INTRODUCTION

1.1 Preliminary Remarks

Fluctuations are ubiquitous in nature. Turbulent water waves in a sea, noise in loudspeakers and electrical circuits, Brownian motion of small colloidal particles when suspended in water are some of the familiar examples. A closer look into these phenomena clearly suggests that a better understanding of systematic or deterministic motion and fluctuations around them, is essential for a correct description of these natural events. These two aspects of motion are naturally intermingled in many phenomena in physics and chemistry. For example, the escape of a particle from a metastable state which lies at the heart of chemical kinetics or spontaneous decay of an excited atom can not be possible without the presence of fluctuations. In the former case one is concerned with thermal fluctuation while in the later vacuum fluctuation plays the key role. Fluctuations induced by stochastic sources are well characterized by their probability distributions. For this it is important to understand the origin of fluctuations or stochasticity from thermodynamics, statistics and quantum physics. The second law of thermodynamics suggests that a component of a macroscopic system kept in a thermal environment at temperature T suffers fluctuations of the order of KT, K being the Boltzmann constant. In statistics central limit theorem asserts that a system of N independent elements exhibits statistical fluctuations of the order N^{1/2}. Finally, uncertainty principle provides us the natural limit on measurement in terms of energy fluctuations of the order of ħ\omega, where ħ is Planck constant divided by 2π and \omega is the characteristic frequency of the system. The fluctuations characterized by these considerations are
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internal in nature, since they depend only on the intrinsic parameters of
the system and therefore can not be avoided under any circumstances.

In the present thesis we deal with these internal fluctuations where
the stochasticity is due to quantum Brownian motion. The microscopic
origin of this stochastic motion may be traced back to an well known
paradigm, the system-reservoir model. A typical variant of this model
is a magnetic dipole coupled to a boson field [1] or a two-level atom
coupled to a continuum of radiation field modes. The system-reservoir
model describes a variety of physical and chemical systems ranging
from laser physics [2], atomic physics [3], quantum optics [4], solid state
physics [5], chemical kinetics [6] and so on, encompassing various phe­
nomena, like spontaneous emission [7], polaron formation [8], defects
in insulator or semiconductor [9], exciton motion [10], Kondo problem
[11], macroscopic quantum tunneling [12], chemical reactions [13, 14], to
name a few. The scope for theoretical treatment of quantum Brownian
motion is therefore very broad. However, the essential description lies on
appropriate elimination of reservoir degrees of freedom from the effec­
tive dynamical evolution of the system which is governed by quantum
dissipation and noise which are connected by fluctuation-dissipation
relationship. This ensures detailed balance and the overall system is
thermodynamically closed.

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In the overwhelming majority of the treatments dealing with quan­
tum dissipative systems as mentioned above, the reservoir acts as a
bosonic heat bath [4, 15, 16] which is dominated by delocalized modes
[7, 17, 18, 19]. However, there often arises situations, particularly, at low
temperatures where one has to take care of the bath characterized by
dominant localized modes. The dynamics of a cavity mode damped by
a reservoir of two-level atoms is an early example suggested by Lamb,
Scully and Sargent [2] in seventies. The spin-bath is a good description
of the underlying stochastic dynamics in such situations. It need not
be over emphasized that a spin bath is a generically distinct quantum
object when compared to a bosonic bath. The present thesis is basically an effort to explore some aspects of quantum Brownian dynamics within the framework of a system-spin-bath paradigm. Our aim here is to derive the basic equations for quantum stochastic evolution of the system under diffusive, inertial and overdamped conditions and apply them for the calculation of diffusive transport, thermally activated rate processes, tunneling and dynamical contribution to thermodynamic properties, like specific heat.

Our work is outlined as follows:

(i) We first propose a scheme for quantum Brownian motion of a particle in a spin bath. Based on the spin coherent state representation of the noise operators and a canonical thermal distribution of the associated c-numbers, we derive a quantum analogue of generalized Langevin equation for quantum mechanical mean position of the particle subjected to an external force field. The approach allows us to map the quantum problem on a classical setting. The quantum dispersion around the mean can be estimated order by order by a set of quantum correction equations up to a desired degree of accuracy for a given nonlinear potential. We then derive a quantum diffusion equation for free particle as an immediate application and show that quantization, in general, enhances the mean square displacement. Increase of temperature leads to suppression of mean square displacement. The method is based on canonical quantization procedure and may be used for understanding diffusive transport and thermally activated processes in a spin bath [20].

(ii) We then extend the treatment to derive the quantum mechanical description of overdamped Brownian motion of a particle in a spin bath of two-level atoms. The resulting Smoluchowski equation is used to calculate the rate of escape of the particle from a metastable state. At 0 K the decay rate is finite. We show that while quantization enhances the decay rate, higher temperatures induce thermal saturation, resulting in effective reduction of the system-bath cou-
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pling. The role of coherence and its consequences are examined [21].

(iii) The spin-bath induced decay of a quantum system out of a metastable state, which can tunnel and undergo thermal activation, is then considered. The treatment is based on the multidimensional transition state theory with the help of a canonical thermal distribution of the c-number variables of the bath degrees of freedom. We show that, apart from the usual frequency prefactor and its dynamical modification in the spatial diffusion-limited regime, i.e., the Grote-Hynes factor, the rate coefficient contains two other factors. One is a quantum correction to the dynamical factor resulting from quantum transmission and reflection of the particle at the finite barrier. This term exhibits exponential rate enhancement at low temperature. The other one is a quantum corrected Arrhenius factor, which incorporates the effect of thermal saturation. At 0 K, dissipation due to tunneling multiplies the tunneling probability by a factor that gets exponentially damped by friction, implying that, at this temperature, the behavior of the spin bath is almost identical to that of a harmonic bath [22].

(iv) We then introduce a simple numerical scheme for generation of c-number noise. The basic idea relies on expressing the noise correlation function by a spectral density function characteristic of the spin bath. The noise correlation function is numerically fitted by a superposition of several exponentials using a parameter set characterising the decay of each exponential. The parameter set obtained is then utilized to express the c-number noise of the bath as a superposition of several Ornstein-Uhlenbeck noise processes. The quantum Langevin equation along with correction equations are solved numerically for harmonic and anharmonic model systems.

(v) Finally we turn to the thermodynamics of a small spin system coupled to an environment of spins. When the system is small and is made open by coupling it to an environment, the system suffers a dissipative energy flow into the environment. It is easy to anticipate that such a flux or flow would give rise to a dynami-
cal correction over and above the usual thermodynamic functions responsible for temperature dependence of the system. We have shown that the specific heat which is a measure of fluctuation of internal energy is a sum of the products of a thermodynamic equilibration factor that carries the signature of temperature dependence and a dynamical factor, characteristic of the dissipative energy flow. These dynamical factors have been correlated with experimental measurements of specific heat on thin films of metal oxides dealing with finite size effects on magnetic ordering temperature.

1.3 Plan of the Thesis

In Chapter 2, we have presented a brief overview of the background theories emphasizing on the system-bath interactions within various approximate schemes.

In Chapter 3, we have introduced a canonical quantization procedure for treatment of quantum Brownian motion of a particle moving in a potential field and kept in contact with a spin bath. [The work in this chapter is covered in the publication; Sinha et al. Physical Review E, 82, 051125 (2010).]

In Chapter 4 we have derived the quantum Smoluchowski equation for a spin bath of two-level atoms. As an application the decay rate of a particle from the metastable state has been calculated. [The work in this chapter is covered in the publication; Sinha et al. Physical Review E, 84, 031118 (2011).]

In Chapter 5, we have presented a multidimensional transition state theoretical approach to derive an analytic expression for the quantum rate of decay of the metastable state induced by spin bath at a finite temperature. The theory unifies the aspects of tunneling and thermal activation on equal footing. [The work in this chapter is covered in the publication; Sinha et al. Physical Review E, 84, 041113 (2011).]

In Chapter 6, we have introduced a simple numerical scheme for generation of c-number noise where the noise correlation is characterized by the spectral density function for the bath. [The work in this chapter

In *Chapter 7* the explicit thermodynamic functions, in particular, the specific heat of a spin system interacting with a spin bath which exerts finite dissipation on the system are determined. The theory has been correlated with experimental measurements of specific heat on thin films of metal oxides dealing with finite size effects. [The work in this chapter is covered in; Sinha et.al. (submitted).]
BIBLIOGRAPHY


