

5-9-2017

A Field Theoretic Description of Non-Equilibrium Chemical Work Relations

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**A FIELD THEORETIC DESCRIPTION OF
NON-EQUILIBRIUM CHEMICAL WORK RELATIONS**

by

Jonathan Pham

A Thesis

Presented to the Faculty of

Bucknell University

in Partial Fulfillment of the Requirements for the Degree of
Bachelor of Science with Honors in Physics & Astronomy

May 7, 2017

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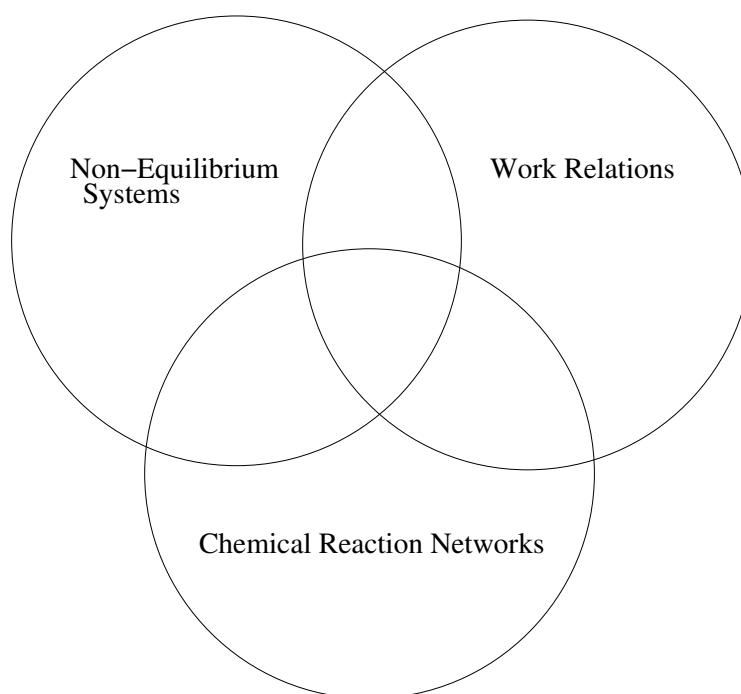
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Abstract

We develop a field theoretic description of non-equilibrium chemical work relations, generalizing the well-known Jarzynski equality using Doi-Peliti field theory. The Jarzynski equality relates the average non-equilibrium work performed on a system to the equilibrium free energy. We consider classical particles undergoing detailed balanced diffusion and chemical reactions in a local potential. The particles are coupled to a chemostat, which is a reservoir of particles, and also a thermal reservoir. Work protocols are imposed by varying the local potential, which drives the system out of equilibrium. We derive the Jarzynski relation in both the Doi representation and in the Doi-Peliti field theory. The Doi representation is a rewriting of the dynamics in terms of creation and annihilation operators, and Doi-Peliti Field theory is an extension of the Doi representation that is convenient for going to the spatial continuum limit. The Jarzynski equality is recovered in the Doi representation due to conditions set by detailed balance. Work relations, in the field theory, appear simply as a result of a gauge-like transformation combined with time reversal. We present the derivation with a one-dimensional system on a lattice and two species of particles but it can be generalized to multiple dimensions with N species of particles. We expect this formalism to be useful in describing spatial chemical reaction networks, for example, sodium-potassium pumps which are distributed along a cell membrane and consume ATP.

Chapter 1

Introduction



We are interested in the intersection of three fields of study: non-equilibrium systems, work relations, and chemical reaction networks. In particular, we are interested in non-equilibrium work relations for chemical reaction networks. We consider situations where we are applying work, positive or negative, via an external control parameter such as an electric field. We vary the external parameter in a prearranged

way known as a work protocol. The amount of work actually performed by this parameter change can itself vary from one realization of the experiment to the next due to the stochastic nature of the chemical reaction. The energetic cost to apply work to the system varies as the dynamics of the system fluctuates the state of the system. As a result, initiating the same work protocol on the system generates a probability distribution of work values, which is highly non-universal and depends on the microscopic details. For large systems near equilibrium, the work is simply equal to the change in free energy, which has been known since the 19th century. On the other hand, for small systems far from equilibrium, particular averages of the work distribution can be related to the equilibrium free energy. This is a striking development in the last 20 years. In synthetic chemistry and biological systems, many chemical reaction networks consist of multiple species and reactions. Additionally, these systems can be spatially non-uniform and far from equilibrium. In the following section, as an example of a spatially varying chemical reaction network, we will be looking at the free energy change in ATPase of sodium-potassium pumps during motor neural conduction.

1.1 ATPase in Sodium Potassium Pumps

Consider the chemical reaction network of ATPase, labeled ‘E’ for enzyme, in Fig. 1.1. ATPase are a class of enzymes that catalyze the decomposition of ATP (adenosine triphosphate) into ADP (adenosine diphosphate) and a free phosphate ion, P_i . ATP is the main source of energy for most cellular processes. Because of the presence of unstable, high energy bonds in ATP, it is readily hydrolyzed in reactions to release large amounts of energy. First ATP is bound to ATPase; then ATP hydrolyzes, resulting in the products, $ADP + P_i$ (inorganic phosphate). P_i is released and finally ADP is released. In the diagram, the transitions are stochastic and can occur in either the forward or reverse direction. Although ATPase reactions are biased in the forward direction to hydrolyze ATP, it can occur in the reverse cycle. The diagram represents the possible discrete states and transitions ATPase can be in and make [1].

Each transition results in a change Gibbs Free energy, ΔG . Gibbs Free energy is the amount of work a system can do and is defined as:

$$G = F + pV = U - TS + pV = \sum_X \mu_X(c_x)N_X \quad (1.1)$$

where F is the Helmholtz free energy, p is the pressure of the system, and V is the volume of the system. The Helmholtz free energy can be expanded to the difference

between the internal energy, U , of the system and the heat provided by the environment, TS . T is the temperature of the system and S is the entropy of the system. From this description, the Helmholtz free energy is the energy needed to create the system excluding the energy provided by the environment. Lastly, the Gibbs free energy can be formulated to the sum on species of the chemical potential, $\mu_X(c_x)$, times the total number of that particular species, N_X , where the chemical potential is dependent on the relative concentration of the species. As a result, the chemical potential can be interpreted as the amount of free energy each molecule adds to the system.

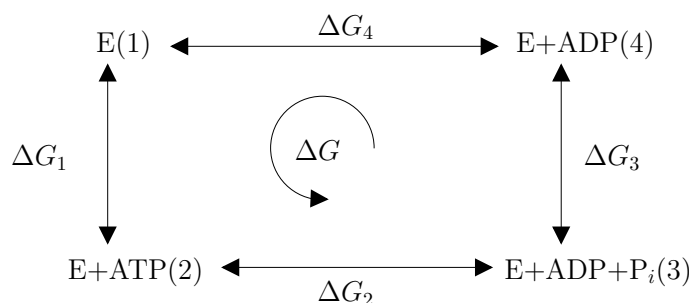


Figure 1.1: Four-state cycle for ATPase, E

During the ATPase cycle, the dephosphorylation, removal of P_i from ATP, releases energy which the enzyme, in most cases, harnesses to drive other processes that would not occur without it. Sodium-potassium pump ($\text{Na}^+/\text{K}^+-\text{ATPase}$) actively use ATP to pump sodium ions out of cells while pumping potassium ions into cells, both against their concentration gradients as seen in figure 1.2. Sodium-potassium pumps play an important role in many cell physiological activities such as motor nerve conduction [2]. Motor signal conduction begins from a stimulus depolarizing (increasing membrane potential from resting membrane potential) upper motor neurons in the brain, triggering a chain of action potentials from the brain to the lower motor neurons of the spinal cord to the targeted muscle fibers. Action potential is the “signal” that must reach the muscle fiber for muscle contraction and can be seen in figure 1.3. The initial stimulus’ depolarization triggers the action potential in the neuron by opening, respectively, sodium and potassium voltage gated ion channels at the start of the axon. These channels allow sodium (Na^+) and potassium (K^+) ions to travel across their concentration gradients. The extracellular environment relative to the neuron’s intracellular environment is rich in sodium ions and deficient in potassium ions, resulting in the sodium ions traveling into the cell and the potassium ions traveling out. During the action potential, sodium channels open first, which further depolarizes the cell. Once depolarization peaks, potassium channels open and repolarize the membrane back to the resting membrane potential. Action potentials are identical

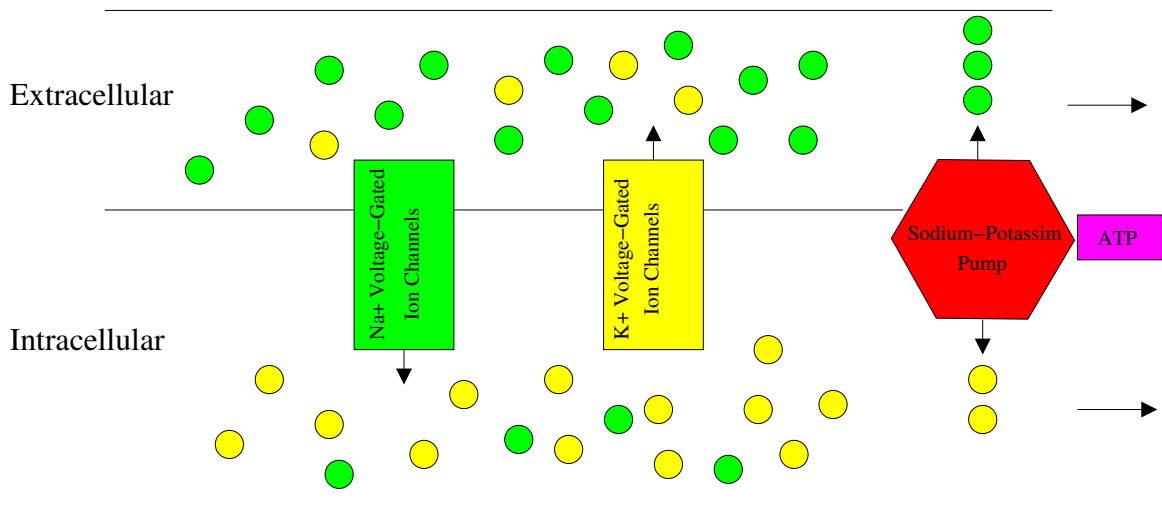


Figure 1.2: Extracellular and intracellular sodium (Na^+) and potassium (K^+) environment of an axon. Na^+ ions are in green and K^+ ions are in yellow. Na^+ and K^+ voltage-gated ion channels and sodium-potassium pumps lie on the plasma membrane of axons and maintain resting membrane potential during motor neural conduction.

and once triggered they continue til completion.

The diffusion of the depolarization and thus the action potential diffuses through the cytoplasm but does not reach the length of the complete axon. To travel across the complete axons, intracellular sodium ions from the initial action potential diffuse to neighboring ion-gated channels and trigger the next action potential, resulting in a chain of action potentials. The action potential chain accomplishes contraction of the muscle fiber and repolarization of the membrane potential, but it disrupts the chemical and electrical gradient, as there are more intracellular sodium ions and extracellular potassium ions. Ultimately, this will disrupt the resting membrane potential and thus the functionality of the neuron. This is where sodium-potassium pumps play a crucial role in pushing their respective ion against its concentration gradient to maintain the chemical and electrical gradient, and most importantly the neural network.

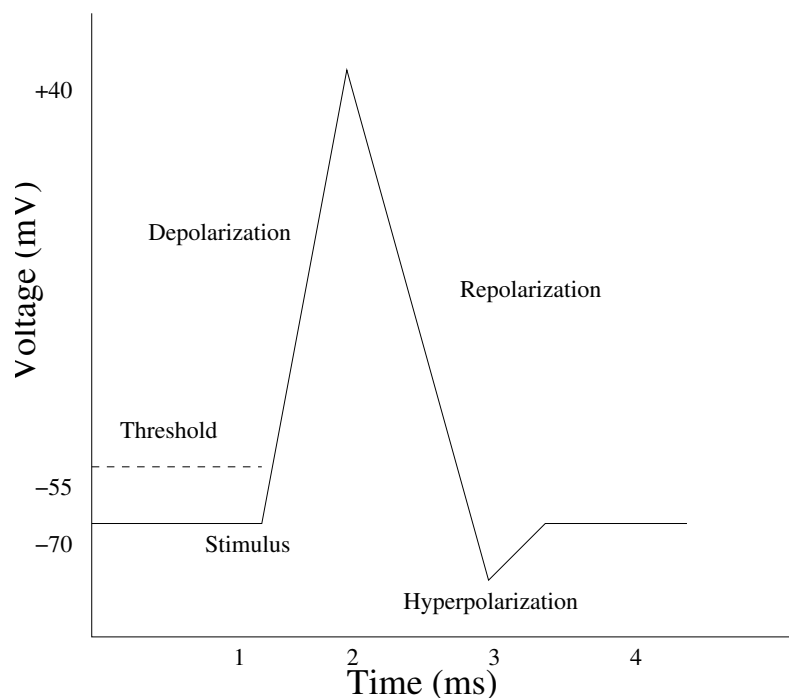


Figure 1.3: Action potential in an neural axon’s plasma membrane. Plasma membrane is resting at -70 mV. Initial stimulus depolarizes the resting membrane potential to a threshold at -55 mV. Once at the threshold, the action potential is initiated and sodium ion channels open and further depolarize the membrane to $+40$ mV. At 40 mV, the sodium channels close and potassium ion channels open and repolarize the membrane and ultimately hyperpolarize the membrane. Sodium-potassium pumps repolarize the membrane to the initial resting membrane potential.

1.2 Our Approach

We now turn to the question of how to mathematically model a chemical reaction network. Macromolecules such as ATPase can be in solution whether it is in a dilute solution or in between extracellular and intracellular environments. These chemical reacting systems, after a period of time with their local environment, reach a thermal equilibrium Gibbs state [3], creating a system that has no net flow of energy nor particles, but rather, a system with constant temperature, pressure, and concentration gradients. Principles from thermodynamics can be used to describe the stochastic dynamics of these systems by developing the Chemical Master Equation (CME), which considers the energetics of the system such as the energy and chemical potential.

Studies have been made using these CMEs for well-stirred mixtures of chemically reacting species [4, 5, 6]. These well-stirred systems, by assumption, exhibit no spatial variation.

In our work, we adopt these CMEs to describe the dynamics of systems with particles undergoing chemical reactions. Moreover, we also map the diffusive properties of these particles in a spatially extended system. We use Doi-Peliti field theory to reinterpret these master equations in the temporal and spatial continuum limit [7, 8, 9, 10]. This is an established theoretical framework for non-equilibrium dynamics, but one which has not been previously applied to chemical systems. Previous work has been done using Doi-Peliti field theory on classical thermal systems with particles under pair interactions [11]. We are now extending the formalism to chemical reaction networks. The spatial variation of such systems is relevant as seen in the sodium-potassium pumps, where ATP must diffuse to these spatially varying pumps to trigger the chemical reaction.

Additionally, we are also interested in the non-equilibrium states of the system and how the system changes due to non-equilibrium processes. For instance, we can apply non-equilibrium work to the system, by initiating a work protocol through a time-varying external electric field to the sodium-potassium system, shifting the energetics of the system and causing the ions to be pushed by the electric force. The time-varying factor evolves the system in a non-quasistatic fashion, resulting in the system never being able to return to an equilibrium state.

1.3 Jarzynski Relation

The use of the free energy of ATP hydrolysis to push ions against their concentration gradient is known as free energy transduction. We are interested in this free energy quantity and how it changes during the non-equilibrium work protocol. The work protocol is a specified sequence of values for the control parameters (i.e. electric field) of the system that occurs regardless of the energetic cost. Classically, for large systems, the change in free energy, ΔF , would be bounded by the second law of thermodynamics: $\langle W \rangle \geq \Delta F$, with equality held for quasistatic processes. However, we are interested in non-equilibrium systems and potentially small systems, such that the inequality does not always hold, resulting in a wide distribution of work values and thus making the second law of thermodynamics inadequate. Therefore, we must turn to a different family of work relations such as the Crook's relation [12, 13], the

fluctuation theorem [14, 15], and the Jarzynski equality [16, 17, 18]. We are most interested in the Jarzynski equality as it provides an equality that is always able to determine the change in free energy from the work distribution. It is given as:

$$\langle e^{-W/k_B T} \rangle = e^{-\Delta F/k_B T} \quad (1.2)$$

where W is the work done on the system, T is the temperature, k_B is Boltzmann's constant, and ΔF is the change in Helmholtz free energy. Note that even for far from equilibrium processes, this relation is an equality rather than an inequality. The angle brackets term in the Jarzynski equality containing the work indicates an average over an infinite number of realizations of the system undergoing the same work protocol. The Jarzynski equality holds true for systems of any size as well as system that are far from equilibrium. However, one caveat of the Jarzynski equality is that the initial state must be an equilibrium state with the same temperature T . Due the universality, the relation has been the focus of many recent studies. The Jarzynski equality applies to variety of systems; both quantum and classical systems obey the relation, whether they are stochastic or deterministic, either on a lattice or taken to the continuum limit.

As mentioned, we will model our system using the Doi-Peliti field theory, thus we will also be deriving the Jarzynski relation in this field theory, which creates the foundation for producing similar relations such as the Crook's relation in this framework. Previous field-theoretic formulations of the Jarzynski relation were found by Mallick, Moshe, and Orland [19] as well as Täuber [20]. Their derivations were phenomenological, and required assumptions about the particle dynamics that are generally only valid for large systems near an equilibrium critical point. Doi-Peliti field theory is based on first principles and is generally valid with no restrictions on system size or location in a phase diagram.

For our derivation, we seek to create a new formulation of the field theory that applies to chemical reaction networks in thermal systems. We generalize the Doi-Peliti field theory developed in [11] to include (i) multiple species of particles, (ii) chemical reactions between the species, (iii) particle exchange with chemostats, and (iv) a Gibbs equilibrium initial state characterize by a fixed chemical potential rather than a fixed number of particles. In doing so, we obtain a generalization of the Jarzynski equation, namely

$$\langle e^{-W/k_B T} \rangle = e^{-\Delta\Phi_G/k_B T} = e^{-(\Delta F - \Delta G)/k_B T}, \quad (1.3)$$

where the grand potential, Φ_G , is given as:

$$\Phi_G = F - \sum_X \mu_X N_X = F - G \quad (1.4)$$

where F is the Helmholtz free energy, μ_X is the chemical potential of the particle species X , and N_X is the total number of particles X . Using our definition of the Gibbs free energy in Eq. 1.1, we can write the grand potential as the difference between the Helmholtz free energy and Gibbs free energy. The equality holds for arbitrarily far from equilibrium processes and for small systems. The generalized Jarzynski relation with the associated grand potential for chemical reaction networks has not been previously obtained in the literature and represents our primary results.

The remainder of the thesis is as follows. In Chapter 2 the model is presented and the Chemical Master Equations (CMEs) are written for our model dynamics. In Chapter 3 we rewrite our master equation in the Doi representation and in Chapter 4 we extend the Doi representation to Doi-Peliti field theory to bring our system to the spatial continuum limit. We then summarize our results in Chapter 5.

Chapter 2

Model

The model we are looking at consists of two species of distinguishable hopping classical particles, particle A and particle B , on a finite 1-D lattice of size of L as seen in Figure 2.1. For simplicity, we examine our theory in one dimension with two species of particles, but it may be extended to a hypercubic lattice of arbitrary dimensions with N distinct species of particles. The system is coupled to a thermostat of temperature T . Furthermore, the system is also coupled to two chemostats held at chemical potential μ_A and μ_B , which allow particles to enter and leave the system. Each lattice site may contain multiple number and species of particles. Each site, i , is paired with a spatially and time varying site potential $U_i(t)$, which affects each particle respectively ($U_i^A(t)$ and $U_i^B(t)$) as seen in Figure 2.2. Experimentally, U can be set by, for instance, an external electric field, and in contrast, theoretically it can take any value, which is useful for developing formalism. The energy landscape sets a bias to where the particles will be on the lattice, as from statistical mechanics, lattice sites with lower energy have a higher probability of being occupied. Work can be applied to the system by varying the site potential. Lastly, we explore chemical reactions of the form $A \longleftrightarrow B$.

2.1 Microstates and Configurations

We can define a particular microstate, α , of the system by giving the lattice coordinate x_i of each particle.

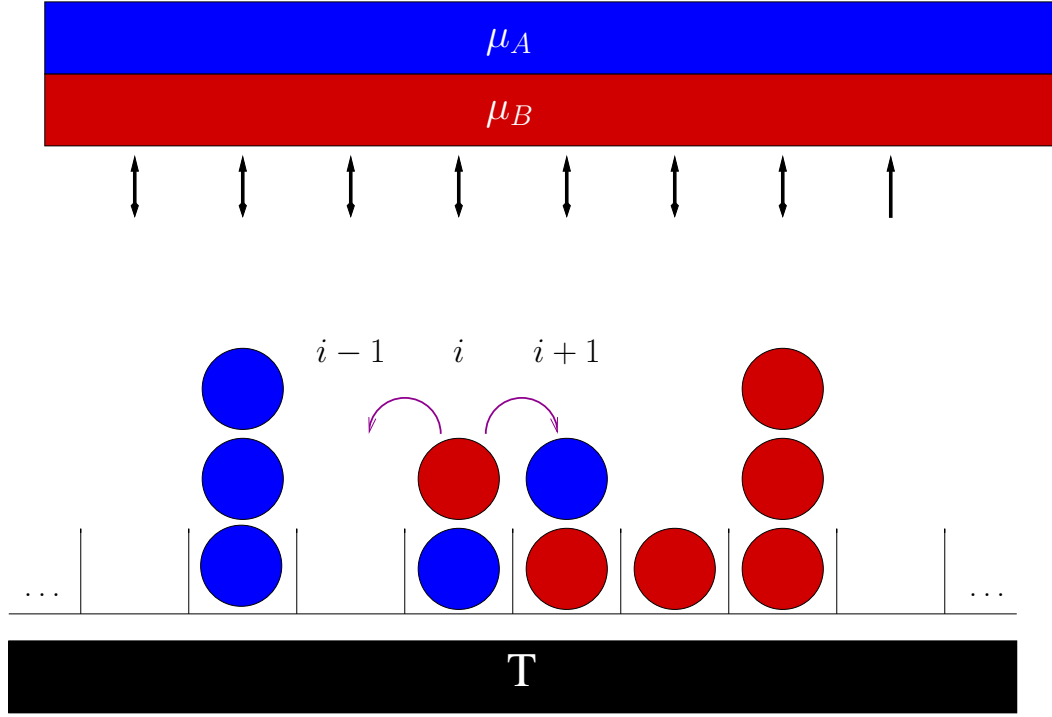


Figure 2.1: System of two types of classical particles, A (blue) and B (red), undergoing stochastic hopping, governed by a coupled thermostat and site potentials. Two chemostats held at chemical potential μ_A and μ_B are also coupled to the system. Particles A and B undergo $A \leftrightarrow B$ chemical reaction.

Furthermore, a set of microstates, $\alpha_1, \alpha_2, \dots$, with the same occupation number, n_{Xi} , for particle X at each site, i , defines a configuration, \mathbf{n}_X :

$$\mathbf{n}_X = (n_{X1}, \dots, n_{Xi}, \dots, n_{XL}) \quad \text{with} \quad \sum_i n_{Xi} = N_X(\mathbf{n}_X) \quad (2.1)$$

where N_X is the total number of particle species X . In configuration space, the associated microstate, α , has multiplicity given by the multinomial coefficient,

$$\Omega_X(\mathbf{n}_X) = \frac{N_X(\alpha)!}{n_{X1}! n_{X2}! \dots n_{XL}!}, \quad (2.2)$$

allowing us to define the multiplicity for our complete system of A and B particles. Let \mathbf{n} be the whole configuration made up of \mathbf{n}_X and the multiplicity of the whole configuration is given as:

$$\Omega(\mathbf{n}) = \prod_X \Omega_X(\mathbf{n}_X) \quad (2.3)$$

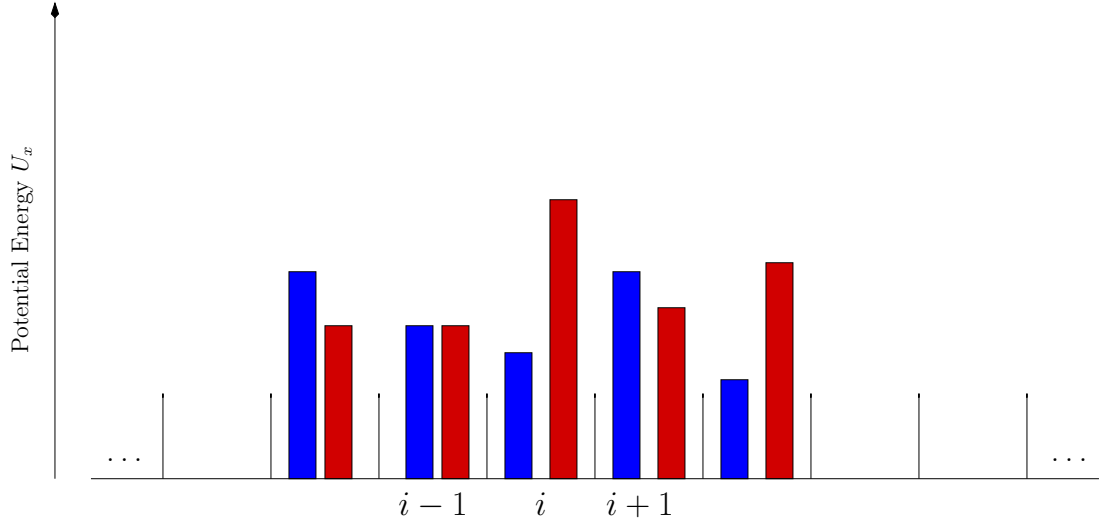


Figure 2.2: Arbitrary spatially and time varying site potentials for particles A (blue) and B (red). These site potentials characterize the energetics of the particle at each site.

2.2 Gibbs distribution

A configuration, \mathbf{n} , of the system in equilibrium can be characterized by the probability distribution of its microstates, $P_{\text{Gibbs}}(\alpha, T)$, which is determined by the Gibbs distribution at temperature T :

$$P_{\text{Gibbs}}(\alpha, T) = \frac{1}{\mathcal{Z} N_A(\alpha)! N_B(\alpha)!} e^{-\beta(E(\alpha) + \mu_A N_A(\alpha) + \mu_B N_B(\alpha))} \quad \beta = \frac{1}{k_B T} \quad (2.4)$$

where \mathcal{Z} is the grand partition function.

$$\mathcal{Z} = \sum_{\alpha} e^{-\beta(E(\alpha, t) + \mu_A N_A(\alpha) + \mu_B N_B(\alpha))} = \sum_{\mathbf{n}} \Omega(\mathbf{n}) e^{-\beta(E(\mathbf{n}, t) + \mu_A N_A(\mathbf{n}) + \mu_B N_B(\mathbf{n}))} \quad (2.5)$$

The sum runs over all possible states of the system, including all possible values of N_A and N_B . The grand partition function acts as a constant normalization factor for the Gibbs distribution.

The Gibbs distribution can be generally defined in configuration space as:

$$P_{\text{Gibbs}}(\mathbf{n}, T) = \frac{\Omega(\mathbf{n})}{\mathcal{Z} \prod_X N_X!} e^{-\beta(E(\mathbf{n}) + \sum_X \mu_X N_X(\mathbf{n}))} \quad \beta = \frac{1}{k_B T} \quad (2.6)$$

Additionally, the energy associated with a configuration in our system is determined by the local site potential, U_i^X , and the number of particles at a site, as

$$E(\mathbf{n}, t) = \sum_X \sum_i^L n_{Xi}(\mathbf{n}) U_i^X(t) \quad (2.7)$$

2.3 Master Equation

The system dynamics, such as nearest neighbor hopping, affects how the system evolves and furthermore affects the time derivative of the probability of the microstate, $P(\alpha, t)$. As a result, the dynamics alter the probability distribution. Initially the system is stationary in equilibrium, but as we vary the local site potential with time, our system moves out of equilibrium and the probabilities of all possible microstates in the system shift.

The dynamics of our system can be mapped to a master equation of the following form:

$$\frac{\partial P(\alpha, t)}{\partial t} = \sum_{\text{Hops, Chemical Reactions}} \left[\sum_{\gamma \neq \alpha} \underbrace{[w_{\gamma \rightarrow \alpha} P(\gamma, t)]}_{\text{Gain Term}} - \underbrace{[w_{\alpha \rightarrow \gamma} P(\alpha, t)]}_{\text{Loss Term}} \right] \quad (2.8)$$

which describes the time evolution of a particular state. Taking note of the master equation's form, it relates the evolution of a particular state to the current state of the system. Each process (hops and chemical reactions) contributes gain and loss terms to the time derivative. A gain term reflects all the different states that can evolve into our particular state and the loss terms reflect all the different states our particular state can evolve out to by the proposed dynamics. The rate constants, $w_{\gamma \rightarrow \alpha}$, represent transition rates due to dynamical processes from state γ to state α . The master equation assumes Markovian dynamics, which means the probability evolution is determined by the present state of the system, with no explicit dependence on earlier states. The master equation models our dynamics but does not include any illuminating information about the rate constants. To define our rate constants, we allow our dynamics to be governed by detailed balance, which states the following:

$$\frac{w_{\alpha \rightarrow \gamma}}{w_{\gamma \rightarrow \alpha}} = \frac{P_{eq}(\gamma)}{P_{eq}(\alpha)} = \frac{N_A(\alpha)! N_B(\alpha)!}{N_A(\gamma)! N_B(\gamma)!} e^{-\beta(\Delta E - \sum_X \Delta(N_X \mu_X))} \quad \text{where} \quad \Delta E = E_\gamma - E_\alpha \quad (2.9)$$

Detailed balance forces the flow into a given state $w_{\gamma \rightarrow \alpha} P_{eq}(\gamma)$ to be equal to the flow out of the state $w_{\alpha \rightarrow \gamma} P_{eq}(\alpha)$ in order to maintain equilibrium. However, as we vary our site potential with time, in a non-quasistatic manner (not allowing the system to re-equilibriate), detailed balance forces our system out of equilibrium. Detailed balance does not fully specify the rate constants as there are many ways of satisfying the equality.

Instead of working with microstates, we can generalize our master equation and detailed balance into configuration space.

$$\frac{\partial P(\mathbf{n}, t)}{\partial t} = \sum_{\text{Hops, Chemical Reaction}} \left[\sum_{\mathbf{m} \neq \mathbf{n}} \underbrace{[w_{\mathbf{m} \rightarrow \mathbf{n}} P(\mathbf{m}, t)]}_{\text{Gain Term}} - \underbrace{[w_{\mathbf{n} \rightarrow \mathbf{m}} P(\mathbf{n}, t)]}_{\text{Loss Term}} \right] \quad (2.10)$$

where

$$P(\mathbf{n}, t) = \Omega(\mathbf{n}) P(\alpha, t) \quad (2.11)$$

as all microstates with the same configuration \mathbf{n} have the same probability. Similarly, detailed balance can then take the form:

$$\frac{w_{\mathbf{n} \rightarrow \mathbf{m}}}{w_{\mathbf{m} \rightarrow \mathbf{n}}} = \frac{P_{eq}(\mathbf{m})}{P_{eq}(\mathbf{n})} = \left(\prod_X \prod_i^L \frac{n_{Xi}!}{m_{Xi}!} \right) e^{-\beta(\Delta E - \sum_X \Delta(N_X \mu_X))} \quad (2.12)$$

where m_{Xi} is the particle X site occupation number for configuration \mathbf{m} .

From this point on, we will assume $\beta = 1$ to simplify expressions.

2.3.1 Master Equation for Hopping Dynamics

From here we consider two species, with the master equation and general transition rates from detailed balance, we can model the dynamics of our system. We will first map out nearest-neighbor particle hopping. Particles are only allowed to hop to adjacent lattice sites and each particle hops independently from all other particles.

We first consider the microstate α of our system with configuration \mathbf{n} :

$$\mathbf{n} = (n_{A1}, n_{B1}, \dots, n_{Ai}, n_{Bi}, n_{A(i+1)}, n_{B(i+1)}, \dots, n_{AL}, n_{BL}) \quad (2.13)$$

Particle A hopping from site i to $i + 1$ results in microstate γ with configuration \mathbf{m}

$$\mathbf{m} = (n_{A1}, n_{B1}, \dots, n_{Ai} - 1, n_{Bi}, n_{A(i+1)} + 1, n_{B(i+1)}, \dots, n_{AL}, n_{BL}) \quad (2.14)$$

For a hop from site i to site $i + 1$ from configuration \mathbf{n} with microstate α there are n_i possible resulting microstates, $\gamma, \dots, \gamma_{n_i}$, all with the same configuration \mathbf{m} as any of the particles from site i can make the hop to microstate γ . This tells us that the configuration transition rate is given by

$$w_{\mathbf{n} \rightarrow \mathbf{m}}^{\text{hop}} = n_{Ai} w_{\alpha \rightarrow \gamma}^{\text{hop}} \quad (2.15)$$

and the reverse reaction transition rate would be

$$w_{\mathbf{m} \rightarrow \mathbf{n}}^{\text{hop}} = (n_{A(i+1)} + 1) w_{\gamma \rightarrow \alpha}^{\text{hop}} \quad (2.16)$$

Detailed balance relates the rates of the $i \rightarrow i + 1$ hop out of configuration \mathbf{n} to \mathbf{m} and a $i + 1 \rightarrow i$ hop into configuration \mathbf{n} from \mathbf{m} . Imposing detailed balance, the simplest choice for the configuration transition rates are

$$w_{\mathbf{n} \rightarrow \mathbf{m}}^{\text{hop}} = -\Gamma_A n_{Ai} e^{U_i^A(t)} \quad \text{and} \quad w_{\mathbf{m} \rightarrow \mathbf{n}}^{\text{hop}} = -\Gamma_A (n_{A(i+1)} + 1) e^{U_{i+1}^A(t)} \quad (2.17)$$

where Γ_A is a constant reflecting how the A particles hop. The chemical potential term is negated as the total number of A particles is conserved during nearest neighbor hopping.

The energy change, ΔE , for adding a particle at site $i + 1$ is U_{i+1}^A ; while removing a particle at site i decreases the energy of the system by U_i^A , resulting in a net energy change of $U_{i+1}^A(t) - U_i^A(t)$, thus our exponential terms in Eq. 2.17 satisfy detailed balance.

Additionally, a separate detailed balance relation exists between an $i + 1 \rightarrow i$ hop out of configuration \mathbf{n} to a microstate γ' with configuration \mathbf{m}' and an $i \rightarrow i + 1$ hop into configuration \mathbf{n} from \mathbf{m}' where \mathbf{m}' is

$$\mathbf{m}' = (n_{A1}, n_{B1}, \dots, n_{Ai} + 1, n_{Bi}, n_{A(i+1)} - 1, n_{B(i+1)}, \dots, n_{AL}, n_{BL}) \quad (2.18)$$

and the configuration transition rates are defines as:

$$w_{\mathbf{n} \rightarrow \mathbf{m}'}^{\text{hop}} = -\Gamma_A (n_{A(i+1)}) e^{U_{i+1}^A(t)} \quad \text{and} \quad w_{\mathbf{m}' \rightarrow \mathbf{n}}^{\text{hop}} = -\Gamma_A (n_{Ai} + 1) e^{U_i^A(t)}. \quad (2.19)$$

To summarize, the hopping dynamics for a configuration, \mathbf{n} , is:

$$\mathbf{n} \begin{array}{c} \xrightarrow{i \rightarrow i+1 \text{ hop}} \\ \xleftarrow{i+1 \rightarrow i \text{ hop}} \end{array} \mathbf{m} \quad \text{and} \quad \mathbf{n} \begin{array}{c} \xrightarrow{i+1 \rightarrow i \text{ hop}} \\ \xleftarrow{i \rightarrow i+1 \text{ hop}} \end{array} \mathbf{m}' \quad (2.20)$$

We are now able to define the hopping master equation for our system.

$$\begin{aligned}
\partial_t P(\mathbf{n}, t) = & \\
- \sum_{X=A,B} \Gamma_X \sum_i & \left[\overbrace{(n_{X(i+1)} + 1) e^{U_{i+1}^X} P(\dots, n_{Xi} - 1, n_{X(i+1)} + 1, \dots, t)}^{\text{gain for } i+1 \rightarrow i \text{ hop}} - \overbrace{n_{Xi} e^{U_i^X} P(\mathbf{n}, t)}^{\text{loss for } i \rightarrow i+1 \text{ hop}} \right. \\
& \left. + \overbrace{(n_{Xi} + 1) e^{U_i^X} P(\dots, n_{Xi} + 1, n_{X(i+1)} - 1, \dots, t)}^{\text{gain for } i \rightarrow i+1 \text{ hop}} - \overbrace{n_{i+1} e^{U_{i+1}^X} P(\mathbf{n}, t)}^{\text{loss for } i+1 \rightarrow i \text{ hop}} \right]. \tag{2.21}
\end{aligned}$$

Each lattice site produces two gain terms and two loss terms in the master equation as a hop from any of the lattice sites can move the system into or out of the configuration \mathbf{n} .

2.3.2 Master Equation for $A \longleftrightarrow B$ Reaction

Similar to constructing the master equation for nearest neighbor hopping, we first consider the same configuration \mathbf{n} as in Eq. 2.24. Furthermore, we examine the configuration/microstate the system evolves into from a forward reaction, $A \rightarrow B$, at site i . We will define this configuration/microstate as \mathbf{m}_R/γ_R :

$$\mathbf{m}_R = (n_{A1}, n_{B1}, \dots, n_{Ai} - 1, n_{Bi} + 1, \dots, n_{AL}, n_{BL}) \tag{2.22}$$

The energy change, ΔE , from a forward reaction is $U_i^B - U_i^A$; the total number of A particles decreases by one and the total number of B particles increases by one. Thus, we can define the forward and reverse configuration rates:

$$w_{\mathbf{n} \rightarrow \mathbf{m}_R}^{A \leftrightarrow B} = \Lambda n_{Ai} e^{U_i^A(t) - \mu_A} \quad \text{and} \quad w_{\mathbf{m}_R \rightarrow \mathbf{n}}^{A \leftrightarrow B} = \Lambda (n_{Bi} + 1) e^{U_i^B(t) - \mu_B} \tag{2.23}$$

where Λ is a constant related to the $A \leftrightarrow B$ reaction. Additionally, we can consider the evolution of the \mathbf{n} configuration by the reverse reaction, $A \leftarrow B$, resulting in the configuration/microstate, \mathbf{m}'_R/γ'_R , given by:

$$\mathbf{m}'_R = (n_{A1}, n_{B1}, \dots, n_{Ai} + 1, n_{Bi} - 1, \dots, n_{AL}, n_{BL}). \tag{2.24}$$

Similarly, we can define the forward and reverse configuration rates into and out of \mathbf{m}'_R :

$$w_{\mathbf{n} \rightarrow \mathbf{m}'_R}^{A \leftrightarrow B} = \Lambda (n_{Bi}) e^{U_i^B(t) - \mu_B} \quad \text{and} \quad w_{\mathbf{m}'_R \rightarrow \mathbf{n}}^{A \leftrightarrow B} = \Lambda (n_{Ai} + 1) e^{U_i^A(t) - \mu_A} \tag{2.25}$$

Grouping the forward and reverse reaction results in the following master equation:

$$\begin{aligned} \partial_t P(\mathbf{n}, t) = \Lambda \sum_i & \left[(n_{Bi} + 1) e^{U_i^B - \mu_B} P(\dots, n_{Ai} - 1, n_B + 1, \dots, t) - n_{Bi} e^{U_i^B - \mu_B} P(\mathbf{n}, t) \right. \\ & \left. + (n_{Ai} + 1) e^{U_i^A - \mu_A} P(\dots, n_{Ai} + 1, n_{Bi} - 1, \dots, t) - n_{Ai} e^{U_i^A - \mu_A} P(\mathbf{n}, t) \right]. \end{aligned} \quad (2.26)$$

2.3.3 Master Equation for Chemostat Exchange

Lastly, we can map the particles leaving and entering through their respective chemostat to the master equation. We will map the A particles exchange interaction with its chemostat. Particle interaction with a chemostat is independent of other particles, so the master equation for B particles will be similar to the A particles.

Starting with a configuration, \mathbf{n} , as in Eq. 2.24 with microstate α . An A particle at site i leaving the system through the A chemostat decreases the energy of the system by U_i^A and results in the microstate and configuration evolving to microstate γ and configuration \mathbf{n} :

$$\mathbf{m}_C = (n_{A1}, n_{B1}, \dots, n_{Ai} - 1, n_{Bi}, \dots, n_{AL}, n_{BL}) \quad (2.27)$$

There are n_{Ai} possible resulting microstates with the same configuration \mathbf{m}_C ; on the other hand, for the reverse process, there is only one possible resulting microstate with configuration \mathbf{n} as the chemostat only has one microstate with a large amount of A particles such that removing or adding one particle does not change its microstate. Therefore the detailed balance configuration rates for the forward and reverse process are:

$$w_{\mathbf{n} \rightarrow \mathbf{m}_C}^{\text{Chemostat}_A} = \lambda n_{Ai} e^{U_i^A(t) - \mu_A} \quad \text{and} \quad w_{\mathbf{m}_C \rightarrow \mathbf{n}}^{\text{Chemostat}_A} = \lambda(1) \quad (2.28)$$

where λ is a constant associated with the chemostat exchange.

From the \mathbf{n} configuration a particle can enter the system at site i through the chemostat, increasing the energy by U_i^A and moving the system to a microstate γ'_C and configuration \mathbf{m}'_C :

$$\mathbf{m}'_C = (n_{A1}, n_{B1}, \dots, n_{Ai} + 1, n_{Bi}, \dots, n_{AL}, n_{BL}). \quad (2.29)$$

The configuration rates are given as:

$$w_{\mathbf{n} \rightarrow \mathbf{m}'_C}^{\text{Chemostat}} = \lambda(1) \quad \text{and} \quad w_{\mathbf{m}'_C \rightarrow \mathbf{n}}^{\text{Chemostat}_A} = \lambda(n_{Ai} + 1) e^{U_i^A(t) - \mu_A} \quad (2.30)$$

where there is only one resulting microstate from evolving the system \mathbf{n} to \mathbf{m}_C whereas there are $n_{Ai} + 1$ microstates for the \mathbf{m}'_C to \mathbf{n} configuration transition.

This results in the master equation:

$$\begin{aligned} \partial_t P(\mathbf{n}, t) = \lambda \sum_i \left[P(\dots, n_{Ai} - 1, n_B + 1, \dots, t) - n_{Ai} e^{U_i^A - \mu_A} P(\mathbf{n}, t) \right. \\ \left. + (n_{Ai} + 1) e^{U_i^A - \mu_A} P(\dots, n_{Ai} + 1, n_{Bi}, \dots, t) - P(\mathbf{n}, t) \right]. \end{aligned} \quad (2.31)$$

Similarly, the B particle chemostat takes the same form as Eq. 2.31, replacing the A scripts for B scripts.

We have now modeled all of our system dynamics and we can sum the right side of equations 2.21, 2.26, 2.31 to form the master equation for our complete system with particle nearest neighbor hopping, $A \longleftrightarrow B$ chemical reaction, and particle chemostat exchange. The techniques presented here generalize straightforwardly to additional species of particles and more complicated chemical reactions.

2.4 Applying Work and The First Law

In our system, the site potential for all particles, $U_i^X(t)$, is time dependent. Through detailed balance, this drives the system out of equilibrium and is how we can do work onto the system. Let us differentiate the average total energy of the system with respect to time to produce an expression similar to the first law of thermodynamics. The average of any quantity, $A(t)$, for instance, is given by:

$$\langle A(t) \rangle = \sum_{\mathbf{n}} P(\mathbf{n}, t) A(\mathbf{n}, t). \quad (2.32)$$

Differentiating the average energy gives:

$$\frac{d}{dt} \langle E \rangle = \sum_{\mathbf{n}} \left[\frac{dP(\mathbf{n}, t)}{dt} E(\mathbf{n}, t) + P(\mathbf{n}, t) \frac{dU(\mathbf{n}, t)}{dt} \right] \quad (2.33)$$

where $P(\mathbf{n}, t)$ is the probability of a given state configuration \mathbf{n} , and $E(\mathbf{n}, t)$ is the energy of the state. This results in the first law of thermodynamics with two terms, one where the probability of the states change and the other where the lattice potential for each particle changes.

The first term on the right of Eq. 2.33 is the heat flow dQ/dt between the system and the thermal reservoir due to being out of thermal equilibrium. Particles will change their state configuration, $P(\mathbf{n}, t)$, to reach equilibrium with the coupled thermal reservoir. As the particles move, they exchange energy with the reservoir. Heat flow stops when the system reaches equilibrium as $dP_{eq}/dt = 0$.

The second term in Eq. 2.33 represents the rate of doing work, dW/dt . Work is the amount of energy we are adding or removing from the system by changing the site potential, thus the total energy of the system varies. By raising or lowering a site's lattice potential, the particles at that site are forced up or down in energy in a manner analogous to doing work on them.

Chapter 3

Doi Representation

The master equation developed in equations 2.21, 2.26, 2.31 are dependent on the occupation numbers, n_i , of the system. This makes it difficult to describe explicitly the time evolution of our system as there are many configurations, each with different occupation numbers. To make these equations more accessible, we exploit that each process for each particle is independent of one another and rewrite the master equation in the Doi representation, which removes the explicit dependence on the occupation number [7].

3.1 Background

We present a brief summary of the Doi presentation. In the Doi representation, annihilation, \hat{x} , and creation, \hat{x}^\dagger , operators are utilized to represent a removal of a particle X and an addition of a particle X respectively. Our system contains two species of particles, A and B, such that for each species there is a pair of annihilation and creation operators (\hat{a} , \hat{a}^\dagger ; \hat{b} , \hat{b}^\dagger). Furthermore, each lattice site, i , will have an associated creation and annihilation operators for each particle, \hat{a}_i , \hat{a}_i^\dagger ; \hat{b}_i , \hat{b}_i^\dagger to increase or decrease the number of particles at a site by, respectively.

Furthermore, in the Doi representation the annihilation and creation operators are similar to quantum mechanical bosonic operators (Ref. [21]) and follows the following

commutation relations ($[A, B] = AB - BA$):

$$[\hat{x}_i, \hat{x}_j^\dagger] = \delta_{ij}, \quad [\hat{x}_i, \hat{x}_j] = [\hat{x}_i^\dagger, \hat{x}_j^\dagger] = 0. \quad (3.1)$$

Additionally, the creation and annihilation operators at the same or different site of different species commute with each other ($[A, B] = 0$).

In the Doi representation a configuration is defined as the following state:

$$|\mathbf{n}\rangle = |n_{A1}, n_{B1}, \dots, n_{Ai}, n_{Bi}, \dots, n_{AL}, n_{BL}\rangle, \quad (3.2)$$

adapting our original notation to Dirac's bra-ket notation [21].

To exemplify the Doi representation operators, we will perform operations on a single lattice site with n X particles in state $|n\rangle$. First, we can define the ground state as $|0\rangle$, where there are zero particles at the site

$$\hat{x}|0\rangle = 0|0\rangle = 0. \quad (3.3)$$

The annihilation operator destroys the ground state. On the other hand, the creation operator has the following property on the ground state:

$$\hat{x}^\dagger|0\rangle = |1\rangle \quad (3.4)$$

which creates a singly occupied state, $|1\rangle$, by increasing the occupation number on the site. We can create the n particle state $|n\rangle$ by applying our creation operator n times on the ground state.

Furthermore, we can increase the occupation number by applying the creation operator onto the $|n\rangle$ state.

$$(\hat{x}^\dagger)^n|0\rangle = |n\rangle, \quad \hat{x}^\dagger|n\rangle = \hat{x}^\dagger(\hat{x}^\dagger)^n|0\rangle = (\hat{x}^\dagger)^{n+1}|0\rangle = |n+1\rangle. \quad (3.5)$$

This defines our creation operator, which differs from the quantum mechanical definition by a normalization constant. The annihilation operator has a unique property with the ground state as it destroys the state. Moreover, the annihilation operator is defined as follows:

$$\hat{x}|n\rangle = n|n-1\rangle, \quad (3.6)$$

decreasing the occupation number by one and producing a constant due to the operator relation. With this general framework introduced, we now proceed to develop the Doi representation for chemical reaction networks. All that follows consists of new formalism that we have developed.

Using the creation operator in conjunction with the annihilation operator creates the number operator, \hat{n} .

$$\hat{n} |n\rangle = \hat{x}^\dagger \hat{x} |n\rangle = \hat{x}^\dagger n |n-1\rangle = n \hat{x}^\dagger |n-1\rangle = n |n\rangle \quad (3.7)$$

The number operator leaves the state unchanged and produces a constant coefficient of n , the occupation number at the site. These operators and states define what is known as Fock space.

3.2 Liouvillian

The purpose of the Fock space is to encode all information of the system at a given time into a single state, $|\psi(t)\rangle$, defined by

$$|\psi(t)\rangle = \sum_{\mathbf{n}} P(\mathbf{n}, t) |\mathbf{n}\rangle \quad \text{with} \quad |\mathbf{n}\rangle = \prod_X \prod_{i=1}^L (x_i^\dagger)^{n_{xi}(\mathbf{n})} |\mathbf{0}\rangle. \quad (3.8)$$

where $|\mathbf{0}\rangle$ is the complete ground state for all lattice sites in our system. The single state, $|\psi(t)\rangle$, contains all the probabilities of any site containing any number of particles at a given time. An important distinction between the quantum mechanics representation and our Doi classical representation is that the probability density, $P(\mathbf{n}, t)$, is linear in the Doi state and not in the quantum mechanical state.

In the Doi representation, we can evolve our system by reexpressing our master equation as the time evolution Liouvillian operator, \hat{L} ,

$$\frac{d}{dt} |\psi(t)\rangle = \hat{L}(t) |\psi(t)\rangle, \quad (3.9)$$

where the Liouvillian \hat{L} depends on the dynamics of the system.

3.2.1 Liouvillian for System Dynamics

Similarly to the master equation dynamics, we can map each of the processes (hopping, chemical reaction, chemostat exchange) to the Doi representation and combine the Liouvillians into the Liouvillian of our system.

To derive the particle hopping Liouvillian operator, \hat{L}_H , that will evolve the single state, $|\psi(t)\rangle$, through nearest-neighbor particle hopping as mentioned in section 2.3.1 we start with Eq. 3.9 and plug in the corresponding master equation, Eq. 2.21:

$$\begin{aligned} \frac{d}{dt} |\psi(t)\rangle &= \frac{d}{dt} \sum_{\mathbf{n}} P(\mathbf{n}, t) |\mathbf{n}\rangle & (3.10) \\ &= \sum_{n_1, \dots, n_L=0}^{\infty} \sum_{X=A,B} \Gamma_X \sum_i \left[(n_{X(i+1)} + 1) e^{U_{i+1}^X} P(\dots, n_{Xi} - 1, n_{X(i+1)} + 1, \dots, t) \right. \\ &\quad \left. - n_{Xi} e^{U_i^X} P(\mathbf{n}, t) + (n_{Xi} + 1) e^{U_i^X} P(\dots, n_{Xi} + 1, n_{X(i+1)} - 1, \dots, t) \right. \\ &\quad \left. - n_{X(i+1)} e^{U_{i+1}^X} P(\mathbf{n}, t) \right] |\mathbf{n}\rangle & (3.11) \end{aligned}$$

where the sums over all possible configurations transforms into the sum over all possible numbers of particles at each lattice site.

The goal of this derivation is to get some operator, \hat{L}_H , acting on the single state, $|\psi(t)\rangle$. So we must recover the single state in each term of Eq. 3.11 to separately define the Liouvillian.

To simplify expression 3.11, we will look at one type of particle hopping between lattice site i and $i + 1$. Furthermore, we will break down the expression into its four terms (two gain, two loss) and re-express each in the Doi representation.

Examining the first loss terms, we can see that it is produced by the application of the number operator on the particular site, \hat{n}_i

$$\sum_{n_{X1}, \dots, n_{XL}}^{\infty} (n_{Xi}) e^{U_i^X} P(\mathbf{n}, t) |\mathbf{n}\rangle = \sum_{n_{X1}, \dots, n_{XL}}^{\infty} (\hat{x}_i^\dagger \hat{x}_i) e^{U_i^X} P(\mathbf{n}, t) |\mathbf{n}\rangle = (\hat{x}_i^\dagger \hat{x}_i) e^{U_i^X} |\psi(t)\rangle. \quad (3.12)$$

Similarly, the second loss term can be expressed as:

$$\sum_{n_{X1}, \dots, n_{XL}}^{\infty} (n_{X(i+1)}) e^{U_{i+1}^X} P(\mathbf{n}, t) |\mathbf{n}\rangle = (\hat{x}_{i+1}^\dagger \hat{x}_{i+1}) e^{U_{i+1}^X} |\psi(t)\rangle \quad (3.13)$$

Conversely, the first gain term is constructed as follows:

$$\begin{aligned} & \sum_{n_{X1}, \dots, n_{XL}}^{\infty} (n_{X(i+1)} + 1) e^{U_{i+1}^X} P(\dots, n_{X_i} - 1, n_{X(i+1)} + 1, \dots, t) |\mathbf{n}\rangle \\ &= \sum_{n_{X1}, \dots, n_{XL}}^{\infty} (\hat{x}_i^\dagger \hat{x}_{i+1}) e^{U_{i+1}^X} P(\dots, n_i - 1, n_{i+1} + 1, \dots, t) |\dots, n_i - 1, n_{i+1} + 1, \dots\rangle. \end{aligned} \quad (3.14)$$

We apply an operator that is similar to the number operator ($\hat{n}_i = \hat{x}_i^\dagger \hat{x}_i$) except it does not have the same site for both operators ($\hat{x}_i^\dagger \hat{x}_{i+1}$) to obtain the necessary coefficient. To recover the general state, we shift the sum $n_{X_i} \rightarrow n_{X_i} - 1$ and $n_{X(i+1)} \rightarrow n_{X(i+1)} + 1$

$$\sum_{n_{X1}, n_{X_i=1}, n_{X(i+1)=-1}, n_{XL}} (\hat{x}_i^\dagger \hat{x}_{i+1}) e^{U_{i+1}^X} P(\mathbf{n}, t) |\mathbf{n}\rangle. \quad (3.16)$$

Because the $n_{X(i+1)} = -1$ state does not exist, we may shift the lower limit at lattice $i + 1$ to zero. Likewise, the $n_i = 0$ state contributes zero to the sum, so we may add it to the sum without affecting it, resulting in:

$$\sum_{n_{X1}, \dots, n_{XL}} (\hat{x}_i^\dagger \hat{x}_{i+1}) e^{U_{i+1}^X} P(\mathbf{n}, t) |\mathbf{n}\rangle = (\hat{x}_i^\dagger \hat{x}_{i+1}) e^{U_{i+1}^X} |\psi(t)\rangle. \quad (3.17)$$

The right side of Eq. 3.17 is our first gain term in the Doi representation. Similarly, the second gain term can be obtained by swapping the operator site indices with its neighbor.

$$\sum_{n_{X1}, \dots, n_{XL}}^{\infty} (n_{X_i} + 1) e^{U_i^X} P(\dots, n_{X_i} + 1, n_{X(i+1)} - 1, \dots, t) |\mathbf{n}\rangle = (\hat{x}_{i+1}^\dagger \hat{x}_i) e^{U_i^X} |\psi(t)\rangle. \quad (3.18)$$

We can now re-express Eq. 3.11:

$$\frac{d}{dt} |\psi(t)\rangle = \sum_{X=A,B} -\Gamma_X \sum_i [\hat{x}_i^\dagger \hat{x}_{i+1} e^{U_{i+1}^X} - \hat{x}_i^\dagger \hat{x}_i e^{U_i^X} + \hat{x}_{i+1}^\dagger \hat{x}_i e^{U_i^X} - \hat{x}_i^\dagger \hat{x}_{i+1} e^{U_{i+1}^X}] |\psi(t)\rangle \quad (3.19)$$

which, from Eq. 3.9 suggests that our hopping Liouvillian is

$$\hat{L}_H = \sum_{X=A,B} -\Gamma_X \sum_i [\hat{x}_i^\dagger \hat{x}_{i+1} e^{U_{i+1}^X} - \hat{x}_i^\dagger \hat{x}_i e^{U_i^X} + \hat{x}_{i+1}^\dagger \hat{x}_i e^{U_i^X} - \hat{x}_i^\dagger \hat{x}_{i+1} e^{U_{i+1}^X}] \quad (3.20)$$

$$= \sum_{X=A,B} -\Gamma_X \sum_i [(\hat{x}_{i+1}^\dagger - \hat{x}_i^\dagger)(e^{U_{i+1}^X} \hat{x}_{i+1} - e^{U_i^X} \hat{x}_i)] \quad (3.21)$$

We write the Liouvillian as in Eq. 3.21 as all parts of the Liouvillian in our system will share this form as each process produced similar gain and loss terms in their respective master equation.

We can take the same steps to derive the hopping Liouvillian to derive the $A \leftrightarrow B$ reaction and chemostat exchange Liouvillian.

Instead of forward and backward hopping dynamics with a neighboring site $i + 1$, during $A \leftrightarrow B$ reactions, the particles undergo forward, $A \rightarrow B$, and reverse, $A \leftarrow B$, reactions in the same site, i . Thus the $A \leftrightarrow B$ Liouvillian has the following form:

$$\hat{L}_{A \leftrightarrow B} = \Lambda \sum_i [(\hat{b}_i^\dagger - \hat{a}_i^\dagger)(e^{U_i^B - \mu_B} \hat{b}_i - e^{U_i^A - \mu_A} \hat{a}_i)] \quad (3.22)$$

and the chemostat exchange involves a particle entering and leaving the system at a site i giving the chemostat Liouvillian as:

$$\hat{L}_{\text{Chemostat}} = \sum_X \lambda_X \sum_i [(\hat{x}_i^\dagger - 1)(e^{U_i^X - \mu_X} \hat{x}_i - 1)]. \quad (3.23)$$

As mentioned at the beginning of the Liouvillian section, once we are able to write the respective Liouvillian for each process, we can sum the Liouvillians to create the Liouvillian, \hat{L} , of our system:

$$\hat{L} = \hat{L}_H + \hat{L}_{A \leftrightarrow B} + \hat{L}_{\text{Chemostat}} \quad (3.24)$$

3.3 Averages and the Projection State

To produce the Jarzynski equality and similar work relations, we need to be able to average quantities in the Doi representation. The average of a quantity at time t is given by

$$\langle A(t) \rangle = \sum_{\mathbf{n}} A(\mathbf{n}) P(\mathbf{n}, t) = \langle \mathcal{P} | \hat{A} | \psi(t) \rangle \quad (3.25)$$

where $A(\mathbf{n})$ is the function of occupation numbers that defines the quantity, and \hat{A} is the operator representation of $A(\mathbf{n})$. This average is linear in terms of the probability as the $|\psi(t)\rangle$ is linear in probability, thus we require a projection state, $\langle \mathcal{P} |$, defined as

$$\langle \mathcal{P} | \hat{x}_i^\dagger = \langle \mathcal{P} | \quad (3.26)$$

That is, $\langle \mathcal{P} |$ is a left eigenstate of all creation operators, with eigenvalue unity. This allows us to act any power of \hat{a}_i^\dagger to the left of the projection state and receive the same state back. It is straightforward to show

$$\langle \mathcal{P} | = \langle 0 | \prod_X e^{\sum_{i=1}^L \hat{x}_i}. \quad (3.27)$$

We can split the projection state up into sectors of definite number projection operators by Taylor expanding the exponential and defining the total number of particles of a species as N_X , giving

$$\langle \mathcal{P} | = \sum_{N_X=0}^{\infty} \prod_X \langle N_X | \quad \text{where} \quad \langle N_X | = \langle 0 | \frac{(\sum_{i=1}^L \hat{x}_i)^{N_X}}{N_X!}. \quad (3.28)$$

Furthermore, it can be shown through a multinomial expansion, the Hermetian conjugate is

$$|N_X\rangle = \frac{(\sum_{i=1}^L \hat{x}_i^\dagger)^{N_X}}{N_X!} |0\rangle = \frac{1}{N_X!} \sum_{\mathbf{n}} \frac{N_X!}{\prod_i n_{iX}} \left(\prod_i (x_i^\dagger)^{n_i} |0\rangle \right) \quad (3.29)$$

$$= \frac{1}{N_X!} \sum_{\mathbf{n}} \Omega_X(\mathbf{n}_X) |\mathbf{n}_X\rangle. \quad (3.30)$$

Thus the expectation value Eq. (3.25) works equally well with $\langle N_X |$ in place of $\langle \mathcal{P} |$ if the state $|\psi(t)\rangle$ is a state of N particles and only contains one type of particles. Our system contains more than one species of particles and allows particles to enter and leave so we will use the full projection state, $\langle \mathcal{P} |$. The projection state contains all possible states for all possible number and types of particles and therefore the overlap between the projection state and any state $|\psi(t)\rangle$ goes to one,

$$\langle \mathcal{P} | \psi(t)\rangle = 1. \quad (3.31)$$

Note then that probability conservation requires

$$0 = \frac{d}{dt} \langle 1 \rangle = \langle \mathcal{P} | \hat{L} | \psi(t)\rangle \quad (3.32)$$

so all Liouvillians must obey

$$\langle \mathcal{P} | \hat{L} = 0. \quad (3.33)$$

3.4 Gibbs State

The Jarzynski equality requires that our system is initially in equilibrium and thus we must redefine our Gibbs distribution, Eq. 2.6, to the Gibbs state, $|\psi_G\rangle$, in the Doi representation.

$$|\psi_G\rangle = \sum_{\mathbf{n}} P_{\text{Gibbs}}(\mathbf{n}) |\mathbf{n}\rangle = \sum_{N_X} \sum_{\mathbf{n}} \frac{\Omega(\mathbf{n})}{\mathcal{Z} \prod_X N_X!} e^{-E(\mathbf{n}) + \sum_X \mu_X N_X(\mathbf{n})} |\mathbf{n}\rangle. \quad (3.34)$$

Expanding the general state $|\mathbf{n}\rangle$ and plugging in the configuration energy Eq. 2.7 gives:

$$\sum_{N_X=0}^{\infty} \sum_{\mathbf{n}} \prod_X \frac{\Omega(\mathbf{n})}{\mathcal{Z} N_X!} e^{\sum_i U_i^X n_{X_i} + \mu_X N_X(\mathbf{n})} = \sum_{N_X=0}^{\infty} \sum_{\mathbf{n}} \prod_X \frac{\Omega(\mathbf{n})}{\mathcal{Z} N_X!} e^{\mu_X N_X} \prod_i^L (e^{-U_i^X} x_i^\dagger)^{n_{X_i}} |0\rangle. \quad (3.35)$$

Using the relation in Eq. 3.29, the Gibbs state simplifies to:

$$\sum_{N_X} \prod_X \frac{e^{\mu_X N_X}}{\mathcal{Z} N_X!} \left(\sum_i^L e^{-U_i^X} x_i^\dagger \right)^{N_X} |0\rangle = \sum_{N_X} \prod_X \frac{1}{\mathcal{Z} N_X!} \left(\sum_i^L e^{-U_i^X + \mu_X} x_i^\dagger \right)^{N_X} |0\rangle \quad (3.36)$$

$$= \prod_X \frac{1}{\mathcal{Z}} e^{\sum_i (-U_i^X + \mu_X) x_i^\dagger} |0\rangle = |\psi_G\rangle. \quad (3.37)$$

The Gibbs state can be expressed in terms of the projection state as from Eq. 3.34 :

$$\sum_{N_X=0}^{\infty} \sum_{\mathbf{n}} \prod_X \frac{\Omega(\mathbf{n})}{\mathcal{Z} N_X!} e^{\sum_i U_i^X n_{X_i} + \mu_X N_X(\mathbf{n})} |\mathbf{n}\rangle = \frac{1}{\mathcal{Z}} e^{\sum_X (\sum_i U_i^X \hat{n}_{X_i} + \mu_X \hat{N}_X)} |\mathcal{P}\rangle, \quad (3.38)$$

where we replace n_{X_i} for the site number operator, \hat{n}_{X_i} and we introduce the total number operator, ($\hat{N}_X = \sum_i \hat{n}_{X_i}$). This symmetry between the equilibrium state and the projection state plays a crucial role when producing the Jarzynski relation.

3.5 Averaging Non-Equilibrium States

Now that we have our system time dependent Liouvillian and Doi representation averaging formulism, we can push our system from an initial equilibrium Gibbs state, $|\psi_G\rangle$,

to a non-equilibrium state at time t with our Liouvillian and average a quantity, \hat{A} , in the non-equilibrium state. Because our Liouvillian is time dependent, we cannot use the analytical solution to Eq. 3.9 to evolve our system from an initial state, but rather we must use a solution that does not require the Liouvillian to be constant as follows:

$$\lim_{\Delta t \rightarrow 0} \frac{|\psi(t + \Delta t)\rangle - |\psi(t)\rangle}{\Delta t} = \hat{L}_t |\psi(t)\rangle \quad (3.39)$$

suggesting, in the limit Δt goes to zero:

$$|\psi(t + \Delta t)\rangle = (1 + \hat{L}_t \Delta t) |\psi(t)\rangle + O(\Delta t^2). \quad (3.40)$$

Furthermore, to evolve our system through our specified dynamics from some time t_1 to another time t_2 , we must continuously multiply the system's state, $|\psi\rangle$, by $(1 + \hat{L}_t)\Delta t$ at the instantaneous Liouvillian. Therefore we are able to create a non-equilibrium state at time t_2 with origins in the Gibbs state at t_1 :

$$|\psi(t_2)\rangle = \lim_{\Delta t \rightarrow 0} (1 + \hat{L}_{t_2} \Delta t) \dots (1 + \hat{L}_{t_1 + \Delta t} \Delta t) (1 + \hat{L}_{t_1} \Delta t) |\psi_G(t_1)\rangle. \quad (3.41)$$

3.6 Jarzynski Average and Hamiltonian Operator

The Jarzynski relation (Eq. 1.3), as mentioned in the introduction, relates the average work done on to the system to the change in grand potential. Furthermore, the Jarzynski relation applies to small and far from equilibrium systems. In our developed formalism, we have set the total number of particles to be arbitrary, meaning our system can be of any size. Additionally, in the Doi representation, we can evolve our system, in increments of Δt , to a non-equilibrium state by applying continuously applying the instantaneous time stepping factor $(1 + \hat{L}_t)\Delta t$ as seen in Eq. 3.41.

We are interested in taking the Jarzynski average of our system in a non-equilibrium state so we must apply the averaging function in Eq. 3.25. To average the work, we must slightly modify the Doi-Peliti averaging procedure. Since the work is a continuous process for our system, we cannot calculate the value of a work function at a final time as the work depends on how the system evolves and at the final time. Hence, we must average the work while we evolve the system forward in time.

We define the work done on the system as the amount of work done between t and Δt :

$$W = \Delta W(t) = W(t + \Delta t) - W(t). \quad (3.42)$$

As mentioned in Eq. 2.33, work is applied to the system by varying the site potential, $U_i^X(t)$ and is related to the number of particles at the site, n_{Xi} . Thus the rate of doing work is:

$$\frac{dW}{dt} = \sum_X \sum_i \frac{dU_i^X(t)}{dt} n_{Xi}, \quad (3.43)$$

which gives the amount of work done as:

$$\Rightarrow \Delta W = \sum_X \sum_i \left(\frac{dU_i^X(t)}{dt} \Delta t \right) n_{Xi} \quad (3.44)$$

$$= \sum_X \sum_i (U_i^X(t + \Delta t) n_{Xi} - U_i^X(t) n_{Xi}) \quad (3.45)$$

$$= E(\mathbf{n}, t + \Delta t) - E(\mathbf{n}, t). \quad (3.46)$$

In the Doi representation we will replace the energy function of the configuration, $E(\mathbf{n}, t)$, with the Hamiltonian energy operator, \hat{H}_t :

$$E(\mathbf{n}, t) |\mathbf{n}\rangle = \sum_X \sum_i U_i^X(t) n_{Xi} |\mathbf{n}\rangle = \hat{H}_t |\mathbf{n}\rangle. \quad (3.47)$$

The Hamiltonian energy operator is hermitian such that if it acts on a state to the left or right of it, it will return that configuration's energy.

Therefore, the Jarzynski average, when we average the work while the system evolves, takes the following form:

$$\begin{aligned} \langle e^{-W} \rangle &= \langle \mathcal{P} | e^{-\hat{H}_{t_2} + \hat{H}_{t_2 - \Delta t}} (1 + \hat{L}_{t_2 - \Delta t} \Delta t) e^{-\hat{H}_{t_2 - \Delta t} + \hat{H}_{t_2 - 2\Delta t}} (1 + \hat{L}_{t_2 - 2\Delta t} \Delta t) \dots \\ &\quad \dots e^{-\hat{H}_{t_1 + \Delta t} + \hat{H}_{t_1}} (1 + \hat{L}_{t_1} \Delta t) | \psi_G \rangle. \end{aligned} \quad (3.48)$$

We have defined the Jarzynski average in the Doi representation, but it is not clear how the Jarzynski Relation arises. In the next section, we will look into general properties of detailed balance Liouvillians, which will make the derivation of the Jarzynski relation more apparent.

3.7 General Detailed Balance Liouvillian

In the first section of this chapter, we mapped the Liouvillians of our system from master equations that are governed by detailed balance. Thus, the Liouvillians generated must also follow detailed balance. We will develop the most general Liouvillian

associated with a detailed balance processes and reveal some underlying restrictions detailed balance sets on the Liouvillian.

Consider starting at state $|\mathbf{q}\rangle$ at time $t = 0$. Then, according to the master equation 2.8, the state a short time δt later is:

$$P(\mathbf{n}, \delta t) = w_{\mathbf{q} \rightarrow \mathbf{n}} \delta t P(\mathbf{q}, 0) \quad (3.49)$$

where $P(\mathbf{q}, 0)$ is equal to 1 as we have defined in the beginning and $\mathbf{q} \neq \mathbf{n}$. We can also define the probability of being in $|\mathbf{q}\rangle$ at δt from probability conservation:

$$P(\mathbf{q}, \delta t) = 1 - \sum_{\mathbf{n}' \neq \mathbf{q}} w_{\mathbf{q} \rightarrow \mathbf{n}'} \delta t. \quad (3.50)$$

Additionally, we can use our Doi representation time stepping (Eq. 3.40), to define the state at time δt

$$|\psi(\delta t)\rangle = (1 + \hat{L} \delta t) |\mathbf{q}\rangle. \quad (3.51)$$

Expanding our states and separating the $|\mathbf{q}\rangle$ state from the sum results in:

$$\sum_{\mathbf{n}} P(\mathbf{n}, \delta t) |\mathbf{n}\rangle = \sum_{\mathbf{n} \neq \mathbf{q}} P(\mathbf{n}, \delta t) |\mathbf{n}\rangle + P(\mathbf{q}, \delta t) |\mathbf{q}\rangle = |\mathbf{q}\rangle + \hat{L} \delta t |\mathbf{q}\rangle. \quad (3.52)$$

We then replace the probabilities with rate constant equations in Eq. 3.49 and Eq. 3.51

$$\sum_{\mathbf{n} \neq \mathbf{q}} w_{\mathbf{q} \rightarrow \mathbf{n}} \delta t |\mathbf{n}\rangle + (1 - \sum_{\mathbf{n}' \neq \mathbf{q}} w_{\mathbf{q} \rightarrow \mathbf{n}'} \delta t) |\mathbf{q}\rangle = |\mathbf{q}\rangle + \hat{L} \delta t |\mathbf{q}\rangle \quad (3.53)$$

$$\Rightarrow \sum_{\mathbf{n} \neq \mathbf{q}} w_{\mathbf{q} \rightarrow \mathbf{n}} |\mathbf{n}\rangle - \sum_{\mathbf{n}' \neq \mathbf{q}} w_{\mathbf{q} \rightarrow \mathbf{n}'} |\mathbf{q}\rangle = \hat{L} |\mathbf{q}\rangle. \quad (3.54)$$

We then take the overlap Eq. 3.54 with a state $|\mathbf{m}\rangle$ such that $|\mathbf{m}\rangle \neq |\mathbf{q}\rangle$:

$$\sum_{\mathbf{n} \neq \mathbf{q}} w_{\mathbf{q} \rightarrow \mathbf{n}} \langle \mathbf{m} | \mathbf{n} \rangle - \sum_{\mathbf{n}' \neq \mathbf{q}} w_{\mathbf{q} \rightarrow \mathbf{n}'} \langle \mathbf{m} | \mathbf{q} \rangle = \langle \mathbf{m} | \hat{L} | \mathbf{q} \rangle. \quad (3.55)$$

Here we introduce the configuration overlap relations such that configuration states are orthogonal to one another:

$$\langle \mathbf{m} | \mathbf{n} \rangle = \delta_{nm} \prod_i n_i! = \delta_{nm} \frac{N!}{\Omega(\mathbf{n})}. \quad (3.56)$$

This gives us:

$$w_{\mathbf{q} \rightarrow \mathbf{m}} \langle \mathbf{m} | \mathbf{m} \rangle = w_{\mathbf{q} \rightarrow \mathbf{m}} \prod_X \prod_i m_{Xi}! = \langle \mathbf{m} | \hat{L} | \mathbf{q} \rangle. \quad (3.57)$$

It can be similarly shown that:

$$\langle \mathbf{q} | \hat{L} | \mathbf{m} \rangle = w_{\mathbf{q} \rightarrow \mathbf{m}} \prod_X \prod_i q_{Xi}!, \quad (3.58)$$

where q_{Xi} is the particle site occupation number for configuration \mathbf{q} .

We can take the ratio of Eq. 3.57 and 3.58:

$$\frac{\langle \mathbf{m} | \hat{L} | \mathbf{q} \rangle}{\langle \mathbf{q} | \hat{L} | \mathbf{m} \rangle} = \frac{w_{\mathbf{q} \rightarrow \mathbf{m}} \prod_X \prod_i m_{Xi}!}{w_{\mathbf{q} \rightarrow \mathbf{m}} \prod_X \prod_i q_{Xi}!}. \quad (3.59)$$

Recognizing the ratio of rate constants as the detailed balance condition (Eq. 2.12), it follows that if our system follows detailed balance, Eq. 3.59 simplifies to:

$$\frac{\langle \mathbf{m} | \hat{L} | \mathbf{q} \rangle}{\langle \mathbf{q} | \hat{L} | \mathbf{m} \rangle} e^{-(\Delta E - \sum_X \Delta(N_X \mu_X))} = e^{-E(\mathbf{m}) + E(\mathbf{q}) + (\sum_X (\mu_X (N_X(\mathbf{m}) - N_X(\mathbf{q})))} \quad (3.60)$$

where we have assumed μ_X to be constant for all species of particles.

Thus,

$$\langle \mathbf{m} | \hat{L} | \mathbf{q} \rangle = \langle \mathbf{q} | \hat{L} | \mathbf{m} \rangle e^{-E(\mathbf{m}) + E(\mathbf{q}) + (\sum_X (\mu_X (N_X(\mathbf{m}) - N_X(\mathbf{q})))} \quad (3.61)$$

$$= \langle \mathbf{q} | e^{\hat{H} - \sum_X \mu_X \hat{N}_X} \hat{L} e^{-\hat{H} + \sum_X \mu_X \hat{N}_X} | \mathbf{m} \rangle \quad (3.62)$$

In the last line we have swapped the energy and total number of particles for the Hamiltonian operator and total number operator. Similar to the Hamiltonian the total number operator is also hermitian. We have also moved the exponential term so the operators are acting on the appropriate states.

Since Eq. 3.62 must hold for any \mathbf{m} and \mathbf{q} , we can define the Liouvillian's hermitian conjugate in terms of the Liouvillian itself as:

$$\hat{L}^\dagger = e^{\hat{H} - \sum_X \mu_X \hat{N}_X} \hat{L} e^{-\hat{H} + \sum_X \mu_X \hat{N}_X}. \quad (3.63)$$

This implies

$$(\hat{L} e^{-\hat{H} + \sum_X \mu_X \hat{N}_X})^\dagger = \hat{L} e^{-\hat{H} + \sum_X \mu_X \hat{N}_X} \quad (3.64)$$

so $\hat{Q} \equiv \hat{L} e^{-\hat{H} + \sum_X \mu_X \hat{N}_X}$ is a hermitian operator. Thus we can write

$$\hat{L} = \hat{Q} e^{\hat{H} - \sum_X \mu_X \hat{N}_X} \quad (3.65)$$

as the general form of a Liouvillian that will satisfy detailed balance, where \hat{Q} is any hermitian operator that annihilates the projection state (recalling Eq. 3.33)

The Liouvillians we derived in Eq. 3.21, 3.22, and 3.23 all share the same form, thus if we prove that one of the Liouvillians satisfy the detailed balance condition 3.65, then all the Liouvillians separately satisfy detailed balance.

Starting with Eq. 3.21 and using the Baker-Campbell-Hausdorff relations [22]

$$e^{-\hat{H}} \hat{x}_i = e^{U_i^X} \hat{x}_i e^{-\hat{H}} \quad \text{and} \quad e^{-\hat{H}} \hat{x}_i^\dagger = \hat{x}_i^\dagger e^{-U_i^X} e^{-\hat{H}}. \quad (3.66)$$

We can rewrite the hopping Liouvillian as:

$$\hat{L}_H = - \sum_{X=A,B} \Gamma_X \sum_i [(\hat{x}_{i+1}^\dagger - \hat{x}_i^\dagger)(e^{U_{i+1}^X} \hat{x}_{i+1} - e^{U_i^X} \hat{x}_i)] \quad (3.67)$$

$$= - \sum_{X=A,B} \Gamma_X \sum_i [(\hat{x}_{i+1}^\dagger - \hat{x}_i^\dagger) e^{-\hat{H}} (\hat{x}_{i+1} - \hat{x}_i) e^{\hat{H}}] \quad (3.68)$$

Then we can multiply the Liouvillian by a factor of $1 = e^{\sum_X \mu_X \hat{N}_X} e^{-\sum_X \mu_X \hat{N}_X}$. The total number operator commutes with its respective species' creation and annihilation operator so we can place each term wherever we want to expression 3.68:

$$\hat{L}_H = - \underbrace{\sum_{X=A,B} \Gamma_X \sum_i (\hat{x}_{i+1}^\dagger - \hat{x}_i^\dagger) e^{-\hat{H} + \sum_{X'} \mu_{X'} \hat{N}_{X'}} (\hat{x}_{i+1} - \hat{x}_i) e^{\hat{H} - \sum_{X''} \mu_{X''} \hat{N}_{X''}}}_{\hat{Q}} \quad (3.69)$$

where the term in the underbrace is hermitian, and thus our hopping Liouvillian and the Eq. 3.22 and 3.23 satisfy detailed balance.

Each Liouvillian satisfies detailed balance, but we must be careful in the case where we superimpose Liouvillians, as in our system in Eq. 3.24. The Liouvillians must satisfy the same detailed balance factors; for instance, if we allowed our chemical reactions to be governed by a different chemical potential, μ , than the chemostat exchange and A \leftrightarrow B Liouvillians would not follow the same detailed balance condition and superimposing these dynamics would break detailed balance in our system.

The Liouvillians defined in Eq. 3.24 all share the same detailed balance condition, so our whole system follows detailed balance.

3.8 Jarzynski Relation in Doi Representation

Now that we have generalized conditions for detailed balance Liouvillians, we can revisit our Jarzynski average in Eq. 3.48 and prove the Jarzynski Relation. We can regroup the terms as follows:

$$\begin{aligned} \langle e^{-W} \rangle &= \langle \mathcal{P} | e^{-\hat{H}_{t_2}} \left[e^{\hat{H}_{t_2-\Delta t}} (1 + \hat{L}_{t_2-\Delta t} \Delta t) e^{-\hat{H}_{t_2-\Delta t}} \right] \\ &\quad \dots \left[e^{\hat{H}_{t_1+\Delta t}} (1 + \hat{L}_{t_1+\Delta t} \Delta t) e^{-\hat{H}_{t_1+\Delta t}} \right] e^{\hat{H}_{t_1}} (1 + \hat{L}_{t_1} \Delta t) | \psi_G \rangle. \end{aligned} \quad (3.70)$$

Similar to when proving the hopping Liouvillian met the detailed balance condition, we can multiply each bracketed term by $1 = e^{\sum_X \mu_X \hat{N}_X} e^{-\sum_X \mu_X \hat{N}_X}$, which gives:

$$\begin{aligned} \langle e^{-W} \rangle &= \langle \mathcal{P} | e^{-\hat{H}_{t_2} + \sum_X \mu_X \hat{N}_X} \left[e^{\hat{H}_{t_2-\Delta t} - \sum_X \mu_X \hat{N}_X} (1 + \hat{L}_{t_2-\Delta t} \Delta t) e^{-\hat{H}_{t_2-\Delta t} + \sum_X \mu_X \hat{N}_X} \right] \\ &\quad \dots \left[e^{\hat{H}_{t_1+\Delta t} - \sum_X \mu_X \hat{N}_X} (1 + \hat{L}_{t_1+\Delta t} \Delta t) e^{-\hat{H}_{t_1+\Delta t} + \sum_X \mu_X \hat{N}_X} \right] \\ &\quad e^{\hat{H}_{t_1} - \sum_X \mu_X \hat{N}_X} (1 + \hat{L}_{t_1} \Delta t) | \psi_G \rangle, \end{aligned} \quad (3.71)$$

resulting in the bracketed terms meeting our Hermitian conjugate Liouvillian condition:

$$e^{\hat{H}_t - \sum_X \mu_X \hat{N}_X} (1 + \hat{L}_t \Delta t) e^{-\hat{H}_t + \sum_X \mu_X \hat{N}_X} = 1 + \hat{L}_t^\dagger \Delta t \quad (3.72)$$

We rewrite our Jarzynski average:

$$\langle e^{-W} \rangle = \langle \mathcal{P} | e^{-\hat{H}_{t_2} + \sum_X \mu_X \hat{N}_X} (1 + \hat{L}_{t_2-\Delta t}^\dagger \Delta t) \dots (1 + \hat{L}_{t_1+\Delta t}^\dagger \Delta t) e^{\hat{H}_{t_1} - \sum_X \mu_X \hat{N}_X} | \psi_G(t_1) \rangle. \quad (3.73)$$

We can expand the Gibbs state and rewrite it in terms of the projection state as in Eq. 3.38 and with our Hamiltonian operator

$$| \psi_G \rangle = \frac{1}{\mathcal{Z}(t_1)} e^{-\hat{H}_{t_1} + \sum_X \mu_X \hat{N}_X} | \mathcal{P} \rangle. \quad (3.74)$$

The exponential terms cancel on the right and only the grand partition function and the projection state is left:

$$\langle e^{-W} \rangle = \frac{1}{\mathcal{Z}(t_1)} \langle \mathcal{P} | e^{-\hat{H}_{t_2} + \sum_X \mu_X \hat{N}_X} (1 + \hat{L}_{t_2-\Delta t}^\dagger \Delta t) \dots (1 + \hat{L}_{t_1+\Delta t}^\dagger \Delta t) | \mathcal{P} \rangle. \quad (3.75)$$

Furthermore, the projection state with its exponential term can be rewritten as a Gibbs state at time t_2 giving an additional Grand partition function at time t_2 :

$$\langle e^{-W} \rangle = \frac{\mathcal{Z}(t_2)}{\mathcal{Z}(t_1)} \langle \psi_G(t_2) | (1 + \hat{L}_{t_2-\Delta t}^\dagger \Delta t) \dots (1 + \hat{L}_{t_1+\Delta t}^\dagger \Delta t) | \mathcal{P} \rangle. \quad (3.76)$$

With the Hermitian conjugate of the Liouvillian, Eq. 3.76 is running from a Gibbs state at time t_2 to a nonequilibrium state at time t_1 . Our system is running in reverse and we have lost the averaging work term, meaning now we are averaging the quantity 1, which averages to 1.

Thus:

$$\langle e^{-W} \rangle = \frac{\mathcal{Z}(t_2)}{\mathcal{Z}(t_1)} \langle 1 \rangle = e^{-\Delta\Phi_G}. \quad (3.77)$$

We have recovered the Jarzynski Relation in the Doi representation for a non-equilibrium system of any size that follows detailed balance dynamics. This is our primary result.

Chapter 4

Peliti Field Theory

While we have so far considered particles hopping on a lattice, we can bring our system to the continuum limit by mapping the Doi representation to the Doi-Peliti field theory. Doi-Peliti field theory is a mathematical framework that can be used to describe classical particles and their dynamics. Most field theories involve phenomenology where they include terms that have been specifically created to satisfy an appropriate symmetry. Doi-Peliti field theory has the advantage that it properly maps classical particle behavior to a field theory without having to make ad hoc assumptions about the dynamics, similar to our development of the Liouvillian from fundamental master equations [10, 7, 8, 9].

4.1 Coherent States

The coherent states for species X and lattice site i are defined by

$$\langle \phi_{Xi} | = \langle 0 | e^{\bar{\phi}_{Xi} \hat{x}_i} e^{-|\phi_{Xi}|^2/2} \quad \text{and} \quad | \phi_{Xi} \rangle = e^{\phi_{Xi} \hat{x}_i^\dagger} e^{-|\phi_{Xi}|^2/2} | 0 \rangle \quad (4.1)$$

where ϕ_{Xi} is a complex number and $\bar{\phi}_{Xi}$ is its complex conjugate. The coherent states are left and right eigenstates of the creation, \hat{x}_i^\dagger and annihilation, \hat{x}_i , respectively. Explicitly,

$$\langle \phi_X | \hat{x}_i^\dagger = \langle \phi_{Xi} | \hat{x}_i^\dagger = \langle \phi_{Xi} | \bar{\phi}_{Xi} \quad \text{and} \quad \hat{x}_i | \phi_X \rangle = \hat{x}_i | \phi_{Xi} \rangle = \phi_{Xi} | \phi_{Xi} \rangle. \quad (4.2)$$

The states are normalized: $\langle \phi_{X_i} | \phi_{X_i} \rangle = 1$ and the coherent states at different lattice sites are orthogonal: $\langle \phi_{X_i} | \phi_{X(i+1)} \rangle = 0$. Also, the coherent states for different species are orthogonal: $\langle \phi_{A_i} | \phi_{B_i} \rangle = 0$.

Additionally, the overlap of two different coherent states for the same species and lattice site, for instance, coherent states at different times $|\phi_{X_i,t}\rangle$ and $\langle \phi_{X_i,t+\Delta t}|$ results in:

$$\langle \phi_{X_i,t+\Delta t} | \phi_{X_i,t} \rangle = \exp(\bar{\phi}_{X_i,t+\Delta t} \phi_{X_i,t}) \exp\left(-\frac{1}{2}|\phi_{X_i,t}|^2 - \frac{1}{2}|\phi_{X_i,t+\Delta t}|^2\right). \quad (4.3)$$

We map the Doi representation of the Jarzynski average Eq. 3.48 to a field theory by inserting a complete set of coherent states at each time slice for each particle and to all lattice sites using the identity:

$$\mathbf{1} = \int \prod_{i=1}^L \frac{d^2 \phi_{X_i}}{\pi} |\phi_X\rangle \langle \phi_X| \quad (4.4)$$

where $d^2 \phi_{X_i} = d(\text{Re} \phi_{X_i}) d(\text{Im} \phi_{X_i})$ and $|\phi_X\rangle$ is the system's coherent state containing the coherent state of each lattice site:

$$|\phi_X\rangle = |\phi_{X1}, \dots, \phi_{XL}\rangle. \quad (4.5)$$

4.2 Jarzynski Average with Coherent States

Every time slice has a different Liouvillian \hat{L}_t , and hence must have a different set of system coherent states $|\phi_{X,t}\rangle$ with that time. Thus we insert at each time slice

$$\mathbf{1} = \prod_X \int \prod_{\tau,i} \frac{d^2 \phi_{X_i}}{\pi} |\phi_{X,\tau}\rangle \langle \phi_{X,\tau}| = \prod_X \int \mathcal{D}\phi_{X,\tau} \mathcal{D}\bar{\phi}_{X,\tau} |\phi_{X,\tau}\rangle \langle \phi_{X,\tau}|, \quad (4.6)$$

where $\mathcal{D}\phi_{X,\tau} \mathcal{D}\bar{\phi}_{X,\tau} = \prod_{x,\tau} d^2 \phi_{X_i,\tau} / \pi$ and τ is the time index. This results in the following average:

$$\begin{aligned} \langle e^{-W} \rangle &= \mathcal{N}^{-1} \prod_X \int \prod_{\tau=t_1}^{t_2} \mathcal{D}\phi_{X,\tau} \mathcal{D}\bar{\phi}_{X,\tau} \langle \mathcal{P} | \phi_{X,t_2} \rangle \langle \phi_{X,t_2} | e^{-(\hat{H}_{t_2} - \hat{H}_{t_2 - \Delta t})} (1 + \hat{L}_{t_2 - \Delta t} \Delta t) | \phi_{X,t_2 - \Delta t} \rangle \\ &\quad \times \langle \phi_{X,t_2 - \Delta t} | e^{-(\hat{H}_{t_2 - \Delta t} - \hat{H}_{t_2 - 2\Delta t})} (1 + \hat{L}_{t_2 - 2\Delta t} \Delta t) \dots \\ &\quad \dots e^{-(\hat{H}_{t_1 + \Delta t} - \hat{H}_{t_1})} (1 + \hat{L}_{t_1} \Delta t) | \phi_{X,t_1} \rangle \langle \phi_{X,t_1} | \psi_G \rangle \end{aligned} \quad (4.7)$$

where \mathcal{N} is a normalization constant determined by ensuring the average $\langle 1 \rangle = 1$. We will write out the work term explicitly to simplify Eq. 4.7,

$$\lim_{\Delta t \rightarrow 0} e^{-(\hat{H}_{t+\Delta t} - \hat{H}_t)} \simeq e^{-\sum_X \sum_i \dot{U}_{i,t}^X \Delta t \hat{n}_{Xi}} \quad (4.8)$$

$$= 1 - \sum_X \sum_i \dot{U}_{i,t}^X \Delta t \hat{n}_{Xi} = 1 - \hat{W}_t \Delta t, \quad (4.9)$$

where we have introduced

$$\hat{W}_t = \sum_X \sum_i \dot{U}_{i,t}^X \hat{n}_{Xi}. \quad (4.10)$$

We rewrite Eq. 4.7 by grouping the work averages and Liouvillian into a product:

$$\begin{aligned} \langle e^{-W} \rangle &= \mathcal{N}^{-1} \prod_X \left[\int \mathcal{D}\phi_{X,t_1} \mathcal{D}\bar{\phi}_{X,t_1} \langle \mathcal{P} | \phi_{X,t_2} \rangle \langle \phi_{X,t_1} | \psi_G \rangle \dots \right. \\ &\times \left. \prod_{\tau=t_1+\Delta t}^{t_2} \left[\mathcal{D}\phi_{X,\tau} \mathcal{D}\bar{\phi}_{X,\tau} \langle \phi_{X,\tau} | \left(1 - \hat{W}_{\tau-\Delta t} \Delta t \right) \left(1 + \hat{L}_{\tau-\Delta t} \Delta t \right) | \phi_{X,\tau-\Delta t} \rangle \right] \right]. \end{aligned} \quad (4.11)$$

Ignoring higher order Δt terms we recover:

$$\begin{aligned} \langle e^{-W} \rangle &= \mathcal{N}^{-1} \prod_X \left[\int \mathcal{D}\phi_{X,t_1} \mathcal{D}\bar{\phi}_{X,t_1} \langle \mathcal{P} | \phi_{X,t_2} \rangle \langle \phi_{X,t_1} | \psi_G \rangle \dots \right. \\ &\times \left. \prod_{\tau=t_1+\Delta t}^{t_2} \left[\mathcal{D}\phi_{X,\tau} \mathcal{D}\bar{\phi}_{X,\tau} \langle \phi_{X,\tau} | \left(1 - \hat{W}_{\tau-\Delta t} \Delta t + \hat{L}_{\tau-\Delta t} \Delta t \right) | \phi_{X,\tau-\Delta t} \rangle \right] \right]. \end{aligned} \quad (4.12)$$

4.3 Temporal Continuum Limit

We can now bring our system into the temporal continuum limit. Consider the time slice in Eq. 4.12:

$$\langle \phi_{X,\tau} | \left(1 - \hat{W}_{\tau-\Delta t} \Delta t + \hat{L}_{\tau-\Delta t} \Delta t \right) | \phi_{X,\tau-\Delta t} \rangle. \quad (4.13)$$

Due to the coherent state on the left and right, we can replace our operators with their respective eigenvalues, thus our Liouvillians (Eq. 3.21, 3.22, 3.23) now take the

following form:

$$\hat{L}_H[\phi, \bar{\phi}] = \sum_{X=A,B} -\Gamma_X \sum_i (\bar{\phi}_{X(i+1),\tau} - \bar{\phi}_{Xi,\tau}) (e^{U_{i+1}^X} \phi_{X(i+1),\tau-\Delta t} - e^{U_i^X} \phi_{Xi,\tau-\Delta t}) \quad (4.14)$$

$$\hat{L}_{A \leftrightarrow B}[\phi, \bar{\phi}] = \Lambda \sum_i (\bar{\phi}_{Bi,\tau} - \bar{\phi}_{Ai,\tau}) (e^{U_i^B - \mu_B} \phi_{Bi,\tau-\Delta t} - e^{U_i^A - \mu_A} \phi_{Ai,\tau-\Delta t}) \quad (4.15)$$

$$\hat{L}_{\text{Chemostat}}[\phi, \bar{\phi}] = \sum_X \lambda_X \sum_i (\bar{\phi}_{Xi,\tau} - 1) (e^{U_i^X - \mu_X} \phi_{Xi,\tau-\Delta t} - 1). \quad (4.16)$$

Our Liouvillian, \hat{L} , is the sum of these three Liouvillians. Furthermore the work term takes the following form:

$$\hat{W}_{\tau-\Delta t} \Delta t = \sum_X \sum_i \left(\frac{dU_{i,\tau-\Delta t}^X}{dt} \Delta t \right) \hat{n}_{Xi} \Rightarrow \sum_X \sum_i \left(\frac{dU_{i,\tau-\Delta t}^X}{dt} \Delta t \right) \bar{\phi}_{Xi} \phi_{Xi} \quad (4.17)$$

where the number operator, $\hat{n} = \hat{x}_i^\dagger \hat{x}_i$ goes to $\bar{\phi}_{Xi,\tau} \phi_{Xi,\tau-\Delta t}$. We are now left with

$$\langle \phi_{X,\tau} | \phi_{X,\tau-\Delta t} \rangle (1 - \hat{W}_{\tau-\Delta t} \Delta t + \hat{L}[\phi, \bar{\phi}]_{\tau-\Delta t} \Delta t) \quad (4.18)$$

where $\langle \phi_{X,\tau} | \phi_{X,\tau-\Delta t} \rangle$ is our overlap relation Eq. 4.3 which results in:

$$\langle \phi_{X,\tau} | \phi_{X,\tau-\Delta t} \rangle = \prod_i \exp\left(-\frac{1}{2} |\phi_{Xi,\tau}|^2 - \frac{1}{2} |\phi_{Xi,\tau-\Delta t}|^2 + \bar{\phi}_{Xi,\tau} \phi_{Xi,\tau-\Delta t}\right) \quad (4.19)$$

$$= \prod_i \exp(-\bar{\phi}_{Xi,\tau} [\phi_{Xi,\tau} - \phi_{Xi,\tau-\Delta t}]) \exp\left(\frac{1}{2} |\phi_{Xi,\tau}|^2 - \frac{1}{2} |\phi_{Xi,\tau-\Delta t}|^2\right). \quad (4.20)$$

Using a Taylor expansion, we can reduce the difference found in the first of Eq. 4.20 to a derivative:

$$\exp(-\bar{\phi}_{Xi,\tau} [\phi_{Xi,\tau} - \phi_{Xi,\tau-\Delta t}]) = \exp\left(-\bar{\phi}_{Xi,\tau} \left[\frac{d\phi_{Xi,\tau}}{dt} \Delta t \right]\right) \quad (4.21)$$

where the higher order powers of Δt vanishes in the limit of $\Delta t \rightarrow 0$.

Inputting Eq. 4.20 back into the average (Eq. 4.12), results in the first and second term of the second exponential canceling with the other time overlaps on the left and

right respectively. Thus,

$$\prod_{\tau} \exp \left(\frac{1}{2} |\phi_{X_i, \tau}|^2 - \frac{1}{2} |\bar{\phi}_{X_i, \tau}|^2 \right) = \exp \left(\frac{1}{2} |\phi_{X_i, t_2}|^2 - \frac{1}{2} |\phi_{X_i, t_1}|^2 \right). \quad (4.22)$$

Our average now has the form:

$$\begin{aligned} \langle e^{-W} \rangle = & \mathcal{N}^{-1} \prod_X \int \mathcal{D}\phi_X \mathcal{D}\bar{\phi}_X \left(\langle \mathcal{P} | \phi_{X, t_2} \rangle \prod_i \exp \left(\frac{1}{2} |\phi_{X_i, t_2}|^2 \right) \right) \\ & \times \left(\prod_i \exp \left(-\frac{1}{2} |\phi_{X_i, t_1}|^2 \right) \langle \phi_{X, t_1} | \psi_G \rangle \right) \\ & \times \prod_{t_1 + \Delta t}^{t_2} \prod_i \left[\exp \left(-\bar{\phi}_{X_i, \tau} \frac{d\phi_{X_i, \tau}}{dt} \Delta t \right) - \frac{dU_{i, \tau - \Delta t}^X}{dt} \Delta t \bar{\phi}_{X_i} \phi_{X_i} + \hat{L}_{\tau - \Delta t} \Delta t \right] \end{aligned} \quad (4.23)$$

where we have rewritten the middle term in between the overlap of Eq. (4.13) as an exponential. Furthermore, we have expanded our work term and have taken the sum on lattice sites, i , out of the work average and all the Liouvillians, resulting in a product over sites outside of the exponential. The sum or product on species in the work average term, projection state (3.27), Gibbs state (3.37), and in the Liouvillians is absorbed by the product over species of particles outside the exponential. Lastly, $\mathcal{D}\phi_X \mathcal{D}\bar{\phi}_X$ now indicates the product of all $\mathcal{D}\phi_{X, \tau} \mathcal{D}\bar{\phi}_{X, \tau}$ from t_1 to t_2 .

$$\mathcal{D}\phi_{X, \tau} = \prod_{t_1}^{t_2} \mathcal{D}\phi_{X, \tau} \mathcal{D}\bar{\phi}_{X, \tau}. \quad (4.24)$$

Focusing on the second line of Eq. (4.23), we can bring the product over time slices into the exponential as the sum over time slices and rewrite the exponential term in the limit $\Delta t \rightarrow 0$ as:

$$\prod_i \exp \left(\int_{t_1}^{t_2} dt \left[-\bar{\phi}_{X_i}(t) \frac{d\phi_{X_i}(t)}{dt} - \frac{dU_i^X(t)}{dt} \bar{\phi}_{X_i}(t) \phi_{X_i}(t) + \hat{L}(t) \right] \right). \quad (4.25)$$

Thus, taking our Jarzynski average into the temporal continuum from t_1 to t_2 .

Separating the work term from Eq. (4.25), we define the bulk action, e^{-S_B} , from t_1 to t_2 as

$$e^{-S_B} = \prod_i \exp \left(\int_{t_1}^{t_2} dt \left[\bar{\phi}_{X_i}(t) \frac{d\phi_{X_i}(t)}{dt} - \hat{L}(t) \right] \right). \quad (4.26)$$

Furthermore, we define the final action, e^{S_F} , as the overlap between the projection state and the coherent state with the exponential term at t_2 in Eq. 4.23.

$$e^{-S_F} = \langle \mathcal{P} | \phi_{X,t_2} \rangle \prod_i \exp \left(\frac{1}{2} |\phi_{X_i,t_2}|^2 \right). \quad (4.27)$$

Conversely, we define the initial action, $\frac{1}{\mathcal{Z}_1} e^{-S_i}$, as the overlap between the Gibbs state and the coherent state with the exponential term at t_1 . We expand the Gibbs state using Eq. (3.37) and define the initial action as:

$$\frac{1}{\mathcal{Z}_1} e^{-S_i} = \frac{1}{\mathcal{Z}_1} \prod_i \exp \left(-\frac{1}{2} |\phi_{X_i,t_1}|^2 \right) \langle \phi_{X,t_1} | e^{\sum_i e^{(-U_i^X + \mu_X) x_i^\dagger}} | 0 \rangle. \quad (4.28)$$

Eq. 4.26, 4.27, 4.28 define the statistical action of the system and we will further develop this in the next few sections.

4.4 Spatial Continuum Limit

We now consider the spatial continuum limit of the Jarzynski average. We will first bring the bulk action and the work term to the spatial continuum limit by rescaling coherent states in the the exponential terms of Eq.4.25 by:

$$\bar{\phi}_{X_i} = \Delta x^{d/2} \bar{\phi}_X(x) \quad \text{and} \quad \phi_{X_i} = \Delta x^{d/2} \phi_X(x) \quad (4.29)$$

where d is the dimension of the system. This results in

$$\exp \left(\int_{t_1}^{t_2} dt \left[\int dx \left(\bar{\phi}_X(x,t) \frac{d\phi_X(x,t)}{dt} - \frac{dU^X(x,t)}{dt} \bar{\phi}_X(x,t) \phi_X(x,t) \right) - \sum_i \hat{L}(t) \right] \right). \quad (4.30)$$

We will now bring the Liouvillians into the spatial continuum limit. Considering the hopping Liouvillian, Eq. 4.14

$$\hat{L}_H[\phi, \bar{\phi}, t] = -\Gamma_X \sum_i (\bar{\phi}_{X(i+1)}(t) - \bar{\phi}_{X_i}(t)) \left(e^{U_{i+1}^X(t)} \phi_{X(i+1)}(t) - e^{U_i^X(t)} \phi_{X_i}(t) \right). \quad (4.31)$$

We can rewrite the two differences in parantheses as spatial derivatives, resulting in:

$$\hat{L}_H[\phi, \bar{\phi}, x, t] = -D_X \int dx \left(\frac{d\bar{\phi}_X(x,t)}{dx} \right) \left(\frac{d(e^{U^X(x,t)} \phi_X(x,t))}{dx} \right). \quad (4.32)$$

where $D_X = \Gamma_X \Delta x^2$ is the diffusion constant.

Combining the first term of Eq. 4.30 and the hopping Liouvillian, Eq. 4.32, we can recover the diffusion equation by using integration by parts and setting periodic boundaries:

$$- \int_{t_1}^{t_2} dt \int dx \left(\bar{\phi}_X(x, t) \frac{d\phi_X(x, t)}{dt} + D_X \left(\frac{d\bar{\phi}_X(x, t)}{dx} \right) \left(\frac{d(e^{U^X(x, t)} \phi_X(x, t))}{dx} \right) \right) \quad (4.33)$$

$$= - \int_{t_1}^{t_2} dt \int dx \left(\bar{\phi}_X \frac{d\phi_X}{dt} + D_X e^{U^X} \left(\frac{d\bar{\phi}_X}{dx} \right) \left(\frac{dU^X}{dx} \phi_X + \frac{d\phi_X}{dx} U^X \right) \right) \quad (4.34)$$

$$(4.35)$$

$$= - \int_{t_1}^{t_2} dt \int dx \left(\bar{\phi}_X \underbrace{\left(\frac{d\phi_X}{dt} - D_X e^{U^X} \frac{d^2 \phi_X}{dx^2} \right)}_{\text{Diffusion Eq.}} + D_X e^{U^X} \left(\frac{d\bar{\phi}_X}{dx} \right) \frac{dU^X}{dx} \phi_X \right) \quad (4.36)$$

where, if we have a non-spatially varying potential, we recover the the diffusion equation alone from purely the hopping Liouvillian and overlap relation.

The continuum $A \leftrightarrow B$ reaction Liouvillian (4.16) falls completely out of the continuum-discrete relation (Eq. 4.29).

$$\hat{L}_{A \leftrightarrow B}[\phi, \bar{\phi}, x, t] = \int \Lambda \left(\bar{\phi}_B(x, t) - \bar{\phi}_A(x, t) \right) \left(e^{U^B(x, t) - \mu_B} \phi_B(x, t) - e^{U^A(x, t) - \mu_A} \phi_A(x, t) \right). \quad (4.37)$$

Lastly, we will convert the chemostat exchange Liouvillian:

$$\hat{L}_{\text{Chemostat}}[\phi, \bar{\phi}, t] = \lambda_X \sum_i \left[(\bar{\phi}_{X_i}(t) - 1) (e^{U_i^X(t) - \mu_X} \phi_{X_i}(t) - 1) \right]. \quad (4.38)$$

Because not all terms in Eq. 4.38 have the same dimensions in the continuum limit, we expand the product and group the terms as follows.

$$\int \left[\lambda_X (e^{U^X(x, t) - \mu_X} \bar{\phi}_X(x, t) \phi_X(x, t) + 1) - \lambda'_X \left(\bar{\phi}_X(x, t) + e^{U^X(x, t) - \mu_X} \phi_X(x, t) \right) \right] \quad (4.39)$$

where $\lambda'_X = \lambda_X / \Delta x^{d/2}$. We have brought our bulk action and work term to the continuum limit.

Next, we will take inner product in the final action, Eq. (4.27). We expand the projection state using Eq. (3.27), and the coherent state using Eq. (4.1):

$$e^{-S_F} = \langle 0 | e^{\sum_{i=1}^L \hat{x}_i} |\phi_{X,t_2}\rangle \prod_i \exp\left(\frac{1}{2} |\phi_{X_i,t_2}|^2\right) \quad (4.40)$$

$$= \langle 0 | e^{\sum_{i=1}^L \phi_{X_i,t_2}} \prod_i \left(e^{\phi_{X_i,t_2} \hat{x}_i} e^{-|\phi_{X_i,t_2}|^2/2} \right) |0\rangle \prod_i \exp\left(\frac{1}{2} |\phi_{X_i,t_2}|^2\right) \quad (4.41)$$

$$= \langle 0 | e^{\sum_{i=1}^L \phi_{X_i,t_2}} e^{\sum_i \phi_{X_i,t_2} 0} |0\rangle = e^{\sum_{i=1}^L \phi_{X_i}(t_2)} \quad (4.42)$$

$$= e^{\sigma \int dx \phi_X(x,t_2)} \quad (4.43)$$

where we introduce $\sigma = \Delta x^{-d/2}$, which takes our final action to the spatial continuum limit.

Lastly, we will take the inner product in the initial action, Eq 4.28, by expanding the coherent state as for the final action:

$$\frac{1}{\mathcal{Z}_1} e^{-S_i} = \frac{1}{\mathcal{Z}_1} \prod_i \exp\left(-\frac{1}{2} |\phi_{X_i,t_1}|^2\right) \langle \phi_{X,t_1} | e^{\sum_i e^{(-U_i^X + \mu_X)} x_i^\dagger} |0\rangle \quad (4.44)$$

$$= \frac{1}{\mathcal{Z}_1} \prod_i \exp\left(-\frac{1}{2} |\phi_{X_i,t_1}|^2\right) \langle 0 | \prod_i \left(e^{\bar{\phi}_{X_i,t_1} \hat{x}_i} e^{-|\phi_{X_i,t_1}|^2/2} \right) e^{\sum_i e^{-U_i^X + \mu_X} \bar{\phi}_{X_i,t_1}} |0\rangle \quad (4.45)$$

$$= \frac{1}{\mathcal{Z}_1} e^{-\sum_i |\phi_{X_i}(t_1)|^2} e^{\sum_i e^{-U_i^X + \mu_X} \bar{\phi}_{X_i}(t_1)} \quad (4.46)$$

$$= \frac{1}{\mathcal{Z}_1} e^{-\int dx |\phi_X(x,t_1)|^2} e^{\sigma \int dx \bar{\phi}_X(x,t_1) e^{-U^X(x,t_1) + \mu_X}}. \quad (4.47)$$

Similarly, we use σ to bring the initial action into the spatial continuum limit. We have completed in bringing the statistical action of S_i , S_B , and S_F , and the work term to the temporal and spatial continuum limit.

4.5 Statistical Action

Using our statistical actions Eq. (4.26), (4.43), and (4.47) and its continuum parts, our Jarzynski average is:

$$\langle e^{-W} \rangle = \frac{\mathcal{N}^{-1}}{\mathcal{Z}_1} \prod_X \left[\int \mathcal{D}\phi_X \mathcal{D}\bar{\phi}_X e^{-S_F - S_B - S_i} e^{-\int_{t_1}^{t_2} dt \int dx \frac{dU^X(x,t)}{dt} \bar{\phi}_X(x,t) \phi_X(x,t)} \right]. \quad (4.48)$$

Conventionally, the statistical action, $S[\bar{\phi}, \phi]$, has the following form in the field average:

$$\langle e^{-W} \rangle = \frac{\mathcal{N}^{-1}}{\mathcal{Z}_1} \prod_X \left[\int \mathcal{D}\phi_X \mathcal{D}\bar{\phi}_X \left(e^{-S[\bar{\phi}, \phi](t_1 \rightarrow t_2)} \right) e^{-\int_{t_1}^{t_2} dt \int dx \frac{dU^X(x,t)}{dt} \bar{\phi}_X(x,t) \phi_X(x,t)} \right] \quad (4.49)$$

where the grand partition function of the initial action is placed outside of the Statistical Action and $S[\bar{\phi}, \phi] = S_i + S_B + S_F$.

Explicitly, we rewrite S_B with its expanded Liouvillians as:

$$\begin{aligned} S_b = \int_{t_1}^{t_2} dt \int dx & \left[\bar{\phi}_X \left(\frac{d\phi_X}{dt} - D_X e^{U^X} \frac{d^2 \phi_X}{dx^2} \right) + D_X e^{U^X} \left(\frac{d\bar{\phi}_X}{dx} \right) \left(\frac{dU^X}{dx} \right) \phi_X \right. \\ & - \Lambda (\bar{\phi}_B - \bar{\phi}_A) \left(e^{U^B(x,t) - \mu_B} \phi_B - e^{U^A(x,t) - \mu_A} \phi_A \right) \\ & \left. - \lambda_X \left(e^{U^X(x,t) - \mu_X} \bar{\phi}_X \phi_X + 1 \right) + \lambda'_X \left(\bar{\phi}_X + e^{U^X(x,t) - \mu_X} \phi_X \right) \right] \quad (4.50) \end{aligned}$$

where the top line is the overlap relationship and hopping Liouvillian re-expressed into the diffusion equation and an additional term, the second line is our $A \leftrightarrow B$ chemical reaction, and lastly the third line is our chemostat exchange. Additionally, we can also write our bulk action with the explicit overlap relation and hopping Liouvillian.

$$\begin{aligned} S_B = \int_{t_1}^{t_2} dt \int dx & \left[\bar{\phi}_X \frac{d\phi_X}{dt} + D_X \left(\frac{d\bar{\phi}_X}{dx} \right) \left(\frac{d(e^{U^X(x,t)} \phi_X)}{dx} \right) \right. \\ & - \Lambda (\bar{\phi}_B - \bar{\phi}_A) \left(e^{U^B(x,t) - \mu_B} \phi_B - e^{U^A(x,t) - \mu_A} \phi_A \right) \\ & \left. - \lambda_X \left(e^{U^X(x,t) - \mu_X} \bar{\phi}_X \phi_X + 1 \right) + \lambda'_X \left(\bar{\phi}_X + e^{U^X(x,t) - \mu_X} \phi_X \right) \right] \quad (4.52) \end{aligned}$$

In the Jarzynski field average (Eq. 4.63), the statistical action acts as a weighting for averages in the field theory. In our case we are averaging the work, $e^{-\frac{dU^X(x,t)}{dt} \bar{\phi}_X(x,t) \phi_X(x,t)}$.

Noting this averaging mechanism will play an important role in recovering the Jarzynski relation in the field theory.

4.6 Jarzynski Relation Field Theory

In the field theoretic representation of the Jarzynski average, we can perform field transformations of the following form:

$$\phi_X(x, t) \rightarrow \bar{\psi}_X(x, t)e^{-U^X(x, t)+\mu_X} \quad \text{and} \quad \bar{\phi}_X(x, t) \rightarrow \psi_X(x, t)e^{U^X(x, t)-\mu_X}. \quad (4.53)$$

These resemble gauge transformations in quantum electrodynamics. They take $\bar{\phi}_X\phi \rightarrow \bar{\psi}_X\psi$. Additionally we perform a time reversal through the variable change, $\tau = t_2 - t$. This results in multiple shifts in our statistical action.

Starting with the initial action, we will define this transformed initial action as S'_i :

$$S'_i = \int dx (|\psi_X(x, \tau = t_2 - t_1)|^2 - \sigma\psi_X(x, \tau = t_2 - t_1)). \quad (4.54)$$

Furthermore, the transformed final action, S'_F takes the following form:

$$S'_F = -\sigma \int dx \bar{\psi}_X(x, \tau = 0)e^{-U^A(x, \tau=0)+\mu_A}. \quad (4.55)$$

Lastly, we will transform the bulk action in 4.52 to the transformed bulk action, S'_B :

$$\begin{aligned} S'_B = \int_{t_2-t_1}^0 -d\tau \int dx \left[\psi_X(x, \tau = t_2 - t)e^{U^X(x, \tau=t_2-t)-\mu_X} \left(\frac{-d\bar{\psi}_X(x, \tau = t_2 - t)e^{-U^X+\mu_X}}{d\tau} \right) \right. \\ \left. + D_X \left(\frac{d\psi_X e^{U^X-\mu_X}}{dx} \right) \left(\frac{d(e^{U^X}\bar{\psi}_X e^{-U^X+\mu_X})}{dx} \right) \right. \\ \left. - \Lambda \left(e^{U^B-\mu_B}\psi_B - e^{U^A-\mu_A}\psi_A \right) (\bar{\psi}_B - \bar{\psi}_A) \right. \\ \left. - \lambda_X \left(e^{U^X(x, t)-\mu_X}\bar{\psi}_X\psi_X + 1 \right) + \lambda'_X \left(e^{U^X-\mu_X}\psi_X + \bar{\psi}_X \right) \right] \quad (4.56) \end{aligned}$$

where under the time reversal $\frac{d}{dt} \Rightarrow -\frac{d}{d\tau}$. The $A \leftrightarrow B$ reaction and chemostat exchange remain invariant under the field transformation. The overlap relation and hopping Liouvillian can be further simplified to:

$$\int_0^{t_2-t_1} d\tau \int dx \left[\psi_X e^{U^X} \left(\frac{-d\bar{\psi}_X e^{-U^X}}{d\tau} \right) + D_X \left(\frac{d\psi_X e^{U^X}}{dx} \right) \left(\frac{d(\bar{\psi}_X)}{dx} \right) \right] \quad (4.57)$$

where under a constant chemical potential, μ_X falls out of the time and spatial derivatives and cancels with its conjugate, thus recovering the hopping term and making it invariant under the chosen transformation. Additionally, we have also swapped the bounds of the time integral absorbing the minus sign in front of $d\tau$.

To recover the coherent state overlap relation terms, we can expand the time derivative with the product rule and apply integration by parts to the resulting product:

$$\begin{aligned} & \int_0^{t_2-t_1} d\tau \int dx \psi_X \left(\frac{-d\bar{\psi}_X}{d\tau} + \frac{dU^X}{d\tau} \bar{\psi}_X \right) \\ &= \int_0^{t_2-t_1} d\tau \int \left(dx \psi_X \frac{-d\bar{\psi}_X}{d\tau} + \frac{dU^X}{d\tau} \bar{\psi}_X \psi_X \right) \\ &= \int_0^{t_2-t_1} d\tau \int \left(dx \bar{\psi}_X \frac{d\psi_X}{d\tau} + \frac{dU^X}{d\tau} \bar{\psi}_X \psi_X \right) + |\psi(x, \tau = 0)|^2 - |\psi(x, \tau = t_2 - t_1)|^2. \end{aligned} \quad (4.58)$$

Through the field transformation and time reversal symmetry we recover the original bulk action, S_B , going in reverse time and with three additional terms in the transformed bulk action, $S'_B[\bar{\psi}, \psi]$:

$$S'_B[\bar{\psi}, \psi] = S_B[\bar{\psi}, \psi](t_2 \rightarrow t_1) + \int_0^{t_2-t_1} d\tau \int dx \frac{dU^X}{d\tau} \bar{\phi}_X \phi_X + |\psi(x, \tau = 0)|^2 - |\psi(x, \tau = t_2 - t_1)|^2 \quad (4.59)$$

where we have shifted the work term from ψ back to ϕ due to $\bar{\phi}_X \phi_X = \bar{\psi}_X \psi_X$. The second term in Eq. 4.59 is our work term with the opposite sign as we have in the Jarzynski average. If we apply the time reversal once more to the work to go from τ back to t , we get an additional minus sign, which is negated by the minus sign in front of the statistical action. Therefore, through the transformation and time reversal, the work terms cancel. Furthermore, if we shift the third and fourth term in Eq. 4.59 into the transformed final (Eq. 4.55) and transformed initial (Eq. 4.54)

action respectively. The transformed initial action takes form of the original final action at t_1 and the transformed final action takes form of the original initial action at t_2 without a grand partition function at t_2 . Thus, to recover the original initial action, we gain an additional grand partition function at t_2 . In summary:

$$S'_i = \int dx -\sigma\psi_X(x, t_1) = S_F(t_1) \quad (4.60)$$

$$S'_F = -\sigma \int dx \bar{\psi}_X(x, t_2) e^{-U^A(x, t_2) + \mu_A} + |\psi(x, t_2)|^2 = -\ln(\mathcal{Z}_2) S_i(t_2) \quad (4.61)$$

$$S'_B = S_B[\bar{\psi}, \psi](t_2 \rightarrow t_1). \quad (4.62)$$

Thus, our Jarzynski average under the transformation and time reversal is:

$$\begin{aligned} \langle e^{-W} \rangle &= \frac{\mathcal{N}^{-1}}{\mathcal{Z}_1} \prod_X \left[\int \mathcal{D}\psi_X \mathcal{D}\bar{\psi}_X \left(e^{-S'[\bar{\psi}, \psi](t_2 \rightarrow t_1)} \right) e^{-\frac{dU^X(x, t)}{dt} \bar{\phi}_X(x, t) \phi_X(x, t)} \right] \\ &= \frac{\mathcal{N}^{-1}}{\mathcal{Z}_1} \prod_X \left[\int \mathcal{D}\psi_X \mathcal{D}\bar{\psi}_X \left(e^{-(S'_i + S'_B + S'_F)} \right) \right] \\ &= \frac{\mathcal{N}^{-1} \mathcal{Z}_2}{\mathcal{Z}_1} \prod_X \left[\int \mathcal{D}\psi_X \mathcal{D}\bar{\psi}_X \left(e^{-(S_F(t_1) + S_B(t_2 \rightarrow t_1) + S_F(t_2))} \right) \right] \\ &= \frac{\mathcal{N}^{-1} \mathcal{Z}_2}{\mathcal{Z}_1} \prod_X \left[\int \mathcal{D}\psi_X \mathcal{D}\bar{\psi}_X(1) \left(e^{-(S[\bar{\psi}, \psi](t_2 \rightarrow t_1))} \right) \right] \\ &= \frac{\mathcal{Z}_2}{\mathcal{Z}_1} \langle 1 \rangle = e^{-\Delta\Phi_G} = e^{-(\Delta F - \Delta G)}. \end{aligned} \quad (4.63)$$

We have recovered the Jarzynski relation in the field theory through a time reversal and field transformation. Our initial and final action swapped and our bulk action remained invariant, up to an additional work term that canceled our original work averaging term. This gives us the Jarzynski relation.

Chapter 5

Conclusion

Our primary results presented in the thesis are the following.

First, we have, using Doi-Peliti field theory, developed the mathematical framework to describe classical particles undergoing chemical reactions in a spatially extended system. This allows us to study spatially varying or diffusion-limited chemical reaction networks, where reactants must travel to certain locations to initiate the chemical reaction. This is applicable to many synthetic chemistry and biological systems such as ATP synthase and sodium-potassium pumps. For example, in our model, $A \leftrightarrow B$ reactions can be limited to certain locations by setting the coefficient Λ in equations 2.26 and 4.37 to be spatially varying such that it is equal to zero at locations where reactions cannot occur and nonzero at locations where reactions can occur. Similarly, in the chemostat exchange, if the particles can only enter and leave the system at the edges of the system, then λ in equations 2.31 and 4.38 is nonzero at site 1 and site L and zero elsewhere. Previous descriptions of chemical reaction networks exhibited no spatial variations and were only considered in well-mixed systems, where all reactants are constantly in range of each other [4, 5, 6] and so all reactions and processes essentially occur all in one site or location. Ultimately, Doi-Peliti field theory allows us to generalize our system into the continuum limit.

Second, we have built into the field theory a way of applying generalized work, capable of describing, for example, a uniform or spatially varying electric field. Moreover, the field descriptions of classical systems allows us to initiate spatially varying non-equilibrium work protocols.

Third, we have demonstrated that chemical reaction networks driven far from equilibrium satisfy a generalized Jarzynski relation, something that was not a priori obvious. We derived this in both the Doi representation and field theory. We are able to recover the change in grand potential, a form of free energy, for chemical reaction system from non-equilibrium work protocols.

Fourth, in the field theory, we showed that the Jarzynski relation follows from a gauge-like transformation combined with time reversal. Additionally, the Jarzynski equality arises from detailed balance dynamics and an initial equilibrium state. This allows us to generate additional, more complex work relations by transforming with different auxiliary fields. This should prove to be a fruitful area of additional study.

Now that we have developed the field theory, our goal is to understand the underlying mechanism so that we can see how the relation holds, if it can be extended, and if it will be broken under any circumstances. In particular we would like to extend the formalism to the Crooks relation [12, 13]. The Jarzynski equality holds for detailed balanced systems, but with our Doi-Peliti formalism, we can incorporate dynamics which does not follow detailed balance. In this case, we are still able to generate equalities and thus, through this formalism, we hope to define new families of non-equilibrium work relations.

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