

A MICROSCOPIC APPROACH TO PHONONIC
ENERGY TRANSFER IN NANO STRUCTURES

A THESIS
SUBMITTED TO THE DEPARTMENT OF PHYSICS
AND THE INSTITUTE OF ENGINEERING AND SCIENCES
OF BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

BY

ALTUĞ ÖZPİNECİ

SEPTEMBER, 1999

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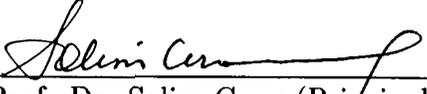
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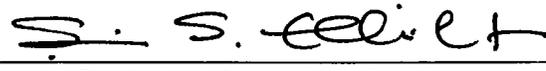
I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.


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ABSTRACT

A MICROSCOPIC APPROACH TO PHONONIC ENERGY TRANSFER IN NANO STRUCTURES

Altuğ Özpineci

M.S. in Physics

Advisor: Prof. Dr. Salim Çıracı

September, 1999

Understanding of mechanisms for the energy transfer from and/or through nano particles in contact with the large samples have become important in various biological processes, molecular electronics and friction. In this thesis, the phononic heat conductance of an atomic wire between two reservoirs, and the vibrational relaxation of an atom adsorbed on a surface is studied. The former problem is studied using the Keldysh formalism which yields the steady state properties of the system. The dependence of the total conductance on temperature, on the number of atoms in the wire and on the coefficient $\sqrt{\frac{k}{m}}$ is studied. It is found that the conductance shows quantal structure similar to the electronic counterpart.

The reduced density matrix is used to study the latter problem. The time evolution of the reduced density matrix has been evaluated for an arbitrary system coupled to a heat bath. The formalism is then applied to study the vibrational relaxation of an atom adsorbed on a surface. The frequency dependence of the relaxation time is also determined.

Keywords and Phrases: Heat Conductance, Keldysh Formalism, Phononic Heat Conductance Quantization, Reduced Density Matrix, Vibrational Relaxation

ÖZET

NANO YAPILARDA FONONLARLA ENERJİ TAŞINIMINA MİKROSKOPİK BİR YAKLAŞIM

Altuğ Özpıneci

Fizik Bölümü Yüksek Lisans

Danışman: Prof. Dr. Salim Çıracı

Eylül, 1999

Daha büyük cisimlere bağı nano cisimlerden ve/veya bunların üzerinden enerji akışının mekanizmalarını anlamak, pek çok biyolojik , moleküler elektronik ve sürtünme ile ilgili olayı anlamak için önemlidir. Bu tezde, iki rezervuara bağı tek boyutlu atomik bir telin fonon kaynaklı ısı iletkenliğı ile bir yüzey üzerine yapışmış bir atomun salınımının sönümü incelendi. İlk problem, incelenen sistemin durağan durumu hakkında bize bilgi veren Keldysh formülasyonu kullanılarak incelendi. Telin toplam ısı iletkenliğinin sıcaklığa, atom sayısına ve $\sqrt{\frac{k}{m}}$ katsayısına bağılığı hesaplandı. Isı iletkenliğinin de, elektrik iletkenliğı gibi kuvantal bir karakter gösterdiğı bulundu.

İkinci problemi incelemede indirgenmiş yoğunluk matrisi kullanıldı. Isı rezervuarına bağı herhangi bir sistemin indirgenmiş yoğunluk matrisinin zaman içinde nasıl geliştiiğı hesaplandı ve bir yüzey üzerine yapışmış bir atomun salınımının sönümü incelendi. Durulma zamanının frekansa bağımlılığı belirlendi.

Anahtar Kelimeler ve İfadeler: Isı İletkenliğı, Keldysh Formülasyonu, Isı İletkenliğı Kuantizasyonu, İndirgenmiş Yoğunluk Matrisi, Salınımsal Sönüm

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Chapter 1

Introduction

Understanding the energy flow through and from substances is essential for a fundamental understanding of various processes in nature ranging from the reactions in the living organisms to various applications in device physics. In itself, controlling the rate of energy flow, being able to increase or decrease it, has a great importance for various applications.

In microelectronics, the quality of growth of silicon wafers and SiGe, Al-GaAs heterostructures is essential for the operation of the devices. Nowadays, significant resources have been allocated to understand the growth mechanisms so that conditions can be established to grow defect-free crystals and wafers. The growth process involves several complex and stochastic phenomenon taking place in the atomic scale. An important and fundamental issue one has to clarify is how the huge energy emerged from the formation of chemical bonds between incoming atoms and surface atoms. The dissipation of this energy is essential for the quality of the surface, where the electronic device will be produced. Clearly the question one has to address here is how the energy released from the bond formation dissipates through the sample, what is the time scale for the dissipation? Another important issue is how the energy generated in an electronic device can dissipate as the size of an electronic device becomes smaller and smaller. In fact, this problem seems to be a factor that limits the miniaturization of devices.

In solar collectors [1], it is important that the collected energy should be transferred into the bulk before it is reemitted to the surrounding. In order to make more efficient solar collectors, the rate of energy transport into the bulk

should be increased. In the case of friction, where two surfaces rub against each other, heat is generated. The rate of heat transfer is important for the dissipation of the mechanical energy and for the wear of surfaces.

In living organisms, most catalytic activity takes place on surfaces [2], hence the reactions can be considered as a set of transitions between various energy levels whose understanding requires a deep understanding for the processes at the surfaces, especially the processes involving energy transfer.

In recent years, there have been extensive theoretical studies on phonon transport and energy relaxations using various methods, including the Kubo formula for heat conductance [3, 4, 5, 6], Landauer type phenomenological energy flux [7, 8, 9, 10], Golden Rule [11, 12], and Langevin type equations [13, 14, 15, 16]. On the experimental side, vibrational relaxations have been studied extensively [17, 18, 19, 20, 21], but to the author's knowledge, there is no experimental study on the conduction of 1D wires (for a review of the present situation see e.g. [22]). The Kubo formula yields just the first order response of the system to an external disturbance, and expresses the conductivity tensor in terms of the current-current correlation functions in equilibrium [6]:

$$\kappa_{\mu\nu} = \lim_{\epsilon \rightarrow 0^+, \omega \rightarrow 0} \frac{1}{k_B T^2 V} \int_0^1 d\lambda \int_{-\infty}^0 dt e^{i(\omega - i\epsilon)t} \langle S_\mu(0) S_\nu(t + i\hbar\beta\lambda) \rangle \quad (1.1)$$

where k_B is the Boltzmann constant, V is the volume of the system, S_μ represents the μ^{th} -component of the heat current, and $\langle \dots \rangle$ denotes the thermal averaging in equilibrium. In cases where the considered system cannot be described by linear response theory, it is not applicable. But in situations where it is applicable, it gives a microscopic description of the phenomenon.

A Landauer-type phenomenological energy flux is given by (for the derivation see [24]):

$$J = \sum_n \int_0^\infty \frac{dk}{2\pi} \hbar \omega_n(k) \frac{d\omega_n(k)}{dk} \{n_1[\omega_n(k)] - n_2[\omega_n(k)]\} \zeta_n(k) \quad (1.2)$$

where $n_{1(2)}$ are the phonon distributions at the left(right) reservoirs, and $\zeta_n(k)$ is the transmission probability for the phonon. Eq. 1.2 gives a macroscopic description for the heat transport. In most cases, the transmission probability, $\zeta_n(k)$, is assumed to be unity or that it is given by matching continuum solutions for the elastic waves at the boundaries. For nanosystems, where the discrete atomic nature of the structure becomes pronounced, the use of continuum theory to determine the transmission coefficients cannot be justified.

Under these circumstances, one has to develop a microscopic theory as done in this thesis to calculate the transmission coefficients and conductance. At the end of this thesis, we will present a microscopic definition for $\zeta_n(k)$.

The Langevin type equation describes the time evolution of the reduced density matrix of the system. They give a microscopic description of the system under study. The density matrix theory will be reviewed in the next section. A broader discussion on the density matrix theory and its applications can be found in eg. [23].

This thesis deals with the microscopic aspects of phononic energy transfer in nanostructures. Two cases are considered are (i) the phononic energy transfer and the related thermal conductance through an atomic chain coupled to two reservoirs; and (ii) the dissipation of excess vibrational energy from an adsorbed atom to the substrate. In both cases the models used to simulate the real systems have been simplified in order to reveal the essential features of heat transfer, but the approaches and formalism developed can easily be extended to more complex systems. On the other hand, in both cases treated in the thesis the approaches developed are unique and hence are expected to contribute to a better understanding of the related physical problems.

For the first case, the Keldysh's approach for non-equilibrium but steady state is used and the energy current through a finite and uniform atomic chain mediated by phonons is calculated. The variations of thermal conductance as a function of chain parameters, and temperature are investigated. A quantum structure of thermal conductance is revealed. For the second case that has a wide range of applicability, in particular it is relevant for the energy dissipation from an adsorbed atom coupled to a substrate through anharmonic interactions, the reduced density matrix approach is used. It is found that the time of equilibration is rather small and most of the excess energy dissipates within 10^{-12} sec. The details of the work is given in Chapters 2 and 3, and conclusions are summarized in Chapter 4.

1.1 Density Matrix

For systems that can be described by a wave function, the wave function gives a complete description. Such systems are said to be in a pure state. Once the

wave function is known, everything about the system, within the limitations of Quantum Mechanics, is known. But for most systems, including systems coupled to the environment, description by a single wave function is not possible, it is not in a pure state. Such systems are said to be in a mixed state. In such cases, the system should be described by the density matrix.

1.2 Definition and Some of the Properties of the Density Matrix

For most system, one can at most know the probabilities, p_i , that the system is in a state described by the wave function $|\psi_i\rangle$. In such cases, in order to calculate the expectation value of an operator, one should take the statistical average besides the quantum average, ie.:

$$\langle \mathcal{O} \rangle = \sum_i p_i \langle \psi_i | \mathcal{O} | \psi_i \rangle. \quad (1.3)$$

If Eq. 1.3 is rearranged as:

$$\begin{aligned} \langle \mathcal{O} \rangle &= \sum_n \sum_i p_i \langle \psi_i | \mathcal{O} | n \rangle \langle n | \psi_i \rangle \\ &= \sum_n \langle n | \left(\sum_i p_i |\psi_i\rangle \langle \psi_i| \right) \mathcal{O} | n \rangle \\ &= \text{Tr} \left(\sum_i p_i |\psi_i\rangle \langle \psi_i| \right) \mathcal{O}, \end{aligned} \quad (1.4)$$

where $\{|n\rangle\}$ is an orthonormal basis for the Hilbert space of wave functions, the definition of the density matrix easily follows as:

$$\rho = \sum_i p_i |\psi_i\rangle \langle \psi_i| \quad (1.5)$$

and the expectation value of any operator can be written as:

$$\langle \mathcal{O} \rangle = \text{Tr} \rho \mathcal{O}. \quad (1.6)$$

Note that the wave functions $|\psi_i\rangle$ need not be orthogonal.

Several properties of the density matrix follows immediately from its definition, Eq. 1.5.

- $Tr\rho = \sum_i p_i = 1$.
- $Tr\rho^2 = \sum_i p_i^2 \leq 1$, and the equality sign holds if and only if it is in a pure state.
- The density matrix is hermitian, i.e. $\rho^\dagger = \rho$. Therefore it is always possible to find a suitable basis in which the density matrix can be represented by a diagonal matrix, the diagonal entries being the classical probabilities. If the system is in a pure state, in its diagonal form, all but one of the diagonal elements will be zero, and the non-zero diagonal element will be 1.

These properties are independent of the representation used for the density matrix. Eq. 1.5 is just one of the representation in which it is easy to show these properties.

Since the density matrix is written in terms of the wave functions, its time evolution is also determined by the time evolution of the wave functions, hence, contrary to other operators in Quantum Mechanics, it is time dependent in Schroedinger picture, and time independent in Heisenberg picture. Its time dependence can be written as:

$$\begin{aligned}
\rho(t) &= \sum_i p_i |\psi_i(t)\rangle \langle \psi_i(t)| \\
&= \sum_i p_i e^{-\frac{i}{\hbar} \mathcal{H} t} |\psi_i(0)\rangle \langle \psi_i(0)| e^{\frac{i}{\hbar} \mathcal{H} t} \\
&= e^{-\frac{i}{\hbar} \mathcal{H} t} \left(\sum_i p_i |\psi_i(0)\rangle \langle \psi_i(0)| \right) e^{\frac{i}{\hbar} \mathcal{H} t} \\
&= e^{-\frac{i}{\hbar} \mathcal{H} t} \rho(0) e^{\frac{i}{\hbar} \mathcal{H} t}
\end{aligned} \tag{1.7}$$

1.3 Systems Interacting with the Environment and the Reduced Density Matrix

In general, one does not deal with an isolated system and it is mostly not necessary to consider all of the interacting parts, which would require one to consider all the universe. In such a case, the density matrix of the whole system contains unnecessary information.

Let ρ be the density matrix of the whole system $A + B$ where the A and B subsystems interact with each other (in fact even if they had interacted for a short time in the past, they have to be described by density matrices). Let \mathcal{O}_A be the operator corresponding to an observable about the A system. Then its expectation value is given by:

$$\langle \mathcal{O}_A \rangle = \text{Tr} \mathcal{O}_A \rho. \quad (1.8)$$

The Tr appearing in Eq. 1.8 can be written in two parts: trace over the degrees of freedom of the A -system, Tr_A , and trace over the degrees of freedom of the B -system, Tr_B . Since, by assumption, \mathcal{O}_A does not affect the degrees of freedom of the B -system, it can be taken out of Tr_B ; ie.

$$\begin{aligned} \langle \mathcal{O}_A \rangle &= \text{Tr}_A \text{Tr}_B \mathcal{O}_A \rho \\ &= \sum_{nm}^A \langle n | \otimes \sum_{m}^B \langle m | \mathcal{O}_A \rho | m \rangle^B \otimes | n \rangle^A \end{aligned} \quad (1.9)$$

$$= \sum_n^A \langle n | \mathcal{O}_A \left(\sum_m^B \langle m | \rho | m \rangle^B \right) | n \rangle^A \quad (1.10)$$

$$= \text{Tr}_A \mathcal{O}_A (\text{Tr}_B \rho) \quad (1.11)$$

The quantity in parenthesis contains all the information about the A -system and is called the Reduced Density Matrix. It will be denoted by ρ_R . It has the same properties listed in the preceding section. Its time dependence is determined by the time dependence of the density matrix of the whole system by

$$\rho_R(t) = \text{Tr}_B \rho(t) \quad (1.12)$$

Chapter 2

Keldysh Formalism Approach to Heat Conduction Through Atomic Wires

In studying non-equilibrium systems, in some cases it is more suitable to deal with a time independent density matrix, in which case one can use the Heisenberg picture, or it can be more suitable to use the time dependent density matrix, i.e. in the Schroedinger picture. In this chapter, heat conduction through an atomic wire between two reservoirs will be studied in the Heisenberg picture, or more precisely the Interaction picture. The formalism employed is the Keldysh formalism.

In equilibrium field theory, the interaction is adiabatically turned on at $t = -\infty$ and it is adiabatically turned off at $t = +\infty$, and it is assumed that the state obtained after this switching on and off of the interaction is the initial state upto a possible phase. This assumption can be justified only in the case of equilibrium and if the considered state is non-degenerate, but breaks down otherwise. In transport, for example, when the interaction is turned on, particles are transferred and they do not come back when the interaction is adiabatically turned off. In the Keldysh formalism, this assumption is not done, the state is first evolved from $t = -\infty$ to $t = +\infty$ and then back to $t = -\infty$ again so that one does obtain the initial state. Keldysh formalism has been applied to the study of electron transport (see eg. [25, 26, 27]), but to the authors' knowledge, it had not been applied to the problem of phonon

transport.

The organisation of this chapter is as follows: in Sec. 2.1, a review of the Keldysh formalism will be presented (see eg. [28]). In Sec. 2.2, an analytical treatment of the heat current through the uniform atomic wire will be carried out and the results will be studied in detail in Sec. 2.3. As much as possible, the details of the calculations will not be presented in the main body of the text but will be given separately at the Appendices at the end of the chapter.

2.1 Keldysh Formalism

The Keldysh formalism gives a means of calculating the properties of systems that are not in equilibrium but are in steady state. In steady state, the expectation value of any operator, \mathcal{O} , can be expressed as:

$$\begin{aligned}
 \langle \mathcal{O} \rangle &= \frac{\text{Tr}(\rho \mathcal{O})}{\text{Tr}(\rho)} \\
 &= \frac{\text{Tr}(\rho_0 \mathcal{T}_{\mathcal{C}} \mathcal{O}(0^+) e^{-\frac{i}{\hbar} \int_{\mathcal{C}} \mathcal{H}_{int}(t) dt})}{\text{Tr}(\rho_0 \mathcal{T}_{\mathcal{C}} e^{-\frac{i}{\hbar} \int_{\mathcal{C}} \mathcal{H}_{int}(t) dt})} \\
 &\equiv \frac{\langle \mathcal{T}_{\mathcal{C}} \mathcal{O}(0^+) e^{-\frac{i}{\hbar} \int_{\mathcal{C}} \mathcal{H}_{int}(t) dt} \rangle_0}{\langle \mathcal{T}_{\mathcal{C}} e^{-\frac{i}{\hbar} \int_{\mathcal{C}} \mathcal{H}_{int}(t) dt} \rangle_0} \quad (2.1)
 \end{aligned}$$

where $\langle \mathcal{O} \rangle_0 = \text{Tr} \rho_0 \mathcal{O}$. In Eq. 2.1, it is assumed that the system has the density matrix ρ_0 and the Hamiltonian \mathcal{H}_0 at $t = -\infty$. Then, the interaction, described by the Hamiltonian \mathcal{H}_{int} , is turned on and the density matrix of the system evolves to the steady state density matrix, ρ . The time loop, \mathcal{C} , is defined to be the path that goes from $t = -\infty$ to $t = +\infty$ and then from $t = +\infty$ back to $t = -\infty$. The times which are on the upper branch that goes from $t = -\infty$ to $t = +\infty$ are labeled by a (+) and the times which are on the lower branch that goes from $t = +\infty$ back to $t = -\infty$ are labeled by a (-). The operator $\mathcal{T}_{\mathcal{C}}$ which appears in Eq. 2.1 is the path ordering operator which orders the operators according to their positions on the time loop. If all the times have the label (+), the $\mathcal{T}_{\mathcal{C}}$ reduces to the time ordering operator and if all the times have the label (-), then it reduces to anti-time ordering operator. Expanding the exponential in Eq. 2.1, yields a perturbation expansion for the average of the operator. By the use of Wick's theorem, the expansion can be given a diagrammatic interpretation. In terms of the diagrammatic expansion,

Eq. 2.1, can be simplified to:

$$\langle \mathcal{O} \rangle = \langle \mathcal{T}_C \mathcal{O}(0^+) e^{-\frac{i}{\hbar} \int_C H_{int}(t) dt} \rangle_{connected} \quad (2.2)$$

where the subscript *connected* indicates that only the connected diagrams should be considered.

Let us define the two point correlation functions of the displacement of the atoms of the wire as:

$$\mathcal{G}_{ij}^{\zeta_1 \zeta_2}(t - t') = \langle \mathcal{T}_C x_i(t^{\zeta_1}) x_j(t'^{\zeta_2}) \rangle \quad (2.3)$$

where x_i is the displacement of the i^{th} wire atom and $\zeta_i = +, -$.

If one defines the matrices

$$\mathcal{G}_{ij}(t - t') = \begin{pmatrix} \mathcal{G}_{ij}^{++}(t - t') & \mathcal{G}_{ij}^{+-}(t - t') \\ \mathcal{G}_{ij}^{-+}(t - t') & \mathcal{G}_{ij}^{--}(t - t') \end{pmatrix} \quad (2.4)$$

$$\Sigma_{ij}(t - t') = \begin{pmatrix} \Sigma_{ij}^{++}(t - t') & \Sigma_{ij}^{+-}(t - t') \\ \Sigma_{ij}^{-+}(t - t') & \Sigma_{ij}^{--}(t - t') \end{pmatrix}, \quad (2.5)$$

where the Σ 's are the self energies, the Dyson equations can be written in a compact form as:

$$\begin{aligned} \mathcal{G}_{ij}(t - t') &= {}^0\mathcal{G}_{ij}(t - t') + \\ &+ \sum_{j'k'} \int dt'' dt''' {}^0\mathcal{G}_{ij'}(t - t'') \Sigma_{j'k'}(t'' - t''') \mathcal{G}_{k'j}(t''' - t') \end{aligned} \quad (2.6)$$

where ${}^0\mathcal{G}_{ij}(t - t')$ is the unperturbed Greens function. In terms of the Fourier transformed Greens function, Eq. 2.6 can be written as:

$$\mathcal{G}_{ij}(w) = {}^0\mathcal{G}_{ij}(w) + \sum_{j'k'} {}^0\mathcal{G}_{ij'}(w) \Sigma_{j'k'}(w) \mathcal{G}_{k'j}(w). \quad (2.7)$$

Diagrammatically, the Dyson equations can be represented by:

where the thin lines represent the free propagators and the solid lines represent the full propagators.

Note that not all the Greens functions and the self energies are independent. They satisfy:

$$\mathcal{G}^{++} + \mathcal{G}^{--} - \mathcal{G}^{+-} - \mathcal{G}^{-+} = 0 \quad (2.8)$$

$$\Sigma^{++} + \Sigma^{--} + \Sigma^{+-} + \Sigma^{-+} = 0 \quad (2.9)$$

Using these relations, the matrices \mathcal{G}_{ij} and Σ_{ij} can be transformed to:

$$\begin{pmatrix} 0 & \mathcal{G}_{ij}^R \\ \mathcal{G}_{ij}^A & \mathcal{G}_{ij}^K \end{pmatrix} = \frac{1}{2}(1 - i\sigma_y)\mathcal{G}_{ij}(1 + i\sigma_y) \quad (2.10)$$

$$\begin{pmatrix} \Sigma_{ij}^K & \Sigma_{ij}^A \\ \Sigma_{ij}^R & 0 \end{pmatrix} = -\frac{1}{2}(1 - i\sigma_y)\Sigma_{ij}(1 + i\sigma_y) \quad (2.11)$$

where σ_y is the second Pauli matrix:

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

After this transformations, the Dyson equations, Eq. 2.6, become:

$$\mathcal{G}_{ij}^R(w) = {}^0\mathcal{G}_{ij}^R(w) - \sum_{i'j'} {}^0\mathcal{G}_{ii'}^R(w)\Sigma_{i'j'}^R(w)\mathcal{G}_{j'j}^R(w) \quad (2.12)$$

$$\mathcal{G}_{ij}^A(w) = {}^0\mathcal{G}_{ij}^A(w) - \sum_{i'j'} {}^0\mathcal{G}_{ii'}^A(w)\Sigma_{i'j'}^A(w)\mathcal{G}_{j'j}^A(w) \quad (2.13)$$

$$\begin{aligned} \mathcal{G}_{ij}^K(w) &= {}^0\mathcal{G}_{ij}^K(w) - \sum_{i'j'} {}^0\mathcal{G}_{ii'}^A(w)\Sigma_{i'j'}^K(w)\mathcal{G}_{j'j}^R(w) \\ &\quad - \sum_{i'j'} {}^0\mathcal{G}_{ii'}^K(w)\Sigma_{i'j'}^R(w)\mathcal{G}_{j'j}^R(w) - \sum_{i'j'} {}^0\mathcal{G}_{ii'}^A(w)\Sigma_{i'j'}^A(w)\mathcal{G}_{j'j}^K(w) \end{aligned} \quad (2.14)$$

2.2 Model

Suppose that we have two reservoirs with temperatures T_L and T_R and are described by the Hamiltonians \mathcal{H}_L and \mathcal{H}_R respectively. Consider a 1D, uniform atomic wire of N atoms connecting the two reservoirs described by the Hamiltonian:

$$\mathcal{H}_S = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=0}^N \frac{k}{2}(x_i - x_{i+1})^2, \quad (2.15)$$

with fixed boundary conditions $x_0 = x_{N+1} = 0$. The system is shown in the figure below.

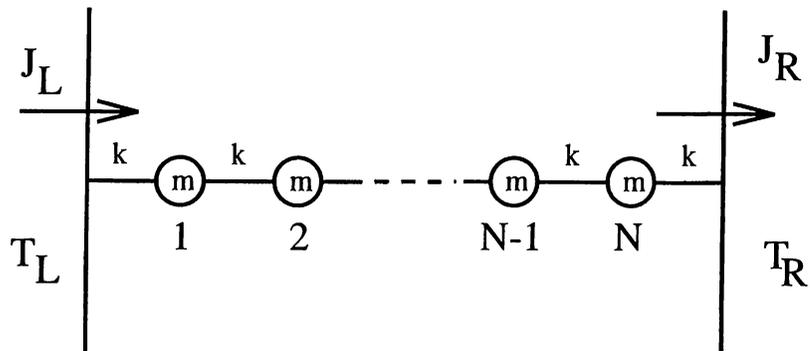


Figure 2.1: A schematic description of the model used in the present study. The balls represent the atoms with mass m .

In this Hamiltonian, we assume N identical masses all of which are connected to its nearest neighbours and the ones at the ends connected to the surfaces, which are assumed to be rigid, by identical springs. This model is over simplified to represent a real physical system quantitatively but we believe that it will grasp the qualitative features of heat conduction through atomic wires. The interaction between the wire and the reservoirs can be described, at the lowest order, by the Hamiltonian:

$$\mathcal{H}_{int} = A_L u_L x_1 + A_R u_R x_N, \quad (2.16)$$

where u 's are the lateral displacements of the reservoir atoms which interact with the wire. In this interaction term, it is assumed that only one atom from each reservoir is interacting with the wire and only the longitudinal modes are considered, generalizations to include other interactions and other modes is possible. Due to this interaction, the states of the wire are broadened. If the interactions of the wire atoms with other reservoir atoms is also taken into account, the broadening will be more pronounced.

At $t = -\infty$, before the interaction is turned on, the initial density matrix is given by,

$$\rho_0 = \frac{1}{Z} e^{-\beta_L \mathcal{H}_L} e^{-\beta_S \mathcal{H}_S} e^{-\beta_R \mathcal{H}_R}, \quad (2.17)$$

where $Z = \text{Tr} e^{-\beta_L \mathcal{H}_L} e^{-\beta_S \mathcal{H}_S} e^{-\beta_R \mathcal{H}_R}$ is the partition function of the whole system at time $t = -\infty$. Note that although at $t = -\infty$, the initial density

matrix depends on the initial temperature of the wire through $\beta_S = (k_B T)^{-1}$, at steady state, no physical quantity should depend on it.

2.2.1 Current Operator

The operator corresponding to the current at the contacts can be obtained from the continuity equation written in the form:

$$\frac{d\epsilon}{dt} = -(J_R - J_L), \quad (2.18)$$

where ϵ is the total energy operator of the wire and $J_{R(L)}$ is the operator for the current leaving(entering) the wire at the junction at the $R(L)$ reservoir. Let $\epsilon = \mathcal{H}_S$, then Eq. 2.18 is satisfied by the choices:

$$J_L = -\frac{A_L}{m} u_L p_1, \quad (2.19)$$

$$J_R = \frac{A_R}{m} u_R p_N. \quad (2.20)$$

Note that the current operators are proportional to the velocity, $v_i = \frac{p_i}{m}$, of the corresponding atom. One might argue that there is no *a priori* reason for the choice $\epsilon = \mathcal{H}_S$. Our attitude was that the energy of the wire appearing in the continuity equation should be a characteristic of the wire only, hence should not contain any operators related to its environment. An alternative argument could be: the energy of the wire should be the sum of all the terms in the Hamiltonian containing the wire operators. Hence it would be the difference in the Hamiltonian if the wire was absent. But the two approaches yields the same result due to the identity:

$$\begin{aligned} \langle p_L(t) x_1(t') \rangle &= M_L \frac{d}{dt} \langle u_L(t) x_1(t') \rangle \\ &= M_L \frac{d}{dt} \langle u_L(0) x_1(t' - t) \rangle \\ &= -M_L \frac{d}{dt'} \langle u_L(0) x_1(t' - t) \rangle \\ &= -M_L \frac{d}{dt'} \langle u_L(t) x_1(t') \rangle \\ &= -\frac{M_L}{m} \langle u_L(t) p_1(t') \rangle, \end{aligned} \quad (2.21)$$

where M_L and p_L are the mass and momentum, respectively, of the left reservoir atom which interacts with the wire. In the derivation, we have used the time

translational symmetry of the steady state. A similar derivation can be used to show:

$$\langle p_R(t)x_N(t') \rangle = -\frac{M_R}{m} \langle u_R(t)p_N(t') \rangle, \quad (2.22)$$

where M_R and p_R are the mass and momentum, respectively, of the right reservoir atom which interacts with the wire. In this work we will concentrate on $J = \langle J_L \rangle$ and by energy conservation $\langle J_R \rangle = \langle J_L \rangle$.

2.2.2 Analytical Calculations

Using the Wick theorem, the current, J can be expressed as (details can be found in Appendix B)

$$J = - \sum_{\alpha=1,N} \int \frac{dw}{2\pi} (\hbar\omega) \left(\Sigma_{1\alpha}^{++}(w) \mathcal{G}_{\alpha 1}^{++}(w) + \Sigma_{1\alpha}^{+-}(w) \mathcal{G}_{\alpha 1}^{-+}(w) \right), \quad (2.23)$$

where the α summation, in fact, represents a summation over all the contacts. In our case there are just two contacts but generalization to the other case is possible. With the interaction described by Eq. 2.16, the self energy can be calculated exactly:

$$\Sigma_{ij}(w) = \Sigma_{11}(w) \delta_{i1} \delta_{j1} + \Sigma_{NN}(w) \delta_{iN} \delta_{jN} \quad (2.24)$$

where $\Sigma_{ii}(w)$ are the Fourier transforms of

$$\Sigma_{11}^{\zeta_1 \zeta_2}(t-t') = (-1)^{\zeta_1 \zeta_2} \left(\frac{-iA_L}{\hbar} \right)^2 \langle \mathcal{T}_C u_L(t^{\zeta_1}) u_L(t'^{\zeta_2}) \rangle_0, \quad (2.25)$$

$$\Sigma_{NN}^{\zeta_1 \zeta_2}(t-t') = (-1)^{\zeta_1 \zeta_2} \left(\frac{-iA_R}{\hbar} \right)^2 \langle \mathcal{T}_C u_R(t^{\zeta_1}) u_R(t'^{\zeta_2}) \rangle_0. \quad (2.26)$$

Here $(-1)^{\zeta_1 \zeta_2} = 1$ if $\zeta_1 = \zeta_2$ and $(-1)^{\zeta_1 \zeta_2} = -1$ if $\zeta_1 \neq \zeta_2$. Substituting the Σ into Eq. 2.7, one can solve for the exact Greens function, \mathcal{G} . Once they are substituted into the expression for the current, the result can be simplified to

$$J = 2\pi \left(\frac{A_L A_R}{\hbar^2} \right)^2 \int_0^\infty dw g^L(w) g^R(w) \times \hbar w \det \mathcal{G}_{1N}(w) \frac{\hbar}{2M_L w} \frac{\hbar}{2M_R w} (n_B^L(w) - n_B^R(w)) \quad (2.27)$$

where $\det \mathcal{G}_{1N}(w) = -\mathcal{G}_{1N}^R(w) \mathcal{G}_{1N}^A(w)$ is the determinant of the 2×2 Greens function matrix and $n_B^{L(R)}(w) = (e^{\beta_{L(R)} \hbar w} - 1)^{-1}$ are the Bose distribution functions at the left(right) reservoirs. The details of the derivation can be found in the Appendix C. The determinant can be decomposed as,

$$\det \mathcal{G}_{1N} = \det \mathcal{G}_{1N}^b + \det \mathcal{G}_{1N}^t, \quad (2.28)$$

where $\det \mathcal{G}_{1N}^b$ describes the contribution of ballistic phonon transport and $\det \mathcal{G}_{1N}^t$ describes the phonon tunneling contribution. Hence the total current can also be decomposed as the sum of the tunneling current and ballistic current.

Note the similarity between this result, Eq. 2.27, and the Landauer type expression, Eq. 1.2 which, after a change of variables, can be written as :

$$J = \frac{1}{2\pi} \sum_m \int dw \hbar w (n_B^L(w) - n_B^R(w)) T_m(w) \quad (2.29)$$

where $T_m(w)$ is the transmission coefficient for a phonon of frequency w at the m^{th} branch to be transmitted from the left reservoir to the right reservoir. In our case, if we allow the reservoirs to have various phonon branches, the total density of states appearing in Eq. 2.27 should be replaced by sums over the density of states of each branch, in which case, we obtain for the transmission coefficient for a phonon of frequency w at the m^{th} branch of the left reservoir to the n^{th} branch of the right reservoir to be:

$$T_{mn} = (2\pi)^2 \left(\frac{A_L A_R}{\hbar^2} \right)^2 g_m^L(w) g_n^R(w) \det \mathcal{G}_{1N}(w) \frac{\hbar}{2M_L w} \frac{\hbar}{2M_R w}, \quad (2.30)$$

so that

$$J = \sum_{mn} \int \frac{dw}{2\pi} \hbar w (n_B^L(w) - n_B^R(w)) T_{mn}(w). \quad (2.31)$$

Eq. 2.30 is important because, to the authors' knowledge, it is the first non-phenomenological microscopic derivation of the transmission coefficient, and contrary to other expressions used in the literature, it takes into account the discrete nature of the system.

2.3 Numerical Analysis and Discussion

In all the calculations, both reservoirs are assumed to be identical Debye solids except their respective temperatures. Let

$$J(T_L, T_R) = \int_0^1 dx J(x\omega_D, T_L, T_R). \quad (2.32)$$

$J(\omega, T)$ can be considered as the heat current density at the frequency ω . Then the heat conductance density at the temperature T can be defined as:

$$\kappa(\omega, T) = \lim_{\Delta T \rightarrow 0} \frac{J(\omega, T + \Delta T, T)}{\Delta T}, \quad (2.33)$$

so that the total conductance is given by,

$$\kappa = \int_0^1 dx \kappa(xw_D, T). \quad (2.34)$$

For the numerical data, we used $\hbar\omega_D^R = \hbar\omega_D^L = \hbar\omega_D = 37.6$ meV, $M_L = M_R = 56$ amu, $m = 28$ amu, and $A_L = A_R = -19$ J/m². The phonon density of states is represented by the 3D Debye density of states,

$$g^{L(R)}(w) = 3 \frac{w^2}{w_D^3} \theta\left(1 - \frac{w}{w_D}\right) \quad (2.35)$$

where w_D is the Debye frequency and θ is the step function. It should be noted that the contribution of the surface phonons are not taken into account.

In Figs. 2.2a, 2.2b and 2.2c, the dependence of the conductance density on the frequency, ω , is shown at various temperatures and for $N = 1$, $N = 5$, and $N = 10$ respectively. The resonances at the eigenfrequencies of the wire and their broadening are clear. The heights of the peaks are almost independent of the number of atoms in the chain, while they become narrower as N becomes larger. This can be understood in terms of the weakening of the coupling constant of each mode to the reservoir modes which is proportional to $\frac{1}{\sqrt{N+1}}$.

In Figs. 2.3a, 2.3b and 2.3c, the dependence of the total conductance on the coefficient $\sqrt{\frac{k}{m}}$ is shown. Contrary to the electronic counterpart, the steps are clear at high temperatures whereas they are lost at lower temperatures. As $\sqrt{\frac{k}{m}}$ increases, the eigenfrequencies of the wire increase, and as one eigenfrequency crosses the Debye frequency, it no longer contributes to the conductance, and hence there is a fast decrease at the total conductance. The more separate the eigenfrequencies are, the longer the plateaus. At high temperatures, all of the eigenmodes contribute to the conductance, hence there are several steps. But as can be seen in Figs. 2.2, at low temperatures, there is very few high frequency phonons at the reservoirs, hence the modes corresponding to the higher eigenfrequencies do not contribute; the corresponding “channel” is closed at lower temperatures. Following comments related with Fig. 2.3 are in order: (i) The step behavior of electrical conductance is obtained by changing the width of the constriction or by stretching the metallic wire between two electrodes. In the present case, the step behavior of κ can be realized to some extent by varying k and m , and also ω_D . Of course ω_D is an artificial cut-off due to the Debye model. In a real crystal, the cut-off of $\omega(\mathbf{k})$ at the zone boundary has to be taken into account. Cut-off frequencies can

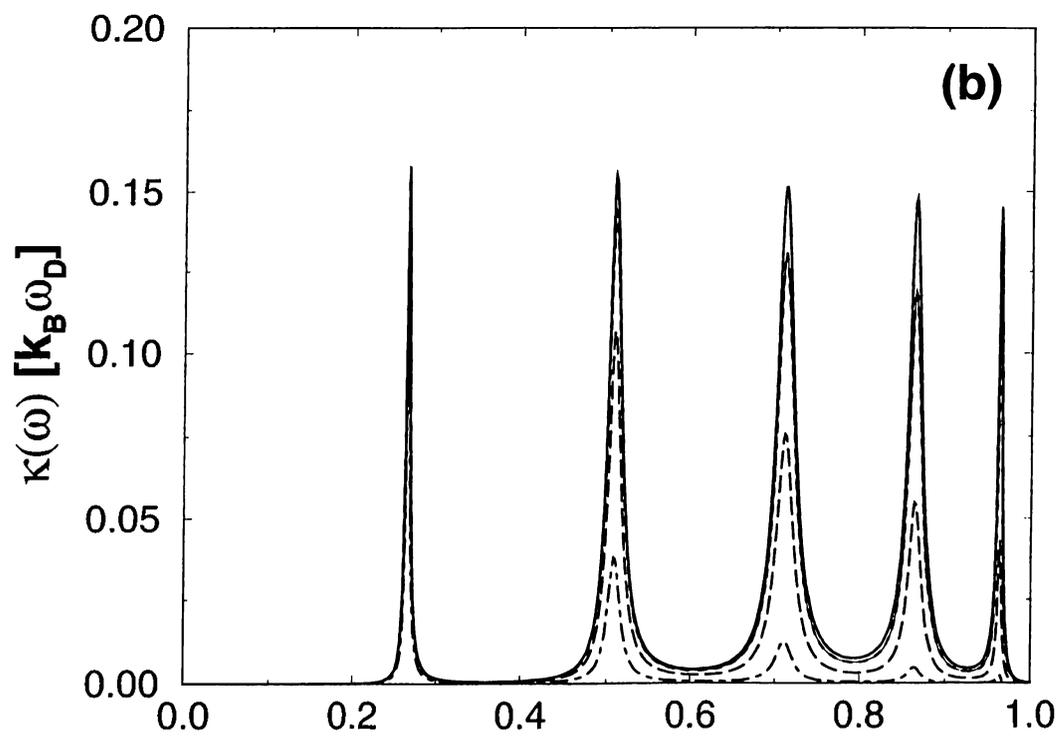
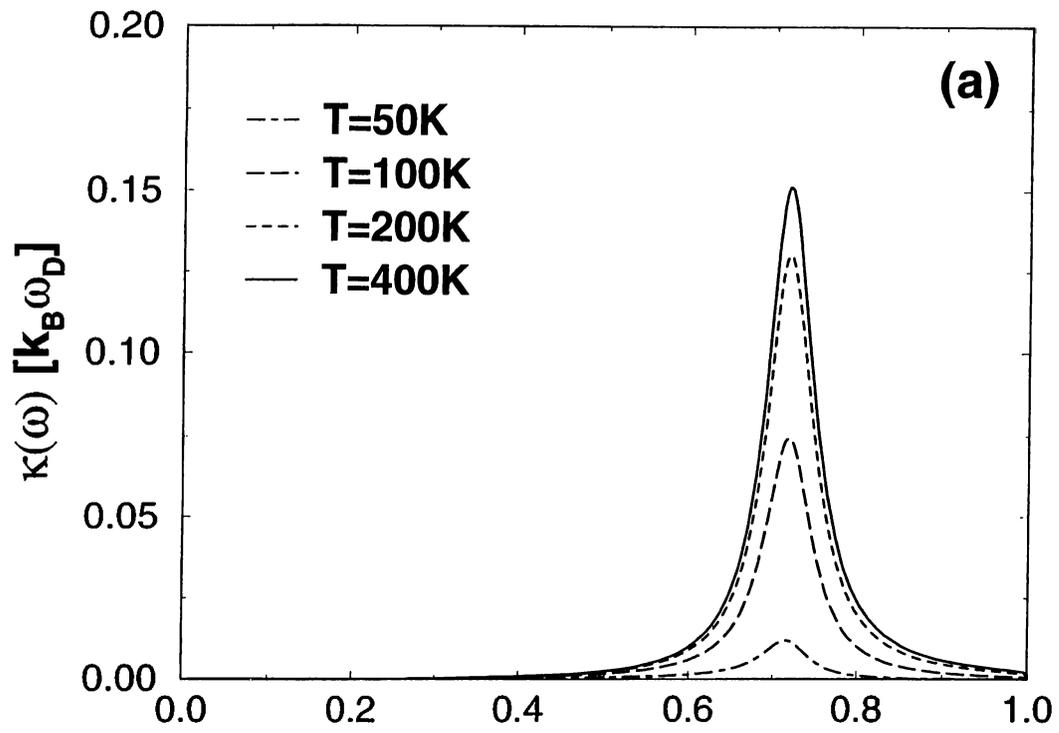
be modified by applying strong external pressure so that the lattice spacing is modified, and the eigenfrequencies of the wire can be modified by stretching the wire. According to the present result, if the atoms of the chain are replaced by their isotopes, the value of κ changes even if all other parameters are kept the same. (ii) In the case of quantum ballistic conductance of electrons, the step heights (or jumps in the electrical conductance, σ , are normally integer multiples of $2e^2/h$ depending on the degeneracy of the channel. The phononic thermal conductance step heights are inversely proportional to N . (iii) The step structure shown in Fig. 2.3 can be modified if there is surface phonons at the gap. It can be argued that the present model and the measurement of conductance can be used to investigate the surface phonons. (iv) In calculating the step structure, the broadening of the modes of the atom is fully taken into account, within our model, which smeared the step. This smearing is more pronounced for the first several steps, since the higher eigenmodes are more closely spaced, and hence they overlap due to the broadening. If interaction with more than one reservoir atom is taken into account, as discussed in the text, the extra broadening would further smear out the steps. Therefore it is possible the this extra broadening, which is present in realistic systems, might cause the steps to disappear completely. (v) The anharmonic coupling which is not taken into account here, may modify the step behavior especially for very large N , and for $\omega_i > \omega_D$

In Fig. 2.4, the dependence of the total conductance on temperature is shown. In this plot it is assumed that $\sqrt{\frac{k}{m}} = \frac{\omega_D}{2}$, and since at this frequency, the conductance is almost independent of the number of atoms, it is only shown for $N = 5$.

In Fig. 2.5, the variation of the total conductance at various temperatures as the number of atoms is increased is shown. As is seen from the figures, for $\sqrt{\frac{k}{m}} = \frac{\omega_D}{2}$, the total conductance is almost independent of the number of atoms. The total conductance for a single atomic wire is less than the total conductance for $N\mathcal{G}^{R2}$. The difference is due to the tail of conductance density which extends beyond the Debye frequency as can be seen in Fig. 2.2a. For $\sqrt{\frac{k}{m}} = \omega_D$, there are fluctuations in the total conductance. This fluctuations are due to the fact that in the first case all the modes contribute to the conductance since the Debye frequency is greater than all the eigenfrequencies of the wire, whereas in the second case, the Debye frequency lies within the spectrum of the wire. Hence the ratio of the contributing modes to the total number of modes

fluctuates, but the fluctuations diminishes as the number of modes increases.

Finally, it may be interesting to find out how the total thermal conductance of the atomic wire with $N \geq 2$ and $\sqrt{\frac{k}{m}} = \frac{w_D}{2}$ is compared with the universal value of conductance [7, 8, 9] $\kappa_0 = \frac{k_B^2 \pi^2}{3h} T$, which is proportional to the temperature T . In our case, if one Taylor expands the conductance expression, Eq. 2.34, in terms of the temperature, the first non-zero term is proportional to T^3 contrary to the results in [7, 8, 9].



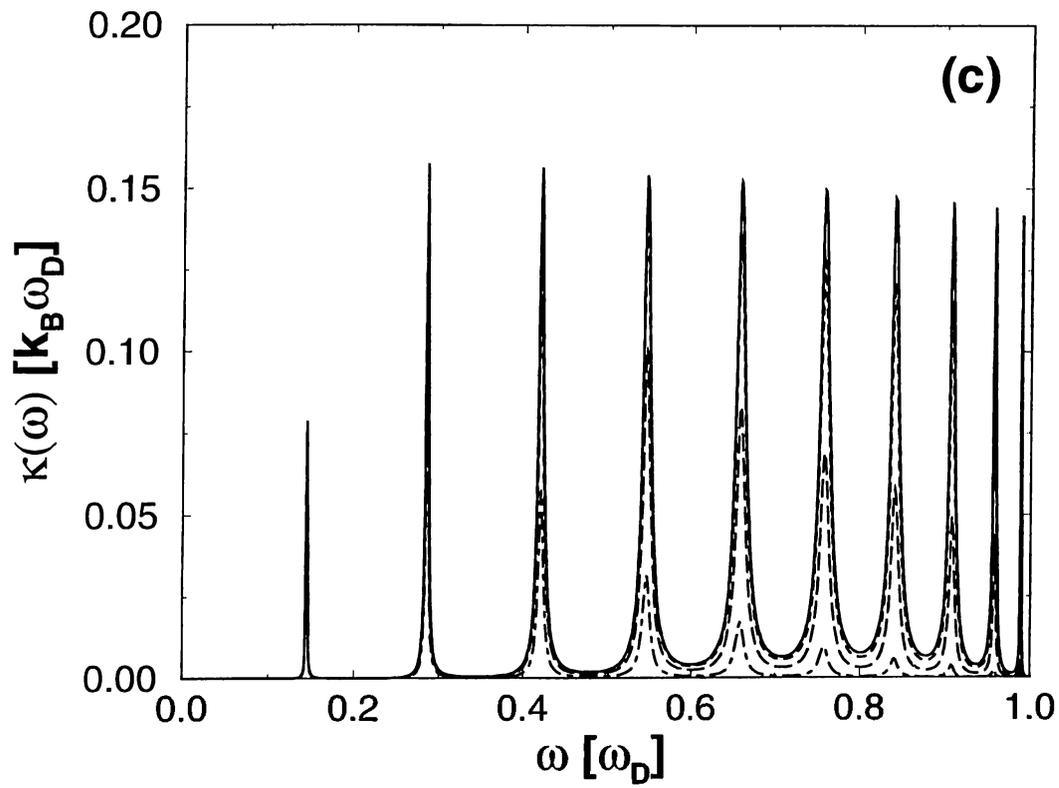
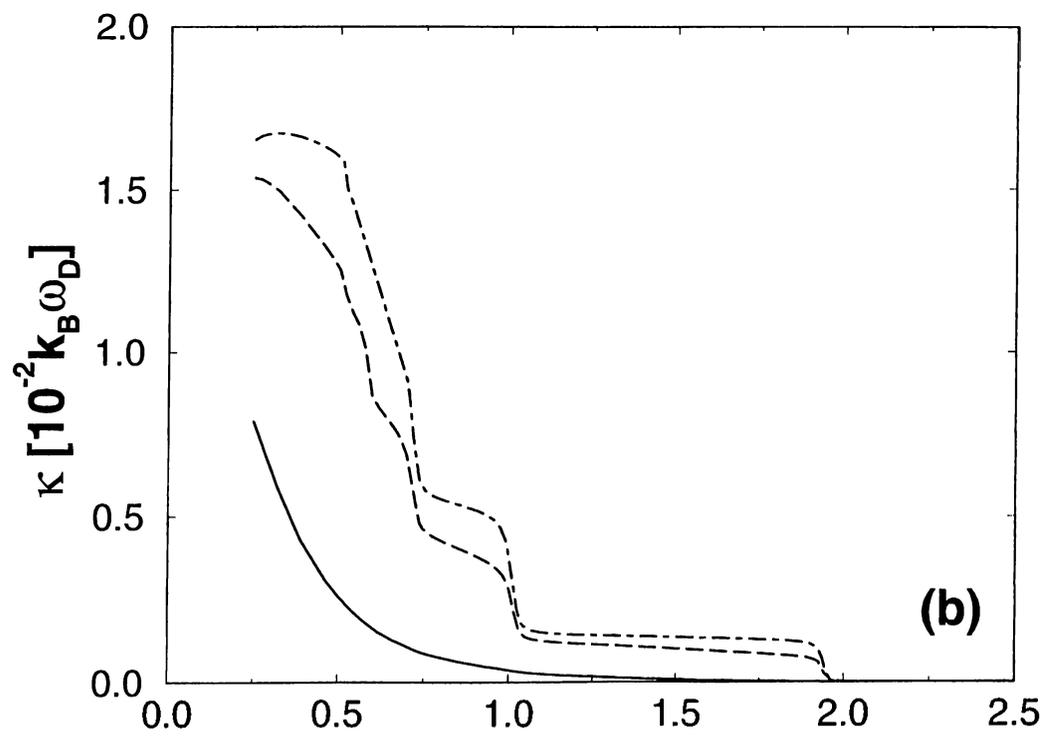
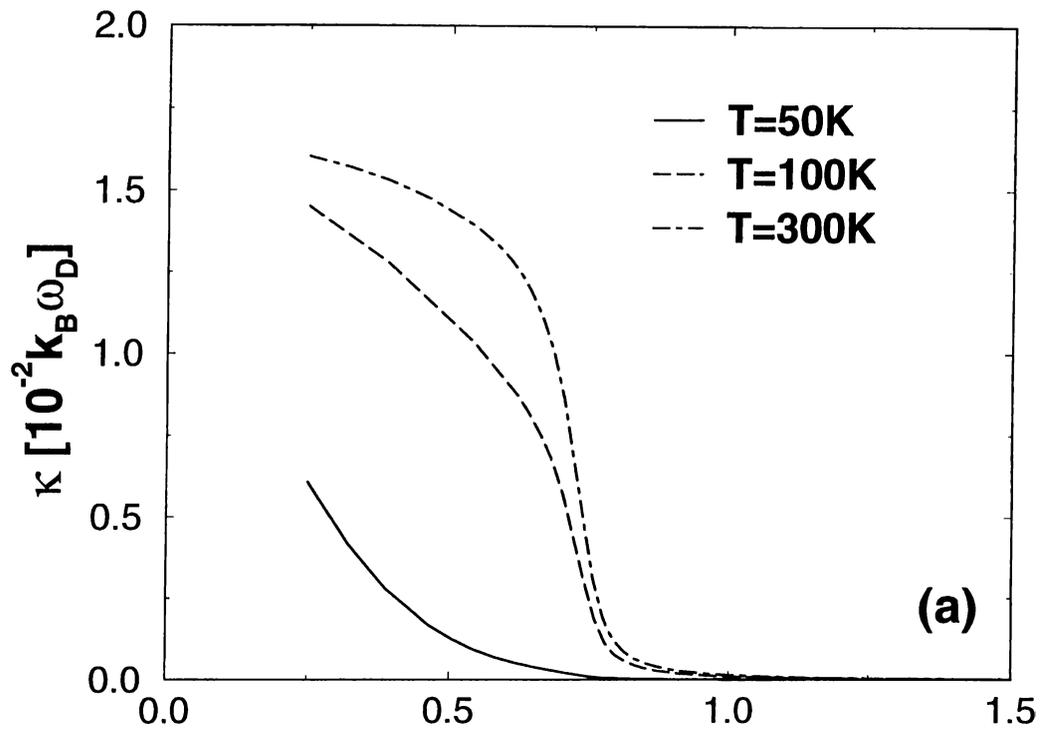


Figure 2.2: The graphs of $\kappa(\omega)$ at various temperatures for $\sqrt{\frac{k}{m}} = \frac{\omega_D}{2}$. (a) $N=1$; (b) $N=5$; (c) $N=10$



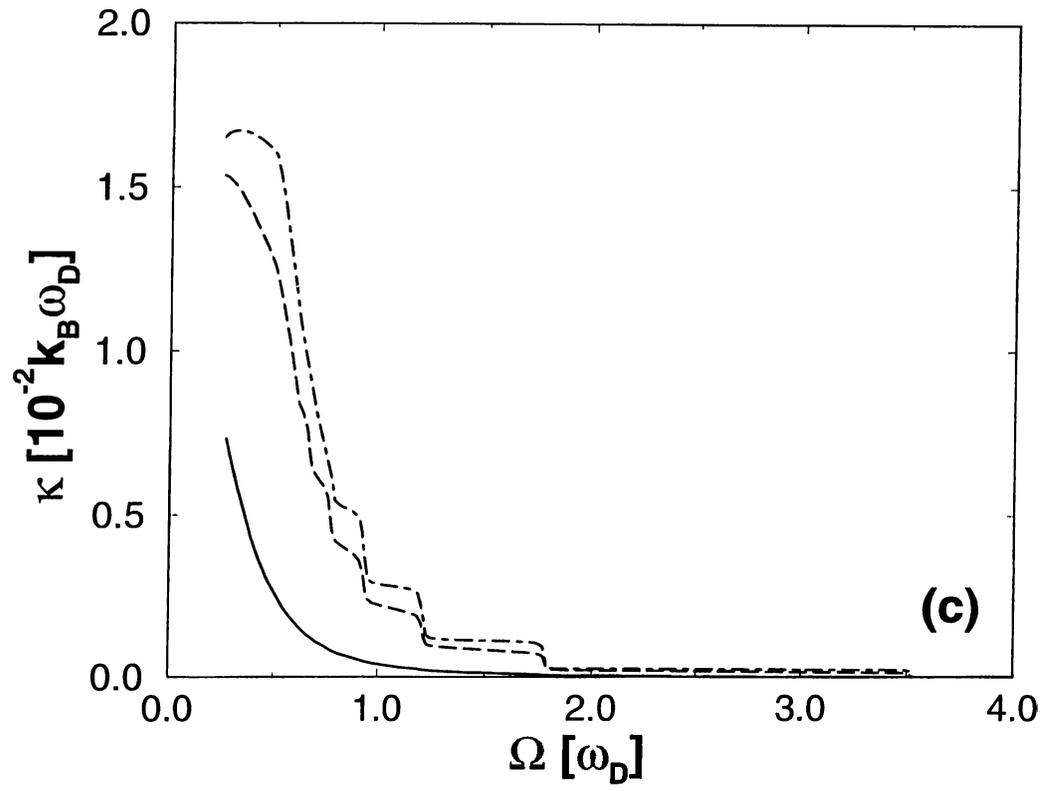


Figure 2.3: The graph of the dependence of the total conductance, κ , on $\Omega = \sqrt{\frac{k}{m}}$ at various temperatures. (a) $N=1$; (b) $N=5$; (c) $N=10$

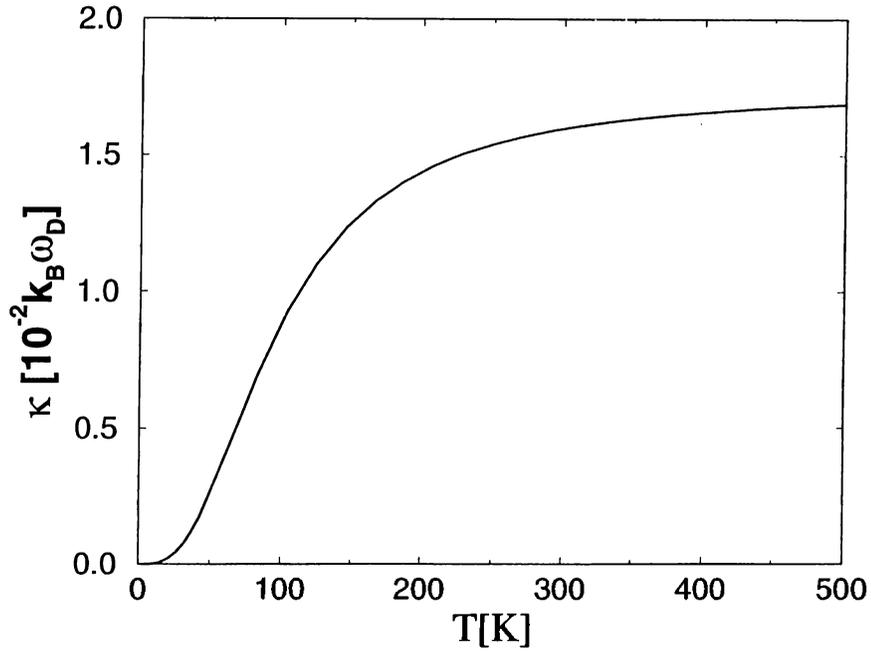


Figure 2.4: The graph of the dependence of the total conductance, κ , on temperature at $\sqrt{\frac{k}{m}} = \frac{w_D}{2}$ for $N = 5$

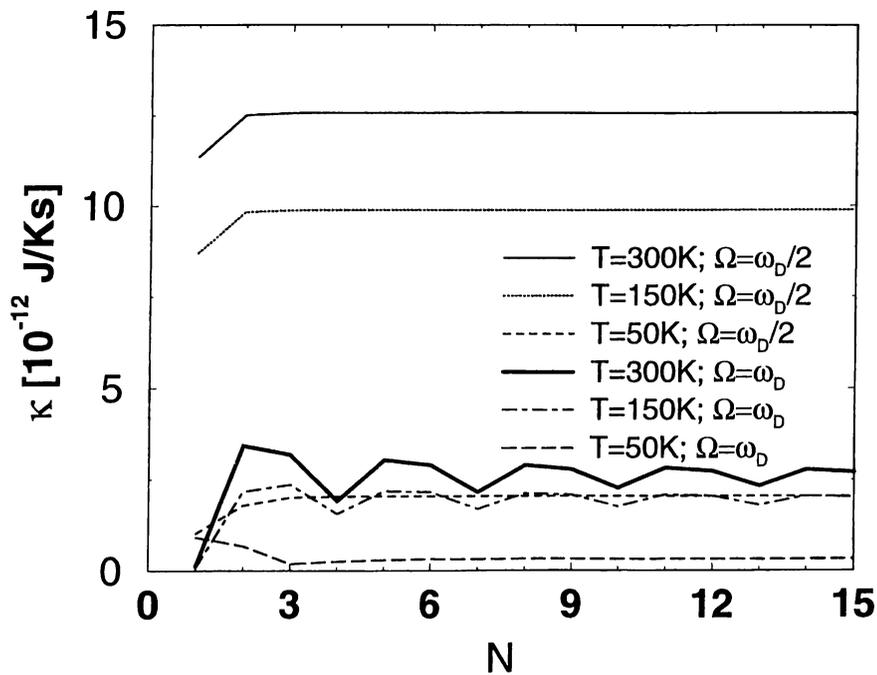


Figure 2.5: The dependence of the total conductance on the number of atoms at various temperatures and for $\Omega = \sqrt{\frac{k}{m}} = w_D$, and $\Omega = \sqrt{\frac{k}{m}} = \frac{w_D}{2}$

Chapter 3

Reduced Density Matrix Approach to Vibrational Relaxations

In this chapter, a Redfield Theory-like approach is developed (for the derivation of the Redfield theory and some of its applications see eg. [33, 34, 23]) for calculating the time evolution of the reduced density matrix in the Schrödinger picture. The result is then applied to study the relaxation of the non-equilibrium phonon distribution taking into account the non-equilibrium properties of the system and then the method is applied to study the vibrational damping of an adsorbed molecule on a surface.

Considering an atom adsorbed on the surface of a sample, with vibration frequency Ω , in general there are two possible decay modes, i) it can create electronic excitations in the metal, eg. create electron-hole pairs, or ii) it can create phononic excitations. In this article our interest will be on the phononic dissipation. If $\Omega \simeq n w_0$ where w_0 is the maximum phonon frequency of the sample (for a Debye solid it is the Debye frequency w_D), the excitations can decay only by the creation of n phonons in the sample [19]. For large n , this contribution is in general negligible. For systems such as the Cu-CO stretch vibration, $\Omega \simeq 1.5 w_0$ and decay by creating two phonons might be an important mechanism for the vibrational damping of the molecule.

In [12] two and three phonon contribution to the dissipation of the Cu-CO

stretch vibrations is studied using Golden Rule formula. In this work we will study the same system using the Redfield theory-like approach for various Ω 's to understand the dependence of the dissipation rate on the coupling between the sample and the adsorbed atom. The organization of the paper is as follows: In Sec. 3.1, we calculate the time evolution of the reduced density matrix which allows one to take into account all non-equilibrium properties of a system and also takes into account possible coherence and incoherence effects (for the properties of density matrices see eg [23]). Possible limitations on the obtained evolution is also discussed. In Sec. 3.2 a model system is proposed which is analyzed and solved in Sec. 3.3.

3.1 Evolution of the Reduced Density Matrix

In studying the dynamics of systems coupled to the environment, it is most natural to use the Reduced Density Matrix (RDM) formalism. The time dependence of the RDM of the system can be obtained from Eq. 1.12. Let

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_r + \mathcal{H}_{int}, \quad (3.1)$$

where \mathcal{H}_s , \mathcal{H}_r are the system and reservoir Hamiltonians, respectively, and \mathcal{H}_{int} describes the interaction between them. We will assume, without loss of generality, that

$$\mathcal{H}_{int} = \sum_s Q_s F_s \quad (3.2)$$

where $Q_s(F_s)$ acts only on the system (reservoir) degrees of freedom. The time evolution of the components of the RDM is given by

$$\rho_{\alpha\beta}(t) = \rho_{\alpha\beta}(0)e^{-i\omega_{\alpha\beta}t} + \sum_{\alpha'\beta'} R_{\alpha\alpha';\beta\beta'}(t)\rho_{\alpha'\beta'}(0)e^{-i\omega_{\alpha\beta}t}, \quad (3.3)$$

where $\hbar\omega_{\alpha\beta} = \epsilon_\alpha - \epsilon_\beta$ and the tensor $R_{\alpha\alpha';\beta\beta'}(t)$ is defined as:

$$R_{\alpha\alpha';\beta\beta'}(t) = \sum_{ij} P(E_j) \langle \alpha i | \mathcal{S}(t) | \alpha' j \rangle \langle \beta' j | \mathcal{S}^\dagger(t) | \beta i \rangle - \delta_{\alpha\alpha'} \delta_{\beta\beta'} \quad (3.4)$$

where the scattering matrix, $\mathcal{S}(t)$, is defined as:

$$\begin{aligned} \mathcal{S}(t) &= e^{\frac{i}{\hbar}\mathcal{H}_0 t} e^{-\frac{i}{\hbar}\mathcal{H} t} \\ &= 1 - \frac{i}{\hbar} \int_0^t dt' \mathcal{H}_{int}(t') \\ &\quad + \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \mathcal{H}_{int}(t_1) \mathcal{H}_{int}(t_2) + \dots \end{aligned} \quad (3.5)$$

Here, \mathcal{H}_0 is defined to be $\mathcal{H}_0 = \mathcal{H}_r + \mathcal{H}_s$. Also $\mathcal{H}_{int}(t) = e^{\frac{i}{\hbar}\mathcal{H}_0 t} \mathcal{H}_{int} e^{-\frac{i}{\hbar}\mathcal{H}_0 t}$, and $|\gamma j\rangle = |\gamma\rangle \otimes |j\rangle$ with,

$$\begin{aligned}\mathcal{H}_s|\gamma\rangle &= \epsilon_\gamma|\gamma\rangle \\ \mathcal{H}_r|j\rangle &= E_j|j\rangle.\end{aligned}\tag{3.6}$$

In the following Greek (Latin) letters will denote the system (reservoir) degrees of freedom. In deriving this result it is assumed that the bath is always in equilibrium so that the density matrix of the whole system could be factorized as:

$$\langle \gamma j | \rho(t) | \delta k \rangle = \delta_{jk} \rho_{R\gamma\delta} P(E_j)\tag{3.7}$$

where the diagonal density matrix elements of the reservoir are defined as

$$P(E_j) = \frac{e^{-\beta E_j}}{Z}.\tag{3.8}$$

Here $Z = \sum_j e^{-\beta E_j}$.

Until this point, the only assumption made is that the density matrix of the whole system is factorizable which resulted in a linear equation for the components of the RDM. The applicability of this approximation should be studied carefully. This assumption is valid only if there exists a weak coupling between the system and the reservoir so that the tensor product states $|\alpha j\rangle$ can be considered as almost the eigenstates of the whole system. If there is a strong coupling between the system and the reservoir, or if the “reservoir” is a finite one, the density matrix of the whole system in general cannot be factorized and one has to do without this simplifying approximation.

Now, the main task is to find a suitable approximation for the tensor $R_{\alpha\alpha';\beta\beta'}(t)$, once it is known, the time evolution of the RDM can be calculated.

Unfortunately, the expression obtained by straightforward application of the second order expansion of the \mathcal{S} matrix yields a result which is valid only if the time t is short enough. To overcome this difficulty we used an iterative scheme in which we calculated the initial RDM and then evolved it one step in time, and then taking the evolved RDM as the initial RDM, we evolved it one step further. At each step, the evolution was for a short enough time. Since energy is not conserved for finite times, one has to impose the energy

conservation by hand. For this reason, the matrix elements of \mathcal{H}_{int} coupling states of different energies are neglected. The calculations are similar to the ones done in scattering theory with the result

$$\rho_{\alpha\beta}(t + \Delta t) = \rho_{\alpha\beta}(t)e^{-i\omega_{\alpha\beta}\Delta t} + \sum_{\alpha'\beta'} R_{\alpha\alpha';\beta\beta'}(\Delta t)\rho_{\alpha'\beta'}(t)e^{-i\omega_{\alpha\beta}\Delta t}, \quad (3.9)$$

$$\begin{aligned} R_{\alpha\alpha';\beta\beta'}(\Delta t) &= \frac{\Delta t}{\hbar^2}\delta_{\alpha-\alpha',\beta-\beta'} \left(\sum_{ss'} Q_s^{\alpha\alpha'} Q_{s'}^{\beta'\beta} j_{ss'}(\omega_{\alpha\alpha'}) - \right. \\ &\quad - \frac{1}{2}\delta_{\alpha\alpha'} \sum_{ss'} \sum_{\gamma} Q_s^{\beta\gamma} Q_{s'}^{\gamma\beta} j_{ss'}(\omega_{\gamma\beta}) - \\ &\quad \left. - \frac{1}{2}\delta_{\alpha\alpha'} \sum_{ss'} \sum_{\gamma} Q_s^{\alpha\gamma} Q_{s'}^{\gamma\alpha} j_{ss'}(\omega_{\gamma\alpha}) \right), \end{aligned} \quad (3.10)$$

$$j_{ss'}(\omega) = \Delta t \sum'_{kj} P(E_j) F_s^{kj} F_{s'}^{jk}, \quad (3.11)$$

where the prime on the summation in Eq. 3.11 indicates that the sum should be carried out over states for which $\hbar\omega = E_{jk}$.

3.2 The Model Hamiltonian

Consider an atom adsorbed on a surface. Let M be the mass of a reservoir atom and m be the mass of the adsorbed atom. Assume that the adsorbed atom is bonded to a single atom of the sample and the interaction between the sample atom and the adsorbed atom is described by the Morse potential:

$$U(u - v) = E_0 \left\{ e^{-2\alpha(u-v)} - 2e^{-\alpha(u-v)} \right\}, \quad (3.12)$$

where u and v are the vertical displacements of the adsorbed atom and the sample atom respectively. E_0 is the binding energy of the adsorbed atom and α can be related to the vibration frequency, Ω , of the adsorbed atom through

$$\alpha = \left(\frac{m\Omega^2}{2E_0} \right)^{\frac{1}{2}}, \quad (3.13)$$

where m is its mass. Expanding the potential and retaining the lowest order terms, we get

$$\mathcal{H}_{int} = Auv + Buv^2 \quad (3.14)$$

where

$$A = -2E_0\alpha^2 \quad (3.15)$$

$$B = -3E_0\alpha^3 \quad (3.16)$$

For $\Omega > \omega_0$, the uv -term has no contribution since it does not conserve energy. If a localized phonon at the adsorbed atom makes a virtual energy non-conserving transition into the reservoir, or vice versa, due to this term, the only possibility for its fate is that it has to go back in order to conserve energy. Hence it would not contribute to dissipation. Note that in the atomic wire case of the preceding chapter, even if a phonon localized at one of the reservoirs makes a virtual transition to the wire, it can then go to the other reservoir and conserve energy, hence in this case, such energy non-conserving transition do contribute to the heat current.

In our case, though, we only have the uv^2 -term. For the other case $\Omega < \omega_0$, in general, compared to the uv term, the uv^2 term is negligible. The decay of the vibrational excitation in this case for the harmonic coupling have been studied by exact diagonalization of the Hamiltonian [35]. The calculated value for the decay rate is two orders greater than the value we have calculated in Sec. 3.3. In this article, this term is omitted even in this case, and only the effects of the uv^2 term are studied. Then the full phononic Hamiltonian of the system becomes:

$$\mathcal{H} = \hbar\Omega b^\dagger b + \sum_{\mathbf{k}\sigma} \hbar\omega_{\mathbf{k}\sigma} b_{\mathbf{k}\sigma}^\dagger b_{\mathbf{k}\sigma} + Buv^2, \quad (3.17)$$

where $\omega_{\mathbf{k}\sigma}$ are the frequencies of the sample phonons with wave vector \mathbf{k} and polarisation vector \mathbf{e}_σ , b and $b_{\mathbf{k}\sigma}$ are the annihilation operators for the phonons at the adsorbed atom and the phonons in the sample, respectively.

3.3 Numerical Analysis and Discussion

We carry out numerical calculations on the model system presented in Fig. 3.1.

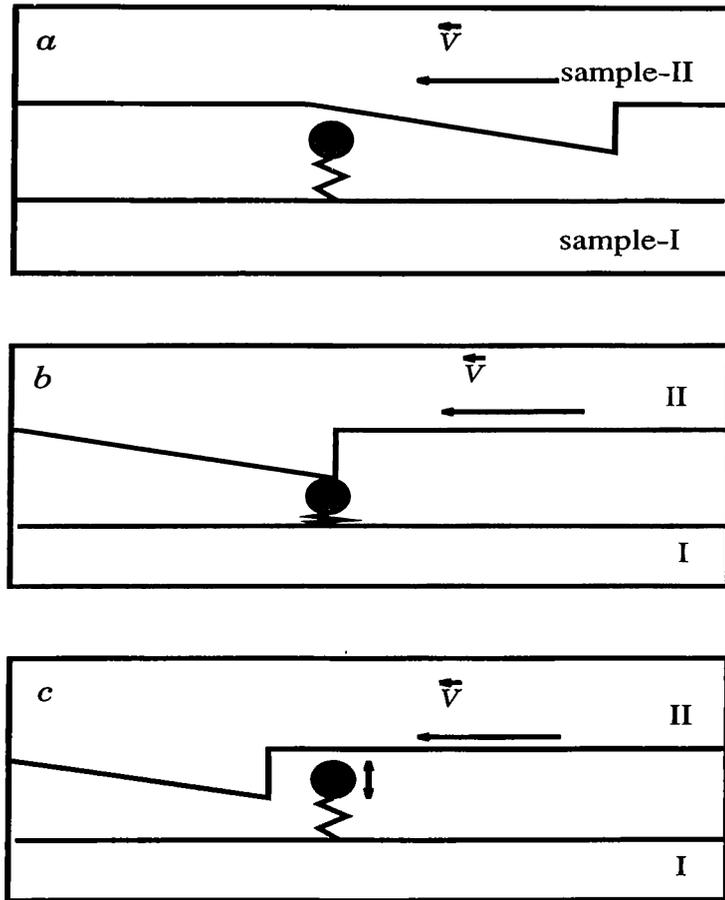


Figure 3.1: An adsorbed atom between the surfaces of two samples, one of which move with a velocity \vec{v} . (a) There is no interaction between the sample-II and the rest of the system. (b) the adatom is squeezed, absorbing some of the translational energy of sample-II. (c) the adatom is suddenly released causing it to oscillate and the interaction between the sample-II and the rest of the system is again neglected.

In order to construct the initial density matrix, consider the following situation: assume that two samples, sample-I and sample-II, are moving on top of one another with an adsorbed layer on the bottom one, and there is no direct interaction between the samples as described in Fig. 3.1. Consider the case when the coverage of the adsorbed layer is so low that the interactions between the adsorbed atoms can be neglected, in which case one can treat each adsorbed atom independently. During the motion of the sample-II, the atom adsorbed on the sample-I will be pushed and released, eg if there is a step dislocation on the bottom surface of the sample-II, the atom will be adiabatically pushed down, due to the wedge shape of the surface, displacing it from its equilibrium position and storing energy in it. And then it is suddenly released. After its release there is no interaction of the adsorbed atom with sample-II. This model is relevant for the energy dissipation through phonons in dry sliding friction or lubrication, and also in the vibration of the adsorbed species. The character of contribution of such a mechanism to the friction between the bodies would depend on the rate of relaxation of this non-equilibrium situation.

Initially, the density matrix of the system plus reservoir is the equilibrium density matrix:

$$\rho = \sum_{\alpha j} \frac{e^{-\beta(\epsilon_{\alpha} + E_j)}}{Z} |\alpha j\rangle \langle \alpha j|, \quad (3.18)$$

$$(3.19)$$

where $Z = \sum_{\alpha j} e^{-\beta(\epsilon_{\alpha} + E_j)}$, α denotes the number of phonons at the atom and j is a multiple index describing the number of phonons in each mode, $k\sigma$ of the sample.

Adiabatically displacing the atom would not cause the atom to go off-equilibrium, the density matrix will still be diagonal with the same diagonal elements but in the displaced basis:

$$\rho = \sum_{\alpha j} \frac{e^{-\beta(\epsilon_{\alpha} + E_j)}}{Z} |\alpha' j\rangle \langle \alpha' j| \quad (3.20)$$

with the same Z and the displaced harmonic oscillator states, $|\alpha'\rangle$, are defined as

$$|\alpha'\rangle = e^{\frac{i}{\hbar} s \hat{p}} |\alpha\rangle = \sum_{\beta} c_{\alpha'\beta} |\beta\rangle \quad (3.21)$$

where s is the displacement of the oscillator and \hat{p} is the momentum operator of the adsorbate. When the adsorbate is suddenly released, the density matrix

does not change, but now, in the absence of the external force due to sample-II, the density matrix is not diagonal in the energy eigenstates, and the adsorbate is off-equilibrium. Denoting the RDM of the system right after it is released by $\rho(0^+)$, we have

$$\begin{aligned}\rho(0^+) &= \text{Tr}_b \sum_{\alpha j} \frac{e^{-\beta(\epsilon_\alpha + E_j)}}{Z} |\alpha' j\rangle \langle \alpha' j| \\ &= \sum_{\beta \gamma} \rho_{\beta \gamma}(0) |\beta\rangle \langle \gamma|\end{aligned}\quad (3.22)$$

where $\rho_{\beta \gamma}(0) = Z^{-1} \sum_{\alpha} c_{\alpha' \beta} c_{\alpha' \gamma}^* e^{-\beta \epsilon_\alpha}$

Following [12], take

$$u = \left(\frac{\hbar}{2m\Omega} \right)^{\frac{1}{2}} (b + b^\dagger), \quad (3.23)$$

$$v = \sum_{\mathbf{k}\sigma} \left(\frac{\hbar}{2M\omega_{\mathbf{k}\sigma} N} \right)^{\frac{1}{2}} (b_{\mathbf{k}\sigma} + b_{\mathbf{k}\sigma}^\dagger) \hat{\mathbf{z}} \cdot \mathbf{e}_{\mathbf{k}\sigma} \quad (3.24)$$

where M and N are the mass and the total number of the sample-I atoms, $\mathbf{e}_{\mathbf{k}\sigma}$ is the polarization vector of the mode $\mathbf{k}\sigma$. As is pointed out in [12], this expression for v does not account for the surface which might reflect bulk phonons, and also does not take into account any surface phonons. With these definitions and choosing

$$F_1 = v^2, \quad (3.25)$$

$$Q_1 = Bu, \quad (3.26)$$

we obtain:

$$\begin{aligned}j_{11}(\omega) &= j(\omega) = \theta(\omega) \left[\left(\frac{\hbar}{2M} \right)^2 \int d\omega' g(\omega') g(\omega' - \omega) 4 \frac{(n_B(\omega') + 1)n_B(\omega' - \omega)}{\omega'(\omega' - \omega)} + \right. \\ &\quad \left. + \left(\frac{\hbar}{2M} \right)^2 \int d\omega' g(\omega') g(\omega - \omega') \frac{n_B(\omega')n_B(\omega - \omega')}{\omega'(\omega - \omega')} \right] + \\ &\quad + \theta(-\omega) \left[\left(\frac{\hbar}{2M} \right)^2 \int d\omega' g(\omega') g(\omega' - \omega) 4 \frac{(n_B(\omega') + 1)n_B(\omega' - \omega)}{\omega'(\omega' - \omega)} + \right. \\ &\quad \left. + \left(\frac{\hbar}{2M} \right)^2 \int d\omega' g(\omega') g(\omega - \omega') \frac{n_B(\omega')n_B(\omega - \omega')}{\omega'(\omega - \omega')} \right], \quad (3.27)\end{aligned}$$

where the integration region in each integration is the region where the density of states is nonzero and ω' is positive. In this result we have assumed the thermodynamic limit and neglected $\mathcal{O}(\frac{1}{N})$ terms. In this study, $g(\omega)$ is represented

by the Debye density of states:

$$g(\omega) = \frac{3\omega^2}{\omega_D^3} \theta\left(1 - \frac{\omega}{\omega_D}\right) \quad (3.28)$$

where ω_D is the Debye frequency and hence $\omega_0 = \omega_D$. In order to obtain Eq. 3.27 from Eq. 3.11, the summations over states are converted to integrations over energies and the integration region is chosen so that only a small energy violation, $\Delta\omega$, is allowed, which is assumed to satisfy $\Delta\omega\Delta t = 1$ from the energy-time uncertainty relation. If one compares Eq. 3.27 with similar results found in the literature (eg. [33]), there is an extra factor of π which arises because of the assumption that Δt is large enough so that one can take the limit $t \rightarrow \infty$ in certain integrals. This factor is not related with the formalism but is just related with the evaluation of Eq. 3.11.

The final result can be compared with the results in [12]. In [12] it is assumed from the beginning that only the diagonal element of the density matrix corresponding to the first excited state, ρ_{11} , is non-zero. In which case, the contribution of the other elements of the density matrix can be neglected in the evolution of ρ_{11} , and we obtain:

$$\rho_{11}(t + \Delta t) = \rho_{11}(t) + R_{11;11}(\Delta t)\rho_{11}, \quad (3.29)$$

which yields a decay rate $-\frac{R_{11;11}}{\Delta t}$ which is nothing but the result derived in [12] using the Golden Rule formula (there is an overall factor of π which is discussed earlier). This feature is quite general in the sense that as long as just the first few elements of the density matrix is important, and for sufficiently low temperatures, the results obtained using this formalism and those obtained by the Golden Rule are almost identical.

For the numerical data, we have used the following values: $\hbar\omega_D = 37.6$ meV; $M = 28$ amu; $m = 28$ amu; $\hbar\Omega_0 = 46$ meV; $E_0 = 1.8$ eV; $F = 10^{-10}$ N and $T = 300$ K. Here F is the maximum vertical force applied to the adsorbed atom and is related to the vertical displacement, s , through

$$s = \frac{F}{m\Omega^2}, \quad (3.30)$$

Ω is changed from $0.2\Omega_0$ up to $1.52\Omega_0$, and the iteration step is chosen to be $\Delta t = \Omega^{-1}$. In Fig. 3.2, we have plotted the decay profiles, $\frac{E(t)}{E(0)}$, for various values Ω . In each case the range of the time axis corresponds to 300 iterations, each iteration corresponding to a time of Ω^{-1} . The exponential character

is obvious. For the numerical calculations, we used only a finite, 16×16 , part of the infinite density matrix. This caused the matrix elements at the edges to evolve incorrectly. But as long as they are negligible compared to the matrix element corresponding to the first few excited states, this does not affect the general profile of the time dependency of the energy which is mainly determined by the evolution of the first few diagonal elements of the density matrix. In most cases after 300 iterations the matrix elements at the edge become nonnegligible. In all cases, we found that the excess energy can be fit almost perfectly into the expression:

$$\Delta E(t) = \Delta E(0)e^{-\frac{t}{\tau}} \quad (3.31)$$

Here, τ is the decay time constant (or the relaxation time)

In Fig. 3.3, the dependence of τ on Ω is shown. In the graph, the frequencies are given in units of Ω_0 . We see that both for large Ω and small Ω , τ diverges. For large Ω limit, the reason is due to the phase space factors; the two phonons created or absorbed has to be in a band of width $2\omega_D - \Omega$ which goes to zero as $\Omega \rightarrow 2\omega_D$. For $\Omega > 2\omega_D$, the adsorbed atom can not decay through the emission of two phonons and one has to consider three or more phonon processes. In the small Ω limit, the coupling constant B becomes very small and the system behaves almost as if it is isolated, and can not decay. In Fig. 3.3, one also sees that in the region $\Omega \simeq \omega_D$ there is a change in τ . For $\Omega < \omega_D$ there is a contribution to the decay process whereby the adsorbate absorbs a low energy phonon from the sample and at the same time emits a high energy phonon into the sample. This process is absent in the $\Omega > \omega_D$ case which causes a sharp change.

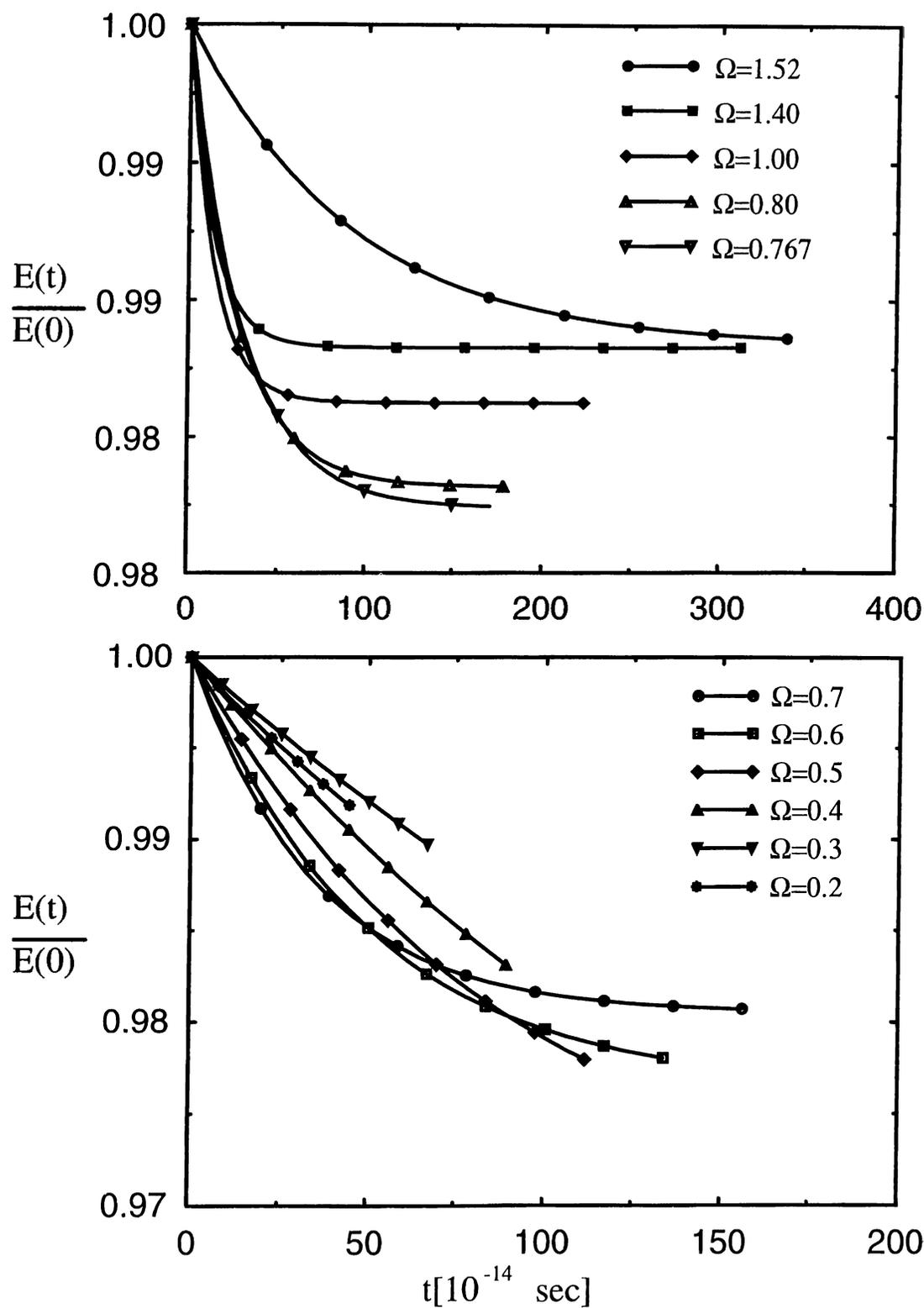


Figure 3.2: Calculated decay profiles, $\frac{E(t)}{E(0)}$, for the energy of the vibrating atom for various Ω 's.

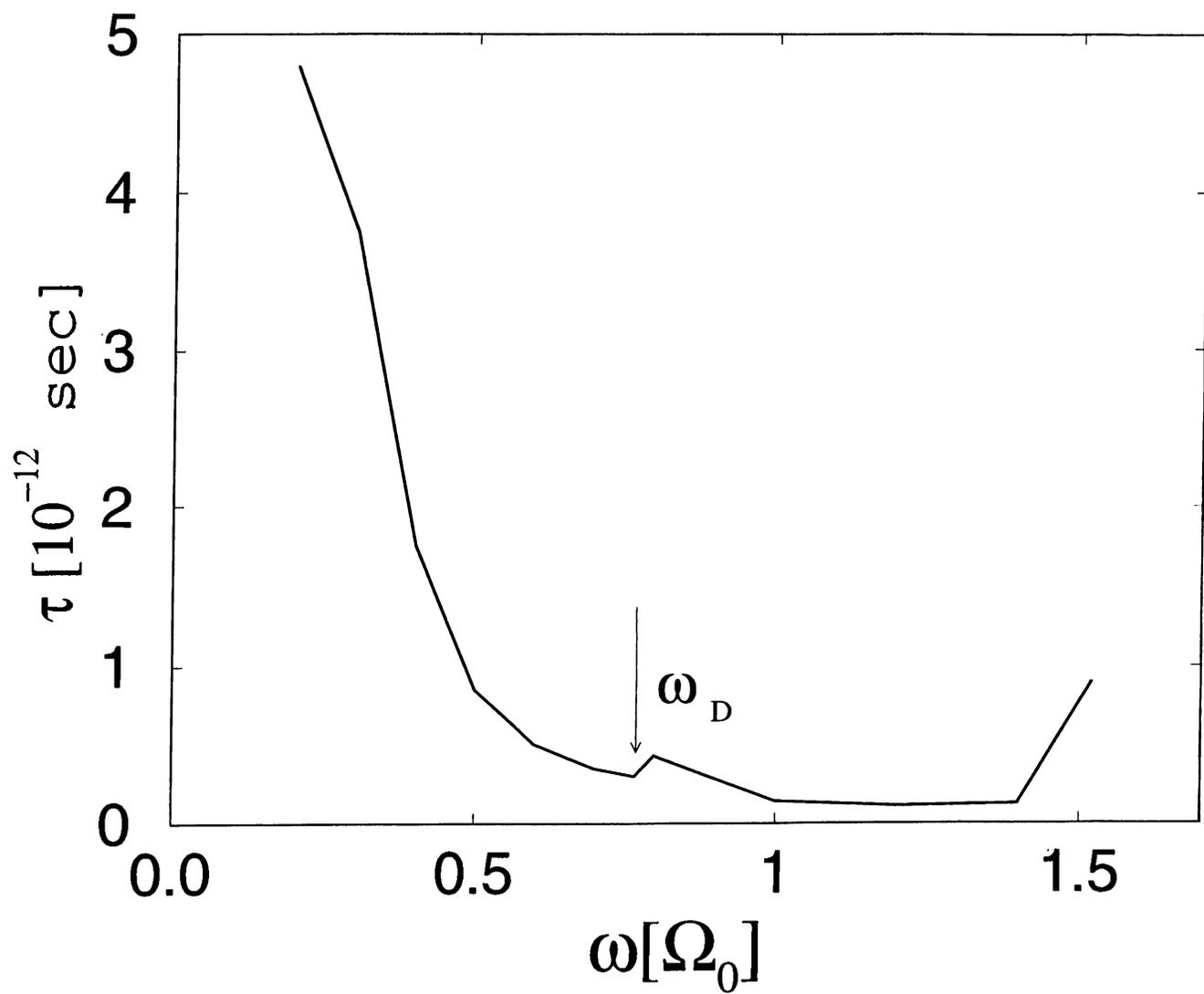


Figure 3.3: Dependence of the relaxation time, τ , on the vibrational frequency, Ω , of the adsorbate.

Chapter 4

Conclusion

We have attacked two different problems using two different methods. In the first chapter, we have used the Keldysh formalism to study the steady state heat current through a 1D atomic wire. Its dependence on temperature and the number of atoms is studied. It is found that most of the current is carried by phonons at the eigenfrequencies of the wire. The total thermal conductance is found to be independent of the total number of atoms. However the conductance is smaller for single atom and for $N = 2$. For $N > 2$, κ is stabilized. Note also that we have not considered unharmonic terms within the wires. It is expected that if one allows for phonon scattering within the wire, the current would decrease as one increases the length of the wire, which we expect from our everyday experience. We also observed step in the total conductance as one makes changes in the structure of the reservoir, similar to the steps seen in the electronic counterpart. Hence although one cannot talk about the universal heat quantum as a fundamental constant, heat conductance still shows some kind of a quantized nature. In view of the recent developments, such as the realization of a linear chain between two electrodes consisting of eight atoms, also fabrication of suspended dielectric bridges with nanometer dimensions and also confining a single molecule between two electrodes, put not only academic interest but also the present results will be used in near future, and may contribute to a rapidly developing field, nanoscience. The formalism developed here can be extended to include multiple contacts and in particular to complex molecules between two electrodes.

In the 3rd chapter, we studied the dissipation of excess energy, $\Delta E(0)$, of

an adsorbed atom on a surface and developed a Redfield-Theory like formalism based on the reduced density matrix. We showed that in all cases, the time variation of the excess energy can be fit almost perfectly into the expression $\Delta E(t) = \Delta E(0)e^{-\frac{t}{\tau}}$, at $T = 300K$. We calculated the decay rate profiles and the corresponding relaxation times for various frequencies. Our results are relevant to various theoretical and applied fields including tribology, molecular biology, molecular electronics, and crystal growth.

As regard to the differences in the methodologies in treating these two problems, the Keldysh formalism only gave the steady state properties of the system. It did not yield information about the transient period, i.e. what happens right after we bring the systems into contact. It is not suitable in studying such systems. On the other hand, the Redfield-like approach gave us information about the transient period. The main fundamental reason for this difference is that, in the Keldysh formalism, one directly attacks the calculation of the expectation value of the operators. But the expectation value of the operators does not specify the state of the system completely. Hence the expectation value of an operator at some time does not give information about its value at following instants. But, in the Redfield theory like approach, the density matrix of the whole system is calculated. As it contains all the information about a system, the density matrix at some moment in time determines its value at a further moment, hence it was possible to use an iterative scheme to obtain its evolution for large enough times.

Appendix A

Eq. 2.1

Let \mathcal{O} be an operator whose expectation value is to be calculated at time t . Let the system be described by ρ_0 at time t_0 (later on the limit $t_0 \rightarrow -\infty$ will be considered). Using the Heisenberg equation of motion

$$\begin{aligned} \langle \mathcal{O}(t) \rangle &= \frac{\text{Tr} \rho_0 \mathcal{O}(t)}{\text{Tr} \rho_0} \\ &= \frac{\text{Tr} \rho_0 e^{\frac{i}{\hbar} \mathcal{H}(t-t_0)} \mathcal{O}(t_0) e^{-\frac{i}{\hbar} \mathcal{H}(t-t_0)}}{\text{Tr} \rho_0 e^{\frac{i}{\hbar} \mathcal{H}(t-t_0)} e^{-\frac{i}{\hbar} \mathcal{H}(t-t_0)}}, \end{aligned} \quad (\text{A.1})$$

where the denominator is substituted for future convenience. Let us consider the numerator only and let $\langle \dots \rangle_0 \equiv \text{Tr} \rho_0 \dots$. Then:

$$\begin{aligned} \text{Tr} \rho_0 e^{\frac{i}{\hbar} \mathcal{H}(t-t_0)} \mathcal{O}(t_0) e^{-\frac{i}{\hbar} \mathcal{H}(t-t_0)} &= \langle e^{\frac{i}{\hbar} \mathcal{H}(t-t_0)} \mathcal{O}(t_0) e^{-\frac{i}{\hbar} \mathcal{H}(t-t_0)} \rangle_0 \\ &= \langle e^{\frac{i}{\hbar} \mathcal{H}(t-t_0)} e^{-\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} e^{\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} \mathcal{O}(t_0) e^{-\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} e^{\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} e^{-\frac{i}{\hbar} \mathcal{H}(t-t_0)} \rangle_0, \end{aligned} \quad (\text{A.2})$$

where we have separated the total Hamiltonian as $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int}$. If the operator $e^{\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} e^{-\frac{i}{\hbar} \mathcal{H}(t-t_0)}$ is differentiated with respect to t , the resultant differential equation can formally be integrated using the boundary condition at $t = t_0$. From the uniqueness of the solution, it can be shown that:

$$e^{\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} e^{-\frac{i}{\hbar} \mathcal{H}(t-t_0)} = \mathcal{T} e^{-\frac{i}{\hbar} \int_{t_0}^t dt' \mathcal{H}_{int}(t')} \quad (\text{A.3})$$

where \mathcal{T} is the time ordering operator and $\mathcal{H}_{int}(t)$ is defined as:

$$\mathcal{H}_{int}(t) = e^{\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} \mathcal{H}_{int} e^{-\frac{i}{\hbar} \mathcal{H}_0(t-t_0)}. \quad (\text{A.4})$$

Similarly:

$$e^{\frac{i}{\hbar} \mathcal{H}(t-t_0)} e^{-\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} = \tilde{\mathcal{T}} e^{\frac{i}{\hbar} \int_{t_0}^t dt' \mathcal{H}_{int}(t')} \quad (\text{A.5})$$

where $\tilde{\mathcal{T}}$ is the anti-time ordering operator. Hence we get:

$$\langle e^{\frac{i}{\hbar}\mathcal{H}(t-t_0)}\mathcal{O}(t_0)e^{-\frac{i}{\hbar}\mathcal{H}(t-t_0)}\rangle_0 = \langle \tilde{\mathcal{T}}e^{\frac{i}{\hbar}\int_{t_0}^t dt'\mathcal{H}_{int}(t')}\mathcal{O}_I(t)\mathcal{T}e^{-\frac{i}{\hbar}\int_{t_0}^t dt'\mathcal{H}_{int}(t')}\rangle_0, \quad (\text{A.6})$$

where

$$\mathcal{O}_I(t) = e^{\frac{i}{\hbar}\mathcal{H}_0(t-t_0)}\mathcal{O}(t_0)e^{-\frac{i}{\hbar}\mathcal{H}_0(t-t_0)} \quad (\text{A.7})$$

The path ordering operator \mathcal{T}_C is defined as the operator which orders the operators in its argument so that if one goes along the time loop shown in the figure below, the operator to the right will be reached later than the operator to the left.

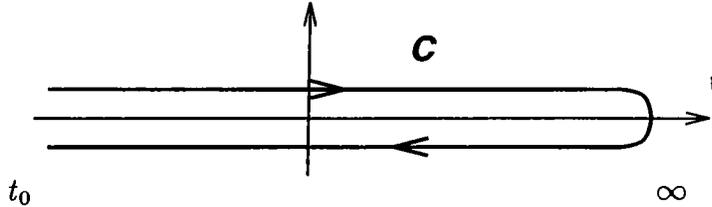


Figure A.1: The time loop along which the operator \mathcal{T}_C orders its arguments.

Note that path ordering reduces to time ordering if all the times are on the upper branch and reduces to the anti-time ordering if all the times are on the lower branch. The times on the upper and lower branches will be distinguished by (+) and (-) superscripts respectively. Then, Eq. A.6 can be re-written in terms of the path ordering operator as:

$$\begin{aligned} \langle e^{\frac{i}{\hbar}\mathcal{H}(t-t_0)}\mathcal{O}(t_0)e^{-\frac{i}{\hbar}\mathcal{H}(t-t_0)}\rangle_0 &= \langle \mathcal{T}_C e^{\frac{i}{\hbar}\int_{t_0}^{t^-} dt'\mathcal{H}_{int}(t')}\mathcal{O}_I(t)\mathcal{T}_C e^{-\frac{i}{\hbar}\int_{t_0}^{t^+} dt'\mathcal{H}_{int}(t')}\rangle_0 \\ &= \langle \mathcal{T}_C e^{\frac{i}{\hbar}\int_{t_0}^{t^-} dt'\mathcal{H}_{int}(t')}\mathcal{T}_C e^{\frac{i}{\hbar}\int_{t^-}^{\infty} dt'\mathcal{H}_{int}(t')}\mathcal{T}_C e^{-\frac{i}{\hbar}\int_{t^+}^{\infty} dt'\mathcal{H}_{int}(t')}\mathcal{O}_I(t)\mathcal{T}_C e^{-\frac{i}{\hbar}\int_{t_0}^{t^+} dt'\mathcal{H}_{int}(t')}\rangle_0, \end{aligned} \quad (\text{A.8})$$

where we have inserted the identity operator $\mathcal{T}_C e^{\frac{i}{\hbar}\int_{t^+}^{\infty} dt'\mathcal{H}_{int}(t')}\mathcal{T}_C e^{-\frac{i}{\hbar}\int_{t^-}^{\infty} dt'\mathcal{H}_{int}(t')}$ to the left of the operator \mathcal{O} . Note that if the time of the operator $\mathcal{O}_I(t)$ is assigned the label (+), all the operators in Eq. A.8 are already path ordered. Hence all of them can be written as the argument of a single path ordering operator. Since we can regroup operators within the path ordering operator, we get:

$$\langle e^{\frac{i}{\hbar}\mathcal{H}(t-t_0)}\mathcal{O}(t_0)e^{-\frac{i}{\hbar}\mathcal{H}(t-t_0)}\rangle_0 = \langle \mathcal{T}_C \mathcal{O}_I(t^+)e^{-\frac{i}{\hbar}\int_C dt'\mathcal{H}_{int}(t')}\rangle_0. \quad (\text{A.9})$$

In order to obtain the denominator in Eq. A.1, it is sufficient to replace the operator \mathcal{O} in Eq. A.9 with the identity operator. For finite t_0 , the system is not time translation invariant, t_0 fixes a reference time. But this is in general not convenient for calculational purposes. Hence the limit $t_0 \rightarrow -\infty$ will be considered. This limit only yields the steady state results. Putting the numerator and the denominator together we obtain Eq. 2.1.

Appendix B

Eq. 2.23

First, note that:

$$\begin{aligned} J_L(t-t') &= -\frac{A_L}{m} \langle u_L(t) p_1(t') \rangle \\ &= -A_L \frac{d}{dt'} \langle u_L(t) x_1(t') \rangle \\ &= -A_L \frac{d}{dt'} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega(t-t')} \langle u_L(t) x_1(t') \rangle_{\omega} \\ &= -A_L \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (-i\omega) e^{i\omega(t-t')} \langle u_L(t) x_1(t') \rangle_{\omega}, \end{aligned} \quad (\text{B.1})$$

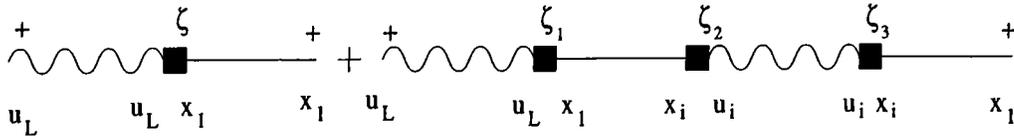
where $\langle u_L(t) x_1(t') \rangle_{\omega}$ is the time Fourier transform of $\langle u_L(t) x_1(t') \rangle = \langle u_L(t-t') x_1(0) \rangle$. Hence if we can calculate this Fourier transform, the current is given by:

$$\begin{aligned} J_L &= \lim_{t \rightarrow 0} J_L(t) \\ &= -A_L \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (-i\omega) \langle u_L(t) x_1(t') \rangle_{\omega}. \end{aligned} \quad (\text{B.2})$$

Note that although in Eq. B.1, we used $J_L(t)$ to denote the function, it is *not* the current at time t .

I will not go into the details of the diagrammatic expansion of correlation functions, and the wick theorem. The diagrammatic expansion for non-equilibrium systems is identical to the equilibrium case, we only have the additional labels (+) and (-) which should be summed over also (see eg. [29, 30, 31, 32]). For concreteness and simplicity, I will only consider the harmonic interaction, Eq. 2.16. The Feynman Diagrams will consist of wavy lines,

representing the free Greens function of the reservoir, straight lines, representing the free Greens functions of the wire, and squares, representing interaction vertices. Each end of a line is labeled: for wavy lines, the label of both ends should be identical, and it is either u_L or u_R . For straight lines, each end should be labeled by an $x_i, i = 1 \dots N$. The vertices would carry the labels (+) or (-) and they will connect the ends of a wavy and a straight line if the labels of the ends are u_L and x_1 or u_R and x_N respectively. In order to calculate $\langle u_L(t^+) x_1(t'^+) \rangle_{w \text{ connected}}$, the Diagrams should start with a u_L and end at x_1 . As regard to the time labels, it should start and end at (+). Two of the contributing diagrams are shown in the figure below.



The contribution of these diagrams can be written as:

$$\begin{aligned}
& {}^0\mathcal{G}_L^{+\zeta} \left(-i\zeta \frac{A_L}{\hbar} \right) {}^0\mathcal{G}_{11}^{\zeta+} \\
& + {}^0\mathcal{G}_L^{+\zeta_1} \left(-i\zeta_1 \frac{A_L}{\hbar} \right) {}^0\mathcal{G}_{1i}^{\zeta_1\zeta_2} \left(-i\zeta_2 \frac{A_i}{\hbar} \right) {}^0\mathcal{G}_i^{\zeta_2\zeta_3} \left(-i\zeta_3 \frac{A_i}{\hbar} \right) {}^0\mathcal{G}_{i1}^{\zeta_3+} \quad (\text{B.3})
\end{aligned}$$

where $\zeta_i = +, -, i = L(1), R(2)$, and all ζ 's and i 's are summed over.

In Eq. B.3, $\mathcal{G}_L^{+\zeta} \left(-i\zeta \frac{A_L}{\hbar} \right)$ can be factored out. But then the remaining terms are nothing but the expansion of the full greens function of the wire, $\mathcal{G}_{11}^{\zeta+}$, and the prefactor $\mathcal{G}_L^{+\zeta} \left(-i\zeta \frac{A_L}{\hbar} \right)$ is proportional to the self energy, Eq. 2.25. Generalization to an arbitrary number of contacts also follows the same line of thought. Putting everything together, one obtains Eq. 2.23

Appendix C

Eq. 2.27

Fortunately, to obtain the result in Eq. 2.27, explicit solution of the Dyson equations, Eqs. 2.12, 2.13, 2.14, are not required. For this reason, let us solve the problem of a general harmonic sample which makes a single contact with the left reservoir, which will be denoted by $i = 1$, and an arbitrary number of contacts with an arbitrary number of reservoirs. And assume that each contact is described by the interaction $\mathcal{O}_i x_i$, where \mathcal{O}_i is an operator acting only on the reservoir of the i^{th} contact, and x_i is the displacement of the sample atom at that contact.

Consider the first Dyson equation, Eq. 2.12. The terms can be rearranged as:

$$\begin{aligned} (\delta_{\alpha'\beta} + {}^0\mathcal{G}_{\beta\beta'}^A \Sigma_{\beta'\alpha'}^A) \mathcal{G}_{\alpha'\alpha}^A &= \mathcal{U}_{\beta\alpha'}^A \mathcal{G}_{\alpha'\alpha}^A \\ &= {}^0\mathcal{G}_{\beta\alpha}^A, \end{aligned} \quad (\text{C.1})$$

where the matrix $\mathcal{U}_{\alpha'\beta}^A = \delta_{\alpha'\beta} + {}^0\mathcal{G}_{\beta\beta'}^A \Sigma_{\beta'\alpha'}^A$ have been introduced. Denote the matrix elements of the inverse of \mathcal{U}^A by superscripts so that:

$$\sum_{\beta} \mathcal{U}_{\alpha\beta}^A \mathcal{U}_A^{\beta\alpha'} = \delta_{\alpha\alpha'}, \quad (\text{C.2})$$

Then the solution of the Dyson equation can formally be written as:

$$\mathcal{G}_{\alpha\beta}^A = \mathcal{U}_A^{\alpha\alpha'0} \mathcal{G}_{\alpha'\beta}^A. \quad (\text{C.3})$$

By interchanging the labels A and R , one obtains the solution of the second Dyson equation, Eq. 2.13:

$$\mathcal{G}_{\alpha\beta}^R = \mathcal{U}_R^{\alpha\alpha'0} \mathcal{G}_{\alpha'\beta}^R, \quad (\text{C.4})$$

where $\mathcal{U}_R^{\alpha\alpha'}$ are the matrix elements of the inverse of the matrix \mathcal{U}^R whose matrix elements are given by $\mathcal{U}_{\alpha'\beta}^R = \delta_{\alpha'\beta} + {}^0\mathcal{G}_{\beta\beta'}^R \Sigma_{\beta'\alpha'}^R$. Note that the matrices \mathcal{U}^A and \mathcal{U}^R have singularities at the eigenfrequencies of the sample which goes like $\frac{1}{\epsilon}$. Hence, their inverses \mathcal{U}_A and \mathcal{U}_R go to zero at the eigenfrequencies like ϵ . For the solution of the third Dyson equation, Eq. 2.14, first rearrange it as:

$$\mathcal{U}_{\beta\alpha'}^A \mathcal{G}_{\alpha'\alpha}^K = {}^0\mathcal{G}_{\beta\alpha}^K - {}^0\mathcal{G}_{\beta\beta'}^A \Sigma_{\beta'\alpha'}^K \mathcal{G}_{\alpha'\alpha}^R - {}^0\mathcal{G}_{\beta\beta'}^K \Sigma_{\beta'\alpha'}^R \mathcal{G}_{\alpha'\alpha}^R \quad (\text{C.5})$$

Multiplying by $\mathcal{U}_{\delta\alpha}^R$, and substitution its explicit form on the right, one obtains:

$$\mathcal{U}_{\delta\alpha}^R \mathcal{U}_{\beta\alpha'}^A \mathcal{G}_{\alpha'\alpha}^K = {}^0\mathcal{G}_{\beta\delta}^K - {}^0\mathcal{G}_{\beta\beta'}^A \Sigma_{\beta'\alpha'}^K {}^0\mathcal{G}_{\alpha'\delta}^R. \quad (\text{C.6})$$

Hence, we get:

$$\mathcal{G}_{\alpha'\alpha}^K = \mathcal{U}_A^{\alpha'\beta'} \mathcal{U}_R^{\alpha\beta 0} \mathcal{G}_{\beta\beta}^K - \mathcal{G}_{\alpha'\beta'}^A \Sigma_{\beta'\delta}^K \mathcal{G}_{\delta\alpha}^R. \quad (\text{C.7})$$

Note that the first term in Eq. C.7, does not contribute, unless it is multiplied by a singular function, since \mathcal{G}^K is non-zero only at the eigenfrequencies of the sample where it behaves as $\frac{1}{\epsilon}$. But its prefactor behaves as ϵ^2 at these frequencies. Hence, in our case, we can omit this term altogether, and we are left with:

$$\mathcal{G}_{\alpha'\alpha}^K = -\mathcal{G}_{\alpha'\beta'}^A \Sigma_{\beta'\delta}^K \mathcal{G}_{\delta\alpha}^R. \quad (\text{C.8})$$

The equation obtained by writing the Eqs. 2.10 and 2.11 can be solved to yield:

$$\begin{aligned} \mathcal{G}^{++}(w) &= \frac{1}{2} (\mathcal{G}^R + \mathcal{G}^A + \mathcal{G}^K) \\ \mathcal{G}^{+-}(w) &= \frac{1}{2} (\mathcal{G}^R - \mathcal{G}^A + \mathcal{G}^K) \\ \mathcal{G}^{-+}(w) &= \frac{1}{2} (-\mathcal{G}^R + \mathcal{G}^A + \mathcal{G}^K) \\ \mathcal{G}^{--}(w) &= \frac{1}{2} (-\mathcal{G}^R - \mathcal{G}^A + \mathcal{G}^K), \end{aligned} \quad (\text{C.9})$$

and similarly for the Σ 's:

$$\begin{aligned} \Sigma^{++}(w) &= \frac{1}{2} (-\Sigma^R - \Sigma^A - \Sigma^K) \\ \Sigma^{+-}(w) &= \frac{1}{2} (\Sigma^R - \Sigma^A + \Sigma^K) \\ \Sigma^{-+}(w) &= \frac{1}{2} (-\Sigma^R + \Sigma^A + \Sigma^K) \\ \Sigma^{--}(w) &= \frac{1}{2} (\Sigma^R + \Sigma^A - \Sigma^K). \end{aligned} \quad (\text{C.10})$$

Note that, these satisfy the (anti) symmetry properties:

$$\begin{aligned}
\mathcal{G}^A(-w) &= \mathcal{G}^R(w) \\
\Sigma^R(-w) &= \Sigma^A(w) \\
\mathcal{G}^K(-w) &= \mathcal{G}^K(w) \\
\Sigma^K(-w) &= \Sigma^K(w)
\end{aligned} \tag{C.11}$$

If Eqs. C.9 and C.10 are substituted into Eq. 2.23, and the result is simplified using Eqs. C.11, the current can be written in the form:

$$J_1 = - \sum_{\beta} \frac{\hbar}{2} \int_{-\infty}^{\infty} \frac{dw}{2\pi} w \left(\Sigma_{1\beta}^R \mathcal{G}_{\beta 1}^K + \Sigma_{1\beta}^K \mathcal{G}_{\beta 1}^A \right). \tag{C.12}$$

If one substitutes Eqs. C.3, C.4 and C.8 into Eq. C.12 and further assumes that $\mathcal{O}_1 \propto u_1$, the current becomes:

$$J_1 = -\frac{\hbar}{2} \int \frac{dw}{2\pi} dw w \left(-\mathcal{G}_{\alpha' 1}^R \mathcal{G}_{1\delta}^A \right) \left(\Sigma_{11}^K \Sigma_{\delta\alpha'}^A + \Sigma_{11}^R \Sigma_{\delta\alpha'}^K \right). \tag{C.13}$$

For systems with just two contacts and harmonic interaction at each contact, the self energy, Σ_{ij} , reduces to the form given in Eq. 2.24. Substituting Eq. 2.24 into Eq. C.13, one obtains:

$$\begin{aligned}
J_1 &= -\frac{\hbar}{2} \int_{-\infty}^{\infty} \frac{dw}{2\pi} dw w \left(-\mathcal{G}_{11}^R \mathcal{G}_{11}^A \right) \left(\Sigma_{11}^K \Sigma_{11}^A + \Sigma_{11}^R \Sigma_{11}^K \right) \\
&\quad -\frac{\hbar}{2} \int_{-\infty}^{\infty} \frac{dw}{2\pi} dw w \left(-\mathcal{G}_{N1}^R \mathcal{G}_{1N}^A \right) \left(\Sigma_{11}^K \Sigma_{NN}^A + \Sigma_{11}^R \Sigma_{NN}^K \right).
\end{aligned} \tag{C.14}$$

Form Eqs. C.11, the integrand of the first integral in Eq. C.14 is antisymmetric, hence this term does not contribute. Note that $-\mathcal{G}_{N1}^R \mathcal{G}_{1N}^A = -\mathcal{G}_{1N}^R \mathcal{G}_{1N}^A = \det \mathcal{G}_{1N}$. Substituting the explicit forms of the self energies obtained from Eqs. 2.25 and 2.26 and Eqs. C.25-C.27 into Eq. C.14, one obtains Eq. 2.27.

For systems with few contacts, once the free Greens' functions are known, the full greens functions can be solved analytically. In the following sections, we give the free Greens function that we used in our calculations.

C.0.1 Free Greens Functions of the Wire

As is seen in Eq. C.13, the current depends only on the greens functions $\mathcal{G}_{1N}^R(w)$ and $\mathcal{G}_{1N}^A(w)$ which in turn can be expressed in terms of their free counterparts and the self energies non of which depends on the initial temperature. To obtain

the free greens function, one has to diagonalize the Hamiltonian describing the isolated system. Let us denote the displacements and momenta of the normal modes of the wire by ξ_m and P_m , and define S_{im} such that:

$$x_i = \sum_m S_{im} \xi_m, \quad (\text{C.15})$$

$$\sum_m S_{im} S_{i'm} = \delta_{ii'}, \quad (\text{C.16})$$

$$\sum_i S_{im} S_{im'} = \delta_{mm'}, \quad (\text{C.17})$$

so that

$$\mathcal{H} = \sum_n \left(\frac{P_n^2}{2m} + \frac{m\omega_n^2}{2} \xi_n^2 \right). \quad (\text{C.18})$$

Then the free greens functions can be expressed as:

$${}^0\mathcal{G}_{ij}^R(\omega) = - \sum_n S_{in} S_{jn} \frac{\hbar}{2m\omega_n} \frac{2i\omega_n}{(\omega - i\epsilon)^2 - \omega_n^2}, \quad (\text{C.19})$$

$${}^0\mathcal{G}_{ij}^A(\omega) = - \sum_n S_{in} S_{jn} \frac{\hbar}{2m\omega_n} \frac{2i\omega_n}{(\omega + i\epsilon)^2 - \omega_n^2}. \quad (\text{C.20})$$

where an infinitesimal ϵ has been inserted to assure the convergence of the Fourier transform. At the end of the calculation the limit $\epsilon \rightarrow 0^+$ should be taken. Note that in this limit, we have the identity:

$$\lim_{\epsilon \rightarrow 0^+} \frac{2i\omega_n}{(\omega - i\epsilon)^2 - \omega_n^2} = \mathcal{P} \frac{2i\omega_n}{\omega^2 - \omega_n^2} - 2\pi\omega_n \delta(\omega^2 - \omega_n^2). \quad (\text{C.21})$$

Hence the Greens functions of the wire can be written as the sum of a purely real part which describes the ballistic transport of phonons and a purely imaginary part which describes the phonon tunneling contribution.

For a wire with identical strings and identical masses, the coefficients S_{im} can be evaluated to be

$$S_{im} = \sqrt{\frac{2}{N+1}} \sin \frac{q_m a i}{2}, \quad (\text{C.22})$$

where a is the spacing between neighbouring atoms and $q_m = \frac{\pi m}{(N+1)a}$

C.0.2 Free Greens Functions of the Reservoirs

The reservoir Greens functions are defined as:

$$\mathcal{G}_i^{\zeta_1 \zeta_2}(t - t') = \langle \mathcal{T}_C u_i(t^{\zeta_1}) u_i(t'^{\zeta_2}) \rangle_0 \quad (\text{C.23})$$

where $i = L, R$ corresponds to the left and right reservoirs respectively. In order to evaluate Eq. C.23, one has to know the expansion of the displacements u_i in terms of the eigenmodes of the reservoirs. Following [12], we take the expansion:

$$u_i = \sum_{\mathbf{k}\sigma} \left(\frac{\hbar}{2m\omega_{\mathbf{k}\sigma}^i N_i} \right)^{\frac{1}{2}} (b_{\mathbf{k}\sigma}^i + b_{\mathbf{k}\sigma}^{i\dagger}) \hat{\mathbf{z}} \cdot \mathbf{e}_{\mathbf{k}\sigma} \quad (\text{C.24})$$

where $N_{L(R)}$ is the number of atoms of the Left(Right) reservoir, $\mathbf{e}_{\mathbf{k}\sigma}$ is the polarization vector of the mode $\mathbf{k}\sigma$, $\hat{\mathbf{z}}$ is the outward unit normal to the surface of the corresponding reservoir and $b_{\mathbf{k}\sigma}^{L(R)}$ ($b_{\mathbf{k}\sigma}^{L(R)\dagger}$) is the annihilation(creation) operator for a phonon with wave vector \mathbf{k} and polarization σ at the left(right) reservoir. Using this expansion and

$$\begin{aligned} \langle b_{\mathbf{k}\sigma}^i b_{\mathbf{k}\sigma}^{i\dagger} \rangle_0 &= (n_B^i(\omega_{\mathbf{k}\sigma}) + 1), & \langle b_{\mathbf{k}\sigma}^{i\dagger} b_{\mathbf{k}\sigma}^i \rangle_0 &= n_B^i(\omega_{\mathbf{k}\sigma}), \\ \langle b_{\mathbf{k}\sigma}^i b_{\mathbf{k}\sigma}^i \rangle_0 &= 0, & \langle b_{\mathbf{k}\sigma}^{i\dagger} b_{\mathbf{k}\sigma}^{i\dagger} \rangle_0 &= 0, \end{aligned}$$

the free Greens functions for the reservoir can be expressed as:

$${}^0\mathcal{G}_i^R(w) = - \int_{-\infty}^{\infty} dw' g^i(w') \frac{\hbar}{2M_i w'} \frac{i}{w - w' - i\epsilon} \quad (\text{C.25})$$

$${}^0\mathcal{G}_i^A(w) = - \int_{-\infty}^{\infty} dw' g^i(w') \frac{\hbar}{2M_i w'} \frac{i}{w - w' + i\epsilon} \quad (\text{C.26})$$

$${}^0\mathcal{G}_i^K(w) = \int_{-\infty}^{\infty} dw' g^i(w') \frac{\hbar}{2M_i w'} (2n_B^i(w') + 1) \frac{2\epsilon}{(w - w')^2 + \epsilon^2} \quad (\text{C.27})$$

where $M_{L(R)}$ is the mass of the atoms of the left(right) reservoir and the density of states of the L(R) reservoir, $g^{L(R)}(w)$ has been continued to negative w by $g^{L(R)}(-w) = g^{L(R)}(w)$.

Bibliography

- [1] C.G. Grandqvist, in Springer Proceedings in Physics Vol 62 Surface Science: Lectures on Basic Concepts and Applications, edited by: F.A. Ponce and M. Cardona (Springer-Verlag Berlin 1991)
- [2] R. Schlögl, in Surface Science: Principles and Current Applications, edited by: R.J. MacDonald, E.C. Taglauer and K.R. Wandelt (Springer-Verlag Berlin 1996)
- [3] P.B. Allen and J.L. Feldman, Phys. Rev. B48 (1993) 12581
- [4] J.K. Flicker and P.L. Leath, Phys. Rev. B7 (1973) 2296
- [5] A. Greiner, L. Reggiani, T. Kuhn and L. Varani, Phys. Rev. Lett. 78 (1997) 1114
- [6] H. Bottger and Th. Damker, Phys. Rev. B50 (1994) 12509
- [7] D.E. Angelescu, M.C. Cross and M.L. Roukes, preprint cond-mat/9801252
- [8] L.G.C. Rego and G. Kirczenow, Phys. Rev. Lett. 81 (1998) 232
- [9] A. Buldum, S. Ciraci and C.Y. Fong, preprint cond-mat/9908204
- [10] A. Kambili, G. Fagas, V.I. Fal'ko and C.J. Lambert, preprint cond-mat/9905171
- [11] G.A. Voth, J. Chem. Phys. 88 (1988) 5547
- [12] B.N.J. Persson, J. Chem. Phys. C17 (1984) 4741
- [13] U. Zürcher and P. Talkner, Phys. Rev. A42 (1990) 3267; U. Zürcher and P. Talkner, Phys. Rev. A42 (1990) 3278
- [14] H. Bottger and T. Damker, Phys. Rev. B52 (1995) 12481

- [15] K. Saito, S. Takesue and S. Miyashita, preprint cond-mat/9810069
- [16] W.T. Pollard and R.A. Friesner J. Chem. Phys. 100 (1994) 5054
- [17] J.A. Leiro, M. Persson, Surface Science 207 (1989) 473
- [18] B.N.J. Persson, Chem. Phys. Lett. 139 (1987) 457
- [19] B.N.J. Persson and R. Ryberg, Phys. Rev. Lett. 54 (1985) 2119
- [20] F.M. Hoffmann and B.N.J. Persson, Phys. Rev. B34 (1986) 4354
- [21] R. Ryberg, Phys. Rev. B40 (1989) 5849
- [22] M.L. Roukes, preprint cond-mat/9811256
- [23] Karl Blum, Density Matrix Theory and Applications 2nd ed. (Plenum Press NY 1996)
- [24] D.C. Langreth and E. Abrahams Phys. Rev. B24 (1981) 2978
- [25] H.M. Pastawski, Phys. Rev. B46 (1992) 4053
- [26] J. Ferrer, A. Martin-Rodero, and F. Flores Phys. Rev. B38 (1988) 10113
- [27] C. Noguere, in Scanning Tunneling Microscopy III Springer Series in Surface Science; edited by: R. Wiesendinger and H.J. Güntherodt (Springer Verlag Berlin 1993), p. 51;
- [28] L.V. Keldysh, Sov. Phys. JETP 20 (1965) 1018
- [29] A.A. Abrikosov, L.P. Gorkov, and I.E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Physics (Prentice-Hall, Englewood Cliffs, N.J., 1963; Pergamon, Elmsford, N.Y., 1965)
- [30] A.L. Fetter, and J.D. Walecka, Quantum Theory of Many Particle Systems (McGraw-Hill, New York, 1971)
- [31] G.D. Mahan, Many-Particle Physics (Plenum Press, New York 1990)
- [32] L.D. Landau, and E.M. Lifshitz, Statistical Physics Part 2 (Oxford; New York ; Pergamon Press , 1980)
- [33] A.G. Redfield, J. Magn. Reson. (1965) 1; R.K. Wangsness and F. Bloch, Phys. Rev. 89 (1953) 728; F. Bloch, Phys. Rev. 102 (1956) 104;

- [34] F.E. Figueirido and M.R. Levy, *J. Chem. Phys* 97 (1992) 704; W.T. Pollard and R.A. Friesner, *J. Chem. Phys* (100) 5054
- [35] M.R. da Costa, A.O. Caldeira, S.M. Dutra and H. Westfahl, Jr. preprint quant-ph/9903022
- [36] B.N.J. Persson and R. Ryberg, *Phys. Rev. Lett.* 48 (1982) 549