THE THERMODYNAMIC PROPERTIES
OF MARKOV PROCESSES

by

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ABSTRACT

In this thesis, we shall develop an axiomatic framework for a theory of thermodynamics. Through a general definition of a thermodynamic system based on a Markov process formulation, we shall demonstrate that thermodynamic relations follow. Consequently, one can identify the essential properties of a thermodynamic system.

This thesis consists of three parts. In Chapter 2, we shall suggest how a Markov process can arise from a classical physical system and we shall show that a general Markov process can be cast in the form of a dissipative dynamical system. In the next chapter, we shall show, as a particular case, how a Markov process results from a reduction in the state space of a classical Hamiltonian system describing the evolution of a microscopic system of a large number of particles. In Chapter 4, we shall construct a framework that captures the required thermodynamic properties of Markov processes—an equilibrium state and forces and fluxes. The dissipation inequality of Chapter 2 can then be shown to correspond to the second law of thermodynamics. Furthermore, we shall obtain a reciprocity theorem stated in an input-output form.

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1. Introduction

Thermodynamics provides a macroscopic description of systems in and near an equilibrium state. Statistical derivations have been advanced as the microscopic foundation upon which thermodynamics rests. As summarized by Lax [LAX 60], a considerable amount of work existed by 1960 on the treatment of a thermodynamic process as a Markov process. Since 1960, the connection between Markov process theory and thermodynamics has continued to be explored and has been extended to systems far from equilibrium [e.g., BRO 79, FOX 79, GRA 78, NIC 77].

Current formulations do not provide a general framework for analyzing thermodynamic systems. Systems are described phenomenologically and with an absence (common to physics [WIL 79]) of a system theoretic treatment of inputs and outputs. To understand what general system properties have as their consequence thermodynamic relations then becomes difficult.

In this thesis, we shall develop an axiomatic framework for a theory of thermodynamics. Through a general definition of a thermodynamic system based on a Markov process formulation, we shall demonstrate that thermodynamic relations follow. Consequently, one can identify the essential properties of a thermodynamic system.

This thesis consists of three parts. In Chapter 2, we shall suggest how a Markov process can arise from a classical physical system and we shall show that a general Markov process can be cast in the form of a dissipative dynamical system in the sense of Willems [WIL 72, WIL 79]. In the next chapter, we shall show, as a particular case, how a Markov process results from a reduction in the state space of a classical Hamiltonian system describing the evolution of a microscopic system of a large number of particles. In Chapter 4, we shall construct a framework that captures the required thermodynamic properties of Markov processes—an equilibrium state can be defined and forces and fluxes follow from a system theoretic input-output setting. The dissipation inequality of Chapter 2 can then be shown to correspond to the second law of thermodynamics. Furthermore, we shall obtain a reciprocity theorem stated in an input-output form.

Three perceived benefits of this research are:

(i) Nonequilibrium thermodynamics can be placed on a sound mathematical footing [WYA 81, p. 2]. The idea that a near-equilibrium thermodynamic system can be modeled as a Gauss-Markov process is well-known [e.g., BRO 79, FOX 79, LAX 60, NIC 77]. For nonlinear, nonequilibrium systems, there is no consensus on an appropriate Markov process formulation (for example, see the above references).

(ii) A cross-fertilization between stochastic control theory and thermodynamics can occur [BRO 79]. Stochastic control provides precise, but often nonintuitive, formulations and solutions of one class of problems while thermodynamics provides imprecise, but often intuitive, formulations and solutions of another class of problems. Both fields can thus benefit from any demonstrated connections.

(iii) An appropriate noise model for a nonlinear resistor can be derived [WYA 82]. A model to represent thermal noise in a nonlinear resistor is a current research topic. A benefit of the proposed approach is an outline of both the constraints such a model must satisfy and the manner of its derivation.

2. The Forward Kolmogorov Equation as a Dissipative Dynamical System

Thermodynamics is concerned with a simplified, macroscopic description of a physical system. The observable dynamical variables of a classical physical system form a small subset of a large but finite set of dynamical variables. Under certain conditions, the observable dynamical variables evolve as a Markov process. The key features of a thermodynamic system can be captured in a Markov process formulation, in particular, through Kolmogorov's forward equation as the evolution equation for the statistical state, a probability distribution or density function. An essential thermodynamic property is a dissipation inequality, which we shall first derive as a property of a system with state dynamics governed by Kolmogorov's forward equation, before providing it with a second-law interpretation in Chapter 4.

2.1. From a Classical Physical System to a Markov Process

Classical physical systems are finite-dimensional, continuous-time, differential systems. The set of dynamical variables is large but finite and evolves according to a system of first-order differential equations.

Thermodynamic quantities are statistical quantities. An ensemble of classical physical systems is a thermodynamic system. However, thermodynamics is concerned with a simplified, macroscopic description of a physical system. The archetypical thermodynamic system is a statistical description of an observable subset of the dynamical variables of a classical physical system. The evolution of the observable dynamical variables is governed by a system of first-order stochastic differential equations. An ensemble of the observable dynamical variables is characterized by a probability measure—the thermodynamic state.

Under appropriate conditions, the reduced description obtained by considering just the observable dynamical variables yields a Markov process. In this thesis, we shall show that the essential features of a thermodynamic system can be captured in a Markov process formulation. Our results follow from the properties of Kolmogorov's forward equation—the evolution equation for the probability distribution or density function which is the thermodynamic state. Although the results are based on Kolmogorov's forward equation, a consideration of the underlying sample-path stochastic differential equations provides insight into why a Markov process formulation so nicely captures thermodynamic properties.

In this section, we shall amplify on this line of reasoning. In the following chapter (Chapter 3), we shall treat a specific example—a description of how Markov processes arise from a Hamiltonian system.

Consider a classical physical system described by a set of $n + N$ dynamical variables

$$x(t) = \begin{pmatrix} y(t) \\ z(t) \end{pmatrix} \in \Re^{n+N},$$

where $y(t)$ is an observable n-dimensional vector, $z(t)$ is an unobservable N-dimensional vector and $n << N$. Let $\Re_+$ be the time set of interest. The evolution equations are the system of first-order differential equations

$$\frac{dx(t)}{dt} = f_N(t, x(t); \lambda). \tag{2.1}$$

We have explicitly indicated the dependences of the function f on both the dimension N of the unobservable vector z and, by assumption, on a characteristic parameter, denoted by λ.

Equation (2.1) can be solved for the observable dynamical variables $y(t)$. Denote the solution by

$$y(t) = \phi_N(t, x(0); \lambda).$$

Assume the dynamical variables are initially distributed according to some probability law, that is, $x(0) = x_0(\omega)$, a random vector. Then $y(t)$ is a stochastic process and

$$y(t) = y(t, \omega) = \phi_N(t, x_0(\omega); \lambda).$$

The stochastic process y depends on both the dimension N of the unobservable vector z and the characteristic parameter λ.

If appropriate regularity assumptions are satisfied, the process $y(t)$ can be decomposed as the sum of a process of finite variation and a martingale. Typically, the regularity assumptions are satisfied in the limits $N \to \infty$ and $\lambda \to \infty$. In the following discussion, we introduce the required regularity assumptions, following the treatment of Nelson [NEL 67].

Let $\mathcal{P}_t$ be an increasing family of σ-algebras, such that $y(t)$ is $\mathcal{P}_t$-measurable for any $t \in \Re_+$. We then say $\{y(t), t \in \Re_+\}$ *is adapted to* $\{\mathcal{P}_t, t \in \Re_+\}$. Note that a suitable choice for $\mathcal{P}_t$ is

$$\mathcal{P}_t = \sigma\{y(s), 0 \leq s \leq t\}.$$

The first two regularity assumptions similarly restrict both the process and what we shall define as its mean forward derivative.

Assumption 2.1. The random variable $y(t, \cdot) \in \mathcal{L}_n^1 \triangleq \mathcal{L}^1(\Omega; \Re^n)$ for all $t \in \Re_+$ (that is, $\mathrm{E}\{|y(t)|\} < \infty$) and the mapping $t \to y(t, \cdot)$ is continuous from $\Re_+ \to \mathcal{L}_n^1$.

Assumption 2.2. For each $t \in \Re_+$, the *mean forward derivative*

$$m(t) \triangleq \lim_{\delta \to 0^+} \mathrm{E}\{\frac{y(t+\delta) - y(t)}{\delta} | \mathcal{P}_t\}$$

exists as a limit in $\mathcal{L}_n^1$ and the mapping $t \to m(t, \cdot)$ is continuous from $\Re_+ \to \mathcal{L}_n^1$.

The mean forward derivative $m(t)$ is a $\mathcal{P}_t$-measurable random variable, by definition of the conditional expectation. As the following theorem shows, $m(t)$ can be considered a best prediction of a derivative of the process $y(t)$.

Theorem 2.1. Let $r, s \in \Re_+$, $r \leq s$. Then

$$\mathrm{E}\{y(s) - y(r) | \mathcal{P}_r\} = \mathrm{E}\{\int_r^s m(\tau) d\tau | \mathcal{P}_r\}.$$

By Assumption 2.2, $t \to m(t, \cdot)$ is continuous from $\Re_+ \to \mathcal{L}_n^1$. Thus the integral exists as a Riemann integral in $\mathcal{L}^1$.

Define the n-dimensional random variable $v(t)$ for all $t \in \Re_+$ by

$$v(t) \triangleq y(t) - y(0) - \int_0^t m(\tau)d\tau.$$

As a consequence of Theorem 2.1, the process $\{v(t), t \in \Re_+\}$ is a martingale with respect to $\{\mathcal{P}_t, t \in \Re_+\}$. The two further assumptions allow us to write the martingale $v(t)$ as a stochastic integral.

Assumption 2.3. For each $r, s \in \Re_+$, $v(s,\cdot) - v(r,\cdot) \in \mathcal{L}_n^2 \triangleq \mathcal{L}^2(\Omega; \Re^n)$. For each $t \in \Re_+$,

$$\Theta(t) \triangleq \lim_{\delta \to 0^+} \mathrm{E}\{\frac{1}{\delta}[v(t+\delta) - v(t)][v(t+\delta) - v(t)]^T | \mathcal{P}_t\}$$

exists as a limit in $\mathcal{L}_{n\times n}^1$ and the mapping $t \to \Theta(t,\cdot)$ is continuous from $\Re_+ \to \mathcal{L}_{n\times n}^1$.

Assumption 2.4. For a.e. $t \in \Re_+$, $\det \Theta(t) > 0$ a.e.

Let $\Sigma(t)$ be the positive square root of $\Theta(t)$. Given Assumption 2.4, the inverse of $\Sigma(t)$ exists, a requirement for the proof of the following decomposition theorem. (Assumption (2.4) is restrictive and is not required for the example of Chapter 3.)

Theorem 2.2. Let $r, s \in \Re_+$, $r \leq s$. Then, given Assumptions 2.1 to 2.4, there exists an n-dimensional martingale w such that

$$\mathrm{E}\{[w(s) - w(r)][w(s) - w(r)]^T | \mathcal{P}_r\} = (s - r)I_{n\times n},$$

where $I_{n\times n}$ is the $n \times n$ identity matrix, and

$$y(s) - y(r) = \int_r^s m(\tau)d\tau + \int_r^s \Sigma(\tau)dw(\tau).$$

In particular, for each $t \in \Re_+$,

$$y(t) = y(0) + \int_0^t m(\tau)d\tau + \int_0^t \Sigma(\tau)dw(\tau). \tag{2.2}$$

We can write Equation (2.2) as the stochastic differential equation

$$dy(t) = m(t)dt + \Sigma(t)dw(t).$$

The notation dw represents the formal derivative of the martingale w—a special case of a white-noise process.

A *white-noise process* is the formal derivative of a process with uncorrelated increments. Its Fourier transform is a frequency-independent spectral density function. The term "white-noise process" is therefore in analogy with white light, which contains all frequency components. The representation of the observable dynamical variables y of a classical physical system as the solution of a stochastic differential equation driven by white noise follows in the limits of the dimension of the unobservable dynamical variables $N \to \infty$ and the characteristic parameter $\lambda \to \infty$, in the examples in the literature (Section 3.2.1.1).

Just as the formal derivative of a martingale is a special case of a white-noise process, the formal derivative of a process with independent increments is a special case of the formal derivative of a martingale. Both Gaussian white noise and Poisson white noise are formal derivatives of processes with independent increments.

If the sample functions of the process y are continuous with probability one, then the martingale w is a Brownian motion process [NEL 67]; hence its formal derivative is Gaussian white noise. For a process y with discontinuous sample functions, the martingale w cannot be specified as a Brownian motion process. When w is a Brownian motion process or a Poisson process, the process y is a Markov process. For example, consider the stochastic differential equation

$$dy = f(y)dt + G(y)d\beta(t), \tag{2.3}$$

where $f(y(t)) \in \mathcal{L}_n^1$, $G(y(t)) \in \mathcal{L}_{n\times n}^1$, and $\beta(t)$ is an n-dimensional Brownian motion process. Then

$$m(t) = f(y(t))$$

$$\Theta(t) = G(y(t))G^T(y(t))$$

$$w(t) = \beta(t)$$

and y is a Markov process. As another example, consider the stochastic differential equation

$$dy = f(y)dt + \sum_{i=1}^{k} h_i(y)dN^i(t), \tag{2.4}$$

where $f(y(t)) \in \mathcal{L}_n^1$, $h_i(y(t)) \in \mathcal{L}_n^1$ for all i, and the $N^i(t)$ are independent Poisson counting processes with intensities $\lambda^i(t)$. Let

$$\gamma^i(t) \triangleq N^i(t) - \int_0^t \lambda^i(\tau)d\tau.$$

Then

$$m(t) = f(y(t)) + \sum_{i=1}^{k} h_i(y(t))\lambda^i(t)$$

$$\Theta(t) = \sum_{i=1}^{k} h_i(y(t))h_i^T(y(t))\lambda^i(t)$$

$$w(t) = \sum_{i=1}^{k} \int_0^t \Sigma^{-1}(t)h_i(y(t))d\gamma^i(t)$$

(where we assume Assumption 2.4), and y is a Markov process. In this thesis, we shall limit our discussion to Markov processes with sample-path functions arising from stochastic differential equations of the form of the above two examples.

2.2. The Forward Kolmogorov Equation

In this thesis, we shall focus on the forward Kolmogorov equations associated with sample-path equations of motion such as (2.3) and (2.4). Kolomogorov's forward equation describes the evolution of the probability distribution or density functions of a Markov process. A detailed development of the following properties of Kolmogorov's forward equation can be found in [DOO 53, GIK 69, KEI 79, KEL 79, WEN 81] for Markov step processes and in [DOO 53, FLE 75, FRI 75, WEN 81, WON 71] for Markov diffusion processes.

A finite-state Markov step process can be described by a stochastic differential equation of the form (2.4). (For example, in [BRO 77], with $f = 0$ in (2.4), choices for the h_i are given for which the process y evolves on a finite set of complex numbers.) Without loss of generality, the finite state space of the stochastic differential equation can be mapped to a subset of the integers

$$\mathrm{E} \triangleq \{1, 2, \ldots, N\}.$$

The set of intensities of the Poisson counting processes similarly can be mapped to a set of rates for transitions $j \to i$ (where $i \neq j$) on the state space E.

A Markov step process on the state space E is also known as a Markov chain. Let $\{\xi(t), \quad t \in \Re_+\}$ be the Markov step process on the state space E. Let $a_{ij}(t)$ be the rate at time t for the transition $j \to i$. The a_{ij} are called *infinitesimal transition rates.* Require that the a_{ij} be piecewise-continuous functions of time. The infinitesimal transition rates satisfy the relation

$$a_{ij}(t)s + o(s) = \Pr\{\xi(t+s) = i \mid \xi(t) = j\},\ i \neq j, \tag{2.5}$$

where $o(s)$ is any function such that $\lim_{s\to 0} \frac{o(s)}{s} = 0$.

Let

$$a_{ii} \triangleq -\sum_{j\neq i} a_{ji} \tag{2.6}$$

and define the infinitesimal matrix $A \triangleq (a_{ij})$. A Markov step process for which (2.6) holds is called *conservative.*

The *transition function matrix* $P(t \mid s)$ is defined to have elements

$$p_{ij}(t \mid s) \triangleq \Pr\{\xi(t) = i \mid \xi(s) = j\}.$$

Equation (2.5) and the *Chapman-Kolmogorov equation*

$$P(u \mid s) = P(u \mid t)\, P(t \mid s),\ 0 \leq s \leq t \leq u,$$

yield [DOO 53] *Kolmogorov's forward equation*

$$\frac{\partial P(t \mid s)}{\partial t} = A(t)\, P(t \mid s),$$

and *Kolmogorov's backward equation*

$$\frac{\partial P(t \mid s)}{\partial s} = -P(t \mid s)\, A(s).$$

The initial condition is $P(s \mid s) = I$, where I is the $N \times N$ identity matrix. The probability distribution of $\xi(t)$ is an N-dimensional vector $p(t)$ with elements

$$p_i(t) \triangleq \Pr\{\xi(t) = i\}.$$

The probability distribution $p(t)$ is the statistical state at time t of the process $\{\xi(t),\ t \in \Re_+\}$. The state space $\mathcal{P}_{\mathrm{E}}$ is the space of all probability distribution functions, that is,

$$\mathcal{P}_{\mathrm{E}} \triangleq \{p_i: \sum_{i=1}^{N} p_i = 1,\ p_i(t) \geq 0 \ \forall\, i \in \mathrm{E}\}.$$

The probability distribution $p(t)$ is related to the probability transition function $P(t \mid s)$ by

$$p(t) = P(t \mid s) p(s),$$

that is,

$$p(t) = \mathrm{E}\{P(t \mid s)\}.$$

Thus $p(t)$ should also satisfy Kolmogorov's forward equation

$$\frac{dp(t)}{dt} = A(t)p(t); \quad p(0) = p_0. \tag{2.7}$$

Given our assumption that the $a_{ij}(t)$ are piecewise continuous, a unique solution exists to the ordinary differential equation(2.7). (Weaker conditions such as integrability will also suffice.) Given our assumption that the Markov step process is conservative, for any initial condition p_0 which is a probability distribution, that is, for any initial condition $p_0 \in \mathcal{P}_{\mathrm{E}}$, the unique solution $p(t) \in \mathcal{P}_{\mathrm{E}}$. We shall further assume intercommunicating states, that is, the $a_{ij}(t)$ are such that every state is reachable with finite probability from every other state. The probability distribution $p(t)$ then has strictly positive elements [GIK 69, KEI 72]. Lastly, we shall assume $a_{ij} = 0$ iff $a_{ji} = 0$, in order for the ratio $\frac{a_{ij}}{a_{ji}}$ to be well-defined. For $a_{ij} = a_{ij} = 0$, we shall adopt the convention that $\frac{a_{ij}}{a_{ji}} = 1$.

We can recast Kolmogorov's forward equation as follows.

Definition 2.1. The *fluxes*

$$J_{ij}(t) \triangleq a_{ij}(t)\, p_j(t) - a_{ji}(t)\, p_i(t).$$

Kolmogorov's forward equation then becomes

$$\frac{d}{dt} p_i(t) = \sum_j J_{ij}(t). \tag{2.8}$$

The flux J_{ij} can be interpreted as the net flow of probability from $j \rightarrow i$ on the state space E. Equation (2.8) is thus a conservation equation for probability.

A continuous-state Markov process can be described by a stochastic differential equation of the form (2.3), also known as an Itô equation. Consider the following Itô equation:

$$dx(t) = m(t, x(t))dt + \Sigma(t, x(t))d\beta(t)\,, \tag{2.9}$$

where $x(t) \in \Re^n$ and $\beta(t)$ is an n-dimensional Brownian motion process. Let the symmetric $n \times n$ matrix

$$\Theta(t, x) \triangleq \Sigma(t, x)\Sigma^T(t, x)\,,$$

and denote the elements of Θ by θ_{ij}. Assume $m(t, x)$ is a C^1-function of x and $\Theta(t, x)$ is a C^2-function of x, $m(t, x)$ and $\Theta(t, x)$ are piecewise-continuous in t, and $\Theta(t, x)$ is positive definite for all $x \in \Re^n$, $t \in \Re_+$. The Markov process $\{x(t),\, t \in \Re_+\}$ is also known as a diffusion process. For this thesis, we shall only consider diffusion processes on the state space $\Re^n$. The *transition function* of the process $\{x(t),\, t \in \Re_+\}$ is denoted by

$$p(t, x \mid s, y) = \Pr\{x(t) < x \mid x(s) = y\}\,.$$

Given suitable restrictions on m and Σ, there exists a *transition density function* $\rho(t, x \mid s, y)$ such that

$$p(t, x \mid s, y) = \int_{-\infty}^{x} \rho(t, u \mid s, y)\, dV_u$$

and $\rho(t, x \mid s, y)$ satisfies *Kolmogorov's forward equation*

$$\begin{aligned}\frac{\partial}{\partial t}\,\rho(t, x \mid x, y) = &-\sum_i \frac{\partial}{\partial x_i}[m_i(t, x)\rho(t, x \mid s, y)]\\ &+ \frac{1}{2}\sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j}\Big[\theta_{ij}(t, x)\rho(t, x \mid s, y)\Big]\end{aligned}$$

and *Kolmogorov's backward equation*

$$\begin{aligned}-\frac{\partial}{\partial s}\rho(t, x \mid s, y) = &\sum_i m_i(s, y)\frac{\partial}{\partial y_i}\rho(t, x \mid s, y)\\ &+ \frac{1}{2}\sum_{i,j}\theta_{ij}(s, y)\frac{\partial^2}{\partial y_i \partial y_j}\rho(t, s \mid s, y)\,.\end{aligned}$$

The initial condition is $\rho(s, x \mid s, y) = \delta(x - y)$, where $\delta(\cdot)$ is Dirac's delta function. The probability density of $x(t), \rho(t, x)$, is a function of $t \in \Re_+$ and $x \in \Re^n$, where, for any region $\Gamma \subset \Re^n$,

$$\Pr\{x(t) \in \Gamma\} = \int_\Gamma \rho(t, x)\, dV_x\,.$$

The probability density $\rho(t, x)$, as a function of x for t fixed, is the statistical state at time t of the process $\{x(t), t \in \Re_+\}$. The state space $\mathcal{P}_{\Re^n}$ is the space of all probability density functions on $\Re^n$, that is,

$$\begin{aligned}\mathcal{P}_{\Re^n} \triangleq \{\rho(t, x)\colon &\int_{\Re^n} \rho(t, x)\, dV_x = 1\,,\\ &\rho(t, x) \geq 0 \ \forall\, x \in \Re^n\}\,.\end{aligned}$$

The probability density $\rho(t,x)$ is related to the transition density function $\rho(t,x \mid s,y)$ by

$$\rho(t,x) = \int_{\Re^n} \rho(t,x \mid s,y)\rho(s,y)\,dV_x\,,$$

that is,

$$\rho(t,x) = \mathrm{E}\{\rho(t,x \mid s,y)\}\,.$$

Thus $\rho(t,x)$ should also satisfy Kolomogorov's forward equation

$$\begin{aligned} \frac{\partial}{\partial t}\rho(t,x) &= -\sum_i \frac{\partial}{\partial x_i}[m_i(t,x)\rho(t,x)] \\ &+ \frac{1}{2}\sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j}\,[\theta_{ij}(t,x)\rho(t,x)]. \end{aligned} \tag{2.10}$$

The existence and uniqueness of a solution to the partial differential equation (2.10) can only be proven in special cases. Consequently, we shall assume the existence of a unique solution $\rho(t,x) \in \mathcal{P}_{\Re^n}$ to (2.10). We shall further assume the probability density $\rho(t,x)$ is strictly positive for all $x \in \Re^n$, $t \in \Re_+$, and sufficiently regular to justify the integrations by parts we perform in the following sections.

We can recast Kolmogorov's forward equation in a more compact form. Define the m-dimensional partial derivative matrix operator

$$\nabla_y \triangleq \left[\frac{\partial}{\partial y_1}\cdots\frac{\partial}{\partial y_m}\right]^T.$$

When $y = \mathfrak{x}$, the sample-path state variable of our diffusion process, we shall denote ∇_x by ∇.

Definition 2.2. The *fluxes*

$$j(t,x) \triangleq m(t,x)\rho(t,x) - \frac{1}{2}\nabla\cdot(\Theta(t,x)\rho(t,x))\,.$$

Kolmogorov's forward equation then becomes

$$\frac{\partial}{\partial t}\rho(t,x) = -\nabla\cdot j(t,x)\,. \tag{2.11}$$

The flux j can be interpreted as a probability density current and Equation (2.11) as a conservation equation.

2.3. A Dissipation Inequality

For both the Markov step process and diffusion process, we can define a function of the statistical state which yields a dissipation inequality. In Section 4.3, we shall provide both the function of state and dissipation inequality with thermodynamic interpretations.

Denote the statistical state of either process by $p(t, y)$. Suppose there are two possibilites for the set of parameters of a Markov process (the set of parameters being either A or m and Θ). Let $p^1(t, y)$ and $p^2(t, y)$ be the solution of the forward Kolmogorov equation for each set of parameters, under equivalent initial conditions. The logarithm of the likelihood ratio

$$\ln \frac{p^1(t,z)}{p^2(t,z)}$$

is well-defined (by assumption, $p(t, y)$ is a strictly positive function of t and y) and is defined as the *information* for discrimination in favour of H_1 against H_2, given the state of the Markov process is z. An argument from Kullback [KUL 58, Sect.1.2] leads to the above definition. Suppose we observe the state of the Markov process at time t to be z (that is, either $\xi(t) = z \in E$ or $x(t) = z \in \Re^n$). The conditional probability that hypothesis H_i is true is then

$$\Pr\{H_i \mid z\} = \frac{\Pr\{H_i\}p^i(t,z)}{\Pr\{H_1\}p^1(t,z) + \Pr\{H_2\}p^2(t,z)} .$$

Thus the logarithm of the likelihood ratio

$$\ln \frac{p^1(t,z)}{p^2(t,z)} = \ln \frac{\Pr\{H_1 \mid z\}}{\Pr\{H_2 \mid z\}} - \ln \frac{\Pr\{H_1\}}{\Pr\{H_2\}}$$

and the information resulting from an observation z is the difference between the logarithms of the likelihood ratio of the two hypotheses after and before the observation.

The information has two interesting properties. The absolute value of the information is a metric on $[0, 1]$, as can be verified by calculation. Furthermore, a conservation relation holds for the information in favour of a time-dependent state $p^1(t, y)$ against a time-independent state $p^2(y)$, given the true state is the time-dependent state. The conservation relation is of the form

$$\begin{aligned} &E\{\frac{d}{dt} \ln \frac{p^1(t,z)}{p^2(z)}\} \\ &= E\{\frac{1}{p^1(t,z)} \frac{d}{dt} p^1(t,z)\} = 0 \quad . \end{aligned}$$

The information leads to a functional of the statistical state which can be considered a distance measure. Consider the quantity

$$E\left\{\ln \frac{p^1(t,z)}{p^2(t,z)}\right\} \quad ,$$

where the expected value is taken given the true state is $p^1(t,y)$, which we shall call the mean information for discrimination in favour of H_1 against H_2, given $p^1(t,y)$, after Kullback [KUL 58, Sect. 2.1]. For $y = i \in E$, the mean information given $p_i^1(t)$ is

$$\sum_i p_i^1(t) \ln \frac{p_i^1(t)}{p_i^2(t)}$$

and for $y = x \in \Re^n$, the mean information given $p^1(t,x)$ is

$$\int_{\Re^n} p^1(t,x) \ln \frac{p^1(t,x)}{p^2(t,x)} \, dV_x \, .$$

Let us call

$$G^r(t) \triangleq E\left\{\ln \frac{p(t,z)}{p^r(z)}\right\}$$

the mean information given $p(t,y)$, with respect to the time-independent reference state $p^r(y)$. This functional of the statistical state $p(t,y)$ has two properties of a measure of the distance of the statistical state from a reference state:

$$\begin{array}{ll} (i) \; G^r(t) \geq 0 & \\ (ii) \; G^r(t) = 0 \quad \text{iff} & p(t,y) = p^r(y) \quad . \end{array}$$

The above two properties follow from the inequality $\ln z \leq z - 1$, for which equality holds iff $z = 1$.

The functional $G^r(t)$ satisfies a dissipation inequality, as follows. First consider the N-state Markov step process. Then

$$\begin{aligned} \frac{d}{dt} G^r(t) &= \frac{d}{dt} \sum_{i=1}^{N} p_i(t) \ln \frac{p_i(t)}{p_i^r} \\ &= \sum_{i=1}^{N} \frac{dp_i(t)}{dt} \ln \frac{p_i(t)}{p_i^r} + \sum_{i=1}^{N} p_i(t) \left[\frac{1}{p_i(t)} \frac{dp_i(t)}{dt}\right] \\ &= \sum_{i=1}^{N} \sum_{j=1}^{N} J_{ij}(t) \ln \frac{p_i(t)}{p_i^r} \\ &= \sum_{i=1}^{N} \sum_{j=1}^{i-1} J_{ij}(t) \ln \frac{p_i(t)/p_j(t)}{p_i^r/p_j^r} \\ &= \sum_{i=1}^{N} \sum_{j=1}^{i-1} J_{ij}(t) \ln \frac{a_{ij}(t)/a_{ji}(t)}{p_i^r/p_j^r} - \sum_{i=1}^{N} \sum_{j=1}^{i-1} J_{ij}(t) \ln \left(1 + \frac{J_{ij}(t)}{a_{ji}(t) p_i(t)}\right) \quad . \end{aligned}$$

Define functionals of the set of fluxes J_{ij}, set of infinitesimal transition rates a_{ij}, and state p by

$$\begin{aligned} W^r(t) &\triangleq \sum_{i=1}^{N} \sum_{j=1}^{i-1} J_{ij}(t) \ln \frac{a_{ij}(t)/a_{ij}(t)}{p_i^r/p_j^r} \\ D(t) &\triangleq \sum_{i=1}^{N} \sum_{j=1}^{i-1} J_{ij}(t) \ln \left(1 + \frac{J_{ij}(t)}{a_{ji}(t) p_i(t)}\right) \quad . \end{aligned}$$

Consider the set of functions of time

$$\ln \frac{a_{ij}(t)/a_{ji}(t)}{p_i^r/p_j^r}.$$

We can write the fluxes J_{ij} to show an explicit dependence on these functions, as

$$J_{ij} = a_{ji}p_i\left(\frac{p_j/p_i}{p_j^r/p_i^r}e^{\ln \frac{a_{ij}/a_{ji}}{p_i^r/p_j^r}} - 1\right).$$

Suppose we consider this set of functions as inputs to a system with Kolmogorov's forward equation (2.8) as a state equation and the set of fluxes $J_{ij}(t)$ as outputs of the system. Then $W^r(t)$ is a memoryless function of the inputs and outputs.

Now consider the functional $D(t)$. If $J_{ij}(t) > 0$, then $\ln\left(1 + \frac{J_{ij}(t)}{a_{ji}(t)p_i(t)}\right) > 0$. Similarly, if $J_{ij}(t) < 0$, then $\ln\left(1 + \frac{J_{ij}(t)}{a_{ji}(t)p_i(t)}\right) < 0$. (Note that $J_{ij}(t)$ will never equal $-a_{ji}(t)p_i(t)$ by the assumptions of intercommunicating states, guaranteeing strictly positive p_i, and a nonzero $a_{ji}(t)$ iff a nonzero $a_{ij}(t)$.) Thus $D(t) \geq 0$, with equality iff $J_{ij}(t) = 0$ for all $i, j \in E$.

Willems' work on dissipative systems [WIL 72, WIL 79] introduces a storage function, supply rate, and dissipation rate. We have constructed a dissipative dynamical system with storage function G^r, supply rate W^r, and dissipation rate D. That is, we have shown

$$\frac{d}{dt}G^r(t) = W^r(t) - D(t) \leq W^r(t),$$

where the supply rate $W^r(t)$ can be considered as a memoryless function of system inputs and outputs and the dissipation rate

$$D(t) \geq 0,$$

with equality iff all system outputs vanish.

We can similarly construct a dissipative dynamical system for the diffusion process. Then

$$\begin{aligned}
\frac{d}{dt}G^r(t) &= \frac{d}{dt}\int_{\Re^n} \rho(t,x)\ln\frac{\rho(t,x)}{\rho^r(x)}\,dV_x \\
&= \int_{\Re^n} \frac{\partial\rho(t,x)}{\partial t}\ln\frac{\rho(t,x)}{\rho^r(x)}\,dV_x + \int_{\Re^n} \rho(t,x)\left[\frac{1}{\rho(t,x)}\frac{\partial\rho(t,x)}{dt}\right]dV_x \\
&= \int_{\Re^n} -\nabla\cdot j(t,x)\ln\frac{\rho(t,x)}{\rho^r(x)}\,dV_x \\
&= \int_{\Re^n} j(t,x)\cdot\nabla\ln\frac{\rho(t,x)}{\rho^r(x)}\,dV_x\,,
\end{aligned}$$

where the last step follows from an integration by parts. A calculation verifies

$$\nabla\ln\rho(t,x) = 2\Theta^{-1}(t,x)\left[m(t,x) - \frac{1}{2}\nabla\cdot\Theta(t,x)\right] - \frac{2}{\rho(t,x)}\,\Theta^{-1}(t,x)j(t,x)\,.$$

So

$$\frac{d}{dt}G^r(t)$$
$$= \int_{\Re^n} j(t,x) \cdot \left\{ 2\Theta^{-1}(t,x)\left[m(t,x) - \frac{1}{2}\nabla \cdot \Theta(t,x)\right] - \nabla \ln \rho^r(x)\right\} dV_x$$
$$- \int_{\Re^n} \frac{2}{\rho(t,x)} j(t,x) \cdot \Theta^{-1}(t,x) j(t,x)\, dV_x.$$

We can similarly define functionals

$$W^r(t) \triangleq \int_{\Re^n} j(t,x) \cdot \{2\Theta^{-1}(t,x)\left[m(t,x) - \frac{1}{2}\nabla \cdot \Theta(t,x)\right] - \nabla \ln \rho^r(x)\} dV_x$$
$$D(t) \triangleq \int_{\Re^n} \frac{2}{\rho(t,x)} j(t,x) \cdot \Theta^{-1}(t,x) j(t,x)\, dV_x .$$

Consider the function of the time t and the sample-path state variable x

$$2\Theta^{-1}(t,x)\left[m(t,x) - \frac{1}{2}\nabla \cdot \Theta(t,x)\right] - \nabla \ln \rho^r(x).$$

We can write the flux j to show an explicit dependence on this function, as

$$j = \frac{1}{2}\Theta\rho\left\{\left[2\Theta^{-1}(m - \frac{1}{2}\nabla \cdot \Theta) - \nabla \ln \rho^r\right] - \nabla \ln \frac{\rho}{\rho^r}\right\}.$$

If we consider this function as the input to a system with Kolmogorov's forward equation (2.11) as a state equation and the flux $j(t,x)$ as the output of the system, then $W^r(t)$ is a memoryless function of the input and output. As $\Theta(t,x)$ is positive definite by assumption, the dissipative rate $D(t) \geq 0$, with equality iff $j(t,x) = 0$ for all $x \in \Re^n$, that is, iff all system outputs vanish. Thus, as above, we have constructed a dissipative dynamical system with storage function G^r, supply rate W^r, and dissipation rate D. In Chapter 4, we shall give this dissipation inequality a thermodynamic interpretation.

3. A Series of Derivations of Markovian Thermodynamic Systems Starting from a Hamiltonian System

A series of Markovian thermodynamic systems can be derived through successive transformations of a Hamiltonian system. The parameters of the Markovian thermodynamic systems are determined by the parameters of the underlying Hamiltonian system. In particular, the equilibrium state associated with a Markovian thermodynamic system follows through knowledge of the original Hamiltonian system.

3.1. The Hamiltonian System

Consider a dynamical system of a large number of particles. In principle, we can describe the microscopic evolution of the system through the laws of classical mechanics. (Our discussion will be only within the framework of classical mechanics.)

In particular, we shall consider a Hamiltonian system of N particles with momentum and position coordinates

$$p_j \in \Re,\ r_j \in \Re, \qquad j = 1, 2, \ldots, N,$$

respectively. The system is described by the Hamiltonian

$$H(p, r) = \frac{1}{2} \sum_{j=1}^{N} \frac{1}{m_j} p_j^2 + V(r),$$

where $p = (p_1, p_2, \ldots, p_N)$, $r = (r_1, r_2, \ldots, r_N)$, and m_j is the mass of particle j. (We consider one-dimensional rather three-dimensional motion only for simplicity.)

Borrowing terminology usually applied to the stochastic processes of the following sections, we shall call a phase-space trajectory of the Hamiltonian system a sample path. Sample-path quantities depend on the coordinates of all particles; that is, a sample-path state is $(r, p) \in \Re^{2N}$. The sample-path equations of motion are

$$\begin{array}{l} \dfrac{dr_j}{dt} = \dfrac{\partial H}{\partial p_j} = \dfrac{1}{m_j} p_j \\ \dfrac{dp_j}{dt} = -\dfrac{\partial H}{\partial r_j} = -\dfrac{\partial V}{\partial r_j} \end{array}, \qquad j = 1, 2, \ldots, N. \tag{3.1}$$

Classical mechanics suggests the following definitions of the sample-path quantities of forces, kinetic energy, and potential energy.

Definition 3.1. The *forces* of a Hamiltonian system are

$$F_j \triangleq -\frac{\partial V}{\partial r_j}, \qquad j = 1, 2, \ldots, N.$$

Definition 3.2. The *kinetic energy* of a Hamiltonian system is

$$K \triangleq \frac{1}{2} \sum_{j=1}^{N} \frac{1}{m_j} p_j^2$$

and the *potential energy* is V.

Note that the Hamiltonian $H = K + V$. Thus the Hamiltonian is the energy in a sample-path sense. As we have defined the Hamiltonian H as a function of only p and r, a simple calculation reveals the Hamiltonian is a constant of motion of (3.1), that is,

$$\frac{dH}{dt} = 0.$$

For large N, we cannot expect to track the path of each particle as a function of time. A statistical description then becomes necessary. Traditionally, one constructs an ensemble of Hamiltonian systems to provide probabilities for the one Hamiltonian system with the physical interpretation of frequencies for a larger system. The ensemble is a collection of identical, noninteracting Hamiltonian systems—a Gibbs ensemble.

Consider an ensemble of identical Hamiltonian systems. Each system is deterministic, but the initial condition is uncertain. The "statistical state" of such an ensemble is a probability measure on $\Re^{2N}$. The state space is some subset of the set of all probability measures on $\Re^{2N}$. We can take the state space as the set of all Borel probability measures on $\Re^{2N}$ that are absolutely continuous with respect to Lesbesgue measure on $\Re^{2N}$ [WON 71]. Then there exists a nonegative Borel function $\rho(t,p,r)$, where $(p,r) \in \Re^{2N}$, such that for all $\Gamma_1, \Gamma_2 \in \Re^N$

$$\Pr\{p(t) \in \Gamma_1, r(t) \in \Gamma_2\} = \int_{\Gamma_2}\int_{\Gamma_1} \rho(t,p,r)\,dp\,dr.$$

The function $\rho(t,p,r)$ is called a probability density function. We can therefore identify the statistical states with their density functions.

The evolution equation for the density function $\rho(t,p,r)$ is the *Liouville equation*

$$\frac{\partial \rho}{\partial t} = -iL\rho,$$

where $i = \sqrt{-1}$ and:

Definition 3.3. The *Liouville operator*

$$L \triangleq i \sum_{j=1}^{N} \left[\frac{\partial H}{\partial r_j}\frac{\partial}{\partial p_j} - \frac{\partial H}{\partial p_j}\frac{\partial}{\partial r_j} \right].$$

The Liouville equation is a Fokker-Planck equation without a diffusion term.

Thermodynamic quantities are statistical quantities. A thermodynamic state is thus a statistical state. We shall call an ensemble of Hamiltonian systems a *thermodynamic system.* The *ensemble average* of a sample-path function $f(p,r)$ is denoted as $\langle f \rangle$ and is defined as

$$\langle f \rangle \triangleq \int_{\Re^{2N}} f(p,r)\rho(t,p,r)\,dp\,dr.$$

Definitions for the thermodynamic quantities of energy, equilibrium, temperature, and entropy rely on the definition of the ensemble average, as we shall show in the remainder of this section.

Definition 3.4. The *energy* of a thermodynamic system

$$\begin{aligned}E(t) &\triangleq \langle H\rangle \\ &= \int_{\Re^{2N}} H(p,r)\rho(t,p,r)\,dp\,dr.\end{aligned}$$

We can calculate

$$\begin{aligned}\frac{dE}{dt} &= \int_{\Re^{2N}} H\frac{\partial \rho}{\partial t}\,dp\,dr \\ &= -i\int_{\Re^{2N}}(L\rho)H\,dp\,dr \\ &= \sum_{j=1}^{N}\left\langle \frac{\partial}{\partial r_j}\left(\frac{\partial H}{\partial p_j}H\right) - \frac{\partial}{\partial p_j}\left(\frac{\partial H}{\partial r_j}H\right)\right\rangle = 0,\end{aligned}$$

where the last step follows from an integration by parts. Thus the energy is time-independent (a constant of motion) for a thermodynamic system which is an ensemble of Hamiltonian systems—a physically obvious conclusion, since the Hamiltonian is time-independent for each system sample path.

We wish to assign a unique equilibrium state to a thermodynamic system. Historically, various arguments have been given to establish a form for such an equilibrium state. We shall give one set of arguments (but only in a nonrigorous setting appropriate to the present discussion).

An equilibrium state should be a steady-state solution to the Liouville equation

$$L\rho^e = 0.$$

A simple calculation shows that any twice-differentiable function is in the kernel of the Liouville operator L iff it is a constant of motion of the Hamiltonian differential equation (3.1) . For, example, any nonnegative twice-differentiable function of the Hamiltonian H, appropriately normalized, is a candidate for an equilibrium state.

Now consider two independent thermodynamic systems characterized by Hamiltonians H_1 and H_2, with equilibrium states ρ_1 and ρ_2. As a second property of an equilibrium state, we should require that $\rho_1 = \rho_2$ if $H_1 = H_2$, for consistency. Thus only a function of the Hamiltonian can be a candidate for an equilibrium state.

Now consider a composite of both systems with Hamiltonian $H = H_1 + H_2$ and equilibrium state ρ^e. As a third property, we should require that the equilibrium state of the composite system be the product of their equilibrium states, or

$$\ln \rho^e = \ln \rho_1^e + \ln \rho_2^e,$$

as follows from their statistical independence. Thus the logarithm of the equilibrium state must be an additive function of the Hamiltonian. Our three requirements have thus led us to the following definition:

Definition 3.5. The *equilibrium state* of a thermodynamic system is the *canonical density function*

$$\rho^e = ce^{-\beta H},$$

where the normalization constant

$$c = \left(\int_{\Re^{2N}} e^{-\beta H}\, dp\, dr\right)^{-1}$$

and

$$\beta > 0.$$

We shall use the notation $\langle f \rangle_e$ to denote the ensemble average of a sample-path function $f(p,r)$ for a thermodynamic system in equilibrium, that is,

$$\langle f \rangle_e \triangleq \int_{\Re^{2N}} f(p,r)\rho^e(p,r)\, dp\, dr.$$

We can define β in terms of a physically-measurable quantity. The average kinetic energy of particle j is $\left\langle \frac{1}{2}\frac{1}{m_j}p_j^2 \right\rangle$. In equilibrium, the average kinetic energy per particle

$$\left\langle \frac{1}{2}\frac{1}{m_j}p_j^2 \right\rangle_e = \frac{1}{2}\beta^{-1}, \qquad (3.2),$$

independent of the particle index j, as revealed by a simple calculation (for one-dimensional motion—for three-dimensional motion, the result is multiplied by 3). We can therefore define β by (3.2).

Definition 3.6. The *temperature* T of a thermodynamic system in equilibrium is defined by

$$T = \frac{1}{k\beta},$$

where k is Boltzmann's constant and $\frac{1}{2}\beta^{-1}$ is the average kinetic energy per particle, in equilibrium.

Note that (3.2) is a form of the equipartition theorem for kinetic energy. We cannot make such a general statement for the potential energy. However, as in equilibrium

$$\begin{aligned} 0 &= \frac{d}{dt}\left\langle p_j r_j \right\rangle_e \\ &= \left\langle \frac{dp_j}{dt} r_j \right\rangle_e + \left\langle \frac{dr_j}{dt} p_j \right\rangle_e \\ &= -\left\langle \frac{\partial V}{\partial r_j} r_j \right\rangle_e + 2\left\langle \frac{1}{2}\frac{1}{m_j} p_j^2 \right\rangle_e, \end{aligned}$$

the relation

$$\left\langle \frac{1}{2}\frac{\partial V}{\partial r_j} r_j \right\rangle_e = \left\langle \frac{1}{2}\frac{1}{m_j} p_j^2 \right\rangle_e = \frac{1}{2} kT \tag{3.3}$$

holds for the potential V. Note that (3.3) can also be written as

$$-\left\langle F_j r_j \right\rangle_e = kT. \tag{3.4}$$

For a quadratic potential, that is, for

$$V(r) = \sum_{j=1}^{N} V_j(r_j) = \frac{1}{2}\sum_{j=1}^{N} \alpha_j r_j^2,$$

an equipartition theorem also holds for the potential energy, that is,

$$\left\langle \frac{1}{2}\frac{\partial V}{\partial r_j} r_j \right\rangle_e = \left\langle \frac{1}{2}\alpha_j r_j^2 \right\rangle_e = \left\langle V_j \right\rangle_e = \frac{1}{2} kT.$$

Definition 3.7. The *entropy* of a thermodynamic system (whether in equilibrium or not) is

$$S \triangleq -k\langle \ln \rho \rangle.$$

We can calculate

$$\begin{aligned}
\frac{dS}{dt} &= -k\int_{\Re^{2N}} \frac{\partial \rho}{\partial t} \ln \rho \, dp\, dr - k\int_{\Re^{2N}} \frac{\partial \rho}{\partial t} \, dp\, dr \\
&= ki \int_{\Re^{2N}} (L\rho) \ln \rho \, dp\, dr \\
&= -k \sum_{j=1}^{N} \left\langle \frac{\partial}{\partial r_j}\left(\frac{\partial H}{\partial p_j} \ln \rho\right) - \frac{\partial}{\partial p_j}\left(\frac{\partial H}{\partial r_j} \ln \rho\right) \right\rangle,
\end{aligned}$$

where the last step follows from an integration by parts. Simplifying, we find

$$\begin{aligned}
\frac{dS}{dt} &= -k \sum_{j=1}^{N} \int_{\Re^{2N}} \left(\frac{\partial H}{\partial p_j}\frac{\partial \rho}{\partial r_j} - \frac{\partial H}{\partial r_j}\frac{\partial \rho}{\partial p_j}\right) dp\, dr, \\
&= k\int_{\Re^{2N}} \frac{\partial \rho}{\partial t} \, dp\, dr = 0.
\end{aligned}$$

Thus the entropy is time-independent for a thermodynamic system which is an ensemble of Hamiltonian systems. A time-independent entropy and energy is a result peculiar to an ensemble of Hamiltonian systems and will not remain valid for the ensembles of Markovian systems introduced in the following sections.

In an equilibrium state

$$\begin{aligned}
S &= -k\langle \ln \rho^e \rangle_e \\
&= -k \ln c(H,T) + k\beta \langle H \rangle_e \\
&= -k \ln c(H,T) + \frac{1}{T} E.
\end{aligned}$$

So in equilibrium

$$\begin{aligned}
\frac{dS}{dE} &= -\frac{k}{c}\frac{dc}{d\beta}\frac{d\beta}{dT}\frac{dT}{dE} - \frac{E}{T^2}\frac{dT}{dE} + \frac{1}{T} \\
&= -\frac{k}{c}\left(c^2 \int_{\Re^{2N}} He^{-\beta H}\, dp\, dr\right)\left(-\frac{1}{k}\frac{1}{T^2}\right)\frac{dT}{dE} - \frac{E}{T^2}\frac{dT}{dE} + \frac{1}{T} \\
&= \langle H\rangle_e \frac{1}{T^2}\frac{dT}{dE} - \frac{E}{T^2}\frac{dT}{dE} + \frac{1}{T} \\
&= \frac{1}{T},
\end{aligned}$$

a classical thermodynamic relation for systems of constant volume (as we have implicitly assumed).

(In the next section, we shall show that, for a Markovian system, the Einstein relation equates equilibrium sample-path fluctuations to intrinsic system properties. A proposed analogue to an Einstein relation in a Hamiltonian system is a combination of Equations (3.3) and (3.4); namely

$$\left\langle\left(\frac{dr_j}{dt}\right)^2\right\rangle_e = -\frac{1}{m_j}\left\langle F_j r_j\right\rangle_e = \frac{kT}{m_j}. \tag{3.5}$$

Probably little significance should be attached to Equation (3.5), but note the similarity to Equation (14.85) of Lax [LAX 60].)

3.2. Diffusion Process Approximations to a Hamiltonian System

The equilibrium state of an ensemble of Hamiltonian systems is described by a simple form of the density function ρ—the canonical density function. To describe a nonequilibrium state, we must use the Liouville equation to calculate the density ρ as a complicated function of all the momentum and position coordinates. However, in thermodynamics we are interested in a simpler, macroscopic description. The simplest macroscopic description is obtained when an ensemble of Hamiltonian systems can be considered as one system of Brownian particles in a heat bath, as occurs when the Hamiltonian has the form of this section.

3.2.1. The Ornstein-Uhlenbeck Process

3.2.1.1. An Outline of a Derivation of the Ornstein-Uhlenbeck Process from a Hamiltonian System

Consider a Hamiltonian system consisting of one observable particle coupled to $2N$ unobservable particles. The two components of interest are then:

(i) the observable particle and

(ii) a process which typifies the behaviour of the $2N$ unobservable particles.

For a particular form of the Hamiltonian, we shall obtain a reduced system consisting only of the two components of interest. The observable particle is often called a *Brownian particle* and the system of $2N$ unobservable particles a *heat bath*.

Let the Brownian particle have mass m, with momentum and position coordinates p_0 and r_0, respectively, and the $2N$ particles of the heat bath have identical masses m', with momentum and position coordinates p' and r', respectively, where

$$p' = (p_{-N}, \dots, p_{-1}, p_1, \dots, p_N),$$
$$r' = (r_{-N}, \dots, r_{-1}, r_1, \dots, r_N).$$

In the reduced system, let the position and velocity of the Brownian particle be

$$x \in \Re,\ v \in \Re,$$

respectively. Let $w(t)$ be a Brownian motion process. Under certain restrictions, mentioned below, Kac [KAC 69] has shown that the sample-path description of the reduced process is the *Ornstein-Uhlenbeck process* (as defined in Section 10 of [NEL 67])

$$dx = v\,dt \tag{3.6a}$$
$$dv = -\frac{1}{m}\frac{\partial V}{\partial x}dt - \frac{f}{m}v\,dt + \frac{1}{m}\sqrt{2kTf}\,dw, \tag{3.6b}$$

where the potential V and frictional coefficient f are defined in terms of the parameters of the Hamiltonian system, and the Brownian motion process $w(t)$ represents the heat bath.

A number of approaches yield the above result (for example, [KAC 69, DUR 81]). We shall follow the approach of Kac. To obtain this result, Kac had to postulate a special form for the Hamiltonian. The Brownian particle has a Hamiltonian

$$H_0 = \frac{1}{2}\frac{1}{m}p_0^2 + V(r_0),$$

the heat bath has a Hamiltonian

$$H_N = \frac{1}{2} \sum_{\substack{j=-N \\ j\neq 0}}^{N} \frac{1}{m'} p_j^2 + V_N(r'),$$

and the Brownian particle is coupled to the heat bath by a coupling Hamiltonian

$$H_c = W(r_0, r').$$

Furthermore, a particular positive-definite quadratic form must be assumed for the sum of the potentials $V_N(r') + W(r_0, r')$. Thus, excluding the potential $V(r_0)$, the system postulated by Kac is linear.

Initially, the Brownian particle and heat bath are a system in equilibrium, that is, the initial state at $t = 0$ is the canonical density function

$$\rho^e = ce^{-\frac{1}{kT}\left[\frac{1}{2}\sum_{j=-N}^{N} \frac{1}{m_j}p_j^2 + V_N(r') + W(r_0, r')\right]}.$$

The external potential $V(r_0)$ is asserted for times $t \geq 0$. Two limiting processes are then required to derive an Ornstein-Uhlenbeck process.

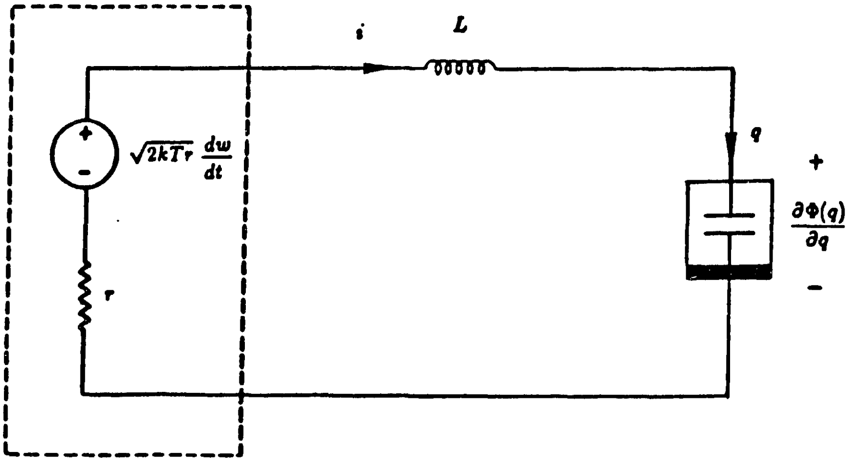
Unlike the ensemble of Hamiltonian systems of the previous section, an ensemble of Ornstein-Uhlenbeck processes exhibits an *irreversible* approach to equilibrium. However, an initial state of a *reversible* dynamical system will recur periodically, to any desired degree of accuracy. The *Poincaré cycle* is the time interval between such recurrences. Thus to obtain irreversible behaviour, the Poincaré cycles of a Hamiltonian system must become infinitely long. Such a requirement is satisfied in the limit of infinitely-many unobservable particles, that is, in the limit of $N \to \infty$.

In the limit of $N \to \infty$, the resulting process is not Markovian. To obtain a Markov process, Kac defines a characteristic parameter ω_0 of the quadratic form for $V(r') + W(r_0, r')$. In the limit of $\omega_0 \to \infty$, the process becomes Markovian. For times t not significantly greater than $\frac{1}{\omega_0}$, the process is not Markovian. Lax notes this point—that a Markov process approximation to a reversible microscopic system is only useful for time scales significantly greater than the forgetting time of microscopic collisions [LAX 60, pp. 40–41].

Given the above limiting processes, the particular form of the Hamiltonian assumed by Kac yields an Ornstein-Uhlenbeck process for the observable particle, with sample-path equations of motion (3.6). The energy in a sample-path sense is that portion of the Hamiltonian which depends on the reduced sample-path state (x, v), that is, $H_0 = \frac{1}{2}mv^2 + V(x)$.

We can construct a circuit model for the Ornstein-Uhlenbeck process (3.6). As in Figure 3.1, consider a series connection of a nonlinear capacitor with energy storage function Φ, a linear inductor of inductance L, a linear resistor of resistance r, and a white-noise voltage source of amplitude $\sqrt{2kTr}$. The resistor in series with the voltage source is the Nyquist-Johnson model for a noisy resistor, which we

Figure 3.1 A Circuit Model for the Ornstein-Uhlenbeck Process



shall describe in Section 3.3.2. Let q be the capacitor charge and i be the inductor current. Identify the circuit analogues as follows:

$x \leftrightarrow q$
$v \leftrightarrow i$
$m \leftrightarrow L$
$f \leftrightarrow r$
$V(x) \leftrightarrow \Phi(q)$.

The above substitutions in Equation (3.6) then yield the Ornstein-Uhlenbeck process corresponding to the circuit.

3.2.1.2. Thermodynamic Quantities

An ensemble of Ornstein-Uhlenbeck processes is a thermodynamic system. The thermodynamic quantities we defined for an ensemble of Hamiltonian systems also apply to an ensemble of Ornstein-Uhlenbeck processes. We shall show that the definitions from the previous section remain consistent, given the following changes:

(i) The Hamiltonian H of Section 3.1 becomes $H_0 = \frac{1}{2}mv^2 + V(x)$. (Note, however, that (3.6) is no longer a conservative system and therefore is no longer derivable from a Hamiltonian H_0 alone.)

(ii) The density function ρ, in Section 3.1 the solution of the Liouville equation, is now the solution of a Fokker-Planck equation.

We can again identify the statistical states with their density functions. However, the evolution equation for the density function is the *Fokker-Planck equation* corresponding to (3.6), that is,

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x}[v\rho] - \frac{\partial}{\partial v}\left[\left(-\frac{1}{m}\frac{\partial V}{\partial x} - \frac{f}{m}v\right)\rho - \frac{kTf}{m^2}\frac{\partial \rho}{\partial v}\right]. \tag{3.7}$$

Clearly the *energy* is

$$E(t) \triangleq \langle H_0 \rangle.$$

The *equilibrium state* is the canonical density function

$$\rho^e \triangleq ce^{-\frac{1}{kT}H_0}. \tag{3.8}$$

The reader can verify that (3.8) satisfies the criteria of Section 3.1, namely, ρ^e is an invariant density of the Fokker-Planck equation (3.7) and the average kinetic energy in equilibrium, $\left\langle \frac{1}{2}mv^2 \right\rangle_e$, is $\frac{1}{2}kT$. Furthermore, (provided $\lim_{|x|\to\infty} xe^{-\frac{1}{kT}V} = 0$, which justifies the required integration by parts) the potential V continues to satisfy the equilibrium relation

$$\left\langle \frac{1}{2}\frac{\partial V}{\partial x}x \right\rangle_e = \frac{1}{2}kT.$$

In contrast to the result of the previous section, for an ensemble of Ornstein-Uhlenbeck processes the equilibrium state not only is an invariant density of the Fokker-Planck equation, but is (under appropriate restrictions) the unique invariant density to which the thermodynamic system evolves. Similarly, both the energy and entropy can vary along trajectories of the Fokker-Planck equation, as we shall now show.

As in the previous section, calculations of the time-dependencies away from equilibrium of the energy and entropy depend on the validity of a series of integrations by parts. Skipping the intermediate steps, calculations of the time-dependencies of the potential and kinetic energies yield:

$$\frac{d}{dt}\langle V(x) \rangle = \left\langle v\frac{\partial V}{\partial x} \right\rangle$$

$$\frac{d}{dt}\left\langle \frac{1}{2}mv^2 \right\rangle = -\left\langle v\frac{\partial V}{\partial x} \right\rangle - f\left(\left\langle v^2 \right\rangle - \frac{kT}{m}\right).$$

Thus

$$\frac{dE}{dt} = -f\left(\left\langle v^2 \right\rangle - \frac{kT}{m}\right) \tag{3.9}$$

and the energy is not a conserved quantity.

Similarly, the entropy is not a conserved quantity. The entropy of the previous section was the entropy of the complete system of the Brownian particle together with the heat bath. In particular, the probability density determining the entropy, as in Definition 3.7, was then a function $\rho(t, p_0, r_0, p', r')$ of all momentum and position coordinates. Now the entropy is the entropy of the Brownian particle—the probability density determining the entropy is a function $\rho(t, p_0, r_0)$ of only the momentum (or equivalently, velocity) and position coordinates of the Brownian particle. As the Hamiltonian $H = H_0 + H_N + H_c$ has a coupling term H_c, the probability density for the complete system $\rho(t, p_0, r_0, p', r')$ is not a product of the probability density of the Brownian particle $\rho(t, p_0, r_0)$ and the probability density of the heat bath $\rho(t, p', r')$. Thus the entropy of the complete system, a conserved quantity, cannot be written as the sum of the entropy of the Brownian particle and an entropy of the heat bath. A third term is needed —an entropy of the interaction of the Brownian particle with the heat bath.

3.2.1.3. A Nyquist Theorem

We can define characteristic parameters of our system in a general way. Consider the Ornstein-Uhlenbeck process (3.6). The white-noise process, formally $\frac{1}{m}\sqrt{2kTf}\frac{dw}{dt}$, is the input to the system. In the case of a free particle, that is, with $V(x) = 0$, the ratio $\frac{m}{f}$ is the time constant of the system. We therefore define a time constant τ as

$$\tau \triangleq \frac{m}{f}$$

and a diffusion constant D, equal to $\frac{1}{2}$ the spectral density of the white-noise input, as

$$D \triangleq \frac{kTf}{m^2}.$$

Equation (3.6b) then becomes

$$dv = -\frac{1}{\tau}v\,dt + \sqrt{2D}\,dw.$$

To account for nonequilibrium effects, Lax introduces a correction factor C, which reduces to unity in equilibrium. For a fluctuating variable $\alpha \in \Re^n$, represented by a column vector, C is defined as

$$C \triangleq \left\langle \alpha\alpha^T \right\rangle \left\langle \alpha\alpha^T \right\rangle_e^{-1}.$$

In our case, we define C as the scalar quantity

$$C \triangleq \frac{\left\langle v^2 \right\rangle}{\left\langle v^2 \right\rangle_e} = \frac{m\left\langle v^2 \right\rangle}{kT}. \tag{3.10}$$

Using the definition for C, the kinetic energy becomes

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{1}{2}m\left\langle v^2 \right\rangle_e C = \frac{1}{2}kTC.$$

As the kinetic energy is the total energy of a free particle, we can rewrite (3.9) to show that the correction factor C satisfies the differential equation

$$\frac{dC}{dt} = -\frac{2}{\tau}(C - 1). \tag{3.11}$$

For a linear system (as we obtain with V set to 0), the *Nyquist theorem* relates the autocorrelation or spectral density of velocity fluctuations due to the extrinsic white-noise input to intrinsic system properties. The time constant τ, particle mass m, and an initial condition for the correction factor C are intrinsic system properties. Define the autocorrelation function

$$R(t_1, t_2) \triangleq \langle v(t_1), v(t_2) \rangle.$$

Then, for $t_1 > t_2$

$$\begin{aligned} R(t_1, t_2) &= e^{-\frac{(t_1 - t_2)}{\tau}} \left\langle v^2(t_2) \right\rangle \\ &= kT \frac{1}{m} e^{-\frac{(t_1 - t_2)}{\tau}} C(t_2). \end{aligned} \tag{3.12}$$

Thus (3.11) and (3.12) relate the autocorrelation of velocity fluctuations to intrinsic system properties and together are a Nyquist theorem.

Furthermore, as the diffusion constant D characterizes the extrinsic white-noise input, the *Einstein relation*

$$D = \frac{1}{\tau} \left\langle v^2 \right\rangle_e = kT \frac{1}{m} \frac{1}{\tau}$$

is a special form of the Nyquist theorem. The precise definition of an Einstein relation is an unsettled question in the literature. The most conventional definition would state that an Einstein relation connects a diffusion constant to a mobility. We use the term more broadly to include any relation between system properties connecting the equilibrium average of the square of a velocity (either a sample-path velocity or a white-noise input) to either an equilibrium average incorporating a force or a parameter associated with a force. This loose interpretation incorporates both the above relation and Equation (3.5).

The above Einstein relation can be established through an equilibrium argument; hence, it remains valid for the case of a nonzero potential $V(x)$. However, in such a case, C can no longer be determined just from intrinsic system properties and our form of the Nyquist theorem is no longer valid.

3.2.2. The Smoluchowski Process

We have seen that a Hamiltonian system reduces to an Ornstein-Uhlenbeck process only for a time scale significantly greater than the forgetting time of microscopic collisions. A further expansion of the time scale yields the Smoluchowski process.

Consider the Ornstein-Uhlenbeck process in the absence of noise, in particular, a modified (3.6b) rewritten as

$$\tau \frac{dv}{dt} = -\frac{1}{f} \frac{\partial V}{\partial x} - v, \tag{3.13}$$

where $\tau = \frac{m}{f}$ as in the previous subsection. The limit $m \to 0$, or equivalently, $\tau \to 0$, yields

$$v = -\frac{1}{f}\frac{\partial V}{\partial x}.$$

The above result, obtained by setting $m = 0$ in (3.13), is called a *singular perturbation.*

Including the noise term, now rewrite (3.6b) as

$$\tau dv = -\frac{1}{f}\frac{\partial V}{\partial x}dt - vdt + \sqrt{\frac{2kT}{f}}dw.$$

The limit $m \to 0$ then yields

$$vdt = -\frac{1}{f}\frac{\partial V}{\partial x}dt + \sqrt{\frac{2kT}{f}}dw.$$

But

$$dx = vdt.$$

Thus a singular perturbation results in the *Smoluchowski process*

$$dx = -\frac{1}{f}\frac{\partial V}{\partial x}dt + \sqrt{\frac{2kT}{f}}dw. \tag{3.14}$$

The above result can also be explained through the circuit model of Figure 3.1. The circuit model for the Smoluchowski process is given in Figure 3.2, which follows in the limit of the inductance $L \to 0$. Nelson [NEL 67] formulates this result as:

Theorem 3.1. Let $\frac{\partial V}{\partial x}$ satisfy a global Lipschitz condition. Let x, v be the solution of (3.6) with

$$x(0) = x_0$$
$$v(0) = v_0$$

and let y be the solution of (3.14) with

$$y(0) = x_0.$$

Then, for all v_0, with probability one

$$\lim_{m \to 0} x(t) = y(t)$$

uniformly for t in compact subintervals of $[0, \infty)$.

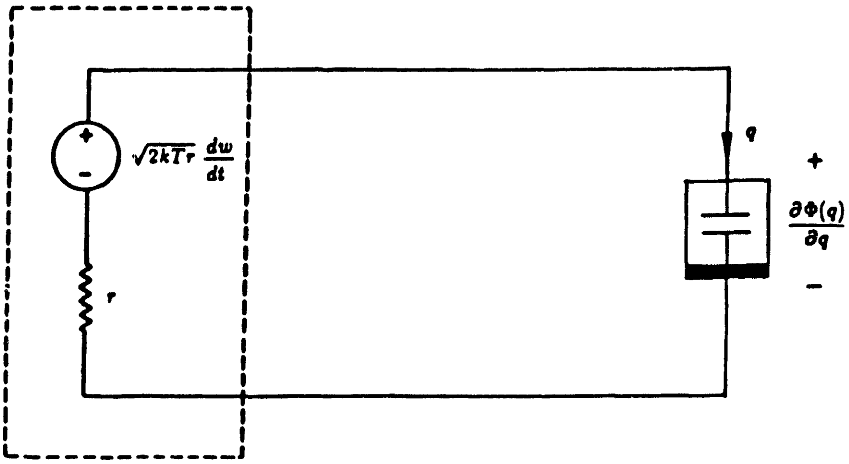
An ensemble of Smoluchowski processes is a thermodynamic system. As we found for the Ornstein-Uhlenbeck process, the definitions of Section 3.1 remain consistent, given the following changes:

(i) $H_0 = \frac{1}{2}mv^2 + V(x)$ of the previous section becomes simply $V(x)$.

(ii) The density function ρ is the solution of the Fokker-Planck equation corresponding to (3.14).

The energy and the equilibrium state have the same form as in Section 3.2.1.2. As before, both the energy and entropy are not conserved quantities. We can obtain

Figure 3.2 A Circuit Model for the Smoluchowski Process



a Nyquist theorem only in the case of a quadratic potential, that is, for $V(x) = \alpha x^2$, for some $\alpha > 0$.

3.2.3. The Nyquist-Johnson Resistor

The Nyquist-Johnson model for thermal noise is based on a theoretical derivation by Nyquist [NYQ 28] of the experimental results reported by Johnson [JOH 28]. The publication of both papers in 1928 provided the study of thermal noise with a rigorous foundation. By considering an equilibrium connection of two resistors and applying the equipartition principle, Nyquist demonstrated that the spectral density $S(\omega)$ of the open-circuit noise voltage in a "noisy" resistor of resistance r is

$$S(\omega) = 2kTr,$$

independent of the frequency ω. A Thevenin-equivalent circuit model for a noisy resistor, as enclosed in the dashed boxes of Figures 3.1 and 3.2, consists of a white-noise voltage source of amplitude $\sqrt{2kTr}$ in series with a (noiseless) resistor of resistance r and is called a *Nyquist-Johnson resistor.*

3.2.4. Appropriate Loads for a Nyquist-Johnson Resistor

Network theory imposes no constraints on the load which can be connected across a Nyquist-Johnson resistor. However, the Nyquist-Johnson resistor connected to a load corresponds to the Smoluchowski process (3.14), derived from the Ornstein-Uhlenbeck process (3.6), in turn derived from the Hamiltonian system of Section 3.2.1.1. The fact that a Nyquist-Johnson resistor is a thermodynamic system derived from a Hamiltonian system imposes a constraint—the load must arise from a potential function in order for equilibrium thermodynamic relations to be satisfied, as we shall now show.

Consider the Smoluchowski process corresponding to the Nyquist-Johnson resistor and its associated load,

$$dq = \frac{1}{r}\xi dt + \sqrt{\frac{2kT}{r}}dw, \tag{3.15}$$

where the charge q corresponds to the position x, the resistance r to the frictional coefficient f, and the voltage ξ to the force $-\frac{\partial V}{\partial x}$.

Suppose we formally write

$$\xi = r\frac{dq}{dt} - \sqrt{2kTr}\eta,$$

where the white-noise process $\eta = \frac{dw}{dt}$. The current $\frac{dq}{dt}$ corresponds to the velocity $v = \frac{dx}{dt}$. The functional form for the voltage ξ determines the nature of the load. Equation (3.15) can only be derived from a Hamiltonian system if the voltage ξ arises from an external potential corresponding to the potential $V(x)$. Let the potential $\Phi(q)$ correspond to the potential $V(x)$. Then

$$\xi(q) = -\frac{\partial\Phi(q)}{\partial q}.$$

Consider two examples of external systems which determine the voltage ξ and hence the external potential Φ. As in Figure 3.3, first consider the connection to a linear capacitor of capacitance C. A linear capacitor determines a potential and voltage as

$$\Phi(q) = \frac{q^2}{C}$$
$$\xi(q) = -\frac{q}{C},$$

consistent with our formalism.

Now consider Figure 3.4, where we connect a Nyquist-Johnson resistor to a linear capacitor of capacitance C in series with a linear resistor of resistance $\mathcal{R}$ (equivalently, to an impedance $Z(\omega) = \mathcal{R} - i\frac{1}{C\omega}$). Then

$$\xi = -(\frac{q}{C} + \mathcal{R}\frac{dq}{dt}).$$

The validity of the connection of Figure 3.4 implies the existence of a potential V such that

$$\frac{\partial V}{\partial x} = ax + bv,$$

for some nonzero constants a and b. But no such potential exists for a Hamiltonian system—thus the connection of Figure 3.4 is invalid. It is not surprising that in Section 10 of [LAX 60], Lax found that a load-independent description of thermal noise could not be found for the connection of a Nyquist-Johnson resistor to a load impedance with a nonzero real part.

We can further compare the consequences of both connections. For the connection to a capacitor

Figure 3.3 A Nyquist-Johnson Resistor Connected to a Capacitor

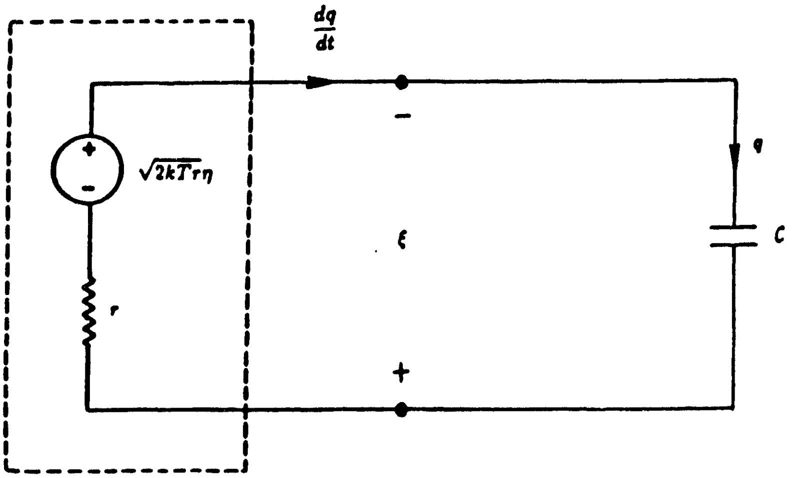
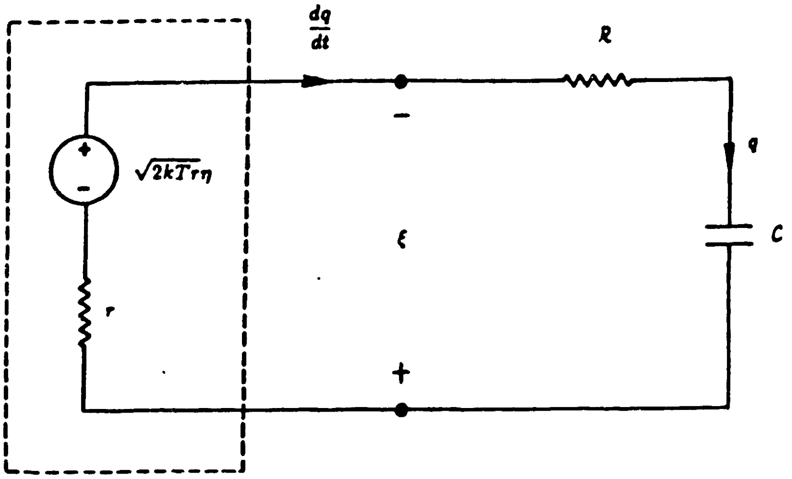


Figure 3.4 A Nyquist-Johnson Resistor Connected to a Capacitor in Series with a Resistor



$$dq = -\frac{1}{rC} q dt + \sqrt{\frac{2kT}{r}} dw$$

and for the connection to a capacitor in series with a resistor

$$dq = -\frac{1}{(r+\mathcal{R})C} q dt + \frac{\sqrt{2kTr}}{r+\mathcal{R}} dw.$$

The diffusion coefficient—$\frac{1}{2}$ the spectral density of the white-noise input—remains unchanged from that of (3.15) in the first case; in the second case, the load modifies it to

$$D = kT\frac{r}{(r+\mathcal{R})^2}.$$

Furthermore, the equipartition theorem fails in the second case—in the first case

$$\frac{1}{2}C\left\langle q^2\right\rangle_e = \frac{1}{2}kT,$$

while in the second case

$$\frac{1}{2}C\left\langle q^2\right\rangle_e = \frac{1}{2}kT(\frac{r}{r+\mathcal{R}}).$$

Thus a violation of an assumption upon which the model is based—its derivation from a Hamiltonian system—results in the vanishing of its equilibrium thermodynamic properties.

This result may be restated as follows. A nonzero real part of a load impedance corresponds to a resistor. The Nyquist-Johnson model of a resistor postulates that a resistor is a thermodynamic system. Hence the connection of a Nyquist-Johnson resistor to a load incorporating a resistor $\mathcal{R}$ is really the interconnection of two thermodynamic systems rather than the connection of one thermodynamic system to a load. The absence of a noise source for the resistor $\mathcal{R}$ implies the connection of a Nyquist-Johnson resistor at temperature T to a Nyquist-Johnson resistor at zero temperature. Equilibrium thermodynamic properties do not hold for the interconnection of two thermodynamic systems at different temperatures.

3.3. Markov Process Approximations to a Hamiltonian System

Both the Ornstein-Uhlenbeck and Smoluchowski process approximations to a Hamiltonian system have position-independent diffusion coefficients, that is, diffusion coefficients independent of the sample-path coordinates. Approximations for a Hamiltonian system composed of distinct potential wells lead to a finite-state Markov step process and, in an appropriate limit, a diffusion process with a position-dependent diffusion coefficient, as we shall now show.

3.3.1. A Markov Step Process

In this section, we shall obtain a Markov step process approximation to a Hamiltonian system, given a potential function with a set of potential wells which, in an expanded time scale, determines only transitions of the Brownian particle from well to well. Consider a Brownian particle in a heat bath under the influence of an external potential composed of M deep potential wells. The spatial extent of each potential well forms one of M identifiable domains, as follows.

Let the position of the Brownian particle be

$$r_0 \in \Re.$$

Denote the external potential by $V(r_0)$. The existence of an equilibrium state (3.8) requires that the potential $V(r_0) \to \infty$ as $r_0 \to \pm\infty$, in such a manner that (3.8) integrates to unity over $\Re$ (for example, $V(r_0) \geq kr_0^2$ as $r_0 \to \pm\infty$, for some positive constant k). Further suppose that the potential has local minima at

$$r_0 = x_{2j}, \qquad j = 1, 2, \ldots, M$$

and local maxima at

$$r_0 = x_{2j+1}, \qquad j = 1, 2, \ldots, M-1,$$

where

$$x_j \in \Re, \qquad j = 2, 3, \ldots, 2M,$$

and global maxima at $r_0 = x_1 = -\infty$ and $r_0 = x_{2M+1} = +\infty$. Then

$$x_1 < x_2 < \cdots < x_{2M+1}$$

and we shall say the Brownian particle is in domain j if

$$x_{2j-1} < r_0 < x_{2j+1}, \qquad j = 1, 2, \ldots, M.$$

As we have shown in the previous section, in a reduced system, the position x of the Brownian particle evolves as the Smoluchowski process

$$dx = -\frac{1}{f}\frac{\partial V}{\partial x}dt + \sqrt{\frac{2kT}{f}}dw. \tag{3.16}$$

As an example, consider a model for the migration of impurity atoms through a crystal. The crystal consists of M identical cells. Each cell contains an interstitial site at which an impurity atom can locate—a potential well. The crystal atoms of each cell are in equilibrium. By successive collisions with the thermally fluctuating crystal atoms, the impurity atom can acquire sufficient energy to escape a potential well and migrate from cell to cell [SCH 79].

Consider the potential wells deep in the sense that transitions from well to well occur on a longer time scale than positional fluctuations within a well. By expanding the time scale to focus only on transitions from well to well, a simplified macroscopic description results. Such a simplification is invaluable in a calculation of the mobility of the impurity atoms in the crystal, for example.

Transformation 1: to a "slowed-down" Smoluchowski process $\bar{x}(s) = x(\frac{s}{Q})$, in a rescaled time $s = Qt$

Let

$$V_j \triangleq V(x_j).$$

Define a dimensionless measure of the depth of the potential wells by

$$Q \triangleq \min_{1 \leq j \leq 2M} \{ \frac{1}{kT} |V_{j+1} - V_j| \}. \tag{3.17}$$

We can then rewrite Equation (3.16) for a rescaled time

$$s \triangleq Qt.$$

For the time scale s, we must introduce the Smoluchowski process

$$\bar{x}(s) \triangleq x(\frac{s}{Q})$$

(a "slowed-down" version of the process x). Note that we can replace the Brownian motion process $w(t)$ in Equation (3.16) by the equivalent Brownian motion process $\frac{1}{\sqrt{Q}} w(Qt)$. (Given $w(t)$ is a Brownian motion process, $\frac{1}{c} w(c^2 t)$ is also a Brownian motion process for any nonzero constant c.) Thus in the expanded time scale s, Equation (3.16) becomes

$$d\bar{x} = -\frac{1}{f} \frac{\partial \Phi}{\partial x} ds + \epsilon dw, \tag{3.18}$$

where

$$\Phi(x) \triangleq \frac{1}{Q} V(x)$$

$$\epsilon \triangleq \sqrt{\frac{2kT}{fQ}}.$$

Transformation 2: to a Markov step process $y(r)$, in a rescaled time $r = \frac{s}{\tau_1}$

With a further transformation of the time scale, we can construct a finite-state, stationary, Markov step process y which approximates the Smoluchowski process x in the sense of describing the sample-path transitions of the Brownian particle from domain to domain. The sample-path state space of the Markov step process therefore consists of M states. We shall label the jth state x_{2j} to correspond to the jth minimum of the potential V. To obtain the Markov step process, we shall define a rescaled time r. The statistical state of this simplified thermodynamic system is the distribution function

$$p_j(r) \overset{\Delta}{=} \Pr\{y(r) = x_{2j}\},$$

in the transformed time scale r. The infinitesimal transition rates characterizing the Markov step process y are defined by

$$\Pr\{y(r+\Delta) = x_{2i} \mid y(r) = x_{2j}\} = a_{ij}\Delta + o(\Delta).$$

Transformation 2a: to a "stochastically-discontinuous" Markov step process

We obtain the Markov step process as follows. Consider an open interval (a,b). Given an initial position $x \in (a,b)$, the mean exit time from (a,b) is, by definition, the expected value of the minimum of the first passage time to the point a and the first passage time to the point b. The probability of exit through the boundary point a (b) is the probability that the first passage time to a (b) is less than the first passage time to b (a). For the Smoluchowski process (3.18) (in the time scale s) and the domain (x_{2j-1}, x_{2j+1}), given an initial position $x \in (x_{2j-1}, x_{2j+1})$, define $\tau_j(x)$ as the mean exit time from (x_{2j-1}, x_{2j+1}) and define $p_{+j}(x)$ as the probability of exit through the boundary point x_{2j+1}. Consider a neighbourhood (a,b) of a boundary point $x_{2j+1}(x_{2j-1})$. Given the Brownian particle starts from $x_{2j+1}(x_{2j-1})$, define p_{exRj} (p_{exLj}) as the probability of exit through the right (left) boundary point b (a) of the neighbourhood. (Note that p_{exRj} and p_{exLj} as defined depend upon the choice of the neighbourhood (a,b).) The transition rates are determined by

$$\begin{aligned} \tau_j &\overset{\Delta}{=} \tau_j(x_{2j}), \\ p_{+j} &\overset{\Delta}{=} p_{+j}(x_{2j}), \end{aligned}$$

p_{exRj}, and p_{exLj}. Assume:

(i) $V(x)$ is twice continuously differentiable (C^2),

(ii) $V''_j \overset{\Delta}{=} \left.\frac{\partial^2 V}{\partial x^2}\right|_{x=x_j} \neq 0, \qquad j = 1, 2, \ldots, 2M+1$, and

(iii) $V_{2j-1} < V_{2j+1}$.

Making these three assumptions, [WIL 82] approximates τ_j, p_{+j}, p_{exRj}, and p_{exLj} asymptotically as $Q \to \infty$. The approximations follow due to the first two assumptions; the form of the following expressions is simplified due to the last assumption. The asymptotic approximations depend only on the local behaviour of $V(x)$ about the maxima and minima and are:

$$\begin{aligned} \tau_j &\sim \frac{Qf\pi e^{\frac{1}{kT}(V_{2j-1}-V_{2j})}}{\sqrt{-V''_{2j-1}V''_{2j}}} \\ p_{+j} &\sim \frac{1}{\sqrt{\frac{V''_{2j-1}}{V''_{2j+1}}}e^{\frac{1}{kT}(V_{2j+1}-V_{2j-1})}+1} \\ p_{exRj} &\sim \frac{1}{2} \\ p_{exLj} &\sim \frac{1}{2}. \end{aligned}$$

The notation $f \sim g$ is read "f is asymptotic to g" and $f \sim g$ as $Q \to \infty$, for functions f and g dependent on both x and Q, is defined, for all x, as

$$\lim_{Q \to \infty} \frac{f}{g} = 1.$$

Define an index γ corresponding to the "least deep" potential well by

$$\min\{V_{2\gamma+1} - V_{2\gamma}, V_{2\gamma-1} - V_{2\gamma}\} = Q,$$

where Q is defined by (3.17). Further transform the time scale to

$$r \triangleq \frac{1}{\tau_\gamma}(Qt).$$

The following theorem, adapted from Theorem 2.4.4 of [WIL 82], describes how the Markov step process $y(r)$, with state space $\{x_{2j} : j = 1, 2, \ldots, M\}$, approximates, as $Q \to \infty$, the Smoluchowski process $x(\frac{\tau_\gamma r}{Q}) = \bar{x}(\tau_\gamma r)$, with state space $\Re$. (Note that the process $y(r)$ is a "sped-up" version of the processes $\bar{x}(s)$ and $x(t)$, because τ_γ grows faster than Q.) We first provide background from Chapter 2 of [WIL 82] and Section 5.4 of [COD 82].

A finite-state, stationary, Markov step process is completely characterized by its transition function matrix $P(t)$, with elements

$$p_{ij}(t) = \Pr\{y(t) = i | y(0) = j\}.$$

For any such transition function matrix, the limit

$$\Pi \triangleq \lim_{t \to 0^+} P(t)$$

always exists (Section 5.4 of [COD 82]). The limit

$$\mathcal{P} \triangleq \lim_{t \to \infty} P(t)$$

is called an ergodic projection and determines a partition of the state space of the Markov step process into ergodic classes and transient states. States in any ergodic class are inaccessible from states in any other ergodic class. The matrix Π satisfies the properties of an ergodic projection, that is,

(i) $\Pi \geq 0$

(ii) $\Pi \cdot \underline{1} = \underline{1}$

(iii) $\Pi^2 = \Pi$

(iv) $\Pi P(t) = P(t)\Pi = P(t)$,

where $\underline{1}$ is a column vector of ones. Therefore Π is called the *ergodic projection at zero.*

A Markov step process can have instantaneous states, that is, states in which the duration of any visit is zero with probability one. However, the process can spend a nonzero amount of time switching among instantaneous states (that is, the set of times spent in any instantaneous state contains no intervals but can have nonzero measure). Thus a Markov step process with instantaneous states is called *stochastically discontinuous* as its sample functions have segments that are nowhere continuous. A Markov step process without instantaneous states is called *stochastically continuous* as its sample functions are piecewise continuous. The states of a stochastically-continuous Markov process are called regular states. The duration of any visit to a regular state is an exponentially-distributed random variable. If $\Pi = I$, the identity matrix, the Markov step process is stochastically continuous; otherwise, it is stochastically discontinuous. An instantaneous state i for which $\pi_{ii} = 0$, where $\Pi = (\pi_{ij})$, is called evanescent, that is, it is a transient state.

Transformation 2b: to the stochastically-continuous Markov step process y

Every stochastically-discontinuous Markov step process uniquely determines a stochastically-continuous Markov process through an *aggregation operation.* Just as the ergodic projection P determines a partition of the state space of the Markov step process into ergodic classes and transient states, the ergodic projection at zero Π determines a partition of the state space of the Markov step process into ergodic classes at zero and evanescent states. An ergodic class at zero can contain any number of instantaneous states and at most one regular state. Evanescent states are visited only in transitions between ergodic classes at zero and can be neglected without affecting the finite dimensional distributions of the process. Once in an ergodic class at zero, the process switches instantaneously among states in the ergodic class. The amount of time spent in any ergodic class at zero is an exponentially-distributed random variable. (In comparison, states in any ergodic class determined by the ergodic projection P are inaccessible from states in any other ergodic class, but within an ergodic class, the time for transitions among states is an exponentially-distributed random variable.) Thus when evanescent states are neglected and the states of each ergodic class at zero are merged into a single state, the resulting Markov step process is stochastically continuous.

The aggregation operation can be formally stated as follows. Let $P(t) = \Pi \exp\{At\}$, where A is the infinitesimal generator of $P(t)$, be the transition function matrix for the stochastically-discontinuous Markov step process. Write the ergodic projection at zero in terms of the matrices of its left and right eigenvectors of eigenvalue one, that is, as $\Pi = V \cdot U$. Then

$$\hat{P}(t) \triangleq UP(t)V = \exp\{UAVt\}$$

is the transition function matrix of the stochastically-continuous Markov step process (Theorem 5.4.5 and Corollary 5.4.6 of [COD 82]), which completely characterizes the process. We can now state the theorem.

Theorem 3.1. In the transformed time scale τ, the finite-dimensional distributions of the process x converge as $Q \to \infty$ to the finite-dimensional distributions of a $2M$-state stochastically-discontinuous Markov step process. Aggregation of the stochastically-discontinuous Markov step process yields an M-state stochastically-continuous Markov step process y with transition rates

$$a_{j+1,j} = \lambda_{j+}p_{exRj}$$
$$a_{j-1,j} = \lambda_{j-}p_{exLj}$$
$$a_{i,j} = 0, \qquad i \neq j \pm 1,$$

where λ_{j+} is the rate for a transition $x_{2j} \to x_{2j+1}$, given by

$$\lambda_{j+} = \frac{p_{+j}}{\tau_j},$$

and λ_{j-} is the rate for a transition $x_{2j} \to x_{2j-1}$, given by

$$\lambda_{j-} = \frac{1 - p_{+j}}{\tau_j}.$$

The evolution equation for the distribution function p_j is the forward Kolmogorov equation

$$\frac{dp_j}{dt} = (a_{j,j+1}p_{j+1} - a_{j+1,j}p_j) + (a_{j,j-1}p_{j-1} - a_{j-1,j}p_j). \tag{3.19}$$

In physics, Equation (3.19) is commonly called a *master equation*.

The form of the equilibrium state p^e follows if we require that the equilibrium state remain an invariant density of the forward Kolmogorov equation. We can calculate

$$\begin{aligned}
\frac{p^e_{j+1}}{p^e_j} &= \frac{a_{j+1,j}}{a_{j,j+1}} = \frac{\lambda_{j+}}{\lambda_{(j+1)-}} \\
&= \frac{p_{+j}}{1 - p_{+(j+1)}} \frac{\tau_{j+1}}{\tau_j} \\
&= \left(\frac{\sqrt{\frac{V''_{2j+1}}{V''_{2j+3}}} e^{-\frac{1}{kT}(V_{2j+1} - V_{2j+3})} + 1}{\sqrt{\frac{V''_{2j-1}}{V''_{2j+1}}} e^{-\frac{1}{kT}(V_{2j-1} - V_{2j+1})} + 1} \right) \sqrt{\left(\frac{V''_{2j+3}}{V''_{2j+1}V''_{2j+2}} \right) \left(\frac{V''_{2j-1}V''_{2j}}{V''_{2j+1}} \right)} \\
&\quad \cdot e^{-\frac{1}{kT}\{[(V_{2j+3} - V_{2j+1}) + V_{2j+2}] - [(V_{2j+1} - V_{2j-1}) + V_{2j}]\}}.
\end{aligned}$$

The equilibrium state is therefore

$$p^e_j = c\left\{ \left(1 + \sqrt{\frac{V''_{2j+1}}{V''_{2j-1}}} e^{-\frac{1}{kT}(V_{2j+1} - V_{2j-1})} \right) \frac{1}{\sqrt{V''_{2j}}} \right\} e^{-\frac{1}{kT}V_{2j}}, \tag{3.20}$$

where c is a normalization constant. The equilibrium state is now a more general form of the canonical density function.

3.3.2. A Diffusion Process with a Position-Dependent Diffusion Coefficient

In a section entitled "Slightly Nonlinear Systems" (Section 14 of [LAX 60]), Lax attributes two properties to nonlinear Markovian systems:

(i) The equilibrium state differs from the canonical density function of Definition 3.5.

(ii) The diffusion coefficient depends on both extrinsic and intrinsic properties of the system.

These two properties of nonlinear systems are properties of Markovian systems with a position-dependent diffusion coefficient. A position-dependent diffusion coefficient appears in a system derived from a Hamiltonian system in a particular manner—by reducing (in an appropriate limit) the spacing between the states of the Markov step process of the previous section.

A *Kramer-Moyal expansion* [NIC 77, Sect. 10.3] of a master equation yields a partial differential equation, called a forward equation. The forward equation models a physical process with a continuous sample-path state space. The discrete sample-path state space of the Markov step process must therefore yield the continuous state space of the physical process. Thus there is an underlying assumption that the state space of the Markov step process is a set of points suitably placed in an n-dimensional Euclidean space (for example).

The forward equation is obtained in the limit of a scaling parameter decreasing to zero. Let $h \in \Re_+$ denote this scaling parameter. The same parameter h scales three different dependencies of the Markov step process—the position coordinates, time, and process parameters. In particular, we shall define a scaling parameter h such that the spacing between the points of the state space placed in an Euclidean space, a transformation of the time scale, and the infinitesimal transition rates all depend on h. The forward equation is obtained from the *infinitesimal transition moments*

$$m_n(z;h) \triangleq \frac{1}{n!} \lim_{\Delta \to 0^+} \frac{1}{\Delta} \mathrm{E}\{[z(r+\Delta) - z(r)]^n \mid z(r) = z\}, \qquad n = 1, 2, \ldots, \quad (3.21)$$

where $z(r)$ is a Markov step process exhibiting the above dependencies on h. Then, in a change of time scale to

$$t = hr\,,$$

the infinitesimal transition moments rescale as

$$m_n(x) = \lim_{\substack{h \to 0 \\ z \to x}} m_n(z;h).$$

In the new time scale, the forward equation can be written formally as an expansion in the rescaled infinitesimal transition moments, that is, as

$$\frac{\partial \rho}{\partial t} = \sum_{n=1}^{\infty} \frac{1}{n!} (-\frac{\partial}{\partial x})^n (m_n \rho),$$

where the density function ρ is the density function of a Markov process x approximating the Markov step process z in the limit of the scaling parameter h decreasing to zero. A Fokker-Planck equation is obtained when the infinitesimal transition moments vanish for $n > 2$.

Consider the Fokker-Planck approximation to the master equation (3.19) on the level of the sample-path equations of motion, that is, consider a diffusion process approximation to the Markov step process of the previous subsection. For a rescaled time τ, the approximating diffusion process is of the form

$$dx = A(x)d\tau + \sqrt{2D(x)}dw, \tag{3.22}$$

where the drift parameter $A(x)$ is the first-order infinitesimal transition moment and the diffusion parameter $D(x)$ is the second-order infinitesimal transition moment.

Transformation 3: to a "sped-up" diffusion process $x(\tau) = y(\delta^2\tau)$, in a rescaled time $\tau = \delta^2 r$

The time and position coordinates of the Markov step process can be scaled to obtain convergence to the diffusion process, as follows. Assume

$$x_{2M+1} - x_{2M} = \cdots = x_{2j+1} - x_{2j} = x_{2j} - x_{2j-1} = \cdots = x_2 - x_1.$$

Set a dimensionless parameter

$$\delta \triangleq x_{2j+2} - x_{2j},$$

that is, δ is defined as the spacing between the minima (or maxima) of the potential function V. Change the time scale to

$$\tau \triangleq \delta^2 r.$$

Thus δ^2 corresponds to the scaling parameter h of Equation (3.21). To obtain the approximating diffusion process (3.22), the measure Q of the depth of the potential wells must have a particular dependence on the scaling parameter δ. In particular, assume

$$Q = \frac{4}{\delta^2}.$$

The diffusion process $x(\tau)$ of Equation (3.22), with state space $\Re$, then approximates, as $\delta \to 0$, the Markov step process $y(\frac{\tau}{\delta^2})$, with state space $\{x_{2j}; j = 1, 2, \ldots, M\}$. (Time is "sped up" and the spacing between states is "shrunk".)

We shall calculate $A(x)$ and $D(x)$ for a specific form of the potential V. For $x \in [x_{2j-1}, x_{2j+1}]$, decompose $V(x)$ as

$$V(x) = Q\phi(x) + \theta(x),$$

where:

(i) $\phi(x)$ and $\theta(x)$ are twice continuously differentiable,

(ii) $\phi''(x_{2j+1}) \neq 0$ and $\theta''(x_{2j}) \neq 0$ for all j,

(iii) $\theta(x_{2j-1}) < \theta(x_{2j+1})$,

(iv) $\phi(x) \sim \alpha(x_{2j})(x - x_{2j})^2$ as $x \to x_{2j}$,

(v) $\phi''(x_{2j+1}) = \phi''(x_{2j-1})$, and

(vi) $V(x) \sim Q\phi(x)$ and $V(x) >> \theta(x)$, as $Q \to \infty$, for $x \neq x_{2j}$.

The first three conditions ensure that our previous assumptions on $V(x)$ are satisfied; the last three conditions determine the form of the limiting expressions for $A(x)$ and $D(x)$. The notation $f \sim g$ as $u \to v$, for functions f and g dependent on u, is defined as

$$\lim_{u \to v} \frac{g}{f} = 1.$$

Similarly, $f >> g$ as $u \to v$ is defined as

$$\lim_{u \to v} \frac{g}{f} = 0.$$

Note that the last three conditions ensure that as $Q \to \infty$, the equilibrium state of the previous section remains both finite and nonzero. The potential $\phi(x)$ varies as function of position on the scale of an individual potential well, while the potential $\theta(x)$ varies on the scale of the composite system. We can call the potential ϕ a local potential and the potential θ a global potential.

With our scaling of the dependencies of the Markov step process y and our specific form for the potential V, the infinitesimal transition moments of order greater than two vanish in the appropriate limits. We can thus determine the parameters of an approximating diffusion process (3.22) by calculating the first-order and second-order infinitesimal transition moments (the drift and diffusion parameters, respectively), using Equation (3.21). For the discrete sample-path state space of the Markov step process y to converge to the continuous state space $\Re$, we must let $\delta \to 0$, $x_{2j} \to x$, and $M \to \infty$. In the limits $\delta \to 0$, $x_{2j} \to x$, and $M \to \infty$, we can calculate the diffusion parameter as

$$\begin{aligned} D(x) &= \lim_{\substack{\delta \to 0 \\ x_{2j} \to x}} \frac{1}{2}(a_{j+1,j} + a_{j-1,j}) \\ &= \lim_{\substack{\delta \to 0 \\ x_{2j} \to x}} (\frac{1}{4\tau_j}) \\ &= \frac{1}{4\pi f} \sqrt{-\phi''_{\mathrm{max}}(x)\phi''_{\mathrm{min}}(x)} e^{-\frac{1}{kT}\alpha(x)}, \end{aligned}$$

where

$$\begin{aligned} \phi''_{\mathrm{max}}(x) &\triangleq \lim_{\substack{x_{2j-1} \to x \\ Q \to \infty}} \frac{1}{Q} V''_{2j-1} \\ \phi''_{\mathrm{min}}(x) &\triangleq \lim_{\substack{x_{2j} \to x \\ Q \to \infty}} \frac{1}{Q} V''_{2j}. \end{aligned}$$

Using the above result, in the same limits we can calculate the drift parameter as

$$\begin{aligned} A(x) &= \lim_{\substack{\delta \to 0 \\ x_{2j} \to x}} \frac{1}{\delta}(a_{j+1,j} - a_{j-1,j}) \\ &= \lim_{\substack{\delta \to 0 \\ x_{2j} \to x}} \frac{1}{\delta}(\frac{2p_{+j} - 1}{2\tau_j}) \\ &= -\frac{1}{kT} D(x) \frac{\partial \theta}{\partial x}. \end{aligned}$$

The approximating diffusion process (3.21) thus becomes

$$dx = -\frac{1}{\mu(x)}\frac{\partial\theta}{\partial x}d\tau + \sqrt{2D(x)}dw, \tag{3.23}$$

where we define a position-dependent frictional coefficient

$$\mu(x) \triangleq kT\frac{1}{D(x)}.$$

Note that

$$D(x) = kT\frac{1}{\mu(x)}$$

is of the same form as the Einstein relation for the Smoluchowski process (3.14) ($D = \frac{kT}{f}$). The diffusion coefficient D is now both a function of extrinsic and intrinsic system properties—the external potential V in addition to the intrinsic parameter f. However, D is independent of the global potential θ and dependent only on the local potential ϕ—the local potential has become a property of a heat bath incorporating the effects of the potential wells.

The density function ρ satisfies the Fokker-Planck equation

$$\frac{\partial\rho}{\partial t} = -\frac{\partial}{\partial x}\left[\left(-\frac{1}{\mu(x)}\frac{\partial\theta}{\partial x} - \frac{\partial D}{\partial x}\right)\rho - D\frac{\partial\rho}{\partial x}\right].$$

As in the previous subsection, we can determine the form of the equilibrium state ρ^e by requiring that the equilibrium state remain an invariant density of the Fokker-Planck equation. We then calculate

$$\begin{aligned}\frac{\partial}{\partial x}\ln\rho^e &= -\frac{1}{D\mu}\frac{\partial\theta}{\partial x} - \frac{\partial}{\partial x}\ln D\\ &= -\frac{1}{kT}\frac{\partial\theta}{\partial x} - \frac{\partial}{\partial x}\ln D.\end{aligned}$$

So

$$\rho^e(x) = c\frac{1}{D(x)}e^{-\frac{1}{kT}\theta(x)}, \tag{3.24}$$

where c is a normalization constant, and the equilibrium state is again a more general form of the canonical density function. A simple calculation verifies the following equilibrium relation (provided $\lim_{|x|\to\infty} xe^{-\frac{1}{kT}\theta} = 0$, which justifies the required integration by parts), a special case of Equation (14.85) of [LAX 60], namely,

$$-\langle A(x)x\rangle_e = \frac{1}{kT}\left\langle D(x)\frac{\partial\theta}{\partial x}x\right\rangle_e = \langle D(x)\rangle_e.$$

3.4. The Equilibrium State

We have constructed a series of Markovian thermodynamic systems through reductions in the state space of an original thermodynamic system consisting of an ensemble of Hamiltonian systems. The original Hamiltonian of Section 3.2.1.1 was of the form

$$H = (K + V) + K' + (V' + W),$$

where K and V are the kinetic and potential energies of the Brownian particle, respectively, K' and V' are the kinetic and potential energies of the unobservable particles of the heat bath, respectively, and W is a coupling Hamiltonian, that is, a potential function of the position coordinates, coupling the Brownian particle to the heat bath.

In the reduction to the Ornstein-Uhlenbeck process, the above three components of the Hamiltonian contribute distinct terms to the reduced system (3.6). The component $K + V$ determines those terms of the equations of motion independent of the effects of the heat bath, that is, the terms $v\,dt$ of (3.6a) and $-\frac{1}{m}\frac{\partial V}{\partial x}\,dt$ of (3.6b). The component K' determines the average kinetic energy per particle, in equilibrium, that is, the temperature T of the heat bath. The component $V' + W$ determines the frictional coefficient f coupling the heat bath to the Brownian particle. In the reduction to the Smoluchowski process, the kinetic energy of the Brownian particle K vanishes.

To obtain the further reduction of Section 3.3.2, the potential energy of the Brownian particle V is broken into two components. In the reduced system, one component determines the now position-dependent frictional coefficient $\mu(x)$ coupling the Brownian particle to the heat bath; the other remains a potential component and determines the term of the equation of motion independent of the heat bath, that is, $-\frac{\partial\theta}{\partial x}\,d\tau$ of (3.23).

We can equivalently consider the contributions of each component of the Hamiltonian to the equilibrium state. The equilibrium state of the original Hamiltonian thermodynamic system was defined in Definition 3.5 as the canonical density function

$$\rho^e = ce^{-\frac{1}{kt}H},$$

where c is a normalization constant. In Section 3.2, the equilibrium state remained the canonical density function, with H becoming $K + V$ for the Ornstein-Uhlenbeck process and V for the Smoluchowski process. In Section 3.3, we obtained a more general form of the equilibrium state, in Equation (3.20) as

$$p_i^e = c(T)\frac{1}{g_i(T)}e^{-\frac{1}{kT}h_i},$$

for the Markov step process, and in Equation (3.24) as

$$\rho^e = c(T)\frac{1}{g(T,x)}e^{-\frac{1}{kT}h(x)},$$

for the diffusion process, where we have indicated the temperature dependences explicitly. The term h is the remaining potential component of the Hamiltonian; the term $\frac{1}{g}$ is the frictional coefficient $\mu(x)$ in (3.24) and what can be considered its analogue in (3.20).

The equilibrium state of a Markovian thermodynamic system is thus determined by the Hamiltonian of an underlying physical system. We can also write the equilibrium state as

$$p^e = c\, e^{-\frac{1}{kT}(h+kT\ln g)},$$

where p^e denotes the equilibrium state of either process. The term $h + kT\ln g$ has the form of a chemical potential, where h is the potential of the Brownian particle independent of the heat bath and $kT\ln g$ is the potential due to coupling to the heat bath. For example, the chemical potential of a species in an ideal mixture is given by

$$\mu = \mu^{\circ} + kT\ln x,$$

where μ° is the chemical potential of the pure species, analogous to h, and $kT\ln x$ is the chemical potential term due to the species being a mole fraction x of the mixture, analogous to $kT\ln g$. Thus we can alternately write the equilibrium state as

$$p^e = c\, e^{-\frac{1}{kT}\mu^e},$$

where

$$\mu^e = h + kT\ln g.$$

When the frictional coefficient is position-independent, the term g vanishes, as it is incorporated in the normalization constant c, and the equilibrium state is the canonical density function. When the frictional coefficient is position-dependent, the equilibrium state is the more general form of the canonical density function.

Based on underlying physical considerations, an equilibrium state can be associated with a thermodynamic system. Three physical properties arising from the original Hamiltonian, in particular, the temperature as measured by the average kinetic energy per heat bath particle, in equilibrium, the potential energy function of the Brownian particle, and possibly a position-dependent frictional coefficient, yield the equilibrium state. Alternately, the equilibrium chemical potential of the Brownian particle gives the equilibrium state. In our model of a thermodynamic system, we shall assume an associated equilibrium state based on either of the above equivalent physical considerations.

4. A Derivation of Fundamental Thermodynamic Relations

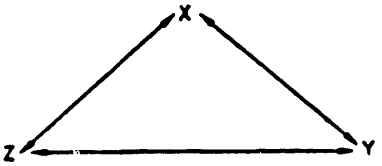
Kolmogorov's forward equation is the evolution equation for the statistical state of a thermodynamic system. We shall augment Kolmogorov's forward equation to construct a state space model of a thermodynamic system. Then, given the parameters of Kolmogorov's forward equation and an associated equilibrium state, both based upon physical considerations, thermodynamic properties follow directly from our model.

4.1. Equilibrium

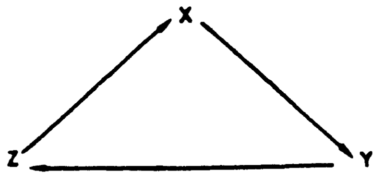
4.1.1. The Equilibrium State in Thermodynamics

In thermodynamics, a *system* is that subset of the universe we isolate from its surroundings for thermodynamic study. A system is described by a set of internal and external parameters. The *state* of the system can be specified by a set of values for these parameters. In *steady state,* the state is time-independent.

A steady state can be maintained by a cyclic mechanism. For example, in a cyclic reaction



a steady state could be maintained by



where a steady flow exists around a cycle. When *detailed balance* holds, there is "on the average, ... the same frequency of transition from the condition $[X]$ to $[Y]$ as from the condition $[Y]$ to $[X]$. ... the transitions from $[X]$ to $[Y]$ do not have to be thought as balanced with the help of some indirect route such as $[Y]$ to $[Z]$ to $[X]$," [TOL 38], that is, a steady flow around a cycle is precluded. When *microscopic reversibility* holds, "any molecular process and the reverse of that process will be taking place on the average at the same rate," [TOL 38] that is, on the average, a microscopic process is invariant under time-reversal. By definition, *equilibrium* is that steady state for which detailed balance holds. The equivalence of detailed balance and microscopic reversibility is a quantum principle.

4.1.2. A Definition of Equilibrium and Equivalent Conditions for Equilibrium

In this section, we shall begin to provide the dissipative dynamical system constructed from Kolmogorov's forward equation in Chapter 2 with thermodynamic properties. An equilibrium state can be defined in terms of a detailed balance condition and shown to be equivalent to a reversibility condition.

Consider first a finite-state Markov step process. Let the infinitesmal matrix A be time-independent. By our assumptions of Section 2.2 on the infinitesimal matrix A, a unique steady-state solution p^s exists, such that, for all $i \in E$,

$$\sum_{j=1}^{N} \left(a_{ij} p_j^s - a_{ji} p_i^s \right)$$
$$= \sum_j J_{ij} = 0 \quad .$$

This steady-state requirement that all fluxes leaving (or equivalently, entering) any state sum to zero does not exclude rotational fluxes. Those steady states for which all fluxes J_{ij} vanish individually for all $i, j \in E$ can be distinguished as equilibrium states.

Definition 4.1. An *equilibrium state* is a steady state for which the fluxes $J_{ij} = 0$ for all $i, j \in E$.

We shall denote an equilibrium state by p^e. The definition of an equilibrium state as a steady state for which all fluxes vanish can equivalently be stated as a steady state p^s for which

$$a_{ij}p_j^s = a_{ji}p_i^s$$

for all $i, j \in E$. In the literature on Markov chains [KEI 79, KEL 79], this condition is known as *detailed balance*. The name arises from the balancing of the flow from any state j to any state i by the flow in the reverse direction from i to j. Note that we use the term *equilibrium* to distinguish a particular type of steady state, as it is used in thermodynamics, distinct from its use in the literature on ordinary differential equations, where it is used synonymously with the term steady state. As in thermodynamics, equilibrium is equivalent to a condition of time reversibility.

Definition 4.2. The process $\{\xi(t), t \in \Re_+\}$ is *invariant under time reversal* if, for all $t, s \in \Re_+$, the transition function matrix

$$P(t \mid s) = P(s \mid t) \quad .$$

Theorem 4.1. The following conditions are equivalent:

(i) The steady state p^s is an equilibrium state.

(ii) The process $\{\xi(t), t \in \Re_+\}$ in the steady state p^s is invariant under time reversal.

A proof of Theorem 4.1 can be found in [KEI 79] or [KEL 79]. Steady state is a necessary condition for both equilibrium (by definition) and time reversal invariance [KEL 79]. Theorem 4.1 duplicates the thermodynamic view of equilibrium we described above (Section 4.1.1). There is a further condition which is equivalent to equilibrium.

Proposition 4.1. The steady state p^s is an equilibrium state iff the infinitesimal matrix A satisfies the intertwining equation.

$$\mathrm{A\ diag}\ \{p^s\} = \mathrm{diag}\ \{p^s\}A^T \,,$$

where diag $\{p^s\}$ is a matrix with diagonal elements p_i^s and zero off-diagonal elements.

Proof. We give a simple proof not found in the literature. Define the matrix of fluxes J to have elements J_{ij} with diagonal elements $J_{ii} = 0$. Then, as the elements

$$J_{ij} = a_{ij}p_j - a_{ji}p_i ,$$

the matrix J satisfies the matrix equation

$$J = A \text{ diag } \{p\} - \text{diag } \{p\}A^T .$$

By definition, a steady state is an equilibrium state iff all fluxes J_{ij} vanish, or equivalently, iff the matrix $J = 0$. But, for any steady state p^s, $J = 0$ iff

$$A \text{ diag } \{p^s\} = \text{ diag } \{p^s\}A^T . \qquad \blacksquare$$

Both the condition of vanishing fluxes and the intertwining equation of Proposition 4.1 allow us to determine whether the steady state of the process $\{\xi(t), t \in \Re_+\}$ is an equilibrium state from the steady state p^s and the infinitesimal transition rates a_{ij}. As a steady state is determined by the infinitesimal transition rates, we should expect to be able to establish whether a steady state is an equilibrium state directly from the infinitesimal transition rates. Such a test exists and is known as Kolmogorov's criteria [KEL 79]. Define a closed path as any sequence of states connected by nonzero infinitesimal transition rates starting and ending with the same state in the state space E. Let the notation

$$\sum_{Closed\,Path} \ln \frac{a_{ij}}{a_{ji}}$$

denote the summation of the natural logarithm of the ratio $\frac{a_{ij}}{a_{ji}}$ of infinitesimal transition rates around a closed path in the state space E. In our language, Kolmogorov's criteria then becomes:

Theorem 4.2. A steady state is an equilibrium state iff the ratios of infinitesimal transition rates satisfy

$$\sum_{Closed\,Path} \ln \frac{a_{ij}}{a_{ji}} = 0$$

for all closed paths in the state space E.

A proof can be found in [KEL 79]. If there are no closed paths in the state space, the theorem is trivially satisfied. Note that Theorem 4.2 implies that the sum of $\ln \frac{a_{ij}}{a_{ji}}$ or the product of the ratio $\frac{a_{ij}}{a_{ji}}$ between any two states is independent of the connecting path for a process which will evolve to the equilibrium state.

Now consider a Markov diffusion process. Let the parameters m and $\sum$ be time-independent. Assume a unique steady-state solution ρ^s exists, such that, for all $x \in \Re^n$,

$$\nabla \cdot \left\{ m(x)\rho^s(x) - \frac{1}{2}\nabla \cdot [\Theta(x)\rho^s(x)] \right\}$$
$$= \nabla \cdot j(x) = 0 \, .$$

This differential steady-state requirement is equivalent to the integral steady-state requirement that, for all regions $\Gamma \subset \Re^n$, the surface integral

$$\int_{\partial\Gamma} n \cdot j(x) dS_x = 0 \, ,$$

where the vector n is the normal to the boundary $\partial\Gamma$. Thus steady state does not exclude circulation around the boundary $\partial\Gamma$. Those steady states for which the flux $j(x)$ vanishes for all $x \in \Re^n$ can be distinguished as equilibrium states.

Definition 4.3. An *equilibrium state is a steady state* for which the flux $j(x) = 0$ for all $x \in \Re^n$.

We shall denote an equilibrium state by ρ^e. The definition of an equilibrium state as a steady state for which the flux vanishes can be equivalently stated as a steady state ρ^s for which

$$\frac{1}{2}\nabla \cdot [\Theta(x)\rho^s(x)] = m(x)\rho^s(x)$$

for all $x \in \Re^n$. Kent [KEN 78] defines these equations as the *detailed balance* equations. Note that as before we use the term *equilibrium* to distinguish a particular type of steady state, distinct from its use in Kent [KEN 78] and the literature on partial differential equations. As for a finite-state Markov step process, equilibrium is equivalent to a condition of time-reversibility.

Definition 4.4. The process $\{x(t), t \in \Re_+\}$ is *invariant under time reversal* if, for all $t, s \in \Re_+$ and $x, y \in \Re^n$, the transition density function

$$\rho(t, x \mid s, y) = \rho(s, x \mid t, y) \quad .$$

Theorem 4.3. The following conditions are equivalent:

(i) The steady state ρ^s is an equilibrium state.

(ii) The process $\{x(t), t \in \Re_+\}$ in the steady state ρ^s is invariant under time reversal.

A proof of Theorem 4.3 follows from Theorems 4.1 and 6.1 of Kent [KEN 78] and our assumption that a steady-state solution exists.

The existence of an intertwining equation is also equivalent to equilibrium. Define the operator $\mathcal{A}$ as the operator of Kolmogorov's forward equation, that is, for any C^2-function $\phi(x)$, let

$$\begin{aligned}\mathcal{A}\phi &\triangleq -\sum_i \frac{\partial}{\partial x_i}[m_i(x)\phi(x)] \\ &\quad + \frac{1}{2}\sum_{i,j}\frac{\partial^2}{\partial x_i \partial x_j}\Big[\theta_{ij}(x)\phi(x)\Big].\end{aligned}$$

The adjoint of $\mathcal{A}$, which we shall denote by $\mathcal{A}^*$, is then the operator of Kolmogorov's backward equation, that is,

$$\begin{aligned}\mathcal{A}^*\phi &= \sum_i m_i(x)\frac{\partial}{\partial x_i}\phi(x) \\ &\quad + \frac{1}{2}\sum_{i,j}\theta_{ij}(x)\frac{\partial^2}{\partial x_i \partial x_j}\phi(x).\end{aligned}$$

We can now state the equivalence of equilibrium and an intertwining operator equation, analogous to the intertwining matrix equation of Proposition 4.1.

Proposition 4.2. The steady state ρ^s is an equilibrium state iff the forward Kolmogorov operator $\mathcal{A}$ satisfies the intertwining equation

$$\mathcal{A}(\rho^s\phi) = \rho^s\mathcal{A}^*\phi,$$

for all C^2-functions ϕ.

Proof. Using our differential notation, we can calculate

$$\begin{aligned}\mathcal{A}(\rho\phi) &= -\nabla\cdot\Big[m\rho\phi - \frac{1}{2}\nabla\cdot(\Theta\rho\phi)\Big] \\ &= -\nabla\cdot(j\phi) + \frac{1}{2}\nabla\cdot[(\Theta\rho)\cdot\nabla\phi] \\ &= -(\nabla\cdot j)\phi - j\cdot\nabla\phi \\ &\quad + \frac{1}{2}[\nabla\cdot(\Theta\rho)]\cdot\nabla\phi \\ &\quad + \frac{1}{2}\rho\sum_{i,j}\theta_{ij}\frac{\partial^2}{\partial x_i\partial x_j}\phi\end{aligned}$$

and

$$\rho\mathcal{A}^*\phi = \rho m\cdot\nabla\phi + \frac{1}{2}\rho\sum_{i,j}\theta_{ij}\frac{\partial^2}{\partial x_i\partial x_j}\phi.$$

Thus, the difference

$$\mathcal{A}(\rho\phi) - \rho\mathcal{A}^*\phi = -(\nabla\cdot j)\phi - 2j\cdot\nabla\phi.$$

By definition, a steady state is an equilibrium state iff the flux j vanishes. But, for any steady state ρ^s, $j = 0$ iff

$$\mathcal{A}(\rho^s\phi) = \rho^s \mathcal{A}^*\phi$$

for all C^2-functions ϕ. ■

We can establish whether a steady state is an equilibrium state directly from the parameters m and Θ, in a theorem analogous to Theorem 4.2 for the Markov step process. For an equilibrium state ρ^e, the flux j vanishes. Equivalently,

$$\frac{1}{2}\nabla \cdot (\Theta\rho^e) = m\rho^e$$

or,

$$\nabla \ln \rho^e = 2\Theta^{-1}(m - \frac{1}{2}\nabla \cdot \Theta).$$

The above equation allows an equilibrium state ρ^e to be determined directly from the parameters m and Θ. Furthermore, for an equilibrium state the quantity $\Theta^{-1}(m - \frac{1}{2}\nabla \cdot \Theta)$ is the gradient of a scalar. Define the *curl* of a vector C^1-function $f(x) \in \Re^n$ by the skew-symmetric matrix $\nabla \times f$ with entries

$$(\nabla \times f)_{ij} = \frac{\partial}{\partial x_i} f_j - \frac{\partial}{\partial x_j} f_i .$$

Note that for any scalar C^2-function $\phi(x)$

$$\nabla \times \nabla\phi = 0 .$$

The following theorem establishes the equivalence of $\Theta^{-1}(m - \frac{1}{2}\nabla \cdot \Theta)$ being the gradient of a scalar and equilibrium.

Theorem 4.4. A steady state is an equilibrium state iff

$$\nabla \times \left[\Theta^{-1}(m - \frac{1}{2}\nabla \cdot \Theta)\right] = 0,$$

or equivalently, for all closed paths $C \subset \Re^n$,

$$\oint_C \left[\Theta^{-1}(m - \frac{1}{2}\nabla \cdot \Theta)\right] \cdot dx = 0 .$$

Theorem 4.4 follows from Theorems 4.1 and 4.2 of [KEN 78].

Given a Markov process with time-independent parameters and the assumption of a unique steady state, we have characterized those steady states which are equilibrium states. In our model of a thermodynamic system, Kolmogorov's forward equation with time-dependent parameters is the evolution equation for the statistical state. An equilibrium state is associated with the system based on the underlying physics, as we have suggested in Section 3.4. That equilibrium state is the steady state to which the system will evolve given a zero nonequilibrium component of external forces, which we shall now define.

4.2. An Input-Output Description of a Thermodynamic System

4.2.1. Forces and Fluxes in Thermodynamics

Thermodynamics does not explicitly provide a system with a state, inputs, and outputs, as does system theory. A thermodynamic system is characterized by a set of internal and external parameters. In equilibrium, the internal parameters vanish. The internal and external parameters are usually synonymous to internal and external forces. Thermodynamic quantities such as work flow and entropy production are written as inner products of forces and fluxes. Thus a flux is defined "conjugate" to each force. The thermodynamic literature does not contain explicit definitions of forces and fluxes. Rather, these quantities are defined by example.

4.2.2. Internal and External Forces

Consider first a finite-state Markov step process.

Definition 4.5. The *external forces*

$$F_{ij}(t) \triangleq \ln \frac{a_{ij}(t)}{a_{ji}(t)}.$$

The external forces F_{ij} are elements of the set $\{F_{ij} : i, j \in E, i > j\}$. For a thermodynamic system which evolves to equilibrium, the external forces are determined exclusively by the equilibrium state p^e, as

$$F_{ij} = \ln \frac{a_{ij}}{a_{ji}} = \ln \frac{p_i^e}{p_j^e}.$$

We shall also define internal forces.

Definition 4.6. The *internal forces*

$$Z_{ij}(t) \triangleq \ln \left(1 + \frac{J_{ij}(t)}{a_{ji}(t)p_i(t)}\right).$$

The internal force Z_{ij} vanishes if and only if the corresponding flux J_{ij} vanishes. Thus all internal forces vanish in steady state if and only if the steady state is an equilibrium state.

Proposition 4.3. The external forces and internal forces satisfy the relation

$$\sum_{ClosedPath} F_{ij} = \sum_{ClosedPath} Z_{ij}$$

for all closed paths in the state space E.

Proof. By definition, the fluxes

$$J_{ij} = a_{ij}p_j - a_{ji}p_i \, .$$

A rearrangement of terms thus yields

$$\begin{aligned} \ln \frac{p_i}{p_j} &= \ln \frac{a_{ij}}{a_{ji}} - \ln\left(1 + \frac{J_{ij}}{a_{ji}p_i}\right) \\ &= F_{ij} - Z_{ij} \, . \end{aligned}$$

But

$$\sum_{Closed Path} \ln \frac{p_i}{p_j} = \ln 1 = 0$$

and the theorem follows. ■

By Theorem 4.2, a steady state is an equilibrium state iff

$$\sum_{Closed Path} F_{ij} = 0$$

for all closed paths in the state space E.

Now consider a Markov diffusion process.

Definition 4.7. The *external forces*

$$f(t,x) \triangleq 2\Theta^{-1}(t,x)\left[m(t,x) - \frac{1}{2}\nabla \cdot \Theta(t,x)\right].$$

For a thermodynamic system which evolves to equilibrium, the external forces are determined exclusively by the equilibrium state ρ^e, as

$$f = 2\Theta^{-1}\left(m - \frac{1}{2}\nabla \cdot \Theta\right) = \nabla \ln \rho^e \, .$$

Definition 4.8. The *internal forces*

$$z(t,x) \triangleq 2\Theta^{-1}(t,x)\,\frac{1}{\rho(t,x)}\,j(t,x) \, .$$

The internal forces vanish in steady state if and only if the steady state is an equilibrium state.

Proposition 4.4. The external forces and internal forces satisfy the relation

$$\nabla \times f = \nabla \times z \, ,$$

or equivalently,

$$\oint_C f \cdot dx = \oint_C z \cdot dx$$

for all closed paths $C \subset \Re^n$.

Proof. By definition, the flux

$$j = m\rho - \frac{1}{2}\nabla \cdot (\Theta\rho).$$

A rearrangement of terms thus yields

$$\begin{aligned}\nabla \ln \rho &= 2\Theta^{-1}\Big(m - \frac{1}{2}\nabla \cdot \Theta\Big) - 2\Theta^{-1}\frac{1}{\rho}j \\ &= f - z.\end{aligned}$$

Thus $f - z$ is the gradient of a scalar and the theorem follows. ■

By Theorem 4.4, a steady state is an equilibrium state iff

$$\nabla \times f = 0,$$

or equivalently,

$$\oint_C f \cdot dx = 0$$

for all closed paths $C \subset \Re^n$.

4.2.3. An Input-Output Thermodynamic System

Although thermodynamics describes systems under the influence of external variables, current formulations do not provide a general framework for treating inputs and outputs. In this section, we shall provide a thermodynamic system with such a system theoretic framework.

Consider the external forces of Definitions 4.5 and 4.7. For a thermodynamic system which evolves to equilibrium, we have shown that the external forces

$$F_{ij} = \ln \frac{p_i^e}{p_j^e} \tag{4.1a}$$

$$f(x) = \nabla \ln \rho^e. \tag{4.1b}$$

In general, such a relation between the external forces and an equilibrium state does not hold.

As we have suggested in Section 2.1 and shown in Chapter 3, a thermodynamic system arises from a classical physical system. As we have shown in Section 3.4, an equilibrium state, determined by either the Hamiltonian of the original physical system or by the equilibrium chemical potential, can be associated with a thermodynamic system. The Hamiltonian or chemical potential and thus the associated equilibrium state will depend upon parameters determined externally to the thermodynamic system. For example, consider Equation (3.15) of Section 3.2.4

$$dq = \frac{1}{r}\xi dt + \sqrt{\frac{2kT}{r}}dw,$$

a sample-path process corresponding to the thermodynamic system of a Nyquist-Johnson resistor and its associated load. The voltage ξ arises from an external potential $\Phi(q)$. Consider a potential $\Phi(q)$ determined by a linear capacitor of capacitance C, that is, a potential

$$\Phi(q) = \frac{q^2}{2C}.$$

The capacitance C is then a parameter which determines the associated equilibrium state

$$\rho^e(q) = ce^{-\frac{1}{kT}\Phi(q)}.$$

The external force $f(x)$ is the voltage ξ (normalized by kT), that is,

$$\begin{aligned} f(x) &= \frac{\partial}{\partial q}\ln\rho^e(q) \\ &= -\frac{1}{kT}\frac{\partial\Phi(q)}{\partial q} \\ &= -\frac{1}{kT}\frac{q}{C} \\ &= \frac{1}{kT}\xi. \end{aligned}$$

Thus for this thermodynamic system, which evolves to its associated equilibrium state, the capacitance C is also a parameter which determines the external force. We shall denote a vector of such external parameters by α and explicitly indicate the dependence of the associated equilibrium state by $p^e(\alpha)$ or $\rho^e(x;\alpha)$.

We shall provide the vector of external parameters α with a time-dependence. Assume $\alpha(t)$ is a differentiable function of time with derivative

$$\frac{d\alpha(t)}{dt} = v(t). \tag{4.2}$$

The derivative $v(t)$ is a control which determines the evolution of $\alpha(t)$ and hence the evolution of the associated equilibrium state.

If the control $v(t) = 0$ for times $t \geq s$, then, for a thermodynamic system with external forces determined by the associated equilibrium state $p^e(\alpha(s))$ or $\rho^e(x;\alpha(s))$, as in Equation (4.1), the system will evolve to that equilibrium state.

In general, the external forces will not be completely determined by Equation (4.1). We shall define two components of the external forces. Let the equilibrium component

$$\begin{aligned} F^e_{ij}(\alpha) &\triangleq \ln\frac{p^e_i(\alpha)}{p^e_j(\alpha)} \\ f^e(x;\alpha) &\triangleq \nabla\ln\rho^e(x;\alpha) \end{aligned}$$

and the nonequilibrium component

$$
\begin{aligned}
F^n_{ij}(t) &\triangleq F_{ij}(t) - F^e_{ij}(\alpha(t)) \\
f^n(t,x) &\triangleq f(t,x) - f^e(x;\alpha(t)).
\end{aligned}
$$

The external forces can then be written as

$$
\begin{aligned}
F_{ij}(t) &= F^n_{ij}(t) + F^e_{ij}(\alpha(t)) \\
f(t,x) &= f^n(t,x) + f^e(x;\alpha(t)).
\end{aligned}
$$

There are two classes of controls which can be applied to our model of a thermodynamic system. The first class is controls which determine the evolution of the associated equilibrium state and hence the equilibrium component of the external forces. The second class is perturbations of the external forces away from that component determined by the associated equilibrium state. We shall append the first-order ordinary differential equation (4.2) to the forward Kolmogorov equation. Then the inputs to our thermodynamic system are the controls $v(t)$ and $F^n_{ij}(t)$ or $f^n(t,x)$. For state dynamics of Kolmogorov's forward equation augmented by Equation (4.2), we shall define an equilibrium state as a steady state for which both the fluxes J_{ij} or j and the control v vanish.

Associated with the control $v(t)$, we shall define additional external forces.

Definition 4.9. The *external forces* due to the control $v(t)$ are

$$
f^v(t) \triangleq \sum_i p_i(t) \nabla_\alpha \ln p^e_i(\alpha(t))
$$

for a finite-state Markov step process and

$$
f^v(t) \triangleq \int_{\Re^n} \rho(t,x) \nabla_\alpha \ln \rho^e(x;\alpha(t))\, dV_x
$$

for a Markov diffusion process.

As we have shown, at equilibrium both the nonequilibrium components of the external forces and the fluxes vanish. Similarly, at equilibrium both the control v and the external forces of Definition 4.9 vanish—the control v by definition and the external forces by the calculation

$$
\begin{aligned}
f^v &= \sum_i p^e_i \nabla_\alpha \ln p^e_i(\alpha) \\
&= \sum_i \nabla_\alpha p^e_i(\alpha) \\
&= \nabla_\alpha \sum_i p^e_i(\alpha) = 0
\end{aligned}
$$

or

$$
\begin{aligned}
f^v &= \int_{\Re^n} \rho^e(x) \nabla_\alpha \ln \rho^e(x;\alpha)\, dV_x \\
&= \int_{\Re^n} \nabla_\alpha \rho^e(x;\alpha)\, dV_x \\
&= \nabla_\alpha \int_{\Re^n} \rho^e(x;\alpha)\, dV_x = 0.
\end{aligned}
$$

We shall consider the fluxes J_{ij} or j and the external forces f^v as the outputs of our thermodynamic system.

We have augmented Kolmogorov's forward equation to construct a state space model of a thermodynamic system. Define the operator $\mathcal{A}$ as the operator of Kolmogorov's forward equation. For the Markov step process, $\mathcal{A}$ is the infinitesimal matrix A; for the diffusion process, $\mathcal{A}$ is an operator, such that, for any C^2-function ϕ,

$$\mathcal{A}\phi = -\nabla \cdot \left[m\phi - \frac{1}{2}\nabla \cdot (\Theta\phi) \right].$$

For both processes, denote the statistical state by p, the fluxes by j, and the nonequilibrium external forces by f^n. Our thermodynamic system is then

$$\frac{d\alpha}{dt} = v \tag{4.3a}$$

$$\frac{\partial p}{\partial t} = \mathcal{A}(\alpha; f^n)p \tag{4.3b}$$

$$j = j(\alpha, p; f^n) \tag{4.3c}$$

$$f^v = f^v(\alpha, p), \tag{4.3d}$$

where the state variables are α and p, the inputs are v and f^n, and the outputs are j and f^v.

4.3. The Dissipation Inequality of Thermodynamics

4.3.1. The First and Second Laws of Thermodynamics

In thermodynamics, with a change in state of a system, the change in a *state function* depends only on the initial and final states, while a *path function* depends on the path through which the change in state is effected. Thus, the differential of a state function is exact and the differential of a path function is inexact. The differential of a state function X can be decomposed (formally) into the sum of the differentials of two path functions, as

$$dX = d_eX + d_iX,$$

where d_eX represents changes in X due to the *flow* of X between the system and its surroundings, and d_iX represents the *production* of X in the system.

Using the terminology of Willems' work on dissipative systems [WIL 72], we say a thermodynamic system with *storage function* X is dissipative with respect to the *supply rate* $\frac{d_eX}{dt}$ and lossless with respect to the difference of the supply rate and the *dissipation rate* $-\frac{d_iX}{dt}$. The corresponding mathematical statements are:

$$\frac{dX}{dt} = \frac{d_eX}{dt} + \frac{d_iX}{dt} \leq \frac{d_eX}{dt}; \quad \frac{d_iX}{dt} \leq 0.$$

The first law of thermodynamics postulates the existence of a state function U called the *internal energy*, such that

$$\frac{dU}{dt} = \frac{d_eU}{dt}$$

$$\frac{d_iU}{dt} = 0,$$

that is, the internal energy of a system is conserved. In a closed system, the flow of energy between the system and its surroundings is equal to the difference of the *heat flow* $\frac{đq}{dt}$ and the *work flow* $\frac{đw}{dt}$, or

$$\frac{dU}{dt} = \frac{đq}{dt} - \frac{đw}{dt}.$$

By thermodynamic convention, a flow from the system to the surroundings is positive for work and negative for heat. In an open system, the heat flow and work flow terms include contributions due to the flow of matter between the system and its surroundings.

The second law of thermodynamics postulates the existence of a state function S called the *entropy*, such that

$$\frac{dS}{dt} = \frac{d_eS}{dt} + \frac{d_iS}{dt} \geq \frac{d_eS}{dt}$$

$$\frac{d_iS}{dt} \geq 0,$$

that is, the entropy produced inside a system is non-decreasing as a function of time. A *temperature* T can be assigned to a system. Then,

$$\frac{d_eS}{dt} = \frac{1}{T}\frac{\text{đ}q}{dt}.$$

We shall use the following notation for heat flow, work flow, and the entropy production rate:

$$\begin{aligned} Q &\triangleq \frac{\text{đ}q}{dt} \\ W &\triangleq -\frac{\text{đ}w}{dt} \\ D &\triangleq \frac{d_iS}{dt}. \end{aligned}$$

Note that we have defined a flow from the system to the surroundings as negative for work, contrary to thermodynamic convention. The first and second laws of thermodynamics can then be written as

$$\begin{aligned} \frac{d}{dt}U &= Q + W \\ \frac{d}{dt}S &= \frac{Q}{T} + D \geq \frac{Q}{T}, \end{aligned}$$

respectively.

For an isothermal change of state, at a constant temperature T,

$$\frac{d}{dt}U - T\frac{d}{dt}S = \frac{d}{dt}(U - TS).$$

If we define a *free energy* G as

$$G \triangleq U - TS,$$

the first and second laws then yield the following dissipation inequality

$$\frac{d}{dt}G = W - TD \leq W.$$

The heat flow Q and work flow W are observable only through effects produced in the system's surroundings. The entropy production rate D is not observable through effects produced in the surroundings. Nonequilibrium thermodynamics gives a structure for the work flow and entropy production—as the inner product of a vector of fluxes and a vector of forces. For example, the flow of electrical work is the product of current and voltage.

4.3.2. The Dissipation Inequality in a Thermodynamic Setting

In this section, we shall use notation applicable to both a Markov step process and a diffusion process as the sample-path process. Suppose q is a sample-path function. For a Markov step process $q = (q_1, q_2, \ldots, q_n)$, an N-dimensional vector, while for a diffusion process, $q = q(x)$, a function of $x \in \Re^n$. Consistent with our definition of Section 3.1, we shall define the *ensemble average* of a sample-path function as

$$\langle q \rangle \triangleq \sum_{i=1}^{N} q_i \, p_i(t)$$

for a Markov step process and as

$$\langle q \rangle \triangleq \int_{\Re^n} q(x)\, \rho(t,x)\, dV_x$$

for a diffusion process. Similarly, consider the $N(N-1)/2$-dimensional vectors Q and R with subscripted elements Q_{ij} and R_{ij}, where $i, j = 1, 2, \ldots, N$ and $i > j$, or the n-dimensional vector functions

$$q(x) = (q_1(x),\ q_2(x), \ldots, q_n(x))$$

and

$$r(x) = (r_1(x), r_2(x), \ldots, r_n(x)),$$

where $x \in \Re^n$. We shall define an inner product as

$$\langle Q, R \rangle \triangleq \sum_{i=1}^{N} \sum_{j=1}^{i-1} Q_{ij} R_{ij}$$

for a Markov step process and

$$\langle q, r \rangle \triangleq \int_{\Re^n} q(x) \cdot r(x)\, dV_x$$

for a diffusion process. For both processes, we shall denote the statistical state by p, the fluxes by j, the internal forces by z, and the external forces by f or by f appropriately superscripted.

Using the notation just introduced, we can rewrite the terms of the dissipation inequality of Section 2.3 as

$$\frac{d}{dt}\mathcal{G}^r = \mathcal{W}^r - \mathcal{D} \leq \mathcal{W}^r,$$

where

$$\mathcal{G}^r \triangleq \langle \ln \frac{p}{p^r} \rangle$$
$$\mathcal{W}^r \triangleq \langle j, f \rangle - \langle j, f^r \rangle$$
$$\mathcal{D} \triangleq \langle j, z \rangle,$$

and f^r is defined similarly to f^e, that is, as either the $N(N-1)/2$-dimensional vector F^r with elements $\ln \frac{p_i^r}{p_j^r}$ or the function $f^r(x) = \nabla \ln \rho^r(x)$. As we stated in Section 2.3, the dissipation rate $\mathcal{D}(t) \geq 0$, with equality iff the flux j vanishes.

In Section 2.3, we defined p^r as a time-independent reference state. Now suppose p^r is time-dependent. In particular, as we have defined an equilibrium state associated with a thermodynamic system, suppose p^r is a function of time-dependent parameters $\alpha(t)$, that is, $p^r = p^r(y; \alpha(t))$, where $\frac{d\alpha(t)}{dt} = v(t)$. Then the supply rate $\mathcal{W}^r$ becomes

$$\mathcal{W}^r = \langle j, f \rangle - \langle j, f^r \rangle - v \cdot \langle \nabla_\alpha \ln p^r \rangle,$$

where the additional term follows from the relation

$$\langle \frac{d}{dt} \ln p^r \rangle = v \cdot \langle \nabla_\alpha \ln p^r \rangle .$$

The storage function $\mathcal{G}^r$ can be decomposed as

$$\mathcal{G}^r = -\langle \ln p^r \rangle + \langle \ln p \rangle .$$

Define the ensemble averages

$$\begin{aligned} \mathcal{U}^r &\triangleq -\langle \ln p^r \rangle \\ \mathcal{S} &\triangleq -\langle \ln p \rangle . \end{aligned}$$

Then

$$\mathcal{G}^r = \mathcal{U}^r - \mathcal{S} .$$

The ensemble average $\mathcal{U}^r \geq 0$, as follows from the inequality $\ln z \leq z - 1$. Define the inner product

$$\mathcal{Q} \triangleq -\langle j, f \rangle .$$

Calculations as in Section 2.3 then yield the equality

$$\begin{aligned} \frac{d}{dt}\mathcal{U}^r &= -\langle j, f^r \rangle - v \cdot \langle \nabla_\alpha \ln p^r \rangle \\ &= \mathcal{Q} + \mathcal{W}^r \end{aligned}$$

and the inequality

$$\begin{aligned} \frac{d}{dt}\mathcal{S} &= -\langle j, f \rangle + \langle j, z \rangle \\ &= \mathcal{Q} + \mathcal{D} \geq \mathcal{Q} . \end{aligned}$$

For an N-state Markov step process (only), using the inequality

$$\mathcal{G} = \langle \ln \frac{p}{p^r} \rangle \geq 0,$$

with $p_i^r = \frac{1}{N}$ independent of i, the inequality $\mathcal{S} \leq \ln N$ follows. Thus $-\mathcal{S} + \ln N$ is nonnegative and consequently $\mathcal{S}$ (strictly $-\mathcal{S} + \ln N$) is a storage function in the sense of Willems [WIL 72] for an N-state Markov step process. Similarly $\mathcal{Q}$ is a supply rate. However, no such upper bound exists for $\mathcal{S}$ for a diffusion process. Thus, in general, $\mathcal{S}$ is not a storage function in the sense of Willems [WIL 72].

The ensemble averages

$$\begin{aligned} \mathcal{U}^r &= -\langle \ln p^r \rangle \\ \mathcal{S} &= -\langle \ln p \rangle \\ \mathcal{G}^r &= \langle \ln \frac{p}{p^r} \rangle = \mathcal{U}^r - \mathcal{S} \end{aligned}$$

and inner products

$$\begin{aligned} \mathcal{W}^r &= \langle j, f \rangle - \langle j, f^r \rangle - v \cdot \langle \nabla_\alpha \ln p^r \rangle \\ \mathcal{Q} &= -\langle j, f \rangle \\ \mathcal{D} &= \langle j, z \rangle \end{aligned}$$

have thermodynamic interpretations. As the time-dependent reference state $p^r(y\,;\,\alpha(t))$, take the equilibrium state $p^e(y\,;\,\alpha(t))$ associated with a thermodynamic system. Then the ensemble averages $\mathcal{U}^r$ and $\mathcal{G}^r$ become

$$\begin{aligned}\mathcal{U}^e &= -\langle \ln p^e \rangle \\ \mathcal{G}^e &= \langle \ln \frac{p}{p^e} \rangle = \mathcal{U}^e - \mathcal{S}\end{aligned}$$

and the inner product $\mathcal{W}^r$ becomes

$$\begin{aligned}\mathcal{W}^e &= \langle j, f \rangle - \langle j, f^e \rangle - v \cdot \langle \nabla_\alpha \ln p^e \rangle \\ &= \langle j, f - f^e \rangle - v \cdot f^v \\ &= \langle j, f^n \rangle - v \cdot f^v .\end{aligned}$$

We have now constructed a first-law equality

$$\frac{d}{dt}\mathcal{U}^e = \mathcal{Q} + \mathcal{W}^e ,$$

a second-law inequality

$$\frac{d}{dt}\mathcal{S} = \mathcal{Q} + \mathcal{D} \geq \mathcal{Q} ,$$

and the resultant dissipation inequality

$$\frac{d}{dt}\mathcal{G}^e = \mathcal{W}^e - \mathcal{D} \leq \mathcal{W}^e .$$

The ensemble averages $\mathcal{U}^e$, $\mathcal{S}$, and $\mathcal{G}^e$ have properties of the energy, entropy, and free energy, respectively. Similarly, the inner products $\mathcal{W}^e$, $\mathcal{Q}$, and $\mathcal{D}$ have properties of the work flow, heat flow, and entropy production rate, respectively. In Section 4.5, we shall reintroduce Boltzmann's constant k and the temperature T as multiplicative factors and define such quantities as applied to physical (as opposed to abstract) systems.

4.4. Reciprocity

4.4.1. Onsager's Reciprocity Relations

Close to equilibrium, thermodynamics assumes a linear relation between forces and fluxes, as

$$\jmath = \mathcal{L} f,$$

where, in the thermodynamic literature, the flux $\jmath$ and force f are n-dimensional vectors and the linear operator $\mathcal{L} = L$, a matrix. However, there is no general definition of fluxes and forces in the literature. Onsager showed that the matrix L is symmetric for processes sufficiently close to equilibrium that such a linear relation could be assumed, as a consequence of the principles of detailed balance and microscopic reversibility (Section 4.1.1). The relations $L_{ij} = L_{ji}$ between the elements of the matrix L are known as *Onsager's reciprocity relations.*

4.4.2. Reciprocity

Consider the dissipation inequality

$$\frac{d}{dt}\mathcal{G}^e = \mathcal{W}^e - \mathcal{D} \leq \mathcal{W}^e.$$

The supply rate is

$$\mathcal{W}^e = \langle \jmath, f^n \rangle - v \cdot f^v,$$

composed of inner products of the inputs f^n and v and outputs $\jmath$ and f^v of the thermodynamic system (4.3) constructed in Section 4.2.3. We can linearize such a system about a steady state. The thermodynamic system is then reciprocal if the linearized operator mapping the inputs to outputs is self-adjoint.

As we have constructed our thermodynamic system (4.3), the state variables are α and $p(t, y)$. We can equivalently consider the statistical state p as parameterized by the vector of external parameters α. A statistical state $p(t, y, \alpha)$ satisfies the partial differential equation

$$\frac{\partial p(t, y, \alpha)}{\partial t} = -v \cdot \nabla_\alpha p(t, y, \alpha) + \mathcal{A}(\alpha; f^n) p(t, y, \alpha),$$

the solution of which maps to the solution of (4.3a) and (4.3b). We can thus alternately take $p(t, y, \alpha)$ as the state of our thermodynamic system. A steady state $p^s(y, \alpha)$ is the solution of

$$v^s \cdot \nabla_\alpha p^s(y, \alpha) = \mathcal{A}(\alpha; f^{n,s}) p^s(y, \alpha).$$

The steady-state inputs are $f^{n,s}$ and v^s and the steady-state outputs are $\jmath^s$ and $f^{v,s}$. Note that in the representation of (4.3a) and (4.3b), a steady state can be a periodic function of time.

We shall define the linearized thermodynamic system as the dynamical system

$$\begin{aligned}\frac{\partial}{\partial t}\delta p &= \mathcal{A}^s\delta p + \mathcal{B}^1\delta f^n + \mathcal{B}^2\delta v; \quad \delta p(0) = 0\\ \delta j &= \mathcal{C}^1\delta p + \mathcal{D}^1\delta f^n\\ \delta f^v &= \mathcal{C}^2\delta p + \mathcal{D}^2\delta v,\end{aligned}$$

where $\mathcal{A}^s \triangleq -v^s \cdot \nabla_\alpha + \mathcal{A}(\alpha; f^{n,s})$. For a Markov step process, the operators are matrices; for a diffusion process, the operators are infinite dimensional.

Let the notation $\mathcal{D}_g$ denote both the partial derivative with respect to the vector g and the Fréchet derivative with respect to the function $g(x)$. Let the notation $\mathcal{D}_g\, h|_s$ denote $\mathcal{D}_g\, h$ evaluated at steady state, that is, at $p = p^s$, $f^n = f^{n,s}$, and $v = v^s$. Then

$$\begin{aligned}\mathcal{B}^1 &= \mathcal{D}_{f^n}\ (-v\cdot\nabla_\alpha + \mathcal{A})p\Big|_s\\ \mathcal{B}^2 &= \mathcal{D}_v\ (-v\cdot\nabla_\alpha + \mathcal{A})p|_s\\ \mathcal{C}^1 &= \mathcal{D}_p\ j|_s\\ \mathcal{C}^2 &= \mathcal{D}_p\ f^v|_s\\ \mathcal{D}^1 &= \mathcal{D}_{f^n}\ j\Big|_s\\ \mathcal{D}^2 &= \mathcal{D}_v\ f^v|_s.\end{aligned}$$

We can now unambiguously define reciprocity as:

Definition 4.10. A thermodynamic system linearized about a steady state p^s is *reciprocal* if the system operator

$$\mathcal{H}^s : (\delta f^n, \delta v) \to (\delta j, \delta f^v)$$

is self-adjoint.

Consider the Markov step process. The explicit dependence of the fluxes J_{ij} on the nonequilibrium forces F^n_{ij} is, for $i > j$,

$$J_{ij} = a_{ji}p_i\left(\frac{p_j/p_i}{p^e_j/p^e_i}e^{F^n_{ij}} - 1\right).$$

The matrix B^1 of the linearized system then follows:

$$B^1 = \left[B^1_{21}\cdots B^1_{N(N-1)}\right],$$

where B^1_{ij} is defined for $i > j$ and has elements

$$\begin{aligned}\left(B^1_{ij}\right)_i &= a_{ji}p^s_j\left(\frac{p^e_i}{p^e_j}\right)e^{F^{n,s}_{ij}}\\ \left(B^1_{ij}\right)_j &= -a_{ji}p^s_j\left(\frac{p^e_i}{p^e_j}\right)e^{F^{n,s}_{ij}}\\ \left(B^1_{ij}\right)_k &= 0, \quad k \neq i, j.\end{aligned}$$

Similarly, calculate:

$$B^2 = -[\nabla_\alpha p_1^s \ldots \nabla_\alpha p_N^s]^T$$

$$C^1 = \left[C_{21}^1 \ldots C_{N(N-1)}^1\right]^T,$$

where C_{ij}^1 is defined for $i > j$ and has elements

$$\begin{aligned} \left(C_{ij}^1\right)_i &= -a_{ji} \\ \left(C_{ij}^1\right)_j &= a_{ij} \\ \left(C_{ij}^1\right)_k &= 0, \quad k \neq i, j, \end{aligned}$$

$$C^2 = [\nabla_\alpha \ln p_1^e \ldots \nabla_\alpha \ln p_N^e]$$

$$D^1 = \text{ diag } \left(d_{ij}^1\right),$$

where d_{ij} is defined for $j > i$ and

$$d_{ij}^1 = a_{ji} p_j^s \left(\frac{p_i^e}{p_j^e}\right) e^{F_{ij}^{n,e}},$$

$$D^2 = 0.$$

Let

$$\begin{aligned} B &\triangleq [B^1 \, B^2] \\ C &\triangleq \begin{bmatrix} C^1 \\ C^2 \end{bmatrix}. \end{aligned}$$

For a thermodynamic system linearized about an equilibrium state, a simple calculation shows

$$\begin{aligned} B &= -\text{diag}(p_i^e) C^T \\ C &= B^T \left(-\text{diag}\left(\frac{1}{p_i^e}\right)\right). \end{aligned}$$

In equilibrium the control $v^s = 0$, so $A^s = A$ and by Proposition 4.1

$$A = \text{diag}(p_i^e) A^T \text{diag}\left(\frac{1}{p_i^e}\right).$$

A further calculation then confirms that the system operator is self-adjoint. In fact, given the linearized thermodynamic system is a continuously controllable and observable realization of the system operator (in the sense of Helton [HEL 76]), we shall prove that a thermodynamic system linearized about a steady state is reciprocal iff the steady state is the equilibrium state.

The state space of the linearized thermodynamic system is actually that of $(N-1)$-dimensional vector functions of α, as $\sum_{i=1}^N \delta p_i = 0$. We can consider the state space as a dense subspace of a Hilbert space X [HEL 76]. As in [HEL 76], we can define a controllability map

$$\mathcal{B}([\delta F^n\ \delta v]^T) \triangleq \int_0^\infty e^{\mathcal{A}^s t} B\,[\delta F^n\ \delta v]^T dt$$

and an observability map

$$\mathcal{C}([\delta J\ \delta f^v]^T) \triangleq \int_0^\infty \left(C e^{\mathcal{A}^s t}\right)^* [\delta J\ \delta f^v]^T dt,$$

where $*$ denotes the adjoint. By definition, if the system is continuously controllable and observable, then the controllability map $\mathcal{B}$ and observability map $\mathcal{C}$ map the space of infinitely-differentiable functions of time to a dense subspace of the Hilbert space X and are continuous. The following lemma gives a necessary condition for reciprocity.

Lemma 4.1. If the linearized thermodynamic system is a continuously controllable and observable realization of the system operator $\mathcal{H}^s$, then reciprocity implies the existence of an operator $\mathcal{T}$ such that

$$\mathcal{A}^s \mathcal{T} = \mathcal{T} \mathcal{A}^{s*}$$

$$C\mathcal{T} = B^T.$$

Proof. Let

$$Q = \begin{bmatrix} 1 & \mathbf{1}^T \\ 0 & I_{N-1\times N-1} \end{bmatrix},$$

where $\underline{1}$ is a column vector with all elements equal to 1. Then

$$Q^{-1} = \begin{bmatrix} 1 & -\mathbf{1}^T \\ 0 & I_{N-1\times N-1} \end{bmatrix}.$$

Let

$$\delta\tilde{p} = \begin{bmatrix} \delta p_2 \\ \vdots \\ \delta p_N \end{bmatrix}$$

and

$$z = Q\delta p = \begin{bmatrix} 0 \\ \delta\tilde{p} \end{bmatrix}.$$

Then, as Q is invertible, another realization of $\mathcal{H}^s$ is

$$\begin{aligned} \frac{\partial z}{\partial t} &= Q\mathcal{A}^s Q^{-1} z + QB^1 \delta F^n + QB^2 \delta v \\ \delta J &= C^1 Q^{-1} z + D^1 \delta F^n \\ \delta f^v &= C^2 Q^{-1} z. \end{aligned}$$

Hence, by assumption, a continuously controllable and observable realization of $\mathcal{H}^s$ can be written as

$$\begin{aligned} \frac{\partial \delta\tilde{p}}{\partial t} &= -v^s \cdot \nabla_\alpha \delta\tilde{p} + \tilde{A}\delta\tilde{p} + \tilde{B}^1 \delta F^n + \tilde{B}^2 \delta v \\ \delta J &= \tilde{C}^1 \delta\tilde{p} + D^1 \delta F^n \\ \delta f^v &= \tilde{C}^2 \delta\tilde{p}, \end{aligned}$$

where the matrices $\tilde{A}$, $\tilde{B}^1$ and $\tilde{B}^2$ have the bottom $N-1$ rows of QAQ^{-1}, QB^1, and QB^2, respectively, and the matrices $\tilde{A}$, $\tilde{C}^1$ and $\tilde{C}^2$ have the left $N-1$ columns of QAQ^{-1}, C^1Q^{-1}, and C^2Q^{-1}, respectively.

By definition, reciprocity implies $\mathcal{H}^s = \mathcal{H}^{s*}$. So, given reciprocity, by Lemma 3 of Willems [WIL 72] and Theorem 4.4 of Helton [HEL 76] there exists an operator $\mathcal{R}$ such that

$$\begin{gathered} \left(-v^s \cdot \nabla_\alpha + \tilde{A}\right)\mathcal{R} = \mathcal{R}\left(v^s \cdot \nabla_\alpha + \tilde{A}^T\right) \\ [\tilde{B}^1 \, \tilde{B}^2] = \mathcal{R}\begin{bmatrix} \tilde{C}^1 \\ \tilde{C}^2 \end{bmatrix}^T . \end{gathered}$$

Let

$$\tilde{\mathcal{R}} \triangleq \begin{bmatrix} 1 & \underline{0}^T \\ 0 & \mathcal{R} \end{bmatrix},$$

where $\underline{0}$ is a column vector with all elements equal to 0, and let

$$\mathcal{T} \triangleq \left(Q^{-1}\tilde{\mathcal{R}}\left(Q^T\right)^{-1}\right)^*.$$

Then a calculation reveals

$$\begin{aligned} \mathcal{A}^s\mathcal{T} &= \mathcal{T}\mathcal{A}^{s*} \\ C\mathcal{T} &= B^T \qquad \blacksquare \end{aligned}$$

Theorem 4.5. A thermodynamic system linearized about the equilibrium state is reciprocal. Furthermore, if the linearized system is a continuously controllable and observable realization of the system operator $\mathcal{H}^s$, then the system linearized about a steady state is reciprocal iff the steady state is the equilibrium state.

Proof. We first prove necessity by calculation. Given the system is linearized about an equilibrium state,

$$\begin{aligned} B &= -\text{diag}(p_i^e)C^T \\ C &= B^T\left(-\text{diag}\left(\frac{1}{p_i^e}\right)\right). \end{aligned}$$

As $v^s = 0$, $\mathcal{A}^s = A$ and by Proposition 4.1

$$A = \operatorname{diag}(p_i^e) A^T \operatorname{diag}\left(\frac{1}{p_i^e}\right).$$

Hence, for the system linearized about an equilibrium state

$$\begin{aligned}
\mathcal{H}^e(t) &= Ce^{At}B + \begin{bmatrix} D^1 & 0 \\ 0 & 0 \end{bmatrix}\delta(t) \\
&= B^T\left(-\operatorname{diag}\left(\frac{1}{p_i^e}\right)\right)\operatorname{diag}(p_i^e)e^{A^T t}\operatorname{diag}\left(\frac{1}{p_i^e}\right) \cdot \\
&\qquad \cdot (-\operatorname{diag}(p_i^e))C^T + \begin{bmatrix} D^1 & 0 \\ 0 & 0 \end{bmatrix}\delta(t) \\
&= B^T e^{A^T t} C^T + \begin{bmatrix} D^1 & 0 \\ 0 & 0 \end{bmatrix}\delta(t) \\
&= \mathcal{H}^{e^*}(t),
\end{aligned}$$

where $\mathcal{H}^e(t)$ is defined for $t \in \Re_+$.

We prove sufficiency, given the assumptions, by proving its contrapositive, that is, we prove that if the steady state is not an equilibrium state, then the system linearized about the steady state is not reciprocal. Using Lemma 4.1, we need only show that no $\mathcal{T}$ exists such that

$$\begin{aligned}
\mathcal{A}^s\mathcal{T} &= \mathcal{T}\mathcal{A}^{s*} \\
C\mathcal{T} &= B^T
\end{aligned}$$

for a nonequilibrium steady state.

If such a $\mathcal{T}$ exists, then

$$\mathcal{A}^s(\mathcal{T}\underline{1}) = \mathcal{T}\mathcal{A}^{s*}\underline{1} = 0,$$

where $\underline{1}$ is a column vector with all elements equal to 1. By assumption, the steady state solution p^s is unique. So

$$\mathcal{T}\underline{1} = p^s$$

But then,

$$B^T\underline{1} = 0$$

while

$$\begin{aligned}
C(\mathcal{T}\underline{1}) &= Cp^s \\
&= \begin{bmatrix} J^s \\ f^{v,s} \end{bmatrix} \neq 0
\end{aligned}$$

for all nonequilibrium steady states. So no such $\mathcal{T}$ exists for a nonequilibrium steady state. ■

A similar theorem should follow for the diffusion process. In fact, a formal calculation verifies that the system linearized about an equilibrium state is reciprocal. However, the operators of the linearized thermodynamic system are infinite dimensional and consequently a proof of the same theorem for the diffusion process lies beyond the machinery introduced in this thesis.

4.5. Physical Thermodynamic Systems

In this chapter, we have constructed a Markovian system with thermodynamic properties—an abstract thermodynamic system. As we shall show in this section, to define quantities as physically measured, the chemical potential, rather than the logarithm of the equilibrium state, and the multiplicative factor of kT must be introduced into the definitions. Our previous definitions will then be seen to define thermodynamic quantities but not those normally measured in an experiment.

We shall continue to use the notation introduced in Section 4.3.2 as applicable to both a Markov step process and a Markov diffusion process as the sample-path process. As we have suggested in Section 3.4, the equilibrium state associated with a thermodynamic system can be written as

$$p^e(y;\alpha(t)) = c(\alpha(t))e^{-\frac{1}{kT}\mu^e(y;\alpha(t))},$$

where the normalization constant

$$c(\alpha(t)) = \left(\sum_{i=1}^{N} e^{-\frac{1}{kT}\mu_i^e(\alpha(t))}\right)^{-1}$$

or

$$c(\alpha(t)) = \left(\int_{\Re^n} e^{-\frac{1}{kT}\mu^e(x;\alpha(t))}\,dV_x\right)^{-1}.$$

The equilibrium chemical potential μ^e is associated with a thermodynamic system based on its underlying physical structure. We can relate μ^e to $\ln p^e$ as follows. Clearly

$$\ln p^e(y;\alpha(t)) = \ln c(\alpha(t)) - \tfrac{1}{kT}\mu^e(y;\alpha(t)). \tag{4.4}$$

However, as

$$\ln \frac{p_i^e}{p_j^e} = -\tfrac{1}{kT}\left(\mu_i^e - \mu_j^e\right) \tag{4.5a}$$

and

$$\nabla \ln \rho^e = -\tfrac{1}{kT}\nabla\mu^e, \tag{4.5b}$$

where either of the above expressions involving $\ln p^e$ appear, the first term of (4.4) drops out. Also, taking the gradient with respect to the vector of external parameters α,

$$\nabla_\alpha \ln p^e = \nabla_\alpha \ln c - \tfrac{1}{kT}\nabla_\alpha\,\mu^e \tag{4.6}$$

and a simple calculation reveals

$$\nabla_\alpha \ln c = \tfrac{1}{kT}\langle\nabla_\alpha\mu^e\rangle_e,$$

where, as before, $\langle f\rangle_e$ denotes the equilibrium ensemble average of a sample-path function $f(y)$. Thus (4.6) reduces to

$$\nabla_\alpha \ln p^e = -\tfrac{1}{kT}(\nabla_\alpha\mu^e - \langle\nabla_\alpha\mu^e\rangle_e). \tag{4.7}$$

Using the above calculations, we can define physically-measured thermodynamic quantities in light of our earlier calculations and relate them to the abstract quantities defined earlier. The internal energy is

$$U \triangleq \langle \mu^e \rangle,$$

the heat flow is

$$Q \triangleq -kT\langle j, f \rangle = kT\mathcal{Q},$$

and the work flow is

$$W \triangleq kT\langle j, f^n \rangle + v \cdot \langle \nabla_\alpha \mu^e \rangle.$$

The internal energy satisfies the first law

$$\frac{d}{dt}U = Q + W.$$

Using (4.7), we can calculate the external forces due to the control $v(t)$, of Definition 4.9, as

$$f^v = -\frac{1}{kT}(\langle \nabla_\alpha \mu^e \rangle - \langle \nabla_\alpha \mu^e \rangle_e).$$

Let

$$W^e \triangleq v \cdot \langle \nabla_\alpha \mu^e \rangle_e$$

denote the work flow done in a *quasi-static trajectory*, that is, a path in the statistical state space consisting only of equilibrium states. We then see that defining the ensemble average $\mathcal{U}^e$ as

$$\mathcal{U}^e = -\langle \ln p^e \rangle = \frac{1}{kT}(U - \ln c)$$

gave a work flow

$$\mathcal{W}^e = \frac{1}{kT}(W - W^e).$$

Thus, using $-\ln p^e$ rather than μ^e resulted in a work flow $\mathcal{W}^e$ referenced to the work flow done in a quasi-static trajectory. We have actually derived two dissipation inequalities:

$$\frac{d}{dt}(kT\mathcal{G}^e) \leq W - W^e$$

using $-\ln p^e$ and

$$\frac{d}{dt}G \leq W$$

using μ^e.

The entropy is

$$S = -k\langle \ln p \rangle$$

and the entropy production rate is

$$D = k\langle j, z\rangle = k\mathcal{D}.$$

The entropy satisfies the second law

$$\frac{d}{dt}S = \frac{Q}{T} + D \geq \frac{Q}{T}.$$

The thermodynamic forces defined in Sections 4.2.2 and 4.2.3 are normalized by kT. Define physically-measured thermodynamic forces as

$$\begin{aligned} \mathcal{F} &\triangleq kTf \\ \mathcal{F}^e &\triangleq kTf^e \\ \mathcal{F}^n &\triangleq kTf^n \\ \mathcal{F}^v &\triangleq -\langle \nabla_\alpha \mu^e\rangle = kTf^v - \langle \nabla_\alpha \mu^e\rangle_e. \end{aligned}$$

The heat flow and work flow can then be written as

$$\begin{aligned} Q &= -\langle j, \mathcal{F}\rangle \\ W &= \langle j, \mathcal{F}^n\rangle - v \cdot \mathcal{F}^v. \end{aligned}$$

We have introduced two modifications to our abstract construction of the previous sections. By replacing the equilibrium state with its underlying chemical potential, obtained from physical considerations, we obtain an absolute work flow, rather than a work flow referenced to a quasi-static trajectory. By introducing the multiplicative factor of kT, we obtain forces defined in physically-measured units. We shall now apply our construction to two nontrivial examples—a variable linear capacitor connected to a Nyquist-Johnson resistor, studied by Brockett and Willems [BRO 79] and muscle contraction, studied by Hill [HIL 74, HIL 75, HIL 77] and the author [PRO 81, PRO 85].

We introduced the Nyquist-Johnson resistor in Section 3.2.3. Consider a Nyquist-Johnson resistor connected to a linear capacitor of variable capacitance $\mathcal{C}$. The sample-path process which models such a thermodynamic system is Equation (3.15) with a voltage $\xi = -\frac{q}{\mathcal{C}}$, that is,

$$dq = -\frac{1}{r}\frac{q}{\mathcal{C}}\,dt + \sqrt{\frac{2kT}{r}}\,dw.$$

The equilibrium chemical potential of the system is the energy stored in the capacitor

$$\mu^e(q) = \frac{q^2}{2\mathcal{C}}.$$

A model of a varying capacitance is a capacitance controlled through

$$\frac{d\mathcal{C}}{dt} = v.$$

We have described a model based on physical considerations. We can apply our construction to this model to obtain its thermodynamic properties. Identifying

$$m = -\frac{1}{r}\frac{q}{C}\,dt$$
$$\theta = \frac{2kT}{r},$$

we see the external force is

$$\mathcal{J} = kTf = kT(2\theta^{-1}m) = -\frac{q}{C}.$$

The equilibrium component of the external force is

$$\mathcal{J}^e = kTf^e = -\frac{\partial}{\partial q}\mu^e = -\frac{q}{C} = \mathcal{J},$$

giving a zero nonequilibrium component. The external force due to the control v

$$\mathcal{J}^v = -\langle\frac{\partial}{\partial C}\mu^e\rangle = \frac{1}{2C^2}\langle q^2\rangle.$$

Thus the heat flow is

$$\begin{aligned} Q &= -\int_{-\infty}^{\infty} j(q)\mathcal{J}(q)\,dq \\ &= \int_{-\infty}^{\infty}\left(\frac{1}{r}\frac{q}{C}\rho + \frac{kT}{r}\frac{\partial\rho}{\partial q}\right)\left(-\frac{q}{C}\right)dq, \end{aligned}$$

which reduces to

$$Q = \frac{kT}{rC} - \frac{1}{rC^2}\langle q^2\rangle,$$

and the work flow is

$$W = -v\frac{1}{2C^2}\langle q^2\rangle.$$

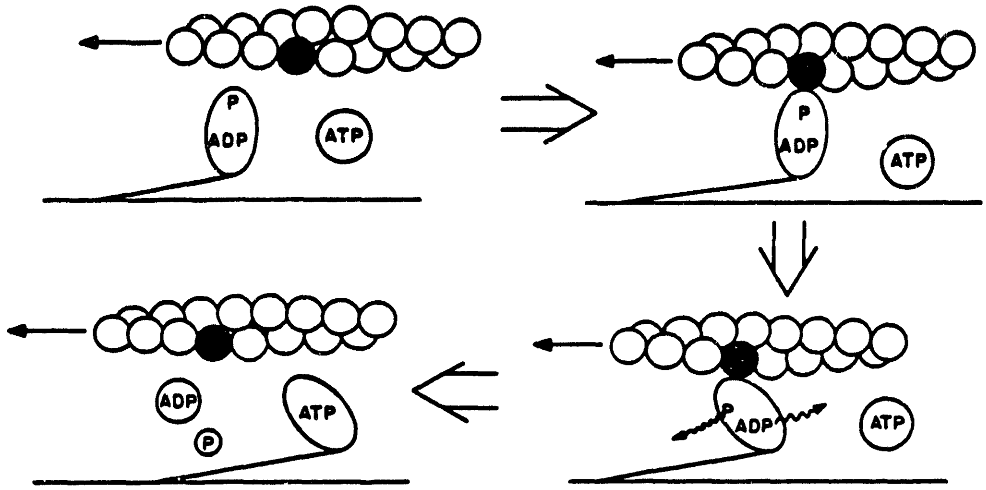
Substituting the voltage ξ for $-\frac{q}{C}$, we can rewrite the heat flow and work flow in the physically intuitive forms

$$Q = \frac{1}{rC}\left(kT - C\langle\xi^2\rangle\right)$$
$$W = -\frac{1}{2}\frac{dC}{dt}\langle\xi^2\rangle.$$

When the capacitance increases, the work flow is negative, that is, work is extracted from the system.

We shall introduce a model of muscle contraction based on its molecular biochemistry and structure, described in much more detail in [HIL 74, HIL 75, HIL 77, PRO 81, PRO 83]. A muscle fibre is composed of myosin cross-bridges and associated binding sites on actin. Muscle can be modelled as an ensemble of a simple structure—a myosin cross-bridge and an associated one-dimensional array of actin binding sites. A cross-bridge cycles through a set of biochemical states, both attached and unattached to actin, as depicted in Figure 4.1. The biochemical states are distinguished by the structural conformation of the cross-bridge and whether the molecules ATP, ADP, and/or P (inorganic phosphate) are bound to the cross-bridge.

Figure 1.1 A Cross-bridge Cycling through Attached and Unattached States



Transitions among the set of biochemical states can be modelled by a Markov step process with transition rates a_{ij}. The transition rates in a set which we shall denote as $(I \times I)^{ATP}$ are dependent on an ATP concentration c. The remaining transition rates are independent of the ATP concentration.

Denote the ***shortening velocity*** of a muscle fibre by $v(t)$. The nearest actin site to a cross-bridge can be referenced by a position $x(t)$. The position $x(t)$ is related to the shortening velocity by

$$\frac{dx}{dt} = -v.$$

The rates for transitions to or from states attached to actin are functions of the position x. As the binding sites on actin are periodic with period λ, we can consider the postion x as only taking values in $[-\lambda/2, \lambda/2]$. A muscle fibre is an ensemble of cross-bridges uniformly distributed among all positions. Any measured quantity is therefore an average over all positions $x \in [-\lambda/2, \lambda/2]$.

At any time t, the statistical state can be represented by the vector function of the position x

$$p = (p_i(t, x)).$$

As

$$\begin{aligned} \frac{dp(t,x)}{dt} &= \frac{\partial p(t,x)}{\partial t} + \frac{dx}{dt}\ \frac{\partial p(t,x)}{\partial x} \\ &= \frac{\partial p(t,x)}{\partial t} - v\frac{\partial p(t,x)}{\partial x}, \end{aligned}$$

the statistical state satisfies the partial differential equation

$$\frac{\partial p(t,x)}{\partial t} = v\frac{\partial p(t,x)}{\partial x} + A(c,x)\,p(t,x).$$

The only parameter which determines whether a steady state is an equilibrium state is the ATP concentration. Denote the equilibrium ATP concentration by c^e. For attached states, the equilibrium chemical potential μ_i^e is a function of the position x. Denote the set of states attached to actin by I^{ACTIN}. Then $\mu_i^e(x)$ is x-dependent only for $i \in I^{ACTIN}$. The external forces are

$$\mathcal{F}_{ij} = kT \ln \frac{a_{ij}(c,x)}{a_{ji}(c,x)}$$

and the equilibrium components are

$$\mathcal{F}_{ij}^e = \mu_j^e(x) - \mu_i^e(x) = kT \ln \frac{a_{ij}(c^e,x)}{a_{ji}(c^e,x)}.$$

The ATP-dependent transition rates are linearly-dependent on the ATP concentration c. For transitions between any two states, the ATP-dependence is only in one direction. Thus the nonequilibrium components are (assuming a direction $j \rightarrow i$ for the ATP-dependence)

$$\begin{aligned} \mathcal{F}_{ij}^n &= kT \ln \frac{a_{ij}(c,x)/a_{ji}(c,x)}{a_{ij}(c^e,x)/a_{ji}(c^e,x)} \\ &= kT \ln \frac{c}{c^e}\ ,\ i,j \in (I \times I)^{ATP}. \end{aligned}$$

and are zero for all other transitions. We can calculate the mechanical force exerted by a muscle fibre as

$$\mathcal{F}^v = -\sum_{i \in I^{ACTIN}} \int_{-\lambda/2}^{\lambda/2} \frac{d\mu_i^e(x)}{dx} p_i(t,x)\, dx,$$

which is an average of the force exerted by a cross-bridge in each attached state. A quadratic potential $\mu_i^e(x)$ models a cross-bridge in each attached state as a linear elastic element.

Combining expressions, the heat flow is

$$Q = -\sum_i \sum_{i<j} \int_{-\lambda/2}^{\lambda/2} J_{ij}(t,x) \ln \frac{a_{ij}(c,x)}{a_{ji}(c,x)}\, dx$$

and the work flow is

$$\begin{aligned} W = &\left(\sum_{i,j \in I^{ATP}} \int_{-\lambda/2}^{\lambda/2} J_{ij}(t,x)\, dx \right) \left(kT \ln \frac{c}{c^e} \right) \\ &- v \left(\sum_{i \in I^{ACTIN}} \int_{-\lambda/2}^{\lambda/2} \frac{d\mu_i^e(x)}{dx} p_i(t,x)\, dx \right). \end{aligned}$$

The heat flow and work flow are the expressions one obtains from a thermodynamic approach [HIL 74, HIL 75, HIL 77]. As the equilibrium constant of a chemical reaction $K_{ij} = \frac{a_{ij}}{a_{ji}}$, the expression for the heat flow is simply an inner product of the net flow in each reaction of a cross-bridge cycle and the logarithm of the reaction's equilibrium constant. The first term of the work flow is the net flow of ATP multiplied by the chemical potential of ATP. The second term is the shortening velocity multiplied by the force exerted by a muscle fibre.

5. Conclusions

We have shown that a thermodynamic system can be modelled as a Markov process. In Chapters 2 and 3, a macroscopic view of a classical physical system led to a Markov process. One must first understand the underlying physics of any thermodynamic system to model it as a Markov process with an associated equilibrium state. However, once a system is so modelled, its thermodynamic properties follow from our formulation. We have not eliminated the need to understand a system before constructing a model. What we have shown is that for the class of models we have constructed, once those parameters due to the underlying physics are identified, thermodynamic behaviour follows as an essential property of the model.

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