Effect of aspect ratio in particle suspensions on spatially and angularly resolved vis-near NIR spectroscopy

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ABSTRACT

The particle characteristics in a suspension affect the performance and quality of the end product of e.g. pharmaceutical formulations. The shape of the suspended particles can be influenced by changes in the manufacturing process conditions. Thus, there is a need in a robust method for continuous monitoring of particle characteristics through the process. This study investigates the feasibility of using spatially and angularly resolved diffuse reflectance measurements as a method of determining particle shape. Towards this aim, a forward calculation algorithm was developed based on using the discrete dipole approximation to estimate single particle optical properties and the diffuse approximation for the reflectance of the particle suspension. This algorithm was used to study aqueous suspensions of randomly-oriented polystyrene ellipsoids. Our objectives were to determine the contribution aspect ratio effect appearance and elucidate the specifics of the effects seen. The results suggest that the method is suitable for determining particle shape for suspensions where the particle and the solvent have significantly different optical properties. For these systems, the work suggests that diffusion reflectance measurements can be developed into an in-line method for particle shape determination

Keywords: Diffuse reflectance, diffuse approximation, DDSCAT, aspect ratio

1. INTRODUCTION

The particle morphology (e.g., size, shape) and concentration of a suspension often critically dictate the performance of a formulation in many areas, such as in the chemical or pharmaceutical industry, and therefore need to be closely controlled. Today, there is a growing number of processes which require techniques for real-time characterisation of particle shape changes.[1] So far, most analytical approaches describe the particles with different

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geometries using the equivalent spherical diameter of the particle.[2] Despite the practicality of these methods, overlooking the particle shape is known to cause difficulties to material flow, homogeneity and performance of the end product.[3–5] In addition, it can noticeably affect the quality of other parameters estimation, like particle size,[6,7] even when the particle shape parameters (like roundness, aspect ratio) lie very close to spherical particle values.

The most accurate techniques in this field are based on image analysis to spot the most subtle differences in particle shapes. The methods often involve manual/semi-automatic image processing, where sampling preparation could be required.[8] Both negatively affect the analysis speed. High-speed methods, on the other hand, often lack of the accuracy due to a varying degree of noise associated with the images from the high-speed cameras.[9] As an alternative, optical measurements are known to provide fast and non-invasive methods for characterising physical and chemical properties of materials. Although optical properties have been reported regarding their sensitivity to particle shape, optical measurement instruments have only made limited progress in identifying these effects.[10,11] Depending on the particular physical measurement, limitations arise due to multiple scattering interruption for laser diffraction, or from the inderect information from the chord length distribution for laser backscattering.[12,13]

Such shortcomings can be addressed by combining an optical theory capable of accounting for multiple scattering and an instrument capable of performing such measurements in real-time. This requires a good understanding of light-particle interaction under multiple scattering and the connection to the shape of the particles. To achieve this, discrete dipole approximation (DDA)[14] was employed in tandem with the diffuse approximation[15] to simulate optical response of a recently developed spatially and angularly resolved diffuse reflectance measurements (SAR-DRM) probe.[16] The following work study the effect of the variation in particle shape on the simulated reflectance. In order to localise the changes caused exclusively by particle shape, the suspensions are assumed to consist of randomly-oriented particles of a constant volume, hence those suspensions differ only in the ratio of length to width (aspect ratio). In this study, the results of modelled SAR-DRM for mentioned above suspensions are reported.

The remainder of this paper is organised as follows. The next section gives an overview of the methods used to calculate the single particle optical properties and the diffuse reflectance of particle suspensions. Then the change in the diffusion reflectance of a suspension with the shape of its constituent particles is examined. This will gauge the feasibility for using the diffuse reflectance to determine particle shape. This is followed by a comparison of the results obtained with a reference calculation of the spherical particles. The results are analysed in the context of optical instrument design and multiwavelength analysis. Finally, the key findings of the paper are summarized and directions for future work are considered in Section 4.

2. METHODOLOGY

2.1 Calculation of bulk optical properties

The first step of describing light-particle interaction is the computation of the optical properties for a single particle. This study was based on the DDA method, available as the *Discrete Dipole SCATtering* open source software (DDSCAT), developed by Draine and Flatau.[14] It is based on the straightforward idea of splitting the scattering body into small spheres of equal size, which is comparable to the size of the radiating dipole. Those dipoles are then placed in the lattice structure to form the desired shape of the particle. Apart from the shape, DDSCAT should be supplied with material properties, such as densities and complex refractive indexes.

Most of the settings related to DDSCAT follow the default routines supplied for each geometry. The alterations that have been made concern the position of the particle in the medium and the wavelength range. The particles analysed are randomly-oriented in the surrounding medium. Hence the DDSCAT simulations were set to five equally spaced samples of each rotation angle and averaged over a total of 125 different positions to account for the different relative orientation between the polarisation of light and the axis of the particle. The computational routine was repeated for 35 wavelengths in the range 450–1000 nm. The gaps in the wavelength grid were then recreated using a cubic spline interpolation available as part of a *scipy* toolset.[17]

For a given single particle volume V_p, DDSCAT provides the scattering σ_s and absorption σ_a cross-sections of the light as well as the cosine of the average scattering angle, $\langle\cos\theta\rangle$, also known as the asymmetry parameter g. For a collection of particles of the same size, these parameters have to be proportional to the concentration of the material in the system, which means, to obtain the bulk coefficients μ_s and μ_a for a monodisperse collection of particles, cross-sections only require to be multiplied by a number of particles N_p.[18] Asymmetry parameter remains the same in this case as it is independent of the number of particles. The end form of bulk optical properties can be expressed as follows:

$$\mu_s'(\lambda) = (\sigma_s(\lambda)N_p)(1-g) \qquad \text{and} \qquad \mu_a(\lambda) = \sigma_a(\lambda)N_p + \frac{4\pi n_{imag}}{\lambda}\phi_w \tag{1}$$

where $\mu_s'(\lambda)$ is the term that combines the scattering coefficient with the directionalty of the scattered light, and $\mu_a(\lambda)$ combines contributions from both material and surrounding medium absorbtion through volume fraction ϕ_w and imaginary part of complex refractive index (n_{imag}) of water. The number of particle per unit volume N_p is derived from the concentration of solids C_p, and the density of the particle and media (ρ_p and ρ_w)as:

$$N_p = \frac{6\rho_w\ V_p}{(\rho_w + \rho_p/C_p - \rho_p)} \qquad \text{where} \qquad C_p = \frac{V_p\rho_p}{V_p\rho_p\ +\ V_w\rho_w} \tag{2}$$

2.2 Calculation of SAR-DRM spectra

The correction for the number of particles in the system, presented in Equation 1, does not reflect the light-particle interaction in the turbid medium accurately because such system exceeds the single scattering regime. The behaviour of the light which undergoes multiple scattering can be described using the radiative transport equation (RTE).[19] However, finding a solution for the RTE is computationally intensive, therefore diffuse approximation to RTE is developed to offer an alternative for solving RTE fully.[15,20]

To provide the solution, diffuse approximation employs bulk optical properties in the form of reduced scattering coefficient and scattering coefficient, described in the previous section as well as parameters related to the measuring instrument. Our model is based on the specifications of the spatially and angularly resolved diffuse reflectance measurements (SAR-DRM) probe that was used in the recent work by Chen and Thennadil.[16] The chosen probe design has a number of receiving fibres, placed in a cross-setting at 0.3 mm from each other, forming a range of the $S-R$ distances. The source fibres are placed in the centre of the probe (normal emittance), and at the corners of the receiving fibres for angular light sources (30° and 45°). The diffuse approximation performance and the comparison of the results with SAR-DRM have been discussed in more detail by Thomson et al.[21]

2.3 Materials

To examine the impact of the alteration of particle form on the light scattering behaviour, the simulations were performed for particles of constant volume but different shape. The measure of non-sphericity was defined as the ratio between the longest (C) and minor(A and B) semi axis, the aspect ratio (AR). This work studied prolate ellipsoids, one of the most common geometries, with three different aspect ratios: 1:1 (sphere), 3:1, and 8:1. These aspect ratios were converted into DDSCAT shape inputs with dipole spacing set to 0.04 Å. Figure 1 illustrates the DDSCAT models of each type of particle studied, the dimensions of their semiaxes (A, B and C) and the number of dipoles N used for each of the particles. To keep the volume constant, semiaxes A and B have to decrease along with the stretch of semiaxis C.

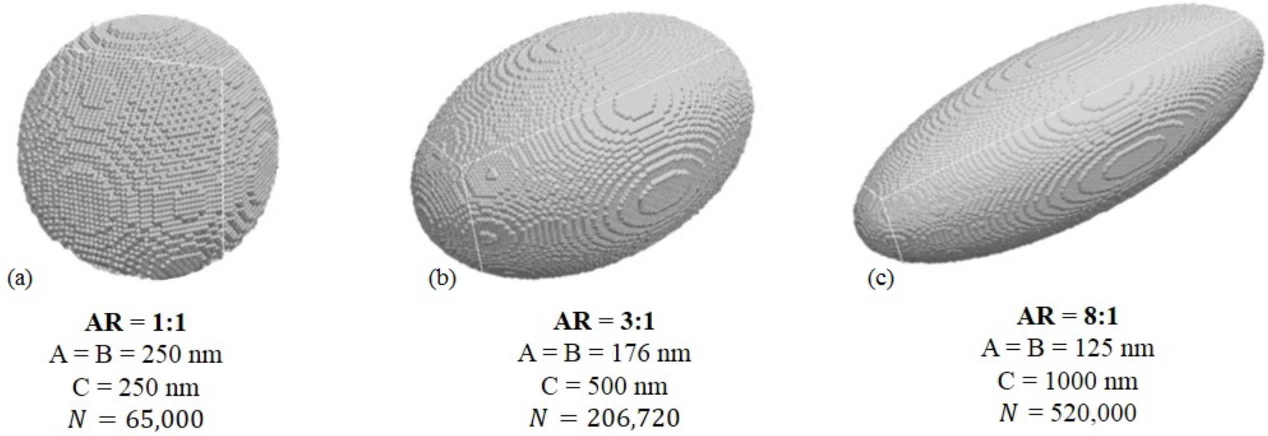

Figure 1: Polystyrene particles simulated by DDSCAT. a: sphere, b: elliptical (AR = 3:1), c: elliptical (AR = 8:1)

The studied particles were assumed to form monodisperse colloid suspensions with 5% of solid loading to ensure conditions are met for the diffuse scattering. The volume of solid and surrounding medium remained constant across the samples, as they differ only in the aspect ratio of the particles they consist of.

The material of the suspension was chosen to polystyrene in water; the complex refractive indexes across the studied wavelength range were taken from the work of Sultanova et al.[22] and Hale and Querry,[23] respectively.

3. RESULTS AND DISCUSSION

To gain an understanding of contribution of the aspect ratio to light-particle interactions, the first analysis was carried out on the simulated bulk optical properties. Figure 2 illustrates the scattering coefficient (a), asymmetry parameter (b) and absorption coefficient (c), where each line corresponds to a suspension with particles of specified aspect ratio (AR).

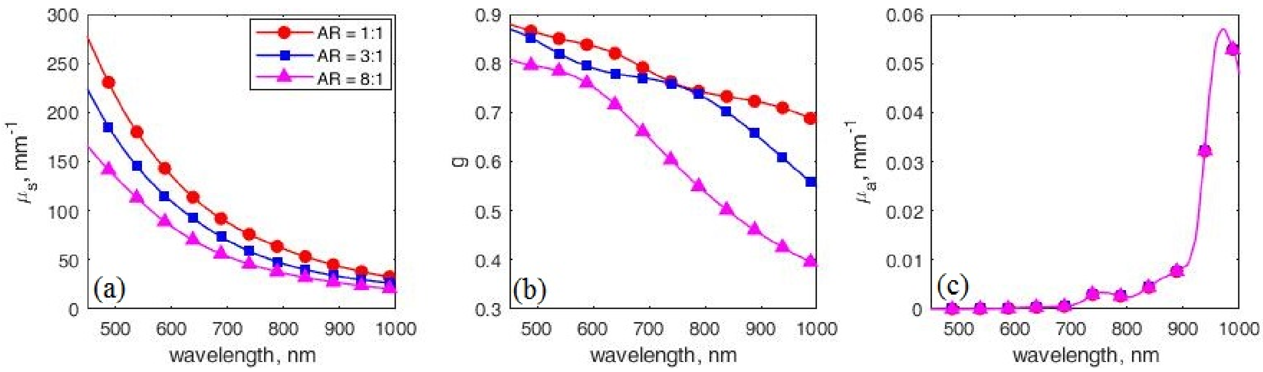

Figure 2: Bulk optical properties for polystyrene colloid suspensions for different particle aspect ratio. Illustrated with (a): scattering coefficient, μ_s, (b): asymmetry parameter, g and (c): absorption coefficient,μ_a

It was found that the effect of particle shapes appears predominantly on the scattering coefficient and asymmetry parameter, whereas the absorption coefficient remains unchanged due to the constant volume fraction of both the scatterers and the surrounding medium. The trend of the effects, however, varies, dependent on properties investigated. The scattering coefficient becomes weaker with an increase in aspect ratio and the effect appears as the change in the magnitude between samples solely. The asymmetry parameter, in contrast, changing in a much more specific manner with the changes in AR. While g for a sphere slowly decreases with increasing wavelengths, showing two distinctive peaks at 650 and 900 nm, the same parameter for AR = 3:1 exhibits a single peak at 700 nm and the magnitude decreases faster than for a sphere. Notably, the asymmetry parameter for AR = 8:1 drastically decrease after 650 nm as the wavelength increases, compared to the other two particles. Overall, it can be concluded that the change in AR affects leads to the specific changes in bulk optical properties in enough extend to distinguish the particle shape changes. However, the effects appeared in the scattering coefficient are not exclusive to the particle shape as the change in the particle size has a similar effect on scattering.The absorption coefficient remains the same (Figure 2(c)), whereas with the change in particle size the simultaneous changes would appear in the absorption coefficient as well.[18]

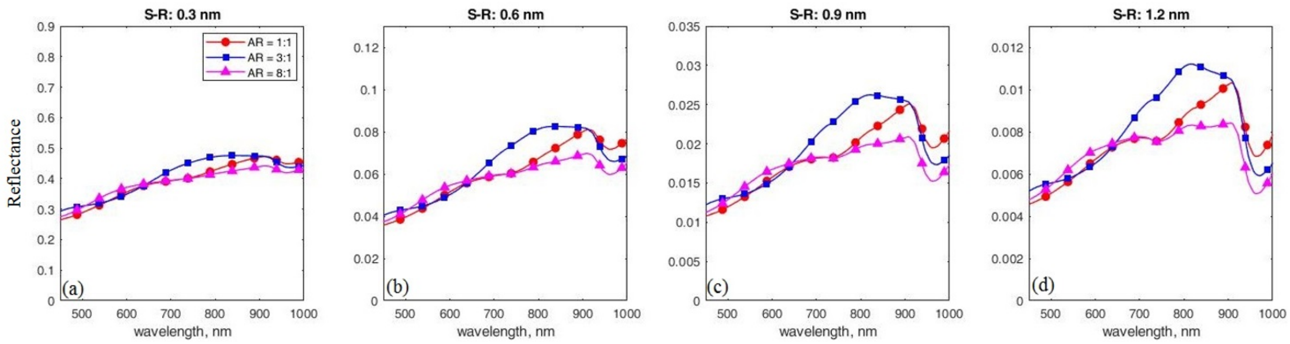

Figure 3: Diffuse reflectance simulated for various source-to-receiver ($S-R$) distances from a normally emitted light. Lines correspond to suspensions with particles of different aspect ratio: 1:1 (circle), 3:1 (square), 8:1 (triangle). (a)-(d) correspond to $S-R$ distance increase from 0.3 to 1.2 mm with 0.3 mm interval

In order to eliminate the effects interference, the simultaneous monitor of other optical properties should be implemented. The effect appears differently at each of the wavelengths studied. The change in the length of particle significantly affects asymmetry parameter between 700 to 1000 nm wavelength, however, the effect of the same parameter on scattering coefficient appears at lower wavelengths, 450–700 nm. The appearance of AR effect implies the strong wavelength dependence which cannot be studied in full with a single wavelength analysis.Firstly, the simulated reflectance is compared using normal emittance for suspensions of particles with different aspect ratio.

In the next step, the optical properties were used to model SAR-DRM spectra. As previously described, the chosen spectroscopic technique emits light at different angles and collects reflected signal at different $S-R$ distances.Figure 3 shows the diffuse reflectance collected at various distance to the light source, $S-R$. With a closer look at Figure 3(a), the overall SAR-DRM differs with change of the aspect ratio, however it transfers the effects from bulk optical properties in low extent.The order of the samples has changed and the magnitude between them visibly reduced. However, signal simulated for 0.6 mm of $S-R$ distance, has an increased separation between samples of different AR, clearly showing the effect of aspect ratio at the same wavelength range as observed in g in Figure 2(b).

The difference in intensity due to AR continues to increase with the increase of the $S-R$ distance. In addition, the reflectance signal also slightly changes over wavelength when approaching the largest $S-R$ distance. It can be concluded, that the difference in particle shape affects the SAR-DRM in the enough extend to initiate the inverse problem solution search, i.e. to estimate aspect ratio of the particles from measured spectra.

The observations in Figure 3 show a clear link between the effect of the aspect ratio and the spatial resolution

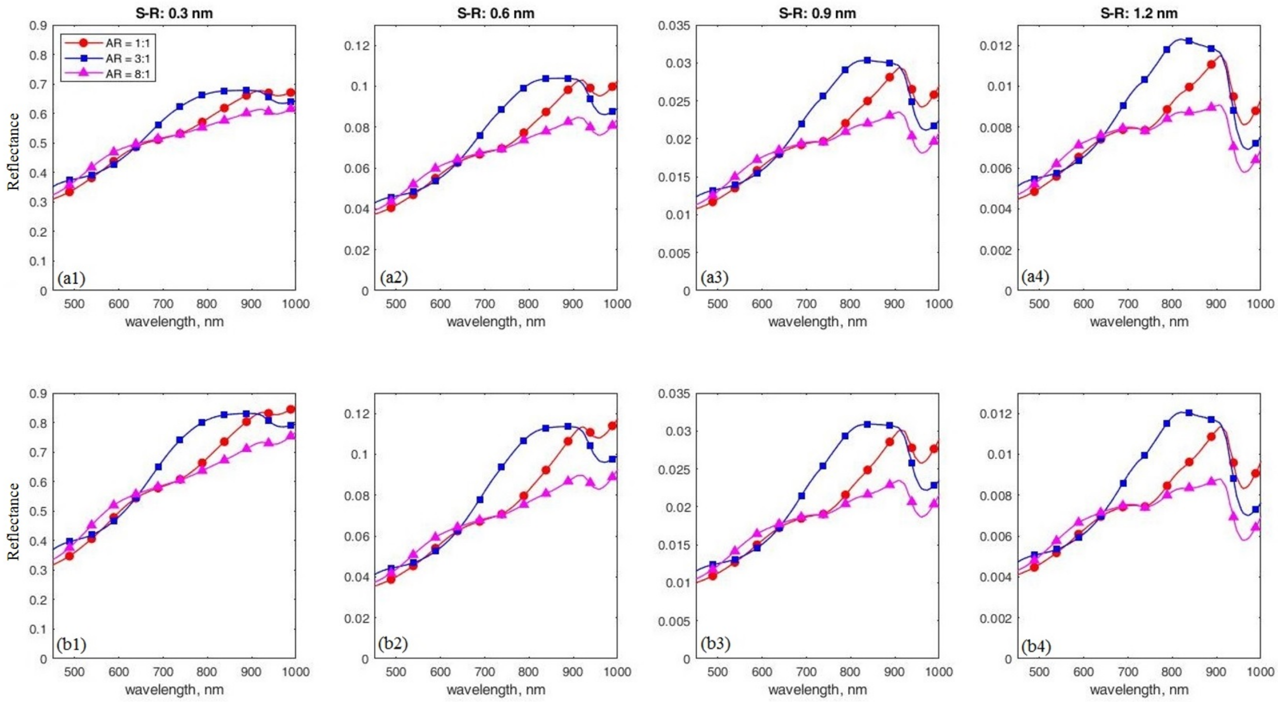

Figure 4: Diffuse reflectance collected at various source-to-receiver ($S - R$) distances from light emitted at a specified angle to the sample, (a1-d1): 30°, (a2-d2): 45°. Lines correspond to suspensions with particles of different aspect ratio: 1:1 (circle), 3:1 (square), 8:1 (triangle). (a)-(d) correspond to $S-R$ distance increase from 0.3 to 1.2 mm with 0.3 mm interval

of the spectra. Incorporation of an additional light source produces two more datasets for analysis. They were compared to normal emittance as well as the difference that angle itself (30° and 45°) makes.

Overall, the pattern of the spectra is similar to what was seen in Figure 3, however, the intensity of the reflectance is slightly higher and the relative difference in its slope has modified as well. Those changes indicate that the signal collected from the angular light source can be distinguished between different aspect ratios of studied particles at the smallest $S-R$ distance, which was not possible when using a normal incident light. The difference between the signal from 30° and 45° is nearly negligible and mostly appear in the relative change of the spectra slope between 750 nm and 900 nm. Increase in the slope relative difference manifests in the more prominent difference between samples with a different aspect ratio. Yet the difference between different angles of incidence is negligible even for relative units and is fading with increase of $S-R$. From observations above, a question is arising regarding the feasibility of the random orientation of particles approximation. If SAR-DRM would be applied to the material, where the orientation of the particles can be estimated, the different angles of emittance would return more specific information depending on the difference between light incidence and scattering angle. The closest receiving fibres would contain information regarding scattering by particles of specified rotation angle. Presumably, such effect will be reducing with propagation through the sample which would be reflected in the measurements from furthest collecting fibre and therefore their approximation to random orientation may still be applied due to simplicity.

Presence of such a strong effect of the parameter of study along with some specific changes between light collection settings substantiates the possibility to track aspect ratio parameter in future studies. The measured signal will become a question of the inverse problem solution. Prior to inversion, the modelling should be continued with a number of aspects of the study, not covered in this work. First, despite the beneficial effect of $S - R$ separation on the appearance of the aspect ratio influence, it is vital to highlight the contribution of other parameters, e.g. material properties to the effects seen. Hence, the SAR-DRM signal for a number of other materials should be simulated in order to evaluate the degree that material has on the aspect ratio effect appearance. In addition, the sensitivity of the method to the different shapes should be considered by comparing the SAR-DRM calculation results for the different geometries of the same volume and/or surface area. Before the final inversion, the simulations presented should be analysed for the presence of multiple minima. This should be done in order to discard the chance of a repetition of the same SAR-DRM pattern by a particle of a shape different to what was used to simulate the signal. By combining the above mentioned studies with the results presented, a suitable inversion methodology can be chosen for the inverting particle shape reliably.

4. CONCLUSION

In this work, the effect of aspect ratio of the ellipsoidal particles on spatially and angularly resolved diffuse reflectance spectra was studied. To achieve this, randomly-oriented ellipsoid suspensions with the same volume with two different aspect ratios and their bulk optical properties were modelled using DDSCAT. The reflectance of the colloid suspensions was then computed using DDA and then, the results were compared with the suspension of spherical particles of the same volume. The asymmetry parameter, g and the scattering coefficient μ_s show the most prominent response to the change in aspect ratio. The effect of the aspect ratio is also manifested in the spatially and angularly resolved diffuse reflectance; it suggests that there is a sufficient differentiation between samples for inversion possibility. The probe design beneficially contributed to the effect appearance as the studied effects were seen the most strongly in SAR-DRM at large source-to-receiver distances. The aspect ratio influence was not focused on narrow wavelength range but rather appeared between 700–1000 nm to a different extent, which emphasises the importance of multiwavelength analysis.

Despite the positive results of this modelling study, there is a number of aspects that have to be clarified in future work. First of all, polystyrene is a highly scattering material and scattering properties of other materials might not show the influence of the aspect ratio influence to the same degree. Another point of interest is the comparability of the effects appearing with effects produced by other shapes or volumes of the particles, in other words, clarification is needed of the likelihood to reproduce the same diffuse reflectance pattern with other particles and whether spatial or angular resolution of spectra have a beneficial effect in the identification of each geometry of particles.

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