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Excitation of surface plasmons in nanotubes

S. Segui · J. L. Gervasoni · N. R. Arista

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Abstract In this work, we describe the excitation of plasmons in nano-systems of cylindrical symmetry when charged particles impinge on them. In particular, we calculate the average number of plasmons excited by electrons in hollow, metallic tubules, using a Drude model to describe the dielectric function of the material. Based on previous results, which show the equivalence between quantum and classical descriptions of the phenomenon, we are able to evaluate in a simple manner the integrals along penetrating trajectories, perpendicular to the cylinder axis. We study the influence of various parameters on the excitation of the different modes available for such geometry, including the variation of the inner radius of the tube, and the impact parameter of the electron beam. We obtain similarities and differences with the already studied cases of solid wires, and hollow capillaries.

Introduction

One of the most relevant processes in the interaction of charged particles with solid samples of nanoscopic dimensions, is the excitation of collective oscillations of the electron gas, or *plasmons* [1, 2]. These oscillations are usually considered to take place both at the surface and in the bulk of the material, and each of them have definite modes and characteristic frequencies. For macroscopic systems, with planar surfaces or interfaces, the contribution of surface modes can be neglected compared with bulk excitations, but decreasing the thickness of the sample increases the importance of the surface excitations. Hence, the particular interest for nanosystems resides in the fact that the surface plasmons may dominate the collective response of the system to an external excitation. Moreover, surface excitations are strongly dependent on the geometry and dimensions of the sample, and may give valuable information about it.

The excitation of plasmons plays a central role in various spectroscopic techniques applied to the study of planar surfaces, thin foils, and small solid samples, such as Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), and Reflected Electron Energy Loss Spectroscopy (REELS) [2–6]. Also, high spatial resolution spectroscopies associated to transmission electron microscopes, such as Electron Energy Loss Spectroscopy (EELS) [7], are increasingly used to study local properties of isolated nanostructures. The refinement of these techniques together with the requirements in the characterization of the novel structures are the main motivations to develop adequate formalisms to describe the excitation of plasmons in such systems.

Most of the recent studies of electron spectroscopy in nanosystems are based on classical descriptions of the medium, dealing in particular with semiclassical dielectric models [8, 9]. Also, hydrodinamical models have been proposed to study particularly the excitation of plasmons in Carbon nanotubes [10, 11]. Alternatively, in previous works, we have studied with great detail the relation

S. Segui and J. L. Gervasoni are members of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) of Argentina.

S. Segui · J. L. Gervasoni · N. R. Arista
Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, 8400 San Carlos de Bariloche, Argentina

J. L. Gervasoni (✉) · N. R. Arista
Instituto Balseiro, Universidad Nacional de Cuyo and Comisión Nacional de Energía Atómica, 8400 San Carlos de Bariloche, Argentina
e-mail: gervason@cab.cnea.gov.ar

between the semiclassical dielectric models and the quantum descriptions based on Hamiltonian models for bulk and surface plasmon excitations [12–14]. We have showed the two methods to produce equivalent results [15].

In the present work, we continue using both, in order to give a detailed description of the excitation of surface plasmons in cylindrical nanotubes, focusing on the dependence with the specific trajectory of the incident particle.

Theoretical description

Let us analyze the excitation of surface plasmons in a hollow, cylindrical tubule of inner radius a and outer radius b, suspended in vacuum, as sketched in Fig. 1. At $t = 0$ an electron is travelling with a trajectory transverse to the lateral surface of the metallic nanotube, which is characterized by a dielectric function $\varepsilon(\omega,k)$, the same as for an infinite medium [16]. In the following, we focus on the interaction with the surface plasmon field, which can be considered to be independent from the bulk plasmon excitation.

The electrostatic surface modes for a given system are obtained from the solutions of the Laplace equation, $\nabla^2\phi = 0$. For cylindrical geometry, these solutions are given by modified Bessel functions $I_m(x)$ and $K_m(x)$, with m = 0,1,2,.... From the boundary conditions for these equations, and using the Drude approximation for the dielectric function of the material,

$$\epsilon(k,\omega) = \epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

where ω_p and γ are the plasmon frequency and damping constant of the plasma, we obtain the corresponding dispersion relation for the allowed frequencies $\omega(k)$ (details of the calculations are provided in [13, 14, 17]).

The excitation of surface plasmon in cylindrical geometries includes a great variety of modes and frequencies, but when the radius of the cylinder increases, the frequencies of all modes tend to that of the surface plasmons characteristic of a flat surface $\omega_s = \omega_p/\sqrt{2}$. As a general rule, a concave surface (as in a capillary) supports modes with frequencies above the planar surface frequency, while in a convex surface (solid wire) the modes show frequencies below the ω_s line. In the case of a tube, the coupling between the outer and the inner surfaces gives place to the splitting of each m-mode in two branches, which we label with a plus or minus sign, $\omega_m^{\pm}(k)$. The plus modes show symmetric charge density and potential distributions, while the minus modes correspond to antisymmetric distributions. Also, the minus modes have frequencies larger than ω_s and can be identified with those of a capillary, while the plus modes can be associated to those of a wire. To illustrate this, we include in Fig. 2 the dispersion relation $\omega(k)$ for the first modes $m = 0$, 1, and 2 [17], corresponding to a tube of radii a = 5 and $b = 8$ nm, and compare them with the corresponding curves for wires and capillaries.

The total energy dissipation rate due to the fields acting on the passing electron is given by [13]

$$\dot{W} = e\frac{\partial\phi_{\text{ind}}(\mathbf{r},t)}{\partial t}\bigg|_{\mathbf{r}=\mathbf{r}_0(t)} = -ie\int\frac{d\mathbf{k}}{2\pi^3}\int d\omega\,\omega\phi_{\text{ind}}(k,\omega)\,e^{i(kr-\omega t)}\bigg|_{\mathbf{r}=\mathbf{r}_0(t)}. \quad (1)$$

The second member is the Fourier transform of the variation with the time of the potential induced by the incident particle $\phi_{\text{ind}}(\mathbf{r},t)$ in the medium and in the vacuum (with adequate matching conditions). To obtain the induced

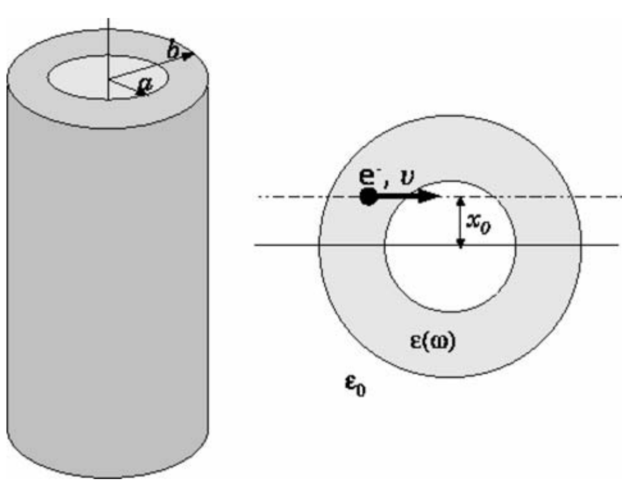

Fig. 1 Scheme of the system: tube of inner radius a and outer radius b. Perspective and axial view

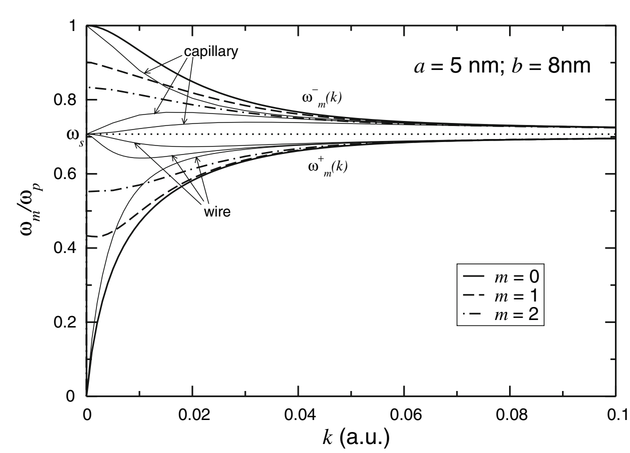

Fig. 2 Dispersion relation $\omega_m(k)$ for surface plasmon modes of a tube, for m = 0, 1, and 2. Inner radius $a = 5$ nm and outer radius $b = 8$ nm. *Thin lines*: corresponding modes for a wire with radius $a_w = 5$ nm, and a capillary with radius $b_c = 8$ nm

field, it is necessary to solve the Poisson equation for the total potential (due to the external charge plus the induced charge distribution) with the usual boundary conditions at the interfaces (for a detailed description of the calculations see [13, 14]).

On the other hand, following a quantum formalism, the plasmon excitation process can be viewed as the result of the interaction between the incident particle and a set of independent quantum oscillators of frequencies $\hbar\omega_m(k)$; within this framework, we calculate the probability of exciting N plasmons of a certain frequency $\hbar\omega_m(k)$, and the average number of plasmons excited by an incident particle. The relation with the semiclassical formulation described in the preceding paragraph is obtained by integrating the energy dissipation rate over time, which should be equal to the total energy absorbed by the plasmon fields,

$$Q = \frac{1}{\hbar}\int dt\dot{W}. \tag{2}$$

The excitation of the different modes has a strong dependence on the trajectory followed by the incident particle. Previous calculations have been developed to describe the excitation of surface plasmons by electrons following straight trajectories along the tube (parallel trajectories [17]) and perpendicular trajectories passing through the tube's axis (impact parameter equal to zero [18]). In this work, we study the dependence of the average number of excited plasmons with impact parameter for transverse trajectories. We consider that the projectile follows a straight trajectory $\mathbf{r}_e = \mathbf{r}_0 + vt$, being $v = (v,0,0)$ the velocity of the electron, perpendicular to the z-axis of the cylinder, with a given impact parameter $\mathbf{r}_0 = (x_0, 0, 0)$. This trajectory remains undisturbed by the plasmon excitation events. This approximation holds for sufficiently large kinetic energies, compared with the plasmon energy ($mv^2/2 \gg \hbar\omega_\mathrm{p}$) [1]. For the case of outer transverse trajectory, the final expression of the number of surface plasmon excitations is:

$$Q^s_{m,v} = \frac{4L}{\pi}\frac{Ze}{\hbar}\int_0^\infty dk\left|\delta_{k,m,v}h^\pm_{k,m,v}\right|^2, \tag{3}$$

with:

$$h^\pm_{kmv} = \int_{y_2/v}^{T} dtK_m(kr(t)) \times \begin{cases} \cos(m\varphi(t) - \omega_{kmv}t) & m\,\mathrm{even} \\ i\sin(m\varphi(t) - \omega_{kmv}t) & m\,\mathrm{odd} \end{cases} \tag{4}$$

for m even or odd, respectively; being $\varphi = \mathrm{Arctan}\ (vt/x_0)$ and $r^2 = x_0^2 + (vt)^2$. For trajectories crossing the tube's wall, similar expressions are obtained with terms including combinations of Bessel functions $I_m(x)$ and $K_m(x)$, depending on the considered region.

Results

With the tools presented in the previous section, we can evaluate the different excitation modes and calculate the average number of plasmon excitations $Q^s_{m,v}$ in the frame of the semiclassical description or using the plasmon quantization technique. The present calculations correspond to an aluminum tube (with $\omega_\mathrm{p} = 0.55$ and $\gamma = 0.035$).

In Fig. 3, we plot the contribution of the modes $m = 0$, 1, and 2 to the average number of surface plasmons, as a function of the particle impact parameter for antisymmetric (a) and symmetric (b) modes. Here we consider external as well as penetrating trajectories for an electron travelling perpendicularly to the tube's axis. The dimensions considered here are inner radius $a = 5$ nm and outer radius $b = 8$ nm, and the velocity of the particle is ≈ 85 a.u. (corresponding 100 keV electrons). Notice that the antisymmetric modes, related to the excitation of plasmons on the inner surface, decay rapidly when the impact parameter crosses the outer surface. That is, the outer interface

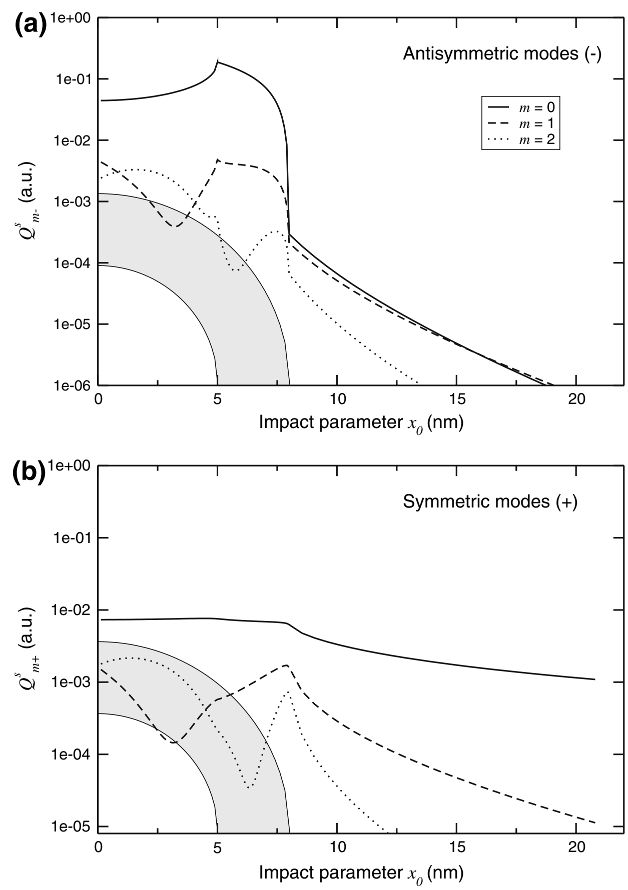

Fig. 3 Average number of surface plasmons excited by an electron on a tube of inner radius $a = 5$ nm and outer radius $b = 8$ nm, as a function of the impact parameter. The first three modes are plotted: (**a**) Antisymmetric modes and (**b**) symmetric modes

screens the interaction of an external particle with the inner surface. The symmetric modes, instead, show (local) maxima at the outer surface, resembling the behavior of the excitation of wire's modes [14]. In both cases, the mode $m = 0$ is the dominant one, but this is not always true as we will see below. We have to mention that, when impact parameter is less than the outer radius b (particle crossing the tube's wall), both types of plasmons, surface and bulk, are excited and should be considered when comparing with experimental spectra.

To study the dependence of the excitation of the surface modes with the relative dimensions of the tube, calculations were performed for different ratios a/b, keeping the outer radius constant ($b = 8$ nm). In this case, only external trajectories were considered with impact parameter $x_0 \geq b$. Some results are presented in Fig. 4, for inner radii $a = 0.1$, 5, and 7.9 nm. As can be seen, the smaller the inner radius, the weaker the coupling between the inner and outer surfaces and the more the symmetric modes resemble the wire's modes (here we include only the $m = 1$ mode for the wire, in circles). The antisymmetric modes are very weakly excited for small inner radii compared with the symmetric modes (notice the logarithmic scale of the ordinates axis). It is worth to mention that for small inner radius (actually, for inner radii less than $\approx b/2$) it is the mode $m = 1$ which dominates over the $m = 0$ and other modes. This behavior is reverted for increasing inner radius, and the mode $m = 0$ gets to dominate the remaining antisymmetric modes. Although the trajectories considered are external (with the corresponding dominance of the symmetric modes), the decreasing thickness of the tube's wall is reflected in the greater contribution of the antisymmetric modes, as can be observed when comparing the lower panels in the figure.

Finally, it is interesting to study the effect of the coupling of the surfaces as a function of the incident particle energy. Figure 5 shows the average number of surface plasmons for the symmetric $m = 1$ mode, for incident electrons with varying energy and impact parameter equal to the outer radius b. The four curves represent different values of the inner radius of the tube: $a = 0.1$, 1, 5, and 7.5 nm. As can be observed, the excitation of plasmons decreases with increasing velocity; nevertheless, it is remarkable that the excitation is greatly influenced by the inner radius for larger velocities. It can be said that for slow projectiles with external trajectories, one can hardly distinguish in the excitation of symmetric modes whether the studied sample is a solid wire or a thin-walled tube of the

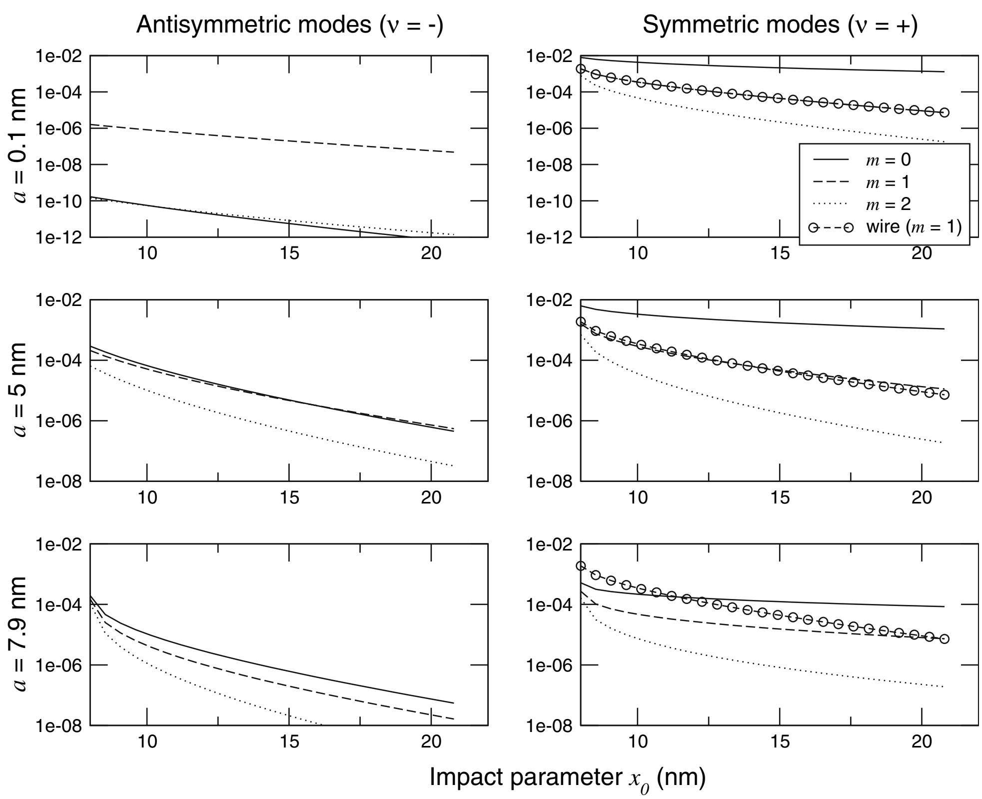

Fig. 4 Average number of surface plasmons excited in modes $m = 0$, 1, and 2 for external transverse trajectories, comparing for different values of the inner radius a. *Left panels*: antisymmetric modes ($\nu = -$); *right panels*: symmetric modes ($\nu = +$). From top to bottom, $a = 0.1$, 5, and 7.9 nm. External radius $b = 8$ nm

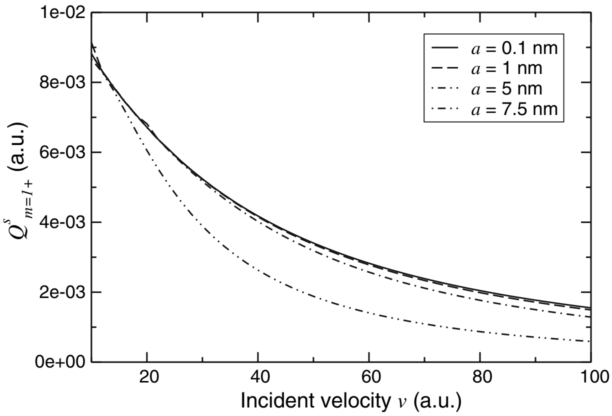

Fig. 5 Average number of surface plasmons excited in the symmetric mode $m = 1$ as a function of the velocity of the incident electron, travelling on a trajectory with impact parameter $x_0 = b = 8$ nm. Different inner radii are considered, $a = 0.1$, 1, 5, and 7.5 nm

same external diameter. Instead, faster projectiles will loss more energy in the excitation of surface plasmons when the inner radius is smaller (for which the limit values are those of a solid wire), than for thin-walled tubes.

Conclusion

In this work we give a description of the excitation of surface plasmons in hollow nanotubes of cylindrical symmetry by charged particles, based on previously determined dispersion relations. We have developed expressions to evaluate the probability of excitation of the different modes for perpendicular trajectories, to study the dependence with the impact parameter including external as well as penetrating trajectories.

We show that the branched modes (±) behave qualitatively different for external and internal trajectories, being the antisymmetric modes hardly excited when the particle travels outside the tube, while the symmetric modes are excited even by particles passing at large distances from the tube. Also, we study the dependence on the relative dimensions of the radii, showing that the symmetric modes can be identified with those of a solid wire when the inner radius is much less than the outer radius. A further comparison is presented for the mode $m = 1+$, as a function of the velocity of the incident electron, for different inner radii.

The results presented here may be useful in current studies of electron energy loss in nanotubes and other related structures. In particular, they can be helpful to design strategies for studying the dielectric response of isolated structures with very focused beams, which allow the definition of an impact parameter.

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