Morphological and Material Effects in Van Der Waals Interactions

Jaime C. Hopkins

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MORPHOLOGICAL AND MATERIAL EFFECTS IN VAN DER WAALS INTERACTIONS

A Dissertation Presented
by
JAIME C. HOPKINS

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Department of Physics
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This work is dedicated to my parents, Ginette and Walter.
ACKNOWLEDGMENTS

I would like to thank my advisors, V. Adrian Parsegian and Rudolf Podgornik, for sharing their passion for science and for their patient guidance and support. I will always be grateful for their selfless contributions to my professional and personal development during my graduate years. Much thanks are also due to the many collaborators with whom I have had the good fortune to work: Daniel M. Dryden, Wai-Yim Ching, Roger H. French, Lin K. Denoyer, Lokendra Poudel, and Nicole F. Steinmetz. I would also like to express my gratitude to the members of my committee, Alfred Crosby, Roger French, and Lori Goldner, for their thoughtful conversations and suggestions during this project and beyond. A special thank you to Eric Lobdell, Lee Walsh, Maritza Mallek, and Ben Gamari, whose curiosity, support, and friendship brightened many of my days in the program.

I am especially grateful to my parents, Walter and Ginette, whose generosity and tireless encouragement and support made all this possible.
Van der Waals (vdW) interactions influence a variety of mesoscale phenomena, such as surface adhesion, friction, and colloid stability, and play increasingly important roles as science seeks to design systems on increasingly smaller length scales. Using the full Lifshitz continuum formulation, this thesis investigates the effects of system materials, shapes, and configurations and presents open-source software to accurately calculate vdW interactions.

In the Lifshitz formulation, the microscopic composition of a material is represented by its bulk dielectric response. Small changes in a dielectric response can result in substantial variations in the strength of vdW interactions. However, the relationship between these changes is complicated and often over-simplified in popular approaches. Three example systems are used to study the effects of material modifications, to characterize important system parameters, and to elucidate this commonly
misunderstood relationship. Modification of example dielectric spectra at a particular frequency influences all terms in the Matsubara summation of the Hamaker coefficient. The terms most affected by the change are distributed doubly non-locally over all frequencies and not confined to terms near to modification. Thus, the possibility of eliminating vdW interactions by spectral variation at a narrow frequency range is very remote.

Orientational dependence of vdW interactions is generally attributed to the effects of anisotropies of body shapes and dielectric responses. In order to disentangle these effects, the angular dependencies for several systems displaying a range of anisotropies are examined and the effects of shape and material anisotropies are mutually isolated in detailed calculations. Shape anisotropy effects are shown to result in torques between arrays of cylinders that are surprisingly stronger than those between half-spaces, even for arrays constructed of isotropic material.

Full Lifshitz’s calculations of vdW interactions, though complicated and lengthy, accurately capture important effects in mesoscale systems. The Gecko Hamaker open-science software and its accompanying open database of optical properties provide users with the accurate vdW calculations that are necessary for deliberate mesoscale design and construction. The Lifshitz formulation gives Gecko Hamaker the unique capability to address orientational degrees of freedom, allowing users to calculate torques and angular-dependencies. The large variety of calculations made possible by Gecko Hamaker provides insights into mesoscale interactions that were previously inaccessible to users, such as DNA-DNA interaction’s dependence on base pair composition and the unusual non-monotonic interactions displayed by certain single-walled carbon nanotubes. This dissertation includes previously published coauthored material.
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CHAPTER 1
INTRODUCTION

Van der Waals interactions, together with more familiar interactions such as hydrogen bonds and Coulomb forces, belong to the set of intermolecular interactions at play in nano- and micro-scale systems. Intermolecular forces generally fall into three categories: electrostatic (Coulomb forces), polarization (e.g., solvent interactions), and quantum mechanical forces (e.g., covalent, steric interactions), see Figure 1.1.

Van der Waals interactions are long-range, relatively weak but substantial when scaled, and, in some form, always present in all materials. In these ways, van der Waals interactions are as much part of our world as the otherwise dissimilar gravi-

![Figure 1.1](image_url)

**Figure 1.1.** Intermolecular forces generally fall into three categories: electrostatic (Coulomb forces, interactions between charges, permanent dipoles, quadrupoles, etc.), polarization forces from the induced dipole moments in atoms and molecules due to electric fields of nearby charges and permanent dipoles (found in all solvent interactions), and quantum mechanical forces (e.g., covalent, chemical bonding (e.g. charge-transfer interactions) and repulsive steric or exchange interactions (due to the Pauli exclusion principle), which balance the attractive forces at very short distances.
Van der Waals interactions result from the correlations between electromagnetic field fluctuations from neutral atoms, molecules, and on the surfaces of dielectric materials. Figure 1.2 [1, 2]. They arise from energy perturbations in the quantum electromagnetic field within a material. The perturbations are caused by the ability of an atom’s dipole field to disturb the electromagnetic field of a material so that the atom’s neighbors experience a field that has been modified by, not only that first atom, but by all its neighbors as well, and so on.

Van der Waals interactions result from the correlations between electromagnetic field fluctuations from neutral atoms, molecules, and on the surfaces of dielectric materials, Figure 1.2 [1, 2]. They arise from energy perturbations in the quantum electromagnetic field within a material. The perturbations are caused by the ability of an atom’s dipole field to disturb the electromagnetic field of a material so that the atom’s neighbors experience a field that has been modified by, not only that first atom, but by all its neighbors as well, and so on.

All molecules and atoms are polarizable, including neutral and non-polar molecules, due to an induced dipole moment actuated by an electric field. The facility with which these atoms can be influenced and are able to influence each other is represented by their frequency-dependent polarizability. In practice, this ability to be influenced appears in the dipole moments (when observing few atoms) or in the frequency-
Figure 1.3. Outline of basic process of computing the Lifshitz formulation of van der Waals interactions. Stylized schematic represents two bodies with material dielectric responses, $\epsilon_{1,3}$, interacting across a separation, $\ell$, of isotropic intervening medium.

...dependent dielectric response (when looking at a bulk material). Consequently, the magnitude, role, and form of van der Waals interactions depend greatly on materials in a system.

The interface between materials with different polarizabilities imposes matching constraints on the possible wave solutions for the boundary, see Figure 1.3. Thus the shape of interacting bodies also plays an important role in van der Waals interactions.

The many-body fluctuations correlations that form the basis of van der Waals interactions occur on a quantum scale. The van der Waals interaction itself acts across the distance separating the interacting bodies, viz on length scales comparable to interatomic spacings up to more than 10 nm. The most important component of the van der Waals interaction is the dispersion interaction due to its omnipresence in all materials. Van der Waals interactions control a range of phenomena such as self-assembly, surface adhesion, friction, and colloid stability [11, 46–57].

They occur on the length scales currently investigated by pioneering theories and techniques in mesoscale engineering, manufacture, biology, and other condensed mat-
ter fields [3, 4]. By studying the physics of van der Waals interactions, it is possible to characterize their strength and role in various systems in these fields of study. Understanding the contributions and effects of variation in a system’s materials, body shapes, and interaction geometry, allows construction and application of mesoscale systems to be designed for deliberate and specific functions. Using the full Lifshitz continuum theory, this thesis investigates how materials, shapes, and configurations effect van der Waals interactions. Chapter 2 contains previously published material with co-authors Daniel M. Dryden, Wai-Yim Ching, Roger H. French, V. Adrian Parsegian, and Rudolf Podgornik, Ref. [137]. Chapter 3 contains previously published material with co-authors Rudolf Podgornik, Wai-Yim Ching, Roger H. French, and V. Adrian Parsegian, Ref. [188]. Chapter 4 contains previously published material with co-authors Daniel M. Dryden, Lin K. Denoyer, Lokendra Poudel, Nicole F. Steinmetz, Wai-Yim Ching, Rudolf Podgornik, V. Adrian Parsegian, and Roger H. French, Ref. [92].

1.1 Motivation

Pioneering techniques and theory in the condensed matter sciences, technology, engineering, and manufacturing are beginning to probe the length regime of van der Waals interactions, where important phenomena in the classical world and quantum world coexist.

Van der Waals interactions are long-range, non-local, and occur on length scales investigated in many fields. In biology, van der Waals interactions govern the structure of packing which is responsible for a variety of self-assembled biological structures [1]. Van der Waals interactions are the dominant interaction binding membranes and proteins, due to role of surface tension at membrane interfaces. They are responsible for attracting membranes together to create membrane multilayers and to enable membranes to adhere to artificial surfaces [1]. They can also result in macroscopic
functionalities, such as those displayed by the gecko foot. A gecko foot uses millions of nm-scale fibers to exploit van der Waals interactions between their setae and surfaces, providing the gecko foot with sufficient attractive force to counter gravity while climbing vertical surfaces [5]. Van der Waals interactions also contribute to the formation of DNA assemblies in viral capsids [6], configuration and conformation of polysaccharides in suspension [7], and the formation of lipid-water liquid crystals [8,9].

They can be used to combine biomolecular and inorganic components to create microstructures, such as DNA-wrapped single-walled carbon nanotubes [10]. They can also be used to engineer inorganic devices using SWCNTs [11], silica nanotubes [12], and colloids [13,14]. Nanotechnological devices such as quantum mechanical actuators [16] and nonlinear micromechanical oscillators [17] have used quantum vacuum forces to construct micromachines. Experiments have studied the role of stiction and adhesion caused by van der Waals interactions in micromechanical systems [15]. Theoretical literature has investigated van der Waals actuated nanomachinery, such as non-contact rack and pinion systems [18]. Torques generated by van der Waals interactions between concentric corrugated cylinders have been used to theorize nanomachine “gears” [19–21]. Van der Waals torques between a disk and plate made of anisotropic materials have been suggested as potential “frictionless bearings” [22].

1.2 History of Derivation and Modern Formulation

Johannes Diderik van der Waals [28] introduced the existence of attractive forces between atoms in his 1873 thesis, where he showed that deviations from the ideal gas law necessitated an interaction between molecules.

1.2.1 London

In 1930, Fritz London [30] further developed the interaction using a quantum-mechanical theory. The development of quantum mechanics was a necessary precursor
to understanding the interactions occurring between neutral atoms and molecules that were first introduced by van der Waals. London derived the interaction between two fluctuating dipoles using second-order perturbation theory. This led to the well-known $1/R^6$ law for interaction energy. However, this derivation is only valid at short distances (roughly, less than 100 nm). This is called the non-retarded regime, where the speed of light is taken to be infinite, and relativistic effects can be ignored. The original London theory is not valid beyond short separations, assumes that atoms and molecules have only one absorption frequency, and does not capture important features, such as solvent effects, which are included in subsequent derivations.

1.2.2 Casimir and Polder

Eighteen years later, Hendrik Casimir and Dirk Polder [33] used quantum electrodynamics to further generalize and develop London’s work. They derived the interaction energies for atom-atom and atom-wall cases at zero temperature. The expressions for the interaction energies between two atoms and between an atom and wall. They showed that London’s $1/R^6$ law, which is valid only for short distances, becomes $1/R^7$ when relativistic retardation effects are included and demonstrated that it is possible to recover London’s equations at small separations.

1.2.3 Casimir

Comments by Niels Bohr first prompted Casimir to re-think the Casimir-Polder formulation in terms of quantum fluctuations of the fields between the two atoms and atom-wall. This led to the formulation of the quantum electrodynamic interaction between two *macroscopic*, neutral, parallel, perfect metal, conducting plates at zero temperature and in vacuum [34,35]. The interaction results in a small but significant attractive force. At a separation of $\ell$, the force/area between the plates is:

$$\frac{\text{Force}}{\text{Area}} = -\frac{\pi^2 \hbar c}{240 \ell^4} = 1.30 \times 10^{-27} \text{Nm}^2/\ell^4.$$
1.2.4 Lifshitz and Contemporaries

In 1955, Evgeny Lifshitz [23] developed, in a continuum approximation, the most general and complete theory between any condensed bodies at any temperature. It is applicable to arbitrary dielectric bodies but assumes vacuum as the intervening material. It includes relativistic retardation effects, uses dielectric and magnetic permeabilities of the bodies, and Maxwell’s equations are solved for the given system’s geometry. The Lifshitz formulation for van der waals interaction in condensed media has its origin in Maxwell’s equations, where the electric and magnetic fields are subjected to fast fluctuations. Lifshitz accounted for these field fluctuations by using Rytov’s fluctuation theorem [39]. By integrating over all allowed frequencies, the Fourier transform of the Maxwell stress tensor components normal to the boundary, Lifshitz derived the van der Waals pressure for two semi-infinite, parallel planes interacting across an intervening medium of finite thickness composed of either a dielectric material or vacuum. In Lifshitz’s formulation, the materials’ properties are represented in terms of macroscopic, continuum properties, to wit, the dielectric response spectra of the system’s materials.

In practice, the full Lifshitz continuum theory of van der Waals interactions employs the molecular scale response of a dielectric material, which is experimentally represented as the materials measured dielectric response spectrum, see Figure 1.3. Maxwell’s equations must satisfy the boundary conditions at the interface of these materials with different polarizabilities, thus only certain frequencies are allowed to occur in the intervening medium. These modes of oscillation exert pressure on the boundaries. van der Waals interactions occur when there are differences in the modes allowed inside and outside the boundaries.

In 1959, Dzyaloshinskii and Pitaevskii [36] generalized Lifshitz’s theory to allow the use of a dielectric material as the intervening medium. Using a sophisticated quantum electrodynamics approach, they provided an alternate derivation of Lif-
shitz’s work which included dielectric materials as the intervening medium. Later, Parsegian developed a heuristic derivation for the interaction free energy in Lifshitz’s formulation by summing the individual oscillator free energies over the full set of frequencies [1].

1.3 Keesom, Debye, and Dispersion Contributions to the Gibbs Free Energy

The Gibbs free energy, $\mathcal{G}$, is the part of a system’s total energy, when pressure and temperature are controlled, that is available to do physical work. For the case of two molecules, the van der Waals interaction free energy, comprises six terms, where three of those terms are inverse sixth power contributions. Five of these six terms represent polarization forces and the sixth term represents the van der Waals interaction.

If the molecules both have a non-zero net charge, then the expression for the interaction free energy is composed of the Keesom (angle averaged) dipole-dipole) and Debye (dipole-induced dipole interaction) contributions to the van der Waals interaction, both of them inverse sixth power of separation contributions.

1.3.1 The Dispersion Contribution to the Free Energy

The third and final contribution is given by the dispersion interaction [3, 40–45]

The “dispersion force” is also known as the “London”, “charge-fluctuation”, “electrodynamic”, or “induced dipole-induced dipole” force, depending on the diction of a given literature. The origin of dispersion forces relates to the dispersion of visible and UV regions of the electromagnetic spectrum.

Unlike the Keesom and Debye contributions, the dispersion term contributes to the van der Waals interaction, even if the net charge is zero and is present between all atoms and molecules. In this way, it composes the most important contribution
to the van der Waals interaction and is sometimes used synomonously for the van der Waals interaction as a whole.

\section*{1.4 Components of van der Waals Interactions}

\subsection*{1.4.1 Types of Charges}

Many types of charges and their fluctuations are responsible for van der Waals interactions. Practically all moving charges can contribute to van der Waals interactions. When the movements of a charge are able to respond to an applied electromagnetic field, they can then generate a transient electromagnetic fields, giving rise to van der Waals interactions. These movements can be motion of electrons around atoms, the oscillations and rotations of dipoles, and the travelling of mobile ions in solutions and metals. However, not all fluctuations contribute equally to the interaction.

\subsection*{1.4.2 Types of Fluctuations and their Time-Scales}

The slowest type of fluctuation that contributes to van der Waals interactions is due to two types of movements: the rotations of dipolar molecules and the translation of ions, which are relatively free and unencumbered by their environments. Slightly quicker movements occur when ions and molecules are not so free to move about and are required to be influenced by their surroundings; these are ionic displacements, molecular rotations, and molecular vibrations. These are the types of slow fluctuations that are able to respond to thermal energy. Their low frequency correlations are robust against screening by relativistic effects and can persist in contributing to the interaction up to it largest separations. Though they span several values, these frequencies are commonly referred to as “zero frequency terms”. Much faster fluctuations, as seen in the UV frequencies of absorption spectra correspond to fast fluctuations. These fluctuations are present in all materials and are generated by the Heisenberg uncertainty principle applied to electron positions, as discussed
above. At small separations, these fast fluctuations are strongly correlated. Unlike low frequency terms, the correlations between fast frequencies are not robust against retardation screening as separations increase. Thus their contributions to the interaction become increasingly screened beyond certain separations.

1.5 Basic Properties of van der Waals Interactions

Unlike the Keesom and Debye contributions, the dispersion term contributes to the van der Waals interaction, even if the net charge is zero and is present between all atoms and molecules. In this way, it composes the most important contribution to the van der Waals interaction and is sometimes used synonymously for the van der Waals interaction as a whole. Dispersion forces govern many properties of mesoscale systems, such as adhesion, surface tension, physical adsorption, wetting, the properties of gases, liquids and thin films, the strengths of solids, self-assembly and flocculation of particles, and the structure of proteins, polymers and other condensed macromolecules.

Dispersion forces, and consequently van der Waals interactions, display the following distinct properties: They exist a length scale that begins at interatomic separations (20 Angstroms) and can act as far as 10 nm in some situations. It is because of this that they are called a “long range interaction”. They can form both attractive or repulsive forces, depending on the composition of the system. They can also generate torques between the interacting bodies. They are nonlocal and non-additive, i.e., the relationship between interaction properties and the composition of the system is dependent on the many-body field in which they act.

A variety of approaches involving a wide range of assumptions, approximations, and complexity have been used to formulate dispersion interactions. For microscopic systems which distinguish individual atoms, few-atom \textit{ab initio} quantum mechanical approaches [132,135,175–177] are useful. The pair-wise summation approach is
only valid for very dilute systems. A most comprehensive formulation is given by the full Lifshitz continuum theory involving a quantum electrodynamic treatment to determine the instantaneous, fluctuating, dipole moments of neutral particles.

1.5.1 Van der Waals Interactions are Always Present

The dipole moment of a non-polar particle time-averages to zero, hence it does not contribute to the interaction, viz. the first order perturbation calculation applied to the Hamiltonian of interacting particles is equal to zero. However, second-order perturbation theory give a non-zero result. Physically, the instantaneous (and fluctuating) dipole moment is non-zero which influences the surrounding electric field. This field then can induce a dipole moment in another neutral atom. The ground state energy of an atom is never zero, i.e., it always has a zero-point energy which can be understood via the Heisenberg uncertainty principle applied to the positions of the electrons about the nuclear protons. These zero-point fluctuations generate a kind of “polarization force” and are the reason that van der Waals interactions are always present in any system. This instantaneous dipole generates an electric field that polarizes any nearby neutral atom and induces a dipole moment in it. The resulting interaction between the two dipoles gives rise to an instantaneous attractive force between the two atoms, and the time average of this force is finite.

1.5.2 Material Effects

For condensed, several-atom bodies, the presence of each atom effects a change in the field through which its neighboring atoms interact, i.e., the interaction occurs in the “medium” of a fluctuating electromagnetic field that is always present in and outside the medium, in the form of exponentially damped standing waves and radiated travelling waves [39].

This interaction, couched in terms of the energy of the electric dipole moment of an atom$_2$ in an electric field created by the dipole moment of atom$_1$, is not caused
by the “action” of the electromagnetic field, i.e., the average dipole moment is zero and there exists no energy change in the first order energy perturbation. Rather, it originates from dispersion of the field due to the electric field, \( E_1 \), of the instantaneous dipole moment of \( \text{atom}_1 \) being felt by \( \text{atom}_2 \), which in turn generates a correlated electric dipole moment due to its electric polarizability, which again in turn generates and electric field, \( E_{1,2} \), due to the \( \text{atom}_2 \)’s dipole moment. \( E_{1,2} \) then acts back on \( \text{atom}_1 \), thus yielding the van der Waals interaction.

In the limit of rarefied media, e.g., a pair of atoms, van der Waals interactions can be formulated directly in terms of the dynamic atomic polarizabilities. However, many-atom condensed media cannot follow a pairwise additive formulation of the this dilute limit. The fluctuation-dissipation theorem relates the fluctuation spectrum of a physical quantity to the reaction of the equilibrium dissipative medium, or susceptibility, to an external field [37]. For condensed media, Lifshitz used the fluctuation-dissipation theorem to represent materials’ properties through their frequency dependent dielectric permittivities, thus addressing the non-additive effects that cannot be represented by summing over pairs of interacting atoms.

1.5.3 Shape Effects

Van der Waals interactions occur at the interface of materials with different polarizabilities. The geometry of those interfaces, to wit, the shape of the interacting bodies, constrains the possible surface mode solutions by demanding that the fields are matched at the boundaries. Hence, van der Waals interactions between bodies inherently carry a complicated dependence on the shape of bodies and the interfaces between them.

1.5.4 The Role of Interfaces

One of van der Waals interactions many influences appears in the forces between dielectrics, conductors, and semiconductors. They play an important role in atom-
surface interactions and are responsible for surface adhesion and wetting, amongst other mesoscale phenomena. Van der Waals interactions occur at the interface of materials with difference polarizabilities. Obviously, if there is no difference in polarizabilities across the interface between materials, then there does not exist a van der Waals interaction.

1.5.5 The Role of Polarizability

In terms of calculations, the ability for a material to accommodate agreement is seen in the material’s polarizability, i.e., the material’s frequency dependent dielectric response spectrum. A highly polarizable material is easily influenced by fields from fluctuating charges while a low-polarizability means the material has little ability to respond. Thus large differences in polarizabilities means a large influence of materials upon each other, e.g., a stubborn, low polarizability material could require large accommodations from a more compliant highly-polarizable material.

1.5.6 Relativistic Retardation Screening

Time retardation effects due to the finite speed of electromagnetic signals begin to effect fluctuation frequencies when the fluctuation’s lifetime, $1/\xi_n$, is smaller than the “round-trip” time of a correlated signal between fluctuations, $2\ell/(c\sqrt{\epsilon_m})$, for a separation distance $\ell$ [1]. Qualitatively, this means that high-frequency contributions to the interaction succumb to retardation screening at large separations (roughly about 100 nm). As the separation is increased, the larger contributions to the interaction that are due to slower fluctuations begin to be screened. Low frequency fluctuations are the most robust against retardation screening. However, the n=0 fluctuation is often lost to ionic screening. The relative amount by which the interaction is reduced by the easy screening of high-frequency terms depends on the particular dispersion spectra of the medium and bodies in the system. Thus, the effects of retardation are highly dependent on material choices.
1.5.7 Debye Screening and Ionic Fluctuations

Free charges, such as free ions in an aqueous buffer or free electrons in a metal, become displaced under polarization. When these free ions travel, they screen electrostatic fields. The zero-frequency contribution to van der Waals interactions represents these slow moving fluctuations and is effectively an electrostatic interaction. The zero-frequency term is screened by free ions at small separations. For example, for a 0.1 M NaCl solution, the zero-frequency contribution nearly vanishes at a separation of just 1 nm. Therefore, for most interactions involving free ions, the zero-frequency term is completely screened.

1.6 The Dielectric Response Functional over Matsubara Frequencies

The complex dielectric function \( \epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) \), is obtained from measured absorption spectra and/or \textit{ab initio} electronic structure calculations. The imaginary part, \( \epsilon''(\omega) \), corresponds to energy dissipation in the material. The Kramers-Kronig relations describe the connection between the real and imaginary parts of complex functions that are analytic in the upper half-plane. Analyticity implies causality in the response function for a stable physical system. Thus the Kramers-Kronig relations encapsulate the important finite limit achievable by electromagnetic signals [32]. Transformation of \( \epsilon''(\omega) \) by the Kramers-Kronig relations yields the London dispersion spectrum, \( \epsilon(i\xi_n) \), which describes the spontaneous field fluctuations that are the origin of the van der Waals interaction. This transforms the dielectric response into the imaginary axis, where \( \xi_n \) are real and are the poles in the upper half plane [30,31].

In the Lifshitz theory the van der Waals interaction is a functional of \( \epsilon(i\xi_n) \), evaluated at the discrete thermal Matsubara frequencies \( \xi_n = 2\pi n k_B T/h \, (n = 0, 1 \ldots) \), where \( k_B \) is the Boltzmann constant. At room temperature Matsubara frequencies
are multiples of $2.4 \times 10^{14}$ Hz or 0.025 eV. The total interaction energy is given by summing over the Matsubara frequencies, $\xi_n = 2\pi n k_B T / \hbar$, where $n$ is an integer, and the $n = 0$ term is counted with a weight 1/2. At room temperature the thermal Matsubara frequencies are a multiple of $2.4 \times 10^{14}$ s$^{-1}$ or 0.025 eV. While only a single $\xi_n$, i.e., $\xi_0$, corresponds to the static response, several for the IR frequencies and a whole band of Matsubara frequencies fall within the optical and UV regimes, it is inadmissible to conclude from this that the optical and UV regimes therefore typically dominate the properties of the vdW interaction. This interaction is a functional of $\epsilon(i\xi_n)$ and not $\epsilon(\xi_n)$.

1.7 Limits, Approximations, and Problems in van der Waals Interactions

1.7.1 Pair-Wise Additivity

There are two approaches to addressing a body’s polarizability. The “pair-wise” approach looks at the influences of a pair of particles on each other. This approach is valid for a single pair and dilute gases, but become increasingly inaccurate for increasing number density of particles. It fails to account for the influence of a third (or fourth, fifth, etc.) particle’s field on the field of the original pair. This approach leads to a van der Waals interaction property called the “Hamaker constant”, which represents the strength of the interaction as being constant over all separations between the interacting bodies. Though shown to be inaccurate, Hamaker constants are still in popular use in some of the scientific community.

The cumulative influences of large numbers of particles on the fields of each other is conveniently incorporated into certain material properties of the optical spectra of materials. Thus, the second approach uses these bulk material properties as a sort of ready-made, mean-field property and thus, more accurately represents the fluctuation correlations between all types of polarizing movements occurring amongst
atomic neighbors comprising the material. This results in a “Hamaker coefficient” (as opposed to the pair-wise “constant”) which carries a dependence on separation, and does not display a simple power-law behavior. This approach is used in the Lifshitz formulation and, in the dilute limit, reduces to the pair-wise approach. For low atomic densities, \( N \), the dielectric response of a medium can be rewritten as a function of \( N \) and an atomic or molecular polarizability coefficient.

1.8 Comparison of Theory and Experimental Measurement

Experimental verification of Lifshitz’s theory has been difficult due to the complicated nature of controlling small objects at very small distances. In 1973, Sabisky and Anderson showed that the force of adhesion of a helium film to a substrate in a helium atmosphere could be described by Lifshitz’s theory, thus using an existing physical phenomenon as a verification of theory [24].

Experimentally, it was found difficult to maintain two plates in a parallel position. In 1997, Lamoreaux gave the first definitive measurement was for the force between conducting plates [25].

Other experiments have been performed using a sphere and plate. Much earlier than these measurements, Derjaguin used the proximity force approximation to deduce the force between a plate and sphere at very short distances from the force between parallel plates [26], but this method fails for all but very small separations.

The systematic errors involved in measurements of the force between parallel plates are relatively large due to difficulties in maintain the parallel positions of the plates. In experiments like these, electrostatic forces may dominant the interaction, thus it is necessary to incorporate an electrostatic calibration for the measurements [27].
2.1 Introduction

This chapter contains previously published material with co-authors Daniel M. Dryden, Wai-Yim Ching, Roger H. French, V. Adrian Parsegian, and Rudolf Podgornik, Ref. [137].

The optical properties of a material, to wit, the imaginary part of the material’s complex dielectric response, is used as input for van der Waals calculations in the Lifshitz formulation. The bulk dielectric response of a material captures quantum structure implicitly in its spectrum. Van der Waals interactions have a doubly non-local relationship to the interacting materials’ dielectric responses. This complicated relationship occludes the consequences of modifications to the spectra on the van der Waals interaction.

A simplified approximate model and two realistic examples of amorphous silica spectrum modified by addition or omission of exciton peaks, are used to show that changes in the dielectric response of a material result in substantial variations in the Hamaker coefficient of the van der Waals interactions, even when the changes are small. The doubly non-local calculations cause a variation in the dielectric response spectra at one particular frequency to influence all the terms in the Matsubara summation, making the total change in the Hamaker coefficient depend on the spectral changes not only at that frequency but also at the rest of the spectrum properly weighted. The Matsubara terms most affected by the addition of a single peak are
not those close to the position of the added peak, but are distributed over the entire range of frequencies. A possibility of eliminating van der Waals interactions or at least drastically reducing them by spectral variation in a narrow regime of frequencies thus seems very remote.

2.1.1 Motivation

There are important issues in the general theory of long-range molecular and macromolecular van der Waals forces and its applications that are both widely misunderstood and deeply entrenched in the colloid and nano-science community. While it is clear that in the Lifshitz theory of van der Waals forces [1, 58] the interaction free energy is a functional of the dielectric response function at imaginary Matsubara frequencies (itself a functional of the imaginary part of the total dielectric response function via the Kramers-Kronig relations), it is seldom appreciated exactly how this non-locality in the dielectric response acts on the properties of van der Waals interaction [2]. What is also often misunderstood are the actual quantitative consequences of variations in the dielectric response of the interacting media on the magnitude of van der Waals interactions.

There are two important contexts in which the appreciation of such issues is a sine qua non for the understanding of the overall features of the interaction between colloidal or nano particles. In the first case, refractive index matching, changes in the dielectric response functions of the medium between the interacting dielectrics are used to modify the interparticle interactions through their van der Waals component [60–67]. Here one often assumes that the dielectric response is dominated by a single absorption peak in the VUV-UV-Vis region of the optical spectrum, corresponding to electronic properties of the materials. The strength of the van der Waals interaction, as codified by the Hamaker coefficient [1], then appears as a simple function of the difference between the squares of the refractive index of the medium and
the interacting bodies [59]. This estimate of the Hamaker coefficient is usually referred to as the Tabor-Winterton approximation (TWA) [60]. If the zero frequency dielectric response is small, matching the refractive index at this single absorption peak should effectively quench the long range van der Waals component of molecular interactions. While a tempting simplification, this can lead to gross underestimation of the overall strength of (macro)molecular interactions, possibly precluding correct interpretation of experimental data on, e.g., wetting.

Another important context for the intricacies of non-locality in the dielectric response function for the variation of the van der Waals interaction, and the one into which we shall delve more deeply, is the effect of excitonic peaks in the ultraviolet and visible (UV/Vis) and higher energy optical region of materials, such as alumina (Al$_2$O$_3$) [79], silica (SiO$_2$) [88], aluminum phosphate (AlPO$_4$) [70], rare gas solids such as Ne [80] and Xe [81], molecular crystals [82,83] and single-walled carbon nanotubes (SWCNTs) [84]. Excitons introduce additional peaks in the energy range below the fundamental absorption edge of the material’s band-gap or slightly shift the position of some other peaks in SWCNTs. Their importance for the strength of van der Waals interaction in the context of SWCNTs remains less clear. Recently Hobbie and co-workers [86] used a simple empirical approach to assess the effect of the excitonic peaks on the strength of van der Waals interactions between SWCNTs. They concluded that in the case of semiconducting nanotubes, neglecting the three excitonic resonances in the optical regime reduces the Hamaker coefficient by roughly 5%. For metallic SWCNTs, neglect of either of these terms reduces the Hamaker coefficient by roughly 3%. In this view, excitonic effects should have a qualitatively small but possibly measurable effect, with its exact magnitude pending on more detailed calculations. It thus appears that the importance of a certain spectroscopic feature in, e.g., the optical regime does not necessarily translate directly into an equally impor-
tant feature of van der Waals interactions. What exactly is the connection remains unclear.

The same problem of excitonic peaks and their influence on the overall strength of van der Waals interaction appears also between condensed media. In this case the theoretical method of choice to evaluate the electronic properties is the orthogonalized linear combination of atomic orbital (OLCAO) variant of density functional theory (DFT), which uses local atomic orbitals for the basis expansion rather than the plane waves [123]. This methodology formulated on a one-electron level of course precludes the inclusion of many-body excitonic corrections, as they are not compatible with the OLCAO-DFT context and may lead to concerns about the underestimation of the band gap as well as a possible rescaling of the complete spectrum. This necessarily implies also modifications in the overall magnitude of the van der Waals interactions between the condensed media. As an example of OLCAO-DFT type of calculation, one can consider the frequency-dependent dielectric function of amorphous silica [77] that can be compared with direct experiments [88]. This comparison shows that the one-electron level OLCAO-DFT calculations can not reproduce the measured excitonic peak. Again the question remains how relevant is this omission in the overall features of the optical response for the quantitative evaluation of the corresponding strength of the van der Waals interaction [2].

In order to address all these issues, we will investigate in detail the effect of variation in the optical properties of the dielectric response function over an interval of frequencies on the strength of the van der Waals interactions as quantified by the Hamaker coefficient. We will confine ourselves to the non-retarded regime as well as to planar interaction geometry, but the analysis can be straightforwardly repeated also for, e.g., small spherical particles or, in fact, for any geometry for which there are explicit Lifshitz’s results [1]. We will first analyse a simple model for the variation of the dielectric response function and then apply the general theory to
an actual dielectric response spectrum with/without the excitonic peak and assess the variation wrought by changes in the dielectric spectrum on the corresponding Hamaker coefficient.

2.1.2 Variation of the Interaction Free Energy: General Theory

Assume that the spectral response of two interacting planar dielectric surfaces is changed from $\epsilon(\omega) \rightarrow \epsilon(\omega) + \delta\epsilon(\omega)$. The Kramers-Kronig transform that enters the van der Waals interaction free energy is defined as [78]

$$\epsilon(i\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon''(\omega)}{\omega^2 + \xi^2} d\omega,$$

(2.1)

with $\epsilon''(\omega)$ the imaginary part of $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$. Quite generally $\epsilon(i\xi)$ is a real, monotonically decreasing function of its argument $\xi$. It follows from the Lifshitz theory of van der Waals interactions [89] that the corresponding interaction free energy change is then defined as $\delta G = G[\epsilon(i\xi) + \delta\epsilon(i\xi)] - G[\epsilon(i\xi)]$. For the planar case of van der Waals interaction between two semi-infinite layers, one obtains to the lowest (linear) order in the dielectric response change $\delta\epsilon$ the simple result [89]

$$\delta G = -\frac{k_B T}{4\pi} \sum_{n=0}^{\infty} \xi_n^2 \left( \text{Tr} \int_{(V)} D_{ik}(i\xi_n, r, r') d^3r \right) \delta\epsilon(i\xi_n),$$

(2.2)

$$= -\frac{k_B T}{4\pi} S \sum_{n=0}^{\infty} \xi_n^2 \left( \text{Tr} \int_{(z)} D_{ik}(i\xi_n, z, z) dz \right) \delta\epsilon(i\xi_n),$$

where the last identity in the above equation stems from the presumed planar geometry with surface area $S$ of the interacting interfaces. $D_{ik}(\omega, r, r')$ is the retarded frequency domain dyadic Green’s function of the electromagnetic field. The sum is over the Matsubara frequencies, $\xi_n = 2\pi nk_B T/\hbar$, where $n$ is an integer, and the $n = 0$ term is counted with a weight $1/2$. At room temperature the thermal Matsubara frequencies are a multiple of $2.4 \times 10^{14} \text{ s}^{-1}$ or $0.025 \text{ eV}$ and thus cover the
whole frequency regime rather unevenly. While only a single $\xi_n$, i.e., $\xi_0$, corresponds to the static response, several for the IR frequencies and a whole band of Matsubara frequencies fall within the optical and UV regimes, it is inadmissible to conclude from this that the optical and UV regimes therefore typically dominate the properties of the van der Waals interaction. This interaction is a functional of $\epsilon(i\xi_n)$ and not $\epsilon(\xi_n)$. Because of this non-locality, variation in the spectral properties of the interacting media at a certain frequency is not directly related to the corresponding frequency term variation in the Matsubara summation over $n$.

Limiting ourselves to the non-retarded case of planar parallel interfaces between two semi-infinite media separated by distance $D$ with dielectric response function $\epsilon(\omega)$ and an intervening medium of $\epsilon_m(\omega)$, the van der Waals interaction free energy $G(D)$ per unit surface area $S$ in the non-retarded limit is given by

$$\frac{G(D)}{S} = -\frac{A}{(12\pi D^2)}$$

where $A$, the *Hamaker coefficient*, is defined as

$$A = -\frac{3}{2} k_B T \sum_{n=0}^{\infty} \text{Li}_3(\Delta_{12}(i\xi_n)) = \sum_{n=0}^{\infty} A(i\xi_n),$$

(2.3)

with the dielectric contrast given by

$$\Delta_{12}(i\xi_n) = \frac{\epsilon(i\xi_n) - \epsilon_m(i\xi_n)}{\epsilon(i\xi_n) + \epsilon_m(i\xi_n)}.$$  

(2.4)

The polylog function $\text{Li}_\nu(z)$ is defined in a standard way [90] and the Kramers-Kronig transforms $\epsilon(i\xi)$ as well as $\epsilon_m(i\xi)$ have been introduced in Eq. 2.1. The variation of this interaction free energy corresponding to a small variation in the dielectric
response functions of the interacting bodies can then be obtained formally from the limit \( c \to \infty \) in Eq. 2.2, as

\[
\delta \left( \frac{\mathcal{G}(D)}{S} \right) = -\frac{k_B T}{8\pi D^2} \sum_{n=0}^{\infty} \text{Li}_2 \left( \Xi_{12}(i\xi_n)^2 \right) \frac{\left( 1 - \Xi_{12}(i\xi_n)^2 \right)}{\Xi_{12}(i\xi_n)} \frac{\delta \epsilon(i\xi_n)}{\epsilon(i\xi_n)} = -\frac{\delta A}{12\pi D^2},
\]

(2.5)

where \( \text{Li}_2(x) \) is the dilogarithm function and the variation of the Hamaker coefficient is given by

\[
\delta A = \frac{3}{2} k_B T \sum_{n=0}^{\infty} \delta A(i\xi_n).
\]

(2.6)

Above \( \delta A(i\xi_n) \) is the partial contribution to the full Hamaker coefficient at the Matsubara frequency \( \xi_n \) whose definition is obvious from comparison with Eq. 2.5.

We next investigate the dependence of the terms in the above Matsubara sum on the value of the frequency. While the relative change in the dielectric response function \( \delta \epsilon(i\xi)/\epsilon(i\xi) \) is a monotonic function, the factor multiplying it in Eq. 2.5, \( \text{Li}_2 \left( \Xi_{12}(i\xi)^2 \right) \left( 1 - \Xi_{12}(i\xi)^2 \right)/\Xi_{12}(i\xi) \), is not. As a consequence, the contribution of the various terms, \( \delta A(i\xi_n) \), to the total Matsubara sum has a maximum whose position depends on the exact form of \( \delta \epsilon(i\xi) \) and \( \epsilon(i\xi) \). This can make the connection between the variation in the dielectric spectrum and the corresponding variation in the van der Waals interaction free energy quite complicated.

### 2.1.3 Interaction Free Energy Variation: a Simple Model

In order to analyze \( \delta A(i\xi) \), we need a form for the frequency dependence of the dielectric function. For this we introduce a simple model that will reveal the salient features of the more realistic problem addressed later. We assume a dielectric response \( \epsilon(\omega) \) for the two semi-infinite dielectric regions, with its imaginary part equal to \( \epsilon''(\omega) \) that we then modify to \( \epsilon(\omega) + \delta \epsilon(\omega) \) by addition of a single narrow absorption peak,
centered at the frequency $\omega_0$ with an area under the peak equal to $A$, approximated as $\delta \epsilon''(\omega) = A \delta(\omega - \omega_0)$. Therefore

$$\omega_0 = \frac{\int_0^\infty \omega \delta \epsilon''(\omega) d\omega}{\int_0^\infty \delta \epsilon''(\omega) d\omega}. \quad (2.7)$$

This defines our simple model. Later we will upgrade it to a realistic calculation for amorphous silica with and without the excitonic peak. From these model assumptions, we then obtain the relevant Kramers-Kronig transforms as

$$\epsilon(i\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon''(\omega)}{\omega^2 + \xi^2} d\omega = 1 + \bar{\epsilon}(i\xi) \quad (2.8)$$

and

$$\delta \epsilon(i\xi) = \frac{2}{\pi} \int_0^\infty \frac{\omega \delta \epsilon''(\omega)}{\omega^2 + \xi^2} d\omega = \frac{2A/\omega_0}{\pi} \frac{\xi}{1 + (\xi/\omega_0)^2}. \quad (2.9)$$

Obviously the transform $\delta \epsilon(i\xi)$ of the dielectric response function depends on $\xi/\omega_0$ and $A/\omega_0$ as scaling variables. Assuming furthermore for convenience that the medium is a vacuum, $\epsilon_m \equiv 1$, we then have

$$\Sigma_{12}(\bar{\epsilon}(i\xi)) = \frac{\bar{\epsilon}(i\xi)}{2 + \bar{\epsilon}(i\xi)}. \quad (2.10)$$

What we are looking for now is the change in van der Waals interaction free energy as the $\omega_0$ peak is added, viz. as the dielectric response changes from $\epsilon(i\xi) = 1 + \bar{\epsilon}(i\xi)$ to $\epsilon(i\xi) = 1 + \bar{\epsilon}(i\xi) + \delta \epsilon(i\xi)$.

We proceed with some general observations. The expression for the Kramers-Kronig transform Eq. 2.8 has the following two limits for $\xi \rightarrow 0$ and $\xi \rightarrow \infty$, respectively

$$\epsilon(i\xi) \simeq \begin{cases} 
1 + \frac{2}{\pi} \int_0^\infty \omega^{-1} \epsilon''(\omega) d\omega = 1 + \frac{2}{\pi} C \\
1 + \frac{2}{\pi} \xi^{-2} \int_0^\infty \omega \epsilon''(\omega) d\omega = 1 + \xi^{-2} \frac{2}{\pi} C'.
\end{cases} \quad (2.11)$$
Figure 2.1. (a) The function $\delta \mathcal{A}(i\xi)$, Eq. 2.5, for six different values of $(\epsilon(0) - 1)$ (from 2 to 12, bottom to top) as a function of $(\xi/\omega_0)$. With increase of $(\epsilon(0) - 1)$ the maximum (purple squares) moves from zero frequency toward non-zero values. The inset shows the complete dependence of the maximum of $\delta \mathcal{A}(i\xi)$, $\xi_{\text{max}}$, on $(\epsilon(0) - 1)$.

For this calculation, we took $r = \omega_0/\omega = 1$. (b) Contour plot of $\text{Max}[\xi/\omega_0]$ as a function of $(\epsilon(0) - 1)$ as well as $r = \omega_0/\omega$. The inset in (a) is obtained by cutting the contour plot (b) with a vertical plane at $r = 1$.

where we introduced

$$C = \int_0^\infty \omega^{-1} \epsilon''(\omega) d\omega = \frac{\pi}{2} (\epsilon(0) - 1)$$

$$C' = \int_0^\infty \omega \epsilon''(\omega) d\omega = \frac{\pi}{2} \omega_p^2$$

(2.12)

These two quantities are obviously connected with the dielectric response sum rules [78]. In the first integral we recognize the static limit sum rule, with $\epsilon(0)$ the static dielectric constant. For substances with the lowest absorption frequency in the optical (visible and UV) region, the static dielectric constant is equal to the square of the optical refraction index. In the second integral we recognize the oscillator strength sum rule (for details see Ref. [78]), where $\omega_p$ is the plasma frequency depending on the effective number of electrons used in transitions at all energies.
The two limits in Eq. 2.11 then suggest a convenient approximation covering the whole range of frequencies that will allow us to analyze the corresponding van der Waals interaction free energy. It has the form

$$\tilde{\epsilon}(i\xi) \simeq \frac{(\epsilon(0) - 1)}{1 + (\xi/\omega_0)^2 (\omega_0/\bar{\omega})^2},$$

(2.13)

with $\bar{\omega}^2 = C'/C$. This approximation is, in fact, quite accurate as long as the dielectric response is given by a single band of frequencies in the optical and/or UV regimes. It becomes inadequate when there are contributions to $\epsilon''(\omega)$ also from the IR and MW regimes. In that case, one should simply revert to the exact definition Eq. 2.8. From the sum rules [78], it follows that $\bar{\omega}$ can be written explicitly as

$$\bar{\omega}^2 = \frac{\int_0^\infty \omega \epsilon''(\omega) d\omega}{\int_0^\infty \omega^{-1} \epsilon''(\omega) d\omega} = \frac{\omega_p^2}{(\epsilon(0) - 1)},$$

(2.14)

and is thus obviously equal to $<\omega^2>$ for the spectral distribution $\omega^{-1} \epsilon''(\omega)$. $r^2 = (\omega_0/\bar{\omega})^2$ thus equals the square of the ratio of the position of the additional peak and the width $<\omega^2>$ of the underlying spectrum.

We expressed the $\xi$ dependence in terms of the dimensionless variable $(\xi/\omega_0)$ because of the assumed form of $\delta\epsilon(i\xi)$, Eq. 2.9, that depends on this dimensionless combination. Therefore $\tilde{\epsilon}(i\xi)$ as well as the variation in the Hamaker coefficient, Eq. 2.5, both depend on the static dielectric constant $\epsilon(0) - 1$ and the ratio $r$.

Having the explicit form of $\tilde{\epsilon}(i\xi)$, we can now calculate the dependence of $\delta A(i\xi)$ on the ratio $\xi/\omega_0$ for $r = 1$ (see Figure 2.1 a). This dependence shows a maximum that depends on the values of $(\epsilon(0) - 1)$ and the ratio $r$. Obviously as $(\epsilon(0) - 1)$ grows past a fixed value, found numerically to be $C_0 \simeq 4.7$ (see below) for $r = 1$, the maximum of $\delta A(i\xi)$ is displaced from $\xi = 0$ to non-zero values. This means that the maximum contribution to the van der Waals interaction free energy is given by the zero frequency term for $(\epsilon(0) - 1) < C_0$ and then depends monotonically on $(\epsilon(0) - 1)$
Figure 2.2. (a) The dielectric dispersion spectrum $\epsilon''(\omega)$ as a function of frequency $\omega$ in eV for amorphous silica without the exciton peak (blue line) and with a simulated exciton peak (green line). The inset shows the difference between the two spectra as a function of frequency. (b) The Kramers-Kronig transform $\epsilon(i \xi_n)$ without (blue line) and with (green line) the exciton peak, as a function of the Matsubara index $n$ of $\xi_n$. The inset again shows the difference.

for larger values. In fact, the behavior of $Max (\delta A(i \xi))$ on $(\epsilon(0) - 1)$ bears a striking formal resemblance to the temperature dependence of the order parameter close to a second-order phase transition [166].

Fitting the calculated dependence of $Max (\delta A(i \xi))$ for $r = 1$ on $(\epsilon(0) - 1)$, it is possible to extract the following behavior for the frequency of this maximum, $\xi_{max}$:

$$
\xi_{max} \sim \begin{cases} 
0 & ; (\epsilon(0) - 1) < C_0 \\
\omega_0 \sqrt{(\epsilon(0) - 1) - C_0} & ; (\epsilon(0) - 1) \geq C_0,
\end{cases}
$$

where $C_0 = 4.7$ can be read off Figure 2.1(a). Obviously, spectra with $(\epsilon(0) - 1) > 4.7$ would lead to a maximum in the van der Waals interaction free energy variation at frequencies that scale linearly with $\omega_0$. Furthermore, the numerical coefficient in Eq. 2.15 as well as $C_0$ are both functions of the ratio $r$. The dependence of $\xi_{max}(\epsilon(0) - 1, r)$
is presented in Figure 2.1(b). It is clear that $C_0$ changes only marginally for $r > 2$ but has an important effect for $r < 1$. Apart from this, qualitatively, the functional form of $\xi_{max}$ is very similar in the whole parameter space. It is indeed quite unexpected that the effect of addition of a lone peak to the dielectric spectrum would effect the different Matsubara terms of the van der Waals interaction free energy in such a non-monotonic fashion.

The relation between the spectral change and the Matsubara frequency at which there is the largest change of the van der Waals interaction free energy is thus quite complicated and extremely indirect. It depends on overall properties of the complete dielectric spectrum as exemplified by $(\epsilon(0) - 1)$ and $r$. Though these results can be derived explicitly only for the very simple model explained above, the salient features revealed remain true even in more realistic cases, as we will elucidate below.

2.1.4 Interaction Free Energy Variation: a Realistic Spectrum

We now apply our general formulation of the dielectric response variation and the consequent van der Waals interaction free energy variation to the case of an exciton peak in amorphous silica. This is aimed at elucidating the often posed, but never properly answered question, what exactly is the effect of addition or removal of a single sharp (exciton) peak on the van der Waals interaction free energy.

For the non-perturbed dielectric dispersion spectrum, we take the imaginary part of the dielectric permittivity, $\epsilon''(\omega)$, of amorphous silica, as calculated with the OLCAO-DFT methodology by Ching et al. [77]. Being a one-electron approximation, the calculated spectrum does not contain any exciton effects; the corresponding peak measured by Tan et al. [88] is missing. In order to simulate an additional excitonic peak, we next synthesize a modified spectrum by adding a Lorentz oscillator peak just below the fundamental absorption edge of the OLCAO-DFT calculated dielectric dispersion spectrum, at a frequency $\hbar\omega_0 = 8.21$ eV. The magnitude, position,
Figure 2.3. The variation of the different Matsubara frequency components in the Hamaker coefficient $A(i\xi_n)$ from Eq. 2.3 for the two spectra from Figure 2.2. The x-axis shows the index $n$ of the Matsubara frequencies $\xi_n$. The biggest change is associated with the lowest frequency terms. The change in the Hamaker coefficient $\delta A(i\xi_n)$ from Eq. 2.6 is shown in the inset as a function of the Matsubara frequency components.

and full width at half maximum (FWHM) of this Lorentz oscillator peak were determined by comparison with experimental spectra [88], so that the ratios of both the position and magnitude of the exciton peak to the first interband transition peak were the same in the experimental spectrum and our synthesized spectrum. The FWHM of the added Lorentz oscillator peak is the same as that of the exciton peak in the measured spectrum. Finally, the whole synthesized spectrum was rescaled so that the total oscillator strength of the spectrum was unchanged by the addition of the Lorentz oscillator peak and that the number of electrons does not depend on the way the spectrum is constructed: the number of electrons involved in transitions up to a certain sufficiently large energy is fixed for a given real material [78].

From Figure 2.2(a) we discern that the addition of the Lorentz oscillator peak affects all or most of the imaginary part of the dielectric spectrum. The imposition
of the oscillator sum rule has the most significant effect only in a narrow frequency interval centered around the fundamental absorption edge, showing a weak tail at larger frequencies. Expectedly the corresponding Kramers-Kronig transform of the dispersion spectrum $\epsilon(i\xi)$ shown in Figure 2.2(b) shows the largest variation close to the static $\xi = 0$ region but has a finite variation distributed throughout the whole range of imaginary frequencies. Obviously the non-local connection between $\epsilon''(\omega)$ and $\epsilon(i\xi)$, provided by the Kramers-Kronig transform, Eq. 2.1, shows up in their quite distinct dependence on the addition of an extra Lorentz oscillator peak.

The effect of peak addition on the corresponding terms in the Matsubara sum for the non-retarded Hamaker coefficient (Eq. 2.6) is shown in Figure 2.3. Clearly, the largest variation of about 10% is observed for lowest Matsubara terms, closest to the static limit. We are thus in the $\xi_{\text{max}} = 0$ limit, see Figure 2.1.

After summing up the Matsubara terms, the total change of the Hamaker coefficient amounts to $\delta A = -5.03 \ zJ$ and is proportional to the area between the two curves in Figure 2.3. The value of the Hamaker coefficient for the original spectrum is 84.9 $zJ$. The relative change in the Hamaker coefficient is thus $\sim 6\%$. Considering that this change is due to the presence of a single narrow Lorentzian peak in the dielectric spectrum of the interacting material, it is non-negligible. Addition of multiple peaks would simply contribute additively to the overall change of the Hamaker coefficient.

We now modify the unperturbed calculated dielectric dispersion spectrum by adding a Lorentz oscillator peak at variable frequency positions, thus avoiding the constraint that the simulated excitonic peak should be just below the fundamental absorption edge. Again the FWHM and the oscillator strength of these added Lorentz oscillator peaks were taken from with experimental spectra [88], while the position was chosen arbitrarily. The background spectrum was multiplied by a scaling factor so that that the oscillator strength at 43 eV ($6.88 \times 10^{16} \text{ s}^{-1}$) for the original spectrum
Figure 2.4. (a) The background dielectric dispersion spectrum \( \epsilon''(\omega) \) of amorphous silica without the exciton peak in the frequency interval 5-30 eV, (black line), and the synthesized spectrum with an added (exciton) Lorentzian peak at various frequencies in units of eV. The dashed curves represent \( n_{\text{eff}}(\omega) \) as a function of frequency for each spectrum. (b) Different Matsubara frequency components as well as their change (inset), as in Figure 2.3, both as a function of the Matsubara frequency index. The biggest change is associated with the low frequency terms and peak position at lower frequencies. Lower energy peaks are larger than high-energy ones despite representing the same number of electrons involved in transitions over their given energy range.

with the additional Lorentzian peak matches the oscillator strength at 43 eV from the experimental spectrum as measured in Ref. [88]. This guarantees that the effective number of electrons up to and including the energy 43 eV remains invariant.

In general the effective number of electrons up to and including the energy \( \hbar \omega \) is related to the oscillator strength sum rule and is given by

\[
n_{\text{eff}}(\omega) = \frac{m_0}{2\pi^2 \hbar c^2} \int_0^{\hbar \omega} u \epsilon''(u) \, du.
\]  

(2.15)

From Figure 2.4(a) it is obvious, that \( n_{\text{eff}}(\omega) \) for a synthesised spectrum becomes effectively identical to the background spectrum without the exciton peak at energies above the added peak. As a result, the added exciton peaks vary in magnitude despite having their oscillator strength invariant, \( i.e., \) lower energy peaks are larger than high
energy ones while representing the same number of electrons involved in transitions over their given energy range.

Figure 2.4(a) shows the rescaled imaginary part of the dielectric spectra for various peak positions and their energy dependent oscillator strengths. At energies above the added Lorentzian peak the oscillator strength becomes universal. The Matsubara frequency components of the Hamaker coefficient are shown in Figure 2.4(b). A broad range of behaviors is observed for the latter, but overall one notices that the peak position at lower $\omega_0$ leads to larger changes in the Hamaker coefficient.

Because of the rescaling implicit in the synthetic spectrum, in order to satisfy the sum rule up to the highest value of the frequency at which data are available for both spectra, the *ab initio* and the experimental results, *i.e.*, 43 eV or $6.88 \times 10^{16}$ s$^{-1}$, the frequency variation of the Matsubara terms in the Hamaker coefficient depends on the position of the peak. For different peak positions the corresponding relative changes in the full Hamaker coefficients are given in Table 2.1. We can thus conclude that the simulation of spectra with an added peak confirms the insight of the model that the addition of peaks at smaller characteristic frequency $\omega_0$ and larger FWHM have a more pronounced effect on the Hamaker coefficient, and make it larger. In fact, one can deduce that the relative changes in the Hamaker coefficient are proportional to FWHM of the added peak and inversely proportional to its frequency $\omega_0$.

<table>
<thead>
<tr>
<th>$\omega_0$ [eV]</th>
<th>4.2</th>
<th>6.2</th>
<th>8.2</th>
<th>10.2</th>
<th>13.2</th>
<th>18.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_0$ [$\times 10^{-16}$ s$^{-1}$]</td>
<td>0.638</td>
<td>0.942</td>
<td>1.245</td>
<td>1.549</td>
<td>2.005</td>
<td>2.764</td>
</tr>
<tr>
<td>$n_{\text{vis}}$</td>
<td>1.7065</td>
<td>1.5926</td>
<td>1.5566</td>
<td>1.5404</td>
<td>1.5289</td>
<td>1.5209</td>
</tr>
<tr>
<td>$\delta A/A$</td>
<td>16.2 %</td>
<td>9.4 %</td>
<td>5.9 %</td>
<td>3.8 %</td>
<td>1.8 %</td>
<td>-1 %</td>
</tr>
</tbody>
</table>

*Table 2.1.* Position of the added (excitonic) peak, index of refraction, $n_{\text{vis}} = \sqrt{\epsilon(\omega_{\text{vis}})}$, at $\hbar \omega_{\text{vis}} = 2$ eV, and the corresponding relative change of the Hamaker coefficient. The index of refraction for the background dispersion spectrum is 1.5222.
2.2 Discussion

2.2.1 Dependence on Properties of the Unperturbed Spectrum and Properties of the Modification

Because the van der Waals interaction free energy is a functional of the Kramers-Kronig transform, itself a functional of the imaginary part of the dielectric function, the relationship between the characteristics of an added peak in the \(\epsilon''(\omega)\) and the Matsubara frequency components of the Hamaker coefficient closest to that frequency is not direct. In fact, the Matsubara frequency component at which the largest change to the Hamaker coefficient occurs varies non-linearly with the frequency of the added peak and depends in a complicated way on the properties of the original spectrum. The overall variation in the Hamaker coefficient is then proportional to the full width at half maximum of the added peak and inversely proportional to its frequency. Its total relative change spans values from a few and up to \(\sim 10\%\), depending on the characteristics of the added peak. In the case of more complicated variations of the dielectric response, corresponding to addition of several peaks, the total variation equals the sum of variations for individual peaks and can be quite large.

2.2.2 Effects of a Single Peak Addition

In order to estimate quantitatively the effect of a single peak addition we synthesized a modified spectrum of amorphous silica by adding a Lorentz oscillator peak just below the fundamental absorption edge of the OLCAO-DFT calculated dielectric dispersion spectrum. For the added exciton peak at 8.21 eV the calculated change in the Hamaker coefficient was established accurately to be 6%. The spectrum was synthesized in such a way that the total oscillator strength \(n_{\text{eff}}(\omega)\) up to 43 eV is held invariant for each spectrum at 12.173 electrons per formula unit of SiO\(_2\). An added peak sweeps up 0.2814 electrons per formula unit from across the whole spectrum into the vicinity of that peak, relocating 2.31% of the total oscillator strength of the
material. Therefore the change in Hamaker coefficient of 6% is quite significant, not only because this change is seen despite oscillator strength being held invariant, but doubly so because of how little oscillator strength was actually relocated into this added excitonic peak.

2.2.3 Effects of Variation of Peak Position

A secondary effect of adding features to the $\epsilon''(\omega)$ spectrum is a change in the visible range index of refraction, $n_{vis}$. This follows directly from the Kramers-Kronig transform which links the real and imaginary parts of any physical variable that obeys causality. Table 2.1 shows the effect on $n_{vis} = \sqrt{\epsilon'(\omega_{vis})}$ evaluated at $\hbar\omega_{vis} = 2eV$ from the addition of each peak. Because the dispersive and absorptive optical properties of a given system are inextricably linked in this manner, any change in the index of refraction (or, equivalently, $\epsilon'(\omega)$) of a material necessarily results in a change of the $\epsilon''(\omega)$ spectrum as well, and thus a change in the Hamaker coefficient for a given system. In this manner the index-matching approach to eliminating van der Waals forces in a system is not totally misguided; however, the implied mechanism is erroneous and the results are imprecise.

Previous results have shown that, in real materials, it is necessary to include transitions up to approximately 20 eV in order to make a reasonable estimate of the Hamaker coefficient for that system [91]. Neglecting features at these higher energies has the consequence of significantly underestimating the strength of van der Waals interactions. This further highlights the danger of index-matching approaches that extrapolate results from low-energy data: without sufficient knowledge of high-energy spectral features in a material, it is not possible to calculate Hamaker coefficients with any accuracy.
2.3 Conclusions

Our calculations of a simplified approximate model as well as of a realistic example of amorphous silica spectrum with and without an exciton peak indicate that even small changes in the dielectric response can show up as substantial variations in the Hamaker coefficient of the van der Waals interactions. However, caution needs to be exercised in making estimates of these variations. Van der Waals interactions are non-local in the frequency response: first through the summation over the Matsubara frequencies in the Lifshitz theory, and then through the imaginary part of the total dielectric response function via the Kramers-Kronig relations. This means that a variation of the dielectric absorption spectrum at one particular frequency influence all the terms in the Matsubara summation of the van der Waals interaction energy, making the total change in the Hamaker coefficient depend on the spectral changes at that frequency but also at the rest of the spectrum properly weighted. For example, the Tabor-Winterton approximation would suggest that matching the refractive index at a single absorption peak should effectively quench the long range van der Waals component of molecular interactions. Our detailed calculations prove that this is certainly not the case.

While it is true that addition of a single peak in the dielectric absorption spectrum can induce a substantial change in the magnitude of van der Waals interactions, the Matsubara terms that are most affected are not those close to the position of the added peak but are distributed over the whole interval of frequencies and can show a maximum whose position is not directly related to the position of the added peak. A possibility of eliminating van der Waals interactions or at least drastically reducing them by spectral variation in a narrow regime of frequencies thus seems very remote.

Some care is therefore necessary when estimating and/or predicting changes in the van der Waals interactions wrought by changes in the dielectric spectrum. There is no
linear correspondence between the interaction free energy variation and the spectral properties of the interacting media.

Figures ?? have been published with coauthors, Ref. [137]. The author performed the calculations and supplied figures. Daniel M. Dryden prepared the synthetic spectra and assisted in data analysis and discussion. Wai-Yim Ching performed ab initio calculations and provided from the unmodified silica spectrum. Roger H. French, V. Adrian Parsegian, and Rudolf Podgornik participated in the analysis, discussion, and manuscript preparation. The research in this chapter was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0008176 and DE-SC0008068. Funding for Wai-Yim Ching’s contributions was provided by the National Energy Research Scientific Computing Center supported by DOE under Contract No. DE-AC03-76SF00098.
CHAPTER 3

DISENTANGLING THE EFFECTS OF SHAPE AND DIELECTRIC RESPONSE IN VAN DER WAALS INTERACTIONS BETWEEN ANISOTROPIC BODIES

This chapter contains previously published material with co-authors Rudolf Podgornik, Wai-Yim Ching, Roger H. French, and V. Adrian Parsegian, Ref. [188].

Van der Waals interactions occur at the interface of materials with different polarizabilities. Consequently, the magnitude, role, and form of van der Waals interactions depend greatly on the materials comprised in a system. In practice, data that represents the (in)ability for materials to influence each other at their interface can be obtained from the measured frequency-dependent dielectric responses of each of the bulk materials. The shape of the interacting bodies also plays an important role in van der Waals interactions. The interfaces between interacting bodies constrain the possible surface mode solutions to Maxwell’s equations by demanding that the fields are matched at the boundaries. Consequently, van der Waals interactions between bodies inherently carry a complicated dependence on the shape of bodies, \textit{i.e.}, the shape of the interfaces formed between materials. Though it is known that the effects of anisotropy on van der Waals interactions [1] between nanoscale bodies [2] are in general a consequence of the morphology of the interacting bodies and the electromagnetic response properties of materials of which they are composed [92], it is unclear how morphological and material anisotropies independently contribute to the vdW interaction energy.

Three system geometries are used to investigate how morphological and material anisotropies each qualitatively and quantitatively contribute to the vdW interaction
energy in the full Lifshitz continuum theory of van der Waals interactions [1]. The free energies, forces, and torques for all separations and mutual orientations are formulated in the full Lifshitz continuum theory of van der Waals interactions. Angular dependence of interactions is characterized for three different interaction geometries of bodies with morphological and/or material anisotropy, interacting across an isotropic aqueous medium: two infinite half-spaces, two half-spaces of composite media comprising parallel cylinder arrays, and an isolated pair of long, thin cylinders. The contributions to van der Waals interaction energy due to shape anisotropy and material anisotropy are isolated in detailed calculations and examined. Inclusion of an orientational degree of freedom in the formulation also permits calculation and comparison of vdW torques experienced in the systems. Surprisingly, the effect of shape on interactions in the retarded regime results in a stronger torque between arrays of cylinders than half-spaces.

3.1 Introduction

Anisotropy effects in the Lifshitz theory of van der Waals interactions were first addressed in the inversed configuration- with isotropic boundaries and anisotropic intervening material [93,94]. Later, Parsegian and Weiss [95] independently solved the problem of bodies with anisotropic dielectric response interacting across an isotropic medium in the non-retarded limit. The complete Lifshitz result including retardation was obtained in the exceptional work by Barash [96,97], leading to renewed interest in the problem and resulting in a series of developments [103–106]. The general Lifshitz formulae for the interaction between two anisotropic half-spaces or an array of finite-size slabs [98] are algebraically untransparent and involved, probably not permitting any further simplification [99]. Effects of morphological anisotropy have also been studied between anisotropic bodies [107–109] or even between surfaces that have anisotropic decorations [110,111].
The Barash results for anisotropic dielectrics were then taken as a point of departure in a dilution process [1] for half-spaces composed of long, oriented cylinders, which considers the presence of dielectric cylinders in the dielectric composite as a small perturbation of the dielectric permittivity [195]. This dilution process then results in a pair-interaction free energy between infinitely long cylinders, of isotropic or anisotropic material, at all mutual angles and separations. The first direct attempt to evaluate the interaction between two parallel isotropic cylinders at all separations came from Barash and Kyasov [112]. The interaction for inclined anisotropic cylinders was later obtained from the dilution process, yielding an explicit formula for the angular dependence of the van der Waals interactions between two infinite cylinders, either with isotropic or anisotropic response, including the non-retarded [113] and retarded limits [114]. These results can be further generalized to cylinders and anisotropic semi-infinite layers [115, 116], a direction we will not pursue here. Orientation dependence of the Casimir, i.e., zero temperature, interaction for perfect metallic cylinders, either parallel [117] or inclined [118], over a wide range of separations was also studied via the scattering approach [119] for non-planar objects at zero temperature and in the classical high-temperature limit.

An unequivocal conclusion of the studies of anisotropies on van der Waals interactions is that their angular dependence shows up in two different ways—corresponding to shape anisotropy and the material anisotropy. The effect is fundamentally non-additive: anisotropic shapes with isotropic material response as well as isotropic shapes with anisotropic material response can both show equally strong anisotropy effects in the van der Waals interactions, i.e., forces and torques. Therefore, what thus remains to be analyzed is what part of the general angular dependence of the van der Waals interaction between anisotropic bodies is due to the shape anisotropy, what part to the material anisotropy, and how to properly disentangle the two closely connected effects.
Figure 3.1. Schematics of the systems of interest with separation, \( \ell \), between bodies in an isotropic medium and angle, \( \theta \), between their principal axes [100]. The isotropic morphology of (a) semi-infinite half-spaces will experience torque only when constructed of anisotropic material. The morphological anisotropy present in (b) composite planes composed of arrays of parallel cylinders and (c) isolated pairs of cylinders will experience torque even when constructed of isotropic material.

In order to answer these queries, we will investigate the van der Waals interactions in the full Lifshitz theory for several separate cases schematically represented in Figure 3.1: two homogeneous semi-infinite planar dielectric bodies with anisotropic dielectric response, two inhomogeneous semi-infinite dielectric composites with embedded arrays either of isotropic or anisotropic cylinders, two interacting cylinders composed of isotropic materials and finally two interacting cylinders composed of anisotropic material. We will investigate the origin and strength of anisotropy effects in van der Waals interactions for all the stated cases and identify the regime and/or configurations in which they are the largest. This will allow us to suggest some specific experimental configurations that could exploit these newly identified features of van der Waals interactions between shape and/or material anisotropic bodies.
3.2 Theoretical Methods

3.2.1 Interaction between two semi-infinite planar anisotropic dielectric materials

The complete solution for the problem of van der Waals interaction between two semi-infinite planar anisotropic dielectric materials interacting across a dielectrically isotropic medium containing no free ions was obtained first by Barash [96, 97]. His result reduces to the non-retarded form of Parsegian and Weiss [95] for small separations (1 - 10 nm) as well as having a fully retarded form for large separations (10-100 nm). The formulae are formidable, mostly due to the fact that, contrary to the isotropic case with polarization degeneracy, the surface waves are a particular linear combination of the polarized ordinary and extraordinary waves, leading to a much more complicated algebra that eventually led to a typographical error in the original formulation. The error was then persistently dragged through the literature until finally rectified in erratum [106]. For this reason, the relevant formulae are fully reproduced in Appendix A.

The Barash derivation leads to the van der Waals interaction free energy for two uniaxial dielectric half spaces as a function of the separation, $\ell$, the angle between the principal directions of the two uniaxial dielectric tensors, $\theta$, and the dielectric responses of all the media involved: that of the isotropic intervening medium, $\epsilon_m$, as well as the perpendicular $\epsilon_\perp$ and the parallel $\epsilon_\parallel$ dielectric responses of the uniaxial semi-infinite media. Their dielectric tensors thus have the form:

$$
\epsilon^{(1)}_{ij} = \begin{bmatrix}
\epsilon_\parallel & 0 & 0 \\
0 & \epsilon_\perp & 0 \\
0 & 0 & \epsilon_\perp \\
\end{bmatrix}
$$

and

$$
\epsilon^{(2)}_{ij} = \begin{bmatrix}
\epsilon_\parallel \cos^2 \theta + \epsilon_\perp \sin^2 \theta & (\epsilon_\perp - \epsilon_\parallel) \sin \theta \cos \theta & 0 \\
(\epsilon_\perp - \epsilon_\parallel) \sin \theta \cos \theta & \epsilon_\parallel \sin^2 \theta + \epsilon_\perp \cos^2 \theta & 0 \\
0 & 0 & \epsilon_\perp \\
\end{bmatrix}.
$$

(3.1)

The frequency dependent dielectric responses involved in Eq. 3.1 in general imply also optical birefringence. The free energy of van der Waals interaction per unit area
for two uniaxial anisotropic half spaces interacting across an isotropic medium is then obtained in terms of the Hamaker coefficient $\mathcal{H}(\ell, \theta)$ (see Appendix A):

$$G(\ell, \theta) = -\frac{\mathcal{H}(\ell, \theta)}{12\pi\ell^2},$$  

(3.2)

where the Hamaker coefficient depends on separation of the bodies and the mutual orientation of the principal directions of the dielectric tensors. It can be evaluated exactly for any value of the separation as well as any anisotropy from formulas Eqs. A.1-A.9 listed in Appendix A. However, a simple analytic dependence on angle can be obtained in the limit of weak anisotropic inhomogeneity, i.e., in the limit

$$\epsilon_\perp = \epsilon_m (1 + \delta_\perp) \quad \text{and} \quad \epsilon_\parallel = \epsilon_m (1 + \delta_\parallel),$$  

(3.3)

for small but otherwise arbitrary $\delta_\perp, \delta_\parallel \ll 1$. One can derive the interaction free energy in the explicit form to the second-order in $\delta_\perp, \delta_\parallel$ as

$$G(\ell, \theta) = \frac{k_B T}{2\pi} \sum_{n=0}^\infty \int_0^\infty QdQ f(Q, \xi_n; \ell, \theta) + \mathcal{O}(\delta_\perp^3, \delta_\parallel^3),$$  

(3.4)

with

$$f(Q, \xi_n; \ell, \theta) = \frac{1}{128} \frac{e^{-2\ell\sqrt{Q^2 + \epsilon_m \xi_n^2}}}{(Q^2 + \epsilon_m \xi_n^2)^2}$$

$$\times \left\{ 2 \left[ (\delta_\parallel + 3\delta_\perp)^2 Q^4 + 2(\delta_\parallel + 3\delta_\perp)(\delta_\parallel + \delta_\perp) Q^2 \epsilon_m \frac{\xi_n^2}{c^2} + 2(\delta_\parallel + \delta_\perp)^2 \epsilon_m \frac{\xi_n^4}{c^4} \right] + (\delta_\parallel - \delta_\perp)^2 \left( Q^2 + 2\epsilon_m \frac{\xi_n^2}{c^2} \right)^2 \cos 2\theta \right\}.$$  

(3.5)

The angular dependence of $G(\ell, \theta)$, and consequently of $\mathcal{H}(\ell, \theta)$, in this limit obviously assumes a particularly simple, explicit analytical form. In the general case, the full
Barash formulae do not yield a simply extractable analytic angular dependence, but numeric results can always be represented with

\[ \mathcal{H}(\ell, \theta) = A^{(0)}(\ell) + A^{(2)}(\ell) \cos(2\theta), \quad (3.6) \]

where the separation-dependent isotropic and anisotropic parts of the Hamaker coefficient, \( A^{(0)}(\ell) \) and \( A^{(2)}(\ell) \), respectively, allow for a straightforward analysis of the angular dependence of the free energy. \( A^{(0)} \) is obtained by choosing the value of \( \theta \) such that the angular contributions to Hamaker coefficient, \( \mathcal{H}(\ell, \theta) \) become zero, i.e., \( \mathcal{H}(\ell, \theta = \pi/4) = A^{(0)}(\ell) \). Subsequently, \( A^{(2)}(\ell) \) is obtained from the resulting difference in \( \mathcal{H}(\ell, \theta) - A^{(0)}(\ell) \).

The force per unit area, \( g(\ell, \theta) \), and the torque per unit area, \( \tau(\ell, \theta) \), can be obtained straightforwardly as

\[
\begin{align*}
g(\ell, \theta) &= -\frac{\partial G(\ell, \theta)}{\partial \ell} \quad \text{and} \quad \tau(\ell, \theta) &= -\frac{\partial G(\ell, \theta)}{\partial \theta} = -\frac{A^{(2)}(\ell) \sin(2\theta)}{6\pi \ell^2} .
\end{align*}
\quad (3.7)
\]

The force per unit area has a complicated dependence on \( \ell \) due to the explicit \( \ell^{-2} \)-dependence of the free energy and the \( \ell \)-dependences of \( A^{(0)}(\ell) \) and \( A^{(2)}(\ell) \). While the \( \ell \)-dependence of \( g(\ell, \theta) \) is complicated, the angular dependence of the torque per unit area can be written as a simple \( \sin(2\theta) \)-dependence with an \( \ell \)-dependent prefactor.

The van der Waals interaction between semi-infinite planes that are made of isotropic dielectric materials, i.e., \( \epsilon_\perp = \epsilon_\parallel \), shows no angular dependence and consequently these isotropic bodies experience no torque. However, this is strictly true only for semi-infinite bodies. Should the two slabs have finite dimensions, the shape anisotropy (see below) would lead to a torque even for isotropic materials.
3.2.2 Interaction Between Two Semi-Infinite Composites Made of Oriented Cylinders

Planes of composite media are constructed from arrays of parallel cylinders of a given volume fraction embedded in an isotropic medium, with the two arrays inclined with respect to one another. While this configuration has been implicated in (non-retarded) van der Waals torques before [101], the relation between the packing density and the strength of van der Waals torques has not been explicitly considered. The arrays interact as a function of their mutual orientation and separation across a gap of isotropic medium. Formulation of the van der Waals interaction free energy for composite media follows that of anisotropic half-spaces but with the modification that the media’s dielectric response functions reflect the composition of the dielectrically inhomogeneous array.

We now assume that both semi-infinite half-spaces are composite materials made of oriented anisotropic cylinders at the volume fraction $v$, with $\epsilon^c_\perp$ and $\epsilon^c_\parallel$ as the transverse and longitudinal dielectric response functions of the cylinder material. For the semi-infinite composite medium of oriented anisotropic cylinders with local hexagonal packing symmetry, the volume fraction is

$$v = \frac{\pi}{\sqrt{3}} \frac{1}{(2 + \frac{\beta}{\alpha})^2} , \quad (3.8)$$

where $\alpha$ is the radius of the cylinder and $\beta$ is the intersurface separation between cylinders. For hexagonal close packing, $v = 0.91$. The anisotropic bulk dielectric response as a function of the imaginary Matsubara frequencies can then be derived in the form [1]

$$\epsilon^{c\perp}(i\xi_n, v) = \epsilon_m(i\xi_n) \left(1 + \frac{2v\Delta_ \perp(i\xi_n)}{1 - v\Delta_ \perp(i\xi_n)}\right) \quad \text{and} \quad \epsilon^{c\parallel}(i\xi_n, v) = \epsilon_m(i\xi_n) \left(1 + v\Delta_ \parallel(i\xi_n)\right) , \quad (3.9)$$
where the relative anisotropy measures in the perpendicular and parallel direction are given by

\[ \Delta_\parallel(i\xi_n) = \frac{\varepsilon^c_\parallel(i\xi_n) - \varepsilon_m(i\xi_n)}{\varepsilon^c_\parallel(i\xi_n) + \varepsilon_m(i\xi_n)} \quad \text{and} \quad \Delta_\perp(i\xi_n) = \frac{\varepsilon^c_\perp(i\xi_n) - \varepsilon_m(i\xi_n)}{\varepsilon_m(i\xi_n)}. \]  

(3.10)

\(\varepsilon_m\) is assumed to be the dielectric function of the isotropic medium between the cylinders as well as between both semi-infinite regions.

The above formula for cylindrical inclusions is due to Rayleigh and is exact to fifth order in volume fraction for any composite. However, higher order terms depend on the exact symmetry of the cylinder packing in the array [3]. While other mixing formulations for the composite dielectric function are possible and have been explored in the context of van der Waals interactions [22,120], they differ mostly in the higher order volume fraction terms. Since the problem of the dielectric response of the composite does not possess a general, universally valid solution, approximations are necessary and should be checked for consistency whenever possible. The Rayleigh form possesses the virtue of yielding the correct van der Waals interaction between a pair of cylinders in the process of dilution [113,114] as described in the next section. Also, in the Rayleigh approach the scattering effects are not taken into account on the level of the dielectric function, which is a drawback of the method, but it does allow for an exact inclusion of the packing symmetry which would be difficult in other approaches. Rayleigh and Maxwell-Garner mixing rules in fact coincide for up to 15% volume fraction [121] and do not differ fundamentally even for much higher packing fractions.

The van der Waals interaction free energy, the force, and the torque per unit area then follow from the same formulae as in the previous section, but taking due notice that now the parallel and the perpendicular dielectric responses of the semi-infinite media are given by the dielectric composite relation
\[ \epsilon_\perp \rightarrow \epsilon_\perp(v) \text{ and } \epsilon_\parallel \rightarrow \epsilon_\parallel(v) \]. \hspace{1cm} (3.11)

To lowest order, the Hamaker coefficient is quadratic in \( v \), as can be seen by expanding the Barash result, Eq. 3.2, and has the explicit form

\[ G(\ell, \theta) = -v^2 \frac{k_B T}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} Q \, dQ \, f(Q, \xi_n; \ell, \theta) + \mathcal{O}(v^4) \), \hspace{1cm} (3.12)\]

where

\[ f(Q, \xi_n; \ell, \theta) = f^{(0)}(Q, \xi_n; \ell) + f^{(2)}(Q, \xi_n; \ell) \cos 2\theta \], \hspace{1cm} (3.13)\]

with

\[ f^{(0)}(Q, \xi_n; \ell) = \frac{\Delta_\parallel^2}{128} e^{-2\ell \sqrt{Q^2 + \epsilon_m \xi_n^2 \ell^2}} \times \left\{ 2 \left[ (1 + 3a)^2 Q^4 + 2(1 + 3a)(1 + a)Q^2 \epsilon_m \xi_n^2 \ell^2 \right] \right\} , \hspace{1cm} (3.14) \]

and

\[ f^{(2)}(Q, \xi_n; \ell) = \frac{\Delta_\parallel^2}{128} e^{-2\ell \sqrt{Q^2 + \epsilon_m \xi_n^2 \ell^2}} \times \left\{ (1 - a)^2 \left( Q^2 + 2\epsilon_m \xi_n^2 \ell^2 \right)^2 \right\} . \hspace{1cm} (3.15) \]

The ratio of the relative anisotropy measures is defined as

\[ a = \frac{2\Delta_\perp}{\Delta_\parallel} = \frac{(\epsilon_\perp - \epsilon_m)\epsilon_m}{(\epsilon_\perp + \epsilon_m)(\epsilon_\parallel - \epsilon_m)} . \hspace{1cm} (3.16) \]

The Hamaker coefficient therefore also acquires an additional dependence on the volume fraction of the interacting composites, quadratic to the lowest order, with the general form

\[ \mathcal{H}(\ell, \theta; v) = \mathcal{A}^{(0)}(\ell; v) + \mathcal{A}^{(2)}(\ell; v) \cos(2\theta) \]. \hspace{1cm} (3.17) \]

Unlike the case of van der Waals interaction between isotropic planes, in the case of dielectric composites made of isotropic cylinders, \( i.e., \epsilon_\perp = \epsilon_\parallel \), we see persistence of
angular dependence stemming from the anisotropic shape of the cylinders, which is present in all configurations of this type of composite media. The origin of dielectric anisotropy can therefore be traced to either material anisotropy of the interacting homogeneous dielectric materials, or to the shapes of the constituent units in the case of dielectric composites.

The force per unit area, $g(\ell, \theta)$, and the torque per unit area, $\tau(\ell, \theta)$, now follow from the same formulae as in the case of two homogeneous anisotropic semi-infinite regions. Again, the force per unit area has a complicated dependence on $\ell$; the angular dependence of the torque per unit area is simply $\sin(2\theta)$ with an $\ell$ dependent prefactor.

### 3.2.3 Interaction between an Isolated Pair of Cylinders

Starting from the interaction free energy of composite media made of arrays of parallel cylinders embedded in an isotropic medium, the interaction free energy of an isolated pair of cylinders is derived by a dilution process, taking the volume fraction of the composite in the dilute limit and expanding the anisotropic dielectric responses to second-order in the number density. The coefficient of this term is proportional to the pair-interaction free energy [1].

To do this, we assume that the two anisotropic half-spaces are composed of identical anisotropic cylinders of radii $R_{1,2} = \alpha$, at volume fraction $v$, with $\epsilon_{\perp}$ and $\epsilon_{\parallel}$ as the transverse and longitudinal dielectric response functions of the cylinder materials. We then expand the Barash interaction free energy $G(\ell, \theta)$ for two half-spaces again as a series in $v$, Eq. 3.12, and evaluate the coefficient multiplying the $v^2$ term. The volume fraction $v$ scales with the area density of the cylinders ($N$) in the direction of their long axes as $v = N \pi \alpha^2$. It then follows [1] that the interaction free energy between two cylinders, $G(\ell, \theta)$, whose axes coincide with the anisotropy axes of the two composites at a separation $\ell$, inclined at an angle $\theta$, can be obtained from a
second derivative of $G(\ell, \theta)$ (see Appendix B) as

$$N^2 \sin \theta \ G(\ell, \theta) = \frac{d^2 G(\ell, \theta)}{d\ell^2} = \nu^2 \frac{k_B T}{2\pi} \sum_{n=0}^{\infty} \int_0^{\infty} Q dQ \frac{d^2 f(Q, \xi_n; \ell, \theta)}{d\ell^2},$$

where $f(Q, \xi_n; \ell, \theta)$ is written explicitly in Eq. 3.13. Note that such an expansion is possible only if the dielectric response at all frequencies is bounded. In the case of an ideal metal Drude-like dielectric response, this expansion is not feasible and our method cannot be transplanted to that case automatically. By noting that

$$f(Q, \xi_n; \ell, \theta) = f^{(0)}(Q, \xi_n; \ell) + f^{(2)}(Q, \xi_n; \ell) \cos 2\theta,$$

$G(\ell, \theta)$ can be finally obtained explicitly and exactly as [114]

$$G(\ell, \theta) = -\frac{(\pi \alpha^2)^2}{2\pi \ell^4 \sin \theta} \mathcal{H}(\ell, \theta) = -\frac{(\pi \alpha^2)^2}{2\pi \ell^4 \sin \theta} (A^{(0)}(\ell) + A^{(2)}(\ell) \cos 2\theta),$$

where the isotropic and the anisotropic parts of the Hamaker coefficient, i.e., $A^{(0)}(\ell)$ and $A^{(2)}(\ell)$, can be obtained in explicit forms (given in Appendix B) and they depend on the relative anisotropy measures in the parallel and perpendicular directions, Eq. 3.10, at imaginary Matsubara frequencies. The ratio of the relative anisotropy measures, Eq. 4.3, can be thought of as a specific measure of the anisotropy of the cylinders compared with the isotropic bathing medium $m$. Note that the relative anisotropy measures vanish when the transverse/longitudinal dielectric response of the cylinder material equals the medium response.

Note also that because of the $\sin^{-1} \theta$ in the free energy, the angular dependence is now associated with both Hamaker coefficients, $A^{(0)}$ and $A^{(2)}$, unlike in the case of the semi-infinite planar and composite bodies which have angular dependence associated only with the orientation term, i.e., $A^{(2)} \cos 2\theta$. Furthermore, the interaction free energy diverges for two parallel cylinders since for two infinite parallel cylinders their
interaction free energy scales as their length, so that the interaction free energy per unit length remains perfectly finite. We will not be specifically dealing with this anomalous situation as perfect alignment is difficult to envision for any realistic nano-objects.

For cylinders, the force, \( \tilde{g}(\ell, \theta) \), and the torque, \( \tilde{\tau}(\ell, \theta) \), can now be obtained straightforwardly as

\[
\tilde{g}(\ell, \theta) = -\frac{\partial G(\ell, \theta)}{\partial \ell} \tag{3.21}
\]

and

\[
\tilde{\tau}(\ell, \theta) = -\frac{\partial G(\ell, \theta)}{\partial \theta} = -\frac{(\pi a^2)^2}{2\pi \ell^4} \left( A^{(0)}(\ell) + A^{(2)}(\ell^2 - \cos 2\theta) \right) \frac{\cos \theta}{\sin^2 \theta} \tag{3.22}
\]

The force per unit area has a complicated dependence on \( \ell \), stemming from the explicit \( \ell^{-4} \) dependence of the free energy, as well as both \( A^{(0)}(\ell) \) and \( A^{(2)}(\ell) \) that also separately depend on \( \ell \). The angular dependence of the torque can be obtained explicitly, and has a complicated angular dependence, partly due to the overall \( \sin^{-1} \theta \) dependence of the interaction free energy and partly from the angular dependence of the Hamaker coefficient.

### 3.3 Results and Discussion

#### 3.3.1 Bulk Dielectric Response Function

In what follows, we specifically consider the dielectric responses of materials that are accessible and relevant to mesoscale interactions in aqueous solutions [92]. As the intervening isotropic solvent, we have taken water with a well known frequency-dependent dielectric response function [1] as provided by the *Gecko Hamaker* software platform, which also contains an extensive spectral database of various relevant materials [122]. We used the *ab initio* orthogonalized linear combination of atomic orbital (OLCAO) method [123] to calculate the electronic structures and optical properties
of [6,5,s] and [9,3,m] carbon nanotube (CNT) materials [11]. The CNTs represent good examples of materials with highly anisotropic optical properties, and we have used them to characterize the bulk dielectric response of two semi-infinite materials. Other choices are also possible [92].

The semi-infinite anisotropic composite materials are constructed as arrays of [6,5,s] and [9,3,m] anisotropic CNT cylinders embedded in water at various volume fractions, given by Eq. 3.8 in terms of the interaxial separation between the cylindrical inclusions in the composite, see Figure 3.2a. We next constructed anisotropic semi-infinite composites out of isotropic cylindrical inclusions. Clearly, here the anisotropic material component is missing and the bulk anisotropy is due only to the morphological anisotropy of the inclusions, see Figure 3.2b. The isotropic dielectric response of the cylindrical inclusions is computed from the isometric average of the perpendicular and parallel responses of the unmodified [6,5,s] and [9,3,m] CNT dielectric spectra. The anisotropic dielectric responses used as inputs for formulae for interacting solid planes or a pair of cylinders are independent of volume fraction, ε∥ (dashed black line) and ε⊥ (solid black line) are shown for [9,3,m] CNT in Figure 3.2a. Calculations for interactions between planes or cylinder pairs with isotropic (I) dielectric responses use ε′∥ = ε′⊥ = (ε∥ + ε⊥)/2, shown as a black solid line in Figure3.2b.

For planes of composite media composed of cylinders embedded in water, the dielectric responses become dependent on the volume fraction of cylinders, see Eq. 3.8. Volume fractions are calculated for separations, β, between cylinders given as multiples of the cylinder radius, e.g., α = 0.42 nm for [9,3,m] CNTs. The parallel responses (dashed lines) and perpendicular responses (solid lines) are plotted in Figure 3.2a for four volume fractions corresponding to cylinder separations of 0, α, 2α and 3α. For composite bodies made of cylinders of isotropic material, ε′∥ = ε′⊥ are used as input for Eqs. 3.9, leading to anisotropic responses, ε∥ ≠ ε⊥, for the composite body. For decreasing volume fractions of cylinders, the magnitude of anisotropy between ε∥
Figure 3.2. Frequency-dependent dielectric response $\epsilon(i\xi)$, with frequency in eV units. (a) The anisotropic bulk dielectric responses, $\epsilon_{||}$ and $\epsilon_{\perp}$, for semi-infinite planes are shown for [9,3,m] CNTs as black dashed and black solid lines, respectively. The responses for composite media with varied volume fractions of cylindrical inclusions, are shown for volume fractions of 0.91 (green), 0.40 (red), 0.23 (cyan), and 0.15 (magenta), corresponding to cylinder separations of 0, $\alpha$, 2$\alpha$ and 3$\alpha$, respectively, with $\alpha = 0.42$ nm as the radius of [9,3,m] CNTs. (b) Isotropic bulk dielectric responses are computed from the isometric average of the anisotropic dielectric responses shown in (a). Though the dielectric responses of the cylindrical inclusions are isotropic (black), the composite dielectric responses become anisotropic due to the anisotropic shape of the cylindrical inclusions.

and $\overline{\epsilon_{\perp}}$, shown as dashed lines and solid lines, respectively, in Figure 3.2b, decreases as $\overline{\epsilon_{||}}$ and $\overline{\epsilon_{\perp}}$ tend toward the isotropic background response, $\epsilon_{water}$, dotted line.

### 3.3.2 Hamaker Coefficient

#### 3.3.2.1 Effects on $A^{(0)}$ term

We now proceed to the evaluation of the Hamaker coefficients as defined above. We present three different interaction geometries with anisotropic and isotropic materials: planar anisotropic half spaces, planar composite half spaces, and two isolated cylinders.

The orientation-independent coefficient, $A^{(0)}$, for materials like [6,5,s] and [9,3,m] CNTs shown in Figure 3.3, is the dominating contributor to the total Hamaker coefficient, $\mathcal{H}$, and consequently, the free energy per unit area for planar and com-
Figure 3.3. (a) The $A^{(0)}$ term of the Hamaker coefficient for planes ([6,5,s] green, [9,3,m] magenta), and composites of volume fractions 0.91 ([6,5,s] red, [9,3,m] black) and 0.15 ([6,5,s] yellow, [9,3,m] orange) of anisotropic (solid lines) or isotropic material (dashed lines) with a mutual angle, $\theta = \pi/4$, is plotted as a function of separation. (b) $A^{(0)}$ as function of separation between an isolated pair of long, thin cylinders made either of anisotropic or isotropic [6,5,s] (blue) or [9,3,m] (cyan) CNT material.

For interacting planes made of anisotropic [6,5,s] and [9,3,m] CNT materials, shown as solid lines in Figure 3.3a, we see large values of $A^{(0)}$ due to the large dielectric contrast at the interface of the bodies and the intervening water medium. For interacting planes made of isotropic material, given by averaging the parallel and perpendicular dielectric responses, the values of $A^{(0)}$, shown as dashed lines, are less than those of the anisotropic case due to a slightly lower dielectric contrast at the interfaces.

For interacting composite bodies, Eqs. 3.6, 3.17, and the free energy per isolated pair of cylinders, Eq. 3.20. For example, at 6 nm separations $A^{(0)}$ constitutes approximately 96 to 99.9 % of the total Hamaker coefficient for interacting planes and for an interacting cylinder pair. For interacting composite bodies separated by a 6 nm gap, $A^{(0)}$ constitutes about 59 % of $H$. For large values of separation, retardation effects are clearly visible and result in smaller values of the Hamaker coefficient.
Figure 3.4. (a) $A^{(2)}$ for an isolated pair of cylinders ([6,5,s] blue, [9,3,m] cyan), planes ([6,5,s] green, [9,3,m] magenta), and composites of volume fractions 0.91 ([6,5,s] red, [9,3,m] black) and 0.15 ([6,5,s] yellow, [9,3,m] orange) of anisotropic (solid lines) or isotropic material (dashed lines) with a mutual angle, $\theta = \pi/4$, is plotted as a function of separation. (b) The ratio of $A^{(2)}$ relative to the total Hamaker coefficient is greatly increased by the morphologically anisotropic cylinders in the composite and pair cylinder cases when compared to the planar cases which contain no morphological anisotropy. The isotropic cases (dashed lines) for composite planes retain their angular dependence because of the shape of the cylindrical inclusions (inset).

For composite bodies with embedded cylinders made either of anisotropic or isotropic dielectric material, dielectric contrast is reduced at the interface between the bodies and the water gap due to Eqs. 3.9 and 3.11. Thus, the values of $A^{(0)}$ are reduced compared to the case of interacting planar bodies, see Figure 3.3a.

For an interacting pair of cylinders, we see $A^{(0)}$ values that are similar to those for planar and composite cases, see Figure 3.3. The $A^{(0)}$ term becomes related to orientation when multiplied by the factor $\sin^{-1} \theta$ in the expression for free energy for a cylinder pair, Eq. 3.20.

3.3.2.2 Effects on $A^{(2)}$ Term

Unlike $A^{(0)}$, the Hamaker coefficient $A^{(2)}$ intrinsically carries dependence on the mutual orientation of interacting anisotropic bodies. For materials like those shown in Figure 3.4a, the magnitude of $A^{(2)}$ is much smaller than that of $A^{(0)}$, thus $A^{(2)}$
typically contributes little to the interaction free energy and normal force between bodies. In cases where the interactions have no angular dependence, such as two isotropic, semi-infinite planar bodies acting across an isotropic gap, $A^{(2)} = 0$. In Figure 3.4a, interacting planes of anisotropic material (solid lines for all systems) show a non-monotonic variation of $A^{(2)}$ with separation. This non-monotonic variation of the Hamaker coefficient, sometimes leading also to non-monotonic dependence of the interaction free energy, has been observed in the case of van der Waals interactions in the system composed of an ice layer, interacting with air across a liquid water layer [124]. In that case, similarly to in our own, the non-monotonicity results from a subtle interplay of dielectric anisotropy, inhomogeneity, and the finite velocity of light, and is thus a signature of the retardation effects.

For interacting composite planes and for an interacting cylinder pair, Figure 3.4a shows non-zero values for both the anisotropic material (solid lines) cases as well as the isotropic material (dashed lines) cases. In general, both the highly anisotropic shape of cylinders as well as the anisotropy of the materials’ responses contribute to the values of $A^{(2)}$. However, in the case of interacting planes, only the material anisotropy contributes to $A^{(2)}$. Figure 3.4b shows that the contribution of $A^{(2)}$ relative to the total Hamaker coefficients, $A^{(2)}/(A^{(0)} + A^{(2)})$, is greatly increased by the inclusions of morphological anisotropy in the composite and pair cases when compared to the planar cases (green and magenta curves) which contain no morphological anisotropy. A detailed view in the inset shows that, for composites and cylinder pairs, even isotropic materials (dashed lines) have large values of $A^{(2)}$ which are comparable in magnitude to their analogous cases with anisotropic materials (solid lines).

### 3.3.3 Effects on van der Waals Interaction Free Energy

The free energies of interaction, $\mathcal{G}(\ell, \theta)$, for planar and composite cases are calculated per unit area, $S$. Figure 3.5a shows similar behavior for the free energies per 1
Figure 3.5. (a) Free energy per unit area, $G$, between planes ([6,5,s] green, [9,3,m] magenta) and composites of volume fractions 0.91 ([6,5,s] red, [9,3,m] black) and 0.15 ([6,5,s] yellow, [9,3,m] orange) of anisotropic (solid lines) or isotropic material (dashed lines) with a mutual angle, $\theta = \pi/4$, is plotted as a function of separation. The free energy between composite bodies with a separation of 6 nm as a function of mutual angle (inset) shows an angular-dependence that is dissimilar to that of planes. (b) Free energy per isolated pair of cylinders, $G$, at a mutual angle of $\theta = \pi/4$, is plotted as a function of separation for cylinders of anisotropic or isotropic [6,5,s] (blue) or [9,3,m] (cyan) material. The cylinder pair shows (inset) a stronger angular dependence than planes and composites.

nm$^2$ as a function of separation for planes and composites for the cases of anisotropic materials (solid lines) and isotropic materials (dashed lines). However, Figure 3.5a (inset) shows that free energies of composites have a much stronger dependence on mutual angle than planar cases. The values of interaction free energies given for two interacting cylinders as a function of separation in Figure 3.5b show a behavior similar to that seen for planes and composites. The free energy expression for a pair of cylinders carries an additional theta dependence of $sin^{-1}\theta$ with both Hamaker coefficients, Eq. 3.20, that is not present in the expressions for planar and composite cases. Therefore, Figure 3.5b (inset) shows a stronger dependence of the free energy between two cylinders on mutual angle than seen in Figure 3.5a (inset) for planes and composites.
Figure 3.6. Composite bodies experience magnitudes of torque greater than those between planar bodies even when the composite’s inclusions are constructed of isotropic material. (a) Torque per unit surface area, $\tau$, between planes ([6,5,s] green, [9,3,m] magenta) and composites of volume fractions 0.91 ([6,5,s] red, [9,3,m] black) and 0.15 ([6,5,s] yellow, [9,3,m] orange) of anisotropic (solid lines) or isotropic material (dashed lines) with a mutual angle, $\theta = \pi/4$, is plotted as a function of separation ($\tau = 0$ for plans of isotropic material). (b) Torque between planes and composite bodies with a separation of 6 nm as a function of mutual angle.

3.3.4 Effects on van der Waals Torque

The interaction free energy per unit area for planes and composites are differentiated with respect to mutual angle and plotted as torque per 1 nm$^2$ area at $\pi/4$ radians as a function of separation for bodies made of anisotropic materials (solid lines) and isotropic materials (dashed lines) in Figure 3.6a. Though the values of free energy are similar for interacting planes and composites at maximum packing fraction, see Figure 3.5a, their torque values are dissimilar at all volume fractions, evidencing the effect of morphological anisotropy introduced by the inclusion of cylinders in composite bodies. Significantly, though the composite case with, e.g., maximum volume fraction (red and black curves), has less interacting material than the planar case (green and magenta curves) it shows much larger values of torque for both cases of anisotropic material and isotropic material in Fig.3.6.
Figure 3.7. (a) Torque per isolated pair of cylinders, $\tilde{\tau}$, at a mutual angle of $\theta = \pi/4$, is plotted as a function of separation for cylinders of anisotropic (solid lines) or isotropic (dashed lines) [6,5,s] (blue) or [9,3,m] (cyan) material. (b) Torque as function of mutual angle, $\theta$, between a pair of cylinders interacting across a 6 nm gap. Cylinders made of either anisotropic or isotropic material will experience torques that drive them to seek parallel alignment of their longitudinal axes.

In Figure 3.7a, the torque experienced between a pair of interacting cylinders inclined at $\pi/4$ radians, is plotted as a function of separation. Torque values show similar dependence on separation compared to those of planes and composites, but of course, lower magnitude due to the reduced dimensionality of the calculation. Comparable magnitudes would be obtained if one would multiply the torque of a lone pair of cylinders by the appropriate surface density in a composite body. The free energy of interaction for a pair of cylinders has two angle-dependent factors and consequently a stronger dependence of torque on mutual angle, shown at a separation of 6 nm in Figure 3.7b.

3.4 Conclusions

The effects of anisotropy on van der Waals interactions are complicated and can be traced to two or fewer properties of a system. Angular dependence of the van der Waals interaction between bodies can originate from either the anisotropy of the
shape of the bodies (morphological anisotropy) or anisotropy of dielectric response of
the materials (materials anisotropy) of the bodies. Each system can have one, both,
or neither of these properties which allow angular dependencies in the interaction free
energy.

3.4.1 Isolation of Material Anisotropy Effects

The case of two interacting anisotropic semi-infinite planar slabs shows angular
dependence of the interactions purely due to the anisotropic material response. When the interfaces are made of isotropic material, the free energy loses all dependence on orientation, the angular dependent term, $A^{(2)}$ drops out of the free energy, and consequently the system displays no torque between the apposed planar interfaces. Two interacting anisotropic semi-infinite planar surfaces are a prime example of anisotropic van der Waals interactions originating solely in the material dielectric response anisotropy of the bodies.

3.4.2 Isolation of Shape Anisotropy Effects

For an isolated pair of cylinders, the van der Waals interaction free energy depends on interaxial separation and its dependence on mutual orientation angle contains both shape anisotropy and material anisotropy effects. Unlike anisotropic planes which carry angular dependence of $\cos 2\theta$ with only the $A^{(2)}$ term in the Hamaker coefficient, cylinders carry an additional $\sin^{-1} \theta$ dependence on mutual angle with both Hamaker coefficients, see Eq. 3.20, due to their anisotropic shape. Two interacting cylinders composed of isotropic material are a prime example of anisotropic van der Waals interactions originating solely in the shape anisotropy of the bodies.

3.4.3 Effects in Composite Bodies

The formulae for interacting composite bodies exhibit both types of anisotropy
effects as a natural consequence of the process of embedding arrays of anisotropic
cylinders into two half-spaces with planar surfaces. The anisotropic shape of the long, thin, embedded cylinders in addition to the anisotropic response of the material from which the cylinders are made, result in strong angular dependence and large van der Waals torques generated between the bodies. Even in cases where the material of the cylinders in the arrays have isotropic dielectric responses, we still see large torque values due to the shape of cylinders. Arrays of cylinders will therefore seek to align their principal dielectric axes even if the material is isotropic.

Larger torque values between composite bodies than between planes is a corollary to the process of embedding cylinder arrays into planes. Unlike the small change effected by this process on the free energies of these two systems, the effect on torque is dramatic. This effect of anisotropy in a composite material can be seen in the increase in the orientational Hamaker coefficient, $A^{(2)}$, see Figure 3.4. The magnitude of $A^{(2)}$ is carried through the differentiation of free energy with respect to the mutual angle, i.e., torque, between the bodies and results in values much larger than those of solid bodies. The increase in anisotropy and torque is largest for close packing and is drastically reduced as the arrays become dilute. The effect of shape in interactions between composite bodies comprising arrays of parallel cylinders results in significantly stronger torques than those seen between solid anisotropic planar spaces. This clearly points to the non-additivity of the shape and material anisotropies in this case, which is an important conclusion to bear in mind when trying to detect the van der Waals torques between anisotropic bodies. The anisotropic shape of the embedded cylinders in composite bodies increases the anisotropy between the bulk dielectric responses in the parallel and perpendicular directions for the composite body, see Figure 3.2. The zero-frequency thermal contribution to the free energy, i.e., the $n = 0$ term in the sum over Matsubara frequencies, is the frequency most affected by this change. For example, the zero-frequency term of the perpendicular dielectric response of a [6,5,s] CNT composite increases by 63% and its parallel response is nearly doubled. For
the [9,3,m] CNT composite at maximum volume fraction, the zero-frequency term in
the perpendicular response increases by 66 % while the parallel response decreases by
3 %. As the separation between cylinders increases (volume fraction decreases) the
zero-frequency term of the dielectric response of the composite begins to approach
the zero-frequency term of the dielectric response of water and thus the dielectric
contrast with the intervening medium is decreased.

3.4.4 Experimental Points

Though the van der Waals torque between anisotropic bodies is small [105,125] it
seems to be measurable, with a direct experiment still lacking [126,127]. From the dis-
cussion above and from related work by Esquivel-Sirvent and Schatz [22] it seems that
the van der Waals torques between ordered arrays of anisotropic nanoparticles embed-
ded in an isotropic matrix would be a good direction for experiments. Such arrays are
well known and have been observed with many biological macromolecules including
DNA, various polysaccharides such as cellulose or hyaluronic acid, and polypeptides
such as microtubules or actin, to name just a few (for details see Yasar, et al. [128]
and references therein). Cylindrical arrays with hexagonal local symmetry observed
in DNA-covered SWCNTs [129] or surfactant-covered SWCNTs [130] well fall within
the confines of our theoretical model of anisotropic arrays. Another possibility that
we do not consider here, though it is implied by the (nematic) ordering of the array
of cylinders, is the action of external fields on the dielectric properties of interacting
bodies [101]. The fact that ordered arrays of cylinders lead to pronounced van der
Waals torques could be exploited in filament-gliding assays above planes composed
of layers of locally aligned microtubules with grain boundaries between regions array
orientation [131]. The van der Waals torque could possibly influence the direction of
motion of the gliding filament as it crosses the orientational grain boundary.
3.5 Summary

Orientational-dependence in the full Lifshitz formulation of van der Waals interactions generally results from two system properties, shown here as: 1. anisotropy of materials’ bulk dielectric responses in the axial and radial directions, and 2. anisotropic morphology demonstrated here by long, thin shape of cylinders in pairs or in arrays embedded in composite planes. The effects of these two properties are isolated through analysis of three interaction geometries—planes, composite planes, and a cylinder pair. Each of the three systems characterizes different strengths of dependencies on the anisotropies of materials’ responses and/or bodies’ shapes. Interacting composite bodies made of arrays of parallel cylinders embedded in a medium display dependence on both material and shape anisotropies, resulting in values of torque between the arrays that, surprisingly, can be stronger than those between planes and may lead to new experimental possibilities.

Figures 3.2-3.7 in this chapter have been published with coauthors, Ref. [188]. The author performed the vdW calculations and supplied figures. Wai-Yim Ching performed ab initio calculations and supplied calculated absorbance spectra. Roger H. French, V. Adrian Parsegian, and Rudolf Podgornik participated in analysis and discussion. The research in this chapter was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Awards DE-SC0008176 and DE-SC0008068. Funding for Wai-Yim Ching’s contributions was provided by the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC03-76SF00098.
CHAPTER 4
ACCESSIBLE, ACCURATE, OPEN-SCIENCE VAN DER WAALS CALCULATIONS

This chapter contains previously published material with co-authors Daniel M. Dryden, Lin K. Denoyer, Lokendra Poudel, Nicole F. Steinmetz, Wai-Yim Ching, Rudolf Podgornik, V. Adrian Parsegian, and Roger H. French, Ref. [92].

Van der Waals interactions govern the organization, orientation, and self-assembly of different types of molecules. By studying the physics of van der Waals interactions, it is possible to characterize their strength and role in various systems, and ultimately, to enable directed and deliberate construction or specific application of molecules or materials. The Gecko Hamaker open-science software [?, 92, 122], along with its open-database of material optical properties, improve on currently available calculations by employing the full Lifshitz continuum theory of van der Waals interactions [11, 119, 132, 134, 135, 176]. Gecko Hamaker calculates the van der Waals forces, torques [187, 188], interaction energies, and Hamaker coefficients that govern the assembly of elements such as DNA, collagen, single-walled carbon nanotubes, and inorganic materials. Lifshitz’s theory accurately captures important effects in mesoscale assembly and design, such as solvent effects, temperature effects, relativistic retardation screening, anisotropy of material’s optical properties, and morphological anisotropy of system elements. The transparency of open-science architecture allows data sharing and increases opportunities for collaboration. User feedback about Gecko Hamaker improves the quality and reproducibility of the science and increases ease of use and versatility of the software.
4.1 Introduction

Van der Waals interactions become increasingly important as nanotechnology [169] and science [170, 171] probe smaller and smaller length scales [2, 167, 168], finding themselves in the regime where the role van der Waals interactions is no longer negligible. Indeed, at the nano- and meso-scales van der Waals interactions can be used to design, drive, and control assembly and functionality of components such as molecular wires and ribbons [46], graphene sheets [173,174], single-walled carbon nanotubes (SWCNTs) [11], linear informational macromolecules [172], fibrous proteins, surfactant monolayers, and biological membranes [1].

Van der Waals calculations are unwieldy and the commonly used alternatives and approximations often fail to incorporate important factors [137], leading to poor representation of the role of van der Waals interactions in mesoscale systems [132,138–142]. The Gecko Hamaker open-science software [122], along with its open-database of material optical properties, uses Lifshitz’s theory to supply the online community with open, accurate, and accessible calculations of van der Waals interactions, Figure 4.1 [11,119,132,134,135,176]. Gecko Hamaker calculates the van der Waals forces, torques, interaction energies, screened terms, and Hamaker coefficients that govern the assembly of elements such as DNA, collagen, single-walled carbon nanotubes,
Figure 4.2. Schematic illustration of the *Gecko Hamaker* work-flow, using a large-radius (24,24,s) SWCNT and Type I collagen in aqueous solvent as examples. Full spectral optical properties (upper left) are taken as input, experimentally measured using optical or electron energy-loss spectroscopy, or calculated using *ab initio* methods. An interaction geometry (lower left) is then chosen, consisting of optically anisotropic cylinders, optically anisotropic half-spaces, multi-layered half-spaces, or graded-interface half spaces. Specific optical properties from the spectral database are then applied to each element in the configuration. The outputs are the isotropic $A^{(0)}_{1w1}(\ell)$ (upper right, bold) and the anisotropic part $A^{(2)}_{1w1}(\ell)$ of the Hamaker coefficients if applicable (upper right, dotted), as well as torques, normal forces, and thermodynamic interaction free energies (lower right). All quantities are given as functions of surface-to-surface separation $\ell$ for a user-specified skew angle $\theta$ (for anisotropic systems) and radii $R_1$ and $R_2$ (for cylinders).

and inorganic materials. We present an open-source, open-data, multi-platform application to calculate van der Waals interactions using the full Lifshitz formulation of van der Waals interactions for a variety of interaction separations and orientations, body morphologies, and materials. Users can select materials from the accompanying MariaDB open source database [136] of optical/UV spectra or users can upload their own spectra and generate their dispersion spectra for use in Gecko Hamaker calculations. Gecko Hamaker allows users to tailor system parameters and material types to represent their specific experiments or design goals, Figure 4.2.
The software improves upon previous isotropic [70] and non-retarded [11] calculations and improves the currently available accuracy of van der Waals calculations of alternative formulation approaches by employing the full Lifshitz continuum theory of van der Waals interactions. It accurately describe solvent and temperature effects, retardation, optically and morphologically anisotropic materials for cylindrical, layered planes, planar arrays [188], and planar interaction geometries [105, 179, 180]. This approach accounts for many-body interactions and permits the use of bulk dielectric responses to capture the role of material properties in the calculations [1].

In the following sections, the versatility of Gecko Hamaker as design tool for the exploration and discovery of novel features of long-range van der Waals interactions is demonstrated for case of an interacting pair of cylinders. In these examples, each of the two cylinders are composed of identical or different materials selected to represent current, promising technological materials such as metallic and semiconducting SWCNTs, [11, 50, 181–183] multiple composites of DNA, [54, 55, 184] collagen, [185] polystyrene, [186] and inorganic materials. The Hamaker coefficients, forces, and torques [187] presented for several cases of cylinder pairs in aqueous media.

4.2 Methods

The properties and capabilities of Gecko Hamaker are demonstrated using an example case of interacting pair of cylinders composed of a variety of materials and interacting across an isotropic aqueous medium. Other geometries, not explored here, are also in the Gecko Hamaker code. Van der Waals interaction energies, Hamaker coefficients, normal forces, are torques, including screening and retardation effects, are presented for pairs of cylinders for symmetric (cylinders are composed of the same material) cases and asymmetric (cylinders are composed of different materials) cases for various separations and orientations. The materials used for these calculations are selected from the 100+ spectra available in the database and include DNA, collagen,
single-walled carbon nanotubes (SWCNTs), and inorganic materials (silica, alumina, polystyrene).

### 4.2.1 Application of Lifshitz’s Theory in Gecko Hamaker

The complex dielectric spectrum, $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, of a material can be obtained from its measured absorption spectrum or from ab initio electronic structure calculations. Full spectral properties are available from the MariaDB open database which accompanies the Gecko Hamaker software. The imaginary part of the dielectric response, $\epsilon''(\omega)$, is required for calculations in the Gecko Hamaker software. After the spectrum is chosen or uploaded by the user, it is transformed by the Kramers-Kronig relations into a form that is a functional, $\epsilon(i\xi_n)$ over the Matsubara frequencies, $\xi_n$, where $\xi_n = 2\pi nk_BT/\hbar = n2.4 \times 10^{14} Hz = n \times 0.025 eV, (n = 0, 1 \ldots)$. This transform greatly simplifies the calculations by representing the input as a well-behaved, monotonically decreasing function over the discrete Matsubara frequencies. Because of this, it is possible to represent the dielectric response function of the intervening isotropic, aqueous medium, $\epsilon_m(i\xi)$, as the combination of Debye and Lorentz oscillators [1].

For a pair of cylinders indexed as 1 and 3, the dielectric responses parallel and perpendicular to the longitudinal axis of a cylinder are denoted by, $\epsilon_{1,3}^{\parallel}(i\xi)$ and $\epsilon_{1,3}^{\perp}(i\xi)$, respectively. The relative anisotropy measures are then provided by

$$
\Delta_{\parallel}^{1,3}(i\xi) = \frac{\epsilon_{1,3}^{\parallel}(i\xi) - \epsilon_m(i\xi)}{\epsilon_m(i\xi)} \quad \text{and} \quad \Delta_{\perp}^{1,3}(i\xi) = \frac{\epsilon_{1,3}^{\perp}(i\xi) - \epsilon_m(i\xi)}{\epsilon_{1,3}^{\parallel}(i\xi) + \epsilon_m(i\xi)}. \quad (4.1)
$$

The van der Waals interaction free energy between two semi-infinite, uniaxial optically-anisotropic, dielectric planes interacting across a finite intervening medium with thickness $\ell$, was derived in the nonretarded formulation by Wiess, et. al. in 1972 [95]. In 2005, Capasso et. al. developed the fully retarded interaction energy, $\mathcal{G}(\ell, \theta)$, as a function of separation $\ell$ and the angle between principal dielectric anisotropy axes $\theta$ [105].
Calculation of the interaction between pairs of anisotropic cylinders of different materials follows the formulation presented in detail in section 3.2.3. The formulation begins by modifying the simple case of two uniaxially anisotropic planar half-spaces acting across an isotropic medium [105] into interacting arrays of oriented cylinders of (an)isotropic materials embedded in the same medium as the intervening space [188, 191, 194]. A dilution process, via the Pitaevskii method, then leads to the interaction energy between a pair of cylinders [1]. It then follows that the interaction free energy between two cylinders, \( G(\ell, \theta) \), whose axes are contained within the two parallel boundaries at a separation \( \ell \), but skewed at an angle \( \theta \) is given by the second derivative \( \frac{d^2 G(\ell, \theta)}{d\ell^2} \) expanded to second-order in the density of the two cylindrical arrays. [1] Note that such an expansion is possible only if the dielectric response at all frequencies is bounded, so that in the case of materials with free charges one needs to model them explicitly [195].

Van der Waals torques will always arise from interactions between optically isotropic or anisotropic cylinders acting across an isotropic medium and the cylinders will seek alignment of their principal axes. Torques and attractive or repulsive normal forces can be found by differentiating the free energy with respect to mutual angle and separation, respectively:

\[
\tau = -\frac{dG(\ell, \theta)}{d\theta} \quad \text{and} \quad F = -\frac{dG(\ell, \theta)}{d\ell}.
\]

The free energy has a periodic dependence on the mutual angle. For \( \theta \to 0 \), the parallel cylinders require a different treatment to properly incorporate the assumption of infinite length [194].

\[
G(\ell, \theta) = -\frac{(\pi R_1^2)(\pi R_2^2)}{2\pi^4 \ell^4 \sin \theta} \left( A^{(0)} + A^{(2)} \cos 2\theta \right), \quad (4.2)
\]
where the inverse \( \sin \theta \) dependence stems from morphological anisotropy and the \( \cos 2\theta \) dependence from the material anisotropy. For both symmetric and asymmetric systems with cylindrical morphology, the Hamaker coefficients, \( A^{(0)} \) and \( A^{(2)} \), are functions of separation, \( \ell \) (see Figure 4.2), as well as of the ratio of relative anisotropy measures, \( a(i\xi_n) \), which depend on the material types and sampling frequencies

\[
a_{1,3}(i\xi) = 2\Delta_{\perp}^{1,3}(i\xi)/\Delta_{\parallel}^{1,3}(i\xi).
\]  

(4.3)

The total Hamaker coefficients as functions of separation are produced from the summation over the Matsubara frequencies, \( \xi_n \), with the \( n = 0 \) term weighted by \( 1/2 \),

\[
A^{(0)} =
\frac{k_BT}{32} \sum_{n=0}^{\infty} \Delta_{\parallel} \Delta_{\parallel} P_n^4(\ell) \int_0^{\infty} t dt \frac{e^{-2p_n(\ell)\sqrt{t^2+1}}}{(t^2+1)} \tilde{g}^{(0)}(t, a_1(i\xi_n), a_3(i\xi_n))
\]  

(4.4)

with

\[
\tilde{g}^{(0)}(t, a_1, a_3) = 2[1+(3a_1)t^2+(1+a_1)]^{1/2} 1^n 3^n + 4(1+a_1)(1+a_3)
\]

and

\[
A^{(2)} =
\frac{k_BT}{32} \sum_{n=0}^{\infty} \Delta_{\parallel} \Delta_{\parallel} P_n^4(\ell) \int_0^{\infty} t dt \frac{e^{-2p_n(\ell)\sqrt{t^2+1}}}{(t^2+1)} \tilde{g}^{(2)}(t, a_1(i\xi_n), a_3(i\xi_n), \theta)
\]  

(4.5)

with

\[
\tilde{g}^{(2)}(t, a_1, a_3, \theta) = (1-a_1)(1-a_3)(t^2+2)^2.
\]

The dimensionless factor \( p_n^2(\ell) = \epsilon_m(i\xi_n)\xi_n^2/\ell^2 \), which depends on the ratio of the travel time of light, \( \ell/c \), across the intervening separation and the fluctuation lifetime, \( \xi_n \),
captures the separation dependence and retardation due to the finite speed of light. For the zero-frequency Matsubara term, the lifetime of the fluctuations is sufficiently long to not be affected by retardation.

4.2.2 Gecko Hamaker

Recent advances in the theory of van der Waals interactions have facilitated the implementation of an open-source, open-data design tool that facilitates understanding and prediction of the magnitude and properties of van der Waals interactions in a wide variety of contexts. The Gecko Hamaker open-source software project is a full implementation of the complete mesoscale Lifshitz theory for isotropic and anisotropic planar multilayer [179], sharp or graded interfaces for modeling of grain boundaries [196] and cylinder-cylinder [191] interaction geometry with an intervening dielectric medium, accompanied by an extensive database of material optical properties spectra.

The Gecko Hamaker software and its source code are distributed freely on Sourceforge [122] under the GNU General Public License [197]. The machine-readable optical property database is available either for download or as a web service and makes available the full spectral properties of over 100 materials from both ab initio calculations [11,198] and experiments, [2,70,199,200] including inorganic as well as organic materials such as Type I collagen and (GC)10 duplex DNA spectra. [123, 198] This open-science architecture is at the forefront of a growing trend, with both the US government [201,202] and the G8 nations [203] emphasizing data sharing for advancing the dialog of scientific discovery. By making the Gecko Hamaker open data science tool with its spectra database freely available, we increase the opportunities for collaboration between researchers focused on long-range interactions and mesoscale design engineers in energy materials, chemistry, physics and biology.
4.3 Results and Discussion

The full Lifshitz formulation of van der Waals interaction energies, Hamaker coefficients, normal forces, and torques are calculated by Gecko Hamaker for several combinations of materials using the cylinder pair geometry as an example configuration. The results for this example case show several trends that are relevant to other materials and configurations. The Hamaker coefficients, $A^{(0)}_{1w1}(\ell)$ and $A^{(2)}_{1w1}(\ell)$, of the van der Waals free energy represent the magnitude and type, i.e., attractive or repulsive, of interaction. They serve as convenient data to study several features of van der Waals interactions. For any system that is morphologically isotropic and constructed of isotropic materials, $A^{(2)}_{123}(\ell)$ makes no contributions to the system’s interaction energy. However, morphological anisotropy always exists in cylindrical bodies. Therefore, all calculations presented here have non-zero $A^{(2)}_{123}$ values. The cylinder pairs used for example calculations are constructed with various amounts of material anisotropies.
and all display strong morphological anisotropy. The angular dependence of van der Waals interactions is examined in the cylinder pair configurations and trends are generalizable to other systems which contain material and/or morphological anisotropies.

All example calculations were performed for two cylinders interacting across an aqueous medium. Contributions to the interaction free energies that are made by the $n = 0$ term of the Matsubara frequencies are assumed to be completely screened by free ions. For an aqueous medium with salt concentrations greater than about $10^{20}$ cm$^{-3}$, i.e., equivalent to about 50 mM univalent ion solution, ion screening will occur for separations larger than 1 nm. It is reasonable to assume that the carrier concentration in aqueous medium is sufficient to screen the $n = 0$ fluctuation contribution to the Matsubara sum. Accordingly, the $A_{n=0}^{(2)}(\ell)$ terms vanish for all the presented calculations.

For many systems of interest, for example, biological systems, it is necessary that the environments of the molecules be maintained at the proper ion concentrations that ensure viability of the molecules. In general, these concentrations are sufficient to produce complete ion screening of the static ($n = 0$) contribution. The $n = 0$ Matsubara term is often relatively large compared to other terms in the summation. Consequently, the strength of the interaction can be greatly reduced by ion screening due to the intervening medium. For highly anisotropic materials, such as metallic SWCNTs, the $n = 0$ term can be large. For example, the $A_{n=0}^{(0)}(\ell)$ term is 50.5 zJ for the symmetric case of (5,2,m) metallic SWCNTs, separated by 5 nm of aqueous medium, see Figure 4.3. The dielectric responses of amorphous silica ($aSiO_2$) are less anisotropic than those of (5,2,m) and the screened term is accordingly smaller: $A_{n=0}^{(0)}(\ell)=2.15$ zJ at 5 nm separation.

The reduction in the interaction due to ion screening can be dramatic, especially for systems constructed of materials with relatively small differences between the dielectric of the materials. For example, $A_{n=0}^{(0)}(\ell)$ the for $aSiO_2$ is about 24.8% of the
unscreened Hamaker coefficient. Ion screening greatly reduces the interaction strength for $aSiO_2$. For the case of (5,2,m) SWCNTs acting across an aqueous medium, dielectric contrasts are large and the $n = 0$ term comprises only 4.4% of the unscreened $\mathcal{A}^{(0)}(\ell)$.

### 4.3.1 Symmetric Systems

For symmetric systems, denoted by $1w1$ subscript, comprising two cylinders constructed of the same material acting acting across and intervening medium (water), the interaction free energy is always attractive. For all practical purposes, the magnitude of the interaction free energy can be represented by the Hamaker coefficients, $\mathcal{A}^{(0)}_{1w1}(\ell)$ and $\mathcal{A}^{(2)}_{1w1}(\ell)$. The magnitudes of $\mathcal{A}^{(0)}_{1w1}(\ell)$ and $\mathcal{A}^{(2)}_{1w1}(\ell)$ can vary greatly, depending on material choices, body morphologies, and system configuration. Values for screened $\mathcal{A}^{(0)}_{1w1}(\ell)$ and $\mathcal{A}^{(2)}_{1w1}(\ell)$ are provided for a pair of identical cylinders in aqueous medium as a function of separation in Figure 4.3. Values for $\mathcal{A}^{(2)}$ are generally much smaller than those for $\mathcal{A}^{(0)}$, and for fully isotropic systems, $\mathcal{A}^{(2)}$ vanishes. However, in the case of interacting cylinders, their highly anisotropic shape ensures that $\mathcal{A}^{(2)}$ is always non-zero, even when the system’s materials are isotropic.

Figure 4.3 shows that the dynamic range of Hamaker coefficients can be large. For the materials evaluated in the cylinder pairs examples, metallic SWCNTs, such as (9,3,m) and (5,2,m), provide the largest values of $\mathcal{A}^{(0)}_{1w1}(\ell)$ and are consistent with published values [11]. $\mathcal{A}^{(0)}_{1w1}(\ell)$ values for (5,2,m) SWCNTs are very large due to their highly anisotropic response spectra. Inorganic ceramics, such as $Al_2O_3$ and $AlPO_4$ exhibit large, but much smaller Hamaker coefficient values than SWCNTs, as shown in Figure 4.3.

In Figure 4.3, proteins, like type 1 collagen, also display significantly large Hamaker coefficients. Polystyrene, $aSiO_2$, and SWCNTs with large radii, such as (24,24,s), display smaller Hamaker coefficients due to their lower dielectric contrasts with the
Figure 4.4. Asymmetric configuration $A_{1w3}^{(0)}(\ell)$ (solid lines) and anisotropic $A_{1w3}^{(2)}(\ell)$ (dotted lines) cylindrical Hamaker coefficients for the interaction of silica nanorods with biological materials in the fully retarded formulation with screened zero-frequency contribution in the case of intervening aqueous medium.

medium. The small values for DNA materials, such as (AT)$^{10}$, (GC)$^{10}$, (AT)$^{5}$,(GC)$^{5}$, and (AT-GC)$^{5}$, exhibit small values of Hamaker coefficients. DNA constructed of the same amino-acids but in different sequences, display different Hamaker coefficients. This indicates a dependence of interaction energy on base-pair sequence and suggests an ability to control self-assembly through deliberate sequencing.

4.3.2 Asymmetric Systems

Mesoscale design and structures often involve interactions between different materials. For example, the interactions between silica nano-rods and biological materials may be used in sensors [192] and nano-bio interfaces [193]. Example asymmetric cases of heterogenous systems comprising cylinders of two different materials are denoted by the subscript $1m3$, Figure 4.4. Particular interaction strengths can be developed through deliberate selection of the types of heterogeneous materials used in a sys-
tem. For example, a silica and collagen cylinder pair separated by 5nm in an aqueous medium exhibits an interaction strength that is 39% larger than the interaction between silica-(GC)10 DNA cylinders. Materials can be chosen such that the interaction is robust against retardation effects. This occurs when silica is combined with a (24,24,s) SWCNT and their interaction persists for relatively large separations. The materials can also be selected such that retardation effects greatly reduce the interaction at large separations, such as in the silica-collagen and silica-(GC)10 cases.

A unique feature of asymmetric systems is that they allow for attractive or repulsive interactions, as well as interactions that change between repulsive and attractive at certain separations and global energy minima. Repulsive interactions depend on the dielectric response spectra of the heterogeneous materials (1 and 3) and medium (m). For dielectric responses that obey $\epsilon_1 < \epsilon_m < \epsilon_3$ the van der Waals interaction between 1 and 3 will be repulsive if the inequality exists over the entire range of Matsubara frequencies. If the inequality is true for only a particular range or ranges of frequencies, then the interaction will be change between repulsive and attractive for certain ranges of separation. The values of separation for which the sign of the interaction occurs depends on region of Matsubara frequencies for which the inequality is true. For example, Hamaker coefficients for a (24,24,s) SWCNT interacting with a cylinder of several different materials, Figure 4.4, exhibits values that increase then decrease with increasing separation. The dielectric response spectra of the particular case of a (24,24,s) SWCNT interacting with a collagen cylinder in an aqueous medium obey the inequality for energies above 10 eV. As these energies are gradually screened out by retardation, they no longer contribute repulsive terms to the interaction, leading to a net increase in $A_{1w3}^{(0)}$. At sufficiently large spacings, even the attractive low-energy contributions are damped by retardation, implying a decrease in $A_{1w3}^{(0)}$ as separation increases.
Figure 4.5. Pairs plot of symmetric and asymmetric interactions of anisotropic cylinders across an aqueous medium. The Hamaker coefficients, $A^{(0)}_{1w3}$ and $A^{(2)}_{1w3}$, and the forces and torques at a skew angle of $45^\circ$, at $\ell = 5$ nm separation are shown for interactions between a wide array of different materials, including biological materials, canonical inorganic materials, and SWCNTs. Cells are shaded according to interaction energy magnitudes. Torques and forces are calculated using commonly accepted literature values for radii of SWCNTs and biomaterials, and 1 nm radius for all other materials. The asterisk indicates that the color scale for $A^{(0)}_{1w3}$ saturates at 121 zJ for clarity, and $A^{(2)}_{1w3}$ saturates at 3.0 zJ, with negative values shaded according to their absolute value.

### 4.3.3 Relativistic Retardation Screening Effects

Time retardation effects due to the finite speed of electromagnetic signals begin to effect fluctuation frequencies when the fluctuation’s lifetime, $1/\xi_n$ is smaller than the “round-trip” time of a correlated signal between fluctuations, $2\ell/(c\sqrt{\epsilon_m})$, for a separation distance $\ell$. Qualitatively, this means that high-frequency contributions to the interaction succumb to retardation screening at large separations (roughly about 100 nm). As the separation is decreased, the larger contributions to the interaction that are due to slower fluctuations begin to be screened. Low frequency fluctuations...
are the most robust against retardation screening, however, the n=0 fluctuation is often lost to ionic screening.

The effects of retardation screening of the different frequency contributions can be seen in the change of the Hamaker coefficients $A_{1w1}^{(0,2)}(\ell)$ as a function of separation in Figures 4.3 and 4.4. High-frequency contributions are the first to be screened at large separations. The relative contribution to the total free energy that is due to high-frequency terms depends on the particular dispersion spectra, $\epsilon_{1,m,3}(\xi_n)$, in the system [1]. Thus, the effects of retardation are highly dependent on material choices.

For (24,24,s) SWCNTs, the strongest optical contrast with water occurs at low frequencies. At about 50 nm, it exhibits minimal time-retardation screening compared to the other materials in Figure 4.3. The optical contrast of type I collagen with water results in contributions from all frequencies (Figure 4.3, blue). Its significant contributions from the higher Matsubara frequencies are screened and it exhibits a dramatic retardation effect as these frequencies are screened with increasing separation.

Retardation screening can sometimes result in a change in the relative magnitudes of dielectric responses of the three bodies in the system [190, 191] (also see “Asymmetric Cases” above). For example, at high frequencies, for a water layer at the interface of ice and vapor (not shown here), the materials have dielectric responses, $\epsilon_i < \epsilon_w < \epsilon_v$. Elbaum and Schick showed that this leads to a repulsive interaction and causes the thickness of the water layer to increase at the interface between ice and vapor [190]. However, because high-frequency contributions are the first to be screened, the repulsive contribution to the interaction vanishes as the thickness of the water increase. The remaining frequency contributions have relative dielectric responses, $\epsilon_v < \epsilon_i < \epsilon_w$, which results in an attractive interaction. At, the very low frequencies, the dielectric spectra return to the repulsive case, however, because low
frequencies are robust against retardation screening, they result in a finite thickness of water between ice and vapor.

The large number of spectra available in Gecko Hamaker’s associated open-database, makes it possible to select and view dispersion spectra of materials such that have relative responses \( \epsilon_1 < \epsilon_m < \epsilon_3 \), and to calculate the consequent repulsive interactions. For spectra choices that have relative responses \( \epsilon_1 < \epsilon_m < \epsilon_3 \) for only a particular range of frequencies, the separation \( \ell \) at which the interaction changes from repulsive to attractive will depend on the frequency(-ies) \( \xi_n \) at which the dielectric responses cross-over according to the relationship between \( 1/\xi_n \) and \( 2\ell/(c\sqrt{\epsilon_m}) \), explained above.

4.3.4 Angular Dependence due to Shape Anisotropy

The example of an interacting pair of cylinders represents the currently most highly anisotropic system morphology available in Gecko Hamaker. By construction, the cylinders are infinitely long in the longitudinal direction and very thin in the radial directions, resulting in a highly anisotropic distribution of material in three-dimensional space. The Lifshitz formulation of van der Waals interactions solves for the surface modes solutions of Maxwell’s equations at the interface between materials. For cylinders, the interface between the cylinder material and the aqueous medium is unlimited in the longitudinal direction but very constraining in the radial directions. For most morphologies, orientational dependence is carried by only the \( A^{(2)} \) term of the free energy equation. However, for the cylinders’ highly anisotropic shape, the free energy equation carries a \( 1/sin(\theta) \) prefactor multiplying both Hamaker coefficients, \( A^{(0)} \) and \( A^{(2)} \). This results in strong values of torque that seek alignment of the cylinders’ longitudinal axes, even when they are constructed of isotropic materials.
4.3.5 Angular Dependence due to Anisotropic Dielectric Responses

Anisotropies in material dielectric responses also contribute to angular dependence of the interaction free energy. Material anisotropy leads to the $A^{(2)}$ term carrying a $\cos(2\theta)$ angular dependence. Highly anisotropic responses, like though seen for (5,2,m) SWCNTs, exhibit large torque values. For isotropic bodies such as semi-infinite half spaces, the $A^{(2)}$ term, and consequently torques, vanish when the planes are constructed of isotropic materials. For the example case of a cylinder pair, torques are always present due to the systems highly anisotropic morphology.

The magnitude of the $A^{(2)}$ term shows a strong dependence on choice of material, to wit, the amount of anisotropy in the dielectric responses of the materials comprising the system. The low anisotropy of the dielectric responses of (AT)10 DNA results in an $A^{(2)}$ of nearly zero and subsequently may exhibit little ability to orient in assemblies. Metallic SWCNTs have highly anisotropy dielectric responses and exhibit large $A^{(2)}$ values. For example, (5,2,m) SWCNTs have an $A^{(2)}$ value of up to 33.6 zJ for (5,2,m) SWCNTs, Figure 4.3.

4.3.6 Open-Science Benefits from Gecko Hamaker and Optical Properties Database

Gecko Hamaker is motivated to provide the scientific knowledge and underlying data necessary for accurate van der Waals calculations to the whole scientific community and public. It seeks to provide opportunities for collaboration across diverse fields, where cross-talk will spread knowledge and ideas, encouraging the development of novel applications of van der Waals interactions. The community is provided with the scientific concepts, methods and example results that are possible with Gecko Hamaker and its associated database through publication of the research already performed with Gecko Hamaker. The Gecko Hamaker software and data are free available online. The data is placed in the public domain with copyright and license
information that clearly explains the free use, re-use, and re-distribution of data, software, and calculations. One of the basic aspects of open-science establishes a practical common framework for data-sharing among participants [204], which is accomplished by the Gecko Hamaker project through the use of MariaDB. Trends in van der Waals interaction properties and how they relate to system parameters and materials are easily visualized via the large number of calculations available in Gecko Hamaker and its database. Users may seek particular interaction properties needed for deliberate design or may “browse” the effects of less familiar materials.

Gecko Hamaker seeks to make its use and sharing accessible and practical. A lack of data-sharing standards and data-repositories are a significant impediment to the public benefiting from open-science [205]. Gecko Hamaker overcomes this barrier by providing its own accompanying database, which is significantly populated, but also allows users to upload their own calculated or measured spectra to the Gecko Hamaker database. A recent survey-based study by Enke et al. showed that though the majority of the survey participants were willing to share data, very few actually did. The percentage of people who actually shared data greatly increased when they had used data shared by other researchers and when they had access to repositories where they could easily share their own data [205].

The Gecko Hamaker software allows users to study the van der Waals properties of multiple systems and to find the parameters necessary to guide material selection and configuration of deliberately constructed systems, Figure 4.5. A number of trends are immediately discernible. Torques and normal forces, which depend on both Hamaker coefficients, show a strong dependence on the cylinder radius as well as on the details of the spectral properties of the interacting materials, Figure 4.5 where forces are shown in yellow and torques are shown in green. This is evident in the case of interactions involving the (24,24,s) SWCNT, that show large torques and normal forces in spite of their modest Hamaker coefficients, while small-radius SWCNTs
exhibit large values of $A_{1w3}^{(0)}$ and $A_{1w3}^{(2)}$ but smaller torques. Nevertheless, in all systems investigated there exists a strong normal force and a modest but always present torque seeking to align the cylinders. $Al_2O_3$ interactions with other inorganic materials tend to have disproportionately large torques despite their relatively modest Hamaker coefficients and radii.

### 4.4 Conclusions

The mesoscale Lifshitz theory of van der Waals interactions has reached a level of refinement where it allows consistent and complete inclusion of solvent and temperature effects, retardation, optical anisotropy, morphology of interacting bodies, and geometry of interaction. In the limit of infinite area planar, and infinitely long cylinder interaction geometries, it yields a full numerical implementation encoded in the Gecko Hamaker open-science software tool.

The Gecko Hamaker software tool integrates a web service for the distribution of detailed optical properties of a broad range of heterogeneous functional materials from the spectral database and the newly implemented analytical solutions to the Lifshitz theory for a range of isotropic and anisotropic system configurations, yielding Hamaker coefficients along with torques, forces, and free energies, Figure 4.2. The calculated Hamaker coefficients for cylindrical interaction geometry may vary by a few orders of magnitude, depending on the materials involved in the systems, with inorganic materials generally having larger Hamaker coefficients, and biomolecular materials exhibiting smaller ones.

The angular dependence of the van der Waals interaction, depending directly on the shape anisotropy and indirectly on the optical property anisotropy through the anisotropic part of the Hamaker coefficient, also varies significantly between materials. $A_{1w3}^{(0)}(\ell)$ and $A_{1w3}^{(2)}(\ell)$ both exhibit dramatic and non-monotonic retardation effects, which vary significantly depending on the high-frequency contributions to the
optical mismatch in a given system and are responsible for a wide array of interesting and unexpected effects. In addition asymmetric systems may exhibit non-monotonic Hamaker coefficients, with distinct characteristics, leading to novel and controllable design paradigms. What is important is the interconnectedness of all these effects that precludes simple approximation schemes that focus on one or the other, but misses the important links between them.

The present mesoscale formulation of the classical Lifshitz theory of van der Waals interactions, taking fully into account the retardation as well as the anisotropy of interacting materials, constitutes a significant advance in accuracy and predictive power for the computation of van der Waals interactions compared with previous implementations of non-retarded, isotropic solutions. Furthermore the calculations accessible via the Gecko Hamaker open-science software tool may provide useful guidance to application engineers, in streamlining the process of calculating appropriate Hamaker coefficients, eliminating the need for rough and misleading approximations, and in making available optical properties of a wide variety of functional materials. This will allow detailed investigation of the long-range interactions between materials and the design of specific model systems.

Figure 4.1 includes artwork displayed on the Gecko Hamaker project page [122] in 2013. Figures 4.3-4.5 in this chapter have been published with coauthors, Ref. [92]. The author performed calculations in Python for Hamaker coefficient tests, participated in analysis, and supplied Figure 4.2. Daniel M. Dryden performed calculations, analysis, and supplied Figures 4.3-4.5. Lin K. Denoyer provided and tested software for Gecko Hamaker. Lokendra Poudel and Wai-Yim Ching performed ab initio calculations and supplied calculated absorbance spectra, and participated in analysis and discussion. Roger H. French performed VUV-LPLS spectroscopy and supplied experimental spectra, and participated in analysis and discussion. Rudolf Podgornik and V. Adrian Parsegian derived formulations and participated in analysis and dis-
discussion. Nicole F. Steinmetz participated in analysis and discussion. The research in this chapter was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0008176 and DE-SC0008068. Funding for Wai-Yim Ching’s contributions was provided by the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC03-76SF00098.
CHAPTER 5
SUMMARY

5.1 Summary

Van der Waals interactions have been investigated in the full Lifshitz formulation in order to understand and quantify the relationships between the various properties of the components of mesoscale systems and van der Waals interactions and to investigate the accuracy and completeness of the Lifshitz formulation. Van der Waals interactions function to control a range of phenomena such as self-assembly, surface adhesion, friction, and colloid stability. They occur on the length scales currently investigated by pioneering theories and techniques in mesoscale engineering, manufacture, biology, and other condensed matter fields. By studying the physics of van der Waals interactions, it is possible to characterize their strength and role in various systems in these fields of study. Understanding the contributions and effects of variation in a system’s materials, body shapes, and interaction geometry, allows construction and application of mesoscale systems to be designed for deliberate and specific functions.

Using the full Lifshitz continuum theory, this thesis investigates how materials, shapes, and configurations effect van der Waals interactions. Unlike other approaches to van der Waals interactions, the full Lifshitz calculations used in this work allow for a uniquely comprehensive and practical investigation of important effects in mesoscale assembly and design, such as solvent effects, temperature effects, relativistic retardation screening, anisotropy of material’s optical properties, and morphological
anisotropy of system elements. This methodology also distinctly addresses orienta-
tional degrees of freedom, allowing calculations of torques and angular-dependencies.

The investigations show that small variations in the dielectric response spectra of materials have a complicated and non-local effect on the strength of van der Waals interactions. Our calculations of a simplified approximate model as well as of a realistic example of amorphous silica spectrum with and without an exciton peak indicate that even small changes in the dielectric response can show up as substantial variations in the Hamaker coefficient of the van der Waals interactions. However, caution needs to be exercised in making estimates of these variations. Van der Waals interactions are non-local in the frequency response: first through the summation over the Matsubara frequencies in the Lifshitz theory, and then through the imaginary part of the total dielectric response function via the Kramers-Kronig relations. This means that a variation of the dielectric absorption spectrum at one particular frequency influence all the terms in the Matsubara summation of the van der Waals interaction energy, making the total change in the Hamaker coefficient depend on the spectral changes at that frequency but also at the rest of the spectrum properly weighted. For example, the Tabor-Winterton approximation would suggest that matching the refractive index at a single absorption peak should effectively quench the long range van der Waals component of molecular interactions. Our detailed calculations prove that this is certainly not the case. While it is true that addition of a single peak in the dielectric absorption spectrum can induce a substantial change in the magnitude of van der Waals interactions, the Matsubara terms that are most affected are not those close to the position of the added peak but are distributed over the whole interval of frequencies and can show a maximum whose position is not directly related to the position of the added peak. A possibility of eliminating van der Waals interactions or at least drastically reducing them by spectral variation in a narrow regime of frequencies thus seems very remote.
Literature on anisotropy effects on van der Waals interactions unequivocally concludes that angular dependence arises from two system properties: shape anisotropy and the material anisotropy. The effect of these two types of anisotropies is fundamentally non-additive: anisotropic shapes with isotropic material response as well as isotropic shapes with anisotropic material response can both show equally strong anisotropy effects in the vdW interactions.

Prior studies did not analyze the nature of the non-additivity of these effects. The work presented in chapter 3 characterizes the part of the general angular dependence of the van der Waals interaction between anisotropic bodies that is due to the shape anisotropy, the part that is due to the material anisotropy, demonstrates how to properly disentangle the two closely connected effects, and identifies the regime and/or configurations in which these effects are the largest. It is possible that these newly identified features of van der Waals interactions between shape and/or material anisotropic bodies may contribute to behaviors in certain existing experimental configurations, see section 3.4.4. The effect of shape on interactions in the retarded regime results in a torque between arrays of cylinders that is surprisingly stronger than that between half-spaces and indicate new possibilities for achieving sufficiently strong torques for nanomachines such as frictionless bearings, see section 3.4.4.

Lifshitz theory accurately captures important effects in mesoscale assembly and design, such as solvent effects, temperature effects, relativistic retardation screening, anisotropy of materials’ optical properties, and morphological anisotropy of system elements. These calculations are unwieldy and the commonly used alternatives and approximations often fail to incorporate important factors, leading to poor representation of the role of van der Waals interactions in mesoscale systems. By using the Lifshitz formulation for van der Waals interactions, the Gecko Hamaker project presented in chapter 4 greatly improves on currently available calculations. The continuum approach of the Lifshitz formulation accounts for many-body interactions and
permits the use of bulk dielectric responses to capture the role of material properties in the calculations. Users can upload their material spectra for use in Gecko Hamaker calculations or they can select materials from the accompanying database of over 100 materials.

The transparency of open-science architecture in Geckco Hamaker increases opportunities for collaboration and allows data sharing in an easy-to-use, standardized database. The project showed that DNA-DNA interactions display an imprint of the DNAs base pair composition. Comparison of Gecko Hamakers highly resolved calculations for many types of SWCNTs showed that certain species of SWCNTs display interaction characteristics stemming from the properties unique in each species. The database of optical properties includes never-before-published spectra such as Type I collagen and (GC)10 duplex DNA.

In summary, the investigations performed in the Lifshitz formulation of van der Waals interactions have provided a further understanding of the role of system properties in mesoscale science. The studies provide new insights into the strength and types of mechanisms that are important in mesoscale systems and opens new possibilities for the construction of systems for deliberate properties or functionalities.

### 5.2 Outlook

Completion of these projects will open several avenues for further investigation. Calculations of lateral forces, in addition to current normal force and torque calculations, will be of interest for the design and construction of mesoscale mechanisms. Mohideen, et al., demonstrated that interaction between corrugated plates introduces a lateral force that seeks to align grooves and peaks of the opposing plates [144,145]. Earlier literature suggests that lateral forces may also be achievable between two planes moving parallel to each other [146,147].
Several methods have attempted to address the difficulties in formulating interactions for complicated shapes and arbitrary boundary conditions [148–151]. Specific shapes have been considered, such as a plane with a sphere [152, 153], a plane with a cylinder [154, 155], and compact objects with a mirrored plane [156, 157]. General shapes have also been investigated through the interactions between arbitrary objects [158–160]. Accurate formulations for the interactions between complicated shapes will allow improve the ability for calculations to better represent real, physical systems.

Experiments have attempted to measure the interaction between an atom and a surface [161, 162] and to trap an atom above complicated bi-layer or multi-layer microstructures [163–165]. Interestingly, these measurements occur at separations lying in the cross-over of the non-retarded and retarded regimes and may lead to investigations toward the unification of some current theoretical approaches.

Nanotechnological devices such as quantum mechanical actuators [16] and nonlinear micromechanical oscillators [17] have used quantum vacuum forces to construct micromachines. Experiments have studies the role of stiction and adhesion caused by van der Waals interactions in micromechanical systems [15]. Theoretical literature has investigated van der Waals actuated nano-machinery such as noncontact rack and pinion systems [18].

Torques generated by vdw interactions between concentric corrugated cylinders have been used to theorize nano-machine “gears” [19–21], and van der Waals torques between a disk and plate made of anisotropic materials have been suggested as potential “frictionless bearings” [22].

5.3 Preparation of this Document

This TeX document was rendered with pdflatex. The author’s calculations were performed in Python and Mathematica. Figures and schematics were created with
Python/matplotlib, Inskape, Blender, TubeGen 3.4, and/or PyMOL Molecular Graphics System.
APPENDIX A

DERIVATION OF THE FREE ENERGY OF INTERACTION FOR TWO SEMI-INFINITE ANISOTROPIC UNIAXIAL PLANES

The full Lifshitz free energy of interaction per unit area for two uniaxial anisotropic half spaces, “1” and “2”, whose principal dielectric axes are inclined at a fixed angle, interacting across an isotropic medium, $G(\ell, \theta)$, is given as a function of separation \( \ell \) and mutual orientation angle, \( \theta \), in the form first derived by Barash [96,97]:

$$G(\ell, \theta) = -\frac{H(\ell, \theta)}{12\pi \ell^2}. \quad (A.1)$$

Where we have explicitly isolated the \( \ell^{-2} \) dependence from

$$G(\ell, \theta) = \frac{3k_BT}{2} \times \sum_{n=0}^{\infty} \int_0^\infty QdQ \int_0^{2\pi} d\phi \log D(\ell, \theta; Q, \phi), \quad (A.2)$$

in order to be able to introduce the standard form of the Hamaker coefficient as in Eq.A.1. $D(\ell, \theta; Q, \phi)$ is the secular determinant of all allowed surface modes with magnitude of the in plane wave-vector $Q$, of the fluctuating electromagnetic field that depends on $\ell$ and $\theta$. The summation over the Matsubara frequencies, $\xi_n = 2\pi nk_BT/\hbar$ with the $n = 0$ term weighted by one-half, stems from the thermal bath of the fluctuating field. At room temperature the Matsubara frequencies are multiples of $2.4 \times 10^{14}$ s\(^{-1}\).
The secular determinant, \( D(\ell, \theta; Q, \phi) \), depends also on two additional parameters: the magnitude \( Q \) and the direction \( \phi \) of the in-plane wave vector, that are both integrated over and is given explicitly as:

\[
D = (A - \epsilon_{2\perp}(\rho_2 - \rho_2)(B - E + C))/\gamma . \tag{A.3}
\]

Where,

\[
\gamma = (\rho_1 + \rho_3)(\rho_2 + \rho_3)((\epsilon_3\rho_1 + \epsilon_{1\perp}\rho_3)(\rho_1^2 - Q^2 \sin^2 \phi) - (\epsilon_{1\perp}(\rho_1 - \rho_1)(Q^2 \sin^2 \phi - \rho_1\rho_3)))
\times ((\epsilon_3\rho_2 + \epsilon_{2\perp}\rho_3)(\rho_2^2 - Q^2(\cos \phi \sin \theta + \sin \phi \cos \theta)(\cos \phi \sin \theta + \sin \phi \cos \theta)) - (\epsilon_{2\perp}(\rho_2 - \rho_2)(Q^2(\cos \phi \sin \theta + \sin \phi \cos \theta)(\cos \phi \sin \theta + \sin \phi \cos \theta) - \rho_2\rho_3))), \tag{A.4}
\]

and

\[
A = ((\rho_1 + \rho_3)(\rho_2 + \rho_3) - (\rho_1 - \rho_3)(\rho_2 - \rho_3)e^{-2\rho_3})((\epsilon_3\rho_1 + \epsilon_{1\perp}\rho_3)(\epsilon_3\rho_2 + \epsilon_{2\perp}\rho_3)
\times ((\epsilon_3\rho_1 - \epsilon_{1\perp}\rho_3)(\epsilon_3\rho_2 - \epsilon_{2\perp}\rho_3)e^{-2\rho_3})(\rho_1^2 - Q^2 \sin^2 \phi)(\rho_2^2 - Q^2 \sin(\phi + \theta) \sin(\phi + \theta))
\times ((\epsilon_{1\perp}(\rho_1 - \rho_1))(\epsilon_{1\perp}(\rho_2 - \rho_2)(\epsilon_{1\perp}(\rho_2 + \epsilon_{2\perp}\rho_3)(\rho_2 + \rho_3)(\rho_1 + \rho_3) + 2(\epsilon_{2\perp} - \epsilon_3)
\times (Q^2 \sin^2 \phi(Q^2\rho_1 - \rho_2\rho_3^2) + \rho_1\rho_3^2(Q^2 - 2Q^2 \sin^2 \phi + \rho_1\rho_2))e^{-2\rho_3}
\times (Q^2 \sin^2 \phi + \rho_1\rho_3)(\epsilon_3\rho_2 - \epsilon_{2\perp}\rho_3)(\rho_1 - \rho_3)(\rho_2 - \rho_3)e^{-4\rho_3}), \tag{A.5}
\]

and

\[
B = ((\epsilon_3\rho_1 + \epsilon_{1\perp}\rho_3)(\rho_1 + \rho_3)(\rho_2 + \rho_3) + 2(\epsilon_{1\perp} - \epsilon_3)(\rho_1\rho_3^2 - 2\rho_2\rho_3^2)e^{-2\rho_3}
\times (\epsilon_3\rho_1 - \epsilon_{1\perp}\rho_3)(\rho_1 - \rho_3)(\rho_2 - \rho_3)e^{-4\rho_3})(\rho_1^2 - Q^2 \sin^2 \phi) + (\epsilon_{1\perp}(\rho_1 - \rho_1))
\times (-Q^2 \sin^2 \phi - \rho_1\rho_3)(\rho_1 + \rho_3)(\rho_2 + \rho_3) + 2(Q^2 \sin^2 \phi(\rho_1\rho_2 + \rho_3^2) - \rho_1^2 \rho_3^2
\times \rho_1\rho_2\rho_3^2)e^{-2\rho_3} - (Q^2 \sin^2 \phi + \rho_1\rho_3)(\rho_1 - \rho_3)(\rho_2 - \rho_3)e^{-4\rho_3})Q^2 \sin(\phi + \theta) \sin(\phi + \theta), \tag{A.6}
\]
\[
C = \rho_2 \rho_3 (- (\epsilon_3 \rho_1 + \epsilon_{1\perp} \rho_3)(\rho_1 + \rho_3)(\rho_2 + \rho_3) + 2 \rho_3 (\epsilon_{1\perp} - \epsilon_3)(r^2 + \rho_1 \rho_2)e^{-2\rho_3}
\]
\[
+ (\epsilon_3 \rho_1 - \epsilon_{1\perp} \rho_3)(\rho_1 - \rho_3)(\rho_2 - \rho_3)e^{-4\rho_3}(\rho_1^2 - Q^2 \sin^2 \phi) + \epsilon_{1\perp}(\tilde{\rho}_1 - \rho_1)\rho_2 \rho_3
\]
\[
((Q^2 \sin^2 \phi - \rho_1 \rho_3)(\rho_1 + \rho_3)(\rho_2 + \rho_3) + 2 \rho_3 (\rho_1^2 \rho_2 + \rho_1 \rho_3^2 + Q^2 \sin^2 \phi(\rho_1 - \rho_2))e^{-2\rho_3}
\]
\[
- (Q^2 \sin^2 \phi + \rho_1 \rho_3)(\rho_1 - \rho_3)(\rho_2 - \rho_3)e^{-4\rho_3}),
\]
(A.7)

and

\[
E = 4 \rho_1 \rho_2 \rho_3^2 \epsilon_{1\perp}(\tilde{\rho}_1 - \rho_1)e^{-2\rho_3}(2Q^2 \sin \phi \cos \theta \sin(\phi + \theta) + \rho_3^2 \sin \theta \sin \theta). 
\]
(A.8)

The dimensionless wave vectors for plane 1, plane 2, and medium 3 are given as:

\[
\rho_1^2 = Q^2 + \epsilon_{1\perp} \frac{\xi^2 \ell^2}{c^2}, \quad \rho_2^2 = Q^2 + \epsilon_{2\perp} \frac{\xi^2 \ell^2}{c^2}, \quad \text{and} \quad \rho_3^2 = Q^2 + \epsilon_3 \frac{\xi^2 \ell^2}{c^2};
\]
\[
\tilde{\rho}_1^2 = Q^2 + (\epsilon_{1\parallel}/\epsilon_{1\perp} - 1)Q^2 \cos^2 \phi + \epsilon_{1\parallel} \frac{\xi^2 \ell^2}{c^2}, \quad \text{and}
\]
\[
\tilde{\rho}_2^2 = Q^2 + (\epsilon_{2\parallel}/\epsilon_{2\perp} - 1)r^2(\cos \phi \cos \theta - \sin \phi \sin \theta)^2 + \epsilon_{2\parallel} \frac{\xi^2 \ell^2}{c^2}.
\]
(A.9)

There appears to be no known simplification of this result. A different form of the interaction free energy was derived in [99] that numerically reduces to the result above, but it was not shown to reduce to it exactly and/or analytically. In the main text, we used the above derivation in the symmetric case of “1” = “2”.
APPENDIX B

DERIVATION OF THE FREE ENERGY OF INTERACTION FOR TWO CYLINDERS

By beginning with the expressions for two composite planar media, “1” and “2”, at a separation $\ell$, made of arrays of parallel cylinders embedded in isotropic medium, the free energy of an isolated pair of inclined cylinders is derived by taking the volume fraction of the composite in the dilute limit and expanding the anisotropic dielectric responses to second-order in the number density [1]. The exact relation is

$$
\frac{d^2 G(\ell, \theta)}{d\ell^2} = N_1 N_2 \sin \theta \ G(\ell, \theta).
$$

where the area density of the cylinders ($N_1, N_2$) in the direction of their long axes is $v_1 = N_1 \pi \alpha_1^2$ ($v_2 = N_2 \pi \alpha_2^2$) and the interaction free energy between the two cylinders whose axes are contained within the two parallel boundaries at a separation $\ell$, but skewed at an angle $\theta$ is $G(\ell, \theta)$. The second derivative can be written furthermore as

$$
\frac{d^2 G(\ell, \theta)}{d\ell^2} = k_B T \frac{2\pi}{\infty} \sum_{n=0}^\infty \int_0^\infty Q dQ \frac{d^2 f(Q, \xi_n; \ell, \theta)}{d\ell^2}.
$$

Where
\[
\frac{d^2 f(Q, \xi_n; \ell, \theta)}{d\ell^2} = -\frac{v_1 v_2 \Delta_{1,\parallel} \Delta_{2,\parallel}}{32} e^{-2\ell \sqrt{Q^2 + \epsilon_m \frac{\xi_n^2}{c^2}}} \frac{\epsilon_c^2}{(Q^2 + \epsilon_m \frac{\xi_n^2}{c^2})} \\
\times \left\{ 2 \left[ (1 + 3a_1)(1 + 3a_2)Q^4 + 2(1 + 2a_1 + 2a_2 + 3a_1 a_2)Q^2 \epsilon_m \frac{\xi_n^2}{c^2} \right. \\
+ 2(1 + a_1)(1 + a_2)\epsilon_m^2 \xi_n^4 + (1 - a_1)(1 - a_2) \left( Q^2 + 2 \epsilon_m \frac{\xi_n^2}{c^2} \right)^2 \cos 2\theta \right\},
\]

(B.3)

and the relative anisotropy measures are:

\[
a = \frac{2\Delta_{\perp}}{\Delta_{\parallel}} = 2 \frac{(\epsilon^c_{\perp} - \epsilon_m)\epsilon_m}{(\epsilon^c_{\perp} + \epsilon_m)(\epsilon^c_{\parallel} - \epsilon_m)} \quad \text{for the two composite materials 1 and 2.}
\]

(B.4)

The van der Waals interaction free energy between the two inclined cylinders of radii \(R_1, R_2\) composed of anisotropic material is given as

\[
G(\ell, \theta) = -\frac{(\pi R_1^2)(\pi R_2^2)}{2\pi \ell^4 \sin \theta} \left( A^{(0)}(\ell) + A^{(2)}(\ell) \cos 2\theta \right). \tag{B.5}
\]

Where the Hamaker coefficients are:

\[
A^{(0)}(\ell) = \frac{k_B T}{32} \sum_{n=0}^{\infty} \Delta_{1,\parallel} \Delta_{2,\parallel} P_n(\ell) \int_0^\infty dt \frac{e^{-2P_n(\ell)\sqrt{t^2 + 1}}}{(t^2 + 1)} \tilde{g}^{(0)}(t, a_1(i\xi_n)a_2(i\xi_n)),
\]

with

\[
\tilde{g}^{(0)}(t, a_1(i\xi_n)a_2(i\xi_n)) = \\
\left[ (1 + 3a_1)(1 + 3a_2)t^4 + 2(1 + 2a_1 + 2a_2 + 3a_1 a_2)t^2 + 2(1 + a_1)(1 + a_2) \right]
\]

(B.6)

and

\[
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\]
\[ \mathcal{A}^{(2)}(\ell) = \frac{k_B T}{32} \sum_{n=0}^{\infty} \Delta_{1,\parallel} \Delta_{2,\parallel} \, p_n^4(\ell) \int_0^\infty t \text{d}t \frac{e^{-2p_n(\ell)\sqrt{t^2+1}}}{(t^2+1)} \tilde{g}^{(2)}(t, a_1(i\xi_n)a_2(i\xi_n)\theta), \]

with

\[ \tilde{g}^{(2)}(t, a_1(i\xi_n)a_2(i\xi_n)\theta) = (1 - a_1)(1 - a_2)(t^2 + 2)^2; \]

(B.7)

with

\[ u = Q\ell, \quad p_n^2(\ell) = \epsilon_m(i\xi_n)\frac{\xi_n^2}{\xi_n^2} \ell^2, \quad \text{thus} \quad u = p_n t. \]

(B.8)

From the form Eq. B.5 for the interaction free energy it is clear that the free energy of a pair of identical cylinders because of the factor \( \sin^{-1} \theta \) thus carries angular dependence with both Hamaker coefficients, \( \mathcal{A}^{(0)} \) and \( \mathcal{A}^{(2)} \), unlike the planar and composite cases which have explicit angular dependence only in the orientation term, \( \mathcal{A}^{(2)} \). In the main text we used the above derivation in the symmetric case of “1” = “2” with \( R_1 = R_2 = \alpha \).


[201] Holdren, J. P. Increasing access to the results of federally funded scientific research (2013).


