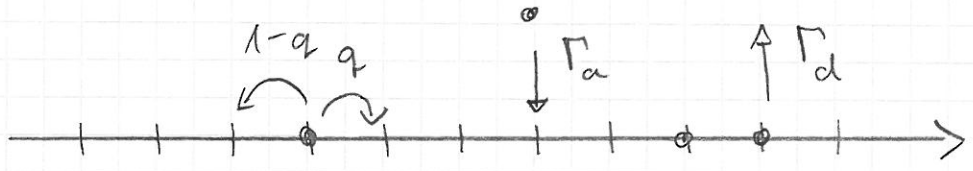
- Langmuir Kinetics: (Parmeggiani et al. 2003)

In addition to hopping, particles are annihilated at rate Γ_d and created at empty sites at rate Γ_a:



⇒ particle density is no longer conserved.

Interesting behavior requires that particle conservation is weakly violated in the sense of

$$\Gamma_a, \Gamma_d \sim \frac{1}{L}$$

2° Continuous time Markov chains

Exclusion processes on finite lattices are examples of (continuous time) Markov chains on finite state spaces. Here we summarize some general properties of such systems. We need the following ingredients:

- states $i = 1, \ldots, C$
- transition rates Γ_{ij}: When system is in state i at time t, a transition to state j occurs in $[t, t+dt]$ with probability $\Gamma_{ij} \cdot dt$

- transition probability:

$$P_{ki}(t) = \text{Prob}[\text{ state } i \text{ at } t \mid \text{ state } k \text{ at } 0]$$

$$=: P_i(t) \quad \text{with} \quad P_i(0) = \delta_{ik}$$

a) Master equation: P_i evolves according to

$$\frac{d}{dt} P_i = \underbrace{\sum_{j\neq i} \Gamma_{ji} P_j}_{\text{gain of probability}} - \underbrace{\sum_{j\neq i} \Gamma_{ij} P_i}_{\text{loss of probability}} = \sum_j A_{ji} P_j$$

with
$$A_{ij} = \begin{cases} \Gamma_{ij} & i \neq j \\ -\sum\limits_{k\neq i} \Gamma_{ik} & i = j \end{cases}$$

- $\hat{A}$ is called the generator of the process and governs the evolution of expectation values. Consider some function $f = \{f_i\}$, then

$$\underline{\frac{d}{dt}\langle f \rangle} = \sum_i f_i \dot{P}_i = \sum_i \sum_j f_i A_{ji} P_j =$$

$$= \underline{\langle \hat{A} f \rangle}$$

In "quantum mechanical" notation:

$$\{f_i\} = |f\rangle, \quad \{P_i\} = |P\rangle, \quad \underline{\langle f\rangle = \langle f|P\rangle} = \sum_i f_i P_i$$

$$\left.\begin{aligned} &\Rightarrow \frac{\partial}{\partial t}|P\rangle = \hat{A}^+ |P\rangle, \\ &\frac{d}{dt}\langle f\rangle = \langle f|\dot{P}\rangle = \langle f|\hat{A}^+ P\rangle = \langle \hat{A} f|P\rangle \end{aligned}\right\}$$

We note that, by conservation of probability,

$$\left.\begin{aligned} &\sum_j A_{ij} = 0 \quad \Rightarrow \quad \hat{A}|\mathbb{1}\rangle = 0 \\ &\qquad\qquad\qquad \text{with } |\mathbb{1}\rangle = (1,1,\dots,1) \end{aligned}\right\}$$

Matrices with this property are called *stochastic*.

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b) *Stationary distribution:* If the Markov chain is *irreducible* (= all states are connected) there is a unique stationary distribution $|P^*\rangle = \{P_i^*\}$ such that

$$\left.\begin{aligned} &\sum_j A_{ji} P_i^* = 0 \quad \Leftrightarrow \quad \hat{A}^+|P^*\rangle = 0 \\ &|P^*\rangle \text{ is a } \underline{\text{left eigenvector}} \text{ of } \hat{A}. \end{aligned}\right\}$$

Any initial distribution converges to P_i^* under the dynamics

(→ Frobenius-Perron thm., Exercise 6).

c) Probability currents

The master equation is a continuity equation for the conserved probability $|P\rangle$:

$$\left.\begin{aligned} \frac{d}{dt} P_i &= \sum_{j \neq i} \left(\Gamma_{ji} P_j - \Gamma_{ij} P_i \right) = - \sum_j K_{ij} \\ K_{ij} &= \Gamma_{ij} P_i - \Gamma_{ji} P_j \\ &\text{net probability current from } i \text{ to } j \end{aligned}\right\}$$

In particular, in the stationary state

$$(K^*) \quad \underline{\sum_j K^*_{ij} = 0} \quad \text{with} \quad K^*_{ij} = \Gamma_{ij} P^*_i - \Gamma_{ji} P^*_j$$

$\Rightarrow$ probability current is <u>divergence free</u>, i.e. net inflow balances net outflow for all i.

There are two ways in which (K^*) can be satisfied:

(i) $\underline{K^*_{ij} = 0 \quad \forall\, i, j}$: This implies

$\Gamma_{ij} P^*_i = \Gamma_{ji} P^*_j \quad \forall\, i, j$, i.e. MC satisfies

$$\left.\begin{aligned} &\circ \text{ detailed balance (physics) or} \\ &\circ \text{ reversibility (mathematics)} \end{aligned}\right\}$$

This describes a <u>equilibrium situation</u> which microscopically symmetric under time reversal.

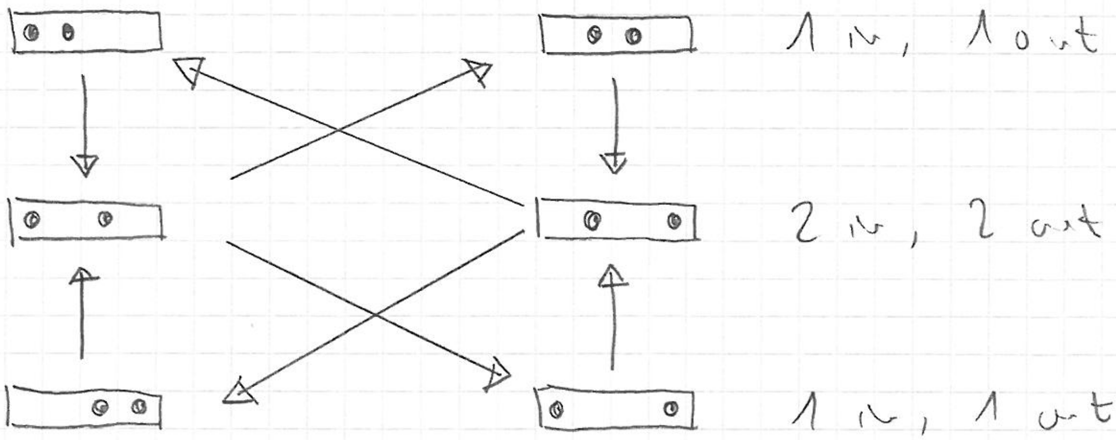
(ii) <u>$K_{ij}^{*} \neq 0$ for at least some i,j</u>:

This describes a <u>nonequilibrium stationary state (NESS)</u>.

<u>Remarks:</u>

- Characterization of a stationary state by $\{P_i^{*}\}$ is not sufficient, as two systems may have the same $\{P_i^{*}\}$ but different $\{K_{ij}^{*}\}$ (see later)
- Because $\{K_{ij}^{*}\}$ is divergence-free, the stationary probability current has to run in cycles.

<u>Example:</u> TASEP with $L=4$, $N=2$,
periodic b.c. $\Rightarrow$ $C=6$ states



<u>Problem:</u> Extend this picture to parallel update

Analogy with electrodynamics: (R. Zia)

$$\left.\begin{array}{ll} \text{Equilibrium} \hat{=} \text{electrostatics:} & \vec{j}=0, \quad \nabla\times\vec{E}=0 \\ \text{NESS} \hat{=} \text{magnetostatics:} & \nabla\cdot\vec{j}=0, \quad \nabla\times\vec{E}\neq0 \end{array}\right\}$$

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d) Entropy production

How to define entropy production for a NESS defined by a stochastic master eq.?

We follow the approach of Schnakenberg (1976). From classical nonequilibrium thermodynamics we expect

$$\sigma = \sum \text{fluxes} \times \text{forces} = \underline{\frac{1}{2}\sum_{ij} K_{ij} X_{ij}}$$

How to identify the forces X_{ij}?

Schnakenberg uses a chemical analogy:

$$\left.\begin{array}{lll} P_i & \rightarrow & \text{concentration } c_i \text{ of chemical species } i \\ \Gamma_{ij} & \rightarrow & \text{reaction rate from } i \text{ to } j \end{array}\right\}$$

At chemical equilibrium

$$K_{ij}^{(0)} = 0 \quad \Rightarrow \quad \Gamma_{ij} c_i^{(0)} = \Gamma_{ji} c_j^{(0)} \quad \Rightarrow \quad \underline{\frac{c_i^{(0)}}{c_j^{(0)}} = \frac{\Gamma_{ji}}{\Gamma_{ij}}}$$

The force X_{ij} is now identified with the (dimensionless) chemical potential difference required to generate a deviation from equilibrium:

$$\frac{c_i}{c_j} = \frac{c_i^{(0)}}{c_j^{(0)}} e^{\beta \Delta\mu_{ij}} = \frac{\Gamma_{ji}}{\Gamma_{ij}} e^{X_{ij}},$$

$$\Rightarrow X_{ij} = \ln\left(\frac{\Gamma_{ij} c_i}{\Gamma_{ji} c_j}\right) = \underline{\ln\left(\frac{\Gamma_{ij} P_i}{\Gamma_{ji} P_j}\right)}$$

$$\Rightarrow \underline{\sigma = \frac{1}{2} \sum_{i,j} \left(\Gamma_{ij} P_i - \Gamma_{ji} P_j\right) \ln\left(\frac{\Gamma_{ij} P_i}{\Gamma_{ji} P_j}\right)}$$

with the following properties:

- $\sigma \geq 0$
- $\sigma^* = 0$ for equilibrium states ($K_{ij}^* = 0$)
- $$\sigma = \underbrace{\frac{1}{2} \sum_{i,j} K_{ij} \ln\left(\frac{P_i}{P_j}\right)}_{\substack{\sigma_{int} \\ \text{internal entropy} \\ \text{production}}} + \underbrace{\frac{1}{2} \sum_{i,j} K_{ij} \ln\left(\frac{\Gamma_{ij}}{\Gamma_{ji}}\right)}_{\substack{\sigma_{ext} \\ \text{export of entropy} \\ \text{to the environment}}}$$

with $\sigma_{int} = \frac{d}{dt}\left(-\sum_i P_i \ln P_i\right)$ [Exercise]

and therefore $\sigma_{int} = 0$ in a NESS.

3° Stationary distribution of the ASEP

Consider the ASEP on a ring of L sites, N particles $\Rightarrow$ $C = \binom{L}{N}$ configurations.

Transition rates:

$$\Gamma(\eta \to \eta') = \begin{cases} \Gamma_0 q & (\ldots \bullet \circ \ldots) \to (\ldots \circ \bullet \ldots) \\ \Gamma_0 (1-q) & (\ldots \circ \bullet \ldots) \to (\ldots \bullet \circ \ldots) \\ 0 & \text{else} \end{cases}$$

with η the configuration on the left and η' the one on the right.

Claim: The stationary distribution $P^*(\eta)$ is uniform on the configuration space, i.e.

$$\underline{P^*(\eta) = \frac{1}{C} = \binom{L}{N}^{-1}}$$

Proof: We need to show that

$$\left.\begin{aligned} &\sum_{\eta'} K^*(\eta \to \eta') = 0 \qquad \forall \eta \\ &K^*(\eta \to \eta') = \binom{L}{N}^{-1} \left(\Gamma(\eta \to \eta') - \Gamma(\eta' \to \eta) \right) \end{aligned}\right\}$$

We distinguish two cases:

(i) $q = \frac{1}{2}$: $\Gamma(\eta \to \eta') = \Gamma(\eta' \to \eta)$ for any η, η'

$\Rightarrow$ detailed balance is satisfied w.r.t. the uniform distribution; the SSEP is a reversible (equilibrium) system.

(ii) $q \neq \frac{1}{2}$: Detailed balance is broken, $K^* \neq 0$; to prove that the uniform distribution is still stationary, consider the total rates ($\Gamma_0 = 1$ for now).

$$\Gamma^{in}_{tot}(\eta) = \sum_{\eta'} \Gamma(\eta' \to \eta) = q\, W_{\circ\bullet}(\eta) + (1-q)\, W_{\bullet\circ}(\eta)$$

$$\Gamma^{out}_{tot}(\eta) = \sum_{\eta'} \Gamma(\eta \to \eta') = q\, W_{\bullet\circ}(\eta) + (1-q)\, W_{\circ\bullet}(\eta)$$

with $W_{xy}(\eta) = \#\{\text{pairs } xy \text{ in conf. } \eta\}$.

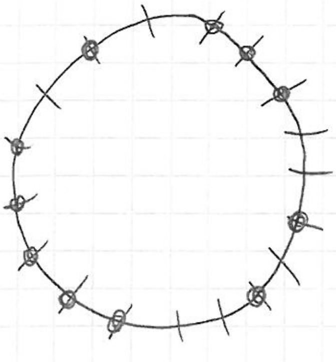
Then we have

$$\sum_{\eta'} K^*(\eta \to \eta') = \binom{L}{H}^{-1} \left(\Gamma^{out}_{tot}(\eta) - \Gamma^{in}_{tot}(\eta) \right) =$$

$$= \underline{\binom{L}{N}^{-1} (2q-1) \left(W_{\circ\bullet}(\eta) - W_{\bullet\circ}(\eta) \right)}$$

so for $q \neq \frac{1}{2}$ we have to show that

$$W_{\circ\bullet}(\eta) = W_{\bullet\circ}(\eta) \quad \forall\, \eta :$$



$$\Rightarrow W_{\circ\bullet} = W_{\bullet\circ} =$$

$= \#$ clusters of particles. $\Box$

Remarks:

(i) The stationary distribution is uniform only on the ring and only for continuous time dynamics. Nontrivial (non-uniform) stationary distributions arise for

- SSEP with open boundaries
- ASEP with open boundaries
- dTASEP

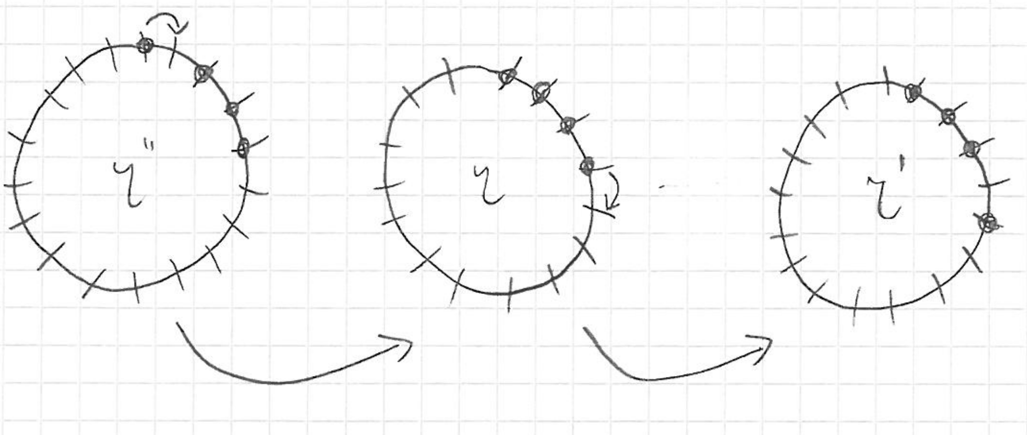
(ii) The ASEP on the ring is an example of pairwise balance: For each pair of configurations η, η' with $\Gamma(\eta \to \eta') > 0$ there is a configuration η'' such that

$$\underbrace{\Gamma(\eta \to \eta')\, P^*(\eta)}_{\text{outflow } \eta \to \eta'} = \underbrace{\Gamma(\eta'' \to \eta)\, P^*(\eta'')}_{\text{inflow } \eta'' \to \eta}$$

$\Rightarrow$ terms in the sum $\sum_{\eta'} K^*(\eta \to \eta')$

cancel pairwise.

Construction of η'':



(iii) The mean stationary particle current can now be calculated.

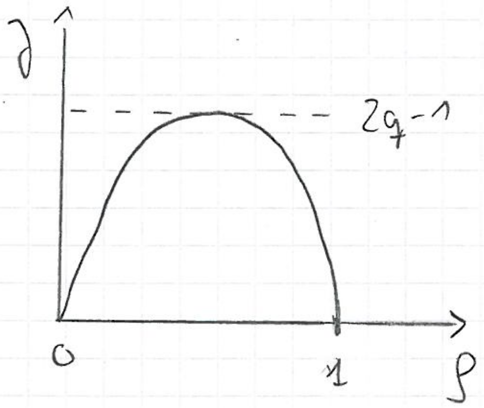
$$J = q \langle \eta_x (1-\eta_{x+1}) \rangle - (1-q) \langle \eta_x (1-\eta_{x-1}) \rangle$$

$$\langle \eta_x (1-\eta_{x+1}) \rangle = \langle \eta_x (1-\eta_{x-1}) \rangle =$$

$= \text{Prob}[\text{ site } x \text{ occupied and site } x+1 \text{ vacant }] =$

$$= \binom{L-2}{N-1} \binom{L}{N}^{-1} = \frac{N(L-N)}{L(L-1)} \xrightarrow[\frac{N}{L}=\rho]{N,L\to\infty} \rho(1-\rho)$$

$$\Rightarrow \quad \underline{J(\rho) = (2q-1)\,\rho(1-\rho)}$$



More generally, it can be shown that the uniform distribution on configuration space implies Bernoulli measure [1]

$$\eta_x = \begin{cases} 1 & \text{prob. } \rho \\ 0 & \text{prob } 1-\rho \end{cases} \quad \text{independently in } x$$

in the limit $N, L \to \infty$ at fixed density $\rho = N/L$. [Exercise 8]. Note that the exact expression for the current is

$$J_L = (2q-1)\,\rho(1-\rho)\left(1-\frac{1}{L}\right)^{-1} > J_\infty$$

[1] or product measure

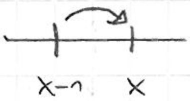
4° Hydrodynamics of the ASEP

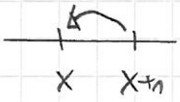
- What can we say about the time evolution of spatially varying (mean or typical) density profiles?
- How do deterministic, autonomous hydrodynamic equations arise on large scales?

a) Evolution of the mean density profile

Start the ASEP in some given initial condition and consider the occupation η_x averaged over many realizations of the stochastic evolution:

$$\frac{d}{dt}\langle \eta_x \rangle = q\langle \eta_{x-1}(1-\eta_x)\rangle + (1-q)\langle \eta_{x+1}(1-\eta_x)\rangle$$





$$- q\langle \eta_x(1-\eta_{x+1})\rangle - (1-q)\langle \eta_x(1-\eta_{x-1})\rangle =$$

$$= q\langle \eta_{x-1}\rangle + (1-q)\langle \eta_{x+1}\rangle - \langle \eta_x\rangle +$$

$$- (2q-1)\left(\langle \eta_{x-1}\eta_x\rangle - \langle \eta_x\eta_{x+1}\rangle\right)$$

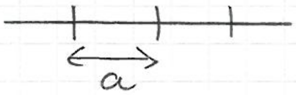
$\underline{q = \frac{1}{2}}$: Closed set of linear equations

$$\frac{d}{dt}\langle \eta_x\rangle = \frac{1}{2}\Big(\underbrace{\langle \eta_{x+1}\rangle + \langle \eta_{x-1}\rangle - 2\langle \eta_x\rangle}_{\substack{\text{discrete second derivative} \\ \text{(Laplace operator)}}}\Big)$$

⇒ hydrodynamic equation is the linear diffusion equation

$$(D) \qquad \frac{\partial \rho}{\partial t} = D \nabla^2 \rho \, , \qquad D = \frac{1}{2} \Gamma a^2$$

Γ: jump rate of particles

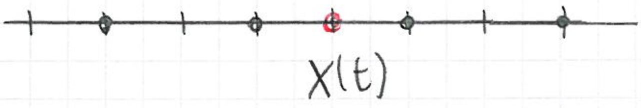
a: lattice spacing 

Remarks: (i) This result holds for symmetric exclusion in arbitrary dimension d, with $D = \frac{1}{2d} \Gamma a^2$.

(ii) (D) is identical to the evolution eq. for the density of independent particles

⇒ collective diffusion is not affected by the exclusion interaction.

(iii) This is not true for the diffusion of a "tagged" tracer particle:



For the SSEP X(t) behaves subdiffusively

$$\langle (X(t) - X(s))^2 \rangle \sim |t-s|^{1/2}$$

"single file diffusion" (Alexander & Pincus 1978)