Synchronicity and detailed balance in Monte Carlo simulations: do they conflict with each other?

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The Group

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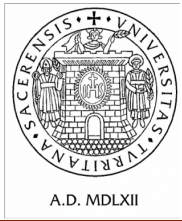
Research Topics

- Confinement
- Force-matching
- Coarse-graining
- Stochastic modelling



Importance sampling Monte Carlo (Classical *NVT*)

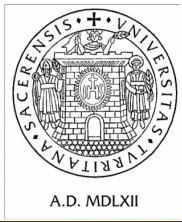
Aim: Sampling of configurations with probability $\propto \exp\{-\beta E(\mathbf{r}^N)\}$
Peculiarity: No need to compute explicitly the partition function,

$$Q_{NVT} = \sum_{\mathbf{r}^N \in \Gamma_{NVT}} \exp\{-\beta E(\mathbf{r}^N)\}. \tag{1}$$

Tool: The principle of *Detailed Balance*. The rate of any 'forward' transformation must balance with the rate of the 'reverse' transformation:

$$K(\mathbf{R} \to \mathbf{S}) = K(\mathbf{S} \to \mathbf{R}), \qquad \mathbf{R} := \mathbf{r}^N, \mathbf{S} := \mathbf{s}^N. \tag{2}$$

Assumption: The underlying Markov Chain to be *ergodic*.
Comment: Detailed Balance is sufficient, but not necessary.



Importance sampling Monte Carlo (Classical *NVT*)

$$K(\mathbf{R} \to \mathbf{S}) = K(\mathbf{S} \to \mathbf{R}), \tag{3}$$

$$p(\mathbf{R})p(\mathbf{S}|\mathbf{R}) = p(\mathbf{S})p(\mathbf{R}|\mathbf{S}), \tag{4}$$

$$p(\mathbf{R})\alpha(\mathbf{S}|\mathbf{R})p_{\mathrm{acc}}(\mathbf{S}|\mathbf{R}) = p(\mathbf{S})\alpha(\mathbf{R}|\mathbf{S})p_{\mathrm{acc}}(\mathbf{R}|\mathbf{S}). \tag{5}$$

Metropolis-Hastings

$\alpha(\mathbf{S}|\mathbf{R})$: probability to generate $\mathbf{S}$ from $\mathbf{R}$ as a *trial configuration*;
$p_{\mathrm{acc}}(\mathbf{S}|\mathbf{R})$: probability to accept the transformation $\mathbf{R} \to \mathbf{S}$.

$$p(\mathbf{R}) \propto e^{-\beta E(\mathbf{R})}, \qquad p(\mathbf{S}) \propto e^{-\beta E(\mathbf{S})}, \tag{6}$$

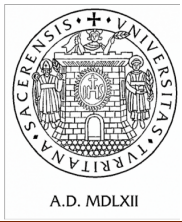
$$p_{\mathrm{acc}}(\mathbf{S}|\mathbf{R}) = \min\left(1, \frac{\alpha(\mathbf{R}|\mathbf{S})}{\alpha(\mathbf{S}|\mathbf{R})} e^{-\beta[E(\mathbf{S})-E(\mathbf{R})]}\right). \tag{7}$$

Importance sampling Monte Carlo (Classical *NVT*)

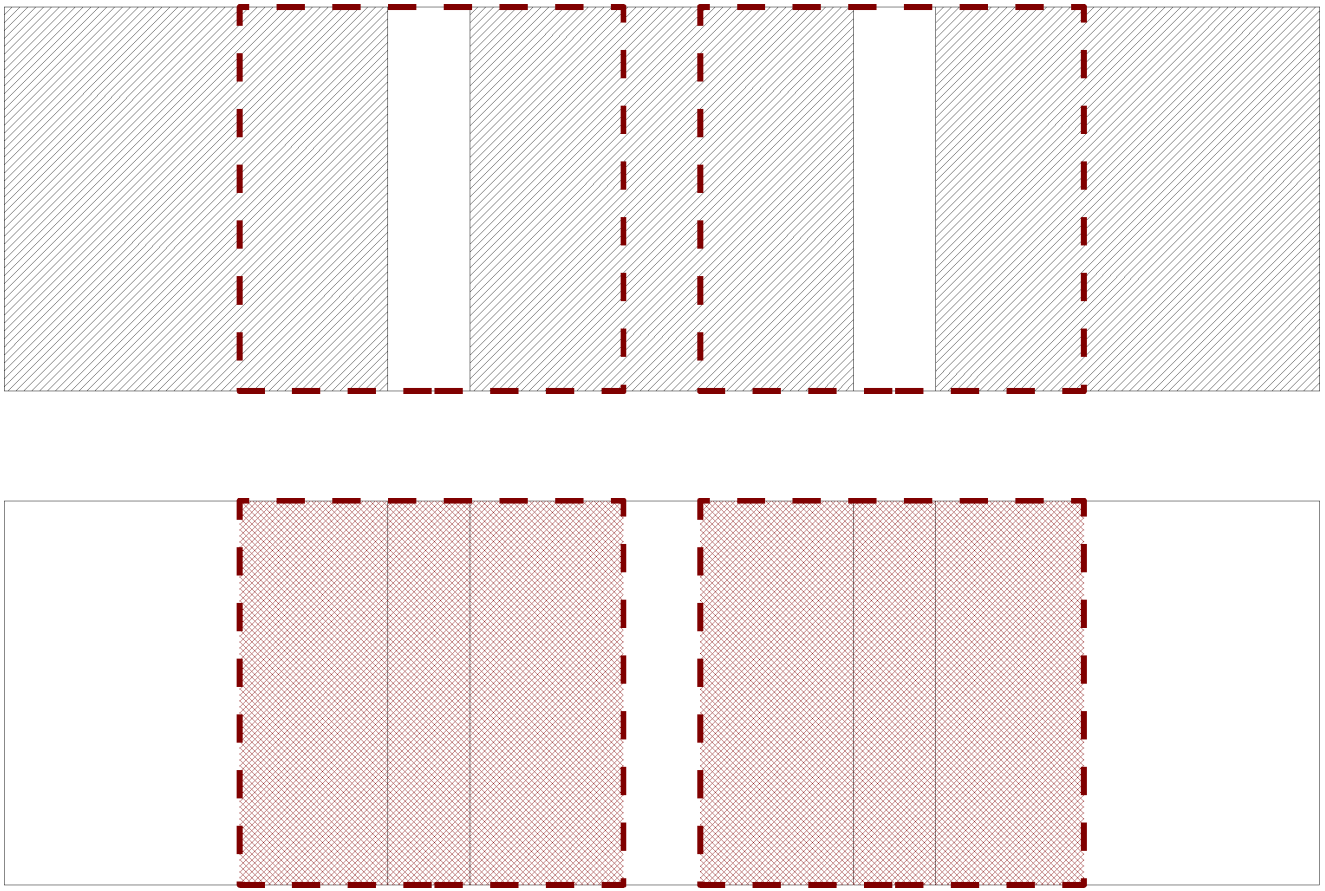
Usually, we construct **S** (from **R**) by changing the position of *one* randomly chosen molecule within a cube of sizes $\Delta x, \Delta y, \Delta z$.

$\Rightarrow E(\mathbf{S}) - E(\mathbf{R})$ is not too large $\Rightarrow$ reasonable $p_{\mathrm{acc}}(\mathbf{S}|\mathbf{R})$.

Cluster algorithms: move more than one molecule at a time, need proper bias in $\alpha(\mathbf{S}|\mathbf{R})$ to retrieve a reasonable acceptance.



Parallelization schemes: Domain decomposition



Parallelization schemes: Domain decomposition

Features:

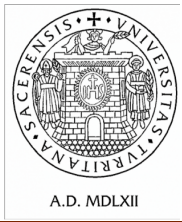
It avoids conflicts at the boundaries.

The sampling algorithm within each subdomain is still the same.

It converges to the same equilibrium measure.

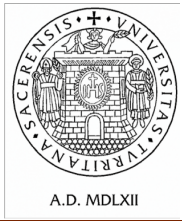
Good for large systems.

The nature of the algorithm is still *asynchronous*.



Question:

Can we build a *synchronous-from-birth* Boltzmannian Monte Carlo algorithm?



Back to basics: cellular automata

Cellular automata (CA): synchronous systems introduced to model non-equilibrium meso- and macroscale phenomena.

Definition

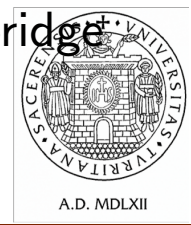
Multi-dimensional grids of identical cells (automata).

At each time step, in each cell a transformation operator, Ω (deterministic or stochastic), processes the state, $\mathbf{s}(r,t)$ of the cell itself, r, together with the state of the neighboring cells, $\mathcal{N}_r$, to produce the new state of r:

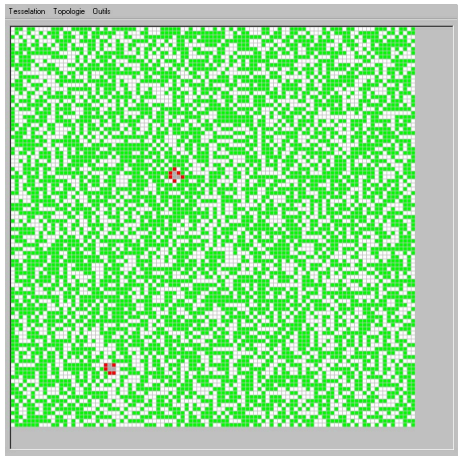
$$\Omega : \{\mathbf{s}(r,t), \mathbf{s}(\mathcal{N}_r,t)\} \mapsto \mathbf{s}(r,t+\tau). \tag{8}$$

At each time step, all the cells are processed simultaneously.

B. Chopard and M. Droz, *Cellular Automata Modeling of Physical Systems*, Cambridge University Press, 1998.



Back to basics: cellular automata



Effective in the simulation of non-equilibrium phenomena.

Conserved quantities might be a problem.

For example: conservation of mass.

Back to basics: cellular automata

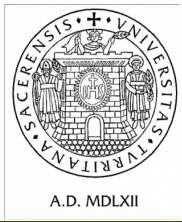
Solution: lattice gas automata

- Also known as *Partitioning Cellular Automata*, they evolve through a Randomization-Propagation algorithm.
- Every cell is made of several channels.
- Randomization ($\mathcal{R}$): changes the internal cell configuration without affecting the local mass.
- Propagation ($\mathcal{P}$): connected channels (belonging to neighboring cells) exchange matter.

$$\Omega = \mathcal{P} \circ \mathcal{R} : \{\mathbf{s}(r,t), \mathbf{s}(\mathcal{N}_r, t)\} \mapsto \mathbf{s}(r, t+\tau). \tag{9}$$

D. Dab et al., *Phys. Rev. Lett.* **64**, 2462-2465 (1990).

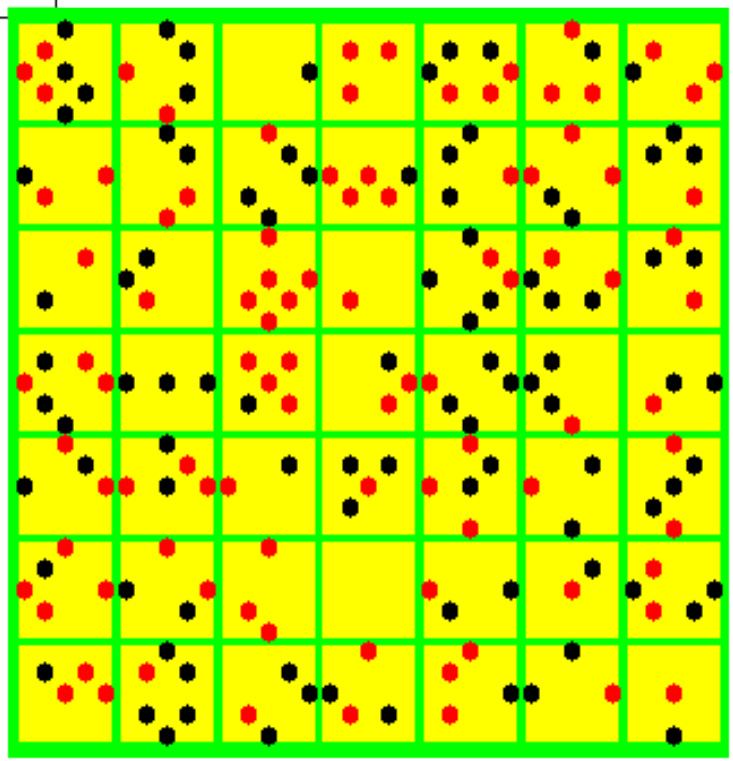
J. P. Boon et al., *Phys. Rep.* **273**, 55-147 (1996).



Back to basics: cellular automata

RANDOMIZATION: each cell independently

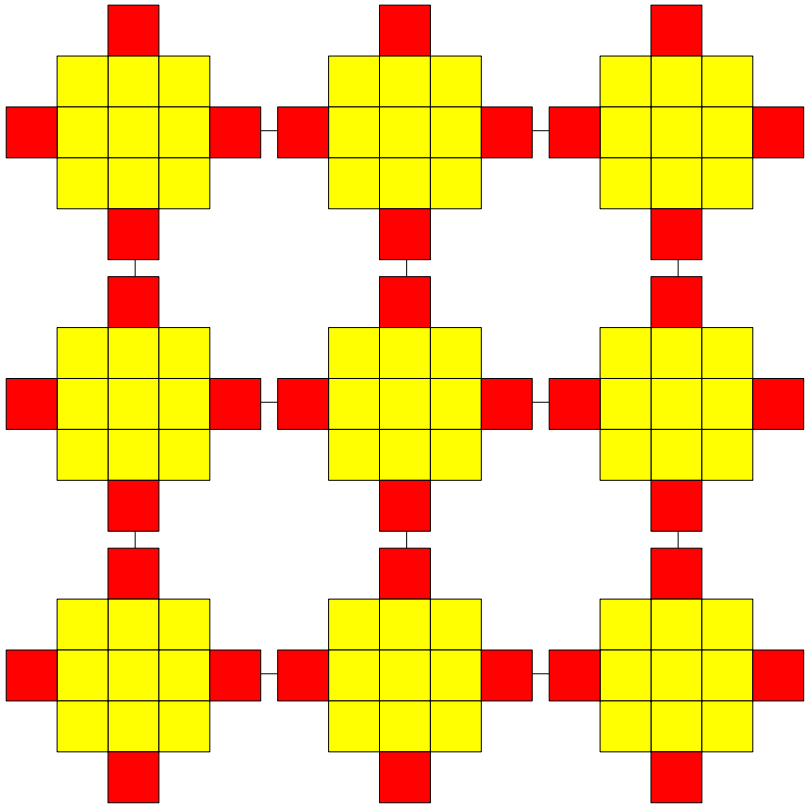
clock=1



P. Demontis, F. G. Pazzona, and G. B. Suffritti, *J. Chem. Phys.* **126**, 194709 and 194710 (2007)

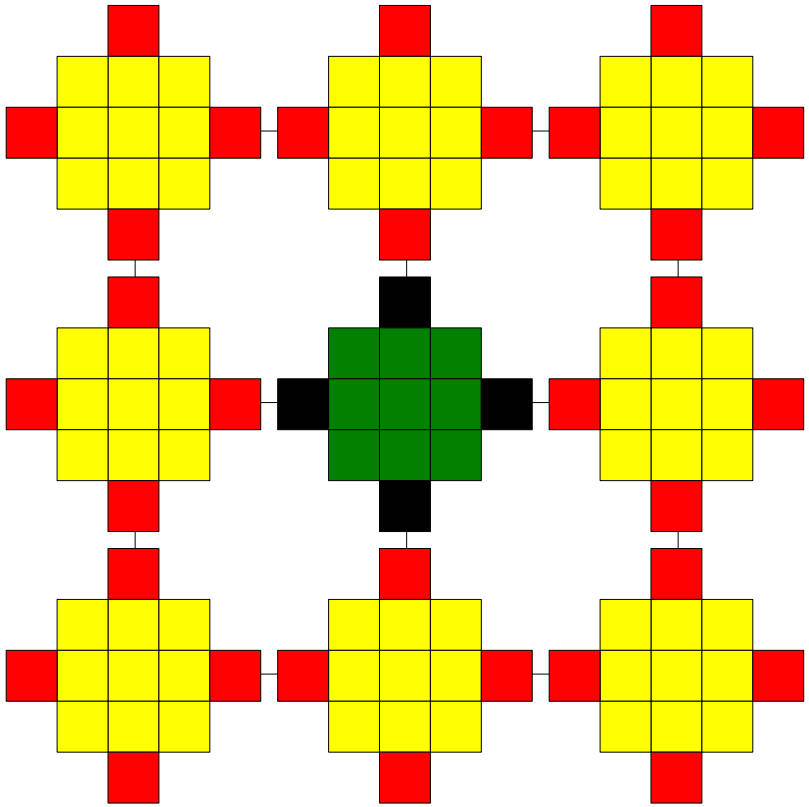
Problem of detailed balance in LGCA

Let us consider a lattice of LGCA cells, evolving through the Randomization-Propagation algorithm:



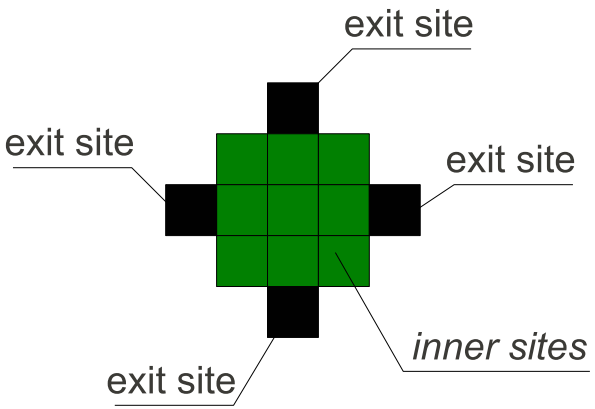
Problem of detailed balance in LGCA

Interactions are defined locally: $H[\mathbf{s}(\mathcal{L}, t)] = \sum_{r \in \mathcal{L}} H[\mathbf{s}(r, t)]$.



Problem of detailed balance in LGCA

To converge to $P(\mathbf{s}_{\mathcal{L}}) \propto e^{-\beta H[\mathbf{s}(\mathcal{L})]}$, the exit sites must *not* interact with each other. Otherwise, Propagation cannot be fully synchronous.



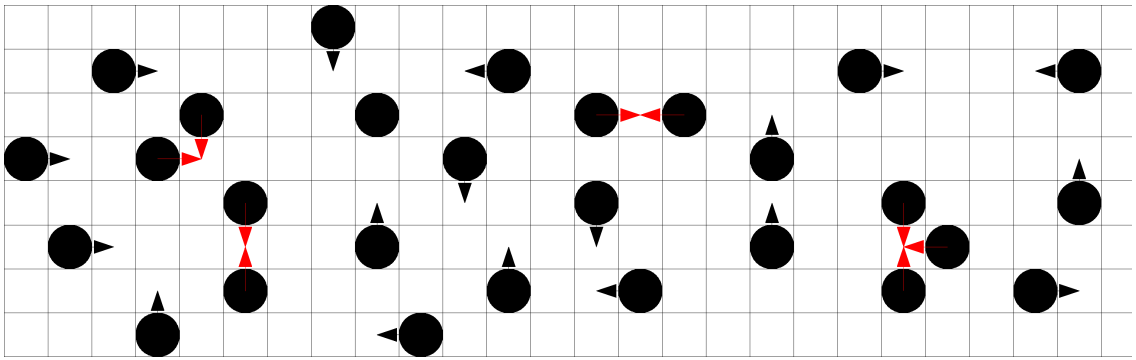
F. G. Pazzona, P. Demontis, and G. B. Suffritti, *J. Chem. Phys.* **131**, 234703 and 234704 (2009).

Synchronous Kawasaki lattice gas: Traditional conflicts

Mutually exclusive particles diffusing synchronously on lattice sites.

Problem:

More than one particle pointing to the same site: overlapping $\Rightarrow$ violation of mutual exclusion.



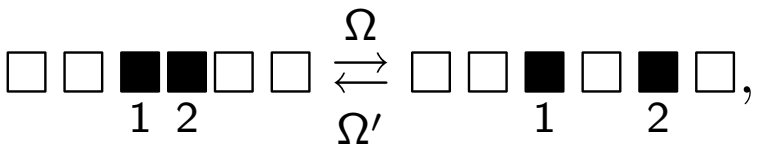
Synchronous Kawasaki lattice gas: Traditional conflicts

Solution:

A particle pointing to a neighboring site can reach it if it is empty and the remaining neighboring sites are empty as well.

New problem:

Full synchronicity $\Rightarrow$ no detailed balance.



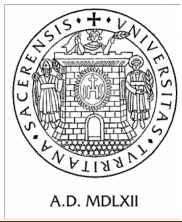
$$\Omega = P(P_0 + P) \qquad \Omega' = 0 \tag{10}$$

Synchronous Kawasaki lattice gas: Traditional conflicts

Conflicts can be solved synchronously and reversibly (under a probabilistic point of view) by means of a 'democratic' criterion:

Prescription ONE:

Empty sites can be pointed to and reached by a particle in a neighboring site, whereas occupied sites can be pointed to but cannot be reached.



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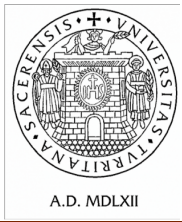
Prescription TWO:

If two or more particles point to the same site, no one of them will be allowed to reach it.



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Prescription TWO:

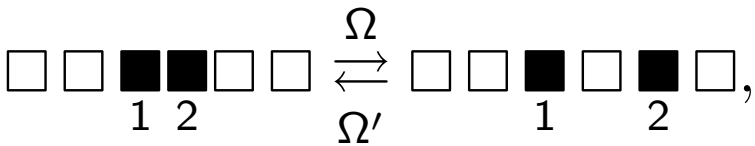
If two or more particles point to the same site, no one of them will be allowed to reach it.

Prescription THREE:

If one or more particles are pointing to a site occupied by another particle, that particle must stay at rest.

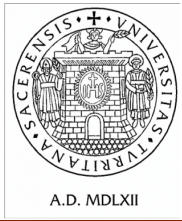
F. G. Pazzona, P. Demontis, and G. B. Suffritti, *Phys. Rev. E* **87**, 063306 (2013).

Synchronous Kawasaki lattice gas: Traditional conflicts



$$\Omega = P_0 P \qquad \Omega' = P_0 P \tag{11}$$

F. G. Pazzona, P. Demontis, and G. B. Suffritti, *Phys. Rev. E* **87**, 063306 (2013).



Synchronous Kawasaki: evolution rule

$$n^{t+\tau}(r) - n^t(r) = \omega^t_{+1}(r)\big[1 - n^t(r)\big] - \omega^t_{-1}(r)n^t(r), \tag{12}$$

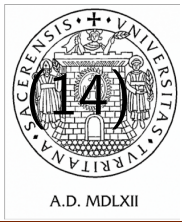
where ω_{+1} and ω_{-1} are creation and annihilation operators:

$$\omega^t_{+1}(r) = \sum_{r' \in \mathcal{I}(r)} \xi^t(r', r) n^t(r') \chi(r, \boldsymbol{\eta}^t),$$

$$\omega^t_{-1}(r) = \sum_{r' \in \mathcal{I}(r)} \xi^t(r, r') \big[1 - n^t(r')\big] \chi(r, \boldsymbol{\eta}^t), \tag{13}$$

The term $\chi(r, \boldsymbol{\eta})$ implements prescriptions (ii) and (iii) into the rule:

$$\chi(r, \boldsymbol{\eta}^t) = \prod_{\substack{r'' \in \mathcal{I}(r') \\ r'' \neq r}} \Big[1 - \xi^t(r'', r') n^t(r'')\Big] \prod_{\substack{r''' \in \mathcal{I}(r) \\ r''' \neq r'}} \Big[1 - \xi^t(r''', r) n^t(r''')\Big],$$



Synchronous Kawasaki: evolution rule

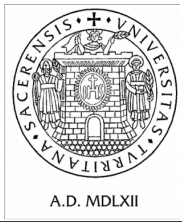
The third prescription, stating that

> *If one or more particles are pointing to a site occupied by another particle, that particle must stay at rest*,

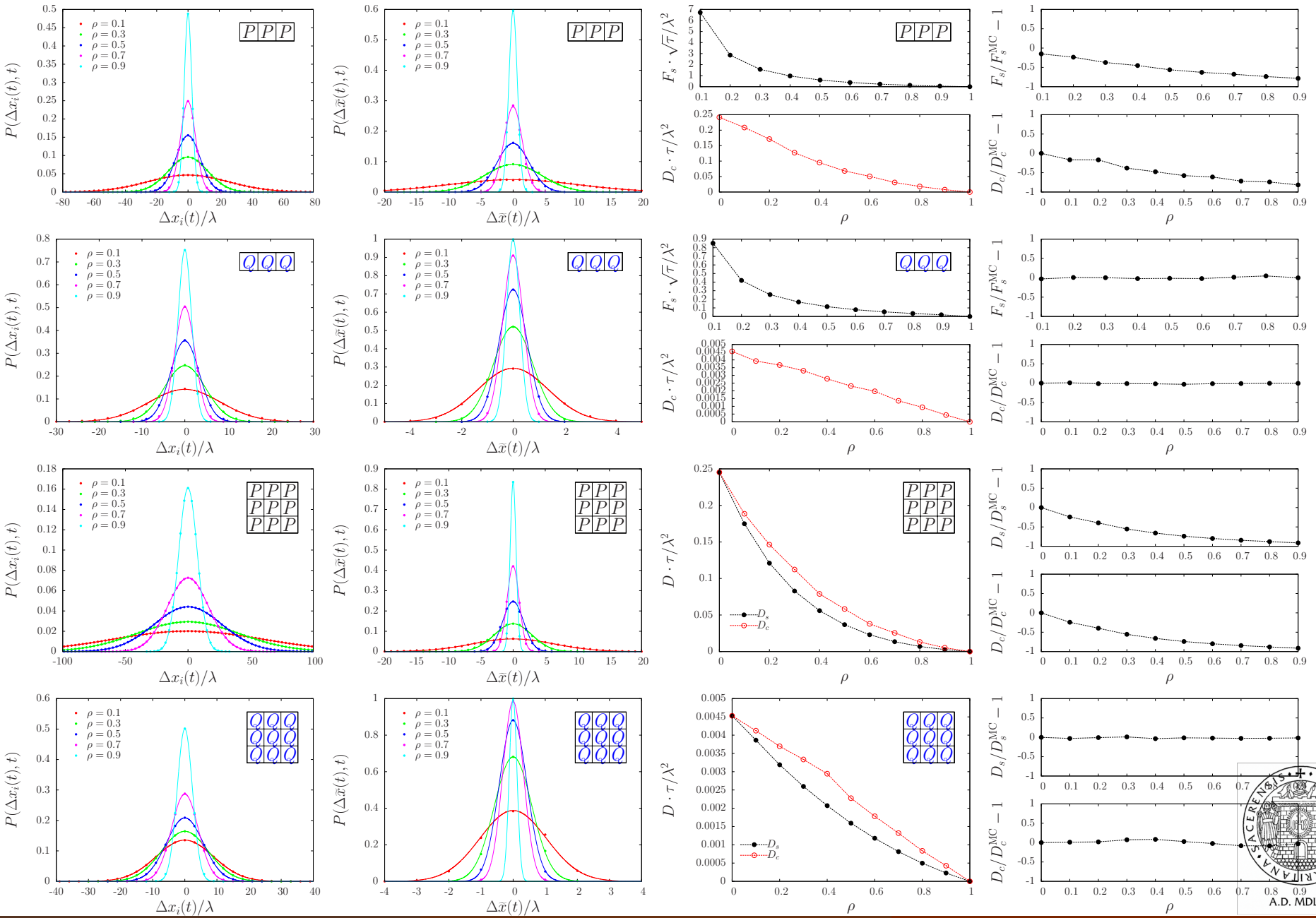
is hard to interpret from a microdynamical point of view.
However, it is necessary to ensure that detailed balance be satisfied,

and

it does not prevent the model from exhibiting 'well behaving' diffusion properties.



Synchronous Kawasaki: evolution rule



Synchronous Kawasaki: Macroscopic limit

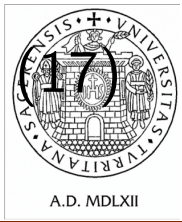
$$\Delta_\tau n_{x,y} = \Delta_\tau n^{\rightarrow}_{x,y} + \Delta_\tau n^{\leftarrow}_{x,y} + \Delta_\tau n^{\uparrow}_{x,y} + \Delta_\tau n^{\downarrow}_{x,y}, \tag{15}$$

where

$$\begin{aligned}
\Delta_\tau n^{\rightarrow}_{x,y} = & [(1-n_{x,y})n_{x+\lambda,y}\xi^{\leftarrow}_{x+\lambda,y} - n_{x,y}\xi^{\rightarrow}_{x,y}(1-n_{x+\lambda,y})] \\
& \times (1-n_{x+2\lambda,y}\xi^{\leftarrow}_{x+2\lambda,y})(1-n_{x+\lambda,y+\lambda}\xi^{\downarrow}_{x+\lambda,y+\lambda}) \\
& \times (1-n_{x+\lambda,y-\lambda}\xi^{\uparrow}_{x+\lambda,y-\lambda})(1-n_{x-\lambda,y}\xi^{\rightarrow}_{x-\lambda,y}) \\
& \times (1-n_{x,y+\lambda}\xi^{\downarrow}_{x,y+\lambda})(1-n_{x,y-\lambda}\xi^{\uparrow}_{x,y-\lambda}),
\end{aligned} \tag{16}$$

$$\begin{aligned}
\Delta_\tau n^{\leftarrow}_{x,y} = & [(1-n_{x,y})n_{x-\lambda,y}\xi^{\rightarrow}_{x-\lambda,y} - n_{x,y}\xi^{\leftarrow}_{x,y}(1-n_{x-\lambda,y})] \\
& \times (1-n_{x-2\lambda,y}\xi^{\rightarrow}_{x-2\lambda,y})(1-n_{x-\lambda,y+\lambda}\xi^{\downarrow}_{x-\lambda,y+\lambda}) \\
& \times (1-n_{x-\lambda,y-\lambda}\xi^{\uparrow}_{x-\lambda,y-\lambda})(1-n_{x+\lambda,y}\xi^{\leftarrow}_{x+\lambda,y}) \\
& \times (1-n_{x,y+\lambda}\xi^{\downarrow}_{x,y+\lambda})(1-n_{x,y-\lambda}\xi^{\uparrow}_{x,y-\lambda}),
\end{aligned} \tag{17}$$

etc.

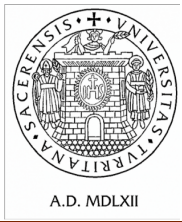


Synchronous Kawasaki: Macroscopic limit

- ε is the site adsorption energy;
- ψ_x, ψ_y are migration barriers along the x and the y directions.

Pointing probabilities:

$$\begin{aligned} \langle \xi^{\leftarrow}_{x+q\lambda,y+w\lambda} \rangle &= \langle \xi^{\rightarrow}_{x+q\lambda,y+w\lambda} \rangle = \frac{1}{4} e^{-\beta\psi_x} e^{\beta\varepsilon}, \\ \langle \xi^{\downarrow}_{x+q\lambda,y+w\lambda} \rangle &= \langle \xi^{\uparrow}_{x+q\lambda,y+w\lambda} \rangle = \frac{1}{4} e^{-\beta\psi_y} e^{\beta\varepsilon}. \end{aligned} \tag{18}$$

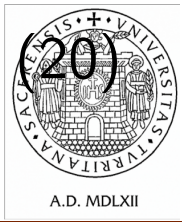


Synchronous Kawasaki: Macroscopic limit

$$\begin{aligned}\langle \Delta_\tau n_{x,y} \rangle = \tfrac{1}{4} e^{\beta\varepsilon} \Big\{ & - \langle n_{x,y} \rangle \left(2e^{-\beta\psi_x} + 2e^{-\beta\psi_y} \right) \\ & + e^{-\beta\psi_x} \left[\langle n_{x+\lambda,y} \rangle + \langle n_{x-\lambda,y} \rangle \right] \\ & + e^{-\beta\psi_y} \left[\langle n_{x,y+\lambda} \rangle + \langle n_{x,y-\lambda} \rangle \right] \\ & + C_1 e^{-\beta\psi_x} + C_2 e^{-\beta\psi_y} + \cdots \Big\}, \end{aligned} \tag{19}$$

where the coefficients $C_1, C_2, \ldots$ are sums of several two- up to seven-body static correlation functions of the form $\langle n_{x_1,y_1} n_{x_2,y_2} \cdots n_{x_k,y_k} \cdots \rangle$.
Assumptions: (i) local densities fluctuating closely around stationarity, and (ii) symmetry of static correlation functions. Taylor expansion:

$$\begin{aligned} \langle n_{i\pm1,j} \rangle &= \rho \pm \lambda \partial_x \rho + \frac{\lambda^2}{2} \partial_x^2 \rho + O(\lambda^3), \\ \langle n_{i,j\pm1} \rangle &= \rho \pm \lambda \partial_y \rho + \frac{\lambda^2}{2} \partial_y^2 \rho + O(\lambda^3), \end{aligned} \tag{20}$$



Synchronous Kawasaki: Macroscopic limit

We get

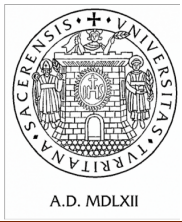
$$\tau\partial_t\rho + \frac{\tau^2}{2}\partial_t^2\rho + O(\tau^3) = \frac{\lambda^2}{4}e^{\beta\varepsilon}\left\{e^{-\beta\psi_x}\partial_x^2\rho + e^{-\beta\psi_y}\partial_y^2\rho\right\} + O(\lambda^3). \quad (21)$$

Diffusion process: $\lambda \to 0$, $\tau \to 0$ with $\lambda^2/\tau = \textit{constant}$.

$$\partial_t\rho = D_x\partial_x^2\rho + D_y\partial_y^2\rho, \quad (22)$$

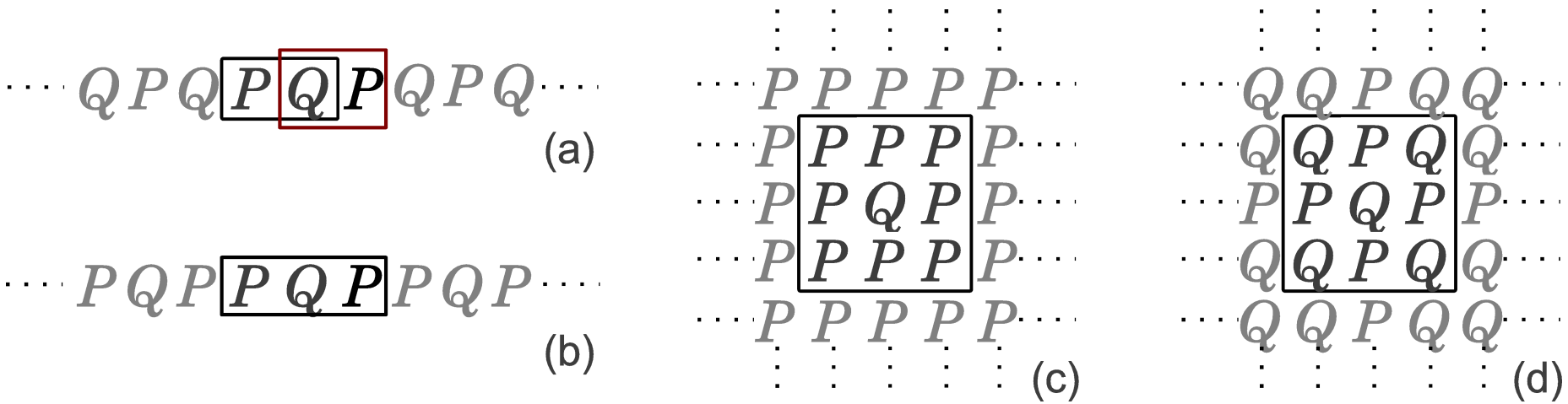
where

$$D_x = \frac{\lambda^2}{4\tau}e^{\beta(\varepsilon-\psi_x)}, \qquad D_y = \frac{\lambda^2}{4\tau}e^{\beta(\varepsilon-\psi_y)}. \quad (23)$$



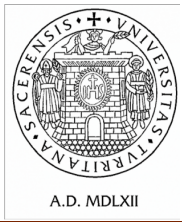
Synchronous Kawasaki: Macroscopic limit

In the presence of heterogeneous adsorption sites



$$D = \frac{\lambda^2}{4K\rho\tau}\left\{ f_P \frac{e^{\beta(\mu-\psi)}}{1+e^{\beta(\mu-\varepsilon_P)}} + f_Q \frac{e^{\beta(\mu-\psi)}}{1+e^{\beta(\mu-\varepsilon_Q)}} \right\}, \tag{24}$$

$$\rho = \frac{K_P}{K}\frac{e^{\beta(\mu-\varepsilon_P)}}{1+e^{\beta(\mu-\varepsilon_P)}} + \frac{K_Q}{K}\frac{e^{\beta(\mu-\varepsilon_Q)}}{1+e^{\beta(\mu-\varepsilon_Q)}}. \tag{25}$$



Synchronous Kawasaki: Explicit interactions

For a lone particle:

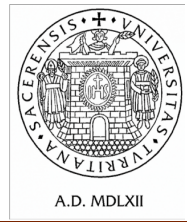
$$p(r,r') = \begin{cases} \dfrac{1}{\nu_{\mathrm{m}}} e^{\beta n(r)[\varepsilon(r)-\psi(r,r')]}, & r \neq r', \\ 1 - \displaystyle\sum_{r'' \in \mathcal{I}(r)} p(r,r''), & r = r'. \end{cases} \tag{26}$$

Neighbor-interacting:

$$\widetilde{p}(r,r') = \begin{cases} \dfrac{p(r,r')}{Z(r,\boldsymbol{\eta}(r))} \Big[\overline{n}(r')\theta + n(r')\phi\Big], & r \neq r', \\ \dfrac{p(r,r)}{Z(r,\boldsymbol{\eta}(r))}, & r = r'. \end{cases} \tag{27}$$

with $Z(r,\boldsymbol{\eta}(r)) = p(r,r) + \displaystyle\sum_{r' \in \mathcal{I}(r)} p(r,r') \Big[\overline{n}(r')\theta + n(r')\phi\Big]$.

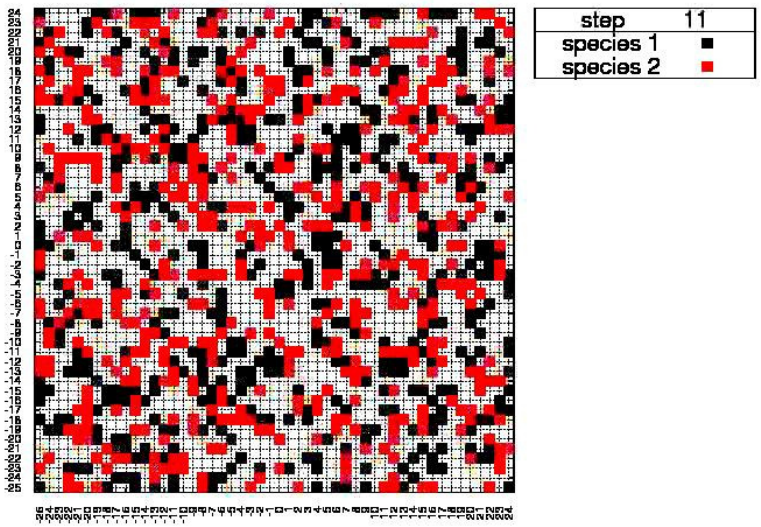
F. G. Pazzona, P. Demontis, and G. B. Suffritti, *Phys. Rev. E* **88**, 062114 (2013).

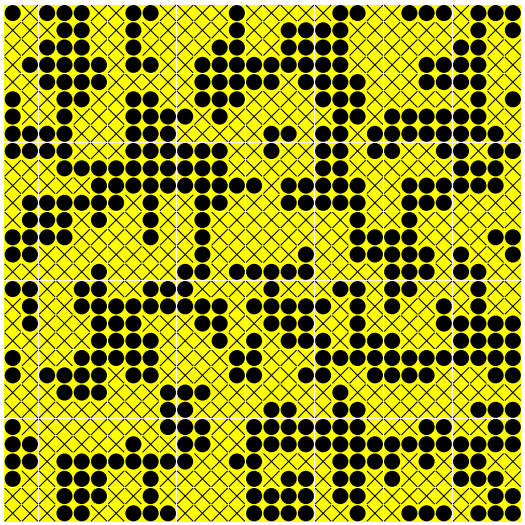


Synchronous Kawasaki: Explicit interactions

θ: multiplies $\overline{n}(r') = 1 - n(r')$. It defines interaction with empty neighbors.
ϕ: multiplies $n(r')$. It defines interaction with occupied neighbors.

- $\theta = \phi = 1$: only mutual exclusion;
- $\theta > 1, 0 \leq \phi < 1$: mutual exclusion + particle-particle repulsion;
- $0 < \theta < 1, \phi > 1$: mutual exclusion + particle-particle attraction.





Synchronous Kawasaki: Explicit interactions

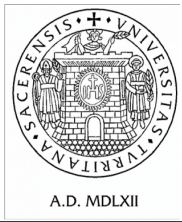
Detailed balance is satisfied.
The price we pay: non-Gibbsian equilibrium distribution.

$$P(\boldsymbol{\eta}) \propto \prod_{r \in \mathcal{L}} \left[e^{-\beta \varepsilon(r)} Z(r, \boldsymbol{\eta}(r)) \right]^{n(r)}. \tag{28}$$

Pseudo-Hamiltonian:

$$\mathcal{H}_\beta(\boldsymbol{\eta}) = \sum_{r \in \mathcal{L}} n(r)\varepsilon(r) - \sum_{r \in \mathcal{L}} \frac{n(r)}{\beta} \ln \left\{ e^{-\beta \varepsilon(r)} \right. \tag{29}$$

$$\left. - \sum_{r' \in \mathcal{I}(r)} \frac{e^{-\beta \psi(r,r')}}{\nu_{\mathrm{m}}} \left[1 - \theta + (\theta - \phi) n(r') \right] \right\}. \tag{30}$$



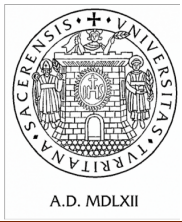
Synchronous Ising model (Little's model)

Pseudo-Hamiltonian of Little's model:

$$\mathcal{H}_\beta(\boldsymbol{\sigma}) = -\beta^{-1} \sum_i \ln \left[2 \cosh \left(\beta \sum_j J_{ij}\sigma_j + \theta_i \right) \right] - \sum_i \sigma_i \theta_i, \qquad (31)$$

J_{ij}: the spin-spin interaction between node i and node j,
θ_i: an external field.

W. A. Little, *Math. Biosci.* **19**, 101 (1974).



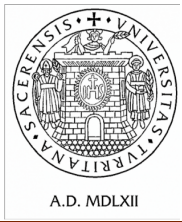
Synchronous Kawasaki: homogeneous 1-D, exact solution

We obtain a third-order finite difference equation for the grand-canonical p.f., Ξ_L, w.r.t. the size variable L:

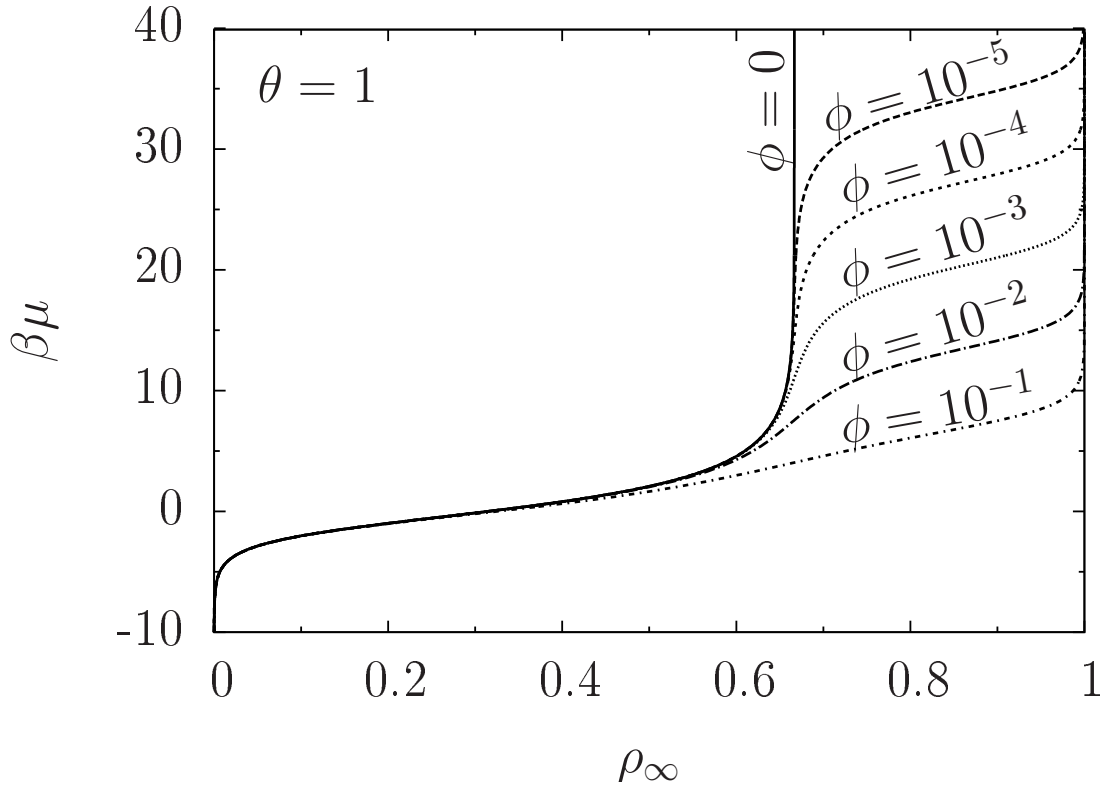
$$\Xi_{L+1} - [1 + \lambda(1 - y - 2x)]\Xi_L - 2\lambda x \Xi_{L-1} - \lambda^2 x^2 \Xi_{L-2} = 0, \qquad (32)$$

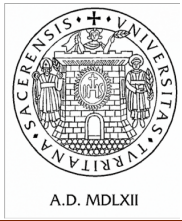
where

$$\lambda = e^{\beta(\mu-\varepsilon)}, \qquad y = e^{\beta(\varepsilon-\psi)}(1-\theta), \qquad x = \frac{e^{\beta(\varepsilon-\psi)}}{\nu}(\theta - \phi). \qquad (33)$$

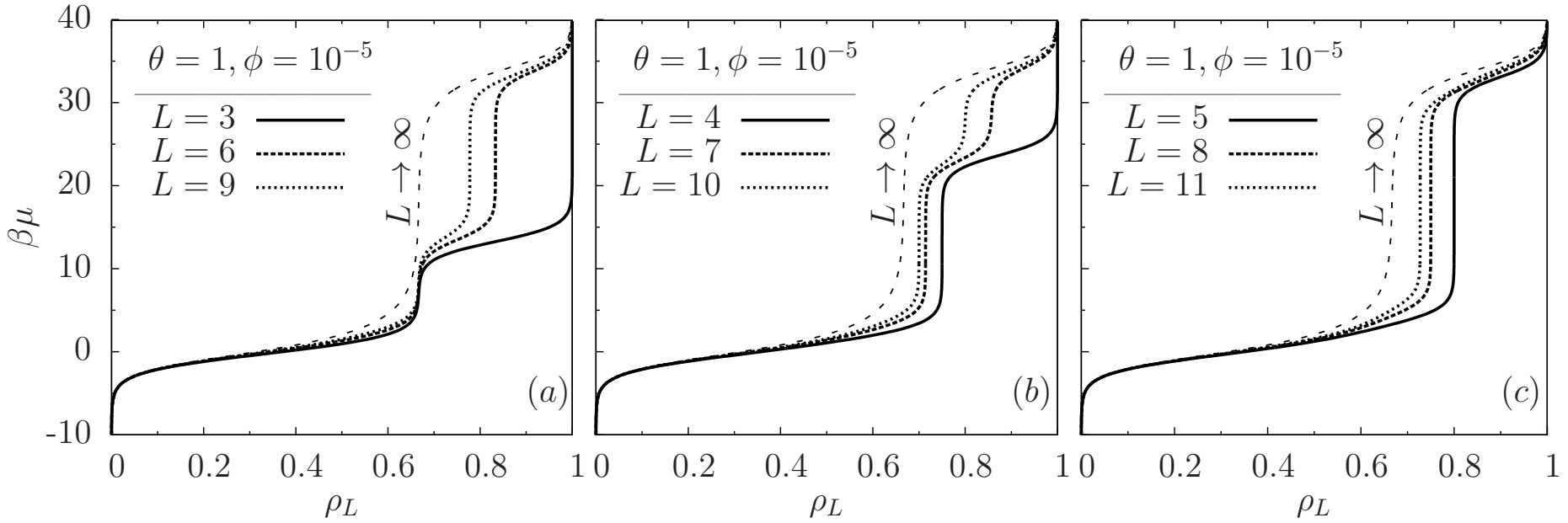


Synchronous Kawasaki: homogeneous 1-D, exact solution





Synchronous Kawasaki: homogeneous 1-D, exact solution



Synchronous Kawasaki

Which ideas can we transfer to off-lattice simulations?

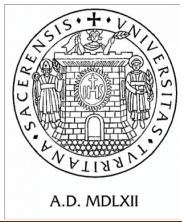
Choice of direction

It can be assumed to represent an intermediate state, **I**, in the transformation $\mathbf{R} \rightarrow \mathbf{S}$.

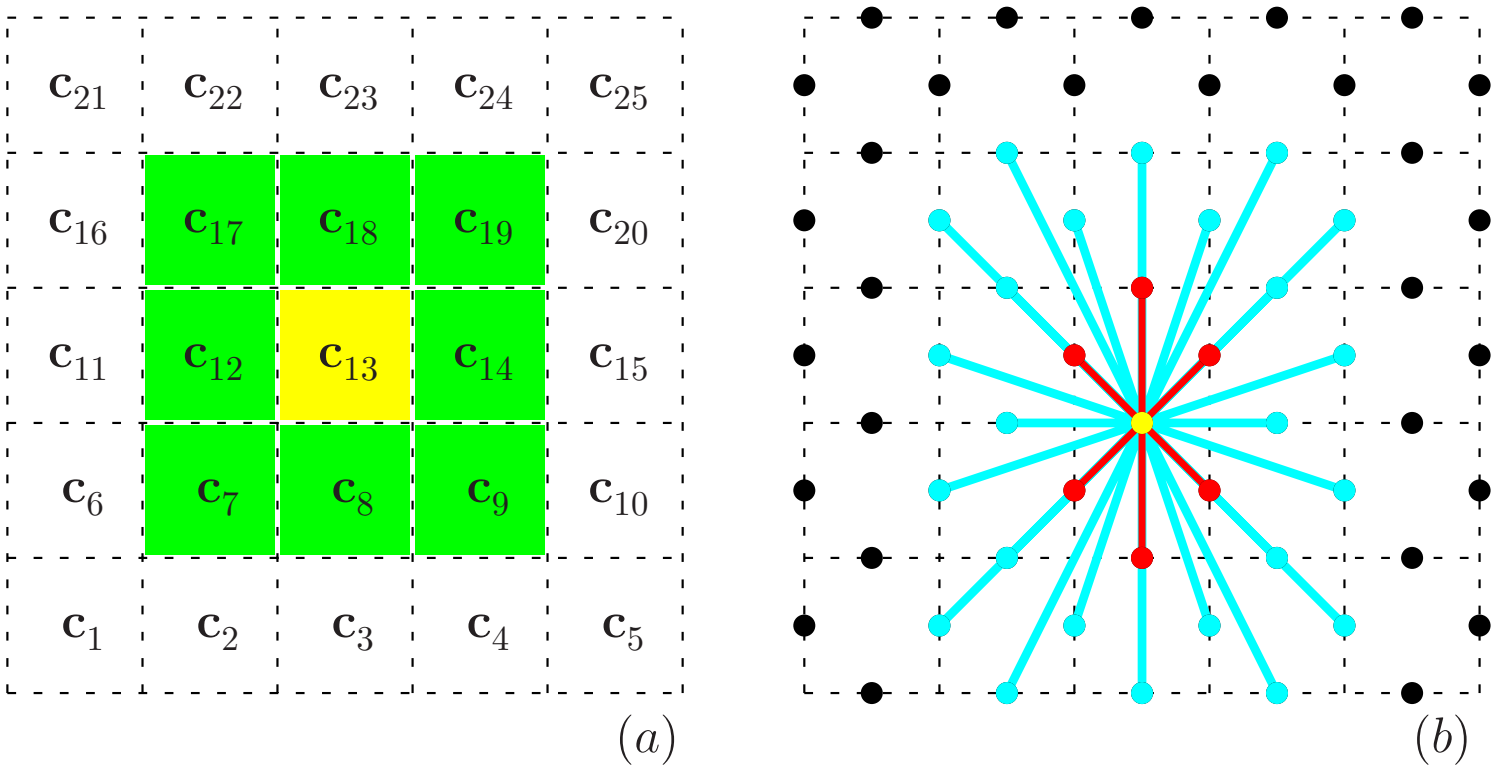
Provided that the intermediate state **I** can be reached with equal probability from both **R** and **S**, we can operate on **I** without breaking detailed balance.

Requirement

Operations on **I** must not depend on $\mathbf{R}, \mathbf{S}$.

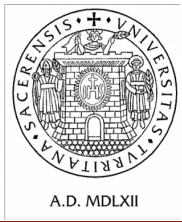


From lattice to off-lattice: Hard-Spheres



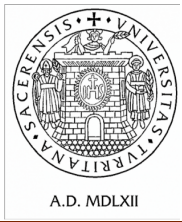
(a) Moore neighborhood (cells);

(b) Moore neighborhood (boundary sites).



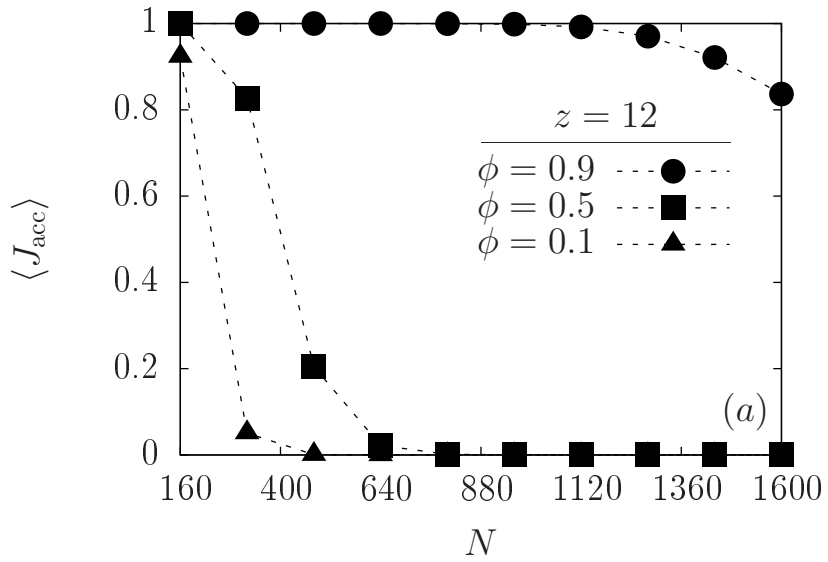
From lattice to off-lattice: Hard-Spheres

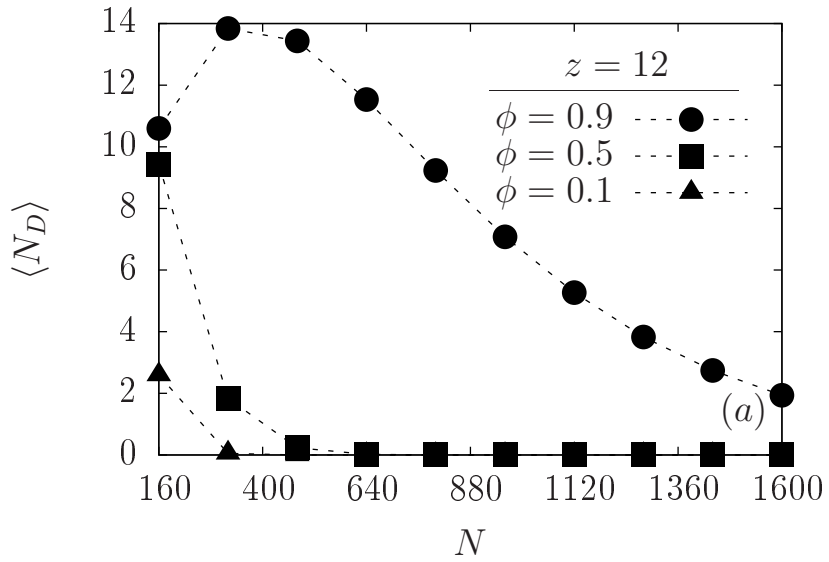
- $\mathcal{I} : \mathbf{R} \mapsto \mathbf{I}$. Every sphere jumps into one of the closest boundary sites w.p. q, or stay at rest w.p. $1 - 6q$.
- $\mathcal{D} : \mathbf{I} \mapsto \mathbf{I}'$. Boundary positions confirmed deterministically and 'democratically'.
- Fine discretization of every pair of connected cells; slight randomization of accessible positions.
- $\mathcal{W} : \mathbf{I}' \mapsto \mathbf{S}$. Every particle moves into an accessible position (*rejection-free*).

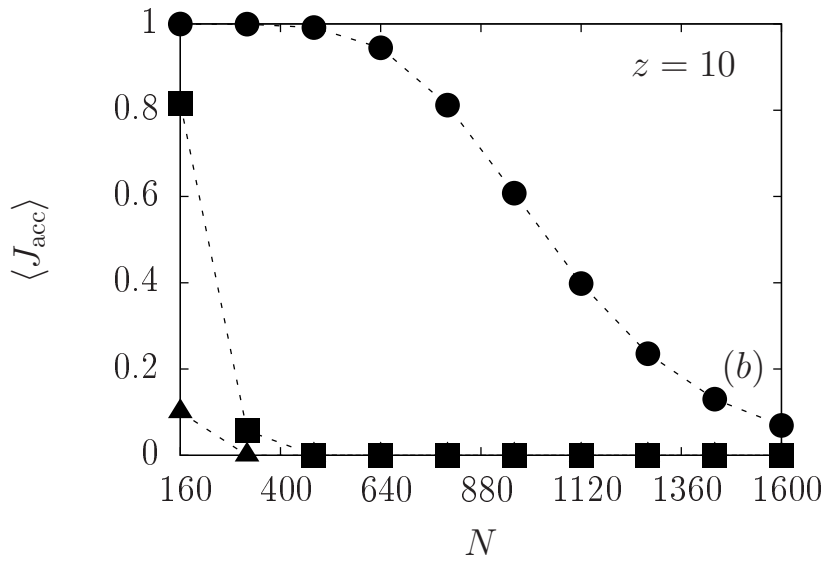


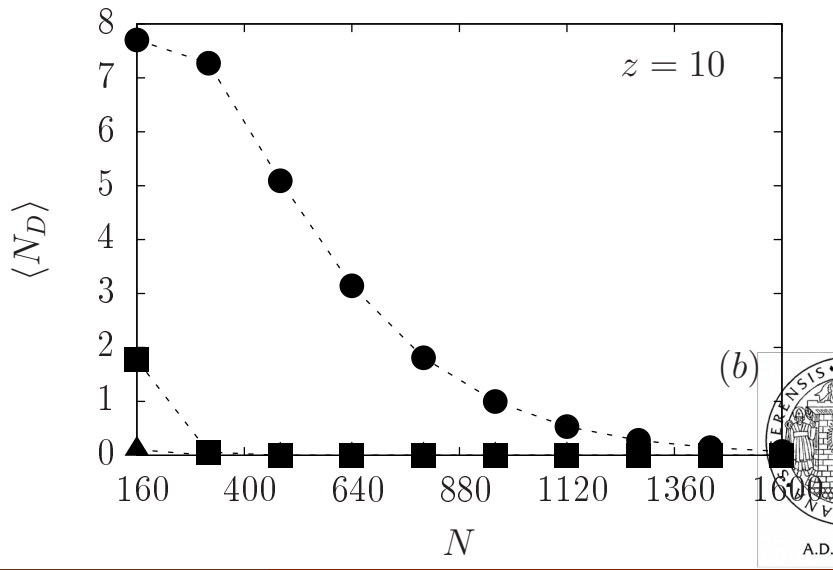
From lattice to off-lattice: Hard-Spheres

z : number of cells per side of the simulation box.









Intermediate states: A formal Markov Chain

Assumption: we are able to explore *all* the configurations that can be accessed from $\mathbf{R}^t$.

A formal Markov Chain with no Detailed Balance

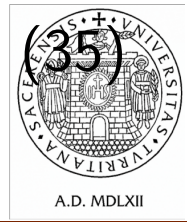
- Weigh every of such configuration (including $\mathbf{R}^t$) as $e^{-\beta U(\mathbf{R}')}$.
- $\mathbf{R}^{t+1} = \mathbf{S}$ with probability (extended Barker's rule)

$$p(\mathbf{S}|\mathbf{R}^t) = \frac{e^{-\beta U(\mathbf{S})}}{\displaystyle\int_{\mathbf{R}' \in \Gamma_{\mathbf{R}^t}} \mathrm{d}\mathbf{R}'\, e^{-\beta U(\mathbf{R}')}}. \tag{34}$$

A. A. Barker, *Aus. J. Phys.* **186**, 224106 (1965).

No detailed balance:

$$\frac{p(\mathbf{R}|\mathbf{S})}{p(\mathbf{S}|\mathbf{R})} = \frac{e^{-\beta U(\mathbf{R})}}{e^{-\beta U(\mathbf{S})}} \frac{\displaystyle\int_{\mathbf{R}' \in \Gamma_{\mathbf{R}}} \mathrm{d}\mathbf{R}'\, e^{-\beta U(\mathbf{R}')}}{\displaystyle\int_{\mathbf{S}' \in \Gamma_{\mathbf{S}}} \mathrm{d}\mathbf{S}'\, e^{-\beta U(\mathbf{S}')}}. \tag{35}$$



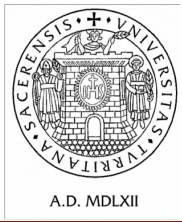
Intermediate states: A formal Markov Chain

$$\frac{\int_{\mathbf{R}' \in \Gamma_{\mathbf{R}}} \mathrm{d}\mathbf{R}'\, e^{-\beta U(\mathbf{R}')}}{\int_{\mathbf{S}' \in \Gamma_{\mathbf{S}}} \mathrm{d}\mathbf{S}'\, e^{-\beta U(\mathbf{S}')}} \text{ represents a bias term.}$$

Not present in the 2-states (original) Barker's rule.

It would disappear if we could manage to restrict the integrals to $\Gamma_{\mathbf{RS}} = \Gamma_{\mathbf{R}} \cap \Gamma_{\mathbf{S}}$.

But again we need to know in advance the trial configuration $\mathbf{S}$
$\Rightarrow$ sequential sampling!



Intermediate states: A formal Markov Chain

Solution: use of an intermediate state, $\mathbf{I}$.

$$\mathbf{R} \to \mathbf{I} \to \mathbf{S}.$$

A formal Markov Chain with Detailed Balance

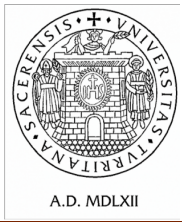
- Select $\mathbf{I}$ from $\Gamma_{\mathbf{R}}$ with *homogeneous* probability $p(\mathbf{I}|\mathbf{R})$.
- List all the possible configurations reachable from $\mathbf{I}$: $\int_{\mathbf{R}' \in \Gamma_{\mathbf{I}}} \mathrm{d}\mathbf{R}'\, e^{-\beta U(\mathbf{R}')}$.
- Any configuration (say $\mathbf{S}$) out of such list can be selected as the new configuration, according to the probability

$$p(\mathbf{S}|\mathbf{I}) = \frac{e^{-\beta U(\mathbf{S})}}{\int_{\mathbf{R}' \in \Gamma_{\mathbf{I}}} \mathrm{d}\mathbf{R}'\, e^{-\beta U(\mathbf{R}')}}. \tag{36}$$

Intermediate states: A formal Markov Chain

Homogeneity: $p(\mathbf{I}|\mathbf{R}) = p(\mathbf{I}|\mathbf{S})$.
Detailed balance between forward and reverse path:

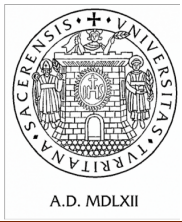
$$\frac{p(\mathbf{I}|\mathbf{S})p(\mathbf{R}|\mathbf{I})}{p(\mathbf{I}|\mathbf{R})p(\mathbf{S}|\mathbf{I})} = \frac{e^{-\beta U(\mathbf{R})}}{e^{-\beta U(\mathbf{S})}} =: \frac{p(\mathbf{R})}{p(\mathbf{S})}. \tag{37}$$



Intermediate states: A formal Markov Chain

Detailed balance for the whole Markov Chain:

$$\mathcal{K}(\mathbf{R} \to \mathbf{S}) = p(\mathbf{R}) \int_{\mathbf{I} \in \Gamma_{\mathbf{R}}} \mathrm{d}\mathbf{I}\, p(\mathbf{I}|\mathbf{R}) p(\mathbf{S}|\mathbf{I}), \tag{38}$$



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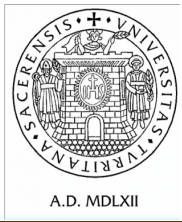
$$\mathcal{K}(\mathbf{R} \to \mathbf{S}) = p(\mathbf{R}) \int_{\mathbf{I} \in \Gamma_{\mathbf{R}} \cap \Gamma_{\mathbf{S}}} \mathrm{d}\mathbf{I}\, p(\mathbf{I}|\mathbf{R}) p(\mathbf{S}|\mathbf{I}). \tag{39}$$



Intermediate states: A formal Markov Chain

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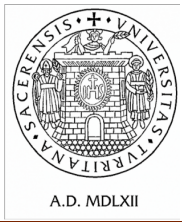
Reverse transition:

$$\mathcal{K}(\mathbf{S} \to \mathbf{R}) = p(\mathbf{S}) \int_{\mathbf{I} \in \Gamma_{\mathbf{R}} \cap \Gamma_{\mathbf{S}}} \mathrm{d}\mathbf{I}\, p(\mathbf{I}|\mathbf{S}) p(\mathbf{R}|\mathbf{I}). \tag{40}$$



Intermediate states: A formal Markov Chain

Detailed balance for the whole Markov Chain:

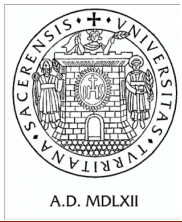
$$\mathcal{K}(\mathbf{R} \to \mathbf{S}) = p(\mathbf{R}) \int_{\mathbf{I} \in \Gamma_{\mathbf{R}}} \mathrm{d}\mathbf{I}\, p(\mathbf{I}|\mathbf{R}) p(\mathbf{S}|\mathbf{I}), \tag{38}$$

$$\mathcal{K}(\mathbf{R} \to \mathbf{S}) = p(\mathbf{R}) \int_{\mathbf{I} \in \Gamma_{\mathbf{R}} \cap \Gamma_{\mathbf{S}}} \mathrm{d}\mathbf{I}\, p(\mathbf{I}|\mathbf{R}) p(\mathbf{S}|\mathbf{I}). \tag{39}$$

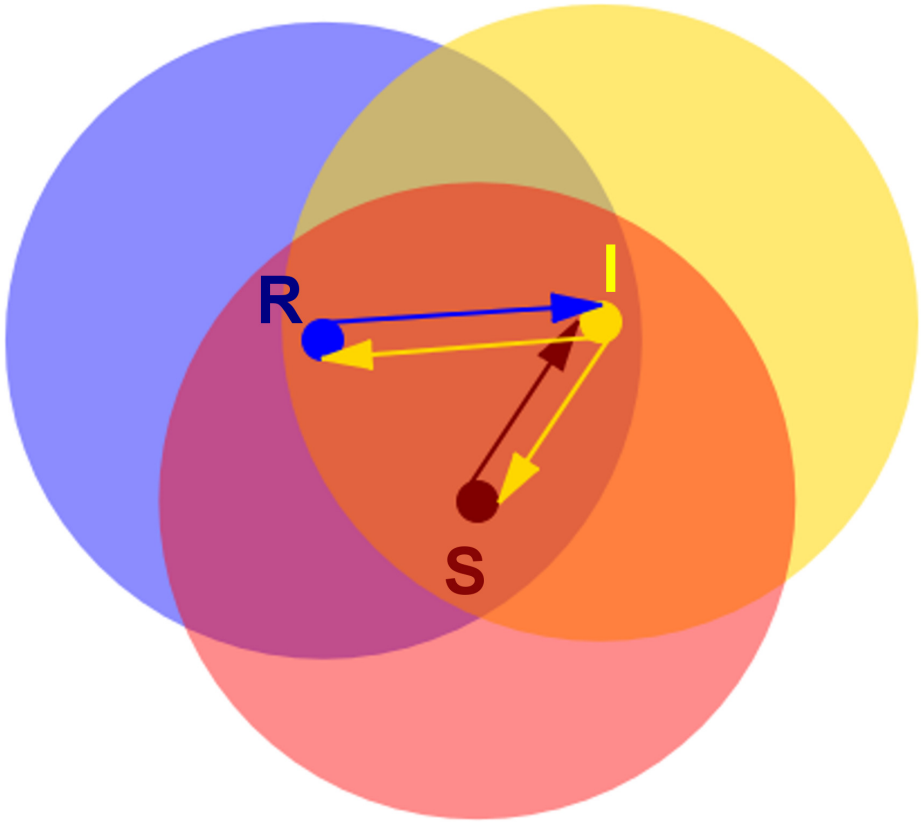
Reverse transition:

$$\mathcal{K}(\mathbf{S} \to \mathbf{R}) = p(\mathbf{S}) \int_{\mathbf{I} \in \Gamma_{\mathbf{R}} \cap \Gamma_{\mathbf{S}}} \mathrm{d}\mathbf{I}\, p(\mathbf{I}|\mathbf{S}) p(\mathbf{R}|\mathbf{I}). \tag{40}$$

By using $p(\mathbf{I}|\mathbf{S})p(\mathbf{R}|\mathbf{I}) = p(\mathbf{I}|\mathbf{R})p(\mathbf{S}|\mathbf{I})\dfrac{e^{-\beta U(\mathbf{R})}}{e^{-\beta U(\mathbf{S})}}$, we get $\mathcal{K}(\mathbf{S} \to \mathbf{R}) = \mathcal{K}(\mathbf{R} \to \mathbf{S})$.



Intermediate states



A Markov Chain with Detailed Balance

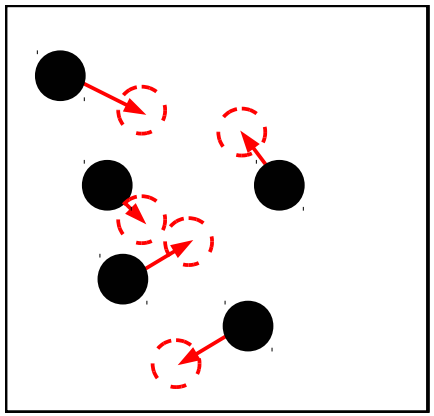
- Construct $\mathbf{I}$ by moving randomly all the particles, each within a maximum distance $\Delta\mathbf{r}$. $p(\mathbf{I}|\mathbf{R}) = q^N$ (homogeneous).
- Construct a set of K possible output configurations,

$$\{\mathbf{R}\}^K := \{\mathbf{R}^{(1)}, \mathbf{R}^{(2)}, \ldots, \mathbf{R}^{(K)}\}, \tag{41}$$

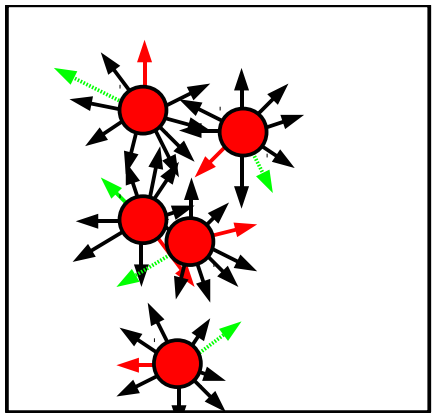
  with probability $p(\{\mathbf{R}\}^K|\mathbf{I}) = q^{NK}$ (again, maximum distance is $\Delta\mathbf{r}$).
- Any configuration (say $\mathbf{S}$) out of the list $\mathbf{R} \cup \{\mathbf{R}\}^K$ can be selected as the new configuration, according to the probability

$$p(\mathbf{S}|\mathbf{I}) = \frac{e^{-\beta U(\mathbf{S})}}{e^{-\beta U(\mathbf{R})} + \sum_{k=1}^{K} e^{-\beta U(\mathbf{R}^{(k)})}}. \tag{42}$$

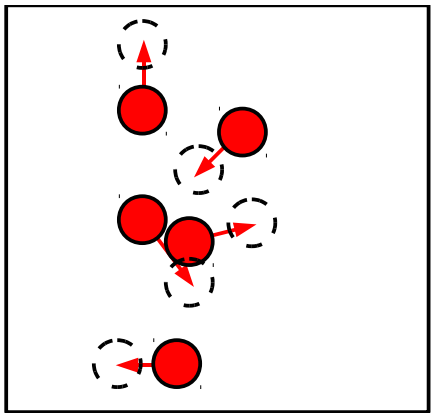
Intermediate states: From *formal* to *feasible*



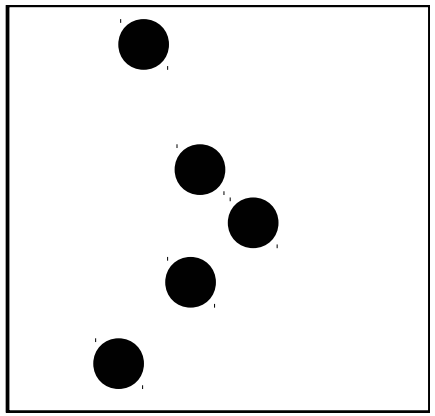
$$\mathbf{R}^t \rightarrow \mathbf{I}^t$$



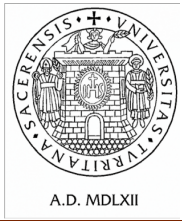
$$\mathbf{I}^t \rightarrow \{\mathbf{R}^t\}^K$$



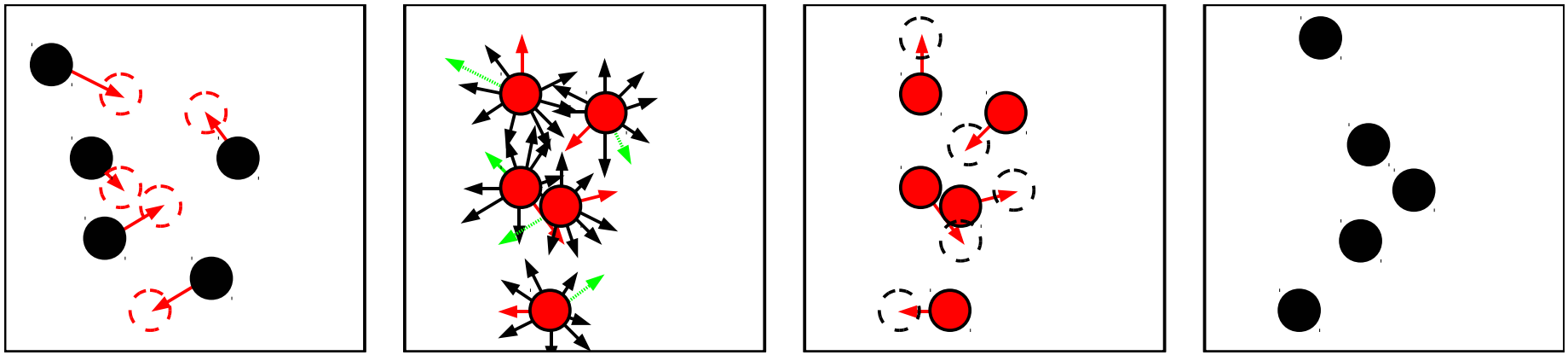
$$\{\mathbf{R}^t\}^K \rightarrow \mathbf{S}^t$$



$$\mathbf{R}^{t+\tau} = \mathbf{S}^t$$



Intermediate states: From *formal* to *feasible*



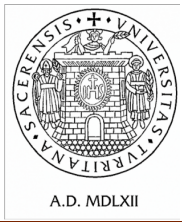
$$\mathbf{R}^t \rightarrow \mathbf{I}^t \qquad \mathbf{I}^t \rightarrow \{\mathbf{R}^t\}^K \qquad \{\mathbf{R}^t\}^K \rightarrow \mathbf{S}^t \qquad \mathbf{R}^{t+\tau} = \mathbf{S}^t$$

No bias $\Rightarrow \Delta\mathbf{r}$ must be small.

Intermediate states: From *formal* to *feasible*

Problem: overflow during the calculation of the statistical weights

$$w(\mathbf{S}^{(\ell)}) = \frac{e^{-\beta U(\mathbf{S}^{(\ell)})}}{e^{-\beta U(\mathbf{S}^{(0)})} + \sum_{k=1}^{K} e^{-\beta U(\mathbf{S}^{(k)})}}. \tag{43}$$



Intermediate states: From *formal* to *feasible*

Problem: overflow during the calculation of the statistical weights

$$w(\mathbf{S}^{(\ell)}) = \frac{e^{-\beta U(\mathbf{S}^{(\ell)})}}{e^{-\beta U(\mathbf{S}^{(0)})} + \sum_{k=1}^{K} e^{-\beta U(\mathbf{S}^{(k)})}}. \tag{43}$$

Solution: recurrence equation for $w(\mathbf{S}^{(\ell)}) =: w(\mathbf{S}^{(\ell)})$

$$w_0(\mathbf{S}^{(0)}) \tag{44}$$

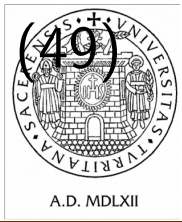
$$w_1(\mathbf{S}^{(0)}), w_1(\mathbf{S}^{(1)}) \tag{45}$$

$$w_2(\mathbf{S}^{(0)}), w_2(\mathbf{S}^{(1)}), w_2(\mathbf{S}^{(2)}) \tag{46}$$

$$\dots \tag{47}$$

$$w_K(\mathbf{S}^{(0)}), w_K(\mathbf{S}^{(1)}), \dots, w_K(\mathbf{S}^{(K)}) \tag{48}$$

$$\tag{49}$$



Intermediate states: From *formal* to *feasible*

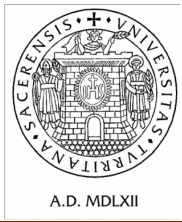
$$\ln \omega_k(\mathbf{S}^{(\ell)}) = \begin{cases} \ln \omega_{k-1}(\mathbf{S}^{(\ell)}), & f_{k-1} < f_{\mathrm{lo}} \\ \ln \omega_{k-1}(\mathbf{S}^{(\ell)}) - \ln\left(1 + e^{f_{k-1}}\right), & f_{\mathrm{lo}} < f_{k-1} < f_{\mathrm{up}} \\ \ln \omega_{k-1}(\mathbf{S}^{(\ell)}) - f_{k-1}, & f_{k-1} > f_{\mathrm{up}} \end{cases}, \tag{50}$$

where

$$f_{k-1} = \ln \omega_{k-1}(\mathbf{S}^{(0)}) - \beta \left[U(\mathbf{S}^{(k)}) - U(\mathbf{S}^{(0)}) \right], \tag{51}$$

starting from

$$\omega_0(\mathbf{S}^{(0)}) = 1. \tag{52}$$



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starting from

$$\omega_0(\mathbf{S}^{(0)}) = 1. \tag{52}$$

The thresholds f_{lo} and f_{up} are defined according to the assumptions

$$\begin{cases} \ln(1 + e^{f_{k-1}}) \approx e^{f_{k-1}} \approx 0 & f_{k-1} < f_{\mathrm{lo}} \\ \ln(1 + e^{f_{k-1}}) \approx f_{k-1} & f_{k-1} > f_{\mathrm{up}} \end{cases}. \tag{53}$$

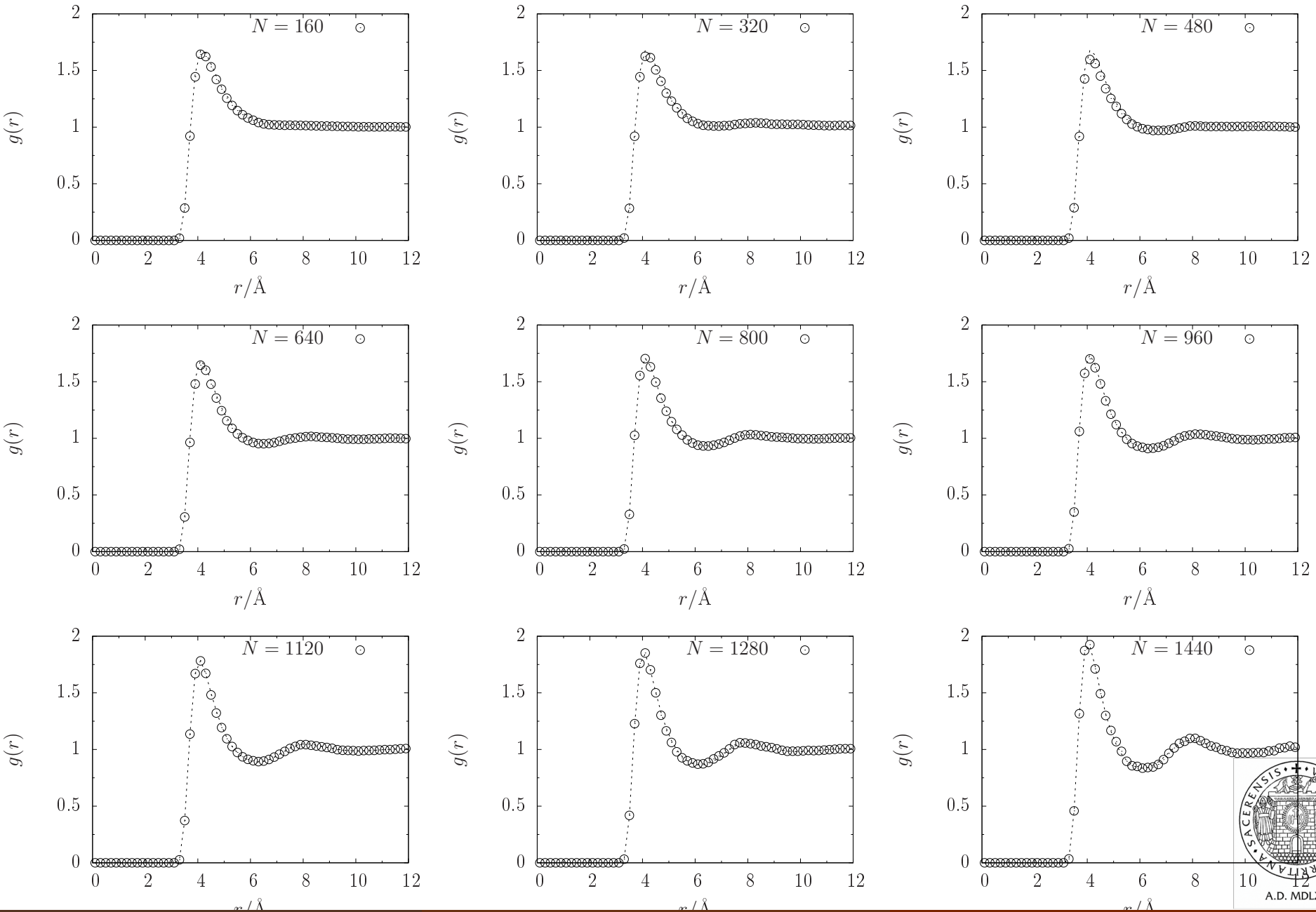
Intermediate states: From *formal* to *feasible*

Introducing a bias

- Generate intermediate configuration: $\mathbf{R} \to \mathbf{I}$ w.p. $p(\mathbf{I}|\mathbf{R})$.
- Modify intermediate configuration: $\mathbf{I} \to \mathbf{I}^{(1)}$ w.p. $p(\mathbf{I}^{(1)}|\mathbf{I})$.
- Generate K possible output (*biased*) configurations: $\mathbf{I}^{(1)} \to \{\mathbf{R}\}^K$ w.p. $p(\{\mathbf{S}\}^K|\mathbf{I}^{(1)})$.
- Select one of the generated configurations while removing the bias: $\{\mathbf{R}\}^K \to \mathbf{S}$ w.p.

$$p(\mathbf{S}|\{\mathbf{R}\}^K) = \frac{e^{-\beta U(\mathbf{S})}}{\sum\limits_{\mathbf{R}' \in \mathbf{R} \cup \{\mathbf{R}\}^K} e^{-\beta U(\mathbf{R}')}} \frac{p(\mathbf{R}|\mathbf{I}^{(1)})}{\max\limits_{\mathbf{R}'' = \mathbf{R} \cup \{\mathbf{R}\}^K} p(\mathbf{R}''|\mathbf{I}^{(1)})}. \tag{54}$$

Intermediate states: From *formal* to *feasible*



From BE to FD and intermediate statistics

- 3-d lattice $\mathscr{L}$ of L^3 sites $\ell = 1, \ldots, L^3$.
- Connectivity ν and lattice parameter λ.
- (Heterogeneous) Adsorption energies $\varepsilon(\ell) \leq 0$.

Probability to jump into a neighboring site:

$$p(\ell) = \frac{1}{\nu} \exp[\beta\varepsilon(\ell)], \tag{55}$$

or null displacement with probability $1 - \nu p(\ell)$.
For the transformations $\mathbf{R} \to \mathbf{S}$ and back we have:

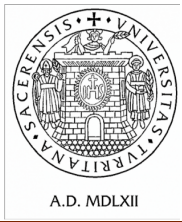
$$p(\mathbf{S}|\mathbf{R}) = \prod_{j=1}^{N} p(\mathbf{r}_j)^{1-\delta(\mathbf{s}_j-\mathbf{r}_j)} \left[1 - \nu p(\mathbf{r}_j)\right]^{\delta(\mathbf{s}_j-\mathbf{r}_j)}, \tag{56}$$

$$p(\mathbf{R}|\mathbf{S}) = \prod_{j=1}^{N} p(\mathbf{s}_j)^{1-\delta(\mathbf{s}_j-\mathbf{r}_j)} \left[1 - \nu p(\mathbf{s}_j)\right]^{\delta(\mathbf{s}_j-\mathbf{r}_j)}, \tag{57}$$

which can be rearranged into

$$\frac{p(S|R)}{p(R|S)} = \frac{\prod_{\ell \in \mathscr{L}} \exp\left[\beta n(\ell; R)\varepsilon(\ell)\right]}{\prod_{\ell \in \mathscr{L}} \exp\left[\beta n(\ell; S)\varepsilon(\ell)\right]}. \tag{58}$$

with $n = 0, 1, 2, \ldots$. (Bose-Einstein statistics)



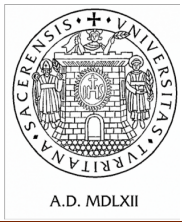
From BE to FD and intermediate statistics

We introduce an intermediate lattice, $\mathscr{I}$, made of $4L^3$ sites:

- L^3 sites located exactly at the same positions of the sites in $\mathscr{L}$, and
- $3L^3$ located in the middle of all the pairs of neighboring nodes (distance $|\lambda/2|$ from every $\mathscr{L}$-node).

Random activated jumps: from $\mathbf{R} := \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$ to $\mathbf{I} := \{\mathbf{i}_1, \ldots, \mathbf{i}_N\}$ w.p.

$$p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{R}) = \prod_{j=1}^{N} p(\mathbf{r}_j)^{1-\delta(\mathbf{i}_j-\mathbf{r}_j)} \left[1 - \nu p(\mathbf{r}_j)\right]^{\delta(\mathbf{i}_j-\mathbf{r}_j)} . \tag{59}$$



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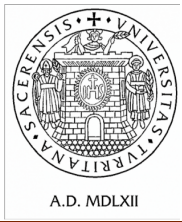
$$p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{R}) = \prod_{j=1}^{N} p(\mathbf{r}_j)^{1-\delta(\mathbf{i}_j-\mathbf{r}_j)} \left[1 - \nu p(\mathbf{r}_j)\right]^{\delta(\mathbf{i}_j-\mathbf{r}_j)}. \tag{59}$$

How many particles, in the configuration $\mathbf{I}$, are located within a distance $\leq \lambda$ from particle j?

$$\widetilde{N}_j(\mathbf{I}) = \sum_{k=1}^{N} \Theta(\lambda - |\mathbf{i}_k - \mathbf{i}_j|), \tag{60}$$

where $\Theta(\cdot)$ is the Heaviside function, i.e.

$$\Theta(x) = \begin{cases} 0, & \text{if } x < 0 \\ 1, & \text{if } x \geq 0 \end{cases}$$



From BE to FD and intermediate statistics

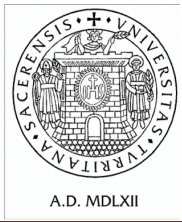
If $\widetilde{N}_j(\mathbf{l}) = 1$ then there are no particles within a distance λ from particle j, thus j can keep its position $\mathbf{i}_j$ in the intermediate lattice.

If otherwise $\widetilde{N}_j(\mathbf{l}) > 1$ then there are particles within the cutoff λ and the particle j must return back to its previous position (coincident with r_j).

Deterministic operation: $F = \{\mathbf{f}_1, \ldots, \mathbf{f}_N\}$ with

$$\mathbf{f}_j = \mathbf{i}_j \left[1 - \delta\left(1 - \widetilde{N}_j(\mathbf{l})\right)\right] + \mathbf{r}_j \delta\left(1 - \widetilde{N}_j(\mathbf{l})\right) \tag{61}$$

for all j.



From BE to FD and intermediate statistics

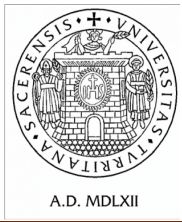
The number of possible outcomes in the $\mathscr{L}$ lattice is

$$\prod_{j=1}^{N} 2^{1-\delta(\mathbf{f}_j-\mathbf{r}_j)}, \tag{62}$$

each chosen starting from $\mathbf{F}$ with probability

$$\begin{aligned} p^{\mathscr{L}|\mathscr{I}}(\mathbf{S}|\mathbf{F}) &= \prod_{j=1}^{N} \left(\frac{1}{2}\right)^{1-\delta(\mathbf{f}_j-\mathbf{r}_j)} \\ &= \prod_{j=1}^{N} \left(\frac{1}{2}\right)^{1-\delta(\mathbf{f}_j-\mathbf{s}_j)} \\ &= p^{\mathscr{L}|\mathscr{I}}(\mathbf{R}|\mathbf{F}), \end{aligned} \tag{63}$$

since for a moving particle $\mathbf{f}_j \neq \mathbf{r}_j$ holds as well as $\mathbf{f}_j \neq \mathbf{s}_j$.



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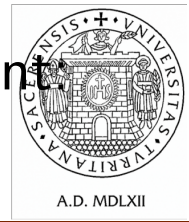
since for a moving particle $\mathbf{f}_j \neq \mathbf{r}_j$ holds as well as $\mathbf{f}_j \neq \mathbf{s}_j$. Crucial point: we can access the $\mathbf{F}$ from $\mathbf{S}$ as well as $\mathbf{R}$.



From BE to FD and intermediate statistics

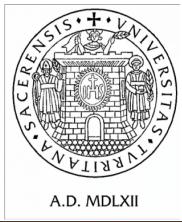
Ratio between the forward and the reverse transition:

$$\frac{p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{R})p^{\mathscr{I}|\mathscr{I},\mathscr{L}}(\mathbf{F}|\mathbf{I},\mathbf{R})p^{\mathscr{L}|\mathscr{I}}(\mathbf{S}|\mathbf{F})}{p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{S})p^{\mathscr{I}|\mathscr{I},\mathscr{L}}(\mathbf{F}|\mathbf{I},\mathbf{S})p^{\mathscr{L}|\mathscr{I}}(\mathbf{R}|\mathbf{F})} = \frac{p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{R})}{p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{S})}$$

$$= \frac{\prod_{j=1}^{N} p(\mathbf{r}_j)^{1-\delta(\mathbf{i}_j-\mathbf{r}_j)}\left[1-\nu p(\mathbf{r}_j)\right]^{\delta(\mathbf{i}_j-\mathbf{r}_j)}}{\prod_{j=1}^{N} p(\mathbf{s}_j)^{1-\delta(\mathbf{i}_j-\mathbf{s}_j)}\left[1-\nu p(\mathbf{s}_j)\right]^{\delta(\mathbf{i}_j-\mathbf{s}_j)}}. \tag{64}$$

Non-moving particles [i.e. those for which $\delta(\mathbf{i}_j-\mathbf{r}_j)=0$ and $\delta(\mathbf{i}_j-\mathbf{s}_j)=0$] have the same coordinates in both R and S:

$$\frac{p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{R})}{p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{S})} = \frac{\prod_{j=1}^{N} p(\mathbf{r}_j)^{1-\delta(\mathbf{i}_j-\mathbf{r}_j)}}{\prod_{j=1}^{N} p(\mathbf{s}_j)^{1-\delta(\mathbf{i}_j-\mathbf{s}_j)}}$$

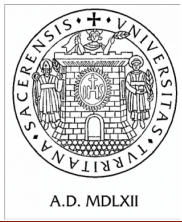


From BE to FD and intermediate statistics

We multiply and divide by the quantity $\prod_{j=1}^{N} p(\mathbf{r}_j)^{\delta(\mathbf{i}_j - \mathbf{r}_j)}$ to get

$$\frac{p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{R})}{p^{\mathscr{I}|\mathscr{L}}(\mathbf{I}|\mathbf{S})} = \frac{\prod_{\ell \in \mathscr{L}} \exp\left[\beta n(\ell; \mathbf{R}) \varepsilon(I)\right]}{\prod_{\ell \in \mathscr{L}} \exp\left[\beta n(\ell; \mathbf{S}) \varepsilon(I)\right]}, \tag{65}$$

with $n = 0 \vee 1$. (Fermi-Dirac statistics)



From BE to FD and intermediate statistics

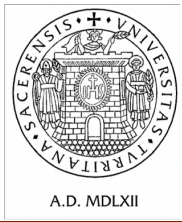
Extended hard-core interactions:

$$\widetilde{N}_j(\mathbf{I}) = \sum_{k=1}^{N} \Theta(\sigma\lambda - |\mathbf{i}_k - \mathbf{i}_j|), \tag{66}$$

Intermediate statistics:

$$f_j = \mathbf{i}_j \left[1 - \Theta\left(n_{\max} - \widetilde{N}_j(\mathbf{I})\right)\right] + \mathbf{r}_j \Theta\left(n_{\max} - \widetilde{N}_j(\mathbf{I})\right), \tag{67}$$

G. Gentile, *Nuovo Cimento*, **17**, 493 (1940).



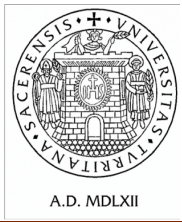
Unanswered questions and w.i.p.

- Modification of the sampling technique

$$p(\mathbf{S}|\{\mathbf{R}\}^K) = \frac{e^{-\beta U(\mathbf{S})}}{\sum_{\mathbf{R}' \in \mathbf{R} \cup \{\mathbf{R}\}^K} e^{-\beta U(\mathbf{R}')}} \mapsto \frac{e^{-\beta U(\mathbf{S})}}{Z} \tag{68}$$

  with $Z \approx \textit{constant}$ to have a quasi-equilibrium rejection-free algorithm?

- Improved bias techniques



Thank you for your patience.