Studies in the optimization of power output of steady-state heat engines

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A dissertation submitted for the partial fulfilment of BS-MS dual degree in Science

Supervised by

Professor R.S. Johal

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Certificate of Examination

This is to certify that the dissertation titled "Studies in the optimization of power output of steady-state heat engines" submitted by Shashank Prakash (MS14057) for the partial fulfilment of BS-MS dual degree programme of the Institute has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Satyajit Jena	Dr. Abhishek Chaudhuri	Prof. R.S. Johal
		(Supervisor)

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Professor R.S. Johal at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Shashank Prakash

(Candidate)

Dated: April 20, 2019

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Prof. R.S. Johal

(Supervisor)

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Abstract

With the advancement in technologies, miniaturization of machines, and using waste energy as an input for heat engines or refrigerator is occurring at a tremendous rate. In today's world, a big challenge is to make these machines more efficient, as even small heat leaks could bring a considerable change in its performance. This thesis is dedicated to studying the power optimization of two kinds of heat engines which operate in the steady-state regime, while being in contact with two heat reservoirs at different temperatures:-

(i) TEG: Thermoelectric generator (TEG) is basically a heat engine that converts heat flux (temperature differences) directly into electrical energy through a phenomenon called the Seebeck effect. Generally, TEGs are quite inefficient and expensive, but considerably less bulky than heat engines. In recent time a lot of research is going on optimizing its power as it could be used in power plants in order to convert waste heat into additional electrical power and in automobiles as automotive thermoelectric generators (ATGs) to increase fuel efficiency. Another application is radioisotope thermoelectric generators which are used in space probes, which has the same mechanism but use radioisotopes to generate the required heat difference. In this report we are trying to optimize the power of a thermoelectric generator (TEG) under a particular model, considering internal and external irreversibilities. Then we find efficiency at maximum power (EMP) and try to infer the series expansion of efficiency around Carnot efficiency.

(ii) Brownian heat engines: In recent times, Brownian microscopic heat engines

have drawn much attention for the utilization of energy resource available at the microscopic scale for nanomachines. Brownian heat engines are spatially asymmetric but periodic structures connected to the reservoirs at different temperatures. The microscopic description of these machines could be given using the Langevin equation. However, for our purposes, we only need a macroscopic description of the system. Our work includes power optimization of the model considering irreversible heat flow due to kinetic energy exchange and infers its behavior near equilibrium. Further, we would like to get a bound in efficiency and investigate conditions where it could achive well-known efficiencies such as Carnot or Curzon-Ahlborn (C.A) efficiency. It may not be important for a practical purpose but it would certainly give insight to the theoretical aspects.

Contents

1 Introduction

This thesis is divided into three sections that are, Theory, TEG (Thermoelectric generator), and B.H.E (Brownian heat engine). The first section is devoted to the study of the underlying theory and mathematical background needed for the succeeding parts, and in the next two sections, we will examine the power optimization of Thermoelectric generator and Brownian heat engine under a particular model considering external and internal irreversibility in the system.

In the first section, we will discuss the early formalism of equilibrium thermodynamics and its application to study theoretical details of heat engines. Further, we will study how the thermodynamic ideas were generalized for the non-equilibrium systems which led to the development of irreversible thermodynamics. At the end of this section, we will discuss the general outline of the thermodynamics for a Brownian particle connected to a heat bath.

In the second section, we will investigate the microscopic transport properties which lead to thermoelectric effects. Then using the microscopic transport equations for thermoelectric material, we will derive the macroscopic heat flux equations for the T.E.G and ultimately use them to get the expression for power. Next, we analytically optimize the power of T.E.G and try to infer it's efficiency near equilibrium.

In the third section will study the microscopic behavior of Brownian particles under the action of periodic and asymmetric potential connected to two reservoirs at different temperatures, and how this set up could be used as a microscopic heat engine. However, we will not study the microscopic description of this model. Instead, we will model it using macroscopic picture analogous to Feynman Ratchet model. Once we set up the model as a heat engine, we analytically optimize its power and find efficiency at maximum power (E.M.P). Then we scrutinize its behavior near equilibrium and compare it to Feynman Ratchet model.

2 Theory

Thermodynamics is a phenomenological description of a macroscopic system. It's like working in a black box. We do not know the internal working of the system, but we could write thermodynamic laws based on the observation, and that's the beauty of the subject. However, the thermodynamic results could be derived from the fundamental laws of physics using a probabilistic approach, which we do in statistical mechanics.

2.1 Equilibrium Thermodynamics

As the name suggests it is a phenomenological description of equilibrium properties of a system. But what is "equilibrium"?

Every system has a tendency to evolve towards a state in which the properties are determined by intrinsic factors and not on previously applied external influence. Such terminal states are called Equilibrium state. These states do not change with time.

For example, consider an ideal gas in adiabatic wall kept as shown in the Fig(2.1). with initial pressure P_1 and atmospheric pressure P_2. Now as time evolves, it expands and comes in equilibrium state as shown in the figure. This state has no memory of past and stays in this state unless otherwise disturbed. Now equilibrium thermodynamics does not comment on how it reaches equilibrium but on the equilibrium properties. It provides an elegant theory to calculate thermodynamic quantities such as heat, work, energy, entropy, etc when the system is in a well defined "equilibrium state".

Now once we define equilibrium state of system we have following laws —

- **Zeroth law:** If two systems A and B are separately in equilibrium with C, then they are in equilibrium with each other. It implies that each system in equilibrium could be specified entirely by its macroscopic parameters such as Internal energy (U), Entropy(S), Volume(V), Temperature(T), etc.

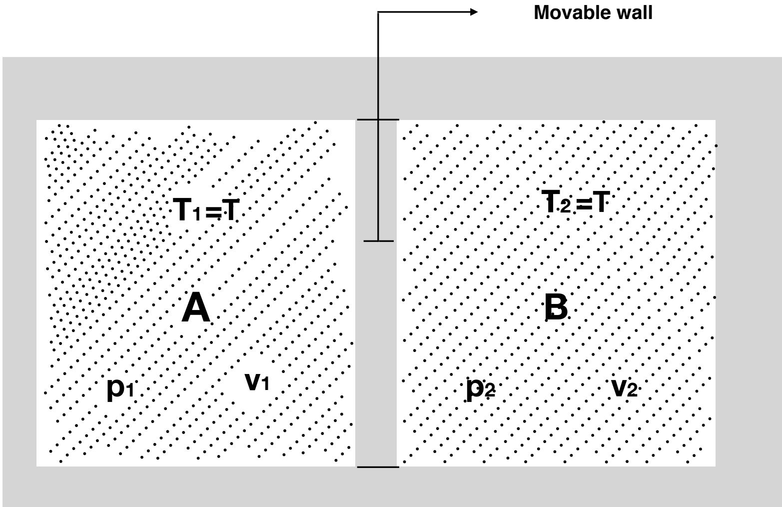


Figure 2.1: Schematic diagram of two gases, at pressure P_1 and P_2 and volume V_1 and V_2 at temperature T, connected to each other by a movable wall.

- **First law:** This law is the energy conservation equation for the system. It states that change in internal energy of the system to go from one equilibrium state to another equals heat supplied to the system plus work done on the system. In differential form it could be written as,

$$du = dq + dw.$$

By further considering the process to be quasi-static (sufficiently slow, so that system is always in an equilibrium state) and reversible we could write,

$$dq = Tds$$
$$dw = \sum_i J_i dx_i.$$

Where J_i is generalized force and dx_i is generalized displacement. For example, if a system is in a magnetic field, then generalized force is the

Types Of Works	Generalized Force	Generalized displacement	Work (F.dX)
Boundary (expansion or compression)	Pressure (P)	Volume (V)	-P.dV
Spring Force	F	Displacement (X)	F.dX
Elastic	F_e	Displacement (é)	F_e.dé
Torsion	F_t	Angle (ø)	F_e.dø
Surface deformation	Ś	Area (a)	Ś.da
Electromotive force	E	Charge (q)	E.dq
Electric Polarization	É	P	E.dP
Magnetic Polarization	H	M	H.dM

Figure 2.2: Table containing list of different generalized forces, generalized displacements and work done by them.

applied magnetic field (H) while generalized displacement is the magnetic moment (M). List of different generalized force and generalized displacement is given in the Fig(2.2).

So our final equation for firsr law of thermodynamics is,

$$du = Tds + \sum_i J_i dx_i.$$

- **Second law:** Second law could be stated in different forms and all of them are equivalent [10].

  (i) The total entropy of an isolated system can never decrease over time.
  (ii) Clausius statement: Heat cannot spontaneously flow from colder body to hotter body.
  (iii) Kelvin statement: It is impossible to devise a cyclically operating thermal engine, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.

This Law gives directionality to a physical process, i.e. nature allows only those process which increase the total entropy of the universe. We will come back to this point later.

- **Third law:** The entropy of a system approaches a constant value as its temperature approaches absolute zero.

2.2 Heat Engines

One of the early triumphs of thermodynamics was to give a limit on maximum useful work that could be extracted from a system. Before the second law was well established, people came up with all sort of theoretical model for the perpetual machine or heat engine where all heat could be transformed into mechanical work. These models followed all the physical laws, but still, never worked. Later on, it was realized that they all violated the second law of thermodynamics and that there is an intrinsic upper bound on the mechanical work that could be extracted from the system.

2.2.1 Carnot Engine:

It is an idealized heat engine which operates between two reservoir with temperature T_h and T_c, with $T_h > T_c$.It takes Q_h amount of heat from hotter reservoir and dumps Q_c amount of heat in colder reservoir and does a work "W", as shown in the Fig(2.3). Where W is,

$$W = Q_h - Q_c$$

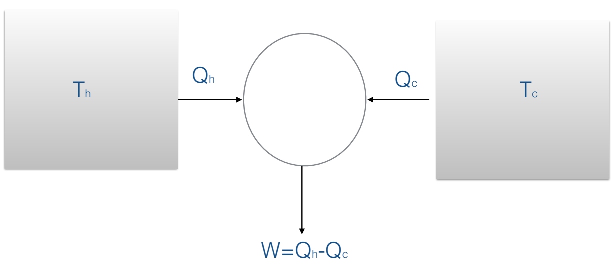


Figure 2.3: Shematic diagram of an heat engine

we define Efficiency(η) of engine as the ratio of work extracted from the engine to heat taken by the engine.

$$\eta_c = 1 - Q_c/Q_h$$

and

$$W = \eta_c Q_h$$

Carnot engine has following properties——

- It is cyclic i.e. the working medium comes back to its initial state after one cycle[10].
- It is reversible i.e., it could be run backward by reversing the input and output.
- Its efficiency depends only on the ratio of operating temperatures.

Now any engine following this criteria is equivalent to a Carnot engine. Next we prove that all such engines have same efficiency, which indeed is the maximum efficiency that could be achieved by any heat engine.

Suppose we have an engine with efficiency greater than that of Carnot engine i.e, $\eta > \eta_c$, where η_c is Carnot efficiency.

Now work extracted from this engine could be used to run the Carnot engine reversibly as shown in the Fig(2.4).

Q'_h= heat extracted by the engine from hotter reservoir.
W'= Work done by the engine. Now by definition,

$$W' = \eta Q'_h \tag{1}$$

and Q'_c= heat dumped by the engine to colder reservoir.

Now this work is used to run the Carnot engine backwards therefore, Q_h= heat

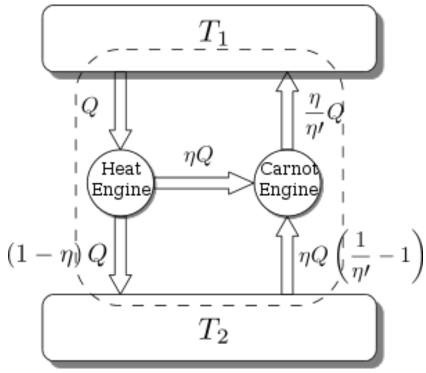


Figure 2.4: Schematic diagram of an engine connected to Carnot engine

dumped by the Carnot engine to hotter reservoir, which is

$$Q_h = W/\eta$$

, now using Eq.(1),

$$Q_h = Q'_h\eta/\eta_c. \tag{2}$$

and Q_c= heat taken from cold reservoir by Carnot engine, Now

$$Q_c = (1-\eta_c)Q_h$$

using equation 2,

$$Q_c = (1-\eta_c)Q'_h\eta/\eta_c. \tag{3}$$

Now, looking at the combined engine of two we see that if

$$Q_h - Q'_h > 0$$

,i.e using Eq.(1) and Eq.(2).

$$Q_h - Q'_h > 0 \Rightarrow Q'_h(\eta/\eta_c - 1) \Rightarrow \eta > \eta_c. \tag{4}$$

then it takes $Q_c - Q'_c$ amount of heat from cold reservoir and dumps it to hot reservoir. where

$$Q_c - Q'_c = Q_h - Q'_h$$

but this violates Kelvin's statement that, it is impossible to devise a cyclically operating thermal engine, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work. Hence our initial assumption must be wrong, So we arrive at the conclusion that Carnot engines have maximum efficiency. Similarly by connecting two Carnot engines we could show that both must have same efficiency.

Next we try to find the upper bound of this efficiency and to do so we construct a Carnot engine using ideal gas. It runs between two isotherms T_h and T_c, joined by adiabatic curve as shown in Fig(2.5)(P-V curve).

So it takes Q_h heat from hot reservoir and expand isothermally $a \rightarrow$ b, then it expands adiabatically from b$\rightarrow$ c, then it compresses isothermally from c$\rightarrow$ d and dumps Q_c heat to cold reservoir and then returns to its initial state adiabatically via d$\rightarrow$ as shown in Fig(2.5). and since the engine is reversible so total entropy

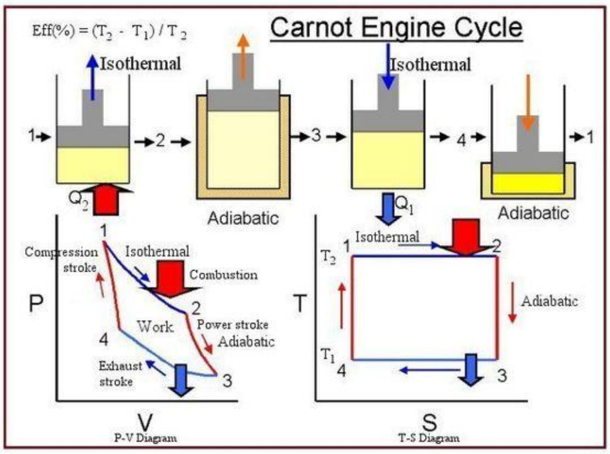


Figure 2.5: P-V diagram and S-T diagram of an Ideal gas Carnot engine.

production must be zero. Now entropy production due to gas is O, as it returns back to its initial state and entropy production due to reservoir is,

$$\frac{Q_c}{T_c} - \frac{Q_h}{T_h} = S$$

where S=total entropy production and,

$$S = 0 \Rightarrow Q_c/T_c = Q_h/T_h \Rightarrow Q_c/Q_h = T_c/T_h \Rightarrow \eta < \eta_c. \quad (5)$$

hence using Eq.(5),

$$\eta_c = 1 - (Q_c/Q_h) = 1 - (T_c/T_h). \quad (6)$$

Now, on surface it may seem that Carnot engine is the best choice for heat engine as its efficiency is maximum that could be achived, but it is quite impractical as it would take infinite time to run through one cycle.

2.2.2 Irreversible heat engines

As we looked earlier that Carnot engine put an upper bound on efficiency But quite impractical as it takes infinite time to make one cycle. In more realistic situations heat engines must incorporate irreversibilities. We, will look more general formalism to incorporate irreversibility in later section. For now we will try to model irreversibility in a heat engine.Now, Irreversibility could either be external or internal.

- **Endoreversible model:** Here we assume that there is no internal irreversibility, like friction, is present in the system and all the irreversibility is external. That is for heat exchange between reservoir and engine, there must be some temperature difference as shown figure.To incorporate external irreversibility we use Finite time thermodynamics(FTT). Here we take into account that it takes finite time for heat to transfer from hotter medium to colder one. This could be understood well using C-A model

  Under C-A model [5], the heat engine operates between two intermediate temperature as shown in the Fig(2.6(a)). Let it takes $\dot{Q}_h$ heat from hot reservoir and dumps $\dot{Q}_c$ heat to cold reservoir per second. We assume that engine runs continuously and heat transfer follows Newton's law of cooling.Then,

$$\dot{Q}_h = K_h(T_H - T_h) \quad (7)$$

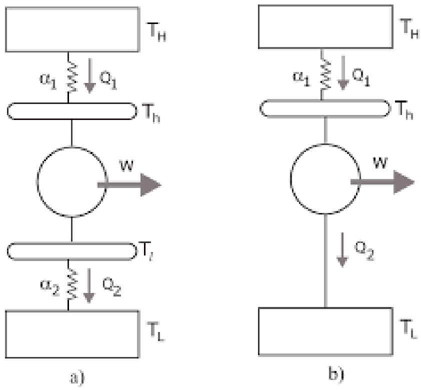


Figure 2.6: (a)Schematic of heat engine with irreversibility at both end of the reservoir and no internal irreversibility. (b) Schematic oh heat engine with irreversibility ony at hotter end of the reservoir

$$\dot{Q}_c = K_c(T_l - T_L) \tag{8}$$

where K_h and K_c is the heat conductance of the system. Now power extracted from the engine is ,

$$\dot{W} = \dot{Q}_h - \dot{Q}_h \Rightarrow W = K_h(T_H - T_h) - K_c(T_l - T_L) \tag{9}$$

hence we see Work is a function of intermediate temperature and it could be optimized according to them, but we need to take in consideration that these temperatures are not independent. As the engine endoreversible so it must follows that entropy production internally is 0, therefore using Eq.(7) and Eq.(8),

$$\dot{S} = 0 \Rightarrow \dot{Q}_c/T_l = \dot{Q}_h/T_h \Rightarrow T_l/T_h = (K_h(T_H - T_h)/K_c(T_l - T_L)). \tag{10}$$

Now using Eq.(10), power could we maximized and efficiency at maximum power (EMP) could be found.

Doing so we get that

$$EMP = \eta_{ca} = (1 - \sqrt{(T_L/T_H)}) = 1 - \sqrt{1 - \eta_c}$$

where η_c is Carnot efficieny. This is known as C.A efficiency and is observed for different classes of systems having no internal heat leaks and Left-right symmetry [7]. expanding it around it we get,

$$E.M.P = \frac{\eta_c}{2} + \frac{\eta_c^2}{8} + 0(\eta_c^3) \tag{11}$$

Here the first term is a consequence of no internal heat leaks while the second term is due to left right symmetry [7].

- **Exoreversible model:** Contrary to endoreversible model, here we assume that all irreversibility present in the system is internal, in form of heat leaks or joule's heating etc and heat conductance to be infinite.

  Similar calculation as former one could be done for exoreversible heat engine based on particular model, which we will see in later section.

2.3 Irreversible Thermodynamics

2.3.1 Flux and Affinities

In the previous section, we mentioned that second law gives directionality to a physical process, i.e. nature allows only those processes which increase the total entropy of the universe. Indeed we see that most of the processes observed in nature are irreversible and things go one way. But that's not the case for system in equilibrium, and at the heart of the equilibrium thermodynamics lies the assumption that processes are reversible. Hence the above formalism is inadequate in explaining such process and we need to modify the above theory to incorporate irreversibilities.

To model irreversibilities in the system, Lars Onsager provided a general formalism for irreversible thermodynamics. But Before moving to Onsager relation we need to define certain terminology of flux and affinities. Suppose we have two systems at temperature T_1 and T_2 connected to each other through the diathermal wall such that they could only exchange energy and total energy(U) of the system is conserved, as shown in Fig(2.7)

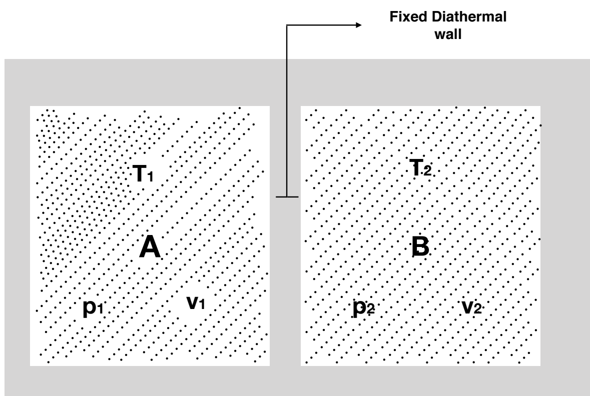


Figure 2.7: Two systems at temperature T_1 and T_2 connected to each other through the diathermal wall such that they could only exchange energy and total energy(U) of the system is conserved

Now as it moves towards equilibrium its entropy increase and we could write the infinitesimal change in entropy as,

$$dS_{tot} = dS_1 + dS_2.$$

where,

$$dS_1 = \frac{\partial S_1}{\partial U_1} dU_1, \tag{12}$$

$$dS_2 = \frac{\partial S_2}{\partial U_2} dU_1, \tag{13}$$

Now we know $\frac{\partial S}{\partial U} = \frac{1}{T}$ Hence, using it

$$dS_{tot} = dS_1 + dS_2 = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2, \tag{14}$$

but as total energy is conserved, therefore

$$dU = dU_1 + dU_2 = 0 \Rightarrow dU_1 = -dU_2.$$

now using the above equation we could write,

$$dS_{tot} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1, \tag{15}$$

Here dU_1 is flux and $(\frac{1}{T_1} - \frac{1}{T_2})$ is difference of intensive parameters.

Similarly if we would have another degree of freedom, say if wall could move such that total volume is conserved then Eq.(15) would be modified accordingly as,

$$dS_1 = \frac{\partial S_1}{\partial U_1} dU_1 + \frac{\partial S_1}{\partial V_1} dV_1.$$

and

$$dS_1 = \frac{\partial S_2}{\partial U_1} dU_2 + \frac{\partial S_2}{\partial V_2} dV_2$$

and following the previous method and using the fact that $\frac{\partial S}{\partial v} = \frac{P}{T}$ we could write,

$$dS_{tot} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1. \tag{16}$$

and if we also allow particle flow, where total particle number is conserved, then we could write

$$dS_{tot} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\mu_1. \qquad (17)$$

Similarly for different degree of freedom we could write,

$$dS = \sum f_k dX_k \qquad (18)$$

where f_k is $\frac{\partial S}{\partial X_k}$ and X_k are different extentensive parameters of the system. also,

$$dS_{tot} = \sum F_k dX_k \qquad (19)$$

where by defnition $F_k =$ affnity and $dX_k =$ flux. For dicrete system affinities are diffrence of f_k of two system. for examaple $F_0 = \frac{1}{T_1} - \frac{1}{T_2}$, $F_1 = \frac{P_1}{T_1} - \frac{P_2}{T_2}$ etc. From above results we see that as affinities vanishes infinitesimal change in entropy turns to zero and equilibrium is attained, and consequently all the fluxes vanishes. Hence as affinities vanish, fluxes also vanish.

2.3.2 Onsager Formalism

In previous section we found how infiitesimal change in entropy is dependent on flux and affinities for a discrete system. Now we want to extend this idea to a continuous system [4]. For this we consider a small volume element(dv) in a continuous system and examine it, as shown in Fig(2.8). We assume that this small volume element is locally in equilibrium.

We define $s = S/v$, which is entropy per unit volume. Now using equation 18 we could write,

$$ds = \sum f_k dx_k \qquad (20)$$

where $x_k = X_k/v$. Now dividing Eq.(20) by area of the element and associating

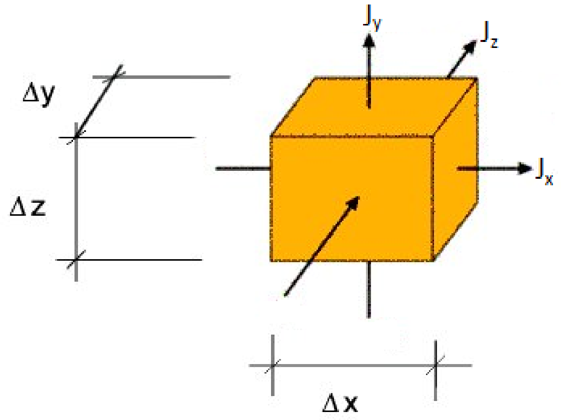


Figure 2.8: particle or energy current passing through infinitesimal volume in a contineous system

an unit vector along the area to it, we could define.

$$\vec{J_s} = \sum f_k \vec{J_k} \tag{21}$$

where $\vec{J_s}$ is entropy current density and $\vec{J_k}$ is current density of x_k extensive variable. for example $\vec{J_{ux}}$ is energy current density along x-axis, $\vec{J_{Ny}}$ is particle current density along Y-axis and so on. Now, using equation of continuity we could write,

$$\dot{s} = \frac{ds}{dt} = \frac{\partial s}{\partial t} + \nabla.\vec{J_s} \tag{22}$$

also using Eq.(20), we could write

$$\frac{\partial s}{\partial t} = \sum f_k \frac{\partial x_k}{\partial t} \tag{23}$$

also we consider system to be in local equilibrium so,

$$\dot{s} = \frac{dx_k}{dt} = \frac{\partial x_k}{\partial t} + \nabla.\vec{J_k} = 0 \tag{24}$$

therefore,

$$\frac{\partial x_k}{\partial t} = -\nabla.\vec{J_k} \tag{25}$$

Now, putting equation 20 and 23 on equation 22,

$$\dot{s} = \sum f_k \frac{\partial x_k}{\partial t} + \nabla . \sum f_k \vec{J_k} \tag{26}$$

$$\dot{s} = \sum f_k \frac{\partial x_k}{\partial t} + \sum f_k \nabla . \vec{J_k} + \sum \vec{J_k} . \nabla F_k \tag{27}$$

Now, putting equation 25 on equation 27 we get,

$$\dot{s} = \sum \nabla f_k . \vec{J_k} . \tag{28}$$

Hence we observe that, same as discrete system we could also write entropy production rate as sum of the product of affinities and fluxes. Here flux turn out to be gradient of intensive parameter in entropy representation.
So here $\vec{F_k} = \vec{\nabla} . f_k$. For eg.

$$\vec{F_u} = \vec{\nabla} \left(\frac{\partial s}{\partial u} \right) \Rightarrow \vec{F_u} = \vec{\nabla} \left(\frac{1}{T} \right).$$

Now, It is phenomenologically it is found that fluxes depend on all the affinities present. It should be noted that a flux tends to depend most strongly on its own affinity, but the dependence on other affinities could not be ignored. Hence,

$$\vec{J_k} = \vec{J_k}(F_0, F_1, F_2 .....F_n).$$

Now we know flux vanishes when affinities vanishes hence we could write,

$$\vec{J_k} = \sum L_{ij} \vec{F_j} + \sum L_{ijl} \vec{F_j} \vec{F_l} + ... \tag{29}$$

Where L_{ij},L_{ijl} etc all are coefficients obtained from Taylor expansion of the above funtion. i.e,

$$L_{ij} = \frac{\partial \vec{J_i}(F_0, F_1, F_2 .....F_n)}{\partial \vec{F_j}}$$

L_{ij},L_{ijl}, etc are called kinetic coefficients. They are funtions of intensive variables.

Next onsager theorem sates that, if a system is in presence of $\vec{B}$ then $L_{ij}(\vec{B}) = L_{ji}(-\vec{B})$. That is, value of kinetic coefficient L_{ij} measured at magnetic field $\vec{B}$ is same as L_{ji} measured at magnetic field $-\vec{B}$. This result becomes very important for linear system, where second order and higher degree dependence on flux could be ignored.

This result is a consequence of a very deep physical law, which tells that Laws of physics remain same when time ”t” is replaced by ”-t” and ”$\vec{B}$” by ”$-\vec{B}$”.

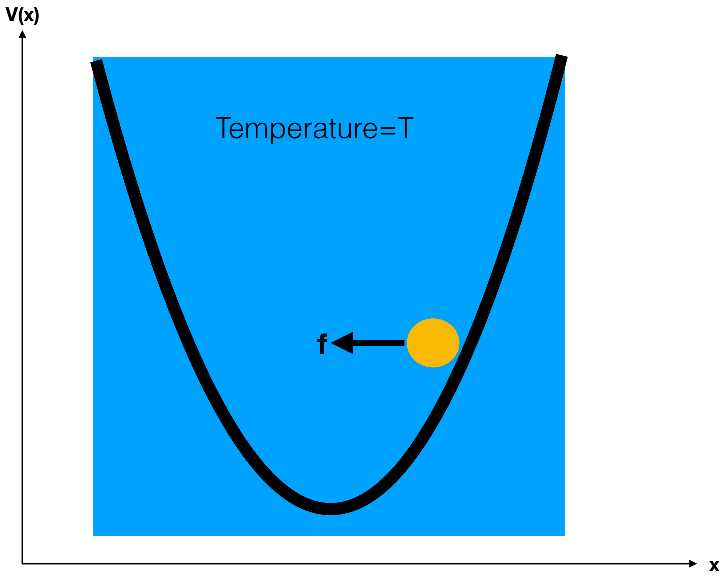


Figure 2.9: Schematic diagram of a Brownian particle at temperature 'T,' under the action of a Potential well (V(x)) and a load force 'f'.

2.4 Thermodynamics of Brownian Particle

Till now we have looked at the microscopic behavior of equilibrium and non-equilibrium system. In this section, we will model the behavior a single Brownian particle connected to a heat bath and try to associate thermodynamic quantities such as heat, work, and entropy production to it. We won't look at these things in much detail as it would not be necessary to study the equilibrium behavior of Brownian heat engine. However its always better to know how the equilibrium properties arise.

Suppose a Brownian particle is under the action of a potential 1-D potential V(x,t) and a force 'f' and is connected to a reservoir at temperature 'T,' as shown in the Fig(2.9).

The microscopic description of the particle could be given using Langevin dynamics [15],[17]. The equation of motion for the particle is,

$$m\ddot{x} + \mu\dot{x} = -\frac{\partial \dot{V}(x,t)}{\partial x} + f + \zeta(t). \tag{30}$$

Where, m= mass of the particle.
μ=friction coefficient.
$\zeta(t)$= Random fluctuation.

Now this Random fluctuation is Gaussian in nature, i.e its average over time is 0.

$$\langle \zeta(t_1)\zeta(t_2)\rangle = 2k_bT\delta(t_1 - t_2) \tag{31}$$

Since the Brownian particle is under the action of a random force, we don't have a deterministic trajectory. Instead we have a probability distribution ($\rho(v,t)$) which is given by Fokker Plank equation. The corresponding fokker plank equation for the above mentioned Langevin equation (Eq.30) is,

$$\frac{\partial \rho}{\partial t} = \mu\frac{\partial \rho v}{\partial v} + \frac{1}{2m^2}\frac{\partial \rho}{\partial v^2}. \tag{32}$$

So solution of this equation gives a probability distribution $\rho(v,t)$ for different trajectories. where, v= velocity of the particle.

For a particular trajectory heat (q) and work (w) could be defined as [15],[17],

$$q = \int \frac{\partial \dot{V}(x,t)}{\partial x}\dot{x}dt - m\int v\dot{v}dt \tag{33}$$

$$w = \int \frac{\partial \dot{V}(x,t)}{\partial t}dt + \int f\dot{v}dt \tag{34}$$

The equation for ρ obtained in equation finally tends to Maxwellian distribution at equilibrium, which we will use for our work.

Further, entropy production could be defined using Eq.(33) and ρ. For such a small system, fluctuations become quite relevant and give rise to essential concepts such as “Jarzynski work relation,” ”Crooks fluctuation theorems,” etc [17,16,10]. Discussion on entropy production and F.T (fluctuation theorems) are outside the scope of this thesis as it requires prior knowledge of ”Stochastic Thermodynamics”[17]. However, we would not need it for our purposes.

3 Thermoelectric Generators

3.1 Thermoelectric material:

Now as a consequence of Onsager formulation we see that one affinity could affect the other flux. This gives rise to interesting phenomena, known as ”Thermoelectric effects,” which include direct conversion of temperature difference to electric current or vice versa and such materials are thermoelectric material [14].

In thermoelectric materials, heat transfer could be done by through two medium, temperature difference, and electrochemical potential. We define J_u and J_n as energy flux and particle flux respectively. Now using Onsager formalism we could write J and J_n as a function of different affinities [3]. For simplicity we assume a 1-D flow of energy and matter along X-axis, so we may not worry about vector components. So using Eq.(21) could write,

$$J_s = \sum f_k J_k$$

or,

$$J_s = \frac{1}{T} J_u - \frac{\mu}{T} J_n \tag{35}$$

and using Eq.(28),

$$\dot{s} = \nabla \frac{1}{T} J_u + \nabla \frac{\mu}{T} J_n \tag{36}$$

where,

$$-J_n = L'11 \nabla \frac{\mu}{T} + L'12 \nabla \frac{1}{T}. \tag{37}$$

$$J_u = L'12 \nabla \frac{\mu}{T} + L'22 \nabla \frac{1}{T}. \tag{38}$$

Here we used the fact that $L_{ij} = Lji$

working in terms of heat flux is easier than that of energy flux, so we would change the variable. we use,

$$T J_s = J_q$$

therefore,

$$J_q = J_u - \mu J_n \tag{39}$$

Now using this equation, we eliminate J_u in Eq.(36) to get,

$$\dot{s} = \nabla\frac{1}{T}(J_q + \mu J_n) + \nabla\frac{\mu}{T}J_n$$
$$\dot{s} = \nabla\frac{1}{T}J_q + \frac{\nabla\mu}{T}J_n \tag{40}$$

and the flux affinity relation becomes,

$$-J_n = L11\frac{\nabla\mu}{T} + L12\nabla\frac{1}{T}. \tag{41}$$

$$J_q = L12\frac{\nabla\mu}{T} + L22\nabla\frac{1}{T}. \tag{42}$$

Now, these kinetic coefficients could be brought in terms of known quantities like electrical conductivity(σ), heat conductivity(k) etc.

3.1.1 Conductivities

Before moving forward we need to understand what does different quantities in our equation mean physically.

J_n=particle flux, could be equated to current density J.

$$J = eJ_n. \tag{43}$$

similarly, μ is sum of two parts electrochemical potential and electrical potential($e\phi$) ie

$$\mu = \mu_e + \mu_c$$

for our case, $\mu_c = 0$. hence

$$\mu = \mu_e = e\phi. \tag{44}$$

also $\nabla\mu = e\nabla\phi = -eE$, where $E =$ electric field.

Now by defnition,at $\nabla T = 0$

$$J = \sigma E$$

or

$$\sigma = eJ_n/\nabla\phi \Rightarrow \sigma = -e^2\frac{J_n}{\nabla\mu} \tag{45}$$

Now, putting $\nabla T = 0$ in Eq.(41),

$$-J_n = L11\frac{\nabla\mu}{T} \Rightarrow -e\frac{J_n}{\nabla\phi} = e^2\frac{L_{11}}{T}$$

Now using Eq.(45),

$$\sigma = e^2\frac{L_{11}}{T} \Rightarrow L_{11} = \frac{T\sigma}{e^2} \tag{46}$$

Similarly heat conductivity ”k” is defined as ratio of heat current and gradient of temperature at $atJ_n = 0$

$$k = \frac{-J_q}{\nabla T}. \tag{47}$$

using Eq.(41),for $J_n = 0$

$$\nabla\mu = \frac{-T\nabla(1/T)L_{12}}{L11}$$

putting it on Eq.(47), we get

$$k = \frac{-J_q}{\nabla T} = \frac{L_{11}L_{22} - L_{11}^2}{T^2L_{11}} \tag{48}$$

Next we define Seebeck coffecient as ratio $\nabla\phi$ and ∇T at $J_n = 0$. i.e

$$\varepsilon = \frac{\nabla\mu}{e\nabla T}$$

now puttiing Eq.(41) to be 0, we get

$$\varepsilon = \frac{\nabla\mu}{e\nabla T} = -\frac{L_{12}}{eTL_{11}} \tag{49}$$

Now putting Eq.(46) on Eq.(49) we get,

$$L_{12} = -\frac{T^2\sigma\varepsilon}{e} \tag{50}$$

now putting expression of L_{12} and L_{11} in Eq.(48) to get expression for L_{22}

$$L_{22} = KT^2 + T^3\varepsilon^2\sigma \tag{51}$$

Now, knowing expression of kinetic coefficients in terms of known quantities we could rewrite equations for current densities as:

$$-J_n = \frac{T\sigma}{e^2}\frac{\nabla\mu}{T} + -\frac{T^2\sigma\varepsilon}{e}\nabla\frac{1}{T}. \tag{52}$$

$$J_q = -\frac{T^2\sigma\varepsilon}{e}\frac{\nabla\mu}{T} + KT^2 + T^3\varepsilon^2\sigma\nabla\frac{1}{T}. \tag{53}$$

3.1.2 Macroscopic Equation for flux

In this section, we will derive macroscopic equation of flux inside thermoelectric material from the microscopic equations [1,6].

For the derivation we assume that flow of energy and particle is one dimensional and cross sectional area of thermoelectric material is 'A' and flow is perpendicular to it, as shown in Fig(3.1). For simplicity we take variation of temperature with length is quadratic. Its two end is connected to reservoir with and total length is 'L'.

Now using Eq.(52), Eq.(53)

$$J_q = T\varepsilon J_n - K\nabla T$$

$$J_q = T\alpha J - K\nabla T. \tag{54}$$

where $\alpha = \frac{\varepsilon}{e}$. Also

$$T = aX^2 + bX + c \tag{55}$$

For $X = 0$, $T = T_h$, Therefore using Eq.(55), $c = T_h$.

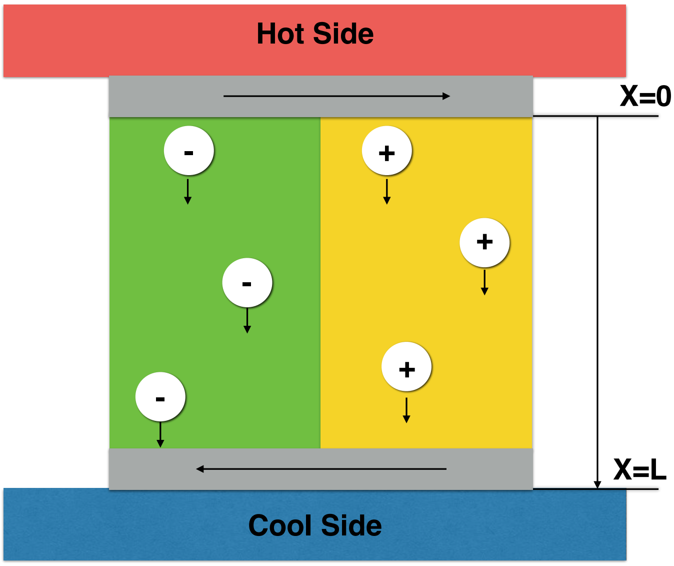


Figure 3.1: Schematic diagram of a 1-D model of Thermoelectric meterial connected to reservoir

Also, $T(L) = T_c$

$$\Rightarrow aL^2 + bL = T_c - T_h \tag{56}$$

taking divergence of Eq.(54), and putting divergence of $J_n = 0$ for condition of local equilibrium.

$$\nabla J_q = -k\nabla^2 T \tag{57}$$

Also, taking divergence of Eq.(39), and putting divergence of $J_n = 0$ and $J_u = 0$ for condition of local equilibrium we get,

$$\nabla J_q = J.E = J^2/\sigma \tag{58}$$

Now equating Eq.(57) and Eq.(58) we get,

$$k\frac{d^2T}{dx^2} = \frac{J^2}{\sigma} \tag{59}$$

Now, using Eq.(55),

$$\frac{d^2T}{dx^2} = 2a$$

Putting it on Eq.(59) we get,

$$a = -\frac{J^2}{2k\sigma} \tag{60}$$

Putting value of a to get b in Eq.(56),

$$b = \frac{T_c - T_h}{L} + \frac{J^2 L}{2k\sigma} \tag{61}$$

putting values of a,b,c in Eq.(55) we get,

$$T = -\frac{J^2}{2k\sigma}X^2 + X + c \tag{62}$$

Now, taking gradient of equation 57, we get

$$\nabla T = \frac{T_h - T_c}{L} + \frac{J^2(L - 2X)}{2\sigma k}. \tag{63}$$

putting ∇T from above equation to Eq.(54) we get an expresion for heat current density.

$$J_q = T\alpha J - +k\frac{T_h - T_c}{L} - \frac{J^2(L - 2X)}{2\sigma}. \tag{64}$$

Now heat flux is AJ_q, hence we multiply Eq.(64), with area

$$AJ_q = TA\alpha J + Ak\frac{T_h - T_c}{L} - A\frac{J^2(L - 2X)}{2\sigma}.$$

Now using the fact, $I = AJ$, where I is current flowing through the system.

$$\Rightarrow Q = T\alpha I + \frac{Ak}{L}(T_h - T_c) - I^2\frac{L(L - 2X)}{2\sigma AL}.$$

Now again renaming the coefficients in known quantities.

$$K = \frac{Ak}{L}$$

$$R = \frac{L}{\sigma A}.$$

Putting these in equation for heat flux we get,

$$Q = T\alpha I + K(T_h - T_c) - \frac{I^2R(1-2X/L)}{2}. \tag{65}$$

Now for X=0 and X=L we have heat flux Q_h and Q_c respectively. where

$$Q_h = T_h\alpha I + K(T_h - T_c) - \frac{I^2R}{2}. \tag{66}$$

$$Q_c = T_c\alpha I + K(T_h - T_c) + \frac{I^2R}{2}. \tag{67}$$

Here the first term signifies Seebeck term. Second term signifies heat leaks and third term signifies joule heating. Here we see heat is dumped to both the reservoir in equal proportion. In general this is not the case, if they dump different fractions of Joule heat in each reservoir, then the flux equations are:

$$Q_h = T_h\alpha I + K(T_h - T_c) - \gamma I^2R. \tag{68}$$

$$Q_c = T_c\alpha I + K(T_h - T_c) + (1-\gamma)I^2R. \tag{69}$$

3.2 Thermoelectric Generators

3.2.1 Different Models

In previous section we saw that, when temperature gradient is applied to a thermoelectric device, it creates a potential difference, which in turn sets up a current in the circuit. This effect is known as 'Seebeck effect'. Now, this current could be used to do work, and the whole system works as a thermoelectric generator as shown in Fig(3.2). Once we set up a TEG, we could optimize its power and observe the trend of efficiency under different models.

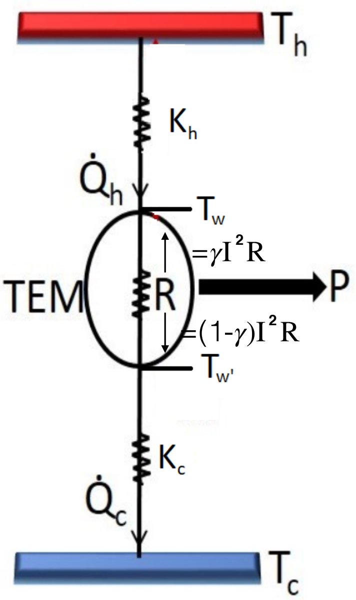


Figure 3.2: Schematic diagram of a thermoelectric generator with external and internal irreversibility and 'γ' fraction of joule heating dumped to the hotter side

The most general model of a thermoelectric generator (TEG), should include all the irreversibilities present in the system [12,6]. To encompass external irreversibility, it should operate between some intermediate temperature. Now the internal irreversibility should consist of Joule heating due to the internal resistance of the device and heat leakage in the device. So the equations for fluxes are,

$$Q_h = K_h(T_h - T_w) = \alpha T_w I - \gamma I^2 R + K_{in}(T_w - T_{w'}) \tag{70}$$

$$Q_c = K_c(T_{w'} - T_c) = \alpha T_{w'} I + (1-\gamma) I^2 R + K_{in}(T_w - T_{w'}) \tag{71}$$

Here γ quantifies the fraction of Joule heating going to either side. Power optimization or calculating efficiency at maximum power(EMP) for such a model becomes quite complex, so to reduce the complexity instead of solving the most general model we solve a certain class of models—

- **Exoreversible model:** As defined earlier, for this model we take external irreversibility to be absent, $K \to \infty$. Hence T_w and $T_{w'}$ approaches T_h and T_c respsetively, Also for simplicity we take heat leaks to be absent and $\gamma = 1$. So using Eq.(71) , flux equation for this case is

  $$Q_h = \alpha T_h I - I^2 R \tag{72}$$

  $$Q_c = \alpha T_c I \tag{73}$$

  Using it,

  $$P = Q_h - Q_c \Rightarrow P = \alpha I(T_h - T_c) - I^2 R$$

  Now maximizing,

  $$\frac{dP}{dI} = 0 \Rightarrow I = \frac{\alpha(T_h - T_c)}{2R} \tag{74}$$

  Now, calculating EMP, we get

  $$\eta_{exo} = \frac{1-\theta}{1+\theta} \tag{75}$$

  here θ is T_c/T_h.

- **Endoreversible model:** Again as defined previously, for this model there are no internal irreversibility i.e. heat leaks and Joule's heating is absent.

Also for simplicity we take $\gamma = 1$ and $K_h = K_c = K$. Hence flux equation for this model is,

$$Q_h = K(T_h - T_w) = \alpha T_w I \tag{76}$$

$$Q_c = K(T_{w'} - T_c) = \alpha T_{w'} I \tag{77}$$

Now using these equation $T_w =$ and $T_{w'} =$ could be written in terms of I,

$$T_w = \frac{KT_h}{K + \alpha I}$$

$$T_{w'} = \frac{KT_c}{K - \alpha I}$$

and equation for power is,

$$P = \alpha I \left(\frac{KT_h}{K + \alpha I} - \frac{KT_c}{K - \alpha I} \right) \tag{78}$$

Again similar to previous problem, this equation could be maximized in terms of current and then we calculate EMP. Which turns out to be same as C-A model.

$$\eta_{endo} = 1 - \sqrt{\theta} \tag{79}$$

For other models reference[12] could be seen.

3.2.2 Model for my case

In our model we use γ =1, i.e all heat is dumped to hotter side, $K_c = K_h = K$ and assume heat leakage to be absent ie $K_{in} = 0$ as shown in Fig(3.3). So for our purpose, the flux equation turns out to be:

$$K(T_h - T_w) = \alpha T_w I - I^2 R \tag{80}$$

$$K(T_{w'} - T_c) = \alpha T_{w'} I \tag{81}$$

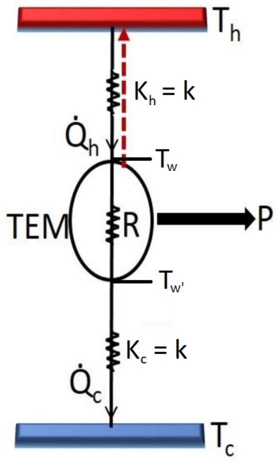


Figure 3.3: Schematic of Thermoelectric Generator with external reversibility(finite K) and internal irreversibility(due to Joule heating, dumped on hot side i.e. γ=1)

now, eliminating T_w and $T_{w'}$ we could write power in terms of current,

$$P = \frac{kR\alpha I^3 - K(\alpha^2(T_h + T_c) + RK)I^2 + K^2(T_h - T_c)\alpha I}{k^2 - \alpha^2 I^2}. \tag{82}$$

Now to optimize power we differentiate the above eqn w.r.t "I". Doing so, we get a quartic equation

$$I^4 - K\left(\frac{3K}{\alpha^2} + \frac{\Delta T}{\alpha R}\right)I^2 + 2K^2\left(\frac{K}{\alpha^3} + \frac{\Gamma}{\alpha R}\right)I - \frac{K^3 \Delta T}{R\alpha 2} = 0 \tag{83}$$

where $\Delta T = T_h - T_c$ and $\Gamma = T_h + T_c$

It has 4 roots and we need to find a physical relevant root(i.e $I > 0$) out of these [2,9], to do so, we are going to use geometrical approach using "Pencil".

3.3 Pencil

Pencil is a family of curve given by [2],

$$ay^2 - by + cx + d + \lambda(y - x^2) = 0. \tag{84}$$

It has a unique property, that every curve passes through 4, 2 or 0 points depending on the root of the quartic equation,

$$ax^4 - bx^2 + cx + d = 0. \tag{85}$$

These points are called base points. Other than base point for every value of λ we get a unique point in co-rdinate space. for eg. consider a particular pencil.

$$y^2 - 7y + 6x + \lambda(y - x^2) = 0, \tag{86}$$

So for different values of λ we get different curves, all of which pass through 4 points. These base points are solutions of the quartic:

$$x^4 - 7x^2 + 6x = 0. \tag{87}$$

From the Fig(3.4) we could see that base points are nothing but intersection of pair of straight line and parabola.

3.3.1 Roots of quartic using Pencil

So for a general quartic equation $ax^4 - bx^2 + cx + d = 0$ the desired pencil is $ay^2 - by + cx + d + \lambda(y - x^2) = 0$ and It's base points i.e roots of the quartic equation is given by intersection of pair of straight line and parabola.

The equation of pair of straight line is given by

$$y + \frac{b + \lambda}{2} = \pm\sqrt{\lambda}\left(x - \frac{c}{2\lambda}\right) \tag{88}$$

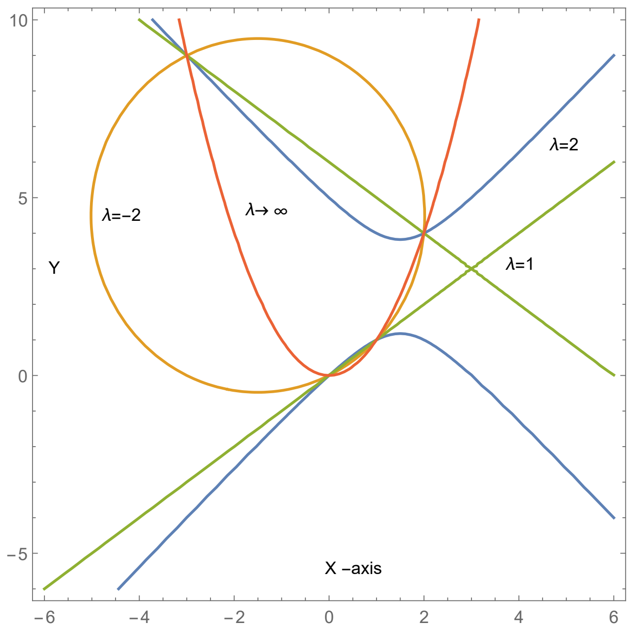


Figure 3.4: plotting Eq.(86) for different values of λ

where λ is root of equation

$$\lambda^3 + 2b\lambda^2 + (b^2 - 4d)\lambda - C^2 = 0$$

Now our equation,

$$I^4 - K\left(\frac{3K}{\alpha^2} + \frac{\Delta T}{\alpha R}\right)I^2 + 2K^2\left(\frac{K}{\alpha^3} + \frac{\Gamma}{\alpha R}\right)I - \frac{K^3 \Delta T}{R\alpha^2} = 0 \tag{89}$$

$b < 0$, $c > 0$ and $d < 0$. Since we expect a physical solution of this model hence $\sqrt{\lambda}$ must be real. Therefore $\lambda > 0$, hence $c/\lambda > 0$. So from Eq.(88) we know that intersection pair of straight line is along positive x-axis.

Now if this point of intersection is in first co-ordinate we get a physically relevant solution irrespective of the slopes of the straight line and solution would be intersection of parabola $y - x^2 = 0$ and line,

$$y + \frac{b + \lambda}{2} = \sqrt{\lambda}\left(x - \frac{c}{2\lambda}\right) \tag{90}$$

Doing so we get our physically relevant root as,

$$I = -\frac{\alpha T_h}{2R}\sqrt{\frac{2(3v^2 - v\eta_c)}{3} + \frac{21/3v^2(3v-\eta_c)^2}{3(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}} + \frac{(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}}{32^{1/3}}}$$
$$+ \frac{\alpha T_h}{2R}\sqrt{\left[\frac{2(3v^2 - v\eta_c)}{3} - \frac{21/3v^2(3v-\eta_c)^2}{3(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}} - \frac{(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}}{32^{1/3}} \right.}$$
$$\left. + \frac{4(v^3 + v^2\check{\eta}_c)}{\sqrt{\frac{2(3v^2 - v\eta_c)}{3} + \frac{21/3v^2(3v-\eta_c)^2}{3(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}} + \frac{(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}}{32^{1/3}}}}\right] \quad (91)$$

where, $\check{\eta}_c = 1 + \theta$ and $v = \frac{KR}{\alpha^2 T_h}$ and

$$D_1 = [108(v^3 + v^2\check{\eta}_c)^2 - 72v^3\eta_c(3v^2 - v\eta_c) - 2(3v^2 - v\eta_c)^3]$$

$$D_2 = [12v^3\eta_c - (3v^2 - v\eta_c)^2]$$

also, EMP(η_{mp})

$$\eta_{mp} = \frac{f^2 - 2(\check{\eta}_c + v)f + 4v\eta_c}{(2-f)(2v-f)} \quad (92)$$

where f is

$$f = -\sqrt{\frac{2(3v^2 - v\eta_c)}{3} + \frac{21/3v^2(3v-\eta_c)^2}{3(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}} + \frac{(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}}{32^{1/3}}}$$
$$+ \sqrt{\left[\frac{2(3v^2 - v\eta_c)}{3} - \frac{21/3v^2(3v-\eta_c)^2}{3(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}} - \frac{(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}}{32^{1/3}} \right.}$$
$$\left. + \frac{4(v^3 + v^2\check{\eta}_c)}{\sqrt{\frac{2(3v^2 - v\eta_c)}{3} + \frac{21/3v^2(3v-\eta_c)^2}{3(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}} + \frac{(D_1^2 + \sqrt{4D_2^3 + D_1^2})^{1/3}}{32^{1/3}}}}\right] \quad (93)$$

3.4 Result

Once the root is selected, we calculate EMP and plot it w.r.t a dimensionless quantity $'v = \frac{KR}{T_h\alpha^2}'$ for a given θ and then match it with two special cases:

- Endoreversible model: For this case $R \to 0$ and $EMP \to \eta_{endo} = 1 - \sqrt{\theta}$.
- Exoreversible model: For this case $K \to \infty$ and $EMP \to \eta_{endo} = \frac{1-\theta}{1+\theta}$.

We find EMP at $\theta = 0.5$, and the value matches for two special cases. Hence we conclude that our selected root is physically relevant one.

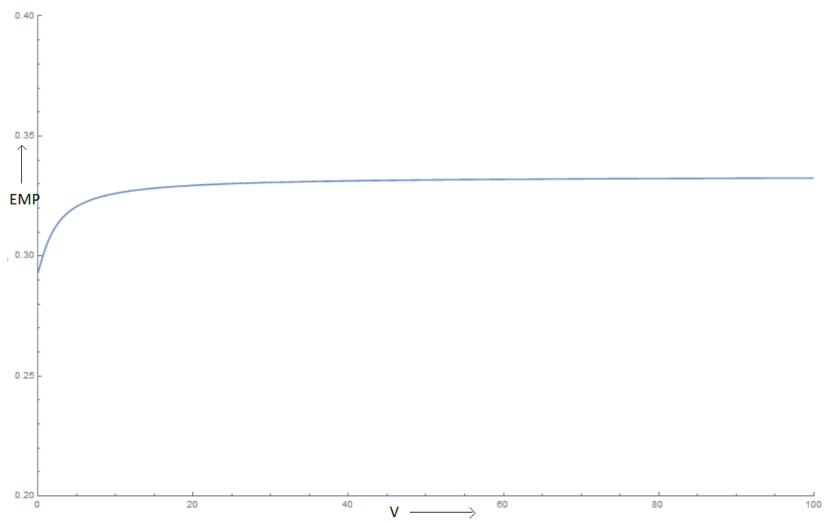


Figure 3.5: Plot of E.M.P vs 'v' for $\theta = 0.5$

3.5 Conclusion

The basic idea of our work was to optimize the power of the given model, then calculate analatycal expression for EMP. To check our expression for EMP (η_{mp}) we match the result with two special cases i.e. endoreversible model ($R \to 0$) and exoreversible model ($K \to \infty$). As the result for our η_{mp} matches with the special cases, we conclude that our selected root was correct and expression for η_{mp} is true expression for EMP

Further we tried to expand the expression of η_{mp} in terms of η_c at $\frac{K_{ex}}{K_{in}} = 1$, where $K_{ex} = \frac{k}{2}$ and $K_{in} = \frac{KR}{2\alpha^2 T_c}$ using Mathematica. But the expression was quite complicated and we couldn't infer the efficiency term further. However we could infer the η_{mp} term numerically.

4 Brownian heat engine

4.1 Feynman ratchet

The model of Feynman's ratchet [8,20] consists of a vane, immersed in a hot reservoir at temperature T_h, and connected through an axle with a ratchet in contact with a cold reservoir at T_c. The ratchet has a preferable direction to move due to a pawl, which, in turn, is connected to a spring. We Assume the direction of rotation when weight moves upward to be positive (forward) and vice versa.

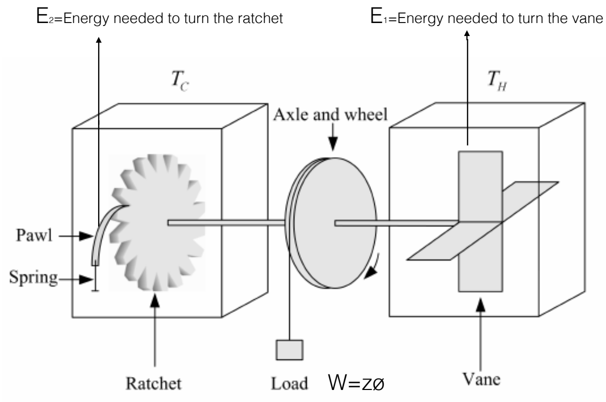


Figure 4.1: Schematic diagram of Feynman ratchet model.

Let E_2 be the amount of energy to overcome the elastic energy of the spring to rotate forward by one step. Also, let Z is the torque induced by weight. Hence for every rotation, it requires an extra $+Z\theta$ energy to rotate forward, where θ is the angle rotated in one forward rotation. Therefore it takes $E_1 = E_2 + Z\theta$ amount of energy for each forward rotation. So, for forward rotation E_1 amount of energy is extracted from the hot reservoir and E_2 amount of energy is dumped into the cold reservoir and meanwhile a work ($w = z\theta$) is extracted. Mathematically it could be written as,

$$q_c^{for} = E_2. \tag{94}$$

$$q_h^{for} = E_1 = E_2 + Z\theta. \tag{95}$$

Similarly when wheel rotates backward it takes E_2 amount of energy from the cold reservoir, a work ($w = -z\theta$) is done by the system (as weight falls down) and $E_1 = E_2 + Z\theta$ amount of energy is dumped into the hot reservoir. So for this case,

$$q_c^{bac} = -E_2. \tag{96}$$

$$q_h^{bac} = -E_1 = -(E_2 + Z\theta). \tag{97}$$

Now assuming the particles to be in equilibrium with reservoirs, the number of forward and backward jumps will be proportional to the corresponding Arrhenius factor. Hence,

$$R_f = e^{-E_1/k_bT_h}. \tag{98}$$

$$R_b = e^{-E_2/k_bT_c}. \tag{99}$$

and Heat flux equation for the system is,

$$Q_h = E_1(e^{-E_1/k_bT_h} - e^{-E_2/k_bT_c}). \tag{100}$$

$$Q_h = E_2(e^{-E_1/k_bT_h} - e^{-E_2/k_bT_c}). \tag{101}$$

$$W = Q_h - Q_c = (E_1 - E_2)(e^{-E_1/k_bT_h} - e^{-E_2/k_bT_c}). \tag{102}$$

For it to operate as a heat engine R_f should be greater than R_b, which implies,

$$e^{E_1/k_bT_h} > e^{E_2/k_bT_c} \Rightarrow E_2/E_1 > T_c/T_h \tag{103}$$

Using this equation we could show that efficiency of this engine is always less than Carnot efficiency.

$$\eta = 1 - \frac{Q_c}{Q_h} = 1 - \frac{E_2}{E_1} < 1 - \frac{T_c}{T_h}. \tag{104}$$

hence $\eta < \eta_c$.

We could optimize Eq.(102) to find maximum power [21] and further calculate Efficiency at maximum power and infer its behavior near equilibrium ($T_c/T_h \to 1$) [18,21].

4.1.1 Power Optimization

Before optimizing Eq.(102) analytically, we should study its behavior at low energy limit. Expanding the Eq.(102) linearly,

- Case 1: Expanding the Eq.(102) linearly

  The equation for work is,

$$W = (E_1 - E_2)\left(\frac{E_2}{k_b T_c} - \frac{E_1}{k_b T_h}\right). \tag{105}$$

  Now optimizing this equation w.r.t E_1 and E_2, we get $E_1 = 0$ and $E_2 = 0$. This suggests that in linear limit it can't be optimized simultaneously w.r.t E_1 and E_2.

- Case 2: Expanding the Eq.(102) quadratically [18].

  The equation for work in this case is,

$$W = (E_1 - E_2)\left(\frac{E_2}{k_b T_c} - \frac{E_1}{k_b T_h} + \frac{E_1^2}{2k_b T_h} - \frac{E_2^2}{2k_b T_c}\right) \tag{106}$$

  Now optimizing this equation with respect to ε,μ and x as we get,

$$E_1^{*q} = \frac{1+3\tau}{3(1+\tau)} \tag{107}$$

$$E_2^{*q} = \frac{(3+\tau)\tau}{3(1+\tau)} \tag{108}$$

  Putting the values of E_1^* and E_2^* to find efficiency at max power (E.M.P) we get,

$$\eta_{mp}^q = 1 - \frac{(3+\tau)\tau}{1+3\tau} \tag{109}$$

  expanding it around carnot efficiency (η_c),

$$\eta_{mp}^q = \frac{\eta_c}{2} + \frac{\eta_c^2}{8} + O(\eta_c^3) \tag{110}$$

- Case 3: General case:

Optimizing the power w.r.t E_1 and E_2 and calculating E.M.P as done in previous cases [20,21], we get,

$$E_1^* = \frac{\tau - \tau^2 - \tau ln\tau}{\tau(1-\tau)} - ln\tau. \tag{111}$$

$$E_2^* = \frac{\tau - \tau^2 - \tau ln\tau}{(1-\tau)}. \tag{112}$$

Calculating E.M.P using E_1^* and E_2^* and expanding it around Carnot efficiency we get,

$$\eta_{mp} = \frac{\eta_c}{2} + \frac{\eta_c^2}{8} + O(\eta_c^3) \tag{113}$$

Optimizing the power w.r.t E_1^{*q} and E_2^{*q} and calculating E.M.P in low energy limit and expanding it around Carnot efficiency we get,

$$\eta_{mp}^q = \frac{\eta_c}{2} + \frac{\eta_c^2}{8} + O(\eta_c^3) \tag{114}$$

Here we see that result for general case matches with low energy limit.

4.2 Thermally driven Brownian microscopic heat engine

In a crude way, we could define microscopic Brownian heat engine as a microscopic setup where work could be extracted due to the transportation of Brownian particles via some nonequilibrium processes [15,13]. Typical examples are external modulation of an underlying potential, an activation of an external force, a non-equilibrium chemical reaction coupled to a change of the potential. The method we are using is a contact with the reservoirs at different temperatures, hence it is called thermally Brownian microscopic heat engine [22].

The model of the thermally driven Brownian microscopic heat engine is as shown in Fig(4.2). The Brownian particles are under the action of a spatially periodic and asymmetric potential $V(x)$ with a constant external force f. Two different regions, shown in the figure, are connected to two reservoirs at different temperatures T_h and T_c. The Brownian Particles could move from the region I to region II due to thermal fluctuations and while doing so they do external work and the whole setup works as a heat engine.

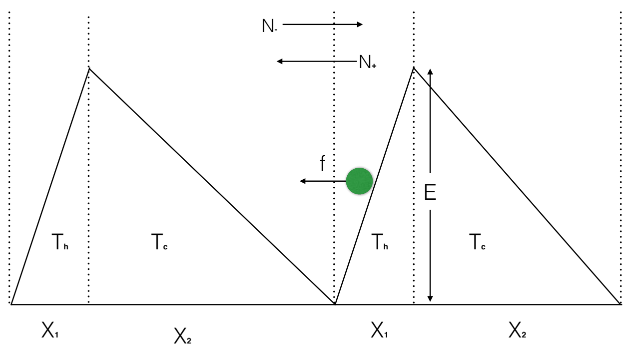


Figure 4.2: The Brownian particles are under the action of a spatially periodic and asymmetric potential $V(x)$ with a constant external force.

Now our next task is to define thermodynamic quantities such as heat and work for the system. These definitions are analogous to Feynman Rachet model. Suppose N_+ particles move from the region I to region II, It takes q_h amount of heat from hot reservoir, does a work w and dumps q_c amount of heat to the cold reservoir. Similarly, when N_- particles move from the region II to region I, it takes q_c amount of heat from cold reservoir, uses a work w and dumps q_h amount of heat to hot reservoir.

Where, q_h = energy needed to go uphill in the region I, q_c= energy needed to go from uphill in region II and by energy conservation $w = q_h - q_c$. Mathematically,

$$q_h = E + fL_1 \tag{115}$$

$$q_c = E - f(L - L_1) \tag{116}$$

Where $L_1 + L_2 = L$. It is assumed that Brownian particles are in equilibrium with the reservoirs, hence the rates of both forward(moving from region I to II) and backward jumps((moving from region II to I)) are proportional to the corresponding Arrhenius factor.

$$\dot{N}_+ = \frac{e^{-(E+fL_1)/k_BT_h}}{t}. \tag{117}$$

$$\dot{N}_- = \frac{e^{-(E-f(L-L_1))/k_BT_h}}{t}. \tag{118}$$

Where t is a constant. Using the above equations we could write the heat exchange due to potential energy as,

$$\dot{Q}_h^{pot} = [E + fL_1][\dot{N}_+ - \dot{N}_-]. \tag{119}$$

$$\dot{Q}_c^{pot} = [E - f(L - L_1)][\dot{N}_+ - \dot{N}_-]. \tag{120}$$

Till here we have considered only the contribution of potential energy term, however as the particles move from I to II, their kinetic energy also changes. To take it into consideration we move one step further. suppose a particle moves from I to II, therefore the change in its K.E is, $\triangle k.E = \frac{K_B(T_h - T_c)}{2}$

Now this energy is supplied by hot reservoir (T_h) and dumped in cold reservoir (T_c). Similarly, if the particle moves from II to I, then also the energy needed to increase its K.E is supplied by the hot reservoir. Hence whether particle moves from I to II or II to I there is an irreversible transfer of heat from the hot reservoir to cold reservoir, which is proportional to the total number of particles transferred. Using this logic,

$$\dot{Q}_h^{kin} = \dot{Q}_c^{kin} = \frac{k_B(T_h - T_c)}{2}[\dot{N}_+ + \dot{N}_-]. \tag{121}$$

So the complete equation for heat flux and power($\dot{W}$) are,

$$\dot{Q}_h = \dot{Q}_h^{pot} + \dot{Q}_h^{kin} = (E + fL_1)(\dot{N}_+ - \dot{N}_-] + \frac{k_B(T_h - T_c)}{2}[\dot{N}_+ + \dot{N}_-]. \tag{122}$$

$$\dot{Q}_c = \dot{Q}_c^{pot} + \dot{Q}_c^{kin} = (E + f(L - L_1))[\dot{N}_+ - \dot{N}_-] + \frac{k_B(T_h - T_c)}{2}[\dot{N}_+ + \dot{N}_-]. \tag{123}$$

$$\dot{W} = \dot{Q}_h - \dot{Q}_c = fL[\dot{N}_+ - \dot{N}_-] \tag{124}$$

$$\eta = \frac{\dot{W}}{\dot{Q}_h} \tag{125}$$

4.2.1 Power Optimization.

Now before moving forward its better to write the expression for power in terms of dimensionless quantities,

$$\frac{\dot{W}}{K_B T_h} = x[e^{-(\varepsilon + x\mu)} - e^{-(\varepsilon - x + x\mu)/\tau}] \tag{126}$$

Where $\varepsilon = E/k_B T_h$, $x = fL/k_B T_h$, and $\mu = L_1/L$.

Initially, it may appear that we have three different parameters for optimization(ε, μ and x). However, looking closely to the equation we find that effectively there is only two energy scale in the system namely $\varepsilon + x\mu$ and x, and this restricts the system to two independent parameters optimization. It will be evident from the equation of optimization. Now we optimize our system for two cases first the general situation and second in the limit where ε and x are small, i.e., in low energy scale.

- Case 1: Here we optimize the general equation for power($\dot{W}$ with respect to ε,μ and x.

$$\frac{\partial \dot{W}}{\partial \varepsilon} = 0 \Rightarrow x(e^{-(\varepsilon+x\mu)} - e^{-(\varepsilon+x\mu-x)/\tau}) = 0 \tag{127}$$

$$\frac{\partial \dot{W}}{\partial \mu} = 0 \Rightarrow x^2(e^{-(\varepsilon+x\mu)} - e^{-(\varepsilon+x\mu-x)/\tau}) = 0 \tag{128}$$

$$\frac{\partial \dot{W}}{\partial x} = 0 \Rightarrow x^2(e^{-(\varepsilon+x\mu)} - e^{-(\varepsilon+x\mu-x)/\tau}) = 0 \tag{129}$$

Solving the above equations to get optimal values of parameters(x^*,ε^* and μ^*) we get,

$$x^* = 1 - \tau \tag{130}$$

$$\varepsilon^* = \frac{1 - \tau - \tau ln\tau}{1 - \tau} - (1 - \tau)\mu. \tag{131}$$

Here we may note that Eq.(24) and Eq.(25) are essentially same. This suggest optimizing w.r.t ε automatically optimizes w.r.t μ. Hence instead of getting particular value for ε^* and μ^* we get a set of ε^* and μ^* for which $\varepsilon^* + \mu^* = constant$ and this constant optimizes the power. Physically it reflects the two energy scales, we mentioned above.

- Case 2: Here we optimize in limit where ε and x are small, such that we could expand the expression for power(Eq.) quadratically. Therefore,

$$\frac{\dot{W}}{k_b T_h} = x\left(\frac{\varepsilon - x + x\mu}{\tau} - (\varepsilon + x\mu) - \frac{(\varepsilon - x + x\mu)^2}{2\tau^2} + \frac{(\varepsilon + x\mu)^2}{2}\right) \tag{132}$$

Now optimizing this equation with respect to ε,μ and x as done in earlier we get,

$$x_q^* = \frac{1-\tau}{3} \tag{133}$$

$$\varepsilon_q^* = \frac{-1-2\tau+3\tau^2}{3(\tau^2-1)} - \frac{(1-\tau)\mu}{3}. \tag{134}$$

4.3 Comparison of Results.

In this section we would compare the efficiency at maximum power (E.M.P) for two different cases near equilibrium (i.e $\tau \rightarrow 1$).

Using Eq.(125), we calculate the efficiency at maximum power (E.M.P) by putting the optimal values of ε and x for two cases. Then expand it around Carnot efficiency and infer the coefficient of linear term.

- Case 1: For this case,

$$\eta_{mp} = \frac{2(1-\tau)^2}{3-2\tau(1+ln\tau)-\tau^2} \tag{135}$$

expanding the above expression in term of Carnot efficiency we get [19],

$$\eta_{mp} = \frac{\eta_c}{3} + \frac{\eta_c^2}{9} + O(\eta_c^3) \tag{136}$$

Near equilibrium,

$\varepsilon^* \rightarrow 2$, $x^* \rightarrow 0$ and $\eta_{mp} \rightarrow \frac{\eta_c}{3}$

- Case 2: For this case,

$$\eta_{mp}^q = \frac{4(2-\eta_c)\eta_c}{136-33\eta_c(4-\eta_c)} \tag{137}$$

expanding it around Carnot efficiency,

$$\eta_{mp}^q = \frac{\eta_c}{17} + \frac{8\eta_c^2}{289} + O(\eta_c^3) \tag{138}$$

Near equilibrium,

$\varepsilon_q^* \rightarrow 2/3$, $x_q^* \rightarrow 0$ and $\eta_{mp}^q \rightarrow \frac{\eta_c}{17}$.

Now this may seem absurd at first. Our model is completely analogous to Feynman Ratchet model discussed in previous section except for the fact that we have included irreversible heat flow due to kinetic energy contribution. In Feynman Ratchet results for both the cases were same, then what's fishy out here?

Our first guess may be, that for quadratic variation ε_q^* and $_q^*$ are not really maxima. But further checking the higher derivative, we found

$$\left.\frac{\partial^2 \dot{W}}{\partial \varepsilon^2}\right|_{\varepsilon=\varepsilon^*, x=x^*} < 0. \tag{139}$$

$$\left.\frac{\partial^2 \dot{W}}{\partial x^2}\right|_{\varepsilon=\varepsilon^*, x=x^*} < 0. \tag{140}$$

$$\left[\left.\frac{\partial^2 \dot{W}}{\partial \varepsilon^2}\right|_{\varepsilon=\varepsilon^*, x=x^*} \left.\frac{\partial^2 \dot{W}}{\partial x^2}\right|_{\varepsilon=\varepsilon^*, x=x^*} - \left(\left.\frac{\partial \dot{W}}{\partial x}\frac{\partial \dot{W}}{\partial \varepsilon}\right|_{\varepsilon=\varepsilon^*, x=x^*} \right)^2 \right] > 0. \tag{141}$$

The problem lies in the fact that the behavior of Eq.(126) and Eq.(132) are entirely different near the true optimal values of the engine. Hence quadratic expansion doesn't give the correct optimal value. This ambiguity could be explained using an analog situation for a function of one variable.

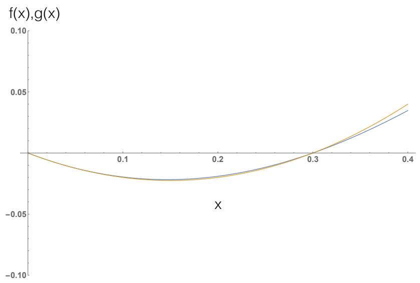
Suppose a function $f(x)$ as defined,

$$f(x) = e^{-ax} - e^{x^2}. \tag{142}$$

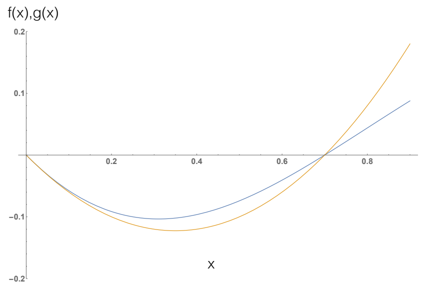
expanding the above function linearly we get,

$$g(x) = -ax + x^2. \tag{143}$$

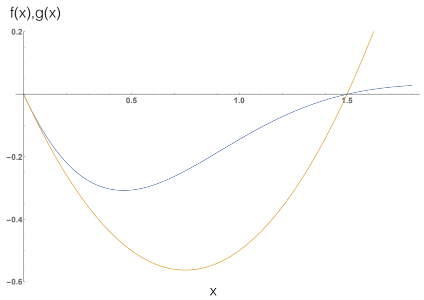
Now plotting the function $f(x)$ and $g(x)$ simultaneously for different values of 'a', as shown in Fig(4.3), we see that the minima of both functions coincide for small values of 'a.' But for large values of 'a' the behavior of g(x) (linear expan-



(a) a=0.3



(b) a=0.7

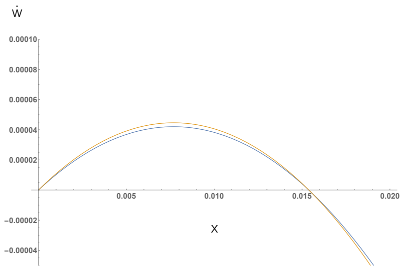


(c) a=1.5

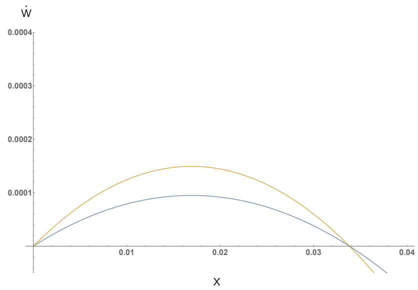
Figure 4.3: plot of $f(x)$ and $g(x)$ simultaneously for for different values of 'a' (near minima).

sion) is completely different from f(x) (initial function) near its minima.

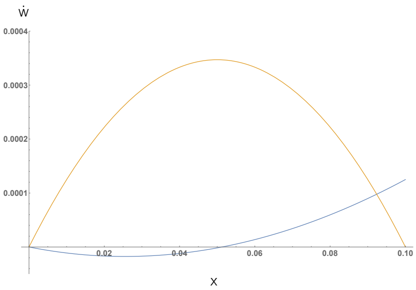
The situation for our case is analogous to the case where 'a' is large. Plotting Eq.(126) (expression for power) and Eq.(132) (expanding power quadratic-ally) as a function of x for different values of ε near equilibrium, as shown in fig(4.4), we could see that the behavior of Eq.(132) changes quite drastically from Eq.(126) for large values of ε. The optimal value of ε for Eq.(132) tends to $\frac{2}{3}$. However, the true optimal value of ε tends to 2. Hence the result of efficiencies for two cases is considerably different. Also note that the efficiency calculated for $\varepsilon \to 2/3$ doesn't correspond to E.M.P for our system.



(a) ε =0.3



(b) ε =0.66



(c) ε =0.66

Figure 4.4: plot of Eq.(126) (expression for power, orange colour) and Eq.(132) (expanding power quadratic-ally, blue colour) as a function of x for different values of ε near equilibrium, for $\mu = 0.5$ and $\tau = 0.5$. Here the negative power implies that heat engine do not operates in following zone.

4.3.1 Revisiting Feynman Rachet:

Now, the next the obvious question arises, why the result of E.M.P matches for quadratic expansion and general case near equilibrium, even though the maxima in two cases are quite far apart? The reason lies in the fact that there is no dissipation term, so efficiency depends only on the ratio E_1 and E_2 and in both case this ratio is almost the same at equilibrium.

Here, we must note that E_1^{*q} and E_1^{*q} does not give efficiency at maximum power for Feynman ratchet. It is given by E_1^* and E_1^*. However, efficiency for both cases is the same at equilibrium.

4.4 Results:

1. The efficiency of the heat engine could never approach to Carnot efficiency as the system has an intrinsic scource of irreversibility due to kinetic energy exhange.

2. At low energy limit power could not be optimized near equilibrium.

3. E.M.P (efficiency at maximum power) tends to $\frac{\eta_c}{3}$ near equilibrium. In general, $\eta_{mp} = \frac{\eta_c}{3} + \frac{\eta_c^2}{9} + O(\eta_c^3)$.

4.5 Conclusion:

In this section, we optimized the power of thermally driven Brownian microscopic heat engine and calculated E.M.P and inferred its behavior near equilibrium. Next, we tried to do the same analysis at low energy scale by expanding the expression of power in quadratic limit and expected the same results for both the cases. However, the result didn't match and the reason being that the behavior quadratic limit is quite different from the complete equation near optimal values of ε^* and x^* .

Even when the result for E.M.P matches near equilibrium for Feynman ratchet model, the optimization in quadratic limit was not giving the true optimal value of ε^* and x^*.

At last, I would like to conclude that while analytically optimizing the power at low energy limit (by approximating to an easily solvable function) we should always check (maybe numerically) the behavior of power at the low energy limit to find if the approximation is good enough.

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