Polarizability of truncated spheroidal particles supported by a substrate: model and applications

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Abstract. The light scattering by three-dimensional clusters supported by a substrate is modelled by representing clusters by truncated spheroids whose polarizability is calculated via a multipolar development of the potential in the quasi-static limit. The determination of the mean island radius, density and aspect ratio from the optical response is examined. The strong influence of both the particle-substrate interaction and the particle shape on the optical behaviour is demonstrated, showing the limits of effective medium and dipolar theories. The Surface Differential Reflectance spectra of silver on MgO(100) and titanium or aluminium on α-Al₂O₃(0001) surfaces have then been modelled by using the above model, illustrating the capability of optical means to deal with various metals, including those belonging to transition series. In all cases, it is highlighted that the aspect ratio is central in modelling the optical response of supported particles.

PACS. 78.20.Bh Theory, models, and numerical simulation – 73.20.Mf Collective excitations (including excitons, polarons, plasmons and other charge-density excitations) – 68.55.Ac Nucleation and growth: microscopic aspects

1 Introduction

Light scattering from small particles is at the origin of many colors effects in nature and affects many reflection-transmission-absorption behaviours. For those reasons, it has received a tremendous attention in the past four decades, both experimentally and theoretically [1], in particular for silver and alkali metals whose behaviour is accurately accounted for by means of the free-electron gas theory. Light scattering offers elegant and non-destructive means to probe particles in very versatile conditions of environment in either vacuum, gas or transparent liquid. In particular, for the study of supported aggregates during either chemical vapor deposition or metal deposition, Surface Differential Reflectance (SDR) has proved to allow for an in situ and in real time characterization of the cluster size, density and aspect ratio via high quality optical spectra, even within the submonolayer range [2–4].

The crucial point is to unambiguously identify the spectral features and to quantitatively interpret the optical data. The effective medium theories, such as Maxwell Garnett or Bruggeman model, fail to describe the experimental spectra in details. Indeed, they assume a strongly simplified picture for the supported particles. In particular, the interaction with the substrate is treated by embedding the particle in an effective medium whose dielectric constant is between that of vacuum and that of the substrate. Yamaguchi et al. [5,6] have first set up an approach including the substrate-induced breaking of symmetry. In their model, each particle is replaced by a point-dipole and its electrostatic image in the substrate. The renormalized polarizability is then obtained by summing the contributions of all the local fields of neighbours and images. However, this description does neither account for the shape of the particle nor for the multipolar coupling with the substrate, which have both been shown to dramatically affect the optical response of supported clusters.

A more sophisticated picture of interacting supported particles can be achieved by means of the theoretical approach of the Fresnel coefficients of a thin film which has been developed by Bedeaux and Vlieger [7–12]. The thin film is represented by a boundary layer lying between two bulk media whose thickness is supposed to be small enough with respect to the wavelength of light for the non-retarded limit to hold. The optical response of this layer is treated by bringing back to the surface, as Dirac terms, all the integrated excess fields from the simple
Fresnel behaviour. The surface being non-magnetic, four coefficients, called surface susceptibility, \( \gamma_e, \beta_e, \tau \) and \( \delta \) are introduced. The reflection and transmission amplitudes, the ellipsometric coefficients can be expressed in terms of these parameters. The susceptibilities \( \gamma \), which gives the integrated surface polarization parallel to the surface in term of the electric field along the surface, and \( \beta \), which relates the integrated surface polarization normal to the surface in terms of the electric displacement field normal to the surface are given as functions of the exact local dielectric constant \( \varepsilon(z) \) along \( z \) by:

\[
\gamma_e = \int_{-\infty}^{+\infty} [\varepsilon(z) - \varepsilon^+ \theta(-z) - \varepsilon^+ \theta(z)] dz, \quad (1.1)
\]

\[
\beta_e = -\int_{-\infty}^{+\infty} [1 - \varepsilon^+ \theta(-z) + \varepsilon^+ \theta(z)] dz, \quad (1.2)
\]

where \( \theta(z) \) is the Heaviside function and \( \varepsilon^+ \) and \( \varepsilon^- \) are the dielectric functions of the two surrounding media. There is a clear connection with the non local dielectric tensor introduced by Barrera et al. [13] for the description of the anisotropic response of a metallic surface in the jellium approximation. The others coefficients \( \tau \) and \( \delta \), which are of second order with respect to the ratio between the thickness of the layer and the wavelength, can be neglected herein. The parameters \( \gamma \) and \( \beta \) are related to the islands polarizabilities parallel and perpendicular to the surface. All the measurable quantities are independent of the choice of the dividing surface so that invariant combinations of them can be introduced as suggested first by Lekner [7,14]. The calculation mostly consists in determining the island polarizability by accounting for all the above-mentioned interactions.

The choice for the particle geometry was currently limited to that of truncated spheres on a substrate [15–17]. However, the model could hardly be run for high aspect ratio, i.e. for spherical caps, because of matrix conditioning [15]. Although this geometry offers a realistic representation of the particles at thermodynamic equilibrium, it does not allow to picture neither partial wetting nor growth modes dominated by kinetics [18]. It is anticipated that a much greater variety of thin films could be represented by approximating particles by truncated spheroids. The aim of the paper is to calculate the polarizability of such objects and to illustrate the capability of the method to deal with experimental cases. The paper is organized as follows. Section 2 is dealing with the calculation of the polarizability of an isolated particle in interaction with the substrate via a spheroidal expansion of the potentials. The expansion coefficients which are then determined can be related to measurable quantities which characterize the optical response. In Section 3 the formalism is applied to differential reflectivity spectra collected in situ during the formation of thin films in the cases of silver on MgO(100), and titanium or silver on \( \alpha \)-Al\(_2\)O\(_3\) (0001).

2 Polarizability of a truncated spheroid

Truncated spheroids, either prolate or oblate, that are symmetric around an axis of revolution normal to the surface of the substrate with its centre either above (island) or below (cap) the substrate, are depicted in Figure 1. The reason to distinguish between islands and caps lies in the expression of the potentials. The symmetry of the problem implies the use of spheroidal coordinates \( (\xi, \eta, \phi) \) [19] defined in more details in Appendix A. It is convenient to locate the origin \( O \) for this spheroidal coordinate system at the centre of the spheroid. In addition, an other spheroidal coordinate system \( (\xi', \eta', \phi') \), whose origin \( O' \) is at the image point of the centre of the spheroid with respect to the surface of the substrate, is introduced. The appropriate changes of variables between these two systems, as well as with the Cartesian system, are given in Appendix A. The Cartesian system \( S \) has its origin \( O \) at the centre of the spheroid with the \( z \)-axis pointing downwards into the substrate. The quantity \( a \) stands for the radius of the ring of foci. The surface of the spheroid corresponds to \( \xi = \xi_0 \) whereas \( z = a\xi\eta = \pm d = \pm a\xi_0 \) defines the surface of the substrate (+ for an island and − for a cap) which separates the vacuum (medium 1) from the substrate (medium 2) and supports the particle (medium 3). For calculation convenience, the buried part of the particle appears as a different medium 4. The limits in spheroidal coordinates of the various domains are given in Appendix A. A dielectric constant \( \varepsilon_t(\omega) \) is assigned to each medium \( i = 1, 2, 3, 4 \).

Several parameters are used to characterize the shape of the particle and its position with respect to the substrate. The axial ratio, \( a_t = R_{z_1}/R_{z_2} \), of the spheroid is the ratio of the parallel radius \( \left( R_{z_2} \right) \) over the normal radius \( \left( R_{x_2} \right) \). A useful quantity which maps all the possible axial ratios onto the interval \([0,1]\) is defined by \( x = 1/(1 + a_t) \).

The truncation parameter \( t_r \) is defined by:

\[
t_r = \frac{d}{R_{z_1}} = \frac{d}{a_\xi} \quad \text{with} \quad 0 \leq t_r \leq 1 \quad \text{(2.1)}
\]

where \( R_{z_1} \) is the radius along the surface normal \( (R_{z_1} = R_{x_1} \text{ for oblate or prolate particle}) \) and \( d \) is the distance from the centre of the spheroid to the surface of the substrate. In all formulae, \( t_r \) is defined as a positive number. However, in figures, to clarify the presentation of data, negative values of \( t_r \) are associated with the spheroidal cap case. For example, \( t_r = -1 \) describes a completely buried particle. Finally, the aspect ratio, \( s_r \), is defined as the cluster diameter seen from above (as in most of the experimental diameter determinations by microscopy techniques) divided by its height \( h = R_{z_1} (1 \pm t_r) \), i.e.:

\[
s_r = \begin{cases} \frac{2a_t}{1 + t_r} & \text{island}, \\ \frac{2a_t}{\sqrt{1 + t_r}} & \text{cap}. \end{cases} \quad \text{(2.2)}
\]

The isovalues of \( s_r \) in logarithmic scale are presented in Figure 2, where the various regions for oblate or prolate island or cap are indicated.