Electron energy-loss spectroscopy in systems of polarizable spheres

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Abstract

We start with a brief presentation of the dielectric formalism used to calculate the energy loss of high-energy electrons (100 keV) passing through a random system of polarizable spheres embedded in a homogeneous matrix. The formalism is then extended to the case of electrons traveling parallel to a homogeneous slab of finite thickness in which either ordered or disordered collections of polarizable spheres are embedded. For an ordered system in which the spheres are in a cubic array, the calculated energy-loss spectra are compared with those of an alternative theory. For a slab with disordered collections of spheres we find the energy-loss spectra using the recursive Green's function method and compare our results with the available experimental data as well as with an extension of the semiclassical-infinite-barrier (SCIB) model. Finally, we discuss the relevance of our work as well as trends for future research.

The problem of calculating the electron energy loss spectra for systems of polarizable spheres has been dealt by several authors \cite{1,2}. In this work we present an approach to this difficult problem by focusing on spectral representations for the nonlocal response functions. Besides computational advantages, the method has the appealing characteristic that the weights and poles of the spectral representation depend only on geometrical information and not on the dielectric functions of the components.

1. Review of the theory for a random system of spheres

Here we give a brief review of the theory of electron energy loss by an unbounded random system of spheres, first derived by Barrera and Fuchs \cite{3}. It is assumed that the system appears to be homogeneous at a length scale $l > a$, where $a$ is the radius of the spheres, although it is highly inhomogeneous at a length scale of the order of $a$. This allows us to describe the system by an effective dielectric function $\varepsilon_M(k, \omega)$. The probability per unit length, per unit energy, for an electron to scatter with energy loss $E$ is

$$\frac{d^2P(E)}{dl dE} = \left( a_0 \frac{m_0 v_I^2}{2} \right)^{-1} \Xi(E),$$

where $a_0$ is the Bohr radius, $m_0$ is the rest mass of the electron and $v_I$ is the speed of the incident electrons. The relation between $\Xi(E)$ and $\varepsilon_M(k, \omega)$ is given by

$$\Xi(E) = \frac{1}{\pi} \int_{\omega/\pi}^{\infty} \text{Im} \left[ 1 - \frac{1}{\varepsilon_M(k, \omega)} \right] \frac{dk}{k},$$

where $k_c$ is an upper cutoff wave vector usually determined by the angular aperture of the electron energy-loss detector.
It was shown [3] that \(1/\varepsilon_m(k, \omega)\) can always be written in the following spectral representation:

\[
\frac{1}{\varepsilon_m(k, \omega)} = \frac{1}{\varepsilon_2} \left[ 1 + f \left( \frac{C_b}{u - 1} + \sum_s \frac{C_s}{u - n_s} \right) \right]
\]

(3)

where \(f = \frac{4}{3} \pi a^3 N/V\) is the filling fraction of the spheres, \(u = -1/(\varepsilon_1/\varepsilon_2 - 1)\) is the spectral variable, and \(\varepsilon_1\) and \(\varepsilon_2\) are the local, frequency-dependent dielectric functions of the spheres and the matrix, respectively. Here \(N\) is the total number of spheres and \(V\) is the total volume of the system. By spectral representation we mean that \(1/\varepsilon_m\) can be written as a sum of terms with simple poles, and these poles are related to the excitation of the normal modes of the electric field within the system. For example, the poles at \(u = 1\) and \(u = n_s\) have strengths \(C_b\) and \(C_s\), and correspond to the excitation of bulk and interfacial modes, respectively. Furthermore, the strengths \(C_b\) and \(C_s\) fulfill the following sum rule [3]:

\[
C_b + \sum_s C_s = 1
\]

(4)

which means that the sum of all mode strengths is conserved, or alternatively, that the strength of the bulk mode is reduced due to the presence of the interface, a fact also known as the Begrenzung effect.

Another appealing feature of the spectral representation given in Eq. (3) is that the properties of the material appear only in the spectral variable \(u\), while the location and strength of the poles depend only on \(k\) and on the geometry of the system. In the mean-field approximation the information about the geometry of the system is given by two statistical parameters [3]: the filling fraction of spheres \(f\) and their two-particle distribution function \(\rho^{12}(r_{12})\), where \(r_{12}\) is the distance between the centers of two spheres. If the two-particle distribution function takes account of only the excluded volume correlation, that is, \(\rho^{12}(r_{12}) = 1\) for \(r_{12} \geq 2a\) and 0 otherwise, it can be shown [3] that the strengths of the modes \(C_b\) and \(C_s\) and the location of the interface modes \(n_s\) become functions of only \(ka\), and can be calculated by a simple procedure.

2. Spheres in a slab

Here we extend the formalism to treat the case of electrons traveling parallel to an homogeneous slab of finite thickness in which either ordered or disordered collections of spheres are embedded.

2.1. Ordered system

First, consider a cubic array of identical polarizable spheres of radius \(a\) and a local dielectric function \(\varepsilon_2(\omega)\) occupying a slab-shaped portion of the region of space \(z < 0\). A fast electron is traveling at speed \(v_t\) on a rectilinear trajectory along the \(y\)-axis, lateral position \(x_l\), and at a distance \(z_0\) above the surface of the slab, as shown in Fig. 1.

![Fig. 1. An electron with charge \(-e\) moves with velocity \(v_t = v_i e_x\) parallel to an ordered array of spheres. The direction \([1 0 0]\) of the lattice makes an angle \(\phi\) with respect to the \(x\)-axis.](image)

We assume a linear relationship between the induced and external potentials which can be written, for systems with crystalline periodicity parallel to the interface, as

\[
\phi^{\text{ind}}(Q, \omega) = -\sum_g g(Q, Q + G; \omega) \phi^{\text{ext}}(Q + G, \omega),
\]

(5)

where \(\omega\) and \(Q = (Q_x, Q_y)\) are the frequency and the two-dimensional wave vector, and \(G\) is the two-dimensional reciprocal lattice vector corresponding to the crystal lattice.

Taking the time average of the energy loss and performing, for simplicity, a lateral scanning of the electron beam, one finds that only the term with \(G = 0\) contributes to the averaged energy loss and we can write

\[
\Xi(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dQ_x e^{-2\pi i z_0 Q_x} Q |g(Q, \omega)|^2 \Im{g(Q, \omega)},
\]

(6)

where \(|g(Q, \omega)|^2 = g(Q, Q; \omega)\), \(Q = (Q_x, Q_y)/v_t\), and \(Q = |Q|\).

The response function \(g(Q, \omega)\) carries information about the interaction among the spheres. Following Ref. [11] the calculation of \(g(Q, \omega)\) is performed to all multipolar orders and expressed as a spectral representation in the following form:

\[
g(Q, \omega) = -\sum_{\ell=\ell_m}^\infty \frac{D_\ell(Q)}{2\pi u(\omega) - n_\ell(Q)},
\]

(7)

where \(u(\omega)\) is the spectral variable defined above but with \(\varepsilon_2 = 1\).

The procedure for calculating \(n_\ell(Q)\) and \(D_\ell(Q)\) can be found in Refs. [7,12]. It turns out that the \(n_\ell(Q)\) correspond to the eigenvalues of an interaction matrix \(H_m^{\text{slab}}(Q)\)
which is independent of the properties of the materials. An expression for \( H_{\text{lim}\{j}}^{m}(Q) \) appears in Ref. [5]. Then, one can show (see Ref. [12]) that the strengths \( D_{i}(Q) \) can be written as

\[
D_{i}(Q) = \sum_{lmi, j} A_{Q, lmi} U_{lmi,s} U_{s,lmi}^{-1} A_{lmi, Q}. \quad (8)
\]

Here, \( U_{lmi,s} \) is the unitary matrix which diagonalizes the matrix \( H_{\text{lim}\{j}}^{m} \), and \( A_{Q, lmi} = (A_{lmi, Q})^{*} \). Expressions for \( A_{lmi, Q} \) appear in Ref. [5].

Now, we present numerical solutions for \( \Sigma(E) \) for a slab of aluminum spheres in vacuum. The dielectric response of aluminum is modeled by a Drude dielectric function \( \varepsilon_{d}(\omega) = 1 - \omega_{p}^{2}/(\omega^{2} + i\omega\tau) \), where \( \omega_{p} \) is the plasma frequency and \( \tau \) the relaxation time. In the results shown below the Drude parameters for aluminum have been taken as \( \hbar\omega_{p} = 16 \text{ eV} \) and \( \omega_{p}\tau = 100 \). Also, we have fixed \( E_{i} = 100 \text{ keV} \), which corresponds to the typical incident energies for electrons produced in a scanning transmission electron microscope, and we have chosen \( a = 2.5 \text{ nm} \) and \( z_{0} = 1 \text{ nm} \).

In Fig. 2 we show the spectra of \( \Sigma(E) \) for systems with a number of layers, \( n_{s} \), chosen sufficiently large to give the response of a half-space. The value of \( L_{\text{max}} \), the maximum multipolar order considered in the calculation, is chosen so that multipolar convergence is achieved. We plot \( \Sigma(E) \) for \( n_{s} = 6 \), \( L_{\text{max}} = 3 \), and \( f = 0.065 \). In this figure we also plot the results obtained using an alternative theory developed by Pendry and Martin-Moreno [6]. The possible sources of discrepancy between these two theories have been thoroughly discussed in Ref. [12].

![Figure 2](image-url)

**Fig. 2.** Energy-loss probability function \( \Sigma(E) \) as a function of the energy loss \( E = \hbar\omega_{s} \) for a slab made of \( n_{s} = 6 \) layers of spheres and with filling fraction \( f = 0.065 \). The dashed line corresponds to results of Pendry and Martin-Moreno (PMM) in Ref. [6] and the solid line corresponds to our theory. The angle between the trajectory of the electron and the [0 1 0] axis of the array is \( \phi = 0^\circ \). The rest of the parameters are the ones reported by PMM in Ref. [6].

### 2.2. Disordered system

In this section we apply the theory to a disordered system of spheres in a slab [7]. The spheres are located so that the density of centers of spheres is constant in the region \( -L_{s} + a < z < -a \) of the slab. Here \( L_{s} \) is the thickness of the slab. The surface response function \( g(Q, \omega) \) is now independent of the direction of \( Q \) and the size of the matrix \( H_{\text{lim}\{j}}^{m} \) that we need to diagonalize to obtain the poles and weights of the spectral representation is \( S = N \times L_{\text{max}} \times (L_{\text{max}} + 2) \). This means that as the number of spheres and multipolar orders increase, the size \( S \) of the matrix becomes much too large to use a diagonalization procedure to obtain the eigenvalues and eigenvectors, since the computation time \( \propto S^{2} \).

Instead of this we use a recursive Green's function method to find \( g(Q, \omega) \) [8,9].

This method consists in expressing \( g(Q, \omega) \) as a continued fraction

\[
g(Q, \omega) = -\frac{1}{2} \frac{b_{0}^{2}}{u - a_{0} - \frac{b_{0}^{2}}{u - a_{1} - \frac{b_{1}^{2}}{u - a_{2} - \frac{b_{2}^{2}}{u - a_{3} - \frac{b_{3}^{2}}{u - a_{4} - \cdots}}}}} \quad (9)
\]

where \( b_{i}^{2}u(u) = (u - 1/2 \pm i\sqrt{u(1 - u)}/2 \) is a terminating function, with the sign of the square root chosen so that \( \text{Im} g(Q, \omega) > 0 \). The coefficients \( b_{0}, a_{0}, b_{1}, a_{1}, \ldots \) are calculated starting with

\[
b_{0} = u_{0}^{2}u_{0} \equiv \sum_{i=1}^{s} A_{v}^{*}A_{v}. \quad (10)
\]

where we have used the simplifying notation \( A_{v} \equiv A_{r,m,j}^{*}A_{j} \), \( A_{v}^{*} \equiv A_{lmi, Q}^{*} \), and the components of the vector \( u_{0} \) are the coefficients \( A_{v} \). The remaining coefficients are calculated recursively as follows:

\[
a_{i} = u_{i}^{2}Hu_{i}u_{i}^{*}u_{i}, \quad (11)
\]

\[
u_{i+1} = (H - a_{i})u_{i} - b_{i}^{2}u_{i-1}, \quad (12)
\]

\[
b_{i+1}^{2} = u_{i+1}^{*}u_{i+1}u_{i}^{*}u_{i}, \quad (13)
\]

for \( i = 0, 1, 2, \ldots, n \), and \( u_{-1} = 0 \). Here \( H \) is the symbol for the matrix whose elements are \( H_{\text{lim}\{j}}^{m} \).

The computation time for each recursive step is \( \propto S^{2} \), and only a small number \( n \) of terms in the continued fraction (9) is needed to give an accurate approximation to \( g(Q, \omega) \). Therefore, the total computation time is \( \propto n S^{2} \), which is much less than the time required for matrix diagonalization.

In Fig. 3 we show the results for a slab of aluminum spheres in vacuum, and make a comparison with the results obtained previously using an effective medium
Fig. 3. Energy-loss probability function $\Xi(E)$ as a function of the energy loss $E = \hbar \omega$ for a slab made of $n_z = 6$ layers of spheres, with filling fraction $f = 0.15$, and $L_{max} = 3$. The solid line corresponds to the theory and the dashed line corresponds to the modified SCIB model of Mendoza et al. [10].

(SCIB) model [10]. The curve labeled “simulation” was obtained using the theory described above for a disordered system. The location of the spheres was generated moving at random an originally ordered system of spheres in a cubic lattice of $n_z$ layers.

If the spheres are immersed in a semiinfinite dielectric matrix then the surface response function is calculated approximately (see Refs. [7,12]) using the formula

$$g_s(Q, \omega) = \frac{g_h(Q, \omega)\left[\varepsilon_2(\omega) + 1\right] + \varepsilon_2(\omega) - 1}{g_h(Q, \omega)\left[\varepsilon_2(\omega) - 1\right] + \varepsilon_2(\omega) + 1}$$

(14)

where $\varepsilon_2$ is the dielectric function of the matrix, $g_h(Q, \omega) = e^{-2\alpha b}g_m(Q, \omega)$, with $(a + b)$ the smallest distance between the sphere centers and the edge of the matrix, and $g_m(Q, \omega)$ is the calculated response function using Eqs. (7) and (8) with $\varepsilon_1/\varepsilon_2$ instead of $\varepsilon_1$ in the spectral variable $\omega$. We recall that Eq. (14) can be used for both, ordered and disordered systems.

In Fig. 4 we plot $\Xi(E)$ for aluminum spheres in aluminum fluoride (AlF$_3$), and we compare with the experimental results of Walsh [4] for a similar system.

3. Conclusion

We have shown approaches for calculating the energy loss of collections of spheres, both unbounded in three dimensions and confined to a slab-shaped region. For the unbounded system, the energy-loss spectrum can be expressed in terms of a nonlocal effective dielectric function. For the slab-shaped configuration, a nonlocal surface response function was used. In both cases, the response functions were written in the form of a spectral representation. For disordered spheres in a slab, a recursive Green’s function method proved to be successful for performing simulations with a large number of spheres and multipolar orders. This method is being used to find the nonlocal effective dielectric function for the three-dimensional unbounded system of spheres without making the mean-field approximation.

References