EMC/FDTD/MD FOR MULTIPHYSICS CHARACTERIZATION OF SEMICONDUCTORS AT THZ FREQUENCIES

by

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EMC/FDTD/MD FOR MULTIPHYSICS CHARACTERIZATION OF SEMICONDUCTORS AT THZ FREQUENCIES

Keely Willis

Under the supervision of Professors Susan Hagness and Irena Knezevic
at the University of Wisconsin-Madison

Doped semiconductors typically have characteristic scattering rates and plasma frequencies in the THz regime. As the stimulating frequency approaches the THz, $\omega \tau \approx 1$, and the conductivity of doped semiconductors becomes complex and strongly frequency-dependent.

We have developed a multiphysics computational technique for semiconductor carrier transport at THz frequencies. The technique combines the ensemble Monte Carlo (EMC) simulation of carrier transport with the finite-difference time-domain (FDTD) solver of Maxwell’s curl equations and the molecular dynamics (MD) technique for short-range Coulomb interaction. At each time step, electric and magnetic fields from FDTD and MD influence EMC carrier motion according to the Lorentz force. Likewise, microscopic currents from carrier motion in the EMC influence FDTD electric field updates according to Ampere’s law, and EMC charge density defines MD fields according to Coulomb’s law.

The strength of the EMC/FDTD solver was first established though characterization of silicon of low doping density. We demonstrated the necessity for rigorous enforcement of Gauss’s law for FDTD solvers with charged particles. This work established new understanding of the capabilities of FDTD to accurately predict the diverging fields surrounding charges in semiconductors. The technique was extended to high carrier density materials through incorporation of MD. A new technique has been developed to combine electric fields from MD with electromagnetic fields from FDTD without double counting the fields. The complex conductivity calculated by EMC/FDTD/MD shows excellent agreement with experimental data for silicon of doping density $n_0 = 5.47 \times 10^{14}$ and $3.15 \times 10^{16}$ cm$^3$ under THz-frequency stimulation.
The EMC/FDTD/MD technique was further extended to describe the exchange interaction between indistinguishable electrons, by assuming a finite electron radius. The addition of this description allows EMC/FDTD/MD to accurately describe carrier dynamics in materials with \( n_0 \geq 10^{18} \text{ cm}^{-3} \). EMC/FDTD/MD was used to predict the complex conductivity of doped silicon at room temperature for \( n_0 = 10^{14} - 10^{19} \text{ cm}^{-3} \) and \( f = 0 - 2.5 \text{ THz} \). The results of this calculation are of immediate value to researchers in THz materials and device design. The prediction establishes the strength of EMC/FDTD/MD for THz-frequency characterization of high-conductivity materials.
ABSTRACT

Doped semiconductors typically have plasma frequencies and characteristic scattering rates in the THz frequency regime. As the frequency of the stimulating electromagnetic wave approaches the THz, $\omega \tau \approx 1$, and the conductivity of doped semiconductors becomes complex and strongly frequency-dependent. In this regime the Drude model is no longer adequate. Several empirical fits have been proposed, but because of the scarcity of experimental data, none is sufficiently parameterized to be broadly adopted.

We have developed a multiphysics computational technique for semiconductor carrier transport at THz frequencies. The technique combines the ensemble Monte Carlo (EMC) simulation of carrier transport with the finite-difference time-domain (FDTD) solver of Maxwell’s curl equations and the molecular dynamics (MD) technique for short-range Coulomb interaction. At each time step, electric and magnetic fields from FDTD and MD influence EMC carrier motion according to the Lorentz force. Likewise, microscopic currents from carrier motion in the EMC influence FDTD electric field updates according to Ampere’s law, and EMC charge density defines MD fields according to Coulomb’s law.

The strength of the EMC/FDTD solver was first established though characterization of silicon of low doping density. We demonstrated the necessity for rigorous enforcement of Gauss’s law for FDTD solvers with charged particles. This work established a new understanding of the capabilities of FDTD to accurately predict the diverging fields surrounding mobile charges. The calculated complex conductivity of doped bulk silicon with doping density $n_0 = 5.47 \times 10^{14} \text{ cm}^{-3}$ under THz-frequency stimulation shows excellent agreement with experimental data.

The technique was extended to high carrier density materials through incorporation of MD. A new technique has been developed to combine electric fields from MD with electromagnetic
fields from FDTD without double counting the fields. The technique demonstrates improved accuracy over previous methods. The complex conductivity calculated by EMC/FDTD/MD shows excellent agreement with experimental data for silicon of doping density $n_0 = 3.15 \times 10^{16} \text{ cm}^3$ under THz-frequency stimulation.

The EMC/FDTD/MD technique was further extended to describe the exchange interaction between indistinguishable electrons, by assuming a finite electron radius. The addition of this description allows EMC/FDTD/MD to accurately describe carrier dynamics in materials with $n_0 \geq 10^{18} \text{ cm}^{-3}$. EMC/FDTD/MD was used to predict the complex conductivity of doped silicon at room temperature for $n_0 = 10^{14} - 10^{19} \text{ cm}^{-3}$ and $f = 0 - 2.5 \text{ THz}$. The results of this calculation are of immediate value to researchers in THz materials and device design. The prediction establishes the strength of EMC/FDTD/MD for THz-frequency characterization of high-conductivity materials.
Chapter 1

Introduction

1.1 Applications of THz frequency radiation

The exploration of the THz frequency range is an exciting area of research in the worldwide scientific community. The THz regime is positioned between the microwave and optical frequency ranges in the electromagnetic spectrum, with wavelengths between 1000-100 $\mu$m (0.3-3 THz) [6]. Like the optical range, it offers high resolution in tomographic and imaging applications, due to its short wavelength. THz radiation is more like microwaves and less like optical waves, however, in its increased depth of penetration into many materials. Further, THz waves have the potential to maintain frequency information in the reflected radiation, allowing for increased specification and examination of systems and materials. Table 1.1 provides a comparison of these and more characteristics for the microwave, optical/infrared, X-ray, and THz regimes. Current applications include tomography imaging [7, 8], semiconductor characterization [9, 10], label-free genetic analysis [11], cellular imaging [12, 13], and nondestructive testing [14, 15], to name a few.

While the nearby microwave and optical regimes have a rich history of exploration and application, the absence of cheap, convenient sources for THz radiation has left that frequency range comparatively underused [16]. The ongoing issue of the development of THz sources is the result of the convergence of several physical limitations. Movement from the “bottom-up”, with the adaptation of microwave and electronics technologies to THz frequencies, is arrested by fundamental electron velocity limits in semiconductors [17]. In “top-down” efforts, or adaptation of optical methods to lower THz frequencies, carrier population inversion becomes more difficult.
as the band gap increases beyond a few $k_B T$. Technologies which utilize frequency coupling and nonlinear effects from both the electronics and optical perspectives have produced some interesting results, but for the most part are too inefficient to be broadly useful [18, 19]. More promising advances include the quantum cascade laser and the traveling wave tube amplifier [20, 21].

1.2 Experimental characterizations of silicon

Contributing to these difficulties are gaps in our understanding of fundamental material characteristics under THz radiation. Since the advent of THz time-domain spectroscopy (THz-TDS) 20 years ago, extensive experimental work has examined the THz characteristics of doped bulk silicon [2, 4, 22–32]. The seminal THz-TDS characterizations extracted the complex transmission spectrum of semiconductor samples through the use of freely-propagating THz beams. The high accuracy of this technique is mainly limited by uncertainties in sample thickness that lead to minor uncertainties in the transmission amplitude, and comparatively large ($\sim 10\%$) uncertainties in the phase [22].

As carrier density increases to around $10^{17} \text{ cm}^{-3}$, the increased opacity of silicon precludes transmission-based characterization [28]. The development of reflection-based THz-TDS in 1996 [33] has since permitted extensive study of optically dense media [24, 28]. In reflecting THz-TDS the exact placement and orientation of the sample is critically important. In analogy to uncertainties from sample thickness in transmission THz-TDS, here small deviations in sample position contribute to uncertainty in the reflection spectrum amplitude and larger uncertainties in phase. This uncertainty may be minimized by analytically sweeping the relative positions of sample and reference plane; see, for example, Ref. [28]. While careful implementation of reflecting THz-TDS produces excellent results, the sensitivity of the technique has prompted research into other THz-regime characterization methods [2, 30–32].

In summarizing available experimental results on the THz characteristics of doped silicon, we consider only those reports which provide sufficient data for comparison: the room temperature $dc$ resistivity or assumed equivalent doping density, as well as THz-range fitting doping density or plasma frequency [4, 22, 24, 27–30]. These data are shown in Table 1.2. In nearly every case,
these results were extracted from observed reflection and transmission spectra assuming Drude model behavior. The Drude model prediction for frequency-dependent complex conductivity is given by

$$\sigma(\omega) = \frac{\sigma(0)}{1 - i\omega\tau},$$  \hspace{1cm} (1.1)

where $\sigma(0)$ is the $dc$ conductivity,

$$\sigma(0) = \frac{n_0q^2\tau}{m^*},$$  \hspace{1cm} (1.2)

$n_0$ is the carrier density, $q$ is the electron charge, $m^*$ is the carrier effective mass in the material, and $\tau$ is the characteristic scattering time. In a realistic material $\tau$ is a function of energy. In this discussion, we use “$\tau$” to represent an appropriate average over the ensemble of electrons [34]. The Drude model conductivity describes the material according to the so-called relaxation time approximation [34]. If we consider only the data in Table 1.2 in which carrier density and mobility are taken as fitting parameters, the fit to the Drude model requires assumed doping densities that average $\sim 27\%$ lower than those calculated from the known $dc$ resistivity, and calculated mobilities $\sim 34\%$ higher than those found at $dc$. This suggests that $\tau$ energy-dependence sufficiently impacts THz-frequency properties that it must be accounted for by the conductivity model [22]. Several other models have been developed to incorporate $\tau$ energy dependence, with promising results [4, 22].

The ill-fit of the Drude model to doped silicon at THz frequencies, and the absence of another well-accepted model, makes prediction of THz-frequency materials properties of arbitrarily doped silicon difficult. Therefore, a comprehensive simulation of THz-frequency conduction in doped semiconductors that is based on a detailed microscopic picture of carrier-field interaction promises to fill an important gap in our understanding of high-frequency transport.

1.3 Carrier dynamics in silicon under electromagnetic stimulation

Pure undoped silicon is almost completely transparent and nondispersive under THz-frequency radiation, more so than quartz, sapphire, or fused silica, making silicon a very attractive THz-optics material [23]. However, this behavior is only observed in extremely pure samples.
Carriers introduced by low-level doping and impurities strongly impact the THz-frequency materials characteristics of silicon [23]. As doping density is increased, silicon becomes quite opaque to THz radiation [22]. Because pure silicon is extremely transparent, it is reasonable to assume that carrier-field dynamics within silicon are solely responsible for silicon’s opacity under THz radiation [23].

In metals and highly doped semiconductors, the strong interactions between densely packed charged particles significantly impact materials properties [35]. These strong interactions cannot be adequately described by grid-based field solvers such as FDTD and Poisson’s equation solvers [36]. At carrier densities above $10^{19}$ cm$^{-3}$, the exchange interaction between indistinguishable electrons can significantly impact bulk materials properties [3, 37–39].

1.3.1 Electrostatic field interaction with high-conductivity silicon

The relevant mechanisms that relax the carrier distribution of doped silicon result from carrier-phonon interactions and Coulomb interactions among carriers and between carriers and stationary ions. For silicon at room temperature with $n_0 < 10^{16}$ cm$^{-3}$, carrier-phonon interactions dominate ensemble relaxation, via acoustic intravalley and intervalley scattering [40]. As $n_0$ increases above $10^{16}$ cm$^{-3}$, Coulomb interactions gain importance and carrier mobility falls rapidly. Carrier-ion scattering is elastic, and so cannot change the mean ensemble energy, but the interaction does randomize carrier momentum and this increases resistivity. Carrier-carrier scattering has only a second-order effect on the $dc$ mobility; it tends to relax the ensemble toward a Maxwellian distribution or Fermi-Dirac distribution, depending on doping, but does not change the mean energy or momentum of the ensemble. In this $n_0$ regime, both Coulomb interactions and carrier-phonon scattering events significantly impact ensemble relaxation.

Above $10^{18}$ cm$^{-3}$, the carrier ensemble becomes degenerate, so the Pauli exclusion principle begins to influence phonon scattering rates. Carrier-phonon scattering events are only permitted if the final carrier momentum state is available. A significant portion of phonon collisions may be forbidden as a result, reducing the impact of lattice interactions on the ensemble [41]. At the same time, the Coulomb interaction among carriers and ions becomes more important as
the charged particles routinely interact at close range. Collective carrier motion begins to significantly impact material properties [3]. Interactions between indistinguishable electrons are influenced both by Coulomb forces and the exchange interaction. The exchange interaction is a geometrical consequence of the Pauli exclusion principle that manifests as a reduction in the force between indistinguishable electrons [3,38,39,42]. At very high doping densities, \( n_0 > 10^{19} \text{ cm}^{-3} \), exchange interactions between indistinguishable electrons can significantly affect bulk materials properties [3, 37–39]. Finally, observe that the effective Bohr radius for a bound electron in the ground state of a phosphorus dopant atom in silicon is \( \approx 13.8 \) Å [43], and at \( 10^{19} \) cm\(^{-3} \) doping density the average radius \( r_s \) of the volume occupied by a single electron, \( r_s = (3/4\pi n_0)^{1/3} \), is about 28 Å, or twice that.

### 1.3.2 Electrodynamic field interaction with high-conductivity silicon

When discussing \( \text{ac} \) material response, we consider the carrier plasma frequency \( \omega_p \), defined as

\[
\omega_p^2 = \frac{n_0 q^2}{\epsilon m^*}.
\]  

(1.3)

\( \omega_p^{-1} \) is the time scale on which the carrier ensemble reacts to applied fields. The relaxation time \( \tau \) is the time scale for ensemble momentum randomization. For doped semiconductors, \( \omega_p \) and \( \tau^{-1} \) are typically in the THz frequency range [44].

For stimulating frequency \( \omega \) significantly below \( \tau^{-1} \) and \( \omega_p \), the ensemble response to the applied field is effectively instantaneous. Ensemble momentum randomization takes place on a time scale much shorter than the period of stimulation, so carrier scattering provides a continuous damping force on the ensemble response to the field. As a result, \( \vec{J} \) and \( \vec{E} \) are in phase and related by a real conductivity.

At THz frequencies where \( \omega \approx \tau^{-1} \) and \( \omega_p \), the ensemble responds strongly to the field, but the response is not effectively instantaneous. As a result, there is a phase shift between \( \vec{J} \) and \( \vec{E} \), and \( \sigma \) is complex [45]. In the classical description, the depth at which the field amplitude is
attenuated by $1/e$ is given by the skin depth $\delta$ of the material [46],

$$\delta = \frac{1}{\omega \sqrt{\mu \epsilon} \left\{ \frac{1}{2} \left[ \sqrt{1 + \left( \frac{\omega^2 \tau}{\omega} \right)^2} - 1 \right] \right\}^{1/2}}$$  \hfill (1.4)

where $\mu$ is permeability and we have used $\sigma = \epsilon \omega^2 p \tau$. Collective carrier motion is much more important in this case. Since radiation penetration into the material is more shallow, surface effects are more important than at low frequency.

### 1.4 Existing work in electrodynamic carrier transport techniques

Outside of the regime where the stimulating frequency is comparable to the carrier relaxation rate, the effects of carrier transport and electromagnetic (EM) wave propagation are sufficiently decoupled to permit independent treatment in numerical models. Accordingly, most of the recent advances and applications of charge transport solvers use simple electrostatic solvers to incorporate electric field effects [34, 41, 47, 48]. At the same time, EM analyses use simpler bulk material models alongside full-wave electrodynamic solvers [49].

As device speeds continue to increase in step with decreasing critical dimensions, electrodynamic effects directly influence high-frequency device performance, and analyses that rely on quasielectrostatic fields lose accuracy [50, 51]. Similarly, as the frequency of stimulating EM fields increases from the lower microwave range, the assumptions inherent to low-frequency material models (namely, that $\omega \tau \ll 1$) lose validity. This prominent interplay between carrier dynamics and electromagnetic wave dynamics in the sub-THz and THz regimes has been the driving force behind advancements in modeling techniques that combine a charge transport kernel with a computational electromagnetic solver, hereafter referred to as global modeling techniques.

Interest in plasma fusion devices prompted early work into the development of global models. In 1966, pioneering work by Langdon and Dawson demonstrated for the first time the viability of an EM-particle solver [52]. Buneman’s 1968 report [53] detailed the advantages of time-integrating Maxwell’s equations using the Yee cell [54]. Several applications of this technique followed [55–57]. Boris gave a detailed account of the global model as it stood in 1970 [58]. Advances in the 1970s addressed self-force [59] and numerical Cherenkov instabilities [60, 61].
The global models resulting from these and other advances are described in detail in Refs. [62–64].

The technique was limited by the computational capabilities of the era. EM calculations exhibited a continual linear increase in noise [65, 66]. Additionally, system timescales varied too greatly to include major relevant interactions without forcing a reduced speed of light and simultaneously increased electron mass. A 1980 review by Buneman et al. suggested that a 3D EM-particle tracking solver could provide qualitative insight, but quantitative results were only possible for reduced systems [67].

For a number of years after the early 1980s, particle tracking models and EM solvers advanced more or less independently. Many of the early EM-particle reports used electromagnetic models that were clearly early finite-difference time-domain (FDTD) implementations. Researchers continued to advance FDTD; a detailed history is available in Refs. [49, 68]. The Monte Carlo technique had already been of great interest for many years, and the discipline continued to mature in this time; for a history of the ensemble Monte Carlo (EMC) technique see Ref. [69].

The need for greater efficiency and decreased memory requirements drove exploration into alternative global modeling approaches. Hydrodynamics transport models and drift-diffusion models have been used successfully in place of EMC in many cases [51, 70–79] offering decreased computational overhead [51]. Numerical simulations combining full-wave electromagnetic solutions via modern FDTD with particle-based transport models via EMC were first reported by El-Ghazaly, Joshi, and Grondin in 1990 [80]. This work provided a more accurate model of sub-picosecond carrier transport in photoconductive switches than had previously been available. A comprehensive review of the global modeling efforts of the 1980s and 1990s was conducted by Grondin, El-Ghazaly, and Goodnick [51].

Modern improvements in computer processing power have eased the restrictions on computational burden in current device and materials simulations, allowing researchers to use more computationally intensive techniques such as EMC and FDTD. Application of a combined 3D full-band cellular Monte Carlo device simulator with a 3D full-wave FDTD solver was first demonstrated in 2003, for modeling the electromagnetic environment surrounding a simple pin
diode [81]. This simulator was used to analyze high-frequency transistor behavior using direct capture of incident and reflected voltage waves from a full-wave analysis of a 3D MESFET device [82]. Further developments include accurate models of electron transport [83, 84] and the full-wave effects [85] in ultrasubmicrometer-gate, pseudomorphic, high-electron mobility transistors (pHEMTs).

1.5 Summary of contributions

This dissertation aimed at developing a multiscale computational technique for high-frequency carrier transport in semiconductors and metals. The technique provides a testbed to examine the relationship between microscopic properties and frequency-dependent conductivity in bulk materials. In the following, we will describe the development of EMC/FDTD/MD technique. To demonstrate the technique’s capabilities, we provide the results for the complex conductivity of doped silicon at room temperature for carrier densities of $10^{14} - 10^{19}$ cm$^{-3}$ at frequencies of $0 - 2.5$ THz. The work performed for this dissertation has led to two journal articles [44, 86] with two more in preparation, six oral conference presentations [87–92], and two poster presentations [93, 94]. The main accomplishments of the project are described below.

1.5.1 Research accomplishments

1) First, a comprehensive computational solver has been developed for high-frequency characterization of materials with low carrier density. The solver combines the ensemble Monte Carlo technique for stochastic representation of carrier dynamics under the Boltzmann transport equation and the finite-difference time-domain technique for Maxwell’s curl equations. This work elucidates the importance of rigorous enforcement of Gauss’s law, in order to avoid unphysical charge buildup and enhance solver accuracy. We have applied an efficient technique to calculate the EMC current density that ensures satisfaction of Gauss’s law in FDTD. This is the first time this technique has been used in the research communities for EMC/FDTD methods of materials and device characterization. Previous research relied on repeated computationally intensive
solutions to Poisson’s equation to ensure accuracy in the diverging fields [81, 82]. We have compared the predicted conductivity calculated by EMC/FDTD with published experimental data for the complex conductivity of silicon at $n_0 = 5.47 \times 10^{14} \text{cm}^{-3}$ [4]. The calculated data show excellent agreement with the experimental data. This work demonstrates the capability of this electrodynamic particle solver to accurately predict the complex conductivity of materials at THz frequencies.

(2) The multiscale computational technique has been extended to materials with high conductivity, through the addition of the molecular dynamics technique for short-range Coulomb interaction among carriers and ions. MD calculates interactions among carriers and ions that occur on length scales shorter than the FDTD grid cell size. These strong interactions significantly impact materials properties for carrier densities above $10^{16} \text{cm}^{-3}$. The EMC/FDTD/MD solver calculates electromagnetic interactions between particles by combined field calculations from FDTD and MD. Both FDTD and MD calculate the Coulomb field between charged particles. We have developed a new technique to allow accurate representation of fields between these two solvers, without double counting the Coulomb fields. We have compared the predicted conductivity calculated by EMC/FDTD/MD with published experimental data for the complex conductivity of silicon at $n_0 = 3.15 \times 10^{16} \text{cm}^{-3}$ [4]. The calculated data show excellent agreement with the experimental data at this moderate doping density.

(3) The final extension that has been made to the technique incorporates a finite-volume treatment of electrons and ions in MD. The exchange interaction between indistinguishable electrons can significantly affect bulk materials properties for carrier densities greater than $10^{18} \text{cm}^{-3}$ [3, 37–39]. The new method describes the exchange interaction between indistinguishable electrons. EMC/FDTD/MD has also been extended to describe the finite radius of dopant ions in the material. EMC/FDTD/MD includes all relevant carrier-phonon interactions, as well as all relevant electromagnetic effects, and effects from the Pauli exclusion principle in materials with high carrier densities. We have used EMC/FDTD/MD to parameterize the electron and ion
radii for doped silicon under \( dc \) stimulation, and then we have calculated the THz-frequency conductivity of silicon for \( n_0 = 10^{14} - 10^{19} \) cm\(^{-3}\). The EMC/FDTD/MD solver is a powerful tool for prediction of THz-frequency conductivity in materials with high carrier density.

### 1.5.2 Organization of chapters

Chapter 2 gives an overview of the three techniques that make up the EMC/FDTD/MD solver. Section 2.1 describes the ensemble Monte Carlo technique for diffusive-regime carrier transport in doped silicon. Section 2.2 describes FDTD for the finite-difference solution to the time-varying Maxwell’s equations. Details are given on boundary condition treatments and current sourcing techniques. Section 2.3 describes the molecular dynamics technique. The section outlines the motivation for using MD instead of a semiclassical scattering rate for carrier-carrier and carrier-ion interaction.

Chapter 3 describes implementation of EMC/FDTD for 2D analysis of lightly doped silicon. In Section 3.1, the accuracy requirements of EMC/FDTD are explored. The section considers the impact of impedance mismatch between the EMC/FDTD coupled region and the pure-FDTD region. Section 3.2 describes the importance of enforcing Gauss’s law, and provides efficient techniques to ensure enforcement of Gauss’s law in the EMC/FDTD solver, without repeated solutions to Poisson’s equation.

In Chapter 4, the EMC/FDTD technique is extended with MD to describe the short-range Coulomb interaction among carriers and between carriers and ions. Section 4.1 describes a new technique to combine FDTD and MD fields without double counting the Coulomb fields. Section 4.2 describes the MD formulation that incorporates exchange interaction between indistinguishable electrons, and the finite size of dopant ions. To determine the appropriate electron and ion radii, in section 4.2 we compare the known \( dc \) conductivity of doped silicon with the calculated \( dc \) conductivity of doped silicon as a function of the two radii, as determined by EMC/FDTD/MD. The results are tabulated and presented in that section.

In Chapter 5, the conductivity of doped silicon under THz-frequency stimulation is given as calculated by EMC/FDTD/MD. First, in Section 5.1, the conductivity predicted by
EMC/FDTD/MD is compared with available experimental data. The technique shows excellent agreement with experiment. In Section 5.2, we extend the prediction to silicon with carrier densities $n_0 = 10^{14} - 10^{19}$ cm$^{-3}$.

Appendix A provides thorough detail on implementation of EMC/FDTD/MD, along with accuracy and stability criteria specific to this combined technique. Appendix B gives derivations of the equations needed for implementation of the exchange interaction in MD.
<table>
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<tr>
<th>Regime</th>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
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<tbody>
<tr>
<td>Microwave</td>
<td>- High sensitivity devices available</td>
<td>- Low resolution</td>
</tr>
<tr>
<td></td>
<td>- Good penetration in many materials</td>
<td>- Require bigger apertures</td>
</tr>
<tr>
<td></td>
<td>- Not hazardous</td>
<td>- Reflected by metal and absorbed by water</td>
</tr>
<tr>
<td></td>
<td>- No contact with the sample</td>
<td></td>
</tr>
<tr>
<td>Infrared</td>
<td>- High sensitivity devices available</td>
<td>- Low penetration in the materials</td>
</tr>
<tr>
<td></td>
<td>- 2D array devices available</td>
<td>- Background noise reduces performance</td>
</tr>
<tr>
<td></td>
<td>- Designs based on optical technique</td>
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<tr>
<td></td>
<td>- Good resolution</td>
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</tr>
<tr>
<td></td>
<td>- Not hazardous</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- No contact with the sample</td>
<td></td>
</tr>
<tr>
<td>X-Ray</td>
<td>- High sensitivity devices available</td>
<td>- Hazardous</td>
</tr>
<tr>
<td></td>
<td>- 2D array devices available</td>
<td>- Strict maintenance policies</td>
</tr>
<tr>
<td></td>
<td>- Highest penetration power</td>
<td>- No spectroscopic information</td>
</tr>
<tr>
<td></td>
<td>- Excellent resolution</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- No contact with the sample</td>
<td></td>
</tr>
<tr>
<td>Terahertz</td>
<td>- Good resolution</td>
<td>- Low scan time</td>
</tr>
<tr>
<td></td>
<td>- Good penetration in many materials</td>
<td>- Reflected by metal and absorbed by liquid water</td>
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<tr>
<td></td>
<td>- Frequency information available</td>
<td></td>
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<tr>
<td></td>
<td>- Highly sensitive</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Not hazardous</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- No contact with the sample</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1 Comparison of terahertz radiation to other frequency regimes in the context of nondestructive topical or subsurface examination of materials. Table adapted from Ref. [1]
Table 1.2 Summary of experimental results on doped bulk silicon under THz radiation, as obtained from THz-TDS, chronologically ordered. Values in bold were calculated for comparison purposes, based on data from the referenced work. The table shows the conductivity model assumed in the original work; the material *dc* characteristics including resistivity, doping density, and mobility; the fitted THz characteristics including doping density and mobility; the percent change from *dc* to THz doping density and mobility values; and the data citation. In most cases, both $n_0$ and $\mu$ are taken as fitting parameters; Ref. [2] assumes known $\mu$ for all calculations.

<table>
<thead>
<tr>
<th>Model</th>
<th>$\rho$ (Ω cm)</th>
<th>$n_0$ (cm$^{-3}$)</th>
<th>$\mu$ (cm$^2$/Vs)</th>
<th>$n_0$ (cm$^{-3}$)</th>
<th>$\mu$ (cm$^2$/Vs)</th>
<th>$\Delta n_0$ %</th>
<th>$\Delta \mu$ %</th>
<th>Ref.</th>
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<td>40</td>
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<td>$3.4 \times 10^{14}$</td>
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<td>34</td>
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<td>$4.0 \times 10^{14}$</td>
<td>2000</td>
<td>23</td>
<td>-47</td>
<td>[4]</td>
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<tr>
<td>Cole-Davidson</td>
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<td>$3.2 \times 10^{16}$</td>
<td>1083</td>
<td>$2.3 \times 10^{16}$</td>
<td>1280</td>
<td>28</td>
<td>-18</td>
<td>[4]</td>
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<td>0</td>
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<td>1350</td>
<td>-6</td>
<td>0</td>
<td>[2]</td>
</tr>
<tr>
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<td>1350</td>
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<td>1280</td>
<td>14</td>
<td>-17</td>
<td>[29]</td>
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Chapter 2

Constituent techniques

In this chapter, we provide an overview of the fundamentals of each of the three constituent techniques – the ensemble Monte Carlo, finite-difference time-domain, and molecular dynamics methods – with details appropriate for the EMC/FDTD/MD method. We direct the interested reader to the references for further details.

2.1 Ensemble Monte Carlo (EMC)

Ensemble Monte Carlo (EMC) is a powerful stochastic method used for numerical simulation of carrier transport in semiconductors in the scattering-limited (diffusive) regime [69]. It has been used for almost four decades to accurately simulate carrier transport properties of bulk semiconductors and semiconductor-based devices, and it provides a benchmark for drift-diffusion and hydrodynamics equations approaches [34]. EMC technique details are discussed below; for more information see Refs. [34, 41, 47, 48, 62, 69, 95, 96].

On timescales longer than typical relaxation times, EMC yields the numerical solution to the Boltzmann transport equation

\[
\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} f + \vec{F} \cdot \nabla_{\vec{p}} f = \frac{\partial f}{\partial t}_{\text{scatter}}
\]  

(2.1)

where \( f(\vec{r}, \vec{p}, t) \) is the semiclassical distribution function, \( \vec{v} \) is the carrier velocity, and \( \vec{F} \) is the total force acting on the carrier. \( f(\vec{r}, \vec{p}, t) \) describes the probability that a carrier exists within \( d^3\vec{r} \) of position \( \vec{r} \) and within \( d^3\vec{p} \) of momentum \( \vec{p} \) at time \( t \). \( f(\vec{r}, \vec{p}, t) \) evolves in time according to Eq. (2.1) as a result of diffusion (included in the second term) and carrier drift due to external
forces (described by the third term). The collision integral (described by the term on the right hand side of the equation) describes the impact of the material-specific scattering mechanisms on the carrier ensemble.

The EMC simulates carrier dynamics in semiconductors by tracking the evolution of a large ensemble of particles [typically O(10^{5})] through time. Each carrier undergoes a series of scattering events and free flights. A random number generator is used to calculate the duration of each free flight, choose the mechanism for the next scattering event, and update the particle’s momentum and energy as needed, according to the appropriate statistical probabilities. Momentum is updated during free flight according to the Lorentz force,

\[ \vec{F} = q(\vec{E} + \vec{v} \times \vec{B}), \]  

(2.2)

where \( q \) the carrier charge, and \( \vec{E} \) and \( \vec{B} \) are the electric and magnetic fields, respectively. Macroscopic quantities of interest (such as charge density and drift velocity) may be readily extracted via ensemble averages.

The majority of EMC implementations employ the quasielectrostatic assumption, where the electromagnetic period of oscillation is sufficiently long compared to carrier scattering times that the field may be considered constant within any time step. A simplified flowchart of the general electrostatic EMC approach, self-consistently coupled to a Poisson’s equation solver, is shown in Fig. 2.1. In this implementation, the Poisson solver calculates the grid-based scalar potential that results from the instantaneous charge density and imposed biasing conditions.

In this work, the EMC describes carrier dynamics in \( n \)-type silicon at room temperature in the low-field regime. We use the effective mass approximation with first-order nonparabolicity [69]. Acoustic intravalley and zeroth-order intervalley phonon scattering are included via semiclassical scattering rates [97]. All material parameters and constants are taken from Ref. [98]. Coulomb interaction is treated via FDTD and MD, and therefore we do not use explicit scattering rates to describe ionized impurity, plasmon, or carrier-carrier scattering. The Pauli exclusion principle is enforced for each scattering event with the rejection technique [69].
2.2 Finite difference time domain (FDTD)

FDTD is a highly accurate and efficient computational technique for modeling electromagnetic wave interactions with physical structures. Advances in absorbing boundary conditions, dispersive and nonlinear materials modeling, low-numerical-dispersion schemes, unconditionally stable schemes, and incident wave source conditions make FDTD a highly attractive tool for electromagnetic analysis. Some details on these advances are given here, and further information is available in Ref. [49].

FDTD is a direct numerical solution of the time-dependent Maxwell’s curl equations,

\[
\mu \frac{\partial \vec{H}}{\partial t} = - \nabla \times \vec{E} - \vec{M}, \quad (2.3a)
\]

\[
\varepsilon \frac{\partial \vec{E}}{\partial t} = \nabla \times \vec{H} - (\vec{J} + \sigma \vec{E}), \quad (2.3b)
\]
where $\vec{E}$ and $\vec{H}$ are the electric and magnetic fields, respectively, $\epsilon$, $\mu$, and $\sigma$ are the permittivity, permeability, and conductivity of the medium, and $\vec{J}$ and $\vec{M}$ are the electric and magnetic source current densities.

The fully explicit FDTD algorithm is obtained by numerically approximating the spatial partial derivatives in Eqs. (2.3) with centered finite differences, and numerically integrating the resulting system of spatial difference equations with respect to time via a centered finite-difference approximation of the temporal partial derivatives. The staggering of $\vec{E}$ and $\vec{H}$ in time yields an efficient leapfrog time-marching scheme wherein all of the $\vec{E}$ components are updated at time step $n$ (corresponding to a physical time of $n\Delta t$) using previously stored $\vec{H}$ data, and then all of the $\vec{H}$ components are updated at time step $n + 1/2$ using the just computed $\vec{E}$ data.

The grid-based vector quantities – $\vec{E}$, $\vec{H}$, $\vec{J}$, and $\vec{M}$ – are positioned relative to each other according to the Yee grid cell shown in Fig. 2.2 [54]. Figure 2.2 illustrates the staggered sampling of $\vec{E}$ and $\vec{H}$ over one grid cell in a 3D Cartesian spatial lattice. Each vector component of $\vec{J}$ is spatially collocated with the corresponding component of $\vec{E}$; $\vec{M}$ and $\vec{H}$ are similarly collocated. Position within the discrete grid is defined in terms of grid indices $(i, j, k)$. The grid point at $(i, j, k)$ has physical location $[x(i), y(j), z(k)]$ where $x(i) = i\Delta x$, $y(j) = j\Delta y$, and $z(k) = k\Delta z$. The 3D FDTD grid used in this EMC/FDTD/MD implementation is defined with cubic grid cells, where $\Delta x = \Delta y = \Delta z$.

The FDTD formulation describes time evolution of $\vec{E}$ and $\vec{H}$ according to initial conditions, sourcing via $\vec{J}$ and $\vec{M}$, and domain boundary conditions [49]. The first two of these points will be discussed in detail in Section 3.2. Domain boundaries may be treated by any of several techniques, the most popular of which is the perfectly matched layer (PML) absorbing boundary condition [99]. This method defines a continuous grading of impedance-matched absorbing material properties over the PML region, which occupies a layer of grid cells typically 10-20 grid cells thick at the boundaries of the FDTD computational grid. There are many variations on the original PML formulation, designed to attenuate outward-propagating radiation and minimize reflections from the domain boundary under various special circumstances [100]. Thus the main grid is electromagnetically isolated from the grid boundary, permitting finite-grid representation
Figure 2.2 Illustration of the staggered electric and magnetic field components about a single Yee cell in a 3D space lattice. The axis origin is positioned at index \((i, j, k)\), and the opposite corner has index \((i+1, j+1, k+1)\). Each electric field component, on the edge of the cell, is surrounded by four circulating magnetic field components. Likewise, each magnetic field component, normal to the face of the cell, is surrounded by four circulating electric field components.

of an infinite space. Other boundary conditions, such as fully reflecting boundaries or transparent periodic boundaries, may alternatively be enforced, to suit a particular application [49].

The total-field/scattered-field (TFSF) formulation launches electromagnetic energy into the FDTD grid via sourced equivalent current densities located at the TFSF boundary [49]. This boundary is typically a closed double layer of electric and magnetic current densities, which source electromagnetic fields into the enclosed space (the total-field region). In the basic implementation, TFSF calculates the desired incident fields \(\vec{E}_{\text{inc}}\) and \(\vec{H}_{\text{inc}}\) in an auxiliary 1D FDTD grid. The equivalent current densities are then given by 

\[
\vec{J}_{\text{TFSF}} = -\hat{n} \times \vec{H}_{\text{inc}} \quad \text{and} \quad \vec{M}_{\text{TFSF}} = \hat{n} \times \vec{E}_{\text{inc}},
\]

where \(\hat{n}\) is the unit vector normal to the TFSF boundary [101]. The TFSF formulation applies these equivalent current densities at the TFSF boundary, according to Eqs. (2.3) [101]. As a result, the fields calculated in the 1D grid are launched as plane waves into the 3D grid total-field region [49]. Radiated fields, from scattering or other current sources in the total-field region, propagate through the grid, and pass through the transparent TFSF boundary into the scattered-field region.
2.3 Molecular dynamics (MD)

In metals and semiconductors with higher doping densities, the strong Coulomb force between charged particles significantly impact materials properties [35]. The difficulty of accurately incorporating the strong Coulomb interaction into computational techniques is a long-standing problem [35]. The molecular dynamics (MD) technique has been described as the ideal and natural way to account for charged particle interactions in materials, and, when combined with EMC, it has predicted materials properties with very high accuracy [37, 102, 103]. However, the technique is very computationally intensive, and for that reason it has generally been avoided in the computational electronics community. Additionally, the fully-classical MD implementation cannot accurately describe high-$n_0$ materials, where the exchange interaction between indistinguishable electrons significantly affects bulk properties [3, 38, 39].

Charged particle interactions may instead be treated via semiclassical scattering rate formulations. Rates are computed individually for binary carrier-carrier scattering, collective carrier-carrier or plasmon scattering, and binary carrier-ion or ionized impurity scattering [41, 42, 47, 97, 104–106]. The binary carrier-carrier rates have in some cases been extended to describe exchange interaction [42, 106].

These semiclassical rates are attractive for their small computational burden (though not always; see Ref [42]) and their incorporation of the Pauli exclusion principle, but they present their own difficulties. Both of the binary scattering rates are usually formulated in the Born approximation, which is recognized to overestimate scattering [41, 97]. Additionally, these two rates assume that each Coulomb interaction involves only two particles, an assumption that can only be valid at low particle densities [102, 103, 107]. In our tests, the carrier-carrier and carrier-ion scattering rates overestimate scattering and artificially lower calculated $\sigma$ in the low-$n_0$ regime where Coulomb interaction should negligibly impact materials properties. It has been shown that plasmon scattering is well described by the long range carrier-field interactions included in most particle-field solvers, so that it need not be addressed with a semiclassical scattering rate in a simulation that also includes long-range fields [42].
Molecular dynamics describes the behavior of collections of particles according to particle-particle interaction [108]. For an ensemble of electrons and ions, MD finds the pairwise electrostatic force between each carrier and all other carriers and stationary ions in the vicinity. In an ensemble of $N_{\text{elec}}$ electrons and $N_{\text{ion}}$ ions, the MD prediction for the net Coulomb force acting on the $i^{th}$ electron is

$$
\vec{F}_i = \sum_{j \neq i}^{N_{\text{elec}}} \frac{q^2}{4\pi\epsilon (\vec{r}_i - \vec{r}_j)^2} \hat{r}_{ij} + \sum_{j=1}^{N_{\text{ion}}} \frac{qQ}{4\pi\epsilon (\vec{r}_i - \vec{r}_j)^2} \hat{r}_{ij}
$$

where $Q$ is the ion charge, $\epsilon$ is the static material permittivity, $\hat{r}_{ij} = (\vec{r}_i - \vec{r}_j)/|\vec{r}_i - \vec{r}_j|$, and $\vec{r}_i$ is the position of the $i^{th}$ particle. In the particle solver, the MD forces describe the full electrostatic system. The MD technique avoids assumptions about screening lengths or the number of particles likely to participate in any particular interaction, and it naturally incorporates all collective ensemble behavior [37, 102]. In addition, the MD technique has been extended to describe exchange interaction between indistinguishable electrons [3, 38, 39]. Even with small numbers of particles, the combined EMC/MD solver has been previously used to accurately predict low-frequency behavior in semiconductors and devices [37, 102, 103].

The fundamental MD calculation is conceptually simple but computationally intensive for large carrier ensembles, scaling with the number of particles as $N^2$ [47, 109]. It is very time consuming to calculate the force on each particle by iterating through the rest of the ensemble. Efforts to reduce the computational load are described in Ref. [110]. When the largest interaction distance between two particles is significantly smaller than the domain length, the computational load can be significantly reduced by eliminating calculations of pairwise interactions over longer distances than the interaction length.

Previous work describing MD combined with electrostatic grid-based field solvers divides the Coulomb interaction into a short-range component, which describes interactions between particles separated by a couple of grid cells, and a long-range component [35,36,103]. The long-range part of the Coulomb interaction is quickly and accurately described by the field solver, and the short-range part is described by MD. The combination of a grid-based solver with MD limits the number of particles involved in each iteration of the MD calculation, significantly reducing the computational load. These solvers have shown excellent representation of $dc$ materials.
properties and semiconductor device characteristics [35, 36, 103]. The novel EMC/FDTD/MD simulation, presented here, calculates long-range Coulomb interaction with FDTD, as described in Section 3.2, and the short-range interaction with MD. Integration of these two field solvers is detailed in Section 4.1.
Chapter 3

EMC/FDTD for 2D analysis of materials with low carrier density

In this section, we explore the use of the EMC/FDTD solver in the context of doped bulk silicon materials characterization. In Sec. 3.1 we describe the specific coupled EMC/FDTD solver used to simulate THz-frequency electromagnetic plane wave interactions with doped bulk silicon, and the method we use to extract the frequency-dependent effective conductivity from the computed fields and currents. We examine simulation performance in the context of predicted conductivity convergence under variation in grid cell size, ensemble size, averaging technique, and impedance mismatch. The following discussion shows the importance of rigorous enforcement of Gauss’s law, in order to avoid unphysical charge buildup and enhance solver accuracy. An efficient technique to calculate the EMC current density that ensures satisfaction of Gauss’s law in FDTD is described. Finally, we compare the simulation results – that is, the predicted effective conductivity – with published experimental results for doped silicon at THz frequencies.

3.1 EMC/FDTD technique characterization

In the combined EMC/FDTD solver, electric and magnetic fields from FDTD influence EMC carrier motion according to the Lorentz force, Eq. (2.2). Microscopic currents resulting from carrier motion in the EMC influence FDTD-computed field values according to Maxwell’s curl equations, Eqs. (2.3). A schematic of the coupling between the solvers is given in Fig. 3.1.
Figure 3.1 Flowchart for the combined EMC/FDTD simulation tool. The carrier transport solver acts on field calculations via the spatially-varying current density $\vec{J}$. The electrodynamic solver acts on charge transport calculations via spatially-varying electric and magnetic fields $\vec{E}$, $\vec{H}$.

3.1.1 Simulation domain

For both EMC and FDTD we use two-dimensional (2D) computational domains defined in the $xy-$plane (Fig. 3.3). The EMC domain is filled with (001) doped silicon with doping density $n_0 = 10^{17}$ cm$^{-3}$. The typical simulation carrier ensemble size is $O(10^5)$. To permit examination of the interaction between these carriers and propagating THz-frequency electromagnetic plane waves, we embed the EMC domain into an FDTD domain.

The FDTD simulation testbed is a semi-infinite half space of doped silicon (Regions B and C in Fig. 3.3) and a semi-infinite half space of air (Region A in Fig. 3.3). Region A is assigned a dielectric constant of 1 and zero conductivity. A dielectric constant of 11.8 is assigned to Regions B and C. Region C is filled with an assumed value for the continuous bulk $dc$ conductivity of doped silicon, $\bar{\sigma}$. Region B contains the embedded EMC domain.

The EMC formulation accounts for the smooth material interface by enforcing specular reflection of carriers at the left and right boundaries of the domain. The top and bottom boundaries are given periodic boundary conditions, to allow unrestricted carrier motion in the vertical direction. Care must be taken at the edges of the coupled region to ensure that EMC current density does not extend beyond the coupled region for any charge assignment scheme.

To allow finite-grid representation of an infinite space, we treat FDTD domain boundaries with convolutional perfectly matched layer (CPML) absorbing boundary conditions which attenuate outward-propagating electromagnetic waves by more than 80 dB [49]. Continuous THz-frequency plane waves are introduced via the analytic field propagation total-field/scattered-field formulation [111]. TE$_z$-polarized plane waves, comprising $E_y$ and $H_z$ components, impinge upon
the coupled region from the left. The plane waves propagate along the $x$–direction, so the dominant force on the carriers is directed along $y$. The periodic boundaries on the top and bottom edges of the EMC domain and the uniform incident field allow bulk EMC simulation within the finite domain. To minimize interaction between EMC charges and FDTD CPML, we define the FDTD domain to be large enough that the diverging fields that surround charges in the coupled region decay significantly before reaching the CPML boundary. The position of the TFSF boundary is arbitrary, so long as it fully encloses the coupled region and does not intersect with the CPML. Fig. 3.2 shows the full simulation flowchart for a coupled EMC/FDTD solver.

Fig. 3.3 shows the 2D spatial distribution of the $E_y$ phasor amplitude, extracted via fast Fourier transform (FFT) over several periods of electromagnetic wave oscillation. The field amplitude is attenuated as a function of depth in both Regions B and C. Amplitude decay in region C corresponds to that expected for a dielectric with conductivity $\bar{\sigma}$. No conductivity is enforced in the coupled Region B; field decay in this region results from the carrier-field interaction, exhibiting the macroscopic phenomenon of the skin effect.

Figure 3.2 Flowchart for the combined EMC/FDTD simulation modeling tool.
Noise in the $E_y$ phasor amplitude in Region B is caused by thermal electron motion; $E_x$, $J_x$, and $J_y$ also exhibit minor fluctuations in phase and amplitude. Transient fields, continually sourced by this noise, propagate to the grid boundary and are attenuated in the CPML. Without high-quality absorbing boundary conditions these simulations would suffer from the same continually increasing noise level that affected the early simulations described in Chapter 1. To reduce the impact of this noise on conductivity calculations, we take spatial averages over small regions surrounding each grid location in the extracted phasor quantities. Increasing the size of the averaging regions decreases phasor quantity noise. The averaging region size must not be increased beyond $\sim 1/20^{th}$ of the smallest electromagnetic feature of interest.

These noise-reduced phasor quantities are used in the effective linear-regime conductivity calculation,

$$\hat{\sigma}(\omega) = \frac{\vec{E}(\omega) \cdot \vec{J}^*(\omega)}{|\vec{E}(\omega)|^2}.$$ (3.1)

The real part of $\hat{\sigma}$ corresponds to power dissipation and is evidenced as the phasor amplitude decay in Fig. 3.3. The imaginary part of $\hat{\sigma}$ corresponds to phase shift between $\vec{E}$ and $\vec{J}$ resulting

![Figure 3.3](image.png)

Figure 3.3 Amplitude of $E_y$ field phasor extracted by FFT over several periods of electromagnetic wave oscillation, where white corresponds to high field amplitude and black corresponds to low field amplitude. The materials interface is indicated by the vertical gray line. The section of the domain shown here lies within the AFP-TFSF boundary; an incident plane wave is sourced from the left boundary. Region B is the EMC/FDTD coupled region, whose boundary is marked by a solid gray box, and Regions A and C are pure-FDTD doped silicon.
Figure 3.4 Average noise of $E_y$ in the EMC/FDTD coupled region for several values of electron ensemble size and grid cell size. $E_y^{\text{noise}}$ is calculated as $\sqrt{\langle |E_y|^2 \rangle - |\langle E_y \rangle|^2}$ and is normalized by $|E_y|$ at the material interface. $\Delta x_{\text{ref}} \approx 400 \text{ nm}$ is a reference grid cell size. Increasing the size of the ensemble reduces noise, as expected, but increasing the grid cell size produces a much larger improvement.

from the delay in material response to applied fields. As the electromagnetic oscillation frequency approaches the carrier scattering rate, we expect the delay in material response to applied fields to increase.

### 3.1.2 Exploration of EMC/FDTD accuracy requirements

Fig. 3.4 shows the variance of $|E_y|$ in Region B as a function of electron ensemble size $N_e$ for several grid cell sizes $\Delta x$. As expected, larger carrier ensembles show decreased phasor quantity noise, at the cost of an increased computational burden. Fig. 3.4 shows dramatic noise reduction for increased $\Delta x$. This improvement directly contrasts the EMC-Poisson solver accuracy requirements, which favor smaller grid cells for improved electrostatic calculations. The EMC/FDTD solver achieves significant noise reduction for larger $\Delta x$ by including a larger number of carriers in each $J_x$ and $J_y$ grid point calculation.
Figure 3.5 Extracted conductivity with varied averaging region size, electron ensemble size, and surrounding bulk conductivity. $N_0$ is a reference ensemble size, typically $O(10^5)$. Larger averaging region size leads to convergence in $\hat{\sigma}$. Level of impedance mismatch between Regions B and C, examined through modified $\bar{\sigma}$, is associated with line type. See text for discussion.

Fig. 3.5 shows $\hat{\sigma}$ as a function of phasor quantity averaging region size, for several values of ensemble size and several levels of impedance mismatch between Regions B and C. As the averaging regions size is increased, $\hat{\sigma}$ converges. Increased ensemble size also leads to convergence in $\hat{\sigma}$, indicating correspondence between decreased phasor quantity noise and convergence in $\hat{\sigma}$.

Finally, Fig. 3.5 allows examination of the impact of impedance mismatch between the EMC/FDTD coupled Region B and the surrounding pure-FDTD Region C. In any single test, the conductivity $\bar{\sigma}$ defined in Region C may not match the conductivity exhibited by the EMC/FDTD coupled region. The resulting impedance mismatch will cause waveguiding and back-reflections within the coupled region. We tested the effect of these reflections on $\bar{\sigma}$ by comparing extracted conductivity values for several tests where $\bar{\sigma}$ was varied through three values, spanning $\hat{\sigma}$. Fig. 3.5 shows the results of this experiment; $\hat{\sigma}$ is insensitive to impedance mismatch between Regions B and C.
3.2 EMC/FDTD, with Gauss’s law

Gauss’s law describes the diverging electric fields surrounding charges, according to

\[ \nabla \cdot \vec{E} = \frac{\rho}{\epsilon}, \]  

(3.2)

where \( \rho \) is the charge density. These fields are responsible for the Coulomb interaction between particles. A typical quasielectrostatic EMC implementation includes the numerical solution of Poisson’s equation which satisfies Gauss’s law by definition. In contrast, there is no explicit solution to Gauss’s law in the FDTD formulation based on Eqs. (2.3).

However, Gauss’s law is implicitly satisfied by FDTD fields for EMC charges if the initial field distribution satisfies Gauss’s law, and if the continuity equation is enforced [44, 86, 112]:

\[ \nabla \cdot \vec{J} = -\frac{\partial \rho}{\partial t}. \]  

(3.3)

In the typical quasielectrostatic EMC implementation which includes the numerical solution of Poisson’s equation, \( \rho \) and \( \vec{J} \) are spatially collocated on the grid and the continuity equation Eq. (3.3) is trivially satisfied. In contrast, in the EMC/FDTD simulation domain, \( \vec{J} \) and \( \rho \) are assigned to two different, spatially staggered grids; see Fig. 3.6.

The combined technique grid cell is defined on a modified Yee grid cell, that includes charge density \( \rho \) at the grid intersections, indicated by the open circles in Fig. 3.6 [63]. All other vector and material quantities are identical to those of the Yee cell that is the basis of FDTD. The small approximations inherent to the grid assignment of \( \vec{J} \) and \( \rho \) in the coupled EMC/FDTD region can result in a violation of Eq. (3.3). Here, we explicitly enforce Eq. (3.3) by calculating a carrier’s contribution to \( \vec{J} \) from its change in position over a time step rather than from its known instantaneous velocity. The resulting \( \vec{J} \) is assigned to the grid according to the carrier’s spatial charge profile [112, 113]. An important advantage of the explicit enforcement of the continuity equation, and thereby the implicit satisfaction of Gauss’s law, is that long-range Coulomb interactions among carriers are automatically accounted for during the simulation. This eliminates the need for repeated solution of Poisson’s equation during runtime and dramatically increases computational speed.
Figure 3.6 3D FDTD grid cell that has been extended to describe charge density $\rho$ at integer grid locations. Vector field and current density components are indicated by arrows, and $\rho$ is indicated by open circles. The vector components are staggered in both space and time, to give low error in the finite-differencing scheme for solving Maxwell’s curl equations.

Figure 3.7 Snapshot of the 2D electrostatic potential $\Phi$ (color bar scale is in mV) throughout the computational domain in the absence of external excitation. The white box encloses the region in which EMC and FDTD simulations are coupled. $\Phi$ varies rapidly within the coupled region due to random placement of electrons and ions. The black dashed lines indicate the boundaries between the FDTD-domain on the inside and the convolutional perfectly-matched-layer absorbing boundary conditions on the outside. The total-field/scattered-field boundary is not shown.
The simulation domain defined in this section is modified in response to the results of the previous section, which demonstrated insensitivity of the calculated conductivity to impedance mismatch between the coupled and pure-FDTD regions. We define a two-dimensional (2D) computational domain in the \(xy\)-plane (Fig. 3.7), with the dielectric constant of silicon \((\varepsilon_r = 11.8)\) assumed throughout. The coupled EMC/FDTD region is enclosed by the white rectangle in Fig. 3.7. In the region between the white solid and dashed black lines, the time evolution of the fields is governed solely by Maxwell’s equations, solved via FDTD with no coupling to EMC. In both regions, we set \(\sigma\) to zero in the FDTD update equations.

The necessity for proper field initialization is illustrated in Fig. 3.8, which shows snapshots in time of \(\Phi\) for a single electron moving from 0 to 25 \(\mu\)m with constant velocity. \(\Phi\) is calculated from line integrals of FDTD electric fields. \(\vec{J}\) is calculated to satisfy Eq. (3.3). In Fig. 3.8a, the FDTD electric field is initialized to zero. As the electron moves away from the starting position, diverging fields develop in the computational domain so that the electron is surrounded by appropriate diverging fields, and the fields for an artificial hole are left behind. In Fig. 3.8b, FDTD electric fields are initialized to satisfy Gauss’s law for the starting position of the electron. As the electron moves away, the diverging fields follow the electron and Gauss’s law is always enforced. Thus, accurate representation of diverging fields in FDTD requires that the initial fields satisfy Gauss’s law.

### 3.2.1 Initialization

The EMC and the electromagnetic solver must interact through a continuous-to-discrete spatial mapping. In EMC-Poisson simulations this is called the charge assignment scheme (CAS) [48, 114]. The charge density associated with each carrier in continuous-space is assigned to discrete grid locations according to the CAS. The Poisson’s equation solver uses this instantaneous charge density, along with the known permittivity, to find the grid-based electrostatic potential. Partial derivatives of the potential produce the grid-based electric field, which is then interpolated in continuous-space to determine the force on the particle, with interpolation weights identical to those in the CAS [62, 114].
Figure 3.8 Electrostatic potential $\Phi$ due to the motion of a single electron, calculated from FDTD electric fields. (a) If the electrostatic field is initialized to zero, the electron’s inception point appears to be charge neutral. As the electron moves, it leaves an artificial immobile hole behind. (b) When the electrostatic fields are initialized according to the solution to Poisson’s equation for the electron’s charge density, FDTD produces appropriate electrostatic fields for the pointlike moving particle.
The charge assignment scheme is the backbone of the simulated carrier-field interaction. Implementation of each scheme may be more or less appropriate depending on local simulation particulars; inappropriate choice of CAS may lead to non-physical electric fields at contacts and dielectric interfaces [114]. Inconsistent coupling may cause a nonphysical carrier self-force [48], where a carrier is acted on by its own potential. Minimization of these effects has driven extensive research in the application of CAS in rectangular-grid EMC-Poisson solvers [48, 114–116]. The conceptual advances resulting from this work have been invaluable in establishing the Ensemble Monte Carlo technique as the benchmark against which other computational electronics methods are gauged.

EMC/FDTD/MD uses the cloud-in-cell (CIC) charge assignment scheme to assign EMC charges to the FDTD grid. This scheme gives excellent representation of the Coulomb interaction between charged particles over length scales longer than a few grid cells [36, 114]. In the CIC scheme, each carrier’s charge is assumed to be evenly distributed over a finite region. In this implementation we assume cubic charge clouds of width \( \Delta x \) and charge density \( q/\Delta x^3 \), so that the total charge of each cloud is \( q \). The CIC scheme assigns a portion of the particle’s charge density to each of the eight \( \rho \) elements at the corners of the EMC/FDTD/MD grid cell shown in Fig. 3.6. For a particle with position \((x, y, z)\) within the grid cell, the portion of the total charge assigned to the \( \rho \) component on the \( n \)th grid cell corner with position \((x_n, y_n, z_n)\) is given by

\[
w_n = \left(1 - \frac{|x_n - x|}{\Delta x}\right) \left(1 - \frac{|y_n - y|}{\Delta x}\right) \left(1 - \frac{|z_n - z|}{\Delta x}\right).
\]

(3.4)

The electrostatic potential \( \Phi \) is calculated as the solution to Poisson’s equation for the initial charge distribution \( \rho \), where \( \Phi \) and \( \rho \) are collocated on the grid in Fig. 3.6. Diverging electric fields are calculated using the gradient of \( \Phi \).

### 3.2.2 Current density calculation

Current continuity is easily satisfied in the typical EMC-Poisson implementation. In that case, \( \rho \) and \( \vec{J} \) are calculated at the same locations on the grid, and as a result current continuity is enforced by using the same weighting scheme for the two quantities. In the EMC/FDTD/MD
grid cell shown in Fig. 3.6, $\vec{J}$ and $\rho$ are assigned to two different, spatially staggered grids. The small approximations inherent to the grid assignment of $\vec{J}$ and $\rho$ in the EMC/FDTD/MD region can result in a violation of Eq. (3.3).

Early contributions to the description of current assignment schemes are given in Refs. [53, 58, 62, 65]. Several current assignment schemes that ensure local charge conservation have been developed. Marder presented a modified version of Maxwell’s equations to prevent violations of Gauss’s law in numerical tests [117]. Villasenor and Buneman’s method forced exact charge conservation in the current density calculation for simply shaped particles [112]. A generalized charge-conserving current calculation technique, for particles of arbitrary shape, was given by Esirkepov [118]. A 2005 comparison showed no difference in the quality of results between the Villasenor-Buneman method or the Esirkepov method for similar particles [113]. That study highlighted the necessity of local charge conservation in particle-in-cell codes.

Here, we describe the fundamental EMC/FDTD/MD current assignment scheme. The method given below assumes the Villasenor-Buneman [112] current conservation technique. We explicitly enforce Eq. (3.3) by calculating a carrier’s contribution to $\vec{J}$ from its change in position over a time step rather than from its known instantaneous velocity. The resulting $\vec{J}$ is assigned to the grid according to the carrier’s spatial charge profile in the CIC scheme, to maintain full consistency between the initial and subsequent field/charge calculations. [44, 86, 112]

During one time step, $\Delta t$, the initialized particle moves from $(x, y, z)$ to $(x', y', z')$, where starting and ending positions are within the same grid cell. There are four elements of $J_x$ in the grid cell shown in Fig. 3.6, with positions given by $(i + 1/2, j, k)\Delta x$, $(i + 1/2, j + 1, k)\Delta x$, $(i + 1/2, j, k + 1)\Delta x$, and $(i + 1/2, j + 1, k + 1)\Delta x$. The $n^{th}$ of these, $J^n_x$, is given by

$$J^n_x = \frac{q(x' - x)}{\Delta t} \left(1 - \frac{|y_n|}{\Delta x}\right) \left(1 - \frac{|z_n|}{\Delta x}\right) \tag{3.5}$$

where $y_{na} = y_n - 0.5(y + y')$, $z_{na} = z_n - 0.5(z + z')$, and $(x_n, y_n, z_n)$ is the position of $J^n_x$. The elements of $J_y$ and $J_z$ are similarly defined. Motion into the neighboring grid cell is treated by dividing the path into sections, so that the motion in each cell is treated individually.

This definition for $\vec{J}$ is fully consistent with the CIC scheme used in the initialization. As a result, the fields may be found at the positions of the mobile carriers during the time-stepping
process from interpolation according to the CIC scheme. Since FDTD fields are offset from the grid intersections, we interpolate the electromagnetic fields to center on the grid intersections prior to second interpolation. This section interpolation finds the field at the location of the carrier using $\vec{E}$ and $\vec{H}$ at the grid cell corners, by interpolating with the weights $w_n$ defined in Eq. (3.4). Because of the consistency between the CIC scheme and the $\vec{J}$ calculation described above, self-force is kept to a minimum [112].

### 3.2.3 Boundary conditions

A second potential source of deviation from Gauss’s law is spurious charge buildup at the boundary between the coupled EMC/FDTD region and the surrounding FDTD-only region (Fig. 3.7). EMC carriers reflect specularly from the left and the right boundary of the coupled region (their velocity normal to the boundary is inverted), in keeping with the expected zero net current through each of these boundaries. In contrast, as the dominant force acting on carriers and the current flow are in the $y$–direction, boundary conditions should allow unrestricted carrier motion and maintain the ensemble momentum in this direction. Therefore, carriers are subject to periodic boundary conditions at the top and bottom boundary of the EMC/FDTD coupled region: as a carrier exits one side of the region, it is injected at the opposite side with unaltered momentum. However, the instantaneous vanishing or emergence of carriers at the top and bottom boundaries of the coupled region is in conflict with Maxwell’s equations. As a result, the electrostatic fields associated with that electron before its disappearance remain tethered to the boundary and act as a residual negative charge. Similarly, as the same electron is injected at the opposite boundary and moves into the coupled EMC/FDTD region, an effective hole’s field is left behind, similar to what we saw in Fig. 3.8. Therefore, effective charge builds up on the top and bottom boundaries, impedes the flow of current along $y$ and results in a lower calculated $\dot{\sigma}$. To eliminate this source of error, every time an electron is removed (injected) at the coupled-region boundary, the electrostatic fields that accompany the electron (artificial hole) are also removed. To avoid repetitious runtime computations and maximize efficiency, in the solver initialization phase we solve Poisson’s equation and calculate the electrostatic fields for a single electron (hole) located
at a grid intersection along the coupled-region boundary. During runtime, we calculate the intercept between the electron trajectory and the boundary and interpolate the precalculated electron (hole) electrostatic field. The interpolated field is then removed from the boundary at which the electron vanishes (emerges).

3.2.4 Comparison with experimental results

In Fig. 3.9, we compare the calculated \( \hat{\sigma} \) for \( n \)-type Si doped to \( 5.47 \times 10^{14} \text{ cm}^{-3} \) with experimental data obtained by Jeon and Grischkowsky via reflecting THz time-domain spectroscopy [4]. EMC/FDTD results show excellent agreement with experiment. The dramatic improvement in the agreement between the EMC/FDTD results and the experiment over those reported previously [44, 87] results directly from the rigorous enforcement of Gauss’s law, as described above. The Drude-model conductivity, calculated by using the doping density and the corresponding low-field mobility, differs significantly from both numerical and experimental data (Fig. 3.9). The disagreement is quite pronounced in the imaginary part of the conductivity, which describes an effective change in the dielectric constant.

In summary, we have presented the THz-regime conductivity calculation for lightly doped silicon using a combined EMC/FDTD simulation tool. We have elucidated the importance of strict enforcement of Gauss’s law to avoid artificial charge buildup and dramatically increase the solver accuracy. As a result, the calculated conductivity data reproduce the experimental data to an outstanding degree. EMC/FDTD is an accurate and efficient simulation tool, holding promise as a highly predictive method for full characterization of semiconductors at THz frequencies.
Figure 3.9 Frequency-dependent conductivity, $\sigma$, of $n$-type silicon doped to $5.47 \times 10^{14} \text{ cm}^{-3}$. Symbols represent the results of the EMC/FDTD numerical calculation, and the dashed line is an analytical best fit to the EMC/FDTD data, to guide the eye. The solid curve represents a faithful analytical fit to the experimental data of Ref. [4]. Conductivity from the Drude model (dotted curve) is calculated using the known doping density and the corresponding electron mobility.
Chapter 4

EMC/FDTD/MD for 3D analysis of materials with high carrier density

In this chapter, we extend the EMC/FDTD technique to describe the short-range Coulomb interaction via the molecular dynamics (MD) technique that has been extended to describe the exchange interaction. The EMC/FDTD/MD technique captures collective carrier motion in conductive materials by using MD to describe the Coulomb interaction between charged particles separated by distances smaller than the FDTD grid cell [35, 36]. This work represented the first comprehensive computational technique where both strong Coulomb interactions and the Pauli exclusion principle are included via MD.

In the EMC/FDTD/MD technique, the three solvers interact in every time step to describe carrier dynamics under applied electromagnetic stimulation with full Coulomb interaction among particles (Fig. 4.1). FDTD electromagnetic fields and MD electrostatic fields accelerate EMC carriers through the Lorentz force, \( \vec{F} \), in Eq. (2.1). EMC carrier motion defines \( \vec{J} \), thereby acting to source FDTD fields in Eq. (2.3), and instantaneous carrier position defines MD fields in Eq. (2.4).

In Chapters 4 and 5 we use the 3D EMC/FDTD/MD solver to examine carrier dynamics in doped silicon under applied electromagnetic fields. We define a 3D FDTD computational domain with the dielectric constant of silicon (\( \epsilon_r = 11.7 \)) specified throughout. Figure 4.2(a) and (b) show cross-sectional slices of the domain. The EMC/FDTD/MD region is embedded within the larger FDTD domain. It is enclosed by the white rectangle in Fig. 4.2(a). This coupled region extends the full height of the larger FDTD domain, shown in Fig. 4.2(b).
Figure 4.1 Conceptual flowchart of the simulation process. FDTD electromagnetic fields and MD electrostatic fields combine according to the scheme described in Section 4.1. The combined fields accelerate EMC carriers through the Lorentz force. EMC carrier motion sources FDTD fields via $\vec{J}$. Instantaneous carrier positions define MD fields.

We drive carrier motion in the coupled region via fields sourced from the TFSF boundary, which extends the height of the FDTD grid in $z$. All applied fields are held constant in $z$. In the $dc$ tests, the sourcing field amplitude increases monotonically over time from $E_{\text{inc}} = 0$ at $t = 0$ to $E_{\text{inc}} = 0.1 \text{kV/cm}$ $\hat{z}$, and this final value is maintained for the duration of the simulation. In the $ac$ tests, the same source profile is used with a sinusoidal carrier wave to launch a TEM plane wave of the frequency of interest with propagation along $x$. In both cases, $E_{\text{inc}}$ is $z$-polarized, so that the dominant force applied to the carriers is directed along $\hat{z}$.

In the open-region simulations discussed here, grid boundaries perpendicular to $\hat{x}$ and $\hat{y}$ are treated with CPML, not shown in Fig. 4.2 [49, 100]. In order to better represent bulk material, EMC enforces specular reflection of carriers from the boundaries of the coupled region that are normal to $\hat{x}$ and $\hat{y}$. The boundaries normal to $\hat{z}$ are treated with periodic boundary conditions in all three solvers, permitting unrestricted carrier motion and continuous electromagnetic interaction in the $\hat{z}$ direction.

4.1 FDTD/MD, without double counting

The CIC technique described in Chapter 3.2 represents $\delta$-function charges as finite-volume charge clouds. The assumption of a finite charge volume is valuable when dealing with $\delta$-function charges in a grid-based field solver. The nearest-grid-point scheme does not require this, and instead assigns each $\delta$-function of charge to whichever grid point is closest to the particle, but this
Figure 4.2 Cross-sectional slices of the initial electrostatic potential $\Phi$ throughout the computational domain in the absence of external excitation. The white box encloses the region in which the EMC, FDTD and MD simulations are combined. $\Phi$ varies rapidly within the coupled region due to random placement of electrons and ions. The black dashed lines indicate the location of the TFSF boundary. (a) Slice in the $xy$–plane. The multiphysics region of the computational domain is surrounded by the TFSF boundary. (b) Slice in the $xz$–plane. The multiphysics region and the TFSF boundary extend the full height of the FDTD domain.

results in very noisy fields and abrupt electron motion, and the CIC scheme is usually preferable [114].

As described in Chapter 3, in the CIC scheme an ion’s $\delta$-function of charge is smoothly divided among the eight corners of the cell containing the ion, before calculation of the grid-based field. When an electron enters the cell during the simulation time stepping process, the CIC scheme calculates the field at the electron’s position by linear interpolation from the grid-based fields that are defined on the boundaries of the cell. Figure 4.3 shows the interpolated field experienced by an electron as it is swept through a grid cell that contains an ion at the center. The resulting nonzero force acting on the electron is very smooth in contrast to the strong, rapidly varying Coulomb force that the electron should experience in this interaction with an ion. In solvers that combine a grid-based field calculation with MD, these strong short-range Coulomb fields are described by MD. When the strong Coulomb field from MD is combined with the nonzero grid-based field, the fields are double counted and the resulting force is larger than the Coulomb force alone.
Figure 4.3 Force on an electron sweeping past a stationary ion. The ion is located at \( x = (i + 1/2)\Delta x \). The dashed line shows the force on the electron found from interpolating the grid-based field according to the CIC scheme. The solid line shows the Coulomb force the electron should experience. Between indices \( i - 1 \) and \( i + 2 \), the Coulomb force is poorly represented by the interpolated field.

The corrected-Coulomb scheme defined in Refs. [35, 36] avoids double counting by precalculating the field that must be added to the grid-based fields to result in the proper Coulomb force. This correcting field is calculated by sweeping a mobile electron past a stationary charge at a known location in the grid cell, as was done to produce Fig. 4.3, and subtracting the force experienced by the electron from the desired Coulomb interaction [35, 36]. This same correction, with appropriate sign, can be used to describe interaction with electrons or ions during the time-stepping process. However, a particle’s contribution to the grid-based field depends on the particle’s position within the grid cell, [48] and as a result a single correcting force cannot be appropriate for interaction with any arbitrarily placed electron or ion.

EMC/FDTD/MD eliminates double counting for any electron-ion interaction that is calculated with MD, by subtracting the ion’s contribution to the grid-based field prior to interpolating the field to the electron’s location. The interaction is then described by MD alone, with no grid-based contribution. Figure 4.4 shows the force on an electron that is swept past a stationary ion, where the ion is positioned at the center of a grid cell. The MD force for the corrected-Coulomb scheme
has been calculated using an ion positioned at the center of the grid cell. Both the corrected-Coulomb scheme (Fig. 4.4a) and the new scheme (Fig. 4.4b) accurately predict the Coulomb force the electron should experience. Figure 4.5 shows the force on an electron that is swept past a stationary ion, where the ion is positioned at the edge of the grid cell. The corrected-Coulomb scheme was initialized as in the previous example, and it now overestimates the combined force on the electron for this offset ion (Fig. 4.5a). The new scheme accurately predicts the combined force, within the portion of the interaction that is calculated with MD.

The next few paragraphs provide detail on the new technique. EMC/FDTD/MD permits MD interactions between carriers and ions within the same cell and in neighboring cells. In the example shown in Fig. 4.3, MD calculates the electron-ion interaction for the three grid cells bounded by grid indices $i-1$ and $i+2$. An ion interacts via MD with every carrier in the surrounding $3 \times 3 \times 3$ block of cells, and no other carriers. In the new scheme, an ion’s local grid-based field contribution within those 27 cells is calculated and stored in the simulation initialization stage.

Every time the field acting on a carrier is needed, EMC/FDTD/MD copies the field components required for interpolation into small auxiliary field grids. These field components include contributions from the applied fields as well as the grid-based Coulomb fields from other particles. Before interpolating from the auxiliary grids, EMC/FDTD/MD subtracts off the stored grid-based Coulomb fields for every ion within the surrounding $3 \times 3 \times 3$ block of cells. We then use interpolation to find the grid-based electromagnetic field at a carrier’s location according to the CIC scheme. The resulting interpolated field has zero contribution from the neighboring ions’ grid-based Coulomb fields. When the interpolated field is combined with the MD field, the entire carrier-ion interaction is calculated with MD. In addition, the carrier still experiences grid-based fields not caused by the ions.

The simplest implementation of this scheme contributes substantially to the computational burden of the initialization stage, as Poisson’s equation must be solved for the full electron and ion charge density, as well as for each individual ion to produce the ions’ local grid-based fields. We exploit the linearity of Poisson’s equation to eliminate the bulk of the computational burden of the technique’s initialization. Prior to calculating the solution to Poisson’s equation, an ion’s
Figure 4.4 Coulomb force from the FDTD-MD field calculation for an electron passing by a stationary ion at the center of a grid cell. The electron is moved along a straight line that passes through the ion position. The black line shows the reference Coulomb force, the red dashed line shows force calculated via the interpolated grid-based field, the blue dashed line shows the contribution to the force from MD, and the circles show the total computed Coulomb force. (a) Corrected-Coulomb scheme. The correcting force is calculated for an ion at the center of the cubic grid cell. The combined force experienced by the electron is accurate. (b) New scheme. In this case, the force calculated by the new method is identical to that of the corrected-Coulomb scheme.
Figure 4.5 Coulomb force from the FDTD/MD field calculation for an electron passing by a stationary ion at the edge of a grid cell. The electron is moved along a straight line that passes through the opposite side of the ion’s grid cell. (a) Corrected-Coulomb scheme. The correcting force is calculated for an ion at the center of the cubic grid cell. The technique overestimates the combined force on the electron for an ion at the edge of the grid cell. (b) New scheme. The FDTD/MD force is identical to the Coulomb force, within the MD-calculated portion of the interaction.
charge is divided among the grid points at the corners of the ion’s cubic grid cell with weights $w_n, n = \{1, 2, ..., 8\}$, according to Eq. (3.4). We consider instead the mathematically equivalent case of eight individual particles with charges $w_n q, n = \{1, 2, ..., 8\}$, positioned at each of the grid cell corners. Given an ion’s position and the Poisson solution $\Phi_0$ for a single charge located at a grid intersection, the ion’s potential $\Phi$ is given by the weighted sum of shifted potentials $\Phi_0$, as

$$\Phi = \sum_{n}^8 w_n \Phi_0^n,$$

where $\Phi_0^n$ is $\Phi_0$ shifted to center on the grid cell’s $n^{th}$ corner. The local fields for each ion in the ensemble are found with a single solution to Poisson’s equation. Since the ions are immobile, these field values are calculated once for each simulation. The calculation to find the local grid-based fields of each ion in the ensemble is significantly expedited.

The only computational burden this scheme adds during run time results from subtracting off the mesh-based field for each carrier-ion interaction. We save significant computational labor in each time step by associating the stored arrays with all ions in a particular grid cell rather than with each ion individually. Instead of subtracting the mesh-based fields for each ion in a cell, we subtract them all at once. This technique contributes more significantly to the computational burden in the electron-electron MD calculation, since electrons move continually and the weights and nearest fields would need frequent recalculation. At the same time, our tests have shown that the exact form of the electron-electron interaction has minimal impact on the overall material properties. Thus, for the electron-electron interaction, we choose the lighter computational load and stronger approximation of the corrected-Coulomb scheme, where we average the correcting fields for stationary electrons at many different positions within the grid cell.

### 4.2 Finite electron and ion size

#### 4.2.1 Exchange interaction

MD accurately describes the Coulomb interaction in bulk materials with $n_0 < 10^{18}$ cm$^{-3}$, where the carrier interaction is well-represented by a fully classical description. As $n_0$ increases,
the exchange interaction between indistinguishable particles increasingly impacts materials properties [3, 38, 39, 106].

The exchange interaction is a geometric consequence of the Pauli exclusion principle that manifests as a reduction in the force between indistinguishable electrons [3, 38, 39, 106]. We adopt the formulation of Refs. [3, 38, 39] to describe this quantum-mechanical effect with molecular dynamics. Carriers are defined as Gaussian wave packets with a finite radius $r_c$; the wave function of the $i^{th}$ electron is

$$\phi_\vec{p}_i(\vec{r}_i) = (2\pi r_c^2)^{-3/4}\exp\left(-\frac{\vec{r}_i^2}{4r_c^2} + i\vec{k}_i \cdot \vec{r}_i\right).$$  (4.2)

The wave packet amplitude is significant only within a few $r_c$ of the electron’s assumed position $\vec{r}_i$ and a few $\hbar/2r_c$ of the assumed momentum $\vec{p}_i = \hbar\vec{k}_i$. The equations of motion for the $i^{th}$ electron in an ensemble of $N$ electrons are then given by

$$\hbar \frac{d\vec{k}_i}{dt} = \vec{F}_0 + \sum_{j \neq i}^N \vec{F}^D_{ij} + \sum_{j \neq i}^N \delta_{\sigma_i\sigma_j} \vec{F}^{XC}_{ij}$$  (4.3)

$$\frac{d\vec{r}_i}{dt} = \frac{\hbar\vec{k}_i}{m^*} - \sum_{j \neq i}^N \delta_{\sigma_i\sigma_j} \vec{G}_{ij}$$  (4.4)

where $\sigma_i$ is the spin of the $i^{th}$ electron, $\delta$ is the Kronecker delta function, the summations include all electrons $j$ where $j \neq i$, and $\vec{F}_0$ includes forces from applied fields and the electron-ion interaction. The new terms are given by

$$F^D_{ij} = -\frac{q^2}{4\pi \epsilon} \nabla_{\vec{r}_i} \left[ \frac{1}{|\vec{r}|} \text{erf} \left( \frac{|\vec{r}|}{2r_c} \right) \right]$$  (4.5a)

$$F^{EX}_{ij} = -\frac{q^2}{8\pi^{3/2}\epsilon r_c^4 |\vec{k}|} \vec{r} \exp\left(-\frac{r^2}{4r_c^2} - k^2 r_c^2\right) \int_0^{kr_c} dt e^{t^2}$$  (4.5b)

$$G_{ij} = -\frac{q^2}{4\pi^{3/2}\epsilon r_c^2 \hbar} \nabla_{\vec{k}_i} \left[ \frac{1}{|\vec{k}|} \exp\left(-\frac{r^2}{4r_c^2} - k^2 r_c^2\right) \int_0^{kr_c} dt e^{t^2} \right]$$  (4.5c)

where $\vec{r} = \vec{r}_j - \vec{r}_i$, $\vec{k} = \vec{k}_j - \vec{k}_i$, and erf$(x)$ is the error function. Appendix B gives the derivation of these equations. $F^D_{ij}$ is the direct Coulomb force between the $i^{th}$ and $j^{th}$ electrons defined by Eq. (4.2). In this formulation, $F^D_{ij}$ defines the direct force of interaction between all electrons, regardless of spin. $F^{EX}_{ij}$ describes the “exchange force”, which acts to reduce the interaction between indistinguishable electrons as a function of the electrons’ proximity in $\vec{r}$ and $\vec{p}$. $G_{ij}$ behaves
as a small modification to the carrier effective mass. All three terms are calculated numerically at the start of the simulation and stored in lookup tables.

We determine the scale of $r_c$ from the Hartree-Fock approximation exchange hole profile, [119]

$$g(r_F) = 1 - 9 \left( \frac{\sin r_F - r_F \cos r_F}{r_F^2} \right)^2$$  \hspace{1cm} (4.6)

where $r_F = q_FR$, $q_F = (3\pi^2 n_0)^{1/3}$ is the Fermi wave vector, $r$ is the radial distance from the center of the electron, and $g(r_F)$ describes the possibility that an identical electron can exist at $r_F$.

We fit the normalized Gaussian envelope of our electron wave function to $1 - g(r_F)$ to determine the Hartree-Fock prescribed electron radius $r_{c, HF}$. This fit produces the following relationship:

$$r_{c, HF} = \exp \left( - \frac{\log n_0}{3} + 17.366 \right)$$  \hspace{1cm} (4.7)

where $n_0$ is carrier density in cm$^{-3}$. Table 4.1 lists the calculated $r_c$ for each doping density of interest here. For comparison the table also includes the $r_{c, MD}$ values used in the MD reference, Ref. [3], as well as the average radius of the volume occupied by a single carrier electron of a particular spin,

$$r_s = \left( \frac{6}{4\pi n_0} \right)^{1/3}.$$  \hspace{1cm} (4.8)

Table 4.1  $r_c$ as a function of $n_0$. We compare the Hartree-Fock exchange hole $r_{c, HF}$, with the carrier radius $r_{c, MD}$ of Ref. [3]. The radius of the volume occupied by one electron of a particular spin $r_s$ is included for reference.

<table>
<thead>
<tr>
<th>$n_0$ (cm$^{-3}$)</th>
<th>$r_{c, HF}$ (Å)</th>
<th>$r_{c, MD}$ (Å)</th>
<th>$r_s$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{14}$</td>
<td>750</td>
<td></td>
<td>1687</td>
</tr>
<tr>
<td>$10^{15}$</td>
<td>350</td>
<td></td>
<td>782</td>
</tr>
<tr>
<td>$10^{16}$</td>
<td>160</td>
<td>7</td>
<td>363</td>
</tr>
<tr>
<td>$10^{17}$</td>
<td>75</td>
<td>14</td>
<td>168</td>
</tr>
<tr>
<td>$10^{18}$</td>
<td>35</td>
<td>16</td>
<td>78</td>
</tr>
<tr>
<td>$10^{19}$</td>
<td>16</td>
<td>17.5</td>
<td>37</td>
</tr>
</tbody>
</table>
The exchange-hole radius $r_{c,HF}$ predicted in this way is always smaller than the radius of the sphere occupied by a single electron where we only consider electrons of the same spin. Both quantities decrease monotonically with increasing $n_0$, in contrast with the values given by Ref. [3] which increase with increasing $n_0$ in the range provided. In Table 4.1 we list the Hartree-Fock exchange hole $r_{c,HF}$ and the carrier radius $r_{c,MD}$, but it is not clear that the two actually represent the same physical quantity. $r_{c,MD}$ is chosen as a compromise between the desire to maintain the Coulomb force for most carrier-carrier interactions, while permitting exchange for very close-range interactions. By choosing $r_c = 750$ Å for simulation at $n_0 = 10^{14} \text{cm}^{-3}$, we describe the carrier-carrier interaction as dominantly quantum mechanical, rather than treating it classically. The question of how to choose the value of $r_c$ is discussed further, below.

### 4.2.2 Finite ion radius

A typical MD implementation treats ions as delta functions of charge [36]. The bare Coulomb force surrounding a delta-function ion applies sufficient force to electrons that such electrons routinely reach relativistic speeds, leading to simulation inaccuracy and instability [120]. Instead, we assume that the dopant ion has a finite radius [42, 97]. We model the dopant ion charge with a Gaussian profile of characteristic half-width $r_d$, so that the Coulomb force experienced by an interacting electron is given by a modification of Eq. (4.5a) as

$$F^{D,\text{ion}}_{ij} = -\frac{qQ}{4\pi\epsilon} \nabla \left[ \frac{1}{|\vec{r}|} \text{erf} \left( \frac{|\vec{r}|}{2r_d} \right) \right]$$  

where we assume an ion of charge $Q$. The maximum force that may be applied to electrons is substantially reduced; see Fig. 4.6 In the case of phosphorous-doped silicon, the approximate radius of the ion’s outer orbitals is given by the effective Bohr radius as 13.8 Å [43]. This is a very approximate value, and is only generally intended to give a qualitative understanding of the extent of the electron cloud.
Figure 4.6 Force between an electron and ion for several values of $r_d$. This method reduces the strength of the interaction, where the degree of reduction depends on $r_d$.

4.2.3 Determining $r_c$ and $r_d$

To determine the appropriate $r_c$ and $r_d$ for doped silicon, we calculate the $dc$ conductivity for $n_0 = 10^{14} - 10^{19}$ cm$^{-3}$ as a function of $r_c$ and $r_d$. As in Chapter 3.2, the effective linear-regime complex conductivity $\hat{\sigma}$ is computed as

$$\hat{\sigma}(\omega) = \frac{\vec{E}(\omega) \cdot \vec{J}^*(\omega)}{|\vec{E}(\omega)|^2},$$

(4.10)

where $\vec{E}(\omega)$ and $\vec{J}(\omega)$ are the electric-field and current-density phasors in the coupled region, after spatial averaging to reduce noise.

Figure 4.7 shows $\text{Re}\{\hat{\sigma}(0)\}/\sigma_0$, where $\sigma_0$ is the known $dc$ conductivity of the material [5], as a function of $r_c$ and $r_d$, for $n_0 = 10^{15}, 10^{16}, 10^{17}$, and $10^{18}$ cm$^{-3}$. At low $n_0$, $\hat{\sigma}(0)$ does not depend on either $r_c$ or $r_d$, as we would expect. We see a moderate dependence on $r_d$ for $n_0 = 10^{16}$ cm$^{-3}$, and no clear dependence on $r_c$. At $n_0 = 10^{18}$ cm$^{-3}$, $\hat{\sigma}(0)$ depends strongly on $r_d$. Table 4.2 shows the resulting values of $r_d$ over $n_0$.

With the $dc$ tests and practical considerations, we have clear values for $r_d$ for each doping density. Our tests show that $r_c$ has little influence on $\hat{\sigma}(0)$. The influence of the carrier-carrier interaction is to relax the ensemble towards a drifted Maxwellian or drifted Fermi-Dirac distribution (depending on doping) without changing the average ensemble energy or momentum (the
Table 4.2 Calculated $r_d$ values from $\hat{\sigma}(0)$. For $n_0 \leq 10^{15}$ cm$^{-3}$ we use $r_d = 1$Å for simulation stability.

<table>
<thead>
<tr>
<th>$n_0$ (cm$^{-3}$)</th>
<th>$10^{14}$</th>
<th>$10^{15}$</th>
<th>$10^{16}$</th>
<th>$10^{17}$</th>
<th>$10^{18}$</th>
<th>$10^{19}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_d$(Å)</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

electron-electron interaction does not directly impact the conductivity of the material). The only situation in which we would expect $r_c$ to impact bulk properties is at very high $n_0$ when electrons are forced to interact at close range. In the next section, we explore $\hat{\sigma}$ at THz frequencies. To test the importance of $r_c$, we calculated the ac conductivity for different values of $r_c$ for several doping densities. The results at low $n_0$ showed no dependence on $r_c$. At high $n_0$ our results are noisiest. As a result, the only conclusion we can draw about impact of $r_c$ on the conductivity is that any changes to $\hat{\sigma}(\omega)$ from $r_c$ occur below the level of the noise in Figs. 5.3-5.8, and the question of how to best choose $r_c$ remains open. In the THz-frequency calculations described in the next Chapter, we use $r_c = r_{c, HF}$. 

Figure 4.7 $\text{Re}\{\hat{\sigma}(0)\}/\sigma_0$ as a function of $r_c$ and $r_d$, for $n_0 = 10^{15}$, $10^{16}$, $10^{17}$ and $10^{18}$ cm$^{-3}$. $\sigma_0$ is the known $dc$ conductivity of silicon [5]. $\text{Re}\{\hat{\sigma}(0)\}/\sigma_0=1$ for acceptable values of $r_c$ and $r_d$. 
Chapter 5

THz conductivity of doped silicon

5.1 Comparison with experimental data

In this section, we compare the effective conductivity calculated by EMC/FDTD/MD with published experimental results for doped silicon at THz frequencies, obtained via reflecting THz-TDS [4]. The complex conductivity is given for two $n-$type silicon samples with $dc$ resistivities of 8.15 $\Omega$ cm and 0.21 $\Omega$ cm, corresponding to $n_0 = 5.47 \times 10^{14}$ cm$^{-3}$ and $n_0 = 3.15 \times 10^{16}$ cm$^{-3}$, respectively [5]. The analytical best fit of the Cole-Davidson model to experimental data is given by Ref. [4]. The Cole-Davidson fit can be regarded as a faithful representation of the experimental data, especially at the lower doping density where the experimental data show low noise. Figure 5.1 compares the EMC/FDTD/MD doped-silicon complex conductivity to the experimental results for $n_0 = 5.47 \times 10^{14}$ cm$^{-3}$. At this low $n_0$, choice of $r_c$ and $r_d$ has little impact on $\tilde{\sigma}$. We use $r_c = 426$ Å, from Eq. (4.7), and $r_d = 1$ Å, for numerical stability (see Appendix A for details on stability criteria). EMC/FDTD/MD results are indicated with open circles and a dashed line to guide the eye. The numerical prediction for conductivity shows excellent agreement with experiment. The Drude-model conductivity, calculated by using the doping density and the corresponding low-field mobility according to Eq. (1.1), differs significantly from both numerical and experimental data.

Figure 5.2 shows the complex conductivity calculated by EMC/FDTD/MD in comparison with the best fit to experimental results for silicon doped to $n_0 = 3.15 \times 10^{16}$ cm$^{-3}$. For the carrier radius we use $r_c = 110$ Å, from Eq. (4.7). Choice of $r_d$ impacts $\sigma$ at this moderate $n_0$, but our tests have shown no dependence on $r_c$. The ion radius is chosen as $r_d = 2.5$ Å,
Figure 5.1 THz conductivity of n-type silicon with $n_0 = 5.47 \times 10^{14}$ cm$^{-3}$. In these tests $r_c = 426$ Å and $r_d = 1$ Å. The dotted line shows the Drude model prediction for the conductivity, based on the known doping density and mobility of the material. The solid line indicates the analytical fit to the experimental data. The calculated by EMC/FDTD/MD is shown with open circles, with a dashed line to guide the eye. The numerical data demonstrates excellent agreement with the experimental conductivity. The Drude model prediction differs significantly from both.
Figure 5.2 THz conductivity of n-type silicon with $n_0 = 3.15 \times 10^{16}$ cm$^{-3}$. In these tests $r_c = 110$ Å and $r_d = 2.5$ Å. The dotted line shows the Drude model prediction for the conductivity, based on the known doping density and mobility of the material. The solid line indicates the analytical fit to the experimental data. Re($\hat{\sigma}$) shows excellent agreement with the experimental data. Im($\hat{\sigma}$) is much more susceptible to small errors in both the computational and experimental systems.
via linear interpolation of $r_d$ as a function of $\log_{10}(n_0)$ in Table 4.2. EMC/FDTD/MD results for $\text{Re}(\hat{\sigma})$ show excellent agreement with experiment. The numerical values for $\text{Im}(\hat{\sigma})$ do not agree quite as well with experiment, though the trend of the prediction is the same as that of the experimental results. The imaginary part of the conductivity describes the phase shift between $\vec{E}$ and $\vec{J}$, and as a result $\text{Im}(\hat{\sigma})$ is highly susceptible to small errors in both the computational and experimental systems. FDTD numerical dispersion could contribute to this error. In the experimental characterization, small inaccuracies in the measured thickness of the sample would also manifest as error in $\text{Im}(\hat{\sigma})$ [22].

Our tests have shown that the results for $n_0 = 5.47 \times 10^{14}$ cm$^{-3}$ can be reproduced without including the short-range Coulomb interaction, by using the EMC and FDTD solvers without MD, as shown in Chapter 3. At the moderate doping density of $n_0 = 3.15 \times 10^{16}$ cm$^{-3}$ the results for doped silicon require MD for accurate prediction of the conductivity. As $n_0$ increases, the short-range Coulomb interaction described by MD becomes even more important to the accuracy of the conductivity prediction. For $n_0 \geq 10^{18}$ cm$^{-3}$, the exchange interaction is relevant as well [3, 37–39]. Ideally, we would establish the accuracy of EMC/FDTD/MD calculations at these high doping densities by comparing the predicted conductivity with experimental conductivity data for silicon with $n_0 \geq 10^{18}$ cm$^{-3}$, but after extensive searching in the literature we have not found the necessary data. While, in the absence of experimental data we cannot be entirely certain that EMC/FDTD/MD is as accurate for $n_0 \geq 10^{18}$ cm$^{-3}$ as it is for lower $n_0$, $dc$ conductivities are predicted accurately in the high as well as low doping density regions, and there is no reason to suspect inaccuracies in the THz calculations. The comparison with experimental data demonstrates the strength of EMC/FDTD/MD as a predictive tool for THz-frequency conductivity of materials. In the following section, we use EMC/FDTD/MD to calculate $\hat{\sigma}(\omega)$ for doping densities where no experimental data exists for THz-frequency conductivity of silicon.

5.2 Extrapolation to other doping densities

In this section we present $\hat{\sigma}$ calculated with EMC/FDTD/MD for n-type silicon at room temperature for doping densities $n_0 = 10^{14} - 10^{19}$ cm$^{-3}$ and $f = 0 - 2.5$ THz. We use $r_e$ and $r_d$ listed
Figure 5.3 THz conductivity of n-type silicon with $n_0 = 10^{14}$ cm$^{-3}$. We have used $r_d = 1\,\text{Å}$ and $r_c = 750\,\text{Å}$. These results required several hundred hours of CPU time. The resulting data is represented by the GD model with $\alpha = 0.03$, $\beta = 0.84$, and $\tau = 0.34$ ps, with normalized error $\varepsilon = 1.39\%$.

in Section 4.2 for each doping density. These data constitute the EMC/FDTD/MD predictions for the THz-frequency conductivity of doped silicon.

Each of the Figs. 5.3-5.8 shows $\hat{\sigma}(\omega)$ calculated by EMC/FDTD/MD (open circles) along with an analytical fit to the data (dashed line) and the Drude model prediction for the complex conductivity (solid line). We have used the analytical fit to provide a quantitative representation of the data, so that the prediction is available for further research where the THz-conductivity of silicon is needed. The analytical curve is the best fit of the generalized-Drude (GD) model for complex conductivity to the EMC/FDTD/MD data, where the GD model conductivity is given by

$$
\sigma_{GD}(\omega) = \frac{\sigma(0)}{(1 - (i\omega\tau)^{1-\alpha})^\beta}.
$$

(5.1)
Figure 5.4 THz conductivity of n-type silicon with $n_0 = 10^{15}$ cm$^{-3}$. We have used $r_d = 1\text{Å}$ and $r_c = 350\text{Å}$. These results required several hundred hours of CPU time. The resulting data is represented by the GD model with $\alpha = 0.02$, $\beta = 0.84$, and $\tau = 0.34$ ps, with normalized error $\varepsilon = 1.37\%$.

Here, $\alpha$ and $\beta$ are positive real numbers $\leq 1$. The GD model reduces to the Drude model conductivity for $\alpha = 0$ and $\beta = 1$. By modifying $\alpha$ and $\beta$, the response function of the ensemble no longer exhibits the Drude model characteristics [121, 122]. This new form for the conductivity incorporates a continuous distribution of relaxation times, where the choice of $\alpha$ and $\beta$ determines the form of that distribution. In the Cole-Cole model (in which $\beta = 1$ and $0 \leq \alpha \leq 1$) the distribution of $\tau$ values is symmetric in $\ln(\tau)$, with a width that increases with $\alpha$ [121]. The Cole-Davidson model (in which $\alpha = 0$ and $0 \leq \beta \leq 1$) describes an asymmetric distribution of $\tau$ values, which is zero for $t > \tau$ and decays for $t < \tau$ [121]. By permitting both $\alpha$ and $\beta$ to vary, we allow both symmetric and asymmetric components of the $\tau$ distribution [121]. We further
Figure 5.5 THz conductivity of n-type silicon with $n_0 = 10^{16} \text{ cm}^{-3}$. We have used $r_d = 2\degree \text{A}$ and $r_c = 160\degree \text{A}$. These results required several thousand hours of CPU time. The resulting data is represented by the GD model with $\alpha = 0.02$, $\beta = 0.88$, and $\tau = 0.26 \text{ ps}$, with normalized error $\varepsilon = 0.95\%$.

permit $\tau$ to vary, to allow for the situation in which the peak of the relaxation time distribution is not given by the Drude $dc$ relaxation time.

The fitting parameters are given in Table 5.1. For each doping density $n_0$ (cm$^{-3}$), Table 5.1 shows the known $dc$ conductivity of $n$–type silicon $\sigma_0$ [5]. Next we show the calculated $dc$ conductivity $\hat{\sigma}(0)$ from EMC/FDTD/MD, along with the corresponding scattering time $\tau_{\hat{\sigma}(0)}$ calculated according to the Drude model. The fitting parameters — $\tau_{\text{fit}}$, $\alpha$, and $\beta$ — are included for each $n_0$. $\varepsilon$ is also included, as calculated by Eq. (5.2).
Figure 5.6 THz conductivity of n-type silicon with \( n_0 = 10^{17} \text{ cm}^{-3} \). We have used \( r_d = 3 \text{ Å} \) and \( r_c = 75 \text{ Å} \). These results required several thousand hours of CPU time. The resulting data is represented by the GD model with \( \alpha = 0.04, \beta = 0.89, \) and \( \tau = 0.17 \text{ ps} \), with normalized error \( \varepsilon = 1.05 \% \).

Table 5.1 also includes an error parameter \( \varepsilon \) in percent, which is the sample standard deviation normalized to \( \hat{\sigma}(0) \),

\[
\varepsilon = \frac{1}{\hat{\sigma}(0)} \sqrt{\frac{1}{S-1} \sum_{i=1}^{S} (\hat{\sigma}_i(\omega) - \sigma_{GD}(\omega))^2}
\]

where we assume \( S \) data points. There are several sources for the noise in \( \hat{\sigma}(\omega) \). Random noise comes from finite EMC ensemble size; an ensemble of \( N \) particles will have statistical noise proportional to \( \sqrt{N} \) [34]. This noise can cause spurious heating in the electron ensemble [96]. In addition, at high \( n_0 \) carrier motion is dominated by the strong Coulomb force between charges, and these strong forces contribute to noise in \( \hat{\sigma} \). The obvious solution is to use a larger ensemble.
Figure 5.7 THz conductivity of n-type silicon with $n_0 = 10^{18}$ cm$^{-3}$. We have used $r_d = 3.5\,\text{Å}$ and $r_c = 35\,\text{Å}$. These results required several thousand hours of CPU time. The resulting data is represented by the GD model with $\alpha = 0.19$, $\beta = 0.82$, and $\tau = 0.07$ ps, with normalized error $\varepsilon = 1.95\%$.

in this case, but for high $n_0$ the computational burden of EMC/FDTD/MD limits the ensemble size. As $n_0$ increases, both $\Delta x$ and $\Delta t$ decrease, as described in Appendix A, and as a result the computational load increases for the same duration of simulation. The data in Figs. 5.3-5.8 were calculated over several tens of thousands of cpu hours, and the majority of that time was spent on the $10^{18}$ and $10^{19}$ cm$^{-3}$ calculations.

We observe $\tau_{\text{fit}} > \tau_{\phi(0)}$ for every $n_0$, so that the peak relaxation time calculated by EMC/FDTD/MD is consistently longer than that predicted by the Drude model. In addition, for $n_0 \leq 10^{17}$ cm$^{-3}$, $\alpha \approx 0$ and $\beta$ is roughly constant. In this case, the GD conductivity reduces to the Cole-Davidson model, which describes an asymmetric distribution of scattering times, where the
Figure 5.8 THz conductivity of n-type silicon with $n_0 = 10^{19} \text{ cm}^{-3}$. We have used $r_d = 5.5\text{Å}$. We have used both $r_c = 16\text{Å}$. These results required several thousand hours of CPU time. The resulting data is represented by the GD model with $\alpha = 0.33$, $\beta = 0.74$, and $\tau = 0.03 \text{ ps}$, with normalized error $\varepsilon = 25.0\%$.

distribution is nonzero for $t \leq \tau_{\text{fit}}$. Our results for $\beta$ do not agree with the predictions of Ref. [4], which describe $\beta$ increasing monotonically with increasing $n_0$ for $n$–type silicon. However, that paper allowed variation in both $\tau$ and $n_0$, so a direct comparison cannot be made with our fits.
Table 5.1 For each doping density $n_0$ (cm$^{-3}$), the table shows the known $dc$ conductivity of $n$–type silicon $\sigma_0$, the calculated $dc$ conductivity $\hat{\sigma}(0)$ from EMC/FDTD/MD, and the corresponding scattering time $\tau_{\hat{\sigma}(0)}$ calculated according to the Drude model. The fitting parameters — $\tau_{\text{fit}}, \alpha$, and $\beta$ — are included for each $n_0$, as is an estimate of the quality of the fit $\varepsilon$ in percent. Conductivities are in units of S/cm, and times are in ps.

<table>
<thead>
<tr>
<th>$n_0$</th>
<th>$10^{14}$</th>
<th>$10^{15}$</th>
<th>$10^{16}$</th>
<th>$10^{17}$</th>
<th>$10^{18}$</th>
<th>$10^{19}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_0$</td>
<td>0.023</td>
<td>0.223</td>
<td>1.912</td>
<td>11.93</td>
<td>42.37</td>
<td>173.0</td>
</tr>
<tr>
<td>$\hat{\sigma}(0)$</td>
<td>0.022</td>
<td>0.219</td>
<td>1.864</td>
<td>11.65</td>
<td>42.17</td>
<td>181.8</td>
</tr>
<tr>
<td>$\tau_{\hat{\sigma}(0)}$</td>
<td>0.209</td>
<td>0.207</td>
<td>0.181</td>
<td>0.110</td>
<td>0.040</td>
<td>0.017</td>
</tr>
<tr>
<td>$\tau_{\text{fit}}$</td>
<td>0.341</td>
<td>0.336</td>
<td>0.264</td>
<td>0.168</td>
<td>0.071</td>
<td>0.032</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.030</td>
<td>0.020</td>
<td>0.023</td>
<td>0.036</td>
<td>0.192</td>
<td>0.331</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.841</td>
<td>0.844</td>
<td>0.883</td>
<td>0.890</td>
<td>0.816</td>
<td>0.739</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>1.39</td>
<td>1.37</td>
<td>0.95</td>
<td>1.05</td>
<td>1.95</td>
<td>25.0</td>
</tr>
</tbody>
</table>
Chapter 6

Summary and future work

6.1 Summary of this dissertation

First, a comprehensive computational solver has been developed for high-frequency materials characterization, in the low carrier density regime. The solver combines the ensemble Monte Carlo technique for stochastic representation of carrier dynamics under the Boltzmann transport equation, with the finite-difference time-domain technique for Maxwell’s curl equations and the molecular dynamics technique for close-range Coulomb interaction. In Chapter 3 the importance of rigorous enforcement of Gauss’s law was described, as was an efficient technique to calculate the EMC current density that ensures satisfaction of Gauss’s law in FDTD. This is the first time this technique has been used in the research community for EMC/FDTD methods for materials and device characterization. We compared the predicted conductivity calculated by EMC/FDTD with published experimental data for the complex conductivity of silicon at $n_0 = 5.47 \times 10^{14} \text{cm}^{-3}$ [4]. The calculated data show excellent agreement with the experimental data. This work demonstrated the capabilities of this electrodynamic particle solver to accurately predict the complex conductivity of low carrier density materials at THz frequencies.

Chapter 4 described incorporating the molecular dynamics technique for short-range Coulomb interaction among carriers and between carriers and ions, thereby extending the multiscale computational technique to materials with high conductivity. MD was used to calculate interactions among carriers and between carriers and ions, which occur on length scales shorter than the FDTD grid cell size. Materials properties are significantly affected by these strong interactions for carrier densities above $10^{16} \text{cm}^{-3}$. The EMC/FDTD/MD solver calculates electromagnetic interactions
between particles by combined field calculations from FDTD and MD. Both FDTD and MD calculate the Coulomb field between charged particles, driving the development of a new technique to permit accurate representation of fields without double counting between these two solvers. We compared the predicted conductivity calculated by EMC/FDTD with published experimental data for the complex conductivity of silicon at $n_0 = 3.15 \times 10^{16} \text{ cm}^{-3}$ [4]. The calculated data shows excellent agreement with the experimental data.

The final extension made to the technique incorporated a finite-volume treatment of electrons and ions in MD. This was described in Chapter 4. The exchange interaction between indistinguishable electrons has been shown to significantly affect bulk materials properties for carrier densities greater than $10^{18} \text{ cm}^{-3}$ [3, 37–39]. The new method describes the exchange interaction between indistinguishable electrons with MD. EMC/FDTD/MD also describes the finite radius of dopant ions in the material. In this final EMC/FDTD/MD, all relevant carrier-phonon interactions are included, as are all relevant electromagnetic effects, and effects from the Pauli exclusion principle in materials with high carrier densities. In Chapter 5, we used EMC/FDTD/MD to parameterize the electron and ion radii for doped silicon at DC, and then we calculated the THz-frequency conductivity of silicon for $n_0 = 10^{14} - 10^{19} \text{ cm}^{-3}$. The EMC/FDTD/MD solver is a powerful tool for the prediction of the THz-frequency conductivity in materials with high carrier density.

### 6.2 Future work

**6.2.1 Apply the EMC-FDTD solver to the examination of copper, incorporating surface roughness and copper material characteristics**

In the context of metals, the Monte Carlo approach has most commonly been used to study the decrease in conductivity that occurs as a result of small physical dimension [123–126]. Bulk
metals are not commonly simulated with the EMC because driving fields cause only small deviations from thermal equilibrium [127], so these systems are usually well-described by simpler models like the relaxation time approximation [125]. The necessity of including the effects of the Pauli exclusion principle can be addressed by the rejection technique implemented in EMC/FDTD/MD [127–130].

A previous representation of metals with Monte Carlo methods used a modified acoustic scattering rate, calculated assuming the wave vector to be independent of frequency [127]. This simulation produced quality results in several limiting cases, and indicated the possibility of application of this technique to broader parameter ranges, given sufficient computing capabilities.

In the THz regime where materials characteristics deviate from those predicted in theory, a more comprehensive description of transport is needed. This work would develop a model for carrier transport in metals and incorporate surface scattering, allowing for the inclusion of surface roughness. Results from this numerical study would be compared with an experimental surface roughness study being completed in tandem by Professor John Booske and Benjamin Yang of the University of Wisconsin-Madison.

6.2.2 Explore the use of the solver for examination of media where surface properties and internal dimensions play a major role in observed material properties

The research described above could be applied to the numerical description of systems where material parameters may not be accurately described by current bulk models. Applicability of this model is not limited to the terahertz frequency range, but may easily be applied in the microwave or optical ranges.

An example of such a system is composed of metallic nanoparticles dispersed in biological tissue. Observed material characteristics of media embedded with metal nanoparticles have been shown not to match with material characteristics before the addition of nanoparticles [131, 132]. Pure FDTD analyses of the material characteristics of biological tissues embedded with metallic nanoparticles have suggested that bulk conductivities may be insufficient to describe the properties
of metal nanoparticles in this context [133]. The EMC/FDTD/MD solver will allow for full consideration of carrier effects on fields and power absorption at the location of the nanoparticle, without the assumptions required by bulk models.
LIST OF REFERENCES


Appendix A: Implementation details

A.1 Initialization

During the initial calculation of the carrier and ion ensembles, electrons are initialized with a randomly chosen spin according to whether a random number is greater or less than 0.5. EMC/FDTD/MD uses a linked-list scheme to calculate pairwise interactions between carriers. In the linked-list scheme, MD maintains lists of the particles close enough to interact through the short-range component of the Coulomb force, so that pairwise forces are only calculated between interacting particles. Associated with each grid cell is a list of the particles in that grid cell, so that interactions among particles within the same cell may be calculated by iterating through the list, rather than by searching the ensemble for nearby particles. In the initialization stage, the electrons in each cell are associated into groups through linked lists, as are the ions in each cell. In order to start the simulation with a realistic carrier ensemble, we check the proximity of each electron to all neighboring ions, to ensure that no electron is initialized in a position of extremely high potential energy.

Once the ensembles are established, the charge density is assigned to the grid via the CIC scheme and Poisson’s equation is solved via an iterative successive over-relaxation scheme for the initial charge density. Local grid-based fields for each ion are calculated as described in Section 4.1. The initial diverging electric fields are found from the gradient of \( \Phi \) (\( \Phi \) being the solution to Poisson’s equation). EMC/FDTD/MD calculates \( F_D \), \( F_{EX} \), and \( G_{ij} \) as functions of \( \vec{x} \) and \( \vec{k} \) and stores the tabulated results for reference. The electron-electron MD force is calculated by averaging solutions to the corrected-Coulomb scheme for many stationary electron positions, where we use \( F_D \) as the reference force, instead of the bare Coulomb force.

A.2 Time-stepping scheme

In our calculation updates, \( \vec{H} \), \( \vec{k} \) and \( \vec{J} \) are defined on the time step, and \( \vec{E} \) and \( \rho \) are defined on the half time step. The \( n^{th} \) time step begins with \( \vec{J}^{n-1} \), \( \vec{k}^{n-1} \), \( E_{FDTD}^{n-1/2} \), \( E_{MD}^{n-1/2} \), \( \rho^{n-1/2} \), and
\( \vec{H}^n \). The scheme is shown in Table A.1. Note that we use \( \vec{H}^{n-1/2} = 0.5(\vec{H}^{n-1} + \vec{H}^n) \), and that

Table A.1 The EMC drift/scatter process takes place in Steps 1 and 2, as carrier momenta and positions are updated. The current density update in Step 3 is formulated to enforce current continuity. Step 4 is the MD calculation. Steps 5 and 6 are the FDTD update.

1. Use \( \vec{E}^{n-1/2} \) and \( \vec{H}^{n-1/2} \) to update \( \vec{k}^{n-1} \rightarrow \vec{k}^n \)
2. Use \( \vec{k}^n \) to update \( \rho^{n-1/2} \rightarrow \rho^{n+1/2} \)
3. Use \( \rho^{n-1/2} \) and \( \rho^{n+1/2} \) to find \( \vec{j}^n \)
4. Use \( \rho^{n+1/2} \) to find \( \vec{E}_F^{n+1/2} \)
5. Use \( \vec{H}^n \) and \( \vec{j}^n \) to update \( \vec{E}_{FDTD}^{n-1/2} \rightarrow \vec{E}_{FDTD}^{n+1/2} \)
6. Use \( \vec{E}_{FDTD}^{n+1/2} \) to update \( \vec{H}^n \rightarrow \vec{H}^{n+1} \)

\( \vec{E} = \vec{E}_{FDTD} + \vec{E}_{MD} \) according to the method described in Sec. 4.1. This time-stepping procedure is adapted from Ref. [134].

In Step 1, FDTD fields are first interpolated to find \( \vec{E} \) and \( \vec{H} \) at integer grid indices, where \( \vec{H} \) is averaged in time as well as space. The field at a carrier is found via interpolation according to the CIC scheme, as described in Section 4.1. After interpolation these grid-based fields are combined with the MD fields where the MD fields are found from \( F_D \) and \( F_{EX} \) lookup tables. The momentum update is then calculated using the following time-centered update equations which incorporate the \( \vec{v} \times \vec{B} \) rotation [135].

\[
\begin{align*}
\vec{k}_1 &= \vec{k}_{n-1} + \frac{q\vec{E}}{2\hbar} \Delta t \quad \text{(A.1a)} \\
\vec{k}_2 &= \vec{k}_1 + \vec{k}_1 \times \vec{t} \quad \text{(A.1b)} \\
\vec{k}_3 &= \vec{k}_1 + \vec{k}_2 \times \vec{s} \quad \text{(A.1c)} \\
\vec{k}_n &= \vec{k}_3 + \frac{q\vec{E}}{2\hbar} \Delta t \quad \text{(A.1d)}
\end{align*}
\]

where

\[
\vec{t} = \frac{q\vec{B}}{2m^*} \Delta t, \quad \text{and} \quad \vec{s} = \frac{2\vec{t}}{1 + \vec{t}^2}
\]

The conduction bands of silicon are ellipsoidal. Implementation of the semiclassical scattering rates requires spherical bands, so \( \vec{k} \) is maintained the Herring-Vogt frame [41]. It is necessary
to return $\vec{k}$ to the true momentum frame before applying Eqs. (A.1). Once carriers have been moved, it is necessary to update the linked lists for any carriers that have moved from one grid cell to another.

Step 2 is calculated including $G_{ij}$ as described in Section 4.2. The current density in Step 3 is calculated according to the description in Section 3.2. In Step 4, the MD fields are calculated according to the new positions of carriers and ions. Steps 5 and 6 are the FDTD update. These steps include use of the TFSF formulation to apply the stimulating fields.

### A.3 Accuracy and stability criteria

Accuracy requires $\Delta x < 0.5\lambda_D$ in the traditional EMC/Poisson. This requirement stems from the need to resolve electrostatic interaction between particles on distances larger than the screening length. The addition of MD relaxes this restriction, since particle interactions are described on length scales smaller than the grid cell size. We are not free of grid-cell-based accuracy considerations, however. FDTD accuracy requires $\Delta x < \lambda/10$ for the shortest wavelength $\lambda$ of interest. This condition is easily satisfied for most situations. In silicon with $n_0 = 10^{14}$ cm$^{-3}$, $\varepsilon_r = 11.7$ and $\sigma_0 = 0.023$ S/cm. When this material is stimulated with radiation of frequency $f_0=1$ THz, the wavelength of interest is $\lambda_0 \approx 87.6\,\mu$m. A simulation of this material with $\Delta x = \lambda_0/10$ would have nearly $1.35 \times 10^5$ carriers and ions in a single grid cell. Clearly, the requirement that $\Delta x < \lambda/10$ gives a very loose upper bound on $\Delta x$. For a lower bound, we require that $\Delta x > 4r_e$ and $\Delta x > 4r_d$, so that the entire profile of the electron and ion is described within the MD formulation.

We find further restrictions on the minimum grid cell size that is reasonable for accuracy that result from the strong forces involved in the carrier-ion interaction. Both FDTD and MD describe these rapidly-varying fields: MD describes the fields within the 27 grid cells surrounding the ion, and FDTD describes the rest. As $\Delta x$ decreases, less of the interacting field is described with MD and more is interpolated from the FDTD grid. This interpolation introduces significant error into the force for the rapidly-varying Coulomb fields close to the ion. To quantitatively determine an appropriate lower-bound on $\Delta x$ based on this effect, we examine a single free electron scattering...
from a single stationary ion. The test defines an electron with thermal initial velocity angled to interact with the ion with impact parameter $b = 1$ nm (Fig. A.1). For each value of $\Delta x$, we find $\Delta v$, where $v = |\vec{v}|$ is the change in the magnitude of electron velocity as a result of the interaction. For $\Delta x \approx 70$ nm, $\Delta v = -0.5\%$, indicating a 0.5% drop in velocity. The change in $\Delta v$ increases monotonically with decreasing $\Delta x$. For $\Delta x < 10$ nm, the electron velocity decreases by a few percent with each interaction with the ion, and at $\Delta x = 3$ nm, such as we would use for 3 carriers per grid cell at $n_0 = 10^{20}$ cm$^{-3}$, $\Delta v = -12\%$. Thus, too small of a grid cell size leads to loss of electron kinetic energy, and eventual trapping around an ion.

As long as these requirements are satisfied, it is relevant to use practical considerations of the computational burden of MD to determine $\Delta x$. As the grid cell size increases for a given doping density, the number of particles in each grid cell increases, and the MD computational burden increases dramatically. Since the traditional accuracy considerations are no longer relevant, we now calculate $\Delta x$ according to $n_0$,

$$\Delta x = \left(\frac{N_{cell}}{n_0}\right)^{1/3} \quad (A.2)$$

where $N_{cell}$ is the number of carriers in a grid cell. Our simulations typically use $N_{cell} = 3$. In essence, the criterion for grid cell size selection is defined to ensure low MD computational burden by having few particles (on average) per grid cell.
The time step $\Delta t$ must satisfy the FDTD stability criterion, given by [49]

$$\Delta t \leq \frac{\Delta x}{c\sqrt{3}} \quad \text{(A.3)}$$

for a cubic grid cell, where $c$ is the speed of light in the material. To give a numerical example, consider again the case of doped silicon with $n_0 = 10^{14}$ cm$^{-3}$, where we allow 3 carriers per grid cell so that $\Delta x = 315.4$ nm. Then, the largest allowable $\Delta t = 2.08$ fs. In this same material, the plasma frequency $\omega_p = 3.20 \times 10^{11}$ rad/s. This satisfies the EMC accuracy and stability requirement that

$$\Delta t_{\text{max}} = \frac{0.5}{\omega_p} \quad \text{(A.4)}$$

by several orders of magnitude. Since MD contributes the bulk of the computational burden, we may reasonably reduce computational load by updating the MD calculation every $n$ EMC/FDTD time steps, where $n < \Delta t_{\text{max}} / \Delta t$. In our simulations we used this further approximation only for the $n_0 = 10^{19}$ cm$^{-3}$ tests.

Stability also establishes a lower bound on the dopant radius $r_d$. In the electron interaction with an ion, the electron may change direction over very small distances and small time scales. If the characteristic distance of these momentum changes is $\delta x$ and the electron’s peak velocity is $\vec{v}_i$, the electron motion must be sampled with a time step $\delta t \leq \delta x / |\vec{v}_i|$ in order to be accurately described. The simulation time step $\Delta t$ is formulated to accurately describe propagation over $\Delta x$ at the speed of light in the material. The highest velocity we expect an electron to obtain is $v_i \approx 10^6$ m/s. Then, for this $\Delta t$, the shortest distance that can be resolved is $\delta x \approx \Delta x / 100$.

We test whether this is enough to describe the electron-ion interaction by observing the scattering angle of an electron that interacts with a stationary ion with known impact parameter $b$ and initial velocity $\vec{v}_i$. The Rutherford scattering angle $\theta$ for the interaction is given by

$$\theta = 2\tan^{-1}\left(\frac{qQ}{4\pi em^*v_i^2b}\right), \quad \text{(A.5)}$$

for an electron of mass $m^*$ scattering from an ion of charge $Q$. We test the response of the EMC/FDTD/MD system for interaction of an electron with an ion described by Coulomb’s law. Accuracy and stability require that the electron-ion interaction be well represented for arbitrarily
small impact parameter $b$. We also test the case where the ion is given finite radius $r_d = 1.1 \ \text{Å}$, the effective Bohr radius of phosphorus in free space. The results are listed in Table A.2.

Table A.2 Test of the scattering angle for a free electron interacting with a stationary ion, where the ion may have $\delta$-function charge or finite volume of radius $r_d = 1.1 \ \text{Å}$, the effective Bohr radius of phosphorous in free space. The impact parameter is $b$. $\theta_{\text{ref}}$ is the Rutherford scattering angle, $\theta_C$ is the scattering angle for the $\delta$-function charge, and $\theta_P$ is the scattering angle for the finite volume charge. All angles are in degrees.

<table>
<thead>
<tr>
<th>$b$ (Å)</th>
<th>670</th>
<th>328</th>
<th>67</th>
<th>34</th>
<th>27</th>
<th>20</th>
<th>13</th>
<th>10</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{\text{ref}}$</td>
<td>4</td>
<td>4</td>
<td>39</td>
<td>71</td>
<td>83</td>
<td>99</td>
<td>121</td>
<td>134</td>
<td>148</td>
</tr>
<tr>
<td>$\theta_C$</td>
<td>4</td>
<td>4</td>
<td>39</td>
<td>71</td>
<td>88</td>
<td>110</td>
<td>150</td>
<td>-168</td>
<td>-7</td>
</tr>
<tr>
<td>$\theta_P$</td>
<td>4</td>
<td>4</td>
<td>39</td>
<td>74</td>
<td>89</td>
<td>111</td>
<td>150</td>
<td>164</td>
<td>113</td>
</tr>
</tbody>
</table>

Both $\theta_C$ and $\theta_P$ give reasonable results for $b \geq 13\text{Å}$. For smaller values of $b$, the $\delta$-function charge produces scattering angles that are completely incorrect, while the finite-volume charge accuracy does not degrade substantially. The interpretation is that the electron reaches speeds during interaction with the $\delta$-function charge that cannot be accurately sampled with the $\Delta t$ of the simulation. The finite-volume charge does not have this problem. In order to resolve interaction with the $\delta$-function charge, we would need to use time-steps smaller than $\Delta t$ for the electron-ion MD calculation.
Appendix B: MD calculation

We describe the $i^{th}$ electron in the ensemble with a minimum-uncertainty wave packet, given by

$$\phi_{\vec{p}_i}(\vec{r}_i) = (2\pi r_c^2)^{-3/4} \exp \left( -\frac{\vec{r}_i^2}{4r_c^2} + i\vec{k}_i \cdot \vec{r}_i \right),$$

where $r_c$ is the electron radius, $\vec{r}_i$ is the position of the $i^{th}$ electron, and $\vec{k}_i$ is its momentum. The Hamiltonian for the electron ensemble is

$$H = E_K + E_D + E_{XC},$$

where $E_K$ is the kinetic energy of the electrons, $E_D$ is the potential energy from the Coulomb interaction among electrons and between electrons and ions, and $E_{XC}$ is the potential energy from the exchange interaction. The Coulomb potential a distance $r = |\vec{r}|$ away from a particle of charge $q$ is given by

$$V = \frac{q}{4\pi \epsilon r},$$

where $\epsilon$ is the permittivity in the material. The equations of motion for the $i^{th}$ electron in an ensemble of $N$ electrons can be calculated from the Hamiltonian, as

$$\frac{d\vec{p}_i}{dt} = -\nabla_{\vec{r}} H,$$

$$\frac{d\vec{r}_i}{dt} = \nabla_{\vec{p}} H.$$

In this case, the equations of motion are given as

$$\hbar \frac{d\vec{k}_i}{dt} = \vec{F}_0 + \sum_{j \neq i}^N \vec{F}_{ij}^D + \sum_{j \neq i}^N \delta_{\sigma_i \sigma_j} \vec{F}_{ij}^{XC},$$

$$\frac{d\vec{r}_i}{dt} = \frac{\hbar \vec{k}_i}{m^*} - \sum_{j \neq i}^N \delta_{\sigma_i \sigma_j} \vec{G}_{ij},$$

where $\sigma_i$ is the spin of the $i^{th}$ electron, $\delta$ is the Kronecker delta symbol, the summations include all electrons $j$ where $j \neq i$, and $\vec{F}_0$ includes all forces from the Coulomb interaction with ions.
The new terms – \(\vec{F}_{ij}^D\), \(\vec{F}_{ij}^{EX}\), and \(\vec{G}_{ij}\) – are defined as

\[
\vec{F}_{ij}^D = -\frac{\partial}{\partial \vec{x}_i} V_r c(\vec{x}_i - \vec{x}_j),
\]

\[
\vec{F}_{ij}^{EX} = \hat{V}_r c(\vec{k}_j - \vec{k}_i) \frac{\partial}{\partial \vec{x}_i} \Delta_r c(\vec{x}_j - \vec{x}_i),
\]

\[
G_{ij} = \frac{1}{\hbar} \left( \frac{\partial}{\partial k_i} \hat{V}_r c(\vec{k}_j - \vec{k}_i) \right) \Delta_r c(\vec{x}_j - \vec{x}_i),
\]

where the auxiliary functions – \(V_r c(\vec{x})\), \(\hat{V}_r c(\vec{k})\), and \(\Delta_r c(\vec{x})\) – are given by

\[
V_r c(\vec{x}) = \int d^3r V(\vec{r} + \vec{x}) \Delta_r c(\vec{r}),
\]

\[
\hat{V}_r c(\vec{k}) = \int d^3r V(\vec{r}) e^{i\vec{k} \cdot \vec{r} - r^2/4\epsilon c},
\]

\[
\Delta_r c(\vec{x}) = (4\pi r_c^2)^{-3/2} e^{-x^2/4r_c^2}.
\]

We calculate \(V_r c(\vec{x})\) and \(\hat{V}_r c(\vec{k})\), and then use the results to define \(\vec{F}_{ij}^D\), \(\vec{F}_{ij}^{EX}\), and \(\vec{G}_{ij}\).

### B.1 \(V_r c(\vec{x})\) calculation

Starting with the above definitions, we have that

\[
V_r c(\vec{x}) = \int d^3r V(\vec{r} + \vec{x}) \Delta_r c(\vec{r})
\]

\[
= \int d^3r \frac{q}{4\pi\epsilon |\vec{r} + \vec{x}|} (4\pi r_c^2)^{-3/2} e^{-r^2/4\epsilon c}
\]

\[
= \frac{q}{4\pi\epsilon} (4\pi r_c^2)^{-3/2} \int d^3\vec{r} \frac{e^{-r^2/4\epsilon c}}{|\vec{r} + \vec{x}|}.
\]

Let \(\vec{z} = \vec{r} + \vec{x}\). Then \(\vec{r} = \vec{z} - \vec{x}\), and \(d\vec{r} = d\vec{z}\).

\[
V_r c(\vec{x}) = \frac{q}{4\pi\epsilon} (4\pi r_c^2)^{-3/2} \int d^3z \frac{e^{-(\vec{z} - \vec{x})^2/4\epsilon c}}{|\vec{z}|}
\]

\[
= \frac{q}{4\pi\epsilon} (4\pi r_c^2)^{-3/2} \int dz \ d\theta \ d\phi \ z^2 \sin\theta \frac{e^{-(\vec{z} - \vec{x})^2/4\epsilon c}}{z}
\]

where we have converted to spherical coordinates. In the new coordinate system the radial variable \(z\) is always positive. Without loss of generality, we assume \(x\) is on the \(\theta = 0\) axis. The
The integrand is then constant in $\phi$.

$$V_{rc}(\vec{x}) = \frac{q}{2e} (4\pi r_c^2)^{-3/2} \int dz \ d\theta \ z \sin\theta \ e^{-(z^2-2xz\cos\theta+x^2)/4r_c^2}$$

$$= \frac{q}{2e} (4\pi r_c^2)^{-3/2} \int_0^\infty dz \ z \ e^{-(z^2+x^2)/4r_c^2} \int_0^\pi d\theta \ \sin\theta \ e^{z\cos\theta/2r_c^2}$$

$$= \frac{q}{2e} (4\pi r_c^2)^{-3/2} \int_0^\infty dz \ z \ e^{-(z^2+x^2)/4r_c^2} \left[ \frac{2r_c^2}{xz} \left( e^{xz/2r_c^2} - e^{-xz/2r_c^2} \right) \right]$$

$$= \frac{q r_c^2}{ex} (4\pi r_c^2)^{-3/2} \left( \int_0^\infty dz \ e^{-(z^2-2xz+x^2)/4r_c^2} - \int_0^\infty dz \ e^{-(z^2+2xz+x^2)/4r_c^2} \right).$$

To evaluate these integrals, note that

$$\int_0^\infty e^{-(ax^2+bx+c)} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} e^{(b^2-4ac)/4a} \text{erfc} \left( \frac{b}{2\sqrt{a}} \right),$$

where \text{erfc} is the complementary error function, given by

$$\text{erfc} \left( \frac{b}{2\sqrt{a}} \right) = \frac{2}{\sqrt{\pi}} \int_{\frac{b}{2\sqrt{a}}}^\infty e^{-x^2} \ dx.$$

Thus we have

$$V_{rc}(\vec{x}) = \frac{q r_c^2}{ex} (4\pi r_c^2)^{-3/2} \sqrt{\pi} r_c \left[ \text{erfc} \left( \frac{-x}{2r_c} \right) - \text{erfc} \left( \frac{x}{2r_c} \right) \right]$$

$$= \frac{2q r_c^2}{ex} (4\pi r_c^2)^{-3/2} \sqrt{\pi} r_c \text{erf} \left( \frac{x}{2r_c} \right)$$

$$V_{rc}(\vec{x}) = \frac{q}{4\pi ex} \text{erf} \left( \frac{x}{2r_c} \right)$$

where we have used the error function

$$\text{erf} \left( \frac{b}{2\sqrt{a}} \right) = \frac{2}{\sqrt{\pi}} \int_{\frac{b}{2\sqrt{a}}}^\infty e^{-x^2} \ dx.$$

The final form of $V_{rc}(\vec{x})$ has no closed form solution. We solve the integral numerically in the EMC/FDTD/MD initialization stage.
B.2 $\hat{V}_{rc}(\vec{k})$ calculation

Starting from the definition of $\hat{V}_{rc}(\vec{k})$, we have,

$$\hat{V}_{rc}(\vec{k}) = \int d^3\vec{r} V(\vec{r}) e^{i\vec{k} \cdot \vec{r} - r^2/4\varepsilon^2}$$

$$= \int d^3\vec{r} \frac{q}{4\pi\varepsilon} e^{i\vec{k} \cdot \vec{r} - r^2/4\varepsilon^2}$$

$$= \frac{q}{2\varepsilon} \int dr \ d\theta \ r \sin \theta e^{ikr \cos \theta - r^2/4\varepsilon^2}$$

$$= \frac{q}{2\varepsilon} \int_0^\infty dr \ r \ e^{-r^2/4\varepsilon^2} \int_0^\pi d\theta \sin \theta e^{ikr \cos \theta}$$

$$= \frac{q}{2\varepsilon} \int_0^\infty dr \ r \ e^{-r^2/4\varepsilon^2} e^{ikr} - e^{-ikr}$$

$$= \frac{q}{2i2k\varepsilon} \int_0^\infty dr \ r \left( e^{-r^2/4\varepsilon^2} e^{ikr} - e^{-r^2/4\varepsilon^2} e^{-ikr} \right)$$

$$= \frac{q}{2i2k\varepsilon} \int_0^\infty dr \ \left( e^{-\left(r/2r_c - ikr\right)^2} - e^{-\left(r/2r_c + ikr\right)^2} \right)$$

$$= \frac{q}{2i2k\varepsilon} e^{-k^2r_c^2} \left( \int_0^\infty dr e^{-\left(r/2r_c - ikr\right)^2} - \int_0^\infty dr e^{-\left(r/2r_c + ikr\right)^2} \right)$$

In this procedure we have employed many of the same techniques of the previous section. We let $u = r/2r_c \mp ikr$ for the first and second terms, so $du = dr/2r_c$. Then,

$$\hat{V}_{rc}(\vec{k}) = \frac{q r_c e^{-k^2r_c^2}}{ik\varepsilon} \left( \int_{-ikr_c}^{\infty} du \ e^{-u^2} - \int_{ikr_c}^{\infty} du \ e^{-u^2} \right)$$

$$= \frac{q r_c e^{-k^2r_c^2}}{ik\varepsilon} \left( 2 \int_0^{ikr_c} du \ e^{-u^2} \right)$$

$$= \frac{2q r_c e^{-k^2r_c^2}}{k\varepsilon} \int_0^{kr_c} dt \ e^{t^2}$$

where we have used $u = it$ in the last equality. To demonstrate that this final form of $\hat{V}_{rc}(\vec{k})$ converges for $kr_c \gg 1$, we show a plot of $\hat{V}_{rc}(\vec{k})$ as a function of $kr_c$, in Fig. B.1. The upper limit of the horizontal axis was chosen for the largest relative wave vector we can reasonably expect in silicon, according to the maximum electron velocity $v \approx 10^6$ m/s.
Figure B.1 $V_{rc}(k)$ as a function of $kr_c$, for $r_c = 10$ Å and $k_{\text{max}} = 4.4 \times 10^{-9}$ m$^{-1}$, the highest reasonable relative wave vector for two interacting electrons in silicon.

### B.3 MD forces with the exchange interaction

Each of the new terms are calculated numerically. The necessary equations are

$$F_{ij}^{D} = -\frac{q^2}{4\pi\varepsilon} \nabla_{\vec{r}_i} \left[ \frac{1}{|\vec{r}|} \text{erf} \left( \frac{|\vec{r}|}{2r_c} \right) \right]$$

$$F_{ij}^{EX} = -\frac{q^2}{8\pi^{3/2}\varepsilon r_c^4 |\vec{k}|} \vec{r} \exp \left( -\frac{\vec{r}^2}{4r_c^2} - k^2 r_c^2 \right) \int_0^{kr_c} dt \: e^{t^2}$$

$$G_{ij} = -\frac{q^2}{4\pi^{3/2}\varepsilon r_c^2 \hbar} \nabla_{\vec{k}_i} \left[ \frac{1}{|\vec{k}|} \exp \left( -\frac{\vec{r}^2}{4r_c^2} - k^2 r_c^2 \right) \int_0^{kr_c} dt \: e^{t^2} \right]$$

where $\vec{r} = \vec{r}_j - \vec{r}_i$ and $\vec{k} = \vec{k}_j - \vec{k}_i$. 