Interface decay channel of particle surface plasmon resonance

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Abstract. Surface plasmon polariton resonance in metallic clusters embedded in a matrix is broadened due to the interface decay channel of the plasmon lifetime. This non-classical broadening effect is caused by adsorbate-induced local density of states near the Fermi level of the cluster. We study theoretically the broadening effect for realistic small noble clusters extending Persson’s theory for adsorbate-induced damping of the plasmon resonance by taking into account the interband transitions in the dielectric function of the cluster. The broadening of the surface plasmon resonance caused by the interface decay channel is significantly influenced by the interband transitions in the metallic cluster.

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1. Introduction

Particle surface plasmon polariton resonance (PSPPR), i.e. collective excitation of conduction electrons in metallic nanoparticles, is a suitable tool for investigations of surface and interface effects in nanoparticle–matrix or cluster–matter systems. In the following, we use the terms nanoparticles and clusters synonymously. Surface and interface effects play an important role in electronic and optical properties of metallic clusters or nanoparticles due to a very large interface area in such systems, the surface-to-volume ratio being proportional to $1/R$, where $R$ is the radius of a cluster. The full-width at half-maximum (FWHM) $\Gamma$ and the frequency $\Omega_{sp}$ of the PSPPR are suitable characteristics for the quantitative study of classical and non-classical interface effects. The frequency $\Omega_{sp}$ is less sensitive for the estimation of non-classical specific interface effects [1, 2]. On the other hand, the FWHM of PSPPR is strongly influenced by various kinds of cluster–matter interface structure [1–4]. This gives a possibility for applications of PSPPR as a sensitive sensor for the surrounding medium as well as for specific interface structures.

If metallic clusters are surrounded by a gas medium, some of the gas molecules are physi- or chemisorbed on the surface of the clusters. At low temperatures, physisorption processes with weaker bonds between the gas molecules and the metallic clusters are more pronounced. When a gas molecule from an ambient medium is situated far enough from the surface of the particle, the overlap between the electronic wave functions of the gas molecule and the wave functions of valence conduction electrons of the metallic particle is very small. In this case, the electronic wave functions of the gas molecule can be considered as well-defined energy eigenstates. During the chemisorption process, the valence-electron eigenstate of a gas molecule is degenerated and shifted and a local projected density of states near the Fermi energy of the metallic particle is induced [5, 6]. The resulting structure of the projected density of states depends on the relative energetic distance between the Fermi level of the metallic particle and the energy level of the valence electron of the adsorbed molecule [7]. This gives a possibility for conduction electrons of the particle to occupy the available positions although these positions are normally separated from the particle’s ‘Fermi sea’ by a barrier, which in turn can be overcome by tunnel effects. After spending some time in these interface regions, electrons can tunnel back to the ‘Fermi sea’. Let us assume that a PSPPR is excited in the metallic particle. Then these electrons will be out-of-phase with other conduction electrons, oscillating as a coherent ensemble driven by the applied electromagnetic field. Thus, a new interface phase decay channel (IDC) of PSPPR is introduced due to adsorbate-induced resonance states. This qualitative picture, also known as a dynamic charge transfer or chemical interface damping (CID), was proposed earlier [1], but still remains quantitatively an unresolved problem, although some attempts were made to get a theoretical description of such effects [1, 2]. If understood quantitatively, this effect can give a deeper insight into physical and chemical phenomena at the interface region between a nanoparticle and a surrounding medium. On the other hand, having a quantitative theory, one can investigate the electronic structure of adsorbate states from optical experimental data, which include PSPPR excitations. If nanoparticles are embedded in some solid matrix where adsorbate atoms are closely packed in an interface layer of complex structure, and where the surrounding matrix has its own electronic band structure, a much more complicated picture can arise due to broad bands of electronic interface states.
Persson [10] developed a theory of adsorbate-induced damping in small metallic particles embedded in a matrix based on the earlier developed theory of resistivity of thin metallic films with adsorbed molecules on the film surface [9]. In his paper, Persson treated a Drude-like dielectric function for the small metallic particle, which is valid only for some alkali elements like Na. For other metals like silver and other noble metals, it is necessary to include the interband transition component in the dielectric function of the metallic particles. In this paper, we give an extension of the jellium-based Persson’s theory [10] including the interband transitions into the dielectric function of the metallic nanoparticles. Furthermore, we treat the problem in a more classical way, avoiding the introduction of a complex quantum ‘self-energy’.

2. Size-dependent dielectric function of a small metallic particle embedded in a matrix

The dielectric function of a bulk metal cannot be used to describe optical or electromagnetic properties of nanoparticles. There are, in principle, many reasons for this, some of them being the quantum confinement of free electrons, size-dependent changes of electronic band structure, changes of optical interband transitions and physisorption/chemisorption/chemical interfacereactions if the particles are imbedded in a matrix [1–3]. There were many theoretical attempts to develop a theory for the dielectric function of small particles from first principles, e.g. by using the time-dependent local density approximation (TDLDA) within the framework of a self-consistent spherical jellium model [1, 2]. Nevertheless, it is still more useful to describe experimental optical spectra of some nanoparticles using a realistic, modified, size-dependent bulk dielectric function, rather than calculating one from first principles, which is restricted to the unrealistic jellium model [1]. Within the framework of Drude–Lorentz–Sommerfeld classical theory, the modified size-dependent dielectric function for a small metallic particle can be obtained, e.g. by solving the equation of motion of a quasi-free electron gas in an external electric field:

\[
m \ddot{r} + \frac{m}{\tau_{\text{bulk}}} \dot{r} + \frac{m}{\tau(R)} \dot{r} = eE, \tag{1}
\]

where \( m \) is the electron mass, \( r \) the position of the electron, \( E = E_0 e^{-i\omega t} \) the applied electric field, \( \tau_{\text{bulk}} \) the relaxation time of the bulk metal, which is mainly due to electron–electron collisions, \( \tau(R) \) the relaxation time due to either the ‘quantum size effect’ [2] or collisions with the surface of the particle, depending on the model applied, and \( R \) the radius of the particle. The validity of the additivity of relaxation terms in equation (1) is due to the independent nature of the relevant relaxation processes. Equation (1) can be rewritten in terms of the velocity of conduction electrons \( \dot{v} = \dot{r} \), which contributes to the current, induced by the applied electric field

\[
\dot{v} + \left( \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau(R)} \right) v = \frac{e}{m} E. \tag{2}
\]
The solution of equation (2) is of the form \( v = v_0 e^{-i\omega t} + \text{c.c.} \). Substituting \( v \) into equation (2) we obtain

\[
\begin{align*}
v &= \frac{e}{m} \frac{E}{\left( \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau(R)} - i\omega \right)},
\end{align*}
\]

(3)

The electric current density \( j = ne\mathbf{v} \) can be written as

\[
\begin{align*}
j &= \frac{ne^2\tau_{\Sigma}}{m} \frac{E}{1 - i\omega\tau_{\Sigma}},
\end{align*}
\]

(4)

where \( 1/\tau_{\Sigma} = 1/\tau_{\text{bulk}} + 1/\tau(R) \). The conductivity \( \sigma \), defined as \( j = \sigma E \), can be obtained from equation (4),

\[
\begin{align*}
\sigma &= \frac{\sigma_0}{1 - i\omega\tau_{\Sigma}},
\end{align*}
\]

(5)

where \( \sigma_0 = ne^2\tau_{\Sigma}/m \) is the dc conductivity. Thus, the total complex-valued size-dependent dielectric function for small metallic particles \( \varepsilon(\omega, R) = 1 + i\varepsilon_0\omega + \chi^{ib}(\omega) \) can be written as

\[
\begin{align*}
\varepsilon(\omega, R) &= 1 - \frac{\omega_p^2}{\omega^2 - i\omega\gamma(R)} + \chi^{ib}(\omega),
\end{align*}
\]

(6)

where the first term is the well-known Drude–Lorentz–Sommerfeld free-electron dielectric function with size correction and the second one is the complex-valued interband contribution, \( \gamma(R) = 1/\tau_{\Sigma} \). The frequency of electron collisions or, alternatively, the quantum size effect, can be written as \( \gamma(R) = \gamma_{\infty} + Av_F/\tau \), where \( \gamma_{\infty} = 1/\tau_{\text{bulk}} \) and \( v_F \) is the Fermi velocity of free electrons. The phenomenologically introduced parameter \( A \) describes size and interface effects in small particles with sizes comparable to the mean free path of the conduction electrons in bulk metal [1]. In equation (6) we neglected an experimentally observed small dependence of interband transitions on the radius of the particle \( \chi^{ib}(\omega, R) \) [4]. In the optical region of PSPPR of metallic clusters \( \gamma(R) \ll \omega \) for \( R \geq 5 \text{ nm} \), and equation (6) can be written as

\[
\begin{align*}
\varepsilon(\omega, R) &\approx \text{Re} \varepsilon(\omega) + i \text{Im} \varepsilon(\omega, R) = \left( 1 - \frac{\omega_p^2}{\omega^2 + \text{Re} \chi^{ib}} \right) + i \left( \frac{\omega_p^2 v_F}{\omega^3} l_\infty + \frac{\omega_p^2 v_F}{\omega^3 R} + \text{Im} \chi^{ib} \right),
\end{align*}
\]

(7)

where \( l_\infty \) is the mean free path of these electrons in the bulk metal. The parameter \( A \) can be written as a sum of two additive terms describing size and interface effects, respectively, \( A = A_{\text{size}} + A_{\text{interface}} \) [1, 12, 13]. We can rewrite equation (7) in another form:

\[
\begin{align*}
\varepsilon(\omega, R) &\approx 1 + \text{Re}[\chi^{\text{bulk}}(\omega) + \chi^{ib}(\omega)] \\
&\quad + i \text{Im}[\chi^{\text{bulk}}(\omega) + \delta\chi^{\text{size}}(\omega, R) + \delta\chi^{\text{interface}}(\omega, R) + \chi^{ib}(\omega)],
\end{align*}
\]

(8)
where

\[ \delta \chi^{\text{size}}(\omega, R) = A^{\text{size}} \frac{\alpha_p^2 v_F}{\omega^3 R}, \]  

(9)

\[ \delta \chi^{\text{interface}}(\omega, R) = A^{\text{interface}} \frac{\alpha_p^2 v_F}{\omega^3 R}. \]  

(10)

Note that, due to approximations, equations (8)–(10) do not contain the slight size dependence of Re \( \varepsilon(\omega) \) which induces a frequency shift of the resonance peak position, and also the slight size dependence of interband excitations [4]. In equations (8)–(10), we see that the real part of the size-dependent dielectric function appears to be independent of the radius of the particle and on the parameter \( A \). On the other hand, the imaginary part of the dielectric function, which defines the broadening due to size and surface/interface effects, depends strongly on the radius and the parameter \( A \), and hence \( \Gamma \) of PSPPR is well suited for studying size and interface effects. It should be mentioned here that the experimental determination of \( A \) can be complicated by inhomogeneous band broadening effects in the particle ensemble. The main object of the present paper is to obtain a correct expression for the parameter \( A^{\text{interface}} \) using the so-called ‘energy loss’ method [10].

3. Light absorption by a spherical metallic nanoparticle embedded in a matrix

Consider a spherical metallic nanoparticle embedded in a homogeneous non-absorbing matrix with a dielectric constant \( \varepsilon_m \). Assume that a plane electromagnetic wave \( \mathbf{E}(\omega) = E_0 e^{-i \omega t} + \text{c.c.} \) with a wavelength much larger than the radius of the particle, \( \lambda \gg R \), irradiates it. Due to the embedding medium, there exists, as described above, an additional interface decay channel, included as an additional term \( \text{Im} \chi^{\text{interface}}(\omega, R) \) in the dielectric function of the particle equation (8). As we are interested here in this additional decay channel, we can rewrite the dielectric function of the particle as the sum of two contributions: the interface susceptibility \( \delta \chi^{\text{interface}}(\omega, R) \) and all other contributions \( \chi^{\text{cluster}}(\omega, R) = \chi^{\text{bulk}} + \delta \chi^{\text{size}} + \chi^{\text{abs}} \):

\[ \varepsilon(\omega, R) = 1 + \chi^{\text{cluster}}(\omega, R) + \delta \chi^{\text{interface}}(\omega, R). \]  

(11)

The time-averaged power absorption in the particle induced by the applied electromagnetic wave is given by

\[ \langle P \rangle_t = \langle I \rangle_t \sigma_{\text{abs}}(\omega, R), \]  

(12)

where \( \langle I \rangle_t = \frac{1}{2} \sqrt{\varepsilon_m} |E_0| \) is the time-averaged intensity of the incident electromagnetic wave and the absorption cross-section is given by [1]

\[ \sigma_{\text{abs}}(\omega, R) = k \text{Im} \alpha(\omega, R) = \frac{\alpha}{c} \varepsilon_m^{3/2} V \frac{\text{Im} \varepsilon(\omega, R)}{[\text{Re} \varepsilon(\omega, R) + 2\varepsilon_m]^2 + [\text{Im} \varepsilon(\omega, R)]^2}, \]  

(13)

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where \( V \) is the volume of the particle and \( c \) the light velocity. Combining equations (11)–(13) we obtain for the time-averaged \( \langle \cdots \rangle \), power absorption [11]

\[
\langle P \rangle_t = \frac{9}{2} \varepsilon_0 \varepsilon_m^2 \omega V |E_0|^2 \frac{\text{Im} \chi^{\text{cluster}}(\omega, R) + \text{Im} \delta \chi^{\text{interface}}(\omega)}{|\varepsilon(\omega, R)+2\varepsilon_m|^2}. \tag{14}
\]

We can rewrite the time-averaged power absorption as two additives

\[
\langle P \rangle_t = \langle P^{\text{cluster}} \rangle_t + \langle P^{\text{interface}} \rangle_t. \tag{15}
\]

### 3.1. Parallel component of the adsorbate-induced damping

An applied electromagnetic field induces an electric current in a spherical metallic particle, which causes power dissipation into the atomic system due to electron–phonon and electron–impurity scatterings, which is described by \( \gamma_\infty \). We are not considering here eddy currents induced in the particle by the magnetic component of the electromagnetic wave. In addition to the usual electron–phonon and electron–impurity dissipations, there is a decay channel of the induced collective motion of conduction electrons caused by interaction of the electrons with adsorbate molecules sitting on the surface of the particle as described in section 2. We are interested here in this additional dissipation and follow in part the procedure of Persson [10]. Consider first the power absorption induced by the electric field component parallel to the surface of the particle. Due to a mutual motion, there is a ‘friction’ force between coherently moving conduction electrons and the adsorbed molecules \( F_\parallel = -M \eta(\omega)v_\parallel \) [10]. Here \( M \) is the mass of the adsorbate molecule, \( \eta(\omega) \) is the frequency-dependent friction coefficient and \( v_\parallel \) is the drift velocity of the electrons. It should be mentioned that the longitudinal dipole PSPPR can be modelled by surface and volume currents. Assuming additivity of the friction dissipation by single adsorbates, the time- and surface-averaged \( \langle \cdots \rangle_{t,s} \) power absorption caused by \( N \) adsorbates is \( \langle P \rangle_{t,s} = N \langle F_\parallel v_\parallel \rangle_{t,s} \). The velocity of the tangential drift motion of conduction electrons \( j_\parallel = \sigma(\omega)E_\parallel = -nev_\parallel \) induced by the applied electric field parallel to the surface of the particle \( E_\parallel \) is given by

\[
v_\parallel = \frac{i \omega \varepsilon_0 (1 - \varepsilon(\omega))}{ne} E_\parallel, \tag{16}
\]

where we used the fact that \( \varepsilon(\omega) = 1 + i\sigma/\varepsilon_0 \omega \), which follows from the Maxwell equation

\[
\Delta \times H = \frac{\partial D}{\partial t} + j. \tag{17}
\]

Substituting the expression for the dielectric function equation (6), with the assumption \( \gamma(R) \ll \omega \) being valid in the optical spectral range of PSPPR, into equation (16) we obtain

\[
v_\parallel = -\frac{i \omega \varepsilon_0}{ne} \left( \frac{\omega_p^2}{\omega^2} - \frac{\text{Re} \chi^{ib}}{\omega_p^2} \right) E_\parallel. \tag{18}
\]
Solving the Laplace equation with appropriate boundary conditions, one obtains an expression for the internal electric field just inside the spherical particle and parallel to its surface

$$E_{\parallel} = \frac{3\varepsilon_m}{\varepsilon(\omega, R) + 2\varepsilon_m} \sin \theta E_0 e^{-i\omega t},$$

(19)

where $E = E_0 e^{-i\omega t}$ is the external electric field and $\theta$ the polar angle between the applied field $E$ and a surface point where we are determining the induced field $E_{\parallel}$. Combining equations (16), (18) and (19) we can write the total surface- and time-averaged absorption caused by the friction of the electron flow with the adsorbed molecules on the surface of the particle

$$\langle P \rangle_{t,\parallel} = \frac{1}{3} NM |E_0|^2 \varepsilon_0^2 \omega^2 \left( \frac{\omega_p^4}{\omega^4} - 2 \frac{\omega_p^2}{\omega^2} \text{Re} \chi^{ib} + (\text{Re} \chi^{ib})^2 \right) \text{Re} \eta(\omega).$$

(20)

Comparing equation (14) with equation (20) one can directly obtain an expression for the imaginary part of the interface susceptibility

$$\text{Im} \delta \chi^{\text{interface}}_{\parallel}(\omega) = \frac{NM \varepsilon_0 \omega}{2\pi R^3 n^2 \varepsilon^2} \left( \frac{\omega_p^4}{\omega^4} - 2 \frac{\omega_p^2}{\omega^2} \text{Re} \chi^{ib} + (\text{Re} \chi^{ib})^2 \right) \text{Re} \eta(\omega).$$

(21)

Substituting into equation (21) the number of adsorbate atoms per unit area, $n_a = N/4\pi R^2$ and introducing the cross-section $\sigma_{\text{diff}}(\omega)$ for the diffuse scattering of an electron from the adsorbed molecule [9]

$$\text{Re} \eta(\omega) = \frac{3}{16} \frac{mn_F}{M} \sigma_{\text{diff}}(\omega),$$

(22)

we can rewrite the formula for the interface susceptibility as follows:

$$\text{Im} \delta \chi^{\text{interface}}_{\parallel}(\omega) = \frac{3}{8} n_a \frac{v_F}{R} \omega_p^2 \omega^3 \left( 1 - 2 \frac{\omega_p^2}{\omega^2} \text{Re} \chi^{ib} + \frac{\omega_p^4}{\omega^4} (\text{Re} \chi^{ib})^2 \right) \sigma_{\text{diff}}(\omega).$$

(23)

Comparing now equation (23) with equation (10) we obtain the formula for the parameter $A^{\text{interface}}_{\parallel}$:

$$A^{\text{interface}}_{\parallel} = \frac{3}{8} n_a (1 - \Delta) \sigma_{\text{diff}}(\omega),$$

(24)

where

$$\Delta = \chi^{ib} \left( 2 \frac{\omega^2}{\omega_p^2} - \frac{\chi^{ib} \omega_4}{\omega_p^4} \right).$$

(25)
We are interested in the interface effects, which cause the damping of PSPPR in the optical region. Hence, substituting the frequency of PSPPR $\Omega_{sp} = \omega_p/\sqrt{1 + 2\varepsilon_m + \text{Re} \chi^{ib}}$, we obtain

$$\Delta(\Omega_{sp}) = \chi^{ib}(\Omega_{sp}) \frac{\chi^{ib}(\Omega_{sp}) + 4\varepsilon_m + 2}{(\chi^{ib}(\Omega_{sp}) + 2\varepsilon_m + 1)^2}$$

(26)

and

$$\text{Im} \delta\chi^{\text{interface}}(\Omega_{sp}) = \frac{3}{8} n_a \frac{v_F}{R\Omega_{sp}} \frac{(1 + 2\varepsilon_m)^2}{(1 + 2\varepsilon_m + \text{Re} \chi^{ib})^2} \sigma_{\text{diff}}(\Omega_{sp}).$$

(27)

Substituting equation (26) into equation (24), we obtain the expressions for the $A_{\parallel}^{\text{interface}}$ parameter at the frequency of PSPPR

$$A_{\parallel}^{\text{interface}}(\Omega_{sp}) = \frac{3}{8} n_a \frac{(1 + 2\varepsilon_m)^2}{(1 + 2\varepsilon_m + \text{Re} \chi^{ib})^2} \sigma_{\text{diff}}(\Omega_{sp}).$$

(28)

3.2. Cross-section of electron scattering from an adsorbed molecule on a metallic surface

In order to calculate the parameter $A_{\parallel}^{\text{interface}}$, one first has to calculate the diffusive cross-section $\sigma_{\text{diff}}(\omega)$ of electron scattering from adsorbed molecules situated on the metallic surface of the cluster. We will discuss now some details of the adsorption process of a foreign atom or molecule on a metallic surface. Consider a molecule or an atom, which is held at a distance more than a few atomic diameters from the metallic surface (see figure 1(a)). We are interested in the potential energy of an electron moving along a line perpendicular to the metallic surface and passing through the core of the foreign atom. Curve 1 of figure 1(a) represents this potential energy obtained with Bloch’s model for the metal and curve 2 obtained with the simplified Sommerfeld model. We assume first that the atom has a valence electron with the energy level situated near the Fermi level of the metal. This is the case for most alkali and alkali earth metals. In order to obtain the allowed energy levels of the electron in such a system, the potential energy depicted in figure 1(a) should be inserted into the Schrödinger equation and the equation solved. For a preliminary treatment, it is sufficient to replace the ‘potential box’ provided by the core of the adsorbed atom by a simpler rectangular box (see curve 3 in figure 1(a)). If we solve the Schrödinger equation we obtain a set of allowed levels, which belong jointly to the metal and to the atom [7] (see figure 1(a), curve 3 and figure 1(b)). In other word, there arises a local projection of a density of states (PDOS) around the adsorbate atom. When the atom approaches the metal surface, the induced density of states will be broadened and shifted (see figure 1(b)). The local projection of the density of states around the adsorbate may be described by a simple Lorentzian

$$\rho_a = \frac{1}{\pi} \frac{\Gamma_a/2}{(E - E_a)^2 + (\Gamma_a/2)^2},$$

(29)

where $\Gamma_a$ is the line width. We have to notice that the Lorentz-like description of the PDOS (equation (28)) is only approved for a qualitative treatment of the interface decay channel.
Figure 1. (a) Profile of the potential energy for an electron at the surface of a metal along a line passing through the core of an adsorbed atom. Curve 1, Bloch model; curve 2, Sommerfeld model for the metallic lattice; curve 3, simplified rectangular potential box of the adsorbed atom. (b) Broadening and shifting of PDOS of an adsorbed atom during an adsorption process.

In order to get quantitative results, one needs more realistic data for PDOS taken, e.g. from \textit{ab initio} calculations \[19\]. Due to the non-availability of such data, only a qualitative treatment of the interface decay channel has been possible to date. The diffuse cross-section of electron scattering from the adsorbed atom given by equation (22) can be written as \[10\]

\[
\sigma_{\text{diff}}(\omega) = \sigma_0 J(\omega),
\]

(30)

where

\[
\sigma_0 = \frac{64 \omega_F Q}{3\pi n v_F},
\]

(31)

and $\hbar \omega_F = E_F$ is the Fermi energy; the number $Q$ depends on the symmetry of the adsorbate resonance state, i.e. $Q = 0.2$ for $s$- or $p_z$-symmetry, while $Q \approx 0.33$ for $p_x$- or $p_y$-symmetry.
Figure 2. The function $J_\parallel(\omega)$ for adsorbed molecule on a silver surface ($E_F = 5.45 \text{ eV}$) with the width $\Gamma = 1 \text{ eV}$ and resonance energies $E_a$.

The frequency-dependent function $J(\omega)$ in equation (29) is given by

$$J(\hbar\omega) = \frac{\pi}{4\varepsilon_F\hbar\omega} \int_{E_F-h\omega}^{E_F} dE [E\Gamma_a\rho_a(E + \hbar\omega) + (E + \hbar\omega)\Gamma_a\rho_a(E)].$$

(32)

The adsorbate-induced resonant states provide a possibility for conduction electrons of the metallic particle to invade these available levels. After spending some time in this region, the electron returns to the particle but it will be out-of-phase with the collective coherent motion of electrons, which constitute the surface plasmon. Thus, the adsorbed molecules provide an additional IDC, which is responsible for the broadening of PSPPR in metallic nanoparticles embedded in a matrix.

The function $J(\omega)$ calculated for a silver metallic surface with $E_F = 5.48 \text{ eV}$ and for different adsorbate molecules with resonant local states $E_a$ relative to $E_F$ is shown in figure 2. We assumed the same resonance width $\Gamma = 1 \text{ eV}$ for different adsorbates. The two variables, which define the electron scattering cross-section $\sigma_{diff}(\omega)$ from the adsorbate molecule and therefore the parameter $A_{interface}$ are the position $E_a$ and the width $\Gamma_a$ of the adsorbate-induced resonance local density of states. It is instructive to study the influence of these parameters on the function $J(\omega)$ for $\hbar\omega = h\Omega_{sp}$ and $\omega = 0$ (which define the dc conductivity of a thin film with adsorbate molecules). The function $J(h\Omega_{sp} = 3.3 \text{ eV})$ is shown in figure 3 for different energies of the adsorbate $E_a - E_F$ and for different adsorbate widths $\Gamma_a$. For the case of small resonance width $\Gamma_a \leq 2 \text{ eV}$, we can distinguish a step-like function $J(h\Omega_{sp})$ with two different values for adsorbate energies $E_a - E_F < h\Omega_{sp}$ and for $E_a - E_F > h\Omega_{sp}$. The reason for such a behaviour is the following. If the energy of PSPPR is larger than the relative energy of the adsorbed molecule, $h\Omega_{sp} > E_a - E_F$, then an electron can acquire enough energy to temporarily occupy this available energetic position and after some time spent in this adsorbate-induced local density of states the electron comes back to the cluster but it loses the phase with other electrons moving coherently and constituting

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the PSPPR. This mechanism defines the IDC in metallic clusters embedded in a matrix. If the adsorbate molecule induces a local density of states with the relative energy larger than the energy of the PSPPR, \( E_a - E_F > \hbar \Omega_{sp} \), then the probability of occupying such a position is much smaller, and the function \( J(\hbar \Omega_{sp}) \) decreases to zero, i.e. \( \sigma_{\text{diff}}(\hbar \Omega_{sp}) \to 0 \) and the IDC becomes unimportant. For more broadened adsorbate-induced resonance density of states, \( \Gamma_a > 2 \text{ eV} \), the \( J(\hbar \Omega_{sp}) \) function becomes monotonic since for such a resonance width the tail of the local density of states overlaps with the occupied conduction band of the particle. The static function \( J(0) \), which defines the dc conductivity of a thin metallic film, is shown in figure 4 for different adsorbate widths \( \Gamma_a \). When an adsorbed molecule has a valence level corresponding to the metal \( E_a - E_F \leq 0 \), the function \( J(0) = 1 \). This is the case, e.g. for silver atoms on a silver surface. For adsorbed atoms with a valence level above the Fermi level, \( E_a > E_F \), the function \( J(0) \to 0 \).

3.3. Perpendicular component of adsorbate-induced damping

The next step in accounting for adsorbate-induced damping in small metallic clusters which are embedded in a matrix is the time- and surface-averaged power absorption \( \langle P_{\perp} \rangle_{t,r} \) caused by an electric field component perpendicular to the surface of the cluster. By analogy with equation (19), the perpendicular component of the electric field just outside the surface of the particle \( r \approx R \) can be obtained from the Laplace equation

\[
E_{\perp} = \frac{3\varepsilon(\omega, R)}{\varepsilon(\omega, R) + 2\varepsilon_m} \cos \theta E_0 e^{-i\omega t}.
\]

The time- and surface-averaged power absorption \( \langle P_{\perp} \rangle_{t,r} = \frac{1}{2} \varepsilon_0 \sqrt{\varepsilon_m} \langle |E_{\perp}|^2 \rangle_{t,r} \sigma_{\text{abs}}(\omega) \) caused by \( N \) adsorbed molecules located on the surface of a cluster and each having polarizability \( \alpha_{\perp} \).
Figure 4. The function $J_{\perp}(\omega = 0)$ for an adsorbed molecule on a silver surface $E_F = 5.45$ eV with different widths $\Gamma$ and resonance energies $E_a$ of the adsorbate-induced resonance density of states.

is then given by

$$\langle P_{\perp} \rangle_{r,t} = \frac{N}{6} \varepsilon_0 \varepsilon_m \left[ \frac{3\varepsilon(\omega, R)}{\varepsilon(\omega, R) + 2\varepsilon_m} \right]^2 |E_0|^2 \text{Im} \alpha_{\perp}. \quad (34)$$

Comparing equation (34) with $\langle P_{\text{interface}} \rangle_{t}$ in equation (15) we obtain the expression for the interface susceptibility

$$\text{Im} \delta \chi_{\perp}^{\text{interface}} = \frac{N}{3 \varepsilon_m V_0} |\varepsilon(\omega, R)|^2 \text{Im} \alpha_{\perp}(\omega). \quad (35)$$

Introducing the surface density of adsorbed molecules on the surface of the cluster $n_a = N/4\pi R^2$ one can write

$$\text{Im} \delta \chi_{\perp}^{\text{interface}} = \frac{n_a}{R} \frac{|\varepsilon(\omega, R)|^2}{\varepsilon_m} \text{Im} \alpha_{\perp}(\omega). \quad (36)$$

The condition for the existence of dipolar PSPPR in a metallic cluster is $\text{Re} \varepsilon = 2\varepsilon_m$. Assuming $\text{Im} \varepsilon(\Omega_{sp}) \ll \text{Re} \varepsilon(\Omega_{sp})$, which holds in the spectral region of interest ($3.0 \text{ eV} < \hbar \Omega_{sp} < 3.8 \text{ eV}$), we have $|\varepsilon(\omega, R)|^2 \approx 4\varepsilon_m^2$ and then

$$\text{Im} \delta \chi_{\perp}^{\text{interface}}(\Omega_{sp}) = 4\varepsilon_m n_a \frac{n_a}{R} \text{Im} \alpha_{\perp}(\Omega_{sp}). \quad (37)$$

Comparing equation (37) with equation (10) we can obtain the formula for the parameter $A_{\perp}^{\text{interface}}$,

$$A_{\perp}^{\text{interface}} = 4n_a \frac{\varepsilon_m \Omega_{sp}}{h \nu_F} \frac{\text{Im} \alpha_{\perp}(\Omega_{sp})}{(1 + 2\varepsilon_m + \text{Re} \chi^{ib})}. \quad (38)$$
The imaginary part of the adsorbate polarizability $\text{Im} \alpha(\omega)$ can be written as [10]

$$\text{Im} \alpha(\omega) = 2\pi(e d)^2 \int_{E_F - \hbar \omega}^{E_F} dE [\rho_a(E) \rho_a(E + \hbar \omega)],$$

(39)

where $d$ is the distance between the centre of the adsorbed molecule and the image plane of the metallic surface.

4. Conclusions

Figure 5 depicts the calculated parameter $A_{\parallel}^{\text{interface}}$ (eV Å) for silver clusters as a function of the dielectric constant of the embedding matrix and the difference between the adsorbate-induced resonance state $E_a$ and the Fermi level $E_F = 5.5$ eV for conduction electrons of the silver clusters. We assumed, for some arbitrary material, the width of the adsorbate-induced PDOS $\Gamma_a = 4$ eV, which appears to be a reasonable value from ab initio calculations [19]. Figure 6 depicts the same calculations for the perpendicular component $A_{\perp}^{\text{interface}}$ (eV Å). We can conclude that the influence of the perpendicular component $A_{\perp}^{\text{interface}}$ is at least ten times smaller than the corresponding parallel parameter $A_{\parallel}^{\text{interface}}$, which is in agreement with the previous calculations [10]. Let us therefore estimate the parameter $A_{\parallel}^{\text{interface}}$ for a Ag/CO cluster–matrix interface. The dielectric function for the CO matrix was $\varepsilon_m \approx 2$. Assuming $E_a - E_F = 2$ eV and $\Gamma_a = 4$ eV, we obtain
Figure 6. Calculated $A^{\text{interface}}$ for Ag clusters as a function of the dielectric constant of the embedding matrix and the difference between the adsorbate-induced resonance state $E_a$ and the Fermi level $E_F = 5.5$ eV for conduction electrons of the silver clusters. The width of the adsorbate-induced PDOS $\Gamma_a = 4$ eV.

$A^{\text{interface}}$ = 2.35 eV Å which is still smaller than the experimental value of $A^{\text{interface}}$ $\approx$ 6.2 eV Å [17]. The discrepancy may be attributed to the absence of exact data for the PDOS of adsorbed molecules on a metallic surface. As one can see from figures 2–5, the value of the parameter $A^{\text{interface}}$ is strongly influenced by the position and width of the induced adsorbate density of states. Therefore, the exact data of the PDOS for a particular cluster–adsorbate system, which may have a much more complicated structure when compared with a simple Lorentz-like resonance state, can give a correct value for the parameter $A^{\text{interface}}$. In conclusion, we developed an extension of Persson’s theory of adsorbate-induced damping of the surface plasmon polariton resonance in metallic clusters for realistic metals by including the interband transitions in the dielectric function of the clusters. We obtained a correction term in the formula for the parameter $A^{\text{interface}}$, which depends on the frequency and the dielectric permittivity of the dielectric-embedding medium. Taking account of interband transitions leads to a decrease in the parameter $A$, i.e. of the electron relaxation frequency, which contributes to the Mie bandwidth $\gamma = \gamma_0 + Av_F/R$, and therefore it leads to a narrower Mie resonance when compared with a free-electron metal cluster. This result is in agreement with general trends of the Mie resonance. The full-width at half-maximum of the Mie resonance is given by [20]

$$\Gamma(R) = \sqrt{\frac{2 \text{Im} \, \varepsilon(\Omega_{sp}, \gamma(R))}{\left| \frac{d \text{Re} \, \varepsilon}{d\omega} \right|_{\Omega_{sp}}^2 + \left| \frac{d \text{Im} \, \varepsilon}{d\omega} \right|_{\Omega_{sp}}^2}(1 + \eta)}.$$  

A low value of the derivative $d(\text{Re} \, \varepsilon(\omega))/d\omega$ leads to a broad Mie resonance, while larger values tend to contribute to a narrower peak. The contribution from the interband transitions
to the dielectric function of a silver nanoparticle leads to a decrease in the parameter $A_{\text{interface}}$ and a steeper curve of the real part of the dielectric function, and thus to a larger derivative $d(\text{Re } \varepsilon(\omega))/d\omega$.

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