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Collective excitations in an infinite set of aligned spheres

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Abstract

We present here electron energy loss spectra (EELS) calculations for an infinite set of aligned dielectric spheres as a first approximation to calculations in a more complex periodic array with small computer cost. The boundary charge method is analytically developed for such a system with use of local dielectric theory. A convenient distribution of surface charge densities at the spherical interfaces, selfconsistently interacting with each other as well as with the external field created by the incoming electron, can provide a solution of the surface collective modes. Energy loss spectra in the valence range (a few eV) are obtained for trajectories parallel and perpendicular to the axis of the aligned spheres and the nature of the excitations is studied by analysing the charge density distribution induced at the spheres, © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Scanning transmission electron microscopy (STEM) has proved to be an adequate tool to study surface collective excitations in many complex systems. Surface collective modes in simple structures as the planar interface [1,2], the sphere [3,4] or the cylinder [5,6] can be analytically described, but as the complexity of a structure increases [7–12] and the coupling between modes plays an important role, an increasingly elaborated analytical basis together with numerical computation is needed. In the non-relativistic approach, a convenient distribution of charges all along the interfaces self-consistently interacting with each other can provide a solution of the collective modes. Here we show the application of the method to calculate surface modes and energy losses by the scattered electrons near a set of aligned spheres. The method developed for this simple system can be easily generalized to more complex ordered inhomogeneous systems. On the other hand, the study of periodic dielectric arrays has been a subject of increasing interest in the last years due to its applications connected with photonic bands. Calculations of energy losses in this type of structures have been performed by Pendry and Martín-Moreno [13] by calculating the response of the complex medium to the external field. Vagov et al. [14] also studied the optical response of arrays of spheres with use of hypercomplex variables. A promising basis for calculation of energy losses suffered by the STEM

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electrons in this type of complex systems is the boundary charge method, also known as boundary element method, whereby a distribution of surface or interface charges is generated, interacting self-consistently with itself as well as with any external field such as that due to a passing electron. This approach has been recently employed to determine normal mode frequencies of dielectric excitations by Fuchs [15,16] for a cube and by Ouyang and Isaacson [17] for bodies of arbitrary shape. In this paper we apply the method to study analytically the collective excitations produced by the scanning electron beam in a one-dimensional set of aligned dielectric spheres for different electron trajectories. Atomic units (a.u., $e=m=\hbar=1$) will be used from now on, unless otherwise specified. The Fourier transform is defined following the convention in Ref. [18].

2. Basic theory and general formula

It is possible to solve Poisson's equation in terms of a convenient distribution of surface charge density $\sigma(\boldsymbol{s}, \omega)$ at the interfaces separating two different media. By writing the potentials in terms of these surface charge distribution one gets the following self-consistent integral equation:

$$\Lambda(\omega)\sigma(\boldsymbol{s}, \omega)=\boldsymbol{n}_s \cdot \nabla \int \mathrm{d}\boldsymbol{r}' \frac{\rho^{\mathrm{ext}}(\boldsymbol{r}', \omega)}{\epsilon(\boldsymbol{r}', \omega)|\boldsymbol{r}-\boldsymbol{r}'|} + \boldsymbol{n}_s \cdot \nabla \int \mathrm{d}\boldsymbol{s}' \frac{\sigma(\boldsymbol{s}', \omega)}{|\boldsymbol{s}-\boldsymbol{s}'|}, \quad (1)$$

where

$$\Lambda(\omega)=2\pi \frac{\epsilon_2(\omega)+\epsilon_1(\omega)}{\epsilon_2(\omega)-\epsilon_1(\omega)} \quad (2)$$

and $\rho^{\mathrm{ext}}(\boldsymbol{r}', \omega)$ is the external charge density, which corresponds to the incoming electron. $\boldsymbol{s}$ denotes a vector which runs over all the interfaces separating two different media, and $\boldsymbol{n}_{\mathrm{s}}$ is the unitary vector perpendicular to the interface at each point. Once this integral equation is solved one can write the induced potential $\phi^{\mathrm{ind}}(\boldsymbol{r}, \omega)$ in terms of the surface charge density, and hence, the energy loss probability which is the function that can be compared with the experimental spectra (EELS) obtained by electron microscopy. The probability of losing energy $\hbar\omega$ is obtained by transforming the potential acting at the incoming electron position as

$$P(\omega)=\frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}t\ \mathrm{Im}[-\phi^{\mathrm{ind}}(\boldsymbol{r}, \omega)|_{r=vt}\ \mathrm{e}^{-\mathrm{i}\omega t}]. \quad (3)$$

In the particular case of an array and due to the spherical shape of the particles, we can express the surface charge density $\sigma(\boldsymbol{s}, \omega)$ in spherical coordinates $(\boldsymbol{r}, \theta, \varphi)$ with the polar axis z parallel to the direction of the array. In terms of associated Legendre functions and exponential functions referred to the origin of each different sphere k, we can express

$$\sigma_k(s, \omega)=\sum_{l,m} \sigma_{lm}^k(\omega) P_{lm}(\mu_k)\ \mathrm{e}^{\mathrm{i}m\varphi_k} \quad (4)$$

where $k=-\infty,\ldots,-2,-1,0,1,2,\ldots\infty$ labels the spheres position and $\mu_k=\cos(\theta_k)$. Positive and negative values correspond to positions at different sides of the central sphere labelled $k=0$. a the radius of the spheres and d the distance between the centres of two neighbouring spheres. We define now the parameter $\alpha=a/d$ which is related to the filling fraction as $f=(4\pi/3)\alpha^3$. After some algebra it is possible to transform the integral Eq. (1) into a set of linear algebraic equations for each m value where it is possible to find the multipolar terms l, m for each sphere k

$$\left(\Lambda-\frac{2\pi}{2l+1}\right)\sigma_{lm}^k=\int \mathrm{d}^3\boldsymbol{r}' \frac{\rho^{\mathrm{ext}}(\boldsymbol{r}'\omega)}{\epsilon(\omega)}\, l a^{l-1}\, \frac{(l-m)!}{(l+m)!} \times \frac{P_{lm}\left[\dfrac{z'-kd}{\sqrt{(kd-z')^2+x'^2}}\right]}{\sqrt{(kd-z')^2+x'^2}^{\,l+1}}\, \mathrm{e}^{-\mathrm{i}m\varphi'} + \sum_{\substack{n-k=-\infty,\\ n-k\neq 0}}^{\infty} (2l+1)\frac{(l-m)!}{(l+m)!} \times \sum_j \frac{2\pi}{2j+1}\, \alpha^{j+2} \times [(j+1)I_{lj(n-k)}^m - Z_{lj(n-k)}^m]\sigma_{jm}^n \quad (5)$$

where the ω dependence of the coefficients σ^k_{lm} is assumed. $I^m_{lj(n-k)}$ and $Z^m_{lj(n-k)}$ are geometrical factors which couple the multipolar term in sphere n with the l multipolar term in sphere k. They are defined as

$$I^m_{lj(n-k)} = \int_{-1}^{1} \frac{d\mu[\alpha-(n-k)\mu]}{[\alpha^2+(n-k)^2-2(n-k)\alpha\mu]^{(j+3)/2}} \times P_{jm}\left[\frac{\mu-\alpha}{\sqrt{\alpha^2+n-k)^2-2(n-k)\alpha\mu}}\right] P_{lm}(\mu) \quad (6)$$

and

$$Z^m_{lj(n-k)} = \int_{-1}^{1} \frac{d\mu(n-k)(1-\mu^2)}{[\alpha^2+(n-k)^2-2(n-k)\alpha\mu]^{(j+4)/2}} \times P'_{jm}\left[\frac{\mu-\alpha}{\sqrt{\alpha^2+(n-k)^2-2(n-k)\alpha\mu}}\right] \times P_{lm}(\mu). \quad (7)$$

Eq. (5) allows us to find any multipolar component of the surface charge density at every sphere by solving the set of linear algebraic equations. The interaction among the spheres is given by the second term in the right side of Eq. (5) through the integrals shown in Eqs. (6) and (7) which are strongly dependent on the filling parameter α. The modes of the system will be the ω values which allow a non-trivial solution of the system in Eq. (5). If one neglects the interaction term the modes of the isolated sphere which are given by $\Lambda-2\pi/(2l+1)=0$ are recovered and from here the induced potential self-consistently acting with the external field produced by the incoming electron. In the same way, the modes of this infinite number of interacting spheres can be obtained when the interaction term in Eq. (5) is taken into account. In general, Eq. (5) involves an infinite number of equations, but due to the decay of the ω component of the interacting potential, it is expected that only the coupling of close neighbours is relevant for the induced potential. This point will be discussed in more detail in the next section in terms of the spectra of losses.

3. Parallel trajectory

We now solve the equation presented in the previous section for the particular case of set of metallic spheres when the electron beam incides parallel to the axis of the aligned spheres considered to be z. We assume that the medium surrounding the spheres is vacuum, i.e. $\epsilon_1(\omega)=1$ and the dielectric spheres will be characterized by the frequency-dependent Drude dielectric function

$$\epsilon_2(\omega)=1-\frac{\omega_p^2}{\omega(\omega+i\gamma)}. \quad (8)$$

We use here $\omega_p=15$ eV and $\gamma=0.5$ eV, typical values for aluminium, but the procedure is general for any couple of frequency-dependent dielectric functions used to describe the response of both media. In the case of an electron beam travelling parallel to the axis of the spheres array the external charge density is $\rho^{ext}(\boldsymbol{r}', \omega)=-1/v\delta(\rho'-\boldsymbol{b})e^{i\omega z'/v}$ where ρ is the coordinate perpendicular to the electron trajectory, $\boldsymbol{b}$ is the impact parameter and v is the electron velocity. In this particular case it makes sense to calculate the energy losses deposited at one sphere. Since any sphere is equivalent in terms of the energy loss per sphere, it arises from the equations that the k label in the surface charge density can be removed with no loss of generality. If one introduces the external charge density expression in Eq. (5) the energy loss probability per sphere is found to be

$$P(\omega)=\frac{16}{v^2}\sum_{l,m>0}(2-\delta_{m,0})\,\mathrm{Im}[A_{lm}(\omega)] \times\frac{a}{2l+1}\frac{(\omega a/v)^l}{\sqrt{(l+m)!}\sqrt{(l-m)!}}K_m^2\left(\frac{\omega}{v}b\right) \quad (9)$$

where $K_m(x)$ is the modified Bessel function of mth order. This expression is formally similar to the one found by Ferrell and Echenique [3] for the isolated sphere. The difference is due to the interaction among spheres via the coefficient $A_{lm}(\omega)$ which has now to fulfill this system of linear

algebraic equations

$$\left(\Lambda-\frac{2\pi}{2l+1}\right)A_{lm}=\frac{l}{\epsilon(\omega)\sqrt{(l+m)!}\sqrt{(l-m)!}}\left(\frac{\omega a}{\upsilon}\right)^{l}+(2l+1)\sum_{j}\frac{2\pi}{2j+1}\alpha^{j+2}\times\sum_{\substack{n=-\infty,\\ n\neq 0}}^{\infty}\times[(j+1)I^{m}_{ljn}-Z^{m}_{ljn}]\mathrm{e}^{(\omega nd/\upsilon)\mathrm{i}}A_{jm} \tag{10}$$

where A_{lm} is directly related with σ_{lm} as

$$\sigma_{lm}=-A_{lm}\frac{2(i)^{l-m}}{\upsilon}K_{m}\left(\frac{\omega b}{\upsilon}\right). \tag{11}$$

In Fig. 1 we show the energy loss probability $P(\omega)$ for an electron travelling parallel to a set of 2 nm Al spheres with different filling fractions. In all the calculations the linear set of algebraic equations has been truncated at $l_{\max}=20$ and a sufficient number of spheres, depending on the filling fraction, was considered in order to get convergence in the spectra.

For a low filling fraction ($\alpha<0.4$), good convergence in spectra is achieved when taking into account 10 neighbouring spheres (five each side).

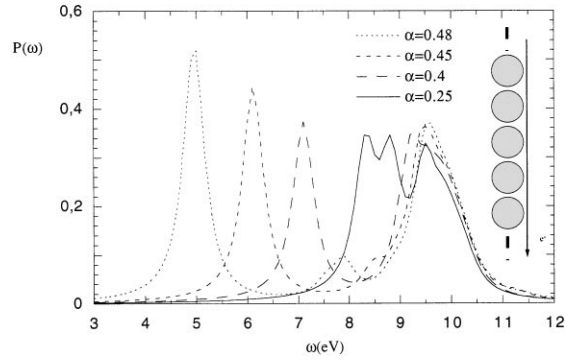

Fig. 1. Loss probability per sphere for 100 keV electrons moving parallel to the axis of an infinite system of spheres. The spheres are surrounded by vacuum and assumed to be made of Al, described via the Drude dielectric function with $\omega_{\mathrm{p}}=15$ eV and damping $\gamma=0.5$ eV. The radii of the spheres are all equal to 2 nm. The electron passes at a distance of 1 nm from the spheres surfaces. Different filling parameters $\alpha=a/d$ have been considered as shown in the labels of the figure. The inset represent the geometry of the system.

For a high filling fraction ($\alpha=0.48$) more spheres are needed, since the coupling among spheres is stronger but, even in this case, the spectra did not change after placing around 20 spheres. In this way, one can consider this system equivalent to a real infinite set of spheres since the presence of the far neighbouring spheres is negligible in terms of the coupled interaction. For this trajectory two main peaks can be clearly observed. For a filling fraction corresponding to $\alpha=0.48$, i.e. 0.16 nm between spheres, the low energy peak is excited at 5 eV. In a two sphere system, the low energy peak for the same filling parameter ($\alpha=0.48$) appears at 6.2 eV [11], therefore, we can conclude that this peak is shifted down as more spheres are introduced in the array. This effect was also reported by Vagov et al. [14] in NaCl arrays. The value of this excitation is shifted up as the filling fraction decreases. In the low filling fraction case ($\alpha=0.25$), the interaction between spheres is weaker and the limit of the dipolar excitation for an isolated sphere is almost recovered (8.6 eV). The high energy peak changes little at 9.5 eV. The surface charge density corresponding to the low energy peaks shows basically a dipolar pattern with the dipole oriented in the direction parallel to the electron trajectory. This peak is a characteristic of the coupled system which allows such an excitation due to the proximity of the neighbouring spheres which help to induce the system of dipoles parallel to the trajectory. The charge is acumulated at both hemispheres with contrary sign in that direction. The low energy of this excitation is due to the high filling fraction which facilitates the simultaneous excitation of many coupled dipoles in the spheres induced by the others. In the limit of very low filling fraction the dipolar excitation of an isolated sphere at 8.6 eV recovered with the dipole oriented in a direction normal to the electron trajectory. On the other hand, the surface charge density associated with the high energy peak at 9.5 eV reveals that many different multipolar terms l and m contribute to this collective excitation. This case is analogous to the high energy peak excited in a isolated sphere [3] but here the excitation of multipolar terms takes also into account the coupling with the rest of spheres.

4. Perpendicular trajectory

For the case of a trajectory perpendicular to the axis of the spheres the position of the spheres in the array plays an important role and the label k for the surface charge density must be maintained. For such a case, the linear set of algebraic equations takes into account more coefficients corresponding to the different positions of the spheres. The external charge density in the perpendicular trajectory case is $\rho^{\mathrm{ext}}(\boldsymbol{r}', \omega) = -1/v\delta(x'-x'_0)\,\delta(z'-z'_0)\,\mathrm{e}^{\mathrm{i}\omega y'/v}$ being x'_0 *and* y'_0 the coordinates of the impact parameter. In Fig. 2 we plot the energy loss probability $P(\omega)$ for a trajectory as shown in the inset for a filling parameter $\alpha = 0.45$. We suppose a different number of neighbouring spheres placed at each side surrounding the sphere in the centre in order to study how many neighbours must be considered in the sphere–sphere interaction. When one neighbouring sphere at each side is considered (dotted line) two main peaks are excited at 7.8 and 9.2 eV. The low energy peak is due to a dipolar-like excitation but the charge is now excited in the direction perpendicular to the axis of the spheres. The high energy peak corresponds to higher multipole orders. When three neighbouring spheres are placed at each side of the sphere in the centre (dashed line) the 7.8 eV excitation changes slightly in weight. If we continue placing more spheres (solid line) the peak is not affected. The high energy peak does not change even with a small number of neighbouring spheres. The only peaks which are affected after placing 5 spheres at each side (solid line) are the very low energy peaks which have a tendency to flatten as we approach to the infinite set. The change in this low energy peaks is logical since the field of this excitations decays like $\mathrm{e}^{-\omega x/v}$ with x distance and, therefore, the number of affected spheres increases as ω decreases. From Fig. 2 one can conclude that a couple of neighbouring spheres is enough to find the main features of the spectra at most values of ω but one should consider more neighbours for the very low energy range in order to get the accurate spectrum.

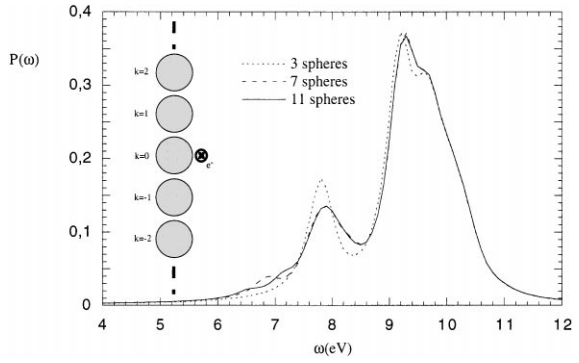

Fig. 2. Loss probability for a 100 keV electron travelling perpendicularly to a set of spheres as depicted in the inset. The total number of spheres considered is shown in the centre.

5. Conclusions

The boundary charge method has been applied to the calculation of low energy losses of electrons passing near a one-dimensional set of aligned spheres. The expansion in the basis of spherical harmonics together with use of this method has allowed us to perform calculations in a complex system with a very reasonable computer time. In that way, this method offers the possibility of calculating more complex structures as periodic ordered systems in two or three dimensions.

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