Theoretical Model for Optical Sensing of a Random Monolayer of Particles

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Abstract— We summarize the derivation of a simple model for the coherent-reflectance of light from a random monolayer of particles using a multiple scattering formalism and an effective field approximation. The resulting model is applicable for low surface-coverage fractions of the monolayer but for all angles of incidence and is suitable for sensing applications.

1. INTRODUCTION

Random monolayers of particles play a fundamental role in diverse physical or chemical processes and devices. For instance, chemical sensors consisting of chemically active particles interacting with their environment may be devised and interrogated using a light beam. An example of such devices is nicely described in Ref. [1].

When light is incident on a random monolayer of particles we may divide the scattered field in two components: a coherent and a diffuse component. The coherent component corresponds to the average scattered field, whereas the diffuse component relates to the fluctuations of the scattered field around the average. The power carried by the average field is commonly referred to as the coherent component. We may then define the coherent reflectance or transmittance of a random monolayer as the ratio between the power carried by the reflected or transmitted component and the incident power. The amount of power carried by the coherent and the diffuse components depend on the particle size, refractive index and angle of incidence. A few models for the coherent reflectance of light from a random monolayer of particles have been devised in the past. The most robust one, valid for larger surface-coverage fractions of the monolayer, is the so called Quasi-Crystalline Approximation [2]. However it is also the most complicated one. There is no formula in closed-form for such model making it rather unsuitable for sensing applications. The simplest model was developed in Refs. [3] to simulate the reflectance of a random monolayer of large particles adsorbed on a glass substrate at an angle of incidence near Brewster's angle of the supporting interface. However this model is valid only for low angles of incidence and ignores the multiple reflections between the substrate and the monolayer and between the particles. Finally, some of us presented a simple heuristic model for the coherent reflectance of a random monolayer of particles which remains well behaved al large angles of incidence in Ref. [4]. The results of this latter model were found to be consistent with some experimental data for reflectivity measurements in an internal reflection configuration from a sparse monolayer of large particles adsorbed at the base of a glass prism. Here we present a formal derivation of this model based on a multiple scattering formalism.

2. MULTIPLE SCATTERING FORMALISM

Let us first consider a free standing random monolayer of particles. That is, let us suppose the particles are embedded in homogeneous, non-magnetic medium of refractive index n_m. We will refer to this medium surrounding the particles as the matrix. For simplicity let us consider all particles are spherical and have the same radius a and refractive index n_p. We will indicate the position of any particle in space with the coordinates of its center, $\vec{r}_n$. In a monolayer of particles, the centers of all particles lie on a plane. Let us place the origin of our coordinate system on the monolayer plane with the x and y axes on the plane as shown in Fig. 1.

Let us suppose a plane wave, $\vec{E}^i(\vec{r}) = E_0 \exp(i\vec{k}^i \cdot \vec{r} - i\omega t)\hat{e}_i$, is incident to the monolayer, where $\vec{k}^i = k_y^i \hat{a}_y + k_z^i \hat{a}_z$ with $k_y^i = k_m \cos\theta_i$, $k_z^i = k_m \sin\theta_i$, $k_m = 2\pi n_m/\lambda$ and λ is the vacuum wavelength. The electric field scattered by the nth particle may be written as,

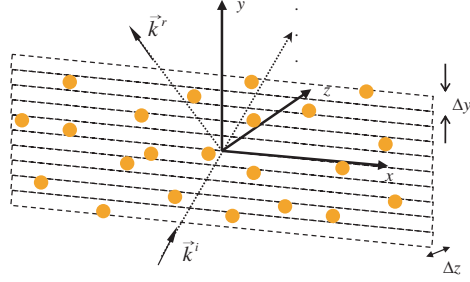$$\vec{E}_n^S(\vec{r}) = \int \vec{\vec{G}}_m(\vec{r}, \vec{r}') \cdot \vec{J}_{ind}^{(n)}(\vec{r}') d^3 r', \tag{1}$$

Figure 1: Coordinate system. Strips along the x axis are indicated.

where $\overset{\leftrightarrow}{G}_m(\vec{r}, \vec{r}')$ is the Green function of the vector wave-equation satisfied by the electric field in the matrix medium, and $\vec{J}_{ind}^{(n)}(\vec{r}')$ is the excess current induced inside the particles, that is, the difference between the current induced inside the particles and the current that would be induced in the matrix without the particle. $\vec{J}_{ind}^{(n)}(\vec{r}')$ includes all excess currents, whether they are polarization, conduction or magnetizations currents. The total scattered field is the sum of the scattered fields by all particles. The current induced in any particle may be related to the exciting field, that is, the net field incident on the particle through the transition operator of a particle centered at the origin, $\overset{\leftrightarrow}{T}(\vec{r}', \vec{r}'')$ (see Ref. [5] and references therein). This operator may be expressed in terms of its momentum representation as,

$$\overset{\leftrightarrow}{T}(\vec{r}', \vec{r}'') = \frac{1}{(2\pi)^6} \int d^3p' \int d^3p'' \exp(i\vec{p}' \cdot \vec{r}') \overset{\leftrightarrow}{T}(\vec{p}', \vec{p}'') \exp(-i\vec{p}'' \cdot \vec{r}''). \tag{2}$$

We can translate this operator to that for a particle centered at $\vec{r}_n$ by replacing $\vec{r}'$ and $\vec{r}''$ with $\vec{r}' - \vec{r}_n$ and $\vec{r}'' - \vec{r}_n$. Then, the scattered field from N particles may be written formally as,

$$\vec{E}^S(\vec{r}) = \sum_{n=1}^{N} \int \overset{\leftrightarrow}{G}_m(\vec{r}, \vec{r}') \cdot \overset{\leftrightarrow}{T}(\vec{r}' - \vec{r}_n, \vec{r}'' - \vec{r}_n) \cdot \vec{E}_n^{exc}(\vec{r}'') d^3r' d^3r'', \tag{3}$$

where $\vec{E}_n^{exc}$ is the exciting field to the nth particle. For a given configuration of N particles in the monolayer we may set up a system of N equations for the exciting fields for each particle. Solving this system of equations, introducing the calculated exciting fields in Eq. (3), performing the indicated integrals and taking the configurational average, yields the coherent scattered fields from the system of particles. Clearly such calculation is limited to a finite number of particles, is time consuming and does not provide physical insight into the process. It would not be suitable, for instance, for inverting the parameters of a monolayer from experimental data in a sensing experiment. To this end, it is desirable to have simple approximate models in closed form.

3. DEVELOPING SIMPLE MODELS

Here we will derive the model reported in Ref. [4] using a multiple-scattering formalism, stating clearly the approximations used, and pointing out a way for improvements while keeping its simplicity.

The idea is to use an effective field approximation previously used for a half-space of a random system of particles [5] but adapted to the monolayer problem. The basic idea is to approximate the exciting field to all the particles as an effective plane wave and setting up a consistency equation from which we may derive the parameters of the exciting field.

Let us assume the center of the particles are confined to a slab of space between $\Delta z/2$ and $-\Delta z/2$, and suppose the exciting field is a plane wave given by $\vec{E}^{exc}(\vec{r}) = E_{exc} \exp(i\vec{k}^{exc} \cdot \vec{r} - i\omega t)\hat{e}_{exc}$. We want to calculate the scattered field from the monolayer on the monolayer. To this end, we divide the monolayer in thin strips of width Δy and calculate the average field scattered by each strip. Then, we may calculate the total average scattered field at a point within the slab containing the monolayer by adding the contributions from all strips.

Considering strips of the slab containing the monolayer along the y-axis (see Fig. 1) it is convenient to work with the following plane-wave expansion of the Green function,

$$\overset{\leftrightarrow}{G}_m(\vec{r}, \vec{r}') = \frac{i}{8\pi^2} \int \int dk_x^s dk_z^s \frac{1}{k_y^s} (\overset{\leftrightarrow}{1} - \hat{k}_\pm^s \hat{k}_\pm^s) \cdot \exp[i\vec{k}_\pm^s \cdot (\vec{r} - \vec{r}')], \tag{4}$$

where $\vec{k}_\pm^s = k_x^s \hat{a}_x \pm k_y^s \hat{a}_y + k_z^s \hat{a}_z$ and $k_y^s = \sqrt{k_m^2 - (k_x^s)^2 - (k_z^s)^2}$ (this is the positive root). Where there is a choice of sign, we should use the upper one when $y > y'$, and the lower one when $y < y'$. The field scattered by all particles may be written as,

$$\vec{E}^S(\vec{r}) = \frac{i}{8\pi^2} E_{exc} \sum_{n=1}^{N} \iint dk_x^s dk_z^s \frac{1}{k_y^s} (\overleftrightarrow{1} - \hat{k}_\pm^s \hat{k}_\pm^s) \cdot \exp[i(\vec{k}^{exc} - \vec{k}_\pm^s) \cdot \vec{r}_n] \overleftrightarrow{T}(\vec{k}_\pm^s, \vec{k}^{exc}) \exp[i\vec{k}_\pm^s \cdot \vec{r}] \hat{e}_{exc}, \quad (5)$$

where we used Eqs. (2) and (4) in Eq. (3) and performed the integrals on d^3r', d^3r'', d^3p' and d^3p''. Now, let us split the thin layer in thin strips of width Δy along the y-axis of the slab containing the monolayer.

Let us take the configurational average of the scattered field from each strip. We will assume the probability density of finding any sphere at $\vec{r}_n$ is constant within the strip and is given by $1/V$, where V is the volume of the strip. Ignoring the exclusion volume between spheres, the average scattered field is N times the average of that for any given sphere, where N is the number of particles in the strip of volume V. The average of the scattered field from any sphere located in a strip around y_n corresponds to integrating on x_n from $-L/2$ to $L/2$ (with $L \to \infty$), on z_n from $-\Delta z/2$ to $\Delta z/2$ and on y_n from $y_o - \Delta y/2$ to $y_o + \Delta y/2$, and multiplying by $1/V$ where $V = \Delta y \Delta z L$. Then, the average scattered field from all particles on a strip around y_o yields,

$$\left\langle \vec{E}^S(\vec{r}) \right\rangle_{strip} = \frac{i}{4\pi} E_{exc} \rho \Delta y \Delta z \int dk_z^s \frac{1}{k_y^s} (\overleftrightarrow{1} - \hat{k}_\pm^s \hat{k}_\pm^s) \cdot \overleftrightarrow{T}(\vec{k}_\pm^s, \vec{k}^{exc}) \exp[i\vec{k}_\pm^s \cdot \vec{r}] \exp[i(k_y^{exc} \mp k_y^s) y_o] \hat{e}_{exc}$$

$$(6)$$

where $\rho = N/V$ is the volume number-density of particles and now $k_y^s = \sqrt{k^2 - (k_x^{exc})^2 - (k_z^s)^2}$. Now, for a monolayer of particles we may take the limit $\Delta z \to 0$ but $\rho \to \infty$ so that the product $\Delta z \rho \to \rho_s$ is the surface number-density of particles. The surface density of particles in the monolayer may be related to the surface coverage fraction, Θ, as $\rho_s = \Theta/(\pi a^2)$.

Now, we add up the scattered field from all strips at a point $\vec{r}_m$ at, or near the monolayer plane and take the limit $\Delta y \to 0$. This corresponds to integrating on dy_o from $-\infty$ to y_m and from y_m to ∞. In the first integral we choose $\hat{k}_+^s$, $\vec{k}_+^s$ and $-k_y^s$ in the integrand, whereas for the second integral we choose $\hat{k}_-^s$, $\vec{k}_-^s$ and k_y^s. We then assume that k_y^s has a small imaginary part and thus, the integrated terms evaluated at $\pm\infty$ are zero. The new integrand becomes, $\exp(ik_x^{exc} x_m + ik_y^{exc} y_m + ik_z^s z_m)$ times, $(\overleftrightarrow{1} - \hat{k}_+^s \hat{k}_+^s) \cdot \overleftrightarrow{T}(\vec{k}_+^s, \vec{k}^{exc}) / i(k_y^{exc} - k_y^s) - (\overleftrightarrow{1} - \hat{k}_-^s \hat{k}_-^s) \cdot \overleftrightarrow{T}(\vec{k}_-^s, \vec{k}^{exc}) / i(k_y^{exc} + k_y^s)$. We may perform the remaining integral on dk_z^s by the method of residues. Note that the first term in the integrand has two poles since $1/i(k_y^{exc} - k_y^s) = -i(k_y^{exc} + k_y^s)/(k_z^s + k_z^{exc})(k_z^s - k_z^{exc})$, whereas there are no singularities in the second term inside the integrand (a physical $\overleftrightarrow{T}$ should not have poles). Now, let us suppose k_z^{exc} has a small imaginary part. Then, there is one pole in the upper half-plane and another in the lower half-plane (of the k_z complex plane). If $z_m > 0$ we may close the contour of integration in the upper half-plane (counter clockwise) and if $z_m < 0$ we may close the contour of integration in the lower half-plane (clockwise). We get,

$$\left\langle \vec{E}^S(\vec{r}_m) \right\rangle = \frac{iE_{exc}\rho_s}{2k_z^{exc}} \begin{cases} (\overleftrightarrow{1} - \hat{k}^{exc}\hat{k}^{exc}) \cdot \overleftrightarrow{T}(\vec{k}^{exc}, \vec{k}^{exc}) \exp[i\vec{k}^{exc} \cdot \vec{r}_m] \hat{e}_{exc} \text{ for } z_m > 0 \\ (\overleftrightarrow{1} - \hat{k}_r^{exc}\hat{k}_r^{exc}) \cdot \overleftrightarrow{T}(\vec{k}_r^{exc}, \vec{k}^{exc}) \exp[i\vec{k}_r^{exc} \cdot \vec{r}_m] \hat{e}_{exc} \text{ for } z_m < 0 \end{cases}, \quad (7)$$

where $\hat{k}^{exc} = k_x^{exc}\hat{a}_x + k_y^{exc}\hat{a}_y + k_z^{exc}\hat{a}_z$ and $\hat{k}_r^{exc} = k_x^{exc}\hat{a}_x + k_y^{exc}\hat{a}_y - k_z^{exc}\hat{a}_z$. This result is nearly they same one obtained in [5] and used in [4], except that here, the scattered field is specified for all values of z_m whereas before the result was obtained formally only for $|z_m| > a$. Note that the scattered field in this approximation is discontinuous at $z_m = 0$. Clearly, this result comes from taking into account, in the dilute limit, the multiple scattering for the average wave among strips of the monolayer.

Now, in the so called effective field approximation, we take the exciting field felt by the particles as the average field. Let us use a slightly different approximation. Let us take the exciting field as given by the average of the fields outside the particles, that is, we do not include the internal field within any given particle as part of the exciting field to the other particles. Then we may write, $\vec{E}^{exc}(\vec{r}) = \vec{E}^i(\vec{r}) + \left\langle \vec{E}^S(\vec{r}) \right\rangle$. Using Eq. (7) in the latter consistency equation requires $\vec{k}^{exc} = \vec{k}^i$ and

$\hat{e}_{exc} = \hat{e}_i$. Now if we consider points with $z_m > 0$, we get, $E_{exc} = E_0[1 - \frac{i\Theta}{4\pi a^2 k_z^i}(\overset{\leftrightarrow}{1} - \hat{k}^i\hat{k}^i)\cdot\overset{\leftrightarrow}{T}(\vec{k}^i, \vec{k}^i)\cdot\hat{e}_i]^{-1}$ which completely specifies the exciting field in this approximation. Using again Eq. (7) we get the average reflected and transmitted fields by the monolayer, and from these, we may obtain a coherent transmission and reflection coefficients, t_{coh} and r_{coh}:

$$t_{coh} = \frac{1}{1 + \alpha S(0)} \quad \text{and} \quad r_{coh} = \frac{\alpha S_j(\pi - 2\theta_i)}{1 + \alpha S(0)}, \tag{8}$$

with $\alpha = 2\Theta/(k_m a)^2 \cos\theta_i$, $j = 1$ or 2 for a TE or a TM polarized incident wave and we used the results, $(\overset{\leftrightarrow}{1} - \hat{k}^i\hat{k}^i)\cdot\overset{\leftrightarrow}{T}(\vec{k}^i, \vec{k}^i)\cdot\hat{e}_i = i\frac{4\pi}{k_m}S(0)\hat{e}_i$, and $(\overset{\leftrightarrow}{1} - \hat{k}^r\hat{k}^r)\cdot\overset{\leftrightarrow}{T}(\vec{k}^r, \vec{k}^i)\cdot\hat{e}_i = i\frac{4\pi}{k_m}S_j(\pi - 2\theta_i)\hat{e}_i$ previously demonstrated in [5], where $S(0)$ is the forward scattering amplitude of an isolated sphere (embedded in the matrix medium), and S_1 and S_2 are the diagonal elements of the amplitude scattering matrix as defined by Bohren and Huffman in [6].

If we now suppose the monolayer is supported by a flat interface, we must take into account the multiple reflections of the average wave between the monolayer and the flat interface. We may construct the coherent reflection coefficient using the well known formula for the compound reflection coefficient of two parallel interfaces, where the reflection coefficient of one of the interfaces is that of the monolayer given in Eq. (9), as shown in Ref. [4]. This is valid whether the monolayer is on one side of the interface or the other.

4. FINAL REMARKS

We obtained Eq. (7) from a multiple scattering formalism in the monolayer and approximating the exciting field to the particles as a simple plane wave. We were able to set up a consistency equation for points in the transmission half-space, from which we obtained t_{coh} and r_{coh} in Eq. (8). With the approach presented here, there is room for some improvements while keeping the same degree of simplicity. For points on the other side of the monolayer (the reflection half-space), no meaningful consistency equation was obtained. A way to improve the present model is to include in the exciting field a plane wave in the direction of coherent reflection. In this way we may be able to set up a consistency equation for all points in space which may yield a more realistic exciting field for the monolayer problem. Also, we may include the internal fields within the particles in the effective field approximation, and thus, in the consistency equation. We believe that such improved models may still be attractive for optical sensing applications and will be published elsewhere in the future.

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