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The scattering of light by a suspension of coated spherical particles: effects of polydispersity on cross sections

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Abstract. The effect of polydispersity on extinction cross sections is studied for a particle system composed of coated, spherical particles. Aden–Kerker equations, governing the light-scattering behaviour of the system, are formulated in a way that makes them more suitable for computation purposes. Differences found between light scattered by non-absorbing and highly absorbing particles show the importance of using accurate refractive indices, especially when dealing with their imaginary part, which accounts for absorption.

1. Introduction

In recent years, use of the light-scattering properties of coated spherical particles has been found to be a useful and non-destructive way to probe and size systems ranging from blood cells to paper whiteners; commercial applications include the study of coated particles as potential drug carriers and as a base for colloidal-type superconducting materials [1–6]. The normal approach is to measure the properties of light scattered by a particle system and solve the so-called inverse problem, namely, given the electric field scattered by a system, describe the particle (or particles) responsible for the scattering.

Light scattered by a coated sphere is described via the Aden–Kerker theory [7], although for actual applications based on that theory the equations can be re-formulated in order to overcome practical computing limitations such as overflow and propagation of errors [8–11]. In many cases, the theory has been applied to real systems assuming that they are composed of identical spherical particles. Since many colloidal dispersions of interest are not perfectly monodisperse, consideration of the effect of different degrees of polydispersity on the scattering properties of core-shell particles can be useful for more accurate optical sizing of such systems.

In this paper the Aden–Kerker method is applied to the study of the extinction cross sections of a system of coated spheres and the effect of polydispersity is examined. Some considerations on the influence of the imaginary part of the refractive index of the particles are presented.

2. The theory and methods

The Aden–Kerker theory for concentric spherical particles will be used [7]. A spherical, coated particle of inner radius x, outer radius y and coating thickness $z = y - x$ is illuminated by a monochromatic beam of radiation of vacuum wavelength λ_0; n_1, n_2 and n_0 are the refractive indices of the core, shell and suspending medium, respectively, $k = 2\pi/\lambda = 2\pi n_1/\lambda_0$ and $X = kx$, $Y = ky$ and $Z = kz$ are the dimensionless size parameters (see figure 1). The Aden–Kerker theory yields the following expressions for the extinction and scattering cross sections:

$$C_{ext} = \frac{\lambda^2}{2\pi}\sum_{n=1}^{\infty}(2n+1)\mathrm{Re}(a_n + b_n) \qquad (1)$$

$$C_{sca} = \frac{\lambda^2}{2\pi}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2). \qquad (2)$$

The extinction and scattering efficiencies are obtained from $Q_{ext} = C_{ext}/G$ and $Q_{sca} = C_{sca}/G$, where $G = \pi y^2$ is the geometrical cross section of a sphere. The functions a_n and b_n contain the dependences of the cross section on the size parameters (X, Y, Z) and on the refractive indices $m_1 = n_1/n_0$ and $m_2 = n_2/n_0$ (see the appendix).

In the absence of multiple scattering, the efficiency for a system of N identical particles is N times that of a single particle. However, when one has to deal with polydispersity, a size distribution $p(d)$ must be used:

$$Q_{ext} = \frac{\int_0^\infty\int_0^\infty C_{ext}(X,Y)p(X)p(Y)\,\mathrm{d}X\,\mathrm{d}Y}{\int_0^\infty\int_0^\infty G(X,Y)p(X)p(Y)\,\mathrm{d}X\,\mathrm{d}Y}. \qquad (3)$$

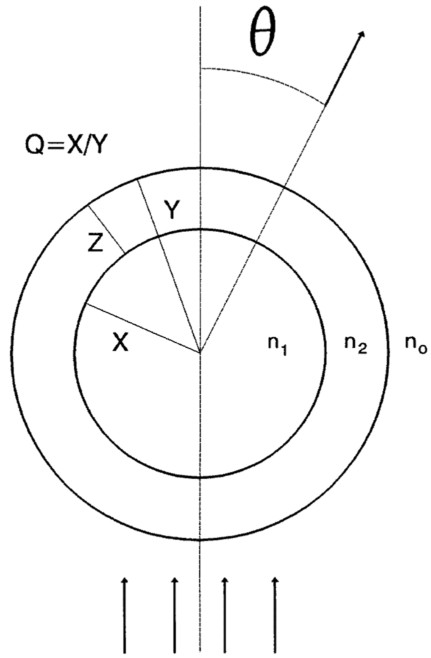

Figure 1. The geometry of the scattering system.

In the present work, a zeroth-order logarithmic distribution (ZOLD) was used [12], which is characterized by its modal diameter (d_m) and width (σ_0):

$$p(d) = \frac{1}{(2\pi)^{1/2} d_m \sigma_0 e^{\sigma_0^2/2}} \exp\left(-\frac{(\ln d - \ln d_m)^2}{2\sigma_0^2}\right). \quad (4)$$

In order to reduce the number of parameters needed to describe the size distribution for the entire particle, some kind of link between X and Y must be assumed. In this work, the ratio $q = X/Y$ is held constant. Under this condition, three numbers (besides the refractive indices) are needed to calculate light-scattering properties of a polydisperse system: (Y_m, σ_0) for the particle-size parameter and q for the X–Y relationship.

The integration was carried out using an adaptive Romberg method with $2^r + 1$ integration points [13]. The number of integration points was successively doubled until the first integral had been found for some r for which the relative error in the calculation of the cross sections $C_{ext}(r)$ and $C_{sca}(r)$ was less than a given quantity:

$$\max\left(\left|1 - \frac{C_{ext}(r)}{C_{ext}(r-1)}\right|, \left|1 - \frac{C_{sca}(r)}{C_{sca}(r-1)}\right|\right) < \Delta \quad (5)$$

where $C_{ext}(r)$ ($C_{sca}(r)$) indicates the extinction (scattering) cross section calculated with $2^r + 1$ integration points. A minimum number of integration points of 65 was imposed. The value adopted for Δ was 10^{-6}; when the number of integration points was greater than 1000, the convergence requirement was relaxed to $\Delta = 10^{-4}$. For ease of computation, the integration interval was reduced by disregarding the sub-intervals within which the size distribution function $p(d)$ fell under 10^{-10} times its minimum value, so the semi-infinite integral $(0, \infty)$ was truncated to $(Y_m/L, Y_m L)$, where $L = \exp(6.78614\sigma_0)$. A Fortran-77 routine was prepared to perform the calculations.

Three sets of refractive indices of the nucleus, shell and surrounding medium were used ($n_0 = 1.3368$ in all cases). The case $n_1 = 3.09 + i0.49$ and $n_2 = 1.65$ closely corresponds to a particle with a haematite core and an yttrium basic carbonate coating for a vacuum wavelength $\lambda_0 = 488$ nm [14, 15]. Since highly absorbing material has a smoothing effect on light-scattering curves, another set of calculations was carried out with $n_1 = 3.09 + i0$ and $n_2 = 1.65$. The third set of refractive indices ($n_1 = 1.48$ and $n_2 = 2.6$) corresponds to titania-coated silica particles that were first prepared by Hsu *et al* [16] and were found to be a useful component of paper whiteners.

3. Results and discussion

The effect of polydispersity on scattering cross sections can be seen in figures 2 and 3. Several conclusions can be drawn from these and similar cross section versus size-parameter representations. First, the ripple structure which occurs for cases in which non-absorbing material is predominant (in our case study, small q) is quickly lost when even a small degree of polydispersity is present. This smoothing effect is less evident with absorbing systems such as those with a large value of q, that is, a large absorbing core (compare figures 2 and 3), because the ripple structure itself appears later (at higher values of Y).

Second, the general oscillatory behaviour of the Q_{ext}–size curves is also affected by polydispersity in a similar way to their ripple structure. Increasing σ_0 brings about a decrease in the amplitudes of extinction maxima and minima. As before, the effect is more important for less absorbing systems (smaller q), since strongly absorbing particles exhibit a flatter extinction behaviour even in the absence of polydispersity (figure 3). Furthermore, figures 2 and 3 demonstrate that maxima and minima in Q_{ext}–Y plots shift towards smaller sizes when the polydispersity increases.

The influence of polydispersity on these core–shell systems can be seen better when the relative core size q is varied for a constant size value Y (figures 4 and 5). It can be seen that, for $Y = 1$, the cross section increases both with the polydispersity σ_0 and with the relative core q. The former is easily atributed to the fact that, for size values such that the cross section curves increase monotonically, a large value of σ_0 means a higher fraction of larger, more scattering particles. For the dependence on q, let us assume that we are not far from the Rayleigh regime, under which, to a first approximation, cross sections depend on the absolute value or the imaginary part of the quantity M, defined as ([17], p 201)

$$M = \frac{(m_2^2 - 1)(m_1^2 + 2m_2^2) + q^3(2m_2^2 + 1)(m_1^2 - m_2^2)}{(m_2^2 + 2)(m_1^2 + 2m_2^2) + q^3(2m_2^2 - 2)(m_1^2 - m_2^2)}. \quad (6)$$

For a homogeneous particle, $M = (m^2 - 1)/(m^2 + 2)$. An average refractive index $\boldsymbol{m}$ can then be defined for which cross sections are equal for a core–shell particle and for a particle with such an average index, that is,

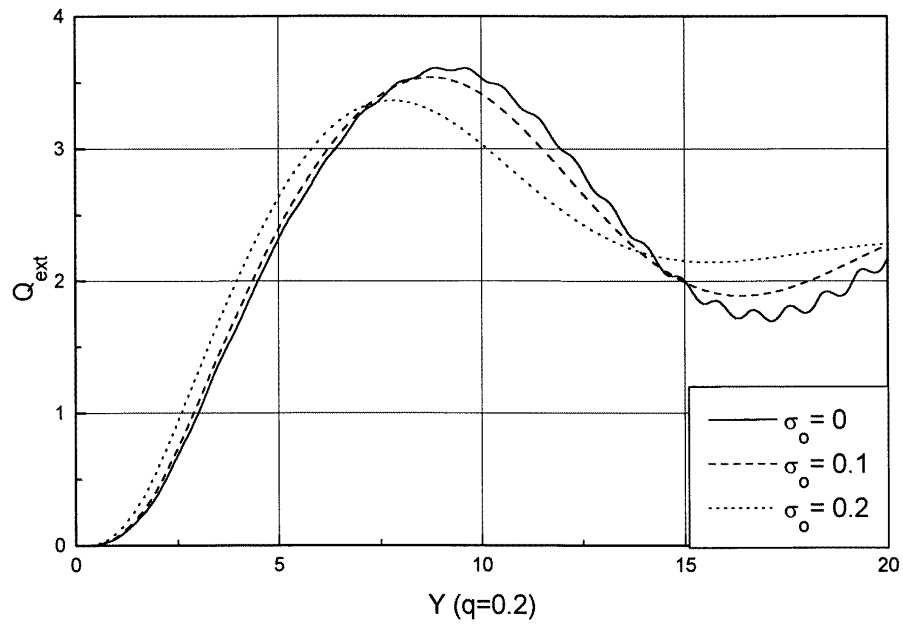

Figure 2. The extinction efficiency versus the size parameter for a coated, spherical particle system with core, shell and medium refractive indices $n_1 = 3.09 + i0.49$, $n_2 = 1.65$ and $n_0 = 1.3368$, for several degrees of polydispersity. A constant core:shell ratio of $q = 0.2$ was assumed.

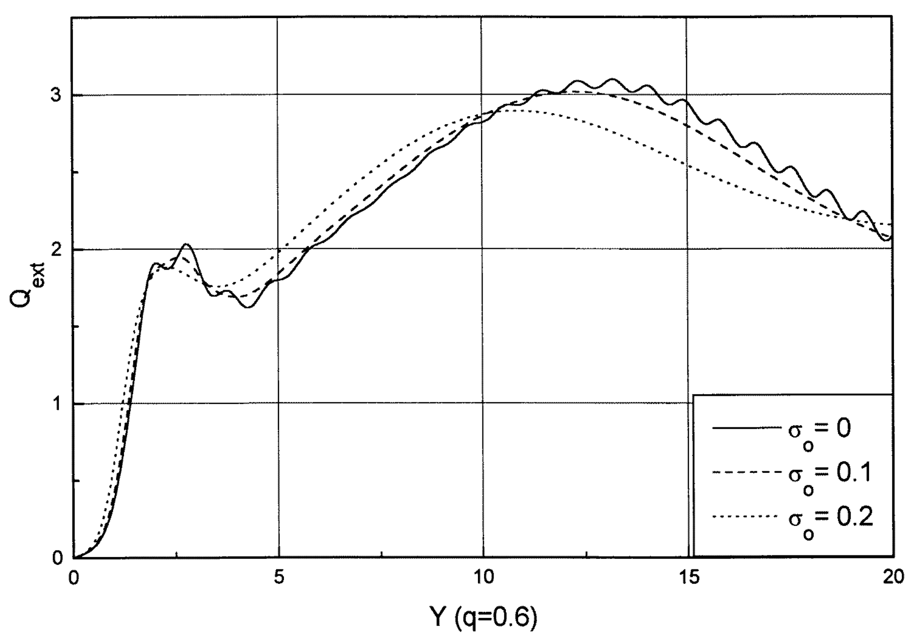

Figure 3. The same as figure 2, but for $q = 0.6$.

$M(m_1, m_2) = M(\boldsymbol{m})$. In most cases of interest within the Rayleigh regime, this is equivalent to defining a volume-weighted refractive index $\boldsymbol{m} = m_1 q^3 + m_2(1 - q^3)$. In our case study, $m_1 > m_2$, so that, for increasing values of q (a higher volume fraction of high-index material), $\boldsymbol{m}$ increases and so do M and Q_{ext} ([17], equations (5.2.1) and (5.2.5)). Figure 4 shows such an increase in Q_{ext} with q for $Y = 1$. At higher size parameter values, Rayleigh approximations are no longer valid and the influence of polydispersity on cross sections does not exhibit a definite trend (figure 5). It can be seen, however, that such influences are generally more noticeable at low values of q, thus indicating that effects on cross sections are larger when refractive indices are real (non-absorbing particles).

In order to outline the effects of polydispersity on purely non-absorbing materials, another set of curves was calculated with $n_1 = 3.09$ (figures 6 and 7). Differences in the size-parameter dependence of cross section curves are barely noticeable for small values of q, which is to be expected since it is there that core effects are small [17].

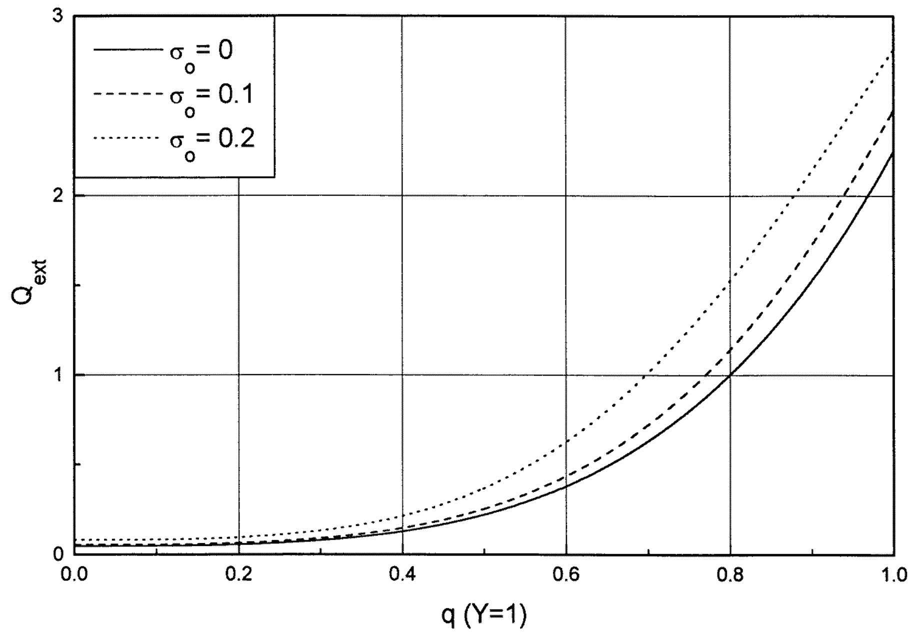

Figure 4. The extinction efficiency versus the relative core size for a coated, spherical particle system with core, shell and medium refractive indices $n_1 = 3.09 + i0.49$, $n_2 = 1.65$ and $n_0 = 1.3368$, respectively, for several degrees of polydispersity and a constant core:shell ratio. A size parameter $Y = 1$ was assumed.

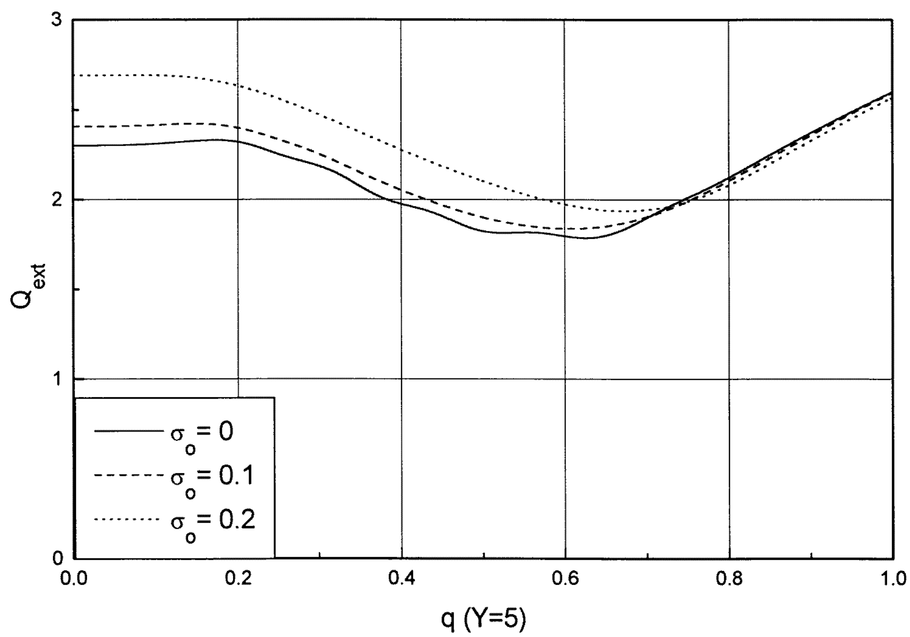

Figure 5. The same as figure 4, but for a size parameter $Y = 5$.

However, there is a strikingly different behaviour for higher values of q. Smoothing effects, which are not pronounced in the highly absorbing case, are now clearly observable. The presence of large numbers of interference maxima and minima in the extinction curve is easily lost when even small amounts of polydispersity are present, as figure 7 shows.

Changes in the optical properties with changing relative shell thickness are shown in figures 8 and 9 for non-absorbing particles. As earlier authors pointed out [18, 19], small cores ($q < 0.2$) have little influence on the overall result, whereas higher values of q result in a high number of narrow resonances. This rapid change in optical cross section with q and Y for a certain range ($q > 0.6$, $Y > 5$) entails severe computational difficulties (narrow size distributions such as $\sigma_0 = 0.05$ and $Y = 10$ require as many as 65 000 integration points). As figures 8 and 9 show, even small values of polydispersity have a

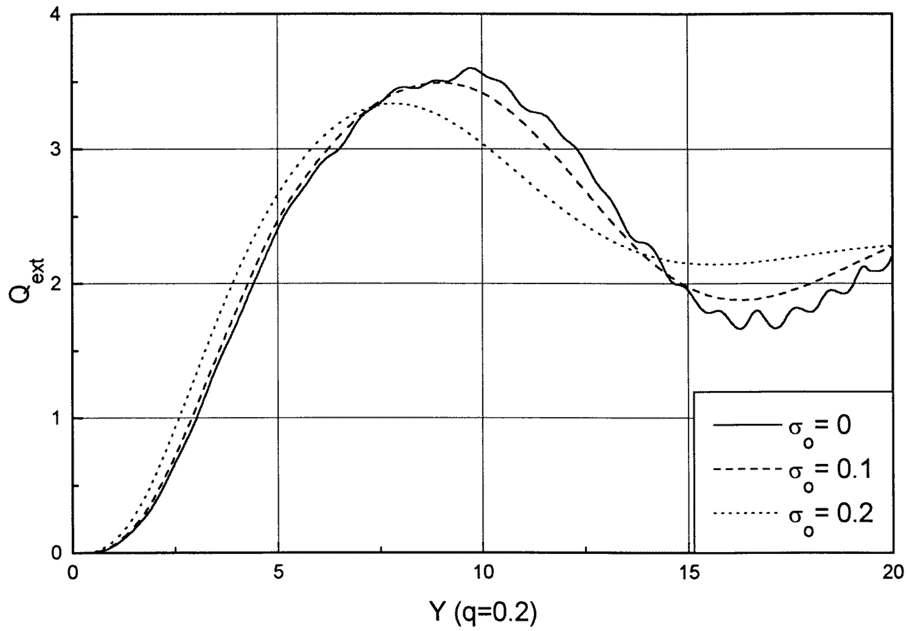

Figure 6. The extinction efficiency versus the size parameter for a coated, spherical particle system with n_1 = 3.09 (core), n_2 = 1.65 (shell) and n_0 = 1.3368 (medium), for several degrees of polydispersity. A constant core:shell ratio of q = 0.2 was assumed.

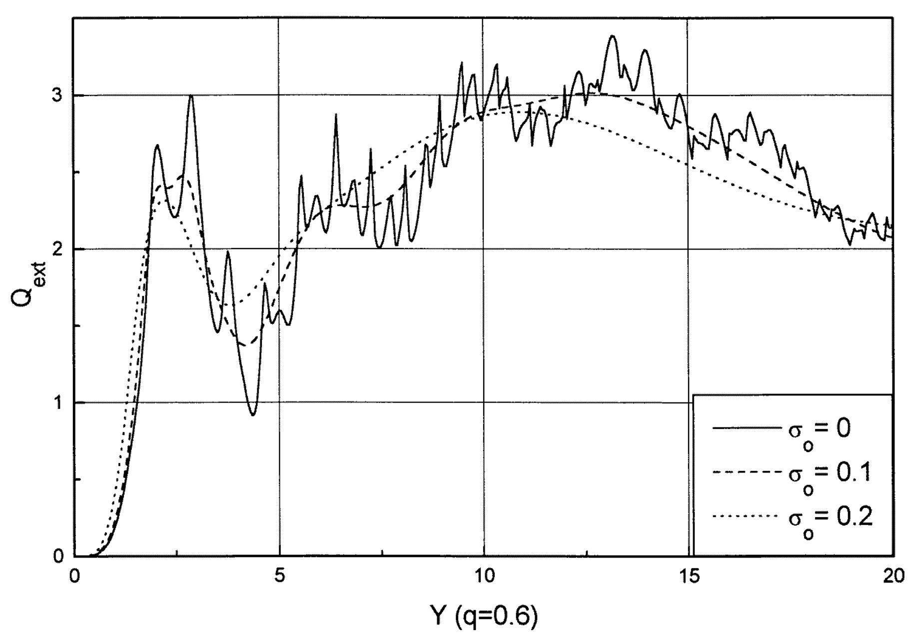

Figure 7. The same as figure 6, but for q = 0.6.

relevant effect on cross section curves, smoothing them out and eliminating, as in the case of homogeneous particles, any information that could be obtained from the presence and location of characteristic peaks.

As mentioned above, the calculations were also performed for particles with core refractive indices not so extreme as those in the case of haematite particles. When $n_1 = 1.48$ (silica) and $n_2 = 2.6$ (titania), the size dependences of Q_{ext} for $q = 0.2$ and $q = 0.6$ are as shown in figures 10 and 11, respectively. Unlike the results of figures 6 and 7, the smoothing effect of even small amounts of polydispersity is significant for small q values (figure 10); furthermore, the main oscillations obtained at $\sigma_0 = 0$ are still visible if σ_0 increases to 0.1, whatever the value of q.

The dependence of Q_{ext} on q for these particles is shown in figures 12 and 13, for $Y = 2$ and 10, respectively. Just like in the case of figures 8 and 9, for low core diameters Q_{ext} is essentially independent of q and, in fact, the whole Q_{ext}–q curve provides little information, even

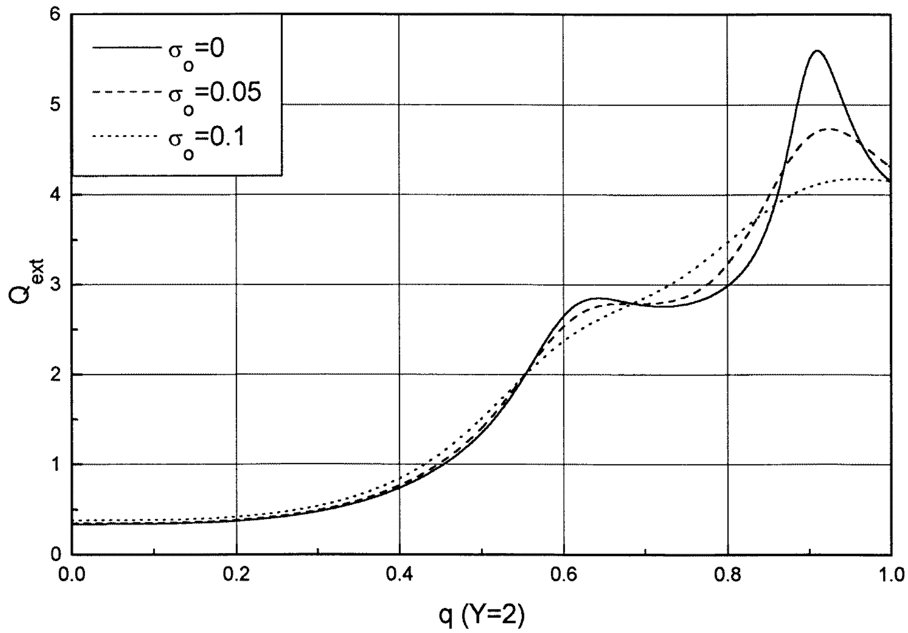

Figure 8. The extinction efficiency versus the relative core size for a coated, spherical particle system with core, shell and medium refractive indices n_1 = 3.09, n_2 = 1.65 and n_0 = 1.3368, for several degrees of polydispersity and a constant core:shell ratio. A size parameter Y = 2 was assumed.

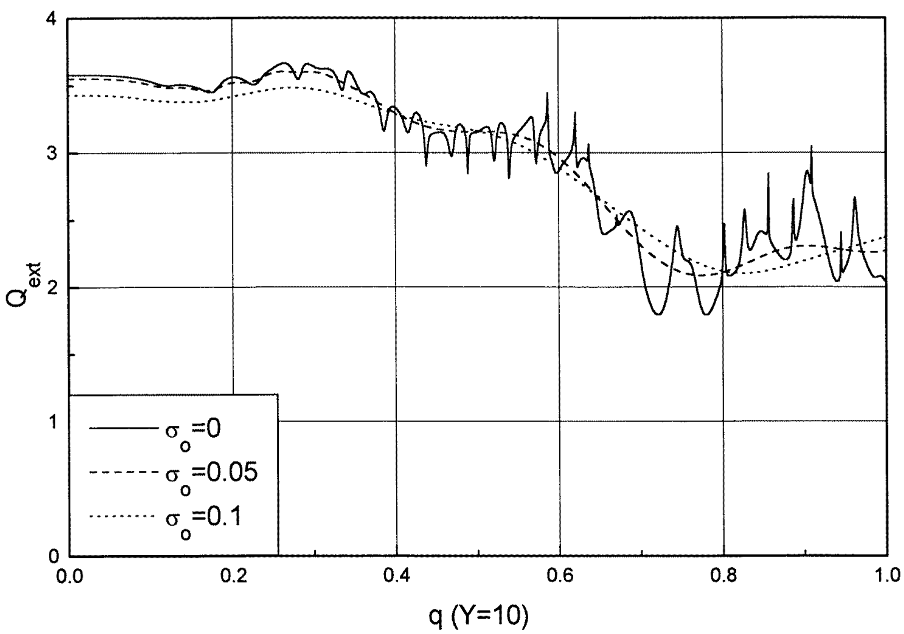

Figure 9. The same as figure 8, but for a size parameter Y = 10.

for monodisperse systems, when Y is small (figure 12). For larger particles (figure 13), the size dependence of the extinction cross section has some significant features (maxima and minima in Q_{ext}) that are smoothed out when the polydispersity increases.

Additional precautions have to be taken concerning the refractive indices used. Particle sizing by cross section methods (so-called turbidity methods) is especially valuable in situations in which the only information available is the attenuation of incoming light at several wavelengths, such as for interstellar clouds. In such cases, the light intensity propagating a distance l through a medium containing N particles per unit volume is attenuated according to

$$I = I_0\, e^{-NC_{ext}l}. \qquad (7)$$

For a given attenuation, assuming that the particle composition (and therefore the refractive index) is known,

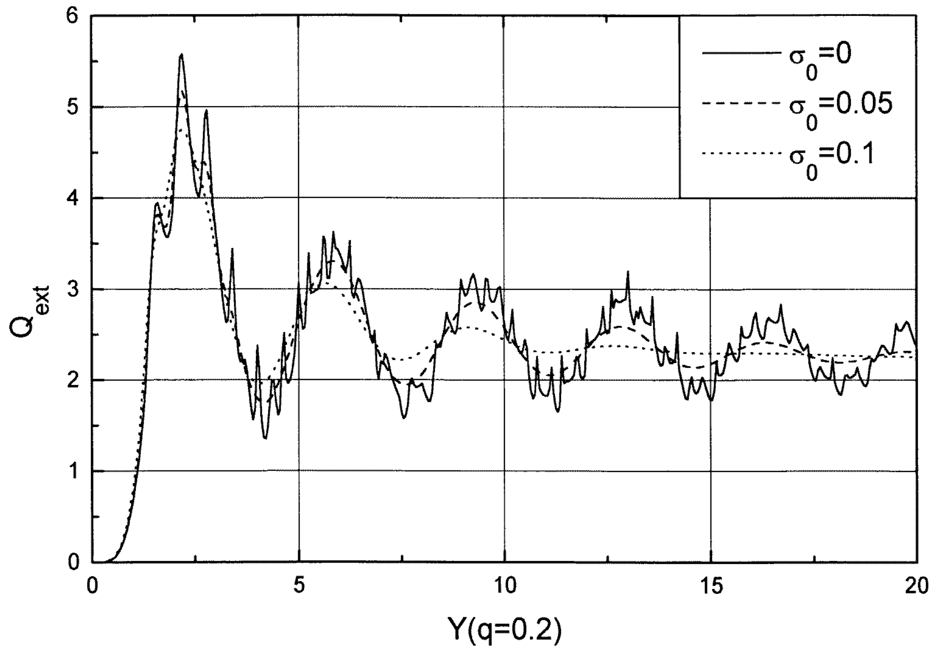

Figure 10. The extinction efficiency versus the size parameter for a coated, spherical particle system with n_1 = 1.48 (core), n_2 = 2.6 (shell) and n_0 = 1.3368 (medium), for several degrees of polydispersity. A constant core:shell ratio of q = 0.2 was assumed.

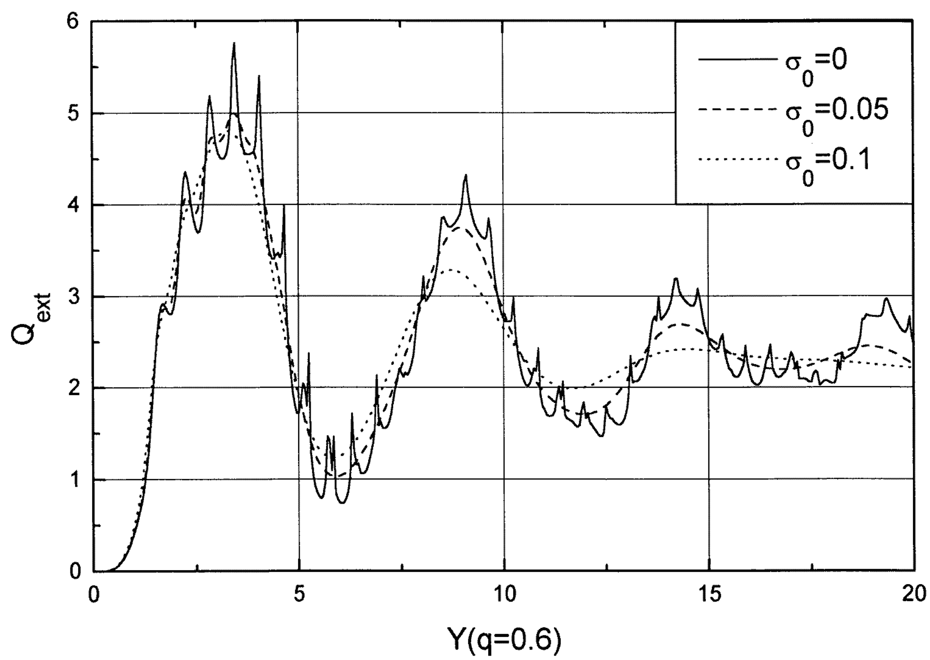

Figure 11. The same as figure 10, but for q = 0.6.

a size distribution of particles that matches the observed cross section can be inferred via the inverse problem. It can be seen from figure 9 above that cross sections are highly dependent on the existence of absorption, which is governed by the imaginary part k in the index of refraction m (the notation $m = n + \mathrm{i}k$ is used). Hence the need to evaluate both parts of the refractive index accurately. On the other hand, even precise measurements of the complex quantity m (either via reflection–refraction or via ellipsometry) are referred to the bulk material and might not always apply accurately to small particles [11, 15]. Last, measurement of cross sections at different wavelengths and therefore different size parameters must take into consideration the fact that refractive indices are generally wavelength-dependent quantities. When this $m(\lambda)$ dependence is not known, a constant refractive index is supposed. This

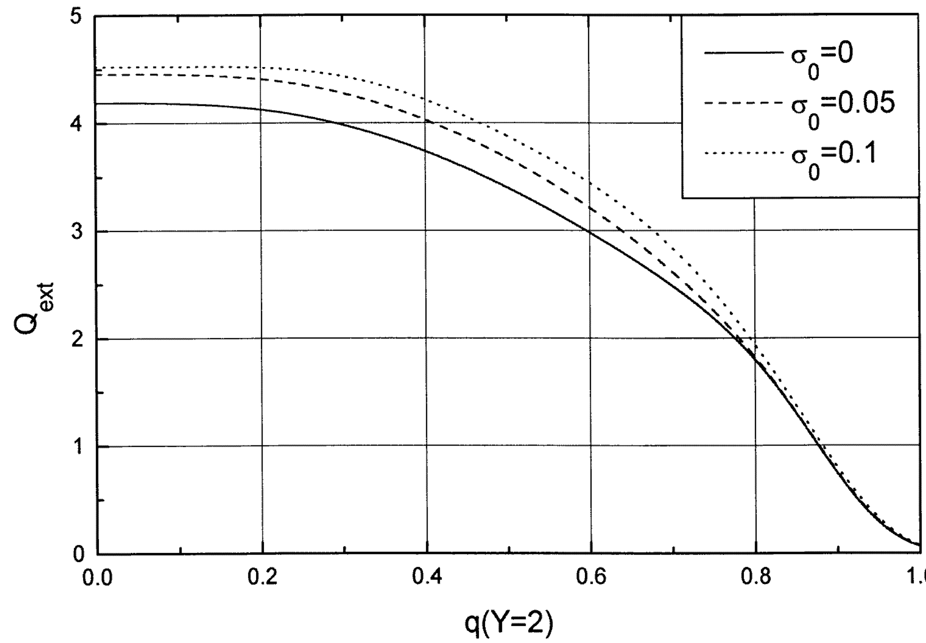

Figure 12. The extinction efficiency versus the relative core size for a coated, spherical particle system with core, shell and medium refractive indices n_1 = 1.48, n_2 = 2.6 and n_0 = 1.3368, for several degrees of polydispersity and a constant core:shell ratio. A size parameter Y = 2 was assumed.

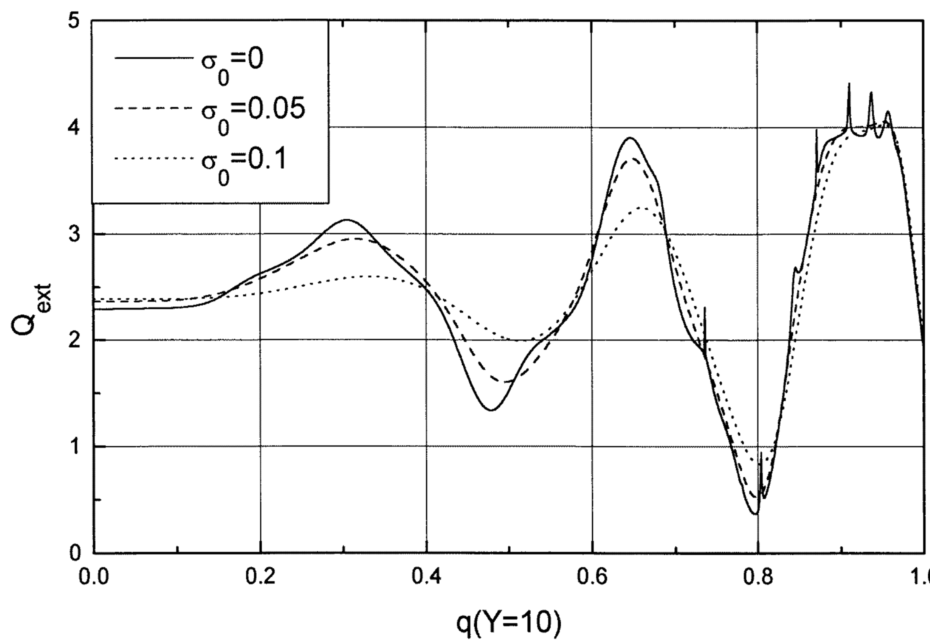

Figure 13. The same as figure 12, but for a size parameter Y = 10.

procedure, which can be used for non-absorbing particles so long as a certain degree of uncertainty can be accepted, is dangerously erroneous for absorbing particles, for in many situations a twofold variation in wavelength results in a change in the imaginary part k of some orders of magnitude. The presence of coated particles does not alter these considerations at all; on the contrary, the presence of two different materials makes it more important to determine the refractive indices of the core, shell and medium accurately if any information of interest is to be obtained from light-scattering sizing methods, especially for applications in which the coating thickness is the parameter of interest.

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Appendix

Here we show the equations used in the calculation of the coefficients a_n and b_n (equations (1) and (2)). They do not follow the original Aden–Kerker formulation [7], but rather are closer to the Bohren and Huffman formalism [11]. The coefficients a_n and b_n are calculated as follows:

$$a_n = \frac{\left(\frac{X_n}{m_2} + \frac{n}{Y}\right)\psi_n(Y) - \psi_{n-1}(Y)}{\left(\frac{X_n}{m_2} + \frac{n}{Y}\right)\xi_n(Y) - \xi_{n-1}(Y)} \tag{A1}$$

$$b_n = \frac{\left(m_2 Y_n + \frac{n}{Y}\right)\psi_n(Y) - \psi_{n-1}(Y)}{\left(m_2 Y_n + \frac{n}{Y}\right)\xi_n(Y) - \xi_{n-1}(Y)} \tag{A2}$$

where

$$X_n = \frac{P_n(m_2Y)D_n(m_2Y) - A_n G_n(m_2Y)}{P_n(m_2Y) - A_n} \tag{A3}$$

$$Y_n = \frac{P_n(m_2Y)D_n(m_2Y) - B_n G_n(m_2Y)}{P_n(m_2Y) - B_n} \tag{A4}$$

$$A_n = P_n(m_2X)\frac{m_2 D_n(m_1X) - m_1 D_n(m_2X)}{m_2 D_n(m_1X) - m_1 G_n(m_2X)} \tag{A5}$$

$$B_n = P_n(m_2X)\frac{m_1 D_n(m_1X) - m_2 D_n(m_2X)}{m_1 D_n(m_1X) - m_2 G_n(m_2X)} \tag{A6}$$

where

$$D_n(z) = \frac{\psi_n'(z)}{\psi_n(z)} \qquad G_n(z) = \frac{\chi_n'(z)}{\chi_n(z)}$$

$$P_n(z) = \frac{\psi_n(z)}{\chi_n(z)} \tag{A7}$$

with $\psi_n(z) = z j_n(z)$, $\chi_n(z) = -z y_n(z)$ and $\xi_n(z) = \psi_n(z) - \mathrm{i}\chi_n(z)$ are the Ricatti–Bessel functions. A time dependence of $\exp(-\mathrm{i}\omega t)$ was assumed.

Equations (A1)–(A3) can then be used to obtain extinction and scattering cross sections for polydisperse systems (the monodisperse case is that of $\sigma_0 = 0$). Romberg integration was found to be a good approach. It is based on the simple trapezoidal integration and it can easily be extended to other, more accurate quadrature methods (such as Simpson's rule). On the other hand, methods such as the Gauss quadrature formula, albeit useful for small degrees of polydispersity, yielded worse results at larger values of σ_0, with a slower convergence and a greater expense in computer time. In order to make the whole Fortran routine self-contained, with no dependence on additional sub-programs, we did not attempt to use subroutine libraries (such as IMSL).

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