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Scattering of intersecting spherical particles in the Rayleigh-Gans approximation

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ABSTRACT

In this work a novel semianalytical procedure to calculate the exact scattering behavior of complex particles made of intersecting spheres in the Rayleigh-Gans approximation is presented. Pickering emulsions, Janus particles, and lock and key particle colloids are particular cases of particles built from intersecting spheres. The proposed methodology is based on the decomposition of the complex particle as a sum of simpler components whose scattering properties can be evaluated using a simple integral. The procedure is developed for any number of spheres that intersect in pairs but it can be directly extended to intersections that involve more than two spheres at the same time. Some examples are presented to illustrate the application of the model to: (i) the study of the sensitivity of scattering spectra to detect complex particles from approximated model particles; (ii) the detection of different degrees of penetration of one particle into the other; (iii) the identification of the location of the cavity in particles that intersect with a spherical surface of contact; and (iv) the follow up of the evolution of a complex particle from a mix of its components.

1. Introduction

Interest in colloidal inhomogeneous particles with complex shapes has increased considerably due to their potential applications in multiple areas of materials science [1]. This type of particle can be used as attractive building blocks to create materials with extraordinary properties to be applied in chemistry, applied optics, or biology. For instance, anisotropic colloidal particles have been shown to be very useful for controlling molecular recognition and self-assembling processes, which are subjects of current interest in materials science. Also, complex colloidal particles with controlled surface structures have been used extensively in studies of controlled formation of hierarchically structured materials due to the wide range of sizes and materials accessible using these particles [2].

Spherical particles are in most cases the building blocks of these complex colloids. These particles are many times organized as a group of intersecting spheres that structure the complex colloidal unit. The number of spheres in this unit may vary from a couple to a many of them. Also many times, the spheres that form the complex colloid are made of different materials and for that reason the type of intersection noted before depends on the application and must be specified. Fig. 1 shows cross sections of two intersecting spheres with different kinds of contact surfaces between them. For instance, Pickering emulsions [3] are colloidal systems in which a large spherical particle is stabilized by the addition of a large number of small ones incrusted on its surface. In this case the spheres intersect in a form such that the small ones occupy the intersecting volume and the large one is deformed to accept the small ones in it, which corresponds to the intersecting spheres of Fig. 1a. Janus particles [4] are another type of colloidal particles that can be thought as a group of intersecting spheres. This is possible when the asymmetry is only due to the surface chemical groups, as well as when biphasic particles such as bicompartmental particles are considered. In this last case, the type of intersection present in the particle is as in Fig. 1b. Recently, colloidal systems that have attracted interest are the ones that follow the lock and key principle [5], in which colloidal spheres as keys and monodisperse colloidal particles with a spherical cavity as locks bind spontaneously and reversibly via the depletion interaction. The morphology of these complex colloidal particles presents intersections also of the type shown in Fig. 1a. Other complex particles that can be described as intersections of spherical ones are dumbbell, snowman, and raspberry particles [2,6–8].

The study of the scattering characteristics of complex colloidal particles is an important topic related to the morphological characterization of the particles and to the understanding of their optical functional behavior. Exact scattering models of complex particles have become available in the last few years [9]. However, these models are difficult to implement and require, in general, lengthy computations. A widely used alternative to the exact model is the Rayleigh-Gans (RG) approximation [10]. This approximation is valid for particles that present a low optical contrast with respect to the ambient medium, and are also sufficiently small so that the

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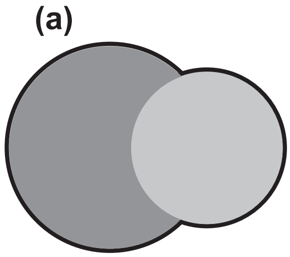

Fig. 1. Cross sections of possible spherical particle–spherical particle intersections: (a) spherical surface of contact between the two spheres; (b) plane surface of contact between the two spheres.

phase shift between incident and scattered light is also small. The conditions of validity for the RG approximation are always fulfilled in X-ray scattering but are more difficult to accomplish in light scattering.

A large variety of complex particles have been modeled in the RG approximation. However, scattering studies of the type of particles described in the previous paragraphs are more limited. For instance, the scattering of Pickering emulsions has been studied very recently using a simplified version of the RG theory [11]. Exact solutions of the RG theory have been obtained for different types of Janus particles [12,13]. These latter results involve the numerical evaluation of integrals of relatively complex functions. However, there is no general methodology available in the literature for calculating exactly the scattering properties of an arbitrary group of intersecting spheres in the RG approximation.

In this work a rather general procedure to calculate the exact scattering behavior of complex particles made of intersecting spheres in the RG approximation is presented. Pickering emulsions, Janus particles, and lock and key particle colloids are particular cases of particles built from intersecting spheres. The proposed methodology is based on the decomposition of the studied particle into a group of particles in which the scattering properties of the individual units can be evaluated using a simple integral, as done when spherical symmetry exists. The procedure is developed for a group of spheres that intersect as in Fig. 1a and it can be directly used to model Pickering emulsions, lock and key particle colloids, snowman particles, and others.

2. Theory

A group of N arbitrary scattering units located at positions given by $\mathbf{R}j$ ($j = 1, \ldots, N$) scatters incident monochromatic light with amplitude electric field, E_S, given by [14]

$$E_S(\mathbf{a}) = -E_0 \frac{\exp(ika)}{a} \sum_{j=1}^{N} b_j(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{R}_j), \tag{1}$$

where vector $\mathbf{a}$ ($|\mathbf{a}| = a$) indicates the position of the detector, E_0 is the magnitude of the incident field which in this case is assumed to be polarized perpendicular to the scattering plane, $\mathbf{q} = \mathbf{q}_s - \mathbf{q}_i$ is the scattering vector ($|\mathbf{q}| = q = \frac{4\pi}{\lambda} \sin 1/2\theta$), $\mathbf{q}_i$ and $\mathbf{q}_s$ are the propagation vectors of the incident and scattering fields, respectively, $k = 2\pi/\lambda$ is the magnitude of the propagation vector of the incident radiation, θ is the scattering angle, λ is the wavelength of the incident radiation in the medium, and b_j is the scattering length of scattering unit j. Note that time dependence has been omitted.

Assume that this group of N scattering units corresponds to a complex particle composed of intersecting spheres as, for instance, the Pickering-type particle shown in Fig. 2. In Fig. 3 a possible schematic decomposition of this particle is considered, in a fashion similar to that used in Ref. [15]. As seen, the intersections correspond to the type described in Fig. 1a. In this example the large sphere has a given contrast and the small ones are all of the same size and contrast, which is different than the contrast of the large sphere.

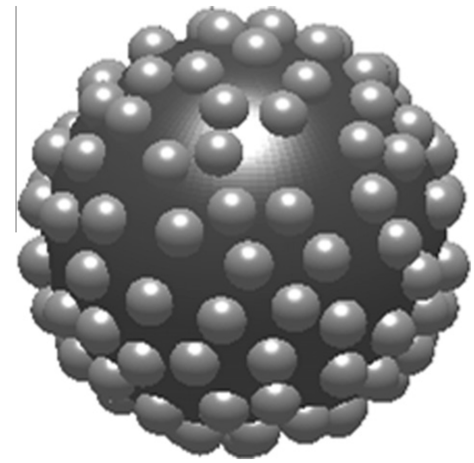

Fig. 2. Inhomogeneous Pickering-type particle composed of intersecting spheres used to develop the model.

According to Fig. 3, the amplitude electric field can now be written as

$$E_S(\mathbf{a}) = -E_0 \frac{\exp(ika)}{a} \left[\sum_{j=1}^{N_i} b_{R_j^*}(\mathbf{q}) + b_r(\mathbf{q}) \sum_{j=1}^{N_i} \exp(-i\mathbf{q} \cdot \mathbf{R}_j) - (N_i - 1) b_R(\mathbf{q}) \right], \tag{2}$$

where $N_i = N - 1$ is the number of small spheres and the scattering lengths of the large and small spheres are given by [10]

$$b_R(\mathbf{q}) = \Delta\rho_1 V_R F(q, R), \tag{3}$$

$$b_r(\mathbf{q}) = \Delta\rho_2 V_r F(q, r), \tag{4}$$

with

$$F(q, x) = \left[\frac{3}{(qx)^3} (\sin qx - qx \cos qx) \right]. \tag{5}$$

Here, $\Delta\rho_1$ and $\Delta\rho_2$ are the contrast scattering length densities (CSLDs) of the large and small spheres, respectively; R is the radius of the large sphere; r is the radius of the small spheres; $V_R = \frac{4}{3}\pi R^3$; and $V_r = \frac{4}{3}\pi r^3$.

Finally, following the decomposition of Fig. 3c, the $b_{R_j^*}(\mathbf{q})$'s ($j = 1, \ldots, N_i$) are the scattering lengths of N_i irregular particles, with each one a spherical particle of the same size and contrast as the large sphere, with a spherical cavity in one of the different N_i positions where the intersecting small spheres are localized. If the plane z–y is taken as the scattering plane, the expression for the scattering length of these particles is [10]

$$b_{R_j^*}(\mathbf{q}) = \Delta\rho_1 \int_{-R}^{R} \exp(i2k\xi \sin\theta/2) A_j(\theta, \xi) d\xi, \quad j = 1, \ldots, N_i, \tag{6}$$

where ξ is the perpendicular distance from the origin of coordinates to intersecting planes which are perpendicular to vector $\mathbf{q}$, and $A_j(\theta, \xi)$ is the area of the intersection of those intersecting planes with the volume of the j sphere with spherical cavity, for a given value of ξ and θ. This area, which for the case of a simple sphere is independent of θ and is given by $A(\xi) = \pi(R^2 - \xi^2)$, cannot be expressed as a simple function for the sphere with spherical cavity.

With the purpose of computing the $A_j(\theta, \xi)$'s for all the spheres with spherical cavity, all possible intersections of the "intersecting planes" with a generic sphere with spherical cavity must be