Chapter 1

Introduction

This Thesis is divided in two parts. Part I comprising Chapters **2** through **4** deals with certain model problems of quantum diffusion and decoherence caused by dissipative coupling to a bath of harmonic oscillators with a view to resolving certain conceptual issues. Part II comprising Chapters *5* and 6 treats the problems of electron relaxation in semiconducting and metallic particles. The aim is to obtain the electron distribution functions for the non-equilibrium non-degenerate gas of photoexcited electrons in the semiconducting particles as also for the "hot" electrons in the metallic particles. The introduction gives a bacground to the contents of the Chapters that follow. Besides, it also includes some technical material that will be made use of in the Thesis, but *is not a part of the original work reported in the Thesis.*

1.1 Introduction to part I

1.1.1 Quantum diffusion on a lattice with tight-binding one-band Hamiltonian in the presence coupling to the environmental degrees of freedom: Introduced phenomenologically through Lindblad operators.

Quantum transport of a charge, or an excitation on a lattice which is potentially disordered in space and in time remains an open problem. Here, the disorder, that ultimately originates dynamically from coupling to the 'bath' degrees of freedom, is often introduced parametrically through a random potential which is generally correlated in space and time. The limit of infinite correlation time then corresponds to a disorder which is purely static. The latter causes multiple elastic scattering – a coherent process. It causes no dephasing of wave interference no matter how strong the disorder is. It can thus, lead to the well known and extensively studied absence of diffusion on random lattices, the Anderson localization, as, e.g., in the impurity band of a doped semiconductor at low temperatures. The opposite limit of zero correlation time and a short spatial correlation length, on the other hand, corresponds to a purely dynamical disorder. The latter involves decoherence, e.g., by inelastic scattering due to the electron-phonon coupling at high temperatures, or to the entanglement with the many dynamical degrees of freedom of the 'bath'. This is an incoherent process that gives classical diffusion in the long-time limit, with a diffusion constant determined by the strength of the dynamical disorder[1, 2, 3, 4, 5, 6, 7, 8, 9]. The general case of a finite correlation time is relevant to dynamics of the charge carriers in semiconductors, and to that of the energy- carrying (Frenkel) excitons in organic molecular solids(the diffusive excitonic verses the wavelike Forster transport[10]), as also to the motion of light adsorbates bound weakly to certain substrates. The problem of quantum transport on dynamically disordered lattices is relatively(relative to the static disorder)much less extensively studied. There do, however, exist several exact analyt-

ical results derived for 1-D lattices (generalization to higher dimensions being rather straightforward because of incoherence, though algebraically quite laborious). In all these studies the dynamical disorder is introduced through the stochastic modulations of certain matrix elements of a tight-binding model Hamiltonians. Thus, e.g., it may be the site-diagonal[1] modulation only, or may include the site-diagonal as well as the site-off-diagonal[2] modulation. The modulation, however was mostly taken to be a gaussian white noise (GWN), and spatially uncorrelated. The long-time(i.e., beyond the time-scale of the initial wavepacket dispersion) mean-squared displacement is found to be diffusive, with a diffusion constant nontrivially depends on the strength of the two (diagonal and off-diagonal) modulations referred to above[2]. These model treatments, however, do not incorporate dissipation which is normally a concomitant of the fluctuations. This, while giving diffusion in the long time limit, also leads to a heating of the carriers. Indeed, treating the interaction of the degree of freedom of interest with the many dynamical degrees of freedom of the bath through a parametric modulation of the potential does not allow the particle to react back on to the bath variables. Such a back-action evasion is well known to give unbounded stochastic heating (an interesting example being that of Fermi-acceleration [12] of charged particles in the astrophysical context). Thus, a delta-time correlated modulation of the potential corresponds to an infinite temperature, and for motion in a spatial continuum(infinite bandwidth), the resulting dynamics turns out to be superdiffusive $(x^2(t)) \sim t^3$ unlike the diffusive behavior obtaining for the tight-binding one-band (bandwidth limited) lattice Hamiltonian[3]. This has been interpreted in terms of the discreteness of the lattice as providing a momentum(Umklapp)sink without exchange of energy, which is off course absent in a continuum. A different interpretation and the treatment of this discrete-vs-continuum behavior has, however, been proposed by Heinrichs[4, 5] through a lattice regularization. In any case, there is no first principle (microscopic) treatment of dissipation for a dynamically disordered lattice available. The treatments based on the phenomenological friction Hamiltonian do not conserve the canonical commutation

relations[13]. The present work is confined to a one-band-tight binding model lattice Hamiltonian in which decoherence has been introduced through the Lindblad operators known well from quantum optics, that project onto the lattice sites. The point here is that what is essential to diffusion on lattice is the decoherence of quantum motion which is well represented by the Lindblad operators. The problem of heating is mitigated by the fact that the lattice- hamiltonian bandwidth will be taken to be small as compared to $k_B T$.

The present study, however, has a limited objective: It aims at generalizing the earlier stochastic lattice models so as to incorporate, non-perturbatively, a uniform potential bias together with a time-harmonic drive of given strength and frequency. The generalization sought here is physically motivated by the now experimentally realizable superlattice heterostructures that support the narrow-bandwidth Stark-Wannier (SW) ladder states [14, 15] in the presence of a longitudinal electric-field bias[14]. As is well known, a strong field normal to the superlattice planes can break up the extended Bloch-like band continuum into energetically well resolved states localized in the potential wells. The stronger the biasing field the more localized are the SW state [14, 15]. The energy mismatch, or, the step between the neighbouring SW states is proportional to the biasing field, and hence is tunable. With this generalization, we have obtained analytical expressions for the time-dependent mean and the mean-squared displacements as function of the bias and the drive amplitude and frequency. Also, dynamical disorder (decoherence) is introduced through a set of Hermitian lindblads[16, 17, 18, 19] chosen so as to project on to the lattice sites. An interesting new result of our calculation is the enhancement of the diffusion coefficient with increasing amplitude of the harmonic drive, and its variation with the increasing detuning of the drive frequency relative to the inter-site energy gap between the neighbouring sites of the lattice −− clearly a non-linear effect. The latter is tunable through the bias field. The analytical results obtained by us correctly specialize to the exact results known in the limit of zero drive and zero-bias. Besides, for such a bandwidth limited systems, the Lindblads

provide a physically valid mechanism for decoherence, as noted above.

1.1.2 Brief introduction to a phenomenological approach to environmentally induced decoherence–the Linbladian approach.

In quantum mechanics the time evolution of a closed physical system (coherent quantum evolution) is given by a unitary time evolution. This is described by the time evolution of the density matrix $\hat{\rho}$ given by (for a time-independent Hamiltonian H):

$$\hat{\rho}(t) = e^{-\frac{i}{\hbar}\hat{H}t}\hat{\rho}(0)e^{\frac{i}{\hbar}\hat{H}t}. \tag{1.1}$$

Once the reduced density matrix $\hat{\rho}$ is known, the quantum-statistical expectation of any one-particle observable A can be obtained as $Tr(\hat{\rho}\hat{A})$. If $\hat{\rho}$ is a pure state $(i.e., \hat{\rho}^2 = \hat{\rho})$ at any initial time t_0, then $\hat{\rho}(t)$ remains a pure state for all t. For an open system, comprising the subsystem of interest coupled to the environment (of no direct interest), however, the time evolution of the subsystem (to be obtained ultimately by integrating out the environmental degrees of freedom) is given by a quantum Master equation (the Liouville equation):

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] + \sum_{k=1}^{n}\{2L_k\hat{\rho}L_k^\dagger - L_k^\dagger L_k\hat{\rho} - \hat{\rho}L_k^\dagger L_k\}, \tag{1.2}$$

which is local in time (the markovian approximation). Here, L_k is the k^{th} Lindblad operator to be discussed below. The first part(the commutator) on the right-hand side of the above equation represents the unitary time evolution(Hamiltonian evolution), and the second term containing the Lindblad operators represents the non-unitary time evolution. The important point to note is that the Lindblad operators introduce the non-unitarity without, (a) violating the complete positivity, (b)hermiticity and (c)the trace-class nature of the density matrix $(\hat{\rho})$. The choice of the Lindblad operator for any specific problem is dictated by the physics of the problem. Thus for the quantum motion of a particle on a dynamically disordered lattice, we will make the choice $L_k =$

$\sqrt{\gamma}|k\rangle\langle k|$ projecting on the lattice site $|k\rangle$. It turns out that the Lindblad operator (used most extensively in quantum optics for the effects of radiation damping etc) actually heats up the system of interest to infinite temperature(it represents coupling to the bath at infinite temperature). This element of unphysicality is, however, rendered ineffective for a bandwidth limited system, with Band Width $\ll kT$. This is indeed expected to be realized in the Stark-Wannier ladder in the superlattice structures. Also, some physical aspects of the finite temperature can be imposed by adding certain phenomenological terms on the R.H.S. of the Lindblad equation that can ensure thermal equilibrium values for the diagonal elements of the density matrix[22]

1.1.3 Quantum diffusion of a charged particle in a magnetic field and the orbital diamagnetic moment – a purely quantum phenomenon without the classical analogue.

The orbital motion of a charged particle, in thermal equilibrium with a heat bath, moving under the influence of an external(static) magnetic field may well be expected to give a non-zero magnetic moment (Figure 4.2a). It is, however, known now that classically there is no orbital (dia) magnetism. This identically vanishing of the orbital diamagnetism in the classical limit is the celebrated Bohr-van Leeuven theorem[23, 24]. Here, in the presence of an external magnetic field (and the associated local Lorentz force $\frac{e}{c}(\mathbf{v} \times \mathrm{B})$), the induced cyclic currents in the bulk (Maxwell cycles) and the skipping orbits (edge currents) at the boundary (internal as well as external) contribute equal and opposite magnetic moments. This classically exact cancellation may be visualized from the schematic in Figure 4.1. This result has been claimed to be one of the surprises of theoretical physics by Rudolph Peierls[25]. This makes the study of orbital diamagnetism in a quantum dissipative system interesting fundamentally.

This vanishing of the orbital diamagnetic moment follows at once from the fact that the equilibrium partition function $Z(B, \beta)$ for the classical system is independent of the magnetic field B (or equivalently, of the vector potential $\mathbf{A}(\mathbf{r})$) inasmuch as the

latter enters minimally through the replacement $\mathrm{p} \rightarrow \mathrm{p} - \frac{e}{c}\mathbf{A}(\mathbf{r})$, and thus the classical trace (integration) over the canonical momentum p makes the partition function independent of $\mathbf{A}(\mathbf{r})$. This, of course, is not permitted quantum mechanically in that the operators p and $\hat{\mathbf{r}}$ do not commute then. This exact cancellation was also derived in a stochastic real space-time treatment[27], where the cancellation was shown to occur in the asymptotic limit of time $\mathrm{t} \rightarrow \infty$ (i.e., in the 'Einsteinian' approach to equilibrium statistical mechanics), and the subtle role of the boundary of the sample was clarified inasmuch as one had to take the limit $\mathrm{t} \rightarrow \infty$ before taking the thermodynamic limit of infinite length scale of the confining potential, assumed harmonic. This ensures that the particle 'sees' the boundary. This classical treatment, based on the stochastic equation of motion in the x – y plane perpendicular to the magnetic field (B):

$$\begin{gathered} \ddot{z} = -\Gamma \dot{z} e\mathbf{B} + \mathrm{f}\,(\mathrm{t}) \\ \text{with } z = x + iy, \quad f(t) = f_1(t) + i f_2(t) \\ \langle f_i(t) f_j(t) \rangle = \delta_{ij} 2 k_B T \Gamma \delta(t - t') \end{gathered} \tag{1.3}$$

was subsequently extended to a quantum treatment[28] based on the phenomenological quantum Langevin equation in the presence of the magnetic field. Again, the above so-called Darwin boundary condition[26] was imposed. A non-zero orbital diamagnetism was obtained that, however, differed from what might be expected from the Landau diamagnetism for a single charged particle at temperature T. For the latter, .having the Hamiltonian $\mathrm{H} = \frac{1}{2m}(\hat{\mathrm{p}} - (e/c)\mathbf{A})^2 +$ a harmonic *confining* term, with the cyclotron frequency $\omega_c = |e|\mathbf{B}/mc$, and V x A = B along z-axis, the partition function $Z(B, \beta) \equiv Tr[e^{-\beta H}]$ gives the diamagnetic moment[27, 29]

$$M_z = -\frac{\partial}{\partial B}\left[-\frac{1}{\beta} ln Z(\beta, B)\right] = \frac{e\hbar}{2mc}\left[\frac{2k_B T}{\hbar\omega_c} - \coth\frac{\hbar\omega_c}{2k_B T}\right], \tag{1.4}$$

(where the harmonic confinement length scale is finally taken to be infinite.) Interestingly, the orbital magnetism derived from the (phenomenological) quantum Langevin Equation turns out to depend on the frictional coupling to the dissipative environment. In fact, the orbital diamagnetism–an equilibrium thermodynamic property- was found

to decrease monotonically with increasing friction- a transport property[29]. It, however, violates no principle (see Sub-section 1.1.5). The orbital diamagnetic moment, being a purely quantum phenomenon, with no classical analogue, provides an excellent 'laboratory' for studying the effect of a dissipative coupling to the environmental degrees of freedom(the heat-bath). A much more subtle question that motivates our present study is the following: In the quantum Langevin-equation based approach to the motion of a charged particle in a given static magnetic field, the latter enter through a local Lorentz force $(e/c)(\mathbf{v} \times \mathrm{B})$, with $\mathrm{B} = \mathrm{V} \times \mathbf{A}$. There is, however, another class of problems where the magnetic field enters as an Aharonov-Bohm flux (ϕ) and acts non-locally through a geometric/topological phase. *The question now is whether or not the orbital diamagnetic moment induced by the purely geometric phase[30] be affected by the dissipative coupling to the environmental degrees of freedom–a continuum of harmonic oscillators.* We treat this problem microscopicaly in Chapter 3 using path integrals. Our calculation re-affirms our conjecture that this geometric-phase induced orbital diamagnetism is essentially unaffected by this dissipative coupling except possibly for a small mass renormalization. It may be of interest to derive this orbital diamagnetism directly from the *phenomenological* quantum Langevin equation.

1.1.4 Effect of dissipative coupling to the environment taken as a bath of harmonic oscillators on the quantum motion of a particle.

Finding the microscopic quantum analogue of the phenomenological classical Langevin equation(that treats the classical Brownian motion as a physical Ornstein-Uhlenbeck Process rather than an idealized stochastic Wiener process), has been[33, 34, 35, 36, 38, 39, 40, 41, 42,431 a continuing issue of theoretical physics—of the Einsteinian approach to the equilibrium statistical mehanics, where the equilibrium state is reached in the time $t \to \infty$ limit of the quantum Brownian motion. it also address the question as to when the environmental degrees of freedom act as a heat bath.

1.1.4.1 The open and the closed quantum systems and the heat bath

An isolated quantum system evolves unitarily under its own time-independent Hamiltonian—-an initially pure state will remain a pure state. By a closed system, however, we only mean that it cannot act on to the external environment. Thus for example, a given external field, electric or magnetic, may act on the system *parametrically* , i.e., the field regarded as not having its own degrees of freedom that may be reacted back upon. The closed system , of course, evolves unitarily. For an open system, or a system comprising the subsystem of interest and the rest of it, the environment with many degrees of freedom (of no interest), however, the subsystem exchanges energy with, and acts upon and is acted upon by the environmental degrees of freedom. Its 'reduced' discription (time-evolution) is non-unitary in general. The environment, often called the heat bath, usually has a large number of (ideally infinitely many) degrees of freedom of which each is taken to be only weakly (idealy infinitesimally) coupled to the subsystem of interest. Thus, in particular, the energy can flow from the subsystem to the environment and cascade away without ever getting refocussed back, on experimental time scales. This is an irreversible process(keeping in mind the all-important consideration of experimental time scales!). The coupling to the environment is then dissipative. Furthermore, while each of the many bath degrees of freedom is only weakly perturbed, and so the bath may be taken to remain essentially unchanged, the subsystem is affected appreciably due to the accumulative effect of the large number of the environmental degrees of freedom that can react back--even its equilibrium properties are afected due to, the renormalization effects (level shifts and level broadenings) that are always there. In fact, it is only in the limit of the coupling to environment $\to 0$ and the time $t \to \infty$, that we have the ideal heat bath[18, 44]. This dissipative coupling to an environment is important in all quantum motions. But, notably it becomes a determining effect for subsystems which are essentially quantum mechanical in nature—have no classical counterparts. The canonical examples are the phenomena involving quantum tunneling out of a metastable state that has been extensively studied

in the past in the context of macroscopic tunneling[38]. Also, the microscopic tunneling inasmuch as it enters the tunneling matrix elements of tight-binding one-band Hamiltonian for the quantum motion on a lattice disordered dynamically by coupling to the vibrational degrees of freedom (the phonon bath). Yet another example is that of the orbital diamagnetic motion of a charged particle in an external magnetic field coupled dissipatively to the environment. The last two have been considered in part I of this thesis (Chapters II - IV).

1.1.4.2 A microscopic model of the dissipative coupling to the environment

An extensively studied model of general validity for the dissipative coupling of the subsystem (coordinate x) to the environment (coordinates q_j) involves the idea of a harmonic oscillator bath with strictly linear coordinate-coordinate coupling. This microscopic quantum model is described by the total Lagrangian[38].

$$L = L_S + L_B + L_{SB}\,, \left\{ \begin{array}{c} L_S = \frac{1}{2}m\dot{x}^2 - V(x) \\ L_B = \sum_j (\frac{1}{2}M_j\dot{q}_j^2 - \frac{1}{2}M_j\omega_j^2 q_j^2) \\ L_{SB} = x\sum_j c_j q_j \end{array} \right\} \tag{1.5}$$

Here a counter term is to be added in order to cancel out the unphysical potential x $\sum_j \frac{c_j^2}{2M_j\omega_j^2}$ that gets generated by the above model (coordinate-coordinate) coupling, giving displaced oscllators. The coupling L_{SB} is usually parametarized through the spectral function

$$J(\omega) = \frac{\pi}{2}\sum_j \frac{c_j^2}{2M_j\omega_j^2}\delta(\omega - \omega_j) \tag{1.6}$$

It turns out that for $J(\omega) = \eta e^{-\omega/\omega_c}$ (for w $\ll \omega_c$ with ω_c a high frequency cut-off for the harmonic oscillator bath), the corresponding classical equation of motion reduces to that for a damped system (Langevin equation)with friction η:

$$m\frac{d^2x}{dt^2} - \eta\frac{dx}{dt} - \frac{\partial V}{\partial x} = f(t)\,, \tag{1.7}$$

with

$$\langle f(t)f(t')\rangle = 2k_B T\eta\delta(t - t') \tag{1.8}$$

Thus, the above choice of $J(\omega)$ is aptly called the 'ohmic bath'. Other choices are possible —the subohmic and the superohmic baths[38].

The above Lagrangian model for the dissipatively coupled system(subsystem + environment) can be treated through the Feynman path integral approach[31, 37]. Here the statistical mechanics(e.g., the partition function) can be obtained by going over to the negative imaginary time-the Euclidian action— as will be done in this Thesis in order to treat the problem of the orbital diamagnetic moment of a charged particle moving diffusively on a ring with Aharonov-Bohm magnetic flux. Another powerful, although phenomenological,approach to treating the subsystem dissipatively coupled to the environment is through the quantum Langevin equation in the operator form[18, 43].

$$m\ddot{x} = -V'(x) - \gamma\dot{x} + \sqrt{2\gamma k_B T}\xi(t), \tag{1.9}$$

where x, x, and x are to be regarded as the Heisenberg operators obeying the canonical commutation relations, with the quantum noise $\xi(t)$ obeying

$$[\xi(t), \xi(t')] = 2i\hbar\gamma\frac{d}{dt}\delta(t - t') \ , \tag{1.10}$$

and

$$([[(t), \xi(t')]_+\rangle = \frac{\hbar\nu}{\pi}\int_{-\infty}^{+\blacksquare\blacksquare} d\omega\omega\coth(\frac{\hbar\omega}{2k_B T})e^{i\omega(t-t')} \tag{1.11}$$

In this approach, the equilibrium (statistical mechanics) is recovered in the limit $t \to \infty$ (the Einsteinian approach to statistical mechanics). Also, the commutation relations are preserved in time. This is not true of many other phenomenological equations proposed so far[13]. It is important to emphasize, that for an ideal heat-bath, we must have $\gamma + 0$ and $t + \infty$. In general, the frictional parameter γ shall enter the equilibrium properties[44].

1.1.5 Brief introduction to the Euclidean action in relation to the partition function.

The partition function $Z(\beta)$ for a system in equilibrium at a temperature $T($ with $\beta = 1/k_B T)$, and having (a necessarily time-independent) Hamiltonian $\mathrm{H} = p^2/2m + V(x)$, say, is given by the trace of the canonical density matrix $\rho = e^{-\beta\hat{H}}$, i.e.,

$$Z(\beta) \equiv Tr[e^{\beta\hat{H}}] = \int dx \langle x|e^{-\beta\hat{H}}|x\rangle, \tag{1.12}$$

where $\{|x\rangle\}$ is a complete orthonormal basis. This suggests a comparison of the off-diagonal matrix element $\langle x_b|e^{-\beta\hat{H}}|x_a\rangle$ with the real time unitary evolution under the Hamiltonian H, namely, $\langle x_b|e^{-iHt/\hbar}|x_a\rangle$, giving $K(x_b, \mathrm{T}; \mathrm{x}_{,,}\ 0) = \langle x_b|e^{-\beta\hat{H}}|x_a\rangle$ with time $\mathrm{T} \to -i\hbar\beta$,i.e., the propagator K with negative imaginary time. Now the propagator(real time), or the kernel, $K(x_b, \mathrm{T}; \mathrm{x}_{,,}\ 0)$ can be written in terms of the Feynman Path integrals[31],

$$K(x_b, T; x_a, 0) = \int_{x_a,0}^{x_b,T} D[x(t)] e^{\frac{i}{\hbar}\int_0^T L(x,\dot{x})dt}, \tag{1.13}$$

where $L(\dot{x}, \mathrm{x})$ is the Lagrangian corresponding to Hamiltonian H,

$$L(x, \dot{x}) = \frac{1}{2}m\dot{x}^2 - V(x) \tag{1.14}$$

It is convenient to introduce here $S = \int_0^T L(x, \dot{x})\mathrm{dt}$, the real-time action along the path $[\mathrm{x(t)}]$. Thus, to go from $K(x_b, \mathrm{T}; \mathrm{x}_{,,}\ 0)$ to the partition function, all we need to do is to perform the analytic continution $\mathrm{t} \to -i\tau$ to negative imaginary time (the Wick rotation) that transforms the real-time action S to the imaginary-time (Euclidean) action $S_E = -\int_0^{\beta\hbar}[\frac{1}{2}m(\frac{dx}{d\tau})^2 + V(x(\tau))]d\tau$, and perform the trace. Thus, we have

$$K(x_b, \beta\hbar; \mathrm{x}_{,,}\ 0) \equiv \int_{x_a,0}^{x_b,\beta\hbar} D[x(\tau)] e^{-\frac{1}{\hbar}S_E[x(\tau)]} \text{ and}$$
$$Z(\beta) = \int K(x_a, \beta\hbar; x_a, 0) dx_a \tag{1.15}$$

In effect, this is how one goes from the Lagrangian to the Hamiltonian description in statistical mechanics. This enables one to use the full power of the Feynman path

integral approach. (It admits generalization to many-body systems, of Fermions as well as the Bosons). In this Thesis, we will make use of the Euclidean Path integral for evaluating the partition function of a charged particle moving on a ring, threaded by an Aharonov-Bohm magnetic flux, and coupled dissipatively to a bath of harmonic oscillators.

1.2 Introduction to part II

1.2.1 Introduction to Two-Temperature model of thermal relaxation of non-equilibrium electron distribution in metals.

The recent advancement in ultrafast (femto-second) laser technology has opened up a new field of time resolved studies of ultrafast thermal relaxation of electrons in the bulk and the nanoscale materials. In metals, because of the large difference between the electronic (C_e) and lattice(phononic C_p) heat capacities (with $C_p \gg C_e$ at room temperature), a femtosecond laser pulse creates nonequilibrium electron distribution, leaving the lattice temperature essentially unchanged $T_p \simeq 300K$. Then, over a time scale of a few pico-seconds, the nonequilibrium electrons redistribute their energies among themselves through electron-electron coulombic interaction, and return to a local equilibrium (among themselves) at a somewhat elevated temperature $T_e > T_p$. This excited degenerate electron gas then cools(relaxes) via the electron-phonon interactions, giving up the excess energy to the phonon bath. Thus, the widely separated time-scales(the intra-electron and the intra-phonon relaxation times $\ll$ the inter-electron-phonon time scale) justifies defining the two temperatures T_e and T_p. This motivates the Two-Temperature model[51, 52, 53]. The Two-Temperature model tries to describe this relaxation process, and has been used extensively by the workers in the field of ultrafast laser spectroscopy in nanoscale materials. Briefly, the two-temperature model assumes

(a) The electron-electron(coulombic) and the phonon-phonon(anharmonic) processes are much faster than the electron-phonon processes, so as to define T_e and $T_p (\neq T_e$ ingeneral) and maintain their local equilibrium distributions giving

$$\begin{aligned} &\text{(for electrons) } N_k = \frac{1}{e^{\beta_e(\varepsilon-\varepsilon_0)}+1} \quad ,\beta_e = \frac{1}{k_B T_e} \\ &\text{(for phonons) } N_f = \frac{1}{e^{\beta\hbar\omega_f}-1} \quad ,\beta = \frac{1}{k_B T_p}, \end{aligned} \tag{1.16}$$

with a fermionic electron distribution at temperature T_e and a bosonic phonon distribution at temperature T_P $(T_p < T,)$.

(b) Homogeneous excitation and no spatial diffusion.

(c) Delta-pulse laser excitation.

Using the Bloch-Boltzmann-Peierls formula[55] for phonon generation rate per unit volume,i.e.,

$$\dot{N}_f = \int \alpha\omega_f\{(N_f+1)N_{k'}(1-N_k)-N_f N_k(1-N_{k'})\}\delta(\varepsilon_{k'}-\varepsilon_k-\hbar\omega)(2/(2\pi)^3)d\tau_{k'}. \tag{1.17}$$

Here, $a = (\pi U^2/\rho V S^2)$. One can show that the rate of energy transfer per unit volume by the electrons to bulk phonons is[52]

$$U_{bulk} = \left[\frac{m^2U^2\omega^4k_B}{2(2\pi)^3\hbar^3\rho S^4}\right][T_e - T]. \tag{1.18}$$

This can be cast in the following form

$$\frac{\partial(C_eT_e)}{\partial t} = -\alpha_{int}(T_e - T) + Q \qquad 1.19(a)$$

$$\frac{\partial(C_pT)}{\partial t} = \alpha_{int}(T_e - T) \qquad 1.19(b)$$

The above coupled differential equations are the defining equations of the two-temperature model of hot electron cooling. Here Q is the specific power absorbed by the photo-excited sample and α_{int} is the electron-phonon interaction coefficient. In Chapter 6, the problem of hot electron relaxation in nanoscale metal films and nanoparticles is considered within two temperature model.

1.2.2 A general stochastic model for the relaxation of the non-equilibrium distribution of a dissipative granular gas: application to photoexcited electrons.

The above Two-Temperature model has a well defined range of applicability — It is a p plicable under the conditions mentioned in the previous section, i.e., when $\tau_{e-e} \ll \tau_{e-p}$ and also $\tau_{p-p} \ll \tau_{e-p}$. Here, τ_{e-e}, τ_{e-p} ,and τ_{p-p} are the electron-electron, electron-phonon and the phonon-phonon relaxation time scales respectively. Typically , $\tau_{e-e} \sim$ sub *picosecod* $\tau_{e-p} \sim$ tens of picosecods, and $\tau_{p-p} \sim$ a few picosecond. In Chapter 6 we develop[45] a stochastic kinetic model which is applicable for all ranges of the electron-phonon interaction strength. Our analytical treatment is based on a generalization of the stochastic model known for a driven dissipative granular gas[48]. This is an interesting model for a granular gas where the particle-particle and the particle-bath collisions are parametrized in detail. More specifically , the total rate of collisions suffered by a given ('tagged') particle is partitioned into the particle-bath collision rate (fraction f) and the particle-particle collision rate (fraction $1-f$). Further, a fraction a of the total energy of the colliding particles is partitioned randomly between the colliding particles, while the remaining fraction $(1-a)$ is dissipated through the frictional contact during the collisions. The system is kept in the dynamic (non-Boltzmannian) non-equilibrium condition by a constant drive. In our generalization to the electronic system,the bath has the obivious identification with phonons, and the drive is to be identified with the photo-excitation. Also, the possibly dissipative electron-electron interaction has to be interpreted in terms of the coulomb interaction as screened by the dissipative polarization of the lattice. We have, however, confined our treatment to the case of $a = 1$. Our generalization is physically realizable in a semiconducting sample where electrons are injected into the conduction band by photoexcitation and removed at the bottom of the conduction band through the electron-hole recombination process. (we assume the sample to be disordered so that energy is the only label for the

1.3 PART I

electronic state). Here the kinetics of the electron-electron and the electron-phonon (bath) scattering processes, as also the partitioning of the total energy in the inelastic collisions, are duly parametrized by certain rate constants. Our analytical results give the steady-state electron distribution function, and the mean energy of the classical non-equilibrium electron gas as function of the phonon (bath) temperature and the rates of injection (cw pump) and depletion (recombination). While, our generalization of the stochastic granular gas model to the electronic system covers time-dependent process relavent to the transient femtosecond photoexcitation, we have actually treated the steady state electron distribution under the cw(continuous wave) drive.