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Markus Mittnenzweig

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Weierstrass Institute
Mohrenstr. 39
10117 Berlin
Germany
E-Mail: markus.mittnenzweig@wias-berlin.de

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Weierstraß-Institut für Angewandte Analysis und Stochastik (WIAS)
Leibniz-Institut im Forschungsverbund Berlin e. V.
Mohrenstraße 39
10117 Berlin
Germany

Fax: +49 30 20372-303
E-Mail: preprint@wias-berlin.de
World Wide Web: <http://www.wias-berlin.de/>

Hydrodynamic limit and large deviations of reaction-diffusion master equations

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Abstract

We derive the hydrodynamic limit of a reaction-diffusion master equation, that combines an exclusion process with a reversible chemical master equation expression for the reaction rates. The crucial assumption is that the associated macroscopic reaction network has a detailed balance equilibrium. The hydrodynamic limit is given by a system of reaction-diffusion equations with a modified mass action law for the reaction rates. We provide the upper bound for large deviations of the empirical measure from the hydrodynamic limit.

1 Introduction

Stochastic reaction-diffusion processes are model systems of interacting particles in statistical physics, for which various aspects, such as hydrodynamic limits [DFL86, DFL85], phase transitions [Tău17], turbulence [CC*08] or stationary non-equilibrium states [BD*07] have been studied. Moreover, stochastic reaction - diffusion models are widely used for the simulation of biochemical reaction networks in cellular biology, where copy numbers of molecules can be small and concentrations can vary across different regions of a cell [AnB04, ErC09].

In this work, we consider the reaction-diffusion master equation for multiple species in the diffusive scaling limit, where particles can react with each other when they find themselves at the same lattice site. The stochastic reaction rates follow a modified chemical master equation expression [GM*76, Isa08]. Furthermore, we will only allow a maximal number of M particles per species per lattice point. Particle jumps between different sites are therefore modeled by an exclusion process. We show that if the associated reaction network satisfies detailed balance, the hydrodynamic limit of the reaction - diffusion master equation is given by a reaction-diffusion partial differential equation with mass action law kinetics. In the second part of this work, we study large deviations from the hydrodynamic limit and prove rigorously the large-deviation upper bound. Our work is a generalization of [JLLV93], in which the authors established a dynamic large deviations principle for a scalar reaction-diffusion master equation. Further results for two species models were obtained in [Per00, BoĀ07].

The crucial observation in this work is, that if the macroscopic reaction network satisfies detailed balance with respect to an equilibrium concentration $\mathbf{w} = (w_1, \dots, w_I)$, then the generator L of the reaction - diffusion master equation is as well in detailed balance with respect to a product binomial distribution. For $M = \infty$, i.e. no restriction on the number of particles per lattice site, the analogous result for the Poisson distribution is known to hold for chemical reaction networks satisfying a complex balance condition (which is a weaker condition than the detailed balance condition). As a result of the detailed balance property for finite M , we can apply the well-developed entropy method of Guo, Papanicalou and Varadhan [GPV88] to derive the macroscopic hydrodynamic limit of the reaction-exclusion process. More precisely, we consider I different species with R different reactions



between them, where $\alpha_r, \beta_r \in \mathbb{N}^I$ are the stoichiometric coefficients of the r th reaction. This reaction network satisfies the (macroscopic) detailed balance condition if

$$\exists \mathbf{w} \in \mathbb{R}_+^I : \quad \kappa_r^{fw} \mathbf{w}^{\alpha_r} = \kappa_r^{bw} \mathbf{w}^{\beta_r} \quad \forall r = 1, \dots, R, \quad (2)$$

with $\mathbf{w}^\alpha = \prod_{i=1}^I w_i^{\alpha_i}$ being the mass action law rate associated to the stoichiometric vector α . The microscopic model on the discrete torus $\mathbb{T}_N^d = \mathbb{Z}^d / N\mathbb{Z}^d$ is a stochastic reaction-exclusion process $\boldsymbol{\eta}_t(\cdot)$ of particle configurations $\boldsymbol{\eta}_t : \mathbb{T}_N^d \rightarrow \mathbb{N}^I$ with $0 \leq \eta_t^i(x) \leq M$ for all i . The generator of the process is given by

$$\begin{aligned} Lf(\boldsymbol{\eta}) &= \sum_{x, |e|=1} N^2 D_i \eta_i(x) \left(1 - \frac{\eta_i(x+e)}{M}\right) [f(\boldsymbol{\eta}_i^{x, x+e}) - f(\boldsymbol{\eta})] \\ &+ M \sum_{x, r} g_r^{fw}(\boldsymbol{\eta}(x)) [f(\boldsymbol{\eta}_x^{\gamma_r}) - f(\boldsymbol{\eta})] + g_r^{bw}(\boldsymbol{\eta}(x)) [f(\boldsymbol{\eta}_x^{-\gamma_r}) - f(\boldsymbol{\eta})] \end{aligned} \quad (3)$$

where $\boldsymbol{\eta}_i^{x, x+e}$ is the new configuration where one particle of type i jumped from x to $x+e$ and $\boldsymbol{\eta}_x^{\gamma_r}$ is the configuration where reaction r took place at lattice site x , i.e. $\boldsymbol{\eta}_x^{\gamma_r}(x) = \boldsymbol{\eta}(x) + \gamma_r$. The reaction rates $g_r^{fw}(\mathbf{n})$ have the form

$$g_r^{fw}(\mathbf{n}) = \kappa_r^{fw} C_r^M \prod_{i=1}^I \frac{n_i!}{(n_i - \alpha_r^i)!} \cdot \frac{(M - n_i)!}{(M - n_i - \beta_r^i)!},$$

with the equivalent expression for $g_r^{bw}(\mathbf{n})$ with exchanged indices α_r and β_r . The constant C_r^M is some normalization constant, see (16). The rates $g_r^{fw/bw}$ are modified versions of the chemical master equation (CME). The standard CME rate for a general reaction of the form (1) would be $t_{\alpha_r}(\mathbf{n}) = \prod_{i=1}^I \frac{n_i!}{(n_i - \alpha_r^i)!}$ times a constant prefactor. However, the rate $t_{\alpha_r}(\mathbf{n})$ can lead to more than M particles per lattice site and therefore it needs to be adapted accordingly. The modified rate $g_r^{fw}(\mathbf{n})$ not only takes into account the number n_i of particles available, but also the number of holes $M - n_i$ available for each species i .

The central object in the study of the hydrodynamic limit is the empirical measure π_t^N associated to a stochastic trajectory $\boldsymbol{\eta}_t(\cdot)$ and defined as

$$\pi_t^N = \frac{1}{MN^d} \sum_{x \in \mathbb{T}_N^d} \boldsymbol{\eta}_t(x) \delta_{x/N}.$$

We show that if the chemical reaction network satisfies the detailed balance condition (2), then the empirical measure π_t^N converges for $N \rightarrow \infty$ in a weak sense to a reaction-diffusion system. More precisely, we show that for all $\delta > 0$ and $\mathbf{G} \in C^{1,2}([0, T] \times \mathbb{T}^d, \mathbb{R}^I)$,

$$\limsup_{N \rightarrow \infty} \mathbb{P}_{\mu^N} \left(\left| \int_0^T \langle \pi_t^N, \mathbf{G}(t, \cdot) \rangle - \langle \mathbf{c}(t, \cdot), \mathbf{G}(t, \cdot) \rangle dt \right| > \delta \right) = 0.$$

where $\mathbf{c}(t, x)$ is the solution of the reaction-diffusion system

$$\dot{\mathbf{c}} = \mathbb{D} \Delta \mathbf{c} - \sum_{r=1}^R (\alpha_r - \beta_r) (\kappa_r^{fw} \mathbf{c}^{\alpha_r} (\mathbf{1} - \mathbf{c})^{\beta_r} - \kappa_r^{bw} \mathbf{c}^{\beta_r} (\mathbf{1} - \mathbf{c})^{\alpha_r}) \quad (4)$$

with $\mathbb{D} = \text{diag}(D_1, \dots, D_I)$ and $\mathbf{1} = (1, \dots, 1)$. Because of the prefactors $\mathbf{c}^{\alpha_r} (\mathbf{1} - \mathbf{c})^{\beta_r}$, the solutions $\mathbf{c}(t, x)$ of (4) are uniformly bounded by $0 \leq \mathbf{c}(t, x) \leq 1$, which is the macroscopic equivalent of the microscopic constraint $0 \leq \eta_t(x) \leq M$.

In the last part, we study dynamic large deviations from the hydrodynamic limit. Because the reaction-exclusion process is reversible with respect to the equilibrium product binomial distribution, we can derive a superexponential estimate and obtain a large-deviation upper bound. Let \mathcal{M}_+^I be the space of positive vector-valued measures on \mathbb{T}^d , i.e. $\pi_t^N \in \mathcal{M}_+^I$ and let $\mathcal{D}([0, T]; \mathcal{M}_+^I)$ be the corresponding Skorohod path space for trajectories $t \mapsto \pi_t^N$. Then we show that

$$\limsup_{N \rightarrow \infty} N^{-d} \log P^N(\pi^N \in \mathcal{C}) \leq - \inf_{\mathbf{c} \in \mathcal{C}} \mathcal{I}(\mathbf{c}) \quad \forall \mathcal{C} \text{ closed.}$$

The rate functional \mathcal{I} consists of a static and dynamic part

$$\mathcal{I}(\mathbf{c}) = \mathcal{I}_0(\mathbf{c}(0, \cdot)) + \mathcal{I}_1(\mathbf{c}).$$

\mathcal{I}_0 characterizes large deviations of the initial distribution μ_0 of $\eta_0(\cdot)$ from the stationary product binomial distribution. It is given by $\mathcal{I}_0(\mathbf{c}) = \int_{\mathbb{T}^d} F(\mathbf{c}(x) | \mathbf{w}) dx$ with the Fermi-Dirac-type entropy

$$F(\mathbf{c} | \mathbf{w}) = \sum_{i=1}^I c_i \log \frac{c_i}{w_i} + (1-c_i) \log \frac{1-c_i}{1-w_i}$$

that is typical for simple exclusion processes. The dynamic rate functional $\mathcal{I}_1(\mathbf{c})$ has the implicit representation

$$\mathcal{I}_1(\mathbf{c}) = \sup_{\mathbf{H} \in C^{1,2}([0, T]; \mathbb{T}^d)} \mathcal{J}_{\text{lin}}(\mathbf{c}, \mathbf{H}) - \mathcal{J}_{\text{re}}(\mathbf{c}, \mathbf{H}) - \mathcal{J}_{\text{ex}}(\mathbf{c}, \mathbf{H})$$

where $\mathcal{J}_{\text{lin}}(\mathbf{c}, \mathbf{H})$ is linear in the function \mathbf{H} and $\mathcal{J}_{\text{ex}}(\mathbf{c}, \mathbf{H})$ and $\mathcal{J}_{\text{re}}(\mathbf{c}, \mathbf{H})$ are convex in \mathbf{H} :

$$\begin{aligned} \mathcal{J}_{\text{ex}}(\mathbf{c}, \mathbf{H}) &= \sum_{i=1}^I \int_0^T \int_{\mathbb{T}^d} |\nabla H_i(t, x)|^2 c_i(t, x) (1-c_i(t, x)) dx dt \\ \mathcal{J}_{\text{re}}(\mathbf{c}, \mathbf{H}) &= \sum_r \int_0^T \int_{\mathbb{T}^d} \mathbf{R}_r^f(\mathbf{c}(t, x)) (e^{\gamma_r \cdot \mathbf{H}(t, x)} - 1) + \mathbf{R}_r^f(\mathbf{c}(t, x)) (e^{-\gamma_r \cdot \mathbf{H}(t, x)} - 1) dx dt. \end{aligned}$$

$\mathcal{J}_{\text{ex}}(\mathbf{c}, \mathbf{H})$ is the typical contribution from the exclusion process [KOV89]. The exponential form of the reaction part $\mathcal{J}_{\text{re}}(\mathbf{c}, \mathbf{H})$ agrees with the large deviations functional for the chemical master equation without spatial degrees of freedom [MP*17]. We do not give a rigorous proof of a large deviations lower bound here. However, it seems reasonable that the lower bound of [JLLV93] for $d = 1$ and $I = 1$ can be generalized to arbitrary d and I . For $d = 1$ and $I = 1$, density large deviations were also extended to joint large deviation principles for the empirical density and empirical current [BoL12] as well as to static large deviations from non-equilibrium stationary states [LaT18].

It remains an open, if one can relax the detailed balance condition (2). For $M = \infty$, the central Proposition 2.4 holds also true for chemical reaction networks satisfying only the weaker complex balanced condition [ACK10, HoJ72, Fei72]. This work leaves also open the convergence to hydrodynamic limit in the case of $M = \infty$, for which particle numbers per lattice site can become arbitrarily large. For the macroscopic reaction-diffusion PDE, weak solutions do globally exist in time in the case of detailed balance and arbitrary quadratic reactions [DF*07].

The paper is structured as follows: In Section 2, we introduce the reaction-diffusion models in detail. In Section 3, we prove the hydrodynamic limit and Section 4 establishes the large deviations upper bound.

Notation

- I is the number of species, R the number of reactions.
- $M \in \mathbb{N}$ is the maximal number of particles per lattice site for each species.
- Bold letters always represent vectors with I components. The bold letters $\mathbf{1} = (1, \dots, 1)$, $\mathbf{M} = (M, \dots, M)$ as well as $\mathbf{c} = (c_1, \dots, c_I)$ for concentrations and $\mathbf{h} = \mathbf{1} - \mathbf{c}$ for hole concentrations will be used throughout the paper.
- $\mathbb{T}^d = \mathbb{R}^d / [0, 1]^d$ is the d -dimensional torus.
- $\mathbb{T}_N^d = \mathbb{Z}^d / N\mathbb{Z}^d$ is the discrete, N -periodic, d -dimensional torus.
- $\pi_t^N = M^{-1} N^{-d} \sum_{x \in \mathbb{T}_N^d} \eta_t(x) \delta_{x/N}$ is the empirical measure associated to the particle configuration $\eta_t(x)$ at time t .
- $\mathcal{N}_M = \{\mathbf{n} \in \mathbb{N}^I \mid \mathbf{n} \leq \mathbf{M}\}$ is the space of allowed lattice site occupation numbers.
- $\mathcal{X}_N = \{\eta(\cdot) \mid \eta : \mathbb{T}_N^d \rightarrow \mathcal{N}_M\}$ space of allowed particle configurations $\eta(\cdot)$.
- \mathcal{M}_+^I is the space of vector-valued positive probability measures on \mathbb{T}^d , i.e. for $\pi \in \mathcal{M}_+^I$ with $\pi = (\pi_1, \dots, \pi_I)$, each π_i is a positive measure on \mathbb{T}^d .
- $\mathcal{D}([0, T]; \mathcal{M}_+)$ is the Skorohod path space for empirical measures π_t^N
- $\eta_i^{x,y}$ is the configuration where a particle of species i moved from point x to point y , see (11).
- η_x^γ is the configuration where $\eta(x)$ is replaced by $\eta(x) + \gamma$, see (10).
- $H(\mu \mid \nu) = \sum_{\eta} \mu(\eta) \log \frac{\mu(\eta)}{\nu(\eta)}$ is the relative entropy.
- P_{μ^N} is the probability measure for empirical measures $\pi_t^N \in \mathcal{D}([0, T]; \mathcal{M}_+)$ as well as particle configurations $\eta_t(\cdot)$.

2 Microscopic and macroscopic reaction-diffusion models

2.1 Chemical reaction networks

We consider I different particle species X_1, \dots, X_I with concentrations $\mathbf{c} = (c_1, \dots, c_I) \in \mathbb{R}_+^I$ that can react with each other according to $r = 1, \dots, R$ different possible reactions

$$\alpha_1^r X_1 + \dots + \alpha_I^r X_I \rightleftharpoons \beta_1^r X_1 + \dots + \beta_I^r X_I. \quad (5)$$

where $\beta^r, \alpha^r \in \mathbb{N}^I$ are the corresponding stoichiometric vectors. In the following $\gamma_r = \beta_r - \alpha_r$ will always denote the difference between the two. The prototypical example is a bimolecular reaction of the form



for instance $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$. When particle numbers are large enough and the whole system is well-mixed, rate equations of the form

$$\dot{\mathbf{c}} = -\mathbf{T}(\mathbf{c})$$

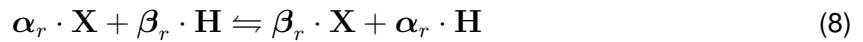
are typically used to model the dynamics of the system. For elementary reactions such as (6), the mass-action law is a good approximation to the kinetics of the reaction. When every reaction (5) follows the mass action law, the reaction rate $\mathbf{T}(\mathbf{c})$ of the reaction network is given by

$$\mathbf{T}(\mathbf{c}) = \sum_{r=1}^R (\boldsymbol{\alpha}_r - \boldsymbol{\beta}_r) (\kappa_r^{fw} \mathbf{c}^{\boldsymbol{\alpha}_r} - \kappa_r^{bw} \mathbf{c}^{\boldsymbol{\beta}_r}) \quad \text{with } \mathbf{c}^{\boldsymbol{\alpha}} = \prod_{i=1}^I c_i^{\alpha_i}. \quad (7)$$

Here $\kappa_r^{fw} \mathbf{c}^{\boldsymbol{\alpha}}$ is the mass action rate associated to the stoichiometric vector $\boldsymbol{\alpha}$ of the r th forward reaction. Typically, the number of reactions R is smaller than the number of species I and the stoichiometric vectors $(\boldsymbol{\beta}_r - \boldsymbol{\alpha}_r)_{r=1}^R$ do not span the full space \mathbb{R}^I . In that case, there exist globally conserved quantities

$$\mathbb{S} = \text{span} \{ \boldsymbol{\beta}^r - \boldsymbol{\alpha}^r \mid r = 1, \dots, R \} \quad \mathbb{S}^\perp = \{ \boldsymbol{\xi} \mid \boldsymbol{\xi} \cdot \mathbf{c} = 0 \quad \forall \mathbf{c} \in \mathbb{S} \}$$

that correspond to atomic species in applications. In the following, we will consider a variation of the mass action kinetics (7), that incorporates an exclusion rule and that guarantees that the concentrations c_i are uniformly bounded by 1, i.e. $c_i \leq 1$ for every i . One possibility is to introduce for every particle type X_i a hole species H_i .



since for every removed particle X_i a corresponding hole H_i is created and vice versa. At any time, the particle and the hole concentrations $c_i(t)$ and $h_i(t)$ satisfy the constraint $c_i(t) + h_i(t) = 1$. The mass action law reaction rate associated to (8) is then given by

$$\mathbf{R}(\mathbf{c}) = \sum_{r=1}^R (\boldsymbol{\alpha}_r - \boldsymbol{\beta}_r) (\kappa_r^{fw} \mathbf{c}^{\boldsymbol{\alpha}_r} \mathbf{h}^{\boldsymbol{\beta}_r} - \kappa_r^{bw} \mathbf{c}^{\boldsymbol{\beta}_r} \mathbf{h}^{\boldsymbol{\alpha}_r}), \quad \mathbf{h} = \mathbf{1} - \mathbf{c}.$$

This reaction rate clearly preserves the positivity of both \mathbf{c} and \mathbf{h} . Next, we will introduce the central notion of a detailed balanced equilibrium of a chemical reaction network.

Definition 2.1. (Detailed balance condition) A chemical reaction network (5) with mass action law reaction rates (7) satisfies the detailed balance condition if

$$\exists \mathbf{w} \in \mathbb{R}_+^I : \quad \kappa_r^{fw} \mathbf{w}^{\boldsymbol{\alpha}_r} = \kappa_r^{bw} \mathbf{w}^{\boldsymbol{\beta}_r} \quad \forall r. \quad (9)$$

Proposition 2.2. If the reaction network (5) without hole species H_i is in detailed balance for $\mathbf{w} > 0$, then the reaction network with holes (8) is in detailed balance for \mathbf{w}_* with $w_{*,i} = \frac{w_i}{1+w_i}$ and vice versa.

Proof. The chemical reaction network with holes is in detailed balance if

$$\exists \mathbf{w}_* \in \mathbb{R}_+^I : \quad \kappa_r^{fw} \mathbf{w}_*^{\boldsymbol{\alpha}_r} (\mathbf{1} - \mathbf{w}_*)^{\boldsymbol{\beta}_r} = \kappa_r^{bw} \mathbf{w}_*^{\boldsymbol{\beta}_r} (\mathbf{1} - \mathbf{w}_*)^{\boldsymbol{\alpha}_r} \quad \forall r.$$

By dividing by $(\mathbf{1} - \mathbf{w}_*)^{\boldsymbol{\beta}_r}$ and $(\mathbf{1} - \mathbf{w}_*)^{\boldsymbol{\alpha}_r}$, we see that this expression is equivalent to

$$\exists \mathbf{w}_* \in \mathbb{R}_+^I : \quad \kappa_r^{fw} \mathbf{w}_*^{\boldsymbol{\alpha}_r} = \kappa_r^{bw} \mathbf{w}_*^{\boldsymbol{\beta}_r} \quad \forall r$$

with $w_i = \frac{w_{*,i}}{1-w_{*,i}}$. □

Proposition 2.2 shows that the existence of a detailed balance equilibrium of the chemical reaction network with holes is equivalent to the existence of a detailed balance equilibrium of the chemical reaction network without holes. An equivalent characterization of detailed balance uses the matrix

$$\mathbb{W} = ((\boldsymbol{\beta}_r - \boldsymbol{\alpha}_r)_{r=1, \dots, R})^T \in \mathbb{Z}^{R \times I}$$

which is called Wegscheider matrix due its first use in [Weg02], see also [GIM12, MHM15]. The detailed balance condition (9) is then equivalent to

$$\mathbb{W} \log \mathbf{w} = \left(\log \frac{\kappa_r^{fw}}{\kappa_r^{bw}} \right)_{r=1, \dots, R} \quad \text{with } \log \mathbf{w} = (\log w_i)_{i=1, \dots, I}.$$

By Fredholm's alternative, this equation is solvable if and only if

$$\xi \cdot \left(\log \frac{\kappa_r^{fw}}{\kappa_r^{bw}} \right)_{r=1, \dots, R} = 0 \quad \forall \xi \in \mathbb{S}^\perp$$

where

$$\mathbb{S} = \text{Ran } \mathbb{W}^T \quad \mathbb{S}^\perp = \ker \mathbb{W}.$$

The last conditions are called Wegscheider conditions [VIR09, ScS89, Weg02] and give polynomial relations on the rates κ_r^{fw} and κ_r^{bw} if the stoichiometric vectors $(\beta_r - \alpha_r)$ are not linearly independent. See [Fei89] for more details on necessary and sufficient conditions of detailed balancing.

2.2 The reaction-diffusion master equation

The reaction-diffusion master equation is a continuous-time Markov chain, where particles can hop on a given lattice and two or more particles can react with each other, when they are at the same lattice position [Isa09, Isa08, WiS16]. In this article, the lattice will always be the discrete torus $\mathbb{T}_N^d = \mathbb{Z}^d / N\mathbb{Z}^d$. A particle configuration $\eta(\cdot)$ is a function

$$\eta : \mathbb{T}_N^d \rightarrow \mathbb{N}^I,$$

where the value $\eta_i(x) \in \mathbb{N}$ describes the number of particles of species i at the lattice point x . We will distinguish between the two cases that either particle numbers per lattice site can be arbitrarily large or that they are uniformly bounded by an integer M , i.e. $\eta_i(x) \leq M$. As explained in the previous section, a reaction is characterized by its stoichiometric vectors $\alpha_r, \beta_r \in \mathbb{N}^I$. If the reaction r takes place at the lattice point x , then the particle configuration $\eta(x)$ will change to $\eta(x) \rightarrow \eta(x) + \gamma_r$ where $\gamma_r = \beta_r - \alpha_r$. We will write $\eta_x^{\gamma_r}$ for this new configuration, i.e.

$$\eta_x^{\gamma_r}(y) = \begin{cases} \eta(x) + \gamma_r & \text{if } y = x \\ \eta(y) & \text{else.} \end{cases} \quad (10)$$

If a particle of species i jumps from x to y , the new configuration will be denoted by

$$\eta_i^{x,y}(z) = \begin{cases} \eta(y) + \mathbf{e}_i & \text{if } z = y \\ \eta(x) - \mathbf{e}_i & \text{if } z = x \\ \eta(z) & \text{else} \end{cases} \quad (11)$$

where $\mathbf{e}_i = (0, \dots, 1, \dots, 0)$ is the i th unit vector. The generator of the reaction-diffusion master equation is given by

$$\begin{aligned} Lf(\eta) = & \sum_{x, |e|=1} N^2 D_i \eta_i(x) [f(\eta_i^{x, x+e}) - f(\eta)] \\ & + \sum_{x, r} \kappa_r^{fw} t_{\alpha_r}(\eta) [f(\eta_x^{\gamma_r}) - f(\eta)] + \kappa_r^{bw} t_{\beta_r}(\eta) [f(\eta_x^{-\gamma_r}) - f(\eta)] \end{aligned} \quad (12)$$

with D_i being the diffusion constant of species i , $\kappa_r^{fw/bw}$ the forward and backward reaction rates and

$$t_\alpha(\mathbf{n}) = \begin{cases} \frac{\mathbf{n}!}{(\mathbf{n}-\alpha)!} & \text{for } \mathbf{n} \geq \alpha \\ 0 & \text{for } \mathbf{n} \not\geq \alpha \end{cases} \quad \text{where } \mathbf{n}! := \prod_{i=1}^I n_i!. \quad (13)$$

The above generator contains a diffusion and a reaction part

$$L = N^2 L_{\text{diff}} + L_{\text{react}}. \quad (14)$$

Note that because $t_\alpha(\mathbf{n}) = 0$ for $\mathbf{n} \not\geq \alpha$, particle numbers $\eta(x)$ will always remain non-negative. Without spatial diffusion, the Kolmogorov forward equation of the above generator is commonly referred to as chemical master equation in the physical literature [Gil07, Gil92]. The specific form of $t_\alpha(\mathbf{n})$ relies on the following combinatorial argument. The idea is, that each lattice point represents a well-mixed volume, in which these particles move rapidly around. Then, the probability that a reaction occurs must be proportional to the number of possibilities to choose a tuple α out of the \mathbf{n} particles. But this is exactly

$$\prod_{i=1}^I n_i(n_i - 1) \cdot \dots \cdot (n_i - \alpha_i + 1) = \frac{\mathbf{n}!}{(\mathbf{n} - \alpha)!}$$

for distinguishable particles. Next, we introduce a variant of the reaction-diffusion process (12), for which only a maximum of M particles is allowed per species per lattice site. Let

$$\mathcal{N}_M = \{ \mathbf{n} \in \mathbb{N}^I \mid 0 \leq n_i \leq M \quad \forall i = 1, \dots, I \}$$

denote the state of allowed lattice occupations $\mathbf{n} \in \mathbb{N}^I$ and let

$$\mathcal{X}_N = \{ \eta(\cdot) \mid \eta(x) \in \mathcal{N}_M \quad \forall x \in \mathbb{T}_N^d \}$$

be the space of all allowed particle configurations $\eta : \mathbb{T}_N^d \rightarrow \mathcal{N}_M$. For each $\eta \in \mathcal{X}_N$, we define then the generator L of the reaction-exclusion process through

$$\begin{aligned} Lf(\eta) = & \sum_{x, |e|=1} N^2 D_i \eta_i(x) \left(1 - \frac{\eta_i(x+e)}{M}\right) [f(\eta_i^{x, x+e}) - f(\eta)] \\ & + M \sum_{x, r} g_r^{fw}(\eta(x)) [f(\eta_x^{\gamma_r}) - f(\eta)] + g_r^{bw}(\eta(x)) [f(\eta_x^{-\gamma_r}) - f(\eta)] \end{aligned} \quad (15)$$

with the reaction rates

$$\begin{aligned} g_r^{fw}(\mathbf{n}) &= \kappa_r^{fw} C_r^M t_{\alpha_r}(\mathbf{n}) t_{\beta_r}(\mathbf{M} - \mathbf{n}) \\ g_r^{bw}(\mathbf{n}) &= \kappa_r^{bw} C_r^M t_{\beta_r}(\eta) t_{\alpha_r}(\mathbf{M} - \mathbf{n}) \end{aligned} \quad (16)$$

where $\mathbf{M} = (M, \dots, M)$ and $C_r^M = [t_{\alpha_r + \beta_r}(\mathbf{M})]^{-1}$. As before, we can write

$$L = N^2 L_{\text{excl}} + L_{\text{react}}. \quad (17)$$

Up to a prefactor, the rates $g_r^{fw/bw}$ are the chemical master equation rate for reactions with holes (8). The prefactor C_r^M is chosen in such a way that the associated macroscopic reaction rates will be of the form $\kappa_r^{fw} \mathbf{c}^{\alpha_r} (\mathbf{1} - \mathbf{c})^{\beta_r}$, see (4) and Proposition 2.7. The hopping of a particle of species i from lattice point x to $x + e$ can also be written as a reaction



Note that particle jumps between neighboring lattice sites are by a factor N^2 faster than the other reactions. Depending on the size of M , the reaction-exclusion master equation (12) can either be viewed as a microscopic description chemical reactions, where only a few particles are allowed on each site, or as a mesoscopic description, where each lattice site is a well-mixed container with several particles in it.

Next, we introduce on \mathcal{N}_M for some $\mathbf{c} \in [0, 1]^I$ the binomial distribution

$$\nu_{\mathbf{c}}(\mathbf{n}) := \prod_{i=1}^I \binom{M}{n_i} c_i^{n_i} (1-c_i)^{M-n_i} \quad \text{for } \mathbf{n} \in \mathcal{N}_M$$

as well as the Poisson distribution

$$\chi_{\mathbf{c}}(\mathbf{n}) := e^{-\sum_{i=1}^I c_i} \cdot \frac{\mathbf{c}^{\mathbf{n}}}{\mathbf{n}!} = \prod_{i=1}^I \chi_{c_i}(n_i) \quad (19)$$

for some $\mathbf{c} \in \mathbb{R}_+^I$. We will also write $\nu_c(n)$ and $\chi_c(n)$ for the one-dimensional binomial and Poisson distributions. Moreover, for particle configurations $\boldsymbol{\eta}(\cdot) \in \mathcal{X}_N$, we define the product distributions

$$\nu_{\mathbf{c}}^N(\boldsymbol{\eta}(\cdot)) := \prod_{x \in \mathbb{T}_N^d} \nu_{\mathbf{c}}(\boldsymbol{\eta}(x)) \quad \chi_{\mathbf{c}}^N(\boldsymbol{\eta}(\cdot)) := \prod_{x \in \mathbb{T}_N^d} \chi_{\mathbf{c}}(\boldsymbol{\eta}(x)). \quad (20)$$

They play an important role, because they are the equilibrium distributions of the pure exclusion and the diffusion processes.

Lemma 2.3. *For every $\mathbf{c} \in [0, 1]^I$ the product binomial distribution $\nu_{\mathbf{c}}^N$ is an equilibrium distribution of L_{excl} and for every $\tilde{\mathbf{c}} \in \mathbb{R}_+^I$, the product Poisson distribution $\chi_{\tilde{\mathbf{c}}}^N$ is an equilibrium of the diffusion process, i.e.*

$$L_{\text{excl}}^* \nu_{\mathbf{c}}^N = 0 \quad L_{\text{diff}}^* \chi_{\tilde{\mathbf{c}}}^N = 0.$$

The next proposition shows that if the chemical reaction network satisfies the detailed balance condition (9) for some $\mathbf{w}_* \in \mathbb{R}_+^I$, then the distributions $\nu_{\mathbf{w}_*}^N(\boldsymbol{\eta}(\cdot))$ (with $w_i = \frac{w_{*,i}}{1+w_{*,i}}$) and $\chi_{\mathbf{w}_*}^N(\boldsymbol{\eta}(\cdot))$ are equilibria of the reaction-exclusion (15) and the reaction-diffusion master equation (12) respectively. For the Poisson distribution, this result is contained in Theorem 4.1 of [ACK10].

Proposition 2.4. *Suppose the reaction network (5) satisfies the detailed balance condition (9) for the concentration \mathbf{w}_* , i.e.*

$$\kappa_r^{fw} \mathbf{w}^{\alpha_r} = \kappa_r^{bw} \mathbf{w}^{\beta_r} \quad \forall r.$$

Then the reaction-diffusion process (12) is reversible with respect to the product Poisson distribution $\chi_{\mathbf{w}_}^N(\boldsymbol{\eta}(\cdot))$ and the reaction-exclusion process (15) is reversible with respect to the product binomial distribution $\nu_{\mathbf{w}_*}^N(\boldsymbol{\eta}(\cdot))$ with $w_i = \frac{w_{*,i}}{1+w_{*,i}}$. In particular, both distributions $\chi_{\mathbf{w}_*}^N(\boldsymbol{\eta}(\cdot))$ and $\nu_{\mathbf{w}_*}^N(\boldsymbol{\eta}(\cdot))$ are equilibrium distributions of the respective processes.*

Proof. Let us start with the binomial distribution. For a general jump process on a finite state space of the form

$$Lf(\boldsymbol{\eta}) = \sum_{\boldsymbol{\eta}' \neq \boldsymbol{\eta}} r(\boldsymbol{\eta}, \boldsymbol{\eta}') (f(\boldsymbol{\eta}') - f(\boldsymbol{\eta})),$$

reversibility of L with respect to a distribution $\mu(\boldsymbol{\eta})$ is defined as

$$\mu(\boldsymbol{\eta}) r(\boldsymbol{\eta}, \boldsymbol{\eta}') = \mu(\boldsymbol{\eta}') r(\boldsymbol{\eta}', \boldsymbol{\eta}) \quad \forall \boldsymbol{\eta}, \boldsymbol{\eta}'.$$

Thus we need to show the two conditions

$$\begin{aligned}\nu_{\mathbf{w}}^N(\boldsymbol{\eta}) \cdot \eta_i(x)(M - \eta_i(y)) &= \nu_{\mathbf{w}}^N(\boldsymbol{\eta}_i^{x,y})(\eta_i(y)+1)(M - (\eta_i(x)-1)) \\ \nu_{\mathbf{w}}^N(\boldsymbol{\eta}) \cdot g_r^{fw}(\boldsymbol{\eta}(x)) &= \nu_{\mathbf{w}}^N(\boldsymbol{\eta}_x^{\gamma_r}) \cdot g_r^{bw}(\boldsymbol{\eta}(x) + \gamma_r).\end{aligned}$$

For the first line, we use that

$$\frac{\nu_{\mathbf{w}}^N(\boldsymbol{\eta}(\cdot))}{\nu_{\mathbf{w}}^N(\boldsymbol{\eta}_i^{x,y}(\cdot))} = \frac{\nu_{w_i}(\eta_i(x)) \cdot \nu_{w_i}(\eta_i(y))}{\nu_{w_i}(\eta_i(x)-1) \cdot \nu_{w_i}(\eta_i(y)+1)}$$

where $\nu_{w_i}(n)$ is the scalar binomial distribution $\nu_{w_i}(n) = \binom{M}{n} w_i^n (1-w_i)^{M-n}$. An explicit calculation for the binomial distribution shows that

$$\frac{\nu_w(n)}{\nu_w(n-1)} = \frac{M - (n-1)}{n} \cdot \frac{w}{1-w}$$

which proves the first line. For the reaction part we note first that

$$\frac{\nu_{\mathbf{w}}^N(\boldsymbol{\eta})}{\nu_{\mathbf{w}}^N(\boldsymbol{\eta}_x^{\gamma_r})} = \frac{\nu_{\mathbf{w}}(\boldsymbol{\eta}(x))}{\nu_{\mathbf{w}}(\boldsymbol{\eta}(x) + \gamma_r)}.$$

Thus, using $\frac{w^\gamma}{(1-w)^\gamma} = \mathbf{w}_*^\gamma$, we obtain

$$\frac{\nu_{\mathbf{w}}(\mathbf{n})}{\nu_{\mathbf{w}}(\mathbf{n} + \gamma_r)} = \frac{\binom{M}{\mathbf{n}} \mathbf{w}^{\mathbf{n}} (1-\mathbf{w})^{M-\mathbf{n}}}{\binom{M}{\mathbf{n} + \gamma_r} \mathbf{w}^{\mathbf{n} + \gamma_r} (1-\mathbf{w})^{M-\mathbf{n} - \gamma_r}} = \frac{(\mathbf{n} + \gamma_r)! (M - \mathbf{n} - \gamma_r)!}{\mathbf{n}! (M - \mathbf{n})!} \cdot \mathbf{w}_*^{-\gamma_r}.$$

On the other hand, using the definition (16) of the reaction rates $g_r^{fw/bw}$, which contain the function $t_{\alpha}(\mathbf{n}) = \frac{\mathbf{n}!}{(\mathbf{n} - \alpha)!}$, it follows that

$$\begin{aligned}\frac{\kappa_r^{fw}}{\kappa_r^{bw}} \cdot \frac{g_r^{bw}(\mathbf{n} + \gamma_r)}{g_r^{fw}(\mathbf{n})} &= \frac{t_{\beta_r}(\mathbf{n} + \gamma_r) \cdot t_{\alpha_r}(M - \mathbf{n} - \gamma_r)}{t_{\alpha_r}(\mathbf{n}) \cdot t_{\beta_r}(M - \mathbf{n})} \\ &= \frac{(\mathbf{n} + \gamma_r)!}{(\mathbf{n} - \alpha_r)!} \cdot \frac{(M - \gamma_r - \mathbf{n})!}{(M - \beta_r - \mathbf{n})!} = \frac{(\mathbf{n} + \gamma_r)! (M - \mathbf{n} - \gamma_r)!}{\mathbf{n}! (M - \mathbf{n})!} \\ &= \frac{\mathbf{n}!}{(\mathbf{n} - \alpha_r)!} \cdot \frac{(M - \mathbf{n})!}{(M - \mathbf{n} - \beta_r)!} = \frac{\mathbf{n}! (M - \mathbf{n})!}{\mathbf{n}! (M - \mathbf{n})!}.\end{aligned}$$

Finally, by using the detailed balance condition $\frac{\kappa_r^{bw}}{\kappa_r^{fw}} = \mathbf{w}_*^{-\gamma_r}$, we thus showed $\frac{g_r^{bw}(\mathbf{n} + \gamma_r)}{g_r^{fw}(\mathbf{n})} = \frac{\nu_{\mathbf{w}}(\mathbf{n})}{\nu_{\mathbf{w}}(\mathbf{n} + \gamma_r)}$, which concludes the proof of reversibility for the binomial distribution. The analogous computation for the Poisson distribution is

$$\frac{\kappa_r^{fw} \cdot \chi_{\mathbf{w}_*}(\mathbf{n})}{\kappa_r^{bw} \cdot \chi_{\mathbf{w}_*}(\mathbf{n} + \gamma_r)} = \frac{\kappa_r^{fw} \mathbf{w}_*^{\mathbf{n}} \cdot (\mathbf{n} + \gamma_r)!}{\kappa_r^{bw} \mathbf{w}_*^{\mathbf{n} + \gamma_r} \cdot \mathbf{n}!} = \frac{t_{\beta_r}(\mathbf{n} + \gamma_r)}{t_{\alpha_r}(\mathbf{n})}$$

which shows reversibility of the reaction part with respect to $\chi_{\mathbf{w}_*}$. Reversibility of the diffusion part follows in the same way. \square

Remark 2.5. For chemical reaction networks, there also exists the notion of a complex balanced equilibrium. Every detailed balance equilibrium is also in complex balance, but not vice versa. The authors of [ACK10] show for the chemical master equation without diffusion, that the Poisson distribution $\chi_{\mathbf{w}_*}$ is an equilibrium of the process if \mathbf{w}_* is a complex balanced equilibrium of the chemical reaction network. It is unclear if a similar statement holds true for the binomial distribution. The notion of complex balanced equilibria might also be more natural if one introduces only one hole species, see Appendix

C. For chemical reaction networks with mass action kinetics, there exists a well-developed theory for complex balanced equilibria [Fei87]. We do not know if a similar theory, such as the deficiency zero theorem, can be developed for reaction rate equations of the form

$$\dot{\mathbf{c}} = \sum_{r,l} (\alpha_l - \alpha_r) \kappa_{r,l} \mathbf{c}^{\alpha_r} (\mathbf{1} - \mathbf{c})^{\alpha_l}$$

for reactions $\alpha_r \cdot \mathbf{X} \rightarrow \alpha_l \cdot \mathbf{X}$.

Remark 2.6. A variant of the exclusion process considered here puts a bound M on the total number of particles, i.e. $\sum_{i=1}^I \eta_i(x) \leq M$. Particles jump between different lattice sites with the rate

$$r(\boldsymbol{\eta}, \boldsymbol{\eta}_i^{x,x+e}) = \eta_i(x) \left(1 - \frac{\sum_{i=1}^I \eta_i(x)}{M}\right).$$

If reaction rates are also adapted accordingly, then the whole reaction-diffusion process is reversible with respect to a multinomial distribution for some parameter \mathbf{w} . See Appendix C for further details.

Proposition 2.4 makes it possible to derive the hydrodynamic limit as well as a superexponential estimate [KiL98]. The macroscopic reaction rate as a function of \mathbf{c} will be given by an average of the microscopic reaction rates $g_r^{fw/bw}(\mathbf{n})$ with respect to the binomial distribution $\nu_{\mathbf{c}}(\mathbf{n})$ with parameter \mathbf{c} . The binomial distribution for general \mathbf{c} appears here, because the binomial product distributions $\nu_{\mathbf{c}}^N(\boldsymbol{\eta}(\cdot))$ are the equilibrium measures of the exclusion process part L_{excl} . The heuristic is that locally, in the neighborhood of a macroscopic concentration $\mathbf{c}(x)$, the system is ergodic with respect to the fast process on small spatial scales, which is the exclusion part L_{excl} . Therefore, the macroscopic rates are the ergodic averages of the microscopic rates with respect to equilibrium measures of the fast process. For later usage, we calculate the macroscopic reaction rates $\mathbb{E}_{\nu_{\mathbf{c}}}[g_r^{fw}(\mathbf{n})]$ in the next proposition.

Proposition 2.7. The average reaction rates follow the mass-action law form

$$\mathbb{E}_{\chi_{\mathbf{c}}}[t_{\alpha}(\mathbf{n})] = \mathbf{c}^{\alpha} \quad \mathbb{E}_{\nu_{\mathbf{c}}}[t_{\alpha}(\mathbf{n})t_{\beta}(\mathbf{M}-\mathbf{n})] = t_{\alpha+\beta}(\mathbf{M}) \cdot \mathbf{c}^{\alpha}(\mathbf{1}-\mathbf{c})^{\beta}.$$

Thus

$$\mathbb{E}_{\nu_{\mathbf{c}}}[g_r^{fw}(\mathbf{n})] = \kappa_r^{fw} \mathbf{c}^{\alpha_r} (\mathbf{1}-\mathbf{c})^{\beta_r} \quad \mathbb{E}_{\nu_{\mathbf{c}}}[g_r^{bw}(\mathbf{n})] = \kappa_r^{bw} \mathbf{c}^{\beta_r} (\mathbf{1}-\mathbf{c})^{\alpha_r}.$$

Proof. The calculation in the Poisson case reads

$$\mathbb{E}_{\chi_{\mathbf{c}}}[t_{\alpha}(\boldsymbol{\eta})] = \mathbf{c}^{\alpha} e^{-|\mathbf{c}|} \sum_{\mathbf{n} \geq \alpha} \frac{\mathbf{c}^{\mathbf{n}-\alpha}}{(\mathbf{n}-\alpha)!} = \mathbf{c}^{\alpha}.$$

For the binomial distribution, we find

$$\begin{aligned} \mathbb{E}_{\nu_{\mathbf{c}}}[t_{\alpha}(\mathbf{n})t_{\beta}(\mathbf{M}-\mathbf{n})] &= \sum_{\mathbf{n} > \alpha, \mathbf{M}-\mathbf{n} > \beta}^K \mathbf{c}^{\mathbf{n}} (\mathbf{1}-\mathbf{c})^{\mathbf{M}-\mathbf{n}} \frac{\mathbf{M}!}{(\mathbf{M}-\mathbf{n})! \mathbf{n}!} \cdot \frac{\mathbf{n}!}{(\mathbf{n}-\alpha)!} \cdot \frac{(\mathbf{M}-\mathbf{n})!}{(\mathbf{M}-\mathbf{n}-\beta)!} \\ &= \mathbf{c}^{\alpha} (\mathbf{1}-\mathbf{c})^{\beta} t_{\alpha+\beta}(\mathbf{M}) \sum_{\mathbf{n} \geq \alpha}^{\mathbf{M}-\beta} \mathbf{c}^{\mathbf{n}-\alpha} (\mathbf{1}-\mathbf{c})^{\mathbf{M}-\mathbf{n}-\beta} \binom{\mathbf{M}-\alpha-\beta}{\mathbf{n}-\alpha} = \mathbf{c}^{\alpha} (\mathbf{1}-\mathbf{c})^{\beta} t_{\alpha+\beta}(\mathbf{M}). \end{aligned}$$

□

2.3 Entropy bounds

We next introduce the relative entropy and the Dirichlet form of a probability distribution as well as an entropy-dissipation inequality relating the two. This inequality will give an a priori bound on both quantities, which will be needed in the derivation of the hydrodynamic limit. For two probability measures μ^N, ν^N on \mathcal{X}_N , the space of all particle configurations $\boldsymbol{\eta}(\cdot)$, we define the relative entropy

$$H(\mu^N | \nu^N) = \sum_{\boldsymbol{\eta} \in \mathcal{X}_N} \mu^N(\boldsymbol{\eta}(\cdot)) \log \frac{\mu^N(\boldsymbol{\eta}(\cdot))}{\nu^N(\boldsymbol{\eta}(\cdot))}.$$

We will write μ_0^N for the probability distribution of $\boldsymbol{\eta}_0(\cdot)$, i.e. the initial distribution of the Markov process $\boldsymbol{\eta}_t(\cdot)$ and μ_t^N for the distribution of $\boldsymbol{\eta}_t(\cdot)$, i.e.

$$\mu_t^N = P_t^* \mu_0^N$$

where P_t^* is the generated semigroup of L^* . The relative entropy between two states is monotonically decreasing under the action of P_t^* , i.e.

$$H(\mu_t^N | \nu_t^N) \leq H(\mu_0^N | \nu_0^N).$$

In particular, the relative entropy $H(\mu_t^N | \nu_w^N)$ to the equilibrium distribution ν_w^N is monotonically decreasing and therefore the entropy production is always positive:

$$-\frac{d}{dt} H(\mu_t^N | \nu_w) \geq 0.$$

A related object is the Dirichlet form $\mathcal{D}(\mu^N)$ of a probability distribution defined through

$$\mathcal{D}(\mu) := - \sum_{\boldsymbol{\eta} \in \mathcal{X}_N} f(\boldsymbol{\eta})(Lf)(\boldsymbol{\eta}) \nu_w^N(\boldsymbol{\eta}(\cdot)) \quad f(\boldsymbol{\eta}) = \sqrt{\frac{\mu^N(\boldsymbol{\eta})}{\nu_w^N(\boldsymbol{\eta})}}. \quad (21)$$

Because L is reversible with respect to ν_w^N , $\mathcal{D}(\mu)$ is a symmetric quadratic form as a function of $f(\boldsymbol{\eta}) = \sqrt{\frac{\mu^N(\boldsymbol{\eta})}{\nu_w^N(\boldsymbol{\eta})}}$. We define \mathcal{D} here as a function of the probability measure μ^N , because we will only need it in this form. Furthermore, we will write

$$\mathcal{D}(\mu) = N^2 \mathcal{D}_{\text{excl}}(\mu) + \mathcal{D}_{\text{react}}(\mu)$$

for the exclusion and reaction process parts. The Dirichlet form of any probability distribution is always bounded from above by the entropy production:

$$\mathcal{D}(\mu^N) \leq -\frac{d}{dt} \Big|_{t=0} H(\mu_t^N | \nu_w).$$

Thus, the following entropy-dissipation inequality holds true.

Proposition 2.8. *The relative entropy and the Dirichlet form satisfy the inequality*

$$H(\mu_t^N | \nu_w^N) + \int_0^t \mathcal{D}(\mu_s^N) ds \leq H(\mu_0^N | \nu_w^N).$$

In particular, if $H(\mu_0^N | \nu_w) \leq CN^d$, then

$$H(\mu_t^N | \nu_w) \leq CN^d \int_0^t \mathcal{D}_{\text{excl}}(\mu_s^N) ds \leq CN^{d-2}. \quad (22)$$

3 The Hydrodynamic limit

In this section, we show convergence of the reaction-exclusion process

$$Lf(\boldsymbol{\eta}) = \sum_{x, |e|=1} N^2 D_i \eta_i(x) \left(1 - \frac{\eta_i(x+e)}{M}\right) [f(\boldsymbol{\eta}_i^{x, x+e}) - f(\boldsymbol{\eta})] \\ + M \sum_{x, r} g_r^{fw}(\boldsymbol{\eta}(x)) [f(\boldsymbol{\eta}_x^{\gamma_r}) - f(\boldsymbol{\eta})] + g_r^{bw}(\boldsymbol{\eta}(x)) [f(\boldsymbol{\eta}_x^{-\gamma_r}) - f(\boldsymbol{\eta})] \quad (23)$$

to the reaction-diffusion equation

$$\dot{\mathbf{c}} = \operatorname{div}(\mathbb{D} \nabla \mathbf{c}) - \sum_{r=1}^R (\boldsymbol{\alpha}_r - \boldsymbol{\beta}_r) (\kappa_r^{fw} \mathbf{c}^{\boldsymbol{\alpha}_r} (\mathbf{1} - \mathbf{c})^{\boldsymbol{\beta}_r} - \kappa_r^{bw} \mathbf{c}^{\boldsymbol{\beta}_r} (\mathbf{1} - \mathbf{c})^{\boldsymbol{\alpha}_r}) \quad (24)$$

with $\mathbb{D} = \operatorname{diag}(D_1, \dots, D_I)$ and $\mathbf{1} = (1, \dots, 1)$ using the entropy method of Guo, Papanicolaou and Varadhan [GPV88]. The central object in this approach is the empirical measure

$$\boldsymbol{\pi}^N = \frac{1}{MN^d} \sum_{x \in \mathbb{T}_N^d} \boldsymbol{\eta}(x) \delta_{x/N} \quad (25)$$

that can be associated to any particle configuration $\boldsymbol{\eta}(\cdot) \in \mathcal{X}_N$. We will denote by

$$\mathcal{M}_+^I = \{ \boldsymbol{\pi} = (\pi_1, \dots, \pi_I) \mid \pi_i \text{ is a positive measure on } \mathbb{T}^d \},$$

the space of vector-valued positive measures on \mathbb{T}^d and write

$$\langle \boldsymbol{\pi}^N, \mathbf{G} \rangle = \frac{1}{MN^d} \sum_{x \in \mathbb{T}_N^d} \sum_{i=1}^I \eta^i(x) G^i(x/N)$$

for the pairing of a measure $\boldsymbol{\pi}^N$ with a function $\mathbf{G} \in C^2(\mathbb{T}^d, \mathbb{R}^I)$. The central theorem of this section is the following.

Theorem 3.1. *Let $\mathbf{G} \in C^{1,2}([0, T] \times \mathbb{T}^d; \mathbb{R}^I)$ and let the initial distribution μ_0^N satisfy for all $\delta > 0$ that*

$$\limsup_{N \rightarrow \infty} P_{\mu_0^N} (|\langle \boldsymbol{\pi}_0^N, \mathbf{G}(0, \cdot) \rangle - \langle \mathbf{c}(0, \cdot), \mathbf{G}(0, \cdot) \rangle| > \delta) = 0$$

for some $\mathbf{c}(0, \cdot) \in C(\mathbb{T}^d, \mathbb{R}_+^I)$. Furthermore, let the entropy of the initial distribution μ_0^N be bounded by $H(\mu_0^N | \nu_w) \leq CN^d$. Then, for every $\delta > 0$,

$$\limsup_{N \rightarrow \infty} P_{\mu^N} \left(\left| \int_0^T \langle \boldsymbol{\pi}_t^N, \mathbf{G}(t, \cdot) \rangle - \langle \mathbf{c}(t, \cdot), \mathbf{G}(t, \cdot) \rangle dt \right| > \delta \right) = 0.$$

where $\mathbf{c}(t, x)$ solves the reaction-diffusion equation (24).

The theorem states that if the initial distribution μ_0^N satisfies an entropic bound and the empirical measure $\boldsymbol{\pi}_0^N$ converges to an initial profile $\mathbf{c}_0(x)$, then $\boldsymbol{\pi}_t^N$ converges in a weak sense to $\mathbf{c}(t, x)$. For a scalar reaction diffusion model, such a hydrodynamic limit was first derived in [DFL85, DFL86] using the BBGKY hierarchy for correlation functions. Below, we will introduce the main steps of the entropy method for the derivation of the hydrodynamic limit in the vector-valued case. The proof of Theorem (3.1) will be given at the end of this section.

The first step consists in showing that the sequence π_t^N of empirical measures is compact in a suitable space. As explained in [KiL98], Chapters 4 and 5, the Skorohod space

$$\mathcal{D}([0, T], \mathcal{M}_+^I)$$

of cadlag trajectories $\pi : [0, T] \rightarrow \mathcal{M}_+^I$, equipped with the Skorohod topology, is a possible choice. It turns $\mathcal{D}([0, T], \mathcal{M}_+^I)$ into a complete separable metric space. Let P^N be the sequence of probability measures on $\mathcal{D}([0, T], \mathcal{M}_+^I)$ induced by the empirical measures π_t^N , i.e. $P^N(\mathcal{O}) = P(\pi_t^N \in \mathcal{O})$. On that space, the following compactness result holds true.

Proposition 3.2. *The sequence of probability measures \mathbb{P}^N is tight and therefore relatively compact in the space of probability measures on $\mathcal{D}([0, T]; \mathcal{M}_+^I)$ (endowed with the weak topology for probability measures).*

We refer to [KiL98, Chapter 4] for a detailed exposition of the proof. Given the existence of a limit probability measure P_* on $\mathcal{D}([0, T]; \mathcal{M}_+^I)$, the entropy method proceeds in showing that the probability measure P_* is concentrated on points $\pi_t \in \mathcal{D}([0, T], \mathcal{M}_+^I)$ that are weak solutions of (24). The principal idea is to decompose the pairing $\langle \pi_t^N, \mathbf{G}(t, \cdot) \rangle$ into a predictable part and a martingale part and to show that the martingale part converges to zero, while the predictable part must converge to a weak solution of (24).

More precisely, to every time-dependent real-valued function $f(t, \boldsymbol{\eta}_t)$ of a Markov process $\boldsymbol{\eta}_t$ on a finite state space, one can associate the two martingales M_t^f and N_t^f defined through

$$\begin{aligned} M_t^f &= f(t, \boldsymbol{\eta}_t) - f(0, \boldsymbol{\eta}_0) - \int_0^t (\partial_s + L)f(s, \boldsymbol{\eta}_s) ds \\ N_t^f &= (M_t^f)^2 - \int_0^t (Lf^2)(s, \boldsymbol{\eta}_s) - 2f(s, \boldsymbol{\eta}_s)Lf(s, \boldsymbol{\eta}_s) ds \end{aligned} \quad (26)$$

We will call

$$\langle M^f \rangle_t := \int_0^t (Lf^2)(s, \boldsymbol{\eta}_s) - 2f(s, \boldsymbol{\eta}_s)Lf(s, \boldsymbol{\eta}_s) ds \quad (27)$$

the (predictable) quadratic variation of M_t^f . We prove in Appendix B that the two functions M_t^f and N_t^f are indeed martingales, see also [Pro05] for more details on quadratic variations of cadlag martingales. We use the martingale decomposition for the linear function $f(t, \boldsymbol{\eta}) = \langle \boldsymbol{\pi}, \mathbf{G}(t, \cdot) \rangle$ with $\mathbf{G} \in C^{1,2}([0, T] \times \mathbb{T}^d; \mathbb{R}^I)$. Let Δ_N denote the discrete Laplacian

$$(\Delta_N \mathbf{G})\left(\frac{x}{N}\right) := N^2 \sum_{e:|e|=1} \mathbf{G}\left(\frac{x+e}{N}\right) - \mathbf{G}\left(\frac{x}{N}\right).$$

Lemma 3.3. *The martingale decomposition of $\langle \pi_t^N, \mathbf{G}(t, \cdot) \rangle$ is given by*

$$\langle \pi_t^N, \mathbf{G}(t, \cdot) \rangle = \langle \pi_0^N, \mathbf{G}(0, \cdot) \rangle + \int_0^t \langle \pi_s^N, \partial_s \mathbf{G} \rangle + L \langle \pi_s^N, \mathbf{G} \rangle ds + M_t^{\mathbf{G}}.$$

with $L = N^2 L_{\text{excl}} + L_{\text{react}}$ and

$$\begin{aligned} N^2 L_{\text{excl}} \langle \pi_s^N, \mathbf{G}(s, \cdot) \rangle &= M^{-1} N^{-d} \sum_{i=1}^I \sum_x D_i \eta_{s,i}(x) \Delta_N G_i(s, \frac{x}{N}) \\ L_{\text{react}} \langle \pi_s^N, \mathbf{G}(s, \cdot) \rangle &= N^{-d} \sum_{x,r} (\mathbf{G}(s, \frac{x}{N}) \cdot \boldsymbol{\gamma}_r) (g_r^{fw}(\boldsymbol{\eta}) - g_r^{bw}(\boldsymbol{\eta})). \end{aligned} \quad (28)$$

The quadratic variation of both terms equals

$$\begin{aligned}\langle M_t^{\mathbf{G}} \rangle_{\text{excl}} &= \frac{1}{M^2 N^{2d-2}} \int_0^t \sum_{x,e,i} D_i \mathbb{E}[\eta_{s,i}(x)] \left(G_i\left(s, \frac{x+e}{N}\right) - G_i\left(s, \frac{x}{N}\right) \right)^2 ds \\ \langle M_t^{\mathbf{G}} \rangle_{\text{react}} &= \frac{1}{MN^{2d}} \int_0^t \sum_{x,r} \mathbb{E} \left[g_r^{fw}(\boldsymbol{\eta}_s(x)) + g_r^{bw}(\boldsymbol{\eta}_s(x)) \right] \left(\mathbf{G}\left(s, \frac{x}{N}\right) \cdot \boldsymbol{\gamma}_r \right)^2 ds.\end{aligned}\tag{29}$$

Proof. We need to calculate $(Lf)(\boldsymbol{\eta})$ for $f(t, \boldsymbol{\eta}) = \langle \boldsymbol{\pi}, \mathbf{G}(t, \cdot) \rangle$. Since

$$f(t, \boldsymbol{\eta}_i^{x,x+e}) - f(t, \boldsymbol{\eta}) = \frac{1}{MN^d} \left(G_i\left(t, \frac{x+e}{N}\right) - G_i\left(t, \frac{x}{N}\right) \right)$$

one obtains

$$\begin{aligned}L_{\text{excl}} \langle \boldsymbol{\pi}_s^N, \mathbf{G}(s, \cdot) \rangle &= \frac{1}{MN^d} \sum_{x,e,i} D_i \eta_{s,i}(x) \left(1 - \frac{\eta_{s,i}(x+e)}{M} \right) \left(G_i\left(t, \frac{x+e}{N}\right) - G_i\left(t, \frac{x}{N}\right) \right) \\ &= \frac{1}{MN^{d-2}} \sum_{i=1}^I \sum_x D_i \eta_{s,i}(x) \Delta_N G_i\left(s, \frac{x}{N}\right).\end{aligned}$$

In going from the first to second line, it was used that the terms with prefactor $\eta_{s,i}(x) \left(1 - \frac{\eta_{s,i}(x+e)}{M} \right)$ cancel each other. The form of the reaction part $L_{\text{react}} \langle \boldsymbol{\pi}_s^N, \mathbf{G}(s, \cdot) \rangle$, follows from

$$f(t, \boldsymbol{\eta}_x^{\gamma_r}) - f(t, \boldsymbol{\eta}) = \mathbf{G}\left(t, \frac{x}{N}\right) \cdot \boldsymbol{\gamma}_r = \sum_{i=1}^I G_i\left(t, \frac{x}{N}\right) \gamma_r^i.$$

It remains to derive the expressions for the quadratic variation. A general Markov jump process of the form

$$Lf(\boldsymbol{\eta}) = \sum_{\boldsymbol{\eta}'} r(\boldsymbol{\eta}, \boldsymbol{\eta}') (f(\boldsymbol{\eta}') - f(\boldsymbol{\eta}))$$

always satisfies the identity

$$2f(\boldsymbol{\eta})(Lf)(\boldsymbol{\eta}) - (Lf^2)(\boldsymbol{\eta}) = \sum_{\boldsymbol{\eta}'} r(\boldsymbol{\eta}, \boldsymbol{\eta}') (f(\boldsymbol{\eta}') - f(\boldsymbol{\eta}))^2.$$

This proves the form (29) for the quadratic variation. \square

The important point about the expression for the quadratic variation is that it vanishes for $N \rightarrow \infty$. Since

$$\left(G_i\left(s, \frac{x+e}{N}\right) - G_i\left(s, \frac{x}{N}\right) \right)^2 \leq C(\mathbf{G}) N^{-2}$$

for $\mathbf{G} \in C^{1,2}([0, T] \times \mathbb{T}^d; \mathbb{R}^I)$ and since all the other terms inside the sums of (29) are of order $O(1)$, the quadratic variation decays on the order

$$\langle M^{\mathbf{G}} \rangle_{t, \text{react}} + \langle M^{\mathbf{G}} \rangle_{t, \text{diff}} \leq C \cdot N^{-d}.$$

As a result, by Doob's martingale inequality, one can conclude that

$$P_{\mu^N} \left(\sup_{t \leq T} |M_t^{\mathbf{G}}| > \delta \right) \leq \frac{4}{\delta^2} \mathbb{E}[\langle M^{\mathbf{G}} \rangle_T] \leq \frac{4C}{\delta^2 N^d}.$$

In summary, the above reasoning shows the following proposition.

Proposition 3.4. For every $\delta > 0$ and $\mathbf{G} \in C^{1,2}([0, T] \times \mathbb{T}^d; \mathbb{R}^I)$

$$\lim_{N \rightarrow \infty} P_{\mu^N} \left(\sup_{t \leq T} \left| \langle \pi_t^N, \mathbf{G}(t, \cdot) \rangle - \langle \pi_0^N, \mathbf{G}(0, \cdot) \rangle - \int_0^t \left(\langle \pi_s^N, \partial_s \mathbf{G} \rangle - L_{\text{react}} \langle \pi_s^N, \mathbf{G}(s, \cdot) \rangle - L_{\text{excl}} \langle \pi_s^N, \mathbf{G}(s, \cdot) \rangle \right) ds \right| > \delta \right) = 0. \quad (30)$$

The next natural step would be to pass to the limit $\pi_t^N \rightarrow \pi_t$ inside the supremum. However, the part $L_{\text{react}} \langle \pi_s^N, \mathbf{G}(s, \cdot) \rangle$ cannot be written as a function of the empirical measure π_s^N , since it contains the functions $g_r^{fw/bw}(\boldsymbol{\eta})$ which are nonlinear in $\boldsymbol{\eta}(x)$. The remedy to this problem is the replacement lemma, which is the crucial part of the entropy method. In order to state it we need to introduce some notation. For a microscopic function $\psi : \mathcal{N}_M \rightarrow \mathbb{R}$, let $\Psi(\mathbf{c})$ denote the average of $\psi(\mathbf{n})$ with respect to the binomial distribution $\nu_{\mathbf{c}}$:

$$\Psi(\mathbf{c}) := \mathbb{E}_{\nu_{\mathbf{c}}}[\psi(\mathbf{n})].$$

Furthermore, let $\boldsymbol{\eta}^l(x)$ be the block average

$$\boldsymbol{\eta}^l(x) = \frac{1}{M(2l+1)^d} \sum_{|y-x| \leq l} \boldsymbol{\eta}(y) \quad (31)$$

of a configuration $\boldsymbol{\eta}(\cdot)$ over a cube of length l . Let τ_x denote the shift operator on \mathcal{X}_N defined by

$$(\tau_x \boldsymbol{\eta})(y) := \boldsymbol{\eta}(y+x).$$

Theorem 3.5. (Replacement lemma) For every $\delta > 0$ and every function $\psi : \mathcal{N}_M \rightarrow \mathbb{R}$

$$\limsup_{\varepsilon \rightarrow 0} \limsup_N P_{\mu^N} \left[\int_0^T \frac{1}{N^d} \sum_{x \in \mathbb{T}_N^d} V_{\varepsilon N}(\tau_x \boldsymbol{\eta}_s) ds \geq \delta \right] = 0 \quad (32)$$

where

$$V_l(\boldsymbol{\eta}) = \left| \frac{1}{(2l+1)^d} \sum_{|y| \leq l} \psi(\boldsymbol{\eta}(y)) - \Psi(\boldsymbol{\eta}^l(0)) \right|.$$

The replacement lemma says, that one can replace a term of the form

$$\int_0^T N^{-d} \sum_{x \in \mathbb{T}_N^d} F(s, \frac{x}{N}) \psi(\boldsymbol{\eta}_s(x)) ds$$

by the Block average

$$\int_0^T N^{-d} \sum_{x \in \mathbb{T}_N^d} F(s, \frac{x}{N}) \Psi(\boldsymbol{\eta}_s^l(x)) ds$$

for large N and l without making a large error. The replacement lemma states in fact, that this error is arbitrarily small for $l = \varepsilon N$ and $N \rightarrow \infty$ for ε small enough. We refer to [Spo91, Lemma II.3.4] for a proof of the replacement that also applies to our model or alternatively to [Kil98, Lemma 5.1.10] where the replacement lemma is shown under more general assumptions. The proof of the replacement lemma is entirely based on the following entropy bounds that were derived for the reaction-exclusion-process in Proposition 2.8:

$$H(\mu_t^N | \nu_{\mathbf{w}}^N) \leq CN^d \quad \text{and} \quad \int_0^t \mathcal{D}_{\text{excl}}(\mu_s^N) ds \leq CN^{d-2}. \quad (33)$$

The replacement lemma is useful because it replaces the term

$$\int_0^T N^{-d} \sum_{x \in \mathbb{T}_N^d} F(s, \frac{x}{N}) \psi(\boldsymbol{\eta}_s(x)) ds$$

by a term that can be written as a function of the empirical measure. Indeed, let

$$\iota_\varepsilon(\cdot) := (2\varepsilon)^{-d} \mathbf{1}_{[-\varepsilon, \varepsilon]^d}$$

be the normalized indicator function of the small cube $[-\varepsilon, \varepsilon]^d$. Then the block average $\boldsymbol{\eta}^{\varepsilon N}(\cdot)$ is a convolution of $\boldsymbol{\eta}(\cdot)$ with ι_ε and the whole sum can be written as

$$\int_0^T N^{-d} \sum_{x \in \mathbb{T}_N^d} F(s, \frac{x}{N}) \Psi(\boldsymbol{\eta}_s^{\varepsilon N}(x)) ds = \int_0^T \int_{\mathbb{T}^d} F(s, y) \Psi((\boldsymbol{\pi}_s^N * \iota_\varepsilon)(y)) dy ds + o(1)$$

for $N \rightarrow \infty$. Note that the right hand side is now a continuous function of the empirical measure in the Skorohod topology and one can pass to the limit $\boldsymbol{\pi}_s^N * \iota_\varepsilon \rightarrow \boldsymbol{\pi}_s * \iota_\varepsilon$. Let us try to explain heuristically why the function

$$\Psi(\mathbf{c}) := \mathbb{E}_{\nu_{\mathbf{c}}}[\psi(\mathbf{n})]$$

appears. Remember from Proposition 2.4, that the product binomial distributions with parameter

$$\nu_{\mathbf{c}}(\boldsymbol{\eta}(\cdot)) = \prod_{x \in \mathbb{T}_N^d} \nu_{\mathbf{c}}(\boldsymbol{\eta}(x))$$

are the equilibrium distributions of the pure exclusion process

$$(L_{\text{excl}} f)(\boldsymbol{\eta}) = \sum_{x, |e|=1} D_i \eta_i(x) \left(1 - \frac{\eta_i(x+e)}{M}\right) [f(\boldsymbol{\eta}_i^{x, x+e}) - f(\boldsymbol{\eta})].$$

The whole reaction-exclusion process has the generator $L = N^2 L_{\text{excl}} + L_{\text{react}}$. On small scales, the exclusion process is very fast and the reaction part is only a small perturbation. In particular, on small spatial scales and averaged over short time $O(1)$, the exclusion process should be ergodic. This means that if we look at the time-averaged marginal distribution of μ_t^N over a block

$$(\boldsymbol{\eta}(x-l), \boldsymbol{\eta}(x-l+1), \dots, \boldsymbol{\eta}(x+l-1), \boldsymbol{\eta}(x+l))$$

then this distribution should be very close to an equilibrium distribution of the exclusion process, i.e.

$$\frac{1}{\Delta t} \int_t^{t+\Delta t} \mu_s^N((\boldsymbol{\eta}(x-l), \boldsymbol{\eta}(x-l+1), \dots, \boldsymbol{\eta}(x+l-1), \boldsymbol{\eta}(x+l))) ds \approx \prod_{|y-x| \leq l} \nu_{\mathbf{c}}(\boldsymbol{\eta}(y)).$$

In other words, the average of a local function $\psi(\boldsymbol{\eta}_t(x))$ over small blocks of size l and small macroscopic times Δt should be equal to

$$\int_t^{t+\Delta t} \sum_{|y-x| \leq l} \psi(\boldsymbol{\eta}_s(y)) ds \approx \Delta t \cdot \mathbb{E}_{\nu_{\mathbf{c}}}[\psi(\mathbf{n})].$$

for some parameter \mathbf{c} , due to ergodicity of the exclusion process. What is the value of the parameter \mathbf{c} ? Since the exclusion process is also ergodic in space, at a given time t , the value $\mathbf{c}(x, t)$ should approximately be equal to block averages of $\boldsymbol{\eta}_t(x)$ for large enough l . This means

$$\mathbf{c}(t, x) \approx \frac{1}{(2l+1)^d} \sum_{x \in \mathbb{T}_N^d} \frac{\boldsymbol{\eta}_t(y)}{M} \quad \text{for large } l$$

and therefore the block averages $\boldsymbol{\eta}^l(x)$ appears. The replacement lemma makes this averaging procedure rigorous up to macroscopic blocks of size εN . The main idea is that due to the $O(N^{d-2})$ bound and a subadditivity property of the Dirichlet form, it can be shown that the Dirichlet form of the time-averaged marginal distributions of μ_t^N on blocks of a fixed size l disappears for $N \rightarrow \infty$ and remains small for small macroscopic blocks εN . This establishes locally convergence to some product binomial distribution with parameter \mathbf{c} , because these are the only distributions for which the Dirichlet form is equal to zero.

Let us now finish the proof the hydrodynamic limit. Remember from Proposition 2.7 that the macroscopic averages of $g_r^{fw/bw}(\boldsymbol{\eta})$ are given by

$$R_r^{fw}(\mathbf{c}) = \kappa_r^{fw} \mathbf{c}^{\alpha_r} (\mathbf{1}-\mathbf{c})^{\beta_r} \quad \text{and} \quad R_r^{bw}(\mathbf{c}) = \kappa_r^{bw} \mathbf{c}^{\beta_r} (\mathbf{1}-\mathbf{c})^{\alpha_r}.$$

The difference between the two will be denoted by $R_r(\mathbf{c}) = R_r^{fw}(\mathbf{c}) - R_r^{bw}(\mathbf{c})$.

Proof. (Proof of Theorem 3.1) Let

$$\begin{aligned} A_N^\varepsilon &= \langle \boldsymbol{\pi}_T^N, \mathbf{G}(T, \cdot) \rangle - \langle \boldsymbol{\pi}_0^N, \mathbf{G}(0, \cdot) \rangle - \int_0^T \langle \boldsymbol{\pi}_s^N, \partial_s \mathbf{G} \rangle + \langle \boldsymbol{\pi}_s^N, \sum_{i=1}^N D_i(\Delta_N \mathbf{G})(s, \cdot) \rangle ds \\ &\quad - N^{-d} \sum_{x,r} (\mathbf{G}(s, \frac{x}{N}) \cdot \boldsymbol{\gamma}_r) (R_r^{fw}((\boldsymbol{\pi}_s^N * \iota_\varepsilon)(\frac{x}{N})) - R_r^{bw}((\boldsymbol{\pi}_s^N * \iota_\varepsilon)(\frac{x}{N}))). \end{aligned}$$

By a combination of the martingale estimate (30) on $|M_t^{\mathbf{G}}|$ with the replacement lemma Thm. 3.5, it follows that

$$\limsup_{\varepsilon \rightarrow 0} \limsup_{N \rightarrow \infty} P_{\mu^N}(|A_N^\varepsilon| > \delta) = 0.$$

Since $\mathbf{G} \in C^{1,2}([0, T] \times \mathbb{T}^d, \mathbb{R}^I)$, we can replace in A_N^ε the discrete Laplacian $\Delta_N \mathbf{G}$ by $\Delta \mathbf{G}$, i.e. $\Delta_N \mathbf{G} = \Delta \mathbf{G} + o_N(1)$, which means $\lim_{N \rightarrow \infty} o_N(1) = 0$. Similarly, because $R_r^{fw}(\cdot) \leq C$ for some C and because $\mathbf{G} \in C^{1,2}([0, T] \times \mathbb{T}^d, \mathbb{R}^I)$, we can replace the discrete sum over $x \in \mathbb{T}_N^d$

$$\int_0^T \sum_{x \in \mathbb{T}_N^d} (\mathbf{G}(s, \frac{x}{N}) \cdot \boldsymbol{\gamma}_r) R_r((\boldsymbol{\pi}_s^N * \iota_\varepsilon)(\frac{x}{N})) ds$$

by the integral

$$\int_0^T \int_{\mathbb{T}^d} (\mathbf{G}(s, y) \cdot \boldsymbol{\gamma}_r) R_r((\boldsymbol{\pi}_s^N * \iota_\varepsilon)(y)) dy ds$$

modulo an error $o_N(1)$. From Proposition 3.2 we know that the probability measures P^N are compact on $\mathcal{D}(0, T; \mathcal{M}_+^I)$. Since all the above integral expressions are continuous in the Skorohod topology, we can pass to the limit $\boldsymbol{\pi}_t^N \rightarrow \boldsymbol{\pi}_t$ inside the probability estimates. Thus, the limit probability measure P_* must be concentrated on trajectories $\boldsymbol{\pi}_t$ satisfying

$$\begin{aligned} \limsup_{\varepsilon \rightarrow 0} \mathbb{P}_* \left(\left| \langle \boldsymbol{\pi}_T, \mathbf{G}(T, \cdot) \rangle - \langle \boldsymbol{\pi}_0, \mathbf{G}(0, \cdot) \rangle - \int_0^T \langle \boldsymbol{\pi}_s, \partial_s \mathbf{G} \rangle + \langle \boldsymbol{\pi}_s, \mathbb{D} \Delta \mathbf{G}(s, \cdot) \rangle ds \right. \right. \\ \left. \left. - \sum_r \int_0^T \int_{\mathbb{T}^d} (\mathbf{G}(s, x) \cdot \boldsymbol{\gamma}_r) R_r((\boldsymbol{\pi}_s * \iota_\varepsilon)(x)) dx ds \right| > \delta \right) = 0. \end{aligned}$$

The only remaining step is the passage $\varepsilon \rightarrow 0$. Let us first remark that every limit measure $\boldsymbol{\pi}_t(dx)$ must have a density $\mathbf{c}(t, x)$ with $0 \leq \mathbf{c}(t, x) \leq 1$, because $0 \leq \boldsymbol{\eta}_t(x) \leq M$ and every $\boldsymbol{\pi}_t$ in

the support of \mathbb{P}_* must be the limit of some sequence of empirical measures π_t^N . For any integrable function $f \in L^1(\mathbb{T}^d)$, $f * \iota_\varepsilon$ converges pointwise to f in L^1 . Thus $(\pi_t * \iota_\varepsilon)(\cdot)$ with $\pi_t(dx) = \mathbf{c}(t, x)dx$ converges pointwise to $\mathbf{c}(t, x)dx$ and by Lebesgue's dominated convergence theorem we know that the whole integral

$$\sum_r \int_0^T \int_{\mathbb{T}^d} (\mathbf{G}(s, x) \cdot \gamma_r) R_r((\pi_s * \iota_\varepsilon)(x)) dx ds$$

converges to $\sum_r \int_0^T \int_{\mathbb{T}^d} (\mathbf{G}(s, x) \cdot \gamma_r) R_r(\mathbf{c}(s, x)) dx ds$. Thus, we can conclude that the limit probability measure P_* is supported on functions $\mathbf{c}(t, x)$ that satisfy

$$\begin{aligned} \mathbb{P}_* \left(\left| \langle \mathbf{c}(T, \cdot), \mathbf{G}(T, \cdot) \rangle - \langle \mathbf{c}(0, \cdot), \mathbf{G}(0, \cdot) \rangle - \int_0^T \langle \mathbf{c}(s, \cdot), (\partial_s \mathbf{G})(s, \cdot) \rangle ds \right. \right. \\ \left. \left. - \int_0^T \int_{\mathbb{T}^d} \mathbf{c}(s, x) \cdot \mathbb{D} \Delta \mathbf{G}(s, x) + (\mathbf{G}(s, x) \cdot \gamma_r) R_r(\mathbf{c}(s, x)) dx ds \right| > \delta \right) = 0. \end{aligned}$$

This shows that any limit point $\pi_t(dx) = \mathbf{c}(t, x)dx$ is a weak solution of 24. \square

We conclude this section with some remarks on the case $M = \infty$. Heuristically one expects trajectories of the reaction-diffusion process (12) to converge to solutions of the reaction-diffusion equation

$$\dot{\mathbf{c}} = \operatorname{div}(\mathbb{D} \nabla \mathbf{c}) - \sum_{r=1}^R (\alpha_r - \beta_r) (\kappa_r^{fw} \mathbf{c}^{\alpha_r} - \kappa_r^{bw} \mathbf{c}^{\beta_r}). \quad (34)$$

The problem is that concentrations $\mathbf{c}(x, t)$ as well as particle numbers $\eta_t(x)$ can now be arbitrarily large. Although we do have global conservation laws at hand, locally, particle numbers $\eta_t(x)$ can still become very large. As a consequence, we cannot show compactness of the probability measures \mathbb{P}^N in the Skorohod space $\mathcal{D}([0, T], \mathcal{M}_+^I)$. The greater difficulty of the problem is also reflected on the PDE level. For finite M , reaction rates $R_r(\mathbf{c})$ are bounded in L^∞ which gives existence and uniqueness of strong solutions globally in time [Pie10]. However, for $M = \infty$, concentrations can blow up locally in space and time [PiS00]. Nonetheless global existence of weak solutions was established in [DF*07] for quadratic reaction-diffusion equations that satisfy the detailed balance condition. The existence of weak solutions [DF*07] uses an $L^2([0, T] \times \mathbb{T}^d)$ a priori bound that is available for reaction-diffusion equations with a mass conservation property. A similar stochastic version of the bound can also be obtained for the reaction-diffusion master equation (12), i.e. one can show that

$$N^{-d} \int_0^T \sum_{i=1}^I \sum_{x \in \mathbb{T}_N^d} \mathbb{E}_{\mu^N} [\eta_t^i(x)^2] dt \leq C.$$

However this seems not good enough to establish compactness of the probability measures \mathbb{P}^N with respect to a strong enough topology. For general non-quadratic reaction-diffusion equations that satisfy a detailed balance condition, global existence of renormalized solutions was obtained recently in [Fis15].

4 Large deviations from the hydrodynamic limit

In this section, P^N will always denote the probability measure on the Skorohod space $\mathcal{D}([0, T]; \mathcal{M}_+^I)$ generated by the empirical measures π_t^N of the reaction-exclusion process with initial distribution

$\mu_0^N(\boldsymbol{\eta}_0(\cdot))$. In the previous section, we established a law of large numbers for the empirical measures $\boldsymbol{\pi}_t^N$ and showed that they converge for $N \rightarrow \infty$ to the solution $\mathbf{c}(t, x)$ of a reaction-diffusion PDE. Thus the probability distribution of P^N on the Skorohod space $\mathcal{D}([0, T]; \mathcal{M}_+^I)$ will concentrate around the solution $\mathbf{c}(t, x)$ with initial condition $\mathbf{c}(0, x)$. If for some closed subset $\mathcal{C} \subset \mathcal{D}([0, T]; \mathcal{M}_+^I)$, the hydrodynamic limit $\mathbf{c}(t, x)$ is not an element of \mathcal{C} , then

$$\lim_{N \rightarrow \infty} P^N(\mathcal{C}) = 0.$$

Large deviation theory has the goal to characterize this decay of $P^N(\mathcal{C})$ - which is typically exponential in some power of N - in a precise way. A full large deviations principle consists of a large-deviation upper bound

$$\limsup_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{C}) \leq - \inf_{\mathbf{c} \in \mathcal{C}} \mathcal{I}(\mathbf{c}) \quad \forall \mathcal{C} \text{ closed}$$

and a large-deviation lower bound

$$\liminf_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{O}) \geq - \inf_{\mathbf{c} \in \mathcal{O}} \mathcal{I}(\mathbf{c}) \quad \forall \mathcal{O} \text{ open.}$$

Below, we will show a large-deviation upper bound for the probability distributions P^N . We conjecture, that similar to [JLLV93], a partial large-deviation lower bound of the form

$$\liminf_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{O}) \geq - \inf_{\mathbf{c} \in \mathcal{O} \cap \mathcal{S}} \mathcal{I}(\mathbf{c}) \quad \forall \mathcal{O} \text{ open}$$

should be true, where $\mathcal{S} \subset \mathcal{D}([0, T]; \mathcal{M}_+^I)$ is a subspace containing sufficiently smooth functions $\mathbf{c}(t, x)$ that are bounded away from 0 and 1, e.g. $\mathbf{c} \in C^{2,3}([0, T] \times \mathbb{T}^d; \mathbb{R}_+^I)$ with $\varepsilon \leq c_i(t, x) \leq 1 - \varepsilon$ for some $\varepsilon > 0$ and all i . Before stating the main theorem concerning the upper bound, let us introduce the rate function \mathcal{I} . Remember that $\mathbf{w} \in \mathbb{R}_+^I$ denoted the detailed balance equilibrium of the chemical reaction network (8). The large deviations principle is typically stated for the process $\boldsymbol{\eta}_t(x)$ starting from the equilibrium distribution. Thus, from now on, we will assume that the initial configuration $\boldsymbol{\eta}_0(\cdot)$ is distributed according to the equilibrium distribution $\nu_{\mathbf{w}}^N$:

$$\mu_0^N(\boldsymbol{\eta}_0(\cdot)) = \prod_{x \in \mathbb{T}^d} \nu_{\mathbf{w}}(\boldsymbol{\eta}_0(x)). \quad (35)$$

The rate function \mathcal{I} contains a static and a dynamic part

$$\mathcal{I}(\mathbf{c}) = \mathcal{I}_0(\mathbf{c}) + \mathcal{I}_1(\mathbf{c}). \quad (36)$$

The static part is given by

$$\mathcal{I}_0(\mathbf{c}) = \int_{\mathbb{T}^d} F(\mathbf{c}(x) | \mathbf{w}) dx$$

with F being the Fermi-Dirac type entropy

$$F(\mathbf{c} | \mathbf{w}) = \sum_{i=1}^I c_i \log \frac{c_i}{w_i} + (1 - c_i) \log \frac{1 - c_i}{1 - w_i}.$$

It depends only on the initial distribution μ_0^N . The dynamic part \mathcal{I}_1 has the form

$$\mathcal{I}_1(\mathbf{c}) = \sup_{\mathbf{H} \in C^{1,2}([0, T] \times \mathbb{T}^d; \mathbb{T}^d)} \mathcal{J}(\mathbf{c}, \mathbf{H}) \quad (37)$$

with $\mathcal{J}(\mathbf{c}, \mathbf{H}) = \mathcal{J}_{\text{lin}}(\mathbf{c}, \mathbf{H}) - \mathcal{J}_{\text{ex}}(\mathbf{c}, \mathbf{H}) - \mathcal{J}_{\text{re}}(\mathbf{c}, \mathbf{H})$ and

$$\mathcal{J}_{\text{lin}}(\mathbf{c}, \mathbf{H}) = \langle \mathbf{H}(T, \cdot), \mathbf{c}(T, \cdot) \rangle - \langle \mathbf{H}(0, \cdot), \mathbf{c}(0, \cdot) \rangle - \int_0^T \langle \partial_s \mathbf{H}(s, \cdot) + \mathbb{D} \Delta \mathbf{H}(s, \cdot), \mathbf{c}(s, \cdot) \rangle ds$$

$$\mathcal{J}_{\text{re}}(\mathbf{c}, \mathbf{H}) = \int_0^T \int_{\mathbb{T}^d} \sum_{r=1}^R R_r^{fw}(\mathbf{c}) \left(e^{\gamma_r \cdot \mathbf{H}(s,x)} - 1 \right) + R_r^{bw}(\mathbf{c}) \left(e^{-\gamma_r \cdot \mathbf{H}(s,x)} - 1 \right) dx ds$$

$$\mathcal{J}_{\text{ex}}(\mathbf{c}, \mathbf{H}) = \sum_{i=1}^I D_i \int_0^T \int_{\mathbb{T}^d} c_i(t, x) (1 - c_i(t, x)) |\nabla H_i(t, x)|^2 dx dt$$

where $R_r^{fw}(\mathbf{c}) = \kappa_r^{fw} \mathbf{c}^{\alpha_r} (\mathbf{1} - \mathbf{c})^{\beta_r}$ and $R_r^{bw}(\mathbf{c}) = \kappa_r^{bw} \mathbf{c}^{\beta_r} (\mathbf{1} - \mathbf{c})^{\alpha_r}$ were the forward and backward reaction rates. The functional \mathcal{J}_{lin} is linear in \mathbf{H} . The terms \mathcal{J}_{ex} and \mathcal{J}_{re} are both nonlinear and convex in \mathbf{H} and come from the exclusion and reaction part of the Markov process. In order to get the above stated form for the static part, it is important that the initial configuration are distributed according to the equilibrium distribution $\nu_{\mathbf{w}}^N$:

$$\mu_0^N(\boldsymbol{\eta}(\cdot)) = \prod_{x \in \mathbb{T}^d} \nu_{\mathbf{w}}(\boldsymbol{\eta}(x)).$$

Theorem 4.1. (Upper bound for large deviations) *The probability measures P^N satisfy for every set closed $\mathcal{C} \subset \mathcal{D}([0, T], \mathcal{M}_+^I)$ the large-deviation upper bound*

$$\limsup_{N \rightarrow \infty} \frac{1}{MN^d} \log P^N(\mathcal{C}) \leq - \inf_{\mathbf{c} \in \mathcal{C}} \mathcal{I}(\mathbf{c})$$

with rate function (36).

Let us explain how to obtain the supremum form (37) for the large deviations functional. The main idea goes back to Donsker and Varadhan and consists in comparing the probability distribution P^N with the probability distribution $P_{\mathbf{H}}^N$ of a perturbed version of the original Markov process with time-dependent generator $L_{\mathbf{H}}$ for some $\mathbf{H} \in C^{1,2}([0, T] \times \mathbb{T}^d; \mathbb{R}^I)$. The perturbation is chosen in such a way that one can calculate explicitly the Radon-Nikodym derivative $\frac{dP_{\mathbf{H}}^N(\{\boldsymbol{\eta}_t^N\}_{0 \leq t \leq T})}{dP^N(\{\boldsymbol{\eta}_t^N\}_{0 \leq t \leq T})}$ of trajectories $\{\boldsymbol{\eta}_t^N\}_{0 \leq t \leq T}$.

In the following, we will shortly write $\frac{dP_{\mathbf{H}}^N(\boldsymbol{\eta}^N)}{dP^N(\boldsymbol{\eta}^N)}$ for the Radon-Nikodym derivative $\frac{dP_{\mathbf{H}}^N(\boldsymbol{\eta}^N)}{dP^N(\boldsymbol{\eta}^N)}$, which is just the ratio between the two probabilities. In fact, as we shall see below, the quotient of the two probabilities is approximately a function of the empirical measure $\boldsymbol{\pi}^N$, namely

$$\frac{dP_{\mathbf{H}}^N(\boldsymbol{\eta}^N)}{dP^N(\boldsymbol{\eta}^N)} \simeq e^{N^d \mathcal{J}(\boldsymbol{\pi}^N, \mathbf{H})}.$$

As a result we can estimate the probability $P^N(\mathcal{O})$ for some $\mathcal{O} \subset \mathcal{D}([0, T]; \mathcal{M}_+^I)$ in terms of the probability $P_{\mathbf{H}}^N(\mathcal{O})$ of the perturbed process:

$$\begin{aligned} P^N(\mathcal{O}) &= \mathbb{E}_{\mu^N} [\mathbf{1}_{\{\boldsymbol{\pi}^N \in \mathcal{O}\}}] \lesssim e^{-N^d \inf_{\boldsymbol{\pi} \in \mathcal{O}} \mathcal{J}(\boldsymbol{\pi}, \mathbf{H})} \mathbb{E}_{\mu^N} \left[\frac{P_{\mathbf{H}}^N(\boldsymbol{\pi}^N)}{P^N(\boldsymbol{\pi}^N)} \mathbf{1}_{\{\boldsymbol{\pi}^N \in \mathcal{O}\}} \right] \\ &= e^{-N^d \inf_{\boldsymbol{\pi} \in \mathcal{O}} \mathcal{J}(\boldsymbol{\pi}, \mathbf{H})} P_{\mathbf{H}}^N(\mathcal{O}) \leq e^{-N^d \inf_{\boldsymbol{\pi} \in \mathcal{O}} \mathcal{J}(\boldsymbol{\pi}, \mathbf{H})} \end{aligned} \quad (38)$$

Thus, by taking the infimum over all possible \mathbf{H} , we will obtain the following upper bound

$$\limsup_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{O}) \leq - \sup_{\mathbf{H}} \inf_{\boldsymbol{\pi} \in \mathcal{O}} \mathcal{J}(\boldsymbol{\pi}, \mathbf{H}). \quad (39)$$

The remaining steps are standard in large deviation theory. By a minimax lemma, one can exchange supremum and infimum in (39) for compact sets \mathcal{C} . The upper bound for compact sets can then be extended to arbitrary closed sets \mathcal{C} , by showing that the family of measures P^N is exponentially tight.

4.1 Change-of-measure formula

The main tool for the construction of tilted versions of the original Markov process with generator L is the following lemma for arbitrary continuous time Markov chains on a finite state space. We give an elementary proof of the lemma in Appendix A. Please see also [KiL98, Appendix 1], for a proof using the Feynman-Kac formula.

Lemma 4.2. *Let $Lf(x) = \sum_y r(x, y)(f(y) - f(x))$ be the generator of a continuous time Markov chain X_t on a finite state space E with initial distribution $\nu_0(x)$. For a given $F \in C^1([0, T] \times E, \mathbb{R})$ let*

$$(L_{F, \mu} f)(x) = \sum_y r(x, y) e^{F(t, y) - F(t, x)} (f(y) - f(x))$$

be a time-dependent perturbation of L with the initial distribution $\mu(x)$. Then the Radon-Nikodym derivative $\frac{dP_{F, \mu}(X(\cdot))}{dP(X(\cdot))}$ for trajectories $X(\cdot) \in \mathcal{D}([0, T]; E)$ is given by

$$\begin{aligned} \frac{dP_{F, \mu}(X(\cdot))}{dP(X(\cdot))} &= \frac{\mu(X_0)}{\nu_0(X_0)} \exp \left\{ F(T, X_T) - F(0, X_0) - \int_0^T \partial_s F(s, X_s) ds \right. \\ &\quad \left. - \sum_y \int_0^T r(X_s, y) (e^{F(s, y) - F(s, X_s)} - 1) ds \right\}. \end{aligned}$$

We will use Lemma 4.2 for the process $\eta_t(\cdot)$ with

$$F(t, \eta) = MN^d \langle \mathbf{H}(t, \cdot), \boldsymbol{\pi} \rangle = \sum_{i=1}^I \sum_{x \in \mathbb{T}_N^d} H_i(t, \frac{x}{N}) \eta_i(x) \quad (40)$$

for some $\mathbf{H} \in C^{1,2}([0, T] \times \mathbb{T}^d; \mathbb{R}^I)$ and a perturbed initial distribution characterized by a function $\mathbf{b} \in C(\mathbb{T}^d, \mathbb{R}_+^I)$ as explained below. The tilted generator $L_{\mathbf{H}}$ then reads

$$\begin{aligned} (L_{\mathbf{H}} f)(\eta) &= \sum_{x, i, |e|=1} N^2 D_i e^{H_i(t, x+e) - H_i(t, x)} \eta_i(x) \left(1 - \frac{\eta_i(x+e)}{M}\right) [f(\eta_i^{x, x+e}) - f(\eta)] \\ &\quad + M \sum_{x, r} e^{\mathbf{H}(t, x) \cdot \boldsymbol{\gamma}_r} g_r^{fw}(\eta(x)) [f(\eta_x^{\boldsymbol{\gamma}_r}) - f(\eta)] \\ &\quad + e^{-\mathbf{H}(t, x) \cdot \boldsymbol{\gamma}_r} g_r^{bw}(\eta(x)) [f(\eta_x^{-\boldsymbol{\gamma}_r}) - f(\eta)]. \end{aligned} \quad (41)$$

The initial distribution of the perturbed Markov process is given by the product binomial distribution $\nu_{\mathbf{b}(\cdot)}^N$ on \mathbb{T}_N^d defined through

$$\nu_{\mathbf{b}(\cdot)}^N(\eta(\cdot)) := \prod_{x \in \mathbb{T}_N^d} \nu_{\mathbf{b}(\frac{x}{N})}(\eta(x)) \quad (42)$$

where $\mathbf{b}(\cdot) \in C_1(\mathbb{T}^d, \mathbb{R}_+^I)$ is some continuous function with $0 \leq b_i(x) \leq 1$ for all i . Finally, we denote by $P_{\mathbf{H}, \mathbf{b}}^N$ the probability distribution on the path space $\mathcal{D}([0, T], \mathcal{X}_N)$ generated by the initial distribution $\nu_{\mathbf{b}(\cdot)}^N$ and the tilted process (41). By Lemma 4.2, the Radon-Nikodym derivative $\frac{dP_{\mathbf{H}, \mathbf{b}}^N(\eta)}{dP^N(\eta)}$ is given by

$$\begin{aligned} \frac{dP_{\mathbf{H}, \mathbf{b}}^N(\eta)}{dP^N(\eta)} &= \exp \left\{ \log \frac{\nu_{\mathbf{b}(\cdot)}^N(\eta_0)}{\nu_{\mathbf{w}}^N(\eta_0)} + MN^d \left(\langle \mathbf{H}(T, \cdot), \boldsymbol{\pi}_T^N \rangle - \langle \mathbf{H}(0, \cdot), \boldsymbol{\pi}_0^N \rangle \right) \right. \\ &\quad \left. - \int_0^T \langle \partial_s \mathbf{H}(s, \cdot), \boldsymbol{\pi}_s^N \rangle ds - \frac{1}{MN^d} \sum_{\eta'} \int_0^T r(\eta_s, \eta') (e^{\langle \mathbf{H}(s, \cdot), \boldsymbol{\pi}' - \boldsymbol{\pi}_s \rangle} - 1) ds \right\}. \end{aligned} \quad (43)$$

The last term contains the contributions from the exclusion process and the reaction process. The exclusion process part was first derived in [KOV89]. By a Taylor expansion up to second order of the exponential, i.e.

$$e^{H_i(s, \frac{x+e}{N}) - H_i(s, \frac{x}{N})} - 1 = H_i(s, \frac{x+e}{N}) - H_i(s, \frac{x}{N}) + \frac{1}{2} \left(H_i(s, \frac{x+e}{N}) - H_i(s, \frac{x}{N}) \right)^2 + O(N^{-3}),$$

one obtains

$$\begin{aligned} & \frac{1}{MN^d} \int_0^T \sum_{x,i,e} N^2 D_i \eta_{s,i}(x) \left(1 - \frac{\eta_{s,i}(x+e)}{M} \right) \left(e^{H_i(s, \frac{x+e}{N}) - H_i(s, \frac{x}{N})} - 1 \right) ds \\ &= \int_0^T N^{-d} \sum_{x,i,e} D_i \frac{\eta_{s,i}(x)}{M} \left(1 - \frac{\eta_{s,i}(x+e)}{M} \right) \left| \partial_e H_i(s, \frac{x}{N}) \right|^2 ds + \int_0^T \langle \pi_s^N, \mathbb{D} \Delta \mathbf{H}(s, \cdot) \rangle ds + o_N(1). \end{aligned} \quad (44)$$

where $o_N(1)$ only depends on \mathbf{H} and other constants and means $\limsup_{N \rightarrow \infty} o_N(1) = 0$. In the above formula, we also replaced the discrete gradients and the discrete Laplacian by their continuous counterparts, i.e.

$$\Delta_N \mathbf{H} = \Delta \mathbf{H} + o_N(1) \quad \text{and} \quad \left(H_i(s, \frac{x+e}{N}) - H_i(s, \frac{x}{N}) \right)^2 = \left| \partial_e H_i(s, \frac{x}{N}) \right|^2 + o_N(1)$$

The contribution of the reaction process is

$$\int_0^t \sum_{x,r} g_r^{fw}(\eta_s(x)) \left(e^{\mathbf{H}(s, \frac{x}{N}) \cdot \gamma_r} - 1 \right) + g_r^{bw}(\eta_s(x)) \left(e^{-\mathbf{H}(s, \frac{x}{N}) \cdot \gamma_r} - 1 \right) ds. \quad (45)$$

Similarly as in the proof of the hydrodynamic limit, both terms (44) and (45) are nonlinear in $\eta_t(\cdot)$ and therefore not a function of the empirical measure π_t^N . Thus, they need to be replaced by block averages $\eta_t^{\varepsilon N}(x)$. The technical tool that allows to do this is the following superexponential estimate. By a local function $\psi(\eta(\cdot))$, we mean a function that only depends on finitely many coordinates $\eta(x_i)$, for instance $\eta(0)$ and $\eta(e)$.

Theorem 4.3. (*Superexponential estimate*) *For each $G \in C([0, T] \times \mathbb{T}^d)$, each local function ψ and each $\varepsilon > 0$, let*

$$V_{N,\varepsilon}^{G,\psi}(t, \boldsymbol{\eta}) = N^{-d} \sum_{x \in \mathbb{T}_N^d} G(t, \frac{x}{N}) \left[\psi(\tau_x \boldsymbol{\eta}) - \Psi(\boldsymbol{\eta}^{\varepsilon N}(x)) \right].$$

Then, for any $\delta > 0$,

$$\limsup_{\varepsilon \rightarrow 0} \limsup_{N \rightarrow \infty} N^{-d} \log P^N \left[\left| \int_0^T V_{N,\varepsilon}(t, \boldsymbol{\eta}_t) dt \right| > \delta \right] = -\infty. \quad (46)$$

The superexponential estimate is a strengthened version of the replacement lemma (32). It says, that the probability for a large difference $V_{N,\varepsilon}^{G,\psi}$ decays superexponentially fast in N^d . Such a superexponentially small error is needed, because we want to apply the replacement lemma for events $P^N(\mathcal{O})$ that are exponentially small.

We will give a detailed proof of the superexponential estimate below. It is exactly the same proof as for the simple exclusion process [KOV89]. It is based on a Feynman-Kac formula, on the reversibility of

the generator L with respect to the invariant measure $\nu_{\mathbf{w}}^N$ and on the replacement lemma in its non-supereponential form. By $L^2(\mathcal{X}_N, \nu_{\mathbf{w}}^N)$, we denote the space of real-valued functions $f(\boldsymbol{\eta})$ equipped with the weighted inner product

$$\langle f, g \rangle_{\nu_{\mathbf{w}}^N} = \sum_{\boldsymbol{\eta} \in \mathcal{X}_N} f(\boldsymbol{\eta})g(\boldsymbol{\eta})\nu_{\mathbf{w}}^N(\boldsymbol{\eta}).$$

Because of the detailed balance condition, the generator L of the reaction-exclusion process is symmetric in $L^2(\mathcal{X}_N, \nu_{\mathbf{w}}^N)$.

Proof. Throughout the proof remember that the state space \mathcal{X}_N is a discrete, finite set of configurations $\boldsymbol{\eta}(\cdot)$, so all the operators appearing in the proof are finite-dimensional matrices. For any N, ε, G, ψ as indicated in Theorem 4.3 and any $a < \infty$, consider the operator $L + aN^d V_{N,\varepsilon}^{G,\psi}$ on $L^2(\mathcal{X}_N, \nu_{\mathbf{w}}^N)$, where $V_{N,\varepsilon}^{G,\psi}$ is to be understood as a multiplication operator $(Vf)(\boldsymbol{\eta}) = V(\boldsymbol{\eta})f(\boldsymbol{\eta})$. The operator $L + aN^d V_{N,\varepsilon}^{G,\psi}$ is symmetric in $L^2(\mathcal{X}_N, \nu_{\mathbf{w}}^N)$. Denote by $\lambda_{N,\varepsilon}(a)$ its largest eigenvalue. By the Feynman-Kac formula and the spectral theorem for symmetric matrices, we obtain

$$\mathbb{E}_{\mu^N} \left[e^{aN^d \int_0^t V_{N,\varepsilon}^{G,\psi}(\boldsymbol{\eta}_s) ds} \right] = \langle P_V^t \mathbf{1}, \mathbf{1} \rangle_{\nu_{\mathbf{w}}^N} \leq e^{t\lambda_{N,\varepsilon}(a)}.$$

Thus, it follows from the exponential Chebychev inequality that

$$P^N \left(\int_0^t V_{N,\varepsilon}^{G,\psi}(\boldsymbol{\eta}_s) \geq \delta \right) \leq e^{t\lambda_{N,\varepsilon}(a) - aN^d \delta}.$$

Therefore, in order to prove the superexponential estimate, it suffices to show

$$\limsup_{\varepsilon \rightarrow 0} \limsup_{N \rightarrow \infty} N^{-d} \lambda_{N,\varepsilon}(a) = 0.$$

The largest eigenvalue of any symmetric matrix A can be calculated through

$$\lambda_{\max}(A) = \sup_{\langle f, f \rangle_{\nu_{\mathbf{w}}^N} = 1} \langle f, Af \rangle_{\nu_{\mathbf{w}}^N}.$$

Remember that the Dirichlet form of a probability measure μ was defined as $D_N(\mu) = -\langle f, Lf \rangle_{\nu_{\mathbf{w}}^N}$ with $\mu(\boldsymbol{\eta}) = (f(\boldsymbol{\eta}))^2 \nu_{\mathbf{w}}^N(\boldsymbol{\eta})$. Thus, by using $A = L + aN^d V_{N,\varepsilon}^{G,\psi}$ in the above variational formula for the largest eigenvalue and by using the probability distribution $\mu(\boldsymbol{\eta})$ instead of $f(\boldsymbol{\eta})$, we obtain the following variational expression for $\lambda_{N,\varepsilon}(a)$:

$$N^{-d} \lambda_{N,\varepsilon}(a) = \sup_{\|\mu\|_1=1} \left\{ \sum_{\boldsymbol{\eta} \in \mathcal{X}_N} aV_{N,\varepsilon}^{G,\psi}(\boldsymbol{\eta})\mu(\boldsymbol{\eta}) - N^{-d} D_N(\mu) \right\}$$

where the supremum is over all probability measures μ on \mathcal{X}_N . Since $a \cdot V_{N,\varepsilon}^{G,\psi}(\boldsymbol{\eta}) \leq C$ for some C , we can restrict the supremum to all μ such that $D_N(\mu) \leq CN^d$. Moreover, remember that

$$D_N(\mu) = D_{\text{react}}(\mu) + N^2 D_{\text{excl}}(\mu) \geq N^2 D_{\text{excl}}(\mu).$$

Taken together, this means that

$$\begin{aligned} & \limsup_{\varepsilon \rightarrow 0} \limsup_{N \rightarrow \infty} N^{-d} \lambda_{N,\varepsilon}(a) \\ & \leq \max \left\{ 0, \limsup_{\varepsilon \rightarrow 0} \limsup_{N \rightarrow \infty} \sup_{\substack{\|\mu\|_1=1 \\ D_{\text{excl}}(\mu) \leq CN^{d-2}}} \sum_{\boldsymbol{\eta} \in \mathcal{X}_N} aV_{N,\varepsilon}^{G,\psi}(\boldsymbol{\eta})\mu(\boldsymbol{\eta}) - CN^{-d+2} D_{\text{excl}}(\mu) \right\}. \end{aligned}$$

Finally, by the replacement lemma, the second term within the maximum must be less or equal zero. \square

4.2 Proof of the upper bound

We first consider the static large deviations that arise from the term $\log \frac{\nu_{\mathbf{b}(\cdot)}^N(\boldsymbol{\eta}_0(\cdot))}{\nu_{\mathbf{w}}^N(\boldsymbol{\eta}_0(\cdot))}$ in (43). Since both measures are product measures and since $\nu_{\mathbf{c}}(\mathbf{n}) = \binom{M}{\mathbf{n}} \mathbf{c}^{\mathbf{n}} (\mathbf{1}-\mathbf{c})^{M-\mathbf{n}}$, we find

$$\begin{aligned} \log \frac{\nu_{\mathbf{b}(\cdot)}^N(\boldsymbol{\eta}_0(\cdot))}{\nu_{\mathbf{w}}^N(\boldsymbol{\eta}_0(\cdot))} &= \sum_{x \in \mathbb{T}_N^d} \log \frac{\nu_{\mathbf{b}(\frac{x}{N})}^N(\boldsymbol{\eta}_0(\frac{x}{N}))}{\nu_{\mathbf{w}}^N(\boldsymbol{\eta}_0(\frac{x}{N}))} \\ &= \sum_{i=1}^I \sum_{x \in \mathbb{T}_N^d} \eta_{0,i}(\frac{x}{N}) \log \frac{b_i(\frac{x}{N})}{w_i} + (M - \eta_{0,i}(\frac{x}{N})) \log \frac{1-b_i(\frac{x}{N})}{1-w_i} = MN^d F_{\mathbf{b}(\cdot)}^N(\boldsymbol{\pi}_0^N) \end{aligned}$$

where $F_{\mathbf{b}(\cdot)}^N$ denotes the function

$$F_{\mathbf{b}(\cdot)}^N(\boldsymbol{\pi}) = \sum_{i=1}^I \langle \pi_i, \log \frac{b_i(\cdot)}{w_i} \rangle + \langle \lambda_N - \pi_i, \log \frac{1-b_i(\cdot)}{1-w_i} \rangle, \quad \lambda_N = N^{-d} \sum_{x \in \mathbb{T}_N^d} \delta_{\frac{x}{N}} \quad (47)$$

Here λ_N is a discrete approximation of the Lebesgue measure, that converges to the Lebesgue measure for $N \rightarrow \infty$. The corresponding functional for $N = \infty$ is

$$F_{\mathbf{b}(\cdot)}(\boldsymbol{\pi}) = \sum_{i=1}^I \langle \pi_i, \log \frac{b_i(\cdot)}{w_i} \rangle + \langle 1 - \pi_i, \log \frac{1-b_i(\cdot)}{1-w_i} \rangle.$$

For a fixed $\mathbf{b}(\cdot)$, the difference between both functionals is of order $o_N(1)$, i.e.

$$F_{\mathbf{b}(\cdot)}^N(\boldsymbol{\pi}) = F_{\mathbf{b}(\cdot)}(\boldsymbol{\pi}) + o_N(1).$$

Remember that every limit point $\boldsymbol{\pi}$ of an empirical measure $\boldsymbol{\pi}^N$ has a density, because only a maximum of M particles is allowed per species per lattice site. For measures with a density $\boldsymbol{\pi}(dx) = \mathbf{c}(x)dx$, the above function $F_{\mathbf{b}(\cdot)}$ can be written as

$$F_{\mathbf{b}(\cdot)}(\mathbf{c}(\cdot)) = \sum_{i=1}^I \int_{\mathbb{T}^d} c_i(x) \log \frac{b_i(x)}{w_i} + (1-c_i(x)) \log \frac{1-b_i(x)}{1-w_i}.$$

In the beginning of this section, we claimed that the static rate function $\mathcal{I}_0(\mathbf{c}(\cdot))$ is the Fermi-Dirac entropy

$$\mathcal{I}_0(\mathbf{c}(\cdot)) = \sum_{i=1}^I \int_{\mathbb{T}^d} c_i(x) \log \frac{c_i(x)}{w_i} + (1-c_i(x)) \log \frac{1-c_i(x)}{1-w_i} dx.$$

It appears because of the following variational representation of \mathcal{I}_0 .

Lemma 4.4. \mathcal{I}_0 has the variational representation

$$\mathcal{I}_0(\mathbf{c}(\cdot, \cdot)) = \sup_{\mathbf{b}(\cdot) \in C(\mathbb{T}^d, \mathbb{R}_+^I)} F_{\mathbf{b}(\cdot)}(\mathbf{c}(\cdot)). \quad (48)$$

Proof. The concave function

$$f(b) = c \log b + (1-c) \log(1-b)$$

attains its unique maximum for $b = c$. □

Theorem 4.5. For every compact set $\mathcal{K} \subset \mathcal{D}([0, T], \mathcal{M}_+^I)$,

$$\limsup_{N \rightarrow \infty} \frac{1}{MN^d} \log P^N(\mathcal{K}) \leq - \inf_{\mathbf{c} \in \mathcal{K}} \mathcal{I}(\mathbf{c}). \quad (49)$$

For the proof of the upper bound, we will need the following minimax lemma, the proof of which can be found in the Appendix 2 of [Kil98].

Lemma 4.6. (Minimax lemma) Consider a polish space \mathcal{E} and a sequence of probability measures P^N on \mathcal{E} . Let $\{\mathcal{J}_s : \mathcal{E} \rightarrow \mathbb{R}, s \in S\}$ be a family of upper semi-continuous functions indexed by some set S . Assume that we are able to prove upper bounds for every open subset \mathcal{O} of \mathcal{E} :

$$\limsup_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{O}) \leq \inf_{s \in S} \sup_{\pi \in \mathcal{O}} \mathcal{J}_s(\pi).$$

Then, for every compact set \mathcal{K} ,

$$\limsup_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{K}) \leq \sup_{\pi \in \mathcal{O}} \inf_{s \in S} \mathcal{J}_s(\pi).$$

Proof. (Proof of Theorem 4.5) Remember that $R_r^{fw/bw}(\mathbf{c}) = \mathbb{E}_{\nu_{\mathbf{c}}} [g_r^{fw/bw}(\mathbf{n})]$ and

$$\mathbb{E}_{\nu_{\mathbf{c}}} [\eta_i(x) (1 - \frac{\eta_i(x)}{M})] = c_i(1 - c_i) = c_i h_i.$$

Let $B_{H, \delta, \varepsilon, N}$ be the set

$$B_{H, \delta, \varepsilon, N} = \{ \boldsymbol{\eta} \in \mathcal{D}([0, T], \mathcal{X}_N) : \int_0^T V_{N, \varepsilon}^H(t, \boldsymbol{\eta}_t) dt \leq \delta \}$$

with

$$\begin{aligned} V_{N, \varepsilon}^H(t, \boldsymbol{\eta}_t) &= \sum_{r=1}^R \left| \sum_{x \in \mathbb{T}_N^d} (g_r^{fw}(\boldsymbol{\eta}_t(x)) - R_r^{fw}(\boldsymbol{\eta}_t^{\varepsilon N}(x))) (e^{\mathbf{H}(s, x) \cdot \boldsymbol{\gamma}_r} - 1) \right| \\ &+ \sum_{r=1}^R \left| \sum_{x \in \mathbb{T}_N^d} (g_r^{bw}(\boldsymbol{\eta}_t(x)) - R_r^{bw}(\boldsymbol{\eta}_t^{\varepsilon N}(x))) (e^{-\mathbf{H}(s, x) \cdot \boldsymbol{\gamma}_r} - 1) \right| \\ &+ \sum_{i, e} D_i \left| \frac{\eta_{t, i}(x)}{M} (1 - \frac{\eta_{t, i}(x+e)}{M}) - \eta_{t, i}^{\varepsilon N}(x) (1 - \eta_{t, i}^{\varepsilon N}(x)) \right| \left(\partial_e H_i(\frac{x}{N}) \right)^2 \end{aligned}$$

where $\eta_{t, i}^{\varepsilon N}(x) = M^{-1} (2\varepsilon N + 1)^{-d} \sum_{|x-y| \leq \varepsilon N} \eta_{t, i}(y)$ was the block average of length εN of $\eta_{t, i}$. Define

$$U(\mathbf{H}, \delta, \varepsilon) = \limsup_{N \rightarrow \infty} N^{-d} \log P^N(B_{\mathbf{H}, \delta, \varepsilon, N}^c)$$

By the superexponential estimate, it follows that

$$\limsup_{\varepsilon \rightarrow 0} U(\mathbf{H}, \delta, \varepsilon) = -\infty.$$

For any measurable $\mathcal{O} \in \mathcal{D}((0, T); \mathcal{M}_+)$ we have

$$P^N(\mathcal{O}) \leq P^N(\mathcal{O} \cap B_{H, \delta, \varepsilon, N}) + P^N(B_{\mathbf{H}, \delta, \varepsilon, N}^c).$$

Thus

$$\limsup_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{O}) \leq \max \left\{ \limsup_{N \rightarrow \infty} N^{-d} \log P^N(O \cap B_{\mathbf{H}, \delta, \varepsilon, N}), U(\mathbf{H}, \delta, \varepsilon) \right\}.$$

and we can restrict ourselves to $O \cap B_{\mathbf{H}, \delta, \varepsilon, N}$. On $B_{\mathbf{H}, \delta, \varepsilon, N}$, we can replace functions by their block averages by making only an error $O(\delta)$. Remember from the introduction, that the main strategy of the proof consists in using the following inequality

$$N^{-d} \log P^N(O \cap B_{\mathbf{H}, \delta, \varepsilon, N}) \leq - \inf_{\pi^N \in \mathcal{O} \cap B_{\mathbf{H}, \delta, \varepsilon, N}} N^{-d} \log \frac{P_{\mathbf{H}, \mathbf{b}}^N(\boldsymbol{\eta}^N)}{P^N(\boldsymbol{\eta}^N)}.$$

Since there is a one-to-one correspondence between empirical measures π^N and configurations $\boldsymbol{\eta}^N$, we can use the two interchangeably. Next we insert above the precise expression (43) for the Radon-Nikodym derivative $\frac{P_{\mathbf{H}, \mathbf{b}}^N(\boldsymbol{\eta}^N)}{P^N(\boldsymbol{\eta}^N)}$. The contributions (44) and (45) from the exclusion and reaction process are replaced by their block averages and therefore an the error term $O(\delta)$ appears. Thus

$$\begin{aligned} \frac{1}{MN^d} \log \frac{P_{\mathbf{H}, \mathbf{b}}^N(\boldsymbol{\eta})}{P^N(\boldsymbol{\eta})} &= \mathcal{J}_{\text{lin}}(\pi^N, \mathbf{H}) + F_{\mathbf{b}(\cdot)}^N(\pi_0^N) \\ &+ N^{-d} \int_0^T \sum_{x, r} R_r^{fw}(\boldsymbol{\eta}_t^{\varepsilon N}(x)) (e^{\mathbf{H}(t, \frac{x}{N}) \cdot \gamma_r} - 1) + R_r^{bw}(\boldsymbol{\eta}_t^{\varepsilon N}(x)) (e^{-\mathbf{H}(t, \frac{x}{N}) \cdot \gamma_r} - 1) ds \\ &+ N^{-d} \int_0^T \sum_{i, e} D_i \boldsymbol{\eta}_{t, i}^{\varepsilon N}(x) (1 - \boldsymbol{\eta}_{t, i}^{\varepsilon N}(x)) (\partial_e H_i(t, \frac{x}{N}))^2 ds + O(\delta) + o_N(1). \end{aligned}$$

Next we proceed as in the proof of the hydrodynamic limit. The block average over macroscopic blocks of length εN can be written as a convolution of the empirical measure with $\iota_\varepsilon = (2\varepsilon)^{-d} \mathbf{1}_{[-\varepsilon, \varepsilon]^d}$, i.e.

$$\boldsymbol{\eta}^{\varepsilon N}(x) = (\pi^N * \iota_\varepsilon)\left(\frac{x}{N}\right).$$

Replacing the sums by integrals with respect to $(\pi^N * \iota_\varepsilon)(\cdot)$ produces an error $o_N(1)$. Moreover we have

$$\mathcal{J}_{\text{lin}}(\pi^N, \mathbf{H}) = \mathcal{J}_{\text{lin}}(\pi^N * \iota_\varepsilon, \mathbf{H}) + o(\varepsilon)$$

where $o(\varepsilon)$ depends only on \mathbf{H} and other constants, but not on π^N . Thus, in conclusion

$$\frac{1}{MN^d} \log P^N(O \cap B_{\mathbf{H}, \delta, \varepsilon, N}) \leq - \inf_{\pi^N \in \mathcal{O}} \left(\mathcal{J}(\pi^N * \iota_\varepsilon, \mathbf{H}) + F_{\mathbf{b}(\cdot)}(\pi_0^N) \right) + O(\delta) + o(\varepsilon) + o_N(1).$$

Note that we replaced the infimum over $\mathcal{O} \cap B_{\mathbf{H}, \delta, \varepsilon, N}$ by a larger infimum over \mathcal{O} . Thus, the infimum does not depend on N anymore and after letting $N \rightarrow \infty$, and minimizing over \mathbf{H} , \mathbf{b} , ε and δ , we obtain

$$\limsup_{N \rightarrow \infty} N^{-d} \log P^N(O) \leq \inf_{\mathbf{H}, \mathbf{b}, \delta, \varepsilon} \sup_{\pi \in \mathcal{O}} \mathcal{J}_{\mathbf{H}, \mathbf{b}, \delta, \varepsilon}(\pi)$$

with

$$\mathcal{J}_{\mathbf{H}, \mathbf{b}, \delta, \varepsilon}(\pi) = \max \left\{ -\mathcal{J}(\pi * \iota_\varepsilon, \mathbf{H}) - F_{\mathbf{b}(\cdot)}(\pi_0) + O(\delta) + o(\varepsilon), U(\mathbf{H}, \delta, \varepsilon) \right\}.$$

For each $\mathbf{H} \in C^{1,2}([0, T] \times \mathbb{T}^d, \mathbb{R}^I)$ and $\mathbf{b} \in C(\mathbb{T}^d, \mathbb{R}^I)$ and $\delta, \varepsilon > 0$, the function $\mathcal{J}_{\mathbf{H}, \mathbf{b}, \delta, \varepsilon}$ is upper semi-continuous. Thus we can apply the minimax lemma 4.6 and obtain for every compact set $\mathcal{K} \subset \mathcal{D}([0, T], \mathcal{M}_+)$ that

$$\limsup_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{K}) \leq \sup_{\pi \in \mathcal{K}} \inf_{\mathbf{H}, \mathbf{b}, \delta, \varepsilon} \mathcal{J}_{\mathbf{H}, \mathbf{b}, \delta, \varepsilon}(\pi).$$

Since $-\mathcal{J}(\boldsymbol{\pi})$ is upper semicontinuous,

$$\lim_{\varepsilon \rightarrow 0} -\mathcal{J}(\boldsymbol{\pi} * \iota_\varepsilon, \mathbf{H}) \leq -\mathcal{J}(\boldsymbol{\pi}, \mathbf{H}).$$

From this we deduce, using $\lim_{\varepsilon \rightarrow 0} U(\mathbf{H}, \delta, \varepsilon)$, that for fixed $\boldsymbol{\pi}, \mathbf{H}, \mathbf{b}, \delta$

$$\lim_{\varepsilon \rightarrow 0} \mathcal{J}_{\mathbf{H}, \mathbf{b}, \delta, \varepsilon}(\boldsymbol{\pi}) \leq -\mathcal{J}(\boldsymbol{\pi}, \mathbf{H}) - F_{\mathbf{b}(\cdot)}(\boldsymbol{\pi}_0) + O(\delta).$$

After taking the limit $\delta \rightarrow 0$, we conclude

$$\limsup_{N \rightarrow \infty} \frac{1}{MN^d} \log P^N(\mathcal{K}) \leq - \inf_{\boldsymbol{\pi} \in \mathcal{K}} \sup_{\mathbf{H}, \mathbf{b}} \mathcal{J}(\boldsymbol{\pi}, \mathbf{H}) + F_{\mathbf{b}(\cdot)}(\boldsymbol{\pi}).$$

By Lemma 4.4, we can perform the supremum over $\mathbf{b}(\cdot)$ explicitly and obtain the static rate functional \mathcal{I}_0 . This finishes the proof of the theorem. \square

The last step consists in extending the upper bound from compact sets to closed sets. This is typically done by showing that the family of probability measures P^N is exponentially tight.

Lemma 4.7. (Exponential tightness) *The family P^N of probability measures on the Skorohod space $\mathcal{D}([0, T]; \mathcal{M}_+^I)$ is exponentially tight, i.e. for every $\alpha < \infty$ there exists a compact set $\mathcal{K}_\alpha \subset \mathcal{D}([0, T]; \mathcal{M}_+^I)$ such that*

$$\limsup_{N \rightarrow \infty} N^{-d} \log \mu_N(\mathcal{K}_\alpha^c) < -\alpha. \quad (50)$$

Exponential tightness of the simple exclusion process is shown in Theorem 4.1 of [KOV89] or [Kil98, page 271 ff.]. Since the proof of exponential tightness the reaction-diffusion process is exactly the same, we do not reproduce it here but refer to the above sources. We conclude this section by showing how to extend the upper bound for compact sets to arbitrary closed sets \mathcal{C} using exponential tightness.

Proof. (Large-deviation upper bound for general closed sets \mathcal{C}). Let $\mathcal{C} \subset \mathcal{D}((0, T); \mathcal{M}_+^I)$ be a closed set and let \mathcal{K}_α be a compact set satisfying (50). Then

$$P^N(\mathcal{C}) \leq P^N(\mathcal{C} \cap \mathcal{K}_\alpha) + P^N(\mathcal{K}_\alpha^c).$$

Thus

$$\begin{aligned} \limsup_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{C}) &\leq \max(\limsup_{N \rightarrow \infty} N^{-d} \log P^N(\mathcal{C} \cap \mathcal{K}_\alpha), -\alpha) \\ &\leq \max\left(- \inf_{\mathbf{c} \in \mathcal{C} \cap \mathcal{K}_\alpha} \mathcal{I}(\mathbf{c}), -\alpha\right). \end{aligned}$$

\square

A Radon-Nikodym formula

Lemma A.1. *Let $Lf(x) = \sum_y r(x, y)(f(y) - f(x))$ be the generator of a continuous time Markov chain X_t on a finite state space E with initial distribution $\nu_0(x)$. For a given $F \in C^1([0, T] \times E, \mathbb{R})$ let*

$$(L_{F, \mu} f)(x) = \sum_y r(x, y) e^{F(t, y) - F(t, x)} (f(y) - f(x))$$

be a time-dependent perturbation of L with the initial distribution $\mu(x)$. Then the Radon-Nikodym derivative $\frac{dP_{F,\mu}(X(\cdot))}{dP(X(\cdot))}$ for trajectories $X(\cdot) \in \mathcal{D}([0, T]; E)$ is given by

$$\frac{dP_{F,\mu}(X(\cdot))}{dP(X(\cdot))} = \frac{\mu(X_0)}{\nu_0(X_0)} \exp \left\{ F(T, X_T) - F(0, X_0) - \int_0^T \partial_s F(s, X_s) ds - \sum_y \int_0^T r(X_s, y) (e^{F(s,y)-F(s,X_s)} - 1) ds \right\}.$$

Proof. Any trajectory $X(\cdot)$ of a continuous time Markov chain is characterized by a sequence

$$X(\cdot) \hat{=} (x_0, t_1, x_1, \dots, t_n, x_n)$$

which means that $X(t)$ jumps from the point x_{i-1} to the point x_i at time t_i . If transition rates $r(x, y)$ between two states do not depend on time, then the probability for the trajectory $X(\cdot)$ is given by

$$P(X(\cdot)) = \nu_0(x_0) \prod_{i=1}^n r(x_{i-1}, x_i) e^{-\sum_y r(x_{i-1}, y)(t_i - t_{i-1})}.$$

Let us explain this expression. For every transition $x \rightarrow y$, we have an independent exponential clock with rate $r(x, y)$. For any exponential random variable T with rate λ , we have

$$P(T = t) = \lambda e^{-\lambda t} \quad \mathbb{P}(T > t) = e^{-\lambda t}.$$

If x_{i-1} jumps to the point x_i at time t_i , then this means that $T_{x_i} = t_i$ and $T_y > t_i$ for all $y \neq x_i$. The probability density of that event is given by

$$P(T_y = t \wedge T_{y'} > t \forall y' \neq y) = r(x_{i-1}, y) e^{-\sum_{y'} r(x_{i-1}, y') t}.$$

This explains the above expression for $P(X(\cdot))$. In the case of an exponential clock with time-dependent rate $\lambda(t)$, the probability distribution follows the law

$$\mathbb{P}(T > t) = e^{-\int_0^t \lambda(s) ds}.$$

Thus, in the case of many time-dependent exponential clocks T_i with rates $\lambda_i(t)$, we obtain the probability

$$P(T_i = t \wedge T_j > t \forall j \neq i) = \lambda_i(t) e^{-\sum_{j=1}^n \int_0^t \lambda_j(s) ds}.$$

Let us now look at the specific time-dependent generator L_F given by

$$L_F f(x) = \sum_y r(x, y) e^{F(t,y)-F(t,x)} (f(y) - f(x))$$

with initial distribution $\mu(\cdot)$. Then the quotient of the probability densities $\frac{dP_{F,\mu}(X(\cdot))}{dP(X(\cdot))}$ of a trajectory $X(\cdot)$ is given by

$$\frac{dP_H(X(\cdot))}{dP(X(\cdot))} = \frac{\mu(x_0)}{\nu_0(x_0)} \prod_{i=1}^N e^{F(t_i, x_i) - F(t_i, x_{i-1})} \cdot \exp \left\{ - \int_{t_{i-1}}^{t_i} \sum_y r(x_{i-1}, y) (e^{F(s,y)-F(s,x_{i-1})} - 1) ds \right\}.$$

By using that $X(s) = x_i$ for $s \in [t_i, t_{i+1})$ and introducing the times $t_0 = 0$ and $t_{N+1} = T$, we can rewrite $\prod_{i=1}^N e^{F(t_i, x_i) - F(t_i, x_{i-1})}$ as

$$\begin{aligned} \sum_{i=1}^N F(t_i, x_i) - F(t_i, x_{i-1}) &= F(t_{N+1}, x_N) - F(t_0, x_0) - \sum_{i=0}^N F(t_{i+1}, x_i) - F(t_i, x_i) \\ &= F(T, X(T)) - F(0, X(0)) - \int_0^T \partial_s F(s, X(s)) ds. \end{aligned}$$

In the last step we use Thus we managed to bring the Radon-Nikodym derivative into a form that does not depend on the jump times t_i . In summary it equals

$$\begin{aligned} \frac{dP_{F,\mu}(X(\cdot))}{dP(X(\cdot))} &= \frac{\mu(x_0)}{\nu_0(x_0)} \exp \left\{ F(T, X_T) - F(0, X_0) - \int_0^T \partial_s F(s, X_s) ds \right. \\ &\quad \left. - \sum_y \int_0^T r(X_s, y) (e^{F(s,y) - F(s, X_s)} - 1) ds \right\} \end{aligned}$$

which proves the lemma. \square

B Martingale Decomposition

Lemma B.1. *Let X_t be a Markov process on finite state space S with generator L and $f(t, X_t)$ be a time-dependent function of the process. Then the functions*

$$\begin{aligned} M_t^f &= f(t, X_t) - f(0, X_0) - \int_0^t (\partial_s + L)f(s, X_s) ds, \\ N_t^f &= (M_t^f)^2 - \int_0^t (Lf^2)(s, X_s) - 2f(X_s)(Lf)(s, X_s) ds \end{aligned}$$

are martingales. We write

$$\langle M^f \rangle_t := \int_0^t (Lf^2)(s, X_s) - 2f(X_s)(Lf)(s, X_s) ds$$

for the predictable quadratic variation of M_t^f .

Proof. Without loss of generality, we assume $f(X_0) = 0$ in the following. In the following, the partial derivatives $\partial_r f(r, X_r)$ or $\partial_s f(s, X_s)$ will always be with respect to the first variable of $f(u, X_t)$. Let P_t be the semigroup of the generator L . By definition of a martingale, we have to show $\mathbb{E} [M_t^f | \mathcal{F}_s] = M_s^f$. This is equivalent to

$$\mathbb{E} [f(t, X_t) - f(s, X_s) | \mathcal{F}_s] = \int_s^t (\partial_r + L)f(r, X_r) dr. \quad (51)$$

For any parametric function $f(u, X_t)$, the conditional expectation with respect to \mathcal{F}_s equals

$$\mathbb{E} [f(u, X_t) | \mathcal{F}_s] = P_{t-s} f(u, X_s),$$

where the semigroup P_τ acts only on the second value. More precisely, let $p_\tau(x, y)$ be the Markov transition kernel of P_τ . Then

$$P_\tau f(u, x) := \sum_y f(u, x) p_\tau(x, y).$$

Thus, the left hand side of (51) equals

$$\mathbb{E} [f(t, X_t) - f(s, X_s) | \mathcal{F}_s] = P_{t-s} f(t, X_s) - f(s, X_s)$$

The right hand side equals

$$\begin{aligned} \mathbb{E} \left[\int_s^t (\partial_r + L)f(r, X_r) dr | \mathcal{F}_s \right] &= \int_s^t P_{r-s} ((\partial_r + L)f)(r, X_s) dr \\ &= \int_s^t \frac{d}{dr} [(P_{r-s} f)(r, X_s)] dr = (P_{t-s} f)(t, X_s) - f(s, X_s) \end{aligned}$$

which shows that M_t^f is a martingale. Regarding the martingale property of N_t^f , we first observe that

$$\begin{aligned} (M_t^f)^2 &= f^2(t, X_t) - 2f(t, X_t) \int_0^t (\partial_s + L)f(s, X_s) ds + \left(\int_0^t (\partial_s + L)f(s, X_s) ds \right)^2 \\ &= f^2(t, X_t) - 2M_t^f \int_0^t (\partial_s + L)f(s, X_s) ds - \left(\int_0^t (\partial_s + L)f(s, X_s) ds \right)^2 \end{aligned}$$

The next crucial step is a martingale integration by parts which gives

$$M_t^f \int_0^t (\partial_s + L)f(s, X_s) ds = \int_0^t \int_0^s (\partial_r + L)f(r, X_r) dM_s^f + \int_0^t M_s^f (\partial_s + L)f(s, X_s) ds.$$

The martingale integration by parts can be avoided by working with conditional expectations instead. Though more elementary, it makes the calculations lengthier. The first term on the right hand side is a martingale since it is an Ito integral with respect to the martingale M_t^f . By reinserting the full expression for M_s^f in the second term and using

$$\left(\int_0^t (\partial_s + L)f(s, X_s) ds \right)^2 = 2 \int_0^t \int_0^s (\partial_s + L)f(s, X_s) \cdot (\partial_r + L)f(r, X_r) dr ds$$

we obtain

$$(M_t^f)^2 = f^2(t, X_t) - 2 \int_0^t f(s, X_s) (\partial_s + L)f(s, X_s) ds + \text{martingale}$$

where martingale stands for some remaining martingale terms. Finally, by using

$$f^2(t, X_t) = M_t^{f^2} + \int_0^t (\partial_s + L)f^2(s, X_s) ds$$

we see that the time derivatives cancel and obtain

$$(M_t^f)^2 = \int_0^t Lf^2(s, X_s) - 2f(s, X_s)Lf(s, X_s) ds + \text{martingale}.$$

□

C Exclusion process with a multinomial equilibrium distribution

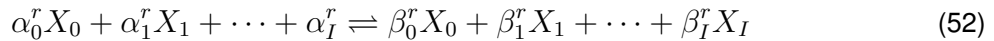
A variant of the exclusion process used in this paper puts a bound on the sum of all particles $\eta_i(x)$ per lattice site, i.e.

$$\sum_{i=1}^I \eta_i(x) \leq M.$$

In this model, there is only one hole species X_0 defined by $\eta_0(x) = M - \sum_{i=1}^I \eta_i(x)$. The rate $r(\boldsymbol{\eta}, \boldsymbol{\eta}_i^{x, x+e})$ for particle jumps is modified to

$$r(\boldsymbol{\eta}, \boldsymbol{\eta}_i^{x, x+e}) = N^2 D_i \eta_i(x) (M - \eta_0(x+e)).$$

A reaction must be complemented by the hole species



in such a way that the number of all particles including the holes is conserved by every reaction. This means that the stoichiometric vectors have to satisfy $\sum_{i=0}^I \alpha_i^r = \sum_{i=0}^I \beta_i^r$. The generator of the corresponding reaction-exclusion process is

$$\begin{aligned} Lf(\boldsymbol{\eta}) &= \sum_{x, |e|=1} N^2 D_i \eta_i(x) \left(1 - \frac{\eta_0(x+e)}{M}\right) [f(\boldsymbol{\eta}_i^{x, x+e}) - f(\boldsymbol{\eta})] \\ &+ \sum_{x, r} \kappa_r^{fw} C_M t_{\alpha_r}(\boldsymbol{\eta}(x)) [f(\boldsymbol{\eta}_x^{\gamma_r}) - f(\boldsymbol{\eta})] \\ &+ \kappa_r^{bw} C_M t_{\eta_r}(\boldsymbol{\eta}(x)) [f(\boldsymbol{\eta}_x^{-\gamma_r}) - f(\boldsymbol{\eta})]. \end{aligned} \quad (53)$$

There exist similar statements to Propositions 2.4 and 2.2, but with the binomial distribution replaced by the multinomial distribution. More precisely, for $\mathbf{c} \leq 1$ with $\sum_{i=0}^I c_i = 1$ we define the multinomial distribution

$$\omega_{\mathbf{c}}(\mathbf{n}) := \sum_{\mathbf{n}: |\mathbf{n}|_1 = M} \binom{M}{\mathbf{n}} \prod_{i=0}^I c_i^{n_i} \quad \binom{M}{\mathbf{n}} := \frac{M!}{n_0! \cdots n_I!}$$

and the product multinomial distribution $\omega_{\mathbf{c}}^N(\boldsymbol{\eta}(\cdot)) = \prod_{x \in \mathbb{T}_N^d} \omega_{\mathbf{c}}(\boldsymbol{\eta}(x))$ on configurations $\boldsymbol{\eta}(\cdot) \in \mathcal{X}_N$. Then the analogue of Proposition (2.4) for the reaction-exclusion process (53) holds true with respect to the multinomial distribution.

Proposition C.1. *If the chemical reaction network (52) satisfies detailed balance with respect to $\mathbf{w} \in \mathbb{R}_+^{I+1}$, i.e.*

$$\kappa_r^{fw} \mathbf{c}^{\alpha_r} = \kappa_r^{bw} \mathbf{c}^{\beta_r}.$$

Then the product multinomial distribution $\omega_{\mathbf{c}}^N$ is a reversible equilibrium of the reaction-exclusion process (53).

The hydrodynamic limit of (53) should be of the form

$$\dot{\mathbf{c}} = \operatorname{div}(\mathbb{D}(\mathbf{c}) \nabla \mathbf{c}) + \sum_{r=1}^R (\beta_r - \alpha_r) (\kappa_r^{fw} \mathbf{c}^{\alpha_r} - \kappa_r^{bw} \mathbf{c}^{\beta_r}) \quad (54)$$

with a nonlinear diffusion tensor $\mathbb{D}(\mathbf{c})$ involving crossdiffusion terms. Similar to [Qua92], see also [KiL98, Chapter 7], it might be possible to prove the hydrodynamic limit (54) and to obtain a variational formula for $\mathbb{D}(\mathbf{c})$.

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