Characterization of metallic nano-particles via surface wave scattering: B. Physical concept and numerical experiments

Mustafa M. Aslan\textsuperscript{a}, M. Pinar Mengüç\textsuperscript{a,\*}, Gorden Videen\textsuperscript{b}

\textsuperscript{a}Radiation Transfer Laboratory, Department of Mechanical Engineering, University of Kentucky, Lexington, KY 40506-0108, USA

\textsuperscript{b}US Army Research Laboratory AMSRL-Cl-EE, 2800 Powder Mill Road, Adelphi, Maryland 20783-1197, USA

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Abstract

We present a methodology to characterize nanometer-size particles on or near a surface via surface-wave scattering. With a series of simulations, we show that the size of nano-particles on a metallic surface can be determined unambiguously from the angular profile of the elliptical polarization of scattered waves expressed as normalized scattering Mueller matrix elements $M_{ij}$. This characterization modality is based on the interaction of particles on a surface with the evanescent waves. The particle–surface interactions become less pronounced with separation distance, and the scattering of evanescent waves by nano-particles does not show any significant size dependence. The results suggest that it is possible to monitor the self-assembly process of metallic particles on metallic surfaces in real time, which is crucial for on-line control in bottom-up nano-manufacturing processes.

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1. Introduction

Nano-particles (1–100 nm in effective diameter) are known for their unusual properties that are due mostly to their small sizes and high percentage of atoms in surface states, which yield unique
properties that differ from those of the same bulk materials [1–4]. Using metallic nano-particles or colloids, it is possible to obtain unprecedented optical, electrical, and structural properties if the composition, structure, shape, and size distribution of nano-building-blocks can be controlled during fabrication. Yet, to be able to engineer bottom-up processes at nanoscale, new approaches need to be developed for measurement and visualization of these particles and structures. Furthermore, such measurements must be incorporated as real-time diagnostic tools for reliable manufacturing applications.

Even though light is used routinely for non-intrusive characterization and visualization of structures and surfaces in real time, it cannot be adapted readily for the identification of nano-structures. The wavelengths of typical light/laser sources available on the market are usually hundreds of times larger than the size of the nano-particles that need to be characterized. Consequently, traditional light scattering/absorption techniques cannot infer the detailed and accurate size and structural information of such small particles.

In this paper, we introduce a different methodology to determine the size and structure of nano-particles. We present an analysis, dubbed elliptically polarized surface-wave scattering (EPSWS) approach, to show that 5–10 nm size particles on or above an interface can be characterized by using the information contained in the scattered evanescent waves. These evanescent waves and surface plasmons are the result of total internal reflection that takes place at the opposite side of the medium from incident light [5,6]. If there are any particles within the reach of the surface waves, the energy is tunneled to the particle and then scattered. An experimental study by

### Nomenclature

- \( a \): diameter of the spherical metallic particle
- \( d \): distance between the center of the particle and the metallic surface
- \( E_{\text{inc}} \): incident electromagnetic radiation vector
- \( E_{\text{sca}} \): scattered electromagnetic radiation vector
- \( h \): thickness of metallic film
- \( I_{\text{inc}} \): normalized electromagnetic wave intensity
- \( I_{\text{sca}} \): stokes vector of scattered light
- \( I_{\text{inc}} \): stokes vector of incident light
- \( k \): wave number
- \( M_{ij} \): normalized scattering matrix elements of the metallic particle
- \( m_i \): complex refractive index of medium \( i \)
- \( n_i \): real part of refractive index \((m)\) of medium \( i \)
- \( r \): distance between the particle and the detector
- \( z_i \): incident angle in medium \( i \)
- \( \mathbf{S} \): scattering matrix
- \( S_{ij} \): scattering matrix elements of the metallic particle
- \( S_l \): the scattering amplitudes \((l = 1, 2, 3 \text{ and } 4)\)
- \( \lambda \): wavelength of incident radiation
- \( \theta_s \): scattering angle
Sterligov et al. [7] indicated that the nano-size particles on a surface can scatter evanescent waves and may cause a change in the polarization of the incident light. However, no potential characterization methodology was offered.

Here, we present a detailed analysis of the problem, based on the theoretical formulation reported in Part A [8], to show that the scattering matrix elements of the evanescent waves scattered by the nano-particles on or near an interface can be used for characterization of such particles. The theory presented in [8] is sufficiently general that the particles can be composed of inhomogeneous material or comprised of multiple sub-particles. In the formulation, only the particle’s scattering response matrix, or $T$-matrix, is required, which can be obtained independently.

In several previous studies, we have shown that characterization of small particles and agglomerates can be described efficiently through polarized light scattering [9–11]. Four scattering matrix elements, $S_{11}$, $S_{12}$, $S_{33}$ and $S_{34}$ are particularly important for this purpose. In the present study, we show for the first time that these patterns are also crucial for characterization of nano-size particles based on scattering patterns of evanescent waves.

2. Surface-wave scattering model

If an electromagnetic wave is incident on an interface at angles larger than the critical angle, we observe total internal reflection (TIR). Even though TIR can be conceptualized using simple Snell’s law, the underlying physics behind it is much richer [6,13] The boundary conditions for the EM-waves at the interface can be satisfied only if the transmitted component is taken into account. Under these conditions, the electric field for the transmitted wave is written as [5]

$$E_1(x_0, \lambda) = E_o(x_0) \left( \exp\left(\frac{-4\pi n_1 z}{\lambda}\right) \sqrt{\left(\frac{n_0}{n_1}\right)^2 \sin^2 x_0 - \left(\frac{n_2}{n_1}\right)^2} \right),$$

where $E_0$ is the amplitude of the EM wave incident on the interface (the time dependence is neglected for brevity). This equation suggests that there is a surface wave along the interface, which decays exponentially. The characteristic length scale for such a decay can be obtained as $z_{\text{characteristic}} = 1/G^{0.5}$, where $G = \left[\left(\sin^2 x_0 / \left(\frac{n_2}{n_1}\right)^2\right) - 1\right]$. For a quartz–air interface, this value is about 200 nm, if a laser with 632 nm wavelength is used. The waves resulting from these interactions are called evanescent waves (EW). If there are any particles within reach of EWs, they scatter the energy after tunneling from the standing wave to the particle or object. Note that the net energy transfer to the second, less-dense medium is always zero on average. Usually the $p$-polarized incident wave is employed to generate strong evanescent waves in Medium 2 [14].

Surface plasmon (SP) waves are the quanta associated with longitudinal waves propagating in matter through the collective motion of large numbers of electrons. As in EWs, the intensity of surface EM radiation (ISW) has a maximum at $z = 0, x = 0$ and exponentially decreases along the $z$-axis. The fundamentals of SP waves are well studied in the literature and relatively well understood [5,6]. SP response of a medium is generally very sensitive to the complex refractive index of the medium [15]. SP waves have been used extensively in the development of optical sensors for measurement of chemical and biological components [14], and characterization of surface and thin films [16]. Recently, considerable progress has been made in the systematic
application of SP waves as a diagnostic tool for obtaining the characteristics of thin films, defects, and coatings [17–19].

To our knowledge, there is no published research in the open literature about the potential use of polarized surface waves for characterization of nano-particles and nano-structures on a metallic thin film, other than a few experimental approaches. Natan’s group studied SP and Au particles experimentally [18]. Their approach, however, is based on the absorption by a thin film, and does not take into account the elliptically polarized scattering signatures of particles for size determination. Sterligov et al. [7] investigated the particle–surface wave interaction and carried out both the near- and far-field measurements. However, they did not suggest any approach to characterize nano-particles in situ. In the present study, we show that the use of Mueller matrix elements allows characterization of nano-particles using the elliptically polarized light-scattering patterns. In a parallel study, a new experimental diagnostic system is developed, which will be reported in a future publication [20].

The geometry of the scattering system considered in this study is shown in Fig. 1. The incident radiation is a plane wave whose wave vector is in the $x$–$z$ plane, oriented at angle $\alpha_0$ with respect to the $z$-axis, traveling from Medium 0 (M-0; bottom) to M-1 (middle). This wave undergoes total internal reflection at the interface between the M-0 and M-1, which results only in standing surface waves in M-1 and M-2. Medium 1 is a thin metallic film with thickness $h$ and M-2 is an ethyl alcohol suspension of metallic nano-particles. For the general case, we consider a particle located a distance $d$ above the interface separating M-1 from M-2. The wave incident on the particle is assumed to be parallel to the interface. The general formulation considered in [8] allows any orientation of the planar wave incident on the particle and accounts for particle–surface interactions. Particles are assumed to convert (tunnel) the standing evanescent wave to the particle and after that to propagate scattering waves, as if they are probes. The wavelength, refractive index, permeability, and wave vector in the media are $\lambda_M$, $n_M$, $\mu_M$, and $k_M$, where the subscript $M$ designates the media number.

The general solution to the surface-wave scattering problem described above is reached by satisfying the boundary conditions at the particle and plane interfaces simultaneously. The
solution is derived using an extension of the Lorenz–Mie theory [20], and it is outlined in detail in [8]. The scattering amplitude matrix elements are solved by expanding the scattered electric fields in terms of the vector wave functions and then expanding the vector wave functions in terms of the polarization directions. In the far-field region, the $r$ component is negligible in comparison with the $\theta$ and $\phi$ components, and the far-field scattering amplitudes can be expressed in the form of the matrix

$$
\begin{pmatrix}
E_{\theta,\text{sca}} \\
E_{\phi,\text{sca}}
\end{pmatrix} = \exp(\pm ik_1r) \begin{bmatrix} S_2 & S_3 \\ S_4 & S_1 \end{bmatrix} \begin{bmatrix} E_{\text{inc}}^{\text{TM}} \\ E_{\text{inc}}^{\text{TE}} \end{bmatrix},
$$

(2)

where the $S_i$ profiles in M-0 are given in [8]. The scattering amplitudes above the interface are composed of the scattered fields plus the interaction fields multiplied by the appropriate Fresnel reflection coefficients. These amplitudes are important for quantifying the amount of light to be received by a detector [8]. The formulation provides a methodology for determining the far-field scattering amplitudes for an arbitrarily shaped particle placed behind the total-reflection interface.

Stokes vector $I_{\text{sca}}$ which contains the flux and polarization information of the medium can be related to the incident light Stokes vector $I_{\text{inc}}$ at given wavelength. This relationship can be written in matrix form for a spherical particle in a symmetric medium [8,13]:

$$
[I_{\text{sca}}]_{\lambda} = \frac{1}{k^2r^2} [S]_{\lambda} [I_{\text{inc}}]_{\lambda} \text{ or }
\begin{bmatrix}
I_{\text{sca}} \\
Q_{\text{sca}} \\
U_{\text{sca}} \\
V_{\text{sca}}
\end{bmatrix} = \frac{1}{k^2r^2} \begin{bmatrix} S_{11} & S_{12} & 0 & 0 \\ S_{12} & S_{11} & 0 & 0 \\ 0 & 0 & S_{33} & S_{34} \\ 0 & 0 & -S_{34} & S_{33} \end{bmatrix} \begin{bmatrix} I_{\text{inc}} \\
Q_{\text{inc}} \\
U_{\text{inc}} \\
V_{\text{inc}} \end{bmatrix},
$$

(3)

where $r$ is the distance between the particle and detector. The scattering matrix elements ($S_{11}$, $S_{12}$, $S_{33}$, and $S_{34}$) can be calculated from the scattering amplitudes using the equations posted in [8]. In order to explain scattering matrix elements’ results better, we define a normalized scattering matrix and its elements are $M_{11} = S_{11}$, $M_{12} = S_{12}/S_{11}$, $M_{33} = S_{33}/S_{11}$, $M_{34} = S_{34}/S_{11}$. In this paper we represent normalized scattering matrix elements of spherical nanoparticle as $M_{11}$, $M_{12}$, $M_{33}$, and $M_{34}$.

3. Numerical experiments

We begin our numerical experiments by considering a thin gold film (Medium 1, M-1) on a glass substrate (M-0). On top of the gold film is an ethyl alcohol solution (M-2) that may contain a suspension of metallic spherical nano-particles. The value of the EM-wave amplitude on the particle depends on several parameters, including the film thickness, refractive indices of M-1 and M-2, as well as the incident angle $\alpha_0$. It is important to note that the material properties of nano-particles alter the overall effective properties of the M-2. Therefore, depending on the nano-particles’ material properties and the volume fraction, the amplitude of the evanescent waves in M-2 also vary. This amplitude is important as the amount of energy scattered by a particle depends on its value. The particle volume-fraction effects on the effective refractive index of the medium may be considered via Maxwell–Garnett theory [20–22]. Both the particle volume fraction and particle refractive index alter the effective index of refraction of the medium, which
change the results. The values we use here are representative and only for the purpose of parametric study; they need to be modified according to the conditions dictated by actual experiments.

Fig. 2 shows how the intensity \( I_1 \) changes as a function of the film thickness if there is only ethyl alcohol on the film. Here initially we assume that there are no metallic particles in the suspension (ethyl alcohol, M-2) and its refractive index is \( m = 1.53 + i0.0 \) at \( \lambda = 632 \text{ nm} \). As discussed above, we also assume that the electromagnetic radiation incident on the sphere is always parallel to the surface of the film; therefore, scattering angle, \( \theta = 0^\circ \) indicates forward scattering and scattering angle, \( \theta = 90^\circ \) indicates side scattering. The wavelength of the incident light is taken as 632 nm (red light). Based on the results shown in Fig. 2, the maximum value of the surface intensity occurs if the angle of incidence of the laser beam that undergoes total internal reflection at the 0–1 interface is around \( 70^\circ \), and up to 20% of the incident-light intensity can be accounted for in the EW-wave amplitudes, depending on the thickness of the gold film and the incident angle. In this paper, the rest of the calculations are reported for \( \alpha_0 = 70^\circ \) and for a gold-film thickness of 50 nm, and all intensity values are normalized with the incident light intensity. In calculations, the refractive index of gold is assumed \( m = 0.216 + i3.445 \) at \( \lambda = 632 \text{ nm} \). The film thickness of 50 nm is selected as it is a reasonable value to use in actual experiments. Scattering angle of \( \alpha_0 = 70^\circ \) is also a representative value, which correspond roughly to the peak intensity for 50 nm film.

### 3.1. Gold nanospheres on gold thin film

Fig. 3 depicts the average surface electromagnetic wave intensity incident on a gold nano-sphere as a function of its diameter and location on the film for incident angle of \( \alpha_0 = 70^\circ \). This intensity is calculated using the EM-wave amplitude at the center-location of the particle, at a distance \( d \) as shown in Fig. 1. This value is obviously very sensitive to particle diameter for diameters between 10 and 35 nm. This sensitivity suggests that the scattered light by these particles can be significantly different and potentially useful for characterization purposes.

![Fig. 2. Transmitted light intensity on the surface of the gold film. Ethyl alcohol (medium 2) has no particles embedded in it.](image-url)
We calculate the angular profiles of the scattering matrix elements following the formulation outlined in [8]. The effect of the diameter of a spherical gold nano-particles on $S_{11}$, $S_{12}$, $S_{33}$ and $S_{34}$ profiles as a function of scattering angle is shown in Fig. 4. Here, it is assumed that the nano-particle is resting on the gold film. These results show that $S_{11}$ profiles peak around $\theta_s = 55^\circ$ and increases with particle size, as the larger particles intersect more of the incident field flux. All three polarization matrix elements show differences with particle size that may be used for detailed characterization.

Fig. 5 depicts the $M_{11}$, $M_{12}$, $M_{33}$ and $M_{34}$ profiles of different diameter gold nano-particles located 100 nm away from the surface of the gold film. In this case, the values of the $M_{11}$ profiles are smaller than those shown in Fig. 4 as the average value of the intensity incident on the nano-particles is smaller. In addition, the profiles are relatively flat, and do not show any profound peaking at all. $M_{12}$, $M_{33}$ and $M_{34}$ profiles show almost no sensitivity to particle size, since the polarized scattering response by such small particles without the wall-interaction is not expected to yield polarization information. For characterization of nano-particles relatively far from the surface, only $M_{11}$ offers some hope for particle characterization.

The results presented so far indicate that it is possible to identify metallic nano-particles from the scattering matrix element profiles, which are affected by both the size and material properties of the particles. The sensitivity of predictions to particle location is depicted in Fig. 6 from a different perspective, where only the results for scattering direction of $45^\circ$ are shown. Note that these are representative results for a single scattering angle; it is possible to combine the results from multiple scattering angles to have more robust characterization. It is obvious that $M_{11}$, $M_{12}$, $M_{33}$, and $M_{34}$ profiles can be used together to identify the particle sizes accurately on the surface of the film. The results suggest that it is possible to identify particle sizes between 10 and 60 nm. On the other hand, if particles are at about 100 nm above the surface, the characterization may not be possible. The combination of determining both particle size and surface separation distances may pose a challenge; however, these cases need to be examined in conjunction with careful experimentation, which is currently being conducted.
In this manuscript, we present a methodology to characterize nanometer-size particles on or near a thin film via scattering of surface waves. Such a characterization has the potential to become the backbone of on-line control of nanostructure self-assembly, and potentially may become significant for future nano-scale manufacturing applications. The concept is based on the general theoretical formulation reported in Part A [8]. That formulation is used to determine the scattering matrix elements ($M_{11}$, $M_{12}$, $M_{33}$ and $M_{34}$) of two different metallic (gold and silver) nano-particles, although only the gold-particle results are presented here. Nano-particles within the diameter range of 10–70nm within an ethyl alcohol solution on a 50-nm thick gold film are considered. The results obtained for the laser wavelength of 632nm show that the $M_{ij}$ elements strongly depend on the size and properties of metallic particles, the incident angle, and the thickness of the thin film, as well as the location of the particle above the thin film.

Fig. 4. $M_{11}$, $M_{12}$, $M_{33}$ and $M_{34}$ profiles of the light scattered by gold nanoparticles on the surface of the gold film ($d - a/2 = 0$ nm).

4. Conclusions

In this manuscript, we present a methodology to characterize nanometer-size particles on or near a thin film via scattering of surface waves. Such a characterization has the potential to become the backbone of on-line control of nanostructure self-assembly, and potentially may become significant for future nano-scale manufacturing applications. The concept is based on the general theoretical formulation reported in Part A [8]. That formulation is used to determine the scattering matrix elements ($M_{11}$, $M_{12}$, $M_{33}$ and $M_{34}$) of two different metallic (gold and silver) nano-particles, although only the gold-particle results are presented here. Nano-particles within the diameter range of 10–70nm within an ethyl alcohol solution on a 50-nm thick gold film are considered. The results obtained for the laser wavelength of 632nm show that the $M_{ij}$ elements strongly depend on the size and properties of metallic particles, the incident angle, and the thickness of the thin film, as well as the location of the particle above the thin film.
Based on these results, we observe that characterization of metallic, spherically shaped nano-particles on a metallic thin film is possible by measuring the normalized scattering matrix elements $M_{ij}$.

The results presented in this paper are encouraging, as there are no other techniques available to characterize such metallic nano-particles reliably. In addition, it is important to extend these results to different size distributions as well as to the agglomerates of metallic particles (colloids). This will require the construction of response matrix $B$ as discussed [8]. In addition, if there are more than one particle scattering the evanescent waves, again, a single response matrix can be used to find the net effect of all particles. These ideas will need to be studied further. In addition, sensitivity analyses to be carried out to determine the size of particles present at different heights from the thin film. The concept proposed here should eventually be evaluated experimentally, and we are currently in the process of building an experimental apparatus to verify the results observed in these numerical simulations.

Fig. 5. Profiles of $M_{11}$, $M_{12}$, $M_{33}$ and $M_{34}$ of light scattered by gold nanoparticles located at $d = 100$ nm above the gold film.
Fig. 6. Profiles of $M_{ij}$ for scattered light by gold nanospheres located on a thin gold film $(d - a/2 = 0)$, and $d - a/2 = 100$ nm; scattering angle is 45°, film thickness is 50 nm, incident angle for the wave is 70°.

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