Quantum Many-Body Interaction Effects In Two-Dimensional Materials

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Abstract

In this thesis, I will discuss three problems related to the novel physics of two-dimensional quantum materials such as graphene, group-VI dichalcogenides family (TMDCs viz. MoS$_2$, WS$_2$, MoSe$_2$, etc) and Silicene-Germanene class of materials. The first problem poses a simple question - how do the quantum excitations in a graphene membrane affect adsorption? Using the tools of diagrammatic perturbation theory, I will derive the scattering rates of a neutral atom on a graphene membrane. I will show how this seemingly naive model can serve as a non-relativistic condensed matter analogue of the infamous infrared problem in Quantum Electrodynamics.

In the second problem, I will move from the framework of a single atom adsorption to a collective behavior of fluids near graphene and TMDC - interfaces. Following the seminal work of Dzyaloshinskii-Lifshitz-Pitaevskii on van der Waals interactions, I will develop a theory of liquid film growth on 2 dimensional surfaces. Additionally, I will report an exotic phenomenon of critical wetting instability which is a result of the dielectric engineering and discuss experimental and technological implications.

Finally, the last problem will see the introduction of spin-orbit coupling effects in the 2D topological insulator family of Silicene-Germanene class of materials. I will present a unified theory for their in-plane magnetic field response leading to “anomalous”, i.e electron interaction-dependent spin-flip transition moment. Can this correction to spin-flip transition moment be measured? I will propose magneto-optical experimental techniques that can probe the effects.
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I need to write a few words about Dr. Kotov now ....
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Preface

The goals of this thesis are the following: (1) To summarize my main research results for the past 3 years, (2) To provide a detailed theoretical framework for understanding few chosen physical phenomena in 2-dimensional quantum materials and (N-1) To successfully receive a Doctoral degree (perhaps, N = 1). The contents of this thesis are mainly related to problems in quantum condensed matter physics. Using the tools of quantum field theory, I will survey the many-body effects related to (i) adsorption phenomenon and (ii) spin-dynamics. These research projects combine analytical studies with numerical techniques, tailored to suit a particular problem at hand.

The thesis is divided into six blocks. Part I introduces the preliminaries - how, what and why. Here, we will introduce the concept behind QFT in a pedagogical manner and review the physical properties of the materials that we will study and finally lay out the main questions of this thesis. Quite naturally this Part is very non-technical. To make up for it, each chapter that follows Part I has a more technical overview of the topic of interest.

Parts II, III, IV form the core of the thesis. In Part II, we explain in excruciating details the mathematical tool kit to solve a 'single atom-surface interaction' problem. The kit includes - diagrammatic perturbation series techniques, Green’s function formalism both at zero and finite temperatures. As with most QFT problems, we will encounter rampant infrared divergences in our mathematical equations. We will finally remove these IR divergences by devising Resummation Techniques based on non-perturbative methods. In Part III, we will move on from single atom-surface inter-
action to liquid-surface interaction phenomenon. Our toolkit would include Random Phase Approximation (RPA) technique in a very simplified manner. Our aim in this section would be to develop a theory of liquid film growth on 2-dimensional quantum materials. We will also look into other 'textbook' phenomena that have previously been absent in the realm of 2D materials research. In Part IV, we will move from many-body adsorption effects to spin dynamics. We will use the celebrated 'Vertex function' calculation in QED to calculate the anomalous spin-flip transition moment for the first time in 2D materials. We will also propose some experimental techniques to verify our results.

Although each chapter and parts include their own technical summary, there is a short Part V that summarizes all the results of this thesis in a single page. All the technical details of most of the calculations are in the Appendix which forms the last part of this thesis - Part VI.
Part I

Preliminaries
Chapter 1

Introduction

1.1 Quantum Field Theory and Many - Body Phenomena

One of my favorite books on quantum field theory by Anthony Zee [159] begins with this remarkable idea - "Quantum field theory arose out of our need to describe the ephemeral nature of life.' The natural question would then be 'What is this ephemeral nature of life?' Or, perhaps, not. From a scientific point of view, one asks why we need Quantum field theory (QFT) and how does it explain the intricate framework of nature?

The starting point of any theory is to understand why we need that theory or what causes it to exist. The existence of QFT lies at the confluence of two of the greatest ideas from Quantum mechanics (QM) and Special theory of relativity (STR). The uncertainty principle in quantum mechanics predicts fluctuating energy within a short time scale, whereas, special theory of relativity gives us the principle of energy-
mass equivalence. Based on these two principles of QM and STR, we can say that
a fluctuating energy field transforms into mass or more precisely into particles that
had no prior existence. These particles are created out of nowhere, they live for a
while and then decay into nowhere - "the ephemeral nature of life!" Remarkably this
is the base of Quantum field theory - the branch of physics that deals with the birth,
life and death of particles. These particles are created because of the fluctuations of
the interacting field. While alive, they mediate interactions between many degrees of
freedom producing profound physical effects and finally, they annihilate back into the
fluctuations. At this point, one might even wonder if any of these is truly observable
in the physical realm.

Well, our best laws in physics tell us that we can imagine the fundamental build-
ing blocks of nature to consist of continuous fluid-like substances that spread out
through out space, we call them - fields. Familiar examples of such fields are the
electric and magnetic fields. Incorporating the effects of quantum mechanics into an
electromagnetic field, quantizes this field producing photons. Thus, as the name sug-
gests the study of quantum field theory in essence deals with quantizing the classical
fields leading to the creation of the corresponding quantum particle. This idea or
process is at play behind the existence of mostly all the particles we know of. As
examples, an electron can be thought of as the ripple of the underlying electron field.
Similarly, there is a quark and a gluon field for the strong interactions existing within
the nucleus and finally a Higgs boson field with its exotic Higgs particle. Thus, every
particle in this Universe is a ripple of the underlying interacting field bundled up into
energy by the principles of quantum mechanics - this is QFT in a nutshell!

Traditionally QFT was developed to study relativistic fields and most importantly
to understand elementary particle physics or high energy physics. With time, theoreticalists and mathematicians extended the field theoretic tool set to its low-energy, non-relativistic counterparts leading to the wide-spread application of the techniques of quantum fields to condensed matter physics. One of the most fascinating aspects of condensed matter physics is the emergence of highly non-trivial many-body effects produced by the low-energy degrees of freedom compared to the individualistic particle that the system starts out with. As for example, the phenomenon of superconductivity could not be explained by the Drude-Lorentz model, instead the collective behavior of the many-electron system provided us with the explanation of its dramatic effects. Current research at the frontiers of condensed matter routinely sees the application of the tools of QFT to solve the many-body problems related to topological phases of matter, quantum Hall effects and superconductors. Other topics include 1D strongly correlated systems, quantum ordered and disordered phases, quantum entanglement and fractional statistics [60].

At this point, we should probably mention that this thesis deals with studying some problems in quantum condensed matter physics which deal with the application of the tools of QFT in investigating the novel many-body physics of 2-dimensional quantum materials. Before we pose the specific questions related to the problems, let us first introduce the different quantum materials and their salient features.

### 1.2 Two-Dimensional Materials

Historically, Landau and Peierls argued that 2D crystals are thermodynamically unstable because of the instability caused by an decreasing melting temperature with
a decreased thickness [84, 119]. Hence, the existence of these crystals were thought of only as "academic" and served as theoretical toy models. However, the successful exfoliation of graphite to graphene, marked the beginning of the era of 2-dimensional materials research. These materials not only exhibit superlative physical properties but are also rich in fundamental physics. In this thesis, our work is focused on three different types of 2D materials and we start off with Graphene, the paradigm of all 2D materials.

1.2.1 Graphene

A revolutionary age in 2-dimensional materials research began in 2004 with the discovery of graphene - a single layer of Carbon atoms closely packed into a benzene ring [115]. This material often referred to as the 'wonder material' was seen to exhibit some of the most fascinating characteristics related to electronic properties, mechanical stability and transport features [24]. From an orbital picture, graphene consists of single layers of $sp^2$ hybridized C-atoms. The exceptional stiffness and mechanical stability of graphene is attributed to the strong $\sigma$ bonds that are formed between the electrons in the in-plane $p_{xy}$ and $s$ orbitals which keep the C-atoms covalently bonded together in a trigonal planar structure with distance between the atoms given by $a = 1.42 \, \text{Å}$. The remaining electron in the $p_z$ orbital perpendicular to the plane of graphene is free to hop between neighboring sites leading to the $\pi$ bands that finally lead to some remarkable electronic and magnetotransport properties.

From the lattice picture [see Fig. 1.1], graphene consists of a single layer of C-atoms arranged in a honeycomb lattice. One can imagine this honeycomb lattice as a triangular Bravais lattice with two atoms per unit cell, or more equivalently as two in-
terpenetrating triangular sublattices. Now a large portion of this thesis is dedicated to studying the lattice dynamics of graphene which alludes to the *phonons* in graphene. Phonon modes of graphene correspond to acoustic and optical branches, according to which atoms of different sublattices vibrate in phase or out-of-plane respectively. The low-energy modes are described by the acoustic phonons which again display both in-plane and out-of-plane vibrations. Dynamics of such low-energy modes are typically governed by the elastic constants of the solid. We will be specifically discussing the effects of the out-of-plane acoustic phonon modes in the subsequent chapters.

Figure 1.1: Honeycomb lattice structure of graphene. Two interpenetrating triangular sublattices are shown by the red open (green filled) dots for A (B) sublattices. The arrows represent the basis vectors of the Bravais lattice [26].
1.2.2 Transition Metal Dichalcogenides (TMDC)

Family of atomically thin 2D crystals goes beyond graphene and includes the insulator family of Transition Metal Dichalcogenides (TMDCs). The transition metal atoms (M) are arranged in a triangular lattice and each one is bonded to six chalcogen atoms (X) [see Fig. 1.2]. From now on we denote these materials by the stoichiometric formula MX2. Bulk TMDCs are composed of X-M-X layers stacked on top of one another and coupled by van der Waals interactions. Similar to graphite, these materials can also be exfoliated down to a single layer [63, 148]. The electronic properties of the materials range from metallic to semiconductor depending on the transition metal. In this thesis, we will concentrate on the semiconducting monolayers [103, 140] such as molybdenum diselenide (MoSe2), molybdenum disulfide (MoS2), tungsten disulfide (WS2) or tungsten diselenide (WSe2). A big difference between the bulk and monolayer materials is that the bulk structure is centrosymmetric whereas the monolayer is not. In terms of the lattice structure, the lattice is a triangular Bravais lattice with 3 atoms comprising of 2 chalcogens and 1 metal. Although the Brillouin zone in TMDCs also consist of a hexagon, the orbital character of the conduction and valence bands are completely different. These bands are dominated by d orbital from the transition metal atom with minute weight in the p orbitals from the chalcogens.
Figure 1.2: (a) shows the two unit cells of MoS$_2$ monolayers and (b) shows a top view of MoS$_2$ monolayer with $R_i$ being the vectors connecting nearest Mo atoms [155].

1.2.3 Silicene - Germanene

The last group of materials in the trio of quantum materials studied in this thesis is the Silicene-Germanene class of topological materials. These elemental 2D materials are of particular interest as they are chemically tractable for synthetic exploration [104]. Quite similar to graphene, Silicene & Germanene are formed on hexagonal lattices with the C-atoms replaced by the respective Silicon & Germanium atoms. While Silicene can be grown on various substrates like Ag, ZrB$_2$, Ir and MoS$_2$ [36, 57, 59, 106, 146], Germanene is synthesized on Au and Pt substrates [39, 98]. Based on first-principles calculations, several proposals on the realization of free-standing silicene & germanene on substrates have also been a topic of recent research[21, 74]. Now, a very important feature of these class of materials is the fact that they are expected to be Topological Insulators (TI). A TI represents a state of matter that is characterized by topological number, and exhibit an insulating gap in the bulk accompanied by topologically protected gapless edge states [55, 66, 122]. These materials thus offer a lucrative playground to explore the physics of topology in quantum condensed
matter in conjunction with Dirac physics. The basic lattice structure is similar to graphene with two interpenetrating trigonal sublattices, however there are two major differences between graphene and Silicene-Germanene class of materials - (i) presence of spin-orbit coupling that makes it a topological insulator [99], (ii) apparently a bigger Si or Ge atom when placed in the honeycomb lattice leads to a buckling in the lattice which produces a layer separation between the respective sub-lattices [see Fig. 1.3]. This separated sub-lattices often produce a staggered potential that can be tuned by an applied electric field. This feature has some profound implications. A tunable electric field applied perpendicular to the plane of the Silicene lattice across this staggered potential results into an evolution of the band gap of the system from a topological insulator (TI) to a bulk insulator (BI) via a valley spin polarized state (VSPM) [42, 50]. In the third problem studied in this thesis, we will talk a bit more about these two features and predict some feasible quantum phenomenon in these class of materials.

Now that we have reviewed the salient features of the 2D quantum materials, let us quickly formulate the three main questions of the thesis.

1.3 Statement of the problems

In previous sections of this introduction, we introduced the concept of quantum field theory and related quantum many-body phenomena in quantum condensed matter physics. We also talked about some salient features of atomically thin quantum materials and now, we think it is time to formulate the main questions that form the base of this thesis. The aim of the thesis is to study the role of quantum particles
leading to quantum many-body phenomena in 2-dimensional materials that can finally give rise to some physically observable effects. For us these observable effects are related to the phenomena of adsorption, thin-film growth and spin dynamics. With that being said, let us begin with the statements of the problems.

1.3.1 What is the effect of phonons on the phenomenon of adsorption?

In Part II of this thesis, namely - "Cold Atom - Surface Interaction", we will investigate the effect of low-energy transverse acoustic phonons on the phenomenon of adsorption. The candidate material chosen for this project happens to be suspended graphene membranes. Although we will discuss and explain the related physics with regards to graphene, we believe our analysis and results will be valid to almost all
the atomically thin materials with proper numerical specifications and considerations. Now let us describe what the problem is.

Let us consider a slowly moving adatom, more specifically a neutral Hydrogen atom impinging on a suspended graphene membrane. Weak forces of van der Waals interaction hold together the atom and the membrane that are now separated from each other by a minute distance. As discussed before, the quantized vibrations of the membrane that appear as ripples in the membrane start to interact with the incoming adatom. The natural question we ask: do these quantum excitations scatter the adatom away or do they actually enhance the adsorption rate? This seems to be an archetype of a collision problem in physics and hence, the natural choices would be to treat it as either an elastic or an inelastic collision. Let us first talk about what may happen if this problem serves as an elastic collision.

Tracing back to the early years of quantum theory, Lennard-Jones [88] predicted a threshold behavior for quantum adsorption. Based primarily on the idea of quantum reflection which is a simple result of the wave-like nature of low-energy particles moving in an attractive potential that falls off sufficiently rapidly with distance from surface, the threshold law states that sticking probability $s(E)$ of a particle with incident energy $E$ is directly proportional to the square of the transition matrix element and varies inversely with the incident particle flux, such that $s(E) \propto \sqrt{E}$. Thus, in our case, if we treat the problem as an elastic collision, we can say that the atom impinging on graphene may undergo quantum reflection from the attractive van der Waals (vdW) tail of the atom-graphene potential. This seems to be a fascinating result both from the point of view of theorists & experimentalists.

However, for inelastic interactions which is the topic of interest in this thesis, the
problem is a little more evolved. The primary channel of energy exchange involves
the creation and annihilation of phonons. Free-standing graphene has two in-plane
acoustic modes and one out-of-plane transverse acoustic mode. For the incoming
atom, it excites the transverse mode and mediates interactions that we would refer
in this thesis as the atom-phonon coupling. Now to derive the adsorption rate of
the atom we do the following: we treat the atom-phonon interaction as perturbation
and derive scattering rates using the tools of perturbation theory expansion. This
expansion will be formulated in a graphical form with each term in the perturbation
series representing a picture - *Feynman diagram*. It is almost never possible to sum
the entire perturbation series to get an exact answer to the scattering rates, however,
one can perform a partial sum but then it is crucial to figure out which term gives
the largest contribution. Also, the entire diagram expansion can be reformulated in
terms of the exact Green’s functions. Thus the first thing we do is to check whether
the individual terms in the series are convergent. Most often than not, it turns out
that the terms in the series are divergent which can be further categorized into either
*infrared* or *ultraviolet* divergence.

Now the UV divergence typically poses a huge challenge for high energy physics,
but for condensed matter system this is generally resolved by setting the system on
a well-defined lattice or by re-organization of the perturbation series. IR divergences
in condensed matter physics are more interesting though. Their presence is always
an indication of an incorrectly chosen reference ground state [143]. Now the general
reader at this point might be wondering why are we digressing from the framework of
adsorption of adatoms on graphene membrane to infrared divergences in perturbation
series. This is because our problem which started off naively as the study of the role of
phonons in adsorption evolves into a much deeper mathematical problem that predicts that on interacting with a suspended membrane, the scattering rates of adatoms predicted by conventional perturbation theory suffer from severe infrared divergences due to the emission of infinitely many low-energy acoustic phonons. Hence, the revised question we ask is the following:

**How do we remedy these IR divergences to predict physically admissible finite adsorption rates for these elastic graphene micromembranes?**

In Chapters 2 & 3, we devise mathematical techniques to remove these IR divergences and provide a well-unified theory that describes the effects of the role of multi-phonon emission in the adsorption phenomena. More interestingly, we will draw parallels of this non-relativistic condensed matter problem to a strikingly similar situation encountered in quantum electrodynamics & quantum chromodynamics. This similarity essentially reflects the great unity of theoretical physics.

Now, so far we have talked about the problem of atom-surface interactions within the framework of a single atom adsorption. What happens when we move towards a collective behavior of atoms impinging on a surface? And what if, instead of a single layer of elastic graphene membrane, we consider a sandwich of dielectrics? Well, these questions form the foundational base of our next problem.

### 1.3.2 What is the effect of polarization on the phenomenon of thin film growth?

In his doctoral thesis back in 1873, van der Waals originally suggested a molecular interaction potential of the form $V(r) = -Ar^{-1}e^{-Br}$ where, $r =$ distance between the
molecules and A and B are positive constants. This interaction potential, later came to be known as the celebrated vdW interaction also, referred to as the "dispersion" force because of the appearance of the molecular polarizability. Now, the most interesting idea behind the vdW interaction is the following: neither molecule in the dispersion interaction has a permanent dipole moment; each has a fluctuating dipole moment induced by the vacuum field at its position and from these fluctuating dipoles emerge a non-vanishing force [35]. Now why is this so? Let us try to understand this from the view point of quantum fluctuations of the electromagnetic field. The dipole moments induced by the fluctuations of the electric field, more precisely the zero-point energy is correlated over finite differences, leading to a non-vanishing expectation value for the inter-molecular interaction energy. Classical electrodynamics owing to the absence of $\hbar$ could never explain such "dispersion forces" existing between charge-neutral molecules.

Well, one might think, why are we considering this idea of quantum fluctuations of the electromagnetic fields here. Well the answer is simple.

Casimir in 1948 predicted that the existence of electromagnetic zero-point energy implies that there is an attractive force between two uncharged perfectly conducting plates [23]. This problem was then generalized by Lifshitz to the case of dielectric media. Using Maxwell’s stress tensor, he derived Casimir’s result for the attractive force between two dielectric half-spaces separated by a vacuum[96]. Lifshitz expression for the force/unit area between 2 dielectric media was then generalized to allow for a third dielectric material between the half-spaces. This problem was then solved by Dzyaloshinskii-Lifshitz-Pitaevskii using diagrammatic field theoretic approach [3, 46]. Their calculation involved the computation of the free energy of the system involving
a summation over all $n$-body vdW interactions, or more precisely, the correction to the free-energy due to the interactions was developed within the Matsubara technique as a set of "ring" diagrams representing the "polarization" loops. This theory known as the Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) theory predicting vdW interaction energy for a system of dielectrics would serve as the starting point for our current problem.

Imagine we introduce a layer of 2D material (either graphene or TMDC) within a system of dielectric. We define this system of dielectric comprising of three layers: layer 1 - vapor of a light atom with dielectric $\epsilon_1$, layer 2 - liquid of the light atom with dielectric $\epsilon_2$ and, layer 3 - substrate with dielectric $\epsilon_3$. Now, let us consider three configurations, where we insert the layer of 2D material (let’s say for eg. the material is graphene) at the interface of layer 2 & 3, such that we have: (i) graphene supported on the substrate, (ii) graphene submerged in liquid (we replace the substrate in layer 3 by liquid) and, (iii) suspended graphene in vacuum (replacing the substrate in layer 2 by vacuum). The question we ask - What is the vdW correlation energy between the 1-2 and 2-3 material surface boundaries for all the three different configurations? Now, we know vdW forces play an important part in the physics of surface phenomena and in the properties of thin film growth, in particular. Quite naturally, a knowledge of the vdW correlation energy at the interface of liquid-2D material interface will thus tell us if we can grow layers of thin film on 2D materials. This forms the content of Chapter 4 in Part III of this thesis named "Fluid - Surface Interaction". Additionally, we will explore an exotic phenomenon of critical wetting instability for the suspended graphene in vacuum. Not only does this exotica have profound physical consequences but also far-reaching technological implications.
Let us now move to our last problem. The question and the calculation that will form the contents of Chapter 5 is similar in essence to a very specific calculation in quantum electrodynamics. Hailed as the "Precision test of QED", Schwinger’s correction to the anomalous magnetic moment due to Coulomb interactions is a groundbreaking proof of the validity of quantum field theory. We will formulate our next problem very much similar in essence to the idea of Schwinger’s calculation.

1.3.3 What is the effect of Coulomb interactions on the phenomenon of Spin-flip transition moment?

Before we set up our last problem, let us first review some of the background topics that form the central ideas of the problem.

Quite similar to classical mechanics, as we all know quantum mechanics allows for two different types of angular momentum - orbital angular momentum (L) & spin angular momentum (S). Now, in quantum mechanics, the spin of an elementary particle is "intrinsic", meaning a specific particle has a fixed value of spin (for examples: spin of electron = 1/2, pi mesons are spin 0, graviton is spin 2, photons & phonons are spin 1), whereas the orbital angular momentum value can change with slight perturbation to the system and takes up only integer values.

Now, one may ask what is the magnetic dipole moment $\vec{\mu}$ of a spinning electron of charge $e$ and mass $m$? Classically, $\vec{\mu}$ of the spinning charge should be proportional to the spin angular momentum ($\vec{S}$), such that, $\vec{\mu} = (e/2m) \vec{S}$, with the gyromagnetic ratio defined as $\gamma = (e/2m)$. However, in Dirac’s relativistic theory of quantum
mechanics, he explained the gyromagnetic ratio of the electron to be $\gamma = (e/m)$ (twice the classical value), thus redefining the magnetic moment of a spin 1/2 electron as $\vec{\mu} = g (e/2m) \vec{S}$, where $g$ is defined as the Lande $g$-factor. So, for a free electron, Dirac’s theory predicts a $g$-factor of 2. However, by late 1940’s with improvements in experimental techniques, the magnetic moment of an electron was measured to be slightly larger than the value predicted by Dirac by a factor of $1.00118 \pm 0.00003$. This anomaly that puzzled physicists of that era is famously referred to as the anomalous magnetic moment of electron. In 1948, finally an explanation to this anomaly was received. Julian Schwinger in his seminal paper, 'On Quantum-Electrodynamics and the Magnetic Moment of the Electron' [136] explained this anomaly by incorporating the effects of the radiative corrections that are produced as a result of the interaction of the electron with the virtual quanta of the Coulomb field. Thus based on the effects of quantum electrodynamics a corrected value of the $g$-factor was given as $g = 2[1 + a]$, with $a = (\alpha/2\pi) = 0.0011614$ represents the anomaly [120] and $\alpha$ represents the fine-structure constant. As we can see the leading term in the corrected $g$ - factor is the value predicted by Dirac’s equation, however the higher order terms are solely explained by interaction of the electron with virtual photons. But this is for a massive free electron in vacuum. Can we predict a correction to the anomalous magnetic moment for electrons in solids for real materials?

In a recent article by Stoof [145], a calculation very similar in essence to Schwinger’s correction for the anomalous magnetic moment was carried out for massless electrons around the band-touching points in 3D Weyl semimetals. Taking the cue, in Part IV of this thesis - "Spin-Orbit Interaction", we will derive the effect of Coulomb interactions on the electromagnetic response of 2D Topological Insulator family of
Silicene-Germanene class of materials. We will develop a well-unified theory for the 'anomalous' response of the spin-flip transition moment and propose experimental methods that can verify our theoretical predictions.

So we have the tools and the problems, I think it’s time to look for the answers.
Part II

Cold Atom - Surface Interactions
Many-body interaction problems in physics are usually first solved in a zero temperature formalism. Although real-world phenomena and experiments never occur at absolute zero, the knowledge that one gains by solving a complex problem at zero temperature facilitates some intuition towards the finite temperature phenomena. Moreover, conceptually, one can map the zero temperature property of the system to its ground state. This makes it indispensable to understand the quantum interaction picture at zero temperature.

In this chapter, we review the quantum many-body effects for ultracold atom - surface interaction within the zero temperature formalism. We begin with an overview and current status of the problem.

2.1 Overview

There is renewed interest in the quantum mechanics of ultracold atoms near surfaces; work is underway to develop new quantum technologies such as chip-scale atomic
clocks, quantum computers, and high-precision nanoscale sensors. Understanding the dynamics of ultracold atoms near surfaces may give insights into optimizing the performance of these quantum devices. There are additional practical considerations that motivate the study of ultracold atoms near surfaces; namely, the ultracold regime offers some advantages for controlling chemical processes. Reaction pathways might be selected by controlling the quantum state of the reactants. Thus, a quantum theory of ultracold adsorption would be desirable for understanding heterogeneous catalysis at ultralow temperatures.

Although theoretical studies of ultracold surface adsorption began nearly eighty years ago, recent results on the adsorption of cold atomic hydrogen on a newly discovered 2-dimensional material, suspended graphene, have been controversial [29, 92]. A numerical study of inelastic scattering from suspended graphene [89] concluded that compared to sticking on graphite, sticking should be enhanced on 2-dimensional graphene. The authors argued that sticking proceeds by the creation of a single graphene phonon. In contrast to 3-dimensional graphite, the vibrations of suspended graphene are essentially completely polarized normal to its surface. Thus, the atom-phonon interaction is stronger for graphene than for graphite.

Another theoretical study found a very different result. The author argued [30] that the frequency dependence of the atom-phonon interaction is also different for graphene than for graphite. An enhanced atom-phonon interaction at low frequencies resulting from the low dimensionality leads to a reduction of the sticking via a phonon orthogonality catastrophe. An atom bound to the surface is accompanied by a deformation that involves a large number of low energy phonons. Such a state has an exponentially small overlap with graphene’s vibrational ground state when the
atom is in the gas phase. As a result, the sticking matrix element for a 1-phonon process is exponentially reduced and tends to vanish as the size of the graphene target becomes large.

Thus, it is clear to us that the recent studies on this topic are debatable with contrasting results. This motivates us to perform an independent investigation on the adsorption dynamics of cold atoms impinging on graphene micromembranes. Using the tools of diagrammatic perturbation theory, we predict adsorption rates. But before we delve into a more detailed calculation, let us introduce the model Hamiltonian and characteristic features related to this physical system.

## 2.2 Model of Cold Atoms on Graphene Membrane

Our focus here is the dynamics of a system consisting of a single atom interacting with an elastic membrane. Such a system can be realized with a cold atom coupled via the van der Waals (vdW) interaction to a suspended two-dimensional material such as graphene. While the vdW interaction between a cold neutral atom and graphene is weak, it is sufficiently strong for a hydrogen atom to bind to graphene at low temperatures.

The quantum excitations of this suspended membrane are represented by the out-of-plane bending vibrations, namely the transverse acoustic (ZA) modes. These modes are not related to in-plane vibrations, and hence play a significant role in mediating an interaction with an incoming atom. We assume that the atom moves slowly in the perpendicular direction toward the elastic, clamped membrane under
tension and transfers energy through force-coupling to the membrane by exciting its circularly symmetric ZA modes (Fig. 2.1). Additionally, the ZA phonons under tension exhibit a linear phonon density of states with constant transverse speed of sound [29, 56, 90].

We take for our model the following Hamiltonian $H = H_a + H_{ph} + H_{ki}$ [29], where

$$H_a = E_k c_k^\dagger c_k - E_b b^\dagger b$$  \hspace{1cm} (2.1)$$

$$H_{ph} = \sum_q \omega_q a_q^\dagger a_q$$  \hspace{1cm} (2.2)$$

$$H_{ki} = -g_{kb}(c_k^\dagger b + b^\dagger c_k) \sum_q (a_q + a_q^\dagger)$$  \hspace{1cm} (2.3)$$

Figure 2.1: Atom impinging on a 2-dimensional elastic membrane. During adsorption, energy is transferred from the atom to the membrane and is radiated away by phonons.
\[ H_{bb} = -g_{bb} b^\dagger b \sum_q (a_q + a_q^\dagger) \]  \hspace{1cm} (2.4)

Here, \( c_k (c_k^\dagger) \) annihilates (creates) an atom in the continuum state \( |k\rangle \) with energy \( E_k \); \( b (b^\dagger) \) annihilates (creates) an atom bound to the static membrane with energy \(-E_b\); \( a_q (a_q^\dagger) \) annihilates (creates) a circularly symmetric ZA phonon in the membrane with energy \( \omega_q \); \( g_{kb} \) is the atom-phonon coupling for an atom in the continuum state \( |k\rangle \) and bound state \( |b\rangle \); \( g_{bb} \) is the atom-phonon coupling for an atom bound to the membrane \[30\].

Formal definitions of the atom-phonon couplings \( g_{kb} \) and \( g_{bb} \) are given in the literature \[29, 160\]. If the structure of the vdW potential \( V_0(z) \) is known along with the continuum \( |k\rangle \) and bound state \( |b\rangle \) wave functions, one defines: \( g_{kb} = \langle k|V'_0(z)|b\rangle \) and \( g_{bb} = \langle b|V'_0(z)|b\rangle \). Hence, the atom-phonon couplings are strongly dependent on the attractive vdW potential between the atom and the membrane. For sufficiently low-energy incident atoms, the coupling \( g_{kb} \) has a strong dependence on the incident energy of the incoming atom, such that: \( g_{kb} \propto \sqrt{E_k} \) for \( E_k \to 0 \). However, for our model of cold atoms impinging on graphene membranes, \( g_{bb} \) is independent of the incident energy and is much larger in magnitude than \( g_{kb} \). This forces us to be restricted in the energy regime\[29\]:

\[ g_{bb}^2 \rho_0 \gg g_{kb}^2 \rho_0 \ , \ E_b \gg g_{bb}^2 \rho_0 \]  \hspace{1cm} (2.5)

where \( \rho_0 \) is the density of axisymmetric vibrational states.

Now, that we have set up our model Hamiltonian and we are more or less aware of the nitty-gritty details of the physical system, we would like to define the statement of the problem:
What is the effect of the graphene ZA phonons on adsorption rate of ultracold atoms?

To answer the above question, we would need to set up a proper mathematical technique that can be employed to derive a solution to our model Hamiltonian. Consequently, we would use those solutions to calculate and predict the phonon-mediated adsorption rates. Now as we know, in quantum mechanics, exact closed solutions can only be obtained in simple or exceptional cases. Quite interestingly, our model Hamiltonian is rich in complexity and does not possess an exact closed-form solution. This brings us to the Green’s function approach which provides us with a unified systematic method for calculating various quantities of physical interest.

In the next Sec. 2.3, we will discuss the ideology of the Green’s function technique and introduce the method of diagrammatic perturbation theory.

2.3 GREEN’S FUNCTION FORMALISM

Green’s functions (also called propagators) are routinely used to deduce and explain various physical insights in many-particle assemblies. For Hamiltonians which cannot be solved exactly, one employs the technique of Green’s function. This section starts off with a basic review of the mathematical method and in subsequent subsections, we show how we tailor the method for our model.
2.3.1 Basic Technique

Let us consider a system described by a Hamiltonian of the form $H = H_0 + H_i$, where the terms $H_0$ and $H_i$ represent the unperturbed and interaction Hamiltonians, respectively. For small interactions, the system is completely described by the unperturbed Hamiltonian $H_0$. Assuming we know the eigenstates of $H_0$, we can derive a solution of $H$ in terms of the bare Green’s function $G_0$. Now, as we turn on the effects of the interaction, the full solution to the total Hamiltonian $H$ is realized by the proper use of Dyson’s equation:

$$G(E) = \frac{1}{[G_0(E)]^{-1} - \Sigma(E)}$$

(2.6)

where, $G(E)$ is the perturbed Green’s function, $G_0(E)$ is the unperturbed/ free Green’s function and $\Sigma(E)$ is the self-energy. Dyson’s equation acts as the starting point for the Feynman-Dyson perturbation theory (see Fig. 2.2).

Figure 2.2: Diagrammatic representation of Dyson’s equation with $G(E) = G_0(E) + G_0\Sigma(E)G(E)$. This diagram is drawn with the convention: thicker lines represent the perturbed Green’s function $G(E)$ and thinner lines are for the free propagator $G_0$.

Now one may ask what exactly is the self-energy of the atom? Well, $\Sigma(E)$ is a complex quantity whose real and imaginary parts bear physical meanings. Because of the interaction, the system undergoes a shift in energy which is contained in the $\text{Re}\Sigma(E)$. Similarly, the imaginary part represents the damping of the motion of the atom. Thus, to understand the dynamics of the many-body assembly, we must study the self-energy. But, how is the self-energy calculated mathematically? It turns out to
all orders in perturbation theory, one can write down a series expansion in self-energy \( \Sigma \) in terms of Feynman diagrams (Fig. 2.3).

*Figure 2.3: Diagrammatic representation of the self-energy \( \Sigma(E) \) in terms of Feynman diagrams. The number of loops \( n \) in the diagrams represent the order of the terms in the series. For example, \( n = 1 \) is the first-order, \( n = 2 \) corresponds to the second-order terms in the perturbation series expansion (see Sec. 2.3.2).*

Analytical expressions corresponding to the self-energy diagrams are derived by invoking Feynman rules. So, as we see, technically it is possible to deduce some basic ideas about the dynamics of the many-body Hamiltonian by evaluating Green’s functions within the perturbative theory, or more precisely, by calculating the self-energy diagrams. However, our interest lies in the adsorption rates of the atoms. So, let us ask if we can calculate the adsorption rate \( \Gamma \) from the self-energy \( \Sigma \)? For the quasiparticle regime, there seems to be a very well-defined formula\[58\] that connects the two:

\[
\Gamma = -2Z(E_0)\text{Im}\Sigma(E_0) \tag{2.7}
\]

Here, \( Z \) is the renormalization factor which is defined as:

\[
Z(E_0) = \left[1 - \left(\frac{\partial\text{Re}\Sigma(E_0)}{\partial E}\right)\right]^{-1} \tag{2.8}
\]

and, \( E_0 \) is the quasiparticle energy. We must mention that Eq. 2.7 is valid for small coupling 'quasiparticle approximation.' Before we proceed to the next subsection on
self-energy, let us very quickly itemize what we have learnt so far:

- Statement of the problem: What is the effect of the graphene ZA phonons on adsorption rate of ultracold atoms?
- Methodology to answer the above question: Calculate the atom self-energy based on perturbative Green’s function formalism.

2.3.2 Atom Self-energy

In our previous subsection, we briefly introduced the perturbation expansion of the self-energy. In this section, we will discuss in details, the Feynman rules to derive mathematical expressions for the atom self-energy. But first, let us look at the different self-energies that pop up in our model.

In this model, we have self-energy of three types: $\Sigma_{kk}$, $\Sigma_{bb}$ and $\Sigma_{kb}$. $\Sigma_{kk}$ gives the self-energy of the system when the particle makes transition from continuum $|k\rangle$ to bound state $|b\rangle$ and back to the continuum state $|k\rangle$. On the other hand, $\Sigma_{bb}$ is concerned with the motion of the particle through bound states only, corresponding to coupling term $g_{bb}$. $\Sigma_{kb}$ corresponds to the transition of the particle from $|k\rangle$ to $|b\rangle$ state. For the purposes of the current work, we study the atom self-energy $\Sigma_{kk}$ in the continuum. The real part of atom self-energy $\Sigma_{kk}$ would physically correspond to the energy shift of the atom due to the interaction with the phonon bath and the imaginary part would represent the decay rate of the atom. Using the imaginary part of the atom self-energy, we can calculate the sticking rates of the atom on the membrane. The rate of transition of the cold atom ($\Gamma$) from the continuum state $|k\rangle$ to the bound state $|b\rangle$ is given by Eq. 2.7 with $\text{Im} \Sigma$ replaced by $\text{Im} \Sigma_{kk}$. Let us now...
review the Feynman rules for the model.

**Feynman Rules**

As stated in the previous section, analytical expressions for the self-energy $\Sigma(E)$ can be derived using the Feynman rules which are summarized below. Schematic representation of the rules is given in the Fig. 2.4.

- Lines labeled by $|b\rangle$ correspond to the bare Green function in the bound state $G_{bb}$
- Lines labeled by $|k\rangle$ correspond to the bare Green function of the atom in the continuum state $G_{kk}$
- The solid dot corresponds to the interaction vertex $g_{kb}$
- The open dot corresponds to the interaction vertex $g_{bb}$
- Wiggly lines correspond to the phonon Green function $D(\omega)$

*Figure 2.4: Feynman diagrams for transition from $|k\rangle$ to $|b\rangle$ state via vertex $g_{kb}$ and from $|b\rangle$ to $|b\rangle$ state via vertex $g_{bb}$, respectively. These transitions are possible through the absorption or emission of a phonon.*
Each diagram is weighted by \((i/\hbar)^n\), where \(n\) is the number of phonon loops (we work in natural units and set \(\hbar = 1\)).

In the next subsection, we derive the bare Green’s functions \(G_{bb},\ G_{kk}\) and the phonon propagator \(D(\omega)\). We also briefly mention some of their properties and pole structures.

**Bare Green’s functions**

We will begin our calculations with the derivation of the bare Green’s functions. For most of this work, we will be concerned with the Green’s functions for the bound state \(|b\rangle\), continuum state \(|k\rangle\) and the phonons.

**Zero Temperature Green’s function for the continuum & bound state**

The time-ordered Green’s function is defined as [135],

\[
G(t) = -i\langle 0|T\{C(t)C^\dagger(0)\}|0\rangle 
\]  

(2.9)

Here, \(|0\rangle\) is the vacuum state for the unperturbed Hamiltonian and \(C(t)\) is the annihilation operator defined in the Heisenberg picture. The time-ordering symbol \(T\) is defined to order chronologically the operators inside the braces so that the operators with earlier times are placed to the right.

In the continuum state, the unperturbed Hamiltonian is \(H_k = E_k c_k^\dagger c_k\) and since, the operators are defined in the Heisenberg picture, therefore, we have,

\[
c_k(t) = c_k(0)e^{-iE_kt}\]  

(2.10)
Therefore, for \( t > 0 \), Eq (2.10) takes up the form:

\[
G_{kk}(t) = -i\langle 0|c_k e^{-iE_k t} c_k^\dagger|0\rangle \Theta(t) \\
= -i\langle 0|c_k c_k^\dagger|0\rangle e^{-iE_k t} \Theta(t) \\
= -ie^{-iE_k t} \Theta(t)
\]

We take Fourier transform of Eq. 3.7 to derive the propagator in the energy domain:

\[
G_{kk}(E) = \frac{1}{E - E_k + i\eta}
\]

where \( \eta \) is an infinitesimal convergence factor (\( \eta \to 0^+ \)).

Similarly, the time-ordered Green’s function in the bound states \( |b\rangle \) is derived using the unperturbed bound state Hamiltonian \( H_b = -E_b b^\dagger b \) and operator \( b(t) = b(0)e^{iE_b t} \),

\[
G_{bb}(E) = \frac{1}{E + E_b + i\eta}
\]

Therefore, we readily see that bare propagators connecting the non-interacting Hamiltonian has poles at the points where the denominator vanishes. These poles correspond to the excitation of the system. For the bare \( G_{bb} \) and \( G_{kk} \), we find simple poles in the complex energy plane at \( E_k \) and \( -E_b \) slightly below the real axis.

**Zero temperature phonon Green’s function**

The time-ordered Green’s function for the phonon is defined as,

\[
D(q, t) = -i\langle 0|T\{A_q(t) A_q^\dagger(0)\}|0\rangle
\]

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The phonon-field amplitude is related to the creation and destruction operators, such that, $A_q = a_q + a_q^\dagger$. Following the Heisenberg representation and the identities $\langle 0 | a_q a_q^\dagger | 0 \rangle = 1$ and $\langle 0 | a_q^\dagger a_q | 0 \rangle = 0$, for $t > 0$, we derive

$$D(q,t) = -i \Theta(t) \langle a_q(t) a_q^\dagger(0) \rangle - i \Theta(-t) \langle a_q(0) a_q^\dagger(t) \rangle$$

Taking the Fourier transform of the above equation, we have an expression for the unperturbed phonon propagator:

$$D(q,\omega) = \int_0^\infty dt e^{i\omega t} D(q,t)$$

$$= \frac{1}{\omega - \omega_q + i\eta} - \frac{1}{\omega + \omega_q - i\eta}$$

$$= \frac{2\omega_q}{\omega^2 - \omega_q^2 + i\eta}$$

In the next section, we invoke Feynman rules for our model and use the bare propagators to derive mathematical expressions for self-energy terms.

### 2.4 Perturbative Expansion of the Atom

#### SELF-ENERGY

Quite simply, Dyson’s equation says to get the exact Green’s function, one calculates the self-energy $\Sigma$. However, $\Sigma$ is a summation of an infinite number of diagrams. Most often, a full calculation of $\Sigma$ is not possible and hence one calculates $\Sigma$ to the first few orders. In this section, we would explicitly derive the first and second order
terms in the perturbative expansion of atom self-energy $\Sigma_{kk}$. Additionally, this loop expansion has Feynman diagrams that are classified by the number of internal loops.

2.4.1 1-LOOP

![Feynman diagram for the 1-loop atom self-energy $\Sigma_{kk}^{(1)}$ (left). Symbolic elements used in the construction of diagrams are pictured (on right).](image)

We begin our calculations for the perturbation series with the derivation of the 1-loop atom self-energy (see Fig. 3.3). This physically corresponds to a transition from continuum $|k\rangle$ to bound $|b\rangle$ state mediated by one phonon of energy $\omega$. With our Feynman rules and Eq. C.29, we find an analytical expression corresponding to Fig. 3.3:

$$\Sigma_{kk}^{(1)}(E) = ig_{kb}^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} D(\omega)G_{bb}^{(0)}(E - \omega)$$

$$= \sum_q \frac{g_{kb}^2}{E + E_b - \omega_q + i\eta} , \eta \rightarrow 0^+$$

(2.17)

From the Wigner-Eckart theorem, we conclude that we need only consider axisymmetric vibrational modes for transitions to bound states that are also axially symmetric [30]. This is because the atom states are restricted to those that are axially symmet-
ric. We evaluate the sum in Eq. 2.17 in the continuum limit ($\sum q \rightarrow \int_0^{\omega_D} \rho_0(\omega) d\omega$) and obtain:

$$\Sigma^{(1)}_{kk}(E) = -g_{kk}^2 \rho_0 \log \left| \frac{\omega_D - E - E_b}{E + E_b} \right| - i\pi g_{kk}^2 \rho_0 \left[ \theta(\omega_D - E - E_b) - \theta(-E - E_b) \right]$$

(2.18)

where $\rho_0$ is the (constant) density of axisymmetric vibrational states and $\omega_D$ is the Debye frequency for the membrane. $\Sigma_{kk}$ has an imaginary part for $-E_b < E < \omega_D - E_b$ corresponding to atom transitions out of the continuum state to the bound state with the emission of a single phonon. Following Eq. 2.7, we obtain the first-order adsorption rate:

$$\Gamma_0 \approx 2\pi g_{kk}^2 \rho_0$$

(2.19)

for atom energies $E_k$ such that $E_k + E_b \leq \omega_D$. Also, we find $Z \approx 1$ which is valid for $g_{kk}^2 \rho_0 \ll E_b$.

We conclude on the basis of Eq. 2.19 that at the 1-loop level, the transition rate is finite, proportional to $g_{kk}^2$ and is independent of the bound atom-phonon coupling $g_{bb}$.

The adsorption rate can also be calculated using Fermi’s Golden Rule, with lowest order transition rate $\Gamma_0$ given by

$$\Gamma_0 = 2\pi \sum_f |\langle f | H_i | i \rangle|^2 \delta(E_f - E_i)$$

(2.20)

with the initial and final states given as $|i\rangle = |k\rangle|q\rangle$ and $|f\rangle = |b\rangle|1_q\rangle$, respectively. The energies corresponding to the final and the initial state are $E_f = -E_b + \omega_q$ and
\( E_i = E_k \). We then calculate the transition matrix element as \( \langle f | H_i | i \rangle = -g_{kb} \). Thus adsorption rate \( \Gamma_0 \) is

\[
\Gamma_0 = 2\pi \sum_q g_{kb}^2 \delta(-E_b + \omega_q - E_k),
\]

(2.21)

which, in the quasicontinuum approximation, becomes

\[
\Gamma_0 = 2\pi g_{kb}^2 \rho_0.
\]

(2.22)

Therefore, we find that the 1-loop result is equal to transition rate given by Fermi’s Golden rule (Eq. 2.22) for \( g_{kb}^2 \rho_0 \ll E_b \). We now examine the next term in the loop expansion of the self-energy.

### 2.4.2 2-LOOP

We begin this section by looking at the next higher order terms which would correspond to 2-phonon processes. The Feynman diagram corresponding to these processes are given in Fig. 2.6. These diagrams correspond to transitions of the particle from \( |k\rangle \) to \( |k\rangle \) via the bound state \( |b\rangle \).

![Feynman diagrams for the 2-loop terms for \( \Sigma_{kk} \): (a) nested (or rainbow), (b) overlap, and (c) loop-after-loop.](image)

Figure 2.6: Feynman diagrams for the 2-loop terms for \( \Sigma_{kk} \): (a) nested (or rainbow), (b) overlap, and (c) loop-after-loop.

Let us begin by introducing a parameter \( \epsilon \), the lowest vibrational frequency of the membrane, that scales as the inverse size of the membrane \( \epsilon \sim v_s/L \), where \( v_s \) is the
transverse speed of sound in graphene membrane and $L$ is the membrane size). We now calculate the $\epsilon$ dependence of the Feynman amplitudes in Fig. 2.6. This cutoff dependence is summarized in Table 1.1. The nested diagram contributes $\Sigma_{kk}^{(2a)}$ to the atom self-energy

$$
\Sigma_{kk}^{(2a)} = \sum_{q} \sum_{q'} g_{kk} g_{bb}^2 G_{bb}^{(0)}(E - \omega) G_{bb}^{(0)}(E - \omega - \omega') G_{bb}^{(0)}(E - \omega)
$$

$$
\times D(q, \omega) D(q', \omega')
$$

$$
= \sum_{q} \sum_{q'} \frac{g_{kk} g_{bb}^2}{(E + E_b - \omega_q + i\eta)^2 (E + E_b - \omega_{q'} + i\eta)^2}
$$

In the quasicontinuum approximation, we evaluate the double integral and find that the real part diverges as a result of the double pole at $\omega = E + E_b$ and the imaginary part suffers from a linear divergence as $\epsilon \to 0$. Detailed calculations for the self-energies are given in the Appendix Sec. A.1.
Similarly, one can derive analytical expressions for the overlap diagram

\[
\Sigma_{kk}^{(2b)} = i^2 \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \sum_q \sum_{q'} g_{kk}^2 g_{bb}^2 G_{bb}^{(0)}(E - \omega)G_{bb}^{(0)}(E - \omega - \omega')G_{bb}^{(0)}(E - \omega') \\
	imes D(q, \omega)D(q', \omega') \\
= \sum_q \sum_{q'} \frac{g_{kk}^2 g_{bb}^2}{(E + E_b - \omega_q + i\eta)(E + E_b - \omega_q - \omega_{q'} + i\eta)(E + E_b - \omega_{q'} + i\eta)}.
\]

(2.24)

In the quasicontinuum approximation, this integral contains a logarithmic divergence for both the real and imaginary parts from low-frequency phonons (\(\epsilon \to 0\)).

In Table 1.1, we specify the \(\epsilon\) dependence from most divergent terms contained in the three 2-phonon diagrams. While the loop-after-loop diagram is finite, we find that the 2-loop nested and overlap diagrams contain contributions that tend to diverge with increasing membrane size (Fig. 2.7). Hence, the loop expansion becomes unreliable for suitably large membranes. According to the Kinoshita-Lee-Nauenberg theorem [79, 86], we know that infrared divergences are specious and are not contained in the true physical adsorption rate as \(\epsilon \to 0\). Thus, approximations to the adsorption rate obtained by truncation of this (divergent) perturbation expansion must be carefully scrutinized for large membranes.

We summarize our current understanding of the problem:
2.5 Resummation Techniques

Given the above structure of perturbation theory, it is clear that in the infrared limit \((E + E_b)/\epsilon \gg 1\), resummation of the series has to be performed. This leads us to set-up our non-perturbative methods which are tantamount to summations over particular classes of diagrams. These schemes take into consideration the strong coupling to low-energy phonons and eliminate the infrared singularities which is equivalent to
summing over contributions corresponding to multiphonon emission.

To investigate the effects of the multiphonon emission on the adsorption rates, we consider three non-perturbative methods: (1) the independent boson model approximation (IBMA), (2) the non-crossing approximation (NCA), and (3) a leading-order soft phonon resummation method (SPR). In the IBMA, we replace in the diagrammatic expansion of the atom self-energy the Green function for the bound atom by the exact IBM Green function. This approximation, equivalent to an infinite sum of diagrams containing the bound state atom-phonon vertices, includes multiphonon contributions to the atom self-energy.

In our second method, we use the non-crossing approximation (NCA) to calculate the atom self-energy. This is equivalent to an infinite sum of 'rainbow' diagrams and also includes multiphonon contributions to the self-energy. We iterate numerically the NCA nonlinear integral equation for the atom self-energy until self-consistency is achieved.

In the third method, we include the interaction of the phonons with the bound atom in the unperturbed Hamiltonian, while the remaining atom-phonon interaction is treated perturbatively. We sum over all emitted phonon states the dominant contributions to the sticking rate in the large membrane regime.

2.5.1 Independent Boson Model Approximation (IBMA)

Our model can be viewed as a generalization of the IBM with two coupling constants $g_{kb}$ and $g_{bb}$. Since, we are in the energy regime $g_{kb}^2 \rho_0 \gg g_{bb}^2 \rho_0$, we aim to derive an exact
solution in the stronger channel ($|b\rangle$) compared to the continuum ($|k\rangle$) which we thus treat perturbatively. An exact solution for the stronger channel with atom-phonon coupling $g_{bb}$ is derived in terms of the IBM. We begin with the IBM Hamiltonian which is basically a subset of our model Hamiltonian but only considers the interaction of the particle of energy $-E_b$ with a set of phonons with energy $\omega_q$:

$$H = -E_b b^\dagger b + \sum_q \omega_q (a_q + a_q^\dagger) - g_{bb} b^\dagger b \sum_q (a_q + a_q^\dagger)$$  \hspace{1cm} (2.25)$$

The exact solution of the IBM Hamiltonian is written as: [102]

$$G_{bb}(t) = -ie^{-it(-E_b-\Delta)}e^{-\phi(t)}$$  \hspace{1cm} (2.26)$$

where, $\phi(t) = \sum_q g_{bb}^2 (1 - e^{-i\omega_q t})/\omega_q^2$ and the self-energy $\Delta$ for $T = 0$ is given as[102],

$$\Delta = \sum_q \frac{g_{bb}^2}{\omega_q} = \int_{\epsilon}^{\omega_D} \frac{g_{bb}^2 \rho_0}{\omega} d\omega$$  \hspace{1cm} (2.27)$$

In the continuum limit, we re-write Eq. 2.26 as:

$$G_{bb}(t) = -i \exp[it(E_b + \Delta)] \exp \left[ -ig_b \int_{\epsilon}^{\omega_D} \left( \frac{d\omega \sin(\omega t)}{\omega^2} \right) \frac{1 - \cos(\omega t)}{\omega^2} \right]$$  \hspace{1cm} (2.28)$$

where, we have used $g_{bb}^2 \rho_0 = g_b$. The Fourier transform of $G_{bb}(t)$ is given as,

$$G_{bb}(E + E_b) = -i \int_0^\infty \left[ e^{it(E_b + E + \Delta)} \exp \left( -ig_b \int_{\epsilon}^{\omega_D} \frac{d\omega \sin(\omega t)}{\omega^2} \right) \frac{1 - \cos(\omega t)}{\omega^2} \right] dt$$  \hspace{1cm} (2.29)$$
Therefore, the imaginary and the real parts of the IBM propagator are given as:

\[
\text{Im}G_{bb}(E_s) = -\int_0^\infty dt \left[ \cos \left( E_s + g_b \int_\epsilon^\omega d\omega \frac{1 - \sin(\omega t)}{\omega^2} \right) \right] \\
\times \exp \left[ -g_b \int_\epsilon^\omega \frac{d\omega (1 - \cos(\omega t))}{\omega^2} \right]
\]

(2.30)

\[
\text{Re}G_{bb}(E_s) = \int_0^\infty dt \left[ \sin \left( E_s + g_b \int_\epsilon^\omega d\omega \frac{1 - \sin(\omega t)}{\omega^2} \right) \right] \\
\times \exp \left[ -g_b \int_\epsilon^\omega \frac{d\omega (1 - \cos(\omega t))}{\omega^2} \right]
\]

(2.31)

where, we have defined \( E_s = E + E_b \). The above integrals are solved numerically and give convergent finite solutions for both the real and imaginary parts for the propagator \( G_{bb}(E_s) \) in the infrared limit \( \epsilon \to 0 \). Fig. 2.8 shows the imaginary and the real parts of the propagator. There are noteworthy features in the propagator for IBM:

- Absence of a \( \delta \)-function corresponding to the pole at the mass shell (-\( E_b \) in this case).

- The density of states is related to the imaginary part of the propagator. A broadened \( \text{Im} G_{bb}(E_s) \) indicates a broadened density of states with a finite width. This is a result of the interaction with phonons.

Armed with our knowledge of the resummed IBM propagator, we proceed to calculate the renormalized atom self-energy \( \Sigma_{kk} \) under the IBMA. Here, we replace the bare bound state propagator \( G_{bb}(E - \omega) \) in Fig. 3.3 by the dressed propagator derived in the IBM. Owing to the relative strength of couplings, the infrared behavior
produced by higher order processes in $g_{kb}$ will be small and thus can be neglected. Hence, we can restrict our calculations for the renormalized self-energy $\Sigma^{IBM}_{kk}$ at the first loop which would contain all orders in the strong coupling $g_{bb}^2 \rho_0$ but only to the lowest order in $g_{kb}^2 \rho_0$. The imaginary part of the atom self-energy is evaluated by numerically integrating the following expression:

$$\text{Im}\Sigma^{IBM}_{kk}(E) = g_{kb}^2 \rho_0 \int_{\epsilon}^{\omega_D} \text{Im}G^{IBM}_{bb}(E_s - \omega)d\omega$$  \hspace{1cm} (2.32)$$

where, we have used the renormalized $G_{bb}(E_s)$ (as given in Eq. 2.30). Once again, the integral is well-behaved and devoid of divergences in the infrared limit $\epsilon \to 0$. 

Figure 2.8: The real and imaginary parts of scaled IBM Green function $g_b G^{IBM}_{bb}(E_s/g_b)$ vs $E_s/g_b$ for $\epsilon = 0$. $G^{IBM}_{bb}(E_s/g_b)$ is a smooth, complex-valued function in the limit $\epsilon \to 0$. 

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Plugging Eq. 2.32 in Eq. 2.20, we derive the transition rate under the IBMA. In our next subsection, we discuss our second resummation technique which involves summation of all the rainbow diagrams.

## 2.5.2 Non-Crossing Approximation (NCA)

In addition to the IBMA, we study another resummation technique that corresponds to the summation of all rainbow diagrams— the non-crossing approximation (NCA). The reason behind using NCA is twofold: firstly, for the zero temperature case, we see that the leading order divergence is rooted in the rainbow (nested) diagram. Hence, we aim to sum all the rainbow diagrams to infinite order with the motive of curing the leading-order divergent contributions. Also, the NCA is a resummation technique which is well suited to account for strong divergences. Secondly, there are successful applications of the NCA in the other fields of many-body physics such as the Anderson impurity problem [69, 117], quantum dot transport [152], and role of phonon interactions in the Anderson-Holstein model, in a quantum antiferromagnet and in Holstein-Hubbard model [27, 76, 151].

We consider the summation of the rainbow diagrams corresponding to two physical situations: the first one represents virtual phonon processes by a bound atom (see Fig. 2.9), while the second corresponds to virtual phonon processes under atomic transition (see Fig. 3.7).

We start by deriving an analytical expression for the self-energy in the bound states ($\Sigma_{bb}$) given by Fig. 2.9:

$$
\Sigma_{bb}(E) = ig_{bb}^2 \rho_0 \int \frac{d\omega}{2\pi} D(\omega) G_{bb}(E - \omega),
$$

(2.33)
where, the dressed bound state propagator $G_{bb}(E - \omega)$ is given as:

$$G_{bb}(E - \omega) = \frac{1}{E - \omega + E_b - \Sigma_{bb}(E - \omega)}, \quad (2.34)$$

Plugging in the phonon propagator and Eq. 2.34 in Eq. 2.33, we get the expression for the non-linear integral equation for $\Sigma_{bb}$:

$$\Sigma_{bb}(E) = \sum_q \frac{g_{bb}^2}{E + E_b - \omega_q - \Sigma_{bb}(E - \omega_q)}, \quad (2.35)$$

The above equation is solved self-consistently until convergence (details of numerical code is given in Appendix Sec. A.4). Similar to the IBMA, the solution for $\Sigma_{bb}(E)$ under the NCA is also found out to be finite in the infrared limit, implying a removal of the infrared divergences.

Diagrammatically one can approximate the atom self-energy $\Sigma_{\text{NCA}}^{kk}(E)$ in terms of the $\Sigma_{\text{NCA}}^{bb}(E)$ as:

$$\Sigma_{\text{NCA}}^{kk}(E) = \frac{g_{bb}^2}{g_{bb}^2} \Sigma_{\text{NCA}}^{bb}(E), \quad (2.36)$$

Following Eq. 2.20, we rewrite the adsoprtion rate under the NCA as:

$$\Gamma = -2Z(E_k)Im\Sigma_{\text{NCA}}^{kk}(E_k) = -2Z(E_k) \frac{g_{bb}^2}{g_{bb}^2} \Sigma_{\text{NCA}}^{bb}(E_k). \quad (2.37)$$
Since $\Sigma_{bb}^{NCA}(E)$ is infrared finite, we clearly see that the adsorption rate of the atom on the elastic membrane corresponding to the physical situation representing transitions via the bound states is also finite in the thermodynamic limit.

Next, we investigate the physical situation related to the transitions involving both bound $|b\rangle$ and continuum states $|k\rangle$ states. As mentioned previously, the Feynman diagram corresponding to this case is shown in Fig. 3.7.

![Figure 2.10: Diagrams in the NCA. Evaluation of these diagrams results in a set of coupled nonlinear integral equations that may be solved self-consistently. This is equivalent to a sum of all diagrams with no phonon lines crossing.](image)

Following the Feynman rules, we derive an analytical expression for the diagram:

$$\Sigma_{bb}(E) = \sum_q \frac{g_{bb}^2}{E + E_b - \omega_q - \Sigma_{bb}(E - \omega_q)} + \sum_q \frac{g_{kb}^2}{E - E_k - \omega_q - \Sigma_{kk}(E - \omega_q)},$$

$$\Sigma_{kk}(E) = \sum_q \frac{g_{kb}^2}{E + E_b - \omega_q - \Sigma_{bb}(E - \omega_q)}.$$ (2.38)

Once again, we solve the above set of coupled nonlinear integral equations self-consistently until convergence. The numerical solution to the atom self-energy $\Sigma_{kk}$ (from Eq. A.30) was also found out to be infrared finite. Following Eq. 2.7, we derive the adsorption rate under this approximation.

Before we introduce our third resummation technique in the next subsection, let
us compare the atom self-energy $\Sigma_{kk}$ derived from the three methods: (1) the loop expansion of the atom self-energy, (2) the non-crossing approximation (NCA), (3) the independent boson model approximation (IBMA). As seen from the Fig. 2.11, the resummed self-energies are infrared finite and are within reasonable agreement with each other.

![Figure 2.11](image)

**Figure 2.11:** Left panel: Real part of the atom self-energy $\text{Re}\Sigma_{kk}(E)$ vs energy $E$. Results are plotted for $\epsilon = 0, g_{k0}^2 \rho_0 = 0.7 \mu\text{eV}$ using three different approximation methods: one-loop self-energy $\Sigma_{kk}^{(1)}$, NCA, and IBMA. Right panel: Imaginary part of the atom self-energy $\text{Im}\Sigma_{kk}(E)$ vs energy $E$. The sticking rate is obtained from self-energy using Eq. 2.7. Signatures of many-body interaction effects are visible in the plots. The real part of the atom self-energy under IBMA and NCA are shifted slightly from the 1-loop result, which we think is caused by the polaron shift ($\Delta$) due to the interaction of the atom with many phonons.
2.5.3 Soft-Phonon Resummation (SPR)

We can calculate the transition rate when the bound atom interaction is included in unperturbed Hamiltonian. The phonon vacuum state is now different from previous partitioning.

We begin by splitting the Hamiltonian in a different way and incorporate the bath atom-phonon coupling term $-g_{bb}b^\dagger b \sum_q (a_q + a_q^\dagger)$ in the unperturbed Hamiltonian $H_0$. The Hamiltonian is written as:

$$H_0 = E_k c_k^\dagger c_k - E_{bb}^\dagger b + \sum_q \omega_q a_q^\dagger a_q - g_{bb}b^\dagger b \sum_n (a_n^\dagger + a_n)$$

$$H_I = -g_{bb}(c_k^\dagger b + b^\dagger c_k) \sum_q (a_q^\dagger + a_q)$$

We solve the above Hamiltonian (Eq. 2.39) by a canonical transformation: $\tilde{H}_0 = e^sH_0e^{-s}$, where $s = -g_{bb}b^\dagger b \sum_q (a_q^\dagger - a_q)/\omega_q$. The transformation is applied to each operator separately. We will use the Baker-Hausdorff lemma [102], $\tilde{A} = e^sAe^{-s} = A + [s, A] + (1/2!)[s, [s, A]] + \cdots$ to evaluate the new operators:

$$\tilde{a}_q = e^s a_q e^{-s} = a_q + \frac{g_{bb}}{\omega_q} b^\dagger b$$

$$\tilde{a}_q^\dagger = e^s a_q^\dagger e^{-s} = a_q^\dagger + \frac{g_{bb}}{\omega_q} b^\dagger b$$

In the above derivation, we have used $[s, a_q] = (g_{bb}/\omega_q)b^\dagger b$.

We see that under the transformation, the previous oscillator operators undergo a shift by an amount $(g_{bb}/\omega_q)b^\dagger b$. This shift physically corresponds to the polarization in the surface caused by the presence of the adatom. Using the shifted oscillator
operators given by Eqs. 2.41 and 2.42, we derive the Hamiltonian in the normal form:

\[ \tilde{H}_0 = E_k c_k^\dagger c_k - E_b b^\dagger b - g_{bb} b^\dagger b \sum_q \left( a_q + a_q^\dagger + \frac{2g_{bb}}{\omega_q} \right) + \sum_q \omega_q \left( a_q^\dagger + \frac{g_{bb} b^\dagger b}{\omega_q} \right) \left( a_q + \frac{g_{bb} b^\dagger b}{\omega_q} \right) \]

\[ = E_k c_k^\dagger c_k - (E_b + \Delta) b^\dagger b + \sum_q \omega_q a_q^\dagger a_q \]

(2.43)

where, \( \Delta = \sum_q g_{bb}^2 / \omega_q \). The ground state energy of \( \tilde{H}_0 \) in the 1-atom sector is \( E_g = -(E_b + \Delta) \) and the final state has energy \( E_f = -(E_b + \Delta) + \omega_q \). Corresponding eigenstate of \( H_0 \) for final state energy \( E_f \) is:

\[ |f\rangle = \exp(s)|0, 1, 1_q\rangle = \exp \left( \sum_q \frac{g_{bb}}{\omega_q} (a_q^\dagger - a_q) \right) |0, 1, 1_q\rangle \]

(2.44)

where, we have used the following definitions: the unperturbed Hamiltonian \( H_0 \) has eigenstates \( |n_k; n_b; n_q\rangle \) with \( n_k \) and \( n_b \) denoting the respective number of atoms in the continuum \( |k\rangle \) and bound \( |b\rangle \) states. The number of phonons in each vibrational mode is given as \( n_q \).

We will use this new final state \( |f\rangle \) which is a result of the shift in the oscillator operator to derive the atom transition rate (\( \Gamma \)).
Shifted Oscillator Method

We will first derive the transition rate that corresponds to a 1-phonon exchange process. This leads us to use the golden rule given by Eq. (2.20):

\[
\Gamma_1 = 2\pi \sum_q |\langle 0, 1, 1_q | e^{s} H_I | 1, 0, 0 \rangle|^2 \delta (-E_b - \Delta + \omega_q - E_k) \\
= 2\pi \sum_q |\langle 0, 1, 1_q | e^{s} H_I e^{-s} | 1, 0, 0 \rangle|^2 \delta (-E_b - \Delta + \omega_q - E_k) \\
= 2\pi \sum_q |\langle 0, 1, 1_q | \tilde{H}_I | 1, 0, 0 \rangle|^2 \delta (-E_b - \Delta + \omega_q - E_k)
\]

Under the canonical transformation we re-write the Hamiltonian of interaction \( H_I \) as:

\[
\tilde{H}_I = -g_{bb}(\tilde{b}^\dagger c + c^\dagger \tilde{b}) \sum_q (\tilde{a}_q + \tilde{a}_q^\dagger)
\]

where, \( \tilde{b} \) is given as:

\[
\tilde{b} = e^{s} b e^{-s} = (1 + s + \cdots) b (1 - s + \cdots)
\]

\[
= b + [s, b] + \frac{1}{2} [s, [s, b]] + \cdots
\]

\[
= b \left( 1 + \sum_q \frac{g_{bb}}{\omega_q} (a_q^\dagger - a_q) + \cdots \right)
\]

\[
= bX
\]

Here, we have used the commutator relation:

\[
[s, b] = \sum_q \frac{g_{bb}}{\omega_q} (a_q^\dagger - a_q) b
\]
The displacement operator $X$ is also introduced:

$$X = \exp \left( \sum_q \frac{g_{bb}}{\omega_q} (a_q^\dagger - a_q) \right)$$  (2.49)

Plugging Eq. 2.47 in Eq. 2.46, we have,

$$\tilde{H}_I = -g_{kb}(c^\dagger b X + X^\dagger b^\dagger c) \sum_q \left( a_q + a_q^\dagger + \frac{2g_{bb}}{\omega_q} b^\dagger b \right)$$  (2.50)

The matrix element to be evaluated in Eq. 2.45 is given as:

$$\langle 0, 1, 1_q | \tilde{H}_I | 1, 0, 0 \rangle = -g_{kb} \langle 1_q | X^\dagger \sum_q a_q^\dagger | 0 \rangle$$  (2.51)

with $X^\dagger$ written as:

$$X^\dagger = \exp \left( \sum_q \frac{g_{bb}}{\omega_q} a_q^\dagger \right) \exp \left( \sum_q \frac{g_{bb}}{\omega_q} a_q \right) \exp \left( -\frac{g_{bb}^2}{2} \sum_q \frac{1}{\omega_q^2} \right)$$  (2.52)

Next we calculate the matrix element for the phonon part:

$$\langle 1_q | X^\dagger \sum_q a_q^\dagger | 0 \rangle = e^{-\alpha} \sum_m \langle 1_q | \exp \left( -\sum_p \frac{g_{bb}}{\omega_p} a_p^\dagger \right) \exp \left( -\sum_p \frac{g_{bb}}{\omega_p} a_p \right) a_m^\dagger | 0 \rangle$$

$$= e^{-\alpha} \sum_m \langle 1_q | \exp \left( \sum_p \frac{g_{bb}}{\omega_p} a_p^\dagger \right) (a_m^\dagger + \frac{g_{bb}}{\omega_m}) | 0 \rangle$$  (2.53)

where,

$$\alpha = \frac{g_{bb}^2}{2} \sum_q \frac{1}{\omega_q^2} = \frac{g_{bb}^2 \rho_0}{2e}$$  (2.54)

52
$\epsilon$ being the relevant lower cut-off. On further simplification the phonon matrix element reduces to:

$$
\langle 1_q | X^\dagger \sum_q a_{q}^\dagger | 0 \rangle = e^{-\alpha} \sum_m \left[ \frac{g_{bb}}{\omega_m} \left( - \frac{g_{bb}}{\omega_q} \right) + \delta_{mq} \right]
$$

Using above equations, the final matrix element is given as:

$$
\langle 0, 1, 1_q | \tilde{H}_I | 1, 0, 0 \rangle = -g_{bb} e^{-\alpha} \left[ 1 - \frac{g_{bb}^2}{\omega_q} \sum_m \frac{1}{\omega_m} \right]
$$

Substituting Eq. 2.56 in Eq. 2.45, we find out the 1-phonon transition rate ($\Gamma_1$):

$$
\Gamma_1 = 2\pi \sum_q g_{bb}^2 e^{-2\alpha} \left( 1 - \frac{g_{bb}^2}{\omega_q} \sum_m \frac{1}{\omega_m} \right)^2 \delta(\omega_q - E_b - \Delta - E_k)
$$

In the continuum limit, Eq. 2.57 takes on the form:

$$
\Gamma_1 = 2\pi g_{bb}^2 e^{-2\alpha} \rho_0 \left( 1 - \frac{g_{bb}^2}{E_b + E_k + \Delta} \sum_m \frac{1}{\omega_m} \right)^2
$$

From the above expression, one can clearly see that the 1-phonon transition rate is exponentially small ($\sim e^{-2\alpha}$) and tends to 0 as $\epsilon \to 0$.

Next, we calculate the 2-phonon transition rate which involves a final state $|f\rangle = e^s|0; 1; 1_p, 1_q\rangle$. The transition rate for a 2-phonon process is written as:

$$
\Gamma_2 = 2\pi \sum_{p,q} |\langle 0; 1; 1_p, 1_q | e^s H_I | 1, 0, 0 \rangle|^2 \delta(-E_b - \Delta + \omega_p + \omega_q - E_k) = 2\pi \sum_{p,q} |M_{pq}|^2 \delta(-E_b - \Delta + \omega_p + \omega_q - E_k)
$$
Following a calculation which is similar to the 1-phonon process, we evaluate the matrix element $M_{pq}$ as:

$$M_{pq} = 2e^{-\alpha}g_{kb}\left(\frac{g_{bb}}{\omega_p}\right)\left[1 - \frac{1}{\omega_q}g_{bb}^2\sum_m \frac{1}{\omega_m}\right]$$

(2.60)

In the continuum limit, combining Eq. 2.59 & Eq. 2.60, we derive the 2-phonon transition rate $\Gamma_2$:

$$\Gamma_2 = 2\pi g_{kb}^2\rho_0 e^{-2\alpha}\left(\frac{g_{bb}\rho_0}{\epsilon}\right)^2\left[1 - \frac{g_{bb}^2}{E_k + E_b + \Delta \sum_m \frac{1}{\omega_m}}\right]^2$$

(2.61)

Once again, the 2-phonon transition rate $\to 0$ in the infrared limit owing to the presence of the exponentially small factor $(e^{-2\alpha})$.

In a similar way, we calculate the 3-phonon transition rate $\Gamma_3$:

$$\Gamma_3 = 2\pi g_{kb}^2\left(\frac{e^{-2\alpha}}{2!}\right)^2\left(\frac{\rho_0 g_{bb}}{\epsilon}\right)^2\left[1 - \frac{g_{bb}^2}{E_k + E_b + \Delta \sum_m \frac{1}{\omega_m}}\right]^2$$

(2.62)

Using a recursion relation, we derive the transition rate $\Gamma_n$ for n-phonon process, such that:

$$\Gamma_n = 2\pi g_{kb}^2\rho_0\left(\frac{\rho_0 g_{bb}}{\epsilon}\right)^{n-1}\left[1 - \frac{g_{bb}^2}{E_k + E_b + \Delta \sum_n \frac{1}{\omega_n}}\right]^2$$

(2.63)

Thus, one can clearly see that as $\epsilon \to 0$, $\Gamma_n \to 0$. This exponentially small factor $e(-g_{bb}\rho_0/\epsilon)$ is a result of the shift of the phonon vacuum and hence is absent in our previous calculations that starts off from a different basis in the unperturbed Hamiltonian.

Although the individual transition rates ($\Gamma_1$, $\Gamma_2$, ···, $\Gamma_n$) are exponentially small,
the total transition rate \( \Gamma^{\text{SOA}} \) of the atom from \( |k\rangle \rightarrow |b\rangle \) via the exchange of infinite number of ZA phonons will be given by the sum of all the transition rates \( \Gamma_1, \Gamma_2, \Gamma_3, \) and so on.

\[
\Gamma^{\text{SOA}} = \Gamma_1 + \Gamma_2 + \Gamma_3 + \cdots
\]

\[
= 2\pi g_{kk}^2 \rho_0 e^{-2\alpha} \left[ 1 - \frac{g_{bb}^2}{E_k + E_b + \Delta} \sum_n \frac{1}{\omega_n} \right]^2 \left[ 1 + \left( \frac{\rho_0 g_{bb}^2}{\epsilon} \right) + \frac{1}{2} \left( \frac{\rho_0 g_{bb}^2}{\epsilon} \right)^2 + \cdots \right] \]

\[
= 2\pi g_{kk}^2 \rho_0 \left[ 1 - \frac{g_{bb}^2}{E_k + E_b + \Delta} \sum_n \frac{1}{\omega_n} \right]^2
\]

(2.64)

where, we have used the series expansion:

\[
e^{2\alpha} = \exp \left( g_{bb}^2 \sum_n \frac{1}{\omega_n^2} \right) = \left[ 1 + \left( \frac{\rho_0 g_{bb}^2}{\epsilon} \right) + \frac{1}{2} \left( \frac{\rho_0 g_{bb}^2}{\epsilon} \right)^2 + \cdots \right]
\]

(2.65)

Thus, from Eq. 2.64, we see that the sum over all the n phonon states leads to a result which is not exponentially small but amounts to a finite result.

In quantum electrodynamics, a similar situation is encountered where the cross section of scattering vanishes for the emission of a finite number of soft photons in collisions (Bremsstrahlung process). This is attributed to the statistically independent nature of the photon emission which is well represented by the Poisson’s distribution \( w(\bar{n}) \) that appears in the scattering cross-section for the charged particle. However the inclusion of emission of infinite number of soft photons results in a finite scattering cross-section.[10]

In a similar way, for our model, as \( \epsilon \rightarrow 0 \), a non-vanishing adsorption rate results only with the emission of an infinite number of phonons. We further note that
multiphonon rate differs from the simplest golden rule estimate \( \Gamma_0 \) by a fractional factor \( \mathcal{R} = (1 + \frac{\Delta}{\hbar \omega})^{-2} \) which depends logarithmically on the IR cutoff \( \epsilon \). We observe that all adsorption rate \( \Gamma \), are finite (specifically, tending to zero) in the infrared limit \( \epsilon \to 0 \) in accord with the KLN theorem [79, 86].

Let us summarize our final understanding of the problem, before we apply our methods to predict results for a physical system of hydrogen atom impinging on graphene membrane.

- **Statement of the problem:** What is the effect of the graphene ZA phonons on adsorption rate of ultracold atoms?
- **Methodology to answer the above question:** Calculate the atom self-energy based on perturbative Green’s function formalism.
- **Preliminary result & new problem:** Higher order contributions to atom self-energies suffer from severe infrared divergences. How does one tame these infinities to obtain physical rates?
- **Mathematical techniques to answer new question:** Non-perturbative methods tantamount to summing infinite orders of Feynman diagrams.
- **Final question to the problem:** Did the resummation techniques work? To answer this, let’s test it on a physical model.
2.6 Test of Resummation Techniques

In this section, we will apply the adsorption rate derived within the IBMA, NCA and SPR to the physical model of cold atomic Hydrogen impinging on graphene micromembranes. This essentially will test the validity of all our techniques.

2.6.1 Adsorption Of Atomic Hydrogen on Graphene

Figure 2.12: Dependence of the (normalized) adsorption rate $\Gamma/\Gamma_0$ with IR cutoff $\epsilon$ (left panel). The two-loop approximation to $\Gamma$ diverges as $\epsilon \to 0$. Under NCA and IBMA, $\Gamma/\Gamma_0$ converges to a constant in this limit (right panel). In SPR, $\Gamma/\Gamma_0$ behaves asymptotically as $\ln^{-2}(\omega_D/\epsilon)$ as $\epsilon \to 0$.

We take the following for the numerical values of the parameters for the model of atomic hydrogen impinging on graphene membranes maintained at zero temperature, we plot the adsorption rates derived in the three techniques in Fig. 2.12. Here, we have considered the following numerical specifications: physisorption well $E_b = 40$ meV.
Figure 2.13: Top panel: Normalized adsorption rate $\Gamma/\Gamma_0$ from the SPR method vs $E_s$ for various membrane sizes ranging 100 nm to 10 µm. Bottom panel: Normalized adsorption rate $\Gamma/\Gamma_0$ from SPR, IBMA and NCA vs $E_s$ for a 1 µm micromembrane. For shallow bound states, the SPR result shows appreciable suppression in adsorption relative to the other methods. However, for deep bound states, the three methods (IBMA, NCA and SPR) give adsorption rates that are in good agreement with each other.

meV, $g_{bb}\rho_0 = 60 \, \mu eV$, $g_{bb} \propto \sqrt{E}$, $g_{bb}\rho_0 = 0.5 - 10 \mu eV$, $\omega_D = 65 \, meV$ and the transverse speed of sound in graphene $v_s = 6.64 \times 10^3 \, m/s$. To test the validity of our resummation techniques, we consider micromembranes whose size ranges from 100 nm to 10 µm. [30, 90]
We compare the numerical results of the adsorption rate obtained by: (1) the loop expansion of the atom self-energy, (2) the non-crossing approximation (NCA), (3) the independent boson model approximation (IBMA), and (4) a leading-order soft-phonon resummation method (SPR). While the one-loop sticking rate gives a result that in the regime of interest is tantamount to the result from the Fermi’s golden rule, the two-loop adsorption rate diverges linearly with increasing membrane size (or equivalently, with vanishing IR cutoff $\epsilon \to 0$). This divergence is seen in the left panel of Fig. 2.12. We conclude that the approximations based on truncation of the loop expansion break down for sufficiently large membranes.

As anticipated, the IBMA sticking rate is slightly less than the golden rule rate $\Gamma_0$ over the range of IR cutoff $\epsilon$ considered (see right panel of Fig. 2.12). The reduction in adsorption under IBMA is a result of the smearing of the bound atom density of states through the interaction with the phonons. In contrast to the two-loop result, the IBMA rate remains finite in the limit of vanishing IR cutoff $\epsilon \to 0$. Therefore, the adsorption in the IBMA which includes the spontaneous emission of an arbitrary number of phonons remedies the infrared problem in the loop expansion.

The NCA sticking rate is also suppressed relative to $\Gamma_0$ and is also consistently lower than the IBMA sticking rate over the range of parameters used (see the right panel of Fig. 2.12). The NCA further broadens the bound atom density of states through the inclusion of virtual transitions of the atom back to the continuum. This further depresses the sticking rate in comparison to the IBMA. We note that the NCA also gives a finite rate as $\epsilon \to 0$.

Lastly, we plot the sticking rate under the SPR method in Fig. 2.12 for comparative purposes. We note that over the parameter range for micromembranes, the SPR
sticking rate lies in between the IBMA and NCA rate. Thus, there is good agreement with the three methods for micromembranes; however, the \( \epsilon \) behavior of the SPR rate differs from both the NCA and IBMA rate. A comparison with SPR results shows that the methods agree to within 3\% of each other for micromembranes. For sufficiently large membranes, IBMA and NCA give a finite rate, while SPR gives a rate that vanishes as \( \ln^{-2} \omega_D/\epsilon \) for \( \epsilon \to 0 \).

2.7 Summary

In summary, we have discussed the dynamics of interactions of cold atoms with 2D elastic membrane. We have encountered failure of conventional perturbation theory due to the emission of infinitely many low-frequency ZA phonons (soft-phonons) which leads to an infrared catastrophe. This infrared catastrophe is similar in spirit to the infrared problem encountered in quantum electrodynamics where the divergence is traced back to the emission of multiple low-energy massless photons. It was previously recognized that there are similarities between the adsorption process and radiative capture[33]. Our work highlights the fact that quantum adsorption is a non-relativistic, condensed matter analogue of QED. We essentially study in this work the phonon analogue to radiative corrections in scattering.

In QED, a solution of the infrared problem is perceived through the Bloch-Nordsieck (BN) model [14, 105] which leads to an analytic solution that cancels the infinities in the infrared regime. In our work, we remedy this infrared catastrophe by considering resummation techniques, similar in nature to the BN scheme. These techniques (IBMA and NCA) involve Green’s function formalism and provide
with a resummation of the leading order divergent contributions/diagrams in the perturbative series. The resulting renormalized self-energy captures the effects of the multiphonon emission and shows significantly different result than the conventional perturbation theory. Employing the technique of Green functions, we have devised two approximation schemes, one of which uses the exact analytical solution of the Independent Boson Model (IBM) and the other engages the self-consistent method of NCA- consistent with summing the infinite orders of rainbow diagrams.

We apply our techniques to study the adsorption of cold atomic hydrogen on 2-dimensional graphene membranes maintained at zero temperature. We investigate the effects of infrared cut-off ($\epsilon$), the bound state energy ($E_b$) on the adsorption rates. We also compare our results with another technique that uses canonical transformation (SPR). Not only do the methods cure the divergences, but also lead to adsorption rates that are different from the conventional perturbation theory. For micromembranes, the adsorption rate derived via all the methods are within 6% of each other and show about 2% variation in adsorption rate for a range of $1 \mu eV < \epsilon < 5 \mu eV$. For a fixed size of the membrane and for $13 \text{ meV} < E_b < 40 \text{ meV}$, the three methods give comparable adsorption rate. We have also predicted a region of validity of IBMA and NCA based on our calculations. We predict that our methods based on Green’s function formalism are best suited to tackle models with deep bound states and weak interactions in the atom-phonon couplings.

In our work, both the IBMA and NCA replace the bare bound atom Green function with a propagator that includes atom-phonon interactions. This dressed propagator leads to a broadened density of states for the bound atom and eliminates infrared divergences in the probability amplitudes. In the SPR method, the inclusion of the
interaction of the bound atom with the phonons in the unperturbed Hamiltonian leads to the use of a coherent state basis for the phonons in the evaluation of the sticking amplitudes. All three of these methods include the spontaneous emission of an arbitrary number of phonons.

Our numerical results for micromembranes show that the IBMA, NCA and SPR methods give results that are in good agreement with each other and yield sticking rates that are mildly suppressed relative to the lowest-order golden rule rate. All three methods produce results that are free of infrared divergences. However, the SPR sticking rate decreases slowly to zero with increasing membrane size, while both the NCA and IBMA rates tend to a nonzero constant as $\epsilon \to 0$. We conclude that approximations to the sticking rate can be sensitive to the effects of soft-phonon emission for large membranes and that cold atom adsorption on a membrane might be viewed as a finite-size effect.

In our next chapter, we extend our studies to a membrane at finite temperature and we will see that with the inclusion of thermal fluctuations, the infrared divergences are more severe. We will derive adsorption rates as a function of temperature for graphene micromembranes.
Chapter 3

Finite Temperature Formalism

In this chapter, we generalize the $T = 0$ to $T \neq 0$ in a straightforward way. As we will see, the finite temperature treatment of our model shows severe infrared divergences because of the emission of infinitely many soft thermal ZA phonons which is understood in terms of the phonon Bose factor. From a mathematical point of view, the thermal distribution of states for the phonons picks up the effects of temperature and hence exhibits damping effects. We will also see that the high temperature formalism of this model bears similarity to the finite temperature ‘hot’ QED and QCD plasmas.

3.1 Overview

The damping of excitations and quasiparticles in finite temperature QED and QCD plasma have been a topic of intense research [6, 12, 18, 75, 121, 133]. The perturbative calculation of damping suffers from severe infrared divergences in both the relevant field theories. Physically, these divergences are rooted in the collision of
long-wavelength quasistatic interactions of soft photons (QED) and soft magnetic gluons (QCD) which are not screened by plasma effects. In contrast to QED, the infrared problem in QCD is less severe because of the presence of gluon magnetic mass which acts as a natural infrared regulator. In principal, these infrared divergences are regulated by resummation techniques. In theoretical physics or mathematics, \textit{Resummation} is a procedure to obtain finite results from a divergent sum (series) of functions. In this chapter, we will discuss resummation techniques that are based on non-perturbative methods.

The seminal work on devising the resummation techniques for the infrared problem in QED was carried out by Bloch-Nordsieck (BN) in their paper on the radiation field of an electron [64]. They considered a non-perturbative treatment that remedied the infrared catastrophe in the interaction of charged particles with soft photons that relies on the exponentiation of infrared-divergent perturbation series. Extending the BN technique to finite temperature, a solution to the infrared problem in thermal QED and QCD has been realized by summing the leading order divergences [133, 150].

Quite remarkably, a non-relativistic, condensed matter analog of this infrared problem is discovered in a model of cold atom interacting with an elastic membrane (Fig. 3.1), which we refer to as the study of Quantum Acoustodynamics (QAD) which studies the interaction of cold atom with phonons. In this case, the damping of the quasiparticle (atom dressed by phonon interactions in the membrane) exhibits severe infrared divergences order by order in the perturbation theory because of the emission of infinitely many soft ZA phonons [31]. At zero temperature, we remedy this IR problem using three non-perturbative methods that include contributions from processes with multiphonon emission: a leading-order soft-phonon resummation
method (SPR) which uses a coherent state phonon basis for the final state [28], numerical techniques based on Non-Crossing Approximation (NCA) and Independent Boson Model Approximation (IBMA).

Figure 3.1: Collisions mediated by ripples of the interacting fields in different finite temperature quantum field theories: (a) Hot QCD: Damping rates of weakly coupled quark-gluon plasma display infrared divergence because of the exchange of long-range gluons. (b) Hot QED: Emission of infinitely many massless photons leads to severe infrared divergence observed in the scattering cross section of an electron in a radiation field. (c) Hot QAD: A neutral, spin polarized cold atom interacts with the ZA phonons in a quantum drum. The transition rate of the atom is seen to suffer from infrared divergence because of the exchange of infinitely many soft ZA phonons.

For the finite temperature formalism, we study the model of QAD in two different regimes: (i) \( T \ll \omega_D \) and (ii) \( T \gg \omega_D \) where \( \omega_D \) is the maximum Debye frequency of the membrane phonons. We will derive adsorption rates in these two regimes following: (i) first-order conventional perturbation theory- Fermi’s Golden rule and (ii) Feynman - Dyson diagrammatic perturbation theory. Similar to the zero temperature formalism, we will see that a closer examination of the diagrammatic perturbation series leads to terms that are infrared divergent. This leads us to treat the problem using resummation techniques that we have devised for our zero temperature formal-
ism. So, in this chapter, we extend the investigation of the resummed atom self-energy to the finite temperature regime. We start off with the detailed calculations related to the low temperature regime.

3.2 LOW TEMPERATURE REGIME

3.2.1 DAMPING IN PERTURBATION THEORY & INFRARED DIVERGENCES

We start this section by reminding ourselves about the features of the model Hamiltonian of Chapter 2. We derive the damping rate of the atom following conventional perturbation theory and proceed to recover the same via diagrammatic perturbation theory invoking Feynman rules.

Features of the model Hamiltonian

The model of QAD considers an impinging cold atom on a clamped graphene membrane maintained at finite temperature (as shown in Fig. 3.1c). The Hamiltonian is written as: \( H = H_0 + H_i \), where \( H_0 \) and \( H_i \) represent the unperturbed and interaction Hamiltonians. We start with \( H_0 \):

\[
H_0 = E_k c_k^\dagger c_k - E_b b^\dagger b + \sum_q \omega_q a_q^\dagger a_q \tag{3.1}
\]

Here, \( c_k (c_k^\dagger) \) annihilates (creates) a particle in the entrance channel \(|k\rangle\) with energy \( E_k \); \( b (b^\dagger) \) annihilates (creates) a particle in the bound state \(|b\rangle\) with energy \(-E_b\) in the
static potential. $a_q (a_q^\dagger)$ annihilates (creates) a ZA phonon in the phonon target bath with energy $\omega_q$. For a graphene membrane under a tension $\gamma$, the phonon dispersion is linear such that $\omega_q = v_s q$, with $v_s = \sqrt{\gamma/\sigma}$. Here, $\sigma$ is the mass density of the graphene membrane [31, 91, 108].

We write the interaction Hamiltonian as: $H_i = H_{bi} + H_{ki}$. The atom-phonon interaction in the continuum is given by $H_{ki}$:

$$H_{ki} = -g_{kb}(c_k^\dagger b + b^\dagger c_k) \sum_q (a_q + a_q^\dagger)$$  \hspace{1cm} (3.2)

with $g_{kb}$ being the corresponding atom-phonon coupling in the entrance channel. Similarly, for the bound channel, the Hamiltonian of interaction is:

$$H_{bi} = -g_{bb} b^\dagger b \sum_q (a_q + a_q^\dagger)$$  \hspace{1cm} (3.3)

here, $g_{bb}$ denotes the atom-phonon coupling for an atom bound to the membrane [31].

We begin our calculation for the damping rate $\Gamma$ of the atom using conventional first order perturbation theory given by Fermi’s Golden rule. Let us mention the energy regime for the low temperature formalism calculation:

$$g_{kb}^2 \rho_0 \ll g_{bb}^2 \rho_0 \ll T \ll E_b \ll \omega_D$$

where, $T$ and $\omega_D$ are the temperature and maximum Debye frequency of the graphene membrane.
Damping from Fermi’s Golden rule

We consider the atom-phonon interaction \( H_i \) as the perturbation. The unperturbed Hamiltonian \( H_0 \) has eigenstates \( |n_k; n_b; \{n_q\} \rangle \) with \( n_k \) and \( n_b \) denoting the respective number of atoms in the continuum \( |k\rangle \) and bound \( |b\rangle \) states. The number of phonons in each vibrational mode is given as \( \{n_q\} \). The initial eigenstate has only one atom in the continuum and the membrane has a thermal distribution of phonons initially with occupancies \( n_q = 1/\exp(\beta \omega_q) - 1 \) such that we can write: \( |i\rangle = |1, 0, \{n_q\}\rangle \). The final state acquires an atom in the bound state with the exchange of a phonon, thus \( |f\rangle = |0, 1, \{n_q\}_{q \neq p}, n_p + 1\rangle \). Following Fermi’s Golden rule, we write the damping rate as:

\[
\Gamma_0 = 2\pi \sum_{f, i} |\langle f | H_i | i \rangle|^2 \delta(E_f - E_i) p_i
\]

\[
= 2\pi \sum_{p, \{n_q\}} |\langle 0, 1, \{n_q\}_{q \neq p}, n_p + 1 | H_i | 1, 0, \{n_q\}\rangle|^2 \delta(E_k + E_b - \omega_p) p(\{n_q\})
\]

\[
= \frac{2\pi g_{bb}^2 \rho_0}{1 - \exp(-\beta E_s)}
\]

where we have used the identity \( a_q |n_q\rangle = \sqrt{n_q + 1} |n_q + 1\rangle \), \( E_s = E_k + E_b \) and \( \rho_0 \) is the partial phonon density of states for the circularly symmetric vibrational modes of the membrane (as defined in Chapter 2) and \( p_i \) is the probability of initial phonon distribution \( i \). Clearly, the damping rate \( (\Gamma_0) \) derived within first-order conventional perturbation theory is finite, independent of \( g_{bb} \) and is of order \( g_{bb}^2 \rho_0 \). It is worthwhile to check if we can recover the damping rate derived within Golden rule by any other technique. In the next subsection, we discuss the damping rate derived by the Feynman Dyson Perturbation theory.
Damping from Feynman Dyson Perturbation Theory

In Chapter 2, we discussed a basic technique to derive an expression of adsorption rate of cold atoms on graphene membranes based on the method of Green’s functions and a series expansion of the atom self-energy $\Sigma_{kk}(E)$. The damping/adsorption rate under the self-energy formalism is given as [58]:

$$\Gamma = -2Z\text{Im}\Sigma_{kk}(E)$$

which is valid in the quasiparticle regime and $\text{Im}\Sigma_{kk}$ gives the imaginary part of the atom self-energy and $Z$ is the renormalization factor related to the real part of the self-energy $\Sigma_{kk}$:

$$Z = \left[1 - \left(\frac{\partial\text{Re}\Sigma_{kk}(E)}{\partial E}\right)\right]^{-1}$$

Following the same methodology as discussed in Chapter 2, we will derive a series expansion of atom self-energy invoking Feynman rules and then use the atom self-energy to derive an expression of $\Gamma$ as given by Eq. 3.5. But first let us specify a main difference for the Feynman rules for the model at $T=0$ with the finite temperature case.

In the finite temperature case, we take the membrane to be initially in thermal equilibrium. For a membrane maintained at $T\neq 0$, there is no guarantee that the open system will return to its initial state for asymptotically large times. This is similar in essence to the situation in surface physics where adatoms exchange charge with the surface and the initial state at $t=\infty$ is very different from the final state at $t=-\infty$ [68]. Thus, the atom self-energy should be calculated using non-equilibrium Green functions, Keldysh or the contour-ordered Green functions. The Feynman rules
using the Keldysh formalism is summarized below for our model (Fig. 3.2):

- The solid dot corresponds to the interaction vertex $g_{kb}$

- The open dot corresponds to the interaction vertex $g_{bb}$

- Lines labeled by $b$ correspond to the bare Green function in the bound state $G_{bb}(E) = 1/(E + E_b + i\eta)$

- Lines labeled by $k$ correspond to the bare Green function of the atom in the continuum state $G_{kk}(E) = 1/(E - E_k + i\eta)$.

- Wiggly lines correspond to the phonon propagators and are given as:

  $D^<(\omega) = -2\pi i[(n_q + 1)\delta(\omega + \omega_q) + n_q\delta(\omega - \omega_q)]$ and $D^r(\omega) = 1/(\omega - \omega_q + i\delta) - 1/(\omega + \omega_q + i\delta)$. 

  Here, $n_q$ is the phonon occupation number with $n_q = 1/(e^{\beta\omega_q} - 1)$, and $\omega_q = v_s q$ is the dispersion (for graphene membrane under tension).

- Each diagram is weighted by $(i/\hbar)^n$, where $n$ is the number of phonon loops.
Finally we mention that the diagram technique constructed above is completely equivalent to simply working with the real-time finite temperature Green’s function for the phonons [97, 102]. Furthermore, it is clear that for the purposes of extracting the leading order terms, it is sufficient to use the small momentum/high temperature limit of the phonon propagator in the form \( D(\omega, q) = -2\pi i(T/\omega_q)[\delta(\omega + \omega_q) + \delta(\omega - \omega_q)] \).

Let us now calculate the perturbative expansion of atom self-energy \( \Sigma_{kk} \). We begin with the 1\(^{st}\) order term which is the 1-loop atom self-energy.

**1-loop Self-energy**

\[ \Sigma_{kk}(E) = \int \frac{d\omega}{2\pi} \sum_q g_{kk}^2 [G_{bb}(E)D^r(\omega) + G_{bb}^r(E)D^< (\omega) + G_{bb}^r(E)D^r(\omega)] \quad (3.7) \]

Here the incoming particle is out of equilibrium with the phonon bath such that, the
Green function $G^{<}_{bb}(E) = 0$, therefore we have:

$$\Sigma_{kk}^{(r)}(E) = i \int \frac{d\omega}{2\pi} \sum_q g^2_{kk} \left[ G^r_{bb}(E)D^{<}(\omega) + G^r_{bb}(E)D^r(\omega) \right]$$  \hspace{1cm} (3.8)

Plugging in the expressions for the Keldysh GFs in Eq. (3.8), we get the atom self-energy as:

$$\Sigma_{kk}^{(r)}(E) = g^2_{kk} \sum_q \left[ \frac{n_q}{E + E_b + \omega_q + i\eta} + \frac{n_q + 1}{E + E_b - \omega_q + i\eta} \right]$$  \hspace{1cm} (3.9)

In the limit of $T \to 0$, the above expression reduces to the atom self-energy to 1-loop for the zero temperature case and is given as:

$$\Sigma_{kk}^{(r)}(E) = g^2_{kk} \sum_q \left[ \frac{1}{E + E_b - \omega_q + i\eta} \right]$$  \hspace{1cm} (3.10)

Next, in the continuum limit, we analytically derive the real and the imaginary part of $\Sigma_{kk}^{(r)}$ for the high temperature case, such that $T \gg \Delta \omega$, therefore, $n_q \approx T/q$ (we choose units where $v_s = 1$ for convenience). Although we are in the low temperature regime for the atoms, it is sufficient to extract the leading order contribution considering a high temperature approximation for the phonons.

Therefore, the real and the imaginary parts are given as:

$$Re \Sigma_{kk}^{(r)}(E) = \frac{2g^2_{kk}\rho_0 T}{E + E_b} \log \left| \frac{E + E_b}{\epsilon} \right|, \quad \epsilon \ll E + E_b$$  \hspace{1cm} (3.11)

$$Im \Sigma_{kk}^{(r)}(E) = -\frac{\pi g^2_{kk}\rho_0 T}{E + E_b}$$  \hspace{1cm} (3.12)

Here $\epsilon$ is the infrared cutoff given by the minimum phonon frequency, $\epsilon \sim v_s/L$,
where $L$ is the characteristic membrane size (radius), which will be a parameter in our model. Although the imaginary part is completely finite, Eq. (3.11) shows that the real part of the finite temperature atom self-energy is log-divergent in the infrared limit ($\epsilon \to 0$). A similar expression can be derived for the 1-loop bound state self-energy $\Sigma_{bb}$ corresponding to a Feynman diagram similar to Fig. 3.3 with $g_{kb}$ replaced with $g_{bb}$. The expressions for the real and imaginary $\Sigma_{bb}$ are given as:

$$Re\Sigma_{bb}^{(r)}(E) = \frac{2g_{bb}^2\rho_0 T}{E+E_b} \log \left| \frac{E + E_b}{\epsilon} \right|$$

(3.13)

$$Im\Sigma_{bb}^{(r)}(E) = -\frac{\pi g_{bb}^2 \rho_0 T}{E + E_b}; \quad E + E_b \gg \epsilon$$

(3.14)

The values of $g_{bb}$ and $g_{kb}$ depend on the form of the attractive (van der Waals) potential between the atom and graphene; for a H atom we will take them from values already specified in Chapter 2. The coupling $g_{kb}$ has a strong energy dependence, $g_{kb} = g_{kb}(E)$ where $E$ is the atom’s energy which will be taken into account in our final results. The coupling $g_{bb}^2\rho_0 = 60\mu eV$ is energy independent and, in addition, is much larger than $g_{kb}^2\rho_0$ (for all energies considered):

$$g_{bb}^2\rho_0 \gg g_{kb}^2\rho_0.$$ 

(3.15)

The ratio of these couplings for H atom is typically $g_{kb}^2/g_{bb}^2 \sim 10^{-2}$. Because of this inequality the bound state self-energy behavior in higher orders will be numerically much more important than the corresponding higher order contributions to the continuum self energy (assuming there are no divergences). Thus we first proceed to investigate the next order in powers of $g_{bb}^2\rho_0$. 

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2-loop Bound Self-energy

Here, we calculate the 2-loop bound state self-energy corresponding to the Feynman diagrams shown in Fig. 3.4. First we evaluate the vertex correction diagram by using the vertex function $\Gamma(E, \omega)$ (see Fig. 3.5). Following the Feynman rules, we derive
analytical expression for $\Gamma(E, \omega)$:

$$
\Gamma(E, \omega) = ig_{bb}^3 \sum_q \int \frac{d\omega'}{2\pi} \frac{T}{\omega_q} (-2\pi i) \left[ \delta(\omega' - \omega_q) + \delta(\omega' + \omega_q) \right] \left[ \frac{1}{[E + E_b - \omega' + i\eta]} \right] 
\times \left[ \frac{1}{[E + E_b - \omega - \omega' + i\eta]} \right] 
\tag{3.16}
$$

In the continuum limit, we call $g_{bb}^2 \rho_0 = g_b$, so that the real and the imaginary parts of the vertex function $\Gamma(E, \omega)$ are written as:

$$
Re \Gamma(E, \omega) = \frac{2g_{bb}^3 \rho T}{(E + E_b)(E + E_b - \omega)} \log \left| \frac{E + E_b}{\epsilon} \frac{E + E_b}{\epsilon} \right| 
\tag{3.17}
$$

$$
Im \Gamma(E, \omega) = -\frac{\pi g_{bb}^3 \rho T}{(E + E_b)(E + E_b - \omega)} 
\tag{3.18}
$$

Using Equations (3.17) and (3.18), we derive the contribution to the vertex correction diagram. The analytical expression for $\Sigma_{bb}$ is written as:

$$
\Sigma_{bb}^{(2)} = ig_{bb} \int \frac{d\omega}{2\pi} G_{bb}(E - \omega) \Gamma(E, \omega) D^<(\omega) 
\tag{3.19}
$$

Plugging Eq. (3.17) and the respective Keldysh GFs in Eq. (3.19), we find an expression for the real part of $\Sigma_{bb}^{(2)}$:

$$
Re \Sigma_{bb}^{(2)} = \frac{2g_b^2 T^2}{(E + E_b)^3} \left[ \log \left| \frac{E + E_b}{\epsilon} \frac{E + E_b}{\epsilon} \right| \right]^2 
\tag{3.20}
$$

A similar expression can be easily derived for the contribution from the rainbow diagram. Thus, the above calculations shows that the real part of $\Sigma_{bb}$ for both the 1-loop and the 2-loop is plagued by log and log-squared infrared divergences,
respectively. Therefore, the perturbative expansion of the real part of the bound state self-energy \( \Sigma_{bb}(E) \), collecting our results up to two loops, is written as:

\[
Re \Sigma_{bb}(E) = \frac{2g_b T}{E + E_b} \log \left| \frac{E + E_b}{\epsilon} \right| + 2 \times \frac{2g_b^2 T^2}{(E + E_b)^3} \left[ \log \left| \frac{E + E_b}{\epsilon} \right| \right]^2 + \cdots \quad (3.21)
\]

Given the above structure of perturbation theory, it is clear that in the infrared limit \((E + E_b)/\epsilon \gg 1\), resummation of the series has to be performed. In fact this turns out to be possible and the infrared dynamics of the result is equivalent to that of the exact Green’s function, \( G_{bb}(E) \), of the independent boson model \([102]\). We can show that one can use Dyson’s Equation \( G_{bb}(E) = G_{bb}^{(0)}(E)/(1 - G_{bb}^{(0)}(E)\Sigma_{bb}(E)) \), where \( G_{bb}^{(0)}(E) \) and \( \Sigma_{bb}(E) \) are the unperturbed bound state Green’s function and the bound state self-energy, respectively, and then derive a perturbative expression for \( G_{bb}(E) \) that matches exactly the perturbative structure of the exact bound state Green’s function corresponding to the IBM. This is indeed natural since both the IBM and the part of our model involving \( bb \) transitions describe physically equivalent situations (phonon bath coupled to a single particle).

Before we proceed to the application of the resummation techniques to the finite temperature cases, let us quickly summarize our perturbative self-energy expansion terms in table 3.1. Contrary, to the zero temperature scenario where the divergences appeared in the 2-loop processes, we encounter severe infrared divergences starting with the 1 phonon processes in the finite temperature regime. In the next section, we discuss resummation schemes based on the Independent Boson Model Approximation (IBMA) and the Non-Crossing Approximation (NCA). Both these methods were found to be successful in treating the infrared problem at zero temperature.
Table 3.1: We summarize the divergences in the self-energy terms for the finite temperature formalism. Here, we have defined: \( g = g_{bb} g_{bb} \rho_0 \) and \( \epsilon \) is the infrared cut-off which is physically related to the size of the membrane as \( \epsilon \sim v_s/L \) with \( v_s = \) speed of sound and \( L = \) the size of the membrane.

### 3.2.2 Resummation Techniques

**Independent Boson Model Approximation (IBMA)**

In our model, it is imperative to derive an exact solution in the bound channel for the following reasons: (i) inclusion of the effects from \( g_{bb} \) in the perturbation series, leads to severe divergences in the higher order self-energy terms (see 2 loop processes in Table. 3.1), (ii) vertex renormalization results indicate an increase in the \( \Gamma_{bb} \) vertex in the infrared limit \( (\epsilon \to 0) \) [See Appendix Sec. A.3 for detailed calculations on vertex renormalization] and (iii) we are in the ultracold regime: \( g_{kb}^2 \rho_0 \ll g_{bb}^2 \rho_0 \). Thus, we aim to devise a resummation technique which will treat the bound channel non-perturbatively in all orders of \( g_{bb}^2 \rho_0 \). Such a scheme is realized in the premise of the Independent Boson Model (IBM). We relate the bound state of our model with the IBM Hamiltonian which represents the interaction of a particle with the phonon bath:

\[
H_{IBM} = -E_b b^\dagger b + \sum_q \omega_q (a_q + a_q^\dagger) - g_{bb} b^\dagger b \sum_q (a_q + a_q^\dagger) \quad (3.22)
\]
Figure 3.6: Variation of the IBM propagator with temperature for the three regimes: $T \gg \omega_D$, $T \ll \omega_D$ and $T = 0$. With the inclusion of the many-body effects from the interaction of the atom with the phonons in the bound state, we observe that the quasiparticle pole is no longer present. Also, an increase in temperature leads to the damping of the propagator. This is similar in essence to the observed damping of propagators in the hot QED and QCD cases.
We write down the propagator for the above Hamiltonian as [102]:

\[ G_{bb}(t) = -ie^{-i(E_b - \Delta)\epsilon - \phi(t)} \]  
(3.23)

where,

\[ \phi(t) = \sum_q \left( \frac{g_{bb}}{\omega_q} \right)^2 \left[ n_q(1 - e^{i\omega_q t}) + (n_q + 1)(1 - e^{-i\omega_q t}) \right] \]  
(3.24)

Plugging Eq. 3.24 in Eq. 3.23, we get:

\[ G_{bb}(t) = -ie^{i(E_b + \Delta)\epsilon} \exp \left[ -\sum_q \left( \frac{g_{bb}}{\omega_q} \right)^2 \left[ 2\sin^2 \left( \frac{\omega_q t}{2} \right) \times (2n_q + 1) \right] \right] \times \exp \left[ -\sum_q \left( \frac{g_{bb}}{\omega_q} \right)^2 i \sin \omega_q t \right] \]  
(3.25)

Using \( \Delta = \sum_q g_{bb}^2/\omega_q \) in the above equation, we re-write Eq. 3.25 as:

\[ G_{bb}(t) = -i \exp \left[ it\left( E_b + \sum_q \frac{g_{bb}^2}{\omega_q} \left( 1 - \sin \frac{\omega_q t}{\omega t} \right) \right) \right] \times \exp \left[ -\sum_q \left( \frac{g_{bb}}{\omega_q} \right)^2 \left[ 2\sin^2 \left( \frac{\omega_q t}{2} \right)(2n_q + 1) \right] \right] \]  
(3.26)

We take the Fourier transform of the above equation to derive the real and imaginary part of the IBM propagator:

\[ Re \ G_{bb}(E_s) = \int_{-\infty}^{\infty} \sin \left[ t \left( E_s + g_b \int_{\epsilon}^{\omega_D} d\omega \frac{1 - \sin \omega t}{\omega t} \right) \right] \exp \left[ -g_b \int_{\epsilon}^{\omega_D} d\omega \frac{2\sin^2 \omega t}{\omega^2} \times \left[ 1 + \frac{2}{\exp(\beta\omega) - 1} \right] \right] dt \]  
(3.27)
\[ |Im \ G_{bb}(E_s)| = \int_{-\infty}^{\infty} \cos \left[ t \left( E_s + g_b \int_{\epsilon}^{\omega_D} \frac{d\omega}{\omega} \left[ 1 - \frac{\sin \omega t}{\omega t} \right] \right) \right] \exp \left[ - g_b \int_{\epsilon}^{\omega_D} \frac{d\omega}{\omega^2} \left( 2 \sin^2 \frac{\omega t}{2} \right) \times \left[ 1 + \frac{2}{\exp(\beta \omega) - 1} \right] \right] \, dt \] (3.28)

where we have defined \( g_b \equiv g_{bb}^2 \rho_0 \). These integrals are solved numerically in the infrared limit (\( \epsilon \to 0 \)) and we study the evolution of the IBM propagator for different temperature regimes. We notice a smearing of the IBM propagator (Fig. 3.6) which we relate to the interaction effect of the atom with the phonons.

Following the procedure given in Chapter 2, we now derive the atom self-energy \( \Sigma_{kk}^{IBM} \) within the IBMA. We replace the bare propagator in one loop self-energy diagram by the effective propagator given by Eq. 3.27 & Eq. 3.28. Therefore, the resummed atom self-energy in the IBMA is given as:

\[ \Sigma_{kk}^{IBMA}(E) = g_{bb}^2 \sum_q \left[ n_q G_{bb}^{IBM}(E + \omega_q) + (n_q + 1) G_{bb}^{IBM}(E - \omega_q) \right] \] (3.29)

Before we derive the transition rate within the IBMA, let us quickly discuss another partial resummation scheme based on the method of NCA which was previously seen to remove the infrared divergence in the zero temperature regime. In the case of zero temperature, we observed a linear divergence (as \( \epsilon \to 0 \)) in the nested diagram in the perturbation series. This led us to sum all the nested diagrams to infinite order with the motive of curing the leading-order divergent contributions. Based on the success of NCA in the zero temperature case, we extend it to the finite temperature regime (\( T \ll \omega_D \)).
Figure 3.7: Diagrams in the NCA. The analytical expressions corresponding to the figures give rise to a set of coupled non-linear integral equations. Symbolic elements used in the construction of diagrams are shown.

Non-Crossing Approximation (NCA)

We begin our calculation in the finite temperature regime by deriving a set of coupled non-linear integral equations given by the Feynman diagrams in Fig. 3.7. As the phonon bath is out-of-equilibrium with the incoming particle, we will use Keldysh formalism to write down the corresponding analytical expression for the Feynman diagrams.

We start with evaluating the $\Sigma_{bb}(E)$ and $\Sigma_{kk}(E)$ using the Keldysh formalism and the Green functions associated with it. Following the Feynman rules, we have:

$$\Sigma_{bb}^{(r)}(E) = i \int \frac{d\omega}{2\pi} \sum_q g_{bb}^2 \left[ G^r(E - \omega)D^<(\omega) + G^r(E - \omega)D^r(\omega) \right],$$

(3.30)
The dressed Green function in the bound state is represented as,

$$G_{bb}^r(E) = \frac{1}{E + E_b - \Sigma_{bb}^r(E)}, \quad (3.31)$$

The finite temperature phonon propagator is given as,

$$D^<(\omega) = -2\pi i[(n_q + 1)\delta(\omega + \omega_q) + n_q\delta(\omega - \omega_q)], \quad (3.32)$$

The retarded phonon propagator is given as,

$$D^r(\omega) = \frac{1}{\omega - \omega_q + i\eta} - \frac{1}{\omega + \omega_q + i\eta}. \quad (3.33)$$

Using Eq. 3.32 and Eq. 3.33 in Eq. 3.30, we get:

$$\Sigma_{bb}^r(E) = g_{bb}^2 \sum_q \left[ n_q G_{bb}^r(E + \omega_q) + (n_q + 1)G_{bb}^r(E - \omega_q) \right], \quad (3.34)$$

Plugging Eq. 3.31 in Eq. 3.34, we derive an expression for the bound state self-energy $\Sigma_{bb}$ in the NCA:

$$\Sigma_{bb}^r(E) = g_{bb}^2 \sum_q \left[ \frac{n_q}{E + \omega_q + E_b - \Sigma_{bb}^r(E + \omega_q)} + \frac{(n_q + 1)}{E - \omega_q + E_b - \Sigma_{bb}^r(E - \omega_q)} \right]. \quad (3.35)$$

Similarly, one can derive the $\Sigma_{kk}^r(E)$ as above,

$$\Sigma_{kk}^r(E) = g_{kb}^2 \sum_q \left[ \frac{n_q}{E + \omega_q + E_b - \Sigma_{bb}^r(E + \omega_q)} + \frac{(n_q + 1)}{E - \omega_q + E_b - \Sigma_{bb}^r(E - \omega_q)} \right]. \quad (3.36)$$

Using Eq. 3.35 & Eq. 3.36, we derive an analytical expression corresponding to
To derive the resummed atom self-energy $\Sigma_{\text{NCA}}^{\Sigma_{kk}}$ we solve Eq. A.31 self-consistently until convergence (see Appendix Sec. A.4 for computational details). As mentioned before, the infrared dynamics of the problem is investigated by changing the membrane size, which is related to the infrared cut-off frequency $\epsilon$. For a particular size of the membrane, we numerically derive the atom self-energy $\Sigma_{kk}(E)$ for two temperatures 10 K and 20 K satisfying our regime of study: $T/\omega_D \ll 1$.

We make a comparative plot of self-energy $\Sigma_{\text{NCA}}^{\Sigma_{kk}}$ shown in Fig. 3.8. This demonstrates the behavior of the real and the imaginary part of $\Sigma_{kk}$, solved self-consistently in Eq. A.31. The important features of the dynamics of the interaction can be easily viewed in these plots. It is clearly seen that the real part of the atom self-energy has a power law decay at $E \to -\infty$. Whereas, the imaginary part of $\Sigma_{kk}$ has a pole at the bound state energy $-E_b$. With the increase in membrane size (L) which corresponds to a decrease in the infrared cut-off frequency, the function for $\text{Im}\Sigma_{kk}$ starts to broaden out more and the quasiparticle nature of the pole is lost. This is similar in essence to the nature of the IBMA propagator and that of hot QED/QCD plasma where the singular nature of the pole in the mass shell is lost and the propagator
Figure 3.8: Comparative plots for the zero and finite temperature NCA results. For $E \to -\infty$, $\text{Re} \Sigma_{kk}$ shows a power law decay. Owing to many-body effects, the $\text{Im} \Sigma_{kk}$ shows no pole at the mass shell $E_b$. Inset plots show the variation of the self-energy for a finite temperature $T \ll \omega_D$ for different infrared cut-off values of $\epsilon$. We observe a broadening of the $\text{Im} \Sigma_{kk}$, similar to the damping of propagators in IBMA.

starts to broaden out. However, we would mention that for $T \gg 2.0$ meV ($\sim 22$ K), we do not have confidence in the NCA result as the divergence from the Bose
factor $n_q = 1/[\exp(\beta \omega) - 1]$ becomes severe in our numerical calculations and the self-consistency can no longer be achieved.

In the next section, we will explicitly discuss the validity of the resummation techniques for the given energy regime in the low temperature formalism.

3.3 Test of Resummation Techniques

Quite similar to the zero temperature case, we will apply the adsorption rate derived within the IBMA and NCA to the physical model of cold atomic Hydrogen impinging on graphene micromembranes and check the validity of all our techniques. In the next subsection, using the resummed atom self-energy $\Sigma_{kk}$, we re-derive the associated damping rates for the experimentally realizable model of atomic hydrogen impinging on graphene micromembranes.

3.3.1 Damping in Resummed Atom Self-Energy

We consider the adsorption rate of cold atomic hydrogen impinging on suspended graphene membranes. In Fig. 3.9, we plot the normalized transition rate $\Gamma/\Gamma_0$ derived within the Golden rule (Eq. 3.4), NCA (Eq. A.31) and IBMA (Eq. 3.29) with the variation of the infrared cut-off $\epsilon$. We observe for micromembranes, our methods of NCA and IBMA are in agreement with each other (Fig. 3.9). However, a close look at the inset plots show us that in the true infrared limit $\epsilon \to 0$ both the NCA and IBMA show an IR divergence (power-law for NCA and a slowly varying logarithmic divergence for IBMA). Within the NCA, as mentioned before the self-consistency is lost with the increase in temperature which is equivalent to decreasing $\omega$ as $n(q) =$
1/\left[ \exp\left(\frac{\omega}{T}\right) - 1 \right] \text{ which is why we are not confident in our NCA results below } \epsilon = 0.1 \text{ K or } T \gg 2 \text{ meV. However, let us investigate the nature of the residue of the slowly varying log in IBMA in more detail in our next subsection.}

Figure 3.9: Variation of the normalized damping/adsorption rate with infrared cut-off (\(\epsilon\)) which is related to the size of the membrane (L). We plug our resummed self-energies \(\Sigma_{kk}^{NCA}\) and \(\Sigma_{kk}^{IBM}\) in Eq. 3.5, to derive a value of the resummed damping rate. For a model of cold atomic hydrogen impinging on graphene membrane, we observe for micromembranes, the two resummation techniques are in agreement with each other, with \(\Gamma/\Gamma_0 \sim 1\). Inset plots show: in the limit of (infinitely large membrane) the IBMA has a slow logarithmic divergence, whereas NCA suffers from a power-law divergence.

Discussion on the residue of the log in IBMA

From Eq. 3.29, we define a function:

\[
F(\omega) = \left[ n_q G_{bb}^{IBM}(E + \omega_q) + (n_q + 1) G_{bb}^{IBM}(E - \omega_q) \right] \tag{3.38}
\]
Figure 3.10: Variation of the function $F(\omega)$ with respect to $\omega$ for different temperatures. With an increase in temperature, there is an accumulation of the density of states at $\omega = 0$. The inset plot shows the corresponding normalized damping rate. For a micromembrane at lower temperatures, we clearly see that the resummed damping rates are similar to the first order conventional golden rule results, obeying the Bloch-Nordsieck sum rule. However, with an increase in temperature, there appears an enhancement which can be related to the temperature effects of the Bose distribution.

We study the evolution of the function $F(\omega)$ with temperatures ranging from $10K \sim 200K$ (Fig. 3.10). For a micromembrane ($L = 1 \mu m$) maintained at $T = 10K$, we observe the usual broadened spectral weight at $\omega = E_s$. However, with the increase in temperature, we notice a broadening of the weight at $\omega = E_s$ with a re-distribution of the left-over spectral weight at $\omega = 0$ (infrared limit). As temperature increases, there is an increased emission of soft phonons at $\omega = 0$ following the identity $a^+_q |n_q \rangle = \sqrt{n_q + 1} |n_q + 1 \rangle$. Thus we relate this feature to the temperature effects coming from Bose distribution such that there is an increased probability
of emission of soft thermal phonons with increasing $T$. The inset plot in Fig. 3.10 shows the variation of the normalized adsorption rate with temperature. For lower temperatures, we observe very little variation with respect to the first-order result which is in agreement with the general idea of the Bloch-Nordsieck sum rule [129, 130]. However, with the increase in temperature, we observe a slow enhancement in the adsorption rate, which can be related to the temperature effects of the Bose function.

Thus, to summarize our low temperature formalism on adsorption rates of cold atoms on graphene membranes, we can say that for micromembranes maintained at sufficiently low temperatures ($\sim 200$K) the resummed adsorption rate is very close to the first-order conventional perturbation theory results. However, as temperature increases, the contribution from the low-frequency phonons to the adsorption rate grows which implies that the infrared problem persists at $T \neq 0$. A recent study on the adsorption rate based on the Soft Phonon Resummation technique at finite temperature remedies the IR divergence but predicts vanishing adsorption rate at $\epsilon \to 0$[32].

Let us conclude this section by a short study on the high temperature formalism to further probe this log behavior and try to extract a physical significance of our results.

### 3.4 High Temperature Regime

Our study on the low temperature formalism clearly shows that there is severe infrared divergence in the normal perturbative structure of the adsorption rates. However, on application of the resummation techniques - NCA and IBMA we derived adsorption
rates for micromembranes at low temperature (10 K ∼ 200 K) that nearly matched the first order conventional theory result. However from Fig. 3.9, we clearly observe an increase in the normalized adsorption rates (Γ/Γ₀) with ϵ → 0. In this section, we will investigate this residual divergence in the resummed IBMA propagator at high temperature and aim to extract some physical significance of our results. Before we proceed to detailed calculations let us quickly define our energy regime:

\[ g_{bb}^2 \rho_0 \ll g_{bb}^2 \rho_0 \ll E_b \ll \omega_D \ll T \]

3.4.1 Resummation Technique: IBMA Propagator

Based on the previous analysis we proceed to calculate the \( bb \) Green’s function which will provide the dominant contribution to the atom damping rate, to be calculated in the next Section. As already mentioned, if we consider only the bound state |\( b \rangle \) contributions, we have the same Hamiltonian as that of the IBM:

\[
H = -E_b b^\dagger b + \sum_q \omega_q a_q^\dagger a_q - g_{bb} b^\dagger b \sum_q (a_q + a_q^\dagger)
\]  

(3.39)

The exact Green’s function \( G_{bb}(t) \) corresponding to Eq. (3.39) is given as: [102]

\[
G_{bb}(t) = -i e^{-i(E_b - \Delta)t} e^{-\phi(t)}
\]  

(3.40)

Here,

\[
\phi(t) = \sum_q \left( \frac{g_{bb}}{\omega_q} \right)^2 \left[ n_q (1 - e^{i \omega_q t}) + (n_q + 1) (1 - e^{-i \omega_q t}) \right]
\]  

(3.41)
where \( n_q \) is the Bose distribution function:

\[
n_q = \frac{1}{e^{\beta \omega_q} - 1} \quad (3.42)
\]

In the limit of \( \Delta \omega \ll T \), \( n_q \approx T/q \). For our model, Eq. (A.1) takes up the form:

\[
\phi(t) = \sum_q \frac{2g_{bb}^2 T}{q^2} \left[ 1 - \cos(qt) \right] \quad (3.43)
\]

Plugging Eq. (3.43) in Eq. (3.40), the Green’s function \( G_{bb}(t) \) takes up the form:

\[
G_{bb}(t) = -ie^{-it(-E_b - \Delta)} \times \exp \left[ - \sum_q \frac{2g_{bb}^2 T}{q^3} \left[ 1 - \cos(qt) \right] \right] \quad (3.44)
\]

In the continuum limit we have:

\[
G_{bb}(t) = -ie^{it(E_b + \Delta)} \times \exp \left[ - 2g_{bb}^2 \rho_0 T \int_\epsilon^{\omega_D} \left[ 1 - \cos(qt) \right] \frac{dq}{q^3} \right] \quad (3.45)
\]

The integral in the parenthesis of Eq. (3.45) is exactly solvable and can be written as:

\[
\int_\epsilon^{\omega_D} \left[ 1 - \cos(qt) \right] \frac{dq}{q^3} = \frac{1}{2q^2} + \frac{\cos(qt)}{2q^2} + \frac{1}{2} t^2 \text{Ci}(qt) - \frac{t \sin(qt)}{2q} \bigg|_\epsilon^{\omega_D} \quad (3.46)
\]

where the function \( \text{Ci}(x) \) is given by [2] and has the following expansion for \( x \ll 1 \),

\[
\text{Ci}(x) \equiv \gamma + \log |x| + \sum_{n=1}^{\infty} \frac{(-1)^n x^{2n}}{2n(2n)!}
\]

and \( \gamma \) is the Euler-Mascheroni constant.
The integral in Eq. (3.46) oscillates and decays rapidly, so the contribution at the upper limit of integration is negligible, especially since $\omega_D/\epsilon \gg 1$. The exponentiated function which appears in Eq. (3.45) oscillates as a function of time around the constant value $\exp\left(-g_{bb}^2 \rho_0 T/\epsilon^2\right)$ which is due to the first term in Eq. (3.47). This number is practically zero for all reasonable values of the cutoff and the other constants.

Next, we take the Fourier transform of Eq. (3.45),

$$G_{bb}(E + E_b) = -i \int_0^\infty dt e^{it(E + E_b + \Delta)} \times \exp \left[-2g_{bb}^2 \rho_0 T \int_{\omega_D}^{\omega} \frac{1 - \cos(qt)}{q^3} dq\right] \tag{3.47}$$

Before performing a full numerical evaluation, it is useful to estimate the decay of the envelope of oscillations. This can be done for large times but subject to the limit $t \ll 1/\epsilon$ (keeping in mind that $\epsilon$ is small), so that in the integral the largest contribution comes from momenta $qt \ll 1$, and the logarithmic term dominates. In this case the above equation reduces to:

$$G_{bb}(E + E_b) = -i \int_0^\infty dt e^{i(E + E_b + \Delta)t} \exp \left[-g_{bb}^2 \rho_0 T t^2 \log \left|\frac{1}{t\epsilon}\right|\right] \tag{3.48}$$

In this limit the oscillations are not visible. We see that for our quasi 1-D model, the damping term is given as $\delta(t) \approx \exp\left[-g_{bb}^2 \rho_0 T t^2 \log \left|1/(t\epsilon)\right|\right]$ which has a different structure than the case of 3D QED, where the damping term is $\delta(t) \approx \exp[-\alpha T t \log(\omega_p t)]$ with $\omega_p$ and $\alpha$ being the plasma frequency and the fine structure constant. [13]

Next, we consider the more general case and numerically solve Eq. (3.47) by using
Figure 3.11: Variation of the real part of the dimensionless Green’s function in the bound state $\tilde{G}_{bb}$ for different values of the effective infrared cutoff $\omega_m = \epsilon/\sqrt{\lambda}$ with $\tilde{E} = (E + E_b + \Delta)/\sqrt{\lambda}$.

Figure 3.12: Variation of the imaginary part of the dimensionless Green’s function in the bound state $\tilde{G}_{bb}$ for different values of the effective infrared cutoff $\omega_m$. 
Eq. (3.46). We use the following transformation of variables: \((E + E_b + \Delta)t = x \) and 
\(q/(E + E_b + \Delta) = y \) and under the approximation that \(\omega_D \gg E_b + \Delta, E \) (this implies a minimum infrared cut-off \(\epsilon \) since \(\Delta \) grows as \(\epsilon \to 0 \)) we re-write a non-dimensional form of the bound state Green’s function \(\tilde{G}_{bb} \):

\[
\tilde{G}_{bb}(\tilde{E}) = -\frac{i}{\sqrt{\lambda}} \int_0^\infty dx \frac{e^{ix}}{E} \times \exp \left[-\frac{1}{E^2} \int_{\omega_m}^{\infty} \frac{1 - \cos(yx)}{y^3} dy \right].
\]

(3.49)

Here we define the dimensionless cutoff \(\omega_m \) and energy \(\tilde{E} \) in the following convenient way:

\[
\lambda = 2g_{bb}^2 \rho_0 T, \quad \omega_m = \epsilon/\sqrt{\lambda}, \quad \tilde{E} = (E + E_b)/\sqrt{\lambda}.
\]

(3.50)

The real and the imaginary parts of Eq. (3.49) are given as follows:

\[
Re\tilde{G}_{bb}(\tilde{E}) = \frac{1}{\sqrt{\lambda}} \int_0^\infty dx \frac{\sin(x)}{E} \times \exp \left[-\frac{1}{E^2} \int_{\omega_m}^{\infty} \frac{1 - \cos(yx)}{y^3} dy \right]
\]

(3.51)

\[
Im\tilde{G}_{bb}(\tilde{E}) = -\frac{1}{\sqrt{\lambda}} \int_0^\infty dx \frac{\cos(x)}{E} \times \exp \left[-\frac{1}{E^2} \int_{\omega_m}^{\infty} \frac{1 - \cos(yx)}{y^3} dy \right]
\]

(3.52)

We solve the above integrals numerically for a graphene membrane with a physisorption well \(E_b = 40 \) meV, \(g_{bb}^2 \rho_0 = 60 \) µeV, and \(\omega_D = 65 \) meV. The variation of the imaginary and the real parts of \(\tilde{G}_{bb} \) with the dimensionless infrared frequency cutoff \(\omega_m \) is captured in Figs. 3.11 and 3.12 respectively.

As discussed in the paragraph before Eq. (3.47), there exists also a constant term \(\exp \left(-g_{bb}^2 \rho_0 T/\epsilon^2 \right) \) in the time domain leading to a singular, \(\delta(\omega) \) function contribution to the imaginary part with spectral weight \(\exp \left(-1/(2\omega_m^2) \right) \). This part is not visible in Fig. 3.12 since for the cutoff values used, the additional \(\delta\)-function spectral weight is practically zero. It can however become appreciable upon further increase of \(\omega_m \).

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beyond 0.2 or so, which would take us beyond the region of validity of our model.

The main conclusion we can draw is that both real and imaginary parts are well-behaved but **still exhibit some infrared cutoff dependence**. Most importantly, there is a vanishingly small quasiparticle pole and the Green’s function is damped. The residual cutoff dependence reflects the 2D nature of the membrane ZA phonon fluctuations.

### 3.4.2 Damping Rates in Resummed Atom Self-Energy

We use the numerically solved $\tilde{G}_{bb}$ to derive the renomalized 1-loop atom self-energy $\Sigma^{r}_{kk}$, which in turn is used to derive the sticking rate $\Gamma$ of the cold atom on finite temperature graphene membranes. We recall, the rate of transition of the cold atom from the continuum state $|k\rangle$ to the bound state $|b\rangle$ is given as:

$$\Gamma = -2Z(E_0)Im\Sigma_{kk}(E_0)$$ (3.53)

where $Z$ is the renormalization factor and is given as: $Z = \left[1 - \left(\partial Re \Sigma_{kk}(E_0)/\partial E\right)\right]^{-1}$ and $E_0$ is the quasiparticle energy, respectively.

As usual, we replace the $G_{bb}^r$ with the $\tilde{G}_{bb}$ derived before, such that the equation to be solved numerically takes up the form:

$$\Sigma^{(1)}_{kk} = g_{kk}^2 \rho_0 T \int_\epsilon^{\omega_D} \left[ \frac{1}{q} \tilde{G}_{bb} \left( \frac{E + E_b - q}{\sqrt{\lambda}} \right) + \frac{1}{q} \tilde{G}_{bb} \left( \frac{E + E_b + q}{\sqrt{\lambda}} \right) \right] dq$$ (3.54)
Our final results, summarized in Eqs. (3.53),(3.54) reflect the idea that, in order to obtain numerically accurate results, it is sufficient to keep the lowest (first) order in the smallest coupling $g_{bb}^2 \rho_0$ while using the fully renormalized $G_{bb}$ which contains all orders in the strong coupling $g_{bb}^2 \rho_0$. However, we are restricted from taking $\epsilon \to 0$, as IR divergences lurk in these expressions.

The above equation is numerically integrated for two different infrared cut-off frequencies which physically correspond to two different sizes of the graphene membrane. We consider 1 $\mu$m and 100 nm sizes. The velocity of ZA phonons sound waves in graphene is taken to be $v_s = \sqrt{\gamma/\sigma} = 6.64 \times 10^3$ m/s, where $\gamma$ and $\sigma$ are defined as the out-of-plane membrane tension and membrane mass-density for graphene [30, 92, 108], so that the physical cut-off corresponding to the two above mentioned membrane sizes are calculated as $\epsilon = 4.33 \times 10^{-3}$ meV and 0.043 meV, respectively. It should be mentioned that anharmonic effects in the ZA phonon dispersion can become important as temperature increases, and are a subject of current research [5, 77, 128, 158]; however if the tension $\gamma$ is large enough, such effects are naturally suppressed. The tension value we use from Refs. [30, 90] is fairly large but lies in the border region where anharmonic corrections could become noticeable; detailed studies of such effects are beyond the scope of the present work.

Now we present the numerical studies conducted for the above mentioned membrane sizes. For each length, we investigate the dependence of $\Gamma$ on temperature. For a membrane size of 100 nm, the dimensionless lower cut-off $\omega_m$ for the selected temperatures 1160K, 928K and 696K are given as 0.0125, 0.0141, 0.01628, respectively. From Figure 3.13 we see that the sticking rate increases with the increase in temper-
Figure 3.13: Variation of the sticking rate $\Gamma$ of the cold atom on graphene membrane (size 100nm), as a function of the atom kinetic energy $E$. An increase in $\Gamma$ is observed for increased temperature of the membrane.

This reflects the physics of damping. A higher temperature corresponds to lower physical cut-off and hence a much broader curve of $\text{Im} \bar{G}_{bb}$ (see Fig. 3.12). The broadening of the curve implies more damping and hence a higher decay rate.

Similar trend is observed for the membrane size of 1 $\mu$m (Fig. 3.14) where $\omega_m$ are given as 0.00125, 0.001397 and 0.00163 for the above mentioned temperatures.

The transition rate can also be calculated using Fermi’s golden rule (GR) both for in the zero-temperature and finite temperature formalism. The golden rule is equivalent to first order in perturbation theory (in $g_{bb}^2 \rho_0$) and obviously does not contain the additional complex physics related to infrared effects discussed previously in higher orders.
Figure 3.14: For a membrane size of 1µm, Γ is seen to increase even further with temperature, which is a clear indication of the increased damping of the wave function leading to higher decay rates.

For the $T = 0$ case:

$$\Gamma = 2\pi \sum_f |\langle f|H_c|i\rangle|^2 \delta(E_f - E_i)$$  \hspace{1cm}(3.55)$$

Here, we use the initial state and energy as: $|i\rangle = |c_k\rangle|0\rangle$ and $E_i = E_k$. The final state and energy is given as: $|f\rangle = |b\rangle|1_q\rangle$, $E_f = -E_b + \omega_q$. The coupling term is given as $H_c = -g_{kk}(c_k^\dagger b + b^\dagger c_k) \sum_q (a_q + a_q^\dagger) - g_{bb} b^\dagger b \sum_q (a_q + a_q^\dagger)$. Therefore, in the continuum limit, the sticking rate $\Gamma$ reduces to:

$$\Gamma_{GR}^{T=0} = 2\pi g_{kk}^2 \rho_0$$  \hspace{1cm}(3.56)$$
Similarly, using the golden rule, an expression for $\Gamma$ can be derived for finite temperature $T \neq 0$. Under the approximation $T \gg E_b$ we obtain:

$$\Gamma_{GR}^{T \neq 0} = 2\pi \sum_{f,i} |\langle f | H_c | i \rangle|^2 \delta(E_f - E_i)p_i$$

(3.57)

where $n_q$ is the Bose-Einstein distribution for the phonons initially. In the limit of $\Delta \omega \ll T$, we have $n_q \approx T/q$, and therefore:

$$\Gamma_{GR}^{T \neq 0} = 2\pi \sum_q g_{bb}^2 \delta(-E_b + \omega_q - E_k) \frac{T}{q}$$

(3.58)

Once again, in the continuum limit, we derive the finite-temperature sticking rate from Fermi’s golden rule as:

$$\Gamma_{GR}^{T \neq 0} = \frac{2\pi g_{bb}^2 \rho_0 T}{(E_k + E_b)}$$

(3.59)

We now compare the transition rates derived from the golden rule both for zero and finite temperatures with the sticking rates obtained using $\bar{G}_{bb}$ for the already mentioned $\omega_m$. We see in Fig. 3.15 that the sticking rates derived by incorporating $\bar{G}_{bb}$ is enhanced compared to the golden rule results, which is natural since it reflects additional damping arising from the emission of phonons which is enhanced because of the presence of a thermal distribution of phonons initially.
Figure 3.15: With the increase in the physical cut-off \( \omega_m \) or decrease in the length of the membrane, the sticking rate \( \Gamma \) is seen to decrease. However, we predict that in our model \( \Gamma \) can not be smaller than the golden rule (GR) results derived for that specific temperature.

### 3.5 Summary

In summary, we have considered the infrared dynamics of atoms interacting with a graphene membrane at finite temperature. This problem exhibits particularly severe infrared divergences order by order in perturbation theory, due to the singular nature of low-energy ZA phonon emission. It is more severe at finite \( T \), compared to \( T=0 \) case. Our model can be viewed as a two channel generalization of the independent boson model, with much weaker atom-phonon coupling constant in one of the channels relative to the other. This allows us to take advantage of the exact non-perturbative solution of the independent boson model in the stronger channel while treating the other one perturbatively. In the low-energy limit, the exact solution can be viewed as
a resummation (exponentiation) of the most divergent diagrams in the perturbative expansion, which we have checked explicitly. As a result of this procedure, we obtain the atom Green’s function which we use to calculate the atom damping rate, this is in turn related to the physical quantum sticking rate. A characteristic feature of our results is that the Green’s function retains some infrared cutoff dependence, which is relatively weak but still detectable by relating the infrared cutoff to the inverse membrane size (we can relate this to the violation of the KLN theorem). We provide detailed predictions for the sticking rate of H atoms as a function of temperature and size. For high temperature $T \gg \omega_D$, sticking is generally enhanced relative to the conventional Fermi golden rule result (which is equivalent to the lowest, one loop perturbative term) which is natural since higher order processes are required to increase damping at finite temperature. Although we observe an enhancement from the golden rule result, we still see the trend of decreasing sticking rates for low energies, contrary to some recent results, where numerical calculations predict an increased sticking rate with low incident energies [92].

It is also worth noticing, as we mention in the Introduction, that our approach is very similar in spirit to the calculation of fermion damping rates in 'hot' QED and QCD, where the gauge structure of the theory is not particularly important as far as infrared properties are concerned. This problem has a long history, and the relevant theoretical approach, based on the finite temperature version of the Bloch-Nordsieck method, relies on exponentiation of infrared-divergent perturbation series (and is thus similar to the solution of the independent boson model in solid state theory.) The role of the long-range gauge propagator is played in our case by the phonon propagator. There are also important differences between our results and
those in hot gauge theories. One difference, which has experimental consequences for the damping rate, is the residual dependence on the infrared cutoff, which can be traced to the low dimensionality model (in the sense that a normally incident atom excites two-dimensional ZA phonons). On the other hand our perturbative expansion does not contain any polarization loop corrections (which are important ingredients of hot gauge theories), since in the case of a single atom interacting with phonon bath those are completely absent from the theory.

We would like to mention a comparison with a recent article. Our results based on the NCA and IBMA show a IR cutoff dependence which is a result of not fully treating the IR problem. As mentioned before, the technique of Soft-Phonon Resummation (SPR) at finite T completely solves the problem [32] and predicts an exponential suppression of sticking. This result in the limit of $\epsilon \to 0$ gives an adsorption rate that is seen to exponentially vanish in contrast to $T = 0$ case [31, 32].

We envisage applications of our approach to related physical systems, such as graphene under additional uniaxial strain, and other atomically thin materials, for example dichalcogenides and similar systems. In these materials various types of strain are expected to exist [4], as well as larger (compared to graphene) spin-orbit interactions. Additional uniaxial strain for example also affects strongly the van der Waals potential near the surface [114]. Therefore the atom damping rate is expected to be very sensitive to the physical characteristics of the atom-surface interactions, such as the strain-modified shape of the ZA phonon modes and the van der Waals interactions between atoms and surfaces which determine the bound state energies and corresponding phonon coupling parameters.

In the next part, we will discuss the collective behavior of atoms near graphene
and TMDC surfaces, in particular, the fluid-surface interaction effects.
Part III

Fluid - Surface Interactions
Chapter 4

Theory of Liquid Film Growth & Critical Wetting Instabilities

Theoretical studies on the formation of liquid film in a multi-layered system of dielectrics is a historic problem and has stimulated active research in the field for many years. The crux of the problem revolves around our understanding of the forces of interaction between different layers of dielectric. In his seminal work, Lifshitz [94] derived an expression for the interaction force between two dielectric half spaces separated by vacuum based on Maxwell’s stress tensor. The foundation of his calculation is established on the consequences of the changes in the zero point electromagnetic field energy due to the presence of the dielectrics. In a parallel work, using diagrammatic approach, Dzyaloshinkii [47] derived an analytical expression of the change in free energy for a system of dielectrics. Their calculation was based on summing over all the many-body vdW interactions. It turns out that the quantum field theoretic approach of Dzyaloshinskii created a well-defined connection between the non-additive, many-body vdW interaction and macroscopic quantum electrody-
nal approaches such as the Maxwell’s stress tensor formulation. Based on the idea of the Dzyaloshinskii-Lifshitz-Pitaevskii[8, 47], we aim to devise a theory of liquid film growth on 2-dimensional surfaces. Simply put, we will extend the DLP theory to include the polarization of a 2D material in an anisotropic layered dielectric sandwich. But before we get into the detailed calculations, let us first review some definitions and the current status of the problem.

4.1 Overview

The wetting of an electrically neutral solid surface by a liquid is controlled by the relative size of attractive van der Waals interactions between molecules in the liquid and those between the liquid and substrate. For weak liquid-substrate interactions, the surface may undergo partial wetting manifest as the coexistence of distinct liquid droplets with an atomically thin layer of adsorbed molecules between them. In the opposite complete wetting regime, the liquid atoms are strongly attracted to the surface resulting in the formation of a macroscopically thick film in equilibrium with the vapor above it [16].

The growth and stability of this film beyond a few atomic layers is dominated by the long range tail of the van der Waals (vdW) interaction which can be thought of as creating an effective repulsion between the liquid-vapor and liquid-substrate boundaries [8, 47, 48]. For intermediate liquid-surface interactions it is possible that at a critical film thickness, $d_c$, (larger than any atomic length scale) this repulsion vanishes and wetting is arrested due to the lack of any energetic gain for molecules in the vapor to adsorb into the liquid – a scenario known as incomplete wetting.
A quantitative characterization of the wetting is possible through the calculation of the contact angle of a bulk droplet that forms on the substrate [62, 87].

In this chapter we report on the physics of wetting in the novel class of geometries depicted in Fig. 4.1, made possible by the ability to readily fabricate and manipulate atomically flat two-dimensional (2D) crystals such as graphene [25], transition-metal dichalcogenides [156] (e.g. MoS$_2$) and representatives of the 2D topological insulator family [43, 51, 53, 113] (silicene and germanene). This includes graphene placed on a substrate, submerged in a liquid, or suspended with a vacuum underneath, realizable due to the impermeability of graphene to even small atoms [20, 111]. Essentially we aim to address the following: (i) scrutinize the vdW interaction forces and predict a relation between the thickness of the film (d) and the chemical potential ($\mu$) (ii) probe the spreading of the droplet and investigate the stability of the films.

We have organized the rest of the chapter as follows: we begin with a derivation of the effective vdW force for the multilayer dielectric system where we review the DLP theory and show how it is modified by the insertion of a graphene sheet (Sec. 4.2). Additionally, we report quantitative results for wetting and film growth in the three configurations in Fig. 4.1. In Sec. 4.3, for the suspended geometry we examine the spreading of droplets on the liquid surface and discuss the formation of long-wavelength surface instabilities. We conclude with a discussion of our main results and the probable experimental measurement of these effects in Sec. 4.4. All detailed calculations are given in the Appendices Sec. B.1.
Figure 4.1: Three geometries that are unique to wetting on two-dimensional materials. From left to right – Substrate: graphene with a momentum and frequency dependent electronic polarization $\Pi(\vec{q}, i\omega)$ is placed on top of an insulating substrate with dielectric constant $\varepsilon_3$ and a macroscopic liquid film with $\varepsilon_2$ grows to a thickness $d$ that is in equilibrium with its vapor ($\varepsilon_1 \approx 1$). Submerged: graphene is floated on top of a liquid with dielectric constant $\varepsilon_2$ and a liquid film of the same substance grows on the top side. Suspended: a liquid film grows on top of a pensile graphene sheet.

4.2 Effective vdW force for the multi-layer dielectric system

The starting point is the calculation of the vdW energy $U(d)$ of a charge neutral system composed of three substances (having dielectric functions $\varepsilon_{1,2,3}$) as shown in Fig. 4.1, with the atomically thin graphene layer, characterized by polarization $\Pi$, inserted at the boundary between regions 2 and 3. $U(d)$ represents the vdW interaction between the 1-2 and 2-3 material surface boundaries separated by distance $d$. It is well-known [8, 73] that $U(d)$ can be related to the momentum ($\vec{q}$) and frequency ($\omega$) dependent effective dielectric function $\mathcal{E}(\vec{q}, i\omega)$ which characterizes the screening of the interlayer Coulomb potential. $U(d) = (\hbar/n)(2\pi)^{-3}\int d^2\vec{q} \int_0^\infty d\omega \ln \mathcal{E}(\vec{q}, i\omega)$, where $n = N/V$ is the density of the liquid (material 2). It should be noted that for a single-material system (i.e. characterized by only one dielectric constant) this formula is
simply the random phase approximation (RPA) correlation energy, while in the case of anisotropic layered structures it represents the fluctuation (vdW) energy. We set ℏ = 1 from now on.

The calculation of $E$ involves the electrostatics of a three layer system. For example, for the configurations of interest in Fig. 4.1 one obtains the following formula \[7, 78\] for the properly screened interlayer Coulomb potential $U_{12}$ between 1 and 2:

$$U_{12} = \frac{V_{12}}{\varepsilon_g}, \quad V_{12} = \frac{8\pi e^2}{q D(q)}$$

and the effect of graphene is in the additional screening characterized by

$$\varepsilon_g(q, i\omega) = 1 - V_2(q) \Pi(q, i\omega).$$ \hspace{1cm} (4.2)

Here, $V_2$ is the Coulomb potential within the lower boundary plane

$$V_2 = \frac{4\pi e^2}{q D(q)} \left[ (\varepsilon_1 + \varepsilon_2)e^{qd} + (\varepsilon_2 - \varepsilon_1)e^{-qd} \right].$$ \hspace{1cm} (4.3)

Then, keeping in mind that $U_{12} \propto e^2 e^{-qd}/[q E(q, i\omega)]$, we obtain:

$E(q, i\omega) = \varepsilon_g(q, i\omega) D(q)e^{-qd}$, and finally

$$U(d) = \frac{1}{n(2\pi)^3} \int d^2 q \int_0^\infty d\omega \ln [\varepsilon_g(q, i\omega) D(q)e^{-qd}].$$ \hspace{1cm} (4.4)

It is instructive to simplify Eq. (4.4) in the limit $(\varepsilon_2 - 1) \ll 1$, which is satisfied with high accuracy for the low-density systems we have studied (such as He and other
light elements). In this case, their vapor can be considered as vacuum \((\varepsilon_1 = 1)\), and suppressing \(\vec{q}\) and \(\omega\) dependence:

\[
U(d) \approx \frac{1}{n(2\pi)^3} \int d^2q \int_0^\infty d\omega (U_d + U_g),
\]

(4.5)

with dielectric:

\[
U_d = \frac{(\varepsilon_2 - 1)(\varepsilon_3 - \varepsilon_2)}{(\varepsilon_2 + 1)(\varepsilon_3 + \varepsilon_2)} e^{-2qd}
\]

(4.6)

and graphene parts:

\[
U_g = \frac{-4\pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)} \frac{(\varepsilon_2 - 1)(\varepsilon_2 + 1)(\varepsilon_3 + \varepsilon_2)}{1 - \frac{4\pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)}} e^{-2qd}.
\]

(4.7)

The corresponding vdW force can be obtained from \(F(d) = -\partial U(d)/\partial d\) which has dimensions of energy due to the normalization factors chosen in Eq. (4.4). [Detailed calculations for the vdW correlation energy \(U(d)\) and force \(F(d)\) are given in Appendix B.1.]

When graphene is absent \((U_g = 0)\), we recover the well known DLP theory expression [47, 48, 95]. In particular it describes the important property of vdW repulsion (a force per unit area known as the disjoining pressure) for \((\varepsilon_3 - \varepsilon_2) > 0\). We note that inserting graphene will always lead to repulsion as \(\Pi < 0\). Eq. (4.7) can be used to describe the three main configurations: graphene on a substrate (characterized by \(\varepsilon_3\)), submerged \((\varepsilon_3 = \varepsilon_2)\), and suspended graphene \((\varepsilon_3 = 1)\). In the next section, we study in detail the effect of substrate which corresponds to our first geometry in Fig. 4.1.
4.2.1 Graphene on Substrate

Recent contradictory research articles on the wettability of graphene lead to debatable questions: (i) is graphene transparent to wetting? (ii) does coating a substrate with graphene impact the wetting properties of the substrate? Conflicting claims of wettability of graphene is examined via molecular dynamics calculation, water contact angle measurements and wetting theory [1, 126]. Employing molecular dynamics simulations and theoretical methods there are atleast two contradictory research results on the wetting transparency of graphene that predicts no effect on the wetting of the substrate due to the presence of intermediate graphene [124, 138, 139]. Here, we use the formalism described in Sec. 4.2, to investigate in detail the effect of substrates on the phenomenon of wetting in presence of graphene.

Effect of Substrates

To calculate $U_d$, we take the dielectric function of light elements to have a single oscillator form: $\varepsilon_2(i\omega) = 1 + C_A/[1 + (\omega/\omega_A)^2]$, where for $^4\text{He}$ we use $\omega_A = \omega_{\text{He}} \approx 27$ eV and $C_{\text{He}} = 0.054$. Parameters for other materials are given in the Appendix B.2. The substrate dielectric function can typically be well fitted to the form, $\varepsilon_3(i\omega) = 1 + C_{IR}/[1 + (\omega/\omega_{IR})^2] + C_{UV}/[1 + (\omega/\omega_{UV})^2]$. For example in the case of SiO$_2$ (quartz): $\omega_{UV} \approx 13.37$ eV, $\omega_{IR} \approx 0.138$ eV, and $C_{IR} = 1.93$, $C_{UV} = 1.359$.

The final result can be conveniently written as:

$$F(d) = \frac{\omega_A}{n16\pi^2} \frac{I(d)}{d^3} \equiv \frac{\Gamma(d)}{d^3}, \quad (4.8)$$

where the dimensionless expression for $I(d)$ is given in the Appendix B.1 and is used
Figure 4.2: Additional liquid film thickness dependence $\Gamma(d)$ (beyond $1/d^3$) of the van der Waals force between the substrate-liquid and liquid-vapor interfaces due to the insertion of graphene on a SiO$_2$ substrate. The dashed line represents the substrate contribution (in the absence of graphene) and a crossover from $1/d^4$ to $1/d^3$ is observed. Left vertical scale corresponds to helium and the right to nitrogen films.

to calculate $\Gamma(d)$. It is clear from Eqs. (4.5)–(4.7) that the dielectric part leads to a pure $1/d^3$ dependence of the force ($\Gamma(d) = \Gamma_0$ as $\varepsilon_{1,2,3}$ do not depend on momentum). However, the graphene contribution has substantial momentum dependence (due to the polarization $\Pi(q, i\omega)$), and causes a $1/d^4$ law above some length-scale. The overall behavior has the scaling form (second term due to graphene):

$$\Gamma(d) = \Gamma_0 + \frac{\Gamma_1}{d + L}. \tag{4.9}$$

Fig. 4.2 shows how the insertion of graphene on a quartz substrate enhances the vDW repulsion between the substrate-liquid and liquid-gas interfaces for helium and
nitrogen gas. Graphene introduces a substantial distance dependence to the force that is larger than that previously reported for graphite [93]. While relativistic corrections can create crossovers in the distance dependence, they happen at larger micron-scales, while here we see a dominant, purely non-relativistic contribution at nanometer lengths. Similar behavior is observed for other substrates such as 6H-SiC (see Fig. 4.3). The crossover length $L$ introduced in Eq. (4.9) is also sensitive to the details of the substrate and for helium we find that $L \sim 10$, i.e. the crossover toward pure $1/d^4$ behavior in the graphene part occurs quite rapidly.

![Figure 4.3: Van der Waals force contribution $\Gamma(d)$ for a 6H-SiC substrate with parameters $C_{IR} = 3.67$, $\omega_{IR} = 0.1$ eV, $C_{UV} = 5.53$, $\omega_{UV} = 7.39$ eV. This can be compared with that of SiO$_2$ (Fig. 4.2). While the magnitude of the van der Waals force shows significant variations between substrates, the overall distance dependence, and crossover length scale remains comparable.](image)

Another important quantity which characterizes the van der Waals force is the
length scale $L$ defined in Eq. (4.9) which sets the crossover from $1/d^3$ to $1/d^4$ behavior.

Due to the Dirac fermion motion in graphene (i.e. the strong momentum dependence of graphene’s polarization) the force crosses over to a stronger power law at distances beyond $L$. In the next subsection, we quickly comment on the effect of uniaxial strain towards the phenomenon of wetting.

**Influence of Uniaxial Strain in Graphene**

The existence of two-dimensional (2D) materials such as graphene opens up the attractive possibility to manipulate van der Waals forces by mechanical manipulation of the substrate – strain. This is due to the strong influence of strain on the electronic motion and consequently substantial change in graphene’s polarization. The case of uniaxial strain is the most straightforward to analyze, in which case graphene’s polarization is

$$\Pi(q, i\omega) = -\frac{1}{4v_xv_y} \frac{v_x^2q_x^2 + v_y^2q_y^2}{\sqrt{v_x^2q_x^2 + v_y^2q_y^2 + \omega^2}}. \quad (4.10)$$

Here we assume strain is in the $y$ (armchair) direction leading to decrease of the electron velocity $v_y$ in that direction (while the velocity in the perpendicular ($x$) direction remains practically unchanged). It is convenient to introduce the ratio $v_\perp = v_y/v_x < 1$ which reflects the strain (relative increase in lattice spacing); this ratio is perturbatively proportional to strain for small values but exhibits non-linear behavior for larger deformations. For example $v_\perp = 0.2$ corresponds to 34% strain, $v_\perp = 0.4$ corresponds to 25% strain, and $v_\perp = 0.75$ corresponds to 10% strain.

Figure 4.4 quantifies the effects of strain. Due to the increase of the graphene polarization Eq. (4.10), the van der Waals interaction increases and thus strain promotes wetting. While at present such strong strain is difficult to achieve in graphene,
mechanical deformations are also expected to be present in a variety of 2D materials, and thus the general tendencies described here could be important in a variety of physical situations. As a consequence of the enhanced van der Waals interaction with strain, the tendency towards film growth is enhanced. In the following subsection, we investigate the other two geometries in Fig. 4.1.

## 4.2.2 Submerged & Suspended Graphene

The vdW force in the submerged and suspended geometries that are unique to 2D materials are evaluated in detail in Appendix. B.1, the corresponding quantitative results are shown in Fig. 4.5 for helium, hydrogen and nitrogen films. In all cases we compare with calculations from Cheng and Cole for adsorption on graphite (dashed
Figure 4.5: Thickness dependence of the van der Waals interaction $\Gamma(d)$ for films formed on submerged and suspended graphene (see Fig. 4.1) composed of helium, hydrogen and nitrogen. The dashed line corresponds to films on graphite taken from Cheng and Cole. For submerged graphene, $\Gamma(d \to \infty) = 0$ and in the suspended geometry, there is an instability causing film growth to be arrested where $\Gamma(d \geq d_c) \leq 0$.

For submerged graphene ($\varepsilon_3 = \varepsilon_2$, filled circles) $U_d = 0$ (see Eq. (4.6)) and $\Gamma(d)$ decays to zero, in stark contrast to the case of a graphene plated substrate. For suspended graphene ($\varepsilon_3 = 1$, squares), we observe a novel physical effect for all elements: there is a critical distance $d_c$ at which graphene’s (always positive) contribution becomes so weak it can no longer compensate the negative dielectric part and $\Gamma(d_c) = 0$. Such an effect is only possible for purely 2D materials that can be suspended without a supporting substrate - graphene [15, 20, 107] is the best (but
not only) candidate in this family. For $d > d_c$ the liquid film growth stops under equilibrium conditions and the system becomes unstable. This is the incomplete wetting scenario discussed in the overview. For $d < d_c$ the characteristic isotherms that determine the change of the chemical potential of the film (relative to bulk), $\Delta \mu = \mu(d) - \mu(d = \infty)$, are determined by the usual equilibrium condition (where $P_0$ is the saturated vapor pressure) [83, 132]

$$\Delta \mu = -\frac{\Gamma(d)}{d^3} = T \ln \frac{P}{P_0}, \quad P \leq P_0. \quad (4.11)$$
Fig. 4.6 shows the resulting chemical potential for helium, hydrogen and nitrogen on suspended graphene which exhibits textbook behavior [83] for an unstable system. The suspended film transition from stable \((d < d_c)\) through a metastable region with \(d > d_c\) where \(\partial \Delta \mu / \partial d > 0\); and finally becomes unstable for \(d > d_c, \partial \Delta \mu / \partial d < 0\). The values of the critical film thickness \(d_c\) are found to be on the order of 3-30 nm and are reported in Table 4.1.

**Influence of Uniaxial Strain in Graphene**

![Graphene Strain Dependence](image)

*Figure 4.7: Strain dependence of critical film thickness \(d_c\) in the suspended graphene geometry. For example the parameter value \(1 - v_\perp = 0.8\) corresponds to 34% strain, while \(1 - v_\perp = 0.6\) corresponds to 25% strain. The general tendency, particularly important for moderate to strong strain, is promotion of film growth (increase of critical \(d_c\)).*

In particular, it is instructive to investigate the effect of uniaxial strain for the suspended geometry to probe the variation of the critical thickness \(d_c\) with strain. In Fig. 4.7, we observe that while in the suspended geometry (suspended graphene with
no supporting substrate) films can grow only up to a finite thickness $d_c$, the value of $d_c$ increases with strain as illustrated in Fig. 4.4 (right). This effect is quite weak for small strain and becomes significant as strain grows. In addition we find substantial dependence on the type of atom (the effect is strongest for helium).

We explore the phenomenon of the wetting instability related to the suspended geometry in Sec. 4.3.

4.3 **CRITICAL WETTING INSTABILITY: A SPECIAL CASE FOR SUSPENDED GEOMETRY**

In our previous section, we observed the special case of suspended graphene where for a certain critical thickness $d_c$, the interface interaction energy is seen to vanish. This calculation was primarily carried out for an undoped suspended graphene. The next natural cause of affair would be to consider the effect of doped (metallic) graphene. We will also carry out a similar investigation for the dielectrics including the insulator family of dichalcogenides. In essence, our aim in this section of the chapter is to understand if the effect of critical wetting instability is universal for all classes of 2-dimensional materials.

4.3.1 **DOPED GRAPHENE**

It is important to investigate the effect of finite carrier concentration $n_e$ in graphene, when the Fermi energy $\varepsilon_F$ is shifted away from the Dirac (charge neutrality) point, and compare with results for undoped graphene ($\varepsilon_F = 0$). Experimentally, in suspended
Figure 4.8: Variation of the van der Waals force $\Gamma(d)$ in the case of He in the suspended geometry, for doped graphene. The densities corresponding to the shown Fermi energies are: $n_e \approx 8 \times 10^9, 10^{11}, 10^{12}, 7 \times 10^{12}, 2 \times 10^{13}$ cm$^{-2}$. For smaller densities ($\varepsilon_F < 40$ meV) the results are indistinguishable from the undoped situation. The Fermi energy is related to the density via $\varepsilon_F = v \sqrt{\pi n_e}$. The overall effect of doping is quite small and becomes noticeable for higher densities only. The general tendency is an increase of $d_c$ due to the increased polarization of doped graphene (inset).

graphene samples [45, 49], the carrier density can be very small $n_e < 10^{10}$ cm$^{-2}$, and thus a close proximity to the Dirac point can be achieved, with $\varepsilon_F \sim 10$ meV.

We use the well-known polarization for doped graphene [9]

$$
\Pi(q, i\omega) = -\frac{q^2}{4\sqrt{\omega^2 + v^2 q^2}} - \frac{2\varepsilon_F}{\pi v^2} + \frac{q^2}{2\pi \sqrt{\omega^2 + v^2 q^2}} \text{Re} \left[ \arcsin \left( \frac{2\varepsilon_F + i\omega}{v q} \right) \right] \\
+ \left( \frac{2\varepsilon_F + i\omega}{v q} \right) \sqrt{1 - \left( \frac{2\varepsilon_F + i\omega}{v q} \right)^2} 
$$

(4.12)

and our results are summarized in Fig. 4.8. It is clear that at small densities the results for doped and undoped graphene are practically identical. Significant modification of
Figure 4.9: Comparison of various members of the dichalcogenides family, showing remarkably similar behavior. The material parameters, $\Delta$ - gap, $v$ - velocity, $g = (\pi/2)e^2/v$ - Coulomb interaction, are: WS$_2$: $\Delta = 1.79$ eV, $v = 4.38$ eV Å, $g = 5.16$; WSe$_2$: $\Delta = 1.6$ eV, $v = 3.94$ eV Å, $g = 5.74$; MoS$_2$: $\Delta = 1.66$ eV, $v = 3.51$ eV Å, $g = 6.44$; MoSe$_2$: $\Delta = 1.47$ eV, $v = 3.11$ eV Å, $g = 7.26$.

d$_c$ starts appearing only in the regime $\varepsilon_F > 100$ meV, which corresponds to substantial density $n_e \gtrsim 10^{12}$ cm$^{-2}$. It is natural that the instability tends to become suppressed with doping (i.e. $d_c$ tends to increase) since the polarization of graphene in the metallic regime increases. Thus the critical wetting instability remains fully present in strongly-doped suspended graphene (Fig. 4.8.)

### 4.3.2 Insulating layers of TMDC

While graphene provides the most well studied example of a 2D material, it is important to assess the applicability of our results to other 2D compounds. Numerous 2D materials have been discovered, forming groups suitable for designing so-called van
der Waals heterostructures [116]. In particular the group-VI dichalcogenides [156] include e.g. MoS\textsubscript{2}, WS\textsubscript{2}, MoSe\textsubscript{2}, etc., which exhibit a significant electronic gap $\Delta$ of order 1 eV, as well as a small spin-orbital interaction. For the purpose of van der Waals calculations, the most significant modification (compared to graphene) to be taken into account is the presence of the gap, while the spin-orbital component can be neglected. The polarization function in this case is [81]

$$\Pi(q, i\omega) = -\frac{|q|^2}{\pi} \left[ \frac{m}{\bar{q}^2} + \frac{1}{2\bar{q}} \left( 1 - \frac{4m^2}{\bar{q}^2} \right) \tan^{-1} \left( \frac{\bar{q}}{2m} \right) \right], \quad \bar{q} \equiv \sqrt{v^2|q|^2 + \omega^2}, \quad m = \Delta/2,$$

(4.13)

where $m$ is the Dirac mass (half of electronic gap). For example for MoS\textsubscript{2} $\Delta = 1.66$ eV, and other materials have similar parameters [156]. Neglecting the small spin-orbit interaction can result in several percent error but our main conclusions will remain intact. We assume the materials are in their insulating phases, i.e. the Fermi energy is in the gap. Fig. 4.9, shows a comprehensive nature of the variation of $d_c$ for the entire class of dichalcogenides.

Overall we conclude that the instability in the suspended geometry, with $d_c$ within several hundred Angstroms, is present in all three main 2D Dirac material groups: (insulating) dichalcogenides, semi-metallic (undoped) graphene, and doped graphene. Figure 4.10 summarizes the main tendencies exhibited by representatives of those groups, namely an increase of the critical film thickness as systems transition from insulating to metallic behavior.
Figure 4.10: Variation of the van der Waals force $\Gamma(d)$ in the case of He in the suspended geometry: MoS$_2$ compared to doped and undoped graphene. The result shows significant decrease of the maximum film thickness $d_c$ (from 300Å to $\approx$ 180Å), caused by the suppression of the force due to the presence of the large electronic gap $\Delta$ in MoS$_2$. A representative (quite substantial) doping value is also shown to illustrate the tendency with doping. The shown value of $\varepsilon_F$ corresponds to graphene carrier density $n_e \approx 7 \times 10^{12}$ cm$^{-2}$, well above the lowest-possible density that can be achieved in suspended graphene ($\approx 10^9$–10 cm$^{-2}$).

### 4.3.3 Surface Instabilities: Spinodal Decomposition

We now concentrate on the properties and implications of the incomplete wetting scenario where a liquid film with thickness $d_c$ is absorbed on suspended graphene. As processes governing the further wetting (partial or complete) of the liquid surface are governed only by the long range tail of the vdW interaction, they can display a
### Table 4.1: Critical film thickness and contact angles for three elements.
The surface tensions were taken to be: $\sigma_{He} \simeq 0.26 \text{ mN/meter}$, $T = 2.5 \text{ K}$; $\sigma_{H_2} \simeq 2 \text{ mN/meter}$, $T = 20 \text{ K}$; $\sigma_{N_2} \simeq 10 \text{ mN/meter}$, $T = 70 \text{ K}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>He</th>
<th>H$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_c$ (Å)</td>
<td>300</td>
<td>120</td>
<td>35</td>
</tr>
<tr>
<td>$\theta$ (°)</td>
<td>0.33</td>
<td>0.83</td>
<td>2.41</td>
</tr>
</tbody>
</table>

Wealth of phenomena of both theoretical and experimental importance [16, 19, 20, 37, 38, 40, 41, 71, 109, 111, 118, 123, 125, 149]. We can formulate an important question regarding wetting of the liquid film via a calculation of the contact angle $\theta$ of droplets which can form its surface. As these droplets are "far" from the substrate, the short-range adsorption potential is irrelevant, opening up the possibility of universal and continuous critical behavior. The value of the contact angle is related to the area under the $\Delta \mu(d > d_c)$ curve [47]:

$$1 - \cos(\theta) = \frac{n}{\sigma_{l-v}} \int_{d_c}^{\infty} \Delta \mu(l)dl = -\frac{n}{\sigma_{l-v}} \int_{d_c}^{\infty} \frac{\Gamma(l)}{l^3}dl$$

(4.14)

where $\sigma_{l-v}$ is the liquid-vapor surface tension. Results are shown in Table 4.1 and we find small angles on the order of a degree that increase with the polarizability of the adsorbant vapor.

The fact that $\theta > 0$ in all cases allows us to consider a remarkable analogy between surface film instabilities and the theory of spinodal decomposition [70, 85, 110, 127, 131, 137, 147]. The characteristic pattern instability length scale is governed by the competition between destabilizing vdW forces and the stabilizing action of the surface tension. The wavelength $\lambda$ which corresponds to amplified surface fluctuations (which
could ultimately cause "spinodal dewetting") in the unstable region ($\partial \Delta \mu / \partial d < 0$) is given by (for $d \gg L$)

$$
\lambda^2 \simeq -8\pi^2 \frac{\sigma_{l-v}}{n \left( \frac{\partial \Delta \mu}{\partial d} \right)} \simeq \frac{8\pi^2 \sigma_{l-v} d^4}{3 \left| \Gamma_0 \right|}.
$$

(4.15)

From Fig. 4.5, for example for H$_2$ we can estimate $|\Gamma_0| \sim 10^3$ KÅ, which yields $\lambda \sim 10^4$-$10^5$ Å for $d \approx 150$-$300$ Å.

Thus we find that the mesoscopic film may exhibit critical surface instabilities including pattern formation in analogy to spinodal decomposition [70, 85, 110, 127, 131, 137, 147].

4.4 Summary

In conclusion we have considered how the relatively weak van der Waals interactions between light atoms and graphene can substantially affect their wetting behavior when graphene is placed on a substrate, submerged in a liquid or suspended above vacuum. We find that placing graphene on a substrate enhances its propensity towards wetting during initial film growth which may have implications for its use as a conductive coating. For suspended graphene, the absence of any substrate material leads to an instability where film growth becomes arrested at a critical thickness. As the vapor pressure above this film is increased, droplets may form, driving surface fluctuations which can potentially have large amplitudes. It is significant that the critical film thickness $d_c$ is dependent on mechanical deformations (e.g. uniaxial strain) in graphene, and is also universally present for other 2D materials, such as members of the group-VI dichalcogenides family (MoS$_2$, WS$_2$, MoSe$_2$, etc.). Quite importantly, we also find that the instability occurs in doped graphene, within a wide
range of experimentally accessible carrier densities. Thus we conclude that this is a universal phenomenon in suspended 2D Dirac materials, ranging from insulating monolayer dichalcogenides to semi-metallic (undoped) and doped graphene. The exact value of $d_c$ itself, which we find to be on the order of several hundred Angstroms, depends on material characteristics such as band gap, quasiparticle velocity, strain and doping level. Experimental confirmation of these effects would involve the measurement of adsorbed film thickness using standard quartz microbalance [109, 144] or interferometry [123] techniques.

In our next part, we introduce the spin-orbit coupling effects on the anomalous response of spin-flip transition moment of Silicene-Germanene class of Topological insulators.
Part IV

Spin-Orbit Interaction
Chapter 5

Anomalous Spin-Flip Transition Moment

Manipulation of the spin degree of freedom of the electron, instead of its charge has led to the revolutionary ideas of *Spintronics*. Spintronics is an emerging paradigm with the aim to replace conventional electronics by utilizing the electron spins as information carriers [72, 153, 154]. The basic idea behind spintronics is based on the coherence of the spin, spin relaxation rates or more precisely the spin dynamics of the system. In this Chapter, we will derive a unified theory of spin-flip transition moment related to the spin relaxation rate for the Topological Insulator family of Silicene-Germanene class of materials. Additionally, we will also predict corrections to this spin-flip transition moment due to the presence of long-range Coulomb interactions.
5.1 Overview

The triumph of quantum field theory is often attributed to the seminal work of Schwinger on the anomalous magnetic moment for an electron in an external magnetic field. Using the tools of QFT, he predicted a correction to the g-factor for a spin 1/2 massive electron due to its coupling to the photon as \( g = 2 + \mathcal{O}[^{\alpha}] \), where \( \alpha \) is the fine structure constant representing the coupling to the electromagnetic field. Seventy years later this prediction in theoretical physics still remains the most accurate and perhaps, the greatest achievements of twentieth century science. Part of its success is attributed to the precision with which the theoretical value matches the experiments, as examples- field theoretic calculations reveals \( g = 2.0023193043617 \) and painstaking experiments measured the corrected g-factor as 2.00231930436 (there is a match till 11 places of decimal !) In this chapter, we will calculate the correction to spin-flip transition moment reminiscent to Schwinger’s correction.

For Silicene-Germanene class of materials, the two sub-lattices are seen to be separated by a minute distance which causes a staggered potential. An applied field across this potential causes the band gap to evolve from a Topological Insulator to a bulk insulator via a Valley Spin Polarized State (VSPM). Indeed, this staggered potential is mapped to the spin-orbit coupling in these materials[52, 141]. Our attempt in this Chapter would be to derive the spin-flip transition moment for these materials as a function of different values of spin-orbit coupling. Remarkably, we will see that for different regimes of spin-orbit coupling, this system will eventually map into (i) Kane - Mele model and (ii) insulator family of TMDC.

We have organized this chapter in the following way: in Section. 5.2, we briefly
discuss the low-energy band structure in Silicene-Germanene and illustrate the general methods related to the calculation of (a) bare spin-flip transition moment and (b) anomalous spin-flip transition moment in the presence of an in-plane magnetic field. In Secs. 5.4 and 5.3, we extend our calculations to two different models that describe the Kane Mele model and the 2D Transition Metal Dichalcogenides (TMDC) which are sub-classes of the Silicene-Germanene class of materials in specific regimes. In Sec. 5.5, we propose possible experimental techniques that can measure both the bare and the corrected spin-flip transition moments.

5.2 Silicene and Germanene

Monolayer arrangement of Silicon and Germanium atoms lead to the possible realization of another group of 2-dimensional materials namely, Silicene and Germanene. These materials exhibit buckled honeycomb lattices that differ from graphene in two major aspects. While graphene acts as a semimetal with massless Dirac electrons, Silicene exhibits characteristic features of a topological insulator with massive Dirac electrons and a large spin-orbit gap [52, 54, 141]. Presumably, one can generate a potential difference across the sublattices in these system of materials by applying an electric field perpendicular to the plane of the lattice [44, 52, 54, 112, 141]. By tuning this electric field, the low-energy band structure of these materials is seen to evolve from a Topological Insulator (TI) to a trivial Bulk Insulator (BI) via a quantum critical Valley Spin Polarized Metal (VSPM) state. Our aim in this section will be to calculate the anomalous spin flip transition moment for these class of materials. We will start our calculations by finding the low-energy band structure and the bare
spin-flip transition moment corresponding to the Silicene-Germanene model Hamiltonian (refer subsection 5.2.1). In subsection 5.2.2, we include the Coulomb interaction effects to find a correction to the bare transition moment which essentially allows us to predict the anomalous spin flip transition moment for these materials. Our main mathematical toolkit for this calculation is based on the method of Green’s function technique.

5.2.1 Low-Energy Band structure and Bare Spin-flip Transition Moment

In this subsection, we study the bare spin-flip transition moment for these type of materials. We begin with the derivation of the eigen energies and eigen functions related to the Hamiltonian that best describes this system [52, 54, 141]:

\[ H = v \sigma \cdot k + \frac{(\Delta - \lambda s_z)}{2} \sigma_z \]  

(5.1)

here, \( v \) is the Fermi velocity in the material, \( \Delta \) is the spin-independent gap which is modulated via the transverse electric field \( E (\Delta = Ed) \) where \( d \) represents the separation between two sub-lattices), \( \lambda \) is the spin-orbit coupling. Also the real spin of the electron is given by \( s = s_z = \pm 1 \) for spin up and spin down and \( \hat{\sigma}_z \) represents the pseudospin associated with the Pauli spin matrices. In our derivations we choose the convenient natural units \( \hbar = v = 1 \), hence otherwise mentioned.

For the above Hamiltonian, the exact wave functions at momentum \( k \) are:
Figure 5.1: Dispersion curves for Silicene-Germanene type of materials. With the proper tuning of electric field ($\Delta = Ed$ where $d$ represents the separation between two sub-lattices), the band structure shows a transition from a topological insulator ($\Delta \ll \lambda$) to a band insulator ($\Delta \gg \lambda$) via the quantum critical VSPM state ($\Delta = \lambda$). Subsequent removal of the spin degeneracy is also observed for the bulk insulator regime ($\Delta \gg \lambda$).

$$\Psi(k)_n = \frac{k}{\sqrt{k^2 + (E_{k,n}^s)^2}} \left( \begin{array}{c} 1 \\ \frac{E_{k,n}^s}{(k_x - ik_y)} \end{array} \right), \quad n = 1, 2$$

(5.2)

$n = 1$ labels the conduction band; $n = 2$ labels the valence band. We define, $E_{k,n}^s$ as:

$$E_{k,n}^s = \varepsilon_{k,n}^s - \frac{(\Delta - \lambda s)}{2}, \quad s = s_z = \pm 1$$

(5.3)

where the eigen energies associated with the conduction and valence band are given by $\varepsilon_{k,n}^s$: 

\begin{align*}
\varepsilon_{k,n}^s &= \varepsilon_{k,n}^s - \frac{(\Delta - \lambda s)}{2}, \\
&= \pm 1
\end{align*}
ε^s_{k,1} = \varepsilon_k^s > 0, \ n = 1 \quad (5.4)

ε^s_{k,2} = -\varepsilon_k^s < 0, \ n = 2 \quad (5.5)

and we use the definition:

ε^s_k \equiv +\sqrt{k^2 + [(\Delta - \lambda s)^2/4]} \quad (5.6)

Fig. 5.1 represents the low-energy band structure corresponding to Eq. 5.6. As, we can see with the increase in the applied electric field \( E \equiv \Delta \), the low-energy band structure evolves from a topological insulator (TI) to the trivial band insulator (BI) with the existence of a Valley Spin Polarized Metallic State (VSPM) at the quantum critical point \( \Delta = \lambda \)[141].

Let us now consider an in-plane magnetic field \( B_x \) such that the bare spin-flip transition moment is given by \( \mu = \langle \downarrow | S_x | \uparrow \rangle \) (see, Fig. 5.3). Here \( | \uparrow \rangle \) and \( | \downarrow \rangle \) are the corresponding conduction band \( (n = 1) \) wave functions given by Eq. 5.2:

\[
| \uparrow \rangle = \Psi(k)^+ = \frac{k}{\sqrt{k^2 + (E_{k,1}^+)^2}} \begin{pmatrix} 1 \\ E_{k,1}^+/(k_x - ik_y) \end{pmatrix} \quad (5.7)
\]

\[
| \downarrow \rangle = \Psi(k)^- = \frac{k}{\sqrt{k^2 + (E_{k,1}^-)^2}} \begin{pmatrix} 1 \\ E_{k,1}^-/(k_x - ik_y) \end{pmatrix} \quad (5.8)
\]

Therefore, the bare spin-flip transition moment is calculated:

\[
\mu = \langle \downarrow | S_x | \uparrow \rangle = \frac{k^2 + E_{k,1}^+ E_{k,1}^-}{\sqrt{(k^2 + |E_{k,1}^+|^2)(k^2 + |E_{k,1}^-|^2)}} \quad (5.9)
\]
Figure 5.2: Variation of the bare spin-flip transition moment $\mu = \langle \uparrow | S_x | \downarrow \rangle$ with the rescaled momentum $2k/\lambda$ for several values of $\Delta/\lambda$. As the coupling parameter $\Delta/\lambda$ increases the system makes a transition from TI to BI via the VSPM state ($\Delta/\lambda = 1$).

We plot the variation of the bare spin-flip transition moment $\mu \equiv \langle \downarrow | S_x | \uparrow \rangle$ with the rescaled momentum described by the dimensionless quantity $(2vk/\lambda)$ for various values of $\Delta/\lambda$ in Fig. 5.2.

In our next subsection, we will incorporate the Coulomb interaction $V(p) = 2\pi e^2/p$ and calculate the correction to the bare spin-flip transition moment.
5.2.2 Anomalous Response to In-plane Magnetic Field

In this subsection, we will use the method of Green’s function to derive the interaction correction to the transition moment. The associated Feynman diagram is given by Fig. 5.3 (right). We begin with the Green’s function $G(k, \omega)$ corresponding to the Eq. 5.1. [Detailed calculations for the derivation of the Green’s functions for the different models are given in Appendix C.1.]

$$G(k, \omega) = \frac{1}{2\varepsilon_k^s} \left[ \frac{\varepsilon_k^s + \sigma \cdot k + \left( \frac{\Delta - \lambda s_z}{2} \right) \sigma_z}{(\omega - \varepsilon_k^s + i\eta)} + \frac{\varepsilon_k^s - \sigma \cdot k - \left( \frac{\Delta - \lambda s_z}{2} \right) \sigma_z}{(\omega + \varepsilon_k^s - i\eta)} \right]$$ (5.10)

Following Feynman rules, the analytical expression for the correction term $\delta \mu$ is
Figure 5.4: Variation of the correction function $F(2k/\lambda)$ with $2k/\lambda$ for various values of coupling $0 < \Delta/\lambda < 2$. The correction term is seen to be large for the topological insulators ($\Delta/\lambda \ll 1$) compared to the VSPM ($\Delta/\lambda = 1$) or bulk insulators states ($\Delta/\lambda \gg 1$).

Given as:

$$
\sum_p i \int \frac{d\omega}{2\pi} \langle \downarrow | G^{s=1}(p,\omega) S_x G^{s=1}(p+q,\omega) | \uparrow \rangle V(|p - k|), \; q \rightarrow 0 \tag{5.11}
$$

Using the expression for Green’s function given in Eq. 5.10, we first evaluate the frequency integral:

$$
i \int \frac{d\omega}{2\pi} \left[ G^- G^+ \right] = \frac{1}{2\varepsilon_p \varepsilon_p^+ (\varepsilon_p^+ + \varepsilon_p^-)} \left[ \varepsilon_p^- \varepsilon_p^+ - (\sigma \cdot p)^2 + \left( \frac{\lambda^2 - \Delta^2}{4} \right) + \lambda (\sigma \cdot p) \sigma_z \right] \tag{5.12}
$$

Finally the correction term $\delta \mu$ is evaluated by plugging Eqs. (5.7), (5.8) and (5.12)
into Eq. (5.11):

$$
\delta \mu = \langle \Downarrow | S_x | \Uparrow \rangle \sum_p \frac{V(|p - k|)}{2\varepsilon_p^+ \varepsilon_p^- (\varepsilon_p^+ + \varepsilon_p^-)} \left[ \varepsilon_p^+ \varepsilon_p^- - p^2 + \frac{\lambda^2 - \Delta^2}{4} + \lambda (p \cdot k) \frac{\varepsilon_k^- - \varepsilon_k^+ - \lambda}{k^2 + E_{k,1}^+ E_{k,1}^-} \right]
$$

$$
= \langle \Downarrow | S_x | \Uparrow \rangle F(2k/\lambda, \Delta/\lambda)
$$

(5.13)

Here, we have introduced a quantity $F(2k/\lambda, \Delta/\lambda)$ in terms of the rescaled momentum, for various couplings $0 < \Delta/\lambda < 2$:

$$
\alpha_0 F(2k/\lambda, \Delta/\lambda) = \sum_p \frac{V(|p - k|)}{2\varepsilon_p^+ \varepsilon_p^- (\varepsilon_p^+ + \varepsilon_p^-)} \left[ \varepsilon_p^+ \varepsilon_p^- - p^2 + \frac{\lambda^2 - \Delta^2}{4} + \lambda (p \cdot k) \frac{\varepsilon_k^- - \varepsilon_k^+ - \lambda}{k^2 + E_{k,1}^+ E_{k,1}^-} \right]
$$

(5.14)

with $\alpha_0 = e^2/\epsilon_0 \hbar v$ is the effective fine-structure constant that defines the strength of the interactions, $\epsilon_0$ is the vacuum permittivity. Therefore, we write the total spin-flip transition moment as a sum of the bare spin-flip transition moment $\mu$ and the interaction correction $\delta \mu$:

$$
\mu + \delta \mu = \langle \Downarrow | S_x | \Uparrow \rangle (1 + \alpha_0 F(2k/\lambda, \Delta/\lambda))
$$

(5.15)

Let us plot the variation of the function $F(2k/\lambda)$ with the rescaled momentum ($2k/\lambda, v = 1$) in Fig. 5.4. It is clear to us that the correction to the spin-flip transition moment is maximum for topological insulators and decreases as the system evolves from the quantum critical state to the bulk insulators.

In our next section, we extend our calculations to the transition metal dichalcogenides (TMDCs) which physically correspond to bulk insulators that describe the
5.3 Atomically Thin Dichalcogenides

Atomically thin layers of MX$_2$ where M = transition metal (Mo, W, etc) and X = chalcogens (S, Se, Te, etc) represent the class of 2D materials namely, the transition metal dichalcogenides (TMDC). Unlike graphene which is a semimetal and shows no band gap, TMDCs show appreciable band gap that can lead to novel spin-valley electronics [22, 67, 155]. Monolayer MX$_2$ presents a honeycomb lattice structure where the metal and the chalcogen are placed on different sublattices. This leads to a broken inversion symmetry causing a large band gap ($\Delta$). In these materials, the origin of the spin-orbit coupling is traced back to the admixture of relevant $d$ - orbitals in the
metals [67]. To calculate the correction effects to the transition moment, we begin with the effective low energy Hamiltonian associated with the monolayer TMDCs:

\[
H = \sigma \cdot \mathbf{k} + (\Delta/2)\sigma_z - (\lambda/2)(\sigma_z - 1)s_z
\]

(5.16)

where, the allowed model parameters for MoS\(_2\) are \(\Delta \approx 1.66\) eV, \(2\lambda \approx 0.15\) eV; for WS\(_2\) are \(\Delta \approx 1.79\) eV, \(2\lambda \approx 0.43\) eV, and for WSe\(_2\) are \(\Delta \approx 1.6\) eV, \(2\lambda \approx 0.46\) eV [67, 155]. From the numerical values, we clearly see that we are in the regime:

\[
\Delta/\lambda \gg 1
\]

(5.17)

Next, we apply our regular procedure given in previous section to derive the exact wave functions at momentum \(k\) are:

\[
\Psi(k)_n^s = \frac{k}{\sqrt{k^2 + (E_{k,n}^s)^2}} \begin{pmatrix} 1 \\ E_{k,n}^s/(k_x - i k_y) \end{pmatrix}, \quad n = 1, 2
\]

(5.18)

As before, \(s\) is the spin index and \(n = 1\) labels the conduction band; \(n = 2\) labels the valence band. The definition of \(E_{k,n}^s\) is:

\[
E_{k,n}^s = \varepsilon_{k,n}^s - \Delta/2, \quad s = s_z = \pm 1
\]

(5.19)

where \(\varepsilon_{k,n}^s\) are the eigen energies (Fig. 5.5):

\[
\varepsilon_{k,1}^s = \lambda s/2 + \varepsilon_k^s > 0, \quad n = 1
\]

(5.20)

\[
\varepsilon_{k,2}^s = \lambda s/2 - \varepsilon_k^s < 0, \quad n = 2
\]

(5.21)
Figure 5.6: Bare spin-flip transition moment for the dichalcogenides for various values of $\lambda/\Delta$. For TMDCs the relevant value of $\lambda/\Delta \lesssim 0.15$, we see that the value of $\mu$ is almost a constant $\approx 1$ and shows negligible variation with the momentum.

and we use the definition:

$$\varepsilon^s_k \equiv + \sqrt{k^2 + [\Delta - \lambda s]^2/4}$$  \hspace{1cm} (5.22)

In Fig. 5.5, we show the low-energy band structure for this group of materials. We can see that this agrees with the bulk insulator regime ($\Delta \gg \lambda$) of the Silicene-Germanene model (Fig. 5.1).

Using the wave functions for the conduction band ($n=1$, $s_z = \pm 1$) given in Eq. 5.18, we derive the bare spin-flip transition moment term corresponding to Fig. 5.3.

$$\mu = \langle \downarrow | S_x | \uparrow \rangle = \frac{k^2 + E^+_{k,1} E^-_{k,1}}{\sqrt{(k^2 + [E^+_{k,1}]^2)(k^2 + [E^-_{k,1}]^2)}}$$  \hspace{1cm} (5.23)

In Fig. 5.6, we plot the variation of the bare spin-flip transition moment $\mu$ with
rescaled momentum described by dimensionless quantity \((2k/\Delta)\) for various values of \(\lambda/\Delta\). For the family of TMDCs, the relevant energy scale is given by the quantity \((\lambda/\Delta) \lesssim 0.15\). From the plot, we see that the value of \(\mu\) is almost constant (and is large) for the small values of \((\lambda/\Delta)\).

Next, we aim to calculate the interaction correction to the transition moment. The mathematical technique is similar to the method given in subsection 5.2.2. The interaction correction in the limit of \(q \to 0\) is given by Eq. 5.11 which corresponds to Fig. 5.3 (right panel). The Green’s function for this model is:

\[
G^s(p, \omega) = \frac{1}{2\varepsilon^s_p} \left[ \frac{\varepsilon^s_p + \sigma \cdot p + \sigma_z(\Delta - \lambda s)/2}{\omega - \varepsilon^s_{p,1} + i\eta} - \frac{-\varepsilon^s_p + \sigma \cdot p + \sigma_z(\Delta - \lambda s)/2}{\omega - \varepsilon^s_{p,2} - i\eta} \right] \quad (5.24)
\]

Using the above green function, we first perform the frequency integral, such that:

\[
i \int \frac{d\omega}{2\pi} \left[ G^- G^+ \right] \approx \frac{1}{4\varepsilon^+_p \varepsilon^-_p} \frac{1}{\lambda^2 - (\varepsilon^-_p + \varepsilon^+_p)^2} \left[ \lambda^2 \varepsilon^-_p (\sigma \cdot p) - 2\lambda^2 \varepsilon^+_p (\sigma_z + 1) - 4\lambda \varepsilon^+_p (\sigma \cdot p) \varepsilon^-_p \sigma_z \right] \quad (5.25)
\]

Here we have expanded the numerator up to \(O[\lambda^2]\). The pre-factors of Eq. 5.25 given by the energy denominators can be taken at \(\lambda = 0\) because their expansion starts from a constant and the next order is \(O[\lambda^2]\). Finally, the interaction correction to the transition moment is derived by taking the expectation value of the above equation with respect to the wave functions \(\Psi(k)^\pm\) (Eq. 5.18):

\[
\delta \mu = \sum_p V(k - p) \frac{(-1)}{16\varepsilon^4_p} \lambda^2 \frac{2}{k^2 + E^2_k} \Gamma(p, k) \quad (5.26)
\]

where the function \(\Gamma(p,k)\) is calculated to be:
\[ \Gamma(p, k) = \frac{1}{\varepsilon_p} \{\Delta E_k(k \cdot p) - 2p^2k^2\} + 2\varepsilon_p(k \cdot p) \left(1 - \frac{\Delta}{2\varepsilon_k}\right) \] (5.27)

In the above expression, we have used the following definitions:

\[ E_k = \varepsilon_k - \Delta/2, \quad \varepsilon_k \equiv +\sqrt{k^2 + [\Delta^2/4]} \] (5.28)

Therefore the sum of bare plus corrected transition moment has the structure:

\[ \mu + \delta\mu = \langle \downarrow | S_x | \uparrow \rangle (1 + \alpha_0(2\lambda/\Delta)^2 H(2k/\Delta)) \] (5.29)

The correction can be written in the form:

\[ \delta\mu = \langle \downarrow | S_x | \uparrow \rangle \alpha_0(2\lambda/\Delta)^2 H(2k/\Delta) \] (5.30)

where \( H(2k/\Delta) \) is a function that can be easily evaluated using Eq. 5.26 & Eq. 5.27, and is plotted in Fig. 5.7. From the figure we observe negligible interaction corrections to the transition magnetic moment for the TMDCs.

In our next section, we will extend our calculations on the correction to the spin-flip transition moment for the Kane-Mele model. This model serves as a prototype for the Topological Insulators and corresponds to a specific regime \((\Delta/\lambda \ll 1)\) associated with the Silicene-Germanene class of materials.
Figure 5.7: The correction function $H(2k/\lambda)$ for the dichalcogenides. Here, we have used the rescaled momentum: $2k/\Delta$. As can be seen from the figure, at $2k/\Delta = 0$, the value of the correction function $H(2k/\Delta)$ is very small ($\sim 0.08$.)

## 5.4 Kane Mele model

The Hamiltonian for the Silicene-Germanene class of materials can be mapped to the Kane-Mele model for $\Delta = 0$, such that:

$$H = v\sigma \cdot k + \lambda \sigma_z s_z$$  \hspace{1cm} (5.31)

The dispersion relation $\varepsilon_k$ and eigen functions at momentum $k$ are given by:

$$\varepsilon_k = \sqrt{k^2 + \lambda^2}$$  \hspace{1cm} (5.32)
\[ |\uparrow\rangle = \Psi(k)^{+1} = \frac{k}{\sqrt{2\sqrt{\varepsilon^2 - \lambda\varepsilon}}} \begin{pmatrix} 1 \\ \varepsilon - \lambda \\ \varepsilon + \lambda \end{pmatrix} \begin{pmatrix} 1 \\ \varepsilon - \lambda \\ \varepsilon + \lambda \end{pmatrix} \begin{pmatrix} (k_x - ik_y) \\ (k_x + ik_y) \end{pmatrix} \]

\[ |\downarrow\rangle = \Psi(k)^{-1} = \frac{k}{\sqrt{2\sqrt{\varepsilon^2 + \lambda\varepsilon}}} \begin{pmatrix} 1 \\ \varepsilon - \lambda \\ \varepsilon + \lambda \end{pmatrix} \begin{pmatrix} 1 \\ \varepsilon - \lambda \\ \varepsilon + \lambda \end{pmatrix} \begin{pmatrix} (k_x - ik_y) \\ (k_x + ik_y) \end{pmatrix} \]

We plot the low-energy band structure for this model in Fig. 5.8. As one can clearly see, this corresponds to the topological insulator regime in the Silicene-Germanene model analogous to \( \Delta/\lambda \ll 1 \).

\[ \begin{array}{c}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{Kane_Mele_Model}
\caption{Low-energy band structure for the Kane Mele model. Presence of the spin-orbit coupling term leads to a gap in the low-energy band structure which otherwise remains gapless at \( \varepsilon_k = \pm|k| \).}
\end{figure}
\end{array} \]

We follow the general procedure outlined in Subsection 5.2.1 to derive the bare transition moment.

\[ \mu = \langle \downarrow | S_x | \uparrow \rangle = \frac{k}{\sqrt{k^2 + \lambda^2}} \]

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For the correction to the transition moment, we start with the Green’s function for this model:

\[ G(k,\omega) = \frac{\omega + (\sigma \cdot k + \lambda \sigma_z s_z)}{\omega^2 - \varepsilon_k^2 + i\eta} \]  

(5.36)

An analytical expression corresponding to the interaction corrections (Fig. 5.3 right panel) is given by Eq. 5.11. Using Eq. 5.11 and Eq. 5.36, we derive an expression for the interaction correction \( \delta \mu \):

\[ \delta \mu = \frac{k}{\sqrt{k^2 + \lambda^2}} \alpha_0 W(k/\lambda) \]  

(5.37)

with

\[ \alpha_0 W(k/\lambda) = \frac{\lambda^2}{2} \int \frac{d^2p}{(2\pi)^2} \frac{V(|p - k|)}{\varepsilon_p^3} \left(1 - \frac{p \cdot k}{k^2}\right) \]  

(5.38)

We plot the correction function \( W(k/\lambda) \) in Fig. 5.9. A quick comparison of this figure with Fig. 5.4 shows that the Kane-Mele model is indeed a subset of the Silicene-Germanene class of materials for \( \Delta/\lambda \ll 1 \).

From Eqs. 5.35, 5.37 & 5.38, we write the total spin-flip transition moment:

\[ \mu + \delta \mu = \frac{k}{\sqrt{k^2 + \lambda^2}} \left\{1 + \frac{\lambda^2}{2} \int \frac{d^2p}{(2\pi)^2} \frac{V(|p - k|)}{\varepsilon_p^3} \left(1 - \frac{p \cdot k}{k^2}\right)\right\} \]  

(5.39)

Before we proceed to investigate the variation of the transition moment with the rescaled momentum, let us quickly consider the effect of substrate screening. The Coulomb interaction effect has so far being quantified by \( \alpha_0 = e^2/\epsilon_0 \hbar v \) which essentially assumes vacuum permittivity \( \epsilon_0 \). However with the presence of a substrate we include the screening effects in the renormalized \( \alpha \):

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Figure 5.9: Variation of the interaction correction function $F(2k/\lambda)$ with rescaled momentum $k/\lambda$. The magnitude of the correction is maximum at $k = 0$ and decays off with the increase in momentum.

\[
\alpha = \frac{\alpha_0}{1 + \frac{2\pi e^2}{k}|\Pi(k; 0)|} \quad (5.40)
\]

where we use the relevant static polarization function for a gapped spectrum $\Pi|(k; 0)|$ [82]:

\[
\Pi(k; 0) = -\frac{1}{\pi} \left( \frac{\lambda}{v^2} \right) - \frac{q}{2\pi v} \left[ 1 - \frac{4\lambda^2}{v^2k^2} \right] \tan^{-1} \left( \frac{vk}{2\lambda} \right), \quad \omega \to 0 \quad (5.41)
\]

Therefore, using Eq. B.27 in Eq. 5.40, we derive the final expression for the renormalized $\alpha$ in rescaled momentum units $(vk/\lambda)$:

\[
\alpha \left( \frac{vk}{\lambda} \right) = \frac{\alpha_0}{1 + 2\alpha_0 f(\frac{\lambda}{vk})} \quad (5.42)
\]
Figure 5.10: Variation of the total spin-flip transition moment ($\mu + \delta \mu$) with rescaled momentum ($vk/\lambda$) for the Kane-Mele Model. With the increase in $\alpha$ we see an enhancement in the total transition moment. We relate this increase to the enlarged correction effects related to Coulomb interactions. The inset plot shows the variation of $\alpha$ with the rescaled momentum. This plot is made with Fermi velocity of Silicene.

where,

$$f\left(\frac{\lambda}{vk}\right) = \frac{\lambda}{vk} + \frac{1}{2}\left[1 - 4\left(\frac{\lambda}{vk}\right)^2\right] \tan^{-1}\left(\frac{vk}{2\lambda}\right)$$

(5.43)

For a model of Silicene with numerical parameters $\lambda = 8$ meV and Fermi velocity $v = 5 \times 10^7$ cm/s [44, 100, 101, 142], we plot the variation of the total transition moment $\mu + \delta \mu$ with rescaled momentum ($vk/\lambda$) for several values of the renormalized $\alpha$ in Fig. 5.10. Additionally, in the inset plot, we show the variation of $\alpha$ with $vk/\lambda$. From the plot we see that with an increase in Coulomb interactions represented by an increasing $\alpha$, the total transition moment increases.

In the following section, we propose experimental methods related to spin precession and spin resonance techniques that can predict a correction to the spin-flip
5.5 EXPERIMENTAL PROPOSALS

Realization of a Spintronic device would thoroughly depend on the spin-relaxation \( (\Gamma_s) \) which is controlled by the spin-orbit coupling. In recent articles [17, 80], for a 4-band Hamiltonian with conduction band splitting, the spin relaxation rate \( (\Gamma_s) \) has been related to the spin-flip transition moment in the conduction band. This leads us to propose experimental techniques that can probe our theoretical predictions. Traditionally, ESR techniques are generally used to measure spin-relaxation rates. But here, we propose two more techniques that we might think will be able to measure our predictions.

Hanle Effects: Based on the idea of spin precession and spin-relaxation, we propose the measurement of spin polarization decay using both Optical Hanle & Electrical Hanle methods [61, 157].

Optical Hanle Method- The optical Hanle method resolves to measuring the spin precession of \( S_z \) owing to a transverse magnetic field \( (B_x) \). This measurement begins with an optical injection of spins by a weak laser pump. The transverse magnetic field is then applied which causes the spins to dephase and undergo spin precession. This induced spin polarization is then detected via a second wavelength tunable probe laser [61, 157]

The phenomenological equation of motion for the spin polarization can be written down in the form [61, 157]:

\[
\frac{dS}{dt} = \Omega_L \times S - \Gamma_s S \tag{5.44}
\]
where $\Gamma_s(\sim 1/\tau_s)$ corresponds to the spin relaxation rate (spin lifetime). The first term corresponds to the spin-precession due to the applied field ($B_x$) such that, $\Omega_L = g\mu_B B_x$. This leads to the Hanle curve which is a Lorentzian of type:

$$\int S_z(t)dt = \frac{S_0(1/\tau_s)}{(\frac{g\mu_B B_x}{\hbar})^2 + 1/\tau_s^2}$$  \hspace{1cm} (5.45)

where, we take $S_0 = 1$, Bohr magneton $\mu_B = 5.78 \times 10^{-5}$ eV T$^{-1}$. Thus, the half-width of the Hanle curve is a measurement of the spin life time ($\tau_s$).

Interestingly, there is a recent study on the spin-valley dynamics on 2D transition metal dichalcogenides [157] which reveal a spin life time $\tau_s \sim 3$ ns at a temperature $\sim 5$K. It will be interesting to see if our theoretical values match with the already published results.

**Electrical Hanle Method** - Here we consider a four-probe lateral spin device as shown in the inset of Fig. 5.11. A spin polarized current is injected through the two terminals on the right and the spins are seen to diffuse through the single-layer Silicene (SL-Si). Application of a perpendicular magnetic field causes the spins to precess. Electrical Hanle spin precession measurement is then carried out on these spins arriving at the detection circuit at the left.[65, 134, 161] The spin precession is characterized by the resistance $R$ which is given as:

$$R \propto \int_{-\infty}^{\infty} \frac{1}{\sqrt{4\pi D t}} \exp \left[ -\frac{L^2}{4Dt} \right] \cos(\omega_L t) \exp \left( -\frac{t}{\tau_s} \right) dt$$  \hspace{1cm} (5.46)

where, the Larmor frequency $\omega_L = g\mu_B/\hbar$. Spin precession is seen to occur across the length $L$ which serves as the distance between the second and third terminal in the four-probe spin device. The spin diffusion co-efficient, $D$ is related to the spin
Figure 5.11: A 4-probe spin device: The terminals on the extreme right are used to electrically inject a spin polarized current. While the spins diffuse through the single layer Silicene, an out-of-plane magnetic field is applied between terminals 2 and 3 which dephases the spins leading to the possibility of an electrical Hanle measurement. The two terminals on the extreme left are used for detection.

relaxation rate via the material parameter $\lambda_s$:

$$\lambda_s = \sqrt{D \tau_s}.$$ 

Relating the probability of spin-flip transition moment to the spin-relaxation rate ($\Gamma_s \sim 1/\tau_s$), we believe the above described experimental techniques can verify our theoretical predictions.

5.6 SUMMARY

In conclusion, we have developed a theory of anomalous response to spin-flip transition moment in 2D topological family of Silicene-Germanene class of materials. Starting from the low-energy Hamiltonian of the systems, our first task was to calculate the bare spin-flip transition moment for these group of materials and investigate its variation with respect to different values of spin-orbit coupling. Our results indicate that the bare transition moment increases as we increase the spin-orbit coupling in these materials. Another notable feature is the variation of the transition moment with the momentum vector. We found at $k = 0$, the bare moment is maximum for TMDC.
and minimum for Kane-Mele model. Additionally, we have calculated for the first time, the vertex term with 1 photon emission corresponding to the correction to the Spin-flip transition moment. Our results indicate minimum correction to spin-flip transition moments for TMDC and maximum for the Kane-Mele model.

We envision our results to have applications in the fields of spintronics-based devices as the spin-flip transition moment is conceptually relevant towards the calculation of the spin-relaxation rates.
Part V

Step 0.1
Chapter 6

Step 0.1 - Where to?

This is going to be the shortest chapter in the thesis. That is because here, I will summarize in a nutshell, what I have learnt and understood so far, presumably I call this the elemental Step 0. Of course, as the name of the chapter suggests, there is an infinitesimal .1 to the foundational Step 0. This point one represents my current questions, questions that have been motivated by the work of this thesis, and hence the natural where to? But before we move to Step point one, let us summarize the contents of Zero.

6.1 Step 0

We began with the idea of quantum field theory, the branch of physics that provides us with the physical explanation of the origin of any particle in this Universe. These particles are sometimes understood as the ripples of the underlying field and hence take part in mediating the forces of interaction. In quantum condensed matter physics, because of the many-body nature of the systems, the interaction effects produced by
These particles are not just interesting but exceptionally counter-intuitive. As for examples one can think about the physical features of superconductivity, superfluidity, fractional statistics and quantum phase transitions.

For this thesis, we chose three modest problems in quantum condensed matter physics related to few exotic 2-dimensional quantum materials.

In Chapter 2 & 3, we studied a model of cold atom impinging on suspended graphene membranes. This problem was studied in both zero and finite temperature formalism. The aim of the game was to derive the adsorption rate of the atom on the membrane. Conventional perturbation theory was seen to suffer severe infrared divergences due to the emission of many soft phonons. This led us to devise resummation techniques based on non-perturbative methods. We have so far devised 3 such techniques - Independent Boson Model Approximation (IBMA), Non-Crossing Approximation (NCA) and Soft-Phonon Resummation (SPR). All the 3 methods remedy the IR problem at $T = 0$ and give finite adsorption rates for micromembranes. However, for membranes maintained at very high temperature, these infrared problems are even more pronounced due to the (infinitely) many soft phonons excited in graphene. We have devised a technique to take account (resummation) of such processes in the spirit of the well-known exact solution of the independent boson model. Remarkably, there is also similarity to the infrared problems and their treatment (via the Bloch-Nordsieck scheme) in finite temperature "hot" quantum electrodynamics and chromodynamics due to the long-range, unscreened nature of gauge interactions. The method takes into account correctly the strong damping provided by the many emitted phonons at finite temperature. In our case, the inverse membrane size plays the role of an effective low-energy scale, and, unlike the above mentioned field theories,
there remains an unusual, highly nontrivial dependence on that scale due to the 2D nature of the problem. We present detailed results for the sticking (atomic damping rate) rate of cold atomic hydrogen as a function of the membrane temperature and size. We find that the rate is very strongly dependent on both quantities.

In Chapter 4, we have developed a theory which presents a universal picture of how graphene, a Dirac semimetal, influences the formation of liquid films (made of light atoms, such as He, H₂, N₂) on a variety of dielectric substrates or in suspended configurations, thus extending the well-known Lifshitz theory of film growth on dielectric substrates to a completely new domain of geometries involving two-dimensional (2D) materials. Applications involving a wide variety of 2D materials, in addition to graphene, can be readily incorporated. Within the regime of mesoscopic film thicknesses where film growth is driven by van der Waals (VDW) interactions, we have discovered that graphene has a profound effect on film formation. This is caused by the significant modification of the VDW interaction distance dependence, due to the motion of Dirac quasiparticles. We have derived and analyzed, for the first time, explicit formulas that incorporate the effects of atomically thin materials on wetting. Graphene as a 2D material also provides a unique novel wetting configuration in the so-called suspended geometry. It is well established that graphene can exist in a suspended or free-standing configuration, without a substrate present. We have discovered a new type of wetting instability: film growth is only possible up to a certain thickness, controlled by graphene’s VDW interaction, whereas beyond this critical thickness a metastable, and ultimately unstable regime develops. The instability is characterized by the formation of long wave-length "spinodal" patterns due to enhanced surface fluctuations. Such "dewetting" patterns are known to exist in
other systems, e.g. thin polymers, liquid crystal and liquid metals films, whereas our work is the first to predict spinodal-type instabilities for liquids (composed of light elements) forming on top of suspended graphene. Other exciting features of our work are: (I) the instability is a 'critical' zero temperature phenomenon, entirely driven by long-range VDW interactions (unlike other known cases), and can be additionally controlled by mechanical deformations, such as strain; (II) the instability is present in a variety of 2D materials "beyond graphene", such as members of the group-VI dichalcogenides family (MoS$_2$, WS$_2$, MoSe$_2$, etc.), currently an active area of solid state physics.

In Chapter 5, we have developed a unified theory of anomalous response of spin-flip transition moment for the Topological Insulator family of Silicene-Germanene class of materials. We have results that predict a large spin-flip transition moment for insulating TMDC compared to the TI system described by Kane-Mele model. However, the inclusion of Coulomb interaction effects show that the correction to the spin-flip transition moment is maximum for Kane-Mele and decreases as we increase the spin-orbit coupling effects. We propose experimental methods that can probe our spin-flip transition moment along with the Coulomb interaction correction effects.

6.2 **Step 0.1**

I have three questions now. I will not provide any technical background on them. Presumably Step 0 is the technical background.

Question 1: Similar to QED, can we predict Faddeev-Kulish Asymptotic states
for the IR problem in QAD?

Question 2: Can we develop a theory of liquid film growth on Weyl Semimetals?

Question 3: The band-gap of Silicene - Germanene class of materials evolves from TI to BI via a quantum critical VSPM. Can our calculations on the anomalous spin-flip transition rate catch this quantum critical state, both theoretically & experimentally?

I think it’s time to find answers to point 1.
Bibilography


model at finite coulomb interaction $U$: Generalized noncrossing approximation. 


Part VI

Appendix
Appendix A

A.1 \( T = 0 \): 2-loop atom self-energy

We show detailed calculation of the atom self-energy \( \Sigma_{kk} \) for the three diagrams - Nested, Overlap and loop-after-loop. We begin with the Nested.

A.1.1 Nested Diagram

Figure A.1: Nested Diagram
The nested diagram contributes $\Sigma^{(2)}_{kk}$ to the atom self-energy

$$\Sigma^{(2)}_{kk} = i^2 \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \sum_q \sum_{q'} g_{kk}^2 g_{bb}^2 G^{(0)}_{bb}(E - \omega)G^{(0)}_{bb}(E - \omega - \omega') G^{(0)}_{bb}(E - \omega) \times D(q, \omega) D(q', \omega')$$

\begin{equation}
\times \sum_q \sum_{q'} \frac{g_{kk}^2 g_{bb}^2}{(E + E_b - \omega_q)^2 (E + E_b - \omega_q - \omega_{q'})}. \tag{A.1}
\end{equation}

In the quasicontinuum limit, the above equation reduces to a double integral over complex $\omega$ and $\omega'$ plane:

$$\Sigma^{(2)}_{kk} = g^2 \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \frac{1}{(E_b - \omega)^2} \frac{1}{(E_b - \omega - \omega')}. \tag{A.2}$$

where we have used our definition of $g = g_{kk} g_{bb} \rho_0$ and $E \ll E_b$. As we see from above, the real part of the above integral always diverges at $\omega = E_b$ as a result of the double pole.

However, let us try to evaluate the double integral. We begin with the integral in complex $\omega'$ plane:

$$I = \int_\epsilon^{\omega_D} \frac{d\omega'}{E_b - \omega - \omega' + i\eta}$$

\begin{equation}
= \int_\epsilon^{\omega_D} \mathcal{P} \frac{1}{E_b - \omega - \omega'} - i\pi \int_\epsilon^{\omega_D} \delta(\omega' + -E_b) \tag{A.3}
\end{equation}

$$= -\log \left| \frac{E_b - \omega - \omega_D}{E_b \omega - \epsilon} \right| - i\pi \left[ \theta(\omega + \omega_D - E_b) - \theta(\omega + \epsilon - E_b) \right]$$

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We plug Eq. A.3 into Eq. A.2:

\[
\Sigma_{kk}^{(2)} = g^2 \int_{\epsilon}^{\omega_D} \frac{d\omega}{(E_b - \omega)^2} \left[ - \log \left| \frac{E_b - \omega_D - \omega}{E_b - \epsilon - \omega} \right| - i\pi \left( \theta(\omega + \omega_D - E_b) - \theta(\omega + \epsilon - E_b) \right) \right]
\]  

(A.4)

We evaluate the imaginary part:

\[
Im \Sigma_{kk}^{(2)} = g^2 \int_{\epsilon}^{\omega_D} \frac{d\omega}{(E_b - \omega)^2} \left[ - \pi \left( \theta(\omega + \omega_D - E_b) - \theta(\omega + \epsilon - E_b) \right) \right]
\]

\[
= g^2 \int_{\epsilon}^{\omega_D} \frac{d\omega}{(E_b - \omega)^2} \left[ \pi \theta(\omega + \epsilon - E_b) \right]; \ \theta(\omega + \epsilon - E_b) = 1; \ \omega > E_b - \epsilon
\]

(A.5)

A.1.2 **Overlap Diagram**

![Overlap Diagram](image)

*Figure A.2: Overlap Diagram*

The mathematical expression corresponding to the above Feynman diagram is given in Sec. 2.4. Let us re-write the expression before showing explicit calculations.
\[ \Sigma_{kk}^{(2)} = i^2 \int \int \frac{d\omega \, d\omega'}{2\pi - 2\pi} \sum_q \sum_{q'} g_{kk}^2 g_{bb}^2 G_b^{(0)}(E - \omega) G_b^{(0)}(E - \omega' - \omega) G_b^{(0)}(E - \omega') \]
\[ \times D(q, \omega) D(q', \omega') \]  
\[ = \sum_q \sum_{q'} \frac{g_{kk}^2 g_{bb}^2}{(E + E_b - \omega_q)(E + E_b - \omega_q - \omega_{q'})(E + E_b - \omega_{q'})}. \]  

(A.6)

In the quasicontinuum limit, the above equation reduces to a double integral over complex \( \omega \) and \( \omega' \) plane:

\[ \Sigma_{kk}^{(2)} = g^2 \int \int d\omega d\omega' \frac{1}{(E_b - \omega)(E_b - \omega - \omega')(E_b - \omega')} \]
\[ = \sum_q \sum_{q'} \frac{g_{kk}^2 g_{bb}^2}{(E + E_b - \omega_q)(E + E_b - \omega_q - \omega_{q'})(E + E_b - \omega_{q'})}. \]  

(A.7)

where we have used \( g = g_{kk} g_{bb} \rho_0 \) and \( E \ll E_b \). Let us begin by calculating the integral over \( \omega' \):

\[ I_1 = \int_\epsilon^{\omega_D} \frac{d\omega'}{(E_b - \omega - \omega')(E_b - \omega')}, \]
\[ = \int_\epsilon^{\omega_D} \frac{d\omega'}{(E_b - \omega - \omega')(E_b - \omega')} - \int_\epsilon^{\omega_D} \frac{d\omega'}{(E_b - \omega')}\omega \]
\[ = \frac{1}{\omega} \left( \log \left| \frac{E_b - \omega - \epsilon}{E_b - \omega - \omega_D} \right| - i\pi \right) + \log \left| \frac{E_b - \epsilon}{E_b - \omega_D} \right|, \quad E_b - \epsilon < \omega < \omega_D \]  

(A.8)

where, we have used the identity: \( 1/(\omega \pm i\eta) = \mathcal{P}(1/\omega) \mp i\pi\delta(\omega), \eta \to 0^+ \). We plug back Eq. A.8 into Eq. A.7, such that:

\[ \Sigma_{kk}^{(2)} = g^2 \int \frac{d\omega}{\omega (E_b - \omega)} \log \left| \frac{E_b - \omega - \epsilon}{E_b - \omega - \omega_D} \right| + g^2 \int \frac{d\omega}{\omega (E_b - \omega)} \log \left| \frac{E_b - \epsilon}{E_b - \omega_D} \right| \]
\[ - i\pi g^2 \int \frac{d\omega}{(E_b - \omega)\omega}. \]  

(A.9)
In the limit of $\omega \to 0^+$ and within energy regime $\omega_D \gg E_b \gg \epsilon$, we evaluate the leading-order divergent term in the real and imaginary part as:

$$Re \Sigma_{kk}^{(2)} = \frac{g^2}{E_b} \log \left| \frac{\omega_D}{E_b} \right| \log \left| \frac{E_b}{\epsilon} \right|$$ \hspace{1cm} (A.10)

$$Im \Sigma_{kk}^{(2)} = -\frac{\pi g^2}{E_b} \log \left| \frac{\omega_D}{\epsilon} \right|, \hspace{0.5cm} E_b - \epsilon < \omega < \omega_D$$ \hspace{1cm} (A.11)

### A.1.3 Loop-after-Loop

![Loop-after-loop Diagram](image)

**Figure A.3: Loop-after-loop Diagram**

Following Feynman rules and propagators given in Sec. 2.3, we derive a mathematical expression corresponding to Fig. A.3.

$$\Sigma_{kk}^{(2)} = i^2 \int \int \frac{d\omega d\omega'}{2\pi 2\pi} \sum_q \sum_{q'} g_{kk}^2 g_{bb}^2 G_b^{(0)}(E - \omega) G_{bb}^{(0)}(E) G_{bb}^{(0)}(E - \omega') D(q, \omega) D(q', \omega')$$

$$= \sum_q \sum_{q'} \frac{g_{kk}^2 g_{bb}^2}{(E + E_b - \omega_q)(E + E_b) (E + E_b - \omega_{q'})} \cdot$$

\hspace{1cm} (A.12)
In the quasicontinuum approximation, the above integral reduces to:

\[
\Sigma_{kk}^{(2)} = \frac{g^2}{E + E_b} \int \frac{d\omega}{E + E_b - \omega} \int \frac{d\omega'}{E + E_b - \omega'}
\]

(A.13)

with \( g = g_{kk} g_{bb} \rho_0 \) and \( E \ll E_b \):

\[
\Sigma_{kk}^2 = \frac{g^2}{E_b} \int \frac{d\omega}{E_b - \omega} \int \frac{d\omega'}{E_b - \omega'}
\]

\[
= \frac{g^2}{E_b} \left[ \mathcal{P} \int \frac{d\omega}{E_b - \omega} - i\pi \theta(\omega - E_b) \right] \times \left[ \mathcal{P} \int \frac{d\omega'}{E_b - \omega'} - i\pi \theta(\omega' - E_b) \right]
\]

\[
= \frac{g^2}{E_b} \left[ \log |E_b - \omega| + i\pi \right] \times \left[ \log |E_b - \omega'| + i\pi \right] \bigg|_{\omega^D}
\]

(A.14)

Considering the energy regime \( \epsilon \ll E_b \ll \omega_D \), the above self-energy \( \Sigma_{kk}^{(2)} \) reduces to:

\[
\Sigma_{kk}^{(2)} = \frac{g^2}{E_b} \left[ \log \left( \frac{\omega_D}{\epsilon} \right) \right] - \pi^2 + \frac{2\pi ig^2}{E_b} \log \left( \frac{E_b - \omega_D}{E_b - \epsilon} \right)
\]

(A.15)

Therefore, the real and imaginary parts are given as:

\[
Re\Sigma_{kk}^{(2)} = \frac{g^2}{E_b} \left[ \log \left( \frac{\omega_D}{\epsilon} \right) \right] - \pi^2
\]

(A.16)

\[
Im\Sigma_{kk}^{(2)} = \frac{2\pi ig^2}{E_b} \log \left( \frac{\omega_D}{\epsilon} \right)
\]

(A.17)
A.2 T ≠ 0: 2-LOOP ATOM SELF-ENERGY

Here we calculate the two loop atom self-energy corresponding to the diagrams shown in Fig. A.4. These are the leading diagrams with two loops which reflect the change of the self-energy in the open $k$ channel due to the influence of the $b$ channel.

Figure A.4: Two-loop atom self-energy diagrams: rainbow (left) and vertex correction (right).

We begin our calculation by deriving an analytical expression for the vertex function $\Gamma(E, \omega)$ which is given by a diagram topologically similar to Fig. 3.5, but in the $kb$ channel:

\begin{align}
\Gamma(E, \omega) &= ig_{bb}^2 \sum_q \int \frac{d\omega'}{2\pi \omega_q} \frac{T}{\omega_q} \left[ \delta(\omega' - \omega_q) + \delta(\omega' + \omega_q) \right] \left[ \frac{1}{E + E_b - \omega' + i\eta} \right] \\
&\quad \times \left[ \frac{1}{E + E_b - \omega - \omega' + i\eta} \right]
\end{align}

(A.18)

In the continuum limit, we have,

\begin{align}
\Gamma(E, \omega) &= g_{bb}^2 \rho_0 \int_{\epsilon}^{E + E_b} \frac{dq}{q} \left[ \frac{1}{(E + E_b - q)(E + E_b - \omega - q + i\eta)} + \frac{1}{(E + E_b + q)} \right] \\
&\quad \times \left[ \frac{1}{E + E_b - \omega + q + i\eta} \right]
\end{align}

(A.19)
Under the approximation, \( q \ll E + E_b \) and calling \( g_{bb}^2 \rho_0 = g_{bb}^2 \), the real and the imaginary parts of the vertex function \( \Gamma(E, \omega) \) are written as:

\[
Re\Gamma(E, \omega) = \frac{2g_{bb}^2 T g_{kk}}{(E + E_b)(E + E_b - \omega)} \log \left| \frac{E + E_b}{\epsilon} \right| \tag{A.20}
\]

Similarly, the imaginary part is given as

\[
Im\Gamma(E, \omega) = -\frac{\pi g_{bb}^2 T g_{kk}}{(E + E_b)(E + E_b - \omega)} \tag{A.21}
\]

Using the vertex function \( \Gamma(E, \omega) \), we derive the contribution from the vertex-corrected self-energy first. The analytical expression can be written as

\[
\Sigma_{kk}^{(2)} = ig_{kk} \int \frac{d\omega}{2\pi} G_{bb}(E - \omega) \Gamma(E, \omega) D^<(\omega) \tag{A.22}
\]

Performing the calculation, we find an expression for the real part of \( \Sigma_{kk}^{(2)} \):

\[
Re\Sigma_{kk}^{(2)} = \frac{2g_{bb}^2 g_{kk}^2 T^2}{(E + E_b)^3} \left[ \log \left| \frac{E + E_b}{\epsilon} \right| \right]^2 \tag{A.23}
\]

A similar expression is derived for the contribution from the rainbow diagram. Thus, the above calculations show that the real part of \( \Sigma_{kk} \) at two-loop order is log squared infrared divergent.

### A.3 \( T \neq 0 \): Vertex Renormalization

Now we calculate the vertex renormalization for the two different types of vertices in our model. The one loop vertex diagrams are shown in Fig. A.5.
Figure A.5: Vertex diagrams corresponding to transitions from: $|k\rangle \to |b\rangle$ states (left), and $|b\rangle \to |b\rangle$ states (right).

The corrections to the vertices are represented as $(g_{kb} + \delta \Gamma^{(1)}_{kb})$ and $(g_{bb} + \delta \Gamma^{(1)}_{bb})$. By evaluating the corresponding diagrams we obtain for the infrared-divergent parts:

\[
\delta \Gamma^{(1)}_{kb}(E) = -\frac{g_{kb}^3 T}{\pi (E + E_b)^2} \log \left| \frac{E + E_b}{\epsilon} \right|, \quad (A.24)
\]

\[
\delta \Gamma^{(1)}_{bb}(E) = \frac{g_{bb}^3 T}{\pi (E + E_b)^2} \log \left| \frac{E + E_b}{\epsilon} \right|. \quad (A.25)
\]

Here the external phonon frequency is set to zero (infrared limit), while $E$ is the external atom energy. The most important feature of these results is that the corrections have different signs, i.e. while the $kb$ vertex decreases, the $bb$ vertex increases.

It is possible to write down and solve the corresponding Dyson equations for the fully renormalized vertex functions, which is equivalent to summing an infinite series of ladder diagrams as is conventionally done in QED [10]. This results in the following
expressions for the effective vertices in the two channels:

\[ \Gamma_{kb}(E) = \frac{g_{kb}}{1 + \frac{g_{kb}^2 T}{\pi (E+E_b)^2} \log \left| \frac{E+E_b}{\epsilon} \right|}, \quad (A.26) \]

and

\[ \Gamma_{bb}(E) = \frac{g_{bb}}{1 - \frac{g_{bb}^2 T}{\pi (E+E_b)^2} \log \left| \frac{E+E_b}{\epsilon} \right|}. \quad (A.27) \]

Again, it is clear that \( \Gamma_{kb}(E) \) decreases while \( \Gamma_{bb}(E) \) increases in the infrared limit. \( \Gamma_{bb}(E) \) in fact contains a Landau pole, although due to the smallness of the effective coupling the system never reaches the pole for physical values of the parameters (coupling, temperature and cutoff).

Finally we consider even higher order renormalization effects. For the \( kb \) vertex, the next level of complexity is represented by the crossed vertex corrections shown in
Fig. A.6. By evaluating the diagram we obtain

\[ \delta \Gamma_{kb}^{(2)}(E) = -\frac{2g_{kk}^3g_{bb}^2T^2}{\pi^2(E + E_b)^3} \log^2 \left| \frac{E + E_b}{\epsilon} \right|, \]  

which confirms that the \( kb \) vertex keeps decreasing. Corresponding results can be derived for the \( bb \) vertex (which experiences an increase). These results are conceptually important because they reaffirm the different tendencies in the two channels, although numerically these diagrams are very small for physical parameter values.

### A.4 Numerical Codes for Non-Crossing Approximation (NCA)

#### A.4.1 T=0

Equations to be solved self-consistently:

Case I: transitions only in the bound states

The non-linear integral equation for \( \Sigma_{bb} \) in this case is given as:

\[ \Sigma_{bb}(E) = \sum_q \frac{g_{bb}^2}{E + E_b - \omega_q - \Sigma_{bb}(E - \omega_q)} , \]  

We solve the equations numerically for the following values: \( g_{bb}^2\rho_0 = 0.06 \text{ meV} \), \( g_{kb}^2\rho_0 = 0.5-10 \mu \text{ eV} \), \( \omega = \epsilon \rightarrow (0,65) \) and in the energy range \(-45 < E < 30\) with the incoming energy of the atom as \( E_k = 2 \text{ meV} \).
The Mathematica code for the above Eq. A.29 is:

```mathematica

gbb = 0.06;
Sbb[x_] := Sum[gbb * 0.01/(x + 40.0 - omega[x - omega[x]])], {omega}, 0.0, 65.0, 0.001];
Sbbnew[x_] := -10 I;
Sbblist = Table[{x, Sbb[x]}, {x, -10, 30, 1}]
Sbbnew = Interpolation[Sbblist]

Case II: transitions within bound to continuum states and vice versa

The non-linear integral equation for $\Sigma_{bb}$ and $\Sigma_{kk}$ in this case is given as:

$$
\Sigma_{bb}(E) = \sum_q \frac{g_{bb}^2}{E + E_b - \omega_q - \Sigma_{bb}(E - \omega_q)} + \sum_q \frac{g_{kb}^2}{E - E_k - \omega_q - \Sigma_{kk}(E - \omega_q)},
$$

$$
\Sigma_{kk}(E) = \sum_q \frac{g_{kb}^2}{E + E_b - \omega_q - \Sigma_{bb}(E - \omega_q)}.
$$

(A.30)

The Mathematica code for the above Eq. A.30 is:

```mathematica

g = 0.06;
h = (4.5)^2 / (2.77 * 10^9);
Sbb21[x_] := Sum[g + 0.01/(x + 40.0 - omega[x] + I 0.1) + h + 0.01 / (x - 2.0 - omega[x] - Sbbnew[x] - omega[x] + I 0.01), {omega}, 0.004, 60, 0.01];
Skk21[x_] := Sum[h + 0.01/(x + 40.0 - omega[x] + I 0.01), {omega}, 0.004, 60, 0.01];
Sbb2021[x_] := If[Abs[x] < 100, -0.01I, 0];
Sbb21[x_] := If[Abs[x] < 100, -0.01I, 0];
Sbblist = Table[{x, Sbb2021[x]}, {x, -100, 100, 1}];
Sbblist = Table[{x, Sbb21[x]}, {x, -100, 100, 1}];
Sbbnew = Interpolation[Sbblist];
Skk21list = Table[{x, Skk21[x]}, {x, -100, 100, 1}];
Sbb21new = Interpolation[Sbb21list];
Skk21list = Table[{x, Skk21[x]}, {x, -45, 15, 1}];
Skk21new = Interpolation[Skk21list];
```
A.4.2 \( T \neq 0 \)

The coupled non-linear integral equations to be solved self-consistently till convergence for transitions within bound and continuum states is given as:

\[
\Sigma_{bb}(E) = g_{bb}^2 \sum_q \left[ \frac{n_q}{E + E_b + \omega_q - \Sigma_{bb}^{(r)}(E + \omega_q)} + \frac{n_q + 1}{E + E_b - \omega_q - \Sigma_{bb}^{(r)}(E - \omega_q)} \right] \\
+ g_{kb}^2 \sum_q \left[ \frac{n_q}{E - E_k + \omega_q - \Sigma_{kk}^{(r)}(E + \omega_q)} + \frac{n_q + 1}{E - E_k - \omega_q - \Sigma_{kk}^{(r)}(E - \omega_q)} \right],
\]

\[
\Sigma_{kk}(E) = g_{kk}^2 \sum_q \left[ \frac{n_q}{E + E_b + \omega_q - \Sigma_{bb}^{(r)}(E + \omega_q)} + \frac{n_q + 1}{E + E_b - \omega_q - \Sigma_{bb}^{(r)}(E - \omega_q)} \right].
\]

The corresponding Mathematica code is given as: here, in the code we have used the notation \( g_{bb}^2 \rho_0 \equiv g_{bb} \) and \( g_{kb}^2 \rho_0 \equiv g_{kb} \).
\[ gbb = 0.06; \]
\[ gkb = (4.5)^2 \times 3.77 \times 10^{-5}; \]
\[ Sbb\{x, \}\) := \text{Sum}\left[ gbb \times 0.1 \times \frac{1.0}{\left( \exp\left[\frac{\text{omega} - 0.002}{0.002}\right] - 1\right)} \times \left( x + 40 \times \text{omega} - \text{Sbbnew}\{x, \text{omega}\}\right), \{\text{omega}, 0.06, 68, .1\}\right) + \]
\[ \text{Sum}\left[ gbb \times 0.1 \times \frac{1.0}{\left( \exp\left[\frac{\text{omega} - 0.002}{0.002}\right] - 1\right)} \times \left( x + 40 \times \text{omega} - \text{Sbbnew}\{x, \text{omega}\}\right), \{\text{omega}, 0.06, 68, .1\}\right) + \]
\[ \text{Sum}\left[ gkb \times 0.1 \times \frac{1.0}{\left( \exp\left[\frac{\text{omega} - 0.002}{0.002}\right] - 1\right)} \times \left( x + 2.0 \times \text{omega} - \text{Skknew}\{x, \text{omega}\}\right), \{\text{omega}, 0.06, 68, .1\}\right) + \]
\[ \text{Sum}\left[ gkb \times 0.1 \times \frac{1.0}{\left( \exp\left[\frac{\text{omega} - 0.002}{0.002}\right] - 1\right)} \times \left( x + 2.0 \times \text{omega} - \text{Skknew}\{x, \text{omega}\}\right), \{\text{omega}, 0.06, 68, 68.1\}\right) + \]
\[ Sbbnew\{x, \} := - I; \]
\[ Skknew\{x, \} := - I; \]
\[ Sbblist = \text{Table}\{\{x, Sbb\{x\}\}, \{x, -45, 30, .1\}\}; \]
\[ Sbbnew = \text{Interpolation}[Sbblist]; \]
\[ Skkleist = \text{Table}\{\{x, Skk\{x\}\}, \{x, -45, 30, .1\}\} \]
\[ Skkknew = \text{Interpolation}[Skkkleist]; \]
Appendix B

B.1 Interface Correlation Energy $U(d)$ & Effective vdW force $F(d)$

We consider a model where an atomically thin graphene sheet with polarization ($\Pi$) is supported on a substrate with dielectric ($\varepsilon_3$) and a layer of liquid of thickness ‘d’ and dielectric ($\varepsilon_2$) is grown on it. This layer of liquid is in equilibrium with another medium of its vapor having dielectric, $\varepsilon_1 = 1$ (refer Fig. 4.1). The following calculation is under the approximation $\varepsilon_2 - \varepsilon_1 << 1$.

Following RPA approach to screening, we relate the vdW potential (correlation energy) to the effective dielectric function ‘$E$’:

$$U(d) = \frac{\hbar}{n(2\pi)^3} \int \int dq_x dq_y \int_0^\infty d\omega \ln E(\tilde{q}, i\omega)$$  \hspace{1cm} (B.1)
The effective dielectric function \( \mathcal{E} \) is given as,

\[
\mathcal{E}(\bar{q}, i\omega) = \varepsilon_g(\bar{q}, i\omega)D(q)e^{-qd}
\]  

(B.2)

where, \( D \) represents the dispersion equation and \( \varepsilon_G \) is the semimetallic screening due to the presence of graphene with polarization function \( \Pi \). We use formal definitions of \( D, \varepsilon_G, V_2 \) and \( \Pi \) from the literature:

\[
D(q) = (\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)e^{qd} + (\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)e^{-qd}
\]  

(B.3)

\[
\varepsilon_g = 1 - V_2\Pi,
\]  

(B.4)

\( V_2 \) represents the Coulomb potential in layer 2 and \( \Pi \) is the polarization of graphene under strain,

\[
V_2 = \frac{4\pi e^2}{qD(q)}\left[(\varepsilon_1 + \varepsilon_2)e^{qd} + (\varepsilon_2 - \varepsilon_1)e^{-qd}\right]
\]  

(B.5)

\[
\Pi(\bar{q}, i\omega) = -\frac{1}{4v_xv_y}\frac{v_x^2q_x^2 + v_y^2q_y^2}{\sqrt{v_x^2q_x^2 + v_y^2q_y^2 + \omega^2}}
\]  

(B.6)

Plugging Eq. B.2 in Eq. B.1 and setting \( \hbar = 1 \) we find:

\[
U(d) = \frac{1}{n(2\pi)^3} \int dq_x dq_y \int_0^\infty d\omega \ln \left[ \varepsilon_g(q, i\omega)D(q)e^{-qd}\right]
\]

\[
= \frac{1}{n(2\pi)^3} \int dq_x dq_y \int_0^\infty d\omega \left[ \ln \varepsilon_g(q, i\omega) + \ln D(q)e^{-qd}\right]
\]  

(B.7)

\[
= \frac{1}{n(2\pi)^3} \int dq_x dq_y \int_0^\infty d\omega \left[ U_g + U_d\right]
\]
We define \( \mathcal{U}_d \) as,

\[
\mathcal{U}_d = \ln D(q) e^{-qd} = \ln \left[ (\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)e^{qd} + (\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)e^{-qd} \right] e^{-qd} \\
= \ln \left[ (\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3) + (\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)e^{-2qd} \right] \\
= \ln \left[ (\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3) + 1 + \frac{(\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)} e^{-2qd} \right] \\
= \ln[(\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)] + \ln \left[ 1 + \frac{(\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)} e^{-2qd} \right] \\
\]

(B.8)

where, we have used Eq. B.3. The first term on the RHS is neglected as it has no ‘d’ dependence. Therefore, Eq. B.8 takes up the form:

\[
\mathcal{U}_d = \ln \left[ 1 + \frac{(\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)} e^{-2qd} \right] \\
\approx \left[ \frac{(\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)} e^{-2qd} \right] \\
\]

(B.9)

Next for the graphene part, we begin by evaluating the Coulomb potential in layer 2, using Eq. B.5 & Eq. B.3, we get,

\[
V_2 = \frac{4\pi e^2}{qD(q)} \left[ (\varepsilon_1 + \varepsilon_2)e^{qd} + (\varepsilon_2 - \varepsilon_1)e^{-qd} \right] \\
= \frac{4\pi e^2}{q(\varepsilon_2 + \varepsilon_3)} \left[ 1 + \frac{(\varepsilon_2 - \varepsilon_1)}{(\varepsilon_1 + \varepsilon_2)} \left( \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + \varepsilon_1} \right) e^{-2qd} \right] \\
\]

(B.10)

Therefore, using the above equation and Eq. B.6, we find the semimetallic screening
\( \varepsilon_g: \)

\[
\varepsilon_g = 1 - V_2 \Pi \\
= 1 - \frac{4 \pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)} \left[ 1 + \frac{(\varepsilon_2 - \varepsilon_1)}{(\varepsilon_2 + \varepsilon_1)} e^{-2qd} \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} \right) e^{-2qd} \right] \\
\leq \frac{4 \pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)} \left[ 1 - \frac{4 \pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)} \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) e^{-2qd} \right] \\
\approx \ln \left[ 1 - \frac{4 \pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)} \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) e^{-2qd} \right] \\
\approx \left[ 1 - \frac{4 \pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)} \right] \\
\]
where we have neglected any term that is independent of 'd'.

F(d) which is defined as the disjoining pressure is given as:

\[ F(d) = \frac{\partial}{\partial d} U(d) \]  

(B.14)

Next, we use Eq. B.8 & Eq. B.13 in Eq. B.7, such that we have:

\[
F = \frac{2}{(2\pi)^3} \int \int dq_x dq_y \int_0^\infty d\omega q \left[ \left( \frac{(\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_2)(\varepsilon_2 + \varepsilon_3)} e^{-2qd} \right) \right. \\
- \left. \left[ \frac{4\pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)} \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2 + \varepsilon_3} \right) e^{-2qd} \right] \right] \\
= \frac{2}{(2\pi)^3} \int \int dq_x dq_y \int_0^\infty q e^{-2qd} \left[ \left( \frac{\varepsilon_2 - 1}{\varepsilon_2 + 1} \right) \left( \frac{1}{\varepsilon_3 + \varepsilon_2} \right) \right] \\
\times \left[ (\varepsilon_3 - \varepsilon_2) - 4\pi e^2 \Pi \left( \frac{2\varepsilon_2}{q(\varepsilon_2 + \varepsilon_3) - 4\pi e^2 \Pi} \right) \right] 
\]

(B.15)

In the next subsections, we will derive the interface force F(d) for cases: undoped, doped & gapped graphene subjected to the following transformation on Eq. B.15:

\[ x = 2qd, \; y = \frac{\omega}{\omega_A}, \; q_x = q \cos(\phi), \; q_y = q \sin(\phi) \text{ and } f(\phi) = \cos^2(\phi) + v_\perp^2 \sin^2(\phi). \]

In addition, we define graphene e-e coupling and anisotropy as: \( v_\perp = \frac{v_y}{v_x} \) and \( g = \frac{\pi e^2}{2v_x}. \)

**B.1.1 Undoped Graphene - Supported, Submerged & Suspended cases**

Using the transformation in Sec. B.1, Eq. B.6 becomes,

\[
\Pi = -\frac{1}{4v_\perp} \left[ \frac{f(\phi)}{\sqrt{v_\perp^2 f(\phi) + \omega^2}} \right] 
\]

(B.16)

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Next, we redefine the dielectric in terms of the transformed parameters, such that: 
\( \epsilon_2(i\omega) \equiv \epsilon_2(y) \) and \( \epsilon_3(i\omega) \equiv \epsilon_3(y) \) and define a characteristic length scale \( \Omega(d) = 2\omega_{He}d/v_x \).

Plugging Eq. B.16 in Eq. B.15, we get:

\[
F = \frac{\omega_A}{16\pi^2d^3} \int \int dx dy \int \frac{d\phi}{2\pi} x^2 e^{-x} \left[ \left( \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right) \left( \frac{1}{\epsilon_2 + \epsilon_3} \right) \right] \\
\times \left[ (\epsilon_3 - \epsilon_2) + \frac{2gx f(\phi) 2\epsilon_2}{v_{\perp}(\epsilon_2 + \epsilon_3) \sqrt{f(\phi)x^2 + y^2\Omega(d)^2 + 2gx f(\phi)}} \right] \] (B.17)

With particle density \( n = 2.12 \times 10^{-2}/AA^3 \) (for He), \( \omega_A \equiv \omega_{He} \) and \( I(d) \) defined as the integral in Eq. B.17 we get:

\[
\frac{F}{n} = \frac{\omega_{He} I(d)}{16\pi^2 n} \frac{d^3}{d^3} = 8.663 \times 10^4 K\text{Å}^3 I(d) \] (B.18)

\[
= \frac{\Gamma(d)}{d^3} [K][\text{Å}]^3
\]

Eq. B.17 serves as the basic equation to solve for the force at the interface. In the consequent subsection, we will just provide with the extension of the above equation to cases for submerged and suspended graphene.

**Submerged Undoped Graphene**

Once again we modify Eq. B.17 subjected to the condition for submerged geometry: \( \epsilon_1 = 1, \epsilon_2 = \epsilon_3 \).
\[
F = \frac{\omega_H e}{16\pi^2 d^3} \int \int dx dy \int \frac{d\phi}{2\pi} x^2 e^{-x} \left[ \frac{\varepsilon_2 - 1}{\varepsilon_2 + 1} \right] \left[ \frac{2gx f(\phi)}{v_\perp(2\varepsilon_2)\sqrt{f(\phi)x^2 + y^2\Omega(d)^2 + 2gx f(\phi)}} \right] \quad (B.19)
\]

**Suspended Undoped Graphene**

Eq. B.17 is modified with the inclusion for the condition of suspended geometry where dielectrics are arranged as: \( \varepsilon_1 = \varepsilon_3 = 1 \). Therefore, we get:

\[
F = \frac{\omega_H e}{16\pi^2 d^3} \int \int dx dy \int \frac{d\phi}{2\pi} x^2 e^{-x} \left[ \frac{\varepsilon_2 - 1}{\varepsilon_2 + 1} \left( \frac{1}{\varepsilon_2 + 1} \right) \right] \left[ (1 - \varepsilon_2) + \frac{2gx f(\phi)2\varepsilon_2}{v_\perp(\varepsilon_2 + 1)\sqrt{f(\phi)x^2 + y^2\Omega(d)^2 + 2gx f(\phi)}} \right] \quad (B.20)
\]

**B.1.2 Suspended Doped Graphene**

We start off with the polarization \( \Pi \) of doped graphene given by: [9]

\[
\Pi(q, i\omega) = \frac{-q^2}{4\sqrt{\omega^2 + v^2q^2}} - \frac{2\varepsilon_F}{\pi v^2} + \frac{q^2}{2\pi\sqrt{\omega^2 + v^2q^2}} \text{Re} \left[ \arcsin \left( \frac{2\varepsilon_F + i\omega}{vq} \right) \right] \\
+ \left( \frac{2\varepsilon_F + i\omega}{vq} \right) \sqrt{1 - \left( \frac{2\varepsilon_F + i\omega}{vq} \right)^2} \quad (B.21)
\]
From Eq. B.15, we see the effect of graphene and polarization $\Pi$ appears in the term $-4\pi e^2 \Pi/q$. Subjected to the transformation given in Sec. B.1, we re-write:

$$-\frac{4\pi e^2 \Pi}{q} = -\frac{2gx}{\sqrt{x^2 + y^2(\Omega(d))^2}} \frac{8g\tilde{\epsilon}_F}{\pi x} + \frac{4gx}{\pi \sqrt{x^2 + y^2(\Omega(d))^2}} \Re \left[ \Phi(x, y) \right] \quad (B.22)$$

where, we have introduced a characteristic length scale: $\tilde{\epsilon}_F = 4\epsilon_F d/v$ and $\Phi(x, y)$ is written as:

$$\Phi(x, y) = \arcsin \left[ \left( \frac{\tilde{\epsilon}_F}{x} + i \left( \frac{y(\Omega(d))}{x} \right) \right) + \left( \frac{\tilde{\epsilon}_F}{x} + i \left( \frac{y(\Omega(d))}{x} \right) \right) \right] \times \sqrt{1 - \left[ \left( \frac{\tilde{\epsilon}_F}{x} + i \left( \frac{y(\Omega(d))}{x} \right) \right)^2 \right]} \quad (B.23)$$

So for the doped case one can write a closed equation for $F$ based on Eqs. B.15, B.22 and Eq. B.23.

**B.1.3 SUSPENDED GAPPED GRAPHENE / TMDC**

Polarization in gapped graphene is given as:

$$\Pi(q, i\omega) = -\frac{|q|^2}{\pi} \left[ \frac{m}{q^2} + \frac{1}{2q} \left( 1 - \frac{4m^2}{q^2} \right) \tan^{-1} \left( \frac{q}{2m} \right) \right] \quad (B.24)$$

Here,

$$q = \sqrt{v^2 |q|^2 + \omega^2} \quad (B.25)$$
The energy gap is represented by ‘m’ which we define as \( \Delta \). Therefore using Eq B.25 in Eq B.24, we get:

\[
\Pi(\vec{q}, i\omega) = -\frac{|\vec{q}|^2}{\pi} \left[ \frac{\Delta}{(v^2|\vec{q}|^2 + \omega^2)} + \frac{1}{2\sqrt{(v^2|\vec{q}|^2 + \omega^2)}} \left( 1 - \frac{4\Delta^2}{(v^2|\vec{q}|^2 + \omega^2)} \right) \right] \tan^{-1} \left( \frac{\sqrt{(v^2|\vec{q}|^2 + \omega^2)}}{2\Delta} \right) 
\]

(B.26)

Next, we evaluate \( 4\pi e^2\Pi \):

\[
4\pi e^2\Pi = -4e^2|\vec{q}|^2 \left[ \frac{\Delta}{(v^2|\vec{q}|^2 + \omega^2)} + \frac{1}{2\sqrt{(v^2|\vec{q}|^2 + \omega^2)}} \left( 1 - \frac{4\Delta^2}{(v^2|\vec{q}|^2 + \omega^2)} \right) \right] \tan^{-1} \left( \frac{\sqrt{(v^2|\vec{q}|^2 + \omega^2)}}{2\Delta} \right) 
\]

(B.27)

Using the transformation as before (Sec. B.1) and characteristic length scales:

\[
\Omega(d) = \frac{2\omega_H d}{v} 
\]

(B.28)

\[
\eta(d) = \frac{4d\Delta}{v} 
\]

(B.29)

Eq. B.27 becomes:

\[
4\pi e^2\Pi = -\frac{2gx^2}{\pi d} \left( \left[ \frac{\eta}{x^2 + y^2(\Omega(d))^2} \right] + \frac{1}{\sqrt{x^2 + y^2(\Omega(d))^2}} \left[ 1 - \frac{\eta^2}{x^2 + y^2(\Omega(d))^2} \right] \right) \tan^{-1} \left( \frac{\sqrt{x^2 + y^2(\Omega(d))^2}}{\eta} \right) 
\]

(B.30)

Recall from Eq. B.15, the effect of graphene polarization \( \Pi \) pops up only in the term:
4\pi e^2 \Pi / q(\varepsilon_2 + \varepsilon_3). Hence, from Eq. B.30 we calculate:

\[
\frac{4\pi e^2 \Pi}{q(\varepsilon_2 + \varepsilon_3)} = -\frac{4gx}{\pi(\varepsilon_2 + \varepsilon_3)} \left( \frac{\eta}{x^2 + y^2(\Omega(d))^2} \right) + \frac{1}{\sqrt{x^2 + y^2(\Omega(d))^2}} \left[ 1 - \frac{\eta^2}{x^2 + y^2(\Omega(d))^2} \right] \\
\times \tan^{-1} \left( \frac{\sqrt{x^2 + y^2(\Omega(d))^2}}{\eta} \right)
\]

(B.31)

We plug the above Eq. B.31 in Eq. B.15 to derive the final expression of the force \( F \).

### B.2 Numerical Specifications for Fluid-Surface Interaction Physical Model

Important conversion factor: 1 au = 0.148Å³; \( g = 2.2 \times (\pi/2.0) \)

#### B.2.1 Gas Parameters

For Helium the dynamical dielectric constant is

\[
\varepsilon_2(i\omega) = 1 + 4\pi n_{\text{He}}\alpha(i\omega), \quad \alpha(i\omega) = \frac{\alpha_{\text{He}}}{1 + (\omega/\omega_{\text{He}})^2},
\]

(B.32)

For Nitrogen and Hydrogen, which have densities comparable to Helium but significantly larger polarizabilities, more accurate formulas based on the Clausius-Mossotti
relation are typically used:

$$
\varepsilon_2(i\omega) = 1 + \frac{4\pi n_A \alpha(i\omega)}{1 - \frac{4\pi}{3} n_A \alpha(i\omega)}, \quad A = \text{N}_2, \text{H}_2, \tag{B.33}
$$

The dynamical polarizability is defined as in Eq. (B.32). Below we classify the numerical values corresponding to the light gases used in this chapter.

**Helium**

Static polarizability $\alpha_0 = 1.38$ au, $M_{\text{He}} = 6.6 \times 10^{-24}$ g, $\rho = 0.14 g/cc$ and $n = 2.12 \times 10^{-2}/\text{Å}^3$, characteristic frequency $\omega_{\text{He}} = 27.21$ eV, $\Omega(d) = 8.245d[\text{Å}],

$$
\Gamma(d) = \frac{\omega_{\text{He}}}{16\pi^2 n \times 8.62 \times 10^{-5}} \times I(d)
= 9.429 \times 10^4 \times I(d) \ [K][\text{Å}^3] \tag{B.34}
$$

For liq. He, however, one should use

$$
\varepsilon_2(\omega) = 1 + 4\pi n \frac{\alpha_0}{1 + \left[\frac{\omega}{\omega_{\text{He}}}\right]^2} \tag{B.35}
$$

**Hydrogen**

Static polarizability $\alpha_0 = 5.439$ au, $M_{\text{H}_2} = 3.34 \times 10^{-24}$ g, $\rho = 0.0708 g/cc$ and $n = 2.04 \times 10^{-2}/\text{Å}^3$, characteristic frequency $\omega_{\text{H}_2} = 14.09$ eV, $\Omega(d) = 4.269d[\text{Å}],

$$
\Gamma(d) = \frac{\omega_{\text{H}_2}}{16\pi^2 n \times 8.62 \times 10^{-5}} \times I(d)
= 5.074 \times 10^4 \times I(d) \ [K][\text{Å}^3] \tag{B.36}
$$
For liq. H\textsubscript{2}, however, one should use

$$
\varepsilon_2(\omega) = 1 + \frac{1}{\left[ \left( \frac{0.537}{n\alpha} \right) \left( 1 + \left( \frac{\omega}{\omega_{H_2}} \right)^2 \right) - \frac{1}{3} \right]} \tag{B.37}
$$

### Nitrogen

Static polarizability $\alpha_0 = 11.74$ au, $M_{N_2} = 4.64 \times 10^{-23} \text{ g}$, $\rho = 0.807\text{g/cc}$ and $n = 1.73 \times 10^{-2}/\text{Å}^3$, characteristic frequency $\omega_{N_2} = 19.319 \text{ eV}$, $\Omega(d) = 5.854d[\text{Å}],$

$$
\Gamma(d) = \frac{\omega_{N_2}}{16\pi^2 n \times 8.62 \times 10^{-5}} \times I(d)
$$

$$
= 8.203 \times 10^4 \times I(d) \text{ [K][Å}^3]\tag{B.38}
$$

For liq. N\textsubscript{2}, however, one should use

$$
\varepsilon_2(\omega) = 1 + \frac{1}{\left[ \left( \frac{0.537}{n\alpha} \right) \left( 1 + \left( \frac{\omega}{\omega_{N_2}} \right)^2 \right) - \frac{1}{3} \right]} \tag{B.39}
$$

### B.2.2 SUBSTRATE PARAMETERS

#### 6H-SiC

It is instructive to investigate the effect of different substrates (medium 3) on wetting. Many dielectric substrates are accurately described by the formula [11]

$$
\varepsilon_3(i\omega) = 1 + \frac{C_{IR}}{1 + (\omega/\omega_{IR})^2} + \frac{C_{UV}}{1 + (\omega/\omega_{UV})^2}, \tag{B.40}
$$
With transformations introduce in Appendix. B.1, we can re-write the above equation as:

$$\varepsilon_3(y) = 1 + \frac{3.67}{1 + y^2 \left[ \frac{\omega_{He}}{\omega_{IR}} \right]^2} + \frac{5.526}{1 + y^2 \left[ \frac{\omega_{He}}{\omega_{UV}} \right]^2} \quad (B.41)$$

where, \( \frac{\omega_{He}}{\omega_{IR}} = 263.286 \), \( \frac{\omega_{He}}{\omega_{UV}} = 3.68 \). We use a gap of \( \Delta = 0.26eV \).
APPENDIX C

C.1 GREEN FUNCTION & CORRECTION TERM

δµ

C.1.1 SILICENE-GERMANENE

\[
G(k, \omega) = \frac{1}{\omega - \left[ \vec{\sigma} \cdot \vec{k} + \left( \frac{\Delta - \lambda s}{2} \sigma_z \right) \right]} \\
= \frac{\omega + \vec{\sigma} \cdot \vec{k} + \frac{\Delta - \lambda s}{2} \sigma_z}{(\omega - \varepsilon_k + i\eta)(\omega + \varepsilon_k - i\eta)}
\] (C.1)

Near the poles:

\[
G(k, \omega) = \frac{u^2}{\omega - \varepsilon_k + i\eta} + \frac{v^2}{\omega + \varepsilon_k - \eta}
\] (C.2)
where, \( u^2 \) and \( v^2 \) give the residues for the function:

\[
f = \frac{\omega + \vec{\sigma} \cdot \vec{k} + \left( \frac{\Delta - \lambda s z}{2} \right) \sigma_z}{(\omega - \varepsilon^s_k)(\omega + \varepsilon^s_k)} \tag{C.3}
\]

\( u^2 \) is the residue of the above function:

\[
u^2 = \lim_{\omega \to \varepsilon^s_k} \left[ \frac{\varepsilon^s_k + \vec{\sigma} \cdot \vec{k} + \left( \frac{\Delta - \lambda s z}{2} \right) \sigma_z}{(\omega - \varepsilon^s_k)2\varepsilon^s_k} \right] \tag{C.4}
\]

Similarly, we get \( v^2 \) in the limit of \( \omega \to -\varepsilon^s_k \):

\[
v^2 = \frac{\varepsilon^s_k - \vec{\sigma} \cdot \vec{k} - \left( \frac{\Delta - \lambda s z}{2} \right) \sigma_z}{2\varepsilon^s_k} \tag{C.5}
\]

Therefore, we derive the Green’s function for the Silicene Germanene as:

\[
G(k, \omega) = \frac{1}{2\varepsilon^s_k} \left[ \frac{\varepsilon^s_k + \vec{\sigma} \cdot \vec{k} + \left( \frac{\Delta - \lambda s z}{2} \right) \sigma_z}{(\omega - \varepsilon^s_k + i\eta)} \right] + \left[ \frac{\varepsilon^s_k - \vec{\sigma} \cdot \vec{k} - \left( \frac{\Delta - \lambda s z}{2} \right) \sigma_z}{\omega + \varepsilon^s_k - i\eta} \right] \tag{C.6}
\]

where, \( \varepsilon^s_k = \sqrt{k^2 + (\Delta - \lambda s)^2/4} \)

Therefore, the correction term to calculate is:

\[
= \sum_p i \int \frac{d\omega}{2\pi} \langle \downarrow | G^{(s=-1)}(p, \omega) S_x G^{(s=+1)}(p + q, \omega \uparrow) \rangle V(|\vec{k} - \vec{p}|) \tag{C.7}
\]
We begin by evaluating the frequency integral at $q \to 0$

$$i \int \frac{d\omega}{2\pi} \left[ G^- G^+ \right] = i \int \frac{d\omega}{2\pi} \left[ \frac{1}{4\varepsilon_p} \left( \frac{\varepsilon_p^- + \vec{\sigma} \cdot \vec{p} + \frac{\Delta + \lambda}{2} \sigma_z}{\omega - \varepsilon_p^- + i\eta} + \frac{\varepsilon_p^- - \vec{\sigma} \cdot \vec{p} - \frac{\Delta - \lambda}{2} \sigma_z}{\omega + \varepsilon_p^- - i\eta} \right) \right]$$

$$\times \left( \frac{\varepsilon_p^+ + \vec{\sigma} \cdot \vec{p} + \frac{\Delta - \lambda}{2} \sigma_z}{\omega - \varepsilon_p^+ + i\eta} + \frac{\varepsilon_p^+ - \vec{\sigma} \cdot \vec{p} - \frac{\Delta + \lambda}{2} \sigma_z}{\omega + \varepsilon_p^+ - i\eta} \right)$$

$$= \frac{1}{2\varepsilon_p} \frac{1}{\varepsilon_p^- + \varepsilon_p^+} \left[ \varepsilon_p^- \varepsilon_p^+ - (\vec{\sigma} \cdot \vec{p})^2 - (\vec{\sigma} \cdot \vec{p}) \left( \frac{\Delta - \lambda}{2} \right) \sigma_z \right]$$

$$- \left( \frac{\Delta + \lambda}{2} \right) \sigma_z (\vec{\sigma} \cdot \vec{p}) - \left( \frac{\Delta^2 - \lambda^2}{4} \right)$$

$$= \frac{1}{2\varepsilon_p} \frac{1}{\varepsilon_p^- + \varepsilon_p^+} \left[ \varepsilon_p^- \varepsilon_p^+ - (\vec{\sigma} \cdot \vec{p})^2 + \left( \frac{\lambda^2 - \Delta^2}{4} \right) + \lambda \sigma_z (\vec{\sigma} \cdot \vec{p}) \right]$$

(C.8)

Now, to get the correction term we plug the frequency integral back into Eq. C.7 and use the wave functions corresponding (5.7), (5.8):

$$\delta \mu = \sum \frac{1}{2\varepsilon_p^- \varepsilon_p^+ + \varepsilon_p^+(\varepsilon_p^- + \varepsilon_p^+)} (\downarrow | S_x \rangle \uparrow) \left[ \varepsilon_p^- \varepsilon_p^+ - p^2 + \frac{\lambda^2 - \Delta^2}{4} + \lambda \left( \vec{p} \cdot \vec{k} \right) \frac{\varepsilon_k^- - \varepsilon_k^+ - \lambda}{k^2 + E_{k,1}^2 - E_{k,1}^-} \right]$$

$$V(\vec{k} - \vec{p})$$

(C.9)

### C.1.2 TMDC

$$G(k, \omega) = \frac{\omega - \frac{\lambda\tau s_z}{2} + v(\vec{\sigma} \cdot \vec{k}) + \frac{\Delta}{2} \sigma_z - \frac{\lambda\tau}{2} \sigma_z s_z}{(\omega - \frac{\lambda\tau s_z}{2})^2 - (\varepsilon_k^2 + \frac{\Delta^2}{4} + \frac{\lambda^2}{4} - \frac{\Delta \lambda}{2} \sigma_z)}$$

(C.10)

Near the poles:

$$G(k, \omega) = \frac{u^2}{(\omega - \frac{\lambda\tau s_z}{2} - \varepsilon_k + i\eta)} + \frac{v^2}{(\omega - \frac{\lambda\tau s_z}{2} + \varepsilon_k - i\eta)}$$

(C.11)
where, $u^2$ and $v^2$ give the residues for the function:

$$f = \frac{\omega - \frac{\lambda \tau}{2}s_z + v(\vec{\sigma} \cdot \vec{k}) + \Delta \sigma_z - \frac{\lambda \tau}{2} \sigma_z s_z}{(\omega - \frac{\lambda \tau}{2}s_z - \varepsilon_k)(\omega - \frac{\lambda \tau}{2}s_z + \varepsilon_k)} \tag{C.12}$$

Poles are given as:

$$\omega_1 = \frac{\lambda \tau}{2}s_z + \varepsilon_k \tag{C.13}$$

$$\omega_2 = \frac{\lambda \tau}{2}s_z - \varepsilon_k \tag{C.14}$$

Therefore, we get, $u^2$ and $v^2$ as:

$$u^2 = \frac{\varepsilon_k + \left[ v(\vec{\sigma} \cdot \vec{k}) + \frac{\Delta}{2} \sigma_z - \frac{\lambda \tau}{2} \sigma_z s_z \right]}{2\varepsilon_k} \tag{C.15}$$

$$v^2 = \frac{\varepsilon_k - \left[ v(\vec{\sigma} \cdot \vec{k}) + \frac{\Delta}{2} \sigma_z - \frac{\lambda \tau}{2} \sigma_z s_z \right]}{2\varepsilon_k} \tag{C.16}$$

$$G(k, \omega) = \frac{\varepsilon_k + \left[ v(\vec{\sigma} \cdot \vec{k}) + \frac{\Delta}{2} \sigma_z - \frac{\lambda \tau}{2} \sigma_z s_z \right]}{2\varepsilon_k[\omega - \frac{\lambda \tau}{2}s_z] - \varepsilon_k + i\eta} + \frac{\varepsilon_k - \left[ v(\vec{\sigma} \cdot \vec{k}) + \frac{\Delta}{2} \sigma_z - \frac{\lambda \tau}{2} \sigma_z s_z \right]}{2\varepsilon_k[\omega - \frac{\lambda \tau}{2}s_z] + \varepsilon_k - i\eta} \tag{C.17}$$

where $\varepsilon_k$ is given as:

$$\varepsilon_k = \pm \sqrt{v^2k^2 + \frac{\Delta^2}{4} + \frac{\lambda^2\tau^2}{4} - \frac{\Delta \lambda \tau}{2}s_z} \tag{C.18}$$
For calculation related to this we only consider the positive energy values:

\[
\varepsilon_k = + \sqrt{v^2 k^2 + \frac{(\Delta - \lambda \tau s_z)^2}{4}} \quad \text{(C.19)}
\]

Correction term to calculate:

\[
\sum_p i \int \frac{d\omega}{2\pi} (\downarrow |G^{(s=-1)}(p, \omega) S_x G^{(s=+1)}(p + q, \omega | \uparrow) V(|\vec{k} - \vec{p}|)) \quad \text{(C.20)}
\]

We begin with: \( q \rightarrow 0 \):

\[
i \int \frac{d\omega}{2\pi} G^- G^+ = i \int \frac{d\omega}{2\pi} \left[ \frac{\varepsilon_p^- + v(\vec{\sigma} \cdot \vec{p})}{2\varepsilon_p^- (\omega + \frac{\lambda \tau}{2} - \varepsilon_p^- + i\eta)} \frac{\Delta - \frac{\lambda \tau}{2} \sigma_z + \frac{\lambda \tau}{2} \sigma_z}{2\varepsilon_p^- (\omega + \frac{\lambda \tau}{2} + \varepsilon_p^- - i\eta)} \right] \times \left[ \frac{\varepsilon_p^+ + v(\vec{\sigma} \cdot \vec{p})}{2\varepsilon_p^+ (\omega - \frac{\lambda \tau}{2} - \varepsilon_p^+ + i\eta)} + \frac{\varepsilon_p^- - v(\vec{\sigma} \cdot \vec{p}) + \frac{\lambda \tau}{2} \sigma_z}{2\varepsilon_p^- (\omega - \frac{\lambda \tau}{2} + \varepsilon_p^- - i\eta)} \right] \quad \text{(C.21)}
\]

Performing the frequency integral:

\[
= \frac{i^2}{4\varepsilon_p^- \varepsilon_p^+} \left[ \frac{\varepsilon_p^- - v(\vec{\sigma} \cdot \vec{p}) - \frac{\Delta}{2} \sigma_z - \frac{\lambda \tau}{2} \sigma_z}{\lambda \tau - \varepsilon_p^- - \varepsilon_p^+} \right] \quad \text{(C.22)}
\]
Simplifying:

\[
= 2\lambda \tau \left[ v(\vec{\sigma} \cdot \vec{p}) + \frac{\Delta}{2} \sigma_z \right] (\varepsilon_p^- - \varepsilon_p^+) - \lambda^2 \tau^2 \sigma_z (\varepsilon_p^+ + \varepsilon_p^-) + 2v^2 p^2 (\varepsilon_p^+ + \varepsilon_p^-) \\
+ \frac{\Delta^2}{2} (\varepsilon_p^+ + \varepsilon_p^-) - \frac{\lambda^2 \tau^2}{2} (\varepsilon_p^+ + \varepsilon_p^-) - 2v \lambda \tau (\varepsilon_p^+ + \varepsilon_p^-)(\vec{\sigma} \cdot \vec{p})\sigma_z - 2\varepsilon_p^- \varepsilon_p^+ (\varepsilon_p^+ + \varepsilon_p^-)
\]

(C.23)

Here, in the limit of \( \varepsilon_p \gg \lambda \), we can expand Eq. C.19 till \( O[\lambda^2] \), such that:

\[
\varepsilon_p^+ = \varepsilon_p - \frac{\lambda \Delta \tau}{4\varepsilon_p} + \frac{\lambda^2 \tau^2}{4\varepsilon_p} \\
\varepsilon_p^- = \varepsilon_p + \frac{\lambda \Delta \tau}{4\varepsilon_p} + \frac{\lambda^2 \tau^2}{4\varepsilon_p}
\]

(C.24)

(C.25)

Therefore,

\[
\varepsilon_p^+ + \varepsilon_p^- = 2\varepsilon_p + \frac{\lambda^2 \tau^2}{2\varepsilon_p}
\]

(C.26)

\[
\varepsilon_p^- - \varepsilon_p^+ = \frac{\lambda \Delta \tau}{2\varepsilon_p}
\]

(C.27)

Using Eqs. C.23, C.25, C.26 we derive the 1st term as :

\[
2\lambda \tau \left[ v(\vec{\sigma} \cdot \vec{p}) + \frac{\Delta}{2} \sigma_z \right] (\varepsilon_p^- - \varepsilon_p^+) = \frac{\lambda^2 \tau^2 \Delta v(\vec{\sigma} \cdot \vec{p})}{\varepsilon_p} + \frac{\lambda^2 \tau^2 \Delta^2 \sigma_z}{2\varepsilon_p}
\]

(C.28)

The 6th term in Eq. C.23 is given as:

\[
- 2v \lambda \tau (\varepsilon_p^+ + \varepsilon_p^-)(\vec{\sigma} \cdot \vec{p})\sigma_z = -4\varepsilon_p \lambda \tau v(\vec{\sigma} \cdot \vec{p})\sigma_z
\]

(C.29)
Collecting the rest of the terms from Eq. C.23, we get:

\[
-\lambda^2 \tau^2 \sigma_z + 2v^2 p^2 + \frac{\Delta^2}{2} - \frac{\lambda^2 \tau^2}{2}(\varepsilon^+_p + \varepsilon^-_p) - 2\varepsilon^-_p \varepsilon^+_p (\varepsilon^+_p + \varepsilon^-_p)
\] (C.30)

\[
= \lambda^2 [-2\varepsilon^-_p \tau^2 \sigma_z - 2\varepsilon^-_p \tau^2 - \tau^2 \varepsilon^-_p + \frac{\Delta^2 \tau^2}{4\varepsilon^-_p}]
\]

Using Eqs. C.30, C.28, C.29 we have:

\[
= \frac{1}{4\varepsilon^-_p \varepsilon^-_p} \left[ \frac{\lambda^2 \tau^2 \Delta v (\vec{\sigma} \cdot \vec{p})}{\varepsilon^-_p} - 4\varepsilon^-_p v \lambda \tau (\vec{\sigma} \cdot \vec{p}) \sigma_z - 2\frac{\lambda^2 \tau^2}{\varepsilon^-_p} v^2 p^2 (\sigma_z + 1) - \frac{\lambda^2 \tau^2}{\varepsilon^-_p} (v^2 p^2 + \frac{\Delta^2}{2}) \right]
\] (C.31)