Large-deviation principles, stochastic effective actions, path entropies, and the structure and meaning of thermodynamic descriptions

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Abstract
The meaning of thermodynamic descriptions is found in large-deviations scaling (Ellis 1985 Entropy, Large Deviations, and Statistical Mechanics (New York: Springer); Touchette 2009 Phys. Rep. 478 1–69) of the probabilities for fluctuations of averaged quantities. The central function expressing large-deviations scaling is the entropy, which is the basis both for fluctuation theorems and for characterizing the thermodynamic interactions of systems. Freidlin–Wentzell theory (Freidlin and Wentzell 1998 Random Perturbations in Dynamical Systems 2nd edn (New York: Springer)) provides a quite general formulation of large-deviations scaling for non-equilibrium stochastic processes, through a remarkable representation in terms of a Hamiltonian dynamical system. A number of related methods now exist to construct the Freidlin–Wentzell Hamiltonian for many kinds of stochastic processes; one method due to Doi (1976 J. Phys. A: Math. Gen. 9 1465–78; 1976 J. Phys. A: Math. Gen. 9 1479) and Peliti (1985 J. Physique 46 1469; 1986 J. Phys. A: Math. Gen. 19 L365), appropriate to integer counting statistics, is widely used in reaction–diffusion theory.

Using these tools together with a path-entropy method due to Jaynes (1980 Annu. Rev. Phys. Chem. 31 579–601), this review shows how to construct entropy functions that both express large-deviations scaling of fluctuations, and describe system–environment interactions, for discrete stochastic processes either at or away from equilibrium. A collection of variational methods familiar within quantum field theory, but less commonly applied to the Doi–Peliti construction, is used to define a ‘stochastic effective action’, which is the large-deviations rate function for arbitrary non-equilibrium paths.

We show how common principles of entropy maximization, applied to different ensembles of states or of histories, lead to different entropy functions and different sets of thermodynamic state variables. Yet the relations among all these levels of description may be constructed explicitly and understood in terms of information conditions. Although the example systems considered are limited, they are meant to provide a self-contained introduction to methods that may be used to systematically construct descriptions with all the features familiar from equilibrium thermodynamics, for a much wider range of systems describable by stochastic processes.

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1. Introduction

Thermodynamics is not fundamentally a theory of energy distribution, but a theory of statistical inference about incompletely constrained or measured systems [9]. While most of our experience and intuition about thermodynamics is drawn from equilibrium statistical mechanics [10–12], which emphasizes the role of energy, we should expect that its fundamental principles apply in much wider domains, outside equilibrium, and even outside mechanics.

Within the last 50 years, a clear conceptual understanding of the nature of thermodynamic descriptions [1, 2] has combined with new methods to analyze a wide variety of stochastic processes, for continuous [13] and discrete systems [4–7], in quantum [14, 15] and classical mechanics [16, 17], both at and away from equilibrium, and even in other areas using information theory such as optimal data compression and reliable communication [18], and via these, robust molecular recognition [19, 20]. These developments confirm that thermodynamics is indeed not restricted to equilibrium or to mechanics. They give us insight into when thermodynamic descriptions should exist, and they provide systematic methods to construct such descriptions in a wide variety of situations.

This paper reviews the aspects of large-numbers scaling and structural decomposition that are essential to thermodynamic descriptions, and presents examples from which each of these may be seen in different forms that are appropriate to equilibrium and non-equilibrium statistical mechanics. It also brings together construction methods (based on generating functions [4–7]), scaling relations (based on ray approximations [3, 21]) and variational methods (based on functional Legendre transforms [22]), which will enable the reader to systematically construct the fluctuation theorems of thermodynamic descriptions from their underlying stochastic processes.

1.1. Key concepts, and source of examples

1.1.1. Entropy underlies large-deviations scaling and reflects system structure. The entropy, as a logarithmic measure of
the aggregate probability of coarse-grained states or processes, is the central quantity in thermodynamics. It arises as the leading term in the log-probability for fluctuations of averaged quantities. At the same time, however, when subsystem components, or a system and its environment, interact, they discover their most probable joint configuration through fluctuations. Therefore, the competition among entropy terms also reflects the structure of system interactions at the macroscale. We are reminded of the importance of this structural role of entropies, by the fact that pure ‘classical’ thermodynamics [10] is entirely devoted to the analysis of entropy gradients. Therefore, we wish to insist on being able to decompose entropy into its subsystem components as a criterion for any fully developed thermodynamic description.

The key property that defines the existence of thermodynamic limits, and the form of their fluctuation theorems, is large-deviations scaling [1, 2]. It is the precise statement of the simplification provided by the law of large numbers, not only in the infinite limit of aggregation, but in the asymptotic approach to infinity. It is well known that averaging over ensembles of configurations for large systems removes almost all (irrelevant) degrees of freedom, and leaves only summary statistics, which are the state variables of the thermodynamic description¹. In finite systems, these summary statistics can still show sample fluctuation, but in the thermodynamic limit, the fluctuation probability takes a simple form.

For an ensemble that possesses large-deviations scaling, it is possible to describe classes of fluctuations as having the same structure under different degrees of aggregation. (An example would be fractional density fluctuations in regions of a gas, whose sample volume may be varied.) The log-probability for any such fluctuation then factors, into a term that depends on overall system scale, and a scale-invariant coefficient that depends only on the structure of the fluctuation. The scale-invariant coefficient is called the rate function of the large-deviations scaling relation [2]. (An example would be the specific entropy of a gas.)

Large-deviations scaling presumes the existence of a separation of scales—between microscopic processes and their macroscopic descriptions—over which aggregation does not lead to qualitative changes in the kinds of fluctuations that can occur. We expect thermodynamic limits to exist where this separation of scales is large. Examples of structural change that can interrupt simple scaling under the law of large numbers include phase transitions, which can change the space of accessible excitations.

Large-deviations scaling permits us to combine fluctuation statistics with entropy decompositions that reflect system structure. In equilibrium thermodynamics, the result is the classical fluctuation theorem for macrostates [1]: the log-probability for fluctuations (of energy, volume, particles, etc) between subsystems with well-defined entropies is the difference between the sum of entropies at the fluctuating value and the maximum value for this sum, which is the equilibrium value.

If we wish to consider the probabilities of fluctuations with more complex structure (whether in equilibrium thermodynamics or in more complicated cases), we will need more flexible methods to compute large-deviations formulae and entropy decompositions. For this, we introduce the notation of the stochastic effective action, which is defined by variational methods that generalize the familiar Legendre transform of equilibrium thermodynamics. The meaning of this quantity, and the way it is used, will be most easily understood by following its construction in the body of the paper, so we postpone further discussion until that point.

1.1.2. The principles in a simple progression: from equilibrium to non-equilibrium statistical mechanics. We will develop examples whose purpose is to show that the definition and properties of the entropy do not change as we extend thermodynamics beyond equilibrium statistical mechanics. Rather, what changes is the state space to which we assign probabilities.

A direct example comes from comparing an equilibrium thermodynamic system with a non-equilibrium description constructed for the same system. A frequent approach [23–26] to non-equilibrium statistical mechanics (NESM) continues to use the equilibrium state variables and equilibrium entropy, but considers their time rates of change. We will see that such an approach, focused on retaining the functional form of the equilibrium entropy, sacrifices its meaning as a large-deviations rate function.

Instead, we will make the transition from equilibrium to NESM by replacing an ensemble of states (in equilibrium) by an ensemble in which entire time-dependent trajectories—termed histories—are the elementary entities (for NESM), and then we will construct the appropriate large-deviations limits for the ensemble of histories. The functional form of the entropy will necessarily change. More importantly, the inventory of state variables will necessarily be enlarged, to include not only the configuration variables of equilibrium, but also a collection of currents that relate to the changes in configuration. Both kinds of variables will be needed as summary statistics for an ensemble of histories, and both will enter as arguments in the non-equilibrium entropy.

NESM is not so far removed from equilibrium thermodynamics that it can really do justice to the generality of large-deviations principles and thermodynamic descriptions. However, it allows us to begin with a completely familiar (equilibrium) construction, then to compare it with a construction with rather different functional forms, and finally to derive the complete set of relations that connect the two descriptions.

1.2. Markovian stochastic processes, the two-state model as an example, and the approach of the paper

Markovian stochastic processes [27] provide a general substrate-independent framework within which to study the
aggregation properties of coarse-grained probabilities and large-deviations scaling. They include models from statistical mechanics, but they may also be used to represent many other random processes, whose structure may have different constraints and interpretations from those of mechanics.

This review will use the two-state random walk, in either discrete or continuous time, as a sample system for which equilibrium and non-equilibrium thermodynamic descriptions will be built and then compared. The two-state random walk is the simplest discrete stochastic process, and most thermodynamic quantities of interest in both ensembles can be computed for this system in closed form. However, the constructions in the examples immediately generalize to more complicated cases, and several generalizations and approximation methods will be covered either in the main text or in appendices.

Section 2 will introduce large-deviations scaling one level ‘below’ the discrete random walk, by supposing that the discrete model emerges as a coarse-grained description from the continuous random walk in a double-well potential. The continuum model illustrates the concept of concentration of measure from large-deviations theory, and sets the parameters (both explicit and implicit) that define the discrete model. It also clarifies the nature and origin of the ‘local-equilibrium’ approximation [26] for coarse-grained descriptions of motion on free-energy landscapes, and illustrates graphically the dual roles that charges and currents must have in non-equilibrium entropy principles.

Sections 3 and 4 present the equilibrium thermodynamics of the two-state model, and its most direct generalization through the master equation of the stochastic process. Section 3 uses the exact solution of the equilibrium distribution to introduce all basic quantities of the large-deviations theory, and derives these using generating functions and their associated variational methods. Section 4 then presents the same construction for the time-dependent probability distribution, in which histories of particle counts rather than counts at a single time are the elementary entities. Neither of these ensembles distinguishes particle identities, either in states or in trajectories. Section 5 presents an alternative construction of a thermodynamics of histories based on the entropy of distinguishable-particle trajectories, and this second construction naturally separates the path entropy from probability terms due to the environment, in a form exactly analogous to the Gibbs free energy for equilibrium.

The rest of the introduction lists sources for the particular methods used in later sections, and explains why they capture different aspects of a full non-equilibrium thermodynamics. Many aspects of the following derivations—the naturalness of the generating-function representation, the role of operator algebras and linear algebra more generally, or the information conditions and counting statistics that relate one ensemble to another—may be understood in conceptual terms that are more fundamental than the particular constructions in which they appear below. We return to these in the discussion, making use of examples from the text.

Numerous diverse studies now contribute to the understanding of methods closely related to those used below.
of collective fluctuation, which we describe with the continuous mean values of Poisson distributions; (3) whether we are describing absolute particle numbers distributed among states, or are separating total number as a scaling variable, from the fractional distributions of particles that have a scale-invariant meaning.

Different choices will lead to objects with quite different mathematical behavior, even if all of them represent particle numbers in one way or another. The notation in the following sections is chosen to reflect the three choices above, while still permitting readable equations.

Ensemble averages of any quantities are denoted by overbars. This convention is easier to incorporate in complicated equations than the $E$ (for expectation value) commonly used in statistics.

The remaining distinctions in the notation are summarized in table 1.

It will be important, in following the D–P construction below, to understand that italic $n_i$ are the mean values of Poisson distributions that are used as a basis in which to expand the actual distribution that evolves under the stochastic process. They remain random variables that are sampled from the ensemble, but they fluctuate with Langevin statistics rather than the Poisson statistics of the integer particle counts $n_i$. The ensemble mean will be denoted $\bar{n}_i$.

The dynamics of a stochastic process may be represented in three ways associated with these different bases, which contain equivalent information and which will all be illustrated in the following sections. These are (1) the transfer matrix of the discrete stochastic process, which shifts probability among indices; (2) the Liouville operator that acts on generating functions, shifting probability among modes and (3) the action functional of the D–P field-theoretic expansion in Poisson distributions, which generates the covariance for Langevin statistics. We will show that, with a suitable choice of dynamical variables, one may skip over the laborious task of interconverting these representations, and simply copy the functional forms from one representation to another. The number variables and shift operators in table 1 are those that substitute for one another under changes of representation.

### Table 1. Notations for particle number in different bases.

| Position variable | Domain       | Measure | Dynamics | Meaning and usage | Conjugate momentum |
|-------------------|--------------|---------|----------|-------------------|--------------------|
| $N$               | [0, $\infty$] | Integer | Fixed    | Total population number | not used |
| $n_i$             | [0, $N$]     | Integer | Stochastic | Values of sample points | $-\partial/\partial n_i$ |
| $n_i/N$           | [0, 1]       | Rational | Stochastic | Mean of Poisson distribution | $\eta_i$ |
| $\bar{n}_i$       | [0, 1]       | Real    | Langevin | Relative values of sample points | $-(1/N)\partial/\partial \bar{n}_i$ |
| $\nu_i$           | [0, 1]       | Real    | Langevin | Distribution normalized by $N$ | $\eta_i$ |

### 2. Coarse graining, emergence of the near-equilibrium approximation, and the dual structure of non-equilibrium state variables

In later sections, the two-state random walk will be the microscopic model, whose thermodynamic descriptions we seek. In this section we will take an even lower-level random walk in a continuum potential to be the microscopic model, for which the two-state model is the coarse-grained thermodynamic description. Starting in the continuum will allow us to relate the dual (charge/current) character of non-equilibrium thermodynamic state variables to graphical features of the underlying free-energy landscape. The particular class of continuum models we will consider—landscapes with basins and barriers—also lead to the asymmetry between states and kinetics in classical discrete stochastic processes, and to the nature of the local-equilibrium approximation in such models.

The main points of the section will be (1) the way large-deviations scaling isolates the fixed points of a stochastic dynamical system as its control points; (2) the difference between the relevant sets of fixed points for equilibrium versus non-equilibrium ensembles and (3) the way the static and kinetic properties of the underlying system become encoded in the discrete representation. We will also cover the origin of the natural scale for a discrete stochastic process, which is never expressed directly within the discrete model, but which can be necessary to regulate and to understand divergences when its stochastic behavior is analyzed.

### 2.1. The free-energy landscape representation bridges scales, and applies to general stochastic processes satisfying detailed balance

Entropy characterizes probabilities for systems that we describe completely (called ‘closed’ systems), while free energies characterize probabilities for systems coupled to incompletely described environments. A review of the basic

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2 This distinction is similar to the distinction between the position basis and the wavenumber basis exchanged by the Fourier–Laplace transform.

3 This asymmetry is not inherent in the classical limit, however, nor is it a common feature of quantum statistical ensembles, where positions and momenta may have much more symmetric roles. The continuum model therefore provides a point of departure for several different macroscopic approximations.
relations of probability to entropy and free energy in classical equilibrium thermodynamics is given in appendix B.

In this and later sections, we will write probabilities of states, and transition rates, in terms of Gibbs free energies [11]. The free-energy representation is not linked to any particular scale, and so provides the map from a continuum potential for a stochastic particle to the parameters of its discrete-state approximation. This representation becomes particularly powerful for extensions from single-particle motion, to the conversion of several species of particles in fixed proportion, which occurs in chemical-reaction networks (considered in appendix D). The origin of free energies need not be mechanical; such a representation may be found for any stochastic process that satisfies detailed balance in its stationary state.

Free energies will also provide a way to interpret the generating functions and functionals used in later sections. A generating function distorts the free-energy landscape by changing the one-particle free energies of stable states and transitions. We will see that the momentum variables that dominate the minimization of the free energy act to change the one-particle free energies of stable states and the barrier maximum (the one-dimensional version of a saddle point).

2.2. Concentration of measure in the large-deviations limit, and fixed points on the free-energy landscape

Consider then the stochastic motion of a particle in the double-well continuum potential illustrated in figure 1. Large-deviations theory for the continuum [3, 21, 28, 38] applies at low temperatures, and characterizes the following three aspects of the probability of trapped motions and escapes.

(1) The probability for a random walker to be found away from the attracting fixed points (the minima of the continuum free-energy potential) decreases exponentially in \( \beta = 1/k_B T \), where \( T \) is temperature and \( k_B \) is Boltzmann’s constant. In particular, escapes from one well to the other are exponentially improbable. The leading term in the log of the escape rate is given by the *quasipotential* of F–W theory [28].

(2) Among escape events, the majority occur along a particular spatio-temporal history of thermal excitations leading uphill from the minima of the potential toward the interior maximum. More precisely, *conditional* on having observed an escape event, the probability that the escape trajectory deviated from this most-probable form decreases exponentially in \( \beta = 1/k_B T \), which is a large-deviations result for histories. The most-likely escape trajectory is the stationary path derived from the F–W dynamical system [28]. For one-dimensional systems, this trajectory is always the time-reverse of the classical diffusion trajectory from the maximum to the minimum.

(3) The most-probable trajectory for any escape requires a specific finite time, which will limit the frequencies at which we can use coarse-grained approximations. In one dimension, the escape time equals the classical diffusive-relaxation time over the path whose time-reverse is the escape.

The large-deviations scaling parameter in these continuum formulae is the inverse temperature \( \beta = 1/k_B T \). \( \beta \) will continue to be a scaling parameter in large-deviations formulae for the discrete approximation, but other parameters such as the number of random walkers in the system will also enter.

The exponential suppression of deviations from either fixed points or stereotypical escape trajectories is the phenomenon known as concentration of measure for the random walk in the potential. It is the property that leads us to make only a finite error\(^4\) even if we replace the infinitely many degrees of freedom of a random walk on the continuum, by a (zero-dimensional!) discrete random walk between two states, written

\[
b \equiv a.
\]

Here \( b \) and \( a \) are coarse-grained labels standing for the left-hand and right-hand wells.

The states in the discrete walk are associated approximately with the positions of the local minima of the continuum potential, as shown in figure 2. Each state also has a Gibbs free energy per particle—known in chemical thermodynamics as the chemical potential [11], and written (for a single particle) as \( \mu \)—near the value at the well minimum.

The continuum large-deviations theory for escapes [28] gives the escape rate from either well, to leading-exponential order, as a function of the chemical potentials in the wells and at the local maximum of the continuum potential between the wells (indicated in figure 1), in the form

\[
k_+ = e^{-\beta(\mu_1-\mu_a)}, \quad k_- = e^{-\beta(\mu_1-\mu_b)}.
\]

Note that the absolute magnitudes of probabilities which are kept to describe transitions are generally (exponentially) smaller than corrections to the mean properties of the fixed points, which are omitted in the large-deviations approximation\(^5\). They are, however, the leading terms in the conditional probability, and therefore the leading contribution to dynamics.

\(^4\) The magnitude of this error decays as powers of \( 1/k_B T \).

\(^5\) See [42, chapter 7] for more on approximations of this kind.
The escape rates appear in the discrete-state continuous-time approximation as the parameters in its master equation, whose form is

$$\frac{\partial \rho_{n_a,n_b}}{\partial t} = \left[ k_+ \left( e^{\beta \mu_a - \beta \mu_b} - 1 \right) n_a - k_- \left( e^{\beta \mu_a - \beta \mu_b} - 1 \right) n_b \right] \rho_{n_a,n_b}. \quad (3)$$

Here, $n_a$ and $n_b$ are possible values for the numbers of particles found in the right and left wells at any instant of time. $\rho_{n_a,n_b}$ is a time-dependent probability density for an ensemble of such observations. The master equation (3) describes the flow of probability among different values of the indices ($n_a$, $n_b$) as particles hop with rates $k_{\pm}$ per particle. Often the right-hand side of a master equation such as equation (3) is written as a sum over all values of ($n_a$, $n_b$). For stochastic processes in which almost all change results from independent single-particle transitions, only adjacent values ($n_a \pm 1$, $n_b \mp 1$) contribute to the change in $\rho_{n_a,n_b}$. Therefore, we have written the shifts of indices in the sum as the action of operators $e^{\beta \mu_a - \beta \mu_b}$, treating the indices ($n_a$, $n_b$) formally as if they lived on a continuum, even though only values separated by integers ever appear in the time evolution of $\rho_{n_a,n_b}$. The operator in square brackets in equation (3) is called the transfer matrix of the stochastic process. Its functional form will reappear throughout the subsequent analyses, in the operators that govern the time evolution of generating functions, and as the Hamiltonian in the F–W dynamical system.

2.3. The discrete-state projections for equilibrium versus non-equilibrium systems

The net effect of concentration of measure in the continuum random walk is to extract the parameters of its discrete approximation from the fixed points of the mean flow on the free-energy landscape. The concentration toward the attracting fixed points is purely spatial, and is easy to visualize for landscapes in any number of dimensions. The concentration of escape trajectories is spatio-temporal, and is not directly illustrated in the static potential of figure 1. Concentration of trajectories takes on a spatial aspect for landscapes in more than one dimension, where transitions are exponentially likely to pass through saddle points, as shown in figure 3.

We may now graphically characterize the difference between static and dynamic ensembles, for random walks on landscapes with basins and barriers. The equilibrium thermodynamic description for any such system is fully specified by the chemical potentials $\mu^1$ at the attracting fixed points (filled dots in figure 3). In this ensemble, there is no role for barriers, and no appearance of their chemical potentials $\mu^2$. The probabilities for state occupancy are determined only by their free energies, because all waiting times for escapes are (by assumption) surpassed.

For systems away from equilibrium, transition rates become essential to determining state occupancies, as well as transition frequencies between pairs of states. These rates are controlled by the saddle points (white dots in figure 3).

With each kind of fixed point we associate a state variable in the thermodynamic description. (See appendix B for discussion of the origin and role of state variables as constraints.) The state variables of the equilibrium theory, which live on attracting fixed points, all have the property of charges: their value would not change if we ran the dynamics in time-reverse. Away from equilibrium, new state variables are introduced, which live on the saddle points, and these have the property of currents: their value would change sign if we ran the dynamics in time-reverse.

Non-equilibrium ensembles require the introduction of additional sets of current-valued state variables [40, 43], which do not arise in equilibrium, and which have their origin in properties of the saddle points of the underlying free-energy landscape.

2.4. The nature of the local-equilibrium approximation

Free-energy landscapes with basins and barriers lead to an extreme asymmetry in the way charge-valued and
current-valued state variables are represented in the discrete model. The asymmetry comes, as noted above, from the fact that the leading probabilities for dynamics are exponentially smaller than corrections to the properties of states that are dropped in the large-deviations approximation. Therefore, in such systems, the charge-valued state variables, even in the non-equilibrium ensemble, are nearly identical to the state variables of equilibrium. The one-particle chemical potentials \( \mu \), and their generalizations to concentration-dependent chemical potentials [11], all have the same relation to Gibbs free energy as in equilibrium. This property defines the local-equilibrium approximation for this class of models.

We note two things about the local-equilibrium approximation, to emphasize its limits. First, the equivalence of the non-equilibrium charge-valued state variables with their counterparts in equilibrium does not extend to the entropy [43]. The non-equilibrium entropy depends on both charges and currents, even at a single time. For ensembles of histories, it depends on the rate of transitions as well as the state-occupancy statistics, as we will show in multiple examples in sections 4 and 5. This fact will be essential to understanding ‘maximum-entropy production’ [26, 44–47] as an approximation but not a principle for non-equilibrium systems.

Second, we note that the asymmetry between states and kinetics need not be a property of free-energy landscapes if they do not have basins and barriers. In particular, it may not be a property of free diffusion, and it is generally not a property of driven dissipative quantum ensembles [43]. Therefore, if the underlying continuum model does not have the features that create asymmetry, we have no ground to expect that even the charge-valued state variables in the non-equilibrium theory will closely resemble those in the corresponding equilibrium limit.

2.5. The implicit ‘natural scale’ for a coarse-grained description

Finally we mention an implicit limit on the use of the discrete-state approximation. Escapes in the continuum model are rare within the intervals that particles spend in either basin. However, they do require a nonzero time, comparable to the diffusive-relaxation time. In the non-equilibrium discrete-state model, we will probe transition probabilities with time-dependent distortions of the chemical potentials \( \mu \) and \( \mu^\dagger \). The model will permit these probes to have arbitrarily high-frequency time-dependence. However, we will see when we consider path entropies in section 5 that such sources lead to divergences in individual entropy terms that should remain finite to be meaningful.

The solution to the problem of divergences is to recognize that the discrete model has a natural scale [48], which is an upper bound on the frequencies that may sensibly appear in probes of the theory. The natural scale is the diffusive-relaxation frequency in the continuum model. For probes with higher frequencies, the constants \( k_a \) describing transition rates no longer retain their meaning or values. They were defined as lumped-parameter representations of escape paths, in a potential which was assumed to be fixed during the period of the escape. Faster probes ‘melt’ the discrete approximation, and require that the description revert to the underlying continuum.

3. Large-deviations analysis of the equilibrium two-state stochastic process

We now begin the analysis of the equilibrium distribution for the two-state system. Since the entire equilibrium distribution may be written down analytically (it is a binomial distribution), the purpose of this ‘analysis’ is to introduce the key quantities expressing large-deviations scaling, along with systematic ways to compute them using generating functions. The methods and the asymptotics will generalize immediately to time-dependent systems that are not exactly solvable, or at least very inconvenient to write in closed form.

The large-deviation result we will derive is that, for any apportionment \( (n_a, n_b) \) of \( N \) particles to the two states, the log-probability of this apportionment in the equilibrium distribution is the difference of the joint entropy from its maximizing value. A more extensive taxonomy of large-deviation results for equilibrium ensembles is given in [1]. Non-maximizing values of \( (n_a, n_b) \) are termed fluctuations, and the relation between entropies and log-probability for sample values is therefore called a fluctuation theorem.

We will isolate this leading-exponential term in the log-probability using the cumulant-generating function to shift the distribution, effectively projecting onto a sub-distribution within which \( (n_a, n_b) \) is the most-likely value. The sub-distribution, when normalized, would be the equilibrium distribution in a two-state system with a shifted chemical potential; the ratio between the generating function and the normalized distribution measures the overlap of the original distribution with the one appropriate to \( (n_a, n_b) \).

It will be the Legendre transform of this cumulant-generating function that gives the fluctuation probability to observe \( (n_a, n_b) \) in the original equilibrium distribution, and expresses this probability as a difference of entropies. The Legendre transform of the cumulant-generating function is known, in some domains of quantum field theory, as the quantum effective action, and we will adapt that term here, calling it the ‘stochastic effective action’. (For more context and the relation to literature, see appendix A.) Although it is only a difference of static entropies in the equilibrium ensemble, the stochastic effective action will become dynamical in ensembles of histories, where it will be the strict counterpart to the quantum effective action.

3.1. The equilibrium distribution of the two-state stochastic process

At an equilibrium steady state the solution to the master equation (3) is the binomial distribution

\[
\rho_{n_a,n_b}^\text{eq} = \frac{k_a^{n_a} k_b^{n_b}}{(k_a + k_b)^N} \binom{N}{n_a} \binom{N}{n_b}
\]

(4)

\[
= \rho_a^n \rho_b^n \binom{N}{n_a} \binom{N}{n_b}.
\]
Total particle number $N = n_a + n_b$ is conserved by all terms in the transfer matrix of equation (3). The equilibrium occupation fractions are

\[
\tilde{\nu}_a \equiv \frac{k_-}{k_+ + k_-} = e^{-\beta \mu_a^b} / Z_1,
\]

\[
\tilde{\nu}_b \equiv \frac{k_+}{k_+ + k_-} = e^{-\beta \mu_b^a} / Z_1,
\]

(5)
in which

\[
Z_1 \equiv e^{-\beta \mu_a^b} + e^{-\beta \mu_b^a}
\]

(6)
is called the partition function \[11\] for a one-particle ensemble in this two-state system.

The Gibbs free energies for non-interacting particles scale linearly (that is, they are ‘extensive’) in particle number \[11\], so the structural terms in the large-deviations formulae for fluctuation probabilities will be functions of the ratios

\[
\hat{n}_a \equiv \frac{n_a}{N},
\]

\[
\hat{n}_b \equiv \frac{n_b}{N}.
\]

(7)

In both steady-state and time-dependent probability distributions, roman $n_a$, $n_b$, $\hat{n}_a$, $\hat{n}_b$ will be used for discrete particle-number indices, respectively, un-normalized or normalized by $N$. When the description of distributions is transferred to the generating function, the corresponding continuous indices will be $n_a$, $n_b$ for absolute number, and $\nu_a$, $\nu_b$ for relative numbers corresponding to the definitions (7).

For dynamical as for static systems, it is convenient to study open-system properties by considering an open system and its environment to be components in a larger closed system. Here the closed system will be defined by $N$ as a parameter, and we introduce the stochastic variable under the reaction $n \equiv (n_b - n_a)/2$, so that

\[
n_a = \frac{N}{2} - n,
\]

\[
n_b = \frac{N}{2} + n.
\]

(8)

When only $n$ is denoted explicitly, the distribution $\rho_{n_a,n_b}$ will be indexed $\rho_n$. The relative particle-number asymmetry is called the partition function \[11\] for a one-particle ensemble in this two-state system.

The equilibrium distribution (4) may be cast in a variety of instructive forms. Using the relation (2) of the rate constants for all numbers will be indicated with overbars.

\[
\rho_{n_a,n_b}^{\text{eq}} \approx \frac{1}{\sqrt{2\pi N \tilde{n}_a \tilde{n}_b}} e^{-N \tilde{D}(\tilde{n}|\tilde{b})}
\]

\[
= \frac{1}{\sqrt{2\pi N \tilde{n}_a \tilde{n}_b}} e^{-N \tilde{D}(n|b)}
\]

\[
= \frac{1}{\sqrt{2\pi N \tilde{n}_a \tilde{n}_b} Z_1^N} e^{-\beta n_a (\mu_a^b + \tau \log \tilde{n}_a) - \beta n_b (\mu_b^a + \tau \log \tilde{n}_b)}
\]

\[
= \frac{1}{\sqrt{2\pi N \tilde{n}_a \tilde{n}_b} Z_1^N} e^{N \log(N/Z_1) \beta} - \beta n_a \mu_a - \beta n_b \mu_b
\]

\[
= e^{N \log(N/Z_1)} \left( \frac{n_a + n_b}{2\pi n_a n_b} \right)^{-N/2} \beta e^{-\beta \tilde{G}_a + \tilde{G}_b}.
\]

(9)

In the second line, $D(\tilde{n} \parallel \tilde{n})$ is the Kullback–Leibler divergence \[49\], in which $\tilde{n}$ and $\tilde{n}$ stand for the distributions with coefficients $(\tilde{n}_a, \tilde{n}_b)$, $(\tilde{n}_a, \tilde{n}_b)$, respectively. The $n_a$- and $n_b$-particle chemical potentials add concentration corrections to the entropy in the one-particle potentials, as

\[
\mu_a = \mu_a^1 + k_B T \log n_a,
\]

\[
\mu_b = \mu_b^1 + k_B T \log n_b.
\]

(10)

By comparing the second with the last-two lines of equation (9), we see that the minimum of the Gibbs free energies of the subsystems over $n$ is

\[
\beta \min_n [G_a + G_b] \equiv \beta \min_n [n_a \mu_a + n_b \mu_b] = N \log \frac{N}{Z_1}.
\]

(11)

The one-particle minimum expressed in terms of fractional occupancies, which is the descaled version at any $N$, gives an $N$-independent relation between the chemical potential per particle and the one-particle partition function:

\[
\min_\tilde{n} \left[ \tilde{n}_a (\mu_a^1 + k_B T \log \tilde{n}_a) + \tilde{n}_b (\mu_b^1 + k_B T \log \tilde{n}_b) \right] = -k_B T \log Z_1.
\]

(12)

These are the standard relations for ideal gases or dilute solutions.

3.1.1. The aggregation of state variables and the fluctuation probability. The local-equilibrium approximation for the two-state system allows us to approximate the log-probabilities for non-equilibrium configurations of $(n_a, n_b)$ by the sum of free energies for the individual wells. At the minimizing value of $(n_a, n_b)$ for this sum, the equilibrium free energy for the composite system is attained. We may therefore express the minimum joint free energy per particle, using equation (11), as a definition for the single-particle chemical potential for the equilibrated system, in a form equivalent to equation (10):

\[
\frac{1}{N} \min_n [G_a + G_b] \equiv \mu_{a,b} = -k_B T \log Z_1 + k_B T \log N
\]

\[
= \mu_{a,b}^1 + k_B T \log N.
\]

(13)

Here $\mu_{a,b}^1$ is the whole-system counterpart to the one-particle chemical potentials $\mu_a^1$ and $\mu_b^1$ for subsystems in the local-equilibrium approximation.

The density values in the equilibrium distribution (9) may then be written as exponentials of the (system + environment) entropies of equation (B5), as

\[
\rho_{n_a,n_b}^{\text{eq}} \approx \frac{n_a + n_b}{2\pi n_a n_b} e^{-\beta (G_a + G_b)}
\]

\[
\approx e^{\beta (G_a + G_b)} \left( \frac{n_a + n_b}{2\pi n_a n_b} \right)^{-N/2} \beta e^{-\beta (G_a + G_b)}.
\]

(14)
As explained in appendix B, all three Gibbs free energies are functions of intensive $k_b T$ and $p$, and of extensive arguments $n_a$, $n_b$, and $N$. Since total energy is controlled by the environment temperature, it is the entropy components of these $G$ values for the subsystems, as functions of $n_a$ and $n_b$, which control the difference of $G_a + G_b$ from $G_{a; b}$.

3.1.2. Entropies of equilibrium and residual fluctuations. The leading-exponential approximation of large-deviations scaling separates extensive entropies of the subsystems, which were defined into the parameters of the two-state stochastic process from coarse-graining the continuum model, from entropies due to chemical fluctuation, which are sub-extensive. To see this, following any standard thermodynamics text [11], we write any of the one-particle chemical potentials $\mu^1 \equiv h^1 - k_b T s^1$, in which $h_i$ is the specific enthalpy and $s^1$ is the specific entropy. This decomposition yields a relation between subsystem and whole-system free energies at equilibrium, which is

$$h_{a; b}^1 \equiv \tilde{n}_a h_a^1 + \tilde{n}_b h_b^1, \quad s_{a; b}^1 \equiv \tilde{n}_a s_a^1 + \tilde{n}_b s_b^1 - \tilde{n}_a \log \tilde{n}_a - \tilde{n}_b \log \tilde{n}_b.$$  

The free energy in the thermodynamic limit is then given by

$$G_{a; b} = N \left( h_{a; b}^1 - k_b T s_{a; b}^1 + k_b T \log N \right),$$

which is extensive in particle number, if we think of the log $N$ term as being set by pressure. In comparison, the Shannon entropy of the full distribution over fluctuations contains a term from the normalization of the exponential in equation (14), due to its width:

$$- \sum_n \rho_n^e \log \rho_n^e \approx \frac{1}{2} \left[ 1 + \log \left( 2 \pi N \tilde{n}_a \tilde{n}_b \right) \right].$$

This correction, being only logarithmic, is sub-extensive in $N$.

3.2. Generating functions and the stochastic effective action

A moment-generating function—or ‘ordinary power-series generating function’ [50]—for a distribution indexed on the two numbers $n_a$ and $n_b$ has two complex arguments, and is written

$$\psi(z_a, z_b) \equiv \sum_{n_a, n_b} z_a^{n_a} z_b^{n_b} \rho_{n_a, n_b}. \quad \text{(18)}$$

To study the properties of $\rho_n$, at fixed $N$, recognizing that $z_a^{n_a} z_b^{n_b} = (z_a z_b)^{n_a + n_b}$, we may set $z_a z_b \equiv 1$ and denote $\tilde{z}_a z_b / z_a \equiv z$. At equilibrium we will be interested only in the one-argument function of $z$. However, as we pass to dynamical descriptions, it will remain convenient in some cases to retain both variables $z_a$ and $z_b$, even if they are applied to a distribution with support on only one value of $N$.

The weight factors $z^n$ have an effect similar to shift in the subsystem chemical potentials, which will recur repeatedly in our analysis. Therefore we denote $z = e^\theta$, and write the one-variable generating function as

$$\psi(z) = \sum_n z^n \rho_n^e = \sum_n \left( \tilde{n}_a \sqrt{z} \right)^n \left( \tilde{n}_b \sqrt{z} \right)^n \frac{N}{n_a} \frac{N}{n_b} \left( \frac{Z_1}{Z_1} \right)^N \sum_n \tilde{n}_a z_a^{n_a} \tilde{n}_b z_b^{n_b} \frac{N}{n_a} \frac{N}{n_b}.$$ \quad \text{(19)}$$

Here new normalized fractions in the presence of $q$—which will be referred to as a source—are defined by

$$\tilde{n}_a \equiv \frac{\tilde{n}_a e^{-q/2}}{\tilde{n}_b e^{-q/2} + \tilde{n}_b e^{q/2}} = \frac{e^{-\beta \mu^1_a + q/2}}{Z_1^{(q)}}, \quad \tilde{n}_b \equiv \frac{\tilde{n}_b e^{q/2}}{\tilde{n}_b e^{-q/2} + \tilde{n}_b e^{q/2}} = \frac{e^{-\beta \mu^1_b - q/2}}{Z_1^{(q)}},$$

and the associated one-particle partition function with source $q$ is

$$Z_1^{(q)} \equiv e^{-\beta \mu^1_a - q/2} + e^{-\beta \mu^1_b - q/2}. \quad \text{(20)}$$

The sum in the third line of equation (19) equates to unity, as for any normalized binomial, but it is instructive to use what was learned in forming equation (14) to recast the sum and prefactor together in terms of a normalized distribution and a ‘penalty’ term, as

$$\psi(z) \approx e^{\beta G_a + \beta G_b - \beta G_{a; b}} \sum_n e^{\beta G_{a; b}^{(n)}} \sqrt{\frac{\tilde{n}_a + \tilde{n}_b}{2 \pi n_a n_b}} e^{-\beta (G_a + G_b + G_{a; b}^{(n)})}. \quad \text{(22)}$$

In equation (22) the subsystem free energies are defined at any $n_a, n_b$ as

$$G_a^{(q)} = G_a + n_b k_b T \frac{q}{2}, \quad G_b^{(q)} = G_b - n_b k_b T \frac{q}{2}. \quad \text{(23)}$$

We wish to introduce $G_{a; b}^{(q)}$ as the minimum of $G_a^{(q)} + G_b^{(q)}$ over $n$, as before. However, for discrete $n$, this gives a discontinuous function of $q$. The thermodynamic usage of $G_{a; b}^{(q)}$ is as a macroscopic function of its intensive state variables, and therefore it will save intermediate steps and notation simply to define $G_{a; b}^{(q)}$ as the minimum over $n$ treated as a continuous variable, whose minimizing argument will then be a continuous function of $q$.

For such binomial distributions or their multinomial generalizations, sources of the form $k_b T \tilde{q} = q / \beta$ behave as shifts in chemical potential, in this case split evenly between subsystems $a$ and $b$. The ‘penalty’ term is expressed as a function of $(G_{a; b} - G_{a; b}^{(q)})$: the minimum chemical work needed to convert the system with potential difference $\mu_b - \mu_a$ and equilibrium $\tilde{n}$ to one with potential difference $\mu_b - \mu_a - q / \beta$ and an equilibrium $\tilde{n}$ determined by the new potentials. $\beta (G_{a; b} - G_{a; b}^{(q)})$ is also the log-probability to obtain the shifted distribution from the original through the set of weights $z^n$.

The penalty function is referred to as the cumulant-generating function and denoted $\Gamma(q)$. It is defined from the moment-generating function $\psi$ by the relation

$$\psi(z) \equiv e^{-\Gamma \log z} = e^{-\Gamma(q)}. \quad \text{(24)}$$
From the definition (19) of the moment-generating function it follows that

\[
\frac{d \log \psi(z)}{d \log z} = - \frac{d \Gamma(q)}{dq} = (n_q) = n^{(q)},
\]

in which we introduce the continuous counterpart \(n^{(q)}\) as both the gradient of \(\Gamma\) and the expectation of \(n\) under the equilibrium distribution shifted by \(z\).

From equation (22), the cumulant-generating function is just the Gibbs free-energy difference

\[
\Gamma(q) = \beta G_{\mu,\mu}^{(q)} - \beta G_{\mu,\mu}.
\]

Recasting equation (25),

\[
- \frac{d \Gamma(q)}{dq} = \frac{d G_{\mu,\mu}^{(q)}}{dq} = n^{(q)},
\]

we recover the usual relation from equilibrium thermodynamics [11], that the gradient of the Gibbs free energy with respect to the chemical potential is the particle number.

For reference in later sections, we may compute closed forms for the various quantities. Define \(\tilde{\mu} = \mu_1 - \mu_2\), dual to the relative particle-number difference \(\bar{n}\). Then

\[
n^{(q)} = \frac{N}{2} \tanh \frac{1}{2} (q - \beta \tilde{\mu}),
\]

and

\[
\Gamma(q) = N \left[ \log \cosh \frac{\beta \tilde{\mu}}{2} - \log \cosh \frac{1}{2} (q - \beta \tilde{\mu}) \right].
\]

In continuum field theories with many particles and nonlinear interactions among them, it is often necessary to approximate the moment- and cumulant-generating functions by series expansions in the variance of the Gaussian approximation to fluctuations. In such an expansion, the gradient of \(\Gamma\) yields all of the connected graphs giving \(n^{(q)}\), while the gradient of \(\psi\) gives a sum over all graphs (see [22, chapter 16]).

3.2.1. The stochastic effective action for single-time fluctuations. Appendix B reviews the fact that the Gibbs free energy is a Legendre transform of the entropy. Thus, the entropy is the converse Legendre transform of the Gibbs free energy. We may therefore expect that by Legendre transforming \(\Gamma(q)\), we will arrive at a direct expression for the entropy differences that govern internal fluctuations of particle number, without reference to external temperature or pressure.

The Legendre transform of the cumulant-generating function \(\Gamma\) is known as an effective action [22]. When it is computed for the single-time binomial distribution it hardly seems to justify its name if we expect an action in the sense of Hamiltonian dynamics. However, it will become just such an action in the time-dependent ensemble. Here we introduce the Legendre transform for its statistical meaning, and later we introduce the dynamical version.

The definition is

\[
S_{\text{eff}}(n) = [\Gamma(q) + n q]_{q=q^{(n)}},
\]

in which \(q^{(n)}\) denotes the inverse function of \(n^{(q)}\) from equation (27)\(^6\). From the gradient relation (25) it follows that

\[
\frac{d S_{\text{eff}}(n)}{dn} = q^{(n)}.
\]

Therefore \(S_{\text{eff}}\) must vanish at the mean value of \(n\) in the distribution \(\rho\) for which it is computed, because no source (i.e. \(q(n) = 0\)) is required to yield the equilibrium value as the mean.

Addition of the term \(n^{(q)} q\) to \(\Gamma\) in equation (30) cancels only the explicit \(q/\beta\) term in the shifted free energy \(G_{\mu,\mu}^{(q)}\), leaving the particle assignments \(n_a^{(q)}, n_b^{(q)}\) unchanged. The terms that remain are precisely those in the fluctuation theorem: they are the subsystem free energies evaluated at shifted \(ns\). The effective action may be written

\[
S_{\text{eff}}(n) = \beta G_{\mu,\mu}^{(q)} + \beta G_{\mu,\mu}^{(n)} - \beta G_{\mu,\mu}^{(N)}.
\]

In equation (32) the free energies \(G\) are now regarded as functions of the continuous-valued \(n_a\) and \(n_b\) rather than the discrete indices \(n_a\) and \(n_b\) on which the distribution is defined.

Referring back to the distribution over fluctuations in the original \(\rho_{n_a,n_b}\) of equation (14), we see that \(\exp(-S_{\text{eff}})\) directly extracts the leading-exponential dependence of the fluctuation probability. It omits sub-extensive normalization factors related to the width of the distribution. Therefore, the effective action directly expresses the large-deviations scaling for fluctuation probabilities. The log-probability approximated by equation (32) scales linearly in \(N\), and its structure is determined by the remaining \(N\)-invariant fractions \(\nu_a\) and \(\nu_b\).

For reference, in comparison with later expressions for the effective actions of fluctuating histories, the effective action for the equilibrium distribution evaluates to

\[
S_{\text{eff}}(n) = N \left[ \log \cosh \frac{\beta \tilde{\mu}}{2} - \log \cosh \frac{1}{2} (q^{(n)} - \beta \tilde{\mu}) \right] + \frac{q^{(n)}}{2} \tanh \frac{1}{2} (q^{(n)} - \beta \tilde{\mu}),
\]

in which \(q^{(n)}\) is evaluated by inversion of equation (28).

4. The Doi–Peliti construction for the dynamical two-state system

We now construct a second generating function and ensemble, for the time-dependent distribution \(\rho\) evolving under the master equation (3), rather than merely for its equilibrium steady state. The equilibrium fluctuation results of section 3 will reappear within this larger construction, as probabilities for histories conditioned on their behavior at a single instant but on no other information. Here, however, the single-time fluctuation probabilities will no longer be computed as

\(^6\) For the equilibrium distribution, and indeed all other distributions computed hereafter, this inverse will be unique. For problems in which it is not unique, such as occurring along the co-existence curves of first-order phase transitions, the Legendre transform is replaced by the Legendre–Fenchel transform [1, 2].
primitive quantities. Instead, they will arise as integrals of log-probability along the entire histories which are, most-likely, conditioned on achieving a particular deviation at a single time.

In keeping with the shift from states to histories, the cumulant-generating function and effective action in this section will be functionals, whose arguments are sequences of occupation numbers \((n_a, n_b)\). The description derived from the master equation will still only count particle numbers, and will not resolve identities. Unlike the equilibrium constructions, the path-space large-deviations formulae will not allow us to identify the natural path-entropy functions, for which we will require the caliber formulation of section 5. However, this section will introduce the remarkable F–W formulation of large-deviations theory as a Hamiltonian dynamical system, in which the stochastic effective action will become a genuine Lagrange–Hamilton action functional\(^7\).

4.1. Liouville time evolution and the coherent-state expansion for its quadrature

The reason to study generating functions at equilibrium is that the moments of the equilibrium distribution may be more relevant and robust descriptions of fluctuations than individual probability values \(\rho_{n_a, n_b}\). Similarly, the reason to use generating functions to study dynamics is that the basis of single-particle hops is often less informative than a basis in the collective motions of many particles.

The master equation formalism acts on probabilities in the basis of single-particle hops. The counterpart, which acts on the moment-generating function, is known as a Liouville equation. When specified in complete detail, the Liouville equation has the same information as its corresponding master equation. However, low-order approximations to the Liouville form will often contain more of the total information than similarly reduced approximations in the basis of single-particle hops. Such approximations are sometimes called the hydrodynamic limit [52]. Therefore, the Liouville form is the starting point for methods of Gaussian integration, Langevin equations, or other commonly used approximation schemes.

4.1.1. The master equation expressed as a function of mass-action rates. The two-state master equation (3) is an instance of a wider class of equations describing single-particle exchanges. A notation for the more general class is introduced here, both because it cleanly divides the particle-hopping terms associated with stochasticity from the probabilities which coincide with mass-action rates, and because it immediately generalizes to more complex reaction stoichiometries, such as those required by chemical-reaction networks. The master equation for the two-state system is written in this general form as

\[
\frac{\partial \rho_{\vec{n}_t}}{\partial t} = \sum_{i,j} \sum_{z_a, z_b} \left( e^{\beta n_i z_i - \beta n_j z_j} - 1 \right) r_{ji} \rho_{\vec{n}_t},
\]

where \(\vec{n}\) is a vector whose components give the number of particles of each type \(i \in [1, \ldots, I]\) (here \(\vec{n} = (n_a, n_b)\)). For the linear reaction model, the mass-action rates \(r_{ji}^8\)

\[
\begin{align*}
    r_{ni} &= k_n n_i \\
    r_{nb} &= k_b n_b 
\end{align*}
\]

describe the probability for particle transfer from state \(i\) to state \(j\). The form (34) extends immediately to arbitrary many-particle exchanges with rates that may involve powers of many different components of \(\vec{n}\), and to arbitrary network connections. The general methods derived below extend immediately to all those cases. Even the shortcuts we will introduce, to pass directly from the form of the master equation to the action functional of F–W theory, apply with no changes\(^9\).

4.1.2. Definition of the Liouville operator from the transfer matrix. This section sketches the conversion from number terms and index shifts in the master equation, to the equivalent polynomials and differential operators in the Liouville equation. It then converts the representation on polynomials to the representation introduced by Masao Doi [4, 5], in terms of raising and lowering operators in an abstract linear vector space. The systematic construction of Liouville forms from master equations is now standard [16, 37], and its form for the linear mass-action kinetics of equation (35) is the simplest possible.

In the vector notation, the generating function at a single time becomes a function of a vector \(\tilde{z}\) whose components correspond to those of \(\vec{n}\). Here the moment-generating function is

\[
\psi (\tilde{z}) = \sum_{\vec{n}} \prod_{i \in \{a, b\}} z_i^{n_i} \rho_{\vec{n}}. 
\]

Time evolution under equation (34) implies time evolution of \(\psi\) according to

\[
\frac{\partial \psi (\tilde{z})}{\partial t} = \sum_{\vec{n}} \prod_{k \in \{a, b\}} z_k^{n_k} \frac{\partial \rho_{\vec{n}}}{\partial t}
\]

\[
= \sum_{i,j} \sum_{z_a, z_b} \left( z_j \frac{\partial}{\partial z_i} - 1 \right) \sum_{k \in \{a, b\}} \prod_{\vec{n}} z_k^{n_k} r_{ji} \rho_{\vec{n}},
\]

\[
= \sum_{i,j} \left( z_j \frac{\partial}{\partial z_i} - 1 \right) r_{ji} \left( z_i \frac{\partial}{\partial z_i} \right) \sum_{\vec{n}} \prod_{k \in \{a, b\}} z_k^{n_k} \rho_{\vec{n}}
\]

\[
= - \mathcal{L} \left( \tilde{z}, \frac{\partial}{\partial z} \right) \psi (\tilde{z}).
\]

\(^8\) We write the mass-action rates as going from \(i\) to \(j\) with this index ordering, because they will appear again later as entries in a transfer matrix, which is naturally written as acting from the left on column vectors of occupation numbers \(n_i\).

\(^9\) The reader is cautioned that in cases where multiple reactants of the same type participate in a reaction, the assumption of separation of timescales may be inconsistent with using equilibrium state variables in the minimal way they are used here. An example is provided in [53], where the local-equilibrium approximation may still be used, but it requires replacing the discrete master equation with a full Boltzmann transport equation for continuous-valued positions and momenta. An alternative solution is to add time-local corrections known as ‘contact terms’ to represent the correct counting of many-particle states. For the linear system such complications do not arise, so we will not expand on them further here.
Here we have written out the functional dependence of $r_{ij}$ on the number indices of the particle species entering half-reactions explicitly, to show how those number indices are replaced by products $z_i \partial / \partial z_i$ acting on the basis polynomials of the generating function. Successive lines of equation (37) reflect the action of successive terms in the master equation (34). The extension of these steps to multi-species reactions also follows a standard form [16], of which our example is representative. The differential operator $L(\vec{z}, \partial / \partial \vec{z})$ is the Liouville operator for this stochastic process.

Time evolution of the density $\rho_0$ over an interval $[0, T]$ is performed by taking the quadrature of equation (37), which we may think of as being performed over a sequence of short time intervals of length $\delta t$:

$$\psi_T = T e^{\int_0^T \! dt \cdot L \cdot \psi_0} = T \prod_{k=1}^T e^{\delta t \cdot L} \cdot \psi_0. \quad (38)$$

$T$ denotes time-ordering in the product, and we will use the same notation when the product of exponential terms $e^{\delta t \cdot L}$ is written as the exponential of a sum or integral. Such expressions are known as time-ordered exponential integrals. For the Liouville operator with constant coefficients, time-ordering serves no explicit purpose, but when time-dependent sources are introduced below it will become necessary.

We may efficiently approximate the product (38) by interposing a complete distribution of generating functions between each of the small increments of time evolution in the second line, which we develop in the next subsection. Doing so, however, introduces a distinct set of arguments at each time, which are cumbersome to work with. Therefore, at intermediate times between 0 and $T$, it is conventional to adopt an abstract notation for the complex vectors and derivatives [4, 5], which more clearly reflect the nature of the generating function as a vector in a normed linear space (a Hilbert space). The correspondence of the elementary monomials,

$$z_j \leftrightarrow a_j^\dagger, \quad \partial / \partial z_j \leftrightarrow a_j^\dagger, \quad (39)$$

reflects the property that complex variables and their derivatives satisfy the algebra of raising and lowering operators familiar from the quantum harmonic oscillator10.

$$\left[ \partial / \partial z_j, z_j \right] \leftrightarrow \left[ a_j^\dagger, a_j \right] = \delta_j^j. \quad (41)$$

Polynomials built from these variables live in a function space built on a ‘vacuum’ which is simply the number 1, denoted

$$1 \leftrightarrow [0]. \quad (42)$$

The conjugate operation to creating a generating function is the evaluation of the trace—generally with moment-sampling operators to extract its moments—so that the conjugate operator to the right-hand vacuum (42) is an integral:

$$\int d^l \vec{z} \cdot \delta(\vec{z}) \leftrightarrow [0]. \quad (43)$$

From these definitions an entire function space with inner product can be built up, as reviewed in [16, 17]11.

### 4.1.3. The coherent-state expansion.

The transformation from discrete number-states to generating functions is the Laplace transform. It may be applied within the discrete time slices of the quadrature (38), where it makes use of the Laplace transforms of intermediate Poisson distributions, which are known as coherent states. It has become conventional in the D–P literature to denote the mean values of these Poisson distributions with the field $\phi$; for a multi-state system, we index them with a complex-valued vector field $\phi$. The conjugate vectors to these Poisson distributions are moment-sampling operators, weighted by Hermitian conjugate field variables denoted $\phi^\dagger$.

The $\phi^\dagger$ will have the property that, dynamically, they propagate information backward in time from final data imposed by the weights $z_a, z_b$. The interpretation of this property is that the moment-sampling operators capture conditional distributions at earlier times, conditioned on the final values they produce. The fields $\phi$ and $\phi^\dagger$ will turn out to be the position fields and their conjugate-momentum fields in one version of the F–W theory, and the Hamiltonian under which they evolve will be the Liouville operator. The way evolution under the dynamical system is made consistent with the ‘backward’ propagation of information, by the conjugate momentum, is that the momentum variables will typically have unstable evolution forward in time, while the position variables will evolve in stable directions.

In this section we construct the coherent-state expansion for the quadrature (38), which is due to Peliti [6, 7].

The Liouville operator is a function of raising and lowering operators $\{a, a^\dagger\}$ so the convenient expansion of equation (38) will be given by a basis of eigenstates of these operators. The coherent states are constructed to be such eigenstates. The right-hand coherent state is defined as

$$|\vec{\phi}\rangle = e^{-(\vec{\phi}^\dagger \cdot \vec{\phi})/2} e^{\vec{\phi}^\dagger \cdot \vec{\phi}} \cdot |0\rangle$$

$$= e^{-(\vec{\phi}^\dagger \cdot \vec{\phi})/2} \sum_{M=0}^{\infty} \left( \frac{\vec{\phi}^\dagger \cdot \vec{\phi}}{M!} \right)^M |0\rangle$$

$$= \prod_{m=1}^{I} \left( e^{-(\phi_m^\dagger \phi_m)/2} \sum_{n_m=0}^{\infty} \frac{\phi_m^{n_m}}{n_m!} a_m^{n_m} \right) |0\rangle. \quad (44)$$

11 It is conventional to denote the inner product for classical stochastic processes with round braces, as in $\langle 0 \rangle$, to distinguish them from the quantum bra-ket notation $|0\rangle$ [54]. This notation reflects the fact that it is not in the operator algebra, but in the space of functions and the inner product, that the distinction between classical and quantum mechanical systems lies, as discussed in the introduction.
The components of its complex parameter vector \( \tilde{\phi} \) correspond to those of \( \tilde{z} \). From the commutator algebra (41), and the fact that all \( \alpha' \leftrightarrow \beta' \) annihilate the right vacuum (42), it follows that equation (44) does define an eigenstate of all the lowering operators \( \alpha' \) with corresponding eigenvalues \( \phi' \):\[ a' \mid \tilde{\phi} \rangle = \phi' \mid \tilde{\phi} \rangle. \] (45)

The left-hand coherent state dual to equation (44) is given by\[ \langle \phi \rangle = (0) \sum_{M=0}^{\infty} \frac{(-\langle \phi \rangle)M}{M!} e^{-\langle \phi \rangle / 2}. \] (46)

Equation (46) is likewise checked to be an eigenstate of the raising operators, with eigenvalues \( \phi_j \):\[ \langle \phi_j \rangle = (0) \langle a_j \rangle = \phi_j \langle \phi \rangle. \] (47)

The presence of \( \bar{\alpha} \) corresponding to \( \partial/\partial \bar{z} \) in equation (46) gives the left-hand coherent state the interpretation of a moment-sampling operator. This state displaces any argument \( a_j \) in the state that it acts on (through the inner product), by a summand \( \phi_j \). It then sets the original \( a_j \) to zero because all left-hand states include the trace defined by the left vacuum (43).

The sum of outer products of a left-hand coherent state and its dual right-hand coherent state gives a representation of the identity operator as an over-complete integral over states: \[ \int d^d\phi d^d\phi \pi^d \langle \phi \rangle \langle \phi \rangle = I. \] (48)

The result of taking the inner product of equation (48) with any state (\( \psi \)) on the right is that the moment-sampling operator (\( \langle \phi \rangle \)) simply transposes the weights that it extracts from \( \psi \) onto the left-coherent states (\( \phi \)) in the expansion (48).

If we insert a complete set of states in this form between every term in the product (38), we express the moment-generating function at time \( T \) as an integral over all intermediate values of the field variables \( \phi, \tilde{\phi} \), of the form \[ \psi(\phi, \tilde{\phi}) \equiv e^{-\frac{1}{2} a^\dagger a + \sum\tilde{\phi}^\dagger 0 \tilde{\phi}} = \int_0^T D\phi_0 D\tilde{\phi}_0 D\phi_T D\tilde{\phi}_T e^{i\int_0^T \left[ -i\tilde{\phi}^\dagger 0 \tilde{\phi} - \phi^\dagger T \phi - \phi_0^\dagger \phi_0 - F_{\psi}(\phi_0, \tilde{\phi}_0, \phi_T, \tilde{\phi}_T) \right]} dt. \] (49)

It requires some algebra, but no conceptual difficulties, to show that the action in equation (49) is given by\[ S = \int dt \left[ -i \left( \partial_t \phi_0^\dagger + \tilde{\phi}_0^\dagger \phi_0 + \tilde{\phi}_0 \phi_0^\dagger \right) + L \right]. \] (50)

The terms \( \partial_t \phi_0, \tilde{\phi}_0 \) come from the inner products of states (\( \langle \phi \rangle \)) and (\( \langle \tilde{\phi} \rangle \)) at successive times, and the evaluation of the Liouville operator sandwiched between these states converts \( \tilde{L} \) into the quantity serving as the Hamiltonian. Its form,\[ L = k_+ \left( \phi_0^\dagger \phi_0 + \phi_0^\dagger \phi_0 \right) + k_- \left( \phi_0^\dagger \phi_0 + \phi_0^\dagger \phi_0 \right) \] (51) is obtained directly from the penultimate line of equation (37) with the mass-action rates (35). It is a general feature, which extends to nonlinear rate equations, that factors of \( \tilde{z}_i \) in the rate functions on the reactant side cancel factors \( 1/\tilde{z}_i \) from the shift operators (the leading parenthesized term in equation (37)).

### 4.2. Standard computations of the Freidlin–Wentzell quasipotential

Equations (49)–(51) are the stochastic-process reformulation of the single-time generation function (18). The Legendre transform \( \log \psi(\phi, \tilde{\phi}) \) continues to be the equilibrium effective action \( S_{\text{eff}}(n_a, n_b) \) of equation (30). The field integral (49) for these quantities will in general be dominated by the stationary paths of the action (50). The value of \( S \) in equation (50), on the stationary path, is known in F–W theory as the quasi-potential, because it generalizes the Gibbs free energy from equilibrium thermodynamics. The quasipotential is widely used to approximate the solutions to diffusion equations on the boundaries of trapping domains [3, 21, 38].

The field integral of the last section has converted an irreversible stochastic process into a deterministic dynamical system perturbed by fluctuations. Any such Hamiltonian system offers several choices of representation, related under the changes of (field) variables known in Hamiltonian dynamics as canonical transformations [51]. In addition to the canonical variables of the Hamiltonian dynamics, this action functional also admits an unusual ‘kinematic’ interpretation, in which escape trajectories are represented as rolling in energy potential, even when they move opposite to the direction of classical diffusion. Finally, the leading expansion about the mean behavior in the integral (49) comes from Gaussian fluctuations, which are readily converted to standard approximation methods such as the Langvin formulation. For the bilinear action, the Langvin approximation in the original fields \( \phi, \tilde{\phi} \) is exact, though in other variables or for more complex reactions it will not be. We will consider each of these aspects of the D–P field integral, and the F–W quasipotential, in turn in this section.

All introductions to F–W theory that I have seen in the reaction–diffusion literature compute the quasipotential by studying the stationary points in the field variables \( \phi, \tilde{\phi} \) [16, 17], or in the equivalent operator expectations [37]. For the two-state system, this choice is technically the easiest, because the bilinear functional integral (49) is manifestly the ‘simple harmonic oscillator’ of stochastic processes. However, field variables are the least intuitive choice, because individually neither \( \phi \) nor \( \tilde{\phi} \) represents an observable quantity. (Recall that the function of \( \phi \) as the expectation value of a Poisson distribution is only propagated through time by the moment-sampling weight given by \( \phi \).) An elementary canonical transformation to action-angle variables [51] will produce fields which, unlike \( \phi \) and \( \tilde{\phi} \), correspond directly to observed average number occupancies, and to a conjugate momentum that has the physical interpretation of a chemical potential.

12 The Gibbs free energy and other Legendre transforms of the entropy are conventionally known as thermodynamic potentials, by yet a further analogy with the potential energy in mechanics.

13 A thorough treatment of this kinematic potential is provided in [55].
4.2.1. Diagonalization and descaling in field variables.

The quasipotential provides the leading log-probability for fluctuations. When large-deviations scaling holds, the value of the quasipotential on its stationary path should factor into an overall scale factor, and a scale-independent rate function. This scaling is particularly easy to achieve for the Gaussian functional integral (49) of the two-state model. The field variable \( \phi \) is rescaled to remove a factor \( N \), which may be moved outside the entire action (50), leaving a bilinear functional integral (49) of the two-state model. The field \( \phi \) and \( \phi^\dagger \) are unchanged.

Field rescaling is one of several changes of variable that may be made in the bilinear field basis given by \( \phi \) and \( \phi^\dagger \). Another is a rotation of components from \( \phi_a, \phi_b \) to a basis in which the independent dynamical quantity \( n \equiv (n_b - n_a)/2 \) may be separated from the non-dynamical conserved quantity \( N \). However, this rotation must be used with care, as certain terms needed to define correlation functions in terms of the equilibrium distribution disappear from the naïve continuous-time limit, and must be reconstructed from the explicit discrete-time forms [39]. We will also see that correct calculation of the cumulant-generating functional can rely on contributions from the apparently non-dynamical number \( N \), depending on how total derivatives are handled in the action (50).

In order to work out the correct treatment of such technical issues, we will begin in this section with the generating function has been understood, and move to a set of transformed basis corresponding in a similar manner to \( n \) and \( N \), by the orthogonal transformation

\[
\phi \equiv (\phi_b - \phi_a)/2, \\
\phi^\dagger \equiv \phi_b^\dagger - \phi_a^\dagger, \\
\Phi \equiv \phi_b + \phi_a, \\
\Phi^\dagger \equiv (\phi_b^\dagger + \phi_a^\dagger)/2.
\]  

Here the relation of absolute to relative number fields repeats the notation used to relate absolute to relative number indices \( n = n/N \). Even though the relation between variables \( \phi, \phi^\dagger \) and the expected number indices is not simple, in general it is the \( \phi \) variables that carry the scaling with total system size.

A final coordinate transformation reflects the fact that the coordinate timescale \( \tau \) is not characteristic of the dynamics for either average behavior or fluctuations. We therefore introduce a rescaled time variable \( \tau \), with Jacobean

\[
d\tau = k_\pm e^{-\beta(\mu_1 - \mu_\pm)} = \frac{e^{-\beta \mu_1}}{\nu_\pm},
\]

as the physically relevant time variable. Note that this natural timescale for rare events relates the transition-state chemical potential to that for the equilibrated joint system, defined from equation (13).

In these new variables the action (50) becomes

\[
S = N \int \, d\tau \left[ -\partial_\tau \Phi^\dagger \dot{\phi} - \partial_\Phi \phi^\dagger \dot{\phi} + \phi^\dagger \left( \phi - \nu \dot{\phi} \right) \right] = N \int \, d\tau \left( -\partial_\Phi \phi^\dagger \dot{\phi} - \partial_\phi \phi^\dagger \dot{\phi} + \dot{\mathcal{L}} \right).
\]  

4.2.2. Calculation of the two-argument cumulant-generating function.

The leading large-\( N \) exponential dependence of the functional integral (49) comes from the stationary point of the action and the boundary terms at times \( 0 \) and \( T \). The stationary-point conditions are vanishing of the first variational derivatives of the action (55), which take the form

\[
\partial_\tau \Phi^\dagger = -\frac{\partial \dot{\mathcal{L}}}{\partial \Phi} = -\nu \phi^\dagger, \\
\partial_\Phi \phi^\dagger = -\frac{\partial \dot{\mathcal{L}}}{\partial \Phi^\dagger} = 0, \\
\partial_\phi \phi^\dagger = \frac{\partial \dot{\mathcal{L}}}{\partial \phi^\dagger} = \phi^\dagger, \\
\partial_\phi \phi = -\frac{\partial \dot{\mathcal{L}}}{\partial \phi} = -\left( \phi - \nu \dot{\phi} \right).
\]  

Equation (56) is the promised conversion of the first-moment dynamics of the stochastic process (34) into a deterministic dynamical system with Hamiltonian \( \dot{\mathcal{L}} \). It follows immediately
from these equations and from the lack of explicit time-dependence in \( \hat{L} \), that this Liouville–Hamiltonian is a constant of the motion along the stationary path:

\[
\frac{d\hat{L}}{d\tau} = 0. \tag{57}
\]

The boundary terms at time \( \hat{T} \equiv T (k_+ + k_-) \) in the variation of the functional integral (49) vanish at \( \phi_{i+} = z_a \), \( \phi_{i-} = z_b \). The intermediate time-dependence of \( \phi^i \) is thus

\[
\phi^i = (z_b - z_a) e^{\tau - T}, \tag{58}
\]

and the corresponding solution for \( \Phi^i \) is

\[
\Phi^i = \frac{1}{2} (z_b + z_a) + \bar{v} (z_b - z_a) (1 - e^{\tau - T}). \tag{59}
\]

The field \( \hat{\Phi} \) is non-dynamical, and a steady-state solution for the relative number field \( \phi \) in terms of \( \hat{\Phi} \) is therefore give by

\[
\hat{\phi} = \bar{v} \hat{\Phi}. \tag{60}
\]

The product \( \phi^a \phi^b + \phi^b \phi^a \) is the expectation of the total number operator, and therefore must equal \( N \). In the rotated and descaled basis, this equality takes the form

\[
1 = \Phi^a \Phi^b + \Phi^b \Phi^a,
\]

which may therefore be used to assign a value to \( \hat{\Phi} \) in terms of the arguments \( z_a, z_b \) of the generating function.

The equivalent expression for the relative number-operator difference \( (\phi^a \phi^b - \phi^b \phi^a) / N \) is then

\[
2v = \frac{1}{2} \phi^a \hat{\Phi} + 2 \phi^b \hat{\Phi}.
\]

Equation (62) is immediately solved from the boundary values (58,59) at time \( \hat{T} \) to recover equation (28) as

\[
2\nu_T = \tanh \frac{1}{2} \left( \log z - \beta \hat{\mu} \right). \tag{63}
\]

In terms of this final value for the function \( \nu \), the functional dependence at earlier times is given by

\[
\nu_T - \bar{v} = (\nu_T - \bar{v}) e^{\tau - \hat{T}}. \tag{64}
\]

The algebra of the preceding solution is simple and linear, and yet it is profoundly obscure as a representation of the physical distributions of random walkers in the two-state model. This obscurity is the reason we will soon abandon coherent-state variables. Note that the field \( \hat{\Phi} \)—naively corresponding to the observable \( n \)—is actually constant by equation (60). All particle-number dynamics in this solution comes from the fields \( \phi^i \) and \( \Phi^i \). These fields, known as response fields in the D–P literature [39], are acting to propagate information from the boundary condition at the final time \( \hat{T} \) backward into the interior of the functional integral, by selecting moments of the intermediate states with time-dependent weights.

The stationary-path solution (64) is the least-improbable sequence of fluctuations to have led to the final value \( \nu \). The single-time probability of \( \nu \) in turn results from the accumulation of probabilities for successive accumulating fluctuations in the integral (55) for \( S \). However, to identify the particle distribution in this solution requires incorporating the response fields, including the (strangely dynamical) response field \( \Phi^i \) associated with the (unchanging) total particle number \( N \).

To show that, despite the difficulties of interpretation, the quasipotential recovers the single-time fluctuation theorems, we evaluate the cumulant-generating function \( \Gamma_T \). The calculation is easiest if we take \( \hat{T} \gg 1 \) so that the initial condition \( \Gamma_0 \) may be evaluated on the equilibrium distribution. For the exact bilinear action (50) a conservation law significantly simplifies the calculations, although it again renders the correct answer in a most cryptic fashion.

We begin with the conservation law (57). To obtain a reference value for \( \hat{L} \) we note that in the equilibrium distribution where the mass-action equations balance, \( \hat{L} = 0 \). The action (55) is bilinear in the fields \( \phi \) and \( \phi^i \), so that it has a simple relation to either of its gradients:

\[
\hat{L} = \sum_{i=a,b} \phi_i \frac{\partial \hat{L}}{\partial \phi_i} = \sum_{i=a,b} \frac{\partial \hat{L}}{\partial \phi_i} \phi_i. \tag{65}
\]

Therefore, the stationary-point conditions, together with \( \hat{L} = 0 \), imply \( S = 0 \) when evaluated on any stationary path. Thus the only contribution to \( \Gamma_T (\log \phi_{a0}, \log \phi_{b0}) \) must come from the boundary term \( \Gamma_0 (\log \phi_{a0}, \log \phi_{b0}) \) in equation (49). Since the initial distribution has support only on a single value \( n_a + n_b = N \), from the definition (18) we may write

\[
e^{-\Gamma_0 (\log \phi_{a0}, \log \phi_{b0})} = e^{\frac{1}{2} \log \phi_{a0} \phi_{b0}} e^{-\Gamma_0 (\log \phi_{a0}, \log \phi_{b0})}, \tag{66}
\]

in which the single-argument cumulant-generating function corresponds to the logarithm of \( \psi (z) \) in equation (19). From equation (58) at \( \tau \to 0 \) and large \( \hat{T} \), \( \phi^b_0 - \phi^a_0 \to 0 \), and as we will see \( \phi^a_0 \) and \( \phi^b_0 \) remain nonzero, so \( \log (\phi^b_0 / \phi^a_0) \to 0 \). Therefore, for the equilibrium distribution \( \Gamma_0 (\log \phi^b_0 / \phi^a_0) \to 0 \) as well. The only contribution to the generating function at time \( \hat{T} \), even with \( z_a z_b \equiv 1 \), is the term \( \frac{1}{2} \log (\phi^a_0 \phi^b_0) \) corresponding to the total number, which is not even dynamical!

In the same limit \( e^{-\hat{T}} \to 0 \), setting \( z_a z_b = 1 \), we have

\[
\phi^a_0 \to \phi^b_0 \to \phi^i_0 \to \frac{\cosh \frac{1}{2} (\log z - \beta \hat{\mu})}{\cosh \frac{1}{2} \beta \hat{\mu}}. \tag{67}
\]

15 Any other initial condition would decay toward the equilibrium distribution for sufficiently large \( \hat{T} \).
The resulting evaluation for the cumulant-generating function is then
\[
\Gamma_\hat{T} (\log z_a, \log z_b) = \Gamma_0 \left( \log \phi_{a0}^+, \log \phi_{b0}^+ \right)
\]
\[
= -\frac{N}{2} \log \left( \phi_{a0}^+ \phi_{b0}^+ \right)
\]
\[
\rightarrow N \left[ \log \cosh \frac{1}{2} \beta \mu - \log \cosh \frac{1}{2} (\log z - \beta \mu) \right],
\] (68)
recovering equation (29). We obtain the correct answer from a collection of surface terms, while the single-argument cumulant-generating functional that should have controlled dynamics dropped out. How shall we understand this?

4.2.3. Cancellation of surface terms, and the quasipotential as an integral of time-local log likelihoods. The puzzle of the Gaussian evaluation of the cumulant-generating function is solved by taking care with the freedom we have to include total derivatives in the field action. The particular choice that moves all fluctuation probabilities into the expected, single-variable cumulant-generating function \( \Gamma (\log z) \) also sets up the action-angle change of variables in the next section, which will isolate only the dynamical observables.

The property \( S = 0, \) together with the general feature \( \hat{L} = 0, \) implies for a bilinear action that the sum of time-derivative terms equals zero independently. In particular, we may decompose these as
\[
0 = \partial_t \phi_a^+ \phi_b + \partial_t \phi_b^+ \phi_a
\]
\[
= \frac{1}{2} \partial_t \log \left( \phi_a^+ \phi_b^+ \right) \left( \phi_a^+ \phi_b + \phi_b^+ \phi_a \right)
\]
\[
+ \partial_t \log \left( \phi_a^+ \phi_b^+ \right) \frac{1}{2} \left( \phi_a^+ \phi_b - \phi_b^+ \phi_a \right).
\] (69)
The combination \( (\phi_a^+ \phi_b + \phi_b^+ \phi_a) \) is nothing more than the conserved number 1, while the combination \( (\phi_a^+ \phi_b - \phi_b^+ \phi_a) \) is precisely the observable expected number asymmetry \( v. \) The total derivative \( -(N/2) \partial_t \log \left( \phi_a^+ \phi_b^+ \right) \) could have been removed from the action to cancel the term in the final generating function, leaving only the argument \( \Gamma_0 (\log (\phi_{a0}^+ / \phi_{b0}^+)) \) and causing the magnitude of \( \Gamma_\hat{T} (\log z) \) to originate from the remaining term in the action rather than from a boundary term.

Let us summarize what has been accomplished so far: we have recovered the value of the single-time generating function and the mean value of its associated distribution, but we have also derived a new inference about the most-probable path of previous observations conditioned on those values at a time \( T. \) The fact that the stationary value \( v_t \neq \bar{v} \) for \( \tau < T \) does not reflect the influence of sources, or in fact any causal influence at times \( \tau < T, \) but rather the conditional probability structure generated by the stationary points of the field functional integral. This very powerful feature makes such functional integrals extremely useful, but it is also the feature that requires us to go through the full exercise of defining the generating functional of continuous-time sources, and then computing the Legendre transform to a stochastic effective action, to identify the history-dependent observations for which we are actually computing probabilities.

4.2.4. Action-angle variables. We next compute the same generating function using a set of transformed variables in which the expected number indices \( \bar{n} \) are given by elementary fields rather than by bilinear forms. In these variables the response field has the physically simple interpretation of a chemical potential. The transformed variables have advantages and disadvantages relative to the coherent-state field variables. The Liouville/Hamiltonian operator in the transformed variables will no longer be bilinear, making solutions to the equations of motion less obvious, even though they may still be found exactly. On the other hand, the kinematic nature of the two-field model as a Hamiltonian system will be clearer. Also—although we have not considered fluctuations yet and have only talked about mean values—the transformed Hamiltonian will show explicitly all terms needed to compute fluctuations, including those that vanished in the continuous-time limit in coherent-state variables \( \phi \) and \( \phi^+. \) In the transformed variables it is no longer necessary to appeal to the underlying discrete-time form to compute correlation functions.

The canonical transformation, from coherent-state fields to action-angle fields (including the now-familiar factoring out of the scale factor \( N \)), is defined by
\[
\phi_i^+ \equiv e^{\bar{n}_i},
\]
\[
\phi_i = e^{-\bar{n}_i} n_i = e^{-\bar{n}_i} N V_i,
\] (70)
for \( i \in \{a, b\}. \) The fields \( n_i \) now correspond to expectation values from equation (25), not only as single insertions, but in general products of fields in the D–P functional integral (49). In the transformed variables, this integral becomes
\[
\psi (z_a, z_b) \equiv e^{-\Gamma_\hat{T} (\log z_a, \log z_b)} = \int_0^T D\eta_a D\eta_b D\eta_b D\eta_b e^{\left( z_a e^{\bar{n}_a} r - 1 \right) n_a + \left( z_b e^{\bar{n}_b} r - 1 \right) n_b - S - \Gamma_0 (\eta_a, \eta_b)}.
\] (71)
The action in transformed variables becomes
\[
S = \int \mathrm{d} \tau \left[ -\left( \partial_\tau \eta_a \eta_a + \partial_\tau \eta_b \eta_b \right) + \hat{L} \right]
\]
\[
= N \int \mathrm{d} \tau \left[ -\left( \partial_\tau \eta_a \eta_a + \partial_\tau \eta_b \eta_b \right) + \hat{L} \right],
\] (72)
in which the Liouville/Hamiltonian has the form
\[
\hat{L} = k_v \left( 1 - e^{\bar{n}_v - \bar{v}} \right) n_a + k_v \left( 1 - e^{\bar{n}_v - \bar{v}} \right) n_b, \quad \text{or}
\]
\[
\hat{L} = \bar{v}_a \left( 1 - e^{\bar{n}_a - \bar{v}} \right) v_a + \bar{v}_b \left( 1 - e^{\bar{n}_b - \bar{v}} \right) v_b.
\] (73)
We now observe an important and general relation between the field action (73) and the transfer-matrix terms in the original master equation (3). (Recall that the Liouville operator is defined with a minus sign relative to the transfer matrix.) The original index shifting operators \( \partial / \partial \bar{n}_i \) have been replaced by momentum fields \( -\bar{n}_i, \) and the discrete indices \( n_i \) have been replaced by field variables \( n_i, \) whose expectation values in the functional integral are those of the indices \( n_i \) in the time-dependent density \( n_{a0}(\tau). \) Thus we see that the tedious task of expressing the operator algebra and coherent-state expansion may be bypassed by a simple notational replacement, to arrive at the functional integral directly. The
glossary indicating which number terms are substituted in passing between the master equation and Liouville operator is given in table 1. The same forms hold for the master equation (34) with more general nonlinear reaction rates, and the forms for large-deviation rates in the more general case are provided in appendix D.

The basis rotation in action-angle variables is now identical to that performed in section 3.1 for the particle numbers and the chemical potentials, with \( \eta \equiv \eta_b - \eta_a \) transforming as the chemical potential dual to \( n \). The resulting action becomes

\[
S = -\frac{N}{2} (\eta_b + \eta_a) \bigg|_0^\tau + N \int \dd{\tau} \left\{ -\partial_\tau \eta \nu + \tilde{v}_b v_a (1 - e^n) + \tilde{v}_a v_b (1 - e^{-n}) \right\}.
\]

(74)

The first term, arising from the total derivative discussed at the end of the preceding subsection, is precisely the one needed to cancel a factor of \((N/2)(\eta_b + \eta_a)\) in the initial generating function \( \Gamma_0(\eta_0, \eta_b) \) in equation (71), leaving only the single-argument function \( \Gamma_0(\eta_b) \) for the response field conjugate to \( \nu \). The net effect of the boundary terms at time \( \tau = \bar{\tau} \) is to set \( \eta_0 = \log \bar{z}_a \) and \( \eta_b = \log \bar{z}_b \) with the result that \( \Gamma_\bar{\tau}(\log \bar{z}_a, \log \bar{z}_b) = \Gamma_\bar{\tau}(\log z) \equiv \Gamma_\bar{\tau}(q) \) from equation (24).

We therefore proceed to solve for the classical stationary paths as in the preceding section, and dispense with further consideration of these extra, canceling terms.

The stationary-path equations, which are the equations of motion with respect to the dynamical system, in action-angle variables are

\[
\partial_\tau \eta = \frac{\partial \tilde{L}}{\partial \nu} \quad \text{and} \quad \partial_\tau \nu = -\frac{\partial \tilde{L}}{\partial \eta}.
\]

(75)

Again \( \tilde{L} \equiv 0 \), but now a non-trivial relation exists between the generating function and the stationary-path action, which may be written

\[
\Gamma_\tau (\log z) = N \int_0^\tau \dd{\tilde{\tau}} \left\{ -\frac{\partial \tilde{L}}{\partial \nu} + \tilde{\nu} + \tilde{L} \right\} + \Gamma_0 (0).
\]

(76)

Here \( \nu \) and (the implicitly present) \( \eta \) are evaluated over a stationary path. Of course the second factor \( \tilde{L} \equiv 0 \) need not have been written, but it serves to emphasize the Legendre-dual relation between the Liouville/Hamiltonian operator and its stochastic ‘Lagrangian’ \(-\partial_\tau \eta \nu + \tilde{L} \), which is similar to the duality between the generating functional and the effective action.

4.2.5. The canonical versus the kinematic description, and its consequences for time-reversal in one-dimensional systems. The cumulant-generating function, evaluated as a stationary-path integral in equation (76), is the quasipotential of F–W theory. For single-time fluctuations, it is a difference of Gibbs free energies, by equation (26). With respect to the underlying dynamical system, however, the quasipotential is an action, with the Liouville operator acting as its conserved Hamiltonian. The Liouville operator, however, still masks the deep simplicity of one-dimensional stochastic processes, which is provided by yet another level of description, in terms of a kinematic potential. The kinematic potential is the counterpart to the familiar potential energy in Hamiltonian dynamics, and it provides the most intuitive connection to finite-temperature instanton methods [42]. Here we show how the kinematic description is extracted, and use it to prove that, for one-dimensional systems, the most likely path to arrive at any fluctuation is the time-reverse of the classical diffusive-relaxation path from that fluctuation. This extension of Onsager’s near-equilibrium results [23, 24] is independent of the magnitude of the fluctuation or the form of the potential.

The ability to prove it so easily in the general case is an example of the power of F–W methods in some circumstances.

In dynamical-systems terms, \( \nu \) is a field with canonical momentum \( \eta \) with respect to the Hamiltonian \( \hat{L} \). While \( \eta \) is a canonical momentum, however, it does not play the role of a kinematic momentum in the stationary-path solutions. To express the kinematic variables, we recall that \( \nu_a/\nu_b = e^{\beta \mu} \) from section 3.1, or equivalently \( 2 \nu = -\tanh (\beta \mu/2) \).

Correspondingly, as a purely notational device, for any instantaneous value of \( \nu \), we may denote

\[
\frac{\nu_a}{\nu_b} \equiv e^{\beta \mu},
\]

(77)

so that \( \mu \) is the chemical potential for which that value of \( \nu \) would result at an equilibrium. With this notation we may recast equation (74)—as promised, now ignoring the surface term—as

\[
S = N \int \dd{\tau} \left\{ -\partial_\tau \eta \nu + 2\sqrt{\nu_a \nu_b} \nu_a \nu_b \right\} \times \left\{ \cosh \left( \frac{\beta \mu}{2} \right) \cosh \left( \frac{\beta \eta}{2} \right) \right\}
\]

\[
= N \int \dd{\tau} \left\{ -\partial_\tau \eta \nu + \sinh (\eta/2) \cosh (\beta \mu/2) \right\} \times \left\{ \sinh \left( \frac{\beta \mu - \eta}{2} \right) + 2 \nu \cosh \left( \frac{\beta \mu - \eta}{2} \right) \right\}.
\]

(78)

The first line of equation (78) shows us that \( \eta - \beta (\mu - \mu)/2 \) is, to leading quadratic order about zero, the term that creates the ‘kinetic energy’ in the Hamiltonian \( \hat{L} \). Its vanishing results in the stationary solution \( \partial_\nu \nu = 0 \) for its conjugate number field. The \( \eta \)-independent part of the Hamiltonian, \(-2\sqrt{\nu_a \nu_b} \nu_a \nu_b \cosh (\beta (\mu - \mu)/2 - 1) \), defines the kinematic potential for the dynamical system. The fields \( \nu, \eta - \beta (\mu - \mu)/2 \) follow a familiar Hamiltonian phase-space dynamics in this potential, with the kinematic momentum vanishing at the turning points \( \hat{L} = 0 \), and the potential vanishing only where the mass-action rates satisfy conditions of detailed balance. These total stationary points are all unstable, just as for problems of barrier penetration or escape in equilibrium Hamiltonian statistical mechanics [42]. A more detailed treatment, for problems with multiple basins of attraction and an interesting instanton structure as a result, is provided in [55].
The very strong consequence of the form in the first line, in one dimension, is that the conservation law \( \dot{L} \equiv 0 \) has only two solutions at any value of \( v \): \( \eta = 0 \) and \( \eta = \beta(\mu - \bar{\mu}) \), by symmetry of the second cosh. Then, by antisymmetry of the gradient of the same cosh, \( \dot{\eta}v \) is equal in magnitude and opposite in sign at these two solutions. Thus, the stationary-path solution at nonzero \( \eta \) is the time-reverse in \( v \) of the classical diffusion solution. Moreover, we have \( \beta\mu = \beta\bar{\mu} - \eta \). at this solution, which together with the form in the second line of equation (78) immediately gives
\[
v = \frac{1}{2} \tanh \left( \frac{\eta}{2} - \beta \bar{\mu} \right).
\] (79)

For these solutions we may recover the value of the single-time cumulant-generating function from the action-angle equations of motion. Vanishing \( \dot{L} \) gives the action as an integral over its kinetic terms along the stationary path, which no longer vanish, namely
\[
\Gamma_T (\log z) - \Gamma_0 (0) = -N \int_0^\infty d\tau \dot{\eta} \eta v
\]
\[
= -N \int_0^{\log z} d\eta \nu.
\] (80)

Using the expression (79) in the last line of equation (80), we then obtain
\[
\Gamma_T (\log z) - \Gamma_0 (0) = -N \log \cosh \left( \frac{\eta}{2} - \beta \bar{\mu} \right)/0, \quad (81)
\]
which again reproduces equation (29).

4.2.6. Langevin approximation and the magnitude of fluctuations about time-dependent solutions. It is important that the equilibrium generating function (19) produces not only an offset equilibrium value, but an entire distribution corresponding to an effective shift in the chemical potential between the \( a \) and \( b \) states. The width of this distribution is identical to the fluctuation variance in \( v \) produced by the Gaussian integral with action (78), as we now show. The easiest demonstration is by means of the Langevin approximation, which is also useful to show how the classical Langevin equation is generated from the more complete D–P functional integral. This construction is particularly elegant in action-angle variables, which lead to a Langevin equation directly for the particle numbers. The coherent-state variables in which the Langevin equation is usually constructed [56] only offer this interpretation for fluctuations about classical diffusion paths, where \( \phi' \equiv 1 \), and they can become quite complicated to compute about other backgrounds. In action-angle variables, the same interpretation is valid in all paths, including those that propagate conditions about single-time fluctuation backward in time.

The fact that the Gaussian integral delivers the fluctuation magnitude (and more generally, the correct correlation structure) even for time-dependent solutions is an important improvement over an approach often taken with Langevin equations, which is simply to ‘guess’ a fluctuation magnitude as an independent input to models [56, 57]. The variance produced is also the unique value for which the terms in the path entropies of section 5 will cancel to produce the continuous-time hydrodynamic limit of [52].

The Langevin stochastic differential equation encodes exactly the same approximations as the Gaussian approximation to fluctuations in the functional integral. About any solutions \( \eta^{cl}, \nu^{cl} \), to the stationary-point equations, we write general \( \eta = \eta^{cl} + \eta' \), \( \nu = \nu^{cl} + \nu' \), and expand \( S \) from equation (74) to second order in primes:
\[
S = S^{cl} + N \int d\tau \left\{ \eta \left[ \partial_t + \left( v_b e^{v^{cl}+\nu^{cl}} + v_a e^{-v^{cl}} \right) \right] \nu' - \frac{1}{2} \left( \left( v_b v^{cl}_a e^{v^{cl}+\nu^{cl}} + \bar{v}_a v^{cl}_b e^{-v^{cl}} \right) \eta' \right] \right\}.
\] (82)

In equation (82) we denote by \( S^{cl} = N \int d\tau \left[ -\partial_t \eta^{cl} v^{cl} + \dot{L}(\eta^{cl}, v^{cl}) \right] \) the action of the classical stationary path. Terms linear in \( \eta' \) and \( \nu' \) vanish as the condition for the stationary-point solutions to hold.

We could complete the square in \( \eta' \) in equation (82), leading to the construction of Onsager and Machlup [58], and we will do this in a later section. An alternative approach, pursued here, is to perform the Hubbard–Stratonovich transformation [22, 59] by introducing an auxiliary field \( \lambda \), with a functional integral (Def[\( v_b^{cl} v^{cl}_a + \bar{v}_a v^{cl}_b \)]1/2 \( \int D\lambda \exp S_{Aux} \)) which is just a representation of unity, in which the auxiliary field action is given by
\[
S_{Aux} = \frac{N}{2} \int d\tau \frac{\lambda^2}{\left( \bar{v}_a v^{cl}_b e^{v^{cl}+\nu^{cl}} + \bar{v}_a v^{cl}_b e^{-v^{cl}} \right)}
\]
\[
\times \left[ \lambda - \left( v_b v^{cl}_a e^{v^{cl}+\nu^{cl}} + \bar{v}_a v^{cl}_b e^{-v^{cl}} \right) \eta' \right]^2.
\] (83)

The sum of actions for the original and auxiliary fields becomes
\[
S + S_{Aux} = \frac{N}{2} \int d\tau \left[ \lambda^2 \left( \bar{v}_a v^{cl}_b e^{v^{cl}+\nu^{cl}} + \bar{v}_a v^{cl}_b e^{-v^{cl}} \right)
\]
\[
+ 2\eta' \left[ \left( \partial_t + \left( \bar{v}_b v^{cl} + \bar{v}_a e^{-v^{cl}} \right) \right] \nu' - \lambda \right] \right\}.
\] (84)

The integral \( \int D\eta' \) in the original functional integral, if rotated to an imaginary contour of integration,16 simply produces the functional \( \delta \)-function
\[
\int D\eta' e^{-\left( S_{Aux} \right)} = \delta \left[ \left( \partial_t + \left( \bar{v}_b v^{cl} + \bar{v}_a e^{-v^{cl}} \right) \right] \nu' - \lambda \right] \exp \left[ \frac{-N}{2} \int d\tau \frac{\lambda^2}{\left( \bar{v}_a v^{cl}_b e^{v^{cl}+\nu^{cl}} + \bar{v}_a v^{cl}_b e^{-v^{cl}} \right)} \right].
\] (85)

The last of the original functional integrals, over \( \nu' \), admits only those solutions which satisfy the Langevin equation
\[
\left[ \partial_t + \left( \bar{v}_b v^{cl} + \bar{v}_a e^{-v^{cl}} \right) \right] \nu' = \lambda.
\] (86)

16 Note that \( \eta' \) is always integrated along an imaginary contour, as the condition for stability of the Gaussian integral. This is true in the Onsager–Machlup construction, and it is also the imaginary part of \( \eta' \) that defines the quantity behaving as a momentum in the kinematic description.
any two times

$$\langle \lambda_\tau \lambda_{\tau'} \rangle = \frac{\bar{v}_a^{\dagger} e^{q_\tau} + \bar{v}_b e^{-q_\tau} \delta (\tau - \tau')}{N},$$

as a result of the Gaussian kernel of integration.

A case of special interest, for its relation to the single-time distribution—at or away from equilibrium—is the fluctuation variance at equal times $$\langle (v'_\tau)^2 \rangle$$ about a constant or long-time persistent background. We will not provide details about the inversion of equation (86) to express $$v'$$ in terms of $$\lambda$$ and a retarded Green’s function, which may be found in [39]. However, the general result is that for backgrounds that persist much longer than the decay time $$\left( \bar{v}_a e^{q_\tau} + \bar{v}_b e^{-q_\tau} \right)$$, the single-time variance is given by

$$\langle (v'_\tau)^2 \rangle = \frac{\bar{v}_a^{\dagger} e^{q_\tau} + \bar{v}_b e^{-q_\tau}}{2N \left( \bar{v}_a e^{q_\tau} + \bar{v}_b e^{-q_\tau} \right)}.$$

We will return in section 4.6 to check that this result agrees with the variance of the single-time distribution given by the equilibrium generating function (22).

We have given a thorough treatment of the single-time generating function to provide multiple points of reference for terms that cause $$\phi^\dagger$$ fields to deviate from unity, or $$\eta$$ to deviate from zero, and to interpret their effect on stationary points. It will now be straightforward to place all such terms entirely within the functional integral rather than in boundary terms. We will do so first for a discrete source with an identical effect to the single-time generating function, and examine the future as well as past properties of the stationary paths. We will then define exact solutions for the more general case of continuous sources, and finally study the analytic structure of the small-fluctuation limit, which is simply a linear expansion in point sources.

4.3. Generating functionals and arbitrary time-dependent sources

When sources interior to functional integrals are used to compute the probabilities of complicated histories, the construction is usually done in two disconnected stages. First, the final-time arguments $$z_i$$ are set to one, so that the moment-generating function $$\psi(z_a, z_b)$$ becomes simply the trace of the probability distribution at time $$T$$. That is, the elaborate field integrals (49) and (71) are simply complicated expressions for the number 1. New terms involving the integration variables and external fields are then simply inserted into the action, with the understanding that these are ‘sources’ that perturb the particle motion.

Here we will introduce sources systematically as part of the construction of the functional integral, to make clear their connection to the original construction of the generating function. The construction involves modifying the map by which we have, up to now, simply reinterpreted intermediate variables $$z$$ and $$\partial / \partial z$$ as operators $$a^\dagger$$ and $$a$$.

A generating functional is the time-evolved product of a sequence of generating functions produced by adding small continuous sources to all previous distributions. That is, we replace the identification (40) with one in which the abstract operators differ from variables $$z$$ by the addition of sources. At any time $$\tau$$, we identify

$$z_j \leftrightarrow a_j e^{q\tau}$$, keeping

$$\frac{\partial}{\partial z_i} \leftrightarrow a^\dagger.$$

Moreover, to separate the discretization time $$\delta \tau$$ from characteristic timescales associated with the sources, we will write

$$q_r = j(\tau) \delta \tau,$$

and take $$j(\tau) \equiv j_s$$, called a current, to be a smooth function of $$\tau$$ in the limit $$\delta \tau \rightarrow 0$$. Because both relaxation and fluctuation effects are governed by timescales in $$\Delta \tau \sim 1$$, we may readily consider sources $$j_s$$ that have large magnitude over some range in $$\tau$$ that is $$\ll 1$$. Currents of this form may be constructed to approximate the point source $$j_{ss} \approx q_s(\tau - \tau_c)$$ for some particular time $$\tau_c$$.

Finally we set values $$z_a = 1$$, $$z_b = 1$$ at time $$\hat{T}$$, keeping only sources from nonzero $$j(\tau)$$ in the range $$0 < \tau < \hat{T}$$. The field integral at $$\tau = T$$ here simply computes a trace, and all correlations are studied internally in the functional integral. The notation $$\psi(z_a, z_b)$$ is no longer needed, and we simply refer explicitly to the cumulant-generating functional $$\Gamma[j]$$ whose argument is the function $$j$$.

Both coherent-state field variables and action-angle variables will be of interest, and so we provide both forms here. Equation (49) is replaced by

$$e^{-\Gamma[j]} = \int_0^T D\phi^0_a D\phi^0_b D\phi_a D\phi_b e^{(1 - \phi^0_a) \phi_a + (1 - \phi^0_b) \phi_b - \delta j \Gamma[\phi^0_a, \log \phi_a, \log \phi^0_b]},$$

in which

$$S_j = N \int d\tau \left[ -\partial_\tau \phi^0_a \phi_a + \partial_\tau \phi^0_b \phi_b \right] - j \phi_a^\dagger \phi_b^\dagger + \delta \hat{\mathcal{L}}.$$  

Likewise, equation (71)—removing the un-needed integration variable $$\eta_a + \eta_b$$, conjugate to $$N$$, and writing the single-argument generating function alone—becomes

$$e^{-\Gamma[j]} = \int_0^T D\eta Dnc(e^{-\eta} - 1) n_\tau - S_j - \Gamma[0,0],$$

in which

$$S_j = N \int d\tau \left[ -\partial_\tau \eta \phi - j \phi + \delta \hat{\mathcal{L}} \right]$$

with Liouville operator

$$\hat{\mathcal{L}} \equiv \bar{v}_a \psi (1 - e^\eta) + \bar{v}_b \psi (1 - e^{-\eta}).$$

The upper time limit $$T$$ may now be taken to infinity and dropped from the notation. If we consider sources $$j_s \rightarrow 0$$,
at both \( \tau \to 0 \) and \( \tau \to \infty \) and which are smooth on the scale of the discrete sum (not a very restrictive condition) it follows from the stationary-path conditions in the presence of the source \( j \) that

\[
\hat{\mathcal{L}}_j \equiv \hat{\mathcal{L}} - j \left( \phi_0 \phi_b - \phi_0^\dagger \phi_b^\dagger \right) / 2
\]

is the Hamiltonian of the dynamical system in the presence of sources. Because \( \hat{\mathcal{L}}_j \) now depends explicitly on time through \( j \), equation (57) is replaced by

\[
\frac{d\hat{\mathcal{L}}}{d\tau} \equiv -\nu \frac{dj}{d\tau}.
\]  

(97)

We also have as boundary conditions that \( \eta_\infty = 0 \) (more generally \( \eta_\infty = 0 \) and \( \eta_{\infty,0} = 0 \) independently if we had kept both sets of integration variables), or equivalently \( \phi_{0,\infty} = 1 \) and \( \phi_{b,\infty} = 1 \). To understand how these conditions lead to stationary-point solutions, which involves the stability structure of the functional integrals, it is easiest to solve some examples. The general exact solution, in coherent-state fields, is given in appendix C.

4.4. General solutions

In all the following cases, we will suppose that the initial distribution is the equilibrium distribution (4). Other initial conditions can easily be considered, but all converge to the equilibrium exponentially in \( \tau \), and so may be decoupled to any desired degree from the influence of \( j \) at later times. We begin with a point source which recovers the single-time generating function, and then consider sources extended in time.

4.4.1. Point sources. Suppose that \( j_\tau \to q \delta(\tau - \tau_c) \) for some time \( \tau_c \) in the sense of convergence of smooth distributions with compact support and fixed area \( q \). The exact solution in this case is most simply expressed in action-angle variables, which can then be converted to coherent-state field variables if desired.

From the action form (94) with this source, stationary solutions are just those of the unperturbed action except at \( \tau_c \), where \( \eta \) has the discontinuity

\[
\eta_{\tau_c+} = \eta_{\tau_c-} - q
\]  

(98)

as \( \epsilon \to 0 \). To understand what this implies, we return to the kinematic form for (78) for the action, using \( \eta^{cl} + \eta' \) as in section 4.2.6. \( \beta \mu \) is a function of \( \nu \) from equation (77), which we indicate on the stationary path by writing \( \mu^{cl} \). For free solutions we already know that \( \dot{\mathcal{L}} = 0 \) requires either \( \eta^{cl} = 0 \) or \( \eta^{cl} = \beta (\mu^{cl} - \mu^{cl}) \). Therefore, we may write

\[
\begin{align*}
\cosh \left( \frac{\beta}{2} (\mu^{cl} - \mu) \right) & - \cosh \left( \eta + \frac{\beta}{2} (\mu^{cl} - \mu) \right) \\
& = \cosh \left( \frac{\beta}{2} (\mu^{cl} - \mu) \right) (1 - \cosh \eta') \\
& + \sinh \left( \eta^{cl} + \frac{\beta}{2} (\mu^{cl} - \mu) \right) \sinh \eta'.
\end{align*}
\]  

(99)

Our concern is with the second line of equation (99). This quantity appears with positive sign in \( \dot{\mathcal{L}} \) and so describes divergent fluctuations for \( \eta' \) integrated along a real contour. As in the case of the Hubbard–Stratonovich transformation, the convergent contour of integration for \( \eta' \) is imaginary, where it behaves like an ordinary momentum variable in finite-temperature field theory [60].

The instability that governs the integration contour for fluctuations also implies that time evolution in the forward direction for real-valued \( \eta \) is unstable in general. This should not be surprising, as we have already seen that the evolution equations for \( \eta \) are stable going backward in time, as \( \eta \) propagates context from observables to their most-likely prior causes. The implication for our stationary path is that if \( \eta^{cl}_\infty = 0 \) and \( j_\tau \equiv 0 \) for \( \tau > \tau_c + \epsilon \), we must have \( \eta^{cl}_\tau \equiv 0 \) for all \( \tau > \tau_c + \epsilon \). Hence \( \eta^{cl}_\tau - \eta \equiv q \) for the stationary path evaluated in section 4.2.5. The consequence for the number field is that its magnitude at \( \tau = \tau_c \) is just that of equation (28), and that for times either before or after \( \tau_c \), \( \nu^{cl} \) satisfies the generalization of equation (64) to

\[
\nu^{cl} = \nu - q \epsilon^{- \tau - \tau_c}.
\]  

(100)

The time-dependence of \( \nu^{cl} \) is shown in figure 4.

The generating functional for the point source has the value already computed:

\[
\Gamma [j] = \Gamma_0 (0) - N \int_0^\infty d\tau \, \partial_\tau \eta^{cl} \nu^{cl}
\]

\[
= -N \log \cosh \left( \frac{\beta}{2} (\eta^{cl} - \beta \mu) \right) |^0_0,
\]  

(101)

again recovering equation (29). Note that although \( \nu^{cl} \neq 0 \) at all times, the integral receives contributions only from \( \tau < \tau_c \) where \( \eta \neq 0 \).

The effective action is numerically just that given in equation (33), because it differs from the generating functional by subtraction of the point source \( q \nu_{\tau_c} \), as before. However, as a Legendre transform on a space of histories, we now regard it as the functional

\[
S_{\text{eff}} [\eta] = S_{\text{eff}} [N \nu^{cl}],
\]  

(102)
whose argument \( v^\text{cl} \) is the whole exponential history given by equation (100) with \( v^\text{cl} \) fixed by equation (28). The entropy difference of equation (32) is now expressed not only as a probability of a fluctuation of given magnitude, but of the most-likely sequence of previous and subsequent configurations consistent with that observed fluctuation but with no other information given.

To understand the meaning of the stochastic effective action as a probability on histories, it is necessary to appreciate the nonlocal relation between histories and the structure of the moment-sampling currents \( j \) which contain the minimal information to specify them. To extend the formulae for the effective action to more general histories, a variety of methods are known which produce both nonlocal and exact, or local but approximate, solutions.

4.4.2. Continuous sources: linear-response approximation and analytic structure. We now return to the second-order expansion of equation (94) in fluctuations, from section 4.2.6, but this time we complete the square directly rather than through a Hubbard–Stratonovich transformation. Following Onsager [23, 24, 58], we will expand about the equilibrium background where \( v^\text{cl} \equiv \bar{v} \) and \( \eta^\text{cl} \equiv 0 \), and will simply write \( \eta' \equiv \eta \). (The more general problem of expanding about non-classical backgrounds conditioned on sources could of course be considered as well.) The quadratic expansion of the action takes the simple form

\[
S_j = -N \bar{v} \int_0^\infty d\tau j, \\
+ \int_0^\infty d\tau \left\{ (v - \bar{v}) \left[ (-\partial_\tau + 1) \eta - \bar{v}_\eta \eta^2 \right] \right\}. \tag{103}
\]

The stationary-point equations are now linear-response equations

\[
(-\partial_\tau + 1) \eta = j, \tag{104}
\]

\( (\partial_\tau + 1) (v - \bar{v}) = 2 \bar{v}_\eta \eta. \)

\( \eta \) is the response to \( j \) through the advanced Green’s function:

\[
\eta_\tau = \int_\tau^\infty d\tau' e^{\tau' - \tau} j_{\tau'}, \tag{105}
\]

while \( v - \bar{v} \) responds through the symmetric Green’s function:

\[
v_\tau - \bar{v} = \bar{v}_\eta \bar{v} \int_\tau^\infty d\tau' e^{-\tau' + \tau} j_{\tau'}. \tag{106}
\]

Equation (106) reproduces the exact time dependence of equation (100) for a point source, and gives the linear small-\( q \) approximation to the magnitude (28).

We now have a closed-form local expression for the generating functional in terms of the response field \( \eta \) and the source \( j \), because in these variables \( \Gamma[j] \) is just \( S_j \) evaluated on the stationary solution. From equation (104), this is

\[
\Gamma[j] = -N \bar{v} \int_0^T d\tau j - \frac{N}{2} \int_0^T d\tau (2 \bar{v}_\eta \bar{v}) \eta^2, \tag{107}
\]

with \( \eta \) given by equation (105). We recognize from equation (9), the quantity \( N \bar{v}_\eta \bar{v} \) as the variance of the equilibrium distribution and hence the susceptibility to perturbations in chemical potential.

From the definition (C11) and use of the equations of motion (104), the effective action is similarly expressed as a local functional:

\[
S_{\text{eff}}[j] = \frac{N}{2} \int_0^\infty d\tau \frac{\left[ (-\partial_\tau + 1) (v - \bar{v}) \right]^2}{2 \bar{v}_\eta \bar{v}} = \frac{1}{2} \int_0^\infty d\tau \frac{\left[ (-\partial_\tau + 1) (n - \bar{n}) \right]^2}{2 N \bar{v}_\eta \bar{v}}. \tag{108}
\]

Equation (108) is the expression first due to Onsager and Machlup [58]. The first line, as usual, makes explicit the separation of large-deviations scaling in \( N \) from the integral that is the rate function, which is a function only of fractional displacements \( v - \bar{v} \).

4.5. The relation to Onsager’s ‘minimum entropy production’ property

Equation (108) is a relation between an offset \( n - \bar{n} \) and a transport current \( \partial_\tau n \), which we might call \( v \), a reaction velocity in appropriate units of time. Recalling equation (32) for the log-probability of single-time fluctuations, we may recognize the combination \( (n - \bar{n})^2/(2N \bar{v}_\eta \bar{v}) \) as none other than \( S_{\text{eff}}(n) \), the entropy deficit from the equilibrium large-deviations principle. Immediately we would then recognize \( (n - \bar{n})/(N \bar{v}_\eta \bar{v}) \) as \( \partial S_{\text{eff}}(n)/\partial n \), and \( (n - \bar{n}) v/(N \bar{v}_\eta \bar{v}) \) as the rate of change in the equilibrium entropy of quasi-equilibrated subsystems. From these associations we could rewrite equation (108) in the form

\[
S_{\text{eff}}[n] = \frac{1}{2} \int_0^\infty d\tau \left\{ S_{\text{eff}}(n) + \frac{\partial S_{\text{eff}}(n)}{\partial n} v + \frac{1}{2} \partial^2 S_{\text{eff}}(n) v^2 \right\}, \tag{109}
\]

in which the term \( \partial^2 S_{\text{eff}}(n)/\partial n^2 \) gives the linear-response coefficients \( 1/(N \bar{v}_\eta \bar{v}) \).

If we chose to regard minimization of \( S_{\text{eff}}[n] \) as an integral over time of two separate criteria—the first being the probability of a fluctuation to \( n \) from \( S_{\text{eff}}(n) \) and the second being a minimization over \( v \)—the minimized function of \( v \) given \( n \) would be the ‘entropy production’ relative to a bilinear form \( v^2 \partial^2 S_{\text{eff}}(n)/\partial n^2 \) parametrized by the near-equilibrium response coefficients. In two papers in 1931 [23, 24], this was the result derived by Onsager as a consequence of microscopic reversibility and referred to as a ‘minimum entropy production’ property. Onsager referred to the bilinear form of currents \( v^2 \partial^2 S_{\text{eff}}(n)/\partial n^2 \) as the ‘dissipation function’.

Note three things: (1) it is not the ‘entropy production’ per se that is minimized, but only its value relative to the dissipation function, which from the form of the system entropy may be arbitrary; (2) there is no obvious reason to interpret the dissipation function as a ‘constraint’ on the entropy production, and thus entropy production is not ‘minimized subject to constraints’, as an analogy to the way the entropy is maximized subject to constraints in equilibrium and (3) the presence of the response coefficients in this form results from the near-equilibrium expansion, as is well known.
We see, then, how we may speak precisely about the range of assumptions needed to make the ‘production’ of the equilibrium entropy a quantity that is informative about dynamics. We have required the particular form of the local-equilibrium approximation that comes from a basins-and-barriers model, so that the dependence of the stochastic effective action \( S_{\text{eff}}[n] \) on its instantaneous configuration variables reduces at leading order to the equilibrium quantity \( S_{\text{eff}}(n) \). We have assumed small fluctuations in order to expand the linear velocity dependence in terms of \( \partial S_{\text{eff}}(n)/\partial n \), and to approximate the linear-response coefficients by their equilibrium values. Had all of these conditions not been satisfied, the expansion (109) need not have been valid. Yet, within the more general framework of the stochastic process, we could readily have derived the correct alternative form from the exact solution, which is derived as equation (C11) in appendix C. In the more general regime of nonlinear response and large perturbations from the equilibrium distribution, the relation between a source \( j(\tau) \) and the path \( \nu(\tau) \) that it induces will generally be nonlocal in \( \tau \).

4.6. A second example: fixed disequilibria and an entropy rate for a large-deviation rate function

We now consider a second problem, aimed at relating dynamics to reference static distributions. Suppose that, rather than assuming free relaxation immediately after a fluctuation of magnitude (28), we ask for the probability of a history at reference static distributions. Figure 5. The source current (dashed) and resulting stationary solution (solid), for a source that raises \( n_t \) to \( n_{q}^{(1)} \) at \( \tau = 0 \), holds it at this value until \( \tau = \tau_C \), and then releases it to free diffusive decay.

\[ S_{\text{eff}}[\nu] = N \int d\tau \left( -\partial_\tau \eta \nu + \hat{\mathcal{L}}_j \right) \]

\[ = \frac{N}{2} \left( \cosh \frac{q}{2} - 1 \right) + \nu \sinh \frac{q}{2} \] (112)

and

\[ S_{\text{eff}}[n] = N \int d\tau \left( -\partial_\tau \eta n + \hat{\mathcal{L}}_j \right) \]

\[ = S_{\text{eff}}(n_{\tau=0, \tau_C}) + \tau_C N \frac{\cosh \frac{q}{2} - 1}{\cosh \frac{q}{2} \cosh \frac{q}{2}} \]

\[ = S_{\text{eff}}(n_{\tau=0, \tau_C}) + \tau_C N \left( \sqrt{v_a v_b} - \sqrt{v_a v_b} \right)^2. \] (113)
Equation (115) is a new result. The combination of square-root dependence on quantities that equal the expected escape rates—\( \bar{v}_b \bar{v}_a \) and \( \bar{v}_a \bar{v}_b \)—and the squared difference of these in the exact entropy rate, extend to general multi-particle chemical reactions as shown in appendix D.

To make contact with the Langevin treatment in section 4.2.6, we check that in the persistent non-equilibrium chemical reactions as shown in appendix D.

\[
\partial_\tau S_{\text{eff}} = \frac{1}{2} \left( \bar{v}_b e^{\nu_a} + \bar{v}_a e^{\nu_b} \right) - \frac{1}{2} \left( \bar{v}_a e^{-\nu_b} + \bar{v}_b e^{-\nu_a} \right) = 2 \sqrt{\bar{v}_a \bar{v}_b} \nu_a \nu_b. \tag{116}
\]

The decay rate in the Langevin equation (86) evaluates to

\[
\bar{v}_b e^{\nu_b} + \bar{v}_a e^{-\nu_a} = \frac{\bar{v}_a \bar{v}_b}{1 + \beta} \tag{117}
\]

Hence the single-time fluctuation expression (88) evaluates to

\[
\langle (\nu_b)^2 \rangle = \frac{\bar{v}_a \bar{v}_b}{N}, \tag{118}
\]

in agreement with the variance obtained from equation (88) for the distribution produced by the equilibrium generating function.

4.6.1. The non-equilibrium entropy rate in relation to gradients of the equilibrium entropy. How does the entropy-rate difference defined from the dynamical stochastic effective action relate to changes in the equilibrium entropy of subsystems under free decay? We may recast equation (32) as

\[
S_{\text{eff}}(n) = N D (\nu \parallel \bar{v}) = \frac{N}{2} \left\{ \log \left( \frac{\bar{v}_b \bar{v}_a}{\bar{v}_b \bar{v}_b} \right) + q (\nu_b - \nu_a) \right\}. \tag{119}
\]

For the period of free decay after \( \tau_C \), the change in equilibrium entropy with \( n \) is

\[
\frac{\partial}{\partial n} S_{\text{eff}}(n) = q. \tag{120}
\]

The time-dependence of the equilibrium-form entropy follows from the time-dependence of \( n \). Its gradient at the moment after the source perturbation is turned off is given by

\[
\partial_t n = - N (\nu - \bar{v}) = - \frac{N}{2} \sinh \frac{\pi}{2} \cosh \frac{\pi \nu}{2} \tag{121}
\]

Therefore, under free diffusion from a chemical-potential perturbation by \( q \), the initial rate of subsystem entropy change is given by

\[
\partial_t S_{\text{eff}}(n) = \frac{\partial S_{\text{eff}}(n)}{\partial n} \partial_t n \]

\[
= - \frac{N}{2} q \sinh \frac{\pi}{2} \cosh \frac{\pi \nu}{2}. \tag{122}
\]

At small \( q \), \( -\partial_t S_{\text{eff}}(n) \to 4 \partial S_{\text{eff}}(n) / \partial n \), as defined in equation (115). Thus the stochastic-process entropy rates, and the rate of change of equilibrium entropies, are not equal even in this limit; more generally they are distinct functions altogether.

We can check from equation (115) that in the interval \([0, \tau_C]\), \( \mathcal{L} \) has the limits \( \mathcal{L} \to \bar{v}_b \) as \( \tanh(q/2) \to 1 \) and \( \mathcal{L} \to \bar{v}_b \) as \( \tanh(q/2) \to -1 \). Thus the entropy rate of the stochastic process is bounded by leaving-rates from the two respective states, while the corresponding rate of entropy change in equation (122) is unbounded.

We may summarize this section as follows. It should not be surprising that the stochastic effective action for histories includes entropy-rate terms that have no simple relation to rates of change in the equilibrium entropy of states. The former measures uncertainty about rates of transition, while the latter measures uncertainty about the occupation frequencies for states. It may be that, in some cases, dynamics is near enough to equilibrium that the state occupancy at successive moments of time places tight constraints on the possible entropy of transitions. However, this is not a general result, and it is not even implied by the local-equilibrium approximation of the form produced by the double-well potential. To say more about the origin of the rate term in the stochastic effective action (113), however, requires a separation between system and environment terms that the continuous-time two-state model does not readily provide. For that separation we turn to the method of maximum caliber.

5. Path entropies and maximum caliber

The construction of equilibrium Gibbs free energies from the entropy, reviewed in appendix B, begins with an explicit division between entropy terms for the system and its environment. The F–W construction of the preceding section does not naturally provide such a decomposition for paths, because the contribution of the ‘environment’ comes from the form of the transition-rate terms \( k_{\alpha \beta} \), which are embedded in the master equation. To separate these two contributions in the ensemble over histories, we require an explicit combinatorial formula for properties of paths, which is defined independently of the probabilities given to such paths by the transition rates set by the environment. The method of maximum caliber, as formulated in \([8, 57, 61, 62]\), provides such a decomposition.

This section will introduce two changes of representation. One is the consideration of histories of an individual random walker, as explained in the introduction. The other, which will be more important to the ability to isolate system–environment interactions, is the replacement of the continuous-time stochastic process of the master equation (3), by a discrete-time two-state Markov process, shown in figure 6. The continuous-time and discrete-time models, in appropriate limits, represent the same stochastic process. However, the discrete-time model has the feature that, in every time interval of length \( \Delta t \), some transition of the particle’s state must occur, even if it is a transition back to the same state.

It may come as a surprise when we find, below, that the entropy rate in the effective action (113) draws its form entirely from the probabilities of no change. When we separate the large-deviations formula into contributions from the path entropy and the environmental probabilities, other terms associated with changes will also appear. However,
These cancel exactly in the hydrodynamic limit represented by equation (113). Thus we will see that, among the many terms that could have been used to probe the generating functional of the previous section, the particular coupling to the field $v$ that we studied was the form that produces the hydrodynamic limit. We return at the end of this section to what such a decomposition implies about the role of ‘energy dissipation’ as an explanation for large-deviations probabilities of histories.

In the next two sections, we will solve for the path ensemble first in its stationary distribution, and then perturbed with sources. With appropriate choices for the transition parameters in the discrete model, the path ensemble will be constructed from the transfer matrix for the single-particle continuous-time model. With a particular choice of perturbing sources in the generating functional for this distribution, we will be able to show that the continuous-time Langevin equation gives the Gaussian approximation to the fluctuating initial state in which the path starts, labeled with index $\sigma$, subject to some set of appropriate constraints on properties of the paths, such as its $M_{\alpha\beta}$ values, which will be denoted $M_{\alpha\beta}$. It will be convenient here to divide the path specification into the state in which the path starts, labeled with index $\sigma$, and the rest of the path conditioned on that starting state, indexed $j \mid \sigma$. We could think, thus, of $j$ as a string denoting the ordered states through which the trajectory passed, and $j \mid \sigma$ as the string excluding its first letter. In this indexing $p_j = p_{j \mid \sigma} \ p_\sigma$.

It simplifies the treatment, without omitting any results that matter here, to exclude the distribution over initial states from the variational problem, and to consider only variations of $p_{j \mid \sigma}$. For any path $j$, the numbers $M_{\alpha\beta}$ count the state-transitions from state $\beta$ to state $\alpha$ along that path. Denote by $\tilde{M}_{\alpha\beta}$ the constraint values on maximum entropy for this path ensemble. Then the Lagrangian for the path-entropy maximization problem becomes

$$\mathcal{L}_{\text{path}} = - \sum_{\sigma} \sum_{j \mid \sigma} p_{j \mid \sigma} \log p_{j \mid \sigma} \ p_\sigma$$

$$- \sum_{\alpha \beta} \lambda_{\alpha\beta} \left( \sum_{\sigma} \sum_{j \mid \sigma} p_{j \mid \sigma} M_{\alpha\beta} - \tilde{M}_{\alpha\beta} \right)$$

$$- \sum_{\sigma} \eta_{\sigma} \left( \sum_{j \mid \sigma} p_{j \mid \sigma} - 1 \right). \quad (124)$$

Lagrangians of the form (124) produce Gibbs (exponential) distributions as their maximizing distributions. Therefore, in terms of the Lagrange multipliers $\{\lambda_{\alpha\beta}\}$, the maximum-entropy probabilities have the form

$$p_j = \frac{1}{Q} \left( y_{\alpha a} M_{\alpha a} + y_{\alpha b} M_{\alpha b} + y_{\beta a} M_{\beta a} + y_{\beta b} M_{\beta b} \right) \ p_\sigma. \quad (125)$$

The entropy on this distribution was given the name "caliber" by Jaynes [8], to reflect the fact that it is a logarithmic measure of the width of a ‘tube’ of microhistories which are typical within the distribution that produces macrohistories characterized by the $\{M_{\alpha\beta}\}$.

Following [61, 62] (apart from a sign convention for the $\{\lambda_{\alpha\beta}\}$) we define

$$y_{\alpha\beta} \equiv e^{-\lambda_{\alpha\beta}}, \quad (126)$$

and choose $p_\sigma$ to be the starting probability appropriate to whichever is the first state in history $j$. For this set of observables, the order in which transitions occur does not affect the weight function, though it does restrict the set of possible paths.

$Q$ is the partition function on histories, defined as the sum over $j$ of the other terms in equation (125). Because histories are in $1 \cdots 1$ correspondence with monomials that arise from the $M$th power of a $2 \times 2$ matrix, the partition function is immediately expressed as the usual trace of a transfer matrix, just as we could have computed working directly from equation (34):

$$Q = \left[\begin{array}{c} 1 \\ 1 \end{array}\right] \left( \left[ \begin{array}{cc} y_{\alpha a} & y_{\alpha b} \\ y_{\beta a} & y_{\beta b} \end{array} \right] \right) M \ p_\sigma = \left[ p_a \right]. \quad (127)$$

Now we may make some simplifying assumptions without loss of generality, to bring the expression (127) into direct correspondence with the transfer matrix of the continuous-time model. The matrix $\gamma$ does not actually have four independent values $\{\gamma_{\alpha\beta}\}$, because the original Lagrangian (124) did not have four independent constraints $\{M_{\alpha\beta}\}$. The sum $\sum_{\alpha \beta} M_{\alpha\beta} \equiv M$, because for each possible path also $\sum_{\alpha \beta} M_{\alpha\beta} \equiv M$. Moreover, for large $M$, it is not possible to set $\tilde{M}_{\alpha\beta} \neq \tilde{M}_{\beta a}$ by more than ±1, so effectively these...
must be chosen equal\(^ {17}\). Therefore two normalizations of the \(\gamma_{\alpha\beta}^{ab}\) may be chosen arbitrarily. These may be chosen so that \(\gamma_{aa}^{ab} + \gamma_{bb}^{ab} = 1\), \(\gamma_{ab}^{ab} + \gamma_{bb}^{ab} = 1\), effectively choosing unit normalization for the partition function \(Q\). The matrix \(\gamma_{\alpha\beta}^{ab}\) is then called a \textit{stochastic matrix}.

Next, in keeping with the omission of the initial state from the variational problem, suppose \(p_{\sigma}\) is chosen to be the stationary distribution of largest eigenvalue preserved by whatever values of \(\gamma_{\alpha\beta}^{ab}\) solve the variational problem. Then it follows immediately—by collapse of the matrix \(\gamma_{\alpha\beta}^{ab}\) with \([1 \ 1]\) on the left, and with \([p_a  \ p_b]^{\top}\) on the right—that

\[
\frac{\partial \log Q}{\partial \log \gamma_{\alpha\beta}^{ab}} = \left(\bar{M}_{\alpha\beta}^{ab}\right) = \gamma_{\alpha\beta}^{ab} p_{\beta}. \tag{128}
\]

We solve for the \(\gamma_{\alpha\beta}^{ab}\) by setting equation (128) equal to \(M_{\alpha\beta}^{ab}\)\(^ {18}\). It follows from our choice to normalize \(\gamma_{\alpha\beta}^{ab}\) to be a stochastic matrix that

\[
\sum_a \bar{M}_{\alpha\beta}^{ab} = p_{\beta}. \tag{129}
\]

The relation of the \(\gamma_{\alpha\beta}^{ab}\) to the \(p_{\beta}\) may now be made explicit. The assumption behind the use of a discrete stochastic-process model is that \(\Delta t\) is a scaling variable that may be changed in the discrete model while leaving important physical observables unchanged, though rescaling \(\Delta t\) may introduce overall renormalization constants associated with the discretization. In general the \(\gamma_{\alpha\beta}^{ab}\) will then depend on the \(\Delta t\) but the stationary distribution of the stochastic process should not. Denote the stationary distribution that is self-consistent with the \(\gamma_{\alpha\beta}^{ab}\) appropriate to the given \(\{M_{\alpha\beta}^{ab}\}\) by \([\pi_{\beta}]\).\(^ {19}\) Then the most general stochastic matrix \(\gamma_{\alpha\beta}^{ab}\) with \([\pi_{\beta}]\) as the dominant eigenvector is

\[
\gamma_{\alpha\beta}^{ab} = \begin{bmatrix} \gamma_{aa}^{ab} & \gamma_{ab}^{ab} \\ \gamma_{ba}^{ab} & \gamma_{bb}^{ab} \end{bmatrix} = \begin{bmatrix} 1 & \pi_{\beta} \\ \pi_{\alpha} & -\pi_{\alpha} \end{bmatrix} \left(1 - r^{-k}\right). \tag{130}
\]

The constant \(R\) sets the frequency of transition events \(M_{\alpha\beta}^{ab} = M_{ba}^{ab}\). To model ensure that the discrete stochastic process has the same continuum limit as the continuous-time model of the previous sections, we require that for sufficiently short \(\Delta t\), \(R\) must converge to

\[
R = (k_+ + k_-) \Delta t. \tag{131}
\]

The form (130) is chosen so that under refinement or coarsening of the time increment, the definition (131) remains consistent.

The interpretation of \(k_\pm\) as rate constants is completed if we set their ratio from the fractions of time intervals in which

\[\text{Note that if we were imposing more finely resolved time-dependent constraints, the same might not be true, but for this finite set of four observables covering indefinite } M, \text{ we have no other choice consistent with only two states.}\]

\[\text{If we had not supposed that } \{p_{\sigma}\} \text{ was the stationary distribution, the same result would be obtained asymptotically in large } M, \text{ through the approximation of } \log Q \text{ by its largest log-eigenvalue, denoted log } \lambda_{\ast}. \text{ This is the approach taken in [61, 62].}\]

\[\text{The distribution } \{\pi_{\beta}\} \text{ clearly corresponds to the number fraction } [\gamma_{\beta}^{\pi}] \text{ of the preceding sections.}\]

The system starts, respectively, in states \(a\) or \(b\):

\[
\pi_a = \frac{k_-}{k_+ + k_-}, \quad \pi_b = \frac{k_+}{k_+ + k_-}. \tag{132}
\]

corresponding to equation (5). Values of \(k_\pm\) are then chosen to satisfy the constraints (129). With these choices the matrix \(\gamma_{\alpha\beta}^{ab}\) becomes precisely the transfer matrix for the continuous-time one-particle problem.

Note that the relation between the rate constants, equilibrium frequencies, and transition numbers may be written

\[
\frac{\bar{M}_{ba}^{ab}}{T} = \frac{\bar{M}_{ab}^{ab}}{T} = \sqrt{\pi_a k_+ \sqrt{\pi_b k_-}}. \tag{133}
\]

This form—a variant expression for either \(\pi_a k_+\) or \(\pi_b k_-\)—which characterizes the equilibrium distribution, will arise again when we use the generating function to probe steady non-equilibrium states.

From the variational property (128) and the original Lagrangian formulation of the problem, we recognize that \(\log Q\) will be the negative of a Gibbs free energy. From the fact that \(\log Q = 0\) when the \(\gamma_{\alpha\beta}^{ab}\) are evaluated at the above conditions, we know that the free energy may be offset by a constant at the entropy-maximizing, equilibrium distribution. We may derive the exact relation by calculating the entropy of the initial distribution, with the time-integral of the entropy rate of the initial distribution, we may express the path entropy as a sum of the entropy of the initial distribution, with the time-integral of the \textit{entropy rate} of the stochastic process in that distribution [49]. This expression is the first in the paper in which the entropy rate is given its familiar form from the stochastic process of a finite-state system.

The combinatorial interpretation of the second line in equation (134) is immediate. Using \(S^0(\{\pi^0\})\) to denote the single-time entropy of the initial distribution, we may express

\[
S^\text{path} \left(\{\bar{M}_{\alpha\beta}^{ab}\}\right) = S^0 (\{\pi^0\}) + \log \left(\frac{M_{\pi_a}}{\bar{M}_{ba}^{ab}}\right) + \log \left(\frac{M_{\pi_b}}{\bar{M}_{ab}^{ab}}\right). \tag{135}
\]

The combinatorial entropy is the Stirling approximation for the logs of the two independent binomial factors for distributing \(\bar{M}_{ba}^{ab}\) transitions \(a \rightarrow b\) among \(M_{\pi_a} = \bar{M}_{aa}^{ab} + \bar{M}_{ba}^{ab}\) total exits.
from state $a$, and similarly for distributing $\bar{M}^{ab}$ exits $b \to a$ among $M_{\pi_b}$ total exits from $b$. Note that the entropy rate term in equation (134) will diverge logarithmically in $\Delta t$ if a finite number of transitions $M^{ba} = \bar{M}^{ab}$ is fixed in a growing number of opportunities $M$.

Finally, from the explicit expression for the entropy either in terms of $\{M_{\alpha\beta}\}$ or the associated Lagrange multipliers $\{\lambda_{\alpha\beta} = -\log \psi_{\alpha\beta}\}$, we may identify the relation between the partition function $Q$ and a free energy that leads to the relations (128):

$$-\log Q = \sum_{\alpha\beta} \lambda_{\alpha\beta} M_{\alpha\beta}^0 - S^{\text{path}} \left( \left[ \frac{\partial \Phi}{\partial M_{\alpha\beta}} \right] \right) + S^0 (\{\pi^0\}). \quad (136)$$

Here each $M_{\alpha\beta}^0$ denotes the $\alpha\beta$-component of the set of $M$ jointly satisfying

$$\frac{\partial S^{\text{path}} \left( \left[ \frac{\partial \Phi}{\partial M_{\alpha\beta}} \right] \right)}{\partial M_{\alpha\beta}} = \lambda_{\alpha\beta}. \quad (137)$$

From the developments of the single-time equilibrium, we may anticipate that the effective action for other configurations $\{M_{\alpha\beta}\}$ that the most-probable ones will have the same form as equation (136), with $\{\lambda_{\alpha\beta}\}$ fixed and $\{M_{\alpha\beta}\}$ permitted to vary independently of them. We will return to that and to its physical and combinatorial evaluation in a moment, but first we do the construction methodically through a generating function for the path-probability distribution.

5.2. Generating function for steady non-equilibrium states, and connection to the continuous-time Langevin equation

A generating function for the discrete-time path ensemble may be constructed as it was in the D–P method. Because we will consider only steady non-equilibrium distributions, we may do this in a direct and simple way, as a modification of the underlying transfer matrix by shifts in the chemical potential. There are many perturbations that could be chosen for the discrete-time model, but only one equivalent to the coupling to the number field in section 4.3 produces the same hydrodynamic limit as $\Delta t \to 0$.

Because the discrete model has four parameters $\{\gamma_{\alpha\beta}\}$ for transition rates, we introduce four complex variables

$$\zeta^{\alpha\beta} \equiv e^{\gamma^{\alpha\beta}} \quad (138)$$
as arguments of the moment-generating function. Suppose that, like the $\lambda^{\alpha\beta}$, all $\zeta^{\alpha\beta}$ scale $\sim (k_+ + k_-) \Delta t \ll 1$. The terms $\zeta^{ba}$ and $\zeta^{bb}$ modify the transition currents, while terms $\zeta^{aa}$ and $\zeta^{bb}$ modify the persistence probabilities. The counterpart to the current $j$ of section 4.3, which effectively modifies the chemical potentials of the states, is the combination $\zeta^{aa} - \zeta^{bb}$. Therefore, to compare the path entropy with this perturbation in the D–P formulation, we set $\zeta^{ba} = \zeta^{ab} \equiv 0$, and consider only the remaining two perturbations.

For constant sources $\zeta^{aa}$ and $\zeta^{bb}$, the path-generating function for non-equilibrium, asymptotically steady transition numbers may simply be written in terms of a transfer matrix that has the same modification in every timestep, as

$$\psi^{\text{path}} (\zeta^{aa}, \zeta^{bb}) = e^{-\Gamma^{\text{path}} (\zeta^{aa}, \zeta^{bb})} = \sum_{\sigma} \sum_{j \sigma} \left( \zeta^{aa} \right)^{M_{\sigma j}^0} \left( \zeta^{bb} \right)^{P_{j \sigma} \pi_{\sigma}} \frac{1}{Q} \left[ 1 \right] \left( \left[ \frac{\partial \Phi}{\partial \zeta^{aa}} \right] \right)^{M_{\sigma j}^0} \left[ \pi_{\sigma} \right]. \quad (139)$$

The starting probabilities $\{\pi_{\sigma}\}$ in equation (139) will no longer be those preserved by the transfer matrix at nonzero $\{\zeta^{\alpha\beta}\}$, so the function $\Gamma^{\text{path}} (\zeta^{aa}, \zeta^{bb})$ will generally differ from the form (136) given for $-\log Q$. The difference will be associated with transient decay from $\{\pi_{\sigma}\}$ to the perturbed stationary state, and will scale as $(T)^0$ at large $T$. If we denote this constant as $\Lambda^0$, the asymptotic expression for the generating function becomes

$$\Gamma^{\text{path}} (\zeta^{aa}, \zeta^{bb}) = \sum_{\alpha\beta} (\lambda + \zeta^{aa}) M_{\alpha\beta}^0 - S^{\text{path}} \left( \left[ \frac{\partial \Phi}{\partial \zeta^{aa}} \right] \right) + \Lambda^0 + \log Q. \quad (140)$$

The asymptotic stationary values $\bar{\rho}^\alpha, \bar{\rho}^\beta$ may be computed as functions of $\lambda + \zeta$ as before, and the functional relation may then be inverted to assign values to the $\zeta^{\alpha\beta}$. It is possible to check that only the combination $\zeta^{aa} - \zeta^{bb}$ appears in any of the transition-number expressions, so we could originally have set $\zeta^{aa} = 1/\zeta^{bb}$ as a single argument to $\psi^{\text{path}}$. This construction exactly follows the construction of the two-argument and the one-argument moment-generating functions in section 3.2.

An important secondary relation, which is not merely a definition but results from the choice $\zeta^{ba} = \zeta^{ab} \equiv 0$, is that the off-equilibrium transition rates satisfy

$$\frac{M_{\sigma j}^{\text{ba}}}{T} = \frac{M_{\sigma j}^{\text{ba}}}{T} = \sqrt{\rho_a k_s} \sqrt{\rho_b k_s}. \quad (141)$$

Equation (141) is the counterpart to equation (133) for the equilibrium distribution. This property will be responsible for the cancellation of terms between the path entropy and external weight factors which could diverge as $\Delta t \to 0$, and recovery of the hydrodynamic limit.

The transition rates (141) equal the rate at which the Langevin field correlation function (87) injects noise into the number-field correlation function (88). Thus we confirm that, for this simple example of non-interacting particles, the Langevin equation (86) describes the fluctuating trajectories of single-particle states. The Langevin description is indirect, as $\nu^\prime$ is formally the expectation value of a Poisson distribution, and not a discrete single-particle trajectory. Following the injection of noise by the correlation function, it is then the classical relaxation time of these fluctuations, given by equation (117), that causes the single-time fluctuations (88) to agree with those in the equilibrium generating-function distribution from equation (22). We thus establish the mutual consistency of all of the approaches used.
5.3. The effective action from caliber and its interpretation

From here we compute the effective action by Legendre transform, just as in section 3 for the single-time equilibrium distribution. The result is

\[ S^{\text{eff}} \left[ \{ \bar{M}^{a\beta} \} \right] = \Gamma^{\text{path}} \left( \bar{x}^{aa} , \bar{x}^{bb} \right) - \int_{\bar{x}^{a\beta}} \bar{x}^{a\beta} \bar{M}^{a\beta} - \int_{\bar{x}^{a\beta}} \bar{x}^{a\beta} \bar{M}^{b\beta} \]

\[ = \sum_{a} \lambda^{a\beta} \bar{M}^{a\beta} - S^{\text{path}} \left[ \{ \bar{M}^{a\beta} \} \right] + \Lambda^0 + \log Q \]

\[ = \sum_{a} \lambda^{a\beta} \bar{M}^{a\beta} - \log \left( \bar{M} \bar{p}_a \right) \]

\[ + \sum_{a} \lambda^{b\beta} \bar{M}^{b\beta} - \log \left( \bar{M} \bar{p}_b \right) \]

\[ + \Lambda^0 + \log Q . \]  \hspace{1cm} (142)

In the last expression we recall the decomposition (135) of the stationary-state path entropy into the logarithms of two independent binomials. For the equilibrium transition rates \( \Lambda^0 \rightarrow S^0(\{ \pi^a \}) \) and the expression vanishes as required. Recalling that \( S^0(\{ \pi^a \}) + \log Q \) in equation (136) is simply the maximizer of the terms written explicitly in equation (142), we recover exactly the difference of Gibbs free energies which was the stochastic effective action in equation (32).

It now remains only to check that the expression (142) recovers the non-divergent entropy rate computed from the master equation, and to assign physical meanings to the terms that appear.

Consider the limit in which \( M^{ba} = M^{ab} \) remains finite as \( \Delta t \rightarrow 0 \) and \( M \rightarrow \infty \), and suppose all \( k_j \Delta t \ll 1 \). The external source term that appears in the effective action (142) evaluates to

\[ \sum_{ab} \lambda^{a\beta} \bar{M}^{a\beta} \frac{M^{ba}}{T} = - \frac{M \bar{p}^b - M^{ba}}{M \Delta t} \log (1 - k_+ \Delta t) \]

\[ = - \frac{M \bar{p}^b - M^{ab}}{M \Delta t} \log (1 - k_- \Delta t) \]

\[ = - \frac{M^{ba}}{T} \log (k_+ \Delta t) + \frac{M^{ab}}{T} \log (k_- \Delta t) \]

\[ = \bar{p}_a k_+ + \bar{p}_b k_- - \sqrt{\bar{p}_a k_+ \bar{p}_b k_-} \log (k_+ k_- \Delta t^2) . \]  \hspace{1cm} (143)

The terms in the purely combinatorial path entropy evaluate to

\[ S^{\text{path}} \left[ \{ \bar{M}^{a\beta} \} \right] = - \frac{M \bar{p}_a - M^{ba}}{M} \log \left( 1 - \frac{M^{ba}}{M \bar{p}_a} \right) \]

\[ - \frac{M \bar{p}^b - M^{ab}}{M} \log \left( 1 - \frac{M^{ab}}{M \bar{p}^b} \right) \]

\[ - \frac{M^{ba}}{M} \log \frac{M^{ba}}{M \bar{p}_a} - \frac{M^{ab}}{M} \log \frac{M^{ab}}{M \bar{p}^b} \]

\[ \approx \frac{M^{ba}}{M} \left[ 2 - \log \left( \frac{M^{ba}}{M^2 \bar{p}_a \bar{p}_b} \right) \right] \]

\[ = \Delta t \sqrt{\bar{p}_a k_+ \bar{p}_b k_-} \left[ 2 - \log (k_+ k_- \Delta t^2) \right] . \]  \hspace{1cm} (144)

We have placed the terms in the same order as those in the internal linear function (143), and the term with the logarithm—again arising from the events where the state changes—is in fact identical in the entropy and in equation (143). The two log terms exactly cancel in the subtraction that defines the effective action (142), leaving a finite remainder, which we will see is the hydrodynamic entropy rate.

It is the first two, non-divergent terms, which differ between the path entropy and the external probabilities. The total numbers \( M^{ba} \) and \( M^{ab} \) are frequencies entering the binomial factors in the path entropy, and both terms contribute identical factors proportional to \( M^{ba} = M^{ab} \). The difference of equation (143) and equation (144) gives the non-divergent effective action by equation (142), which goes at large \( T \) (ignoring the contribution of terms \( \sim (T)^0 \)) to

\[ \frac{S^{\text{eff}} \left[ \{ \bar{M}^{a\beta} \} \right]}{T} \rightarrow \bar{p}_a k_+ + \bar{p}_b k_- - 2 \sqrt{\bar{p}_a k_+ \bar{p}_b k_-} \]

\[ = \left( \sqrt{\bar{p}_a k_+} - \sqrt{\bar{p}_b k_-} \right)^2 . \]  \hspace{1cm} (145)

Equation (145) recovers precisely the one-particle coefficient of \( T \) in equation (113), when converted to descaled time \( T \) by the factor \( k_+ + k_- \).

Thus we again find that \( T \) is the scaling variable in the large-deviations principle associated with independent path fluctuations for a single particle. This scaling applies only to the extended-time partition function. It acts independently of the scaling with \( N \), which is the same in the extended-time and single-time levels of thermodynamic description.

5.4. Discretization divergences and the natural scale

As was explained in section 2.5, the discrete time interval \( \Delta t \) may be taken only down to a certain scale before the approximation by a discrete two-state theory becomes inappropriate. The lower limit to \( \Delta t \) from the continuum double-well model will come from the diffusive-relaxation time, for a trajectory starting at the saddle point and ending in whichever well is most-quickly reached. On timescales shorter than this it becomes invalid to characterize escapes as elementary events counted by \( M^{ba} \) or \( M^{ab} \).

We expect that when the discretization scale is set to this value—termed the natural scale of the problem following
The exponential waiting times in $k_{\pm}$ are not affected, but the factor $\Delta t$ cancels the dimensional prefactors in $k_{\pm}$, which have dimensions $1/$time, and have a characteristic scale set by the diffusive-relaxation rate.

If we plug the approximation (146) into the formula (143) for the environment terms in the path-space Gibbs free energy, this term evaluates approximately to

$$\begin{align*}
\sum_{\alpha\beta} \lambda^{\alpha\beta} M^{\alpha\beta} / T &\approx \bar{p}_a k_+ + \bar{p}_b k_- \\
&+ \bar{M}^{a0} / T (\mu_+ - \mu_{b+}) + \bar{M}^{ab} / T (\mu_+ - \mu_b).
\end{align*}$$

(147)

We have thus arrived at a mathematical expression of the graphical heuristic for thinking about dynamical ensembles given in figure 3 of section 2.3. The attracting fixed points of the underlying free-energy landscape carry charge-valued, extensive state variables such as the occupation frequencies $\bar{p}_a$, $\bar{p}_b$ for states. They are related under Legendre transform to dual, intensive entropy gradients from the environment—here $k_+$ and $k_-$, respectively—which determine the probabilities for each state. The extensive, current-valued state variables—here the numbers $M^{a0}$ and $M^{ab}$ of transition events—live on the saddle points of the landscape. Under Legendre transform, they should be coupled to the dual chemical potentials that determine the probability of transitions: here $\mu_+ - \mu_{b+}$ and $\mu_+ - \mu_b$. The asymmetry between states and transitions arises because chemical potentials appear exponentially in the leaving rates $k_{\pm}$, and only linearly in the transition-state terms involving $\mu_{\pm}$.

5.5. Connection to energy dissipation

The path-space Gibbs free energy (142) has separated events into categories, which we can associate with different kinds of energy transfers. The events in which the particle exchanges wells could correctly be associated with either absorption of energy from the bath, or dissipation to it, depending on the sign of the free-energy difference in the starting and ending well. However, these terms entirely cancel between the path entropy and the environment-mediated probability, and do not contribute to the entropy rate expression in equation (113) in the hydrodynamic limit. This cancelling term may be ascribed to ‘entropy production’ in the path ensemble which is exported to the environment, but it does not appear in the large-deviations formula. Moreover, we are lucky that we do not need it to compute path probabilities, because it appears to depend on the model resolution $\Delta t$, which is not physically meaningful.

The terms that survive in the entropy rate, and contribute to its distinctive form (115), come from all the moments when thermal fluctuations do not lead to escapes. For all these, energy is neither absorbed nor dissipated. In summary, we acknowledge that there are cases [63] in which a collection of non-equilibrium transitions is constrained by consistency with the equilibrium distribution that is their starting or ending point. Since the equilibrium distribution is dictated by energy, these constrained transformations must also have characterizations in terms of energy. However, for a large collection of non-equilibrium fluctuation theorems, energy alone is not serving as the primary constraint on kinetics, and we must look for the explanation of path probabilities in terms of other parameters of the stochastic process.

6. Discussion and conclusions

6.1. Why generating functions for large-deviations formulae?

We remarked in section 4.1 that generating functions provide a more natural representation for large-deviation formulae, and better approximation methods, than the discrete probability distribution because generating functions expand in moments of collective many-particle motion, rather than in single-particle hops. We have also seen, comparing equation (14) with equation (32), that the cumulant-generating function extracts the leading-exponential term in from the probability distribution, bypassing sub-leading terms from normalization. But how does it perform this separation? We may understand that the isolation of leading exponentials is in fact a direct reflection of the way the generating function expands in moments.

In elementary statistical mechanics [11], we argue that the microcanonical and canonical ensembles produce the same entropy, because the probability of the most-likely element in a sharply peaked distribution is equal at leading-exponential order to the weight of all typical elements in that distribution. The two probabilities differ only by the width of the distribution, which is sub-leading as we saw in equation (17).

The moment-generating function may be understood as extracting, not only the probability to observe a single sample-fluctuation from the equilibrium distribution, but in fact the projection of the original distribution onto the entire sub-distribution within which that sample fluctuation is typical. This is the shifted binomial distribution appearing in equation (19). The constant of proportionality between the two distributions, whose logarithm is the cumulant-generating function, is then precisely the leading-exponential difference of probabilities, because normalization terms in the original distribution and the projected distribution have canceled.

6.2. Operator algebras in the Doi formalism: two-field methods in general, and the difference between classical and quantum systems

The Doi [4, 5] construction of time-dependent ensembles uses a further property of generating functions which can lead to confusion on first exposure, but which is important to understand in order to assign the correct meaning to the operators and states used in the construction.

Any probability distribution may be written as a sum of modes, and the generating function associated with that
probability distribution may likewise be written as a sum of polynomials. Therefore, generating functions satisfy a property of superposition, similar in many respects to the superposition satisfied by states in quantum mechanics. Time evolution acts on superpositions, either of quantum states, or of the modes of a generating function, independently. Much of the time-dependence in either quantum mechanics or stochastic processes can therefore be understood from the sequencing of the time-evolution operators, without reference to the particular function-spaces in which they act. Doi’s contribution was to distill the dependence in the order of time-evolution operators into an operator algebra, which has the same form as the algebra of the simple harmonic oscillators of quantum mechanics or quantum field theory.

For this reason, Doi–Peliti methods are sometimes [16] termed ‘quantum field theory’ methods for stochastic processes. However, the operator algebra itself carries no implication of a physical property of quantum-superposition of distinct eigenstates of observables, and derives only from the linearity of time evolution. The physical commitment to the classical or quantum nature of a system comes from specifying the space of functions representing states and their observable properties, and on the inner product in that space. For further discussion of the many similarities implied, solely by superposition and causality, between classical and quantum systems, see [39]. It is under the correspondence of operator algebras that the stochastic effective action and the quantum effective action are equivalent objects.

The use of time-dependent sources to probe complex histories with the stochastic effective action does not seem common in reaction–diffusion applications of Doi–Peliti theory. We hope that such methods can come to be used to ask a wider range of structurally explicit questions about non-equilibrium paths.

As the simplest non-trivial examples, this paper has demonstrated new entropy-rate formulae for steady non-equilibrium paths, both for independent-particle random walks, and for stoichiometrically non-trivial chemical reactions. An area for future work is to extend such formulae to study the large-deviations behavior of random walks on graphs or the fluctuations of realistic chemical-reaction networks.

6.3. The information conditions that embed single-time ensembles within ensembles of histories

The equilibrium (canonical) thermodynamic ensemble was recovered in section 4.3 as the projection of the larger ensemble over histories onto a single-time slice, in a region where the histories had settled into their stationary distribution over both states and transitions. ‘Fluctuations’ in the equilibrium ensemble have no dynamical connotation, and are simply sample values. Histories have both dynamical correlation—a property of a path itself—and stochastic fluctuation that represents sampling from the ensemble over paths.

Fluctuation values in the equilibrium ensemble, when embedded within the larger ensemble of histories, have the interpretation of instantaneous conditions on histories accompanied by no other information. These information conditions imply distributions over histories conditioned on the single-time fluctuation, which appears as an independent variable. Freidlin–Wentzell theory reproduces the probabilities for such single-time fluctuations from the integrals, over the most-probable histories, of conditional probabilities for each successive increment of change.

The equilibrium distribution is not the only ensemble that can be recovered from an ensemble of histories by projection onto single instants. Projections onto slices where paths have not settled into their stationary distribution result in non-equilibrium entropies at single times. These entropies require both charge and current state variables as arguments [40, 43], and they can be written in terms of the Wigner distribution, considered in [55]. We may say then that there is a hierarchy of ensembles, from the most-complete ensemble over histories to single-time non-equilibrium ensembles, which lose the time-correlation of histories but preserve current-valued state variables, finally reaching the equilibrium ensemble which projects onto only the charge-valued state variables. By connecting state variables to fixed points of free-energy landscapes in figure 3, and to Legendre duality in equation (147), we have attempted to provide several perspectives to understand this duality.

6.4. Thermodynamics beyond Zeno

The incompleteness of the time-reversal-invariant state variables of equilibrium thermodynamics is analogous, in the domain of stochastic processes, to the incompleteness of spatial geometry as a representation for mechanics, as expressed in Zeno’s paradox of the arrow. If a geometric description can assign only a position as a property of the arrow at any single instant, this description offers no way to distinguish states of motion that the arrow may have, which in a dynamical theory are required as initial conditions. Unlike the other Zeno paradoxes which emphasize subdivision of space or time, the arrow paradox highlights the inadequacy of dynamical descriptions that cannot represent both position and momentum as independent but inherent properties at a single instant. The dynamical system of Freidlin–Wentzell theory, with its conjugate momentum field, completes this dual formulation for thermodynamics much as Hamiltonian dynamics completes it for mechanics.

In quantum mechanics the independence of position and momentum as both inherent properties is manifest—traveling waves are distinct superpositions from standing waves—but it comes at the price that position and momentum are non-commuting observables [40, 43]. The correspondence between operator algebras for stochastic processes and dissipative quantum systems (annotated bibliography in appendix A), shows that the Doi–Peliti construction is revealing essentially the same form of inherent duality as the standing/traveling wave duality in quantum mechanics. The remarkable insight from Freidlin–Wentzell theory, not obvious beforehand, is that this dual momentum variable for classical stochastic processes should be an ‘inference field’, and that in reversible random walks it takes the form of a chemical potential.
References [57, 61, 62] emphasize the potential for master equations to give only a coarse-grained description compared with maximum-caliber methods that track distinguishable particle trajectories. For interacting particles, this difference may be important. However, for non-interacting particles, the $N$-particle moment-generating function is simply the $N$th power of the one-particle moment-generating function [50]. Indeed, this relation is what causes the field normalizations (53) and (70) to lead to an exact (and not merely asymptotic) factorization of scale-factor $N$ from the remaining large-deviation rate functions for relative numbers, not only for the two-state system, but for any non-interacting particle system. We also see that the Doi–Peliti construction ‘contains’ a description of single-particle trajectories, from the agreement of the transition rates (141) in the discrete-time model with the correlation function (87) of the Langevin stochastic differential equation, whose solution is the Gaussian approximation to discrete random walk.

6.6. On the necessity of thermodynamic limits

Our rather conservative extension of large-deviations calculations, from equilibrium to non-equilibrium statistical mechanics, has the advantage of starting in well-known territory, and taking a small step across which we can construct all relations between the different ensembles explicitly. It does not do justice to the generality of large-deviations formulae, emphasized in [2], and up to now we have not adequately expressed the dependence throughout science on the existence of thermodynamic descriptions.

The ability to coarse-grain has been our most important tool to bring an infinitely complicated world within reach of analysis and comprehension. In the early years of statistical mechanics, when the formulations of Boltzmann [64, 65] and Gibbs [66] were seen as ‘replacing’ classical thermodynamics, Fermi [10] was quick to emphasize that thermodynamic descriptions have their own internal consistency and, at the appropriate level of scale, are self-contained with respect to empirical validation. We have learned over the last half-century that this point is true and important to a degree that Fermi could not have foreseen. As renormalization methods have become well-understood conceptually [67], we have learned that all descriptions are—or may as well be—thermodynamic descriptions [48, 59]20.

Our view of the meaning of fundamental theory has changed accordingly. All theories once regarded as fundamental have been effective theories, and at the same time, from criteria of scale-dependent statistical reduction, each has been fundamental. Whether the series terminates is now understood not to be critical; any level at which one can form a thermodynamic description is a valid starting point for deduction at that scale and larger scales of aggregation.

Hierarchies of nested phase transitions [68, 69], connected by regions of large-deviations scaling, govern the behavior of equilibrium matter at all scales now known, within theories that are already understood. Recognizing that neither large-deviations scaling nor phase transition are phenomena linked inherently to equilibrium, we may ask how many non-equilibrium cases of symmetry breaking and large-deviations scaling are responsible for complex dynamics in nature that are not yet well understood in terms of collective phenomena [70].

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Appendix A. Survey of approaches to large-deviations theory for non-equilibrium processes

The main text brings together Doi–Peliti construction methods, the larger framework of Freidlin–Wentzell theory, and Jaynes’s methods of defining combinatorial entropies for paths. Mathematical differences among the methods are small; Doi–Peliti theory may be seen simply as a construction method for the Freidlin–Wentzell quasipotential, and the only important addition from path entropies is the finer resolution it gives to distinguishable-particle trajectories.

What will not be apparent in the main text is that several distinct studies exist for these nearly identical mathematical methods, which have been repeatedly discovered for quantum mechanics, and for discrete- and continuous-variable classical stochastic processes. From the collection of different special cases, it has become clear [39] that a single framework of two-field functional integrals subsumes all the different approaches. Moreover, all integrals of this type share particular structural features, which reflect superposition or causality, independently of the physical substrate to which they apply.

We summarize in order the key ideas behind two-field methods, functional Legendre transforms, and entropy-rate methods, and finally mention a parallel treatment within the mathematics literature that emphasizes observables rather than states.

Appendix A.1. Two-field functional integral methods

The most widely used (formally exact)21 methods in the physics literature to compute both deterministic and

20 Properly they are called effective theories. The class of equilibrium mechanical theories generally recognized within the conventional term “thermodynamics” is a class of effective theories. The defining properties used in this review are, however, properties of the whole class, and so the terms “thermodynamic description” and “effective theory” could be used interchangeably to refer to them. This concept of “effective” theory is also the source of the name for the quantum and stochastic effective actions.

21 With this condition we exclude very widely used but intentionally approximate methods such as Langevin equations or the van Kampen expansion [71]. Any of the fall methods cited here may be reduced to Langevin or van Kampen approximations by standard methods of Gaussian integration.
fluctuation properties of non-equilibrium systems are a class of generating-functional methods, all of which have expressions as two-field, coherent-state functional integrals. The earliest of these were the density-matrix methods of Schwinger [14] and Keldysh [15, 41] to combine dissipation and dynamics in quantum systems. The Schwinger–Keldysh form was later proposed as a general framework to handle dissipative dynamics in classical or quantum systems by Martin, Siggia and Rose (MSR) [13]. It was observed by Doi [4, 5] that the superposition principle for generating functions for multiparticle classical stochastic processes is similar enough to that for quantum density matrices that the same operator algebra may be used to describe both, and only their Hilbert spaces differ. The Doi operator algebra for discrete Markov processes was later expanded as a coherent-state functional integral of MSR form by Peliti [6, 7]. Kamenev has recently emphasized [39] that the causal structure originally recognized by Keldysh, and reflected in a characteristic ‘tri-diagonal’ form of the MSR action functional, is the unifying physical commitment that all field-theoretic methods of this kind share.

Explanations of the common elements of superposition and operator algebras are given in the main text in section 4.3, and the tri-diagonal form of Gaussian kernels and Green’s functions is illustrated in appendix C.

Among the two-field methods, the one that most explicitly emphasizes the large-deviations structure of the macroscopic approximation is the ray-theoretic, or eikonal-based, approach of Freidlin and Wentzell [3, 21, 37, 38, 73]. This approach, introduced in basic form by Eyring [74] to understand chemical-reaction rates, has been most extensively developed for escape and first-passage problems [28–36]. It refines and generalizes the equilibrium barrier-penetration formulae of Wentzel, Kramers and Brillouin (WKB) [54]. More generally the Freidlin–Wentzell method is of interest to mathematicians for the solution of boundary-value problems for diffusion in potentials. Freidlin–Wentzell theory introduces a quantity known as the quasipotential, so-named because it is thought of as a generalization of the equilibrium thermodynamic potentials. The quasipotential is a large-deviations rate function, appropriately scaled for system size. It may be evaluated as an action-functional integral along a ray or ‘eikonal’ of the diffusion operator [21, 38], which has the interpretation of the most-probable trajectory leading to an escape or boundary value.

Appendix A.2. Functional Legendre transform and stochastic effective actions

Generating-functional methods for dynamical systems—especially emphasizing efficient approximation—have been extensively refined in vacuum quantum field theory (QFT) and to some extent in condensed-matter physics. They are used in these domains to extract the leading deterministic approximation to fluctuating quantum-mechanical observables, a use very close to the extraction of leading-exponential dependence of probabilities in large-deviations theory. The functional Legendre transform of the cumulant-generating functional is known in QFT as the quantum effective action [22]. It is the basis of background-field methods used to identify the ground states or vacua of field theories, and it is the starting point for a variety of renormalization schemes. Efficient and elegant graphical methods have been derived to approximate it within the moment expansions of Gaussian functional integrals.

In the Doi–Peliti construction for discrete stochastic processes, the counterpart to the quantum effective action is the deficit in entropy for any configuration from the maximum entropy attainable under the same constraints. This entropy deficit is precisely the large-deviations rate function for fluctuations in macrostates [1]. For closed equilibrium systems this rate function is simply a difference between two entropies. For open equilibrium systems the contribution from entropies of the environment leads to the expression of the rate function as a difference of Gibbs free energies. The latter case leads to the forms developed in the main text.

In the large-deviations limit for non-equilibrium stochastic processes, where probabilities are defined on histories rather than on instantaneous states, the rate function becomes the difference between a combinatorial entropy defined on a path, and an entropy rate from the Markov process that generates the path in a stationary environment, as we have illustrated in section 5.

We have termed this large-deviations rate function, counterpart to the quantum effective action in QFT, the stochastic effective action. The quasipotential used in Freidlin–Wentzell theory to compute boundary values of diffusion equations in potentials is an instance of the stochastic effective action. For a one-dimensional system it is the form produced by the moment-generating function for observations at a single time. The general stochastic effective action, for arbitrary path fluctuations, is computed as the self-consistent expectation value of the Freidlin–Wentzell field action, in which the Liouville operator acts as Hamiltonian.

Appendix A.3. Path entropies and maximum caliber

The approach to non-equilibrium thermodynamics taken by Jaynes [8] is a direct outgrowth of methods based on the entropy rate of a stochastic process. (Related methods were developed for chaotic deterministic dynamical systems, where the entropy rate was replaced by the Kolmogorov–Sinai, or metric, entropy.) Probabilities are assigned to histories, and the measure on the space of histories, together with any constraints, then determines the path-space entropy. Jaynes coined the term caliber for the path entropy, to suggest the fluctuation width of a tube of microhistories about any coarse-grained macrohistory.

In the main text, we have used a formulation of the maximum-caliber principle developed in [57, 61, 62], suitable for computing the probability of steady non-equilibrium distributions. In cases where the transition probabilities
The methods used in this paper are those common in the literature. Appendix A.4. Large-deviations theory within the probability arguments of the entropy:

\[ \text{The entropy is the state function maximized subject to the energy in classical thermodynamics.} \]

\[ \text{Appendix B. State variables, entropy and Gibbs free energy in classical thermodynamics} \]

The entropy is the state function maximized subject to the constraints on the system configurations. The values of the constraints are given by the state variables that are the arguments of the entropy:

\[ S(U, V, \{n_i\}) \]

Common sources of constraint are internal energy \( U \), volume \( V \), or the numbers \( \{n_i\} \) of different kinds of particles.

The entropy arises as the leading-exponential term in the relative probabilities of different states of the system, grouped according to the values of the constraints \( U, V \), for which that entropy would be maximum:

\[ e^{S(U, V, \{n_i\})} \]

In this respect, the relative probability is a more fundamental quantity than the normalized probability. The normalization is the sum or integral of terms \( e^{S} \) over whichever states the system can take, which can depend on the setting. For independent systems, the relative probabilities multiply, so that the sum of the entropies is maximized at the overall-most-likely state. It is this relation between entropy and relative probability that defines the macroscopic fluctuation properties of ensembles [1].

The way entropy governs the structure of interacting systems comes from the properties of its gradients. The manipulation of these gradients is the main enterprise of classical thermodynamics [10].

The equation of state is merely a definition of the gradients of the entropy in terms of observable quantities:

\[ \delta S = \frac{\partial S}{\partial U} \delta U + \frac{\partial S}{\partial V} \delta V + \sum_i \frac{\partial S}{\partial n_i} \delta n_i \]

\[ \equiv \beta \delta U + \beta p \delta V - \sum_i \beta \mu_i \delta n_i. \] (B1)

In chemical thermodynamics \( 1/\beta = k_B T \) corresponds to the temperature in energy units, \( p \) is the pressure, and \( \{\mu_i\} \) are the chemical potentials. These gradients of \( S \) with respect to its extensive arguments are the intensive state variables in the thermodynamic description.

Equation (B1) may be rearranged to express entropy change in the units of any of the constraining state variables that are shared between system sub-components, or between the system and its environment. When energy is chosen as the unit of measure—a natural choice since it is conserved among nearly all forms of systems in contact—the result is the usual thermodynamic statement of ‘conservation of energy’:

\[ \delta U = k_B T \delta S - p \delta V + \sum_i \mu_i \delta n_i. \] (B2)

In this representation \( p \delta V \) and \( \{\mu_i, \delta n_i\} \) are interpreted respectively as mechanical and chemical increments of work, and \( k_B T \delta S \) labeled ‘heat’. Equation (B2) is only a ‘conservation law’ in the sense that \( \delta U \) is a lower bound on the energy change required to permit a change \( \delta S \), in the context where volume also changes by \( \delta V \) and particle numbers by \( \{\delta n_i\} \).

The expression of competition of entropy terms in the relative probability, when a small system is coupled to a much larger environment, is that we may often expand the entropy in the environment to linear order in the exchanged amounts of any conserved quantity that the system and environment dynamically apportion between them. The result for the total relative probability of an apportionment that leaves \( U \) and \( V \) in the system is

\[ e^{S(U,V,\{n_i\})-\beta_E U-\beta_E p V}. \] (B3)

We have supposed in the expression (B3) that energy and volume can be exchanged, but not particle number, and that intra-system equilibration leads to the relative probability \( e^{S} \) that would be maximum with \( U \) and \( V \) as constraints. Here \( \beta_E \) and \( p_E \) are regarded as fixed descriptors of the environment, by supposing that it is large compared with the system, so that only the first derivative of its entropy need be known. \( \beta_E \) and \( p_E \) therefore are not functions of \( U \) or \( V \).

The expected or stable state of the system is the one that maximizes the joint probability (B3) over \( U \) and \( V \). Ordinarily this maximization is regarded to take place within the fluctuations of the ensemble, and values other than the maximizers are never used in the combination \( S(U, V, \{n_i\})-\beta_E U-\beta_E p_E V \) in classical thermodynamics.

If we wish to use the classical theory to understand the effects of constraints on system states, we think of...
using $\beta_E$ and $p_E$ as control variables, imposed through the interaction between the system and the environment. The log-probability as a function of these control variables then becomes $\max_{U, V} [S(U, V, \{n_i\}) - \beta_E U - \beta_E p_E V]$. At the maximizers, $\beta = \beta_E$ and $p = p_E$. If we continue to denominate entropy changes in units of energy, and if we choose signs so that the $U$, $V$ extrema is a minimum, then the log-probability is proportional to the Gibbs free energy

$$G(k_B T, p, \{n_i\}) \equiv \min_{U, V} [U + p V - k_B T S(U, V, \{n_i\})].$$

(B4)

Now $p$ and $\beta$ have been set equal in the system and environment. The subscripts $p_E$, $\beta_E$ have therefore been dropped, and the minimizing $U$ and $V$ are now functions of $p$ and $\beta$.

If we wish to express classical thermodynamic relations in the form that relates most directly to the fluctuation-origins of the entropy, we may simply work directly with the logarithm of the relative probability, which is

$$-\beta G(k_B T, p, \{n_i\}) \equiv \max_{U, V} [S(U, V, \{n_i\}) - \beta (U + p V)].$$

(B5)

We will take the sign and normalization from equation (B5) to define a standard Legendre transform of $S$.

The fluctuation theorems in section 3, for particle exchange, are similar in structure to the intermediate expression (B3) for exchanges of energy or volume. $-\beta G$ takes the place of $S$, because it is assumed that energy and volume equilibrate on times much shorter than the equilibration times for particle exchange. In addition, the two states of the system exchange particles only with each other and not with the environment, so the two reference Gibbs free energies in the subsystems are not evaluated only to linear order.

**Appendix C. Exact solution for continuous sources in the time-dependent generating functional**

The nonlocal relation between current sources and the non-equilibrium paths they produce makes computation of the functional Legendre transform technically challenging for all but simple cases. However, the simplicity of the Gaussian integral in coherent-state variables makes it possible to understand this nonlocality with exact solutions. The coherent-state variables in this appendix will follow the diagonalization of section 4.2.

The coherent-state field action $\langle 92 \rangle$ may be recast in the matrix form $[39]$ characteristic of all two-field action functionals, as

$$S_j = N \int \text{d}r \left[ \frac{\partial}{\partial \tilde{\phi}_b} \phi_a \right]$$

$$\times \left[ -\hat{\alpha}_r + \hat{\nu}_a - j/2 \right]^{-\hat{v}_a} \left[ -\hat{\alpha}_r + \hat{\nu}_b - j/2 \right] \left[ \phi_a \right]$$

$$= N \int \text{d}r \left[ \sqrt{2 \hat{\phi}} \sqrt{1 / 2 \hat{\phi}} \right] - \hat{\alpha}_r + 1/2 \sigma_0$$

$$+ 1/2 \sigma_3 - \left( \tilde{v} + j/2 \right) \sigma_1 + i \tilde{v} \sigma_2. \quad \text{(C1)}$$

In the second line, $\sigma_0$ designates the $2 \times 2$ identity matrix and the other $\sigma_i$ are the Pauli matrices $\{54\}$

$$\sigma_1 = \left[ \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right],$$

$$\sigma_2 = \left[ \begin{array}{cc} i & 0 \\ 0 & -i \end{array} \right], \quad \text{(C2)}$$

$$\sigma_3 = \left[ \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right].$$

The solution to the stationary-point conditions, and for the effective action more generally, follows closely what has already been done for the single-time generating function. The major difference is that we must replace the solution of scalar differential equations with the time-ordered matrix solution of a linear differential equation expressed in terms of the matrix in equation (C1). The $2 \times 2$ matrix kernel, which depends on parameters of the potential and on $j$, will be denoted by

$$\sigma [\tilde{v}, j] \equiv \frac{1}{2} \sigma_0 + \frac{1}{2} \sigma_3 - \left( \tilde{v} + j/2 \right) \sigma_1 + i \tilde{v} \sigma_2. \quad \text{(C3)}$$

The expression of the boundary conditions at time $T$ (here again $T$ will be assumed finite but large) may be written

$$\left[ \sqrt{1 / 2 \hat{\phi}} \right]_r = \sqrt{2} \left[ \begin{array}{c} 0 \\ 1 \end{array} \right], \quad \text{(C4)}$$

and in terms of these, the general solution for the $\phi^\dagger$ fields propagates this constraint backward in time, as

$$\left[ \sqrt{1 / 2 \hat{\phi}} \right]_r = \sqrt{2 T^{-1}} e^{-j_1 j r} \left[ \begin{array}{c} 1 \\ 0 \end{array} \right]. \quad \text{(C5)}$$

Here $T^{-1}$ denotes the inverse time-ordering operator which arranges terms in the exponential from right to left in order of decreasing time. The solution (C5) is the direct generalization of the solutions (58) and (59).

In the same manner, for continuous sources (no $\delta$-functions, so we do not have to worry about exponential tails) $j_{r < 0} \equiv 0$, and the equilibrium state as the initial distribution, the lower boundary condition for the $\phi$ fields is

$$\left[ \sqrt{2 \hat{\phi}} \right]_0 = \frac{\phi_0}{\sqrt{2}} \left[ 2 \tilde{v} \right]. \quad \text{(C6)}$$

25 For relations among these, see the literature review in appendix A.
and the general time-dependent solution is

\[ \left[ \sqrt{2\dot{\Phi}} \right. - \left. \sqrt{T/2\Phi} \right] \tau = \frac{\delta_0}{\sqrt{2}} \left[ 2\tilde{v} - 1 \right] T^{-1} e^{-\int_0^\tau \text{d}\tau' \text{d}\sigma[i,j,1]} \]. \tag{C7} \]

Equation (C7) generalizes the constant solution (60) due to nonzero \( \dot{\tau} \).

The constraint of total number fixes the normalization of \( \dot{\Phi}_0 \) as before, through the relation

\[ 1 = \left[ \sqrt{2\dot{\Phi}} \right. - \left. \sqrt{T/2\Phi} \right] \tau \left( \text{at any } \tau \right) \]

\[ = \dot{\Phi}_0 \left[ 2\tilde{v} - 1 \right] T^{-1} e^{-\int_0^\tau \text{d}\tau' \text{d}\sigma[i,j,1]} \begin{bmatrix} 0 \\ 1 \end{bmatrix}. \tag{C8} \]

(corresponding to equation (61). The general time-dependent number expectation \( n_{\tau} \) is immediately seen to satisfy

\[ 2n_{\tau} = N \left[ \sqrt{2\dot{\Phi}} \right. - \left. \sqrt{T/2\Phi} \right] \tau \left[ 1 \right. \left. \begin{bmatrix} 1 \\ 1 \end{bmatrix} \begin{bmatrix} \sqrt{T/2\Phi} \Phi \end{bmatrix} \right] \tau \]

\[ = N \dot{\Phi}_0 \left[ 2\tilde{v} - 1 \right] T^{-1} e^{-\int_0^\tau \text{d}\tau' \text{d}\sigma[i,j,1]} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \]

\[ = 2\frac{\delta}{\delta \dot{\tau}} N \log \left[ \left[ 2\tilde{v} - 1 \right] T^{-1} e^{-\int_0^\tau \text{d}\tau' \text{d}\sigma[i,j,1]} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \right] \]

\[ = -2\frac{\delta}{\delta \dot{\tau}} \Gamma [j]. \tag{C9} \]

The functional form in the first two lines of equation (C9) directly generalizes equation (100) for the point source. The last two lines are the functional equivalent, with a variational derivative replacing the partial derivative, of the single-time relation (25). And indeed, by exactly the evaluation leading to equation (68), we find that the cumulant-generating functional is given by

\[ \Gamma [j] = -N \log \left[ \left[ 2\tilde{v} - 1 \right] T^{-1} e^{-\int_0^\tau \text{d}\tau' \text{d}\sigma[i,j,1]} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \right] \]. \tag{C10} \]

We now have an exact expression for the effective action which generalizes the single-time expression (33). Drawing \( \nu_\tau = n_{\tau}/N \) from equation (C9), the stochastic effective action is

\[ S_{\text{eff}} [n] = N \int_0^T \text{d}\tau \nu_\tau + \Gamma [j]. \tag{C11} \]

Equation (C11) is the promised functional which correctly generalizes the notion of an entropy difference from equation (32) to a space of histories. It represents a large-deviations principle for the stochastic process from equation (3), with a rate function \( \int_0^T \text{d}\tau \nu_\tau + \Gamma [j]/N \) which is strictly \( N \)-independent for Gaussian fluctuations. In this sense the linear reaction is the analog of the Gaussian distribution, and its large-deviations principle is simply the central limit theorem for a system with finite variance. The residual functional determinant for fluctuations about the mean value—though it will not be computed here—would introduce sub-extensive corrections in \( N \) just like those of the residual entropy in equation (17). (See [22, chapter 16], [39], and [42, chapter 7] for good treatments of such calculations).

**Appendix D. Entropy-rate formulae for multi-particle reactions**

Independent random walks between wells, by a particles of a single type, may be modeled in the discrete-state approximation by diffusion on an ordinary graph. If the mass-action rates satisfy detailed balance in the steady state, the graph may be considered undirected; otherwise it is directed. Chemical reactions in which multiple particles jointly move through a transition state from reactants to products generalize this relation from graphs to hypergraphs. A graph need not be directed in the case of detailed balance, because the nodes at either end of a link are naturally complementary. Hypergraphs, in contrast, are defined to permit arbitrary collections of nodes as the ‘boundary’ of a hyper-edge. We therefore require directed hyper-edges to model chemistry, which distinguish a subset of nodes as inputs and a second subset as outputs.

The surprising formula (115) for the probability rate of persistent non-equilibrium paths may immediately be extended to arbitrary networks of chemical reactions, hence, from graphs to directed hypergraphs. Global network topology will not be considered here, but the rate formulae for arbitrary multi-particle reactions at steady-state disequilibria will be given.

Consider a general collection of bi-directional reactions indexed by their reactant and product sides as \( r \) and \( p \). Individual species participating in the reaction generalize the wells \( a \) and \( b \) of the two-state system, to a many-well problem where indices \( a_i \) and \( b_j \) are drawn from a common set of species. The reaction formula is

\[ p_{b_1} + \cdots + p_{b_n} \xrightleftharpoons[r_{a_1} + \cdots + r_{a_n}]{k_{ba}} r_{a_1} + \cdots + r_{a_n}. \tag{D1} \]

To simplify the notation, rather than writing stoichiometric coefficients other than unity, it will be assumed that the coefficients \( a_i \) or \( b_j \) can repeatedly take the same values as needed. The order in which the indices \( ab \) are written defines the relation between the sign of the current and the changes of concentrations, so that \( ab \) and \( ba \) denote the same reaction but with opposite sign conventions for the current. When only the pair matters, without respect to sign, the pair-index will be denoted by \( \langle ab \rangle \).

The complexes of reactants and products behave in the transition state as a single ‘particle’, for which the one-particle free energy (or chemical potential) will be denoted \( \mu_{i}^{\langle ab \rangle} \). The half-reaction rate constants are then defined from the transition-state and single-species one-particle chemical potentials as

\[ k_{ba} = e^{-\beta (\mu_{i}^{\langle ab \rangle} - \sum_{j=1}^{n} \mu_{j}^{\langle ab \rangle})}. \]

\[ k_{ab} = e^{-\beta (\mu_{i}^{\langle ab \rangle} - \sum_{j=1}^{n} \mu_{j}^{\langle ab \rangle})}. \tag{D2} \]

The forward and backward half-reaction rates associated with the reaction (D1), with the simplified dilute-solution
assumption that activities are proportional to concentrations, are then given by
\[ r_{ba} = k_{ba} \prod_{i=1}^{m} n_{a_i} \]
\[ = e^{-\beta \mu_{a_i}} e^{\sum_{i=1}^{m} \left( \mu_{a_i} \log n_{a_i} \right)} \]
\[ \equiv e^{-\beta \left( \mu_{a_i} - \sum_{i=1}^{m} \mu_{a_i} \right) \log n_{a_i}} \].

The construction of the field functional integral proceeds to determine such backgrounds can then be inferred. The equation for \( n_k \) is
\[ \partial_t n_k = \sum_{ab} e^{-\beta \left( \mu_{a_i} - \sum_{i=1}^{m} \mu_{a_i} \right) \frac{\partial}{\partial \eta_k} \left( e^{\sum_{j=1}^{n} \beta \mu_{b_j} - \sum_{i=1}^{m} \eta k \beta \mu_{a_i} \log n_{a_i}} \right)} \].

Again, the sum is symmetric under exchange of \( a \) and \( b \), so wherever \( \partial_t / \partial \eta_k \) acts, it acts equally and with opposite sign in two terms. Cancellation of all such pairs of terms corresponds to detailed balance, except that the \( \eta \) variables in the exponential can take nonzero values.

Equation (D7) can be solved with \( \partial_t n_k \equiv 0 \) for any configuration of the \( \{n_k\} \) by setting
\[ \eta_k = \frac{1}{2} \beta \mu_k = \frac{1}{2} \left( \beta \mu_k + \log n_k \right) \].

A sequence of evaluations identical to those leading to equation (113) then produces an equivalent form for the set of many-particle reactions, now expressed as a sum over reactions only (so unordered pairs \( \{ab\} \)):
\[ \mathcal{L} = \sum_{\{ab\}} e^{-\beta \mu_{a_i}} \left( e^{\sum_{j=1}^{n} \beta \mu_{b_j} - \sum_{i=1}^{m} \eta k \beta \mu_{a_i} \log n_{a_i}} \right)^2 \]
\[ = \sum_{\{ab\}} \left( k_{ba} \prod_{i=1}^{m} n_{a_i} - k_{ab} \prod_{j=1}^{n} n_{b_j} \right)^2 \].

Equation (D9) generalizes equation (115) for the single linear reaction. Other terms in the effective action vanish on a constant-\( n \) history, and so this is the expression from Freidlin–Wentzell theory that governs fluctuations in the manner of an entropy-rate difference. A topic for future work is to extend the Jaynes path-entropy methods to many-particle reactions, to determine whether combinatorial and environment entropy rates may be isolated for these as for the double-well.

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