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► **To cite this version:**

Segun Goh, Junhyuk Woo, Jean-Yves Fortin, Mooyoung Choi. Grand canonical description of equilibrium and non-equilibrium systems using spin formalism. *Physica A: Statistical Mechanics and its Applications*, 2020, 558, pp.124983. 10.1016/j.physa.2020.124983 . hal-02906059

**HAL Id: hal-02906059**

**<https://hal.science/hal-02906059>**

Submitted on 24 Jul 2020

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# Grand canonical description of equilibrium and non-equilibrium systems using spin formalism

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## Abstract

We consider an open system in contact with a reservoir, where particles as well as energies can be exchanged between them, and present a description of the dynamics in terms of mixed (pseudo)spin and state variables. Specifically, a master equation is constructed out of the exchange rates for particles and for energies, which allows us to probe the system in the grand canonical description. In particular, employing the state resummation analysis, we obtain coupled time evolution equations for the probability distributions of the system as well as the environment. This is exemplified by a standard growth model, where the steady-state density function exhibits power-law behavior with the exponent depending on the microscopic parameters of the rate equations.

*Keywords:* statistical mechanics, stochastic dynamical systems, master equations, open systems

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## 1. Introduction

Many systems in equilibrium or in non-equilibrium can be described by stochastic processes for which the configuration probabilities satisfy master equations with appropriate reaction rates [1, 2]. For instance, applied to chemical reaction kinetics in biological systems [3], this approach gives the concentrations of reactants as solutions of the time-dependent (evolution) equations obtained from the master equation. From the theoretical point of view, statistical mechanics, especially in the framework of the recently developed stochastic thermodynamics [4, 5, 6], connects such stochastic nature of many particle systems to their macroscopic non-equilibrium dynamics. Accordingly, the second law of thermodynamics as well as the fluctuation theorems and entropy production rates have been addressed [7, 8, 9, 10].

Usually, the number of particles in the system is taken to be conserved (i.e., leading to the canonical ensemble) but in reality, particles may leak out. Such a case of particle exchange with external sources under open boundaries can also be considered [11, 12, 13], for which the description by means of a grand canonical ensemble is more adequate [14]. In general, the choice of an ensemble does not make any difference for a large system in equilibrium. Note, however, that there are some model systems exhibiting differences between microcanonical and canonical ensembles [15, 16]. Also in the presence of particle exchange, the dynamics of the number of particles may not be described by the canonical ensemble. Further, properties of a small system, e.g., in confinement [17, 18] may depend on the ensemble used. In this study, we aim at the extension of a master equation formalism including particle exchange, which is applicable to a broader range of settings. Specifically, we propose a master equation formulation, which can incorporate the dynamics of the reservoir.

In physics, various growth phenomena [19, 20, 21, 22] can be described in terms of non-conserved particle systems, in which new elements are added through stochastic processes [23, 24, 25, 26]. In particular, in a

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non-equilibrium steady-state system a driving force produces growth or destruction of particles via chemical reactions and boundary sources or sink [27, 28]. The distribution or concentration of particles is essential for studying criticality in an evolving system [29, 30, 31], derived from a master equation. Integrating over all possible configurations in general leads the distribution to satisfy functional equations [32]. While the number of particles is not conserved, competition between growth and production of particles may give rise to power-law distributions with exponents depending on the microscopic parameters of the transition rates.

In this work, we focus on a system in contact with a reservoir, described by an extended master equation with additional variables. This may be relevant for Bose condensates where a fraction of the atoms from a reservoir can condensate in the normal state [33], and therefore deriving a master equation in the grand canonical ensemble is an appropriate approach to obtaining thermodynamic quantities such as the average number of particles in the condensate. To describe such a grand canonical system in contact with a particle reservoir as well as a heat reservoir, the number  $N_i$  of particles in given state  $i$  can be used as a dynamical variable. In this way, macroscopic laws of non-equilibrium systems have been derived from stochastic models within the framework of stochastic thermodynamics [9, 6, 10]. In microscopic pictures, e.g., for molecular dynamics or Monte-Carlo simulations, on the other hand, it is necessary to assign the state to each and every individual particle. Combining these two perspectives, we extend the master equation formulation to a microscopic level in this study, by introducing a pseudo-spin state for the location of each particle. Such an additional state variable depicts whether the particle is in the system or in the environment, consequently determining the numbers of particles in the system and in the environment. This master equation describing a grand canonical ensemble allows particle exchange as well as usual energy exchange. Summing over the extended variables then leads to the master equation with energy exchange only, thus recovering the usual description in the canonical ensemble. The particle exchange rates account for the growth or decline of the system in the evolution equation for the distribution function, depending on the parameters chosen. In other cases, there may exist a natural particle exchange rate depending also on the local energy exchange between the system and the reservoir. In the equilibrium state, this defines the proper number of particles at a given chemical potential.

This paper is organized as follows: Section 2 introduces additional occupation variables for the system and its reservoir and establishes the general master equation in the grand canonical ensemble for an extended version of the probability distribution function in Sect. 3. In Sect. 4, via partial resummation of the states from the reservoir, projection onto the canonical ensemble is carried out; this leads to novel time-dependent equations for the non-equilibrium dynamics of the probability distribution functions in Sect. 5. Section 6 presents examples of physical systems in the grand canonical ensemble. Specifically, we consider a growth process with constant production rates, exhibiting a power-law size distribution of its elements, as well as two Ising systems exchanging particles. Finally, a summary is given in Sect. 7.

## 2. Microstates and master equation

To write down a master equation, one should define the microscopic state variables in advance. As we attempt to describe the dynamics of the reservoir as well, the degrees of freedom corresponding to the particles in the reservoir need to be taken into account explicitly. Accordingly, we consider a system of  $N_{\text{tot}}$  particles with  $N$  particles in system  $\mathcal{S}$  and  $N_{\text{env}} \equiv N_{\text{tot}} - N$  particles in reservoir  $\mathcal{S}_{\text{env}}$ . Following the standard formalism for the grand canonical ensemble [34, 35], we assume that the total number  $N_{\text{tot}}$  of particles is a constant. Then the state of particle  $i$  is represented by  $x_i$  (or more generally by a vector  $\vec{x}_i$ ) which can be a discrete or continuous variable ( $i = 1, 2, \dots, N_{\text{tot}}$ ). Before we proceed, we note here that the number  $N$  of particles is by no means a microscopic variable. It is a macroscopic variable (see, e.g., [34]), which is subject to an average, just like the energy or entropy. Therefore, one should consider an alternative variable to formulate a microscopic-level description of grand canonical systems. To this end, a pseudo-spin variable for particle locations is introduced in this study.

Now we discuss how to represent the location of a particle, namely, whether a particle is located in the system  $\mathcal{S}$  or in the reservoir  $\mathcal{S}_{\text{env}}$ . In principle, the total phase space of a particle can be separated into two subspaces, one of which corresponds to the state space of the particle being in the system and the other in the reservoir. The location of each particle is determined accordingly. Therefore, it is necessary

to introduce an interface separating the whole phase space. Then, for instance, one may consider a specific system and develop a model for the interface capturing its permeability responsible for the particle exchange dynamics.

Instead of that, in this study, we take rather a general approach to the case that particles have the same state variables in the same phase space, regardless of their locations. We then simply introduce an additional independent state variable, which represents the location of each particle. Such a type of state variable was introduced to the implementation of a Monte Carlo simulation algorithm for grand canonical systems [36, 37]. Here we extend this idea and include dynamics of the particles in the reservoir as part of the model, in order to illuminate the contributions of the reservoir to the non-equilibrium dynamics of the system.

Specifically, the Ising-type (pseudo-)spin variable  $s_i$  is assigned to particle  $i$ , taking the value  $+1$  or  $-1$  according to whether the particle is in system  $\mathcal{S}$  ( $s_i = 1$ ) or in  $\mathcal{S}_{\text{env}}$  ( $s_i = -1$ ), respectively. Each particle is thus described by state  $(x_i, s_i)$ , depending on whether it belongs to system  $\mathcal{S}$ , in the same manner as the lattice-gas model, as well as on the continuous or discrete energy state  $x_i$ . In the case of a chemical reaction system with several species [10], one may introduce, e.g., Potts spin variables in place of the Ising-type spin variables. The microscopic state of the whole system ( $\mathcal{S} \cup \mathcal{S}_{\text{env}}$ ) is then specified by  $(x_1, x_2, \dots, x_{N_{\text{tot}}}, s_1, \dots, s_{N_{\text{tot}}}) \equiv \{x_i, s_i\}_{\text{tot}}$ . For convenience, we adopt the following notation for state variables:  $\{x_i\}$  and  $\{x_i\}_{\text{env}}$  representing the  $N$  variables in the system and the  $N_{\text{env}}$  variables in the reservoir, respectively, out of the total  $x_{N_{\text{tot}}}$  variables  $\{x_i\}_{\text{tot}} \equiv (x_1, x_2, \dots, x_{N_{\text{tot}}})$  of the whole system.

Once the microscopic states of the whole system are specified, the dynamics of the system can then be described by the master equation for the probability distribution function  $P(\{x_i, s_i\}_{\text{tot}}; t)$  at time  $t$ :

$$\begin{aligned} \frac{\partial P(\{x_i, s_i\}_{\text{tot}}; t)}{\partial t} = & \sum_{j=1}^{N_{\text{tot}}} [w_s(-s_j \rightarrow s_j)P(R_j\{x_i, s_i\}_{\text{tot}}; t) - w_s(s_j \rightarrow -s_j)P(\{x_i, s_i\}_{\text{tot}}; t)] \\ & + \sum_{j=1}^{N_{\text{tot}}} \sum_{x'_j} [w_x(x'_j \rightarrow x_j)P(Q_j\{x_i, s_i\}_{\text{tot}}; t) - w_x(x_j \rightarrow x'_j)P(\{x_i, s_i\}_{\text{tot}}; t)], \end{aligned} \quad (1)$$

where  $w_s$  and  $w_x$  are the transition rates corresponding to particle location and state changes, respectively, with the notation  $R_j\{x_i, s_i\}_{\text{tot}} \equiv (x_1, \dots, x_{N_{\text{tot}}}, s_1, \dots, -s_j, \dots, s_{N_{\text{tot}}})$  and  $Q_j\{x_i, s_i\}_{\text{tot}} \equiv (x_1, \dots, x'_j, \dots, x_{N_{\text{tot}}}, s_1, \dots, s_{N_{\text{tot}}})$ . Henceforth, we omit the time-dependence in the probability distribution function  $P$  for simplicity.

As apparent from its form, simultaneous transitions of two (or more) particles are not included in Eq. (1). Since such a simultaneous transition probability during a short time interval  $\delta t$  is of the order  $(\delta t)^2$ , its contribution vanishes as we take the limit  $\delta t \rightarrow 0$  to obtain the continuous-time dynamics described by Eq. (1) [2, 38, 39]. In the same manner, transitions between states ( $x_i \rightarrow x'_i$ ) and those between locations ( $s_i \rightarrow -s_i$ ) are described separately. We note that equilibrium Monte Carlo simulation algorithms for grand canonical systems consist of two separate steps as well [40, 41]: the transition in its configurational energy with a fixed number of particles and the insertion/removal of a particle. In short, as far as microstates of the system are specified by  $\{x_i, s_i\}_{\text{tot}}$ , our master equation provides rather a general description at the level of the corresponding stochastic process.

Henceforth we use the notation for discrete state variables; however, replacing the summation  $\sum_{\{x_i\}_{\text{tot}}}$  by the integration  $\int d^{N_{\text{tot}}}x$  makes it straightforward to consider continuous state variables as well.

With the master equation proposed, one can probe how the average value of a quantity of interest changes

in time. For instance, the number of particles in system  $\mathcal{S}$  evolves according to

$$\begin{aligned}
\frac{d\langle N \rangle}{dt} &= \sum_{j=1}^{N_{\text{tot}}} \sum_{\{s_i\}_{\text{tot}}} \sum_{\{x_i\}_{\text{tot}}} \delta_{s_j,1} \frac{\partial}{\partial t} P(\{x_i, s_i\}_{\text{tot}}) \\
&= \sum_{j=1}^{N_{\text{tot}}} \sum_{\{s_i\}_{\text{tot}}} \delta_{s_j,1} \sum_{\{x_i\}_{\text{tot}}} \sum_{k=1}^{N_{\text{tot}}} [w_s(-s_k \rightarrow s_k) P(R_k \{x_i, s_i\}_{\text{tot}}) - w_s(s_k \rightarrow -s_k) P(\{x_i, s_i\}_{\text{tot}})] \\
&+ \sum_{j=1}^{N_{\text{tot}}} \sum_{\{s_i\}_{\text{tot}}} \delta_{s_j,1} \sum_{\{x_i\}_{\text{tot}}} \sum_{k=1}^{N_{\text{tot}}} \sum_{x'_k} [w_x(x'_k \rightarrow x_k) P(Q_k \{x_i, s_i\}_{\text{tot}}) - w_x(x_k \rightarrow x'_k) P(\{x_i, s_i\}_{\text{tot}})], \quad (2)
\end{aligned}$$

where the master equation in Eq. (1) has been used. Here the second term on the right-hand side vanishes after the double summation over energy states; only the first term describing spin processes gives non-vanishing contributions. In consequence, Eq. (2) takes the simple form:

$$\frac{d\langle N \rangle}{dt} = - \sum_{j=1}^{N_{\text{tot}}} \langle (\delta_{s_j,1} - \delta_{s_j,-1}) w_s(s_j \rightarrow -s_j) \rangle, \quad (3)$$

where the bracket  $\langle \dots \rangle$  stands for the average over all states.

Closing this section, we make a few remarks on the characteristics of Eq. (1) and its potential applications. First, one may add an overall “super” heat bath, coupled to the whole system  $\mathcal{S} \cup \mathcal{S}_{\text{env}}$ . In Sect. 3, for example, we consider a canonical heat bath to confirm that the conventional grand canonical description is recovered from our formalism. Such a heat bath with given temperature seems to be a reasonable option especially for the non-equilibrium dynamics of biological systems. However, the additional reservoir may not necessarily be assumed. As apparent from the example of the growth problem described in Sect. 6.1, it is the transition rates  $\omega_s$  and  $\omega_x$  that are prescribed as input parameters of the model [see, e.g., Eq. (42)], independently of the “super” heat bath.

We also note that in general there could be two different mechanisms responsible for the particle exchange. To facilitate the discussion, we consider here a Hamiltonian system and write the total energy as the sum of the energy of the system and that of the reservoir as well as the interaction energy:  $E(\{x_i, s_i\}_{\text{tot}}) = E(\{x_i\}) + E(\{x_i\}_{\text{env}}) + E_{\text{int}}(\{x_i\}_{\text{tot}})$ . Obviously, direct interactions between particles in  $\mathcal{S}$  and in  $\mathcal{S}_{\text{env}}$  would lead to the subsequent particle exchange, mediated by the term  $E_{\text{int}}$ . As already discussed, however, this term, corresponding to the interfacial contributions, is neglected in this study; otherwise the transition rate  $\omega_s$  should be taken as a function of the state variables  $x_i$ . We also note that the interfacial contributions are usually neglected in the conventional formulation for equilibrium statistical mechanics of a bulk system. Here the other mechanism mediates the particle exchange, via the energy difference in the system:  $\delta E \equiv E(x_1, \dots, x_{N \pm 1}) - E(\{x_i\})$ , which gives rise to state-independent transition rates  $\omega_s(1 \rightarrow -1)$  and  $\omega_s(-1 \rightarrow 1)$ . According to the Widom insertion formula [42], the energy difference  $\delta E$  quantifies the chemical potential of the system.

Lastly, the assumption that the state variables of particles in  $\mathcal{S}$  and  $\mathcal{S}_{\text{env}}$  are the same may impose restrictions on the applicability of our formalism. First of all, in the uncommon case that the system and reservoir are spatially separated, our master equation does not apply because the state spaces corresponding to the positions of particles should be different. In fact, the assumption corresponds to the absence of interfacial contributions which may mediate a transition between the system and reservoir with different state variables. In our formulation, all state variables but the location are kept fixed while a particle is moving from the reservoir to the system or vice versa. Nevertheless, there are a few classes of systems for which our formulation can be utilized. For instance, if the system and reservoir have the same geometry, one can characterize both of them with the same state variables. The transition between the system and reservoir can be prescribed in such a trivial way that the particle in  $\mathcal{S}$  simply jumps to the same position in  $\mathcal{S}_{\text{env}}$  (and vice versa) keeping all the other state variables fixed. Potential applications may include the material exchange between two capillaries, coupled thin layers of metallic materials with different electric/magnetic

properties, and the spread of a (traffic) jam across road lanes. Further, our formulation is also suitable to a mean-field level description where the position of each particle is irrelevant (see, e.g., Ref. [43]).

### 3. Connection to the equilibrium grand canonical description

In this section, we describe how our formulation is connected to the equilibrium grand canonical description. In the equilibrium description, the transition rates can be specified by the help of the detailed balance conditions:

$$w_s(s_j \rightarrow -s_j) P_{eq}(\{x_i, s_i\}_{tot}) = w_s(-s_j \rightarrow s_j) P_{eq}(R_j\{x_i, s_i\}_{tot}) \quad (4)$$

and

$$w_x(x_j \rightarrow x'_j) P_{eq}(\{x_i, s_i\}_{tot}) = w_x(x'_j \rightarrow x_j) P_{eq}(Q_j\{x_i, s_i\}_{tot}). \quad (5)$$

If the system is in contact with a heat reservoir at temperature  $T$ , the equilibrium distribution is given by  $P_{eq}(\{x_i, s_i\}_{tot}) \propto \exp[-\beta E(\{x_i, s_i\}_{tot})]$  with the inverse temperature  $\beta \equiv 1/k_B T$ . Here rewriting the probability density  $P(\{x_i, s_i\}_{tot})$  in the grand canonical ensemble requires a two-step projection, consisting of

$$P(\{x_i\}_{tot}, N) = \sum_{\{s_i\}_{tot}} \delta \left[ \sum_{k=1}^{N_{tot}} s_k - (2N - N_{tot}) \right] P(\{x_i, s_i\}_{tot}) \quad (6)$$

and

$$P(\{x_i\}, N) = \sum_{\{x_i\}_{env}} P(\{x_i\}_{tot}, N), \quad (7)$$

as well as  $P(N) = \sum_{\{x_i\}} P(\{x_i\}, N) = \sum_{\{x_i\}_{tot}} P(\{x_i\}_{tot}, N)$ . The derivation of the equation governing the dynamics of  $P(\{x_i\}, N)$  is one of the main issues to be addressed in this paper.

Before proceeding to such non-equilibrium dynamics in a more general setting, we first examine how the equilibrium description of the whole system ( $\mathcal{S} \cup \mathcal{S}_{env}$ ) represents the grand canonical description of system  $\mathcal{S}$ . Supposing that particles are indistinguishable, we have

$$P_{eq}(\{x_i, s_i\}_{tot}) = \frac{1}{N_{tot}!} \frac{1}{Z_{N_{tot}}} e^{-\beta E(\{x_i, s_i\}_{tot})}, \quad (8)$$

with the partition function

$$Z_{N_{tot}} \equiv \frac{1}{N_{tot}!} \sum_{\{x_i, s_i\}_{tot}} e^{-\beta E(\{x_i, s_i\}_{tot})} = \frac{1}{N_{tot}!} \sum_{N=0}^{N_{tot}} W_N \sum_{\{x_i\}_{tot}} e^{-\beta [E(\{x_i\}) + E(\{x_i\}_{env})]}, \quad (9)$$

where  $W_N$  is the number of  $N_{tot}$ -particle states for the whole system corresponding to the  $N$ -particle states for system  $\mathcal{S}$  in the grand-canonical description and the interactions between the system and the reservoir have been assumed weak enough for the energy to be separable:  $E(\{x_i, s_i\}_{tot}) = E(\{x_i\}) + E(\{x_i\}_{env})$ . As the particles are indistinguishable, we simply have  $W_N = \binom{N_{tot}}{N} = N_{tot}!(N!N_{env}!)^{-1}$ . Then writing the partition function in the form

$$Z_{N_{tot}} = \sum_{N=0}^{N_{tot}} \frac{1}{N!} \sum_{\{x_i\}} e^{-\beta E(\{x_i\})} Z_{N_{env}}, \quad (10)$$

where  $Z_{N_{env}} \equiv (N_{env}!)^{-1} \sum_{\{x_i\}_{env}} e^{-\beta E(\{x_i\}_{env})}$  is the partition function for reservoir  $\mathcal{S}_{env}$ , and defining the Helmholtz free energy  $A_{N_{tot}} \equiv -k_B T \ln Z_{N_{tot}}$ , one arrives at the standard grand-canonical description of

system  $\mathcal{S}$ , with the chemical potential  $\mu$  given by the derivative of the Helmholtz free energy with respect to the particle number. To be specific, in equilibrium Eqs. (6) and (7) lead to

$$P_{\text{eq}}(\{x_i\}, N) = \frac{1}{N!} \frac{Z_{N_{\text{env}}}}{Z_{N_{\text{tot}}}} e^{-\beta E(\{x_i\})}, \quad (11)$$

where Eq. (8) has also been used. Further, for  $N_{\text{tot}} \gg N$ , we can perform the Taylor expansion of the Helmholtz free energy:

$$\begin{aligned} k_B T \ln(Z_{N_{\text{env}}}/Z_{N_{\text{tot}}}) &= A_{N_{\text{tot}}}(V_{\text{tot}}, T) - A_{N_{\text{tot}}-N}(V_{\text{tot}} - V, T) \\ &\simeq N \frac{\partial A_{N_{\text{tot}}}(V_{\text{tot}}, T)}{\partial N_{\text{tot}}} + V \frac{\partial A_{N_{\text{tot}}}(V_{\text{tot}}, T)}{\partial V_{\text{tot}}} \simeq N\mu + pV, \end{aligned}$$

where  $V$  and  $V_{\text{tot}}$  are the volume of  $\mathcal{S}$  and  $\mathcal{S} \cup \mathcal{S}_{\text{env}}$ , respectively,  $\mu$  is the chemical potential, and  $p$  the pressure (see, e.g., Ref. [44]). We note that the condition  $N_{\text{tot}} \gg N$  should be assumed in this procedure of defining the chemical potential. Accordingly, the equilibrium probability indeed takes the grand-canonical form:

$$P_{\text{eq}}(\{x_i\}, N) = \frac{1}{N!} \frac{1}{Q} e^{-\beta[E(\{x_i\}) - \mu N]}, \quad (12)$$

where the relation  $pV = k_B T \ln Q$  with the grand partition function  $Q = \sum_N e^{\beta \mu N} Z_N$  has been used, and

$$Z_N = \frac{1}{N!} \sum_{\{x_i\}} e^{-\beta E(\{x_i\})}. \quad (13)$$

Note also that  $Q$  may not be expressed as the summation over  $N$  as above, if the energy contributions of particles in  $\mathcal{S}_{\text{env}}$  depend on the particle index  $i$ . In such a case,  $\mathcal{S}_{\text{env}}$  may not behave like a usual thermal particle reservoir, and a more detailed description of the environment, besides the chemical potential, should be provided. In a similar context, albeit in terms of coarse-graining rather than indistinguishability of particles, it has already been reported that the entropy may not be an extensive variable of the system [45].

On the other hand, we can specify the transition rate  $w_s$  from the equilibrium probability distribution. For the purpose, we multiply Eq. (4) by  $\delta \left[ \sum_{k=1}^{N_{\text{tot}}} s_k - (2N - N_{\text{tot}}) \right]$  and take the summation over  $\{s_i\}_{\text{tot}}$ . The left-hand side then becomes  $W_N^{-1} \left[ \binom{N_{\text{tot}}-1}{N-1} w_s(1 \rightarrow -1) + \binom{N_{\text{tot}}-1}{N} w_s(-1 \rightarrow 1) \right] P_{\text{eq}}(\{x_i\}_{\text{tot}}, N)$ , which reduces, upon summation over  $\{x_i\}_{\text{tot}}$ , to  $[r w_s(1 \rightarrow -1) + (1-r) w_s(-1 \rightarrow 1)] P_{\text{eq}}(N)$  with  $r \equiv N/N_{\text{tot}}$ . Similarly, the right-hand side of Eq. (4) takes the form  $(1-r) w_s(-1 \rightarrow 1) P_{\text{eq}}(N-1) + r w_s(1 \rightarrow -1) P_{\text{eq}}(N+1)$  for  $N \gg 1$ . To sum up, we have

$$[r w_s(1 \rightarrow -1) + (1-r) w_s(-1 \rightarrow 1)] P_{\text{eq}}(N) = (1-r) w_s(-1 \rightarrow 1) P_{\text{eq}}(N-1) + r w_s(1 \rightarrow -1) P_{\text{eq}}(N+1)$$

or

$$r w_s(1 \rightarrow -1) = (1-r) w_s(-1 \rightarrow 1) e^{\beta \mu}, \quad (14)$$

where the probability for the particle number has been related to the chemical potential via  $P(N \pm 1) = P(N) e^{\mp \beta \mu}$  (see, e.g., Ref. [42, 46]). More generally, Eq. (14) can be expressed in terms of the chemical potential:

$$\frac{w_s(s_j \rightarrow -s_j)}{w_s(-s_j \rightarrow s_j)} = \frac{W_N}{W_{N-s_j}} e^{s_j \beta \mu}, \quad (15)$$

for  $s_j = \pm 1$ .

#### 4. Projection onto the canonical ensemble

In the standard description of the  $N$ -particle system  $\mathcal{S}$ , one is concerned with the probability  $P(\{x_i\})$  for the system in state  $(x_1, x_2, \dots, x_N)$ . It corresponds to the conditional probability  $P(\{x_i\}|\{s_i=\zeta_i\}_{\text{tot}}) \equiv P(\{x_i\}|\{\zeta_i\}_{\text{tot}})$  in the grand canonical description, where  $\zeta_j \equiv 1$  and  $-1$  for  $1 \leq j \leq N$  and for  $N+1 \leq j \leq N_{\text{tot}}$ , respectively. In this section, we examine how the conventional (canonical) description is recovered from the grand canonical description.

Summing over all possible states in system  $\mathcal{S}_{\text{env}}$  yields

$$P(\{x_i\}) = \frac{\sum_{\{x_i\}_{\text{env}}} \sum_{\{s_i\}_{\text{tot}}} \prod_{j=1}^{N_{\text{tot}}} \delta_{s_j, \zeta_j} P(\{x_i, s_i\}_{\text{tot}})}{\sum_{\{x'_i\}_{\text{tot}}} \sum_{\{s_i\}_{\text{tot}}} \prod_{j=1}^{N_{\text{tot}}} \delta_{s_j, \zeta_j} P(\{x'_i, s_i\}_{\text{tot}})}. \quad (16)$$

To obtain the master equation for  $P(\{x_i\})$ , we introduce the projection operator  $P_s \equiv \prod_{j=1}^{N_{\text{tot}}} \delta_{s_j, \zeta_j}$  and write Eq. (16) in the form

$$\sum_{\{x_i\}_{\text{env}}} \sum_{\{s_i\}_{\text{tot}}} P_s P(\{x_i, s_i\}_{\text{tot}}) = P(\{x_i\}) \sum_{\{x'_i\}_{\text{tot}}} \sum_{\{s_i\}_{\text{tot}}} P_s P(\{x'_i, s_i\}_{\text{tot}}), \quad (17)$$

which, upon differentiation with respect to time, gives

$$\sum_{\{x_i\}_{\text{env}}} \sum_{\{s_i\}_{\text{tot}}} P_s \frac{\partial P(\{x_i, s_i\}_{\text{tot}})}{\partial t} = \sum_{\{x'_i\}_{\text{tot}}} \sum_{\{s_i\}_{\text{tot}}} P_s \left[ \frac{\partial P(\{x'_i, s_i\}_{\text{tot}})}{\partial t} P(\{x_i\}) + P(\{x'_i, s_i\}_{\text{tot}}) \frac{\partial P(\{x_i\})}{\partial t} \right]. \quad (18)$$

Substitution of Eq. (1) leads the left-hand side of Eq. (18) to take the form

$$\begin{aligned} & \sum_{\{x_i\}_{\text{env}}} \sum_{\{s_i\}_{\text{tot}}} P_s \sum_{j=1}^{N_{\text{tot}}} \left\{ [w_s(-s_j \rightarrow s_j) P(R_j \{x_i, s_i\}_{\text{tot}}) - w_s(s_j \rightarrow -s_j) P(\{x_i, s_i\}_{\text{tot}})] \right. \\ & \quad \left. + \sum_{x'_j} [w_x(x'_j \rightarrow x_j) P(Q_j \{x_i, s_i\}_{\text{tot}}) - w_x(x_j \rightarrow x'_j) P(\{x_i, s_i\}_{\text{tot}})] \right\} \\ &= \sum_{j=1}^N w_s(-1 \rightarrow 1) P(\{x_i\}, R_j \{\zeta_i\}_{\text{tot}}) + \sum_{j=N+1}^{N_{\text{tot}}} w_s(1 \rightarrow -1) P(\{x_i\}, R_j \{\zeta_i\}_{\text{tot}}) - \sum_{j=1}^N w_s(1 \rightarrow -1) P(\{x_i\}, \{\zeta_i\}_{\text{tot}}) \\ & \quad - \sum_{j=N+1}^{N_{\text{tot}}} w_s(-1 \rightarrow 1) P(\{x_i\}, \{\zeta_i\}_{\text{tot}}) + \sum_{j=1}^N \sum_{x'_j} [w_x(x'_j \rightarrow x_j) P(Q_j \{x_i\} | \{\zeta_i\}_{\text{tot}}) - w_x(x_j \rightarrow x'_j) P(\{x_i\})], \end{aligned} \quad (20)$$

where Eq. (17) has been used and it has also been recognized that  $\sum_{\{x_i\}_{\text{env}}} \sum_{x'_j} [w_x(x'_j \rightarrow x_j) P(Q_j \{x_i, s_i\}_{\text{tot}}) - w_x(x_j \rightarrow x'_j) P(\{x_i, s_i\}_{\text{tot}})] = 0$  for  $N+1 \leq j \leq N_{\text{tot}}$ , due to the symmetry between  $x'_j$  and  $x_j$  included in the partial sum  $\sum_{\{x_i\}_{\text{env}}}$ . It is of interest that the projection operator  $P_s$  would actually make the sum of particle transfer rates a constant:

$$P_s \sum_{j=1}^{N_{\text{tot}}} w_s(s_j \rightarrow -s_j) = \sum_{j=1}^N w_s(1 \rightarrow -1) + \sum_{j=N+1}^{N_{\text{tot}}} w_s(-1 \rightarrow 1). \quad (21)$$



Next the first term on the right-hand side of Eq. (18) reads

$$\begin{aligned}
& \sum_{\{x'_i\}_{\text{tot}}} \sum_{\{s_i\}_{\text{tot}}} P_s P(\{x_i\}) \times \sum_{j=1}^{N_{\text{tot}}} \left\{ w_s(-s_j \rightarrow s_j) P(R_j\{x'_i, s_i\}_{\text{tot}}) - w_s(s_j \rightarrow -s_j) P(\{x'_i, s_i\}_{\text{tot}}) \right. \\
& \left. + \sum_{x''_j} [w_x(x''_j \rightarrow x'_j) P(Q_j\{x'_i, s_i\}_{\text{tot}}) - w_x(x'_j \rightarrow x''_j) P(\{x'_i, s_i\}_{\text{tot}})] \right\} \\
& = P(\{x_i\}) \left[ \sum_{j=1}^N w_s(-1 \rightarrow 1) P(R_j\{\zeta_i\}_{\text{tot}}) + \sum_{j=N+1}^{N_{\text{tot}}} w_s(1 \rightarrow -1) P(R_j\{\zeta_i\}_{\text{tot}}) \right. \\
& \left. - \sum_{j=1}^N w_s(1 \rightarrow -1) P(\{\zeta_i\}_{\text{tot}}) - \sum_{j=N+1}^{N_{\text{tot}}} w_s(-1 \rightarrow 1) P(\{\zeta_i\}_{\text{tot}}) \right],
\end{aligned} \tag{22}$$

since the sum over all energy states vanishes.

We now combine Eqs. (19) and (22) to derive the projected master equation governing the dynamics of  $\mathcal{S}$ :

$$\begin{aligned}
\frac{\partial P(\{x_i\})}{\partial t} & = \frac{1}{P(\{\zeta_i\}_{\text{tot}})} \left[ \sum_{\{x_i\}_{\text{env}}} \sum_{\{s_i\}_{\text{tot}}} P_s \frac{\partial P(\{x_i, s_i\}_{\text{tot}})}{\partial t} - \sum_{\{x'_i\}_{\text{tot}}} \sum_{\{s_i\}_{\text{tot}}} P_s \frac{\partial P(\{x'_i, s_i\}_{\text{tot}})}{\partial t} P(\{x_i\}) \right] \\
& = \sum_{j=1}^N w_s(-1 \rightarrow 1) \frac{P(R_j\{\zeta_i\}_{\text{tot}})}{P(\{\zeta_i\}_{\text{tot}})} \times [P(\{x_i\} | R_j\{\zeta_i\}_{\text{tot}}) - P(\{x_i\})] \\
& + \sum_{j=N+1}^{N_{\text{tot}}} w_s(1 \rightarrow -1) \frac{P(R_j\{\zeta_i\}_{\text{tot}})}{P(\{\zeta_i\}_{\text{tot}})} \times [P(\{x_i\} | R_j\{\zeta_i\}_{\text{tot}}) - P(\{x_i\})] \\
& + \sum_{j=1}^N \sum_{x'_j} [w_x(x'_j \rightarrow x_j) P(Q_j\{x_i\} | \{\zeta_i\}_{\text{tot}}) - w_x(x_j \rightarrow x'_j) P(\{x_i\})].
\end{aligned} \tag{23}$$

Here the equilibrium with respect to particle exchanges, in which those terms associated with  $w_s$  vanish, is attained if the condition  $P(\{x_i\} | R_j\{\zeta_i\}_{\text{tot}}) = P(\{x_i\})$  is fulfilled. In other words, if  $P(\{x_i\})$  is independent of  $N$ , particle exchanges become irrelevant. Then the standard (canonical) master equation for a system of  $N$  particles relaxing toward the equilibrium with respect to particle states is recovered in a straightforward manner:

$$\frac{\partial}{\partial t} P(\{x_i\}) = \sum_{j=1}^N \sum_{x'_j} [w_x(x'_j \rightarrow x_j) P(Q_j\{x_i\}) - w_x(x_j \rightarrow x'_j) P(\{x_i\})]. \tag{24}$$

Otherwise, particle exchanges with  $\mathcal{S}_{\text{env}}$  as well as particle states in  $\mathcal{S}$  are yet to equilibrate. As given in Eq. (23), the additional terms associated with  $w_s$ , which correspond to the particle exchange, should be included in the proper description of the nonequilibrium dynamics of the system.

## 5. Macroscopic dynamics of the system

### 5.1. Transformation from spin variables to the particle number

Usually, it is not possible to measure directly the dynamics of microscopic variables. In this section, we describe the macroscopic dynamics with the number  $N$  of particles as an independent variable, instead of the pseudo-spin variable  $\{s_i\}_{\text{tot}}$ , via the transformation defined in Eq. (6), which is generally applicable to any system exchanging particles. In particular, for indistinguishable particles, the definition

can be cast into a simplified form. Namely, provided that  $P(\{x_i\}_{\text{tot}}, s_1, \dots, s_{N_{\text{tot}}}) = P(x_{\pi(1)}, \dots, x_{\pi(N_{\text{tot}})}, s_{\pi(1)}, \dots, s_{\pi(N_{\text{tot}})})$  with  $\pi$  being the permutation operator, the probability in terms of  $N$  reads

$$P(\{x_i\}_{\text{tot}}, N) = W_N P(\{x_i, s_i = \zeta_i\}_{\text{tot}}), \quad (25)$$

where we have  $W_N = \binom{N_{\text{tot}}}{N}$  as noted already in Sect. 2.

In this case, the master equation can be obtained via differentiating explicitly both sides with time:

$$\begin{aligned} \frac{\partial P(\{x_i\}_{\text{tot}}, N)}{\partial t} &= N W_N w_s(-1 \rightarrow 1) \frac{P(\{x_i\}_{\text{tot}}, N-1)}{W_{N-1}} - N w_s(1 \rightarrow -1) P(\{x_i\}_{\text{tot}}, N) \\ &+ (N_{\text{tot}} - N) W_N w_s(1 \rightarrow -1) \frac{P(\{x_i\}_{\text{tot}}, N+1)}{W_{N+1}} - (N_{\text{tot}} - N) w_s(-1 \rightarrow 1) P(\{x_i\}_{\text{tot}}, N) \\ &+ \sum_{j=1}^{N_{\text{tot}}} \sum_{x'_j} [w_x(x'_j \rightarrow x_j) P(Q_j \{x_i\}_{\text{tot}}, N) - w_x(x_j \rightarrow x'_j) P(\{x_i\}_{\text{tot}}, N)]. \end{aligned} \quad (26)$$

To probe the time evolution of  $P(\{x_i\})$ , we make use of the projection  $\sum_{\{x_i\}_{\text{env}}} P(\{x_i\}_{\text{tot}}, N) = P(N) P(\{x_i\} | N)$ , which leads directly to

$$P(N) \frac{\partial P(\{x_i\} | N)}{\partial t} = \sum_{\{x_i\}_{\text{env}}} \left[ \frac{\partial P(\{x_i\}_{\text{tot}}, N)}{\partial t} - \frac{\partial P(N)}{\partial t} P(\{x_i\} | N) \right]. \quad (27)$$

At first, summing over  $\{x_i\}_{\text{tot}}$ , one can rewrite Eq. (26) in the form

$$\begin{aligned} \frac{\partial P(N)}{\partial t} &= N W_N w_s(-1 \rightarrow 1) \frac{P(N-1)}{W_{N-1}} - N w_s(1 \rightarrow -1) P(N) \\ &+ (N_{\text{tot}} - N) W_N w_s(1 \rightarrow -1) \frac{P(N+1)}{W_{N+1}} - (N_{\text{tot}} - N) w_s(-1 \rightarrow 1) P(N) \\ &= \omega(N-1 \rightarrow N) P(N-1) - \omega(N \rightarrow N-1) P(N) \\ &+ \omega(N+1 \rightarrow N) P(N+1) - \omega(N \rightarrow N+1) P(N), \end{aligned} \quad (28)$$

where  $\omega(N-1 \rightarrow N) \equiv (N_{\text{tot}} - N + 1) w_s(-1 \rightarrow 1)$ ,  $\omega(N \rightarrow N-1) \equiv N w_s(1 \rightarrow -1)$ ,  $\omega(N+1 \rightarrow N) \equiv (N + 1) w_s(1 \rightarrow -1)$  and  $\omega(N \rightarrow N+1) \equiv (N_{\text{tot}} - N) w_s(-1 \rightarrow 1)$ . Note here that setting  $\partial P(N) / \partial t = 0$  for  $P(N) = P_{\text{eq}}(N)$  results in Eq. (14) as expected.

On the other hand, Eq. (26) allows to rewrite the first term on the left-hand side of Eq. (27):

$$\begin{aligned} \sum_{\{x_i\}_{\text{env}}} \frac{\partial P(\{x_i\}_{\text{tot}}, N)}{\partial t} &= \omega(N-1 \rightarrow N) P(\{x_i\} | N-1) P(N-1) - \omega(N \rightarrow N-1) P(\{x_i\} | N) P(N) \\ &+ \omega(N+1 \rightarrow N) P(\{x_i\} | N+1) P(N+1) - \omega(N \rightarrow N+1) P(\{x_i\} | N) P(N) \\ &+ \sum_{j=1}^{N_{\text{env}}} \sum_{x'_j} [w_x(x'_j \rightarrow x_j) P(Q_j \{x_i\} | N) - w_x(x_j \rightarrow x'_j) P(\{x_i\} | N)] P(N). \end{aligned} \quad (29)$$

Inserting Eqs. (28) and (29) into Eq. (27), we obtain

$$\begin{aligned} \frac{\partial P(\{x_i\} | N)}{\partial t} &= \omega(N-1 \rightarrow N) \frac{P(N-1)}{P(N)} \times [P(\{x_i\} | N-1) - P(\{x_i\} | N)] \\ &+ \omega(N+1 \rightarrow N) \frac{P(N+1)}{P(N)} \times [P(\{x_i\} | N+1) - P(\{x_i\} | N)] \\ &+ \sum_{j=1}^{N_{\text{env}}} \sum_{x'_j} [w_x(x'_j \rightarrow x_j) P(Q_j \{x_i\} | N) - w_x(x_j \rightarrow x'_j) P(\{x_i\} | N)]. \end{aligned} \quad (30)$$

As before, one can identify that  $P(\{x_i\}|N) \equiv P(\{x_i\})$ , regardless of  $N$ , in equilibrium with respect to particle exchanges. In this case, Eq. (24) is recovered straightforwardly once again. At this stage, the dynamical equation governing the probability density in the grand canonical ensemble, given by Eq. (7), is simultaneously obtained from Eq. (29) as follows:

$$\begin{aligned} \frac{\partial P(\{x_i\}, N)}{\partial t} &= \omega(N-1 \rightarrow N)P(\{x_i\}, N-1) - \omega(N \rightarrow N-1)P(\{x_i\}, N) \\ &\quad + \omega(N+1 \rightarrow N)P(\{x_i\}, N+1) - \omega(N \rightarrow N+1)P(\{x_i\}, N) \\ &\quad + \sum_{j=1}^N \sum_{x'_j} [w_x(x'_j \rightarrow x_j)P(Q_j\{x_i\}, N) - w_x(x_j \rightarrow x'_j)P(\{x_i\}, N)]. \end{aligned} \quad (31)$$

## 5.2. Distribution function

In this section we consider the distribution function  $F(x|N; t)$  of variables  $\{x_i\}$  at time  $t$ :

$$F(x|N; t) \equiv \sum_{\{x_i\}} \sum_{j=1}^N \delta(x-x_j)P(\{x_i\}|N), \quad (32)$$

where  $\delta(x-x_i)$  is to be understood as the Kronecker delta in the case of discrete variables. Then, as before, taking the time derivative, substituting Eq. (1) for  $\partial P(\{x_i, s_i\})/\partial t$  and following similar procedures, one obtains the evolution equation for the distribution function  $F(x; t)$  or the normalized distribution function  $f(x|N; t) \equiv N^{-1}F(x|N; t)$ . Similarly, we also define the distribution function  $G(x|N; t) \equiv \sum_{\{x_i\}_{\text{env}}} \sum_{j=N+1}^{N_{\text{tot}}} \delta(x-x_j)P(\{x_i\}_{\text{env}}|N)$  and the normalized distribution function  $g(x|N; t) \equiv (N_{\text{tot}} - N)^{-1}G(x|N; t)$  for  $\mathcal{S}_{\text{env}}$ .

When there are no correlations between the exchange and the state of a particle, in other words,  $f(x|N; t)$  is independent of  $N$ , the system is described by the (canonical) master equation in Eq. (24) and it is straightforward to derive

$$\begin{aligned} \frac{\partial f(x; t)}{\partial t} &= \frac{1}{N} \sum_{\{x_i\}} \sum_{j=1}^N \delta(x-x_j) \times \sum_{k=1}^N \sum_{x'_k} [w_x(x'_k \rightarrow x_k)P(Q_k\{x_i\}|N) - w_x(x_k \rightarrow x'_k)P(\{x_i\}|N)] \\ &= \sum_{x'} [w_x(x' \rightarrow x)f(x', t) - w_x(x \rightarrow x')f(x; t)], \end{aligned} \quad (33)$$

where the density function, independent of  $N$ , is defined as follows:

$$f(x; t) \equiv \sum_{N=1}^{N_{\text{tot}}} f(x|N; t)P(N). \quad (34)$$

Here particle exchanges between  $\mathcal{S}$  and  $\mathcal{S}_{\text{env}}$  do not bring on any additional dynamics to the density function of the system.

We next take into account the correlations between the exchange and the state of a particle. In such a case additional effects arise due to particle exchanges as described in Eq. (23). To find the corresponding terms, we first show that

$$\begin{aligned} \sum_{\{x_i\}} \sum_{j=1}^N \delta(x-x_j)P(\{x_i\}|N-1) &= \sum_{\{x_i\}} \sum_{j=1}^{N-1} \delta(x-x_j)P(\{x_i\}|N-1) + \sum_{x_N} \delta(x-x_N)P(x_N|N-1) \\ &= (N-1)f(x|N-1; t) + g(x|N-1; t) \end{aligned} \quad (35)$$

and

$$\sum_{\{x_i\}} \sum_{j=1}^N \delta(x - x_j) P(\{x_i\}|N+1) = Nf(x|N+1; t), \quad (36)$$

as we have assumed that the particles are indistinguishable. Making use of the above equations together with Eq. (30), we thus obtain

$$\begin{aligned} N \frac{\partial f(x|N; t)}{\partial t} &= \sum_{\{x_i\}} \sum_{j=1}^N \delta(x - x_j) \frac{\partial P(\{x_i\}|N)}{\partial t} \\ &= w(N-1 \rightarrow N) \frac{P(N-1)}{P(N)} \times [(N-1)f(x|N-1; t) + g(x|N-1; t) - Nf(x|N; t)] \\ &\quad + w(N+1 \rightarrow N) \frac{P(N+1)}{P(N)} \times [Nf(x|N+1; t) - Nf(x|N; t)] \\ &\quad + N \sum_{x'} [w_x(x' \rightarrow x) f(x'|N; t) - w_x(x \rightarrow x') f(x|N; t)]. \end{aligned} \quad (37)$$

Now we are ready to address the time evolution of  $f(x; t)$ , which reads

$$\frac{\partial f(x; t)}{\partial t} = \sum_{N=1}^{N_{\text{tot}}} f(x|N; t) \frac{\partial P(N)}{\partial t} + \sum_{N=1}^{N_{\text{tot}}} \frac{\partial f(x|N; t)}{\partial t} P(N). \quad (38)$$

As the first and the second terms on the right-hand side are given by Eqs. (28) and (37), respectively, we finally obtain:

$$\begin{aligned} \frac{\partial f(x; t)}{\partial t} &= \sum_{N=1}^{N_{\text{tot}}} \frac{N_{\text{tot}} - N}{N} w(-1 \rightarrow 1) \times [g(x|N; t) - f(x|N; t)] P(N) \\ &\quad + \sum_{x'} [w_x(x' \rightarrow x) f(x'; t) - w_x(x \rightarrow x') f(x; t)]. \end{aligned} \quad (39)$$

Similarly, we obtain the equation governing the dynamics of  $g(x; t)$  as well:

$$\begin{aligned} \frac{\partial g(x; t)}{\partial t} &= \sum_{N=1}^{N_{\text{tot}}} \frac{N}{N_{\text{tot}} - N} w(1 \rightarrow -1) \times [f(x|N; t) - g(x|N; t)] P(N) \\ &\quad + \sum_{x'} [w_x(x' \rightarrow x) g(x'; t) - w_x(x \rightarrow x') g(x; t)]. \end{aligned} \quad (40)$$

It is remarkable that the dynamics of the system  $\mathcal{S}$  and the reservoir  $\mathcal{S}_{\text{env}}$  are coupled together and governed by the particle exchanges between  $\mathcal{S}$  and  $\mathcal{S}_{\text{env}}$  as well as the state changes inside  $\mathcal{S}$  and  $\mathcal{S}_{\text{env}}$ . Here we make two additional remarks. First, if  $N_{\text{tot}} \gg N$ , as expected from statistical mechanics of systems in contact with a thermal reservoir, the density function  $f(x; t)$  of  $\mathcal{S}$  is dominated by  $g(x; t)$  of  $\mathcal{S}_{\text{env}}$  while  $g(x; t)$  is rather independent from  $f(x; t)$ . Second, if the transition rate is proportional to  $N/(N_{\text{tot}} - N)$ , for instance  $w(-1 \rightarrow 1) \equiv w_s N/(N_{\text{tot}} - N)$  [see also Eq. (42) in the next section], Eq. (38) takes the simple form

$$\frac{\partial f(x; t)}{\partial t} = -w_s [f(x; t) - g(x; t)] + \sum_{x'} [w_x(x' \rightarrow x) f(x'; t) - w_x(x \rightarrow x') f(x; t)]. \quad (41)$$

## 6. Physical systems in the grand canonical ensemble: Examples

### 6.1. Systems with constant production rates

As an example, we consider a simple growth process, where each particle in the system tends to produce a new one and to decay with given rates. As for production each of the  $N$  particles in system  $\mathcal{S}$  produces a new one by choosing one among the  $N_{\text{tot}} - N$  particles in reservoir  $\mathcal{S}_{\text{env}}$  to be transferred to system  $\mathcal{S}$ . The former brings on factor  $N$  in the corresponding transition (growth) rate while the latter leads to the probability, associated with the selection, proportional to  $(N_{\text{tot}} - N)^{-1}$ . On the other hand, decay is described by the process that a particle among the  $N$  particles in system  $\mathcal{S}$  leaves the system and enters reservoir  $\mathcal{S}_{\text{env}}$ . As a result, the transition rate is given by

$$w_s(s_j \rightarrow -s_j) = \frac{kN}{N_{\text{tot}} - N} \delta_{s_j, -1} + \lambda \delta_{s_j, 1}, \quad (42)$$

with appropriate growth and decay rate constants  $k$  and  $\lambda$ , which reduces Eq. (21) to

$$P_s \sum_{j=1}^{N_{\text{tot}}} w_s(s_j \rightarrow -s_j) = (k + \lambda)N, \quad (43)$$

for the sum of particle transfer rates and Eq. (3) to the balance equation

$$\frac{d\langle N \rangle}{dt} = (k - \lambda)\langle N \rangle, \quad (44)$$

for  $N \neq N_{\text{tot}}$ . In case that decay is dominant over growth ( $k < \lambda$ ), the particle number  $N$  decreases to zero. In the opposite case of  $k > \lambda$ ,  $N$  increases to  $N_{\text{tot}}$ : When all the  $N_{\text{tot}}$  particles are transferred to  $\mathcal{S}$  (i.e.,  $N = N_{\text{tot}}$ ), the first term on the right-hand side of Eq. (42) is absent, reducing the balance equation to  $dN/dt = -\lambda N$ . Accordingly,  $N$  cannot exceed  $N_{\text{tot}}$  as expected.

It is of interest to examine the chemical potential in the growth process. Equation (15) can be rewritten in the form

$$\frac{w_s(s_j \rightarrow -s_j)}{w_s(-s_j \rightarrow s_j)} \approx \exp \left[ s_j \ln \frac{N_{\text{tot}} - N}{N} + s_j \beta \mu \right], \quad (45)$$

for large  $N$  while Eq. (42) reads

$$\begin{aligned} \frac{w_s(s_j \rightarrow -s_j)}{w_s(-s_j \rightarrow s_j)} &= \frac{\lambda \delta_{s_j, 1} + kN(N_{\text{tot}} - N)^{-1} \delta_{s_j, -1}}{\lambda \delta_{s_j, -1} + kN(N_{\text{tot}} - N)^{-1} \delta_{s_j, 1}} \\ &= \exp \left\{ s_j \ln \left[ \frac{\lambda(N_{\text{tot}} - N)}{kN} \right] \right\}. \end{aligned} \quad (46)$$

Comparing the above two equations, we can identify the chemical potential:

$$\mu = k_B T \ln \left( \frac{\lambda}{k} \right), \quad (47)$$

which depends only on the growth parameters  $\lambda$  and  $k$ . It is now apparent that the chemical potential vanishes in the case of a symmetric process ( $k = \lambda$ ), which results in  $dN/dt = 0$ . When  $k > \lambda$ , the chemical potential  $\mu$  is negative, leading to  $N \approx N_{\text{tot}}$ , as the free-energy could be further reduced by adding additional particles. In contrast, for  $k < \lambda$ , we have  $N \approx 0$  in equilibrium. These observations indeed coincide with the consequences of Eq. (3).

We now consider growth of the size measured by the variable  $x_i$  (which may represent, for example, local heights), with the rate  $w_x(x_i \rightarrow x'_i) = r \delta[x'_i - x_i - \Delta(x_i)]$ , where  $\Delta(x) = bx + c$  is a linear function of  $x$ . As a simple example, we consider the reservoir  $\mathcal{S}_{\text{env}}$  to be sufficiently large, so that its distribution function does

not change  $[\partial g(x;t)/\partial t = 0]$ , with  $\omega_x(x_i \rightarrow x'_i | s_i = -1) = 0$  and  $N_{\text{tot}} \gg N$  assumed. In this case Eq. (41) gives a proper description of the dynamics of the system with  $w_s = k$ .

With the growth rate  $w_x(x \rightarrow x') = r\delta[x' - x - \Delta(x)]$ , Eq. (41) in the steady state reads

$$\begin{aligned} kf(x) &= kg(x) + r \sum_{x'} \delta[x - x' - \Delta(x')] f(x') - r \sum_{x'} \delta[x' - x - \Delta(x)] f(x) \\ &= kg(x) + \frac{r}{1+b} \sum_{x'} \delta\left(\frac{x-c}{1+b} - x'\right) f(x'; t) - rf(x) \\ &= kg(x) + \frac{r}{1+b} f\left(\frac{x-c}{1+b}\right) - rf(x). \end{aligned} \quad (48)$$

If  $\mathcal{S}_{\text{env}}$  contains only those particles smaller than  $x_0$ , namely,  $g(x > x_0) = 0$ , we obtain

$$(k+r)f(x > x_0) = \frac{r}{1+b} f\left(\frac{x-c}{1+b} > \frac{x_0-c}{1+b}\right), \quad (49)$$

which yields the steady-state functional equation

$$\left(1 + \frac{k}{r}\right) f(x) = \frac{1}{1+b} f\left(\frac{x-c}{1+b}\right), \quad (50)$$

in the range of  $x \gg x_0$ . To solve the functional equation in Eq. (50), we first translate the variable and the function according to  $x \equiv y + d$  and  $f(x) \equiv \tilde{f}(y)$ , with  $d \equiv -c/b$ . This leads to the reduced form

$$\left(1 + \frac{k}{r}\right) \tilde{f}(y) = \frac{1}{1+b} \tilde{f}\left(\frac{y}{1+b}\right), \quad (51)$$

the solution of which is given by  $\tilde{f}(y) = y^{-\alpha}$  [47] with exponent  $\alpha = 1 + \ln(1+k/r)/\ln(1+b)$ , up to a constant factor determined by the normalization of  $f$ . Therefore, for  $b \neq 0$ ,  $f(x)$  has the form of the power-law distribution

$$f(x) = \frac{\alpha-1}{a} \left(1 + \frac{x}{a}\right)^{-\alpha}, \quad (52)$$

with  $a = c/b$ . The distribution is normalizable as long as  $k > 0$  (corresponding to the case that there are particles transferring from  $\mathcal{S}_{\text{env}}$  to  $\mathcal{S}$ ). When  $b = 0$ , on the other hand, a general solution of Eq. (50) is given by the exponential distribution

$$f(x) = \frac{1}{\xi} \exp(-x/\xi), \quad (53)$$

with the characteristic size  $\xi = c[\ln(r+k) - \ln r]^{-1}$ . Therefore in this case, where each element ceases to grow in proportion to the current size and increases its size rather slowly by adding the constant amount  $c$ , the probability of finding a large size is exponentially small. Note that the characteristic size becomes large only when the particle transfer from  $\mathcal{S}_{\text{env}}$  to  $\mathcal{S}$  is slight ( $k \ll r$ ).

## 6.2. Two Ising systems exchanging particles

The Ising model is one of the simplest models for many-particle systems. We consider two Ising systems  $\mathcal{S}_1$  and  $\mathcal{S}_2$ , which exchange particles with each other. Each particle in the model is represented by their spin state  $\sigma = \pm 1$  and pseudo-spin variable  $s = \pm 1$ ; the latter represents whether the particle is in system  $\mathcal{S}_1$  or in system  $\mathcal{S}_2$ . This model provides an additional example of the system in the grand canonical description. Since it was studied in our previous work [48], we here introduce only the formulation briefly, just for completeness. The energy  $E$  of the whole system is defined by

$$E = -\frac{1}{2} \sum_{i,j} J_1 \sigma_i \sigma_j \frac{(1+s_i)(1+s_j)}{4} - \frac{1}{2} \sum_{i,j} J_2 \sigma_i \sigma_j \frac{(1-s_i)(1-s_j)}{4}. \quad (54)$$

Then Eq. (1) leads to the master equation for the model in the form

$$\begin{aligned} \frac{\partial P(\{\sigma_i, s_i\})}{\partial t} = & \sum_{j=1}^{N_{\text{tot}}} [w_s(-s_j \rightarrow s_j)P(R_j\{x_i, s_i\}) - w_s(s_j \rightarrow -s_j)P(\{x_i, s_i\})] \\ & + \sum_{j=1}^{N_{\text{tot}}} [w_\sigma(-\sigma_j \rightarrow \sigma_j)P(Q_j\{\sigma_i, s_i\}) - w_\sigma(\sigma_j \rightarrow -\sigma_j)P(\{\sigma_i, s_i\})]. \end{aligned} \quad (55)$$

From the relation  $P_{eq}(\{\sigma_i, s_i\}) \propto e^{-\beta H}$  and the detailed balance condition

$$\frac{w_s(s_j \rightarrow -s_j)}{w_s(-s_j \rightarrow s_j)} = \frac{\exp[-\beta E(R_j\{\sigma_i, s_i\})]}{\exp[-\beta E(\{\sigma_i, s_i\})]}, \quad (56)$$

we obtain the transition rate of the form

$$w_s(s_j \rightarrow -s_j) = \frac{1}{2\tau_s} \left[ 1 + s_j \sigma_j \tanh\left(\frac{\Delta h}{2}\right) \right]. \quad (57)$$

Here  $\tau_s$  is the relaxation time and  $\Delta h \equiv h_1 - h_2$  is the local field difference, with

$$\begin{aligned} h_1 & \equiv -\beta m_1 J_1 = -\frac{\beta J_1}{2N_{\text{tot}}} \sum_{j=1}^{N_{\text{tot}}} (1 + s_j) \sigma_j, \\ h_2 & \equiv -\beta m_2 J_2 = -\frac{\beta J_2}{2N_{\text{tot}}} \sum_{j=1}^{N_{\text{tot}}} (1 - s_j) \sigma_j. \end{aligned} \quad (58)$$

Similarly, we have

$$w_\sigma(\sigma_j \rightarrow -\sigma_j) = \frac{1}{2\tau_\sigma} \left[ 1 + \sigma_j \tanh\left(\frac{1+s_j}{2}h_1 + \frac{1-s_j}{2}h_2\right) \right]. \quad (59)$$

Accordingly, in the mean-field approximation, the master equation for the distribution function reads

$$\begin{aligned} \frac{\partial P(\sigma, s)}{\partial t} = & -\frac{1}{2\tau_s} \left[ 1 + \sigma s \tanh\left(\frac{\Delta h}{2}\right) \right] P(\sigma, s) + \frac{1}{2\tau_s} \left[ 1 - \sigma s \tanh\left(\frac{\Delta h}{2}\right) \right] P(\sigma, -s) \\ & - \frac{1}{2\tau_\sigma} \left[ 1 + \sigma \tanh\left(\frac{1+s}{2}h_1 + \frac{1-s}{2}h_2\right) \right] P(\sigma, s) + \frac{1}{2\tau_\sigma} \left[ 1 - \sigma \tanh\left(\frac{1+s}{2}h_1 + \frac{1-s}{2}h_2\right) \right] P(-\sigma, s). \end{aligned} \quad (60)$$

Solving this master equation, one may obtain equilibrium and non-equilibrium behaviors of this coupled systems, the detailed analysis of which can be found in Ref. [48].

## 7. Conclusion

We have provided a grand canonical description of equilibrium and non-equilibrium systems in terms of a master equation, introducing the environment system as a reservoir of particles (constituents) as well as energy. Using extended variables (occupation numbers or pseudo-spins), which introduces additional transition rates associated with particle exchange, creation or destruction, we have obtained a generalized master equation governing the particle transfer as well as the energy transfer. The conversion from the grand canonical description to the canonical one has been examined by partial resummation of states, which is equivalent to the Legendre transformation between the grand potential and the free energy. In this way, we have successfully extended the master equation formalism to the system in which the number of particles is not conserved. In particular, correlations between the exchange and the state of a particle lead to coupled equations governing the dynamics of the density functions of the system and of the reservoir (environment).

The coupling terms explicitly describe the particle exchanges between the system and the environment. This description is useful for system growth where particles are added as well as new sites are created, leading to critical phenomena. In most existing studies, the environment is usually assumed to be infinitely large and its dynamics left rather unspecified. However, the environment of a complex system is expected to perform a significant role as resources or buffers for the system. In the grand canonical formalism, dynamics of the environment or coupling between the system and the environment can be handled in detail and therefore the formalism may provide a concrete base for modeling of more realistic complex systems, elucidating the role of the environment. For instance, one might examine the effects of the resource depletion, considering the case  $N \approx N_{\text{tot}}$ . In the same manner, the entropy production in the environment can be tracked explicitly. This may pave the way towards an extended understanding of the relaxation dynamics of systems in contact with finite-size reservoirs. Such applications to various relevant systems and subsequent calculations of the entropy production rates are left for future study.

## Acknowledgements

This work was supported by the National Research Foundation of Korea through the Basic Science Research Program (Grant No. 2019R1F1A1046285).

## References

## References

- [1] R. Kubo, M. Toda, N. Hashitsume, *Statistical Physics II: Nonequilibrium Statistical Mechanics*, Springer, Berlin, 1991.
- [2] R. Zwanzig, *Nonequilibrium Statistical Mechanics*, Oxford university press, New York, 2001.
- [3] P. Érdi, J. Tóth, *Mathematical Models of Chemical Reactions: Theory and Applications of Deterministic and Stochastic Models*, Manchester University Press, Manchester, 1989.
- [4] U. Seifert, Stochastic thermodynamics, fluctuation theorems and molecular machines, *Rep. Prog. Phys.* 75 (12) (2012) 126001. doi:10.1088/0034-4885/75/12/126001.
- [5] C. Van den Broeck, M. Esposito, Ensemble and trajectory thermodynamics: A brief introduction, *Physica A* 418 (2015) 6 – 16. doi:https://doi.org/10.1016/j.physa.2014.04.035.
- [6] H. Qian, S. Kjelstrup, A. B. Kolomeisky, D. Bedeaux, Entropy production in mesoscopic stochastic thermodynamics: nonequilibrium kinetic cycles driven by chemical potentials, temperatures, and mechanical forces, *J. Phys.: Condens. Matter* 28 (15) (2016) 153004. doi:10.1088/0953-8984/28/15/153004.
- [7] M. Esposito, C. Van den Broeck, Three faces of the second law. i. master equation formulation, *Phys. Rev. E* 82 (2010) 011143. doi:10.1103/PhysRevE.82.011143.
- [8] C. Jarzynski, Equalities and inequalities: Irreversibility and the second law of thermodynamics at the nanoscale, *Ann. Rev. Condens. Matter Phys.* 2 (1) (2011) 329–351. doi:10.1146/annurev-conmatphys-062910-140506.
- [9] T. Tomé, M. J. de Oliveira, Stochastic approach to equilibrium and nonequilibrium thermodynamics, *Phys. Rev. E* 91 (2015) 042140. doi:10.1103/PhysRevE.91.042140.
- [10] T. Tomé, M. J. de Oliveira, Stochastic thermodynamics and entropy production of chemical reaction systems, *J. Chem. Phys.* 148 (22) (2018) 224104. doi:10.1063/1.5037045.
- [11] H. J. Kreuzer, Kinetic lattice-gas model: Time-dependent generalization of the grand-canonical ensemble, *Phys. Rev. B* 44 (1991) 1232. doi:10.1103/PhysRevB.44.1232.
- [12] W. J. Heuett, H. Qian, Grand canonical markov model: A stochastic theory for open nonequilibrium biochemical networks, *J. Chem. Phys.* 124. doi:10.1063/1.2165193.
- [13] A. Agarwal, J. Zhu, C. Hartmann, H. Wang, L. D. Site, Molecular dynamics in a grand ensemble: Bergmann?lebowitz model and adaptive resolution simulation, *New J. Phys.* 17 (2015) 083042.
- [14] C. M. Van Vliet, *Equilibrium and Non-equilibrium Statistical Mechanics*, World Scientific, Singapore, 2008.
- [15] M. Y. Choi, J. Choi, Stability and ensemble inequivalence in a globally coupled system, *Phys. Rev. Lett.* 91 (2003) 124101.
- [16] T. Squartini, J. de Mol, F. den Hollander, D. Garlaschelli, Breaking of ensemble equivalence in networks, *Phys. Rev. Lett.* 115 (2015) 268701.
- [17] R. Evans, Fluids adsorbed in narrow pores: phase equilibria and structure, *J. Phys.: Condens. Matter* 2 (1990) 8989–9007. doi:10.1088/0953-8984/2/46/001.
- [18] A. González, J. A. White, F. L. Román, S. Velasco, R. Evans, Density functional theory for small systems: Hard spheres in a closed spherical cavity, *Phys. Rev. Lett.* 79 (1997) 2466–2469. doi:10.1103/PhysRevLett.79.2466.
- [19] J. Jo, M. Y. Choi, D.-S. Koh, Size distribution of mouse langerhans islets, *Biophys. J.* 93 (2007) 2655– 2666.
- [20] D. Sarkar, M. Chu, S.-J. Cho, Y. I. Kim, B. Basu, Synthesis and morphological analysis of titanium carbide nanopowder, *J. Am. Ceram. Soc.* 92 (2009) 2877–2882.
- [21] Y. Loewenstein, A. Kuras, S. Rumpel, Multiplicative dynamics underlie the emergence of the log-normal distribution of spine sizes in the neocortex in vivo, *J. Neurosci.* 31 (2011) 9481–9488.



- [22] K. Lee, S. Goh, J. S. Park, W.-S. Jung, M. Y. Choi, Master equation approach to the intra-urban passenger flow and application to the metropolitan seoul subway system, *J. Phys. A* 44 (2011) 115007.
- [23] M. Y. Choi, H. Choi, J.-Y. Fortin, J. Choi, How skew distributions emerge in evolving systems, *Europhys. Lett.* 85 (2009) 30006.
- [24] S. Goh, H. W. Kwon, M. Y. Choi, J.-Y. Fortin, Emergence of skew distributions in controlled growth processes, *Phys. Rev. E* 82 (2010) 061115.
- [25] J.-Y. Fortin, S. Mantelli, M. Y. Choi, Dynamics of interval fragmentation and asymptotic distributions, *J. Phys. A* 46 (2013) 225002.
- [26] S. Goh, H. W. Kwon, M. Y. Choi, Discriminating between weibull distributions and log-normal distributions emerging in branching processes, *J. Phys. A* 47 (2014) 225101.
- [27] V. Privman, *Nonequilibrium Statistical Mechanics in One Dimension*, Cambridge University Press, Cambridge, 1997.
- [28] M. Henkel, H. Hinrichsen, S. Lübeck, *Non-equilibrium Phase Transitions: Absorbing Phase Transitions*, Springer, Dordrecht, 2008.
- [29] G. K. Zipf, *Human Behavior and the Principle of Least Effort*, Addison-Wesley, Cambridge, 1949.
- [30] V. Pareto, *Cours d'Économie Plitique*, Droz, Geneva, 1896.
- [31] R. Gibrat, *Les Inégalités Économiques*, Sirey, Paris, 1931.
- [32] J. Jo, J.-Y. Fortin, M. Y. Choi, Weibull-type limiting distribution for replicative systems, *Phys. Rev. E* 83 (2011) 031123. doi:[10.1103/PhysRevE.83.031123](https://doi.org/10.1103/PhysRevE.83.031123).
- [33] A. N. Jordan, C. H. R. Ooi, A. A. Svidzinsky, Fluctuation statistics of mesoscopic bose-einstein condensates: Reconciling the master equation with the partition function to reexamine the uhlenbeck-einstein dilemma, *Phys. Rev. A* 74 (2006) 032506. doi:[10.1103/PhysRevA.74.032506](https://doi.org/10.1103/PhysRevA.74.032506).
- [34] R. K. Pathria, *Statistical Mechanics*, Butterworth-Heinemann, Boston, 1996.
- [35] J. Sethna, *Statistical Mechanics: Entropy, Order Parameters, and Complexity*, Vol. 14, Oxford University Press, 2006.
- [36] J. Yao, R. Greenkorn, K. Chao, Monte carlo simulation of the grand canonical ensemble, *Mol. Phys.* 46 (1982) 587–594.
- [37] A. Papadopoulou, E. D. Becker, M. Lupkowski, F. van Swol, Molecular dynamics and monte carlo simulations in the grand canonical ensemble: Local versus global control, *J. Chem. Phys.* 98 (1993) 4897–4908.
- [38] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, 3rd Edition, Elsevier, Amsterdam, 2007. doi:<https://doi.org/10.1016/B978-044452965-7/50001-5>.
- [39] R. Toral, P. Colet, *Stochastic numerical methods: an introduction for students and scientists*, John Wiley & Sons, 2014.
- [40] D. Frenkel, B. Smit, *Understanding Molecular Simulation*, 2nd Edition, Academic Press, San Diego, 2002. doi:<https://doi.org/10.1016/B978-012267351-1/50007-9>.
- [41] M. Clark, S. Meshkat, J. S. Wiseman, Grand canonical free-energy calculations of protein - Ligand binding, *J. Chem. Inf. Model.* 49 (2009) 934–943.
- [42] B. Widom, Some topics in the theory of fluids, *J. Chem. Phys.* 39 (1963) 2808–2812. doi:[10.1063/1.1734110](https://doi.org/10.1063/1.1734110).
- [43] J.-Y. Fortin, S. Goh, C. Kim, M. Choi, Density distribution in two ising systems with particle exchange, *Euro. Phys. J. B* 91 (2018) 309.
- [44] K. Huang, *Statistical Mechanics*, 2nd Edition, Wiley, New York, 1987.
- [45] S. Goh, J. Choi, M. Y. Choi, B.-G. Yoon, Time evolution of entropy in a growth model: Dependence on the description, *J. Korean Phys. Soc.* 70 (2017) 12–21. doi:[10.3938/jkps.70.12](https://doi.org/10.3938/jkps.70.12).
- [46] J.-P. Hansen, I. R. McDonald, *Theory of simple liquids: with applications to soft matter*, 4th Edition, Academic Press, Oxford, 2013.
- [47] A. D. Polyanin, A. V. Manzhirov, *Handbook of integral equations*, 1st Edition, CRC Press, 1998.
- [48] S. Goh, J.-Y. Fortin, M. Y. Choi, Phase transitions and relaxation dynamics of ising models exchanging particles, *Physica A* 466 (2017) 166 – 179. doi:<http://dx.doi.org/10.1016/j.physa.2016.09.007>.