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Plasmon damping in the free-electron gas model of solids

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ABSTRACT

We address the problem of quantifying the decay of plasmons excited in the electron gas of a condensed medium. Within the dielectric formalism, we thoroughly describe the theoretical framework in which we define the damping parameter γ. We present two detailed procedures to assess it as a function of the momentum transfer q, one based on a classical description of the excitation process and the second based on a quantum formulation of it. We present results corresponding to aluminum and magnesium, and compare them with experimental data obtained from the literature.

1. Introduction

Plasmons are collective excitations of the valence electrons of a solid and, along with individual excitations, are one the main causes of the energy loss of an external charged particle traversing a condensed medium [1,2]. The excitation of plasmons and their subsequent decay are of great interest in many branches of fundamental and applied physics [3–5]. Charged-particle spectroscopic techniques, such as EELS, REELS, XPS, etc. [6] show distinct features corresponding to the activation of plasmon modes by the interaction with the incident particle. The shape of the detected signals is determined to a large extent by the way plasmons interact with the medium and ultimately decay. In particular, the width of plasmon characteristic peaks is mainly given by the way the plasmon energy is dissipated.

A widely used quantum model to describe these processes was originally proposed by Lindhard [7], assuming a random phase approximation (RPA) for the free electron gas. This model takes into account both types of electronic excitations (individual and collective), and supplies a very good approximation to the dielectric response of real metals [8]. Within this frame, plasmons decay into a single electron–hole pair and it only occurs when the momentum transfer exceeds a critical value [9,10]. Below this value, plasmons are long-lived excitations with a well defined dispersion relation and negligible decay rate. They can be described using the so-called plasmon pole approximation [11], which models the typical narrow peak centered at a characteristic frequency ω_P and includes a small damping parameter γ to account for its width. In the transition to the individual-excitations regime, the damping increases and the sharp peak widens. Experimental data show that the dependence of γ with the momentum transfer reflects this transition with a threshold behaviour around a critical value [12–14].

The theoretical description of plasmon's decay has been studied in several works and with different approaches [15–18]. However, to our knowledge, an accurate quantitative theoretical model to calculate the damping rate γ remains an open question.

In this work, we explore different methods (from classical to quantum approaches) for quantifying γ in order to determine its value for realistic situations. The paper is structured as follows: in Section 2 we briefly develop the theory related to the response of the electron gas of a solid to the perturbation represented by an external charged particle. Section 3 is devoted to explain the different methods considered for the calculation of γ and to compare their results between them and with experimental data. Finally, we make some concluding remarks in Section 4.

2. Theoretical description of plasmon excitation

As we mentioned above, plasmons are one of the most significant effects in the response of the electron gas in a solid to an external perturbation (e.g., a charged particle). In classical electrodynamic theory, this response is mediated by the complex dielectric function $\epsilon(\mathbf{q},\omega)$, which gives the relation between the induced and the external charge densities in the reciprocal Fourier space with variables $\{\mathbf{q},\omega\}$. These variables are to be identified with

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the momentum transfer and the frequency of the excitations. Here we consider an homogeneus and isotropic medium, where the relevant variable is the modulus of the wave vector $q = |\mathbf{q}|$, so the induced charge density ρ_{ind} can be written in terms of the external charge density ρ_{ext} as

$$\rho_{\text{ind}}(\mathbf{q},\omega) = \rho_{\text{ext}}(\mathbf{q},\omega)\left(\frac{1}{\epsilon(q,\omega)} - 1\right). \tag{1}$$

The zeroes of $\epsilon(q,\omega)$ yield the resonances identified as plasmon modes, which correspond to the poles of the energy loss function $ELF(q,\omega)$:

$$ELF(q,\omega) = \text{Im}\left[-\frac{1}{\epsilon(q,\omega)}\right]. \tag{2}$$

Lindhard's model gives for $\epsilon(q,\omega)$ the following expression in terms of the reduced variables $u = \omega/kv_F$ and $z = q/2k_F$:

$$\epsilon_L(u,z) = 1 + \frac{\chi^2}{z^2}\left[f_1(u,z) + if_2(u,z)\right] \tag{3}$$

with v_F and k_F are the Fermi velocity and Fermi wave vector respectively, $\chi = e^2/\pi\hbar v_F$ is a density parameter and f_1 and f_2 are given by

$$f_1(u,z) = \frac{1}{2} + \frac{1}{8z}\left[g(z-u) + g(z+u)\right] \tag{4}$$

$$f_2(u,z) = \begin{cases} \frac{\pi}{2}u & z+u<1 \\ \frac{\pi}{8z}(1-(z-u)^2) & |z-u|<1<z+u \\ 0 & |z-u|>1, \end{cases} \tag{5}$$

with

$$g(x) = (1+x^2)\ln\left|\frac{x+1}{x-1}\right|.$$

This formulation divides the plane (q,ω) in three regions corresponding to the allowed excitations due to the energy and momentum transfers from the incident particle. Individual excitations take place in the band region with $|u-z|<1$, where the imaginary part of ϵ is different from zero ($\text{Im}[\epsilon_L] \neq 0$). In the other regions there is no contribution to the *ELF*, except along a line defined by the condition $\epsilon_L = 0$, where the plasmon excitations occur. This line defines the dispersion curve $\omega_{pl}(q)$, as shown in Fig. 1 for a typical metal. This figure presents a map of the *ELF* calculated for aluminum using the Lindhard model for $\epsilon(q,\omega)$. The plasmon resonance $\omega_{pl}(q)$ distinctively shows up in the region $q<q_c, \omega<\omega_c$, being (q_c,ω_c) a critical point determined by the intersection of the plasmon line and the upper boundary of the region of individual excitations; beyond this critical point, the line widens as it enters the region where plasmons are heavily damped by the individual excitations. The width of these resonances is determined by the way the plasmon energy is dissipated.

In the context of the plasmon-pole approximation (PPA) the dielectric function is represented as [11]:

$$\epsilon_{PPA}(q,\omega) = 1 - \frac{\omega_P^2}{\omega(\omega+i\gamma) + \omega_p^2 - \omega_q^2}, \tag{6}$$

Here, ω_P is the resonant plasma frequency, and $\omega_q = \omega_{pl}(q)$ is the dispersion relation. The damping is introduced here with γ playing the role of the imaginary part of a complex frequency ($\omega \to \omega + i\gamma$) and gives the width of the plasmon resonance in the *ELF*. A usual approach for the dispersion relation is given by $\omega_q^2 = \omega_p^2 + \beta^2q^2 + \alpha^2q^4$ where β is a typical velocity, related to the Fermi speed as $\beta^2 = (3/5)v_F^2$, and $\alpha = \hbar/2m_e$. Notice that, in the limit $q \to 0$ we obtain from Eq. (6) the well-known Drude's approximation [19] which describes the non-dispersive case $\omega_q = \omega_P$:

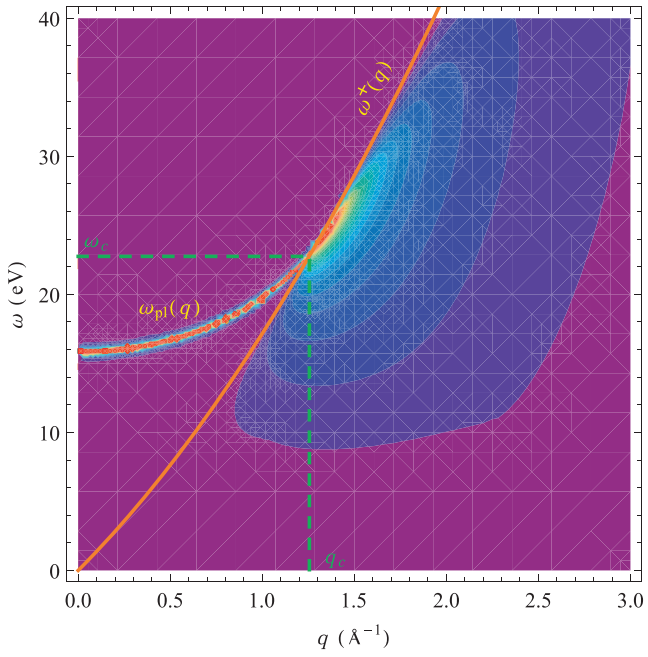

Fig. 1. Map of the ELF using Lindhard's model. The plasmon dispersion relation $\omega_{pl}(q)$ emerges in the $q<q_c$ region with a sharp but finite width since we have considered a complex frequency $\omega = \omega + i\eta$ in the Lindhard's equation for $\epsilon(q,\omega)$. The line $\omega^+(q)$ limits the region where individual excitations are allowed from that where they are forbidden.

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega+i\gamma)}. \tag{7}$$

Continuing the analysis of Fig. 1, we observe that in the transition zone it is still possible to follow the plasmon line beyond the critical point, in a sort of fuzzy dispersion relation $\widetilde{\omega}_{pl}(q)$; energy loss spectra will show a wide peak but with a defined maximum at a certain value $\widetilde{\omega}_q$. In this sense we will be able to determine the value of γ as a function of q for $q>q_c$. In the following we explore different approaches to accomplish this task.

3. Determination of the damping parameter γ

3.1. The plasmon decay process

The damping of plasmons can be easily visualized through the following thought experiment. Let us consider an external charge density, oscillating in an arbitrary direction x with amplitude A, that is switched off at $t=0$,

$$\rho_{\text{ext}}(\mathbf{r},t) = Ae^{ik_1x-\omega_1t}e^{\eta t}H(t), \tag{8}$$

with $H(t)=1$ for $t\leqslant 0$ and $H(t)=0$ for $t>0$, and let η be a smallness parameter that will be taken as zero at the end of the calculation. If we take k_1 and ω_1 as those corresponding to a plasmon (using the dispersion relation $\omega_1 = \omega_{pl}(k_1)$), we ensure that it will excite a pure plasmon mode of frequency ω_1 in the x direction. Now, since the perturbation is switched off at $t=0$, we can study how the plasmon decays for $t>0$.

We write the external charge density in Fourier space

$$\rho_{\text{ext}}(\mathbf{q},\omega) = \frac{A(2\pi)^3\delta(\mathbf{q}_\perp)\delta(q_x-k_1)}{i(\omega-\omega_1-i\eta)} \tag{9}$$

where $\mathbf{q}_\perp$ and q_x are the components of momentum in the directions perpendicular and parallel to the arbitrary direction x. We use Eq. (2) to obtain the induced charge density,

$$\rho_{\mathrm{ind}}(\mathbf{r},t) = \frac{A}{2\pi i} e^{i(k_1 x - \omega_1 t)} \int_\infty^\infty d\omega \frac{e^{i(\omega+\omega_1 t)}}{\omega - \omega_1 - i\eta} \left[\frac{1}{\epsilon(q,\omega)} - 1\right]_{q=k_1}. \tag{10}$$

This expression shows the decay of the oscillatory induced charge density, identified with the plasmon propagating into the solid. The first factor yields the amplitude of the external charge and its oscillatory behavior. The integral includes the effects of the damping due to internal processes governed by the response of the medium through the dielectric function. Fig. 2 shows an example of a calculation of ρ_{ind} using the Lindhard's dielectric function (Eq. (3)), for a value of k_1 greater than k_c, that is within the region where individual excitations are present. As can be seen, the induced charge is damped for $t > 0$, and can be fitted with an exponential decay with γ as a parameter.

Now, we are interested in finding a sistematic procedure that allows us to calculate the behavior of γ as a function of k, for a given metal of known electron density n_0. To this end, we consider two different approaches: (1) fitting ELF's data obtained from Lindhard's model using Drude's expression (Eq. (7)); and (2) using a quantum calculation of transition probabilities.

3.2. Study of ELF: fitting Lindhard with Drude

Lindhard's model allows us to build a map of the energy loss functions, where the plasmon resonance $\omega_{pl}(q)$ distinctively shows up in the region $q < q_c$ (see Fig. 1). At the critical point, the line broadens as it enters the region where plasmons are heavily damped by the individual excitations. We propose that, for a given value of the momentum transfer q, it is possible to fit the ELF obtained with Lindhard's dielectric function $\epsilon(q,\omega)$, using a Drude-like expression where ω_P and γ are fitting parameters. In this way, we can obtain the damping constant γ as a function of

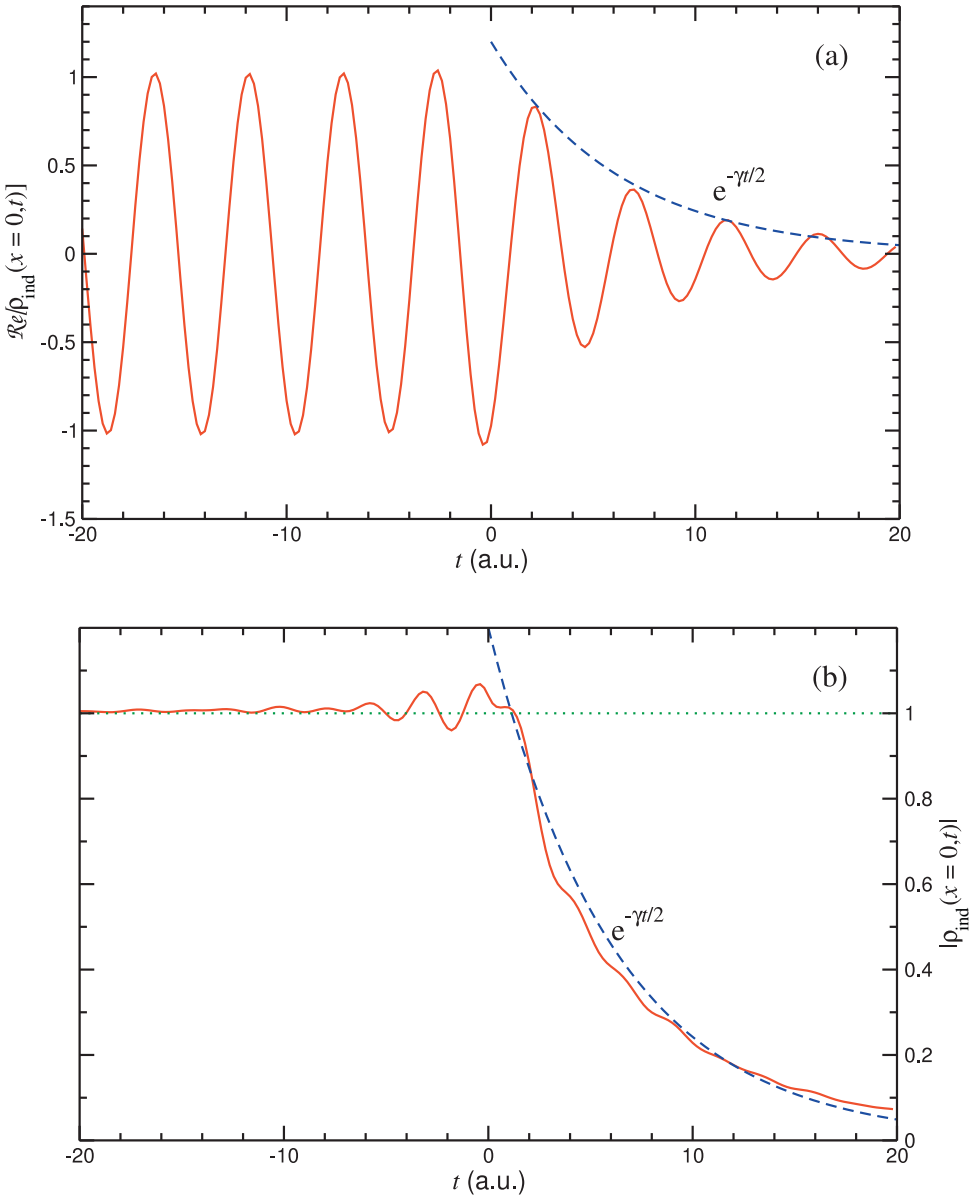

Fig. 2. Attenuation of the induced charge density calculated for aluminum, with $\eta = 0.01$ a.u. and $k_1 = 1$ a.u. (≈ 1.88 Å). Left panel: real part of ρ_{ind}; right panel: square absolute value of ρ_{ind}. Fitted exponential decay yields a value of $\gamma \approx 0.81$ a.u.

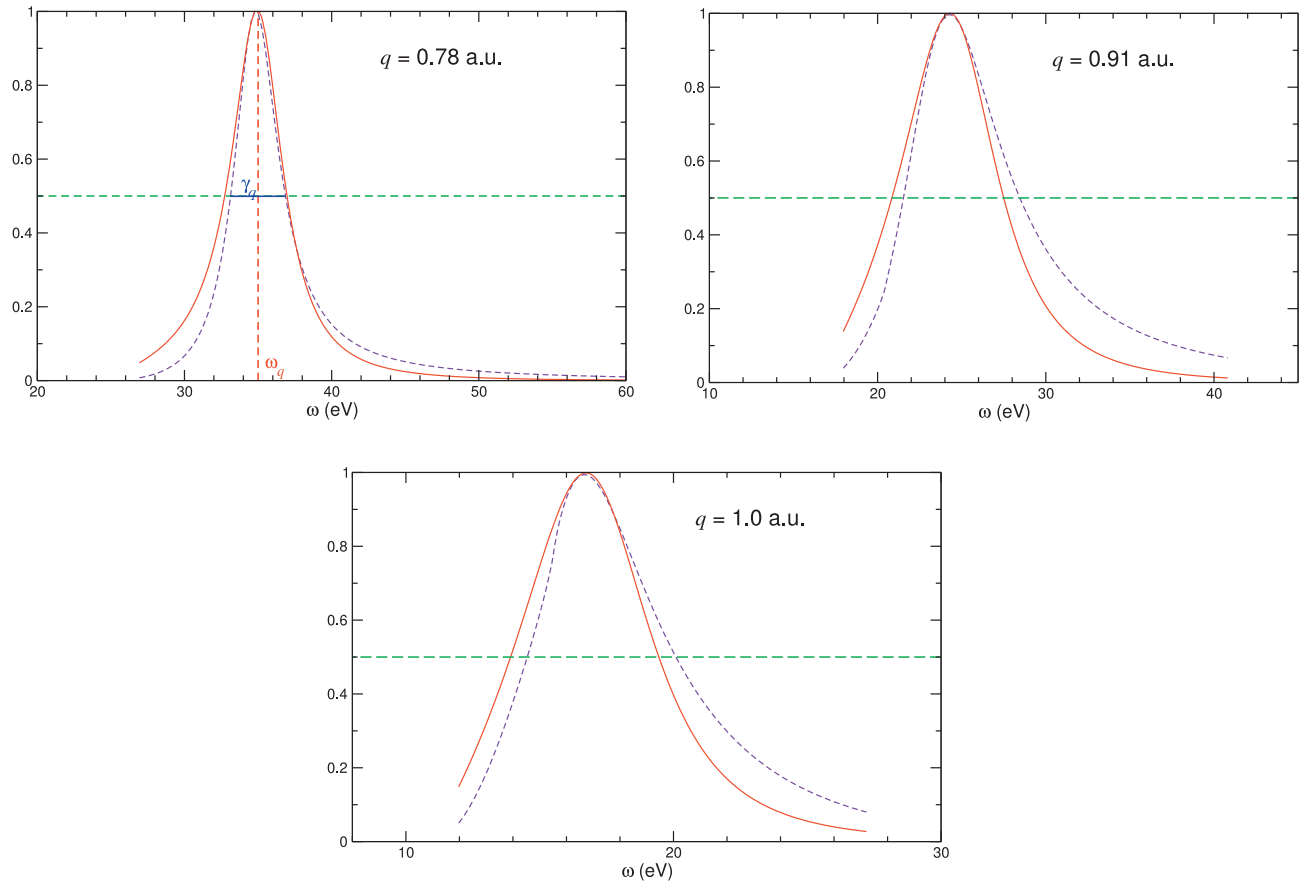

Fig. 3. Fitting Lindhard's curves for *ELF* (dashed blue lines) using Drude's expression (Eq. (4), red lines) for aluminum; three representative curves corresponding to $q = 0.78, 0.81$ and 1.0 a.u. For each value of q, we obtained a value for ω_{pl} (from the position of the maximum) and γ, from the width of the *ELF* at half its height. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

q, as well as the dispersion relation $\omega_{pl}(q)$, even beyond the q_c point where it enters the damping region.

Fig. 3 (a-c) show a series of curves for $ELF(\omega)$ for fixed values of q as a function of ω, calculated with Lindhard's model for aluminum ($\omega_P = 15.5$ eV), and fitted using the Drude expression. Notice that, even when Lindhard model yields an asymmetric ELF, Drude's model yield a reasonable approach for the general shape, at least in the range of q considered where the contributions of the excitation of plasmons is still relevant (right above the critical value q_c). The critical value of q is determined from the intersection of the plasmon line $\omega_{pl}(q)$ and the upper boundary of the region of individual excitations (see Fig. 1). Although this method does not provide a closed expression for γ, it allows us to extract quantitative information of the decay process which is not explicitely given in Lindhard's formulation.

3.3. Quantum calculation

Now, we turn to the quantum formulation of the plasmon decay process, considering the interaction of the quantum fields correspondig to plasmons and electronic states [20]. In this context, the damping rate can be associated to the transition probability between an initial state of the system with one plasmon in eigenstate $\{\mathbf{q}, \omega_{\mathbf{q}}\}$ and one electron with momentum $\mathbf{k}$, and a final state with zero plasmon in the state $\mathbf{q}$ and an electron emitted with $\mathbf{k}+\mathbf{q}$ (notice that here we take $\mathbf{q}$ and $\mathbf{k}$ as vectors for geometrical considerations of momentum conservation). We consider the hamiltonian of this system in terms of second-quantization operators [21],

$$H_0 = H_{\rm pl} + H_{\rm e} + H_{\rm int}. \tag{11}$$

where we have included the contribution from the plasmon field ($H_{\rm pl}$), the electron field (H_e), and the interaction term between them, H_{int}. They can be written in terms of the corresponding creation and annihilation operators $a^\dagger_{\mathbf{q}}, a_{\mathbf{q}}$ and $c^\dagger_{\mathbf{k}}, c_{\mathbf{k}}$ for plasmon and electron states respectively:

$$H_{\rm pl} = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} \left(a^\dagger_{\mathbf{q}} a_{\mathbf{q}} + \frac{1}{2} \right), \tag{12}$$

$$H_e = \sum_{\mathbf{k}}^{S_{Fermi}} E_{\mathbf{k}} c^\dagger_{\mathbf{k}} c_{\mathbf{k}} \tag{13}$$

$$H_{\rm int} = e \sum_{\mathbf{k}} \sum_{\mathbf{q}} \lambda_{\mathbf{q}} \left(a_{\mathbf{q}} c^\dagger_{\mathbf{q}+\mathbf{k}} c_{\mathbf{k}} + a^\dagger_{\mathbf{q}} c^\dagger_{\mathbf{k}-\mathbf{q}} c_{\mathbf{k}} \right). \tag{14}$$

with

$$\lambda_q = \sqrt{\frac{2\pi}{L^3} \frac{\hbar\omega_p^2}{q^2 \omega_q}}.$$

Here L^3 is the volume of the system considered. In this context, we can calculate γ using the transition probability from the initial state with one plasmon in a given mode $|\mathbf{q}\rangle$ and a free electron in the state $|\mathbf{k}\rangle$, to a final state with an electron with momentum $|\mathbf{k}+\mathbf{q}\rangle$ and zero plasmons in mode $|\mathbf{q}\rangle$:

$$\gamma = \frac{2\pi}{\hbar} \sum_{\mathbf{k}}^{S_{Fermi}} |\langle f | H_{\rm int} | i \rangle|^2 \delta(\hbar\omega_q - \Delta E(\mathbf{k}, \mathbf{q})) \tag{15}$$

with $\Delta E = E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}}$. We sum upon all the possible electron states $\mathbf{k}$ close to the Fermi energy level such that, when absorbing the plasmon momentum q, their energy falls outside the Fermi sphere. By making the usual replacement of the discrete summation by a volume integral $\left(\sum_{\mathbf{k}} \rightarrow \int \frac{d^3k}{(2\pi/L)^3}\right)$, and applying the creation and annihilation operators involved in Eq. (14) to the plasmon and electron states described above, we rewrite Eq. (15) as:

$$\gamma = \frac{4\pi e^2}{\hbar}\left(\frac{L}{2\pi}\right)^3 |\lambda_q|^2 \int_{E_F} d^3k\, \delta(\hbar\omega_q - \Delta E(\mathbf{k},\mathbf{q})), \tag{16}$$

The integral is solved taking into account the conditions specified above [22], and we obtain the following expression for γ:

$$\gamma = \frac{m_e e^2 \omega_p^2}{\hbar^2 q^3 \omega_q}(k_F^2 - k_1^2) \tag{17}$$

with $k_1 = \frac{m_e}{\hbar q}\left(\omega_q - \frac{\hbar q^2}{2m_e}\right)$.

In contrast with the previous method (Section 3.2), the quantum calculation gives an analytical expression for γ as function of momentum q. Notice that the dispersion relation ω_q needed to evaluate this formula is external to the theory, and in particular is not well defined for $q > q_c$. In the following assessment we use the dispersion relation obtained from the Lindhard's ELF maxima.

3.4. Comparison of results

In order to validate the methods described above, we compare the present results with available experimental data [12–14]. In particular we compare with data obtained from energy loss spectroscopy for aluminum and magnesium, which are good examples of metallic and alkaline earth elements. These experimental values of γ for both elements show the expected threshold behaviour around a critical point, which is charateristic of each material. We have calculated values of γ for Mg (with plasma frequency $\hbar\omega_P = 10.35$ eV) and Al (with $\hbar\omega_P = 15.5$ eV) using the methods described in the previous sections. In Fig. 4 we show the results obtained for aluminum, which is usually taken as a reference since its metallic behaviour is almost ideal. Experimental data are those given in references [12,13] (we have included representative error bars when available). The critical value q_c, according to the Lindhard's model, shows the point where the plasmon resonance merges into the region of single-particle excitations. The curves of gamma show a sharp threshold behavior at $q = q_c$ and a step increase for larger q values. We observe that the values calculated with Eq. (17) provide the correct qualitative trend above the critical q and explain the sudden increase of the damping rate observed experimentally. The experimental points, however, show a softer transition; the reason for this behavior lies outside the description of the single particle scheme contained in the present analysis and is probably due to interband transitions not considered here [3]. Regarding the values obtained with the fitting method described in Section 3.2, we observe that this gives a worse approximation than the quantum calculation; nevertheless, as stated before, the method allows to highlight some implicit information contained in the Lindhard's model.

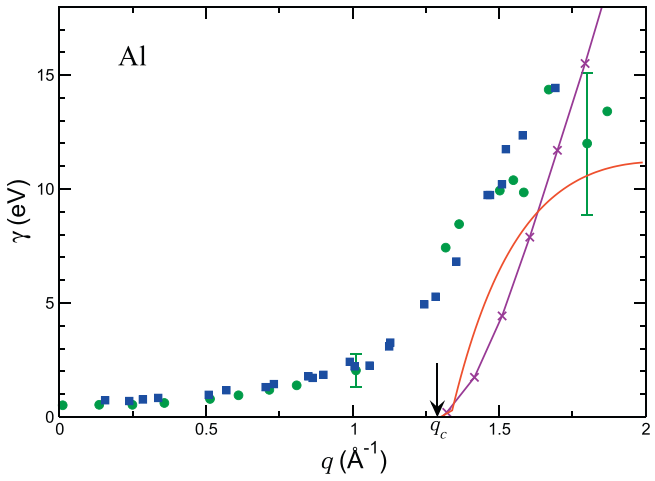

Fig. 4. γ values for aluminum obtained from the fitting method (violet line with crosses), and the quantum method (red line). Experimental γ values from Zacharias [12] (green circles) and from Gibbons et al. [13] (blue squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

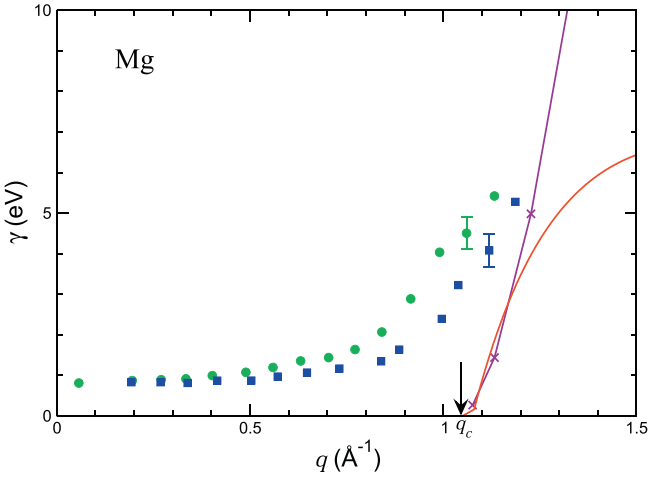

Fig. 5. γ values for magnesium obtained from the fitting method (violet line with crosses), and the quantum method (red line). Experimental γ values from Chen [14] (green circles and blue squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

A similar analysis can be done for the case of magnesium (Fig. 5), where we have included data from reference [14]. In this case there is greater plasmon damping in the limit $q \rightarrow 0$ in comparison with aluminum (the plasmon width of magnesium is more than twice the one for aluminum) and a softer transition around the q_c point.

4. Conclusions

In this work we have explored different methods to assess the damping constant γ for plasmons defined within the dielectric and hamiltonian formulations. In the first place we have studied the decay process of plasma oscillations describing the physical process from a phenomenological point of view. Then we analyzed two procedures to quantitatively determine the value of γ as a function of fundamental parameters with clear physical meaning, and compared the results with experimentally available data.

The first procedure was to fit Lindhard's *ELF* using Drude's approximation, which does not provide a closed expression for γ, but it allows us to extract quantitative information of the decay not explicitely given in Lindhard's formulation.

Quantum formalism yields a rather simple expression for γ which can be easily evaluated using the metal parameters; nevertheless, systematic differences are observed that can be ascribed to the approximations considered. In particular we notice a very different behavior of the two theoretical curves with opposite curvatures. One relevant difference between both calculations is that the method based on the Lindhard function includes in a self consistent way the effects of the collective screening of the electron

gas, as a function of q and ω, while the hamiltonian method yields a more schematic representation of the electron-plasmon interaction parameterized in terms of the λ_q coefficient in Eq. (14). The existing experimental data do not allow us to conclude which of the two behaviors is more realistic. This poses an interesting question for possible future experiments.

As final remarks, we can state that while a better agreement between theory and experiment remains to be achieved, we think the present study represents a significative contribution to the understanding of the process of volume plasmon decay of importance for spectroscopic techniques. On the other hand, and due to its own relevance, a complementary analysis for surface plasmon decay is under way,

Acknowledgments

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