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## Electron energy-loss spectroscopy of inhomogeneous systems

Ronald Fuchs<sup>a,\*</sup>, Carlos I. Mendoza<sup>b</sup>, Rubén G. Barrera<sup>b</sup>,  
José Luis Carrillo<sup>c</sup>

<sup>a</sup> *Ames Laboratory and Department of Physics and Astronomy, Iowa State University,  
Ames, IA 50011, USA*

<sup>b</sup> *Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364,  
01000 México, Distrito Federal, Mexico*

<sup>c</sup> *Instituto de Física "Luis Rivera Terrazas", Universidad Autónoma de Puebla, Apartado Postal J-48,  
72570 Puebla, Puebla, Mexico*

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### Abstract

After beginning with a brief review of the theory of electron energy loss by an unbounded random system of spherical inclusions characterized by a local dielectric function, we examine several extensions of this theory. We first treat an inhomogeneous system of spherical particles confined to a half-space. A surface response function, which can be used to calculate the energy-loss spectrum for charged particles moving outside the system, is defined, and this response function is written in a spectral representation. We discuss different approaches to this problem: the semiclassical infinite barrier model, an exact formal theory, and a continuous effective medium theory. Finally, we develop a theory of electron energy loss for a mixture of two components with arbitrary geometry, unbounded in three dimensions.

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### 1. Introduction

The theoretical problem of calculating the local effective dielectric function  $\epsilon_M(\omega)$  of a heterogeneous mixture in terms of the dielectric functions  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  of its constituents has a long history. Only recently have there been some electron energy-loss measurements of such mixtures [1], and Barrera and Fuchs [2] were the first to study this problem theoretically. We begin with a short review of this theory, which

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\* Corresponding author. Fax: (44)1223336117; e-mail: fuchs@iastate.edu.

addresses the problem of calculating the nonlocal effective dielectric function  $\varepsilon_M(k, \omega)$  of a random system of spherical particles. Throughout this paper we emphasize spectral representations, which give a direct connection between the effective dielectric response and the geometry of the system. Next, we consider the problem of finding the surface response function  $g(Q, \omega)$  of a disordered system of spheres confined to a half-space, and discuss several methods which may be useful for solving this problem. The fact that correlation functions depend on distances from the surface, not only on distances between particles, is a challenging feature of such systems. In the final section of this paper, we find the spectral representation of  $\varepsilon_M(k, \omega)$  for a heterogeneous mixture with arbitrary geometry.

## 2. Review of theory for random system of spheres

We begin with a brief review of the theory of electron energy loss by an unbounded random system of spherical inclusions, first derived by Barrera and Fuchs [2]. It was assumed that the system appears to be homogeneous at a length scale  $l \gg a$ , 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  $\varepsilon_M(k, \omega)$ , from which the electron energy-loss spectrum can be calculated.

It was shown [2] that  $1/\varepsilon_M(k, \omega)$  can be written in the following spectral representation:

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

where  $f = (N/V)4\pi a^3/3$  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 [2]:

$$C_b + \sum_s C_s = 1 \quad (2)$$

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. (1) 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 [2]: the filling fraction of spheres  $f$  and their two-particle distribution function  $\rho^{(2)}(R_{12})$ , 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,  $\rho^{(2)}(R_{12}) = 1$  for  $R_{12} \geq 2a$  and 0 otherwise, it can be shown [2] 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.

### 3. Inhomogeneous systems in a half-space

#### 3.1. Surface response function $g(Q, \omega)$

We consider a system of spherical inclusions randomly located in the half-space  $z < 0$ . The inclusions have local dielectric function  $\varepsilon_1$ , and the matrix has local dielectric function  $\varepsilon_2 = 1$ . The surface response function  $g(Q, \omega)$ , in which  $\mathbf{Q}$  is the wave vector parallel to the surface, has been applied to study energy-loss processes by homogeneous media in a half-space [3], and this quantity appears in expressions for the energy-loss spectrum of electrons moving on trajectories confined to the half-space  $z > 0$ ; for example, a trajectory parallel to the surface [4], or reflected from the surface [5]. For the inhomogeneous system we are considering,  $g(Q, \omega)$  must be regarded as an effective response function, describing the system which is effectively homogeneous and isotropic parallel to the surface after an appropriate configurational average over the sphere positions.

One takes an external potential produced by an external charge infinitely distant from the interface in the region  $z > 0$ , with a single wave-vector component  $\mathbf{Q} = Q\mathbf{i}$ . The external potential satisfies Laplace's equation, and is of the form

$$V^{ext}(\mathbf{r}) = V_0 e^{Qz} e^{iQx}. \quad (3)$$

The time dependence  $e^{-i\omega t}$  is omitted for simplicity. This external potential induces charges on the system of spheres, giving rise to an induced potential. The surface response function is defined in terms of this induced potential in the region outside the spheres,

$$V^{ind}(\mathbf{r}) = -g(Q, \omega) V_0 e^{-Qz} e^{iQx}, \quad z > 0. \quad (4)$$

If a homogeneous medium filling the half-space  $z < 0$  is described by a local dielectric function  $\varepsilon(\omega)$ , one finds that  $g(Q, \omega) = (\varepsilon(\omega) - 1)/(\varepsilon(\omega) + 1)$ .

It will be shown in Section 3.3 that the surface response function can be written in the form of a spectral representation

$$g(Q, \omega) = -\frac{f}{2} \sum_s \frac{d_s}{u - n_s}, \quad (5)$$

where  $u$  is the same spectral variable as in Eq. (1) and  $f$  is the volume fraction of spheres infinitely far from the surface,  $f = \lim_{z \rightarrow -\infty} f(z)$ . The mode strengths  $d_s$  and positions  $n_s$  depend only on geometry and the wave vector  $Q$ . In fact, Eq. (5) should be valid for any system of particles of any shape confined to the half-space  $z < 0$ , which is uniform in the  $x$  and  $y$  directions after configurational averaging, so that the volume fraction is a function only of  $z$ . One can derive a sum rule for the strengths  $d_s$  by going to the high-frequency limit, where  $\epsilon_1(\omega) - 1 \sim O(\omega^{-2})$  and  $u \rightarrow \infty$ . In this limit, the polarization of the dielectric is due to the electrons, which can be considered free, and the coulomb interaction between the electrons can be neglected. Each electron (labelled by the index  $i$ ) moves independently in response to the external potential, and produces an induced dipole moment which gives the induced potential  $V_i^{ind}(\mathbf{r})$ . The  $Q$ th Fourier component of this potential is found by taking a two-dimensional Fourier transform,

$$V_i^{ind}(Q, z) = \frac{1}{L^2} \int e^{-iQx} V_i^{ind}(\mathbf{r}) dx dy, \quad (6)$$

where we are assuming a period length  $L$  in the  $x$  and  $y$  directions. One finds

$$V_i^{ind}(Q, z) = -L^{-2} V_0 \alpha 4\pi Q e^{-Qz} e^{2Qz_i}, \quad (7)$$

where  $\alpha = -e^2/m\omega^2$  is the polarizability associated with each electron. The total induced potential  $V^{ind}(Q, z)$  from all electrons is found by changing the sum over  $i$  to an integral over volume, using the expression  $dN = f(z)n_0 dv$  for the average number of electrons  $dN$  in a volume element  $dv = dx dy dz$ , where  $n_0$  is the electron density in the material 1. Since  $V^{ind}(\mathbf{r}) = V^{ind}(Q, z) e^{iQx}$ , comparison with Eqs. (4) and (5) gives the desired sum rule,

$$\sum_s d_s = \frac{2Q}{f} \int_{-\infty}^0 e^{2Qz} f(z) dz. \quad (8)$$

For a constant volume fraction  $f(z) = f$ ,  $-\infty < z < 0$ , Eq. (8) gives the simple result  $\sum_s d_s = 1$ .

### 3.2. SCIB model for a random system of spheres

A simple procedure for calculating the surface response function is to use a model known in the literature as the *specular reflection* or *semiclassical infinite barrier* (SCIB) model [6,7]. This model was originally used in theories of the anomalous skin effect for a metal surface and has also been proposed to calculate optical properties and screening of external charges for metal surfaces. The advantage of this model is that the surface response function  $g(Q, \omega)$  is given as a functional of the bulk longitudinal dielectric function  $\epsilon(k, \omega)$  of the unbounded system, which is already known [Eq. (1)]. Therefore, the model correctly takes into account the nonlocal ( $k$ -dependent) effects that arise from the size of the spheres and the two-particle distribution function. However, it implicitly assumes a model for the surface region in which the surface is terminated abruptly.

The idea of the SCIB model is to extend the system of spheres that is actually confined to the half-space  $z < 0$  into an unbounded system of spheres, whose dielectric response is correctly given by  $\varepsilon(k, \omega)$ . Then, in order to model the presence of the surface, one introduces at  $z = 0$  a fictitious external charge of the form  $\rho(\mathbf{r}) = A e^{iQx} \delta(z)$ , where  $A$  is an unknown constant. The potential  $V(\mathbf{r})$  and electric displacement  $\mathbf{D}(\mathbf{r})$  are determined throughout the entire infinite medium. One assumes that the potential and displacement within the half-space  $z < 0$ , in which the system is actually located, are given correctly by this procedure, and that on the vacuum side the potential is the sum of the external and induced potentials [Eqs. (3) and (4)]. Imposing the boundary conditions that the potential and the normal component of the displacement are continuous across the interface at  $z = 0$ , one can find both unknowns, the constant  $A$  and the surface response function,

$$g(Q, \omega) = \frac{\tilde{\varepsilon}(Q, \omega) - 1}{\tilde{\varepsilon}(Q, \omega) + 1}, \tag{9}$$

where

$$\frac{1}{\tilde{\varepsilon}(Q, \omega)} = \frac{Q}{\pi} \int_{-\infty}^{+\infty} \frac{dk_z}{(Q^2 + k_z^2) \varepsilon_M(k, \omega)}. \tag{10}$$

From the surface response function we find a quantity  $S(Q, \omega) = \text{Im} g(Q, \omega)$ , called the surface-loss function, which is used to calculate the energy loss of an electron traveling parallel to the interface of the system, with impact parameter  $z_0$  and speed  $v_l$  in the  $y$  direction. The probability per unit path length, per unit energy, of scattering with energy loss  $E$ , is given by [4]

$$F(E) \equiv \frac{d^2P}{dl dE} = \frac{1}{a_0 E_l} \Xi(E), \tag{11}$$

where  $a_0$  is the Bohr radius,  $E_l$  is the kinetic energy of the incident electron,  $E = \hbar\omega$ , and

$$\Xi(E) = \frac{1}{\pi} \int_0^\infty \frac{e^{-2Qz_0}}{Q} S(Q, \omega) dk_x, \tag{12}$$

with  $Q = \sqrt{k_x^2 + \omega^2/v_l^2}$ .

In the local limit, that is when one assumes that  $\varepsilon_M(k, \omega)$  is independent of  $k$  and sets  $\varepsilon_M(k, \omega) = \varepsilon_M(k = 0, \omega) \equiv \varepsilon_M(\omega)$ , one gets  $1/\tilde{\varepsilon}(Q, \omega) = 1/\varepsilon_M(\omega)$ , and consequently the surface loss function  $S(Q, \omega)$  becomes independent of  $Q$  and given by  $S(\omega) = \text{Im}[(\varepsilon_M(\omega) - 1)/(\varepsilon_M(\omega) + 1)]$ . Now, substituting  $S(\omega)$  into Eqs. (10) and (11) and performing the integration over  $k_x$ , one gets the well-known local result [4],

$$F(E) = \frac{1}{a_0 E_l} \Xi_{loc}(E), \tag{13}$$

where

$$\Xi_{loc}(E) = \frac{1}{\pi} K_0 \left( \frac{2z_0}{v_l/\omega} \right) \text{Im} \left[ \frac{\varepsilon_M(\omega) - 1}{\varepsilon_M(\omega) + 1} \right]. \quad (14)$$

Here  $K_0$  is the modified Bessel function of order zero. In this case  $\Xi(E)$  has a pole at  $\varepsilon_M(\omega) = -1$ , coming from the excitation of surface plasmons, and the argument of  $K_0$  establishes the characteristic length  $v_l/\omega$  of approach for their excitation.

We now present results for electron energy loss of electrons travelling parallel to the interface of a half-space of a system with spherical inclusions described by an effective bulk dielectric response  $\varepsilon_M(k, \omega)$  given by Eq. (1). The bulk dielectric response  $\varepsilon_M(k, \omega)$  is found in the mean-field approximation and we consider only the excluded volume correlation between spheres. Also, for simplicity in the calculation of  $\varepsilon_M(k, \omega)$  we use a single-mode approximation [8], in which all interfacial modes in Eq. (1) are replaced by a single effective mode located at an average position  $n_\sigma$  and with an average strength  $C_\sigma$ . In order to have a more transparent picture of the underlying physics, we consider a half-space of aluminum spheres in vacuum. In this case, one sets  $\varepsilon_2 = 1$  and  $\varepsilon_1(\omega)$  will be given by a Drude dielectric function, that is,

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}, \quad (15)$$

where  $\omega_p$  is the bulk plasma frequency and  $\tau$  is the relaxation time coming from dissipation processes. For aluminum  $\hbar\omega_p$  is taken as 16 eV and  $\tau$  will be taken as a parameter which simply controls the width of the excitation peaks. The surface plasmon energy  $\hbar\omega_s = \hbar\omega_p/\sqrt{2}$  is then equal to 11.3 eV, and the energy of dipolar mode of an isolated sphere  $\hbar\omega_d = \hbar\omega_p/\sqrt{3}$  is 9.2 eV.

In Fig. 1 we show a 3D-plot of  $S(Q, \omega)$  as a function of  $Qa$  and  $\hbar\omega$  for  $f = 0.1$ , sphere radius 25 Å and  $\omega_p\tau = 100$ . We can see that for  $Q = 0$  there is a single pole around 9.4 eV. Then, as  $Qa$  increases, this pole shifts a little to higher energies. There is also another pole located a little below 16 eV, whose strength is zero at  $Q = 0$ , and then starts to grow, while its location shifts a bit to lower energies, as  $Qa$  increases. The strength of the low-energy peak decreases, as  $Qa$  increases, while that of the high-energy peak increases.

One can identify the low-energy peak with the usual surface mode coming from the presence of the interface. For example, in the local limit  $\varepsilon_M(\omega) \equiv \varepsilon_M(k = 0, \omega) = 1 - f/[u - (1 - f)/3]$  becomes the Maxwell Garnett dielectric response [2], which according to Eq. (14) has a pole when  $\varepsilon_M(\omega_0) = -1$ , due to the presence of the interface. For Drude spheres this yields  $\omega_0 = \omega_d \sqrt{1 + f/2}$ , where  $\omega_d = \omega_p/\sqrt{3}$  is the dipolar resonance of an isolated sphere. For aluminum  $\hbar\omega_p = 16$  eV, thus  $\hbar\omega_0 = 9.4$  eV for  $f = 0.1$ . The physical nature of the other peak which appears at finite  $Q$  close to the bulk plasmon energy is more subtle and is due to the fact that  $\varepsilon_\infty(\omega) \equiv \lim_{k \rightarrow \infty} \varepsilon_M(k, \omega) \neq 1$ , because the bulk mode strength  $C_b \rightarrow 1$  in this limit.

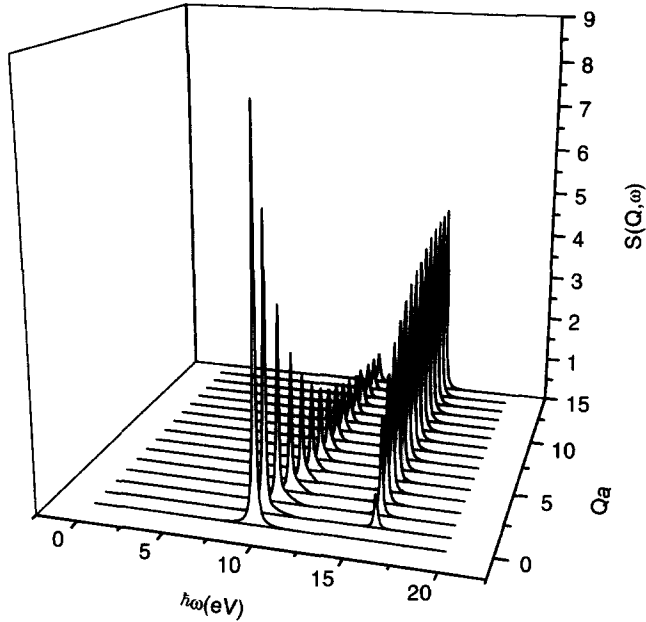


Fig. 1. Surface loss function  $S(Q, \omega)$  as a function of  $Qa$  and  $\hbar\omega$  for aluminum spheres of radius  $25 \text{ \AA}$  in vacuum. The volume fraction of spheres is  $f=0.1$  and  $\omega_p\tau=100$ .

Finally, we substitute the results for  $S(Q, \omega)$ , shown in Fig. 1, into Eq. (12) and perform the  $k_x$  integration to get  $\Xi(E)$ . In Fig. 2 we plot  $\Xi(E)$  as a function of  $E$  for three different values of the impact parameter,  $z_0=0.1, 5,$  and  $10$ . One can clearly see two peaks, which correspond, obviously, to the low- and high-energy peaks of  $S(Q, \omega)$ . Although the strength of both peaks decreases as  $z_0$  increases, it is also clear that the strength of the high-energy peak decreases faster; for  $z_0=10$ , the strength of the high-energy peak is already very small in comparison with that of the low-energy peak.

The question about the physical reality of the high-energy peak in  $\Xi(E)$  still remains open. It is possible that this high-energy peak is an artifact of the SCIB model, which abruptly terminates the system at the surface plane  $z=0$ . It can be shown that for the SCIB model, the sum rule in Eq. (8) has the value 1, corresponding to a constant volume fraction  $f(z)=f$  for  $z < 0$ . This is not physically possible for a half-space containing spheres of finite radii, where  $f(z)$  must be a continuous function of  $z$ , and cannot jump discontinuously from a constant value inside the system to zero outside, assuming that the spheres cannot actually penetrate into the region  $z > 0$ . In the unbounded system assumed for the SCIB model  $f$  is indeed constant, but the  $z=0$  plane will cut through the interiors of the spheres near the surface in an unphysical way. However, it still has not been proven that this is the reason for the appearance of the high-energy peak.

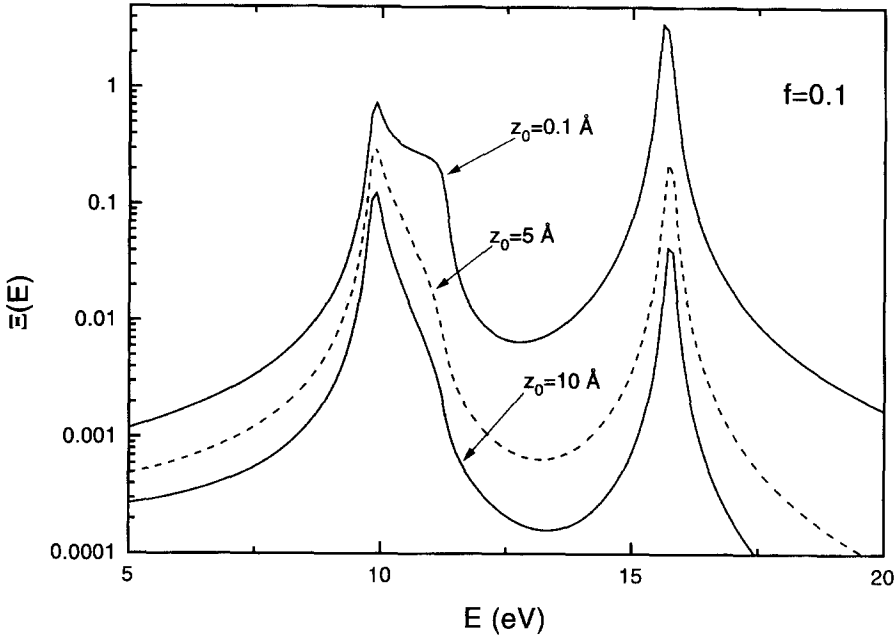


Fig. 2. Energy loss probability  $\Xi(E)$  as a function of  $E$  for 25 Å aluminum spheres,  $f=0.1$  and three different values of the impact parameter  $z_0$ .

### 3.3. Exact formal solution for spheres

In this section we derive an exact solution for the surface response function, in the form of the spectral representation in Eq. (5), of spherical inclusions with a local dielectric function  $\epsilon_1$  contained in a matrix with local dielectric function  $\epsilon_2 = 1$ . The spheres have radii  $a_i$  and the centers are at arbitrary fixed locations  $r_i$ , such that no sphere penetrates into the region  $z > 0$ . This exact solution will be a useful starting point for various approximations, and illustrates nicely how the sum rule in Eq. (8) is satisfied.

We first expand the external potential in Eq. (3) about the sphere whose center is at  $r_i$  in a multipole series

$$V^{ext}(\mathbf{r}) = \sum_{lm} V_{lmi}^e(r')^l Y_{lm}(\theta', \phi'), \quad (16)$$

where  $\mathbf{r}' = \mathbf{r} - \mathbf{r}_i$ . For brevity, the expression for the coefficients  $V_{lmi}^e$  will not be given here. The induced potential acting on sphere  $i$  which arises from the multipole moments  $q_{l'm'j}$  on all other spheres  $j$  can similarly be written in a multipole series

$$V^{ind}(\mathbf{r}) = \sum_{lm} V_{lmi}^1(r')^l Y_{lm}(\theta', \phi'), \quad (17)$$



where the coefficients  $V_{lmi}^1$  are given by

$$V_{lmi}^1 = \sum_{l'm'j} B_{lmi}^{l'm'j} q_{l'm'j} . \tag{18}$$

An expression for the quantities  $B_{lmi}^{l'm'j}$  appears in [2]. In the linear approximation, the multipole moment  $q_{lmi}$  is proportional to the  $lm$  multipole coefficient of the total potential acting on sphere  $i$ :

$$q_{lmi} = - \frac{2l+1}{4\pi} \alpha_{li} (V_{lmi}^e + V_{lmi}^1) , \tag{19}$$

$\alpha_{li}$  being the  $l$ -polarizability of sphere  $i$ . We remove the common phase factor  $e^{iQx_i}$  from the multipole moments by defining  $q_{lmi} = t_{lmi} e^{iQx_i}$ , and solve Eqs. (18) and (19) using the procedure described in Ref. [2]. This is an eigenfunction expansion of the Green function, which appears in the form of a spectral representation. Having solved for the multipole moments on all spheres, we find the induced potential and calculate its two-dimensional Fourier transform using Eq. (6). The result is of the form

$$V^{ind}(Q, z) = - \sum_{lmi} F_{lmi} t_{lmi} e^{-Qz} , \quad z > 0 , \tag{20}$$

from which  $g(Q, \omega)$  is found using Eq. (4).

The surface response function  $g(Q, \omega)$  appears in the form of the spectral representation (5). The mode positions  $n_s$  are eigenvalues of the Hermitian matrix

$$H_{lmi}^{l'm'j} = n_i^2 \delta_{ll'} \delta_{mm'} \delta_{ij} + \frac{1}{4\pi} \sqrt{l! a_i^{2l+1} a_j^{2l'+1}} e^{iQ(x_j - x_i)} B_{lmi}^{l'm'j} , \tag{21}$$

with  $n_i^0 = l/(2l+1)$ , whereas the mode strengths  $d_s$  are given by

$$d_s = \frac{4\pi}{fL^2} \sum_{lmi, l'm'j} i^{m-m'} \beta_{ll'mm'} \sqrt{l! a_i^{2l+1} a_j^{2l'+1}} Q^{l+l'-1} U_{lmi,s} U_{s,l'm'j}^{-1} e^{Q(z_i+z_j)} . \tag{22}$$

Here,  $U_{lmi,s}$  is the unitary matrix which diagonalizes the matrix  $H$  in Eq. (21) and  $\beta_{ll'mm'} = [(2l+1)(2l'+1)(l+m)!(l-m)!(l'+m')!(l'-m')!]^{-1/2}$ .

The sum rule (8) is a convenient test for the validity of the above result. The filling fraction  $f(z)$  that appears in the sum rule is the fraction of the area  $L^2$  that is occupied by the spheres in the plane at the given value of  $z$ . For a single sphere  $i$  with radius  $a_i$  and center at  $z_i$ , one has  $f_i(z) = (\pi/L^2) [a_i^2 - (z - z_i)^2]$  for  $(z_i - a_i) < z < (z_i + a_i)$  and  $f_i(z) = 0$  for  $z$  outside this range. The filling fraction for all spheres is  $f(z) = \sum_i f_i(z)$ ; inserting this function into Eq. (8), and doing the integration over  $z$ , one finds

$$\sum_s d_s = \frac{2\pi Q}{fL^2} \sum_i I(\lambda_i) e^{2Qz_i} , \tag{23}$$

where

$$I(\lambda_i) = 4a_i^3 \left( \frac{\cosh \lambda_i}{\lambda_i^2} - \frac{\sinh \lambda_i}{\lambda_i^3} \right) , \tag{24}$$

with  $\lambda_i = 2Qa_i$ . On the other hand, one can calculate  $\sum_s d_s$  from Eq. (22) using the completeness relation for the  $U$  matrices, and show that the result is the same as Eq. (23).

Finally, it is useful to examine the relation between the density of sphere centers  $\rho(z)$  and the filling fraction  $f(z)$ , for a system where all spheres have the same radius  $a$ . For an unbounded medium, with  $\rho$  and  $f$  constant, one has  $f = (4\pi a^3/3)\rho$ . However, for the system with a surface at  $z = 0$ ,

$$f(z) = \pi \int_{z-a}^{z+a} \rho(z') [a^2 - (z' - z)^2] dz'. \quad (25)$$

Here, one must have  $\rho(z') = 0$  for  $-a < z' < 0$  since no sphere can penetrate into the region  $z > 0$ . Also,  $f(z)$  must fall continuously to 0 at  $z = 0$  for any reasonable distribution  $\rho(z)$ , as we pointed out in Section 3.2.

The formal theory developed above may serve as a reliable framework for the introduction of different kinds of approximations or the performance of numerical calculations. For example, the mean-field approximation is obtained by replacing  $H_{lmi}^{l'm'j}$  in Eq. (21) by its configurational average. However, this is not a simple calculation, since performing this configurational average requires detailed statistical information about the pair correlations between spheres near the nominal surface of the system.

#### 3.4. Impedance transfer method using $\varepsilon(z)$

An approximate solution for the surface response of the random system of spheres in a half-space can be found by keeping only dipole ( $l = 1$ ) terms and neglecting correlations between spheres. Thus, all effects of the finite size of the spheres and correlations between spheres on the  $Q$ -dependence of  $g(Q, \omega)$  are disregarded, leaving only the effects of the  $z$  dependence of the filling fraction  $f(z)$ . It can be shown that when these approximations are made, the exact theory of the previous section reduces to a problem in which the system of spheres is replaced by a continuous effective medium with a  $z$ -dependent dielectric function  $\varepsilon(z)$  given by the expression for the Maxwell–Garnett effective dielectric function with the constant filling fraction replaced by the  $z$ -dependent filling fraction  $f(z)$ ,

$$\frac{\varepsilon(z) - 1}{\varepsilon(z) + 2} = f(z) \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}. \quad (26)$$

This continuous medium problem is most easily solved using an impedance transfer method. One imagines breaking the medium into many thin layers and defines an impedance  $W(z) = iD_z(z)/E_x(z)$ , with  $D_z(z) = \varepsilon(z)E_z(z)$ . Using the fact that the potential in each layer (in which  $\varepsilon(z) \approx \text{const.}$ ) is of the form  $V(z) = [C_1 \exp(Qz) + C_2 \exp(-Qz)] \exp(iQx)$  one can derive an impedance transfer equation which relates

the values of  $W(z)$  at the two sides of the layer,  $z = z_1$  and  $z = z_2$ ,

$$W(z_2) = \varepsilon(\bar{z}) \frac{[\varepsilon(\bar{z}) + W(z_1)]e^{2Q(z_2-z_1)} - [\varepsilon(\bar{z}) - W(z_1)]}{[\varepsilon(\bar{z}) + W(z_1)]e^{2Q(z_2-z_1)} + [\varepsilon(\bar{z}) - W(z_1)]}, \quad (27)$$

with  $\bar{z} = (z_1 + z_2)/2$ . Sufficiently far into the material that  $f(z) = f = \text{const.}$  for  $z \leq z_0$ , the starting value of  $W$  is  $W(z_0) = \varepsilon(z_0)$ . Then, since  $W(z)$  is continuous at the interfaces between layers, Eq. (27) is used iteratively to find  $W$  at the each interface, starting from the known value at  $z = z_0$  and ending at the surface, where its final value is  $W(0)$ . The surface response function is then given by

$$g(Q, \omega) = \frac{W(0) - 1}{W(0) + 1}. \quad (28)$$

For a system with a large number of spheres in the area  $L^2$ , the surface modes are numerous and closely spaced, so the discrete modes with strengths  $d_s$  can be replaced by a continuous spectral function  $D(n)$ , and the spectral representation (5) becomes

$$g(Q, \omega) = -\frac{f}{2} \int \frac{D(n)}{u - n} dn. \quad (29)$$

This is also the appropriate form for the spectral representation that is found using the impedance transfer method. The spectral function  $D(n)$  can be found by calculating  $g(Q, \omega)$  from Eq. (28) not as a function of  $\varepsilon_1(\omega)$ , but as a function of the spectral variable  $u = n' + i\delta$ . Then Eq. (29) gives  $D(n') = [2/(\pi f)] \text{Im} g(Q, u)$  in the limit as  $\delta \rightarrow 0$ .

We have used this procedure to calculate  $D(n)$  for a simple filling fraction profile  $f(z)$  that is derived by assuming that the density of spheres  $\rho(z) = \rho = \text{const.}$  for  $z < -a$  and  $\rho(z) = 0$  for  $z > -a$ . Eq. (25) gives  $f(z) = \frac{3}{4}f[(z/a)^2 + (z/a)^3/3]$  for  $0 > z > -2a$ , and  $f(z) = f$  for  $z < -2a$ , where  $f = \frac{4}{3}\pi a^3 \rho$ . This filling fraction profile  $f(z)$  increases smoothly from the value 0 at the surface ( $z = 0$ ) to the value 0.4 at  $z = -2a$ . Fig. 3 shows the spectral function  $D(n)$  for the selected values  $f = 0.4$  and  $Qa = 0.05, 0.2, 1.0$ , and 5.0. The behavior of  $D(n)$  can be understood by noting that  $D(n)$  for a constant value of  $f$  would have a single sharp peak located at  $n_s = \frac{1}{3}(1 + \frac{1}{2}f)$ , i.e.,  $n_s = \frac{1}{3}$  for  $f = 0$  and  $n_s = 0.4$  for  $f = 0.4$ . For the largest value of  $Qa$  the external potential samples only the outermost region where  $f(z) \sim 0$ , and  $D(n)$  is indeed quite sharply peaked at  $n \sim \frac{1}{3}$ . For  $Qa = 0.05$ , the external potential samples deeply into the system, where  $f = 0.4$ , and  $D(n)$  is quite sharply peaked at the corresponding value  $n = 0.4$ . For intermediate values of  $Qa$  the entire surface profile  $f(z)$  is sampled, so the spectral function is much broader.

It can be shown that the spectral function found using the impedance transfer method satisfies two sum rules: a zeroth moment sum rule

$$\int D(n) dn = \frac{2Q}{f} \int_{-\infty}^0 f(z) e^{2Qz} dz, \quad (30)$$

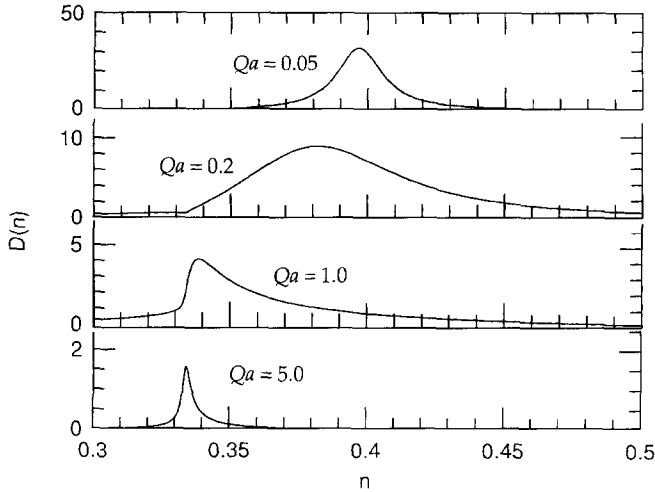


Fig. 3. Spectral function  $D(n)$  as a function of  $n$  for  $Qa=0.05, 0.2, 1.0,$  and  $5.0$ , with a filling fraction profile  $f(z)$  discussed in the text.

which is the same as the exact sum rule (8), and a first moment sum rule

$$\int n D(n) dn = \frac{Q}{3f} \int_{-\infty}^0 f(z) [2 + f(z)] e^{2Qz} dz. \quad (31)$$

The sum rule (31) is not exact, since it would change if the effects of finite sphere sizes and correlations between spheres were included.

#### 4. Infinite system with arbitrary geometry

In this section we consider an unbounded system consisting of a mixture of two components with local dielectric functions  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$ , and arbitrary geometry. Calculations of electron energy loss by objects of various shapes have been performed by Ouyang and Isaacson [9,10], using a method similar to ours, but those papers emphasized scanning transmission microscopy, where the electrons are imagined to move classically with constant velocity on a well-defined path. In our theory we assume that the electrons travel randomly through the system, which appears homogeneous on some length scale, and can therefore be described by an effective dielectric function  $\epsilon_M(k, \omega)$ . Just as for the system of spheres,  $\epsilon_M(k, \omega)$  can be written as a spectral representation of the form (1), with mode strengths that satisfy the sum rule (2).

### 4.1. Separation of bulk and surface modes

The method which we shall present allows us to find the bulk mode strength  $C_b$  independently of the surface modes, and then, having solved the bulk mode problem, to find the surface mode positions  $n_s$  and strengths  $C_s$ . For the sake of simplicity, we will write the dielectric function  $\epsilon_1(\omega)$  as  $\epsilon$  and take  $\epsilon_2(\omega) = 1$ . The external potential is  $V^{ext}(\mathbf{r}) = V_0 e^{ikz}$  and associated with this, there is an external charge density  $\rho^{ext}(\mathbf{r}) = \rho_0 e^{ikz}$ , with  $\rho_0 = k^2 V_0 / 4\pi$ . The total potential  $V(\mathbf{r})$  is the sum of the external and induced potentials,  $V(\mathbf{r}) = V^{ext}(\mathbf{r}) + V^{ind}(\mathbf{r})$ , where  $V^{ind}(\mathbf{r})$  can be expressed in terms of its charge sources, a volume charge  $\rho^{ind}(\mathbf{r})$  inside medium 1 and a surface charge density  $\sigma^{ind}(\mathbf{r})$  on the interface of the two media:

$$V^{ind}(\mathbf{r}) = \int_1 \frac{\rho^{ind}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} dv' + \int \frac{\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} dS', \tag{32}$$

where the subscript 1 signifies that the volume integral is to be taken over region 1, which contains the dielectric medium 1, and the surface integral is over the interface between the two media. Using the identity  $1/(u - 1) = (1/\epsilon - 1)$ , we can write  $\rho^{ind}(\mathbf{r}) = \rho^{ext}(\mathbf{r})\Phi_1(\mathbf{r})/(u - 1)$ , where  $\Phi_1(\mathbf{r}) = 1$  (0) inside (outside) medium 1. We also have  $\sigma(\mathbf{r}) = (1/4\pi)(\epsilon - 1)\mathbf{E}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r})$ , where  $\mathbf{E}(\mathbf{r}) = -\nabla V(\mathbf{r})$  is to be calculated just inside the surface of medium 1 and  $\mathbf{n}(\mathbf{r})$  is a unit vector pointing outward from the surface of medium 1.

The key step in separating the bulk mode, which appears as the term containing  $1/(u - 1)$  in the spectral representation (1), is to write the surface charge density as the sum of two terms,  $\sigma(\mathbf{r}) = \sigma^0(\mathbf{r})/(u - 1) + \sigma^1(\mathbf{r})$ . Here  $\sigma^0(\mathbf{r})$ , the surface charge density associated with the bulk mode, is independent of  $u$ , and  $\sigma^1(\mathbf{r})$ , which can depend on  $u$ , is associated with the surface modes. After doing some algebra we find separate equations for the bulk mode,

$$\sigma^0(\mathbf{r}) = \frac{1}{4\pi} \left[ \int_1 \rho^{ext}(\mathbf{r}') \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \mathbf{n}(\mathbf{r}) dv' + \int \sigma^0(\mathbf{r}') \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \mathbf{n}(\mathbf{r}) dS' \right] \tag{33}$$

and the surface modes,

$$u \sigma^1(\mathbf{r}) - \frac{1}{4\pi} \int \sigma^1(\mathbf{r}') \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \mathbf{n}(\mathbf{r}) dS' = \frac{1}{4\pi} \mathbf{E}^{ext}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) + \sigma^0(\mathbf{r}). \tag{34}$$

If medium 1 consists of isolated inclusions, the bulk mode equation (33) is equivalent to an electrostatics problem in which each inclusion is a vacuum-filled hole containing the external charge density  $\rho^{ext}(\mathbf{r})$ , cut into a perfectly conducting matrix 2. The surface charge density  $\sigma^0(\mathbf{r})$  is exactly what is needed to make the surface of each hole an equipotential ( $V = 0$ ). Solving the equivalent problem, one would write  $V(\mathbf{r}) = V^{ext}(\mathbf{r}) + V^{ind}(\mathbf{r})$ , where  $V^{ext}(\mathbf{r}) = V_0 e^{ikz}$ , and find the potential  $V^{ind}(\mathbf{r})$  (satisfying Laplace's equation) which makes  $V(\mathbf{r}) = 0$  at the surface. Thus, the bulk mode excitations are

confined completely to the interior of the medium 1 inclusions, so the bulk mode strength depends on the sizes and shapes of the inclusions but not on their positions.

The surface mode equation (34) can be solved for  $\sigma^1(\mathbf{r})$  by converting the  $dS'$  surface integral into a sum over discrete surface areas  $\Delta S(\mathbf{r}_j)$ . The solution can be written in terms of a Green function containing denominators  $u - n_s$ , where the mode positions  $n_s$  are related to eigenvalues of the interaction matrix  $R_{ij} \equiv \nabla(1/|\mathbf{r}_i - \mathbf{r}_j|) \cdot \mathbf{n}(\mathbf{r}_i) \Delta S(\mathbf{r}_j)$ , and the numerators are related to eigenvectors of this matrix. We can gain some physical insight into why Eq. (34) involves only surface modes by thinking of the two terms on the right-hand side of the equation as forcing terms for the surface charge density. The source of the first term, the normal component of  $\mathbf{E}^{ext}$ , is the external charge density  $\rho^{ext}(\mathbf{r}) = \rho_0 e^{ikz}$ , which is present in both media. The term  $\sigma^0(\mathbf{r})$  on the right-hand side cancels the part of the first term that is produced by the external charge inside medium 1, so the effective driving charge on the right-hand side is the external charge that resides outside medium 1, and such a charge cannot excite the bulk mode in this medium.

The effective dielectric function of the system is calculated from  $1/\varepsilon_M(k, \omega) = 1 + \rho^{ind}(k)/\rho_0$ , where  $\rho^{ind}(k)$  is found using an inverse Fourier transform of the bulk and surface charge densities,  $\rho^{ind}(k) = v^{-1}[\int \rho^{ind}(\mathbf{r}) \exp(-ikz) dv + \int \sigma(\mathbf{r}) \exp(-ikz) dS]$ ,  $v$  being a large periodic volume. The result is

$$\frac{1}{\varepsilon_M(k, \omega)} = 1 + \left[ f + \frac{1}{\rho_0 v} \int e^{-ikz} \sigma^0(\mathbf{r}) dS \right] \frac{1}{u-1} + \frac{1}{\rho_0 v} \int e^{-ikz} \sigma^1(\mathbf{r}) dS. \quad (35)$$

This is in the desired form of a spectral representation; the second term is bulk mode contribution  $f C_b/(u-1)$  and the third term, the surface mode contribution  $f \sum_s C_s/(u-n_s)$ .

We illustrate an application of this theory by calculating the bulk mode strength  $C_b$  for a rectangular parallelepiped as a function of  $kc$ , where the wave vector  $\mathbf{k}$  is in the  $z$  direction and the parallelepiped has dimensions  $a$ ,  $b$ , and  $c$  in the  $x$ ,  $y$ , and  $z$  directions, respectively. It is easiest to use the point of view that the potential must satisfy Poisson's equation with the charge density  $\rho^{ext}(\mathbf{r}) = \rho_0 e^{ikz}$  inside the parallelepiped, and with the boundary condition  $V=0$  on the surface. To solve this electrostatics problem it is convenient to use a Fourier sine transform method described by Press et al. [11].

The results of the calculation are shown in Fig. 4, where the bulk mode strength is plotted as a function of  $kc$  for five different shapes, which are specified by three integers proportional to the lengths ( $abc$ ). The curve marked  $(\infty \infty 1)$  is an infinite slab of thickness  $c$ . The basic trend of these curves is that  $C_b$  is an increasing function of  $kc$  that rises more slowly as the shape becomes more elongated in the field ( $z$ ) direction. At  $k=0$ ,  $C_b=0$  for any isolated inclusion because of complete cancellation of the two terms inside the square brackets in Eq. (35): the quantity  $f$ , which is the Fourier transform of the bulk induced charge inside the inclusion, cancels the second term, which is the Fourier transform of the induced surface charge. As  $k$  increases, this

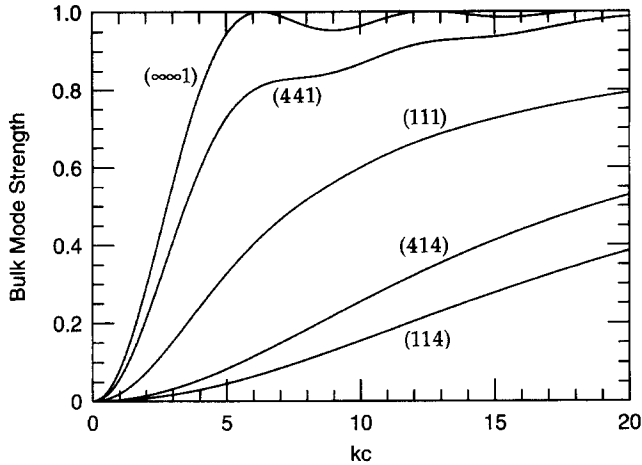


Fig. 4. Bulk mode strength  $C_b$  as a function of  $kc$  for rectangular parallelepipeds. The three integers that specify the shape of a parallelepiped are proportional to  $a$ ,  $b$ , and  $c$ , the lengths of the sides in the  $x$ ,  $y$ , and  $z$  directions, respectively.

cancellation is no longer complete, but a partial cancellation is more easily attained for an elongated inclusion because of the induced charge on the side surfaces of the inclusion.

## 5. Conclusion

We have described several approaches to the theory of electron energy-loss spectroscopy of inhomogeneous systems, both unbounded in three dimensions and confined to a half-space. The energy-loss spectrum can be expressed in terms of a bulk or surface response function, and we have been able to write these response functions in the form of spectral representations. What is still missing is a correct inclusion of a configurational average, which would yield a relation between the mode positions and strengths and the spatial correlations in the system. These problems will be addressed in future work.

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