The Pervasive Maxwell Demon

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Abstract

Today, we find an increasing interest in Brownian motors – theoretical “thermal ratchets” that rectify random motion to do work. This interest stems not only from possible applications to cellular transport mechanisms and nanoscale mechanics but from the more intricate understanding of entropy and non-equilibrium dynamics they offer. In an attempt to bring Brownian motors one step closer to reality, the primary goal of this paper is to propose an experimental realization of an (electronic) thermal ratchet and predict its behavior numerically; with a secondary goal of exploring the practicality and properties of this ratchet and putting this research in the context of existing thermal ratchet work. To these ends, we present a general discussion of non-equilibrium dynamics and the state-of-the-art in thermal ratchet research. Following this, we explain the electronic ratchet, a diode and resistor in parallel where the diode rectifies the Nyquist noise across the resistor, in detail. Finally, we determine that an experimental electronic ratchet using off-the-shelf components can exhibit a measurable voltage difference $14.5pV/K$, which could confirm this effect experimentally. We also show that this effect is independent of the Seebeck effect, meaning that there are unlikely to be any other “antagonistic” thermoelectric effects to muddle any experimental results.
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Chapter 1

Introduction

Feynman’s ratchet and pawl system is the most well-known example of a mechanical Maxwell demon, a device whose purpose is to convert random thermal motion into some sort of useful work. The idea is simple: set up a ratchet and pawl such that a wheel or axle is allowed to turn in only one direction. Now attach a windmill to this axle. If the windmill is immersed in a gas at a finite temperature, every so often an accumulation of collisions of the gas molecules against the vanes of the windmill will cause one notch of motion in the preferred motion of the ratchet, but presumably never in the opposite direction. Harnessing this work, we would be rectifying thermal noise into useful energy — in clear violation of the Second Law. Feynman resolves this paradox by showing that the probability of thermal fluctuations driving our microscopic windmill forward is the same as the probability of it driving our microscopic ratchet backward (this mechanism is discussed in detail in Chapter 3). Thus, there is no mean movement in equilibrium and the Second Law is saved [Feynman 1964].

Feynman eventually goes on to show that, should the ratchet and pawl be at a different temperature than the windmill, the probabilities are no longer the same and the system can create directed work as a ΔT engine. Although Feynman shows that this engine could be run in such a way that it would consist of reversible processes, he does not investigate the properties of such a system running in reverse – as a heat pump – nor does he investigate the practicality or power output.
If both reservoirs are held at the same temperature $T_1 = T_2 = T$, no net work is done and the load (in this case, a somewhat confused flea) does not move. If $T_1 > T_2$ the flea will be raised and if $T_1 < T_2$, the flea will be lowered [Feynman 1964].

In fact, Maxwell demons in general have historically been investigated out of peculiarity, not practicality. Maxwell demons are usually considered a nuisance, to be sought out and debunked. However, recent interest in the mechanics of cellular transport and other nanoscale locomotion has created a serious experimental interest in these demons. This interest has not only spurred experimental exploration into the properties of some Brownian motors (Maxwell demons that do work) and their associated biological systems, but has engendered theoretical work detailing a series of reversible Brownian motors. Nevertheless, there has been a dearth of experimental results in this field, and for good reason – thermal fluctuations are traditionally tiny, hard to measure, and systems at fluctuation scales are exceedingly difficult to build.

Our investigation is concerned primarily with taking the intermediary step between theory and experiment. We conduct a numerical simulation which, modeling an electronic ratchet (a ratchet that works by using a diode to rectify the Nyquist noise across a resistor), shows us that an experiment using common components could confirm this ratcheting effect in the lab.

Furthermore, with practicality in mind, we explore the possibility of running our Brownian motors in reverse (using them as refrigerators) as well as comparing them to the more common thermoelectric effect – the Seebeck effect. Finally, we end with some general insight into the vagaries of these systems and some short proposals for future work.

The theory behind these results is divided into general Brownian motion and Brownian motor specifics. A reader versed in statistical mechanics may elect to skip to chapter 3, *Thermal Ratchet Systems*
Chapter 2

General Theory:
Non-Equilibrium Dynamics

Thermodynamic quantities (temperature, pressure, etc) should be constant for a system in thermal equilibrium. However, if we manage to measure these values with higher and higher precision, eventually we find that they undergo small fluctuations. Pressure is due to atomic collisions along a surface – this value fluctuates due to the randomness of the collisions. Similarly, the internal energy of the system might fluctuate due to the randomness of the heat exchange between a system and the heat bath enclosing it.

These fluctuations are classified generally as thermal noise – two well known examples of which are Brownian motion (random particle motion due to thermal fluctuations) and Nyquist noise (random electrical noise due to thermal fluctuations). This effect is generally small, but can become important as the shrinking size of system increasingly reflects the granular nature of matter.

An excellent illustration of the effects of noise is provided by Huang’s Introduction to Statistical Physics [Huang 2001]. Using results from the grand canonical ensemble, we find the mean-square fluctuation in the number of particles in a volume $V$ is

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{NkT}{V^2} \kappa_T,$$  \hspace{1cm} (2.1)
where $\kappa_T$ is the isothermal compressibility. For an ideal gas, we get:

$$\sqrt{\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2}} = \frac{1}{\sqrt{N}}.$$  \hfill (2.2)

For a standard mole of gas, this is utterly insignificant. However, if we consider a volume dimension of 400 nm, the order of the wavelength of visible light, the number of atoms is about $10^6$ and the fractional rms fluctuation is almost 0.1%. This fluctuation is observed in the scattering effects of sunlight in the atmosphere – it’s why the sky is blue! Thus, whether thermal noise is of importance depends on the scale at which we choose to study the system. In fact, in the thermal ratchets we will soon describe, fluctuations are the dominant effect.

To analyze the complex noise effects at work in these thermal ratchets, we will be modeling an electronic ratchet using the master equation describing state transition probability and approximating it with an effective Fokker-Planck equation. In this section, General Theory, we will introduce the Langevin equation (as a prerequisite to using the Fokker-Planck equation), then the Fokker-Planck equation itself. The Langevin equation, which describes the mean evolution of a thermal system over time, will help build our basic understanding of thermal fluctuations in equilibrium. The Fokker-Planck equation will then allow us to model closely the evolution of our system in a non-equilibrium state – this will be crucial when we (eventually) calculate the power output and efficiency of our ratchet system.

Note that two derivations which may seem conspicuously missing are those of Nyquist noise (across a linear resistor) [Huang 2001], and a more general solution of the Fokker-Planck equation (which we will eventually use) [van Kampen 1961]. The first is not included because of its very limited use in analyzing our system’s non-equilibrium dynamics. The second is not included because of its lengthy, awkward, (and physically uninteresting) mathematics – if we believe that the Fokker-Planck equation we set up is a good model of what’s going on, it seems beyond the scope of this paper to go into unending detail of how to solve this differential equation analytically.
2.1 The Langevin Equation

Before we can ask questions about the probability of a system evolving to a particular state after some time $t$ it is helpful to consider a slightly simpler question: what is the state (on average) we will find our system in after some time $t$? We approach this problem with the goals of (i) some basic understanding of Brownian (noise based) movement, and (ii) finding the mean-squared displacement $\langle x^2 \rangle$ of a particle after a time $t$ (noting that the average displacement $\langle x \rangle$ is zero).

To do this, we will consider the case of a “free” Brownian particle, surrounded by some liquid (of non-zero viscosity); the particle is free in that sense that it is not restricted by any external force (only the frictional forces arising from its diffuse movement). The equation of motion we will begin with is in terms of velocity $v = \frac{dv}{dt}$, but could just as easily be another change in state, like electrical current $i = \frac{di}{dt}$.

$$M \frac{dv}{dt} = F(t), \quad (2.3)$$

with $M$ the particle’s mass, $v(t)$ the particle velocity and $F(t)$ the force acting on the particle from collision-based forces.

The equation of motion should include the driving term from the random collisions with the fluid molecules as well as a damping term due to the viscosity, so let us decompose our above equation into:

$$M \frac{dv}{dt} = -\frac{v}{B} + F_{\text{noise}}(t), \quad (2.4)$$

where $F_{\text{noise}}(t)$ is the rapidly fluctuating “random collisions” term (which will average to zero over long periods of time, $\langle F_{\text{noise}}(t) \rangle = 0$) and $-v/B$ is the viscous drag (where $B$ is the mobility of system).  

Before we solve for displacement or mean-squared values, let’s examine the

\[1\]Note that most texts will immediately point out that for a spherical particle in a viscous liquid we can use Stoke’s law to define $B = 1/(6\pi \eta a)$, where $\eta$ is the coefficient of viscosity of the fluid and $a$ is radius of this spherical particle – we are somewhat less interested in this relation, as our eventual system of interest is electrical (where the mobility of the system is just the electrical conductance).
basic behavior of the system by just taking the ensemble average of both sides of Eq. 2.4, eliminating our $F_{\text{noise}}$ term and giving us a nice, clean differential equation:

$$M \frac{d\langle v \rangle}{dt} = -\frac{\langle v \rangle}{B} \quad (2.5)$$

which we can easily solve for

$$\langle v(t) \rangle = v(0) \exp(-t/\tau); \tau = MB. \quad (2.6)$$

In other words, if we give our particle some initial velocity $v(0)$ through some external force, it will lose this velocity at characteristic rate $\tau$ that is determined by both the mass of the particle as well as the mobility of the system. So, the diffusive nature of the system will dissipate any motion we throw into it as waste heat after some characteristic time.

To solve for the displacement of the particle, we begin by dividing Eq. 2.4 by $M$:

$$\frac{dv}{dt} = -\frac{v}{\tau} + A(t), \quad (2.7)$$

where $\langle A(t) \rangle = 0$ just like $\langle F(t) \rangle = 0$. From Pathria [Pathria 1980] we will now multiply Eq. 2.7 by the instantaneous position $x$ of the particle and then take the ensemble average. In order to do this effectively we use three relations: (i) $x \cdot v = \frac{1}{2}(dx^2/dt)$, (ii) $x \cdot (dv/dt) = \frac{1}{2}(d^2x^2/dt^2) - v^2$, and (iii) $\langle x \cdot A \rangle = 0$. We now have

$$\frac{d^2}{dt^2} \langle x^2 \rangle + \frac{1}{\tau} \frac{d}{dt} \langle x^2 \rangle = 2\langle v^2 \rangle. \quad (2.8)$$

But, if this system is already in thermal equilibrium (and we assume a one dimensional system for simplicity), we can use $\frac{1}{2}kT = \frac{1}{2}M\langle v^2 \rangle$ to solve for $\langle v^2 \rangle$. The resulting expression is easily integrated to solve for $\langle x^2 \rangle$,

$$\langle x^2 \rangle = \frac{2kT \tau^2}{M} \left[ \frac{t}{\tau} - (1 - \exp^{-t/\tau}) \right]. \quad (2.9)$$
where we have chosen constants such that at \( t = 0 \) both \( \langle x^2 \rangle = 0 \) and \( \frac{d\langle x^2 \rangle}{dt} = 0 \). Now, we explore this solution for two cases of particular interest to our basic understanding of fluctuation dynamics. For \( t \ll \tau \),

\[
\langle x^2 \rangle \approx \frac{kT}{M} t^2 = \langle v^2 \rangle t^2.
\]  
(2.10)

which means that in a very short period of time, the particle behaves essentially as an ordinary, free Newtonian particle which is governed by \( x = vt \). This is, of course, before it gets knocked around by any of the particles colliding with it. What happens after a long time? If we set \( t \gg \tau \),

\[
\langle x^2 \rangle \approx \frac{2kT \tau}{M} t = (2BkT) t.
\]  
(2.11)

which gives us a nice solution for our mean-square displacement over a “long” period of time.\(^2\)

Now, because we have only been putting this Langevin theory of Brownian motion to work by clever use of ensemble averages, we still have no ability to analyze particular states and their probabilities. Also, since we have made assumptions of this system being in equilibrium, we cannot explore a system approaching equilibrium (step by step) with this theory. To do that, we will derive an equation detailing every little step from state to state. That is – up until now, we’ve been working with equilibrium results – now we will explore non-equilibrium results.

### 2.2 The Fokker-Planck Equation

To explore these Brownian motors, we need to ask questions not only about what the system is doing at equilibrium, but: how does it get there, and how long does it take? It is interesting that of all the heat engines we traditionally learn of (Stirling, Carnot, etc) we don’t require this non-equilibrium analysis for

\(^2\)Note that solving for \( \langle x^2 \rangle \) using the Smoluchowski equation we get that \( \langle x^2 \rangle = 2D t \) [Pathria 1980]. This gives us a simple correlation between two important values, \( D \) the diffusion constant and \( B \) the mobility of the system, \( D = BkT \) called the Einstein relation. The details of this derivation is of little importance in our ratchet analysis, though the Einstein relation will be used several times.
us to determine their steady state efficiency (or work per cycle, etc) – we can do it with PV and ST graphs, or a variety of much simpler methods. This is because these macroscopic heat engines are discrete cycles. Move the ideal gas to the heat source $T_H$, let it expand to equilibrium, move the ideal gas to the heat drain $T_C$, let it contract to equilibrium, rinse and repeat; not much need of non-equilibrium dynamics.

Here, we don’t get off that easy. Thermal ratchets are held in contact with both their heat source and heat drain at the same time so the system we consider contains both $T_H$ and $T_C$! If we were to analyze its equilibrium behavior it would be doing exactly nothing (on average, anyway). So here, we will discuss what will end up being the only simple way we can model the ratchets that we study: the master equation and its approximation.

### 2.2.1 The Master Equation

Let us consider a system with various states and whose evolution can be described by the transitions between these states. This could be one of many different types of systems: an electron excited to different energy levels, an atom that moves from one position to the next along a random walk, etc. Now we say that for each of these very small transitions, there is a well-defined transition probability $W_{rs}$ per unit time for a particle in a state of $r$ to to move to the state $s$.

Furthermore, we would expect any particle that has a transition probability $W_{rs}$ of going from $r$ to $s$ to have an symmetric probability $W_{sr} = W_{rs}$.

And, though we will not perform the derivation presently, one can find in Reif [Reif 1965] that, considering the canonical ensemble, we get the relation:

$$\exp^{-\beta E_r} W_{sr} = \exp^{-\beta E_r} W_{rs}. \tag{2.12}$$

Ah, now things get interesting. Under the authority of a thermal bath, our particles stop being so lazy – they bounce around from state to state with reckless abandon (or, at least until the lower energy levels are filled and we eventually come to thermal equilibrium.)

Now that we have established some form for the probability of movement
from state to state, we can write a very intuitive equation describing the probability of being in a certain state (in this case, just $r$ or $s$) at a certain time $t$:

$$\frac{dP_r}{dt} = P_s W_{sr} - P_r W_{rs}. \quad (2.13)$$

This equation, known as the master equation, simply says that over any unit time $t$ the $r$ state has a [probability] rate of gaining a particle $P_s W_{sr}$ and a [probability] rate of losing a particle $P_r W_{rs}$. Integrate this master equation, solve for $P_r(t)$ and we should see this two-state system evolve to thermal equilibrium. In a system with more than just two states, however, we sum over all $N$ states and get a master equation that looks like:

$$\frac{dP_r}{dt} = \sum_N (P_r W_{sr} - P_r W_{rs}). \quad (2.14)$$

We have increased the power of what our equation can describe but unfortunately have also made solving our equation much more difficult. So difficult, in fact, that for most systems we could not possibly solve the master equation exactly. Enter the Fokker-Planck approximation.

### 2.2.2 The Fokker-Planck Approximation

To perform this brilliant approximation of the master equation, let’s first recast Eq. 2.14 into a continuous spectrum of states – let’s use displacement, $x$, for this example.

$$\frac{\partial P(x,t)}{\partial t} = \int_{-\infty}^{\infty} [-p(x,t)W(x,x') + p(x',t)W(x',x)] \, dx' \quad (2.15)$$

Now, the transition probabilities $W(x,x')$ and $W(x',x)$ are actually just incarnations of the probability function $P$! After all, the probability function tells you, given an initial condition, how any state will evolve (including how it will evolve into other states). Actually putting this inspiration into equation form is tough, though – what follows quotes Reif [Reif 1965], since I feel completely incapable of making this as accessible he does.
We first create a form for the probability equation that conveys a little more information than our $P(x,t)$. We say that a probability function given by

$$P(x,t|x_0)dx,$$

indicates the probability of finding a particle that was once at $x_0$ in between $x$ and $x + dx$ after some time $t$.

Now, we write down a general condition that must be satisfied by the probability $P(x,t|x_0)$. In a small time interval $\delta t$, the [increase in the probability that the particle has a displacement between $x$ and $x + dx$] must be equal to the [decrease in this probability because of particles who originally had a displacement between $x$ and $x + dx$ have a probability $P(x_1, \delta t|x)dx_1$ of changing its displacement to some other value between $x_1$ and $x_1 + dx_1$ plus the [increase in this probability because of particles who were originally between $x_1$ and $x_1 + dx_1$ have a probability of $P(x, \delta t|x_1)dx$ of changing its displacement to some value between $x$ and $x + dx]$. This complex description is just a statement of conservation. Symbolically, this becomes

$$\frac{\partial P}{\partial t} dx\delta t = -\int_{x_1} P(x,t|x_0)dx\cdot P(x_1, \delta t|x)dx_1 + \int_{x_1} P(x_1, t|x_1)dx_1 \cdot P(x, \delta t|x_1)dx_1$$

(2.17)

where the integrals extend for all values of $x_1$.

This is still a daunting equation, though definitely solvable. To simplify it, we first note that

$$\int_{x_1} P(x_1, \delta t|x_1)dx_1 = 1$$

(2.18)

from the normalization condition. Also, in the first integral, the $P(x,t|x_0)$ function has no dependence on $x_1$. Noting that we are only considering slow movement from state to state, we can set $x_1 = x - \xi$ (with $\xi \to 0$), and we make our first set of simplifications to Eq. 2.17
\[
\frac{\partial P}{\partial t} \delta t = -P(x, t|x_0) + \int_{-\infty}^{\infty} P(x - \xi, t|x_0)P(x, \delta t|x - \xi) d\xi
\]  
(2.19)

We now Taylor expand the remaining integral about \(\xi\), as an expression of the integrand for only small values of \(\xi\) seems sufficient. This expansion gives:

\[
P(x - \xi, t|x_0)P(x, \delta t|x - \xi) = \sum_{n=0}^{\infty} \frac{(-\xi)^n}{n!} \frac{\partial^n}{\partial x^n} [P(x, t|x_0)P(x + \xi, \delta t|x)]
\]  
(2.20)

Now, Eq. 2.19 becomes

\[
\frac{\partial P}{\partial t} \delta t = -P(x, t|x_0) + \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} \left[ P(x, t|x_0) \int_{-\infty}^{\infty} d\xi \xi^n P(x + \xi, \delta t|x) \right]
\]  
(2.21)

Here we note that the term \(n = 0\) in the sum is just \(P(x, t|x_0)\) from the normalization condition, thus canceling with the negative term out front.

For the rest of the terms, we introduce an abbreviation

\[
\mu_n = \frac{1}{\delta t} \int_{-\infty}^{\infty} d\xi \xi^n P(x + \xi, \delta t|x) = \frac{\langle \delta x^n \rangle}{\delta t}
\]  
(2.22)

Now, Eq. 2.21 becomes

\[
\frac{\partial P(x, t|x_0)}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} [\mu_n P(x, t|x_0)]
\]  
(2.23)

When \(\delta t\) is macroscopically infinitesimal the terms involving \(\mu_n\) with \(n > 2\) can be neglected. Thus, we obtain the FP approximation to the master equation:

\[
\frac{\partial p(x, t)}{\partial t} = -\frac{\partial}{\partial x} [\mu_1(x)p(x, t)] + \frac{1}{2} \frac{\partial^2}{\partial x^2} [\mu_2(x)p(x, t)]
\]  
(2.24)

where
\[ \mu_1(x) = \frac{\langle \delta x \rangle}{\delta t} = \langle v \rangle \]  \hfill (2.25)

and

\[ \mu_2(x) = \frac{\langle (\delta x)^2 \rangle}{\delta t} \]  \hfill (2.26)

Eq. 2.24 is known as the Fokker-Planck equation and occupies a classic place in the field of Brownian motion.

Let us now consider a system of Brownian particles, each particle being acted upon by a linear restoring force, \( F_x = -\lambda x \), and immersed in a medium with a mobility \( B \). The mean viscous force, \( -(\langle v \rangle) / B \) must be balanced by the restoring force; thus,

\[ \frac{\langle v \rangle}{B} + F_x = 0 \]  \hfill (2.27)

such that

\[ \mu_1 = \langle v \rangle = -\lambda Bx. \]  \hfill (2.28)

To solve for \( \mu_2 \) we need only refer back to our discussion of the Langevin equation; Eq. 2.11 tells us that

\[ \mu_2 = \frac{\langle (\delta x)^2 \rangle}{t} = 2BkT. \]  \hfill (2.29)

Substituting everything back in the Fokker-Planck equation we are left with

\[ \frac{\partial P}{\partial t} = \lambda B \frac{\partial}{\partial x} (xP) + BkT \frac{\partial^2 P}{\partial x^2}. \]  \hfill (2.30)

### 2.2.3 Solving for Diffusive Brownian Motion

As an example, let us apply this to an ensemble of Brownian particles, initially concentrated at \( x = x_0 \), and allowed to diffuse. Here, in the absence of a
restoring force, $F_x = \lambda x = 0$, our equation reduces to

$$\frac{\partial P}{\partial t} = BkT \frac{\partial^2 P}{\partial x^2}, \quad (2.31)$$

known as the diffusion equation.

This expression will end up giving us back a “random walk” probability distribution function when integrated:

$$P(x, t) = \frac{1}{(4\pi Dt)^{1/2}} \exp \left[ -\frac{(x - x_0)^2}{4Dt} \right], \quad (2.32)$$

with

$$\langle x \rangle = x_0; \langle x^2 \rangle = x_0^2 + 2Dt. \quad (2.33)$$

This result implies that without a restoring force, the mean square distance traveled by a particle in this system will increase without limit. A restoring force, on the other hand, can put an upper limit on this diffusion.

In a system with a restoring force $\lambda$, we show that in the limiting distribution (where $t = \infty$, and thus $\frac{\partial P}{\partial t} = 0$),

$$\frac{\partial}{\partial x} \langle xP_\infty \rangle + \frac{kT}{\lambda} \frac{\partial^2 P_\infty}{\partial x^2} = 0. \quad (2.34)$$

Integrating this, we find

$$P_\infty(x) = \left( \frac{\lambda}{2\pi kT} \right)^{1/2} \exp \left( -\frac{\lambda x^2}{2kT} \right), \quad (2.35)$$

with

$$\langle x \rangle = 0; \langle x^2 \rangle = kT/\lambda. \quad (2.36)$$

Where the last result agrees with the equipartition theorem:
\[ \langle \frac{1}{2} \lambda x^2 \rangle = \frac{1}{2} kT. \] (2.37)

Now that we’ve laid out the tools that we need to tackle the problem of analyzing our ratchet, let’s move on to a discussion and history of thermal ratchets.
Chapter 3

Thermal Ratchet Systems

We should try and put our work into context before we jump into analysis of the thermal ratchet of interest. I know that, when I first began researching this subject I found one of my biggest problems was just figuring out what was out there. What systems have been studied and to what extent? Why do people care?

To answer those questions, let’s start at the very beginning (it’s a very good place to start): Feynman’s ratchet.

3.1 Maxwell’s Paradox and Feynman’s Solution

While not actually the first person to study or discuss a ratchet, Feynman did develop a physical system (as opposed to a fanciful gedanken experiment) and mathematical model. His system and his analysis were actually a response to a paradox proposed by James Clerk Maxwell whereby a “Maxwell Demon”, an imaginary creature that can reduce entropy, violates the Second Law.

To see why this demon poses a problem, imagine a box with filled with gas held at some temperature. The average speed of the gas molecules depends on this temperature, with some variance from this average (some particles slightly faster, some slightly slower) at a given moment in time. Suppose we now place a partition in the middle of the box, separating the box into two chambers,
Figure 3.1: There's the evil demon (the stick figure) slowly separating the once in-equilibrium box into two chambers of differing temperatures while requiring no external work! What a dastardly villain. It’s ok though, because Feynman eventually kills him. Also note the heat engine pictured, which can generate free energy if the demon can actually do what he’s supposed to.

left and right. Maxwell proposes a molecule-sized trapdoor somewhere on the partition wall, where a mischievous demon waits for molecules coming from the left chamber to the right – all the molecules moving at a speed greater than some threshold speed \( v_0 \) he allows through; for all those lower than \( v_0 \) he closes the trapdoor, rejecting them. Likewise, he watches for molecules moving from the right chamber to the left – all the molecules moving at a speed lower than \( v_0 \) he allows through, all those higher he rejects. [von Baeyer 1999]

Eventually the right chamber becomes full of fast moving molecules (making it hot) and the left chambers fills with slow moving molecules (cold). The trick is that the demon doesn’t appear to require any external source of work to operate: he’s reducing the total entropy of the universe! That’s bad, of course, for the second law. What are we to do? Here’s where Feynman’s recasting of this famous second-law paradox into a physically realizable system comes in.

3.1.1 The (Physical) Problem

Feynman proposes a device to that emulates the effects of the imaginary demon: a machine that can generate work from a single heat reservoir at a single tem-
If the two components of our system (windmill and ratchet) are at a single temperature such that $T_1 = T_2 = T$ our load (the flea) may get jostled about, but will be essentially forever doomed to hang at the same spot. [Feynman 1964]

temperature (note that this device was actually based on an idea originally proposed by Smoluchowski [Smoluchowski 1912]). We first imagine a box which contains gas at a certain temperature. The gas molecules, moving with Brownian motion, oscillate and otherwise move about, colliding at random with a windmill which is attached to an axle running outside of the box. Now, we simply hook this axle to a ratchet and pawl mechanism in another box, allowing the axle to turn only one way. Now, when the windmill jiggles one way, it will not turn, but when it jiggles the other way, it will. With our slowly moving axle, we can attach a belt and use it to power a toy car. We now have a device to amuse children for hours on end – the amazing entropy reducing toy car.

How is this possible? According to the laws of thermodynamics, it is clearly impossible. Yet it seems, here, quite plausible. In order to disprove this clever construction (and with it the original Maxwell demon paradox) we must look closer, at the small elements composing the system.

### 3.1.2 The Solution

In order to analyze the ratcheting mechanism, we need to make a set of assumptions. The first is that all parts in the device are made of perfectly elastic parts (lest we get caught up with issues of friction). The second is that the temperature is at a perfectly equal distribution about all components of the system: the ratcheting mechanism, axle, and windmill.

Each time the windmill turns a gear tooth, it will drive the pawl up. In turn, a spring will push the pawl back down, and the pawl will bounce against the gear.
If the motion is not damped then, come a random turn in the opposite direction, the pawl will still be up, and the gear will be allowed to move in reverse. Thus, without a dampening mechanism, our system fails. The dampening effect on the pawl is energy lost in the system, and shows up as heat. Thus, which each turn of the axle, the ratchet and pawl becomes hotter and hotter.

The motion can not continue forever – the ratchet and pawl mechanism is affected by Brownian motion as well (of the same magnitude as the windmill). Every once in a while this Brownian motion lifts the pawl and allows our system to slip “backwards” against the ratcheting action. As things get hotter, this will become more and more likely.

So, every time the windmill turns with the ratcheting action, it is also quite likely that when it turns against the ratcheting action, the pawl will be lifted by its own Brownian motion. The net result is no motion on average, just as we would expect. Following that explanation in words is tricky, but it becomes clearer when told in a slightly more quantitative manner.

In order for the gear tooth to do work on the spring holding the pawl down, the gear must expend energy. Let us label the energy needed to move the pawl over the gear tooth energy, $\varepsilon$. The chance that the system will accumulate enough energy, (from the windmill) to move the spring, $\varepsilon$ is proportional to $e^{-\varepsilon/kT}$. But the probability that the spring will be lifted by random Brownian motion in its own environment is also $e^{-\varepsilon/kT}$ (since the temperature in either system is equal). Thus, the number of times the pawl is up and the wheel can turn backwards is equal to the number of times the pawl will have enough energy to push itself up when it is down, on average. Thus, balance is struck, and the gear will average zero motion.\(^1\)

### 3.1.3 Consequences of Feynman’s Solution

The first consequence of this explanation is just what is sets out to do: elimination of the law-breaking demon. The second consequence is that this model brings to our attention the possibility of this system as a heat engine. Remember: the failure of the ratchet to rectify thermal fluctuation was due to

\(^1\)This, admittedly is still not all that a “quantitative” solution – this is as good a solution as Feynman provides us with, though. For a more in depth analysis of the ratchet system which uses the Fokker-Planck equation to model the system in a more rigorous manner, see Parrondo [Parrondo 1996].
the ratchet and pawl being as jostled as the windmill. What if the ratchet were colder than the windmill? Feynman shows that we should then expect the windmill to turn, on average, in the direction of the ratcheting action. The hot windmill would slowly dump heat to the cold ratchet, but for a time (before equilibration) it could function as an ordinary heat engine.

Spoken in the language of the original demon: the sensing element (the trap door) must be at temperature $T_C$, which is lower than the temperature $T_H$ of the fluctuations it is rectifying. However, as it senses, it approaches $T_H$, and thus the ratchet loses some of its $\Delta T$, bringing it closer to equilibrium. Until it reaches equilibrium, however, it is a perfectly valid, law-abiding engine.

So therein lies the purpose of this background explanation and the importance of Feynman’s seminal work: how the ratchet-based heat engine came about as a result of an investigation in second law breaking demons.

### 3.2 Brownian Motors

Since Feynman, work has progressed on a variety of thermal ratchets, three of the most popular being the original mechanical ratchet, Brillouin’s electronic ratchet, and a “flashing” or “rocking” ratchet.

Most of the work has been on the energetics of these ratchets. In specific, there has been great interest in the efficiency of such ratchets. In order to study these energetics, the popular method of analysis involves pitting the ratcheting motion against some small (load) force to find work done, and then using a non-equilibrium equation (most typically the Fokker-Planck) to analyze their steady-state behavior. It is typical in literature to refer to a system as a thermal “ratchet” if it has no load and a thermal “motor” if has a load.

J.M.R. Parrondo [Parrondo 2002] points out three reasons for this interest in ratchets in general and their energetics in specific:

1. **Waste Heat Reduction**

   Highly efficient motors are desirable both to decrease energy consumption and/or decrease the heat dissipation. In biological systems, this second characteristic is of particular interest. General wisdom holds that energy
is not a scarce resource in a biological system. However, when there are a
large number of motors in close proximity (as, perhaps, cellular transport
pumps), disposing of waste heat does become an important issue. Nano-
technology and cell biology applications are the ultimate goal of much of
the research in this field, so this efficiency research is of critical importance.

2. Fundamental Statistical Mechanics

Ratchets are related to fundamental problems of thermodynamics and
statistical mechanics: the Maxwell demon, the entropy/information trade-
off, the arrow of time, and non-equilibrium dynamics. We have already
seen that the first practical system came from a need to address some of
those issues.

3. Experimental Realization

Study into efficiency implies a tangential research of power output and
implementation – including understanding the physical nature of the ex-
ternal agents in some of these systems (there are no real “external” agents
in the Feynman ratchet, but we shall soon see an example of one that does
use one: flashing ratchets).

In the following subsections we will discuss the efficiencies of these systems,
some more of their history, and experimental success (if any).

3.2.1 Feynman’s Ratchet

In Feynman’s original Lectures [Feynman 1964], Feynman presented a system
that consisted of a ratchet that was forced by a pawl to turn in only one direction,
connected to a windmill immersed in some heat bath $T_H$. The fluctuations from
the windmill are then rectified by the pawl that is at some lower temperature
heat bath $T_C$. Feynman shows that in the case of $T_H > T_C$ rectification does
indeed take place, while in the Maxwell demon case of $T_H = T_C$ rectification
does not occur. Moreover, he shows that the efficiency for this system (when
set up as a heat engine) is Carnot efficiency for a quasistatic load (e.g. a load
of the correct size such that the ratchet turns infinitely slowly).

It is shown in a later work by Parrondo [Parrondo 1996] that Feynman’s
analysis was incomplete – that the Feynman ratchet actually exhibits nonzero
heat conduction\textsuperscript{2} even under the no work condition (where the load is perfectly balanced by the power output of the motor and thus no work is done). The result was confirmed by Sekimoto [Sekimoto 1997] with a numerical simulation, as well Magnasco and Stolovitzky [Magnasco 1998] through an analytical approach. Thus, Feynman’s ratchet actually exhibits far-below Carnot efficiency.

There has been no real attempt at an experimental implementation of a Feynman ratchet, or even a system loosely based on a Feynman ratchet. The difficulties involved with constructing a mechanical system on the characteristic scale of these fluctuations seems prohibitive.

3.2.2 Brillouin’s Paradox

Feynman’s ratchet is a close cousin of Brillouin’s paradox [Brillouin 1950]. Suppose we have an electrical circuit that consists of a diode in parallel with a resistor working against some current load, all held at some temperature $T$. It seems that the resistor, with some Nyquist noise across it, will suddenly become an AC power source, with its voltage rectified by the diode. This voltage is created over the load and we once again run into an issue of power output from a single bath. The solution to this problem is very similar to that of the Feynman ratchet: as the diode heats up, it loses its ability to rectify the noise across the resistor.

The circuit does work as a ratchet, however, if you keep the diode at a lower temperature $T_C$ and the resistor at a higher temperature $T_H$. This was shown by Sokolov [Sokolov 1998] using a Fokker-Planck equation to model the probability distribution of the voltage. Later, Sokolov extends his analysis to two diodes in parallel (no resistor) and shows that for two ideal diodes, the system can exhibit Carnot efficiency under the quasistatic load condition.

There has been no experimental success with this electronic ratchet either, though there seem to be no fundamental problems with attempting such an experiment. To this end, this paper will propose an experiment and makes

\textsuperscript{2}This heat conduction is not due to conduction through device elements. We assume, for example, that the axle connecting the ratchet and windmill is a perfect insulator. This heat conduction is rather “virtual” in the sense that it is heat moved through work done by the windmill on the ratchet or vice versa that is not in the direction of the desired movement (as it is eventually dissipated as heat). And not due to the usual method of conduction through molecular vibration.
some predictions on the results thereof.

3.2.3 Flashing Ratchets

A slightly different class of ratchets are those based on a flashing potential (a potential that is “flashed” in and out over time). Here, the system is held at only one temperature but, the non-equilibrium-ness is induced by the introduction of an external agent – an acting potential.

If this potential is modeled as a discontinuous sawtooth, we can see in figure 3.4 how turning it on and off at random (or, even along a deterministic schedule) will cause a net current of particles in a particular direction (in this example, to the left) [Reimann 2002].

To follow why they diffuse in this direction, we need to consider what happens at each step of the process.

1. Potential Trapped
   At the beginning of the cycle \( t = 0 \), all the particles should be at the bottom of the “wells” between the potential peaks.

2. Free Diffusion
   When the potential is turned off, the particles are allowed to freely diffuse along the dimension of freedom.

3. Work Done
Figure 3.4: Here, we can follow the three discrete steps of the flashing ratchet’s mechanism: (i) at $t = 0$ the Brownian particles all sit in the potential wells between the sawteeth, (ii) at $t = 0.5$ the particles are allowed to diffuse into a uniform distribution about the dimension of freedom, and (iii) at $t = 1.0$ the potential is brought back and does work on the particles – moving more to the left than the right, producing a net current. [Reimann 2002]

When the potential is brought back, a “power stroke” is done as the potential will move more particles along the long (left) slope compared to the particles moved by the short (right) slope.

We also expect that the force this potential puts on the particles should allow them to work against a load (which it does).

Analyzing the flashing ratchet’s response to a load, Parrondo goes on to model this system with an effective Fokker-Planck equation and determine the efficiency of this sawtooth potential ratchet (which he finds to be far from Carnot) as a function of load. Parrondo then shows that there exist adiabatic potentials for the flashing ratchet which will result in Carnot efficiency under the quasi-static load condition [Parrondo 1998]. Parrondo’s results for these two systems are shown in figure 3.5.

The flashing ratchet, unlike the previous two types described, has actually been realized experimentally: an optical ratchet which uses a sweeping laser to create a sawtooth potential in a Brownian particle bath showed that this ratchetting effect is indeed present and physically significant [Faucheux 1995]. In fact, one of the original aims of this thesis was to extend that experiment by altering Faucheux’s experiment to accept dynamically created potentials (allowing us to model adiabatic potentials instead of just the original sawtooth).

While a model of my adiabatic optical ratchet was completed, it soon became
Figure 3.5: a) *Irreversible ratchet*: the numerical results for the efficiency of a ratchet consisting of the sawtooth potential discussed earlier as a function of load force $F$ and different values for the time per cycle $T$: $T = 0.00125 \, (\circ)$, $0.025 \, (\square)$, $0.05 \, (\diamond)$, $0.25 \, (\times)$, and $0.5 \, (\triangle)$. b) *Reversible ratchet*: numerical and analytical results for the efficiency for an adiabatic potential as a function of $\alpha = FT$ where $F$ is the load force and $T$ is time per cycle and $T = 1 \, (\times)$, $2 \, (\circ)$, $10 \, (\square)$, $40 \, (\diamond)$. The thick solid line is the analytical result for the limit as $T \to \infty$ and $F \to 0$. Note that $\eta$ is an increasing function of $T$ in the reversible case. [Parrondo 2002]

obvious that it would be impossible to complete both my [writeup of this optical ratchet setup] and [the investigation and writeup of the electronic ratchet]. I eventually settled on the electronic ratchet because I feel that both the Feynman and Brillouin ratchets are slightly more fundamental than this flashing ratchet – or at least more complete. The flashing ratchet has a nebulous “external agent” that provides the potential doing the work. This external agent (in the case of the optical ratchet, a complex array of electronics and the laser itself) is often even harder to fully analyze than our ratchet itself! Whereas, in the electronic ratchet, everything is there: load, heat baths, etc. – it is complete unto itself.

### 3.2.4 Ratchets Everywhere

There are more ratchets, of course – an infinite number, really.

Chemical ratchets are of increasingly interest for use in biological applications. In these systems, the non-equilibrium-ness usually comes from chemical potentials and Gibbs free energy (instead of just temperature and heat). For further reading see Reimann [Reimann 1997] or Humphrey [Humphrey 2002].

There has been no experimental realization of quantum ratchets, but theoretical proposals come as varied as a Fermi gas exchange-based ratchets to quantum dot flashing ratchets printed on a chip. For further reading see Parmeg-
A ratchet is just any device that can produce work from thermal (random) energy. As long you are increasing entropy and producing work, you are a ratchet. A good, simple test for a system that generates work is - if you bring the system to equilibrium does it still generate work? Of course it won’t. And it’s interesting to note that not only do heat engines stop producing work, so do chemical batteries, or any other power source. So really, pretty much everything is a ratchet.

This is just a restatement of the Second Law – things have to be out of equilibrium to evolve. Equilibrium is stagnant. The importance of these ratcheting systems is not in what they say (the Second Law has already stated it more succinctly!) but in how they say it. They tell the details of the story and allow us better access to the practical applications and physical intuition missing from the Second Law.

A laser trapping and cooling set-up is a (backwards) ratcheting effect. The laser trap limits the directions of movement and, by doing work on the system, slows the particles down. Traders in a financial market rectify price fluctuations (risk) into profit. Evolution is a sort of ratcheting effect – where the thermal motion is the drift in our genetics and death is the non-linear frictional element.

The way the world changes from the smallest to largest, from the quantum to the abstract is governed by ratchets operating in non-equilibrium systems.
Chapter 4

The Electronic Ratchet

The system I chose to work with in exploring the vagaries of the thermal ratchets consists of a diode in parallel with a resistor and a capacitor; the diode and resistor are held at different temperatures $T_1$ and $T_2$. Besides being easier to analyze than Feynman's mechanical ratchet, it also has the distinct advantage of being physically realizable – building a true ratchet-pawl system at a scale where thermal fluctuations were significant would be quite a feat of engineering. Since one of the primary goals of this paper is to explore the practicality of realizing these systems experimentally, the electronic ratchet seemed the obvious choice.

In this chapter we strive to introduce the current state-of-the-art in electronic ratchet research. We then lay out a direction for our research: investigation of the properties of a “realistic” electronic ratchet and comparison to other thermoelectric effects. Finally, we present a numerical simulation of the behavior of such a ratchet.

4.1 Previous Work

This system was introduced in Brillouin's Paradox [Subsection 3.2.2], but it is worth giving a more detailed recount of its history at this point. The original explanation of the paradox was described by Brillouin: his method of detailed balance showed the ineffectiveness of a diode rectifying the thermal noise of a resistor for a system in equilibrium [Brillouin 1950]. However, his analysis does
not give us much insight into the system’s approach to equilibrium.

In order to answer questions of efficiency and power output we turn to Sokolov’s analysis [Sokolov 1998]. Here, the circuit is shown to act as an ordinary $\Delta T$ heat engine if the diode is colder than the resistor, using an effective Fokker-Planck equation for probability distribution of voltage. Moreover, Sokolov extends the theory to circuits with two diodes [Sokolov 1999], finding that ideal diodes yield zero thermal conductivity under a no-work condition and hence, exhibit Carnot efficiency.

4.1.1 Energetics of the Non-Linear Resistor System

Because of the critical importance of the equations describing the electronic ratchet, I will present a slightly simplified version of Sokolov’s derivation [Sokolov 1998] here, rather than relegate it to an appendix.

The system is a convenient toy model – represented in figure 4.1. We can see that it looks much like the Brillouin system, with two minor additions. The first addition is the ideal current source: a theoretical power source which maintains a constant current regardless of potential difference. Without this current source, any thermal noise will show up as voltage but won’t be working against any load. Adding this current source makes it possible to determine power output and hence, efficiency.

The second addition is the capacitor $C$ which makes the system’s energy
a function of one variable, the capacitor’s charge \( q \), given by \( E = \frac{q^2}{2C} \). Note that the presence of the capacitor implicitly brings the system closer to an accurate physical system, as any real system would have some capacitance over it. Thus, we can rest our fears of some unknown “fluctuation smoothing” or other capacitance effect destroying our thermal drift. In fact, the only basic circuit component that is missing from this model is an inductor. Luckily, this inductance effect is proportional to change in current, and we are assuming a constant current load.

The system is also composed of a linear resistor \( R \) (kept at a temperature \( T_1 \)) and a semiconductor diode, presumably some sort of non-linear resistor (kept at some temperature \( T_2 \)). We give the non-linear resistor a differential resistance as a function \( R_n(u) \), where \( u \) is voltage across the capacitor.

We follow Van Kampen’s approach [van Kampen 1961] to noise in diode systems and break our “continuous” thermal system into discrete objects and actions. We use single classical electrons residing on the plates of the capacitor as our basic elements. We assume that electrons can pass from the upper plate to the lower plate of the capacitor (and vice versa) through one of two possible channels: through the resistor or through the diode. Each process is given by the corresponding rates \( W_{i,i+1}^{(1)} \) and \( W_{i,i+1}^{(2)} \). We assume the two transport channels to be independent, such that the transition rates sum up to 1. We can describe the overall process by a master equation,

\[
\frac{dp_i}{dt} = -p_i (W_{i,i+1} + W_{i,i-1}) + p_{i-1}W_{i-1,i} + p_{i+1}W_{i+1,i},
\]

(4.1)

with \( W_{i,i\pm 1} = W_{i,i\pm 1}^{(1)} + W_{i,i\pm 1}^{(2)} \). The two channels each satisfy their own detailed balance conditions

\[
W_{i,i+1} = W_{i+1,i} \exp \left[ \frac{E_{i+1} - E_i}{kT} \right],
\]

(4.2)

and

\[
W_{i-1,i} = W_{i-1,i} \exp \left[ \frac{E_i - E_{i-1}}{kT} \right],
\]

(4.3)

for temperatures \( T = T_1 \) and \( T = T_2 \), respectively.

We will now go about approximating the (intractable) master equation with a continuous Fokker-Planck (FP) equation by taking the limit as \( \xi \to 0 \). To do this, we introduce the functions \( W(q) = W(n\xi) = W_{n+1,n}, E(q) = E(n\xi) = E_n \).
and \( p(q) = p(n \xi) = p_n \) and expand eq. (1) around \( q \) up to order \( \xi^2 \). This is a standard procedure for approximating the master equation, and it leaves us with the FP equation we’re after:

\[
\frac{\partial p(q)}{\partial t} = \frac{\partial}{\partial q} \left( W(q)\xi^2 f(q)p(q) + W(q)\xi^2 \frac{\partial p(q)}{\partial q} \right).
\] (4.4)

with \( f(q) = \frac{\partial E}{\partial q} \), the restoring force. Now we just make two more substitutions and we can attain some physical intuition of this system. \( W(q)\xi^2 = D(q) \), the fluctuation term, and \( W(q)\xi^2/kT = D(q)/kT = \mu(q) \), the classical mobility (for this electronic system, conductivity\(^1\)). Now eq. 4 takes a familiar form:

\[
\frac{\partial p(q)}{\partial t} = \frac{\partial}{\partial q} \left( \mu(q)f(q)p(q) + D(q)\frac{\partial p(q)}{\partial q} \right).
\] (4.5)

Now, finding the conductivity of the system is trivial, given our initial values: \( \mu(u) = \left( \frac{1}{R} + \frac{1}{R_{n}(u)} \right) \), we’ll be recasting our FP in terms of voltage \( u \), shortly, so don’t worry too much about \( \mu \) being a function of \( u \) (not \( q \)). We also have \( f(q) = u = q/C \), the voltage across the capacitor. Finally, we have a current source running at \( i \) amps. Microscopically, this generator takes \( i \) unit charges per unit time and moves them from the top plate of the capacitor and places them on the bottom. This is represented as an additional system drift \(-i\):

\[
\frac{\partial p(q)}{\partial t} - i \frac{\partial p(q)}{\partial q} = \frac{\partial}{\partial q} \left\{ \left( \frac{1}{R} + \frac{1}{R_{n}(u)} \right) \frac{q}{C} \right\} p(q) + \left( \frac{kT_1}{R} + \frac{kT_2}{R_{n}(u)} \right) \frac{\partial p(q)}{\partial q}.
\] (4.6)

Note that the sign of \( i \) is chosen such that when that the power output of the engine is positive when both \( u \) and \( i \) are positive. Now, we make the substitution \( q = uC \), simplify our term for drift from the current source, and are left with the FP equation as a function of the fluctuating voltage \( u \):

\(^1\)The reader may be troubled by the units of conductance, which is clearly different than the units of mobility! In this system, however, our units are in terms of charge \( \delta q \) and not \( \delta x \). In this “native” charge-based system, conductance can be used as the mobility directly, and the units do end up working out.
\[
\frac{\partial p(u)}{\partial t} = \frac{\partial}{\partial u}\left\{ \left[ \left( \frac{1}{R} + \frac{1}{R_n(u)} \right) u + \frac{i}{C} \right] p(u) + \left( \frac{kT_1}{RC^2} + \frac{kT_2}{R_n(u)C^2} \right) \frac{\partial p(q)}{\partial u} \right\},
\]

(4.7)

A typical form for a Fokker-Planck and whose stationary solution is easily found [van Kampen 1961]

\[
p(u) \propto \exp\left\{ -\int du \left[ \left( \frac{1}{RC} + \frac{1}{R_n(u)C} \right) u + \frac{i}{C} \right] / \left( \frac{kT_1}{RC^2} + \frac{kT_2}{R_n(u)C^2} \right) \right\}.
\]

(4.8)

As Sokolov immediately points out, this equation satisfies our simplest intuitive test. In equilibrium, where \( T = T_1 = T_2 \) and \( i = 0 \), Eq. 4.8 reduces to a normal distribution: \( p(u) = \exp[-Cu^2/2kT] \). This represents, of course, the Boltzmann distribution of the energy of the capacitor in equilibrium. Note that this Boltzmann nature in equilibrium is completely independent of our resistor and diode properties, as it should be. Using this distribution, it is a simple matter to find that the mean voltage is given by \( V = \int_{-\infty}^{\infty} up(u)du \) and the mean power is given by \( P = iV \).

### 4.1.2 Generalization to the Two Diode system and Analytical Results

Sokolov further extends his analysis to the two diode system pictured in figure 4.2. As we did not assume any special conditions to allow for the non-linear resistor in our previous example, and the linear resistor \( R \) is just a particular case of the non-linear resistor \( R(u) \), this extension is rather straightforward. Now, we can represent this new system using a slightly altered version of Eq. 4.8 – while we’re at it, we’ll throw in a normalization constant to change our “\( \infty \)” to a “\( \vdash \)” . The stationary solution of the two diode system is given by

\[
p(u) = A\exp\left\{ -\int du \left[ \left( \frac{1}{R_1(u)} + \frac{1}{R_2(u)} \right) u + i \right] / \left( \frac{kT_1}{R_1(u)C} + \frac{kT_2}{R_2(u)C} \right) \right\}
\]

(4.9)
where $A$ is the normalization constant.

We already have expressions describing mean voltage and mean power – the only value we have left to find is the heat absorbed by the diodes from each of their respective heat baths. This is, once again, a standard procedure derivable from the standard Fokker-Planck equation [Sokolov 1998]. The heat absorbed from the reservoir at temperature $T_1$ per unit time is given by

$$Q_1 = - \int_{-\infty}^{\infty} u \left[ \frac{kT_1}{R_1(u)C} \frac{\partial p(u)}{\partial u} + \frac{u}{R_1(u)} p(u) \right] du \quad (4.10)$$

At this point, we have what we need to go forward with a numerical simulation to investigate this system: an expression for probability distribution $p(u)$, power output $P$, and rate of heat absorption $\dot{Q}_1$ from one heat bath. Note that solving for the rate of heat absorption from the other bath $\dot{Q}_2$ is straightforward: just find the power output $P$ and $\dot{Q}_1$ and satisfy the detailed balance, $P = \dot{Q}_1 + \dot{Q}_2$, to solve for $\dot{Q}_2$.

However, we will first pause a moment and review some analytical results that come from these equations [Sokolov 1999]. Besides the fact that you can analyze ideal diodes (infinite backward resistance) only in an analytical example, these results will be an important benchmark with which to test the accuracy
Figure 4.3: The efficiency of the engine as a function of the current source $i$. The heat bath temperatures are given by $T_1 = 10$ and $T_2 = 1$ for this example. The thick line corresponds to $R_- \to \infty$. The thinner lines correspond to $R_- = 1000$, $R_- = 100$, $R_- = 10$, respectively, from top to bottom. Note that at $i = 0$ and an ideal diode with $R_- \to \infty$, we attain Carnot efficiency of $\eta = 0.9$. [Sokolov 1999]

and precision of our numerical simulation – we want to be sure we are seeing physical effects, not a programming bug.

To solve these nasty integrals analytically, it pays to use a piecewise (ideal) function for the non-linear resistances of these two diodes.

$$R_1(u) = \begin{cases} R_+ & \text{for } u > 0, \\ R_- & \text{for } u < 0, \end{cases} \quad (4.11)$$

and

$$R_2(u) = \begin{cases} R_- & \text{for } u > 0, \\ R_+ & \text{for } u < 0, \end{cases} \quad (4.12)$$

In figure 4.3, efficiency is given for various values of $R_-$ and $R_+$. Note
the intriguing result Sokolov leaves us with: for two ideal diodes, arranged as a ratcheting Brownian motor, we can achieve Carnot efficiency as we reduce current \( i \) to zero.

### 4.2 Current Goals

In spite of Sokolov’s great steps forward in understanding this Brownian motor, it is still mainly a theoretical construct. The goals of this investigation will revolve around proposing a physical experiment to measure this effect as well as try and probe its properties in detail – could this be a significant effect with practical applications? Any new insights into efficiency, power output, or otherwise will be catalogued as they are found.

Our efforts can be broken down into four directions:

1. **Detecting the Ratcheting Effect Experimentally**
   
   Given reasonable values for electronic ratchet system described above, temperatures near room temperature, real resistors, non-ideal diodes, reasonable capacitances and current sources, would the power output of such a system be measurable?

2. **Determining Whether The System is Capable of Pumping Heat**
   
   Could this system *pump* heat rather than produce energy? What sort of efficiencies could it exhibit running in this reverse-direction?

3. **Comparison to the Thermoelectric (Seebeck) effect**
   
   A shrewd reader might already be asking himself, “Does this have anything to do with the Seebeck effect? It sounds awfully familiar – semiconductors, thermoelectrics, electrical current from temperature difference, etc.” Does this effect contribute to or perhaps explain microscopically the phenomenological Seebeck effect? Or, if it is an independent effect – is it overpowered by the Seebeck effect in any practical implementation (that is, are they antagonistic effects?).

4. **General Insight into Efficiency and Power Output**
   
   Along the way, we hope to pick up some insights that will allow us to choose better components or design better circuit set-ups that will max-
imize this effect experimentally. e.g. Is a diode with a lower threshold voltage but higher back current more effective than a diode with higher threshold but lower back current?

4.3 Simulation Setup and Discussion

The questions posed in the previous section, will be addressed with a Matlab based numerical simulation. In this section, we will discuss why we picked a numerical simulation as our vehicle of choice in this research and then discuss the development and testing process that left us with the computer program eventually used to produce the results in Results and Discussion [Section 5.4].

4.3.1 Why a Numerical Simulation?

In exploring a system with as many unknowns as this one – where, in many ways, you’re not sure what you’re even looking for, the most critical requirement of your investigation method is flexibility.

An analytical approach has a very low fixed cost – whatever values and functions we chose, we can immediately attempt to solve the equations Sokolov left us with. Unfortunately, our variable cost – how long it will take to derive new solutions every time we think of new functions and new values will be prohibitively high. We need to allow for the flexibility to try different values and graphs at a whim – a numerical method. The analytical approach also sometimes suffers from an issue with transcendental equations, limiting the range of the initial values and functions we can work with.

An experimental approach suffers from a high fixed cost and a high variable cost. The experimental approach also introduces the possibility of other, antagonistic effects – what if the Seebeck effect serves to completely cancel what we hope to see? Better to predict what we expect to see so we can sort through competing effects once we get to an experiment. In addition, at this point we have little idea of what kind of power output we hope to see – the instruments we chose may simply not have the precision necessary to reflect these ratcheting effects.
4.3.2 The Approach

The program seeks to numerically calculate three key properties of the system:

1. \( p(u) \): the probability distribution function for any \( u \), as given by Eq. 4.9.
2. \( V \): the mean voltage across the capacitor, as given by \( V = \int_{-\infty}^{\infty} up(u)du \).
3. \( \dot{Q}_1 \): the heat absorbed from reservoir at temperature \( T_1 \) per unit time, as given by Eq. 5.10.

With these, it is easy to calculate other interesting values: heat absorbed from the other reservoir \( \dot{Q}_2 \), power output \( P \), the system efficiency \( \eta = P/\dot{Q}_1 \), etc.

What difficulties are there in evaluating these expressions? There is an indefinite integral \( p(u) \) that is always nested within a definite integral, \( V \) or \( \dot{Q}_1 \). There is also one partial derivative \( \frac{\partial p(u)}{\partial u} \), in the expression for \( \dot{Q}_1 \). Since we’d like to avoid taking numerical derivatives (as it is difficult, relative to numerical integrals), we simply take this derivative analytically:

\[
\frac{\partial p(u)}{\partial u} = \frac{\partial}{\partial u} A \exp \left( - \int du \left\{ \left( \frac{1}{R_1(u)} + \frac{1}{R_2(u)} \right) u + i \right\} / \left( \frac{kT_1}{R_1(u)C} + \frac{kT_2}{R_2(u)C} \right) \right) \tag{4.13}
\]

\[
= -p(u) \left\{ \left( \frac{1}{R_1(u)} + \frac{1}{R_2(u)} \right) u + i \right\} / \left( \frac{kT_1}{R_1(u)C} + \frac{kT_2}{R_2(u)C} \right) \tag{4.14}
\]

Presto – no more derivatives. Now the only thing we need to do is take some numerical integrals and we’ll have our values. Since there is an exponential function involved, choosing ‘bad’ values that cause the probability distribution to blow up is easy to do. However, every case that is interesting (where the drift due to the thermal noise is significant) ends up having a fairly well behaved probability function. The only easy way to check this is to graph the probability function before your program does any other work – if it looks continuous and has a reasonable normalization constant, you’re ok. Because of the different requirements in precision, it is sufficient to perform a quadrature integration method on the probability function \( p(u) \) and a simple trapezoid integration on mean voltage \( V \) and heat absorbed \( \dot{Q}_1 \).
Figure 4.4: The un-normalized numerical solution to $p(u)$, given $T = T_1 = T_2 = 300$; elegantly Gaussian. Note that plotting the analytical solution, $p(u) = \exp\left(-Cu^2/2kT\right)$, would give an identical graph.

Initial values (temperatures of the two thermal baths, capacitance, current sources, etc.) are all hard-coded into the source (not set at runtime, although still easily editable). The differential resistances for the two linear/non-linear resistors are set via two functions conveniently named $r_1(u)$ and $r_2(u)$ respectively. All the code is designed to be easily modified, with graphs and output at each stage of runtime – for a more complete discussion of the inner workings of the code, follow the comments through the actual source in *Source Code for Electronic Ratchet Simulation* [Appendix B].

### 4.3.3 Comparison of Numerical Results to Prior Work

Before we delve into any unknowns, we will attempt to reproduce Sokolov’s analytical results with our program.

First, we will set $i = 0$ and $T = T_1 = T_2$. This puts the system into equilibrium and our program should return a Boltzmann distribution irrespective of our resistance functions. The results are shown in figure 4.4: looks like our program has passed its first test.
Figure 4.5: Note the familiar efficiency curves mirroring those from figure 4.3, Sokolov’s analytic results. The lines correspond to $R_\infty = 1000, R_\infty = 100, R_\infty = 10$, respectively, from top to bottom. There is no line corresponding to $R_\infty \to \infty$ in this numerical analysis, although it is easy to imagine where it would fall, and that it would cross the $y$-axis at $\eta = 0.9$. Finally, note that the scale of $i$ is not quite the same as in figure 4.3; this may be due to approximations Sokolov makes which I do not – nevertheless, it is not of too much concern, as we are only interested in the qualitative features of these results. Since our goals are identifying order of magnitude values and qualitative behaviors, these discrepancies are fairly meaningless.
Second, we attempt to recreate the efficiency versus current graph pictured in figure 4.3. For this test we use stepwise diode functions, exactly as Sokolov did. While we are unable to mathematically set $R_- \rightarrow \infty$ as we could with an analytical solution, we can clearly see the trend towards $\eta = 0.9$ as $i = 0$ and $R_- \rightarrow \infty$. Our results are illustrated in figure 4.5: once again, it looks like our program has passed the test.

We are fairly confident that, having reproduced Sokolov’s analytic results numerically, our program is bug-free and ready to explore some uncharted territory.
Chapter 5

Results and Discussion

Using our numerical simulation, we can find answers to the first two questions posed in our Current Goals [Section 4.2] (1. Detecting the Ratcheting Effect Experimentally and 2. Determining Whether The System is Capable of Pumping Heat) as well as gain a few insights into our fourth line of questions (4. General Insight into Efficiency and Power Output). The third direction of questioning (3. Comparison to the Thermoelectric Effect), that regarding the Seebeck effect’s correlation to this ratcheting effect, finds minimal assistance from our computer program. We will address that third question analytically, instead.

5.1 Detecting the Ratcheting Effect Experimentally

Using an experimental setup that is cheap, easy to build, and composed of off-the-shelf parts, we want to be able to detect an indication of this ratcheting effect – the voltage across the capacitor. To show this, we will discuss how we attempted to include realistic experimental issues in detail, and then present the predictions made by the numerical simulation on what sort of results we could expect to see with a “realistic” setup.

Throughout this section we try and keep our eye on the “prize”: bridging the gap between the theoretical ratchet and an experimental realization.
5.1.1 Realistic Experimental Considerations

The most obvious effects that must be considered are those relating to the circuit: non-idealities in resistance, inductance, capacitance and the current source. For example, pretending our current source draws exactly 0A (e.g. no load) or that the diode(s) can be represented by differential resistance functions that are discontinuous Eq. 4.11, 4.12 is going to cause us to make inaccurate predictions.

A secondary set of effects that must be considered are any “external” effects (external in that they are outside the realm of our circuit analysis) that could serve to dominate or antagonize this one. The only obvious culprit here is the thermoelectric effect. We find that this is, in fact, an independent and (for this set-up) a negligible effect – this is explained in Comparison to the Thermoelectric (Seebeck) Effect [Section 5.3]. The thermoelectric effect will simply be assumed to be non-existent for the purposes of this section.

1. Real Resistors and Diodes

The most pressing and obvious issue with simulating a “real” experiment is that diodes are not step functions – they are described by a continuous function. Instead of using an ideal (step) function we will use a diffusion/recombination model to represent the diode, the model in which minority-carrier flow is approximated to occur by some linear ratio of diffusion and recombination [Linvill 1963]. Pictured in figures 5.1 and 5.2 are the ideal diode and its volt-ampere characteristics and that of a diffusion/recombination model based graph, respectively.

On the basis of the diffusion/recombination model for the behavior of a silicon junction as a function of applied voltage, we find that the current-voltage characteristic for direct current is:

\[ I = I_s(\exp AV - 1), \]  

(5.1)

where \( A = \frac{qA}{kTn} \approx 40/n \) at room temperature and \( n \) is the ideality factor and varies between 1 and 2 for various diodes of different construction [Wilson 2003].

We will use this as the basis of our modeling effort. But, before we use this to curve fit experimentally determined current-voltage characteristics of a diode,
Figure 5.1: The ideal diode current-voltage curve: a step function with a discontinuity about zero. This is clearly unrealistic and, with the small numbers we're dealing with, can drastically reduce the accuracy of our predictions [Linvill 1963].

Figure 5.2: The diffusion/recombination model for the diode I-V curve: a smooth function that can very closely model the diode's characteristics down to the scale that we will be analyzing (nano and pico volts) [Linvill 1963].
we must consider threshold voltage. While typically of minor importance, most diodes have a “turn-on” voltage $V_T$ of approximately 0.7V. In our system we are exclusively interested in the resistance characteristics within a small range of zero (where the thermal fluctuations occur) so this threshold voltage can possibly make or break us. To try and avoid this problem, it seems obvious that a bias equal to the threshold voltage should be applied so that fluctuations occur about the threshold voltage, rather than about zero voltage. We can add a small “bias” factor $V_T$ in our equation for current/voltage Eq. 5.1 such that we now model our diode as:

$$I = I_s(\exp A(V + V_T) - 1).$$

(5.2)

Of course, the $V_T$ can be factored out of the exponent:

$$I = I_s(\exp A(V + V_T) - 1) = I_s(\exp AV_T \exp AV - 1)$$

(5.3)

So, biasing this diode only affects the magnitude of the current (and hence, the resistance), not the functional form of its I-V curve. Whether or not the diode is biased by any outside voltage source, the diode response will be as non-linear as ever, and this effect will occur. Of course, the lower the resistance of the diode, the larger load we can put on the system, so it’s in our best interest to bias the diode anyway. We’ll keep these biasing factor there and use it to keep the resistance of the system low in our simulation.

If we use the differential form of resistance ($\frac{1}{R} = \frac{\partial I}{\partial V}$) we can create a function of resistance using this modified diffusion model of the diode from Eq. 5.2:

$$R = \frac{1}{I_s A(\exp A(V + V_T))}.$$  

(5.4)

At this point, we will confirm our modeling efforts by using Eq. 5.4 to curve fit the voltage-ampere characteristics of a real diode. If we can successfully curve fit it with a very low (less than 1%) error, we will use this approximation as our differential resistance expression inside our simulation. The diode chosen is a 1N4123 Silicon Diode. It was chosen because it is one of the cheapest and easiest to acquire diodes in our college shop – we want to show that this effect
Figure 5.3: Using our equation for the diffusion/recombination model of diode voltage response, we curve fit our experimental diode data to a fairly high degree of accuracy. We are left with values of $I_s = 2.1203 \times 10^{-9}$ and $A = 21.298$.

is nothing special, but rather a very fundamental phenomena.

As we can see from figures 5.3 and 5.4, Kaleidagraph has fitted our data with less than 1% error and given us values for $I_s$ and $A$. This leaves us with a “realistic” expression for our diode:

$$ r_2(u) = \frac{1}{I_s A \exp(A(V + V_T))}, $$

with $I_s = 2.1203 \times 10^{-9}, A = 21.298$. It may be troubling that (relatively) little care has been paid to error bars and significant figures of these experimental values. The thing to realize is the exact values for these two constants is almost irrelevant as long as they’re in the right ball-park order of magnitude. After all, we can always find a different diode with an $I_s$ at least ten times greater than this one’s, or at least ten times less than this one’s. And, $A$ varies between less than 20 to almost 40 for various diodes. The purpose of this experimental data
is not to show that this particular diode will produce rectification efficiencies of
a specific value but rather to show the general behavior and magnitude of this
rectification effect.

It is important to note that these tests were conducted at room temper-

ture ($T \approx 300K$) and that diode resistance characteristics change as their
temperature changes. In addition, most diodes have a fairly narrow functional
temperature range (typically in the range of $270K - 400K$) out of which they
burn, crack, or otherwise physically break. Thus, to effectively model this sys-
tem over a range of temperatures we would need to also curve fit the diode's
characteristics over changes in temperature. This, in turn, would allow us to
determine the system's properties over a range of possible heat bath tem-
peratures. Besides the obvious functional temperature limits mentioned, this is a
pretty big pain.

To avoid this problem altogether we will make only one resistor non-linear.
This will be our room-temperature heat bath (so, let's say $T_2 = 300K$). The
other resistor will be an ordinary linear resistor whose resistance is essentially

![Image: 1N4123 Silicon Diode Differential Resistance Curve](image)

Figure 5.4: When we plot our differential resistance equation we can see the general
(non-linear) form of our resistance curve.
governed by Ohm’s law and does not change much as we heat it to 400K, 500K or whatever other relatively high test temperatures we’d like to try\(^1\). In addition, it will be less prone to thermal damage than a diode as we crank up the heat. This simplifies our simulation significantly, as we can represent \(r_1\) as:

\[
 r_1(u) = R. \tag{5.6}
\]

The optimal value of \(R\) will be determined shortly.

2. Capacitor not Included

The size of the thermal fluctuations in this system are proportional to \(kBT\) (the resistance values also factor into this, but in a more complicated way). Given that we cannot alter \(k\), and the range of operating values for \(T\) is determined somewhat by what we can achieve easily in a lab, the only way we can increase the size of these fluctuations (and thus, the power output of our system) is by reducing \(C\) as low as it will go. Thus, we must determine how low we can physically take the capacitance.

Besides the fact that in a real system the wires themselves will have some non-zero capacitance (on the order of one picofarad), the diode we use will have some non-negligible capacitance (a few picofarads). This means that choosing a capacitor value of \(C = 1^{-12}F = 1pF\) would give us misleading (and inaccurate) results as the diode’s capacitance would be a dominant factor in the circuit’s behavior. It becomes obvious that we don’t want to include a separate capacitor at all, but rather we should use the diode’s internal capacitances as our capacitor \(C\). Since the diode’s internal capacitance can be modeled as a capacitor in parallel with a diode, we can simply take the internal capacitance of the diode as our system’s \(C\). This particular diode has a measured capacitance of approximately \(3pF\) – we will round up to \(5pF\) just to be on the safe side. Note that rounding up capacitance will only reduce our expected power output, if it ends up being lower than we expected, great – more voltage to measure!

\[
 C = 5pF = 5 \times 10^{-12}. \tag{5.7}
\]

\(^1\)Since we are only interested in \(\Delta T\), lower temperatures are also possible, but it seems significantly more difficult to cool something a couple hundred degrees below room temperature than heat it to above.
Figure 5.5: A diode can be modeled as a diode and a capacitor in parallel to account for its internal capacitance (shown in 5.5a). For our diode, we find an internal capacitance \( C \approx 3\, \mu F \), which we round up to \( 5\, \mu F \) for the whole system (wires, etc) and represent in 5.5b. Thus, there is no physical “capacitor” component we add to the system – we just use the system’s built-in capacitance (via the diode and wiring), representing it as the ubiquitous \( C \) value.

3. Pulling a Current Load

We cannot choose a current source of zero \( (I = 0) \) since, to measure anything (even voltage) we would need to draw a small amount of current. And, in this system even a tiny current could potentially affect the predictions that we make about it. An upper limit on what a volt-meter would draw is in the range of \( I = 10^{-9} \, A = 1\, nA \). It later becomes apparent that any current around this order of magnitude will produce approximately the same change in voltage, so this is not as important as we’d think. Still, it pays to use realistic values, just in case. For now, we will model our current source as a constant source of:

\[
I = 1\, nA = 10^{-9}.
\]  

(5.8)

4. No Steady-State Inductance

The final effect that we must consider is the inductance of the circuit – is this a significant enough effect that our predictions could be rendered inaccurate? We will posit here that, if our current source is truly close to constant (e.g. we are pulling the maximum current from a current-limited source), than the
inductance of the circuit is given by:

\[ V_{\text{induced}} = -L \frac{dI_{\text{constant}}}{dt} = 0, \quad (5.9) \]

or that it is essentially zero in the steady-state.

We’ve covered a lot of effects and are now left with some reasonable, realistic values to model our experiment on. To reiterate our conclusions:

1. **Resistance**: To make sure we’re using a realistic diode model, we curve fit experimental data detailing our diode’s current-voltage characteristics. This diode is the non-linear resistor element in heat bath \( T_2 \). The second resistor is just a linear resistor – this serves to simplify our “real” experimental setup, if we were to build it. We thus model our two resistance functions \( r_1(u) \) and \( r_2(u) \) by:

\[
\begin{align*}
    r_2(u) &= \frac{1}{I_s \exp \left( V + V_T \right)}, \\
    r_1(u) &= R,
\end{align*}
\]

with \( I_s = 2.1203 \times 10^{-9}, A = 21.298. \)

2. **Capacitance**: We choose a capacitance value \( C \) that is sufficiently large that it is greater than the internal capacitance of the diode. This value will also easily dominate any residual line capacitance. We use \( C = 5pF = 5 \times 10^{-12} \).

3. **Current Source**: We assume a current source that is sufficiently large that it can account for the (small) draw that even a volt-meter using an op-amp will require. Looking at the usual draw of instruments we’d find in any given lab, we find an upper limit at \( I = 1nA = 10^{-9} \).

4. **Inductance**: We find that if our current source is close to ideal we get \( V_{\text{induced}} = -L \frac{dI_{\text{constant}}}{dt} = 0 \), meaning that in the steady state any induced EMF is probably going to be negligible and that we can safely ignore this issue.

A schematic of this circuit is shown in figure 5.6.
\[ r_{2}(u) = \frac{1}{1 + 5.0 \mu F} \]

**Figure 5.6:** The system of interest, where \( T_2 = 300 \), \( I_s = 2.1203 \times 10^{-9} \), \( A = 21.298 \), \( V_T = 0.7 \), \( R \) is to be determined, and \( T_1 \) is a variable set in the lab. Also note that the volt-meter probes will be touched on either side of the capacitor/circuit at junctions \( V_+ \) and \( V_- \) respectively.

### 5.1.2 Simulation Results

So it’s time to put our simulation to the test and see some real mean voltage values.

Using the circuit described in the previous subsection, we run our simulation first to create a graph of average voltage over the capacitor for various values of the unknown linear resistor \( R \). Note that in figure 5.6 every initial value except \( T_1 \) and \( R \) have already been defined – we will take those values as given for this entire subsection.

We will set the linear resistor heat bath to \( T_1 = 301 \) to get the approximate change in voltage per change in degree (we will show shortly that this relation between \( \Delta V \) and \( \Delta T \) is highly linear). We will bias the diode by \( V_T = 0.7V \) to drive down its resistance and allow us to increase our load. This diode has a fairly low maximum voltage/current limit so we have to be careful not to bias it too much; 0.7V is pretty safe\(^2\).

\(^2\)0.7V is not arbitrary – it is chosen because it is an operating range that we are confident will provide us with low resistance but no current limiting or diode damaging effects. Not biasing the diode at all would result in very small loads destroying the effect, biasing the diode too much would either burn the diode or “max out” it’s current limit (eliminating the
Figure 5.7: There is a certain value for $R$ which will produce the greatest ratcheting effect – not so big as to overwhelm the diode’s path and not so small as to render the resistor’s path irrelevant. Here we can see it is approximately $R = 200\Omega$, and produces $\frac{\Delta V}{\Delta T} \approx 15\mu V/°K$. We won’t concern ourselves with finding the exact peak since it will probably end up being a non-standard resistance value anyway – the approximation is sufficient for our purposes. The resistor bath is held at $T_1 = 301$, in this example, with all other initial values as given in figure 5.6.
From Fig. 5.7 we see that the maximum average voltage is found when $R \approx 200$, and reaches a voltage of approximately $15pV/K$. So we’ve almost struck gold: we can just heat the resistor to $500K - 600K^3$ and detect a voltage change in the lab using a lock-in method or simply run the system for several hours and average out the instrument noise.

To confirm the validity of these results, let us also use our simulation to analyze what happens if the load $I$ is less (or, even, slightly higher) than our assumed $I = 10^{-9}A = 1nA$. In Fig. 5.8 we can see plainly that under less load our voltage results are always at least as great in magnitude as those under higher load.

Finally, let’s see what the relationship between temperature and voltage is. To do this, we calculate the voltage across the capacitor for various values of $T_1$ from $300K$ to $500K$ (so, values of $\Delta T$ from $0K$ to $200K$).

We can see there is a near linear relationship and that the voltage clearly increases as temperature increases – Fig. 5.9 shows a linear curve fit of these calculated voltage values, so that we can characterize this system as having a “Sokolov” coefficient of $C_S = 14.5pV/K$ and the relationship can be described as:

$$C_S = \frac{dV}{dT},$$

(5.10)

where the $\Delta T$ is the difference between the two paths, not the two points (as in the Seebeck effect). By path, we mean that each electron can travel through either the resistor or diode on its way to the opposite plate of the capacitor. There is no net temperature gradient to speak of between the two plates of the capacitor – it is the paths which are held at different temperatures. This will be discussed in more detail in Comparison to the Thermoelectric effect [Section 5.3].

Over several hundred degrees of temperature difference between the two heat baths (easily achievable in the lab), we should see several nanovolts of voltage change. An experiment performed in the lab should confirm the above linear fit

---

3We could heat our sample to less than 500K or significantly more. 500K is chosen because $(200K)(15pV/K) = 3000pV = 3nV$, and “several nanovolts” is what is often considered a heuristic range of what is barely detectable in an average lab.
Figure 5.8: It appears that for a load current in the range of $I = 10^{-9} = 1nA$ we observe a change of approximately $\Delta V = 14.501 \times 10^{-12} = 1.45pV$ per degree $K$. There is a slight downward trend which is difficult to explain, but is probably due to the fact that, as we send more current through the system, we begin to “break” the effect as we force electron movement. The resistor bath is held at $T_1 = 301$ and $R = 200$, in this example, with all other initial values as given in figure 5.6.
Figure 5.9: We see here a plot of the characteristics of our circuit with $\Delta V$ by $\Delta T$. We do a curve fit and find that to a great approximation, out to nearly $\Delta T = 200K$, our relation is linear with a slope of $14.5 \times 10^{-12}$. The resistor bath $T_1$ is varied from $0K$ to $200K$ and $R = 200$, all other initial values are given in figure 5.6.
and in so doing confirm the presence of this effect.

Our simulation predicts that there exists a simple, cheap, and common system that should exhibit this effect. Our only remaining question is: will any antagonistic thermoelectric effect cancel it? Read on to Comparison to the Thermoelectric effect [Section 5.3].

5.2 Determining Whether The System is Capable of Pumping Heat

An important and interesting possible application of this effect could be in its ability to pump heat. While its power output may be significantly less than that of a Peltier cooler, it has an interesting property in that the two linear/nonlinear resistance elements can be as remote as we like – as long as they are connected by a sufficiently electrically conductive line. Thus, the problem that high power Peltier coolers have with heat conducting back from the hot pad to the cold pad is significantly reduced.

Investigation into the applications of this cooling effect and characterizing it would be another thesis in itself – instead I chose to simply show that it could pump heat. The simplest way to do this is to extend our simulation’s efficiency graphs (looking at efficiency saves us from having to question magnitudes of heat pumping, etc etc) into the negative $I$ range, where we are doing work on the system instead of trying to measure the work it does on us.

In figure 5.10, setting $T_2 = 299$ and $T_1 = 300$, we can see that in a certain region the efficiency ($\eta = P/Q_1$) is positive and less than 1. This implies that more heat is being dumped to $T_1$ than is coming from outside work done on it ($P$). Where is the extra heat coming from? $T_2$, the colder heat bath! Thus, we are moving heat from a lower temperature heat bath to a higher one – clearly indicating this system’s ability to pump heat. Note that this is a graph of a simulation of ideal diodes, with $R_+ = 1$ and $R_- = 10$.

In figure 5.11 we leave $T_2 = 299$ and $T_1 = 300$, but use our “real” diode model. Unfortunately, we do not see the positive, less than 1, region of efficiency. The reason is that the heat pumping ability of the system is very sensitive to the degree of non-linearity of the diodes – real diodes are far more linear than our
Figure 5.10: For an *ideal* diode system we set $T_2 = 299$ and $T_1 = 300$ and explore the negative region of the load current $I$. Here, we do work on the system and expect that we pump heat. Where $0 < \eta < 1$ we do, in fact, pump heat from the colder $T_2$ to the warmer $T_1$. Note that this ideal diode system converges to $\eta \approx 1.1$ as $I \rightarrow -\infty$, this is because $R_+ = 1$ and $R_- = 10$ for this example. If $R_- \rightarrow \infty$ we would see $\eta \rightarrow 1.0$. 
Figure 5.11: For our “real” diode system, we set $T_2 = 299$ and $T_1 = 300$ and explore the negative region of the load current $I$. Here, we do work on the system and expect that we pump heat. Unfortunately, there appears to be no region where $0 < \eta < 1$. This is probably due to lackluster non-linearity of our silicon diode (compared to an ideal diode). We hope in future work to identify a different non-linear resistance element that will more effectively facilitate this heat pumping capability.
ideal diodes. Thus, we predict that this heat pumping effect will most likely not be observed with our current “off-the-shelf” diode/resistor system. However, if we can “stack” several of these systems, or if we can find a more non-linear resistor (e.g., a field-effect transistor) we may be able to eventually measure this effect. See General Insight into Efficiency and Power Output [Section 5.4] for more on this and future work.

5.3 Comparison to the Thermoelectric (Seebeck) effect

In order to prove that this ratcheting effect is independent of the Seebeck effect (and in the process show that we can measure this ratcheting effect without worrying that the Seebeck effect will get in our way) it is sufficient to show two things. First, that there is a system where the Seebeck effect is present and this ratcheting effect is not. Second, that there is a system where this effect is present and the Seebeck effect is not.

The two systems we are looking for happen to be elementary examples of each effect and are thus easy to identify and describe.

Note that we do not go into describing the Seebeck effect here. For a more in-depth background discussion of the thermoelectric effect and the Seebeck coefficient, consult The Seebeck Effect [Appendix A].

5.3.1 No Ratcheting Effect in a Linear Resistor

To streamline this discussion, we will begin with an assumption of some level of familiarity with thermocouples, Peltier coolers, and the definition of the Seebeck coefficient:

\[ S = \frac{dV}{dT}, \]  

which can be understood as “the potential difference between two points is proportional to the temperature difference by a coefficient \( S \).”

Now, assume we have a bar of copper and hold one end at a temperature
$T_H = 400$ and one end at a temperature $T_C = 300$. Copper has a Seebeck coefficient of $S \approx 6.5 \mu V/°K$ when it is near room temperature [Kasap 1997] – its exact value is irrelevant, as we shall see shortly. With a $\Delta T = 100$ and Seebeck coefficient $S = 6.5$ we would expect a $\Delta V = 650 \mu V$.

Of course, we notice that in this system (which is just two heat baths touching a bar of copper) there are no non-linear resistors. All we have is a very very linear resistor: copper. Since the only material present is copper, we must assume that, were we to try and measure a ratcheting effect in this Seebeck system our two resistors would be made of copper.

Returning to our probability distribution Eq. 4.9 for the ratcheting system and replacing our resistance equations $R_1(u)$ and $R_2(u)$ with some totally linear $R$ (the resistance of some bit of copper), we get:

$$ p(u) = A \exp \left\{ - \int_0^\infty du \left[ \left( \frac{1}{R} + \frac{1}{R} \right) u + i \right] \left/ \left( \frac{kT_1}{RC} + \frac{kT_2}{RC} \right) \right\} \right] $$

The denominator of the integral $(\frac{kT_1}{RC} + \frac{kT_2}{RC})$ is now a constant divisor – no matter what we change $T_1$ and $T_2$ to, this denominator cannot shift the average value of voltage. Now that we have shown that a ratcheting system built on two linear resistors has no temperature dependence we can be fairly certain that we have identified a system where the Seebeck effect is present and the ratcheting effect is not.

Just to be thorough, however, let’s set $i = 0$ in this system (we won’t disturb the system so no load is required).

$$ p(u) = A \exp \left\{ - \left[ \left( \frac{1}{R} + \frac{1}{R} \right) / \left( \frac{kT_1}{RC} + \frac{kT_2}{RC} \right) \right] \int_0^\infty u du \right\} $$

Which is a basic Gaussian form centered about zero – taking the average from $-\infty$ to $\infty$ will always give a mean voltage of zero.

Thus, linear resistors can exhibit the Seebeck effect but never the ratcheting
5.3.2 No Seebeck Effect Without a Temperature Gradient

In the model we use for the ratcheting system, we measure voltage as the potential across the capacitor. In order to show that there is no voltage that is due to the Seebeck effect, we must analyze in detail what happens at the two points where our voltmeter probes touch the lines connecting to the plates of the capacitor.

If we consider the wires that our probes are touching as small linear resistors of resistance $R_{small}$ that are held at some third temperature $T_3$ (these wires will be exposed to the air in the room, so $T_3$ will be room temperature) such that we say $T_3 = 300K$, we can now effectively model what is going to happen to each effect.

For the ratcheting effect, adding two linear resistors of the same resistance and held at the same temperature to each of the two possible paths won’t do much. That is, adding these cannot alter the probability of an electron taking one path (say through the diode) as opposed to taking the other. Nor can adding these alter the probability of an electron jumping from the top plate to the bottom plate and vice versa – the addition to the paths is symmetrical. If the resistance was large or the temperature of this heat bath $T_3$ was large compared to that of $T_1$ and $T_2$ we might adversely affect the load we could put on the system (that is, the rate at which electrons move from plate to plate) but never the voltage.

For the Seebeck effect, if we refer back to Eq. 5.11 we see that, should the temperature difference between two points be zero ($\Delta T = 0$), we expect the voltage difference to be zero as well. However, our two probe points are both held at exactly the same temperature ($T_3 = 300K$), room temperature, so $\Delta T$ between our two probe points is zero as well. Note that the only places where temperature gradients do occur, between $T_1$ and $T_3$ as well as $T_2$ and $T_3$, they occur symmetrically and cancel.

Why there can be a ratcheting voltage when there is no Seebeck voltage is somewhat easier to understand than why there is a Seebeck voltage in a linear resistor. Essentially, the ratcheting effect depends on the temperature
Figure 5.12: We consider essentially the same model system except that now we explicitly hold both the voltage probe junctions ($V_+$ and $V_-$) at the same temperature ($T_3 \approx 300$), room temperature. This essentially does not affect our path-based ratcheting effect since the two junction points (even if they have some non-zero resistance) add to both paths in a symmetric manner. However, it means that the temperature gradient between the two voltage probe point is obviously zero. No temperature gradient means no Seebeck voltage. The only temperature gradients that exist are those between $T_1$ and $T_3$ as well as $T_2$ and $T_3$ – however, these are symmetric on either side and cancel nicely. Thus, this system has allowed the ratcheting effect to flourish while defeating the Seebeck effect.
differences between different paths between two points – not the temperature difference between those two points directly. Note that the path is only well defined for cases where there is a single element along each path (just a resistor, or just a diode), so this intuition doesn’t apply well past this basic example.

This result is doubly important because it implies that we should see a near zero interference from the Seebeck effect while we measure the ratcheting effect.

5.4 General Insight into Efficiency and Power Output

The foremost insight that studying this system has brought to me is why the ideal two diode system works at Carnot efficiency. The answer is simple – as always, we want to exchange heat along isotherms. The complication is, unlike in a Stirling or Carnot cycle, we cannot touch our system to the warmer heat bath, then move it over to the colder heat bath; it is, in fact, touching both at once. Having two linear resistors, one in a bath $T_H$ and one in a bath $T_C$ is tantamount to having the gas in a Stirling cycle piston touching both heat baths at once: nothing happens.

The more non-linear the response of the resistor the closer the continuous ratchet is to a familiar reversible thermodynamic cycle – physically moving the ideal gas in the piston from $T_H$ to and $T_C$ and back again. The more linear, the closer to a cycle where the gas is touching both $T_H$ and $T_C$ at once all throughout the cycle. This is what is meant by “no heat transfer under a no work condition” [Sokolow 1999] in the ideal diode system. It is comforting to know that our only requisite for reversibility, dumping heat along an isotherm, is still the only requisite for these slightly more complex microscopic engines – it’s just figuring out how to do it that’s a little harder.

In the following subsections I present an interesting but haphazard collection of insights into this system. While not as concrete or meaningful as the other results we have presented, they form the basis for future work that we would like to pursue.
5.4.1 Methods of Increasing Power Output

In the results section above it was already hinted at that, to increase the power output of our system, we'd like to both decrease resistance and decrease capacitance (beyond the trivial method of just increasing the temperature difference). The low capacitance requirement fell out of the probability distribution equation, and the low resistance requirement was mentioned in the discussion of load current.

It is insufficient to just leave it at that, though. The dependence of the system on these two factors is complex and a more detailed physical understanding is critical towards choosing components or implementations of this system which may eventually produce useful power output. My insights into this problem are incomplete, but nevertheless useful to an elementary investigator into this field.

The first statement we will make is that: 1. Under a no load condition the resistance values of the system are irrelevant. “Wait!”, you say, “didn’t you just say we wanted to keep resistance low?” We do, but only for the purposes of balancing our load; without a load it is irrelevant. There are two simple ways to understand why this is and to also understand what role capacitance plays, physically, in this system.

The first method of showing this involves a reference back to an old friend: the probability distribution of the electronic ratchet as a function of voltage $u$, Eq. 4.9. Under a no-load $i = 0$ condition, any resistance change to the whole system (both diodes/resistors equally) given by $R_{\text{change}}$ divides out

$$p(u) = A \exp \left\{- \int du \left[ \left( \frac{R_{\text{change}}}{R_1(u)} + \frac{R_{\text{change}}}{R_2(u)} \right) u \right] / \left( \frac{k T_1 R_{\text{change}}}{R_1(u) C} + \frac{k T_2 R_{\text{change}}}{R_2(u) C} \right) \right\}$$

$$= A \exp \left\{- \int du \left[ \left( \frac{1}{R_1(u)} + \frac{1}{R_2(u)} \right) u \right] / \left( \frac{k T_1}{R_1(u) C} + \frac{k T_2}{R_2(u) C} \right) \right\}$$

where we have already shown earlier in this chapter that, for a particular function $R_2(u)$ there is a unique magnitude for $R_1(u)$ that maximizes our power output – meaning that we must increase/decrease the resistances of both resistors in-ratio.

The second way to show this involves reviving Nyquist noise, a perspective
on this problem we decided was insufficient to model our system early on in our General Theory [Chapter 2] chapter. I stick by that assessment, although it does provide some insight into the role of capacitance in our system.

For the spontaneous voltage fluctuation across the free ends of an open resistor, Nyquist [Nyquist 1928] derived the result

\[ \langle V^2 \rangle = 4RkT\Delta \nu \] (5.17)

where \( R \) is the resistance of the resistor, \( T \) is the temperature of the system, and \( \Delta \nu \) is the bandwidth - the frequency range of the fluctuations. This result relates the voltage fluctuation to the resistance, and is an example of a fluctuation-dissipation theorem [Huang 2001].

We understand that increasing this rms voltage fluctuation increases the power output of our system. Yet, we see no reference to \( C \) at all – how does \( C \) play such a critical role? The key is the bandwidth term \( \Delta \nu \). In theory, if the noise was integrated over all frequencies from \(-\infty \) to \( \infty \) it would have an infinite rms voltage! What limits this bandwidth is our capacitor, which serves as a restoring force. This can be understood explicitly (and experimentally) by noting that a resistor and capacitor in series is a low-pass filter. A low-pass filter is an electronic circuit element that allows through all frequencies lower than a value proportional to \( 1/RC \). Plugging this back in to Nyquist’s theorem we get

\[ \langle V^2 \rangle = 4RkT \frac{1}{RC} = \frac{4kT}{C}. \] (5.18)

We have shown that while resistance is irrelevant in a no-load system: 2. The power output of the system is inversely proportional to the capacitance \( C \).

So then, when is resistance important? When we came to the conclusion that resistance was irrelevant, we looked at Nyquist’s theorem and noted that the resistance \( R \) canceled out because: while the noise was directly proportional to \( R \), the bandwidth was inversely proportional. In order to understand why resistance is important when current is present we have to look at why this canceling occurs.

In a system with a very high resistance we know that the bandwidth is cut down, but at the same time very small drifts in charge (small thermal
fluctuations in electron current) still produce large voltage changes: $V_{\text{large}} = I_{\text{small}}R_{\text{large}}$. In a system with very low resistance we know that the bandwidth is larger, but at the same time even large drifts in charge (a lot of thermal electron current) produce relatively small voltage changes across the resistor: $V_{\text{small}} = I_{\text{large}}R_{\text{small}}$. In either case, when bandwidth is taken into account the $(V^2)$ is the same. The electron drift is the fundamental manifestation of this thermal noise – the potential is a consequence of that drift.

Thus, in the low resistance device we have more current to work with. Ignoring superconductors and other anomalies we see that this makes sense – lower resistance means fatter resistors with more free electrons. Heat up a bigger resistor and you get more current to oppose a load with: 3. The load the system can take is inversely proportional the resistance of the system.

The complications arise when we do the next logical thing to try and increase the power output of the system: put lots of these systems in parallel or in series. Put them in parallel and we’ll increase the load it can take, put them in serial and we should increase the voltage over it, right? Wrong, unfortunately. Decreasing only the capacitance or only the resistance unambiguously increases the power output, but putting two systems in parallel halves the resistance but doubles the capacitance! Likewise, putting two systems in series halves the capacitance but doubles the resistance.

Understanding why putting these into series doesn’t just give us more power is hard to understand intuitively – after all, what if we just black boxed all of these? How do they know that they’re strange thermoelectric power sources and not just ordinary power supplies? Part of the answer to this is the fact that we’re working against an ideal current source which we have to load-match to. If we working against a dissipative resistor or some traditional load, our intuition would be more accurate. Unfortunately, analyzing a system with a dynamic load is incredibly hard to do with the Fokker-Planck equation. In addition, we run into the problem that putting two systems into parallel and then two of those systems into series would halve the resistances and then double them again (vice versa with capacitance) – so that we would have a system with essentially the same properties but that we would expect to produce four times the power.

I have yet to find a palatable theoretical answer for this problem, although for now I have been able to find optimal capacitance and resistance values (measures of parallel-ism and serial-ism if there is such a thing) using numerical
methods. There is an optimal balance for any given load – and yes, increasing the load and rebalancing these values does increase the power output. I just don’t quite understand why yet.

Future work would involve further investigation (theoretical and experimental) into these phenomena and continuing the search for a scale and system where an electronic Brownian motor could produce useful power output.

5.4.2 Methods of Increasing Efficiency

Increasing efficiency is not so complicated as increasing power output. Simply:

4. Efficiency is directly proportional to the non-linearity of the resistors’ voltage response. We commented on this briefly at the start of this section – essentially, the closer our resistors come to step functions with infinite back-resistance the closer we get to our reversibility condition of no heat conductance under a no work condition.

If the resistor did NOT have an infinite backward resistance, it could conduct (and dissipate as heat) electricity which was working with (not against) the load current.

Future work in this direction involves investigating more exotic non-linear resistance elements beyond the traditional silicon diodes. Of particular interest in the near future are field effect transistors (FETs), crystal rectifiers, and Josephson junctions.

5.4.3 Tradeoff between Efficiency and Load

One of the interesting theoretical consequences of analyzing heat engines with a non-equilibrium (Fokker-Planck) equation is that there is an explicit dependence on time. Using a P-V or S-T diagram to determine the work done per cycle for a Carnot or Stirling engine is useful, but does not give a direct dependence on time. To facilitate the reversibility of a Carnot cycle we must allow heat to move “very slowly”; how slowly is very slowly, though? How fast can we repeat the cycle and still maintain high efficiency?

In the electronic ratchet, we note in our results a quantitative tradeoff between efficiency and current load. One can see, in the reversible case of $R_+ = \infty$
in figure 4.3, that the efficiency takes a very characteristically inverse dependence on the current load $i$. Sokolov also derives the following relation analytically

$$\eta \approx \eta_{\text{Carnot}} (1 + 1/i)^{-1}$$

(5.19)

showing the exact quantitative tradeoff between load and efficiency [Sokolov 1999]. This tradeoff is also present in another reversible ratchet, the adiabatic flashing ratchet [Parrondo 1998], which has an even more explicit relation

$$\eta \approx \eta_{\text{Carnot}} (1 + t^{-1})$$

(5.20)

where $t$ is the relaxation time for a single “cycle”. Note that as the time of the cycle gets large $t \gg 1$, the efficiency quickly approaches Carnot, and extending the cycle time exhibits extreme diminishing returns.

This direction of insight doesn’t have any particular application to it – it was just a good answer to a question I’ve had for a long time regarding the quantitative nature of this tradeoff between cycle time and efficiency.

5.4.4 Fluctuation versus Pressure

It is important to note one last direction of inquiry regarding the properties of the ratchet. How do Brownian motors compare to our macroscopic (traditionally ideal gas) heat engines?

To perform this comparison, we will first calculate the magnitude of fluctuation (in a grand canonical ensemble) in relation to number of particles in a system, then magnitude of pressure in relation to the number of particles in a system.

Considering the fluctuations in energy of a grand canonical ensemble, once again from Huang’s discussions [Huang 2001], we find that the variance of energy is given by

$$\sigma_E^2 = \frac{\partial \langle E \rangle}{\partial \beta} = kT^2 \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} = kT^2 C_v$$

(5.21)
The spread in energy about the mean is given by the ratio of the square root of the variance relative to the energy

\[ \frac{\sigma_E}{E} = \frac{\sqrt{kT^2 C_v}}{E}, \]

(5.22)

for an ideal gas \( C_v = 3/2Nk \) and \( E = 3/2NkT \) so that

\[ \sigma_E \frac{E}{E} = \frac{\sqrt{kT^2(3/2)Nk}}{(3/2)NkT} = \frac{1}{\sqrt{3N/2}} \]

(5.23)

So the fluctuations are proportional to \( 1/\sqrt{N} \). However, this is only the percent fluctuation about the energy \( E \) – the absolute rms is simply given by \( \sigma_E = \sqrt{3/2kT \sqrt{N}} \). So we say that the real rms goes up by \( \sqrt{N} \).

The pressure for an ideal gas is given by the ubiquitous

\[ P = NkT/V \]

(5.24)

such that pressure is directly proportional to the number of particles in the system \( N \).

While these results are culled from different ensembles, they are still useful and provide important insights.

The first issue highlighted is that pressure based systems will always provide more output for the same “sized” system, except in the case of a single particle. Pressure is a macroscopic variable anyway, so this may be a contrived example, but it does show that as the a system scales down a fluctuation based engine begins to become comparable to a pressure based engine.

The second issue highlighted is a bizarre property of these fluctuation systems: ten ratchet systems operating each on systems of \( N \) particles produce a different total power output than one ratchet operating on one system with \( 10N \) particles. The ten systems with each \( N \) particles will produce power proportional to \( 10\sqrt{N} \) where the one system will produce power proportional to \( \sqrt{10N} \). This characteristic may shed light on the problems discussed earlier with trying to optimize power output of the electronic ratchet using traditional
circuit analysis techniques.

We believe that the exploration of this relationship between fluctuation and pressure based engines is extremely important and hope to pursue theoretical work on this subject in the near future.
Chapter 6

Unification and Conclusion

Starting from a humble beginning describing non-equilibrium dynamics and explaining the Maxwell demon, we have made significant progress in our endeavor to explore the practicality of an experimental Brownian motor.

Using a numerical simulation, we have predicted that an off-the-shelf diode/resistor based electronic ratchet should provide a measurable voltage due to a thermal ratcheting effect. Furthermore, we predict that the voltage response will be linear with respect to temperature difference by a proportionality constant $C_S = 14.5 \text{pV/}^\circ \text{K}$. An experiment confirming this voltage/temperature relation should also confirm the presence of this effect.

Exploring the region of negative power output (where work is done on the system), we find that: while this electronic ratchet should theoretically be able to act as a refrigerator, the effect is negligible in our “real” diode/resistor system.

We have probed the relation between this thermoelectric ratcheting effect and what is traditionally known as the thermoelectric effect: the Seebeck effect. We have shown that there exists a system where there is a Seebeck voltage but no ratcheting voltage and, conversely, there exists a system where there is a ratcheting voltage and no Seebeck voltage. Thus, we have shown that these effects are indeed independent and also show that for the particular diode/resistor system of interest the Seebeck effect is negligible, giving us just a little bit more confidence in our ability to measure this effect experimentally.
Finally, we have explored a variety of methods to eventually increase both the power output and efficiency of our system. In the process, we’ve gained some strong insight into and understanding of non-equilibrium dynamics, entropy, and the thermodynamic laws.

Now, more than ever, research and understanding of these micro-scale thermodynamics is important. Not just for our own quest for knowledge, but for applications in the coming nanotechnology and biotech revolutions. Misunderstandings of basic physical laws at these scales – or even the ubiquitous macroscopic thermodynamic laws, is sure to cause much woe in the near future.

In fact, this entire thesis came about after reading a popular *Wall Street Journal* recommended book on nanotechnology investment. In one chapter on nanoscale powersupplies the author makes a reference to a Brownian motor/ratchet as a possible solution to our macroscopic energy woes, lauding it as producing free energy! Part of the purpose of this thesis is to bridge this gap between these physics and industry goals and know-how (which will soon intersect).

Of course, we do not limit our thoughts to just industries that may use these results in a very direct way. If you truly consider what a ratchet means, it is nothing more than a device which takes advantage of a non-equilibrium state to produce useful energy. Or, vice versa – using energy to create a non-equilibrium state. This is not in any way limited to mechanical motion, or even electron motion. It finds itself used in any space where any system creates such an effect - from laser cooling apparatuses to a trader on Wall Street. Our ability to understand, unify, and optimize these devices allow us to better comprehend the evolution of the world around us.
Bibliography


Appendix A

The Seebeck Effect

A temperature difference between two points in a conductor or semiconductor will give rise to a corresponding voltage difference between these two points. That is, a temperature gradient in a conductor or semiconductor produces a “built-in” electric field [Kasap 1997]. The effect is known as the Seebeck effect or thermoelectric effect. The Seebeck coefficient denotes the magnitude of this effect in a given material. The thermoelectric voltage created per unit temperature difference between two points is the Seebeck coefficient. Finally, only the net Seebeck voltage between two different conductors can be measured – the thermocouple is based on this principle.

We will presently discuss the basic theory behind the Seebeck voltage in a conductor, in that hopes that we can provide an understanding sufficient to follow arguments made in Comparison to the Thermoelectric (Seebeck) effect [Section 5.3].

A.1 The Seebeck Effect in Conductors

Imagine an aluminum rod that is heated at one end and cooled at the other end, as pictured in figure A.1. If we model the aluminum as an ideal conductor, with a “sea” of free electrons, the hot electrons are more energetic and thus have higher rms velocities than those of the cold ones. Thus, much like ideal gas molecules moving in a convection oven, there is a net diffusion of electrons from
Figure A.1: A temperature gradient along a conductor causes electron diffusion towards the colder end. This non-uniform charge distribution, in turn, gives rise to a potential difference which is known as the Seebeck voltage. [Kasap 1997]

the hot end toward the cold end of the aluminum rod. This electron movement leaves behind exposed positive metal ions in the hot region and simultaneously accumulates electrons in the cold area. This electron movement will continue until the electric field developed between the positive ions and the excess electrons prevents further electron motion. A voltage is thus developed between the hot and cold ends. This potential difference $\Delta V$ across a conductor due to a temperature difference $\Delta T$ is called the Seebeck Effect.

The magnitude of this effect, for a given material, is then given by the Seebeck coefficient and is defined as the potential difference per unit temperature difference

$$S = \frac{dV}{dT}. \quad (A.1)$$

This understanding, while intuitive, is incomplete. In some conductors, the Seebeck coefficient is positive – something which a free electron sea model cannot explain (a positive coefficient implies that electrons diffuse towards the hot end). The complete explanation extends to lattice structures, semi-conductor
physics, Fermi energies, etc. See *Solid State Physics*, by Ashcroft and Mermin [Ashcroft/Mermin 1976] for a more complete discussion.

Nevertheless, this explanation is sufficient for us to see that the Seebeck effect is more similar to a traditional heat engine in its dependence on pressure and convention, not fluctuation (as our ratchet does).
Appendix B

Source Code for Electronic Ratchet Simulation

Included below is the source code that we used to calculate the results presented in Chapter 5. This particular version of the code was used to explore the heat pumping capability of the electronic ratchet, Determining Whether The System is Capable of Pumping Heat [Section 5.2].

The functions of importance, including the two resistance functions \( r_1(u) \) and \( r_2(u) \), probability distribution function, and heat transfer equations, are all located near the end (after the Main function).

All the pertinent values in the simulation: \( k, \) resistance, \( T_1, T_2, \) capacitance, current, etc. are global and defined at the start of the program.

The Main function itself changes depending what we are exploring (for example, it graphed different variables to calculate optimal \( R \) in section 5.1). In this example, it creates an array of \( I \) values, then finds the efficiency for each of these values, graphing these against each other.

Much of the intricacies of the code can be understood by following the comments through the code.
Appendix C

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% Main function/loop
function output = Main(u)
%Global constant
global k
global I
global C
global T1
global T2
global A
global infinity
global resistance

% Init useful variables
k = 1.3806503 * 10^-23; % Boltzmann constant
I = 10^-9; % I is the ideal current source we're doing work against 1-nanoamp
resistance = 200; % backward resistance assuming a forward resistance of 1
C = 5 * 10^-12; % C is the capacitance of the power sink
T1 = 300.0; % Temperature of bath 1 (source bath)
T2 = 299.0; % Temperature of bath 2 (drain bath)
A = 1; % start our normalization constant at something reasonable

% the VALUE for infinity is very testy, it is not always the same it is
% very dependent on starting parameters
infinity = 10^-3; % this has to be determined per case based on the graph check below

% sanity check via graph
% this graph is the probability distribution function
x = linspace(-infinity, infinity, 100);
y = p(x);
plot(x, y)

% create an array of (negative) current values to analyze heat pumping
% ability
In = linspace(-10^-9, 0, 100);

% loop through current values
for n = 1:100
% set current for this run
I = In(n);

% First off, calculate A, the normalization constant of our probability
% distribution function
A = 1;
y = p(x);
% Calculate the normalization constant using a trapezoid rule
Normalization = 1/trapz(x, y);
A = Normalization
n
% reset the probability distribution array we're working with
y = p(x);

% give some output
% find the power output of the system
length = size(y);
for j = 1:length(2)
z(j) = x(j) * y(j);
end
P = trapz(x, z) * I

%find the heat drawn from bath 1
w = heat(x);
Q1 = -trapz(x, w)

%output the efficiency of the system
effic(n) = P/Q1;
end

%plot a graph of efficiency Eta versus current I
figure(2)
plot(In, effic)
output = 0;
end

%Resistor Functions%

%function for the diode
function resist = r1(u)
global resistance

%set threshold bias
V_T = 0.7;

%calculate diode resistance
length = size(u);
for n = 1:(length(2))
    resist(n) = 1 / ( (2.1203 * 10^-9) * (exp(21.298*(u(n) + V_T))) )
end

end

%function for second resistor
function resist = r2(u)
global resistance

resist = resistance;
end

%Probability Distribution Functions%

%function of the integrand take in the p(u) distribution
function integrand = phi(u)

%global variables this integrand needs
global k % Boltzmann constant
global I % I is the ideal current source we're doing work against
global C % C is the capacitance of the power sink
global T1 % Temperature of bath 1 (source bath)
global T2 % Temperature of bath 2 (drain bath)

length = size(u);
for n = 1:length(2)
    numer(n) = ((1/r1(u(n)) + 1/r2(u(n))) * u(n)) + I;
    denom(n) = (((k*T1)/(r1(u(n))*C)) + ((k*T2)/(r2(u(n))*C)));
    integrand(n) = numer(n)/denom(n);
end
end

%function of the probability distribution p(u)
function probability = p(u)
    global A %where A is the normalization constant
    length = size(u);
    for n = 1:length(2)
        probability(n) = A * exp(-quadl( @phi, 0, u(n)));  
    end
end

%heat absorption functions%

%integrand
function integrand = heat(u)

%init the global variables we need
global k
global T1
global T2
global C

%just adapting this setup for use with vectors
length = size(u);
for n = 1:length(2)
    integrand(n) = (((k*T1)/(r1(u(n)*C)) * (p(u(n)) * -phi(u(n))) + (u(n)/r1(u(n))) * p(u(n)))) * u(n);
end
end