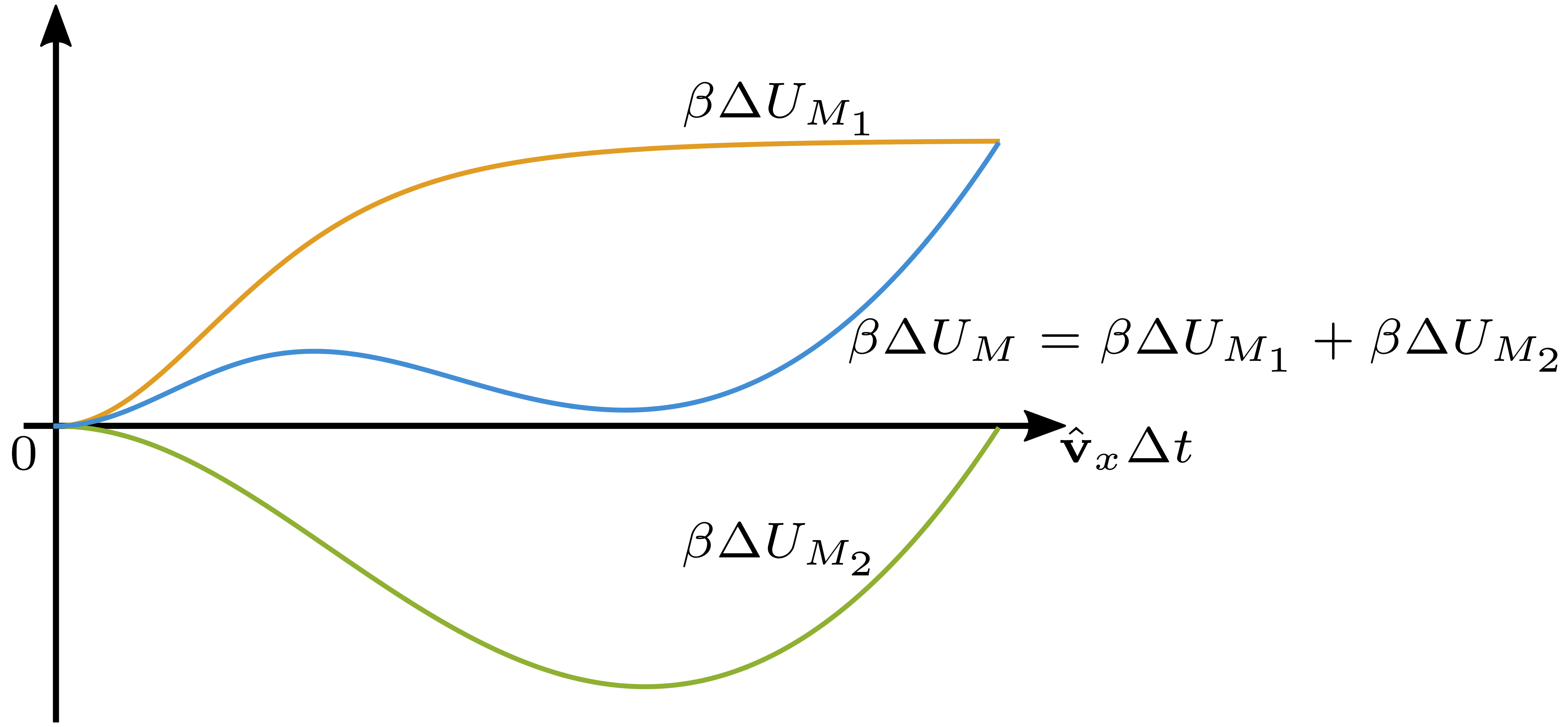
- For every factor M containing a, sample a candidate event time Δt_M .

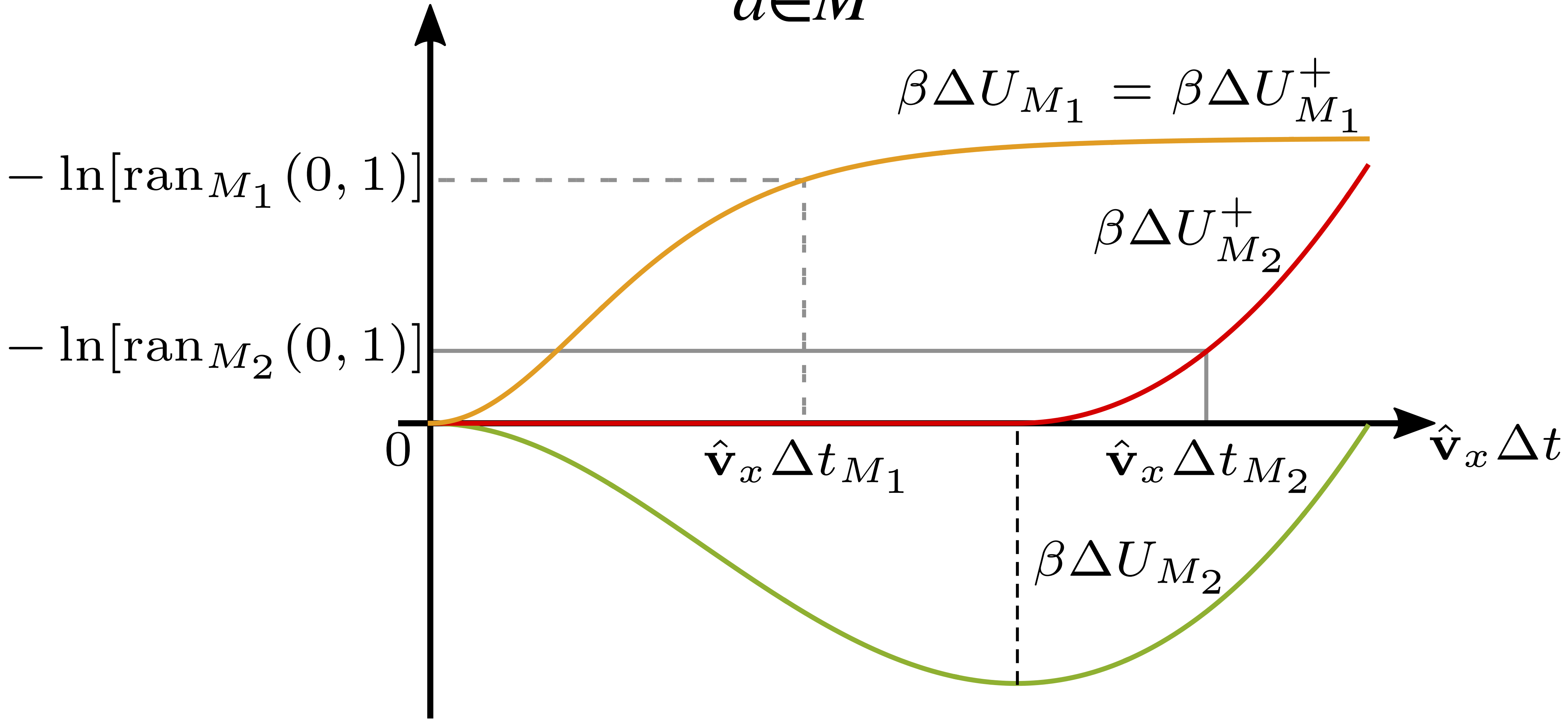
  → Proposed configuration $c'_M : c_M = \{\mathbf{r}_a, \mathbf{r}_t\} \to c'_M = \{\mathbf{r}_a + \Delta t_M \mathbf{v}, \mathbf{r}_t\}$.

  → Invert equation for $\Delta t_M : -\ln\left[\mathrm{ran}_M(0,1)\right] = \beta \Delta U_M^+(c_M \to c'_M)$.

  → Integrate event rate $\Delta U_M^+(c_M \to c'_M) = \int_0^{\Delta t_M} \mathrm{d}t \, \max\left[0, \mathbf{v} \cdot \nabla_{\mathbf{r}_a} U_M(\mathbf{r}_a + t\mathbf{v}, \mathbf{r}_t)\right]$.

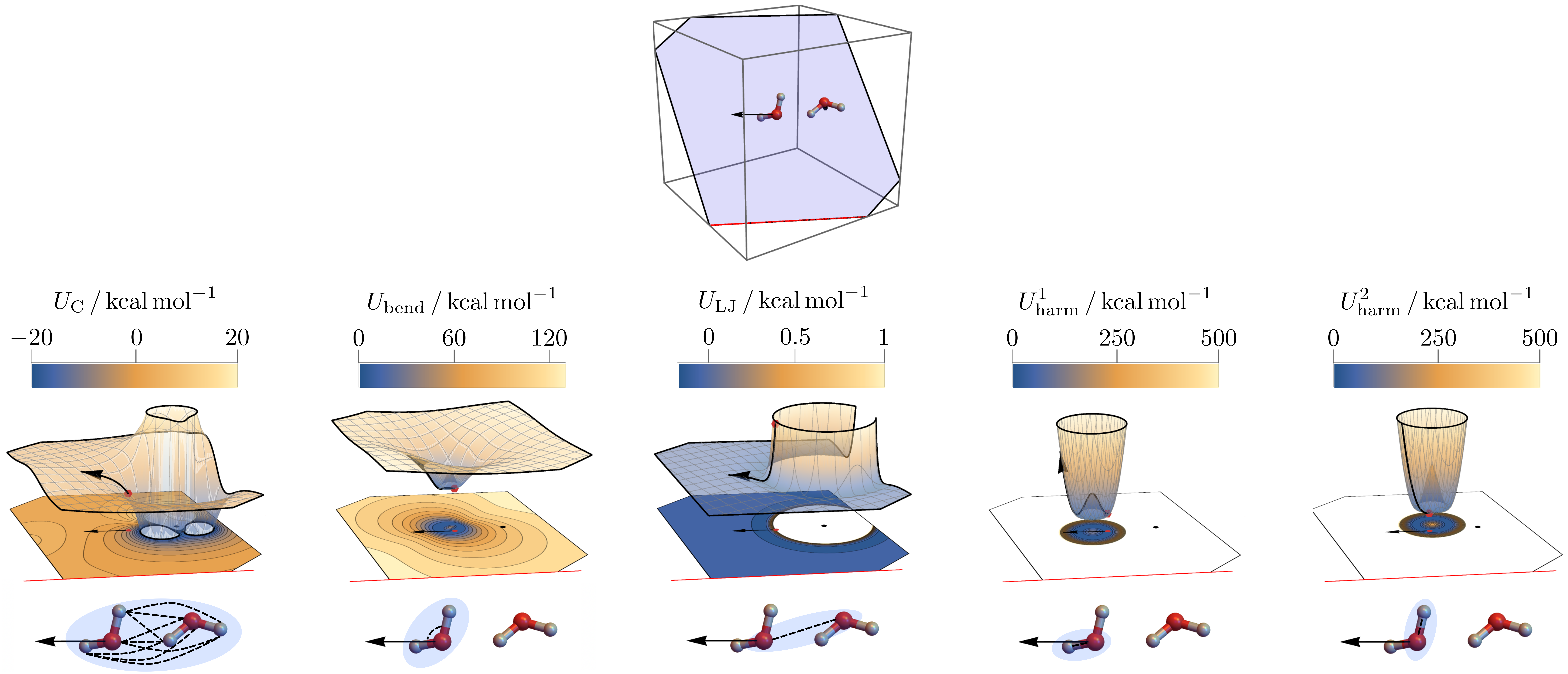
- Event takes place at minimum candidate event time $\Delta t_{\mathrm{Event}} = \min_{a \in M} \Delta t_M$.





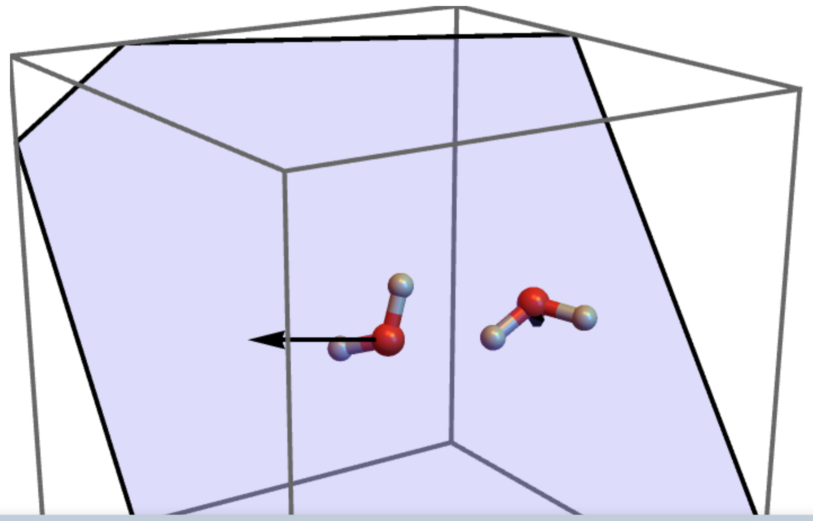
PH, *All-Atom Event-Chain Monte Carlo — Designing a General-Purpose Python Application* (Master's thesis, 2019)

ECMC for SPC/Fw Water Model



PH, Maggs, and Krauth, *Bringing the Power of Monte Carlo methods to Long-Range-Interacting Molecular Systems* (2022, manuscript in preparation)

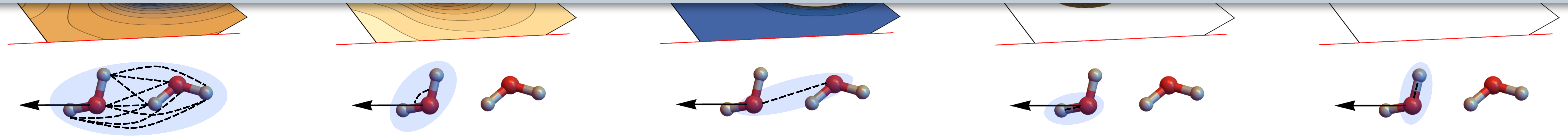
ECMC for SPC/Fw Water Model



Problems

- Integration and inversion of event rate can be tedious.
- In long-range-interacting N-body systems, consensus considers $\mathcal{O}(N)$ factors per event.

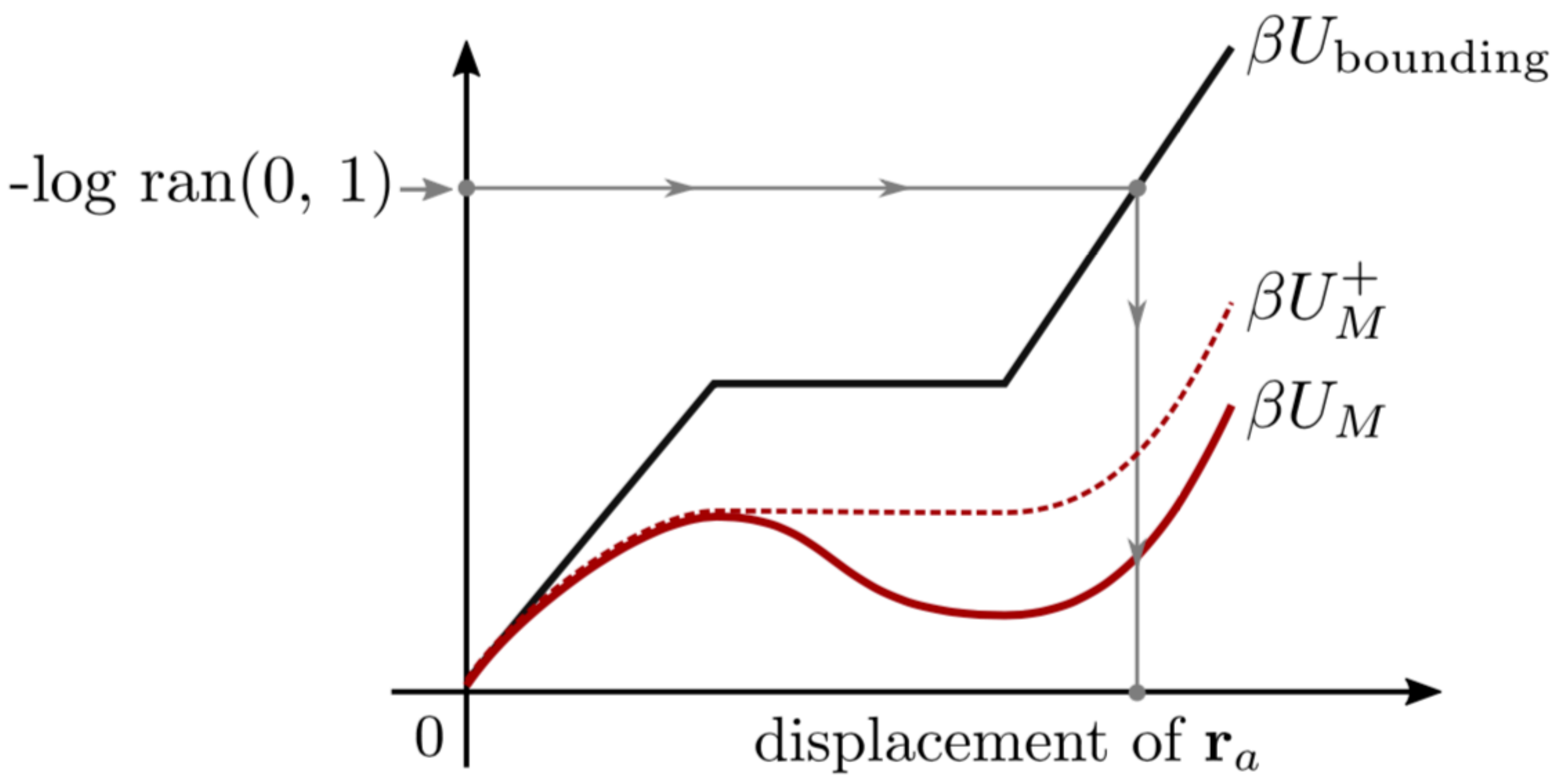
$\rightarrow$ Problematic long-range merged-image Coulomb potential.

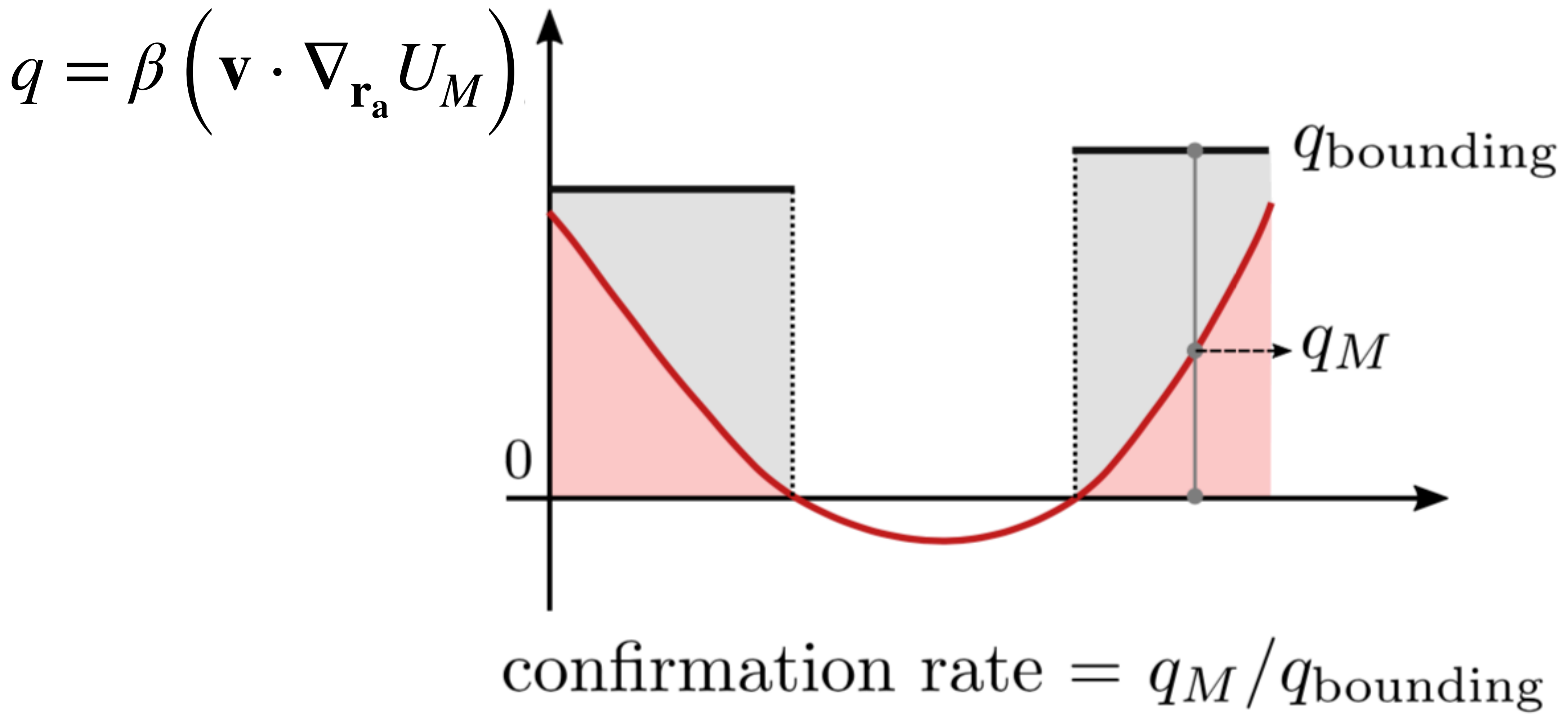


PH, Maggs, and Krauth, *Bringing the Power of Monte Carlo methods to Long-Range-Interacting Molecular Systems* (2022, manuscript in preparation)

Bounding Potentials

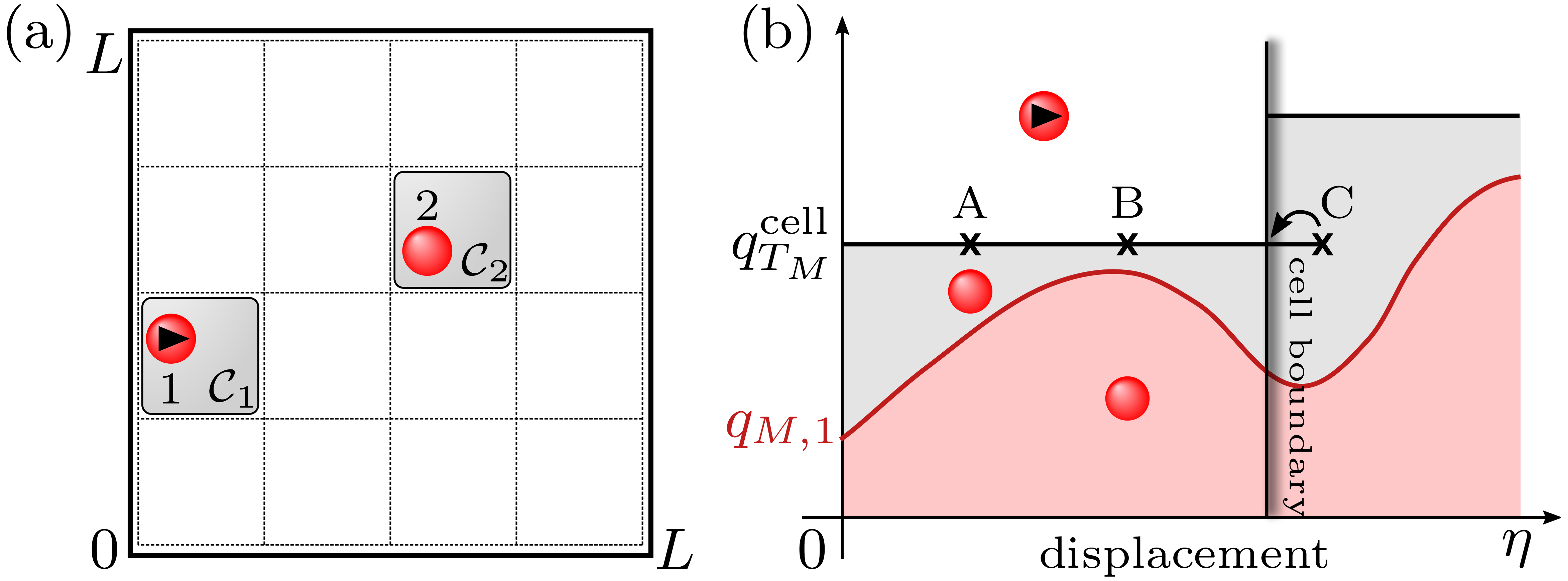
- Bounding potentials bound the event rate of their factor potential.
  → Events of bounding potentials have to be confirmed.





Cell-Veto Algorithm

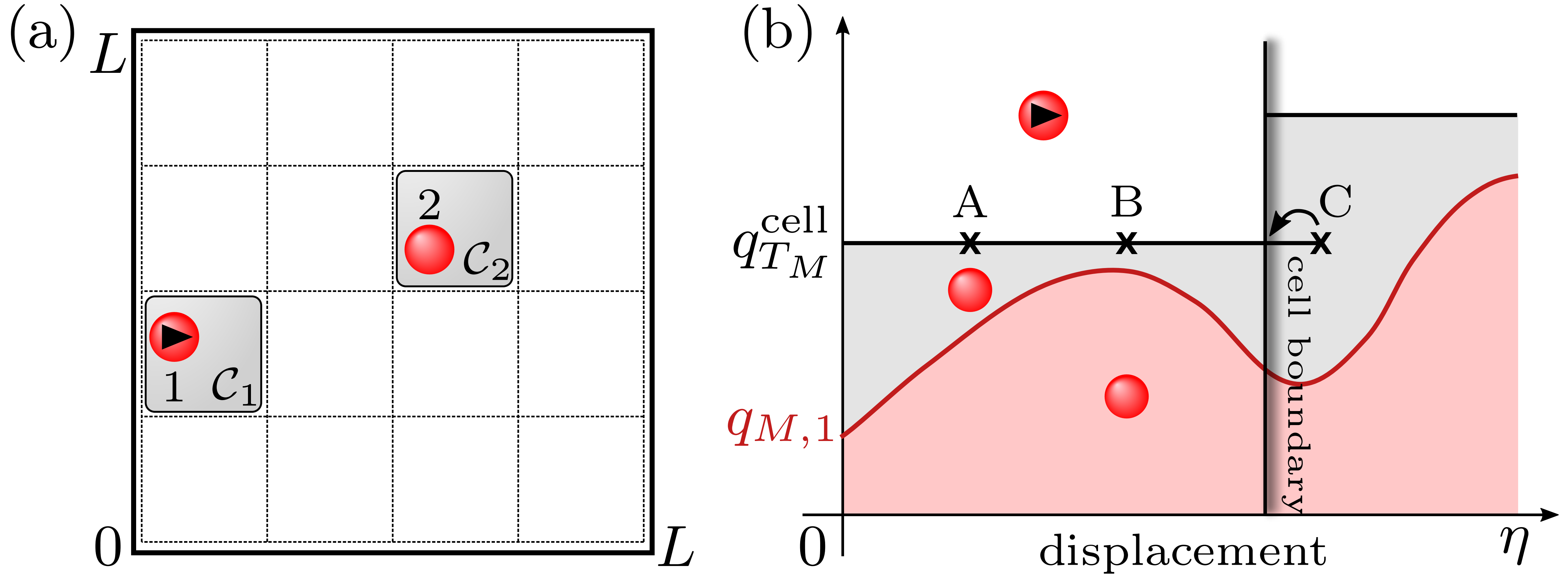
- Cell-based bounding potentials can be precomputed.



Faulkner et al., J. Chem. Phys. **149**, 064113 (2018)

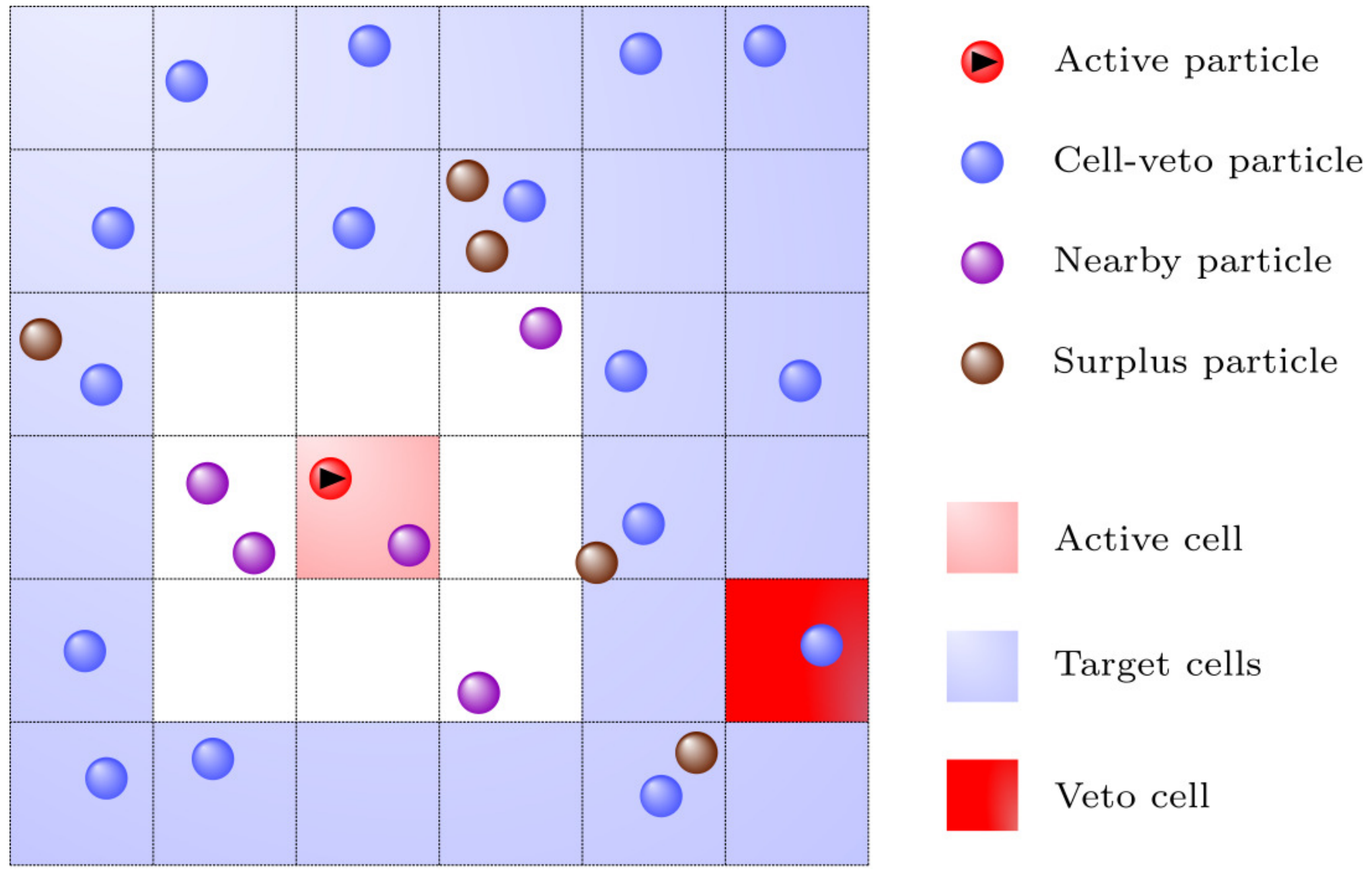
Cell-Veto Algorithm

- Cell-based bounding potentials can be precomputed.



Faulkner et al., J. Chem. Phys. **149**, 064113 (2018)

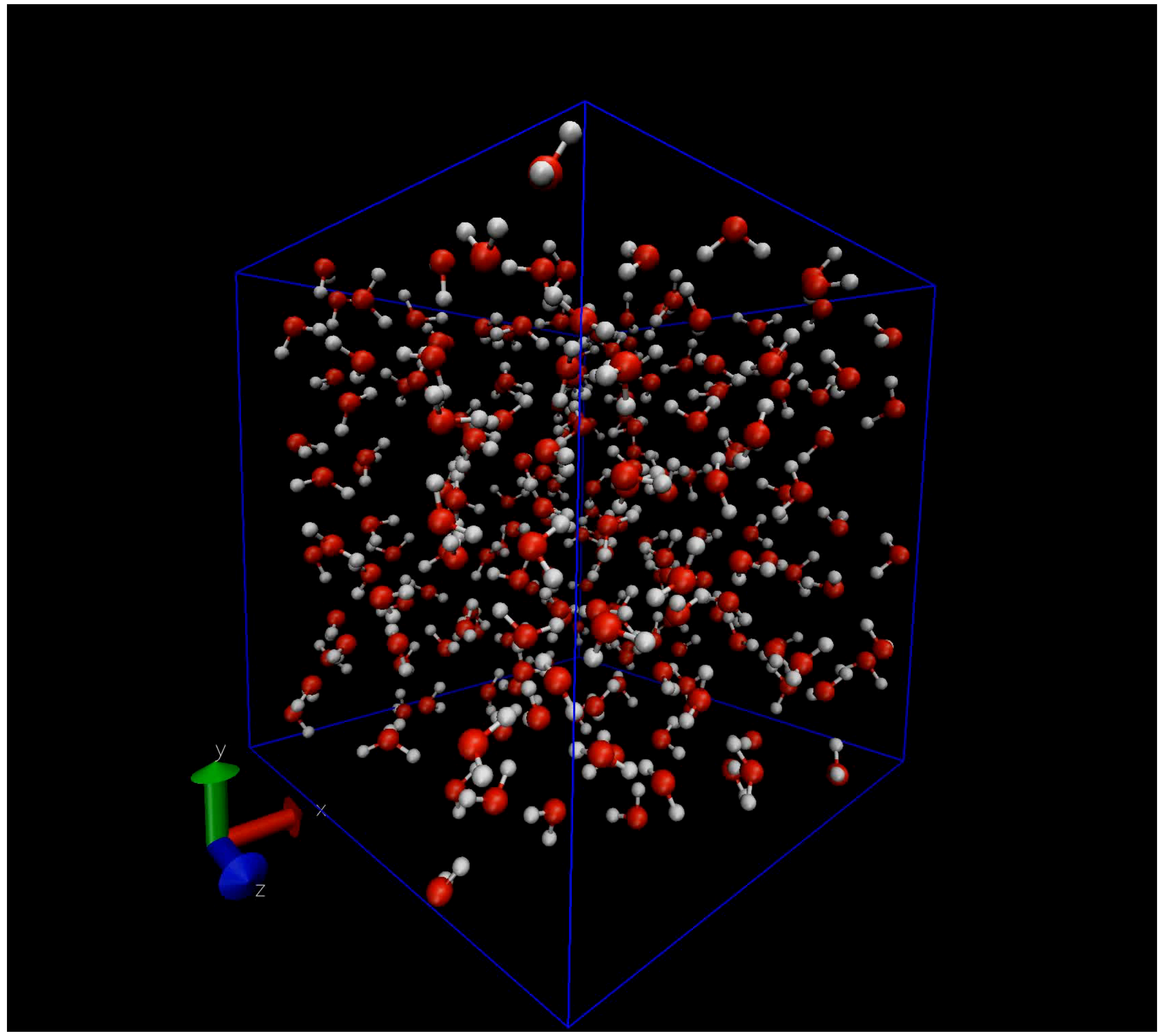
- Cell-veto algorithm considers all non-nearby interactions at once with $\mathcal{O}(1)$ complexity per event.



PH, *All-Atom Event-Chain Monte Carlo — Designing a General-Purpose Python Application* (Master's thesis, 2019)

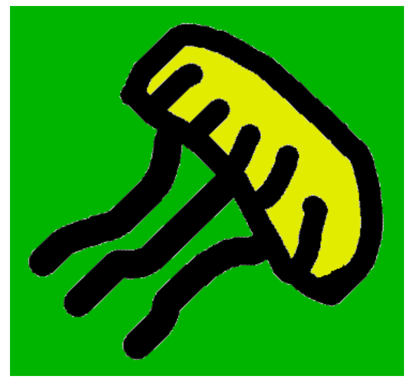
ECMC for Molecular Systems

- ECMC with cell-veto algorithm samples the Boltzmann distribution $\exp(-\beta U)$...
  $\rightarrow$ ...without ever knowing U.
  $\rightarrow$ ...numerically exact without discretizing time (or space).
  $\rightarrow$ ...using non-equilibrium dynamics.

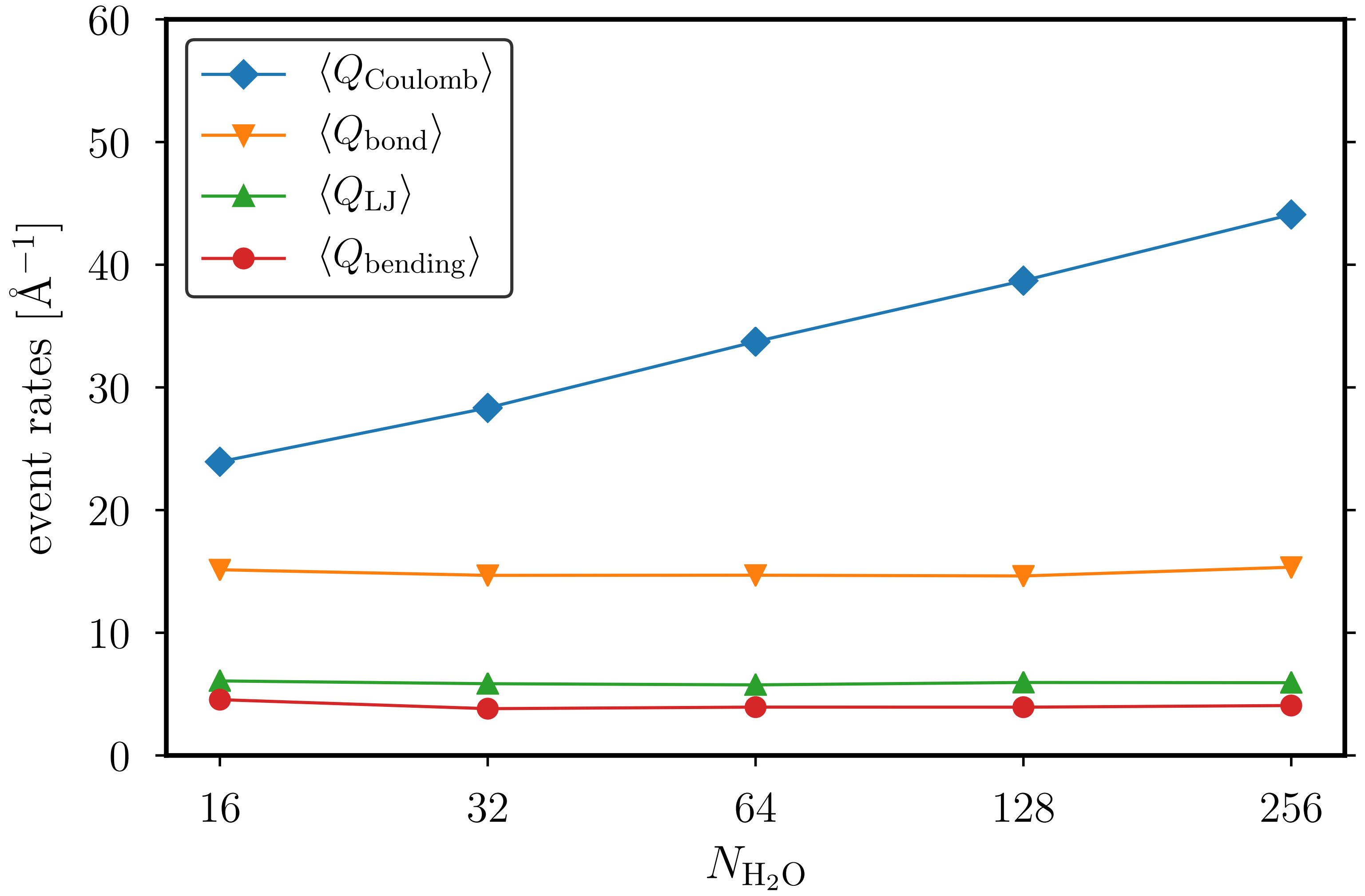


ECMC for Molecular Systems

- ECMC with cell-veto algorithm samples the Boltzmann distribution $\exp(-\beta U)$...
  $\rightarrow$ ...without ever knowing U.
  $\rightarrow$ ...numerically exact without discretizing time (or space).
  $\rightarrow$ ...using non-equilibrium dynamics.
- General-purpose open-source ECMC application JeLLyFysh for molecular simulations available [**PH** et al., Comput. Phys. Commun. **253**, 107168 (2020)].



- Factors involving more than three atoms can be treated in a variety of ways (e.g., have most liftings within a water molecule).
- ECMC advances N SPC/Fw water molecules with $\mathcal{O}(N \log N)$ complexity.



Faulkner et al., J. Chem. Phys. **149**, 064113 (2018)

ECMC for Molecular Systems

- ECMC with cell-veto algorithm samples the Boltzmann distribution $\exp(-\beta U)$…
  → …without ever knowing U.
  → …numerically exact without discretizing time (or space).
  → …using non-equilibrium dynamics.
- General-purpose open-source ECMC application JeLLyFysh for molecular simulations available [**PH** et al., Comput. Phys. Commun. **253**, 107168 (2020)].
- Factors involving more than three atoms can be treated in a variety of ways (e.g., have most liftings within a water molecule).
- ECMC advances N SPC/Fw water molecules with $\mathcal{O}(N \log N)$ complexity.

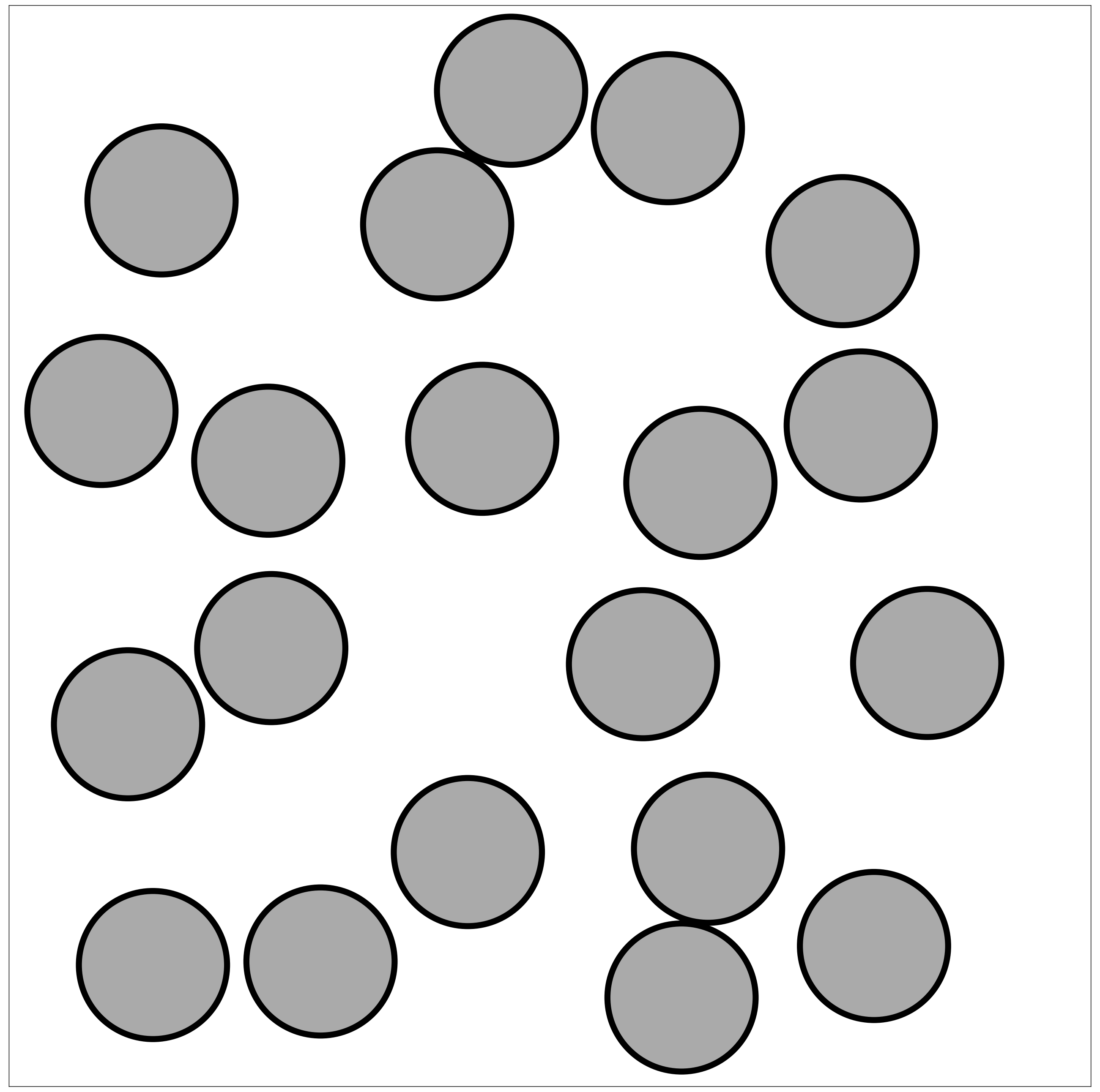
MD	ECMC
• Computational complexity per MD time step: $\mathcal{O}(N \log N)$.	• Computational complexity per MCMC sweep: $\mathcal{O}(N \log N)$. ✓
• Superior (Newtonian) exploration of configuration space.	• ?

Newtonian ECMC

- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.

  → Every atom has a velocity, but only one is active.

  → Consider both involved velocities in an event.

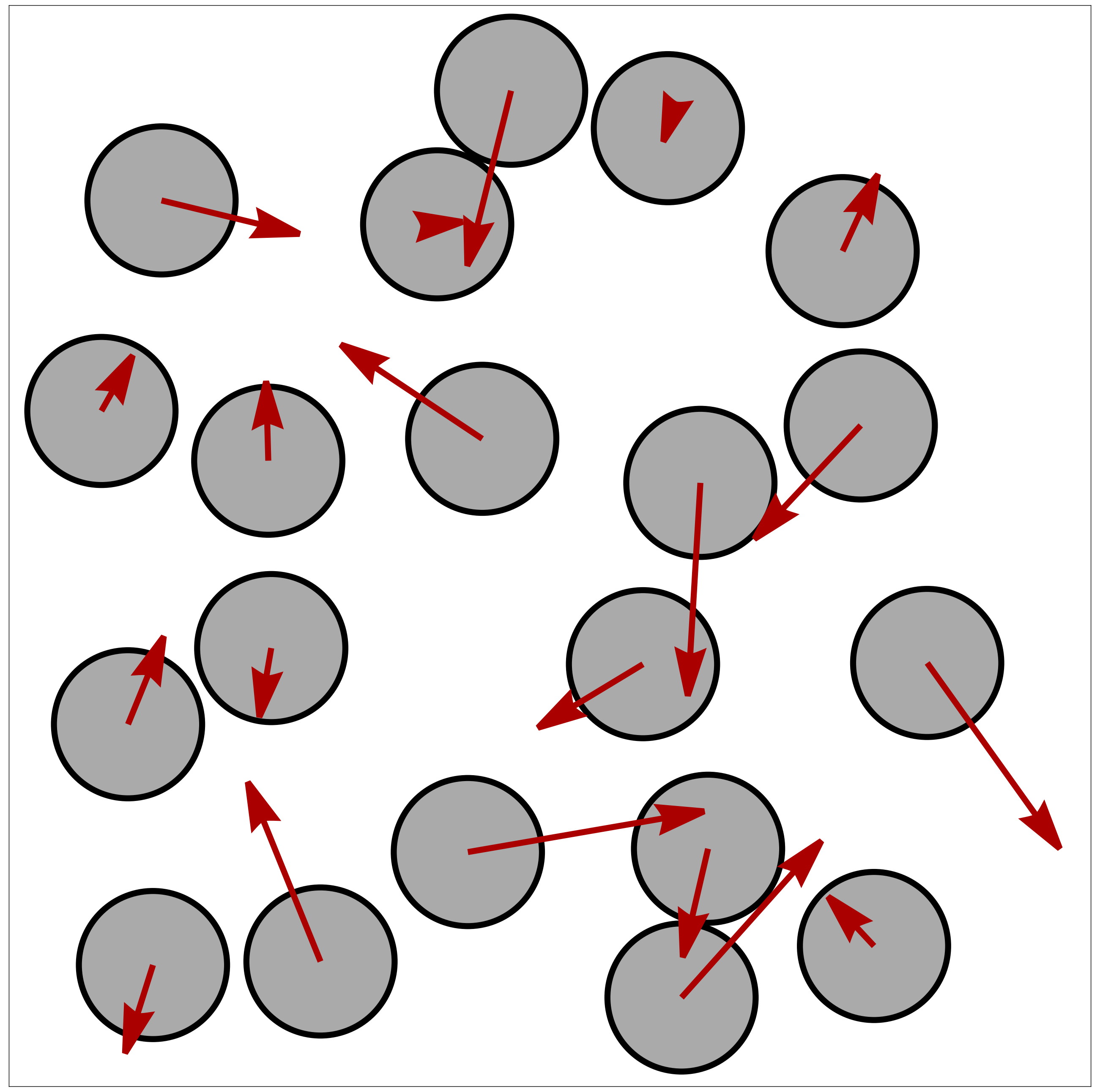


Newtonian ECMC

- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.

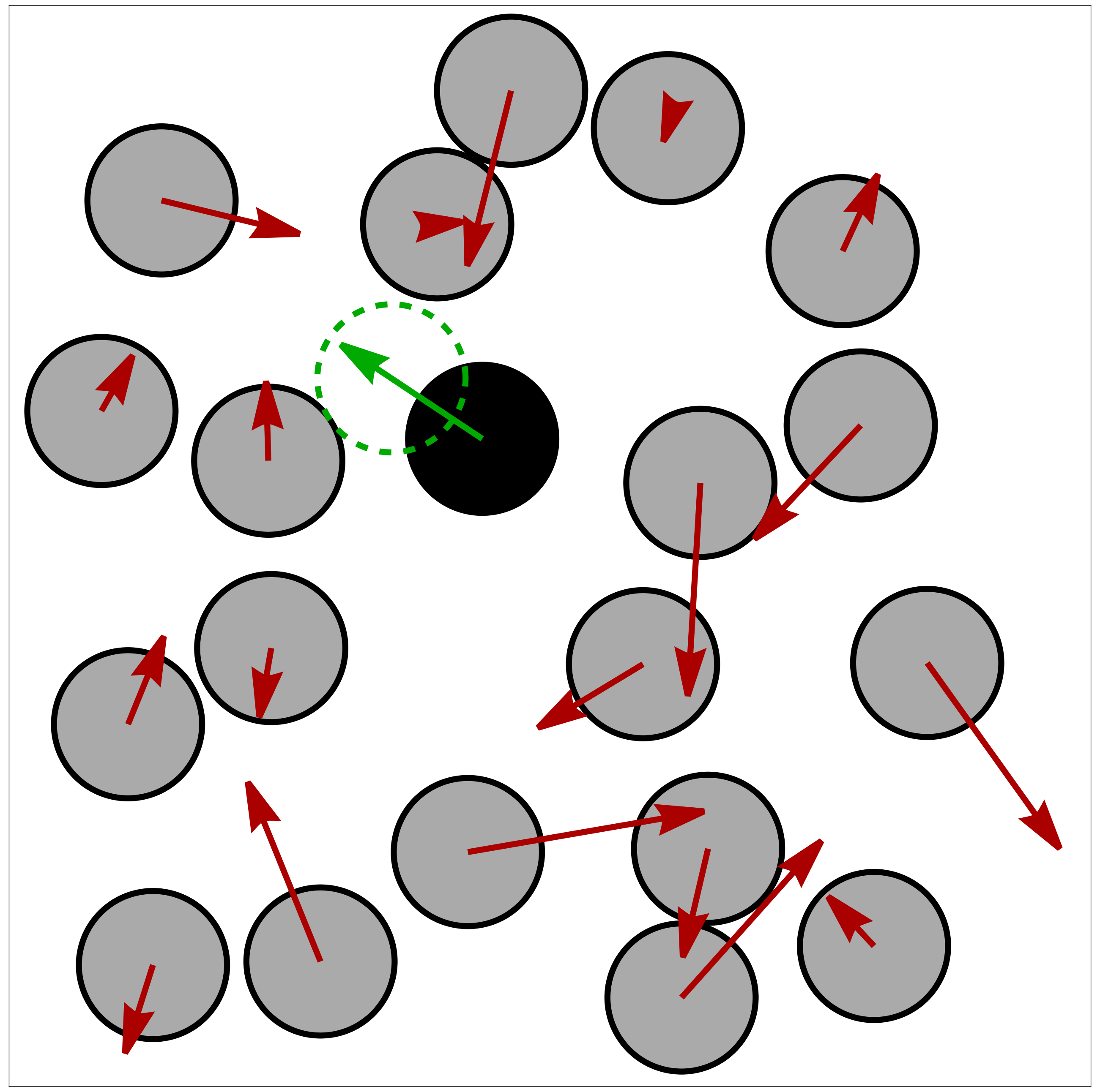
  → Every atom has a velocity, but only one is active.

  → Consider both involved velocities in an event.



Newtonian ECMC

- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.
  → Every atom has a velocity, but only one is active.
  → Consider both involved velocities in an event.

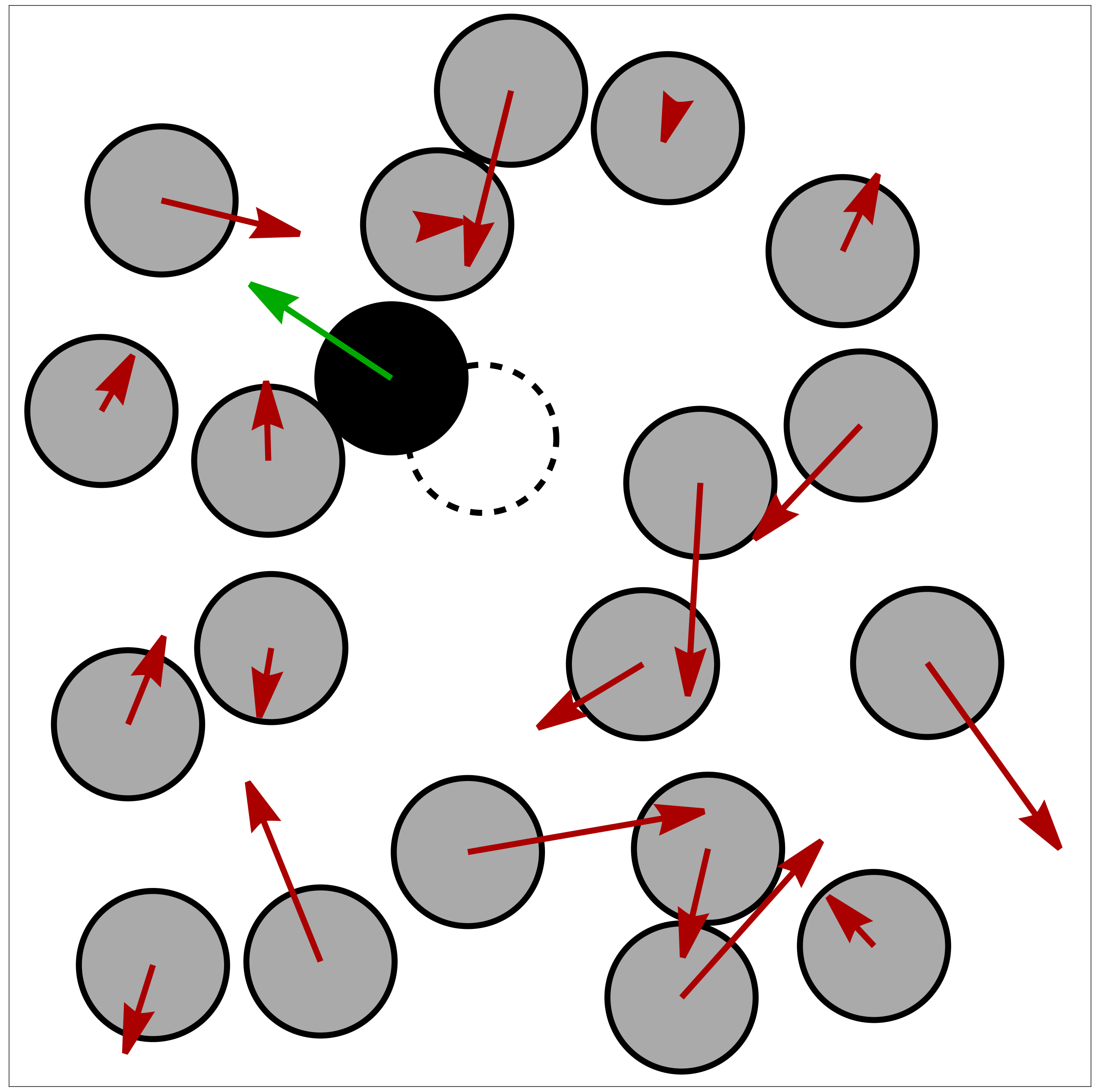


Newtonian ECMC

- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.

  → Every atom has a velocity, but only one is active.

  → Consider both involved velocities in an event.

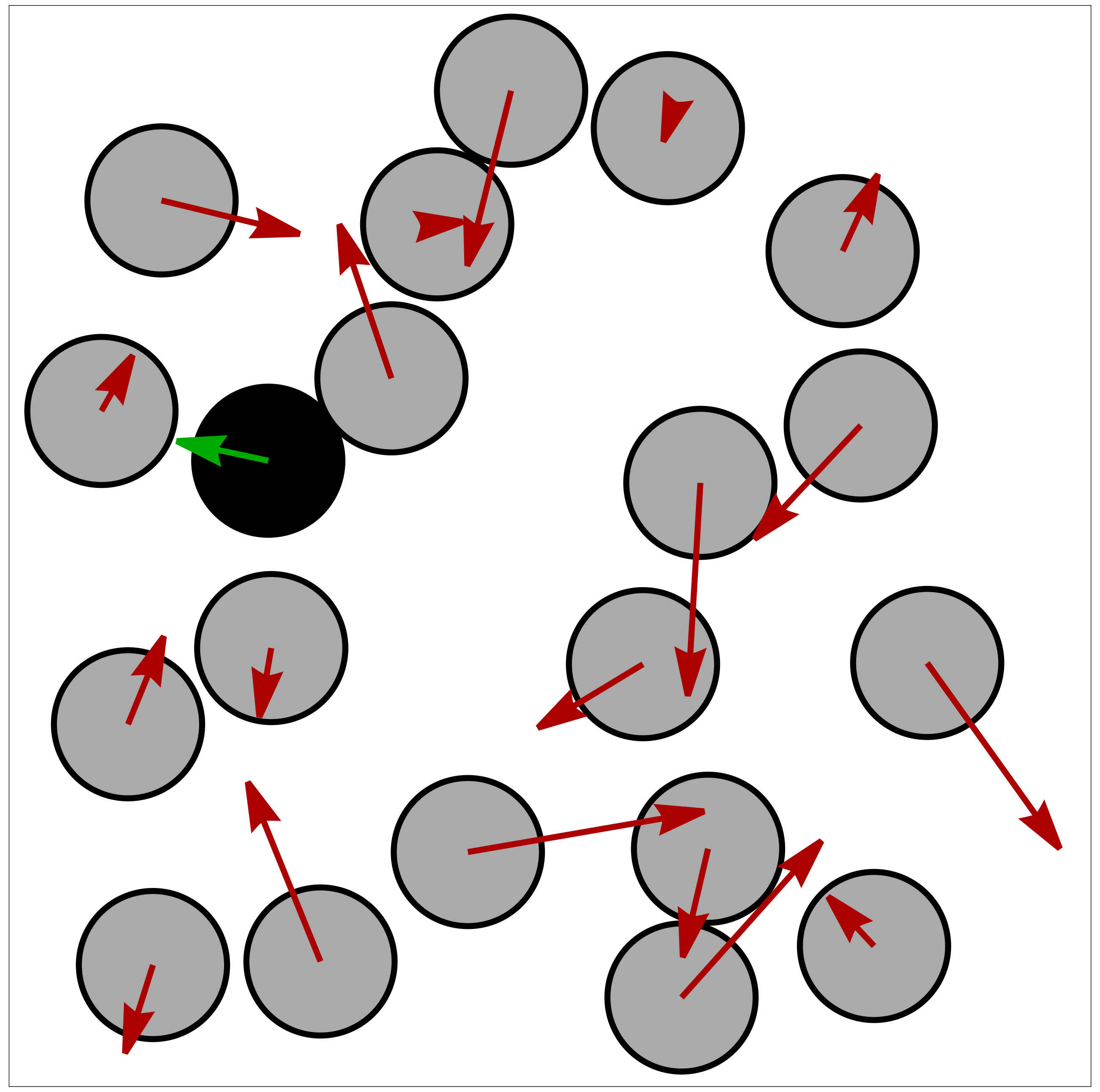


Newtonian ECMC

- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.

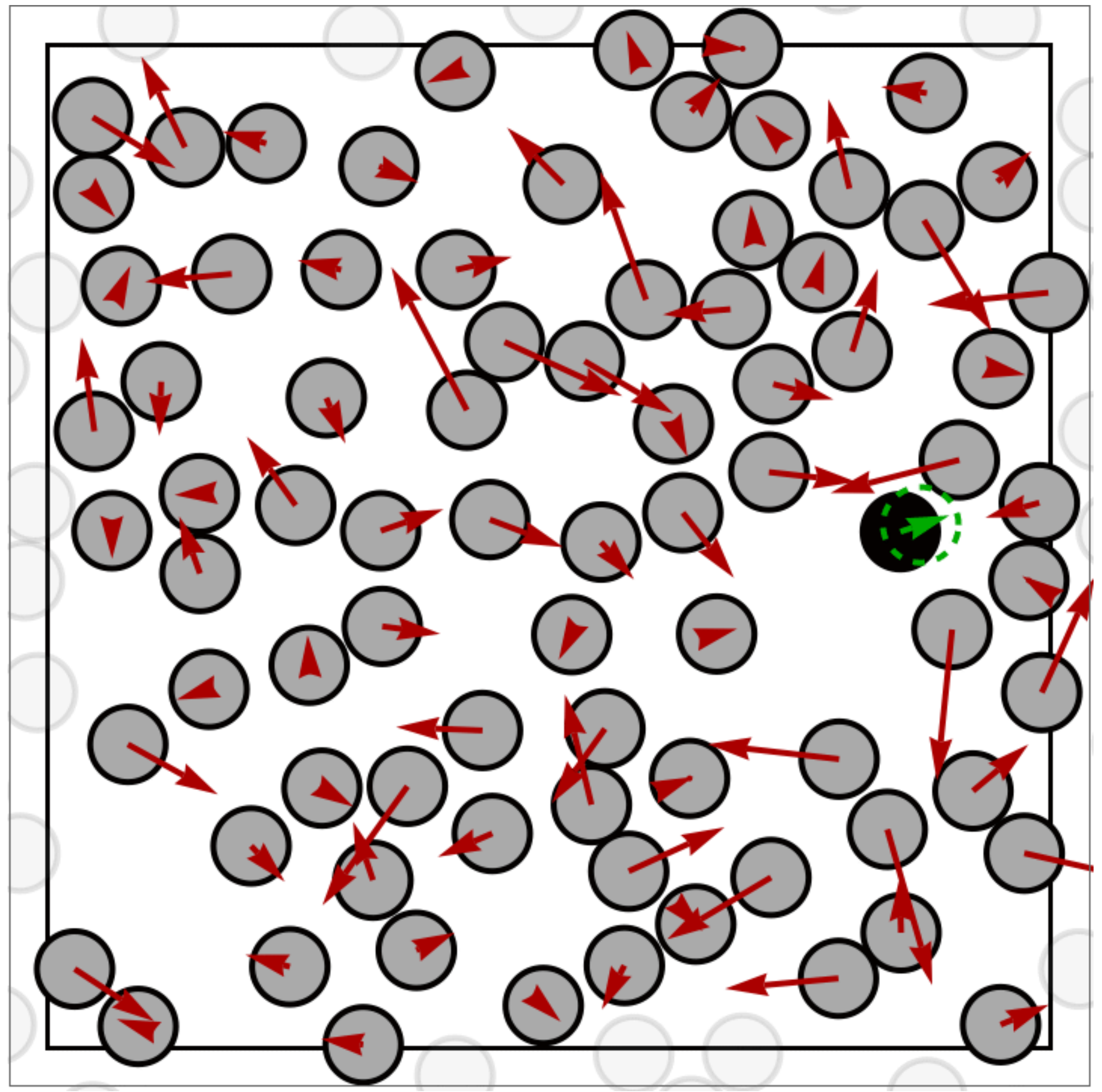
  → Every atom has a velocity, but only one is active.

  → Consider both involved velocities in an event.



Newtonian ECMC

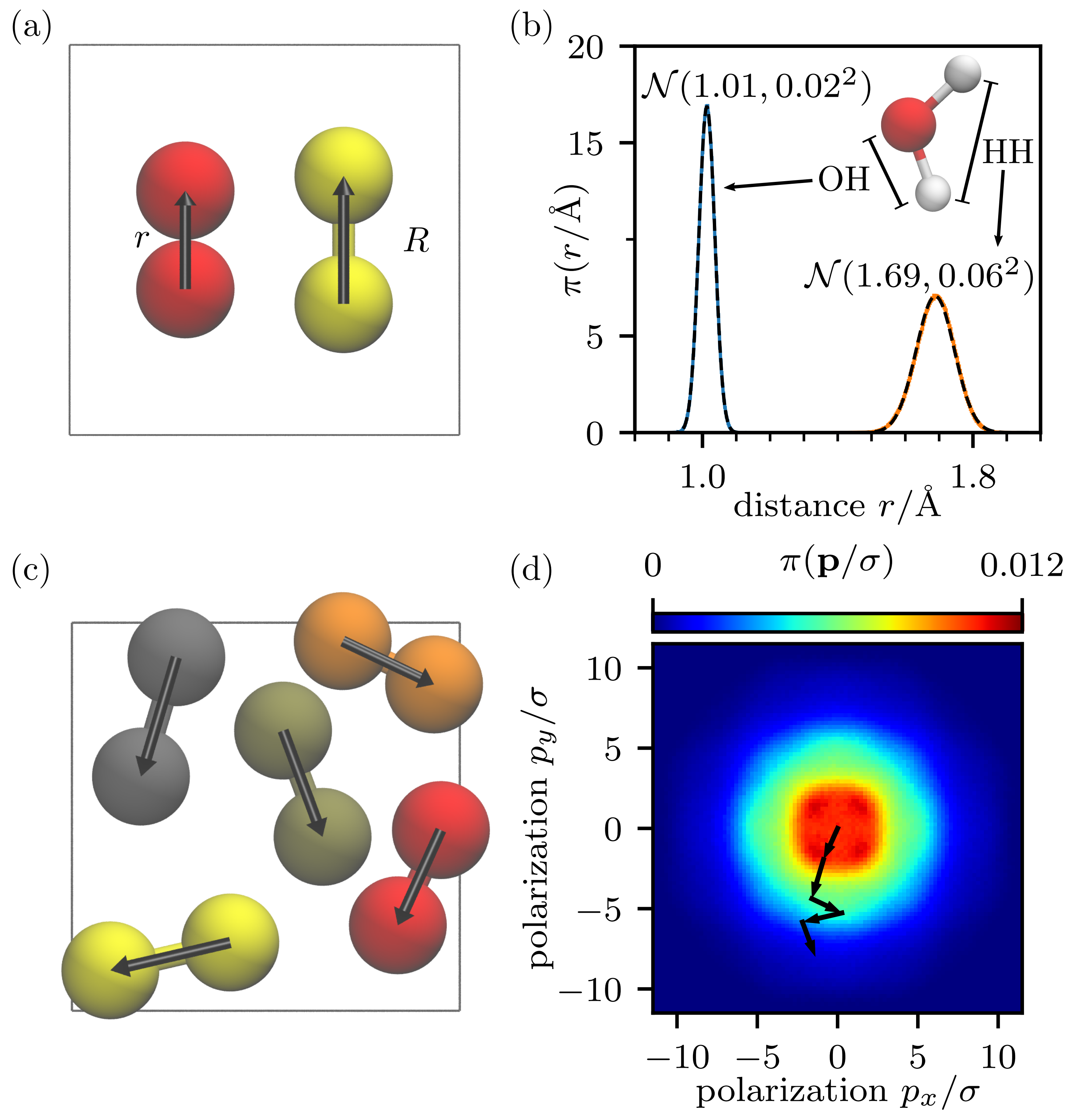
- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.
  → Every atom has a velocity, but only one is active.
  → Consider both involved velocities in an event.

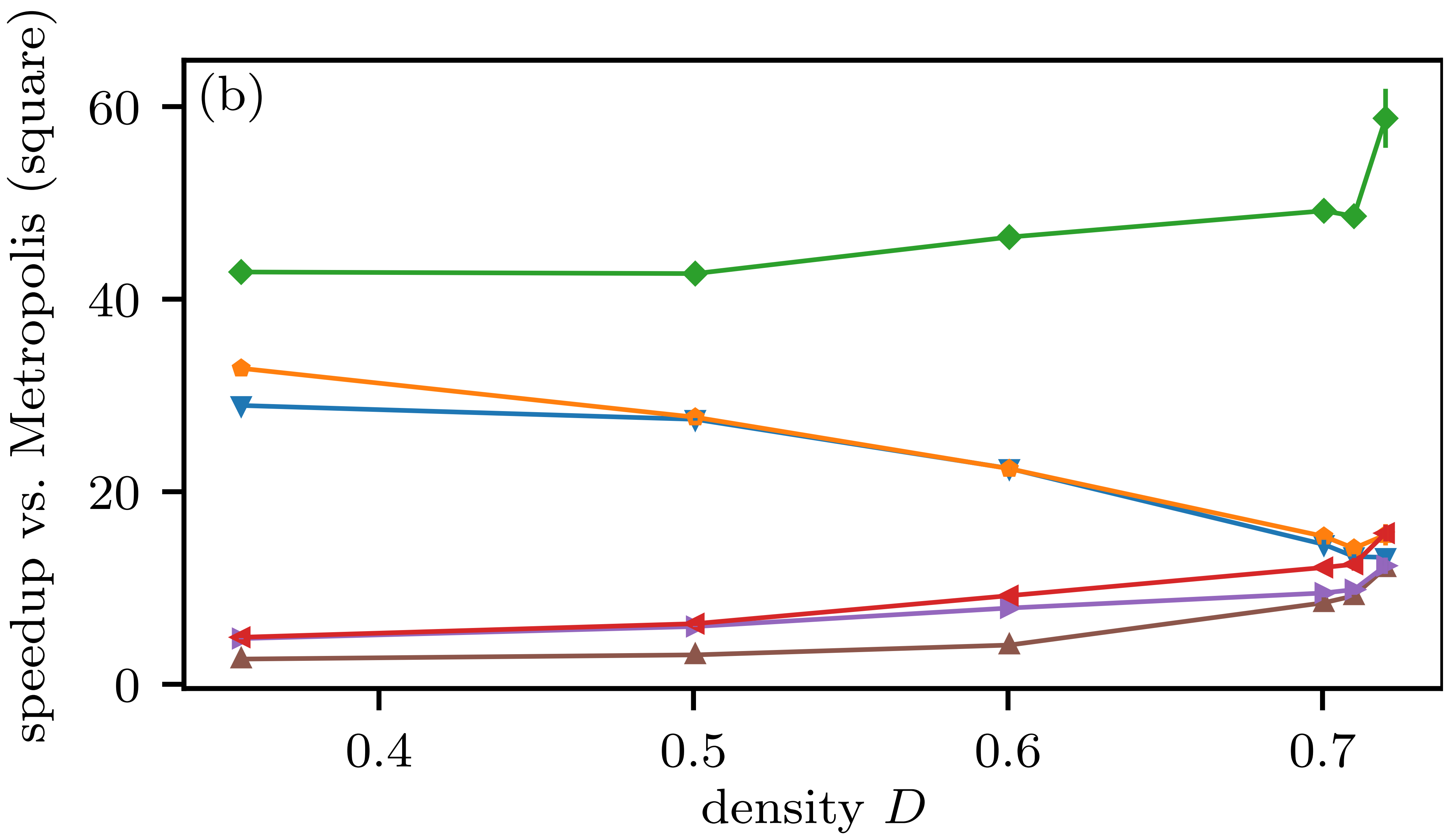


Newtonian ECMC

- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.
  $\rightarrow$ Every atom has a velocity, but only one is active.
  $\rightarrow$ Consider both involved velocities in an event.

- Strongly improves rotation dynamics of dense tethered hard-disk dipoles.





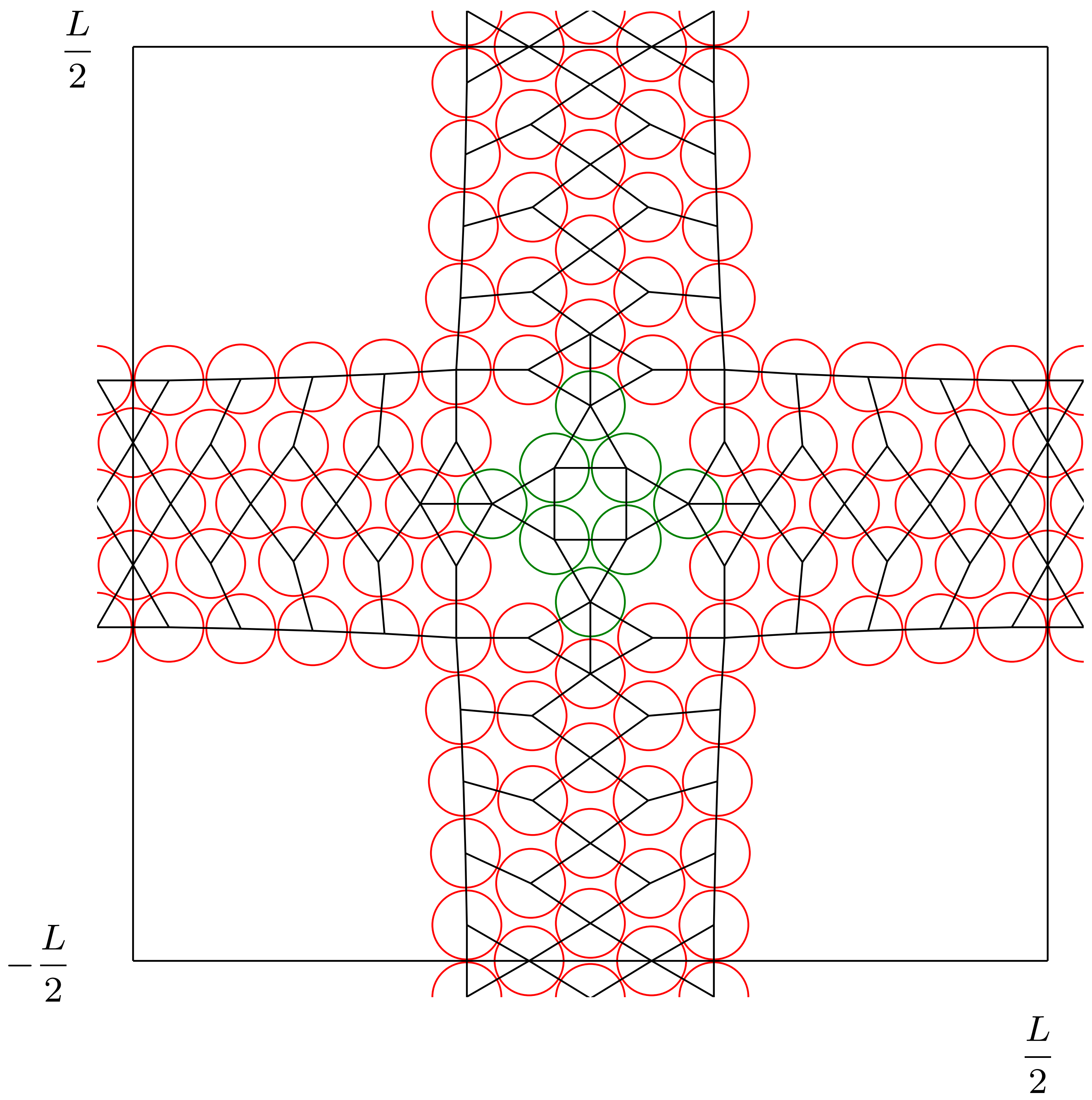
PH et al., J. Chem. Phys. **156**, 084108 (2022)

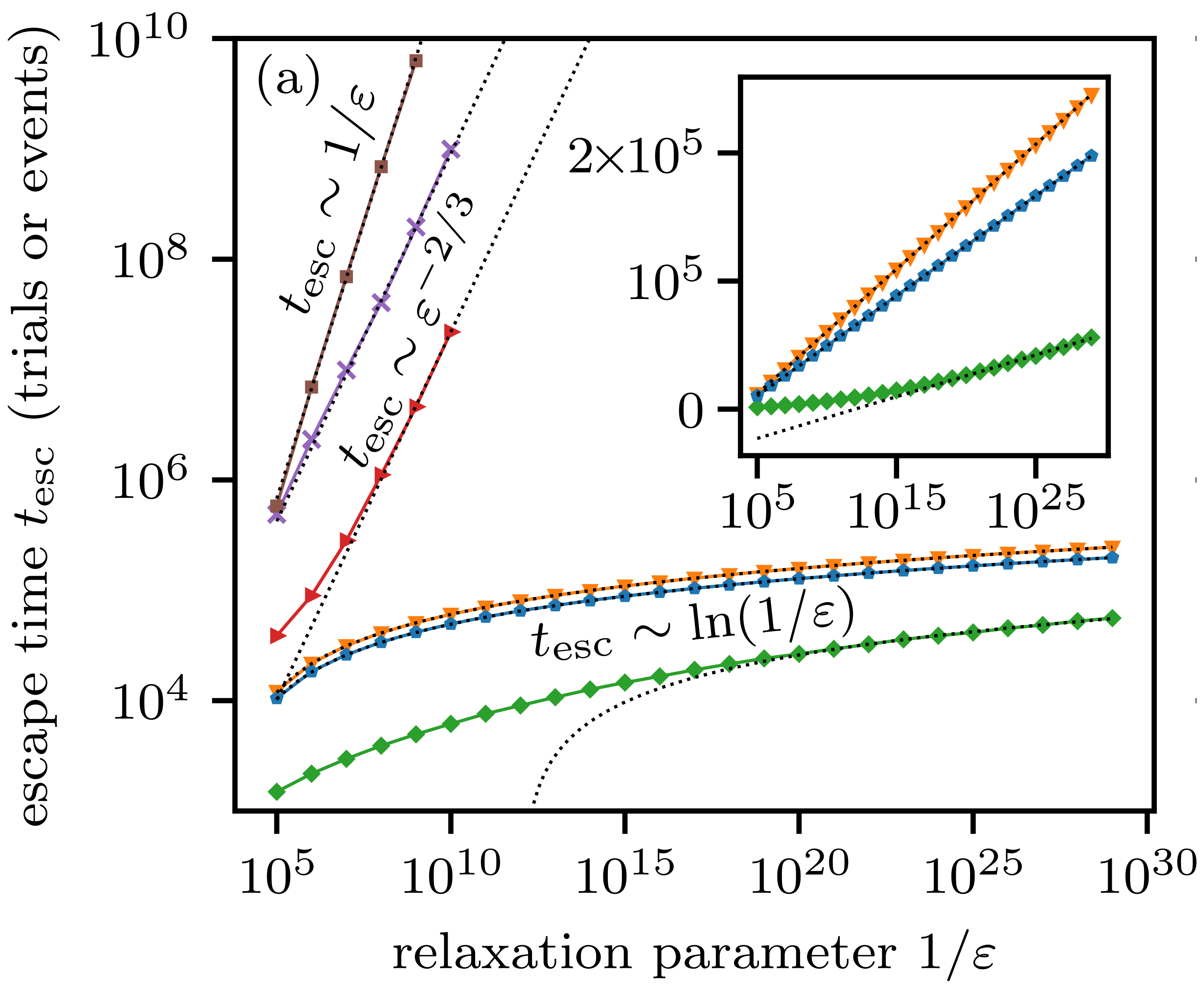
Newtonian ECMC

- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.
  → Every atom has a velocity, but only one is active.
  → Consider both involved velocities in an event.

- Strongly improves rotation dynamics of dense tethered hard-disk dipoles.

- Entirely different escape behavior from locally stable hard-disk Böröczky packings.





PH et al., J. Stat. Phys. **187**, 31 (2022)

Newtonian ECMC

- Incorporate Newtonian dynamics into the non-reversible Monte Carlo method.
  → Every atom has a velocity, but only one is active.
  → Consider both involved velocities in an event.
- Strongly improves rotation dynamics of dense tethered hard-disk dipoles.
- Entirely different escape behavior from locally stable hard-disk Böröczky packings.
- Trivial choice of the optimal chain time (very large or even infinite).
  → No fine-tuning of internal parameters required.

Conclusion

- ECMC with cell-veto algorithm samples the Boltzmann distribution $\exp(-\beta U)$…

  $\rightarrow$ …without ever knowing U.

  $\rightarrow$ …numerically exact without discretizing time (or space).

  $\rightarrow$ …using non-equilibrium dynamics.

- ECMC overcomes disadvantages of traditional reversible MCMC in long-range-interacting molecular systems:

  $\rightarrow$ Decorrelate N water molecules in $\mathcal{O}(N \log N)$ computational complexity.

Conclusion

- ECMC with cell-veto algorithm samples the Boltzmann distribution $\exp(-\beta U)$…
  → …without ever knowing U.
  → …numerically exact without discretizing time (or space).
  → …using non-equilibrium dynamics.
- ECMC overcomes disadvantages of traditional reversible MCMC in long-range-interacting molecular systems:
  → Decorrelate N water molecules in $\mathcal{O}(N \log N)$ computational complexity.

Outlook

- Direct comparison with MD that considers the precision in the MD algorithm.
- Improve dynamics beyond Newtonian dynamics (e.g., with factor fields).
- Efficiently parallelize ECMC.