Plasmonic Nanoparticles Project - Notes

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1 Introduction

1.1 Hot charge generators

What follows is a translation of the project's abstract [1]:

When electromagnetic radiation "hits" a plasmonic nanoparticle it causes the free electron density to oscillate with the same frequency as the incident radiation. This, near the resonance frequency, can excite a great number of electrons, that then decay back to their equilibrium state, producing highly energetic electron-hole pairs. These hot charge generators can be absorbed by nearby molecules to induce a chemical reaction, and it follows that these nanoparticles can be used as a light dependent catalyst. One possible such reaction is the chemical reduction from carbon dioxide to carbon monoxide, diminishing the levels of carbon dioxide in the atmosphere and producing a valuable component for industrial use.

In the group of Dr. Jonhanes Lischner in the Department of Materials of Imperial College London, a code was developed that utilizes spectral methods to calculate the charge carriers generation rate. It consists of 3 steps:

1. The shape of the nanoparticle that one intends to study is chosen (cubes, spheres, tetrahedra), and one finds all the compatible atom positions.
2. The electric potencial is obtained for an incident finite frequency electric field. We shall use the Discrete Dipole Approximation to find the electric field at each point, which can then be integrated to find the electric potential - another approach would be to use the quasi-static approximation and solve Laplace's equation inside the nanoparticle.
3. Finaly, this potential is used in Fermi's golden rule to calculate the rate of generation of charge carriers.

The aim of this project is to develop an open source code in Julia to execute the second step, since, at the time of writing, Dr. Jonhanes' group uses proprietary software.

1.2 Discrete Dipole Approximation (DDA)

The discrete-dipole approximation for computing scattering and absorption by particles, originally developed by Purcell and Pennypacker [2], is a general method for computing scattering and absorption by a particle of arbitrary shape [3]. It replaces the continuum by a grid of N point dipoles, such that the spacing between the dipoles is small compared to the wavelength. Each dipole has an oscillating polarization in response to both an incident plane wave and the electric fields due to all of the other dipoles in the array; the self-consistent solution for the dipole polarizations can be found solving a set of coupled linear equations.

Since we are considering nanoparticles, with a volume of $1000 - 100000$ Å^3, and, depending on the structure of the material we are considering, each atom in a nanoparticle takes up between $1 - 10$ Å^3, there are between 100 and 10000 atoms on the nanoparticle. For a good approximation of the electric field, one should expect to use at least that many dipoles.

For the discrete dipole approximation, we shall consider $\mathbf{p}_j = \hat{\alpha}\mathbf{E}_j$, where $\mathbf{p}_j$ is the instantaneous (complex) dipole moment at the jth dipole's position, $\mathbf{E}_j$ is the instantaneous (complex) electric field at that dipole, and $\hat{\alpha}$ is the (symmetric [4]) polarizability tensor. The assumption $\mathbf{p}_j = \hat{\alpha}\mathbf{E}_j$ this is not entirely correct, but is a good approximation for a big number of dipoles and big wavelengths [3].

Then, a self consistent solution for the electric field is given by:

$$\mathbf{p}_j = \hat{\alpha}\left(\mathbf{E}_{inc,j} + \mathbf{E}_{ind,j}\right), \tag{1.1}$$

where $\mathbf{E}_{inc,j}$ is the incident electromagnetic field at the jth dipole and $\mathbf{E}_{ind,j}$ is the field induced by the other dipoles. For a given angular wave vector $\mathbf{k}$ and angular frequency ω, with $w/c = |\mathbf{k}|$, we can represent $\mathbf{E}_{inc,j}$ as $\mathbf{E}_{inc,j} = \mathbf{E}_0 e^{i(k\cdot\mathbf{r}_j - \omega t)}$.

Since the fields produced by the other oscillating dipoles depend linearly on their magnitude and the distance between dipoles is fixed, we can write this induced field as a matrix product:

$$\mathbf{p}_j = \hat{\alpha}\left(\mathbf{E}_{inc,j} - \sum_{k\neq j} A_{jk}\mathbf{p}_k\right) \tag{1.2}$$

Here A_{jk} is a matrix that when applied to the polarization $\mathbf{p}_k$ gives the symmetric of the electric field of the kth dipole at the jth position.

Let $\mathbf{r}_{jk} = \mathbf{r}_j - \mathbf{r}_k$, the distance between the jth and kth dipoles, and $\hat{\mathbf{r}}_{jk} =$

$\frac{\mathbf{r}_j - \mathbf{r}_k}{|\mathbf{r}_j - \mathbf{r}_k|}$. The electric field produced by these oscilating dipoles is given by:

$$A_{jk}\mathbf{p}_k = e^{ikr_{jk}}\frac{1}{4\pi\epsilon_0}\left[\frac{k^2}{r_{jk}}\Big(\hat{\mathbf{r}}_{jk}\times(\hat{\mathbf{r}}_{jk}\times\mathbf{p}_k)\Big) + \left(\frac{1}{r_{jk}^3} - \frac{ki}{r_{jk}^2}\right)\Big(\mathbf{p}_k - 3(\mathbf{p}_k\cdot\hat{\mathbf{r}}_{jk})\,\hat{\mathbf{r}}_{jk}\Big)\right] \quad (1.3)$$

We shall derive this expression in section 1.8. Note that this is the exact dipolar field for point dipoles, and retardation efects are fully taken into account. In this regard, this method is superior to solving Laplace's equation, since that method ignores retardation efects. This matrix is not defined for $j = k$, but if we define $A_{jj} = \hat{\alpha}^{-1}$, then we can rewrite equation (1.2) as:

$$\sum_k A_{jk}\mathbf{p}_k = \mathbf{E}_{inc,j} \implies A\mathbf{p} = \mathbf{E}_{inc}, \quad (1.4)$$

where we now see $\mathbf{p}$ and $\mathbf{E}$ as $3N$ dimensional vectors, and A as a $3N$ by $3N$ matrix. A consistent set of polarizations obeys:

$$A\mathbf{p} = \mathbf{E}_{inc} \quad (1.5)$$

The standard solutions for this kind of problem can be tried, as direct matrix inversion and relaxation methods.

1.3 Calculating the matrix

The matrix A has two kinds of symmetry: it's immediate from equation (1.3) that $A_{jk} = A_{kj}$, since $\mathbf{r}_{jk} = -\mathbf{r}_{kj}$ and the vector always appears in pairs; and each entry A_{jk} is a 3×3 symmetric matrix, in the sense that $(A_{jk})_{lm} = (A_{jk})_{ml}$.

We can check this. To simplify notation, let us define two $N \times N$ matrices and a constant: B, C, and D, respectively. For given indices j, k, we define them as follows:

$$B_{jk} = \frac{e^{ikr_{jk}}}{r_{jk}^3}\frac{1}{4\pi\epsilon_0}, \qquad C_{jk} = \left(\frac{1}{r_{jk}^2} - \frac{ki}{r_{jk}}\right), \qquad D = k^2, \qquad \mathbf{r} = \mathbf{r}_{jk}.$$

Note that the k that appears not in indices is the wave vector magnitude. Let $\mathbf{p}_{k_m} := (\mathbf{p}_k\cdot\hat{\mathbf{x}}_m)\hat{\mathbf{x}}_m$, the mth component of the kth dipole. Therefore, we can write $(A_{jk})_{lm}\mathbf{p}_{k_m}$, the contribution to the lth component of the electric field at the jth dipole by the mth component of the kth dipole, as:

$$(A_{jk})_{lm}\mathbf{p}_{k_m} = B_{jk}\Big[D\big(\mathbf{r}\times(\mathbf{r}\times\mathbf{p}_{k_m})\big) + C_{jk}(r^2\mathbf{p}_{k_m} - 3(\mathbf{p}_{k_m}\cdot\mathbf{r})\mathbf{r})\Big]\cdot\hat{\mathbf{x}}_l \quad (1.6)$$

This follows quickly from (1.3).

Let's simplify the parcel on the right.

$$\left(r^2\mathbf{p}_{k_m} - 3(\mathbf{p}_{k_m}\cdot\mathbf{r})\mathbf{r}\right)\cdot\hat{\mathbf{x}}_l = (\delta_{ml}\,r^2 - 3x_l x_m)\,p_m, \tag{1.7}$$

where p_m is the magnitude of $\mathbf{p}_{k_m}$, and x_i the magnitude of the ith component of $\mathbf{r}$. We can see this parcel is the same if we switch l and m.

The vector product component can be quickly obtained using Einstein's index notation:

$$\begin{aligned}(\mathbf{r}\times(\mathbf{r}\times\mathbf{p}_{k_m}))\cdot\hat{\mathbf{x}}_l &= \epsilon_{lab}\,x_a\,(\epsilon_{bcd}\,x_c\,p_m\,\delta_{md})\\ &= (\delta_{lc}\delta_{am} - \delta_{lm}\delta_{ac})\,x_a x_c p_m\\ &= (x_l x_m - x_a x_a \delta_{lm})p_m\\ &= (x_l x_m - r^2\delta_{lm})p_m\end{aligned} \tag{1.8}$$

Again, this parcel is the same if we switch m and l. The symmetry for $A_{jj} = \hat{\alpha}^{-1}$ is assured, since the inverse of a symmetric matrix is also symmetric. It follows that A has the symmetry we wanted to prove.

We are now able to write to define the entries of the matrix A in a single expression, defining $B_{jj} = 0 = C_{jj}$:

$$(A_{jk})_{lm} = \delta_{jk}\,\hat{\alpha}^{-1}_{lm} + B_{jk}\Big[D\left(x_l x_m - r^2_{jk}\delta_{lm}\right) + C_{jk}\left(r^2_{jk}\delta_{lm} - 3x_m x_l\right)\Big] \tag{1.9}$$

It should be noted that, for a given geometry and number of dipoles, the distances r_{jk} are fixed. With some changes, one could define the matrices B and C "free" from dependencies in frequency and then adjust them with the necessary dependence with ω.

The matrix can be rewritten as:

$$\begin{aligned}(A_{jk})_{lm} = \delta_{jk}\,\hat{\alpha}^{-1}_{lm} + e^{ikr_{jk}}\frac{1}{4\pi\epsilon_0}\Bigg[&-k^2\,\frac{1}{r_{jk}}\left(\delta_{lm} - \frac{x_l x_m}{r^2_{jk}}\right) +\\ &+\frac{1}{r^3_{jk}}\left(\delta_{lm} - 3\frac{x_l x_m}{r^2_{jk}}\right) - k\,\frac{i}{r^2_{jk}}\left(\delta_{lm} - 3\frac{x_l x_m}{r^2_{jk}}\right)\Bigg].\end{aligned} \tag{1.10}$$

Then, we can define new matrices F, G, and H that don't depend on ω such that:

$$(A_{jk})_{lm} = \delta_{jk}\,\hat{\alpha}^{-1}_{lm} + e^{ikr_{jk}}\frac{1}{4\pi\epsilon_0}\Bigg[-k^2(F_{jk})_{lm} + (G_{jk})_{lm} - ik(H_{jk})_{lm}\Bigg], \tag{1.11}$$

where $F_{jj} = G_{jj} = H_{jj} = 0$, and:

$$\begin{cases} (F_{jk})_{lm} = \dfrac{1}{r_{jk}} \left(\delta_{lm} - \dfrac{x_l x_m}{r_{jk}^2} \right) \\ (G_{jk})_{lm} = \dfrac{1}{r_{jk}^3} \left(\delta_{lm} - 3\dfrac{x_l x_m}{r_{jk}^2} \right) \\ (H_{jk})_{lm} = r_{jk} (G_{jk})_{lm} \end{cases} \tag{1.12}$$

This approach has the advantage that we can calculate the matrices F, G, H once and then obtain the entries of A for each frequency that we consider.

1.4 The Purcell-Pennymaker way

Let's try relaxation. Let

$$\mathbf{E}_i = \mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}_i} + \sum_{j \neq i} \frac{e^{i(kr)}}{4\pi\epsilon_0 r_{ij}^3} \Bigg[k^2 (\mathbf{r}_{ij} \times (\mathbf{p}_j \times \mathbf{r}_{ij})) + \\ + \left(\frac{1}{r^2} - \frac{ki}{r_{ij}} \right) \left(3(\mathbf{p}_j \cdot \mathbf{r}_{ij})\, \mathbf{r}_{ij} - r_{ij}^2 \mathbf{p}_j \right) \Bigg] \tag{1.13}$$

and

$$\mathbf{p}_i = \alpha \mathbf{E}_i \tag{1.14}$$

be the $6N$ linear equations we want to solve.

We can find a solution by using an iterative method to find the $\mathbf{p}_i$ and $\mathbf{E}_i$ that satisfy both these equations. Let $\mathbf{p}_j^{(n)}$ and $\mathbf{E}_j^{(n)}$ be our guesses for the polarizations and electric field after n iterations. Then, we define the next iteration of polarizations as:

$$\mathbf{p}_i^{(n+1)} = \gamma\alpha \mathbf{E}_i^{(n)} + (1-\gamma)\mathbf{p}_i^{(n)}. \tag{1.15}$$

and fields as:

$$\mathbf{E}_i^{(n+1)} = \mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}_i} + \sum_{j \neq i} \frac{e^{i(kr)}}{4\pi\epsilon_0 r_{ij}^3} \Bigg[k^2 (\mathbf{r}_{ij} \times (\mathbf{p}_j^{(n)} \times \mathbf{r}_{ij})) + \\ + \left(\frac{1}{r^2} - \frac{ki}{r_{ij}} \right) \left(3(\mathbf{p}_j \cdot \mathbf{r}_{ij})\, \mathbf{r}_{ij} - r_{ij}^2 \mathbf{p}_j^{(n)} \right) \Bigg] \tag{1.16}$$

Following Purcell and Pennymaker [2], we use the parameter γ to aid convergence. The solution we desire is a fixed point of these iterations. For our inicial guesses we shall use $\mathbf{p}_j^0 = 0$, $\mathbf{E}_j^0 = \mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}_i}$ for all j.

1.5 The Clausius-Mossotti Equation

One can approximate the polarization of a molecule, knowing its relative electric permeability, using the Clausius-Mossotti relation [5]. It's valid for isotropic linear dielectrics, with relative magnetic permeability close to unity ($\mu \approx 1$). We shall now derive it.

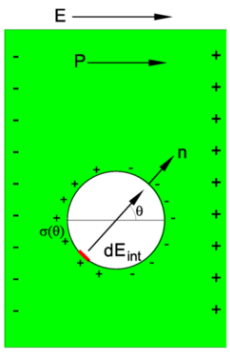
Let's consider a linear dielectric with n molecules per unit volume. The electric polarization vector $\mathbf{P}$ is the sum of the induced dipoles in a unit of volume:

$$\mathbf{P} = n\mathbf{p}_{\text{ind}} \tag{1.17}$$

In a linear dielectric, there's a linear relation between the macroscopic electric field inside the dielectric $\mathbf{E}$ and the polarization vector $\mathbf{P}$:

$$\mathbf{P} = \epsilon_0(1 - \epsilon_r)\mathbf{E} \tag{1.18}$$

Since we are considering only induced dipoles, we have $\mathbf{p}_{\text{ind}} = \alpha\mathbf{E}_m$, where α is the atomic polarizability, and $\mathbf{E}_m$ is the electric field in the position of the molecule. This suggests a relation between the polarization and dielectric constant using equation (1.17):



$$\epsilon_0(\epsilon_r - 1)\mathbf{E} = \mathbf{P} = n\mathbf{p}_{\text{ind}} = n\alpha\mathbf{E}_m,$$

and, if $\mathbf{E} = \mathbf{E}_m$, then:

$$\epsilon_0(\epsilon_r - 1) = n\alpha \tag{1.19}$$

This is not a bad approximation for low dielectric constants ($\epsilon_r \approx 1$) , but it is a poor one for other values of it. This is because the electric field at the molecule, $\mathbf{E}_m$, is different from the average macroscopic field at the points around it. Consider a small empty sphere in the dielectric around the molecule, small enough so that the polarization vector is approximately constant at its surface. The field at the the center of the sphere is:

$$\mathbf{E}_m = \mathbf{E} + \frac{1}{3\epsilon_0}\mathbf{P}, \tag{1.20}$$

where $\mathbf{E}$ is the electric field inside the dielectric. We can obtain this result solving Laplace's equation (there will be a bound charge $\sigma(\theta)$ on the surface given by $\sigma(\theta) = \mathbf{P} \cdot \hat{\mathbf{n}}$), but we can solve the problem quicker if we assume that the solution for the field inside the sphere is approximately constant. Note that the electric field is the superposition of the field in the dielectric and the field inside a sphere with opposite polarization. It's known (see [5]) that the average electric field inside a sphere due to the contributions to the charges in its interior is:

$$\mathbf{E}_{\text{avg}} = -\frac{\mathbf{p}}{4\pi\epsilon_0 R^3}, \tag{1.21}$$

where $\mathbf{p} = \int d\mathbf{r}'\mathbf{r}'\rho(r')$ is the dipole moment of the sphere, and R its radius. If we consider a small enough sphere such that $\mathbf{p} = \mathbf{p}_{ind}$, the dipole moment of the sphere is given by $\mathbf{P}\cdot = -\frac{4}{3}\pi R^3\mathbf{P}$, and we get equation (1.20).

Then, we can use equations (1.17) and (1.18) to obtain:

$$\mathbf{p} = \alpha\mathbf{E}_m = \frac{1}{\epsilon_0(1-\epsilon_r)}\mathbf{P} + \frac{1}{3\epsilon_0}\mathbf{P} \implies \alpha = \frac{n}{\epsilon_0(1-\epsilon_r)} + \frac{n}{3\epsilon_0} \tag{1.22}$$

The Clausius-Mossotti relation quickly follows:

$$\frac{n\alpha}{3\epsilon_0} = \frac{\epsilon_r - 1}{\epsilon_r + 2} \tag{1.23}$$

This relation is exact in the zero frequency limit for oscillating incident fields, but not correct if the Polarization (and hence the field) varies significantly at the boundary of the molecule.

1.6 An alternate Clausius-Mossotti derivation

This alternate derivation makes the approximation the Clausius-Mossotti derivation makes more evident.

For a start, what is the electric dipole field? We know the electric dipole potential:

$$V_{\text{dip}} = \frac{1}{4\pi\epsilon_0}\frac{\mathbf{p}\cdot\hat{\mathbf{r}}}{r^2} \implies \mathbf{E}_{\text{dip}} = \frac{1}{4\pi\epsilon_0}\nabla\left(\mathbf{p}\cdot\nabla\left(\frac{1}{r}\right)\right) \tag{1.24}$$

This way of writing the r dependence will be useful later. The gradient of a scalar product can be obtained using the following identity:

$$\nabla(a\cdot b) = (a\cdot\nabla)b + a\times(\nabla\times b) + (b\cdot\nabla)a + b\times(\nabla\times a) \tag{1.25}$$

Then, since $\mathbf{p}$ is a constant:

$$\mathbf{E}_{\text{dip}} = \frac{1}{4\pi\epsilon_0}\left[(\mathbf{p}\cdot\nabla)\left(\nabla\frac{1}{r}\right) + \mathbf{p}\times\left(\nabla\times\left(\nabla\frac{1}{r}\right)\right)\right] \tag{1.26}$$

The curl of a gradient is zero, so all that remains is the term on the left. Using Einstein's notation, we see that:

$$(a\cdot\nabla)(\nabla b)_i = a_j\frac{\partial}{\partial x_j}\frac{\partial}{\partial x_i}b = a_i\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_i}b + a_{j\neq i}\frac{\partial}{\partial x_{j\neq i}}\frac{\partial}{\partial x_i}b \tag{1.27}$$

Here the first term is analogous to a dot product between a and the Laplacian of b. What's the Laplacian of $1/r$? Using spherical coordinates one gets zero, but if we integrate in a spherical volume we get that it is a delta function.

$$\int_V \nabla^2\left(\frac{1}{r}\right)\,dV = \oint_A \nabla\left(\frac{1}{r}\right)\cdot\,d\mathbf{A} = \oint_A\left(\frac{-\hat{\mathbf{r}}}{r^2}\right)\cdot\,d\mathbf{A} = -4\pi \tag{1.28}$$

Since $1/r$ is differentiable everywhere in that domain except at zero, necessarily the only contribution to the integral comes from there. Then, one gets that $\nabla^2\left(\frac{1}{r}\right) = -4\pi\delta^3(\mathbf{r})$. Since $1/r$ is symmetric for x, y, z, we expect the same contribution from each component, and we can write

$$\frac{\partial^2}{\partial x^2}\frac{1}{r} = \frac{\partial^2}{\partial y^2}\frac{1}{r} = \frac{\partial^2}{\partial z^2}\frac{1}{r} = -\frac{4\pi}{3}\delta^3(\mathbf{r})$$

It follows that the electric field "picks up" a discontinuity at the origin. One can show that there are no more contributions to the field at the origin from the other derivatives. Then we can calculate the field as usual, writing nabla in spherical coordinates.

$$\begin{aligned}\mathbf{E}'_{\text{dip}} &= \frac{1}{4\pi\epsilon_0}(\mathbf{p}\cdot\nabla)\left(\nabla\frac{1}{r}\right) = \frac{1}{4\pi\epsilon_0}\left[(\mathbf{p}\cdot\hat{\mathbf{r}})\frac{\partial}{\partial r} + \frac{(\mathbf{p}\cdot\hat{\theta})}{r}\frac{\partial}{\partial\theta}\right]\left(-\frac{\hat{\mathbf{r}}}{r^2}\right) \\ &= \frac{1}{4\pi\epsilon_0}\left[2(\mathbf{p}\cdot\hat{\mathbf{r}})\frac{\hat{\mathbf{r}}}{r^3} + \frac{(\mathbf{p}\cdot\hat{\theta})}{r^3}\frac{\partial(-\hat{\mathbf{r}})}{\partial\theta}\right] = \frac{1}{4\pi\epsilon_0}\left[\frac{2(\mathbf{p}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}} - (\mathbf{p}\cdot\hat{\theta})\hat{\theta}}{r^3}\right]\end{aligned} \tag{1.29}$$

We can rewrite this in a more concise manner, using the fact that:

$$\mathbf{p} = (\mathbf{p}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}} + (\mathbf{p}\cdot\hat{\theta})\hat{\theta} \implies (\mathbf{p}\cdot\hat{\theta})\hat{\theta} = \mathbf{p} - (\mathbf{p}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}},$$

to write:

$$\mathbf{E}'_{\text{dip}} = \frac{1}{4\pi\epsilon_0}\left[\frac{3(\mathbf{p}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}}{r^3}\right]. \tag{1.30}$$

The apostrophe is to remind us that this field is not the correct one, since it is missing the term at the origin. This term is the component of the Laplacian at the origin in the direction of $\mathbf{p}$.

$$\begin{aligned}\mathbf{E}_{\text{dip}} &= \frac{1}{4\pi\epsilon_0}\left[\frac{3(\mathbf{p}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}}{r^3} - \frac{4\pi\mathbf{p}}{3}\delta^3(\mathbf{r})\right] \\ &= \frac{1}{4\pi\epsilon_0}\left[\frac{3(\mathbf{p}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}}{r^3}\right] - \delta^3(\mathbf{r})\frac{\mathbf{p}}{3\epsilon_0}\end{aligned} \tag{1.31}$$

This term can be deduced in other ways, but the underlying physics is simple. We can approximate a point dipole by considering two charges, q and $-q$, letting the distance between them d go to zero and their charge go to infinity, such that $dq = p$ is constant. The field we get is the dipole field, and the delta function tells us the field between the charges, where there is a discontinuity in the field (above and bellow an electric charge there's a discontinuity in the field). We can now obtain a different derivation of Clausius-Mossotti.

In a linear dielectric, we have

$$n\mathbf{p} = (\epsilon_r - 1)\epsilon_0\mathbf{E}, \tag{1.32}$$

where n is the dipole volume density, and $\mathbf{E}$ is the average macroscopic field in a certain point in the dielectric. We define a polarizability tensor α such that

$$\mathbf{p} = \alpha \mathbf{E}' \tag{1.33}$$

As before, E' is not the average macroscopic field in a certain point, it is the field that affects the dipole. If we assume that the dipole doesn't "see" its or its neighbours' delta function fields, and in each point that term contributes $-\frac{\mathbf{p}}{3\epsilon_0}\delta^3(\mathbf{r})$, then the average field E, averaged in a small volume around a point, is:

$$\mathbf{E} = \mathbf{E}' - \frac{n}{3\epsilon_0}\mathbf{p} \implies n\frac{\mathbf{p}}{\epsilon_0(\epsilon_r - 1)} = \frac{\mathbf{p}}{\alpha} - \frac{n}{3\epsilon_0}\mathbf{p} \tag{1.34}$$

Rewriting, we get Clausius-Mossotti.

$$\epsilon_r - 1 = \frac{\frac{\epsilon_0}{n\alpha}}{1 - \frac{\epsilon_0}{3n\alpha}} \quad \text{or} \quad \frac{n\alpha}{3\epsilon_0} = \frac{\epsilon_r - 1}{\epsilon_r + 2} \tag{1.35}$$

This equivalence (between the dipoles ignoring the delta term and the Clausius-Mossotti equation) implies that when we obtain the polarizations, we can't just divide by the polarizability constant to obtain the electric field, and must be mindful of the delta term.

1.7 Time Dependent Potentials and Fields

The four Maxwell equations carry within them some redundancies: we have two vector equations and two scalar equations, which amount to eight component equations, for six unknowns, the six components of the two vector fields $\mathbf{E}$ and $\mathbf{B}$.

$$\begin{cases} \nabla \cdot \mathbf{E} = \dfrac{\rho}{\epsilon_0} \\ \nabla \cdot \mathbf{B} = 0 \\ \nabla \times \mathbf{E} = -\dfrac{\partial \mathbf{B}}{\partial t} \\ \nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \dfrac{\partial \mathbf{E}}{\partial t} \end{cases} \tag{1.36}$$

The second of these equations implies that $\mathbf{B} = \nabla \times \mathbf{A}$, for some $\mathbf{A}$. Therefore, we can rewrite the third equation as:

$$\nabla \times \mathbf{E} + \nabla \times \frac{\partial \mathbf{A}}{\partial t} = 0 \implies \nabla \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = 0,$$

which implies that $\mathbf{E} + \dfrac{\partial \mathbf{A}}{\partial t} = -\nabla V$ for some V. It follows:

$$\begin{cases} \mathbf{B} = \nabla \times \mathbf{A} \\ \mathbf{E} = -\nabla V - \dfrac{\partial \mathbf{A}}{\partial t} \end{cases} \tag{1.37}$$

where $\mathbf{A}$ and V are given by the two following differential equations:

$$\begin{cases} \nabla^2 V + \dfrac{\partial}{\partial t} \nabla \cdot \mathbf{A} = -\dfrac{\rho}{\epsilon_0} \\ \nabla^2 \mathbf{A} - \mu_0 \epsilon_0 \dfrac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla\big(\nabla \cdot \mathbf{A} + \mu_0 \epsilon_0 \dfrac{\partial V}{\partial t}\big) = -\mu_0 \mathbf{J} \end{cases} \tag{1.38}$$

The first of these equations is obtained by taking the divergence of $\mathbf{E}$ in (1.37), and the second one taking the curl of $\mathbf{B}$, using the vector identity $\nabla \times (\nabla \times \mathbf{A}) = \nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$.

The Maxwell equations, with suitable boundary conditions for $\mathbf{A}$ and V, are contained in the solutions of (1.38).

We can choose an appropriate gauge for our potentials: from (1.37) the fields don't change for some changes of potential. Consider

$$\begin{cases} \mathbf{A}' = \mathbf{A} + \alpha \\ V' = V + \beta \end{cases}$$

It can be easily checked that if the fields are invariant then $\alpha = \nabla \chi$, $\beta = -\frac{\partial \chi}{\partial t}$ for some scalar field χ. We can choose χ so that $\nabla \cdot \mathbf{A} + \mu_0 \epsilon_0 \frac{\partial V}{\partial t} = 0$, since the divergence of A can be varied at will. It follows that we can simplify extensively equations (1.38), obtaining the following two:

$$\begin{cases} \Box^2 V = -\dfrac{\rho}{\epsilon_0} \\ \Box^2 \mathbf{A} = -\mu_0 \mathbf{J}, \end{cases} \tag{1.39}$$

where $\Box^2$ is the D'Alembert operator, $\Box^2 = \nabla^2 - \dfrac{1}{c^2} \dfrac{\partial^2}{\partial t^2}$. The solutions to these potential equations are given by:

$$V(\mathbf{r}, t) = \frac{1}{4\pi\epsilon_0} \int\int d\mathbf{r}'\, dt'\, \frac{\rho(r', t')}{|\mathbf{r} - \mathbf{r}'|}\, \delta(t' - t_r) \tag{1.40}$$

$$\mathbf{A}(\mathbf{r}, t) = \frac{\mu_0}{4\pi} \int\int d\mathbf{r}'\, dt'\, \frac{\mathbf{J}(r', t')}{|\mathbf{r} - \mathbf{r}'|}\, \delta(t' - t_r). \tag{1.41}$$

Here, $t_r = t - \frac{|\mathbf{r} - \mathbf{r}'|}{c}$ is the retarded time, meaning the information from currents and charge densities takes some time to affect the potentials at some other points.

On a side-note, for an oscillating electric field, $\mathbf{E} = e^{-i\omega t} \mathbf{E}'(\mathbf{r})$, outside of a source, meaning no currents or charge densities, the fields can be calculated using only $\mathbf{A}$ as follows:

$$\begin{cases} \mathbf{B} &= \nabla \times A \\ \mathbf{E} &= c\, \dfrac{i}{k} \nabla \times B, \end{cases} \tag{1.42}$$

where $k = \dfrac{\omega}{c}$.
The second of these equations can be deduced using the fourth of Maxwell's equations (1.36), since $\frac{\partial \mathbf{E}}{\partial t} = -i\omega\mathbf{E}$.

1.8 Harmonic dipole fields

Since we are analyzing the effects of electromagnetic waves on molecules, we can retrieve the idea that the induced dipole caused by an electric field is proportional to the field (in apolar molecules), and, since the field has a sinusoidal time dependence, it would be natural to assume the charge density (which varies due to the aplied field) has a similar time dependency.

Let $\rho(\mathbf{r}, t) = e^{-i\omega t}\rho(\mathbf{r})$. Then, we get:

$$\begin{aligned} V(\mathbf{r}, t) &= \frac{1}{4\pi\epsilon_0} \int\int d\mathbf{r}'\, dt'\, \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, e^{-i\omega t'}\, \delta(t' - t_r) = \\ &= e^{-i\omega t} \frac{1}{4\pi\epsilon_0} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} e^{ik|\mathbf{r}-\mathbf{r}'|} \end{aligned} \tag{1.43}$$

From the continuity equation, we have $\dfrac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{J}$, so:

$$i\omega\rho = \nabla \cdot \mathbf{J}, \tag{1.44}$$

and we can see that $\mathbf{J}$ must have the same time dependency (apart some phase we can add to its spatial dependence). Then $\mathbf{J}(\mathbf{r}, t) = e^{-i\omega t}\mathbf{J}(\mathbf{r})$, and

$$\mathbf{A}(\mathbf{r}, t) = \frac{\mu_0}{4\pi} e^{-i\omega t} \int d\mathbf{r}' \frac{\mathbf{J}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} e^{ik|\mathbf{r}-\mathbf{r}'|} \tag{1.45}$$

We can now do multipolar expansion on these potentials to find the dipolar fields. If the domain of integration is very small in comparison with the distance to the source, then the first non-zero multipolar term dominates outside the source. In the Discrete Dipolar Approximation we shall be considering point dipoles to approximate the continuum, and so the dipole approximation is exact.

See [6] for a thorough examination of the various approximations that can be done for different distances from the source, and also the higher multipole terms.

The order zero approximation we can do is $|\mathbf{r} - \mathbf{r}'| \approx r$. Calculating the potentials from (1.43) and (1.45), we obtain:

$$V(\mathbf{r}, t) = e^{i(kr-\omega t)} \frac{1}{4\pi\epsilon_0 r} \int d\mathbf{r}' \rho(\mathbf{r}') = e^{i(kr-\omega t)} \frac{q}{4\pi\epsilon_0 r} = 0, \tag{1.46}$$

where q is the electrostatic monopolar moment, the total charge in the given molecule, which is zero (also, the monopolar moment must be zero for oscilating charges that produce oscilating fields, see [6]). For the vector potential, we get:

$$\mathbf{A}(\mathbf{r},t) = \frac{\mu_0}{4\pi r} e^{i(kr-\omega t)} \int d\mathbf{r}' \mathbf{J}(\mathbf{r}'), \tag{1.47}$$

This integral can be rewritten with "integration by parts":

$$\int d\mathbf{r}' \mathbf{J}(\mathbf{r}') = \oint \mathbf{r}' (\mathbf{J} \cdot d\mathbf{a}) - \int \mathbf{r}' (\nabla' \cdot \mathbf{J})\, d\mathbf{r}' \tag{1.48}$$

Observe that $\nabla \cdot (x_i \mathbf{J}) = J_i + x_i (\nabla \cdot \mathbf{J})$. If we sum over the components, we get $\sum_i \hat{\mathbf{e}}_i \nabla \cdot (x_i \mathbf{J}) = \mathbf{J} + \mathbf{r}(\nabla \cdot \mathbf{J})$.

Since we are considering confined sources (molecules), the second integral is null. Then, using (1.44), we have:

$$\mathbf{A}(\mathbf{r},t) = e^{i(kr-\omega t)} \frac{\mu_0}{4\pi r} (-i\omega) \int d\mathbf{r}' \mathbf{r}' \rho(r'), \tag{1.49}$$

where the integral is the electrostatic dipole moment of the molecule,

$$\mathbf{p} = \int d\mathbf{r}' \mathbf{r}' \rho(r') \tag{1.50}$$

We can now obtain the electric and magnetic fields by differentiation:

$$\begin{cases} \mathbf{B} &= \nabla \times \mathbf{A} \\ \mathbf{E} &= c \dfrac{i}{k} \nabla \times \mathbf{B}. \end{cases} \tag{1.51}$$

Finally (after a train of differentiations):

$$\begin{cases} \mathbf{B} = (\hat{\mathbf{r}} \times \mathbf{p}) \dfrac{k^2}{4\pi\epsilon_0 c} \dfrac{e^{i(kr-wt)}}{r} \left(1 - \dfrac{1}{ikr}\right) \\ \mathbf{E} = e^{i(kr-wt)} \dfrac{1}{4\pi\epsilon_0} \left[\dfrac{k^2}{r} (\hat{\mathbf{r}} \times (\mathbf{p} \times \hat{\mathbf{r}})) + \left(\dfrac{1}{r^3} - \dfrac{ki}{r^2} \right) (3(\mathbf{p} \cdot \hat{\mathbf{r}})\, \hat{\mathbf{r}} - \mathbf{p}) \right] \end{cases} \tag{1.52}$$

The next page takes care of the full derivation of the equation for the electric field, which make use of the two following identities (see [6], for example):

$$\nabla \cdot \hat{\mathbf{r}} = \frac{2}{r} \qquad (\mathbf{a} \cdot \nabla)\hat{\mathbf{r}} = \frac{1}{r} \left(\mathbf{a} - \hat{\mathbf{r}} (\mathbf{a} \cdot \hat{\mathbf{r}}) \right). \tag{1.53}$$

With which we may derive the following:

$$\nabla \times (\hat{\mathbf{r}} \times \mathbf{p}) = -\frac{1}{r} \left(\mathbf{p} + (\mathbf{p} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} \right) \tag{1.54}$$

Let α be defined as $\alpha = \dfrac{e^{ikr}}{r} \left(1 - \dfrac{1}{ikr}\right) (\hat{\mathbf{r}} \times \mathbf{p})$. Then we have:

$$\nabla \times \alpha = -\frac{ik}{r}e^{ikr}(\hat{\mathbf{r}} \times (\mathbf{p} \times \hat{\mathbf{r}})) + e^{ikr}\left(-\frac{2}{r^2} + \frac{2}{kir^3}\right)(\hat{\mathbf{r}} \times (\hat{\mathbf{r}} \times \mathbf{p})) - \frac{e^{ikr}}{r^2}\left(1 - \frac{1}{ikr}\right)((\mathbf{p} \cdot \hat{\mathbf{r}})\,\hat{\mathbf{r}} + \mathbf{p}) \tag{1.55}$$

Now, notice that $(\hat{\mathbf{r}} \times (\hat{\mathbf{r}} \times \mathbf{p})) = (\hat{\mathbf{r}} \cdot \mathbf{p})\,\hat{\mathbf{r}} - \mathbf{p}$, and we get:

$$\nabla \times \alpha = -\frac{ik}{r}e^{ikr}(\hat{\mathbf{r}} \times (\mathbf{p} \times \hat{\mathbf{r}})) + e^{ikr}\left(-\frac{1}{r^2} + \frac{1}{kir^3}\right)(3(\mathbf{p} \cdot \hat{\mathbf{r}})\,\hat{\mathbf{r}} - \mathbf{p}) \tag{1.56}$$

All we're missing is multiplication by constants:

$$\mathbf{E} = e^{-i\omega t}\,\frac{c\omega\mu_0}{4\pi}\,i\,\nabla \times \alpha = \\ = e^{i(kr-wt)}\frac{1}{4\pi\epsilon_0}\left[\frac{k^2}{r}(\hat{\mathbf{r}} \times (\mathbf{p} \times \hat{\mathbf{r}})) + \left(\frac{1}{r^3} - \frac{ki}{r^2}\right)(3(\mathbf{p} \cdot \hat{\mathbf{r}})\,\hat{\mathbf{r}} - \mathbf{p})\right] \tag{1.57}$$

For $r >> \lambda$ we get the radiation field, which goes as $1/r$, and for $\lambda >> r$ we get the static dipolar field, although oscillating in time. Meaning, if we drop every term that contains k (as $k = 2\pi/\lambda$), we get:

$$\mathbf{E}(\mathbf{r}, t) = \frac{e^{-i\omega t}}{4\pi\epsilon_0 r^3}\left(3(\mathbf{p} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}\right) \tag{1.58}$$

1.9 Dirac Delta term for oscilatig dipoles

Following what we did to concerning the static dipole field, we should check for a Dirac Delta term in the oscillating dipole field. Since we are dealing with source terms we can not ignore the current. From Maxwell's laws and the oscillating time dependence of the electric field, we get:

$$\mathbf{E} = i\frac{c^2}{\omega}\left(\nabla \times (\nabla \times A) - \mu_0\mathbf{J}\right), \tag{1.59}$$

where $\mathbf{A}$ is given by (1.49):

$$\mathbf{A}(\mathbf{r}, t) = \frac{-i\mu_0\omega e^{-i\omega t}}{4\pi}\left[\frac{e^{ikr}}{r}\mathbf{p}\right] \tag{1.60}$$

Let's ignore the multiplicative constants and the source current for now. Let $a = \frac{e^{ikr}}{r}$. Then we can write the electric field, ignoring the $i\frac{c}{k}$ constants, as:

$$\nabla(\nabla \cdot (a\mathbf{p})) - \nabla^2(a\mathbf{p}) \tag{1.61}$$

This can be calculated using known identities, and using the fact that p is constant.

$$\nabla(\nabla \cdot (a\mathbf{p})) = \nabla(a(\nabla \cdot \mathbf{p}) + \mathbf{p} \cdot \nabla a) = \nabla(\mathbf{p} \cdot \nabla a) \tag{1.62}$$
$$= (\mathbf{p} \cdot \nabla)\nabla a + \mathbf{p} \times (\nabla \times \nabla a)$$
$$= (\mathbf{p} \cdot \nabla)\nabla a$$
$$\nabla^2(a\mathbf{p}) = \mathbf{p}\ \nabla^2 a \tag{1.63}$$

The Laplacian of a is easily calculated, and it has a delta function dependency that comes from the Laplacian of $\frac{1}{r}$.

$$\nabla^2 \frac{e^{ikr}}{r} = -4\pi\delta(r)e^{ikr} - 2ik\frac{e^{ikr}}{r^2} + e^{ikr}\left[2\frac{ik}{r^2} - \frac{k^2}{r}\right]$$
$$= -4\pi\delta(r)e^{ikr} - \frac{k^2}{r}e^{ikr} = -4\pi\delta(r) - \frac{k^2}{r}e^{ikr} \tag{1.64}$$

The other term is similar to the one we calculated for the static case. Again, using Einstein's notation:

$$(\mathbf{p}\cdot\nabla)\nabla a = p_j \frac{\partial}{\partial x_j}\frac{\partial}{\partial x_i} a\ \hat{\mathbf{e}}_i = p_i \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_i} a\ \hat{\mathbf{e}}_i + p_{j\neq i}\frac{\partial}{\partial x_{j\neq i}}\frac{\partial}{\partial x_i} a\ \hat{\mathbf{e}}_i, \tag{1.65}$$

and that left term is analogous to a dot product between p and the Laplacian of a. Similarly, the resulting delta term will be $\frac{-4\pi}{3}\mathbf{p}e^{ikr}\delta(r)$. Once again, the other derivatives don't contribute to the term at the origin. With a bit of patience, the other terms will give us the electric dipole field we obtained before. Therefore, the resulting origin terms are:

$$\mathbf{E} = \mathbf{E}_{dip} + i\frac{c^2}{\omega}\frac{-i\mu_0\omega e^{-i\omega t}}{4\pi}\left(-\frac{4\pi}{3}\mathbf{p}\delta(r) + 4\pi\mathbf{p}\delta(r)\right) - i\frac{\mu_0 c^2}{\omega}\mathbf{J} \tag{1.66}$$
$$= \mathbf{E}_{dip} + \frac{e^{-i\omega t}}{\epsilon_0}\left(-\frac{\mathbf{p}}{3}\delta(r) + \mathbf{p}\delta(r)\right) - \frac{i}{\omega\epsilon_0}\mathbf{J} \tag{1.67}$$

We can now recall the contents of equation 1.48, that tells us that, letting $\mathbf{J}(r',t) = e^{-i\omega t}\mathbf{J}(r')$:

$$\int d\mathbf{r}'\mathbf{J}(\mathbf{r}') = -i\omega\mathbf{p} \tag{1.68}$$

which implies, since $\mathbf{J}$ is only non zero at the origin, that $\mathbf{J} = -iw\delta(r)e^{-i\omega t}\mathbf{p}$. The delta term that comes from the Laplacian banishes and the result is analogous to the static case, with an oscillation in time:

$$\mathbf{E} = \mathbf{E}_{dip} - e^{-i\omega t}\frac{\mathbf{p}}{3\epsilon_0}\delta(r) \tag{1.69}$$

The argument for the derivation of the Clausius-Mossotti can be applied.

1.10 Possible tests for the approximation

If we have $\lambda >>> d$, where d is the characteristic (or largest) distance between two points of the nanoparticle, then the field inside the nanoparticle is approximately constant at a given time, since $e^{kr} - e^{k(r+d)}$ is close to zero. Then we should recover the classical results for a dielectric in a constant uniform field if we use a great number of dipoles. For example, the field inside a dielectric sphere in a constant uniform field is given by:

$$\mathbf{E}_{\text{in}} = \frac{3}{\epsilon_r(\omega) + 2}\,\mathbf{E} \tag{1.70}$$

One should recover this result with DDA. It may be helpful to know that the field outside the sphere is given by:

$$\mathbf{E} = \mathbf{E}_0 + \frac{\epsilon_r - 1}{\epsilon_r + 2} R^3 \frac{3(\hat{\mathbf{r}} \cdot \mathbf{E}_0)\hat{\mathbf{r}} - \mathbf{E}_0}{r^3} \tag{1.71}$$

One might be able to use the analytical result for the polarization to aid convergence. Since the electric field at a certain dipole is given by:

$$\mathbf{E} = \frac{3}{\epsilon_r + 2}\mathbf{E}_0 = \frac{\mathbf{p}}{\alpha} - \frac{n}{3\epsilon_0}\mathbf{p} \tag{1.72}$$

This can be written in terms of our external field as:

$$\frac{\dfrac{3}{\epsilon_r + 2}\mathbf{E}_0}{\dfrac{1}{\alpha} - \dfrac{n}{3\epsilon_0}} = \mathbf{p} \implies \mathbf{p} = \alpha \frac{\dfrac{3}{\epsilon_r + 2}\mathbf{E}_0}{1 - \dfrac{\epsilon_r - 1}{\epsilon_r + 2}} = \alpha \mathbf{E}_0 \tag{1.73}$$

This result makes sense since the electric dipole field at any point in the sphere, ignoring the contributions from the point itself, is zero.

Another (more elementary) exemple is the infinite dielectric slab with an incident electromagnetic wave perpendicular to one of its sides. The field is given by:

$$\mathbf{E}_{\text{in}} = \frac{1}{\epsilon_r(\omega)}\mathbf{E} \tag{1.74}$$

With this last example, (computationally easier because of its many symmetries), one could also test the validity of the Clausius–Mossotti approximation for high frequencies.

1.11 Adimensionalizations

For calculations, proper adimensionalizations should be made. Considering electric fields in units of $\frac{1}{4\pi\epsilon_0}$, as in cgs units, is the first simplification.

Besides the electric field, the expression for the polarizability also changes, since $\mathbf{p} = \alpha\mathbf{E}$. In cgs, the Clausius-Mossotti (1.23) is given by

$$\alpha = \frac{3}{4\pi n}\frac{\epsilon_r - 1}{\epsilon_r + 2}, \tag{1.75}$$

setting $\frac{1}{4\pi\epsilon_0} = 1$.

The following simplification is the units of distance. If the distance between successive dipoles in the square grid is d_0, one can use that as a unit of distance. The respective changes to the other physical quantities will depend on the constants of our calculation. Since the strength of the external field is a given parameter of it, we should consider the following changes:

$$
\begin{aligned}
\bar{k} &\to k\ d_0 \\
\bar{r} &\to r/d_0 \\
\bar{\alpha} &= \alpha/d_0^3 \\
\implies \bar{p} &= p/d_0^3 \\
\implies \bar{E} &= E
\end{aligned} \tag{1.76}
$$

The last equality should be valid if we use the given value of the electric field directly in calculations, or there would be a contradiction in how we compare values of E. Other choices of dependence in d are possible. After calculations, we must revert the last changes to get the real polarizations, if needed.

2 The Discrete Dipole Approximation as a field integral discretization

2.1 The field integral

If we consider a linear dieletric medium with $\mathbf{P} = \epsilon_0 \chi \mathbf{E}$, and we disregard the magnetic moments, then Maxwell's equations (1.36), together with $J_p = \frac{\partial \mathbf{P}}{\partial t}$, give us:

$$\nabla \times (\nabla \times \mathbf{E}(\mathbf{r})) - k^2 \mathbf{E}(\mathbf{r}) = \mathbf{S}(\mathbf{r}) + k^2 \chi(\mathbf{r}) \mathbf{E}(\mathbf{r}), \tag{2.1}$$

where $\mathbf{S}$ is a source term equal to $i\omega\mu_0 \mathbf{J}_f(\mathbf{r})$, $\mathbf{J}_f(\mathbf{r})$ being the free current density. We assume a time dependency of the kind $\mathbf{E}(\mathbf{r}, t) = e^{-i\omega t}\mathbf{E}(\mathbf{r})$. If we consider the electric field the sum of an incident component and a diffracted one,

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_d, \tag{2.2}$$

then the incident field satisfies the following equation in all space:

$$\nabla \times (\nabla \times \mathbf{E}_0(\mathbf{r})) - k^2 \mathbf{E}_0(\mathbf{r}) = \mathbf{S}(\mathbf{r}). \tag{2.3}$$

We'll represent $\chi(\mathbf{r})$ as a scalar, as in an isotropic medium, although the results are still valid for anisotropic mediums. To solve equation (2.1), following [7], we introduce the Green tensor $\bar{G}$ as the solution of the diferential equation:

$$\nabla \times [\nabla \times \bar{G}(\mathbf{r}, \mathbf{r}')] - k^2 \bar{G}(\mathbf{r}, \mathbf{r}') = k^2 \delta(\mathbf{r} - \mathbf{r}'). \tag{2.4}$$

Then the solutions of (2.1) are given by [1] :

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \int \bar{G}(\mathbf{r}, \mathbf{r}') \chi(\mathbf{r}') E(\mathbf{r}') d\mathbf{r}' \tag{2.5}$$

[1] According to D. Yaghjian, this is not true, since the Green tensor is only the free space solution of the differential equation outside of the origin, and so the exchange of order of operators of the curls and integral is not correct. This mistake is fixed later with the introduction of the the principal volume. A rigorous derivation is given in [8].

since if we apply $[\nabla \times (\nabla \times) \ - k^2]$ to both sides we can verify that the equation (2.1) is verified.

We have already obtained a solution to equation (2.4), although not in tensor form. If we consider equation (1.57) as a tensor equation acting on the polarization vector, we can write, using the vector identity:

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c})\mathbf{b} - (\mathbf{a} \cdot \mathbf{b})\mathbf{c},$$

the following equation:

$$\mathbf{E}_{dip}(\mathbf{r}, t) = e^{i(kr - wt)} \frac{1}{4\pi\epsilon_0} \left[\frac{k^2}{r} (I - \hat{\mathbf{r}} \otimes \hat{\mathbf{r}}) + \left(\frac{1}{r^3} - \frac{ki}{r^2} \right) (3\hat{\mathbf{r}} \otimes \hat{\mathbf{r}} - I) \right] \mathbf{p}, \quad (2.6)$$

where I is the identity matrix and $\otimes$ is the outer product. This will be the Green's tensor for our differential equation (Note that this differential equation came about as a linear approximation for Maxwell's equations, where we assume some oscillating dipole density, with oscillating dipole fields). What we mean is:

$$\bar{G}(\mathbf{r}, \mathbf{r}') = \frac{e^{ikr}}{4\pi} \left[\frac{k^2}{r} (I - \hat{\mathbf{r}} \otimes \hat{\mathbf{r}}) + \left(\frac{1}{r^3} - \frac{ki}{r^2} \right) (3\hat{\mathbf{r}} \otimes \hat{\mathbf{r}} - I) \right], \quad (2.7)$$

where $r = |\mathbf{r} - \mathbf{r}'|$. The Dirac delta term will appear in the same way as in subsection 1.9's deduction. The algebra to show that this is indeed a solution is quite long, and similar to what has been done in the preceding sections. In [9] a deduction of this solution without using the electric dipole field is obtained.

Solving (2.5) we know that $\chi(\mathbf{r}') = 0$ if we're outside the dielectric volume, where are all the contributions. To compute this integral one could use Riemann integration, subdividing the volume into a grid of small subunits and summing all the components. One would then have the following sum:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \sum_i^N \int_{V_i} \bar{G}(\mathbf{r}, \mathbf{r}') \chi(\mathbf{r}') \mathbf{E}(\mathbf{r}') d\mathbf{r}' \quad (2.8)$$

To obtain the Discrete Dipole Approximation, we have to do a couple of approximations. First, we must assume that the electric field and permittivity is constant inside each sub unit, which is to be expected if the sub units have dimensions smaller than the wavelength of the radiation and the material hasn't got too variable of a dieletric constant. We will also assume that for different sub units, the Green's function will take on a constant value. The electric field is now, for $\mathbf{r}$ in V_j:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \sum_{i \neq j}^N \bar{G}(\mathbf{r}, \mathbf{r}_i) V_i \, \chi(\mathbf{r}_i) \mathbf{E}(\mathbf{r}_i) + \int_{V_j} \bar{G}(\mathbf{r}, \mathbf{r}') \chi(\mathbf{r}_j) \mathbf{E}(\mathbf{r}_j) d\mathbf{r}' \quad (2.9)$$

We now face a problem with this integral. The Green function has a singularity at $\mathbf{r} = \mathbf{r}'$, and even in the limit as the sub units go to zero volume, it will still depend on the shape of the sub units (for example, it is quite variable for

cuboids [8]). We shall assume a cubic grid for calculation. We follow [10] for the following.

The last integral can be rewritten in the following manner:

$$\int_{V_j} \bar{G}(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}_j)d\mathbf{r}' = \int_{V_j} d\mathbf{r}' \left(\bar{G}(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}_j) - \bar{G}^s(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}_j)\right) - \frac{1}{4\pi}\oint_{\partial V_j} d\mathbf{s}'\hat{\mathbf{n}}\left[\frac{\mathbf{r}'-\mathbf{r}}{|\mathbf{r}'-\mathbf{r}|^3}\cdot\mathbf{E}(\mathbf{r}_j)\right], \quad (2.10)$$

where

$$\bar{G}^s = \frac{1}{4\pi}\frac{3\hat{\mathbf{r}}\otimes\hat{\mathbf{r}} - I}{r^3} = \frac{1}{4\pi}\nabla\nabla\frac{1}{|\mathbf{r}-\mathbf{r}'|} \quad (2.11)$$

is the Green's tensor the static case, i.e, for $k = 0$. Here, as before, the versors are in the direction of $\mathbf{r} - \mathbf{r}'$. Note that the gradients correspond to $\mathbf{r}$, even thought the the scalar is symmetric in $\mathbf{r}, \mathbf{r}'$, and the the change in sign is due to switching to a diferentiation in $\mathbf{r}$. As before, assuming constancy of χ and $\mathbf{E}$, we have that, for $\mathbf{r}$ in V_j:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \sum_{i\neq j}^{N} \bar{G}(\mathbf{r},\mathbf{r}_i)V_i\,\chi(\mathbf{r}_i)\mathbf{E}(\mathbf{r}_i) + (\bar{M}_j - \bar{L}_j)\chi(\mathbf{r})\mathbf{E}(\mathbf{r}), \quad (2.12)$$

for

$$\bar{M}_j = \int_{V_j} d\mathbf{r}' \left(\bar{G}(\mathbf{r},\mathbf{r}') - \bar{G}^s(\mathbf{r},\mathbf{r}')\right) \quad (2.13)$$

$$\bar{L}_j = \frac{1}{4\pi}\oint_{\partial V_j} d\mathbf{s}'\hat{\mathbf{n}}\left[\frac{\mathbf{r}'-\mathbf{r}}{|\mathbf{r}'-\mathbf{r}|^3}\right], \quad (2.14)$$

where $\hat{\mathbf{n}}$ is the external normal versor to the surface. Note that, while we arrived at these tensors as results of discretization, the last of the tensors doesn't go to zero with decreasing volume. It depends only on the geometry of the principal volume in the dielectric, the depolarization factor of the "middle of the dipole". Then, we should amend the equation of the electric field, in the limit as V_0 goes to zero, to:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \int_{V-V_0} dV\bar{G}(\mathbf{r},\mathbf{r}')\chi(\mathbf{r})\mathbf{E}(\mathbf{r}) \;-\; \bar{L}(\mathbf{r})\chi(\mathbf{r})\mathbf{E}(\mathbf{r}) \quad (2.15)$$

This can be re-written in terms of the bound current $\mathbf{J}$ as:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \frac{i}{\omega\epsilon_0}\int_{V-V_0} dV\bar{G}(\mathbf{r},\mathbf{r}')\mathbf{J}(\mathbf{r}) + \frac{\bar{L}(\mathbf{r})\mathbf{J}(\mathbf{r})}{i\omega\epsilon_0} \quad (2.16)$$

2.2 The Discrete Dipole Approximation

The discrete dipole approximation follows from equation (2.12), with more or less approximations made. It doesn't calculate the total field, but the exciting

fields, meaning:

$$\begin{aligned} E_i^{exc} &= \left(I - (\bar{M}_i - \bar{L}_i)\chi_i\right) E_i \\ E_i^{self} &= (\bar{M}_i - \bar{L}_i)\chi_i E(\mathbf{r}_i) \\ E_i &= E_i^{self} + E_i^{exc} \end{aligned} \tag{2.17}$$

Re-writing the the equation with simplified indices and letting $\mathbf{E}_0 = \mathbf{E}^{inc}$ we have that:

$$\mathbf{E}_i = \mathbf{E}_i^{inc} + \sum_{j \neq i} \bar{G}(\mathbf{r}_i, \mathbf{r}_j) V_j \chi_j \mathbf{E}_j + \mathbf{E}_i^{self} \tag{2.18}$$

We're looking to incorporate the self-interacting field into our polarizability, and re-writing the equation in order to the exciting field, we get:

$$\mathbf{E}_i^{exc} = \mathbf{E}_i^{inc} + \sum_{j \neq i} \frac{\bar{G}(\mathbf{r}_i, \mathbf{r}_j)}{\epsilon_0} \bar{\alpha_j} \mathbf{E}_j^{exc} \iff \mathbf{E}_i^{inc} = \mathbf{E}_i^{exc} - \sum_{j \neq i} \frac{\bar{G}(\mathbf{r}_i, \mathbf{r}_j)}{\epsilon_0} \bar{\alpha_j} \mathbf{E}_j^{exc} \tag{2.19}$$

Defining the electric dipole at the jth position as $\bar{\alpha}_j \mathbf{E}_j^{exc}$, we get:

$$\mathbf{E}_i^{inc} = \frac{\mathbf{p}_i}{\bar{\alpha}_i} - \sum_{j \neq i} \frac{\bar{G}(\mathbf{r}_i, \mathbf{r}_j)}{\epsilon_0} \mathbf{p}_j, \tag{2.20}$$

our familiar linear equations, if one checks the value of G. It makes sense that the tensor $\bar{\alpha}$ will play the role of polarizability. It must be equal to:

$$\bar{\alpha}_j = \epsilon_0 \chi_j V_j \left(I + (L_j - M_j)\chi_j\right)^{-1}. \tag{2.21}$$

If we consider cubic cells, then L_j is equal to $\frac{1}{3}I$ [8], and as the cells' volume goes to zero, $\bar{M}$ also goes to zero. It is then costumary to approximate M_j as zero. It follows that we can take the polarization as:

$$\alpha_j = \frac{\epsilon_0 \chi_j V_j}{\left(1 + \frac{1}{3}\chi_j\right)} = \frac{3\epsilon_0}{n} \frac{\epsilon_r - 1}{\epsilon_r + 2} \tag{2.22}$$

and we recover the Clausius-Mossotti relation.

Equation (2.19) can be re-written in matrix form in a form analogous to what was done in subsection 1.2.

$$\bar{\mathbf{E}}^{inc} = (I - \bar{A}\bar{D}_\alpha)\bar{\mathbf{E}}^{exc}, \tag{2.23}$$

where $\bar{A}$ is an $3N \times 3N$ matrix that contains the Green tensor entries, and $\bar{D}_\alpha$ is a $3N \times 3N$ matrix that contains the polarization entries. It will be diagonal by 3×3 blocks. The discrete dipole approximation we are using consists in solving equation (2.23), and using equations (2.17) to obtain the real electric field at the dipoles. We also use equation (2.7) to obtain the entries of $\bar{A}$. Once that process is complete, it's easy to obtain the electric field in any point by using

equation (2.8), since both $\bar{M}$ and $\bar{L}$ are zero outside of the source. And, for the sake of completion, note that the real electric field is given by, for spherical or cubical principal volumes:

$$\mathbf{E} = \frac{3}{2+\epsilon_r}\mathbf{E}^{exc} \tag{2.24}$$

2.3 Properties of $\bar{L}$ and $\bar{M}$

The dyadic $\bar{L}$ is responsible for the dependency of the integral on the shape that is used for integration. It is a real symmetric tensor with trace equal to 1 and for cubes and spheres it is equal to $\frac{1}{3}I$. To check this, note that the trace of the tensor is equal to

$$\mathrm{Tr}(\bar{L}) = \frac{1}{4\pi}\oint_{\partial V_j} \hat{\mathbf{n}} \cdot \frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2} = \frac{1}{4\pi}\int_{V_j} \nabla \cdot \frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2}$$

and that divergence is equal to $4\pi\delta(\mathcal{R}')$.

The symmetry of a dyadic tensor is characterized by it's "vector", the sum of the vector products of the diads that compose it. Let $\bar{M}$ be:

$$\bar{M} = a_1 \otimes a_1' + a_2 \otimes a_2' + \cdots,$$

Then its vector is:

$$\mathrm{vec}(\bar{M}) = a_1 \times a_1' + a_2 \times a_2' + \cdots. \tag{2.25}$$

A dyadic is symetric if and only if its vector is zero [8]. This can easily be proven for the finite sum case. The difference of $\bar{M}$ to its transpose is:

$$\bar{M} - \bar{M}^t = \sum_{n,i,j,k} \varepsilon_{ijk} e_{ij} (a_n \times a_n')_k, \tag{2.26}$$

which will be zero if and only if its vector is zero. Here e_{ij} is the matrix with only the entry ij equal to 1 and the rest equal to 0. The vector of the $\bar{L}$ dyadic is:

$$\mathrm{vec}(\bar{L}) = \frac{1}{4\pi}\oint_{\partial V_j} d\mathbf{s}'\hat{\mathbf{n}} \times \left[\frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2}\right] = -\frac{1}{4\pi}\int_{V_{out}} dV\ \nabla \times \left[\frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2}\right] = 0, \tag{2.27}$$

where the second to last equality comes from the application of the divergence theorem to each component of the vector field. It's not very hard to obtain the values of $\bar{L}$ for spheres and cubes. The result is the same for any orientation of the axis and position in the sphere of $\mathbf{r}$ [8], but we'll show it for $\mathbf{r}$ centered. Letting $\mathcal{R}' = \mathbf{r}' - \mathbf{r}$, we need to calculate the integral:

$$\hat{L}_{sphere} = \frac{1}{4\pi}\oint_{\partial V_j} \hat{\mathbf{n}}\frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2} = \frac{1}{4\pi}\oint_{\partial V_j} \frac{\hat{\mathcal{R}}' \otimes \hat{\mathcal{R}}'}{|\mathcal{R}'|^2} = \frac{1}{4\pi}\frac{4\pi}{3}I = \frac{1}{3}I. \tag{2.28}$$

The second to last equality is showed bellow. The result is the same for $\mathbf{r}$ in the center of a cube. We'll show it for axis aligned with the sides of the cube. Consider first the an x face.

$$\frac{1}{4\pi}\oint_{\partial x_f} ds\hat{\mathbf{n}}\frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2} = \frac{1}{4\pi}\oint_{\partial x_f} ds \begin{pmatrix} \frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2}\cdot\hat{x} & \frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2}\cdot\hat{y} & \frac{\hat{\mathcal{R}}'}{|\mathcal{R}'|^2}\cdot\hat{z} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{2.29}$$

For each point of the face, consider the point with inverted x coordinate. Since the opposite face has a symmetric $\hat{\mathbf{n}}$, the sum of the matrices will be null except on the diagonal. By symmetry, the tensor will be a multiple of the identity tensor, or its trace divided by three multiplied by the identity. Then $\hat{L} = \frac{1}{3}I$.

Obtaining the value of $\bar{M}$ for a cube is complicated, but for a sphere with the same volume we can more rapidly calculate it.

$$\bar{M} = \frac{1}{4\pi}\int_V d\mathbf{v}\left[\frac{k^2}{r}(I-\hat{\mathbf{r}}\otimes\hat{\mathbf{r}})e^{ikr} + \left(\frac{e^{ikr}-1}{r^3} - \frac{e^{ikr}ki}{r^2}\right)(3\hat{\mathbf{r}}\otimes\hat{\mathbf{r}} - I)\right] \tag{2.30}$$

If we write $\hat{\mathbf{r}}\otimes\hat{\mathbf{r}}$ in polar coordinates it's easy to see that the resulting tensor will be diagonal:

$$\begin{aligned}\int_0^{2\pi} d\varphi \begin{pmatrix} \sin^2(\theta)\cos^2(\varphi) & \sin^2(\theta)\cos(\varphi)\sin(\varphi) & \sin(\theta)\cos(\varphi)\cos(\theta) \\ \sin^2(\theta)\cos(\varphi) & \sin^2(\theta)\sin^2(\varphi) & \sin(\theta)\sin(\varphi)\cos(\theta) \\ \cos(\varphi)\cos(\theta) & \sin(\theta)\sin(\varphi)\cos(\theta) & \cos^2(\theta) \end{pmatrix} = \\ = \begin{pmatrix} \pi\sin^2\theta & 0 & 0 \\ 0 & \pi\sin^2\theta & 0 \\ 0 & 0 & 2\pi\cos^2\theta \end{pmatrix}\end{aligned} \tag{2.31}$$

That it is a multiple of the identity comes from the other angular integral:

$$\int_0^{\pi} d\theta\sin\theta \begin{pmatrix} \pi\sin^2\theta & 0 & 0 \\ 0 & \pi\sin^2\theta & 0 \\ 0 & 0 & 2\pi\cos^2\theta \end{pmatrix} = \frac{4\pi}{3}I \tag{2.32}$$

It follows that the term $3\hat{\mathbf{r}}\otimes\hat{\mathbf{r}} - I$ is zero, and the integral is:

$$\bar{M}_{\text{sphere}} = \frac{1}{4\pi}\int_0^R \left[rk^2e^{ikr}\left(\frac{8\pi}{3}\right)\right] I = \frac{2}{3}\left[e^{iRk}(1-iRk)-1\right] I \tag{2.33}$$

For the cube with side a to have the same volume we would have $a^3 = \frac{4\pi}{3}R^3$. If we consider the Taylor expansion until the third order of a, the side of the cube with the same volume as the sphere, we get that:

$$\bar{M}^{(3)} = \left[\frac{k^2a^2}{3}\left(\frac{3}{4\pi}\right)^{2/3} + \frac{1}{6\pi}ik^3a^3\right] I \tag{2.34}$$

The imaginary term is the "radiation" term necessary for the optical term of Draine [3].

One could obtain this result in another, perhaps easier, fashion. First, let's verify than we can write the Green's tensor as a double gradient. I claim that:

$$\bar{G}(\mathbf{r},\mathbf{r}') = \left(\nabla\nabla + k^2 I\right)\frac{1}{4\pi}\frac{e^{ikr}}{r}, \quad \text{where } r = |\mathbf{r}-\mathbf{r}'|. \tag{2.35}$$

Let's check:

$$\begin{aligned}
\partial^i\partial_j\frac{e^{ik\sqrt{x_k x^k}}}{\sqrt{x_k x^k}} &= \partial^i\left[ik\frac{x_j}{x_k x^k}e^{ik\sqrt{x_k x^k}} - e^{ik\sqrt{x_k x^k}}\frac{x_j}{(x_k x^k)^{3/2}}\right] \\
&= e^{ik\sqrt{x_k x^k}}\left[ik\frac{\delta^i_j x_k x^k - 2x_j x^i}{(x_k x^k)^2} + ik\frac{x_j}{x_k x^k}ik\frac{x^i}{\sqrt{x_k x^k}} - \right. \\
&\left. ik\frac{x^i}{\sqrt{x_k x^k}}\frac{x_j}{(x_k x^k)^{3/2}} - \frac{\delta^i_j(x_k x^k)^{3/2} - 3x_j\sqrt{x_k x^k}x^i}{(x_k x^k)^3}\right] \\
&= e^{ikr}\left[ik\frac{\delta^i_j - 2\hat{\mathbf{r}}\otimes\hat{\mathbf{r}}}{r^2} - k^2\frac{\hat{\mathbf{r}}\otimes\hat{\mathbf{r}}}{r} - ik\frac{\hat{\mathbf{r}}\otimes\hat{\mathbf{r}}}{r^2} - \frac{\delta^i_j - 3\hat{\mathbf{r}}\otimes\hat{\mathbf{r}}}{r^3}\right] \\
&= 4\pi\hat{G}^i_j(\mathbf{r}-\mathbf{r}') - e^{ikr}k^2\frac{\delta^i_j}{r}.
\end{aligned}$$

Then, one could rewrite the tensor $\hat{M}$ as:

$$\bar{M}_j = \int_{V_j} d\mathbf{r}'\left(\bar{G}(\mathbf{r},\mathbf{r}') - \bar{G}^s(\mathbf{r},\mathbf{r}')\right) \tag{2.36}$$

$$= \int_{V_j} d\mathbf{r}'\nabla\nabla\frac{(e^{ik|\mathbf{r}-\mathbf{r}'|}-1)}{4\pi|\mathbf{r}-\mathbf{r}'|} + I\frac{1}{4\pi}\int_{V_j} d\mathbf{r}' k^2\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \tag{2.37}$$

$$= \oint_{\partial V_j} d\mathbf{a}'\hat{\mathbf{n}}\nabla\frac{(e^{ik|\mathbf{r}-\mathbf{r}'|}-1)}{4\pi|\mathbf{r}-\mathbf{r}'|} + IO(k^2) \tag{2.38}$$

$$= \frac{1}{4\pi}\oint_{\partial V_j} d\mathbf{a}'\ \hat{\mathbf{n}}\otimes\hat{\mathbf{r}}'\left(\frac{1-e^{ikr}}{r^2} + \frac{ike^{ikr}}{r}\right) + IO(k^2) \tag{2.39}$$

This result seems easier to use for non symmetric principal volumes.

2.4 Approximation of M for cubes and considerations of order

We shall obtain values of $\bar{M}$ for cubes to compare with the one of the sphere. Notice we can easily prove that $\bar{M}$ is diagonal (and by symmetry a multiple of the identity): if we consider the sum of the matrix $\hat{\mathbf{r}}\otimes\hat{\mathbf{r}}$ for a particular value of $\hat{\mathbf{r}}$ and the ones with a symmetric coordinate ($x\to -x, y\to -y, z\to -z$) we get a diagonal matrix. It's enought to calculate the integral for one entry. If we expand the integrand until second order terms, and substitute for one

coordinate, we get:

$$\begin{aligned}
\bar{M} &= \frac{1}{4\pi}\int_V d\mathbf{v}\frac{e^{ikr}}{r}\left[k^2(I-\hat{\mathbf{r}}\otimes\hat{\mathbf{r}})+\left(\frac{1-e^{-ikr}-ikr}{r^2}\right)(3\hat{\mathbf{r}}\otimes\hat{\mathbf{r}}-I)\right] \\
\implies \bar{M}_{11}^{(2)} &= \frac{1}{4\pi}\int_V d\mathbf{v}\left[\frac{k^2}{r}\left(1-\frac{x^2}{r^2}\right)+\left(\frac{k^2r^2}{2r^3}\right)\left(3\frac{x^2}{r^2}-I\right)\right] \\
&= \frac{k^2}{8\pi}\int_V d\mathbf{v}\frac{1}{\sqrt{x^2+y^2+z^2}}\left(1+\frac{x^2}{x^2+y^2+z^2}\right) \qquad (2.40)
\end{aligned}$$

This integral is equal to a long algebraic expression, but it can be represented in a concise manner as, if a is the side of the cube (and the integration was done from $-a/2$ to $a/2$):

$$\bar{M}_{11}^{(2)} = \frac{k^2a^2}{8\pi}\left[4\log\left(\frac{\sqrt{3}+1}{\sqrt{3}-1}\right)-\frac{2\pi}{3}\right] \qquad (2.41)$$

To properly compare with the value encountered for the sphere, we should also obtain the third order terms. The integral is trivial in this case.

$$\begin{aligned}
\bar{M}_{11}^{(3)}-\bar{M}_{11}^{(2)} &= \frac{1}{4\pi}\int_V d\mathbf{v}\left[\frac{ik^3r}{r}\left(1-\frac{x^2}{r^2}\right)+\left(\frac{k^2r^2(ikr)}{2r^3}-\frac{k^2r^2(-ikr)}{6r^3}\right)\left(3\frac{x^2}{r^2}-I\right)\right] \\
&= \frac{1}{4\pi}\int_V d\mathbf{v}\ ik^3\frac{2}{3} = \frac{1}{6\pi}ik^3a^3 \qquad (2.42)
\end{aligned}$$

This is the same third order coefficient we obtained for the sphere with the same volume. The second order coefficients differ by a significant margin:

$$\frac{M_{11}^{(2)}{}_{cube}}{M_{11}^{(2)}{}_{sphere}} \approx \frac{0.1263}{0.5902} = 0.2140, \qquad (2.43)$$

and so M is considerably smaller for the cube for small values of kr. Calculations for higher orders will depend on the accuracy of the DDA with its other approximations. For example, if the field inside the dieletric has an harmonic spacial dependency, it could change by a factor of ka in a unit cell.

Consider again our integral equation with principal volume term:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \int_{V\setminus V_0}\bar{G}(\mathbf{r},\mathbf{r}')\chi(\mathbf{r}')E(\mathbf{r}')d\mathbf{r}' + \left(\bar{M}(V_0,\mathbf{r})-\bar{L}(\partial V_0,\mathbf{r})\right)\chi(\mathbf{r})\mathbf{E}(\mathbf{r}) \qquad (2.44)$$

We should not write the $\bar{M}$ component like this, since the electric field and dieletric constant should be integrated in the volume, but consider it to shorten the expression. The assumption of a smooth dieletric constant is reasonable, and ignoring the incident field, we discretized the equation:

$$\mathbf{E}(\mathbf{r}) = \sum_i^N\int_{V_i}\bar{G}(\mathbf{r},\mathbf{r}')\chi(\mathbf{r}')\mathbf{E}(\mathbf{r}')d\mathbf{r}' + \left(\bar{M}(V_0,\mathbf{r})-\bar{L}(\partial V_0,\mathbf{r})\right)\chi(\mathbf{r})\mathbf{E}(\mathbf{r}) \qquad (2.45)$$

If we can also assume that the electric field is constant in each volume (for small enough dipole volumes), we get:

$$\mathbf{E}(\mathbf{r}) = \sum_i^N \bar{G}'(\mathbf{r}, V_i) V_i \ \chi_i \mathbf{E}_i d\mathbf{r}' + \left(\bar{M}(V_0, \mathbf{r}) - \bar{L}(\partial V_0, \mathbf{r})\right) \chi(\mathbf{r}) \mathbf{E}(\mathbf{r}), \tag{2.46}$$

where

$$\bar{G}'(\mathbf{r}, V_i) = \frac{1}{V_i} \int_{V_i} d\mathbf{r}' \bar{G}(\mathbf{r}, \mathbf{r}'). \tag{2.47}$$

We assumed in the discretization above that this term is equal to $G(\mathbf{r}, \mathbf{r}'_i)$ for $\mathbf{r}'_i$ in the center of the cell. This is quite correct for distant dipoles, but is not accurate for nearby ones. The reason this doesn't greatly affect the result is because only the total sum matters. If we're not near the surface, the integral of the nearby dipole cells will be approximately the integral of the static electric dipole field in a symmetric cubic volume, which is zero. In [11], the error is said to be $O(kd)$. This is another factor, beyond just the L dyadic, that influences the convergence of the dda. For a rectangular grid, the integral is not zero, and adaptations would have to be made.

3 Other methods for solutions of the system of equations

We will focus mainly on iterative methods: obtaining the solution via direct inversion or similar approaches is very memory intensive.

3.1 Gradient descent and the associated quadratic form

Let $A\mathbf{x} = b$ be the linear system we're trying to solve. We claim that it's a critical point of its associated quadratic form, if the matrix A is symmetrical:

$$f(\mathbf{x}) = \frac{1}{2}\mathbf{x}^T A \mathbf{x} - b^T \mathbf{x} + \mathbf{c} \tag{3.1}$$

This can be easily checked using tensor notation:

$$\frac{\partial}{\partial x_l} f = \frac{\partial}{\partial x_l} \left(\frac{1}{2} A_{ij} x_i x_j - b_k x_k + c \right) = \frac{1}{2}(A_{lj} x_j + A_{il} x_i) - b_l, \tag{3.2}$$

and so,

$$\nabla f = \frac{1}{2}\left(A\mathbf{x} + A^T\mathbf{x}\right) - \mathbf{b} \implies A\mathbf{x} = \mathbf{b} \quad \text{for symmetrical A and } \nabla f = 0. \tag{3.3}$$

If the matrix is positive-definite, $\mathbf{x}^T A \mathbf{x} > 0$ for non-zero $\mathbf{x}$, then it's also a global minimum of f. Let's check this by calculating the Hessian:

$$\frac{\partial^2}{\partial x_m \partial x_l} f = \frac{\partial}{\partial x_m} \frac{1}{2}(A_{lj} x_j + A_{il} x_i) - b_l = \frac{1}{2}(A_{lm} + A_{ml}). \tag{3.4}$$

The Hessian is just the symmetric component of A, in our case, just A. Since A is positive-definite the Hessian also is, and that implies f attains a local minimum at its critical points.

It follows one could use gradient descent to find the solution of the linear system (we will talk later of the positive-definiteness of the dda matrix). If we're searching for a minimum, we "walk" in the opposite direction of the gradient.

$$\mathbf{x}_{n+1} = \mathbf{x}_n - \alpha \, \nabla f(\mathbf{x}_n) = \mathbf{x}_n + \alpha(\mathbf{r}_n), \quad \text{where we define:} \tag{3.5}$$

$$r_n = \mathbf{b} - A\mathbf{x}_n \tag{3.6}$$

The value of α will be chosen so that we minimize the error of the next step. Setting the derivative to zero, we get:

$$\begin{aligned} 0 = \frac{\partial}{\partial \alpha} f(\mathbf{x}_{n+1}) = \nabla f(\mathbf{x}_{n+1}) \cdot \frac{\partial}{\partial \alpha} \mathbf{x}_{n+1} &= (\mathbf{b} - A\mathbf{x}_{n+1})^T(-\mathbf{r}_n) \\ &= (\mathbf{b} - A\mathbf{x}_n - \alpha A\mathbf{r}_n)^T(-\mathbf{r}_n) \\ &\implies \alpha_{(n)} = \frac{\mathbf{r}_n^T \mathbf{r}_n}{\mathbf{r}_n^T A \mathbf{r}_n} \end{aligned} \tag{3.7}$$

With the 3 equations we have so far we could iterate until the error is bellow a certain value, but we can reduce them by one. Notice that to equation (3.5) we can add $\mathbf{b}$ and multiply by $-A$.

$$\mathbf{r}_{n+1} = \mathbf{r}_n - \alpha A \mathbf{r}_n. \tag{3.8}$$

We can then use just these last two equations, that share the vector matrix multiplication, and then recover the value of $\mathbf{x}$. This method can run into convergence problems with eigenvalues of significantly different magnitudes.

3.2 Convergence Analysis

Let e_i be an eigenvector of the matrix, with eigenvalue λ_i, and let x_0 be the solution of the system. If our x_i is $x_0 + e_i$, then:

$$x_{i+1} = x_i + 1/\lambda(b - A(x_0 + e_i)) = x_0 + e_i - e_i = x_0 \tag{3.9}$$

Or, in a more general faction, letting $\mathbf{x}_n = \mathbf{x}_0 + \beta_{in}\mathbf{v}_i$, where the $\mathbf{v}_i$ are the orthogonal eigenvalues of the symmetric matrix, then:

$$\mathbf{r}_n = -\lambda_i \beta_{in} \mathbf{v}_i, \qquad \alpha_n = \frac{\lambda_j^2 \beta_{jn}^2}{\lambda_k^3 \beta_{kn}^2}, \qquad r_{n+1,i} = \left(1 - \frac{\lambda_j^2 \beta_{jn}^2}{\lambda_k^3 \beta_{kn}^2} \lambda_i\right) r_{n,i} \tag{3.10}$$

The squared components β turn the sum into a kind of weighted average of $1/\lambda$. To better evaluate the convergence, let's consider the following norm for the error: $||e|| = \sqrt{e^T A e}$. Since A is positive definite, this is works as a norm. Also, we can verify that:

$$f(\mathbf{p}) - f(\mathbf{x}) = \frac{1}{2}(\mathbf{p} - \mathbf{x})^T A (\mathbf{p} - \mathbf{x}), \tag{3.11}$$

so that:

$$f(\mathbf{x}_0 + \mathbf{e}) - f(\mathbf{x}) = \frac{1}{2}||e||^2 \tag{3.12}$$

Minimizing the norm minimizes the error. Then, we can check, with a little algebra, that:

$$||e_{n+1}||^2 = ||e_n||^2 \left(1 - \frac{(\sum_i \beta_{ni}^2 \lambda_i^2)^2}{(\sum_i \beta_{ni}^2 \lambda_i^3)(\sum_i \beta_{ni}^2 \lambda_i)}\right) = ||e_n||^2 \omega_n \tag{3.13}$$

We can now seek to maximise this parameter, to find the worst case scenario convergence. Naming the sums L_1, L_2, L_3, according to if the eigenvalues are raised to those powers, if we take its derivative with respect to β_i we get:

$$(\nabla\omega)_i = 2\lambda_i \beta_i L_2 \frac{-2L_3 L_1 \lambda_i + L_2 L_3 + L_1 L_2 \lambda_i^2}{L_1^2 L_3^2} \tag{3.14}$$

Equaling this to zero for all i, and ignoring the trivial solutions ($\beta_i = 0$ for example), leads to a complicated system, in which the solution is non-obvious. Let's consider the 2-dimensional case first. Let $\mu = \frac{\lambda_1}{\lambda_2}$ and the inverse ratio for the coefficients $\kappa = \frac{\beta_2}{\beta_1}$. Then we can check that:

$$\omega = 1 - \frac{(\kappa^2 + \mu^2)^2}{(\kappa + \mu^2)(\kappa^3 + \mu^2)} \tag{3.15}$$

It's not hard to see that, in this case, the worse value of ω is for $\kappa^2 = \mu^2$. That gives, for $\kappa = \pm\mu$,

$$\omega = 1 - \frac{4k}{1 + 2\kappa + \kappa^2} = \frac{(\kappa - 1)^2}{(\kappa + 1)^2} \tag{3.16}$$

This means that, since μ is a property of the system, we get that:

$$||e_i||^2 \leq \left[\frac{(\mu - 1)}{(\mu + 1)}\right]^{2i} ||e_0||^2 \tag{3.17}$$

This equation also works for n-dimensional systems, if we redefine μ as $\mu = \lambda_{\max}/\lambda_{\min}$. We will prove this later.

3.3 On the positive-definiteness of A

The matrix of the DDA problem, as we saw it in equation (2.20),

$$\mathbf{E}_i^{inc} = \frac{\mathbf{p}_i}{\bar{\alpha}_i} - \sum_{j \neq i} \frac{\bar{G}(\mathbf{r}_i, \mathbf{r}_j)}{\epsilon_0} \mathbf{p}_j \implies \mathbf{E}_i^{inc} = \sum_j \bar{A}_{ij} p_j \tag{3.18}$$

This way of constructing the matrix implies:

$$\bar{A}_{ij} = \alpha^{-1} - \bar{G}_{ij}, \tag{3.19}$$

where $\bar{A}_{ij}$ is a 3×3 block. As mentioned before, if we define the matrix $\bar{A}'$ we use in calculations as:

$$\bar{A}'_{3i+l,3j+k} = (\bar{A}_{ij})_{kl} \tag{3.20}$$

this new matrix is still symmetric. The diagonal matrices will not be positive definite for $\epsilon_r \leq 1$, since α will take a negative or null value. I don't know if the matrix will be positive definite for all positive values of α (it will be at least for ϵ_r very close to 1, using the fact that a matrix is positive definite if the diagonal terms are all positive and each is greater than the sum of the absolute values of the respective columnn and row), and as such we will use methods that don't require positive-definiteness explicitly.

3.4 Conjugated Gradients

In the gradient descent method, we may take multiple r_i steps in the same direction. It would be nice if every step we took was orthogonal to the previous one, and if every step minimized error in its respective direction, we would be done after n steps. This can be achieved b

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