Extreme enhancement and reduction of the dielectric response of polymer nanoparticulate composites via interphasial charges

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An analytical solution is constructed for the homogenized (i.e., macroscopic) dielectric response of particulate composites comprising a random distribution of particles bonded to a matrix material through interphases of finite size that contain space charges. By accounting for interphasial charges, the solution is able to describe and explain both the extreme enhancement and the reduction of the dielectric response typically exhibited by emerging polymer nanoparticulate composites. More generally, the solution reveals that judicious manipulation of interphasial charges provides a promising path forward for the design of materials with exceptional dielectric properties. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4884368]

Over the past ten years, a host of experiments[1–7] have shown that the macroscopic (i.e., homogenized) permittivity of polymers filled with nanoparticles can be drastically different—higher or lower—from that of the same polymers unfilled or filled with microparticles. Motivated by prior work on suspensions of particles in electrolytic solutions,[8,9] in this Letter, we show theoretically how such "anomalous" behavior can be described and explained by the presence of interphasial charges. More generally, we show that the manipulation of interphasial charges (possibly via particle surface treatments or coatings) provides a promising path forward for the design of materials with exceptional dielectric properties.

The basic idea rests on a generalization of the "coated-sphere-assemblage" approach pioneered by Hashin[10] to the realm of particulate composites with interphases that contain *space charges*, or, in homogenization parlance, source terms that oscillate at the microscale.[11] Specifically, the first step is to idealize[12,21] the random microstructure of filled polymers as assemblages of homothetic multicoated spheres made up of a core (the particle), an inner shell (the interphase), and an outer shell (the matrix), all with different isotropic permittivities $\varepsilon_p\mathbf{I}$, $\varepsilon_i\mathbf{I}$, and $\varepsilon_m\mathbf{I}$, respectively. Further, the inner shell is taken to contain a distribution of space charges $Q(\mathbf{X})$—heterogeneous but with equal amount of positive and negative charges—per unit volume of the material; see Fig. 1 for a schematic depiction. Having idealized the microstructure of filled polymers as such assemblages, their macroscopic permittivity can then be determined *exactly* and in *closed-form* by making use of a neutral-inclusion strategy.

Consider a homogeneous material with unknown isotropic permittivity $\varepsilon_*\mathbf{I}$ that occupies a domain Ω and is subjected to the electric potential

$$\varphi(\mathbf{X}) = -\bar{\mathbf{E}} \cdot \mathbf{X} \qquad (1)$$

on its boundary $\partial\Omega$, where $\bar{\mathbf{E}}$ is a prescribed constant vector. We seek to find the permittivity ε_* such that when a multicoated sphere made up of a core (the particle) with permittivity $\varepsilon_p\,\mathbf{I}$, an inner shell (the interphase) with permittivity $\varepsilon_i\,\mathbf{I}$ that contains a distribution of charges $Q(\mathbf{X})$, and an outer shell (the matrix) with permittivity $\varepsilon_m\,\mathbf{I}$ is inserted in Ω, the electric field remains unaltered $(\mathbf{E}(\mathbf{X}) = \bar{\mathbf{E}})$ outside the multicoated sphere. Since the multicoated sphere acts as a *neutral inclusion* in such a medium, the sought-after permittivity ε_* corresponds precisely to the macroscopic permittivity of a fully dense assemblage of homothetic multicoated spheres that fills the entire domain Ω (see, e.g., the seminal work of Hashin and Shtrikman,[13] Chapter 7 in Milton[14]).

For convenience, we choose the origin of the laboratory axes to coincide with the center of the multicoated sphere and write its heterogeneous permittivity in the compact form

$$\varepsilon(\mathbf{X})\mathbf{I} = [\theta_p(\mathbf{X})\varepsilon_p + \theta_i(\mathbf{X})\varepsilon_i + \theta_m(\mathbf{X})\varepsilon_m]\mathbf{I}, \qquad (2)$$

where $\theta_p(\mathbf{X}) = 1$ if $|\mathbf{X}| \leq R_p$ and zero otherwise, $\theta_i(\mathbf{X}) = 1$ if $R_p \leq |\mathbf{X}| \leq R_i$ and zero otherwise, $\theta_m(\mathbf{X}) = 1$ if $R_i \leq |\mathbf{X}| \leq R_m$ and zero otherwise. Here, R_p, R_i, and R_m stand, respectively, for the radii of the core, the inner shell, and the outer shell; see Fig. 2. Similarly, the charge density is conveniently written as

$$Q(\mathbf{X}) = \theta_i(\mathbf{X})\,Q_i(\mathbf{X}). \qquad (3)$$

In the sequel, for definiteness, we restrict attention to charge densities of the form

$$Q_i(\mathbf{X}) = q_i\,\frac{\bar{\mathbf{E}} \cdot \mathbf{X}}{R_p\,|\mathbf{X}|}, \qquad (4)$$

where again R_p denotes the radius of the filler particle and q_i is any constant of choice (of units F/m) that physically can be viewed as a measure of charge content. The functional form of (4) is consistent with the interphasial charge distributions found in suspensions of dielectric spherical particles in electrolytic solutions under an external uniform electric field.[8] It is also consistent with the charge distributions that develop on the surface of conducting spherical particles under the same

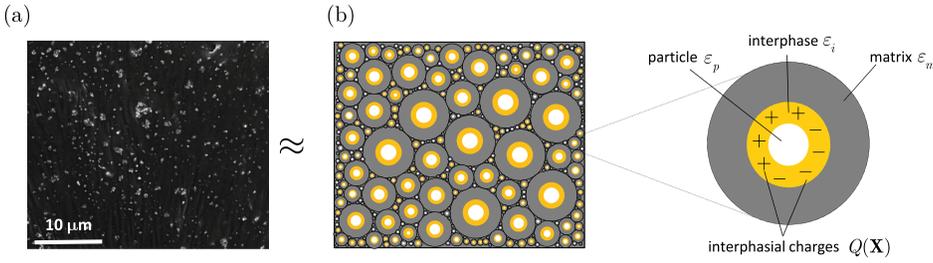a)Electronic mail: pamies@illinois.edu

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FIG. 1. (a) Electron micrograph of a PDMS elastomer filled with titania nanoparticles and (b) its idealization as an assemblage of multicoated spheres with interphasial charges. All the multicoated spheres in the assemblage are homothetic in that they are scale-up or scale-down replicas of each other.
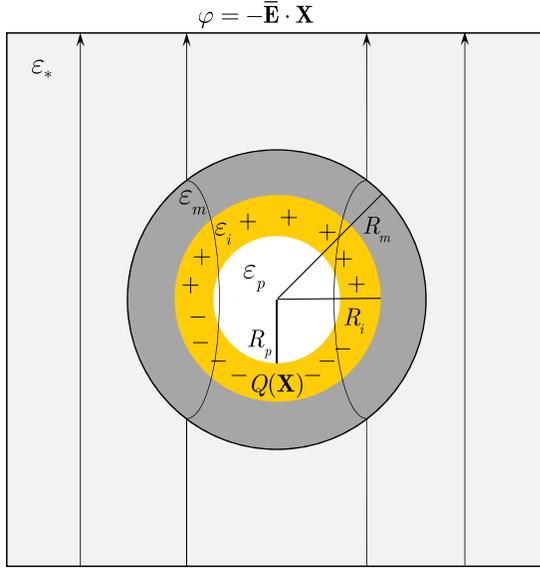

FIG. 2. Schematic of a multicoated sphere with interphasial charges embedded in the homogeneous material with permittivity $\varepsilon_* \mathbf{I}$ under the affine boundary condition $\varphi(\mathbf{X}) = -\bar{\mathbf{E}} \cdot \mathbf{X}$ on $\partial\Omega$. The multicoated sphere acts as a neutral inclusion in that it does not alter the uniform electric field $\mathbf{E}(\mathbf{X}) = \bar{\mathbf{E}}$ outside of it.

boundary conditions.[15] While sufficiently general for our purposes, the charge distribution (4) has the further merit to be simple enough to lead to fully explicit results.

The next step is to solve Gauss equations

$$\mathrm{Div}[-\varepsilon(\mathbf{X})\mathrm{Grad}\,\varphi] = Q(\mathbf{X}) \quad \text{for} \quad \mathbf{X} \in \Omega/\Gamma \qquad (5)$$

and

$$[\![-\varepsilon(\mathbf{X})\mathrm{Grad}\,\varphi]\!] \cdot \mathbf{N} = 0 \quad \text{for} \quad \mathbf{X} \in \Gamma. \qquad (6)$$

Here, $\mathbf{N} = \mathbf{X}/|\mathbf{X}|$ and $\Gamma = \{\Gamma_p, \Gamma_i, \Gamma_m\}$ have been introduced to denote the set of surfaces of material discontinuity $\Gamma_p = \{\mathbf{X} : |\mathbf{X}| = R_p\}$, $\Gamma_i = \{\mathbf{X} : |\mathbf{X}| = R_i\}$, and $\Gamma_m = \{\mathbf{X} : |\mathbf{X}| = R_m\}$. Making use of spherical coordinates, we look for solutions of the form

$$\varphi(\mathbf{X}) = \begin{cases} a_p R \cos\Phi & \text{for} \quad R \leq R_p \\ \left[a_i R + \dfrac{b_i}{R^2} - \dfrac{q_i|\bar{\mathbf{E}}|}{4R_p\varepsilon_i}R^2 \right] \cos\Phi & \text{for} \quad R_p \leq R \leq R_i \\ \left[a_m R + \dfrac{b_m}{R^2} \right] \cos\Phi & \text{for} \quad R_i \leq R \leq R_m \\ -|\bar{\mathbf{E}}|R \cos\Phi & \text{for} \quad R \geq R_m \end{cases}, \qquad (7)$$

where $R = |\mathbf{X}|$ and Φ denotes the angle between the applied electric field $\bar{\mathbf{E}}$ and the position vector $\mathbf{X}$. It is straightforward to verify that the electric potential (7) satisfies identically the Poisson's equation (5). The jump conditions (6) entail that

$$\varepsilon_p a_p = \varepsilon_i \left[a_i - 2\frac{b_i}{R_p^3} - \frac{q_i|\bar{\mathbf{E}}|}{2\varepsilon_i} \right],$$

$$\varepsilon_i \left[a_i - 2\frac{b_i}{R_i^3} - \frac{q_i|\bar{\mathbf{E}}|}{2R_p\varepsilon_i}R_i \right] = \varepsilon_m \left[a_m - 2\frac{b_m}{R_i^3} \right], \qquad (8)$$

$$\varepsilon_m \left[a_m - 2\frac{b_m}{R_m^3} \right] = -\varepsilon_*|\bar{\mathbf{E}}|,$$

while the continuity of the electric potential entails further that

$$a_p R_p = a_i R_p + \frac{b_i}{R_p^2} - \frac{q_i|\bar{\mathbf{E}}|}{4\varepsilon_i}R_p,$$

$$a_i R_i + \frac{b_i}{R_i^2} - \frac{q_i|\bar{\mathbf{E}}|}{4R_p\varepsilon_i}R_i^2 = a_m R_i + \frac{b_m}{R_i^2}, \qquad (9)$$

$$a_m R_m + \frac{b_m}{R_m^2} = -|\bar{\mathbf{E}}|R_m.$$

Relations (8)–(9) constitute a system of six linear algebraic equations for the six unknowns $a_p, a_i, b_i, a_m, b_m, \varepsilon_*$, and thus admit a unique solution. After introducing the notation $c_p \doteq R_p^3/R_m^3$ and $c_i \doteq (R_i^3 - R_p^3)/R_m^3$ for the volume fractions of the particle c_p and the interphase c_i, the solution for the permittivity ε_* can be written explicitly as

$$\varepsilon_* = \varepsilon_m + \frac{3\varepsilon_m(c_i + c_p)\left[c_i(\varepsilon_i - \varepsilon_m)(2\varepsilon_i + \varepsilon_p) + 3c_p\varepsilon_i(\varepsilon_p - \varepsilon_m)\right]}{\varepsilon_p[\varepsilon_i(1 - c_i - c_p)(c_i + 3c_p) + c_i\varepsilon_m(c_i + c_p + 2)] + \varepsilon_i[\varepsilon_m(c_i + c_p + 2)(2c_i + 3c_p) - 2c_i\varepsilon_i(c_i + c_p - 1)]}$$

$$+ \frac{3\varepsilon_m c_p(c_i + c_p)\left[\left(\frac{c_i}{c_p} + 1\right)^{4/3}(2\varepsilon_i + \varepsilon_p) + 4\left(\frac{c_i}{c_p} + 1\right)^{1/3}(\varepsilon_i - \varepsilon_i) + 3(\varepsilon_p - \varepsilon_i)\right]q_i}{4\varepsilon_p[\varepsilon_i(1 - c_i - c_p)(c_i + 3c_p) + c_i\varepsilon_m(c_i + c_p + 2)] + 4\varepsilon_i[\varepsilon_m(c_i + c_p + 2)(2c_i + 3c_p) - 2c_i\varepsilon_i(c_i + c_p - 1)]}. \qquad (10)$$

The *exact closed-form* solution (10) constitutes the main result of this Letter. It characterizes the macroscopic permittivity of a matrix material with permittivity ε_m, filled with polydisperse spherical particles with permittivity ε_p, and volume fraction c_p, that are bonded to the matrix through finite-size interphases with permittivity ε_i and volume fraction c_i containing space charges of the form (4). The following theoretical and practical remarks are in order:

1. In the absence of interphases altogether when $c_i = 0$ and $q_i = 0$, the macroscopic permittivity (10) reduces to the Maxwell-Garnett (MG) formula

$$\varepsilon_* = \varepsilon_m + \frac{3c_p\varepsilon_m(\varepsilon_p - \varepsilon_m)}{2\varepsilon_m + \varepsilon_p + c_p(\varepsilon_m - \varepsilon_p)}. \qquad (11)$$

When $\varepsilon_m \geq \varepsilon_p \, (\varepsilon_m \leq \varepsilon_p)$, this result also agrees with the Hashin-Shtrikman[13] upper (lower) bound for two-phase dielectrics with arbitrary (not necessarily particulate) isotropic microstructures. While the result (11) is unable to describe the permittivities of nanoparticulate composites observed in experiments, it does describe reasonably well the macroscopic permittivity of dielectrics filled with micron-sized spherical particles over large ranges of volume fractions of particles.[16]

2. In the absence of charges when $q_i = 0$, the macroscopic permittivity (10) reduces to the result of Milton[17]

$$\varepsilon_* = \varepsilon_m + \cfrac{3(c_p + c_i)\varepsilon_m}{1 - c_p - c_i + \cfrac{3\varepsilon_m}{\varepsilon_i - \varepsilon_m + \cfrac{3c_p\varepsilon_i}{c_i + \cfrac{3(c_p + c_i)\varepsilon_i}{\varepsilon_p - \varepsilon_i}}}}, \qquad (12)$$

for an assemblage of homothetic doubly coated spheres. While expression (12) accounts for finite-size interphases with homogeneous permittivity ε_i, possibly higher or lower from that of the matrix and particles, it is unable by itself to explain many of the unusually high and low permittivities of nanoparticulate composites observed in experiments. To see this, it suffices to recognize that the result (12) is bounded from above by

$$\varepsilon_* \leq \varepsilon_m + \frac{3(c_p + c_i)}{1 - c_p - c_i}\varepsilon_m, \qquad (13)$$

and from below by

$$\varepsilon_* \geq \varepsilon_m - \frac{3(c_p + c_i)}{2 + c_p + c_i}\varepsilon_m. \qquad (14)$$

Thus, even in the limiting cases when $\varepsilon_i/\varepsilon_0 = +\infty$ or $\varepsilon_i/\varepsilon_0 = 1$ (with $\varepsilon_0 \approx 8.85 \times 10^{-12}$ F/m denoting the permittivity of vacuum), the enhancement or reduction in the macroscopic permittivity (12) is—away from percolation—only of order $O(\varepsilon_m)$.

3. The macroscopic permittivity (10) is *linear* in q_i, a measure of the amount of charges in the interphases. Accordingly, given that the coefficient multiplying q_i is positive, large positive values of q_i can lead to a great enhancement of the macroscopic permittivity, whereas

large negative values of q_i can lead to a great reduction (possibly rendering negative permittivities). Physically, these two behaviors can be understood as follows. Positive values of q_i imply that the interphasial charges form an overall dipole that is aligned in the same direction with the applied electric field $\bar{\mathbf{E}}$ and thus enhances the macroscopic permittivity. On the other hand, negative values of q_i imply that the charges form an overall dipole that is in the opposite direction to $\bar{\mathbf{E}}$ and thus reduces the macroscopic permittivity. In short, the result (10) reveals that the presence of interphasial charges can indeed describe and explain both, the enhanced as well as the reduced, dielectric response exhibited by emerging polymer nanoparticulate composites. More generally, it reveals that judicious manipulation of interphasial charges—by means, for instance, of particle surface treatments or coatings—provides a promising path forward for the design of materials with exceptional dielectric properties (and, by the same token,[1,18,19] exceptional electromechanical properties).

To gain further physical insight into the properties of the formula (10), we now present some illustrative results within the context of comparisons with two representative sets of experiments, one exhibiting enhancement and one exhibiting reduction of the dielectric response.

Figure 3 shows results for the relative permittivity $\varepsilon_*/\varepsilon_0$ of a nanocomposite material made up of a P(VDF-TrFE-CTFE) matrix filled with PANI (polyaniline) particles, for a range of small volume fractions of particles c_p. P(VDF-TrFE-CTFE) is a dielectric polymer with permittivity approximately given by $\varepsilon_m/\varepsilon_0 = 52$. On the other hand, PANI is a conductive polymer. The permittivity of PANI particles is therefore modeled here as unbounded, $\varepsilon_p/\varepsilon_0 = +\infty$.
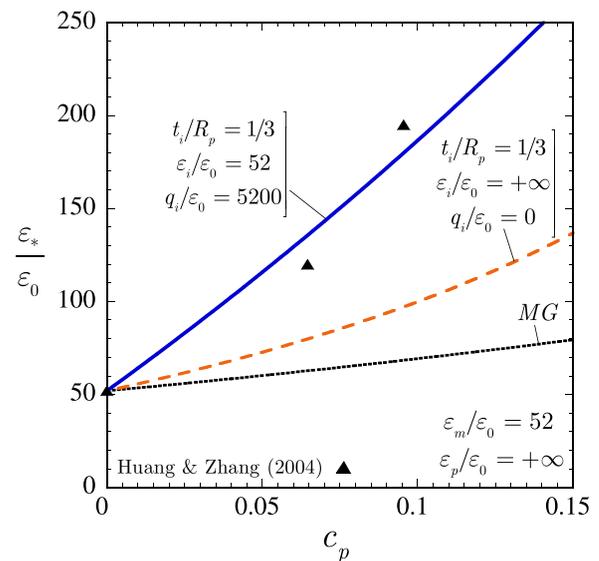

FIG. 3. Relative permittivity $\varepsilon_*/\varepsilon_0$ of a nanocomposite made up of a P(VDF-TrFE-CTFE) matrix ($\varepsilon_m/\varepsilon_0 = 52$) filled with PANI particles ($\varepsilon_p/\varepsilon_0 = +\infty$), as a function of the volume fraction of particles c_p. The data shown correspond to the theoretical result (10) accounting for interphasial charges (solid line), the experiments of Huang and Zhang[1] (triangles), the result (12) of Milton accounting for interphases with much higher permittivity than that of the matrix (dashed line), and the MG formula (dotted line).

There are four sets of data displayed in Fig. 3. The solid line corresponds to the full theoretical result (10) for the basic case when the permittivity of the interphases is equal to that of the P(VDF-TrFE-CTFE) matrix, $\varepsilon_i/\varepsilon_0 = \varepsilon_m/\varepsilon_0 = 52$, the thicknesses of the interphases are one-third the size of the radius of the particles that they surround, $t_i/R_p \doteq (R_i - R_p)/R_p = (c_i/c_p + 1)^{1/3} - 1 = 1/3$, and the charge-content parameter is $q_i/\varepsilon_0 = 5200$, two orders of magnitude larger than the matrix permittivity. The triangles correspond to the experiments (measured at room temperature and 1000 Hz) of Huang and Zhang.[1] The dashed line corresponds to the Milton formula (12), which, again, accounts for a finite-size interphase between the particles and the matrix but *not* for interphasial charges. In particular, the result displayed in the figure corresponds to interphases of infinite permittivity, $\varepsilon_i/\varepsilon_0 = +\infty$, whose thicknesses are one-third the size of the particles that they surround, $t_i/R_p = 1/3$. Finally, the dotted line corresponds to the MG formula (11), which does not account for any interphasial phenomena whatsoever.

The main observation from Fig. 3 is that the theoretical result (10) is able to describe the drastic enhancement exhibited by the experimental data when evaluated at physically sound values of the size of the interphases ($t_i/R_p = 1/3$) and their charge content ($q_i/\varepsilon_0 = 5200$). Another key observation is that interphases with (infinitely) high permittivity but that do not contain space charges can generate a substantial enhancement of the macroscopic dielectric response but not in any way as substantial as that generated by interphases that do contain charges. From the glaring disagreement of the MG formula with the other three results, Fig. 3 also makes it plain that interphasial phenomena, as expected, dominate the dielectric response of nanocomposites.

Figure 4 shows results for the relative permittivity $\varepsilon_*/\varepsilon_0$ of a PDMS (polydimethylsiloxane) elastomer filled with polycrystalline anatase titania particles, for a range of small volume fractions of particles c_p. PDMS is a dielectric elastomer with permittivity approximately given by $\varepsilon_m/\varepsilon_0 = 3.5$. The permittivity of the polycrystalline anatase titania utilized here is much higher, $\varepsilon_p/\varepsilon_0 = 100$.

The triangles and circles in Fig. 4 correspond to new[20] experimental data (obtained at room temperature and at 1000 Hz). In particular, the triangles correspond to nanocomposites wherein the titania particles are spheres of radius $R_p = 10$ nm; Fig. 1 shows a representative electron micrograph of one of the samples with particle volume fraction $c_p = 0.01$. The circles, on the other hand, correspond to microcomposites wherein the titania particles are only roughly spherical in shape (since they were synthesized in the form of a fine powder) and about 1 μm in average radius. Moreover, the solid line in Fig. 4 corresponds to the theoretical result (10) for the case when the permittivity of the interphases is equal to that of the PDMS matrix, $\varepsilon_i/\varepsilon_0 = \varepsilon_m/\varepsilon_0 = 3.5$, the interphase-thickness-to-particle-radius ratio is $t_i/R_p = 0.35$, and the charge-content parameter is $q_i/\varepsilon_0 = -350$. The dashed line pertains to the Milton formula (12) for the case of interphases with the limiting permittivity of vacuum, $\varepsilon_i/\varepsilon_0 = 1$, whose ratio of thickness to particle radius is $t_i/R_p = 0.35$. The dotted line stands again for the MG formula (11).

It is plain from Fig. 4 that the MG formula correlates well with the experimental results for the microcomposite—where interphases are expected to be negligible—but *not* with those for the nanocomposite, which, consistent with earlier observations,[2] are seen to exhibit a reduction in permittivity with the addition of titania particles (in spite of the fact that titania has a much higher permittivity than PDMS). The Milton result accounting for interphases of physically plausible size (3.5 nm in thickness, since $t_i = 0.35 \times R_p = 3.5$ nm) with much lower permittivity (that of vacuum in fact, $\varepsilon_i/\varepsilon_0 = 1$) than that of the matrix is seen to lead to slightly lower permittivities with the addition of particles, but not in any way as low as those experimentally displayed by the nanocomposite. By contrast, the theoretical result (10) accounting for interphases with the same physically plausible size (3.5 nm in thickness) that contain a small content of charges ($q_i/\varepsilon_0 = -350$) is able to describe the drastic reduction in dielectric response exhibited by the nanocomposite.

FIG. 4. Relative permittivity $\varepsilon_*/\varepsilon_0$ of a PDMS elastomer ($\varepsilon_m/\varepsilon_0 = 3.5$) filled with polycrystalline anatase titania particles ($\varepsilon_p/\varepsilon_0 = 100$), as a function of the volume fraction of particles c_p. The data shown correspond to the theoretical result (10) accounting for interphasial charges (solid line), experiments wherein the particles are 10 nm (triangles) and 1 μm (circles) in radius, the result (12) of Milton accounting for interphases with much lower permittivity than that of the matrix (dashed line), and the MG formula (dotted line).

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[11]In this regard, it is important to emphasize that the vast majority of homogenization techniques and results currently available[14] make critical use of the assumption that source terms (such as, for instance, space charges, body forces, and heat sources) oscillate only at the macroscale.

[12]For definiteness, we restrict attention here to the case of *isotropic* microstructures and *isotropic* constitutive properties. However, the arguments apply more generally to particulate composites with anisotropic microstructures and anisotropic constitutive properties.[21]

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