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Conductivity calculation for a two-phase composite with spheroidal inclusions

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Abstract. An analytical solution is presented for the electrical conductivity of a material composed of spheroidal particles embedded in a matrix. The particles are arranged on a simple-cubic lattice with their axes of rotation aligned with one of the lattice vectors. In this arrangement, there are two independent components of the conductivity tensor; one for the electric field applied parallel to the rotation axis of the spheroids and one for the electric field applied perpendicular to this axis. Both components are calculated using a method in which each particle is replaced by a singular multipole source which gives rise to the electric potential in the interstitial domain. This potential can readily be written as a sum of spherical harmonics but, in order to treat spheroidal particles, it is necessary to transform the solution into one in terms of spheroidal harmonics. The calculation of the matrix elements required for this transformation is described and the solution for each component of the conductivity tensor is given in analytic form. Results are presented for various values of particle aspect ratio, volume fraction and conductivity ratio between the two phases. Very good agreement is observed with experimental data and the results of an independent calculation.

1. Introduction

Electrically conducting composite materials have a variety of important applications such as electrostatic shielding of electronic components and electrical stress relief in high-voltage devices. For these applications, the composite is typically formed by adding conducting particles to a polymer with low conductivity. This results in a material which is both electrically conducting and mechanically similar to the polymer. In order to design composite materials for specific applications, it is useful to be able to model the properties theoretically, based on knowledge of the constituent phases and their relative distribution.

The design of a composite material is usually a compromise between the desire to raise the conductivity as much as possible, and the need to retain flexibility so that the material can be moulded or extruded. Types of filler commonly used in practice are carbon-black particles, carbon fibres and metal flakes or fibres. Adding increasing amounts of filler has the effect of increasing the conductivity of the composite, but consequently it also becomes less flexible. At a certain threshold value of volume fraction of the filler, the particles or fibres are sufficiently close-packed to form an unbroken conducting pathway through the composite, and the conductivity of the material increases sharply. The threshold at which this occurs is known as the percolation threshold. A way of maximizing the material conductivity while retaining flexibility would be to control the arrangement of the filler particles such that percolating networks form for relatively low volume fractions. This is an ideal which is difficult to achieve in practice.

An early model of the bulk conductivity of a composite material was devised by Maxwell [1], who assumed that the particles were well spaced in the matrix and did not interact with one another. Using this assumption, each particle acts as a dipole source and the following result is obtained

$$\sigma^* = 1 - 3f\frac{\alpha - 1}{\alpha + 2} + \mathcal{O}(f^2) \tag{1}$$

which is independent of the size and spatial distribution of the particles. In (1), σ^* is the ratio of the bulk conductivity to that of the interstitial matrix, σ/σ_i, f is the volume fraction of the particle phase and α is the ratio σ_p/σ_i, where σ_p is the conductivity of the particles. Equation (1) holds for f less than about 0.3. In order to determine σ^* for larger values of f, higher-order terms must be included in the calculation. The higher-order terms typically depend on the size, shape and distribution of the particles. In this paper, a method is presented for calculating σ^* up to order $f^{14/3}$ for spheroidal particles arranged on a simple-cubic lattice. Spheroidal geometry has the advantage of being representative of some useful limiting cases, approximating the behaviour of rods or fibres and discs. There is good agreement with experimental data and the results of an independent calculation, confirming that the result is valid for volume fractions up to the limit in which the particles nearly touch.

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2. Lattice model

A simple model of a composite material is one in which the filler particles are arranged on the sites of a regular lattice. Due to the periodic nature of the lattice, an infinite number of particles is treated. This is a classical problem of theoretical physics and has been considered by many authors using a variety of methods. In one approach, Zuzovsky and Brenner [2] replaced the particles by a singular multipole source distribution located at their centres and determined a solution for a simple-cubic lattice of spheres. Simple-cubic, body-centred-cubic (bcc) and face-centred-cubic (fcc) lattices of spheres have been treated by McPhedran, McKenzie and Derrick [3, 4] by extending Rayleigh's method [5] to include the effects of multipoles of arbitrarily high order. Recently, the lattice model has been generalized in a number of ways. Sangani and Yao [6] have reduced the ordering in the microstructure by distributing N spherical particles in a cubic unit cell and replicating it to form an infinite simple-cubic lattice with a quasi-random distribution of particles. An orthogonal lattice of aligned spheroids has been treated by Kushch [7], with some anisotropy in the material of the matrix and the inclusions permitted. These methods are analytical in nature and have the advantage of short computation times. In this work, the multipole expansion method of Zuzovsky and Brenner is adapted and applied to a simple-cubic lattice of aligned spheroidal particles. Each particle is replaced by a singular multipole source which gives rise to the electric potential in the interstitial domain. The potential can readily be written in terms of spherical harmonics but, in order to treat spheroidal particles, it is helpful to transform the solution into one in terms of spheroidal harmonics so that the continuity conditions at the particle surface can be applied in a straightforward manner. The matrix elements required for this transformation are calculated and the coefficients in the expansion determined by solving the resulting infinite set of linear algebraic equations. It can be shown by using Green's theorem that only the first coefficient in the expansion is required to calculate the bulk conductivity of the material. This coefficient is determined by solving a truncated equation set and the solution for each component of the conductivity tensor is given in analytic form. There is no restriction on the relative conductivities of the two phases; the conductivity of the filler particles may be greater or less than that of the matrix.

This calculation differs from that for the lattice of spheroids given in [7] in the way that the infinite number of particles is accounted for. In [7], an addition theorem derived in the Russian literature is used to sum the effects of particles arranged on a triple-periodic lattice. The method adopted here, of representing each particle by a multipole expansion and transforming the solution to deal with spheroidal geometry, is currently restricted to the simple-cubic array but lends itself to extension to more general cases in which distributions of particle orientation, size and shape can be considered.

The accuracy of this method depends on the number of harmonics used in the expansion for the potential. For low volume fractions, and/or a low conductivity ratio between the phases, only a few terms are required to describe the field accurately everywhere in the material. On the other hand, when there is high contrast between the conductivity of the phases, and when the particles approach one another closely, higher-order terms are required. In principle, the method given here can be made as accurate as desired by including terms of sufficiently high order. The example solution given later is of relatively low order, however, so there is some loss of accuracy in certain cases.

The analytical approaches mentioned may be contrasted with a purely numerical technique in which the composite is reduced to an effective impedance network [8]. This alternative scheme has the advantage of simplicity; the partial differential equation governing the electric potential is reduced by discretization to an equivalent of Kirchhoff's Laws for a square or cubic conductance network (square for a two-dimensional (2D) array and cubic for three dimensions). The accuracy of results obtained in this way depends on the density of the network used to treat a single unit cell, and is limited only by the available computing power and memory.

Another approach worthy of mention is the boundary integral equation method. In [9], boundary integral equations are derived from Green's theorem and are solved for the local field. Particular care is taken with the numerical evaluation of the field in order to overcome the loss of accuracy associated with traditional boundary-value methods when the volume fraction is large. This is a powerful method with the ability to deal with particles of arbitrary shape, possibly fused together, as well as any type of lattice. The technique can also be applied to treat a random distribution of inclusions.

As well as being suitable for calculating electrical conductivity, these methods are equally valid for the calculation of a number of other physical properties, for example, thermal conductivity, magnetic permeability or dielectric constant, due to mathematical equivalence in the formulations.

3. Formulation

3.1. Constitutive relation

Consider a medium composed of spheroidal particles of conductivity σ_p embedded in a matrix which fills the interstices and has conductivity σ_i. The particles and matrix are assumed to be homogeneous. The aim is to determine $\overline{\overline{\sigma}} = \{\sigma_{ij}\}$, the second-order tensor describing the effective conductivity of the composite. This is done without loss of generality by solving for the electric potential in the medium when an electric field of unit magnitude is applied. As a consequence of the linearity of this system, there exists a linear macroscopic constitutive relation between the macroscopic current density and electric field

$$\langle \boldsymbol{J} \rangle = \overline{\overline{\sigma}} \cdot \langle \boldsymbol{E} \rangle. \tag{2}$$

For a lattice of spheroids oriented like the one shown in figure 1, $\overline{\overline{\sigma}}$ has only two independent components

$$\overline{\overline{\sigma}} = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}. \tag{3}$$

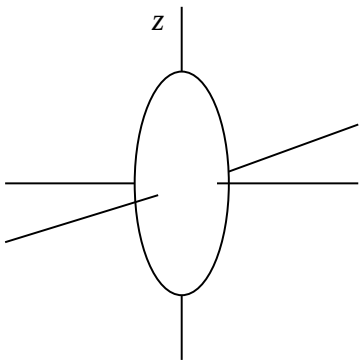

Figure 1. Prolate spheroid with axis of rotation parallel to z.

The problem of determining $\overline{\overline{\sigma}}$ can, therefore, be reduced to two similar scalar problems in which σ_{xx} and σ_{zz} are determined for a unit electric field applied parallel to x and then parallel to z

$$\langle J_x \rangle = \sigma_{xx} \langle E_x \rangle \tag{4}$$

$$\langle J_z \rangle = \sigma_{zz} \langle E_z \rangle. \tag{5}$$

3.2. Laplacian problem

The basic equations governing steady-state flow are the relation

$$\boldsymbol{J}_m(\boldsymbol{r}) = -\sigma_m \nabla \Phi_m(\boldsymbol{r}) \tag{6}$$

and the zero divergence of the current density

$$\nabla \cdot \boldsymbol{J}_m(\boldsymbol{r}) = 0 \tag{7}$$

where $\boldsymbol{J}_m$ is the local current density vector, Φ_m is the local electric potential at $\boldsymbol{r}$ and $m = i$ or p denotes values in the interstitial or particle domains, respectively. Equations (6) and (7) combine to show that the potential obeys the Laplace equation

$$\nabla^2 \Phi_m(\boldsymbol{r}) = 0 \tag{8}$$

everywhere.

If a uniform electric field is applied to the material, it gives rise to a potential distribution with average gradient $\langle \boldsymbol{E} \rangle$. The potential at any point in the composite can be expressed

$$\Phi_m(\boldsymbol{r}) = \breve{\Phi}(\boldsymbol{r}) - \boldsymbol{r} \cdot \langle \boldsymbol{E} \rangle \tag{9}$$

where $\breve{\Phi}(\boldsymbol{r})$ is a spatially periodic function

$$\breve{\Phi}(\boldsymbol{r}) = \breve{\Phi}(\boldsymbol{r} + \boldsymbol{r}_n) \tag{10}$$

and particles are located at lattice points defined by the following set of position vectors

$$\boldsymbol{r}_n = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2 + n_3 \boldsymbol{a}_3 \qquad n_1, n_2, n_3 = 0, 1, 2, \ldots \tag{11}$$

with $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$ a triad of basic lattice vectors characterizing the unit cell. This system of equations possesses a unique solution if either the macroscopic electric field $\langle \boldsymbol{E} \rangle$ or the macroscopic current density $\langle \boldsymbol{J} \rangle$ is prescribed.

3.3. Multipole expansion

Equations (6)–(10) can be solved by analytically continuing the interstitial fields into the interior of the space occupied by the particles and replacing the particles themselves by singular multipole source distributions located at their centres [10]. The sum over all lattice sites is achieved using Fourier analysis, following Hasimoto [11]. The details of this development have been given previously [12] so only key results are given here. This approach is distinct from that of Kushch [7], in which the potential due to the infinite lattice of particles is calculated by means of an addition theorem established in Russian literature.

The periodic potential $\breve{\Phi}$ can be expressed as follows [2, 11]

$$\breve{\Phi} = \Phi_0 - \frac{1}{4\pi} \sum_{j=1}^{\infty} \nabla_{(2j-1)} S(\cdot)^{2j-1} \overline{B}_{(2j)} \cdot \langle \boldsymbol{E} \rangle \tag{12}$$

where Φ_0 is a constant, $\nabla_{(j)}$ is the jth gradient polyadic operator, $(\cdot)^j$ is a j-fold inner product, $\overline{B}_{(j)}$ is a constant tensor of rank j and

$$S = \frac{1}{\pi \tau_0} {\sum_{\boldsymbol{m}}}' \frac{\mathrm{e}^{-2\pi \mathrm{i} \boldsymbol{k}_m \cdot \boldsymbol{r}}}{k_m^2}. \tag{13}$$

In (13), τ_0 is the volume of the unit cell and

$$\boldsymbol{k}_m = \frac{1}{\tau_0}(m_1 \boldsymbol{b}_1 + m_2 \boldsymbol{b}_2 + m_3 \boldsymbol{b}_3)$$

$$m_1, m_2, m_3 = 0, \pm 1, \pm 2, \ldots \tag{14}$$

with $(\boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ the basic vectors characterizing the unit cell of the reciprocal lattice. The sum over $\boldsymbol{m}$ excludes the value $\boldsymbol{m} = 0$, as indicated by the prime. The function S is the periodic, singular solution of Laplace's equation

$$\nabla^2 S = 4\pi \left[\frac{1}{\tau_0} - \sum_{n} \delta(\boldsymbol{r} - \boldsymbol{r}_n) \right]. \tag{15}$$

In principle, one can proceed to solve in general terms with the lattice described in (11), but here matters will be simplified by treating the simple-cubic lattice.

The polyadic operator in (12), $\nabla_{(j)}$, regarded as a Cartesian tensor, is completely symmetric in all its indices. This same symmetry property may be ascribed to $\overline{B}_{(j)}$ and, further, the Cartesian tensor $\overline{B}_{(j)}$ possesses symmetry properties based on the fact that its components must remain invariant under group operations appropriate to the symmetry of the cube. It is found that $\overline{B}_{(2)}$ possesses only one independent component and $\overline{B}_{(4)}$ only two, for example. Continuing in this manner it can be established that (12) may be written [2]

$$\breve{\Phi} = \Phi_0 - \frac{1}{4\pi} B \nabla S \cdot \langle \boldsymbol{E} \rangle \tag{16}$$

with B the partial differential operator

$$B = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} b_{mnp} \frac{\partial^{2(m+n+p)}}{\partial x^{2m} \partial y^{2n} \partial z^{2p}}. \tag{17}$$

The b_{mnp} are scalar coefficients to be determined by applying the continuity conditions at the particle–matrix interface. As shown in section 4, the bulk conductivity can be calculated from b_{000}.

In order to apply the continuity conditions at the particle surface in a straightforward way, (16) will be written in terms of spheroidal harmonics. An important step in this process is to use an expansion of S in spherical harmonics to write (16) first as a sum of spherical harmonics. Expanding about $r = 0$ [11]

$$S = \frac{1}{r} - c + \frac{2\pi r^2}{3\tau_0} + \sum_{n=2}^{\infty} \sum_{m=0}^{m \leqslant n/2} a_{nm} r^{2n} P_{2n}^{4m}(\mu) \cos 4m\phi \quad (18)$$

in which c is a constant and x, y and z are Cartesian coordinates parallel to the axes of cubic symmetry

$$x = r \sin\theta \cos\phi \qquad y = r \sin\theta \sin\phi \qquad z = r \cos\theta \quad (19)$$

and $\mu = \cos\theta$. Combining (9), (16) and (19) gives, for an electric field applied parallel to the z axis

$$\Phi_i = \Phi_0 - \langle E \rangle \left(\frac{1}{4\pi} B \frac{\partial S}{\partial z} + r \cos\theta \right). \quad (20)$$

The Cartesian derivatives of S which appear in (20) may be evaluated by transforming to derivatives with respect to r, μ and ϕ using the following relations

$$\begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} = \begin{pmatrix} \sqrt{1-\mu^2}\cos\phi & -\frac{1}{r}\mu\sqrt{1-\mu^2}\cos\phi & -\frac{\sin\phi}{r\sqrt{1-\mu^2}} \\ \sqrt{1-\mu^2}\sin\phi & -\frac{1}{r}\mu\sqrt{1-\mu^2}\sin\phi & \frac{\cos\phi}{r\sqrt{1-\mu^2}} \\ \mu & \frac{1}{r}(1-\mu^2) & 0 \end{pmatrix} \times \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \mu} \\ \frac{\partial}{\partial \phi} \end{pmatrix}$$

and then using the relations between contiguous Legendre functions given in [13, section 3.8]. Taking derivatives of S gives, to order r^7

$$\begin{aligned} \Phi_i = \Phi_0 + \langle E \rangle r P_1 - \frac{\langle E \rangle}{4\pi} \Bigg\{ & \frac{b_{000}}{r^2} \Bigg[- P_1 + \frac{4\pi r^3}{3\tau_0} P_1 \\ & + 4a_{20} r^5 P_3 + 6a_{30} r^7 P_5 + 10 a_{31} r^7 P_5^4 \cos 4\phi + \mathcal{O}(r^9) \Bigg] \\ & + \frac{b_{001}}{r^4} [-6P_3 + 24 a_{20} r^5 P_1 + 120 a_{30} r^7 P_3 + \mathcal{O}(r^9)] \\ & + \frac{b_{110}}{r^6} [-15 P_5 + P_5^4 \cos 4\phi + 5130 a_{30} r^7 P_1 + \mathcal{O}(r^9)] \\ & + \frac{b_{002}}{r^6} [-120 P_5 + 720 a_{30} r^7 P_1 + \mathcal{O}(r^9)] + \mathcal{O}(r^9) \Bigg\}. \end{aligned} \quad (21)$$

In (21), the argument of the Legendre functions is μ and the relation [14]

$$a_{30}/a_{31} = -360 \quad (22)$$

has been used. Further, an algebraic error in Zuzovsky and Brenner's paper [2, equation (59)], has been corrected.

3.4. Harmonic expansion

In the spheroidal coordinate system, spheroidal surfaces are surfaces of constant ξ. The polar angle is related to η and the azimuthal angle is ϕ. In general, harmonic solutions of Laplace's equation in a spheroidal system take the form of combinations of Legendre functions of degree n and order m where n and m are integers such that $m = 0, \ldots, n$. For a simple-cubic lattice of spheroids whose axes of rotation (parallel to z) coincide with one of the lattice vectors, the azimuthal symmetry dictates that the order of the Legendre functions must be an integral multiple of four. If the electric field is also applied parallel to this axis, the potential Φ is odd in the polar variable and consequently, the degree of the Legendre functions is odd. In the case of a prolate spheroid, the potential in the interstitial domain can be written

$$\begin{aligned} \Phi_i = \Phi_0 + \langle E \rangle \sum_{n=1}^{\infty} \sum_{m=0}^{m<n/2} c_{nm} [& P_{2n-1}^{4m}(\xi) P_{2n-1}^{4m}(\eta) \\ & + \mathcal{L}_{2n-1}^{4m} Q_{2n-1}^{4m}(\xi) P_{2n-1}^{4m}(\eta)] \cos 4m\phi \end{aligned} \quad (23)$$

where

$$\mathcal{L}_s^t = \frac{1-\alpha}{\alpha[Q_s^t(\xi_0)/P_s^t(\xi_0)] - [Q_s^t(\xi_0)'/P_s^t(\xi_0)']}. \quad (24)$$

In these equations, P_s^t and Q_s^t are Legendre functions of the first and second kinds, respectively. The c_{nm} are unknown coefficients. The coefficients $\mathcal{L}_s^t$ have been determined by applying the conditions that the tangential electric field and normal current density are continuous at the particle–matrix interface. Coefficients in an expansion for Φ_p are eliminated to yield (23). The expansion for Φ_p contains only growing harmonics, which are of the form $P_{2n-1}^{4m}(\xi) P_{2n-1}^{4m}(\eta)$, since the potential in the particle interior is finite at its centre. The coordinate ξ_0 denotes the surface of the particle and the prime indicates the derivative normal to the surface, i.e.

$$Q_s^t(\xi_0)' \equiv \left. \frac{\mathrm{d}Q_s^t(\xi)}{\mathrm{d}\xi} \right|_{\xi=\xi_0}.$$

For an electric field applied perpendicular to the axis of rotation of the spheroids, the potential in the interstitial domain takes the form

$$\begin{aligned} \Phi_i = \Phi_0 + \langle E \rangle \sum_{n=1}^{\infty} \sum_{m=1}^{n} c_{nm} [& P_{2n-1}^{2m-1}(\xi) P_{2n-1}^{2m-1}(\eta) \\ & + \mathcal{L}_{2n-1}^{2m-1} Q_{2n-1}^{2m-1}(\xi) P_{2n-1}^{2m-1}(\eta)] \sin(2m-1)\phi. \end{aligned} \quad (25)$$

The symmetry is now such that the order of the Legendre functions based on the local spheroidal coordinate system is odd, as well as the degree.

The solution for oblate spheroids can be obtained directly from that for prolate spheroids by formally replacing ξ with $\mathrm{i}\xi$ and d with $-\mathrm{i}d$ in (23) and (25), where $2d$ is the distance between the foci of the elliptic cross section.

4. Solution

As shown elsewhere [2, 12], the bulk conductivity can be determined from the constant tensor of rank 2, $\overline{B}_{(2)}$, which appears in the multipole expansion for the interstitial

potential, equation (12). In the following relation, $\overline{\overline{I}}$ is the unit tensor of rank 2 and $\overline{\overline{\sigma}}^*$ is the normalized bulk conductivity $\overline{\overline{\sigma}}/\sigma_i$

$$\overline{\overline{\sigma}}^* = \overline{\overline{I}} - \frac{\overline{B}_{(2)}}{\tau_0}. \tag{26}$$

For a lattice of spheroids whose axes of rotation are aligned with one of the lattice vectors, $\hat{z}$

$$\overline{B}_{(2)} = \begin{pmatrix} B_{xx} & 0 & 0 \\ 0 & B_{xx} & 0 \\ 0 & 0 & B_{zz} \end{pmatrix}$$

and (26) reduces to

$$\sigma^*_{jj} = 1 - \frac{B_{jj}}{\tau_0} \tag{27}$$

with $j = x$ or z. From (17), $B_{jj} = b_{000}$ [2] and we have

$$\sigma^* = 1 - \frac{b_{000}}{\tau_0}. \tag{28}$$

Note that the value of b_{000} (and hence σ^*) depends on the direction in which the electric field is applied.

In order to solve for the coefficients b_{mnp} defined in (17) and hence determine the bulk conductivity using equation (28), it is necessary to write (20) in terms of spheroidal harmonics. The growing and decaying terms can then be matched with those in (23) and (25) and c_{nm} can be eliminated in each case to give a set of linear equations which can be solved for b_{mnp}. This can be achieved by transforming the spherical harmonics in (21) into spheroidal harmonics by means of appropriate transformation relationships. The way in which this is done is described in the following two sections.

4.1. σ^*_{zz}

As established in [12], the following relationships can be employed in transforming between spherical and spheroidal coordinate systems in which the polar axes coincide (see figure 2). For the growing harmonics, if s and t are both even, or s and t both odd

$$R^s P^t_s(\mu) = \sum_{j=0}^{(s-t)/2} A^t_{s,t+2j} P^t_{t+2j}(\xi) P^t_{t+2j}(\eta). \tag{29}$$

The inverse relationship is

$$P^t_s(\xi) P^t_s(\eta) = \sum_{j=0}^{(s-t)/2} \alpha^t_{s,t+2j} R^{t+2j} P^t_{t+2j}(\mu). \tag{30}$$

The coordinate R is the radial coordinate scaled with the distance between the centre of the spheroid and one of its foci, d, such that $R = r/d$. If s is even and t is odd, or s odd and t even

$$R^s P^t_s(\mu) = \sum_{j=0}^{(s-t-1)/2} A^t_{s,t+1+2j} P^t_{t+1+2j}(\xi) P^t_{t+1+2j}(\eta) \tag{31}$$

with

$$P^t_s(\xi) P^t_s(\eta) = \sum_{j=0}^{(s-t-1)/2} \alpha^t_{s,t+1+2j} R^{t+1+2j} P^t_{t+1+2j}(\mu). \tag{32}$$

For each order, t, the coefficients α^t_{su} and A^t_{su} form a lower diagonal checkerboard matrix. The growing spherical harmonics can thus be represented as a finite series of growing spheroidal harmonics, and *vice versa*. For the decaying harmonics

$$R^{-(s+1)} P^t_s(\mu) = \sum_{j=0}^{\infty} B^t_{s,s+2j} Q^t_{s+2j}(\xi) P^t_{s+2j}(\eta) \tag{33}$$

and the inverse relationship is

$$Q^t_s(\xi) P^t_s(\eta) = \sum_{j=0}^{\infty} \beta^t_{s,s+2j} R^{-(s+1+2j)} P^t_{s+2j}(\mu). \tag{34}$$

In this case, the coefficients β^t_{su} and B^t_{su} form an upper diagonal checkerboard matrix for each order. This means that the decaying spherical harmonics are represented as an infinite series of decaying spheroidal harmonics, and *vice versa*. The following expressions for the coefficients α and β can be obtained using the orthogonal properties of the Legendre functions [12]. In general

$$\alpha^m_{nu} R^u = c_{um} \int_{-1}^{1} P^m_n(\xi) P^m_n(\eta) P^m_u(\mu)\, \mathrm{d}\mu \tag{35}$$

and

$$\beta^m_{nu} R^{-(u+1)} = c_{um} \int_{-1}^{1} Q^m_n(\xi) P^m_n(\eta) P^m_u(\mu)\, \mathrm{d}\mu \tag{36}$$

where

$$c_{um} = \frac{2u+1}{2} \frac{(u-m)!}{(u+m)!} \tag{37}$$

$\xi = \xi(r, \mu)$ and $\eta = \eta(r, \mu)$. For α^m_{nn} and β^m_{nn}, the integrals in (35) and (36) can be evaluated analytically to give [12]

$$\alpha^m_{nn} = \frac{1.3.5.7 \ldots (2n-1)}{(n-m)!} \tag{38}$$

$$\beta^m_{nn} = \frac{(-1)^m (n+m)!}{1.3.5.7 \ldots (2n+1)}. \tag{39}$$

In other cases (35) and (36) are evaluated numerically. The coefficients A^m_{nu} and B^m_{nu} are obtained by numerical inversion of the arrays of coefficients α^m_{nu} and β^m_{nu}. Since (33) and (34) are infinite series, the arrays of coefficients B^m_{nu} and β^m_{nu} are truncated to a suitable accuracy.

In this solution, only the first four non-zero terms in the second term of (20) are considered, to give a solution for b_{000} accurate to λ^7, where $\lambda = d/l$ with l the side length of the unit cell. This approach parallels that of Zuzovsky and Brenner [2] who obtained a solution accurate to γ^7 with $\gamma = r_0/l$, r_0 being the radius of the spherical particles. Greater accuracy can be obtained by including higher order terms, as in the calculation of Sangani and Acrivos [14].

Evaluating the first few derivatives in (16) gives (21). This equation may be used as it stands to obtain the following

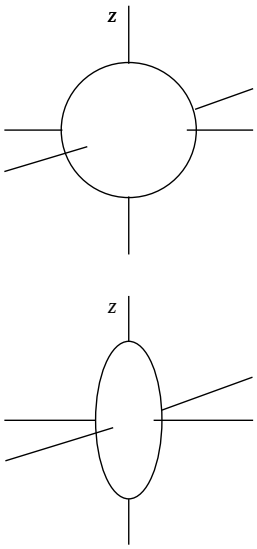

Figure 2. Geometry for transformation between spherical and spheroidal harmonics.

result for a cubic lattice of spheres [2], or may be transformed to treat spheroids. For spheres

$$b_{000} = 4\pi r_0^3\left[\mathcal{L}_1^{-1} + \frac{4\pi r_0^3}{3\tau_0} - \frac{16(a'_{20})^2\gamma^{10}}{(\mathcal{L}_3^{-1} + 20a'_{30}\gamma^7)} - 176\mathcal{L}_5(a'_{30})^2\gamma^{14} + \mathcal{O}(\gamma^{18})\right]^{-1} \tag{40}$$

with r_0 the sphere radius, $\gamma = r_0/l$, $a'_{nm} = l^{2n+1}a_{nm}$

$$\mathcal{L}_s = \frac{1-\alpha}{\alpha + (s+1)/s} \tag{41}$$

and, from [15, table 13],

$$a_{20} = 3.108\,227 \qquad a_{30} = 0.573\,3293. \tag{42}$$

The bulk conductivity can now be obtained by substituting (40) into (28).

In order to treat spheroidal particles, (21) is transformed using relations (29), (31) and (33) to yield an expression containing terms with the following combinations of Legendre functions

$$P_1P_1 \qquad P_3P_3 \qquad P_5P_5 \qquad P_5^4P_5^4\cos 4\phi$$
$$Q_1P_1 \qquad Q_3P_3 \qquad Q_5P_5 \qquad Q_5^4P_5^4\cos 4\phi.$$

The argument of the first Legendre function in each term is ξ and that of the second is η. Matching terms with those in (23) allows elimination of c_{nm} and determination of b_{mnp}. Finally, one obtains

$$b_{000} = 4\pi d^3\left\{\Gamma_1(\mathcal{L}_1^0)^{-1} + \frac{4\pi d^3}{3\tau_0} + 4a'_{20}\Gamma_2\lambda^5 + 6a'_{30}\Gamma_3\lambda^7 - [4a'_{20}B_{13}^0(\mathcal{L}_3^0)^{-1}\lambda^5 + 2a'_{30}\Gamma_6B_{13}^0(\mathcal{L}_3^0)^{-1}\lambda^7 + 16(a'_{20})^2A_{33}^0\lambda^{10} + 8a'_{20}a'_{30}A_{33}^0\Gamma_7\lambda^{12} + 12(a'_{30})^2A_{53}^0\Gamma_6\lambda^{14}][B_{33}^0(\mathcal{L}_3^0)^{-1} + 20a'_{30}A_{33}^0\lambda^7]^{-1} - (a'_{30})^2[36\Gamma_4\mathcal{L}_5^0 + 140\Gamma_5\mathcal{L}_5^4]\lambda^{14} + \mathcal{O}(\lambda^{18})\right\}^{-1} \tag{43}$$

with

$$\Gamma_1 = B_{11}^0/A_{11}^0 \qquad \Gamma_2 = A_{31}^0/A_{11}^0$$
$$\Gamma_3 = (A_{51}^0/A_{11}^0) - (B_{15}^0/B_{55}^0) \qquad \Gamma_4 = A_{55}^0/B_{55}^0$$
$$\Gamma_5 = A_{55}^4/B_{55}^4 \qquad \Gamma_6 = 10(A_{31}^0/A_{11}^0) - 3(B_{35}^0/B_{55}^0)$$
$$\Gamma_7 = 3(A_{53}^0/A_{33}^0) + 10(A_{31}^0/A_{11}^0) - 3(B_{35}^0/B_{55}^0). \tag{44}$$

To obtain (43), relation (22) has again been used.

The bulk conductivity of the material can now be calculated by evaluating (43) and substituting into (28). The result for oblate spheroids is obtained from (43) by replacing ξ with $i\xi$ and d with $-id$. For spherical particles, the argument ξ_0 in the Legendre functions and their derivatives in $\mathcal{L}_s^t$, equation (24), becomes large and it is better to use the dedicated expressions given in (40) and (41).

4.2. σ_{xx}^*

In this section, the previous solution method will be extended to calculate the bulk material conductivity for an electric field applied perpendicular to the major axes of the spheroids. The simplest way of achieving this is to introduce an intermediate transformation which rotates the polar axis of the local spherical coordinate system in (21) through $\pi/2$ radians. The transformation from spherical to spheroidal coordinates can then be performed using the relationships given in the previous section, resulting in a spheroidal system whose polar axis lies perpendicular to the applied electric field. The detailed derivation of the matrix elements involved in this transformation is given in the appendix. The key results of interest in this particular example are

$$P_s^t(\mu)\cos t\phi = \begin{cases} \displaystyle\sum_{j=0}^{2j\leqslant s} A_s^{t,2j}P_s^{2j}(\mu')\cos 2j\phi' \\ \qquad s \text{ even}, t \text{ even} \\ \displaystyle\sum_{j=0}^{2j+1\leqslant s} \widetilde{A}_s^{t,2j+1}P_s^{2j+1}(\mu')\sin(2j+1)\phi' \\ \qquad s \text{ odd}, t \text{ even} \\ \displaystyle\sum_{j=1}^{2j+1\leqslant s} \widetilde{A}_s^{t,2j+1}P_s^{2j+1}(\mu')\sin(2j+1)\phi' \\ \qquad s \text{ even}, t \text{ odd} \\ \displaystyle\sum_{j=0}^{2j<s} A_s^{t,2j}P_s^{2j}(\mu')\cos 2j\phi' \\ \qquad s \text{ odd}, t \text{ odd} \end{cases} \tag{45}$$

where $x = z'$, $y = x'$ and $z = y'$.

Now (21) is transformed using the above relations. For the terms which appear in (21), (45) gives rise to

$$P_1(\mu) = \widetilde{A}_1^{01}P_1^1(\mu')\sin\phi'$$
$$P_3(\mu) = \widetilde{A}_3^{01}P_3^1(\mu')\sin\phi' + \widetilde{A}_3^{03}P_3^3(\mu')\sin 3\phi'$$
$$P_5(\mu) = \widetilde{A}_5^{01}P_5^1(\mu')\sin\phi' + \widetilde{A}_5^{03}P_5^3(\mu')\sin 3\phi' + \widetilde{A}_5^{05}P_5^5(\mu')\sin 5\phi'$$
$$P_5^4(\mu)\cos 4\phi = \widetilde{A}_5^{41}P_5^1(\mu')\sin\phi' + \widetilde{A}_5^{43}P_5^3(\mu')\sin 3\phi' + \widetilde{A}_5^{45}P_5^5(\mu')\sin 5\phi'.$$

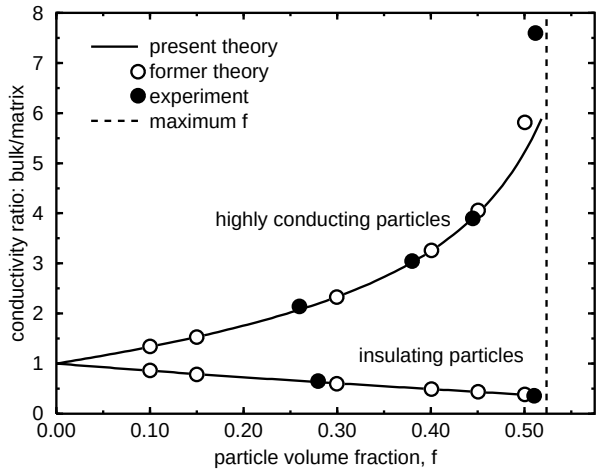

Figure 3. Bulk conductivity as a function of particle volume fraction for high-conductivity and insulating spherical particles in a low-conductivity matrix. The results of former theory are taken from [7] and the experimental data is taken from [16].

Substituting these relationships into (21), the resulting expression is transformed again using relations (29), (31) and (33). Terms are then matched with those in (25) and c_{nm} are eliminated to yield a system of linear equations which can be solved for b_{mnp}. The final result is

$$b_{000} = 4\pi d^3 \Big\{ S_1(\mathcal{L}_1^1)^{-1} + \frac{4\pi d^3}{3\tau_0} + 4a'_{20}S_2\lambda^5 + 2a'_{30}S_8\lambda^7 + C(24a'_{20}\lambda^5 + 120a'_{30}S_2\lambda^7) - 6a'_{30}\lambda^7[\chi - S_6(\widetilde{A}_5^{05}\chi - 2a'_{30}S_7\lambda^7)] + \mathcal{O}(\lambda^{18}) \Big\}^{-1} \quad (46)$$

with

$$C = -\frac{S_9 B_{13}^1(\mathcal{L}_3^1)^{-1} + 4a'_{20}A_{33}^1\lambda^5 + 2a'_{30}S_{10}\lambda^7}{6[B_{33}^1(\mathcal{L}_3^1)^{-1} + 20a'_{30}A_{33}^1\lambda^7]} \quad (47)$$

$$\chi = S_3 + 6CS_4 + 2a'_{30}S_5\mathcal{L}_5^1\lambda^7 \quad (48)$$

and

$$S_1 = \frac{B_{11}^1}{A_{11}^1} \qquad S_2 = \frac{\widetilde{A}_3^{01}A_{31}^1}{\widetilde{A}_1^{01}A_{11}^1} \qquad S_3 = \frac{\widetilde{A}_1^{01}B_{15}^1}{\widetilde{A}_5^{01}B_{55}^1}$$

$$S_4 = \frac{\widetilde{A}_3^{01}B_{35}^1}{\widetilde{A}_5^{01}B_{55}^1} \qquad S_5 = \frac{A_{55}^1}{B_{55}^1}\left(3 - \frac{\widetilde{A}_5^{41}}{72\widetilde{A}_5^{01}}\right)$$

$$S_6 = \frac{840\widetilde{A}_5^{01} + \widetilde{A}_5^{41}}{\widetilde{A}_5^{05}\widetilde{A}_5^{41} - \widetilde{A}_5^{01}\widetilde{A}_5^{45}} \qquad S_7 = 3\widetilde{A}_5^{05} - \frac{\widetilde{A}_5^{45}}{72}$$

$$S_8 = \frac{A_{51}^1}{A_{11}^1}\left(3\frac{\widetilde{A}_5^{01}}{\widetilde{A}_1^{01}} - \frac{\widetilde{A}_5^{41}}{72\widetilde{A}_1^{01}}\right) \qquad S_9 = \frac{\widetilde{A}_1^{01}}{\widetilde{A}_3^{01}}$$

$$S_{10} = A_{53}^1\left(3\frac{\widetilde{A}_5^{01}}{\widetilde{A}_3^{01}} - \frac{\widetilde{A}_5^{41}}{72\widetilde{A}_3^{01}}\right). \quad (49)$$

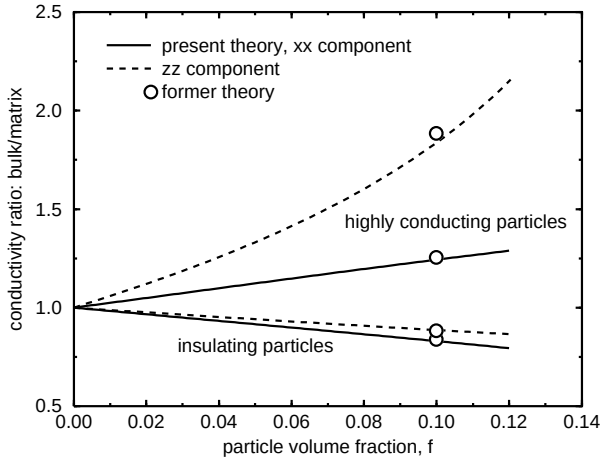

Figure 4. As for figure 3 but with prolate spheroidal particles with aspect ratio 2.0.

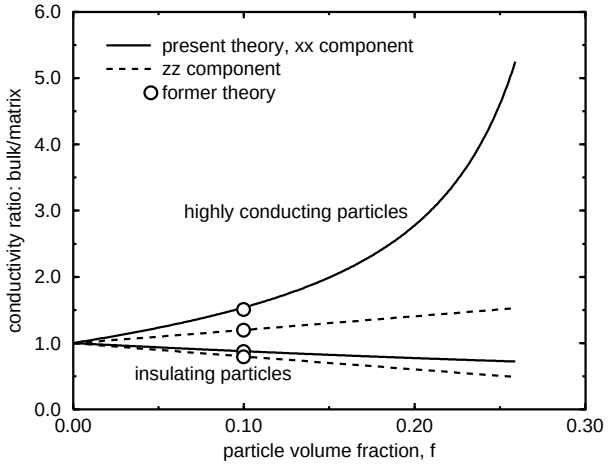

Figure 5. As for figure 3 but with oblate spheroidal particles with aspect ratio 0.5.

5. Calculations and validation

The aspect ratio, ϵ, of a spheroid is defined by

$$\epsilon = a/b \quad (50)$$

where a and b are the lengths of the semi-major and semi-minor axes, respectively. Therefore $\epsilon = 1$ describes a sphere, $\epsilon > 1$ describes a prolate spheroid and $0 \leqslant \epsilon < 1$ describes an oblate spheroid. In principle, the bulk conductivity of a composite formed of a simple-cubic lattice of spheroids can be calculated from (43) and (46) for any value of ϵ. Here, results are presented for bulk conductivity as a function of particle volume fraction for ϵ with values 0.5 (oblate spheroid), 1.0 (sphere) and 2.0 (prolate spheroid), in order to make comparisons with former theory and experimental data available in the literature. The variation in bulk conductivity as a function of ϵ and as a function of the conductivity ratio of the two phases, α, is also shown.

The volume fraction is defined as the ratio of the volume occupied by the inclusions to the total volume. For this system in which one spheroidal particle occupies each unit

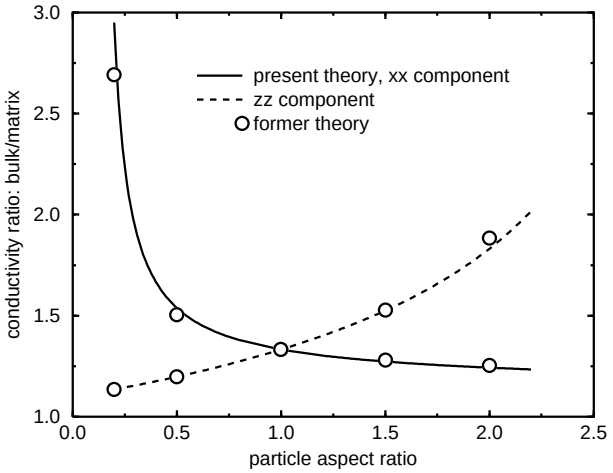

Figure 6. Bulk conductivity as a function of the particle aspect ratio ϵ for high-conductivity particles and volume fraction 0.1. The results of former theory are taken from [7].

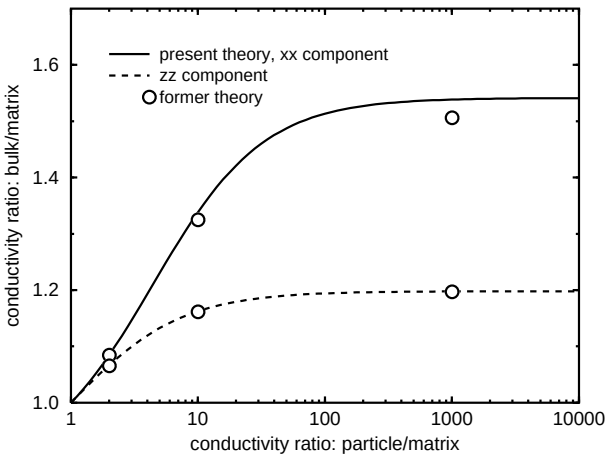

Figure 7. Bulk conductivity as a function of the particle/matrix conductivity ratio α for oblate spheroids with aspect ratio 0.5, $\alpha \geqslant 1$ and volume fraction 0.1. The results of former theory are taken from [7].

cell, the volume fraction has an analytic expression

$$f = \frac{4\pi ab^2}{3l^3}. \tag{51}$$

The maximum volume fraction is achieved when the particles are sufficiently large to touch one another. For prolate spheroids arranged on a cubic lattice, this occurs for $a = l/2$ and for oblate spheroids when $b = l/2$. From (51), the maximum value of f can be expressed

$$f_{max} = \begin{cases} (\pi\epsilon)/6 & 0 \leqslant \epsilon < 1 \quad \text{oblate spheroid} \\ \pi/6 & \epsilon = 1 \quad \text{sphere} \\ \pi/(6\epsilon^2) & \epsilon > 1 \quad \text{prolate spheroid.} \end{cases} \tag{52}$$

The maximum volume fraction tends to zero as $\epsilon \to 0$, in the limit in which the oblate spheroids become infinitesimally thin discs, and as $\epsilon \to \infty$, when the prolate spheroids become infinitesimally thin rods or fibres.

In figure 3, predictions of bulk conductivity as a function of volume fraction are compared with experimental data and former theoretical work for highly conducting and insulating spherical particles in a low-conductivity matrix ($\alpha \to \infty$ and $\alpha = 0$, respectively). The independent theoretical results were taken from [7] and the experimental data was obtained from [16].

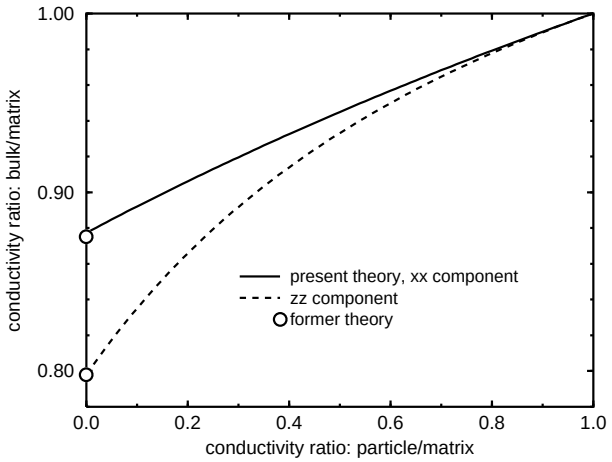

Figure 8. As for figure 7 but with $0 \leqslant \alpha \leqslant 1$.

In figures 3, 4 and 5, predictions are shown for values of f approaching f_{max}, i.e. up to the limit in which the particles are nearly touching each other. From (52), $f_{max} = \pi/12$, $\pi/6$ and $\pi/24$ for $\epsilon = 0.5$, 1.0 and 2.0, respectively. There is good agreement between this theory and the experimental data and former theoretical work. The discrepancy between these predictions and other work for the highly conducting particles as f approaches f_{max} is due to the fact that in this example only four terms are used in obtaining b_{000}. As the particles approach one another closely, and when the conductivity ratio between the two phases is large, this is an insufficient number of terms to accurately describe the field in the interstitial region. The accuracy could be improved by using a larger number of terms.

From figures 4 and 5 it is clear that, for a particular value of f and with highly conducting particles, the bulk conductivity is higher for particles whose greatest dimension is parallel to the direction of the applied field. In other words, σ_{zz} is greater than σ_{xx} for prolate spheroids, which are elongated in the z direction, whereas for oblate spheroids σ_{xx} is greater than σ_{zz}. This point is made clearly in figure 6 in which the bulk conductivity is shown as a function of the particle aspect ratio ϵ.

In figures 7 and 8, calculations of bulk conductivity are shown as a function of α for fixed volume fractions $f = 0.1$ and $\epsilon = 0.5$. As before, there is excellent agreement between this theory and former theoretical work [7]. The discrepancy observed for σ_{xx} in the high-conductivity limit (figure 7) is again explained by the low number of terms used in the solution.

6. Conclusion

Analytical expressions have been derived for the bulk conductivity of a material composed of aligned spheroidal particles arranged on a simple-cubic lattice. The material properties which form the input parameters of the model are

the conductivity ratio of the two phases, the particle shape and the volume fraction. The formulation given here is in terms of electrical conductivity, but the model is equally valid for the calculation of other material properties, such as thermal conductivity and permittivity, due to mathematical equivalence in the formulations. Results have been presented for various values of particle aspect ratio, volume fraction and conductivity ratio between the two phases, and very good agreement has been observed with the results of an independent calculation [7] and experimental data [16].

This model generalizes the work of Zuzovsky and Brenner [2], who treated a simple-cubic lattice of spheres by representing each particle as a singular multipole source distribution. The generalization to spheroidal particles is a useful one since the spheroid can be used to model a variety of particle shapes, including discs and fibres in limiting cases. The method also lends itself to further generalization. For example, spheroids whose axes of rotation are tilted with respect to the lattice vectors and/or the applied field can be treated by computing the appropriate transformation matrix. In addition, following the approach of Sangani and Yao [6], more than one particle can be distributed in each unit cell to create a less regular microstructure. In this way, the effect of distributions of particle size, shape and orientation can be modelled. A mixture of particle types can also be considered by assigning different values of conductivity to different particles. Finally, through a modification of the coefficient given in (24), the effect of a layer coating the surface of the particles can be modelled.

Acknowledgments

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Appendix: Transformation matrices

To transform an expression in spherical harmonics, referred to axes x, y and z, into an equivalent expression referred to axes x', y' and z', we begin with the addition theorem for spherical harmonics described in [17, section 5.24]. This expresses a surface zonal harmonic $P_n(\mu')$ in terms of general surface harmonics, referred to another axis. If the two axes intersect at the origin, we let the coordinates of the θ'-axis be $\theta = \Theta$ and $\phi = 0$. The expansion then takes the following form

$$P_n(\mu') = \sum_{p=0}^{n} \alpha_n^p P_n^p(\mu) \cos p\phi \tag{53}$$

where $\mu = \cos\theta$ etc. The coefficients α_n^p can be determined analytically as shown by Smythe [17]. The first step in the procedure is to multiply both sides of this by $P_n^t(\mu)\cos t\phi$ and integrate over the surface of a unit sphere. Eventually one finds

$$P_n(\mu') = P_n(\cos\Theta)P_n(\mu) + 2\sum_{p=1}^{n} \frac{(n-p)!}{(n+p)!} P_n^p(\cos\Theta) P_n^p(\mu)\cos p\phi. \tag{54}$$

For $m = 0$, (54) is required for transforming between spherical harmonics referred to coordinate systems which are rotated with respect to one another. For $m > 0$, (54) must be generalized. We write

$$P_n(\mu')\cos m\phi' = \sum_{p=0}^{n} P_n^p(\mu)[\alpha_n^{mp}\cos p\phi + \tilde{\alpha}_n^{mp}\sin p\phi]. \tag{55}$$

Multiplying both sides of (55) by $P_n^t(\mu)\cos t\phi$ and integrating over the surface of a unit sphere yields

$$\alpha_n^{mt} = \begin{cases} \dfrac{c_{n0}}{2\pi}\displaystyle\int_0^{2\pi} \mathrm{d}\phi \int_{-1}^{1} \mathrm{d}\mu\, P_n(\mu) P_n^m(\mu')\cos m\phi' \\ \qquad t = 0 \\ \dfrac{c_{nt}}{\pi}\displaystyle\int_0^{2\pi} \mathrm{d}\phi \cos t\phi \int_{-1}^{1} \mathrm{d}\mu\, P_n^t(\mu) P_n^m(\mu')\cos m\phi' \\ \qquad \text{otherwise} \end{cases} \tag{56}$$

with c_{nt} given in (37). Multiplying instead by $P_n^t(\mu)\sin t\phi$ gives

$$\tilde{\alpha}_n^{mt} = \begin{cases} 0 \\ \qquad t = 0 \\ \dfrac{c_{nt}}{\pi}\displaystyle\int_0^{2\pi} \mathrm{d}\phi \sin t\phi \int_{-1}^{1} \mathrm{d}\mu\, P_n^t(\mu) P_n^m(\mu')\cos m\phi' \\ \qquad \text{otherwise.} \end{cases} \tag{57}$$

If the primed and unprimed coordinate systems are related by

$$(x', y', z') = (y, z, x) \tag{58}$$

it can be shown that

$$\mu' = \sqrt{1-\mu^2}\cos\phi$$

and

$$\cos^2\phi' = \frac{1-\mu^2}{1+\mu^2\cot^2\phi}.$$

Using these relations, the integrals in (56) and (57) have been evaluated numerically with an algorithm based on [18, section 25.4.62]. For even m, $\tilde{\alpha}_n^{mt}$ are zero and for odd m α_n^{mt} are zero. This means that, for each m, the matrix of coefficients α_n^{mt} can be directly inverted to yield A_n^{mt} in (45). Similarly, $\tilde{\alpha}_n^{mt}$ can be inverted to give $\tilde{A}_n^{mt}$.

The analytic results available from (54) can be used to check the numerical calculation of α_n^{0t}. For the coordinate relationships given in (58), Θ in (54) is $\pi/2$ and the first few values are

$$\begin{pmatrix} \alpha_0^{00} & & & \\ \alpha_1^{00} & \alpha_1^{01} & & \\ \alpha_2^{00} & \alpha_2^{01} & \alpha_2^{02} & \\ \alpha_3^{00} & \alpha_3^{01} & \alpha_3^{02} & \alpha_3^{03} \end{pmatrix} = \begin{pmatrix} 1 & & & \\ 0 & -1 & & \\ -1/2 & 0 & 1/4 & \\ 0 & 1/4 & 0 & -1/24 \end{pmatrix}.$$

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