

Modelling Nanocomposite Dielectrics - Polarization and Inclusions At The Atomic
Scale

by

Archita Adluri
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We acknowledge and respect the Lək'wəŋən (Songhees and X^wsepsəm/ Esquimalt)
Peoples on whose territory the university stands, and the Lək'wəŋən and W̱SÁNEĆ
Peoples whose historical relationships with the land continue to this day.

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ABSTRACT

This thesis details the computational investigations into molecular-nanoparticle based nanocomposite dielectric candidate materials. Mainly silver-based nanoparticles under 32 atoms in metal-oxide and polymer model materials to understand how encapsulation affects local and bulk dielectric function and how to model such candidates.

Chapter 1 introduces the ideas behind molecular nanoparticles (MNP) and functional dielectrics at the sub-100nm range. Emphasis on bridging gaps present in the literature at present and potential novel uses between atomic-doping and traditional larger nanoparticles.

Chapter 2 delves into theory and background as this is an entirely theoretical and computational thesis. An explanation of both static and optical dielectric starting from electronic structure and ending in a comparison of methods. Further computational details provided in relevant next chapters.

Chapter 3 contains details of the major topic of this thesis: How to model a molecular nanoparticle inclusion in a solid-state dielectric. The candidates of Ag inclusion and MgO candidate metal-oxide were modelling using Car-Parinello Molecular Dynamics to obtain a size and shape correlation in nanoparticles as well as some guidelines for computing charge distribution and quantum of polarization effects.

Chapter 4 contains details of the optical polarization of Ag-PVDF nanocomposites with a focus on interacting particles and non-homogeneity in MNP distribution. This project aimed to move towards a more realistic model with two nanoparticles interacting at various distances.

Chapter 5 is an attempt to push the boundaries of highly detailed molecule-level polarization calculations and a discussion on their usefulness without experimental backing.

Chapter 6 summarizes this thesis followed by some QuantumEspresso code and parameters used.

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List of Abbreviations

mnp		m olecular n anoparticle
NC		n anocomposite
NP		n anoparticle
MD		m olecular d ynamics
CPMD		C ar - P arinello m olecular d ynamics
GGA		g eneralized g radient a pproximation
LDA		l ocalized d ensity a pproximation

Chapter 1

Introduction

Understanding the atom and sub-atomic particles has lead to the greatest acceleration in technology in human history. Once we were able to harness electricity, we used it to light up the world, heat our homes, and build machinery to industrialize our society. Energy is thus the most fundamental currency we have.

Semiconductors, dielectrics, supercapacitors, and transistors are all designed for storing, discharging, and moving energy to suit a variety of specifications. As computing needs grow increasingly niche across industries, functional dielectrics for a wide array of applications demand a deeper understanding of charge storage and movement in materials.

This thesis presents various investigations in the theme of molecular scale nanoparticles in nanocomposite dielectric materials and the modelling and calculations thereof. Specifically the problem of calculating the dielectric capability of materials with molecular scale metal inclusions and how the size, shape and dispersity might be accounted for computationally. Included are a series of introductory chapters on various dielectric materials in industry both present and future predictions, theory chapters to guide the reader through both computational methods and quantum mechanical phenomena and the results of 2 main investigations - static dielectric constant in metal-oxide dielectric composites and optical dielectric function in polydisperse polymer-metal composites.

Using simulation we can learn how to model polarization in complex nanocomposite structures efficiently, build an understanding of trends in charge storage at the atomic scale across a wide variety of solid state dielectrics and various combinations and inclusion types to inform industry R&D and also work toward greener materials

overall.

The basis of this work started from the Modern Theory of Polarization and moved through various currently available computational methods and this thesis will follow that logic. The entirety of this work in theoretical - no experimental work has been conducted to build an understanding of material properties in the quantum regime and how to conduct calculations from first-principles.

All computational work must be interpreted within heavy context as we make many assumptions and generalizations in the quest to join theory (here, quantum and classical mechanics) with its observable and practical application in the material world. This especially includes assumptions about bulk structure in order to gain understanding of electronic movement and to quote Sir Arthur Eddington ‘an electron is no more and no less theoretical than a star’ and to quote existential grad students ‘what exactly is electron?’.

Using simulation we can learn how to model polarization in complex nanocomposite structures efficiently, build an understanding of trends in charge storage at the atomic scale across a wide variety of solid state dielectrics and various combinations and inclusion types to inform industry R&D and also work toward greener materials overall.

1.1 Functional Dielectric Materials

A dielectric material is an insulator with electric dipoles that are that are induced or reoriented by an applied field. The higher the bulk dielectric permittivity the more charge can be held within the material. The research so far has shown that at the atomic scale, even a point defect or a single atom defect leads to noticeable changes in polarization potential of a material. While this has minimal effect in a bulk solid, as industry demands smaller materials to increase density and these issues are becoming more relevant to research.

Doping semiconductors to tune properties is well known in the literature with n-type and p-type dopants - and by controlling defects as we would dopants we can also mitigate any issues that may arise. In order to be effective however a material must have high dielectric permittivity but also high dielectric breakdown strength. Theoretical investigations have been used to attempt to predict and optimize the many possibilities for nanoparticle/matrix distributions, structural arrangements and even elemental composition. Effective medium approximations are suitable for

macro-scale mixtures where experimental data is broadly available such as for polymer or aqueous systems [73, 67, 42]. Classical approaches as discussed in the computational methods below work at the nanoscale but fail to incorporate the quantum response of the MNP and local field effects [7, 71, 14]. Direct DFT approaches have been used for doped materials with single-element dopants such as nitrogen or potassium but a complete treatment of the quantum polarization of the mixed material is complex.

The continuous scaling of transistors, as described by Moore’s Law, predicts a doubling of transistor density approximately every two years. This relentless miniaturization has driven advancements in computational power, energy efficiency, and device capabilities. However, as the size of transistors shrinks to the nanometer scale, the classical understanding of material behaviour gives way to quantum mechanical effects. This shift is especially pronounced in multi-phase and composite dielectrics. Combinations of phases (e.g., crystalline and amorphous) and heterogeneous systems with molecular-scale inclusions or engineered interfaces introduce complex interactions [57, 117, 132, 77].

At the current stage, miniaturization no longer answers the need for advancing device performance, and the focus has shifted on the development and integration of new materials, with improved properties and connectivity [1]. One area in high need of development is that of materials with tunable dielectric constant (κ) for electrical and computational devices that rely on metal-oxide semiconducting materials: transistors, high-density charge storage super-capacitors, and emerging technologies in quantum computing [80, 119, 152, 111, 9].

1.1.1 Towards Molecular Nanocomposites

Traditional Si/SiO₂ gates have given way to more complex materials such as silicon-germanium and hafnium oxides[158], multilayered ‘sandwich’ materials such as embedded graphene sheets [101, 112], polymer enriched metal oxides and other multiphase materials in order to address this. Industrially, mixed SiO₂/HfO₂/Si chips, ZnO and thin-film ‘sandwich’ semiconductors have also been of great interest.

Additionally, several quantum computer architectures are built around silicon metal-oxide ‘quantum wells’.

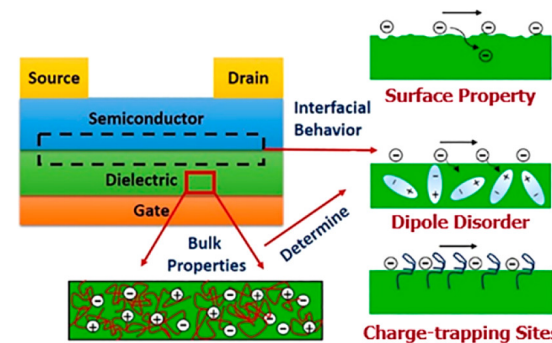
Metallic nanoparticles in the molecular regime (nanoclusters with up to 100 or so atoms) bridge the gap between single-atom dopants in classical semiconductors and

traditional nanoparticles with ‘metallic properties’, while providing a range of unique features.[47, 129] Molecular nanoparticles (MNPs) are insulating, do not present a band structure and the high-electron density of traditional nanoparticles, which often leads to low percolation thresholds and tunneling. Essentially a source of highly polarizable electron density, their quantum behaviour requiring quantum mechanical treatments to model their contribution to local polarization effects. In recent years, methods for synthesis of noble metal MNPs (Ag, Au, Pt) with atomic precision have been developed, and their distinctive properties have been capitalized in applications such as heterogeneous catalysis [28, 70, 60, 148], photo-catalysis [153], chemical and medical sensing [156, 43, 130, 62], and in composite materials with intriguing functionalities [39, 22, 40].

Traditional nanoparticles suffer from issues of hotspots, distortion of local field [8, 141, 126] and are large(r) relative to thin-film transistors which are in the sub-100 nm range. A solution to this would be the use of metal molecular nanoparticles (up to 100 atoms) in traditional dielectrics. These bridge the gap between single-atom dopants in classical semiconductors and traditional nanoparticles with ‘metallic properties’, while providing unique features that can be capitalized on. The issues with hotspots and local field effects can also be used to our advantage as at such small sizes the local field effects can be controlled and isolated. Molecular nanoparticles are insulating, do not present a band structure but have the high-electron density of traditional metal nanoparticles. MNPs exist in the atomic range, have separate molecular states, and therefore require quantum mechanical treatments to model their electron dynamics and contribution to local polarization effects.

The bulk polarization of candidate nanocomposites dielectric and differs from interfacial effects of trapping and surface charge that exists between the dielectric and semiconductor [142, 57] as seen in Figure 1.1. The semiconductor is usually Si to complement the SiO₂ dielectric and changing this introduces other issues such as amorphous structure, bonding and subsequent creation of dipoles.

Treating all these effects in the proposed research would require simulations of several length scales at different levels of theory that would be unfeasible. Additionally, simulations are highly controlled in



terms of structure and defect formation
and without experimental data on
crystal structure it would be unrealistic.

There exists a discussion on the ability
or computational power to complete a
computation versus the utility of results
and environmental impact of using
resources and energy. Theory must
always be done with an aim to support

experimentation and design and the fact we might be able to brute-force a
calculation is not reason enough to do it.

To address limitations in silicon-based technology, researchers are exploring
alternative materials that offer superior properties for miniaturized electronic
devices:

High-dielectric-constant materials, such as perovskite oxides, provide enhanced
charge storage and insulation properties. Examples include metal-halides, layered
and hybrid perovskites [30, 77, 138]. Modifying the electronic and ionic structure by
introducing controlled impurities can enhance conductivity, dielectric properties,
and thermal stability. For example, doped hafnium oxide shows promise as a high-k
dielectric [151].

Beyond silicon we see a transition to materials like gallium nitride (GaN), silicon
carbide (SiC), and even carbon-based systems such as graphene [123, 32, 157].
These materials offer advantages in high-speed, high-power, or flexible electronics
while overcoming silicon's scaling limitations.

While significant progress has been made in modelling and understanding
polarization, challenges persist at the molecular scale. Polarization in applied fields
involves complex interactions among electrons, ions, and defects, which are
complicated especially in multi-phase and composite materials.

1.1.2 Defect Control at the Atomic Level

Defects play a dual role: they can either enhance material performance (e.g.
dopants creating local polarization effects) or degrade it (e.g. unwanted charge
trapping). Current advancements in nanotechnology are enabling precise control of
defects, moving toward designing materials with predictable and reproducible

properties however it is still crucial to understand and work with defects. Carefully controlling the size and distribution of nanoparticles can help reduce the occurrence of defects like charge-hopping or hole formation. In molecular nanocomposites, due to their high surface area to volume ratio smaller particles have the potential to exhibit more surface defects [155, 58, 50]. Therefore an optimal balance between particle size and surface treatment is necessary to minimize defects while maximizing the dielectric enhancement.

One particular issue in composite dielectrics - particularly for capacitors - arises when a large difference in permittivity between layered materials leads to loss of breakdown strength due to field effects at the interface. This necessitates a filler or intermediary to 'bridge the gap'. In ceramic materials this includes TiO_2 , Al_2O_3 , and SiO_2 however they do not work in polymer composites as poor adhesion at the interface can result in poor dispersion of the filler, creating localized stress concentrations that promote electric field hotspots and reduce the physical and dielectric strength [143, 61, 57].

At the atomic scale, defects in nanocomposites can arise from several sources, including the synthesis process, filler-particle interaction, polymer-filler or crystal-crystal interfaces, and structural imperfections in the nanoparticles/inclusions themselves. One common type of defect is the interface defect which occurs when there is a mismatch between structures that becomes apparent at an interface leading to holes or amorphicity. Poor adhesion at the interface can result in poor dispersion of the filler, creating localized stress concentrations in polymer that promote electric field hotspots and reduce the dielectric strength. In solid-state systems, it may induce internal fields that affect the movement of charge carriers, leading to unique polarization behaviour. This can be attributed to charge redistribution and accumulation at the interface, which alters the dielectric response.

In solid-state dielectrics, particularly those used in electronic devices, p-type and n-type semiconductors are the two fundamental types, named for their defects and dopants behaviour.

P-type semiconductors are materials that have been doped with elements that have fewer valence electrons than the semiconductor's base material (e.g., boron-doped silicon). This creates "holes" in the material's valence band where there should be electrons allowing for some current flow but not as a conductor. This can also be seen as positive holes for electrons to occupy when a field is applied. In dielectrics,

the goal is often to minimize free charge carrier flow (whether holes or electrons), but p-type doping can be useful when the dielectric material is also meant to undergo charge/discharge cycles [118].

In contrast to p-type materials, n-type semiconductors are created by doping the semiconductor with donor atoms that have more valence electrons than the semiconductor itself (e.g., phosphorus-doped silicon). This introduces extra electrons into the conduction band making electrons the primary charge carriers. These extra electrons in the conduction band can move freely when an electric field is applied, leading to electrical some conductivity. In solid-state dielectrics, n-type behaviour can be useful in creating composite materials where electron conduction is desired, such as in some energy storage devices, where charge transport is an essential factor. While the goal for many dielectric materials is still to suppress free electron movement, n-type materials can influence the overall properties of composite materials designed for applications like sensors, and are often used at the interface of p-type semiconductors [9, 81].

Electron holes play a critical role in dielectric breakdown and charge transport behaviour, particularly under high electric fields. In some high-performance dielectric materials, the presence of these holes can create pathways for breakdown, leading to the failure of the dielectric under stress [154, 104]. In some cases, electron-hole recombination can occur when an electron from the conduction band falls into a hole, releasing energy in the form of light or heat. This recombination can impact the efficiency and stability of dielectric materials used in energy harvesting or other specialized applications.

Both p-type and n-type semiconductor regions within a solid-state dielectric can contribute to dielectric breakdown when exposed to high electric fields. In these cases, the material may allow the movement of free charge carriers (electrons or holes), which can cause local conduction, leading to breakdown. The mobility of electrons and holes will affect how effectively the material polarizes in response to the field [77]. Charge trapping can also occur when electron density becomes caught in holes with nowhere to go without impacting the integrity of the bulk material. Materials that can maintain high polarization without significant carrier movement are considered ideal dielectrics [144]. Managing the number and mobility of these holes becomes crucial in designing solid-state dielectrics for high voltage or high-frequency applications. In creating crystal-structures for computation, it is extremely important to control the formation of unwanted holes and the balance of

valence electrons especially at interfaces.

1.1.3 Multilayered Sandwich Materials

Stacking two-dimensional materials like graphene with dielectric layers creates high-performance composites. For example, Graphene sandwiched between dielectric layers offers promising electronic and mechanical properties [123, 39]. The challenges include edge effects in graphene-based materials introduce variability, such as localized charge density and defect-induced scattering. These issues complicate uniform device performance and especially complicate computation as the simulation cell size needs to be very large to capture the edge and bulk.

1.1.4 Polymer-based Dielectrics

In addition to solid-state dielectrics, polymer based dielectrics with either polymer-as-filler, blended or as a nanocomposite. They have especially gained attention for their physical flexibility useful in wearable electronics, medical ‘biodevices’ and in ‘green’ materials [103, 27]. Generally exhibiting high breakdown strength and low dielectric loss, polymer-based dielectrics are useful as medium- κ dielectrics, tuned via blending polymers or used as fillers in conjunction with ceramics or metals [104].

Linear polymer dielectrics are often PVDF (polyvinylidene fluoride), polyimide or a glass polymer based on poly-methacrylate or poly-itaconate [143]. PVDF in particular is useful as it has a large dielectric constant ($\kappa \approx 10$) and low dielectric loss in its α -phase [29]. Significant improvements have been made by atomic substitutions or adding inclusions to the polymer matrix to control the interfacial effects and charge trapping. Blending n- and p-type doped polymers [104] has been shown to improve breakdown strength. Inclusions such as elemental dopants (ex: Ni [78], Au & Cu [27], nanotubes [123]).

Metal-oxide and metal-silicone nanorod and core-shell nanoparticles such as $\text{Bi}_2\text{S}_3@\text{SiO}_2$ [50], have been shown to similarly improve the function at heterojunctions [50]. The study of trapped inclusions has even prompted exploration of machine-learning models to design materials based on PVDF/ BaTiO_3 molecular nanoparticle composites [122].

1.2 Functional Dielectric "Trapped" Composites

Trapping all the edges in a nanoparticle while keeping the low-dimensions or small sizes means we can compute the effects without worrying about leakage or approximations in the computation. Smaller materials approaching quantum limits mean we will have effects arising that are not found in 'classical materials as we see the following advantages:

1. Localized Polarization Effects: Nanoparticles introduce local distortions in the lattice, modifying the material's overall polarization response.
2. Defect Mitigation: Since nanoparticles are uniformly distributed within the matrix, they reduce the likelihood of macroscopic defects while introducing tunable, controlled nanoscale defects.
3. Dielectric Property Modulation: By embedding surfaces and interfaces within the bulk material, the impact of nanoparticles on dielectric behaviour can be studied systematically.

Molecular nanoparticles enable precise examination of how inclusions alter electronic and ionic polarization, paving the way for materials with engineered dielectric properties. The ability to manipulate atomic-scale defects and inclusions opens pathways for tuning dielectric behaviour, polarization anisotropy, and other critical properties. Examining molecular-scale inclusions as a tool for engineering dielectric properties. The investigations found within this work will focus on how to model atomic-scale engineered 'defects' and a theoretical discussion on how to extend and extrapolate the data.

Chapter 2

Theory and Computational Details

The theory driving computational chemistry methods and computations are integral to the work presented here, and the following chapter covers all theoretical topics as they pertain to polarization, permittivity, and dielectric function(s). Discussion on computing polarization for charge storage capabilities of molecular nanoparticles (MNp) along with challenges with code, availability and improvements to the methods developed.

2.1 Note on Notation

A brief clarification on the notation used: polarization and permittivity have many different notations across fields of study. Here, both $\mathbf{P}$ and ϵ refer to a polarization quantity, where $\mathbf{P}$ is polarization of a defined state or time (for example, in the middle of a polarization calculation) and ϵ is the relative dielectric of the material as either the static dielectric (ϵ_r , $\epsilon_{||}$, $\epsilon_{\perp}$) or frequency dependent optical dielectric function (ϵ_1 or ϵ') and dielectric loss (ϵ_2 or ϵ''). In some disciplines, the measured dielectric constant is denoted as κ [21, 112]; however, an issue arises when discussing the relative and absolute change within the confines of simulation. We are unable to model the absolute value due to DFT issues such as bandgap underestimation, especially when using generalized gradient approximation(s).

Attempts made to correct the potential errors are discussed in Chapter 3.

It is important to distinguish between two dielectric tensors. The static dielectric tensor ϵ_r encompasses both ionic and electronic polarization contributions and is the quantity of interest when characterizing insulating matrix materials. A second

tensor, $\vec{\epsilon}_{\infty}$, captures only the electronic polarization and is referred to as the high-frequency dielectric tensor [109]. As this work concerns composite materials in which the insulating matrix plays a significant role, ionic contributions cannot be neglected; all references to the static dielectric constant herein refer to ϵ_r .

Additionally, microscopic polarization will refer to point charges relating to the frozen core approximations and macroscopic polarization requires a defined volume Ω equal to the volume of the periodic cell and not a sum over atomic volumes.

Applied fields will always be $\mathcal{E}$ referring to a linear potential (not a sawtooth potential present in calculations of polarization in molecules or surfaces).

2.2 Electronic Structure Calculations

Classical MD uses numerical methods to solve for motion or dynamics of a system of many particles taking into account potential energy through force fields implementation and solving Newtons' equations of motion for large systems (100 Å) at large time scales (up to ~ 10 ns). Useful for calculating bulk physical properties of materials like tensile strength, thermal stability, or simulating crystal growth or atomic layer deposition [82]. The calculated properties rely on the potentials chosen, the degree of assumptions or level of theory. Even at high levels of theory, it will not provide details of electron dynamics as there are no explicit degrees of freedom given to the electrons, so we only see effects that are the result of atomic movement. Any 'electronic' effects are the result of artificially imposed constraints and these properties must be known and parametrized beforehand. Therefore, it would not be suitable to take this approach to understand electron dynamics of polarizing nanocomposites.

First-principles quantum chemical methods, including wavefunction-based approaches and Density Functional Theory (DFT), attempt to solve the Schrödinger equation to compute energies based on a material's structure and physical constants. Using the Born-Oppenheimer approximation the nuclear and electronic dynamics are treated separately, giving us an understanding of properties that relate to electron movement and not just atomic movement. This is possible because the time scales of electronic and atomic/nuclear movement are very different and by separating them only the electrons need to be treated using the Schrödinger equation. In the Kohn-Sham approach [69] the electron density $\rho(r)$ is the sum of N non-interacting orbitals ϕ_i which would be exact if orbitals are exact.

In order to solve this 3N-dimensional problem the many-body wavefunction must be considered which is computational expensive and unnecessary.

$$\rho(r) = \sum_i^N |\phi_i(r)|^2 \quad (2.1)$$

Hohenberg-Kohn [55] then circumvent the need for dealing with the many-body wavefunction by looking only at the ground state and therefore the simpler $\rho(r)$. They state that for any system of electrons under perturbation the total energy is a functional of the electron energy. The ground state gives the total energy and therefore all properties of the system, including the many-body wavefunction can be found from the ground state. The Kohn Sham potential $V_{KS}(r)$ fleshes out the many-body problem even if approximations for the exchange-correlation are taken.

$$V_{KS}(r) = -\sum_{\alpha} \frac{Z_{\alpha} e^2}{|r - R_{\alpha}|} + \frac{e^2}{2} \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc}(r) \quad (2.2)$$

This potential includes (from left to right) the electron-nucleus interaction (effective nuclear charge Z_a and radii r and R), the average (mean-field) Coulomb energy (using electron density $\rho(r')$) and the exchange-correlation potential V_{xc} .

Now we have simplified a complex many-body 3N-dimensional problem to a 3 dimensional ground state system of non-interacting particles. As stated, we must take approximations such as LDA (local density approximation) and GGA (generalized gradient approach) or the GGA extensions PBE and PBEsol (Perdew-Burke-Ernzerhof and extension for solids) [100]. LDA assumes that the exchange-correlation potential at a given state depends only on the electron density at that same state. It is computationally efficient but can be inaccurate for systems with significant electron density variations. GGA improves upon this by including the gradient of the electron density to account for the inhomogeneity of the electron distribution. This leads to better agreement with experimental results [160, 21]. Pseudopotentials replace the effects of core potentials with an effective potential. Pseudopotential files were not generated for any investigation in this investigation but used from pre-tested and tested publicly repositories [23, 72, 137] created by obtaining Kohn-Sham orbitals (all-electron, fully atomistic). Then a distinction between valence and core states can be made as core states changes are trivial.

Within the core, the nucleus and core electrons are treated as a model potential corresponding to the atom/element configuration. This is an appropriate assumption to make outside of high energy situations where core electrons may be excited to higher energy levels. Therefore discussion of ‘electron density’ from here only involves the valence electrons explicitly defined via a pseudo-wavefunction. Theoretically, any property of the system should be obtainable given the energy of the system and its components. Ab-initio methods can calculate properties such as bonding, charge transfer, and polarization intrinsically, while in classical MD they are artificially imposed. These methods can also calculate electronic structure, density-of-states, and band structure. The limits on size in ab-initio MD are due to computational expense. At each perturbation, the electronic structure must be solved for the entire system, which puts a limit on size and number of electrons. The ab-initio code SIESTA [125] is primarily used here for calculating projected density-of-states and optical dielectric properties for transparent materials. Car-Parinello MD or CPMD [15] is a highly parallelized method that allows for solving electronic structure of larger systems. Traditional DFT methods solve for electronic positions given nuclear positions, calculate forces on each and then displace according to the forces (for example, the force of an electric field acting on the system). This iterative method is extremely expensive as stated above for ab-initio. Car and Parinello proposed that it is not necessary to solve the electronic Hamiltonian at each step by keeping the electrons close to the ground state by initially assigning ‘fake’ masses and dynamics to the electrons and assuming there is minimal transfer of energy between the electrons and the ion. The ion is the nucleus plus core electrons described by a pseudo-potential while the valence electrons are treated explicitly in plane-wave basis as in other ab-initio codes. By keeping the system dynamics damped for as long as possible the convergence to the correct electronic structure is accelerated. This is therefore close to hybrid methods. The CPMD code used here is QuantumEspresso [37, 34] for its accurate implementation of applied electrical fields and parallelization on computing clusters.

2.3 Theories of Polarization

The simplest model of an atom and valence electrons can approximate them as two masses attached by a spring with the lighter valence electron bound to the nucleus + core electrons. Thus a dampening factor describes the relationship between the

two and can be used in approximating the possible displacement of valence electrons and therefore the polarizability.

In an open system (non-periodic) the net electric dipole moment (d) or polarization $\mathbf{P}$ of N particles with charge q_i and positions $\mathbf{r}_i$:

$$d = \sum_{i=1}^N q_i r_i \quad (2.3)$$

We can often think of polarization as the net electric dipole moment per unit volume as a vector quantity - which works for small atomic systems. This is a limited descriptor for condensed matter systems for several reasons.

In a free or bulk metal (i.e conductor) the electrons are accelerated by an applied field and can freely move; however near the plasma frequency metals are susceptible to electron loss and this poses a significant limitation for optical metamaterials. In applications such as semiconductors, capacitors, or ferroelectric devices, the performance depends not on a single dipole value but on the material's bulk polarization and dielectric response therefore simple models are insufficient [127].

Equation 2.3 is invariant to translation from the origin so long as the system is charge-neutral, which does not work in periodic systems as neighbouring image cells should not be invariant to translation. Periodic boundary conditions (PBCs) are in effect a mathematical trick to expand a finite space model to an infinite-space one by mirroring space-filling unit cells in all directions. The vector $\mathbf{r}$ from 2.3 also does not conform to boundary conditions and we need to use another definition.

Another issue is the failure to capture the complexities of periodic systems and the interactions within a material. We see issues such as ambiguity in dipole definition as the dipole moment depends on the choice of the origin in a periodic structure - any shift in the unit cell can change the calculated net dipole. Also, in large uniform crystals the local dipoles may cancel out, leading to a net dipole of zero despite significant polarization effects at the microscopic scale.

Net dipoles also fail to account for local effects such as ionic displacements and interfacial effects. In polar materials, ionic displacements at the atomic scale can contribute significantly to the material's response to electric fields, which the net dipole cannot describe - this requires a dynamic handling of the polarization.

Interfacial effects in heterogeneous materials or nanostructures mean local polarization at interfaces or boundaries significantly influences dielectric behavior,

especially in thin films or low dimensions. Lastly, the net dipole moment assumes a uniform electric field, which is rarely the case in real systems. Localized electric fields, gradients, and anisotropies in polarization require a more nuanced treatment than a single net value can provide.

The Modern Theory of Polarization gives us a theoretical framework in which to investigate polarization effects in periodic systems. This is explained in detail through the works of Vanderbilt and King-Smith, Resta and Spaldin [127, 108] and is an evolution from classical theories (e.g., Lorentz model) to quantum mechanical approaches to allow complex, condensed phases and functional materials modelling.

2.4 Berry Phase Theory

According to the modern theory of polarization *the macroscopic polarization is best defined (and calculated) as a Berry phase of the electronic Bloch wavefunctions* [110]. Also known as the Berry phase theory, it redefines electronic polarization in terms of the geometric phase of the electronic wavefunctions. Therefore, instead of relying on the ill-defined position operator, polarization is treated as a bulk property emerging from the topology of the occupied electronic states in reciprocal space.

The formulation in continuous k-space is explained in detail by Resta and Vanderbilt [110]. The change in internal polarization $\Delta\mathbf{P}$ where polarization $\mathbf{P}$ is the adiabatic flow of current within a periodic system is described by (2.4) where j is the macroscopic (i.e., cell-averaged) current density.

$$\Delta P = P(\Delta t) - P(0) = \int_0^{\Delta t} dt j(t) \quad (2.4)$$

The context of the time dependence shown in (2.4) is of an adiabatic field $\mathcal{E}$ switched on to perturb the system and induce a 'current'. The induced polarization is the time-integrated value of the macroscopic current. This definition is applicable to all polarization related phenomena, whether treated with open or periodic boundary conditions; however, we will only consider periodic conditions - the requirement is that the Hamiltonian and wavefunction be periodic over the cell. The essential point is that polarization relates to the response of a material to some perturbation and is not defined by charge density but by a current.

Polarization is a ground state property, so summing over all occupied states in

continuous k -space we end up with this analogous equation for effective polarization given electronic polarization is the time-dependent one.

$$P_{eff} = \Delta P_{ion} + [P_{el}(1) - P_{el}(0)] \quad (2.5)$$

This equation forms the basis of both static and optical polarization computations as a function of change between an initial (zero-field) and final (polarized or clamped-ion state).

The electronic contribution $\Delta \mathbf{P}_{el}$ to the macroscopic polarization $\Delta \mathbf{P}$ is given as a sum over occupied bands n and the integral taken over the Brillouin zone (BZ) and is generally a complex number ($\Im$ denotes the imaginary part).

$$P_{el} = \frac{e}{(2\pi)^3} \Im \sum_n \int dk \langle u_{nk} | \nabla_k | u_{nk} \rangle \quad (2.6)$$

Here k is a wavevector in the Brillouin zone (reciprocal space) and u_{nk} is a periodic function of the states (zero-field and equilibrium polarized states). The integral itself is known as the 'Berry Phase'.

The full derivation is fleshed out between Resta, Vanderbilt and King-Smith [110, 107, 65] and a practical explanation present in the Spaldin paper "A beginners guide to the modern theory of polarization" [127].

The ion part or the nuclear contribution $\Delta \mathbf{P}_{ion}$ arises due to nuclear displacement within the crystal structure.

$$P_{ion} = + \frac{e}{\Omega} \sum_s Z_s^{ion} r_s \quad (2.7)$$

When using pseudopotential theory (i.e frozen core approximation) this includes all the frozen core electrons. Only the outermost shell of electrons are included in the $\Delta \mathbf{P}_{el}$ computation for efficient use of computing resources. This holds as polarization is a ground state property.

Quantum Of Polarization and Limits

One of the key insights of the modern theory is that absolute polarization is not uniquely defined in a periodic system. The Berry phase is only well defined modulo $\frac{e\mathbf{R}}{\Omega}$ with $\mathbf{R}$ as any lattice vector and Ω as the cell volume of the primitive cell.

Polarization is therefore multivalued as a lattice of vectors. Another approach is these value(s) are only valid within the limits of one quantum of polarization best illustrated by Figure 2.1.

As

our polarization lattice is now defined in all three directions with lattice vectors ($\mathbf{R}$) equal to the dimensions of the simulation cell, one polarization quantum P_i equals one vector value.

$$P_i = \frac{1}{\Omega} e R_i \quad (2.8)$$

Another

way of imagining this is if an ion is near the edge of a cell, the electrons may polarize into the neighboring cell as shown in figure 2.2. Since periodic conditions are a construct where the same cell is repeated/mirrored - 'seen' mathematically

as the valence electrons jumping the length of the cell to the other side.

This means perturbations from the left atom will also be 'seen' on the right atom and the quantum of polarization will equal the distance or lattice vector. This is generally not an issue for highly symmetric crystal structures, but nanocomposites have amorphous and disordered regions which makes tracking these "jumps" important.

Symmetry and amorphicity both play a large role in the practicality of setting up any atom-level polarization calculation from the size of sampling mesh to quantum of polarization corrections. In centrosymmetric materials such as GaN and some

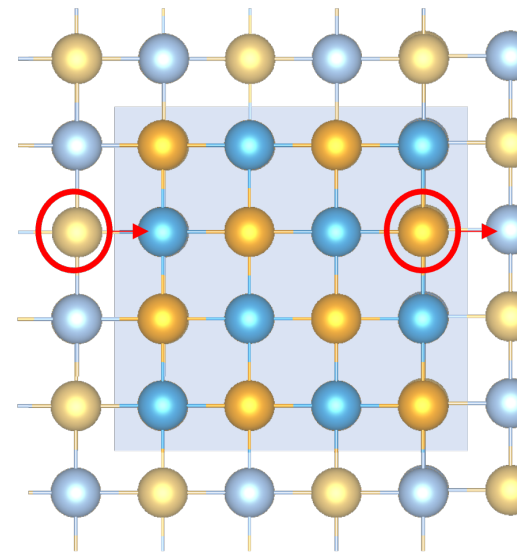


Figure 2.2: A crystal cell (center, background) with periodic 'ghost' images surrounding it. The circled atoms are periodic images of each other

silicon crystals [161], inversion symmetry ensures the electronic polarization is exactly zero in the absence of an external field ($\mathbf{P}_{el}(0)$ from (2.5). In contrast, non-centrosymmetric materials such as perovskite or ferroelectrics BaTiO₃ [6, 41, 77], doped metal oxides (HfO₂ [151, 86], ZrO₂ [138], ZnO [158]) or doped graphene-based dielectrics [101] lack symmetry and will see spontaneous polarization. The Berry Phase framework described above will capture this spontaneous polarization.

The Berry phase formulation of polarization is implemented in various plane-wave based DFT codes using discretization schema to translate from 1-dimensional systems to 3-dimensional. The King-Smith and Vanderbilt schema [65] for such systems is given as

$$\gamma = \text{Im} \left[\ln \prod_k \det \langle u_{n,k_j} | u_{n,k_{j+1}} \rangle \right] \quad (2.9)$$

Where k_j is the j -th k-point in the brouillon zone. This can then be generalized to 3-dimensions by computing integrals along either high-symmetry bands and averaging over the k-point 'mesh'. K-points are points in k-space or reciprocal space at which the Brillouin zone is to be sampled (defined via k-point meshes). They tell us how the wavefunction evolves throughout the crystal cell. A single Berry phase computation involved computing overlap matrices of the occupied Bloch states, evaluating their determinant across a k-point path and summing the resulting across real-space. This routine is standard in various codes such as QuantumEspresso [37, 34] and Siesta [125].

2.5 Dielectric Function in Materials

2.5.1 Static Dielectric Constant in Solids

The static dielectric constant ϵ_r , is a critical parameter that characterizes the intrinsic ability of a material to polarize in response to an applied electric field in the absence of atomic vibrations. Starting from our definition of $\mathbf{P}_{\text{eff}}$ (2.5) we treat the applied electrical field by integrating based on the plane wave basis sets and pseudopotentials. The relative ϵ_r within the linear regime of a finite electrical field

$\mathcal{E}$ is

$$\epsilon_R = 1 + \frac{4\pi\Delta P}{\Omega\epsilon} \quad (2.10)$$

Where ΔP is the difference between the zero-field and polarized and relaxed ion states [135]. There is a middle calculation needed in the QuantumEspresso code called clamped-ion, where the ionic degrees of freedom are artificially damped and only the electrons polarize, also referred to as high-frequency polarization.

Solid-State Materials

Material class, atomic structure, and bonding characteristics all influence the static dielectric constant. In ionic solids such as alkali halides and alkaline earth oxides, the dielectric constant is governed largely by the displacement of ions under an electric field. For example MgO and CaO [112] exhibit moderate dielectric constants due to their strong ionic bonds and simple crystal structures. They are useful as models for computing properties and establishing trends as they don't exhibit any anisotropy and formation of amorphous regions / short-range disorder is easy to track.

In contrast, transition metal oxides like TiO, SrTiO, and BaTiO₃ [40, 66] often exhibit significantly higher dielectric constants. These materials can support large displacements of ions (especially transition metal cations in octahedral coordination) and display high polarizability due to the involvement of partially filled d-orbitals. Some, such as BaTiO₃ also exhibit ferroelectricity where spontaneous polarization arises even in the absence of an external field, and this behavior further enhances the dielectric response. It is much harder to predict the local structure of molecular nanocomposites within these types of structures due to their already complex nature.

In general, materials with greater bond polarity, complex unit cells, and soft phonon modes tend to have higher dielectric constants. The ability of atoms to displace under an electric field and the electronic structure (e.g., band gap size) play key roles. Smaller band gaps allow easier electronic polarization.

2.6 Optical Dielectric Function

In contrast to the static dielectric constant, which describes the material response to low-frequency or DC electric fields, the optical dielectric function characterizes how materials respond to high-frequency electromagnetic radiation, particularly in the visible and ultraviolet regions. The frequency-dependent optical dielectric function is calculated using the interband transitions [11]. In (2.11) below, ω is the frequency of the incident photon, ϵ_1 is the real part of the dielectric and ϵ_2 as the absorptive 'loss'.

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (2.11)$$

Neglecting any excitonic effects and assuming independent particle transitions between occupied and unoccupied Kohn-Sham states from (2.1) and (2.2), we can compute ϵ_2 :

$$\epsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2} \right) \sum_{ij} \int i |M|^2 f_i (1 - f_j) \delta(E_f - E_i - \omega) d^3 K \quad (2.12)$$

Here, M is the dipole matrix, f_i is the Fermi distribution function for its state and E_i is the energy of electron in the i^{th} state. This is now used along with the Kramers-Kronig relation to find the ϵ_1 :

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon_2(\omega') d\omega'}{\omega'^2 - \omega^2} \quad (2.13)$$

It is important to use this relationship as it accounts for intraband (note, different to interband) transitions which are important for metals. It is also necessary in practice for the computation to account for additional bands, especially when working with metals, and include a Drude term with the square of the plasma frequency ω_p^2 :

$$\omega_p^2 / \omega(\omega + i\gamma) \quad (2.14)$$

It is especially important to include this term when computing MO diagrams/energies or the projected density-of-states.

2.6.1 Static vs. Optical Dielectric Response

The primary distinction between static and optical dielectric behaviour lies in the timescale and nature of the electric field interaction. The former includes both electronic and ionic contributions, as the field changes slowly enough to allow ions to displace and generally describes a transition to an equilibrium state. The optical dielectric constant, on the other hand, reflects purely electronic polarization, as ionic motions cannot follow the rapid oscillations of optical fields. For instance, materials like SiO_2 exhibit a large difference between their optical and static dielectric constants due to the added ionic contribution.

Metal oxides typically offer high dielectric constants, chemical and thermal stability, and well-defined electronic structures. These attributes make them ideal for applications in transistors, capacitors, and other solid-state devices. However, they are often brittle and require high-temperature processing [112].

Polymers, in contrast, are mechanically robust, lightweight, and easily processed, even into flexible or stretchable forms. While they exhibit lower dielectric constants and limited thermal endurance, they excel in applications requiring mechanical adaptability and large-area coatings, such as in organic electronics, sensors, and flexible displays [144].

In metal oxides, both ionic and electronic polarizations contribute to the dielectric response. Materials with soft phonon modes (ferroelectrics, superionic conductors [151, 121] can show large static dielectric constants due to the ease of ion displacement. Phonon modes relate to the collective vibrations within a lattice from a quantum mechanical perspective and soft phonon modes refer to low-frequency vibrational modes in crystal lattices that will become unstable/amorphous near phase transitions. They will more easily lose their physical order enabling large ionic displacements - leading to the importance of ionic contributions to polarization. Contrastingly, in polymers the dielectric response is predominantly electronic and depends on the polarizability of the constituent molecules and their arrangement. The interplay of these polarization mechanisms is critical in understanding how dielectric behaviour scales with temperature, frequency, and structural ordering. The presence of defects, grain boundaries, and interfaces also

introduces local field effects that can strongly modulate dielectric properties, particularly in thin films and nanostructured materials.

Current Challenges and Emerging Research

Despite the utility of existing computational models, several challenges persist in accurately predicting and characterizing dielectric behaviour. As stated previously, DFT often underestimates band gaps and may not fully capture correlation effects or excitonic phenomena, which are important in optical spectra. Corrections using hybrid functionals, scissor functions, Hubbard+U corrections are all computationally expensive, even if we had all the parameters tested and validated at this moment in time. It makes more sense to establish general trends in materials and obtain experimental data on the structures of nanocomposites of interest, especially with regard to polydispersity and trapped interfaces as feedback to computation. Emerging research is exploring hybrid materials that combine the advantages of metal oxides and polymers. These hybrid dielectrics can exhibit tunable permittivity, improved mechanical properties, and enhanced interface control. Additionally, the study of dielectric behaviour at the nanoscale—where confinement and interface effects dominate—is an active area, particularly for next-generation electronics and photonics [95, 117, 29].

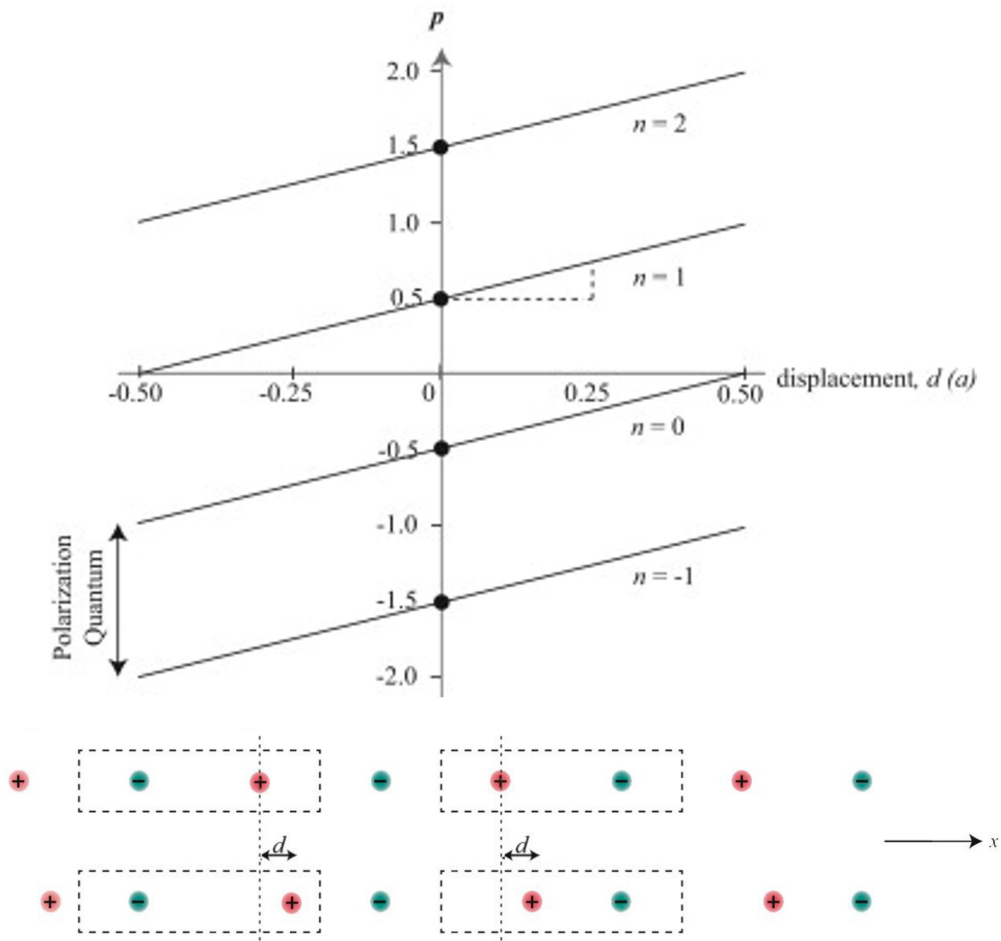


Figure 2.1: Polarization as a function of the displacement (d) between repeated periodic images of the cell (n) separated by 1 quantum of polarization. Lower panel shows displacement of charges before and after perturbation of the system by an external field for a one-dimensional string of charges. Reprinted with permission from Spaldin [127]

Chapter 3

Ag/MgO Molecular Scale inclusions in Metal Oxide Matrix

3.1 Overview

This project concerns the polarization of molecular-scale silver inclusions in a magnesium oxide matrix, using the Modern Theory of Polarization and Car-Parrinello Molecular Dynamics (CPMD). Details of the implementation and method development are laid out, including the handling of current jumps due to the distortion of the matrix during the simulation. Several trends in the dielectric response are considered in this project, including the effects of nanoparticle size, shape, and orientation relative to the applied field. Dielectric permittivity enhancements of 30-100% are observed with inclusion sizes varying from 8 to 32 atoms, considering both rod-like and disk-like inclusions, with alignment either parallel or perpendicular to the external field.

As stated in Chapter 1, 'metal' nanoparticles in the molecular regime (nanoclusters with up to 100 or so atoms) bridge the gap between single-atom dopants in classical semiconductors and traditional nanoparticles with 'metallic properties', while providing a range of unique features [47, 129]. Molecular nanoparticles (MNPs) are insulating, do not exhibit a band structure, and possess a high-electron density compared to traditional nanoparticles, which often leads to low percolation thresholds and tunnelling. This project can therefore treat MNPs as a source of highly polarizable electron density 'trapped' within our material of choice. Their quantum behaviour requires quantum mechanical treatments to model their

contribution to local polarization effects, which was done via the planewave code QuantumEspresso and the LCAO code SIESTA [125, 35].

3.2 Introduction

In recent years, methods for the synthesis of noble metal MNPs (Ag, Au, Pt) with atomic precision have been developed, and their distinctive properties have been capitalized on in applications such as heterogeneous catalysis and photo-catalysis [28, 70, 60, 148, 153], chemical and medical sensing [156, 43, 130, 62], and in composite materials with intriguing functionalities [39, 22, 40]. As methods for their synthesis have been developed in recent years, Ag nano-clusters have become a popular choice for materials' synthesis due to their enhanced optoelectronic properties, low cost, and reduced toxicity [150, 17]. From a computational standpoint, Ag is a well understood metal with a lower electron count than Au and Pt and does not require consideration of relativistic effects in calculations. MgO is a naturally abundant, common ceramic dielectric with a high permittivity for a single-metal oxide ($\epsilon_r \approx 9$), with applications generally driven by its high thermal conductivity, a high coefficient of thermal expansion compatible with metal contact layers, and a high melting point [18, 154, 49, 155, 149, 102]. More recently, highly ordered MgO crystals have been found to exhibit giant magneto-resistance [94, 79, 54] and high transparency [19], making them suitable matrix components for new categories of multifunctional materials for electronic and optical applications. Moreover, its simple face-centred cubic lattice with a low unit cell occupancy, its predominantly ionic polarization, and its wide band gap (around 7 eV) make MgO relatively straightforward to treat computationally and thus a good model dielectric material for metal/oxide nanocomposites. Particularly, the lower number of polarizable d-electrons compared to those of other mid/high- κ materials, such as HfO_2 , is important in Car-Parinello molecular dynamics, where valence electrons in matrix atoms greatly increase the computational cost.

Previous research from our group [46] used the modern theory of polarization [84, 127] to develop a model for describing the polarization of MNP NCs. We sought to unravel the contributions of the inclusion and matrix to the overall response of a model Ag_8/MgO NC and found significant interfacial effects between the MNP and matrix, contributing to a greater than expected polarization response.

This project uses Ag as a stand in for other potential metals and MgO as a test

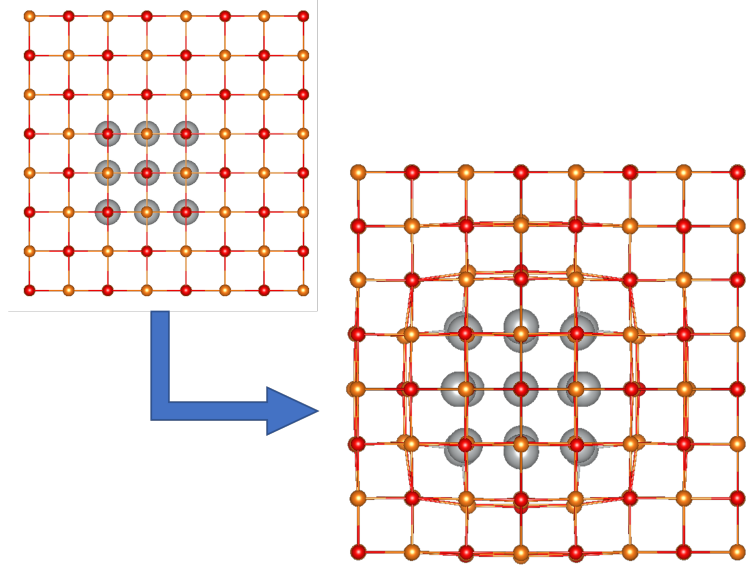


Figure 3.1: The unit cell of the $\text{Ag}_{18}/\text{MgO}$ NC, before and after geometry optimization. Mg, O and Ag are shown in orange, red and grey, respectively.

matrix due to the ease of computation.

3.2.1 Models

We considered a series of NCs based on an MgO matrix containing inclusions of silver MNPs' of varying shapes and sizes. Models were built using the Avogadro software [48], based on an ideal face-centered cubic (FCC) MgO lattice. An example NC with an Ag_{18} inclusion is shown in Figure 3.1.

Three rod-like inclusions and five disk-like inclusions were considered, as shown in Figures 3.2 and 3.3. Inclusions were built initially by replacing MgO ions with Ag atoms, and the entire structure was allowed to relax during the structural optimization phase of the calculation, as described in Section 3.2.2. The matrix extended at least 2 Mg-O layers beyond the edge of the inclusion in each direction.

This was done to prevent the cell from conducting into its periodic images while maintaining control of loading and cell size and ensuring appropriate lattice continuation at the boundaries. %Loading ratios were between 3-5.5%. Atom-based %loading values are slightly lower than volume-based values. However, for atomistic calculations, the definitions of atomic and thus inclusion volumes are ambiguous [52], and moreover, inclusion volumes are subject to change during the simulation.

For consistency, we report atomic number %loading here.

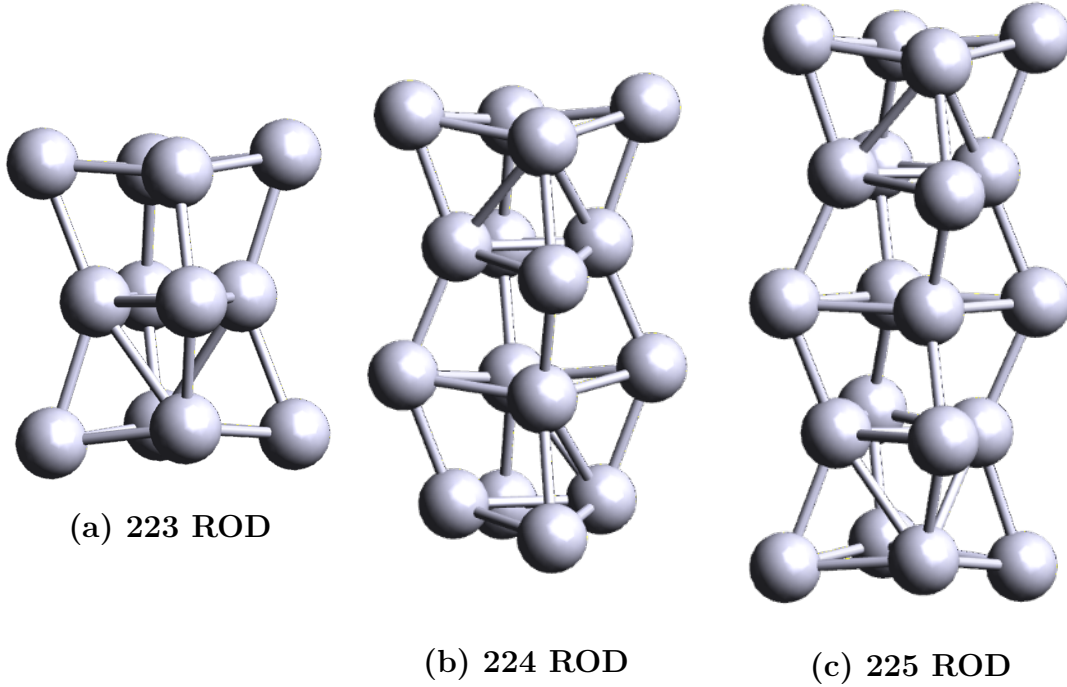


Figure 3.2: Rod-shaped nanoparticles used in this work. The nanoparticles were named for the number of repeating units in the x , y , and z directions, and include 12, 16 and 20 atoms for panels (a), (b) and (c), respectively.

3.2.2 Low-frequency Ionic and Electronic polarization

The process for calculating the low-frequency polarization of a NC material using the modern theory of polarization, as well as our methodology of partitioning the complex material's response, are also described in detail in Ref [46]. The CPMD method is used in the Quantum Espresso (QE) code [15, 36], with the two major stages of the calculation, structural relaxation and polarization, outlined in the following two subsections.

Electronic Structure Calculations and Structural Relaxation

The relaxed geometry of the periodic NC and its electronic structure were found using QE. CPMD requires sequential optimization of the electronic structure, nuclei and periodic cell boundaries [24], as shown in Figure 3.4. Each new system (new inclusions, new matrix materials, etc.) requires extensive trial and error in establishing a minimization scheme and appropriate runtime parameters. Furthermore, tight convergence criteria are required by the subsequent polarization

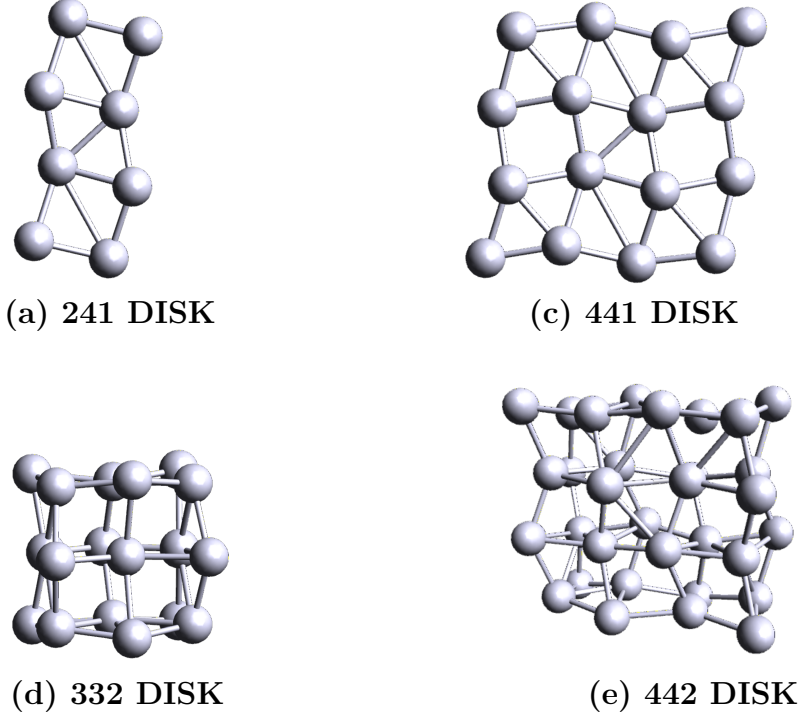


Figure 3.3: Disk-shaped molecular nanoparticles used in this work. The nanoparticles were named for the number of repeating units in the x , y , and z directions, and include 8, 16, 18 and 32 atoms for panels (a)-(d), respectively.

calculation [46]. Steepest descent initial electron minimization using a Gram-Schmidt orthogonalization was followed by a series of clamped and damped dynamics steps to allow both ions and electrons to reach a minima. For several of the steps, it is difficult to achieve perfect convergence; however, it is absolutely imperative to maintain low convergence thresholds for the ion movement steps, as complications will arise if the ions move erratically in the field.

An additional step to relax lattice vectors and remove additional stress on the cell must also converge due to the presence of the inclusion within the matrix. This is imperative as these models were created using substitution methods instead of MD to replicate the sintering or annealing processes—i.e., the atoms were replaced in the matrix with the inclusion until the desired shape (rod/disk) was formed. Excess strain on the cell vectors can be misread as electron density, especially when visualising induced fields and Born-Effective charges. Another consideration is the balance of atoms at the interface. Several other shapes of inclusion were considered; however, they may result in uneven hole formation or an imbalance of oxygen atoms

at one interface, which skews the apparent charge movements. It is important when creating the initial system to consider the symmetry of metal-oxygen contacts to reduce bias and the risk of failed computations.

Input files are available in the Appendix A.

Initialize System: Initial electron minimization conducted using Gram-Schmidt orthogonalization. This will begin the process of bringing electrons and ions from a frozen state to a reasonable minima. This yields incorrect eigen-energies; cell vectors will appear to indicate stress on the cell, and however, all these will be corrected in subsequent steps. This step must converge with a low total energy threshold of 10^{-9} a.u. that can be raised to 10^{-8} a.u. Electrons are explicitly given a mass of 300 a.u. which is used in the Car-Parinello Lagrangian term. Once converged, a quick geometry optimization is conducted with damped electron dynamics - both conducted as steepest descent. Here there may be 2 errors: firstly, the material must be an insulator with no unpaired electrons. Secondly, the material cannot be too far from a reasonable starting geometry, otherwise these damped dynamics steps will be computationally unfeasible. A good starting place is an existing crystal structure of the matrix modified using point-deletion methods to create the composite. The idea is to quickly get to a reasonable minima with minimal computational resources. Both electronic and geometric minimization can be repeated if they do not converge properly. There is no temperature control, and it corresponds to steps 1 and 2 in the appendix code.

Quick Geometry Minimization: Now that we have an initialised system, we quickly and iteratively relax any forces and stresses on the cell as a result of the inclusion. This occurs by conducting a steepest descent minimization and then slightly changing the cell vectors between scf-steps. Electrons are still damped with a fake mass; the wavefunction and density kinetic energy cutoffs should be taken from the pseudo-potential file (typically the softest one; here, it was usually oxygen that was the limiter). This step may not converge to a point but may end in an oscillating set of values; this is fine so long as the ΔE_{tot} is minimal. This step can be rerun to minimize forces.

Initialize System for Accurate Geometries Now that the ions are approximately in their lowest energy state, a zero-field minimization is performed with damped electron and ion dynamics, given the cell vectors. A Parrinello-Rahman dampening scheme is used on the cell vectors. The Wannier

function/centres (maximally localised) can be computed at this stage using the “vc-cp-wf” flag (variable cell - Car-Parrinello - wannier function). We alternate between an undamped and damped dynamics calculation to fine-tune the electronic structure, with 10 electronic relaxation steps between every ionic step. It is important that the material is not conductive at this stage; if it is not, the computation will most likely fail before this stage.

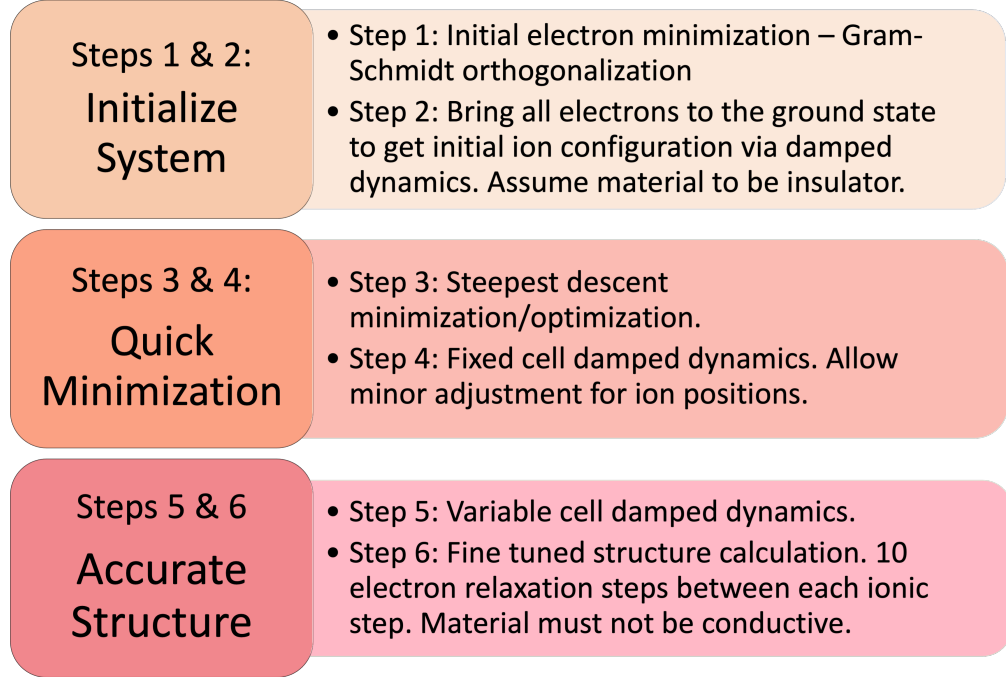


Figure 3.4: Structure calculation steps using QuantumEspresso.

Polarization

Dielectric constants were calculated from the polarization change of the periodic material upon the application of a finite electric field, following the modern theory of polarization as described in previous chapters. The low frequency dielectric constant (ϵ_r) [135, 147] is calculated as:

$$\epsilon_r = 1 + \frac{4\pi(P_{\text{relaxed}} - P_{\text{zerofield}})}{\Omega E} \quad (3.1)$$

where ϵ_r is the static dielectric constant of the NC, Ω is the simulation cell volume, and E is the applied static field. $P_{\text{zerofield}}$ and P_{relaxed} represent the polarization of

the relaxed cell prior to the application of the finite static field, and after the full geometric relaxation in the field, respectively.

Zero Field Polarization: Prior to applying an electric field, the reference polarization $P_{\text{zero field}}$ is calculated in Step 7 (Figure 3.5) for the relaxed geometries and electronic structures produced in Step 6 (Figure 3.4). This damped polarization is prone to computational errors due to sudden movements and high electron velocities that can cause integration/orthogonalization errors. This is fixed by manually adjusting velocities and dampening parameters in Step 7. It is vital this step not only converges but several (1–200 steps with $dt = 8$ a.u). It should be noted here that the Car-Parinello cp.x code from QuantumEspresso uses Hartree atomic units and the plane wave code pw.x uses Rydberg atomic units. If translating between the two methods one must not only transfer the structures but also translate the units.

Clamped and Relaxed Polarization: The field-induced electronic and ionic polarization were calculated using damped dynamics. A homogeneous electric field $E = 0.001$ a.u. is applied in the z direction in Step 8 (3.4), and the electronic density is allowed to relax while holding the ions fixed (Figure 3.4, step 8). This step models the high frequency dielectric response ϵ_{∞} and is necessary for calculating the Born Effective Charges discussed below. Finally, the ions and electrons are allowed to relax together in step 9, which allows calculation of the field-induced polarization P_{relaxed} and the low-frequency dielectric constant. Note that the infinite-dimensions assumption of periodic boundary conditions (PBCs) calculations result in differences between calculated and measured values for ϵ_r : in the infinite bulk (PBC) calculation, surface charge and edge effects are not taken into account and resulting ϵ_r value is a loading-dependent volume average.

Quantum Of Polarization

One issue for consideration in calculating the polarization of periodic solids is the quantum of polarization.[127] The polarization calculated for a periodic system is multiply defined, and dependent on the choice of unit cell and of coordinate system.

Spaldin[127] discusses this in some detail. For the case of an infinite one-dimensional chain of alternating unit-charge anions and cations, different choices for the unit cell and the coordinate system return an infinite number of equally-spaced polarization values: $...-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}...$ That spacing is the

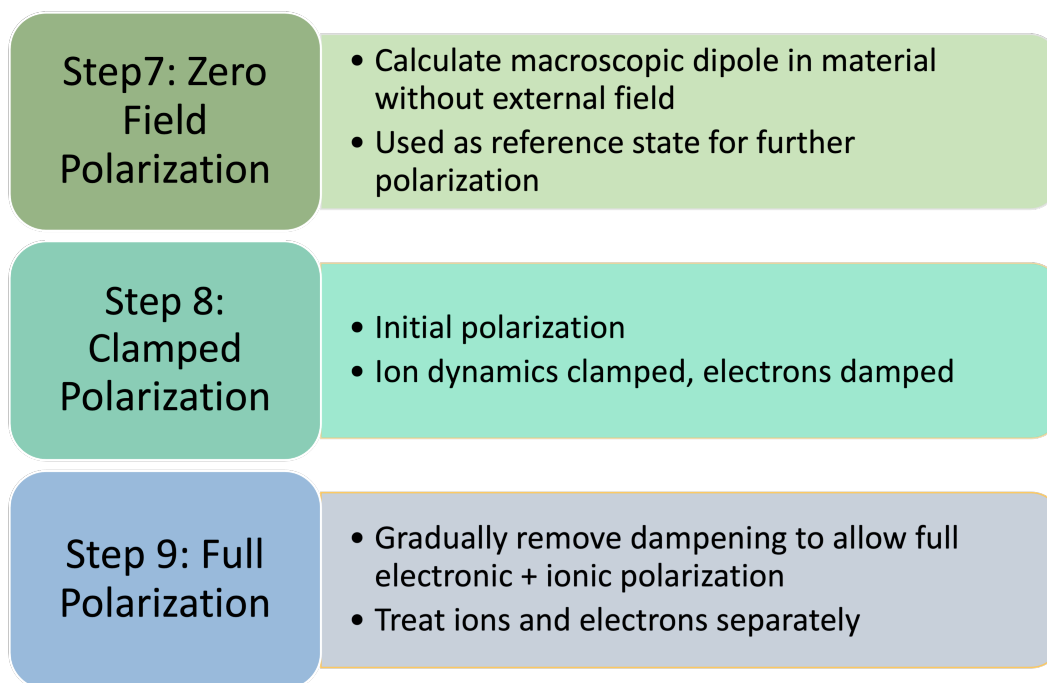


Figure 3.5: Polarization steps using QuantumEspresso – step numbers continued from Structure calculation (Figure 3.4)

polarization quantum. That the absolute polarization of an infinite solid is undetermined is not an issue in practice: What normally needs to be calculated is the change in polarization, such as upon application of an electric field. Provided that a consistent choice of unit cell and coordinate system is made in the reference and the polarized states, this polarization change is, in principle, single-valued. The requirement of a consistent choice of unit cell becomes problematic when that unit cell is stressed during the polarization process, or when charges are displaced beyond cell boundaries. In the periodic calculations described here, some of the charge density will polarize into neighbouring image cells (or, more specifically, to the other side of the simulation box), shifting the charge distribution relative to the coordinate system in which the “reference” polarization was calculated. The reported polarization then shifts by a positive or negative multiple of the quantum of polarization (in this case, one box length along the polarization direction for each displaced electron). These effects are more likely to arise when the matrix is deformed by larger, anisotropic inclusions, thus monitoring and correction of cell polarization becomes essential. However, it is important to note that monitoring cell polarization for quantum of polarization discontinuities should be performed

regardless of the system's anisotropy.

Consequently, care must be taken when calculating the effective polarization, particularly for anisotropic, low-symmetry systems or deformed crystal lattices. As discussed in Spaldin [127] however, the system follows a single ‘polarization branch’ as it structurally and electronically adapts to the applied field - i.e., the evolution of polarization during the field-on simulation should be smooth. The corrections for polarization jumps can be done during post-processing by checking the full simulation run for discontinuities and inconsistencies of the total dipole of the simulation cell [see Figure 3.6(a) for an example], followed by shifting its value (and respectively the value of the volume-adjusted permittivity) by the required number of polarization quanta [Figure 3.6(b)].

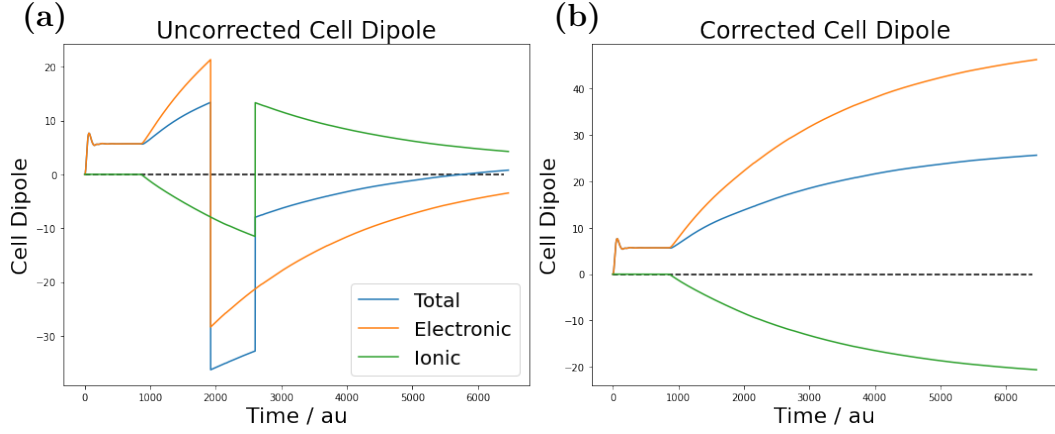


Figure 3.6: Correction of cell polarization due to cell distortion effects. The uncorrected cell dipole displays polarization jumps due to polarization of electrons across cell boundaries [panel (a)], which upon correction lead to the continuous corrected cell dipole [panel (b)].

3.2.3 Born Effective Charge

To understand the electronic polarization effects in the composite, we examine its

Born effective charge tensor ($Z_{\alpha,ij}^*$, BEC). BECs reflect the changes in the polarization of a material as a result of ionic displacements. The BEC of an individual atom or ion is defined as the change in the force acting on that atom or ion as a result of the application of an external electric field:

$$Z_{\alpha;ij}^* = -e \frac{\partial F_{\alpha;i}}{\partial E_j} \quad (3.2)$$

where $Z_{\alpha;ij}^*$ are the BEC tensor elements at the nucleus α , E_j is the j -direction component of the external field, and $F_{\alpha;i}$ is the i -direction component of the force acting on α .

In a bulk ionic crystal, the static charges of constituent elements (or ions) are their nominal valence charge [76] (−2 for oxygen, +2 for magnesium in the case of MgO).

Upon application of an electric field, the average overall BEC tensor remains the same, as all the atoms experience the field uniformly. In a NC, however, significant changes in the charge distribution of the matrix ions arise from the influence of MNP electrons, especially under an applied field. This impact is strongest for the ions near the MNP - matrix interface, where the local field effects of the polarizable MNP electrons are strongest. BEC maps are thus a useful tool for depicting the local charge density and spatial distribution of induced fields at small scales. Here, BECs are calculated using Eq. 3.2. Forces were normalized to the bulk matrix to highlight the effect of the NP.

Mapping BECs was a major sideproject for this work and some details are given in 3.4.1.

3.2.4 Numerical Details

Electronic structure calculations were carried out in a zero-field environment.

Electronic structure, relaxed crystal structures and polarization were calculated using the CPMD methodology implemented in the Quantum Espresso code versions 6.0 and 6.6, with a plane wave-basis and the LDA functional. Test calculations were run using GGA functionals such as PBE. However, the structural minimization steps were significantly slower in these calculations, and furthermore, convergence of the polarization was impeded in GGA-based calculations. Later iterations of PBESOL and PBE- based pseudopotentials are more accurate and available via Materials Cloud [72] however they were not available when these computations were initially completed. Mg atoms were described using Bachelet–Hamann–Schluter [137] norm-conserving pseudopotentials, whereas Rappe–Rabe–Kaxiras–Joannopoulos [23] ultra-soft pseudopotentials from MaterialsCloud[72] were used for oxygen and

silver. The total energy convergence criterion was increased from the standard 10^{-4} to 10^{-8} and a force threshold of 10^{-4} was used. A wavefunction cutoff (*wfcut*) of 50-60 Ry and charge density (*rhocut*) cutoffs of 560 Ry were used for all calculations. Electron masses were set initially at 300 a.u., and increased to 450 a.u. after initial damped minimizations, to accelerate convergence of the initial structure.

All calculations were done using periodic boundary conditions (PBCs), and the Brillouin zone was sampled at the Γ point, there is no discernable symmetry in the crystal structure. The size and volume of the simulation cell were allowed to relax with the matrix structure throughout the zero-field dynamics and structure minimization.

A thermostat was not applied nor were temperatures controlled for the runs reported herein. No specific ensemble is implemented. Instead, CPMD-based damped dynamics[68] is used to relax ion positions and electronic structure. Test runs using thermostats between 200 and 600 K found that temperature effects, especially those on geometry were negligible in these systems. We attribute this to the intrinsic rigidity of the lattice due to high ionic charges, as well as the high melting temperature of the ionic matrix.

3.3 Results and Discussion

Two types of effects accompany the inclusion of silver clusters within a uniform MgO matrix, both contributing to the dielectric response of the material in applied electric fields. On one hand, the inclusion distorts local structure in the matrix (as shown in Figure 3.1 for example). In the cases considered here, the somewhat compacted MNPs push outward against the ionic layers of the matrix. Other types of lattice mismatch will lead to inward buckling at the interface. Generally, this distortion only encompasses the nearest neighbours of the inclusions (up to around 3 Å from the edge of the MNP), since the doubly charged ions of the matrix create a rigid lattice. This rigidity, as well as the relatively low %volume loadings of 4-5% ensure that the MNP-induced distortion does not extend to neighbouring simulation cells, in all cases. However, disruption of local structure in the strongly ionic matrix changes the electronic structure at the interface (defined here as the roughly 3 Å-thick layer of matrix atoms neighbouring the inclusion), and its response to the applied field.

The second class of effects has to do with the specifics of the charge density in the

two mixture components, and at the interface. In broad terms, the MNP electrons mobilize along the applied external field, creating strong local fields at the NP-matrix interface, further impacting the ionic and electronic polarization of the matrix. For the small Ag₈ inclusion considered in our previous work,[46] the field of the polarized MNP resembled that of a point dipole located at the MNP centre. In this analogy, using larger, anisotropic inclusions should further enhance the dielectric response of the NC by creating stronger induced dipoles through polarization of a larger charge density over longer distances. We discuss the electronic structure of the composites, and the various effects impacting the materials' response to applied fields, in the following paragraphs.

3.3.1 Electronic structure of the NC

Calculated bandgaps of polarizable materials require careful consideration of the errors arising from the DFT formalism – particularly when using the LDA functional. The calculated bandgap is generally expected to be significantly lower than the corresponding experimental bandgap, due to DFT's known underestimation of virtual orbital energies.[99, 100] For bulk MgO, the electronic structure calculations described in Section 3.2.4 yield a bandgap of 5.5 eV [See Figure 3.7(a)], compared to the experimental value of ≈ 7 eV.

In large-bandgap materials (over 4-5 eV), metallic inclusions introduce additional states in the bandgap.[116, 115] These states are generally located in the vicinity of the Fermi level, and occupied by the many MNP electrons. In Ag/MgO NCs, the bandgap of the pure MgO [Figure 3.7(a)] is populated. Comparison of the Fermi regions in the NC DOS (blue line in Figure 3.7(b) and the matrix- and MNP-projected DOSs in the composite [blue lines in Figure 3.7(a) and (c), respectively] suggests that all the states within ~ 2 eV of the Fermi level are mainly localised on the MNP. Interaction between the NP and the matrix is reflected in the splitting of NP states [Figure 3.7(c)], particularly in the region of overlap with the matrix conduction band. Thus we expect that the response properties of the NC are dominated by MNP effects, and thus DFT performance for these properties will mirror more closely its performance for nanoparticles,[74, 140] than that of bulk materials.

3.3.2 Dielectric response of NCs with rod and disk-shaped inclusions

We have shown previously that the inclusion of “spherical” Ag₈ MNPs at 4 %loading increased the dielectric constant of the MgO matrix by 30% [46]. Larger, anisotropic NPs with rod-like and disk-like geometries can further enhance the dielectric response, both by increasing the inclusion volume ratios, and through specific local field enhancements. Dielectric constants for the series of Ag/MgO NCs with rod-like and disk-like inclusions are presented in Table 3.1. The data indicate that asymmetric inclusions bring on dielectric enhancements that are, depending on orientation, larger than expected based on volume ratios alone. For example, multi-layer disks (Disks 332, 432 and 442) exhibit more than 70% enhancement in ϵ_r over the matrix permittivity, at loadings of around 4% (see Table 3.1).

The series of rod-like inclusions considered here have similar cross-sections, with longer MNPs featuring additional atom planes along the inclusion’s principal axis (See Figure 3.2). NCs with rod-like inclusions exhibit stronger response when the applied field is parallel to the principal axis of the inclusion ($\epsilon_{\parallel}$) than when the field is applied perpendicular to the inclusion ($\epsilon_{\perp}$). This is because of the larger polarization distance available along the principal axis in the longer rods. The polarisation distance within the inclusion is an important factor in the field response of these NCs, as illustrated by the discrepancy between the size dependence of $\epsilon_{\parallel}$

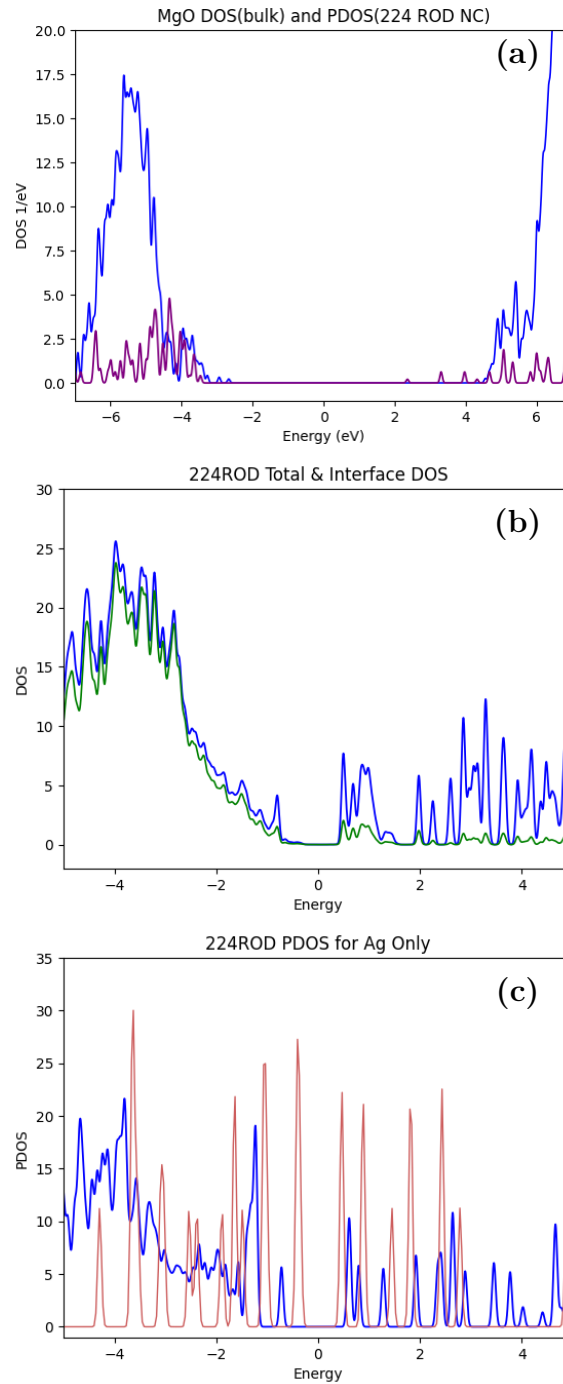


Figure 3.7: Density Of States (DOS) graphs for the Ag/MgO NC with the 224 rod-like inclusion. Panel (a) shows the DOS of the pure bulk MgO (purple line) and the matrix-projected DOS (blue). Total and interface-projected NC DOSs are presented in (b) in blue and green, respectively. Panel (c) shows the MNP-projected DOS, in vacuum (red) and in the NC (blue).

Table 3.1: Dielectric constants of Ag/MgO nanocomposites with anisotropic inclusions.

Inclusion	N_{inc}	N_{atoms}	%Loading ¹	$\epsilon_{\parallel}$ ²	$\epsilon_{\perp}$ ³
None (bulk MgO)	0			9.8	
SPHERE 222 [46]	8	216	3.7	11.9	
ROD 223	12	288	4.2	12.9	12.2
ROD 224	16	288	5.6	13.9	12.3
ROD 225	20	360	5.6	14.9	12.8
DISK 332	18	384	4.7	15.0	13.3
DISK 432	24	800	3	15.9	14.8
DISK 442	32	800	4	16.9	15.9
DISK 241	8	192	4	11.3	10.7
DISK 441	16	384	4.2	12.6	11.0

* Calculated as a ratio of the number of atoms in the MNP to the total number of atoms in the cell.

[†] $\parallel$ indicates that the field is applied parallel to the longest axis of the inclusion.

[‡] $\perp$ indicates that the field is applied perpendicular to the longest axis of the inclusion.

and that of $\epsilon_{\perp}$ (Table 3.1). Whereas $\epsilon_{\parallel}$ increases significantly with MNP length, $\epsilon_{\perp}$ remains roughly constant in the series of rod-shaped inclusions.

However, dielectric enhancement, in general, is more complex than a simple correlation to the MNP length or the availability of polarizable electrons. This is evidenced by comparison of $\epsilon_{\parallel}$ (Table 3.1) for Rod225 and Disk332. The MNPs have similar atom numbers but different shapes, and Rod225 has a longer dimension parallel to the field with two more atoms than Disk332. Despite this, NCs containing Disk332 inclusions have similar $\epsilon_{\parallel}$ values to those containing Rod225.

Moreover, response to transverse applied fields ($\epsilon_{\perp}$) is generally stronger in multilayer disks and increases with MNP size, in contrast with the relatively constant transversal response of rods of varying sizes.

When the polarizing field is applied along the MNP's longest axes, NCs with disk-shaped inclusions show an increased response for larger nanoparticles, with marked increases in $\epsilon_{\parallel}$ over their rod-like counterparts. The effect can be attributed to the larger number of electrons and polarization length in the larger MNPs.

Moreover, NCs with disk-like inclusions show stronger dependence of dielectric response on the field direction and NP shape than those with rod-like inclusions.

NCs with 3-dimensional MNPs (Disk332, Disk432 and Disk442) had stronger response than rod inclusions with similar axis ratios, a fact that can be traced back

to the availability of larger numbers of polarizable electrons, with greater overall space to move in the disk-like MNP. On the other hand, dielectric response is weaker in NCs with 2-dimensional NPs (Disk421 and Disk441), regardless of the applied field direction. This observation holds even when accounting for the fewer metal atoms in these MNPs, and is attributed to the small polarization distance in the direction of the smallest NP axis, and the overall lower number of electrons for these MNPs (see Table 3.1).

Broadly, disk-like inclusions do not conform as much as rods to the induced-point-dipole analogy, from both electronic and structural perspectives. In these cases, consideration of polarization volumes instead of polarization lengths, as well as a more sophisticated classical model, such as a polarizable metal disk or ellipsoid, are necessary to help interpret many of the observed trends.[52]

3.3.3 Local Polarization Fields and Born Effective Charges

Beyond the MNP polarization, the dielectric response of the Ag/MgO NCs presented in Table 3.1 includes significant interfacial and matrix contributions. The different contributions (NP electrons, interface, matrix ions, and electrons) are not directly separable, as polarization modes are coupled. One such coupling, between the electronic polarization in the NP and that of the matrix, is described by the matrix-ion BECs. The BECs reflect the influence of the NP polarization on the charge distribution within the matrix ions. To illustrate this effect, three-dimensional lattice interpolated plots of BECs were generated. These serve as effective maps of the local electrostatic field created by the NP's polarization in the matrix (Figures 3.8, 3.9 and 3.10).

Figures 3.8, 3.9 and 3.10 shows the interpolated BEC maps for NCs with a 224 rod-like inclusion and a 332 disk-like inclusion. Enhancement of the matrix polarization field (blue regions in the figures) is observed in regions adjacent to the NP poles, in the applied field direction. In the equatorial regions, a depolarization arises (red/yellow regions in BEC plots), where the effective ionic charge is weaker than in the absence of the external field. The enhancement is intense and mainly localised to two layers of matrix ions at the interface. Depolarization fields are weaker, often extend over broader swaths of the cell, but also often decay within two layers of matrix ions from the interface. The increased charge density in the MNP close to the interface, particularly strong along the polarization direction, leads to

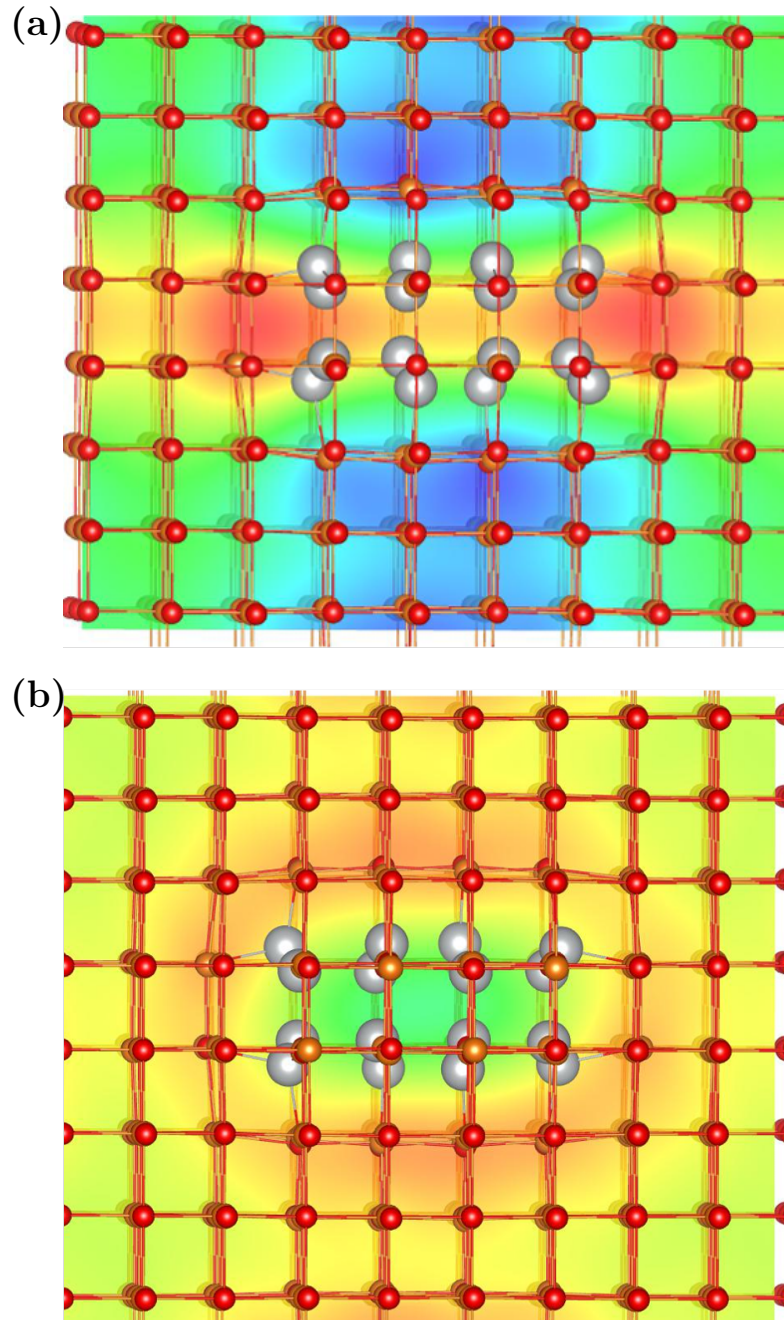


Figure 3.8: Interpolated BEC plots for NCs with rod-like and disk-like inclusions (continued in 3.9, 3.10). Plots show Rod224/MgO [panels (a)–(d)]. Blue and red show areas of increased and decreased polarization compared to bulk matrix values, respectively. The static field is parallel to the longest MNP axis in in both (c) and (d). Two sections are shown for each Rod-inclusion simulation: (a) and (c) are sections along the field direction, whereas (b) and (d) are taken perpendicular to the field.

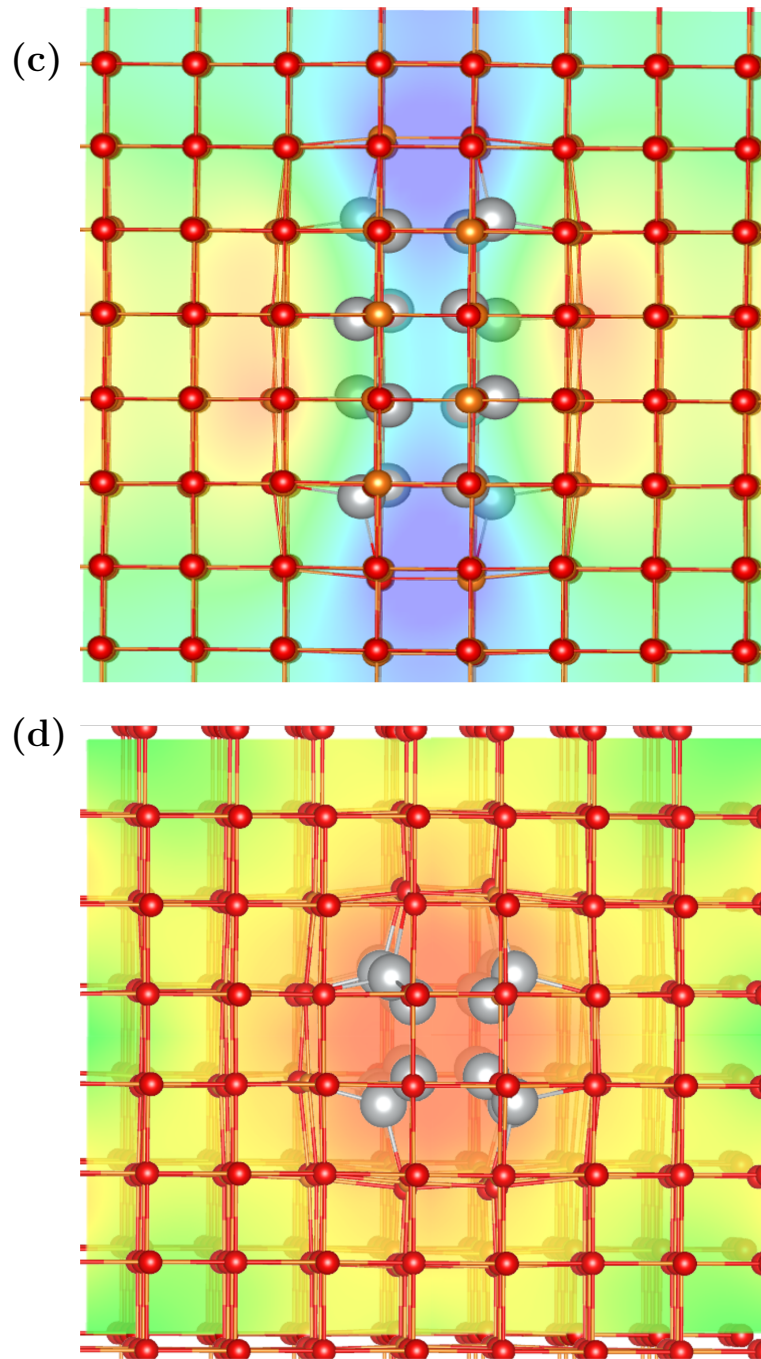


Figure 3.9: Interpolated BEC plots for NCs with rod-like and disk-like inclusions (continued from 3.8). Plots show Rod224/MgO [panels (a)–(d)]. Blue and red show areas of increased and decreased polarization compared to bulk matrix values, respectively. The static field is parallel to the longest MNP axis in both (c) and (d). Two sections are shown for each Rod-inclusion simulation: (a) and (c) are sections along the field direction, whereas (b) and (d) are taken perpendicular to the field.

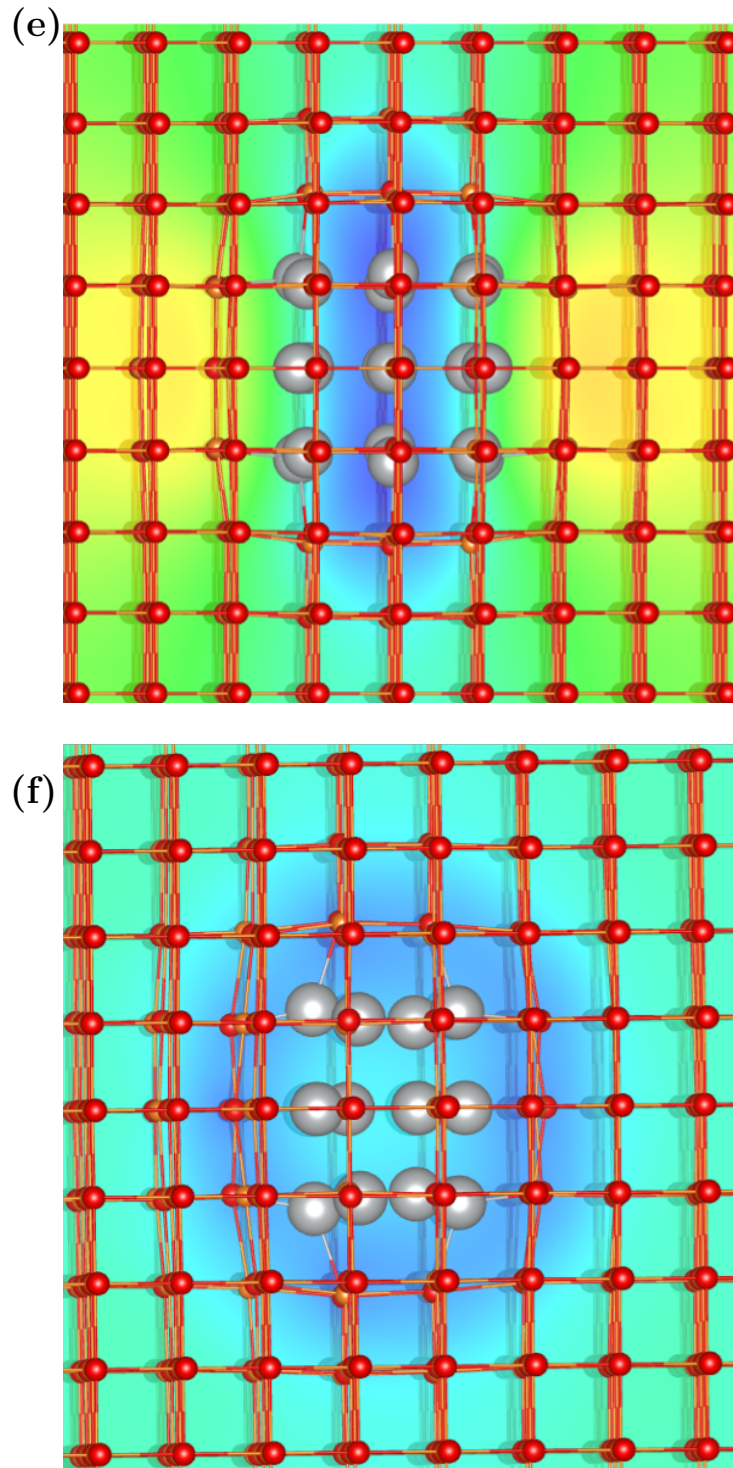


Figure 3.10: Interpolated BEC plots for NCs disk-like inclusions (continued from 3.8, 3.9). Plots show Disk332/MgO, along the direction of applied field. Blue and red show areas of increased and decreased polarization compared to bulk matrix values - in particular an induced field shown as a blue ring from both directions. The static field is perpendicular to the longest MNP axis in panels (a), (b) and (e) and parallel to the longest axis in (c), (d) and (f).

increased forces acting on the nearby ions along the direction of polarization [see Figures Figures 3.8 and 3.9 (a) and (c)]. This raises the overall dipole moment in the cell, beyond the NP polarization, and prior to ionic movement in the overall field. The opposite effect arises perpendicular to the polarization direction [Figures 3.9 and 3.10 (b) and (d)].

From a classical perspective, the polarization of the NP creates an electric field, similar to the field of a dipole, which modifies the local field in which matrix ions polarize. However, the classical picture neglects the quantum coupling of the MNP electrons and those of the matrix ions- particularly coupling to the electrons in the oxygen ions. The BECs capture this interaction, *in the clamped ion regime*. The movement of nuclei in Step 9 (Figure 3.5) further modifies this polarization picture.

Nevertheless, the BEC plots highlight the significance of the interface in the polarization of nanocomposite materials. Interfacial effects also impact the ionic movement under the field, as ions at the interface are not bound in the crystal lattice in the same fashion as bulk ions, and lattice mismatches between the inclusion and the matrix can further modulate this effect. In the systems considered here, the larger interfacial area present in NCs with disk-like inclusions enhances further the overall polarization of the material. The relative importance of these effects would have to be reconsidered for matrix materials with more diffuse charges, or with weaker ionic or even covalent bonding.

3.4 Conclusions

This work examines the effects of nanoparticle size and shape on optimizing dielectric response in metal/metal oxide nanocomposite materials, aiming to develop an understanding of how polarization in molecular-scale metallic inclusions, in turn, affects the polarization of the metal oxide matrix. The introduction of molecular scale metal inclusions of silver in a magnesium oxide matrix is found to increase the dielectric capacity of the material by up to 80% at below 5%volume loading, with the enhancement depending on the shape, size, and orientation of the inclusion relative to the external field. As the inclusions are small enough to behave as molecules, their polarization behaviour is quantized, requiring quantum approaches to model the material's response to an applied static field. Calculation of electron dynamics and Born effective charges provide a picture of the local fields generated around the polarized inclusions. The electronic and ionic

polarization modes are coupled and cannot be individually described; However, the BEC picture suggests that induced fields at the matrix-inclusion interface enhance the matrix response to the applied field beyond the bulk level. The extent of the interface is particularly important, both as it relates to the accumulation of charges, and as it affects the mobility of nearby ions. The balance of polarization enhancement and destruction in the vicinity of the inclusion points towards a specificity of the outcome to individual matrix materials.

The qualitative trends discussed above should be applicable to a broad range of composites, particularly those based on ionic matrices with a large band gap. Lower-bandgap matrix materials will exhibit further interaction with nanoparticle states, likely leading to a more pronounced effect of nanoparticle polarization on the dielectric response of the composite. Other oxide matrix materials exhibit more covalent bonding, altering the matrix polarization mode. In these systems, the interfacial effects should be distinct from those observed here. The next steps would be to extend our calculations to other relevant matrix materials, including SiO_2 , Al_2O_3 and HfO_2 , as well as other inclusion options. These calculations are extremely lengthy, rely on highly uniform MNP distributions and are discussed in Chapter 5. Such distributions are challenging to achieve experimentally, particularly from the point of view of nanoparticle alignment with the field. We are working on developing alternative, quantum/classical approaches for estimating polarization response in nanocomposite materials, to mitigate these problems and enable studies of polydisperse, non-uniform systems, including broader nanoparticle size and orientational distributions.

3.4.1 BEC Mapping Details

The Born-Effective charges mapping was a major part of understanding charge dynamics and the induced fields around molecular nanoparticle based composites.

The visuals (Figures 3.8, 3.9, 3.10) were generated from the QuantumEspresso output using the PyBEC Python module [13]. Using the output files (.out, .xyz and .xsf files) of zero-field and fully relaxed polarization as a grid of values overlaid on the ionic coordinates we are able to subtract the inherent dipole moments in the matrix.

First, we compute the dipole field for a point dipole centered at the nanoparticle centroid and plot the values up to the limits of the cell. Computing the dipole at

each atomic position, excluding the effects of the MNP inclusion gives us a baseline for which to conduct interpolation and regression analysis. We perform a simple linear regression [97] to interpolate the values across a slice of the 3-dimensional grid that passes through the volumetric centre of the cell. Depending on the crystal lattice, this is either the 1,0,0 or 0,0,1 plane. The interpolators used were the spatial regression model Universal Kriging [87], a radial basis function (RBFs) interpolator and LinearND interpolator [139], and a minimal linear dipole-based interpolator. All plots shown here used the Universal Kriging interpolation method, which is why small artefacts at the edges of the plots can be seen.

Interpolation of BEC

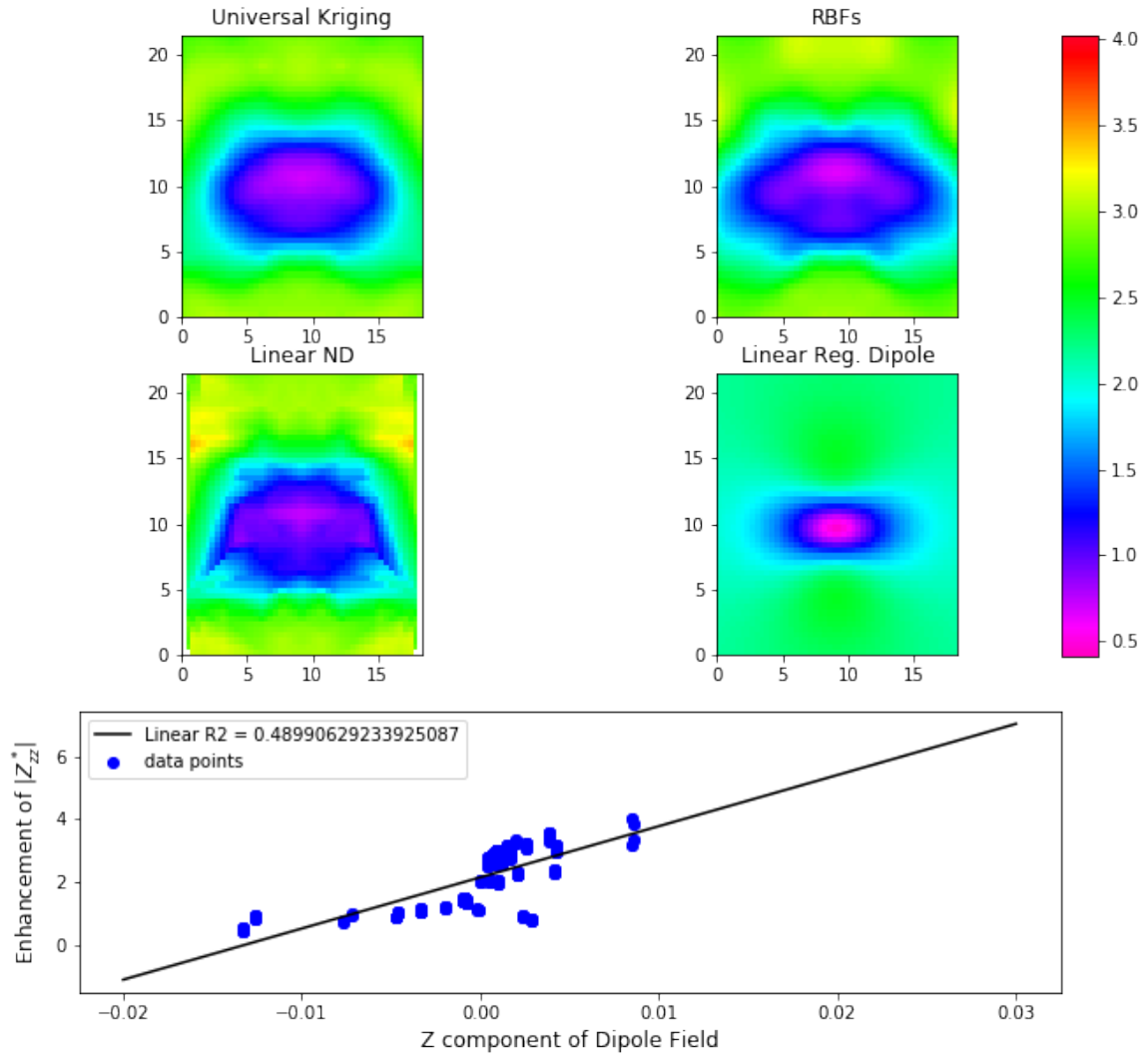


Figure 3.11: BEC interpolation: various regression models are plotted and the smoothest one was chosen for each model. Includes Universal Kriging, Radial Distribution Function (RBF), LinearND and regular linear dipole-based interpolation.

Chapter 4

Polymer Models and Polydispersity of Inclusions

4.1 Overview

This project studies optical polarization of molecular metal inclusions (Ag) in a PVDF matrix to investigate polydispersity effects on the optical dielectric function.

Meant as a model for other systems with more complex polarization modes or complicated multiphase or highly doped materials, especially with molecular metal nanoparticles (molecular meaning they do not act as proper conductors as they are so small in size; in this case all are 30 Ag atoms). Various displays of polydispersity

by “pulling apart” an inclusion and polarizing within the material give us an understanding of how polydispersity and directional polarization of atom-scale or molecule-scale metal inclusions will affect the dielectric function of a polymer.

Simulations on the polydispersity of inclusions within nanoscale materials show the effect of various issues in deforming a molecular nanoparticle (MNP) in a PVDF polymer matrix and its effect on the optical dielectric function: energetic materials, vacuum/hole states, defects, charge hopping, and potential tunnelling issues. This work deals with a minimal set of models showing the effect of deforming a molecular nanoparticle (MNP) in a polymer matrix and its effect on the optical dielectric function. We found that unlike previous investigations in strongly-correlated metal-oxide matrices, these polymer-based nanocomposites showed a change in dielectric response only with changing length of metal relative to light propagation/applied field.

4.2 Introduction

Nanocomposites are two- or multi-phase materials in which at least one of the phases has dimensions in the nanometre range. These mixed materials have the capability of incorporating the desirable properties of each of the constituents [56, 96]. Organic-inorganic nanocomposites have been the subject of intense investigations because of the ability of combining the optical, mechanical and electrical properties of metals or semiconductors with the process-ability and flexibility of organic materials such as polymers. As a result, nanocomposite materials have been fabricated with application in opto-electronics [4], electronics [56], intracellular manipulation [96], as thermoelectric materials, high-strength and high-toughness structural materials, electrolytes in batteries, insulation, coatings, gas separation [85], fire barriers etc.

Polymer-metal, polymer-semiconductor and biomolecule-semiconductor nanocomposites are promising materials for a number of opto-electronic applications. These take advantage of the special electro-optical properties of the inorganic nanoclusters (high dielectric constant, conductivity or unusual refractive index), as well as a number of convenient properties characteristic to polymers, such as dielectric properties, transparency and flexibility. The characteristics of the components may be enhanced in the blend as a result of the large interfacial area and interfacial field effects such as Maxwell-Wagner polarization. New dielectric materials for transistors and capacitors, ultrahigh/low refractive index materials for fiber optics, nonlinear optical materials for photonics, biosensors and other applications have been realized [64, 89, 33, 159, 91, 128, 90, 16].

To design new materials with enhanced optical response, two properties of metal nanoparticles (NPs) have been exploited in particular: size-dependent light-absorption properties in the visible range of the spectrum and their medium-dependent surface plasmon resonance. Molecular nanocomposites can absorb electromagnetic radiation in the optical frequency range when the energy of the incident light excites electrons. Incorporating metal molecular nanoparticles (MNP) much smaller than the wavelength of light into polymers can alter the absorption spectra - the signal enhancement arises due to collective oscillations. This effect is due to the wavelength of light being much longer than the dimension of the NP (< 30 nm), known as the quasi-static limit, such that the NP uniformly experiences the field, with alternations in phase.

The polymer may serve simply as a substrate or binding material in exploiting the NP properties, such as in the use of polyvinyl alcohol as a matrix for surface-enhanced Raman spectroscopy applications of metal nanoparticles [105, 63]. Several solar-cell concepts used a conducting polymer blended or layered with metal or metal oxide nanoparticles as a material for photon adsorption, charge injection and conduction.[88, 81, 75, 59]. Spectroscopic changes upon addition of metal nanoparticles, as well as enhanced chemical reactivity, have been leveraged to devise a broad range of chemical sensors [12, 2, 145].

Initially developed as a dielectric, ferroelectric and piezoelectric material, polyvinylidene fluoride (PVDF) and its blends have a series of promising optical properties [131, 3, 31] and is relatively easy to model. PVDF is chemically inert and transparent, depending on preparation, with a band gap of roughly 6.5 eV. It exhibits unusual polymorphism, with five distinct crystalline phases α , β , γ , σ and ϵ . Structural, dielectric and optical properties change drastically between phases, prompting the materials' use in optical storage devices [31]. PVDF blends with trifluoroethylene and nanocomposites with ZnO exhibit strong nonlinear optical response [120, 31].

We previously applied density functional theory (DFT) to the study of the optical response properties of Ag/PVDF nanocomposites [113, 114]. as well static dielectric constant of nanocomposite Ag/MgO [5].

In ideal, monodisperse systems, we found that the optical properties of the NC were by and large determined by those of the metallic inclusions. The small, molecular Ag inclusions provided numerous discrete states and electrons in the vicinity of the nanocomposite Fermi level.

These new states led to the appearance of optical transitions in the NC where there were none in the polymer, in the UV-Vis region of the excitation spectrum. Because of the wide polymer band gap, states within 2 – 3 eV of the Fermi level strongly resembled those presented by the nanoparticle in vacuum. As a result, ϵ_2 absorption spectra in the UV-Vis region also mirrored those of the NP, with some broadening, particularly in the near-UV region, due to the effect of polymer states.

Trends in optical response with changing inclusion shape and dimensions also mirrored well-known nanoparticle trends, described by simple confinement models: using larger NPs led to red-shifted response in the NC, whereas for anisotropic NPs, polarization along the longer axis resulted in red-shifted NC adsorption peaks. Loading had no effect on spectral position if below percolation thresholds, with

increased NP loading only increasing spectral intensity. Whereas spectral location was solely determined by NP length along the polarization axis, spectral features were influenced by the crystallographic cut and geometric features of the NP, via changes in the availability of states for optical transitions in the DOS.[113, 114] In calculations of static dielectric constant in solid Ag/MgO systems we saw that changing size/shapes of inclusions lead to various ‘induced polarization’ fields [5, 45]. This was dependant largely on the surface area available for charge accumulation which is possible in a solid metal-oxide dielectric material. These models relied on artificially imposed monodispersity of metal inclusions, they cannot interact and therefore resultant ‘induced field’ effects cannot take into account charge transfer or ‘hopping’ between metal nanoparticles even within an insulator. Whereas our previous work established several baseline trends in nanocomposite behaviour, they were mainly limited to monodisperse, regular systems, where a unit simulation box with one inclusion was repeated to infinity by use of periodic boundary conditions. Here we set out to investigate the impact of multi-dispersity in NC optical response.

4.3 Methods and models

4.3.1 NP and NC models

Starting with a 32-atom rod-like NP, composed of 5 Ag(111) layers with 6 or 7 atoms each, we created two NP sections: a 2-layer, 13-atom disk and a 19-atom, roughly spherical 3-layer NP as seen in 4.1. Created using Avogadro [48] software these inclusions were initially minimized in vacuum then were placed at various distances and relative locations, in a PVDF matrix with a total of 1250 atoms, corresponding to a NP loading of 4.2% vol. This volume loading was used to allow enough separation between

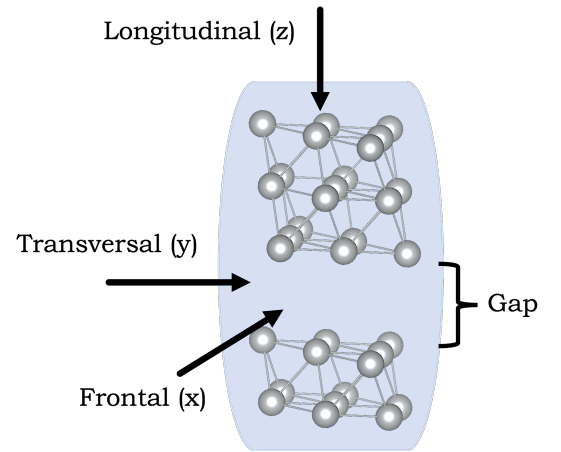


Figure 4.1: Longitudinal, transverse and frontal mode polarization in rod-like inclusions with gap between ‘interacting’ segments of nanoparticle shown.

periodic cells and is similar to the loading used in the previous chapter 3.

The relative distances between inclusions will be referred to by their z and y separation distances (with a singular nanoparticle at $z=0$). Several representative examples of the NC systems considered here are shown in 4.2. Note that all inclusions used in the present work were direct cuts from the fcc crystal structure, rather than minimum-energy structures: structural minimizations would lead to maximum binding, near-spherical structures that would invalidate the geometric analysis which constitutes the purpose of the present study.

4.3.2 NC structural relaxation using molecular dynamics

The structure of the initial nanocomposite was compressed to a target density, calculated from the bulk density of the two materials. For this purpose, we used a classical molecular dynamics methodology within the Gromacs [136] software package, with periodic boundary conditions (PBC). Lennard-Jones parameters for the structure optimization were taken from the Universal Force Field [106]. Partial atomic charges were based on those of Chen and Shew [20], modified to fit small charge groups; silver atoms had zero charge. The construction of suitable simulation cells and computational details has been explained in greater detail in our previous work [113]. The optimization of NCs including the two separated NP fragments was then performed by successive molecular dynamics relaxation of NC structures containing the two fragments separated in a stepwise fashion along the z and y axis, as shown in Figure 4.2. Separation steps of $0.5\text{\AA}$ were found sufficiently small so that steric effects created during the NP relocation were not catastrophically repulsive for the simulation.

In the following pages, systems will be described by the nature of the nanoparticle gap given the z and y displacement in Angstrom compared to the singular 32-atom nanoparticle (gap of 0).

4.3.3 Optical Response

The macroscopic dielectric permittivity is a complex function (ϵ_∞) dependant on the applied fields' frequency (ω). It includes both the real (ϵ_1) and imaginary (ϵ_2) parts which correspond to the polarization (in optical range means mainly electronic

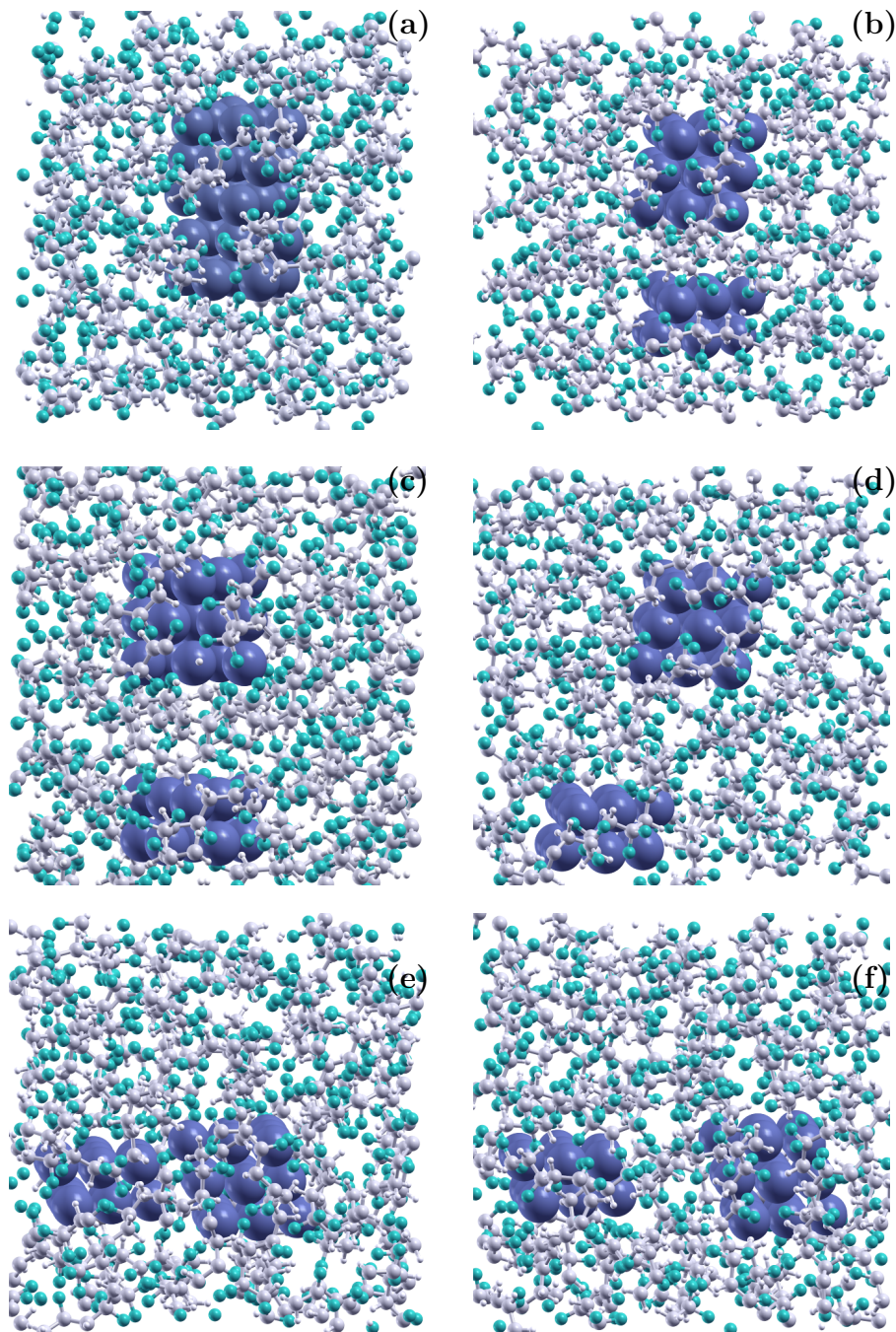


Figure 4.2: Selection of NCs studied in this work. The initial $\text{Ag}_{32}/\text{PVDF}_{1250}$ NC is shown in (a). Shifts along the z axis, by 3.5 and 5.5 Å in systems L_3 and L_5 are shown in (b) and (c), respectively. Further shift along z (6.5 Å from initial position) and along y (by 6 Å) in system LT_6 is shown in panel (d). Particles centred along the same z axis were also considered. Panels (e) and (f) had a y -shift from the initial position by 9 and 13 Å, respectively.

dipoles) and loss function respectively and are related via the Eqn 4.1:

$$\hat{\epsilon}(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \left| \frac{D_0}{E_0} \right| (\cos \delta - i \sin \delta) \quad (4.1)$$

SIESTA calculates ϵ_2 from direct, allowed interband transitions [93, 26]. For periodic materials, the eigenfunctions of self-consistent Hamiltonian are calculated for the entire system in momentum space. Allowed transition dipole matrix elements are then calculated between the different eigenfunctions, in a local field considered to be equal to the macroscopic field. The imaginary part of the dielectric constant is given by a sum of these transitions:

$$\begin{aligned} \epsilon_2(\omega) = & 1 - \frac{e^2 \hbar^2}{\epsilon_0 m_e^2 V} \sum_{\mathbf{k}} \sum_{i,j} \frac{|\mu_{i,j}(\mathbf{k})|^2}{E_{ij}^2} \\ & \times \frac{f_0(E_j(\mathbf{k})) - f_0(E_i(\mathbf{k}))}{E_{ij} - \hbar\omega - i\hbar\Gamma}, \end{aligned} \quad (4.2)$$

where e is the electronic charge, $\hbar = h/2\pi$, h is Planck's constant, ϵ_0 is the dielectric constant of vacuum, m_e is the mass of the electron and V is the volume of the cell. The sum is taken over all $\mathbf{k}$ -points in reciprocal space, and over all pairs of electronic energy values i and j . $\mu_{i,j}(\mathbf{k})$ are transition dipole matrix elements, f_0 is the Fermi distribution function, $E_{ij} = E_i(\mathbf{k}) - E_j(\mathbf{k})$, ω is the angular frequency and Γ is a peak broadening term. All reported ϵ_2 spectra used a broadening factor of 0.05 eV. The method as used here does not consider collective modes such as plasmons or electron-hole interactions such as excitons. Also we will describe the applied field not in terms of angle but along the x, y and z planes parallel to the faces of the inclusion.

We also consider the shifts in the absorption edge the infrared region. Sets of dipoles in a semiconductor can couple to an applied field when the frequency equals the vibrational mode of the dipole(s) – which is seen as a peak on the absorption spectra.

Optical Calculations

Optical calculations were performed using SIESTA version 3.2 and 4.0 [124] using polarized electric fields directed along the three symmetry axes of the original

rod-like NP, as shown in Figure 4.1. Longitudinal fields were directed along the principal (z) axis, and transverse fields were along a perpendicular (y) axis. NP fragments were shifted along these two directions. Frontal mode polarization along the x axis was also considered. A PBE/DZP formalism [98] was used, with core electrons modelled using norm-conserving Troullier-Martins pseudopotentials [134] from the SIESTA documentation.

Further details of the optical SIESTA/DFT calculations, their advantages and limitations, are given in Refs [113, 114] and references therein. As most standard DFT methods, the PBE Hamiltonian underestimates band gaps [44, 83, 10].

Empirical scissor operators are often applied [51, 38] to compensate for this tendency. They were not used in this work, because of a lack of comparable experimental data. Consequently, spectra and relevant excitations discussed in this work will be considered relative to one another, rather than as absolute values.

4.4 Results and Discussion

The variety of NP arrangements explored here can be grouped in three distinct regimes: (i) Minimal interparticle distances, when insufficient space exists for accommodating any polymer between the NPs; (ii) Intermediate layer-to-layer inter-particle distances (between 1.5–3.5 Å), when the NPs are separated by a thin (1–2 atom thick) layer of polymer; (iii) Well-separated NPs, in a variety of relative positions when the layer-to-layer distance is more than 6.5 Å. The Ag-Ag bond distance is approximately 2.8 Å, thus the difference between the second and third regimes is roughly equal to two bond lengths.

The first two of these are plotted in Figures 4.3 and 4.4. The peaks correspond to allowed transitions and while we were not able to extract the exact transitions present from metal-metal to metal-polymer, we are able to establish several trends.

4.4.1 The Small-Gap, Highly Interacting Regime

When the gap between the particles is small enough to prohibit any polymer intercalation, their field response is coupled and the behaviour is similar to that of a single, longer nanoparticle. The small gap region shows a dramatic blueshift and change in nature of peaks in optical dielectric function in both z and y directions - which can be followed left to right of Figures 4.3 and 4.4. In the longitudinal or

z-direction the field is applied vertically to the plane of the figure(s) as seen and we see from $z = 1.5$ to $z = 3.5$ the peaks entirely shift out of infrared. It also appears that as the gap begins to grow the dielectric function collapses into distinct allowed transitions in the visible region only ($z3.5/y3$). The discrete nature of these transitions begins to collapse as the gap widens but they stay in the visible region. In the application of a y-direction or transverse field (Figure 4.4) we see different behaviour with no peak shifting. The magnitude of the peaks increases as it appears the allowed optical transitions combine to form discrete peaks in the infrared to visible range. They only arise as the gap forms, then collapse at $6.5 \text{ \AA}$ - when the gap is larger than either nanoparticle. It appears the change in surface area with transverse translations makes little difference to the nature of optical dielectric function (y-direction movement, plotted down the columns of Figure 4.4). We also see the absorption edge blue-shifting in Figure 4.9 as the gap widens along the length of polarization, with a significant 'break' in the character of absorption spectra at $3.5\text{-}4.5\text{ \AA}$ when the gap is approximately the size of the nanoparticle(s). The absorption spectra is quite messy and likely not indicative of the true nature of the bulk material.

4.4.2 Well-separated nanoparticles

We also studied the effects of large gaps up to $14\text{ \AA}$ on the dielectric function in all three directions and saw relatively consistent behaviour as shown in Figures 4.6 and 4.7. The longitudinal or z-direction polarization remains consistent with the small no-gap ($z=1, y=0$) nanoparticle and the large gap ($6\text{-}14\text{ \AA}$). This is to be expected, as any non-interacting silver nanoclusters should behave similarly at such small cluster sizes. The transverse or y-direction polarization shows a change in behaviour up to $6\text{ \AA}$, but beyond this we see mainly infrared transition peaks that are indistinguishable from each other. The plots shown in Figure 4.7 demonstrate that with a gap in the same direction as the applied field, there is virtually no change in the optical function, regardless of how far the nanoparticles are pushed in the perpendicular direction.

4.4.3 Band bending and PDOS

The Projected Density-Of-States plots shows significant band bending as the gap between nanoparticles widens. Figure 4.5 and 4.8 have a 'normalised' fermi level at

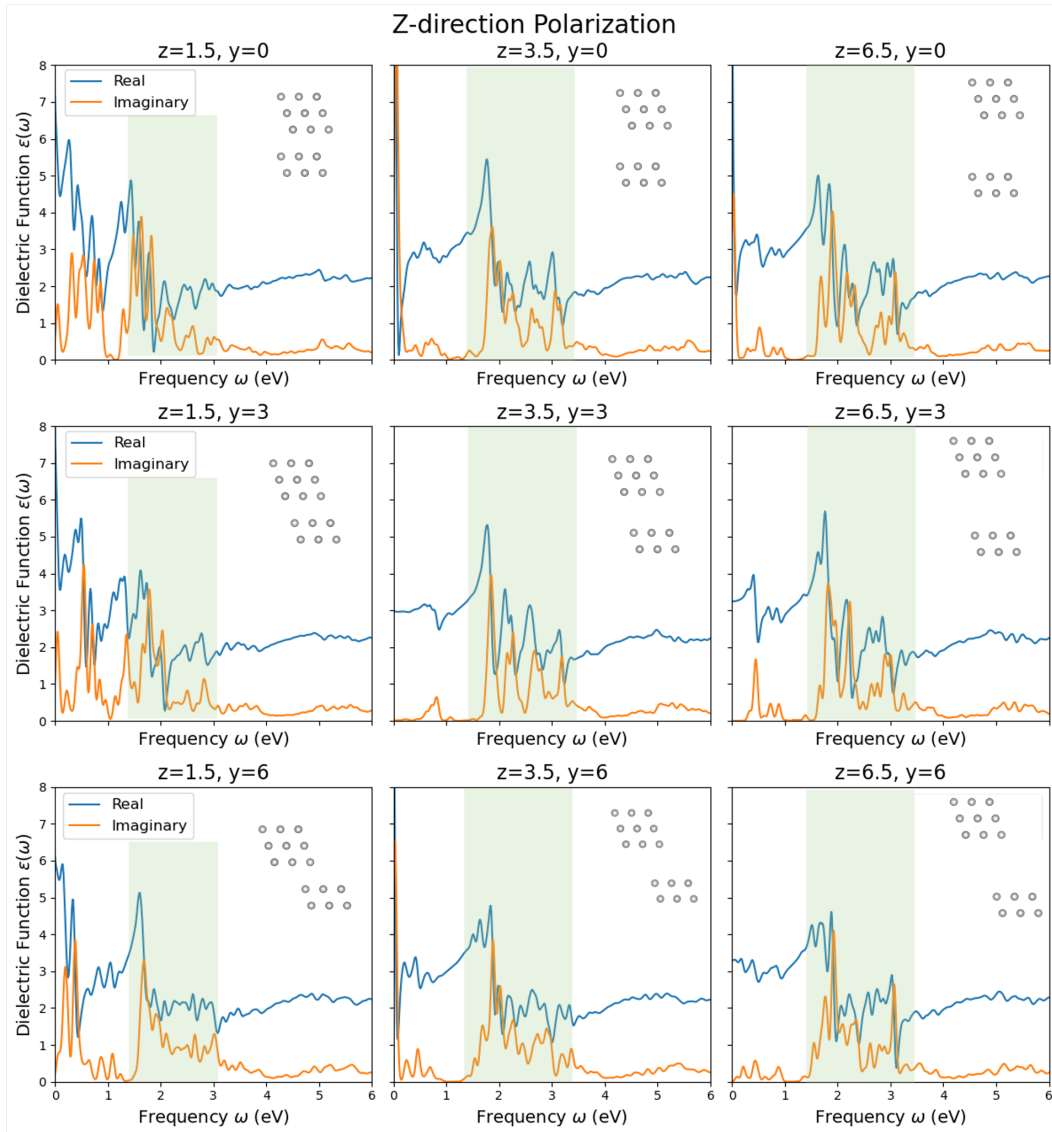


Figure 4.3: Z direction polarization plots show the shifting optical dielectric function (ϵ_1 (real) and ϵ_2 (imaginary)) from infrared to ultraviolet region with the visible region highlighted in green. The relative nanoparticle separations are also shown on each plot (minus the polymer)

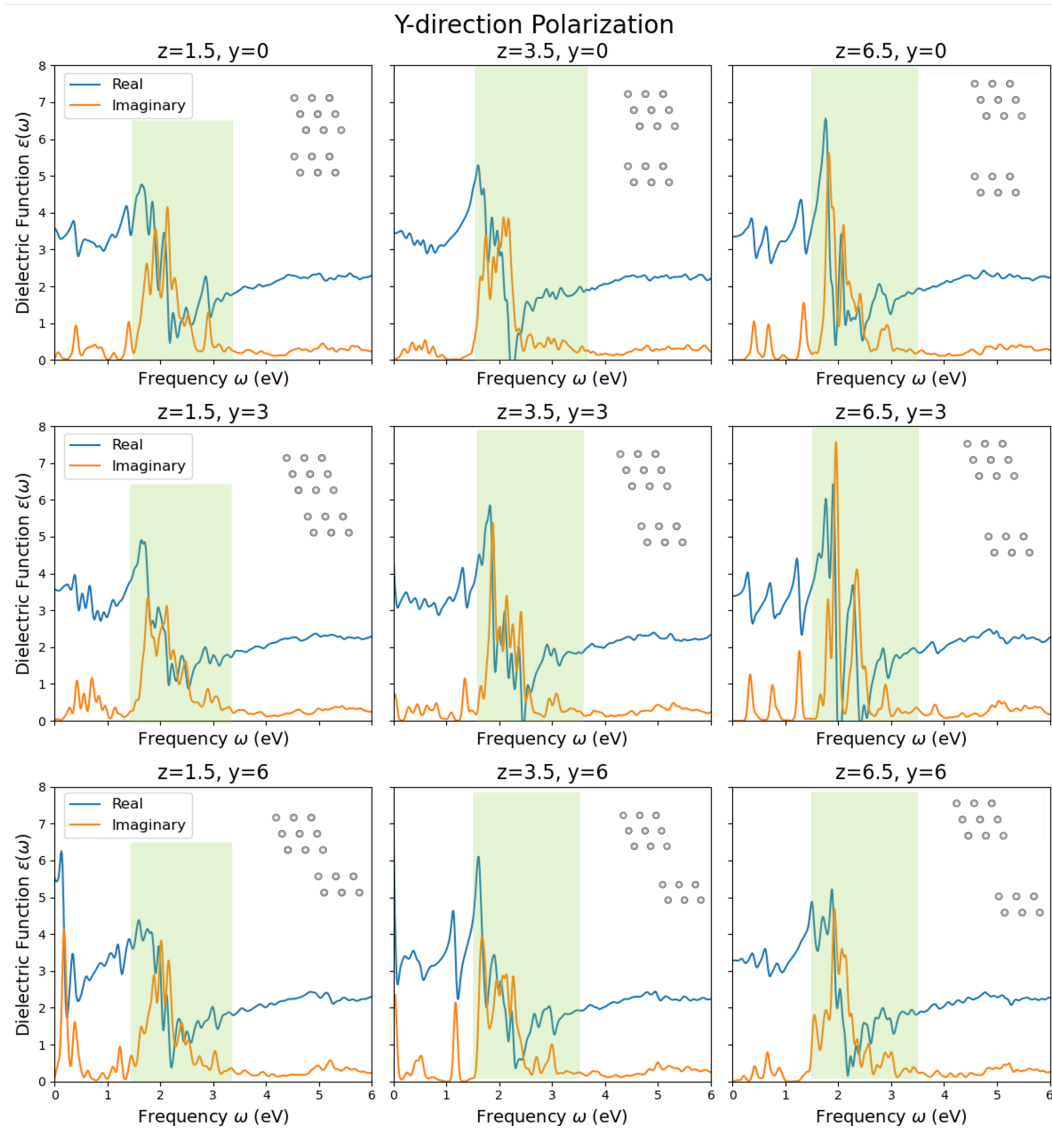


Figure 4.4: Y direction polarization plots show the shifting optical dielectric function (ϵ_1 (real) and ϵ_2 (imaginary)) from infrared to ultraviolet region with the visible region highlighted in green. The relative nanoparticle separations are also shown on each plot (minus the polymer)

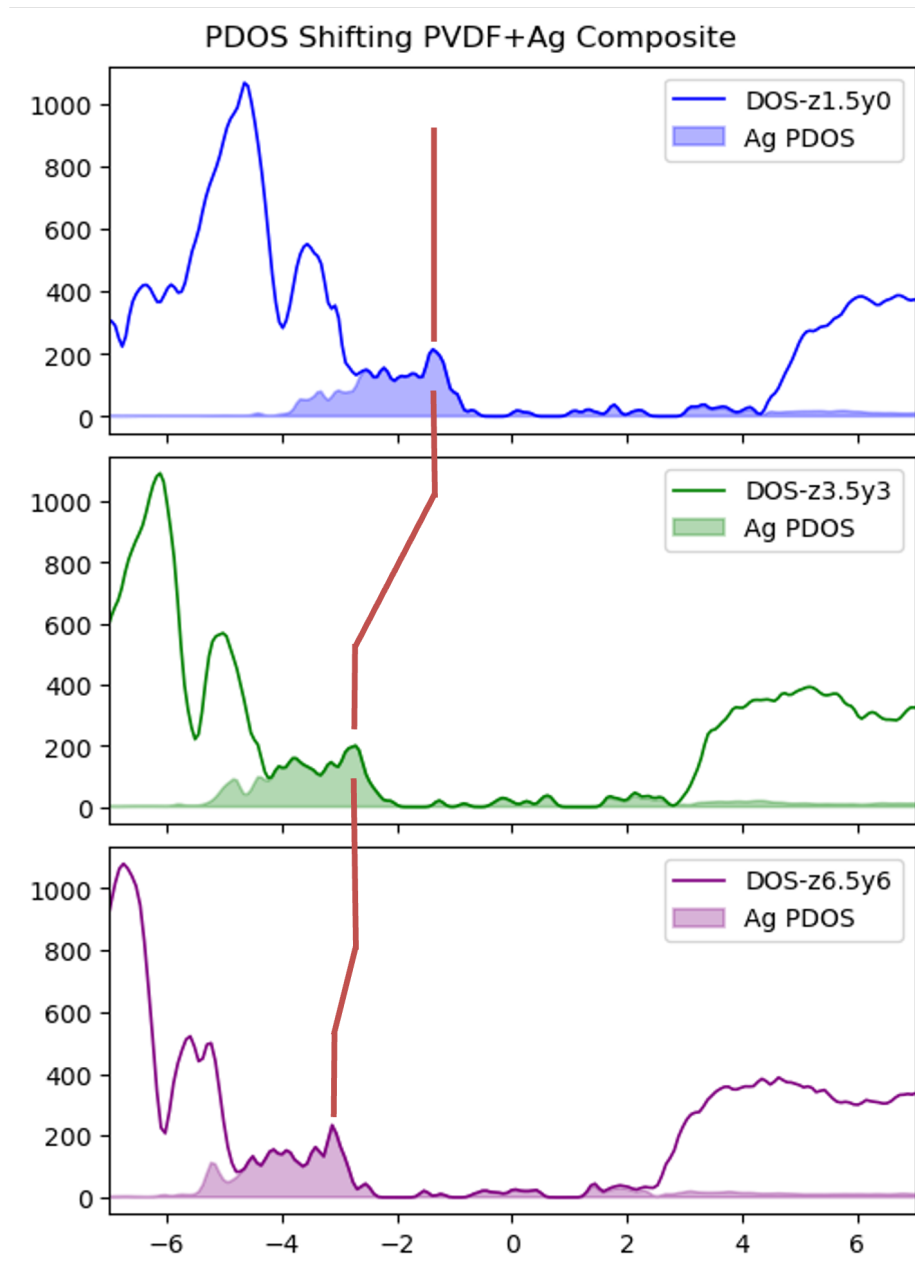


Figure 4.5: PDOS plot of Silver valence electrons vs Full PDOS including polymer (models are the diagonal of Figures 4.3 and 4.4). The fermi level shifts as the inter-particle gap widens and metal-metal interaction passes through more polymer. Normalized fermi level kept at 0 so bending of HOMO peak can be followed. The states around the fermi level and just below are from the silver inclusion.

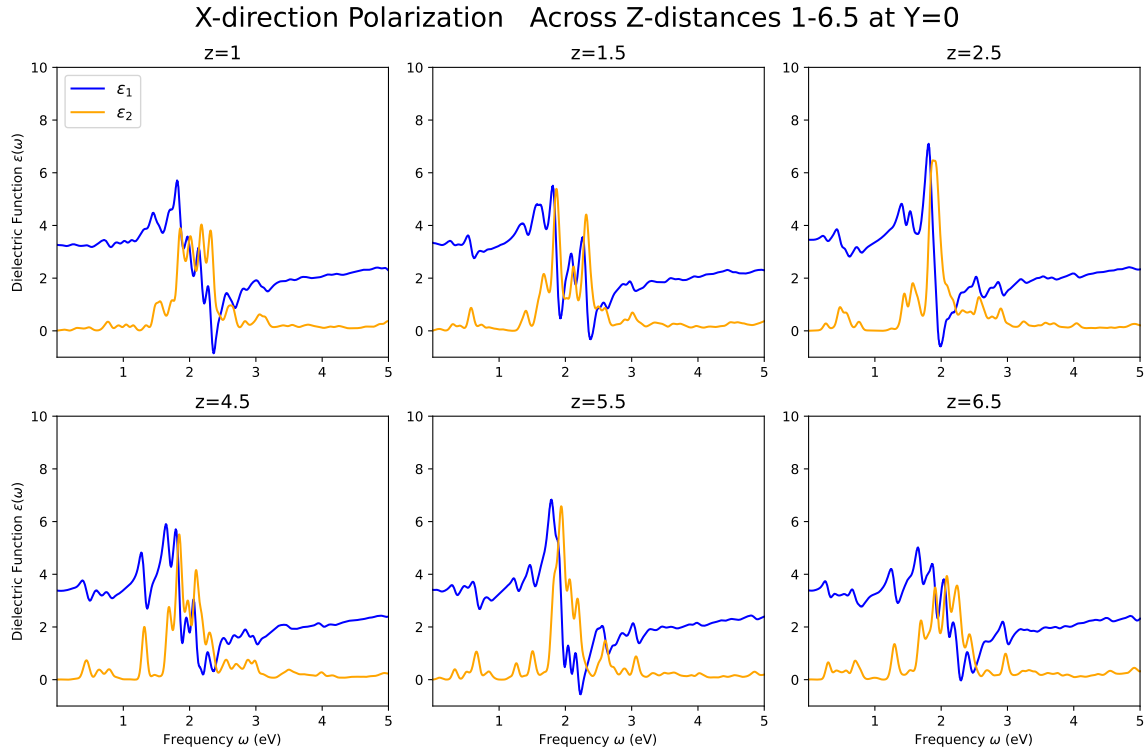


Figure 4.6: Polarization across a small range of separation distances perpendicular to applied polarization field, with no gap parallel to applied field. The nanoparticle is only being ‘stretched’ in z -direction with the y -separation kept at zero. Shows a discontinuity and change in behaviour at the small gap regime ($z = 2.5 - 5.5$) and a return to normal polarization at large separation ($z = 6.5$).

0, which shows the bandgap shifting lower in energy, with the HOMO and interband states (shaded in the figure) comprising Ag orbitals, as expected. This is a phenomenon usually seen near the interfaces of junctions in layered semiconductors.

While this material isn’t “layered” in a traditional sense, it does show that even with small clusters of metal, we can have a pseudo-interfacial layer when polarised similar to a heterojunction.

The absorption edge analysis (Figure 4.9) provides additional insight into the field-induced behaviour of these systems. We observe a systematic blue-shift in the absorption onset as the nanoparticle gap increases, suggesting reduced optical coupling and a suppression of low-energy transitions. The shift is not linear but shows a sharp transition around $3.5 - 4.5 \text{ \AA}$, corresponding to a gap comparable to the length of the nanoparticles themselves. This may indicate a transition from hybridised metal-metal states to more localised intra-cluster transitions, driven by

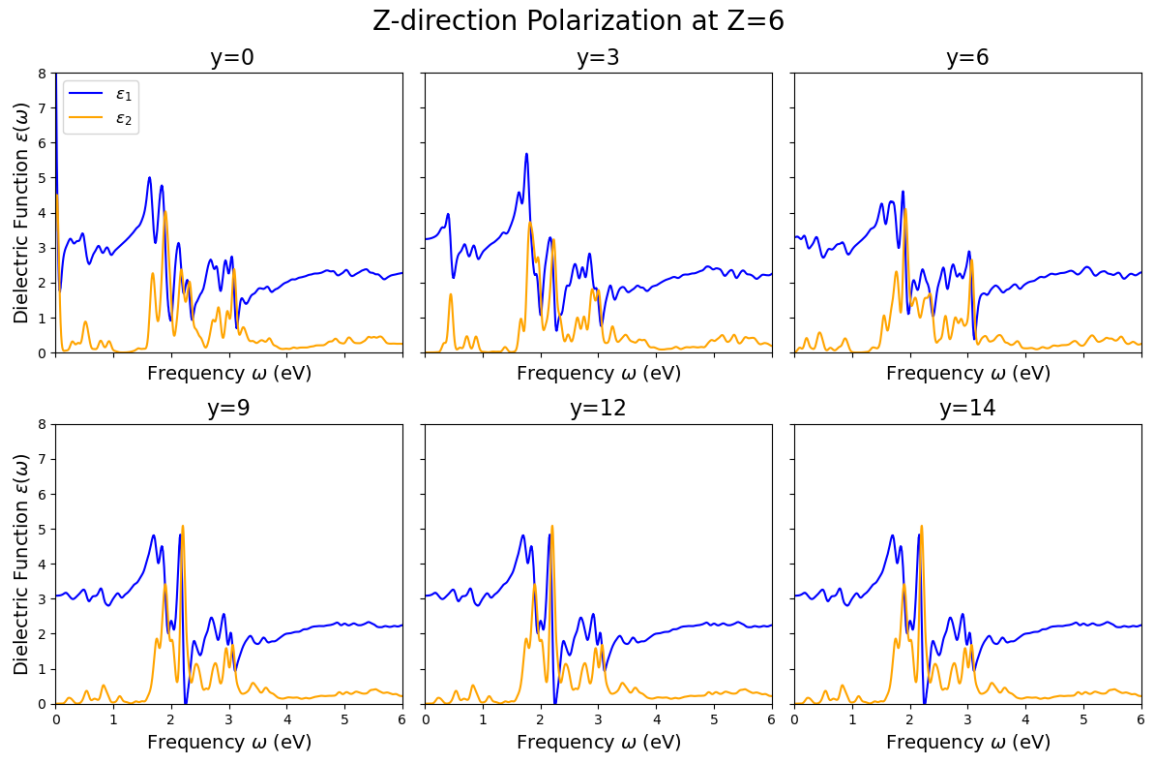


Figure 4.7: Polarization across a broad range of separations with a large gap (approximately $6\text{\AA}$) along the direction of applied field. Shows that with large gaps there is minimal difference between one nanoparticle and two halved nanoparticles and therefore they are not interacting.

the loss of charge overlap and tunnelling pathways. While the overall shape of the absorption spectra remains broad and diffuse, likely due to disorder, surface effects, and the semi-metallic nature of the fragments. These trends highlight the role of spatial configuration in modulating optical thresholds.

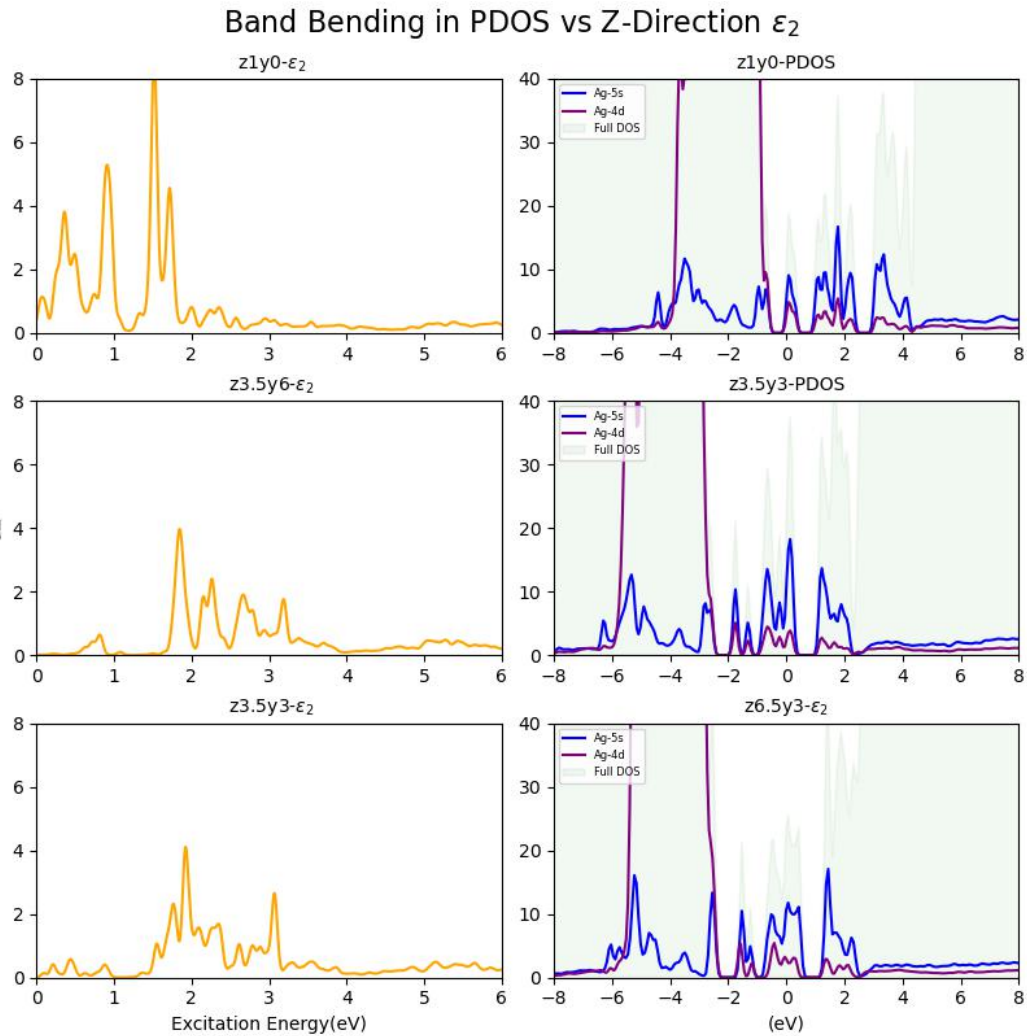


Figure 4.8: PDOS vs ϵ_2 including polymer (models are the diagonal of Figures 4.3. The fermi level shifts as the inter-particle gap widens and metal-metal interaction passes through more polymer. Normalized fermi level kept at 0 so bending of HOMO peak can be followed. The states around the fermi level and just below are from the silver inclusion.

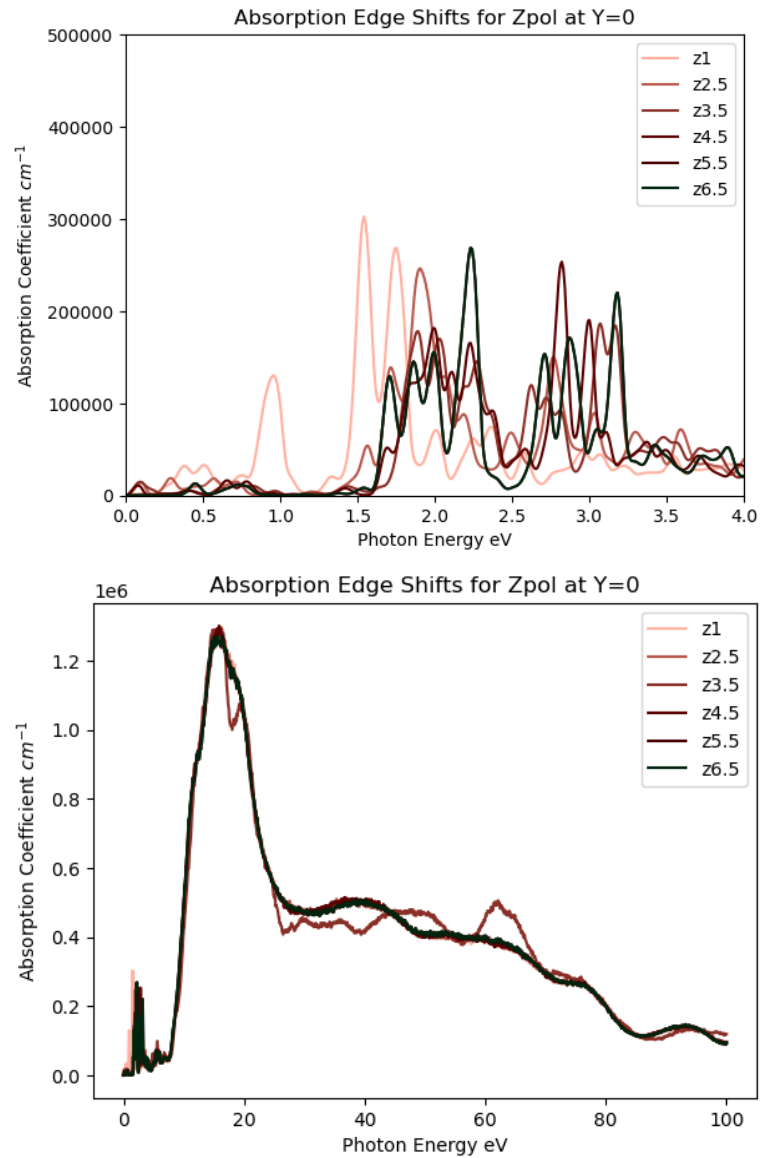


Figure 4.9: Absorption coefficient as a function of incident photon energy. Shows that show latitudinal movement (z-dir) creating a vacancy between the nanoparticles results in a blueshifting of the absorption coefficient at the edge (from z1 to z6.5 at 6.5 Å gap. Bottom plot shows across a large incident photon energy range only issue is at $z = 3.5$ Å

4.5 Conclusions

In this study, we have explored the optical dielectric response of polydisperse molecular-scale silver nanoparticles (MNPs) embedded in a PVDF matrix, focusing on the consequences of nanoparticle disassembly and relative displacement within the polymer bulk. This work extends beyond the previous monodisperse and idealised nanocomposite models seen in Chapter 3 by incorporating the effects of spatial separation, orientation, and non-cubic particle symmetry. Using density functional theory and optical response calculations within the SIESTA framework, we have identified how varying the gap between nanoparticle fragments modulates the directionality and magnitude of the dielectric response in longitudinal, transverse, and frontal field geometries.

There are several limitations to this model, mostly due to the idealised starting structures, forced interactions, and size constraints. The simulations begin with ideal particles that are small enough for feasible computation. despite attempts at energy minimisation, it is still a forced 'ideal' that does not take into account pressure, stress, strain, and atomic movements due to repeated charge-discharge cycles. Moreover, a lack of experimental absorption spectra for comparison precludes corrections to the DFT band gaps, limiting our results to trends instead of predictions.

Lastly, while these simulations provide some mechanistic insight into localised polarization, they are inherently limited by size, boundary conditions, and computational tractability. the absence of collective phonon modes, long range Coulomb effects, and inter-particle tunnelling (useful when looking at conductive filler polymer) suggests that future work must be validated experimentally. Nonetheless, this work demonstrates that even subtle changes in nanoparticle connectivity and orientation at the molecular scale can lead to substantial modulations in dielectric response.

Chapter 5

Extended Models, Further Matrix-Inclusion studies and Polydispersity

5.1 Overview

Thus far two major projects have been detailed, and this chapter details the attempts at expanding those projects and the future of nanocomposite dielectric modelling. First, the development and modelling of Ag/MgO nanocomposites and exploring the size, shape, and orientation effects in an applied field are discussed in

Chapter 3. Several attempts at expanding the static dielectric model to include both interacting particles for polydispersity and alternative materials such as TiO_2 , SiO_2 , HfO_2 and SnO_2 etc... were performed to no avail. The polydispersity project lead to the PVDF/Ag project outlined in Chapter 4 with a silver rod MNP interactions with optical polarization. This chapter will detail those projects.

5.2 Expansion of Matrix Metal-Oxide Candidates

Modelling embedded nanocomposites within crystalline matrices such as SiO_2 presents unique challenges, especially when the host material does not possess a cubic or highly symmetric crystal structure. In contrast to cubic systems, which often allow for straightforward replication and embedding due to their isotropic lattice parameters and translational symmetry, non-cubic structures like hexagonal,

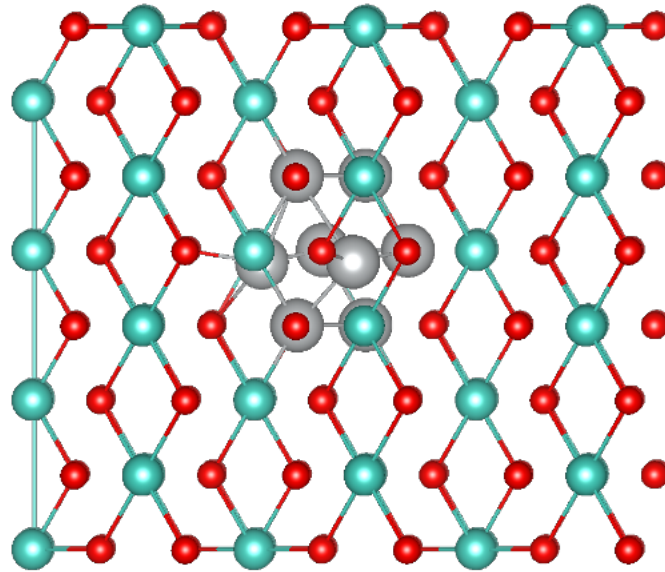
tetragonal, or orthorhombic polymorphs of SiO_2 (e.g., α -quartz or cristobalite) introduce significant complications in lattice matching, strain minimization, and defect mitigation. When embedding nanoparticles or clusters into such anisotropic matrices, lattice distortions are difficult to evenly distribute, often resulting in artificial strain gradients or local structural instabilities.

One critical issue encountered during this work was the development of holes or areas of high strain around embedded nanoparticles. These emerge due to imperfect lattice relaxation and volume mismatch between the filler and matrix atoms. In low-symmetry systems, it becomes much harder to distribute the structural relaxation around the nanoparticle, leading to asymmetric bonding environments and under-coordinated atoms, especially near curved interfaces. These defects not only distort the local electronic structure but can also introduce artificial mid-gap states, thereby compromising the predictive accuracy of simulations aimed at assessing dielectric or electronic properties. Attempts to fix these geometries using simple relaxation often result in overcompensation or further destabilisation, highlighting the limits of classical minimisation methods in complex crystal environments.

One method employed was the creation of a cavity by deleting units of the matrix (i.e for SnO_2 , two oxygens per tin removed for electron/bonding balance) and inserting a pre-minimized MNP. Shown in Figure 5.1, there is a large disruption in short-range order and crystal structure, even with a flexible cell and lattice vectors that can expand to accommodate movement and update atomic positions. The Sn-O bonds are 2.0-2.7 Å in length, and Ag-Ag bonds are generally 2.8-2.9 Å [92], which should be accounted for given the variable-cell parameters. Both Sn and Ag are period 5 elements, with Sn being the only tested matrix metal of a similar size to the inclusion silver atoms—the most ideal candidate. No matter the size of the cavity or orientation however, it was not possible to both preserve the crystal structure and keep the cell small enough to feasibly complete computations.

Another method was to replace some atoms in the matrix metal-oxide with the inclusion atoms, delete surrounding atoms to balance the valence electrons and bonding, and attempt to create an inclusion that would fit the natural structure of the crystal. This is illustrated in Figure 5.2 which shows a similar level of disorder throughout the 792-atom cell. In MgO , an 8-atom inclusion only requires 216 matrix atoms as padding to avoid interaction errors, and the full calculation takes approximately 30 hours of total computing time on a 48-core computing node with

(a)



(b)

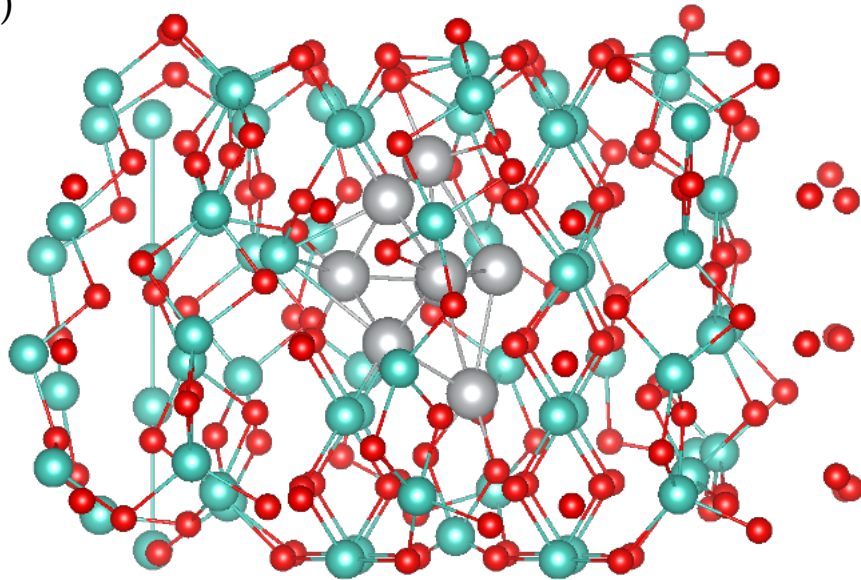


Figure 5.1: Lattice mismatch in engineered defects using cavity method shown in SnO_2 with a small Ag_8 molecular nanoparticle. Matrix+cavity+inclusion shown in a), and disordered behaviour with variable cell parameters shown in b).

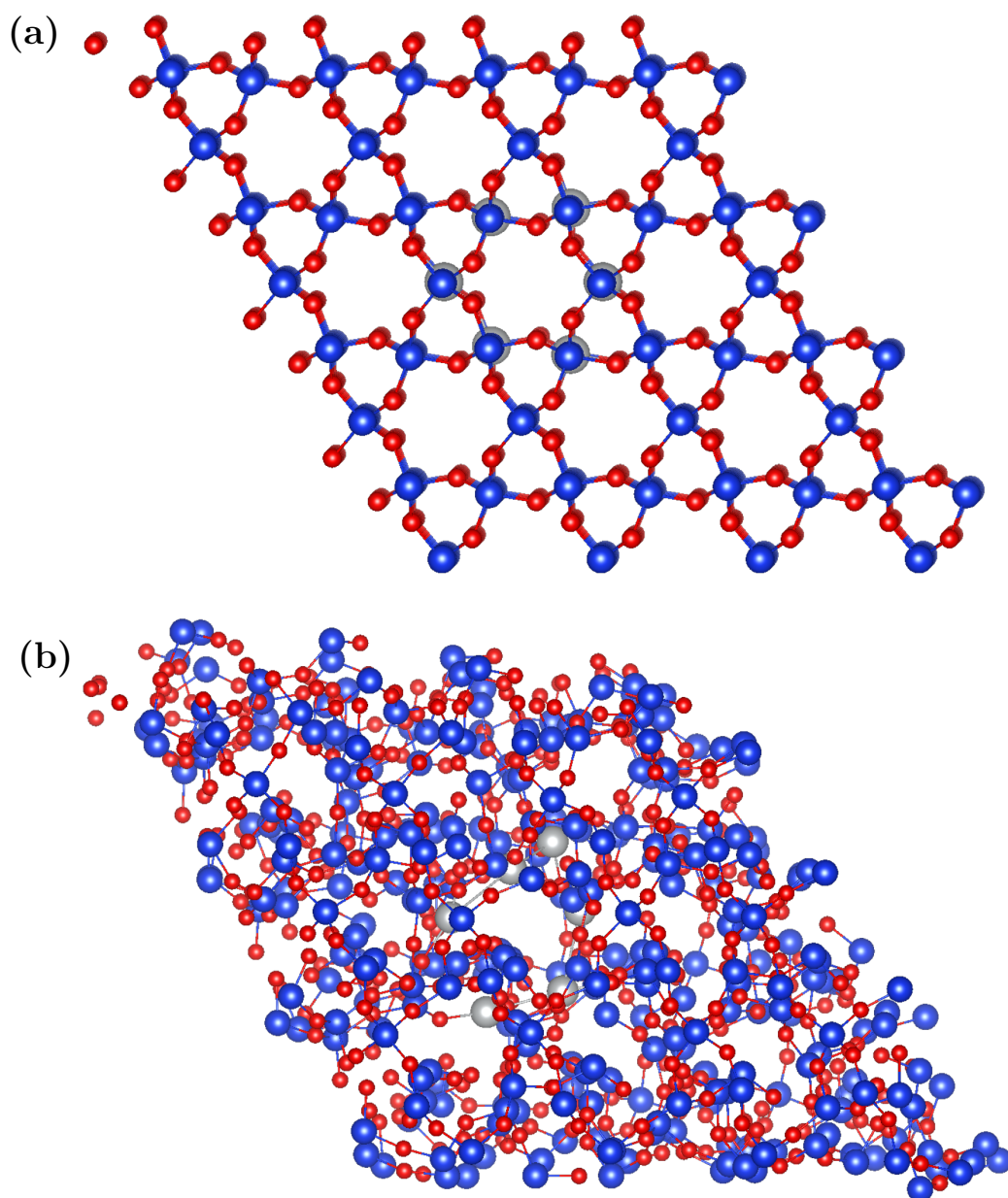


Figure 5.2: Disorder in crystal lattice for SiO_2 using replacement method for plate-shaped MNP inclusion. 6 Ag atoms are present in the center of the 792-atom cell.

all the available memory. Any feasible SiO_2 model would require computations multiple times this for structure alone, so large they would not be feasible. Another issue with non-symmetric structures is the size of k-point mesh and lattice parameters needed to get an accurate computation. K-point meshes are a grid of discrete points used in reciprocal space for approximations related energy calculations. A highly disordered system - at least in electronic structure methods - requires a large mesh. Adding to this the prospective crystal cells used here were over 800 atoms means there was a lot of expensive computations needed and the mesh sizes were difficult to narrow down.

After this project was published, several updates were made to the available code and pseudopotentials. Small calculations were re-run using both PBE and PBESOL pseudopotentials. Both worked well with no changes to the method or code and ran in similar computational resources as the described systems, the only change needed was benchmarking for appropriate cutoff energies and k-point meshes which was insignificant compared to the initial benchmarking. This would be a significant factor to consider when expanding or using this method to validate results from finite element or experimental models. For future work, including experimental crystal structures, binding energies, and polarization behaviour, Hubbard +U terms would be useful for model building. As they must be parameterized for each system, they were not included here.

5.2.1 Computational Models and Real Data - A Discussion

There are major considerations and discussions to be had about the use of computational models without sufficient experimental backup here. Embedded molecular nanoparticles have limited real data to support the model development and the existing data is not broad enough to make generalizations about such fine atomic-level details. Without experimental characterisation of interface structures such as high-resolution TEM or XPS data; assumptions about bonding, particle morphology, or orientation are largely speculative. While first-principles methods provide atomic-level detail it also means the “freedom” to construct arbitrary interfaces which introduces the risk of generating structures that are energetically stable in simulation but physically implausible. For instance, the use of ideal filler shapes (e.g., spherical nanoparticles) or periodic embedding patterns may satisfy convergence criteria but fail to replicate realistic surface chemistry.

If the idea is that computational frameworks should help narrow down the field of experiments to conduct, they must be somewhat accurate to begin with. If computational models are meant to complement experimental/wet-lab/engineered material design processes, they should start from a 100% experimentally derived crystal structure. This gap between theory and realism becomes more critical as the scale of the simulation increases. Larger supercells designed to accommodate entire nanoclusters within periodic boundaries require trade-offs in terms of computational cost and structural fidelity. Too small a matrix introduces artificial interactions between periodic images, especially in systems with significant long-range polarization or charge redistribution. On the other hand, making the matrix large enough to capture interface physics accurately demands thousands of atoms and becomes computationally intractable with hybrid functionals or DFT+U corrections. Small models with other metal-oxides such as SiO₂ or TiO₂ were computed, but larger plate or rod nanoparticles proved tricky to rationalise.

5.3 Size Constraints in Periodic Simulation Cells

A central challenge in using periodic boundary conditions (PBCs) for embedded systems is managing self-interaction artefacts between the periodic images of the filler. If the matrix is not sufficiently large in all three dimensions, especially around the filler, electrostatic fields, defect states, or strain patterns can artificially overlap with themselves across the simulation cell boundaries. This is particularly problematic in dielectric studies where long-range polarization effects are significant. The consequence is an overestimation of interaction energies and dielectric response, leading to misleading conclusions about the material’s intrinsic properties.

To mitigate this, a large bulk matrix region is required around the embedded nanoparticle (in all directions) depending on the dielectric screening length of the material. In cubic and symmetrical MgO, this only required a few atoms to return to a non-strained structure and “average” dipole moment. In non-cubic structures like SiO₂, generating such large supercells while preserving lattice continuity and low-strain boundaries is far more complex. Even slight lattice mismatches can propagate through the cell, requiring careful tuning of lattice vectors or the use of quasi-random interface structures, both of which introduce additional uncertainty. Again, without experiemntal data this project was quickly abandoned however the framework developed and outlined in Chapter 3 and Appendix A

In sum, while theoretical modelling of embedded nanocomposites is an invaluable tool in CPMD, systems with non-cubic matrices like SiO_2 expose the limits of current modelling frameworks. Addressing these challenges requires either hybrid multi-scale approaches or validation from experimental structures to ensure that the predicted properties are not artefacts of modelling assumptions or computational constraints.

5.3.1 Polydispersity and Interactions in Static Dielectric Models

As mentioned, the solid-state Ag/MgO models imposed artificial mono dispersity as all inclusions were equally spaced apart in the periodic crystal and any interaction between images was minimized to get a volume-accurate picture of the induced field and polarization. Several attempts were made to create a larger simulation cell with interacting rods and plates however the size of the computation needed exceeded reasonable computational ability even with CPMD. The systems needed >1200 atoms, with several thousand valence electrons especially the non-cubic crystal structures such as SiO_2 to ensure non-interaction between periodic images. This is not feasible and ended up taking months of computational time - raises the question about the ability to brute force computation and the need for it. As this was a theoretical investigation and not a supplement to experimental data, it did not seem a prudent path. It appears a finite element or other mathematical method where material parameters are logged and applied model that can predict the interaction of different dielectrics strengths in a field would be the logical next step.

5.3.2 Hubbard+U and Bandgap Underestimation

In the computational studies presented in this thesis, there is a severe underestimation of the bandgap. Bulk MgO should have a bandgap of >7.8 eV, and while a nanocomposite would reduce that, the computed bandgap of ~ 1.2 eV is a severe underestimation. Accurate prediction of electronic structure is critical, as key properties such as dielectric permittivity, polarization behaviour, and breakdown strength are directly tied to the underlying electronic band structure, especially when expanding into other crystal structures and materials with narrower bandgaps or a propensity to develop “holes” at the interface of an embedded molecular

nanoparticle. This is especially true for “classical” semiconducting materials like SiO₂. Traditional implementations of density functional theory (DFT), particularly within the local density approximation (LDA) or generalized gradient approximation (GGA), often severely underestimate the bandgap of semiconductors and insulators. This limitation stems from the self-interaction error and the absence of derivative discontinuity in the exchange-correlation functional, which results in delocalised electron densities and inaccurately low conduction band energies.

This bandgap underestimation becomes particularly problematic when material screening and optimisation rely heavily on the fidelity of first-principles calculations. If looking to expand the model to charge transfer, trap state formation, and local field enhancement effects, it is essential to develop routines that include corrections to capture the effective dielectric response.

To address this, the Hubbard U corrections were introduced via the DFT+U formalism [133, 53]. Originally developed for strongly correlated systems with localised d or f orbitals, the DFT+U method introduces a corrective on-site Coulomb interaction term that penalises partial orbital occupancies and restores proper localisation. The total energy in the DFT+U approach is modified as:

$$E_{DFT+U}[\rho(r)] = E_{DFT}[\rho(r)] + \sum_{I,\sigma} \frac{U^I}{2} Tr[n^I(1 - n^I)] \quad (5.1)$$

In the equation above, U is the on-site repulsion Hubbard +U energy, and n represents the occupancy of the localised orbital I [25]. This correction shifts occupied and unoccupied localised states further apart, thereby widening the bandgap and improving agreement with experimental observations.

In dielectric nanocomposite systems, the application of DFT+U has been shown to yield more reliable estimates of the bandgaps of transition metal oxides (e.g., TiO₂, ZrO₂, HfO₂), which are commonly used as high-k dielectric fillers. Moreover, the accurate prediction of band offsets at matrix-filler interfaces, which control carrier confinement and leakage currents, is only feasible when the band structure is correctly modelled.

By incorporating the Hubbard U correction in CMPD workflows, researchers can significantly enhance the predictive power of computational screening studies. This enables a more informed selection of filler-matrix combinations that optimise dielectric performance metrics such as permittivity, loss tangent, and dielectric

strength. Therefore, DFT+U is not just a corrective tool but an essential component in the reliable computational design of next-generation dielectric nanocomposites.

Despite the theoretical improvements provided by the DFT+U approach, the accuracy and transferability of simulations in CPD models ultimately depend on the choice of U parameters and the realism of input structures. The effective Hubbard U value is not universal; it is material-specific and often sensitive to the local chemical environment. While semi-empirical methods exist to determine U_{eff} , they often require calibration against experimental data, such as photoemission spectra or measured bandgaps.

In this project, several attempts were made to model polymer-based nanodielectrics using standard DFT and DFT+U methods. These approaches failed to produce realistic dielectric behaviour or band alignment, primarily due to the lack of accurate experimental input parameters. Without experimentally calibrated U values or validated interfacial structures, the electronic properties predicted by CPD models diverged from known behaviours, such as overestimated charge transfer or artificial mid-gap states at the polymer-filler interface. This highlights a critical limitation in purely ab initio modelling approaches: accurate results demand hybrid workflows where first-principles methods are grounded in experimentally derived data.

Ultimately, the failure of purely theoretical modelling in this context underscores the necessity for integrated computational-experimental pipelines. Future efforts should prioritise the use of experimental bandgap measurements, spectroscopic data, and interface characterisation as benchmarks for parameter tuning, thereby enabling the development of more predictive frameworks for complex dielectric nanocomposites.

Chapter 6

Conclusions

This thesis has explored the origins of dielectric behaviour in heterogeneous materials and our ability to model them at the atomic scale. With particular emphasis on systems composed of metallic inclusions embedded in dielectric matrices, the central goal was to establish a quantitative and conceptual understanding of polarization phenomena in encapsulated nanocomposites through the development and application of first-principles models.

The research unfolded across three interconnected studies. The first examined the electronic polarization and local field effects in Ag/MgO composites, serving as a well-defined model system for metal–oxide interfaces. The second expanded the analysis to polymer-based dielectrics, investigating the impact of polydispersity and inter-particle interactions of Ag nanoparticles dispersed within polyvinylidene fluoride (PVDF). The third explored extensions of these models to other matrices and inclusions and the limits thereof. Methodological and computational limitations revealed the boundaries of current approaches and underscored the complexity inherent in predicting dielectric behaviour across material classes.

Collectively, these studies have resulted in new insights into the coupling between microscopic polarization, interfacial structure, and macroscopic dielectric response while also delineating the computational frontiers of first-principles modelling of complex composites.

Major Findings and Contributions

The principal findings of this work can be summarised as follows:

1. **Establishment of a quantum-mechanical framework for interfacial polarization.** A formalism was developed to evaluate the electronic contribution to the dielectric tensor in periodic systems containing interfaces, based on the modern theory of polarization. This framework was implemented in a first-principles context and successfully applied to Ag/MgO composites, enabling the decomposition of polarization into interfacial and bulk components.
2. **Identification of non-linear polarization enhancement in Ag/MgO systems.** Simulations revealed that Ag inclusions induce significant local field amplification at the metal–oxide boundary, leading to non-linear polarization and enhanced dielectric constants. These findings quantitatively confirm long-standing experimental observations of dielectric enhancement in metal–oxide composites and provide a microscopic explanation grounded in charge redistribution and screening behaviour.
3. **Demonstration of inter-particle coupling effects in Ag–PVDF nanocomposites.** Building upon the insights from the oxide systems, the second project examined polymer-based composites containing polydisperse metallic nanoparticles. It was shown that both particle size distribution and inter-particle separation critically determine the effective dielectric constant, with strong coupling between inclusions leading to collective polarization modes. These results highlight the necessity of accounting for both polydispersity and interaction range in any predictive model of composite dielectrics.
4. **Assessment of model generality and computational limitations.** Efforts to extend the modeling framework to alternative matrices (including SiO₂) and to different metallic inclusions revealed several challenges. In particular, convergence issues and computational expense associated with large supercell representations limited the accessible parameter space. Moreover, differences in interface chemistry led to substantial deviations from the simplifying assumptions made in the MgO- and PVDF-based systems. These limitations, while constraining in scope, provide valuable guidance for the design of next-generation models that balance accuracy with computational feasibility.

Through these advances, the thesis contributes both a methodological foundation and a set of benchmark insights for the study of dielectric phenomena in heterogeneous materials.

6.1 Scientific Implications

The findings presented in this work hold several important implications for materials design and for the interpretation of dielectric phenomena at the nanoscale. First, the demonstration that interfacial polarization dominates dielectric behavior in metal–oxide composites establishes a new benchmark for rational interface engineering. By tailoring the electronic structure and morphology of metal–oxide boundaries, dielectric performance can be systematically optimized. Second, the discovery of collective polarization effects in polydisperse Ag–PVDF composites bridges the conceptual gap between isolated nanoparticle models and realistic, interaction-dominated composites. This insight is particularly relevant to emerging high-energy-density capacitors, where trade-offs between processability, breakdown strength, and permittivity are often governed by microstructural heterogeneity. Finally, the identification of methodological limits in extending these models to new material systems underscores the importance of hierarchical modeling strategies. The computational constraints encountered in the final project are not failures, but rather defining boundaries that motivate the coupling of first-principles accuracy with coarse-grained or continuum-scale descriptions.

6.2 Concluding Remarks

In conclusion, this thesis has worked towards a framework for understanding polarization and dielectric behavior in heterogeneous materials. Through the study of Ag/MgO and Ag–PVDF systems, it has elucidated the development of induced fields at trapped interfaces of dielectric enhancement, the role of interfacial structure, and the impact of particle interactions and size dispersion. The work integrates theory, computation, and materials interpretation into a coherent picture of dielectric phenomena that extends from the atomic to the macroscopic scale. Beyond its immediate findings, the research provides a methodological template for future investigations of complex dielectrics. By combining rigorous first-principles formalisms with statistically informed models of structural heterogeneity, it points toward a new generation of multiscale approaches capable of capturing the richness of real materials.

Ultimately, the contributions of this thesis lie not only in the specific results

obtained, but in the conceptual and computational bridges it has built—linking electronic structure, interfacial physics, and materials design in the pursuit of predictive dielectric science.

Appendix A

Additional Information

Outline of my Quantum Espresso Input Codes. Each script corresponds directly to a step as outlined in 3.4 or 3.5. These scripts were developed in the Paci group as a result of several years of experimentation with Quantum Espresso and other codes. Some of the cutoff values have been left in, and system-specific values such as bands and number of atoms are blank. All cutoff values must be benchmarked for each system (matrix+inclusions combination) but these are a starting point.

```
# INITIAL ELECTRON MINIMIZATION WITH GRAM-SCHMIDT
  ORTHOGONALIZATION
#      More stable orthogonalization technique for electrons far
      from the minimum.
#      Yields incorrect eigenenergies; used only for first few
      steps.

# Submit using cp.x < 1_emin_gram.in > 1_output.out and
      QuantumEspresso Version 6.0

&CONTROL
  calculation = 'cp',
  restart_mode = 'restart',
  ndr = 51,
  ndw = 51,
  nstep = 50,
  iprint = 10,
  isave = 10,
  tstress = .FALSE.,
```

```

    tprnfor = .FALSE.,
    dt      = 4,
    etot_conv_thr = 1.d-9,
    ekin_conv_thr = 1.d-5,
    prefix = '4jobname'
    pseudo_dir = './'
/
&SYSTEM
    ibrav = 0,
    nbnd= ,
    nat  = ,
    ntyp =3,
    ecutwfc = 70,
    ecutrho = 560,
    nr1b= 30, nr2b = 30, nr3b = 30,
    nspin=1,
/
&ELECTRONS
    emass = 300.d0,
    emass_cutoff = 2.5d0,
    orthogonalization = 'Gram-Schmidt',
    electron_dynamics = 'sd',
/
&IONS
    ion_dynamics = 'none',
    ion_temperature = 'not_controlled',
/
ATOMIC_SPECIES

ATOMIC_POSITIONS (angstroms)

CELL_PARAMETERS (angstroms)

```

```

&CONTROL
  calculation = 'cp',
  restart_mode = 'reset_counters',
  ndr = 51,
  ndw = 52,
  nstep = 1000,
  iprint = 50,
  isave = 50,
  tstress = .FALSE.,
  tprnfor = .FALSE.,
  dt = 8,
  etot_conv_thr = 1.d-9,
  ekin_conv_thr = 1.d-5,
  prefix = '$jobname'
  pseudo_dir = './'
/
&SYSTEM
  ibrav = 0,
  nbnd= ,
  nat = ,
  ntyp = ,
  ecutwfc = 70,
  ecutrho = 560,
  nr1b= 30, nr2b = 30, nr3b = 30,
  nspin=1,
/
&ELECTRONS
  emass = 300.d0,
  emass_cutoff = 2.5d0,
  orthogonalization = 'ortho',
  ortho_max = 100
  electron_dynamics = 'damp',
  electron_damping = 0.05
/
&IONS
  ion_dynamics = 'none',

```

```
    ion_temperature = 'not_controlled',  
/  
ATOMIC_SPECIES  
  
ATOMIC_POSITIONS (angstroms)  
  
CELL_PARAMETERS (angstroms)
```

```

# ZERO-FIELD GEOMETRY OPTIMIZATION WITH STEEPEST DESCENT
#   Quickly relax the highest forces

&CONTROL
  calculation = 'cp',
  restart_mode = 'reset_counters',
  ndr = 52,
  ndw = 53,
  nstep = $n_ionsd,
  iprint = 10,
  isave = 100,
  tstress = .TRUE.,
  tprnfor = .TRUE.,
  dt = $ionsd_step,
  etot_conv_thr = 1.d-7,
  ekin_conv_thr = 1.d-5,
  prefix = '$job_name'
  pseudo_dir = './'
/
&SYSTEM
  ibrav = 0,
  nbnd=$bands,
  nat = $atoms,
  ntyp = $types,
  ecutwfc = $wfcut,
  ecutrho = $rhocut,
  nr1b= $soft_box, nr2b = $soft_box, nr3b = $soft_box,
  nspin=1,
/
&ELECTRONS
  emass = 300.d0,
  emass_cutoff = 2.5d0,
  orthogonalization = 'ortho',
  ortho_max = 100,
  electron_dynamics = 'damp',
  electron_damping = $e_damp

```

```
    electron_temperature = 'not_controlled',  
/  
&IONS  
    ion_dynamics = 'sd',  
    ion_temperature = 'not_controlled',  
/  
ATOMIC_SPECIES  
  
ATOMIC_POSITIONS (angstroms)  
  
CELL_PARAMETERS (angstroms)
```

```

&CONTROL
  calculation = 'cp',
  restart_mode = 'restart',
  ndr = 53,
  ndw = 54,
  nstep = 2000,
  iprint = 50,
  isave = 200,
  tstress = .TRUE.,
  tprnfor = .TRUE.,
  dt = 8,
  etot_conv_thr = 1.d-7,
  ekin_conv_thr = 1.d-5,
  prefix = '442'
  pseudo_dir = './'
/
&SYSTEM
  ibrav = 0,
  nbnd=,
  nat =,
  ntyp =,
  ecutwfc = 70,
  ecutrho = 560,
  nr1b= 30, nr2b = 30, nr3b = 30,
  nspin=1,
/
&ELECTRONS
  emass = 300.d0,
  emass_cutoff = 2.5d0,
  orthogonalization = 'ortho',
  ortho_max = 100
  electron_dynamics = 'damp',
  electron_damping = 0.05
!  electron_velocities = 'zero'
  electron_temperature = 'not_controlled',
/

```

```
&IONS
  ion_dynamics = 'damp',
  ion_damping = 0.05,
!  ion_velocities = 'zero'
  ion_temperature = 'not_controlled',
/
ATOMIC_SPECIES

ATOMIC_POSITIONS (angstroms)

CELL_PARAMETERS (angstroms)
```

```

&CONTROL
  calculation = 'vc-cp',
  restart_mode = 'reset_counters',
  ndr = 54,
  ndw = 55,
  nstep = 2000,
  iprint = 10,
  isave = 100,
  tstress = .TRUE.,
  tprnfor = .TRUE.,
  dt = 8,
  prefix = '$jobname',
  pseudo_dir = './',
  etot_conv_thr = 1.d-6,
  ekin_conv_thr = 1.d-5,
  forc_conv_thr = 1.d-4
/
&SYSTEM
  ibrav = 0,
  nbnd=,
  nat =,
  ntyp =,
  ecutwfc = 70,
  ecutrho = 560,
  nr1b= 30, nr2b = 30, nr3b = 30,
  nspin=1,
/
&ELECTRONS
  emass = 300.d0,
  emass_cutoff = 2.5d0,
  orthogonalization = 'ortho',
  ortho_max = 100
  electron_dynamics = 'damp',
  electron_damping = 0.05
  electron_velocities = 'zero'
  electron_temperature = 'not_controlled',

```

```
/
&IONS
  ion_dynamics = 'damp',
  ion_damping = 0.05,
  ion_velocities = 'zero'
  ion_temperature = 'not_controlled',
/
&CELL
  cell_dynamics = 'damp-pr'
  cell_velocities = 'zero'
  cell_dofree = 'all'
  cell_damping = 0.01
  press = 1.0d-3
/
ATOMIC_SPECIES

ATOMIC_POSITIONS (angstroms)

CELL_PARAMETERS (angstroms)
```

```

&CONTROL
  calculation = 'vc-cp',
  restart_mode = 'restart',
  ndr = 55,
  ndw = 56,
  nstep = 3000,
  iprint = 50,
  isave = 100,
  tstress = .TRUE.,
  tprnfor = .TRUE.,
  dt = 6, # can be 4,6,8
  prefix = '$jobname',
  pseudo_dir = './',
  etot_conv_thr = 1.d-6,
  ekin_conv_thr = 1.d-5,
  forc_conv_thr = 1.d-4
/
&SYSTEM
  ibrav = 0,
  nbnd=,
  nat =,
  ntyp =3,
  ecutwfc = 70,
  ecutrho = 560,
  nr1b= 30, nr2b = 30, nr3b = 30,
  nspin=1,
/
&ELECTRONS
  emass = 300.d0,
  emass_cutoff = 2.5d0,
  orthogonalization = 'ortho',
  ortho_max = 100
  electron_dynamics = 'damp',
  electron_damping = 0.05
  electron_velocities = 'zero'
  electron_temperature = 'not_controlled',

```

```
/
&IONS
  ion_dynamics = 'damp',
  ion_damping = 0.05,
  ion_velocities = 'zero'
  ion_temperature = 'not_controlled',
  ion_nstepe = 10,
/
&CELL
  cell_dynamics = 'damp-pr'
  cell_velocities = 'zero'
  cell_dofree = 'all'
  cell_damping = 0.01
  press = 1.0d-3
/
ATOMIC_SPECIES

ATOMIC_POSITIONS (angstroms)

CELL_PARAMETERS (angstroms)
```

```

&CONTROL
  calculation = 'cp',
  restart_mode = 'from_scratch', #to restart, set to 'restart'
  ndr = 56,
  ndw = 57,
  nstep = 1500,
  iprint = 10,
  isave = 100,
  tprnfor = .TRUE.,
  tstress = .TRUE.,
  tefield = .TRUE.,
  dt = 8, #can also be 4, check what works for your system
  etot_conv_thr = 1.d-9,
  ekin_conv_thr = 1.d-5,
  prefix = '$jobname'
  pseudo_dir = './'
/
&SYSTEM
  ibrav = 0,
  nbnd=,
  nat =,
  ntyp =,
  ecutwfc = ,
  ecutrho = ,
  nr1b= 30, nr2b = 30, nr3b = 30,
  nspin=1,
/
&ELECTRONS
  emass = 300.d0,
  emass_cutoff = 2.5d0,
  orthogonalization = 'ortho',
  ortho_max = 100
  electron_dynamics = 'damp',
  electron_damping = 0.05
  electron_velocities = 'zero'
  epol = 3

```

```
    efield = 0.0
/
&IONS
    ion_dynamics = 'none',
    ion_temperature = 'not_controlled',
/

ATOMIC_SPECIES

ATOMIC_POSITIONS (angstroms)

CELL_PARAMETERS (angstroms)
```

&CONTROL

```
calculation = 'cp',
restart_mode = 'reset_counters',
ndr = 57,
ndw = 58,
nstep = 3000,
iprint = 20,
isave = 100,
tprnfor = .TRUE.,
tstress = .TRUE.,
tefield = .TRUE.
dt = 8, # can start with 4 and increase.
etot_conv_thr = 1.d-9,
ekin_conv_thr = 1.d-5,
prefix = '$jobname'
pseudo_dir = './'
```

/

&SYSTEM

```
ibrav = 0,
nbnd=,
nat =,
ntyp =,
ecutwfc =,
ecutrho = ,
nr1b= 30, nr2b = 30, nr3b = 30,
nspin=1,
```

/

&ELECTRONS

```
emass = 300.d0,
emass_cutoff = 2.5d0,
orthogonalization = 'ortho',
ortho_max = 100
electron_dynamics = 'damp',
electron_damping = 0.05
```

```
    electron_velocities = 'zero'  
    epol = 3  
    efield = 0.001  
/  
  
&IONS  
    ion_dynamics = 'none',  
    ion_temperature = 'not_controlled',  
/
```

&CONTROL

```

    calculation = 'cp',
    restart_mode = 'reset_counters', #to restart, set to "restart"
    ndr = 58,
    ndw = 59,
    nstep = 10000,
    iprint = 10,
    isave = 100,
    tstress = .TRUE.,
    tprnfor = .TRUE.,
    prefix = '$jobname',
    tefield = .TRUE.,
    dt = 8, #can start lower and increase if encountering errors
    pseudo_dir = './',

```

/

&SYSTEM

```

    ibrav = 0,
    nbnd=,
    nat =,
    ntyp =,
    ecutwfc = 70,
    ecutrho = 560,
    nr1b= 30, nr2b = 30, nr3b = 30,
    nspin=1,

```

/

&ELECTRONS

```

    emass = 300.d0,
    emass_cutoff = 2.5d0,
    orthogonalization = 'ortho',
    ortho_max = 100
    electron_dynamics = 'damp',
    electron_damping = 0.05
    electron_velocities = 'zero'
    epol = 3

```

```
    efield = 0.001
/

&IONS
    ion_dynamics = 'verlet',
    ion_temperature = 'not_controlled',
/

ATOMIC_SPECIES

ATOMIC_POSITIONS (angstroms)

CELL_PARAMETERS (angstroms)
```

Bibliography

- [1] IrdS 2020: International roadmap for devices and systems 2020 edition: Beyond cmos. <https://irds.ieee.org/editions/2021/beyond-cmos>, 2020. (Accessed on 07/27/2021).
- [2] Rafael Abargues, Pedro J. Rodriguez-Canto, Sandra Albert, Isaac Suarez, and Juan P. Martínez-Pastor. Plasmonic optical sensors printed from ag-PVA nanoinks. *J. Mater. Chem. C*, 2(5):908–915, 2014.
- [3] E.M. Abdelrazek and Rudolf Holze. Structural, optical and some physical properties of PVDF films filled with LiBr/MnCl₂ mixed fillers. *Physica B: Condensed Matter*, 406(4):766–770, feb 2011.
- [4] M. Abdullah, I. W. Lenggoro, K. Okuyama, and F. G. Shi. *J. Phys. Chem. B*, 107:1957, 2003.
- [5] Archita N. S. Adluri, Brett Henderson, and Irina Paci. Tuning the dielectric response in a nanocomposite material through nanoparticle morphology. *RSC Advances*, 12(17):10778–10787, 2022.
- [6] L. M. B. Alldredge, Wontae Chang, Steven W. Kirchoefer, and Jeffrey M. Pond. Microwave dielectric properties of BaTiO₃ and ba_{0.5}sr_{0.5}tio₃ thin films on (001) MgO. *Applied Physics Letters*, 95(22):222902, November 2009.
- [7] F. Aryasetiawan, O. Gunnarsson, M. Knupfer, and J. Fink. Local-field effects in NiO and ni. *Physical Review B*, 50(11):7311–7321, September 1994.
- [8] Reuben M. Bakker, Dmitry Permyakov, Ye Feng Yu, Dmitry Markovich, Ramón Paniagua-Domínguez, Leonard Gonzaga, Anton Samusev, Yuri Kivshar, Boris Luk’yanchuk, and Arseniy I. Kuznetsov. Magnetic and electric hotspots with silicon nanodimers. *Nano Letters*, 15(3):2137–2142, February 2015.

- [9] F Balestra and G Ghibaudo. Physics and performance of nanoscale semiconductor devices at cryogenic temperatures. *Semiconductor Science and Technology*, 32(2):023002, January 2017.
- [10] V. Barone, O. Hod, J. E. Peralta, and G. E. Scuseria. *Acc. Chem. Res.*, 44:269, 2011.
- [11] Y. Benkrima, S. Benhamida, and D. Belfennache. Theoretical study of structural and optical properties of zno in wurtzite phase. *Digest Journal of Nanomaterials and Biostructures*, 18(1):11–19, January 2023.
- [12] Priya Bhatia, Parul Yadav, and Banshi D. Gupta. Surface plasmon resonance based fiber optic hydrogen peroxide sensor using polymer embedded nanoparticles. *Sensors and Actuators B: Chemical*, 182:330–335, jun 2013.
- [13] brett rhenderson. brett rhenderson/pybec. <https://github.com/brettrhenderson/pybec>, nov 6 2021.
- [14] Lingzhou Li Canfield. *Local field effects on dielectric properties of solids*. PhD thesis, 1992.
- [15] R. Car and M. Parrinello. Unified approach for molecular dynamics and density-functional theory. *Physical Review Letters*, 55(22):2471–2474, November 1985.
- [16] W. Caseri. *Macromol. Rapid Commun.*, 21:705, 2000.
- [17] Indranath Chakraborty and Thalappil Pradeep. Atomically precise clusters of noble metals: Emerging link between atoms and nanoparticles. *Chemical Reviews*, 117(12):8208–8271, June 2017.
- [18] Cheng Chen, Limei Pan, Senchuan Jiang, Shuang Yin, Xiaoyun Li, Jingxian Zhang, Yongbao Feng, and Jian Yang. Electrical conductivity, dielectric and microwave absorption properties of graphene nanosheets/magnesia composites. *Journal of the European Ceramic Society*, 38(4):1639–1646, April 2018.
- [19] Xianqiang Chen and Yiquan Wu. Fabrication and optical properties of highly transparent MgO ceramics by spark plasma sintering. *Scripta Materialia*, 162:14–17, March 2019.
- [20] Y. Chen and C.-Y. Shew. *J. Mol. Model.*, 9:379–389, 2003.

- [21] Kyeongjae Cho. First-principles modeling of high-k gate dielectric materials. *Computational Materials Science*, 23(1–4):43–47, April 2002.
- [22] Hanbao Chong, Peng Li, Ji Xiang, Fangyu Fu, Dandan Zhang, Xiaorong Ran, and Manzhou Zhu. Design of an ultrasmall au nanocluster–CeO₂ mesoporous nanocomposite catalyst for nitrobenzene reduction. *Nanoscale*, 5(16):7622, 2013.
- [23] Andrea Dal Corso. Pseudopotentials periodic table: From h to pu. *Computational Materials Science*, 95:337–350, December 2014.
- [24] N. Drakos and R. Moore. *CP User’s Guide*.
- [25] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton. Electron-energy-loss spectra and the structural stability of nickel oxide: an lsd+u study. *Physical Review B*, 57(3):1505–1509, January 1998.
- [26] H. Ehrenreich and M. H. Cohen. *Phys. Rev.*, 115:786–790, 1959.
- [27] Parisa Fakhri, Haroon Mahmood, Babak Jaleh, and Alessandro Pegoretti. Improved electroactive phase content and dielectric properties of flexible pvdf nanocomposite films filled with au- and cu-doped graphene oxide hybrid nanofiller. *Synthetic Metals*, 220:653–660, October 2016.
- [28] Jun Fang, Bin Zhang, Qiaofeng Yao, Yang Yang, Jianping Xie, and Ning Yan. Recent advances in the synthesis and catalytic applications of ligand-protected, atomically precise metal nanoclusters. *Coordination Chemistry Reviews*, 322:1–29, September 2016.
- [29] Qi-Kun Feng, Shao-Long Zhong, Jia-Yao Pei, Yu Zhao, Dong-Li Zhang, Di-Fan Liu, Yong-Xin Zhang, and Zhi-Min Dang. Recent progress and future prospects on all-organic polymer dielectrics for energy storage capacitors. *Chemical Reviews*, 122(3):3820–3878, December 2021.
- [30] Marina R. Filip, Giles E. Eperon, Henry J. Snaith, and Feliciano Giustino. Steric engineering of metal-halide perovskites with tunable optical band gaps. *Nature Communications*, 5(1), December 2014.
- [31] Chun gang Duan, W N Mei, Wei-Guo Yin, Jianjun Liu, J R Hardy, Mengjun Bai, and Stephen Ducharme. Theoretical study on the optical properties

- of polyvinylidene fluoride crystal. *Journal of Physics: Condensed Matter*, 15(22):3805, 2003.
- [32] Hengjie Gao. Advancements and future prospects of gallium nitride (gan) in semiconductor technology. *Applied and Computational Engineering*, 65(1):37–44, May 2024.
- [33] Matthew Genovese and Keryn Lian. Polyoxometalate modified inorganic–organic nanocomposite materials for energy storage applications: A review. *Current Opinion in Solid State and Materials Science*, 19(2):126–137, apr 2015.
- [34] P Giannozzi, O Andreussi, T Brumme, O Bunau, M Buongiorno Nardelli, M Calandra, R Car, C Cavazzoni, D Ceresoli, M Cococcioni, N Colonna, I Carnimeo, A Dal Corso, S de Gironcoli, P Delugas, R A DiStasio Jr, A Ferretti, A Floris, G Fratesi, G Fugallo, R Gebauer, U Gerstmann, F Giustino, T Gorni, J Jia, M Kawamura, H-Y Ko, A Kokalj, E Küçükbenli, M Lazzeri, M Marsili, N Marzari, F Mauri, N L Nguyen, H-V Nguyen, A Otero de-la Roza, L Paulatto, S Poncé, D Rocca, R Sabatini, B Santra, M Schlipf, A P Seitsonen, A Smogunov, I Timrov, T Thonhauser, P Umari, N Vast, X Wu, and S Baroni. Advanced capabilities for materials modelling with quantum espresso. *Journal of Physics: Condensed Matter*, 29(46):465901, 2017.
- [35] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano de Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sclauszero, Ari P Seitsonen, Alexander Smogunov, Paolo Umari, and Renata M Wentzcovitch. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39):395502, sep 2009.
- [36] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano de Gironcoli, Stefano Fab-

- ris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sciauzero, Ari P Seitsonen, Alexander Smogunov, Paolo Umari, and Renata M Wentzcovitch. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39):395502, September 2009.
- [37] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano de Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sciauzero, Ari P Seitsonen, Alexander Smogunov, Paolo Umari, and Renata M Wentzcovitch. Quantum espresso: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39):395502 (19pp), 2009.
- [38] X. Gonze and C. Lee. *Phys. Rev. B*, 55:10355, 1997.
- [39] Tapas Goswami, Navpreet Kamboj, Amarnath Bheemaraju, Aditya Kataria, and Ramendra Sundar Dey. Supercapacitive behaviour of a novel nanocomposite of 3, 4, 9, 10-perylenetetracarboxylic acid incorporated captopril-ag nanocluster decorated on graphene nanosheets. *Materials Advances*, 2(4):1358–1368, 2021.
- [40] Tapas Goswami, K. Mohan Reddy, and Amarnath Bheemaraju. Silver nanocluster anchored tio2/nb2o5 hybrid nanocomposite as highly efficient and selective visible-light sensitive photocatalyst. *ChemistrySelect*, 4(22):6790–6799, June 2019.
- [41] Elzbieta Gradauskaite, Quintin N. Meier, Natascha Gray, Martin F. Sarott, Tizian Scharsach, Marco Campanini, Thomas Moran, Alexander Vogel, Karla Del Cid-Ledezma, Bryan D. Huey, Marta D. Rossell, Manfred Fiebig, and Morgan Trassin. Defeating depolarizing fields with artificial flux closure in ultrathin ferroelectrics. *Nature Materials*, 22(12):1492–1498, October 2023.

- [42] Grzegorz Grzela, Djamil Hourlier, and Jaime Gómez Rivas. Polarization-dependent light extinction in ensembles of polydisperse vertical semiconductor nanowires: A mie scattering effective medium. *Phys. Rev. B*, 86:045305, Jul 2012.
- [43] Shaojun Guo and Erkang Wang. Noble metal nanomaterials: Controllable synthesis and application in fuel cells and analytical sensors. *Nano Today*, 6(3):240–264, June 2011.
- [44] D. Guzman, M. Cruz, and C. Wang. *Microelectr. J.*, 39:523–525, 2008.
- [45] David J. T. Hally and Irina Paci. Low-frequency polarization in molecular-scale noble-metal/metal-oxide nanocomposites. *Nanoscale*, 10(20):9583–9593, 2018.
- [46] David J.T. Hally and Irina Paci. Low-frequency polarization in molecular-scale noble-metal/metal-oxide nanocomposites. *Nanoscale*, 10(20):9583–9593, 2018.
- [47] W. P. Halperin. Quantum size effects in metal particles. *Reviews of Modern Physics*, 58(3):533–606, July 1986.
- [48] Marcus D Hanwell, Donald E Curtis, David C Lonie, Tim Vandermeersch, Eva Zurek, and Geoffrey R Hutchison. Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *Journal of Cheminformatics*, 4(1), August 2012.
- [49] Daniel C. Harris, Lee R. Cambrea, Linda F. Johnson, Robert T. Seaver, Meghan Baronowski, Richard Gentilman, C. Scott Nordahl, Todd Gattuso, Stephanie Silberstein, Patrick Rogan, Thomas Hartnett, Brian Zelinski, Wayne Sunne, Eric Fest, W. Howard Poisl, Charles B. Willingham, Giorgio Turri, Cori Warren, Michael Bass, David E. Zelmon, and Steven M. Goodrich. Properties of an infrared-transparent MgO:y2o3 nanocomposite. *Journal of the American Ceramic Society*, 96(12):3828–3835, September 2013.
- [50] Dalong He, Yao Wang, Silong Song, Song Liu, Yu Luo, and Yuan Deng. Polymer-based nanocomposites employing bi2s3@sio2 nanorods for high dielectric performance: Understanding the role of interfacial polarization in semiconductor-insulator core-shell nanostructure. *Composites Science and Technology*, 151:25–33, October 2017.

- [51] Y. He and T. Zeng. *J. Phys. Chem. C*, 114:18023, 2010.
- [52] Brett Henderson, Archita Adluri, and Irina Paci. Finite element modeling of the dielectric response of metal/metal oxide nanocomposites: Coarse-graining the quantum response. *ChemRxiv: 10.33774/chemrxiv-2021-s0vqp*, October 2021.
- [53] Burak Himmetoglu, Andrea Floris, Stefano De Gironcoli, and Matteo Cococcioni. Hubbard-corrected dft energy functionals: The lda+ u description of correlated systems. *International Journal of Quantum Chemistry*, 114(1):14–49, 2014.
- [54] Atsufumi Hirohata, Keisuke Yamada, Yoshinobu Nakatani, Ioan-Lucian Prejbeanu, Bernard Diény, Philipp Pirro, and Burkard Hillebrands. Review on spintronics: Principles and device applications. *Journal of Magnetism and Magnetic Materials*, 509:166711, September 2020.
- [55] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical Review*, 136(3B):B864–B871, November 1964.
- [56] C. Huang, Q. M. Zhang, J. Y. Li, and M. Rabeony. *Appl. Phys. Lett*, 87:182901, 2005.
- [57] Xingyi Huang, Bin Sun, Yingke Zhu, Shengtao Li, and Pingkai Jiang. High-k polymer nanocomposites with 1d filler for dielectric and energy storage applications. *Progress in Materials Science*, 100:187–225, February 2019.
- [58] Hongjin Jiang, Kyoung Sik Moon, Yi Li, and C. P. Wong. Surface functionalized silver nanoparticles for ultrahigh conductive polymer composites. *Chemistry of Materials*, 18(13):2969–2973, 2006.
- [59] Xiaomei Jiang, Richard D. Schaller, Sergey B. Lee, Jeffrey M. Pietryga, Victor I. Klimov, and Anvar A. Zakhidov. PbSe nanocrystal/conducting polymer solar cells with an infrared response to 2 micron. *Journal of Materials Research*, 22(08):2204–2210, aug 2007.
- [60] Rongchao Jin, Gao Li, Sachil Sharma, Yingwei Li, and Xiangsha Du. Toward active-site tailoring in heterogeneous catalysis by atomically precise metal nanoclusters with crystallographic structures. *Chemical Reviews*, 121(2):567–648, September 2020.

- [61] So-Yeon Jun, SeungHun Park, Nam Wuk Baek, Tae-Young Lee, Sehoon Yoo, Donggeun Jung, and Jin-Young Kim. Enhancement of dielectric performance of encapsulation in barium titanate oxide using size-controlled reduced graphene oxide. *RSC Advances*, 12(26):16412–16418, 2022.
- [62] Xi Kang and Manzhou Zhu. Tailoring the photoluminescence of atomically precise nanoclusters. *Chemical Society Reviews*, 48(8):2422–2457, 2019.
- [63] B. Karthikeyan. Optical studies on thermally surface plasmon tuned au, ag and au:ag nanocomposite polymer films. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 96:456–460, oct 2012.
- [64] Ajeet Kaushik, Rajesh Kumar, Sunil K. Arya, Madhavan Nair, B. D. Malhotra, and Shekhar Bhansali. Organic–inorganic hybrid nanocomposite-based gas sensors for environmental monitoring. *Chem. Rev.*, 115(11):4571–4606, jun 2015.
- [65] R. D. King-Smith and David Vanderbilt. Theory of polarization of crystalline solids. *Physical Review B*, 47(3):1651–1654, January 1993.
- [66] J.A. Kittl, K. Opsomer, M. Popovici, N. Menou, B. Kaczer, X.P. Wang, C. Adelman, M.A. Pawlak, K. Tomida, A. Rothschild, B. Govoreanu, R. Degraeve, M. Schaekers, M. Zahid, A. Delabie, J. Meerssaut, W. Polspoel, S. Clima, G. Pourtois, W. Knaepen, C. Detavernier, V.V. Afanas’ev, T. Blomberg, D. Pierreux, J. Swerts, P. Fischer, J.W. Maes, D. Manger, W. Vandervorst, T. Conard, A. Franquet, P. Favia, H. Bender, B. Brijs, S. Van Elshocht, M. Jurczak, J. Van Houdt, and D.J. Wouters. High-k dielectrics for future generation memory devices. *Microelectronic Engineering*, 86(7–9):1789–1795, July 2009.
- [67] Vladimir Kochergin, Vladimir Zaporozhchenko, Haile Takele, Franz Faupel, and Helmut Föll. Improved effective medium approach: Application to metal nanocomposites. *Journal of Applied Physics*, 101(2):024302, January 2007.
- [68] A. Kohlmeier. *CPMD Tutorial*.
- [69] Walter Kohn and Lu Jeu Sham. Self-consistent equations including exchange and correlation effects. *Physical review*, 140(4A):A1133, 1965.
- [70] Kyuju Kwak and Dongil Lee. Electrochemistry of atomically precise metal nanoclusters. *Accounts of Chemical Research*, 52(1):12–22, November 2018.

- [71] L. Lajaunie, F. Boucher, R. Dessapt, and P. Moreau. Strong anisotropic influence of local-field effects on the dielectric response of α - moo_3 . *Phys. Rev. B*, 88:115141, Sep 2013.
- [72] K. Lejaeghere, G. Bihlmayer, T. Bjorkman, P. Blaha, S. Blugel, V. Blum, D. Caliste, I. E. Castelli, S. J. Clark, A. Dal Corso, S. de Gironcoli, T. Deutsch, J. K. Dewhurst, I. Di Marco, C. Draxl, M. Du ak, O. Eriksson, J. A. Flores-Livas, K. F. Garrity, L. Genovese, P. Giannozzi, M. Giantomassi, S. Goedecker, X. Gonze, O. Granas, E. K. U. Gross, A. Gulans, F. Gygi, D. R. Hamann, P. J. Hasnip, N. A. W. Holzwarth, D. Iu an, D. B. Jochym, F. Jollet, D. Jones, G. Kresse, K. Koepnik, E. Kucukbenli, Y. O. Kvashnin, I. L. M. Locht, S. Lubeck, M. Marsman, N. Marzari, U. Nitzsche, L. Nordstrom, T. Ozaki, L. Paulatto, C. J. Pickard, W. Poelmans, M. I. J. Probert, K. Refson, M. Richter, G.-M. Rignanese, S. Saha, M. Scheffler, M. Schlipf, K. Schwarz, S. Sharma, F. Tavazza, P. Thunstrom, A. Tkatchenko, M. Torrent, D. Vanderbilt, M. J. van Setten, V. Van Speybroeck, J. M. Wills, J. R. Yates, G.-X. Zhang, and S. Cottenier. Reproducibility in density functional theory calculations of solids. *Science*, 351(6280):aad3000, March 2016.
- [73] J. Y. Li, L. Zhang, and Stephen Ducharme. Electric energy density of dielectric nanocomposites. *Applied Physics Letters*, 90(13):132901, March 2007.
- [74] M. Li and J.C. Li. Size effects on the band-gap of semiconductor compounds. *Materials Letters*, 60(20):2526–2529, September 2006.
- [75] Shanghua Li, Meng Meng Lin, Muhammet S. Toprak, Do Kyung Kim, and Mamoun Muhammed. Nanocomposites of polymer and inorganic nanoparticles for optical and magnetic applications. *Nano Reviews*, 1(0), aug 2010.
- [76] Y.F. Li, B. Xiao, L. Sun, Y.M. Gao, and Y.H. Cheng. A theoretical study of dielectric tensor, born effective charges, LO-TO splitting and infrared response of al_4sic_4 and $\text{al}_4\text{si}_2\text{c}_5$. *Journal of Alloys and Compounds*, 692:713–719, January 2017.
- [77] Chi Liu, William Huhn, Ke-Zhao Du, Alvaro Vazquez-Mayagoitia, David Dirkes, Wei You, Yosuke Kanai, David B. Mitzi, and Volker Blum. Tunable semiconductors: Control over carrier states and excitations in layered hybrid organic-inorganic perovskites. *Physical Review Letters*, 121(14), October 2018.

- [78] Fan Liu, Qing-Qing Ni, and Yasushi Murakami. Preparation of magnetic polyvinyl alcohol composite nanofibers with homogenously dispersed nanoparticles and high water resistance. *Textile Research Journal*, 83(5):510–518, December 2012.
- [79] Xiaoyong Liu, Dipanjan Mazumdar, Weifeng Shen, B. D. Schrag, and Gang Xiao. Thermal stability of magnetic tunneling junctions with MgO barriers for high temperature spintronics. *Applied Physics Letters*, 89(2):023504, July 2006.
- [80] Maria R. Lukatskaya, Bruce Dunn, and Yury Gogotsi. Multidimensional materials and device architectures for future hybrid energy storage. *Nature Communications*, 7:1–13, 2016.
- [81] A Malinauskas, J Malinauskiene, and A Ramanavičius. Conducting polymer-based nanostructurized materials: electrochemical aspects. *Nanotechnology*, 16(10):R51–R62, aug 2005.
- [82] Qian Mao, Muye Feng, Xi Zhuo Jiang, Yihua Ren, Kai H. Luo, and Adri C.T. van Duin. Classical and reactive molecular dynamics: Principles and applications in combustion and energy systems. *Progress in Energy and Combustion Science*, 97:101084, July 2023.
- [83] R. M. Martin. *Electronic Structure: Basic Theory and Practical Methods*. Cambridge University Press, 2004.
- [84] Nicola Marzari and David Vanderbilt. Maximally localized generalized Wannier functions for composite energy bands. *Physical Review B - Condensed Matter and Materials Physics*, 56(20):12847–12865, 1997.
- [85] T. C. Merkel, B. D. Freeman, R. J. Spontak, Z. He, I. Pinnau, P. Meakin, and A. J. Hill. *Science*, 296:519, 2002.
- [86] S. Mueller, C. Adelmann, A. Singh, S. Van Elshocht, U. Schroeder, and T. Miko-lajick. Ferroelectricity in gd-doped hfo2thin films. *ECS Journal of Solid State Science and Technology*, 1(6):N123–N126, 2012.
- [87] Sebastian Müller, Roman Yurchak, Benjamin Murphy, nannau, Malte Ziebarth, Sudipta Basak, Marcelo Albuquerque, Mark Vrijlandt, Matthew Peveler, Daniel Mejía Raigosa, Harry Matchette-Downes, Jordan Porter, Rhilip, Scott

- Staniewicz, Will Chang, and kvanlombek. Geostat-Framework/PyKrige. <https://github.com/GeoStat-Framework/PyKrige>, sep 3 2024.
- [88] N. Mustapha, K.H. Ibnaouf, Z. Fekkai, A. Hennache, S. Prasad, and A. Alyamani. Improved efficiency of solar cells based on BEHP-co-MEH-PPV doped with ZnO nanoparticles. *Optik - International Journal for Light and Electron Optics*, 124(22):5524–5527, nov 2013.
- [89] Amara Nasir, Ayesha Kausar, and Ayesha Younus. Polymer/graphite nanocomposites: Physical features, fabrication and current relevance. *Polymer-Plastics Technology and Engineering*, 54(7):750–770, dec 2014.
- [90] J. K. Nelson and Y. Hu. *J. Phys. D: App. Phys.*, 38:213–222, 2005.
- [91] L. Nicolais and G. Carotenuto. *Metal-Polymer Nanocomposites*. Wiley, New Jersey, 2005.
- [92] None Available. Materials data on tl18ag59se39 by materials project, 2018.
- [93] P. Nozieres and D. Pines. *Phys. Rev.*, 113:1254–1267, 1959.
- [94] Stuart S. P. Parkin, Christian Kaiser, Alex Panchula, Philip M. Rice, Brian Hughes, Mahesh Samant, and See-Hun Yang. Giant tunnelling magnetoresistance at room temperature with MgO (100) tunnel barriers. *Nature Materials*, 3(12):862–867, October 2004.
- [95] B.A. Parviz, D. Ryan, and G.M. Whitesides. Using self-assembly for the fabrication of nano-scale electronic and photonic devices. *IEEE Transactions on Advanced Packaging*, 26:233–241, 2003.
- [96] T. Paunesku, T. Rajh, G. Wiederrecht, J. Maser, S. Vogt, N. Stojicevic, M. Protic, B. Lai, J. Oryhon, M. Thurnauer, and G. Woloschak. *Nature Mats.*, 2:343, 2003.
- [97] F. Pedregosa, G. Varoquaux, A. Gramfort, V. Michel, B. Thirion, O. Grisel, M. Blondel, P. Prettenhofer, R. Weiss, V. Dubourg, J. Vanderplas, A. Passos, D. Cournapeau, M. Brucher, M. Perrot, and E. Duchesnay. Scikit-learn: Machine learning in Python. *Journal of Machine Learning Research*, 12:2825–2830, 2011.

- [98] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, 77:3865–3868, 1996.
- [99] John P. Perdew. Density functional theory and the band gap problem. *International Journal of Quantum Chemistry*, 28(S19):497–523, June 1985.
- [100] John P. Perdew, Weitao Yang, Kieron Burke, Zenghui Yang, Eberhard K. U. Gross, Matthias Scheffler, Gustavo E. Scuseria, Thomas M. Henderson, Igor Ying Zhang, Adrienn Ruzsinszky, Haowei Peng, Jianwei Sun, Egor Trushin, and Andreas Görling. Understanding band gaps of solids in generalized kohn–sham theory. *Proceedings of the National Academy of Sciences*, 114(11):2801–2806, March 2017.
- [101] Tanut Pettong, Pawin Iamprasertkun, Atiweena Krittayavathananon, Phansiri Sukha, Pichamon Sirisinudomkit, Anusorn Seubsai, Metta Chareonpanich, Paisan Kongkachuichay, Jumras Limtrakul, and Montree Sawangphruk. High-performance asymmetric supercapacitors of MnCo₂O₄ nanofibers and n-doped reduced graphene oxide aerogel. *ACS Applied Materials & Interfaces*, 8(49):34045–34053, November 2016.
- [102] A. Posadas, F. J. Walker, C. H. Ahn, T. L. Goodrich, Z. Cai, and K. S. Ziemer. Epitaxial MgO as an alternative gate dielectric for SiC transistor applications. *Applied Physics Letters*, 92(23):233511, June 2008.
- [103] Manojit Pusty and Parasharam M. Shirage. Gold nanoparticle–cellulose/PDMS nanocomposite: a flexible dielectric material for harvesting mechanical energy. 10(17):10097–10112, 2020.
- [104] Rui Qiao, Chao Wang, Sheng Chen, Guanghu He, Zijin Liu, Hang Luo, and Dou Zhang. High-temperature dielectric polymers with high breakdown strength and energy density via constructing the electron traps in blends. *Composites Part A: Applied Science and Manufacturing*, 152:106679, January 2022.
- [105] V. Kesava Rao and T. P. Radhakrishnan. Tuning the SERS response with ag–au nanoparticle-embedded polymer thin film substrates. *ACS Appl. Mater. Interfaces*, 7(23):12767–12773, jun 2015.
- [106] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, and W. M. Skiff. *J. Am. Chem. Soc.*, 114:10024–10035, 1992.

- [107] R. Resta, M. Posternak, and A. Baldereschi. First-principles theory of polarization in ferroelectrics. *MRS Proceedings*, 291, January 1992.
- [108] Raffaele Resta. Why are insulators insulating and metals conducting? *Journal of Physics Condensed Matter*, 14(20), 2002.
- [109] Raffaele Resta. Electrical polarization and orbital magnetization: the modern theories. *Journal of Physics: Condensed Matter*, 22(12):123201, March 2010.
- [110] Raffaele Resta and David Vanderbilt. *Theory of Polarization: A Modern Approach*, page 31–68. Springer Berlin Heidelberg.
- [111] J. Robertson. High dielectric constant oxides. *The European Physical Journal Applied Physics*, 28(3):265–291, December 2004.
- [112] John Robertson and Robert M. Wallace. High-k materials and metal gates for CMOS applications. *Materials Science and Engineering: R: Reports*, 88:1–41, February 2015.
- [113] C. K. Rowan and I. Paci. *J. Phys. Chem. C*, 115:8316, 2011.
- [114] C. K. Rowan and I. Paci. *Theor. Chem. Acc.*, 131:1078, 2012.
- [115] Christopher K. Rowan and I. Paci. Nanoparticle morphology and aspect ratio effects in ag/pvdf nanocomposites. *Theoretical Chemistry Accounts*, 131:1–11, 2012.
- [116] Christopher K. Rowan and Irina Paci. Optical properties of ag/polyvinylidene fluoride nanocomposites: A theoretical study. *The Journal of Physical Chemistry C*, 115(16):8316–8324, March 2011.
- [117] Jyoti Sahu, Hemant Kumar, Deepti Pateria, Swati Verma, and Mohan L. Verma. Interface layer dft study of first transition series xo oxides (x = ti, cr, mn, fe, co, ni, cu and zn). *Materials Today: Proceedings*, 59:1831–1838, 2022.
- [118] Numan Salah, Neazar Baghdadi, Ahmed Alshahrie, Abdu Saeed, A.R. Ansari, Adnan Memic, and Kunihiro Koumoto. Nanocomposites of cuo/swcnt: Promising thermoelectric materials for mid-temperature thermoelectric generators. *Journal of the European Ceramic Society*, 39(11):3307–3314, September 2019.

- [119] D Shamiryan, T Abell, F Iacopi, and K Maex. Low-k dielectric materials. *Materials Today*, 7(1):34–39, January 2004.
- [120] Haider Mohammed Shanshool, Muhammad Yahaya, Wan Mahmood Mat Yunus, and Ibtisam Yahya Abdullah. Measurements of nonlinear optical properties of PVDF/ZnO using z-scan technique. *Brazilian Journal of Physics*, 45(5):538–544, jul 2015.
- [121] Xingchen Shen, Chun-Chuen Yang, Yamei Liu, Guiwen Wang, Huan Tan, Yung-Hsiang Tung, Guoyu Wang, Xu Lu, Jian He, and Xiaoyuan Zhou. High-temperature structural and thermoelectric study of argyrodite ag₈ge₆s₆. *ACS Applied Materials and Interfaces*, 11(2):2168–2176, December 2018.
- [122] Zhong-Hui Shen, Zhi-Wei Bao, Xiao-Xing Cheng, Bao-Wen Li, Han-Xing Liu, Yang Shen, Long-Qing Chen, Xiao-Guang Li, and Ce-Wen Nan. Designing polymer nanocomposites with high energy density using machine learning. *npj Computational Materials*, 7(1), July 2021.
- [123] Inderpreet Singh, P.K. Bhatnagar, P.C. Mathur, Inderpreet Kaur, L.M. Bharadwaj, and Ravindra Pandey. Optical and electrical characterization of conducting polymer-single walled carbon nanotube composite films. *Carbon*, 46(8):1141–1144, July 2008.
- [124] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejón, and D. Sanchez-Portal. *J. Phys.: Condens. Matter*, 14:2745, 2002.
- [125] José M Soler, Emilio Artacho, Julian D Gale, Alberto García, Javier Junquera, Pablo Ordejón, and Daniel Sánchez-Portal. The siesta method for ab initio order-n materials simulation. *Journal of Physics: Condensed Matter*, 14(11):2745–2779, March 2002.
- [126] Ivo Souza, Tim Wilkens, and Richard M. Martin. Polarization and localization in insulators: Generating function approach. *Physical Review B*, 62(3):1666–1683, July 2000.
- [127] Nicola A. Spaldin. A beginner's guide to the modern theory of polarization. *Journal of Solid State Chemistry*, 195:2–10, November 2012.
- [128] T. Tanaka, G. C. Montanari, and R. Mulhaupt. *IEEE Trans. Dielectr. Electr. Insul.*, 11:763, 2004.

- [129] Jia Tang, Haihong Shi, Guanyu Ma, Liangping Luo, and Zhenghua Tang. Ultra-small au and ag nanoclusters for biomedical applications: A review. *Frontiers in Bioengineering and Biotechnology*, 8, October 2020.
- [130] Yu Tao, Mingqiang Li, Jinsong Ren, and Xiaogang Qu. Metal nanoclusters: novel probes for diagnostic and therapeutic applications. *Chemical Society Reviews*, 44(23):8636–8663, 2015.
- [131] A. Tawansi, A. H. Oraby, E. Ahmed, E. M. Abdelrazek, and M. Abdelaziz. Effect of na-light radiation on the optical gap and crystal structure of agno3-diffused pvdf sensor. *Journal of Applied Polymer Science*, 70(9):1759–1767, 1998.
- [132] John T. Titantah and Mikko Karttunen. Ab initio calculations of optical properties of silver clusters: cross-over from molecular to nanoscale behavior. *The European Physical Journal B*, 89(5), May 2016.
- [133] Sarah A. Tolba, Kareem M. Gameel, Basant A. Ali, Hossam A. Almossalami, and Nageh K. Allam. *The DFT+U: Approaches, Accuracy, and Applications*. InTech, May 2018.
- [134] N. Troullier and J. L. Martins. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B*, 43:1993 – 2006, 1991.
- [135] P. Umari and Alfredo Pasquarello. Ab initio molecular dynamics in a finite homogeneous electric field. *Phys. Rev. Lett.*, 89:157602, Sep 2002.
- [136] D. van der Spoel, E. Lindahl, B. Hess, A. R. van Buuren, E. Apol, P. J. Meulenhoff, D. P. Tieleman, A. L. T. M. Sijers, K. A. Feenstra, R. van Drunen, and H. J. C. Berendsen. *Gromacs User Manual version 4.0*. The GROMACS development team, Groningen, Netherlands, 2006.
- [137] M.J. van Setten, M. Giantomassi, E. Bousquet, M.J. Verstraete, D.R. Hamann, X. Gonze, and G.-M. Rignanese. The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table. *Computer Physics Communications*, 226:39–54, May 2018.
- [138] David Vanderbilt, Xinyuan Zhao, and Davide Ceresoli. Structural and dielectric properties of crystalline and amorphous zro2. *Thin Solid Films*, 486(1–2):125–128, August 2005.

- [139] Pauli Virtanen, Ralf Gommers, Travis E. Oliphant, Matt Haberland, Tyler Reddy, David Cournapeau, Evgeni Burovski, Pearu Peterson, Warren Weckesser, Jonathan Bright, Stéfan J. van der Walt, Matthew Brett, Joshua Wilson, K. Jarrod Millman, Nikolay Mayorov, Andrew R. J. Nelson, Eric Jones, Robert Kern, Eric Larson, C J Carey, İlhan Polat, Yu Feng, Eric W. Moore, Jake VanderPlas, Denis Laxalde, Josef Perktold, Robert Cimrman, Ian Henriksen, E. A. Quintero, Charles R. Harris, Anne M. Archibald, Antônio H. Ribeiro, Fabian Pedregosa, Paul van Mulbregt, and SciPy 1.0 Contributors. SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nature Methods*, 17:261–272, 2020.
- [140] Aron Walsh, Juarez L. F. Da Silva, and Su-Huai Wei. Origins of band-gap renormalization in degenerately doped semiconductors. *Physical Review B*, 78(7), August 2008.
- [141] Jian Wang and Zhong-Hui Shen. Modeling-guided understanding microstructure effects in energy storage dielectrics. *Microstructures*, 2021.
- [142] Jian Wang and Zhong-Hui Shen. Modeling-guided understanding microstructure effects in energy storage dielectrics. *Microstructures*, 2021.
- [143] Shuai Wang, Cao Yang, Xiaomeng Li, Hanyu Jia, Shuiren Liu, Xuying Liu, Takeo Minari, and Qingqing Sun. Polymer-based dielectrics with high permittivity and low dielectric loss for flexible electronics. *Journal of Materials Chemistry C*, 10(16):6196–6221, 2022.
- [144] Shuai Wang, Cao Yang, Xiaomeng Li, Hanyu Jia, Shuiren Liu, Xuying Liu, Takeo Minari, and Qingqing Sun. Polymer-based dielectrics with high permittivity and low dielectric loss for flexible electronics. *Journal of Materials Chemistry C*, 10(16):6196–6221, 2022.
- [145] Xiaoyu Wang, Fang He, Xi Zhu, Fu Tang, and Lidong Li. Hybrid silver nanoparticle/conjugated polyelectrolyte nanocomposites exhibiting controllable metal-enhanced fluorescence. *Sci. Rep.*, 4, mar 2014.
- [146] Yuxin Wang, Xingyi Huang, Tao Li, Liqiang Li, Xiaojun Guo, and Pingkai Jiang. Polymer-based gate dielectrics for organic field-effect transistors. *Chemistry of Materials*, 31(7):2212–2240, March 2019.

- [147] Nathan Wiser. Dielectric constant with local field effects included. *Phys. Rev.*, 129:62–69, Jan 1963.
- [148] Juanzhu Yan, Boon K. Teo, and Nanfeng Zheng. Surface chemistry of atomically precise coinage-metal nanoclusters: From structural control to surface reactivity and catalysis. *Accounts of Chemical Research*, 51(12):3084–3093, November 2018.
- [149] L. Yan, C. M. Lopez, R. P. Shrestha, E. A. Irene, A. A. Suvorova, and M. Saunders. Magnesium oxide as a candidate high- gate dielectric. *Applied Physics Letters*, 88(14):142901, April 2006.
- [150] Jie Yang and Rongchao Jin. Advances in enhancing luminescence of atomically precise ag nanoclusters. *The Journal of Physical Chemistry C*, 125(4):2619–2625, December 2020.
- [151] Wanwang Yang, Chenxi Yu, Haolin Li, Mengqi Fan, Xujin Song, Haili Ma, Zheng Zhou, Pengying Chang, Peng Huang, Fei Liu, Xiaoyan Liu, and Jinfeng Kang. Ferroelectricity of hafnium oxide-based materials: Current status and future prospects from physical mechanisms to device applications. *Journal of Semiconductors*, 44(5):053101, May 2023.
- [152] X. Yang, Z. Zhou, T. Nan, Y. Gao, G. M. Yang, M. Liu, and N. X. Sun. Recent advances in multiferroic oxide heterostructures and devices. *Journal of Materials Chemistry C*, 4(2):234–243, 2016.
- [153] Haizhu Yu, Bo Rao, Wan Jiang, Sha Yang, and Manzhou Zhu. The photoluminescent metal nanoclusters with atomic precision. *Coordination Chemistry Reviews*, 378:595–617, January 2019.
- [154] Chi Zhang, Ying Chen, Xin Li, Haishen Ren, Genshui Wang, and Xianlin Dong. Effect of LiF addition on sintering behavior and dielectric breakdown mechanism of MgO-based microwave dielectric ceramics. *Journal of Materiomics*, 7(3):478–487, May 2021.
- [155] Chi Zhang, Ying Chen, Mingxing Zhou, Xin Li, Lei Wang, Liansheng Xia, Yi Shen, and Xianlin Dong. Achieving ultrahigh dielectric breakdown strength in MgO-based ceramics by composite structure design. *Journal of Materials Chemistry C*, 7(26):8120–8130, 2019.

- [156] Libing Zhang and Erkang Wang. Metal nanoclusters: New fluorescent probes for sensors and bioimaging. *Nano Today*, 9(1):132–157, February 2014.
- [157] Lin Zhang and Zhen Cui. Electronic, magnetic, and optical performances of non-metals doped silicon carbide. *Frontiers in Chemistry*, 10, April 2022.
- [158] S. B. Zhang, S.-H. Wei, and Alex Zunger. Intrinsic n-type versus p-type doping asymmetry and the defect physics of zno. *Phys. Rev. B*, 63:075205, Jan 2001.
- [159] Yingying Zheng, Jonathan Monty, and Robert J. Linhardt. Polysaccharide-based nanocomposites and their applications. *Carbohydrate Research*, 405:23–32, mar 2015.
- [160] Paul Ziesche, Stefan Kurth, and John P. Perdew. Density functionals from lda to gga. *Computational Materials Science*, 11(2):122–127, April 1998.
- [161] Jesús Zúñiga-Pérez, Vincent Consonni, Liverios Lymperakis, Xiang Kong, Achim Trampert, Sergio Fernández-Garrido, Oliver Brandt, Hubert Renevier, Stacia Keller, Karine Hestroffer, Markus R. Wagner, Juan Sebastián Reparaz, Fatih Akyol, Siddharth Rajan, Stéphanie Rennesson, Tomás Palacios, and Guy Feuillet. Polarity in gan and zno: Theory, measurement, growth, and devices. *Applied Physics Reviews*, 3(4), November 2016.