Polarizability calculation of vibrating nanoparticles for intensity of low frequency Raman scattering

Daniel B. Murray, Caleb H. Netting, Robin D. Mercer, and Lucien Saviot

1 Mathematics, Statistics and Physics Unit, University of British Columbia Okanagan
3333 University Way, Kelowna, British Columbia, Canada V1V 1V7
2 Laboratoire de Recherche sur la Réactivité des Solides, UMR 5613 CNRS - Université de Bourgogne
9 avenue A. Savary, BP 47870 - 21078 Dijon - France

(Dated: July 27, 2021)

A new numerical method is introduced for calculating the polarizability of an arbitrary dielectric object with position dependent complex permittivity. Three separate numerical approaches are provided to calculate the dipole moment of a nanoparticle embedded in a dielectric matrix in the presence of an applied electric field. Numerical tests confirm the accuracy of this method when applied to several cases for which an exact solution is available. This method is especially well suited for the calculation of absolute Raman scattering intensities due to acoustic phonons in metallic and dielectric nanoparticles embedded in transparent matrices.

PACS numbers:

Key words: Nanoparticle, Raman intensity, polarizability, dipole moment, permittivity

I. INTRODUCTION

Spectral features of low frequency Raman scattering from nanoparticles (NP) can be explained in terms of the vibrational frequencies of acoustic phonons which are confined in those NPs. Calculation of the displacement fields of the modes permits prediction of the Raman selection rules. Variation of Raman intensity when parallel or perpendicular polarization is selected can also be understood.

Past theoretical work on the intensity of Raman scattering from NPs has not produced quantitative estimates of scattering intensities. However, key qualitative features, such as the distinction between NP volume and surface mechanisms, have been pointed out. In the NP volume mechanism, deformation potential coupling modulates the bulk dielectric response. In the surface coupling mechanism, changes of the NP’s size or shape modulate the NP’s polarizability.

Calculation of the absolute intensity of low frequency Raman scattering from an NP requires the values of the polarizability matrix, α, of the NP, in particular the modulation of the polarizability with time due to the acoustic phonon degrees of freedom. Our approach incorporates both the NP volume and surface coupling mechanisms. In addition, our general approach includes an additional qualitative mechanism which has not been previously pointed out: Variations of the density of the matrix material surrounding the NP will lead, through deformation potential coupling, to a new matrix volume mechanism.

It is a reasonable approximation in many cases to hope to determine the polarizability of an object in terms of a local permittivity function, ε(\r) such that \[ \mathbf{D}(\r) = \varepsilon(\r) \mathbf{E}(\r). \] Our discussion only applies to this case.

In some kinds of NPs this approach will not work. It is not always the case that the dielectric response of an object can be described in terms of a local permittivity function. An example of this is when the Raman scattering of a NP is dominated by acoustic phonon modulation of electron hole excitons, as in semiconductor NPs when the Raman laser is close to the exciton energies. In addition, local dielectric response cannot be expected for distance scales comparable to the Thomas-Fermi length. Such situations will not be considered further in what follows.

What is needed is a method which can handle: (1) small variations in shape of an object; (2) complex permittivity; (3) permittivity which is an arbitrary function of position; (4) non-spherical shape; (5) permittivity with a large magnitude.

Quite a number of methods are available to calculate the polarizability of an object. However, none of these methods are suitable for the requirements of low frequency Raman scattering from NPs.

The exact solution due to Mie is for homogeneous spherical objects only. The most general method is Finite Difference Time Domain (FDTD). However, FDTD cannot handle very small changes in the object since it must use a coarse grid of spatial points. The discrete dipole approximation (DDA) requires a mesh to approximate the object, and is not suitable to reflect small changes in shape due to vibration. The dipole-induced-dipole (DID) method is applicable only when the permittivity is small.

No presently available numerical method meets all of these criteria. This paper introduces a new method which satisfies all of these requirements. The application of this method will permit quantitative estimates of the intensity of low frequency Raman scattering due to acoustic phonons in NPs.

This paper is restricted only to the problem of calculating the polarizability tensor for a given static configuration of a NP. Repetition of this method for a sequence of configurations associated with the motion of an acous-
tic phonon will allow the modulation of the polarizability tensor to be determined. This leads directly to the scattered Raman intensity, which is the ultimate justification for this work.

NPs are very small compared to the wavelength of the laser light used to excite them in Raman and Brillouin light scattering experiments. Thus, at an instant of time the electric field in the region enclosing a NP may be regarded as a uniform static electric field. The NP has a dielectric constant which differs from that of the surrounding glass matrix. For this reason there will be a spatial variation of the electric field in the interior and vicinity of the NP. This electric field induces polarization and consequently bound charge on the NP which leads to a dipole moment. It is this electric dipole that oscillates so as to radiate, emitting Rayleigh scattered light (with the same wavelength as the incident light). Acoustic vibrations of the NP lead to variations in the dielectric response of the NP. Their frequency is very low compared to the laser as the NP slowly vibrates, its dielectric response leads to Raman or Brillouin scattered light (with the same wavelength as the incident light).

An electrostatic (also called “quasistatic”) description of a system is justifiable if the characteristic frequencies applied are much less than the speed of light divided by the diameter of the system. For a NP, this intrinsic frequency would be roughly $10^{17}$ Hz, whereas the frequency of light is below $10^{15}$ Hz. Consideration of retardation effects is not important if we are considering small NPs. In addition, note that the NP oscillates very slowly compared to the incident electric field.

To understand the physical situation in question, consider a single instant in time. Consider also a region surrounding the NP over which the incident electric field is approximately constant. The incident electric field $E_{\text{inc}}$ has components $E_{\text{incx}}, E_{\text{incy}},$ and $E_{\text{incz}}$. If the region under consideration contained only glass without a NP, then the electric field would be constant within the region. The effect of the variation of the dielectric response of the NP material relative to that of the glass is that the electric field varies in and close to the NP.

In the following sections, a numerical method is introduced for determining the resulting electric field associated with the NP as well as the dipole moment of the NP. This can be used to find the polarizability of the NP.

II. DIPOLE RADIATION

Before continuing on to the main point of this paper, which is the calculation of the polarizability of a NP, we will here present the key relationships that will permit these results to be applied to the problem of the calculation of the intensity of Raman scattering.

First, note that, for a small object, the radiation emitted by it is completely dominated by its dipole moment, and that higher order moments such as quadrupole are negligible. If an object in vacuum has dipole moment $z$-component varying with time as $p_z = p_{0z} \cos(\omega t)$ then the radiated power per unit area of the detector is

$$\mathcal{S} = \frac{\mu_o p_{0z}^2 \omega^4}{32\pi^2 c^2} \frac{\sin^2 \theta}{r_{pd}^2} \tag{1}$$

where $\mu_o$ and $c$ are the permeability and speed of light, respectively, of free space. $r_{pd}$ is the distance from the NP to the photon detector. $\theta$ is the angle between the axis of the dipole and the ray from the dipole to the photon detector.

Even though the results of this paper may be applied to the situation of a NP in vacuum, it is more common in experimental situations that the NP is embedded in a macroscopic matrix such as a block of glass. It is straightforward to adapt Eq. (1) to this situation:

$$\mathcal{S} = \frac{\mu_m p_{0z}^2 \omega^4}{32\pi^2 c_m^2} \frac{\sin^2 \theta}{r_{pd}^2} \tag{2}$$

where $\mu_m$ is the permeability of the matrix and $c_m$ is the speed of light in the matrix. $c_m = 1/\sqrt{\mu_m \epsilon_m}$ and $\epsilon_m = \epsilon_{mro} \epsilon_o$, where $\epsilon_{mro}$ is the relative permittivity of the matrix, $\epsilon_o$ is the permittivity of free space.

As an aside, we add the “o” to $\epsilon_{mro}$ to signify that this is the equilibrium value of this quantity, which is necessary because our later calculations can involve situations where the vibrations of the NP cause variations in the density of the matrix material and consequently result in changes of the permittivity of the matrix in the immediate vicinity of the NP. The formalism in later sections allows the permittivity of the matrix in the immediate vicinity of the NP to be a function of position.

When dealing with the macroscopic behavior of dielectrics, charge may be viewed as “free”, “bound”, or “total”. Charge which is artificially added to a preexisting neutral dielectric material is certainly “free”. The response of the dielectric is to rearrange its own charge so as to partly screen the “free” charge. Concentrations of this redistributed charge are “bound” charge. Specifically, if $\rho_f$, $\rho_b$, and $\rho$ are, respectively, the free, bound, and total charge densities, then $\rho_f + \rho_b = \rho$, $\nabla \cdot \mathbf{E} = \rho/\epsilon_o$ and $\nabla \cdot \mathbf{D} = \rho_f$.

A point charge $q_f$ (“f” stands for “free”) in vacuum creates an electric field with magnitude $E = kq_f/\mathbf{r}^2$ where $k = 1/(4\pi \epsilon_o)$. If the same point charge is artificially added into an initially neutral block of dielectric material of relative permittivity $\epsilon_{mro}$, it creates an electric field $E = kq_f/(\epsilon_{mro} \mathbf{r}^2)$. The reduction in $E$ is due to bound charge $q_b = -((\epsilon_{mro} - 1)/\epsilon_{mro}) q_f$. The total charge contained in the vicinity immediately surrounding the free charge is $q = q_f + q_b$, and is given by $q = q_f/\epsilon_{mro}$.

In like manner, when speaking of a point dipole in a dielectric matrix, we must distinguish between the free, bound, and total dipole moments. Let these three (vector) quantities be denoted respectively by $\mathbf{p}_f$, $\mathbf{p}_b$, and $\mathbf{p}$. For specificity, suppose that the dipole is oriented along the $z$-axis with respective moments $p_{fz}$, $p_{bz}$, and
If a free dipole $p_{fz}$ is artificially inserted into a neutral dielectric, it will be screened by bound dipole moment $p_{bz} = -((\epsilon_{mro} - 1)/\epsilon_{mro})p_{fz}$.

In subsequent sections of this paper, we will always be dealing with situations where there is no free charge present. As a result, all of the dipole moments which we will calculate involve bound charge only. When these dipoles oscillate, they radiate electromagnetic energy. This is the fundamental mechanism for all Rayleigh and Raman scattering from NPs. It is important to note that Eq. (1) and Eq. (2) cannot be used to find the energy radiated from such NPs because the relative permittivity of the dielectric surrounding the NP must be considered.

The correct way to obtain the radiated energy from a NP embedded in a dielectric matrix is as follows. Given the bound dipole moment $p_{bz} = p_z$, we find the equivalent free dipole ($p_{fz}$) which would create the same fields in the immediate vicinity of the NP. These are related by $p_{fz} = \epsilon_{mro}p_z$.

Thus, in the absence of any free dipole moment, for an oscillating point dipole $p_z = p_{oz}\cos(\omega t)$ in a dielectric matrix, the radiated power density is:

$$S = \left(\frac{\mu_m(\epsilon_{mro}p_{oz})^2\omega^4}{32\pi^2\epsilon_m} \right) \sin^2 \theta \frac{\epsilon_{fzd}}{r_{pol}^2}$$  \hspace{1cm} (3)

**III. SPHERICAL HARMONIC TRANSFORM**

Consider a NP that is approximately spherical in shape and approximately centered at the origin of the coordinate system. The electric field is $E(r)$. Because of the static approximation, $E = -\nabla V$ where $V(r)$ is the electric potential.

The motivation for introducing the word “approximately” twice above is to justify the use of a spherical harmonic expansion for the potential $V$ which is dominated by components with slow angular variation. In such a situation, we can hope for a useful approximation with a finite number of spherical harmonics. However, with generality any potential whatsoever could be expressed in the form:

$$V(r, \theta, \phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} a_{\ell m}(r) S_{\ell m}(\theta, \phi)$$  \hspace{1cm} (4)

where $S_{\ell m}(\theta, \phi)$ are “real spherical harmonics” which are real-valued functions here defined as:

$$S_{\ell m} = -\sqrt{2} \Re(Y_{\ell m}^m) \quad [m > 0]$$

$$S_{00} = Y_0^0 \quad [m = 0]$$

$$S_{\ell m} = -\sqrt{2} \Im(Y_{\ell m}^m) \quad [m < 0]$$

The $Y_{\ell m}^m(\theta, \phi)$ are conventionally defined complex-valued spherical harmonic functions.\footnote{There are orthonormality conditions}

There are orthonormality conditions

$$\int \int S_{\ell m} S_{LM} \sin \theta d\theta d\phi = \delta_{LL} \delta_{mM}$$  \hspace{1cm} (5)

where $\delta_{ij}$ is the Kronecker delta. In particular, $S_{00} \approx 0.2821$, $S_{10} \approx 0.4886 \cos \theta$, $S_{11} \approx 0.4886 \sin \theta \cos \phi$, and $S_{1-1} \approx 0.4886 \sin \theta \sin \phi$. Finally, note that:

$$\nabla^2 S_{\ell m} = -\frac{\ell(\ell+1)}{r^2} S_{\ell m}$$  \hspace{1cm} (6)

In macroscopic electrostatics the permittivity $\epsilon$ and the fields $E$, $D$ and the polarization $P$ are related through $D = \epsilon E$ and $D = \epsilon_o E + P$ so that $P = \epsilon_o (\epsilon - 1) E$ where $\epsilon_o$ is the permittivity of free space and $\epsilon = \epsilon_r \epsilon_o$, where $\epsilon_r$ is the “relative permittivity.”

The permittivity is a function of position, varying for two reasons: (1) The permittivity of the NP is different from the permittivity of the surrounding glass matrix. (2) Vibrations of the NP will lead to elastic strains which will cause small time dependent variations of the permittivity. (These periodic variations have a time scale on the order of 3 ps, which is 1000 times longer than the period of the incident laser light beam.)

Motivated by the roughly spherical shape of the NP about the origin, a real spherical harmonic expansion is employed:

$$\epsilon(r, \theta, \phi) = \epsilon_o \sum q_{\ell m}(r) S_{\ell m}(\theta, \phi)$$  \hspace{1cm} (7)

It also turns out to be convenient to introduce the logarithm (base e) of the relative permittivity $b = \log(\epsilon/\epsilon_o) = \log(\epsilon_r)$ which has the expansion:

$$\log (\epsilon_r(r, \theta, \phi)) = b(r, \theta, \phi) = \sum c_{\ell m}(r) S_{\ell m}(\theta, \phi)$$  \hspace{1cm} (8)

The permittivity can, in general be complex-valued, so the complex analytic continuation of the logarithm function will be used. Note that the coefficients $c_{\ell m}(r)$ and $q_{\ell m}(r)$ are dimensionless, while the $a_{\ell m}(r)$ are in volts.

The permittivity is assumed to be initially specified at all points within the NP and the matrix. The coefficients are found using:

$$q_{LM}(r) = \frac{1}{\epsilon_o} \int b(r, \theta, \phi) S_{LM} \sin \theta d\theta d\phi$$  \hspace{1cm} (9)

and

$$c_{LM}(r) = \int \log(\epsilon_r(r, \theta, \phi)) S_{LM} \sin \theta d\theta d\phi$$  \hspace{1cm} (10)

While $V(r)$ may have non-analytic variation in the vicinity of the surface of the NP due to rapid spatial changes in $\epsilon(r)$, we suppose that $V(r)$ is smooth at the origin with the following series expansion:

$$\lim_{r \to 0} V(r, \theta, \phi) = \sum d_{\ell m} r^\ell S_{\ell m}(\theta, \phi)$$  \hspace{1cm} (11)

Finally, we suppose that sufficiently far away from the NP the permittivity again becomes constant. In this region the electric field is supposed to reach a spatially constant value, but formally the potential can be expanded.
in the large $r$ limit as:

$$\lim_{r \to \infty} V(r, \theta, \phi) = \sum \varepsilon_{\ell m} r^\ell S_{\ell m}(\theta, \phi)$$  \hspace{1cm} (12)$$

The $x$, $y$, and $z$ incident (far away) electric field components are related to $e_{10}$, $e_{11}$, and $e_{1-1}$ as follows: $E_{incz} \simeq -0.4886 e_{10}$, $E_{incx} \simeq -0.4886 e_{11}$, and $E_{incy} \simeq -0.4886 e_{1-1}$.

IV. INTEGRATING THE COULOMB EQUATION

The basis for this paper’s calculations is that there are no free charges associated with the NP, although there will be some bound charge as a result of the induced polarization. Thus $\rho_f = 0$, in which case $\nabla \cdot \mathbf{D} = 0$ but $\mathbf{D} = \varepsilon \mathbf{E}$, so $\nabla \cdot (\varepsilon \mathbf{E}) = 0$. Note further that $\mathbf{E} = -\nabla V$, so that $\nabla \cdot (\varepsilon (\nabla V)) = 0$. Differentiating, $\varepsilon \nabla^2 V + (\nabla V) \cdot (\nabla \varepsilon) = 0$  \hspace{1cm} (13)$$

Next, divide this through by $\varepsilon(r)$. If $b = \log(\varepsilon/\varepsilon_o) = \log(\varepsilon_r)$ then $\nabla b = (\nabla \varepsilon)/\varepsilon$. In this case

$$\nabla^2 V + (\nabla V) \cdot (\nabla b) = 0$$  \hspace{1cm} (14)$$

The boundary value problem that we are solving is as follows: Supposing $b(r)$ to be known, it will be Eq. (14) which will be solved to yield $V(r)$. The boundary condition is that $\mathbf{E}$ approaches a specified constant value $\mathbf{E}_{inc}$ in the limit of large $r$.

To do this, we next insert the real spherical harmonic expansions of $V$ and $b$ into Eq. (14). The result is multiplied by a given $S_{\ell m}(\theta, \phi)$, and then integrated over $\theta$ and $\phi$. This yields a set (indexed by $\ell$ and $m$) of coupled ordinary differential equations as follows:

$$- r^2 a''_{\ell m} = 2r a'_{\ell m} - \ell (\ell + 1) a_{\ell m} + \sum_{LM} \sum_{\lambda\mu} \left\{ a_{LM}^2 c_{\lambda\mu}^2 H(\ell m; LM; \lambda\mu) + a_{LM} c_{\lambda\mu} K(\ell m; LM; \lambda\mu) \right\}$$  \hspace{1cm} (15)$$

where

$$H(\ell m; LM; \lambda\mu) = \int S_{\ell m} S_{LM} S_{\lambda\mu} d\Omega$$  \hspace{1cm} (16)$$

and

$$K(\ell m; LM; \lambda\mu) = \int S_{\ell m} \left( \frac{\partial}{\partial \theta} S_{LM} \frac{\partial}{\partial \theta} S_{\lambda\mu} + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} S_{LM} \frac{\partial}{\partial \phi} S_{\lambda\mu} \right) d\Omega$$  \hspace{1cm} (17)$$

where $d\Omega$ denotes $\sin \theta d\theta d\phi$. The constants $H(\ell m; LM)$ and $K(\ell m; LM)$ have to be numerically integrated in advance and stored in a lookup table. $a''_{\ell m}$ is the second derivative and $a'_{\ell m}$ is the first derivative of $a_{\ell m}(r)$.

For the initial small $r$ value in each integration of Eq. (15), only one of the constants $d_{\ell m}$ (from Eq. (11)) will be 1, and the others are all zero. (Later on, we will be able to determine the actual values of all of the $d_{\ell m}$ so as to satisfy the large-$r$ boundary conditions of the original boundary value problem.)

For a given choice of initial conditions in terms of the constants $d_{\ell m}$, these coupled second order ordinary differential equations, (Eq. (15)), can be integrated outwards from $r=0$ until large $r$ is reached, at which point the constants $\varepsilon_{\ell m}$ can be found.

Because of the linearity of the equations, these are related by

$$\varepsilon_{\ell m} = \sum_{LM} F_{\ell m LM} d_{LM}$$  \hspace{1cm} (18)$$

where $F$ is a matrix. All of the coefficients of $F$ can be calculated through successive integrations of the coupled equations (i.e. varying $\ell$ and $m$).

Suppose the desired solution corresponds to the case where $e_{10} \simeq -2.047 E_{incz}$ and all other $e_{\ell m}$ are 0. Let $G$ be the inverse of the matrix $F$. Then

$$d_{\ell m} = \sum_{LM} G_{\ell m LM} e_{LM}$$  \hspace{1cm} (19)$$

The next step is to repeat the integration of the coupled differential equations with the resulting values of $d_{\ell m}$, in which case all of the values of $a_{\ell m}(r)$ can be found for all values of $r$. Using Eq. (14), this then yields $V(r)$, from which the electric field, polarization, bound charge density and dipole moment can all be calculated.

V. OBJECTS IN VACUO

In order to understand how the dipole moment of a NP in a dielectric is calculated later in this paper, we first review the simpler case of a NP in a vacuum. The dipole moment of the NP is $p$, with Cartesian components $p_x$, $p_y$, and $p_z$. Since there is no free charge, the dipole moment arises from the bound charge, whose volume density is $\rho_b(r)$. The polarization of the material is $P(r)$, and $\rho_b = -\nabla \cdot P$. Since polarization is dipole moment per unit volume, dipole moment can also be calculated from:

$$p = \int P d^3r$$  \hspace{1cm} (20)$$

But $p$ can also be obtained directly from its definition, given that $\rho = \rho_b$ in this situation:

$$p = \int r \rho_b d^3r$$  \hspace{1cm} (21)$$

In addition, since $\nabla^2 V = -\rho/\varepsilon_o$

$$p = -\varepsilon_o \int r \nabla^2 V d^3r$$  \hspace{1cm} (22)$$
Equations (21), (21), and (22) will serve as the basis of three independent numerical methods for calculating the dipole moment (and hence the polarizability tensor) of a NP. These methods are presented in Sections VII VIII and IX respectively. This threefold redundancy of our method serves as a check on the numerical reliability of its results.

To see that Eq. (20) and Eq. (21) give the same answer, consider an arbitrary closed region \( U \) enclosing the NP in its interior. Let \( \partial U \) denote the surface of \( U \). In this case, \( \mathbf{P} \) is zero everywhere on \( \partial U \).

Next, consider the vector field \( \mathbf{B} = z\mathbf{P} \), where \( z \) is the \( z \)-component of position. According to the divergence theorem:

\[
\int_{\partial U} \mathbf{B} \cdot d\mathbf{A} = \int_U (\nabla \cdot \mathbf{B}) d^3r
\]  

(23)

Therefore, \( \int (\nabla \cdot \mathbf{B}) d^3r = 0 \), since \( \mathbf{P} = 0 \) on the boundary of this closed region.

However, since \( \nabla \cdot (z\mathbf{P}) = P_z + z\nabla \cdot \mathbf{P} \) thus

\[
\mathbf{P} = \int_U r \rho_o d^3r = \int_U \mathbf{P} d^3r
\]  

(24)

VI. EMBEDDED DIPOLES

Unfortunately, the formulas of Section V do not all apply to the situation of interest for an embedded NP, where the surrounding material (a glass matrix, for example) has a susceptibility, so that the polarization in the matrix is nonzero, and must be taken into account when finding the dipole moment of the NP. The dipole moment that is relevant to light scattering experiments when finding the dipole moment of the NP. The dipole moment in this case.

As for the incident field part \( \mathbf{B}_{\text{dip}} \cdot d\mathbf{A} \) is equal to \( B_{\text{dip}} \cdot d\mathbf{A} \). We now want to integrate this over the sphere of radius \( R \).

\[
\int \mathbf{B}_{\text{dip}} \cdot d\mathbf{A} = \int B_{\text{dip}} R^2 \sin \theta d\theta d\phi = \int (\epsilon_{\text{mro}} - 1) 2p_z \cos^2 \theta \sin \theta d\theta d\phi = \frac{2(\epsilon_{\text{mro}} - 1)}{3} p_z
\]  

(30)

As for the incident field part \( \mathbf{B}_{\text{inc}} \), it is:

\[
\mathbf{B}_{\text{inc}} = z\mathbf{P}_{\text{inc}} = z\epsilon_o(\epsilon_{\text{mro}} - 1)\mathbf{E}_{\text{inc}}
\]  

(31)

To evaluate the surface integral \( \int \mathbf{B}_{\text{inc}} \cdot d\mathbf{A} \) we need only the radial component:

\[
B_{\text{incr}} = \epsilon_o(\epsilon_{\text{mro}} - 1) R \cos \theta \mathbf{E}_{\text{incz}} \cos \theta
\]  

(32)

where \( E_{\text{incz}} \) is the \( z \)-component of the incident field. We need to integrate this over the same sphere of radius \( R \):

\[
\int \mathbf{B}_{\text{inc}} \cdot d\mathbf{A} = \epsilon_o(\epsilon_{\text{mro}} - 1) \int E_{\text{incz}} R^3 \cos^2 \theta \sin \theta d\theta d\phi
= \frac{4\pi}{3} (R^3 \epsilon_o(\epsilon_{\text{mro}} - 1) E_{\text{incz}})
= \int P_{\text{incz}} d^3r
\]  

(33)
where \( P_{\text{incz}} = \epsilon_o(\epsilon_{\text{mro}} - 1)E_{\text{incz}} \) is the polarization in the matrix if the NP were not present.

We now combine results:

\[
\int \mathbf{B} \cdot d\mathbf{A} = \int \mathbf{B}_{\text{dip}} \cdot d\mathbf{A} + \int \mathbf{B}_{\text{inc}} \cdot d\mathbf{A} + \int P_{\text{incz}} d^3r \quad (34)
\]

\[
= \frac{2(\epsilon_{\text{mro}} - 1)}{3} p_z + \int P_{\text{incz}} d^3r
\]

Once again, because \( \nabla \cdot (z\mathbf{P}) = P_z + z\nabla \cdot \mathbf{P} \) then

\[
\int \mathbf{B} \cdot d\mathbf{A} = \int (\nabla \cdot \mathbf{B}) d^3r
\]

\[
= \int z(\nabla \cdot \mathbf{P}) d^3r + \int P_z d^3r
\]

\[
(35)
\]

Next, since \( \rho_0 = -\nabla \cdot \mathbf{P} \) and \( p_z = \int z\rho_0 d^3r \), we get

\[
\frac{2(\epsilon_{\text{mro}} - 1)}{3} p_z + \int P_{\text{incz}} d^3r = -p_z + \int P_z d^3r \quad (36)
\]

and finally

\[
p_z = \frac{3}{2\epsilon_{\text{mro}} + 1} \int (P_z - P_{\text{incz}}) d^3r
\]

\[
(37)
\]

which can then be vector generalized as follows:

\[
p = \frac{3}{2\epsilon_{\text{mro}} + 1} \int (\mathbf{P} - \epsilon_o(\epsilon_{\text{mro}} - 1)E_{\text{incz}}) d^3r
\]

\[
(38)
\]

**VII. DIPOLE MOMENT: POLARIZATION**

Finally we address the central problem of calculating the dipole moment of an object with inhomogeneous permittivity. The object has an arbitrary shape. In the case of a vibrating NP, the region of inhomogeneous permittivity extends outside the NP into the glass matrix since density variations resulting from the vibrations will affect the permittivity of the glass as well as that of the NP. Only at sufficient distance from the NP will the relative permittivity reach its homogeneous value of \( \epsilon_{\text{mro}} \). Note that \( \epsilon_{\text{mro}} \) is the square of the index of refraction of the glass.

There is some given incident electric field \( \mathbf{E}_{\text{inc}} \). By repeating calculations of \( p \) for different orientations of \( \mathbf{E}_{\text{inc}} \) we can obtain the polarizability tensor \( \alpha \).

We begin by calculating \( p_z \) using Eq. (37). We first make the substitution \( E_z = -\partial V/\partial z \), yielding

\[
p_z = \frac{3\epsilon_o}{2\epsilon_{\text{mro}} + 1} \int \left\{ (1 - \epsilon_r) \frac{\partial V}{\partial z} + (1 - \epsilon_{\text{mro}})E_{\text{incz}} \right\} d^3r
\]

\[
(39)
\]

The following seven steps will re-express Eq. (39) in terms of an explicit quadruple summation over indices \( \ell, m, L, \) and \( M \), as shown in Eq. (41):

Step 1: Recall the expansion of \( \epsilon_r \) in terms of the summation of the \( q_{\ell m} \) in Eq. (17).

Step 2: We want to put the summation for \( (1 - \epsilon_r) \) into a neat form. Note that \( 1 = \sqrt{4\pi}S_{00} \), so that

\[
(1 - \epsilon_r) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left[ \sqrt{4\pi}\delta_{00} - q_{\ell m} \right] S_{\ell m}
\]

\[
(40)
\]

Step 3: Note that

\[
\frac{\partial V}{\partial z} = \cos \theta \frac{\partial V}{\partial r} - \sin \theta \frac{\partial V}{\partial \theta}
\]

\[
(41)
\]

Step 4: Recall the expansion of \( V \) in terms of the summation of the \( a_{\ell m} \) in Eq. (1). Step 5: Take the derivative with respect to \( r \):

\[
\frac{\partial V}{\partial r} = \sum_{L=0}^{\infty} \sum_{M} a'_{LM}(r)S_{LM}(\theta, \phi)
\]

\[
(42)
\]

Step 6: And with respect to \( \theta \) as well:

\[
\frac{\partial V}{\partial \theta} = \sum_{L=0}^{\infty} \sum_{M} a_{LM}(r) \left( \frac{\partial S_{LM}}{\partial \theta} \right)
\]

\[
(43)
\]

Step 7: Substitute Eq’s. (10), (12), and (13) all into Eq. (39) so as to get:

\[
p_z = \frac{3\epsilon_o}{2\epsilon_{\text{mro}} + 1} \int \sum_{\ell m LM} \left\{ \left[ \sqrt{4\pi}\delta_{00} - q_{\ell m}(r) \right] S_{\ell m}(\theta, \phi) \right\} r^2 dr \Omega
\]

\[
(44)
\]

where \( d^3r \) has been replaced with \( r^2 dr \Omega \) and \( d\Omega = \sin \theta d\theta d\phi \). Next, we want to carry out the angular part of the integration. First, note that \( \cos \theta \approx 2.047 \) \( S_{00} \approx \sqrt{4\pi}/3S_{00} \) and second note that \( \sin \theta = -d(d/d\theta) \cos \theta = -\sqrt{4\pi}/3(\partial/\partial \theta)S_{00} \). Third, refer to the definitions of \( H(\lambda) \) in Eq. (16) and \( K(\lambda) \) in Eq. (17). Putting these all together,

\[
p_z = \frac{3\epsilon_o}{2\epsilon_{\text{mro}} + 1} \int \sum_{\ell m LM} \left\{ \left[ \sqrt{4\pi}\delta_{00} \right] - q_{\ell m}(r) \right\} \left( a'_{LM} H(LM; 10, \ell m) + \frac{1}{r} a_{LM} K(\ell m; 10; LM) \right) \right\} r^2 dr \Omega
\]

\[
(45)
\]

Note that Eq. (16) still applies in the situation where \( E_{\text{incz}}=0 \) and \( E_{\text{incx}} \) or \( E_{\text{incy}} \) is nonzero. This would be the situation when calculating the off-diagonal elements of the polarizability, \( \alpha \).
The other components \( p_x \) and \( p_y \) can be found by analogous expressions: \( x \leftrightarrow 1 \) and \( y \leftrightarrow -1 \).

\[
p_x = \frac{3\varepsilon_o}{2\epsilon_{mro} + 1} \int \sum_{\ell m L M} \left\{ \frac{4\pi}{3} \sqrt{4\pi}\delta_{\ell 0} \\
- q_{\ell m} \left[ a'_{LM}(H(LM; 1\ell; \ell m) + 1 \right] \rho_{\ell m} K(\ell m|1\ell; \ell M) \right) \\
+ 4\pi \delta_{\ell 0} \delta_{m0} \delta_{L1} \delta_{M0}(1 - \epsilon_{mro})E_{incx} \right\} r^2 dr \quad (46)
\]

\[
p_y = \frac{3\varepsilon_o}{2\epsilon_{mro} + 1} \int \sum_{\ell m L M} \left\{ \frac{4\pi}{3} \sqrt{4\pi}\delta_{\ell 0} \\
- q_{\ell m} \left[ a'_{LM}(H(LM; 1\ell; \ell m) + 1 \right] \rho_{\ell m} K(\ell m|1\ell; \ell M) \right) \\
+ 4\pi \delta_{\ell 0} \delta_{m0} \delta_{L1} \delta_{M0}(1 - \epsilon_{mro})E_{incy} \right\} r^2 dr \quad (47)
\]

The dipole moment \( \mathbf{p} \) and applied electric field \( \mathbf{E}_{inc} \) are related by \( \mathbf{p} = \alpha \mathbf{E}_{inc} \) where \( \alpha \) is the polarizability tensor of the NP.

It makes things more compact to label vector components by the subscript \( \mu \) which runs from \(-1 \) to \( 1 \). For example, \( p_{\mu} \) and specifically \( p_1, p_0 \) and \( p_1 \), where the correspondence to usual Cartesian notation is as follows: \( (p_1, p_0, p_1) = (p_x, p_y, p_z) \) and \( (E_{incx}, E_{incy}, E_{incz}) = (E_{incx}, E_{incy}, E_{incz}) \).

In this way, it is possible to write a single formula which can calculate any of the three components of the dipole moment of the NP, where \( \mu \in \{1, -1, 0\} \):

\[
p_{\mu} = \frac{3\varepsilon_o}{2\epsilon_{mro} + 1} \int \left\{ \sum_{\ell m L M} \left\{ \frac{4\pi}{3} \sqrt{4\pi}\delta_{\ell 0} \\
- q_{\ell m}(r) \left[ a'_{LM}(r)H(LM; 1\mu; \ell m) + 1 \right] \rho_{\ell m} K(\ell m|1\mu; \ell M) \right) \\
+ 4\pi(1 - \epsilon_{mro})E_{inc\mu} \right\} r^2 dr \quad (48)
\]

**VIII. DIPOLE MOMENT: CHARGE**

For redundancy, the calculation of Section VII is repeated, but this time based on the charge-based expression for dipole moment, Eq. (21). The bound charge density is \( \rho_b = -\nabla \cdot \mathbf{P} \) where the polarization \( \mathbf{P} \) is given by \( \mathbf{P} = \varepsilon_o(\epsilon_r - 1)\mathbf{E} \). Also, \( \mathbf{E} = -\nabla V \). So

\[
\rho_b = \varepsilon_o \nabla \cdot ((\epsilon_r - 1)\nabla V) \quad (49)
\]

From this, and using Eqs. (40) and (47),

\[
\rho_b = \varepsilon_o \left\{ \sum \sum (q_{\ell m} - \sqrt{4\pi}\delta_{\ell 0})S_{\ell m} \nabla^2(a_{LM}S_{LM}) \\
+ \sum \sum 1 \frac{\partial}{\partial r}(q_{\ell m}S_{\ell m}) \frac{\partial}{\partial r}(a_{LM}S_{LM}) \\
+ \sum \sum \frac{r}{\sin^2 \theta \partial \phi}(q_{\ell m}S_{\ell m}) \frac{\partial}{\partial \theta}(a_{LM}S_{LM}) \right\} \quad (51)
\]

Carrying out these derivatives, and also using Eq. (49), we get

\[
\rho_b = \varepsilon_o \left\{ \sum \sum (q_{\ell m} - \sqrt{4\pi}\delta_{\ell 0}) \frac{1}{r^2} [r^2 a'_{LM} + 2 ra_{LM} \\
- L(L + 1)a_{LM}]S_{LM} \\
+ \sum \sum q_{\ell m}a'_{LM} \frac{1}{r^2} \frac{\partial S_{\ell m}}{\partial \theta} \frac{\partial S_{LM}}{\partial \theta} \\
+ \frac{1}{\sin^2 \theta \partial \phi}(q_{\ell m}S_{\ell m}) \frac{\partial}{\partial \phi}(a_{LM}S_{LM}) \right\} \quad (52)
\]

This last equation can now be inserted into Eq. (21) to obtain the dipole moment.

Suppose we want to calculate a single component of the dipole moment, \( \rho_{b\mu} \) where \( \mu \) could be \(-1, 0 \) or \( 1 \). If \( \mu = 0 \) then we multiply \( \rho_b \) by \( z = r \cos(\theta) \simeq 2.047rS_1 \). In general we multiply by \( 2.047rS_1 \). The integrand is then integrated over all space. It is convenient to carry out the angular integrations first:

\[
\rho_{b\mu} = \varepsilon_o \left\{ \sum \sum (q_{\ell m} - \sqrt{4\pi}\delta_{\ell 0})[r^2 a'_{LM} + 2 ra_{LM} \\
- L(L + 1)a_{LM}]H(1\mu; LM; \ell m) \\
+ r^2 q_{\ell m}a'_{LM}H(1\mu; LM; \ell m) \\
+ q_{\ell m}a_{LM}K(1\mu; LM; \ell m) \right\} r dr \quad (53)
\]

Results obtained using this equation can be compared to those obtained from Eq. (15). This provides a guard against programming errors and numerical problems in the integrations over \( r \).

**IX. DIPOLE MOMENT: POTENTIAL**

A third independent method for obtaining dipole moment is presented in this section. Starting from
Coulomb’s law in differential form: \( \nabla \cdot \mathbf{E} = \rho / \varepsilon_0 \), and using \( \mathbf{p} = \int r \rho d^3r \) as well as \( \mathbf{E} = -\nabla V \), we get:

\[
p = -\varepsilon_0 \int r (\nabla^2 V) r^2 drd\Omega \quad (54)
\]

Next, use Eq. (48) to express \( V \) in terms of \( a_{\ell m} \) and real spherical harmonics. Also, specialize to \( p_z \):

\[
p_z = -\varepsilon_0 \sum_{\ell m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} a_{\ell m} \right)
- \frac{\ell (\ell + 1)}{r^2} a_{\ell m} S_{10} S_{\ell m} r^3 drd\Omega \quad (55)
\]

Recall that \( \cos \theta \simeq 2.047 S_{10} \). Also, make use of Eq. (56). So this becomes:

\[
p_z = -2.047 \varepsilon_0 \int r \cos \theta \nabla^2 [a_{\ell m} S_{\ell m}] r^2 drd\Omega \quad (56)
\]

It is now apparent how to generalize from the \( z \)-axis to the \( \mu \) axis where \( \mu = -1, 0, 1 \). Also, the angular integration can be performed (employing Eq. (5)), followed by the summation over \( \ell \) and \( m \):

\[
p_{\mu} = -\sqrt{4 \pi / 3} \varepsilon_0 \int [r^3 a''_{1\mu} + 2r^2 a'_{1\mu} - 2ra_{1\mu}] dr \quad (57)
\]

Equation (57) for dipole moment is far simpler than Eq. (38) and Eq. (52). In particular, the \( q_{\ell m} \) coefficients are no longer required. In theory the range of integration is from \( r = 0 \) to \( \infty \). However, Eq. (57) is not susceptible to numerical error buildup in the high \( r \) region compared to the other two methods, and the upper limit of integration has to be carefully restricted. The integration step should also be kept small. Even so, it tends to give much more accurate results than the other two methods when tested on prolate ellipsoids.

**X. NUMERICAL METHODS**

In practice, the expansion for \( V \) in Eq. (41) has a limited value of \( \ell \), here denoted as \( \ell_{maxa} \). In a similar way, the expansion for \( \log(\varepsilon_r) \) in Eq. (3) is limited to a finite value of \( \ell \), denoted \( \ell_{maxc} \).

It was found that \( \ell_{maxa} \) must be chosen jointly with \( \ell_{maxc} \). Best results are obtained when \( \ell_{maxa} \) is less than \( \ell_{maxc} \). Further increasing \( \ell_{maxa} \) while holding \( \ell_{maxc} \) constant does not improve the results.

It is desirable to make careful comparisons with the exact solution for a homogeneous dielectric ellipsoid in a homogeneous matrix. However, in such a situation the permittivity is a singular function which is not suitable for integration. To get around this problem, the dielectric ellipsoid is approximated by a smoothed permittivity. The smoothing must be carried out over a short distance (surface thickness) in order to accurately approximate the ideal shape. In addition, this smoothing should be done in such a way that the derivatives of permittivity are also smooth. This is implemented in a C++ program named varpr27e. However when the eccentricity is nonzero the functions become smooth, and in these cases even zero-order smoothing (continuous, but 1st derivative discontinuous) seems to work.

The coefficients \( c_{\ell m} \) and \( q_{\ell m} \) that are obtained from the smoothed permittivity function are now smooth functions of \( r \). Even so, they change sharply near certain points. It is necessary to use integration with variable step size where a much smaller step is used near the difficult points.

It is practical to first obtain the functions \( c_{\ell m} \) and \( q_{\ell m} \). These functions of \( r \) can be stored in a look-up table. However, because of the sharp variation at certain points the step size between entries in the table must be variable. This is taken care of in the program varpr27e which generates a file as output which is read by varpr28j.

The lookup table for \( H(\cdot; \cdot) \) and \( K(\cdot; \cdot) \) can grow to several hundred entries, and access time can be minimized through use of a hash index (likely first guess) method as implemented in the functions \( H(\cdot; \cdot) \) and \( K(\cdot; \cdot) \) in varpr28j. Most computation time ends up being spent in the evaluation of the right side of Eq. (15) because of the triple nested loop required. This is why the access time of \( H(\cdot; \cdot) \) and \( K(\cdot; \cdot) \) is so important.

It is preferable to carry out the actual numerical integration of Eq. (15) in terms of the variables \( w_{\ell m}(r) \), such that \( a_{\ell m}(r) = r^\ell w_{\ell m}(r) \). This is because these variables are constant both at large and small \( r \).

It is not possible to handle the situation where the permittivity inside the NP is a purely negative number. That is because smoothing at the boundary would result in a point where the permittivity is zero, so that the logarithm is singular. However, if the permittivity inside is complex valued then this problem is avoided.

**XI. CHECKS OF CORRECTNESS**

The three methods for determining the dipole moment given as Eqs. (38), (52), and (57), do not give identical results when finite \( \ell \) cutoffs (\( \ell_{maxa} \) and \( \ell_{maxc} \)) are used. However, mutual convergence of the three methods to calculate dipole moment is an indication of convergence as the two \( \ell \) cutoffs are increased.

Given the length of this paper, we have chosen not to present specific numerical results. But we can mention the numerical tests that we have done as a check of correctness of the equations presented here. We compared our numerical results to exact ones for the (1) dielectric sphere, with positive and complex valued permittivity (2) prolate spheroid (3) oblate spheroid and (4) dielectric sphere with its center not located at the origin of coordinates.

All of these cases have an exact solution that comes from Eq. (8.10) on page 41 of Landau’s book. This is
for the dipole moment of a homogeneous ellipsoid (with semiaxes \(a, b, \) and \(c\)) in a vacuum with an asymptotically uniform electric field along the \(z\)-axis. When translated from cgs to SI units and into our notation it becomes:

\[
p_z = (volume) E_{inc} \frac{\epsilon_o(\epsilon_{inr} - 1)}{1 + (\epsilon_{inr} - 1)n(z)}
\] (58)

where \(n(z)\) is the \(z\)-axis depolarization factor which is equal to \(1/3\) for a sphere and “volume” is \((4\pi/3)abc\). \(\epsilon_{inr}\) is the relative permittivity of the ellipsoid. Using our Eq. (A7) (in the Appendix) the formula for the case of a homogeneous dielectric ellipsoid embedded in a homogeneous dielectric is:

\[
p_z = (volume) E_{inc} \frac{\epsilon_o(\epsilon_{mro} - \epsilon_{inr})}{\epsilon_{mro} + (\epsilon_{inr} - \epsilon_{mro})n(z)}
\] (59)

For an oblate spheroid where \(a = b\) and \(c < a\), the eccentricity is \(e = \sqrt{a^2/b^2 - 1}\).

\[
n(z) = \frac{1 + e^2}{e^3}(e - \arctan(e))
\] (60)

\[
n(x) = n(y) = \frac{1}{2}(1 - n(z))
\] (61)

There is an increase in numerical error as the condition for dipole surface plasmon resonance is approached. This is because \(F_{1010}\) approaches zero after many positive and negative contributions so that numerical errors become predominant when \(l\) cutoffs are used.

In order to see the pattern of convergence as \(\ell_{max}\) and \(\ell_{max}\) increase, some series of values have been calculated to see if the percentage error goes to zero. The percentage error does decrease monotonically.

**Acknowledgments**: This work was supported by the Natural Sciences and Engineering Research Council of Canada.

**APPENDIX A: HOMOGENEOUS OBJECTS**

We present a fourth method to calculate the dipole moment, however this one is specialized to the situation of a homogeneous dielectric embedded in a homogeneous dielectric. There is no bound charge density \(\rho_b\) at interior points of a homogeneous dielectric, but bound surface charge \(\sigma_b\) can exist at dielectric surfaces. To see why, note that \(\mathbf{P} = (\epsilon_r - 1)/\epsilon_r \mathbf{D}\), and \(\nabla \cdot \mathbf{D} = \rho_f\) where \(\rho_f\) is the free charge density. In a region where \(\epsilon_r\) is constant and there is no free charge \(\nabla \cdot \mathbf{D} = 0\) so that \(\nabla \cdot \mathbf{P} = 0\) as well. Thus \(\rho_b = 0\).

In this case, the volume integral for dipole moment \(\mathbf{p} = \int \mathbf{r} \rho_b d^3r\) can be replaced with the surface integral

\[
\mathbf{p} = \int r \sigma_b dA
\] (A1)

The bound surface charge density is given by

\[
\sigma_b = P_{in} - P_{out}
\] (A2)

where \(P_{out}\) is the normal (outward pointing) component of the polarization just outside the surface, while \(P_{in}\) is the normal (outward pointing) component of the polarization just inside the surface. This can be related to the electric field at the surface since \(\mathbf{P} = \epsilon_o(\epsilon_r - 1)\mathbf{E}\). Thus:

\[
\sigma_b = \epsilon_o[(\epsilon_{in} - 1)E_{in} - (\epsilon_{out} - 1)E_{out}]
\] (A3)

where \(E_{in}\) is the normal component of the electric field just inside the surface. This is equivalent to:

\[
\sigma_b = \frac{D_{in} - D_{out} + \epsilon_o(E_{out} - E_{in})}{2}
\] (A4)

The absence of free charge means that \(D_{in} = D_{out}\). Therefore

\[
\sigma_b = \epsilon_o(E_{out} - E_{in})
\] (A5)

This provides a formula for dipole moment in terms of the electric field:

\[
\mathbf{p} = \epsilon_o \int \mathbf{r}(\mathbf{E}_{out} - \mathbf{E}_{in}) \cdot d\mathbf{A}
\] (A6)

The electric field at great distances is \(\mathbf{E}_{inc}\). It can also be noted that the electric field in and near the object in this situation depends only on \(\epsilon_{in}/\epsilon_{out}\). To see why, note that \(\nabla \cdot \mathbf{D} = 0\). Therefore, \(\nabla \cdot (\epsilon_r(\mathbf{E}(\mathbf{r})) = 0\). Consequently, a given electric field still solves the boundary value problem if both \(\epsilon_{in}\) and \(\epsilon_{out}\) are multiplied by the same constant.

Because of Eq. (A6), the same also holds true for the dipole moment:

\[
\mathbf{p} = f(\mathbf{E}_{inc}, \epsilon_{in} \epsilon_{out})
\] (A7)

where \(f()\) is some (non-scalar) function that also depends on the size, shape, and orientation of the object.

Thus, if the dipole moment is theoretically calculable for the situation of a homogeneous object sitting in a vacuum, Eq. (A7) can be used to find the dipole moment when permittivities inside and outside are multiplied by the same constant. The dipole moment will be the same, in fact.

* Electronic address: daniel.murray@ubc.ca  
† Electronic address: calebnetting@gmail.com
Electronic address: lucien.saviot@u-bourgogne.fr

1 E. Duval, A. Boukenter, and B. Champagnon, Phys. Rev. Lett. 56 (1986) 2052.
2 J. I. Gersten, D. A. Weitz, T. J. Gramila, and A. Z. Genack, Phys. Rev. B 22 (1980) 4562.
3 M. Montagna and R. Dusi, Phys. Rev. B 52 (1995) 10080.
4 G. Bachelier and A. Mlayah, Phys. Rev. B 69 (2004) 205408.
5 N. Del Fatti, C. Voisin, M. Achermann, S. Tzortzakis, D. Christofilos, and F. Vallee, Phys. Rev. B 61 (2000) 16956.
6 G. Mie, Ann. Physik 25 (1908) 377.
7 A. Taflove, Computational Electrodynamics: The Finite-Difference Time-Domain Method. Norwood, MA: Artech House, 1995.
8 E. M. Purcell and C. R. Pennypacker, Astrophys. J 186 (1973) 705.
9 B. T. Draine, Astrophys. J 333 (1988) 848.
10 K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, J. Phys. Chem. B 107 (2003) 668.
11 D. J. Griffiths, Introduction to Electrodynamics. Prentice Hall, 3rd ed., 1999.
12 J. D. Jackson, Classical Electrodynamics. New York: John Wiley, 2nd ed., 1985.
13 L. D. Landau, E. M. Lifshitz, and L. P. Pitaevskii, Electrodynamics of Continuous Media. Pergamon, 2nd ed., 1984. (volume 8 in Landau and Lifshitz Course of Theoretical Physics) See section 4 (pages 19-25) and section 8 (pages 39-42).