Plasmons in simple-metal slabs: a semiclassical approach.

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Abstract

Collective excitations in simple metal systems can be described successfully in terms of a local one-body excitation operator \( Q \), due to the long range nature of the coulomb interaction. For the plasmon modes of a simple-metal slab, momentum expansions of \( Q \) are calculated using a variational procedure, equivalent to a restricted RPA calculation. The dispersion relation and the density fluctuation for each mode are found in the sudden approximation using the proper \( Q \) operator and the RPA sum-rule formalism. The contribution of the exchange and correlation energy is estimated using a local density functional. The positive background is described within a jellium model while the ground-state electronic density is approximated by a double step profile. The density fluctuation of the plasmon modes above the plasma frequency form standing waves across the slab. The spectra below the plasma frequency is qualitatively different to that of local optics calculations, due to the appearance of two multipole plasmon modes that shift down the origin of the \( \omega_p \) plasmon. The dependence of the results on the width of the slab, the density of the simple-metal and the surface diffuseness is discussed. Throughout, we compare our results with previous RPA and TDLDA calculations.

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1 Introduction.

There are several ways in which the dispersion relation of the plasmon modes in systems with translational invariance can be measured. The first experiments on simple metal slabs used a dielectric substrate to support the metal film and measured the light transmittance [1] or the photoelectric yield [2]. More recently, molecular-beam epitaxy has been applied to grow thin metallic layers between two insulators [3] or Al_{x}Ga_{1-x}As heterostructures simulating a positive jellium background [4]. Also electron energy loss spectroscopy (EELS) has been used to study adsorbed simple-metal layers on an aluminium substrate [3].

The spectrum of a simple-metal slab has two distinct parts: the plasmon modes that lie above $\omega_p$, corresponding to standing waves across the slab, and the surface plasmon modes, with lower frequencies. Some theoretical calculations have been done using the random-phase approximation (RPA) [3, 4, 5, 6, 7, 8, 9, 10] and the time-dependent local density approximation (TDLDA) [11, 12, 13]. The $\omega_-$ and the $\omega_+$ plasmons are studied thoroughly in all these references, but only two of them discuss the existence of an additional multipole plasmon mode. Liebsch [12], in a calculation of the plasmon modes of a simple-metal overlayer on an aluminium substrate, finds a multipole plasmon that hybridizes with the $\omega_+$ plasmon. Schaich and Dobson [13] also obtain a peak in the response function at frequencies between $\omega_p$ and $\omega_p/\sqrt{2}$ but they do not conclude whether the cause is a collective mode or is due to intersubband excitations.

This multipole plasmon mode has been detected in simple-metal clean surfaces using EELS [14]. Its dispersion relation has a positive slope when the momentum $k$ parallel to the surface is zero while the frequency at this point is $0.8\omega_p$. This value agrees with theoretical calculations [14, 15]. Multipole plasmon modes are associated with electronic-density fluctuations that are peaked at the surface region and have decreasing oscillating amplitude towards the interior of the metal. It can be shown [16] that the integral of the electronic density perpendicular to the surface is zero. Unlike ordinary surface plasmons, they are optically active because they carry momentum on the normal direction. All this properties were found for simple-metal surfaces but one expects that at least some of them should be valid for slabs.

The aim of this work is to study the existence of multipole plasmon modes on simple-metal slabs and its coupling to the other surface modes. We will use the RPA sum-rule formalism (SR) that previously has been able to produce useful results for different geometries [17, 18, 19, 20]. In particular, a good agreement has been obtained between experimental data and the dispersion relation of surface plasmons [21] and multipole plasmons [15] on a plane simple-metal surface. It has some advantages over other methods. The different contributions to the energy of each mode can be analyzed on
its own and semiclassical approximations for the kinetic energy are easily implemented. It can incorporate electronic exchange and correlation interactions using a local density approximation. Within the SR formalism it is not difficult to employ realistic electronic profiles. In fact the results have RPA precision as long as a self-consistent ground-state electronic profile is used, although only an average of the response function can be obtained.

Usually, when working within the SR method, it is assumed that for every collective mode exists a local one-body observable that excites that mode without mixing it with others. In order to obtain useful results an appropriate excitation operator $Q$ must be found and the system must have well-defined collective modes. Otherwise it would not be possible to get any valuable information from the averaged response function. There is not a unique way to find such an operator. Sometimes the properties of a given operator $Q$ determine the kind of mode that it excites. For example, an operator that fulfills Laplace's equation can only excite surface modes. A restricted variation of $Q$ on a parameter can be useful if a sufficiently general form of $Q$ is employed. In RPA calculations an excitation operator $Q$ can be found for each mode but although it will be an observable, in general it is not a local operator. Nevertheless, the fact that the interaction responsible for the existence of well-defined collective excitations, the coulomb interaction, has a long range, allows to approximate $Q$ as a local operator. This approximation is called local-RPA and has been applied successfully to nuclei and metal clusters. We use local-RPA to find a proper $Q$ operator as a momentum expansion.

Instead of a self-consistent electronic profile, a double step profile is used to describe the ground-state. This leads to a simplification of the calculations which can be performed analytically without a great loss of precision because it has been shown that there is little quantitative difference between the results from any of the two models.

2 Application of local RPA to a metal slab

In this section we first give a short review of the method as it was stated in (see this reference for more details). Then we expatiate on the particularities that we have had to devise to adapt it to our problem, the most important being the choice of the form of the functions that give rise to the sought-after excitation operators.

Both local and full RPA demand as a starting point a description of the vacuum of the system at issue. Within the quasi-bosonic approximation this description is furnished by working out the Hartree-Fock approximation to the vacuum state $|\psi_0\rangle$. This approximation is acceptable as long as one assumes that correlations are small. Once
the Hartree-Fock problem is solved, the essence of the method is to build the excitation operators as linear combinations of one-particle–one-hole operators, and determine the coefficients of the expansion by solving the equation of motion

\[ \langle \phi_0 | [C_m, [H, C_n^\dagger]] | \phi_0 \rangle = \delta_{nm} \hbar \omega_m, \]  

where \( C_n^\dagger \) is an excitation operator. By this name we mean that when it acts on the ground state, an elementary excitation of the system with a well defined energy is created. An alternative description of RPA can be made based upon the operator

\[ Q_n = \frac{C_n^\dagger + C_n}{\sqrt{2}} \]  

\[ [H, [H, Q_n]_{ph}]_{ph} = (\hbar \omega_n)^2 Q_n, \]  

The \( ph \) symbol means that the operator is projected onto the linear space spanned by one-particle–one-hole states. Local RPA assumes that the operator \( Q_n \) can be expanded in terms of a function \( f_n \) as follows,

\[ Q_n = \sum_{i=1}^{N} f_n(\hat{r}_i), \]  

where \( N \) is the number of electrons and \( \hat{r}_i = (x_i, y_i, z_i) \) is the position operator of the \( i \)-th particle. In order to determine \( f_n \) we shall consider that it is a linear combination of the elements of a basis of functions that we shall choose taking advantage of the particular problem we are facing at. We will focus on the problem of a gas of electrons in a simple metal slab of very large area \( A \) and thickness \( d \). If the gas is made of \( N \) electrons, then the operator of total momentum \( \hat{q}_{tot} \) of the gas will be;

\[ \hat{q}_{tot} = \sum_{i=1}^{N} \hat{q}_i \]  

We will assume the slab to be parallel to the \( XY \) plane and consequently write any vector as \( q = (k, p) \), \( k \) being the 2 dimensional vector that lives in the \( x - y \) plane and \( p \) is the projection along the \( z \) axis. Translation invariance in the \( x \) and \( y \) axis leads to the conservation law;

\[ [H, \hat{k}_{tot}] = 0 \]  

So, the eigenvalues \( k \) of operator \( \hat{k} \) are good quantum numbers for our system. As \( k \) is a true quantum number of the problem, we may advance that each \( Q_n \) operator has a well defined \( k \), in other words, it has the form

\[ Q_n = \sum_{j=1}^{N} e^{ik\hat{R}_j} \phi_n(\hat{z}_j). \]
This observation suggests that we relabel $Q_n$ as $Q_{k,n}$ in the sequel.

As for the $f_n$ functions, which we haste to relabel in accordance with the previous discussion, we may write

$$f_{k,n}(R, z) = \exp (ikR)\phi_n(z).$$

(8)

The electronic profile vanishes for distances far enough from the boundaries of the slab. We can think the gas of electrons to live in a linear box of size $L$. We must take $L$ to be larger than $d$ as there are electrons wandering outside the slab, but provided $L$ is large enough, the physical results are $L$-independent. Nevertheless the value of $L$ must not be larger than necessary because this would increase the number of terms needed in the expansion.

Now we have a physically motivated choice for the basis which generates $\phi_n$; we take $\phi_n$ to be expanded in terms of a Fourier basis

$$\phi_n(z) = \sum_l a^l_n e^{ip_l z},$$

(9)

with $p_l = \frac{2\pi l}{L}$. Equivalently, we may expand the $Q_{k,n}$ operators

$$Q_{k,n} = \sum_l a^l_n Q_{k,p_l},$$

(10)

with

$$Q_{k,p_l} = \sum_{j=1}^N \exp (ik \hat{R}_j) \exp (ip_l \hat{z}_j).$$

(11)

By construction, the $Q$ operator will have a period $L$. This is done just for mathematical convenience. We have truncated the previous Fourier series ((9) or (10)) making sure that the terms we do not consider are really negligible. This can be done checking the convergence of the results as the number of terms is increased. It is clear that $L$ cannot be too small as we would cut the tails of the electronic density, but it should not be larger than necessary because this would increase the number of terms needed in the preceding expansion. $a^p_n$ are coefficients that can be obtained by minimizing the energy functional $\mathcal{K}$. Written in terms of the Fourier coefficients eq. 3 reads

$$\left[ K_{\alpha\beta} - (\hbar \omega_n)^2 B_{\alpha\beta} \right] a^\alpha_n = 0,$$

(12)

$K_{\alpha\beta}$ and $B_{\alpha\beta}$ being respectively;

$$B_{\alpha\beta} = \langle \Phi_0 \left[ Q_\alpha, [H, Q_\beta] \right] | \Phi_0 \rangle,$$

(13)

$$K_{\alpha\beta} = \langle \Phi_0 \left[ [Q_\alpha, H], [H, Q_\beta] \right] | \Phi_0 \rangle.$$
$H$ is the Hamiltonian of the system and $|\Phi_0\rangle$ the (Hartree-Fock) ground state. Needless to say that the sum-rule approach

$$m_1 = \frac{1}{2} \langle \Phi_0 | [Q, [H, Q]] | \Phi_0 \rangle,$$  

(15)

$$m_3 = \frac{1}{2} \langle \Phi_0 | [[Q, H], [H, [H, Q]]] | \Phi_0 \rangle,$$  

(16)

$$E_3 = \sqrt{\frac{m_3}{m_1}},$$  

(17)

is a particular case of eq. 12 because if we could find a series expansion such that every term would couple to a different eigenmode, eq. 12 would be separated into a set of equations like eq. 17, one for each term of the series. It can be shown [27] that $E_3$ is an upper bound to the energy of the mode excited by $Q$.

Solving equation 12 for a fixed value of $k$ does not only deliver the optimal operator $Q$ but also the dispersion relations of the collective excitations $\omega_n(k)$. We calculate the dispersion relation in an equivalent, but more transparent way. As the Hamiltonian

$$H = \int dr \left[ \frac{\hbar^2}{2m_c} \tau(r) + \frac{n(r)}{2} \left( c^2 \int dr' \frac{n(r')}{\|r - r'\|} + 2v_j(r) \right) \right]$$

(18)

contains a kinetic and a coulomb term, we can evaluate separately the contribution of each part of the Hamiltonian to the $m_3$ sum-rule. When the $Q$ operator used is that obtained solving eq. 12, the eigenvalues of this equation are, by construction, the $E_3$ energy obtained from eq. 17 taking into account all the contributions to $m_3$. If $E_3$ is calculated using only a contribution to $m_3$, the quantity obtained gives an idea of the relative importance of that term in the total energy. The inclusion of an exchange and correlation term when solving eq. 12 is done in a perturbative way, as explained later on.

Another important magnitude in the sum-rule formalism is the sudden approximation to the density fluctuation given by

$$n_1 = -\hbar \nabla \left[ n \nabla Q \right].$$

(19)

It is the first-order contribution to the density fluctuation of the $|\eta\rangle$ state described in the appendix and usually gives a reliable description of the eigenstates of the system.

At this point we just need to solve equation 12 and we will do so by expressing $K_{\alpha\beta}$ and $B_{\alpha\beta}$ in terms of the local density $n(r)$ and the kinetic-energy density $\tau(r)$ (due to the symmetry discussed so far the only dependence of this quantities is on the $z$ axis)

$$n(r) = \sum_i |\phi(r)|^2, \quad \tau(r) = \sum_i |\nabla \phi(r)|^2,$$  

(20)
To compute the kinetic term the most direct approach consists in taking the kinetic energy of a free gas of electrons;

\[ \tau = an(r)^{5/3}. \]  

(21)

The coulomb part contains the coulomb interaction between electrons (of charge e) and the interaction with the jellium through a potential \( v(r) \). An estimation of the exchange and correlation energy is made using the following Slater- and Wigner-type expressions

\[ \epsilon_{ex} = -\frac{3}{4}an(r)^{1/3} - b\frac{n(r)^{1/3}}{cn(r)^{1/3} + d} \]

(22)

with \( a = \sqrt{3/\pi}, b = .44, c = 7.8 \) and \( d = a/2 \). Although this term is not included in the Hamiltonian when computing \( Q \), a contribution to the \( m_3 \) sum-rule is calculated just as if it were another part of eq. \[ \text{18} \] and added to the other contributions. So the final values of the dispersion relation are slightly different to the ones obtained in eq. \[ \text{12} \]. In this way the exchange and correlation interactions are included in the results. The main drawback is that the self-consistency of the calculation is lost to a certain extent but this is acceptable because exchange and correlation do not play a crucial role in the existence of the collective excitations in an electron gas.

The details necessary to solve equation \[ \text{12} \] and improvements to the kinetic energy functional are postponed to the appendix as they become rather technical and do not contain any new physics.

3 Results and discussion

We have applied the method described in the preceding section to simple metal slabs. A double step electronic profile is used as a description of the ground state

\[ n(z) = \frac{n_b}{2} \left[ \theta(z + \frac{d + \delta}{2}) + \theta(z + \frac{d - \delta}{2}) - \theta(z - \frac{d + \delta}{2}) - \theta(z - \frac{d - \delta}{2}) \right]. \]  

(23)

The length of the step \( \delta \) has been adjusted in all the cases by a minimal squares procedure to an improved Thomas-Fermi electronic profile \[ \text{20} \] calculated for each system. In this section atomic units are used throughout.

Figure 1 (a) represents the dispersion relation of the plasmon modes below \( \omega_p \) for a typical system. The lower mode is the \( \omega_- \) mode. It begins at \( \omega = 0 \) for \( k = 0 \) and tends to the surface plasmon frequency \( \omega_p/\sqrt{2} \) as \( k \) tends to infinite. This behaviour is completely in agreement with Local Optics, not like the next mode, that we identify as the \( \omega_+ \) mode of Local Optics. In our calculation it has a frequency of approximately \( \omega = 0.8\omega_p \) for \( k = 0 \) when according to Local Optics, and most RPA
and TDLDA calculations, it should tend to $\omega = \omega_p$ for a small $k$. For large values of $k$ it becomes degenerate with the $\omega_-$ mode. There is another mode whose frequency tends to $0.8\omega_p$ for a low $k$. We call it the even multipolar mode and it has a qualitative behaviour very similar to that of multipolar modes in a surface. Its dispersion relation has a positive slope when $k = 0$ and tends to the same value as in the semi-infinite case. In our calculation it becomes degenerate for large $k$ with a mode that we call the odd multipolar mode. This last mode has its origin at the plasma frequency $\omega_p$.

Although this scheme is not the usual one in semiclassical or fully quantum-mechanical calculations of collective excitations in metal slabs, a nearly identical behaviour has been reported for plasmons in a simple-metal overlayer \cite{12}. Figure 1 (b) displays the dispersion relation of the first four bulk resonances. These dispersion relations are qualitatively similar to those obtained by discretization of the $z$ component of the momentum in a bulk plasmon dispersion relation but the slopes are flatter than those obtained with other methods, even classical \cite{2}. Also the position of the origins does not seem to be quadratic as a reasoning of this type would indicate.

Further insight can be gained looking at the sudden approximation of the density fluctuation for each mode. Every one of the four discontinuities in the ground-state electronic profile produces an avoidable discontinuity in the density fluctuation. In those points the first derivative of the density fluctuation is also discontinue. A more realistic profile should be used to obtain quantitatively correct results but as the double-step model includes the most important physical aspects, such as diffuseness, qualitative information like symmetry and number of nodes is reliable. The density fluctuation of the $\omega_-$ and the $\omega_+$ modes is shown in Fig. 2 (a). The symmetry and the number of nodes of this modes are the same as those of the even multipole and the odd multipole respectively, in Fig. 2 (b). All these modes are clearly surface modes and the main difference between them is that in the multipole modes the density fluctuation is not constant in the middle of the slab. The decreasing oscillating amplitude that multipole plasmons show in a semi-infinite medium is not found in our calculation for thin slabs. The density fluctuation of the bulk resonances is represented in Fig. 2 (c)-2 (d). The first resonance has two nodes and presents the typical profile of a standing wave across the slab. In fact, we can label a resonance with its number of nodes because any resonance has one more node than the previous one.

The key part of the calculation is to choose the number $M$ of terms of the $Q$ expansion. This is done, for a given momentum $k$ parallel to the surface, examining the energy of the modes in front of $M$. The value of $M$ necessary to attain the convergence depends on a great number of physical factors. As the main assumption of Local RPA is the existence of well defined collective excitations, the convergence will be difficult or even impossible in all those situations where a severe damping of the plasmon modes
is expected. Because the relative importance of the coulomb energy increases with the electronic density, in high-density metals like aluminium the convergence will need lower values of $M$ than low-density metals like cesium. Also when the momentum $k$ approaches the Landau cutoff value, given approximately by $q_c = \omega_p/v_F$, the convergence must be harder. The surface diffuseness also plays its role because an increasing diffuseness tends to lower the coulomb energy. All these general trends are present in our calculations. The size of the system is also an important factor. This is mainly because the expansion series of a bigger system needs more terms to be accurate. This puts an upper bound on the size of the slabs that can be treated within this method.

Taking advantage of the transparency of the method, the contributions of the kinetic and the coulomb parts of the hamiltonian to the dispersion relation are represented in Fig. 3. The ratio between the coulomb and the kinetic energy is different for each mode. The $\omega_-\!$ mode has a negligible kinetic energy in front of the coulomb contribution while they are comparable in the $\omega_+\!$ mode. In fact, looking at Fig. 3 one can expect the $\omega_+\!$ mode to have the worse convergence of all, as it really happens in our calculation. This agrees with TDLDA results [13] that show how the peaks in the excitation spectra are noticeably wider for the $\omega_+\!$ mode than for the $\omega_-\!$ mode.

The dependence of the dispersion relation on the width $d$ of the slab can be seen in Fig. 4 (a)-4 (b). The $\omega_-\!$ and the $\omega_+\!$ modes tend to degenerate when $k >> d^{-1}$ and the same is true for the even and the odd multipole modes. This is due to the fact that the symmetry of the mode is not a real difference when the density fluctuation of two modes is concentrated on the two surfaces of the slab and these are enough apart in comparison with the wavelength of the mode. Obviously, for larger values of $d$ plasmons will tend to degenerate for smaller values of $k$. The $\omega_-\!$ and the $\omega_+\!$ modes degenerate at an energy close to $\omega_p/\sqrt{2}$. In the semi-infinite medium limit their dispersion relations will join at the origin and they will form the well known surface plasmon. The even and the odd multipole modes will also join in a unique multipole plasmon mode [13] for extremely large slabs. In Fig. 4 (b) can be seen that the dispersion relation of the odd plasmon mode is much more affected by the change of the width of the slab than that of the even multipole mode, so the dispersion relation of the surface multipole mode will be closer to that of this last mode.

In Fig. 5 (a) the dispersion relations of two slabs with a different electronic density are plotted. The sodium slab has a greater electronic density and the energy of its modes is higher than those of the potassium slab. Surface modes degenerate for lower values of $k$ in slabs of this last metal. The increase in the energy of the modes in a high-density metal is due to both kinetic and coulomb energies although in relative terms the coulomb term is more responsible of this feature. Moreover, the density also influences the diffuseness of the electronic profile. As discussed earlier, these two
factors have an important effect on the convergence of the expansion series. A plot of the plasmon modes for an aluminium slab is displayed in Fig. 5 (b). Besides the rise of the energies of the modes we can notice a greater gap between the origin of the odd multipole mode and the first bulk resonance. This is not due directly to the higher electronic density but to the steeper slope of the electronic profile as will be seen soon. In order to distinguish the effects due to the change of electronic density and those caused by a different diffuseness of the profile we have studied three systems where we have changed only the length of the intermediate step. The results are represented in Fig. 6. When the length of the step is reduced the origins of the $\omega_+$ and of the even multipole tend to rise, they are no longer at $0.8\omega_p$, and a gap appears between them. It is clear that the origin $0.8\omega_p$ depends strongly on the diffuseness of the surface and can be used as a test on how good is an electronic profile. The odd multipole and the first bulk resonance also have higher energies for $k = 0$ and the gap between their origins also increases. The slopes of the dispersion relations of the even and the odd multipole modes suffer a significant change and are closer than before. Finally, for a system with no diffuseness, the origin of the $\omega_+$ mode has risen up to $\omega_p$ and the two dispersion relations of the multipole modes are in the same place as the first and second bulk resonances in the previous systems. The result of the reduction of the diffuseness is, then, the gradual conversion of the even and the odd multipole modes into the first two bulk resonances.

4 Summary and conclusions

We have succeeded in developing a semi-classical calculation that includes as solutions the even and the odd multipole modes, that are not usually considered in related calculations. In the semi-infinite medium they are brought together into the by now well studied multipole plasmon mode. These multipole modes modify the classical origin of the $\omega_+$ mode and are closely dependent on the diffuseness of the electronic profile. Their origin is shifted upwards when the diffuseness is reduced and they disappear when it is set to zero.

The $\omega_-$ plasmon is far more observable, for intermediate values of $k$, than the $\omega_+$ plasmon. This can be stated either examining the convergence of the results on the number of terms of the expansion series or taking into account the relative contribution of the coulomb and the kinetic energies. The bulk resonances closer to $\omega_p$ are also realistically described. The Thomas-Fermi density functional gives a too flat slope of the kinetic energy. The exchange and correlation contribution lowers the energy for large values of $k$.

Local RPA is a useful and economic method for finding the excitation operator
whenever well-defined collective excitations are expected. The size of the system determines, among other factors, the number of terms needed in the expansion series. If a strong damping acts on the plasmon modes due to high diffuseness of the electronic profile, low electronic density or whatever other cause, the convergence can be difficult to reach or even non-existent at all.

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A Appendix

In this appendix we will present the formulae which were used in the solution of equation 12.

The first object to compute, that is $B$, is a straightforward calculation;

$$B_{(k,p),(k',p')} = A(k^2 + pp') \int dz \exp(-i(p - p')z) n(z)$$

To compute $K_{\alpha\beta}$ we start by considering;

$$M_{\alpha\beta} \equiv M_{\alpha\beta}^k + M_{\alpha\beta}^{ex} + M_{\alpha\beta}^c = \langle \Phi_0 | \exp(\eta [Q_\alpha, H]) \exp(\eta' [Q_\beta, H]) (H_k + H_{ex} + H_c) \times \exp(-\eta' [Q_\beta, H]) \exp(-\eta [Q_\alpha, H]) | \Phi_0 \rangle \equiv \langle \eta\eta' | H_k + H_{ex} + H_c | \eta\eta' \rangle$$

The previous object is useful as it is connected to the one we are interested in through formulae;

$$K_{\alpha\beta} = \left( \frac{\partial^2}{\partial \eta \partial \eta'} M_{\alpha\beta} \right)_{\eta=0,\eta'=0}$$

At this point we have reduced the problem of calculating the expressions in formula 14 to the evaluation of expressions such as $\langle \eta\eta' | F(n) | \eta\eta' \rangle$ which are still quite intractable. Some approximations are needed to go any further. We will approximate terms like this one as

$$\langle \eta\eta' | F(n) | \eta\eta' \rangle = F(\langle \eta\eta' | n | \eta\eta' \rangle) + ...$$

and keep just the first term.

The rest of the computation is straightforward but lengthy. We arrive at

$$K_{c,(k,p),(k',p')} = 4\pi A p' \int dz n(z)^2 \exp(-i(p - p')z)$$

$$+ 2\pi A \int dz' n(z)n(z') \exp(-i(p - p')z) \exp(-|z - z'|k) \times$$

$$\left( k^3 - pp'k + i(p + p')k^2 \text{sgn}(z - z') \right)$$

$$- 4\pi A p' \int dz (n(z) - n_j(z')) n(z) \exp(-i(p - p')z)$$

$$- 2i\pi A \left( pp' + k^2 \right) p' \int dz dz' (n(z) - n_j(z')) n(z) \exp(-iz(p - p')z) \text{sgn}(z - z')$$

(28)
The exchange term is easily computed with the result;

\[ \mathcal{K}^{ex}_{(k,p),(k,p')} = A(k^2 + p'^2)(k^2 + p^2) \int dz n(z)^2 \frac{\partial^2 \epsilon_x(n)}{\partial n(z)^2} \]

\[ -(k^2 + p'^2)p(p - p') \int dz \exp(-i(p - p')z) \left( n(z) \frac{\partial \epsilon_x(n)}{\partial n(z)} - \epsilon_x(n) \right) \]

The kinetic part does not show up any further complication as compared to the exchange term since where one reads \( \epsilon_{ex} \) one substitutes \( \tau(n) \) and the rest is exactly the same.
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Figure captions

**Figure 1 (a):** Dispersion relation of the plasmon modes below the plasma frequency in a sodium slab \((d = 25a_0)\) where \(a_0\) is the Bohr radius. From bottom to top can be seen the \(\omega_-, \omega_+, \) even multipole and odd multipole modes. Thin lines represent, from bottom to top, \(\omega_p/\sqrt{2}, 0.8\omega_p\) and \(\omega_p.\)

**Figure 1 (b):** Dispersion relation of the four lowest bulk plasmon resonances in the same case as Fig. 1 (a). The thin line represents the plasma frequency.

**Figure 2 (a):** Sudden approximation to the density fluctuation calculated as explained in the text for a sodium slab \((d = 40a_0)\). The dashed line represents the \(\omega_-\) mode while the solid line is the \(\omega_+\) mode.

**Figure 2 (b):** The dashed line represents the density fluctuation of the even multipole mode in the same case as Fig. 2 (a). The solid line is the odd multipole mode.

**Figure 2 (c):** Density fluctuation of the two lowest bulk plasmon resonances for the same system as Fig. 2 (a). The dashed line represents the lowest resonance and the solid line represents the next resonance.

**Figure 2 (d):** The dashed line is the third bulk resonance with lowest energy and the solid line is the fourth. Calculation for the same system as previous cases.

**Figure 3:** The energy contributions of the same mode are plotted in the same type of line. The upper one is the coulomb contribution and the lower one is the kinetic contribution. The solid line corresponds to the \(\omega_-\) mode, the long-dashed to the \(\omega_+\) mode, the short-dashed to the even multipole mode, the dotted line to the odd multipole mode and the dot-dashed line corresponds to the lowest bulk resonance. The calculations are made for the same case as Fig. 1 (a).

**Figure 4 (a):** Dispersion relation of the \(\omega_-\) and the \(\omega_+\) modes for a sodium slabs of different widths. The solid line represents a width \(18a_0\), the long-dashed line stands for \(25a_0\) and the short-dashed line is the result for \(40a_0\).

**Figure 4 (b):** Same as Fig. 4 (a) but with the even and the odd multipole plasmon modes.

**Figure 5 (a):** Dispersion relation of the plasmon modes of two slabs of different metals and the same width \((d = 25a_0)\). The solid line corresponds to a potassium slab. The dashed line is used for the sodium slab.

**Figure 5 (b):** Dispersion relation of the plasmon modes of an aluminium slab. The width is \(25a_0\).

**Figure 6:** Dispersion relation of the four modes with lowest energy. The solid line represents the modes with an intermediate step set to \(\delta = 2.11a_0\). The long-dashed lines are calculated with \(\delta = 1a_0\) while while short-dashed lines stand for a system with \(\delta = 0.\)
