Abstract

The coupled dipole method is used to calculate the circular intensity differential scattering (CIDS) from chiral particles. The particles are described by a collection of spherical or ellipsoidal dipoles. In the case of ellipsoidal dipoles, it is shown that triaxial polarizabilities have to be used to quantitatively describe the scattering matrix of the particle. For certain collections of ellipsoidal dipoles, the dipolar interactions may be neglected in calculating CIDS from the structure. The coupled dipole approximation also provides a convenient method for calculating CIDS from a one dimensional helical crystal.

Polarizabilities for light scattering from chiral particles

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I. INTRODUCTION

In a recent work,[1] the coupled dipole approximation was shown to be a suitable method for the calculation of the entire scattering matrix of an arbitrary particle or collection of particles. The approximate method was found to give results which were in good quantitative agreement with Mie calculations for a sphere and spherical shell. In describing the spherical shell, both spherical and ellipsoidal dipoles were used and found to be equally effective. The comparisons with Mie theory for a very thin spherical shell also showed that triaxial polarizabilities were more appropriate than biaxial polarizabilities even though extremely thin oblate ellipsoids were used in the dipolar calculation. This use of triaxial polarizabilities was found to be particularly crucial in obtaining agreement with Mie results for the magnitude of the S_{34} matrix element of the shell.

In this paper, we extend these results to scattering from chiral particles. For complicated geometric shapes, e.g., helical structures, a Mie theory solution for the scattering matrix is not known. Such geometries are usually described by the dipolar approximation using anisotropic dipoles in appropriate orientations. The circular intensity differential scattering (CIDS) is the difference in scattered intensities for incident left and right circularly polarized light divided by the total, i.e., CIDS $= -S_{14}/S_{11}$. The CIDS from helical structures has been extensively studied by Bustamante and co-workers[2–5] using oriented uniaxial point polarizabilities. These calculations have been done for oriented and rotationally averaged helices within the first and second Born approximations[6,7] and have provided much insight into the dependence of CIDS on chiral parameters. This model has also been used to establish a superposition principle for CIDS from hierarchical chiral structures.[8] Isotropic and anisotropic polarizabilities have also been used in calculations of the scattering matrix of model geometries (within the first Born approximation) and found to be useful in relating the elements of the scattering matrix to structural parameters.[9]

The focus of this work is to establish a method for assigning point polarizabilities which are appropriate for a quantitative description of scattering from chiral particles. We are particularly interested in the CIDS parameter of chiral structures for which some experimental data is available.[10] We start by assuming that small isotropic (spherical) polarizabilities which are allowed to interact provide a good approximation for scattering from a chiral structure. The model is then extended to anisotropic (ellipsoidal) polarizabilities and our results indicate that triaxial polarizabilities for ellipsoids used to describe helices and other chiral structures yield quantitatively different results from the same structures described by uniaxial or biaxial polarizabilities.

We also examine the importance of dipolar interactions in calculating the CIDS for chiral structures; these interactions are included self-consistently and with retention of retardation effects.[11] In the Mie comparisons,[1] it was found that dipolar interactions were negligible in calculating some of the matrix elements for structures which were very small compared to the wavelength or very "thin" as in the case of a very thin shell. This neglect of retardation effects is known to give zero values for the matrix elements S_{13}, S_{23}, and S_{34} for rotationally averaged structures.[12] However, CIDS is obtained in this approximation for oriented and rotationally averaged chiral structures described by appropriately oriented anisotropic dipoles.[2,5] We find that a sufficiently thin helix can be equivalently described by interacting spheres or a smaller number of noninteracting prolate ellipsoids directed tangentially to the helix. Again, the appropriate triaxial polarizabilities must be used for the ellipsoids. The calculation of CIDS from such a rotationally averaged helix composed of noninteracting dipoles can then be related to the rotationally averaged expression in the first Born approximation[5] and is considerably simplified. However, a thick helix cannot be approximated in a similar fashion and the dipolar interactions are necessary for calculating appropriate values for CIDS from such oriented or rotationally averaged structures.

We also use the coupled dipole approximation to calculate CIDS from a one dimensional helical crystal. An important consequence of describing a thin helix with noninteracting prolate ellipsoids is that the CIDS of a one dimensional crystal comprised of such a thin helix will be independent of length. When the helix is no longer continuous but com-

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posed of discrete spherical units, it is not possible to neglect dipolar interactions between the units. However, we find that the CIDS of such a structure calculated with inclusion of interactions converges to a constant value as the length of the helical crystal is increased. Thus, the coupled dipole approximation provides a convenient method for calculating CIDS from crystals as well as from oriented or rotationally averaged chiral particles of finite size.

II. THE COUPLED DIPOLE APPROXIMATION

In the coupled dipole approximation described by Purcell and Pennypacker,[11] an arbitrary particle is subdivided into units on a cubic lattice such that each unit is small relative to the wavelength of incident light. Each unit is assumed to behave as a point dipolar oscillator which responds to the incident field as well as to the field generated by the other dipoles. For a collection of m units, the field ($\mathbf{E}^i$) at unit i (position $\mathbf{r}^i$) is due to the incident field ($\mathbf{E}^0$) as well as the scattered fields from the other dipoles, i.e.,

$$\mathbf{E}^i = \sum_{j\neq i}^{m} [a^{ij}\hat{\alpha}^j\mathbf{E}^j + b^{ij}(\hat{\alpha}^j\mathbf{E}^j\cdot\mathbf{n}^{ji})\mathbf{n}^{ji}] + \mathbf{E}^0 e^{i\mathbf{k}\cdot\mathbf{r}^i}, \tag{1}$$

where

$$a^{ij} = \frac{e^{ikr^{ij}}}{r^{ij}}\left(k^2 - \frac{1}{(r^{ij})^2} + \frac{ik}{r^{ij}}\right)$$

and

$$b^{ij} = \frac{e^{ikr^{ij}}}{r^{ij}}\left(\frac{3}{(r^{ij})^2} - k^2 - \frac{3ik}{r^{ij}}\right).$$

Here, the electric dipole moment is given by $\mathbf{p}^j = \hat{\alpha}^j\mathbf{E}^j$, where $\mathbf{E}^j$ is the field at the scattering center and $\hat{\alpha}^j$ is, in general, a complex polarizability tensor. k is the wave number of the radiation, r^{ij} is the distance, and $\mathbf{n}^{ji}$ the unit vector from the jth to the ith dipole. The explicit time dependence of the fields is omitted. Retardation effects are completely accounted for in this model, self-radiative effects are neglected, and only elastic scattering is considered.

For the m dipolar oscillators, Eq. (1) yields a set of $3m$ linear equations which are solved self-consistently to give the resultant field at each dipole. That is, Eq. (1) can be rewritten as

$$\mathbf{E} = \hat{A}^{-1}\mathbf{B}, \tag{2}$$

where $\mathbf{E}$ is a $3m\times 1$ matrix containing the resultant fields at the dipoles, $\mathbf{B}$ is a $3m\times 1$ matrix given by

$$B^i_\mu = E^0_\mu e^{i\mathbf{k}\cdot\mathbf{r}^i}, \tag{3}$$

and $\hat{A}^{-1}$ is a $3m\times 3m$ matrix obtained from

$$A_{i\mu,j\nu} \equiv \delta_{ij}\delta_{\mu\nu} + (\delta_{ij}-1)\left[a^{ij}\alpha^j_{\mu\nu} + b^{ij}n^{ji}_\mu\left(\sum_\lambda \alpha^j_{\lambda\nu}n^{ji}_\lambda\right)\right]. \tag{4}$$

The field, $\mathbf{E}^d$, at the detector in the far-field region is then given by the sum of the amplitudes of the far-field contributions from the m dipoles, i.e.,

$$\mathbf{E}^d = \frac{k^2 e^{ikr^d}}{r^d}(\hat{1} - \mathbf{n}^d\mathbf{n}^d)\sum_j^m e^{-ik\mathbf{n}^d\cdot\mathbf{r}^j}\hat{\alpha}^j\mathbf{E}^j, \tag{5}$$

where r^d is the distance and $\mathbf{n}^d$ the unit direction of the detector from the origin.

For point dipoles arranged on a cubic lattice, a value for the polarizabilities can be obtained rigorously by using the Clausius–Mossotti relationship.[13] In the previous work,[1] the calculations for a spherical shell made up of spherical point dipoles not arranged on a cubic lattice were found to be in good agreement with Mie results. Thus, the use of a cubic arrangement for the dipoles does not appear to be essential for a good approximation. Further, it was also found that ellipsoidal shaped dipoles could be used to define the volume of the particle. In using such dipolar subunits it is necessary to use the Maxwell–Garnett[14] (or other) theory to obtain a dielectric constant for the ellipsoid which will suitably account for the dielectric constant of the material of the particle. The polarizability tensor of each ellipsoidal dipole can then be obtained from the dimensions of the ellipsoid together with the dielectric constant.[14] The use of spherical or ellipsoidal shaped dipoles appear to be equally good approximations, the only differences arising from variations in describing the overall shape of the particle. Anisotropy in the dielectric constant of the material of the particle can be explicitly accounted for by calculating the polarizability tensor of either a spherical or ellipsoidal dipole with the appropriate dielectric tensor.

The scattered field given in Eq. (5) can be resolved into components parallel (unit vector $\mathbf{e}^s_\parallel$) and perpendicular (unit vector $\mathbf{e}^s_\perp$) to the scattering plane which is defined as the plane containing $\mathbf{r}^d$ and the direction of propagation of the incident light. These components have to be calculated for incident light of two orthogonal polarizations, e.g., left (superscript L) and right (superscript R) circularly polarized light. For an azimuthal angle of zero they are given by[15]

$$E^\beta_\alpha = C'\sum_{ij\mu\nu} V^\alpha_\mu L^\beta_\nu M^{ij}_{\mu\nu} e^{-ik\mathbf{n}^d\cdot\mathbf{r}^j} e^{i\mathbf{k}\cdot\mathbf{r}^i}, \tag{6}$$

where

$$C' = k^2\frac{e^{ikr^d}}{r^d}$$

and α,β take values 1,2 with

$$\mathbf{V}^1 = \mathbf{e}^s_\parallel, \quad \mathbf{V}^2 = \mathbf{e}^s_\perp,$$
$$\mathbf{L}^1 = \mathbf{E}^{0R}, \quad \mathbf{L}^2 = \mathbf{E}^{0L},$$

and

$$M^{ij}_{\mu\nu} = \sum_\lambda \alpha^j_{\mu\lambda} A^{-1}_{j\lambda,i\nu}. \tag{7}$$

The tensors $\hat{M}^{ij}$ are the interaction tensors which contain information about the interactions between the pairs of dipoles i and j. In the limit of noninteracting dipoles, $\hat{A}$ becomes a unit matrix and $\hat{M}^{ij} = \delta_{ij}\hat{\alpha}^j$. In this limit (first Born approximation), the field at the dipoles is only determined by the incident field.

The amplitude scattering matrix elements (S_j) are then calculated from the values of E^β_α and the scattering matrix elements (S_{ab}) are obtained from linear combinations of products of S_j.[14] Numerical and analytic orientation averages for these scattering matrix elements calculated within

the coupled dipole approximation have been recently obtained.[15]

III. POLARIZABILITIES FOR CHIRAL PARTICLES

A. Continuous helix

The position vector and a coordinate system for the polarizability tensor of a helix have been described previously.[2] The position vector for a right-handed helix of radius R and pitch P may be described parametrically by

$$\mathbf{r} = R\cos\theta\mathbf{x} + R\sin\theta\mathbf{y} + (P\theta/2\pi)\mathbf{z}\,. \tag{8}$$

The polarizability for each point is described in terms of a coordinate system with unit vectors normal ($\mathbf{n}$), tangential ($\mathbf{t}$), and perpendicular ($\mathbf{p}$) to the helix, i.e.,

$$\begin{aligned}\mathbf{n} &= \cos\theta\mathbf{x} + \sin\theta\mathbf{y}\,,\\ \mathbf{t} &= -(R/N)\sin\theta\mathbf{x} + (R/N)\cos\theta\mathbf{y} + (P/2\pi N)\mathbf{z}\,,\\ \mathbf{p} &= \mathbf{t}\times\mathbf{n} = -(P/2\pi N)\sin\theta\mathbf{x}\\ &\quad + (P/2\pi N)\cos\theta\mathbf{y} - (R/N)\mathbf{z}\,,\end{aligned} \tag{9}$$

where $N = (R^2 + P^2/4\pi^2)^{1/2}$. The polarizability tensor for any point of the helix is then given by

$$\hat{\alpha} = \alpha_n\mathbf{nn} + \alpha_t\mathbf{tt} + \alpha_p\mathbf{pp}\,, \tag{10}$$

where α_n, α_t, and α_p are the principal components. For a helix made up of spherical dipoles, the principal values of the polarizability tensor are equal yielding a scalar polarizability.

The equivalence of spherical and ellipsoidal dipoles in describing the shape of a chiral particle is shown in Fig. 1(a). The model helix is continuous with a radius and pitch of 500 nm and cylindrical thickness of 50 nm. The helical axis is oriented along the direction of propagation of the incident light which has a wavelength of 975 nm. A total of 64 spherical dipoles (radius 25 nm) is used to define the shape of the particle. The material of the helix is taken to have a dielectric constant of 1.4 and the surrounding medium is vacuum. The Maxwell–Garnett theory is used to obtain a suitable value for the dielectric constant of the spherical dipoles ($\epsilon = 1.64$). The same helix is then described by 32 prolate ellipsoids oriented tangentially to the helix. It is seen in Fig. 1(a) that the coupled dipole approximation yields virtually identical results for the spherical and prolate ellipsoidal models, the very slight differences being attributable to variations in descriptions of the shape of the particle.

We have also used a similar comparison to examine the importance of the size of the subunits for the dipolar model. Subunits which are about a tenth of the incident wavelength or smaller are usually considered appropriate for the dipolar approximation. We find that subunits with a maximum dimension of about a fifth of the wavelength or even larger do not cause serious error in calculating CIDS from chiral particles, e.g., prolate ellipsoids with a length of a fifth of the wavelength oriented tangentially to the helix appear to be suitable. This comparison is shown in Fig. 1(b) for the model helices considered above where the wavelength is now taken to be 500 nm. We also find that oblate ellipsoids with their short axes directed tangentially to the helix do not suitably describe the shape of the helix.

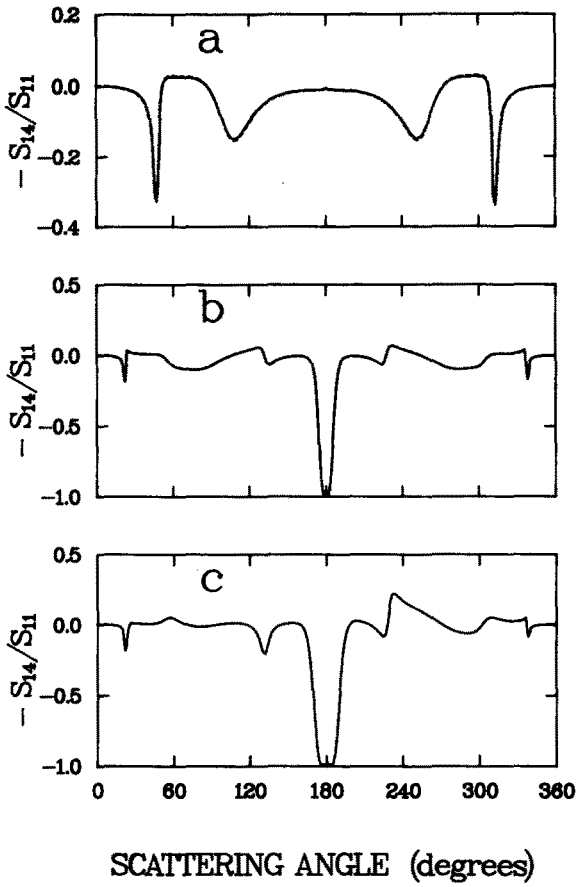

FIG. 1. (a) CIDS from an oriented continuous helix with radius and pitch of 500 nm and cylindrical thickness of 50 nm. The helical axis is oriented along the direction of incident light which has a wavelength of 975 nm; the azimuthal angle of the detector is 0°. The dielectric constant of the helix is 1.4 and that of the surrounding medium is 1.0. *Solid line*–CIDS for the structure described by 64 spherical dipoles with radius 24.85 nm ($\alpha = 2.708\times10^3$ nm^3); *dashed line*–CIDS for the same structure described by 32 prolate ellipsoids ($a = 49.7$ nm, $b = c = 24.85$ nm) oriented tangentially to the helix ($\alpha_t = 5.908\times10^3$ nm^3, $\alpha_n = \alpha_p = 5.190\times10^3$ nm^3). (b) Same as (a) except that the wavelength is now 500 nm. (c) CIDS from an oriented thick helix with radius, pitch, and wavelength equal to 500 nm and the helical axis oriented along the incident light direction. The thickness is 200 nm. The helix is modeled by 124 prolate ellipsoids where each has approximate dimensions of $a = 51.3$ nm and $b = c = 50$ nm ($\alpha_t = 2.271\times10^4$ nm^3, $\alpha_n = \alpha_p = 2.259\times10^4$ nm^3). Four dipoles are used for the cross section of the cylindrical thickness of the helix.

Very thick helices are common structures for biological organisms. A helix with radius and pitch of 500 nm and cylindrical thickness of 200 nm will not be very well described by spherical subunits of radius 100 nm if the wavelength is 500 nm. We model such a helix by using four dipoles on the cross section of the cylindrical thickness and, as before, accounting for the excess volume of the true helix when compared with the volume of the dipoles. A total of 124 prolate ellipsoidal dipoles were used for a single turn of the helix where each ellipsoid had approximate dimensions of $a = 51.3$ nm and $b = c = 50$ nm; the CIDS from this structure is shown in Fig. 1(c).

We now compare the CIDS for a helix described by dipoles with triaxial polarizabilities with that obtained using (uniaxial) tangential polarizabilities. A helical turn with radius and pitch of 500 nm is modeled by 32 tangential polarizabilities with $\alpha_t = 5.908\times10^3$ nm^3 and 64 tangential polar-

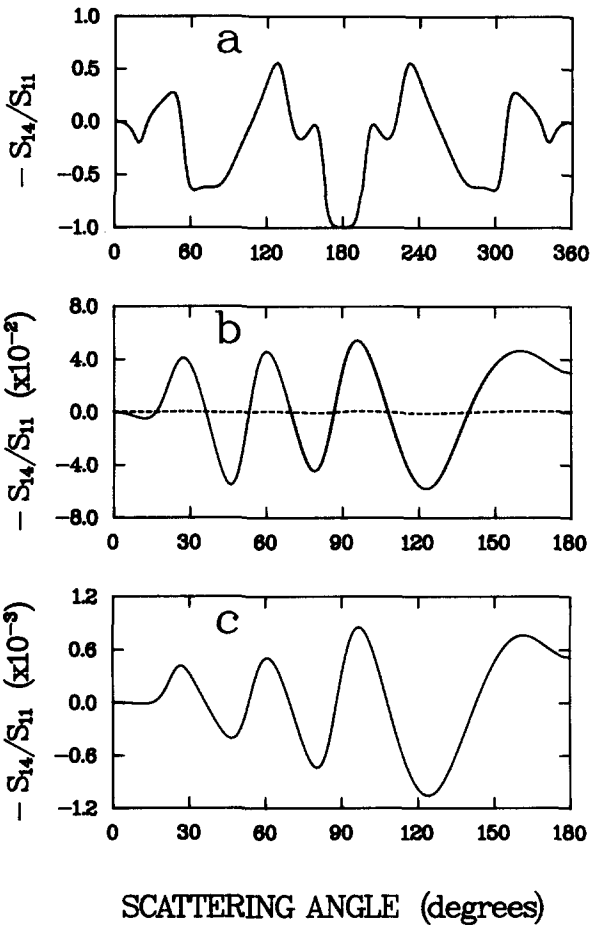

FIG. 2. (a) CIDS from an oriented helix described by tangential polarizabilities with the helical axis along the direction of light. The azimuthal angle of the detector is 0° and the radius, pitch, and wavelength of the helix are 500 nm. *Solid line*–64 tangential polarizabilities with $\alpha_t = 2.708 \times 10^3$ nm^3; *dashed line*–32 tangential polarizabilities with $\alpha_t = 5.908 \times 10^3$ nm^3. (b) CIDS for rotationally averaged helices. *Solid line*–CIDS for helix described by 32 tangential polarizabilities as used for (a); *dashed line*–CIDS for helix described by 32 ellipsoids (triaxial polarizabilities) used for Fig. 1(b). (c) Same as dashed line in (b).

izabilities with $\alpha_t = 2.708 \times 10^3$ nm^3. These magnitudes for tangential polarizabilities were obtained from the calculated values of α_t for the same helix with a thickness of 50 nm. The CIDS from these model structures is shown in Fig. 2(a) for incident light of 500 nm and it is clear that the uniaxial structures with 32 or 64 polarizabilities yield identical results. However, it is evident that the magnitude of the calculated CIDS is very different at some scattering angles from that calculated using spherical polarizabilities or triaxial ellipsoidal polarizabilities [Fig. 1(b)]. These differences become more pronounced at all scattering angles for other orientations of the helix relative to the direction of incident light and we compare the CIDS of the rotationally averaged structures in Figs. 2(b) and 2(c). The solid line in Fig. 2(b) is the calculated CIDS for the rotationally averaged helical structure described by 32 tangential polarizabilities while Fig. 2(c) shows the CIDS for the same structure described by 32 prolate ellipsoids with triaxial polarizabilities. Both angular distributions show the detailed structure expected for a helix with chiral parameters equal to the wavelength but the relative magnitudes of the peaks are different and, more importantly, the absolute magnitude of CIDS is very different for the two cases. Thus, it appears that the tangential polarizability model for a rotationally averaged helix, while displaying the qualitative features of CIDS, is not suitable for calculating a quantitative estimate for CIDS. To calculate CIDS for comparison with experimental data it is then necessary to use triaxial polarizabilities which are evaluated using the thickness of the helical structure.

B. Other chiral structures

We have studied the differences in calculated CIDS for a triaxial polarizability model compared with uniaxial or biaxial models for two other chiral structures—a helical ribbon and twisted ladder. The helical ribbon model is a very thin ribbon with rectangular cross section wrapped along a helical turn of radius and pitch 500 nm. The width of the ribbon is taken to be 50 nm and the thickness is 0.5 nm. This structure is modeled by 64 oblate ellipsoids with the short axis of each ellipsoid along the thickness of the ribbon (i.e., along **p**). A biaxial polarizability model is obtained by assigning the polarizability for spherical dipoles of radius 24.85 nm to the tangential and normal polarizability components and assigning zero to the perpendicular component. The axis of the helical ribbon is rotated by Euler angles $\varphi = \theta = \psi = 45°$ from the direction of incident light (wavelength 500 nm) and a comparison of the CIDS calculated for the two models is shown in Fig. 3(a). It is observed that the CIDS calculated by the biaxial model is relatively insensitive to the magnitude of the polarizabilities used. As in the previous case, it is evident that there are differences in the magnitude of CIDS calculated by the two models and it appears that the biaxial model is not very good even though the ratio of $a = b$ to c in the oblate ellipsoids is 100:1.

We perform a similar comparison for the twisted ladder of polarizabilities[7] which has been used as a model for some liquid crystals. Again, very thin cylindrical subunits (length = 50 nm and diameter = 0.5 nm) are used in the model helix which has zero radius and a pitch of 500 nm with 50 polarizabilities per turn of the helix and the helical axis is rotated to some arbitrary angle (Euler angles $\varphi = \theta = \psi = 45°$) with respect to the direction of incident light. The comparison of CIDS for the twisted ladder composed of triaxial polarizabilities with the same structure modeled by only a normal polarizability is shown in Fig. 3(b) and, as in the other cases, large differences are seen for the two models.

Quantitative differences in models with triaxial compared with uniaxial or biaxial polarizabilities can be observed to different extents in all the scattering matrix elements. From the Mie comparison of the spherical shell[1] it was clear that better agreement was observed for the triaxial polarizabilities and that these polarizabilities were essential to obtain agreement for the S_{34} matrix element. In the case of CIDS, we find that only triaxial polarizabilities for ellipsoids are in agreement with the results obtained with spherical polarizabilities. The differences observed for CIDS of chiral structures modeled with triaxial polarizabilities when compared with uniaxial or biaxial polarizabilities are significant

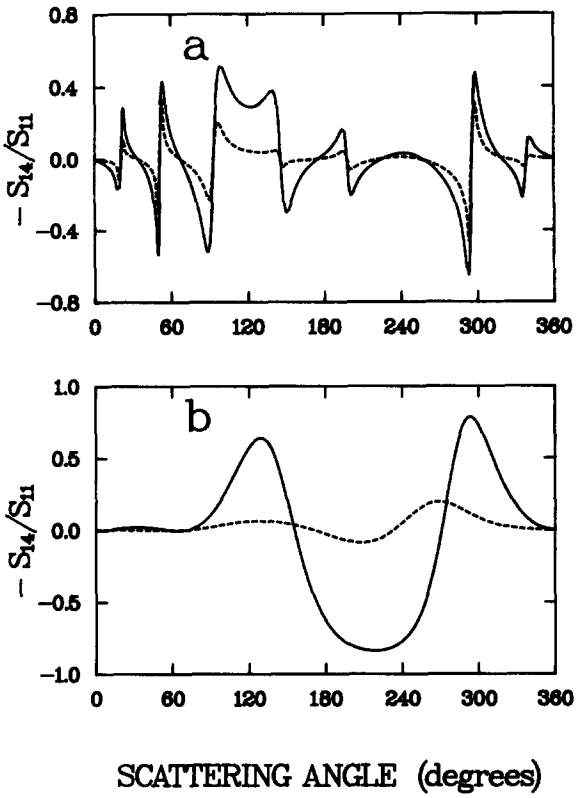

FIG. 3. (a) CIDS for a helical ribbon ($\epsilon = 1.4$) with rectangular cross section wrapped along a helical turn of radius and pitch 500 nm. The width of the ribbon is 50 nm and the thickness is 0.5 nm. The ribbon is modeled by 64 oblate ellipsoids ($a = b = 25$ nm, $c = 0.25$ nm) and the surrounding medium is taken to be vacuum. The helical axis is rotated by Euler angles $\varphi = \theta = \psi = 45°$ from the direction of incident light (wavelength 500 nm); the azimuthal angle of the detector is 0°. *Solid line*–CIDS using biaxial polarizabilities with $\alpha_n = \alpha_t = 3.448\times10^3$ nm^3 and $\alpha_p = 0.0$ nm^3; *dashed line*–CIDS using triaxial polarizabilities with $\alpha_n = \alpha_t = 4.245\times10^1$ nm^3 and $\alpha_p = 2.351\times10^1$ nm^3. (b) CIDS for a twisted ladder of thin cylindrical subunits of length 50 nm and diameter 0.5 nm modeled by prolate ellipsoids with $a = 25$ nm, $b = c = 0.25$ nm. The structure has zero radius and a pitch of 500 nm with 50 polarizabilities per turn of the helix which is oriented at Euler angles $\varphi = \theta = \psi = 45°$ with respect to the direction of incident light (wavelength 500 nm). *Solid line*–CIDS using uniaxial normal polarizabilities with $\alpha_n = 3.324\times10^{-1}$ nm^3 and $\alpha_t = \alpha_p = 0.0$ nm^3; *dashed line*–CIDS using triaxial ellipsoidal polarizabilities for the cylindrical subunits, i.e., $\alpha_n = 3.324\times10^{-1}$ nm^3, $\alpha_n = \alpha_p = 2.521\times10^{-1}$ nm^3.

although not nearly as large as the differences observed for S_{34} of the spherical shell.

IV. DIPOLAR INTERACTIONS

In this section, the importance of dipolar interactions in calculating the scattering matrix elements is discussed. It is known that inclusion of these interactions with retention of retardation effects is essential to obtain nonzero values of S_{13}, S_{23}, and S_{34} for rotationally averaged structures.[12] However, nonzero CIDS (and S_{24}) is observed for both oriented and rotationally averaged chiral structures described by noninteracting dipoles provided that the dipoles are anisotropic and appropriately oriented. The diagonal matrix elements and S_{12} appear with or without interactions for isotropic or anisotropic dipoles.

In the coupled dipole approximation, the interactions between dipoles appear through the interaction tensors $\hat{M}^{ij}$ given in Eq. (7). The magnitude of these tensors depend on several factors—the wavelength of incident light, the distance of separation between dipolar centers, and the magnitude of the elements of the polarizability tensors. We have calculated the elements $\hat{M}^{ij}$ for collections of dipoles and find that the dependence on wavelength is slight, i.e., the magnitude of $\hat{M}^{ij}(i\neq j)$ decreases slowly with increasing wavelength. The effect of dipolar separation is much more pronounced with the magnitude of $\hat{M}^{ij}(i\neq j)$ decreasing sharply with increasing separation. An increase in the magnitude of the polarizability tensor also has the effect of increasing $\hat{M}^{ij}$.

Calculation of $\hat{M}^{ij}$ for a pair of touching spheres shows that the self-interaction tensor $\hat{M}^{ii}$ is very different from the polarizability of each sphere and that the $\hat{M}^{ij}(i\neq j)$ tensors have significant magnitudes when compared with $\hat{M}^{ii}$. A similar, more pronounced, effect is observed for two oblate or prolate ellipsoids touching along their *short* axes. However, the calculation for two prolate or oblate ellipsoids touching along their *long* axes shows a much smaller effect with $\hat{M}^{ii}\simeq\hat{\alpha}^i$ and $\hat{M}^{ij}$ fairly small when compared with $\hat{M}^{ii}$. We have calculated CIDS for structures in which dipolar interactions result in significant variations for $\hat{M}^{ii}$ from $\hat{\alpha}^i$ and a relatively large magnitude for $\hat{M}^{ij}$ and find differences in CIDS calculated with and without interactions. However, as expected, for structures where $\hat{M}^{ij}\simeq\delta^{ij}\hat{\alpha}^j$ is satisfied for all the dipoles, there is virtually no difference in the calculated CIDS with or without interactions. The conditions for neglect of dipolar interactions in CIDS appear to be that $\hat{M}^{ii}\simeq\hat{\alpha}^i$ and that the elements of $\hat{M}^{ij}$ are less than 10^{-2} of the largest elements of $\hat{M}^{ii}$. This neglect of interactions always yields identically zero for the CIDS in the forward scattering direction in contrast to the coupled dipole method which gives a small, nonzero component in the forward direction for both oriented and rotationally averaged chiral structures.

The effect of dipolar interactions in calculating the CIDS of an arbitrarily oriented helical turn is shown in Fig. 4. The radius and pitch of the helix is 500 nm and the calculations are done for three thicknesses–0.5, 50, and 200 nm. In the former two cases, 32 prolate ellipsoids are used with their long axes tangential to the helix and the 200 nm thick helix is made of 124 dipoles as discussed previously. The calculated CIDS for these oriented structures with and without interactions show virtually no differences for the very thin helix but significant differences for the thicker helices. These differences are also observed for the rotationally averaged calculations and it appears that dipolar interactions have to be retained to get an accurate description of CIDS from such structures. Dipolar interactions are found to be unimportant for prolate ($b = c$) ellipsoids which have a:b of 4:1 or larger and have centers displaced by $2a$ when the difference between the dielectric constants of the material and medium is 0.4 or less. Therefore, the CIDS from such a thin helical particle which can be well described by noninteracting dipoles can be very easily calculated using the results of Bustamante *et al.*[5] for the first Born approximation.

The conditions for neglect of dipolar interactions are also valid for the other scattering matrix elements except for S_{13}, S_{23}, and S_{34} from rotationally averaged structures. They

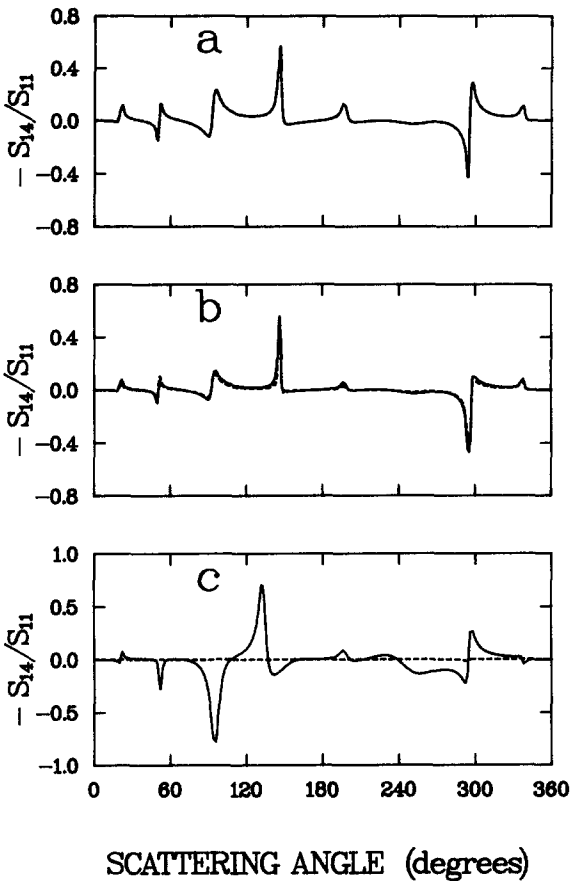

FIG. 4. (a) CIDS of a turn of a continuous helix (radius and pitch of 500 nm) oriented at Euler angles $\varphi = \theta = \psi = 45°$ from the direction of incident light (wavelength 500 nm); the azimuthal angle of the detector is 0°. The helix is modeled by 32 prolate ellipsoids with triaxial polarizabilities. The cylindrical thickness of the helix is 0.5 nm; for a dielectric constant of 1.4 compared with 1.0 for the medium the principal polarizability components for the ellipsoids with $a = 49.7$ nm and $b = c = 0.25$ nm are $\alpha_t = 6.610 \times 10^{-1}$ nm^3 and $\alpha_n = \alpha_p = 5.011 \times 10^{-1}$ nm^3. *Solid line*–CIDS with retention of all dipolar interactions; *dashed line*–CIDS with neglect of dipolar interactions (first Born approximation). (b) CIDS for the helix described in (a) except that the thickness is now 50 nm. The principal polarizabilities are $\alpha_t = 5.976 \times 10^3$ nm^3 and $\alpha_n = \alpha_p = 5.254 \times 10^3$ nm^3. *Solid line*–CIDS with retention of dipolar interactions; *dashed line*–CIDS with neglect of interactions. (c) CIDS for the helix described in (a) except that the thickness is now 200 nm. This helix is modeled by 124 dipoles as described in the caption for Fig. 1(c). The helical axis is oriented at Euler angles $\varphi = \theta = \psi = 45°$ from the direction of propagation of incident light. *Solid line*–CIDS with retention of dipolar interactions; *dashed line*–CIDS with neglect of interactions.

are also applicable to any chiral (or other) structure. We find that for oblate ($a = b$) ellipsoids placed along a long axis (as in a helical ribbon) an a:c ratio of 8:1 or larger is necessary for neglect of interactions and, for the twisted ladder, the distance of separation of dipolar centers is the critical factor.

V. HELICAL CRYSTALS

It has been previously shown that the CIDS of a helical crystal composed of discrete spherical units cannot be easily calculated using an iterative approach for the internal fields.[16] The lack of convergence results from the fact that CIDS for systems of isotropic scatterers is very sensitive to the details of the internal field which depends on the induced interactions between scatterers. In the coupled dipole approximation, the field of the unit cell is calculated self-consistently using the interactions among all the dipoles. As a result, the CIDS in the central unit cell resulting from successively larger crystals will indeed converge.

For simplicity we calculate the CIDS for a linear crystal comprised of several turns of a helix. One turn of the helix then represents the unit cell and we observe the CIDS of the unit cell resulting from an odd number of turns of the helix. The dipoles in the unit cell are allowed to interact with all the dipoles in the crystal and successively longer helices are used until the CIDS of the unit cell converges.

For a crystal comprised of a continuous thin helix with isotropic dielectric constant, the CIDS is approximately the same as that from one turn of the helix. This is a consequence of the fact that a continuous *thin* helix can be approximated by a string of noninteracting prolate ellipsoids as discussed in the previous section. It is known that the CIDS from a crystal of *noninteracting* dipoles is the same as that from a single unit cell.[6] If the crystal is composed of a continuous thick helix, then interacting dipoles have to be used and we observe that the CIDS is now more sensitive to the number of helical turns but the CIDS from the central unit cell still converges to a constant value with an increase in the number of unit cells.

For a crystal comprised of a few discrete spherical units on one turn of a helix the CIDS is again calculated by including interactions between the units. For example, in Fig. 5 we show the CIDS for 7, 11, and 15 turns of a helix with three spherical units per turn. The radius, pitch, and wavelength are all set equal to 250 nm while the radius of the spherical unit is 31 nm. The helical axis is oriented at Euler angles $\varphi = 0°, \theta = 45°, \psi = 0°$ from the direction of incident light. It is assumed that each unit satisfies the dipole approximation and has a dielectric constant of 1.6 with the surrounding medium being vacuum. This leads to an isotropic polarizability for each dipole of 5×10^3 nm^3. In Fig. 5 we see that the CIDS from the central unit cell is reasonably well converged

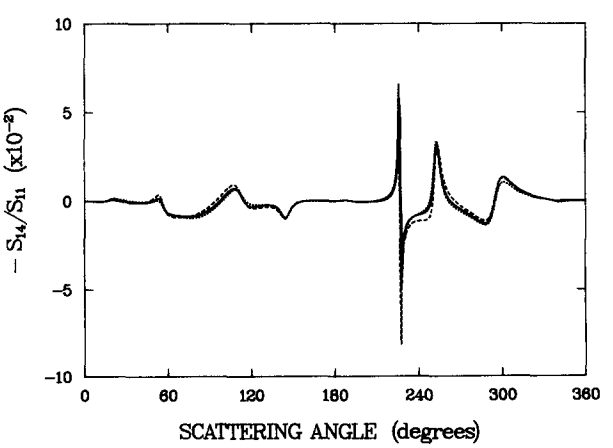

FIG. 5. CIDS for the central unit cell of a helix composed of three discrete spherical units per turn. The helical axis is oriented at Euler angles $\varphi = 0°, \theta = 45°, \psi = 0°$ from the direction of incident light. The azimuthal angle of the detector is 0°. The radius, pitch, and wavelength are all 250 nm and the radius of a unit is 31 nm. The dielectric constant is 1.6 while that of the surroundings is 1.0. The polarizability for each unit is 5×10^3 nm^3. *Dashed line*–7 turns of the helix; *dotted line*–11 turns; *solid line*–15 turns.

after 15 turns of the helix. The coupled dipole approximation thus appears to be suitable for calculating CIDS from both discrete and continuous helical crystals.

VI. ROTATIONALLY AVERAGED HELICES

We use our results on appropriate polarizabilities for chiral particles to examine the CIDS dependence on the length of randomly dispersed species. Previous calculations on helices described by uniaxial polarizabilities showed that CIDS was relatively independent of length if the chiral parameters were less than the wavelength of light and more dependent on length when the parameters were on the order of the wavelength.[5,7] We have used triaxial polarizabilities to model helices with chiral parameters smaller than and equal to the wavelength and find that the CIDS dependence on length appears to be about the same in both cases. Approximately ten helical turns are required for convergence. Inclusion of dipolar interactions does not significantly affect the length dependence of CIDS; i.e., the thickness of the helix is not an important factor.

In calculating CIDS for comparison with experimental data from helical particles, the magnitudes of the chiral parameters (radius and pitch) are obviously important. We have studied the relevance of helical thickness (using triaxial polarizabilities) on the magnitude of the calculated CIDS and find slight variations when the chiral parameters are smaller than the wavelength of incident light. However, more significant differences are observed when the parameters are of the order of the wavelength. Figure 6 shows the CIDS of a single turn of a thick and thin continuous helix with dielectric constant 1.4. The calculations are done in vacuum for incident light with wavelength 600 nm. The radius and pitch of the helices are 400 nm and thicknesses of 127 and 16 nm are modeled using 20 spheres ($r = 63.6$) and 20 ellipsoids ($a = 63.6$ nm, $b = c = 8.0$ nm), respectively. It is clear from Fig. 6 that the calculated CIDS from these structures show some differences. It then appears that the thickness of the chiral structure is another parameter that is of importance in calculating CIDS quantitatively; this is particularly important for structures in which the chiral parameters are of the order of the wavelength.

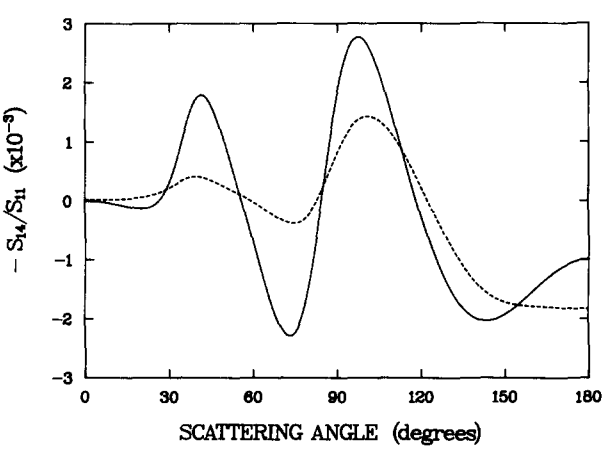

FIG. 6. CIDS from a rotationally averaged turn of a continuous helix in vacuum with radius and pitch of 400 nm and dielectric constant 1.4. The wavelength of incident light is 600 nm. *Solid line*–cylindrical thickness of 16 nm modeled by 20 ellipsoids ($a = 63.6$ nm, $b = c = 8.0$ nm) with $\alpha_t = 8.516 \times 10^2$ nm^3, $\alpha_n = \alpha_p = 6.618 \times 10^2$ nm^3; *dashed line*–cylindrical thickness of 127 nm modeled by 20 spheres with $\alpha = 4.540 \times 10^4$ nm^3.

VII. CONCLUSIONS

The coupled dipole approximation has been used to calculate the scattering matrix of chiral particles. The structures can be described by spherical dipoles or by a lesser number of appropriately oriented ellipsoidal dipoles. For the special case of a very thin chiral particle, e.g., a thin helix or flat helical ribbon, long prolate ellipsoidal dipoles, or flat oblate ellipsoidal dipoles can be used to simulate the geometry. The ellipsoidal polarizabilities that have to be used in all structures are triaxial polarizabilities calculated using the geometry of the ellipsoid and the appropriate dielectric constants. These polarizabilities have significant relative magnitudes along the three principal axes even when the ellipsoids are very thin. The CIDS calculated by this method shows quantitative differences from that calculated using uniaxial or biaxial polarizabilities.

Dipolar interactions are found to be unimportant in calculating CIDS of structures made up of appropriately oriented thin ellipsoids. The conditions for neglect of interactions are that each self-interaction tensor should be very nearly equal to the polarizability tensor of the ellipsoid and that the elements of the other interaction tensors should have magnitudes less than 10^{-2} of the largest values of the self-interaction tensors. This neglect of dipolar interactions leads to simplification in the calculation of CIDS from randomly distributed particles.

The CIDS from rotationally averaged helices has been calculated and found to converge after ten helical turns for chiral parameters which are equal to or less than the wavelength of light. The results also show that the thickness of the helix is a parameter which may be of importance in calculating CIDS quantitatively for comparison with experimental data.

We have also shown that the coupled dipole approximation can be used to calculate CIDS from one dimensional crystals composed of unit cells with chiral geometries. The geometries studied were continuous structures as well as structures made up of discrete subunits. In all cases, the CIDS was found to converge with an increasing number of unit cells. The coupled dipole approximation is thus found to be applicable to the calculation of CIDS from both oriented and randomly dispersed chiral species.

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