1 Introduction.

Any system in equilibrium can be fully described by the Boltzmann-Gibb's theory of ensembles. For a system in contact with a heat bath, the phase-space probability distribution is given by the canonical distribution. This expression is very general and can be applied to any given equilibrium system. One can then calculate the partition function and from this the free energy of the system. From this all equilibrium properties of a system can, in principle, be calculated. In practice of course this can be difficult and an explicit calculation of specific properties may not always be possible.

There is a large class of phenomena which cannot be described by the Boltzmann-Gibb's ensemble theory. These include non-equilibrium phenomena in glassy systems, granular material, electrical and thermal transport. The reasons that the equilibrium description breaks down in these systems can be various: for example there may be no Hamiltonian description; or the Hamiltonian is time-dependent; or relaxation times are extremely slow, etc.

There are few theories, such as those of non-equilibrium thermodynamics and theory of linear response, to describe some of these non-equilibrium phenomena. However, they work only in the linear regime where the perturbed system is slightly out of equilibrium. These theories thus have a very limited range of applicability. There is no general framework to treat non-equilibrium phenomena which is valid for systems far from equilibrium. In the absence of a general theory for such systems, one approach is to take simple but nontrivial model systems and understand their behaviour from first principles.

In the last decade the situation has changed somewhat. Certain general relations have been discovered which are valid independent of how far a system is driven out of equilibrium. These results include (1) the Jarzynski equality $[3-6]$ and (2) the fluctuation theorems

[7 − 17]. These results are now being extended and shown to be valid for many different systems, dynamics (deterministic as well as stochastic) and ensembles. They have been verified for a variety of systems theoretically [18 − 20] as well as experimentally [21 − 24]. After the work by Crooks [10] and Seifert [11], it is now understood that many of these relations are closely related and are the manifestations of a single theorem, the theorem which connects the path probability of a thermostatted system to its time reversed trajectory. In Sec. (1.1) we will briefly describe these results on non-equilibrium fluctuations and state the new results obtained by us.

Another class of problems in non-equilibrium physics, which cannot be treated by conventional theories, is that of ratchet systems and of molecular pumps and engines. These are systems which are driven out of equilibrium by some external parameter and exhibit many interesting phenomenas like uni-directional current, resonances etc. Among their applications it has been proposed to model the behaviour of molecular motors and pumps in biological systems. There have also been many studies on the quantum version of such particle and heat pumps. So it is interesting to look at whether the quantum nature of a system is an essential requirement. In Sec. (1.2) we will briefly describe some known results on these systems and discuss our contribution.

1.1 The Jarzynski equality and the fluctuation theorems

Consider a system in contact with a heat reservoir. Let some parameter, λ, for example the external field on a magnet or the volume of a gas etc. be varied in time from an initial point λ_A to a final point λ_B (in general there can be many time-dependent parameters $\boldsymbol{\lambda} = \{\lambda_1, \lambda_2, ..., \lambda_n\}$ in the system). With this parameter variation, work is done on the system. Then, conventional thermodynamics tells us that the work done W, on the system is always greater than or equal to the free energy (Helmholtz free energy) difference. Thus:
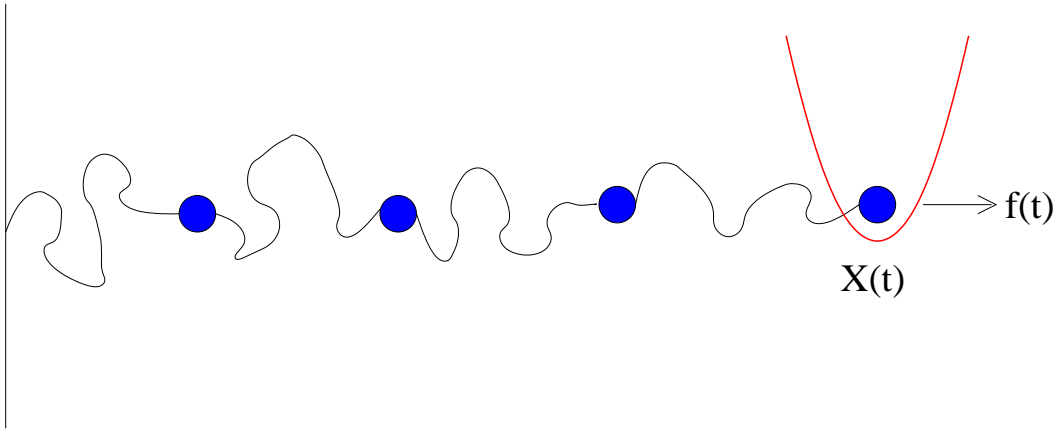
$$W \geq \Delta F, \tag{1.1}$$

Figure 1.1: A polymer being stretched by an optical trap potential.

where, $\Delta F = F(\lambda_B) - F(\lambda_A)$. This result basically follows from the second law. The equality holds for a quasi-static, reversible process. For example consider a system as shown in Fig. (1.1). This is an example of a polymer placed in a bath at temperature T and stretched by an external time-dependent force $f(t)$ (thus $\lambda(t) = f(t)$ in this case) by means of, for example, an optical trap. The process is done in the following way. At time $t = 0$ the system is in equilibrium at a temperature T. Then the force is applied from time $t = 0$ to $t = \tau$. This stretching process is done for large number of times, every time starting the system in equilibrium and with the force following the same protocol $f(t)$. If such a process is done at a finite rate, then since we start with different initial equilibrium conditions and also because of the stochastic dynamics, we will get different amount of work done in different realizations. Hence we can find the distribution of work $P(W)$. Though the average work $\langle W \rangle$ is always greater than ΔF for all rates, the distribution may have a large negative part. This negative part implies that for some realizations of the experiment, system is doing work on the external agent while extracting heat from the reservoir. This contribution can be large if the system is non-thermodynamic, and can be viewed as transient violation of the second law. This observation of apparent violation of second law also startled early observers of Brownian motion. In his book [2], Perrin discusses this point. Here we give a paragraph from the same book:

It is clear that this agitation (of a Brownian particle) is not contradictory to the principle

of conservation of energy. It is sufficient that every increase in the speed of a granule is accompanied by a cooling of the liquid in its immediate neighbourhood, and like wise every decrease of speed by a local heating, without loss or gain of energy.

Perrin also stresses the following point that the Brownian motion (or motion at small scales) is not reconcilable with rigid enunciations too frequently given to Carnot's principle, because in a given realization a particle can spontaneously do work at the expense of the surrounding medium (heat bath).

So it must not any longer be said that perpetual motion of the second sort is impossible, but one must say: " On the scale of size (macroscopic) which interests us practically, perpetual motion of the second sort is in general so insignificant that it would be absurd to take into account."

But at the microscopic scales this fluctuations about the most probable behaviour are important and their study might provide us with a better understanding of the second law.

Let us now go back to our discussion of the Jarzynski equality. We consider a general Hamiltonian of a system given by $H_\lambda(\mathbf{x}, \mathbf{p})$, where $\mathbf{x} = \{x_1, x_2, ...x_n\}$ and $\mathbf{p} = \{p_1, p_2, ...p_n\}$ are usual phase-space variables and λ is the parameter which is varied in time from λ_A to λ_B in time τ following a fixed protocol $\lambda(t)$. Then Jarzynski considers the following definition of work done on the system:

$$W_J = \int_0^\tau \frac{\partial H_\lambda(\mathbf{x}, \mathbf{p})}{\partial t} \, dt = \int_0^\tau \frac{\partial H_\lambda(\mathbf{x}, \mathbf{p})}{\partial \lambda} \frac{d\lambda}{dt} \, dt. \tag{1.2}$$

We take an ensemble of such processes, with initial conditions for the system generated from a canonical distribution at temperature T. Then the work done W_J can be calculated for every trajectory in the phase-space given by $(\mathbf{x}(t), \mathbf{p}(t))$. This work is a fluctuating quantity because of two reasons:

1. The initial conditions are generated from a canonical distribution, hence we get different work for different initial conditions.

2. The heat bath generates stochastic forces, which cause fluctuations in the phase-space

paths taken by the system.

It was proved by Jarzynski, that the distribution $P(W_J)$ satisfies the following equality:

$$\langle \exp\{-\beta W_J\} \rangle = \int_{-\infty}^{\infty} dW_J \exp\{-\beta W_J\} P(W_J) = \exp\{-\beta \Delta F\}, \qquad (1.3)$$

where $\beta = 1/k_B T$. We now give a proof that of the Jarzynski equality, for the case where the system is in contact with a heat bath at time $t = 0$ and in equilibrium, but the heat bath is then removed during the driving process. Then the evolution of the system is deterministic and described by the phase-space trajectory $(\mathbf{x}(t), \mathbf{p}(t))$ which evolves according to $H_\lambda(\mathbf{x}(t), \mathbf{p}(t))$, with λ taken from λ_A to λ_B in time τ. Let the ensemble of such trajectories be described by the initial phase-space density given by:

$$\rho_{\lambda_A}(\mathbf{x}(0), \mathbf{p}(0)) = \frac{1}{Z_{\lambda_A}} \exp\{-\beta H_{\lambda_A}(\mathbf{x}(0), \mathbf{p}(0))\}, \qquad (1.4)$$

where $Z_\lambda = \int exp\{-\beta H_\lambda\} \, d\mathbf{x} \, d\mathbf{p}$. For a particular phase-space trajectory starting from $(\mathbf{x}(0), \mathbf{p}(0))$ at time $t = 0$, the work done in time τ is given by Eq. (1.2). The probability of the initial state is $\rho_{\lambda_A}(\mathbf{x}(0), \mathbf{p}(0))$. Hence we get the following average:

$$\langle \exp\{-\beta W_J\} \rangle = \int \rho_{\lambda_A}(\mathbf{x}(0), \mathbf{p}(0)) \, \exp\{-\beta W_J\} \, d\mathbf{x}(0) \, d\mathbf{p}(0). \qquad (1.5)$$

Since the system is isolated, we can write $\partial H/\partial t = dH/dt$, and hence the work done, Eq. (1.2) on the system is nothing but the change in the total energy of the system, i.e., $W_J = H_{\lambda_B}(\mathbf{x}(\tau), \mathbf{p}(\tau)) - H_{\lambda_A}(\mathbf{x}(0), \mathbf{p}(0))$. This gives us:

$$\langle \exp\{-\beta W_J\} \rangle$$
$$= \frac{1}{Z_{\lambda_A}} \int_0^\tau \exp\{-\beta H_{\lambda_A}(\mathbf{x}(0), \mathbf{p}(0))\} \, \exp\{-\beta [\, H_{\lambda_B}(\mathbf{x}(\tau), \mathbf{p}(\tau)) - H_{\lambda_A}(\mathbf{x}(0), \mathbf{p}(0)) \,]\} \, d\mathbf{x}(0) \, d\mathbf{p}(0).$$
$$(1.6)$$

Using Liouville's theorem, giving conservation of phase-space volume we get $d\mathbf{x}(0) \, d\mathbf{p}(0) = d\mathbf{x}(\tau) \, d\mathbf{p}(\tau)$ and the above equation then gives:

$$\langle \exp\{-\beta W_J\} \rangle = \frac{1}{Z_{\lambda_A}} \int \exp\{-\beta H_{\lambda_B}(\mathbf{x}(\tau), \mathbf{p}(\tau))\} \, d\mathbf{x}(\tau) \, d\mathbf{p}(\tau) = \frac{Z_{\lambda_B}}{Z_{\lambda_A}}. \qquad (1.7)$$

Since $F_\lambda = -k_B T \ln(Z_\lambda)$, we then get the Jarzynski equality, given by Eq. (1.3). This equality can also be proved for the situation where system remains in contact with the heat bath during the driving process. In this case, the system and the reservoir are considered to be a larger isolated system, with Hamiltonian given by, $\mathcal{H}_\lambda = H_\lambda + H_B + h_I$, where H_λ is the system Hamiltonian, H_B is the reservoir Hamiltonian and h_I is the coupling between the system and the reservoir. The result in Eq. (1.3) was proved for weak coupling between the system and reservoir in [3] then for the general case in [6]. This relation can also be proved for discrete Markovian process [10], with heat bath dynamics and for Langevin dynamics [15] (we will outline this proof later in this section). It is remarkable that the result in Eq. (1.3) is valid independent of the rate at which the external parameter is varied. The only requirement is that the system should be in the equilibrium when the driving process starts. Unlike Eq. (1.1), this is an *equality* which relates a non-equilibrium quantity to an equilibrium free energy difference.

We will now give a simple example of a driven system with Langevin dynamics, where one can explicitly calculate the work distribution function and verify the Jarzynski equality. Consider a Brownian particle in a harmonic trap, which is moved with a constant velocity u. The Hamiltonian of the system is given by:

$$H = \frac{p^2}{2m} + \frac{1}{2} k(x - \alpha(t))^2, \tag{1.8}$$

where $\alpha(t) = ut$ is now the external control parameter. We consider the over-damped limit in which case the inertial term drops out and the Langevin equation of motion is given by:

$$\gamma \dot{x} = -k \left[x - \alpha(t) \right] + \eta(t), \tag{1.9}$$

where $\eta(t)$ is a Gaussian white noise, satisfying, $\langle \eta(t) \rangle = 0$ and $\langle \eta(t)\eta(t') \rangle = 2k_B T \gamma \delta(t - t')$. Using the Jarzynski definition of work, Eq. (1.2), we get for the work done in time τ:

$$\begin{aligned} W_J &= \int_0^\tau \frac{\partial H}{\partial \alpha} \dot{\alpha} \, dt = -k \int_0^\tau \dot{\alpha} \left[x - \alpha(t) \right] dt \\ &= \frac{k}{2} \left[\alpha^2(\tau) - \alpha^2(0) \right] - k \int_0^\tau \dot{\alpha} \, x \, dt. \end{aligned} \tag{1.10}$$

The general solution of Eq. (1.9) is given by:

$$x(t) = e^{-(k/\gamma) t} x_0 + \frac{1}{\gamma} \int_0^t e^{-(k/\gamma) (t-t')} [k\alpha(t') + \eta(t')] dt'. \qquad (1.11)$$

We choose $x_0 = x(t = 0)$ from the initial equilibrium distribution $P(x_0) = \exp\{-\beta H_{\alpha(0)}\}/Z_{\alpha(0)}$. It can be seen from Eq. (1.10) that W_J is linear in x, while x itself is linear in both, x_0 and $\eta(t)$ which are Gaussian variables. Hence it follows that the distribution of W_J will also be Gaussian. We thus just need to find the first and second moments of this distribution. We have:

$$P(W_J) = \frac{1}{\sqrt{2\pi\sigma_{W_J}^2}} \exp\left[- \frac{(W_J - \langle W_J \rangle)^2}{2\sigma_{W_J}^2} \right]. \qquad (1.12)$$

Using Eqs. (1.10) and (1.11), it is straightforward to calculate $\langle W_J \rangle$ and $\sigma_{W_J}^2 = \langle (W_J - \langle W_J \rangle)^2 \rangle$, where we note that $\langle ... \rangle$ denotes an average over initial conditions as well as over noise. We find:

$$
\begin{aligned}
\langle W_J \rangle &= \gamma u^2 \tau \left[1 + \frac{\gamma}{k\tau} (e^{-(k/\gamma)\tau} - 1) \right], \\
\sigma_{W_J}^2 &= 2 k_B T \gamma u^2 \tau \left[1 + \frac{\gamma}{k\tau} (e^{-(k/\gamma)\tau} - 1) \right] = 2k_B T \langle W_J \rangle.
\end{aligned}
\qquad (1.13)
$$

For this particular Hamiltonian given by Eq. (1.8), it is easy to show that the free energy is independent of α and hence $\Delta F = 0$. Using Eqs. (1.12, 1.13), we immediately get:

$$\langle \exp\{-\beta W_J\} \rangle = 1 = \exp\{-\beta\Delta F\}. \qquad (1.14)$$

Thus we have verified that the Jarzynski equality Eq. (1.3) is satisfied.

Now we will discuss the fluctuation theorems which are somewhat more general than the Jarzynski equality and give information about the fluctuations of the entropy production in a non-equilibrium system. In fact we will see that the Jarzynski equality can be derived from one of the fluctuation theorems. There are various versions of the fluctuation theorems. All of them start with some definition of the entropy produced S in a particular realization of a non-equilibrium process in time τ. As discussed earlier (for the work done W), we

expect this entropy S to be also a fluctuating quantity with a distribution, say $P(S)$. The transient fluctuation theorem (TFT) [8, 12 − 15], states that for a system initially in thermal equilibrium, $P(S)$ satisfies the following equation:

$$\frac{P(S)}{P(-S)} = e^{S/k_B}. \tag{1.15}$$

This result is valid for any time interval τ. Another version of TFT, due to Crooks [10] gives:

$$\frac{P_F(S)}{P_R(-S)} = e^{S/k_B}, \tag{1.16}$$

where $P_F(S)$ and $P_R(S)$ are the probabilities in forward and time reversed processes respectively. This theorem is also true for all times τ. The steady state fluctuation theorem (SSFT) looks at the case where the initial state is chosen from a non-equilibrium steady state, rather from an equilibrium state as in TFT. In this case, the statement of the theorem as obtained by Cohen and Gallavotti [9] is

$$\frac{P(\sigma)}{P(-\sigma)} = e^{\tau\sigma}, \tag{1.17}$$

where $\sigma = S/(k_B\tau)$ is rate of entropy production and one looks at the limit $\tau \to \infty$.

Here we will give a proof of Crooks' fluctuation theorem for a single particle following Langevin dynamics. Then we will also show how to obtain the Jarzynski equality from this theorem. Consider a Brownian particle in the presence of an external potential $U(x)$. The Hamiltonian of the system is given by:

$$H = \frac{p^2}{2m} + U(x). \tag{1.18}$$

This particle is driven by an external time-dependent force $f(t)$, doing work on the particle. We also assume that the system is in contact with a heat bath at temperature T and it's time evolution is described by Langevin dynamics. The Langevin equation of motion is thus given

by:

$$m\ddot{x} = -\frac{\partial U}{\partial x} + f(t) - \gamma\dot{x} + \eta(t) = -\frac{\partial H_f}{\partial x} - \gamma\dot{x} + \eta(t),$$

$$\text{with} \quad H_f = H - f(t)x, \tag{1.19}$$

where $\eta(t)$ is a Gaussian noise satisfying $\langle\eta(t)\rangle =$ and $\langle\eta(t)\eta(t')\rangle = 2k_BT\gamma\delta(t-t')$. For such stochastic systems the proof of Crooks' fluctuation theorem and the Jarzynski equality can be shown to follow from the principle of microscopic reversibility. For discrete systems, evolving for example through Monte Carlo dynamics, this principle has been proved by Crooks. Here we give a proof for Langevin dynamics [15].

We first state the principle of microscopic reversibility. Consider the evolution of the system from time $t = 0$ to $t = \tau$, through a path in phase-space given by $\{x(t), p(t), f(t)\}$. This path will correspond to a particular realization of the noise $\eta(t)$. The probability of this path is then given by:

$$P_+ = \mathcal{N} \exp\{-\frac{1}{4k_BT\gamma} \int_0^\tau \eta_+^2 \, dt\} = \mathcal{N} \exp\left\{ -\frac{1}{4k_BT\gamma} \int_0^\tau (m\ddot{x} + \frac{\partial U}{\partial x} - f(t) + \gamma\dot{x})^2 \, dt \right\},$$

$$\tag{1.20}$$

where $\mathcal{N}$ is a normalization factor. Now consider the time reversed trajectory given by $\{x'(t), p'(t), f'(t)\} = \{x(\tau - t), -p(\tau - t), f(\tau - t)\}$. The probability of this path is:

$$P_- = \mathcal{N} \exp\{-\frac{1}{4k_BT\gamma} \int_0^\tau \eta_-^2 \, dt\} = \mathcal{N} \exp\left\{ -\frac{1}{4k_BT\gamma} \int_0^\tau (m\ddot{x}' + \frac{\partial U}{\partial x'} - f'(t) + \gamma\dot{x}')^2 \, dt \right\}$$

$$= \mathcal{N} \exp\left\{ -\frac{1}{4k_BT\gamma} \int_0^\tau (m\ddot{x} + \frac{\partial U}{\partial x} - f(t) - \gamma\dot{x})^2 \, dt \right\}. \tag{1.21}$$

We then get after some simplification:

$$\frac{P_+}{P_-} = \exp\left\{ -\frac{1}{k_BT} \int_0^\tau (-\gamma\dot{x} + \eta)\,\dot{x}\,dt \right\} = \exp\{ -\beta Q \}, \tag{1.22}$$

where $Q = \int_0^\tau (-\gamma\dot{x} + \eta)\,\dot{x}\,dt$, is the amount of heat transferred from the heat bath to the system in time τ. The identification of Q as heat transferred follows from the fact that $(-\gamma\dot{x} + \eta)$ is the force from the heat bath on the particle.

Eq. (1.22) is the principle of microscopic reversibility. This principle is similar to that of detailed balance principle. The principle of microscopic reversibility relates the probability of a specified path in phase-space to the probability of the time reversed path. The detailed balance condition refers to the probability of transition between two points in phase-space say C and C' and states that $P(C \to C') = P(C' \to C)\, e^{-\beta\,[E(c')-E(c)]}$ and does not make reference to any specific path in phase-space.

Now we proceed to prove Crooks' fluctuation theorem. Following Crooks we will first motivate the definition of the entropy produced, S, for a given trajectory. This entropy S consists of two parts: a contribution from change in entropy of the bath which is $-\beta Q$ and another contribution coming from the change in entropy of the system. The entropy change of the system is found in the following way. Let some parameter $f(t)$, be switched from an initial value $f_A = f(0)$ to a final value $f_B = f(\tau)$. Let the equilibrium distributions corresponding to the parameters f_A and f_B be ρ_{f_A} and ρ_{f_B} respectively, where $\rho_f = e^{-\beta H_f}/Z_f$. Then the equilibrium entropy of the ensemble is given by:

$$S = -k_B \int \rho_f(x, p)\ln\rho_f(x, p)\, dx\, dp. \tag{1.23}$$

One can think of $-k_B\ln\rho_f(x, p)$ as the entropy of a micro-state and the change in entropy of the system is given by $-k_B\ln\rho_{f_B} + k_B\ln\rho_{f_A}$. Thus for a given path, Crooks' definition of the *total* entropy generated is:

$$S/k_B = \ln\rho_{f_A} - \ln\rho_{f_B} - \beta Q. \tag{1.24}$$

Then $P_F(S)$, the probability of entropy S generated in time τ, in time forward process is given as:

$$
\begin{aligned}
P_F(S) &= \int D[x, p]\, dx(0)\, dp(0)\, dx(\tau)\, dp(\tau)\, \rho_{f_A}\, P_+\, \delta(S_F - S) \\
&= \int D[x, p]\, dx(0)\, dp(0)\, dx(\tau)\, dp(\tau)\, \rho_{f_A}\, P_-\, e^{-\beta Q}\, \delta(S_F - S),
\end{aligned}
\tag{1.25}
$$

where S_F is the entropy generated for a given forward trajectory and $D[x, p]$ denotes a sum over all paths $\{x(t), p(t)\}$ between $\{x(0), p(0)\}$ and $\{x(\tau), p(\tau)\}$. Also from Eq. (1.24) we can

write $\rho_{f_A} \, e^{-\beta Q} = e^{S_F/k_B} \, \rho_{f_B}$. Note that under time reversal S changes sign hence we can write $S_R = -S_F$. Substituting these relations in Eq. (1.25), we get:

$$P_F(S) = \int D[x, p] \, dx(0)dp(0) \, dx(\tau)dp(\tau) \, \rho_{f_B} \, P_- \, e^{-S_R/k_B} \, \delta(S_R + S) = e^{S/k_B} \, P_R(-S),$$

(1.26)

thus proving Eq. (1.16).

Now we show how the Jarzynski equality can be derived from the Crooks' fluctuation theorem. To do this we note that, $\rho_{f_A} = \exp\{-\beta H_{f_A}\}/Z_{f_A}$ and $\rho_{f_B} = \exp\{-\beta H_{f_B}\}/Z_{f_B}$, where $H_f(x, p) = p^2/2m + U(x) - f(t)x$. This implies, using Eq. (1.24):

$$
\begin{aligned}
S/k_B &= \beta H_{f_B} + \ln Z(f_B) - \beta H_{f_A} - \ln Z(f_A) - \beta Q \\
&= -\beta(F_{f_B} - F_{f_A}) + \beta(H_{f_B} - H_{f_A}) - \beta Q,
\end{aligned}
$$

(1.27)

where, H_{f_A} and H_{f_B} are initial and final Hamiltonians, F_{f_A} and F_{f_B} are initial and final free energies. Using the equation of motion Eq. (1.19) and the definition of $H_f(x, p)$, it is easily seen that:

$$\frac{dH_f(x, p)}{dt} = \frac{\partial H_f(x, p)}{\partial t} + \frac{dQ}{dt}.$$

(1.28)

Which then gives $H_{f_B} - H_{f_A} = W_J + Q$. Hence from Eq. (1.27) we get:

$$S/k_B = -\beta \, \Delta F + \beta \, W_J = \beta \, W_d,$$

(1.29)

where we have defined $W_d = W_J - \Delta F$ as the dissipated work. Thus from the Crooks' identity we have:

$$\frac{P_F(W_d)}{P_R(-W_d)} = e^{\beta W_d}.$$

(1.30)

This is the Crooks' fluctuation theorem for work distribution and from this we get:

$$\int_{-\infty}^{\infty} P_F(W_d) \, e^{-\beta W_d} \, dW_d = \int_{-\infty}^{\infty} P_R(-W_d) \, dW_d = 1.$$

(1.31)

Thus

$$\langle \exp\{-\beta W_d\} \rangle = \langle \exp\{-\beta(W_J - \Delta F)\} \rangle = 1, \tag{1.32}$$

which is the Jarzynski equality in Eq. (1.3).

Let us see the validity of this Crooks' fluctuation theorem for the example we considered previously, namely a Brownian particle in a moving harmonic trap. In this example we proved that the distribution of work W_J is Gaussian. For Gaussian distribution it can be shown that [15] the distribution for forward trajectory $P_F(W_J)$ is same as that for time reversed trajectory $P_R(W_J)$ and therefore the Crooks' fluctuation theorem also implies the transient fluctuation theorem. Since $\Delta F = 0$ for this system, dissipated work W_d is nothing but the Jarzynski work W_J. Hence from the distribution given in Eqs. (1.12) and (1.13), we get:

$$\frac{P(W_J)}{P(-W_J)} = \exp\left[\frac{2\langle W_J \rangle W_J}{\sigma_{W_J}^2}\right] = e^{\beta W_J}, \tag{1.33}$$

which is the transient fluctuation theorem.

Contribution of this thesis: The fluctuation theorems have been proved for a large class of systems. However, their general validity has not been established and is still an open question. Here we look at the validity of these relations, namely the Jarzynski equality and the fluctuation theorems, for a single classical spin in the presence of a time-dependent magnetic field and where the dynamics of the spin is modeled by Glauber dynamics. Also, we note that the Jarzynski equality and the fluctuation theorems are general relations satisfied by the probability distribution function of some non-equilibrium quantity like work, and do not make any reference to the actual form of these distributions. There have been very few earlier studies which have explicitly looked at the form of the distribution functions, except in linear systems where the distributions are Gaussian. We have performed Monte-Carlo simulations to obtain the distributions for different driving protocols such as ramped magnetic field and periodically varied fields which can be symmetric or asymmetric. In general we find that the distributions are broad and have non-trivial forms. In some special limits, namely fast and

slow driving rates we show that the work distributions can be analytically calculated. We verify that Crooks' fluctuation theorem is always satisfied while the usual TFT and a steady state version is not.

1.2 Ratchets, heat engines and molecular motors

Ratchet models have been studied for a long time to examine how directed motion occurs in non-equilibrium systems even in the absence of any net external bias. Among its applications it has been proposed that Brownian ratchets could provide a possible mechanism of transport of motors in biological cells. An example of a molecular motors is kinesin which moves uni-directionally on microtubules inside the cell. Also molecular pumps, like sodium or potassium pumps maintain active transport across membranes against a concentration gradient. Note that these motors and pumps work in a very noisy environment and still they exhibit directed motion. It is thus of interest to understand the functioning of these highly complex systems by studying simple microscopic models. In this context several ratchet models like flashing ratchets, rocking ratchets, correlation ratchets, frictional ratchets etc. have been proposed [75]. In all these models one tries to get a net motion, by combining the effects of thermal (or a-thermal) fluctuations, spatial or temporal anisotropy and external non-directed driving. In some cases, the system is in contact with several thermal baths (thermal ratchets) at different temperatures. One of the first example of a ratchet is in fact Feynman's ratchet and pawl machine [49], where the machine is kept in contact with two baths at different temperatures, and is able to extract work from the heat transferred. In many of these models, one is interested in the dependence of the particle current on system parameters like temperature, diffusion constant, amplitude of external driving etc. Also one is interested in finding out the efficiency of these motors, a question which is of obvious practical interest. Many studies have been done to understand these aspects [64 − 66, 79]. The efficiency has mainly been studied as a function of temperature and external load in rocking, frictional ratchets. There have been lot of studies on improving the efficiency of such ratchet models. It turns out that this efficiency is small due to the non-equilibrium and irreversible

nature of the system. Questions like whether irreversibility can be suppressed, and whether a system can be made to achieve Carnot efficiency, have also been studied [69, 74]. To study efficiency of such ratchets models one usually uses the method of stochastic energetics developed by Sekimoto [64]. In this framework all the quantities like work done, input energy, output energy etc. can be understood and computed by the Langevin equation approach.

In the following sections we discuss a few ratchet models. We begin with the well known Feynman's ratchet and pawl model and then we look at some other models of externally driven ratchets, namely flashing, rocking and inhomogeneous ratchets.

1.2.1 Feynman's ratchet and pawl model

In this section we will look at a model discussed in *Feynman lectures on Physics, Vol. 1*. This model was devised to understand, from a molecular or kinetic point of view, how much maximum amount of work could be extracted from a heat engine. As we know from thermodynamics, there is a maximum limit to this efficiency, given by the Carnot efficiency. Feynman was trying to understand this through a microscopic mechanical model and using statistical mechanics. Feynman's ratchet and pawl device is shown in Fig. (1.2). This consists of two compartments containing gases at temperatures T_1 and T_2. The compartment (**I**), at temperature T_1, contains vanes which are able to rotate freely in both directions. The compartment (**II**), at temperature T_2, contains a ratchet and a pawl as shown. This ratchet with the pawl (with a spring) pressing on its teeth is an *asymmetric* object. With the pawl pressing on it, the ratchet can move only in one direction. The ratchet and the vanes are connected by a rigid rod. Let us consider a situation where both the temperatures are same, i.e., $T_1 = T_2 = T$. In compartment (**I**), gas molecules bombard on the vanes and make it rotate randomly. When the vanes try to move in one direction it is allowed but the other direction appears to be forbidden due to the presence of ratchet and pawl to which it is connected. Thus we should see the vanes moving only in one direction and the load moves up. It apparently looks like we get a directed motion out of random motion in thermal equilibrium. The flaw in above argument lies in the fact that, in our analysis we haven't considered the motion
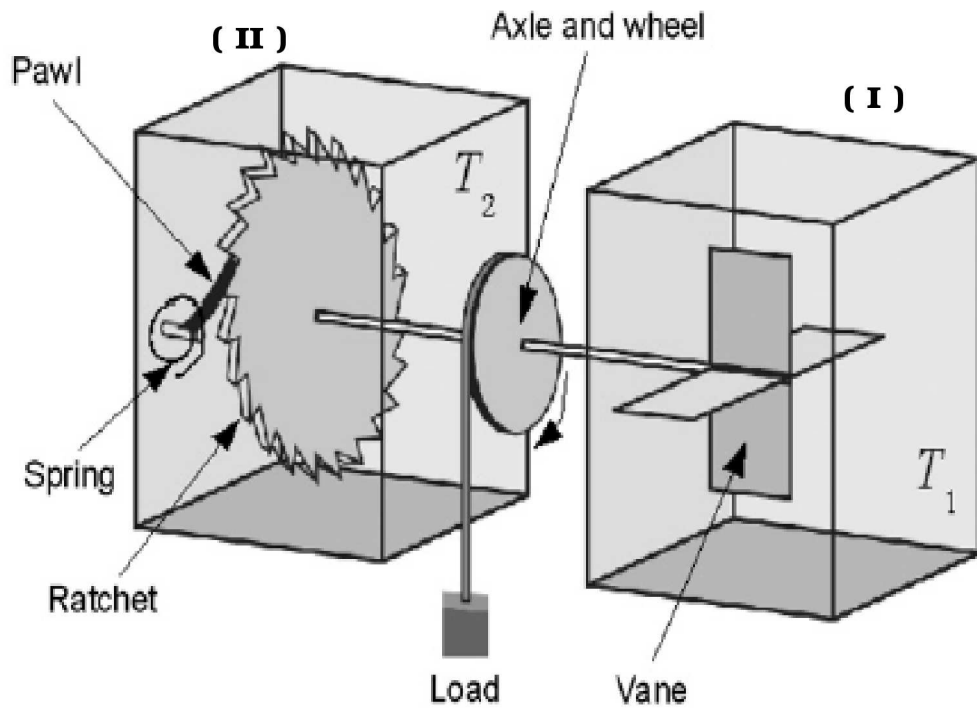
Figure 1.2: Feynman's ratchet and pawl engine.

of the pawl at all. Just as the vanes are getting kicks from the gas molecules, the pawl in the other compartment is also getting bombarded by the gas molecules in its compartment. Due to these kicks the pawl could be pressing against the ratchet, but it can also get lifted above the ratchet once in a while. At this particular instant when the pawl is lifted, if vanes get the kick in other direction (so called *forbidden*) then the ratchet is free to rotate. Thus we can see that in fact there can be motion in both the directions. Hence if we look at the load tied to the rigid rod, we will see it moving up and down at various instances, but on an average there will be no net motion.

Now let us see what happens when the temperatures are different. Let $T_1 > T_2$, that is the pawl is colder than the vanes. In this case, Feynman shows that directed motion is possible. Roughly the argument is as follows. The probability of a forward motion, by one tooth of the ratchet is $e^{-\epsilon/k_B T_1}$, where ϵ is the energy required to lift the pawl. On the other hand the probability of a reverse motion is $e^{-\epsilon/k_B T_2}$. Hence, as the rate of these jumps are no longer

equal, when $T_1 > T_2$, there can be a net forward motion of the ratchet. This can be used to do work, thus working as an engine.

Feynman then argues that in the reversible mode of operation, the efficiency of this model reaches a Carnot efficiency. In this analysis there are some flaws, which were pointed out by Parrondo [50] and Magnasco [51]. The point of their criticism was that, this system unlike other usual heat engines, is in contact with two heat baths at two different temperatures *simultaneously*, thus it can never work in a reversible way.

Actual analysis, of the Feynman's ratchet and pawl system turns out to be quite difficult, so different models have been proposed to model this engine [48 − 52]. A simple way of modeling is that given by Magnasco [51]. Consider a system with two degrees of freedom, x and y, where x is a cyclic coordinate representing the ratchet motion and y representing the pawl. These two coordinates are in contact with heat baths, at different temperatures T_1 and T_2 respectively, corresponding to the two compartments with gas in Feynman's model, and modelled by Langevin equation. An asymmetric periodic potential $U(x, y)$ is included to represent the asymmetry and periodicity of ratchet tooth and the interaction of ratchet and pawl degree of freedom. When the pawl is pressing against the ratchet, this potential is infinite. For a particular choice of $U(x, y)$ considered by Magnasco [51], the system works as an engine depending on the two temperatures, similar to Feynman's model. Also it was shown that the efficiency of this model is quite low, and it doesn't reach Carnot efficiency.

In such devices it is important to note the following points. A difference between such microscopic engines and thermodynamic engines like Carnot engines is that here effects of thermal fluctuations are important. The second important difference is that the system is simultaneously in contact with two (or more) heat baths at different temperatures and hence is essentially always a non-equilibrium system.

1.2.2 Other ratchet models

In the last section we discussed the ratchet and pawl model which is an example of an engine driven by temperature differences, with no external driving. Work is extracted solely from the

heat baths at different temperatures. There are other class of ratchets where an external time-dependent driving drives the system into a non-equilibrium steady state, and useful work is done. These models usually look at particle transport. In such models the general situation is as follows. Consider a Brownian particle placed in an asymmetric periodic potential such as shown in Fig. (1.3). Then, even if the potential is asymmetric, the system equilibrates at the temperature of the bath and reaches Boltzmann distribution. In this equilibrium situation there will be no net particle current. Thus we need to make the system non-equilibrium, and this can be done by various means and below we will discuss three examples.

I. Flashing ratchet: Suppose now that the asymmetric potential is made time-dependent [55]. This will drive the system into a non-equilibrium state and in such a situation we can have a uni-directional current in the system. In general such a system can be described by a Langevin equation as follows:

$$m\ddot{x} = -\frac{\partial U(x,t)}{\partial x} - \gamma \dot{x} + \eta(t), \qquad (1.34)$$

where, m is the mass of the particle, γ is the dissipation in the bath, $U(x,t)$ is the external asymmetric time-dependent periodic potential. For flashing ratchets one takes $U(x,t) = U(x)f(t)$. Also $\eta(t)$ is the noise due to the heat bath. This noise is usually taken to be a Gaussian white noise satisfying $\langle \eta(t) \rangle = 0$ and $\langle \eta(t)\eta(t') \rangle = 2k_B T \gamma \delta(t-t')$. A simple example of a time-dependent potential is one shown in Fig. (1.3). In this case this potential is switched on (for time T_{on}) and off (for time T_{off}) and this is repeated periodically.

When the potential is off (during T_{off}), then particles are free to diffuse. Suppose we choose, $T_{off} \sim X_s^2/2D$, where D is the diffusion constant. Then, during this time, many particles starting from close to the potential minima would have diffused to the peak on the left hand side while few particles would have reached the peak on the right. Now when we switch on the potential, the particles on the left will slide down the slope to the next minima while those on the right return to the same minima (see Fig. (1.4)). Hence we get a net motion to the left. It is important to note that *we require diffusion* in order to get a directed motion.
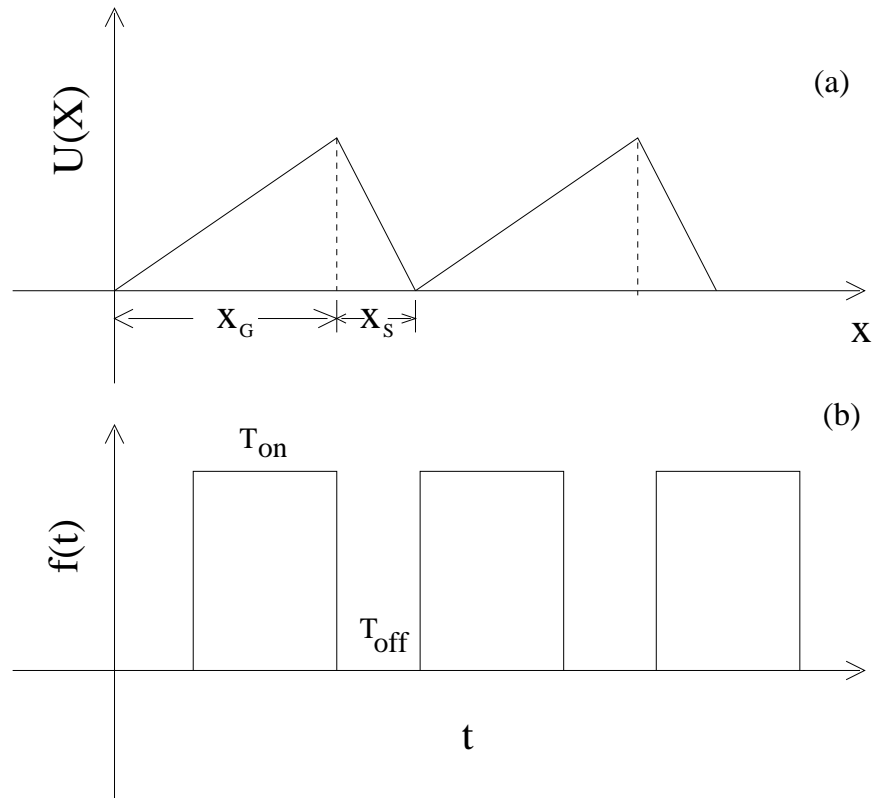
Figure 1.3: Part (*a*) of the figure shows a saw-tooth potential, an example of an asymmetric potential. Part (*b*) shows a switching function used to generate a time-dependent potential $U_t(x) = U(x)f(t)$, where $V(x)$ is as given in part (*a*). For time T_{on} potential in on and for time T_{off}, $U(x) = 0$. Such a driving can lead to an uni-directional particle current.
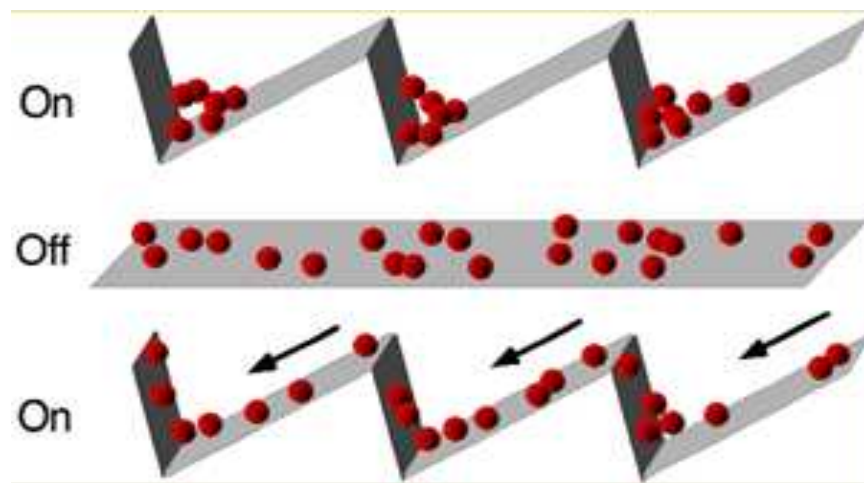

Figure 1.4: Brownian particles are trapped in a periodic, asymmetric potential that can be turned on and off. The random diffusion when the potential is off is converted into net motion to the left when the ratchet is switched on.
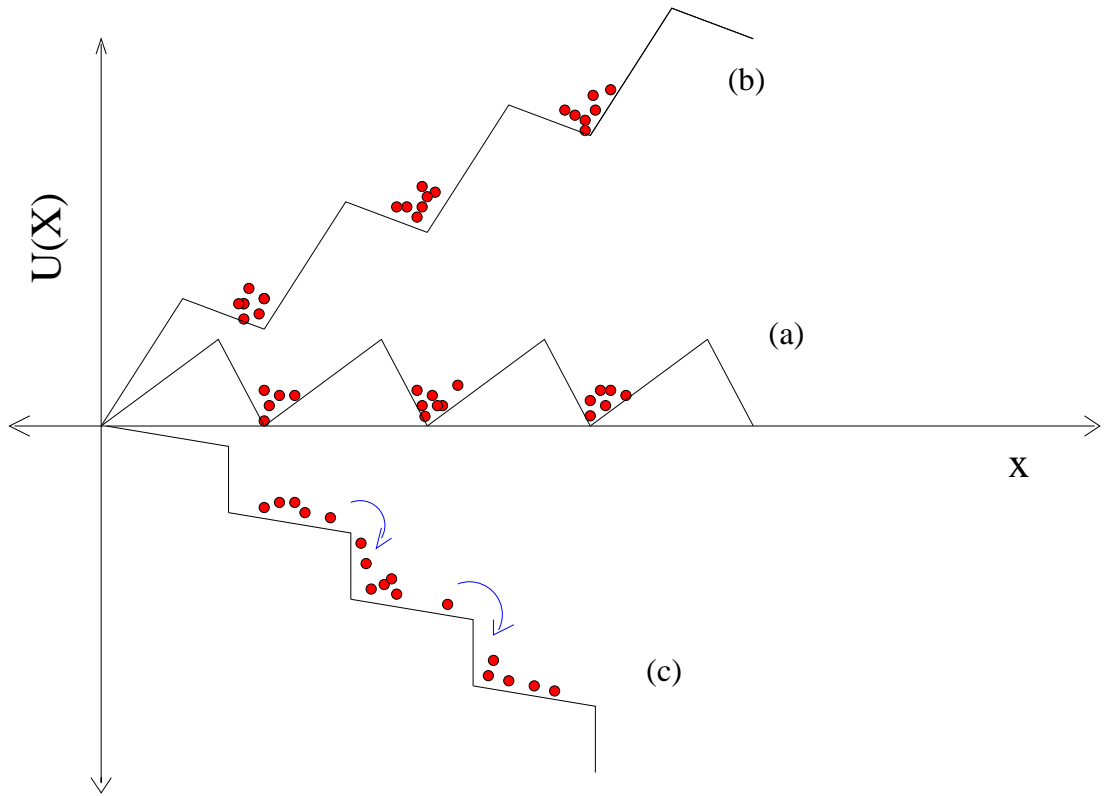
Figure 1.5: A rocking ratchet model where the external force is varied periodically in time. Because of the asymmetry of the potential, the situation (*b*) is not same as that of (*c*). In this case we get a motion in the direction of steeper slope.

Now suppose there is a gradient in the potential (which opposes the current, usually called as *load*). Then till some maximum load called as *stalled* load, the particles are able to move against this gradient and thus useful work can be done.

II. Rocking ratchet: In the case of flashing ratchets, discussed above, the potential fluctuates between on and off states. In another class of ratchets known as rocking ratchets [56], where one applies a time-dependent force with zero mean (see Fig. (1.5)). For example such a potential can be given by $U(x,t) = U(x) - \sin(\omega t)x$. This corresponds to a situation where the slope of the saw-tooth potential is periodically varied in time. More generally, this variation of slope can be done in a random or periodic way, the only requirement being that the average slope is zero. Consider the zero temperature case. Then, when the force is negative, (part (*b*) in Fig. (1.5)), particles can remain trapped in the valley of the potential, where local force there is positive. On the other hand, when the external force is positive (part (*c*)
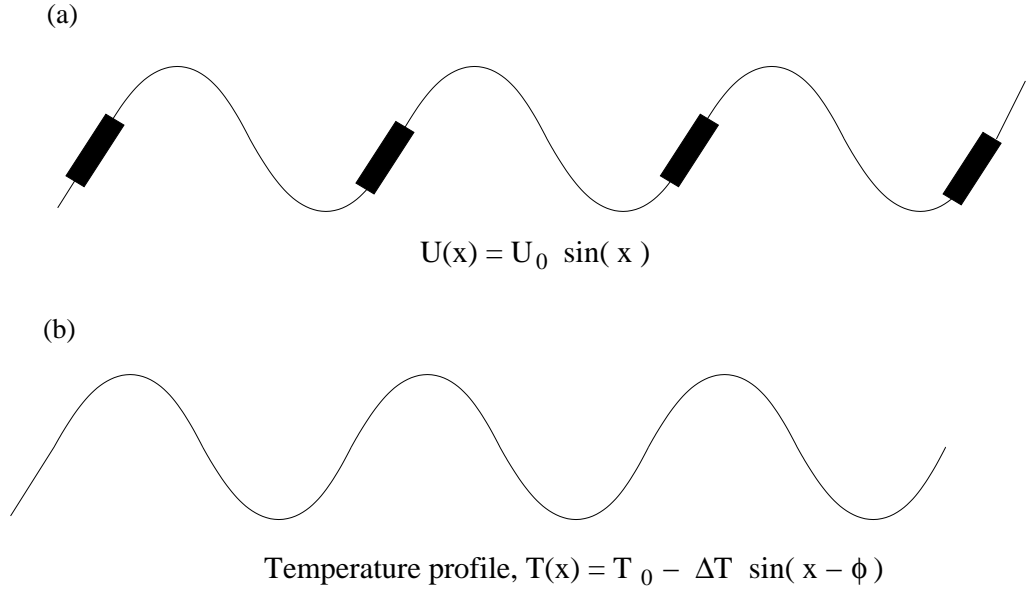
(a)

$$U(x) = U_0 \, \sin(\, x \,)$$

(b)

Temperature profile, $T(x) = T_0 - \Delta T \, \sin(\, x - \phi \,)$

Figure 1.6: Inhomogeneous ratchet model where a periodic potential (*a*), and a temperature profile (*b*), is separated by a phase difference ϕ. Dark regions in (*a*) correspond to the higher temperature regions. Direction of the current depends on this phase difference.

in Fig. (1.5)), then particles slide down the slope. Thus the situations $+F$ and $-F$ are not equal and opposite to each other, which happens due the asymmetry of the potential, and we get a net current. This can be shown to be true even for finite temperatures. Unlike the case of flashing ratchets, the direction of the current in this case is in the direction of the steeper slope. Note that the flashing and rocking ratchets can be thought of as examples where a $\mathcal{DC}$ current is generated by applying an $\mathcal{AC}$ field.

III. Inhomogeneous ratchet: A third type of ratchet is the inhomogeneous ratchets [57, 58], which unlike flashing and rocking ratchets, have spatially symmetric periodic potential $U(x)$. They show directional transport due to the presence of space dependent diffusion coefficient $D(x)$. This space dependence can arise, for example from a spatially varying temperature $T(x)$ [57 − 60], since the diffusion constant is given by $D(x) = k_B T(x)/\gamma$. These systems are common in nature. For example, colloidal particles diffusing near any surface have space dependent diffusion coefficient, molecular motors moving on the microtubules experience space dependent mobility [63]. In this case, the ratchet effect arises because the system dissipates energy differently at different places due to the space dependent temperature $T(x)$. In this case the only criterion to be satisfied is that both the potential $U(x)$ and the

temperature $T(x)$ have to be periodic, and should be separated by a phase difference other than 0 or π.

Consider part (*a*) in Fig. (1.6), where dark regions corresponds to higher temperature (this is sometimes called as Landauer torch) corresponding to the maxima of temperature profile. Particles try to settle at the minima of the potential but, all the time they fluctuate around this minima due to noise from the bath. Thus when particles come into the contact with these higher temperature regions they get enough energy to cross the barrier and jump to next valley on the right. Thus particles in any minima will find it easier to jump to the right than to the left. Hence this temperature anisotropy produces a net particle transport in the system, whose direction and magnitude depends on the phase ϕ.

Contribution of this thesis: Here we look at models of both heat and particle pumps. These models are somewhat different from various ratchet models which we have described above and are motivated by models of quantum pumps. Unlike the flashing and rocking ratchets, there is no asymmetric potential in the examples we study. These models have external time-dependent magnetic field, forces etc. doing work on the system and driving the system in to non-equilibrium steady state. The ratchet effect is achieved through the fact that the external driving is both time, as well as space dependent.

In chapter (3) we study following two classical models of heat pump,

1. A spin system consisting of two coupled Ising spins each driven by periodic magnetic fields with a phase difference, and connected to two heat reservoirs.

2. An oscillator system of two interacting particles driven by periodic forces with a phase difference and connected to two reservoirs.

In both these models we drive the system by external periodic time-dependent magnetic fields or forces, with a phase difference and connected to multiple reservoirs. We find that though these models are based on same designing principles, one of them (Ising system) is able to work both as a heat pump and as an engine but the other is not. As discussed earlier for ratchet systems, to work, require spatial or temporal asymmetry. In these models there is

no built-in asymmetry but the phase different driving leads to an overall symmetry breaking.

In chapter (4) we study a model of a particle pump. We look at the symmetric exclusion process (SEP), with time-dependent hop-out rates at two or more sites. These hop-out rates are periodic in time and with a phase difference. We find that in this system, in the steady state we get a non zero $\mathcal{DC}$ current. Unlike previous models studied in chapter (3), here there is a particle transport. The hop-out rate is related to the diffusion constant and the modulation of this diffusion constant can be thought of as arising from a spatial and temporal modulation of the temperature or friction coefficient. We study this model by simulations and also analytically by doing a perturbation theory in driving strength around the exactly known time-independent SEP. We calculate general current expression and study its behaviour in few special cases. We look at the behaviour of this current as a function of driving frequency and the phase difference and also get a formal expression in adiabatic and fast driving limits.