Effective conductivity of composites of graded spherical particles

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Abstract

We have employed the first-principles approach to compute the effective response of composites of graded spherical particles of arbitrary conductivity profiles. We solve the boundary-value problem for the polarizability of the graded particles and obtain the dipole moment as well as the multipole moments. We provide a rigorous proof of an \textit{ad hoc} approximate method based on the differential effective multipole moment approximation (DEBMA) in which the differential effective dipole approximation (DEDA) is a special case. The method will be applied to an exactly solvable graded profile. We show that DEDA and DEMMA are indeed exact for graded spherical particles.

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I. INTRODUCTION

In functionally graded materials (FGM), the materials properties can vary spatially. These materials have received considerable attention in various engineering applications [1]. The variation in the composition yields material and microstructure gradients, and makes the FGM very different in behavior from the homogeneous materials and conventional composite materials [1,2]. The great advantage is that one can tailor the materials properties via the design of the gradients. Over the past few years, there have been a number of attempts, both theoretical and experimental, to study the responses of FGM to mechanical, thermal, and electric loads and for different microstructure in various systems [1–8]. In Nature, graded morphogen profiles can exist in a cell layer [4]. In experiments, graded structure may be produced by using various approaches, such as a three-dimensional X-ray microscopy technique [7], deformation under large sliding loads [8], and adsorbate-substrate atomic exchange during growth [6]. Thus, gradation profiles exist in both natural materials and artificial FGM. Interestingly, gradation profiles may further be controlled according to our purpose, such as a specific power-law gradation profile and so on. It has reported recently that the control of a compatibility factor can facilitate the engineering of FGM [5].

There have been various different attempts to treat the composite materials of homogeneous inclusions [9] as well as multi-shell inclusions [10–13]. These established theories for homogeneous inclusions, however cannot be applied to graded inclusions. To this end, we have recently developed a first-principles approach for calculating the effective response of dilute composites of graded cylindrical inclusions [14] as well as graded spherical particles [15]. The electrostatic boundary-value problem of a graded spherical particle has been solved for some specific graded profiles to obtain exact analytic results. Along this line, exact analytic results are available so far for the power-law graded profile [14,15], linear profile [14], exponential profile [16,17] as well as some combination of the above profiles [18]. For arbitrary graded profiles, we have developed a differential effective dipole approximation (DEDA) to estimate the effective response of graded composites of spherical particles
numerically. The DEDA results were shown to be in excellent agreement with the exact analytic results [15]. However, the excellent agreement is difficult to understand because DEDA method was based on an *ad hoc* approximation [19].

The object of the present investigation is two-fold. Firstly, we will extend the first-principles approach slightly to deal with graded particles of arbitrary profiles. We will solve the boundary-value problem for the polarizability of the graded particles and obtain the dipole moment as well as the multipole moments. Secondly, we will provide a rigorous proof of the *ad hoc* approximation from first-principles. To this end, we extend the proof to multipole polarizability and derive the differential effective multipole moment approximation. As an illustration of the method, application to the power-law profile will be made. Thus, both DEDA and DEMMA are indeed exact for graded spherical particles.

II. FIRST-PRINCIPLES APPROACH

In this work, we will focus on a model of a graded conducting particle, in which the conductivity of the particle varies continuously along the radius of the spherical particle. We consider the electrostatic boundary-value problem of a graded spherical medium of radius $a$ subjected to a uniform electric field $E_0$ applied along the $z$-axis. For conductivity properties, the constitutive relations read $\vec{J} = \sigma_i(r)\vec{E}$ and $\vec{J} = \sigma_m\vec{E}$ respectively in the graded spherical medium and the host medium, where $\sigma_i(r)$ is the conductivity profile of the graded spherical medium and $\sigma_m$ is the conductivity of the host medium. The Maxwell’s equations read

$$\vec{\nabla} \cdot \vec{J} = 0, \quad \vec{\nabla} \times \vec{E} = 0.$$  

To this end, $\vec{E}$ can be written as the gradient of a scalar potential $\Phi$, $\vec{E} = -\vec{\nabla}\Phi$, leading to a partial differential equation:

$$\vec{\nabla} \cdot [\sigma(r)\vec{\nabla}\Phi] = 0,$$  

(1)

where $\sigma(r)$ is the dimensionless dielectric profile, while $\sigma(r) = \sigma_i(r)/\sigma_m$ in the inclusion, and $\sigma(r) = 1$ in the host medium.
In spherical coordinates, the electric potential $\Phi$ satisfies
\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \sigma(r) \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \sigma(r) \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \varphi} \left( \sigma(r) \frac{\partial \Phi}{\partial \varphi} \right) = 0. \tag{2}
\]

As the external field is applied along the $z$-axis, $\Phi$ is independent of the azimuthal angle $\varphi$. If we write $\Phi = f(r)\Theta(\theta)$ to achieve separation of variables, we obtain two distinct ordinary differential equations. For the radial function $f(r)$,
\[
\frac{d}{dr} \left( r^2 \sigma(r) \frac{df}{dr} \right) - (l + 1)\sigma(r)f = 0, \tag{3}
\]
where $l$ is an integer, while $\Theta(\theta)$ satisfies the Legendre equation \cite{9}. Eq.(3) is a homogeneous second-order differential equation; it admits two possible solutions: $f_+^l(r)$ and $f_-^l(r)$ being regular at the origin and infinity respectively. Exact analytic results can be obtained for a power-law profile \cite{14,15}, linear profile \cite{14}, and exponential profile \cite{16}. The general solution for the potential in the spherical medium is thus given by
\[
\Phi_\text{i}(r, \theta) = \sum_{l=0}^{\infty} \left[ A_l f_+^l(r) + B_l f_-^l(r) \right] P_l(\cos \theta). \tag{4}
\]

In the host medium, the potential is given by
\[
\Phi_\text{m}(r, \theta) = \sum_{l=0}^{\infty} \left[ C_l r^l + D_l r^{-(l+1)} \right] P_l(\cos \theta). \tag{5}
\]
Thus the problem can be solved by matching the boundary conditions at the spherical surface.

**III. BOUNDARY-VALUE PROBLEM**

By virtue of the regularity of the solution at $r = 0$, the general solution inside the particle becomes:
\[
\Phi_\text{i}(r, \theta) = \sum_{l=0}^{\infty} A_l f_+^l(r) P_l(\cos \theta), \quad r \leq a, \tag{6}
\]
The external potential ($r \geq a$) is:
\[
\Phi_m(r, \theta) = -E_0 r \cos \theta + \sum_{l=0}^{\infty} D_l r^{-(l+1)} P_l(\cos \theta), \quad r \geq a. \tag{7}
\]

We can rewrite \(r \cos \theta\) as \(\sum_l \delta_l r^l P_l(\cos \theta)\). Thus \(C_l = -E_0 \delta_l\) and no multipole moment will be induced in a uniform applied field. However, in a nonuniform applied field as in dielectrophoresis of graded particles, multipole moments will be induced. Matching boundary conditions at \(r = a\),

\[
\Phi_i(a) = \Phi_m(a), \quad \sigma(a) \Phi_i'(a) = \Phi_m'(a),
\]

where prime denotes derivatives with respect to \(r\), we obtain a set of simultaneous linear equations for the coefficients

\[
A_l f_i^+(a) = -E_0 a^l \delta_l + D_l a^{-(l+1)}, \tag{8}
\]

\[
\sigma(a) A_l f_i'^+(a) = -E_0 a^{l-1} \delta_l - D_l (l+1) a^{-(l+2)}. \tag{9}
\]

Solving these equations,

\[
A_l = -\frac{(2l + 1) a^l E_0 \delta_l}{a \sigma(a) f_i^+(a) + (l+1) f_i'^+(a)} = -\frac{(2l + 1) a^l E_0 \delta_l}{f_i^+(a)[l(F_i + 1) + 1]}, \tag{10}
\]

\[
D_l = \frac{a^{2l+1} [a \sigma(a) f_i'^+(a) - l f_i^+(a)] E_0 \delta_l}{a \sigma(a) f_i'^+(a) + (l+1) f_i^+(a)} = a^{2l+1} [l(F_i - 1) E_0 \delta_l] / l(F_i + 1) + 1, \tag{11}
\]

where

\[
F_i = \frac{\sigma_i(a) a f_i'^+(a)}{\sigma_m a f_i^+(a)}. \tag{12}
\]

When the radial equation is solved for a specified graded profile, the potential distribution can generally be expressed in terms of \(f_i^+(r)\) and \(F_i\). For a uniform applied field, the potential becomes

\[
\Phi_i(r, \theta) = -\frac{3 a f_i^+(r) E_0}{f_i^+(a)(F_i + 2)} \cos \theta, \quad r \leq a, \tag{13}
\]

\[
\Phi_m(r, \theta) = -E_0 r \cos \theta + \frac{a^3(F_i - 1) E_0}{r^2(F_i + 2)} \cos \theta, \quad r \geq a. \tag{14}
\]

The second term in the potential in Eq. (14) can be interpreted as the potential due to an induced dipole moment \(p = \sigma_m b_1 a^3 E_0\). Thus we identify the dipole factor:
\[ b_1 = \frac{F_1 - 1}{F_1 + 2}, \quad F_1 = \frac{\sigma_i(a) a f_1^{+}(a)}{\sigma_m f_1^{+}(a)}. \] (15)

For a homogeneous (non-graded) particle, the well known result recovers:

\[ b_1 = \frac{\sigma_i - \sigma_m}{\sigma_i + 2\sigma_m}. \]

Thus, \( F_1 \) can be interpreted as the equivalent conductivity ratio of the graded spherical particle.

**IV. DIFFERENTIAL EFFECTIVE MULTIPOLe MOMENT APPROXIMATION**

We should remark that in general \( F_l \) is the equivalent conductivity ratio of the \( l \)th multipole moment. Let us extend the definition [Eq.(12)] slightly for a graded spherical particle of variable radius \( r \):

\[ F_l(r) = \sigma(r) \frac{r f_l^{+}(r)}{l f_l^{+}(r)}. \] (16)

Thus, the multipole factor reads:

\[ b_l(r) = \frac{l(F_l(r) - 1)}{l(F_l(r) + 1) + 1}. \] (17)

Physically it means that we construct the graded particle by a multi-shell procedure [19]: we start out with a graded particle of radius \( r \) and keep on adding conducting shell gradually. The change in \( F_l \) and \( b_l \) can be assessed. In this regard, it is instructive to derive differential equations for \( F_l(r) \) and \( b_l(r) \). Let us consider (ignoring the superscript + and subscript \( l \) in \( f_l^{+}(r) \) for simplicity):

\[ \frac{d}{dr}[rF_l(r)] = \frac{1}{l} \frac{d}{dr} \left[ r^2 \sigma(r) \frac{f_l(r)}{f(r)} \right] = \frac{1}{l f(r)} \frac{d}{dr} \left[ r^2 \sigma(r) f_l'(r) \right] - \frac{r^2 \sigma(r) f_l'(r)^2}{lf(r)^2}. \]

From Eq.(3) and Eq.(16), we obtain the differential equation:

\[ \frac{d}{dr}[rF_l(r)] = (l + 1)\sigma(r) - \frac{lF_l(r)^2}{\sigma(r)}, \] (18)

which is just the generalized Tartar formula [20]. From Eq.(17) and Eq.(18), we obtain the DEMMA:
\[
\frac{db_l(r)}{dr} = -\frac{1}{(2l+1)r\sigma(r)}[(b_l(r) + l + b_l(r)l) + (b_l(r) - 1)l\sigma(r)] \times [(b_l(r) + l + b_l(r)l) - (b_l(r) - 1)(l + 1)\sigma(r)].
\] (19)

When \( l = 1 \), we recover the Tartar formula and DEDA [19]:
\[
\frac{d}{dr}[rF_1(r)] = 2\sigma(r) - \frac{F_1(r)^2}{\sigma(r)},
\] (20)
\[
\frac{db_1(r)}{dr} = -\frac{1}{3r\sigma(r)}[(2b_1(r) + 1) + (b_1(r) - 1)\sigma(r)] \\
\times [(2b_1(r) + 1) - 2(b_1(r) - 1)\sigma(r)].
\] (21)

Let us consider a graded particle in which the conductivity profile has a power-law dependence on the radius, \( \sigma(r) = cr^k \), with \( k \geq 0 \) where \( 0 < r \leq a \). Then the radial equation becomes
\[
\frac{d^2f}{dr^2} + \frac{k + 2}{r} \frac{df}{dr} - \frac{l(l + 1)}{r^2} f = 0.
\] (22)

As Eq.(22) is a homogeneous equation, it admits a power-law solution [15],
\[
f(r) = r^s.
\] (23)

Substituting it into Eq.(22), we obtain the equation \( s^2 + s(k + 1) - l(l + 1) = 0 \) and the solution is
\[
s_k^\pm(l) = \frac{1}{2} \left[ -(k + 1) \pm \sqrt{(k + 1)^2 + 4l(l + 1)} \right].
\] (24)

There are two possible solutions:
\[
f_l^+(r) = r^{s_k^+(l)}, \quad f_l^-(r) = r^{s_k^-(l)}.
\]

Thus the \( l \)-th order equivalent conductivity becomes:
\[
F_l = \frac{\sigma_i(a) a f_l^+(a)}{\sigma_m l f_l^+(a)} = \frac{s_k^+(l)}{l}ca^k.
\] (25)

When \( k \to 0 \), \( s_k^+(l) \to 0 \), \( F_l \to c \), the result for a homogeneous sphere recovers.
V. DISCUSSION AND CONCLUSION

Here a few comments are in order. We have employed the first-principles approach to compute the multipole polarizability of graded spherical particles of arbitrary conductivity profiles and provided a rigorous proof of the differential effective dipole approximation.

We are now in a position to propose some applications of the present method. We may attempt the similar calculation of the multipole response of a graded metallic sphere in the nonuniform field of an oscillating point dipole at optical frequency. The graded Drude dielectric function will be adopted [21]. The similar approach may also be extended to anisotropic medium with different radial and tangential conductivities [22]. Similar work can be extended to ac electrokinetics of graded cells [23]. We can also study the interparticle force between graded particles [24].

In summary, we have solved the boundary-value problem for the polarizability of the graded particles and obtained the dipole moment as well as the multipole moments. We provided a rigorous proof of the differential effective multipole moment approximation. We showed that DEDA and DEMMA are indeed exact for graded spherical particles. Note that an exact solution is very few in composite research and to have one yields much insight. Such solutions should be useful as benchmarks. Finally, we should remark that the exact derivation of DEDA and DEMMA is for graded spherical particles only. For graded nonspherical particles, these ad hoc approaches may only be approximate.

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