Scattering Properties of Core–Shell Particles in Plastic Matrices

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ABSTRACT: Blending submicron rubber particles with plastics can enhance the mechanical strength of the composite material. However, the difference in refractive index between the particle and matrix scatters light, making the material more opaque. We consider the possibility of reducing a particle's scattering cross section by adding coatings. We find that adding coatings can reduce the amount of scattering by changing the effective dielectric contrast between the particle and the matrix. We also found that, when the refractive index of the particle is very close to that of the matrix the order of the layers can have significant effects on the transmitted light. Such effects may be useful for engineering the optical properties of particle-doped plastics. Resonant effects akin to those found in antireflection coatings on planar surfaces are difficult to obtain and rarely provide a significant reduction in scattering. We discuss theoretical models that can qualitatively explain some of our results.
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INTRODUCTION

Polymer scientists frequently find it useful to incorporate heterogeneous particles into a plastic matrix. Indeed, most commercial plastics today are inhomogeneous blends or alloys. A typical example of such heterogeneous systems is rubber-toughened plastics. The rubbery domain enhances the mechanical strength of the composite material.[1–6] However, incorporating particles into an otherwise homogeneous material causes light to be scattered rather than transmitted, altering the appearance of the material. In many cases scattering is undesirable, as it tends to make the material more opaque, but in some cases scattering might be a tool that one uses to tune the appearance of a material.

Most work on the optical properties of plastic composites has been guided by two observations: that smaller particles scatter more light than larger particles, and that decreasing the refractive index contrast between the particle and the surrounding matrix tends to reduce the amount of light scattered by a particle.[7,8] These observations, while valid under a wide range of conditions, are based on the assumption that the only adjustable variables are the size and refractive index of homogeneous particles. One could ask, however, if particles with more complex (i.e. lay-

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ered) morphologies might give us greater flexibility. It is known that a properly designed coating on a planar surface can significantly reduce the amount of light reflected over a range of visible wavelengths and angles.[9] Synthetically, particles with defined layer morphology are possible by emulsion polymerization,[10] suspension polymerization methods,[11] or self-assembly approaches.[12,13] We will therefore explore the possibility of producing antireflection coatings for small particles.

Most of the work done on scattering by coated dielectric spheres has been undertaken with the goal of identifying and exploiting resonances that increase the scattering strength. Much of the current interest comes from colloidal chemists who are interested in self-assembly of colloidal crystals from particles that scatter strongly.[14] Other groups have studied fluorescent particles made with multiple layers to take advantage of the different properties of the core, the fluorescent inner shell, and the surface.[15] Astronomers have also taken an interest in core–shell particles, as the various layers of a particle of interstellar dust may yield information on the environments that the particle has encountered.[16]

We are aware of only one study undertaken with the goal of understanding how coatings might *reduce* scattering.[17] That study focused on particles with two layers (core and shell), a volume-averaged dielectric constant close to that of the surrounding medium, and a diameter comparable to or smaller than the wavelength of light. We describe here a computational study or particles with a wider range of sizes and refractive indices, as well as the possibility of reducing scattering by adding multiple shells to a core particle. We restrict our attention to materials and particle sizes that are commonly encountered when making composite plastics, and we use our computational findings to inform general design rules.

We find that, in most cases, the general guideline of minimizing the refractive index contrast applies to coated particles as well as homogeneous particles. Coatings that minimize the difference between the matrix and the volume-averaged dielectric constant of the particle tend to produce the least scattering. Resonant effects akin to those found in antireflection coatings on planar surfaces are rare and usually weak when present. We also find that a single coating is usually more effective at reducing scattering than adding multiple coatings. The principal exception is when the volume-averaged dielectric constant of a particle approximately matches that of the matrix, in which case the scattering properties can be sensitive to morphology (e.g., the order of the layers). We will explain some of these findings in terms of analytical theories that help inform design rules.

Theory

Useful Parameters

For the purpose of this work, the three most important characteristics of a particle are the scattering cross section (denoted σ), asymmetry parameter (denoted g), and the volume-average of the dielectric constant (denoted $\bar{\varepsilon} - \varepsilon_b$).[18]

The cross section σ is proportional to the total amount of light scattered by a particle when illuminated by a plane wave, and it has units of area. Suppose that we illuminate a particle with a plane wave of intensity I_0 (which has units of energy/area/time), and with an array of detectors we measure the power scattered in each direction. By integrating the measured over all directions, we can obtain the total scattered power W (which has units of energy/time). We can then define the scattering cross section σ as:

$$\sigma \equiv W/I_0 \tag{1}$$

It is clear that σ has units of area and is proportional to the total amount of light scattered by a particle.

We will frequently find it convenient to discuss the scattering efficiency Q_{scatt}, which is just σ normalized to the particle's geometrical cross section:

$$Q_{\text{scatt}} \equiv \frac{\sigma}{\pi r^2} \tag{2}$$

where r is the outer radius of the particle. Q_{scatt} has the advantage of being a dimensionless number that we can use to compare particles of different sizes. It is important to note that Q frequently exceeds 1, and for very large particles, it tends toward 2. The reason for this is that, in addition to scattering light incident on their geometrical cross section, particles also diffract light at their edges, so a particle can effectively "look" larger than its geometrical cross section.

The second parameter of interest, known as the asymmetry parameter and denoted g, is a

measure of the angular distribution of scattered radiation (when the particle is illuminated by a plane wave), and is defined as:

$$g \equiv \langle \cos\theta \rangle \tag{3}$$

where θ is the scattering angle and the average is taken over all directions, weighting according to the scattered intensity in each direction.

The last parameter, the average dielectric contrast, is a measure of the difference between the particle and the surrounding medium. The dielectric constant of a medium is the square of the refractive index n and is denoted ε. When it is spatially inhomogeneous it is often called the dielectric function rather than dielectric constant and denoted as $\varepsilon(\mathbf{r})$. The volume average of $\varepsilon(\mathbf{r})$ is frequently denoted $\bar{\varepsilon}$, and the average dielectric contrast is just $\bar{\varepsilon} - \varepsilon_b$, where ε_b is the dielectric constant of the surrounding background medium. Finally, we will sometimes make reference to the volume-averaged refractive index of a particle, which we define as $\sqrt{\bar{\varepsilon}}$.

Light in a System of Particles

Once we know the scattering parameters g and σ for a given particle morphology, we can ask how light will behave in a system of such particles, and what the resulting appearance will be. Qualitatively, if most photons entering the system are either unscattered or only scattered by a single particle before exiting then the system will look transparent, with a slight sheen determined by the wavelength dependence of σ.

Quantitatively, most light will be either unscattered or scattered only once if the sample dimensions are comparable to or larger than the mean free path $\ell \equiv (\sigma\rho)^{-1}$, where ρ is the number density of particles per unit volume. The mean free path is the average distance that a photon will travel before being scattered by a particle. Once a sample's thickness is larger than ℓ, photons will in general be scattered multiple times before exiting the sample. Multiply scattered photons can, under a very wide range of circumstances, be described as undergoing a random walk.[19] Photons executing a random walk exhibit many of the same properties as atoms and molecules executing random walks, and many of the same results from diffusion theory apply.

The most important parameter to describe a random walk is not the average distance between scattering events ℓ. Rather, it is the average distance that a photon travels before its direction of propagation is randomized, which is given the name *transport mean free path* and denoted with the symbol ℓ^*. If the particles scatter isotropically then that distance will be equal to ℓ, but if scattering is biased in the forward direction, then a photon may have to undergo several scattering events (and, on average, travel a distance $\ell^* > \ell$) before its direction of propagation is randomized. Clearly the value of ℓ^* will depend on the angular distribution of scattered radiation, and it turns out that the relationship between ℓ^* and ℓ is

$$\ell^* = \ell/(1-g) \tag{4}$$

Qualitatively, the relationship between ℓ^* and ℓ is similar to the relationship between the bond length and persistence length in polymers.

Materials tend to look white when the sample thickness is larger than ℓ^*. The fraction of incident light transmitted through a sample of thickness $L \gg \ell^*$ is proportional to ℓ^*/L. Polymers that have a natural color due to absorption of light also tend to assume a less saturated (less colorful) appearance when doped with scattering particles. For both of these reasons, the natural question to ask will be how can we modify the properties of polymer particles to maximize ℓ^* and hence minimize $\sigma(1-g)$.

Theory of Scattering from Layered Spherical Particles

The parameters σ and g can be calculated by solving Maxwell's equations for a plane wave incident on a layered spherical particle. The exact analytical solution for scattering from a homogeneous particle was originally worked out by Mie,[20] and is outlined in a number of good books.[18,21] The theory of scattering from a layered particle was first worked out by Aden and Kerker[22] for a particle with a single coating, and various algorithms have been developed since then to describe scattering from particles with an arbitrary number of layers. We use the algorithm of Wu and Wang[23] to perform the calculations. The algorithm is described in detail in their paper; what we present here is an outline of the Mie theory in a form that will be useful for making analogies with waves in planar dielectric coatings.

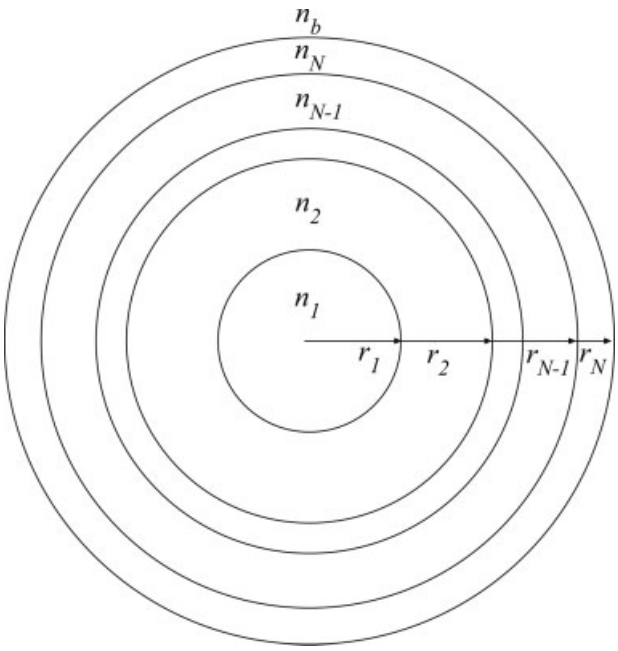

Figure 1. Diagram of layered particle with variables r_j, n_j, and n_b illustrated.

We consider a spherical particle with N layers, with layer 1 being the core and layer N the outermost shell. (See Fig. 1) Each layer has radius r_j and refractive index n_j (and hence dielectric constant $\varepsilon_j = n_j^2$). The particle is embedded in a background matrix of refractive index n_b (and dielectric constant $\varepsilon_b = n_b^2$). Because of spherical symmetry, the incident, scattered, and internal fields can be expanded as a superposition of vector spherical harmonics, special functions similar to the spherical harmonics used to solve the Schrödinger equation for the hydrogen atom.

We have to solve a boundary value problem to determine the expansion coefficients of the vector spherical harmonics. Using notation similar to that of Smith and Fuller,[24] we use the symbol $\mathbf{N}_{mp}^{(3)}(k_0 nr,\theta,\phi)$ for waves radiating outward from the origin and $\mathbf{N}_{mp}^{(3)*}(k_0 nr,\theta,\phi)$ for waves converging inward toward the origin, where the superscript * denotes complex conjugation, k_0 is 2π divided by the wavelength of light in vacuum, n is the refractive index of the medium that the wave is traveling in, and r, θ, and ϕ are the usual spherical coordinates. The subscript p refers to the polarization of the wave and is 1 for transverse magnetic waves and 2 for transverse electric waves. The subscript m refers to the order of the Hankel function of the first kind (a type of spherical Bessel function) governing the radial dependence of the vector spherical harmonic.

At large distances from the origin the Hankel functions are proportional to $\frac{\exp(\pm ik_0 nr)}{k_0 nr}$, where the sign of the exponent depends on whether the wave radiates outward from the origin (+) or converges inward toward the origin (−). When the thickness of a layer is much smaller than the distance r from the origin we can approximate the radial dependence of the field in that layer with a sinusoidal function, a fact that we will use later in our discussions of the properties of particles large compared with the wavelength of light.

The plane wave incident on the particle can be written in the following form:

$$\mathbf{E}_{inc} = \hat{\mathbf{e}}_x \exp(ik_0 n_b z) = \frac{1}{2}\sum_{p=1}^{2}\sum_{m=1}^{\infty} q_{mp}\left(\mathbf{N}_{mp}^{(3)}(k_0 n_b r,\theta,\phi) + \mathbf{N}_{mp}^{(3)*}(k_0 n_b r,\theta,\phi)\right) \quad (5)$$

where $q_{mp} = -[i^{n+p}\ (2n+1)/n(n+1)]$.[24] We have written this field in terms of incoming and outgoing spherical waves for convenience when making analogies with waves in planar dielectric coatings. The scattered field can be written as

$$\mathbf{E}_{scatt} = \sum_{p=1}^{2}\sum_{m=1}^{\infty} q_{mp} a_{mp} \mathbf{N}_{mp}^{(3)}(k_0 n_b r,\theta,\phi) \quad (6)$$

where a_{mp} is proportional to a scattering amplitude. (The factor of q_{mp} has been inserted for convenience when matching boundary conditions.) Calculating the set of coefficients $\{a_{mp}\}$ is the principle task when studying scattering by a particle, as these coefficients completely determine the scattered field. Once the scattered field is known it is straightforward to calculate the parameters σ and g.

The field in the jth layer of the particle can be written in the following form:

$$\mathbf{E}_{int}^{(j)} = \sum_{p=1}^{2}\sum_{m=1}^{\infty} q_{mp}\left(u_{mp}^{(j)}\mathbf{N}_{mp}^{(3)}(k_0 n_j r,\theta,\phi) + v_{mp}^{(j)}\mathbf{N}_{mp}^{(3)*}(k_0 n_j r,\theta,\phi)\right), \quad 2 \le j \le N \quad (7)$$

$$\mathbf{E}_{\text{int}}^{(1)} = \sum_{p=1}^{2}\sum_{m=1}^{\infty} q_{\text{mp}} u_{\text{mp}}^{(1)} \left(\mathbf{N}_{\text{mp}}^{(3)}(k_0 n_1 r, \theta, \phi) + \mathbf{N}_{\text{mp}}^{(3)*}(k_0 n_1 r, \theta, \phi) \right) \quad (8)$$

where $u_{\text{mp}}^{(j)}$ and $v_{\text{mp}}^{(j)}$ are coefficients of the outgoing and incoming fields, and once again the factor of q_{mp} has been included for ease when matching boundary conditions. Finally, the magnetic field $\mathbf{H}$ in any layer can be obtained using Faraday's law: $\mathbf{H} = \frac{-i}{k_0} \nabla \times \mathbf{E}$.

In eq 8 we impose our first boundary condition. At the core of the particle $u_{\text{mp}}^{(j)} = v_{\text{mp}}^{(j)}$. An incoming spherical wave front that converges toward the center of the particle will, upon reaching the center, diverge outward, and so the amplitudes of the incoming and outgoing fields must be equal at the center of the particle. The other boundary conditions that we must apply are that the transverse components of the electric and magnetic fields are continuous across the boundary between layers j and $j + 1$ ($1 \leq j \leq N - 1$) and between layer N and the surrounding matrix. These conditions yield a set of $2N$ equations that we can solve to obtain the set of coefficients $\{a_{\text{mp}}\}$, which can then be used to obtain σ and g for a given particle morphology.

The process that we have just described is in general tedious, but excellent software is available to implement these calculations.

EXPERIMENTAL

Computational Methods

We calculated σ and g for a variety of particle morphologies. We used code developed by Voshchinnikov[16,22] to implement the algorithm of Wu and Wang.[23] Our only significant modification to the code, aside from customizing the input and output formats, was to allow for the possibility that the matrix might have a larger refractive index than any layer of the particles. In Voshchinnikov's code it is assumed that the refractive index of the matrix is smaller than the refractive index of any layer in the particle, and so the algorithm only checks the layers of the particle when searching for the largest refractive index in the problem. We modified the code to also check the matrix refractive index. Results for homogeneous particles and particles with a single coating were checked against the freeware program Scatlab, and agreement was found to at least one part in 10^{-3}.

Parameters

All calculations assume light with a wavelength of 550 nm, the center of the visible range. Searching for a resonance by varying the particle size is equivalent to searching for resonance by varying λ. Also, the typical design problem facing a plastics engineer is one where the wavelength range of interest is fixed, and the adjustable parameters are the thicknesses of the various particle layers. One can determine the optical properties at some other wavelength $\lambda_2 \neq 550$ nm by rescaling the diameters (and layer thicknesses) of the particles described here by a factor $\lambda_2/550$ nm.

For convenience we assume a particle volume fraction $\phi = 5\%$ relative to the matrix. One can calculate ℓ and ℓ^* at some other volume fraction ϕ_2 by rescaling ℓ or ℓ^* by a factor $0.05/\phi_2$, as long as $\phi_2 \leq 0.1$. For volume fractions above 0.1, particle positions become correlated because of excluded volume effects, and correlations can modify scattering in a manner that tends to increase ℓ^*. Also for convenience, we do all calculations for particles in a matrix with a refractive index of 1.500. This is comparable to typical refractive indices of commercially important polymers. To implement the systems described here in a matrix with some other refractive index n_2, rescale the refractive index of each layer by a factor $n_2/1.500$, and rescale the particle diameters and layer thicknesses by a factor $(n_2/1.500)^{-1}$.

Finally, for the most part we will consider particles with outer diameters between 50 nm and 5 μm, and cores or layers with refractive indices between 1.35 and 1.65. These parameters are representative of the range of materials frequently used in commercial plastics.

RESULTS

Our key findings are

1. Coatings on small to midsize ($d \approx 50$ nm to 1 μm) particles tend to decrease σ and bring g closer to 0, provided that the coating decreases the dielectric contrast between the medium and the particle. A single coating is generally more effective than

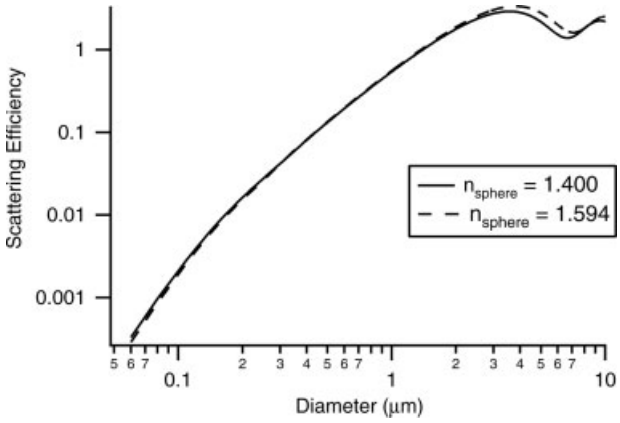

Figure 2. Scattering efficiency Q_{scatt} *versus* particle diameter for homogeneous spheres of different refractive indices in a medium of refractive index $n_b = 1.5$.

multiple coatings, and the scattering properties tend not to depend sensitively on the thickness of the coating if the volume-averaged dielectric constant of the particle differs from that of the surrounding matrix by more than ≈0.02.

2. When the volume-averaged dielectric constant of the particle matches or nearly matches that of the surrounding matrix, σ and g can depend sensitively on particle morphology.
3. For larger particles, the effect of a coating can be more complicated, but typically σ is unaffected while g can be modified slightly.

Homogeneous Particles

We begin by showing in Figure 2 a plot of Q_{scatt} *versus* particle diameter for homogeneous spheres with refractive indices 1.400 and 1.594. These numbers were chosen because the dielectric contrast is the same in both cases, and in many cases Q_{scatt} and σ are proportional to the square of the dielectric contrast. We see that as long as the particle diameter is less than 2 μm, the high-index and low-index particles scatter with the same efficiency. This fact is useful for studying coated particles. If we want to ask whether coatings are more useful on core particles with refractive indices higher or lower than that of the surrounding medium, it helps to compare core particles with similar scattering properties. For particle diameters larger than 2 μm, the high-index and low-index particles differ in their scattering efficiencies. The difference is due to interference effects: waves that scatter from different portions of the particle interfere with each other, and the phase shift between different waves depends on the refractive index of the particle.

Single Coatings on Particles Smaller than or Comparable to λ

Arbitrary Choices of Refractive Indices

We now consider the effect of adding a single coating to a spherical particle. We begin by studying core particles with refractive indices of 1.400 and 1.594 and outer diameters of 100, 320, and 1000 nm. We chose these parameters because homogeneous high-index and low-index particles of these sizes and refractive indices have nearly identical scattering efficiencies.

On the low-index particles ($n_1 = 1.400$) we consider coatings with refractive indices 1.350, 1.449, and 1.546. On the high-index particles ($n_1 = 1.594$) we consider coatings with refractive indices 1.449, 1.546, and 1.650. The values 1.449 and 1.546 were chosen to facilitate comparisons with antireflection coatings on planar surfaces: these are the optimum refractive indices for antireflection coatings on planar samples of the low-index and high-index materials (respectively) surrounded by a medium of background refractive index $n_b = 1.500$. (The optimum refractive index n_{coat} for an antireflection coating on a slab of refractive index n_{core} in a background medium of refractive index n_b is $\sqrt{(n_{\text{core}} n_b)}$.) The values 1.350 and 1.650 were chosen arbitrarily, to study the effect of a coating that provides a larger contrast compared with the surrounding matrix.

Figures 3–5 show our results. We calculated the scattering efficiency *versus* the volume fraction ϕ of the core material for the particle sizes, refractive indices, and coatings discussed in the previous paragraph. In every case, we find that adding a coating with a refractive index closer to that of the surrounding matrix reduces the scattering efficiency, while adding a coating with a refractive index further from that of the surrounding matrix increases the scattering efficiency of the particle. The scattering efficiency is minimized when the volume average of the dielectric constant is approximately equal to the dielectric constant of the surrounding medium. (We did not sample enough data points to determine if the dielectric constant must be *exactly* matched to minimize Q_{scatt}, but for our practical

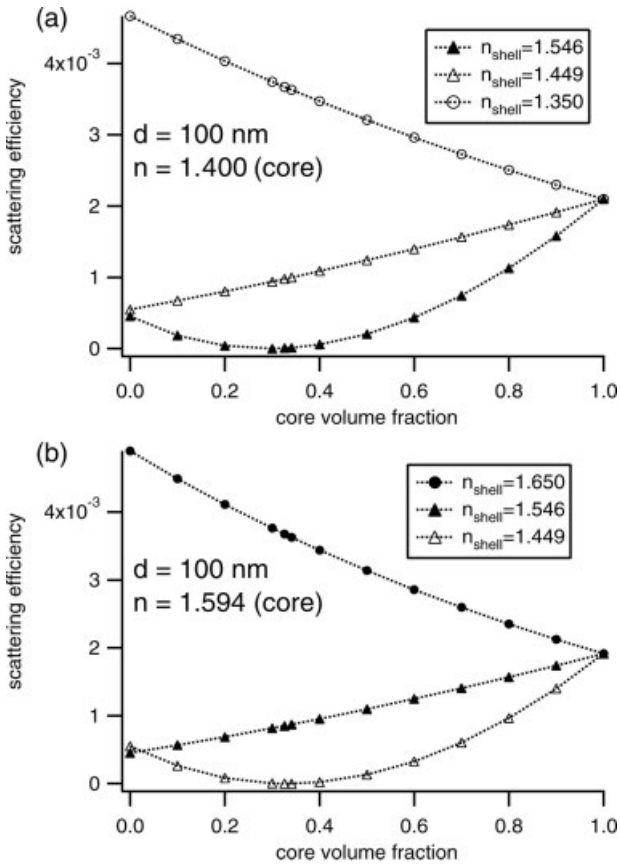

Figure 3. Scattering efficiency Q_{scatt} of a core–shell particle *versus* volume fraction of core material. Particles have an outer diameter of 100 nm and coatings with various refractive indices, and are embedded in a background medium of refractive index $n_b = 1.50$.

concerns any small discrepancy is irrelevant.) Varying the volume fraction of the core only *minimizes* Q_{scatt} when it is possible to make the volume-averaged dielectric contrast zero. Otherwise varying the volume fraction of the core (or, equivalently, the thickness of the particle) only changes the scattering efficiency monotonically.

We can deduce that the mechanism by which coatings reduce the scattering efficiency of a core–shell particle is very different from the mechanism by which antireflection coatings reduce scattering from planar surfaces. Antireflection coatings on planar surfaces operate by destructive interference of scattered waves. Interference effects are very sensitive to phase shifts and coating thicknesses. In Figures 3–5, however, the minimum scattering efficiency does not occur at the same coating *thickness* irrespective of particle diameter. Rather, it always occurs at approximately the same *volume fraction* of core material. In all of the cases that we have examined involving particle diameters less than 2 μm (including cases not shown here), the scattering efficiency is minimized when the volume-averaged dielectric constant of the particle matches or nearly matches that of the surrounding medium. Later we shall discuss a simple analytical model that predicts this behavior.

We now consider how coatings on particles affect transport of light through a system of particles. We calculate ℓ^* for light propagating through a system of core shell particles, varying the particle morphology. We will concentrate on particle morphologies that minimize the scattering efficiency. We do not assume that minimizing Q_{scatt} maximizes ℓ^*, since ℓ^* depends on the angular distribution of scattered radiation as well as the total amount of light scattered.

In Figure 6(a) we calculate ℓ^* for light propagating through a system of core–shell particles

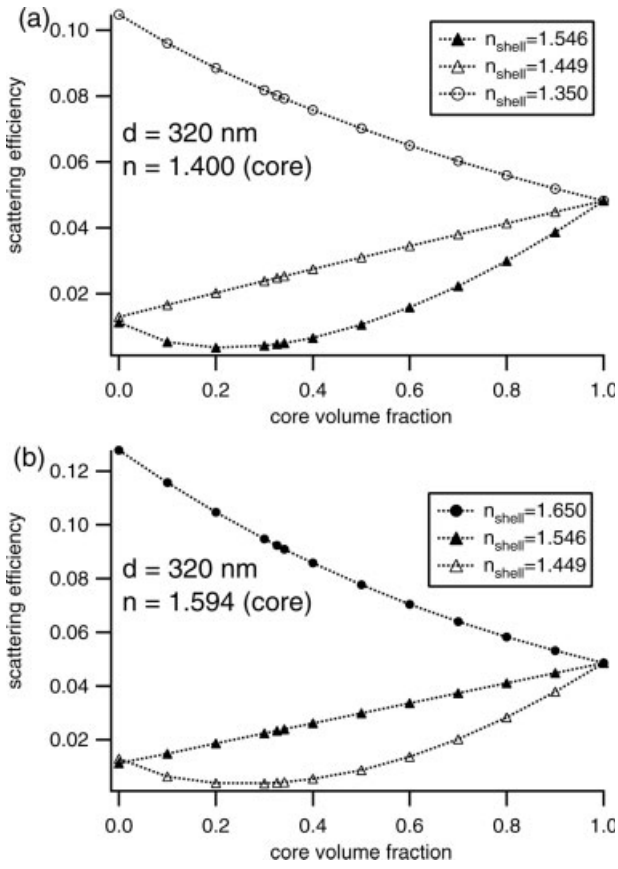

Figure 4. Scattering efficiency Q_{scatt} of a core–shell particle *versus* volume fraction of core material. Particles have an outer diameter of 320 nm and coatings with various refractive indices, and are embedded in a background medium of refractive index $n_b = 1.50$.

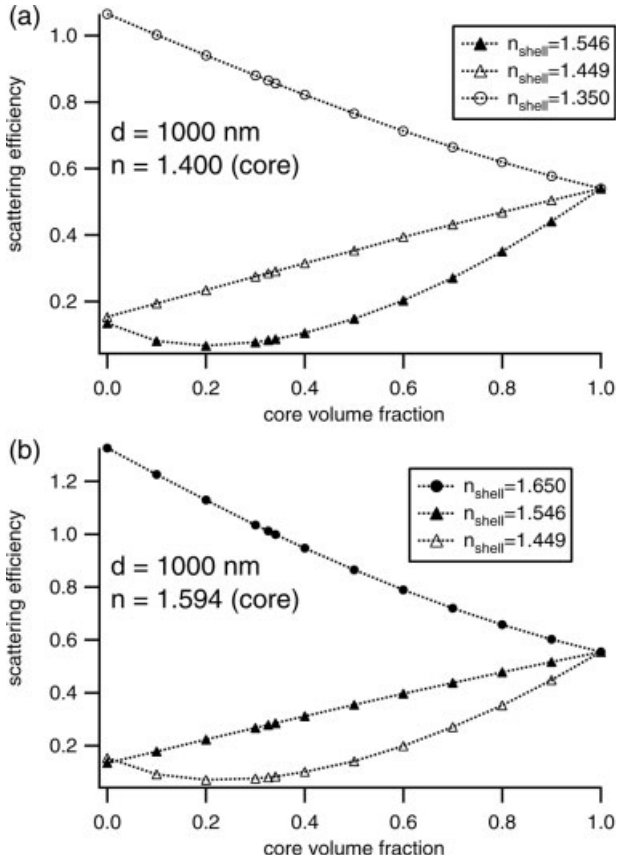

Figure 5. Scattering efficiency Q_{scatt} of a core–shell particle *versus* volume fraction of core material. Particles have an outer diameter of 1000 nm and coatings with various refractive indices, and are embedded in a background medium of refractive index $n_b = 1.50$.

with a core that has a refractive index of 1.4 and a coating that has a refractive index of 1.546, and we vary the particle diameter and the volume fraction of the core material. In Figure 6(b) we do the same, except that the core material has a refractive index of 1.594 and the coating has a refractive index of 1.449. For both particle types, we find that the morphology that minimizes Q_{scatt} sharply maximizes ℓ^* only in the case of the smallest particles (100-nm diameter). In this case, ℓ^* is enhanced by nearly 3 orders of magnitude. For larger particles (320- and 1000-nm diameters) ℓ^* is only weakly affected by the presence of a coating.

Volume-Averaged Dielectric Constant Nearly Matches Matrix

In many industrial applications, such as impact-modified transparent poly(methylmethacrylate) and poly(vinyl chloride), multi-layered core–shell particles are used, and the refractive indices and volume fractions of the layers frequently result in a volume-averaged dielectric constant that nearly matches that of the surrounding matrix. In such cases, the volume-averaged dielectric constant of the particle is not the only important parameter for coated particles smaller than or comparable to λ. We have found that when the volume-averaged dielectric constant of a small particle nearly matches the dielectric constant of the surrounding medium, the order of the layers can significantly affect Q_{scatt} and g and hence ℓ^*.

As an example, in Figure 7 we show calculations of l^* for core–shell particles in which the core and shell have equal volume fractions, and one of the layers has a refractive index of 1.45

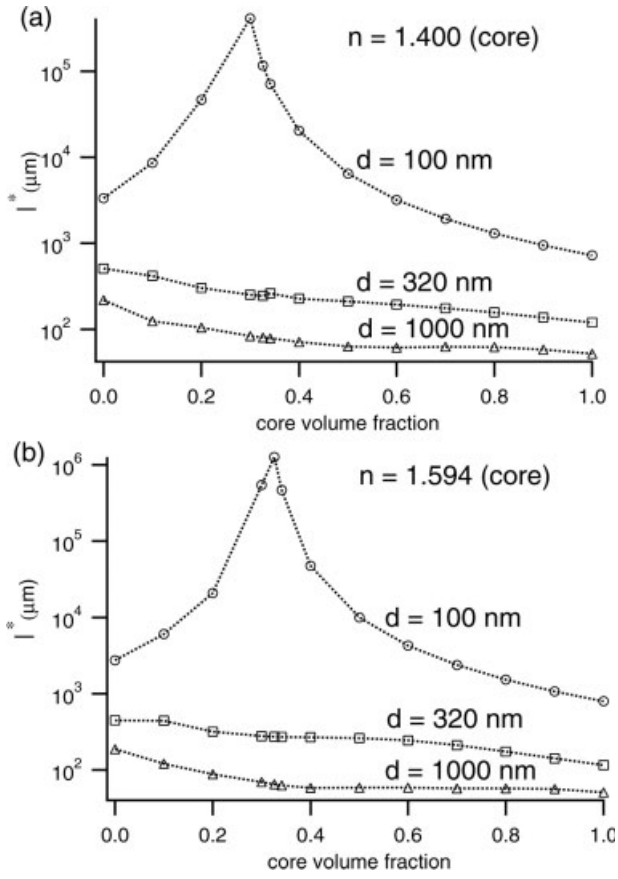

Figure 6. Transport mean free path l* for light diffusing through a system of core–shell particles. We show calculations of l* for a variety of particle sizes and morphologies (background medium $n_b = 1.5$). (a) Particles with a core material having a refractive index 1.4 and coating having a refractive index 1.546. (b) Particles with a core material having a refractive index 1.594 and coating having a refractive index 1.449.

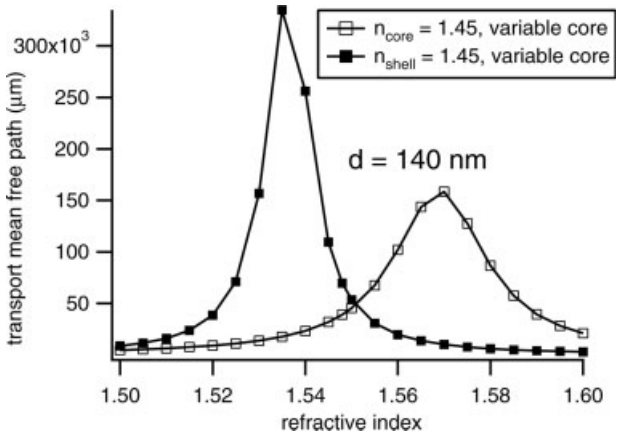

Figure 7. Transport mean free path for light diffusing through a system of core–shell particles with an outer diameter of 140 nm. The volume fractions of the core and shell are 50% in both plots, and for each plot one of the components (core or shell) is fixed at a refractive index of 1.45 while the refractive index of the other component is varied (background medium $n_b = 1.5$).

while the other layer has a variable refractive index. The outer diameter is 140 nm. We see that interchanging the core and shell materials can, in some cases, alter ℓ^* by a factor of 10. Depending on the situation the weakest scattering can be obtained with either a high-index core or a high-index shell. In all cases, ℓ^* is quite large, on the order of a millimeter or more.

We attribute this morphology-dependent phenomenon to the effective size of the particle. When the refractive index of the shell is close to that of the matrix, incoming light waves "see" an effectively smaller particle, because the outer shell scatters only weakly. If we then interchange the core and shell materials, the new particle will "appear" larger to incoming light waves because the edges will scatter more strongly. Interestingly, this effect can cause ℓ^* to be shorter for particles on which the shell's refractive index nearly matches that of the surrounding medium: a smaller particle scatters light less efficiently (which tends to increase ℓ^*), but it also scatters less light in the forward direction (which tends to *decrease* ℓ^*). The only way to determine which of these competing effects dominates is to perform a numerical calculation with the Mie theory, as we have done in Figure 7.

We also observe that the effect of interchanging the core and shell is actually weakest when the volume average of the dielectric constant matches the dielectric constant of the surrounding medium (i.e., when the refractive index of the variable layer is $\sim$1.548). This is consistent with our interpretation in terms of an effective size: when the volume average of the dielectric constant matches the surrounding medium, the dielectric constants of the core and shell will differ significantly from the surrounding medium and in either morphology the edges of the particle will scatter relatively strongly. We have found similar effects in particles with multiple layers.

Another interesting phenomenon occurs when we look at the wavelength dependence of the mean free path. In Figure 8 we show a plot of ℓ^* *versus* wavelength for core–shell particles with

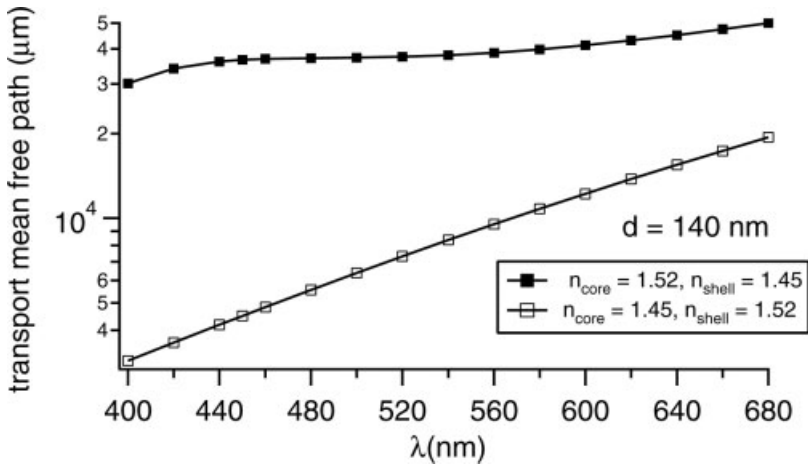

Figure 8. Transport mean free path *versus* wavelength for light diffusing through a system of core–shell particles with an outer diameter of 140 nm. The volume fractions of the core and shell are 50% in both plots (background medium $n_b = 1.5$).

an outer diameter of 140 nm and two layers, the layers having refractive indices 1.45 and 1.52 and volume fractions of 50% for each layer. The only difference between the two plots in Figure 8 is the order of the layers. The difference is striking: interchanging the layers of the particle can change the red–blue contrast by a factor of 4.

In both cases the transport mean free path is longer for red light (long wavelengths), as would be expected for light diffusing through a system of small, weakly scattering particles. (Rayleigh scattering) However, the ratio $\ell^*(700\text{ nm})/\ell^*(400\text{ nm})$ is 1.64 when the outer layer has a refractive index of 1.45, and 6.24 when the outer layer has a refractive index of 1.52. When the ratio of mean free paths for red and blue light is large, the appearance of the plastic material is reddish when viewing transmitted light and bluish when viewing scattered light. When the ratio is closer to unity, both the scattered and transmitted light will have a more neutral appearance. The parameters used here are only examples, and similar phenomena are observed for other choices of parameters. The key point is that by coating the particles one can control the color of a material as well as the transparency.

Coatings on Particles Large Compared with λ

Next we turn our attention to particles significantly larger than λ. We begin by studying particles with an outer diameter of 4 μm, for which size the two types of core materials ($n_{\text{core}} = 1.400$ and $n_{\text{core}} = 1.594$) lead to significantly different scattering efficiencies, as seen in Figure 2. We consider the same types of coating materials as for small spheres with single coatings ($n_{\text{core}} = 1.35$, 1.449, and 1.594 for low-index cores, $n_{\text{core}} = 1.449$, 1.546, and 1.65 for high-index cores). In Figure 9 we plot Q_{scatt} *versus* core volume fraction for the two types of core materials.

As before, we find that the only significant reduction in Q_{scatt} is achieved when the refractive index of the medium is intermediate between the refractive indices of the core and shell. However, there are two major differences between this case and the smaller particles that we examined earlier. The first is that Q_{scatt} varies by only a factor of 3 in Figure 9. On the smaller particles a coating that reduced the volume-averaged dielectric contrast to zero could reduce Q_{scatt} by an order of magnitude or more. The second is that the optimal coating thickness

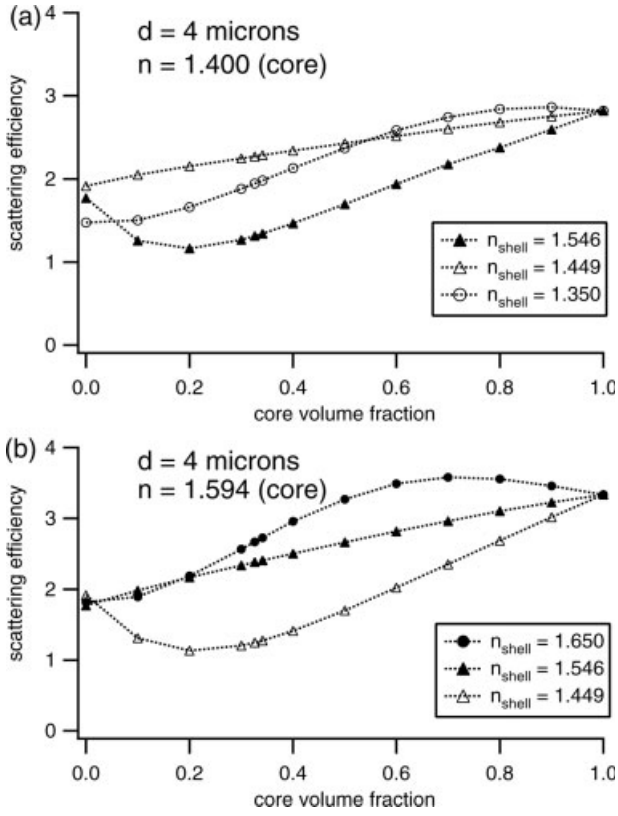

Figure 9. Scattering efficiency Q_{scatt} of a core–shell particle *versus* volume fraction of core material. Particles have an outer diameter of 4 μm and coatings with various refractive indices, and are embedded in a background medium of refractive index $n_{\text{b}} = 1.50$.

does *not* bring the volume-averaged dielectric contrast to zero. In these larger particles Q_{scatt} is sensitive to interference of waves as well as the volume average of the dielectric constant, so we cannot use any simple heuristic to estimate the optimal coating thickness; only a full Mie calculation can give accurate predictions. Our calculation shows that, for the parameters studied here, a particle with a core volume fraction of $\sim$20% produces the optimal (minimum) scattering efficiency when the coating material is chosen so that the refractive index of the matrix is intermediate between the refractive indices of the core and shell.

When we consider light propagation in a system of such particles, we find a third difference between these large particles and the smaller particles that we studied above: adding a coating to a particle does not optimize ℓ^*. In Figure 10 we plot ℓ^* *versus* the volume fraction of core material for light propagating through a system of particles with various core and coating refrac-

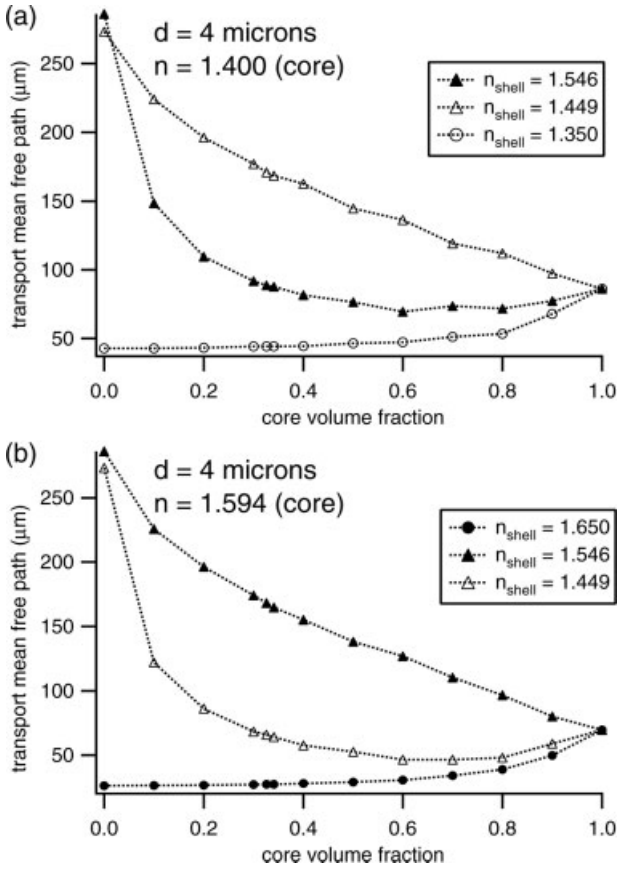

Figure 10. Transport mean free path ℓ^* for light diffusing through a system of core–shell particles. Particles have an outer diameter of 4 μm and coatings with various refractive indices, and are embedded in a background medium of refractive index $n_b = 1.50$. (a) Core refractive index = 1.400, (b) core refractive index = 1.594.

tive indices, surrounded by a medium with refractive index 1.5. For all particle types considered here, ℓ^* (and hence the amount of transmitted light) is maximized when the volume fraction of the core material is either 0 or 1, depending on the choice of parameters. The modest reduction in Q_{scatt} achieved by the coating cannot compensate for the effect on the angular distribution of scattered light, and so ℓ^* changes monotonically as a function of the core volume fraction.

We have also considered a wide variety of other large particles with single coatings, varying the particle size, the volume fraction of the core material, and the refractive indices of the core and shell. In general, it is very difficult to find a combination of parameters that cause ℓ^* to deviate from the trend seen in Figure 10: ℓ^* is almost always a monotonically increasing or decreasing function of the core volume fraction. The most frequent exceptions occur when ℓ^* is approximately the same for core volume fractions of either 0 or 1, and in those cases the maximum value of ℓ^* achievable by coating the particles is rarely more than 10% larger than the value achievable with homogeneous particles.

The implications for particle design are clear: when doping a polymer with large particles, if the goal is to minimize scattering then use homogeneous particles whenever possible. If homogeneous particles are not feasible for the application, then use either the thickest or thinnest coating possible, depending on the circumstances.

Multiple Coatings

Finally, we have also considered the possibility of reducing scattering from particles in various size regimes by incorporating more layers. We have found that adding multiple coatings to a particle can indeed increase ℓ^*. However, in almost all cases that we have examined, particles with multiple coatings scatter more strongly than homogeneous particles or particles with a single judiciously chosen coating. In rare cases where particles with multiple coatings did scatter less than homogeneous or single-coated particles, we never found a case where adding more coatings reduced ℓ^* by more than a factor of 2.

DISCUSSION

Having illustrated the typical ways in which coatings can modify the scattering properties of spherical particles, our next goal is to develop a conceptual understanding of these results. We want to be able to formulate design rules that are supported by our calculations as well as a conceptual understanding of the phenomenon. We will use approximate models to study the properties of coated particles in two limits: The Rayleigh–Gans approximation (RGA, applicable in the case of low refractive index contrast and small particles), and a combination of geometrical optics and planar coating theory to study particles large compared with the wavelength of light. From the Rayleigh–Gans model we will deduce why the volume-averaged dielectric contrast is the most important parameter to optimize when trying to reduce scattering by small particles. From the geometrical optics approxi-

mation we will deduce why a coating on a large particle rarely produces significant changes in σ or g.

Rayleigh–Gans Approximation

In the RGA, the intensity of light scattered from a particle in a given direction is proportional to the Fourier transform of the particle's spatially inhomogeneous dielectric contrast $\varepsilon(\mathbf{r}) - \varepsilon_b$. The spatial frequency and direction at which we compute the Fourier transform depends on the direction of scattering. We define the scattering vector $\boldsymbol{q}$ as the difference between the wavevector of the incident wave and the wavevector of a wave scattered in a given direction (θ, ϕ):

$$\mathbf{q} \equiv \mathbf{k}_{\text{incident}} - \mathbf{k}_{\text{scattered}} \tag{9}$$

The intensity of the wave scattered in a given direction is proportional to square of the scattering amplitude $f(\mathbf{q})$, and in the RGA one can show that[18]

$$f(\mathbf{q}) \propto \int_{\text{particle volume}} (\varepsilon(\mathbf{r}) - \varepsilon_b)\ \exp(i\mathbf{q}\cdot\mathbf{r})\mathrm{d}V \tag{10}$$

We omit factors of 2, π, k_0, and so forth because we are primarily interested in qualitative trends. Equation 10 is approximately valid as long as

$$|\varepsilon(\mathbf{r})/\varepsilon_b - 1|,\ n_b k_0 r_N |\varepsilon(\mathbf{r})/\varepsilon_b - 1| \ll 1 \tag{11}$$

Even within this domain of applicability, however, eq 10 may not be quantitatively accurate when $\mathbf{q} = \mathbf{0}$, especially if it predicts that $f(\mathbf{0}) \approx 0$.

The significance of $f(\mathbf{0})$ is two-fold: we can see from eq 10 that in the RGA $f(\mathbf{0})$ is the volume-averaged dielectric contrast $\bar{\varepsilon} - \varepsilon_b$, and in the previous section we saw that coated particles scatter more weakly when a coating reduces $\bar{\varepsilon} - \varepsilon_b$. The optical theorem, which is discussed in books on light scattering and electromagnetism,[18,25] states that σ is proportional to $f(\mathbf{0})$. The fact that $f(\mathbf{0})$ and hence σ is proportional to $\bar{\varepsilon} - \varepsilon_b$ explains why scattering from small particles is minimized when the dielectric contrast is minimized.

We can also understand why a single coating will, in general, be more effective at reducing scattering than can multiple coatings. Suppose that, for a given material, we have the ability to synthesize several different types of coatings. $\bar{\varepsilon} - \varepsilon_b$ will be minimized if we pick the coating material with the refractive index that is closest to that of the matrix and make the thickest possible layer. Any other coating materials will have refractive indices that are closer to that of the particle, and will hence increase the dielectric contrast compared with the single-coating design.

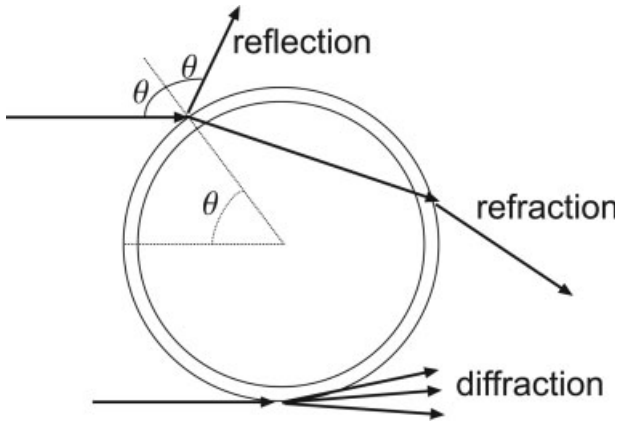

Figure 11. Illustration of mechanisms for scattering from a large particle. Two rays of light are shown hitting the particle. One is split into refracted and reflected rays; the other is incident on the edge of the particle and is diffracted. The angle of incidence for the top ray is θ.

Large Particles

On particles too large to be modeled by the RGA, we have found that coatings rarely reduce Q_{scatt} (or σ) by more than a factor of 2, and that the effect becomes weaker as the particle size increases. Here we seek to explain why the effect of a coating becomes negligible in the limit of very large particles. If a spherical particle is significantly larger than the wavelength of light, then we can apply traditional notions and methods used to study scattering of light from objects large compared with the wavelength of light. We assume that scattering can be attributed to three distinct mechanisms, as illustrated in Figure 11:

1. Reflection from the surface of the particle.
2. Any light not reflected from the surface is refracted in accordance with Snell's law upon entering the particle. Regardless of whether the light undergoes internal reflections before exiting the particle, refraction upon entering the particle has already changed the direction of propagation, and so the light is considered scattered.
3. Diffraction at the edges of the particle.

Of these mechanisms, only the first one, reflection at the surface, can be enhanced or diminished by a coating. The angular distribution of light that scatters after entering the particle may also be affected by a coating (due to the effect on internal reflections), but any light that enters the particle is by definition scattered by refraction, regardless of how many (if any) internal reflections it undergoes. We therefore deduce that a coating on a large particle cannot significantly reduce Q_{scatt}, but it may bias scattering in the forward direction (by slightly reducing scattering at the rear surface) and bring g closer to 1. This will have the effect of increasing ℓ^* for light diffusing through a system of coated particles, somewhat decreasing the opacity.

To verify our deduction we calculated the angular distribution of light reflected from the back surface of a large spherical particle with and without a thin coating. We used standard formulas for off-normal reflection from planar coatings to calculate the amount of light from each point on the surface, and integrated over the back surface of the particle to obtain the average cosine of the scattering angle.[9] We average the reflectance over the two possible polarizations and integrate the reflected light over the back surface of the particle to obtain a reflectance efficiency which we call Q_{reflect}. Q_{reflect} is the portion of incident light reflected by the back surface of the particle, and is given by:

$$Q_{\text{reflect}} = \int_{-90^\circ}^{90^\circ} R(\theta)\ \sin\theta\ \cos\theta\ \mathrm{d}\theta \qquad (12)$$

where θ is the angle of incidence in Figure 11, $R(\theta)$ is the reflectance for light incident at an angle θ, the factor of sin θ accounts for solid angle in the integration, and the factor of cos θ accounts for energy flux at off-normal incidence.

To model a coating's effect on the angular distribution of scattered radiation we also consider the contribution of reflected light in the calculation of g, and define a parameter g_{partial}:

$$g_{\text{partial}} = \frac{1}{2}\int_{-90^\circ}^{90^\circ} R(\theta)\ \cos(180 - 2\theta)\ \sin\theta\ \cos\theta\ \mathrm{d}\theta \qquad (13)$$

where cos $(180 - 2\theta)$ is the cosine of the scattering angle in Figure 11, the factor of 1/2 is a normalization, and the other factors are the same as in eq 12.

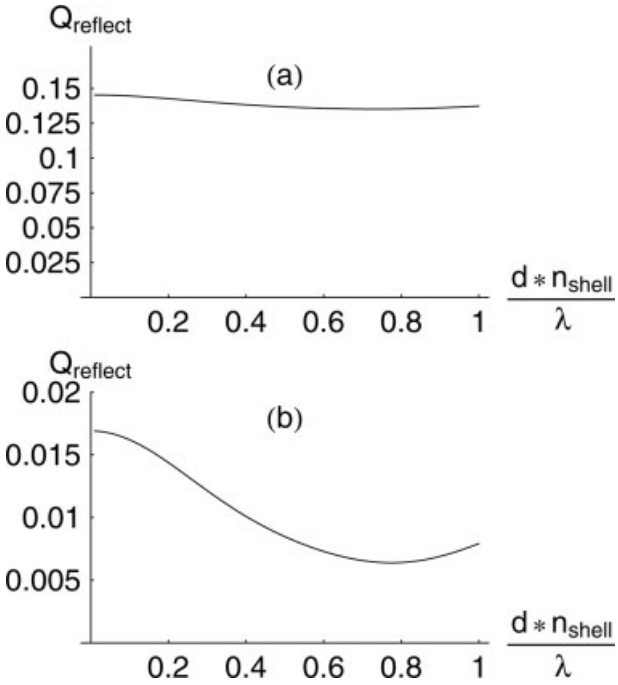

Figure 12. Calculated reflectance efficiency as a function of coating thickness for large-core shell particles in a medium with refractive index 1.5. (a) $n_{\text{core}} = 1.4$, $n_{\text{shell}} = 1.45$, (b) $n_{\text{core}} = 1.594$, $n_{\text{shell}} = 1.547$.

In Figure 12 we plot Q_{reflect} *versus* coating thickness for high-index ($n_{\text{core}} = 1.594$) and low-index ($n_{\text{core}} = 1.4$) particles in a matrix of background refractive index 1.5, and coated with materials that would minimize reflection from a planar surface ($n_{\text{core}} = 1.547$ for high-index spheres and 1.45 for low-index spheres). The coating thickness is normalized to the wavelength of light inside the coating. For light hitting a planar system at normal incidence the optimum coating thickness would be $\lambda/4$.

As we would expect, the low-index particle reflects more light than a high-index particle, because of total internal reflection. That neither particle's scattering efficiency is minimized when the coating thickness is $\lambda/4$ may seem dubious, but keep in mind that not all of the light hitting the particle is coming in at normal incidence. Reflection at off-normal incidence is minimized by thicker coatings, and so this result is not surprising.

In Figure 13 we plot g_{partial} *versus* coating thickness for the same parameters as in Figure 12. In both cases, the reflection contribution to g is small compared with g (g is of order 0.98 for large particles). The reflectance contribution is only weakly modulated by varying the coating

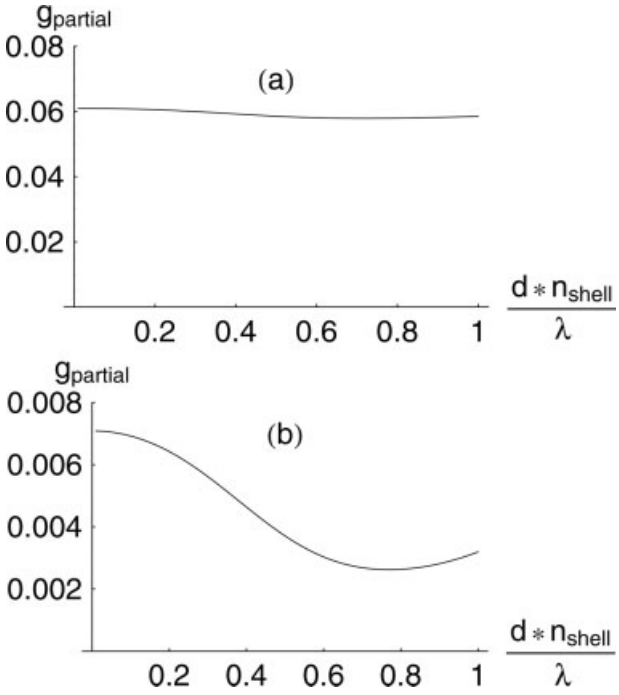

Figure 13. Calculated reflection contribution to angular distribution of radiation (g_{partial}) as a function of coating thickness for large-core shell particles in a medium with refractive index 1.5. (a) $n_{\text{core}} = 1.4$, $n_{\text{shell}} = 1.45$, (b) $n_{\text{core}} = 1.594$, $n_{\text{shell}} = 1.547$.

thickness (modulation of order 0.001 or smaller), so a coating should have only a negligible effect on $1 - g$ and hence l*. Also, the reflection contribution to g is positive, so most reflected light is scattered in the forward direction. This may seem counterintuitive, but light that hits a spherical particle near the edges (and hence at a glancing angle) will undergo a glancing angle reflection into the forward direction.

If we add additional layers, it is still possible to calculate the reflectance at each point on the coated sphere, but the calculation is much more tedious. Fortunately, most multiple-layer coatings share a universal feature: the overall reflectivity tends toward 1 irrespective of angle as the number of layers increase. At specific angles and frequencies resonant transmission may happen, but these resonances become quite narrow (both as a function of angle and frequency) as the number of layers increases, and so integrating the reflected light over the back surface of the particle will tend to "average out" the effects of such resonances. We therefore conclude that, in general, adding additional coatings to a large spherical particle will not reduce reflectance, but will rather increase the amount of light reflected in the backward direction. The net result is to decrease g and hence decrease ℓ^*, making a system of such particles less transparent rather than more transparent.

We can make this analysis more rigorous by looking at qualitative features of the boundary value problem for waves incident on spherical particles. In eqs 7 and 8 we described the field inside each layer as a superposition of outward propagating ($\mathbf{N}_{\text{mp}}^{(3)*}(k_0nr,\theta,\phi)$) and inward converging ($\mathbf{N}_{\text{mp}}^{(3)}(k_0nr,\theta,\phi)$) waves. We know that the asymptotic form of these waves at large distances from the origin ($r \gg \lambda$) is $\frac{\exp(\pm ik_0nr)}{k_0nr}$, and within a layer of thickness much smaller than r the factor of r^{-1} will be approximately constant and the waves will be approximately sinusoidal. The problem for waves of a given order m and polarization p is then formally identical to a sinusoidal plane wave incident on a multilayer dielectric coating. Waves incident on a planar dielectric coating of many layers tend to be more strongly reflected as we increase the number of layers.

We are therefore confident of our prediction that multilayer dielectric coatings on spheres will rarely or never produce a significant reduction in σ (or, equivalently, Q_{scatt}). This result has been demonstrated by exact calculations based on the wave equation, and supported by approximate calculations based on a simple model of scattering from large coated particles.

CONCLUSIONS

Adding a coating to a polymer particle only leads to a significant reduction in the particle's scattering cross section if the coating reduces the volume-averaged dielectric contrast between the particle and the surrounding matrix. The scattering cross section and angular distribution of scattered radiation are relatively insensitive to morphological details unless the volume-averaged dielectric constant of the core–shell particle exactly or nearly matches that of the surrounding matrix. In addition, for large diameter particles, homogenous particles provide the least scattering than particles with multiple layers. These computational findings can be explained by simple theoretical models, confirming that our findings are broadly applicable rather than a relic of the parameters that we investigated in this work. Finally, the current work also pro-

vides a tool for predicting the optical behavior of systems filled with homogenous or multi-layered spherical particles.

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