NOISE IN NANOSYSTEMS

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Timothy Patrick Mehay
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Declaration

I declare that this Thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

Timothy Patrick Mehay
October 2018

Abstract

With the increasing interest in nanosystems in various branches of science, the question naturally arises as to whether such systems will have practical applications. At the nano-scale all physical measurements are fundamentally constrained by the Heisenberg uncertainty relations. In addition to these fundamental limitations, fluctuations or noise arising from various physical processes act so as to further obscure the accuracy with which we can perceive the physical world. The goals of this thesis are to investigate the consequences of these fluctuations in physical systems, and to develop methods enabling the study of physical processes associated with these fluctuation phenomena. I begin by developing the necessary framework with which to describe these random fluctuations. After discussing the necessary prerequisites, I develop a probabilistic model of charge-density fluctuations. This model draws on results from kinetic theory and Eulerian perturbation theory. It is found that under certain assumptions regarding the nature of the fluctuations, the equation of motion governing charge-density fluctuations may be solved analytically. I then develop a method enabling the study of the statistical correlation of density fluctuations using the fluctuation-dissipation theorem. This approach is then applied to the study of density fluctuations in graphene using the electron energy-loss spectrum (EELS) of ideal graphene. It is found that the autocorrelation function (ACF) of density fluctuations contains information related to both plasmonic resonance and to the noise present in the EELS. I conclude this thesis by developing a formalism which allows for the calculation of the dephasing rate of a system using only the EELS. This approach has the benefit of enabling a uniform treatment of dephasing in both high-temperature and low-temperature regimes, and contains both electron-electron and electron-phonon interactions by virtue of the EELS, which are the primary contributions to the dephasing rate in low-dimensional semiconductor systems. The use of this approach is then illustrated using the EELS of ideal graphene. Given the generality of the fluctuation-dissipation theorem, many of the methods discussed in this work may be extended to study arbitrary fluctuation phenomena in a wide variety of systems.

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On a more personal note I thank my family, particularly my parents Shawn and Claudia, for their endless support, and for fostering my intellectual curiosity at a young age. Last but not least, I thank my wife Chia, for her love and devotion, and for listening to my late-night ramblings about meaningless mathematics.

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Nomenclature

Probability Theory

$\mathfrak{A}$	Sample space
$\mathfrak{P}$	Probability measure over $\mathfrak{A}$
$\mathfrak{S}$	σ-algebra over $\mathfrak{A}$
η	Event in sample space
$Z(\tau)$	Continuous stochastic process
Z_τ	Discrete stochastic process
z	Realization of the stochastic process Z
Φ_Z	Cumulative distribution function of Z
$\mathfrak{T}$	Indexing set
ϕ_Z	Probability density function of Z
$\langle g(Z) \rangle$	Expectation value of quantity $g(Z)$
$\langle Z \rangle$	Mean of Z
σ_Z^2	Variance of Z
$\lambda(Z, V)$	Covariance of Z and V
$\langle Z, V \rangle$	Correlation of Z and V
W	Wiener process
w	White noise process
g_i	Filter weight
$\mathbb{R}$	The set of real numbers
$\mathbb{Z}$	The set of integers

$\mathbb{N}$ The set of natural numbers

Classical Theory

Γ Phase space volume

$\mathbf{q}$ Generalized coordinate

$\dot{\mathbf{q}}$ Generalized velocity corresponding to $\mathbf{q}$

$\mathbf{p}$ Generalized momentum

Φ Ensemble density function

ϕ_N N-body joint-probability density function

$\mathcal{N}$ Number of occupied states in phase space

$\langle A \rangle$ Ensemble average of the dynamical variable A

C Boltzmann collision term

K Conservative force field

$\mathcal{Z}$ Canonical partition function

x Comoving position

v Particle velocity

m Particle mass

r Particle position

u Comoving velocity

Quantum Theory

$|n\rangle$ State ket

$\langle n|$ State bra

$\hat{A}$ Quantum operator corresponding to observable A

$\hat{A}_{\mathbf{q}}$ Spectral decomposition of $\hat{A}$

$\mathbf{q}$ Momentum transfer

$\langle n|m\rangle$ Inner product of states n and m

$\langle n|\hat{A}|n\rangle$ Quantum expectation value of $\hat{A}$

$\hat{\rho}$ Density matrix operator

$\hat{H}$	Hamiltonian operator
$\hat{V}$	Interaction term
$[\hat{A}, \hat{B}]$	Quantum commutator of operators $\hat{A}$ and $\hat{B}$
$\mathrm{Tr}\hat{A}$	Trace of operator $\hat{A}$
$\hat{A}^\dagger$	Hermitian conjugate of $\hat{A}$
$\hat{U}$	Unitary transformation
$\|0\rangle$	Ground state
Ψ	Response function
χ	Generalized susceptibility
Λ	Dephasing rate
S	Structure factor
L^d	Volume of d-dimensional system in real space
Ω	Volume in reciprocal space

Miscallaneous

t	Time
f	Frequency
ω	Angular frequency
S	Spectral density
n	Number density
ρ	Charge density
D	Electric displacement field
ϵ	Dielectric function
φ	Electrostatic potential
a	Position fluctuation parameter
$\delta\xi$	Fluctuation of ξ
i	Imaginary unit
$\Im$	Imaginary component

$\Re$ Real component

$\delta(\xi - \xi')$ Dirac delta function centered about ξ'

∇_ξ Gradient with respect to ξ

$\nabla_\xi \cdot$ Divergence with respect to ξ

∇_ξ^2 Laplacian with respect to ξ

$\mathcal{L}\{g(t)\}$ Laplace transform of $g(t)$

Physical Constants

β Reciprocal of thermodynamic temperature $k_B T$

ϵ_0 Permittivity of free space

$\hbar$ Reduced Planck constant

e Fundamental charge

k_B Boltzmann constant

Acronyms

EELS Electron energy-loss spectrum

AR Autoregressive model

ACF Autocorrelation function

Chapter 1

Introduction

In numerous scientific domains, particularly those concerned with experimental observation, the accuracy to which any measurement can be made is determined solely by the fluctuations of the quantity of interest. These fluctuations are due to random changes of quantities from their statistical mean and are observed as noise in measurements. Indeed all physical measurements are fundamentally constrained by the Heisenberg uncertainty relations. In addition to these fundamental limitations, fluctuations or noise arising from various physical processes act so as to further obscure the accuracy with which we can perceive the physical world. Some examples of these fluctuations include Johnson Nyquist noise arising from thermal motion[63][85], generation-recombination noise arising from creation and annihilation of electron-hole pairs [2][76][75][104], and $1/f$ noise, which arises due to a wide variety of physical processes [4][5][6][7][10][16][17][18][19][20][21][22][24][25][26][28][38][53][69]. A practical consequence of these limitations is that the sensitivity of many devices is fundamentally limited. Further, from the results of density functional theory, all system properties can be obtained from the charge density. Thus, charge-density fluctuations are of fundamental importance in the study of fluctuation phenomena. Hence the study of fluctuation phenomena, in particular charge-density fluctuations is of both theoretical and practical importance. The aim of this work is to develop various methods to investigate charge-density fluctuations and the associated physical processes, in order to explore the consequences of noise in nanosystems.

The pioneering works of Einstein [42][41][40], Sutherland [101], and Smoluchowski [95][105] on the theory of Brownian motion, are the earliest known works attempting to understand the mechanisms governing random fluctuations. This work was later extended by Langevin[77] who presented a stochastic differential equation describing Brownian motion known as the Langevin equation. Despite its success, the Langevin approach to particle kinetics is inherently restrictive[73], however, these limitations may be over-

come by generalizing the Langevin equation, as shown by Mori[81][82]. Another alternative is to use the Fokker-Planck-Kolmogoroff formalism based on the theory of Markov processes and developed independently by Fokker[45], Planck[89], and Kolmogoroff[70]. In contrast to the Langevin approach, which describes the time evolution of random processes, the Fokker-Planck-Kolmogoroff approach involves calculating transition probabilities of a diffusion process by solving the Fokker-Planck-Kolmogoroff equation. Using the probability density the expectation value of observables associated with the process may then be calculated. While the generalized Langevin and Fokker-Planck-Kolmogoroff approaches are powerful, a more elegant formalism is available when we consider equilibrium systems with sufficiently weak external perturbations. This formalism is based on the fluctuation-dissipation theorem, originally proposed by Nyquist[85] and proven by Callen and Welton [27]. The most natural framework in which to describe the fluctuation-dissipation theorem is linear-response theory as developed by Kubo in his seminal work in statistical mechanics[73][72][74]. In this theory the dissipative response of a system to external perturbations is studied using the generalized susceptibility, a quantity containing information related to the fluctuation processes. Much of the work discussed in this thesis is based on the results of the linear-response formulation of the fluctuation-dissipation theorem.

Due to the random nature of noise, the natural language to discuss such ideas is the theory of stochastic or random processes. I begin Chapter 2 with an overview of elementary concepts and results from probability theory following the measure theoretic approach developed by Kolmogoroff[71]. The measure theoretic formulation of probability theory has the benefit of providing a unified approach to the study of both continuous and discrete stochastic processes. I then give an elementary introduction to stochastic differential equations. The discussion of stochastic processes is concluded with an overview of some important classes of stochastic processes. I then describe classical and quantum correlation functions, which are at the center of all of the work presented in this thesis. Following this I present the basics of linear-response theory as developed by Kubo[73] in order to obtain the fluctuation-dissipation theorem, which forms the basis of Chapters 4 and 5. In Chapter 3 I develop a stochastic differential equation governing charge-density fluctuations. This model is based on results from kinetic theory. It is assumed that the particle trajectory is of the form $r(x,t) = a(t)x(t)$, where $a(t)$ is a random process and $x(t)$ is the co-moving coordinate of the particle. Similar assumptions have been used in the study of two-level quantum systems[12] and in the analysis of the Stern-Gerlach experiment using an inhomogeneous magnetic field[94], where it is assumed that the state of the system is of the form $\Psi_n(r,t) = f(r,t)g(t)$, where $f(r,t)$ is a wave-packet and $g(t)$ is some function of time. By combining this ansatz with results from Eulerian perturbation theory[14][23][83][88][111], and the theory of stochas-

tic processes, I illustrate the derivation of a stochastic differential equation governing charge-density fluctuations. The resulting equation is similar in form to the equation for a randomly-damped harmonic oscillator. By making assumptions regarding the nature of the noise driving the process, this equation is exactly solved[48]. It is discovered that the resulting particle trajectories are described by a geometric Brownian process.

In chapter 4 I begin with a discussion of the dielectric response of a fermionic system based on the work of Nozières and Pines[84]. I then present a numeric method allowing the calculation of the number density autocorrelation function (ACF) using the electron energy-loss spectrum (EELS). This is a useful method as the EELS is obtainable both numerically and experimentally and so may allow for more accurate studies of the density ACF by combining the results of such studies. The use of this method is illustrated using the EELS of graphene obtained from linear-response time-dependent density functional theory calculations[107]. Analysis of the resulting data indicates that the density ACF can be used to investigate both plasmonic resonance, and the noise characteristics of density fluctuations.

Chapter 5 begins with an introduction to the many-body approach to dephasing as developed by Cohen et. al.[32][29][30][31][33][34][58]. By combining the results of this approach with the fluctuation-dissipation theorem I present a novel method for the calculation of dephasing rates requiring only the EELS. This approach has the benefit of enabling a uniform treatment of dephasing in both high-temperature and low-temperature regimes, and contains both electron-electron and electron-phonon interactions by virtue of the EELS, which are the primary contributions to the dephasing rate in low-dimensional semiconductor systems. The use of this approach is then illustrated using the EELS of graphene.

While this work focuses on the study of density fluctuations, many of the methods presented can easily be generalized to study arbitrary fluctuation processes as a result of the generality of the fluctuation-dissipation theorem.

Chapter 2

Review of Elementary Concepts

2.1 Stochastic Processes

In order to develop the language necessary for the study of fluctuations, I begin with an overview of some fundamental results from probability theory. Much of this discussion is based on the expositions given in [64][87][109].

2.1.1 Basic Concepts

Probability Space, Random Variable, and Stochastic Process

Probability theory is the quantitative study of stochastic or random processes. In other words, probability theory is the analysis of the outcomes of random experiments. In modern probability theory, as pioneered by Kolmogorov[71], random experiments are associated with a probability space. A probability space is formally defined as a triplet $(\mathfrak{A}, \mathfrak{S}, \mathfrak{P})$, composed of the sample space $\mathfrak{A}$, defined as the set of all conceivable results of an experiment, a σ-algebra[1] $\mathfrak{S}$ on $\mathfrak{A}$, and a probability measure $\mathfrak{P}$ on $\mathfrak{A}$, which maps each event to a non-negative real number. A random variable is a function $Z : \mathfrak{A} \to \mathfrak{E}$, where $\mathfrak{E}$ is a measurable space[2]. Intuitively, a random variable is simply the outcome of a random experiment. Subsets of the sample space $\{\eta : \eta \in \mathfrak{A}\}$ are called events. A stochastic process is defined as any collection $\{Z(\tau) : \tau \in \mathfrak{T}\}$, where $Z(\tau)$ is a random variable, and $\mathfrak{T}$ is an indexing set, such that for each $\tau \in \mathfrak{T}$, each random variable $Z(\tau)$ is defined on the same sample space $\mathfrak{A}$. In particular, when $\mathfrak{T}$ represents time, we refer to the process as a stochastic time-series, or more simply, a time-series.

[1] Qualitatively, a σ-algebra is used to define measures, which essentially describe systematic procedures for assigning numbers to subsets of a set

[2] A measurable space is defined as a sample space equipped with a σ-algebra

If the index set $\mathfrak{T}$ contains a continuous range of variables, the process is called a continuous stochastic process. If instead the set contains a range of discrete variables, the process is called a discrete stochastic process. In what follows, I denote continuous stochastic processes using the functional notation $Z(\tau)$, while discrete processes are denoted using the subscript notation Z_τ. A realization of a stochastic process, denoted $z(\tau)$ is the set of outcomes $\{Z(\tau, \eta) : \tau \in \mathfrak{T}\}$ for fixed $\eta \in \mathfrak{A}$. Qualitatively, the realization of a time-series is simply the set of values occurring during the observation of a single event.

Ensemble, Distribution Function, and Probability Density

The collection of all possible realizations of a time-series is called an ensemble. The cumulative distribution function Φ_Z of the stochastic process Z is defined as

$$\Phi_Z(z) = \mathfrak{P}(\{\eta \in \mathfrak{A} : Z(\eta) \leq z\}) \tag{2.1}$$

The stochastic process Z has probability density function ϕ_Z if

$$\Phi_Z(\xi) = \int_{-\infty}^{\xi} \mathrm{d}z\, \phi_Z(z) \tag{2.2}$$

Intuitively $\phi_Z(z)$ gives the probability of Z falling within a neighbourhood of z. The probability density function contains all the statistical information about a given stochastic process. Consider now a finite collection of stochastic processes $\{Z_i : i \in \mathbb{N}\}$. The joint cumulative distribution function of this collection is given by

$$\Phi_Z(z_1, \ldots, z_N) = \mathfrak{P}(\{\eta \in \mathfrak{A} : Z_i(\eta) \leq z_i\}) \tag{2.3}$$

If $\Phi(z_1, \ldots, z_N) = \Pi_i \Phi(z_i)$ then the random variables Z_i are said to be independent. The joint probability distribution function is then given by

$$\Phi_Z(z_1, \ldots, z_N) = \int_{-\infty}^{\xi_1} \cdots \int_{-\infty}^{\xi_N} \mathrm{d}z_1 \ldots \mathrm{d}z_N\, \phi(z_1, \ldots, z_N) \tag{2.4}$$

Expectation, Co-variance, and Correlation

Related to the probability distribution function is the expectation of some function $g(Z)$ of the process Z, defined as

$$\langle g(Z) \rangle = \int_{\mathbb{R}} d\Phi_Z(z)\, g(z) \tag{2.5}$$

The n-th moment of Z is then defined as $\langle Z^n \rangle$. Qualitatively the expectation of a process is the long-run average of repeated experiments. The mean and variance of the process Z are defined as $\langle Z \rangle$ and $\sigma_Z^2 = \langle (Z - \langle Z \rangle)^2 \rangle$

respectively. Using the expectation, the co-variance of processes Z and V is defined by

$$\lambda(Z,V) = \langle (Z - \langle Z \rangle)(V - \langle V \rangle \rangle \tag{2.6}$$

The co-variance is a measure of the statistical dependence of Z and V. If Z and V are the same process then the co-variance is called the autocovariance of the process. A quantity closely related to the co-variance is the correlation function, defined as

$$\langle Z,V \rangle = \frac{\lambda(Z,V)}{\sigma_Z(t)\sigma_V(t)} \tag{2.7}$$

As with the co-variance, if Z and V denote the same process, the correlation function is called the autocorrelation function. The correlation function returns 1 if Z and V are totally correlated, 0 if Z and V are uncorrelated, and -1 if Z and V are anti-correlated.

Stationary and Ergodic Process

Let Z be a stochastic process with joint probability distribution function $\Phi_Z(z_{\tau_1}, \ldots, z_{\tau_k})$. Then Z is called a stationary process if for all k, for all t and for all $\tau_t, \ldots, \tau_k$,

$$\Phi_Z(z_{\tau_1+t}, \ldots, z_{\tau_k+t}) = \Phi_Z(z_{\tau_1}, \ldots, z_{\tau_k}) \tag{2.8}$$

Clearly stationary processes are stochastic processes whose probabilistic laws remain unchanged through time translations. Consequently, the mean and variance of stationary processes are time invariant. Such processes arise naturally in systems with no inherent time origins. The co-variance of a stationary process for times t_1 and t_2 depends only on $t_1 - t_2$ since the time origin may be chosen arbitrarily.
Consider now a sequence $V_0, \ldots, V_N$ of independent random variables and the stochastic process $Z_N = V_N$. Then Z_N is called an ergodic process[3] if for every function g such that $\langle g(V_0) \rangle$ is finite, we have

$$\lim_{N\to\infty} \frac{1}{N} \sum_{i=0}^{N-1} g(Z_i) = \langle g(V_0) \rangle \tag{2.9}$$

Qualitatively an ergodic process is a stochastic process whose statistical characteristics may be obtained from a single, sufficiently long, realization. All processes discussed in this work are assumed to be ergodic.

Spectral Density

Until now our discussion has focused on quantities describing the temporal aspects of stochastic processes. It is possible to gain further insights into the

[3]This result is known as the Birkhoff ergodic theorem

nature of a process by analyzing its spectral decomposition. The frequency spectrum analog of the autocorrelation function is the spectral density $S(\omega)$. Using the Wiener-Khinchin theorem[66][108], we define the spectral density of a stationary process $Z(t)$ as the Fourier transform of the autocorrelation function

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\tau \, e^{-i\omega\tau} \langle Z(\tau) Z(\tau + t) \rangle \tag{2.10}$$

with corresponding inverse transform given by

$$\langle Z(\tau) Z(\tau + t) \rangle = \int_{-\infty}^{\infty} \mathrm{d}\omega \, e^{i\omega\tau} S(\omega) \tag{2.11}$$

Qualitatively, the spectral density gives the intensity of a signal at a given frequency.

2.1.2 Stochastic Differential Equations

Wiener Process

Before giving the basic definition of a stochastic differential equation, it is necessary to define the Wiener process. The Wiener process, denoted $W(t)$, is defined as a stochastic process satisfying [109]

i $W(0) = 0$

ii $W(\tau)$ is almost surely[4] continuous

iii $W(\tau)$ has independent increments $W(\tau_i) - W(\tau_{i-1})$

iv $W(\tau_1) - W(\tau_2)$ has a Gaussian distribution

Stochastic Differential Equation

A stochastic differential equation (SDE) is simply a differential equation containing one or more terms which are stochastic processes. As stochastic processes are in general nowhere differentiable, the solution of stochastic differential equations requires an extension of calculus. In this thesis, I adopt the convention of conforming to the Itô stochastic calculus[59][60]. More formally, a stochastic differential equation is defined as

$$\mathrm{d}Z_\tau = \gamma(\tau, Z_\tau)\mathrm{d}\tau + \kappa(\tau, Z_\tau)\mathrm{d}W_\tau \tag{2.12}$$

with initial condition $Z_0 = z_0$ where Z_τ is a real-valued d-dimensional vector, and W_τ is a Wiener process. Eq. 2.12 is understood to represent the process given by

$$Z_t = z_0 + \int_0^t \mathrm{d}\tau \, \gamma(\tau, Z_\tau) + \int_0^t \mathrm{d}W_\tau \, \kappa(\tau, Z_\tau) \tag{2.13}$$

[4] An event is said to occur almost surely if it occurs with probability one.

A stochastic process which can be expressed as in Eq. 2.13 is called a diffusion process.

2.1.3 Examples of Stochastic Processes

White Noise

A process $\{Z(\tau) : \tau \in \mathfrak{T}\}$ with autocovariance function $\lambda(\tau_1, \tau_2)$ is called white noise if [109]

i Each Z_i has a common distribution function

ii $\lambda(\tau_1, \tau_2) = 0$ for $\tau_1 \neq \tau_2$

iii $\lambda(\tau, \tau)$ is constant and finite

White noise can also be defined as the time-derivative of the Wiener process.

Gaussian Processes

An important class of stochastic processes are those known as Gaussian processes. Formally a process $\{Z(\tau) : \tau \in \mathfrak{T}\}$ is Gaussian if the random vector $Z = (Z_{\tau_1}, \cdots, Z_{\tau_d})$ has a probability density function of the form[5] [87]

$$\phi_Z(Z) = \frac{1}{\sqrt{(2\pi)^d \det\lambda}} \exp\Big(-\frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \lambda_{ij}^{-1} \delta z_i \delta z_j \Big) \tag{2.14}$$

where $\delta z = z - \langle z \rangle$ is the fluctuation of z, and λ is the co-variance matrix. A useful property of Gaussian processes is that they are completely characterized by the mean and co-variance functions. Gaussian processes are an example of an Ornstein-Uhlenbeck process, defined as any process governed by [87]

$$\mathrm{d}Z_\tau = -\gamma Z_\tau \mathrm{d}\tau + 2\kappa \mathrm{d}\tau \tag{2.15}$$

with initial condition $Z_0 = z_0$. The solution of the above equation is given by

$$Z_t = e^{-\gamma t} z_0 + \sqrt{2\kappa} \int_0^t \mathrm{d}W_\tau \, e^{-\alpha(t-\tau)} \tag{2.16}$$

A white noise process with a Gaussian probability density function is called Gaussian white noise. Fig. 2.1 shows several realizations of a Gaussian white noise process.

[5] It is assumed that λ is non-singular.

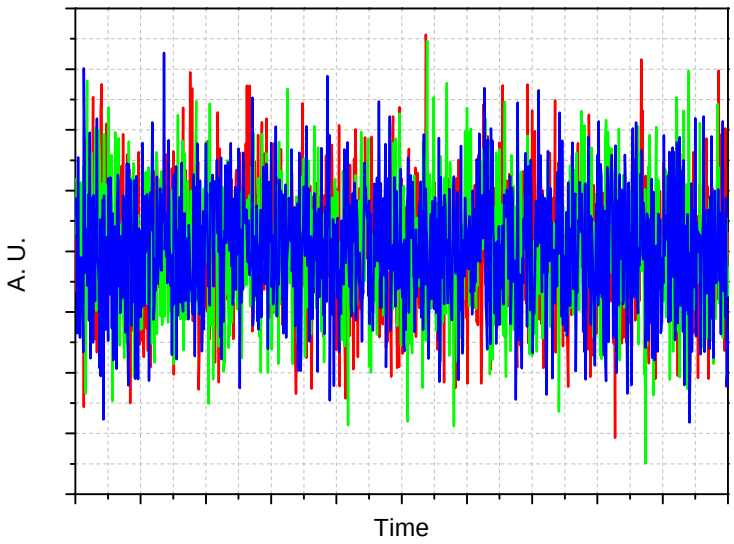

Figure 2.1: Realizations of Gaussian white noise process

Brownian Motion

Perhaps the most significant of all stochastic processes is Brownian motion. It appears in many contexts in all of the natural sciences. Brownian motion is an example of a Wiener process. The SDE governing Brownian motion is given by [87]

$$\mathrm{d}Z_t = \sqrt{2\kappa}\mathrm{d}W_t \tag{2.17}$$

with initial condition $Z_0 = z$, where κ is the diffusion coefficient. The above equation is solved by

$$Z_t = z + \sqrt{2\kappa}W_t \tag{2.18}$$

Fig. 2.2 shows several realizations of a Brownian process.

Geometric Brownian Motion

Another important process is geometric Brownian motion. This process is given by the solution of

$$\mathrm{d}Z_t = \gamma Z_t\,\mathrm{d}t + \sigma Z_t \mathrm{d}\,W_t \tag{2.19}$$

with initial condition $Z_0 = z_0$. This SDE has the solution [87]

$$Z(t) = z_0 \exp\left((\gamma - \frac{\sigma^2}{2}t + \sigma W(t)\right) \tag{2.20}$$

Fig. 2.3 shows several realizations of geometric Brownian motion.

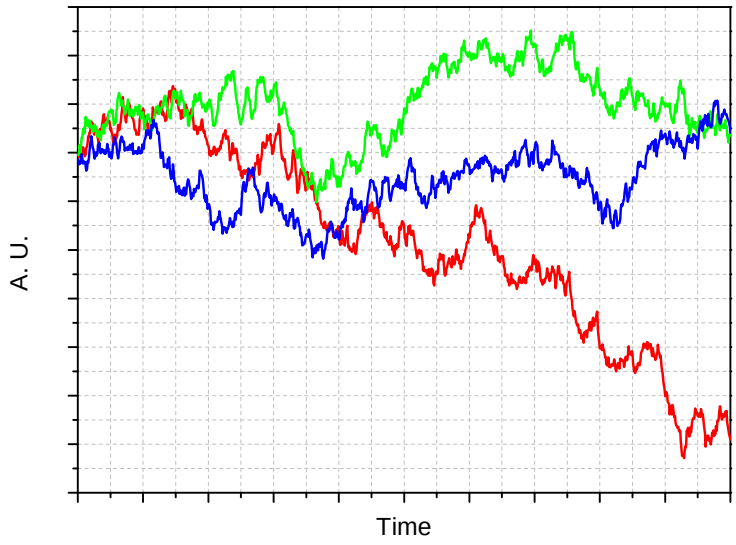

Figure 2.2: Realizations of Brownian process

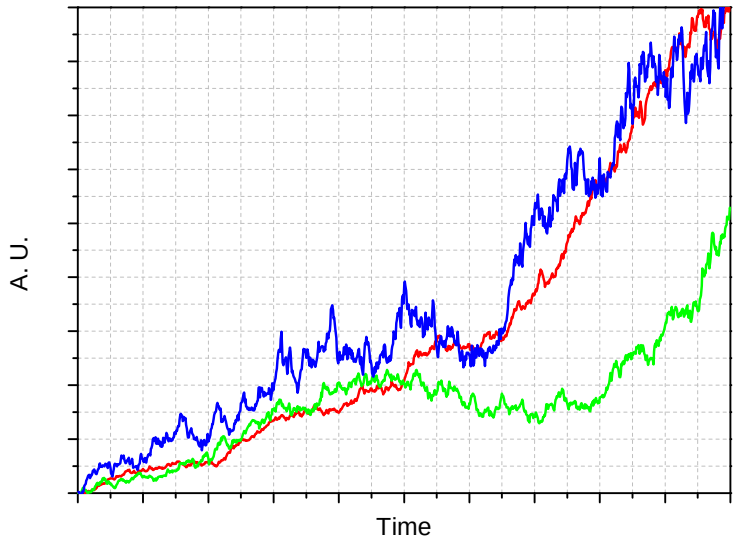

Figure 2.3: Realizations of geometric Brownian process.

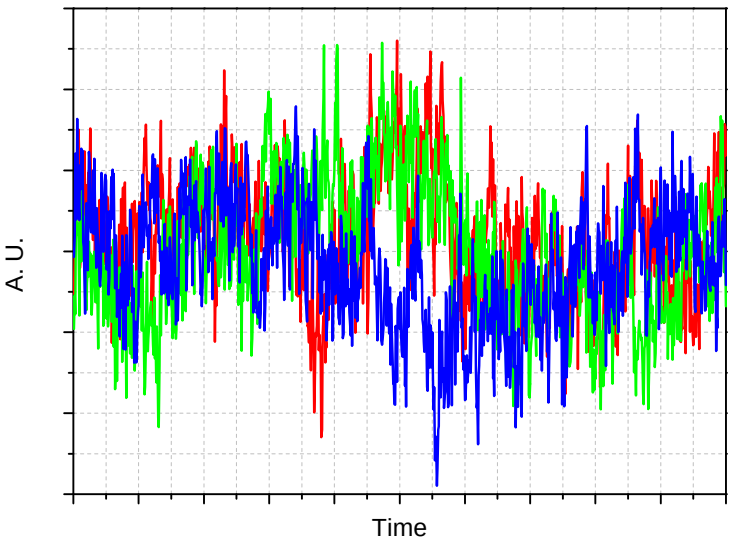

Figure 2.4: Realizations of $1/f$ noise process

$1/f$ Noise

Another ubiquitous class of stochastic processes is the family of processes known as $1/f$ noise. This process is also called "pink" or "flicker" noise. Systems exhibiting $1/f$ noise include electronic systems[11][26], spin glases [18][44][90], amorphous metals[20], biological systems[35] and various other systems of interest[38][39]. The study of $1/f$ noise presents difficulty as no general theory of $1/f$ noise exists, consequently, the models used to study the statistical properties of these processes vary according to the context in which the noise occurs[55][68]. The spectral density of $1/f$ noise is of the form $S(f) \propto f^{-1}$ hence its name. While no general theory of $1/f$ noise exists, it is possible to model processes with a $1/f$ spectrum using the following SDE[91]

$$\mathrm{d}Z_t = \sigma^2\left(1 - \frac{\nu}{2}\right) Z_t \mathrm{d}t + \sigma Z_t \mathrm{d}W_t \tag{2.21}$$

where ν characterizes the stationary probability distribution function. Fig. 2.4 shows several realizations of the time-series of generic $1/f$ noise.

2.2 The Correlation Function

Time-correlation functions are a powerful formalism and play a central role in statistical mechanics. They appear in many contexts including the study of transport coefficients and time-dependent perturbation theory. I begin this section with a discussion of correlation functions for classical systems. These results are then extended to the case of quantum systems. An understanding of quantum time-correlation functions is prerequisite for a proper discussion of linear response theory and for the derivation of the fluctuation dissipation relations.

2.2.1 Classical Correlation Functions

In this section I develop the time-correlation formalism for classical systems. This discussion is based on [78] and [79]. Consider a classical many-body system with N degrees of freedom. To completely describe the spatial orientation of such a system requires N generalized coordinates, given by

$$\mathbf{q} = (q_1, q_2, \ldots, q_N) \tag{2.22}$$

The associated generalized velocities are then given by

$$\dot{\mathbf{q}} = (\dot{q}_1, \dot{q}_2, \ldots, \dot{q}_N) \tag{2.23}$$

The state of the system is then completely described by the vector $(\mathbf{q}, \dot{\mathbf{q}})$. We define the phase-space, also known as the Γ-space, as a $2N$-dimensional Euclidean space whose axes are given by each $\{q_i, \dot{q}_i\}$. The dynamics of the system are given by the Hamiltonian equations of motion. We define a micro-canonical ensemble as a collection of independent replicas of a system in phase-space. The ensemble density function $\Phi(\mathbf{q}, \mathbf{p}, t)$, describes the statistical distribution of systems in phase-space, and is defined by

$$\Phi(\mathbf{q}, \mathbf{p}, t)\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p} = \Phi(\mathbf{q}, \mathbf{p}, t)\mathrm{d}\Gamma \tag{2.24}$$

Qualitatively this function describes the number of system points in the phase-volume $\mathrm{d}\Gamma$ in the neighbourhood of point $(\mathbf{q}, \mathbf{p})$ at time t. The time-evolution of Φ is given by the Liouville equation:

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = 0 \tag{2.25}$$

From the definition of Φ it follows that the total number of occupied states in the volume Γ is

$$\mathcal{N} = \int_{\Gamma} \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\, \Phi(\mathbf{q}, \mathbf{p}, t) \tag{2.26}$$

Similarly, the total number of occupied states in volume $\partial\Gamma$ is

$$\partial\mathcal{N} = \int_{\partial\Gamma} \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\, \Phi(\mathbf{q}, \mathbf{p}, t) \tag{2.27}$$

Following the work of Gibbs[47] we define the probability that an arbitrary state is occupied in the volume $\partial\Gamma$ by

$$\int_{\partial\Gamma} \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\, \phi_N = \frac{\int_{\partial\Gamma} \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\, \Phi(\mathbf{q},\mathbf{p},t)}{\int_{\Gamma} \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\, \Phi(\mathbf{q},\mathbf{p},t)} \tag{2.28}$$

The function ϕ_N is the N-body joint-probability density function of a single N-body system. Using this probability density we define the ensemble average of a dynamical variable A by

$$\langle A \rangle = \int \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\, \phi_N(\mathbf{q},\mathbf{p}) A(\mathbf{q},\mathbf{p},t) \tag{2.29}$$

The classical two-time correlation function of two dynamical variables A and B is given by

$$\langle A(t)B(0)\rangle = \int \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\, \phi_N(\mathbf{q},\mathbf{p}) A(\mathbf{q},\mathbf{p},t) B(\mathbf{q},\mathbf{p},0) \tag{2.30}$$

Qualitatively, classical correlation functions give a statistical measure of the time-evolution of a dynamical variable at equilibrium. The spectral density is then given by

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}t\, e^{-i\omega t} \langle A(t)A(0)\rangle \tag{2.31}$$

2.2.2 Quantum Correlation Functions

In this section I develop the definition of the quantum correlation function, which plays a fundamental role in much of the work presented in later chapters. This discussion is based on the expositions given in [15] and [93]. In quantum mechanics, we describe the state of the system using the state vector or state ket $|\Psi\rangle$, which defines an N-dimensional vector in Hilbert space. In the Schrödinger representation, the dynamics of the state ket are given by

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \tag{2.32}$$

We define a pure ensemble as an ensemble where every member is characterized by the same state ket. In contrast, a mixed ensemble can be thought of as a mixture of pure ensembles, where relative population w_i is characterized by $|i\rangle$, and the fractional populations satisfy

$$w_i = \frac{e^{\beta\hbar\omega_i}}{\mathcal{Z}} \tag{2.33a}$$

$$\sum_i w_i = 1 \tag{2.33b}$$

where $\mathcal{Z}$ is the canonical partition function. We define the density operator of a mixed ensemble by

$$\hat{\rho} = \sum_i w_i |i\rangle\langle i| \tag{2.34}$$

whose time evolution is give by the von Neumann equation

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = -[\hat{\rho}, \hat{H}] \tag{2.35}$$

This quantity contains all information about a given ensemble, and can be thought of as the quantum mechanical extension of the ensemble density function Φ defined previously. In analogy with the classical case, we define the ensemble average, or expectation of the observable $\hat{A}$ by

$$\langle \hat{A} \rangle = \sum_i w_i \langle i|\hat{A}|i\rangle \tag{2.36}$$

$$= \mathrm{Tr}\hat{\rho}\hat{A} \tag{2.37}$$

Consider now the observables $\hat{A}$ and $\hat{B}$ with Fourier decomposition

$$\hat{A}_{\mathbf{q}} = \sum_n \frac{1}{2}\{\hat{A}_n, e^{i\mathbf{q}\cdot\mathbf{r}_n}\} \tag{2.38}$$

$$\hat{B}_{\mathbf{q}} = \sum_n \frac{1}{2}\{\hat{B}_n, e^{i\mathbf{q}\cdot\mathbf{r}_n}\} \tag{2.39}$$

where the curly braces denote the anticommutator, and the A_n and B_n denote single particle properties. Then, the quantum time-correlation function[6] is given by

$$\langle \hat{A}_{\mathbf{q}}(t)\hat{B}^\dagger_{\mathbf{q}}(0)\rangle = \mathrm{Tr}\hat{\rho}e^{it\hat{H}/\hbar}\hat{A}_{\mathbf{q}}e^{it\hat{H}/\hbar}\hat{B}^\dagger_{\mathbf{q}} \tag{2.40}$$

If we expand the trace the expression for the quantum correlation function becomes

$$\langle \hat{A}_{\mathbf{q}}(t)\hat{B}^\dagger_{\mathbf{q}}(0)\rangle = \sum_{mn} \hat{\rho}_m \langle m|\hat{A}_{\mathbf{q}}|n\rangle\langle n|\hat{B}^\dagger_{\mathbf{q}}|m\rangle e^{i\omega_{mn}t} \tag{2.41}$$

where $\omega_{mn} = (E_n - E_m)/\hbar$, E_n is the n-th energy eigenvalue, and ρ_m is the Boltzmann factor. At $T = 0$ the above reduces to

$$\langle \hat{A}_{\mathbf{q}}(t)\hat{B}^\dagger_{\mathbf{q}}(0)\rangle = \sum_n \langle n|\hat{A}_{\mathbf{q}}|0\rangle\langle 0|\hat{B}^\dagger_{\mathbf{q}}|n\rangle e^{i\omega_{n0}t} \tag{2.42}$$

I present without proof some properties of the quantum correlation function

(i) $\langle \hat{A}^\dagger_{\mathbf{q}}(0)\hat{B}_{\mathbf{q}}(t)\rangle = \langle \hat{A}^\dagger_{\mathbf{q}}(-t)\hat{B}_{\mathbf{q}}(0)\rangle$

(ii) $\langle \hat{A}^\dagger_{\mathbf{q}}(0)\hat{B}_{\mathbf{q}}(t)\rangle = \theta_A\theta_B\langle \hat{B}_{\mathbf{q}}(-t)\hat{A}^\dagger_{\mathbf{q}}(0)\rangle$

[6] Also called the canonical correlation function

(iii) $\langle \hat{A}^{\dagger}_{\mathbf{q}}(0)\hat{B}_{\mathbf{q}}(t)\rangle^* = \langle \hat{B}^{\dagger}_{\mathbf{q}}(t)\hat{A}_{\mathbf{q}}(0)\rangle$

where θ_A and θ_B are the time-reversal signatures of operators A and B respectively. The spectral density is defined analogously to the classical case

$$S(\mathbf{q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, e^{-i\omega t}\langle A_{\mathbf{q}}(t)A_{\mathbf{q}}(0)\rangle \tag{2.43}$$

2.3 Linear Response Theory

In this section I present the central results of linear-response theory. This discussion follows the work of R. Kubo [73][72][74]. Following the discussion of linear response theory I present the famous fluctuation dissipation theorem. This theorem was originally presented by H. Nyquist[85] and later proven by H. Callen and T. A. Welton[27]. This theorem provides a powerful relationship between dissipative forces and fluctuation phenomena and will play a central role in much of the work presented in this thesis.

2.3.1 The Response Function and Generalized Susceptibility

Consider now a system described by the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}(t). \tag{2.44}$$

where $\hat{H}_0$ represents the unperturbed Hamiltonian, and the interaction term is given by

$$\hat{V}(t) = -\int \mathrm{d}\mathbf{r}\hat{A}(\mathbf{r})\hat{K}(\mathbf{r},t) \tag{2.45}$$

where $\hat{A}(\mathbf{r})$ is some property and $\hat{K}(\mathbf{r},t)$ is a field acting on $\hat{A}(\mathbf{r})$ at point $(\mathbf{r},t)$ and the expectation $\langle\hat{A}\rangle$ vanishes in the absence of $\hat{K}$. The expectation value of some operator $\hat{B}$ due to the perturbation is given by

$$\delta\langle\hat{B}(\mathbf{r},t)\rangle = \int_{-\infty}^{t}\mathrm{d}t'\int \mathrm{d}\mathbf{r}'\,\Psi(\mathbf{r}-\mathbf{r}',t-t')\hat{K}(\mathbf{r}',t') \tag{2.46}$$

where Ψ is the response function[7]. The response function is independent of the nature of the perturbations as it is an inherent property of the system. Taking the spatial Fourier transform of the above yields

$$\delta\langle\hat{B}_{\mathbf{q}}(t)\rangle = \int_{-\infty}^{t}\mathrm{d}t'\Psi(\mathbf{q},t-t')\hat{K}_{\mathbf{q}}(t') \tag{2.47}$$

In order to obtain the response function, we must solve the von Neumann equation, Eq. 2.35, of the system. We impose the initial condition $\hat{\rho}(-\infty) = \hat{\rho}_0$ where

$$\hat{\rho}_0 = \mathcal{Z}^{-1}\exp[\hat{H}_0/kT] \tag{2.48}$$

[7] Also called the after-effect function

The solution of the von Neumann equation, to first order in the perturbation, is then

$$\hat{\rho}(t) = \hat{\rho}(-\infty) + \delta\hat{\rho}(t) \tag{2.49}$$

$$= \hat{\rho}_0 + \frac{1}{i\hbar}\int_{-\infty}^{t} \mathrm{d}t' \hat{U}_0(t-t')[\hat{V}(t'), \hat{\rho}(t')]\hat{U}_0^{-1}(t-t') \tag{2.50}$$

In the above $\hat{U}_0(t-t')$ is the unitary time translation operator. Using the expression for $\hat{\rho}(t)$ and Eq. 2.47 gives

$$\delta\langle\hat{B}_{\mathbf{q}}(t)\rangle = \int_{-\infty}^{t} \mathrm{d}t' \left\langle \frac{i}{\hbar}[\hat{B}_{\mathbf{q}}(t-t'), \hat{A}_{-\mathbf{q}}(0)] \right\rangle \hat{K}_{\mathbf{q}}(t') \tag{2.51}$$

from which it follows that the response function has the form

$$\Psi(\mathbf{q}, t) = \left\langle \frac{i}{\hbar}[\hat{B}_{\mathbf{q}}(t-t'), \hat{A}_{-\mathbf{q}}(0)] \right\rangle \tag{2.52}$$

Finally we may define the susceptibility of the system as

$$\chi(\mathbf{q}, \omega) = \int_0^\infty \mathrm{d}t e^{i\omega t}\Psi(\mathbf{q}, t) \tag{2.53}$$

$$= \int_0^\infty \mathrm{d}t\, e^{i\omega t} \left\langle \frac{i}{\hbar}[\hat{B}_{\mathbf{q}}(t-t'), \hat{A}_{-\mathbf{q}}(0)] \right\rangle \tag{2.54}$$

For a system with translational invariance the susceptibility becomes

$$\chi(\mathbf{q}, \omega) = \frac{1}{L^d}\int_0^\infty \mathrm{d}t\, e^{i\omega t} \left\langle \frac{i}{\hbar}[\hat{B}_{\mathbf{q}}(t-t'), \hat{A}_{-\mathbf{q}}(0)] \right\rangle \tag{2.55}$$

where L^d is the volume of the system.

2.3.2 The Fluctuation Dissipation Theorem

It follows that $\chi(\mathbf{q}, \omega)$ satisfies[15]

$$\Im\{\chi(\mathbf{q}, \omega)\} = -\frac{\pi}{\hbar L^d}\sum_n |\langle n|\hat{A}_q|0\rangle|^2[\delta(\omega - \omega_{n0}) - \delta(\omega + \omega_{n0})] \tag{2.56}$$

An important quantity in the study of fluctuations and dissipation is the dynamic structure factor, $S(q, \omega)$, defined by

$$S(\mathbf{q}, \omega) = \sum_n |\langle n|\hat{A}_q|0\rangle|^2\delta(\omega + \omega_{n0}) \tag{2.57a}$$

$$= \frac{1}{2\pi}\int \mathrm{d}t e^{-i\omega t}\langle\hat{A}_{\mathbf{q}}(t), \hat{A}_{-\mathbf{q}}(0)\rangle \tag{2.57b}$$

where the second line follows from the definition of the quantum correlation function. The dynamic susceptibility satisfies the principle of detailed balance, which is embodied in the relation

$$S(\mathbf{q}, -\omega) = e^{-\beta\hbar\omega}S(\mathbf{q}, \omega) \tag{2.58}$$

Combining Eqs. 2.56 - 2.58 gives

$$\Im\{\chi(\mathbf{q},\omega)\} = -\frac{\pi}{\hbar L^d}(1 - e^{-\beta\hbar\omega})S(\mathbf{q},\omega) \tag{2.59}$$

The relation given in Eq. 2.59 is known as the fluctuation dissipation theorem. It relates the dissipative response of the system, characterized by the susceptibility, to the fluctuation processes, characterized by the structure factor. The exact form of the fluctuation dissipation theorem depends on the definition of $S(\mathbf{q},\omega)$. Another commonly used convention is to define $S(\mathbf{q},\omega)$ by

$$S(\mathbf{q},\omega) = 2\pi L^d \sum_n |\langle n|\hat{A}_q|0\rangle|^2 \delta(\omega + \omega_{n0}) \tag{2.60a}$$

$$= L^d \int \mathrm{d}t e^{-i\omega t} \langle \hat{A}_{\mathbf{q}}(t), \hat{A}_{-\mathbf{q}}(0)\rangle \tag{2.60b}$$

In this case we have

$$\Im\{\chi(\mathbf{q},\omega)\} = -\frac{1}{2\hbar L^d}(1 - e^{-\beta\hbar\omega})S(\mathbf{q},\omega) \tag{2.61}$$

2.4 Ab-intio calculation of the electron energy-loss spectrum

In this section I give an overview of the numerical methods used to calculate the electron energy-loss spectrum. This is achieved using the linear-response time-dependent density functional theory package provided by the Generalized Projector Augmented Wave (GPAW) simulation package[43][62][106][110]. In this method, the interacting density response is calculated using the Dyson equation in reciprocal space

$$\chi_{QQ'}(\mathbf{q},\omega) = \chi^0_{QQ'}(\mathbf{q},\omega) + \sum_{Q_1Q_2} \chi^0_{QQ_1}(\mathbf{q},\omega) V_{Q_1Q_2}(\mathbf{q}) \chi_{Q_2Q'}(\mathbf{q},\omega) \tag{2.62}$$

where $\chi^0_{QQ'}$ is the non-interacting density response, $\mathbf{q}$ denotes the momentum transfer, Q denotes the reciprocal lattice vectors, and V is the interaction kernel given by

$$V_{Q_1Q_2}(\mathbf{q}) = \frac{4\pi}{|\mathbf{q}+\mathbf{Q}_1|^2}\delta_{Q_1Q_2} + \frac{1}{L^d}\int \mathrm{d}\mathbf{r}\, e^{i(Q_1-Q_2)\cdot\mathbf{r}} \left.\frac{\partial^2 E_{xc}[n]}{\partial n^2}\right|_{n_0(\mathbf{r})} \tag{2.63}$$

where L^d is the system volume, n is the number density, and E_{xc} is the exchange-correlation energy. The dielectric function is then given by

$$\epsilon^{-1}_{QQ'}(\mathbf{q},\omega) = \delta_{QQ'} + \frac{4\pi}{|\mathbf{q}+\mathbf{Q}|^2}\chi_{QQ'}(\mathbf{q},\omega) \tag{2.64}$$

Using the dielectric function, the EELS is then given by $-\Im\{\epsilon^{-1}_{00}(\mathbf{q},\omega)\}$.

Chapter 3

Stochastic Kinetic Model of Charge Density Fluctuations

3.1 Introduction

In this chapter I present a probabilistic model of charge-density fluctuations based on kinetic theory. This is achieved by applying methods from Eulerian perturbation theory to results from kinetic theory, resulting in a stochastic differential equation governing charge-density fluctuations. This equation is then solved under special conditions.

3.2 Boltzmann Equation of the Electron Gas

The Boltzmann equation gives the equation of motion for the single-particle distribution function. Using the many-particle distribution function ϕ_N, we define the single-particle distribution function by [78]

$$\phi(\mathbf{r}_1, \mathbf{v}_1, t) = \frac{1}{N} \int \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_N \mathrm{d}\mathbf{v}_2 \cdots \mathrm{d}\mathbf{v}_N \phi_N(\mathbf{x}_1, \cdots, \mathbf{x}_N, \mathbf{v}_1, \cdots, \mathbf{v}_N, t) \tag{3.1}$$

The Boltzmann equation is given by[13][78][79]

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = C(\phi) \tag{3.2}$$

where C is the Boltzmann collision term, which contains the inter-molecular potential and describes particle collisions. This equation describes the statistical behaviour of non-equilibrium systems. Expanding the total derivative yields

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \phi + \frac{K}{m} \cdot \nabla_{\mathbf{v}} \phi = C(\phi) \tag{3.3}$$

In the above K is a conservative, external force-field, and $\nabla_{\mathbf{r}}$, $\nabla_{\mathbf{v}}$ denote differentiation with respect to r and $\mathbf{v}$ respectively. In the case of an electron

gas, assuming zero external magnetic field and ignoring particle collisions, the Boltzmann equation becomes the Klimontovich equation

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \phi + \frac{e}{m} \nabla_{\mathbf{r}} \varphi \cdot \nabla_{\mathbf{v}} \phi = 0 \tag{3.4}$$

where φ is the electrostatic potential satisfying

$$\nabla^2_{\mathbf{r}} \varphi = -\frac{1}{\epsilon_0} \rho \tag{3.5}$$

with ϵ_0 the vacuum permittivity, and ρ the electron gas charge density. Following the work of Bouchet[23] we derive the fluid equations as velocity moments of Eq. 3.4. The n-th velocity moment of the Klimontovich equation is given by

$$\int \mathrm{d}\mathbf{v}\, \mathbf{v}^n \left(\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \phi + \frac{e}{m} \nabla_{\mathbf{r}} \varphi \cdot \nabla_{\mathbf{v}} \phi \right) = 0 \tag{3.6}$$

In taking the velocity moments of the Klimontovich equation it is implicit that we are taking the continuum limit of Eq. 3.4, in which case it is referred to as the Vlasov equation. Taking the zeroth velocity moment of Eq. 3.4 yields the continuity equation[13]

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{r}} \cdot (\rho \mathbf{u}) = 0. \tag{3.7}$$

where $u(\mathbf{r}, t)$ is the mean velocity, defined by

$$\mathbf{u}(\mathbf{r}, t) = \frac{1}{n(\mathbf{r}, t)} \int d\mathbf{v} \Big(\mathbf{v}\, \phi(\mathbf{r}, \mathbf{v}, t) \Big). \tag{3.8}$$

and $n(\mathbf{r}, t)$ is the number density, defined by

$$n(\mathbf{r}, t) = \int d\mathbf{v}\, \phi(\mathbf{r}, \mathbf{v}, t). \tag{3.9}$$

Assuming friction and pressure are negligible, the first moment yields the momentum conservation or Euler equation[13]

$$\left(\frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla_r \right) \mathbf{u} + \frac{e}{m} \nabla_r \varphi = 0 \tag{3.10}$$

3.3 Eulerian Perturbation Theory

Following a similar approach to that used in cosmological perturbation theory[14][23][83][88][111], we make the ansatz that the particle trajectory may be described as the initial particle position $\mathbf{x}(t)$ coupled to the random process $a(t)$,

$$\mathbf{r}(\mathbf{x}, t) = a(t)\mathbf{x}(t). \tag{3.11}$$

In the context of gravitational instability the quantity $a(t)$ describes the inflation of space and the quantities $\mathbf{r}(\mathbf{x},t)$ and $\mathbf{x}(t)$ are known respectively as the physical (Eulerian) and co-moving (Lagrangian) coordinates. We adopt this naming convention for $\mathbf{r}$ and $\mathbf{x}$, however, for our purposes, $a(t)$ contains the fluctuation characteristics of the particles in the system. As a direct consequence of Eq. 3.11 we have the following relations,

$$\nabla_{\mathbf{x}} = a(t)\nabla_{\mathbf{r}} \tag{3.12}$$

$$\mathbf{u}(\mathbf{r},t) = \frac{d\mathbf{r}}{dt} = a\frac{d\mathbf{x}}{dt} + \mathbf{x}\frac{da}{dt} \tag{3.13}$$

Assuming the fluid has a uniform background density $\tilde{\rho}(t)$, we define the density fluctuations $\delta\rho(\mathbf{x},t)$ by

$$\delta\rho(\mathbf{x},t) = \rho(\mathbf{x},t) - \tilde{\rho}(t) \tag{3.14}$$

where $\rho(\mathbf{x},t)$ is the fluid charge density in co-moving coordinates. Similarly, we define the electrostatic potential perturbation by

$$\varphi(\mathbf{x},t) = \varphi(\mathbf{r},t) - \tilde{\varphi(t)}, \tag{3.15}$$

Taking the perturbations to first order, and noting that the velocity in co-moving coordinates is $\mathbf{v}(\mathbf{x},t) = a(t)\dot{\mathbf{x}}$, where the dot indicates differentiation with respect to time, Eqs. 3.5, 3.7, and 3.10 become[23][88], respectively,

$$\nabla^2_{\mathbf{x}}\varphi(\mathbf{x},t) = -\frac{1}{\epsilon_0}a^2\delta\rho(\mathbf{x},t) \tag{3.16}$$

$$\frac{\partial\delta\rho(\mathbf{x},t)}{\partial t} + \frac{\tilde{\rho(t)}}{a}\nabla_x\cdot\mathbf{v}(\mathbf{x},t) = 0 \tag{3.17}$$

$$\frac{\partial\mathbf{v}(\mathbf{x},t)}{\partial t} + \frac{\dot{a}}{a}\mathbf{v}(\mathbf{x},t) + \frac{1}{a}\frac{e}{m}\nabla_x\varphi(\mathbf{x},t) = 0 \tag{3.18}$$

Taking the divergence of Eq. 3.18 and using Eqs. 3.16 and 3.17 gives the equation of motion of the charge density fluctuations.

$$\frac{\partial^2\delta\rho}{\partial t^2} + \frac{\dot{a}}{a}\frac{\partial\delta\rho}{\partial t} + \frac{\tilde{\rho}e}{\epsilon_0 m}\delta\rho = 0 \tag{3.19}$$

3.4 Analytic Solution of the Charge-Density Fluctuations Equation of Motion

In order to solve Eq. 3.19 we impose the constraint

$$\frac{\dot{a}}{a} = b[1 + w(t)] \tag{3.20}$$

where b is a real constant, and $w(t)$ is a random noise process. In principle, the noise process in Eq. 3.19 can be characterized by an arbitrary correlation function. However, for mathematical simplicity, we assume it is a white noise process with correlator

$$\langle w(t)w(\tau)\rangle = D\delta(t-\tau) \tag{3.21}$$

The random variable a is then described by

$$\mathrm{d}a_t = ba_t\mathrm{d}t + ba_t dW_t \tag{3.22}$$

where W_t is a Brownian process, defined as time integrated white-noise. The relation given in Eq. 3.22 indicates that with the constraint given in Eq. 3.20 where w satisfies Eq. 3.21, the particle trajectory is described by geometric Brownian motion. The solution of Eq. 3.22 is given by[87]

$$a(t) = a_0\exp\left(\left(b-\frac{b^2}{2}\right)t + bW(t)\right) \tag{3.23}$$

If we assume that the physical and co-moving coordinates coincide at $t=0$, then the particle position at time t is

$$\mathbf{r}(\mathbf{x},t) = \exp\left(\left(b-\frac{b^2}{2}\right)t + bW(t)\right)\mathbf{x}(t). \tag{3.24}$$

With the constraint given in Eq. 3.20, and assuming the density fluctuations are isotropic, we can rewrite Eq. 3.19 as[48]

$$\frac{\mathrm{d}^2\langle\delta\rho\rangle}{\mathrm{d}t^2} + b(1-bD)\frac{\mathrm{d}\langle\delta\rho\rangle}{\mathrm{d}t} + \omega_p^2\langle\delta\rho\rangle = 0 \tag{3.25}$$

where ω_p is the plasma frequency, given by

$$\omega_p^2 = \frac{\tilde{\rho}e}{\epsilon_0 m} \tag{3.26}$$

The equation of motion of density fluctuations, Eq. 3.25, has solution[1]

$$\begin{aligned}\langle\delta\rho(t)\rangle = e^{\alpha t}\Bigg[&\left(\cos(\beta t) - \frac{\alpha}{\beta}\sin(\beta t)\right)\langle\delta\rho(0)\rangle \\ &+ \frac{1}{\beta}\sin(\beta t)\langle\delta\dot{\rho}(0)\rangle\Bigg]\end{aligned} \tag{3.27}$$

where α and β satisfy

$$\alpha = -\frac{1}{2}b(1-bD) \tag{3.28}$$

$$\beta^2 = \omega_p^2 - \frac{1}{4}(b(1-bD))^2 \tag{3.29}$$

[1]See appendix B for a derivation of the solution

and

$$\langle \delta\dot{\rho}(0)\rangle = \left.\frac{\mathrm{d}\langle\delta\rho\rangle}{\mathrm{d}t}\right|_{t=0} \tag{3.30}$$

The stability condition of Eq. 3.27 is given by $bD < 1$[48]. In the absence of the perturbation, $b = 0$, the physical and comoving coordinates coincide at all times, and Eq. 3.25 reduces to the equation of motion of plasmons with solution

$$\langle \delta\rho(t)\rangle = \cos(\omega_p t)\langle\delta\rho(0)\rangle + \frac{1}{\omega_p}\sin(\omega_p t)\langle\delta\dot{\rho}(0)\rangle \tag{3.31}$$

Comparing Eq. 3.27 and Eq. 3.31, we see that the perturbations have the effect of exponentially damping the oscillations of the density fluctuations.

3.4.1 Numerical Results

In this section I investigate the consequences of varying the parameters of the solution of the density fluctuations equation of motion, Eq. 3.27 and Eq. 3.31. Fig. 3.1 shows the density fluctuations normalized by the background charge-density ρ_b as given by Eq. 3.31 for different values of the plasma frequency ω_p, and initial conditions $\langle\delta\dot{\rho}(0)\rangle\tau = \rho_b$ and $\langle\delta\rho(0)\rangle = \rho_b$, where τ denotes the unit time interval. As is expected given the form of Eq. 3.31, ω_p determines both the frequency of oscillation, and the amplitude of the density fluctuations. Clearly in the absence of the perturbation the density fluctuations exhibit simple harmonic oscillation.

The influence of the perturbation on the density fluctuations is illustrated in Fig. 3.2 for various values of b, with plasma frequency $\omega_p = 1$ eV and initial conditions as given previously. Clearly, the perturbation acts so as to dampen the density fluctuations. Fig. 3.3 shows the particle displacements as well as the cumulative sum of the displacements corresponding to the density fluctuations shown in Fig. 3.2. Clearly there is a direct correlation between the particle displacements, in particular the distance covered, and the magnitude of the damping of the density fluctuations.

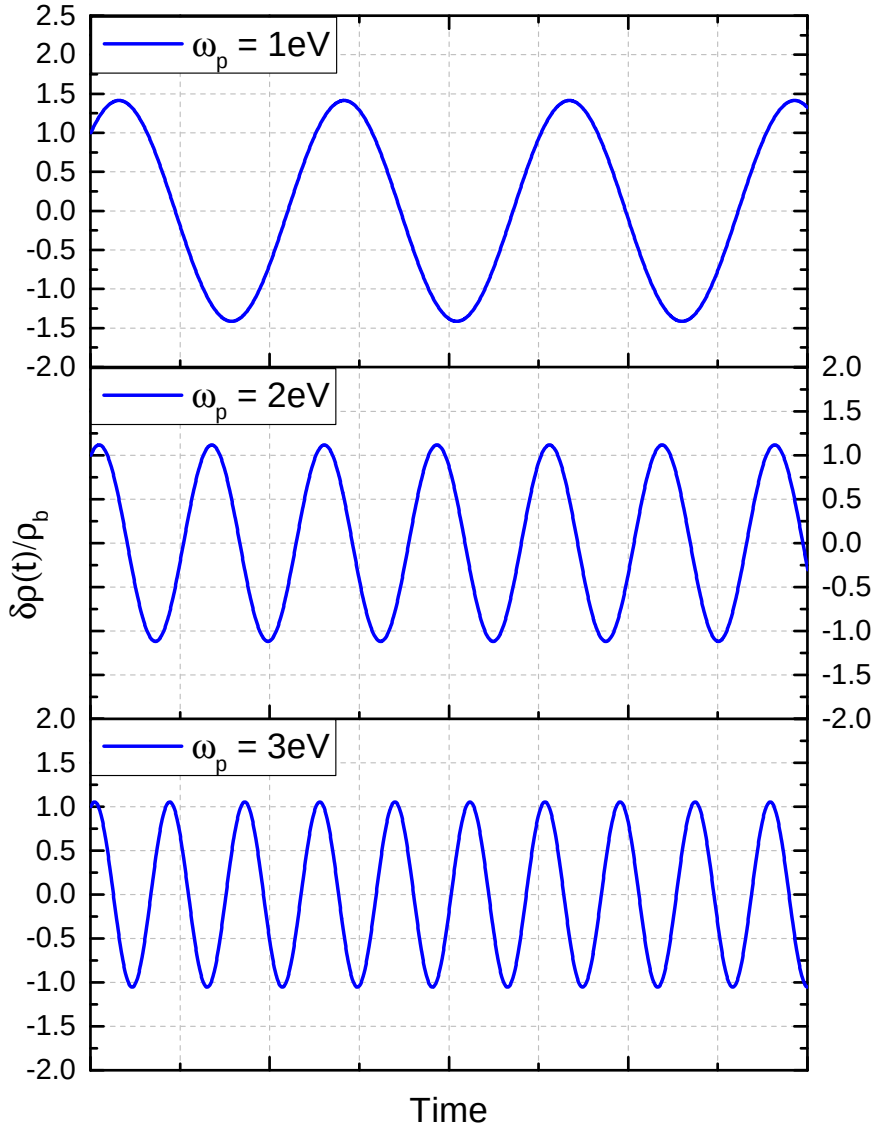

Figure 3.1: Density fluctuations with no perturbations and initial conditions $\langle \delta\dot{\rho}(0)\rangle\tau = \rho_b$ and $\langle \delta\rho(0)\rangle = \rho_b$, and plasma frequency $\omega_p = 1\text{eV}, 2\text{eV}, 3\text{eV}$.

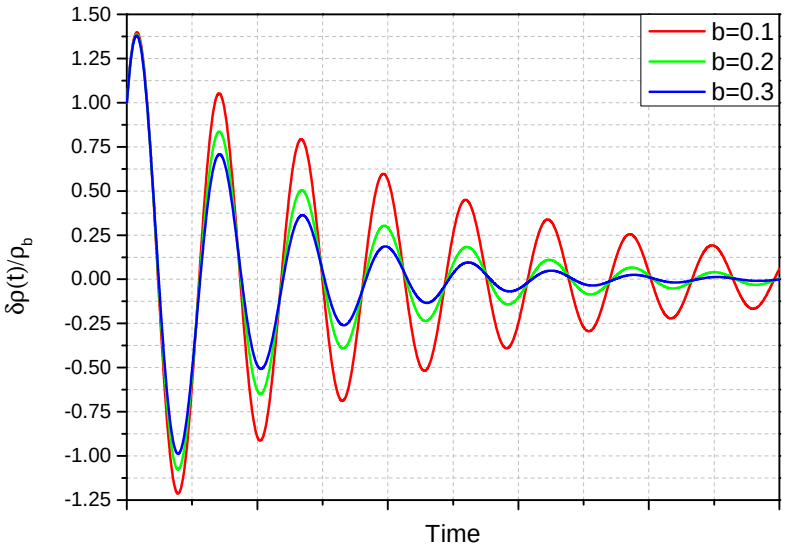

Figure 3.2: Density fluctuations with initial conditions $\langle \delta\dot{\rho}(0) \rangle = \langle \delta\rho(0) \rangle = \rho_b$, showing $b = 0.1, 0.2, 0.3$ and plasma frequency $\omega_p = 1\text{eV}$.

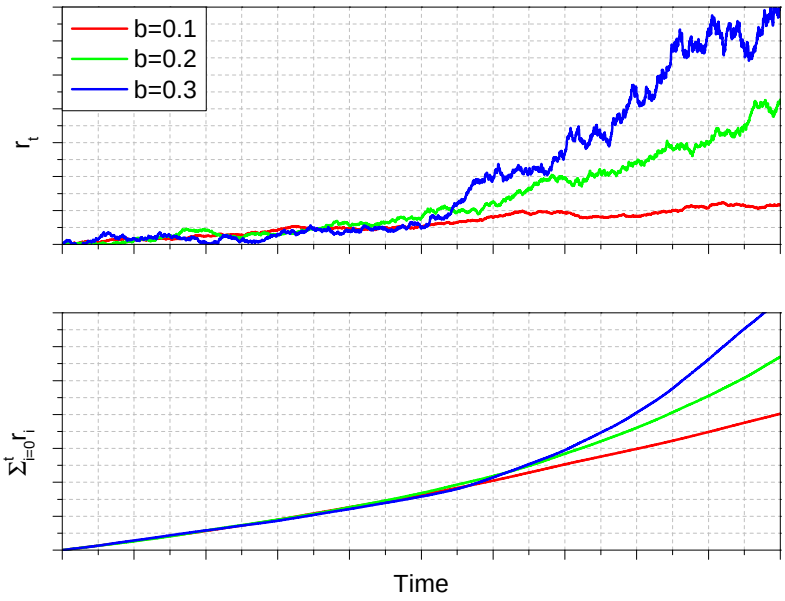

Figure 3.3: Particle displacement (top) and cumulative sum of displacements (bottom).

3.5 Conclusions

In this chapter I gave an overview of the derivation of a probabilistic model of charge-density fluctuations. This was achieved by combining results from kinetic theory and Eulerian perturbation theory with the assumption that the particle displacement can be decomposed into the product of a random variable with the comoving coordinate of the particle, as described by Eq. 3.11. This resulted in a stochastic differential equation governing the time-evolution of the charge-density fluctuations, Eq. 3.19. This equation was then solved analytically by making simplifying assumptions regarding the noise governing the stochastic process, Eq. 3.21. With these assumptions it was found that the particle trajectory was given by a special case of geometric Brownian motion. The influence of the various parameters of the model on the solution of the equation of motion were then investigated numerically. It was found that the perturbation has the effect of damping the oscillations of the density fluctuations. While the model developed in this chapter was investigated for a specific set of assumptions regarding the noise characteristics, it is possible in principle to extend this model to account for arbitrary noise characteristics, although the equation of motion of the density fluctuations may or may not be solvable in general.

Chapter 4

Density Fluctuations and the Electron Energy-Loss Spectrum

In this chapter I describe a method enabling the numerical calculation of the charge-density ACF. This method is based on linear response theory and makes use of the fluctuation-dissipation relations. From the results of density functional theory, all system properties can be obtained from the charge density, thus charge-density fluctuations determine all other fluctuation processes in a system. Therefore, this approach provides a significant method for the study of noise in systems.

4.1 The Dielectric Function

Consider a homogeneous electron gas perturbed by an inhomogeneous charge density $\rho_{ext}(\mathbf{r}, t)$ which generates an external potential $\varphi_{ext}(\mathbf{r}, t)$. The total charge density of the system is given by

$$\rho(\mathbf{r}, t) = \rho_{ext}(\mathbf{r}, t) + \rho_{ind}(\mathbf{r}, t) + \rho_b(\mathbf{r}, t) \tag{4.1}$$

where $\rho_{ind}(\mathbf{r}, t)$ is the induced charge density resulting from the redistribution of electrons due to the external charge, and $\rho_b(\mathbf{r}, t)$ is the background charge-density. Gauss' law then yields

$$\nabla \cdot \mathbf{D} = 4\pi\rho_{ext} \tag{4.2}$$

Assuming local-field corrections are negligible the dielectric function is then given by [98]

$$\frac{1}{\epsilon(\mathbf{q}, \omega)} = 1 + \frac{4\pi e^2}{q^2} \frac{n_{ind}(\mathbf{q}, \omega)}{\varphi_{ext}(\mathbf{q}, \omega)} \tag{4.3}$$

where $n_i(\mathbf{r}) = -\rho_i(\mathbf{r})/e$ and $\varphi_i(\mathbf{r}) = -e\varphi_i(\mathbf{r})$. Using linear response theory, the response function is given by [98]

$$n_{ind}(\mathbf{q},\omega) = \chi(\mathbf{q},\omega)\varphi_{ext}(\mathbf{q},\omega) \tag{4.4}$$

Combining the above relation with Eq. 4.3 gives

$$\frac{1}{\epsilon(\mathbf{q},\omega)} = 1 + \frac{4\pi e^2}{q^2}\chi(\mathbf{q},\omega) \tag{4.5}$$

4.2 The Generalized Susceptibility of an Electron Gas

Using the fluctuation-dissipation theorem, Eq. 2.59, and ignoring the volume normalization, it immediately follows that the generalized susceptibility of an electron gas is given by

$$\Im\{\chi(\mathbf{q},\omega)\} = \frac{\pi}{\hbar}(e^{-\beta\hbar\omega} - 1)S(\mathbf{q},\omega) \tag{4.6}$$

where the dynamic structure factor is defined as

$$S(\mathbf{q},\omega) = \sum_m |\langle m|n^\dagger_{\mathbf{q}}|0\rangle|^2\delta(\omega - \omega_{m0}) \tag{4.7}$$

$$= \frac{1}{2\pi}\int \mathrm{d}t\, e^{-i\omega t}\langle n_{\mathbf{q}}(t), n^\dagger_{\mathbf{q}}(0)\rangle \tag{4.8}$$

where $n_{\mathbf{q}}$ is the many-body number density. The electron energy-loss spectrum (EELS) is defined as $\Im\{\epsilon^{-1}(\mathbf{q},\omega)\}$. Combining Eq. 4.3 and Eq. 4.6 gives

$$\Im\{\epsilon^{-1}(\mathbf{q},\omega)\} = \frac{4\pi^2 e^2}{q^2\hbar}[e^{-\beta\hbar\omega} - 1]S(\mathbf{q},\omega) \tag{4.9}$$

which is the fluctuation-dissipation relation for the density fluctuations. Using Eq. 4.8 and the definition of the spectral density, we obtain an explicit relation for the density ACF

$$\langle n_{\mathbf{q}}(t), n^\dagger_{\mathbf{q}}(0)\rangle = \int \mathrm{d}\omega\, e^{i\omega t}\frac{q^2\hbar}{4\pi^2 e^2}\frac{\Im\{\epsilon^{-1}(\mathbf{q},\omega)\}}{e^{-\beta\hbar\omega} - 1} \tag{4.10}$$

The above relation allows us to study density fluctuations using a knowledge of the EELS, which is both experimentally and numerically accessible. This gives us a useful tool for the study of density fluctuations and associated processes.

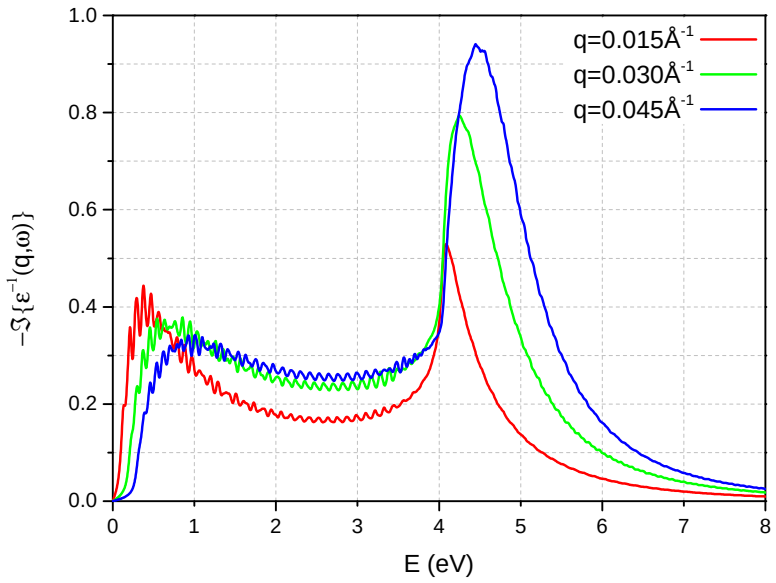

Figure 4.1: EELS of ideal graphene for energys below 8eV at $q = 0.003\text{Å}^{-1}$, $q = 0.006\text{Å}^{-1}$, and $q = 0.010\text{Å}^{-1}$.

4.3 Density Fluctuations in Graphene

In this section Eq. 4.10 is applied to numerical EELS data of ideal graphene calculated using linear-response time-dependent density functional theory [43][106][62][110][107]. Graphene was chosen as graphene based electronic devices exhibit low-frequency $1/f$ noise[8], and since its dielectric properties have been studied extensively[1][110][61]. The results presented in this section are based on[80].

4.3.1 Numerical Results

Eq. 4.10 specifies the density ACF at a single point in reciprocal space, thus for the present analysis we will investigate the density ACF at points $q = 0.003\text{Å}^{-1}$, $q = 0.006\text{Å}^{-1}$, and $q = 0.010\text{Å}^{-1}$ in the irreducible zone, where $q = ||\mathbf{q}||$[1]. Fig. 4.1 shows the EELS at these points for energies ranging between 0eV and 8eV. The noise visible in Fig. 4.1 may be due to a combination of physical processes and numerical error related to the sampling of the Brillouin zone. The second peak in Fig. 4.1 is related to the plasmonic resonance in graphene[107]. The density ACF corresponding

[1] In graphene the EELS is virtually independent of direction for small values of $\mathbf{q}$. Thus using $q = ||\mathbf{q}||$ is sufficient.

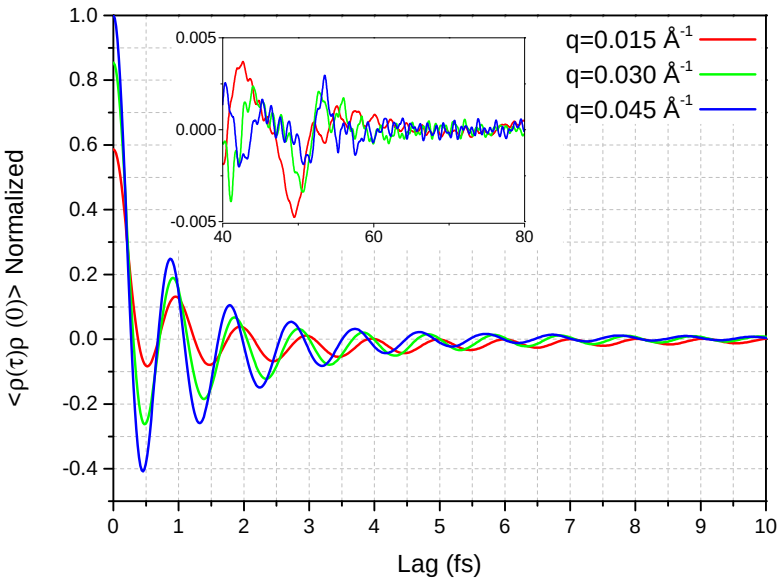

Figure 4.2: Density ACF of ideal graphene at $q = 0.003\text{Å}^{-1}$, $q = 0.006\text{Å}^{-1}$, and $q = 0.010\text{Å}^{-1}$, with inset showing long-time behaviour.

to the EELS of Fig. 4.1 is shown in Fig. 4.2, where the ACF has been normalized as we are primarily interested in the temporal behaviour. The initial decay of the ACF has a period of approximately 1fs. This corresponds to a resonance of approximately 4eV, which corresponds to the second peak of the EELS in Fig. 4.1. This suggests that the initial decay of the density ACF is related to plasmonic resonance. At long-time lags, the periodic behaviour of the density ACF is dominated by random fluctuations. These fluctuations are a direct consequence of the noise present in the EELS. This indicates that the long-time behaviour of the density ACF may be used to investigate the characteristics of the noise processes associated with density fluctuations. For comparative purposes, we compute the EELS of a Lorentz oscillator. The Lorentz oscillator model gives the imaginary component of the dielectric function as

$$\Im\{\epsilon(\omega)\} = \frac{\omega_p^2 \gamma \omega}{(\omega_0 - \omega^2)^2 + \omega^2 \gamma^2} \tag{4.11}$$

The parameters for the Lorentz model are obtained using a least-squares fit of the Lorentzian to the EELS of ideal graphene. Fig. 4.3 shows the EELS obtained using the Lorentz oscillator model. Comparing Fig. 4.1 and Fig. 4.3 we see that the EELS of the Lorentz model has no noise, and has its first peak at slightly higher energy than the corresponding peak of the graphene

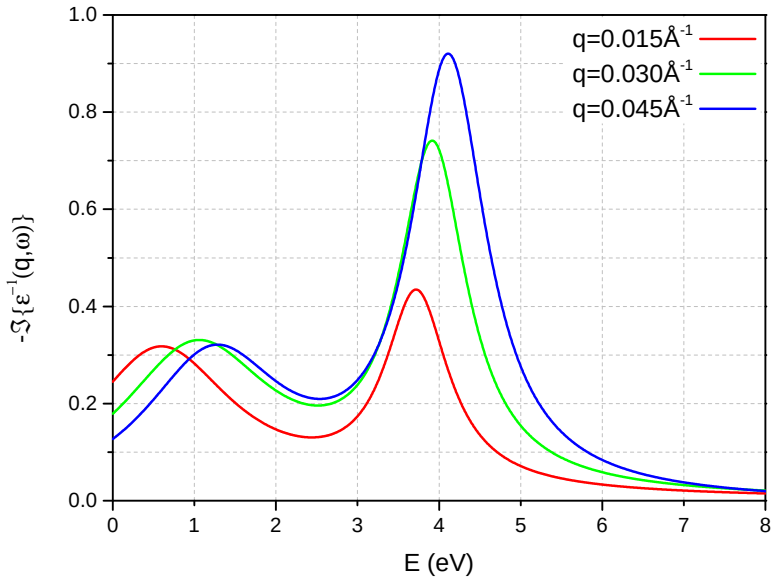

Figure 4.3: EELS of Lorentz oscillator model

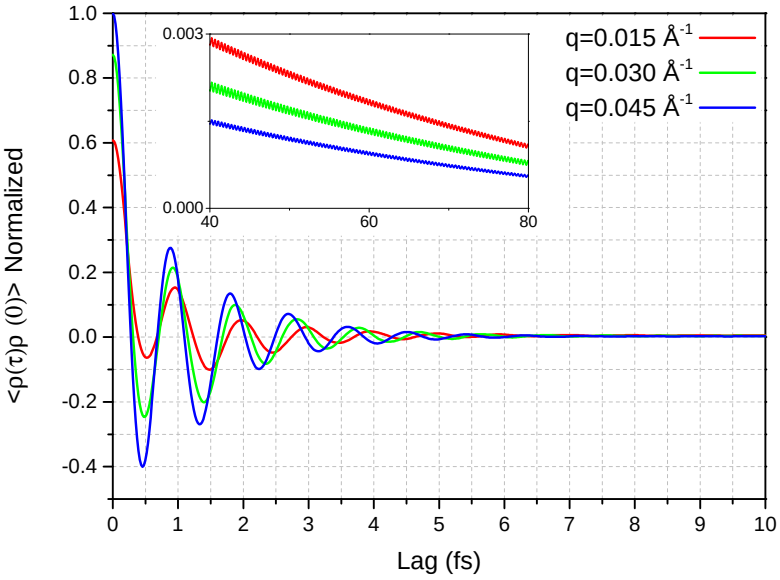

Figure 4.4: Density ACF of Lorentz oscillator model, with inset showing long-time behaviour.

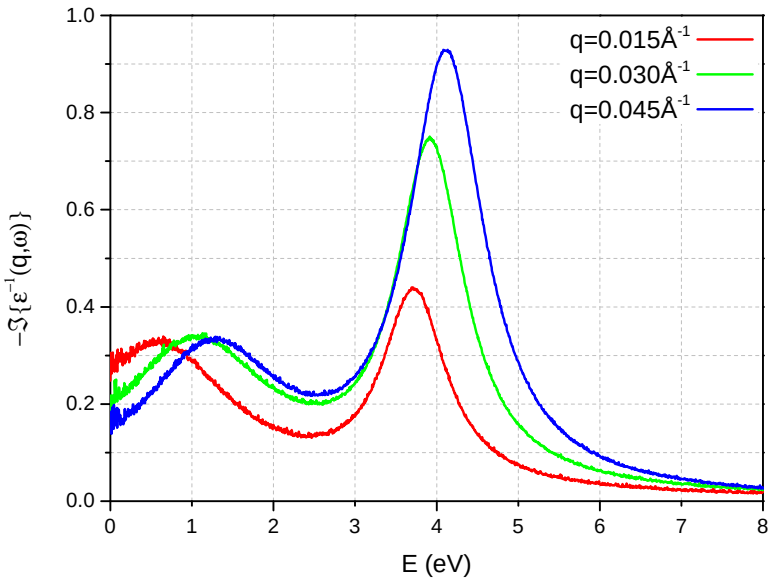

Figure 4.5: EELS of Lorentz model with additive $1/f$ noise.

EELS, while the second peaks are virtually identical. The density ACF obtained from the Lorentz EELS is shown in Fig. 4.4. We note that the initial decay is almost identical to that of ideal graphene, further implying that it is the second peak of the EELS, related to plasmonic resonance, which most strongly determines the initial decay of the density ACF, with the period of the ACF being directly related to the resonance frequency. The long-time behaviour of the Lorentz density ACF, shown in the inset of Fig. 4.4 shows a drastic departure from that of Fig.4.2. While the long-time behaviour of the graphene density ACF displays random noise, the long-time behaviour of the Lorentz density ACF displays sinusoidal behaviour enveloped by an exponential decay. From this observation it is clear that the long-time behaviour of the density ACF displays the noise characteristics contained in the EELS. In order to further investigate the noise characteristics of the density ACF of graphene, we insert additive $1/f^2$ noise and additive white noise into the Lorentz EELS. Fig. 4.5 and Fig. 4.7 show the results for $1/f$ and white noise respectively, with the corresponding density ACF shown in Fig. 4.6 and Fig. 4.8 respectively. Even with the addition of artificial noise, the initial decay of the density ACF in Fig. 4.6 and Fig. 4.8 is virtually unchanged. The long-time behaviour of the density ACF of the Lorentz model with $1/f$ noise and white noise, shown in the insets of Fig. 4.6 and Fig. 4.8

[2]See appendix A for a discussion of the $1/f$ noise algorithm

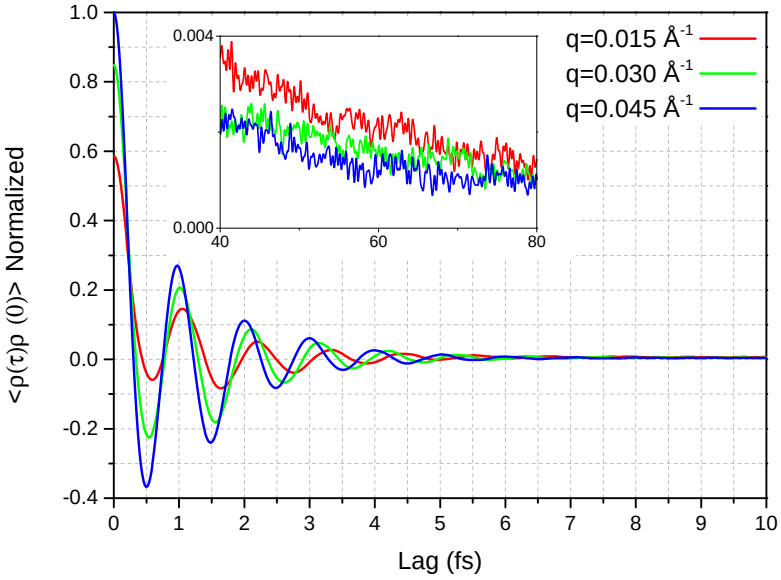

Figure 4.6: Density ACF of Lorentz model with additive $1/f$ noise, with inset showing long-time behaviour.

respectively clearly shows the influence of the artificial noise on the long-time behaviour. Clearly the tail of the density ACF is highly sensitive to the characteristics of the noise present in the EELS, and may thus be used to further investigate noise characteristics associated with density fluctuations. Comparing the long-time behaviour shown in Fig. 4.2, Fig. 4.6, and Fig. 4.8, it is clear that the noise present in the graphene EELS is neither of white noise nor $1/f$ noise, and is likely a combination of several noise processes, due to both physical processes and numerical limitations.

4.4 Conclusions

The relation given in Eq. 4.10 was used to study density fluctuations using the EELS of ideal graphene, computed using linear-response time-dependent density functional theory, at various points in reciprocal space. It was found that the initial decay of the density ACF is related to plasmonic resonance, and that the long-time behaviour of the density ACF is sensitive to the characteristics of the noise in the EELS. As the EELS may be obtained both numerically and experimentally, the current approach provides a useful method for studying density fluctuations using the EELS, and the associated noise. In principle it is possible to model the noise associated with density

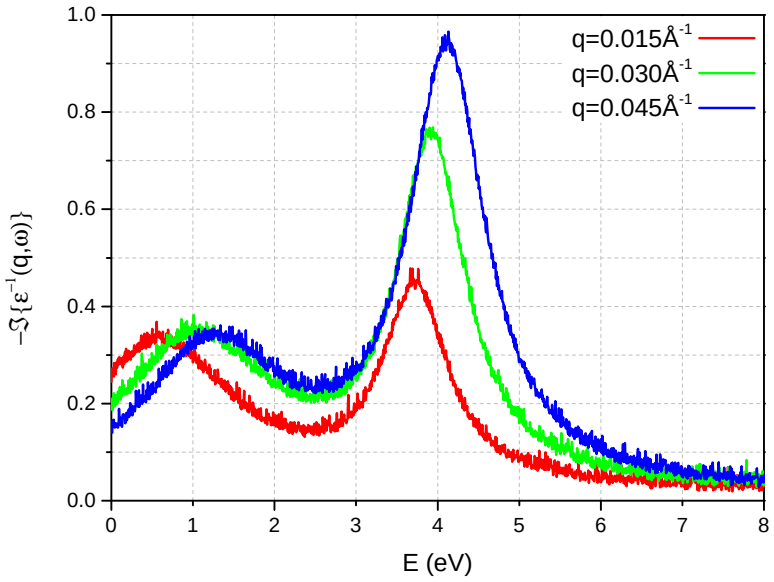

Figure 4.7: EELS of Lorentz model with additive white noise.

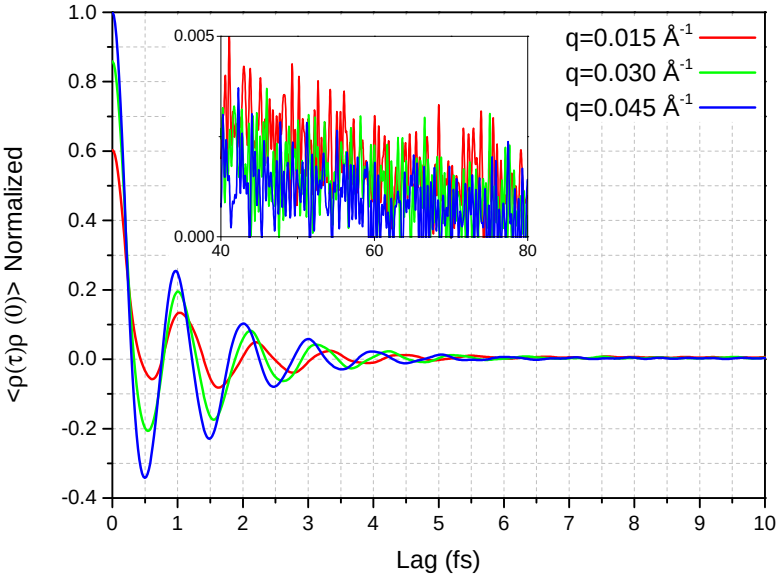

Figure 4.8: Density ACF of Lorentz model with additive white noise, with inset showing long-time behaviour.

fluctuations using more sophisticated regression models, and by combining results from numerical and experimental studies of the EELS.

Chapter 5

Dephasing and the Electron Energy-Loss Spectrum

When a system is coupled to an external heat bath, the coherence of the quantum states decays as a function of time due to its degrees of freedom becoming entangled with those of the environment[34]. This effect is due to quantum interference and is known as dephasing. Many different approaches have been developed to study dephasing in a variety of contexts[30][33][34][46][52][50][86][100]. This discussion is limited to the dephasing of fermionic systems, in particular the electron gas. The discussion of dephasing presented here is based on the work of Cohen et al.[32][29][30][31][33][34][1]

5.1 Many-Body Formulation of Dephasing

Consider an electron gas coupled to an environment with an interaction term of the form

$$\hat{V}(t) = \int \mathrm{d}\mathbf{r}\, \hat{n}(\mathbf{r},t)\hat{K}(\mathbf{r},t) \tag{5.1}$$

In the above $\hat{n}(\mathbf{r},t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t))$ is the many-body number density and $\hat{K}(\mathbf{r},t)$ represents the fluctuations of the environment. The spectral functions describing the fluctuations of the environment and electron gas are respectively given by

$$S_{\hat{K}}(\mathbf{q},\omega) = \int \mathrm{d}t e^{-i\omega t}\langle \hat{K}_{\mathbf{q}}(t), \hat{K}_{-\mathbf{q}}(0)\rangle \tag{5.2}$$

$$S_{\hat{n}}(\mathbf{q},\omega) = L^d \int \mathrm{d}t e^{-i\omega t}\langle \hat{n}_{\mathbf{q}}(t), \hat{n}_{-\mathbf{q}}(0)\rangle \tag{5.3}$$

where $\hat{K}_{\mathbf{q}}(t)$ and $\hat{n}_{\mathbf{q}}(t)$ are the spacial Fourier transforms of $\hat{F}(x,t)$ and $\hat{n}(x,t)$ respectively, and L^d is the volume of the system. Following [34]

[1] To conform with the notation used in [34] we use natural units, i.e. $\hbar = k_B = 1$

we define the probability of the system-environment coupling inducing a transition in terms of the two-time correlation function of the interaction term $\hat{V}$ for times t_1 and t_2:

$$p(t) = \int_0^t \mathrm{d}t_2 \int_0^t \mathrm{d}t_1 \langle \hat{V}(t_2), \hat{V}(t_1) \rangle \tag{5.4a}$$

$$\approx t \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \int \frac{\mathrm{d}\omega}{2\pi} S_{\hat{K}}(\mathbf{q}, \omega) S_{\hat{n}}(-\mathbf{q}, -\omega) \tag{5.4b}$$

where the second line follows by using the definitions of $S_{\hat{K}}$ and $S_{\hat{n}}$, and taking the appropriate limiting procedure as specified in [34]. Using the above, we define the dephasing rate Λ of the system by [34]

$$\Lambda = \frac{1}{(2\pi)^4} \int_0^\infty \mathrm{d}^3 q \int_0^\infty \mathrm{d}\omega \, S_{\hat{K}}(\mathbf{q}, \omega) S_{\hat{n}}(-\mathbf{q}, -\omega) \tag{5.5}$$

Using the principle of detailed balance, Eq. 2.58, the dephasing rate becomes

$$\Lambda = \frac{1}{(2\pi)^4} \int_0^\infty \mathrm{d}^3 q \int_0^\infty \mathrm{d}\omega \, S_{\hat{K}}(\mathbf{q}, \omega) e^{-\omega/T} S_{\hat{n}}(\mathbf{q}, \omega) \tag{5.6}$$

If we take into account the screening effect of the long-range Coulomb interaction, we can express $S_{\hat{K}}(\mathbf{q}, \omega)$ in terms of $S_{\hat{n}}(\mathbf{q}, \omega)$[34]

$$S_{\hat{K}}(\mathbf{q}, \omega) = \frac{1}{L^d} \left(\frac{4\pi e^2}{q^2} \right)^2 S_{\hat{n}}(\mathbf{q}, \omega) \tag{5.7}$$

Combining Eq. 5.6 with Eq. 5.7 gives

$$\Lambda = \frac{1}{(2\pi)^4} \int_0^\infty \mathrm{d}^3 q \int_0^\infty \mathrm{d}\omega \, \frac{1}{L^d} \left(\frac{4\pi e^2}{q^2} \right)^2 e^{-\omega/T} |S_{\hat{n}}(\mathbf{q}, \omega)|^2 \tag{5.8}$$

Using the fluctuation-dissipation theorem, Eq. 2.61, and the relation between the dielectric function and the density response, Eq. 4.5, we may rewrite $S_{\hat{n}}(\mathbf{q}, \omega)$ as

$$S_{\hat{n}}(\mathbf{q}, \omega) = 2L^d \frac{q^2}{4\pi e^2} \frac{\Im\{\epsilon^{-1}(\mathbf{q}, \omega)\}}{e^{-\omega/T} - 1} \tag{5.9}$$

Using the above the dephasing rate becomes

$$\Lambda = \frac{4L^d}{(2\pi)^4} \int_0^\infty \mathrm{d}^3 q \int_0^\infty \mathrm{d}\omega \, e^{-\omega/T} \left(\frac{\Im\{\epsilon^{-1}(\mathbf{q}, \omega)\}}{e^{-\omega/T} - 1} \right)^2 \tag{5.10}$$

The above relation is a completely new result and allows us to calculate dephasing rates for arbitrary materials using nothing more than the EELS, which is accessible both numerically and experimentally. Further, by virtue of the EELS, the above relation contains both electron-electron interactions,

and electron-phonon interactions. While an expression relating the dephasing rate to the EELS has been derived previously using the path-integral formalism[51]. The result presented in that work requires the additional knowledge of the diffusion coefficient of the system. In contrast the present formalism requires only the EELS and allows for simple calculations in practice. In order to use Eq. 5.10 in practice, we restrict the k-space integral to the first Brillouin zone. Using the relation between the volume of a primitive cell in real space L^d, and the corresponding volume in reciprocal space $\Omega = (2\pi)^3 L^{-d}$, the dephasing rate becomes

$$\Lambda = \frac{2}{\pi}\frac{1}{\Omega}\int_{BZ} \mathrm{d}^3 q \int_0^\infty \mathrm{d}\omega\, e^{-\omega/T}\left(\frac{\Im\{\epsilon^{-1}(\mathbf{q},\omega)\}}{e^{-\omega/T}-1}\right)^2 \tag{5.11}$$

where the integral over the Brillouin zone is computed as a weighted sum over k-points, i.e.

$$\frac{1}{\Omega}\int_{BZ} \mathrm{d}^3 q \rightarrow \sum_i \omega_{\mathbf{q}_i} \tag{5.12}$$

where $\omega_{\mathbf{q}_i}$ is the weight of the reciprocal space point $\mathbf{q}_i$. Finally, noting that the EELS is defined as $-\Im\{\epsilon(\mathbf{q},\omega)\}$ we rewrite Eq. 5.11 as

$$\Lambda = \frac{2}{\pi}\sum_i \omega_{\mathbf{q}_i}\int_0^\infty \mathrm{d}\omega\, e^{-\omega/T}\left(\frac{-\Im\{\epsilon^{-1}(\mathbf{q},\omega)\}}{1-e^{-\omega/T}}\right)^2 \tag{5.13}$$

5.2 Dephasing in Graphene

In this section I illustrate the use of Eq. 5.13 for the calculation of dephasing rates using the EELS of ideal graphene. Fig. 5.1 shows the first Brillouin zone of graphene with the shaded region showing the irreducible wedge over which the EELS of ideal graphene was computed. The EELS over the irreducible wedge of the first Brillouin zone of graphene, computed using linear-response time-dependent density functional theory calculations [107] is shown in Fig. 5.2. These calculations were done at the temperature $T = 0.025$ eV. As can be seen in Fig. 5.2, the EELS varies sufficiently smoothly such that numerical integration may be used to compute the frequency integral of Eq. 5.13. The dephasing rate computed using the EELS of Fig. 5.2 is $\Lambda \approx 0.0016$ eV, corresponding to a dephasing time of $\Lambda^{-1} \approx 2.6$ ps.

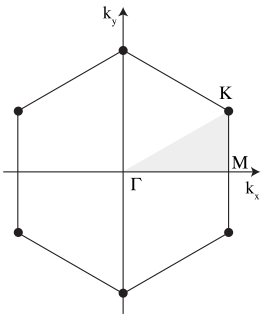

Figure 5.1: Brillouin zone of graphene with irreducible wedge shown by shaded region.

In the study of dephasing in mesoscopic systems it is common practice to treat the low-temperature

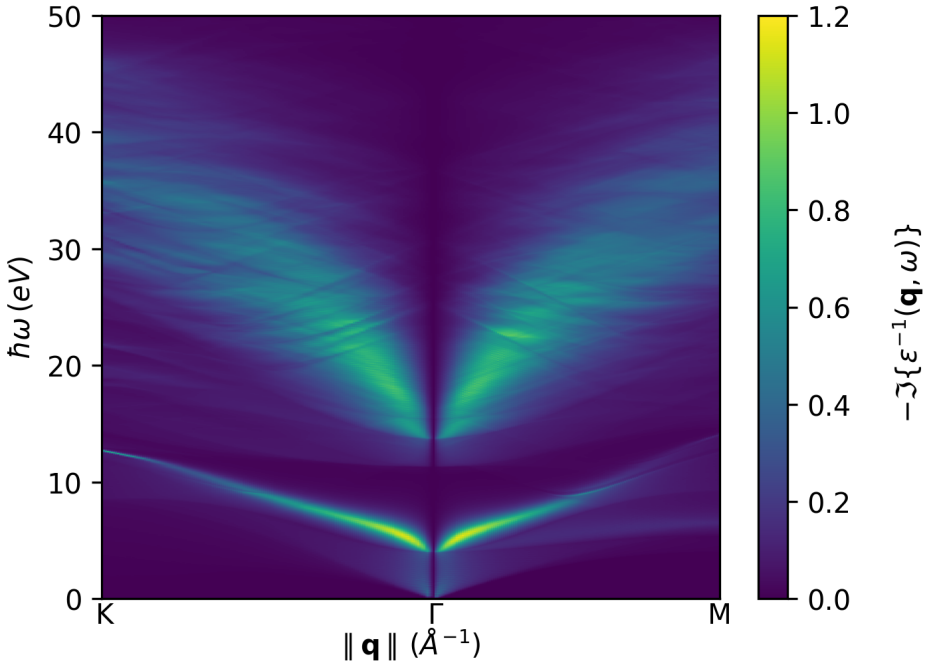

Figure 5.2: EELS of ideal graphene over irreducible wedge of Brillouin zone.

and high-temperature regimes separately [33][56]. This is not necessary when using the current formalism. Further, the formalism developed here has the benefit of including both electron-electron and electron-phonon couplings by virtue of the EELS. In semiconductors, the main contributions to the dephasing time are electron-electron and the electron-phonon interactions [56], with the electron-electron coupling dominating at high temperatures in graphene [99][57][102]. The electron-electron scattering rate Λ_{ee} is given by [102]

$$\Lambda_{ee} = \alpha \frac{T}{2\epsilon_F \tau_p} \ln(2\epsilon_F \tau_p) + \beta \frac{\pi}{4} \frac{T^2}{\epsilon_F} \ln\left(\frac{2\epsilon_F}{T}\right) \tag{5.14}$$

where α and β are constants determined by the system, ϵ_F is the Fermi-energy, and τ_p is the momentum relaxation time. Studies of dephasing in graphene using the above relation have yielded dephasing times $\Lambda^{-1} \sim$ ps [102], which are in agreement with the result obtained using Eq. 5.13.

5.3 Conclusions

The dephasing rate of a system has important implications for the scalability of solid-state quantum computers [56] as well as the detection of defects in systems [102], and so is of great importance in the study of nano-devices. In this section I derived a new relation enabling the calculation of dephasing rates using the EELS, a quantity which is accessible both via numerical calculations and experiment. This was achieved by combining results from the many-body formulation of dephasing with the fluctuation dissipation theorem. Further, the relation obtained is particularly well suited for practical use. The formalism developed in this chapter has the benefit of including both electron-electron interactions and electron-phonon interactions by virtue of the EELS, and thus allows for a uniform treatment of the study of dephasing in both the high-temperature and low-temperature regimes. Another benefit of the current approach is the absence of extraneous system-specific constants. For illustrative purposes this relation was applied to the study of dephasing in graphene. It was found that the results predicted by Eq. 5.13 are in agreement with previous studies of dephasing in graphene[102].

Chapter 6

Summary

The main focus of this work was on the development of methods for the study of fluctuation phenomena in systems. Several novel methods were developed enabling the study of physical processes related to charge-density fluctuations. In chapter 3 I developed a stochastic model of charge-density fluctuations based on the Boltzmann equation. In this model it was assumed that the particle position is given by the product of the particle's comoving coordinate with a random process. Using results from Eulerian perturbation theory I then derived an equation of motion for the density fluctuations. Under simplifying assumptions regarding the random process coupled to the comoving coordinates, this equation can be solved. Using these assumptions, the resulting particle trajectories were found to be given by a geometric Brownian process, and the equation of motion was solved analytically. In chapter 4 I derived a numerical method enabling the calculation of the ACF of density fluctuations using the dielectric response of an electron gas. This approach was then illustrated using the EELS of ideal graphene. It was found that the density ACF contains information regarding plasmonic resonance of materials, as well as the characteristics of noise present in the EELS. By combining results from numerical and experimental studies of the EELS with the method developed, it is hoped that new valuable insights into the nature of noise in systems may be obtained via the ACF of the fluctuation process. In chapter 5 I extended the many-body formalism of dephasing using the fluctuation-dissipation theorem, allowing for the calculation of dephasing rates using the EELS. This approach has the benefit of enabling a uniform treatment of dephasing in both high-temperature and low-temperature regimes, and contains both electron-electron interactions and electron-phonon interactions by virtue of the EELS, which are the primary contributions to the dephasing rate in low-dimensional semiconductor systems. Further, the formalism developed is particularly well suited to practical use, and is independent of system-specific constants. The use of this approach was illustrated using the EELS of graphene. It was found

that the results predicted by this model were in agreement with previous studies of dephasing in graphene. Due to the generality of the fluctuation-dissipation theorem, many of the approaches developed in this thesis may be extended to study both arbitrary materials and the effects of different fluctuation phenomena in physical systems. It is hoped that the use of the methods developed in this work will allow for a deeper understanding of fluctuation phenomena and the associated noise in nanosystems.

Appendix A

Simulation of $1/f^{\gamma}$ Noise

In this section I present an outline of the algorithm used to generate $1/f^{\gamma}$ noise, as presented by N. Kasdin[65]. Before presenting the algorithm I give a brief overview of some concepts and results associated with the discrete simulation of time-series based on [109]. A stochastic process $\{X_t : t \in \mathbb{Z}\}$ is called a linear process if it is defined by

$$X_t = \sum_{i=-\infty}^{\infty} g_i Y_{t-i} \tag{A.1}$$

where the g_i are constants, and Y_t is a zero mean stochastic process. Given the above linear process, we call Y_t the input, X_t the output, and g_i the filter weights, with the impulse response of the filter given by the set $\{g_i : i \in \mathbb{Z}\}$. We call a process an autoregressive model of order n, AR(n), if it can be expressed as

$$X_t = \sum_{i=1}^{n} g_i X_{t-i} + w_t \tag{A.2}$$

where g_i are nonzero real constants, and w_t is a white noise process. To simulate discrete noise with a power spectra of the form $1/f^{\gamma}$, we use an AR model with impulse response given by

$$\begin{aligned} g_0 &= 1 \\ g_n &= \left(n - 1 - \frac{\gamma}{2}\right)\frac{\gamma_{n-1}}{n} \end{aligned} \tag{A.3}$$

With the above model we are able to simulate discrete time-series of various noise types including white noise with $\gamma = 0$, $1/f$ noise with $\gamma = 1$, and Brownian noise with $\gamma = 2$. Realizations of these different noise types are shown in Figs. 2.1 - 2.3.

Appendix B

Solution of Equation of Motion of Density Fluctuations

In this section I give a detailed solution of Eq. 3.25. Consider the second order differential equation

$$g''(t) + ug'(t) + v^2 g(t) = 0 \tag{B.1}$$

where the coefficients u and v^2 are real. The Laplace transform of $g(t)$ is defined by[3]

$$G(s) = \mathcal{L}\{g(t)\} = \int_0^\infty \mathrm{d}t\, e^{-st} g(t) \tag{B.2}$$

with inverse transform given by

$$g(t) = \mathcal{L}^{-1}\{G(s)\} = \frac{1}{2\pi i} \lim_{\epsilon\to\infty} \int_{l-i\epsilon}^{l+i\epsilon} \mathrm{d}s\, e^{st} G(s) \tag{B.3}$$

where $l \in \mathbb{R}$. The Laplace transform of the n-th derivative of $g(t)$ satisfies [3]

$$\mathcal{L}\{g^{(n)}(t)\} = s^n G(s) - \sum_{i=0}^{n-1} s^{n-(i+1)} G^{(i)}(0) \tag{B.4}$$

Applying the Laplace transform to Eq. B.1 gives

$$s^2 G(s) - sg(0) - g'(0) + u(sG(s) - g(0)) + v^2 G(s) = 0 \tag{B.5}$$

or equivalently

$$G(s) = \frac{u+s}{s^2 + us + v^2} g(0) + \frac{1}{s^2 + us + v^2} g'(0) \tag{B.6}$$

If we define α and β such that

$$\alpha = -\frac{1}{2}u \tag{B.7}$$

$$\beta^2 = v^2 - \frac{1}{4}u^2 \tag{B.8}$$

then $s^2 + us + v^2 = (s-\alpha)^2 + \beta^2$ and $u + s = (s-\alpha) - \alpha$ and so we can rewrite Eq. B.6 as

$$G(s) = \left[\frac{s-\alpha}{(s-\alpha)^2+\beta^2} - \frac{\alpha}{(s-\alpha)^2+\beta^2}\right]g(0) + \frac{1}{(s-\alpha)^2+\beta^2}g'(0) \tag{B.9}$$

Using the properties of the inverse Laplace transform[3] it follows that

$$\mathcal{L}^{-1}\left\{\frac{s-\alpha}{(s-\alpha)^2+\beta^2}\right\} = e^{\alpha t}\cos(\beta t) \tag{B.10}$$

$$\mathcal{L}^{-1}\left\{\frac{\alpha}{(s-\alpha)^2+\beta^2}\right\} = \frac{\alpha}{\beta}e^{\alpha t}\sin(\beta t) \tag{B.11}$$

$$\mathcal{L}^{-1}\left\{\frac{1}{(s-\alpha)^2+\beta^2}\right\} = \frac{1}{\beta}e^{\alpha t}\sin \tag{B.12}$$

Hence the solution of Eq. B.1 is given by

$$g(t) = e^{\alpha t}\left[\left(\cos(\beta t) - \frac{\alpha}{\beta}\sin(\beta t)\right)g(0) + \frac{1}{\beta}\sin(\beta t)g'(0)\right] \tag{B.13}$$

Appendix C

Source Code Listing

In all code listings it is assumed numpy has been imported as np.

```
"""
file: autocorr.py

Computes autoccorrelation function
"""


def autocorr(data, method="data"):
    """
    Compute autocorrelation function.

    Args
    ----
    data: numpy array

    method: string, "data" or "pow"
        Specify method used, "data" computes autocorrelation
        from autocorrelation of time-series, "pow" computes
        autocorrelation from inverse fft of power spectrum.
    """
    if not (type(data).__module__ == np.__name__):
        raise TypeError("Input must be of type numpy.ndarray")
    if (np.count_nonzero(data) == 0):
        raise ValueError("Input must be nonzero numpy.ndarray")

    if method == "data":
        data = np.array([i - np.mean(data) for i in data])
        autocorr = np.correlate(data, data, mode='full') / np.
    sum(data**2)
        autocorr = autocorr[len(autocorr)/2:]

    elif method == "pow":
        # Specification of np.fft.ifft requires data
        # to be symmetric about zero frequency
        if np.array_equal(data[1:len(data)/2 + 1],
                data[len(data)/2 + 1:][::-1]):
```

```
            autocorr = np.fft.ifft(data)
        else:
            data = np.append(data, data[1:][::-1])
            autocorr = np.fft.ifft(data)
            autocorr = autocorr[:len(autocorr)/2 + 1]
    else:
        raise ValueError("Argument method must be in (\"data\",
    \"pow\").")

    return autocorr
```

Listing C.1: Code to compute autocorrelation function

```
"""
file: noise.py

Routines to generate random noise
"""


def pink_noise(n):
    """
    Generates 1/f (pink) noise

    Args
    ----
    n : int
        number of samples to produce

    Notes
    -----
    * The following uses n*2 due to the symmetry of the FFT
    * h is array containing coefficients for coloured noise
      generation
    * noise output is a convolution of h coefficients with
      white noise process
    * This routine is based on the algorithm discussed
      in Appendix A
    """
    if n <= 0:
        raise ValueError("Input must be greater than zero")

    h = np.zeros(n*2)
    h[0] = 1
    for i in range(1, n*2):
        h[i] = (0.5 + i - 1) * h[i-1] / float(i)
    h = np.fft.fft(h)

    seed = np.random.normal(0, 1, size=n*2)
    seed = np.fft.fft(seed)

    for i in range(0, n*2, 2):
        if i < 2:
            seed[i] = seed[i] * h[i]
```

```
        else:
            seed[i] = seed[i] * h[i] - seed[i+1]*h[i+1]
            seed[i+1] = seed[i] * h[i+1] - seed[i+1]*h[i]

    noise = np.fft.ifft(seed)

    return noise[:n] / max(noise)


def geom_brownian_noise(n, drift=0.1, vol=0.1, init=1,
        timestep=0.01):
    """
    Generate geometric Brownian noise

    n : int
        Number of samples

    drift : float
        Drift factor

    vol : float
        Volatility

    init : float
        Initial condition

    timestep : float
        Time-step
    """
    if n < 0:
        raise ValueError("Input must be greater than zero")

    time = np.linspace(0, n*timestep, n)
    bnoise = np.random.standard_normal(size=n)
    bnoise = np.cumsum(bnoise)*np.sqrt(timestep)

    return np.array([init*np.exp((drift - 0.5*vol**2)*t + \
            vol*w) for t, w in zip(time, bnoise)])
```

Listing C.2: Code to generate random noise

```
"""
file: dephasing.py

Routine to generate dephasing rate using eels.
"""


def dephasing_rate(energy, eels, weights, T = 0.02585199105):
    """Computes dephasing rate in eV using eels

    Input
    -----
    energy : ndarray
```

```
    1-dimensional array corresponding to energy scale
    values are in units of eV

eels : ndarray
    2-dimensional array spanning different q-points
    and energy values given in energy

weights : ndarray
    k-point weights of irreducible Brillouin zone

T : float
    Thermodynamic temperature in natural units
"""

temp_eels = np.array(copy.deepcopy(eels))

for integrand in temp_eels:
    for i in range(1, len(energy)):
        integrand[i] /= (1 - np.exp(-energy[i]/T))
        integrand[i] *= integrand[i]
        integrand[i] *= np.exp(-energy[i]/T)

integrand = np.trapz(temp_eels[:, 1:], axis=1)

return 2*pow(np.pi, -1)*sum(w*i for w, i in zip(weights,
        integrand))
```

Listing C.3: Code to compute dephasing rate

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