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AUTHOR(S) Shermila Brito Singham

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MASTER

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

LIGHT SCATTERING BY ORIENTED AND RANDOMLY DISPERSED CHIRAL PARTICLES

Shermila Brito Singham
Life Sciences Division, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545.

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ABSTRACT

The use of coupled dipoles in modelling light scattering by oriented and randomly dispersed chiral particles is examined in this paper. The chirality considered here is form chirality which results from macroscopic structural mirror asymmetry in the particle. For a chiral particle described by spherical dipoles, it is shown that large magnitude terms that contribute to the chiral matrix elements of an oriented particle do not contribute at all in the orientation average. This result will be used in future work to obtain a more efficient method of evaluating light scattering by randomly dispersed chiral particles.

The coupled dipole method[1] is known to be a good approximate technique for evaluating light scattering by arbitrarily shaped particles. In this method, an arbitrary particle is subdivided into units where each unit is small compared with the wavelength of light. Each unit is then assumed to behave like a spherical dipolar oscillator with its polarizability specified by its dimension and the bulk dielectric constant of the particle. The fields at the dipoles are determined by the incident field and interactions among all the dipoles in the collection. These resultant fields are obtained by solving, self-consistently, a set of linear, coupled equations and retardation effects are taken fully into account. The scattered field at the detector is then evaluated by summing the fields scattered by the dipolar oscillators.

For a set of N optically inactive dipoles, the field $\underline{E}_i$ at an oscillator i is determined by the incident field ($\underline{E}^o e^{i\underline{k}\cdot\underline{r}_i}$) as well as by the scattered fields from the other dipolar oscillators, i.e.,

$$\underline{E}_i = \underline{E}^o e^{i\underline{k}\cdot\underline{r}_i} + \sum_{i\neq j}^{N} [a_{ij}\, \hat{\alpha}_j \underline{E}_j + b_{ij}\, (\hat{\alpha}_j \underline{E}_j \cdot \underline{n}_{ji})\, \underline{n}_{ji}] \qquad (1)$$

where $a_{ij} = \frac{e^{ikr_{ij}}}{r_{ij}} (k^2 - \frac{1}{r_{ij}^2} + \frac{ik}{r_{ij}})$

and $b_{ij} = \frac{e^{ikr_{ij}}}{r_{ij}} (\frac{3}{r_{ij}^2} - k^2 - \frac{3ik}{r_{ij}})$.

k is the wavenumber of the radiation, r_{ij} is the distance and $\underline{n}_{ji}$ the unit vector from j to i. The explicit time dependence of the fields is omitted and only elastic light scattering is considered. Retardation effects are completely accounted for in this model. The electric dipole moment is given by $\underline{p}_j = \hat{\alpha}_j \underline{E}_j$, where $\underline{E}_j$ is the field at the scattering center and $\hat{\alpha}_j$ is, in general, a complex polarizability tensor. If the dipolar units are taken to be spherical, the polarizability of each unit (α) is a scalar.

The scattered field at the detector ($\underline{E}_d$) is the sum of the amplitudes of the far field contributions from the N spherical dipoles, i.e.,

$$\underline{E}_d = k^2 \frac{e^{ikr_d}}{r_d} (\hat{I} - \underline{n}_d \underline{n}_d)\, \alpha \sum_j^N e^{-ik\underline{n}_d\cdot\underline{r}_j}\, \underline{E}_j \qquad (2)$$

where r_d is the distance and n_d the unit direction of the detector from the origin. The amplitude scattering matrix elements[2] of the particle can be obtained by determining $\underline{E}_d$ for two orthogonal polarizations of the incident light. The incident light propagates in the positive z direction and the xz plane is chosen to be the scattering plane; the amplitude scattering matrix elements can be obtained from

$$S_1 = C\, E_y^y\,, \qquad S_2 = C\,[E_x^x \cos\theta - E_z^x \sin\theta],$$
$$S_3 = -C\,[E_x^y \cos\theta - E_z^y \sin\theta], \qquad S_4 = -C\, E_y^x \tag{3}$$

where, $C = \frac{-ikr}{e^{ik(r-z)}}$, and θ is the scattering angle. The scattered field components of $\mathbf{E}_d$ along the x, y and z axes are specified by $E_{x,y,z}$ and the superscript refers to the incident light which is linearly polarized in the x or y directions.

The elements of the 4 x 4 scattering matrix[2] are obtained by linear combinations of products of the amplitude scattering matrix elements. The products

$$\begin{aligned}
\mathrm{Re}\,[(S_2 - S_1)(S_3^* - S_4^*)] &= S_{13} - S_{31}\\
\mathrm{Im}\,[(S_2 - S_1)(S_3^* - S_4^*)] &= S_{24} + S_{42}\\
\mathrm{Re}\,[(S_2 + S_1)(S_3^* - S_4^*)] &= S_{23} - S_{32}\\
\mathrm{Im}\,[(S_2 + S_1)(S_3^* - S_4^*)] &= S_{14} + S_{41}
\end{aligned} \tag{4}$$

contain only the 2 x 2 off-block-diagonal matrix elements which are sensitive to chirality and will be referred to as chiral matrix elements. For a collection of randomly oriented particles, these products become $2S_{13}(=-2S_{31})$, $2S_{24}(=2S_{42})$, $2S_{23}(=-2S_{32})$ and $2S_{14}(=2S_{41})$.[2]

We write equation (1) in the form

$$\mathbf{E}_i = \mathbf{E}_i^o + \sum_{\substack{j\\ i\neq j}} \mathbf{E}_j^i + \sum_{\substack{jk\\ i\neq j\neq k\\ j<k}} \mathbf{E}_{jk}^i + \sum_{\substack{jk\ell\\ i\neq j\neq k\neq \ell\\ j<k<\ell}} \mathbf{E}_{jk\ell}^i + \ldots \tag{5}$$

where $\mathbf{E}_i^o$ is the incident field at dipole i ($= \mathbf{E}^o e^{i\mathbf{k}\cdot\mathbf{r}_i}$), $\mathbf{E}_j^i$ is the field at i due to interactions (to all orders) with only the j^{th} dipole, $\mathbf{E}_{jk}^i$ is the field at i due to interactions involving both the j^{th} and k^{th} dipoles and the other fields in the series are similarly defined. The summations are over the total number of dipoles, i.e., N. In this series, the field at a given dipole is determined by the incident field and the fields due to many center interactions with the other dipoles which are used to describe the particle. Equation (5) is a finite series in which the last term is a summation over the field at i due to interactions with the remaining (N-1) dipoles. As the interactions are retained to all orders, equation (5) is simply equation (1) with the interaction fields specified in terms of the dipolar centers involved.

The scattered field at the detector can also be written in terms of a series over many center terms and the product $(S_2 - S_1)(S_3^* - S_4^*)$ can then be written as

$$
\begin{aligned}
(S_2 - S_1)(S_3^* - S_4^*) = k^6 \alpha\alpha^* \Big[& \sum_{\substack{ijk\\ j\neq k}} E^i E_k^{jb} + \sum_{\substack{ijk\ell\\ j\neq k\neq \ell\\ k<\ell}} E^i E_{k\ell}^{jb} + \ldots \\
& + \sum_{\substack{ijk\ell\\ i\neq j\ k\neq \ell}} E_j^{ia} E_\ell^{kb} + \sum_{\substack{ijk\ell m\\ k\neq \ell\neq m\\ i\neq j\ \ell<m}} E_j^{ia} E_{\ell m}^{kb} + \ldots \\
& + \sum_{\substack{ijk\ell m\\ i\neq j\neq k\\ \ell\neq m\ j<k}} E_{jk}^{ia} E_m^{\ell b} + \sum_{\substack{ijk\ell mn\\ i\neq j\neq k\\ \ell\neq m\neq n\\ j<k\ m<n}} E_{jk}^{ia} E_{mn}^{\ell b} + \ldots \Big]
\end{aligned} \tag{6}
$$

$$
\begin{aligned}
\text{with}\quad E^i &= e^{-ik\underline{n}_d\cdot\underline{r}_i} e^{ikz_i} (\cos\theta - 1) \\
E_j^{ia} &= e^{-ik\underline{n}_d\cdot\underline{r}_i} [E_{jx}^{ix} \cos\theta - E_{jz}^{ix} \sin\theta - E_{jy}^{iy}] \\
E_j^{ib} &= e^{ik\underline{n}_d\cdot\underline{r}_i} [-E_{jx}^{iy*} \cos\theta + E_{jz}^{iy*} \sin\theta + E_{jy}^{ix*}]
\end{aligned} \tag{7}
$$

and E_{jk}^{ia}, E_{jk}^{ib}, ... defined similarly. The other product $(S_2 + S_1)(S_3^* - S_4^*)$ is given by a similar series with a diffrrent linear combination for the E^i and E^{ia} terms, i.e.,

$$
\begin{aligned}
E^i &= e^{-ik\underline{n}_d\cdot\underline{r}_i} e^{ikz_i} (\cos\theta + 1) \\
E_j^{ia} &= e^{-ik\underline{n}_d\cdot\underline{r}_i} [E_{jx}^{ix} \cos\theta - E_{jz}^{ix} \sin\theta + E_{jy}^{iy}]
\end{aligned} \tag{8}
$$

and so on.

For a collection of randomly oriented particles, the orientation averages of the products $(S_2 - S_1)(S_3^* - S_4^*)$ and $(S_2 + S_1)(S_3^* - S_4^*)$ are required. These averages are zero unless the particle is chiral. The orientation averages are obtained by numerically summing the magnitudes of the products over a large number of orientations until convergence is reached or, equivalently, by using an analytic averaging method.

The orientation average of $(S_2 - S_1)(S_3^* - S_4^*)$ can also be obtained from the sum of the orientation averages of the field products in the series given in equation (6). That is, the average can be obtained by summing the integrals over all space of each of the field products $E^i E_k^{jb}$, $E^i E_{k\ell}^{jb}$, etc., in equation (6). Some of these field products become <u>identically zero</u> when integrated over all space. This is found to be the case for those products which derive from dipolar centers which do not form a chiral structure.

The first term in the series in equation (6), $E^i E_k^{jb}$, is derived from fields involving at most three dipolar centers. For a given orientation of the structure described by the three dipoles, its mirror image in the scattering plane exists if all possible orientations of the particle are allowed, i.e., the particle can be rotated to another orientation such that the three dipoles now form the mirror image of the original three dipole structure. This is always possible when the subunits are not optically active. The y coordinates of the three dipoles change sign while the x and z coordinates are unchanged in the mirror image in the scattering plane (xz). The term $e^{-ik\mathbf{n}_d \cdot \mathbf{r}_i}$ is unchanged on reflection in the scattering plane because $\mathbf{n}_d$ lies in this plane; E^i is then the same for the original and reflected structures. The field E_j^{ia} is also unchanged on reflection in the scattering plane because E_{jx}^{ix}, E_{jz}^{ix} and E_{jy}^{iy} are unaffected on changing the sign of the y axis. However, E_j^{ib} changes sign on reflection because E_{jx}^{iy}, E_{jz}^{iy} and E_{jy}^{ix} change sign with reflection of i,j,k in the xz plane. The product $E^i E_k^{jb}$ then has opposite signs for a pair of mirror symmetric structures and goes to <u>zero</u> when it is averaged over all space because the mirror symmetric pair exists in the orientation average.

The products $E^i E_{k\ell}^{jb}$ and $E_j^{ia} E_\ell^{kb}$ involve two, three or four dipolar centers. The terms involving two or three dipolar centers will again average to zero because the mirror images of the structures in the scattering plane exist in the orientation average. The products involving four dipolar centers will also average to zero if the four dipoles do not form a chiral structure. However, if the four dipoles do form a chiral arrangement, the mirror image of the structure is not present in the orientation average and the field products will be non-zero when averaged over all space. For the same reasons, all other field products in the series described in equation (6) will also average to zero unless the dipolar centers involved in the products form a chiral structure. The same result is true for $(S_2 + S_1)(S_3^* - S_4^*)$ because the same symmetry considerations hold and the only difference is that E^i and the E^{ia} terms are different linear combinations from those in $(S_2 - S_1)(S_3^* - S_4^*)$.

The large difference in the magnitudes of the 2 x 2 off-block-diagonal matrix elements for oriented and orientationally averaged chiral structures is now evident. Many of the field products which contribute to the matrix elements of the oriented structure, do not contribute at all in the orientation average. In particular, the leading term in the series given in equation (6) is of large magnitude and expected to be a major component of the 2 x 2 off-block-diagonal matrix elements of oriented particles and this term goes to zero in the orientation average.

In order to illustrate this difference in oriented and orientationally averaged scattering, we describe a model calculation for a simple chiral structure. Four spherical dipoles which form a chiral structure are chosen as a model and the dipoles form one third of a turn of a helix with a radius of 100 nm and a pitch of 200 nm. The (x,y,z) coordinates of the four dipoles in the oriented structure are (100, 0, 0), (86.6, 50, 16.67), (50, 86.6, 33.33) and (0, 100, 50) and the polarizability of each dipole is 3×10^3 nm^3. The incident light has a wavelength of 600 nm and is propagating along the positive z direction.

The fields corresponding to interactions among specific dipolar centers were evaluated by obtaining the self-consistently coupled fields for each group of dipoles. Thus, the field at dipole i due to j was obtained by evaluating the final field at i in the 'particle' described by i and j and subtracting the incident field at i (i.e., E_i^o). In a similar manner, the field at i due to all interactions with j and k was obtained by finding the final field at i from the self-consistent solution for interactions with j and k and subtracting the incident field at i and the fields at i due to two center interactions with j and two center interactions with k. The fields due to four center interactions were obtained similarly.

Figures 1 and 2 show the angular distributions of the real and imaginary parts of $(S_2 \pm S_1)(S_3^* - S_4^*)$ for the oriented particle composed of four spherical dipolar units. The solid lines are the total calculated values of the chiral matrix elements while the dashed lines are two and three center field products and the chain-dashed lines are the four center field products. From the results, it is evident that the two and three center field products dominate and that the four center terms are an extremely small component at most angles of the angular distributions for the oriented particle.

The cancellation of the field products that do not contribute to the orientation averages of the chiral matrix elements is a source of the slow convergence that has been observed for these elements when calculated by summing the magnitudes over a large number of orientations. The chiral matrix elements when calculated this way are contained as small differences between large magnitude field products. When the orientation averages of the chiral matrix elements for a simple model were calculated using only the field products that survive the averaging, convergence was rapidly achieved. If this feature, i.e., retention of only the field products that contribute to the average, can be efficiently incorporated into an orientation averaging method for arbitrarily shaped chiral particles, it is probable that the computational difficulties in calculating the chiral matrix elements will be significantly improved.

References:

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FIGURE CAPTIONS

Figure 1.

Angular distributions of two chiral matrix elements of a helical structure. A third of a turn of a helix with a radius of 100 nm and a pitch of 200 nm is modelled by four spherical dipoles each with a polarizability of 3 x 10^3 nm^3. The incident light is in the z direction and has a wavelength of 600 nm. The xz plane is the scattering plane. (a) Solid line - angular distribution of the real part of $(S_2 - S_1)(S_3^* - S_4^*)$ for the oriented particle. Dashed line - two and three center field products. Chain-dashed line - four center products. (b) Solid line - angular distribution of the imaginary part of $(S_2 - S_1)(S_3^* - S_4^*)$ for the oriented particle. Dashed line - two and three center field products. Chain-dashed line - four center field products.

Figure 2.

Two chiral matrix elements for the helical particle described in the caption for Figure 1. (a) Solid line - angular distribution of the real part of $(S_2 + S_1)(S_3^* - S_4^*)$ for the oriented particle. Dashed line - two and three center field products. Chain-dashed line - four center field products. (b) Solid line - angular distribution of the imaginary part of $(S_2 + S_1)(S_3^* - S_4^*)$ for the oriented particle. Dashed line - two and three center field products. Chain-dashed line - four center field products.

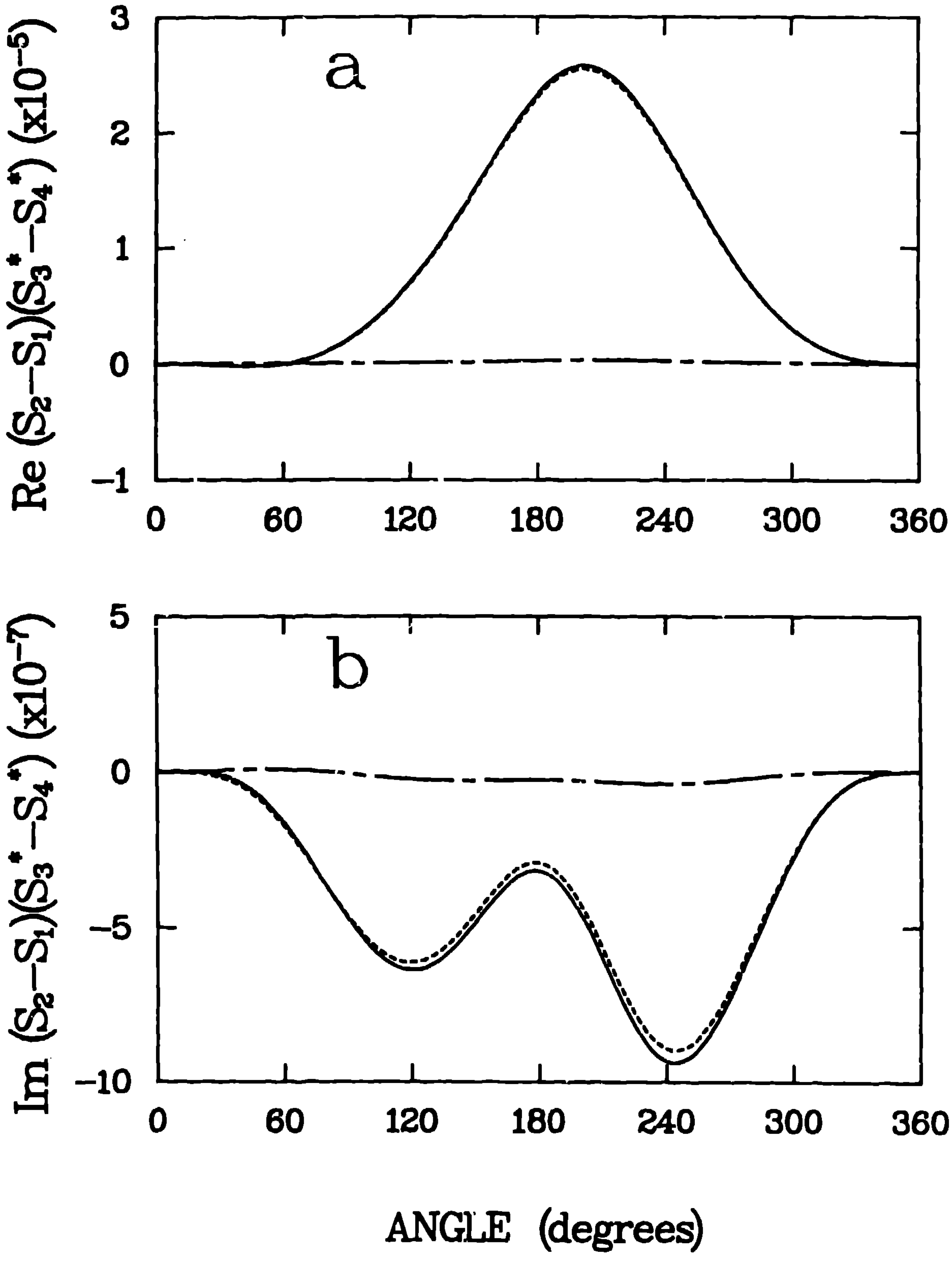
a
Re $(S_2-S_1)(S_3^*-S_4^*)$ (x10^{-5})
3
2
1
0
−1
0
60
120
180
240
300
360
b
Im $(S_2-S_1)(S_3^*-S_4^*)$ (x10^{-7})
5
0
−5
−10
0
60
120
180
240
300
360
ANGLE (degrees)

Figure 1.

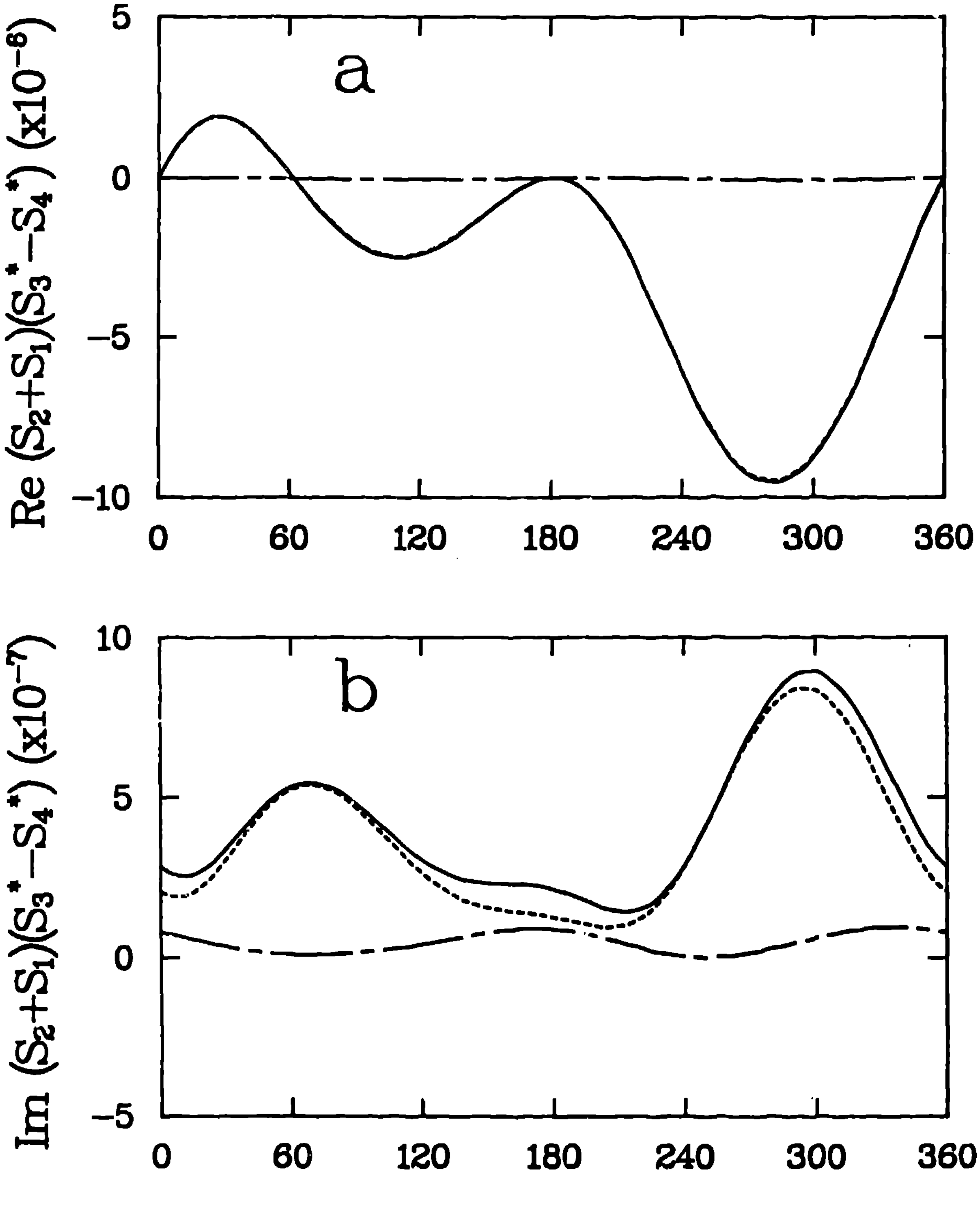
a
b
Re $(S_2+S_1)(S_3^*-S_4^*)$ (x10^{-6})
Im $(S_2+S_1)(S_3^*-S_4^*)$ (x10^{-7})
5
0
−5
−10
10
5
0
−5
0
60
120
180
240
300
360
ANGLE (degrees)

Figure 2.