LINEAR IRREVERSIBLE THERMODYNAMICS, EFFICIENCY AND COEFFICIENT OF PERFORMANCE OF THERMAL BROWNIAN MOTORS IN TIGHT COUPLING

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By

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The undersigned hereby certify that they have read and recommended to the Faculty of Science School of Graduate Studies for acceptance a thesis entitled "**Linear irreversible thermodynamics, efficiency and coefficient of performance of thermal brownian motors in tight coupling** " by **Anteneh Getachew** in partial fulfillment of the requirements for the degree of **Master of Science in Physics**.

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To my entire parent,especially Girmish and Fitse.

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"..........I love you Eyobed.................."

....my be loved, Tigist M.this is yours and my sister and my brothers........

Addis Ababa, Ethiopia — Anteneh Getachew

Abstract

We analytically study a thermal Brownian motor and calculate exactly the Onsager's coefficients in equilibrium and steady state conditions. We show that the reciprocity relation holds and the determinant of the Onsager's matrix vanishes. Such a condition implies that the device is built with tight coupling. This tells us why Carnot's efficiency can be achieved in the limit of infinitely slow velocities (quasistatic process). We also find the efficiency and the coefficient of performance for our model at these conditions using Onsager's coefficients. The efficiency and the coefficient of performance that we found using the tools of LIT is exactly the same as the Carnot's efficiency and coefficient of performance. Also we find the efficiency (at maximum power) and the maximum coefficient of performance of the Brownian refrigerator to be exactly identical with the the corrosponding results of Curzon - Alhborn and Carnot's refrgerator for perfectly tight coupling model.

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Chapter 1

Introduction

In the most general sense thermodynamics is the study of energy - its transformations and its relationship to the properties of matter. In its engineering applications thermodynamics has two major objectives. One of these is to describe the properties of matter when it exists in what is called an equilibrium state, a condition in which its properties show no tendency to change. The other objective is to describe processes in which the properties of matter undergo changes and to relate these changes to the energy transfers in the form of heat and work which accompany them. Thermodynamics is unique among scientific disciplines in that no other branch of science deals with subjects which are as commonplace or as familiar. Concepts such as "heat", "work", "energy", and "properties" are all terms in everyone's basic vocabulary. Thermodynamic laws which govern them originate from very ordinary experiences in our daily lives. One might think that this familiarity would simplify the understanding and application of thermodynamics.

Basic thermodynamics tells us that a heat engine, while extracting some work, has to transform some amount of heat from a hot reservoir, at temperature T_h, to a cold reservoir, at a lower temperature T_c. The ratio of the useful work, W, extracted to the heat taken from the hot reservoir, Q_h, is called the efficiency, η, of the heat engine; i.e.

$$\eta = \frac{W}{Q_h}. \tag{1.1}$$

It was Carnot who first showed that no heat engine could convert heat to work better than the Carnot engine whose efficiency, η, is given by

$$\eta_c = 1 - \frac{T_c}{T_h}. \tag{1.2}$$

The thermodynamic efficiency increases as T_c decreases. In other words, the lower the temperature of the cold system (to which heat is delivered), the higher the engine efficiency. The maximum possible efficiency, $\eta_c = 1$, occurs if the temperature of the cold source is equal to zero and the temperature of hot source is nonzero. If the reservoir at zero temperature were available as a heat repository, heat could be freely and fully converted into work and the world "energy storage" would not exist [1].

A refrigerator is simply a heat engine operated in reverse. The purpose of this device is to extract heat from the cold system with an input of work and eject that heat into a comparatively hot system. The fraction of the heat taken from the cold reservoir, Q_c, to the applied work, W_{ap}, is called the coefficient of performance of the refrigerator, P_{ref}; i.e.

$$P_{ref} = \frac{Q_c}{W_{ap}}. \tag{1.3}$$

The coefficient of performance of the Carnot refrigerator is given by

$$P_{ref}^{(carnot)} = \frac{T_c}{T_h - T_c}. \tag{1.4}$$

If the temperatures T_h and T_c are equal, the coefficient of performance of the refrigerator becomes infinite; no work is then required to transfer heat from one system to the other. The coefficient of performance becomes progressively smaller as the temperature T_c decreases relative to T_h. And if the temperature T_c approaches zero, the COP approaches zero assuming T_h nonzero. It therefore requires huge amount of work to extract even trivially small quantities of heat from a system near $T_c = 0$.

Even though both macroscopic as well as microscopic engines work with the same principle, extensive studies have been done in the performance of mainly macroscopic heat engine [2]. Nowadays, there is much interest in the study of microscopic heat engines. Some of this interest lies on the need to have microscopic engine in order to utilize energy resources available at microscopic scale, and miniaturization of devices demanding tiny engines operating on the small scale [3]. As such, modelling microscopic engines and finding how well they work (efficiency) is the primary task that has to be considered at present. To understand how microscopic heat engines operate, it is important to take the model that has minimum ingredients. Feynman came up with such a model a few decades ago which is usually called 'ratchet and pawl'. Feynman's 'ratchet and pawl' system [4] is the famous but it was not the first model for microscopic heat engine. Much earlier, Smoluchowski [5] proposed a device called 'Smoluchowski's trap door' which converts motion in a heat reservoir to a useful work. In Feynman's 'ratchet and pawl' system, vanes are put in a box where inside the box there is gas at certain temperature, T_1. The ratchet and pawl sit in another box at different temperature, T_2, and attached to the vanes through an axle.The system is illustrated as shown in Fig.1. The random kick of the gas against the vanes makes the wheel to rotate in the allowed direction enabling it to lift the load, L.

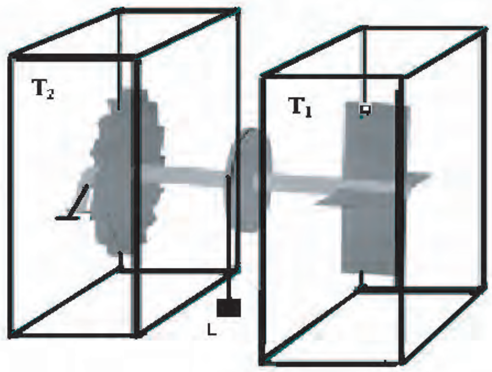

Figure 1.1: Feynman ratchet and pawl [4]

Understanding the Feynman's 'ratchet and pawl' system is important because microscopic heat engine work with the same basic mechanism. In Feynman's 'ratchet and pawl' system the rotation of the wheel (ratchet) can be seen as motion of a Brownian particle in a saw-tooth potential assisted by random kick it gets from the reservoir in which it is in contact. Feynman showed that the efficiency of the system could approach the Carnot efficiency without considering a quasistatic process. However, detailed study of the model by Parrondo et al. [6] showed that this is not so because the device (engine) is simultaneously in contact with two reservoirs that are at different temperature and cannot function as Carnot engine.

Microscopic engines (or molecular motors) can be driven either chemically or thermally. We can model a microscopic engine that moves a Brownian particle in a periodic sawtooth potential under some non-equilibrium process [7]. This non-equilibrium process could come into being due to either external modulation of the potential, or contact with reservoirs at different temperatures or non-equilibrium chemical reaction.

To determine the efficiency of a microscopic engine one can conventionally supply an external load. The work done against the external load in comparison with the heat taken from the hot reservoir determine the efficiency of the engine. However some of the microscopic engines are designed to achieve a high velocity without carrying a load. Eventhough there is no load, work can be done against the viscous frictional force while the particles get transported. We can use the definition of generalized efficiency proposed by Deréneyi et al. [8] to find the efficiency of such an engine.

The idea of a Brownian heat engine working due to nonhomogenous temperature first came up with the works of Büttiker [9], van Kampen [10] and Landauer [11] while they were involved in exposing the significance of the influential papers of Landauer on blow torch effect [12 ,13]. Millionas studied the kinetics of heat engine, which he called as "information engine", relating it to the underlying microscopic thermodynamics [14]. Following Büttiker's work, Matsuo and Sasa [15] took a Brownian heat engine as an example to show that it acts as a Carnot heat engine at quasistatic limit.

Derényi and Astumian [16], after analyzing the details of heat flow in a Brownian heat engine, found that its efficiency can, in principle, approach that of a Carnot engine. The same group later used a model of Brownian heat engine as an example to apply their newly introduced definition of generalized efficiency and find its implications [8]. Later, Hondou and Sekimoto [16] claimed that such a heat engine cannot attain Carnot efficiency due to inevitable irreversible heat flow over the temperature boundary.

There are three arrangements for one dimensional Brownian heat engines. The first arrangement is the Feynmam's 'ratchet and pawl' system where the particle is in contact with two reservoirs, having different temperatures, simultaneously. In the second arrangement, temperature is constant in space but alternates in time between two different temperatures; i.e. the particle is in contact with different reservoirs alternately in time. The third arrangement is where the temperature is constant in time but vary spatially. Our work will consider the third arrangement where we have modelled a thermally driven microscopic engine that moves the Brownian particle in a periodic sawtooth potential assisted by the thermal kick it gets when it is in contact with the hot and cold baths placed alternately along the path.

One of the key concepts in the study of the performance characteristic of Brownian engine is the notion of the efficiency of the energy transduction from the fluctuation [17]. The primary need for the efficient motors arises either to decrease the energy consumption rate and/or to decrease the heat dissipation rate in the processes of operation. The latter concept is of more importance in a nonequilibrium state since there is always an unavoidable and irreversible transfer of heat via fluctuations (in coordinate and accompanying velocity) thereby making less efficient as a motor. Any irreversibility or finite entropy production will reduce the efficiency. Due to this the actual microscopic heat engine that will be designed must consider all these .

For practical application the Carnot efficiency has a limited significance, Indeed a reversible power having no preferred direction in time has to be infinitely slow. Hence the corresponding power is zero (finite work divided by infinite time). Due to this Curzon and Alhborn [18] investigated the problem of efficiency at nonzero power by constructing a Carnot cycle in finite time, in which the only irreversible steps are assumed to be during the transfers of heat between reservoir and auxiliary work-performing system (the so called endoreversible approximation). Also Van de Broeck [19] proposed a general derivation within the realm of linear irreversible thermodynamics. This is the most important feature because it paves the way for analyzing the nonisothermal heat engines using the linear irreversible thermodynamics frame work, a field upto now almost limited to isothermal energy converters. Curzon and Alhborn [18] took an endoreversible engine that exchanges heat linearly at finite rate with the two reservoirs and found its efficiency, η_{CA}, to be

$$\eta_{CA} = 1 - \sqrt{\frac{T_c}{T_h}}. \tag{1.5}$$

On the other hand, B. Jiménez de Cisneros et al. [20] extended the proposal of Van de Broeck [19] to refrigeration cycle and found the maximum coefficient of performance (COP), using the tools of linear irreversible thermodynamics (LIT), to be

$$P_{ref}^{max} = P_{ref}^{carnot}\Phi(q), \tag{1.6}$$

where $\Phi(q) = (\frac{q}{1+\sqrt{1-q^2}})^2$ with the parameter $q^2 = \frac{L_{12}^2}{L_{11}L_{22}}$ defined as the coupling strength and L_{12}, L_{11} and L_{22} are the Onsager's coefficients. The coefficient of performance of the refrigerator becomes 0 (when q = 0) and approaches to that of the Carnot refrigerator COP $P_{ref}^{carnot} = \frac{T_c}{\triangle T}$ when $|q| \longrightarrow 1$. But all did for the efficiency and COP by taking (or constructing) a Carnot type model.

Recently, A. Gomez-Marin and J.M. Sancho [21] studied about tight coupling in thermal Brownian motors. They studied analytically a model of thermal Brownan motor, calculated Onsager's coefficients and showed how the reciprocity relation holds and the determinant of the Onsager matrix vanishes. To do this they considered a Brownian particle moving alternately in hot and cold reservoirs along space and in the limit where the width of the cold region tends to zero. Using the tools of LIT they obtained the Onsager's coefficients around the equilibrium (where the external load is zero, F = 0 and the difference in temperature, $\triangle T$=0). From this they checked Onsager's reciprocity relation and found that the determinant of the Onsager's matrix vanishes.

In our work here, on the other hand, we consider the equilibrium (F = 0 and $\triangle T = 0$) as well as the steady state ($F \neq 0$ and $\triangle T \neq 0$) states in the LIT regime to evaluate the Onsager's coefficients, to check Onsager's reciprocity relation and find whether the determinant of the Onsager's matrix vanishes. Such condition tells us that the device is built with tight coupling and we can operate it in a reversible way at zero entropy production. This agrees with the second law of thermodynamics. Since this explains why Carnot's efficiency can be achieved in the quasistatic process (in the limit of infinitely slow velocities) and gives the fact that the system reaches the Carnot and the Curzon-Alhborn's efficiency bounds.

We have to know that when F = 0 and $\triangle T = 0$, the system is in equilibrium state and therefore no drift of average particles as well as heat flows. But in steady state where $F \neq 0$ and $\triangle T \neq 0$, there is a flow but the **net** flow is zero.

The main goal of this work is to extend the proposal of A.Gomez-Marin and J.M. Sancho [21] for different values of ϵ (temporal asymmetry) of ratchet potential profile. In addition to the above stated, we study the theoretical model for a Brownian motor to show that it has the so called tight coupling property using the tools of LIT. This gives us the basic explanation for the fact that the system reaches Carnot and Curzhon-Alhborn efficiency bounds.

The rest of the thesis is organized as follows. In Chapter two we introduce about irreversible thermodynamics especially the LIT and explain the parameter which is used for defining the Onsager's theory. In Chapter three we consider a model sawtooth potential with hot and cold temperatures alternating periodically along the path in the presence of external load and we find the exact expression for the current generated and thus average drift velocity. In Chapter four we calculate the Onsager's coefficients for the at equilibrium and steady states and also the efficiency and the COP of the Brownian motors and check whether it has tight coupling property or not. In the last Chapter we summarize and conclude the results of our work.

Chapter 2

NON EQUILIBRIUM THERMODYNAMICS

2.1 Introduction

As useful as the characterization of equilibrium states by thermostatic theory has proven to be, it must be conceded that our primary interest, is frequently in processes rather than in states. In biology, particularly, it is the life process that captures our imagination, rather than the eventual equilibrium state to which each organism inevitably proceeds. Thermostatic does provide two methods that permit us to infer some limited information about the process, but each of these methods is indirect and each yields only the most meager return. First, by studying the initial and terminal equilibrium states it is possible to bracket a process and thence to determine the effect of the process, in its totality. Second, if some process occurs extremely slowly, we may compare it with an idealized, nonphysical, quasistatic process. But neither of these methods confronts the central problem of rates of real physical processes. The extension of thermodynamics that has reference to the rate of physical processes is the theory of Irreversible thermodynamics. Irreversible thermodynamics is based on the postulates of equilibrium thermostatic plus the additional postulate of time reversal symmetry of physical laws .

Macroscopic thermodynamics of equilibrium referred to as classical thermodynamics is concerned with macroscopic states of matter, with experimentally observable properties and with energetics of systems exchanging heat, work and/or matter with the surroundings. It rests on two fundamental laws: the balance of energy and the ed second law of thermodynamics. The latter introduces two new concepts, absolute temperature and entropy, and states that entropy never decreases in an isolated system. Classical thermodynamics does not enquire into the mechanism of the phenomena and thus is unconcerned with molecular structure of the systems under investigation. It is a theoretically well founded theory and in the practice a very successful method. Classical thermodynamics is restricted to equilibrium situations. It is correct for equilibrium systems, for reversible (equilibrium) processes and for processes between equilibrium states. Absolute temperature and entropy are defined rigorously and unambiguously only in equilibrium. Outside equilibrium, entropy enters the theory through an inequality only and it is not uniquely defined. The relationships in classical thermodynamics between state variables (e.g. the Gibbs equation) lose their validity in nonequilibrium. The range of application of classical thermodynamics is therefore very narrow. It is in particular unable to describe situations far from equilibrium and the behavior of continuous systems or of complicated materials (materials with memory, nonuniform systems, etc.). Their treatment falls under the head of thermodynamics of irreversible processes which originally tried to overcome these difficulties in two ways: either the existence of absolute temperature and of entropy outside equilibrium was simply assumed or different hypotheses, for example the local equilibrium, were used.

Unlike classical thermodynamics, which is one universal theory, thermodynamics of irreversible processes presents several faces. We shall review besides classical irreversible thermodynamics only the most important macroscopic theories, the extended irreversible thermodynamics and the rational thermodynamics. Some other theories, such as the so-called entropy-free thermodynamics or the theory of hidden variables, will not be discussed as they are of a rather special nature. In addition to the phenomenological macroscopic theories there exist also microscopic theories of irreversible thermodynamics. They facilitate a deeper insight and their importance will in our opinion still grow in the future. We mention the methods based on the kinetic theory of gases and on the fluctuation theories, and in particular the more general methods and theories rooted in nonequilibrium statistical mechanics. For example, the linear response theory based on the fluctuation-dissipation theorem which relates the phenomenological parameters to the nature of microscopic dynamics and fluctuations. These theories lie beyond the scope of this treatise, however, and they will not be analyzed here.

2.2 Classical irreversible thermodynamics

Classical irreversible thermodynamics (CIT) as developed by Onsager, Prigogine (Nobel prize winners for chemistry in 1968 and 1977, respectively) and many others, forms the base for all the later formulations of irreversible thermodynamics. It has to be emphasized that it is based on the concept of local equilibrium. This fundamental hypothesis assumes that the system can be split mentally into cells which are sufficiently large to be treated as macroscopic thermodynamic subsystems but, at the same time, sufficiently small that equilibrium is very close to being realized in each cell. The hypothesis thus postulates that the local and instantaneous relations between the thermal and mechanical properties of a physical system are the same as for a uniform system at equilibrium. This implies that all the variables of equilibrium thermodynamics remain significant and that all the relationships of classical thermodynamics between state variables remain valid outside equilibrium provided that they are stated locally at each instant of time. That means particularly that entropy outside equilibrium depends on the same variables as at equilibrium and that the Gibbs equation is here correct. The central concept of CIT is the rate at which entropy is produced during an irreversible process. It has been since the origin of irreversible thermodynamics related experimentally to the well- known empirical laws like Fourier's, Fick's or Ohm's. The rate of local entropy production σ follows from the general entropy balance equation

$$\frac{\partial(s)}{\partial t} = -\nabla.J + \sigma, \tag{2.1}$$

with

$$\sigma \geqslant 0. \tag{2.2}$$

Here s is the local specific entropy, J_s is the local entropy flux (contains two terms: one is due to heat conduction and the other is due to matter flow) and σ which can be related to irreversible process such as heat conduction, diffusion and chemical reaction. Eq :(2.2) is in agreement with the second law of thermodynamics. The basic distinction here between reversible and irreversible processes, since only the irreversible ones contribute to entropy production.

The basic formula for the rate of entropy production of the irreversible process can be written in the simple form,

$$\frac{dS}{dt} = \sum_k J_k \mathcal{F}_k \tag{2.3}$$

where J_k is the thermodynamic fluxes (for example heat flux, diffusion, chemical reaction) and $\mathcal{F}_k$ is the conjugated generalized forces (gradients of temperature, gradients of chemical potential, affinities). That means, the rate of production of entropy is the sum of products of each flux with the associated force. Evidently, all J_k and $\mathcal{F}_k$ vanish at equilibrium. The existence of a non-negative entropy production is one of the main points underlying CIT. The further is the existence of linear constitutive laws. They postulate that the fluxes J_k and the generalized forces $\mathcal{F}_j$ are related linearly as

$$J_k = \sum_j L_{kj} \mathcal{F}_j. \tag{2.4}$$

The equations are called phenomenological equations and the coefficients L_{kj} phenomenological (kinetic)coefficients. Experimental evidence and theoretical considerations in statistical mechanics have confirmed that a wide class of processes can be described by means of linear relations between fluxes and forces. This is true in particular for transport processes. The phenomenological coefficients are subjected to the rule of selectivity limiting the possibility of interference between irreversible processes of different tensorial character and they are dominated by the Onsager's reciprocal relations which state that

$$L_{kj} = L_{jk}. \tag{2.5}$$

It is, when the flow J_k corresponding to the irreversible process k is influenced by the force $\mathcal{F}_j$ of the irreversible process j, then the flow J_j is also influenced by the force F_k through the same coefficient. The Onsager's relation belongs to the most significant results of CIT. They were originally based only on experiments, but they are motivated today usually on a molecular base and were shown to be a consequence of the time-reversal invariance of the microscopic dynamics. The validity of these relations has been challenged on the microscopic level, but they are generally accepted to be correct at the macroscopic level. Experimental tests showed that they are particularly a powerful tool for linear processes and studying coupled phenomena, like thermodiffusion, thermoelectric and thermomagnetic effects. CIT is the most successful method of irreversible thermodynamics and it turned out to be very useful in many practical situations. Its current tasks are the linear transport phenomena, the coupled phenomena, the mixtures and chemical kinetics. It must be conceded however that the theories underlying it are not general and are of an approximative character. They are correct only near equilibrium and the hypothesis of local equilibrium is only consistent with local and instantaneous relations between fluxes and forces. There are also several limitations on the microscopic level, but they will not be discussed here. Efforts have been made to enlarge the range of applications of CIT and they led to the formulations of Extended irreversible thermodynamics and Rational thermodynamics.

Generally we conclude that classical (linear) irreversible thermodynamics is based on the fundamental hypothesis of local equilibrium. The validity of the results of equilibrium thermodynamics is thus anticipated at the outset. The classical method turned out to be very useful in many practical situations, but the theories underlying it are not general and they are of an approximative character. The method is inadequate to treat situations far from equilibrium or systems with complicated inner structures (example: bodies with memory).

Extended irreversible thermodynamics is no longer based on the local-equilibrium hypothesis but it generalizes and enlarges the classical theory. It introduces besides the classical thermodynamic variables the dissipative fluxes as new independent variables. To compensate for the lack of evolution equations, supplementary rate equations for the dissipative fluxes are introduced. The central thermodynamic result is the generalized Gibbs equation. The statements behind this theory are confirmed by the kinetic theory of gases and by statistical mechanics.

Rational thermodynamics presents a very rigorous mathematical formalism and it abandons the hypothesis of local equilibrium. It is a phenomenological and macroscopic theory which ignores the molecular structure and assumes that materials have a memory. Its main objective is to derive constitutive equations which must meet a certain number of a priori postulates.

The thermodynamics theory of irreversible processes is based on the Onsager reciprocity theorem and Onsager's theory begins with the assumption that the linear phenomenological laws are valid. In the following sections we will discuss about affinities and fluxes, the linear phenomenological laws, reciprocal relation and irreversible process and the symmetry principle and finally we will get an expression for the total rate of entropy production which help us to find the fluxes and the flows for efficiency calculation.

2.3 Affinities and fluxes

De Donder defined the affinity as the product of a thermodynamic force and a thermodynamic flow. Or it is the driving force for chemical reactions. A nonzero affinity implies that the system is not in equilibrium and that the chemical reactions will continue to occur driving the system towards equilibrium.

To start our discussion of Onsager's theorem, we define certain quantities that appropriately describe irreversible processes. Basically we require two parameters: One is to describe the "force" that drives a process and the other is to describe the response to this force. The processes of most general interest occur in continuous systems such as the flow of energy in a bar with a continuous temperature gradient. However, to suggest the proper way to choose parameters in such continuous systems, we first consider the relatively simple case of a discrete system. A typical process in discrete system would be the flow of energy from one homogeneous subsystem to another through an infinitely thin diathermal partition. Consider a composite system composed of two subsystems. An extensive parameter has values X_k and $X_{k'}$ in the two subsystems, and the closure condition requires that

$$X_k + X_{k'} = X_k^0, \tag{2.6}$$

be a constant. If X_k and $X_{k'}$ are constrained, their equilibrium values are determined by the vanishing of the quantity

$$\mathcal{F}_k = (\frac{\partial S^0}{\partial X_k})_{X_k^0}, \tag{2.7}$$

$$\mathcal{F}_k = (\frac{\partial (S + S')}{\partial X_k})_{X_k^0}, \tag{2.8}$$

$$\mathcal{F}_k = \frac{\partial S}{\partial X_k^0} - \frac{\partial S'}{\partial X_{k'}}, \tag{2.9}$$

$$\mathcal{F}_k = F_k + F_{k'}. \tag{2.10}$$

where F_k, S, S' and $F_{k'}$ are the thermodynamic force and the entropy of k and k' subsystems, respectively. Thus, if $\mathcal{F}_k$ is zero the system is in the equilibrium, but for nonzero $\mathcal{F}_k$ an irreversible process occurs, taking the system toward the equilibrium. The quantity $\mathcal{F}_k$, which is the entropy representation of intensive parameter, acts as a "generalized force" which "drives" the process. Such generalized forces are called *affinities*. For definiteness, consider two subsystems separated by a diathermal wall, and let X_k be the energy U. Then the affinity is

$$\mathcal{F}_k = \frac{1}{T} - \frac{1}{T'}. \tag{2.11}$$

No heat flows across the diathermal wall if the difference in inverse temperature vanishes. But a nonzero difference in inverse temperature, acting as a generalized force, drives a flow of heat between the subsystems. For example, if X_k is the volume, the affinity, $\mathcal{F}_k$, is $[\frac{P}{T} - \frac{P'}{T'}]$, where P and P' are the pressures of the corresponding subsystem and if X_k is the mole number, the associated affinity is $[\frac{\mu'_k}{T'} - \frac{\mu_k}{T}]$, where μ and μ' are the chemical potential of the corresponding subsystem. We characterize the response to the applied force by the rate of change of the extensive parameter X_k. The flux J_k is defined by

$$J_k = \frac{dX_k}{dt}. \tag{2.12}$$

Therefore, the flux vanishes if the affinity vanishes or constant in time, and a nonzero affinity leads to a nonzero flux. It is the relation between fluxes and affinities that characterizes the rates of irreversible processes. The identification of the affinities in a particular type of system is frequently rendered more conveniently by considering the rate of production of entropy. Differentiating the entropy $S(X_0, X_1, ...)$ with respect to the time, we have

$$\dot{S} = \sum_k \frac{\partial S}{\partial X_k} \frac{dX_k}{dt}, \tag{2.13}$$

from which one can write

$$\dot{S} = \sum_k \digamma_k J_k. \tag{2.14}$$

The entropy production equation is particularly useful in extending the definition of affinities to continuous system rather than to discrete systems. If heat flows from one homogeneous subsystem to another, through an infinitely thin diathermal partition, the generalized force is the difference $[\frac{1}{T} - \frac{1}{T'}]$; but if heat flows along a metal rod, in which the temperature varies in a continuous fashion it is difficult to apply the previous definition of the affinity.

2.4 The linear phenomenological laws

When a system is close to equilibrium, both forces and flows have linear relations and the rate of entropy production per unit volume is defined in Eq:(2.3). In which $\digamma_k$ are forces, such as the gradient of $\frac{1}{T}$ and J_k are flows, such as the heat flow. The forces drive the flows; a non vanishing gradient $\frac{1}{T}$ causes the flow of heat. At equilibrium all forces and the corresponding flows vanish, i.e. the flows J_k are function of forces $\digamma_k$ such that they vanish when $\digamma_k = 0$. For a small deviation in the forces from their equilibrium value of zero, the flows can be expected to be linear functions of the forces. In other words the flows are assumed to be analytic functions of the forces as in the case with most physical variables. From equation Eq:(2.4) we must note that not only can a force such as gradient $\frac{1}{T}$ cause the flow of heat but it can also drive other flows such as a flow of matter or an electrical current. The thermoelectric effect is one of such cross effect, in which a thermal gradient drives not only a heat flow but also an electrical current and vice versa. For conditions under which the linear phenomenological laws are valid, entropy production takes the quadratic form which can be found by combining Eq:(2.3) and (2.4) as

$$\dot{S} = \sum_{k} \sum_{j} \mathcal{F}_k L_{kj} \mathcal{F}_j. \tag{2.15}$$

Here $\mathcal{F}_k$ can be positive or negative. A matrix that satisfied the condition Eq: (2.4)is known as positive definite. The properties of positive definite matrices are well characterized. For example, a two dimensional matrix L_{jk} is positive definite only when the conditions: $L_{11} > 0$, $L_{22} > 0$ and $(L_{12} + L_{21})^2 < 4L_{11}L_{22}$. are satisfied. In general, the diagonal elements of a positive definite matrix must be positive. In addition, a necessary and a sufficient condition for a matrix L_{kj} is that its determinant and all the determinants of the lower dimension obtained by deleting one or more rows and columns must be positive. Thus according to the Second law " the proper coefficients", L_{kk} should be positive; the "cross coefficients", can have either definite.

2.5 The symmetry principle

Though forces and flows are coupled in general, the possible coupling is restricted by general symmetry principle. This principle which states that macroscopic causes always have fewer or equal symmetries than the effects they produce was originally proposed by Pierre Curie but not in the context of thermodynamics. It was introduced by Pigogine into non-equilibrium thermodynamics because it enables us to eliminate the possibility of coupling between certain forces and flows on the basis of symmetry. For example a scalar thermodynamic force such as chemical affinity which has the high symmetry of isotropy, can not drive a heat current which has lower symmetry because of its directionality. As an Example, let us consider a system in which there is heat transport and chemical reaction. The entropy production is

$$\dot{S} = J_q.\nabla\frac{1}{T} + \frac{A}{T}v, \tag{2.16}$$

where A is the affinity and v is the velocity of the reaction. The general phenomenological laws that follow from this are

$$J_q = L_{qq}\nabla\frac{1}{T} + L_{qc}\frac{A}{T}, \tag{2.17}$$

and

$$v = L_{cc}\frac{A}{T} + L_{cq}\nabla\frac{1}{T}. \tag{2.18}$$

According to the symmetry principle, the scalar processes of chemical reaction, due to its higher symmetry of isotropy and homogeneity, cannot generate a heat current which has a direction and hence an isotropy. Another way of stating this principle is that a scalar cause can not produce a vectorial effect. There fore L_{qc}= 0. As a consequence of the reciprocal reactions, we have L_{qc}=L_{cq} = 0.

In general, irreversible processes of different tensorial character (scalars, vectors, and higher order tensors) do not couple to each other. Because of the symmetric principle, the entropy production due to scalar, vectorial and tensorial process should each be positive. In the above case, we must have $J_q.\nabla\frac{1}{T} \geq 0$ and $\frac{A}{T}v \geq 0$. Thus, the symmetry principle provides constraints for the coupling and entropy production, due to irreversible process.

2.6 Reciprocal relation and irreversible process

When two or more irreversible transporting process (heat conduction, electrical conduction and diffusion) take place simultaneously in a non equilibrium thermodynamic the process may interfere with each other. Thus an electric current in a circuit that consist of different metallic conductors will in general cause evolution or absorption of heat at the junctions (Peltier effect). Conversely, if the junctions are maintained at different temperatures an electromotive force will usually appear in the circuit, the thermoelectric force: the flow of heat has tendency to carry the electricity along. Linear irreversible thermodynamics is based on the assumption of local equilibrium and the linear relation between the fluxes and the forces as

$$J_1 = L_{11}X_1 + L_{12}X_2, \tag{2.19}$$

and

$$J_2 = L_{21}X_1 + L_{22}X_2. \tag{2.20}$$

From which the total rate of entropy production becomes

$$\dot{S} = X_1J_1 + X_2J_2. \tag{2.21}$$

and this can be rewritten in a compact form as

$$\dot{S} = \ (X_1, X_2)\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} . \tag{2.22}$$

From this Chapter we have got basic tools about LIT, such as Onsager's coefficient and the linear relationship between the flows and the forces and also we have good expression for the total rate of entropy production which will help us for Chapter four.[1]

[1] *This Chapter on nonequilibrium thermodynamics is based on the works of [1], [22], [23] and [24] .

Chapter 3

STOCHASTIC MODEL AND EQUATION OF MOTION

3.1 Introduction

In this Chapter using the condition we have, we are going to derive the Steady State Solution and Probability Current Density and the average drift velocity.

3.2 Stochastic model and equation of motion

Consider the Brownian particle in a highly viscous medium moving along one dimensional asymmetric sawtooth potential of period λ with the external load of period λ, the potential due to external force (load) and barrier height, U_0 which is subjected to a nonhomogenous temperature background that changes periodically with the same as the potential (see Fig.3.1). The potential and the temperature profiles are given

by

$$U(q) = \begin{cases} \frac{U_0}{\lambda_1} q + Fq & \text{for } 0 \leq q < \lambda_1 \\ \frac{U_0}{\lambda_2}(-q + \lambda) + Fq & \text{for } \lambda_1 \leq q < \lambda, \end{cases} \tag{3.1}$$

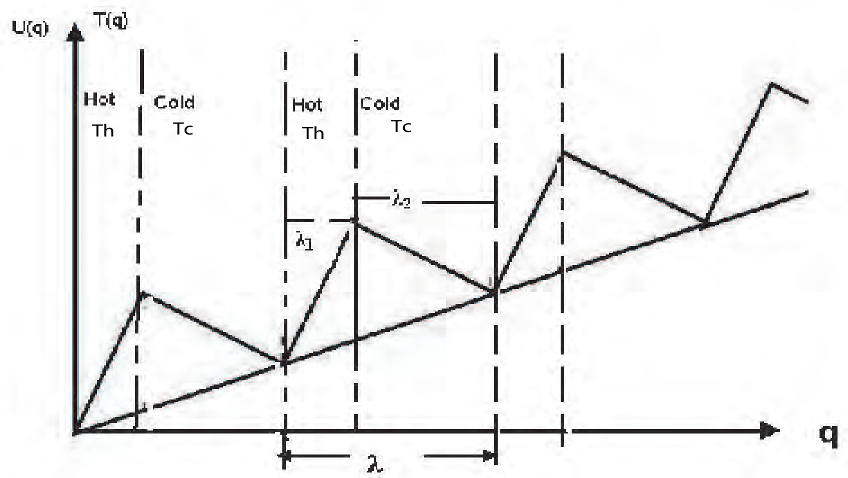

Figure 3.1: periodic sawtooth potential with load where hot and cold regimes alternate in space.

and

$$T(q) = \begin{cases} T_h & \text{for } 0 \leq q < \lambda_1 \\ T_c & \text{for } \lambda_1 < q \leq \lambda, \end{cases} \tag{3.2}$$

respectively. Here $\lambda = \lambda_1 + \lambda_2$ where λ_1 is the length of the hot reservoir and λ_2 is the length of the cold reservoir. The dynamic of the Brownian particle is governed by the Langeivin equation

$$m\ddot{q}(t) = -\gamma\dot{q}(t) - U'(q) - F + \eta(t), \tag{3.3}$$

where γ is the coefficient of friction, F is the external load, m is the mass of the Brownian particle, q(t) is the position of the particle, $U'(q)$ is the space derivative of the potential, $\ddot{q}(t)$ is the acceleration of the particle, $\dot{q}$(t) is the velocity of the particle and $\eta(t)$ is a randomly fluctuating force satisfying the Gaussian white noise with mean zero and autocorrelation

$$\langle \eta(t)\eta(t') \rangle = 2k_B T(q)\gamma\delta(t-t'). \tag{3.4}$$

Here k_B is the Boltzmann's constant and $\delta(t-t')$ is the Dirac delta function where the coefficient with the Dirac delta function is called the noise intensity.

In the high friction limit the dynamics of Eq: (3.3) is over damped so that the inertial term, $m\ddot{q}(t)$, can be neglected and Eq: (3.3) reduces to:

$$\dot{q}(t) = -\frac{U'(q)+F}{\gamma} + \frac{1}{\gamma}\eta(t). \tag{3.5}$$

3.3 The steady state probability current density

Due to the asymmetric saw-tooth potential and the position dependant temperature background shown in Fig.(3.1), there is a directed transport of Brownian particle in the foreword direction provided that the parameter used in our model is of interest. In this section, using the Fokker-Planck equation corresponding to the Langevin equation Eq: (3.5) the steady state solution of probability density which is normalized over the period λ is calculated. Then the constant probability current density, J_0, is obtained in the presence of load.

We can rewrite Eq: (3.5) following Ito's prescription [25] as

$$dq(t) = -(\frac{U'(q)+F}{\gamma})dt + \sqrt{\frac{2k_B T(q)}{\gamma}}dW(t), \tag{3.6}$$

where

$$\eta(t) = \sqrt{2k_B T(q)\gamma}\xi(t), \tag{3.7}$$

and

$$dW(t) = \xi(t)dt, \tag{3.8}$$

is the Wienner process.

In order to obtain the probability density of finding the Brownian particle at a position q and at time t, we have to find the FPE corresponding to the Langevin equation Eq: (3.5). The Fokker-Planack equation corresponding to the Langevin equation Eq: (3.6) is

$$\partial_t P(q,t) = \frac{\partial}{\partial q}\Big[\frac{U'(q)+F)P}{\gamma} + \frac{\partial}{\partial q}(\frac{k_B T(q)P}{\gamma})\Big], \tag{3.9}$$

where P(q , t) is the probability density of finding the particle at position q and time t and γ is taken to be the same through out the medium. In the presence of thermal source, the probability density induced by Langevin equation obey the Fokker-Planck equation in the form of conservation law for probability [26] as

$$\partial_t P(q,t) + \partial_q J(q,t) = 0, \tag{3.10}$$

where J(q , t) is the probability current density at position q and time t. Comparing Eq: (3.9) and Eq: (3.10) one can obtain the expression for current, J, to be

$$J(q,t) = -\frac{(U'(q)+F)P}{\gamma} - \frac{\partial}{\partial q}(\frac{k_B T(q)P}{\gamma}). \tag{3.11}$$

In the steady state condition the probability density is independent of time, i.e $\partial_t P(q,t) = 0$, and the steady state solution for the probability density, $P_s(q)$, can be solved first to get the constant steady state current density from the equation

$$\frac{dP_s(q)}{dq} + \frac{(U'(q)+F)P_s}{k_BT(q)} = -\frac{\gamma J_0}{k_BT(q)}. \tag{3.12}$$

Multiplying both sides of equation Eq: (3.12) by an integrating factor

$$\psi(q) = \exp \int_0^q \frac{(U'(q)+F)}{k_BT(q)}dq', \tag{3.13}$$

and using the periodicity condition for probability density as

$$P_s(q) = P_s(q+\lambda). \tag{3.14}$$

along with the normalization condition

$$\int_0^\lambda P(q)dq = 1, \tag{3.15}$$

we get the expression for the steady state current density, J_0, to be

$$J_0 = \frac{\frac{k_B}{\gamma}(1-\exp(\frac{V_1}{k_BT_h} - \frac{V_2}{k_BT_c}))}{k_BD(\frac{\lambda_1^2}{V_1} - \frac{\lambda_2^2}{V_2}) + k_B^2AB(\frac{\lambda_1}{V_1}+\frac{\lambda_2}{V_2})(\frac{\lambda_1T_h}{V_1}+\frac{\lambda_2T_c}{V_2})}. \tag{3.16}$$

(The expressions for values V_1, V_2, A, B and D are given in Appendix .)

For asymmetric potential profile ($\lambda_1 \neq \lambda_2$) one can redefine λ_1 and λ_2 such that, $\lambda_1 = \frac{\lambda}{2}(1+\epsilon)$ and $\lambda_2 = \frac{\lambda}{2}(1-\epsilon)$ for $|\epsilon| \leq 1$ and get an expression for the mean velocity interms of the steady state current (for k_B=1) to be

$$v = \frac{\frac{\lambda}{\gamma}(1-\exp(-U_0\alpha + \frac{F\lambda}{2}(-\alpha\epsilon+\beta)))}{D_1\frac{\lambda^2}{4}(4U_0\epsilon - F\lambda\epsilon^3) + A_1B_1C_1}, \tag{3.17}$$

where

$$\alpha = \frac{1}{T_c} - \frac{1}{T_h},$$
$$\beta = \frac{1}{T_c} + \frac{1}{T_h},$$

$$A_1 = 1 - \exp(-U_0 + \frac{F\lambda(1-\epsilon)}{2T_c}),$$
$$B_1 = 1 - \exp(U_0 + \frac{F\lambda(1-\epsilon)}{2T_h}),$$
$$D_1 = 1 - \exp(-U_0\alpha + \frac{F\lambda}{2}(-\alpha\epsilon + \beta)),$$

and

$$C_1 = (\frac{U_0\lambda^2}{2})(U_0\frac{\lambda}{2}(T_h + T_c) - \frac{F\lambda}{2}(1-\varepsilon^2)\triangle T + U_0\epsilon\triangle T).$$

In a symmetric potential profile (i.e. $\lambda_1 = \lambda_2 = \frac{\lambda}{2}$) with zero constant load the expression for current density in Eq: (3.16) reduces to a simple expression

$$J_0 = \frac{U_0^2}{2k_B\gamma\lambda_1^2(T_h + T_c)}(\frac{1}{\exp\frac{U_0}{k_BT_h} - 1} - \frac{1}{\exp\frac{U_0}{k_BT_h} - 1}). \tag{3.18}$$

Therefore, once we get the average drift velocity of the Brownian particle, we can easily calculate the total rate of entropy production, rate of work done, mean rate of heat flux released from the hot reservoir and absorbed by the cold reservoir.

Chapter 4

Stochastic Energetics

4.1 Introduction

An engine is designed to perform a certain task. How efficiently the engine performs the task given to it is an essential issue. Conventionally, some force (or load) should be applied so that the work done against the load compared with the input energy determines the efficiency of the engine. However some of the microscopic engines like motor protein are designed to achieve a high velocity with out carrying load [27]. When such an engine moves with a velocity, v, work can be done against the viscous friction even in the absence of load. The engine dissipates an energy, $\gamma v \lambda$ or power γv^2 due to friction, where γ is the coefficient of friction and λ is the distance that the engine moves. In order to maintain the motion, the engine should get a minimum input heat or energy (or input power) other wise no drift will occur. Even if there is no external force (or load) one can take the minimum energy input, E_{in}^{min} (or minimum power in put, P_{in}^{min}), as the energy output E_{out} (or power out put ,P_{out}) and compare it with the input energy source (or power source). If the task is performed in the most favorable condition, the efficiency goes to unity. In the absence of load, the efficiency,

η, of such a microscopic heat engine will be given by

$$\eta = \frac{P_{out}}{P_{in}} = \frac{\gamma v^2 \lambda}{P_{in}}. \tag{4.1}$$

The expression for the minimum power input or power output in the presence of the external force (load), F, is given by

$$P_{out} = P_{in}^{min} = (F + \gamma v)\lambda v. \tag{4.2}$$

from which efficiency will be given by

$$\eta = \frac{P_{out}}{P_{in}} = \frac{(F\lambda + \gamma v \lambda)v}{P_{in}}. \tag{4.3}$$

These Eq:(4.2) and Eq:(4.3) enable us to compare and characterize the efficiency of the microscopic heat engines in various conditions.

4.2 Stochastic Energetics

The main importance in the study of microscopic engine is their energetics such as the power consumption of the machine, efficiency of energy conversion of the machine and so on. In this section we will try to find the energy extracted by the Brownian particle from the hot reservoir Q_h, work done by the engine W, efficiency η, and coefficient of performance per cycle in the regime of linear irreversible thermodynamics (see Fig. 4.1 and 4.2 below).

As we can see the model acts as a heat engine when the current is to the right and as a refrigerator when the current is to the left. The particle undergoes a cyclic motion, during each cycle it is in contact with the hot region of length λ_1 and then with the cold region of length λ_2. During this we consider energy flows between the

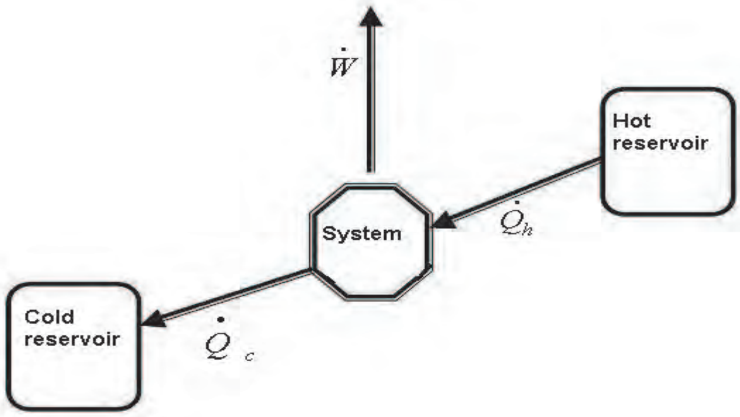

Figure 4.1: Energetics of a thermal motor: rate of heat flow $\dot{Q}_h$ from the hot source at T_h gets into the system S and mechanical work at a rate of $\dot{W}$ is performed at the same time that rate of heat flow $\dot{Q}_c$ is delivered to the cold source at T_c.

region by neglecting energy transfer via kinetic energy when the particle crossing the boundary between the two regions[7,8]. When the particle moves through the hot region, it gains energy, Q_h, which enables it to climb up the potential, U_0 + F λ_1, and to over come the viscous drag force $\gamma v \lambda_1$ (v is its average drift velocity). That is

$$Q_h = U_0 + (F + \gamma v)\lambda_1. \tag{4.4}$$

Similarly, the cold region will absorb energy as the particle moves through the cold region while some energy will be lost due to the drag force in the cold region. Therefore the net heat absorbed by the cold region, Q_c, will be

$$Q_c = U_0 - (F + \gamma v)\lambda_2. \tag{4.5}$$

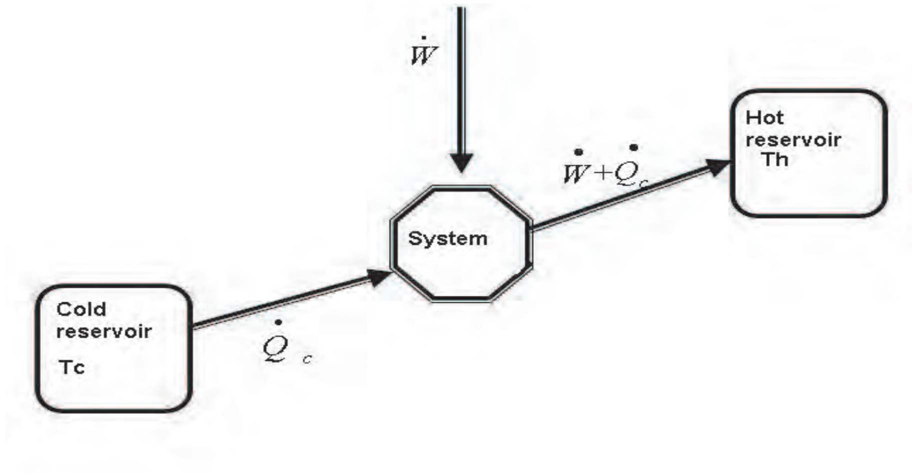

Figure 4.2: Energetics of a refrigerator motor: rate of heat extracted $\dot{Q}_c$ from the cold source at T_c by doing mechanical work at a rate of $\dot{W}$ on the system S and delivered to the hot source at T_h.

The net work done, W, by the system (engine) in one cycle is

$$W = (F + \gamma v)\lambda, \tag{4.6}$$

where $\lambda = \lambda_1 + \lambda_2$.

Multiplying both sides of Eqs: (4.4), (4.5) and (4.6) by J, where the average drift velocity, v = J λ and taking the case where $\lambda_1 = \lambda_2 = \frac{\lambda}{2}$, we have the expression for the rate of work done against an external load and viscous force

$$\dot{W} = -(F + \gamma v)v, \tag{4.7}$$

and mean rate of heat flux released from the hot reservoir

$$\dot{Q}_h = \Big(\frac{2U_0}{\lambda} + F + \gamma v\Big)\frac{v}{2}, \tag{4.8}$$

while the mean rate of heat flux absorbed by the cold reservoir

$$\dot{Q}_c = \Big(\frac{2U_0}{\lambda} - (F + \gamma v)\Big)\frac{v}{2}. \tag{4.9}$$

According to the the non equilibrium thermodynamics the rate of entropy production is given by

$$\dot{S} = \frac{-\dot{Q}_h}{T_h} + \frac{\dot{Q}_h}{T_c} - \frac{\dot{W}}{T_c}. \tag{4.10}$$

Now this expression can be recast in terms of second order form involving the thermodynamic forces as

$$X_1 = \frac{(F + \gamma v)}{T_c}, \tag{4.11}$$

and

$$X_2 = \frac{\triangle T}{T_c T_h}. \tag{4.12}$$

where the difference in temperature $T_h - T_c = \triangle T$, therefore in the linear response regime we have

$$\dot{S} = -X_1 v + X_2 \dot{Q}_h. \tag{4.13}$$

Let us write a heat flux, $\dot{Q}_h$, and a drift velocity, v, in terms of X_1 and X_2 to the leading order of X_1 and X_2 near equilibrium up to first order. That is

$$\begin{pmatrix} v \\ \dot{Q}_h \end{pmatrix} = \begin{pmatrix} \frac{\partial v}{\partial X_1} & \frac{\partial v}{\partial X_2} \\ \frac{\partial \dot{Q}_h}{\partial X_1} & \frac{\partial \dot{Q}_h}{\partial X_2} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \tag{4.14}$$

which leads to the identification of the corresponding Onsager's coefficients. We obtain the coefficients with the derivation of V and $\dot{Q}_h$ and evaluate near equilibrium at two different cases (at $v = 0$, i.e. $\triangle T$ =0 and $\triangle T \neq 0$). Using Eq: (4.13) the rate of entropy production can be written as

$$\dot{S} = \ (X_1, X_2)\begin{pmatrix} v \\ \dot{Q}_h \end{pmatrix}. \tag{4.15}$$

From phenomenological laws, near equilibrium we have

$$\dot{S} = \ (X_1, X_2) \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix}. \tag{4.16}$$

Using Eq: (4.14), (4.15) and (4.16) we have

$$L_{11} = \frac{\partial v}{\partial X_1}, L_{12} = \frac{\partial v}{\partial X_2}, L_{21} = \frac{\partial \dot{Q}_h}{\partial X_1}, L_{22} = \frac{\partial \dot{Q}_h}{\partial X_2}. \tag{4.17}$$

Now let us define the new parameter, τ,to describe T_h in terms of T_c as

$$T_h = (1+\tau)T_c, \tag{4.18}$$

where $\tau \geq 0$.

And from Eq: (3.16) the condition at which the current changes its direction is the boundary demarcating the domain of operation of the engine as a refrigerator from that as a heat engine. The force at which this demarcating boundary occurs is known as the stall force and is given by

$$F_0 = \frac{2U_0\alpha}{\lambda(2+\tau(1-\epsilon)}. \tag{4.19}$$

Evaluating the derivatives of v and $\dot{Q}_h$ with respect to X_1 and X_2 at F = F_0 as

$$\frac{\partial v}{\partial X_i}|_{F=F_0}, \tag{4.20}$$

and

$$\frac{\partial \dot{Q}_h}{\partial X_i}|_{F=F_0}, \tag{4.21}$$

where $i = 1, 2$ we get explicit expression for Onsager's coefficients by considering four different cases.

CASE 1: For $\epsilon = 1$, we have $\lambda_2 = 0$ and F $= \triangle T = 0$ and $T_c \backsimeq T_h$ the matrix elements of L are:

$$L_{11} = \frac{T_h}{\gamma}\Big(\frac{\frac{U_0}{2T_h}}{\sinh(\frac{U_0}{2T_h})}\Big)^2, \tag{4.22}$$

$$L_{12} = \frac{-U_0 T_h}{\lambda\gamma}\Big(\frac{\frac{U_0}{2T_h}}{\sinh(\frac{U_0}{2T_h})}\Big)^2, \tag{4.23}$$

$$L_{21} = \frac{-U_0 T_h}{\lambda\gamma}\Big(\frac{\frac{U_0}{2T_h}}{\sinh(\frac{U_0}{2T_h})}\Big)^2, \tag{4.24}$$

and

$$L_{22} = \frac{U_0^2 T_h}{\lambda^2\gamma}\Big(\frac{\frac{U_0}{2T_h}}{\sinh(\frac{U_0}{2T_h})}\Big)^2. \tag{4.25}$$

This is the work of A. Gomez-Marin and J.M. Sancho [21] studied about tight coupling of thermal Brownian motors by taking the case in the limit of the cold region going to zero which is trivial and couldn't generally explain the tight coupling property of the thermal Brownian motors.

CASE 2: For ϵ=1, we have $\lambda_2 = 0$ and the force F=F_0 written as

$$F_0 = \frac{U_0\alpha}{\lambda}. \tag{4.26}$$

The expression for the matrix elements are, therefore, given as

$$L_{11} = \frac{T_c}{\gamma}\Big(\frac{\frac{U_0}{2T_c}}{\sinh(\frac{U_0}{2T_c})}\Big)^2, \tag{4.27}$$

$$L_{12} = \frac{-U_0(1+\tau)T_c}{\lambda\gamma}\Big(\frac{\frac{U_0}{2T_c}}{\sinh(\frac{U_0}{2T_c})}\Big)^2, \tag{4.28}$$

$$L_{21} = \frac{-U_0(1+\tau)T_c}{\lambda\gamma}\Big(\frac{\frac{U_0}{2T_c}}{\sinh(\frac{U_0}{2T_c})}\Big)^2, \tag{4.29}$$

and

$$L_{22} = \frac{U_0^2(1+\tau)^2 T_c}{\lambda^2\gamma}\Big(\frac{\frac{U_0}{2T_c}}{\sinh(\frac{U_0}{2T_c})}\Big)^2. \tag{4.30}$$

CASE 3: For $\epsilon = 0$, we have λ_1 =λ_2=$\frac{\lambda}{2}$ and F = $\triangle T = 0$ (i.e. $T_c \backsimeq T_h$) the matrix elements of L are:

$$L_{11} = \frac{T_h}{\gamma}\Big(\frac{\frac{U_0}{2T_h}}{\sinh(\frac{U_0}{2T_h})}\Big)^2, \tag{4.31}$$

$$L_{12} = \frac{-U_0 T_h}{\lambda\gamma}\Big(\frac{\frac{U_0}{2T_h}}{\sinh(\frac{U_0}{2T_h})})^2, \tag{4.32}$$

$$L_{21} = \frac{-U_0 T_h}{\lambda\gamma}(\frac{\frac{U_0}{2T_h}}{\sinh(\frac{U_0}{2T_h}\Big)})^2, \tag{4.33}$$

and

$$L_{22} = \frac{2U_0^2 T_h}{\lambda^2\gamma}\Big(\frac{\frac{U_0}{2T_h}}{\sinh(\frac{U_0}{2T_h})}\Big)^2. \tag{4.34}$$

CASE 4: For $\epsilon = 0$, λ_1=λ_2=$\frac{\lambda}{2}$ and F = F_0 that is at

$$F_0 = \frac{2U_0\tau}{\lambda(2+\tau)}, \tag{4.35}$$

we have

$$L_{11} = \frac{T_c}{\gamma}\Big(\frac{\frac{U_0}{T_c(2+\tau)}}{\sinh(\frac{U_0}{T_c(2+\tau)})}\Big)^2, \tag{4.36}$$

$$L_{12} = \frac{-2U_0T_c}{\lambda\gamma}(\frac{1+\tau}{2+\tau})\Big(\frac{\frac{U_0}{T_c(2+\tau)}}{\sinh(\frac{U_0}{T_c(2+\tau)})}\Big)^2, \tag{4.37}$$

$$L_{21} = \frac{-2U_0T_c}{\lambda\gamma}(\frac{1+\tau}{2+\tau})\Big(\frac{\frac{U_0}{T_c(2+\tau)}}{\sinh(\frac{U_0}{T_c(2+\tau)})}\Big)^2, \tag{4.38}$$

and

$$L_{22} = \frac{4U_0^2T_c}{\lambda^2\gamma}\Big(\frac{1+\tau}{2+\tau}\Big)^2\Big(\frac{\frac{U_0}{T_c(2+\tau)}}{\sinh(\frac{U_0}{T_c(2+\tau)})}\Big)^2. \tag{4.39}$$

By comparing Eq: (2.22) and Eq: (4.15) we have the particle flux which is given as

$$J_1 = v, \tag{4.40}$$

and the heat flux given as

$$J_2 = \dot{Q}_h. \tag{4.41}$$

The Onsager coefficients offer a lot of information about the intrinsic non equilibrium thermodynamic properties of the system. From above we have checked that the reciprocity relation $L_{12} = L_{21}$ (the cross coupling), is full filled and this tells us the system is reversible and the diagonal elements L_{11} and L_{22} are positive as they should be. And from Eq: (2.19) and Eq: (2.20) these elements have direct physical meaning. For $X_1 = 0$, we have $\dot{Q} = L_{22}\frac{\triangle T}{T^2}$, so that $\frac{L_{22}}{T^2}$ is the coefficient of thermal conductivity. Similarly, for $X_2 = 0$, we have V $= L_{11}\frac{F}{T}$, therefore $\frac{L_{11}}{T}$ is the mobility of the system in response to the external force.

4.3 Calculating the efficiency and coefficient of performance using Onager's coefficients

The thermodynamic engine efficiency is defined in terms of fluxes of heat and work and this consequently operationally measurable. Thus a Carnot cycle provides us with an operational method of measuring the two temperature. The Carnot efficiency is the efficiency at zero power out put and an ideal one. But to obtain a non zero power out put the extraction of heat from the high temperature reservoir and the insertion of heat in to the low temperature reservoir must each be done irreversibly. An endoreversible engine is defined as one in which the two process of heat transformation (from and to the heat reservoir) are the only irreversible process in the cycle.

Efficiency:

$$\eta = \frac{-X_1 T_c J_1}{J_2}. \tag{4.42}$$

Substituting the value of J_1 and J_2 in the above equation from Eq: (2.19) and Eq: (2.20) we get

$$\eta = \frac{\triangle T}{T}\Big(-\zeta\frac{L_{11}}{L_{21}}\Big)\Big(\frac{\zeta+\frac{L_{12}}{L11}}{\zeta+\frac{L_{22}}{L_{21}}}\Big), \tag{4.43}$$

where $\zeta = \frac{X_1}{X_2}$.

When v= 0, it means that there is no flow such that such that

$$X_1 = \Big(\frac{-L_{12}}{L_{11}}\Big)X_2. \tag{4.44}$$

From $det(L) = 0$, and Eq: (4.44) we get an expression for Eq: (4.31) to be

$$\eta = \frac{\triangle T}{T_h}\Big(\frac{L_{12}}{L_{21}}\Big). \tag{4.45}$$

This tells us unless $L_{12} = L_{21}$ we will not attain the Carnot efficiency. Therefore, for the four cases of our model the reciprocity relation holds and our result becomes the

Carnot efficiency. That is

$$\eta = \frac{\triangle T}{T_h}. \tag{4.46}$$

By imposing

$$\frac{\partial \dot{W}}{\partial X_1} = 0, \tag{4.47}$$

for fixed value of X_2 to the equation to Eq: (4.7) we have maximum power at

$$X_1^{max} = \Big(\frac{-L_{12}}{2L_{11}}\Big)X_2. \tag{4.48}$$

By substituting the force X_1^{max}, the efficiency evaluated at maximum power to be

$$\eta = \frac{1}{2}\frac{\triangle T}{T_h}\Big(\frac{q^2}{2-q^2}\Big). \tag{4.49}$$

In the optimal limit of perfectly coupled systems, $|q| \to 1$, it is half of the Carnot efficiency and this value coincides with the Curzon-Alhborn efficiency when $\frac{T_c}{T_h}$ is very small.

Coefficient of Performance(COP): We start with analysis of the heat engine shown in the Fig.(4.2). This device extracts a refrigeration load Q_c from a cold space at a temperature T_c by the the expenditure of power $\dot{W}$. So referring the definition of COP in chapter one we have

$$P_{ref} = \frac{\dot{Q}_c}{\dot{W}}. \tag{4.50}$$

$$P_{ref} = \frac{J_2}{X_1 T_h J_1}. \tag{4.51}$$

Assuming that X_2 be constant and from the usual linear relation between forces and fluxes through the direct and cross coupling coefficients, we have

$$P_{ref} = \frac{T_c}{\triangle T}\Big(\frac{-1}{\zeta}\frac{L_{21}}{L_{11}}\Big)\Big(\frac{\zeta + \frac{L_{22}}{L_{21}}}{\zeta + \frac{L_{12}}{L11}}\Big). \tag{4.52}$$

From $det(L) = 0$ and Eq: (4.52) we get an expression for Eq: (4.57) as

$$P_{ref} = \frac{T_c}{\triangle T}\Big(\frac{L_{21}}{L_{12}}\Big). \tag{4.53}$$

For the four cases of our model the reciprocity relation holds true near equilibrium and thus the coefficient of performance of the model converges to the coefficient of performance the Carnot refrigerator. That is

$$P_{ref} = P_{ref(carnot)} = \frac{T_c}{\triangle T}. \tag{4.54}$$

also by imposing

$$\frac{\partial \dot{Q}_c}{\partial X_1} = 0, \tag{4.55}$$

for fixed value of X_2 to the equation to Eq: (4.9) we have maximum COP at

$$X_1 = -X_2\sqrt{\frac{L_{22}}{L_{11}}}\Big(\frac{1+\sqrt{1-q^2}}{q}\Big). \tag{4.56}$$

By substituting the force X_1, the maximum COP evaluated to be

$$P_{ref}^{max} = \frac{T_c}{\triangle T}\Big(\frac{q}{1+\sqrt{1-q^2}}\Big)^2 \tag{4.57}$$

For $|q| \rightarrow 1$,it will converge to COP of Carnot's refrigerator.

The above results imply that, near equilibrium, a macroscopic device operating between two reservoirs either can act as a heat engine and as a refrigerator if L_{12}=L_{21} $\neq$o or will exhibit neither behavior if L_{12}=$L_{21} = 0$. For instance, in a microscopic ratchet and pawl device, if the sawtooth on the wheel have a symmetric shape, the system cannot behave as a heat engine: $L_{12} = 0$, as is obvious by symmetry. What is not so immediately obvious but follows from the condition L_{12}=L_{21}, is that it is impossible for a system with symmetric teeth to operate as a refrigerator.

Chapter 5

Summary and discussion

We consider a simple model of microscopic thermal engine that is the extension of the Feynman's ratchet and pawl system described by a Langevin equation which allows us to find closed form of expression of the thermodynamic quantities (for example: free energy, rate of entropy producton, heat flux, current density etc) . We designed them to transport Brownian particle in a periodic sawtooth potential with external load driven by the thermal kicks the particle gets from alternately placed hot and cold heat reservoirs along the path. In our model, we assumed the particle to be moving in a highly viscous medium and found the exact expression for the stationary current density, J_0 and the average velocity, v. Using the tools of LIT, we found the matrix elements of Onsager's coefficients and checked that the determinant vanishes. This indicates that our model can operate in a reversible regime at zero entropy production which agrees with the second law of thermodynamics both in equilibrium and steady state conditions. Using this law we found the coupling strength of our model which is equal to one and this tells us that the force and the flows are perfectly coupled. Moreover, the efficiency converges to the exact limit of Carnot efficiency in the quasistatic limit.

As we mentioned in Chapter one, the works of Van de Broeck [18], the efficiency at maximum power goes to the Curzon-Alhborn efficiency when the coupling strength is one ($|q| = 1$). Similarly, on the works of the Cisneros et al. [20] the COP of a refrigerator goes to the COP of the Carnot refrigerator. Therefore, for a perfectly tight models, we can achieve the Carnot efficiency and COP of the Carnot refrigerator. For nonperfectly tight coupling ($|q| < 1$), since there will be a leak of heat, efficiency becomes far lower than the Carnot's efficiency.

We can anticipate two scenarios in which our system acts as "useful" device.

1. For $\dot{W} > 0$ and $\dot{Q}_c > 0$, the system acts as a heat engine, causing the particle to drift to the colder regime. When $v = 0$, "the thermal force" exerted on the particle due to the temperature difference between the reservoirs, exactly balances the external load acting against it at the boundary and as such the system no longer acts as a heat engine.

2. For $\dot{W} < 0$ and $\dot{Q}_c < 0$ the system acts as a refrigerator, since the effect of doing work on the system leads to a heat flux leaving the cold system. In other words, since a thermal gradient drives the system against an external mechanical force, due to the cross coupling of the system (L_{12} and L_{21} coefficients), then an external mechanical force can lead to a thermal gradient opposing the one that already exists. Therefore, any system that can work as an engine, has a region in the parameter space (which may be too small to set, nearly impossible) in which it will work as a refrigerator. The transition from the engine mode of operation to that of refrigerator is determined by Eq: (4.19).

In conclusion, we believe that our work has, for the first time, found analytic expression of Onsager's coefficient, rate of entropy production, efficiency and coefficient of performance for the thermal Brownian motors in equilibrium and steady state conditions for different values of spatial asymmetry(ϵ) of sawtooth potential in the presence of external force. Microscopic heat engines require minimum ingredients for the engine to work properly. These theoretical results proposes the extents and the limits to be considered in the design of actual microscopic heat engine. Lastly,there are two points to be mentioned in connection with this work. Firstly, we have limited our consideration to the overdamped motion of the Brownian particle. Secondly, we have neglected the transfer of energy between the hot and the cold sources via kinetic energy when the particles recross the boundaries. For the future, we will extend our study without neglecting the transfer of energy via kinetic energy in the underdamped regime.

Appendix

$$V_1 = U_0 + F\lambda_1, \tag{5.1}$$

$$V_2 = U_0 - F\lambda_2, \tag{5.2}$$

$$A = 1 - \exp\frac{V_2}{k_B T_c}, \tag{5.3}$$

$$B = 1 - \exp\frac{V_1}{k_B T_h}, \tag{5.4}$$

$$D = \exp\frac{V_1}{k_B T_h} - \exp\frac{V_2}{k_B T_c}. \tag{5.5}$$

Bibliography

[1] H.B. Callen, *Thermodynamics and introduction to thermostatistics* 2^{nd} edition (John Wiley and Sons, 1985).

[2] B. Anderson, P. Salamon, and R. S. Berry, Phys. Today **37**, 62 (1984).

[3] Mesfin Asfaw and Mulugeta Bekele Eur. Phys. J. B **38**, 456 (2004).

[4] R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, Vol. **I**, Chapter 46 (Addison-Wesely, MA, 1963).

[5] P. A. Sordos and W. H. Zurek, Am. J. Phys. **60**, 867 (1992).

[6] J.M.R. Parrando and P. Espanol, Am. J. Phys. **64**, 1125 (1996).

[7] I. Derènyi, and R. D. Astumain, Phys. Rev.E **59**, 6219 (1999).

[8] I. Derènyi, M. Bier and R. D. Astumain, Phys. Rev. Lett. **83**, 903 (1999).

[9] M. B*ü*ttiker, Z. Phys. **68**, 161 (1987).

[10] N. G. van Kampen, IBM J. Res. Dev. **32**, 107 (1988).

[11] R. Landauer, J. Stat. Phys. **53**, 233 (1988).

[12] R. Landauer, Phys. Rev. A **12**, 636 (1975).

[13] R. Landauer, Helv. Phys. Acta **56**, 847 (1083) .

[14] M. M. Millonas, Phys. Rev. Lett. **74**, 10 (1995).

[15] Miki Matsuo and Shin-ichi Sasa, Physica A **276**, 188 (1999).

[16] Tsuyoshi Hondou and Ken Sekimoto, Phys. Rev. E **62**, 6021 (2000).

[17] Linke H., Downtown M. and Zuckermann M. Choas **15**, 026111 (2005).

[18] F. L. Curzon and B.Alhborn, Am. J. Phys. **43** 22 (1975).

[19] Van de Broeck, Phys. Rev. Lett. **95**, 190602 (2006).

[20] B. Jim*é*nez de Cisneros, L. A. Arias-Hern*á*dez and A. Calvo Hern*á*ndez Phys. Rev. E. **73**, 057103 (2006).

[21] A.Gomez-Marin and J.M. Sancho Phys. Rev. E **74**, 062102 (2006).

[22] Dilip Kondepudi, *Modern Thermodynamics From Heat Engine to Dissipative Structures* (John Wiley and Sons, 1998).

[23] A.B. Pippard, *Elements of Classical Thermodynamics* (Cambridge University Press, Cambridge, 1966).

[24] IVAN VAVRUCH Chem.Listy **96**, 271-275 (2002) .

[25] C. W. Gardiner, *Handbook of stochastic methods for Physcis, Chemistry and Natural science* 2^{nd} edition (Spiringerverlag, Berlin, 2003).

[26] H.Risken, *The Fokker Planck equation: Methods of Solution and Applications* (Springer-Verlag. Berlin 1989).

[27] F. Julicher A. Ajdari and J. Prost Rev. Mod. Phys. **69**, 1269 (1997).

DECLARATION

I hereby declare that this thesis is my original work and has not been presented for a degree in any other university. All sources of material used for the thesis have been duly acknowledged.

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