

Non-equilibrium thermodynamics, organizations, and the use of asymptotically effective theories

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1 Introduction

This paper is the formal conclusion of my REU internship. It is just a piecemeal snapshot of work in progress. The purpose is to roughly communicate the current state of my research, and what I learned, to those responsible for granting me the pleasure of working on it. This paper contains too much dislocation and possible errors than would be reasonable for anyone to rely on without validation; caveat lector.

At the onset of my research I sought to find interesting connections between topological features of chemical reaction networks and their non-equilibrium thermodynamic qualities. Each topic turns out to be more than sufficiently challenging separately; the resolution was to learn as much as I could about thermodynamics, using chemical reaction networks as an intuitive substrate on which to apply the methods of non-equilibrium thermodynamics. This is inherently an interesting topic for its application toward understanding complicated chemical processes such as those in biology, including the spontaneous formation of life from early geochemistry.

Chemistry is also useful as a ready foundation on which to build intuitions about non-equilibrium thermodynamics, since mass-action chemical reactions are fairly well-understood (in equilibrium) and their thermodynamics are grounded in simple physical quantities.

Section 2 of this paper discusses one approach to non-equilibrium statistical mechanics based on Freidlin-Wentzell theory [4], emphasizing what I found to be interesting or especially departing from my intuition about traditional, equilibrium thermodynamics. Section 3 discusses the generalization of those thermodynamic methods that are applicable to chemical reactions, and Section 4 considers chemical organization theory.

Finally, I sketch some of the ways I am currently applying this paper's contents to original work on: assigning invariant sets of mean-field equations to each "chemical organization", a way to apply approximations of distributed computing failure modes, and non-equilibrium behavior of one-dimensional nearest-neighbor diffusion on a ring.

2 Thermodynamics

2.1 Applicability to complex systems

The tools of thermodynamics are important in the study of systems one might label ‘complex’. For the confounding aspects of complex systems often arise in the form of stochastic dynamics, imperfect measurement or specification of dissipative systems, sensitive interactions with an incompletely specified environment, and related necessity to describe phenomena as probabilistic.

2.2 Terminology

Thermodynamics began as a study of equilibrium distribution of energy and flows toward it. A few formulations of the topic were developed, most notably those which differentially relate various aggregate extensive and averaged intensive quantities such as temperature and total internal energy. These effective theories are extraordinarily useful for a wide variety of problems. However these “laws of thermodynamics” are now explained by statistical mechanics as macroscopic consequences of deeply simple microscopic interactions; they are the limiting behavior of a probability distribution contracting to a narrow band about a combinatorial peak.

For example, when microscopic objects probabilistically exchange units of energy, the equilibrium energy distribution of these objects can be found exactly for many systems, as can the dynamics of this probability distribution. From this microscopic theory, one can recover the ordinary differential relations between various thermodynamic variables by applying limits. In this sense, the traditional “laws of thermodynamics” supervene on the microscopic description insofar as, within the confines of certain approximations applicable for many applications, the empirical

laws are the most probable behavior of the microscopic description in the limit as the system comprises a large number of objects.

One might ask whether we can apply the tools of statistical mechanics, similar to those used to prove the convergence of many-particle equilibrium behavior to the empirical thermodynamic laws, to determine properties about typical behavior that is not equilibrium behavior. Indeed this is possible. But first it is important to understand the nature of the aforementioned approximations, and to emphasize the meaning of a misnomer.

Taking the number of particles to be large is known as the *thermodynamic limit*. This limit is, as the name implies, a fundamental point of what has come to be called thermodynamics. Thermodynamics is a corpus of methods to study this limiting behavior for systems that are stochastic, or otherwise incompletely determined, that have such broad applicability beyond energy exchange that the word is somewhat misleading.

Another important approximation assumed in the empirical laws of thermodynamics is that of *equilibrium*. This assumption takes the timescale of observations to be much greater than that of fluctuations departing from equilibrium. Again, this is a good approximation for a great deal of situations. But in fully non-equilibrium thermodynamics, we obviously eschew it (but note that some approaches use near-equilibrium approximations).

To do so, we must be more careful about the thermodynamic limit. For by strictly taking the number of particles to be infinite, the probability of deviations from the most probable behavior becomes zero. However with some more delicate handling we can get useful results about the most probable of these vanishingly unlikely events. Many systems obey exponential scaling

that we can exploit easily. For this we turn to *large-deviations*.

2.3 Large deviations

To say that a process *obeys a large deviations principle* generalizes the notion that it obeys a law of large numbers. Whereas a law of large numbers is a statement about the existence of one or more limiting behaviors, a large deviations principle specifies the rate to which probability contracts to those limits. We will follow the lead of Ref. [3] in this subsection to give the reader a slightly more concrete (but terse) version of these concepts and language.

To be more specific, large deviations can be considered a study of the rate at which probability density, evaluated sufficiently far from stationary distributions, exponentially decays in the tail of a sequence of probability distributions. It therefore is of direct concern to the limiting behavior of some stochastic processes, which in turn motivates its use in statistical mechanics.

In fact Touchette summarizes the deep relationship of large deviations to physics by calling it the “mathematics of statistical mechanics”. And due to the broad utility of thermodynamic descriptions, as mentioned above, large deviations is also deeply applicable to many problems outside the realm of mechanics.

To sketch the idea behind large deviations, particularly as they apply to the kind of stochastic systems considered later, we introduce first the notion of a rate function $I(x)$. This function quantifies the rate of exponential scaling, with respect to a large parameter n , as approximated by large deviations:

$$I(x) = \lim_{n \rightarrow \infty} -\frac{1}{n} \ln \rho(X_n = x).$$

Here x is a postulated outcome and X_n is a random variable drawn from the probability distribution corresponding to a given n from the family of distributions in question, and ρ is a probability density. The rate function for measurement outcomes from a thermodynamic process is the familiar microcanonical entropy up to an additive constant.

Another important quantity is the *scaled cumulant generating function* $\lambda(k)$ of the random variable X_n , given by

$$\lambda(k) = \lim_{n \rightarrow \infty} \frac{1}{n} \ln \langle e^{nkX_n} \rangle,$$

which for a thermodynamic process represents its free energy. As expected, and further demonstrating how large deviations explains thermodynamics, the rate function and scaled cumulant generating function are interchangeable by Legendre transform (in most elementary cases). More specifically, the rate function is given by the Legendre-Fenchel transform of the scaled cumulant generating function when λ exists and is differentiable; the s.c.g.f. is given by the Legendre-Fenchel transform of the rate function. The former result is known in literature as the Gärtner-Ellis Theorem; the latter is a special case of Varadhan’s Theorem.

2.4 Generating functions and stochastic effective action

We begin discussion of large deviations with the rate function and s.c.g.f. only to illustrate what is meant by exponential limiting behavior. As large deviations applies to the chemical reaction systems we consider, it is helpful to look at it another way [1, 2].

Computational and conceptual advantages motivate starting instead with a *moment-generating function* of the stochastic process,

given by:

$$\psi(\vec{z}) \equiv \sum_{\vec{n}} \left(\prod_{m=1}^D z_m^{\vec{n}_m} \right) \rho_{\vec{n}},$$

with D specifying the number of complex arguments, each corresponding to one of the coarse-grained states whose population is counted by an element of the vector \vec{n} , and $\rho_{\vec{n}}$ specifies the probability density of that specific state configuration.

For concision, arrows will not always be written over z and n , and quantities such as $\log z$ will implicitly denote elementwise operation, but their meaning should be clear in context.

In making this change of basis we pass from discrete variables that count population number, to continuous complex variables z that mimic shifted chemical potentials. The moment-generating function is a change of representation from the basis of state configuration, to the basis of stationary (equilibrium) probability distributions for systems given by these shifted chemical potentials. It is in this way that low-order approximations of the moment-generating function are more relevant to bulk changes in population.

It is important to understand that the M^{th} derivative (gradient) of the moment-generating function gives the M^{th} moment of the probability distribution. That is, $\frac{d^M}{dz^M} = \langle \rho^M \rangle$.

To be more explicit about the role of these chemical potential shifts, Ref. [1] notes that the moment-generating function is proportional to the exponent of the difference between free energies of the original system and the system perturbed by a “source” q that stands for shifts in chemical potentials. We therefore rewrite the moment-generating function in terms of this source:

$$\psi \equiv e^{-\Gamma(\log z)} = e^{-\Gamma(q)}. \quad (1)$$

The function Γ is known as the *cumulant generating function*, which serves a practically identical role as the “scaled” version above in the sense that its Legendre-Fenchel transform is a rate function, called the *effective action* [22].

$$S^{\text{eff}}(n) = \sup_q [\Gamma(q) + nq]$$

As do all convex rate functions, the effective action vanishes at the mean value for its argument. Its name will become more clear when considering the time-dependent version, wherein the action’s variational properties determine the structure of transitions.

2.5 Time dependence

The transition to non-equilibrium thermodynamics involves assigning probabilities not only to fixed points in state configuration, but also to entire trajectories that are conditioned on initial and final states.

Non-equilibrium behavior, for example transitions between different classical steady states, imposes necessary differences in the way we think of thermodynamic descriptions. In particular, we are forced to consider state more state variables: not only the familiar charge-like population statistics (signs of which are invariant under time reversal), but also current-like variables (with signs reversing under time reversal) that generate changes in the charge-like variables. These additional state variables are Hamiltonian conjugate momenta of the charge-like variables.

Utilizing *both* sets of variables, the Freidlin-Wentzell methods provide a way to compute probabilities for *histories* of quantities that are macroscopically aggregated or averaged over the microscopic contributions given by constituent particles.

Consider a master equation of a Markov process, giving the probability distribution's time rate of change as a linear operation on the probability density $\rho_{\vec{n}}$ indexed by a vector \vec{n} representing population of each coarse-grained state in the set \mathcal{M} :

$$\frac{\partial \rho_{\vec{n}}}{\partial t} = \sum_{i,j \in \mathcal{M}} \left(e^{\partial/\partial n_i - \partial/\partial n_j} - 1 \right) r_{ji} \rho_{\vec{n}}$$

The quantity r_{ji} is the directional rate of transition from species i due to conversion from species j . The operator is written in terms of exponentials of $\partial/\partial n_i$ as a shorthand to encode all moments of the dynamic into the operator, which is called a *transition matrix*.

To rewrite the master equation in the polynomial basis of a generating function, we recall the form of (1) and compute the time derivative just as [1] does:

$$\begin{aligned} \frac{\partial \psi(\vec{z})}{\partial t} &= \sum_n \prod_{k \in \mathcal{M}} z_k^{n_k} \frac{\partial \rho_{\vec{n}}}{\partial t} \quad (2) \\ &= \sum_n \prod_{k \in \mathcal{M}} z_k^{n_k} \sum_{i,j \in \mathcal{M}} \left(e^{\partial/\partial n_i - \partial/\partial n_j} - 1 \right) r_{ji}(n_i) \rho_{\vec{n}} \\ &= \sum_{i,j \in \mathcal{M}} \left(\frac{z_j}{z_i} - 1 \right) \sum_n \prod_{k \in \mathcal{M}} z_k^{n_k} r_{ji}(n_i) \rho_{\vec{n}} \\ &= \sum_{i,j \in \mathcal{M}} \left(\frac{z_j}{z_i} - 1 \right) r_{ji} \left(z_i \frac{\partial}{\partial z_i} \right) \sum_n \prod_{k \in \mathcal{M}} z_k^{n_k} \rho_{\vec{n}}. \end{aligned}$$

Notice that the last line of (2) is arranged with a matrix on the left and the moment-generating function of $\rho_{\vec{n}}$ on the right. The matrix-valued operator, called the *Liouville operator* acting on the generating function serves to determine the time rate of change of the generating function:

$$\frac{\partial \psi(\vec{z})}{\partial t} \equiv -\mathcal{L} \left(z, \frac{z}{\partial z} \right) \psi(\vec{z}) \quad (3)$$

This time evolution is readily reduced to quadrature by successively operating on an initial state ψ_0 by many increments of $e^{\delta t \mathcal{L}}$, with small timesteps δt . A change of representation makes this computation simpler.

Causality and superposition of probability distributions satisfy the same rules as operator algebra of quantum harmonic oscillators, as do complex variables and derivatives. Furthermore, generating functions exist as elements of normed linear spaces. These facts motivate changing representation from explicit complex variables, derivatives thereof, and generating functions, to abstract linear operators acting on vectors in a Hilbert space. It is therefore conventional to introduce operators,

$$\begin{aligned} z_i &\leftrightarrow a_j^\dagger \\ \frac{\partial}{\partial z_i} &\leftrightarrow a^i, \end{aligned}$$

obeying familiar ladder-operator commutation relations

$$\left[\frac{\partial}{\partial z_i}, z_i \right] \leftrightarrow [a^i, a_j^\dagger].$$

Even though the operator algebra is identical, the Hilbert space on which these “raising” and “lowering” operators act is fundamentally different from the space applicable to quantum fields. The classical space is, however, still constructible from a “ground” or “vacuum” state:

$$1 \leftrightarrow |0\rangle.$$

Just as it is convenient to work in the eigenbasis of raising and lowering operators for quantum fields [5], it is conventional to use a basis of classical fields in which the basis elements $\vec{\phi}$ are eigenstates of a^i and a_i^\dagger :

$$a^i \left| \vec{\phi} \right\rangle = \phi^i \left| \vec{\phi} \right\rangle. \quad (4)$$

We may express the identity as an outer product integral over these coherent states,

$$\int \frac{d^I \phi^\dagger d^I \phi}{\pi^I} \left| \vec{\phi} \right\rangle \left\langle \vec{\phi}^\dagger \right| = I. \quad (5)$$

Although this is just a complicated way to write the identity, the expression projects arbitrary states into this algebraically simple basis of eigenstates and permits one to directly compute a path integral for ψ_T . With that, one can find a Hamiltonian action functional

$$S = \int dt \left[- \sum_{i \in \mathcal{M}} \partial_t \phi_i^\dagger \phi_i + \mathcal{L} \right], \quad (6)$$

for which a stationary path (with vanishing first-order variation [6]) corresponds to either a classical thermodynamic path to equilibrium or to one of the “least unlikely” trajectories, given some specific initial condition, that yield a given specific final state. The Hamiltonian \mathcal{L} recovers mean-field dynamics, i.e. classical solutions, via solutions of Euler-Lagrange equations.

For general reactions, rate dependence that is nonlinear in particle number diminishes what is advantageous of using coherent state bases for a two-state reaction with linear rate dependence. Furthermore, working in these variables makes the meaning of these conjugate fields abstruse. Instead we may work in *action angle coordinates*, a canonical transformation similar to rotating to complex polar coordinates. The fields n_i , indicating expectation values, and their conjugate momenta η_i , now to be interpreted as chemical potentials, are related to coherent-state fields by:

$$\begin{aligned} \phi_i^\dagger &\equiv e^{\eta_i} \\ \phi_i &\equiv e^{-\eta_i} n_i. \end{aligned}$$

For concision, we delay writing the action and Hamiltonian in these coordinates until after introducing more general notation.

3 Stoichiometry

In this section we consider large-deviations thermodynamics of reaction systems with arbitrarily many particle types and reaction rates that have arbitrary (possibly nonlinear) dependence on particle number.

3.1 Mass-action

Mass-action kinetics provides a familiar starting point for describing important type-conversion problems, most notably in chemistry. In this model, the rate of conversion between different species of agents (such as chemical types) due to a single directed reaction is taken to be equal to the product of the reaction rate and the probability of interaction between each species involved in that reaction, which is approximated by the product of (continuously varying) concentrations.

3.2 Directed hypergraphs

We represent a mass-action stoichiometric reaction of discrete types as a directed hypergraph with weighted edges, described by the tuple

$$G = (\mathcal{M}, \mathcal{R}, \alpha, \omega, k). \quad (7)$$

Here \mathcal{M} denotes a set of species, \mathcal{R} represents a set of edges. Symbols α and ω stand for functions mapping edges (elements of \mathcal{R}) to multisets of elements in \mathcal{M} . The multisets in the target of these functions stand for reactants and products, respectively, of each reaction in \mathcal{R} . The collection k contains a real-valued reaction rate, denoted k_j for each (directed) reaction $j \in \mathcal{R}$.

This representation is translatable to kinetics introduced in any basic chemistry reference. To be general,

$$\frac{d\vec{c}}{dt} = \mathbf{M} \mathbf{J}(\vec{c}), \quad (8)$$

where \vec{c} is a vector of concentrations of species, and a stoichiometric matrix \mathbf{M} encodes the number of each chemical species consumed or produced in each reaction. $J(\vec{c})$ is called a *flux vector* [9] and should be interpreted as a vector of the rate at which each reaction occurs (as a function of its reactant’s concentrations). For some systems, particularly those comprising very few molecules (e.g. in sub-cellular biological processes), mass-action reaction rates are not a good approximation of the flux vector. However for our purposes we ought not complicate things further.

$$\mathcal{L} = \sum_{j \in \mathcal{R}} \left(k_j \prod_{a' \in \alpha(j)} n_{a'} \right) \left[1 - \exp \left(\sum_{b \in \omega(j)} \eta_b - \sum_{a \in \alpha(j)} \eta_a \right) \right]. \quad (10)$$

The first parentheses surround the reaction rate, expressed to mass-action approximation, but can in principle be generalized.

4 Chemical organizations

Literature contains a number of qualitative approaches to stoichiometric systems, which ignore reaction rates and species’ concentrations to retain only the structural aspects of interacting reactions.

Chemical organization theory is of particular interest to me. Fontana argues in [10] that selection and transmission alone are an incomplete theory of biology. Together these emphasize the role of traits of organisms rather than the organisms themselves. That seems insufficient in seeking answers to questions about disruptive changes, which fundamentally change the state

3.3 Mass-action thermodynamics

The action (6), written in action-angle coordinates and the hypergraph notation introduced in this section, takes the form

$$S = \int dt \left(- \sum_{i \in \mathcal{M}} \partial_t \eta_i n_i + \mathcal{L} \right). \quad (9)$$

For mass-action kinetics, the Hamiltonian (which is also the Liouville operator) takes a simple form:

space for a fitness landscape, such as the genesis of life itself.

Ref. [9] is one approach toward a more comprehensive biological theory. Using the framework of chemical reaction network theory (CRNT) [7, 8], Speroni di Fenizi emphasizes the hierarchical nature of *chemical organizations*, which each represent a set of chemical species that satisfy certain algebraic constraints: *closure* and *self-maintenance*.

Closure is defined by [9] in a simple way. A set of chemical species $C \in \mathcal{M}$ is called *closed* if all reactions possible on multisets of elements in C produce only more multisets of elements in C .

Self-maintaining sets C of chemical species are those for which there exists a flux vector J that satisfies three conditions:

- the reaction rate is positive for all reactions

with educts that are multisets of chemical species in C ,

- the rate is identically zero for all reactions with reactants that are *not* in C , and
- the rate of production MJ of any species in the set C must be nonnegative.

These chemical organizations have a lattice structure (provisional on “consistency” of the chemical system at hand), with “upward movement” and “downward” movement” representing addition and total removal of species, respectively.

Not surprising, but still interesting, is that fixed points of the mean-field mass-action kinetics correspond to chemical organizations.

Such an algebra of chemistry seems like a promising way to realize Fontana’s vision. Chemical organizations treated in this manner can be understood as coarse-grained representations for robust ecologies of chemical species. Mean-field microscopic detail at this level of equivalence becomes inconsequential; *qualitative changes in the state space* of the microscopic description are all that remain.

Transitions between organizations therefore represent either interactions with an environment, or stochastic effects of an incompletely describable closed system. Either of these could lead to annihilation of one or more species necessary to regenerate the organization, or to the spontaneous generation of a new species via a route that is almost impossible (and therefore would be excluded from the set of “spontaneous” reactions).

5 Ongoing work

5.1 Chemical organizations as invariant sets

Speroni di Fenizi and collaborators do not appear to feel that the relation from fixed points to organizations can be reversed. Their counterexample is of exponential growth (e.g. of an auto-catalyzing system), which is an organization but is certainly not a fixed point (without compactification of the reals, that is).

I am more optimistic. However the correspondence would require expanding the menu of invariant sets to consider as possible mean-field behavior to which a chemical organization may be mapped.

The counterexample mentioned above is simple: a regime of exponential growth is still a well-defined region of the microscopic state space. It is an invariant set of the dynamical system to which that organization can be identified.

The number of chemical species is enormous, and the reactions that act on them impose complicated, coupled, nonlinear interactions. For this reason I wish to seek correspondence with more complicated invariant sets such as limit cycles and exotics like hyperchaotic toroidal attractors. Whether this goal is tenable using existing methods such as those of Freidlin-Wentzell is unclear so far, particularly in the case of non-compact limit sets.

Uniqueness of the map from organization to invariant set is not possible using the definition of organization above. For example, there are chemistries which support multiple stable concentrations of the same set of species [11].

5.2 Distributed computation

Load balancing, the dynamic redirection or reallocation of computing resources, has become

prevalent in critical services in recent years. It is used in virtually all large real-time computing environments from logistics to stock exchanges to scientific experiment control. Algorithms used are often conceived and implemented without any consideration of what possible behaviors they can induce, nor what unpredictability they inherently exhibit.

Analytical analysis of a load-balanced system is necessary in cases wherein one wants to anticipate behavior that is sufficiently unlikely to occur during conditions or timescales within budget for simulation. Often, however, mathematical analysis is extremely difficult in practice.

A standard way to circumvent that problem is to make very rough estimates of what measurable quantities of the system indicate something unacceptable. This can be costly, since conservatism in these estimates can cause underutilization of resources and, therefore, increases overhead. It can also result in overcompensation for inconsequential deviations from what the model defines as permissible, which wastes resources and can decrease responsiveness (or even reliability) of the service. Perhaps thermodynamics can help.

Suppose it *is* possible to create a mathematical model for a computing system that is exponentially accurate, as the system size grows large, near saddle-points between normal operating modes and self-organizing undesirable behavior (“cascading failure”) of a distributed computing system. For sufficiently smooth separatrices of exponentially ergodic systems (or even those with broken exponential ergodicity), it is near these saddle points through which transition from good to bad is exponentially likely to occur. Therefore these are the locations in state space near which a load-balancing system must be most pessimistic about its predictions and most preemptive in its actions. By isolating

these regions, it may become possible to relax constraints far away from them.

This selective weighting of predictions, made by the approximation accurate near the most likely failure modes, may provide a way to better tune the tradeoff between availability and overhead cost.

5.3 Locality

If we are to accept thermodynamics as always arising from the aggregation or averaging of a large number of stochastic processes, it would be nice to identify what the process are and directly form the thermodynamic description from them. That might be intractable in practice; even a simple model has me vexed on how to deal with a particular kind of spatial locality.

The “ABC model” uses spatially-local exchange of three different particle types on a one-dimensional periodic lattice as a thermodynamic tinker-toy [12]. It is also an example that tinker-toys can still be fun. This is an example of a system that behaves very much like a mass-action chemical system that is not mixed. Species types are in this case not just the single objects of $\{A, B, C\}$, but quadruplets from that alphabet. This is because exchange of the middle two particles necessarily changes the adjacent pairs. Long-distance correlation depends only on the rate at which particles diffuse around the ring due to stochastic interchange of location.

Ref. [12] aggregates over the local configurations by assuming the particle number is sufficiently large. But it is not clear to me that this is still valid under generalization to large deviations. It may become necessary to describe the dynamics using a stochastic partial differential equation, though I am not yet familiar with these methods (e.g. [13]).

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