Scattering pattern of a quasitransparent core-shell particle

Roberto Alexander-Katz
Departamento de Física, División de Ciencias Básicas Ingeniería, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, 09340 México, Distrito Federal, Mexico
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Nonisotropic scattering patterns showing a minimum for small and almost transparent core-shell particles are discussed. It is shown that the Rayleigh-Gans theory will not predict accurately the scattering by such particles. A law of corresponding patterns is established for small core-shell particles with an effective index of refraction as close as possible to that of the medium. Based on this nonisotropic scattering phenomenon, a method for determining the thickness itself and its distribution of very thin coatings on small colloidal particles is proposed.

I. INTRODUCTION

It is well known that light scattered by particles much smaller than the wavelength of light (smaller than λ, $\sim\lambda/20$) do not show any angular dependence in a plane perpendicular to the axis of polarization of the incident beam. Another well-established fact is that for such a size, the Rayleigh approximation is sufficient to explain scattering phenomena. On the other hand, the Rayleigh-Gans theory of scattering extends its application to larger particles with an index of refraction near to that of the medium. Within this approximation, the intensity is proportional to the form factor $P(\theta)$, which, in the case of a core-shell spherical particle of radius R_2 and core radius R_1, where m_1 and m_2 are the index of refraction of the core and the shell, respectively, relative to the medium, is given by

$$P(\theta)=\mathcal{N}\left[G_2(q)+\frac{m_1-m_2}{m_2-1}\frac{R_1^3}{R_2^3}G_1(q)\right]^2 , \quad (1)$$

where

$$G_i(q)=\frac{3}{(qR_i)^3}(\sin qR_i-R_i\cos qR_i) , \quad (2)$$

$$q=\frac{4\pi}{\lambda}\sin\frac{\theta}{2} , \quad (3)$$

and

$$\mathcal{N}=\frac{R_2^6(m_2-1)^2}{[(m_1-m_2)R_1^3+(m_2-1)R_2^3]^2} . \quad (4)$$

As one can see from Eq. (1), $P(\theta)=0$ when the scattered electric-field amplitude of the shell cancels exactly that of the core, that is,

$$\frac{(m_2-1)[R_2^3G_2(q)-R_1^3G_1(q)]}{(m_1-1)R_1^3G_1(q)}=-1 , \quad (5)$$

which implies that, while their magnitudes are the same, they are out of phase. This means that there exists a collection of indices of refraction such that at some specific angles the scattering pattern exhibits a minimum. This is illustrated in Fig. 1 for a particle of radius 0.005 μm with indices of refraction $m_1=0.993\,732\,87$ and $m_2=1.01$.[1] Hence, even for extremely small particles, there are situations where the scattering pattern is far from being isotropic. This situation normally occurs when the particle *effective* index of refraction is very near that of the medium. As we shall see, the position of the minimum is extremely sensitive to structural parameters such as the indices of refraction and the ratio of the core radius to the shell, which implies that in order to be able to predict such patterns accurately we should use Mie's theory to determine the contribution of the local fields with the required accuracy. In the same figure we compare the predictions of the Rayleigh-Gans approximation with that of an exact Mie calculation[2] for the same set of parameters, and we observe that they differ notably one from the other. Therefore, in this quasitransparent region, the Rayleigh-Gans approximation is not accurate, even for small particles which are effectively almost transparent. The purpose of the present paper is to study the properties of the scattering patterns in this quasitransparent region.

All the calculations that follow will be made with five

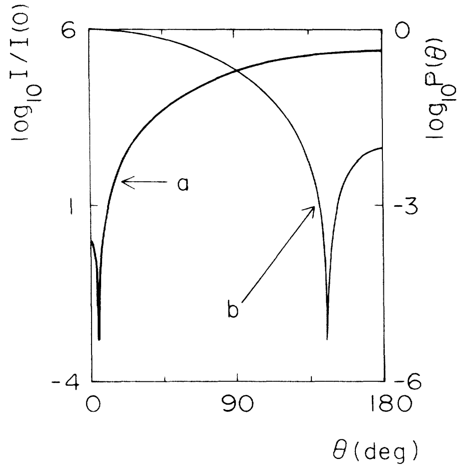

FIG. 1. Scattering patterns according to Mie (curve *a*) and Rayleigh-Gans (curve *b*) theories for $R_2=0.005$ μm, $Q=0.85$, $m_1=0.993\,732\,87$, and $m_2=1.01$.

electrical and magnetic Mie terms, which, up to the precision required, is enough for the particle sizes chosen in this paper. To simplify matters we shall only refer to the nonabsorbing particles.

II. EFFECTIVE INDEX OF REFRACTION OF A STRUCTURED PARTICLE: THE CONDITION OF MAXIMUM TRANSPARENCY

Let us first define the concept of effective index of refraction of a structured particle by a procedure similar to the random unit cell[3–6] (RUC) concept for a composite media. We shall say that the effective index of refraction of a coated sphere of radius R_2 is equal to the index of refraction of a homogeneous sphere of the same radius with the same extinction coefficient. That is, the effective index of refraction, m_{eff}, relative to the medium will be given by

$$C_{\text{ext}}(R_1,R_2,m_1,m_2,\lambda)=C_{\text{ext}}(R_2,m_{\text{eff}},\lambda) \ . \tag{6}$$

In the case of very small particles compared with the wavelength of light,[7,8] C_{ext} can be approximated by

$$C_{\text{ext}}(R_1,R_2,m_1,m_2,\lambda)=\frac{3}{2\pi}\lambda^2 v^6 p_1^2 \ , \tag{7}$$

where

$$v=2\pi R_2/\lambda \tag{8}$$

and

$$p_1=-\frac{2}{3}\frac{(m_2^2-1)(m_1^2+2m_2^2)+Q^3(2m_2^2+1)(m_1^2-m_2^2)}{(m_2^2+2)(m_1^2+2m_2^2)+Q^3(2m_2^2-2)(m_1^2-m_2^2)} \ , \tag{9}$$

and where

$$Q=R_1/R_2 \ . \tag{10}$$

Substituting Eqs. (7)–(10) into Eq. (6), we get, for m_{eff},

$$m_{\text{eff}}^2=m_2^2\frac{(m_1^2+2m_2^2)+2Q^3(m_1^2-m_2^2)}{(m_1^2+2m_2^2)-Q^3(m_1^2-m_2^2)} \ . \tag{11}$$

If we replace in this expression Q by the volume fraction of the particles in the medium, it will become identical to that of Maxwell-Garnett effective index of refraction of a composite. Within this approximation, the maximum transparency is obtained with values of m_1 and m_2 that satisfy the condition $m_{\text{eff}}=1$, that is,

$$m_1^2=m_2^2\frac{2(Q^3-1)m_2^2+(Q^3+2)}{(2Q^3+1)m_2^2+(Q^3-1)} \ . \tag{12}$$

It is interesting to note first that, under this approximation, the relation between the index of refraction is independent of the radius of the particle, and second, that for a whole range of values of m_1 and m_2 one could obtain total transparency. Of course, at higher-order approximations one will not be able to find a collection of m_1 and m_2 such that $C_{\text{ext}}=0$, yet the values predicted by Eq. (12), for some morphologies, will be close to those that give a minimum value for the extinction coefficient.

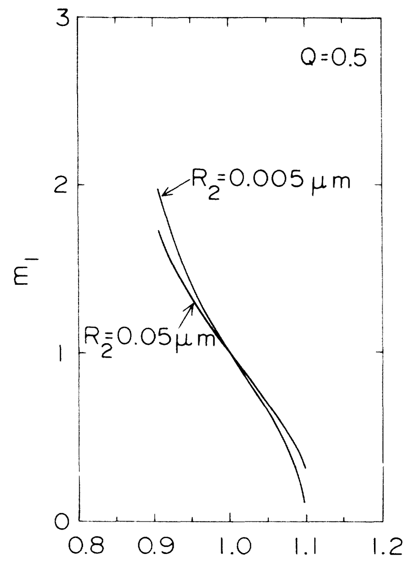

FIG. 2. Values of m_1 and m_2 that minimize the extinction coefficient for different R_2's.

In order to yield the maximum transparency for a given R_2, m_2, Q, and λ, one should look for an m_1 that satisfies

$$\left.\frac{d}{dm_1}C_{\text{ext}}(Q,R_2,m_1,m_2,\lambda)\right|_{R_2,m_2,Q,\lambda}=0 \ , \tag{13}$$

rather than $C_{\text{ext}}=0$. This will give the value of the core refractive index that will make the particle almost transparent. Using then Eq. (6), one can calculate the value of

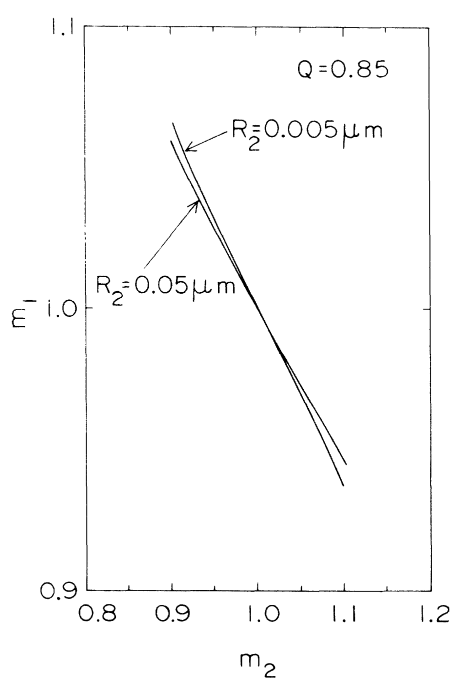

FIG. 3. Values of m_1 and m_2 that minimize the extinction coefficient for different R_2's.

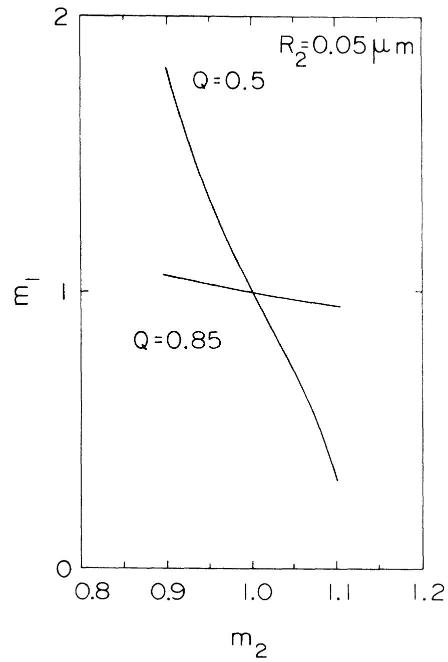

FIG. 4. Values of m_1 and m_2 that minimize the extinction coefficient for different Q's.

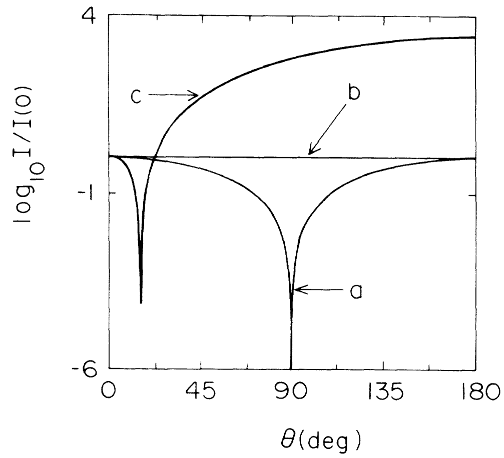

FIG. 5. Scattering patterns for a particle of radius 0.005 μm. *a*: $Q=0.85$, $m_1=0.938\,195\,54$, and $m_2=1.1$; *b*: homogeneous equivalent particle with the same effective index of refraction; *c*: $Q=0.85$, $m_1=0.938\,106\,56$, and $m_2=1.1$ [solution of Eq. (12)].

m_{eff} for such particle; this corresponds to the closest effective refractive index to that of the medium.

In Figs. 2–4 we show the set of values of m_1 and m_2 that minimizes C_{ext} for different values of R_2 and Q. The values obtained from Eq. (12) will superimpose those of $R_2=0.005$ μm up to the second significant figure in the case of $Q=0.5$, and for $Q=0.85$ they will match the third significant figure. The latter differences look as negligible, yet as we shall see, they will have a profound effect on the scattering pattern of such particles. These deviations from Eq. (12) can give values for the extinction coefficient 3–6 times smaller.

III. SCATTERING PATTERNS OF QUASITRANSPARENT COATED SPHERICAL PARTICLES

In this section we shall discuss the main properties of the scattering patterns for particles whose effective index of refraction is very near that of the medium.

Figure 5 shows the scattering pattern of a particle of 50 Å radius with $Q=0.85$, $m_2=1.1$, and $m_1=0.938\,195\,54$ (this m_1 minimizes the extinction coefficient for that choice of R_2, m_2, and Q). The effective index of refraction for this particle, according to Eq. (6), is $m_{\text{eff}}=1.000\,037\,23$. As one can see, the light scattered by such particle is far from being isotropic, showing a deep minimum at 90°. This is contrasted with the pattern of the equivalent homogeneous particle, shown in the same figure, with m_{eff} mentioned above, which is isotropic as expected. In order to show how sensitive the position of the minimum is with respect to the index of refraction, we compare, in the same figure, the previous scattering patterns with that obtained by changing m_1 to $0.938\,106\,56$, which is the solution of Eq. (12) for $Q=0.85$ and $m_2=1.1$, that is, a change of only $8.897\,344\times10^{-5}$ in the relative index of refraction. As we see, the minimum moves all the way to 16° for such a minute change. It is interesting to note the strong backscattering present for the latter choice of parameters, which also is quite surprising.

The sensitivity to changes in index of refraction varies with the particle size and the closeness of the indices of refraction of the core and shell compared to that of the medium. For instance, for a thin shell as that shown in the previous figure, the sensitivity will diminish 2 orders of magnitude for particles 1 order of magnitude larger; for indices of refraction m_1 and m_2 very close to that of the medium (say, around $m_1=0.993\,741\,74$, $m_2=1.01$, and $R_2=0.005$ μm), a change in $\Delta m_2=10^{-6}$ will lead to displacement of the minimum of the order of 6.5°, 1 order of magnitude more sensitive than the case shown in Fig. 5.

The behavior of scattering patterns with particle size depends on the angle at which the minimum appears and also whether $m_2>m_1$ or $m_1>m_2$. As a general rule, a pattern having a minimum at low angles is less sensitive to changes in size than a pattern where the minimum appears at higher angles; the higher the angle, the more sensitive the pattern becomes to changes in external radius. When we are at the condition of the best matching of refraction indices, which we shall discuss later, the minimum appears around 90°; in this case the sensitivity is of the order of 1° per 1% change in R_2 in all cases. This increases to several degrees (from ~3° to ~7°) when the minimum appears at higher angles (say, 150°), the latter trend being almost independent of other parameters such as the indices of refraction, thickness, or whether the particles are small (say, 0.005 μm) or larger (0.05 μm). When the minimum is at low angles and $m_1>m_2$, the sensitivity is in most cases below 1° (except in some cases for very thick shells); however, when $m_2>m_1$ the

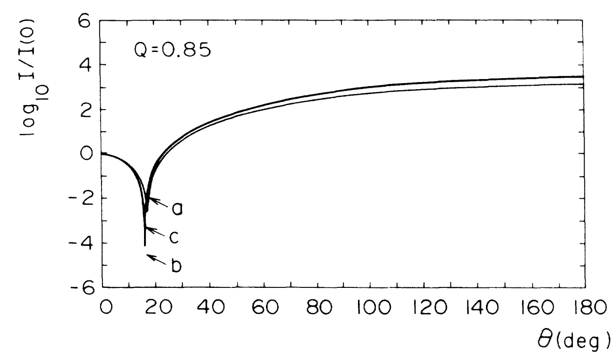

FIG. 6. Sensitivity of the scattering patterns with a change in radius. $m_1=0.938\,106\,56$ and $m_2=1.1$. *a*: $R_2=0.05$ μm; *b*: $R_2=0.01$ μm; *c*: $R_2=0.005$ μm.

patterns with a low-angle minimum are almost insensitive [except for the normalizing factor $I(0)$] to particle size as shown in Fig. 6. Even in the cases of very thick shells ($Q=0.5$) for $m_2>m_1$, low-angle minima are quite insensitive (less than 0.4° for a change of 1% in R_2) to particle size.

When we change the thickness of the shell, leaving R_2 and the indices of refraction constant, it is equivalent to a direct change in index of refraction since we are changing the global composition of the particle, and therefore we expect the same sensitivity as for the indices of refraction. Figure 7 shows a typical response to this parameter for small particles ($R_2=0.005$ μm, $m_1=0.938\,196$, and $m_2=1.1$), where Q was varied slightly. As one can see, the position of the minimum is extremely sensitive to Q, having a displacement of 37.5° for a ΔQ of 10^{-4}. In the same way as with the index of refraction, for larger particles, say, of 1 order of magnitude larger, this sensitivity reduces by about 2 orders of magnitude. The latter is shown in Fig. 8 where we have chosen a larger particle with $R_2=0.05$ μm in the same range of indices of refraction $m_1=0.946\,221$ and $m_2=1.1$; we see from this figure that a $\Delta Q=0.01$ displaces the position of the minimum by about 30°. Apart from this particle size dependence,

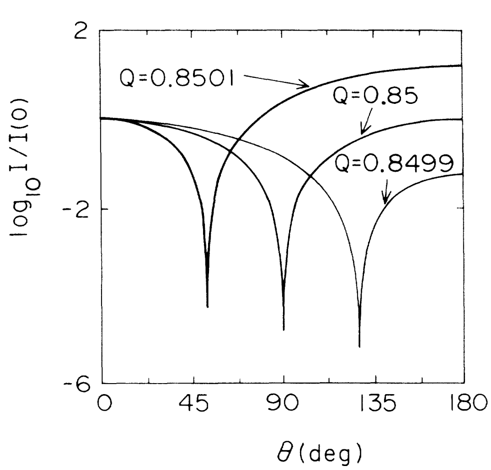

FIG. 7. Sensitivity of the minimum to a change in Q. $R_2=0.005$ μm, $m_1=0.938\,196$, and $m_2=1.1$.

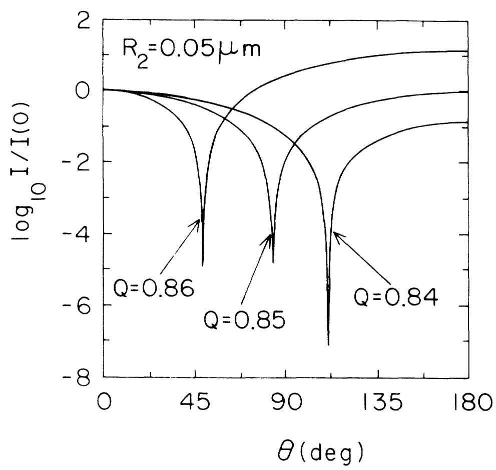

FIG. 8. Sensitivity of the minimum to a change in Q. $R_2=0.05$ μm, $m_1=0.946\,221$, and $m_2=1.1$.

the sensitivity of the position of minimum with respect to Q can also increase when we do not have the best index-matching choice (the minimum appears at lower or higher angles than 90°) and decrease with an increase in thickness of the shell; however, it will not change in both cases by more than a factor of 2.

Another interesting feature of this region, for the case of small particles, is that, as long as we choose a pair of m_1 and m_2 that minimizes C_{ext}, the scattering patterns are identical (except for the scaling factor mentioned above and the depth of the minima) no matter how different the pair of index of refraction are and independently of the values of Q or R_2, as long as $R_2 \ll \lambda$. In Fig. 9 we show the superposition of 12 patterns whose parameters are described in Table I.

As is evident from this figure, all of these patterns can

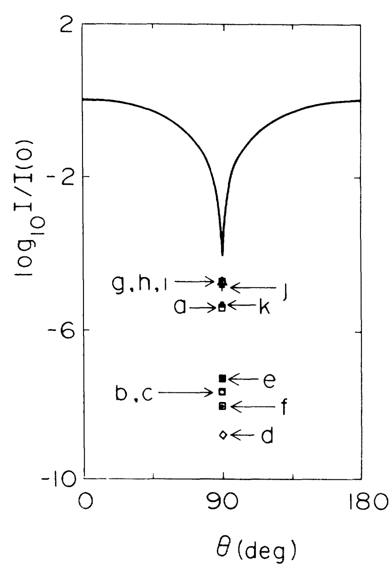

FIG. 9. Superposition of 12 scattering patterns corresponding to the parameters shown in Table I, which minimize the extinction coefficient.

TABLE I. Different values of indices of refraction and radii that minimize the extinction coefficient and the corresponding pattern shown in Fig. 9.

Pattern	R_2 (μm)	Q	m_1	m_2
a	0.01	0.5	0.413 832 6	1.08
b	0.002	0.5	2.041 004 72	0.9
c	0.002	0.85	1.065 522 111	0.9
d	0.002	0.85	0.993 734 293	1.01
e	0.002	0.85	0.938 120 807	1.1
f	0.002	0.5	0.930 807 1	1.01
g	0.01	0.85	1.065 175 443	0.9
h	0.01	0.85	0.993 768 261	1.01
i	0.01	0.85	0.938 461 58	1.1
j	0.01	0.5	2.028 696 95	0.9
k	0.01	0.5	0.931 242 511	1.01

be superimposed on each other, and one can hardly distinguish between them except in that the depth of the minima are different. The latter implies that the perfect cancellation occurs at 90° in the limit of the radius going to zero. However, within reasonable accuracy this law can be extended up to diameters of the order of $\lambda/15$ as shown in Fig. 9.

Therefore, for small particles, compared to the incident wavelength, we can state a law of corresponding patterns as follows: Any pair of index of refraction of a core and shell particle that minimizes the extinction coefficient, for any given particle radius and ratio between the radii of the core and the shell, will have an identical scattering pattern shape with a minimum at 90°.

For larger particles the law of corresponding patterns does not hold so well; however, the patterns come very close to each other as shown in Fig. 10 for a particle of 0.05 μm of radius and different core-shell morphologies that minimize the extinction coefficient for the given parameters. For this particle size, the minima move slightly from 90°, being at 84° for $Q=0.85$; when $Q=0.5$ the minimum is around 85.5° for $m_2=0.9$ and $m_1=1.789\,498$, and at 87° for $m_2=1.1$ and $m_1=0.331\,404\,6$.

In real colloidal systems such as polymer latex, it is reasonably easy to control the core radius (e.g., monodisperse polystyrene latex). However, the shell thickness (a second polymerization grafting the seed particles) is not a parameter with which one can have the same degree of control. From the above discussion, variations in this parameter have a stronger effect on the scattering pattern than the actual size and would not allow us to see such sharp minima as the one already shown. In any case, if we have a colloidal system with a fixed core radius and with a distribution in thickness (and concomitantly a distribution of particle sizes), where the medium has its index of refraction as close as possible to the most probable m_{eff}, one should observe an anisotropy in the scattering by such systems, although not as sharp, but sufficiently pronounced to be observed. To illustrate such behavior, Fig. 11 shows the scattering patterns of a core radius of fixed particles for several distributions of shell thickness shown in Fig. 12, where the effect of the

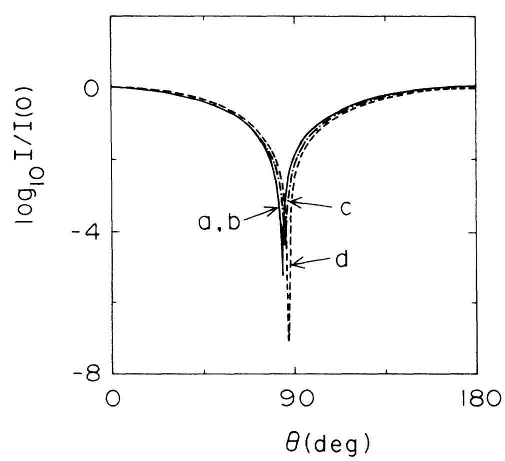

FIG. 10. Scattering patterns for $R_2=0.05$ μm for different core-shell morphologies which minimize the extinction coefficient. *a*: $Q=0.85$, $m_1=1.057\,297$, and $m_2=0.9$; *b*: $Q=0.85$, $m_1=0.946\,221$, and $m_2=1.1$; *c*: $Q=0.5$, $m_1=1.789\,498$, and $m_2=0.9$, *d*: $Q=0.5$, $m_1=0.331\,404\,661$, and $m_2=1.1$.

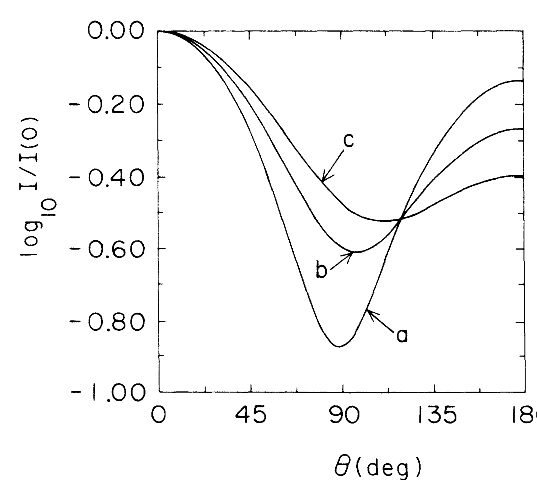

FIG. 11. Scattering patterns for particles with a distribution in Q given in Fig. 12. $R_1=0.0425$ μm, $m_1=1.022\,214$, and $m_2=0.96$. The curves *a*, *b*, and *c* refer to the corresponding distributions of Fig. 12 used to generate the scattering patterns.

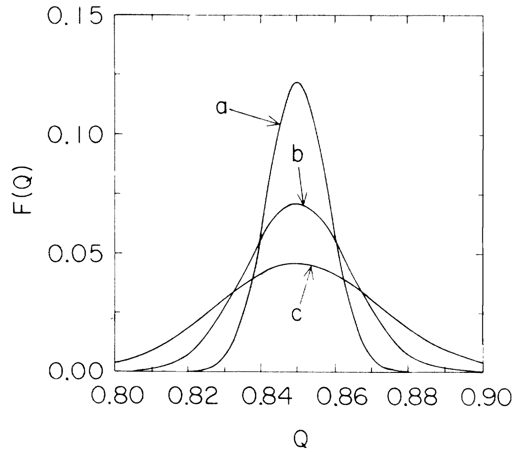

FIG. 12. Truncated normalized Gaussian distribution for Q.

particle-size distribution has also been taken into account. As one can see, even for a distribution as broad as c, the scattering pattern shows a minimum, which has about a third of the intensity of an experimentally easily accessible small angle (say, at 30°). As the distribution becomes narrower, the minimum becomes more pronounced, signaling the potential use of this technique in determining narrow-shell-thickness distributions. In order to obtain the distribution of Q's, one has to solve the inversion problem, which as in most scattering cases is ill conditioned; however, just by changing slightly the medium index of refraction, one can generate a whole family of patterns with minima at different angles but associated with the same sample, and therefore, in principle, one can construct a well-conditioned inversion problem. Furthermore, if we had a sample with $m_2 > m_1$, we know from the previous discussion that when the minimum appears at low angles, it is practically insensitive to the particle size, and therefore, if we choose a medium whose index of refraction is such that the minimum appears at low angles, then one can apply this technique to determine narrow-thickness distributions in wildly polydisperse (particle-size-wise) systems. This could be the case for instance of vesicles with a thin shell of a lipid.

There are other experimental problems that can have an effect on the pattern described, yet one can isolate them or they are second-order effects. For instance, if our temperature control within the scattering volume is of the order of 10^{-2} °C, then there will be an indetermination of the indices of refraction in the sixth significant feature (for most polymers, $dn/dT \approx 10^{-4}$ °C^{-1}), and for the case shown in Fig. 11 ($R_2 = 0.05$ μm), this will only displace the minimum by about 0.1°, which is negligible in our analysis. Density fluctuations of the index-matching medium will also contribute to the total scattering, yet the turbidity due to these, for most organic solvents, is of the order of 10^{-4} cm^{-1}, while the turbidity of a dilute (10^{13} particles per cc) suspension of particles of mean radius of 0.05 μm of the type (curve c) described in Fig. 11 is 5.67×10^{-3} cm^{-1}. Even for an ideal suspension of the best refractive-index-matching particles used in Fig. 11, the turbidity for the same particle concentration will be 10 times greater than for most common organic solvents. If the index-matching medium consists of a mixture of solvents, we will have, in addition to the density fluctuations, concentration fluctuations that will add to the total scattering measured. Although the contribution to the scattering of the latter can be larger than that from the density fluctuations, in many cases this is not more than 1 order of magnitude higher, and for mixtures that are not highly concentrated this is just 2–3 times larger. This means that in the example chosen, even in the worst case, the scattering due to concentration fluctuations will still be below or at most the same order as that coming from the particles, and therefore, although the depth of the minimum will be reduced, the effect described above can still be directly observed without data treatment. In any case, the contribution coming from density and concentration fluctuations can be measured independently and then subtracted from the total scattering measured, and the excess scattering will follow the patterns shown in Fig. 11.

Furthermore, Fig. 13 shows the values of m_2 and Q that minimize the extinction coefficient for a given core radius and index of refraction. For very thin shells the values of Q in this figure seem to be quite insensitive to the index of refraction of the shell. For instance, if $R_1 = 0.0425$ μm and $m_1 = 1.03$, and we roughly know the index of refraction of the shell to be $m_2 = 0.946 \pm 0.01$, then the error in Q is only of the order of 3%. For the same R_1 and m_1, a rough estimate of $m_2 = 0.81 \pm 0.06$ will reflect itself only in an error $\approx 2.5\%$ in the determination of Q. Even if we did not know m_1 with precision, say, m_1 is in between 1.03 and 1.02, for $m_2 = 0.917 \pm 0.03$ the maximum error in Q will be about 2.8% around $Q = 0.9$. This means that a very simple experimental method can be set up to determine the thickness of very thin coating films on small particles when we do not know with precision both indices of refraction. We would only have to match the media index of refraction until we reach a minimum in the extinction coefficient. From the knowledge of the matching refractive index and the best estimate of m_1 and m_2, we can determine Q from curves such as in Fig. 13. This will not

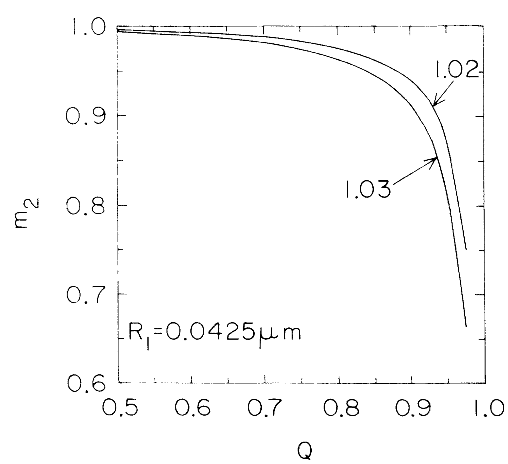

FIG. 13. m_2 and Q values that minimize the extinction coefficient for $R_1 = 0.0425$ μm and different m_1's.

require more than standard instrumentation such as a spectrophotometer and a refractometer. The experimental difficulties described before will also apply to this determination, yet as in the scattering experiment, their effects are negligible or can be subtracted as already discussed above.

IV. CONCLUSIONS

In this paper we have shown that for a core-shell particle there is a region that we have designated quasi-transparent (that is, when the effective index of refraction is very close to that of the surrounding media) where the scattering pattern, in the plane perpendicular to the incident polarization direction, is not isotropic, no matter how small the particle is with respect to the incident wavelength. We also showed that the theory of Rayleigh and Gans did not apply in this region for such core-shell particles, even those that are small and almost transparent. It was established that in that region, for the case of particles that are small with respect to the incident wavelength ($\leq \lambda/15$), no matter what values of Q or R_2 are adopted, as long as the pair of refraction indices minimized the extinction coefficient for such parameters, its scattering pattern shape will be the same with a minimum at 90°. If the particles are not that small, say, a third of the incident wavelength in the medium, the shape of the pattern will not differ much from those of very small particles for pairs of refraction indices that minimize the extinction coefficient for a given R_2 and Q. Although these will not superimpose on one another, yet they will be awfully close to each other and having their minima at angles close to 90°.

We discussed the sensitivity of the position of the minimum, showing in all cases that this was greater for changes either in the indices of refraction or in the thickness of the shell than for variations of the same order in the particle size. The smaller the particle, the greater this sensitivity of the position of the minimum with respect to Q and m values. Moreover, we showed that for $m_2 > m_1$ the position of the minimum at low angles was quite insensitive to the radius of the particle. All this suggests that the position of the minimum could be employed, in principle, for the determination of the index of refraction or the thickness of film coatings on small particles.

We showed that, even in the case of particles with relatively broad distributions of thickness, this phenomenon could be observed experimentally and proposed a method to determine the thickness and its distribution by light scattering. This was applicable from relatively broad to very narrow distributions in thickness, being extremely sensitive in the last case. If $m_2 > m_1$ and the minimum of the most probable particle indices appears at low angles, then the method would be almost particle-size independent.

Finally, we also suggested another experimental method, based on determining the index of refraction of the index-matching fluid, which gives rise to the smallest extinction coefficient for the particles, that could be used to measure the thickness of a very thin shell with reasonable accuracy when we know the refraction indices of the core and the shell only roughly.

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[1]The wavelength used in this paper is 488 nm in a medium with 1.54 as index of refraction.

[2]For a better graphical display, all the Mie patterns in this paper have been normalized with $I(0)$.

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