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UMI
TOPICS IN THE STATISTICAL PHYSICS OF DISORDERED AND INHOMOGENEOUS SYSTEMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By

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*$ * * * *$

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ABSTRACT

The principal aim of this thesis is to study the physics of systems that are disordered and inhomogeneous. The systems we study fall under two categories: A) Liquid semiconductors and semiconductor surfaces B) Simple model systems with disorder. In the following, we summarize the problems studied.

A) In recent years, due to the exponential increase in computational power and the development of innovative techniques of computation, it has become possible to carry out 'first principles' studies of the properties of materials. By first principles studies, we mean that there are no adjustable parameters in the theory and the only necessary inputs are the atomic numbers and electronic configurations of the atoms involved. These studies are generally referred to as *ab initio* calculations and the principal aim of this thesis is to carry out *ab initio* studies of semiconductors and to determine their properties in the liquid phase. We look at liquid Germanium, liquid Gallium-Germanium alloys and liquid Gallium Arsenide, and for these materials we obtain structural properties such as the structure factor, transport properties such as the diffusion constant, and electronic properties such as the low-frequency conductivity.

A related aim is to apply the techniques so developed to the study of semiconductor surfaces. The study of these surfaces involves a complex interplay between the atomic and the electronic structure which necessitates the use of first principles approaches. We will study in particular the growth of Silicon on Ge(001) surfaces, for which we
study the energetics and scanning tunneling microscopy (STM) images pertaining to the initial stages of growth.

B) While *ab initio* techniques are very useful in obtaining quantitative information for materials, there are many complex systems which cannot be studied using these techniques. We are often interested in qualitative insights for such systems, and an alternate approach is to study simple models. In the rest of this thesis we study two such simple models for disordered systems. We will look at a class of networks called small-world networks which have attracted a lot of attention lately due to their applications to a wide range of systems with disorder and randomness. For these systems we will derive some exact relations which greatly aid in numerical computation of properties of small-world networks. We will also consider their application to a simple model of biological evolution. The other model system we study is the frustrated XY-model which is relevant in modeling a class of granular high-$T_c$ superconductors. For these systems we propose a novel way of characterizing the ground state and we confirm our ansatz numerically.
To my parents
ACKNOWLEDGMENTS

I would like to express my deepest thanks to my adviser, David Stroud, for his unflagging support and guidance through all these years. He gave me the freedom to work on various topics and ably guided and aided me through all of them. It has been a pleasure working with him.

I would also like to thank the other faculty members at OSU who have taught me physics and with whom I've had many helpful discussions: Daniel Cox, John Wilkins, Jonathan Pelz, Robert Perry, William Saam, Fernand Hayot, C. Jayaprakash and Jason Ho.

I would also like to express my deep gratitude towards Matthias Scheffler and the research group at the Fritz-Haber Institut in Berlin. I will never forget their hospitality while I was visiting them in Berlin. It was there that I learnt about 'first-principles' calculations (which occupy the bulk of this thesis) and their continued support, computationally and otherwise, has meant a lot to me.

When I started physics research, I had a highly individualistic bent of mind. Over the years, I have learnt physics research is done best when you have good collaborators. I would like to thank all my collaborators who have worked with me on different projects: Eivind Almaas, Sanjay Khare, Wilfried Aulbur and Kent Fisher. Working with Eivind, in particular, has been a very rewarding experience which we both hope will continue.
Thanks also to my group members Roman Sasik, Seungoh Ryu, Wenbin Yu, Ingye Hwang, Eric Roddick, Kent Harbaugh, Greg Mohler, Sergei Barabash for numerous helpful discussions and their constant support and encouragement. I would also like to thank other graduate students and postdocs with whom I have shared many interesting talks and with whom it has been fun interacting with: Stefan Turneaure, Matt Trawick, Al Mieth, Avik Ghosh, Rudra Bandhu, Manoj Kaplinghat, Jim Kneller, John Phillips, Dallas Trinkle, Daniel Cociorova, Wei Wang, Roger Sakhel, Hsung-Jai Ihm, Jon-Frederick Neilsen, Jens Andersen, Viktor Martisovits Vivek Shenoy, Krystof Gorny, Mihai Girtu, Jian Chen, Jeongnim Kim, Florian Kirchoff and Jeff LePage. My extended gratitude goes to to Brenda Mellett and Shelley Palmer for their help on innumerable occasions.

Words cannot adequately express my gratitude towards my parents and my sister Pallavi. It has been their love and constant support that has been the source of strength and inspiration for me through both good times and bad times. Their faith in my abilities and continued encouragement has made my journey through physics, and life, so much more worthwhile.
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R. V. Kulkarni, E. Almaas, and D. Stroud, “Exact results and scaling properties of small-world networks”. cond-mat/9908216 *to be published in Phys. Rev. E*
FIELDS OF STUDY

Major Field: Physics
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CHAPTER 1

INTRODUCTION

Condensed matter physics, as the name implies, involves the study of matter in a solid or liquid state such that each of the constituent particles interacts with many of its neighbours. The constituent particles are generally electrons and nuclei and loosely speaking, a condensed matter system may be defined as an assembly of positively charged nuclei with a compensating number of electrons (typically \(10^{23}\)). Thus the problems of condensed matter physics are essentially many-body problems which are intrinsically quantum mechanical in nature and thereby rather intractable. Clearly one has to make certain approximations (and often seemingly drastic assumptions like the independent electron approximation) in dealing with these problems. One approach is to look at simplified model systems which elucidate the basic physics of the real system(s) being studied e.g. the Anderson model for magnetic impurities in a metal. The study of simplified model systems has been a source of great insights into the nature of condensed matter systems. While this approach is both insightful and appealing, one is often interested in properties of the systems studied where 'the devil lies in the details'. It is also desirable, based upon practical as well as aesthetic grounds, to have an approximation scheme which is generic to all condensed matter
systems. At first glance this would seem to be a rather difficult task since what we want is an approximation scheme which is at once universal (i.e. independent of the particulars of the system being studied) and capable of providing us with detailed information about the electronic and structural properties of a wide variety of systems and materials. The good news is that such a scheme does exist and it has been used extensively (and often successfully) to calculate the ground state properties of condensed-matter systems. Such calculations are frequently referred to as \textit{ab initio} calculations and the fundamental theory behind these calculations is density-functional theory (DFT).

The major aim of this thesis is to apply the techniques of DFT to the study of semiconductors, both in the liquid and solid state. Specifically we shall study the following systems: 1) Liquid Germanium (Ge) 2) Liquid Gallium-Germanium alloys 3) Liquid GaAs, on and off stoichiometry. The electronic charge density in these systems is strongly inhomogeneous which makes analysis more difficult and the liquid state is further complicated by the fact that the system is disordered. In the solid state, the study of semiconductor surfaces is of great interest, both theoretically and technologically. Accordingly we shall also study the problem of growth processes on Si(001) and Ge(001) surfaces using the techniques of DFT. In the Appendix, we also explore some aspects of the newly introduced Polarization Density-Functional theory (PDFT) and discuss its relevance to the optical properties of semiconductors.

Another aim is to study simplified model systems from which general insights into the nature of condensed matter systems can be drawn. In particular we shall look at a version of the frustrated XY-model which is of particular relevance to high-$T_c$ cuprate superconductors. We will introduce a novel set of excitations for the XY-model which
feature in the ground state of the frustrated version. We shall also look at a class of networks called "small-world" networks which were introduced very recently and have generated a lot of interest since. This stems from their possible application to wide range of systems ranging from social networks to genetic regulatory nets. For these networks we derive some exact relations and explore their scaling properties. We also consider their application to a simple model of evolution.

The outline of this thesis is as follows: In Chapter I we discuss the basics of DFT and ab initio molecular dynamics. In Chapters 2-4 we apply these techniques to the study of liquid semiconductors. In Chapter 5 we use the same techniques to study the problem of growth on Silicon and Germanium surfaces. Chapters 6 and 7 involve the study of simplified model systems with disorder. In Chapter 6 we study the properties of an important class of networks with disorder, i.e. the small-world networks referred to in the preceding paragraph. Finally in Chapter 7, we look at a particular example of the frustrated XY-model.

We begin with a very brief historical overview of DFT. The origins of DFT can be traced to the Thomas-Fermi theory [1] of the inhomogeneous electron gas which showed that the many-body problem can be statistically dealt with as a one-body problem by relating the local electron density \( n(\mathbf{r}) \) to the average potential \( V(\mathbf{r}) \) felt by the electrons. Subsequently there were many attempts to use the ground-state density (as opposed to the many-body wavefunction) as the basic variable to study properties of the many-body system, however a rigorous mathematical foundation for density-based theories was established only in 1964 by two theorems by Hohenberg and Kohn.[2] These theorems form the basis of density-functional theory. In the
following sections we shall state these theorems and discuss a scheme for implementing practical calculations using the same.

1.1 Hohenberg-Kohn Theorems

The many-body problem we want to investigate is that of a system of electrons moving under the influence of an external potential $v(\vec{r})$ and of their mutual Coulomb repulsion. In atomic units the Hamiltonian for the system has the form

$$ H = T + V + U $$

(1.1)

where

$$ T = \frac{1}{2} \int \nabla \psi^*(\vec{r}) \cdot \nabla \psi(\vec{r}) d\vec{r} $$

(1.2)

$$ V = \int v(\vec{r}) \psi^*(\vec{r}) \psi(\vec{r}) d\vec{r} $$

(1.3)

$$ U = \frac{1}{2} \int \frac{1}{|\vec{r} - \vec{r'}|} \psi^*(\vec{r}) \psi^*(\vec{r'}) \psi(\vec{r'}) \psi(\vec{r}) d\vec{r} d\vec{r'} $$

(1.4)

The density operator is given by

$$ n(\vec{r}) = \psi^*(\vec{r}) \psi(\vec{r}) $$

(1.5)

The Hohenberg-Kohn theorems establish the ground state density of the system (which is the expectation value of the density operator defined above) as a basic variable from a knowledge of which all other properties of the many-body system
can be derived. In the following we shall discuss these theorems which we shall state without proof.

**Theorem I**

If the ground state of the many-body system is non-degenerate then the external potential $v(\vec{r})$ is (to within an additive constant) uniquely determined by the ground-state density $n(\vec{r})$.

Thus there is a one-one correspondence between the density $n(\vec{r})$ in the ground state (assumed nondegenerate) and the external potential $v(\vec{r})$. Furthermore, since $n(\vec{r})$ determines the potential $v(\vec{r})$, it also determines the ground state uniquely as well as all the other electronic properties of the system. This is, in some sense, a very remarkable statement; it implies that all the information contained in the many-body wavefunction (which for a $N$-particle system is defined on a $3N$ dimensional configuration space) is effectively stored in a simple $3$ dimensional function $n(\vec{r})$. Of course, the fact that every physical quantity can be calculated from the ground state density, while interesting in itself, wouldn't be particularly useful unless we had a means of obtaining the ground state density. This is where the second Hohenberg-Kohn theorem comes in.

**Theorem II**

For a given external potential $v(\vec{r})$, the correct $n(\vec{r})$ minimizes the ground state energy, which is a unique functional of $n(\vec{r})$.

The above can be stated mathematically by defining the following energy functional

$$E[n'(\vec{r})] = \int v(\vec{r})n'(\vec{r})d\vec{r} + F[n'(\vec{r})]$$  \hspace{1cm} (1.6)
where

\[ F[n(\vec{r})] = \langle \Psi | T + U | \Psi \rangle \]  

(1.7)

\( \Psi \) is the ground state wavefunction which, according to the Theorem I, is uniquely determined by the ground state density. It should be noted that \( F[n(\vec{r})] \) is a universal functional of the density. For a fixed \( v(\vec{r}) \), Theorem II states that

\[ E[n(\vec{r})] < E[n'(\vec{r})] \]  

(1.8)

for the corresponding ground state density \( n(\vec{r}) \) and that the minimum value \( E[n] \) is the ground state energy associated with \( v(\vec{r}) \).

So now we have a means of calculating the ground state density corresponding to a fixed external potential, we simply have to do a variational search in the space of all possible densities to determine the density which minimises the energy functional defined above. However we are still a long way off from carrying out any practical calculations using this scheme for the following reasons:

1) We don't know the exact form of the functional \( F[n(\vec{r})] \), indeed it is doubtful if we ever will since all the many-body effects are contained in this functional and knowing it exactly would be tantamount to solving the many-body problem.

2) We haven't got a practical scheme to implement the variational search which will give us the ground state density.

In the following section we shall address the second point noted above by presenting a set of equations which effectively carry out the variational search. These are the so-called Kohn-Sham equations and we shall see that the formalism will also lead naturally to an approximation for the functional \( F[n(\vec{r})] \).
1.2 **Kohn-Sham equations**

The key assumption going into the Kohn-Sham procedure [3] is that the ground state density of any interacting system can be reproduced by the ground state density of non-interacting electrons in the presence of a local single particle potential. Thus we make the ansatz that the ground-state density can be constructed from some fictitious single-particle normalised orbitals $\psi_i(\vec{r})$ as

$$ n(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2 $$

(1.9)

The total energy functional $E[n(\vec{r})]$ can be factorised as follows

$$ E[n(\vec{r})] = T_0[n(\vec{r})] + \int v(\vec{r})n(\vec{r})d\vec{r} + \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{\text{xc}}[n(\vec{r})] $$

(1.10)

where $T_0[n(\vec{r})]$ is the kinetic energy of non-interacting electrons with ground-state density $n(\vec{r})$ and all the many-body effects have been transferred onto an unknown functional $E_{\text{xc}}[n(\vec{r})]$. Now minimising $E[n(\vec{r})]$ with respect to variations of $n(\vec{r})$ (using equation (9) above) and subject to the constraint

$$ \int n(\vec{r})d\vec{r} = N $$

(1.11)

we get the following set of self-consistent equations

$$ \left[ -\frac{1}{2} \nabla^2 + v_{\text{eff}}(\vec{r}) \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) $$

(1.12)

$$ n(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2 $$

(1.13)

where

$$ v_{\text{eff}}(\vec{r}) = v(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}d\vec{r}' + \frac{\delta E_{\text{xc}}[n(\vec{r})]}{\delta n(\vec{r})} $$

(1.14)

These are the celebrated Kohn-Sham self-consistent equations. They demonstrate that a complex many-body problem with interacting electrons can be mapped *exactly*
onto a problem of noninteracting electrons in an effective field. Furthermore this effective potential is a local potential, so the degree of complexity involved in solving the Kohn-Sham equations self-consistently is no greater than that involved in solving the self-consistent Hartree equations (at the Hartree-Fock level one has to deal with a non-local potential). The catch of course is that we don't know the exact form of the exchange-correlation potential defined as

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}$$  \hspace{1cm} (1.15)

So what we need now is some approximation for the exchange-correlation functional $E_{xc}[n(\vec{r})]$, knowing which we can obtain $v_{xc}(\vec{r})$ and thereby solve the Kohn-Sham equations. As was remarked in the introduction, one has to make approximations at some stage; the great appeal of DFT in the Kohn-Sham scheme lies in the fact that it reduces the task to that of approximating a single universal functional. Furthermore, it turns out that the simplest approximation, which we shall discuss in the next section, seems to give results in excellent agreement with experiments for a wide range of systems.

### 1.3 The Local Density Approximation (LDA)

Our task now is to find the ground-state energy for a system of interacting electrons which, in general, will be inhomogeneous. The Local Density Approximation (LDA) corresponds to assuming that the exchange-correlation contribution to the ground state energy of the inhomogeneous system can be approximated as a sum of contributions from locally homogeneous parts. Mathematically speaking, LDA corresponds to

$$E_{xc}[n(\vec{r})] = \int \varepsilon_{xc}(n(\vec{r}))n(\vec{r})d\vec{r}$$  \hspace{1cm} (1.16)
where $\varepsilon_{xc}(n)$ is the exchange-correlation energy per particle of a homogeneous electron gas of density $n$. Now the homogeneous electron gas is probably one of the most-studied systems in many-body physics, its role can be likened to that of the harmonic oscillator in quantum mechanics. The earliest attempt to obtain its ground state energy as a function of density can be traced back to Wigner[4] who postulated an interpolation formula connecting analytical results in the high and low-density limits. Over the years increasingly sophisticated approaches have been developed to tackle this problem, one of the formulae which has gained wide popularity in recent years is the parametrization by Perdew and Zunger[5] of the results from Quantum Monte-Carlo simulations by Ceperley and Alder.[6]

Now that we have a functional form for the exchange correlation energy we can attempt to solve the Kohn-Sham equations self-consistently. While this is not an easy task in itself, the meteoric rise in computational power coupled with the development of sophisticated procedures for solving the equations has made it possible to perform calculations for even complicated systems such as amorphous materials and liquids. For most part these calculations employ LDA although it would seem at first glance that LDA is really the simplest approximation one can make and one would require more sophisticated approximations for strongly inhomogeneous systems. Nevertheless LDA continues to give results in good agreement with experiments for systems ranging from atoms to bulk solids. [7]

1.4 The Exchange-Correlation Hole

The surprising success of LDA can be better understood by examining an exact expression for $E_{xc}[n]$ [8]
where \( n_{xc}(\vec{r}_1, \vec{r}_2) \) is the so-called exchange-correlation hole density. It represents the depletion of charge due to exchange and correlation (i.e. Coulomb repulsion) effects around a test charge centred at \( \vec{r}_1 \). In the case of perfect screening the depletion of charge is equal in magnitude to the charge being screened and hence we have the sum rule

\[
\int d\vec{r}_2 n_{xc}(\vec{r}_1, \vec{r}_2) = -1
\]  

It is customary to partition the exchange-correlation hole density in the following manner

\[
n_{xc}(\vec{r}_1, \vec{r}_2) = n(\vec{r}_2) g_{xc}(\vec{r}_1, \vec{r}_2)
\]  

where \( g_{xc}(\vec{r}_1, \vec{r}_2) \) is the exchange-correlation hole distribution function. The local density approximation (LDA) corresponds to

\[
n_{xc}(\vec{r}_1, \vec{r}_2) = n(\vec{r}_2) g_0(|\vec{r}_1 - \vec{r}_2|; n(r_1))
\]

where \( g_0(|\vec{r}_1 - \vec{r}_2|; n) \) is the exchange-correlation hole distribution function for the uniform electron gas at density \( n \). Since we have perfect screening in the case of a uniform electron gas LDA satisfies the sum rule mentioned above. Furthermore if we define the spherical average \( n_{xc}(\vec{r}_1, R) \) of the exchange-correlation hole density \( n_{xc}(\vec{r}_1, \vec{r}_1 + \vec{R}) \) as

\[
n_{xc}(\vec{r}_1, R) = \int n_{xc}(\vec{r}_1, \vec{r}_1 + \vec{R}) \frac{d\Omega_R}{4\pi}
\]

we see that

\[
E_{xc}[n] = \frac{1}{2} \int n(\vec{r}_1) d\vec{r}_1 \int \frac{1}{R} n_{xc}(\vec{r}_1, R) dR
\]
So the exchange-correlation energy only depends on the spherical average of the exchange-correlation hole.

The reasons LDA works so well in most cases is

1) Although it does a poor job of reproducing the exact exchange-correlation hole, it tends to approximate the spherical average quite well.

2) It satisfies the sum rule for the exchange-correlation hole density. Thus even if one makes errors in using LDA there seems to be a cancellation of errors that takes place by virtue of the fact that LDA satisfies the exact sum rule.

Having discussed the remarkable success of LDA and the probable causes for it, we should point out that two its significant failures are the overestimation of the dielectric constant of semiconductors and also the underestimation of the band gap. The band-gap problem is by now well understood [10, 11] and the possible resolution of the dielectric constant problem using a new development called Polarization Density-Functional Theory (PDFT) will be discussed in Appendix A.

So far we have focussed on the theory underlying DFT calculations. We have seen that if we are able to solve the Kohn-Sham equations within LDA then we obtain the ground-state energy and electronic density for a given configurations of ionic positions. Furthermore the Kohn-Sham orbitals, i.e solutions to the KS equations, yield information about the electronic structure in the ground state. In the next section we expand upon how the computations are actually performed.

1.5 Plane-Wave Pseudopotential Approach

In addition to the local density approximation (LDA), we have to make some more approximations in order to solve the Kohn-Sham equations in practice. Among these
Figure 1.1: Pseudo wavefunctions vs the true valence wave functions for the 3s and 3p orbitals of Aluminium

we discuss first the 'pseudopotential' approximation. This approximation has its basis in the observation that most of the electronic behavior of the solid is determined by the electrons occupying the valence bands, and the core electrons are for most part inert. The pseudopotential approximation exploits this by removing the core electrons and replacing them and the strong ionic potential by a weaker pseudopotential which acts on a set of pseudo wavefunctions rather than the true valence wavefunctions. An example of this is indicated in Fig. 1.1.

The figure indicates that there is a core region beyond which pseudo wavefunctions and the true valence wavefunctions are identical. However the true valence
wavefunctions oscillate rapidly within the core region whereas the pseudo wavefunctions vary smoothly and are nodeless. This corresponds to the fact that the strong ionic potential has been replaced by a weaker pseudopotential. The pseudopotential is constructed such that its scattering properties for the pseudo wavefunctions are identical to the scattering properties of the ion and the core electrons for the valence wavefunctions. We shall not discuss the construction of pseudopotentials here, the details of this procedure can be found in the literature [12].

Having made life easier by working with pseudopotentials, we are still faced with the formidable task of obtaining wavefunctions for all the electrons in the system we wish to study. In order to do this, we perform calculations on periodic systems and use Bloch's theorem in the calculation of the wavefunctions. This states that in a periodic solid each electronic wavefunction can be written as a product of a cell-periodic part and a wavelike part

\[
\psi_i(r) = e^{ik \cdot r} \psi_i(r)
\]  

(1.23)

Now, the cell-periodic part of the wavefunction can be expanded in a basis of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the periodic lattice. Thus we can write

\[
f_i(r) = \sum_G c_{i,G} e^{iG \cdot r}
\]

(1.24)

where \(G\) is a reciprocal lattice vector. Using the above equations, we see that the electronic wavefunction can be written as a sum of plane waves

\[
\psi_i(r) = \sum_G c_{i,k+G} e^{i(k+G) \cdot r}
\]

(1.25)

This equation now leads us to our second approximation. In principle, an infinite plane-wave basis set is required to expand the electronic wavefunctions. However,
typically the coefficients of plane-waves with small kinetic energy \( \propto |\mathbf{k} + \mathbf{G}|^2 \) are more important than those with large kinetic energy. Thus we are led to introduce a plane-wave cutoff so as to include only those plane-waves which have kinetic energies less than some cutoff energy. Thus we now have to work with a finite basis set. In actual calculations, one has to vary the cutoff to check that the results obtained are not dependent on the cutoff. This approach of approximating the ionic potential by a pseudopotential and using a finite plane-wave basis set to expand the electronic wavefunctions is often called the 'plane-wave pseudopotential approach'. Finally, we note that the cases where the system is not periodic are converted by repeating a large volume (or supercell) of the disordered material periodically in space. Thus, we can still make use of Bloch's theorem and the procedure outlined above. This is called the supercell approximation and implicit in it is the assumption that the supercell size is large enough so as to be representative of the disordered system.

1.6 \textit{Ab Initio} Molecular Dynamics

In order to do molecular dynamics simulations within DFT one has to invoke the Born-Oppenheimer approximation. This states that since the ions are much slower than the electrons, the electrons can always be taken to be in the ground-state corresponding to the ionic configuration. The task of finding the ground-state electronic configuration is often referred to as 'converging to the Born-Oppenheimer surface' in the literature. In order to do this we have to solve the Kohn-Sham equations self-consistently. Using the plane-wave pseudopotential approach reduces the KS equations to
\[ \sum_{G'} \left[ \frac{1}{2} |k + G|^2 \delta_{GG'} + V_{\text{ion}}(G - G') + V_{\text{KS}}(G - G') \right] c_{i,K+G'} = \epsilon_i c_{i,K+G'} \]  

(1.26)

The above equation is now in the form of a matrix equation which can be solved by matrix diagonalization and iterating this procedure until it is self-consistent (i.e. till the ground-state density used in determining the KS Hamiltonian is identical to that obtained by solving the above matrix equation). In practice however, matrix diagonalization is computationally prohibitive for most systems, and alternate procedures are used to obtain the self-consistent ground-state. The details of these procedures can be found in the literature [13], here we simply note that they result in giving us the ground-state electronic structure for a fixed ionic configuration.

While it is necessary to calculate the electronic structure quantum-mechanically, we can use classical mechanics to describe the ionic motion. In order to do so though, we must calculate the force acting on a given ion due to the other ions and the electrons. By definition this force is given by

\[ f_i = -\frac{dE}{dR_i} \]  

(1.27)

In calculating the above force, we are aided by the Hellmann-Feynman theorem [14] which implies that, if the electrons are in the ground-state corresponding to the ionic configuration, then the partial derivative of the KS energy with respect to the position of the ion gives the real physical force acting on that ion. Having obtained this force, the ions are moved using classical dynamics to their new positions. The for this new configuration of ions, the electronic structure is reconverged to the Born-Oppenheimer surface and the these steps are repeated. This process is referred to as
'ab initio molecular dynamics' and in the next Chapters we shall see examples of the its application to liquid semiconductors.
2.1 Introduction

We now apply the techniques discussed in the previous chapter to study liquid Germanium. Liquid Ge (ℓ-Ge) has a number of unusual properties, which have prompted several experimental and theoretical studies. In the crystalline phase, Ge is a diamond-structure semiconductor with a direct band gap of about 0.9 eV. Upon melting, Ge undergoes a semiconductor-metal transition accompanied by significant structural changes. The density increases by about 4.7%, and its coordination number, as determined by x-ray diffraction, grows from 4 in the solid phase to about 6.8 in the liquid. Similarly, the electrical conductivity increases on melting by more than an order of magnitude, to about $1.6 \times 10^{-4} \ \Omega^{-1} \ \text{cm}^{-1}$. A range characteristic of metallic behaviour.

Despite its metallic nature, however, the behaviour of ℓ-Ge is more complicated than that of a simple liquid metal. Simple liquid metals usually have structure factors similar to that of a fluid of hard spheres, with a temperature-dependent packing fraction and a coordination number of about 10 – 12. Apart from having a lower
coordination number. \( \ell \)-Ge also has a structure factor with a shoulder on the high-\( k \) side of the first peak, a feature which cannot be reproduced by a hard sphere model. These differences have been interpreted as indications that covalent bonding persists in the liquid state. [16] This interplay between metallic and covalent bonding makes \( \ell \)-Ge of particular theoretical interest.

The properties of liquid semiconductors are also important from a technological point of view. Since most semiconductors are grown from the melt, the transport coefficients of the liquid, such as the diffusion constant, are needed as inputs in the fluid-dynamic equations used to model crystal growth. However these properties are difficult to determine experimentally. Typical experiments to measure such diffusion constants are based on tracer diffusion through capillary tubes. [18] Such experiments suffer from uncertainties arising from the contributions of convection and of gravity. These uncertainties can be overcome, in principle, by carrying out the experiments in microgravity.

On the theoretical side, most numerical studies of \( \ell \)-Ge have been carried out using molecular dynamics simulations. One approach is to obtain the interatomic forces using empirical potentials which include three-body terms to model the covalent contributions. While such simulations[19, 20] can reproduce the observed structure factors for liquid semiconductors, they tend to overestimate the degree of tetrahedral bonding in the liquid state. Also, the empirical potentials used are independent of both density and temperature, whereas the actual many-body potential for \( \ell \)-Ge depends on both.

An alternative approach is to derive the interatomic forces by expanding the total energy to second order in the electron-ion pseudopotential, using the linear response
function of the electron gas. [21] The pair correlation function and structure factor obtained from this method agree fairly well with experiment. But this method omits the many-body contributions to interatomic forces, which are important in $\ell$-Ge. Thus to understand the effects of covalent bonding in $\ell$-Ge, one must treat the interatomic forces at a level beyond second-order perturbation theory.

Since the pioneering work of Car and Parrinello, [22] several molecular dynamics schemes have been developed which treat the interatomic forces in a microscopic, fully quantum-mechanical manner. The feature common to all is that the electronic degrees of freedom are treated quantum mechanically to determine the forces on the ions, after which the ionic motion itself is handled using classical dynamics. This approach, i.e. $ab\ initio$ molecular dynamics, has recently been applied by several groups to study liquid semiconductors, including $\ell$-Ge. [23, 24, 25] Most of these studies have, however, emphasized the properties at only one temperature in the liquid state, and thus omit possibly important temperature-dependent changes in the atomic and the electronic structure.

In this Chapter, we report the results of $ab\ initio$ simulations for liquid Ge at five temperatures ranging from 1250 K to 2000 K, thereby obtaining information about the temperature-dependence of various observables in the liquid state. At each temperature, we study a range of structural, electronic, and atomic properties of liquid Ge. Among these are the electronic density of states, the static structure factor, the atomic self-diffusion diffusion coefficient and the d. c. and a. c. conductivities. Our simulations carried out over a time interval of more than 1.5 ps at each temperature.

Besides considering several temperatures, our simulations also differ from previous work in various technical details. In particular, we avoid treating Fourier coefficients
of electronic wave functions as fictitious dynamical variables, as is done in the Car-Parinello approach, and, in order to converge the electronic structure at each step, we use the so-called Williams-Soler algorithm [28] instead of the conjugate-gradient approach.

The rest of this Chapter is organized as follows. In Section II we discuss the computational details. Our results are presented in Section III. Section IV describes our results and gives some conclusions.

2.2 Computational Details

The method used in our calculations has already been elaborated in the previous chapter. We now proceed to discuss the computational details. A detailed description of the molecular dynamics code used in the calculations can be found in the literature.[29, 30] We carry out the electronic structure calculations in the local density approximation (LDA), together with the Ceperley-Alder exchange-correlation functional as parametrized by Perdew and Zunger.[5] We use the Bachelet-Hamann-Schlüter norm conserving pseudopotentials [31] in the Kleinman-Bylander form,[32] choosing the $d$-wave part of the pseudopotential as the local component. We take the $4s$ and $4p$ states of Ge as the valence states, and we apply non-linear core-valence corrections.[33] To check this pseudopotential, we determined the ground-state properties of crystalline Ge, using an energy cutoff of 20 Ry and a set of six $k$-points in the irreducible wedge of the Brillouin zone. The resulting zero-temperature lattice constant, bulk modulus, and binding energy of Ge are in reasonably good agreement with experiment [cf. Table I]. (The binding energy is somewhat larger than experiment, as is characteristic of LDA calculations.)
To generate the initial configurations in the liquid state, we use a classical molecular dynamics code[34] based on empirical potentials of the Stillinger-Weber form.[19] Our simulations are carried out in a 64-atom supercell with simple cubic periodic boundary conditions. Note that such a cell size is commensurate with a possible diamond-structure ground state. The densities for the different temperatures are chosen to match published experimental data.[16] The plane-wave energy cutoff in the liquid state is 10 Ry, and we use Γ-point sampling for the supercell Brillouin zone integration. The ionic equations of motion are integrated by means of the Verlet algorithm, using an ionic time step of 125 a. u. (~ 3 fs). The ionic temperature is controlled by means of the Nosé-Hoover thermostat.[35, 36] using a thermostat mass parameter $Q$ of about $1 \times 10^6$ a. u. The fictitious temperature for the electronic subsystem is $k_B T^{el} = 0.1$ eV, and we calculate the electronic wave functions for the lowest 134 bands, i. e., including six empty bands.

Using this approach, we converge the total energy until the change in the energy in successive steps falls below $5 \times 10^{-6}$ eV/atom. Since our starting ionic configurations are already close to equilibrium at the temperature considered, we find that

<table>
<thead>
<tr>
<th>Property</th>
<th>Calculated</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{lat}$ (bohr)</td>
<td>10.63</td>
<td>10.68</td>
</tr>
<tr>
<td>$B$ (GPa)</td>
<td>69.4</td>
<td>76.5</td>
</tr>
<tr>
<td>$E_B$ (eV)</td>
<td>4.29</td>
<td>3.85</td>
</tr>
</tbody>
</table>

Table 2.1: Lattice constant $a_{lat}$, bulk modulus $B$, and binding energy per valence electron $E_B$ for diamond-structure Ge at temperature $T = 0$, as calculated in the present work, and as obtained experimentally (quoted by Ref. 9).
Figure 2.1: Pair correlation function $g(r)$ for liquid Ge at $T = 1250$ K. Dashed lines: calculated $g(r)$ as obtained from present simulations. Circles: experiment (ref. 1).

simulations of only 1.5 ps are adequate to extract the self-diffusion coefficients at these temperatures.

2.3 Results

2.3.1 Structural Properties

We begin by describing our results for the pair correlation function $g(r)$. Figs. 1 and 2 show $g(r)$ at the temperatures $T = 1250$ K and $T = 2000$ K. As can be seen from Fig. 1, the results agree well with experiment.

At this temperature, the principal peak in the calculated $g(r)$ occurs at $r = 2.63$ Å, in good agreement with the experimental values of 2.70 Å [15] and 2.66 Å. [37] An
effective coordination number $N_c$ can be obtained by integrating $n \times 4\pi r^2 g(r)$ from $r = 0$ to the first minimum, $r_m$, where $n$ is the number density. If we choose $r_m$ to be 3.2 Å, which is the experimentally observed value for the first minimum, we get $N_c = 6.0$. In our simulation, however, the first minimum falls between 3.35 Å and 3.45 Å. If we therefore choose as a cutoff $r_m = 3.4$ Å, we obtain $N_c = 7.1$. Clearly, $N_c$ is rather sensitive to the choice of $r_m$, a quantity which is not sharply defined for liquid Ge. Bearing this ambiguity in mind, we can still see that both $r_m$ and $N_c$ grow with increasing $T$. At $T = 2000$ K, for example, using $r_m = 3.6$ Å, we obtain a coordination number of $N_c = 8.0$. By comparison, $N_c$ is 4 in diamond-structure Ge, 12 in a close-packed solid, and about 10 in a typical hard-sphere liquid.
At $T = 1250$ K, $g(r)$ has a weak intermediate peak at $r = 4.1$ Å lying between the two principal peaks. This peak flattens with increasing $T$, disappearing completely at $T = 2000$ K (cf. Fig. 2). The height of the first peak of $g(r)$ also diminishes with increasing $T$, but occurs at roughly the same $r$ which is in good agreement with experiments done by A. Filipponi et al. [38]

Figs. 3 and 4 show the calculated static structure factor $S(k)$ for the same temperatures. $S(k)$ is defined by the relation

$$S(k) = \frac{1}{N} \langle \rho_k \rho_{-k} \rangle - N \delta_{k,0}.$$  \hspace{1cm}(2.1)
Here $\rho_k$ is a Fourier component of the atomic density, defined by

$$\rho(k) = \sum_n e^{-ik\cdot R_n},$$  \hspace{1cm} (2.2)

where $R_n$ is the position of the $n^{th}$ atom, and $N$ is total number of atoms. In calculating $S(k)$, we average over the last 450 simulation time steps, and also over all $k$-vectors of equal magnitude.

At the lowest temperatures, our calculated $S(k)$ shows the characteristic feature of the structure factor for liquid Ge observed in neutron diffraction studies: a distinct shoulder on the high-$k$ side of the principal peak which occurs at $k = 3.45 \text{ Å}^{-1}$. The results are in excellent agreement with the measured $S(k)$ at $T = 1250$ K. As $T$ increases, the principal peak is reduced in height, and the shoulder becomes less
Table 2.2: Structure factor $S(0)$ at wave vector $k=0$, ionic number density $n$, and height of principal peak in $g(r)$, as calculated at five temperatures.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>1250</th>
<th>1400</th>
<th>1500</th>
<th>1600</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S(0)$</td>
<td>0.05</td>
<td>0.11</td>
<td>0.12</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>$n$ (Å$^{-3}$)</td>
<td>0.04526</td>
<td>0.04457</td>
<td>0.04413</td>
<td>0.04370</td>
<td>0.04250</td>
</tr>
<tr>
<td>$g(r_{max})$</td>
<td>2.39</td>
<td>2.23</td>
<td>2.13</td>
<td>2.08</td>
<td>2.00</td>
</tr>
</tbody>
</table>

distinct. By $T = 2000$ K, the shoulder has completely disappeared [cf. Fig. 4], and the structure factor resembles that of a simple liquid metal well above melting.

As $T$ increases, our calculations also predict an increase in small-angle X-ray or neutron scattering, as measured by $\lim_{k \to 0} S(k)$. In turn, $S(0)$ is related to the isothermal compressibility $\chi_T$ by the compressibility sum rule

$$\lim_{k \to 0} S(k) = S(0) = nk_BT \chi_T$$

(2.3)

where $n$ is the ionic number density. Now Egelstaff et al [39] have shown that in practice, for liquid metals, $S(0) \approx S(k_1/4)$, where $k_1$ corresponds to the principal peak of $S(k)$. Using this estimate, we can calculate the isothermal compressibility of $\ell$-Ge at $T=1250$ K as $\chi_T = 6.4 \times 10^{-11} m^2 N^{-1}$. Table II lists the calculated $S(0)$'s, as obtained from the Egelstaff estimate, along with the corresponding $n(T)$ and the height of the first peak in $g(r)$.

More information about the structural properties can be obtained from the bond angle distribution function $g^{(3)}(\theta, r_c)$. $g^{(3)}$ gives the distribution of the angle formed by pairs of vectors drawn from a reference atom to any two other atoms within a cutoff radius $r_c$ of that atom. Figs. 5 and 6 show $g^{(3)}(\theta, r_c)$ for $T = 1250$ K and $T = 2000$ K.
Figure 2.5: Calculated bond angle distribution function $g^3(\theta, r_c)$ for liquid Ge at $T = 1250$ K for $r_c = 2.8\text{ Å}$ and for $r_c = 3.2\text{ Å}$.

If $r_c$ is chosen as the first minimum in $g(r)$, $g^{(3)}(\theta, r_c)$ shows two peaks at $T = 1250$ K: one at $\theta \sim 60^\circ$, and a second broader peak centered at $98^\circ$. If instead $r_c = 2.8$ Å (equal to the covalent bond length in crystalline Ge), the $60^\circ$ peak disappears while that near $98^\circ$ persists.

As $T$ increases, we observe several changes in $g^{(3)}(\theta, r_c)$. (a) For the larger cutoff radius $r_c$, the $60^\circ$ peak becomes slightly more pronounced while that at $\sim 98^\circ$ becomes slightly less so. (b) For the smaller cutoff radius ($r_c = 2.8$ Å), there is a change from a single broad peak near $98^\circ$ at $T = 1250$ K to an almost uniform distribution in the bond angles at $T = 2000$ K, slightly peaked near $60^\circ$. The $98^\circ$ peak suggests a 'flattened' tetrahedral arrangement of the atoms, similar to the so-called $\beta$-tin.
structure.[40] whereas that at 60° is typical of metallic bonding and represents a more close packed structure. In short, the structure gradually changes from an open structure, with tetrahedral bonding for shorter bond lengths, just above melting, to a more close packed structure with very little tetrahedral bonding at very high temperatures ($T = 2000 K$).

2.3.2 Atomic Self-Diffusion

We now turn to our results for the atomic self-diffusion coefficient $D(T)$ in liquid Ge. To study $D(T)$, we first follow the time-dependent mean-square ionic displacement in the liquid. We start from the equilibrium liquid configuration generated by classical molecular dynamics. For sufficiently long time intervals, $D(T)$ can be
Figure 2.7: Mean-square atomic displacements $\langle r^2 \rangle \equiv \langle |\mathbf{R}_I(t) - \mathbf{R}_I(0)|^2 \rangle$ (in Å²) versus time t (in ps), calculated at $T = 1250$ K and $T = 2000$ K.

extracted from the equation

$$D(T) = \lim_{t \to \infty} \frac{\langle |\mathbf{R}_I(t) - \mathbf{R}_I(0)|^2 \rangle}{6t},$$

(2.4)

where $\mathbf{R}_I(t)$ denotes an ionic position at time $t$. The angular brackets denote an average over all the ions, and also over all time origins. In our calculations we have computed the average taking the beginning of each time step as a different time origin.

Our calculated mean square displacements are shown in Fig. 7 for two representative temperatures: $T = 1250$ K and $T = 2000$ K. $D(T)$ is obtained from a linear-regression fit of the last 0.6 ps of data to a straight line. Table III show the resulting $D(T)$ for all temperatures considered, along with the experimental results.
Table 2.3: Calculated and measured atomic self-diffusion coefficients \( D(T) \).

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>1250</th>
<th>1400</th>
<th>1500</th>
<th>1600</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D(T) ) (10^{-4} \text{ cm}^2/\text{s})</td>
<td>1.2^a</td>
<td>1.7^a</td>
<td>2.0^a</td>
<td>2.1^a</td>
<td>2.3^a</td>
</tr>
<tr>
<td>( D(T) ), other calcs.</td>
<td>1.0^b, 0.44^c</td>
<td>1.0^d</td>
<td>1.2^e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D(T) ), exp't</td>
<td>1.21, 0.78^f</td>
<td>1.62^f</td>
<td>3.21^f</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Results of present calculations, carried out by \textit{ab initio} molecular dynamics at five temperatures. \(^b\) Kresse and Hafner, Ref. 23 (at \( T = 1230 \) K). \(^c\) Yu et al, Ref. 34 (empirical potential). \(^d\) Godlevsky et al, Ref. 25 (at \( T = 1350 \) K). \(^e\) Takeuchi and Garzón, Ref. 24. \(^f\) P. V. Pavlov and E. V. Dobrokhotov, Fiz. Tverd. Tela (Leningrad) 12, 281 (1970) [Sov. Phys. Solid State 12, 225 (1970)].

As expected, \( D(T) \) is a monotonically increasing function. Our results agree well with experiment, and also with the \textit{ab initio} calculations of Kresse and Hafner for \( T = 1250K \)[23], but at the other temperatures are somewhat higher than other \textit{ab initio} predictions.[24, 25] Possibly some of these differences arise from the fact that the densities chosen in the various simulations are different. Previous calculations at elevated temperatures have used the density of liquid Ge at melting, whereas we choose a lower density appropriate to the temperature, determined from experiment.[16] In addition, of course, each of the simulations uses a slightly different \textit{ab initio} method.

\( D(T) \) may also be obtained from the velocity autocorrelation function \( \psi(t) \), defined by

\[
\psi(t) = \frac{\langle v_i(t) \cdot v_i(0) \rangle}{\langle v_i(0) \cdot v_i(0) \rangle}
\]  

(2.5)
Here, the angular brackets again denote an average over all the atoms and over different time origins. The diffusion constant $D$ is then obtained from the relation

$$D = \frac{k_BT}{M} \int_0^\infty \psi(t)dt.$$  

(2.6)

The resulting $D(T)$ agrees to within 5-10% with the values extracted from the mean-square displacement; both are shown in Fig. 8.

A notable feature of our results is that the diffusion constant rises sharply between $T = 1250$ K and $T = 1500$, and more slowly at higher temperatures. Possibly this is related to a corresponding behavior reported in the kinematic viscosity $\eta$. Experimental data for the $\eta(T)$ in liquid Ge shows a sharp drop just above the
melting point, followed by a more gradual decline at higher temperatures. [16] $D$ can be related to $\eta$ using the Stokes-Einstein relation

$$D = \frac{k_B T}{2\pi a \eta}, \quad (2.7)$$

which is quite successful in connecting the two coefficients for a liquid of hard spheres of diameter $a$. If $a$ is assumed to decrease only slightly with temperature, then a sharp decrease in $\eta$ is connected to a corresponding increase in $D$. Thus, the sharp rise in $D$ is in qualitative agreement with the experiment for $\eta$.

### 2.3.3 Electronic Properties

Next, we discuss the electronic density of states $N(E)$ at the same five temperatures. $N(E)$ is calculated from the approximate expression

$$N(E) = \sum_{k,E_k} w_k g(E - E_k). \quad (2.8)$$

Here $E(k)$ denotes the energy eigenvalues for the single-particle wave functions at a particular k-point of the supercell Brillouin zone, and $w_k$ is the weight of that k point (as defined below). $g(E)$ is a Gaussian function of width $\sigma = 0.2$ eV, used in order to give better statistics to the density of states. To carry out the calculation we sampled the supercell Brillouin zone using the set of eight special k-points, with equal weights $w_k$, used by Holender et al [42] in their simulation of liquid Ga and we have included the lowest 168 eigenvalues $E_k$ for each $k$. For each temperature, the final results were then obtained by averaging over five representative configurations in the liquid state.

Fig. 9 shows the calculated density of states for $T = 1250$ K and $T = 2000$ K. At these, and all intermediate temperatures, we find that $N(E)$ is finite at the Fermi energy, indicating that liquid Ge is metallic. Another characteristic feature of $N(E)$ is
the presence of a pseudogap at -4.6 eV which separates the s-like and p-like bands.[43, 44] Even though there is short-range covalent bonding in liquid Ge this feature is not obviously reflected in the density of states. Furthermore, $N(E)$ does not show much variation with temperature in the range considered. However two significant points should be noted: 1) The pseudogap occurs at a binding energy which corresponds to \( \frac{1}{2}(k_m/2)^2 \) (in atomic units) where $k_m$ is the wave-vector corresponding to the position of the first peak in the structure factor. 2) The shoulder in the structure factor for $T = 1250$ K occurs roughly at the Fermi wave-vector $2k_f$. Correspondingly we also see a dip in the electronic density of states at $E = E_f$. Furthermore, corresponding to
the disappearance of the shoulder in the structure factor at $T = 2000$ K, we see that
the dip in the electronic density of states also disappears. The observations imply that
the pseudogaps and dips seen in the electronic density of states are structure-induced.

Another quantity of interest is the frequency dependent electrical conductivity
$\sigma(\omega)$, and its low-frequency limit, the d. c. conductivity. $\sigma(\omega)$ can be calculated from
the Kubo-Greenwood formula [45]

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2\omega\Omega} \sum_i \sum_j \sum_\alpha \langle f_j - f_i \rangle \langle \psi_i | p\alpha | \psi_j \rangle |^2 \delta(E_j - E_i - \hbar\omega). \quad (2.9)$$

Here $m$ is the electron mass, and $\psi_i$ and $\psi_j$ are the single particle Kohn-Sham wave
functions with occupancies $f_i$ and $f_j$ and energy eigenvalues $E_i$ and $E_j$. $p\alpha$ is the
component of the momentum operator in the direction $\alpha$. We have calculated the
conductivity using the same set of eight special k-points used for $N(E)$, and again
averaged over five representative ionic configurations for each temperature. As in the
density of states calculation, we have included the lowest 168 eigenvalues; the highest
of these lies $\sim 2.5$ eV above the Fermi energy.

The resulting $\sigma(\omega)$ is shown for two temperatures in Fig. 10. At both tempera-
tures, $\sigma(\omega)$ decreases monotonically with $\omega$, showing no absorptive peaks in the
observed frequency range. By extrapolating to $\omega = 0$, we estimate the d. c. conduc-
tivity at $T = 1250$ K as $1.5 \times 10^4 \Omega^{-1} cm^{-1}$, in good agreement with the measured value
of $1.66 \times 10^4 \Omega^{-1} cm^{-1}$. [16] The calculated temperature-dependent d. c. conductivity
is shown in Table IV.
Figure 2.10: Calculated a. c. conductivity $\sigma(\omega)$ for liquid Ge at $T = 1250 \text{ K}$ and 2000 K, as obtained by averaging over five typical atomic configurations at each temperature.

2.4 Discussion and Conclusions

We now turn to some possible interpretations of the results presented in the preceding section, especially the unusual temperature-dependent structure. It has been argued [46] that the structural properties of liquid metals are basically determined by two length scales: an effective hard sphere diameter $\sigma$, which determines the position of the principal peak in $g(r)$, and the wavelength of Friedel oscillations in the pair potential ($\lambda = \pi/k_F$), where $k_F$ is the Fermi wave vector. This picture has been successfully applied to explain trends in the structural properties of liquid metals, [47]. In the following, we use this view to offer some speculations about our own results.
<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$1250$</th>
<th>$1400$</th>
<th>$1500$</th>
<th>$1600$</th>
<th>$2000$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{dc}$ ($10^4$ ohm$^{-1}$ cm$^{-1}$)</td>
<td>$1.54$</td>
<td>$1.45$</td>
<td>$1.42$</td>
<td>$1.35$</td>
<td>$1.27$</td>
</tr>
</tbody>
</table>

Table 2.4: D. c. conductivity at the five temperatures, obtained by extrapolating low frequency a. c. conductivity results.

For a simple liquid metal like Na, the two length scales set by $\sigma$ and $\lambda$ are commensurate. Hence, in this picture, the behavior of $g(r)$ can be explained as a consequence of the constraints of hard sphere packing. But for tetravalent liquid metals, it has been shown [47] that the two length scales are incompatible. In particular, the first maximum of the hard-sphere $g(r)$, coincides with the repulsive part of the effective pairwise interaction. Thus it becomes energetically favorable to shift some atoms from the first shell to a neighbouring shell which corresponds to a minimum of the pair potential. This explains the low coordination numbers of tetravalent liquid metals and also the intermediate peak observed in $g(r)$ in both experiment and our simulations, without the necessity of invoking specifically three-body (or bond-angle-dependent) forces. In the static structure factor, this shift is reflected in the appearance of a shoulder at $q = 2k_F$, distinct from the primary peak of $S(q)$ which occurs roughly at $q = 2\pi/\sigma$.

As the temperature increases the following changes take place: (a) because of the increased ionic kinetic energy, the effective hard-sphere diameter $\sigma$ decreases; and (b) the lowering of the ionic number density leads to a corresponding decrease in $k_F$. Thus the two peaks in $S(q)$, corresponding to $2\pi/\sigma$ and $2k_F$, tend to approach each other. The increased thermal disorder also lowers and broadens the first peak in $S(q)$ and makes it broader. These two effects conceivably combine to make shoulder in the $S(q)$
disappear with increasing temperature. In real space, this behavior is reflected in the disappearance or "flattening" of the intermediate peak in \( g(r) \), and a corresponding broadening of the first peak. As the intermediate maximum disappears, the first shell gains atoms, so that the coordination number increases at higher temperatures.

There are other possible explanations for the shoulder in the structure factor. Three-body forces among the ions, such as are predicted by the pseudopotential theory of interatomic forces in metals, may conceivably produce such a shoulder. A recent paper\[48\] has shown that a shoulder can be produced by a model in which several Ge ions are assumed to form a single tetrahedral dynamical entity which moves through the liquid as a unit, at least over diffusive time scales. Our calculations, while they do produce the observed shoulder, cannot easily discriminate between these explanations.

Finally, we mention briefly the recent \textit{ab initio} calculations of Stich \textit{et al}\[49\] for \( \ell \)-Si. These authors find that the explicit inclusion of spin in the density-functional theory tends to enhance the diffusion coefficient in \( \ell \)-Si by about 50\%. It seems likely, however, that in \( \ell \)-Ge, where the degree of covalent bonding is significantly reduced, \( D(T) \) should be less influenced than in Si.

In conclusion, we have carried out \textit{ab initio} molecular dynamics simulations for several properties of \( \ell \)-Ge at five different temperatures: 1250K, 1400K, 1500K, 1600K and 2000K. Our results are in very good agreement with available experimental data. They indicate that liquid Ge is a good metal, but with some special short-range order arising from residual covalent bonding which persists into the liquid state. At the highest temperatures, however, the liquid seems to evolve into a more conventional close-packed liquid metal. Our computed values of the atomic self-diffusion coefficient
$D(T)$ are higher than those previously obtained using empirical potentials, but are in good agreement with results from other \textit{ab initio} calculations.

Finally, the present approach suggests a number of possible applications. For example, it can be used to treat the diffusion coefficients of impurities such as Ga and Si in $\ell$-Ge. The same approach may be useful for treating liquid versions of technologically important compound semiconductors, such as $\ell$-GaAs and $\ell$-CdTe, both on and off stoichiometry. The latter materials might be especially worthwhile to study, because the electronic structure here should be strongly dependent on both temperature and concentration. We will turn to the study of these systems in the following Chapters.
CHAPTER 3

LIQUID GA-GE ALLOYS

3.1 Introduction

In the previous Chapter, we have looked at the structural, dynamic and electronic properties of liquid Ge. In this Chapter, we present the results of a simulation study of liquid Ge$_x$Ga$_{1-x}$ at four concentrations just above the melting temperature of pure Ge. In the previous Chapter, we have calculated a number of properties of pure liquid Ge (ℓ-Ge) [53], including the ionic structure factor, electronic density of states, bond-angle distribution, frequency-dependent conductivity $\sigma(\omega)$, and atomic self-diffusion coefficient at several temperatures. The present work extends the same approach to ℓ-Ga$_x$Ge$_{1-x}$. This alloy system is of interest because Ga is a common impurity in ℓ-Ge, whose transport properties are of interest in order to model crystal growth. In addition, of course, Ga is a common p-type dopant in solid semiconductors. Furthermore, the properties of liquid Ga are markedly different from those of liquid Ge. While liquid Ga has a coordination number of $\sim 9$ and an electronic density of states that is almost free-electron like; liquid Ge has a much lower coordination number and an electronic density of states which has a pseudogap, as was seen in
the previous Chapter. So it would be interesting to see how these properties vary systematically as the concentration of the alloy is changed. Another source of interest in this system is change in behavior of the electrical conductivity with increasing Gallium concentration. Previous theoretical calculations on this system, using the Faber-Ziman theory of liquid alloys [17], have predicted a minimum in the conductivity at 50% Ga concentration. Experimentally however the change seems to be monotonic, so it is interesting to see the behavior predicted by \textit{ab initio} simulations.

The remainder of this Chapter is organized as follows. In Section II, we briefly review our method of calculation. Section III describes our results, and a discussion follows in Section IV.

3.2 Method and Computational details

The exchange-correlation potential is calculated within local-density approximation (LDA), using the Ceperley-Alder form as parameterized by Perdew and Zunger[5]. We use generalized norm conserving pseudopotentials [55] in the Kleinman-Bylander [32] form with the $d$-wave part treated as the local component.

In order to test the pseudopotentials we have calculated some of the structural properties for both Ga and Ge in the crystalline phase. The results for Ge were obtained with a plane-wave energy cutoff of 25 Ry and using 10 special $k$-points in the irreducible wedge of the Brillouin zone. To determine the lattice constants and bulk moduli, we fitted the calculated energies to the functional form [56]

$$E = A + BV^{-\frac{1}{2}} + CV^{-\frac{3}{2}} + DV^{-1}$$

(3.1)

where $E$ and $V$ are the energy and volume per atom respectively. The resulting calculated values of the lattice constant and the bulk modulus were 5.59 Å and 72.3
GPa. in good agreement with the experimental values of 5.65 Å and 76.5 GPa. For Ga, we carried out these tests on the α phase. This crystal structure has a base-centered orthorhombic Bravais lattice specified by the experimentally determined[57] lattice parameters $a = 4.52$ Å, $b = 4.53$ Å, $c = 7.66$ Å. In our tests, we have fixed the ratios of these three lengths at their experimental values and varied the single parameter $a$. Using a plane-wave cutoff of 20 Ry and 39 special $k$-points, we obtained the calculated values $a = 4.38$ Å, $b = 4.37$ Å, $c = 7.40$ Å. These are nearly identical to the values obtained in previous ab initio simulations [42, 58].

We carry out the liquid-state molecular dynamics simulations at 1273 K at four concentrations of Ga in Ge ranging from ~ 20% to ~ 80% and a 64-atom supercell with periodic boundary conditions. These concentrations correspond to 13, 26, 38 and 51 Ga atoms. For each concentration, the initial configurations are generated from the results of a previously reported molecular dynamics simulation of of liquid Ge [53] at 1250 K, but with the appropriate number of Ge atoms randomly replaced by Ga. The densities for the four concentrations are determined from the experimental densities [15] of pure liquid Ge and Ga, using Vegard's law (linear interpolation of atomic volumes) to obtain the densities for the alloys. We use a plane-wave energy cutoff of 10 Ry and Γ-point sampling for the supercell Brillouin zone. Since we expect the liquid system to be metallic, we use standard Fermi-surface broadening, taking the temperature of the electronic subsystem as $k_BT^e = 0.1$ eV . In calculating the electronic wave functions we include eight empty bands for each concentration. The ionic temperature is controlled by means of a Nosé-Hoover thermostat [35, 36] and the equations of motion are integrated using the Verlet algorithm with an ionic time-step.
of 125 a. u. (~ 3 fs). After an initial equilibration period of about 0.2 ps, simulations were carried out for more than 3 ps at each concentration.

3.3 Results

Fig. 1 shows the partial pair-correlation function $g_{Ge-Ge}(r)$ for the four alloys $Ge_{1-x}Ga_x$ with $x = 0.2, 0.4, 0.6,$ and $0.8$. For comparison, we have shown in Fig. 2 the pair-correlation function $g_{Ge-Ge}(r)$ with $x = 0.2$ contrasted with the experimental results [15] for pure $\ell$-Ge at a similar temperature. A number of features deserve mention. First, the position of the principal peak, which occurs at $r = 2.61 \text{Å}$, is virtually unchanged from the value calculated for pure $\ell$-Ge ($r = 2.63 \text{Å}$) [53].
Figure 3.2: Partial pair correlation function $g_{Ge-Ge}(r)$ for liquid Ge$_{1-x}$Ga$_x$ with $x = 0.2$ at $T = 1273$ K compared to experimental pair-correlation function for pure $\ell$-Ge at $T = 1253$ K. Dashed lines: present calculations. Circles: experiment (ref. 1). The inset shows the results of previous calculations (ref. 14) for pure liquid Ge as compared to experiment (ref. 1).

However, the height of that peak is reduced, from $\sim 2.4$ to $\sim 2.2$. In pure $\ell$-Ge, $g_{Ge-Ge}(r)$ also shows a weak intermediate peak between the two principal peaks. This intermediate peak reflects the characteristic feature of the structure factor in pure $\ell$-Ge, namely, the presence of a shoulder occurring at $k = 2k_F$ distinct from the primary peak in the structure factor $S(k)$ (see below).

However, as can be seen from Fig. 2, this intermediate peak has already flattened out at $x = 0.2$. One would expect that this flattening would correspond to a weakening of the shoulder in the structure factor at nonzero $x$. This is indeed the case, as
will be discussed below. A final point is that $g_{Ge-Ge}(r)$ is becoming noisier as the concentration of Ge is reduced. This is simply a consequence of the smaller number of Ge atoms which are included at these lower concentrations.

Fig. 3 shows the partial correlation functions $g_{Ga-Ga}(r)$ at the same concentrations. The principal peak seems to show a slight shift to smaller $r$ as the concentration of Ga diminishes; in general, this peak occurs at about the same $r$ as that of $g_{Ge-Ge}(r)$, suggesting that the "atomic sizes" are similar in the liquid. The data is, as expected, noisier at the lowest concentrations of Ga. We can compare the results obtained by us for $g_{Ga-Ga}(r)$ with $x = 0.8$ with the experimental results [59] and simulations [42] for pure $\ell$-Ga obtained at $T = 982$ K. Since our simulations are at a higher temperature
than the experimental results, it is instructive to note the temperature dependence seen in previous simulations [42] for pure \(\ell\)-Ga. With increasing temperature, the height of the principal peak in \(g_{Ga-Ga}(r)\) shows a marked reduction (from \(\sim 2.6\) at \(T = 702\) K to \(\sim 2.2\) for \(T = 982\) K) and shows a slight shift to smaller \(r\). Our results for \(g_{Ga-Ga}(r)\) with \(x = 0.8\) show a principal peak at \(r = 2.55\) Å with a peak height of \(\sim 1.9\) as compared to \(r = 2.67\) Å and \(\sim 2.2\) for the simulations for the pure liquid at \(T = 982\) K. These values seem to be consistent with the trend noted above.

We turn next to the partial structure factors \(S_{Ge-Ge}(k)\) and \(S_{Ga-Ga}(k)\), shown in Figs. 4 and 5 for the four alloy concentrations. The most striking feature in the calculated \(S_{Ge-Ge}(k)\) is the shoulder on the large-\(q\) side of the principal peak. This
Figure 3.5: Partial structure factor $S_{Ge\rightarrow Ge}(k)$ for liquid $Ge_{1-x}Ga_x$ at the concentration $x = 0.2$ compared to the experimental structure factor for pure $\ell$-Ga at $T = 1253$ K (ref. 1). The inset shows the results of previous calculations (ref. 14) for pure liquid Ge as compared to experiment (ref. 1).

shoulder is quite pronounced in pure $\ell$-Ge, in agreement with experiment, but it disappears rapidly with increasing Ga concentration $x$. In fact, it has almost disappeared by $x = 0.2$ as indicated in Fig. 6, a fact that is also reflected in the flattening of the intermediate peak in $g_{Ge\rightarrow Ge}(r)$ as mentioned earlier. Also, there is a distinct increase in the low-$k$ values of $S_{Ge\rightarrow Ge}(k)$ in comparison to the structure factor for the pure liquid. By $x = 0.8$, in spite of the poor statistics, Fig. 4 shows that $S_{Ge\rightarrow Ge}(k)$ is similar to that of a dilute gas, being close to unity except at very small $k$. The partial structure factor $S_{Ga\rightarrow Ga}(k)$ behaves similarly to that of a conventional (hard-sphere-like) liquid metal at $x = 0.8$, crossing over to nearly ideal-gas-like behavior at
Figure 3.6: Partial structure factor $S_{Ga-Ga}(k)$ as a function of wave vector $k$ (in Å$^{-1}$) for liquid Ge$_{1-x}$Ga$_x$ at the four concentrations, $x = 0.2, 0.4, 0.6,$ and 0.8.

$x = 0.2$. Comparing our results for $x = 0.8$ with the published experimental results for pure liquid Ga at $T = 982$ K [59] we see that the positions of the principal and secondary peaks are basically unchanged; however the height of the principal peak is reduced and there is a distinct increase in the low-$k$ values of the structure factor.

In Figs. 7 and 8, we show the bond angle distribution - that is, the distribution of angles formed by triplets of Ge atoms for $x = 0.2$ and of Ga atoms at $x = 0.8$, such that all three atoms lie within a suitable cutoff radius $r_c$. For comparison, we also show the corresponding distribution for pure $\ell$-Ge in the inset for Fig. 7. For $x = 0.2$, the bond angle distribution, like that of pure Ge, shows a slight peak at $\sim 60^0$, corresponding to a close-packing arrangement. However, the peak observed
in our pure Ge simulations at $\sim 100^\circ$ has been reduced to a barely detectable and rather broad plateau at $x = 0.2$. This indicates that the addition of only $\sim 20\%$ of Ga already reduces the degree of covalent bonding present in pure $\ell$-Ge, in agreement with the disappearance of the shoulder in $S_{Ge-Ge}(k)$ at that concentration. The bond-angle distribution for Ga clusters at $x = 0.8$ is quite uniform except for a weak peak near $\sim 60^\circ$. This indicates close-packed bonding characteristic of simple liquid metals.

We have also calculated the values of the self-diffusion coefficients for Ge atoms $D_{Ge-Ge}$ (at 20\% Ga) and $D_{Ga-Ga}$ (at 20\% Ge), obtained in both cases by examining
the mean square displacements of the respective atoms as a function of time as in our previous work for pure Ge (cf. Fig. 9). The self-diffusion coefficients can be extracted from the equation

$$D = \lim_{t \to \infty} \frac{\langle |R_I(t) - R_I(0)|^2 \rangle}{6t},$$  \hspace{1cm} (3.2)$$

where $R_I(t)$ denotes an ionic position at time $t$. The angular brackets denote an average over all the ions of the same species, and also over all time origins. In our calculations we have computed the average taking the beginning of each time step as a different time origin. For Ge self-diffusion, we obtain $D_{Ge-Ge} \sim 1.1 \times 10^{-4} \text{ cm}^2/\text{s}$, very close to the previously calculated values for pure $\ell$-Ge of $1.2 \times 10^{-4} \text{ cm}^2/\text{sec}$ (our work[53]) and $1.0 \times 10^{-4} \text{ cm}^2/\text{sec}$ (Kresse and Hafner[23]) It is mildly surprising that
Figure 3.9: Mean-square atomic displacements \( \langle r^2 \rangle \equiv \langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle \) (in Å²) versus time \( t \) (in ps) for Ge atoms in liquid Ge\(_{1-x}\)Ga\(_x\) at \( x = 0.2 \) and for Ga atoms at \( x = 0.8 \).

The reduction in covalent bonding at \( x = 0.2 \) does not translate into a more significant change in \( D_{\text{Ge-Ge}} \). For Ga, we obtain \( D_{\text{Ga-Ga}} \sim 1.7 \times 10^{-4} \text{ cm}^2/\text{s} \) for 80\% Ga at \( T = 1273 K \). This value seems to be in rough agreement with some old experimental values of \( 0.9 \times 10^{-4} \) (702 K) and \( 1.3 \times 10^{-4} \) (982 K) in pure \( \ell \)-Ga .[60]

We now turn to the electronic properties of \( \ell \)-Ge\(_{1-x}\)Ga\(_x\), which show a striking concentration-dependence. We calculate the electronic density of states \( N(E) \) from the standard expression

\[
N(E) = \sum_{k,E_k} w_k g(E - E_k).
\] (3.3)
Figure 3.10: Calculated electronic density of states \( N(E) \) (in states/ev-atom) for liquid \( Ge_{1-x}Ga_x \) at the four concentrations \( x = 0.2, 0.4, 0.6, \) and 0.8. Each curve is obtained by averaging over twelve characteristic atomic configurations: the supercell Brillouin zone is sampled using eight special k-points.

Here \( E_k \) denotes the energy eigenvalues for the single-particle wave functions at a particular k-point of the supercell Brillouin zone, and \( w_k \) is the weight of that k point (as defined below). As discussed in the previous chapter, \( g(E) \) is a Gaussian function of width \( \sigma = 0.2 \) eV, used in order to give a smooth variation to the calculated density of states. To carry out the calculation we sampled the supercell Brillouin zone using the same set of eight special k-points, with equal weights \( w_k \), as used by Holender et al [42] in their simulation of pure \( \ell - Ga \), and we have included 40 conduction band states for each \( k \). For each concentration, the final results were then obtained by averaging over twelve representative configurations in the liquid state.
Fig. 10 shows the resulting calculated $N(E)$ for $x = 0.2, 0.4, 0.6,$ and 0.8 as well as for pure $\ell$-Ge for comparison. For pure $\ell$-Ge, $N(E)$ shows a pseudogap at -4.6 eV separating the $s$-like and $p$-like bands [61]. On the other hand the density of states for $\ell$-Ga at elevated temperatures is known to be almost free-electron like [42]. Thus we would expect a gradual progression towards free-electron-like behavior in $N(E)$ as $x$ increases. This behavior is precisely what is seen in Fig. 10. The pseudogap is already substantially reduced below its value for pure $\ell$-Ge, even at $x = 0.2$. With increasing concentration of Ga, $N(E)$ loses even more of its structure and approaches the free-electron-like behavior seen in pure $\ell$-Ga at these temperatures. Of course, at all concentrations, $N(E)$ shows clear metallic behavior - that is, it is finite, with no dips, at the Fermi energy.

Finally, we have calculated the frequency dependent electrical conductivity $\sigma(\omega)$, and its low-frequency limit, the d. c. conductivity, as a function of concentration. As in our previous work, we obtain $\sigma(\omega)$ from the standard Kubo-Greenwood formula [45]

$$
\sigma(\omega) = \frac{2\pi e^2}{3m^2\omega\Omega} \sum_i \sum_j \sum_\alpha (f_j - f_i) |\langle \psi_i | \hat{p}_\alpha | \psi_j \rangle|^2 \delta(E_j - E_i - \hbar \omega). \tag{3.4}
$$

Here $m$ is the electron mass, and $\psi_i$ and $\psi_j$ are the single particle Kohn-Sham wave functions with Fermi occupancies $f_i$ and $f_j$ and energy eigenvalues $E_i$ and $E_j$. $\hat{p}_\alpha$ is the component of the momentum operator in the direction $\alpha$. We have calculated the conductivity using the same set of eight special $k$-points employed for $N(E)$, and again averaged over twelve representative ionic configurations for each concentration. As in the density of states calculation, we have included 40 conduction band states at each $k$.

By extrapolating $\sigma(\omega)$ to $\omega = 0$, we can estimate the d. c. conductivity. The calculated values of $\sigma(0)$ for the four concentrations are shown in Table I, along with
that for pure $\ell$-Ge. We note that $\sigma(0)$ shows a weak minimum at 40% and then increases for higher concentrations of Ga. This behavior is in qualitative agreement with that predicted by calculations based on the weak-scattering Faber-Ziman theory of liquid alloys[50], and presumably arises for the same reason: stronger scattering near $x = 0.5$ due to differences between the Ge and Ga scattering potentials. However, there is no clear evidence in the experimental data reported [62] of the weak minimum in conductivity seen in our calculations.

3.4 Conclusions

In conclusion we have carried out ab initio molecular dynamics simulations for liquid Ga-Ge alloys at four different concentrations. The basic picture emerging from these calculations is that, as the concentration of Ga is increased at the temperatures considered, the alloy rapidly becomes more free electron-like. This transformation manifests itself in a variety of ways. The atomic structure, which shows some residue of tetrahedral local arrangement in pure $\ell$-Ge in both $g(r)$ and the distribution of bond angles, quickly becomes more close-packed and is almost entirely so for 40% or more atomic concentration of Ga. The structure factor $S_{Ge-Ge}(k)$, which has a noticeable shoulder in pure $\ell$-Ge in both our calculations and experiment, becomes more hard-sphere-like with increasing Ga concentration, as does $S_{Ga-Ga}(k)$. Most noticeably, the deep pseudogap between p-like and s-like states in pure $\ell$-Ge quickly fills in as the Ga concentration $x$ increases, leading to a nearly free-electron-like density of states for $x = 0.8$. The electrical conductivity looks similar to what might have been obtained from a Faber-Ziman calculation: a weak minimum near $x = 0.4$ coming
from enhanced alloy scattering. At all concentrations, the alloy is a reasonably good metal, with resistivities in the range of 70 $\mu\Omega\cdot\text{cm}$.

The present work can be extended in a number of way. Of probably greatest interest would be to study such liquid alloy systems as CdTe or GaAs. In the next Chapter we shall study liquid GaAs, both on and off stoichiometry.
CHAPTER 4

LIQUID GALLIUM ARSENIDE

4.1 Introduction

In the previous chapters, we have studied an example of a "liquid semiconductor" in $\ell$-Ge (and the effects produced by alloying it with Ga). By "liquid semiconductors", we mean liquids of materials which are semiconducting in their solid phases, such as Si, Ge, GaAs, and CdTe. Somewhat surprisingly, most of these are reasonably good metals in their liquid phases. For example, Si, Ge, and GaAs all have conductivities near melting which lie in the metallic range, and which tend to decrease with increasing temperatures, as is characteristic of metals. This metallic behavior is correlated with an increase in coordination number on melting, the liquid is thus more close-packed than the solid and has a higher density. By contrast, $\ell$-CdTe is poorly conducting in its liquid state and its conductivity increases with increasing temperature, characteristic of semiconductors.

Recent $ab\ initio$ calculations for several of these materials give behavior which is in good agreement with these experiments. Godlevsky $et\ al$[64] have found, in agreement with experiment, that stoichiometric GaAs is metallic, whereas stoichiometric CdTe
is a reasonable insulator. These differences in the electronic properties were related to the differences in the structural properties occurring within the melt. An earlier calculation by Zhang et al.[65] studied stoichiometric $\ell$-GaAs using the Car-Parrinello version of ab initio molecular dynamics. In this calculation too, it was found that $\ell$-GaAs is a metallic, weakly ionic liquid, with a larger coordination number than the insulating solid phase.

In this Chapter, we describe our numerical study of $\ell$-Ga$_x$As$_{1-x}$ over a range of concentrations, using the techniques discussed in previous chapters. Such a study is of interest for a variety of reasons. The properties of $\ell$-Ga and $\ell$-As stand in marked contrast to each other. $\ell$-Ga is a close-packed liquid metal with a coordination number of $\sim 9$ and its electronic density of states is almost free-electron like. In contrast, $\ell$-As has the same coordination number as in the crystalline phase ($\sim 3$), and is a narrow band-gap semiconductor in the liquid state. Thus while we expect $\ell$-Ga to show metallic bonding, $\ell$-As is expected to retain the covalent character of the bond upon melting. Previous ab initio calculations for these liquids [66, 42] have indeed confirmed this picture. Thus as the stoichiometry is varied for $\ell$-Ga$_x$As$_{1-x}$, we would expect interesting changes both structurally and electronically. It is also of interest to compare the structures of $\ell$-Ga$_x$As$_{1-x}$ for $x = 0.2$ and $x = 0.8$ with the structure for the corresponding pure liquids (As and Ga respectively) to see how changes in structural properties are correlated with changes in electronic properties.

Our method of carrying out the ab initio simulations is similar to the one outlined in the previous chapters and we summarize it below. Our liquid-state molecular dynamics (MD) simulations were carried out at a temperature $T = 1600$ K, just above the melting point of GaAs ($T = 1515$ K). We have considered five concentrations of
Ga$_x$As$_{1-x}$: $x = 0.2, 0.4, 0.5, 0.6,$ and $0.8$. In each case, we used a cubic 64-atom supercell with periodic boundary conditions. For this size cell, the actual numbers of Ga atoms in the five samples were 13, 26, 32, 38, and 51. The atomic densities for the five concentrations were obtained from the measured density of $\ell$-GaAs at this temperature[16], together with Vegard's Law (i.e. linear interpolation of atomic volumes). We use a 10-Ry cutoff for the energies of the plane waves included in the wave function expansion, and $\Gamma$-point sampling for the supercell Brillouin zone. For the electronic structure, we used Fermi-surface broadening corresponding to an electronic subsystem temperature of $k_B T^{el} = 0.1$eV. In calculating the electronic wave functions, at each concentration we include eight empty bands. We control the ionic temperature using the Nosé-Hoover thermostat. The equations of motion are integrated by means of the Verlet algorithm, using an ionic time step of 125 a.u. ($\sim 3$ fs). For each concentration, the samples were equilibrated for about 0.2ps, following which simulations were carried out for more than 3ps.

### 4.2 Results

Fig. 1 shows the three partial pair correlation functions $g_{GaGa}(r)$, $g_{AsAs}(r)$ and $g_{GaAs}$ for liquid Ga$_x$As$_{1-x}$ at the concentration $x = 0.5$ and a temperature $T = 1600$ K. A number of features deserve mention. First, at $x = 0.5$, the principal peaks of all three partial pair correlation functions occur at about the same separation, namely 2.5Å. This indicates the non-ionic character of the bonds; in ionic liquids the partial pair correlation functions for like atoms are out of phase with the corresponding function for unlike atoms [67]. Our results for $g_{aa}(r)$ are in close agreement with the recent calculation by Godlevsky et al [64]; an earlier calculation by Zhang et al [65]
Figure 4.1: Pair correlation functions $g_{\text{GaGa}}(r)$ and $g_{\text{AsAs}}(r)$ for $\ell$-Ga$_x$As$_{1-x}$ at a temperature of 1600 K and concentration $x = 0.5$. All calculations are carried out for a 64-atom sample with periodic boundary conditions in all three directions.

also gives the same features although these authors get a much stronger principal peak for $g_{\text{GaAs}}(r)$ than is found in either our calculations of that of Ref. [64]. While the principal peaks are in phase, there are some differences among the partial $g(r)$'s. For example, at $x = 0.5$, $g_{\text{AsAs}}(r)$ has a slightly higher and narrower first peak, and a stronger second peak, than $g_{\text{GaGa}}(r)$, while $g_{\text{GaGa}}(r)$ has a broad first peak and no obvious peak beyond that. We have also calculated the coordination numbers for the first shell of neighbors, defined as the integral of $4\pi r^2 g(r)$ from zero out to the minimum after the first maximum in $g(r)$. [Here $g(r)$ is the total pair correlation function, which does not distinguish between the two species, normalized so that it
approaches unity at large $r$. The coordination we calculate in this way at $T = 1600$ K is 5.8, in good agreement with the experimental estimate of $5.5 \pm 0.5$. Note also that this value is larger than the diamond-structure value of 4 but significantly smaller than the value expected in a close-packed liquid, which would be in the range of 9 or 10. This value indicates the persistence of covalent bonding in $\ell$-GaAs.

Fig. 2 shows $g_{\text{GaGa}}(r)$ at $x = 0.8$ and $g_{\text{AsAs}}(r)$ at $x = 0.2$. The latter shows more short-range order than the former - specifically, a sharper main peak and a broad second peak, rather than a single broad principal peak. We believe that there are several causes for these differences. First, pure Ga has a much lower melting temperature than either $\text{Ga}_{0.5}\text{As}_{0.5}$ or As. Thus, at the same temperature of 1600
K, we expect less short-range order for $g_{GaGa}(r)$ at $x = 0.8$ than for $g_{AsAs}(r)$ at $x = 0.2$, as seen in our calculations. In addition, we expect the $x = 0.2$ sample to show some residue of the complex local structure seen in pure $\ell$-As, which is, in turn, quite similar to that of the crystalline phase [66, 68]. Indeed, our calculated $g_{AsAs}(r)$ at $x = 0.2$ has some of the same features as those in the calculated $g(r)$ for pure $\ell$-As [66]. However, there are also some observable differences, which may be related to the fact that pure $\ell$-As is semiconducting while $\ell$-Ga$_{0.2}$As$_{0.8}$ is calculated to be metallic (as shown later when we calculate the electronic structure). First, if we integrate $g_{AsAs}(r)$ for the $x = 0.2$ sample out to the first minimum beyond the main peak, we obtain a coordination number of 3.2 As atoms for the first shell of nearest neighbors surrounding an As atom. This is slightly larger than the value 3 reported for pure $\ell$-As (at $T=1150$ K) experimentally and in previous calculations [66, 69]. A more important difference is that pure $\ell$-As has a sharp second peak in $g(r)$ [68], whereas for $g_{AsAs}(r)$ in our simulations this second peak is very broad. While some of this broadening may result from the higher temperature ($T=1600$K) in our simulations for $x = 0.2$, these results suggest that the local structure seen in $\ell$-As is preserved only out to the first shell of neighbors in $\ell$-Ga$_{0.2}$As$_{0.8}$.

On the other hand, the features we see for $g_{GaGa}(r)$ at $x = 0.8$ are qualitatively similar and consistent with those seen for liquid Ga at lower temperatures [42, 59]. Using the procedure indicated above, we get a Ga coordination number of 5.8 for the first shell. If we integrate the total $g(r)$ up to the first shell (i.e., including both As and Ga neighbors of Ga), we obtain a Ga coordination number of 6.9. While these values are smaller than the coordination number of 9.0 reported for pure $\ell$-Ga [59], we attribute the difference to the lowering of the first peak due to the higher temperature.
Figure 4.3: Partial structure factors $S_{GaGa}(k)$, $S_{AsAs}(k)$, and $S_{GaAs}(k)$ for $x = 0.5$ and the same temperature as above of our simulations ($T = 1600$ K) compared to those for pure $\ell$-Ga ($T = 702$ K and $T = 982$ K) [42].

Figs. 3-5 show information about the various partial alloy structure factors at the same temperature. The partial structure factors $S_{ij}(k)$ are defined in one of the standard ways[15, 70]:

$$S_{ij}(k) = (N_iN_j)^{-1/2}\left(\sum_i \sum_j e^{-ik\cdot(R_i-R_j)} - (N_iN_j)^{-1/2}\delta_{k,0}\right)$$  \hspace{1cm} (4.1)

where $i$ and $j$ denote the two components of the binary alloy. Fig. 3 shows the calculated total structure factor $S(k)$, as weighted by neutron scattering factors at a
Figure 4.4: Calculated neutron structure factor $S(k) = \sum_{\alpha \beta=Ga} f_{\alpha \beta}(k) S_{\alpha \beta}(k)$, where $f_{\alpha \beta}(k)$ is the neutron form factor, for $x = 0.5$. Open circles: measured $S(k)$ as obtained by neutron diffraction.

concentration $x = 0.5$. $S(k)$ is defined by

$$S(k) = \frac{b_i^2 S_{ii}(k) + 2b_i b_j S_{ij}(k) + b_j^2 S_{jj}(k)}{b_i^2 + b_j^2}$$

(4.2)

where $b_i$ and $b_j$ are the corresponding experimental neutron-scattering lengths ($b_{Ga} = 7.2$ and $b_{As} = 6.7$) For comparison, we also show in Fig. 3 the quantity $S(k)$ as measured by neutron diffraction[71]. As can be seen from the Figure, the two agree quite well. In particular, the calculations convincingly reproduce the experimentally observed shoulder on the high-$k$ side of the principal peak in $S(k)$.

Fig. 4 shows the three partial alloy structure factors $S_{GaGa}(k)$, $S_{AsAs}(k)$, and $S_{GaAs}(k)$ at $x = 0.5$ and $T = 1600K$. The structure factor for like pairs is always
positive, with a conspicuous first peak, while the structure factor between opposite pairs is negative for small k, becoming positive at k values corresponding to the peaks in the other two partial structure factors. It is of interest to compare these results to those found in other model calculations. For a mixture of hard spheres of packing fraction 0.45 (characteristic of the liquid near melting) and ratio of hard sphere diameters of 0.9[72], the cross-correlation function is negative at small k and has a peak near that of the two same-species functions, as in our calculations. By contrast, for liquid NaCl, which is strongly ionic), the cross-correlation function has a strong negative peak at the same k as the peaks of the same-species partial structure factors. Thus, our results are more similar to the hard-sphere structure factors, suggesting that liquid GaAs is at most only weakly ionic.

Finally, Fig. 5 shows $S_{GaGa}(k)$ at $x = 0.8$ and $S_{AsAs}(k)$ at $x = 0.2$. Once again, like the real-space correlation functions at the same concentrations, the Ga-Ga structure factors show slightly less correlation (i.e., a lower principal peak and a less conspicuous second peak) than do the corresponding As-As structure factors. One possible reason for this behavior, as for the corresponding real-space correlation functions, is that the $x = 0.8$ sample is further from melting than is the $x = 0.2$ liquid.

$S_{AsAs}(k)$ for $x = 0.2$ shows characteristic differences from that for pure $\ell$-As, which are analogous to those discussed earlier for the g(r)'s. Specifically, S(k) for pure $\ell$-As[68] has a split principal peak with maxima at $k = 2.45 \text{Å}^{-1}$ and $k = 3.74 \text{Å}^{-1}$. By contrast, $S_{AsAs}(k)$ for $x = 0.2$ has a peak at 2.5 Å, but the second peak is reduced to only a shoulder at about 3.5 Å. The fact that the second of the split peaks is smoothed to a shoulder at $x = 0.2$ indicates a change in the local structure which is also reflected in the reduction of the second peak of partial g(r) as noted earlier.
We next discuss the $x = 0.8$ sample, comparing our results with those for pure $\ell$-Ga at lower temperatures [42, 59]. The partial structure factor show the same qualitative features as the structure factors for the pure liquid, but there are some quantitative differences. Our results for $x = 0.8$ (at 1600 K) show a first peak in $S_{GaGa}(k)$ with a maximum of only about 1.3, which is lower than the experimental one seen in pure Ga at 959 K ($\sim 1.7$). We attribute the lowering of the first peak to the increased temperature, as seen experimentally in most liquid metals.

Further information about the short-range order in the liquid alloy may be obtained from bond angle distribution functions, shown in Figs. 6 and 7. These functions
are defined by analogy with our previous work in liquid Ge[53, 63]. Namely, one considers a group of three atoms. Of these, one is denoted as the central atom; the other two atoms (denoted as "side atoms"), with the central atom, define a bond angle $\theta$. $g_3(\theta, r_c)$ is the distribution of bond angles formed by all such groups of three atoms, such that both the side atoms lie within a cutoff distance $r_c$ of the central atom. Fig. 6 shows $g_3(\theta, r_c)$ for the Ga-Ga-Ga angles at $x = 0.8$, and for the As-As-As angles at $x = 0.2$, each for two different choices of the cutoff radius $r_c$. Fig. 7 shows the same functions for Ga-Ga-Ga and for As-As-As at $x = 0.5$. 

Figure 4.6: Calculated bond angle distribution functions $g(\theta, r_c)$ for (a) groups of three Ga atoms at a concentration $x = 0.8$, and (b) groups of three As atoms at a concentration $x = 0.2$, both for two different cutoff radii, $r_c = 3.4\text{Å}$ and $r_c = 3.8\text{Å}$, as defined in the text.
Figure 4.7: Same as for Fig. 4.6 but for $x = 0.5$.

The peaks in these distribution functions give hints about the short-range bond-order in the liquids. For example, a peak near $\theta = 60^\circ$ corresponds to a relatively close-packed arrangement of the corresponding atomic group, with many nearest neighbors. In contrast, a peak near $100^\circ$ indicates a more tetrahedral structure, typical of covalent bonding. Thus, the upper part of Figs. 6 and 7 suggest that the Ga ions form a rather close-packed arrangement at $x = 0.8$ and $x = 0.5$, since there is a strong peak near $60^\circ$ for both values of the cutoff $r_c$. By contrast, the lower parts of Figs. 6 and 7 suggest that, as expected, the As atoms have a more open arrangement at $x = 0.2$, since there are two peaks in $g_3$ at this concentration: a side peak near $50^\circ$, and another noticeable peak near $97^\circ$. We also observe the peak at $97^\circ$ for As atoms.
at $x = 0.5$. However it is broader and less pronounced than at $x = 0.2$. In both Figs. 6 and 7, the Ga-Ga-Ga bond angle distribution depends little on $r_c$.

At $x = 0.2$, the As-As-As distributions show noticeable $50 - 60^\circ$ peaks only at the larger cutoff values. At the smaller cutoff radius, the $50 - 60^\circ$ peak is missing. Thus, at short distances, the As clusters tend to maintain the local version of the structure they have in the pure liquid phase (and the crystalline phase) which shows a strong peak at $97^\circ$, but at larger cutoffs the local structure differs from that of pure $\ell$-As. We have made the same observation in connection with $g_{\text{As-As}}(r)$ at the same concentrations, and with the shoulder in $S_{\text{As-As}}(k)$. The $97^\circ$ peak implies some tetrahedral order persisting to $x = 0.2$, though this peak is less pronounced than in pure $\ell$-As[66].

We have also calculated the electronic properties of $\ell$-$\text{Ga}_x\text{As}_{1-x}$. We calculate the single-particle electronic density of states $N(E)$ in the standard way, by using the expression

$$N(E) = \sum_{k,E_k} w_k g(E - E_k).$$

In this expression $E_k$ denotes one of the energy eigenvalues of the single-particle wave functions at a particular $k$ point within the supercell Brillouin zone, $w_k$ is the weight of that $k$ point (defined below), and $g(E)$ is a Gaussian smoothing function of width $\sigma = 0.2eV$. Our calculation is carried out by sampling the supercell Brillouin zone at eight special $k$ points, using the same choice of special points and weights as that of Holender et al in their calculations for pure $\ell$-Ga[42]. For each $k$-point we include 40 conduction band states, and for each concentration, we obtain our final results by averaging over twelve representative liquid state configurations.
Figure 4.8: Single-particle electronic density of states $N(E)$ for $\text{Ga}_x\text{As}_{1-x}$ at $x = 0.2$, 0.4, 0.6, and 0.8. The Fermi energy in each case is shown as a dashed vertical line.

The resulting calculated density of states $N(E)$ is shown for the four concentrations $x = 0.2, 0.4, 0.6, \text{ and } 0.8$ in Fig. 8. [We do not show our calculated $N(E)$ for $x = 0.5$, but it interpolates smoothly between $x = 0.4$ and $x = 0.6$.] As in our previous studies, the alloy has a clearly metallic density of states for all concentrations $x$. However, just as in our previous results for $\text{Ga}_x\text{Ge}_{1-x}$, the density of states becomes more and more free-electron like as the concentration $x$ of the metallic component (Ga in this case) increases. Pure $\text{l-As}$ is semiconducting and has been calculated to have deep minima in the electronic density of states at the Fermi energy ($E_F$), and also at an energy of $\sim -7$ eV (measured from $E_F$) [66], which separates the $s$ and $p$ bands. Liquid Ga, on the other hand, has an almost free-electron like density of states. We
Figure 4.9: Calculated electrical conductivity $\sigma(\omega)$ for $\text{Ga}_x\text{As}_{1-x}$ at $x = 0.2$ and $x = 0.8$.

see these features reflected in our simulations; as the figures indicate, the electronic density of states (DOS) has a pseudogap in the As rich phase which progressively fills up as the Ga concentration is increased, so that for $x = 0.8$ it is hardly noticeable. But even at low Ga concentration ($x = 0.2$), there is no minimum in the density of states at the Fermi energy. As for the pseudogap, we find that its position changes monotonically to lower energies (relative to $E_F$) with increasing Ga concentration.

A similar pseudogap is reported in calculations for pure $\ell$-Ge [53, 61], for the same reason, i. e., a partial separation between s-like and p-like bands.

We have also computed the frequency-dependent electrical conductivity $\sigma(\omega)$ for $x = 0.2, 0.4, 0.5, 0.6$, and $0.8$, at frequencies ranging up to $2eV$. $\sigma(\omega)$ is given by the
Table 4.1: D. c. conductivity at the four concentrations, obtained by extrapolating low frequency a. c. conductivity results.

<table>
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<th>Concentration (%)</th>
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<th>40</th>
<th>50</th>
<th>60</th>
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<td>0.9</td>
<td>0.84</td>
<td>0.91</td>
<td>1.1</td>
</tr>
</tbody>
</table>

standard Kubo-Greenwood expression\[45\]

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2\omega\Omega} \sum_i \sum_j (f_j - f_i) |\langle \psi_i | \hat{p} \alpha | \psi_j \rangle|^2 \delta(E_j - E_i - \hbar\omega).$$  \tag{4.4}$$

where $\psi_i$ and $\psi_j$ are the single particle Kohn-Sham wave functions with Fermi occupancies $f_i$ and $f_j$ and energy eigenvalues $E_i$ and $E_j$. Once again, we calculate the conductivity using the same set of eight special $k$ points used for $N(E)$, and averaging over the same twelve representative ionic configurations, including 40 conducting band states for each $k$. The frequency-dependent conductivity is shown in Fig. 9 for $x = 0.2$ and $x = 0.8$, and its calculated zero-frequency limit is listed in Table I for the five concentrations $x = 0.2, 0.4, 0.5, 0.6$ and $0.8$, all at $T = 1600K$.

Several features of the conductivity graphs, and of the tabulated d. c. limits, deserve mention. First, the calculated value of the d. c. conductivity at $x = 0.5$ is very close to the experimental value: $0.84 \times 10^4$ ohm$^{-1}$cm$^{-1}$, compared to the experimental value of $0.79 \times 10^4$ ohm$^{-1}$cm$^{-1}$\[16\]. Secondly, the conductivity has a weak minimum near $x = 0.5$. This is consistent with expectations based on second-order perturbation theory\[17\] which would predict that alloy scattering (due to concentration fluctuations) would be a maximum near $x = 0.5$. Thirdly, the frequency-dependence of $\sigma(\omega)$ becomes more metallic as $x$ increases. Specifically, at $x = 0.8$, $\sigma(\omega)$ clearly

70
Figure 4.10: Calculated mean-square displacement \( \langle |R_\alpha(0) - R_\alpha(t)|^2 \rangle \), plotted as a function of \( t \) for \( x = 0.5 \) and \( \alpha = \text{Ga}, \text{As} \). One-sixth the long-time slopes of these functions give the partial diffusion coefficients \( D_{a\alpha} \), shown in Table 2.

decreases with increasing frequency, characteristic of a Drude metal, while for the highest As concentration (\( x = 0.2 \)), the conductivity is nearly frequency-independent in the range of calculation. This behavior is closer to the nonmetallic behavior in which the conductivity increases with increasing frequency.

Finally, we have computed one important atomic transport coefficient, namely, the atomic self-diffusion coefficients \( D_{ii} \) for the majority species in the two liquids \( \text{Ga}_{0.2}\text{As}_{0.8} \) and \( \text{Ga}_{0.8}\text{As}_{0.2} \). In both cases, the \( D_{ii} \)'s can be extracted from a plot of the mean-square atomic displacement versus time, which approaches a straight line.
in the limit of large time. The expression is

\[ D_{ii} = \lim_{t \to \infty} \frac{\langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle}{6t}, \] (4.5)

where \( \mathbf{R}_i(t) \) denotes the position of an ion of species \( i \) at time \( t \), and the triangular brackets denote an average over all atoms of species \( i \) and over initial times. Plots of the mean-square atomic displacement as a function of time are shown in Fig. 10 for both types of atoms at \( x = 0.2 \) and 0.8 as indicated above; From these we obtain

\[ D_{Ga} = 2.1 \times 10^{-4} \text{ cm}^2/\text{sec} \text{ at } x = 0.8; \quad D_{As} = 1.7 \times 10^{-4} \text{ cm}^2/\text{sec} \text{ at } x = 0.2. \]

The value for \( D_{As} \) at \( x = 0.2 \) is about three times larger than that obtained by Li [66] for pure \( \ell \)-As (\( D \sim 0.6 \times 10^{-4} \text{ cm}^2/\text{sec} \)). This difference is probably due to a combination of several factors. First, the calculations by Li are carried out at a temperature \( \sim 450 \text{ K} \) lower than ours. Secondly, pure \( \ell \)-As seems to have more covalent bonding than \( Ga_{0.2}As_{0.8} \), which probably impedes atomic motion, giving a lower atomic diffusion coefficient for As. Thus, in short, this behavior seems to be consistent with the rest of our picture, which is that \( \ell \)-Ga\(_x\)As\(_{1-x} \) rapidly acquires metallic conductivity, and corresponding structural properties for \( x \) as small as 0.2.

### 4.3 Discussion and Conclusions

The most striking results of these calculations is that Ga\(_x\)As\(_{1-x} \) remains metallic at all concentrations between \( x = 0.2 \) and \( x = 0.8 \), including the As rich value \( x = 0.2 \). Thus even low Ga concentrations are sufficient to render \( \ell \)-Ga\(_x\)As\(_{1-x} \) metallic (recall that pure \( \ell \)-As is semiconducting). This is reflected in the electronic density of states which shows no minimum at the Fermi energy for all concentrations studied. The liquid structure is also consistent with metallic behavior at all concentrations between \( x = 0.2 \) and 0.8, although there are some clear deviations from the behavior seen in
simple metallic alloys. Specifically, although the coordination number at all concentrations is larger than the value of four that might be expected in a predominantly covalent liquid, it is still smaller than that of a typical close-packed hard-sphere mixture. At $x = 0.2$ and $0.8$, the pair correlation functions and structure factors resemble those of the corresponding pure liquids, except that the split first peak in $S(k)$ of $\ell$-As becomes a single peak with a weak shoulder in As.

It has been suggested [73] that semiconducting properties persist in a liquid only if the liquid has the same short-range order as the crystalline phase. In the alloys we study, the liquid state has a short range order which is distinctly different from the solid. We also find that all these alloys are metallic, in agreement with the suggestion of Ref. [73]. By contrast, again in agreement with the picture advanced in [73], another compound semiconductor, stoichiometric CdTe, appears to preserve the crystalline short-range order, and also to retain its semiconducting characteristics in the liquid state. Such semiconducting behavior was indeed found in the \textit{ab initio} calculation by Godlevsky et al.[64]. It would be of interest to extend their calculations off stoichiometry, where metallic behavior is likely.

The other characteristics of $\ell$-Ga$_x$As$_{1-x}$ reflect its fundamentally liquid-metallic character. For example, the resistivity is predicted to exhibit typical Faber-Ziman behavior: a weak positive deviation from a linear concentration dependence near stoichiometry, which is caused by alloy scattering. The calculated values of the partial atomic diffusion coefficients are comparable to the diffusion coefficients of those other liquid semiconductors which are metallic in their liquid states. We find no evidence of a strong reduction in this value because of formation of clusters near stoichiometry;
such cluster formation is not expected for Ga$_x$As$_{1-x}$ because of the small electronegativity differences between the two species. One might speculate that, in other liquid semiconductors, such as stoichiometric $\ell$-CdTe, which remain poorly conducting in the liquid state, the local structure is much more ionic near melting and the atomic diffusion coefficients are correspondingly lower.

In summary, our calculations show that Ga$_x$As$_{1-x}$ is a reasonable metal at all concentrations between $x = 0.2$ and $x = 0.8$. In particular, there is no evidence of strong compound formation in the liquid state near $x = 0.5$. The electrical conductivity shows a concentration dependence typical of a liquid metallic alloy, with evidence of weak scattering from concentration fluctuations which reaches a maximum near $x = 0.5$. The electronic density of states shows no minimum at the Fermi energy; instead, it has a pseudogap between $s$-like and $p$-like occupied state which persists at all concentrations, though it is considerably weaker in the Ga-rich alloys. The atomic diffusion coefficient is calculated to be similar to that of other liquid semiconductors which are metallic in their liquid state. Finally, the liquid structure shows some indications of deviation from the behavior of simple liquid metal alloys[70]. The principal evidence of deviation from behavior characteristic of a simple liquid alloy formation comes from the calculated pair correlation functions, structure factors, and bond angle distribution functions, all of which show some weak indications of departure from close-packed behavior: smaller coordination functions than in typical hard-sphere liquids, and a weak residue of tetrahedral bonding.

In the next Chapter, we apply the ab initio techniques to the study of solid semiconductor surfaces, in particular to the growth of Si on Ge(001) surfaces.
CHAPTER 5

ENERGETICS AND STM IMAGES OF SI ON GE(001)

5.1 Introduction

So far, we have used ab initio techniques to look at liquid semiconductors and alloys. We now turn to the application of these techniques to the surfaces of solid semiconductors. These systems are of great interest both technologically and from a fundamental point of view. With semiconductor-based devices growing smaller and smaller, the physics of semiconductor surfaces has become increasingly important. One of the issues of interest is the initial stages of growth on these surfaces. In the following we address this issue for the case of growth on Ge(001) surfaces.

The growth of Si (or Ge) on Si(001) and Ge(001) surfaces has recently been extensively studied, spurred by interest in GeSi superlattices [74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84]. Despite numerous studies of film growth in these systems however, the initial stages of growth are not well understood [82, 83, 84]. Most studies, both theoretical and experimental, have been carried out on the system of Si on Si(001) [75, 76, 77, 78, 79, 80, 81, 82, 83]. They may be summarized as follows. In the earliest growth stage, no isolated ad-atoms are observed at room temperature; the smallest
stable adsorbed unit is a dimer[76, 77]. By ad-atom we mean a single atom added on top of the surface, whereas the ad-dimer will refer to the addition of a dimerized pair of atoms. Fig. 1 shows the four plausible local energy minima available for these ad-dimers, three of which (A, B, and C) have been experimentally detected[82, 83]. Two of these (A and B configurations) consist of isolated dimers directly adsorbed on top of the substrate dimer rows; of these, the B dimer is found to be the most stable[79, 80, 81, 82, 83]. In addition to these, C dimers are also detected, both in isolation and in the form of diluted dimer rows. Multi-atom structures oriented along the (130) surface direction are also observed[77, 83]. These structures are thought to be composed either of C dimers or of pairs of ad-atoms[83, 84]. The fourth possible (D) configuration for isolated dimers has not been observed experimentally in isolation [83]. This is consistent with the results of \textit{ab initio} calculations for isolated ad-dimers which find that the D dimer is highest in energy[78, 79, 80]. Experimental observations of Ge on Si(001) exhibit similar features[84].

Recently Wulfhekel et al. [85] (WHZRP) carried out a quantitative analysis of structures formed by deposition of 0.01 monolayer at 300K of Si on Ge(001). Just as in the growth of Si and Ge on Si(001), they found no stable isolated ad-atoms but only stable ad-dimers. They also observed multi-atom structures oriented along the (130) direction. However, in contrast to growth on Si(001), they found no isolated ad-dimers in the C configuration. They found that D dimers are the most commonly observed dimers on the surface, and that they become even more numerous on annealing. By contrast, they found that dimers in the A and B configurations, which lie atop the substrate dimer rows, are less common and become even rarer on annealing. These
In this Chapter, we describe ab initio simulations of Si ad-dimers on the Ge(001) surface. The goal of these calculations is to understand the surprising contrasts between the results of Wulfhekel et al. and those found for adsorption of Si or Ge on Si(001). For comparison, we have also carried out analogous studies of Ge dimers on Si(001). Our results show that the D dimer is the highest in energy for Si on Ge(001), contrary to the experimental deduction of WHZRP, but in keeping with the trend seen in theoretical and experimental results for Si (or Ge) growth on Si(001). We
suggest two possible ways of reconciling our result with experimental observations. We then propose an experimental test which will unambiguously distinguish between these two possibilities.

5.2 Results

Our total energy calculations for the various surface structures were carried out using density functional theory in the local density approximation (LDA). We used generalized norm-conserving pseudopotentials[86] with a plane wave basis set and the Ceperley-Alder exchange-correlation potential in the form parameterized by Perdew and Zunger [87]. Our supercell consists of a $4 \times 4$ surface unit cell with six Si (or Ge) layers and six vacuum layers. Of the six layers, the bottom two layers were held fixed at their bulk lattice positions with the theoretical lattice constant of 5.58Å for Ge and 5.38Å for Si, while the remaining four layers were allowed to relax fully. The clean surface was taken to have the c(4×2) reconstruction. The dangling bonds of the bottom layer were saturated by H atoms. We used an energy cut-off of 10 Ry in our plane wave expansion and two special k points in the irreducible part of the surface Brillouin zone. The calculated forces on the atoms were converged to less than 0.0005 Hartree/Bohr. By varying parameters such as Brillouin zone sampling and energy cut-off, we estimate that our calculated energy differences are converged to better than 0.05 eV. The computations were performed using the \textit{ab initio} code \textit{fhi96md}[88].

The calculated energies of the different ad-dimers relative to the B dimer are shown in Table I. From these results we make the following observations: (1) In all
### Table 5.1: Energies in eV of the dimer configurations of Fig. 1 on Si and Ge substrates, relative to the stable B dimer. In each case the isolated D dimer is theoretically found to be the highest in energy. On the Si(001) substrate this isolated dimer is not observed experimentally[83, 84]. On Ge(001) WHZRP[85] report the existence of this dimer in isolation and also identify it to be the most stable.

"Theoretical values from Ref. [78]. "Theoretical values from Ref. [79]. "Experimental values from Refs. [81, 82] (in italics).

<table>
<thead>
<tr>
<th>Ad-dimer</th>
<th>Si/Si(001)</th>
<th>Si/Ge(001)</th>
<th>Ge/Si(001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1.11&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.76&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.18</td>
</tr>
<tr>
<td>C</td>
<td>0.3</td>
<td>0.18</td>
<td>0.06&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>-0.01</td>
<td>0.07</td>
<td>0.11</td>
</tr>
</tbody>
</table>

three systems i.e. Si/Si(001), Si/Ge(001) and Ge/Si(001), we notice that the D ad-dimer has the highest energy. Our results for Ge/Si(001) are consistent with the experimental observation that no isolated D dimers are seen[84]. Previous <i>ab initio</i> calculations[78, 79, 80] for the Si/Si(001) system also indicate that the D dimer has the highest energy, consistent with experimental observations[80, 83]. By contrast, WHZRP conclude that in Si/Ge(001) the D dimer is energetically the most favored amongst the different dimer types. (2) The energies of the B and C dimers for Si/Ge(001) are nearly degenerate, whereas for adsorbates on Si(001) the energies of these dimers are calculated to differ substantially. (3) Finally, we observe that the calculated energy of the D dimer relative to the B dimer is much smaller in the Si/Ge(001) system than in the Ge/Si(001) and Si/Si(001) systems.

We now discuss the experimental results of WHZRP[85], in light of these calculations. As mentioned before, WHZRP found that isolated D ad-dimers are the most common species found in the Si/Ge(001) system at low coverage, making up 39% of the deposited material when 0.01 monolayers of Si was grown on Ge(001) at 300K.
and 50% of the material when that same surface was annealed for five minutes at 350K. Furthermore the predominant species when Si is deposited at 350K are the D dimers. From these and related results, WHZRP conclude that the D dimer is the isolated dimer of lowest energy on this surface. While we compute the C dimer to be considerably lower in energy than the D dimer (cf. Table I) they observed no isolated C dimers. Despite the absence of isolated C dimers, WHZRP do report metastable multi-atom ("CC") structures lying along (130), comprised of several C dimers. The experimental observation of stable D dimers, the absence of isolated C dimers, and the presence of CC structures, seems somewhat puzzling. Not only does it seem inconsistent with the calculated energy sequences of Table I for Si/Ge(001): it also contrasts with the behavior of Si (or Ge) dimers on Si(001), where experimentally no isolated D dimers are found [83, 84], in agreement with calculated dimer energies[78, 79, 80].

In an effort to resolve this puzzle, we generated STM images of our relaxed geometries for the D and C dimers (cf. Fig. 2c and Fig. 2d). Fig 2 shows the calculated STM images at constant height for the Si/Ge(001) system. These images were generated in the Tersoff-Hamann approximation [89, 90]. In this scheme, the tunneling current is proportional to the local density of states at the tip position integrated over the energy range allowed by the applied bias voltage. If we denote the local density of state at the tip position by $\rho_s(r^t, \epsilon)$ and the applied voltage bias is $V$, then the tunneling current is given by

$$I(r^t, V) \propto \int_{E_{\text{Fermi}}}^{E_{\text{Fermi}}+eV} \rho_s(r^t, \epsilon) d\epsilon$$  \hspace{1cm} (5.1)

A positive bias gives us the STM images of the empty states (in the specified energy range) and a negative bias does the same for the filled states. By mapping surfaces
of constant $I(r', V)$ an isocurrent picture can be simulated. Alternatively, we can fix the tip height and evaluate the above integral for that value. Both procedures yield essentially the same STM images in terms of qualitative features [90], and we shall follow the latter approach.

Figs. 2e and 2a show the computed filled and empty state STM images respectively for the D dimer. Note that the empty state image of the D dimer (Fig. 2a) shows buckling consistent with the relaxed atomic geometry (Fig. 2c). Comparing with experiment we notice that the STM images of D dimers, as observed in Refs. [85, 91], have four distinguishing characteristics: (i) in empty-state images, the ad-dimers lie in the troughs between dimer rows; (ii) they appear much brighter in empty state images than in filled state images; (iii) in filled-state images, they show a ring like feature with a faint intensity in the middle; and (iv) in empty-state images, they appear elongated along the dimer rows. All four of these characteristics are seen in our theoretical images. Hence, these results are consistent with the fact that the most frequently occurring dimer reported by WHZRP in Si/Ge(001) is indeed the D dimer.

On the other hand, Table I indicates that the D configuration is theoretically always found to be energetically the least favored ad-dimer. One possible resolution of this apparent discrepancy is that the D dimer, although not the most stable energetically, is favored to form kinetically. This would be similar to the case of Si/Si(001), where the C dimer, though higher in energy than the A and B dimers is argued to be favored kinetically[80, 83]. Such a resolution would be consistent with the energetics of Table I, since then the D dimer need not be the dimer of lowest energy. This would also be in accordance with the agreement between our theoretical STM images of the
D dimer and the experimental ones of WHZRP. However, we should note that experimental STM images probe only the local electronic density of states, and care must be exercised when inferring the corresponding atomic geometry\cite{92}. Consider, as an example, the conclusion drawn earlier from the experimental STM images\cite{85} that all four substrate atoms nearest to the D dimer recede into the Ge(001) surface. On the contrary our \textit{ab initio} computation for the D dimer shows that two of these four Ge atoms rise \textit{upwards} by about 0.5\AA\ compared to their positions in clean Ge(001).

Keeping such considerations in mind, we now examine an alternate possibility: that the isolated ad-dimers identified by WHZRP \cite{85} as D dimers are actually dimers in the C configuration. Figs. 2f and 2b show our computed filled and empty state STM images for the C dimer which, consistent with the underlying relaxed atomic geometry (cf. Fig. 2d), show no buckling. These images of the C dimer clearly exhibit the same first three characteristic features of the experimental dimer images. Only the fourth characteristic (i.e. elongation of the ad-dimer image along the dimer rows in empty state images) distinguishes the two types of dimer images, since the C dimer empty-state image shows that it extends perpendicular to the substrate dimer rows. This distinction is clear in our theoretical STM images, which are generated assuming a perfectly sharp tip. However as Fig. 2b suggests, a slight distortion in this empty state image of the C dimer can make it appear extended along the direction parallel to the dimer rows. In practice such distortions could arise from real finite-size effects of the STM tip. Thus the C and D dimer images could well be confused, since they share three common characteristics and differ only in the fourth. It is therefore possible that the dimer in the trough observed by WHZRP is the C dimer. If so, this result would be consistent not only with our calculated results for the Ge(001)
substrate (cf. Table I), but also with the theoretical and experimental trend observed for Si and Ge grown on Si(001)[78, 79, 80, 82, 83, 84].

To distinguish further between these two possibilities we generated theoretical STM images of these two dimers at varying biases. We found the main features of the C and D dimer empty state images to be nearly independent of bias in the range of +0.5V to +2.0V. Furthermore, the filled-state images of the D dimer do not change much in the bias range from -0.5V to -2.0V. This is seen in Figs. 2e and 2g, which show nearly identical filled-state images generated at biases of -1.6V and -0.6V. However, the filled state image of the C dimer at low bias shows a dramatic change. The C dimer, which is very visible at a bias of -1.6V (cf. Fig. 2f), shows a distinct reduction in intensity below a bias of -0.8V and nearly disappears at the low bias of -0.6V (cf. Fig. 2h).

We now propose an experimental test based on this difference. If such low-bias filled-state images of the Si/Ge(001) system show that the dimer lying in the trough between the substrate dimer rows almost disappears at low bias, then it is a C dimer. If, on the other hand, the image remains principally unchanged in character, then this result indicates that it is a D dimer. Thus a low-bias imaging of this system should serve as a test to indicate unambiguously whether it is a C or a D dimer which has been observed. Such low-bias STM imaging can now be carried out, with a sufficiently sharp tip [93].

If the proposed test detects a D dimer, then its formation would presumably be due to some kinetic mechanism. This would suggest a rather different growth mechanism for the Si/Ge(001) system than that found for Si/Si(001), where isolated C dimers have been argued to play a crucial role in the initial stages of growth[78, 79, 83].
Otherwise, if the test detects a C configuration, then the behavior of Si/Ge(001) would be consistent with our results in Table I for Si/Ge(001) and would suggest that Si/Ge(001) and Si (or Ge) on Si(001) have similar growth patterns.

To summarize, we have calculated the energies of Si dimers on Ge(001) and Ge dimers on Si(001), in various configurations. The D dimer is found to have the highest energy in both systems. This result is consistent with STM observations in the Ge/Si(001) system and Si/Si(001) system, in both of which no D dimers were seen. In the Si/Ge(001) system, STM experiments have identified D dimers as the most stable[85]. To account for this apparent discrepancy, we generated theoretical STM images for both the C and D dimers for Si/Ge(001). Our results suggest that the images of these two dimer types can be difficult to distinguish. Thus, the existing experiments may be consistent with either C or D dimers. We have also proposed an experimental test (low-bias STM imaging) which, if carried out, should permit the two configurations to be unambiguously distinguished.

So far in this thesis, we have looked at the properties of materials such as Ge and GaAs and obtained useful quantitative information about them. We now turn to the study of model systems, which is a complementary approach to understanding properties of condensed matter systems. In the next Chapter, we will look at the properties of a particular class of networks with disorder, which are widely applicable as models for real-life networks, and obtain some interesting properties characterizing these networks.
Figure 5.2: STM images and fully relaxed geometries for Si dimers on the Ge(001) surface. Relaxed configurations of the ad-dimer and top layer atoms are shown for (c) the D dimer and (d) the C dimer. The height is represented by the size of the filled circles. Above the respective geometries are shown the empty state images in (a) and (b). Below the relaxed geometries are shown the respective filled state images at high bias [(e) and (f)] and low bias [(g) and (h)]. The images were generated at a distance of 3 Å from the uppermost substrate atom. The maximum(minimum) charge densities are 15(1), 14(0.9), 4(0.2), 4(0.2), 3(0.2), 2(0.1) for the images a, b, e, f, g, and h respectively, in units of $10^{-4}$ e/Å$^3$. Notice that the charge densities for the empty state images are significantly larger than for the corresponding filled state images, consistent with experiment [80].
6.1 Properties of small-world networks

An idea which has become increasingly popular in this age of global interconnectedness is that there are "six degrees of separation" between any two individuals on the planet. While the exact number six might be somewhat speculative, most social networks do seem to exhibit the property that there is a surprisingly short number of "links" necessary to make a connection between its most distant members. This is a property also seen in random graphs [112], however one would think that social networks are not random at all. When viewed on a local basis they seem, for most part, to be quite structured. So the puzzle here is how systems that appear ordered locally can resemble disordered or random systems globally.

Recently Watts and Strogatz [94] have studied a class of networks which can be 'tuned' from being ordered to being random by varying a single parameter. In doing so, they discovered that for a range of parameter values the networks resembled ordered networks locally but random networks globally. They named this class of networks "small-world" networks because of their relevance to the problem in sociology mentioned above [95]. There were able to show that surprisingly diverse
group of real-life networks such as the power grid of the western United States, the neural network of the worm *Caenorhabditis elegans*, the collaboration graph of film actors can all be characterized as small-world networks. Since their introduction, small-world networks and their properties have received a lot of attention, in part due to their possible application to a broad spectrum of systems ranging from social networks [95] to coupled dynamic oscillators [96]. Hence there has been considerable effort spent lately in understanding the properties and applications of these networks. [97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111].

Much of the work characterizing the properties of small-world networks has focused on the average minimal distance, $\bar{l}$, separating two randomly chosen points in the network. Previous work has shown that $\bar{l}$ has two scaling regimes: for small systems sizes $L$, it is found that $\bar{l} \sim L$, whereas for large $L$, $\bar{l} \sim \log(L)$, [112]. A scaling form for $\bar{l}$ has been proposed and numerically confirmed; however the nature of the crossover between the two scaling regimes has been the subject of debate[98, 101, 103, 105, 107, 108]. In this work, we will focus on some basic probability distributions for small-world networks, and as a consequence obtain an exact result for $\bar{l}$ and its variance $\sigma^2$.

We generate the networks following the prescription of Newman and Watts [101]. We start with a 1-d periodic lattice with $L = 2N$ sites and nearest neighbor connections. We then add short-cuts uniformly with probability $p$ such that the average number of short-cuts added is $x = pL$. By a short-cut we mean an added link which connects a given site to another randomly chosen site in the network. The somewhat surprising result found by Watts and Strogatz is that it takes only a small number of short-cuts to make the network a “small-world” network. We now proceed with some
definition which will aid further analysis of these networks. We denote the distance between two sites, counted along the lattice using only nearest neighbor links, as the \textit{Euclidean distance}. By contrast, the shortest distance between two sites, counted along any bond including short-cut bonds, is called the \textit{minimal distance}.

Using these definitions, we now introduce the following probability functions: (i) $P(n|m)$, the probability that two sites are separated by Euclidean distance $n$ given that their minimal distance is $m$; (ii) $P(m|n)$, the probability that two sites have minimal separation $m$ given that their Euclidean distance is $n$; and (iii) $Q(m)$, the probability that two randomly chosen sites have a minimal separation $m$. Recently, Dorogovtsev \textit{et al} [111] have introduced two exactly solvable models similar to small-world networks. For these models they derive the explicit form of $P(m|n)$, from which they obtain $\bar{l}$ and other properties of their networks. In this Section, we derive the general form of $P(m|n)$ for small-world networks, and we confirm it numerically. Using this form, we derive an exact expression for $\bar{l}$ and for the variance of $\bar{l}$, $\sigma^2 = \bar{l}^2 - \bar{P}^2$. We also study the scaling properties of $P(m|n)$ and obtain some approximate results for it in the limit of large $L$. Note that in describing the networks, we have considered the case of coordination number of $2k = 2$ for each site. However, our arguments for the general form of $P(m|n)$ are valid for arbitrary $k$. For simplicity we will consider the case $k = 1$ in the rest of this Letter and generalizations to arbitrary $k$ will be indicated as appropriate.

We begin by deriving the general form of $P(n|m)$. First, since the minimal distance cannot exceed the Euclidean distance, $P(n|m) = 0$ for $n < m$. For $n > m$, the minimal path must use at least one short-cut. But taking a short-cut is equivalent to randomizing the position along the network, since the short-cuts are uniformly
distributed. Hence, $\bar{P}(n|m)$ must be independent of $n$ for all $n > m$. Finally, for $n = m$, it is not necessary to use any short-cuts in the minimal path; so the arguments invoked for $n > m$ do not apply. Instead, $\bar{P}(n|n)$ is determined by the constraint that the probability distribution is normalized.

We now derive the general form of $P(m|n)$. From elementary probability theory, we have

$$\bar{P}(n|m) \ast Q(m) = \begin{cases} \frac{2}{L-1}P(m|n) & ; \ n < N \\ \frac{1}{L-1}P(m|n) & ; \ n = N \end{cases} \tag{6.1}$$

From Eqn. (6.1) and the properties discussed in the previous paragraph, $P(m < n|n) \equiv f(m)$ is independent of $n.$ and $P(m > n|n) = 0$. Thus the general form of $P(m|n)$ is

$$P(m|n) = \Theta(n - m)f(m) + [1 - \sum_{m' = 1}^{n-1} f(m')]\delta_{m,n}, \tag{6.2}$$

where $\Theta(x)$ is defined by $\Theta(x) = 0$ for $x \leq 0$ and $\Theta(x) = 1$ for $x > 0$. We have numerically confirmed the validity of this form, as shown in Fig. 6.1.

The fact that $P(m|n)$ is completely determined by $f(m)$ has some surprising consequences, regardless of the exact form of $f(m)$. To explore these consequences, we examine some other properties of small-world networks. For example, besides $\bar{l}$, the quantity $\langle \ell(n) \rangle$, which is the average minimal distance separating two sites with Euclidean distance $n$, has been discussed in the literature[107, 108]. We can express both these quantities in terms of $P(m|n)$ as follows:

$$\langle \ell(n) \rangle = \sum_{m=1}^{n} mP(m|n) \tag{6.3}$$

$$\bar{l} = \frac{1}{L-1} \left[ 2 \sum_{n=1}^{N-1} \sum_{m=1}^{n} mP(m|n) + \sum_{m=1}^{N} mP(m|N) \right] \tag{6.4}$$
Figure 6.1: The values of \( f(m) \) as obtained from \( P(m|n) \), which is calculated from simulations for the \( n \)-values \( n = 5 \) (○), \( n = 10 \) (*), \( n = 15 \) (*), and \( n = 500 \) (○). This figure confirms the statement that \( P(m < n|n) \) is independent of \( n \). The parameters for the figure are \( L = 1000, p = 0.25 \). Similar confirmation has been obtained from simulations for a wide range of parameter values.

Similar expressions hold for \( \langle \ell^2(n) \rangle \), \( \langle \ell^3(n) \rangle \), and \( \bar{\ell}^2 \). Substituting the form of \( P(m|n) \) [Eqn. (6.2)] into the expression for \( \bar{\ell} \) [Eqn. (6.4)], we obtain

\[
\bar{\ell} = \frac{1}{L-1} \left[ 2 \sum_{n=1}^{N-1} \sum_{m=1}^{n-1} mf(m) + 2 \sum_{n=1}^{N} n[1 - \sum_{m=1}^{n-1} f(m)] \right.
\]

\[
+ \sum_{m=1}^{N-1} mf(m) + N[1 - \sum_{m=1}^{N-1} f(m)] \right]
\]

which can be simplified to give the following exact expression:

\[
\bar{\ell} = \langle \ell(N) \rangle \left( 1 + \frac{1}{L-1} \right) - \frac{\langle \ell^2(N) \rangle}{L-1}
\]

(6.5)

Similarly, we also obtain an exact expression for the variance of the distribution of minimal distances, \( \sigma^2 = \bar{\ell}^2 - \bar{\ell}^2 \):

\[
\sigma^2 = \langle \ell^2(N) \rangle \left( 1 + \frac{1}{L-1} \right)
\]

(6.6)
Figure 6.2: The average minimal separation, $\bar{l} = Lg(x)$, vs. average number of shortcuts $x = pL$, as obtained from (a) numerical simulation by averaging over all pairs (*): (b) numerical simulation using Eqn. 6.6 (o), and (c) Padé-fit as given by Ref. [12] (solid line). This confirms the exact expression Eqn. (6.6).

$$
\begin{align*}
&= \frac{1}{3(L-1)} \left[ <\ell(N)> - 4 <\ell^3(N)> \right] \\
&- \left[ <\ell(N)> (1 + \frac{1}{L-1}) - \frac{<\ell^2(N)>}{L-1} \right]^2 \\
\end{align*}
$$

(6.7)

The surprising aspect of the above equations is that $\bar{l}$ and $\sigma^2$, which are average properties of the entire network, are completely determined by the mean separation of ‘diametrically opposite sites’ (d.o.s.), $<\ell(N)>$, and its higher moments $<\ell^2(N)>$ and $<\ell^3(N)>$. Note that Eqns. (6.6) and (6.7) can readily be generalized to any $k$ by performing the substitution $L \mapsto [L/k]$.

When the network has exactly one short-cut, $\bar{l}$ can be calculated analytically using Eqn. (6.6). In this case, in the limit of large $N$, we get $<\ell(N)> = \frac{2}{3}N$ and $<\ell^2(N)> = \frac{1}{2}N^2$ which gives $\bar{l} = \frac{5}{12}N$. As expected, this is in perfect agreement with
Figure 6.3: This figure confirms the proposed scaling form of \( f(m, N, p) \) (Eqn. (6.10)) for \( x = pL = 10 \) and system sizes: (a) \( L = 500 \) (*), (b) \( L = 750 \) (o), and (c) \( L = 1000 \) (o). We have confirmed this scaling collapse for a wide range of \( x \)-values.

The results obtained by Strang et al [105, 113]. We have further confirmed Eqn. (6.6) by numerically computing \( \tilde{l} \) using the following two procedures: (i) Averaging the minimal distance over all pairs of sites, and (ii) considering only pairs of d.o.s. and using Eqn. (6.6). The results, which are presented in Fig. 6.2, indicate that the two procedures are equivalent.

The results obtained so far have been independent of the functional form of \( f(m) \). To gain further insight, we consider the scaling properties of \( f(m) \), following the real-space renormalization group (RG) analysis of Newman and Watts [101]. This procedure consists of blocking pairs of adjacent sites while preserving the total number of short-cuts in the network. This gives for the transformed lattice: \( N' = N/2 \) and \( p' = 2p \). We note the following features of this transformation [101]: (i) the geometry
of the minimal paths is unchanged in almost all cases, and the number of site-pairs for which the geometry does change is negligible for large $L$ and small $p$. and (ii) the distance along the minimal path is halved, i.e. $m' = m/2$ for large $L$ and small $p$. Now, by definition $f(m) = P(m|N)$ ($m < N$); thus to evaluate $f(m)$ we need to calculate the average number of minimal paths of length $m$ between two d.o.s. in the network. Furthermore we note that the RG-transformation maps two pairs of d.o.s. into a single pair. This fact, in conjunction with points (i) and (ii) above gives us

$$f'(m, N, p) = 2f(m, N, p)$$

(6.8)

For large $N$, taking the continuum limit, we can generalize the above expression to

$$f'(m, N, p) = \lambda f(m, N, p)$$

(6.9)

These observations can now be summarized in the following scaling form:

$$f(m, N, p) = \frac{1}{N} h(x)$$

(6.10)

where $y = \frac{m}{N}, x = 2pN$

By fixing $x$, we have observed the scaling collapse of $f(m)$ for different values of $N$ and $p$. This is demonstrated numerically for $x = 10$ in Fig.6.3. Our simulations indicate that for any given $x$, this scaling collapse holds for large enough $N$.

It is interesting to note that the scaling properties of $I$ can be derived from the scaling form of $f(m)$. Using the definition of $I$ (Eqn. (6.4)) and the scaling form for $f(m)$, we get

$$I = \frac{L}{4}[1 - \int_0^1 dy (1 - y)^2 h(y, x)]$$

(6.11)

$$= L g(x)$$

(6.12)
Figure 6.4: $f(m)$ vs. $m$ for $x = pL = 250$ and $L = 2000$. The solid line is the gaussian fit to the calculated data. The inset shows the gaussian fit for $x = 500$ and $L = 2000$. Note that with increasing $x$, the gaussian becomes more sharply peaked.

which is consistent with the scaling form proposed in previous works. Similar scaling forms hold for $\bar{\ell}^2$, $\langle \ell(N) \rangle$, and $\langle \ell^2(N) \rangle$.

We now consider the limit of large system sizes such that $x \gg 1$. In this limit, we have observed numerically that we can approximate $f(m)$ by a gaussian distribution function:

$$f(m) = \frac{1}{\sqrt{2\pi}\sigma_g^2} e^{-\frac{(m-\mu_g)^2}{2\sigma_g^2}}$$

(6.13)

where $\mu_g$ and $\sigma_g^2$ are respectively the mean and variance of the distribution. The corresponding fit for $x = 250$ and $x = 500$ is shown in Fig. 6.4. Our simulations indicate that as $x$ increases, $(\mu_g/\sigma_g)$ also increases, as can be seen from the figure.

Using the gaussian approximation for $f(m)$, we are now able to calculate the function $\langle \ell(n) \rangle$, which has been discussed elsewhere [107, 108]. From Eqn. (6.3)
Figure 6.5: The mean distance $<\ell(n)>$ between two sites having Euclidean separation $n$ for $x = pL = 250$. Results are shown for: (a) numerical simulation ($\circ$), and (b) analytic expression (Eqn. (6.14)) (solid line). The analytic expression is an excellent fit for $x \gg 1$.

and (6.13) in the limit $\mu_g \gg \sigma_g$, we obtain

$$<\ell(n)> = n - \frac{1}{2} (n - \mu_g) \left[ \Phi \left( \frac{n - \mu_g}{\sqrt{2}\sigma_g} \right) + 1 \right]$$

$$+ \frac{\sigma_g}{\sqrt{2\pi}} e^{-\frac{(n-\mu_g)^2}{2\sigma_g^2}}$$

(6.14)

where we have assumed $\Phi(\mu_g/\sqrt{2}\sigma_g) = 1$. In this limit, substituting the above form of $f(m)$ into the definitions of $<\ell(N)>$ and $<\ell^2(N)>$, we get

$$\mu_g = <\ell(N)>$$

(6.15)

$$\sigma_g^2 = <\ell^2(N)> - <\ell(N)>^2$$

(6.16)

In particular, these equations imply that $\mu_g$ and $\sigma_g$ have the following scaling forms:

$\mu_g \sim L g_1(x)$ and $\sigma_g \sim L g_2(x)$

Using these relations, we see that the gaussian ansatz
for \( f(m) \) (Eqn. (6.13)) is consistent with the scaling form proposed in Eqn. (6.10).

In Fig. 6.5, we compare Eqn. (6.14) to results from our simulations for \( x = 250 \). In the limit \( L \to \infty \), we have \( \sigma_g/\mu_g \to 0 \), which upon substitution into Eqn. (6.14) gives us

\[
\langle \ell(n) \rangle = \begin{cases} 
  n & : n < \langle \ell(N) \rangle \\
  \langle \ell(N) \rangle & : n \geq \langle \ell(N) \rangle 
\end{cases}
\]  

(6.17)

This expression for \( \langle \ell(n) \rangle \) is consistent with that derived in Ref. [107, 108] in the same limit.

In this Section we have derived some important relations for small-world networks using the basic probability distributions that we introduced. In the next Section we turn to a possible application of small-world networks when we consider a simple model of evolution [118] and the insights that arise from combining it with the idea of small-world networks.

### 6.2 Applications to a simple model of evolution

The theory of punctuated equilibrium (PE) [114] states that (i) most evolutionary change associated with life on Earth occurs during speciation events, and (ii) the time scale for these speciation events is very brief compared to the lifetimes of the individual species. Thus the evolutionary history of most species is characterized by long periods of stasis punctuated by relatively brief intervals of rapid evolutionary activity. Mayr’s theory of allopatric speciation [115], which forms the basis of PE, suggests that the rapid evolutionary activity leading to speciation generally occurs in small isolated populations, whereas more widespread populations exhibit little evolutionary change over the same time scale. Understanding why the rates of evolutionary change differ so drastically in these two types of populations is one of the important
problems of evolutionary biology. A related problem is the study of patterns of extinctions in biological history, which seem to show scale-free behavior as discussed by Raup\cite{116}. Stanley \cite{117} has argued that these problems, and most large-scale trends in evolutionary history, can be understood by using the species as a fundamental unit of evolution.

Bak and Sneppen \cite{118} have introduced a simple model aimed at understanding these evolutionary patterns using the species as the fundamental unit. The model is based on coevolution of species and exhibits "intermittent dynamics" - that is, species undergo long periods of little change, called stasis, which are punctuated by sudden bursts of activity called avalanches. It provides a natural explanation for the apparent scale-free behavior of the extinctions - the system evolves into a self-organized critical (SOC) state with avalanches (which are correlated with extinction events) occurring at all scales. The same model can also be used to understand the scale-free behavior of seemingly unrelated phenomena such as earthquakes, as noted by Ito\cite{119}. Aside from its applications to various problems, the Bak-Sneppen model is of intrinsic interest, since it is one of the simplest models giving rise to SOC behavior.

The Bak-Sneppen model, as elaborated below, has been extensively studied for regular networks \cite{120}. However, as argued by Watts and Strogatz\cite{121}, most real-life networks are neither perfectly ordered nor completely disordered but fall under the category of "small-world" networks which interpolate smoothly between the two extremes. In the context of species interacting in an ecosystem, examples of food webs indicate that the interactions are better represented by small-world networks rather than by a simple ordered topology.

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In this Section we examine the dynamics of the Bak-Sneppen model on small-world networks. In our analysis, we find it useful to define a site-dependent property which we call "connectance." We find that the patterns of activity at each site are correlated with the connectance. In particular, the minimally connected site in a given network shows activity characteristic of intermittent dynamics, whereas the maximally connected site shows uniform activity on the same time scale. Furthermore, for the maximally connected site we see a drastic reduction in the stasis times in going from the ordered topology to the small-world networks. We discuss the implications of these results for speciation events.

We begin by recalling the definition of the Bak-Sneppen model. Each species is represented by a site on a 1-d lattice with periodic boundary conditions. Each lattice site is connected to its $2k$ nearest neighbors by a bond (so that for $n$ interacting sites, or species, we have $nk$ bonds). With each site we associate a random number, called the barrier value, between 0 and 1; this number plays the role of a barrier against evolutionary change for that species. The dynamics of the Bak-Sneppen model is carried out by the following rule. At each time step, we select the site with the minimal barrier value (denoted the minimal site), and assign new barrier values to this site and its $2k$ neighboring sites. We refer to a reassignment of the barrier value at a site as activity at that site. This set of rules, called extremal dynamics, leads the system into a SOC state where the distribution of barrier values is uniform above a critical barrier value $f_c [120]$.

The small-world networks are generated using the procedure outlined by Watts and Strogatz [121]. We start with the 1-d lattice described above and "rewire" each bond with a probability $p (0 \leq p \leq 1)$. The rewiring consists of taking a given bond
Table 6.1: The functions $L(p)/L(0)$ and $C(p)/C(0)$ as defined in the text, calculated for a system with $n = 2000$ sites and $k = 2$. For each $p$, we averaged over 25 different realizations.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$L(p)/L(0)$</th>
<th>$C(p)/C(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.14</td>
<td>0.97</td>
</tr>
<tr>
<td>0.04</td>
<td>0.06</td>
<td>0.89</td>
</tr>
<tr>
<td>1.00</td>
<td>0.02</td>
<td>0.04</td>
</tr>
</tbody>
</table>

and moving it so that, instead of connecting two neighbors, one end of the bond is moved so as to connect with another site chosen at random, with the constraint that double bonds are forbidden. The network so formed can then be characterized by the functions $L(p)$, which is defined as the number of bonds in the shortest path between two sites, averaged over all pairs of sites, and $C(p)$ which is a measure of clustering in the graph [121]. The network is said to fall in the small-world regime if it satisfies the conditions $C(p)/C(0) \sim 1$ and $L(p)/L(0) \sim 0$. Table 6.2 shows the values of these two ratios for the networks we studied, all of which were characterized by $n = 2000$ and $k = 2$. A recent study on food webs [122] suggests that our choice of $k$ is often realized in practice. Finally, for each site, we define the connectance $g_i$ by

\[
g_i = 1 - \frac{D_i - \min_{\{j\}} D_j}{\max_{\{j\}} D_j - \min_{\{j\}} D_j}; \quad p > 0
\]  

\[
D_i = \sum_{j=1}^{N} d(i, j)
\]

where $d(i, j)$ is the minimal distance between sites $i$ and $j$, that is, the minimal number of bonds which must be traversed in going from $i$ to $j$. 

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Figure 6.6: Number of avalanches (*) and number of sites covered (full line without symbols: $N_{cov}$) by an avalanche vs. duration $s$ of the avalanche, for $p = 0.01$. The influence of short-cuts, or small-world behavior, is reflected in the slope changes between regions A and B. In region C, finite-size effects dominate. The inset shows the same plots for $p = 0.0$.

We carried out our simulations for $n = 2000$ and for $p = 0.0, 0.01, 0.04,$ and 1.0. For each disordered network ($p \neq 0$) we studied the dynamics for 10 different realizations. Remarkably, even though the topologies for a given $p$ value were distinct, our calculated quantities all collapsed onto the same set of curves. The results we present were obtained by sampling for $5 \times 10^9$ time steps after the stationary state characteristic of SOC had been reached. In the following, we discuss results for $p = 0.0$ and $p = 0.01$ since these capture the essential features in going from ordered to small-world networks.

In the Bak-Sneppen model, an avalanche is defined as the sequence of time steps for which the minimal site has a barrier value smaller than a threshold value $f_0$. 

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The avalanche thus ends when the minimal site has a barrier value greater than $f_0$. For each $p$-value, we choose $f_0$ such that $\Delta f = f_c - f_0 = 0.01$. Fig. 6.6 shows the distribution of avalanche durations and the average number of sites covered ($N_{cov}$) by an avalanche of a given duration for $p = 0.0$ and $p = 0.01$. For $p = 0.0$ (inset) we see the expected power-law behavior with a cut-off for large avalanche sizes. For $p = 0.01$, on the other hand, we see novel features arising from the small-world properties of the network. In particular, we now see two power-law regimes, denoted by regions A and B. As the avalanche size grows, it increasingly "senses" the short-cuts in the system, and becomes more delocalized: this delocalization produces an increased slope in $N_{cov}$ in going from regime A to regime B.

In Fig. 6.7, we show the so-called first-return plots, i.e., the distribution of waiting times between subsequent returns of activity, at the maximally connected sites for $p = 0.0$ and $0.01$. All the plots show power-law behavior followed by a cut-off which corresponds to the maximal stasis time. We note that the maximal stasis time decreases by roughly two orders of magnitude in going from $p = 0.0$ to $p = 0.01$. Thus the transition from ordered to small-world networks is marked by a drastic reduction of the maximal stasis times. The inset shows the first-return plots for the maximally and the minimally connected sites in a $p = 0.01$ network. From these plots we see that the cut-off is correlated with the connectance: higher connectance leads to a smaller cut-off time for a given network.

A dramatic consequence of the reduction in stasis times can be seen in Fig. 6.8, where we show the activity plots at the maximally connected sites for $p = 0.0$ and $p = 0.01$. For $p = 0.0$, the cumulative activity at a particular site shows a pattern of "punctuated equilibrium:" long periods of stasis interrupted by much shorter periods
Figure 6.7: Distribution of first-return (stasis) times for the maximally connected sites for $p = 0.0$ (o) and $p = 0.01$ (*). Note that the cut-off, which corresponds to the maximal stasis time, is reduced by 2 orders of magnitude in going from $p = 0.0$ to $p = 0.01$. The inset shows the distribution of stasis times for the maximally (*) and the minimally (+) connected site in a $p = 0.01$ network.

of activity. By contrast, the maximally connected site at $p > 0$ shows a uniform pattern of activity on the same time scale. This behavior results from the decrease in maximal stasis time (cf. Fig. 6.7) with increasing $p$. This relationship is clearly indicated in the inset, which shows that the same pattern now exhibits “punctuated equilibrium” behavior on a much smaller time scale. The correlation between maximal stasis time and connectance for a given network can be seen in Fig. 6.9, where the activity is plotted for the sites with maximal and minimal connectance at $p = 0.01$. The minimally connected site shows a pattern of “punctuated equilibrium,” whereas the site with maximal connectance exhibits uniform behavior. In short, the periods of stasis are significantly reduced when either $p$ or $g$ is increased.
The uniform activity pattern seen for $p > 0$ may appear to be at variance with the theory of punctuated equilibrium. But in fact, we argue that this behavior actually supports that theory in the form postulated by Gould and Eldredge [114]. We first clarify the correspondence between our idealized model and an ecosystem. As already noted, the sites correspond to species, while the network of connections between them can be viewed as representing the food web of the ecosystem. Activity at a site represents a significant change for the corresponding species population in the ecosystem: an accumulation of activity can lead to either speciation or extinction. Our model does not distinguish between the two, and we expect instances of both speciation and extinction to be proportional to the amount of activity. Finally we note that a bond between two species represents a dependency link between them, which is typically, but not exclusively, a predator-prey relationship.

We now discuss the correspondence between the activity patterns described above and the theory of punctuated equilibrium. We note that the staircase pattern seen in Fig. 6.8(a) corresponds to an evolutionary process called anagenesis, in which the entire ancestral species evolves into a new species. But, as noted by Stanley [117], most speciation processes in nature are actually branching processes (called cladogenesis), in which a new species is created from a geographically isolated sub-population of the ancestral species. During cladogenesis, the ancestral species shows little change (stasis), whereas the isolated sub-population undergoes rapid evolutionary change. This is the basic process involved in the theory of punctuated equilibrium. Thus, what is required is that the periods of stasis be greatly reduced for the isolated population, in comparison to the ancestral species. This behavior is precisely what is seen in Fig.
Figure 6.8: Calculated cumulative activity at the maximally connected sites for (a) $p = 0.0$ and (b) $p = 0.01$. While (a) shows a “punctuated equilibrium” pattern, (b) appears uniform on the same time scale. The inset shows that actually (b) also exhibits a “punctuated equilibrium” pattern, but on a much reduced time scale.

6.8: in these plots, increasing $p$ results in much shorter periods of stasis and hence, an activity plot which has the appearance of uniformity in time.

Thus, our scenario for the time sequence of allopatric speciation events, as motivated by our simulations, is the following. (1) A sub-population migrates to a peripherally isolated region, such as an island. We expect the island ecology to have a higher value of $p$ for the interaction network; hence, the periods of stasis for the isolated sub-population should be much smaller than those of the ancestral population. (2) The migration event itself initiates a period of activity on the island [123], while stasis continues to prevail for the ancestral population. The combination of these two effects gives rise to rapid evolutionary change leading to speciation for the island population, and simultaneously stasis in the ancestral population.
Note that this model does not exclude other proposed mechanisms, such as the "founder effect" proposed by Mayr[115], but instead is complementary to them. Our scenario focuses on the coevolutionary activity in different ecosystems and thus on effects *external* to the species populations, whereas the other mechanisms focus on the internal characteristics of the species populations. For example, the founder effect requires that the peripherally isolated population be small, and therefore more amenable to rapid change. Speciation can, however, occur rapidly over a large area containing many millions of individuals. In particular, Williamson [124] has shown that, in a group of African lakes in the Turkana basin, which shrank and became separated from the parental water bodies, the species underwent significant phylogenetic change over only $5 \times 10^4$ years, whereas the ancestral populations remained virtually unchanged in their parental waters. In this case, the observed speciation events cannot be explained by the founder effect, as argued by Williamson, but they do seem consistent with our proposed scenario.

Our calculations show that, for a given network, the patterns of activity are strongly correlated with the connectance. How is this observation reflected in studies of real ecosystems? One possibility is the following: since the bonds in the network corresponds to dependency links, the species with high connectance have a high degree of dependency - i. e., they are specialists (*stenotypic*) - whereas species with low connectance are generalists (*eurotypic*). As already noted in Fig. 6.9, the cumulative activity is an order of magnitude larger for the maximally connected site than for the one with minimal connectance. Based on our model, we therefore expect *stenotypic* species to speciate or go extinct more often than their *eurotypic* counterparts. This
correlation between ecological specialization and speciation and extinction rates has been observed in numerous studies [125].

In summary, we have extended the 1-d Bak-Sneppen model to small-world networks. This extension allows us to distinguish different sites in the network, and thereby the species in an ecosystem, based on a site-dependent property which we call connectance. We find that the activity patterns are strongly correlated with the topology of the network and with the connectance. Finally, we discuss the possible implications of these results for speciation events.

In this Chapter, we have seen that there is a lot of interesting physics associated with systems with even small amounts of disorder in them. Small-world networks in particular is a field which is still in its infancy, and we hope that the results we have
discussed in this Chapter will further spur research in this area. In the next Chapter, we will look at a different kind of disordered system, one which is relevant to High-$t_c$ superconductors.
7.1 Introduction

We have seen in the previous chapters how DFT combined with LDA can yield a host of interesting properties for the systems considered. However there are limitations to this approach. While it can be readily applied to 'simple' systems like Si and Ge, its limitations become apparent when dealing with more complex systems. Consider a system like Rb₂Mn₁₋ₓCrₓCl₄ has been studied experimentally as an example of a randomly mixed quasi-two-dimensional antiferromagnet and ferromagnet \[126\]. It would be hopeless at present to try to understand the properties of this system using the techniques we have described. In such cases one often has to resort to simple models, as described in the Introduction, which can yield much insight into the physics of these systems. In this Chapter we shall discuss one such model which is currently generating a lot of interest and propose a novel variational guess for the ground state of this model.
The classical XY Hamiltonian is one of the most studied models in statistical physics. In its simplest form, it is written
\[ H = -\sum_{(ij)} J_{ij} \cos(\theta_i - \theta_j), \]  
where \( \theta_i \) is an angle variable \((-\pi \leq \theta_i < \pi)\) on the \( i \)th site, the sum runs over distinct pairs \((ij)\), and \( J_{ij} \) is a coupling energy between \( i \) and \( j \), which can be construed as the angle of an effective two-component spin variable of fixed length relative to some specified axis in the XY plane. In the ferromagnetic, nearest-neighbor case, \( J_{ij} \) vanishes except between nearest-neighbor sites and all the \( J_{ij} \)'s are equal to a single positive constant \( J \). In this case, for spatial dimensionality \( d \geq 3 \), there is a phase transition to a ferromagnetic state at a critical temperature with conventional critical phenomena. If \( d = 2 \), there is instead a Kosterlitz-Thouless-Berezinskii phase transition, consisting of unbinding of pairs of integer vortices of opposite charge, which occurs at a finite temperature \( T_{KTB} \). This model has been found to describe a wide variety of systems with complex scalar order parameters, including liquid He\(_4\) and bulk superconductors in \( d = 3 \), and He\(_4\) films, superconducting films, and Josephson junction arrays, among others, in \( d = 2 \).

Recently, the XY model with antiferromagnetic bonds (also called \( \pi \) bonds) has begun to receive attention. In this model, some of the bond strengths \( J_{ij} \) are negative. Such a model may be physically relevant in high-\( T_c \) superconductors. For example, consider a Josephson junction array in which some of the superconducting grains are high-\( T_c \) materials. In this case, each “spin” in the XY model might represent a superconducting grain, while the bonds represent the Josephson junctions between two grains. If, as thought for some high-\( T_c \) materials, the grains have a \( d_{x^2-y^2} \) order parameter, then, for certain grain orientations, \( J_{ij} < 0 \)[127]. An XY
model with some negative $J_{ij}$'s is a possible model for such an array. Similarly, a string of $\pi$ bonds might represent an extended Josephson $\pi$ junction in a high-$T_c$ material, such as a grain boundary junction. Such grain boundary junctions have lately been studied in a variety of experiments, in several geometries. A wide variety of exotic experimental results, such as apparent trapping of half-integer or other fractional flux quanta [128, 129], have been described in terms of hypothetical strings of $\pi$ junctions. Similar explanations have also been developed to explain such phenomena as the paramagnetic Meissner effect [130], also observed in samples of high-$T_c$ superconductors.

In this Chapter we propose a new set of excitations in the XY model which we call "fractional vortices". We show that these fractional vortices can be used to characterize the ground-state of the XY model with $\pi$-bonds in it. We also derive an expression for the interaction energy of two fractional vortices in the XY model.

The rest of the Chapter is organized as follows: In Section II we describe the fractional vortex excitations and derive an expression for the interaction energy of a bound pair of fractional vortices. In Section III we look at the ground-state properties of the XY model with one and two $\pi$-bonds and compare our results with previous analytical calculations as well as our numerical simulations. In Section IV we consider chains of $\pi$-bonds and again compare our analytical results using the fractional vortices ansatz to our numerical simulations. Finally in Section V we summarize our results and discuss the possible significance to recent experiments by Kirtley et al.
7.2 Fractional vortices

We begin with the Hamiltonian for the XY-model defined on a 2-d square lattice with $N \times N$ sites

$$H = -J \sum_{<ij>} \left(1 - \cos(\theta_i - \theta_j)\right)$$  \hspace{1cm} (7.2)

where $\theta_i$ refers to the phase at site $i$. In modeling granular high-$T_c$ superconductors, the phase at a site corresponds to the phase of the order parameter for the grain and $J$ denotes the strength of the Josephson coupling between neighbouring grains. For convenience we shall, in subsequent discussion, set $J = 1$. We now describe what we mean by a fractional vortex configuration. The phase angle $\theta_i$ at point $(x_i, y_i)$ due to a fractional vortex of charge $q$ at point $(x_0, y_0)$ is given by

$$\theta_i = q \times \tan^{-1} \left( \frac{y_i - y_0}{x_i - x_0} \right)$$  \hspace{1cm} (7.3)

For $q = 1$ we recover the standard configuration for an integer vortex. Note that while the bond-angles change continuously for the integer vortex, for the fractional vortex configuration, we have a branch cut across which the bond-angles change discontinuously. Thus this configuration is not well-defined for a continuum model but poses no problems on a lattice. Now, the energy of a single integer vortex goes as $\ln(N)$ which leads to the Kosterlitz-Thouless (KT) vortex unbinding transition [131]. In contrast, the energy of an unbound fractional vortex is $\propto N$ since the number of bonds along the branch cut is $\propto N$. Hence there is no unbinding transition associated with single fractional vortices. However if we have a bound pair of fractional vortices with charges $q$ and $-q$, then we note that the branch cut is restricted to the line joining the two charges. So for the energy of a bound pair of fractional vortices, we
expect the leading term to be proportional to the separation between the vortices. For finite separations, the energy is correspondingly finite (in the thermodynamic limit), so the fractional vortices serve as distinct excitations in the XY model. In the following we shall derive an expression for the energy of a bound pair of fractional vortices and compare it with numerical results obtained by calculating the energy explicitly for the configuration.

We begin by considering a bound pair of integer vortices. To derive the KT expression for their energy, one assumes that the bond-angles are all small enough such that the Hamiltonian can be approximated by

\[ H = \frac{1}{2} \sum_{\langle ij \rangle} (\theta_i - \theta_j)^2 \tag{7.4} \]

The Kosterlitz-Thouless formula for the interaction energy \( E_{kt} \) of two integer vortices (with charges +1 and -1) separated by a distance \( n \) (we set the lattice constant \( a = 1 \)) is then given by

\[ E_{kt}(n) = 2\pi(\ln(n) + \frac{\pi}{2}) \tag{7.5} \]

Fig. 1. shows the results of the numerical computation for a pair of bound vortices compared with the energy calculated using the formula above. The discrepancy arises from the fact that we use the approximation \( \cos(\theta) \sim 1 - \theta^2/2 \) for all the bond-angles. However, for the bonds closest to the vortices this is not a good approximation. This can be remedied by performing a 'core-correction': from the expression above we subtract out the approximated contributions from the bonds constituting the plaquettes surrounding the vortices and add the exact contributions. As shown in Fig. 1 this gives much better agreement with the numerical results.
Figure 7.1: Energy of a bound pair of integer vortices as a function of the separation \( n \) obtained using (a) numerical computation (solid line) (b) KT formula (dot-dashed line) and (c) KT formula with core-corrections (*).

We now turn to the expression for the energy of a pair of bound fractional vortices separated by a distance \( n \). Let \( q \) denote the absolute value of the charge of the fractional vortices i.e \( 0 \leq q < 1 \). To obtain this, we classify the bonds into two groups: A) The set of bonds intersected by the line-segment joining the two vortex centers, and B) the rest of the bonds. Let \( E_A(q, n) \) and \( E_B(q, n) \) be the corresponding energy contributions from these two regions. This dichotomy is useful because, as we shall see, the exact energy contributions from region B are well approximated using Eqn. 7.4. whereas in region A we have to use the exact Hamiltonian (Eqn. 1) in the case of fractional vortices. Correspondingly the total energy is given by
\[ E(q,n) = E_A(q,n) + E_B(q,n) \]

Note that \( E(1,n) \) is the same as the KT energy \( E_{kt}(n) \) as given in Eqn. 7.5.

We now outline the general procedure we use to determine the total energy when we have a pair of fractional vortices, where the phases are determined using Eqn. 2. The procedure consists of the following steps.

I) Calculate \( E_A(1,n) \). This is simply the contribution to the total energy from all the bonds along the branch cut. The contribution from each bond is given according to the Eqn. 7.4. From this we get \( E_B(1,n) = E_{kt}(n) - E_A(1,n) \).

II) To obtain \( E_B(q,n) \) we proceed as follows. Let \( \phi_b(q,n) \) denote the difference in phases across a bond (bond-angle) in region B. From our definition of the fractional vortex configuration it can be seen that \( \phi_b(q,n) = q\phi_b(1,n) \). This gives us \( E_B(q,n) = q^2E_B(1,n) \).

III) Finally we determine \( E_A(q,n) \) as follows. We note that, for arbitrary \( q \), the bond-angles in region A are not small and we have to use Eqn. 1 to determine their contribution to the energy.

We now use the outlined procedure to obtain \( E(q,d) \).

I) Let \( \phi_{i,a}(1,d) \) denote the \( i^{th} \) bond-angle in region A. The expression for \( \phi_{i,a}(1,n) \) is

\[ \phi_{i,a}(1,n) = 2 \left( \tan^{-1}\left( \frac{1}{2i - 1} \right) + \tan^{-1}\left( \frac{1}{2n - 2i + 1} \right) \right) \]

(7.6)

The energy contribution \( E_A(1,n) \) is given by

\[ E_A(1,n) = \frac{1}{2} \sum_{i=1}^{n} \phi_{i,a}(1,n)^2 \]

(7.7)
We can evaluate the above sum making the approximation \( \tan^{-1}\left(\frac{1}{2n-1}\right) \sim \frac{1}{2n-1} \) for \( i \geq 2 \). Using this we get

\[
E_A(1, n) = \frac{\pi^2}{2} + \left(\frac{\pi}{2} + \frac{2}{2n-1}\right)^2 + \frac{2}{n} \left(\gamma + 2 \ln(2) - 2 - 2n\right) + \frac{2}{n} \psi(n - \frac{1}{2}) - \psi'(n) \left(\frac{1}{2}\right)
\]

\[
E_B(1, n) = E_{kl}(n) - E_A(1, n)
\]

(7.9)

where \( \psi(x) \) is the Digamma function and \( \gamma \) is the Euler constant.

II) Using the results of I) and Eqn. 7.5 we get

\[
E_B(q, n) = q^2(2\pi \ln(n) + \pi^2 - E_A(1, n))
\]

(7.10)

III) We now turn to calculating \( E_A(q, n) \). The bond-angles in region \( A \) are given by

\[
\phi_{i,a}(q, n) = q \left(2\pi - \phi_{i,a}(1, n)\right)
\]

(7.11)

Correspondingly the energy \( E_A(q, n) \) is given by

\[
E_A(q, n) = \sum_{i=1}^{n} (1 - \cos(\phi_{i,a}(q, n)))
\]

(7.12)

For an arbitrary \( q \), \( \phi_{i,a}(q, n) \) is not small and hence we cannot approximate the \( \cos \) term in the equation above. However for all \( q \)'s we note that \( \phi_{i,a}(q, n) - \phi_{n/2,a}(q, n) \) is a small parameter for \( i \geq 2 \). Expanding the \( \cos \) term in the above equation to second order in this parameter, we get an expression for \( E_A(q, n) \) which can then be summed to give

\[
E_A(q, n) = (n - 2) \left[ (1 - \cos \alpha_n) + \frac{8q^2}{n^2} \cos \alpha_n + \frac{4q}{n} \sin \alpha_n \right]
\]
\[ E(q,n) = E_A(q,n) + E_B(q,n) - q^2 \phi_c^2 + 2(1 - \cos(q\phi_c)) \]  
where  \[ \phi_c = \frac{\pi}{2} - \frac{2}{2n + 1} \]  

Comparing the above expression with the results of numerical computation in Figs. 2 and 3, we see that the agreement is excellent. Based on this agreement for arbitrary values of \( q \) and \( n \), we claim that we have derived the expression for the interaction energy of two fractional vortices. This is a generalization of the integer vortex excitations proposed by Kosterlitz and Thouless.

For large \( n \), we can further simplify the above expression by dropping terms of \( \mathcal{O}\left(\frac{1}{n}\right) \) and smaller to get
Figure 7.2: Energy of a bound pair of fractional vortices obtained using numerical computation (*) and the analytical expression Eqn. 16 (solid line) for fixed separation $n = 50$

$$E(q, n) = (n - 2) \left[ 1 - \cos(2\pi q) \right] + 2\ln(n) \left[ \pi q^2 - q \sin(2\pi q) \right]$$
$$+ \frac{3}{4} \pi^2 q^2 + 2 \left[ 1 - \cos \left( \frac{3\pi q}{2} \right) \right]$$

(7.19)

7.3 XY model with $\pi$-bonds

We now turn to the XY model with $\pi$-bonds. We shall see that the fractional vortex configurations introduced in the previous section provide a natural way of characterizing the ground state of the system. We do this by making a variational guess for the ground-state configuration using fractional vortices. We then compare
Figure 7.3: Energy of a bound pair of fractional vortices obtained using numerical computation (*) and the analytical expression Eqn. 16 (solid line) for fixed charge $q = 0.8$

our results with those obtained by numerically relaxing to the ground state configuration and find excellent agreement. For the case of 1 and 2 $\pi$-bonds, we also compare our results with those from previous studies by Vanneminus et al [132].

In order to check the results of our variational approach, we have carried out an independent minimization approach to calculate the ground-state of the system. The details of this approach will be discussed elsewhere [133], we note that it involves numerically relaxing to the ground-state by solving the dynamical equations for an overdamped Josephson junction array.
7.3.1 1 π-bond

We first consider the case of a single π-bond i.e an antiferromagnetic bond in a host of ferromagnetic bonds. As before the bond strength for the normal (ferromagnetic) bonds is taken to be 1 and we denote the bond strength of the antiferromagnetic bond by \( \lambda \) (\( \lambda \geq 0 \)). Our problem is to obtain the ground-state configuration for arbitrary strength \( \lambda \) of the π-bond. To this end, we make an ansatz for the ground-state configuration: it is the configuration of phases corresponding to a bound state of fractional vortices (with charges +/- \( q \)) located at the centers of the plaquettes adjacent to the π-bond thus giving \( n = 1 \). The charge \( q \) of the vortices is a variational parameter which is varied to obtain the ground-state configuration for a given \( \lambda \).

We now obtain the total energy of our variational configuration using the procedure outlined in the previous section. The only difference is that we have to correct for the fact that we have a π-bond instead of a normal bond. In the following analysis we ignore the 'core-correction' terms but shall include them subsequently.

Now, the bond-angle across the π-bond (\( \theta_\pi \)) is given by \( \theta_\pi = q\pi \). Using Eqns. 7.7 and 7.10 we get

\[
E_B(q) = \frac{1}{2} q^2 \pi^2
\]  

(7.20)

and using Eqn. 7.12 we get

\[
E_A(q) = 1 + \lambda \cos(q\pi)
\]  

(7.21)

Adding the two terms we get the total energy of the configuration. Minimizing this energy with respect to \( q \) we find
For $\lambda \leq 1$ the ground-state configuration corresponds to $q = 0$ i.e all the spins are perfectly aligned. For $\lambda > 1$ the ground-state configuration corresponds to a bound pair of fractional vortices with charge $q$ given by solving the equation above. Thus the critical value of the bond-strength ($\lambda_c$) above which the ferromagnetic ground-state is unstable is given by $\lambda_c = 1$. The same value has been obtained previously using a different approach.

Furthermore, we obtain the ground-state energy and $q$ for a given value of $\lambda$ using the numerical simulations as outlined in the beginning of this Section. In Figs. 4 and 5 we compare the results so obtained with the results from our variational guess using fractional vortices. As can be seen from the figures the agreement is excellent, thereby indicating that the ground-state is characterised by a bound pair of fractional vortices.

7.3.2 2 $\pi$-bonds

We first consider the case of two adjacent $\pi$-bonds. As before, our variational guess for the ground-state is the configuration corresponding to a bound pair of fractional vortices. The total energy corresponding the this configuration is calculated using the procedure outlined in Section II. In this case there are 2 $\pi$-bonds in region A. For the variational configuration both of them have the same bond-angle $\phi = \frac{\pi}{2} + 2 \tan^{-1}(\frac{1}{3})$. Correspondingly using Eqns. 7.7 and 7.10 we get

$$E_B(q) = q^2(2\pi \ln(2) + \pi^2 - (\frac{\pi}{2} + 2 \tan^{-1}(\frac{1}{3}))^2)$$

(7.23)
and using Eqn. 7.12 we get

\[ E_A(q) = 2 + 2\lambda \cos(2q[\pi - (\frac{\pi}{4} + \tan^{-1}(\frac{1}{3}))]) \]  

(7.24)

Adding the two contributions, we get the total energy which upon minimization gives us the value of \( q \) for a given \( \lambda \). This gives us the critical value \( \lambda_c = 0.563 \) which is in good agreement with the exact value \( \lambda_c = \frac{\pi}{2} - 1 \) obtained by Vanneminus et al [132].

As in the case of one \( \pi \)-bond we obtain the ground state configuration using (i) our variational ansatz with fractional vortices and (ii) numerical simulations. The results obtained from these two methods for the total energy and the bond-angle across the \( \pi \)-bonds are shown if Figs. 6 and 7. As before they are in excellent agreement.
Now, we consider the case of 2 parallel non-adjacent \( \pi \)-bonds. The bond-centers are taken to have the coordinates \((0,0)\) and \((m,n)\). With this configuration we calculate the energy using the procedure described earlier. For large separation between the bonds, this gives us

\[
E_B(q) = q^2(2\pi^2 - 2\alpha_{mn} - (\pi - \alpha_{mn})^2) \tag{7.25}
\]

and

\[
E_A(q) = 2(1 + \lambda \cos(q(\pi + \alpha_{mn}))) \tag{7.26}
\]

where

\[
\alpha_{mn} = \frac{m^2 - n^2}{(m^2 + n^2)^2} \tag{7.27}
\]
Minimizing the total energy, we get for the critical bond-strength

$$\lambda_c = \frac{1 - 2\alpha_{mn}/\pi}{1 + 2\alpha_{mn}/\pi}$$  \hspace{1cm} (7.28)

Similarly for 2 non-adjacent $\pi$-bonds perpendicular to each other, we get the following results

$$E_B(q) = q^2(2\pi^2 - 2\beta_{mn} - (\pi - \beta_{mn})^2)$$  \hspace{1cm} (7.29)

and

$$E_A(q) = 2(1 + \lambda \cos(q(\pi + \beta_{mn})))$$  \hspace{1cm} (7.30)

where

$$\beta_{mn} = \frac{2mn}{(m^2 + n^2)^{1/2}}$$  \hspace{1cm} (7.31)
In this case the critical bond-strength is

\[ \lambda_c = \frac{1 - \beta_{mn}/\pi}{1 + \beta_{mn}/\pi} \]  

(7.32)

These results are identical to those obtained previously by Vanneminus et al using a different approach. This lends confirmation to our claim that the ground-state configuration of such systems can be characterized by a set of fractional vortices. Besides having the merit of simplicity, our approach also easily yields the ground-state configuration and energy for arbitrary \( \lambda \). Furthermore it can readily be generalized to longer \( \pi \)-bond chains, as we shall see in the next section.
7.3.3 Chains of $\pi$-bonds

We now consider chains of $\pi$-bonds of length $n$ ($n \geq 3$). In this case, our variational ansatz for the ground state consists of $\frac{n}{2} \left( \frac{n+1}{2} \right)$ pairs for fractional vortices for even (odd) $n$. As before we proceed by calculating the contribution to the total energy from regions A and B. However, the procedure outlined in Section II has to be generalized to include many pairs of fractional vortices. To minimize the total energy, which is a multi-dimensional function of $q_i$, we used two procedures: (i) Powell’s multidimensional direction set method and (ii) a Genetic algorithm. Both methods successfully converged to the same minimum. From this we obtained the critical bond-strength $\lambda_c$ for various values of $n$. Fig. 8 shows our results for $\lambda_c(n)$ which can be fitted very well to the approximate expression $\lambda_c \approx \frac{1.16}{n}$. The inset shows the log-log plot of the same data, clearly indicating that $\lambda_c$ falls off as $1/n$. A consequence of this is that if the system has a finite concentration of $\pi$-bonds, then in the thermodynamic limit we have $\lambda_c = 0$. This is so because we will always have a finite probability of having a arbitrarily large chain-size $n$ and since $\lambda_c$ falls off as $1/n$, we get $\lambda_c = 0$.

7.4 Summary

The most exciting possible application of these calculations is, of course, to $\pi$ junctions occurring in real materials, such as high-temperature superconductors. It is now widely believed that many high-$T_c$ materials have a $d_{x^2-y^2}$ order parameter. If a Josephson junction is formed between two grains of such a material, it will be a $\pi$ junction if the grains have suitable crystallographic orientations. Kirtley and collaborators have studied such grain boundaries using SQUID magnetometry. They have considered two geometries: (i) a single grain boundary forming a junction
Figure 7.8: Critical bond-strength ($\lambda_c$) as function of chain length, compared to the approximate fit $\lambda_c = \frac{1.16}{n}$.

of finite length, and (ii) a triangular crystal of high-$T_c$ material embedded in the same high-$T_c$ material oriented differently. In both cases, they observe spontaneously generated flux (at the ends of the grain boundary or the corners of the triangular crystal) in amounts corresponding to fractions of a flux quantum.

Our calculations for a chain of $\pi$ bonds might be relevant to a single grain boundary of finite length. There is a caveat about the geometry we have considered: our chain is embedded in a host of 0 bonds. This geometry insures that our model calculation has frustrated plaquettes. But to create it in a real material, the $\pi$ grain boundary would have to be embedded in an unfrustrated host. Notwithstanding this caveat, our results do show some features also seen in experiment. In particular, for a sufficiently
long chain of \( \pi \) junctions, even very weak \( \pi \) junctions, we find that the ground state always contains pairs of fractional vortices. Since we are not including inductive effects in our calculations, we cannot calculate the corresponding induced flux, as measured in experiments. Nevertheless, the presence of pairs of fractional vortices would imply induced flux.

In summary, we have introduced a new set of excitations in the XY-model which we term fractional vortices, and derived an expression for the interaction energy for a bound pair of fractional vortices. These vortices appear naturally in characterizing the ground-state configuration for the XY-model with \( \pi \)-bonds. We have verified this by calculating the ground state configuration by a) using a variational ansatz involving fractional vortices and b) performing numerical simulations using the RSJ model. So far we have only focussed on these excitations in regards to the frustrated XY-model, however we hope to use these insights to explore the physics of fractional flux entrapment in high-\( T_c \) superconductors with grain boundaries.
A.1 The Dielectric Constant problem

One of the most basic properties of a semiconductor is its response to an electric field. This is expressed in terms of the dielectric constant $\varepsilon$ which has contributions coming from both the electronic and ionic subsystems. In what follows we shall concentrate only on the electronic contribution to the dielectric constant. In a semiconductor this primarily arises from interband transitions caused by the electric field. In general when we study dielectric response we end up looking at the dielectric function $\varepsilon(q, \omega)$ which in the static, long-wavelength limit gives us the dielectric constant.

Simply put, the dielectric constant problem refers to the fact that for medium and small-band-gap materials the dielectric constant is overestimated by at least 10% using LDA-based calculations. While this discrepancy is not as striking as the one encountered in the band gap problem, it is still sufficiently large so as to merit closer attention. Again, calculations done with more sophisticated approximations such as GGA do not yield any significant improvement over the LDA result.
the other hand, $\varepsilon$ is a ground-state property of the system and can in principle be exactly calculated within DFT. One is then faced with the question as to whether the discrepancy is an artifact of the approximations used or if it is reflective of a more basic error in our application of DFT. To date, this is still an open question and it has been the subject of some controversy of late.

Before we proceed further, it will be necessary to define certain quantities relating to dielectric response. This is sometimes the source of some confusion since different people tend to use different symbols for the same quantities and often the terms ‘polarizability’ and ‘susceptibility’ are used interchangeably which adds to the confusion. Of course as long as one uses a consistent set of definitions it’s fine and so we shall proceed with our set of definitions. Let us consider the response of the system to an external field with wave-vector $\vec{q}$ and frequency $\omega$. The external potential $\delta V_{\text{ext}}$ is screened by the electrons in the system and the total potential inside the system and the fourier components of the quantities are related by

$$\delta V(q, \omega) = \frac{\delta V_{\text{ext}}(\vec{q}, \omega)}{\varepsilon(\vec{q}, \omega)} \quad (A.1)$$

which defines the dielectric function $\varepsilon(\vec{q}, \omega)$. Now the response function or susceptibility is defined as

$$\delta n(\vec{q}, \omega) = \chi(\vec{q}, \omega)\delta V_{\text{ext}}(\vec{q}, \omega) \quad (A.2)$$

where $\delta n(\vec{q}, \omega)$ is the fourier component of the induced charge density. The dielectric function is connected to the response function by the following relation

$$\frac{1}{\varepsilon(\vec{q}, \omega)} = 1 + \frac{4\pi}{q^2} \chi(\vec{q}, \omega) \quad (A.3)$$

For notational simplicity we consider here the case of a homogeneous system.
Meanwhile the polarizability is defined as the response function to the total potential

$$\delta n(\vec{q}, \omega) = \pi(\vec{q}, \omega)\delta V(\vec{q}, \omega).$$  \hspace{1cm} (A.4)

So in terms of the polarizability the dielectric function is given by

$$\varepsilon(\vec{q}, \omega) = 1 - \frac{4\pi}{q^2} \pi(\vec{q}, \omega)$$  \hspace{1cm} (A.5)

In the next section we shall study the formal expression for the susceptibility of the system within the Kohn-Sham scheme treated for the general case of an inhomogeneous system.

A.2 Linear response formalism in DFT

We would like to look at the response of the interacting system to an external perturbation $\delta V_{ext}$. In the Kohn-Sham scheme the problem is mapped on to the problem of noninteracting electrons in an effective field $V_{eff}$ and the result of the perturbation is to change $V_{eff}$ to $V_{eff} + \delta V_{eff}$. The resulting change in density is given by

$$\delta n(r) = \int d\vec{r}' \chi_0(\vec{r}, \vec{r}') \delta V_{eff}(\vec{r}')$$  \hspace{1cm} (A.6)

where

$$\chi_0(\vec{r}, \vec{r}') = \sum_{E_j > E_f} \sum_{E_i < E_f} \frac{\psi_i(\vec{r})\psi_j^*(\vec{r}')\psi_j(\vec{r})\psi_j^*(\vec{r}')}{E_j - E_i} + c.c$$  \hspace{1cm} (A.7)

is the response function for noninteracting electrons. For the homogeneous electron gas $\chi_0$ is the familiar Lindhard function.

In the above equations it should be noted that the change in the effective potential $\delta V_{eff}$ is also a functional of the change in density $\delta n(r)$ and is given by
\[
\delta V_{\text{eff}}(\vec{r}) = \delta V_{\text{ext}}(\vec{r}) + \int d\vec{r}' \left[ \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta n(\vec{r})\delta n(\vec{r}')} \right] \delta n(\vec{r}')
\] (A.8)

Now the response function for the interacting system, by definition, is given by

\[
\delta n(\vec{r}) = \int d\vec{r}' \chi(\vec{r}, \vec{r}') \delta V_{\text{ext}}(\vec{r}').
\] (A.9)

So combining the above equations we get the following integral equation for the response function

\[
\chi(\vec{r}, \vec{r}') = \chi_0(\vec{r}, \vec{r}') + \int d\vec{r} d\vec{r}' \left[ \frac{1}{|\vec{r} - \vec{r}'|} + K_{\text{xc}}(\vec{r}, \vec{r}') \right] \chi(\vec{r}, \vec{r}') \chi_0(\vec{r}, \vec{r}')
\] (A.10)

where

\[
K_{\text{xc}}(\vec{r}, \vec{r}') = \frac{\delta^2 E_{\text{xc}}}{\delta n(\vec{r})\delta n(\vec{r}')}
\] (A.11)

In the homogeneous case all quantities appearing in the above equations become functions of relative distance only and the integral equations are trivially solved in reciprocal space giving

\[
\chi(q) = \frac{\chi_0(q)}{1 - [4\pi / q^2 + K_{\text{xc}}(q)] \chi_0(q)}
\] (A.12)

Now that we have set up the formalism we return to the question as to whether the discrepancy is due to the approximations invoked by using LDA or whether there is something missing in the formalism developed. This is as yet an unresolved issue and in the following section we shall discuss a possible resolution.
A.3 Polarization Density Functional Theory

A rather radical approach to this problem was taken by Gonze et al [135, 139] who suggested that the Hohenberg-Kohn theorems, considered by many DFT practitioners to be sacrosanct, were invalid in the case of the static response of an insulator to a constant electric field. They went on to suggest that the proper extension of DFT would have include the dependence of the total energy functional on the macroscopic polarization $\mathbf{P}$ of the system. This additional dependence would give rise to an effective 'exchange-correlation electric field' acting on the Kohn Sham electrons which was ignored in previous calculations of the dielectric constant and it was proposed that the inclusion of this term would correct for the discrepancy in the dielectric constant. The existence of this correction term was demonstrated by Gonze et al. with calculations on a 1D semiconductor model. Further verification of this theory was somewhat hampered by the fact that the form of the polarisation dependence in the energy-functional was unknown.

It should be mentioned that this approach too has met with some criticism although that has been primarily directed at the claim that the Hohenberg-Kohn theorems are violated. Current research along these lines has concentrated upon possible consequences of the polarization dependence and the explicit form of $E_{xc}(\mathbf{P})$. This issue is addressed in the rest of the appendix.

To apply these concepts to real materials, Aulbur et al [134] introduced a phenomenological parameter $\gamma_1$ which is determined by the polarization contribution to the exchange-correlation energy; they also derived an expression for $\gamma_1$ in terms of the experimental and LDA susceptibilities. Resta [136] showed that long-range correlations between bulk and surface charges would give rise to the polarization dependence

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proposed by GGG. However, it was pointed out by Martin and Ortiz [137] and by Gonze et al [138] that this was not the only way to get the polarization-dependence: the same could be achieved by assuming that the surface charge, while not correlated with the bulk charge density, polarizes the exchange-correlation hole around a charge in the bulk. In later work by Martin et al [140], a generalization of the Kohn-Sham equations has been proposed which includes the polarization dependence in order to correctly describe dielectric properties. Ortiz et al [143] have demonstrated, through explicit computation in a 1-d system, that the exchange-correlation hole depends on the macroscopic polarization.

In the rest of this Appendix, we investigate how the polarization of the exchange-correlation hole is related to the discrepancy between the experimental and LDA susceptibilities. We first define ‘polarization-dependence’ in terms of constraints on the long-wavelength part of the exchange-correlation kernel, as proposed by Ghosez et al [142]. Next, we explore the connection to the exchange-correlation hole and demonstrate how the two mechanisms proposed by Resta [136] and Martin et al [137] can give rise to the polarization dependence. We also obtain an expression for the phenomenological parameter $\gamma_1$ introduced by Aulbur et al and discuss its scaling properties. Finally we discuss how the polarization of the exchange-correlation hole might affect the calculated non-linear susceptibilities of semiconductors.

Consider a dielectric with a lattice-periodic ground-state density given by the Fourier components $\{n_G\}$ (where $G$ is a reciprocal lattice vector). In the presence of a long-wavelength static external potential $V_q e^{iqr}$, the induced charge density within linear response is given by the Fourier components $\{\delta n_{q+G}\}$. In the following we shall consider only the electronic contribution to the polarization. We shall work with the
units $e = 1$ so that the number density is the same as the charge density. Now the change in the exchange-correlation potential ($V_{xc}(r)$) due to the induced change in density is, by definition, given by

$$\delta V_{xc}(r) = \int K_{xc}(r, r') \delta n(r') dr'$$  \hspace{1cm} (A.13)$$

where

$$K_{xc}(r, r') = \frac{\delta^2 E_{xc}[n]}{\delta n(r) \delta n(r')}$$  \hspace{1cm} (A.14)$$

is the exchange-correlation kernel. For the case being considered the above equation can be recast as

$$\delta V_{xc}(r) = K_{xc}(q, q) \delta n(q) e^{iq \cdot r} + \sum_{G \neq 0} K_{xc}(q, q + G) \delta n(q + G) e^{iq \cdot r}$$
$$+ e^{iq \cdot r} \sum_{G \neq 0} \sum_{G' \neq 0} e^{iG \cdot r} K_{xc}(q + G, q + G') \delta n(q + G')$$  \hspace{1cm} (A.15)$$

In order to have an exchange-correlation electric field $\mathcal{E}_{xc} e^{iq \cdot r}$ we must have

$$\mathcal{E}_{xc} = K_{xc}(q, q)(q^2 P) + \sum_{G \neq 0} K_{xc}(q, q + G) \delta n(q + G)(iq)$$  \hspace{1cm} (A.16)$$

where we have used $\delta n(q) = -i q \cdot P$ [145] in the above equation. Eq. (A.16) indicates that the presence of a finite exchange-correlation electric field requires that, in the long-wavelength limit, $K_{xc}(q, q)$ diverges as $1/q^2$ or that $K_{xc}(q, q + G)$ diverges as $1/q$ for some reciprocal lattice vector $G$. In the case of a model 1-d semiconductor Ghosez et al. [142] have computed $K_{xc}(q, q)$ exactly and shown that it has a $O(\frac{1}{q^4})$ divergence. Furthermore they have argued, on the basis of the so-called DFT metal/insulator paradox [144], that the exact $K_{xc}(q, q)$ for real materials must also
exhibit a similar divergence. Based on the above arguments, we shall assume hence­forth that the presence of an exchange-correlation electric field implies that the exact exchange-correlation kernel diverges in the long-wavelength limit as $1/q^2$. This is to be contrasted with the LDA behavior where

$$\lim_{q \to 0} K^{\text{LDA}}_{\text{xc}}(q, q) = \kappa$$  \hspace{1cm} (A.17)

where $\kappa$ is a constant (given by the compressibility sum rule). This precludes the existence of an exchange-correlation electric field in LDA and other local approxima­tions such as GGA and WDA [142].

Let us now investigate the implications of the divergence in $K_{\text{xc}}(q, q)$ in terms of properties of the average exchange-correlation hole (xc-hole). We start with the exact expression for the exchange-correlation energy functional in terms of the xc-hole [146]

$$E_{\text{xc}}[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}') [\tilde{g}(\mathbf{r}, \mathbf{r}') - 1].$$  \hspace{1cm} (A.18)

The exchange-correlation potential and the exchange-correlation kernel are ob­tained by functional differentiation of the above expression

$$v_{\text{xc}}(\mathbf{r}) = \int \frac{n(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} [\tilde{g}(\mathbf{r}, \mathbf{r}_1) - 1] d\mathbf{r}_1 + \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \left[ \frac{\delta \tilde{g}(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r})} \right] d\mathbf{r}_1 d\mathbf{r}_2 \hspace{1cm} (A.19)$$

$$K_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \frac{\tilde{g}(\mathbf{r}, \mathbf{r}') - 1}{|\mathbf{r} - \mathbf{r}'|} + 2 \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}' - \mathbf{r}_1|} \left[ \frac{\delta \tilde{g}(\mathbf{r}', \mathbf{r}_1)}{\delta n(\mathbf{r})} \right] d\mathbf{r}_1 + \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \left[ \frac{\delta^2 \tilde{g}(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \right] d\mathbf{r}_1 d\mathbf{r}_2 \hspace{1cm} (A.20)$$

Eq. (A.20) is an exact expression for the exchange-correlation kernel. It indi­cates how the two mechanisms proposed by Resta and by Martin et al bring about
the polarization-dependence of the exchange-correlation energy. Consider each term on the right-hand side of Eq. (A.20). The first term indicates that if \( \tilde{g}(r, r') \) shows long-range correlation then \( K_{xc}(r, r') \) falls off as \( 1/|r - r'| \). This in turn implies that \( K_{xc}(q, q) \) diverges in the long-wavelength limit as \( 1/q^2 \). Thus long-range correlation in the xc-hole gives rise to an exchange-correlation electric field in accordance with our previous discussion. The field so obtained is coupled to the macroscopic polarization to give a non-vanishing ( in the thermodynamic limit ) contribution to the exchange-correlation energy as demonstrated by Resta. However as pointed out by Martin and Ortiz the exchange-correlation energy can have a more subtle polarization-dependence. On physical grounds they argued that in the presence of an electric field the xc-hole should polarize thereby giving an exchange-correlation energy which differs from the exchange-correlation energy in the absence of an electric field. It is not clear however, whether the dependence on the polarization proposed above can give rise to the exchange-correlation electric field (which is crucial for a resolution of the dielectric constant problem ). The conditions under which this proposed polarization dependence can give rise to an exchange-correlation electric field can be seen by looking at the second term on the right-hand side of Eq. (A.20). It indicates that we can get an effective exchange-correlation electric field if the functional derivative \( \delta \tilde{g}(r', r_1)/\delta n(r) \) is long-ranged as a function of \( |r - r'| \). That this corresponds to a polarization of the xc-hole is best demonstrated by noting that, by definition, the functional derivative of the xc-hole is given by

\[
\frac{\delta \tilde{g}(r', r_1)}{\delta n(r)} = \lim_{\varepsilon \to 0} \left[ \frac{\tilde{g}(r', r_1, [n(r_2) + \varepsilon \delta(r_2 - r)]) - \tilde{g}(r', r_1, [n(r_2)])}{\varepsilon} \right] \tag{A.21}
\]
The above identity indicates that a finite value of $\delta \tilde{g}(r', r)/\delta n(r)$ corresponds to a polarization of the xc-hole at $r'$ due to a charge at $r$. Note that the long-ranged behavior of $\delta \tilde{g}(r', r)/\delta n(r)$ is not inconsistent with $\tilde{g}(r', r)$ being short-ranged; thus, it is possible to have an exchange-correlation electric field without having long-range correlations in the xc-hole as argued by Martin and Ortiz.

Now let us try to cast the arguments in the previous paragraph into a more rigorous form. We are interested in looking at $K_{xc}(q, q)$ which is given by

$$K_{xc}(q, q) = \frac{1}{\Omega} \int dr' \int dr K_{xc}(r, r') e^{i q \cdot (r - r')}$$

Substituting Eq. (A.20) into the above equation we get the exact expression for $K_{xc}(q, q)$. Let us look at the contribution to this coming only from the first term on the r.h.s of Eq. (A.20). Let

$$f(r', r - r') = \tilde{g}(r, r') - 1.$$  (A.23)

Furthermore let $\xi$ be the length scale over which $f(r', r - r')$ exponentially decays to zero. If $f(r', r - r')$ decays according a power law then $\xi \sim L$ where $L$ is the linear dimension corresponding to the system size. Let us first consider the case when $f$ decays exponentially over a finite length $\xi$. Using the Schwartz inequality for Eq. (A.22) we get

$$K_{xc}(q, q) < \frac{1}{\Omega} \int dr' \int dr \frac{|f(r', r - r')|}{|r - r'|}$$  (A.24)

The r.h.s of the above equation is clearly finite since $f$ is an exponentially localized function. Thus $K_{xc}$ does not diverge in the long-wavelength limit and there is no corresponding exchange-correlation electric field. When $f$ shows power law correlations, the integral in the above expression extends over the entire system and the preceding
argument is no longer valid. In this case, using the following change of variables

\[ d(\mathbf{r} - \mathbf{r}') = R^2 dR dx d\phi \quad x = \cos \theta \]

and also using \( y = qR \) we get the following expression

\[ K_{xc}(q, q) = \frac{1}{q^2 \Omega} \int d\mathbf{r}' \int y dy dx d\phi \ e^{iyx} f(\mathbf{r}', \frac{y}{q}, x, \phi) \quad (A.25) \]

From the above equation we see that if \( f(\mathbf{r}', \mathbf{R}) \) tends to a finite constant as \( R \) approaches \( L \) i.e the system shows long-range correlations. then \( K_{xc} \) diverges in the long-wavelength limit as \( 1/q^2 \). Thus the system shows a crossover in the behavior of \( K_{xc} \) as one goes from short-range correlations to long-range correlations.

However, as pointed out by Martin and Ortiz [137], it is unusual for the exchange-correlation hole to exhibit such long-range correlations. Instead they argued that the exchange-correlation electric field arises due to the polarization of the xc-hole. [140, 143] This corresponds to the second term on the r.h.s of Eq. (A.20). In the following analysis we consider the contribution to \( K_{xc} \) due to this term only. Using the definition

\[ \frac{\delta \tilde{g}(\mathbf{r}', \mathbf{r}_1)}{\delta n(\mathbf{r})} = \frac{f_1(\mathbf{r}', \mathbf{r}_1, \mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (A.26) \]

and carrying out the same change of variables as before, we get

\[ K_{xc}(q, q) = \frac{1}{q^2 \gamma_1} \quad (A.27) \]

where

\[ \gamma_1 = \frac{2}{\Omega} \int d\mathbf{r}' \int d\mathbf{r}_1 \frac{n(\mathbf{r}_1)}{|\mathbf{r}' - \mathbf{r}_1|} \int y dy dx d\phi \ e^{iyx} f_1(\mathbf{r}', \mathbf{r}_1, \frac{y}{q}, x, \phi) \quad (A.28) \]

The above equation relates the parameter \( \gamma_1 \), first discussed by Aulbur et al, to the polarization of the xc-hole. Note that, while the point has been made previously
[137, 140] that the xc-hole has to be long-ranged in order for $\gamma_1$ to be finite, the above expression clearly indicates what the constraints on long-ranged behaviour are. i.e $\delta \tilde{g}(\mathbf{r}', \mathbf{r}_1)/\delta n(\mathbf{r})$ must fall off as $1/|\mathbf{r} - \mathbf{r}'|$.

Aulbur et al [134] have shown that the parameter $\gamma_1$ can be related to the difference in the inverse experimental and LDA susceptibilities, assuming that the exchange-correlation electric field solely accounts for the discrepancy between the LDA and experimental dielectric constants. However, they neglect local field effects in their analysis. In the following we show that the above result concerning $\gamma_1$ is more general and can be derived without neglecting local-field effects. Our starting point is the density-functional perturbation theory introduced by Baroni et al [147]. Let us consider the linear response to an external potential $\Delta V$ with periodicity $\mathbf{q}$. The linear variation in the Kohn-Sham orbitals $\Delta \phi_i$ and the corresponding change in the Kohn-Sham potential $\Delta V_{KS}$ is obtained by solving the following set of equations self-consistently [148]

$$\Delta \phi_i = \sum_{j \neq i} \phi_j \frac{\langle \phi_j | \Delta V_{KS} | \phi_i \rangle}{E_i - E_j} \tag{A.29}$$

$$\Delta V_{KS} = \Delta V + \int d\mathbf{r}' \frac{\delta n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r}' K_{xc}(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}) \tag{A.30}$$

where $\delta n$ is the change in the electronic density. In order to look at the response to a macroscopic electric field $\mathbf{E}_0$ we have to take the long-wavelength limit $\mathbf{q} \to 0$ of the above equation. In this case the corresponding electronic potential $\Delta V = -\mathbf{E}_0 \cdot \mathbf{r}$ is not lattice periodic and hence its matrix elements are ill-defined when periodic boundary conditions are used. However the matrix elements can be cast into a boundary-insensitive form and then evaluated as discussed in detail by Giannozzi et al [145].
With this in mind we take the long-wavelength limit for Eq. (A.30) and recast it to get [148]

$$\Delta V_{\text{KS}} = -\mathbf{E} \cdot \mathbf{r} + \int d\mathbf{r}' \frac{\Delta n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r}' K_{\text{xc}}(\mathbf{r}, \mathbf{r}') \Delta n(\mathbf{r})$$  \hspace{1cm} (A.31)

where $\mathbf{E}$ is the screened macroscopic electric field and $\Delta n$ now corresponds to the lattice-periodic density. The above set of equations is iterated to self-consistency while keeping $\mathbf{E}$ fixed. The solution can then be used to obtain the susceptibility which is given by $\chi = \delta \mathbf{P} / \delta \mathbf{E}$. We note that in solving the above equations, typically local approximations such as LDA are used in evaluating the exchange-correlation kernel $K_{\text{xc}}$. Hence there is no macroscopic contribution from the exchange-correlation part of the response. However we have seen that PDFT states that, for insulators, $K_{\text{xc}}$ diverges in the long-wavelength limit, so a better approximation to the 'exact' exchange-correlation kernel is given by

$$K_{\text{xc}}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = K_{\text{xc}}^{\text{LDA}}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') \quad \mathbf{G}, \mathbf{G}' \neq 0$$

$$= \frac{\gamma_1}{q^2} \quad \mathbf{G}, \mathbf{G}' = 0$$  \hspace{1cm} (A.32)

where $\gamma_1$ is a finite constant related to the polarization of the xc-hole as argued previously. The effect of the above approximation for $K_{\text{xc}}$ is that in taking the long-wavelength limit of Eq. (A.30) above, there is an additional term to the macroscopic response which is the exchange-correlation electric field ($E_{\text{xc}}$). So the change in the effective potential is now given by

$$\Delta V_{\text{KS}} = -e(\mathbf{E} + E_{\text{xc}}) \cdot \mathbf{r} + \int d\mathbf{r}' \frac{\Delta n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r}' K_{\text{xc}}(\mathbf{r}, \mathbf{r}') \Delta n(\mathbf{r})$$  \hspace{1cm} (A.33)
Note that Eqs. (A.31) and (A.33) are identical apart from the macroscopic response terms which are kept fixed during the iteration to self-consistency. Now, let $\chi_{\text{LDA}}$ be the linear susceptibility obtained by solving Eqs. (A.29) and (A.30) self-consistently and let $\chi$ be the same obtained by solving Eqs. (A.29) and (A.31) self-consistently. In the linear response regime, the macroscopic polarization $P$ obtained by solving Eqs. (A.29) and (A.31) is given by

$$P = \chi E = \chi_{\text{LDA}}(E + E_{xc})$$

(A.34)

Substituting for $E_{xc}$ in terms of $\gamma_1$ and $E$ we get [134]

$$\gamma_1 = \frac{1}{\chi_{\text{LDA}}} - \frac{1}{\chi}$$

(A.35)

Aulbur et al. have estimated $\gamma_1$ using the above equation and assuming that the PDFT linear susceptibility is the same as the experimental susceptibility. They observed a roughly linear scaling of $\gamma_1$ with lattice constant for a range of semiconductors. In the following we offer some speculations regarding the scaling properties of $\gamma_1$.

Let us consider a range of dielectric materials with the same crystalline structure, for example the tetrahedrally bonded semiconductors in zincblende structure. We are interested in seeing how $\gamma_1$, for a particular semiconductor, is changed when the lattice constant changes from $a$ to $\lambda a$. Let us introduce a new length scale $a_c$ which is the lattice parameter at which the system becomes metallic. This value can be determined, in principle, by $GW$ calculations and for Silicon it is estimated to be $a_c = 0.8 \cdot a_0$, where $a_0$ is the equilibrium lattice constant [144]. Note that since LDA consistently underestimates the true band-gap of the semiconductor, LDA calculations done at the lattice constant $a_c$ will also yield a metallic system. Now
from Eq. (A.35) for $\gamma_1$ it is easy to see that

$$\gamma_1 = 0 \quad a < a_c$$  \hspace{1cm} (A.36)

Thus the lattice parameter $a_c$ serves as a cutoff length scale for $\gamma_1$. We now make the following scaling ansatz: $\gamma_1$, being dimensionless, is a function only of the dimensionless variable $a/a_c$ such that

$$\gamma_1 = \Phi\left(\frac{a}{a_c}\right)$$  \hspace{1cm} (A.37)

For $a$ close to $a_c$ we can do a Taylor expansion to get

$$\gamma_1 = \left[\left(\frac{a}{a_c}\right) - 1\right] \times \Phi'(1)$$  \hspace{1cm} (A.38)

and thereby obtain a simple linear scaling for $\gamma_1$. In order to test the validity of this approximation we have to calculate $\gamma_1$ for different values of the lattice constant $a$ for a given semiconductor. For a homogenous function $\Phi\left(\frac{a}{a_c}\right)$ we expect

$$\Phi\left(\frac{\lambda a}{a_c}\right) = \lambda \epsilon \Phi\left(\frac{a}{a_c}\right)$$  \hspace{1cm} (A.39)

The calculations of $\gamma_1$ at different values of $a$ should either confirm or disprove this conjecture. Furthermore it would be interesting to do the same calculation for other semiconductors in the zincblende structure. The observation of linear scaling by Aulbur et al can be explained by the following conjectures: a) $\Phi$ is a universal function for the semiconductors considered. b) $\epsilon = 1$ for all the semiconductors. It would be interesting to see if the calculations bear out these conjectures. Unfortunately these are very challenging calculations and only a few group across the world have the resources to carry them out. We hope that in the future these calculations will be done and if so they will shed new light on the dielectric constant problem.
Finally let us look at the implications of the polarization of the xc-hole for the non-linear response functions for dielectrics. In this case we have to consider higher-order terms for the change in the exchange-correlation potential which is given by

$$
\delta V_{xc}(r) = \int K_{xc}(r,r')\delta n(r')dr' + \frac{1}{2} \int \int M_{xc}(r,r',r'')\delta n(r')\delta n(r'')dr'dr''
$$  \hspace{1cm} (A.40)

where

$$
M_{xc}(r,r',r'') = \frac{\delta^2 V_{xc}(r)}{\delta n(r')\delta n(r'')}
$$  \hspace{1cm} (A.41)

By fourier-transforming the above equations and carrying out the same analysis as in Eqs. (A.13)-(A.16) we see that the exchange-correlation electric field is now given by

$$
\mathcal{E}_{xc} = \gamma_1 P + \gamma_2 P^2
$$  \hspace{1cm} (A.42)

where

$$
\gamma_2 \propto \lim_{q \to 0}[q^3 M_{xc}(q,q,q)]
$$  \hspace{1cm} (A.43)

and

$$
M_{xc}(q,q,q) = \frac{1}{\Omega^2} \int \int dr dr' dr'' M_{xc}(r,r',r'') e^{iq \cdot r} e^{-iq \cdot r'} e^{-iq \cdot r''}
$$  \hspace{1cm} (A.44)

$M_{xc}$ can be obtained by functional differentiation of Eq. (A.20). Dropping terms proportional to $[\frac{\delta^2 \tilde{g}(r_1,r_2)}{\delta n(r)}\delta n(r')]$ and higher order derivatives we get

$$
M_{xc}(r,r',r'') = 2 \left[ \frac{\delta \tilde{g}(r',r'')}{\delta n(r)} \right] \frac{1}{|r' - r''|}
$$  \hspace{1cm} (A.45)

Now for $\tilde{g}(r,r')$ short-ranged and $\delta \tilde{g}(r',r_1)/\delta n(r)$ long-ranged i.e falling off as $1/|r' - r|$ we see from the above equation that $M_{xc}(q,q,q)$ diverges as $(1/q^2)$. This, in conjunction with Eq. (A.43) above, implies that $\gamma_2 = 0$. By assuming $\gamma_2 = 0$,
Aulbur et al. have derived a relation between the LDA and experimental non-linear susceptibilities which agrees well with the experimental results [134]. We have shown that this assumption is consistent with the properties of the xc-hole proposed by Martin and Ortiz [137]

In conclusion, we have looked at polarization density functional theory from the point of view of polarization of the exchange-correlation hole as proposed by Martin and Ortiz. We have related this polarization of the exchange-correlation hole to the parameter $\gamma_1$ introduced by Aulbur et al. Finally we have looked at the effect of this polarization on the calculated nonlinear susceptibilities of semiconductors and speculated about the scaling properties of $\gamma_1$. Further calculations investigating this scaling form could be a big step towards confirming the validity of PDFT. It is thus hoped that further calculations along these lines will add to the understanding of dielectric response in DFT.


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