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Electromagnetic Response of Small Metal Particles Made Simple

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Abstract. We give a unifying picture of a number of characteristic response properties of small metal particles. The static polarizability and the surface plasmon peak position are discussed with respect to surface and quantum size effects. The surface and bulk collective modes are investigated in a multipole framework and finally a relation between the surface plasmon resonance and the static polarizability is commented upon.

Resumen. Se presenta un esquema unificador para las propiedades de respuesta característica de partículas metálicas pequeñas. La polarizabilidad estática y la posición del pico del plasmón superficial se discuten en relación a los efectos de superficie y los efectos cuánticos de tamaño. Se investigan los modos colectivos de superficie y de volumen en un marco multipolar y, finalmente, se comenta una relación entre la resonancia del plasmón de superficie y la polarizabilidad estática.

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1. Introduction

In recent years several groups [1–3] have invested a considerable effort in providing a realistic self-consistent picture of the electromagnetic response of small metal particles, notably the impressive and elegant numerical undertaking by Ekardt [1]. Much of this work is inspired by experimental results indicating that particles in the 10–100 Å range show unusual properties such as large far-infrared absorption [4], anomalous van der Waals interaction [5], enormous photoyield [6], etc. However, being a difficult experimental set-up some care has to be taken in viewing what is "unusual" as recent result for the far-infrared absorption experiment has shown [7]. Even in the light of this, these small particles do deviate in their behaviour from what classical (Mie) optical theory predicts [8]. This means that they themselves deserve a theoretical effort, which at the present time due to the complexity of the problem can be difficult to compare to a realistic (experimental) situation. This complexity makes those calculations very demanding with respect to computing power limiting the present particles to "large atoms" with a radius of roughly 10 Å.

In order to present a general overview of the electrodynamical response of small particles in the so far inaccessible region 10–100 Å and the present 10 Å region and less, we will make use of an earlier developed formalism [9] which with the recent numerical calculations available has proven its predictive capability. Using black box arguments together with Maxwell equations we showed how to take into account a smooth variation in the dielectric properties of a vacuum particle interface. The scheme developed correctly predicted a red-shift of the surface plasmon peak [10], an order of magnitude increased optical absorption compared to Mie theory [11] and a static polarizability larger than the classical one [12], where it in its lower limit of applicability overlaps with the numerical calculations at hand. Thus, containing qualitative as well as quantitative predictions, as referred to the present experimental accuracy, we will in this paper elucidate the consequence of the theory for the static polarizability, extending it to take into account the effects of having a discrete excitation spectrum which is the case for very small particles. We also investigate the role this quantum size effect (QSE) has on the surface plasmon resonance, the bulk plasmon excitation and its importance relative to surface effects.

The classical Mie theory is adequate for particles with a radius of the order of 100 Å and larger. When we are dealing with particles in the size-range 10–100 Å the surface starts to become more and more important compared to the bulk. Where as the classical theory characterized by bulk properties through the length-scale R (R being the particle radius) the surface enters to lowest order as a length d_r whose real part is a measure of the center of gravity of the screening charge induced in response to the external perturbation.

Red_r is of the order of Ångströms and will start to contribute significantly when R goes down to 10–30 Å. However there is also an imaginary part connected to d_r (causality) which describes surface absorption coming about because the spatial variation of the induced electromagnetic field at the particle surface (not accounted for in the Mie theory) makes an approach based on the dipole approximation for the total electromagnetic field invalid. This is an extra absorption mechanism and it turns out to dominate over the classical absorption (induced currents scattering against phonons, impurities, etc.) for particles ≤ 100 Å.

Reducing the radius even further we enter a region where again the bulk becomes important in that for $R \lesssim 10$ Å we enter a quantum size effect region where the discrete energy level spectrum makes it possible to set up standing electron-hole pair waves [13] whose existence are determined by the size of the system, *i.e.* R. These QSE influence the particle response to a significant degree and compete with the effect coming from the smooth variation in the dielectric properties at the interface. In the next section we treat the effects of this on the static polarizability and in the following section for the bulk and surface plasmon resonance frequencies. Finally we combine those two measures; the static polarizability with the dynamical surface plasmon oscillation. Gaussian units are used throughout the paper.

2. Static Polarizability and Quantum Size Effects

The dipolar polarizability $\alpha(\omega)$ of a small metal particle with an unspecified, but frequency-dependent, dielectric function $\epsilon(\omega)$ can be written in the form [9,14]

$$\alpha(\omega) = R^3 \frac{(\epsilon(\omega) - 1)(1 - \tilde{d})}{\epsilon(\omega) + 2 + 2(\epsilon(\omega) - 1)\tilde{d}}, \tag{1}$$

where $R^3(\epsilon - 1)/\epsilon + 2$ is the corresponding classical result and the normalized length $\tilde{d}$ is d_r/R, where

$$d_r(\omega)/R = \frac{\int dr\, r(R - r)\delta\rho(r,\omega)}{\int dr\, r^2 \delta\rho(r,\omega)} \tag{2}$$

integrated over all space, is a correction because of the spreading out of the singular classical surface charge at $r = R$, which takes place in a realistic description of a vacuum-metal interface. In Eq. (1) we have neglected the contribution coming from current fluctuations along the surface (d_θ). Those give no contribution for a rotationally invariant sphere surface but play a non-negligible role if surface roughness is present [15]. The surface correction d_r is seen to be expressed in terms of a microscopic quantity, the induced electron density $\delta\rho(r,\omega)$ in response to an electromagnetic perturbation of frequency ω. In this sense different calculations of $\alpha(\omega)$ for a small particle are only different approximations for $\delta\rho$ while they all have to conform to the general structure in Eqs. (1) and (2) which are but only another way of writing Maxwell equations, separating out the classical part through $\epsilon(\omega)$. Red_r is the effective surface position of the particle.

For a metal particle, described by the Drude model,

$$\epsilon(\omega) = 1 - \omega_p^2/\omega^2 \tag{3}$$

(ω_p being the plasma frequency; $\epsilon(\omega_p) = 0$) diverges in the static limit and we can write

$$\alpha(0) = R^3 \frac{1 - \tilde{d}}{1 + 2\tilde{d}} \approx R_{\text{eff}}^3, \tag{4}$$

where

$$R_{\text{eff}} = R - d_r(0).$$

As is evident from Eq. (2) if the indiced density has its main weight outside $r = R$, the classical particle radius, d_r becomes negative and the effective size of the particle $R_{\rm eff}$ is larger than R. To lowest order we can replace d_r by its value $d_\perp$ for a planar surface [11], since as long as $Rk_{\rm F} \gg 1$, $k_{\rm F}$ being the Fermi momentum, we do not expect the electrons involved in setting up the induced density $\delta\rho(r,\omega)$ to be affected to any significant degree by the surface curvature. Indeed for an electron gas with sodium density $d_\perp \approx -1.3$ a.u. [16] is very close to $d_r = -1.182$ a.u. [1]. These considerations give an estimated static polarizability of $\alpha(0) \approx 1.18\alpha_{\rm cl}(0)$ for a 12 Å radius sodium particle. We thus expect a somewhat larger polarizability for a small metal particle than predicted by classical theory. This conclusion is opposite to earlier model calculations [17–19]. However, in these models by construction there is no chance for the induced density to relax outside the classical radius R, by necessity giving an $\alpha(0) < \alpha_{\rm cl}(0) = R^3$. An early non-self-consistent variational calculation [20] and the self-consistent calculations in reference 1 however include this relaxation of the induced charge and do indeed get $\alpha(0) > \alpha_{\rm cl}(0)$.

Thus our simple formula Eq. (1) both contains a microscopic mechanism for making $\alpha(0)$ different from $\alpha_{\rm cl}(0)$ as well as it is able to predict that $\alpha(0)$ has to be larger than $\alpha_{\rm cl}(0)$ since it is a well-known fact from planar surfaces that the induced electronic charge relaxes outwards from the "classical" surface within a realistic description of the metal surface [16]. With reference to a planar calculation we are also able to make a quantitative prediction within a few % of the correct result without actually doing any calculation at all. However we can ask what it is that makes $d_\perp$ larger than d_r. Of course, for very small particles we do indeed expect them to be very different ($Rk_{\rm F} \gg 1$ not fulfilled). But what physical effect can counteract the outward charge relaxation? In the actual numerical calculation one has a discrete excitation spectrum so as the particle gets smaller and smaller, it is no longer the case that $\epsilon(0)$ diverges without lower bound. The situation is similar to a semiconductor system with an excitation gap, consequently having $\epsilon(0)$ finite. An inspection of

Eq. (1) shows at once that a finite $\epsilon(0)$ indeed will decrease the value of $\alpha(0)$ as compared to $\alpha_{\mathrm{cl}}(0)$, and we now proceed to make those general statements a bit more specific. The semiconductor analogy is very close to what happens in a particle being in the QSE regime, since it was shown by Gorkov and Eliashberg [21] that in this limit $\epsilon(0)$ is on a form which is the same as for a semiconductor in the Penn model [22]:

$$\epsilon(0) = 1 + \omega_p^2/\Delta^2. \tag{5}$$

Eq. (5) is the static limit of Eq. (3) extended to include a gap $(\omega^2 \to \omega^2 - \Delta^2)$.

For the small particle the gap depends on the radius since for $R \to \infty$, Δ has to vanish. In other words we choose to write for our discussion the gap on the form

$$\Delta^2 = \omega_p^2 f(R/R_0), \tag{6}$$

where $f(R)$ is a dimensionless function with the property that it vanishes when $R \to \infty$, and R_0 is the length-scale associated with the QSE. An example is [21]:

$$f = (R_0/R)^2, \tag{7}$$

with $R_0 \cong 1.1\sqrt{r_s}\,a_0$, a_0 being the Bohr radius and $r_s a_0$ is the radius of a sphere containing one electron (the electron gas density parameter). Inserting $\epsilon(0)$ from Eq. (5) into Eq. (1) we get for the static polarizability

$$\alpha(0) = \alpha_{\mathrm{cl}}(0)/[1 + (\Delta/\omega_0)^2] \tag{8}$$

letting $d_r = 0$ for the moment, and where $\omega_0^2 = \omega_p^2/3$ is the Mie surface plasmon frequency. It is obvious that the QSE will reduce $\alpha_{\mathrm{cl}}(0)$. An estimate of the reduction for a 12 Å sodium particle is 3%, the reduction increasing rapidly with decreasing radius R. Including also the density profile effects we can write down the following result for the effective radius in Eq. (4):

$$R_{\mathrm{eff}} = R - d_r(0) - R_0^2/R \tag{9}$$

which apparently is like an expansion in $1/R$ if we were to replace d_r by $d_\perp$. Since R_0 and $d_\perp(0)$ are both in the Ångström range this means that for particles where $R \gtrsim 10$ Å the QSE play a very minor role the main effect being d_r. When making our conclusions we have made the implicit statement that $d_r(0)$ is roughly independent of QSE. The argument for this is that since we are at zero frequency there is no standing electron-hole pairs excited and consequently the induced density has only the surface to reside at and this we then approximate with the value taken from the semi-infinite medium which is a reasonable approximation seen in the context of our qualitative approach.

It is interesting however to make an estimate of the QSE on $d_r(\omega)$. As soon as we reach the frequency where we can satisfy the condition for having a standing electron density excitation in the particle we can take the induced density $\delta\rho$ as only corresponding to this part, neglecting all other non-resonant contributions. We also neglect specific surface effects since when we meet the QSE oscillation condition d_r must scale with the size of the system (*i.e.* R) and it is then to lowest order irrelevant what the exact surface position is. For this matter we take $\delta\rho \propto j_l(k_n r)$, the spherical Bessel function of first kind, where the form comes from the general spatial dependence of the dipolar solution inside a sphere and where we use $j_l(k_n R) = 0$, the vanishing of the induced density at the surface of the particle. For the first eigenmode $n = 1$ we then get $d_r = 0.73R$, *i.e.*, the QSE will make the sphere to "shrink" in size at the particular frequency the $n = 1$ electron-hole pair can be excited. Thus a QSE oscillation at a very low frecuency can have an influence on $\alpha(0)$ but it is the task of a more detailed calculation to determine the exact magnitude of this influence as well as the true coefficient in d_r/R.

3. Bulk and Surface Plasmon Peak Positions

When N non-interacting electrons are allowed to interact we get $N - 1$ new single-particle modes and one collective mode, the plasmon [23]. For the finite sphere their spatial extension has to conform with the size of the sphere. This leads to a QSE dependence on both wave functions and energies. Above we discussed the effect of QSE on the electron-hole pair wave functions. Here we will see what happens to d_r when $\delta\rho(r,\omega)$ is the induced density associated with the bulk plasmon excitation. For the semi-infinite solid this plasma oscillation occurs at $\omega = \omega_p$ but is shifted in the case of a small particle. Evidently if we have QSE present the resonance $(\epsilon(\omega) = 0)$ now occurs at $\sqrt{\omega_p^2 + \Delta^2}$ since Eq. (5) has the form

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - \Delta^2} \tag{10}$$

for finite frequencies.

This means that we get a blue-shifted plasmon which in the limit of a very large particle, when $\Delta \to 0$, approaches the ordinary bulk plasma frequency ω_p. In an optical experiment one does not measure ϵ directly, instead one probes $\operatorname{Im}\alpha(\omega)$ in Eq. (1) and we have to see if there is a pole in the vicinity of $\omega = \sqrt{\omega_p^2 + \Delta^2}$ when d_r is present.

In the vicinity of the plasma frecuency the hydrodynamical model which only contains the plasmon as an electronic excitation is believed to be a good approximation for the dielectric response. It has been found earlier that for this model [18]

$$d_r(\omega) = R j_1(\rho)/\rho j_1'(\rho), \tag{11}$$

j_1 being the spherical Bessel function of first kind and $\rho = Rq_L$, q_L being the plasmon wave number:

$$q_L = \sqrt{(\omega^2 - \Delta^2 - \omega_p^2)/\beta^2} = \omega\sqrt{\epsilon}/\beta, \tag{12}$$

β being the dispersion coefficient ($\propto v_F$) and ϵ is given in Eq. (10). When $\epsilon \to 0$, $d_r(\omega)$ in Eq. (11) approaches R, and this means according to Eq. (1) that there is a pole at $\epsilon(\omega) = 0$ in the polarizability, *i.e.* a pole at the blue-shifted plasma frecuency and this has been seen in the detailed calculations in reference 1. However it is a rather weak structure, a reason for this being that the numerator of Eq. (1) is such that this pole has a very weak strength. In what follows we now turn to the surface plasmon, which has a much larger spectral strength than the bulk plasmon and we will study its peak position in frequency with respect to QSE and surface effects. An irradiated small metal particle will exhibit a large resonance absorption at a frequency very close to $\omega_0(\omega_p/\sqrt{3})$, the classical prediction. However there is a definite frequency shift and we will use Eq. (1) together with our QSE model for $\epsilon(\omega)$ in Eq. (10) to investigate this. $\alpha(\omega)$ has a pole at a frecuency ω_R determined from

$$\omega_R^2 = \omega_0^2[1 + 3R_0^2/R + 2d_r/R], \tag{13}$$

where d_r should be evaluated at ω_R and depending on how strong the frequency dispersion of d_r is, this equation might have to be solved by iteration. There is a competition in Eq. (13) between the QSE gap in general leading to a blue-shift while the density effect at the surface generally acts in the opposite direction, if the induced electron density relaxes outward (d_r negative) from the particle with $r = R$ as the reference position. Clearly the red-shift dominates for larger particles ($R > R_0$) while the blue-shift is important for the smaller ones. Of importance here is also, as we concluded in the previous section, if ω_R is close to a resonance condition for a single-particle QSE excitation d_r will act as to reinforce the ordinary blue-shift term, to give an overall blue-shift. Thus there can be interesting variations in ω_R as we move along in R. It is also evident from the contributions to ω_R that it must be very sensitive to whatever is absorbed on the surface of the particle, or the medium adjacent to the particle, since this affects d_r directly.

So far we have in this paper mainly been concerned with shifts, *i.e.* the real part of the response. We also have an imaginary part which manifests itself in broadening of the spectral features we have discussed. We will here make a brief discussion of the limit when the surface and bulk excitations cease to be well-defined physical eigenmodes of the system. Using bulk arguments one has found [24] that when the surface and bulk plasmons with dispersion reach a certain wave vector q_c they will decay into single-particle excitations; they enter the electron-hole pair excitation spectrum. For our modest purposes it is enough to use the simple estimate [25] $q_c \approx \omega_p/v_F$. Now we have shown earlier in reference 9 that the result for the planar surface response can be transferred to the sphere by the replacement $k_{\parallel} \leftrightarrow l/R$ [26], $k_{\parallel}$ being the wave vector parallel to the metal surface. Thus for a sphere of a given R a mode of given l has a wave vector $\approx l/R$ by geometrical necessity [9]. This immediately leads to, if $l \geq l_c = R\omega_p/v_F \approx (R/a_0)/\sqrt{r_s}$ within a factor of order unity, these excitations will have to decay into electron-hole pairs and they start to become so broad that they are no longer well-defined collective excitations. Needless to say this is again in accordance with the numerical work of Ekardt, where for a 12 Å sodium particle it was found that $l_c \approx 8$ [27].

4. Surface Plasmon and Static Polarizability

We now turn to our final discussion topic, the relation between the static polarizability $\alpha(0)$ and ω_R, the surface plasmon frequency. Equation (1) can be rewritten on the form

$$\alpha(\omega) = \alpha_{\rm cl}(0)(1 - \tilde{d})/g(\omega), \tag{14}$$

where we have defined

$$g(\omega) = 3/(\epsilon - 1) + 1 + 2\tilde{d}(\omega). \tag{15}$$

Neglecting the imaginary parts in Eq. (15), since we are primarily interested in the relation between two real quantities where the first term in Eq. (15) provides the main result, $g(\omega)$ is even in ω in what follows. It is evident from a comparison between Eqs. (9) and (13) that the resonance frequency ω_R can be related to the static quantity $\alpha(0)$. The resonance frequency of $\alpha(\omega)$, ω_R is defined by $g(\omega_R) = 0$. Now $\alpha(0) = \alpha_{\rm cl}(0)(1 - \tilde{d}_{\rm o})/g_{\rm o}$, o denoting the $\omega = 0$ result. Adding and subtracting an expansion of $g(\omega) = g_{\rm o} + \omega^2 g_{\rm o}''/2\ldots$, letting $\omega = \omega_R$, we can write

$$\omega_R^2 = \omega_a^2/(\alpha(0)/\alpha_{\rm cl}(0)), \tag{16}$$

where

$$\omega_a^2 = (1 - \tilde{d}_\text{o})/(-g_\text{o}''/2). \tag{17}$$

For our choice of $\epsilon(\omega)$ in Eq. (10) we have $-g_\text{o}''/2 = (1/\omega_\text{o}) - d_\text{o}''$ leading to

$$\omega_R^2 = \omega_\text{o}^2 (R^3/\alpha(0))(1 - \tilde{d}_\text{o})/(1 - \omega_\text{o}^2 \tilde{d}_\text{o}''), \tag{18}$$

where in general $\tilde{d}$ is small so that to a good approximation is ω_R expresable in terms of $\alpha(0)$. Notice that to lowest order the quantum size effects only enter through $\alpha(0)$.

5. Summary

Optical properties of small metal particles is a field which has received lots of interest and where currently much research is done, both theoretically and experimentally. These systems are interesting both by themselves and as model systems to study the influence of surface roughness. They have rather different properties compared to planar surfaces following from the fact that their shape makes it possible to couple to collective surface excitations. The (dipolar) spherical surface plasmon is the dominant feature of their optical absorption spectra. We have considered the dipolar polarizaibility of a jellium sphere expressing it in terms of its bulk dielectric function and a correction coming from the center of gravity of the induced electron density in response to the external field. Further we examined the bulk and surface plasmon poles and their dependence on surface effects and QSE, effects of a discrete excitation spectrum. Then we indicated when they cease to exist over a critical multipole order decaying into electron-hole pairs. We have also considered the static polarizability and its dependence on surface and QSE; the major finding being that it is larger than the classical prediction. This means that the particle appears larger in an electrodynamical sense than classical Mie theory would indicate. Finally we linked the static polarizability and the surface plasmon frequency and in fact to a rather high degree of accuracy the latter dynamical quantity can in fact be obtained directly from the static polarizability.

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