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Scattering of Light from Cylindrical Particles: Coupled Dipole Method Calculations and the Range of Validity of the Rayleigh–Gans–Debye Approximation

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We calculate the single particle scattering properties of cylindrical particles with the iterative version of the Coupled Dipole Method (CDM), and using these results we discuss the validity regime of the Rayleigh–Gans–Debye (RGD) theory. The CDM includes, contrary to RGD scattering, the higher order intraparticle multiple scattering contributions, which become more important when the dimensions of the rods increase and/or the refractive index difference with the solvent increases. The range of validity of the RGD approximation is assessed from the deviations from the CDM, which becomes exact in the limit of infinitely small distances between the subunits. Systematic calculations are performed for rods with a diameter smaller than one-tenth of and a length smaller than two times the wavelength of the light in the solvent, and a refractive index relative to the solvent that lies between 1 and 1.5.

1. INTRODUCTION

In this paper, we consider the single particle scattering properties of cylindrical particles. When the refractive index difference between particle and medium is small and the particle size is limited to a certain range (1–3), these properties can be calculated using the Rayleigh–Gans–Debye (RGD) theory. The RGD theory is a simple approximate theory, which is often used in colloid science. With this theory the scattering properties of finite cylinders can be calculated analytically. Our interest is in the scattering properties of cylinders with a length of the order of the wavelength of the light, a diameter smaller than the wavelength of the light, and a refractive index relative to the solvent which is smaller than 1.5. Particles with dimensions and relative refractive indexes within this range are, for instance, aqueous dispersions of boehmite (4), imogolite (5), tobacco mosaic virus (6), fd-virus (7), and cellulose microcrystals (8). As far as we know, no systematic calculations are available on the validity of the RGD theory for cylinders with these dimensions and refractive indexes.

To calculate these deviations, an exact theory for the scattering of cylinders is needed. For the scattering of light from *spheres* the exact Mie theory (1–3) can be used, and along similar lines an exact theory for *infinitely long cylinders* (1–3) and *ellipsoidal particles* (9) has been derived. These theories are not applicable to *finite cylinders*, however. Two theories that can be used for arbitrary shaped particles are the Extended Boundary Condition Method (EBCM) (10, 11) and the Coupled Dipole Method (CDM) (12). From these two methods, the CDM is chosen, because it appeared more easy to implement in a computer program than the EBCM.

The CDM is a numerical method for the calculation of light scattering properties of a particle of arbitrary shape and refractive index, which was introduced by Purcell and Pennypacker (12) in the context of applications in astrophysics. The particle is modeled by an assembly of electrically polarizable subunits on a cubic lattice, from which the scattering is calculated including the coupling between the subunits (12–20). The CDM is exact in the limit of infinitely small distances between the subunits. The restrictions of the CDM are determined by the computational power and the memory of the computer used. Therefore, this relatively simple method has become more widely used only recently. Some examples are the study of scattering by interstellar grains (17), the scattering of ice crystals (18), light scattering by inhomogeneous particles (16, 19), and the calculation of the circular intensity differential scattering from chiral particles (20).

After an introduction of the CDM and the link to the RGD theory in the next paragraph, systematic calculations are given to determine the validity regime of the RGD theory. Although the numerical results obtained by the CDM are not exact, they are very accurate as long as one uses sufficiently small distances between the subunits. Therefore the deviations between the CDM and RGD results are referred to here as "errors" in the latter. The calculations are restricted

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to nonabsorbing rods, although the extension of the calculations to include absorption is straightforward. All equations in the present paper are given in Gaussian units, which are also used in most of the referred articles on the CDM.

2. THEORY

In the CDM, the particle is modeled by an assembly of electrically polarizable subunits on a cubic lattice, analogous to a crystalline particle built of atoms. The main difference with an atomic assembly is the larger distance (d) between the subunits, keeping the number of subunits relatively small and hence the calculations manageable. As long as the subunits are small compared to the wavelength of the light their precise size is not very important. How small the subunits have to be depends on the scattering parameter calculated (16).

The polarizability (α) of the subunits can be obtained from the Clausius–Mosotti (CM) relation (21)

$$\alpha = \frac{3d^3}{4\pi}\left(\frac{n_r^2 - 1}{n_r^2 + 2}\right), \qquad [1]$$

which links the bulk refractive index n of a cubic array to the polarizability of its subunits. In the case of colloidal particles ($n = n_p$) immersed in a solvent ($n = n_m$), the relative refractive index $n_r = n_p/n_m$ is the relevant quantity. For absorbing particles the refractive index is a complex quantity and hence α is complex.

Each subunit is polarized by the electric field component $\mathbf{E}^0$ of the incident light. This gives rise to an oscillating electric dipole moment $\mathbf{p} = \alpha\mathbf{E}^0$, which in turn emits an electromagnetic field $\mathbf{E}(\mathbf{r})$ at position $\mathbf{r}$ relative to the subunit given by (21)

$$\mathbf{E}(\mathbf{r}) = k^2(\mathbf{n} \times \mathbf{p}) \times \mathbf{n}\frac{e^{ikr}}{r} + [3\mathbf{n}(\mathbf{n}.\mathbf{p}) - \mathbf{p}]\left(\frac{1}{r^3} - \frac{ik}{r^2}\right)e^{ikr}, \qquad [2]$$

where r is the distance from the oscillating dipole, $\mathbf{n} = \mathbf{r}/r$, and k is the wave number of the light in the medium.

In this formula the r^{-1} term describes the electromagnetic radiation, that is, the dominant part of the dipole field at distances greater than the wavelength of the radiation. This far field term also describes the Rayleigh scattering of small particles, which are actually dipole scatterers. The r^{-3} term describes the electrostatic field of a dipole. At distances much smaller than the wavelength of the light this term is the dominant one. For intermediate distances (induction zone) the r^{-2} term has to be taken into account.

The RGD scattering of an arbitrary shaped and oriented particle can be described as follows. The incident wave polarizes the subunits of which the particle is composed. These subunits each radiate a dipole field, the scattered amplitude of which is calculated by merely adding the far field part of the scattered waves with the proper phase difference.

Whenever the polarizability of the subunits is high (corresponding to a high refractive index) and/or the particle is large, the fields of the subunits can no longer be neglected with respect to the incident electric field. Therefore, the influence of all dipoles on each other has to be taken into account, which can be regarded as intraparticle multiple scattering. This can be done either by the calculation of a large interaction matrix, which then has to be inverted, or by iteration. The former method applies also to particles for which the iterative scheme no longer converges, and furthermore allows efficient orientation averaging (13). It demands however large computer memory for the storage of the interaction matrix, which restricts the particle size that can be treated. We use the iterative scattering order formulation (14), as the calculations on cylindrical particles do not have convergence problems.

Consider first, as a simple example, a rod with a length-over-width ratio of two, where the length is taken much smaller than the wavelength of the light. The particle can be modeled by just two subunits (Fig. 1). Because of the small particle size, only the electrostatic part of the dipole field is required to determine the influence of the dipoles on each other. Furthermore, the incident field is constant over the particle (but oscillating in time). It is now possible to calculate the scattering of this particle (in one orientation) as follows. The electric field of the incident light $\mathbf{E}^0$ polarizes the subunits. The dipoles produced by this polarization generate an electrostatic field as shown in Fig. 1. Now, an effective electric field can be calculated at both subunits by adding the field of the other dipole to $\mathbf{E}^0$. This gives the

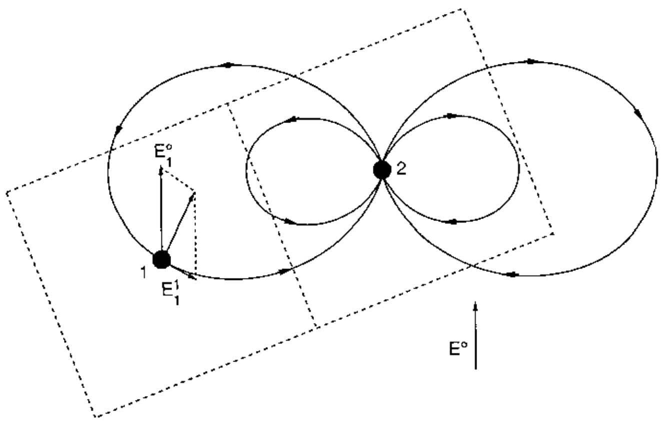

FIG. 1. First-order coupling between the dipoles in a rod consisting of two subunits. The dashed lines indicate the modeled rod. Only the effect of dipole two on subunit one is shown. $\mathbf{E}_1^0$ is the incident field $\mathbf{E}^0$ at subunit 1, and $\mathbf{E}_1^1$ is the first-order coupling field at subunit 1. Note that the field at subunit 1 is rotated in the direction of the particle's long axis. The effect at subunit 2 is the same.

internal field in the particle including the first-order coupling between the dipoles. The scattered amplitude to first order can now be calculated by adding the far fields from both dipoles due to the polarization by this internal field. To second order, one has to include the additional polarization of subunit 1 and 2 resulting from the first-order dipole fields of subunit 2 and 1, respectively. This process can be continued indefinitely, and in practice is truncated by some convergence criterion.

For an arbitrary particle, let $\mathbf{E}_i^a$ be the ath order electric field strength at subunit i, resulting from all the other subunits. The exact value for the electric field strength at subunit i is then

$$\mathbf{E}_i = \mathbf{E}_i^0 + \sum_{a=1}^{\infty} \mathbf{E}_i^a. \quad [3]$$

The superscript a is thus the number of the iteration, c.q. the scattering order. The electric dipole fields of increasing scattering order, as calculated from each other by iteration, are given by

$$\mathbf{E}_i^{a+1} = \sum_{i \neq j} k^2(\mathbf{n}_{ij} \times \alpha_j \mathbf{E}_j^a) \times \mathbf{n}_{ij} \frac{\exp(ikr_{ij})}{r_{ij}} + [3\mathbf{n}_{ij}(\mathbf{n}_{ij} \cdot \alpha_j \mathbf{E}_j^a) - \alpha_j \mathbf{E}_j^a] \left(\frac{1}{r_{ij}^3} - \frac{ik}{r_{ij}^2} \right) \exp(ikr_{ij}). \quad [4]$$

When the final electrical fields ($\mathbf{E}_i$) at the subunits are determined, the total scattered amplitude can be obtained by adding the far field waves of the subunits with the proper phase differences, just as with RGD scattering. The electrical field at the detector, $\mathbf{E}_d$, is given by

$$\mathbf{E}_d = \frac{k^2 \exp(ikr_d)}{r_d} (\mathbf{I} - \mathbf{n}_d \mathbf{n}_d) \sum_j \exp(-ik\mathbf{n}_d . \mathbf{r}_j) \alpha_j \mathbf{E}_j, \quad [5]$$

where $\mathbf{n}_d$ is the unit vector pointing from the particle to the detector, and $\mathbf{r}_j$ is the position vector of subunit j. The intensity is determined by the square of the amplitude.

The above discussed simple example of the two subunit rod can be compared with a small ellipsoidal rod for which the scattering can be calculated exactly, by calculating the polarizability of the particle using basic electrostatics (2). Here too, just as for the rod consisting of two subunits, one observes that the polarization of the particle is rotated in the direction of the particle's long axis with respect to $\mathbf{E}^0$. This effect gives rise to the form birefringence of an ordered assembly of rod-like particles, with zero intrinsic birefringence (22).

Of course, convergence becomes worse when the particle is larger, or the refractive index difference is higher. Convergence also depends on the shape of the particle. Anisometric particles (e.g., rods) can give convergence while a sphere of the same volume and refractive index does not give convergence (14). This is easy to understand, because in compact structures the subunits are closer together, so that the coupling between the dipoles is stronger. Especially the sum of the r^{-1} and r^{-2} terms in Eq. [4] may lead to a nonconvergence of the iterative procedure for large massive structures, because the number of subunits at a distance r increases as r^2. In these cases the incident field is not even a moderately good first approximation for the internal field any more, and the internal field must be calculated by the matrix inversion method.

In the limit where the subunits are taken infinitely small, the CDM result can be shown to give an exact integral equation for the scattering problem. This integral equation is also the basis for the multiple light scattering analysis near the gas–liquid critical point of Oxtoby and Gelbart (23), and the interparticle double scattering correction for colloidal particles, as developed by Dhont (24).

If the refractive index is small enough, then $\mathbf{E}_i - \mathbf{E}_i^0$ is small and the internal field can be approximated by $\mathbf{E}^0$, leading to Rayleigh–Gans–Debye scattering. For a cylinder, the form factor can be calculated analytically, but orientation averaging yields an integral which has to be evaluated numerically. The orientationally averaged RGD form factor (1) is given by (where J_1 is the Bessel function of the first kind of integral order 1)

$$P(q) = \int_0^1 \left[\frac{2J_1((1/2)qD\sqrt{1-x^2})}{(1/2)qD\sqrt{1-x^2}} \times \frac{\sin((1/2)qLx)}{(1/2)qLx} \right]^2 dx, \quad [6a]$$

with

$$q = \frac{4\pi n_m}{\lambda_0} \sin(\theta/2), \quad [6b]$$

where λ_0 is the wavelength of the light in vacuum and θ is the scattering angle. In the limit of qD going to zero, the quotient with the Bessel function goes to one, and the form factor for an infinitely thin rod is obtained. For qL going to zero, on the other hand, the quotient with the sine function goes to one, yielding the form factor for an infinitely thin disc.

3. SCATTERING CALCULATIONS

The CDM has been implemented in Pascal on a 80486-25 MHz personal computer. Calculation times (including orientational averaging) were between a few minutes and a few hours. First of all, calculations were performed for a homogeneous sphere and compared with Mie theory. The

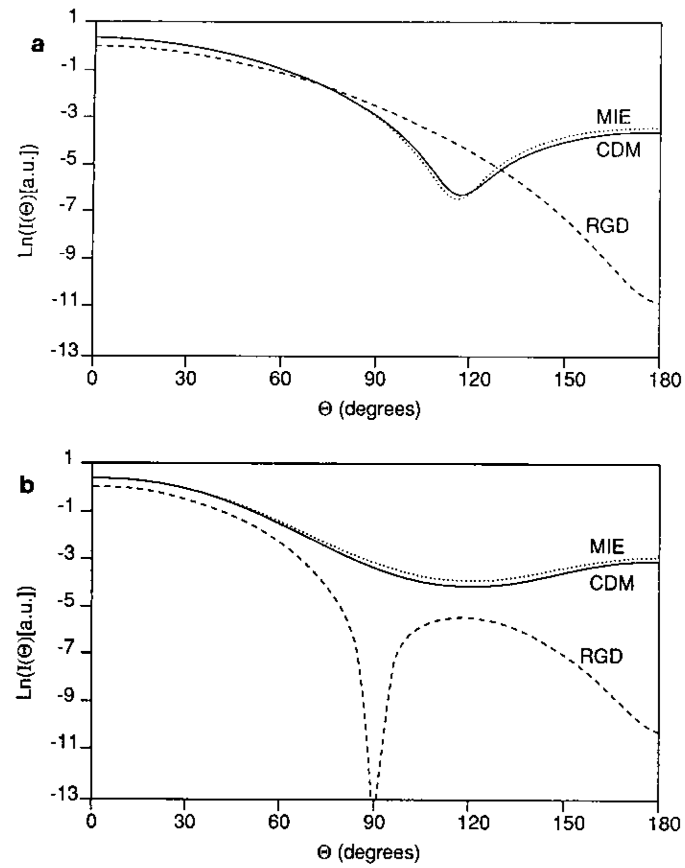

FIG. 2. (a) Light scattering curves of a sphere with radius $rn_m/\lambda_0 = 0.355$ and $n_r = 1.33$ on RGD (– – –), Mie (· · ·), and CDM (—) levels. The CDM sphere consists of 739 subunits (size, $0.063\lambda_0/n_m$) and the incident and scattered light are both vertically polarized. (b) The same as (a), but with horizontally polarized incident and scattered light.

sphere consisted of 739 subunits and the distance between the subunits was adjusted, so that the volume of the sphere was equal to the total volume of all the subunits. For this choice of subunit size good agreement was found between the Mie and the CDM results, as is shown in Figs. 2a and 2b, together with the RGD result for comparison. Clearly, for the scattering parameters used, there is a large discrepancy between RGD and the CDM/Mie results. As a check, a CDM calculation with vertically polarized incident light and horizontally polarized scattered light was performed, and found to give no scattering intensity for the sphere (within numerical errors).

For the calculations on rods, orientation averaging was added, using numerical integration with Simpson's rule. For small refractive indexes, the CDM results correspond to the RGD scattering as calculated with Eq. [6].

It was considered that convergence was reached when the field strength of the last iteration step was a factor 10,000 smaller than the incident field, at every subunit. All calculations showed convergence within 10 iterations. For the orientationally averaged calculations on rods only the average number of iterations for different orientations was recorded.

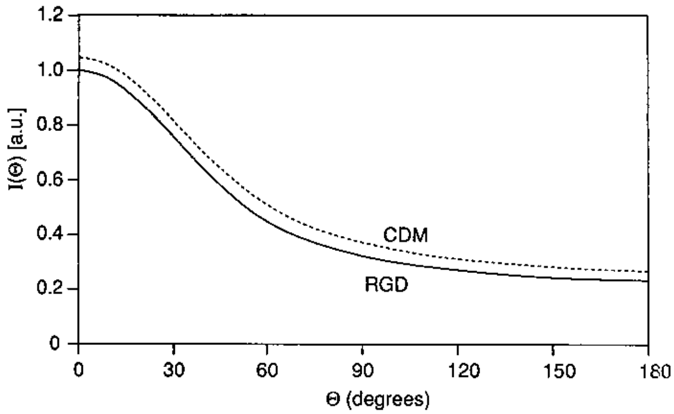

FIG. 3. RGD (—) and CDM (– – –) light scattering curves for an infinitely thin rod with $n_r = 1.25$ and $L_r = 1$. The distance between the subunits was $0.025\lambda_0/n_m$.

Hereafter, the dimensionless size parameters $n_m L/\lambda_0$ and $n_m D/\lambda_0$ are used, which are referred to as L_r and D_r, respectively. The refractive index of the particle is taken relative to the refractive index of the medium as discussed in Section 2. All calculations relate to vertically polarized incident and scattered light, and the particles are nonabsorbing.

An infinitely thin rod is a good approximation for scattering calculations on rods with a diameter much smaller than the wavelength of the light. In the CDM such a thin rod is modeled by a single row of subunits. The distance between the subunits was $0.025\lambda_0/n_m$ unless stated otherwise. The diameter for the corresponding cylinder is found by taking the square of the distance between the subunits equal to the cross-sectional area of the cylinder. For calculations on rods with a finite thickness, the rod is modeled by four parallel

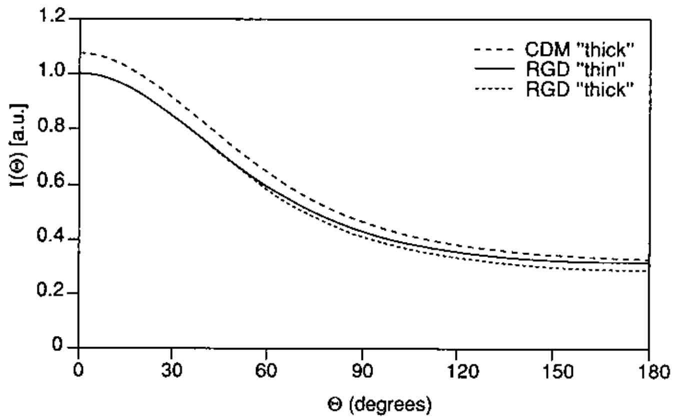

FIG. 4. Scattering curves of an infinitely thin rod on the RGD (—) level and a 2 × 2 subunits thick rod ($D_r = 0.11$) on RGD (----) and CDM (– – –) levels. The length $L_r = 0.75$ and $n_r = 1.20$ and the distance between the subunits was $0.05\lambda_0/n_m$.

TABLE 1

Comparison between "Thick" and Infinitely Thin Rods Concerning the Relative Error (Δ_I) in the RGD Results of $I(0)$

L_r	n_r	Δ_I (thin) (%)	Δ_I (thick) (%)
0.3	1.2	7.6	10.8
0.75	1.2	8.0	12.6
1.5	1.2	8.1	13.2
2	1.2	8.1	13.3

TABLE 2

Comparison between "Thick" and Infinitely Thin Rods Concerning the Relative Error (Δ_z) in the RGD Results of $z(30)$

L_r	n_r	Δ_z (thin) (%)	Δ_z (thick) (%)
0.3	1.50	5	2.1
0.75	1.20	5	4.1
1.5	1.30	5	3.3

rows of subunits. The distance between the subunits was $0.05\lambda_0/n_m$ in each case (corresponding to a D_r of 0.11 for a cylinder). Hereafter, these rods are referred to as "thick" rods.

Figures 3 and 4 show the results for scattering calculations on RGD and CDM levels for an infinitely thin and a "thick" rod. The figures show a significant but small difference between the CDM and the RGD curves. To allow verification of the RGD theory for use with experimental studies, the error in the RGD result is evaluated more systematically.

The first parameter of interest is the scattering intensity $I(\theta)$ at zero scattering angle ($\theta = 0$). The error in the RGD result is given as $\Delta_I = |I(0)_{CDM} - I(0)_{RGD}|/I(0)_{RGD}$. Table 1 shows a comparison between four thick and infinitely thin rods, which demonstrates that the error in the RGD result is larger for the thick rods. Therefore, systematic calculations on Δ_I as a function of L_r and n_r were performed for the thick rods. The results are shown in the contour plot of Fig. 5. The contour lines are accurate to within 0.5%. All intensities on the CDM level are larger than the corresponding RGD intensity. The contour plot shows that the error in the RGD result is mainly determined by n_r.

In practice, however, the shape of the light scattering curve can be just as important or even more important than the absolute scattering intensity. Therefore, calculations have been performed for the dissymmetry ratio at 30 degrees $z(30)$. This dissymmetry ratio (1) is defined as

$$z(\theta) = I(\theta)/I(180° - \theta). \quad [7]$$

The angle of 30° is chosen because 30° and 150° often are the limiting angles in light scattering measurements. First, a comparison is made between the errors in the RGD results of infinitely thin and thick rods. The result is shown in Table 2. Contrary to the absolute intensity, the error in the RGD result for $z(30)$ decreases for the thick rods. Therefore, the systematic calculations on the error of the RGD value for $z(30)$ are performed for infinitely thin rods. The result for the relative difference $\Delta_z = |z_{CDM} - z_{RGD}|/z_{RGD}$ is shown in the contour plot of Fig. 6. Within the range of $L_r < 2$ and $n_r < 1.5$ no errors larger than 15% are found. It should be noted here that the upward shift of the CDM curve in Figs. 3 and 4 results in a decrease of the dissymmetry ratio. Indeed, all $z(30)$ values calculated with the CDM are smaller than the ones calculated with the RGD theory.

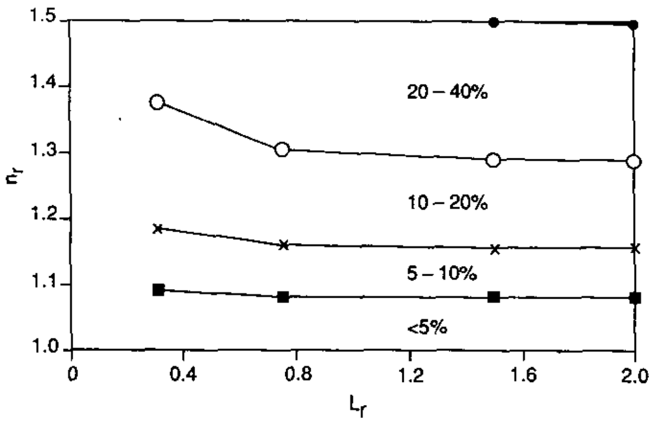

FIG. 5. The relative error (Δ_I) in the RGD results for the scattering intensity at zero scattering angle of a thick rod calculated by the CDM, as a function of L_r and n_r. The 5% (■), 10% (×), 20% (○), and 40% (●) contour lines are shown. A 10% error means that $I(0)$ of the CDM is 10% larger than the corresponding RGD value. The distance between the subunits was $0.050\lambda_0/n_m$. The symbols indicate the points that were calculated.

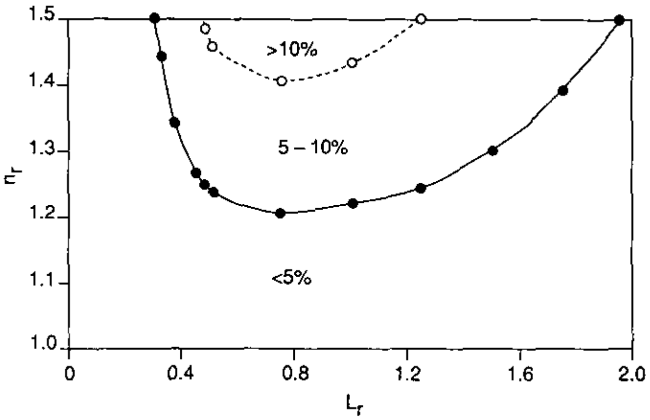

FIG. 6. The relative error (Δ_z) in the RGD results of the dissymmetry ratio $z(30)$ of an infinitely thin rod calculated by the CDM, as a function of L_r and n_r. The 5% (●) and 10% (○) contour lines are shown. A 5% error means that $z(30)$ of the CDM is 5% lower than the corresponding RGD value. The distance between the subunits was $0.025\lambda_0/n_m$. The dots indicate the points that were calculated.

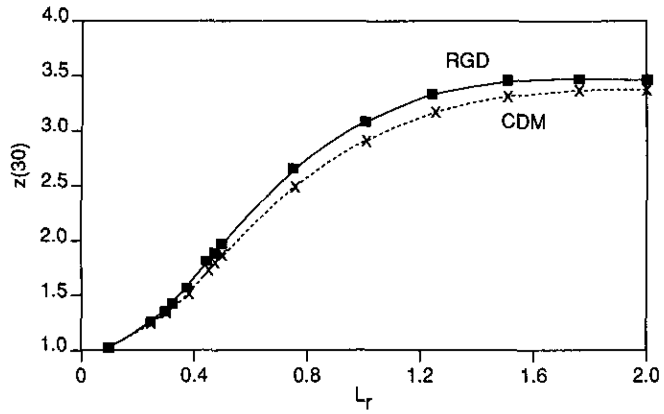

FIG. 7. Dissymmetry ratio $z(30)$ for an infinitely thin rod as a function of L_r on the RGD level (■), compared to the CDM values for $n_r = 1.25$ (×). The distance between the subunits was $0.025\lambda_0/n_m$.

The dissymmetry ratio on the RGD level is shown in Fig. 7 as a function of L_r and compared to the CDM result for $n_r = 1.25$. As can be seen, the error in the RGD result reaches its maximum at intermediate L_r values, where the derivative of $z(30)$ to L_r is high. Furthermore, $z(30)$ increases only very slowly for large rod lengths, reaching a limiting value of 3.732 for infinitely long rods in the RGD approximation. The limits of the dissymmetry ratios for infinitely long and thin rods can be derived from Eq. [6] and is given by

$$\lim_{L_r \to \infty} z(\theta) = \frac{\sin(90° - \theta/2)}{\sin(\theta/2)}. \qquad [8]$$

The calculations described above set the validity range of the RGD theory for cylindrical particles, in the parameter range $L_r < 2$, $n_r < 1.5$, and $D_r < 0.11$. The errors for longer particles, however, can probably be extrapolated somewhat, and even longer (but still thin) particles become flexible and can no longer be described by a cylinder.

4. CONCLUSIONS

The principle result of this paper is summarized in Figs. 5 and 6, which show the range of validity of the RGD theory for cylindrical particles, in terms of the relative error in the scattering intensity at zero scattering angle and the relative error in the dissymmetry ratio at 30° ($z(30)$), as a function of the length and the relative refractive index, for rods with a diameter relative to the wavelength of the light (D_r) which is smaller than 0.11. It is found that the error in the scattering intensity at zero scattering angle increases with the thickness of the rod, contrary to the error in $z(30)$, which decreases with the thickness of the rod.

For $L_r < 2$, $n_r < 1.2$, and $D_r < 0.11$ the error in $z(30)$ is smaller than 5%. In this parameter range the maximum error in the absolute scattering intensity at zero degrees scattering angle is 13.3%.

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