Chemical potentials in driven steady-state systems in contact : a large deviation approach

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Potentiels chimiques dans des systèmes stationnaires hors d'équilibre en contact : une approche par les grandes déviations

Chemical potentials in driven steady-state systems in contact: a large deviation approach

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À mes grands-pères,
Maurice et André

Résumé

Cette thèse porte sur la physique statistique des systèmes hors d'équilibre maintenus dans un état stationnaire. Plus spécifiquement, ce travail s'intéresse à des quantités macroscopiques conservées (le volume, la masse, etc.) qui peuvent être échangées entre plusieurs systèmes hors d'équilibre en contact. Cette mise en contact d'un ou plusieurs systèmes est une situation fondamentale en thermodynamique classique des systèmes à l'équilibre, en ce qu'elle permet de définir la notion de paramètre thermodynamique conjugué comme la température, la pression, le potentiel chimique, etc., qui dérivent d'un même potentiel thermodynamique. Dans les systèmes hors d'équilibre stationnaires, l'existence de tels paramètres conjugués dérivant d'un potentiel thermodynamique (énergie libre) demeure une question ouverte.

En se focalisant sur la situation du contact entre deux systèmes stochastiques hors d'équilibre quelconques de particules sur réseau dans des états homogènes, nous montrons l'existence d'une fonction de grande déviation attachée aux densités globales des deux systèmes, lorsque la fréquence d'échange de particules entre ces derniers est faible. Cette fonction de grandes déviations hors d'équilibre, analogue de l'énergie libre, vérifie une équation dite de Hamilton-Jacobi. Nous identifions les conditions naturelles pour lesquelles la fonction de grandes déviations est additive, menant ainsi à la définition de potentiels chimiques hors-équilibre. Néanmoins, nous montrons que ceux-ci dépendent de façon générique de la dynamique au contact et ne vérifient donc pas d'équation d'état. En l'absence de bilan détaillé macroscopique, l'équation de Hamilton-Jacobi est beaucoup plus difficile à résoudre. Une analyse perturbative par rapport aux forçages hors-équilibres permet de se convaincre que l'additivité est génériquement brisée dès les premiers ordres de perturbation en l'absence de bilan détaillé. Au-delà de la propriété d'additivité, cette fonction de grandes déviations peut être liée dans un certain nombre de cas au travail exercé par un potentiel extérieur à travers une relation de type second principe de la thermodynamique. Nous discutons également différentes façons d'y avoir accès expérimentalement.

Fort de cette analyse théorique générale, nous illustrons celle-ci sur des systèmes stochastiques sur réseau classiques (Zero Range Process et Driven Lattice Gases) ainsi que sur un modèle de transport de masse original, exactement soluble. Nous appliquons

également notre analyse sur des systèmes de particules auto-propulsées indépendantes. Dans chaque cas, l'importance du contact est alors pleinement révélée, en accord avec la littérature récente, que ce soit au niveau de la dynamique elle-même ou de la position de ce dernier vis à vis des systèmes.

Summary

This thesis deals with the statistical physics of out-of-equilibrium systems maintained in a steady state. More specifically, this work focuses on macroscopic conserved quantities (volume, mass, etc.) that can be exchanged between several out-of-equilibrium systems brought into contact. The contact between two systems is a fundamental situation in classical thermodynamics of equilibrium systems, since it allows one to define the notion of intensive thermodynamic parameters such as temperature, pressure, chemical potential, etc., derived from the same thermodynamic potential. For non-equilibrium steady state systems, the general existence of such intensive parameters remains an open issue.

By focusing on the contact situation between two out-of-equilibrium stochastic systems on lattice in homogeneous states, we show the existence of a large deviation function attached to the overall densities of both systems, when the frequency of particle exchange between them is low. This large deviations function, analogous to a free energy, satisfies a so-called Hamilton-Jacobi equation. We identify the natural conditions for which the large deviation function is additive, leading to the definition of non-equilibrium chemical potentials. Nevertheless, we show that the latter generically depends on the contact dynamics and therefore do not obey any equation of state. In the absence of a macroscopic detailed balance, the Hamilton-Jacobi equation is much more difficult to solve. A perturbative analysis with respect to the driving forces allows one to show that additivity is generically broken. Beyond this additivity property, this large deviations function can – under certain assumptions – be related to the work applied by an external potential through a generalisation of the second law. We also discuss different ways to get access experimentally to this out-of-equilibrium free energy.

Based on this general theoretical analysis, we eventually provide several illustrations on standard stochastic lattice models (Zero Range Process and Driven Lattice gases in particular) as well as a detailed analysis of an original, exactly solvable, mass transport model. Standard models of independent self-propelled particles are also discussed. The importance of the contact is eventually fully revealed, in agreement with recent literature, either in terms of the dynamics at contact itself or because of its position with respect to both systems.

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Contents

CHAPTER 1

General introduction

1.1 Thermodynamics, non-equilibrium systems and large deviations

Let us consider a cup of hot coffee closed with a lid in order to prevent evaporation. If you leave this cup of coffee on your desk and come back an hour later, you will eventually find a cold coffee whose temperature is the same as the room's temperature.

Consider now a bicycle pump that you want to test, to be sure it is not leaking. For this, you obstruct the valve and push the piston to compress the air inside, and stay like this for a certain time. Then, if you stop to hold the piston, the latter will move until the air in the pump gets the same pressure as the air in the room.

Eventually, take a glass of water and let a drop of blue ink fall in the water. After a while, you can witness that all the water is blue and that the ink has diffused across the whole glass.

All these everyday life experiments have in common to be instances of irreversible phenomena: nobody has ever witnessed a spontaneous warming of the coffee after the latter has been cooled, or has ever witnessed a spontaneous compression of the air inside the pump, or, eventually, has ever witnessed a spontaneous formation of a drop of ink after the latter has diffused throughout the liquid.

In order to grasp these irreversible phenomena and to use the mechanical force that they can produce[1], physicists of the XIX$^{\text{th}}$ century have developed a general theory, namely Thermodynamics [Callen, 1998]. Thermodynamics deals with equilibrium

[1] For instance, you could heat the air inside the pump by putting it in contact with the hot coffee, in order to move the piston by using the work produced by the expansion of the hot air; or you could build a selective elastic membrane, permeable to the water but not to the ink, separating the glass of water into two parts: in diffusing, the ink will apply an extra force on the membrane that prevent its diffusion.

states and transitions that lead an initial equilibrium state to another equilibrium state. Equilibrium states are not clearly defined at this stage, but they can be easily imagined: they correspond to dead calm bodies which do not contain any current. In our example about coffee for instance, initial equilibrium states are the hot coffee initially in its thermos flask and the air that is at a different temperature. When the coffee is poured in the cup and thus brought in contact with air, both systems change their state to eventually reach a new equilibrium state where they both are at the same temperature. The first step was to recognise that equilibrium bodies can be characterised by a few macroscopic observables, that mainly are energy (E), volume (V) and mass (N) (or number of molecules) and that the latter quantities are conserved. This was pretty obvious for the volume and the mass but it was only after series of systematic experimental and theoretical work that energy was recognised to be conserved and could be exchanged between body either through work or heat flow. Coming back to our examples, the transformation of their state is precisely understood as an *exchange* of these quantities. For the coffee, clearly its volume and its mass have not changed. Only its energy has changed and has been transfered to the surrounding air. For the air in the pump, its mass has stayed the same, but not its volume, nor its energy. Eventually, the case of ink is a bit more challenging. One can isolate – by thought – a certain volume which initially contains all the ink molecules and which does not move in time. While diffusing, the quantity of ink inside this fixed volume decreases until the density becomes the same inside the fixed volume as outside. This fictitious volume stayed nevertheless, by definition, fixed, and the energy of the ink molecules is also the same (if one assumes that their concentration is sufficiently small). The second step – which in fact started before historically – was to grasp all these different types of irreversibility introduced in our three different examples into a unique, although quite abstract, framework: that is to say the necessary increase of entropy during a thermodynamic evolution of an *isolated* system. This entropy, generally called S, is attached to every homogeneous system, already fully characterised by its energy, its volume and its mass. S is then a function of the system's state (E, V, N). One of the most important property of entropy is that it is *additive*, meaning that if system A has an entropy S_A and state B has an other S_B, the assembly made of both systems has then an entropy equal to $S_A + S_B$. Let us come back to our first example about coffee to illustrate the second law. Initially, the coffee and the air in the room are separated. Their entropy is initially $S_c(E_c^{\text{ini}}, V_c, N_c) + S_a(E_a^{\text{ini}}, V_a, N_a)$, where c refers to "coffee" and a to "air". When everything reaches its final equilibrium state, the second law states that the final state is the one for which the entropy is maximal – given the constraints applied on the system – (since it can only increase during the evolution and must stop at some point). The final entropy $S_c(E_c^{\text{fin}}, V_c, N_c) + S_a(E_a^{\text{fin}}, V_a, N_a)$ is

thus maximal when $E_a^{\rm fin}$ and $E_c^{\rm fin}$ are such that[2]

$$\frac{\partial S_c}{\partial E_c}(E_c^{\rm fin}, V_c, N_c) = \frac{\partial S_a}{\partial E_a}(E_a^{\rm fin}, V_a, N_a) \ . \tag{1.1}$$

But what quantities are equal when the final equilibrium state is reached? The temperature of course: the abstract quantity $T^{-1} = \partial S/\partial E$ has indeed been recognised as the inverse of the temperature T. The same analysis could have been done for the other two examples and one would have found that in the final state, the derivatives of the entropy with respect to the volumes or with respect to the numbers of particles should equalise. The former derivatives have been recognised as the pressure P divided by the temperature T and the latter as the chemical potential μ divided by the temperature T.

Even if this will be refined henceforth, the general issue to which the present work aims at contributing has been expounded above and can be summarised like this: is there a thermodynamic structure for out-of-equilibrium systems in a steady state? ***Or more precisely: is there a function of state variables that plays a role analogous to the entropy and which is additive? Can one attach to conserved quantities intensive parameters like pressure or chemical potentials that equalise when two non-equilibrium systems are brought into contact?***

1.1.1 Non-equilibrium systems: brief panorama

Before going further, however, we need to specify what these non-equilibrium systems in a steady state are. We have already given a picture of an equilibrium state. Without wishing to be pejorative, equilibrium state can be characterised by their tranquillity: they are dead calm and do not contain any global current. In contrast, non-equilibrium states can be considered at first sight as states that do display currents (in configuration space, not directly observable in all cases). These currents appear because of a lack of equilibrium between different systems. They always corresponds to relaxation toward an equilibrium state. For lots of systems, this relaxation is generally quite fast[3] and one is just interested in the initial and final equilibrium states. This is the subject matter of equilibrium thermodynamics. But sometimes this relaxation is quite long and becomes the topics of interest. The diversity of non-equilibrium situations is very large but one can classify them in basically three types.

[2] The extremal point is characterised by the vanishing of the derivative of the entropy with respect to, say, E_a since E_c is automatically known by the energy conservation: $E_c = E_{\rm tot} - E_a$.

[3] Recall for example the cup of coffee in which you put a little piece of sugar. If you stir it to help the dissolution of the sugar, you do not have to wait for long time in order to the coffee returns to its equilibrium state.

- With this relaxation process in mind, the most natural example is an isolated system which is relaxing toward its equilibrium state. When the latter is very frustrated, the relaxation phenomenon may be very slow and, at our human time scale, one can only witness the transient state. This is the large topic of glassy behaviours, whose main illustration is the window glass for instance.

- However, the most common way to be out of equilibrium is certainly the situation in which the system of interest, say water, is brought into contact with two heat baths at different temperatures, like for instance when this water is in a pot which is heated at the bottom and in contact with the cooler air at the top. The driving force can be also in bulk as for instance in a copper electric wire where electrons are driven by an applied electric field. All these cases can also be seen as very slow transient phenomena: the water in contact with two heat baths is actually only the medium through which the warm heat bath cools itself by discharging its energy into the cold heat bath. As experienced with the coffee, the heat current will end up vanishing when both heat baths will reach the same temperature. But if the latter are very big, this globally transient phenomenon may actually becomes a steady-state phenomenon for a significant time during which the temperatures of both heat baths do not change significantly. Non-equilibrium systems belonging to this category are generally referred to as non-equilibrium systems in a steady state.

- Eventually, a third kind of out of equilibrium systems are those for which the driving force takes place at the level of the particles composing the system. A striking example which has attracted a lot of attention recently, is the emerging field of active matter. Here each unit – which are already quite complicated in themselves – experiences its own driving force generally produced by an internal transfer of energy, often from chemical to mechanical.

Clearly, all these phenomena are very diverse and it appears hopeless to describe them in a unified framework as the equilibrium one. Hence, it seems sound to look at simple situations where the non-equilibrium systems at stake can be described by few quantities at a macroscopic level. Following this approach, we will focus in this thesis on non-equilibrium steady-state systems, mostly driven by non-conservative uniform external forces. Even in the presence of long-range correlations, these systems may remain uniform as equilibrium systems in certain situations. If so, one can expect to describe them at a macroscopic level by few global quantities only. In a second step, we will also consider active particle systems in their steady homogeneous phase.

Furthermore, an important feature of these steady-state systems is that there is necessary a driving force that brings energy (work) into the system and a dissipation

mechanism that removes energy (heat) in order to sustain a global balance, necessary to achieve a steady state.

1.1.2 A phenomenological approach?

As for thermodynamics, one could try to build a phenomenological framework to describe and predict transformations of these non-equilibrium states. For instance, let us come back to the heat flow across the water. For a fixed temperature difference between the two heat baths, the water is crossed by a certain heat current. If the temperature of the warm bath is raised, one eventually gets another – stronger – current and one may ask: what is the supplemental heat absorbed by the water during the transient process between the initial and the final steady state?

To build such a phenomenological framework, similar to the thermodynamics, for non-equilibrium systems in a steady-state, was the purpose of two important works of Oono & Paniconi [Oono and Paniconi, 1998] and then Sasa & Tasaki [Sasa and Tasaki, 2006]. One of the main outcome of these works was to recognise, based on very general hypotheses, the main quantities necessary to describe non-equilibrium uniform steady states. Contrary to equilibrium systems, energy is no longer a good parameter since it is only fixed in average by the environment of the system. Also, in addition to volume and mass (or particles number) which are still conserved, non-equilibrium states display currents that need to be taken into account through a specific out of equilibrium variable. They also gave operational definitions of generalised intensive parameters such as pressure and chemical potentials, with which one can build a generalised entropy function – or rather a free energy in this case, since energy is not conserved.

Nevertheless, exactly in the same way as classical thermodynamics relied on many experimental studies to be justified, such a phenomenological framework finds its ultimate justifications from careful and systematic experiments and does not contain in itself its domain of application [Sekimoto, 2010, Chapter 2] and [Callen, 1998; Kubo, 1968]. Also, one should emphasise the fact that this phenomenological approach only deals with global quantities without taking into account their fluctuations. The latter can however be crucial to understand some phenomena as for instance the adiabatic piston problem[4], needless to say that they naturally appear in small systems.

[4]The adiabatic piston problem, presented in [Feynman et al., 2011; Fruleux et al., 2012; Gruber et al., 2004; Sekimoto et al., 2013], corresponds to the situation where two gases, initially at different temperatures and different pressures, are enclosed in a container and separated by a mobile piston, assumed adiabatic. When the latter is released, the piston moves because of the pressure difference. But even if mechanical equilibrium is reached, temperatures are in general still different since the piston does not allow the heat to flow across itself and classical thermodynamic is not sufficient to predict the final state. Nevertheless, in a real situation with a massive – but not infinitely massive with respect to particles mass – piston, it is observed that gases eventually (after a long time compared to the relaxation times of gases in both systems) achieve the same temperature. It has been recognised

Eventually, the range of prediction of this phenomenological approach is only operational. It says nothing about the quantities involved, in particular about their connection with the microscopic components of the systems at stake. This is already the case for equilibrium thermodynamics which says nothing about the temperature or the chemical potential concepts, except that they equalise in equilibrium and they can be both understood – by construction – as first derivatives of a single function, the entropy, whose meaning is only operational and conceptual as it summarised in only one quantity so many irreversible phenomena. Because of its operational feature, the thermodynamic approach says nothing about equations of states, which relates thermodynamic parameters between them. For instance, the ideal gas law was independently discovered in an empirical way before the birth of thermodynamics.

All these comments do not intend to criticise the thermodynamic approach which is of course very predictive and very robust. They rather aim at emphasising that the core of a thermodynamic approach is empirical and that the latter can only be justified through experiments. In parallel to these essential empirical studies, it is also instructive to examine theoretically macroscopic features of simple models, well defined microscopically. Besides, the history of thermodynamics and statistical mechanics actually shows similar studies: the study of the kinetic theory of gases (actually the seed of the statistical mechanics) was revived by Clausius, the inventor of the entropy, leading to the great achievements of Maxwell and Boltzmann (see [Barberousse, 2002] for a short historical account of statistical mechanics).

1.1.3 Our approach: mesoscopic stochastic systems

It is now time to refine the issue that will be addressed in this thesis. Indeed, as mentioned above, the main question is to define an entropy function (or equivalently at this stage, a free energy function) that would describe the macroscopic state of large *homogeneous* non-equilibrium systems. In equilibrium, this entropy function is additive when two systems (with short-ranged interactions) are brought into contact and together with the conservation of quantities at stake (energy, number of particles, volume, *etc.*), the extremalisation of the thermodynamic potential leads to the equalisation of intensive thermodynamic parameters (temperatures, chemical potentials, pressures, *etc.*). *Is this still valid for uniform non-equilibrium systems in a steady-state?*

To address this question, we will mainly focus on simple stochastic Markov sys-

quite recently [Fruleux et al., 2012; Gruber et al., 2004; Sekimoto et al., 2013] that the well defined equilibrium state, for which all intensive parameters are equal, is indeed reached because of the finite but non-zero asymmetric fluctuations of the massive piston that transfers energy from the hot to the cold gas. Even if the example of the adiabatic piston is maybe too academic, it is a situation where classical thermodynamics does not allow to conclude and for which fluctuations, no matter how small, are necessary to predict the ultimate physical stationary state.

tems composed of microscopic particles. The main idea underlying the modelling of non-equilibrium systems by stochastic Markov models is to describe the system at a mesoscopic level. Certainly, starting from the microscopic Hamiltonian dynamics would be the best. But except for particular very simple situations, it is often impossible to deal with it. This is so because of the non-conservative forces that are often involved, but also because of the contact with at least one heat bath, that is necessary to absorb the energy supplied by the external forces. Hence, an intermediate way to proceed is to imagine mesoscopic models – virtually obtained by space-time coarse-graining over the true microscopic dynamics – that describe the average dynamics as well as fluctuations around the law of large number.

To be specific, let us discuss very briefly the paradigm of such a mesoscopic description : the Langevin dynamics of colloids immersed in a solvent [Oono, 2017; Reif, 2009]. Because of the large – but finite – mass and size difference between the colloids and the solvent's particles, the typical space-time scale along which colloids move is much larger than the one of the solvent's particles. Hence, at the colloid time-scale, an infinitesimal move corresponds to a huge number (at microscopic space-time scale) of collisions with the solvent's molecule: if the space-time scale separation were infinite, the law of large number would exactly apply and colloids would not move at all. However, since the latter is large but finite, the law of large number needs to be completed by fluctuations that can be modelled as a Gaussian white noise in many cases. Of course, one needs some additional information to make the link with the underlying microscopic mechanics. In this case, this is done by relating the variance of the noise to the temperature of the solvent, which characterised the velocity distribution of the solvent's molecules. We will see that for more general Markov stochastic processes, there exists a general condition, namely the *local detailed balance* condition, which allows one to relate the prescribed noise to a physical description. This will be detailed in the first chapter.

Coming back to our main question, one should directly discard as of now the possibility to define a non-equilibrium temperature [Casas-Vázquez and Jou, 2003; Cugliandolo, 2011; Martens et al., 2009; Palacci et al., 2010] in this way: for non-equilibrium stochastic Markov systems in contact, energy is not conserved since systems of interest is exchange energy between them but also with their respective heat baths (if different). Nevertheless, the total number of particles or the volume are still conserved and it remains sound to ask if generalised intensive parameter can be defined to characterise the balance (and the unbalance) of such conserved quantities.

The pressure, which is the conjugate intensive parameter associated with the volume, has always a mechanical definition as it can be derived as a force per unit area exerted on a wall. Nevertheless, the definition of a chemical potential seems to be more delicate to consider generically otherwise than by considering the latter as the

conjugate quantity associated with the number of particles. *For this reason, we will mostly focus our attention to the notion of chemical potential in this thesis.*

In the last decades, several series of studies on stochastic Markov models focusing on thermodynamic issues, and particularly on intensive thermodynamic parameters, have been conducted. In particular, two of them are of particular importance for the issue we want to address:

- The first has been conducted on mass transport models and driven lattice gases, which are lattice models where particles locally jump from site to site according to a Poisson process. The main theoretical contributions on this subject contains: [Hayashi and Sasa, 2003; Sasa and Tasaki, 2006] on the KLS model ; [Bertin et al., 2006, 2007] was a theoretical study on the Zero Range Process, an exactly solvable non-equilibrium mass transport model, whose stationary microscopic distribution completely factorises and thus allows one to define chemical potentials using the same procedure as for equilibrium statistical mechanics. The latter contribution was recently extended to a specific class of short-ranged correlated non-equilibrium systems by [Chatterjee et al., 2015]. The other relevant studies have essentially consisted in numerical simulations on the KLS models [Pradhan et al., 2010, 2011] as well as other driven lattice gases with exclusion [Dickman, 2014, 2016; Dickman and Motai, 2014].

- The second series of study is concerned by active matter models in continuous space and more specifically self-propelled particles like Active Brownian Particles and Run-&-Tumble Particles [Fodor and Marchetti, 2018; Marchetti et al., 2013]. In particular, the question of the definition of the pressure has been addressed quite extensively in recent work [Fily et al., 2017; Solon, Fily, Baskaran, Cates, Kafri, Kardar and Tailleur, 2015; Solon, Stenhammar, Wittkowski, Kardar, Kafri, Cates and Tailleur, 2015; Speck and Jack, 2016; Takatori et al., 2014; Winkler et al., 2015].

The purpose of the present work will be mainly to extend and discuss in a more systematic way the first series of studies on lattice Markov models. In particular, the main results of our work will be to define in an unambiguous and general way a thermodynamic potential from which chemical potential could emerge. We will then address briefly the definition of chemical potentials for (almost) homogeneous self-propelled independent particles models.

1.1.4 From the mesoscopic modelling to thermodynamics: large deviations

Eventually, we present here the main tool that we will use to address the questions introduced above, namely the *Large Deviations* formalism [Ellis, 2007; Freidlin and Wentzell, 1998; Graham, 1987; Oono, 1989; Sasa, 2012; Touchette, 2009]. The latter is particularly suited to study macroscopic variables at the thermodynamic limit. For instance, let us consider the main quantity of interest in our study, namely the total number of particles N_Λ within a given macroscopic domain Λ.

First, when the thermodynamic limit is actually taken, one expects the law of large number to hold. Indeed, for the stochastic models mentioned above, the number of particles is a stochastic variable which thus fluctuates as long as particles enter and leave the domain Λ. If one now looks at the empirical density $\rho_\Lambda = N_\Lambda/|\Lambda|$ ($|\Lambda|$ refers to the volume of the domain Λ) which is an intensive stochastic variable, one expects that $\rho_\Lambda \to \langle\rho\rangle$ when $|\Lambda| \to \infty$ in probability, where $\langle\rho\rangle$ is the average value of the density inside the domain Λ. Interestingly, this law of large numbers can be heuristically rephrased in terms of probability distributions. Indeed, this law states that the probability distribution of the stochastic variable ρ_Λ narrows toward a Dirac delta distribution centred around its mean value $\langle\rho\rangle$.

But how can one refine this law and describe fluctuations around the mean value? A first answer is given by the Central Limit Theorem which deals with Gaussian fluctuations around the mean. However, it turns out that a more natural extension, directly related to the singular limit toward the Dirac delta (*i.e.* the Law of Large Numbers), is provided by the Large Deviations Principle. To illustrate this framework on a simple situation – but relevant for our concern –, let us consider the canonical situation of two systems A and B, in contact in equilibrium, maintained at the same temperature, that can exchange particles across their contact area. According to statistical mechanics [Reif, 2009], the probability to have N_A particles in A (or rather a density ρ_A) and N_B particles in B (or rather a density ρ_B in B), knowing that $N = N_A + N_B$ is kept fixed, reads

$$P_V(\rho_A, \rho_B) = \frac{e^{-\beta[V_A f_A(\rho_A) + V_B f_B(\rho_B)]}}{Z_V(\bar{\rho})} \tag{1.2}$$

where V_k is the volume of region k, f_k is the free energy of region k ($k = A, B$), and $Z(\bar{\rho})$ is the partition function of the whole system, which normalises the probability distribution ($\bar{\rho} = N/V$, $V = V_A + V_B$). This equality can be easily derived from the Gibbs-Maxwell-Boltzmann probability distribution of the micro-states, providing that the interaction energy between the two regions A and B remains local and thus negligible with respect to bulk energies of each systems. Let us now examine this

distribution (1.2) when $V_k \to \infty$. Indeed, $Z(\bar{\rho})$ can be computed using the asymptotic saddle-point approximation:

$$Z(\bar{\rho}) \sim e^{-\beta\left[V_A f_A(\rho_A^*)+V_B f_B(\rho_B^*)\right]} , \tag{1.3}$$

where ρ_k^* are such that $f_A'(\rho_A^*) = f_B'(\rho_B^*)$. Bringing all the quantities together, one can see that the main contribution of the distribution $P_V(\rho_A, \rho_B)$ when V_k are very large reads

$$P(\rho_A|\bar{\rho}) \sim e^{-\beta V I(\rho_A|\bar{\rho})} \tag{1.4}$$

with

$$I(\rho_A|\bar{\rho}) = \gamma_A \left(f_A(\rho_A) - f_A(\rho_A^*)\right) + \gamma_B \left(f_B(\rho_B) - f_B(\rho_B^*)\right) ,$$

where $\gamma_k = V_k/V$ the relative size of volume k ($k = A, B$) with respect to the whole volume.

Equation (1.4) is what one calls a *large deviation principle* associated with the stochastic variable ρ_A (ρ_B is in fact known as soon as ρ_A is because of mass conservation) and $I(\rho_A|\bar{\rho})$ is called a large deviation function or large deviation rate. When $V \to \infty$ (with γ_A, γ_B fixed) one can notice that the distribution is more and more peaked around the value for which $I(\rho_A|\bar{\rho})$ is *minimal* and thus equates to 0. According to (1.4), this point that minimises $I(\rho_A|\bar{\rho})$ is $\rho_A^* = \langle \rho_A \rangle$ for which $f_A'(\rho_A^*) = f_B'(\rho_B^*)$, which have been recognised to be the chemical potentials of systems A and B that equalise at the thermodynamic limit.

Hence, the large deviation framework allows one to derive *variational principles* (or minimisation principle, of the free energy here) that are useful to characterise the average value around which the probability distribution narrows. Since the large deviation function I is additive, *i.e.* that it is a sum of a contribution depending on A and another depending on B, the minimisation procedure allows one to define chemical potentials that equalise in the stationary state.

The link between equilibrium thermodynamics and equilibrium statistical physics can in fact be rationalised through this large deviation formalism [Ellis, 2007; Touchette, 2009, 2015]. It thus appears quite promising to try to derive a thermodynamic formalism for stochastic non-equilibrium systems.

1.2 Outline

The main purpose of this thesis is to extend and rationalise the first series of studies mentioned at the end of subsection 1.1.3, centred around the definition of chemical

potentials and the zeroth law for non-equilibrium systems in steady-state. This first chapter (chapter 2) is then devoted to the presentation of a formal general framework – asymptotically valid when the relaxation time-scales inside the bulks of both systems are much larger than the typical time-scale to exchange a particle across contact – to study the large deviation function associated with the probability distribution of densities ρ_A and ρ_B of two uniform non-equilibrium mass transport or lattice gas models (which belong to the general class of jump Poisson processes).

The chapter 3 is the core of this thesis. Using the general framework expounded in the first chapter, we propose a general condition in order to obtain an additive large deviation function of densities as in equilibrium (see equation (1.4)). Under this additivity property, generalised non-equilibrium chemical potentials can be defined. We discuss their relation with equilibrium chemical potentials as well as prospective chemical potentials attached to the virtually separated systems. Eventually, the thermodynamic meaning of the large deviation function (and possibly its related chemical potentials) is investigated. We show that for certain rule of transition rates, the large deviation function of the densities play a role of a free energy since it obeys a second law with respect to the work supplied by the variation of external potentials. We close this chapter by providing some methods to measure either the large deviation function or its associated chemical potentials. In particular, we inspect the particular case of the contact between a non-equilibrium system and a reservoir of particles (which can be at or out of equilibrium).

After the abstract and general studies of chapters 2 and 3 comes applications to specific mass transport and lattice gas models. A short review of the pioneering work of [Bertin et al., 2006, 2007] is illustrated on the Zero Range Process. Nevertheless, the stationary distribution of the latter is invariant with respect to a variation of the applied driving force. Hence, the driving force dependence on the large deviation function cannot be studied. In order to overcome this situation, we present an original mass transport model, exactly solvable, which displays a dependence on the external drive (more details are available in appendix C). Extensive studies on chemical potentials and their generic dependence on the dynamic at contact are expounded, together with some numerical simulation results. Then, to go beyond these exact solvable models and explore systems with dimension greater than one, we discuss the main relevant papers of the literature, using our unifying framework developed in chapters 2 and 3. Eventually, we briefly tackle the question of the contact in the Macroscopic Fluctuation Theory framework [Bertini et al., 2015*a*]: we show that the effects observed in previous microscopic models cannot be restored by this general mesoscopic theory.

As for the last chapter 5, it moves to continuous space models and more specifically to colloids and self-propelled particles which have recently attracted a lot of attention. These works correspond to the second series of studies mentioned above

(see the end of subsection 1.1.3). We study in particular independent particles, either externally driven (colloids) or self-propelled (Run-&-Tumble and Active Brownian particles), which are brought into contact with a permeable membrane or more generically with a high energy barrier. Eventually, a general conclusion and some perspectives are given.

CHAPTER 2

General framework: contact in the thermodynamic limit

This introductory chapter aims at introducing the main objects of this thesis, on the simple stochastic framework of driven lattice gas or mass transport models that both belong to the realm of Markov jump processes which obey *local detailed balance*. We will consider the situation where two such systems are brought into contact and thus reach a new steady state, in a similar way as previous studies available in the literature [Bertin et al., 2007; Dickman, 2014; Dickman and Motai, 2014; Hayashi and Sasa, 2003; Pradhan et al., 2010, 2011; Sasa and Tasaki, 2006]. An important assumption necessary for our framework to hold will be a time-scale separation between the exchange of particles at contact and the bulk dynamics within the systems, as already advocated in [Sasa and Tasaki, 2006, Appendix B.]. This limitation may appear quite restrictive but is actually physically motivated if one imagines the contact as a high energy barrier that particles have to cross (see [Sasa and Tasaki, 2006]). We will nevertheless consider more general contact types that could be relevant, still in this vanishing exchange rate limit at contact (compared to the bulk rates).

The main achievement of this chapter is the introduction of the large deviations function $\mathcal{I}(\rho_A, \rho_B|\bar{\rho})$ associated with the global densities ρ_A and ρ_B of the two systems in contact (called A and B). The latter is considered as a solution of what one may call an Hamilton-Jacobi equation for Markov jump processes. This results are not new ([Kubo et al., 1973; Maes and Netočný, 2007] and [Ge and Qian, 2017] for a recent survey with emphasis on chemical reactions) but seem to have received – as far as the author knows – little attention for the study of macroscopic phenomena in simple lattice gases and other mass transport model.

The last part of the chapter is devoted to the different available ways to solve the Hamilton-Jacobi equation and then find its solution $\mathcal{I}(\rho_A, \rho_B|\bar{\rho})$. In particular, we

highlight the important situation of the detailed balance (at a macroscopic level, which will be detailed henceforth), as well as its natural link with time-reversal symmetry. We conclude by presenting a general perturbation method to solve the Hamilton-Jacobi equation, that mimics the one presented in [Bouchet et al., 2016] in the context of diffusive systems. Here again, we emphasise that the ideas presented in this chapter are not new [Bertini et al., 2015*a*; Ge and Qian, 2017; Kaiser et al., 2018] – even if its presentation may have its part of originality in the specific setting considered here.

2.1 Definition of the dynamics

We begin with the general definition of the models that will be considered in this thesis. Stochastic lattice gases and mass transport models are formally continuous time stochastic Markovian systems defined on lattice [Liggett, 2012; Spitzer, 1970] composed of interacting particles that jump from site to site, see figure 2.1. Particles are assumed to be indistinguishable and thus one can describe microscopic state or configuration by the occupation number in each site x of the lattice as shown on figure 2.1.

To visualise the dynamics, let us consider the most simple model of this kind, namely a single particle performing a random walk in one dimension. The particle is assumed to start at site, say, x_0, at time $t = 0$. The particle will stay at site x_0 for a random time drawn in an exponential distribution before jumping instantly to the left $(x_0 - 1)$ or the right $(x_0 + 1)$ with equal probability (in the absence of any bias). Then, the particle stays at its new location for another random time drawn in the same exponential distribution before jumping to another site, *etc.* When several particles, interacting with each other, are present, the average waiting time to jump that controls the exponential distribution of jump times at each occupied site, as well as the probability to jump to an other site, generally depend on the occupation numbers of neighbouring sites (local configurations). In the framework of interacting Markov systems, this is generally summarised in the local configuration dependence of the transition rates, since the latter completely describe the dynamics sketched above [Spitzer, 1970].

Examples of such mass transport models are: the well known Asymmetric Simple Exclusion Process (ASEP) as well as its variant [Derrida, 1998, 2007; Spitzer, 1970], the Katz-Lebowitz-Spohn (KLS) model [Katz et al., 1984; Zia, 2010], the Zero Range Process [Evans and Hanney, 2005; Levine et al., 2005] as well as its numerous variants [Evans et al., 2004, 2006*a*,*b*; Zia et al., 2004], *etc.*

For one system, we note $\Lambda \subset \mathbb{Z}^{\mathrm{d}}$ the space grid (d being the space dimension), $V = |\Lambda|$ the number of sites, N the number of particles and $\mathcal{C} = \{n_x\}_{x\in\Lambda}$ a configuration of the system, $n_x \in [\![0, n_{\max}]\!]$ being the number of particles at site x ($n_{\max}$ can be finite

or infinite). If n_x is generically an integer for most models, one will also consider in the following continuous masses for which $n_x \geq 0$ is real. We point out that periodic boundary conditions are assumed at least in the driving direction (detailed are given below).

The dynamics is entirely prescribed by the transition rates $T(\mathcal{C}'|\mathcal{C})$ to jump from a configuration $\mathcal{C}$ to an other one $\mathcal{C}'$. For instance, for stochastic lattice gases, $\mathcal{C}'$ corresponds to a single move of one particles from its former site to its new site. As these simple models intend to be mesoscopic modellings of the dynamics of particles, one imposes the *local detailed balance* [Katz et al., 1984; Maes, 2003; Maes and Netočnỳ, 2003] condition which restricts the class of systems that can be modelled by Markov processes. It states that

$$\frac{T(\mathcal{C}'|\mathcal{C})}{T(\mathcal{C}|\mathcal{C}')} = \exp\left[-\beta\left(E(\mathcal{C}') - E(\mathcal{C}) - W(\mathcal{C},\mathcal{C}')\right)\right] \tag{2.1}$$

where $E(\mathcal{C})$ is the energy of the configuration $\mathcal{C}$ and $W(\mathcal{C},\mathcal{C}')$ refers to the non-conservative work associated with the driving. Physically, this assumption is reminiscent of the contact between the particles and the heat bath producing the noise which is such that the latter stays in equilibrium at inverse temperature β (see introduction of [Wynants, 2010]).

The energy E is generically prescribed by a given interacting potential sometimes supplemented by an external potential. The non-conservative work W depends on the driving but we will mostly consider a constant driving force f for which

$$W(\mathcal{C},\mathcal{C}') = f \cdot j(\mathcal{C},\mathcal{C}'),$$

$j(\mathcal{C},\mathcal{C}')$ being the total current flowing in the system for the transition $\mathcal{C} \to \mathcal{C}'$ (the latter is thus generally localised if only one particle jumps at a time). We note that explicit functional form of transition rates T is not completely specified by the local detailed balance property. We will consider in specific examples below some common choices obeying local detailed balance such as the exponential rule, the Kawasaki rule, the Metropolis rule or the Sasa-Tasaki rule (defined in chapter 3) [Tasaki, 2004].

2.2 Putting two systems into contact

2.2.1 Definition of the microscopic dynamics

We define in this subsection the contact dynamics between two systems A and B defined by their own Hamiltonians $E_A(\mathcal{C}_A)$, $E_B(\mathcal{C}_B)$ and their own driving force f_A, f_B. One calls Λ_k the space grid of system k, $V_k = |\Lambda_k|$ the number of sites of system

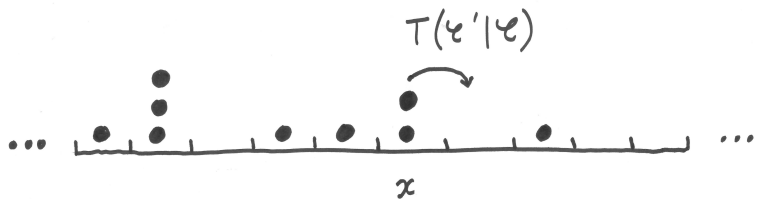

Figure 2.1 – Sketch of a one dimensional mass transport model on lattice. Sites $x \in \Lambda$ are occupied by n_x particles. For most models, the dynamics is asynchronous, meaning that only one particle is moving during a transition. That being said, synchronous dynamics for which all sites are updated at each transition can be also considered. Even if the latter does not concern driven lattice gases, it has been investigated in generalisation of the Zero Range Processes. This is also the natural dynamics of Probabilistic Cellular Automata [Lebowitz et al., 1990].

k and $N_k = \mathcal{N}(\mathcal{C}_k)$ the actual number of particles in system k, $k = A, B$. One sets $\gamma_A = V_A/V$ and $\gamma_B = V_B/V$ ($\gamma_A + \gamma_B = 1$) the relative sizes of system A and B with respect to the total volume of $A \cup B$ which reads $V = V_A + V_B$. The contact dynamics is defined through a transition rate $T_c(\mathcal{C}'_A, \mathcal{C}'_B | \mathcal{C}_A, \mathcal{C}_B)$ obeying local detailed balance as well. The total number of particles $N = \mathcal{N}(\mathcal{C}_A) + \mathcal{N}(\mathcal{C}_B)$ is assumed to be fixed.

As already mentioned in the general introduction, our main goal is to investigate the situation of two uniform non-equilibrium systems in contact. Since we have chosen to look at the simple situation of externally driven systems for which periodic boundary conditions along the driving forces are necessary, the natural contact geometry one can think of is the one sketched in figure 2.2 that shows a contact *orthogonal* to the driving forces f_A and f_B. Hence, microscopic transition rates at contact, T_c, are thus assumed not to depend on driving forces f_A, f_B. The case with an additional dependence on the forcing at contact will be briefly discussed later (see subsection 3.1.3).

***Remark*: there is an effect!** Since we will not consider particular examples before chapter 4, we shall not prolong the suspense and hence point out that even if the contact is perpendicular to both driving forces, the stationary densities in the two systems A and B are indeed observed to be significantly affected by the drives (see numeral simulation results of section 4.2 or detailed numerical investigations of R. Dickman in [Dickman, 2014; Dickman and Motai, 2014]).

The dynamics of the whole system composed of systems A and B is thus prescribed by transition rates in the bulk as well as the contact ones. The stochastic process is a Poisson Markov jump process and the probability to observe a configura-

tion $\mathcal{C} = (\mathcal{C}_A, \mathcal{C}_B)$ at time t, $P_t(\mathcal{C})$, obeys the following master equation

$$\begin{aligned}\frac{\mathrm{d}P_t}{\mathrm{d}t}(\mathcal{C}_A,\mathcal{C}_B) = &\sum_{\mathcal{C}'_A\neq\mathcal{C}_A} T_A(\mathcal{C}_A|\mathcal{C}'_A)P_t(\mathcal{C}'_A,\mathcal{C}_B) - \lambda_A(\mathcal{C}_A)P_t(\mathcal{C}_A,\mathcal{C}_B) \\ &+ \sum_{\mathcal{C}'_B\neq\mathcal{C}_B} T_B(\mathcal{C}_B|\mathcal{C}'_B)P_t(\mathcal{C}_A,\mathcal{C}'_B) - \lambda_B(\mathcal{C}_B)P_t(\mathcal{C}_A,\mathcal{C}_B) \\ &+ \sum_{\substack{\mathcal{C}'_A\neq\mathcal{C}_A \\ \mathcal{C}'_B\neq\mathcal{C}_B}} T_c(\mathcal{C}_A,\mathcal{C}_B|\mathcal{C}'_A,\mathcal{C}'_B)P_t(\mathcal{C}'_A,\mathcal{C}'_B) - \lambda_c(\mathcal{C}_A,\mathcal{C}_B)P_t(\mathcal{C}_A,\mathcal{C}_B)\ .\end{aligned} \tag{2.2}$$

with $\lambda_k(\mathcal{C}) = \sum_{\mathcal{C}'\neq\mathcal{C}} T_k(\mathcal{C}'|\mathcal{C})$ the escape rates associated with the configuration $\mathcal{C}$, $k = A$, B or c. The subscripts A and B stands for the bulks of both systems A and B whereas the subscript c is referring to the contact (*i.e.* transitions $(\mathcal{C}_A,\mathcal{C}_B) \to (\mathcal{C}'_A,\mathcal{C}'_B)$ that corresponds to exchange of particles between A and B).

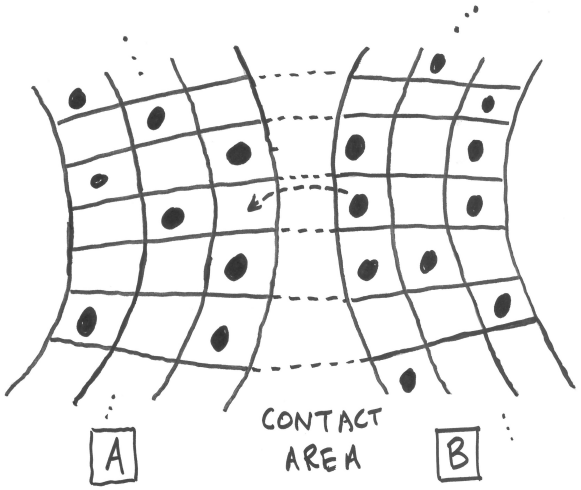

Figure 2.2 – Picture of the two particle models on lattice brought into contact. The latter is generally localised but one does not restrict its extension at this stage. As long as the exchange rates at contact are small, all sites of each systems can be connected (in a supplemental dimension)

2.2.2 Coarse-grained dynamics of the densities

Our goal is to compute the stationary distribution of the number of particles in each systems, knowing the total number of particles $N = N_A + N_B$ or rather the density $\bar{\rho} = \gamma_A\rho_A + \gamma_B\rho_B$. If microscopic detailed balance holds, one can solve straightforwardly the stationary master equation (2.2) and thus derive directly the distribution of densities ρ_A, ρ_B in each systems. However, since both systems are out-of-equilibrium, detailed balance does not hold. The strategy is then to derive an evolution equation on the probability distribution on ρ_A ($\rho_B = \gamma_B^{-1}(\bar{\rho} - \gamma_A\rho_A)$) as we will see henceforth.

Proceeding straightforwardly, one can easily derive an evolution equation on $P_t(\rho_A|\bar{\rho})$, $P_t(\rho_A|\bar{\rho})$ being the probability to observe a density $\rho_A = N_A/V_A$ (and $\rho_B = \gamma_B^{-1}(\bar{\rho} - \gamma_A\rho_A)$ since mass is conserved), by summing over all the micro-states $\mathcal{C} = (\mathcal{C}_A, \mathcal{C}_B)$ that give the actual density in (2.2). Since the dynamics in the bulks of A and B conserve the number of particles in each system, the coarse-grained master equation over (ρ_A, ρ_B) only involves the dynamics at contact encoded in T_c. It yields

$$\frac{\mathrm{d}P_t}{\mathrm{d}t}(\rho_A|\bar{\rho}) = \sum_{\rho'_A \neq \rho_A} \pi_{\bar{\rho},t}(\rho_A|\rho'_A)P_t(\rho'_A|\bar{\rho}) - \pi_{\bar{\rho},t}(\rho'_A|\rho_A)P_t(\rho_A|\bar{\rho}) \; . \tag{2.3}$$

$\pi_{\bar{\rho},t}(\rho'_A|\rho_A)$ refers to the coarse-grained transition rate associated with the coarse-grained transition $\rho_A \to \rho'_A$, $\rho'_A = \rho_A - \Delta N_A/V_A$. It reads

$$\pi_{\bar{\rho},t}(\rho'_A|\rho_A) = \sum_{\substack{\mathcal{C}'_A \in \mathcal{E}^{V_A}_{\Delta N_A}(\rho_A) \\ \mathcal{C}'_B \in \mathcal{E}^{V_B}_{-\Delta N_A}(\rho_B)}} \sum_{\substack{\mathcal{C}_A \in \mathcal{E}^{V_A}_{0}(\rho_A) \\ \mathcal{C}_B \in \mathcal{E}^{V_B}_{0}(\rho_B)}} T_c(\mathcal{C}'_A, \mathcal{C}'_B|\mathcal{C}_A, \mathcal{C}_B)P_t(\mathcal{C}_A, \mathcal{C}_B|\rho_A, \bar{\rho}) \; . \tag{2.4}$$

with $\mathcal{E}^V_{\Delta N}(\rho) = \{\mathcal{C} \,|\, \mathcal{N}(\mathcal{C}) = \rho V + \Delta N\}$, the set of configurations that contains exactly $\rho V + \Delta N$ particles.

The knowledge of the coarse-grained transition rates thus rests upon the knowledge of the conditional probability distributions $P_t(\mathcal{C}_A, \mathcal{C}_B|\rho_A, \bar{\rho})$ whose coupled evolutions can be obtained from the microscopic dynamics (2.2). Of course, this series of equations is completely equivalent to the microscopic one and this approach would be a deadlock without further approximations.

Let us stop here for a moment, in order to discuss physically the situation. Contrary to the equilibrium situation for which detailed balance holds and all currents between every transitions $\mathcal{C} \to \mathcal{C}'$ vanish, non-equilibrium systems host non-vanishing currents. Hence, when systems A and B are brought into contact, the global balance of currents of the configurations $\mathcal{C}$ have to adjust to a new balance which takes into account the currents at contact.

One cannot avoid in general that the perturbation at contact remains local. In particular, long-range correlations along the flux are ubiquitous in non-equilibrium systems [Bertini et al., 2007; Dorfman et al., 1994; Garrido et al., 1990; Spohn, 1983] and local perturbation may produce long-range effect [Maes et al., 2009] thus leading to a strong coupling between systems. Clearly, one would not expect any additivity property to hold if such a strong coupling were present. The two systems in contact would be rather a non-homogeneous global system built upon the two initially isolated systems.

Even if these long-range effects are less expected to happen when the contact is local and the extension in the directions perpendicular to the driving forces are large enough, this coupling remains too difficult to be studied in a general setting. Following

the phenomenological study of [Sasa and Tasaki, 2006], as well as their detailed study on the KLS model [Hayashi and Sasa, 2003; Sasa and Tasaki, 2006], we will then focus on the simpler situation for which the transition rates at contact are very small compared to the bulk ones. We will see that this limiting case is also the more likely to enable a thermodynamic structure since the stationary probability density happens to be almost factorised.

Eventually, this vanishing exchange rates limit at contact is also quite likely to be realised in physical experiment. Indeed, this could be realised – for the exchange of particles – by any system that displays a high energy barrier compared to the typical energy barrier in systems A and B. One can think for instance of a porous membrane whose pores exert a repulsive interaction that needs to be overcome. But beyond this case of an high energy barrier – which led Sasa & Tasaki to propose their transition rates that will be discussed henceforth –, one can also imagine that the small-rate limit can be achieved by low frequency openings of a gate without any repulsive or attractive force exerted by the membrane itself. In the latter case, the particles that jump from one system to the other may feel forces applied by the particles belonging to the other system when the gate is open. Eventually, in the same spirit of the gate dynamics, low frequency can be achieved by a strong conformation selection[1] of particles without any additional forces performed by pores.

To summarise this physical discussion, the low frequency exchange limit can be reached either by a high energy barrier that screens the interactions between both systems at contact, or by a low opening rate of a gate or strong conformation selection of particles that decreases the attempt rate of jumps without screening the interactions between systems in contact. Whatever the situation, one will consider in the following that the rates at contact are very small compared to the bulk ones. One will thus enforce explicitly this low frequency by introducing a small parameter $\epsilon \ll 1$ in front of the transition rates at contact: $T_c(\mathcal{C}'|\mathcal{C}) \to \epsilon T_c(\mathcal{C}'|\mathcal{C})$. It is thus natural to introduce the re-scaled time $\tau = \epsilon t$ for the dynamics over the number of particles N_A. Note that we keep writing $P_\tau(\rho_A|\bar{\rho})$ and $\pi_{\bar{\rho},\tau}$ for the re-scaled function but not for the microscopic distribution $P_t(\mathcal{C}_A, \mathcal{C}_B|\rho_A, \bar{\rho})$. That being said, one obtains

$$\pi_{\bar{\rho},\tau}(\rho'_A|\rho_A) = \sum_{\substack{\mathcal{C}'_A \in \mathcal{E}^{V_A}_{\Delta N_A}(\rho_A) \\ \mathcal{C}'_B \in \mathcal{E}^{V_B}_{-\Delta N_A}(\rho_B)}} \sum_{\substack{\mathcal{C}_A \in \mathcal{E}^{V_A}_{0}(\rho_A) \\ \mathcal{C}_B \in \mathcal{E}^{V_B}_{0}(\rho_B)}} T_c(\mathcal{C}'_A, \mathcal{C}'_B|\mathcal{C}_A, \mathcal{C}_B) P_{\epsilon^{-1}\tau}(\mathcal{C}_A, \mathcal{C}_B|\rho_A, \bar{\rho}) \,. \tag{2.5}$$

Before looking at a more rigorous treatment, one can already guess heuristically

[1] For instance, particles could have a specific shape or a marker that would be rejected by the pores of the membrane if they do not appear with the suited position, or the marker activated, etc. If one does not follow these extra degrees of freedom assumed to be stochastic too, averaging over them should give this selective behaviour

what happens when $\epsilon \to 0$. We introduce τ_b^{-1} the typical rate at which bulks evolve. According to our assumption, the typical rate at contact reads $\tau_c^{-1} = \epsilon \tau_b^{-1}$. For ϵ small enough, τ_c can become very large compared to the largest relaxation time of the bulk dynamics. Hence, jumps of particles between A and B are typically spaced out from a very large time interval τ_c during which bulk dynamics is mostly drawn from its stationary state (since one assumes that it has relaxed very quickly to its steady state). At a resolution time of order τ_c (very large compared to the bulk time τ_b) – which can be achieved by averaging the signal in time (filtering) over a typical time large compared to τ_c –, the coarse-grained transition rate reads

$$\pi_{\bar{\rho}}(\rho'_A|\rho_A) = \sum_{\mathcal{C}'_A,\mathcal{C}'_B} \sum_{\mathcal{C}_A,\mathcal{C}_B} T_c(\mathcal{C}'_A,\mathcal{C}'_B|\mathcal{C}_A,\mathcal{C}_B) P(\mathcal{C}_A,\mathcal{C}_B|\rho_A,\bar{\rho}) \; . \tag{2.6}$$

At zeroth order in ϵ, the stationary distribution $P(\mathcal{C}_A,\mathcal{C}_B|\rho_A,\bar{\rho}) = P(\mathcal{C}_A,\mathcal{C}_B)$ is the stationary solution of the master equation (2.2) with $\epsilon = 0$. It is equal to the stationary distribution one would reach if the systems were completely isolated from each other, which is completely factorised: $P(\mathcal{C}_A,\mathcal{C}_B|\rho_A,\bar{\rho}) = P_A(\mathcal{C}_A|\rho_A) P_B(\mathcal{C}_B|\rho_B)$.

***Remark*: about the finite ϵ case.** The $\epsilon \to 0$ limit ensures that the typical time between two exchange of particles between systems in contact is very large compared to the typical time for both systems to relax to their respective stationary states. For finite ϵ such that the typical exchange time is of order of the time for both systems to relax to their respective steady state, one can intuitively guess that an approximate Markovian description of the dynamics upon densities will involve relaxation modes of the bulk dynamics [Wang et al., 2016*a*,*b*]. This much more complicated situation will not be considered in this thesis and is postponed for future works.

***Remark*: breaking of the detailed balance at microscopic level.** One will have the opportunity to come back to this point latter, but let us make one important comment at this stage. Indeed, we can note heuristically that in the vanishing rate limit, one may avoid the "equilibration" at contact. Since the stationary distribution $P(\mathcal{C}_k|\rho_k)$ ($k = A, B$) is generally different from the equilibrium one when driving forces are turned on, one can expect a breaking of detailed balance for the microscopic transitions involved in the exchange of particles. Yet, we will see thereafter that this allows a null current of particles at contact.

Along with the precedent remark on the finite ϵ situation, one can expect that increasing ϵ may reduce the breaking of the detailed balance at contact. Indeed, in the $\epsilon \to \infty$ limit case, the sites connected through the contact reach equilibrium very quickly whereas the remaining part evolves very slowly. It is difficult to discuss the situation in a general way since it strongly depends on the specific interactions between

sites at contact but one can imagine that approaching this limit may allow a better balance of the currents at contact since transition rates at contact are assumed to be the same as in equilibrium. This effect will be discussed in section 4.3.3 regarding the numerical simulations performed by R. Dickman in [Dickman, 2014; Dickman and Motai, 2014].

2.2.3 Time-scale separation in the weak contact limit: multi-scale analysis

Even if the heuristic discussion above might be sufficient at an intuitive level – at least for the expression of the final coarse-grained transition rate – we propose here to look in more details into the multi-scale analysis of the problem. Even if we will stop at the first non-trivial order in ϵ, such an approach can be extended in principle beyond this order. To do so, we first lighten notations and rewrite the master equation describing the probability distribution of configurations of the two coupled systems in vector notations:

$$\frac{\mathrm{d}|P_t\rangle}{\mathrm{d}t} = \mathcal{W}_b|P_t\rangle + \epsilon\mathcal{W}_c|P_t\rangle \tag{2.7}$$

where $\mathcal{W}_b$ and $\mathcal{W}_c$ are respectively the evolution matrices associated with the bulk transition rates $T_b(\mathcal{C}|\mathcal{C}') = T_A(\mathcal{C}_A|\mathcal{C}_A{}')\delta_{\mathcal{C}_B,\mathcal{C}'_B} + T_B(\mathcal{C}_B|\mathcal{C}_B{}')\delta_{\mathcal{C}_A,\mathcal{C}'_A}$ and the contact transition rates $T_c(\mathcal{C}|\mathcal{C}')$. $|P_t\rangle$ is the vector whose coordinates are $P_t(\mathcal{C}) = \langle\mathcal{C}|P_t\rangle$, $\langle\mathcal{C}|$ being the row vector associated with the configuration $\mathcal{C}$ (full of 0 except at the configuration label $\mathcal{C}$ for which it is equal to 1).

In order to get the solution of this master equation (2.7) in the weak contact limit $\epsilon \to 0$, one can perform a perturbative expansion

$$|P_t\rangle = |P_t^{(0)}\rangle + \epsilon|P_t^{(1)}\rangle + \mathcal{O}(\epsilon^2)\,. \tag{2.8}$$

The master equations at each order read

$$\begin{aligned} \mathcal{O}(\epsilon^0)\ :&\quad \frac{\mathrm{d}|P_t^{(0)}\rangle}{\mathrm{d}t} = \mathcal{W}_b|P_t^{(0)}\rangle \\ \mathcal{O}(\epsilon^1)\ :&\quad \frac{\mathrm{d}|P_t^{(1)}\rangle}{\mathrm{d}t} = \mathcal{W}_b|P_t^{(1)}\rangle + \mathcal{W}_c|P_t^{(0)}\rangle\,, \end{aligned} \tag{2.9}$$

whose formal solutions are

$$\begin{aligned} |P_t^{(0)}\rangle &= e^{t\mathcal{W}_b}|P_0\rangle \\ |P_t^{(1)}\rangle &= \int_0^t \mathrm{d}s\, e^{(t-s)\mathcal{W}_b}\mathcal{W}_c e^{s\mathcal{W}_b}|P_0\rangle\,, \end{aligned} \tag{2.10}$$

initial conditions being $|P_{t=0}\rangle = |P_0\rangle$ with $|P_0\rangle \sim \mathcal{O}(\epsilon^0)$. The initial condition is quite

arbitrary and can always be decomposed as

$$|P_0\rangle = \sum_{\rho_A} P_0(\rho_A)|SS,\rho_A\rangle_b + \sum_{\rho_A} |T_0,\rho_A\rangle_b \tag{2.11}$$

where $|SS,\rho_A\rangle_b$ is a short notation for a stationary solution of the bulk dynamics with densities ρ_A and ρ_B chosen initially: $\langle\mathcal{C}|SS,\rho_A\rangle_b = P_A(\mathcal{C}_A|\rho_A)P_B(\mathcal{C}_B|\rho_B)$ for any $\mathcal{C}=(\mathcal{C}_A,\mathcal{C}_B)$ such that $\mathcal{N}(\mathcal{C}_A)=\rho_A V_A$ and $\mathcal{N}(\mathcal{C}_B)=\rho_B V_B = N-\rho_A V_A$. As one notices, we will omit the fixed total density $\bar{\rho}$ in order to lighten notations. Technically, $|SS,\rho_A\rangle_b$ is a right eigenvector of $\mathcal{W}_b$ associated with the eigenvalue 0. As for $|T_0,\rho_A\rangle_b$, it refers to a transient part that will vanish at large time ($\lim_{t\to\infty} e^{t\mathcal{W}_b}|T_0,\rho_A\rangle_b = 0$). Eventually, $P_0(\rho_A)$ is a weight to start with densities ρ_A, ρ_B in the steady states of A and B.

Inserting $|P_0\rangle$ in equations (2.10), one obtains

$$\begin{aligned}
|P_t^{(0)}\rangle &= \sum_{\rho_A} P_0(\rho_A)|SS,\rho_A\rangle_b + \sum_{\rho_A} e^{t\mathcal{W}_b}|T_0,\rho_A\rangle_b \\
|P_t^{(1)}\rangle &= t\sum_{\rho_A,\rho'_A} P_0(\rho_A)\,{}_b\langle -,\rho'_A|\mathcal{W}_c\,|SS,\rho_A\rangle_b\,|SS,\rho'_A\rangle_b \\
&\quad + \sum_{\rho_A} P_0(\rho_A)\int_0^t \mathrm{d}s\, e^{(t-s)\mathcal{W}_b}|R_{SS},\rho_A\rangle_b \\
&\quad + \sum_{\rho_A}\int_0^t \mathrm{d}s\, e^{(t-s)\mathcal{W}_b}\mathcal{W}_c e^{s\mathcal{W}_b}|T_0,\rho_A\rangle_b
\end{aligned} \tag{2.12}$$

where one has used $\mathcal{W}_c|SS,\rho_A\rangle_b = \sum_{\rho'_A} {}_b\langle -,\rho_A|\mathcal{W}_c|SS,\rho_A\rangle_b\,|SS,\rho'_A\rangle_b + |R_{SS},\rho_A\rangle_b$, $|R_{SS},\rho_A\rangle_b$ being the transient component (with respect to the bulk dynamics) and ${}_b\langle -,\rho_A|$ being the left eigenvector of $\mathcal{W}_b$ for fixed densities ρ_A, ρ_B with eigenvalue 0. One has ${}_b\langle -,\rho_A|\mathcal{C}\rangle = 1$ if $\mathcal{N}_A(\mathcal{C}) = V_A\rho_A$ and ${}_b\langle -,\rho_A|\mathcal{C}\rangle = 0$ otherwise.

The second and the third term of $|P_t^{(1)}\rangle$ in equation (2.12) converge when $t\to\infty$ but the first, proportional to t, is clearly a *secular* term which breaks the validity of the perturbation expansion as soon as $\epsilon t \sim \mathcal{O}(1)$: for $t\sim\mathcal{O}(\epsilon^{-1})$, $\epsilon|P_t^{(1)}\rangle$ becomes of the same order as $|P_t^{(0)}\rangle$ and the expansion is no more uniform [Bender and Orszag, 1999; Nayfeh, 2008]. Such discrepancy is the consequence of the fact that the perturbation series is slowly convergent and that all terms are needed to obtain a bounded result for any time t. In order to regularise the perturbation series for large time, one can use the fact that the initial condition cannot be observed when t is large [Chen et al., 1994, 1996; Oono, 2012]: one can take advantage of it to renormalise the series.

In order to perform this procedure, one introduces an arbitrary time $\tilde{t}$ which will be the new initial time: $t = (t-\tilde{t})+\tilde{t}$. Absorbing the term proportional to $\epsilon\tilde{t}$ of the secular term in the coefficients $P_0(\rho_A)$, which leads to a renormalised term $P_{\tilde{t}}(\rho_A)$,

allows us to write the solution $|P_t\rangle$ (equation (2.8)) as

$$\begin{aligned}|P_t\rangle = &\sum_{\rho_A} P_{\tilde{t}}(\rho_A)|SS,\rho_A\rangle_b + \sum_{\rho_A} e^{t\mathcal{W}_b}|T_0,\rho_A\rangle_b \\ &+ \epsilon(t-\tilde{t})\sum_{\rho_A,\rho'_A} P_{\tilde{t}}(\rho_A)\,{}_b\langle -,\rho'_A|\mathcal{W}_c\,|SS,\rho_A\rangle_b\,|SS,\rho'_A\rangle_b \\ &+ \epsilon\mathcal{R}_t + \mathcal{O}(\epsilon^2)\end{aligned} \tag{2.13}$$

where $\mathcal{R}_t$ refers to non-secular terms at order $\mathcal{O}(\epsilon^1)$ in equation (2.8). The secular term $\propto \epsilon(t-\tilde{t})$ can now be deleted by a suitable choice of $P_{\tilde{t}}$. Indeed, decomposing $P_{\tilde{t}} = P_t + (t-\tilde{t})\partial P_{\epsilon t}/\partial t + o\Big((t-\tilde{t})\Big)$ in equation (2.13), one observes that – after a projection on ${}_b\langle -,\rho_A|$ – the secular term of order $\epsilon(t-\tilde{t})$ can be removed if P_t satisfies

$$\frac{\mathrm{d}P_t(\rho_A)}{\mathrm{d}t} = \epsilon\sum_{\rho'_A} \pi(\rho_A|\rho'_A)P_t(\rho'_A) - \pi(\rho'_A|\rho_A)P_t(\rho_A) \tag{2.14}$$

where one has introduced, similarly with notations of the previous section,

$${}_b\langle -,\rho'_A|\mathcal{W}_c\,|SS,\rho_A\rangle_b = \pi(\rho'_A|\rho_A) - \lambda(\rho_A)\delta_{\rho_A,\rho'_A}\,, \tag{2.15}$$

with $\rho'_A = \rho_A + \Delta N_A/V_A$, $\pi(\rho'_A|\rho_A)$ being the transition rate associated with the transition from ρ_A to ρ'_A ($\pi(\rho_A,\rho_A)=0$) and $\lambda(\rho_A) = \sum_{\rho'_A}\pi(\rho'_A|\rho_A)$, the escape rate.

Eventually, the final regularised solution reads then

$$\begin{aligned}|P_t\rangle = &\sum_{\rho_A} P_{\epsilon t}(\rho_A)|SS,\rho_A\rangle_b + \sum_{\rho_A} e^{t\mathcal{W}_b}|T_0,\rho_A\rangle_b \\ &+ \mathcal{O}(\epsilon)\,.\end{aligned} \tag{2.16}$$

where the probability distribution $P_\tau(\rho_A)$ obeys the coarse-grained master equation (2.14):

$$\frac{\mathrm{d}P_\tau}{\mathrm{d}\tau}(\rho_A) = \sum_{\rho'_A} \pi(\rho_A|\rho'_A)P_\tau(\rho'_A) - \pi(\rho'_A|\rho_A)P_\tau(\rho_A)\,, \tag{2.17}$$

with $\tau = \epsilon t$, the relevant slow time associated with the dynamics of the number of particles.

For large time compared to the relaxation time of the bulk dynamics, the stationary solution $\lim_{t\to\infty}|P_t\rangle = |P\rangle$ reads, for all configurations $\mathcal{C}$,

$$P(\mathcal{C}) = P(\rho_A|\bar{\rho})P_A(\mathcal{C}_A|\rho_A)P_B(\mathcal{C}_B|\rho_B) + \mathcal{O}(\epsilon)\,, \tag{2.18}$$

with $P(\rho_A|\bar{\rho})$ the stationary solution[2] of equation (2.17).

[2]The dependence with respect to the total density has been reintegrated to not forget that P describes the density ρ_A in A as well as in B, with $\rho_B = \gamma_B^{-1}(\bar{\rho} - \gamma_A\rho_A)$.

Expression of the coarse-grained transition rates. As we will very often consider coarse-grained transition rates $\pi(\rho'_A|\rho_A)$ in the following, we repeat here their expression with explicit notations:

$$\pi(\rho'_A|\rho_A) = \sum_{\substack{\mathcal{C}'_A \in \mathcal{E}^{V_A}_{\Delta N_A}(\rho_A) \\ \mathcal{C}'_B \in \mathcal{E}^{V_B}_{-\Delta N_A}(\rho_B)}} \sum_{\substack{\mathcal{C}_A \in \mathcal{E}^{V_A}_{0}(\rho_A) \\ \mathcal{C}_B \in \mathcal{E}^{V_B}_{0}(\rho_B)}} T_c(\mathcal{C}'_A, \mathcal{C}'_B|\mathcal{C}_A, \mathcal{C}_B)\, P_A(\mathcal{C}_A|\rho_A) P_B(\mathcal{C}_B|\rho_B)\,, \tag{2.19}$$

with $P_k(\mathcal{C}_k|\rho_k)$ the stationary density of the isolated system k.

2.3 Large deviations analysis of the density dynamics

The time-scale separation being settled, one is interested in the thermodynamic limit for which volumes and particle numbers tend to infinity, with fixed densities.

2.3.1 Volume dependence of the macroscopic transition rates at contact

Until now, all the expressions of the coarse-grained transition rates π, probability distribution P_t and so on have been computed – even if it has not been specified explicitly – at fixed volume V_A, V_B. Hence, let us first shed light on the volume dependence of the transition rates $\pi(\rho'_A|\rho_A)$ involved in the master equation ruling the dynamics of the densities (2.17). We will also take advantage of this clarification to write properly the explicit system B dependence of the quantities at stake.

$\pi(\rho'_A|\rho_A)$ corresponds to the transition rates associated with the following transition

$$\begin{aligned} \rho_A = \frac{N_A}{V_A} &\to \rho'_A = \frac{N_A + \Delta N_A}{V_A} \\ \rho_B = \frac{N_B}{V_B} &\to \rho'_B = \frac{N_B - \Delta N_A}{V_B}\,. \end{aligned} \tag{2.20}$$

In all this work we will naturally assume that the number of particles that can be exchanged per unit time (during a transition) is bounded and does not scale with the volume of the system. We will then call

$$\pi(\rho'_A|\rho_A) \equiv \nu(V)\varphi_V(\rho_A, \rho_B; \Delta N_A) \tag{2.21}$$

where we have explicitly introduced the ρ_B dependence as well as the volume V which refers to the potential volume dependence of the transition rate (according to notations introduced before, $V_A = \gamma_A V$ and $V_B = \gamma_B V$, with γ_A, γ_B that are hidden since they

are kept finite at the thermodynamic limit). The V-dependence of the transition rate is potentially twofold. The first contribution, encoded in the factor $\nu(V)$ corresponds to the contact area and how it grows as $V \to \infty$. The second which will have to be considered case by case may appear through the stationary probability distribution $P_k(\mathcal{C}_k|\rho_k)$ $(k = A, B)$ as a possible finite-size effect. If the number of sites that connect both systems is fixed, then φ_V is not proportional to V and $\nu(V) = \nu$. The remaining V-dependence in φ_V is expected to vanish as $V \to \infty$ so that $\lim_{V\to\infty} \varphi_V$ exists. In this case, the dynamics in large system size is slower than the one at small system size: this V dependence will have to be absorbed in the time scale. However, if the contact area grows with volumes, the frequency factor $\nu(V)$ is expected to be proportional to V^α, $\alpha \leqslant 1$ (for instance, if the contact is proportional to the external surface, $\alpha = d/2$, d being the space dimension), in addition to potential finite-size contributions. This V dependence will be discussed explicitly with specific systems in chapter 4 but we make the assumption here that beyond the factor $\nu(V)$, $\lim_{V\to\infty} \varphi_V$ is well defined.

2.3.2 Evolution equation of the large deviations function of densities

The study of thermodynamic limit $V \to \infty$ for a jump stochastic processes might remind one of the so-called expansion of the Master equation popularised by Van Kampen in his seminal book [Van Kampen, 1992]. Nevertheless, as stressed in the introduction, a thermodynamic analysis based on stochastic dynamics needs large deviations analysis that is not captured by the Van Kampen expansion (at least if one stops the expansion at a finite order). Even if we are not interested in rare events *per se*, the large deviations framework is the relevant one to study the dominant extensive contribution to the probability distribution of density ρ_A (and ρ_B), exactly as it is for the equilibrium statistical mechanics (see for instance [Touchette, 2009]). One should note that this large deviations analysis, on the same kind of Master equations considered by Van Kampen, was first considered – with a somewhat different emphasis – in [Kubo et al., 1973] (see also [Maes and Netočný, 2007]). Also, even if the work presented here as been developed independently, we should mention the recent study of Ge & Qian [Ge and Qian, 2017] which deals with the same kind of large deviations analysis in the context of chemical reactions.

The simplest way (even though not rigorous) to look at a large deviations scaling is to introduce the large deviations ansatz directly in the master equation (2.17). To treat systems A and B on the same footing, we introduce

$$P_t(\rho_A|\bar{\rho}) = P_t(\rho_A, \rho_B|\bar{\rho}) \asymp e^{-V\mathcal{I}_t(\rho_A,\rho_B|\bar{\rho})} , \tag{2.22}$$

where $\asymp$ refers to a logarithmic equivalence[3] for large $V = V_A + V_B$. It yields

$$V\frac{\mathrm{d}\mathcal{I}_t}{\mathrm{d}t}(\rho_A,\rho_B|\bar{\rho}) = \nu(V)\sum_{\Delta N_A}\varphi_V(\rho_A,\rho_B;\Delta N_A)\left[\exp\left\{\Delta N_A\left(\gamma_A^{-1}\frac{\partial\mathcal{I}_t}{\partial\rho_A}-\gamma_B^{-1}\frac{\partial\mathcal{I}_t}{\partial\rho_B}\right)\right\}-1\right] + \mathcal{O}(V^{-1})$$

After re-scaling the time t into $\nu(V)V^{-1}t$, one obtains at the lowest order in V the following equation over $\mathcal{I}_t$:

$$\frac{\mathrm{d}\mathcal{I}_t}{\mathrm{d}t}(\rho_A,\rho_B|\bar{\rho}) = \sum_{\Delta N_A}\varphi(\rho_A,\rho_B;\Delta N_A)\left[\exp\left\{\Delta N_A\left(\gamma_A^{-1}\frac{\partial\mathcal{I}_t}{\partial\rho_A}-\gamma_B^{-1}\frac{\partial\mathcal{I}_t}{\partial\rho_B}\right)\right\}-1\right], \tag{2.23}$$

with $\varphi = \lim_{V\to\infty}\varphi_V$. The latter equation generally bears the name of a Hamilton-Jacobi equation by analogy to the classical mechanics since the stationary large deviations function $\mathcal{I}(\rho_A,\rho_B|\bar{\rho})$ can be interpreted as the weight (also called action) of the most probable trajectory $\{\rho_A(s),\rho_B(s)\}_{s=0}^{s=t}$ starting at the stationary point (ρ_A^*,ρ_B^*) of the dynamics and ending at the desired point (ρ_A,ρ_B) at time t. We will briefly come back to this kind of trajectory/path analysis in the following (see section 2.4.4) but one can as of now consult [Maes and Netočný, 2007] for a short presentation.

The large deviations function allows one to have access to rare events *i.e.* to deviations of densities of order $\mathcal{O}(V^0)$. But it can also be seen as an extension of the law of large numbers as it gives the rate at which the stochastic variable ρ_A approaches its average (or formally, in other words, how the probability distribution $P(\rho_A|\bar{\rho})$ contracts into a Dirac measure centred around the average density). One can thus use it to characterise also the stationary state in a variational way since by definition the stationary state belongs to the set of the most probable values of the densities. According to (2.22), the latter can be seen as the set of points which correspond to minima of the large deviations function $\mathcal{I}(\rho_A,\rho_B|\bar{\rho})$. In the absence of first order phase transition, the large deviations function I is expected to be convex and to display only a single minimum characterised by the vanishing of the derivative of I [Ellis, 2007; Touchette, 2009].

Eventually, we mention that the derivation of the Hamilton-Jacobi equation for more than two systems in contact is available in appendix B.

***Notation*: implicit ρ_B dependence.** The introduction at this point of the explicit ρ_B-dependence allows one to see more clearly the dependence in the relative sizes of the systems as well as the parallel with the situation at equilibrium that we remind one

[3] Precisely, $\mathcal{I}_t = \lim_{V\to\infty}\ln(P_t)/V$.

of here very briefly. Indeed, at equilibrium, the large deviations function $\mathcal{I}$ is closely linked to the free energies of both systems, up to a temperature factor β, as already discussed in the general introduction (see equation (1.4)). One has

$$\mathcal{I}_{\rm eq}(\rho_A,\rho_B|\bar{\rho}) = \beta\gamma_A\left[f_A(\rho_A) - f_A(\rho_A^*)\right] + \beta\gamma_B\left[f_B(\rho_B) - f_B(\rho_B^*)\right] , \tag{2.24}$$

where f_k refers to the equilibrium free energies per unit of volume of system k and ρ_k^* the most probable density of system k (which corresponds to the average density). The most probable densities are fixed by the vanishing of the derivative of $\mathcal{I}$ which reads $f_A'(\rho_A^*) = f_B'(\rho_B^*)$ (or, in other words, that chemical potentials defined as the derivative of the free energies, are equal).

Nevertheless, in order to lighten notations, we will come back from now on to our former convention and omit the ρ_B dependence – which will be implicitly assumed through mass conservation – and simply write

$$I_t(\rho_A|\bar{\rho}) = \gamma_A^{-1}\mathcal{I}_t(\rho_A,\rho_B|\bar{\rho}) \tag{2.25}$$

This implies

$$I_t'(\rho_A|\bar{\rho}) = \gamma_A^{-1}\frac{\partial\mathcal{I}_t}{\partial\rho_A} - \gamma_B^{-1}\frac{\partial\mathcal{I}_t}{\partial\rho_B} , \tag{2.26}$$

where the $'$ symbol indicates a derivative with respect to ρ_A. In this way,

$$P_t(\rho_A|\bar{\rho}) \asymp e^{-V_A I_t(\rho_A|\bar{\rho})} . \tag{2.27}$$

With this new notation, the Hamilton-Jacobi equation (2.23) simply reads

$$\frac{\mathrm{d}I_t}{\mathrm{d}t}(\rho_A|\bar{\rho}) = \sum_{\Delta N_A\neq 0}\varphi(\rho_A;\Delta N_A)\left[e^{\Delta N_A I_t'(\rho_A|\bar{\rho})} - 1\right] . \tag{2.28}$$

The stationary solution $I = \lim_{t\to\infty} I_t$ thus obeys

$$\sum_{\Delta N_A\neq 0}\varphi(\rho_A;\Delta N_A)\left[e^{\Delta N_A I'(\rho_A|\bar{\rho})} - 1\right] = 0 . \tag{2.29}$$

This translation being made, we will come back to the explicit notation $\mathcal{I}(\rho_A,\rho_B|\bar{\rho})$ each time we will need to take into account the explicit dependence in system B.

2.3.3 Stationary state: link between the vanishing of $I(\rho_A|\bar{\rho})$ and the current $J(\rho_A)$

One can wonder naturally why we have not mentioned the current of particles until now. Indeed, the stationary state of the system at the average level is very natu-

rally defined by the vanishing of the particle current $J(\rho_A^*) = 0$ through the contact. The latter deterministic current is defined in the infinite volume limit through the deterministic relaxation equation of the density ρ_A (see [Van Kampen, 1992, chapter X])

$$\frac{\mathrm{d}\rho_A(t)}{\mathrm{d}t} = J(\rho_A(t)) = \sum_{\Delta N_A} \varphi(\rho_A, \Delta N_A)\, \Delta N_A \,. \tag{2.30}$$

Of course, the description of the stationary state as the minimum of a large deviations function ρ_A^* must agree with the vanishing of the current at the same density ρ_A^*. Formally, one must have

$$I'(\rho_A^*|\bar{\rho}) = 0 \qquad \Longleftrightarrow \qquad J(\rho_A^*) = 0$$

This relationship is known for a long time (see [Ge and Qian, 2017] for a recent account) but we show it here succintly for completness. To prove this equivalence, we can use the stationary Hamilton-Jacobi equation (2.29) evaluated along the deterministic path obeying (2.30). Indeed, for $\rho_A(t)$ solution of (2.30), one has

$$\begin{aligned} \frac{\mathrm{d}I(\rho_A(t)|\bar{\rho})}{\mathrm{d}t} &= J(\rho_A(t))I'(\rho_A(t)|\bar{\rho}) \\ &= \sum_{\Delta N_A \neq 0} \varphi(\rho_A(t), \Delta N_A)\Delta N_A I'(\rho_A(t)|\bar{\rho})\,. \end{aligned} \tag{2.31}$$

One should stress that $I(\rho_A(t)) \neq I_t(\rho_A)$ here. $I(\rho_A)$ is the stationary large deviations function, solution of (2.29). But since the inequality $e^x - 1 \geqslant x$ holds for all x with equality only when $x = 0$, $\Delta N_A I'(\rho_A(t)|\bar{\rho}) \leqslant e^{\Delta N_A I'(\rho_A(t)|\bar{\rho})} - 1$, the last equality in (2.31) yields

$$\frac{\mathrm{d}I(\rho_A(t)|\bar{\rho})}{\mathrm{d}t} \leqslant \sum_{\Delta N_A} \varphi(\rho_A(t), \Delta N_A) \left(e^{\Delta N_A I'(\rho_A(t)|\bar{\rho})} - 1\right) = 0 \tag{2.32}$$

since the last term is the left-hand side term of the Hamilton-Jacobi equation (2.29). As a corollary, we have demonstrated that the stationary large deviations function $I(\rho_A|\bar{\rho})$ plays the role of a *Lyapunov function* for the macroscopic dynamics. The equality stands if and only if $I'(\rho_A(t)|\bar{\rho}) = 0$. Thus, if $J(\rho_A) = 0$ then $\mathrm{d}I(\rho_A(t)|\bar{\rho})/\mathrm{d}t = 0$ and the system is at the minimum of I characterised by $I' = 0$.

Conversely, taking the derivative with respect to ρ_A of the stationary Hamilton-Jacobi equation (2.29) leads to

$$\begin{aligned} 0 = \sum_{\Delta N_A} \frac{\mathrm{d}\varphi}{\mathrm{d}\rho_A}(\rho_A, \Delta N_A) \left(e^{\Delta N_A I'(\rho_A|\bar{\rho})} - 1\right) \\ + I''(\rho_A|\bar{\rho}) \sum_{\Delta N_A} \varphi(\rho_A, \Delta N_A)\, \Delta N_A\, e^{\Delta N_A I'(\rho_A|\bar{\rho})} \,. \end{aligned} \tag{2.33}$$

At the stationary point ρ_A^* for which $I'(\rho_A^*|\bar{\rho}) = 0$, the last equation reads

$$J(\rho_A^*)I''(\rho_A^*) = 0 \tag{2.34}$$

Then, if $I''(\rho_A^*|\bar{\rho}) \neq 0$, one sees that $I'(\rho_A^*|\bar{\rho}) = 0$ implies that $J(\rho_A^*) = 0$. We recognise here a stability condition needed to assert the vanishing of the current. In fact, one even needs $I'' \geqslant 0$ in order to guarantee the convexity of the stationary large deviations function.

Our purpose in the remaining part of this chapter and in the next one is to study the stationary properties of our contact set-up through this large deviations rate function $\mathcal{I} = \lim_{t\to\infty} \mathcal{I}_t$. A central issue that will be the core of the second chapter is to know when the large deviations function $\mathcal{I}$ is additive as in the equilibrium situation (2.24) and if this allows one to define proper chemical potentials. The remaining part of the present chapter is devoted to the different available ways to solve the Hamilton-Jacobi equation (2.29) and then to obtain the stationary large deviations function $I(\rho_A|\bar{\rho})$ that enables one to predict the stationary densities as well as their fluctuations when the volume is large but not infinite.

2.4 Macroscopic detailed balance

2.4.1 Formal approach

To start at a formal level, one can notice that the Hamilton-Jacobi equation (2.29) can be easily solved if each term under the rearranged sum cancels one by one for any ρ_A:

$$\begin{aligned}\sum_{\Delta N_A \neq 0} \varphi(\rho_A, \Delta N_A) \left[e^{\Delta N_A I'(\rho_A|\bar{\rho})} - 1\right] \\ = \sum_{\Delta N_A \neq 0} \underbrace{\left[\varphi(\rho_A, \Delta N_A) e^{\Delta N_A I'(\rho_A|\bar{\rho})} - \varphi(\rho_A, -\Delta N_A)\right]}_{=0 \text{ if detailed balance}} = 0 \,.\end{aligned}$$

One gets a generalised detailed balance condition, that we will call *macroscopic detailed balance* in the following. It reads

$$I'(\rho_A|\bar{\rho}) = \frac{1}{\Delta N_A} \ln \frac{\varphi(\rho_A, -\Delta N_A)}{\varphi(\rho_A, \Delta N_A)} \,. \tag{2.35}$$

Importantly, one can note that for most lattice gas models – that deal with the dynamics of particles on lattice in continuous time – (and potentially more realistic systems) only one particle can be exchanged per unit time. Thus $\Delta N_A = \pm 1$ at most and one can easily check that the macroscopic detailed balance condition is always

verified. However, for more general situations where $\max(\Delta N_A) \geq 2$ (or even when ΔN_A is continuous), this condition is not at all guaranteed. In the remaining part of this section we discuss on a physical ground how one can see whether this condition holds or not.

In subsections 2.4.2, 2.4.3 and 2.4.4, our purpose is to discuss what this condition means at a more physical level. We will in particular suggest experimental way to see whether it does hold or not.

2.4.2 Time-reversal symmetry and adjoint process

Without surprise, one can easily see that this macroscopic detailed balance condition is reminiscent of a global time-reversal symmetry. Indeed, the usual detailed balance is another way to name the equality, for all trajectories, of the probability to observe a certain trajectory with the probability to observe the exact time-reversed trajectory. In particular, the time-reversal symmetry for a two-time infinitesimal trajectory (on the time interval $[t, t + \mathrm{d}t]$) of the density $\rho_A(t)$ reads

$$\begin{aligned} P(\rho'_A, t + \mathrm{d}t; \rho_A, t) &= P(\rho_A, t + \mathrm{d}t; \rho'_A, t) \\ \pi(\rho'_A|\rho_A)P(\rho_A|\bar{\rho}) &= \pi(\rho_A|\rho'_A)P(\rho'_A|\bar{\rho})\,. \end{aligned} \tag{2.36}$$

Thus, if $P(\rho_A|\bar{\rho}) \sim e^{-V_A I(\rho_A|\bar{\rho})}$, and recalling that $\rho'_A = \rho_A + \Delta N_A/V_A$, one gets at leading order in V_A the macroscopic detailed balance (2.35).

Now that the importance of this time-reversal symmetry has been recognised, we would like to investigate in more details the structure of the coarse-grained transition rates as well as some of its consequences, in particular fluctuations and relaxation paths (that will be defined henceforth). Several new notations will be introduced in the following.

In order to analyse the time-reversibility of the dynamics and its consequences on the large deviations function, it is helpful to introduce what one can call the corresponding *adjoint* process. Writing $\omega = \{\rho_A(t)\}_{0\leq t\leq T}$ a trajectory, $\mathcal{R}\omega = \{\rho_A(T - t)\}_{0\leq t\leq T}$ its time-reversed counterpart and $\mathcal{P}_P(\omega)$ the probability density to observe the trajectory ω along the bare process with the stationary distribution $P(\rho_A|\bar{\rho})$ as the initial distribution, the adjoint process can be characterised by its trajectory probability density $\mathcal{P}^\dagger_P(\omega)$ which is defined to be

$$\mathcal{P}^\dagger_P(\omega) = \mathcal{P}_P(\mathcal{R}\omega)\,. \tag{2.37}$$

Thus, this new stochastic process is simply built from the sampling of the time-reversed trajectory of the bare process. By definition, the dynamics is time-reversible if $\mathcal{P}^\dagger_P(\omega) = \mathcal{P}_P(\omega)$, *i.e.* if the adjoint and the bare process are the same. The intro-

duction of the adjoint process may appear quite formal but the reader can just see it as a way to compare the probability of trajectories with respect to their time-reversed counterparts.

For a two-time trajectory, equation (2.37) gives

$$\varphi_V^\dagger(\rho_A, \Delta N_A) = \varphi_V(\rho_A + \tfrac{\Delta N_A}{V_A}, -\Delta N_A) \times \frac{P(\rho_A + \frac{\Delta N_A}{V_A}|\bar{\rho})}{P(\rho_A|\bar{\rho})} .$$

The adjoint process is defined by the transition rates $\varphi_V^\dagger$ given by equation (2.38) and has the same stationary distribution as the bare process.

That being said, it is simpler to discuss the meaning of the adjoint process and to express the macroscopic detailed balance condition by decomposing transition rates in terms of force and activity [Maes et al., 2008; Maes and Netočný, 2008]. Furthermore, this decomposition will be extensively used in the next chapter, when we will discuss the second law 3.3

2.4.3 Analysis in terms of force and activity

Each transition rate $\varphi_V(\rho_A, \Delta N_A)$ can indeed be decomposed as

$$\varphi_V(\rho_A, \Delta N_A) = a_V(\rho_A, \Delta N_A) e^{\frac{1}{2} F_V(\rho_A, \Delta N_A)} \tag{2.38}$$

where

$$\begin{aligned} F_V(\rho_A, \Delta N_A) &= \ln \frac{\varphi_V(\rho_A, \Delta N_A)}{\varphi_V(\rho_A + \frac{\Delta N_A}{V_A}, -\Delta N_A)} \\ a_V(\rho_A, \Delta N_A) &= \sqrt{\varphi_V(\rho_A, \Delta N_A)\varphi_V(\rho_A + \tfrac{\Delta N_A}{V_A}, -\Delta N_A)} . \end{aligned} \tag{2.39}$$

$F_V(\rho_A, \Delta N_A)$ is interpreted as a *bias* or a *generalised force* and is anti-symmetric with respect to the transition $\rho_A \to \rho_A + \Delta N_A/V_A$: $F_V(\rho_A, \Delta N_A) = -F_V(\rho_A + \frac{\Delta N_A}{V_A}, -\Delta N_A)$. As for $a_V(\rho_A, \Delta N_A) = a_V(\rho_A + \frac{\Delta N_A}{V_A}, -\Delta N_A)$, it is generally refered as an *activity*. One should stress that this decomposition is just a more physical – and practical – rewriting of the coarse-grained transition rates φ_V and has nothing to do with the adjoint process for the moment.

In the thermodynamic limit, when $V \to \infty$, expressions converge in

$$\begin{aligned} F(\rho_A, \Delta N_A) &= \ln \frac{\varphi(\rho_A, \Delta N_A)}{\varphi(\rho_A, -\Delta N_A)} = -F(\rho_A, -\Delta N_A) \\ a(\rho_A, \Delta N_A) &= \sqrt{\varphi(\rho_A, \Delta N_A)\varphi(\rho_A, -\Delta N_A)} = a(\rho_A, -\Delta N_A) . \end{aligned} \tag{2.40}$$

The exact same decomposition can be done on the adjoint process defined by its

transition rates $\pi_V^\dagger$. Comparing π_V and $\pi_V^\dagger$, one verifies that

$$\begin{aligned} F_V^\dagger(\rho_A, \Delta N_A) &= -F_V(\rho_A, \Delta N_A) + 2\ln \frac{P(\rho_A + \frac{\Delta N_A}{V_A})}{P(\rho_A)} \\ a_V^\dagger(\rho_A, \Delta N_A) &= a_V(\rho_A, \Delta N_A)\,, \end{aligned} \tag{2.41}$$

which, at large deviations level, leads to

$$\begin{aligned} F^\dagger(\rho_A, \Delta N_A) &= -F(\rho_A, \Delta N_A) - 2I'(\rho_A|\bar{\rho}) \\ a^\dagger(\rho_A, \Delta N_A) &= a(\rho_A, \Delta N_A)\,, \end{aligned} \tag{2.42}$$

One can thus see the interest of all this rewriting of transition rates. Now, the asymmetry between the bare and the adjoint processes can be simply measured through the difference between F_V and $F_V^\dagger$. To measure their distance, it is thus interesting to introduce a symmetric and an anti-symmetric forces

$$\begin{aligned} F_V^{(S)}(\rho_A, \Delta N_A) &= \frac{F_V(\rho_A, \Delta N_A) + F_V^\dagger(\rho_A, \Delta N_A)}{2} = \ln \frac{P(\rho_A + \frac{\Delta N_A}{V_A})}{P(\rho_A)} \\ &\xrightarrow[V\to\infty]{} \quad F^{(S)}(\rho_A, \Delta N_A) = -I'(\rho_A|\bar{\rho})\Delta N_A \\ F_V^{(A)}(\rho_A, \Delta N_A) &= \frac{F_V(\rho_A, \Delta N_A) - F_V^\dagger(\rho_A, \Delta N_A)}{2} \\ &= F_V(\rho_A, \Delta N_A) - \ln \frac{P(\rho_A + \frac{\Delta N_A}{V_A})}{P(\rho_A)} \\ &\xrightarrow[V\to\infty]{} \quad F^{(A)}(\rho_A, \Delta N_A) = F(\rho_A, \Delta N_A) + I'(\rho_A|\bar{\rho})\Delta N_A\,. \end{aligned} \tag{2.43}$$

This kind of decomposition are not new in the literature. What has been expounded above was in fact inspired by [Kurchan, 1998] or more recently by [Bertini et al., 2015*a*] in the context of the Macroscopic Fluctuation Theory which deals with the diffusive dynamics of a conserved field quantity. It is sometimes referred to as the transverse decomposition in the context of small noise limit of diffusive systems [Bouchet et al., 2016; Graham, 1995]. Nevertheless, to the knowledge of the author, this decomposition in terms of symmetric and anti-symmetric forces is more original in the context of large deviations of Poisson processes. One should however note the very recent work of [Jack et al., 2017; Kaiser et al., 2018] which discusses a very similar decomposition in the context of Markov chains, even though with a different emphasis.

Interpretation of the macroscopic detailed balance in terms of force. Along with this definitions, one can notice that the formal macroscopic detailed balance (2.35) turns into $F^{(A)}(\rho_A, \Delta N_A) = 0$, since, by definition of $F(\rho_A, \Delta N_A)$ (2.40), the macroscopic detailed balance (2.35) reads $I'(\rho_A|\bar{\rho})\Delta N_A = -F(\rho_A, \Delta N_A)$. In this case,

the derivative of the large deviations function of the densities simply reads $I'(\rho_A) = -\Delta N_A^{-1} F(\rho_A, \Delta N_A)$.

Until now, we just have recognised that the formal detailed balance condition (2.35) was simply the translation at a large deviations level of a time-reversal symmetry of the underlying process. As a consequence, we have introduced – in line with the studies on macroscopic fluctuation theory [Bertini et al., 2015*a*] – an equivalent but more physical decomposition of transition rates, more suitable to express the macroscopic detailed balance condition. As we will see, the above formulation will be useful for the thermodynamic investigations that will be performed in the next chapter.

However, until now, the only way one has to see if macroscopic detailed balance holds is to check directly, knowing the form of the transition rates $\varphi(\rho_A, \Delta N_A)$, if $-\Delta N_A^{-1} F(\rho_A, \Delta N_A)$ is independent of ΔN_A and if the resulting function of ρ_A is a well-defined derivative of a large deviations function I (it should always increase to get a convex large deviations function I for instance). Since the measure of the transition rates is not easy in realistic systems, we would like to lay out in the following another way to assess the macroscopic detailed balance applicable at large deviations level.

2.4.4 Large deviations analysis of density trajectories

When the volumes increase, fluctuations of the densities are naturally tightened. If one starts at a density $\rho_A(0) = \rho_A \neq \rho_A^*$ (ρ_A^* being the most probable density) and lets the system evolves for a time t, it turns out that the probability to observe a certain trajectory ending at $\rho_A(t) = \rho_A^*$ condenses around the most probable trajectory which simply follows the deterministic relaxation dynamics. By contrast, the time-reversed trajectory starting at the most probable density ρ_A^* and ending at a point ρ_A can only be realised at the expense of a noise contribution. However its probability to be observed condenses as well around a certain trajectory which follows a so-called fluctuation dynamics (see for instance the introduction of [Bouchet et al., 2016]). When detailed balance holds, it will be shown in the following that both – relaxation and fluctuation – most probable trajectories are the same, albeit travelling in opposite direction. Conversely, when macroscopic detailed balance is broken, both trajectories differ.

Although it may be delicate to measure such fluctuation path in realistic systems (since such fluctuations are rare at the thermodynamic limit), such an effect can be considered as a signature of the breaking of detailed balance that can probably be more easily observed than the non-linearity in the amount of particle exchanged in the force (2.40).

The probability density $\mathcal{P}_{\rho_A}(\omega)$ of a trajectory starting at a density ρ_A can be written in the form of a Martin-Siggia-Rose-Janssen-De Dominicis (MSRJD) path

integral (see [De Dominicis, 1978; Janssen, 1976] in the context of diffusive systems). Path integrals for Poisson processes have often been considered in line with the Doi-Peliti formalism [Peliti, 1985; Weber and Frey, 2017]. We do not want to enter into these discussions here and we will adopt a formal approach advocated in [Andreanov et al., 2006; Lefevre and Biroli, 2007; Thompson et al., 2011] for Poisson processes (with the slight difference that ours is treated at large deviations level):

$$\mathcal{P}_{\rho_A}(\omega) \asymp \int \mathcal{D}\theta \, e^{-V_A \int_0^t \mathrm{d}s \, [\theta(s)\dot{\rho}_A(s) - H(\rho_A(s),\theta(s))]} , \tag{2.44}$$

where

$$H(\rho_A, \theta) = \sum_{\Delta N_A} \varphi(\rho_A, \Delta N_A) \left(e^{\theta \Delta N_A} - 1 \right) . \tag{2.45}$$

The term $S(\omega) = \int_0^t \mathrm{d}s \, [\theta(s)\dot{\rho}_A(s) - H(\rho_A(s), \theta(s))]$ in the exponential in (2.44) is generally referred to as the action of the path ω in the statistical physics literature [Andreanov et al., 2006; Bouchet et al., 2016; Cardy, 1999; Freidlin and Wentzell, 1998; Lefevre and Biroli, 2007; Peliti, 1985], by analogy with analytical mechanics and with its use in Feynman's quantum path integral. Pursuing the mechanical analogy, the function H refers to the Hamiltonian of the stochastic process [Andreanov et al., 2006; Lefevre and Biroli, 2007]. The presence of an exponential of the response function $\theta(s)$ in the action is a signature of the underlying Poisson process. By contrast, the classical gaussian noise path integral related to diffusive processes only involves terms up to quadratic order in the response function $\theta(s)$.

Let us now consider the probability to reach a density ρ'_A at large time t, knowing that one starts at ρ_A at time 0. This conditional probability reads

$$P(\rho'_A, t | \rho_A, 0) = \int \mathcal{D}\rho_A \mathcal{P}_{\rho_A}(\omega) \delta \left(\omega(t) - \rho'_A \right) . \tag{2.46}$$

At the thermodynamic limit, only trajectories following the so-called instanton equations (which minimise the action) matters at the leading order in the volume V [Bertini et al., 2015*a*; Bouchet et al., 2016; Freidlin and Wentzell, 1998; Tailleur et al., 2007, 2008]. They are formally the same as the Hamilton equations and read

$$\begin{aligned} \frac{\mathrm{d}\rho_A}{\mathrm{d}t} &= \frac{\partial H(\rho_A(t), \theta(t))}{\partial \theta} \\ &= \sum_{\Delta N_A} \Delta N_A \varphi(\rho_A(t), \Delta N_A) e^{\theta(t) \Delta N_A} \end{aligned} \tag{2.47}$$

$$\begin{aligned} \frac{\mathrm{d}\theta}{\mathrm{d}t} &= -\frac{\partial H(\rho_A(t), \theta(t))}{\partial \rho_A} \\ &= \sum_{\Delta N_A} \frac{\partial \varphi(\rho_A(t), \Delta N_A)}{\partial \rho_A} \left(e^{\theta(t) \Delta N_A} - 1 \right) \end{aligned} \tag{2.48}$$

which must be supplemented by appropriate boundary conditions, ρ_A at time 0 and ρ'_A at time t. If the final point ρ'_A is equal to the most probable one ρ^*_A and the initial density ρ_A is a less probable density, one can show that the associated instanton trajectory is simply a relaxation dynamics for which the response field $\theta(t)$ is uniformly vanishing. Intuitively, $\theta(s)$ can be interpreted as a deterministic force that skews the dynamics[4] in order to make the targeted trajectory the most probable in this biased dynamics whereas this trajectory may be rare in the natural, unbiased, dynamics. So to speak, the presence of $\theta(t)$ indicates the need of a work from the noise (physically performed by a thermostat) to explore the targeted region in phase space. With this interpretation in mind, one can understand quite intuitively that the relaxation dynamics (which does not need noise in a sense) is realised for $\theta(t) = 0$.

In the opposite case, to realise the time-reversed path that leads to $\rho_A \neq \rho^*_A$ starting from the stationary state of the system (*i.e.* the most probable density ρ^*_A), the system needs work (or rather heat) from the noise. Since this trajectory starts at the final point and ends at the initial point of a relaxation dynamics, it should belong to the set of time-reversed trajectories that realise the relaxation. The latter trajectories correspond to those of the adjoint dynamics and it can be shown [Bertini et al., 2015*a*; Bouchet et al., 2016] that the most probable trajectory that connects ρ^*_A to ρ_A matches the most probable trajectory of the adjoint dynamics which corresponds to the bare dynamics biased by $\theta(t) = I'(\rho_A|\bar{\rho})$ for all t.

According to the Hamilton equations (2.47), the relaxation dynamics thus reads

$$\begin{aligned} \frac{\mathrm{d}\rho_A}{\mathrm{d}t}(t) = J(\rho_A(t)) &= \frac{\partial H}{\partial \theta}(\rho_A(t), 0) \\ &= \sum_{\Delta N_A} \Delta N_A \varphi(\rho_A(t), \Delta N_A) \ , \end{aligned} \tag{2.49}$$

with $\rho_A(0) = \rho_A \neq \rho^*_A$ and $\rho_A(t) = \rho^*_A$. As for the fluctuation dynamics, it obeys the equation

$$\begin{aligned} \frac{\mathrm{d}\rho_A}{\mathrm{d}t}(t) = J^\dagger(\rho_A(t)) &= \frac{\partial H}{\partial \theta}(\rho_A(t), I'(\rho_A)) \\ &= \sum_{\Delta N_A} \Delta N_A \varphi^\dagger(\rho_A(t), \Delta N_A) \ , \end{aligned} \tag{2.50}$$

with $\rho_A(0) = \rho^*_A$ and $\rho_A(t) = \rho_A \neq \rho^*_A$.

If macroscopic detailed balance holds, $J = J^\dagger$ and one can see that the relaxation path and the fluctuation path are the same, modulo time-reversal. However, when they are different, *i.e.* when macroscopic detailed balance does not hold, the paths are different. Even if the observation of such fluctuations is certainly difficult in real experiment, this symmetry – or its absence – should be observed if resolution and data

[4] Formally it is a Lagrange multiplier.

amount are sufficient enough. As shown in the appendix A, the current can be also expressed in terms of symmetric and anti-symmetric forces. The vanishing of $F^{(A)}$ leads to the equalisation of J and $J^\dagger$.

Summary of the conditions to get the macroscopic detailed balance. The macroscopic detailed balance condition (2.35) is thus related to the time-reversibility of the dynamics at a large deviations level. Such time-reversibility can be observed theoretically and, possibly experimentally, at several equivalent but different levels

- The vanishing of the anti-symmetric force of the coarse-grained transition rates[5]: $F^{(A)} = 0$.
- The time-reversal symmetry of the relaxation and the fluctuation paths dynamics.

2.4.5 Relationship with microscopic detailed balance

As already mentioned at the end of section 2.2, one should notice that the macroscopic detailed balance relation can *a priori* hold without requiring that the microscopic, local, detailed balance holds as well. Indeed, the ratio between the probability to observe a transition $\mathcal{C} = (\mathcal{C}_A, \mathcal{C}_B) \to \mathcal{C}' = (\mathcal{C}'_A, \mathcal{C}'_B)$ involving an exchange of particle between A and B, and its time-reversal counterpart reads

$$\lim_{\mathrm{d}t\to 0} \frac{P(\mathcal{C}', t+\mathrm{d}t; \mathcal{C}, t)}{P(\mathcal{C}, t+\mathrm{d}t; \mathcal{C}', t)} = \frac{P(\mathcal{C})T_c(\mathcal{C}'|\mathcal{C})}{P(\mathcal{C}')T_c(\mathcal{C}|\mathcal{C}')} \neq 1 \tag{2.51}$$

since $P(\mathcal{C}) \neq P_{eq}(\mathcal{C})$ in general.

Of course, if the probabilities to observe microscopic transitions involving a positive transfer of particles from A to B is always greater than those to transfer of particles from B to A, and such that this is the case for any densities allowed by the constraints (hard repulsion between particles for instance), it will happen a net transfer from A to B until the system reaches the bound enforced by the constraints, if any. Otherwise, even with a net circulation (*i.e.* a non-vanishing current) between the microscopic configurations at contact, it is perfectly possible to obtain a balance of densities

These remarks are here to emphasise that microscopic and macroscopic detailed balance are only partially related and that the first can be broken without breaking the second. A detailed study of these loops of configurations should be performed in order to assess if indeed a macroscopic detailed balance holds or not but it seems to be very difficult to establish a general result, for a general contact dynamics. The only statement that can be certain is the propagation of microscopic detailed balance to the macroscopic level: this is nothing but the equilibrium situation.

[5]It is shown in appendix A that $F^{(A)}$ is related to the so-called house-keeping entropy production.

2.5 Breaking of macroscopic detailed balance: perturbation expansion

When macroscopic detailed balance does not hold, one has to come back to the complete Hamilton-Jacobi equation (2.29) whose solution is $I(\rho_A|\bar{\rho})$. In our setting we are focused on exchanges of particles, that is a discrete quantity. One has seen in section 2.4 that when only *one* particle can be exchanged, the dynamics necessary obeys macroscopic detailed balance. But if one can exchange more than one particle at a time by some participation mechanism at contact, macroscopic detailed balance may not hold. This is also the case when the exchanged (conserved) quantity is continuous, like volume for instance. We will see explicit examples in chapter 4.

For convenience, we use in this section the Hamilton-Jacobi equation formulated in terms of forces and activity (see section 2.4.3 and equation (2.55) below). In the case where one can only exchange two particles at most ($\Delta N_A = \pm 1, \pm 2$), the Hamilton-Jacobi equation is a polynomial equation in $e^{I'(\rho_A|\bar{\rho})}$ of order 4 whose solution is already not simple. Beyond, for more than two particles exchanged and generally for a continuous quantity, there is no general way to solve exactly the Hamilton-Jacobi equation. One must then perform a perturbation expansion around some known reference solution, generally taken to be a solution verifying macroscopic detailed balance. Such a detailed balance solution always exists, at least in our set up: the equilibrium situation plays this role.

2.5.1 Perturbative expansion

Our following perturbation expansion is greatly inspired by a discussion performed – with much more details – for diffusive systems in the weak noise limit in the recent article [Bouchet et al., 2016]. Our rigour requirements are much weaker and we will stay at a formal level. More details that are directly importable from the diffusive framework can be found in this article [Bouchet et al., 2016].

We start with a description of our notations. We call ξ the parameter which characterises the "distance" between the solution $I^{(\mathrm{DB})}(\rho_A) = I^{(0)}(\rho_A)$ (we omit the $\bar{\rho}$-dependence here, to lighten notations) that verifies the macroscopic detailed balance and the one we are looking for, $I(\rho_A)$. We set

$$I(\rho_A) = \sum_{n\geqslant 0} \xi^n \, I^{(n)}(\rho_A) \tag{2.52}$$

$$F(\rho_A, \Delta N_A) = \sum_{n\geqslant 0} \xi^n \, F^{(n)}(\rho_A, \Delta N_A) \tag{2.53}$$

$$a(\rho_A, \Delta N_A) = \sum_{n\geqslant 0} \xi^n \, a^{(n)}(\rho_A, \Delta N_A) \tag{2.54}$$

where $F^{(0)}(\rho_A, \Delta N_A) = -\Delta N_A I'(\rho_A)$ according to macroscopic detailed balance.

Since we would like to perform this perturbation expansion in terms of F, a and $I(\rho_A)$ – which happens to be easier to handle –, we write here the Hamilton-Jacobi equation (2.23) in terms of the latter quantities:

$$\sum_{\Delta N_A>0} \sinh\left(I'(\rho_A)\Delta N_A\right) a(\rho_A, \Delta N_A) \sinh\left(F(\rho_A, \Delta N_A) + I'(\rho_A)\Delta N_A\right) = 0\,. \tag{2.55}$$

Performing the expansion order by order gives

- $\mathcal{O}(\xi^0)$:
$$I^{(0)\prime}(\rho_A) = -\frac{1}{\Delta N_A} F^{(0)}(\rho_A, \Delta N_A) = F^{(0)}(\rho_A, -1)\,, \tag{2.56}$$
according to detailed balance.

- $\mathcal{O}(\xi^1)$:
$$\begin{aligned} &I^{(1)\prime}(\rho_A) J^{(0)}(\rho_A) \\ &\quad = -\sum_{\Delta N_A>0} a^{(0)}(\rho_A, \Delta N_A) \sinh\left(I^{(0)\prime}(\rho_A)\Delta N_A\right) F^{(1)}(\rho_A, \Delta N_A)\,, \end{aligned} \tag{2.57}$$
with $J^{(0)}(\rho_A) = 2\sum_{\Delta N_A} \Delta N_A\, a^{(0)}(\rho_A, \Delta N_A) \sinh(F^{(0)}(\rho_A, \Delta N_A))$, the macroscopic current of the dynamics at order $\mathcal{O}(\xi^0)$.

- $\mathcal{O}(\xi^2)$:
$$\begin{aligned} &I^{(2)\prime}(\rho_A) J^{(0)}(\rho_A) = \\ &\quad -\sum_{\Delta N_A>0} a^{(0)}(\rho_A, \Delta N_A) \sinh\left(I^{(0)\prime}(\rho_A)\Delta N_A\right) F^{(2)}(\rho_A, \Delta N_A) \\ &\quad -\sum_{\Delta N_A>0} \left(F^{(1)}(\rho_A, \Delta N_A) + I^{(1)\prime}(\rho_A)\Delta N_A\right) \\ &\qquad \times \Big[a^{(0)}(\rho_A, \Delta N_A) \cosh\left(I^{(0)\prime}(\rho_A)\Delta N_A\right) I^{(1)\prime}(\rho_A)\Delta N_A \\ &\qquad\quad + a^{(1)}(\rho_A, \Delta N_A) \sinh\left(I^{(0)\prime}\Delta N_A\right)\Big] \end{aligned} \tag{2.58}$$

- $\mathcal{O}(\xi^3)$: ...

One notices that the perturbation expansion expresses itself as

$$I^{(k)\prime}(\rho_A) J^{(0)}(\rho_A) = \mathcal{F}^{(k)}\left[I^{(0)}, I^{(1)}, \ldots, I^{(k-1)}\right](\rho_A(t)) \qquad k \geqslant 1\,. \tag{2.59}$$

which allows one to compute $I^{(k)}$ iteratively by integrating $I^{(k)\prime}$ along the fluctuation paths of the reference dynamics (for $\xi = 0$) since

$$\mathrm{d}I^{(k)}(\rho_A(t)) = I^{(k)\prime}(\rho_A(t)) J^{\dagger\,(0)}(\rho_A(t))\mathrm{d}t$$

for $\rho_A(t)$ a solution of $\dot{\rho}_A = J^{\dagger\,(0)}(\rho_A(t))$ and because $J^{\dagger\,(0)}(\rho_A) = J^{(0)}(\rho_A)$ when detailed balance holds. Performing the integration along the fluctuating path starting from the stationary point $\rho_A^{*(0)}$ at $t = 0$ of the reference dynamics and ending at a point ρ_A at $t \to \infty$, one obtains

$$I^{(k)}(\rho_A) = C^{(k)} + \int_0^\infty \mathrm{d}t\, \mathcal{F}^{(k)}\left[I^{(0)}, \ldots, I^{(k-1)}\right](\rho_A(t))\,, \tag{2.60}$$

where $C^{(k)} = I^{(k)}(\rho_A^{*(0)})$ is an unknown constant to be determined. A simple way to compute this constant is to remember that the stationary point $\rho_A^{*(\xi)}$ of the perturbed dynamics verifies $I^{(\xi)}(\rho_A^{*(\xi)}) = 0$. The stationary point $\rho_A^{*(\xi)}$ itself can be computed by looking for the stationary solution of the macroscopic dynamics

$$J^{(\xi)}(\rho_A^{*(\xi)}) = 0\,, \tag{2.61}$$

which allows one to look for $\rho_A^{*(\xi)}$ as $\rho_A^{*(\xi)} = \sum_{n\geqslant 0} \xi^n \rho_A^{*(n)}$. Then, Taylor expanding $I^{(\xi)}(\rho_A^{*(\xi)}) = 0$ allows us to express $C^{(k)} = \mathcal{I}_{\mathrm{SS}}^{(k)}(\rho_A^{*(0)})$ as function of $\rho_A^{*(0)}$, the coefficients $\rho_A^{*(n)}$ of the Taylor expansion of $\rho_A^{*(\xi)}$, the functions $I^{(n)}(\rho_A)$ and their derivatives for $n < k$.

2.5.2 Conclusion on this perturbation expansion

Such formal expansion have been sketched here to show how one can try to solve the general Hamilton-Jacobi equation in case of the dynamics of the density ρ_A would not obey detailed balance. We will use the first order of this expansion in chapter 3 when we will discuss the additivity property of the large deviations function I when the latter does not verify macroscopic detailed balance.

CHAPTER 3

Additivity property of the large deviations function

The purpose of this whole chapter is to address the issue of the additivity of the large deviations function $I(\rho_A|\bar{\rho})$ defined in the chapter 2 for two systems in contact. This additivity condition is very reminiscent to the additivity of the free energy for equilibrium systems interacting through short-ranged potential, reminded in equation (2.24). It reads

$$\mathcal{I}(\rho_A, \rho_B|\bar{\rho}) \equiv \gamma_A I(\rho_A|\bar{\rho}) = \gamma_A I_A(\rho_A) + \gamma_B I_B(\rho_B) \tag{3.1}$$

where $\rho_B = \gamma_B^{-1}(\rho - \gamma_A\rho_A)$. If such additivity condition holds, the derivative of the large deviations function reads

$$I'(\rho_A|\bar{\rho}) = I'_A(\rho_A) - I'_B(\rho_B) \ , \tag{3.2}$$

and the steady-state densities ρ_A^* and ρ_B^* satisfies $I'_A(\rho_A^*) = I'_B(\rho_B^*)$. Hence it offers the possibility to attach to each system a quantity, $I'_k(\rho_k)$ $(k = A\,, B)$ – rather noted $\mu_k(\rho_k)$ henceforth – that will be called *generalised chemical potential* at contact.

Contrary to what one may think intuitively in the vanishing exchange rate limit at contact, it is not always guaranteed that this condition holds in any circumstances. Besides, even when it holds we will see that the so-called generalised chemical potential $I'_k(\rho_k)$ strongly depends on local properties at contact and thus cannot be utterly associated with the isolated systems (in other words, the present chemical potentials do not verify any bulk equation of state). We thus confirm and significantly extend preliminary results obtained by S.-I. Sasa, K. Hayashi and H. Tasaki [Hayashi and Sasa, 2003; Sasa and Tasaki, 2006] on the KLS model, although the latter was not recognised as resulting from a large deviations analysis.

On another hand, we explore the thermodynamic meaning of this large deviations function (being additive or not). In particular, we show that for a certain class of transition rates, the large deviations function I verifies a second law with respect to the work supplied by uniform external potentials applied on each systems A and B. Here again, our derivation, albeit – up to our knowledge – original in this context, is greatly inspired by the work of [Bertini et al., 2015*a*,*b*, 2012, 2013]. We then discuss the particular case when one of the system, say B, is very large compared to the other and plays the role of a reservoir. Eventually, we close this chapter by discussing different possible experimental ways to measure this large deviations function, at least for a certain range of densities.

The two first sections of this chapter have been subject to a recently published letter [Guioth and Bertin, 2018].

3.1 Additive case

First, we identify sufficient conditions in order for the large deviations function $I(\rho_A|\bar{\rho})$ to be additive. Then, assuming that the additivity condition holds, we discuss expressions and properties of the chemical potentials thus defined. In particular, we make connection with chemical potentials of isolated systems and discuss the zeroth law of thermodynamics.

3.1.1 Chemical potential of systems in contact

Factorisation condition of the contact dynamics

When macroscopic detailed balance (2.35) holds, the additivity property of the large deviations function $I(\rho_A|\bar{\rho})$ should be directly related to the coarse-grained transition rates φ. It appears as a matter of fact that if each transition rate factorises as

$$\varphi(\rho_A, \Delta N_A) = \nu_0 \phi_A(\rho_A, \Delta N_A)\phi_B(\rho_B, \Delta N_B) \tag{3.3}$$

with $\Delta N_B = -\Delta N_A$ and ν_0 an arbitrary common frequency scale, the macroscopic detailed balance (2.35) enables one to split the derivative of the large deviations function into two contributions that respectively depend on each systems $k = A, B$. It reads

$$I'(\rho_A|\bar{\rho}) = \mu_A^{\mathrm{cont}}(\rho_A) - \mu_B^{\mathrm{cont}}(\rho_B) \tag{3.4}$$

with the chemical potentials

$$\mu_k^{\mathrm{cont}}(\rho_k) \equiv \ln \frac{\phi_k(\rho_k, -1)}{\phi_k(\rho_k, 1)} \tag{3.5}$$

with $k = A, B$. One notes that we have set $|\Delta N_A| = 1$ since the large deviations function $I(\rho_A|\bar{\rho})$ given by the macroscopic detailed balance condition (2.35) does not depend on ΔN_A. At the most probable values of the densities ρ_A^*, ρ_B^* – around which the probability density $P(\rho_A|\bar{\rho})$ is more and more peaked when system sizes increase –, $I'(\rho_A^*|\bar{\rho}) = 0$, resulting in the equalisation of the chemical potentials:

$$\mu_A^{\text{cont}}(\rho_A^*) = \mu_B^{\text{cont}}(\rho_B^*)\,. \tag{3.6}$$

One can wonder where the factorisation assumption (3.3) of the coarse-grained transition rates does come from. According to the microscopic expression of coarse-grained transition rates (2.19), an answer should without doubt be sought in the microscopic transition rates' expression T_c.

A remark on fugacity and its stochastic interpretation at equilibrium. At equilibrium, one often introduces the notion of *fugacity* which corresponds to the exponential of the chemical potential: $\zeta = e^{\mu}$. As recalled in a footnote of [Sekimoto, 2010, p. 77], the fugacity is interpreted as the "probability to escape" of a randomly chosen particle. Let us interpret our expression (3.5) is that respect. Indeed, the framework developed here is indeed still valid to describe equilibrium situations for which the drives are null. At equilibrium, the coarse-grained transition rates are simply averages over the canonical probability distributions for the given densities ρ_A, ρ_B. Exactly as for the present non-equilibrium situation, the expressions of equilibrium coarse-grained transition rates strongly depend on the choice of the microscopic dynamics at contact which does not necessarily factorise as in (3.3). If this is so, it appears difficult to interpret the exponentials of the chemical potentials as a "a probability to escape". The hint resides in the microscopic detailed balance condition.

Indeed, as one will be able to see it henceforth, it turns out that as long as the microscopic detailed balance holds with respect to the same equilibrium distribution, the ratio $\varphi(\rho_A, -1)/\varphi(\rho_A, +1)$ is invariant with respect to any changes of the dynamics at contact. Hence, the equilibrium chemical potentials (3.5) can be computed with the help of any transition rates satisfying microscopic detailed balance. In particular, Arrhenius-like transition rates for which an exchange of one particle from A to B only depends on A and symmetrically, an exchange from B to A only depends on B would be completely acceptable (see Sasa-Tasaki rule (3.11) below). In that case,

$$\varphi(\rho_A, -1) = \nu_0 \phi_A(\rho_A, -1) \qquad \text{and} \qquad \varphi(\rho_A, +1) = \nu_0 \phi_B(\rho_B, -1) \tag{3.7}$$

that gives

$$\mu_k^{\text{eq}}(\rho_k) = \ln \phi_k(\rho_k, -1)\,, \tag{3.8}$$

which can thus be interpreted as the logarithm of a "probability (per unit time) to escape" from the system k, knowing that the density is ρ_k, according to (3.7).

That being said, the absence of the microscopic detailed balance for our out-of-equilibrium set up is thus expected to break this escape probability interpretation for transition rates different from the one just expounded above.

Microscopic transition rates: factorisation condition

As shown in section 2.2.3, the transition rates $\varphi(\rho_A, \Delta N_A)$ are averages of the microscopic transition rates over the product of stationary distributions of the isolated systems. One then can observe that a sufficient condition is simply that the microscopic transition rates factorise in a similar way as the macroscopic ones

$$T_c(\mathcal{C}'_A, \mathcal{C}'_B|\mathcal{C}_A, \mathcal{C}_B) = \nu_0 \theta_A(\mathcal{C}_A, \mathcal{C}'_A)\theta_B(\mathcal{C}_B, \mathcal{C}'_B) \ . \tag{3.9}$$

At this stage this condition is quite abstract and the reader might expect some physical motivations. Local detailed balance assumption, discussed in the introduction, imposes a constraint on the ratio between transition rates of a transition $\mathcal{C} \to \mathcal{C}'$ and its time-reversed counterpart $\mathcal{C}' \to \mathcal{C}$: the logarithm of the latter ratio is related to (β times) the work supplied by the environment (from operator and heat bath) to make the transition. But, as already seen, the local detailed balance hypothesis does not entirely define transition rates and we will assume more generally that the latter only depends on (β times) the work necessary to make the transition. One notes that this assumption is consistent with most of the common choices of transition rates present in the literature [Katz et al., 1984; Tasaki, 2004]. It reads:

$$\begin{aligned} T_c(\mathcal{C}'|\mathcal{C}) &= \tau\left(\beta W(\mathcal{C}, \mathcal{C}')\right) \\ &= \tau\left(\beta W_A(\mathcal{C}_A, \mathcal{C}'_A) + \beta W_B(\mathcal{C}_B, \mathcal{C}'_B) + \beta W^{\text{int}}_{AB}(\mathcal{C}_A, \mathcal{C}'_A\,; \mathcal{C}_B, \mathcal{C}'_B)\right) \ , \end{aligned} \tag{3.10}$$

with $W(\mathcal{C}, \mathcal{C}')$ the supplied work which has been split in several contributions which depend on systems A and B as well as their interactions. According to the local detailed balance condition, the function $\tau(x)$ should satisfy $\tau(x) = e^x\tau(-x)$. Clearly, the presence of the interaction term which mixes A and B configurations does not allow the above factorisation property to hold in general. One should thus assume that the latter is negligible with respect to the other contributions. Among the classical choices that satisfy local detailed balance (*e.g.* the exponential rule, the metropolis rule, the Kawasaki/heat-bath rule and the Sasa-Tasaki rule, *etc.*), only two of them verify the factorisation condition (3.9).

Sasa-Tasaki dynamics. The first one, discussed in [Sasa and Tasaki, 2006, Appendix B], will be called the Sasa-Tasaki rule[1]. This rule is claimed to model a high energy barrier separating systems A and B. If the energy barrier is very high, the work necessary to make a transition of one particle from system A to system B only involves a change of energy in system A due to interactions with other particle as well as work to climb the barrier. However, once the particles is at the top of the barrier, there is no more cost to overcome to go down to B. In short, one gets an Arrhenius expression of the transition rates. They read

$$T_c(\mathcal{C}'_A, \mathcal{C}'_B|\mathcal{C}_A, \mathcal{C}_B) = \epsilon \begin{cases} e^{-\beta\Delta E_A} \text{ if } \Delta N_A = -1 \\ e^{-\beta\Delta E_B} \text{ if } \Delta N_A = +1 \end{cases} , \tag{3.11}$$

$\Delta E_k = E_k(\mathcal{C}'_k) - E_k(\mathcal{C}_k)$ and $\Delta N_A = \mathcal{N}(\mathcal{C}'_A) - \mathcal{N}(\mathcal{C}_A)$, $k = A, B$, $E_{A,B}$ being the respective energies of systems A and B. We point out that mass conservation $\mathcal{N}(\mathcal{C}'_A) - \mathcal{N}(\mathcal{C}_A) = -(\mathcal{N}(\mathcal{C}'_B) - \mathcal{N}(\mathcal{C}_B))$ is implicitly enforced in Eq. (3.11). Also, $\epsilon = e^{-\beta\Delta V}$ where ΔV is the height of the energy barrier separating A and B. When the barrier is very high, $\epsilon \ll 1$ and one gets a natural realisation of the slow frequency exchange limit as already devised in the first chapter (see section 2.2).

Exponential rule. Eventually, another classic rule for which the factorisation condition holds is when $\tau(x) = e^{\frac{x}{2}}$. It reads

$$T_c(\mathcal{C}'_A, \mathcal{C}'_B|\mathcal{C}_A, \mathcal{C}_B) = \epsilon\, e^{-\frac{\beta}{2}\Delta E_A} e^{-\frac{\beta}{2}\Delta E_B} , \tag{3.12}$$

where one has used the same notations as for the Sasa-Tasaki dynamics. The latter could be relevant in the case when interactions between A and B are negligible compared to the interactions within each system but when the weak contact is generated by a conformation selection or a small frequency openings of a gate but not by any high energy barrier as explained in the first chapter 2.

Even if these two cases appear to be the most common transition rates that satisfy the factorisation property (3.9), one could certainly imagine other rules that might be relevant. That being said, we will nevertheless discuss the implication of the factorisation property (3.9) in its general formulation without any reference to a specific choice, unless mentioned otherwise. Specific instances of transition rates will be encountered in chapter 4.

[1] Nevertheless, this choice of dynamics has been considered for long time. According to [Sekimoto, 2010, p. 112], the latter has already been considered in [Bergmann and Lebowitz, 1955; Lebowitz and Bergmann, 1957].

3.1.2 Relationships between chemical potentials of systems in contact and of isolated systems

We expound here the relationships between the chemical potentials of systems in contact (see equation (3.5)) and those of isolated systems.

First, one can notice that when macroscopic detailed balance condition (2.35) as well as the factorisation condition (3.9) hold, it is sufficient to compute quantities for $\Delta N_A = \pm 1$ only since

$$\begin{aligned} I'(\rho_A|\bar{\rho}) &= \frac{1}{\Delta N_A} \ln \frac{\varphi(\rho_A, -\Delta N_A)}{\varphi(\rho_A, \Delta N_A)} = \ln \frac{\varphi(\rho_A, -1)}{\varphi(\rho_A, +1)} \\ &= \ln \frac{\phi_A(\rho_A, -1)}{\phi_A(\rho_A, +1)} - \ln \frac{\phi_B(\rho_B, -1)}{\phi_B(\rho_B, +1)} \end{aligned}$$

Assuming a factorisation of the transition rates at the microscopic level as in equation (3.9), the macroscopic transition rates factorise as in (3.3) with the factors $\phi_k = \lim_{V_k \to \infty} \phi_{V_k,k}$ that stem from the finite volume exact expression which reads

$$\phi_{V_k,k}(\rho_k, \pm 1) = \sum_{\substack{\mathcal{C}'_k \in \mathcal{E}^{V_k}_{\pm 1}(\rho_k) \\ \mathcal{C}_k \in \mathcal{E}^{V_k}_{0}(\rho_k)}} \theta_k(\mathcal{C}'_k, \mathcal{C}_k) P_{V_k}(\mathcal{C}_k|\rho_k) \,. \tag{3.13}$$

One recalls that $\mathcal{E}^{V_k}_{\Delta N}(\rho_k) = \{\mathcal{C}_k \,|\, \mathcal{N}(\mathcal{C}_k) = \rho_k V_k + \Delta N_k\}$ is the set of configurations $\mathcal{C}_k$ that exactly contain $\rho_k V_k + \Delta N_k$ particles.

Also, in the absence of any direct interaction energy between A and B, the microscopic detailed balance reads, in terms of θ_k factors,

$$\prod_{k=A,B} \theta_k(\mathcal{C}'_k, \mathcal{C}_k) = \prod_{k=A,B} e^{-\beta \Delta E_k(\mathcal{C}'_k, \mathcal{C}_k)} \theta_k(\mathcal{C}_k, \mathcal{C}'_k) \tag{3.14}$$

with $\Delta E_k(\mathcal{C}'_k, \mathcal{C}_k) = E_k(\mathcal{C}'_k) - E_k(\mathcal{C}_k)$. Hence, it still holds for each isolated factor θ_k

$$\theta_k(\mathcal{C}'_k, \mathcal{C}_k) = e^{-\beta(E_k(\mathcal{C}'_k) - E_k(\mathcal{C}_k))} \theta_k(\mathcal{C}_k, \mathcal{C}'_k) \,. \tag{3.15}$$

In order to get a more insightful expression for $\mu_k^{\text{cont}} = \ln [\phi_k(\rho_k, -1)/\phi_k(\rho_k, +1)]$, one should relate $\phi_k(\rho_k, -1)$ to $\phi_k(\rho_k, +1)$. According to the equation (3.13), $\phi_{V_k,k}(-1, \rho_k + \frac{1}{V_k})$ reads

$$\phi_{V_k,k}(-1, \rho_k + \tfrac{1}{V_k}) = \sum_{\substack{\mathcal{C}_k \in \mathcal{E}^{V_k}_{+1}(\rho_k) \\ \mathcal{C}'_k \in \mathcal{E}^{V_k}_{0}(\rho_k)}} \theta_k(\mathcal{C}'_k, \mathcal{C}_k) P_{V_k}\left(\mathcal{C}_k \middle| \rho_k + \tfrac{1}{V_k}\right) \,. \tag{3.16}$$

Using the microscopic detailed balance relation (3.15) and changing $\mathcal{C}_k$ into $\mathcal{C}'_k$ and

vice versa, one can write

$$\phi_{V_k,k}(-1,\rho_k+\tfrac{1}{V_k}) = \sum_{\substack{\mathcal{C}_k\in\mathcal{E}_0^{V_k}(\rho_k)\\ \mathcal{C}'_k\in\mathcal{E}_{+1}^{V_k}(\rho_k)}} \theta_k(\mathcal{C}'_k,\mathcal{C}_k)e^{\beta\left(E_k(\mathcal{C}'_k)-E_k(\mathcal{C}_k)\right)} \times \frac{P_{V_k}\left(\mathcal{C}'_k\middle|\rho_k+\frac{1}{V_k}\right)}{P_{V_k}\left(\mathcal{C}_k|\rho_k\right)} \times P_{V_k}\left(\mathcal{C}_k|\rho_k\right) . \tag{3.17}$$

To go further, one should now insert expressions of the stationary probability distributions of system $k = A, B$ before taking the infinite volume limit. Even if this is a definitely prominent fact, one should stress that the stationary probability distribution of the isolated system k is quite difficult to compute in general. Several examples will be discussed in chapters 4 and 5 but we would like now to keep a broad perspective and to consider general links between chemical potentials of isolated systems.

The first idea, quite natural, is to express the out-of-equilibrium stationary distribution $P_{V_k}(\mathcal{C}_k|\rho_k)$ as an expansion with respect to the equilibrium distribution. This approach is particularly suited when the non-equilibrium systems are close to equilibrium. Such expansion of the stationary probability was first introduced by McLennan [McLennan Jr, 1959; Zubarev, 1974] and has been revived quite recently with significant development by [Colangeli et al., 2011; Komatsu and Nakagawa, 2008; Komatsu et al., 2008, 2009, 2015, 2010; Maes and Netočnỳ, 2010; Maes et al., 2008]. Since equilibrium is considered as the reference process here, one naturally gets a connection with equilibrium chemical potentials of isolated systems.

The second perspective aims at making a link with proper out-of-equilibrium chemical potentials attached to isolated systems only. We should stress that one does not know how to define in a general way any genuine out of equilibrium partition function from which a non-equilibrium chemical potential could be derived. Nonetheless, we will see in chapter 4 that a so-called non-equilibrium partition function can be explicitly computed for specific mass transport models on lattice. Broadly speaking, one expects to be able to define chemical potentials attached to isolated systems when static stationary spatial correlations are short-ranged, leading to an asymptotic factorisation of the steady state probability distribution of the number of particles (or mass) in macroscopic sub-parts of the system. This is indeed the case for the Zero Range Process [Evans and Hanney, 2005; Evans et al., 2004, 2006*b*] or some generalised mass transport models that will be encountered in chapter 4. However, when long-range static correlations are present – for a broad range of external parameters as it is generically the case for non-equilibrium systems [Bertini et al., 2007; Dorfman et al., 1994; Garrido et al., 1990; Spohn, 1983], or maybe near a second order phase transition – the stationary probability distribution no longer factorises and one cannot apply the

previous procedure to define a chemical potential attached to an isolated system. As we will see, one can nevertheless try to renormalise the perturbative expansion with respect to equilibrium in order to obtain a non-equilibrium partition function.

Relation between μ^{cont} and μ^{eq}

If one takes the equilibrium state as the reference, $P_{V_k,k}(\mathcal{C}_k)$ can be obtained from a perturbative expansion with respect to the equilibrium distribution. This idea was first the one of McLennan [McLennan Jr, 1959] who computed corrections due to the driving force up to first order. Based on this idea to compute perturbatively the non-equilibrium stationary distribution, extensive developments, based on dynamical fluctuations studies, have been performed recently [Colangeli et al., 2011; Komatsu and Nakagawa, 2008; Komatsu et al., 2008, 2009, 2010; Maes and Netočnỳ, 2010; Maes et al., 2008]. Without more details, one can generally write

$$P_{V_k,k}(\mathcal{C}_k) = \frac{1}{Z_k^{\text{eq}}} e^{-\beta E_k(\mathcal{C}_k)+\Upsilon_k^{\text{eq}}(\mathcal{C}_k)}\,, \tag{3.18}$$

which defines the supplemental term $\Upsilon_k^{\text{eq}}(\mathcal{C}_k)$ that accounts for the non-equilibrium correction to the Gibbs-Maxwell-Boltzmann equilibrium probability distribution. Introducing this ansatz into Eq. (3.17) leads to

$$\phi_{V_k,k}(\rho_k+\tfrac{1}{V_k},-1) = \frac{Z_k^{\text{eq}}(\rho_k)}{Z_k^{\text{eq}}\left(\rho_k+\frac{1}{V_k}\right)} \sum_{\mathcal{C}_k,\mathcal{C}_k'} \theta_k(\mathcal{C}_k',\mathcal{C}_k) e^{\Upsilon_k^{\text{eq}}(\mathcal{C}_k')-\Upsilon_k^{\text{eq}}(\mathcal{C}_k)} P_{V_k,k}\left(\mathcal{C}_k|\rho_k\right)\ . \tag{3.19}$$

Thus, at the thermodynamic limit $V_k \to \infty$,

$$\phi_k(\rho_k,-1) = e^{\mu_k^{\text{eq}}(\rho_k)} \lim_{V_k\to\infty} \sum_{\substack{\mathcal{C}_k'\in\mathcal{E}_{+1}(\rho_k)\\ \mathcal{C}\in\mathcal{E}_0(\rho_k)}} \theta(\mathcal{C}_k',\mathcal{C}_k) e^{\Upsilon_k^{\text{eq}}(\mathcal{C}_k')-\Upsilon_k^{\text{eq}}(\mathcal{C}_k)} P_{V_k,k}(\mathcal{C}_k|\rho_k)\,. \tag{3.20}$$

As for $\phi_k(\rho_k,+1)$, one obtains

$$\phi_k(\rho_k,+1) = \lim_{V_k\to\infty} \sum_{\substack{\mathcal{C}_k\in\mathcal{E}_0(\rho_k)\\ \mathcal{C}_k'\in\mathcal{E}_{+1}(\rho_k)}} \theta_k(\mathcal{C}_k',\mathcal{C}_k) P_{V_k,k}(\mathcal{C}_k|\rho_k)\,. \tag{3.21}$$

One then notices that $\phi_k(\rho_k,-1)$ can be related to a biased transition rate factor. Indeed,

$$\phi_k(\rho_k,-1) = e^{\mu_k^{\text{eq}}(\rho_k)} \phi_{k,\Delta\Upsilon_k^{\text{eq}}}(\rho_k,+1)\,, \tag{3.22}$$

with $\phi_{k,\Delta\Upsilon_k^{\text{eq}}}(\rho_A,+1)$ the analogue of $\phi_k(\rho_A,+1)$ where $\theta_k(\mathcal{C}_k',\mathcal{C}_k)$ has been biased by $\Delta\Upsilon_k^{\text{eq}} = \Upsilon_k^{\text{eq}}(\mathcal{C}_k') - \Upsilon_k^{\text{eq}}(\mathcal{C}_k)$, leading to $\theta_k(\mathcal{C}_k',\mathcal{C}_k)e^{\Upsilon_k^{\text{eq}}(\mathcal{C}_k')-\Upsilon_k^{\text{eq}}(\mathcal{C}_k)}$.

Eventually, according to equation. (3.5) and (3.22), the chemical potential at con-

tact $\mu_k^{\rm cont}$ reads

$$\mu_k^{\rm cont}(\rho_k) = \mu_k^{\rm eq}(\rho_k) + \ln \frac{\phi_{k,\,\Delta\Upsilon_k^{\rm eq}}(\rho_k,+1)}{\phi_k(\rho_k,+1)} \,, \tag{3.23}$$

where $\ln[\phi_{k,\,\Delta\Upsilon_k^{\rm eq}}(\rho_k,+1)/\phi_k(\rho_k,+1)]$ can be interpreted as an excess chemical potential with respect to the equilibrium one.

One recovers $\mu^{\rm cont} = \mu^{\rm eq}$ when the excess non-equilibrium term $\Upsilon_k^{\rm eq}(\mathcal{C}_k)$ is vanishing. This is of course the case if the systems at stake are at equilibrium: our expression is thus consistent with the equilibrium situation. But one can also find $\mu^{\rm cont} = \mu^{\rm eq}$ when the stationary distribution of the non-equilibrium isolated systems does not differ from the equilibrium one. Even if such a dependence is expected to be generic [Colangeli et al., 2011; Maes et al., 2009], one can nevertheless find full-fledged non-equilibrium systems whose stationary solution is not affected at all by the driving (and is thus equal to the equilibrium one). This is for instance the case for the Asymmetric Simple Exclusion Process (ASEP) on a ring in one dimension [Derrida, 1998]. For these latter non-equilibrium systems, no shift in stationary densities is expected to be observed when the drives are switched on.

Relation between $\mu^{\rm cont}$ and $\mu^{\rm iso}$

Rather than taking equilibrium as the reference situation, one can consider also the out-of-equilibrium state on its own. Indeed, even if a general procedure to define a non-equilibrium free energy is not yet established, one can sometimes – but rarely – directly compute the non-equilibrium stationary distribution which brings directly an "out-of-equilibrium partition function" different from the equilibrium one. Some examples are the Zero Range Process and its extensions [Evans and Hanney, 2005; Evans et al., 2004, 2006*b*; Levine et al., 2005; Zia et al., 2004], the Simple Exclusion Processes [Derrida, 1998, 2007], etc. We will provide an extensive study of an original solvable model in the next chapter 4.

To our knowledge, it does not exist any consensus on a general definition of a genuine non-equilibrium partition function $Z_k(\rho)$ for any general system. As already pointed out, however, when correlations are *short-ranged* — which is a non-generic situation when a system is driven by permanent non-conservative forces —, such a non-equilibrium partition function can be computed by cutting the isolated system into a small, local, macroscopic part, the rest acting as a reservoir. In this case, the stationary probability distribution of the configurations $\mathcal{C}^\ell$ of this local part is given by

$$P_k^\ell(\mathcal{C}_k^\ell) = F_k(\mathcal{C}_k^\ell) e^{\mu_k^{\rm iso}(\rho_k)\mathcal{N}(\mathcal{C}_k^\ell)} \,, \tag{3.24}$$

with F_k the non-equilibrium weight. The chemical potential $\mu_k^{\rm iso}$ defined in that respect is thus associated with the control of mass inside the isolated system k.

In any case, we will postulate in the following, without proof, that the stationary distribution P_k of the whole system k can be written as

$$P_{V_k,k}(\mathcal{C}_k|\rho_k) = \frac{1}{Z_k^{\mathrm{Neq}}(\rho_k)} e^{-\beta E_k(\mathcal{C}_k)+\Upsilon_k^{\mathrm{Neq}}(\mathcal{C}_k)} , \tag{3.25}$$

where $Z_k^{\mathrm{Neq}}(\rho_k)$ refers to a non-equilibrium partition function of system k, different from the equilibrium one. As observed in a simple but non-trivial non-equilibrium mass transport model [Guioth and Bertin, 2017], a potential non-equilibrium partition function could be defined such that $\partial Z_k^{\mathrm{Neq}}/\partial f$ is equal to β times the average (both in space and in probability) current, as one would expect for a generalisation from the equilibrium non-equilibrium free energy (see [Sasa and Tasaki, 2006] for a very detailed discussion on the phenomenological definition of a genuine non-equilibrium free energy). One notices that this expression of the stationary probability distribution can then be obtained from the perturbative expansion (3.18) simply by introducing the term $e^{-\beta\sigma}$ in (3.25) where σ refers (up to a multiplicative constant length that one takes to be equal to the lattice spacing) to the entropy production equals to $f \cdot J$ when f, the non-conservative force, is homogeneous along the system and J is the average current. In this case, $\Upsilon_k^{\mathrm{Neq}} = \Upsilon_k^{\mathrm{eq}} + \beta\sigma$. We refer the reader to the appendix C for a detailed example of such expression. Assuming that the non-equilibrium partition function $Z_k^{\mathrm{Neq}}(\rho_k)$ obeys a large deviations principle with respect to ρ_k at the thermodynamic limit, the same calculation as in the subsection 3.1.2 leads to

$$\phi_k(\rho_k,-1) = e^{\mu_k^{\mathrm{iso}}(\rho_k)} \lim_{V_k\to\infty} \sum_{\substack{\mathcal{C}_k'\in\mathcal{E}_{+1}^{V_k}(\rho_k) \\ \mathcal{C}\in\mathcal{E}_0^{V_k}(\rho_k)}} \theta(\mathcal{C}_k',\mathcal{C}_k) e^{\Upsilon_k^{\mathrm{Neq}}(\mathcal{C}_k')-\Upsilon_k^{\mathrm{Neq}}(\mathcal{C}_k)} P_{V_k,k}(\mathcal{C}_k|\rho_k) , \tag{3.26}$$

which itself gives

$$\mu_k^{\mathrm{cont}}(\rho_k) = \mu_k^{\mathrm{iso}}(\rho_k) + \ln \frac{\phi_{k,\,\Delta\Upsilon_k^{\mathrm{Neq}}}(\rho_k,+1)}{\phi_k(\rho_k,+1)} . \tag{3.27}$$

This expression is almost identical to the previous one (3.23) for which the reference situation was the equilibrium. Different normalisation of the stationary probability distribution can thus lead to different chemical potentials in excess with respect to the chosen reference configuration.

Contact dependence of the excess chemical potential

In every case, one sees that the chemical potential at contact $\mu_k^{\mathrm{cont}}(\rho_k)$ is equal to a chemical potential related to the isolated system (either the equilibrium one or the stationary non-equilibrium one) and an *excess* chemical potential which generically

reads

$$\eta_k(\rho_k) = \ln \frac{\phi_{k,\,\Delta\Upsilon_k}(\rho_k,+1)}{\phi_k(\rho_k,+1)}\,. \tag{3.28}$$

The excess chemical potential η_k clearly depends on $\Delta\Upsilon_k$ that has to be different from 0 to get η_k non-vanishing.

We should however recognise that one cannot avoid any *generic* dependence of $\theta_k(\mathcal{C}'_k,\mathcal{C}_k)$ in the expression of η_k as long as the steady-state measure of isolated systems are affected by the drives. That is to say, the details of the contact (which involves activity (symmetric part) and force/bias (anti-symmetric part) of the contact) do contribute to the chemical potential $\mu_k^{\rm cont}$. We will extensively study this dependence on specific situations in the next chapters but one cannot exclude as of now that the chemical potential at contact $\mu_k^{\rm cont}$ may depend on the specificity of the contact dynamics, beyond the specificities of stationary probability distributions of the isolated systems.

Eventually, since long-range correlations are ubiquitous in non-equilibrium systems and have been questioned several times in the literature which has considered the question of the contact [Chatterjee et al., 2015; Pradhan et al., 2010, 2011; Sasa and Tasaki, 2006], we propose a brief comment about their potential impact on our set-up.

Effect of long-range correlations?

Long-range correlations are ubiquitous in non-equilibrium systems [Bertini et al., 2007; Dorfman et al., 1994; Garrido et al., 1990; Spohn, 1983]. If the usual observable is the static (or equal time) two-point correlation function, such a weak decay transfers itself to the stationary probability distribution. Indeed, as discussed in [Derrida, 2007], this can be seen easily by considering the following cumulant generating function defined as

$$\mathcal{G}(\{\alpha_x\}_{x\in\Lambda}) = \ln\left\langle e^{\sum_{x\in\Lambda}\alpha_x\eta_x}\right\rangle = \ln\sum_{\{\eta_x\}_{x\in\Lambda}}\frac{1}{Z}e^{\sum_{x\in\Lambda}\alpha_x\eta_x-\beta H(\{\eta_x\}_{x\in\Lambda})+\Upsilon(\{\eta_x\}_{x\in\Lambda})}\,, \tag{3.29}$$

where H is the energy of the configuration $\mathcal{C}=\{\eta_x\}_{x\in\Lambda}$ and $\Upsilon(\{\eta_x\}_{x\in\Lambda})$ is the non-equilibrium part either from the McLennan approach (3.18) or from Eq. (3.25). Taking derivatives with respect to α_x in (3.29) at $\alpha=0$ leads to

$$\rho_x = \langle\eta_x\rangle = \left.\frac{\partial\mathcal{G}}{\partial\alpha_x}\right|_{\alpha=0} \tag{3.30}$$

$$C_{x,y} = \langle\eta_x\eta_y\rangle - \langle\eta_x\rangle\langle\eta_y\rangle = \left.\frac{\partial^2\mathcal{G}}{\partial\alpha_x\partial\alpha_y}\right|_{\alpha=0}\,, \tag{3.31}$$

higher order derivatives being related to higher order correlation functions. Put another way, expanding $\mathcal{G}$ with respect to α_x leads to

$$\mathcal{G}(\{\alpha_x\}) = \sum_{x\in\Lambda} \alpha_x \rho_x + \frac{1}{2} \sum_{\substack{x\in\Lambda \\ y\in\Lambda}} \alpha_x \alpha_y C_{x,y} + \dots \tag{3.32}$$

Non-local contributions in $\mathcal{G}(\{\alpha_x\})$ appear when the correlation function $C_{x,y}$ does not decay fast enough. Typically, $\forall x$, $\sum_{y\in\Lambda} C_{x,y}$ should be of order $\mathcal{O}(|\Lambda|^0)$: this includes weak long-range correlations but also short-range correlations leading to local contributions in $\mathcal{G}(\{\alpha_x\})$.

Clearly, the potential non-locality of $\mathcal{G}$ is inherited from the non-locality of the stationary distribution function. For short-range interactions, the energy E is a local function, meaning that it can be written as $E(\{\eta_x\}_{x\in\Lambda}) = \sum_{x\in\Lambda} \varepsilon(\eta_x, \{\eta_y\}_{y\in\mathcal{V}_x})$, $\mathcal{V}_x$ being a local neighbourhood of site x. Except for long-range interactions — present in gravitational systems for instance — that we will not consider here, this will always be assumed. Away from second order phase transition, the non-local contribution is only present in Υ which intervenes in the excess chemical potential (3.28).

If such long-range correlations are present, the coarse-grained transition rates potentially depend on the fluctuations quite far from the contact area (if the latter is localised). However, this presence does not break the validity of the expression (3.28) as long as we consider the vanishing transition rates limit at contact. One should note however that the relaxation dynamics in bulk systems might be much slower than the equilibrium relaxation (outside any phase transition) in this situation of long-range correlations. In real situations (either experimental or numerical) for which the parameter that controls the rates at contact, ϵ, is small but finite, one has to pay attention that ϵ is sufficiently small to keep two well-separated time scales between bulk and contact dynamics. If this is so, our framework remains valid even when long-range correlations are present.

Otherwise, if ϵ is not sufficiently small, one can expect that in the presence of such long-range correlations, local perturbations due to small but finite exchange rates at contact, may significantly modify the stationary states of each systems in contact on length scales much larger than the contact area [Maes et al., 2009]. In this case, thinking of two well-defined systems in contact may not be relevant anymore and one may prefer to consider one, big, inhomogeneous system instead. If this big picture is correct, it would be worth having detailed studies of such an effect on simple models. This is however beyond the scope of the work presented here.

3.1.3 What if the contact dynamics involves an additional work or depends on the drives?

Until now, we have considered a contact orthogonal to the non-conservative driving forces, leading to transition rates at contact independent of the driving forces of systems A and B and verifying detailed balance with respect to the equilibrium distributions. One can nevertheless wonder what happens when microscopic transition rates at contact do depend on the driving forces or when there is an extra-work performed at contact. In that respect, if one assumes that transition rates at contact obey a local detailed balance with extra work in addition to the local energy difference present at equilibrium, the same reasoning still applies. Let us discuss it in more details.

We assume that the microscopic transition rates at contact, $T_c(\mathcal{C}'|\mathcal{C})$ obey local detailed balance with additional work $w^{\rm cont}(\mathcal{C},\mathcal{C}')$ that can depend on the driving forces themselves. We consider also a possible extra-influence of the driving forces on the symmetric part of the transition rates $a(\mathcal{C},\mathcal{C}')$. One then obtains

$$T_c(\mathcal{C}'|\mathcal{C}) = a^{\rm Neq}(\mathcal{C},\mathcal{C}')e^{-\frac{\beta}{2}\left(E(\mathcal{C}')-E(\mathcal{C})-w^{\rm cont}(\mathcal{C},\mathcal{C}')\right)}\,. \tag{3.33}$$

Assuming that both the factorisation condition (3.9) and macroscopic detailed balance hold, the same calculation presented in last subsection 3.1.2, valid at the vanishing exchange rate limit, leads to

$$\mu_k^{\rm cont}(\rho_k) \equiv \ln\frac{\phi_k(\rho_k,-1)}{\phi_k(\rho_k,+1)} = \mu_k(\rho_k) + \ln\frac{\phi_{k,\,\Delta\Upsilon_k+w_k^{\rm cont}}(\rho_k,+1)}{\phi_k(\rho_k,+1)}\,. \tag{3.34}$$

Not surprisingly, one can see that the excess chemical potential due to the additional work $w_k^{\rm cont}$ adds to the out-of-equilibrium term $\Delta\Upsilon_k$ (that appears as the breaking term of the detailed balance at micro-scale when $P(\mathcal{C}_k|\bar{\rho_k})$ is different from the equilibrium distribution).

It may happen that the presence of the additional work $w^{\rm cont}$ to realise the transition $\mathcal{C}\to\mathcal{C}'$ could break the factorisation property. If this is so, one has to come back to the global expression of the derivative of the large deviations function which would thus be non-additive. For situations when this extra-work is only exerted through the contact by external agents and thus is not a function of energies or applied work in each systems – in short, when $w^{\rm cont}$ depends neither on A nor on B –, one can notice that the splitting into two contributions to get the factorisation property could still be made, even though perhaps in a quite arbitrary way, by considering the work needed to move particles from A to B and conversely to move a particle from B to A.

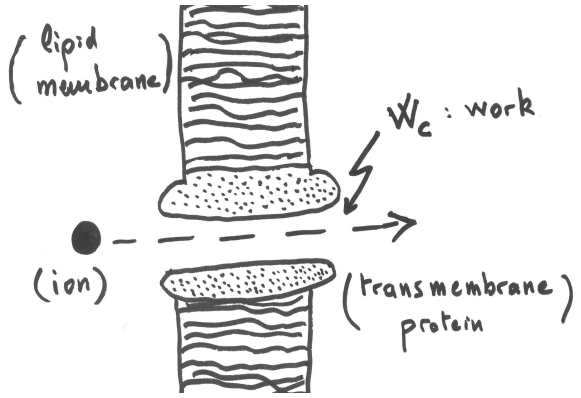

Figure 3.1 – Sketch of ion pump in a cell membrane (lipid bilayer). The ion pump is a protein attached to the membrane that can exert a work W_c on a ion to counter-balance the the natural diffusion (entropic flux).

***Remark*: in equilibrium.** Even in equilibrium, the case where the microscopic transition rates involve an extra-work is quite interesting. In particular, this situation happens in biological systems and more specifically in cells. Indeed, let us consider two compartments separated by a membrane punctured by channels that allow the transfer of particles (ions here) from one side to another (see figure 3.1. Two type of channels have been observed [Gadsby, 2009; Siwy and Fuliński, 2002]. The first type concerns passive channel (called *ion channel*) that let the ions follow the local electro-chemical potential gradient (which basically embeds, if one neglects interactions between ions, simple diffusion and possible complex electric potential across the membrane). But, in several situations, it is observed that the transfer of particles is not passive and does not follow the electro-chemical potential gradient. At a microscopic level, this is due to the fact that the channel is active and consumes metabolic energy to transport ions. These are usually referred to as *ion transporters* or *ion pumps*. Thus, this active transport involves an extra work w^{cont} which is localised in the channel. If the frequency of exchange is very small and if one takes for reference an equilibrium situation where in each system k the stationary probability distribution reads $P_k^{\text{eq}}(\mathcal{C}_k|\rho_k) = e^{-\beta E_k(\mathcal{C}_k)}/Z_k^{\text{eq}}$, one obtains

$$\mu_k^{\text{cont}}(\rho_k) = \mu_k^{\text{eq}}(\rho_k) + \ln \frac{\phi_{k,\, w_k^{\text{cont}}}(\rho_k, +1)}{\phi_k(\rho_k, +1)}\,, \tag{3.35}$$

if both macroscopic detailed balance and factorisation conditions hold. In the case where the active transports is switch off, w_k^{cont} vanishes, and one recovers the passive equilibrium potentials $\mu_k^{\text{eq}}(\rho_k)$.

3.1.4 About the Zeroth law of thermodynamics

We have provided detailed expressions and some properties of the chemical potentials at contact in last subsections. We would like now to go beyond definitions and explore

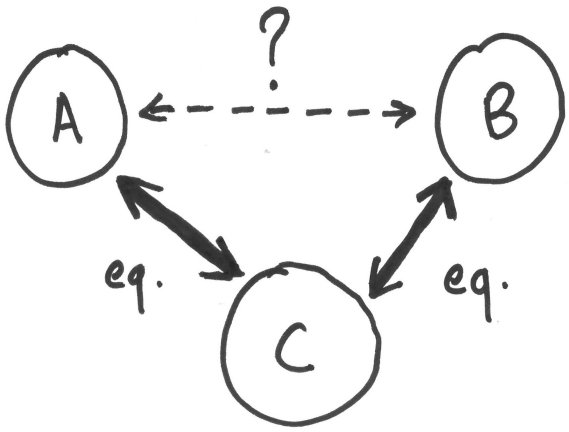

Figure 3.2 – Sketch of the Zeroth law procedure. It asks if systems A and B are in equilibrium with each other when their are separately both in equilibrium with a third system C. This law is fundamental in the equilibrium realm since it ensures the universality of the intensive thermodynamic parameter (such as temperature, pressure, chemical potential, etc).

their thermodynamic meaning. If one follows the phenomenology of thermodynamics, chemical potentials are very intricately linked with the zeroth law. What happens for our non-equilibrium set-up?

The zeroth law is indeed at the heart of equilibrium thermodynamics and deals with the issue of the contact between equilibrium systems. People generally refer to it as the transitivity property of equilibrium states, meaning that if two systems A and B are in equilibrium with a third one C, then they are in equilibrium with each other (a sketch of this procedure is drawn in figure 3.2). If it holds, it can serve as an operational definition of the existence of intensive thermodynamic parameters related to exchange of conserved quantities through the contact, like temperature (for the exchange of energy), pressure (for the exchange of volume) or chemical potentials (for the exchange of particles), that equalise when systems are in equilibrium with each other.

For contact between non-equilibrium driven systems in steady-state, one has seen the importance of the contact dynamics as it exerts a strong influence on the stationary densities in each system. In certain situations when macroscopic detailed balance holds and when macroscopic transition rates factorise, one can define intensive thermodynamic parameters, namely chemical potentials, that are associated with each systems and equalise when the stationary state is reached. However, this does not necessarily lead to the zeroth law as stated above since the chemical potential defined here may depend on the specificity of the contact between systems. For instance, if A and B are separately in contact with C through different contact dynamics, it is not at all guaranteed that the final stationary states of A and B (in contact with C)

can still be stationary states – or say differently, the final states of A and B coexist – when A and B are now brought into contact through a certain contact dynamics. This issue has been addressed in different papers [Chatterjee et al., 2015; Dickman, 2016; Pradhan et al., 2010] and a more detailed discussion will be given later in chapter 4, section 4.3.1.

That being said, in the case when chemical potentials at contact can be defined, one can tune the contact so that the macroscopic transition rates factorise in terms made of the ϕ_k and then attach to each system k its macroscopic transition rates $\phi_k(\rho_k, \Delta N_k)$. One will thus get a class of systems that satisfy the zeroth law with respect to each other. Physically speaking, it corresponds to virtually associate one half of the contact to each isolated system in order for its chemical potential to become its chemical potential at contact μ_k^{cont}. This procedure is however very sensitive to the choice of the contact dynamics which thus needs to be measured in details.

In brief, the zeroth law of thermodynamics in our non-equilibrium situations is not expected to hold in full generality. Nonetheless, when additivity of the large deviations function holds it is formally possible to attach to each systems its chemical potential at contact. Yet, such chemical potential does generically depend on the local contact dynamics and thus cannot be assigned to the separated systems but only to the systems *as well as* part of the contact – that hence need to be attached to the system. This is reminiscent to the fact that chemical potential at contact do not generally obey any equation of state involving only bulk quantities as an equilibrium system does.

3.2 Non-additive case: general results

Before going further in thermodynamic considerations, we take a short break here and turn now to the general case for which the large deviations function $I(\rho_A|\bar{\rho})$ is not additive. As already seen in the previous section, the additivity property is a necessary consequence of two properties: the macroscopic detailed balance (2.35) and a factorisation condition on the macroscopic transition rates (3.3). We will thus see in this section that there are two main ways to break this additivity condition: either by breaking the factorisation condition on the transition rates or by breaking the macroscopic detailed balance itself.

3.2.1 Macroscopic detailed balance with non-factorised contact dynamics

When macroscopic transition rates $\varphi(\rho_A, \Delta N_A)$ are not factorised into two parts, there is no reason that one can define in a general way chemical potentials at contact attached to systems A and B. If macroscopic detailed balance (2.35) still holds, the large

deviations function of the density reads

$$I'(\rho_A) = \ln \frac{\varphi(\rho_A, -1)}{\varphi(\rho_A, +1)} \tag{3.36}$$

where $\varphi(\rho_A, \pm 1) \neq \phi_A(\rho_A, \pm 1)\phi_B(\rho_B, \mp 1)$. This condition is in general reminiscent of the non-factorisation of the transition rate at contact $T_c(\mathcal{C}'|\mathcal{C})$ itself. This can be the case because of direct interaction between A and B or because of a non-factorisation of the activity $a_c(\mathcal{C}, \mathcal{C}')$ of the transition rates T_c, as it is always the case for the Heat-bath rule or the Metropolis rule for instance.

A calculation very similar to the one made for the factorisation case leads in this situation to the following expression of the large deviations function I'

$$I'(\rho_A|\bar{\rho}) = \mu^{(A)}(\rho_A) - \mu^{(B)}(\rho_B) + \ln \frac{\varphi_{\Delta\Upsilon^{(A)}+\Delta\Upsilon^{(B)}}(\rho_A, +1)}{\varphi(\rho_A, +1)}\,, \tag{3.37}$$

where $\varphi_{\Delta\Upsilon}$ refers to the macroscopic transition rate (2.19) where the microscopic transition rate T_c has been tilted by $e^{\Delta\Upsilon_A + \Delta\Upsilon_B}$. Even if the contribution of the stationary distributions of each system is still factorised, the $\varphi_{\Delta\Upsilon^{(A)}+\Delta\Upsilon^{(B)}}/\varphi$ has no reason to do so since T_c does not factorise. Explicit examples will be given in chapter 4.

3.2.2 Absence of macroscopic detailed balance

If this time macroscopic detailed balance breaks, it appears to be much more difficult to solve the Hamilton-Jacobi equation (2.23) in order to obtain $I(\rho_A|\bar{\rho})$. One has seen in the first chapter a general way to proceed, which essentially consists in performing a perturbative expansion with respect to a reference situation, assumed to satisfy the macroscopic detailed balance. At first order in the perturbation, the derivative of the large deviations function reads

$$I'(\rho_A|\bar{\rho}) = I^{(0)\prime}(\rho_A|\bar{\rho}) + \xi I^{(1)\prime}(\rho_A|\bar{\rho}) + \mathcal{O}(\xi^2)\,. \tag{3.38}$$

Let us assume that at $\xi = 0$, both systems are at equilibrium and that their driving forces increase together with ξ, albeit potentially at different rates. One thus has $I^{(0)\prime} = \mu_A^{\mathrm{eq}} - \mu_B^{\mathrm{eq}}$. Let us assume now that the macroscopic transition rates completely factorise at each order in ξ. Contrary to what is expounded in 2.5, it is easier to formulate things in terms of transition rates $\varphi(\rho_A, \Delta N_A)$ directly. $I^{(1)\prime}(\rho_A|\bar{\rho})$ reads

$$I^{(1)\prime}(\rho_A|\bar{\rho}) = \frac{\sum_{\Delta N_A \neq 0} \varphi^{(1)}(\rho_A, \Delta N_A)\left(e^{I^{(0)\prime}(\rho_A|\bar{\rho})\Delta N_A} - 1\right)}{\sum_{\Delta N_A \neq 0} \varphi^{(0)}(\rho_A, \Delta N_A)\Delta N_A}\,. \tag{3.39}$$

Hence, even if $\varphi^{(1)}(\rho_A, \Delta N_A)$ and $\varphi^{(0)}(\rho_A, \Delta N_A)$ factorise as in (3.3), it is not expected that this factorisation property still holds for the large deviations function $I(\rho_A|\bar{\rho})$, even at the first order beyond the equilibrium situation for which the large deviations function is additive.

Explicit examples of this lack of additivity when macroscopic detailed balance breaks will be discussed in chapter 4. We shall now explore in more details the relation between external potentials and the large deviations function $I(\rho_A|\bar{\rho})$, or the chemical potentials if they are well defined.

3.3 Chemical Potential and external potential

In order to progress in our understanding of the thermodynamic properties of chemical potentials at contact and more generally to the large deviations function of densities, we would like now to investigate the relations between chemical potentials and uniform external potentials that can be applied over each sub-systems. Our main motivations are

- Quite importantly, first, such external potential difference can be a way to probe rare events of the unperturbed stationary dynamics and thus allows one to have access experimentally to the large deviations function, exactly as in equilibrium (see [Touchette, 2009]).

- It is also a natural thermodynamic transformation that has its own interest. We will in particular show henceforth that, similarly to other analysis for diffusing systems at hydrodynamic space-time scale [Bertini et al., 2002, 2015*a*], the large deviations function $I(\rho_A|\bar{\rho})$ obeys a second law, meaning that the average work provided by the evolution of the external potential difference is always larger or equal to the difference of the large deviations function between the final and the initial stationary state. In that respect, the large deviations function $I(\rho_A|\bar{\rho})$ plays the role of a non-equilibrium free energy.

Let us in the first place remind the situation at equilibrium. The balance of mass between two systems in contact, controlled by the chemical potentials of each system, can be biased by uniform external potentials. Indeed, adding a potential $U(x) = U_A$ for all $x \in \Lambda_A$ and $U(x) = U_B$ for all $x \in \Lambda_B$ leads to a balance of mass governed by the equalisation of generalised chemical potentials — sometimes called *electro-chemical potentials* — $\mu_k^{\mathrm{eq}} + U_k$, $k = A, B$. Furthermore, when an operator changes $\Delta U = U_A - U_B$ over time, the latter applies a work on the system which brings the densities to a new equilibrium at the end of the transformation. If the transformation is quasi-static, *i.e.* the transformation speed is infinitely slow, then the average supplied

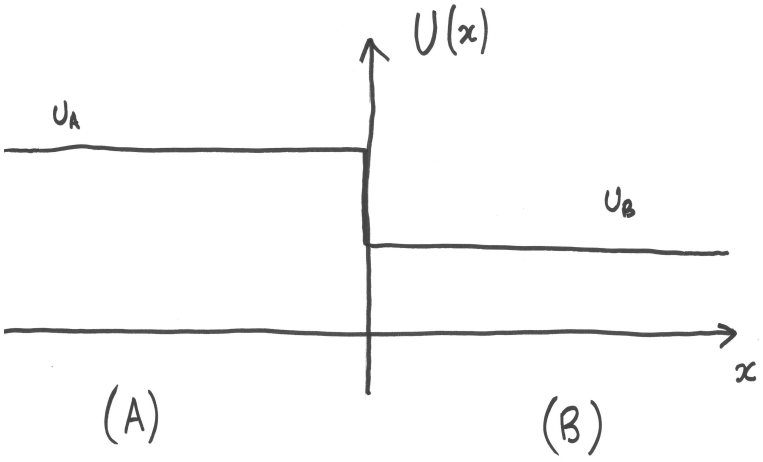

Figure 3.3 – Uniform external potentials U_A and U_B apply on each systems A and B.

work is equal to the difference in the free energy of the whole system. Otherwise, the average supplied work is greater than the difference of free energies. This is what the second law states.

How does this external potential enter our non-equilibrium framework? Of course, applying such uniform piecewise external potential over the two systems in contact tilts the dynamics only at the interface between systems A and B, that is at the contact. If transition rates at contact reads $T_c(\mathcal{C}'|\mathcal{C}) = \tau(\beta(E(\mathcal{C}') - E(\mathcal{C}))$ as assumed previously (see equation (3.10)), the tilted transition rates $T_c^{\Delta U}$ read

$$T_c^{\Delta U}(\mathcal{C}'_A, \mathcal{C}'_B|\mathcal{C}_A, \mathcal{C}_B) = \tau\left[\beta\left(E_A(\mathcal{C}'_A) - E_A(\mathcal{C}_A) + E_B(\mathcal{C}'_B) - E_B(\mathcal{C}_B)\right.\right. \\ \left.\left. + \Delta U(\mathcal{N}(\mathcal{C}'_A) - \mathcal{N}(\mathcal{C}_A))\right]\right. , \tag{3.40}$$

with τ is *a priori* an arbitrary function that must satisfy $\tau(x) = \tau(-x)e^x$ according to the local detailed balance. One should notice that this kind of bias is of the same kind of the general extra-work tilting consider in section 3.1.3. The only difference is that it derives here explicitly from a potential and is thus compatible with equilibrium, in the sens that microscopic detailed balance holds if both systems are undriven.

Before going into details, one should also remark the particularity of our framework, that is to say the vanishing exchange rate at contact. It clearly conditions the response of the system to a perturbation by external potentials: as long as the force generated by ΔU does not increase the microscopic rate $T_c^{\Delta U}$ such that it is no longer of order $\mathcal{O}(\epsilon^1)$, *i.e.* that ΔU doesn't scale with ϵ, the response will be slow. In the vanishing exchanged rate limit, we have seen in 2.2.3 that the systems evolve in a quasi-static way, going back to their steady states after each (rare) exchange. We will assume here that the presence of ΔU will not change this property and that the time variations of ΔU are at the same time scale as the density dynamics (which is slow compared to

the bulk dynamics).

Let us now put this discussion into equations. First, we specify the protocol that the operator performs to go from the initial value ΔU_i and ΔU_f: $\forall\, s \in [0,1]$, one defines the function ΔU_s such that $\Delta U_0 = \Delta U_i$ and $\Delta U_1 = \Delta U_f$. Assuming that the total real time to apply this transformation is T, the instantaneous macroscopic transition rate $\varphi^{\Delta U}_{V,\tau}$ reads

$$\varphi^{\Delta U}_{V,\tau} = \varphi_V(\Delta U(\tfrac{\tau}{T}); \rho, \Delta N) \tag{3.41}$$

for all $\tau \in [0,T]$. Depending on the context and our need of explicit notation, we will use both notations. The biased transition rates $\varphi_V(\Delta U, \rho, \Delta N)$ are average of the tilted microscopic transition rates $T_c^{(\Delta U)}$ with respect to the stationary microscopic distribution of the isolated systems, as in (2.19). Since external potentials are uniform over both sub-systems, the bulk transition rates are not perturbed by their presence and the stationary distribution of isolated systems $P_k(\mathcal{C}_k|\rho_k)$ are the same as in the absence of any external potential tilting.

As we will see henceforth, a crucial property is how the coarse-grained transition rates depend on the external potential difference, and especially its associated force $F^{\Delta U}_V(\rho_A, \Delta N_A)$ defined in equation (2.40). According to the definition (2.19) of the coarse-grained transition rates, one has

$$\varphi^{\Delta U}_V(\rho_A, \Delta N_A) = \sum_{\substack{\mathcal{C}'_A \in \mathcal{E}^{V_A}_{\Delta N_A}(\rho_A) \\ \mathcal{C}'_B \in \mathcal{E}^{V_B}_{-\Delta N_A}(\rho_B)}} \sum_{\substack{\mathcal{C}_A \in \mathcal{E}^{V_A}_0(\rho_A) \\ \mathcal{C}_B \in \mathcal{E}^{V_B}_0(\rho_B)}} T_c^{\Delta U}(\mathcal{C}'_A, \mathcal{C}'_B|\mathcal{C}_A, \mathcal{C}_B) P_{V_A}(\mathcal{C}_A|\rho_A) P_{V_B}(\mathcal{C}_B|\rho_B)\,. \tag{3.42}$$

The bias or generalised force associated with this coarse-grained transition rate reads, at the thermodynamic limit,

$$F^{\Delta U}(\rho_A, \Delta N_A) = F(\Delta U; \rho_A, \Delta N_A) \equiv \ln \frac{\varphi^{\Delta U}(\rho_A, \Delta N_A)}{\varphi^{\Delta U}(\rho_A, -\Delta N_A)} \tag{3.43}$$

At equilibrium, the force $F^{\Delta U}(\rho_A, \Delta N_A)$ would read $-\left(\mu^{\mathrm{eq}}_A(\rho_A) - \mu^{\mathrm{eq}}_B(\rho_B) + \Delta U\right)\Delta N_A$ and thus, the force would be linear in ΔU. But out of equilibrium, it is not at all obvious that such a linearity in the force still holds. As it can be seen in the microscopic definition of the tilted coarse-grained transition rate (3.42), this is naturally a consequence of the choice of $T_c^{\Delta U}$. This led us to consider two classes of transition rates.

1. The first one is the one for which the coarse-grained generalised force (3.43) is linear in ΔU. Hence, the coarse-grained transition rate reads

$$\varphi(\Delta U; \rho_A, \Delta N_A) = a^{\Delta U}(\rho_A, \Delta N_A) e^{\frac{1}{2}\left(F(\rho_A, \Delta N_A) - \beta \Delta U \Delta N_A\right)}\,, \tag{3.44}$$

with $F(\rho_A, \Delta N_A)$ the force in the absence of any tilting, which thus does not depend on the external potentials U_k, $k = A, B$. Interestingly, both the Sasa-Tasaki rule (3.11) and the classical exponential rule (3.12) belong to this class.

2. The second one allows a more complex dependence in ΔU. It reads, in full generality,
$$\varphi(\Delta U; \rho_A, \Delta N_A) = a^{\Delta U}(\rho_A, \Delta N_A) e^{\frac{1}{2}F(\Delta U; \rho_A, \Delta N_A)} , \tag{3.45}$$
where the force $F(\Delta U; \rho_A, \Delta N_A)$ is not linear in ΔU. This is for instance the case for other rules, different from the Sasa-Tasaki and the exponential ones, such as the metropolis rule or the heat-bath (or Kawasaki) rule.

In both classes, one eventually introduces the macroscopic current $J_V(\Delta U, \rho)$ associated with the dynamics in presence of a time-dependent bias $\Delta U(\frac{\tau}{T})$. It reads
$$J_V(\Delta U, \rho_A) = \sum_{\Delta N_A} \Delta N_A \, \varphi_V(\Delta U; \rho_A, \Delta N_A) . \tag{3.46}$$
The most probable relaxation path (which coincides with the average one at the thermodynamic limit) in the presence of a time-dependent forcing thus follows the relaxation dynamics
$$\frac{\mathrm{d}\rho_A(t)}{\mathrm{d}t} = J(\Delta U; \rho_A(t)) , \tag{3.47}$$
with $J = \lim_{V\to\infty} J_V$.

Notations being settled, one can enter the heart of this section which is the study of the work supplied by the protocol ΔU_s for $s \in [0, 1]$. The infinitesimal (stochastic) work supplied by the external operator with the potential difference $\Delta U(s)$ between a time τ and $\tau + \mathrm{d}\tau$ reads
$$\widehat{\delta W}_\tau = -\Delta U(\tfrac{\tau}{T})(\mathcal{N}_A(\mathcal{C}_{\tau+\mathrm{d}\tau}) - \mathcal{N}_A(\mathcal{C}_\tau)) . \tag{3.48}$$
But the stochastic variable $\mathcal{N}_A(\mathcal{C}_\tau)$ follows a Poisson process[2] whose conditionally averaged infinitesimal increments read
$$\langle \mathcal{N}_A(\mathcal{C}_{\tau+\mathrm{d}\tau}) - \mathcal{N}_A(\mathcal{C}_\tau) | \mathcal{N}_A(\mathcal{C}_\tau) = N_A \rangle = \sum_{\Delta N_A \neq 0} \varphi_V(\Delta U(\tfrac{\tau}{T}); \rho_A, \Delta N_A) \Delta N_A . \tag{3.49}$$

[2]More precisely, one should write the following equation
$$\widehat{\delta W}_\tau = -\sum_{\Delta N_A \neq 0} \Delta U(\tfrac{\tau}{T}) \Delta N_A \mathbb{Y}_{\Delta N_A} \left[\varphi_V(\Delta U(\tfrac{\tau}{T}); \widehat{\rho_A}(\tau), \Delta N_A) \mathrm{d}\tau \right] ,$$
with $\mathbb{Y}_{\Delta N_A}[u]$ is a stochastic Poisson variable of parameter u: $\mathrm{Prob}(\mathbb{Y}_{\Delta N}[u] = k) = u^k e^{-u}/k!$ for $k \in \mathbb{N}$. See for instance the presentation of Kurtz in [Kurtz, 1971, 1978].

Thus, the average infinitesimal work reads

$$\left\langle \widehat{\delta W} \right\rangle_\tau = \delta W_\tau = - \sum_{\Delta N_A \neq 0} \sum_{\rho_A} \Delta U(\tfrac{\tau}{T}) \Delta N_A \varphi_V(\Delta U(\tfrac{\tau}{T}); \rho_A, \Delta N_A) P^{\Delta U}_{V,\tau}(\rho_A|\bar{\rho}) \mathrm{d}\tau \,, \tag{3.50}$$

which at large deviations level leads to the following integral work

$$W_{[0,T]} = \int_0^T \delta W_\tau = - \int_0^T \sum_{\Delta N_A \neq 0} \Delta U(\tfrac{\tau}{T}) \Delta N_A \varphi(\Delta U(\tfrac{\tau}{T}); \rho_A(\tau), \Delta N_A) \mathrm{d}\tau \,, \tag{3.51}$$

where $\rho_A(\tau)$ is the solution of the macroscopic equation $\dot{\rho}_A(\tau) = J(\Delta U(\frac{\tau}{T}); \rho_A(\tau))$, as well as the minimum (saddle-point) of the large deviations function $I_\tau(\Delta U(\frac{\tau}{T}), \rho_A)$ associated with the distribution $P^{\Delta U}_{V,\tau}(\rho_A)$ when $V \to \infty$.

In order to be perfectly clear when later on taking the quasi-static limit $T \to \infty$, it is fruitful to change variable from τ to $s = \tau/T$. In this case,

$$W_{[0,T]} = -T \int_0^1 \mathrm{d}s \sum_{\Delta N_A \neq 0} \Delta U(s) \Delta N_A \varphi(\Delta U(s); \rho_A^{(T)}(s); \Delta N_A) \,, \tag{3.52}$$

where $\rho_A^{(T)}(s) = \rho_A(sT)$.

On this basis, our aim is to connect the supplied work $W_{[0,T]}$ with the large deviations function $I(\rho_A|\bar{\rho})$ of the unperturbed dynamics. Although different in several aspects, one can achieve this goal by following the strategy developed by [Bertini et al., 2015*a*,*b*, 2012, 2013] in the context of the Macroscopic Fluctuation Theory[3]. In our setting, the main idea is to replace $\Delta U(s)\Delta N_A$ in the expression of the work (3.52) by the generalised forces $F(\rho_A, \Delta N_A)$ and $F(\Delta U; \rho_A, \Delta N_A)$. As discussed previously, $F(\Delta U; \rho_A, \Delta N_A)$ can be either linear in ΔU or not. It is thus interesting to isolate this linear dependence by introducing

$$F^{\mathrm{NL}}(\Delta U; \rho_A, \Delta N_A) = F(\Delta U; \rho_A, \Delta N_A) + \beta \Delta U \Delta N_A \,. \tag{3.53}$$

The two classes introduced in (3.44) (3.45) thus differ in the ΔU dependence of $F^{\mathrm{NL}}(\Delta U; \rho_A, \Delta N_A)$: for the first class, $F^{\mathrm{NL}}(\Delta U; \rho_A, \Delta N_A)$ is independent of ΔU and is equal to $F(\rho_A, \Delta N_A)$, the force associated with the unbiased transition rates. As for the second class, $F^{\mathrm{NL}}(\Delta U; \rho_A, \Delta N_A)$ does depend on ΔU.

In both cases, one can write $-\Delta U \Delta N_A = F(\Delta U; \rho_A, \Delta N_A) - F^{\mathrm{NL}}(\Delta U; \rho_A, \Delta N_A)$

[3]Even if the frameworks are different, the kind of decomposition we will encounter dates back to the pionneering works of Oono & Paniconi, later developed by Sasa & Hatano, Sasa & Tasaki, [Hatano and Sasa, 2001; Oono and Paniconi, 1998; Sasa and Tasaki, 2006].

and the supplied work (3.52) reads

$$\beta W_{[0,T]} = T\int_0^1 \mathrm{d}s \sum_{\Delta N_A\neq 0}\Big[F(\Delta U(s);\rho_A^{(T)}(s),\Delta N_A) - F^{\mathrm{NL}}(\Delta U(s);\rho_A^{(T)}(s),\Delta N_A)\Big] \times \varphi(\Delta U(s);\rho_A^{(T)}(s);\Delta N_A)\,. \quad (3.54)$$

Some work is still needed to make the connection with the large deviations function of the unperturbed dynamics $I(\rho_A|\bar{\rho})$. Nevertheless, one already expects that if the properties $F^{\mathrm{NL}}(\Delta U;\rho_A,\Delta N_A = F(\rho_A,\Delta N_A)$ and the macroscopic detailed balance both hold, F^{NL} will be equal to $F(\rho_A,\Delta N_A) = -I'(\rho_A|\bar{\rho})\Delta N_A$ which may be a good departure to connect the work with the large deviations function mentioned above. Hence, we first consider this simple case for which a second law holds before briefly moving toward the more complex case for which F^{NL} is genuinely non-linear in ΔU, and thus different from the unperturbed dynamic force F.

3.3.1 Linear tilting in the coarse-grained transition rates

We start with the first class of dynamics for which $F^{\mathrm{NL}}(\Delta U;\rho_A,\Delta N_A) = F(\rho_A,\Delta N_A)$ is independent of ΔU. Then, the average work reads

$$\beta W_{[0,T]} = T\int_0^1 \mathrm{d}s \sum_{\Delta N_A\neq 0}\Big[F(\Delta U(s);\rho_A^{(T)}(s),\Delta N_A) - F(\rho_A^{(T)}(s),\Delta N_A)\Big] \times \varphi(\Delta U(s);\rho_A^{(T)}(s);\Delta N_A)\,. \quad (3.55)$$

As suggested just above, one can glimpse a connection with the large deviations function by remembering now the symmetric and anti-symmetric decomposition of the forces F. Indeed, according to (2.43), one can decompose F into $F^{(S)} + F^{(A)}$ with

$$\begin{aligned} F^{(S)}(\rho_A,\Delta N_A) &= -I'(\rho_A|\bar{\rho})\Delta N_A \\ F^{(A)}(\rho_A,\Delta N_A) &= F(\rho_A,\Delta N_A) - F^{(S)}(\rho_A,\Delta N_A)\,. \end{aligned} \quad (3.56)$$

A natural decomposition follows in the same way for the perturbed process by introducing the associated adjoint dynamics. However, since transition rates depend on time[4] through the perturbation $\Delta U(\tau/T)$, the stationary dynamics is not very well defined. The natural way to proceed is rather to define an adjoint process for each dynamics with a fixed value of the tilting ΔU. It will help to measure the lack of quasi-staticity of the perturbed dynamics, *i.e.* how far the state of the perturbed systems is from the instantaneous stationary point $\rho_A^{*\Delta U}$ of the perturbed dynamics at time τ for which $\Delta U(\tau/T) = \Delta U$. Reproducing the argument outlined in section

[4]Technically speaking, one sometimes says that the process is not autonomous.

2.4.3, one can thus introduce

$$F^{(S)}(\Delta U;\rho_A,\Delta N_A) = -I'_{\Delta U}(\rho_A|\bar{\rho})\Delta N_A \tag{3.57}$$
$$F^{(A)}(\Delta U;\rho_A,\Delta N_A) = F(\Delta U;\rho_A,\Delta N_A) - F^{(S)}(\Delta U;\rho_A,\Delta N_A)\ ,$$

with $I'_{\Delta U}(\rho_A|\bar{\rho})$ the large deviations function associated with the dynamics at *fixed* value of the external potentials difference ΔU.

Using the above decomposition, the work (3.55) reads now

$$\begin{aligned}\beta W_{[0,T]} = T\int_0^1 \mathrm{d}s\ \Big(I'(\rho_A^{(T)}(s)|\bar{\rho}) - I'_{\Delta U(s)}(\rho_A^{(T)}(s)|\bar{\rho})\Big)\, J(\Delta U(s);\rho^{(T)}(s)) \\ + T\int_0^1 \mathrm{d}s \sum_{\Delta N_A\neq 0}\Big[F^{(A)}(\Delta U(s);\rho_A^{(T)}(s),\Delta N_A) - F^{(A)}(\rho_A^{(T)}(s),\Delta N_A)\Big] \\ \times\,\varphi(\Delta U(s);\rho_A^{(T)}(s),\Delta N_A)\ .\end{aligned} \tag{3.58}$$

As we have seen in 2.4.3, the presence of the second term on the right hand side is related to the breaking of time-reversal symmetry or, to put it another way, to the non-vanishing entropy production as shown in appendix A. Thus, it will disappear if macroscopic detailed balance holds.

Let us focus for the moment to the first term involving $I'_{\Delta U}(\rho_A|\bar{\rho}))$ and $I'(\rho_A|\bar{\rho})$. First, one immediately notices that the first term under the integral is a total derivative in time since $\rho_A^{(T)}(s)$ obeys the equation (3.47). The second term is however not a total time derivative since $I'_{\Delta U(s)}$ depends on time. The term in which $I'_{\Delta U}$ is involved can be seen as the large deviations contribution to what can be called the free energy dissipation rate (see [Ge and Qian, 2017]):

$$\dot{\mathcal{F}}_{\mathrm{diss}}(\Delta U;\rho_A) \equiv -I'_{\Delta U}(\rho_A|\bar{\rho})J(\Delta U;\rho_A)\,. \tag{3.59}$$

which happens to be always positive [Ge and Qian, 2017].

Then, the first term in (3.58) reads

$$\Big[I(\rho_A^{(T)}(1)|\bar{\rho}) - I(\rho_A^{(T)}(0)|\bar{\rho})\Big] + T\int_0^1 \mathrm{d}s\,\dot{\mathcal{F}}_{\mathrm{diss}}(\Delta U(s),\rho_A^{(T)}(s))\ . \tag{3.60}$$

A partial conclusion of our analysis at this stage already allows one to write the second law when macroscopic detailed balance holds. Indeed, if so, $F^A = 0$ and one gets

$$\begin{aligned}\beta W_{[0,T]} &= \Big[I(\rho_A^{(T)}(1)|\bar{\rho}) - I(\rho_A^{(T)}(0)|\bar{\rho})\Big] + T\int_0^1 \mathrm{d}s\,\dot{\mathcal{F}}_{\mathrm{diss}}(\Delta U(s),\rho_A^{(T)}(s) \\ &\geqslant \Big[I(\rho_A^{(T)}(1)|\bar{\rho}) - I(\rho_A^{(T)}(0)|\bar{\rho})\Big]\end{aligned} \tag{3.61}$$

since the last term is positive. One would expect that the last term vanishes in the quasi-static limit when $T \to \infty$. Nevertheless, it does not appear completely obvious. To solve this issue, one should look at a perturbative analysis with respect to the small parameter T^{-1}. This is the subject of the next paragraph.

Quasistatic limit and corrections. We analyse what happens when the protocol $\Delta U(s)$ is very slow, *i.e* when $T \to \infty$. $\rho_A^{(T)}(s)$ is solution of the time-dependent macroscopic dynamics

$$\frac{1}{T}\frac{\mathrm{d}\rho_A^{(T)}}{\mathrm{d}s}(s) = J(\Delta U(s); \rho_A^{(T)}(s))\,. \tag{3.62}$$

Looking for a perturbative solution of the form

$$\rho_A^{(T)}(s) = \rho_A^{(0)}(s) + \frac{1}{T}\rho_A^{(1)}(s) + \mathcal{O}(T^{-2}) \tag{3.63}$$

gives

$$J(\Delta U(s); \rho_A^{(0)}(s)) = 0 \quad \Longrightarrow \quad \rho_A^{(0)}(s) = \rho_A^{*\,\Delta U(s)} \tag{3.64}$$

$$\frac{\mathrm{d}\rho_A^{(0)}(s)}{\mathrm{d}s} = \rho_A^{(1)}(s)\frac{\partial J}{\partial \rho_A}(\Delta U(s), \rho_A^{(0)}(s)) \tag{3.65}$$

$$\Longrightarrow \ \rho_A^{(1)}(s) = \frac{\mathrm{d}\rho_A^{(0)}(s)}{\mathrm{d}s}\left(\frac{\partial J}{\partial \rho_A}\right)^{-1}\,. \tag{3.66}$$

Injecting this expansion in the last term involving $\dot{\mathcal{F}}_{\rm diss}$ in equation (3.60) gives, at first order in T^{-1}:

$$\int_0^1 \mathrm{d}s\, \dot{\mathcal{F}}_{\rm diss}(\Delta U(s), \rho_A^{(T)}(s)) = \frac{1}{T}\int_0^1 \mathrm{d}s\, \rho_A^{(1)}(s)\frac{\partial \dot{\mathcal{F}}_{\rm diss}}{\partial \rho}(\Delta U(s), \rho_A^{(0)}) + \mathcal{O}(T^{-2}) \tag{3.67}$$

One has used the fact that $\dot{\mathcal{F}}_{\rm diss}(\Delta U(s); \rho_A^{(0)}(s)) = 0$ since $\rho_A^{(0)}(s) = \rho_A^{*\,\Delta U(s)}$ and that $I'_{\Delta U(s)}$ vanishes at this point.

Eventually, one gets for the first term of (3.60)

$$\Big[I(\rho_A^{(T)}(1)|\bar{\rho}) - I(\rho_A^{(T)}(0)|\bar{\rho})\Big] + \int_0^1 \mathrm{d}s\, \dot{\mathcal{F}}_{\rm diss}(\Delta U(s), \rho_A^{(T)}(s)) \xrightarrow[T\to\infty]{} I(\rho_A^{(T)}(1)|\bar{\rho}) - I(\rho_A^{(T)}(0)|\bar{\rho})\,. \tag{3.68}$$

We have thus demonstrated that the last term of the first equality of (3.61) vanishes at the quasi-static limit.

A second law when macroscopic detailed balance holds

We have already seen that the large deviations function $\beta^{-1}I(\rho_A|\bar{\rho})$ plays the role of a non-equilibrium free energy function and satisfies the second law:

$$W_{[0,T]} \geqslant \beta^{-1}I(\rho_A^{(T)}(1)|\bar{\rho}) - \beta^{-1}I(\rho_A^{(T)}(0)|\bar{\rho})\,. \tag{3.69}$$

As a by-product of our analysis, one has derived, when detailed balance holds, that

$$I'_{\Delta U}(\rho_A|\bar{\rho}) = I'(\rho_A|\bar{\rho}) + \beta\Delta U\,. \tag{3.70}$$

This simply comes from the decomposition of the forces (3.56), (3.57) for $F^{(A)} = 0$ (since macroscopic detailed balance holds), as well as the hypothesis that $F(\Delta U; \rho_A, \Delta N_A)$ is linear in ΔU. Evaluating this expression at $\rho_A = \rho_A^{*\Delta U}$, *i.e* at the stationary state of the dynamics with a presence of a fixed tilt ΔU, cancels $I_{\Delta U}(\rho_A|\bar{\rho})$ and one obtains

$$I'(\rho_A^{*\Delta U}|\bar{\rho}) + \beta\Delta U = 0\,. \tag{3.71}$$

If, in addition to macroscopic detailed balance, additivity holds, the above relation implies the relation postulated on phenomenological grounds by Sasa and Tasaki in their seminal paper [Sasa and Tasaki, 2006] that relates chemical potentials at contact and external potentials

$$\mu_A^{\rm cont}(\rho_A^{*\Delta U}) + \beta U_A = \mu_B^{\rm cont}(\rho_B^{*\Delta U}) + \beta U_B\,. \tag{3.72}$$

This relation can be used to measure the chemical potentials of, say system A, as we will see in a next section devoted to the possible experimental way of measuring the large deviations $I(\rho_A|\bar{\rho})$.

When macroscopic detailed balance does not hold

When macroscopic detailed balance does not hold, the supplied work $W_{[0,T]}$ (3.58) involves house-keeping [Ge and Qian, 2017; Hatano and Sasa, 2001; Oono and Paniconi, 1998] terms that do not vanish, even at the quasi-static limit. They read, according to (3.58),

$$T\int_0^1 {\rm d}s \sum_{\Delta N_A \neq 0} \Big[F^{(A)}(\Delta U(s); \rho_A^{(T)}(s), \Delta N_A) - F^{(A)}(\rho_A^{(T)}(s), \Delta N_A)\Big] \\ \varphi(\Delta U(s); \rho_A^{(T)}(s), \Delta N_A)\,. \tag{3.73}$$

Before going further, one should make an important remark. Indeed, it would be tempting to try to assert a relation between $F^{(A)}(\Delta U; \rho_A, \Delta N_A)$ and $F^{(A)}(\rho_A, \Delta N_A)$

when F is linear in ΔU. Nevertheless, this cannot be done since we do not know *a priori* the dependence in ΔU of $I'_{\Delta U}$. The latter can be determined in general by the Hamilton-Jacobi equation (2.23) of the tilted dynamics. But when macroscopic detailed balance is broken, it is not obvious that the large deviations function stays linear in ΔU, even when $F(\Delta U; \rho_A, \Delta N_A)$ is linear in ΔU and the activity $a^{\Delta U}(\rho_A, \Delta N_A) = a(\rho_A, \Delta N_A)$ does not depend on ΔU. This can be guessed by a perturbation calculation from the Hamilton-Jacobi (2.23) for small ΔU: the term of order ΔU^2 has no reason to vanish.

That being said, the presence of these terms (3.73) – that are sometimes referred to as house-keeping entropy productions (see appendix C and [Ge and Qian, 2017; Hatano and Sasa, 2001; Oono and Paniconi, 1998]) – cannot be avoided even at the quasi-static limit and have to be subtracted in order to have access to the work $W_{[0,T]}$. If one knows by another mean the large deviations function (see next section about the possible experimental measures of the large deviations $I(\rho_A|\bar{\rho})$), a measure of the work could thus be another possibility to assess the presence of a non-zero anti-symmetric force and thus the breaking of the macroscopic detailed balance.

3.3.2 Non-linear bias in the force

We now discuss very briefly the case for which the force $F(\Delta U, \rho_A, \Delta N_A)$ is non-linear in ΔU. Basically, the same calculation as for the linear case still holds but now $F(\rho_A, \Delta U)$ should be replaced by $F^{NL}(\Delta U; \rho_A, \Delta N_A)$ as written in (3.55). Assuming the simple case, *i.e.* the case for which macroscopic detailed balance holds for both dynamics defined by the two forces $F(\Delta U; \rho_A, \Delta N_A) = -I'_{\Delta U}(\rho_A|\bar{\rho})\Delta N_A$, $F^{NL}(\Delta U; \rho_A, \Delta N_A) = -I^{NL\prime}_{\Delta U}(\rho_A|\bar{\rho})\Delta N_A$, and for the same activity $a^{\Delta U}(\rho_A, \Delta N_A)$, one gets in the quasi-static limit,

$$\beta W_{[0,T]} = -\int_0^1 \mathrm{d}s\, I^{NL\prime}_{\Delta U(s)}(\rho_A^{(T)}(s)|\bar{\rho})\dot{\rho}_A^{(T)}(s)\ , \tag{3.74}$$

where $\rho_A^{(T)}(s)$ is the trajectory followed by the perturbed dynamics. Since $I^{NL\prime}_{\Delta U}$ does depend on ΔU, one does not recognise in general a total time derivative and it seems that there does not exist any second law for this non-linear ΔU dependence in the force $F(\Delta U, \rho_A, \Delta N_A)$.

3.3.3 Conclusion on the second law

This rather long discussion aimed at looking for a second law in which the large deviations function of the densities $I(\rho_A|\bar{\rho})$ would play the role of a non-equilibrium free energy. We have found that it is indeed the case if the force $F(\Delta U, \rho_A, \Delta N_A)$ reads $F(\rho_A, \Delta N_A) + \beta\Delta U\Delta N_A$ and if macroscopic detailed balance holds. If the latter con-

straint does not hold, we have seen that new terms involving the anti-symmetric part of the forces F should be considered. Eventually, if the tilted force $F(\Delta U, \rho_A, \Delta N_A)$ involves non-linear contributions of ΔU, it has been sketched that one cannot expect a second law involving the unperturbed large deviations function $I(\rho_A|\bar{\rho})$. This thus questioned the physical meaning of transition rates that would not lead to a linear dependence in ΔU, but this issue will not be treated here and is postponed for future work.

3.4 Contact with a reservoir

We have discussed with some details the general situation where two different systems, whose size ratio $\gamma_A = 1 - \gamma_B$ is arbitrary but finite, are in contact. We would like here to investigate the situation where one of the two systems, say B, is infinitely large compared to the other and plays the role of a reservoir of particles. It corresponds to taking the limit $\gamma_A \to 0$ (and $\gamma_B \to 1$).

Indeed, we have seen that for finite γ_A, the stationary large deviations function of the density ρ_A is solution of the Hamilton-Jacobi equation which involves macroscopic transition rates $\varphi(\rho_A; \Delta N_A)$. The transition rates do not depend explicitly on the volumes of systems A and B which means that $I'(\rho_A|\bar{\rho})$ is independent of γ_A. The only dependence on the size ratio γ_A is hidden in $I'(\rho_A|\bar{\rho})$ through $\rho_B = \gamma_B^{-1}(\bar{\rho} - \gamma_A \rho_A)$. As a consequence, when $\gamma_A \to 0$, $\rho_B \to \bar{\rho}$ which simply means that when B becomes very large compared to A, the difference of mass is such that B does not see its density changed by any exchange of particles of the order of magnitude of the number of particles that A contains.

At the vanishing exchange rate limit, the global stationary probability distribution (2.18) reads, when $\gamma_A \to 0$

$$P(\mathcal{C}_A, \mathcal{C}_B) \sim e^{-V_A I(\rho_A|\bar{\rho})} P_A(\mathcal{C}_A|\rho_A) P_B(\mathcal{C}_B|\bar{\rho}) \,, \tag{3.75}$$

where $\rho_A V_A = \mathcal{N}(\mathcal{C}_A)$ and $\bar{\rho} V_B = \mathcal{N}(\mathcal{C}_B)$. Summing over $\mathcal{C}_B$ at fixed $\mathcal{C}_A$ and inserting $P_A(\mathcal{C}_A|\rho_A) = F_A(\mathcal{C}_A)/Z_A(\rho_A)$ with $F_A(\mathcal{C}_A) = e^{-\beta H(\mathcal{C}_A) + \upsilon(\mathcal{C}_A)}$ the out-of-equilibrium weight of the non-equilibrium stationary measure of the isolated system A (see section 3.1.2), the stationary probability distribution of system A in contact with B is thus given by

$$P(\mathcal{C}_A) \sim F_A(\mathcal{C}_A) e^{V_A(-I(\rho_A|\bar{\rho}) + \psi_A(\rho_A))} \,, \tag{3.76}$$

where $\psi_A(\rho_A) = \lim_{V_A \to \infty} \frac{1}{V_A} \ln Z_A(\rho_A)$. This expression can be read as a generalised grand-canonical distribution. Nevertheless, as one can see in (3.76), the term in the exponential that would be the chemical potential of the reservoir times the number of particles in A if one were at equilibrium is generally very different. Indeed, one can

see that

$$\nu(\rho_A) = \psi_A(\rho_A) - I(\rho_A|\bar{\rho}) \tag{3.77}$$

is generally not linear in ρ_A. When I is additive, $I'(\rho_A|\bar{\rho}) = \mu_A^{\text{cont}}(\rho_A) - \mu_B^{\text{cont}}(\rho_B)$, and ν reads

$$\nu(\rho_A) = \mu_B^{\text{cont}}(\bar{\rho})\rho_A - \int_{\rho_A^*}^{\rho_A} \mathrm{d}\rho \left[\mu_A^{\text{cont}}(\rho) - \mu_A^{\text{iso}}(\rho)\right] , \tag{3.78}$$

where $\mu_A^{\text{iso}} = \mathrm{d}\psi_A/\mathrm{d}\rho_A$. One gets a contribution similar to the equilibrium grand-canonical distribution, namely $\mu_B^{\text{cont}}\rho_A$, but the supplemental term is in general still nonlinear in ρ_A and thus cannot be interpreted as a meaningful correction to the chemical potential of the reservoir: standard grand-canonical mass fluctuations no longer hold in this setting.

To conclude this section, one would like to discuss the notion of ensemble equivalence in our setting. Even if the mass fluctuation term $\nu(\rho_A)$ is not linear in A, the microscopic fluctuations of the configurations $\mathcal{C}_A$ are the same as in the isolated systems as long as the slow exchange limit holds (see (3.75)). Thus, the observed fluctuations of an isolated system A containing a fixed number of particles $N = V_A\rho_A$ can be reproduced in the "grand-canonical" ensemble – *i.e.* with a reservoir – at the thermodynamic limit if $I(\rho_A|\bar{\rho})$ has its minimum at the same target density as the isolated system. In this sense, the vanishing exchange rate at contact guarantees a certain notion of equivalence between ensemble. However, as for the differences between internal fluctuations of mass and global fluctuations of mass (when the system of interest is brought into contact with a reservoir of particles), one can see that the fluctuations are very different if the chemical potential at contact is different from the one attached to the isolated system – when the latter can be defined, *i.e.* generally when there is not any long-ranged correlations inside the system. This later case – which in short reproduces the equilibrium situation – will be discussed in more details in 4.3.2.

3.5 Measure of the large deviations function

An essential issue about the chemical potentials we defined in this out-of-equilibrium context —when they exist!— is our ability to measure them. We briefly discuss here several ways to perform such a measurement. Similarly to the situation at equilibrium, one can think about:

1. putting the system of interest in contact with a “thermometer” whose chemical potential at contact is known. Of course, in our non-equilibrium situation, the property of the contact are important and need to be taken into account when the measure is performed.

2. measuring the stationary densities to get access to the derivative of the large deviations I by biasing the dynamics (with external potentials for instance).

3. measuring the supplied work associated with a given protocol, starting from a known configuration of densities.

Even if our focus will be on the situation for which chemical potentials can be defined, the last two measurement allow us to access the large deviations function in general, additive or not.

3.5.1 Contact with a thermometer

The first natural way one may think of to measure the chemical potential of a system is to put it in contact with a very small known system whose density can be easily measured and thus be calibrated. This situation is exactly the reversed one of the set-up where the system of interest is put in contact with a reservoir. Here, the system of interest, says A, plays the role of the reservoir and the thermometer, says B, is the "small system". This corresponds to the limit $\gamma_A \to 1$ (thus $\gamma_B \to 0$) which intuitively means that the density of system A does not change in this asymptotic limit: the thermometer does not perturb the system of interest. As long as chemical potentials at contact can be defined, *i.e.* that detailed balance and factorisation of transition rates hold, they equalise at the stationary state, leading to

$$\mu_A^{\text{cont}}(\bar{\rho}) = \mu_{\text{therm}}^{\text{cont}}(\rho_{\text{therm}}) \ . \tag{3.79}$$

Thermometer at equilibrium. A particular case is when the thermometer is itself an equilibrium system. Hence, $\mu_{\text{therm}}^{\text{cont}} = \mu_{\text{therm}}^{\text{eq}}$. The equality (3.79) above does depend on the specificity of the contact only through θ_A, the factor that depends on system A, involved in the microscopic transition rates T_c. Anyhow, one has to pay attention to the contact design which needs to produce factorised transition rates at contact. This natural way to measure intensive thermodynamic parameters was the one advocated on a phenomenological ground by [Sasa and Tasaki, 2006].

3.5.2 Biasing the dynamics

Another natural and interesting way to have access to the large deviations function I, already considered in the last section 3.3 by using external potential (see also [Sasa and Tasaki, 2006] for a phenomenological account), is to bias the dynamics to explore rare events of the unbiased dynamics. In contrast with section3.3, we would like to emphasise here the connections between a general bias (which can be different from an external potential difference) and the large deviations function I.

Considering the generating moment function

$$\mathcal{Z}(\lambda) = \left\langle e^{\lambda V_A \rho_A} \right\rangle_{\rm SS} = \sum_{\rho_A} P(\rho_A|\bar{\rho}) e^{\lambda V \rho} \asymp e^{V_A \inf_{\rho_A}(\lambda\rho_A - I(\rho_A|\bar{\rho}))} \tag{3.80}$$

and its associated large deviations rate

$$\chi(\lambda) = \lim_{V_A\to\infty} \frac{1}{V_A} \ln \mathcal{Z}(\lambda) = \lambda\rho_A^*(\lambda) - I(\rho_A^*(\lambda)|\bar{\rho})\,, \tag{3.81}$$

where $\rho^*(\lambda) = mathrmarg\max_{\rho_A}(\lambda\rho_A - I(\rho_A|\bar{\rho})))$. This means that $\rho_A^*(\lambda)$ is the solution, supposed unique in the absence of phase transition, of the equation

$$\lambda = I'(\rho_A^*(\lambda)|\bar{\rho})\,. \tag{3.82}$$

Hence, if one knows the bias λ and is able to measure ρ_A^* by an other mean, the value of the derivative of the large deviations function is straightforward according to (3.82).

But naturally, equation (3.82) is just formal and with no use if the tilting $\lambda V_A\rho_A$ cannot be implemented physically in a real experiment. In section 3.3.1 which has discussed a generalised form of the second law in our specific context, we have seen that biasing the macroscopic transition rates with $\lambda = \beta\Delta U$ such that the tilted force $F(\Delta U; \rho_A, \Delta N_A)$ reads $F(\rho_A, \Delta N_A) - \beta\Delta U$ and assuming macroscopic detailed balance, led to a tilt $\beta\Delta U$ of the large deviations function such that $\beta\Delta U = I'(\rho_A^{*\Delta U}|\bar{\rho})$.

Is it the case for a different modification of the transition rates or without detailed balance? To discuss generally this issue, one considers macroscopic transition rates $\varphi(\lambda; \rho_A, \Delta N_A)$ that depend on an extra-parameter λ that can be controlled by an external operator. λ is a generic name and may be an external potential difference applied on each part of the whole system, or even the driving force applied on one or both systems, etc. We choose λ such that $\varphi(\lambda = 0; \rho_A, \Delta N_A) = \varphi(\rho_A, \Delta N_A)$.

To capture the change induced by such an external parameter on the large deviations function, one can look at its derivative with respect to λ. To be clear, a tilt λ acts linearly as in (3.82) if and only if $\partial I'/\partial\lambda$ is a constant, say[5] $-K$. In general, one can compute $\partial I'/\partial\lambda$ directly from the Hamilton-Jacobi equation (2.23) of the modified dynamics

$$\sum_{\Delta N_A\neq 0} \varphi(\lambda; \rho_A, \Delta N_A) \left(e^{I'(\lambda;\rho_A|\bar{\rho})\Delta N_A} - 1\right) = 0\,. \tag{3.83}$$

[5]In this circumstances, by integration, $I'(\lambda; \rho_A|\bar{\rho}) = I'(\rho_A|\bar{\rho}) - K\lambda$. Evaluating the last equality at $\rho = \rho_A^{*\lambda}$ which is the saddle-point associated with the modified dynamics with λ, one obtains $I'(\rho_A^{*\lambda}|\bar{\rho}) = K\lambda$.

Taking the derivative of (3.83) with respect to λ gives

$$\frac{\partial I'}{\partial \lambda} = \Big(J^\dagger(\lambda;\rho_A)\Big)^{-1}\left[\sum_{\Delta N_A\neq 0}\frac{\partial\varphi}{\partial\lambda}(\lambda;\rho_A;\Delta N_A)\left(e^{I'(\lambda;\rho_A|\bar\rho)\Delta N_A}-1\right)\right] . \tag{3.84}$$

The right hand side of the last equation is not constant in general. When $\varphi(\lambda;\rho_A,\Delta N_A)=\varphi(\rho_A,\Delta N_A)e^{\frac{\lambda}{2}\Delta N_A}$, the latter equation (3.84) reads

$$\frac{\partial I'}{\partial \lambda} = -\frac{J(\lambda;\rho_A)+J^\dagger(\lambda;\rho_A)}{2\,J^\dagger(\lambda;\rho_A)} . \tag{3.85}$$

Of course, when macroscopic detailed balance holds, $J=J^\dagger$ and $\partial I'/\partial\lambda=-1$.

One thus eventually notices that the effect of an external parameter λ leads generally to a perturbation of I which is not linear in λ. Even when the perturbation only changes the "force" $F(\rho;\Delta N_A)$ and not the activity of the macroscopic transition rate, the perturbation is quite complex. The only case for which a linear perturbation holds is when detailed balance holds. Hence, measuring the derivative of the large deviations through the perturbation λ is not always an easy task and generally imposes to possess additional information on its response (see (3.84)).

3.5.3 Work measure

As discussed in section 3.3, when macroscopic detailed balance holds as well as factorisation of transition rates, one can have access to rare events of the unperturbed dynamics by applying uniform external potentials over each sub-systems. By measuring the supplied work necessary to reach in a quasi-static way a certain stationary state, one can have access to the value of the large deviations function for this new stationary state. According to (3.69), one obtains in the quasi-static limit

$$W_{[0,T]} = \beta^{-1}\Big(I(\rho_A^{(f)}|\bar\rho)-I(\rho_A^{(i)}|\bar\rho)\Big) = \beta^{-1}I(\rho_A^{(f)}|\bar\rho) , \tag{3.86}$$

if $\rho_A^{(i)}$ is chosen to be the stationary state of the unperturbed dynamics.

One can also remark that a similar measurement can be performed when macroscopic detailed balance does not hold, if one knows by another mean the anti-symmetric term (3.73) (related to the house-keeping entropy production) that hence needs to be removed to get access to the large deviations function $I(\rho_A|\bar\rho)$.

3.5.4 Conclusion on the measurement procedures

One notices that the measure of the work in the quasi-static limit, as well as the measure of the derivative of the large deviations function through the tilting expounded in 3.5.2, allows one only to measure the whole large deviations function or its derivative

and not chemical potentials directly. Nevertheless, if the latter is additive and known for every accessible densities ρ_A, ρ_B, the two contributions (3.1) can be isolated if one of them is known, for instance if one of the system is at equilibrium.

CHAPTER 4

Lattice models in contact

In this chapter, we investigate the framework proposed in the last chapters 2, 3 on specific lattice models in contact. Examples considers are mostly classic models in the literature [Evans and Hanney, 2005; Katz et al., 1984; Liggett, 2012; Spitzer, 1970; Zia, 2010]. We begin (section 4.1) with a short review of previous studies on two *Zero Range Processes* (ZRP) in contact [Bertin et al., 2006, 2007]. This exactly solvable system is one of the few non-equilibrium examples that reproduces an equilibrium-like situation. Nevertheless, this model has the drawback that its stationary probability distribution does not depend on the driving force[1] and thus does not enable one to observe a genuine difference between chemical potential at contact, μ^{cont}, and chemical potential of the isolated system μ^{iso} (see 3.1.2). This is also the case for other, well-known, simple lattice models uniformly driven on a ring, such as the *Asymmetric Simple Exclusion Model* (ASEP) for instance [Derrida, 1998], for which the stationary probability distribution is outright the equilibrium one. For this reason, we have imagined, with Éric Bertin, an original mass transport model, exactly solvable, which displays a generic dependence of the external driving (also the latter acts a bit differently than a simple uniform driving field). A short presentation of this original model (more details can be found in [Guioth and Bertin, 2017], which is reproduced in appendix C as well as an extensive study of the contact between two of such systems is the subject of the second section (section 4.2). We provide also some numerical simulations that confirms the suitability of the theoretical framework expounded in the first chapters 2 and 3. Then, moving (section 4.3) to space dimensions larger that one, we interpret the most relevant numerical results available in the literature in light with our analysis developed in chapters 2 and 3. The latter would need detailed numerical simulations to be completely validated (since exact solutions of the models considered are not available) but we believe that the analysis available here already gives an interesting

[1] At least for a simple tilting as the one considered in (4.8).

new insight of the available literature on the subject matter. Eventually, we change scale and propose in the last section (section 4.4) a short presentation of the contact between two non-equilibrium systems described by the quite recent *Macroscopic Fluctuation Theory* (MFT) [Bertini et al., 2002, 2015*a*]. The latter finds a natural place here since it was imagined on the basis of studies on driven lattice gases and other lattice models. We will nevertheless see that MFT does not account for the effect observed in microscopic stochastic models since it is actually a framework that deals with weakly driven systems and assumed a local equilibrium hypothesis.

4.1 Case of the Zero Range Process (ZRP)

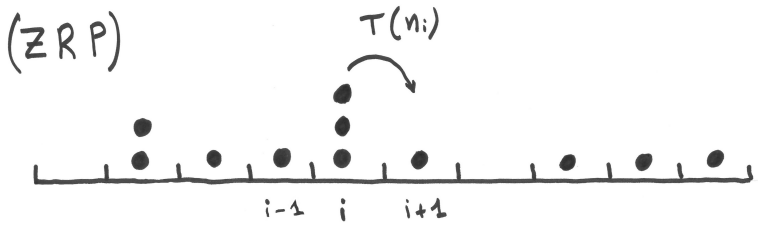

Figure 4.1 – Sketch of a Zero Range Process.

The contact between two non-equilibrium systems has first been investigated on a theoretical side by a work on *Intensive Thermodynamic Parameters* (ITP) [Bertin et al., 2006, 2007; Martens and Bertin, 2011]. The authors considered the particular case of the Zero Range Process (ZRP) that presents a very simple factorised structure. We review principal results of this model in this section.

The ZRP belongs to the general category of mass transport models on lattice [Evans and Hanney, 2005; Evans et al., 2004, 2006*b*; Levine et al., 2005; Zia et al., 2004]. Many different versions of the ZRP[2] exist but we will consider here a model very close to the original model introduced by Spitzer [Spitzer, 1970] which involves discrete masses in one dimension. Each site $i \in [\![1, |\Lambda|]\!]$ is occupied by a mass $n_i \in \mathbb{N}$. Several update rules are possible but one distinguishes in general a *parallel* dynamics for which all sites are updated simultaneously, compared to an *asynchronous* dynamics for which a single particle jumps at a time, randomly chosen. For the latter dynamics that will be considered here, a particle is transfered from site i to site $i+1$ according to the following rate:

$$T(n_i) = a\frac{f_i(n_i - 1)}{f_i(n_i)} \,, \tag{4.1}$$

where a is a site-independent activity parameter, f_i an arbitrary positive function. Of course, mass is conserved and $T(n) = 0$ if $n < 1$. Thus, the explicit transfer reads:

[2]There exist in particular different versions depending on whether the mass exchanged between sites which is discrete or continuous.

$n'_{i+1} = n_{i+1} + 1$ and $n'_i = n_i - 1$, n'_i being the mass at site i after the jump. With this rule, the transport is totally biased and generates a total flux along the ring. As already announced, the stationary probability distribution is completely factorised:

$$P\left(\{n_i\}_{i=1}^{|\Lambda|}\right) = \frac{1}{Z(N)} \prod_{i=1}^{|\Lambda|} f_i(n_i)\, \delta\left(\sum_{i=1}^{|\Lambda|} n_i - N\right) . \tag{4.2}$$

Now, we would like to consider two of such ZRP systems and put them into contact. To simplify the discussion, both systems will be considered to be homogeneous and f_i will not depend on each site i but only on the system $k = A, B$. Also, the activity parameter $a = a_k$ will also depend on the system $k = A, B$. One needs to define explicitly the dynamics at contact which can be chosen to take place at few sites of the two rings. Since both systems are homogeneous, the sites belonging to the contact region are all equivalent. We note $\mathsf{C} = \{(i_A, j_B)\}$ the set of sites (i_A, j_B) of each systems that are linked together. For a transfer of one particle from A to B or from B to A, the microscopic transition rates on the link $(i_A, j_B) \in \mathsf{C}$ read respectively

$$T_{i_A \to j_B}(n_{i_A}) = a_A^{\mathrm{c}} \frac{f_A(n_{i_A} - 1)}{f_A(n_{i_A})} \qquad \text{and} \qquad T_{j_B \to i_A}(n_{j_B}) = a_B^{\mathrm{c}} \frac{f_B(n_{j_B} - 1)}{f_B(n_{j_B})} . \tag{4.3}$$

Even in this heterogeneous contact dynamics, the ZRP model is one of the few model that is exactly solvable. That explains without doubt its strong interest for the first studies published on the subject [Bertin et al., 2006, 2007]. For the set-up described above, the steady-state distribution can be found in the appendix of [Pradhan et al., 2011]. It reads

$$P\left(\{n_{i_A}\}, \{n_{i_B}\}\right) = \frac{1}{Z(N)} \left[\prod_{i_A \in \Lambda_A} f_A(n_{i_A}) \prod_{i_B \in \Lambda_B} f_B(n_{i_B})\right] e^{-\ln(a_A^{\mathrm{c}})\mathcal{N}_A} \times e^{-\ln(a_B^{\mathrm{c}})\mathcal{N}_B}\, \delta\left(\mathcal{N}(\{n_{i_A}\}) + \mathcal{N}_B(\{n_{i_A}\}) - N\right) . \tag{4.4}$$

with $\mathcal{N}(\{n_{i_k}\}) = \sum_{i_k \in \Lambda_k} n_{i_k}$.

Hence, one can compute exactly the stationary probability distribution $P(N_A|N)$ from the distribution of the micro-state without assuming a vanishing exchange rate limit at contact. The latter reads

$$P(N_A|N) = \frac{Z_A(N_A) Z_B(N_B)}{Z(N)} e^{-\left(\ln(a_A^{\mathrm{c}})N_A + \ln(a_B^{\mathrm{c}})N_B\right)} , \tag{4.5}$$

where

$$Z_k(N_k) = \sum_{\{n_i\}_{i\in\Lambda_k}} \prod_{i\in\Lambda_k} f_k(n_i)\delta\left(\sum_{i\in\Lambda_k} n_i - N_k\right) \asymp \exp\left[-|\Lambda_k|\left(\mu_k(\rho_k)\rho_k - \ln g_k(\mu_k(\rho_k))\right)\right] , \tag{4.6}$$

with $\rho_k = N_k/|\Lambda_k|$, $g(\mu) = \sum_{n\geqslant 0} f(n)e^{\mu n}$. The chemical potential $\mu_k(\rho_k)$ is implicitly defined such that such that

$$\frac{g'(\mu_k(\rho_k))}{g(\mu_k(\rho_k))} = \frac{\sum_{n\geqslant 0} nf(n)e^{\mu_k(\rho_k)n}}{\sum_{n\geqslant 0} f(n)e^{\mu_k(\rho_k)n}} = \rho_k$$

The chemical potentials μ_k, $k = A,\ B$, are then chemical potentials associated with isolated systems. The stationary densities are then given by the equalisation of chemical potentials which reads [Pradhan et al., 2011, see appendix]

$$\mu_A(\rho_A) + \ln(a_A^{\mathrm{c}}) = \mu_B(\rho_B) + \ln(a_B^{\mathrm{c}}) . \tag{4.7}$$

The excess chemical potential $\ln(a_k^{\mathrm{c}})$ are reminiscent of the difference in the activity of the jumps from A to B compared to from B to A. They can be interpreted as (the logarithm of) effective temperatures which are not uniform over the two systems, thus producing a bias. Nevertheless, we should stress that this bias is already present in the microscopic transition rates and corresponds to an additional force in the contact region, as discussed in section (3.1.3). The latter is thus not due to a genuine breaking of the microscopic detailed balance at contact as discussed in chapter 2.

These exact computations are made possible by the factorisation property of the stationary distribution which is definitely not ubiquitous in the realm of non-equilibrium driven systems. Also, the transport is totally biased and leads to an infinite entropy production which is thus not controlled by any parameter like a driving force for instance. This totally biased dynamics can be relaxed if one also allows exchange from to the left from site i to site $i-1$ with a probability p_{L}. The probability to jump to the right is then $p_{\mathrm{R}} = 1 - p_{\mathrm{L}}$. The transition rates reads in this case

$$T_{i\to i+1}(n_i) = p_{\mathrm{R}}T(n_i) \qquad T_{i\to i-1}(n_i) = p_{\mathrm{L}}T(n_i) . \tag{4.8}$$

When $p_{\mathrm{R}} = p_{\mathrm{L}} = \frac{1}{2}$, the system is unbiased and one can recover the totally biased system when $p_{\mathrm{R}} = 1$. But whatever the choice of p_{R}, p_{L}, it can be shown that the stationary probability distribution does not depend on the bias and takes the same form as in the totally biased system (4.2) [Evans and Hanney, 2005; Evans et al., 2004, 2006*b*]. In particular, the unbiased system verifies detailed balance with respect to the same probability distribution as the totally biased system. Hence the stationary

probability distribution does not depend on the forcing and so the chemical potentials (4.7) defined above.

However, several numerical simulations of different driven lattice gas that will be discussed henceforth (see [Dickman, 2014, 2016; Dickman and Motai, 2014]) as well as general theoretical arguments [Colangeli et al., 2011; Maes and Netočnỳ, 2010; McLennan Jr, 1959] have shown that one could expect a generic dependence of the external driving force (see related discussion in chapter 3). In order to study such a dependence we have imagined a new mass transport model inspired by the ZRP whose stationary distribution can also be exactly computed and shows an explicit dependence on the driving force. A brief description of this system is the object of the next section.

4.2 A new mass transport model

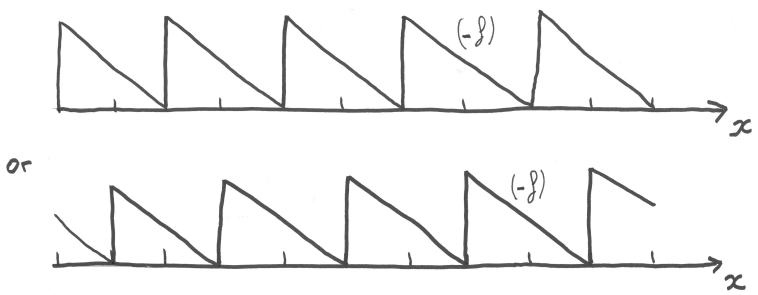

Figure 4.2 – Sketch of the of the oscillating driving force of our mass transport model.

As for the ZRP, one considers a one dimensional lattice Λ of $|\Lambda|$ sites. The number of sites is assumed to be even and we write $|\Lambda| = 2L$ with L an integer. Each site i is occupied by $n_i \geqslant 0$ particles that cannot exceed a maximum number of $n_{\max}$ particles per site, that may be infinite. The dynamics of this new model is inspired by an equilibrium KCM (Kinetically Constrained Models) model [Bertin et al., 2005] as well as by the ZRP [Evans and Hanney, 2005]. Contrary to most of the standard mass transport models, the dynamics is *synchronous* and involves two partitions of the lattice, namely $\mathcal{P}_1 = \{(2k, 2k+1)\}_{k\in[\![0,L]\!]}$ and $\mathcal{P}_2 = \{(2k+1, 2k+2)\}_{k\in[\![0,L]\!]}$ which gather alternate adjacent pairs of sites. A partition is selected – at a rate that will be defined henceforth – randomly between $\mathcal{P}_1$ and $\mathcal{P}_2$ with equal probability. Once a partition $\mathcal{P}_j$ has been chosen, all links belonging to $\mathcal{P}_j$ are updated in parallel and independently. A link $(i, i+1)$ is updated according to the following transition rate

$$T(n'_{i+1}, n'_i | n_{i+1}, n_i) = K(d'_i|\bar{n}_i) = \frac{\exp\left\{-\left[\varepsilon\left(\bar{n}_i + \frac{d'_i}{2}\right) + \varepsilon\left(\bar{n}_i - \frac{d'_i}{2}\right)\right] + \frac{f}{2}d'_i\right\}}{Q(\bar{n}_i)}. \quad (4.9)$$

with $n'_{i+1} + n'_i = n_{i+1} + n_i$ since mass is conserved ($T = 0$ otherwise). One has called

$d'_i = n'_{i+1} - n'_i$ and $\bar{n}_i = (n_i + n_{i+1})/2 = (n'_i + n'_{i+1})/2$. $Q(\bar{n}_i)$ is a normalisation factor such that $\sum_{n'_1,n'_2} T(n'_2, n'_1|n_1, n_2) = 1$. We emphasise that the net transfer of particles $\Delta n_i = (n'_i - n_i) = -(n'_{i+1} - n_{i+1})$ from site i to site $i+1$ is given by $\Delta n_i = (d'_i - d_i)/2$ with $d_i = n_{i+1} - n_i$. One then notices that the probability to choose a density gap d'_i between site i and $i+1$ is independent of d_i which means that the probability to transfer Δn_i particles does not depend on the initial difference in density of the two sites as one might expect intuitively for a mass transport model. In the absence of f, the uniform energy $\varepsilon(n)$ attached to each site tends to flatten the density over the link (if we assume $\varepsilon(n)$ convex). The parameter f can be interpreted as a driving force since it pushes particles toward the site $i+1$ whatever the initial configuration. In terms of local detailed balance, on has:

$$\ln \frac{T(n'_{i+1}, n'_i|n_{i+1}, n_i)}{T(n_{i+1}, n_i|n'_{i+1}, n'_i)} = -\Delta\varepsilon_{i+1} - \Delta\varepsilon_i + f\Delta n_i \tag{4.10}$$

with $\Delta\varepsilon_i = \varepsilon(n'_i) - \varepsilon(n_i)$. Hence, equation (4.10) confirms the interpretation of f as a driving force since $f\Delta n_i$ can be interpreted as the non-equilibrium work needed to move a mass Δn_i from site i to site $i+1$. As for the alternation of the partition choice, one can imagine that this is produced by an oscillating confining potential of two sites period. In the presence of a driving force f, the oscillating potential would look more like a saw-tooth potential of slope $-f$ as shown on figure 4.2.

The stationary probability density function can be exactly computed (see [Guioth and Bertin, 2017], reproduced in appendix C for the continuous mass version of this model but the calculations are the same) and reads

$$P\left(\{n_i\}_{i\in\Lambda}\right) = \frac{2}{Z(|\Lambda|, N)} \exp\left(-\sum_{i\in\Lambda} \varepsilon(n_i)\right) \cosh\left(\sum_{i\in\Lambda} (-1)^i f n_i\right) . \tag{4.11}$$

One thus observes that the stochastic oscillating forcing produces long-range static correlations that can be guessed by the presence of the hyperbolic cosine term in (4.11) (see [Guioth and Bertin, 2017] or appendix C for detailed calculations of the static two-points correlation function).

4.2.1 Isolated chemical potential

Even if the distribution P is not factorised, one can define a chemical potential associated with one isolated system, related to the partition function $Z(|\Lambda|, N)$. Indeed, from the normalisation of the stationary probability (4.11) the partition function of

our model reads

$$Z(|\Lambda|,N)=2\sum_{\{n_i\}_{i\in\Lambda}}\left[\prod_{k=1}^{L}f_+(n_{2k})f_-(n_{2k+1})\right]\delta_{\sum_{i\in\Lambda}n_i,N} \tag{4.12}$$

where $f_+(n)=\exp\left[-\varepsilon(n)+fn\right]$ and $f_-(n)=\exp\left[-\varepsilon(n)-fn\right]$. Introducing the Fourier transform of the Kronecker delta, one obtains

$$Z(|\Lambda|,N)=2\int_{-\pi}^{\pi}\mathrm{d}\theta e^{-|\Lambda|\left[i\theta\bar{\rho}-\frac{1}{2}\ln(z_+(i\theta)z_-(i\theta))\right]}, \tag{4.13}$$

where one has introduced $z_\alpha(x)=\sum_n f_\alpha(n)e^{xn}$, $\alpha=\pm$ and $\bar{\rho}=N/|\Lambda|$. Assuming that there is only one saddle-point at $\mu(\bar{\rho})$, the partition function eventually reads

$$Z(|\Lambda|,N)\asymp e^{-|\Lambda|\left[\mu(\bar{\rho})\bar{\rho}-\frac{1}{2}\ln(z_+(\mu(\bar{\rho}))z_-(\mu(\bar{\rho})))\right]} \tag{4.14}$$

with the implicit equation verified by $\mu(\bar{\rho})$ reading

$$\bar{\rho}=\frac{1}{2}\left(\frac{z'_+(\mu(\bar{\rho}))}{z_+(\mu(\bar{\rho}))}+\frac{z'_-(\mu(\bar{\rho}))}{z_-(\mu(\bar{\rho}))}\right). \tag{4.15}$$

The quantity $\mu(\bar{\rho})$ is naturally interpreted as the chemical potential associated with the isolated system.

Single site marginal distribution. Integrating over all except one site the stationary distribution (4.11), the single site probability distribution reads

$$\begin{aligned}P(n|\bar{\rho})&=\frac{\exp\left[\mu(\bar{\rho})n\right]}{2}\left(\frac{f_+(n)}{z_+(\mu(\bar{\rho}))}+\frac{f_-(n)}{z_-(\mu(\bar{\rho}))}\right)\\&=\frac{\exp\left[\mu(\bar{\rho})n-\varepsilon(n)\right]}{z_0(\mu(\bar{\rho}))}\exp\left(\upsilon[\mu,f](n)\right)\end{aligned} \tag{4.16}$$

with

$$\exp\left(\upsilon[\mu,f](n)\right)=\frac{z_0(\mu)}{2}\left(\frac{e^{fn}}{z_+(\mu)}+\frac{e^{-fn}}{z_-(\mu)}\right).$$

The quantity $z_0(x)$ reads $\sum_n f_0(n)e^{xn}$, where $f_0(n)=\exp\left[-\varepsilon(n)\right]$, *i.e.* the stationary weight for the driving force $f=0$.

4.2.2 Definition of the contact

We now move to the study of the contact between two different systems say A and B. As for the ZRP case, one needs to define precisely the dynamics at contact since

only isolated systems have been defined insofar. We naturally adopt the framework expounded in chapter 2. We want to connect both systems to each other with at least one link, say $i_A \in \Lambda_A$ and $j_B \in \Lambda_B$. But contrary to the bulk dynamics for which all links are updated in parallel, the contact dynamics is assumed not to be synchronous with respect to the bulk. An exchange between both systems is thus selected at a rate very small compared to the bulk one of each system. The dynamics at contact needs to satisfy local detailed balance without any forcing since there is *a priori* no reason that the transition rates change when systems are driven out-of-equilibrium *orthogonally* to the contact. Since an energy $e(n_i)$ is attached to each site filled by n_i particles, we set T_c, the transition rate at contact, such that it satisfies the local detailed balance that reads

$$\frac{T_{\mathrm{c}}(n'_{i_A}, n'_{j_B}|n_{i_A}, n_{j_B})}{T_{\mathrm{c}}(n_{i_A}, n_{j_B}|n'_{i_A}, n'_{j_B})} = \exp\Big\{-\Big[\varepsilon_A(n'_{i_A}) - \varepsilon_A(n_{i_A})\Big]\Big\} \exp\Big\{-\Big[\varepsilon_B(n'_{j_B}) - \varepsilon_B(n_{j_B})\Big]\Big\} \ , \tag{4.17}$$

if the mass conservation $n'_{i_A} + n'_{j_B} = n_{i_A} + n_{j_B}$ holds, and $T_c = 0$ otherwise. From here we will consider different dynamics that will differ by a different choice of the "activity" parameter [Maes et al., 2008; Maes and Netočný, 2008] (we recall that the activity refers to the parameter a in the decomposition $T_c(\mathcal{C}'|\mathcal{C}) = a(\mathcal{C}, \mathcal{C}')e^{\frac{F(\mathcal{C},\mathcal{C}')}{2}}$ according to which $a(\mathcal{C}, \mathcal{C}') = a(\mathcal{C}', \mathcal{C})$ and $F(\mathcal{C}, \mathcal{C}') = -F(\mathcal{C}', \mathcal{C})$).

Natural Dynamics. In this case, one chooses a transition rate at contact that looks like the dynamics in the bulk, *i.e.* the transition rates depends on the final configuration:

$$T_{\mathrm{c}}(n'_{i_A}, n'_{j_B}|n_{i_A}, n_{j_B}) \propto \exp\Big[-\varepsilon_A(n'_{i_A})\Big] \exp\Big[-\varepsilon_B(n'_{j_B})\Big] \ . \tag{4.18}$$

Sasa-Tasaki's rule. For the Sasa-Tasaki's rule which models a high energy barrier separating both systems, the probability to transfer a particle from A to B (resp. from B to A) only depends on the energy to go from the A side (resp. B side) bottom of the barrier to its top. Hence, it reads:

$$T_{\mathrm{c}}(n'_{i_A}, n'_{j_B}|n_{i_A}, n_{j_B}) \propto \begin{cases} \exp\Big\{-\Big[\varepsilon_A(n'_{i_A}) - \varepsilon_A(n_{i_A})\Big]\Big\} & \text{if } n'_{i_A} < n_{i_A} \\ \exp\Big\{-\Big[\varepsilon_B(n'_{j_B}) - \varepsilon_B(n_{j_B})\Big]\Big\} & \text{if } n'_{i_A} > n_{i_A} \end{cases} \tag{4.19}$$

Kawasaki-Heat bath rule. This choice of transition rate is a classic one and does not factorise in two terms that respectively depend on A and B:

$$T_{\mathrm{c}}(n'_{i_A}, n'_{j_B}|n_{i_A}, n_{j_B}) \propto \frac{2}{1 + \exp\Big\{\Big[\varepsilon_A(n'_{i_A}) - \varepsilon_A(n_{i_A})\Big] + \Big[\varepsilon_B(n'_{j_B}) - \varepsilon_B(n_{j_B})\Big]\Big\}} \ . \tag{4.20}$$

The symbol $\propto$ means here that the transition rates are equal to the right hand side up to a constant factor that set the typical time scale associated with the transition. In the slow contact limit, the latter factor will be infinitesimally small.

4.2.3 Large deviations function and chemical potentials

Having specified the dynamics, we will compute here the large deviations function of the density. Under the hypothesis that the exchange of particles between systems are very rare, the coarse-grained transition rates (2.19) reads

$$\varphi(\rho_A, \Delta n) = \sum_{n_{i_A}, n_{j_B}} T(n_{i_A} + \Delta n, n_{j_B} - \Delta n | n_{i_A}, n_{j_B}) P(n_{i_A}|\rho_A) P(n_{j_B}|\rho_B) \ . \tag{4.21}$$

The notations used are the same as in chapter 2.

One-particle exchange

When only one particle can be exchanged, the macroscopic detailed balance (2.35) always holds. To illustrate the dependence of the large deviations function – and thus the possible chemical potentials – with respect to the dynamics at contact, we compute the latter for the three contact dynamics presented in section 4.2.2.

Natural Dynamics. For the natural dynamics, the coarse-grained transition rates reads

$$\begin{aligned}
\varphi(\rho_A, +1) &= \left[\sum_{n_{i_A}=0}^{n^A_{\max}-1} e^{-\varepsilon_A(n_{i_A}+1)} P(n_{i_A}|\rho_A) \right] \left[\sum_{n_{j_B}=1}^{n^B_{\max}} e^{-\varepsilon_B(n_{j_B}-1)} P(n_{j_B}|\rho_B) \right] \\
\varphi(\rho_A, -1) &= \left[\sum_{n_{i_A}=1}^{n^A_{\max}} e^{-\varepsilon_A(n_{i_A}-1)} P(n_{i_A}|\rho_A) \right] \left[\sum_{n_{j_B}=0}^{n^B_{\max}-1} e^{-\varepsilon_B(n_{j_B}+1)} P(n_{j_B}|\rho_B) \right]
\end{aligned} \tag{4.22}$$

with $|\Lambda_B|\rho_B = N - |\Lambda_A|\rho_A$. Since microscopic transition rates are factorised, chemical potentials associated with each system can be defined and reads, according to (3.5),

$$\mu_k^{\text{cont}}(\rho_k) = \ln \frac{\sum_{n_k=0}^{n^k_{\max}-1} e^{-\varepsilon_k(n_k)} P(n_k+1|\rho_k)}{\sum_{n_k=0}^{n^k_{\max}-1} e^{-\varepsilon_k(n_k+1)} P(n_k|\rho_k)} \ . \tag{4.23}$$

where $k = A,\ B$. Using the expression of the single site probability distribution (4.16), one finally obtains

$$\mu_k^{\text{cont}}(\rho_k) = \mu_k^{\text{iso}}(\rho_k) + \ln \frac{\sum_{n_k=0}^{n^k_{\max}-1} e^{-\left[\varepsilon_k(n_k)+\varepsilon_k(n_k+1)+\mu_k^{\text{iso}} n_k\right]} e^{\upsilon[\mu_k^{\text{iso}}, f_k](n+1)}}{\sum_{n_k=0}^{n^k_{\max}-1} e^{-\left[\varepsilon_k(n_k)+\varepsilon_k(n_k+1)+\mu_k^{\text{iso}} n_k\right]} e^{\upsilon[\mu_k^{\text{iso}}, f_k](n)}} \ . \tag{4.24}$$

One recognises the excess chemical potential that adds to the chemical potential $\mu_k^{\rm iso}$ of the isolated system k.

Sasa-Tasaki's rule. For the Sasa & Tasaki's dynamics rule, the coarse-grained transition rates reads

$$\varphi(\rho_A,+1) = \left[\sum_{n_{i_A}=0}^{n_{\max}^A-1} P(n_{i_A}|\rho_A)\right]\left[\sum_{n_{j_B}=1}^{n_{\max}^B} e^{-\left[\varepsilon_B(n_{j_B}-1)-\varepsilon_B(n_{j_B})\right]}P(n_{j_B}|\rho_B)\right] \tag{4.25}$$
$$\varphi(\rho_A,-1) = \left[\sum_{n_{i_A}=1}^{n_{\max}^A} e^{-\left[\varepsilon_A(n_{i_A}-1)-\varepsilon_A(n_{i_A})\right]}P(n_{i_A}|\rho_A)\right]\left[\sum_{n_{j_B}=0}^{n_{\max}^B-1} P(n_{j_B}|\rho_B)\right]$$

with again $|\Lambda_B|\rho_B = N - |\Lambda_A|\rho_A$. One can also notice that the exclusion rule, *i.e.* that there can be at most $n_{\max}$ particle on a single site, adds a dependence of the recipient system although the transition rates only involve energy exchanges from the sender system. The term reminiscent to the exclusion rule reads $\sum_{n_k}^{n_{\max}} P(n_k|\rho_k) = 1 - P(n_{\max}^k|\rho_k)$ by normalisation. When $n_{\max}\to\infty$, one expects $P(n_{\max}^k|\rho_k)\to 0$ and this extra-dependence vanishes. Beyond this remark, the situation appears to be the same as in the previous case and chemical potentials read

$$\mu_k^{\rm cont}(\rho_k) = \ln \frac{\sum_{n_{i_A}=1}^{n_{\max}^A} e^{-\left[\varepsilon_A(n_{i_A}-1)-\varepsilon_A(n_{i_A})\right]}P(n_{i_A}|\rho_A)}{1-P(n_{\max}^k|\rho_k)}\,. \tag{4.26}$$

In terms of $\mu_k^{\rm iso}$, the chemical potential at contact reads this time

$$\mu_k^{\rm cont}(\rho_k) = \mu_k^{\rm iso}(\rho_k) + \ln \frac{\sum_{n_k=0}^{n_{\max}^k-1} e^{-\varepsilon_k(n_k)+\mu_k^{\rm iso}n_k}e^{v[\mu_k^{\rm iso},f_k](n_k+1)}}{\sum_{n_k=0}^{n_{\max}^k-1} e^{-\varepsilon_k(n_k)+\mu_k^{\rm iso}n_k}e^{v[\mu_k^{\rm iso},f_k](n_k)}}\,. \tag{4.27}$$

The excess chemical potential reads thus different from the "natural dynamics" case.

Kawasaki rule. Eventually, for the Kawasaki rule, the coarse-grained transition rates reads

$$\varphi(\rho_A,+1) = \sum_{n_{i_A}=0}^{n_{\max}^A-1}\sum_{n_{j_B}=1}^{n_{\max}^B} \frac{2P(n_{i_A}|\rho_A)P(n_{j_B}|\rho_B)}{1+e^{\varepsilon_A(n_{i_A}+1)-\varepsilon_A(n_{i_A})+\varepsilon_B(n_{j_B}-1)-\varepsilon_B(n_{j_B})}} \tag{4.28}$$
$$\varphi(\rho_A,-1) = \sum_{n_{i_A}=1}^{n_{\max}^A}\sum_{n_{j_B}=0}^{n_{\max}^B-1} \frac{2P(n_{i_A}|\rho_A)P(n_{j_B}|\rho_B)}{1+e^{\varepsilon_A(n_{i_A}-1)-\varepsilon_A(n_{i_A})+\varepsilon_B(n_{j_B}+1)-\varepsilon_B(n_{j_B})}}\,.$$

Here the microscopic rates do not factorise and one cannot define proper chemical potential. The derivative of the large deviations function (2.35) nevertheless reads

$$I'(\rho_A|\bar{\rho}) = \mu_A^{\text{iso}} - \mu_B^{\text{iso}} + \ln\left[\sum_{n_{i_A}=0}^{n_{\max}^A-1}\sum_{n_{j_B}=0}^{n_{\max}^B-1}\frac{2e^{\mu_A^{\text{iso}}n_{i_A}+\mu_B^{\text{iso}}n_{j_B}}e^{\upsilon[\mu_A^{\text{iso}},f_A](n_{i_A}+1)+\upsilon[\mu_B^{\text{iso}},f_B](n_B)}}{e^{\varepsilon_A(n_{i_A}+1)+\varepsilon_B(n_{j_B})}+e^{\varepsilon_B(n_{j_B}+1)+\varepsilon_A(n_{i_A})}}\right] - \ln\left[\sum_{n_{i_A}=0}^{n_{\max}^A-1}\sum_{n_{j_B}=0}^{n_{\max}^B-1}\frac{2e^{\mu_A^{\text{iso}}n_{i_A}+\mu_B^{\text{iso}}n_{j_B}}e^{\upsilon[\mu_A^{\text{iso}},f_A](n_{i_A})+\upsilon[\mu_B^{\text{iso}},f_B](n_B+1)}}{e^{\varepsilon_A(n_{i_A}+1)+\varepsilon_B(n_{j_B})}+e^{\varepsilon_B(n_{j_B}+1)+\varepsilon_A(n_{i_A})}}\right]. \quad (4.29)$$

Some comments

When $n_{\max} = 1$. The first comment we would like to make is that when there is at most one particles on each site, *i.e.* that $n_{\max}^k = 1$ for both systems, $P(n_k|\rho_k) = \rho_k$ by translation symmetry and is thus independent of the driving force f. In this case, one recovers an equilibrium situation and stationary densities are given by the equality of the equilibrium chemical potential $\mu_k^{\text{cont}}(\rho_k) = \mu_k^{\text{eq}}(\rho_k) = \ln(\rho_k/(1-\rho_k))$.

Contact along several links. The contact we defined heretofore was built along one single link involving only two sites. Of course, in general, several links can be involved in the contact area. But since the dynamics is asynchronous, *i.e.* that only one link can be chosen at a time, and rare, one does not expect to observe any effect related to the extension of the area. Numerical simulations performed confirm this hypothesis (see below).

Numerical simulations & explicit examples

In all cases studied, the excess chemical potentials – or excess large deviations derivative – is non-zero because of the presence of the non-equilibrium term $e^{\upsilon[\mu^{\text{iso}},f](n)}$. But one can wonder what is the magnitude of these correction terms compared to the chemical potential of the isolated systems. In order to address this question, we provide some plots of the chemical potentials at contact in different situations.

We fix the maximum number of particles at $n_{\max} = 2$ and we choose a simple linear energy function $\varepsilon(n) = \varepsilon n$. The first figure (see figure 4.3) represents the isolated chemical potential as well as the "excess" chemical potential. One can observe that for $f \geqslant 0.5$, μ^{ex} becomes of the same order of magnitude as μ^{iso} and one thus may expect a clear effect of the forcing coupled to the particular dynamics at play. Furthermore, one can observe that for a sufficiently high driving force f, a significant difference between the excess chemical potential associated with both dynamics, namely the "natural dynamics" and the "Sasa & Tasaki" dynamics, appears.

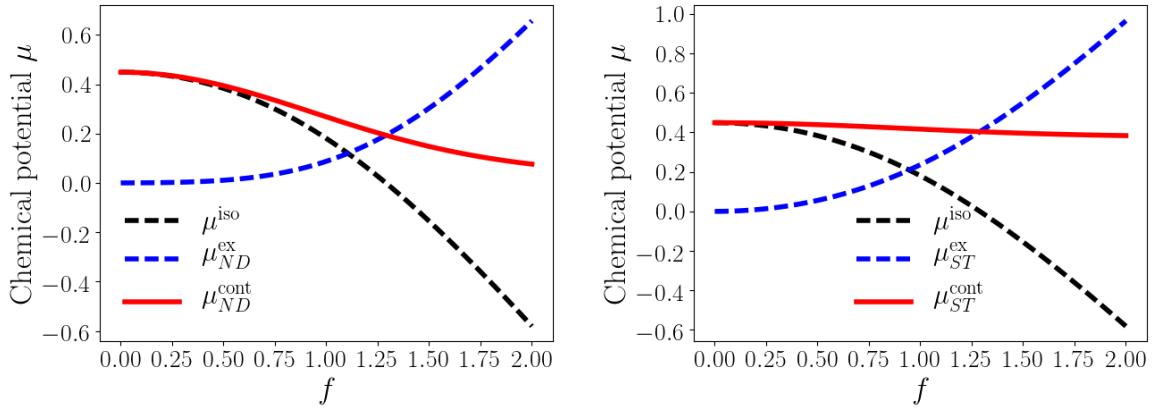

Figure 4.3 – Plots of the chemical potentials associated with one system. The parameters are $n_{\max} = 2$, $\rho = 0.65$, and an energy parameter $\varepsilon = 1$ (for $\varepsilon(n) = \varepsilon n$). The chemical potentials μ^{iso} (dashed-black curve), μ^{ex} (blue-dashed curve) and μ^{cont} (red curve) are plotted as functions of the forcing f. Left panel: natural dynamics (ND), right panel: Sasa-Tasaki (ST).

In order to show how this non-equilibrium effect can strongly perturb the equilibrium stationary state of the system, we provide some plots (see figure 4.4) directly stemmed from direct numerical simulations of our model. We mention that we used 50 links at contact with a typical exchange frequency at contact $\epsilon = 0.01$ in order to guarantee an effective time-scale separation between the bulk and the contact. We put two systems of same size ($|\Lambda| = 10000$ sites) in contact and keep the driving force of the system B equal to $f_B = 2$. By symmetry, for $f_A = 2$, the densities in each system should be the same, namely $\rho_A = \rho_B = \bar{\rho} = 0.5$. This is what we observe. But when f_A moves away from $f_B = 2$, one can observe that the stationary density difference grows as well, leading to a significant effect. Also, as one can see on figure 4.4, the agreement between theory and simulations is very good for this non-zero – but small – value of ϵ.

More than one particle exchange

After all, more than one particle can be exchanged in the bulk of each system: there is no reason for it to be different at contact for our set-up. Assuming that $n_{\max} = 2$ in each system A and B, at most two particles can be exchanged along one link. Hence, one assumes that two particles are also able to be exchanged at contact at a time. The expressions for $\varphi(\rho_A, \Delta n = \pm 1)$ stay the same as in (4.22), (4.25) and (4.28). Our goal here is to provide expressions for $\varphi(\rho_A, \Delta n = \pm 2)$ for each transition types described above and discuss whether macroscopic detailed balance holds or not.

Natural Dynamics. Since, $|\Delta n| = 2 = n_{\max}$, there is only one initial local configuration that can lead to an exchange of two particles. Coarse-grained transition rates

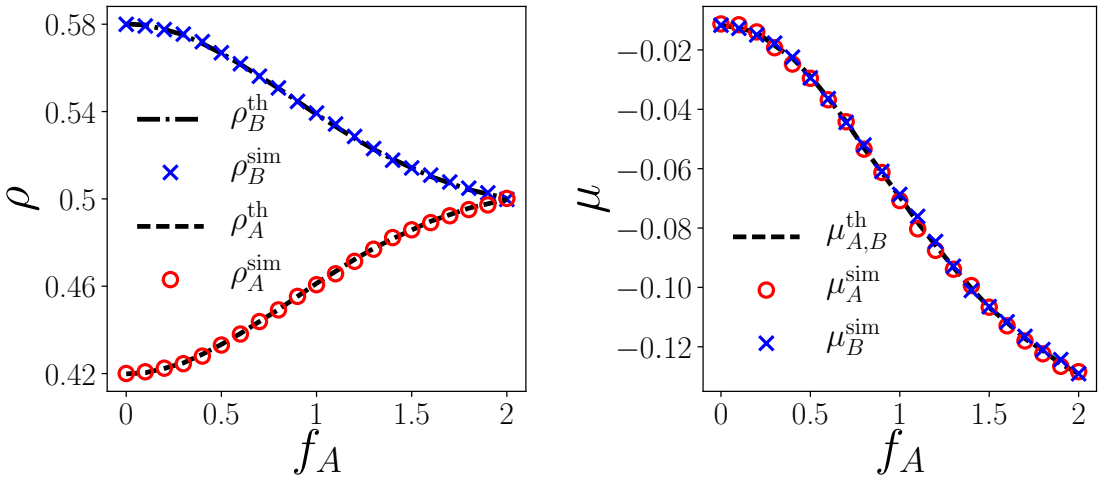

Figure 4.4 – Numerical simulations of two lattice models A and B in contact, with different drivings. Left: Densities ρ_A (red) and ρ_B (blue) versus time. Right: Chemical potentials $\mu_A^{\rm cont}$ (red) and $\mu_B^{\rm cont}$ (blue). The dashed lines are the theoretical predictions. Parameters: $|\Lambda_A| = |\Lambda_B| = 10000$, $\bar{\rho} = 0.5$. The dynamics that has been used is the "Natural Dynamics" (ND).

read

$$\begin{aligned}\varphi(\rho_A,+2) &= e^{-\varepsilon_A(2)-\varepsilon_B(0)}P(0|\rho_A)P(2|\rho_B)\\ \varphi(\rho_A,-2) &= e^{-\varepsilon_A(0)-\varepsilon_B(2)}P(2|\rho_A)P(0|\rho_B)\end{aligned} \tag{4.30}$$

Inserting the exact expression of the stationary single site distribution (4.16), one obtains

$$\begin{aligned}\frac{1}{2}\ln\frac{\varphi(\rho_A,-2)}{\varphi(\rho_A,+2)} &= \mu_A^{\rm iso}(\rho_A)-\mu_B^{\rm iso}(\rho_B)\\ &+\frac{(v[\mu_A^{\rm iso},f_A](2)-v[\mu_B^{\rm iso},f_B](2))-(v[\mu_A^{\rm iso},f_A](0)-v[\mu_B^{\rm iso},f_B](0))}{2}\,.\end{aligned} \tag{4.31}$$

This expression should be compared with

$$\begin{aligned}\ln\frac{\varphi(\rho_A,-1)}{\varphi(\rho_B,+1)} &= \mu_A^{\rm iso}(\rho_A)-\mu_B^{\rm iso}(\rho_B)\\ &+\ln\left[\frac{e^{-\varepsilon_A(0)-\varepsilon_A(1)+v[\mu_A^{\rm iso},f_A](1)}+e^{\mu_A^{\rm iso}}e^{-\varepsilon_A(1)-\varepsilon_A(2)+v[\mu_A^{\rm iso},f_A](2)}}{e^{-\varepsilon_A(0)-\varepsilon_A(1)+v[\mu_A^{\rm iso},f_A](0)}+e^{\mu_A^{\rm iso}}e^{-\varepsilon_A(1)-\varepsilon_A(2)+v[\mu_A^{\rm iso},f_A](1)}}\right]\\ &-\ln\left[\frac{e^{-\varepsilon_B(0)-\varepsilon_B(1)+v[\mu_B^{\rm iso},f_B](1)}+e^{\mu_B^{\rm iso}}e^{-\varepsilon_B(1)-\varepsilon_B(2)+v[\mu_B^{\rm iso},f_B](2)}}{e^{-\varepsilon_B(0)-\varepsilon_B(1)+v[\mu_B^{\rm iso},f_B](0)}+e^{\mu_B^{\rm iso}}e^{-\varepsilon_B(1)-\varepsilon_B(2)+v[\mu_B^{\rm iso},f_B](1)}}\right]\,.\end{aligned} \tag{4.32}$$

One can then notice that in general for our model

$$\ln \frac{\varphi(\rho_A,-1)}{\varphi(\rho_A,+1)} \neq \frac{1}{2}\ln \frac{\varphi(\rho_A,-2)}{\varphi(\rho_A,+2)} \tag{4.33}$$

which confirms that macroscopic detailed balance does not hold. The large deviations function can then only be characterised as the stationary solution of the Hamilton-Jacobi equation (2.23). Therefore, one does not expect for the large deviations function to be additive (see section 3.2).

Sasa-Tasaki's rule. The same calculation applies for the Sasa-Tasaki dynamics. Even if the latter was claimed to be the relevant physical one, representing a high energy barrier between systems in contact, one can see here that the additivity that it provides for a one-particle exchange is not robust to an exchange of more than one particle. Briefly,

$$\begin{aligned}\varphi(\rho_A,+2) &= e^{\varepsilon_B(2)-\varepsilon_B(0)}P(0|\rho_A)P(2|\rho_B)\\ \varphi(\rho_A,-2) &= e^{\varepsilon_A(2)-\varepsilon_A(0)}P(2|\rho_A)P(0|\rho_B)\end{aligned} \tag{4.34}$$

which gives

$$\begin{aligned}\frac{1}{2}\ln \frac{\varphi(\rho_A,-2)}{\varphi(\rho_A,+2)} &= \mu_A^{\mathrm{iso}}(\rho_A)-\mu_B^{\mathrm{iso}}(\rho_B)\\ &+\frac{\upsilon[\mu_A^{\mathrm{iso}},f_A](2)-\upsilon[\mu_A^{\mathrm{iso}},f_A](0)}{2}-\frac{\upsilon[\mu_B^{\mathrm{iso}},f_B](2)-\upsilon[\mu_B^{\mathrm{iso}},f_B](0)}{2}\,.\end{aligned} \tag{4.35}$$

A comparison with the expression of $\ln[\varphi(\rho_A,-1)/\varphi(\rho_A,+1)]$ leads us to the same conclusion as before: macroscopic detailed balance is broken.

4.2.4 Continuous mass version of our model

The mass transport model presented heretofore was originally introduce in its continuous mass version as presented in appendix [Guioth and Bertin, 2017] (reproduced in appendix C). The stationary solution of an isolated system looks the same as for the particle case. In order to point out that the mass is continuous, we change notations and call $m_i \geqslant 0$ the mass at site i. For an exchange of a mass Δm along the link (i_A, j_B), the coarse-grained transition rates in the weak contact limit reads

$$\begin{aligned}\varphi(\rho_A,\Delta m) = &\int_0^{m_{\max}^A}\mathrm{d}m_{i_A}\int_0^{m_{\max}^B}\mathrm{d}m_{j_B}T_{\mathrm{c}}(m_{i_A}+\Delta m, m_{j_B}-\Delta m|m_{i_A},m_{j_B})\\ &\times P(m_{i_A}|\rho_A)P(m_{j_B}|\rho_B)\mathbb{1}_{[0,m_{\max}^A]}(m_{i_A}+\Delta m)\mathbb{1}_{[0,m_{\max}^B]}(m_{j_B}-\Delta m)\,.\end{aligned} \tag{4.36}$$

In the sequel, we will consider only a very simple case already mentioned before for which $\varepsilon_A(m) = \varepsilon_A m$ and $\varepsilon_B(m) = \varepsilon_B m$. For this very specific choice, the single site probability distribution (see equation (B.18) in appendix C) reads

$$P(m|\bar{\rho}) = \frac{(\varepsilon - \mu^{\mathrm{iso}}(\bar{\rho}))^2 - f^2}{\varepsilon - \mu^{\mathrm{iso}}(\bar{\rho})} e^{[\mu^{\mathrm{iso}}(\bar{\rho}) - \varepsilon]m} \cosh(fm) \tag{4.37}$$

Sasa-Tasaki's rule. For the microscopic Sasa & Tasaki transition rate, the coarse-grained transition rate reads, in the limit where $m_{\max} \to \infty$,

$$\varphi(\rho_A, \Delta m) = \begin{cases} e^{\mu_B^{\mathrm{iso}} \Delta m} \left[\cosh(f_B \Delta m) + \lambda_B^{-1} f_B \sinh(f_B \Delta m)\right] & \text{if } \Delta m > 0 \,, \\ e^{\mu_A^{\mathrm{iso}} |\Delta m|} \left[\cosh(f_A \Delta m) + \lambda_A^{-1} f_A \sinh(f_A |\Delta m|)\right] & \text{if } \Delta m < 0 \,, \end{cases} \tag{4.38}$$

with $\lambda_k(\rho_k) = \varepsilon_k - \mu_k^{\mathrm{iso}}(\rho_k)$.

From (4.38), it thus appears very clearly that macroscopic detailed balance cannot hold since $\ln[\varphi(\rho_A, -\Delta m)/\varphi(\rho_A, \Delta m)]$ is generically nonlinear in Δm for $f_A \neq f_B$. The derivative of the large deviations function $I'(\rho_A|\bar{\rho})$ can therefore only be seen as the solution of the Hamilton-Jacobi equation that reads in this case

$$\int_{\Delta m \geqslant 0} \mathrm{d}\Delta m \, \varphi(\rho_A, \Delta m) \left(e^{I'(\rho_A|\bar{\rho})\Delta m} - 1\right) + \int_{\Delta m \geqslant 0} \mathrm{d}\Delta m \, \varphi(\rho_A, -\Delta m) \left(e^{-I'(\rho_A|\bar{\rho})\Delta m} - 1\right) = 0 \,. \tag{4.39}$$

Due to the exponential character of the transition rates (4.38), the integrals of the Hamilton-Jacobi equation (4.39) can be reckoned and an algebraic equation over I' can be found. However, in order to keep a simple discussion and tractable calculations, we have performed a perturbative expansion over the driving forces f_A and f_B. Since the symmetry $f \leftrightarrow -f$ holds, the first non-zero order is $\mathcal{O}(f^2)$. The solution reads

$$I'(\rho_A|\bar{\rho}) = \mu_A^{\mathrm{eq}}(\rho_A) - \mu_B^{\mathrm{eq}}(\rho_B) + (f_A^2 - f_B^2) \frac{(\mu_A^{\mathrm{eq}})^2 + \mu_A^{\mathrm{eq}}\mu_B^{\mathrm{eq}} + (\mu_B^{\mathrm{eq}})^2}{(\mu_A^{\mathrm{eq}})^2 + 2\mu_A^{\mathrm{eq}}\mu_B^{\mathrm{eq}} + (\mu_B^{\mathrm{eq}})^2} + \mathcal{O}({f_{A,B}}^4) \tag{4.40}$$

One can thus check again that the large deviations function is not additive as long as f_A or f_B are different from 0 and from each other.

4.3 Discussion of the literature

In light of the general large deviations framework of chapter 2 and 3 and our previous examples of mass transport models, we would like now to discuss the main important studies closely related to the notion of out-of-equilibrium chemical potentials available in the literature. This will also be a good opportunity to see our framework at work

in systems of spatial dimension greater that one and the subtleties that can appear. Proceeding in a chronological order, we first discuss in this section an important work around the zeroth law conducted by P. Pradhan, U. Seifert *et al.* [Pradhan et al., 2010, 2011]. In a second step, we consider a more recent paper of P. Pradhan *et al.* [Chatterjee et al., 2015] dealing with a necessary condition that needs to be satisfied in order to define chemical potentials attached to non-equilibrium systems that mimic the equilibrium structure. Their condition, that appears to be a particular instance of our framework, is analysed here. Eventually, we will emphasise the importance of edge effects that may appear in two (or greater) dimensional systems by considering very detailed numerical experiments achieved by R. Dickman [Dickman, 2014, 2016; Dickman and Motai, 2014].

4.3.1 Around the zeroth law – influence of the dynamics at contact

Few years after the precursor analysis of the contact between two ZRP systems [Bertin et al., 2006, 2007], extensive numerical analysis on the KLS model [Katz et al., 1984] followed [Pradhan et al., 2010, 2011]. The authors discussed most specifically the zeroth law and how it could be used to settle an approximate thermodynamic structure. Before discussing their results around the zeroth law, one will first consider the KLS model and comment some of their results regarding our approach expounded in chapter 2.

Results of [Pradhan et al., 2010, 2011] Authors of [Pradhan et al., 2010, 2011] have performed numerical investigations on the KLS driven lattice gas (on a square two-dimensional lattice) in its disordered phase – to obtain a homogeneous phase – which we would like to investigate here, in order to compare our formalism to the theoretical ideas suggested in [Pradhan et al., 2011]. For this classic model, microscopic transition rates have been chosen along the Metropolis dynamics:

$$T(\mathcal{C}'|\mathcal{C}) = \min\left[1, e^{-\beta(H(\mathcal{C}')-H(\mathcal{C})-E\cdot\Delta_y)}\right] . \tag{4.41}$$

where it is implicitly assumed that the new configuration is drawn from the old one by the move of one particle at a site x to one of its open neighbouring site y, supposed empty. More precisely the notations are the following: the configuration $\mathcal{C}$ reads $\mathcal{C} = \{n_x\}_{x\in\Lambda}$, $n_x = 0, 1$ being the number of particle at each site x. The energy $H(\mathcal{C}) = -K\sum_{x\in\Lambda\,;\,y\in\mathcal{V}_x} n_x n_y$ ($\mathcal{V}_x$ refers to the set of nearest neighbours of site x), and $E\cdot\Delta_y$ is equal to E (resp. $-E$) if the displacement is along (resp. at the opposite) of the driving field, but equal to 0 if the displacement is orthogonal to the drive, thus producing a bias toward the direction of the drive. K is the coupling constant between

neighbouring sites ($K > 0$ corresponds to a repulsive dynamics whereas $K < 0$ refers to an attractive dynamics).

They chooses to put two different systems in contact (with different parameters K, E) along a small contact area compared to system sizes. Even if they did not impose a slow frequency of exchange across the contact, they measure the stationary two-point correlation function between two sites belonging to different systems that was found to be small compared to the correlation among neigh-boring sites in the individual systems. Thus, even if further investigations would be necessary to completely specify this point (the absence of correlation does not imply independence of variables), we assume that the stationary distribution of the two systems in contact generally reads

$$P(\mathcal{C}_A, \mathcal{C}_B) = P(N_A, N_B) P(\mathcal{C}_A | N_A) P(\mathcal{C}_B | N_B) \ , \tag{4.42}$$

where $N_k = \mathcal{N}(\mathcal{C}_k)$ is the number of particles associated with the configuration $\mathcal{C}_k$ of the system $k = A, B$ and $P(\mathcal{C}_k | N_k)$ the stationary probability distribution of the isolated system k. As seen in the first chapter 2 the same equality holds in the slow exchange limit and simply means that the two systems are linked through the conservation of mass only and not through the details of their microscopic configurations as it would be at equilibrium. We point out that the hypothesis we make here is different from the one made in [Pradhan et al., 2011]. Indeed, the authors rather assumed that the vanishing of correlations at contact led to the additivity of the large deviations function of the global densities ρ_A and ρ_B. But as we have seen it in the chapter 2, the additivity of the large deviations function is not dictated by the level of independence of each system as an equilibrium-like reasoning would suggest if the interacting potential is short-ranged. It is a consequence of the explicit form of the microscopic transition rates at contact.

With the Metropolis transition rates above that are assumed to be also at play at contact and assuming the factorisation condition (4.42), one can compute the coarse-grained transition rates (2.19) which read in this case (reminding that only one particle

can be exchanged at a time):

$$\varphi(\rho_A,+1) = \sum_{x_A,x_B\in\mathsf{C}_{\mathsf{A,B}}} \sum_{n_{x_A}=0}^{1} \sum_{\{n_{j_A}\}_{j_A\in\mathcal{V}_A(x_A)}} \sum_{n_{x_B}=0}^{1} \sum_{\{n_{j_B}\}_{j_B\in\mathcal{V}_B(x_B)}} n_{x_B}(1-n_{x_A}) \tag{4.43}$$
$$\exp\left\{-\frac{\beta}{2}\left[\left(K_A\sum_{j_A\in\mathcal{V}_A(x_A)} n_{j_A} - K_B\sum_{j_B\in\mathcal{V}_B(x_B)} n_{j_B}\right) - \left|K_A\sum_{j_A\in\mathcal{V}_A(x_A)} n_{j_A} - K_B\sum_{j_B\in\mathcal{V}_B(x_B)} n_{j_B}\right|\right]\right\}$$
$$\times P(n_{x_A},\{n_{j_A}\}_{j_A\in\mathcal{V}_A(x_A)}|\rho_A)P(n_{x_B},\{n_{j_B}\}_{j_B\in\mathcal{V}_B(x_B)}|\rho_B)$$
$$\varphi(\rho_A,-1) = \sum_{x_A,x_B\in\mathsf{C}_{\mathsf{A,B}}} \sum_{n_{x_A}=0}^{1} \sum_{\{n_{j_A}\}_{j_A\in\mathcal{V}_A(x_A)}} \sum_{n_{x_B}=0}^{1} \sum_{\{n_{j_B}\}_{j_B\in\mathcal{V}_B(x_B)}} n_{x_A}(1-n_{x_B})$$
$$\exp\left\{-\frac{\beta}{2}\left[\left(K_B\sum_{j_B\in\mathcal{V}_B(x_B)} n_{j_B} - K_A\sum_{j_A\in\mathcal{V}_A(x_A)} n_{j_A}\right) - \left|K_B\sum_{j_B\in\mathcal{V}_B(x_B)} n_{j_B} - K_A\sum_{j_A\in\mathcal{V}_A(x_A)} n_{j_A}\right|\right]\right\}$$
$$\times P(n_{x_A},\{n_{j_A}\}_{j_A\in\mathcal{V}_A(x_A)}|\rho_A)P(n_{x_B},\{n_{j_B}\}_{j_B\in\mathcal{V}_B(x_B)}|\rho_B)$$

with C_{AB} the pairs of sites of systems A and B forming the contact, assumed to be localised (only a small regions at the edges of both systems are involved in the contact). $\mathcal{V}_k(x_k)$ refers to the set of neighbour belonging to the system k surrounding the site x_k.

One clearly notices that, due to the absolute value $|\cdot|$ (which stems from a rewriting of the metropolis transition rate (4.41)), one cannot expect that the factorisation property (3.3) does hold. Hence, even if macroscopic detailed balance does hold since only one particles can be exchanged per time step, the derivative of the large deviations function $I'(\rho_A,\rho_B) = \ln\varphi(\rho_A,-1)/\varphi(\rho_A,+1)$ has no reason to be additive contrary to what is assumed in [Pradhan et al., 2011]. Furthermore, if the perfect factorisation condition (4.42) breaks due to microscopic correlations at contact between systems, there is no reason that microscopic detailed balance holds and propagates to the macroscopic level since the stationary probability distribution of micro-state is different from the equilibrium one. As a consequence, excess chemical potentials (see (3.28)) cannot be defined properly in this situation.

Zeroth law. We move now to the main part of the paper which deals with the zeroth law (see section 3.1.4 for a general presentation). Numerical investigations of the KLS model performed by the authors in [Pradhan et al., 2011] leads to the conclusion that the zeroth law holds only in an approximate way outside equilibrium. More specifi-

cally, they performed numerical tests of the zeroth law with three different equilibrium systems. If the zeroth law has been observed to hold for a large parameter (K, the coupling constant, and E, the driving field) range, significant deviations have been noticed, especially at highly negative coupling constant K (attractive interactions). As shown on figure 11 of [Pradhan et al., 2011], the authors put a non-equilibrium system successively in contact with three different equilibrium systems with different coupling constant $K_{\rm eq} = 0, -0.8, -0.9$. For each equilibrium system, they measure the density $\rho_{\rm neq}$ and assign a chemical potential $\mu_{\rm neq}(\rho_{\rm neq}) = \mu_{\rm eq}(\rho_{\rm eq})$ to the non-equilibrium systems (μ_{eq} assumed to be known), thus measuring a curve $\rho_{\rm neq}(\rho_{\rm neq})$ for a $\rho_{\rm neq} \in [0, 1]$. If the zeroth law was satisfied, every chemical potential curve $\mu_{\rm neq}(\rho_{\rm neq})$ would have collapsed one a single curve since the non-equilibrium system stay the same. The non-collapse of the different chemical potential curves can be attributed to the excess term $\eta_{\rm ex}$ in the derivative of the large deviations function. Indeed, as discussed in the chapter 3, section 3.2.1, the derivative of the large deviations function associated with the contact between an equilibrium and a non-equilibrium system, generally reads, when macroscopic detailed balance holds,

$$I'(\rho_{\rm neq}, \rho_{eq}) = \mu^{\rm iso}_{\rm neq}(\rho_{\rm neq}) - \mu_{\rm eq}(\rho_{eq}) + \eta^{\rm ex}(\rho_{\rm neq}, \rho_{\rm eq}) \ . \tag{4.44}$$

Here, $\eta_{\rm ex}$ cannot be split into two parts since the metropolis microscopic rates do not factorise (see (4.43) above) and thus depends on the equilibrium system as well as the non-equilibrium one through the detail of the contact dynamics. Since the non-equilibrium system stays the same, the function $\mu^{\rm iso}_{\rm neq}$ (of the density $\rho_{\rm neq}$) does not change. At stationarity, $I'(\rho^*_{\rm neq}, \rho^*_{\rm eq}) = 0$ and

$$\mu_{\rm eq}(\rho^*_{eq}) = \mu^{\rm iso}_{\rm neq}(\rho^*_{\rm neq}) + \eta^{\rm ex}(\rho^*_{\rm neq}, \rho^*_{\rm eq}) \tag{4.45}$$

where of course $V_{\rm eq}\rho_{\rm eq} + V_{\rm neq}\rho_{\rm neq}$ is fixed by conservation of the total number of particles. Varying the final densities ρ^*, one can have access to $\mu^{\rm iso}_{\rm neq} + \eta^{\rm ex}$ by the knowledge of $\mu_{\rm eq}$. If $\eta^{\rm ex}$ was null, the different curves should be the same since $\mu^{\rm iso}_{\rm eq}$ stay the same. But since $\eta_{\rm ex}$ is *a priori* different from 0 and depends on $K_{\rm eq}$, it is not surprising that the curves depend on $K_{\rm eq}$.

We eventually stress that such an effect could be avoided by choosing a factorised dynamics at contact as discussed in a general setting in section 3.1.4. In that case, $\eta_{\rm ex}$ would not depend on the coupling constant $K_{\rm eq}$ and the same procedure described above would give the same curve, representing $\mu^{\rm cont}_{\rm neq} = \mu^{\rm iso}_{\rm neq} + \eta^{\rm ex}_{\rm neq}$.

4.3.2 Macroscopic detailed balance at contact & ensemble equivalence

In [Chatterjee et al., 2015], S. Chatterjee, P. Pradhan and P.K. Mohanty discuss the restricted case of non-equilibrium steady-state systems having short-ranged spatial correlations. Under this assumption, they have found a condition – reminiscent of a detailed balance condition – under which well-defined non-equilibrium chemical potentials can be defined. We point out that they do not assume any slow frequency exchange at contact, as we do. Nevertheless, even if the hypothesis are physically different, they are formally commensurable. As a consequence of their short-ranged correlation assumption, they explicitly demand that the stationary probability distribution of a configuration of the combined system reads,

$$P(\mathcal{C}_A, \mathcal{C}_B) = \frac{\omega_A(\mathcal{C}_A)\omega_B(\mathcal{C}_B)}{W(\bar{\rho})}\delta\left(\mathcal{N}(\mathcal{C}_A) + \mathcal{N}(\mathcal{C}_B) - N\right) \ . \tag{4.46}$$

with $W(\bar{\rho})$ the normalisation factor and where ω_k, the weight associated with the subsystems, are also assumed to display short-ranged correlations. We note that this assumption already assumed a factorisation of the probability distribution of the density. Also, contrary to what we have assumed in our framework expounded in chapter 2, they supposed that the stationary state can only be achieved through macroscopic detailed balance

$$\begin{aligned} &P(\rho_A, \rho_B)\pi(\rho_A + \tfrac{\Delta N}{V_A}, \rho_B - \tfrac{\Delta N}{V_B}|\rho_A, \rho_B) \\ &\qquad = P(\rho_A + \tfrac{\Delta N}{V_A}, \rho_B - \tfrac{\Delta N}{V_B})\pi(\rho_A, \rho_B|\rho_A + \tfrac{\Delta N}{V_A}, \rho_B - \tfrac{\Delta N}{V_B}) \ . \end{aligned} \tag{4.47}$$

which in the thermodynamic limit reads (see equation (2.35))

$$\frac{\varphi(\rho_A, \rho_B, -\Delta N)}{\varphi(\rho_A, \rho_B, \Delta N)} = e^{(\mu_A - \mu_B)\Delta N} \tag{4.48}$$

with μ_k defined to be the chemical potentials associated with the partition function

$$W(N_k) = \sum_{\mathcal{C}_k} \omega_k(\mathcal{C}_k)\delta\left(\mathcal{N}(\mathcal{C}_k) - N_k\right)$$

These equations are the equations numbered (9) and (10) in [Chatterjee et al., 2015]. Under the short-ranged spatial correlations hypothesis which allows one to define isolated chemical potentials – characterising the distribution of mass – inside each subsystem, they demand – in short – that microscopic detailed balance[3] holds with respect to

[3]We notice that one should rather write "mesoscopic" since they consider only exchange of mass at a level which is large compared to the microscopic distance but small with respect to the whole

the same chemical potential associated with the macroscopic detailed balance, itself a consequence of the completely factorised distribution (4.46). This strong demand can be interpreted very clearly in our framework: it simply corresponds to the situation where microscopic detailed balance holds and then propagates to a macroscopic detailed balance condition. In other word, this situation exactly mimics the equilibrium one for which there is no excess chemical potential and thus no difference between isolated chemical potentials and contact chemical potentials. It is merely a generalisation of the precursor analysis based on the ZRP of [Bertin et al., 2007]. That being said, in the absence of any slow frequency exchange assumption, this context seems indeed to be the only one for which one can associate a thermodynamic structure similar to the equilibrium one.One can also notice that it is the only case for which ensemble equivalence holds (more precisely an ensemble equivalence of the level of probability distributions, see [Touchette, 2015] for a recent survey). Indeed, according to (3.78), if the chemical potential at contact is the same as the isolated one, the equivalence of ensemble holds since internal fluctuations of mass (in the canonical ensemble, for an isolated system) are governed by the same chemical potential as the one defined by the contact with the external reservoir (grand canonical ensemble).

4.3.3 On the position of the contact (in a weak contact limit) in two dimensional systems

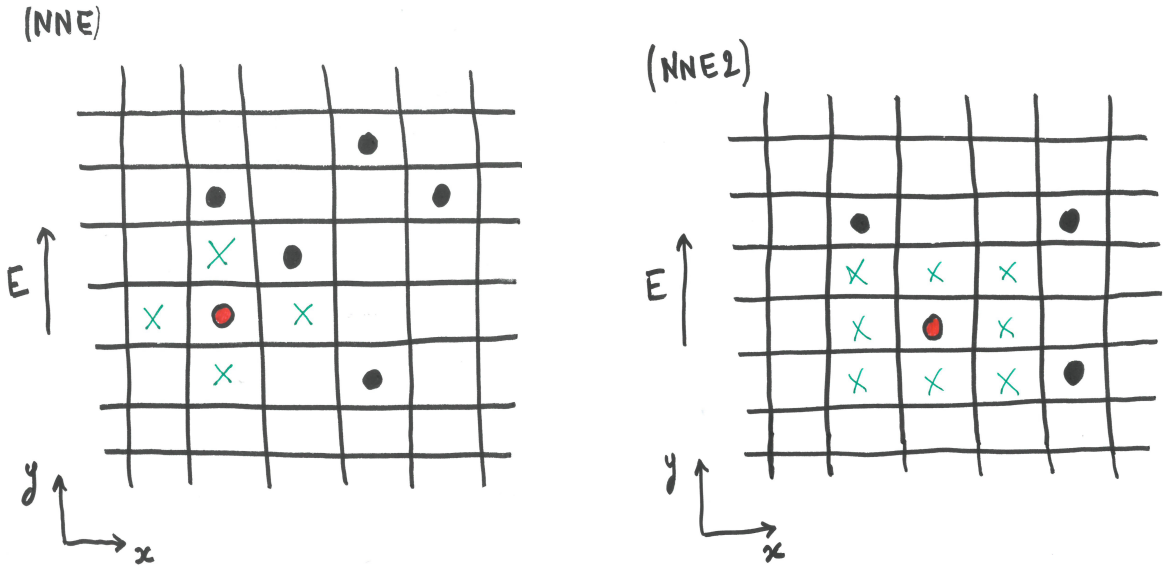

Figure 4.5 – Sketches of NNE (left) and NNE2 (right) dynamics. Green crosses materialise the excluded region around the (arbitrary) red particle for each dynamics.

We now move to the last series of papers we would like to discuss. It concerns a

volume.

quite recent numerical work performed by R. Dickman [Dickman, 2014, 2016] which – in light of the framework presented in chapters 2 and 3 – can be seen as the numerical proof that the non-uniformities at the edges (that in general affect the stationary state of any system) plays a major role for two non-equilibrium (almost) uniform systems in contact. In these papers, R. Dickman has mainly discussed driven lattice gases with nearest-neighbour exclusion (NNE) and next-nearest-neighbours exclusion (NNE2) as well as the KLS model that has been discussed in the previous section. The main purpose of his work is to test and discuss the Steady State Thermodynamics proposed by Sasa & Tasaki [Sasa and Tasaki, 2006] on a numerical simulation ground. First [Dickman and Motai, 2014], the author discussed the case of an extended contact, that is when every site of system A is in contact with corresponding sites of system B (see figure 4.6 for a sketch). He emphasised – as we have shown in subsection 4.3.1 – the importance of the transition rates at contact, showing that the Metropolis rule led to a breaking of the zeroth law, contrary to the Sasa and Tasaki's rule for instance. In a second paper [Dickman, 2014], R. Dickman discussed this time the case of localised contacts (see figures 4.7 for a sketch) and showed that even for the same factorised contact dynamics (which could be of Sasa & Tasaki's type), different contact (pointwise, at the edge, etc.) can lead to different final stationary states, emphasising the strong influence of the localisation of the contact area. In a slow exchange rate limit, these localisation subtleties – even if they are a bit hidden in our general presentation of chapter 2, and necessarily absent in our previous discussion of one dimensional systems – are perfectly present in our framework. Our goal is to expound them in this section, along the precious detailed numerical investigations presented by R. Dickman.

The dynamics of the KLS model has been briefly presented above. First, we briefly lay out the dynamics of the NNE and NNE2 models in two dimensions (see figure 4.5 for a sketch). As for classic driven lattice gas, each site x can be occupied by at most one particle, so $n_x = 0, 1$. One jump from configurations $\mathcal{C}$ to $\mathcal{C}'$ corresponds to the move of one particle toward an empty neighbouring site $y \in \mathcal{V}(x)$ ($\mathcal{V}(x)$ being the set of the nearest neighbours of x) that satisfies the potential constraints. For NNE dynamics, these constraints are the existence of an infinite interaction energy between two particles at a distance lower or equal to one site width, or, in another words, the nearest-neighbour sites need to be empty so that a site can be occupied. For an exchange between site x and $y \in \mathcal{V}(x)$, transition rates that embed this exclusion rules read

$$T(\mathcal{C}'|\mathcal{C}) = \frac{1 + \Delta_{y-x}E}{4} n_x(1 - n_y) \prod_{\substack{z \in \mathcal{V}(y) \\ z \neq x}} (1 - n_z)\,, \tag{4.49}$$

with Δ_{x-y} the projection of norm 1 of the replacement $y - x$ along the driving force; E characterises the strength of the driving.

For NNE2 Dynamics, the exclusion rule is the same as for NNE but displacements are also allowed to next nearest-neighbours. Thus, for an exchange between site x and $y \in \mathcal{V}_+(x)$ ($\mathcal{V}_+(x)$ being the set of nearest as well as next-nearest neighbours of x), transition rates read

$$T(\mathcal{C}'|\mathcal{C}) = \frac{1+\tilde{\Delta}_{y-x}E}{8} n_x(1-n_y) \prod_{\substack{z\in\mathcal{V}(y)\\ z\neq x}} (1-n_z) \,, \tag{4.50}$$

with $\tilde{\Delta}_{y-x}$ being equal to 1 (*resp.* -1) if the projection of the displacement $y-x$ along the driving force has a strictly positive (*resp.* strictly negative) component. If the displacement is orthogonal to the driving force, $\tilde{\Delta}_{y-x} = 0$.

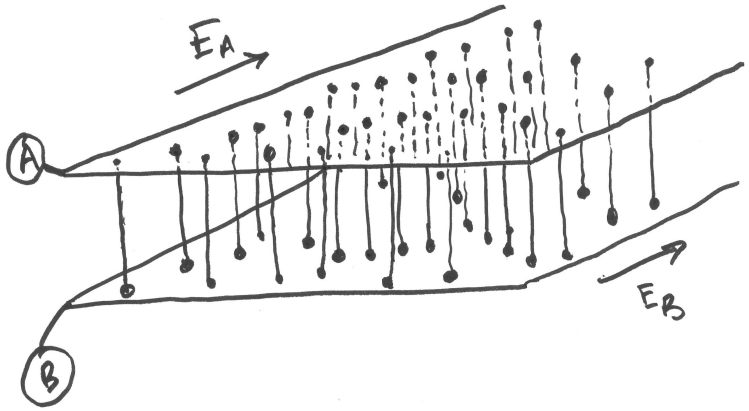

Figure 4.6 – Sketch of a "global" contact between systems A and B. Every sites of A are connected to one site on B (and *vice versa*).

Global contact. If one imagines a global contact between two systems A and B of same size as shown on figure 4.6, with a dynamics at contact similar to the bulk one (without any bias), the coarse-grained transition rates read

$$\begin{aligned} &\varphi(\rho_A,+1) \\ &\quad = \sum_{(x_A,x_B)\in\mathsf{C}_{AB}} \sum_{n_{x_B}} \sum_{\{n_{y_A}\}_{y_A\in\bar{\mathcal{V}}(x_A)}} n_{x_B}(1-n_{x_A}) \prod_{y_A\in\mathcal{V}(x_A)} (1-n_{y_A}) \\ &\qquad\qquad \times P(n_{x_B}|\rho_B) P(n_{x_A},\{n_{y_A}\}_{y_A\in\mathcal{V}(x_A)}|\rho_A) \\ &\quad = \sum_{(x_A,x_B)\in\mathsf{C}_{AB}} \bar{n}_{\rho_B}(x_B)\bar{n}^{\mathrm{av}}_{\rho_A}(x_A) \end{aligned} \tag{4.51}$$

and

$$\varphi(\rho_A,-1) = \sum_{(x_A,x_B)\in\mathsf{C}_{AB}} \bar{n}_{\rho_A}(x_A)\bar{n}^{\mathrm{av}}_{\rho_B}(x_B)$$

with $\bar{\mathcal{V}}(x) = \mathcal{V}(x) \bigcup \{x\}$ and $\bar{n}_\rho(x) = \langle n_x \rangle_\rho$ being the average density at point x and

$$\bar{n}_\rho^{\mathrm{av}}(x) = \left\langle (1 - n_x) \prod_{y \in \mathcal{V}(x)} (1 - n_y) \right\rangle_\rho$$

being the average of what one can call the average availability of site x (since x is actually available to receive a particle when $(1 - n_x) \prod_{y \in \mathcal{V}(x)} (1 - n_y)$ is equal to 1).

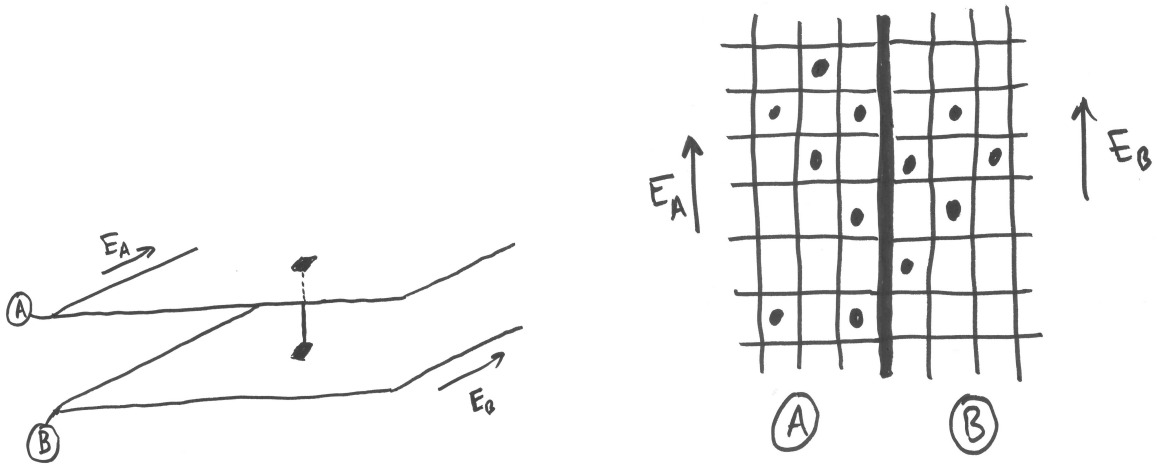

Figure 4.7 – Sketch of a "local" contact between two systems A and B. Left: a pointwise contact corresponds to a contact which is realised with two sites of each system only; latter can be in the bulk or at the edges. Right: contact along edges of both systems.

Local contact. For a local contact between A and B (see figure 4.7), the situation needs to be precise, depending on the exact geometry of the contact. Following R. Dickman [Dickman, 2014], the contact can be pointwise or along edges of both systems. For a pointwise exchange, say along connected sites x_A and x_B, coarse-grained transition rates at contact read, using the same notations as in equation (4.51),

$$\begin{aligned} \varphi(\rho_A, +1) &= \bar{n}_{\rho_B}(x_B) \bar{n}_{\rho_A}^{\mathrm{av}}(x_A) \\ \varphi(\rho_A, -1) &= \bar{n}_{\rho_A}(x_A) \bar{n}_{\rho_B}^{\mathrm{av}}(x_B) \,. \end{aligned} \tag{4.52}$$

For an extended contact dynamics along the edge, the transfer of particles happen in the same dimensions as the systems (for instance in the same plane here, for 2 dimensional systems). Thus for a contact perpendicular to the driving force, the

coarse-grained transition rates read

$$\begin{aligned}\varphi(\rho_A,+1) &= \sum_{(x_A,\,x_B)\in \mathsf{C}_{AB}} \bar{n}_{\rho_B}(x_B)\tilde{n}^{\mathrm{av}}_{\rho_A}(x_A;x_B) \\ \varphi(\rho_A,-1) &= \sum_{(x_A,\,x_B)\in \mathsf{C}_{AB}} \bar{n}_{\rho_A}(x_A)\tilde{n}^{\mathrm{av}}_{\rho_B}(x_B;x_A)\,,\end{aligned} \tag{4.53}$$

with this time a modified availability

$$\tilde{n}^{\mathrm{av}}_{\rho}(x;y) = \left\langle (1-n_x) \prod_{z\in\mathcal{V}(x),\, z\neq y} (1-n_z) \right\rangle$$

meaning that this time the average availability must not take into account the site already occupied in the initial configuration.

First of all, one can notice that the derivative of the large deviations function $I'(\rho_A,\rho_B|\bar{\rho})$ is not *a priori* additive for all the case considered above even if microscopic transition rates factorise:

$$\begin{aligned} I'_{\mathrm{glob}}(\rho_A,\rho_B) &= \ln \frac{\sum_{(x_A,\,x_B)\in \mathsf{C}_{AB}} \bar{n}_{\rho_A}(x_A)\bar{n}^{\mathrm{av}}_{\rho_B}(x_B)}{\sum_{(x_A,\,x_B)\in \mathsf{C}_{AB}} \bar{n}_{\rho_B}(x_B)\bar{n}^{\mathrm{av}}_{\rho_A}(x_A)} \\ I'_{\mathrm{pw}}(\rho_A,\rho_B) &= \ln \frac{\bar{n}_{\rho_A}(x_A)\bar{n}^{\mathrm{av}}_{\rho_B}(x_B)}{\bar{n}_{\rho_B}(x_B)\bar{n}^{\mathrm{av}}_{\rho_A}(x_A)} \\ I'_{\mathrm{edges}}(\rho_A,\rho_B) &= \ln \frac{\sum_{(x_A,\,x_B)\in \mathsf{C}_{AB}} \bar{n}_{\rho_A}(x_A)\tilde{n}^{\mathrm{av}}_{\rho_B}(x_B;x_A)}{\sum_{(x_A,\,x_B)\in \mathsf{C}_{AB}} \bar{n}_{\rho_B}(x_B)\tilde{n}^{\mathrm{av}}_{\rho_A}(x_A;x_B)}\,. \end{aligned} \tag{4.54}$$

The subscripts refers respectively to the "global", the "pointwise" and the "edge" contacts.

Let us inspect what happens when the steady state of each systems is globally uniform, *with a potential exception at the edges*.

For the global contact case, each sum over $(x_A,\, x_B) \in \mathsf{C}_{AB}$ in (4.54) can be split into a bulk contribution and an edge contribution. In the thermodynamic limit, where the edge contributions become negligible compared to the uniform bulk contribution, the derivative of the large deviations function reads

$$I'_{\mathrm{glob}}(\rho_A,\rho_B) = \ln \frac{\rho_A}{\bar{n}^{\mathrm{av}}_{\rho_A,\,\mathrm{bulk}}} - \ln \frac{\rho_B}{\bar{n}^{\mathrm{av}}_{\rho_B,\,\mathrm{bulk}}}\,. \tag{4.55}$$

It is then additive and the chemical potentials $\mu^{\mathrm{cont}}_k(\rho_k) = \ln[\rho_k/\bar{n}^{\mathrm{av}}_{\rho_k,\,\mathrm{bulk}}]$ correspond to the ones postulated on a physical ground by Dickman. Furthermore, they equalise well upon contact [Dickman and Motai, 2014].

As for the pointwise contact, it is also clearly additive but the chemical potentials read this time $\mu^{\mathrm{cont}}_k(\rho_k;x_k) = \ln[\bar{n}_{\rho_k}(x_k)/\bar{n}^{\mathrm{av}}_{\rho_k}(x_k)]$. They thus clearly depend on the localisation of the contact: if the latter is located in the bulk, the chemical potentials

are the same as for the global contact at the thermodynamic limit. But if the contact is localised on the edge, chemical potentials may become different since the stationary state becomes in general non-uniform near the edges, here made of hard walls. At equilibrium, chemical potentials stay uniform despite a manifest non-uniformity of the density close to the walls. But out-of-equilibrium, as illustrated numerically by Dickman [Dickman, 2014], the chemical potential are no-longer uniform due to non-trivial edge effects (see in particular figures 4, 6 and 7 of [Dickman, 2014]). We will see in more details in the case of self-propelled particles the role of edge effects.

The contact along an edge proceeds in a similar way as the pointwise contact. If one assumes that the steady state in each system is uniform along the edge, I' is additive but the chemical potential depends on the density and the "availability" near the contact area that can be seen as a hard wall in the weak exchange rate limit. Hence, chemical potentials strongly depend on what happens on the edge and are not necessarily uniform as in equilibrium, then breaking the existence of an equation of state (along which chemical potential would only depend on uniform bulk quantities (density here)). For the edge contact case, with the assumption that the stationary state is uniform along the edge, chemical potential reads $\mu_k^{\rm cont}(\rho_k) = \ln[\bar{n}_{\rho_k,\rm edge}/\tilde{n}^{\rm av}_{\rho_k,\rm edge}]$. One notices the difference between $\bar{n}^{\rm av}_\rho$ and $\tilde{n}^{\rm av}_\rho$ that may also be a source of disagreement between a pointwise contact (in the bulk) and an edge contact.

Conclusion

Eventually, our large deviations approach allows us to rationalise – in the weak exchange rate limit – the non-uniformity subtleties emphasised by R. Dickman. As the author pointed out, different contacts can lead to different stationary state although the systems stay the same. This violates the zeroth law and is reminiscent of the fact that no equation of state exists for non-equilibrium driven systems. For each type of contact, depending on its localisation, it exists an associated chemical potential that is not necessarily the same for other contact type. We here again see a manifestation of the influence of the contact which this time has focused on its position.

To conclude, one can summarise the role of the contact by noticing two main effects: the particular dynamics at contact – through the microscopic transition rate – and, the dynamics being fixed, the position of the contact when the stationary states of both systems are not perfectly uniform (at the edge in particular). These two effects both lead in general to the existence of an excess chemical potentials (with respect to isolated systems) that need to be taken into account to describe the balance of densities.

4.4 Macroscopic fluctuation theory

To conclude this chapter, we would like to discuss very briefly the situation of the contact between two out-of-equilibrium systems in the context of the Macroscopic Fluctuation Theory (MFT). The latter framework has been developed during the 2000s years (see [Bertini et al., 2002; Derrida, 2007] for reviews from the main investigators of this theory), mostly inspired by stochastic lattice gases like the ones presented along this chapter. As emphasised in a recent review [Bertini et al., 2015*a*], this theory can be seen as an extension of the Onsager theory by considering space-time fields and non-linear evolution equations, valid at a mesoscopic level. However, even if the Macroscopic Fluctuation Theory goes beyond the standard linear non-equilibrium theory, it strongly stands on the local equilibrium assumption as we will see.

Our aim in this section is to discuss the situation of the contact between two systems, exactly in the same setting as the one discussed previously. More precisely, we will assume periodic boundary conditions along the parallel fields and the contact will be materialised by an energy barrier $U(\boldsymbol{x})$ which only varies in the transverse direction with respect to the fields one. We first provide a very short presentation of the MFT framework. We will then analyse briefly the situation of the contact before giving a short opening. In particular, we will focus as previously on the definition of chemical potentials.

4.4.1 Presentation of the framework

In the context of driven lattice gases and mass transport models, the relevant conserved variable is the density field $\rho(\boldsymbol{x}, t)$. MFT is then a small noise fluctuating theory valid in a specific coarse-grained space-time scale (called hydrodynamic scale), which itself holds when the driving force decreases inversely with the size (in microscopic unit) of the mesoscopic fluid particles (which correspond to the typical "boxes" on which the coarse-graining procedure is performed). The equation governing the dynamics of this density field $\rho(\boldsymbol{x}, t)$ is a field Langevin equation and reads

$$\begin{aligned} &\frac{\partial \rho_t(\boldsymbol{x})}{\partial t} + \nabla \cdot \left[J_t(\rho_t(\boldsymbol{x}), \boldsymbol{x}) + \xi_t(\boldsymbol{x}) \right] = 0 \\ &J_t(\rho, \boldsymbol{x}) = -D(\rho)\nabla\rho + \chi(\rho) F_t(\boldsymbol{x}) \,. \end{aligned} \tag{4.56}$$

with J_t the current, $D(\rho)$ is the diffusion matrix and $\chi(\rho)$ the mobility matrix. $F_t(\boldsymbol{x})$ refers to an external force that can contain conservative and non-conservative forces. We call Λ the space domain to which $\boldsymbol{x}$ belongs. Eventually, $\xi_t(\boldsymbol{x})$ is a Gaussian white

noise characterised by

$$\begin{aligned} \langle \xi_{t,\,i}(\boldsymbol{x}) \rangle &= 0 \\ \langle \xi_{t,\,i}(\boldsymbol{x}) \xi_{t',\,j}(\boldsymbol{x}) \rangle &= 2\epsilon^d \chi_{ij}(\rho_t(\boldsymbol{x}))\, \delta(t-t') \delta(\boldsymbol{x}-\boldsymbol{x}') \,. \end{aligned} \tag{4.57}$$

where d is the space dimension and $\epsilon \ll 1$ is the ratio between the microscopic length scale and the macroscopic one (it is then a dimensionless scaling factor). Hence, the noise $\xi_t(\boldsymbol{x})$ is a *small* noise. Also, equations (4.56) need to be supplemented by appropriate boundary conditions. For the case we will consider here, the boundary conditions will mostly consist in assuming the vanishing of the current orthogonal to the boundaries. The second equation of (4.56) linking the current J to the diffusion matrix D and mobility matrix χ is the constitutive relation of the system, embedded in the ρ dependence of $D(\rho)$ and $\chi(\rho)$. Because of the small driving force considered in the MFT framework, the local equilibrium assumption stays valid and is embedded in the following local Einstein relation

$$D(\rho) = f''(\rho)\chi(\rho) \,, \tag{4.58}$$

where f is the equilibrium free energy of the system per unit volume.

When $F_t(\boldsymbol{x}) = F(\boldsymbol{x})$ does not depend on time, a stationary state can be achieved. Because of the small-noise limit, the large deviations analysis is particularly suited to study the behaviour of the probability distribution. Indeed, the probability distribution to observe a profile $\rho(\boldsymbol{x})$ in the stationary state can be written

$$P(\rho) \asymp \exp\left[-\epsilon^{-d} V(\rho)\right] \,. \tag{4.59}$$

The large deviations functional $V(\rho)$ is often called the "quasi-potential" in the large deviations literature [Bertini et al., 2015*a*] and satisfies an Hamilton-Jacobi equation in a very similar way as the one derived in chapter 2 (see (2.23)). The latter reads

$$\int_\Lambda \mathrm{d}\boldsymbol{x} \left[\nabla \frac{\delta V}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta V}{\delta \rho} - \frac{\delta V}{\delta \rho} \nabla \cdot J(\rho, \boldsymbol{x}) \right] = 0 \,, \tag{4.60}$$

which can be transformed into

$$\int_\Lambda \mathrm{d}\boldsymbol{x} \left\{ \nabla \frac{\delta V}{\delta \rho} \cdot \left[\chi(\rho) \nabla \frac{\delta V}{\delta \rho} + J(\rho, \boldsymbol{x}) \right] \right\} = 0 \,, \tag{4.61}$$

when $J(\rho, \boldsymbol{x})$ vanishes at the boundary of the domain Λ, $\partial\Lambda$. The profile $\rho^*(\boldsymbol{x})$ minimising the quasi-potential V is then the most probable profile.

4.4.2 Discussion about the contact in the MFT framework

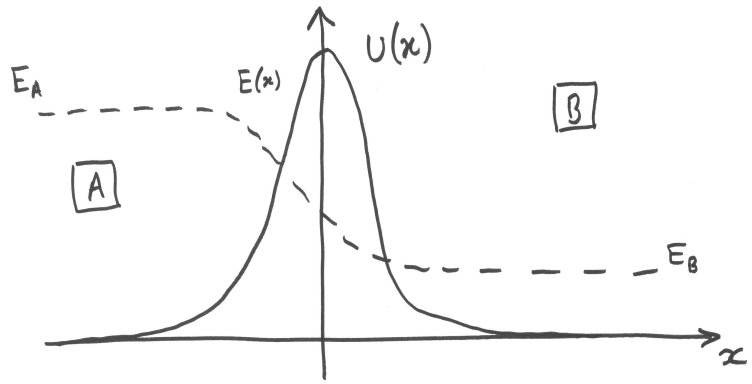

Figure 4.8 – Sketch of the external potential barrier that separates the two systems brought into contact.

We consider here two 2-dimensional systems in contact along the x direction. Periodic boundary conditions along the y direction, which is also the direction of the drives, are assumed. For both systems, the forces are such that $F(\boldsymbol{x}) = E(x)\boldsymbol{e}_y - U'(x)\boldsymbol{e}_x$, $\boldsymbol{x} = (x, y)$, with $E(x)$ and $U(x)$ smoothly varying inside the contact area only, as shown on figure 4.8. For $\boldsymbol{x}$ in the bulk of systems k ($\boldsymbol{x} \in \Lambda_k$), one sets $E(x) = E_k$ and $U(x) = 0$, $k = A, B$. Also, we assume that both systems are isotropic. Matrices $\chi(\rho)$ and $D(\rho)$ then become bare coefficients. We point out that we do not consider non-uniform diffusion and mobility coefficient: systems A and B are the same but forced by different external fields. This assumption is clearly restrictive compared to previous studies but it is already a situation where one can see whether deviations from equilibrium can be expected or not. With these assumptions, the current $J(\rho, \boldsymbol{x})$ reads

$$J(\rho, \boldsymbol{x}) = -D(\rho)\nabla\rho + \chi(\rho)\left(E(x)\boldsymbol{e}_y - U'(x)\boldsymbol{e}_x\right) \ . \tag{4.62}$$

At stationary state one expects to have only currents (uniform along y) along the external fields E_k but not along the orthogonal direction. Indeed,

$$\begin{aligned} J_x(\rho^*, \boldsymbol{x}) &= -D(\rho^*)\partial_x\rho^* - \chi(\rho^*)U'(x) \\ J_y(\rho^*, \boldsymbol{x}) &= -D(\rho^*)\partial_y\rho^* + \chi(\rho^*)E(x)\,. \end{aligned} \tag{4.63}$$

For a given x, systems are invariant in the y direction so we look for a solution $\rho^*(\boldsymbol{x}) = \rho^*(x)$. In this case, $J_y(\rho^*, \boldsymbol{x}) = \chi(\rho^*(x))E(x)$ and the stationary condition $\nabla \cdot J = 0$ implies

$$J_x(\rho^*, x) = 0 \qquad i.e \quad D(\rho^*)\partial_x\rho^* + \chi(\rho^*)U'(x) = 0\,, \tag{4.64}$$

since both systems are bounded in the x direction. According to the local Einstein

relation (4.58), the vanishing of the current along x reads

$$\partial_x \left[f'(\rho^*(x)) + U(x) \right] = 0 \quad \Longrightarrow \quad f'(\rho^*(x)) + U(x) = \text{Cst} \, . \tag{4.65}$$

Hence, the situation is perfectly the same as in equilibrium where local chemical potentials read $\mu^{\text{eq}}(\rho^*(x)) = f'(\rho^*(x)) + U(x)$. For two points $\boldsymbol{x}_A^* \in \Lambda_A$ and $\boldsymbol{x}_B^* \in \Lambda_B$ in the bulks of each systems such that $\rho^*(x_A^*) = \bar{\rho}_A$ and $\rho^*(x_B^*) = \bar{\rho}_B$, one has

$$\mu_A^{\text{eq}}(\bar{\rho}_A) = \mu_B^{\text{eq}}(\bar{\rho}_B) \tag{4.66}$$

since $U(x_k^*) = 0$ for $k = A, \, B$.

One should remark that we have not mentioned the quasi-potential $V(\rho)$. The approach expounded here is in fact more intuitive but one can also show [Bertini et al., 2015*a*, p. 614] that the solution $V(\rho)$ that solve the Hamilton-Jacobi equation is in fact the equilibrium quasi-potential, related to the equilibrium free energy such that

$$\frac{\delta V}{\delta \rho} = f'(\rho) - f'(\rho^*) \, . \tag{4.67}$$

Conclusion

Eventually, the MFT thus does not account for the genuine non-equilibrium effects encountered in the last chapters. This can be understood by the fact that MFT is actually a theory which describes non-linear out-of-equilibrium systems which are in fact close to equilibrium. Even if both systems are spanned by currents, the profile along the potential barrier remains the equilibrium one and no deviation at contact occurs. This preliminary very direct result invites us to look for fluctuating field theories beyond the MFT that could account for the effect at contact observed in the previous sections and chapters. This probably requires to go beyond linear response and then probes deviations from the local equilibrium hypothesis[4]. We will see in the last chapter 5 simple examples of independent active particles for which local equilibrium is broken (at least near walls as we will see).

[4]These very interesting issues are actually a work in progress, but unfortunately, it is not enough mature to be presented here at this stage.

CHAPTER 5

Application to diffusive and self-propelled independent particles

In this chapter, we investigate systems made of independent particles that can be externally driven by an external field or that can be self-propelled in different manners. Physically, these are models of colloidal particles immersed in a solvent that can be driven by external electric fields or self-propelled by the presence of an inhomogeneity of chemical reactant on their surface for instance. As we are interested in putting two systems of this kind of particles in contact, we now draw a list up of contact types that can be physically realisable (see figure 5.1).

- The first type of contact one can think of for the exchange of colloidal particles is a porous membrane that can be possibly selective and lead to osmosis effect. In a idealised situation, one could think of a perfect infinitely thin wall modelled by an infinite potential drilled with perfect holes that require no energetic cost to be passed through by particles of smaller size than the diameter of the pores.

- The second one, more generic, simply corresponds to a homogeneous high barrier of potential separating both systems. As we will see henceforth, the absence of symmetry of the barrier with respect to its top will play an important role.

Our aim is to compute the distribution of the number of particles on both sides of the contact for several simple non-interacting particle models (Driven Diffusive Particles) [Barany, 2009; Figliuzzi et al., 2014; Hunter and White, 1987], Active Brownian Particles (ABP) and Run-&-Tumble particles (RTP) (see [Fodor and Marchetti, 2018] for a recent review). These models have been introduced for long time in the literature [Cates and Tailleur, 2013; Tailleur and Cates, 2008] but we focus here our attention on the contact between these systems and particularly about the definition of chemical potentials. We will see in particular that the contact specificities, as for

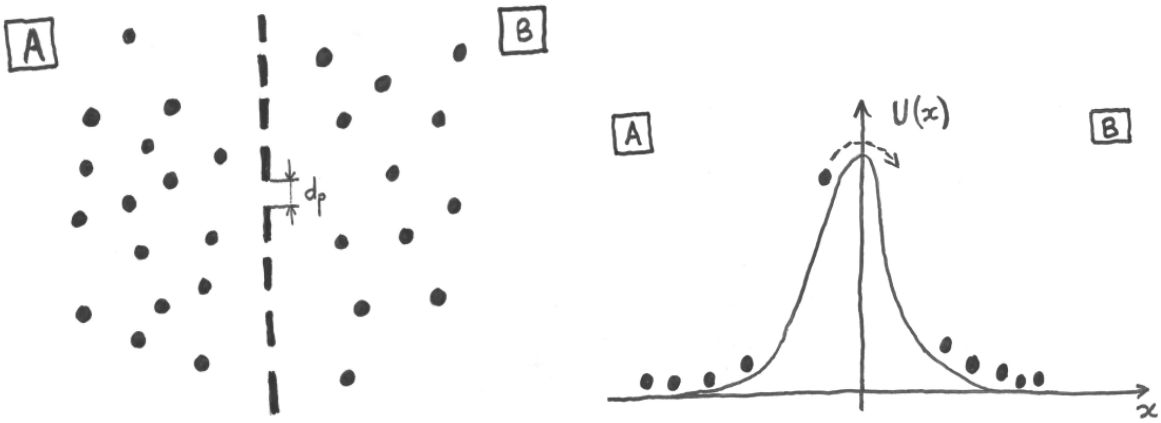

Figure 5.1 – Scheme of the two types of contact that will be considered henceforth.

the mass transport models discussed in preceding chapters, often plays a significant role for the control of the densities on both sides of the contact. Interestingly, we should as of now mention recent studies about the pressure which shows a similar behaviour [Fily et al., 2017; Solon, Fily, Baskaran, Cates, Kafri, Kardar and Tailleur, 2015; Solon et al., 2018*a*; Solon, Stenhammar, Wittkowski, Kardar, Kafri, Cates and Tailleur, 2015; Speck and Jack, 2016; Takatori et al., 2014; Winkler et al., 2015].

5.1 Introductory model of passive particles with a porous membrane

Let us start with a very simple conceivable physical system. We consider in this section a simple model of colloidal particles that are in contact with a solvent and forced by a non-conservative electric field (in a geometric domain with periodic boundary conditions) [Barany, 2009; Figliuzzi et al., 2014; Hunter and White, 1987]. It is not at all obvious that the colloids will always respond to the electric field but this is the case in several situations. Microscopically, a possible mechanism is the one in which the solvent contains free ions and the colloids can absorbed either the cations or the anions on its surface, leading to an electric surface charge [Hunter and White, 1987]. This surface charge is screened by ions of the liquid, then forming a diffusive electric double layer surrounding colloids, which may be also affected by polarisability or metallic properties of the colloid itself. When the electric field is switched on, the charges attached to the solid particle and those of the electric double layer are propelled in opposite directions, leading to a modulated drag force with respect to the external electric field. For small driving force, one expects the linear response theory to hold. However, for sufficient magnitudes of the external field, non-linear response may happen. It appears in particular conceivable for colloids displaying metallic or polarisability properties [Barany, 2009; Bazant and Squires, 2004; Figliuzzi et al.,

2014].

Assuming that the colloidal particles can still feel thermal fluctuations, in spite of the presence of strong forces, we model the dynamics of one particles with a Langevin equation reading

$$m\mathrm{d}\boldsymbol{V}(t) = -\gamma(E)\boldsymbol{V}(t)\mathrm{d}t + Q(E)\boldsymbol{E}\mathrm{d}t + \boldsymbol{\sigma}(E)\cdot\mathrm{d}\boldsymbol{W}(t) \tag{5.1}$$

$$\mathrm{d}\boldsymbol{X}(t) = \boldsymbol{V}(t)\mathrm{d}t \tag{5.2}$$

where $\boldsymbol{\sigma}(E)$ is the diffusion matrix, m the mass, $\gamma(E)$ the friction coefficient, $Q(E)$ the coupling constant with the electrical field. We assume the diffusive matrix $\boldsymbol{\sigma}(E)$ is diagonal (which means that $\mathrm{d}W_x$ and $\mathrm{d}W_y$ are independent) but due to the non-linear effect discussed above, we let the possibility that it is not proportional to the unity matrix. We write $\boldsymbol{x}(t) = (x(t), y(t))$ the space coordinates, $\sigma_{xx} = \sqrt{2D_x(E)}$ and $\sigma_{yy} = \sqrt{2D_y(E)}$. $\boldsymbol{W}(t) = (W_x(t), W_y(t))$ refers to the vector built upon two independent Gaussian white noises whose variance reads $\langle \mathrm{d}W_i(t)\mathrm{d}W_j(t')\rangle = \mathrm{d}t\,\delta_{i,j}\delta(t-t')$, $i, j = x, y$.

In the absence of the external field, $E = 0$, colloids are at equilibrium and the Einstein relation holds: $\beta = 2\gamma/D$. But when the electric field is high enough to produce the non-linear response suggested above, one does not expect that the Einstein relation sill hold. We thus assume that is indeed not the case here.

Having defined the dynamics of one particle, we now describe the whole system we consider. At low density limit, we assume the particles to be independent of each other and we consider initially N_A particles in the left system, say A, and N_B particles in the right system, say B, such that the total number of particles is fixed at $N = N_A + N_B$. The non-conservative field $\boldsymbol{E} = E\boldsymbol{e}_y$ is aligned along the y direction where periodic boundary conditions are assumed. In the transverse direction x, perfect hard walls are settled at the left side of the system A and the right side of the system B. The separation between the two systems is assumed to be made of a porous membrane (see figure 5.1), infinitely thin, whose "hard" part are supposed perfect as well, meaning that the repulsive potential symbolising the wall becomes infinite at contact but is null elsewhere. Furthermore we assume that an operator can vary independently the uniform electric field in the two parts A and B of the system. We call E_A and E_B the magnitude of the fields in each part respectively.

Focusing on the steady state, the stationary density probability distribution $P(\{\boldsymbol{x}_i, \boldsymbol{v}_i\}_{i=1}^N)$ verifies the stationary Kramers equation, which reads

$$0 = -\sum_{i=1}^{N} \boldsymbol{\nabla}_{\boldsymbol{x}_i}\cdot(\boldsymbol{v}P) + \boldsymbol{\nabla}_{\boldsymbol{v}_i}\cdot\left[\left(Q(E)\boldsymbol{E} - \gamma(E)\boldsymbol{v}\right)P - \boldsymbol{\sigma}(E)\cdot\boldsymbol{\nabla}_{\boldsymbol{v}_i}P\right]. \tag{5.3}$$

Particles being independent and the currents being homogeneous, one can look for a factorised solution $P(\{\boldsymbol{x}_i, \boldsymbol{v}_i\}_{i=1}^N) = \prod_{i=1}^N P(\boldsymbol{x}_i, \boldsymbol{v}_i)$, with $P(\boldsymbol{x}, \boldsymbol{v})$ also factorised (*cf.* equation (5.4) below).

At first sight, let us imagine that the systems are isolated from each other with a perfect wall — *i.e.* that the holes of the membrane are "filled". In this case, the boundary conditions are the following. Because of the walls, particles are prevented to leave the respective system they belong to. Thus, $\boldsymbol{J}^{(\boldsymbol{x})} = \boldsymbol{v}P = 0$ for $\boldsymbol{x} \in \partial\Lambda_{A,B}, \partial\Lambda_{A,B}$, corresponding to the edges of domains $\Lambda_{A,B}$. Also, we assume that the momentum probability current vanishes uniformly, which is a sound assumption here since walls are not supposed to provide or absorbed momentum. Eventually, the one particle stationary solution reads

$$P(\boldsymbol{x}, \boldsymbol{v}) \propto e^{-\frac{\gamma}{D_x} v_x^2} e^{-\frac{\gamma}{D_y}\left(v_y - \frac{Q}{\gamma}E\right)^2}. \tag{5.4}$$

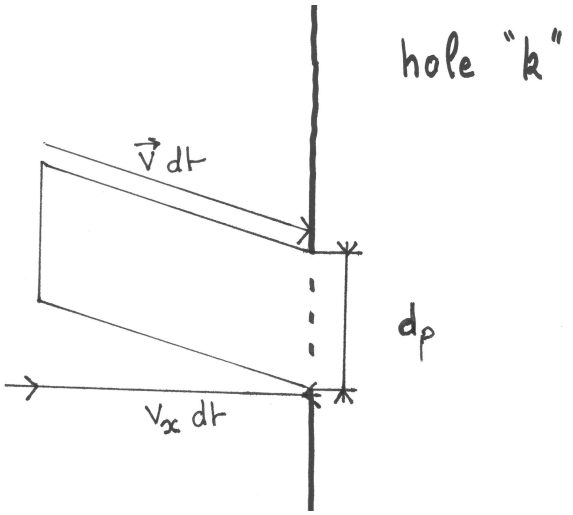

Figure 5.2 – Transfer of particles through one pore from A to B during t and $t + \mathrm{d}t$.

If one now allows exchange of particles through the pores of the porous membrane, a new stationary state settles, depending on the parameters of each systems. Our goal is now to compute the probabilities to exchange a particle from B to A (respectively from A to B) between t and $t + \mathrm{d}t$, knowing that there is N_A (or $N_B = N - N_A$) particles at time t. Let us focus first on one pore. A classical computation from kinetic theory [Reif, 2009] gives that, between t and $t + \mathrm{d}t$, the number of particles going from A to B is the number of particle with velocity $\boldsymbol{v}$ such that $v_x > 0$ that are in the parallelogram of small side d_p (the diameter of one hole) and length $\boldsymbol{v}\mathrm{d}t$ whose surface reads $v_x \mathrm{d}t d_p$ (see figure 5.2). Calling $\mathcal{S}^{(k)}_{v_x \mathrm{d}t d_p}$ the surface of the parallelogram related to the hole number k of the membrane, the probability that one particle goes

from A to B through the pore k, knowing that there is N_A particles in A reads

$$p_{\mathrm{d}t}(N_A - 1|N_A) = \mathrm{d}t\rho_A S_p \int_{v_x>0} \mathrm{d}v_x v_x P_A(v_x) \tag{5.5}$$

$$= \mathrm{d}t\rho_A S_p \frac{1}{2}\sqrt{\frac{D_x(E_A)}{\pi\gamma(E_A)}} \tag{5.6}$$

where $S_p = N_p d_p$, N_p being the total number of pores. Symmetrically,

$$p_{\mathrm{d}t}(N_A + 1|N_A) = \mathrm{d}t\rho_B S_p \frac{1}{2}\sqrt{\frac{D_x(E_B)}{\pi\gamma(E_B)}}\,. \tag{5.7}$$

One notices that the probability of having a transfer of two particles or more between t and $t + \mathrm{d}t$ is of order $\mathrm{d}t^{\geqslant 2} = o(\mathrm{d}t)$ (because the probability that two particles are in parallelograms of area $v_x \mathrm{d}t d_p$ is $\propto (\rho \mathrm{d}t)^2$ since particles are independent). Thus, beyond the two above events where only one particle is exchanged, the only other event is simply that nothing happens which reads, according to the normalisation of probability, $1 - (p_{\mathrm{d}t}(N_A + 1|N_A) + p_{\mathrm{d}t}(N_A - 1|N_A))$. Also, we should stress that we made the assumption that the distribution of particles position corresponds to the stationary density value $\rho_{A,B}$, which, as explained in the first chapter, is a sound assumption only when the jump frequency is very small compared to the frequency associated with the bulk relaxation time. Furthermore, we emphasise that these densities ρ_A, ρ_B corresponds to the bulk value of the densities, meaning that the membrane is assumed to not perturbed the local density of particles close to it. This is without doubt an idealisation and we will see henceforth what may happen in presence of a high energy barrier for overdamped active particles.

Calling $N_A = V_A \rho_A$, the master equation associated with this Markov process reads

$$\frac{\mathrm{d}P_t}{\mathrm{d}t}(\rho_A|\bar{\rho}) = \frac{\rho_A S_p}{2}\sqrt{\frac{D_x(E_A)}{\pi\gamma(E_A)}}\left(P_t(\rho_A + \tfrac{1}{V_A}|\bar{\rho}) - P_t(\rho_A|\bar{\rho})\right)$$
$$+ \frac{\rho_B S_p}{2}\sqrt{\frac{D_x(E_B)}{\pi\gamma(E_B)}}\left(P_t(\rho_A - \tfrac{1}{V_A}|\bar{\rho}) - P_t(\rho_A|\bar{\rho})\right)\,,$$

such that $\rho_A V_A + \rho_B V_B = (V_A + V_B)\bar{\rho}$. At large deviations limit, one can derive a stationary Hamilton-Jacobi equation (2.23) for the stationary large deviations function I (defined by $P(\rho_A|\bar{\rho}) \asymp e^{-V_A I(\rho_A|\bar{\rho})}$), which reads

$$I'(\rho_A|\bar{\rho}) = \ln \frac{\rho_A\sqrt{D_x(E_A)\gamma(E_A)^{-1}}}{\rho_B\sqrt{D_x(E_B)\gamma(E_B)^{-1}}}\,. \tag{5.8}$$

Chemical potentials attached to system $k = A, B$ then reads

$$\mu_k^{\rm cont}(\rho_k) = \ln \rho_k + \frac{1}{2} \ln \frac{D_x(E_k)}{\gamma(E_k)} \ . \tag{5.9}$$

The equalisation of chemical potentials gives the stationary densities in each systems, generally different when external driving fields are different.

To conclude, this simple example has shown that a non-linear effect produced by an applied electric field on certain colloids could modify the Maxwellian velocity distribution by introducing an effective temperature $\propto D/\gamma$ that depends on the external driving force. For this very simple case, chemical potentials attached to each system can be defined and are independent of the contact properties (because of our assumption that the density near the membrane is not perturbed by the latter). One is able to recognise the standard chemical potential related to independent particles, namely $\ln \rho$, but an extra parameter related to the effective temperature D/γ needs to be added. The latter is generally responsible for a shift in the stationary densities since their ratio reads

$$\frac{\rho_A^*}{\rho_B^*} = \frac{D_x(E_B)\gamma(E_A)}{D_x(E_A)\gamma(E_B)} \, . \tag{5.10}$$

At equilibrium, the Einstein relation between D and γ is satisfied and one gets $\beta = 2\gamma/D$. The additional part in the chemical potential depending on the temperature is always there but blank at equilibrium since temperature is uniform along the whole system.

5.2 Active particle systems in contact

After this simple example involving a perfect contact made of a permeable membrane, we would like to move to more realistic types of contact made of a general potential barrier. For this, we will consider other models of independent self-propelled particles [Cates and Tailleur, 2013; Fodor and Marchetti, 2018; Schnitzer, 1993; Tailleur and Cates, 2008] whose chemical potentials exhibit a strong dependence on the contact dynamics. We will see in particular that this effect is the exact counter-part for the exchange of particles of what has been seen to happen for the exchanged of volume (controlled by the pressure) in active systems [Fily et al., 2017; Solon, Fily, Baskaran, Cates, Kafri, Kardar and Tailleur, 2015; Solon et al., 2018*a*; Solon, Stenhammar, Wittkowski, Kardar, Kafri, Cates and Tailleur, 2015; Speck and Jack, 2016; Takatori et al., 2014; Winkler et al., 2015].

5.2.1 Some generalities about self-propelled particles

Self-propelled particles are part of what people call active matter, which has attracted lot of attention recently [Fodor and Marchetti, 2018; Marchetti et al., 2013]. Contrary to the systems encountered so far, particles (or rather colloids in the following) are not propelled by an external driving force but host in themselves their own self-propulsion mechanism. Such kind of driving is ubiquitous in the biological realm (cells, molecular motor, etc.) and in colloids science (self-catalytic colloids).

Most of self-propelled particles are small objects whose dynamics is usually described by an overdamped Langevin equation (when inertial effects are neglected). A general equation for one self-propelled particle evolving in a potential $U(\boldsymbol{x})$ reads

$$\mathrm{d}\boldsymbol{X}(t) = \boldsymbol{V}(t)\mathrm{d}t - \mu_{\mathrm{tr}}\boldsymbol{\nabla}U(\boldsymbol{X}(t))\mathrm{d}t + \sqrt{2D_{\mathrm{tr}}}\mathrm{d}\boldsymbol{W}_{\mathrm{tr}}(t) \tag{5.11}$$

where $\mathrm{d}\boldsymbol{W}_{\mathrm{tr}}(t)$ is a two dimensional Gaussian white noise with a variance

$$\langle \mathrm{d}W_{tr,\,i}(t')\mathrm{d}W_{tr,\,j}(t)\rangle = \mathrm{d}t\delta(t'-t)\delta_{i,j}\ ,$$

μ_{tr} the (translational) mobility, D_{tr} the (translational) diffusion coefficient and $\boldsymbol{V}$ encodes the self-propulsion. Different models of self-propulsion exist and mostly vary on the prescribed stochastic dynamics of its *direction*, keeping its norm fixed. We will consider in particular *Run-&-Tumble particles* (RTP) as well as *Active Brownian particles* (ABP) (see [Solon, Cates and Tailleur, 2015] for a comparative study). One then write $\boldsymbol{V}(t) = v_0\boldsymbol{e}(\theta(t))$ where $\theta(t)$ is the angle, $\boldsymbol{e}(\theta) = (\cos\theta, \sin\theta)$ in two dimensions, and $v_0 > 0$ the amplitude of the self-propulsion, homogeneous to a velocity.

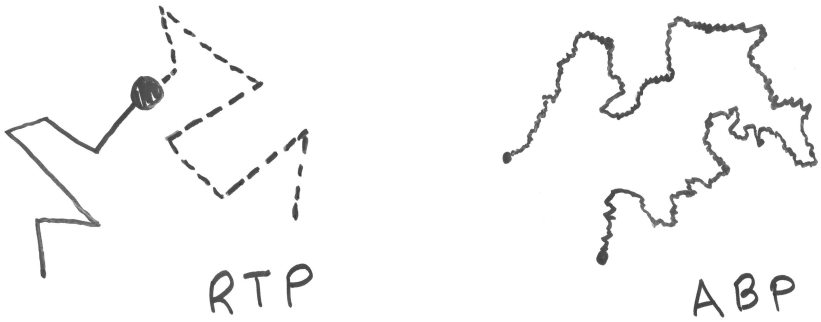

Figure 5.3 – Sketch of trajectories of Run-&-Tumble particles (left) and Active Brownian Particles (right).

Run-&-Tumble particles (RTPs). RTPs model was firstly inspired by the dynamics of bacteria. Basically, RTPs alternate between straight moves ("run") for a random time before reorienting its direction ("tumble") to perform a second straight move ("run"), *etc.* (see figure 5.3). A simple modelling then consists in assuming that

$\theta(t)$ follows a simple jump Poisson process at a rate α, with a probability to draw a new angle between θ and $\theta + \mathrm{d}\theta$ that reads $\mathrm{d}\theta/2\pi$.

Active Brownian particles (ABPs). As for the ABPs, they were introduced to mimic the dynamics of colloidal particles with asymmetric chemical or physical properties causing its (self-)propulsion. Here, the angle follows a Brownian dynamics which reads $\mathrm{d}\theta(t) = \sqrt{2D_\mathrm{r}}\mathrm{d}W_\mathrm{r}(t)$, D_r being the (rotational) diffusion coefficient and $\mathrm{d}W_\mathrm{r}$ a one-dimensional Gaussian white noise of variance

$$\langle \mathrm{d}W_\mathrm{r}(t')\mathrm{d}W_\mathrm{r}(t)\rangle = \mathrm{d}t\,\delta(t'-t)\ .$$

Even for independent particles, the lack of time-reversibility – which appears in presence of a non-uniform potential as we will see henceforth – in the dynamics makes it difficult to compute the stationary probability density distribution of the position (lack of detailed balance in the Master or Fokker-Planck equation). If perturbative computations are feasible for certain limits of the parameters, for instance when the reorientation time scale is very small compared to the translational time scales as we will see in next sections, we shall begin with one of the few available exact results, namely RTP in one dimension [Schnitzer, 1993; Tailleur and Cates, 2008].

5.2.2 Run-&-Tumble particles in 1D

In one dimension, there are only two possible directions of motion, namely left or right. Calling $P_L(x,t)$ and $P_R(x,t)$ the probability density distributions associated with a velocity oriented to the left or to the right respectively, the master equation reads

$$\frac{\partial P_R}{\partial t}(x,t) = -\frac{\partial}{\partial x}\left[\left(v_0(x) - \mu_\mathrm{tr}U'(x)\right)P_R(x,t)\right] - \alpha\left(P_R(x,t) - P_L(x,t)\right) \tag{5.12}$$

$$\frac{\partial P_L}{\partial t}(x,t) = -\frac{\partial}{\partial x}\left[\left(-v_0(x) - \mu_\mathrm{tr}U'(x)\right)P_L(x,t)\right] + \alpha\left(P_R(x,t) - P_L(x,t)\right)\ . \tag{5.13}$$

Writing $P(x,t) = P_R(x,t) + P_L(x,t)$ and $D(x,t) = P_R(x,t) - P_L(x,t)$, equations (5.27) read

$$\frac{\partial P}{\partial t}(x,t) = -\frac{\partial J}{\partial x}(x,t) \qquad \text{with} \qquad J(x,t) = v_0(x)D(x,t) - \mu_\mathrm{tr}U'(x)P(x,t) \tag{5.14}$$

$$\frac{\partial D}{\partial t}(x,t) = -\frac{\partial}{\partial x}\left[v_0(x)P(x,t) - \mu_\mathrm{tr}U'(x)D(x,t)\right] - 2\alpha D(x,t)\ . \tag{5.15}$$

Now, let us formally split our system into two parts A and B that are separated

by a high barrier $U(x)$ as drawn in figure 5.1. One can also assume that $v_0(x) = v_A$ if $x \in \Lambda_A$ and $v_0(x) = v_B$ if $x \in \Lambda_B$, *i.e.* that the velocities in A and B can be different. This situation may be particularly relevant for light-controlled self-catalytic propulsion as described for instance in [Buttinoni et al., 2013; Gomez-Solano et al., 2016; Palacci et al., 2013; Stenhammar et al., 2016].

In the bulk of each system, where the potential $U(x)$ is flat, the current reads $J(x,t) = v_{A,B}D(x,t)$. Since the boundaries are closed, the current is vanishing at boundaries and one can look for a stationary solution whose current is null. Then, $P(x) = p_A$ or p_B for x in the bulk of A or B respectively. The question we ask is how the two densities ρ_A and ρ_B in the bulk of each system are related to each other when particles are allowed to cross the potential barrier $U(x)$ centred at $x = 0$.

To address this question, we look for a solution in the presence of the potential barrier. When the potential barrier $U(x)$ is such that $v_0(x) > \mu_{\rm tr}|U'(x)|$ for[1] all x, it has been shown in [Tailleur and Cates, 2008] that a steady state solution of equations (5.14) reads

$$P(x) \propto \frac{1}{1-\left(\frac{\mu_{\rm tr}U'(x)}{v_0(x)}\right)^2} \exp\left[-\int^x \mathrm{d}q \left(\frac{\mu_{\rm tr}\alpha}{v_0^2(q)}\right) \frac{U'(q)}{1-\left(\frac{\mu_{\rm tr}U'(q)}{v_0(q)}\right)^2}\right] , \tag{5.16}$$

with $P(x) = 0$ if $v_0(x) < \mu_{\rm tr}|U'(x)|$. One can see that this solution is associated with a vanishing current $J(x)$. We should also note that the latter displays an accumulation of particles near the potential (see [Fodor and Marchetti, 2018] for instance), which already suggests that something different from the equilibrium happens near the separating barrier.

Entropy production of 1D RTPs. One should make a remark at this stage. The reader might indeed wonder where the non-equilibrium character of this model resides since the noise is symmetric and the force $-\mu_{\rm tr}U'(x)$ derives from a potential. Let us then compare trajectories with their time-reversal counterpart to examine the non-equilibrium character of this model (the study of time-reversal symmetry in self-propelled particles and active matter has attracted recently a lot of interest, see for instance [Fodor et al., 2016; Nardini et al., 2017]). For one particle, a trajectory of length T corresponds to the position $x(t)$ as well as the direction of its velocity $\pm v_0$, or equivalently the instants of velocity reversal $\{t_k\}_{k=1}^{\mathcal{N}_j}$, for each time $t \in [0,T]$, $\mathcal{N}_j$ being the number of jumps during $[0,T]$. The position $x(t)$ thus obeys the equation of motion

$$\dot{x}(t) = -\mu_{\rm tr}U'(x(t)) + \iota(t)v_0 \,, \tag{5.17}$$

[1] This means that the propulsion must be sufficient so that a particle can overcome the barrier and go to the other side.

with

$$\iota(t) = \iota_k \in \{+1, -1\} \qquad \text{for } t_k \leqslant t < t_{k+1}\,.$$

Calling $x^{\mathrm{R}}(t) = x(T-t)$ the time-reversed trajectory, it necessarily obeys the equation

$$\dot{x}^{\mathrm{R}}(t) = -\mu_{\mathrm{tr}} U'(x^{\mathrm{R}}(t)) + \underbrace{2\mu_{\mathrm{tr}} U'(x^{\mathrm{R}}(t)) - \iota(T-t)v_0}_{\notin\{+v_0,-v_0\}}\,. \tag{5.18}$$

But clearly, the last term cannot be realised by the natural noise present in the system since the latter is only bi-valued, unless the external force vanishes ($U'(x) = 0$). Thus, the presence of an external potential breaks the time-reversal symmetry and the entropy production gets infinite (because the probability to observe the time-reversed trajectory is simply zero). One should note that this entropy production is not related to any global current flowing in the system, but is necessary to maintain the non-equilibrium state.

In order to compute the stationary distribution of density in A (and B), one can proceed in two ways. The first one is straightforward: as one knows the exact stationary distribution for the whole system, one can compute exactly the probability density of a configuration $\{X_i\}_{i=1}^N$ and then find the probability to have N_A particles in A. In a word, this way is the one someone would apply in an equilibrium situation where the Gibbs-Maxwell-Boltzmann distribution is known. The second one proceeds in a similar fashion as in section 5.1 and focus directly on the exchange dynamics at the contact area.

Direct computation

The stationary solution $\rho(x) = NP(x)$ reads

$$\begin{aligned}
&\text{For } x \in \Lambda_A, \quad \rho(x) = \frac{\rho_A^*}{1 - \left(\frac{\mu_{\mathrm{tr}} U'(x)}{v_A}\right)^2} \exp\left[-\int_{x_A^*}^{x} \mathrm{d}q\, \frac{\mu_{\mathrm{tr}}\alpha}{v_A^2} \frac{U'(q)}{1 - \left(\frac{\mu_{\mathrm{tr}} U'(q)}{v_A}\right)^2}\right] \\
&\text{For } x \in \Lambda_B, \quad \rho(x) = \frac{\rho_B^*}{1 - \left(\frac{\mu_{\mathrm{tr}} U'(x)}{v_B}\right)^2} \exp\left[-\int_{x_B^*}^{x} \mathrm{d}q\, \frac{\mu_{\mathrm{tr}}\alpha}{v_B^2} \frac{U'(q)}{1 - \left(\frac{\mu_{\mathrm{tr}} U'(q)}{v_B}\right)^2}\right]\,.
\end{aligned} \tag{5.19}$$

with x_A^* and x_B^* two points respectively in the bulk of A and B where the potential barrier $U(x) = 0$; and ρ_A^*, ρ_B^* the densities in the bulks to be determined. The current being continuous at contact between A and B, the constants ρ_A^* and ρ_B^* are not independent from each other but are related by the equalisation of the stationary currents from A to B and from B to A. The latter equality reads

$$v_A \rho_A^* e^{-\Delta Q_A} = v_B \rho_B^* e^{-\Delta Q_B} \tag{5.20}$$

with

$$\Delta Q_k = \int_{x_k^*}^{0} \mathrm{d}q \, \frac{\alpha \mu_{\mathrm{tr}}}{v_k^2} \frac{U'(q)}{1 - (\mu_{\mathrm{tr}} U'(q)/v_k)^2} \, . \tag{5.21}$$

At the thermodynamic limit where L_A and L_B tend to infinity, the normalisation condition of $\rho(x)$ reads

$$N = \int_{\Lambda_A \cup \Lambda_B} \mathrm{d}x \rho(x) = L_A \rho_A^* + L_B \rho_B^* + o(L_A, L_B) \, . \tag{5.22}$$

since the non-uniformity caused by the external potential $U(x)$ stays localised around the contact area. Equations (5.20) and (5.22) of course completely determine ρ_A^* and ρ_B^* but one would like to see how chemical potentials of systems in contact can be defined in this simple case.

Knowing the density $\rho(x)$ (or $P(x) = \rho(x)/N$), one can now calculate the probability to observe N_A particles in the region Λ_A (and thus $N_B = N - N_A$ particles in Λ_B). Indeed, particles being independent, the probability distribution is simply a binomial

$$P(N_A|N) = \frac{1}{N^N} \binom{N}{N_A} \left(\int_{\Lambda_A} \mathrm{d}x \, \rho(x) \right)^{N_A} \left(\int_{\Lambda_B} \mathrm{d}x \, \rho(x) \right)^{N - N_A} \, . \tag{5.23}$$

The associated large deviations function which is the meaningful quantity at the thermodynamic limit then reads

$$P(\rho_A|\bar{\rho}) \asymp e^{-L\mathcal{I}(\rho_A, \rho_B)} \quad \text{with} \quad \mathcal{I}(\rho_A, \rho_B) = \gamma_A \rho_A \ln \frac{\rho_A}{\rho_A^*} + \gamma_B \rho_B \ln \frac{\rho_B}{\rho_B^*} \tag{5.24}$$

with $\gamma_A \rho_A + \gamma_B \rho_B = \bar{\rho}$ and $L = L_A + L_B$.

Eventually, the stationary densities – that we already know! – are dictated by the minimum of the large deviations function $\mathcal{I}$, characterised by the vanishing of its derivative:

$$\mathcal{I}'(\rho_A^*, \rho_B^*) = 0 \implies \mu_A^{\mathrm{cont}}(\rho_A^*) = \mu_B^{\mathrm{cont}}(\rho_B^*) \tag{5.25}$$

with

$$\mu_k^{\mathrm{cont}}(\rho_k) = \ln \frac{\rho_k v_k e^{-\Delta Q_k}}{\alpha} \, , \tag{5.26}$$

where α as been introduced as a typical rate (or typical inverse time scale) to get an dimensionless argument in the logarithm. One thus notices that beyond the expected "perfect gas" contribution $\ln \rho_k$, a non-trivial dependence on the contact appears in the expression of a chemical potential at contact. Even when the velocities in each side are equals ($v_A = v_B$), ΔQ_A and ΔQ_B (see equation (5.21)) are different as soon as the potential barrier $U(x)$ is asymmetric.

Computation with the explicit Poisson dynamics over the particle number

To make the link with the previous chapters, we would like here to compute the large deviations function $I(\rho_A|\bar{\rho})$ for this model, by directly using a model of the exchange dynamics. Following section 5.1, the independence of the particles implies that the number of particles N_A in the system A obeys a Poisson process. Its associated Master equation reads

$$\frac{\mathrm{d}P_t}{\mathrm{d}t}(\rho_A|\bar{\rho}) = v_A\rho(0^-)\left(P_t(\rho_A+\tfrac{1}{V_A}|\bar{\rho}) - P_t(\rho_A|\bar{\rho})\right) + v_B\rho(0^+)\left(P_t(\rho_A-\tfrac{1}{V_A}|\bar{\rho}) - P_t(\rho_A|\bar{\rho})\right) , \tag{5.27}$$

with

$$\rho(0^-) = \rho_A e^{-\Delta Q_A} \qquad \text{and} \qquad \rho(0^+) = \rho_B e^{-\Delta Q_B} ,$$

ρ_k being the actual densities in the bulk of system k such that $\gamma_A\rho_A + \gamma_B\rho_B = \bar{\rho}$, and ΔQ_k being defined in equation (5.21). $v_k\rho_k e^{-\Delta Q_k}$ is nothing but the average current of particles (and also the transition rates here for this very simple Poisson process) from $k \to k' \neq k$, $k, k' = A, B$.

The derivative of the large deviations function associated with $P(\rho_A|\bar{\rho})$, solution of the Hamilton-Jacobi equation (2.23), reads

$$I'(\rho_A|\bar{\rho}) = \ln\frac{v_A\rho_A e^{-\Delta Q_A}}{v_B\rho_B e^{-\Delta Q_B}} . \tag{5.28}$$

We thus retrieve the chemical potentials μ_k^{cont} of (5.26).

In line with previous chapters, we note that the additivity of the large deviations function is again a consequence of the factorisation of the macroscopic transition rates (which are of Sasa-Tasaki type (see equation (3.11)) as well as macroscopic detailed balance (only one particle can be exchanged per unit time).

Relation between chemical potential and the pressure

This situation is very reminiscent to what happens to the pressure in the same kind of active systems. As mentioned in the introduction, several studies on the notion of pressure in active systems has been conducted quite recently [Fily et al., 2017; Solon, Fily, Baskaran, Cates, Kafri, Kardar and Tailleur, 2015; Solon et al., 2018*a*,*b*; Solon, Stenhammar, Wittkowski, Kardar, Kafri, Cates and Tailleur, 2015]. The pressure can be computed as the mean force applied by the particles onto the external operator who is interacting with the system through the external potential $U(x)$ at the interface:

$$P_{k\to U(x)}(\rho_k^*) = \int_{x_k^*}^{0} \rho(x)U'(x)\,\mathrm{d}x . \tag{5.29}$$

If the system is at equilibrium (this can be achieved by taking the limit $\alpha \to \infty$, $D = v_0^2/\alpha$ kept fixed with $\beta = \mu_{\rm tr}/D$ the effective temperature), $\rho(x) = e^{-\beta U(x)}/Z(\beta)$ and $P_{k\to U(x)} = \beta^{-1}\rho_k^*$ as one would expect for a perfect gas. But since, $\rho(x)$ is non-local in $U(x)$ for RTPs in 1D, $P_{k\to U(x)}$ has been shown to strongly depends on the external potential barrier profile $U(x)$. Indeed, it appears that the pressure can be exactly computed here (see appendix of [Solon, Fily, Baskaran, Cates, Kafri, Kardar and Tailleur, 2015] for instance):

$$P_{k\to U(x)}(\rho_k^*) = \frac{\rho_k^* v_k^2}{\mu_{\rm tr}\alpha}\left(1 - e^{-\Delta Q_k}\right) . \tag{5.30}$$

At equilibrium, there is a well known relationship between pressure and chemical potentials which is often called a Maxwell relation (see [Sekimoto, 2010, Chapter 2], [Sasa and Tasaki, 2006] or [Takatori and Brady, 2015; Takatori et al., 2014] in the context of active matter). The latter reads

$$\frac{\partial P(\rho)}{\partial \rho} = \rho \frac{\partial \mu(\rho)}{\partial \rho} . \tag{5.31}$$

However, for independent RTPs in 1D, one has

$$\rho_k \frac{\partial \mu_k}{\partial \rho_k} = 1 \qquad \text{and} \qquad \frac{\partial P_{k\to U(x)}}{\partial \rho_k} = \frac{v_k^2}{\alpha \mu_{\rm tr}}\left(1 - e^{-\Delta Q_k}\right) , \tag{5.32}$$

which thus show that the Maxwell equation does not hold for the chemical potential defined above. In the case where $v_A = v_B = v_0$, part of the discrepancy can be absorbed by a redefinition of the chemical potential μ_k. Indeed, the chemical potential μ_k is in fact a *dimensionless* chemical potential and one could define $\mu_k \to (\alpha\mu_{\rm tr}/v_0^2)\mu_k$, the parameter $v_0^2/(\alpha\mu_{\rm tr})$ playing the role of an effective temperature shared by both systems (otherwise, this redefinition of μ_k with $v_A \neq v_B$ would destroy the equalisation at stationarity since the effective temperature would be different). But even with this redefinition, $1 \neq (1 - e^{-\Delta Q_k})$ and the Maxwell equation does not hold.

The breaking of the Maxwell relation could have actually been expected. Indeed, as shown in [Sasa and Tasaki, 2006], the latter relation is intimately related to a balance between forces applied by an external potential on the particles and by the pressure exerted by the particles. Nevertheless, since ρ_k^* for $k = A, B$ are related through the equality of currents (5.20), one can notice that

$$\left|\frac{P_{B\to U(x)}}{P_{A\to U(x)}}\right| = \frac{v_B}{v_A}\frac{e^{\Delta Q_B} - 1}{e^{\Delta Q_A} - 1} \neq 1 , \tag{5.33}$$

as long as $v_A \neq v_B$ and $\Delta Q_A \neq \Delta Q_B$. Hence, there exists a net force applied on the external operator producing the external potential $U(x)$ which needs to be balanced

by something else to keep $U(x)$ centred at $x = 0$.

Eventually, no link seems to emerge between the mechanical pressure (5.29) and the chemical potentials at contact. This is expected to be so because of the lack of balance between the forces exerted by the external potential and the pressure of the particles, but further studies in this direction should definitely be performed to validate more systematically this result.

5.2.3 Active dynamics in 2D: perturbative evaluation

As already said in the introduction of the previous section, very few situations even for independent particles allow explicit exact calculations. To see if the effect of the potential described before is not specific to the run-&-tumble dynamics and the dimension one, we would like to look at what happens in dimension 2 again for a run-&-tumble dynamics (RTPs) as well as for active Brownian particles (ABPs). We consider first the RTP dynamics. Techniques used in this subsection are borrowed from [Bertin et al., 2009; Peshkov et al., 2014].

Run-&-Tumble in 2D

In two dimensions, relevant variables are the position $\boldsymbol{x} = x\boldsymbol{e}_x + y\boldsymbol{e}_y$ and the angle $\theta \in [0, 2\pi[$. The master equation which describes the evolution of the probability density function $P_t(\boldsymbol{x}, \theta)$ reads

$$\frac{\partial P_t}{\partial t}(\boldsymbol{x}, \theta) = -\boldsymbol{\nabla}_{\boldsymbol{x}} \cdot [(v_0(x)\boldsymbol{e}(\theta) - \mu_{\mathrm{tr}} \boldsymbol{\nabla}_{\boldsymbol{x}} U(\boldsymbol{x}))P_t(\boldsymbol{x}, \theta)] + \frac{\alpha}{2\pi} \int_0^{2\pi} \mathrm{d}\tilde{\theta} P_t(\boldsymbol{x}, \tilde{\theta}) - \alpha P_t(\boldsymbol{x}, \theta) \, . \tag{5.34}$$

To find a general stationary solution seems out of reach at this stage. However, one can intuitively expect an equilibrium-like limit behaviour where an infinite tumbling rate over the angle would lead to a translational diffusive-like behaviour if the velocity v_0 scales in the proper way. With straightforward dimensional analysis, one expects that in this limiting behaviour, the effective diffusion coefficient $D \sim v_0^2/\alpha$ should remain finite while $\alpha \to \infty$. Our goal is then to compute the first order correction in α of this equilibrium-like limit. Note that v_0 is supposed here to be piecewise constant ($v_0(\boldsymbol{x}) = v_A$ for $\boldsymbol{x} \in \Lambda_A$ and $v_0(\boldsymbol{x}) = v_B$ for $\boldsymbol{x} \in \Lambda_B$).

To perform this study, we introduce several quantities and notations (see [Peshkov et al., 2014] for an extensive review of these techniques). First, we define the Fourier transform over the angle θ:

$$P_t(\boldsymbol{x}, \theta) = \frac{1}{2\pi} \sum_{k \in \mathbb{Z}} f_{k,\,t}(\boldsymbol{x}) e^{-ik\theta} \quad \text{and} \quad f_{k,\,t}(\boldsymbol{x}) = \int_0^{2\pi} \mathrm{d}\theta \, P_t(\boldsymbol{x}, \theta) e^{ik\theta} \tag{5.35}$$

with $\bar{f}_{k,\,t} = f_{-k,\,t}$, $\bar{z}$ being the complex conjugate of $z \in \mathbb{C}$. With these notations, one

gets $P_t(\boldsymbol{x}) = \int_0^{2\pi} \mathrm{d}\theta P_t(\boldsymbol{x},\theta) = f_{0,t}(\boldsymbol{x})$. Projecting the master equation (5.34) onto the Fourier basis we have just introduced, gives a hierarchy of equations on $f_{k,t}$, $k \in \mathbb{Z}$:

$$\frac{\partial f_{k,t}}{\partial t} = -v_0\left(\partial f_{k+1,t} + \bar{\partial} f_{k-1,t}\right) + \mu_{\mathrm{tr}}\boldsymbol{\nabla}\cdot\left(f_{k,t}\boldsymbol{\nabla}U\right) + \alpha\left(f_{k,t}\delta_{k,0} - f_{k,t}\right) \ , \tag{5.36}$$

where one has introduced the complex derivatives $\partial = (\partial_x - i\partial_y)/2$ and $\bar{\partial} = (\partial_x + i\partial_y)/2$. In order to perform the perturbative expansion, let us write the first three equations:

$$\begin{aligned}
\frac{\partial P_t}{\partial t} &= -v_0\left(\bar{\partial} f_{1,t} + \partial \bar{f}_{1,t}\right) + \mu_{\mathrm{tr}}\boldsymbol{\nabla}\cdot\left(P_t\boldsymbol{\nabla}U\right) \\
\frac{\partial f_{1,t}}{\partial t} &= -\alpha f_{1,t} - v_0\left(\bar{\partial} P_t + \partial f_{2,t}\right) + \mu_{\mathrm{tr}}\boldsymbol{\nabla}\cdot\left(f_{1,t}\boldsymbol{\nabla}U\right) \\
\frac{\partial f_{2,t}}{\partial t} &= -\alpha f_{2,t} - v_0\left(\bar{\partial} f_{1,t} + \partial f_{3,t}\right) + \mu_{\mathrm{tr}}\boldsymbol{\nabla}\cdot\left(f_{2,t}\boldsymbol{\nabla}U\right) \ .
\end{aligned} \tag{5.37}$$

For $k \geqslant 1$, it is not difficult to see that $f_{k\geqslant 1}$ relax quickly to their stationary state for large α. Hence, one can assume that at a time scale very large compared to α^{-1},

$$\begin{aligned}
f_{1,t} &= -\frac{v_0}{\alpha}\left(\bar{\partial} P_t + \partial f_{2,t}\right) + \frac{\mu_{\mathrm{tr}}}{\alpha}\boldsymbol{\nabla}\cdot\left(f_{1,t}\boldsymbol{\nabla}U\right) \\
f_{2,t} &= -\frac{v_0}{\alpha}\left(\bar{\partial} f_{1,t} + \partial f_{3,t}\right) + \frac{\mu_{\mathrm{tr}}}{\alpha}\boldsymbol{\nabla}\cdot\left(f_{2,t}\boldsymbol{\nabla}U\right)
\end{aligned} \tag{5.38}$$

Fixing $D = v_0^2/2\alpha$, one obtains that $v_0 \sim \alpha^{1/2}$. Thus, if one wants to keep only up to first order corrections in α^{-1}, f_1 and f_2 read

$$\begin{aligned}
f_{2,t} &= \frac{2D}{\alpha}\bar{\partial}\bar{\partial}P_t \\
f_{1,t} &= -\left[\frac{(2D)^{1/2}}{\alpha^{1/2}}\bar{\partial}P_t + \frac{(2D)^{3/2}}{\alpha^{3/2}}\partial\bar{\partial}\bar{\partial}P_t \right. \\
&\qquad \left. + \mu_{\mathrm{tr}}\frac{(2D)^{1/2}}{\alpha^{3/2}}\boldsymbol{\nabla}\cdot\left(\bar{\partial}P_t\boldsymbol{\nabla}U\right)\right] \ .
\end{aligned} \tag{5.39}$$

Using the identities $\partial\bar{\partial} = \Delta/4$ and $2\Re(\bar{\partial} f_{1,t}) = \partial\bar{f}_{1,t} + \bar{\partial} f_{1,t}$, one eventually gets a closed equation on $P_t(\boldsymbol{x})$ which reads

$$\frac{\partial P_t}{\partial t} = D\boldsymbol{\nabla}\cdot\left[\boldsymbol{\nabla}\left(P_t + \frac{D}{2\alpha}\Delta P_t\right)\right] + \frac{\mu_{\mathrm{tr}}D}{\alpha}\boldsymbol{\nabla}\cdot\left[\Delta P_t\boldsymbol{\nabla}U + (\boldsymbol{\nabla}P_t\cdot\boldsymbol{\nabla})\boldsymbol{\nabla}U\right] + \mu_{\mathrm{tr}}\boldsymbol{\nabla}\cdot\left(P_t\boldsymbol{\nabla}U\right) \ . \tag{5.40}$$

Looking for a stationary perturbative solution, we propose the following ansatz

$$P(\boldsymbol{x}) \propto \exp\left(-\phi_0(\boldsymbol{x}) - \frac{1}{\alpha}\phi_1(\boldsymbol{x})\right) \ , \tag{5.41}$$

where ϕ_0 and ϕ_1 do not depend on α. Assuming that $U(\boldsymbol{x}) = U(x)$, *i.e.* that U does

not depend on y, one gets

$$\phi_0(x) = \frac{\mu_{\rm tr}}{D} U(x) \tag{5.42}$$

$$\phi_1(x) = -\frac{1}{2}U''(x) - \frac{1}{4D}\left(U'(x)\right)^2 + \frac{1}{2D^2}\int^x \mathrm{d}q\,\left(U'(q)\right)^3 \ . \tag{5.43}$$

One thus notices the presence of a non-local contribution of the external potential barrier at order α^{-1}. This contribution is quite similar to the 1D case at order α^{-1} and gives different contributions to ΔQ_k in (5.21) depending on $k = A,\, B$. Particles being independent, results of the 1D case can be easily extended to this 2D situation.

Active Brownian Particles in 2D

For the active Brownian particles, the dynamics is very similar except for the angle that follows a Brownian motion rather than a jump process. The corresponding master equation reads

$$\frac{\partial P_t}{\partial t}(\boldsymbol{x},\theta) = -\boldsymbol{\nabla}_{\boldsymbol{x}}\cdot\left((v_0(x)\boldsymbol{e}(\theta) - \mu_{\rm tr}\boldsymbol{\nabla}_{\boldsymbol{x}}U(\boldsymbol{x}))P_t(\boldsymbol{x},\theta)\right) + D_r\frac{\partial^2 P_t}{\partial\theta^2} \ . \tag{5.44}$$

Projecting this Fokker-Planck equation on the Fourier basis (5.35), one obtains

$$\frac{\partial f_{k,t}}{\partial t} = -v_0\left(\partial f_{k+1,t} + \bar{\partial} f_{k-1,t}\right) + \mu_{\rm tr}\boldsymbol{\nabla}\cdot\left(f_{k,t}\boldsymbol{\nabla}U\right) - k^2 D_{\rm r} f_{k,t} \tag{5.45}$$

This time, we look at the limit where $D_{\rm r}\to\infty$ and we keep $D = v_0^2/2D_{\rm r}$ fixed. One can recognise that up to $k=2$, the hierarchy of equations is the same if one changes $D_{\rm r}\leftrightarrow\alpha$ except for $k=2$ where a factor $2^2 = 4$ appears. This does not affect the fast relaxation of the $f_{k\geqslant 1}$ and the final equation over $P_t(\boldsymbol{x})$ reads

$$\frac{\partial P_t}{\partial t} = D\boldsymbol{\nabla}\cdot\left[\boldsymbol{\nabla}\left(P_t + \frac{D}{8D_{\rm r}}\Delta P_t\right)\right] + \frac{\mu_{\rm tr}D}{D_{\rm r}}\boldsymbol{\nabla}\cdot\left[\Delta P_t\boldsymbol{\nabla}U + (\boldsymbol{\nabla}P_t\cdot\boldsymbol{\nabla})\boldsymbol{\nabla}U\right] + \mu_{\rm tr}\boldsymbol{\nabla}\cdot(P_t\boldsymbol{\nabla}U) \tag{5.46}$$

Eventually, looking for a stationary solution with a similar ansatz (5.41) as in the RTP case,

$$P(\boldsymbol{x}) \propto \exp\left(-\phi_0(\boldsymbol{x}) - \frac{1}{D_{\rm r}}\phi_1(\boldsymbol{x})\right) \ , \tag{5.47}$$

one gets

$$\phi_0(x) = \frac{\mu_{\rm tr}}{D} U(x) \tag{5.48}$$

$$\phi_1(x) = -\frac{1}{8}U''(x) - \frac{13}{16D}\left(U'(x)\right)^2 + \frac{7}{8D^2}\int^x \mathrm{d}q\,\left(U'(q)\right)^3 \ . \tag{5.49}$$

Conclusions are the same as for RTPs in 2D since the expressions are very closed to each other, except for numerical prefactors.

5.3 Conclusion & relations with chapter 2 and 3

All the systems presented in this chapter are independent particles systems for which at most one particle can be exchanged at a time between A and B subsystems. This naturally led to the macroscopic detailed balance (2.35). Associated macroscopic transition rates were found to be of Sasa-Tasaki type or Arrhenius type (3.7) which naturally led to the additivity property. Nevertheless, one has seen that additional contributions to the bulk or equilibrium chemical potential were present. These additional contributions can be organised in two types for the simple models considered here (cases investigated in this chapter have often mixed this two contributions):

1. A non-uniformity of the effective temperature. For the first model of externally driven colloids, these effective temperatures of both systems were controlled each by the external driving fields. As for the RTPs and ABPs, the effective temperature-like parameters were rather controlled by the fixed value of the non-uniform velocity $v_0(x) = v_A$ or v_B. In all these situations, the consequence of this non-uniformity was to induce a bias in the microscopic transition rates, hence leading to a bias in the macroscopic transition rates. This situation is thus very similar to the one described in 3.1.3 for which an extra-tilting of the microscopic transition rates at contact has been considered.

2. The second contribution corresponds to a modification of the stationary distribution value at the top of the high energy barrier, compared to the equilibrium situation. When $P(0^-) \neq P(0^+)$, which has been noticed to be the case when the potential barrier $U(x)$ is not symmetric, macroscopic transition rates are then tilted and provide an extra-contribution to the perfect gas chemical potential. By analogy with driven lattice gas cases, this contribution corresponds to a departure from equilibrium of the local probability distributions, thus breaking the local detailed balance condition with respect to equilibrium transition rates.

However, one should eventually emphasise that this two types of extra-contributions are ambiguous and strongly depend on the definition of the frontier between both systems. Indeed, if the contact area containing the high potential barrier would have been considered as a contact region separated from both systems A and B, the difference in $P(0^{\pm})$ would have been included in the coarse-grained transition rates involving the work to climb the potential barrier, thus leading to an asymmetry of the macroscopic transition rates.

Eventually, contrary to mass transport models and other driven lattice gas models, the notion of mechanical pressure can be defined without any ambiguity. We have seen that the latter was not related to the chemical potential at contact through a Maxwell relation as one may have expected (see [Sasa and Tasaki, 2006]). Even if

further studies would be necessary to assess a definitive conclusion, one can suspect that this is so because of the lack of balance of mechanical forces exerted on the high energy barrier.

CHAPTER 6

Conclusion and outlook

6.1 General conclusion

The work presented in this thesis aimed at looking at a thermodynamic structure for non-equilibrium (almost) uniform systems in a steady-state, focusing on a particular situation, namely the contact between two systems. Following previous studies [Bertin et al., 2006, 2007; Dickman, 2014; Dickman and Motai, 2014; Pradhan et al., 2010, 2011; Sasa and Tasaki, 2006], we mainly concentrated on mass transport models and driven lattice gases for which the most natural conserved quantity is the number of particles, volume being fixed.

In chapter 2, we expounded in a quite general way the large deviations analysis of the densities in each systems, which is the relevant framework to derive variational principles and more generally to study the thermodynamic limit. The latter analysis has been performed in the idealised limit of the vanishing exchange rate at contact, as first suggested by [Sasa and Tasaki, 2006]. In this limit, we have performed a multi-scale analysis which has led to the main equation of the chapter, namely the equation over the stationary large deviations function $\mathcal{I}(\rho_A, \rho_B)$, which was called the Hamilton-Jacobi equation. Eventually, the macroscopic detailed balance condition (which is formally a particular condition for which the Hamilton-Jacobi equation is very easy to solve) has been discussed in terms of time-reversal symmetry. All these ideas are clearly not new, but we should stress that some have not been discussed (at least to the knowledge of the author) in the context of Poisson processes (but rather on diffusive processes).

After having defined the tools and main objects of our analysis, the chapter 3 focused on the core of the thesis, namely the thermodynamics analysis of the densities. At equilibrium, the main feature of the free energy is to be additive. Together with the conservation of mass, the latter property allows one to define chemical potentials

attached to each systems, useful to characterise stationarity as well as to predict the direction of mass flow. We thus derived on general grounds general sufficient conditions, namely macroscopic detailed balance as well as factorisation of transition rates, for the large deviations function $\mathcal{I}(\rho_A, \rho_B)$ to be additive. In particular, this result extensively generalised the pioneering study of the KLS model by Sasa & Tasaki (see [Hayashi and Sasa, 2003] and [Sasa and Tasaki, 2006, Appendix B.]). Assuming that the latter conditions hold, we have provided a general definition of out-of-equilibrium chemical potentials. Their potential relations with equilibrium chemical potentials or, if defined, with chemical potentials of isolated systems has been also discussed: it has led to the notion of excess chemical potential that has been shown to be generically strongly dependent on the dynamics at contact. We then investigate the relation between the large deviations function $\mathcal{I}(\rho_A, \rho_B)$ and external potentials through which an operator can shift stationary densities. Inspired by the thermodynamics analysis performed in the MFT context [Bertini et al., 2015*a*], we use the large deviations analysis presented in chapter 2 to derive a second law relating the work performed by an external potential and the difference in large deviations functions. Here again, ideas are not original but it seems that this kind of derivation has never been performed (to the author's knowledge) previously. We close the chapter by a discussion around the different ways to measure experimentally this large deviations function and, if defined, the related chemical potentials.

The third chapter 4 was devoted to applications and discussions of the most important studies of the literature in light with the framework presented in previous chapters. After a short review of exact results on the Zero Range Process [Bertin et al., 2007; Pradhan et al., 2011], we have presented a new mass transport model in one dimension, exactly solvable, whose stationary distribution does depend on the magnitude of the external driving force (more details about the continuous version of the model is available in [Guioth and Bertin, 2017], reproduced in appendix C). The contact between two such systems has then been extensively studied and the importance of the dynamics at contact has been explicitly emphasised. The analysis of the literature was then the occasion to discuss specific more complex systems, in particular in two dimensions. With the help of the framework developed in chapter 2 and 3, we notably have managed to rationalise most of the discrepancies observed in numerical simulations (at the vanishing exchange rate limit) presented in [Dickman, 2014; Dickman and Motai, 2014]. We nevertheless recognise that extensive numerical simulations on these models would be necessary to assert a definitive conclusion. This is intended to be the subject matter of future work. Eventually, we have found interesting to consider briefly this situation of two non-equilibrium systems brought into contact in the context of the Macroscopic Fluctuation Theory which deals with non-linear out-of-equilibrium diffusive systems at local equilibrium. The latter theory was after all

motivated by the same kind of lattice gases discussed above. Nevertheless, it turns out that the latter cannot account for the effect previously observed. The reason is without doubt because of the local equilibrium, valid for small external driving forces.

The last chapter 5 leaves the realm of lattice models to enter the one of continuous space stochastic models. We have discussed in particular independent passive colloids as well as independent self-propelled particles which have raised a lot of attention recently. The models considered as well as the situation of the contact allowing exchange of particles are not new but our large deviations approach apparently is. In particular, we have discussed extensively the exactly solvable models of RTPs in one dimension as well as a two dimensional model of externally driven colloids. In the same way as for lattice models, the contact is shown to play a major role in the density balance between both macroscopic regions A and B. In the case where the contact is realised with a high energy barrier, a dependence in the latter has been observed for RTPs in one dimension as well as RTPs and ABPs in two dimensions: this is perfectly in correspondence with recent results about the mechanical pressure exerted on a wall [Solon, Fily, Baskaran, Cates, Kafri, Kardar and Tailleur, 2015], albeit no general link between the mechanical pressure and our chemical potential has been found. This issue nevertheless deserves future work.

6.2 Some perspectives

We list here some perspectives that would be interesting to explore in the future:

- The preliminary results obtained about the links between the pressure and chemical potentials for self-propelled particles should be continued for other models as well as in a more systematic way.

- One has mainly focused on only one conserved quantity, namely the number of particles. In relation with the previous point, looking at the pressure as the quantity conjugated to the exchange of volume would be interesting too. It may also be a way to relate the chemical potentials and the pressure. However, we can already point out that the macroscopic detailed balance is less obvious since the volume is a continuous quantity. For instance, going beyond the close to equilibrium (detailed) analysis of the adiabatic piston performed in [Itami and Sasa, 2015] could be an interesting clue.

- Eventually, one has observed all along this thesis the crucial importance of the contact for the balance of the density between two (almost) uniform systems. Contrary to the behaviour of equilibrium systems (actually quite singular in

light of our work!)[1] for which the necessary local perturbations of the equilibrium state near walls and edges do not play any role, allowing a description in terms of (uniform) bulk quantities only, out-of-equilibrium systems, even (almost) uniform, cannot in general be only described by bulk quantities: the knowledge of the behaviour at contact is also required.

For this reason, it seems appealing to consider fields (even if the latter are almost uniform) rather than simple macro-variables to describe spatially extended thermodynamic states in a systematic way, in the same vein as the Macroscopic Fluctuation Theory for instance. Since the latter does not account for the situations expounded above, it raises the interesting (and probably difficult) issue to look at field descriptions that go beyond the local equilibrium hypothesis[2].

[1] Eventually, one should emphasise that it is not so surprising for the balance of mass through the contact to be determined by the property of the contact itself. Along this line, the equilibrium situation appears quite singular.

[2] In this respect, we should mention a recent work of Barré *et al.* [Barré et al., 2015] about a small noise field description of interacting self-propelled particles.

APPENDIX **A**

Entropy production and currents at large deviations level

A.1 Entropy definitions

Having explored how transition rates could be decomposed with respect to the time-reversal symmetry in 2.4.3, we discuss here the influence of this decomposition for the expressions of the entropy production in average, at a large deviations level. In particular, we will see that the vanishing of the "anti-symmetric" part of the generalised forces in (2.43) can be seen in average without knowing the exact form of the transition rates $\pi_V(\rho'_A|\rho_A)$. Our discussion is largely inspired by a recent paper of Ge and Quian [Ge and Qian, 2017].

Using the same notations as before, we define the entropy related to the transition $\rho_A \to \rho'_A$ between t and $t + \mathrm{d}t$ as

$$\mathcal{S}_{t,\,\mathrm{d}t}(\rho_A, \rho'_A) = \ln \frac{P_t(\rho_A) P_{\mathrm{d}t}(\rho'_A|\rho_A)}{P_{t+\mathrm{d}t}(\rho'_A) P_{\mathrm{d}t}(\rho_A|\rho'_A)} \tag{A.1}$$

which measures the asymmetry between the probability of the transition $\rho_A \to \rho'_A$ and its time-reversal counterpart $\rho'_A \to \rho_A$ (see for instance [Gaspard, 2004] and [Maes, 2003; Maes and Netočnỳ, 2003]). The ratio of the infinitesimal propagator vanishes when $\rho'_A = \rho_A$ and thus only transitions $\rho_A \to \rho'_A$ matter for its calculation. For $\rho'_A \neq \rho_A$, $P_{\mathrm{d}t}(\rho'_A|\rho_A) = \pi_V(\rho'_A|\rho_A)\mathrm{d}t$ and one gets

$$\mathcal{S}_{t,\,\mathrm{d}t}(\rho_A, \rho'_A) = F_V(\rho_A, \rho'_A) - \ln \frac{P_{t+\mathrm{d}t}(\rho'_A)}{P_t(\rho_A)} \,. \tag{A.2}$$

In average, one obtains

$$\langle \mathcal{S} \rangle_{t,\,\mathrm{d}t} = \sum_{\rho_A,\rho'_A} P_t(\rho_A) P_{\mathrm{d}t}(\rho'_A|\rho_A) F_V(\rho_A,\rho'_A) - \sum_{\rho_A,\rho'_A} P_t(\rho_A) P_{\mathrm{d}t}(\rho'_A|\rho_A) \ln \frac{P_{t+\mathrm{d}t}(\rho'_A)}{P_t(\rho_A)} \tag{A.3}$$

which leads when $\mathrm{d}t \to 0$ to

$$\langle \mathrm{d}\mathcal{S} \rangle_t = \sum_{\rho'_A \neq \rho_A} P_t(\rho_A) \pi_V(\rho'_A|\rho_A) F_V(\rho_A,\rho'_A)\mathrm{d}t - \sum_{\rho_A,\rho'_A} P_t(\rho_A) \pi_V(\rho'_A|\rho_A) \ln \frac{P_t(\rho'_A)}{P_t(\rho_A)} \mathrm{d}t + o(\mathrm{d}t)\,. \tag{A.4}$$

Eventually, introducing the decomposition $F = F^{(S)} + F^{(A)}$ of equation (2.43) into equation (A.4) and writing $\left\langle \dot{\mathcal{S}} \right\rangle_t = \lim_{\mathrm{d}t\to 0} \langle \mathrm{d}\mathcal{S} \rangle_t / \mathrm{d}t$ gives

$$\left\langle \dot{\mathcal{S}} \right\rangle_t = \left\langle \dot{\mathcal{S}}_{hk} \right\rangle_t - \frac{\mathrm{d}}{\mathrm{d}t} \left\langle \ln \frac{P_t(\rho_A)}{P(\rho_A)} \right\rangle_t \tag{A.5}$$

where

$$\left\langle \dot{\mathcal{S}}_{hk} \right\rangle_t = \sum_{\rho_A,\rho'_A} P_t(\rho_A) \pi_V(\rho'_A|\rho_A) F_V^{(A)}(\rho_A,\rho'_A) \tag{A.6}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \left\langle \ln \frac{P_t(\rho_A)}{P(\rho_A)} \right\rangle_t = \sum_{\rho_A,\rho'_A} P_t(\rho_A) \pi_V(\rho'_A|\rho_A) \left[\ln \frac{P_t(\rho'_A)}{P_t(\rho_A)} - F_V^{(S)}(\rho_A,\rho'_A) \right]. \tag{A.7}$$

$\left\langle \dot{\mathcal{S}}_{hk} \right\rangle_t$ refers to the house-keeping entropy production (see [Hatano and Sasa, 2001; Oono and Paniconi, 1998]).

Interpretation of $\dot{\mathcal{S}}_{hk}$. As one can easily see from (A.5) that at stationarity, the total entropy derivative is equal to the house-keeping contribution. When detailed balance holds *i.e.* when dynamic is time-reversible, the total entropy derivative should vanish and $\left\langle \dot{\mathcal{S}}_{hk} \right\rangle = 0$. Otherwise, the stationary state can be kept with a non-zero house-keeping entropy meaning that non-conservative forces are in play.

We will see in next subsections that the presence of a non-vanishing $F^{(A)}$ — *i.e.* that macroscopic detailed balance holds — is equivalent to the non-zero house-keeping entropy production at large deviations level.

A.2 Expressions of entropies at large deviations level

We examine here how these quantities are transformed at a large deviations level. First of all, the probability to observe a density ρ_A at time t, $P_t(\rho_A) \asymp e^{-V_A I_t(\rho_A)}$, leads, for any observable $\mathcal{O}(\rho_A)$, to

$$\sum_{\rho_A} P_t(\rho_A)\mathcal{O}(\rho_A) \xrightarrow[V\to\infty]{} \mathcal{O}(\rho_A(t)) \tag{A.8}$$

where $\rho_A(t)$ is the argument of the minimum of I_t for which $I_t(\rho_A(t)) = 0$ and $I_t'(\rho_A(t)) = 0$. This come from the fact that P_t becomes more and more peaked and formally tends to a Dirac delta centred at $\rho_A(t)$.

Applying this last equality to equation (A.3) and (A.6), leads to the following expressions:

$$\left\langle \dot{\mathcal{S}}_{hk} \right\rangle_t \xrightarrow[V\to\infty]{} \dot{\mathcal{S}}_{hk}(\rho_A(\tau)) = \sum_{\Delta N_A \neq 0} \varphi(\rho_A(\tau), \Delta N_A) F^{(A)}(\rho_A(\tau), \Delta N_A) \tag{A.9}$$

$$\left\langle \dot{\mathcal{S}} \right\rangle_t \xrightarrow[V\to\infty]{} \dot{\mathcal{S}}(\rho_A(\tau)) = \sum_{\Delta N_A \neq 0} \varphi(\rho_A(\tau), \Delta N_A) F(\rho_A, \Delta N_A) \tag{A.10}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \ln \frac{P_t(\rho_A)}{P(\rho_A)} \right\rangle \xrightarrow[V\to\infty]{} \frac{\mathrm{d}I(\rho_A(\tau))}{\mathrm{d}\tau} = -\left(\sum_{\Delta N_A \neq 0} \varphi(\rho_A(t), \Delta N_A)\Delta N_A \right) I'(\rho_A(\tau)) \tag{A.11}$$

where the time t has been rescaled to $\tau = V^{-1}t$. The last quantities is sometimes called the "free energy dissipation rate" [Ge and Qian, 2017] and reads:

$$\dot{\mathcal{F}}_{\text{diss}} = -I'(\rho_A(\tau))J(\rho_A(\tau)) \tag{A.12}$$

with $J(\rho_A(\tau)$ is the macroscopic current $\sum_{\Delta N_A \neq 0} \varphi(\rho_A(t), \Delta N_A)\Delta N_A$.

$F^{(A)}$ and F are equals to

$$F(\rho_A, \Delta N_A) = \lim_{V\to\infty} \ln \frac{\pi_V\left(\rho_A + \frac{\Delta N_A}{V} \middle| \rho_A\right)}{\pi_V\left(\rho_A \middle| \rho_A + \frac{\Delta N_A}{V}\right)} = \ln \frac{\varphi(\rho_A, \Delta N_A)}{\varphi(\rho_A, -\Delta N_A)} \tag{A.13}$$

$$F^{(A)}(\rho_A, \Delta N_A) = \lim_{V\to\infty} \ln \frac{\pi_V\left(\rho_A + \frac{\Delta N_A}{V} \middle| \rho_A\right) P(\rho_A)}{\pi_V\left(\rho_A \middle| \rho_A + \frac{\Delta N_A}{V}\right) P\left(\rho_A + \frac{\Delta N_A}{V}\right)} \tag{A.14}$$

$$= \ln\left(\frac{\varphi(\rho_A, \Delta N_A)}{\varphi(\rho_A, -\Delta N_A)} e^{I'(\rho_A)\Delta N_A} \right). \tag{A.15}$$

One notices that the total entropy derivative $\dot{\mathcal{S}}$ and the house-keeping entropy $\dot{\mathcal{S}}_{hk}$ are

positive quantities since F and $F^{(A)}$ are anti-symmetric in ΔN_A. Eventually, (A.5) becomes

$$\frac{\mathrm{d}I(\rho_A(\tau))}{\mathrm{d}\tau} = \dot{\mathcal{S}}_{hk}(\rho_A(\tau)) - \dot{\mathcal{S}}(\rho_A(\tau))\,. \tag{A.16}$$

We can thus show the equivalence between $\dot{\mathcal{S}}_{hk}(\rho_A) = 0$ and the macroscopic detailed balance condition.

Link between $\dot{\mathcal{S}}_{hk} = 0$ and (2.35). Using the standard inequality $\ln x \geqslant 1 - \frac{1}{x}$ for $x > 0$, where equality holds only for $x = 1$ one obtains

$$\dot{\mathcal{S}}_{hk}(\rho_A) \geqslant -\sum_{\Delta N_A \neq 0} \varphi(\rho_A, \Delta N_A)\left[e^{I'(\rho_A)\Delta N_A} - 1\right] \tag{A.17}$$

$$= H(\rho_A, I') = 0 \quad \forall \rho_A\,. \tag{A.18}$$

The transition rate φ being always strictly positive for $\Delta N_A \neq 0$, the equality in (A.17) holds only when (2.35) holds. Trivially, if the macroscopic detailed balance is satisfied, $\dot{\mathcal{S}}_{hk} = 0$.

A.3 Decomposition of the current at large deviations level

According to equations (2.49) and (2.50), the macroscopic current $J(\rho_A)$ and $J^\dagger(\rho_A)$ reads

$$J(\rho_A) = \sum_{\Delta N_A} \varphi(\rho_A, \Delta N_A)\Delta N_A \tag{A.19}$$

$$= \sum_{\Delta N_A > 0} \Delta N_A a(\rho_A, \Delta N_A) \sinh\left(F(\rho_A, \Delta N_A)\right)$$

$$J^\dagger(\rho_A) = \sum_{\Delta N_A} \varphi^\dagger(\rho_A, \Delta N_A)\Delta N_A \tag{A.20}$$

$$= \sum_{\Delta N_A > 0} \Delta N_A a(\rho_A, \Delta N_A) \sinh\left(F^\dagger(\rho_A, \Delta N_A)\right)$$

Using the decomposition in terms of force and activity (see equations (2.38) and (2.43)), one can decompose J and $J^\dagger$ in a symmetric and anti-symmetric components

as

$$J^{(S)}(\rho_A) = \frac{J(\rho_A) + J^\dagger(\rho_A)}{2} \tag{A.21}$$
$$= \sum_{\Delta N>0} \Delta N a(\rho_A, \Delta N) \cosh\left[\frac{F_A(\rho_A, \Delta N_A)}{2}\right] \sinh\left[\frac{F_S(\rho_A, \Delta N_A)}{2}\right]$$
$$J^{(A)}(\rho_A) = \frac{J(\rho_A) - J^\dagger(\rho_A)}{2} \tag{A.22}$$
$$= \sum_{\Delta N>0} \Delta N a(\rho_A, \Delta N) \cosh\left[\frac{F_S(\rho_A, \Delta N_A)}{2}\right] \sinh\left[\frac{F_A(\rho_A, \Delta N_A)}{2}\right]$$

A.4 Hamilton-Jacobi in terms of forces and activity

The stationary Hamilton-Jacobi equation (2.23) can be reformulated in terms of $F^{(A)}$ and $F^{(S)}$ or in terms of I' and F. They read

$$\sum_{\Delta N_A>0} \sinh\left[F^{(A)}(\rho_A, \Delta N_A)\right] a(\rho_A, \Delta N_A) \sinh\left[F^{(S)}(\rho_A, \Delta N_A)\right] = 0 \tag{A.23}$$

or, equivalently,

$$\sum_{\Delta N_A>0} \sinh\left[F(\rho_A, \Delta N_A) + I'(\rho_A)\Delta N_A\right] a(\rho_A, \Delta N_A) \sinh\left[I'(\rho_A)\Delta N_A\right] = 0\,. \tag{A.24}$$

These expressions are completely equivalent to Eq (2.23). One should also note that the above version of the Hamilton-Jacobi equation can be interpreted as the counterpart of the orthogonality between anti-symmetric and symmetric forces already found in the Macroscopic Fluctuation Theory (see [Bertini et al., 2015*a*]) in the context of Markov jump processes (see [Kaiser et al., 2018] for a very recent study of an almost identical decomposition in the context of Markov chains).

Appendix A. Entropy production and currents at large deviations level

APPENDIX B

More than two systems in contact

Insofar, we have only considered the most simple case of two systems in contact with each other. Even if the case of more than two systems in contact is much more complicated, we show here how the framework discussed all along this chapter for the two systems case can be extended to the general case of an arbitrary number of systems in contact.

We consider a simple graph made of vertex that symbolise the different systems and links that symbolise the contact between the different systems. The systems are numbered by $i \in \{1, 2, \dots, S\}$, and the links are called $\{\ell = (i, j)\}$. Of course, as we adopt a coarse-grained point of view, we assume that there exist only one link $\ell = (i, j)$ between two adjacent systems i and j. Each system i exchange mass with its neighbours j according to a coarse-grained transition rate $\varphi_\ell(\Delta N_i, \rho_i, \rho_j)$ with $\rho_i = N_i/V_i$, N_i being the number of particles in system i and V_i its volume. We note ΔN_i the number of particles received or loosed by the system i after the exchange: $N_i' = N_i + \Delta N_i$, $N_j' = N_j - \Delta N_i$. We also introduce $\gamma_i = V_i/V$ which verify $\sum_{i=1}^{S} \gamma_i = 1$ since $V = \sum_{i=1}^{S} V_i$. The dynamics is supposed to be asynchronous. The master equation reads

$$\begin{aligned}\frac{\mathrm{d}P_t(\{N_i\})}{\mathrm{d}t} = \sum_{\ell} \sum_{\Delta N_{\ell_1}} \varphi_\ell \left(\Delta N_{\ell_1}, \rho_{\ell_1} - \tfrac{\Delta N_{\ell_1}}{V_{\ell_1}}, \rho_{\ell_2} + \tfrac{\Delta N_{\ell_1}}{V_{\ell_2}} \right) \\ \times P_t(N_1, \dots, N_{\ell_1} - \Delta N_{\ell_1}, \dots, N_{\ell_2} + \Delta N_{\ell_1}, \dots, N_S) \\ - \sum_{\ell} \sum_{\Delta N_{\ell_1}} \varphi_\ell(\Delta N_{\ell_1}, \rho_{\ell_1}, \rho_{\ell_2}) P_t(\{N_i\}) \quad \text{(B.1)}\end{aligned}$$

with $\ell_1 = i$ and $\ell_2 = j$ the "coordinates" of the link $\ell = (i, j)$. At the thermodynamic limit for which $V \to \infty$, keeping γ_i fixed, we expect that the distribution $P_t(\{N_i\})$

verifies a large deviations principle:

$$I_t(\rho_1,\dots,\rho_S) = \lim_{V\to\infty} \frac{1}{V} \ln P_t(V\gamma_1\rho_1,\dots,V\gamma_S\rho_S) \ . \tag{B.2}$$

The equation obeyed by the latter large deviations function is an Hamilton-Jacobi equation that reads

$$\frac{\mathrm{d}I_t}{\mathrm{d}t}(\{\rho_i\}) = \sum_{\ell} \sum_{\Delta N_{\ell_1}} \varphi_\ell(\Delta N_{\ell_1},\rho_{\ell_1},\rho_{\ell_2}) \left[\exp\left\{\Delta N_{\ell_1}\left(\gamma_{\ell_1}^{-1}\frac{\partial I_t}{\partial\rho_{\ell_1}} - \gamma_{\ell_2}^{-1}\frac{\partial I_t}{\partial\rho_{\ell_2}}\right)\right\} - 1\right] \ . \tag{B.3}$$

Some comments can already be made from (B.3). One notices that if the number of systems in contact is greater than 2, the exchange of one particle at most between two adjacent systems is no more a sufficient condition to obtain macroscopic detailed balance[1]. The latter yet reads

$$\gamma_{\ell_1}^{-1}\frac{\partial I}{\partial\rho_{\ell_1}} - \gamma_{\ell_2}^{-1}\frac{\partial I}{\partial\rho_{\ell_2}} = \frac{1}{\Delta N_{\ell_1}} \frac{\varphi_\ell(-\Delta N_{\ell_1},\rho_1,\rho_2)}{\varphi_\ell(\Delta N_{\ell_1},\rho_1,\rho_2)} \ . \tag{B.4}$$

If the factorisation (3.3) of the macroscopic transition rates holds, the large deviations function I is then additive as for the case of only two systems in contact. If factorisation does not hold but macroscopic detailed balance does, one can already see that the additivity property has no reason to be verified.

Beyond this particular case, only a perturbative solutions as expounded in section 2.5 seems to be available in general. Even if detailed study are not available, one can reasonably expect that long range effects – which can be seen through the slow decay of correlation functions or the non-local response to a local perturbation by an external potential – emerge as long as the large deviations function is a non-local function of the systems $i \in \{0,\dots,S\}$ (see [Bertini et al., 2015*a*] for a presentation of such effects in the context of continuous-space diffusive dynamics).

[1] As discussed for the case of two systems in contact, the macroscopic detailed balance can be evaluate by looking at the vanishing of the house-keeping heat released in the heat bath or the asymmetry between fluctuation and relaxation path, etc.

APPENDIX C

"A mass transport model with a simple non-factorized steady-state distribution"

This appendix is a duplication of [Guioth and Bertin, 2017] (see below).

A mass transport model with a simple non-factorized steady-state distribution

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Abstract. We study a mass transport model on a ring with sublattice-parallel update, where a continuous mass is randomly redistributed along distinct links of the lattice. The redistribution process on a given link depends on the masses on both sites, in contrast to the Zero Range Process and its continuous mass generalizations. We show that the steady-state distribution takes a simple non-factorized form that can be written as a sum of two inhomogeneous product measures. A factorized measure is recovered for a symmetric mass redistribution, corresponding to an equilibrium process. A non-equilibrium free energy can be explicitly defined from the partition function. For a certain class of transition rates, a condensation transition is obtained, with a critical density which depends on the driving force. We also evaluate different characterizations of the 'distance' to equilibrium, either dynamic or static: the mass flux, the entropy production rate, the Gibbs free-energy difference between the equilibrium and non-equilibrium stationary states, and the derivative of the non-equilibrium free energy with respect to the applied driving force. The connection between these different non-equilibrium parameters is discussed.

1. Introduction

One of the goals of non-equilibrium statistical physics is to be able to describe the statistical properties of systems driven in a non-equilibrium steady state by an external non-conservative force. As no general statistical formalism is available to deal with driven systems, exactly solvable models have played an important role in the development of this field. A paradigmatic exactly solvable model is the Asymmetric Simple Exclusion Process (ASEP) [1], either with periodic [2] or open boundary conditions [3, 4, 5, 6]. Generalizations with several types of particles have also been proposed, with periodic [7, 8, 9] or open geometries [10, 11, 12, 13]. The ABC model [14], which includes three types of particles, also falls into this class. The solution of the ASEP model requires in most cases the use of matrix product states [15], often with infinite size matrices, making its analysis relatively involved. Such matrix product state solutions are required even with a periodic geometry, when the model includes several types of particles [7, 8, 9] —except if some restrictive conditions are imposed [16].

Simpler models, like the Zero-Range Process (ZRP) [1, 17, 18] and related mass transport models [19, 20, 21, 22], have also been considered, often in relation to condensation transitions [23, 24, 17, 25]. Multispecies generalizations of these models have also been proposed [23, 26, 27]. When the transition rates satisfy certain conditions [19, 20, 21, 25], these models have the advantage that their steady-state distribution factorizes, making their analytical study much easier. However, in a closed geometry, they have the drawback that the distribution does not depend on the driving force, and thus remains identical to the equilibrium distribution obtained for unbiased dynamics. Note that the same property also holds for the (single-species) ASEP on a ring [2].

In this paper, we propose a class of mass transport models for which the steady-state distribution takes a simple form (a sum of two inhomogeneous product measures) and explicitly depends on the local driving force. The present model is inspired by the equilibrium model considered in [28], though it differs from the latter in several respects, notably the presence of a driving force and of a synchronous dynamics. The simple form of the steady-state probability distribution makes calculations easy, as illustrated below on several examples including the evaluation of a non-equilibrium free energy. For a certain class of transition rates, our model exhibits a condensation transition similar to the one appearing in mass transport models with factorized steady states [25], but with a condensation threshold depending on the driving force. In addition, the dependence of the steady-state probability distribution on the forcing allows us to compare dynamical characterizations of the 'degree of non-equilibrium' (mass flux and entropy production rate) with static characterizations like the difference of Gibbs free energy functional (or Kullback-Leibler divergence [29]) between the non-equilibrium distribution and the corresponding equilibrium one. We also evaluate the non-equilibrium order parameter introduced by Sasa and Tasaki [30], defined as a derivative of the non-equilibrium free energy with respect to the driving force, and discuss the relationship between these different measures of the 'distance' to equilibrium.

2. Definition of the model

We consider a one-dimensional lattice with N sites, labelled by $i = 1, \ldots, N$, with periodic boundary conditions ($i \pm N \equiv i$); N is assumed to be even, namely $N = 2N'$ with N' integer. On each site i, one defines a real positive mass m_i. The model is endowed with a sublattice parallel-update dynamics‡ The dynamics proceeds, at each discrete time step $t = 0, 1, 2, \ldots$, by parallel redistributions of mass between neighboring sites i and $i{+}1$ on one of the two partitions $\mathcal{P}_1 = \{(2k, 2k{+}1)\}$ and $\mathcal{P}_2 = \{(2k{+}1, 2k{+}2)\}$, randomly chosen with equal probability. Once a partition $\mathcal{P}_j$ has been selected, all links belonging to the partition $\mathcal{P}_j$ are simultaneously updated. To update a link $(i, i+1)$, a

‡ Note that although the asynchronous, continuous time dynamics is most often used in this context, synchronous dynamics has also been used in the ASEP [31, 32, 33] and related particle models [27], as well as in mass transport models [19, 26].

new value m'_i of the mass on site i is randomly drawn from the distribution

$$K(m'_i|S_i) = \frac{v(m'_i)w(S_i - m'_i)}{v * w(S_i)}, \qquad S_i \equiv m_i + m_{i+1} \tag{1}$$

where $v(m)$ and $w(m)$ are arbitrary positive functions, and $v * w(S)$ is the convolution product of v and w,

$$v * w(S) = \int_0^S \mathrm{d}m\, v(m)w(S-m)\,, \tag{2}$$

which has to be non-zero for any $S > 0$ for the model to be well-defined. From mass conservation, the mass on site $i+1$ is, after redistribution, $m'_{i+1} = S_i - m'_i$.

3. Master equation and steady-state solution

3.1. Discrete time master equation

To describe the statistical evolution of the system under the above dynamics, we write down the corresponding master equation. A configuration of the system is given by the ordered list $\mathbf{m} = (m_1, \ldots, m_N)$ of all the masses in the system. The probability density $P(\mathbf{m}, t)$ evolves according to the discrete time master equation

$$P(\mathbf{m}', t+1) = \int \mathrm{d}\mathbf{m}\, T(\mathbf{m}'|\mathbf{m})\, P(\mathbf{m}, t) \tag{3}$$

with $\mathrm{d}\mathbf{m} = \prod_{i=1}^N \mathrm{d}m_i$, and where $T(\mathbf{m}'|\mathbf{m})$ is the probability (density) to jump from configuration $\mathbf{m}$ to configuration $\mathbf{m}'$ in a single time step. This transition probability is normalized according to

$$\int \mathrm{d}\mathbf{m}'\, T(\mathbf{m}'|\mathbf{m}) = 1\,. \tag{4}$$

For the present mass transport model, the transition probability is given by

$$T(\mathbf{m}'|\mathbf{m}) = \frac{1}{2}\, T_1(\mathbf{m}'|\mathbf{m}) + \frac{1}{2}\, T_2(\mathbf{m}'|\mathbf{m}) \tag{5}$$

where

$$T_1(\mathbf{m}'|\mathbf{m}) = \prod_{k=1}^{N'} K(m'_{2k}|S_{2k})\, \delta(S'_{2k} - S_{2k})\,, \tag{6}$$

$$T_2(\mathbf{m}'|\mathbf{m}) = \prod_{k=1}^{N'} K(m'_{2k+1}|S_{2k+1})\, \delta(S'_{2k+1} - S_{2k+1})\,, \tag{7}$$

with the shorthand notations $S_i \equiv m_i + m_{i+1}$ and $S'_i \equiv m'_i + m'_{i+1}$.

3.2. Steady-state distribution

In the following, we show that the distribution

$$P(\mathbf{m}) = \frac{1}{Z_N(M)} \left(\prod_{k=1}^{N'} v(m_{2k})w(m_{2k+1}) + \prod_{k=1}^{N'} w(m_{2k})v(m_{2k+1}) \right)\, \delta\left(\sum_{i=1}^{N} m_i - M \right) \tag{8}$$

is a stationary solution of the master equation Eq. (3). In Eq. (8), M is the (constant) total mass, and $Z_N(M)$ is a normalization factor. In some cases, it may be convenient to write $P(\mathbf{m})$ in the form $P(\mathbf{m}) = \frac{1}{2}[P_1(\mathbf{m}) + P_2(\mathbf{m})]$ with, for $j \in \{1, 2\}$

$$P_j(\mathbf{m}) = \frac{2}{Z_N(M)}\, Q_j(\mathbf{m})\, \delta\left(\sum_{i=1}^{N} m_i - M\right), \tag{9}$$

having defined

$$Q_1(\mathbf{m}) = \prod_{k=1}^{N'} v(m_{2k}) w(m_{2k+1})\,, \qquad Q_2(\mathbf{m}) = \prod_{k=1}^{N'} w(m_{2k}) v(m_{2k+1})\,. \tag{10}$$

The partition functions $Z_N(M)$ then reads

$$Z_N(M) = \int \mathrm{d}\mathbf{m}\, [Q_1(\mathbf{m}) + Q_2(\mathbf{m})]\, \delta\left(\sum_{i=1}^{N} m_i - M\right). \tag{11}$$

Using Eq. (8), the master equation (3) reads, taking into account the fact that the dynamics conserves the total mass,

$$\begin{aligned} &Q_1(\mathbf{m}') + Q_2(\mathbf{m}') \\ &\quad = \frac{1}{2} \int \mathrm{d}\mathbf{m}\, [T_1(\mathbf{m}'|\mathbf{m}) + T_2(\mathbf{m}'|\mathbf{m})]\, [Q_1(\mathbf{m}) + Q_2(\mathbf{m})] \end{aligned} \tag{12}$$

where, to lighten notations, the Dirac delta function accounting for the total mass conservation is understood.

Expanding the r.h.s. of Eq. (12) into four terms, we evaluate these terms separately, obtaining for $j, k \in \{1, 2\}$ (see Appendix A)

$$\int \mathrm{d}\mathbf{m}\, T_k(\mathbf{m}'|\mathbf{m})\, Q_j(\mathbf{m}') = Q_k(\mathbf{m})\,. \tag{13}$$

The sum of the four contributions appearing in the r.h.s. of Eq. (12) is thus equal to $Q_1(\mathbf{m}') + Q_2(\mathbf{m}')$, so that Eq. (12) is satisfied. Hence the distribution $P(\mathbf{m})$ given in Eq. (8) is the stationary solution of the model.

3.3. Physical interpretation of the dynamics

Without loss of generality, one can rewrite the functions $v(m)$ and $w(m)$ as

$$v(m) = e^{-\beta\varepsilon(m) - \beta h(m)}, \qquad w(m) = e^{-\beta\varepsilon(m) + \beta h(m)} \tag{14}$$

where we have defined

$$e^{-\beta\varepsilon(m)} = \sqrt{v(m) w(m)}, \qquad e^{-\beta h(m)} = \sqrt{\frac{v(m)}{w(m)}}\,. \tag{15}$$

The parameter $\beta > 0$, to be thought of as an inverse temperature, is arbitrary here, and has only been introduced to facilitate the comparison with equilibrium. A symmetric redistribution process, obtained for $v(m) = w(m)$, corresponds to $h(m) = 0$, and the stationary distribution Eq. (8) boils down to an equilibrium distribution,

$$P(\mathbf{m}) = \frac{2}{Z_N(M)}\, e^{-\beta \sum_{i=1}^{N} \varepsilon(m_i)}\, \delta\left(\sum_{i=1}^{N} m_i - M\right). \tag{16}$$

The function $\varepsilon(m)$ thus appears as an effective local energy associated to a local density m. The function $h(m)$ describes the asymmetry of the dynamics. In the linear case $h(m) = h_0 m$, having in mind *local detailed balance*, the term $2h_0(m_i - m_i')$ that enters the ratio $K(m_i'|S_i)/K(m_i|S_i')$ (with $S_i = S_i'$) can be interpreted as the work done by a driving force $f = 2h_0$ associated with a displaced mass $m_i - m_i'$ on a unit distance (one lattice spacing). This case is thus physically meaningful, and we will focus on it when dealing with specific examples (keeping f rather than h_0 as the driving parameter).

When $h(m) \neq 0$, the non-equilibrium steady-state distribution $P(\mathbf{m})$ given in Eq. (12) can be rewritten as

$$P(\mathbf{m}) = \frac{2}{Z_N(M)}\, e^{-\beta E(\mathbf{m})}\, \cosh[\beta H(\mathbf{m})]\, \delta\left(\sum_{i=1}^{N} m_i - M\right) \tag{17}$$

where one has introduced the global observables

$$E(\mathbf{m}) = \sum_{i=1}^{N} \varepsilon(m_i), \qquad H(\mathbf{m}) = \sum_{i=1}^{N} (-1)^i h(m_i). \tag{18}$$

The presence of the hyperbolic cosine in Eq. (17) yields long-range correlations as can be seen explicitly by a calculation of the two-points spatial correlation function $G_j = \langle m_i m_{i+j}\rangle - \rho^2$ ($\rho = \langle m_i\rangle$) for a particular choice of $\epsilon(m)$ and $h(m)$ (see Appendix B). In more intuitive terms, these correlations are generated by the synchronous dynamics over two different partitions of the lattice.

Note that more details on the evaluation of the correlation function and on the expression of the pair and single mass distributions can be found in Appendix B.

In the following, the arbitrary inverse temperature scale β is set to unity, unless stated otherwise.

4. Partition function: non-equilibrium free energy and condensation transition

4.1. Expression of the partition function in the thermodynamics limit

It is natural to define from the partition function given in Eq. (11) a non-equilibrium (intensive) free energy $\varphi(\rho)$ at an average density ρ as

$$\varphi(\rho) = -\lim_{N\to\infty} \frac{1}{N} \ln Z(N\rho), \tag{19}$$

if this limit exists.

To evaluate $\varphi(\rho)$, we apply the classical saddle-node approximation. Plugging into Eq. (11) the Laplace representation of the delta function,

$$\delta(s) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \mathrm{d}\zeta\, e^{\zeta s} \tag{20}$$

with a an arbitrary real number, we end up with

$$Z_N(N\rho) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \mathrm{d}\zeta\, e^{N(\lambda(\zeta)-\rho\zeta)} \tag{21}$$

where we have introduced the functions§

$$\lambda(\zeta) = \frac{1}{2}\ln[\hat{v}(\zeta)\hat{w}(\zeta)] \tag{22}$$

and

$$\hat{v}(\zeta) = \int_0^\infty \mathrm{d}m\, e^{\zeta m} v(m), \qquad \hat{w}(\zeta) = \int_0^\infty \mathrm{d}m\, e^{\zeta m} w(m). \tag{23}$$

Note that the real part of ζ (equal to a) is chosen small enough for the integrals to converge. Note that a possible restriction on v and w may appear at this stage: $\hat{v}$ and $\hat{w}$ should exist for a free energy to be properly defined.

Assuming that these restrictions are satisfied and that $\lambda(\zeta) - \rho\zeta$ has a *unique real* saddle-point for a fixed $\rho = M/N$, $\zeta^*(\rho)$, given by

$$\frac{d\lambda}{d\zeta}(\zeta^*) = \rho, \tag{24}$$

one gets

$$Z_N(N\rho) \underset{N\to\infty}{\asymp} e^{-N[\rho\zeta^*(\rho) - \lambda(\zeta^*(\rho))]}. \tag{25}$$

The intensive free energy $\varphi(\rho)$ introduced in Eq. (19) is then given by

$$\varphi(\rho) = \rho\zeta^*(\rho) - \lambda(\zeta^*(\rho)). \tag{26}$$

As in equilibrium, one can define a non-equilibrium chemical potential μ and a non-equilibrium pressure p, derived as usual as derivatives of the extensive free energy $F(M,N) = N\varphi(M/N)$ [30, 34]. Moving to the intensive free energy, one gets

$$\mu(\rho) = \varphi'(\rho) = \zeta^*(\rho)\,, \qquad p(\rho) = -\varphi(\rho) + \rho\varphi'(\rho)\,. \tag{27}$$

Assuming that the mass M and the volume N are the only extensive parameters, one shows, using the Euler relation for a homogeneous function [30], that

$$\varphi(\rho) = -p(\rho) + \rho\mu(\rho)\,. \tag{28}$$

As an example, we evaluate explicitly the free energy in the specific case of linear functions $\varepsilon(m) = \varepsilon_0 m$ and $h(m) = \frac{1}{2}fm$, using the parameterization Eq. (14) of the functions $v(m)$ and $w(m)$. For $-\infty < \zeta < \epsilon_0 - f/2$, one obtains

$$\hat{v}(\zeta) = \frac{1}{\varepsilon_0 - \zeta + \frac{1}{2}f}, \qquad \hat{w}(\zeta) = \frac{1}{\varepsilon_0 - \zeta - \frac{1}{2}f} \tag{29}$$

and

$$\lambda(\zeta) = -\frac{1}{2}\ln\left((\varepsilon_0 - \zeta)^2 - \frac{f^2}{4}\right). \tag{30}$$

The saddle-point $\zeta^*(\rho)$, as defined in Eq.(24), is given by

$$\zeta^*(\rho) = \varepsilon_0 - \frac{1 + \sqrt{1 + \rho^2 f^2}}{2\rho}, \tag{31}$$

§ We take here a determination of the logarithm in the complex plane such that the integration path does not cross the branch cut.

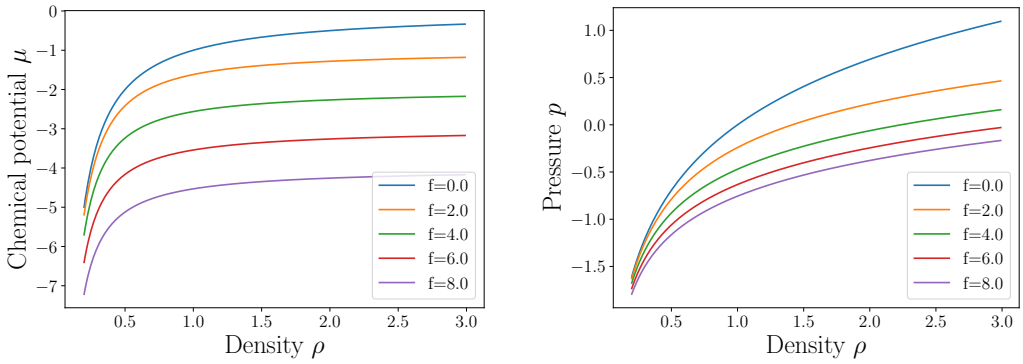

Figure 1. (Color online) Chemical potential $\mu(\rho)$ (left panel) and pressure $p(\rho)$ (right panel) as a function of the density ρ, for different values of the driving force f (from top to bottom, $f = 0$, 2, 4, 6 and 8).

which is always strictly lower than $\epsilon_0 - f/2$ for any positive ρ. Then, the free energy reads, from Eq. (26),

$$\varphi(\rho, f) = \varepsilon_0 \rho - \frac{1 + \sqrt{1 + \rho^2 f^2}}{2} + \frac{1}{2} \ln \left(\frac{1 + \sqrt{1 + \rho^2 f^2}}{2\rho^2} \right). \tag{32}$$

According to Eq. (28), one reads from the last equation

$$\mu(\rho) = \varepsilon_0 - \frac{1 + \sqrt{1 + \rho^2 f^2}}{2\rho} \tag{33}$$

$$p(\rho) = -\frac{1}{2} \ln \left(\frac{1 + \sqrt{1 + \rho^2 f^2}}{2\rho^2} \right). \tag{34}$$

The chemical potential $\mu(\rho)$ and the pressure $p(\rho)$ are plotted in Fig. 1 for the sake of illustration.

Note that here and in what follows, we emphasize the f-dependence of the free energy density by denoting it as $\varphi(\rho, f)$ when considering the specific case $h(m) = \frac{1}{2} f m$. At equilibrium, for $f = 0$, one recovers the equilibrium free energy $\varphi(\rho, 0) = \epsilon_0 \rho - 1 - \ln \rho$ (we recall that temperature is set to unity).

4.2. Condensation transition

Another choice of $v(m)$ and $w(m)$ can lead to the phenomenon of condensation, well studied for different versions of the Zero Range Process [17]. Indeed, it may happen that the saddle-point equation Eq. (24) has no real solution ζ^* for a density ρ greater than a critical value ρ_c. The ensemble equivalence (between "grand canonical" and "canonical" ensembles) is therefore broken and the condensation of a macroscopic fraction of the total mass then occurs on a randomly selected site [35]. For our model, the exact

single-site probability distribution is given by (see Appendix B)

$$p(m) = v(m) \int_0^{+\infty} \mathrm{d}m' \frac{Z_{N-2}(M-m-m')}{Z_N(M)} w(m') + w(m) \int_0^{+\infty} \mathrm{d}m' \frac{Z_{N-2}(M-m-m')}{Z_N(M)} v(m') \; . \tag{35}$$

As explained in [35], the phenomenon of condensation is closely related to the existence of a saddle-point for the evaluation of $Z_N(M)$, leading to different distributions $p(m)$.

As a specific example, we consider $\epsilon(m) = \epsilon_0 m + \ln(1+m^\gamma)$, $h(m) = \frac{1}{2} f m$. One obtains,

$$\hat{v}(\zeta) = \int_0^\infty \frac{\mathrm{d}m}{1+m^\gamma} e^{-(\epsilon_0 + \frac{f}{2} - \zeta)m} \; , \qquad \hat{w}(\zeta) = \int_0^\infty \frac{\mathrm{d}m}{1+m^\gamma} e^{-(\epsilon_0 - \frac{f}{2} - \zeta)m} \; , \tag{36}$$

and the saddle-point equation Eq. (24) reads

$$\rho = \frac{1}{2} \left(\frac{\hat{v}'(\zeta^*)}{\hat{v}(\zeta^*)} + \frac{\hat{w}'(\zeta^*)}{\hat{w}(\zeta^*)} \right) . \tag{37}$$

Clearly, as in the previous example, ζ has to be lower than or equal to $\epsilon_0 - f/2$ for $\hat{w}$ to exist‖. Now, the existence of a critical value $\rho_c < +\infty$ in Eq. (37) depends on γ. Indeed, for ζ tending to its upper bound $\epsilon_0 - f/2$, the associated ρ in Eq. (37) can be infinite or finite, depending on the actual value of γ.

If $\gamma \leq 2$, one has

$$\lim_{\zeta \to \epsilon_0 - f/2} \frac{\hat{w}'(\zeta)}{\hat{w}(\zeta)} = +\infty \; , \tag{38}$$

and thus, there exist a solution ζ^* of Eq. (37) for each $\rho < +\infty$: a saddle-point always exists.

If $\gamma > 2$, one has on the contrary that

$$\lim_{\zeta \to \epsilon_0 - f/2} \frac{\hat{w}'(\zeta)}{\hat{w}(\zeta)} < +\infty \tag{39}$$

and thus Eq. (37) has a solution ζ^* only for $\rho \leq \rho_c$ where ρ_c is given by

$$\rho_c = \frac{1}{2} \left(\frac{\hat{v}'(\epsilon_0 - f/2)}{\hat{v}(\epsilon_0 - f/2)} + \frac{\hat{w}'(\epsilon_0 - f/2)}{\hat{w}(\epsilon_0 - f/2)} \right) \; . \tag{40}$$

This implies that condensation occurs for $\rho > \rho_c$ [35].

The threshold density ρ_c appearing when $\gamma > 2$ can be rewritten more explicitly as

$$\rho_c = \frac{1}{2} \left(\frac{\int_0^{+\infty} \mathrm{d}m (1+m^\gamma)^{-1} m e^{-fm}}{\int_0^{+\infty} \mathrm{d}m (1+m^\gamma)^{-1} e^{-fm}} + \frac{\int_0^{+\infty} \mathrm{d}m (1+m^\gamma)^{-1} m}{\int_0^{+\infty} \mathrm{d}m (1+m^\gamma)^{-1}} \right) . \tag{41}$$

We emphasize that the dependence on the driving force of the stationary distribution leads to a dependence on the driving force of the threshold (or critical) density ρ_c for condensation to appear. The threshold density ρ_c is plotted as a function of the driving force f in Fig. 2.

‖ Note that $\hat{v}$ automatically exists if this restriction is satisfied.

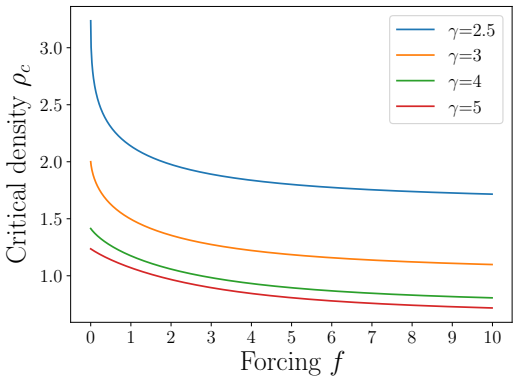

Figure 2. (Color online) Threshold density ρ_c for condensation, plotted as a function of the driving force f, for several values of γ (from top to bottom, $\gamma = 2.5$, 3, 4 and 5).

5. Characterization of the 'distance' to equilibrium

We have seen in the previous section that the presence of a non-zero driving force has observable consequences, for instance by shifting the threshold density for condensation. This suggests to try to further characterize the non-equilibrium character of the dynamics by computing several quantities that can be thought of as different evaluations of a 'distance' to equilibrium. The fundamental characterization of a non-equilibrium stationary stochastic process relies on the breaking of detailed balance, which can be macroscopically quantified through observables like the mass flux or the entropy production rate. These two quantities are evaluated in sections 5.1 and 5.2 respectively. We call these observables 'dynamical' (although they are time-independent) in the sense that they involve fluxes, either of mass or of probability. In addition, one may compute 'static' observables that characterize the distance to equilibrium only based on the stationary measure, by comparing the non-equilibrium stationary measure with the equilibrium one. Although such static observables do not reveal an intrinsic non-equilibrium character of the system, one expects that this out-of-equilibrium dependence of the stationary measure is rather typical as suggested for instance by the McLennan formula in a close-to-equilibrium regime [36, 37]. It is then of interest to compare these static observables to the dynamical ones to see whether both are connected. We thus discuss in section 5.3 the Gibbs free energy difference with the equilibrium state, and in section 5.4 the non-equilibrium order parameter defined as a derivative of the non-equilibrium free energy with respect to the driving force.

5.1. Stationary mass flux

We start by evaluating the stationary mass flux between two sites i and $i+1$ (which, due to mass conservation, is independent of i). During a given time step, a mass is

transferred between i and $i+1$ only if the link $(i, i+1)$ belongs to the chosen partition ($\mathcal{P}_1$ or $\mathcal{P}_2$) of the lattice; mass transfer on this link thus occurs with probability $\frac{1}{2}$. The average flux Φ then reads

$$\Phi = \frac{1}{2}(\langle m_i \rangle - \langle m_i' \rangle) \tag{42}$$

where m_i is the mass on site i before a redistribution occurs on the link $(i, i+1)$, while m_i' is the mass on site i after the redistribution. The masses m_i and m_{i+1} before redistribution are assumed to follow the steady-state distribution $P(m_i, m_{i+1})$ given in Appendix B —see Eq. (B.3); one thus has $\langle m_i \rangle = \rho$. Note that the time step has been set to unity.

The average mass $\langle m_i' \rangle$ after redistribution can be expressed as

$$\langle m_i' \rangle = \int_0^\infty \mathrm{d}m_i \int_0^\infty \mathrm{d}m_{i+1}\, P(m_i, m_{i+1}) \int_0^\infty \mathrm{d}m_i'\, m_i'\, K(m_i'|m_i + m_{i+1}). \tag{43}$$

After some algebra, one finds

$$\langle m_i' \rangle = 2C_2(\rho) \int_0^\infty \mathrm{d}S\, e^{-\mu S} \int_0^S \mathrm{d}m'\, m'\, v(m') w(S - m')\,. \tag{44}$$

The calculation can be carried out explicitly on the example $\varepsilon(m) = \varepsilon_0 m$ and $h(m) = \frac{1}{2} f m$, yielding

$$\langle m_i' \rangle = \frac{1}{\varepsilon_0 - \mu + f}. \tag{45}$$

The average mass flux Φ then reads, using Eqs. (33) and (42),

$$\Phi = \frac{1}{2}(\rho - \langle m_i' \rangle) = \frac{f}{4(\varepsilon_0 - \mu)^2 - f^2}. \tag{46}$$

Also, using the explicit expression of $\mu(\rho)$ given in Eq. (33), one finds

$$\Phi = \frac{\rho^2 f}{2 + 2\sqrt{1 + \rho^2 f^2}}\,. \tag{47}$$

Furthermore, one can notice that the flux, which can be interpreted as a response of the system to the driving force f (when $h(m) = \frac{1}{2} f m$), is directly related to the free energy I (19) as explicitly shown in Appendix C :

$$\Phi = -\frac{\partial \varphi(\rho, f)}{\partial f} \tag{48}$$

We will comment on this relation in the next subsection, in connection to the entropy production rate.

5.2. Entropy production rate

An alternative dynamical measure of the degree of irreversibility is given by the entropy production rate. For a discrete time Markov process, the (time-dependent) entropy

production rate (i.e., the entropy production per time step) is defined as [38]¶

$$\Delta_{\rm int} S_t = \frac{1}{2} \int {\rm d}\mathbf{m}\, {\rm d}\mathbf{m}' [T(\mathbf{m}'|\mathbf{m}) P_t(\mathbf{m}) - T(\mathbf{m}|\mathbf{m}') P_t(\mathbf{m}')] \ln \frac{T(\mathbf{m}'|\mathbf{m}) P_t(\mathbf{m})}{T(\mathbf{m}|\mathbf{m}') P_t(\mathbf{m}')} \,. \tag{49}$$

The advantage of this form is that the positivity of $\Delta_{\rm int} S$ is visible, as it involves products of factors of equal sign. In steady state, the entropy production rate simplifies to [38]

$$\Delta_{\rm int} S = \int {\rm d}\mathbf{m}\, {\rm d}\mathbf{m}'\, T(\mathbf{m}'|\mathbf{m}) P(\mathbf{m}) \ln \frac{T(\mathbf{m}'|\mathbf{m})}{T(\mathbf{m}|\mathbf{m}')} \,. \tag{50}$$

The entropy production rate $\Delta_{\rm int} S$ can be evaluated in the present model, yielding (technical details are reported in Appendix D):

$$\Delta_{\rm int} S = \frac{1}{2} \int {\rm d}\mathbf{m}\, [P_1(\mathbf{m}) - P_2(\mathbf{m})]\, H(\mathbf{m}), \tag{51}$$

where $P_j(\mathbf{m})$ is defined in Eq. (9). One thus recovers, as expected, that $\Delta_{\rm int} S = 0$ at equilibrium, when $P_1(\mathbf{m}) = P_2(\mathbf{m})$. Eq. (51) can be rewritten in terms of the observables E and H defined in Eq. (18), as

$$\Delta_{\rm int} S = \frac{1}{Z_N(M)} \int {\rm d}\mathbf{m}\, H(\mathbf{m})\, e^{-E(\mathbf{m})}\, \sinh\left(H(\mathbf{m})\right) \delta\left(\sum_{i=1}^N m_i - M \right). \tag{52}$$

Since the entropy production rate is extensive with system size, it is convenient to define the density of entropy production rate $\sigma = \lim_{N\to\infty} \Delta_{\rm int} S/N$, when this limit exists. A way to evaluate σ in practice is to introduce the generalized partition function $Z_N(M,\theta)$, obtained by replacing $h(m)$ by $\theta h(m)$ where θ is a real parameter, yielding

$$Z_N(M,\theta) = \int {\rm d}\mathbf{m}\, e^{-E(\mathbf{m})}\, \cosh\left(\theta H(\mathbf{m})\right) \delta\left(\sum_{i=1}^N m_i - M \right). \tag{53}$$

Assuming a thermodynamic form $Z_N(N\rho,\theta) \asymp e^{-N\widetilde{\varphi}(\rho,\theta)}$, one can then write

$$\sigma = -\frac{\partial \widetilde{\varphi}}{\partial \theta}(\rho, \theta = 1) \,. \tag{54}$$

The free energy $\widetilde{\varphi}(\rho,\theta)$ can be evaluated in the same way as $\varphi(\rho)$, simply replacing $h(m)$ by $\theta h(m)$ in the calculation of $\lambda(\zeta)$ —see Eq. (22).

In the specific case $h(m) = \frac{1}{2} f m$, one can also write the entropy production rate in terms of the non-equilibrium free energy $\varphi(\rho, f)$ as

$$\sigma = -f \frac{\partial \varphi}{\partial f}. \tag{55}$$

Given that the flux Φ is equal to $-\partial\varphi/\partial f$, the entropy production σ reads

$$\sigma = f\, \Phi \tag{56}$$

using Eq. (48). One then recovers the usual expression of the local entropy production interpreted as the average local work injected in the system (times the inverse

¶ Note that notations in [38] do not follow the same convention, as $P(\omega|\omega')$ denotes there the probability of a transition from a configuration ω to a configuration ω', while we use here a (somehow more standard) conditional probability notation where $T(\mathbf{m}|\mathbf{m}')$ is the transition probability from $\mathbf{m}'$ to $\mathbf{m}$.

temperature that is equal to 1 here). Note that if the inverse temperature $\beta \neq 1$, one finds $\sigma = \beta f \, \Phi$. This result is consistent with the local detailed balance interpretation of the dynamics briefly discussed in Sect. 3.3.

Having discussed dynamical characterizations of the distance to equilibrium, we now turn to static characterizations of this distance, namely, measures of the 'degree of non-equilibrium' that are based only on the steady-state probability distribution $P(\mathbf{m})$, without any explicit reference to the dynamics.

5.3. Difference of Gibbs free energy functional

One possible such measure is the difference of Gibbs free energy functional between the non-equilibrium and equilibrium distributions, for the same temperature of the thermal bath. Note that for the sake of clarity, we explicitly take into account in this subsection the temperature $T = \beta^{-1}$ (previously set to $T = 1$). For an arbitrary probability distribution $P(\mathbf{m})$ over the configuration space of the model, the Gibbs free energy functional $\mathcal{F}[P]$ is defined as

$$\mathcal{F}[P] = \int \mathrm{d}\mathbf{m} \, P(\mathbf{m}) E(\mathbf{m}) - T \int \mathrm{d}\mathbf{m} \, P(\mathbf{m}) \ln P(\mathbf{m}). \tag{57}$$

Given that the equilibrium distribution $P_{\mathrm{eq}}(\mathbf{m})$ at temperature T minimizes the functional $\mathcal{F}[P]$, the quantity

$$\Delta\mathcal{F} = \frac{1}{N}\Big(\mathcal{F}[P] - \mathcal{F}[P_{\mathrm{eq}}]\Big) \tag{58}$$

satisfies $\Delta\mathcal{F} \geq 0$ for any distribution P (note that we have introduced the factor $1/N$ to make $\Delta\mathcal{F}$ an intensive quantity). It is thus natural to interpret $\Delta\mathcal{F}$ as a measure of the distance to equilibrium. Note that $\beta N \Delta\mathcal{F}$ identifies with the Kullback-Leibler divergence

$$\mathbb{D}[P||P_{\mathrm{eq}}] = \int \mathrm{d}\mathbf{m} \, P(\mathbf{m}) \ln \frac{P(\mathbf{m})}{P_{\mathrm{eq}}(\mathbf{m})}. \tag{59}$$

In the present model, a straightforward calculation yields

$$\Delta\mathcal{F} = \frac{1}{N} \ln Z_N^{\mathrm{eq}}(M) - \frac{1}{N} \ln Z_N(M) + \frac{1}{N} \int \mathrm{d}\mathbf{m} \, P(\mathbf{m}) \, \ln\cosh[\beta H(\mathbf{m})] \, . \tag{60}$$

The last integral can be evaluated explicitly in the case $h(m) = \frac{1}{2} f m$, where one has

$$\begin{aligned} &\int \mathrm{d}\mathbf{m} \, P(\mathbf{m}) \, \ln\cosh[\beta H(\mathbf{m})] \\ &\qquad = \int \mathrm{d}M' \int d\mathbf{m} \, P(\mathbf{m}) \, \delta\left(\sum_{k=1}^{N'} m_{2k} - M'\right) \ln\cosh[\beta f (M - 2M')] \\ &\qquad = \int \mathrm{d}M' \, \Psi(M'|M) \, \ln\cosh[\beta f (M - 2M')] \end{aligned} \tag{61}$$

where $\Psi(M'|M)$ is the distribution of the total mass over even sites $M' = \sum_{k=1}^{N'} m_{2k}$, given the total mass M in the system. By symmetry, the most probable value of M' is

$M/2$, so that by a saddle-point argument, the last integral in Eq. (61) is equal to zero at order N, with only possible subextensive corrections. One thus finds from Eqs. (60) and (19), for $N \to \infty$,

$$\Delta\mathcal{F} = \varphi(\rho, f) - \varphi(\rho, 0) \tag{62}$$

so that $\Delta\mathcal{F}$ also identifies in this case with the difference of free energy as defined by the non-equilibrium free energy $\varphi(\rho, f)$ of the partition function $Z_N(M)$ —a quantity a priori distinct from the Gibbs free energy functional, as seen from Eq. (60).

5.4. Non-equilibrium order parameter

A non-equilibrium order parameter Ψ has been introduced by Sasa and Tasaki [30] as (the opposite of) the derivative of the non-equilibrium free energy with respect to the driving force. In the present model with $h(m) = \frac{1}{2}fm$, this definition leads to

$$\Psi = -\frac{\partial\varphi}{\partial f}(\rho, f)\,. \tag{63}$$

Several remarks are in order here. First, this definition is similar to the relation linking, at equilibrium, an order parameter like the magnetization to its conjugate field, hence the name 'non-equilibrium order parameter'. Second, an alternative definition, involving the derivation with respect to the (mass or particle) flux, has also been proposed in [30]. Third, we use here an intensive order parameter instead of the extensive order parameter originally introduced in [30].

Since the non-equilibrium free-energy $\varphi(\rho, f)$ is, from symmetry arguments, an even function of f, $\Psi(\rho, f)$ is an odd function of f, and thus vanishes for $f = 0$, consistently with the interpretation of Ψ as a non-equilibrium order parameter.

Using Eq. (48), the non-equilibrium order parameter Ψ simply boils down to the mass flux,

$$\Psi(\rho, f) = \Phi(\rho, f)\,. \tag{64}$$

Although the non-equilibrium parameter Ψ turns out to be numerically equal to the mass flux Φ, the two quantities differ in essence: Ψ is a static order parameter, while the flux Φ is a dynamical quantity. Introducing explicitly a time step Δt in the model (this time step is been set to $\Delta t = 1$ up to now), we would have $\Phi = \Psi/\Delta t$, showing that both quantities have different dimensions. In any case, Eq. (64) provides an interesting connection between static and dynamic measures of the 'distance' to equilibrium.

6. Discussion and conclusion

In this paper, we have introduced a one-dimensional mass transport model on a ring geometry with sublattice-parallel dynamics for which the steady-state distribution takes a non-factorized form. In contrast to other models with a non-factorized distribution like the Target process [39] (see also [25] for a general discussion of the conditions for factorized steady states), the steady-state distribution can here be determined explicitly

—which constitutes the main contribution of this work— and is found to take a simple form as a sum of two inhomogeneous product measures. The knowledge of the steady-state distribution allows for a straightforward evaluation of local distributions of mass, and, if it exists, of a non-equilibrium free energy. Also, we showed that, like for other similar systems, our model may exhibit a condensation transition. As already emphasized, the explicit dependence of the stationary measure on the driving force is a main advantage of this model —at odds with, for instance, the Zero Range Process and related mass transport models [17]— since this behavior is expected to be generic. It has allowed us to exhibit the explicit dependence on the driving field of different quantities, like the threshold density for condensation.

In addition, we have evaluated several quantities, either static or dynamic, that characterize the 'degree of non-equilibrium' of the steady state of the system. These include the mass flux Φ, the entropy production rate per site σ, the difference $\Delta\mathcal{F}$ of Gibbs free energy functional (per site) between the non-equilibrium and equilibrium states, as well as the non-equilibrium order parameter Ψ introduced by Sasa and Tasaki [30] as the derivative of the non-equilibrium free-energy with respect to the driving force. We have found that all these non-equilibrium parameters are closely related one to the other, and that (at least in the case of a density-independent driving force f) the non-equilibrium order parameter Ψ may be seen as a key parameter from which the others can be evaluated. In particular, we have found that

$$\Phi(\rho, f) = \Psi(\rho, f), \qquad \sigma = f\Psi(\rho, f), \qquad \Delta\mathcal{F}(\rho, f) = \int_0^f \mathrm{d}f'\, \Psi(\rho, f')\,. \quad (65)$$

For a non-zero applied force f, all these parameters have a non-zero value. This is to be contrasted, for instance, with more standard mass transport models [19, 17] (including the ZRP) which, in spite of the presence of a non-zero particle flux, have vanishing values of Ψ and $\Delta\mathcal{F}$, because their steady-state distribution is independent of the driving.

Future work may consider possible extensions of the model with asynchronous dynamics, where more complicated forms of the steady-state distribution (involving, e.g., matrix-product states) are likely to be needed. Applications of the model to the field of glassy dynamics could also be considered, by including kinetic constraints in the spirit of the model introduced in [28].

Appendix A. Evaluation of the integral terms in the master equation

Calculations of the integrals appearing in the steady-state master equation, as formulated in Eq. (12), are straightforward. We provide here the explicit calculation in the case $j = k = 1$ [see Eq. (13)], using again the short notation $S_i \equiv m_i + m_{i+1}$ and $S'_i \equiv m'_i + m'_{i+1}$:

$$\int \mathrm{d}\mathbf{m}\, T_1(\mathbf{m}'|\mathbf{m})\, Q_1(\mathbf{m}) \quad (A.1)$$

$$= \frac{1}{Z} \prod_{k=1}^{N'} \int_0^\infty \mathrm{d}m_{2k} \int_0^\infty \mathrm{d}m_{2k+1}\, K(m'_{2k}|S_{2k})\, v(m_{2k}) w(m_{2k+1})\, \delta(S'_{2k} - S_{2k})$$

$$= \frac{1}{Z}\prod_{k=1}^{N'}\left[\frac{v(m'_{2k})w(m'_{2k+1})}{v*w(S'_{2k})}\int_0^\infty \mathrm{d}m_{2k}\int_0^\infty \mathrm{d}m_{2k+1}\, v(m_{2k})w(m_{2k+1})\,\delta(S'_{2k}-S_{2k})\right].$$

Given that

$$\int_0^\infty \mathrm{d}m_{2k}\int_0^\infty \mathrm{d}m_{2k+1}\, v(m_{2k})w(m_{2k+1})\,\delta(S'_{2k}-S_{2k}) = v*w(S'_{2k}) \qquad \text{(A.2)}$$

one eventually obtains

$$\int \mathrm{d}\mathbf{m}\, T_1(\mathbf{m}'|\mathbf{m})\, Q_1(\mathbf{m}) = Q_1(\mathbf{m}). \qquad \text{(A.3)}$$

Calculations for other values of j, k follow the same lines. For instance, for $k = 1$ and $j = 2$, v and w are exchanged in the l.h.s. of Eq. (A.2), but the result is the same since the convolution product is commutative.

Appendix B. One- and two-site mass distributions in the thermodynamic limit

We derive in this appendix the one- and two-site mass distributions in the thermodynamic limit, provided that the saddle-point approximation discussed in section 4.1 can be performed.

Appendix B.1. Joint mass distribution on a pair of sites

The easiest distribution to compute is the joint distribution of masses $P(m_i, m_{i+1})$ on neighboring sites. Integrating Eq. (8) over the $N-2$ remaining variables m_j ($j \neq i, i+1$), one finds

$$P(m_i, m_{i+1}) = \frac{Z_{N-2}(M - m_i - m_{i+1})}{Z_N(M)}\left[v(m_i)w(m_{i+1}) + w(m_i)v(m_{i+1})\right]. \qquad \text{(B.1)}$$

Using the "thermodynamic limit" form of Z_N, one finds

$$\lim_{N\to\infty}\frac{Z_{N-2}(M - m_i - m_{i+1})}{Z_N(M)} = \exp\left[-2\varphi(\rho) + \mu(\rho)(m_i + m_{i+1} - 2\rho)\right]. \qquad \text{(B.2)}$$

Hence the distribution $P(m_i, m_{i+1})$ can be written as

$$P(m_i, m_{i+1}) = C_2(\rho)\, e^{\mu(\rho)(m_i+m_{i+1})}[v(m_i)w(m_{i+1}) + w(m_i)v(m_{i+1})], \qquad \text{(B.3)}$$

where $C_2(\rho)$ is a normalization constant. It is convenient at this stage to introduce the auxiliary distributions $p_v(m)$ and $p_w(m)$ defined as

$$p_v(m) = c_v(\rho)\, e^{\mu(\rho)m} v(m), \qquad p_w(m) = c_w(\rho)\, e^{\mu(\rho)m} w(m), \qquad \text{(B.4)}$$

where c_v and c_w are normalization constants. In this way, the distribution $P(m_i, m_{i+1})$ given in Eq. (B.3) can be reformulated as

$$P(m_i, m_{i+1}) = \frac{1}{2}[p_v(m_i)\, p_w(m_{i+1}) + p_w(m_i)\, p_v(m_{i+1})]. \qquad \text{(B.5)}$$

The same calculation holds for the joint distribution $P_j(m_i, m_{i+j})$ of the masses m_i and m_{i+j} on distant sites i and $i+j$, as long as j is odd. One thus has

$$P_j(m_i, m_{i+j}) = \frac{1}{2}[p_v(m_i)\, p_w(m_{i+j}) + p_w(m_i)\, p_v(m_{i+j})] \qquad (j = 2k-1,\, k > 0)\,. \tag{B.6}$$

When j is even, the calculation is slightly more complicated; one has

$$P_j(m_i, m_{i+j}) = \frac{Z_{N'-2,N'}(M - m_i - m_{i+j})}{Z_N(M)}\, v(m_i)v(m_{i+j}) + \frac{Z_{N',N'-2}(M - m_i - m_{i+j})}{Z_N(M)}\, w(m_i)w(m_{i+j}) \tag{B.7}$$

with $N' = N/2$ and where the quantity $Z_{N_1,N_2}(M)$ is defined as

$$Z_{N_1,N_2}(M) = \int \prod_{i=1}^{N_1+N_2} \mathrm{d}m_i \prod_{i=1}^{N_1} v(m_i) \prod_{i=N_1+1}^{N_2} w(m_i)\; \delta\left(\sum_{i=1}^{N_1+N_2} m_i - M\right). \tag{B.8}$$

However, in the thermodynamic limit $N' \to \infty$, the two prefactors $Z_{N'-2,N'}/Z_N$ and $Z_{N',N'-2}/Z_N$ have the same limit, again given by Eq. (B.2). Hence the distribution reduces in the thermodynamic limit to

$$P_j(m_i, m_{i+j}) = \frac{1}{2}[p_v(m_i)\, p_v(m_{i+j}) + p_w(m_i)\, p_w(m_{i+j})] \qquad (j = 2k,\, k > 0)\,. \tag{B.9}$$

Using the more physically meaningful parameterization in terms of the functions $\varepsilon(\rho)$ and $h(\rho)$, the distribution $P_j(m_i, m_{i+j})$ can also be written for all $j > 0$ in the form

$$P(m_i, m_{i+1}) = 2\, C_2(\rho)\, e^{-\varepsilon(m_i) - \varepsilon(m_{i+j}) + \mu(\rho)(m_i + m_{i+j})} \cosh\left[h(m_i) + (-1)^j h(m_{i+j})\right]. \tag{B.10}$$

As an explicit example, $P_j(m_i, m_{i+j})$ reads in the specific case $\varepsilon(m) = \varepsilon_0 m$ and $h(m) = h_0 m$

$$P(m_i, m_{i+j}) = \frac{[(\varepsilon_0 - \mu(\rho))^2 - h_0^2]^2}{(\varepsilon_0 - \mu(\rho))^2 + (-1)^j h_0^2}\, e^{-(\varepsilon_0 - \mu(\rho))(m_i + m_{i+j})} \times \cosh\left(h_0 m_i + (-1)^j h_0 m_{i+j}\right) \tag{B.11}$$

where $\mu(\rho)$ is given by Eq. (33). We remind here that $(\epsilon_0 - \mu(\rho))^2 - h_0^2$ is always strictly positive as can be checked from the expression of $\mu(\rho)$ in Eq. (33).

Appendix B.2. Two-point correlation

The two-point correlation function G_j between the masses m_i and m_{i+j}, defined as

$$G_j = \langle m_i m_{i+j} \rangle - \rho^2 \tag{B.12}$$

then takes a simple form. From Eqs. (B.6) and (B.9), one has for $k > 0$

$$G_{2k-1} = \langle m \rangle_v \langle m \rangle_w - \rho^2 \tag{B.13}$$

$$G_{2k} = \frac{1}{2}(\langle m \rangle_v^2 + \langle m \rangle_w^2) - \rho^2 \tag{B.14}$$

where $\langle \ldots \rangle_v$ and $\langle \ldots \rangle_w$ are averages over the distributions $p_v(m)$ and $p_w(m)$ respectively. Obviously, G_j is 2-periodic for $j > 0$. In the example $\varepsilon(m) = \varepsilon_0 m$ and $h(m) = h_0 m$, G_j is given by

$$G_j = \left(\frac{\rho h_0}{\varepsilon_0 - \mu(\rho)} \right)^2 \frac{h_0^2 + (2 + (-1)^j)(\varepsilon_0 - \mu(\rho))^2}{(\varepsilon_0 - \mu(\rho))^2 + (-1)^j h_0^2} \,. \tag{B.15}$$

In the limit where $f = 2h_0$ is small, one can expand G_j to leading order, yielding

$$G_j \underset{f\rho \ll 1}{=} \frac{(2 + (-1)^j)}{(\varepsilon_0 - \mu(\rho))^2} \rho^2 f^2 + \mathcal{O}\left((\rho f)^4\right) . \tag{B.16}$$

Appendix B.3. Single-site distribution

The single-site distribution $p(m)$ is obtained by integrating the two-site distribution over one of the masses. Using for instance Eq. (B.5), we get

$$p(m) = \frac{1}{2}[p_v(m) + p_w(m)] \tag{B.17}$$

or equivalently, in terms of $\varepsilon(m)$ and $h(m)$,

$$p(m) = c(\rho)\, e^{-\varepsilon(m) + \mu(\rho) m} \cosh h(m), \tag{B.18}$$

with $c(\rho)$ a normalization constant.

Appendix C. Link between the flux ϕ and the non-equilibrium free energy φ

When one goes from a configuration $\mathbf{m}$ to another one $\mathbf{m}'$, the local instantaneous current $\Delta_{i,i+1}(\mathbf{m}, \mathbf{m}')$ that goes to the right on the link $(i, i+1)$ is

$$\Delta_{i,i+1}(\mathbf{m}, \mathbf{m}') = -(m_i' - m_i) = m_{i+1}' - m_{i+1} \,. \tag{C.1}$$

Summing over all links, the total mass transferred during the transition $\mathbf{m} \to \mathbf{m}'$, $\Delta(\mathbf{m}, \mathbf{m}')$, is given by

$$\Delta(\mathbf{m}, \mathbf{m}') = \begin{cases} -\sum_{k=1}^{N'} (m_{2k}' - m_{2k}) = \frac{1}{2} \sum_{i=1}^{N} (-1)^i (m_i - m_i') & \text{for part. } \mathcal{P}_1 \\ -\sum_{k=0}^{N'-1} (m_{2k+1}' - m_{2k+1}) = \frac{1}{2} \sum_{i=1}^{N} (-1)^i (m_i' - m_i) & \text{for part. } \mathcal{P}_2 \end{cases} \tag{C.2}$$

On average,

$$\begin{aligned} \langle \Delta(\mathbf{m}, \mathbf{m}') \rangle = \frac{1}{4} \int \mathrm{d}\mathbf{m}\, \mathrm{d}\mathbf{m}' \left(\sum_{i=1}^{N} (-1)^i (m_i - m_i') \right) T_1(\mathbf{m}'|\mathbf{m}) P(\mathbf{m}) \\ + \frac{1}{4} \int \mathrm{d}\mathbf{m}\, \mathrm{d}\mathbf{m}' \left(\sum_{i=1}^{N} (-1)^i (m_i' - m_i) \right) T_2(\mathbf{m}'|\mathbf{m}) P(\mathbf{m}) \,. \end{aligned} \tag{C.3}$$

Since $\int \mathrm{d}\mathbf{m}'\, T_k(\mathbf{m}'|\mathbf{m}) = 1$ $(k = 1, 2)$, the terms involving $\sum_{i=1}^{N} m_i$ cancel out. Using Eq. (10) and (13), one gets

$$\begin{aligned} \langle \Delta(\mathbf{m}, \mathbf{m}') \rangle = \frac{1}{2Z_N(M)} \int \mathrm{d}\mathbf{m}' \left(\sum_{i=1}^{N} (-1)^i m_i' \right) Q_2(\mathbf{m}') \\ - \frac{1}{2Z_N(M)} \int \mathrm{d}\mathbf{m}' \left(\sum_{i=1}^{N} (-1)^i m_i' \right) Q_1(\mathbf{m}') \,. \end{aligned} \tag{C.4}$$

To go further, one needs to use the physical interpretation of the dynamics, given in Sect. 3.3. Indeed, using Eq. (10) and (14), one can notice that in the (linear) case where $h(m) = \frac{1}{2}fm$,

$$\int \mathrm{d}\mathbf{m} \left(\sum_{i=1}^{N} (-1)^i m_i \right) Q_k(\mathbf{m}) = 2 \int \mathrm{d}\mathbf{m} \frac{H(\mathbf{m})}{f} Q_k(\mathbf{m}) = 2(-1)^k \frac{\partial Q_k}{\partial f}(\mathbf{m}) \; . \tag{C.5}$$

Eventually, using Eq. (11), the total averaged mass transferred is equal to

$$\langle \Delta(\mathbf{m}, \mathbf{m}') \rangle = \frac{\partial \ln Z_N}{\partial f} \; , \tag{C.6}$$

leading to the final expression of the mass current Φ (mass transferred per link and per time step)

$$\Phi = \frac{\langle \Delta(\mathbf{m}, \mathbf{m}') \rangle}{N} = \frac{1}{N} \frac{\partial \ln Z_N}{\partial f} = -\frac{\partial I}{\partial f}(\rho, f) \; , \tag{C.7}$$

thus proving the relation given in Eq. (48).

Appendix D. Evaluation of the entropy production rate

In this appendix, we evaluate the entropy production rate in the model defined in Sect. 2. From Eq. (5), the transition rate $T(\mathbf{m}'|\mathbf{m})$ takes the form

$$T(\mathbf{m}'|\mathbf{m}) = \frac{1}{2} T_1(\mathbf{m}'|\mathbf{m}) + \frac{1}{2} T_2(\mathbf{m}'|\mathbf{m}) \tag{D.1}$$

where $T_1(\mathbf{m}'|\mathbf{m})$ and $T_2(\mathbf{m}'|\mathbf{m})$ respectively describe redistributions over the partitions $\mathcal{P}_1$ and $\mathcal{P}_2$ of the lattice. For a given configuration $\mathbf{m}$, we define the sets $\mathcal{D}_1(\mathbf{m})$ and $\mathcal{D}_2(\mathbf{m})$ as the subsets of configurations $\mathbf{m}'$ accessible from $\mathbf{m}$ through redistributions over the partitions $\mathcal{P}_1$ and $\mathcal{P}_2$. More formally, one has for $j \in \{1, 2\}$,

$$\mathcal{D}_j(\mathbf{m}) = \{\mathbf{m}' | \forall k = 1, \ldots, N', \; m'_{2k+j-1} + m'_{2k+j} = m_{2k+j-1} + m_{2k+j}\}. \tag{D.2}$$

Using the subsets $\mathcal{D}_1(\mathbf{m})$ and $\mathcal{D}_2(\mathbf{m})$, one can express the ratio of reciprocal, nonzero transition probabilities, so that the entropy production reads, in steady state,

$$\begin{aligned} \Delta_{\mathrm{int}} S = \frac{1}{2} \int \mathrm{d}\mathbf{m} \, P(\mathbf{m}) \Bigg\{ & \int_{\mathcal{D}_1(\mathbf{m})} \mathrm{d}\mathbf{m}' \, T_1(\mathbf{m}'|\mathbf{m}) \ln \frac{T_1(\mathbf{m}'|\mathbf{m})}{T_1(\mathbf{m}|\mathbf{m}')} \\ & + \int_{\mathcal{D}_2(\mathbf{m})} \mathrm{d}\mathbf{m}' \, T_2(\mathbf{m}'|\mathbf{m}) \ln \frac{T_2(\mathbf{m}'|\mathbf{m})}{T_2(\mathbf{m}|\mathbf{m}')} \Bigg\} . \end{aligned} \tag{D.3}$$

The ratios of transition rates can be expressed as

$$\ln \frac{T_1(\mathbf{m}'|\mathbf{m})}{T_1(\mathbf{m}|\mathbf{m}')} = [E(\mathbf{m}) - E(\mathbf{m}')] + [H(\mathbf{m}) - H(\mathbf{m}')] \, , \tag{D.4}$$

$$\ln \frac{T_2(\mathbf{m}'|\mathbf{m})}{T_2(\mathbf{m}|\mathbf{m}')} = [E(\mathbf{m}) - E(\mathbf{m}')] - [H(\mathbf{m}) - H(\mathbf{m}')] \, . \tag{D.5}$$

The restriction of the integration domains to the subsets $\mathcal{D}_1(\mathbf{m})$ and $\mathcal{D}_2(\mathbf{m})$ in Eq. (D.3) was needed only to be able to properly define the ratio of reverse transition probabilities. Once Eq. (D.3) is rewritten in terms of the observables $E(\mathbf{m})$ and $H(\mathbf{m})$, the integration

domains no longer need to be restricted to these subsets since the transition probabilities $T_1(\mathbf{m}'|\mathbf{m})$ and $T_2(\mathbf{m}'|\mathbf{m})$ appearing in the integrals vanish by definition outside the subsets $\mathcal{D}_1(\mathbf{m})$ and $\mathcal{D}_2(\mathbf{m})$. Hence one has

$$\Delta_{\rm int}S = \frac{1}{2}\int {\rm d}\mathbf{m}\,{\rm d}\mathbf{m}'\,P(\mathbf{m})\left[T_1(\mathbf{m}'|\mathbf{m})\Big(E(\mathbf{m})-E(\mathbf{m}')+H(\mathbf{m})-H(\mathbf{m}')\Big)\right. \tag{D.6}$$
$$\left. +T_2(\mathbf{m}'|\mathbf{m})\Big(E(\mathbf{m})-E(\mathbf{m}')-H(\mathbf{m})+H(\mathbf{m}')\Big)\right].$$

The part of the integral involving E is easily shown to vanish. Using the form $P(\mathbf{m}) = \frac{1}{2}[P_1(\mathbf{m}) + P_2(\mathbf{m})]$ of the probability distribution —see Eq. (9)— one has thanks to Eq. (13) that $\int {\rm d}\mathbf{m}\, T_k(\mathbf{m}'|\mathbf{m})P_j(\mathbf{m}) = P_k(\mathbf{m})$. The H-dependent part in Eq. (D.6) can then be simplified, after a straightforward calculation, to

$$\Delta_{\rm int}S = \frac{1}{2}\int {\rm d}\mathbf{m}\,[P_1(\mathbf{m})-P_2(\mathbf{m})]\,H(\mathbf{m}), \tag{D.7}$$

which is precisely Eq. (51).

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APPENDIX D

Introduction, conclusion et résumés des chapitres

Nous fournissons dans cet annexe une brève version française de l'introduction, de la conclusion ainsi que des brefs résumés de chaque chapitre.

D.1 Introduction Générale

Considérons une tasse de café chaude fermée par un couvercle afin d'éviter l'évaporation. Si vous laissez cette tasse de café sur votre bureau et revenez une heure plus tard, la température de votre café sera la même que celle de la pièce. Pensez maintenant à une pompe à vélo que vous voulez tester pour vous assurer qu'elle ne fuit pas. Pour cela, vous obstruez la valve et poussez le piston afin de comprimer l'air à l'intérieur. Ensuite, si vous relâcher le piston, ce dernier bougera jusqu'à ce que l'air dans la pompe obtienne la même pression que l'air dans la pièce. Finalement, prenez un verre d'eau et laissez tomber une goutte d'encre, disons bleue, dans le verre. Au bout d'un certain temps, l'eau devient bleue : la goutte a diffusé dans tout le verre. Toutes ces expériences de la vie quotidienne ont en commun d'être des phénomènes irréversibles : personne n'a jamais été témoin d'un réchauffement spontané du café après son refroidissement, ni d'une compression spontanée de l'air dans la pompe, ni, enfin, d'une formation spontanée d'une goutte d'encre après sa diffusion dans l'eau. Pour saisir ces phénomènes irréversibles et utiliser les forces qu'ils peuvent générer[1], les physiciens du XIX^{e} siècle ont développé une théorie générale, la thermodynamique [Callen,

[1]Par exemple, on pourrait chauffer l'air à l'intérieur de la pompe en le mettant en contact avec une source chaude, afin de déplacer le piston en utilisant le travail produit par l'expansion de l'air chaud ; ou on pourrait construire une membrane élastique sélective, perméable à l'eau mais pas à l'encre, séparant le verre d'eau en deux parties : en cherchant à diffuser, l'encre appliquerait une force supplémentaire sur la membrane qui empêcherait sa diffusion.

1998]. La thermodynamique traite des états d'équilibre et plus précisément des transitions qui conduisent un état d'équilibre initial vers un autre état d'équilibre. Les états d'équilibre ne sont pas clairement définis à ce stade, mais on peut facilement les imaginer : ils correspondent à des états de la matière très calmes, qui ne contiennent aucun courant moyen, quelle que soit l'échelle à laquelle on regarde le système.

D'après le second principe de la thermodynamique, ces états d'équilibre finaux d'un système isolé peuvent être prédits en maximisant l'entropie, généralement appelée S. La maximisation de l'entropie donne lieu, de par la conservation de l'énergie, du volume ainsi que du nombre de particules, à l'égalisation de quantités que sont justement la température, la pression et le potentiel chimique. Si ces quantités peuvent par ailleurs avoir une définition opérationnelle, leur lien avec cette fonction entropie permet de les définir de façon non ambiguë.

Très généralement, la problématique à laquelle le présent travail vise à contribuer est la suivante : existe-t-il une structure thermodynamique pour les systèmes hors de l'équilibre en régime permanent ? Ou, plus précisément : existe-t-il une fonction des variables d'état qui joue un rôle analogue à l'entropie ? Peut-on associer à des quantités conservées des paramètres intensifs comme la pression ou les potentiels chimiques qui s'égalisent lorsque deux systèmes hors d'équilibre sont mis en contact ?

Contrairement aux systèmes à l'équilibre, les systèmes hors de l'équilibre présentent des courants (dans l'espace des configurations, pas toujours directement observables) crées par des forces extérieures ou simplement parce qu'ils n'ont pas encore atteint leur état d'équilibre. Ces diverses situations peuvent être complexes. Afin de simplifier notre discussion, nous nous intéresserons principalement à des systèmes maintenus hors de l'équilibre, dans un état stationnaire, par des forces externes non-conservatives. Si ces systèmes sont homogènes, de même que les forces extérieures, on peut s'attendre à pouvoir les décrire macroscopiquement par quelques quantités globales seulement, à l'instar des systèmes thermodynamiques à l'équilibre.

Comme mentionné plus haut, la problématique principale de cette thèse est de définir une fonction entropie (ou plutôt ici, une fonction énergie libre) qui décrirait l'état macroscopique des systèmes hors d'équilibre à la limite thermodynamique. À l'équilibre, cette fonction entropie est additive lorsque deux systèmes (avec des interactions de courte portée) sont mis en contact. De part les lois de conservation des quantités échangeables (énergie, nombre de particules, volume, *etc.*), l'extrémalisation du potentiel thermodynamique entraîne l'égalisation de paramètres thermodynamiques intensifs (températures, potentiels chimiques, pressions, *etc*). Cette structure est-elle toujours valide pour des systèmes hors d'équilibre en régime stationnaire ?

Pour répondre à cette question, nous nous concentrerons principalement sur des systèmes stochastiques simples modélisant la dynamique de particules en interaction. L'idée principale qui sous-tend la modélisation des systèmes hors d'équilibre par des

modèles stochastiques est de décrire le système à un niveau mésoscopique, à une échelle plus large que la dynamique hamiltonienne sous-jacente, trop compliquée à traiter. Pour faire le lien avec la dynamique hamiltonienne, nous ferons l'hypothèse classique que la dynamique stochastique obéit a un bilan détaillé local.

L'énergie n'étant pas une quantité conservée entre deux (ou plusieurs) systèmes hors d'équilibre dans un état stationnaire en contact, étendre la notion de température aux systèmes hors d'équilibre de cette façon paraît sans espoir. Ce n'est néanmoins pas le cas pour des quantités comme le nombre de particules ou encore le volume qui demeurent conservées. Le volume étant la quantité conjuguée à la pression, qui dispose d'une définition mécanique généralement bien définie, nous nous focaliserons principalement dans ce manuscrit sur la notion de potentiel chimique, quantité conjuguée au nombre de particules, qui a moins été explorée.

Plusieurs études sur ces questions ont été menées durant les dernières décennies. En particulier, deux d'entre elles sont particulièrement pertinentes :

- La première a été menée sur des modèles de transport de masse et des gaz sur réseau, qui sont des modèles où les particules sautent localement d'un site à l'autre selon un processus de Poisson. Les principales contributions théoriques sur ce sujet contiennent : [Hayashi and Sasa, 2003; Sasa and Tasaki, 2006] sur le modèle KLS ; [Bertin et al., 2006, 2007], une étude théorique sur le Zero Range Process (un modèle de transport de masse hors de l'équilibre exactement soluble, dont la distribution microscopique factorise complètement et permet ainsi de définir des potentiels chimiques en utilisant la même procédure que pour la mécanique statistique d'équilibre). Cette dernière contribution a récemment été étendue à une classe spécifique de systèmes hors d'équilibre comportant des corrélations à courte portée par [Chatterjee et al., 2015]. Les autres études pertinentes ont essentiellement consisté en des simulations numériques sur les modèles KLS [Pradhan et al., 2010, 2011] ainsi que sur d'autres gaz sur réseau avec exclusion [Dickman, 2014, 2016; Dickman and Motai, 2014].

- La deuxième série d'études porte quant à elle sur des modèles de matière active dans l'espace continu et plus particulièrement sur des particules autopropulsées comme des particules browniennes actives (ABP) ou des particules « Run-&-Tumble » [Fodor and Marchetti, 2018; Marchetti et al., 2013]. En particulier, la question de la définition de la pression a été abordée en détail dans des travaux récents [Fily et al., 2017; Solon, Fily, Baskaran, Cates, Kafri, Kardar and Tailleur, 2015; Solon, Stenhammar, Wittkowski, Kardar, Kafri, Cates and Tailleur, 2015; Speck and Jack, 2016; Takatori et al., 2014; Winkler et al., 2015].

L'objectif de cette thèse est d'étendre et de discuter de façon plus systématique la première série d'études susmentionnée. En particulier, le principal résultat de ce travail

sera de définir un potentiel thermodynamique à partir duquel une notion de potentiel chimique pourra être dérivée. Dans un second temps nous aborderons brièvement la notion de potentiel chimique pour des gaz de particules autopropulsées.

Pour se faire, nous utiliserons abondamment le formalisme des grandes déviations [Touchette, 2009] qui est l'outil naturel pour analyser des variables macroscopiques à la limite thermodynamique (grand nombre de particules) dans des systèmes stochastiques.

D.2 Chapitre 1 : contact entre deux systèmes à la limite thermodynamique

Ce chapitre d'introduction vise à présenter les principaux objets de cette thèse, dans le cadre simple des gaz sur réseau et autres modèles de transport de masse qui obéissent à un bilan détaillé local. Nous examinerons la situation dans laquelle deux de ces systèmes sont mis en contact et atteignent ainsi un nouvel état stationnaire, de la même façon que plusieurs études précédentes [Bertin et al., 2007; Dickman, 2014; Dickman and Motai, 2014; Hayashi and Sasa, 2003; Pradhan et al., 2010, 2011; Sasa and Tasaki, 2006]. Une hypothèse importante nécessaire à notre cadre de travail et déjà préconisée dans [Sasa and Tasaki, 2006, Annexe B.] consiste en une séparation bien définie entre, d'une part, le temps caractéristique d'échange de particules au contact, et, d'autre part, le temps caractéristique d'évolution des particules au sein de chaque système. Cette hypothèse peut sembler plutôt restrictive mais elle est en fait physiquement motivée si l'on imagine le contact comme une haute barrière de potentiel que les particules doivent franchir (voir [Sasa and Tasaki, 2006]). Nous considérerons néanmoins des types de contact plus généraux qui pourraient demeurer physiquement pertinents, toujours dans cette limite de faible taux d'échange au contact. Sauf mention contraire, la dynamique au contact sera supposée ne pas être perturbée par les forces externes.

Le principal objectif de ce chapitre est l'introduction de la fonction de grandes déviations $\mathcal{I}(\rho_A, \rho_B|\bar{\rho})$ associée aux densités globales ρ_A et ρ_B des deux systèmes en contact (appelés A et B). Cette dernière est introduite comme solution d'une équation de Hamilton-Jacobi pour les processus markoviens à sauts. Ces résultats ne sont pas nouveaux (voir [Kubo et al., 1973; Maes and Netočný, 2007] et [Ge and Qian, 2017] pour une étude récente portant sur les réactions chimiques) mais semblent avoir reçu peu d'attention dans le cadre des gaz sur réseau et autres modèles de transport de masse.

Enfin, ce chapitre discute différentes façons de résoudre l'équation de Hamilton-Jacobi et ainsi trouver sa solution $\mathcal{I}(\rho_A, \rho_B|\bar{\rho})$. En particulier, nous détaillons la situation importante du bilan détaillé (au niveau macroscopique), ainsi que son lien

naturel avec la symétrie par renversement du temps. Nous concluons en présentant une méthode de perturbation générale pour résoudre l'équation de Hamilton-Jacobi en l'absence de bilan détaillé, qui reprend celle présentée dans [Bouchet et al., 2016] dans le contexte des systèmes diffusifs.

D.3 Chapitre 2 : propriété d'additivité de la fonction de grandes déviations

Ce second chapitre aborde la question de l'additivité de la fonction de grandes déviations $I(\rho_A|\bar{\rho})$ pour deux systèmes en contact. Cette condition d'additivité est très proche de l'additivité de l'énergie libre pour les systèmes à l'équilibre avec interactions à courte portée. Celle-ci s'écrit :

$$I(\rho_A|\bar{\rho}) \sim I_A(\rho_A) + I_B(\rho_B) \tag{D.1}$$

où ρ_B est fixée par la conservation du nombre de particules, connaissant ρ_A. La dérivée de la fonction de grandes déviations I est alors

$$I'(\rho_A|\bar{\rho}) = I'_A(\rho_A) - I'_B(\rho_B)\ . \tag{D.2}$$

Dans l'état stationnaire, on obtient $I'_A(\rho_A) = I'_B(\rho_B)$. Cette approche offre donc la possibilité d'associer à chaque système une quantité $I'_k(\rho_k)$ $(k = A\,, B)$ – notée $\mu_k(\rho_k)$ désormais – que l'on appellera potentiel chimique généralisé au contact.

Néanmoins, la limite d'un faible taux d'échange au contact n'est pas suffisante pour garantir cette propriété d'additivité. Nous montrons dans ce chapitre qu'une condition suffisante pour garantir l'additivité correspond à la présence d'un bilan détaillé macroscopique, au niveau de la dynamique du nombre de particules, ainsi qu'à une propriété de factorisation des taux de transition au contact. Sans ces hypothèses qui ne sont pas automatiquement valides lorsqu'il est possible d'échanger plus d'une particule par unité de temps, nous ne pouvons nous attendre à obtenir cette propriété d'additivité nécessaire à la définition de potentiels chimiques. En outre, même lorsque ces hypothèses sont vérifiées, nous montrons que le potentiel chimique généralisé $I'_k(\rho_k)$ dépend fortement des propriétés locales au contact et ne peut donc pas être totalement associé aux systèmes isolés (autrement dit, les potentiels chimiques ainsi définis ne vérifient aucune équation d'état). Nous confirmons et étendons donc significativement les résultats préliminaires obtenus par S.-I. Sasa, K. Hayashi et H. Tasaki [Hayashi and Sasa, 2003; Sasa and Tasaki, 2006] sur le modèle KLS, bien que ce dernier n'ait pas été reconnu comme résultant d'une analyse en grandes déviations.

D'autre part, nous explorons les propriétés thermodynamiques générales de cette

fonction de grandes déviations I (additive ou non). En particulier, nous montrons que pour une certaine classe de taux de transition, cette fonction de grandes déviations I vérifie un second principe de la thermodynamique, par rapport au travail fourni par des potentiels externes uniformes appliqués sur chaque système A et B. Notre dérivation, bien qu'originale dans ce contexte, est largement inspirée par les travaux exposés dans [Bertini et al., 2015*a*,*b*, 2012, 2013]. Nous discutons ensuite le cas particulier où l'un des systèmes, disons B, est très grand par rapport à l'autre et joue le rôle d'un réservoir. Finalement, nous terminons ce chapitre en discutant différentes façons expérimentales d'avoir accès à cette fonction de grandes déviations : en biaisant la dynamique au contact (à l'aide par exemple de potentiels extérieurs), en plaçant le système en contact avec un petit système à l'équilibre jouant le rôle d'un thermostat, ou encore, à l'aide du second principe, en mesurant le travail reçu par les systèmes lors d'une transformation adiabatique.

D.4 Chapitre 3 : modèles sur réseau en contact

Nous examinons à présent le cadre proposé sur des exemples de modèles sur réseau en contact. Les modèles considérés sont surtout des modèles classiques de la littérature [Evans and Hanney, 2005; Katz et al., 1984; Liggett, 2012; Spitzer, 1970; Zia, 2010].

Nous commençons par une brève discussion des études précédentes sur deux modèles *Zero Range Processes* (ZRP) en contact [Bertin et al., 2006, 2007]. Ce modèle exactement soluble est l'un des rares exemples de système hors d'équilibre qui reproduit une situation formellement équivalente à l'équilibre. Néanmoins, ce modèle a l'inconvénient d'avoir sa distribution de probabilité stationnaire non dépendante du forçage. Il n'est alors pas possible d'observer une différence réelle entre le potentiel chimique au contact, μ^{cont}, et le potentiel chimique du système isolé μ^{iso}, qui correspondent d'ailleurs au potentiel chimique d'équilibre. C'est également le cas pour d'autres modèles simples sur réseau tels que le *Modèle d'exclusion simple asymétrique* (ASEP) [Derrida, 1998], dont la distribution de probabilité stationnaire est la distribution d'équilibre.

Pour cette raison, nous avons élaboré avec Éric Bertin un modèle original de transport de masse, exactement soluble, dont la distribution de probabilité stationnaire dépend génériquement du forçage extérieur. Une brève présentation de ce modèle original (voir [Guioth and Bertin, 2017] pour plus de détails) ainsi qu'une étude approfondie du contact entre deux de ces systèmes sont exposées. Nous fournissons également quelques simulations numériques qui confirment la pertinence de notre analyse dans le cadre de ce modèle.

Ensuite, afin d'explorer des dimensions spatiales supérieures à l'unité, nous interprétons les résultats numériques disponibles dans la littérature à la lumière de notre

analyse. Ces interprétations nécessiteraient des simulations numériques détaillées pour être complètement validées (puisque les solutions exactes des modèles considérés ne sont pas disponibles) mais nous croyons que l'analyse disponible ici donne déjà un nouvel aperçu pertinent de la littérature disponible sur le sujet. En accord avec les résultats de R. Dickman [Dickman, 2014, 2016; Dickman and Motai, 2014], nous montrons qu'en plus du détail des taux de transition, l'étendue et la position du contact jouent un rôle important.

Enfin, nous changeons d'échelle et proposons une brève présentation du contact entre deux systèmes hors d'équilibre décrits par la *Macroscopic Fluctuation Theory* (MFT), exposée par exemple dans [Bertini et al., 2002, 2015*a*]. Cette dernière trouve ici une place naturelle puisqu'elle a été imaginée sur la base d'études de modèles sur réseau. Nous montrons néanmoins que la MFT ne tient pas compte de l'effet observé dans les modèles stochastiques microscopiques compte tenu de l'hypothèse d'équilibre local qui est faite.

D.5 Chapitre 4 : application à quelques modèles de particules indépendantes diffusives et autopropulsées

Finalement, nous appliquons dans ce chapitre les idées précédentes à des systèmes constitués de particules indépendantes qui peuvent être forcées par un champ extérieur ou qui peuvent être autopropulsées de différentes manières. Physiquement, il s'agit de modèles de particules colloïdales immergées dans un solvant qui sont entraînées par des champs électriques externes ou autopropulsées par la présence d'une hétérogénéité de réactifs chimiques sur leur surface par exemple. Deux systèmes différents constitués de ces particules peuvent être mis en contact selon plusieurs protocoles différents. Nous nous focaliserons sur deux types de contact :

- Le premier type de contact auquel on peut penser est une membrane poreuse. Dans une situation idéalisée, on pourrait penser à une paroi infiniment mince modélisée par un potentiel infini percé de trous parfaits qui ne nécessitent aucun coût énergétique pour être traversés par des particules de taille inférieure à leur diamètre.

- Le second, plus homogène, correspond simplement à une haute barrière de potentiel séparant les deux systèmes. Comme nous le montrons dans le contexte des particules autopropulsées, l'absence de symétrie de la barrière par rapport à son sommet joue un rôle important.

Nous calculons perturbativement le profil de densité (proportionnel à la densité de probabilité pour des particules indépendantes) pour plusieurs modèles simples de particules indépendantes : particules diffusives forcées par un champ externe au-delà de la réponse linéaire [Barany, 2009; Figliuzzi et al., 2014; Hunter and White, 1987], particules browniennes actives (ABP) et particules Run-&-Tumble (RTP) (voir [Fodor and Marchetti, 2018] pour une revue récente). Ces modèles ont été introduits il y a longtemps dans la littérature [Cates and Tailleur, 2013; Tailleur and Cates, 2008] mais nous concentrons ici notre attention sur la situation d'un contact entre ces systèmes et en particulier sur la définition des potentiels chimiques. Nous montrons que les spécificités du contact, comme pour les modèles de transport de masse discutés dans les chapitres précédents, influencent significativement les densités moyennes des deux côtés du contact. Aucune équation d'état n'est ainsi vérifiée, à l'instar de la pression dans certains systèmes de particules actives [Fily et al., 2017; Solon, Fily, Baskaran, Cates, Kafri, Kardar and Tailleur, 2015; Solon et al., 2018*a*; Solon, Stenhammar, Wittkowski, Kardar, Kafri, Cates and Tailleur, 2015; Speck and Jack, 2016; Takatori et al., 2014; Winkler et al., 2015].

D.6 Conclusion et ouverture

En examinant la situation de deux systèmes macroscopiques en contact, nous avons montré dans cette thèse que l'existence de potentiels chimiques associés à chaque sous systèmes, qui s'égaliseraient en atteignant l'état stationnaire, était sujette à plusieurs restrictions. Plus précisément, nous avons montré, sous une hypothèse de très faible fréquence d'échange de particules au contact pour des systèmes markovien à sauts, que l'existence d'un bilan détaillé macroscopique et la factorisation des taux de transition constituait une condition suffisante pour obtenir l'additivité de la fonction de grandes déviations. Néanmoins, même lorsque la propriété d'additivité est valide, une dépendance explicite de la dynamique au contact est toujours présente dans l'expression des potentiels chimiques : ceux-ci ne vérifient aucune équation d'état. Malgré cette dépendance de la dynamique au contact, il est possible – lorsqu'ils existent – d'avoir accès expérimentalement aux potentiels chimiques. Ces résultats ont été vérifiés et illustrés sur différents modèles stochastiques de particules. En particulier, l'étude de systèmes de dimension spatiale supérieure à un ont montré, en plus de la dépendance explicite des taux de transition au contact, l'influence de la position et de l'étendue du contact, corroborant ainsi des résultats de simulations antérieures [Dickman, 2014, 2016; Dickman and Motai, 2014].

Quelques perspectives

- Cette thèse s'est principalement concentrée sur une seule quantité conservée, à savoir le nombre de particules. Il serait également intéressant de considérer la pression comme la quantité conjuguée à l'échange de volume, lui aussi conservé. Il pourrait s'agir d'un moyen de mettre en relation les potentiels chimiques et la pression. Le problème du piston adiabatique (voir par exemple [Itami and Sasa, 2015] pour une étude récente) en contact avec des gaz hors de l'équilibre pourrait être une étude préliminaire intéressante.

- Finalement, nous avons observé tout au long de cette thèse l'importance cruciale du contact dans la répartition du nombre de particules dans chaque sous-système. Contrairement à l'équilibre, la thermodynamique des systèmes hors d'équilibre ne peut pas être décrite par des quantités globales simples, faisant abstraction du contact. Pour cette raison, il semble intéressant de considérer des champs spatiaux (même si ces derniers sont presque uniformes) plutôt que de simples macro-variables pour décrire de façon systématique des états thermodynamiques, dans la même veine que la MFT par exemple. Comme cette dernière ne tient pas compte des situations exposées ci-dessus, il serait intéressant (mais sans aucun doute difficile) d'élaborer une théorie des champs de densité au-delà de l'hypothèse de l'équilibre local[2].

[2]Par exemple, voir cet article récent [Barré et al., 2015] à propos d'une description en terme de champ de densité de particules autopropulsées en interaction dans la limite de petit bruit.

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