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Influence of interfacial surface conduction on the DC electrical conductivity of particle reinforced composites

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We describe new effects associated with electrical conduction along phase interfaces for particle reinforced conductors. For particles of general shape we introduce a new quantity β_1 called the 'surface to volume dissipation' of a particle. This quantity is a measure of the particle's ability to dissipate energy on its surface relative to the energy dissipated in its interior. It is described mathematically as the minimum value of a suitably defined Rayleigh quotient and is related to an eigenvalue problem posed on the particle surface. We consider the overall conductivity of a particle reinforced conductor when the particle conductivities are less than that of the matrix. It is shown that the overall conductivity will be increased by the presence of a specific particle when the particle's 'surface to volume dissipation' lies above a critical value. We calculate the surface to volume dissipation for a sphere and for starlike particles we provide a lower bound in terms of particle dimensions. These estimates allow for the prediction of new particle size effects. Second, we present a new criterion on the particle size distribution for which the overall conductivity lies below the matrix conductivity.

Keywords: surface-to-volume dissipation; interfacial surface conductivity

1. Introduction

We consider particle reinforced composite materials. The case when electrical conduction occurs along phase interfaces as well as inside the particle and matrix phases is addressed. The interfacial surface conductivity has dimensions of 'conductivity $\times$ length' and is denoted by α. The conductivity of each particle is allowed to be different. Both matrix and particles are assumed to have anisotropic conducting properties. We focus on a specific particle and denote its conductivity tensor by $\boldsymbol{c}_{\mathrm{p}}$. We denote the matrix conductivity by $\boldsymbol{c}_{\mathrm{m}}$ and suppose that the conductivity of the particle is less than the matrix, i.e. $\boldsymbol{c}_{\mathrm{p}} < \boldsymbol{c}_{\mathrm{m}}$. This inequality holds in the sense of quadratic forms. We identify a new quantity called the 'surface to volume dissipation' associated with the particle. It is shown that the overall conductivity is increased by the presence of the particle when the particle's surface to volume dissipation lies above a critical value. This result holds independently of the location and conductivities of the other particles in the suspension. The second result presented is a new criterion on the suspension geometry for which the overall conductivity lies below the

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conductivity of the matrix material. New results relating the size distribution of a polydisperse suspension of spheres to its effective conductivity are found.

The composite domain is denoted by Ω and its volume is given by $|\Omega|$. For a suspension of N particles, the conductivity inside the composite is described by $\boldsymbol{c}(\boldsymbol{x})$ taking the values $\boldsymbol{c}_{\mathrm{p}}^{i}$ in the ith particle and $\boldsymbol{c}_{\mathrm{m}}$ in the matrix. The electric potential in the composite is denoted by φ. On the boundary of Ω we suppose that the potential is given by the linear function $\boldsymbol{E}\cdot\boldsymbol{x}$, where $\boldsymbol{E}$ is a constant vector. Inside the particle and matrix phases the current is denoted by $\boldsymbol{j}$. The current is related to the potential by the constituitive law $\boldsymbol{j}=\boldsymbol{c}(\boldsymbol{x})\nabla\varphi$ and in each phase we have

$$\operatorname{div}(\boldsymbol{j})=0. \tag{1.1}$$

The potential is continuous across phase interfaces and on the matrix-particle interface we have:

$$\boldsymbol{j}_{\mathrm{m}}\cdot\boldsymbol{n}-\boldsymbol{j}_{\mathrm{p}}\cdot\boldsymbol{n}=-\alpha\Delta_{\mathrm{s}}\varphi. \tag{1.2}$$

Here Δ_{s} denotes the surface Laplacian on the interface, the subscripts indicate on which side of the interface the normal component of the current is evaluated, and $\boldsymbol{n}$ is the unit normal pointing into the matrix phase.

We observe from (1.2) that the jump in the normal component of the current produces an interfacial surface charge density that is coupled to the electric potential through a Poisson equation on the interface. The interface jump condition given by (1.2) models, to first approximation, the effects of a thin highly conducting interphase layer between the matrix and particle phases. Indeed one can show rigorously that (1.2) is obtained in the distinguished limit of vanishing layer thickness and increasing interphase conductivity (see Pham Huy & Sanchez-Palencia 1974). The effective conductivity $\boldsymbol{c}_{\mathrm{e}}$ is given by

$$\boldsymbol{c}_{\mathrm{e}}\boldsymbol{E}=|\Omega|^{-1}\int_{\partial\Omega}c(\boldsymbol{x})\nabla\varphi\cdot\boldsymbol{n}\boldsymbol{x}\,\mathrm{d}s. \tag{1.3}$$

Here $\mathrm{d}s$ is the element of surface area, and the vector $\boldsymbol{n}$ is the exterior unit normal.

We denote the region occupied by the particle phase by A_{p} and the region occupied by the matrix by A_{m}. The interface between the particle and matrix phase is assumed sufficiently regular in order for the jump condition (1.2) to hold and is denoted by Γ.

The energy dissipated inside the composite is given by the variational principle:

$$\boldsymbol{c}_{\mathrm{e}}\boldsymbol{E}\cdot\boldsymbol{E}=\min_{\phi\in V}\{C(A_{\mathrm{p}},\phi)\}, \tag{1.4}$$

with

$$C(A_{\mathrm{p}},\phi)=|\Omega|^{-1}\left\{\int_{\Omega}\boldsymbol{c}(\boldsymbol{x})\nabla\phi\cdot\nabla\phi\,\mathrm{d}x+\alpha\int_{\Gamma}|\nabla_{\mathrm{s}}\phi|^{2}\,\mathrm{d}s\right\}, \tag{1.5}$$

and

$$V=\left\{\phi:\int_{\Omega}|\nabla\phi|^{2}+|\phi|^{2}\,\mathrm{d}x<\infty,\quad \phi=\boldsymbol{E}\cdot\boldsymbol{x},\quad \text{on } \partial\Omega\right\}. \tag{1.6}$$

Here ∇_{s} is the gradient operator on the interfacial surface and the minimzer of (1.4) is precisely the electric potential φ.

The effect of a particular particle on the overall conductivity is considered. The conductivity of the particle is denoted by $\boldsymbol{c}_{\mathrm{p}}$ and $\boldsymbol{c}_{\mathrm{p}}<\boldsymbol{c}_{\mathrm{m}}$. We provide the geometric criterion that determines the length scale at which interfacial conduction compensates for the lower conductivity of the particle. This criterion is general and applies to any particle shape. In order to give the criterion, we introduce the matrix $\boldsymbol{P}_{\mathrm{cr}}$ given by

$$\boldsymbol{P}_{\mathrm{cr}} = \alpha(\boldsymbol{c}_{\mathrm{m}} - \boldsymbol{c}_{\mathrm{p}})^{-1}. \tag{1.7}$$

Here each element of $\boldsymbol{P}_{\mathrm{cr}}$ has dimensions of length. This quantity provides a measure of the relative magnitude of the interfacial conductance with respect to the mismatch between the conductivity tensors of the matrix and particle. Denoting the domain of the particle by Σ, we introduce a geometric quantity called the 'surface to volume dissipation' of the particle. The 'surface to volume dissipation' is denoted by $\beta_1(\boldsymbol{c}_{\mathrm{p}})$ and has dimensions of (conductivity $\times$ length)$^{-1}$. It is given by the following quotient:

$$\beta_1(\boldsymbol{c}_{\mathrm{p}}) = \min_{\phi\in\mathcal{U}} \frac{\displaystyle\int_{\partial\Sigma} |\nabla_{\mathrm{s}}\phi|^2 \,\mathrm{d}s}{\displaystyle\int_{\Sigma} \boldsymbol{c}_{\mathrm{p}}\nabla\phi\cdot\nabla\phi\,\mathrm{d}x}. \tag{1.8}$$

Here the class of admissable functions is given by

$$\mathcal{U} = \left\{\phi \middle| \operatorname{div}(\boldsymbol{c}_{\mathrm{p}}\nabla\phi) = 0, \quad \int_{\partial\Sigma}\phi\,\mathrm{d}s = 0, \quad \phi \neq 0\right\}.$$

The minimizer of (1.8) is the 'surface to volume dissipation potential' denoted by φ_{β_1}. Taking the first variation of the quotient (1.8) shows that β_1 is the first eigenvalue of the eigenvalue problem on the particle surface given by

$$-\,\Delta_{\mathrm{s}}\varphi_\beta = \beta\boldsymbol{n}\cdot\boldsymbol{c}_{\mathrm{p}}\nabla\varphi_\beta, \quad \text{on } \partial\Sigma, \tag{1.9}$$

where $\operatorname{div}(\boldsymbol{c}_{\mathrm{p}}\nabla\varphi_\beta) = 0$ inside the particle. Since $\operatorname{div}(\boldsymbol{c}_{\mathrm{p}}\nabla\varphi_{\beta_1}) = 0$ inside the particle, we see that equation (1.9) shows that the surface Laplacian of φ_{β_1} is proportional to the Dirichlet to Neumann map of the potential φ_{β_1}.

The 'surface to volume dissipation' is a measure of the particle's ability to dissipate energy on its surface relative to the energy dissipated in its interior. For spherical particles filled with isotropic material of conductivity c_{p} we show in § 3 that this ratio is proportional to the reciprocal of the sphere radius a and is given by $\beta_1 = 2/(c_{\mathrm{p}}a)$. For more general shapes we provide lower bounds on the 'surface to volume dissipation' in terms of the physical dimensions of the particle (see § 3).

For a fixed configuration of particles occupying the region A_{p} we add the new particle Σ of conductivity $\boldsymbol{c}_{\mathrm{p}}$ to the suspension. We assume that the particle Σ is compactly contained in the matrix, (i.e. $\Sigma \subset A_{\mathrm{m}}$ and $\partial\Sigma \cap \partial A_{\mathrm{m}} = \emptyset$). The region occupied by the particle phase is now given by $A_{\mathrm{p}} \cup \Sigma$ and the associated effective conductivity tensor is denoted by $\tilde{\boldsymbol{c}}_{\mathrm{e}}$. The principal result given in this paper is the following criterion on the particle geometry.

Theorem 1.1. (Energy dissipation inequality). *Given a reinforcement particle Σ, if its 'surface to volume dissipation' β_1 satisfies*

$$\boldsymbol{P}_{\mathrm{cr}}^{-1} \leqslant \boldsymbol{c}_{\mathrm{p}}\beta_1(\boldsymbol{c}_{\mathrm{p}}), \tag{1.10}$$

then

$$\tilde{\boldsymbol{c}}_{\mathrm{e}} \geqslant \boldsymbol{c}_{\mathrm{e}}. \tag{1.11}$$

Here (1.10) and (1.11) hold in the sense of quadratic forms. No assumptions on the topological nature of the particle domain Σ is made. Indeed it can be a disjoint union of multiply connected components. We emphasize that this result holds independently of the location and conductivities of the other particles in the suspension. This inequality is established in § 2. The 'surface to volume dissipation' of a sphere is calculated in § 3. For particles that are starlike we provide explicit lower bounds on β_1 in § 3. These observations together with the energy dissipation inequality are applied in § 4 to obtain energy dissipation inequalities in terms of the physical dimensions of the particle. Such size-effect inequalities predict the existence of a critical particle dimension below which the particle will always increase the overall conductivity of the composite. These predictions apply to a wide class of particle shapes. We remark that the lower bound on β_1 given in § 3 when applied to a sphere lies strictly below the actual value. In § 5 we provide tighter lower bounds that agree with the actual value of β_1 for spherical particles. For more general particle shapes, like sphereoids or chopped fibres, the tighter bound is not explicitly given by a formula, but can be computed numerically.

Earlier size effects have been found in the context of isotropic monodisperse suspensions of isotropically conducting spheres in an isotropically conducting matrix. The conductivities of the matrix and particles are given by the scalars c_{p} and c_{m} and the quantity $\boldsymbol{P}_{\mathrm{cr}}$ reduces to the scalar $P_{\mathrm{cr}} = \alpha(c_{\mathrm{m}} - c_{\mathrm{p}})^{-1}$. For this case the results have focused on critical radii for a monodisperse suspension of spheres. Here the critical radius is precisely $2P_{\mathrm{cr}}$ and is that for which the overall conductivity of the composite equals that of the matrix conductivity. The critical radius was found by Lipton (1995) and by Torquato & Rintoul (1995) using different methods. In Lipton (1995), this effect is shown to persist even if the suspension is not isotropic. Moreover, the electric field is shown to be uniform throughout the composite and is precisely $\boldsymbol{E}$ (see Lipton 1995). For isotropic monodisperse suspensions of isotropically conducting spheres Torquato & Rintoul (1995) have shown that the overall conductivity lies above the matrix value when the common sphere radii are below $2P_{\mathrm{cr}}$ and that the overall conductivity is decreased when the radii lie above $2P_{\mathrm{cr}}$. More recently, results involving the statistics of the size distribution of spheres have been found in the context of isotropic polydisperse suspensions of spheres (see Lipton 1996*a*). There it is shown that if the arithmetic mean of the sphere radii lie below $2P_{\mathrm{cr}}$ then the effective conductivity lies above the matrix value. It is also shown that if the harmonic mean of the sphere radii lie above $2P_{\mathrm{cr}}$ then the effective conductivity lies below that of the matrix. In § 6 we show that this phenomenon persists even when the suspension is anisotropic. We conclude the paper with an application to ionic diffusion in concrete structures.

2. Energy dissipation inequality

We establish the energy dissipation inequality given in § 1. For any constant vector $\boldsymbol{E}$ in R^3, we can write the difference $\delta = \tilde{\boldsymbol{c}}_{\mathrm{e}}\boldsymbol{E}\cdot\boldsymbol{E} - \boldsymbol{c}_{\mathrm{e}}\boldsymbol{E}\cdot\boldsymbol{E}$ as

$$\delta = C(A_{\mathrm{p}}, \tilde{\varphi}) - C(A_{\mathrm{p}}, \varphi) + R(\Sigma, \tilde{\varphi}), \tag{2.1}$$

where $\tilde{\varphi}$ is the potential associated with the configuration of particles given by $A_{\mathrm{p}} \cup \Sigma$ and the remainder $R(\Sigma, \tilde{\varphi})$ is given by

$$R(\Sigma, \tilde{\varphi}) = \alpha \int_{\partial\Sigma} |\nabla_{\mathrm{s}}\tilde{\varphi}|^2 \,\mathrm{d}s - \int_{\Sigma} (\boldsymbol{c}_{\mathrm{m}} - \boldsymbol{c}_{\mathrm{p}})\nabla\tilde{\varphi}\cdot\nabla\tilde{\varphi}\,\mathrm{d}x. \tag{2.2}$$

Noting that $\tilde{\varphi}$ is an admissable trial for the variational principle (1.4) we have

$$C(A_\mathrm{p}, \tilde{\varphi}) - C(A_\mathrm{p}, \varphi) \geqslant 0, \tag{2.3}$$

thus

$$\delta \geqslant R(\Sigma, \tilde{\varphi}). \tag{2.4}$$

From (1.8) it follows that

$$\int_{\partial\Sigma} |\nabla_\mathrm{s}\phi|^2 \, \mathrm{d}s - \beta_1 \int_\Sigma \boldsymbol{c}_\mathrm{p} \nabla\phi \cdot \nabla\phi \, \mathrm{d}x \geqslant 0, \tag{2.5}$$

for every function ϕ such that $\mathrm{div}(\boldsymbol{c}_\mathrm{p}\nabla\phi) = 0$. Comparing the right-hand side of (2.2) with (2.5), we discover that

$$\delta \geqslant 0, \tag{2.6}$$

for

$$\alpha^{-1}(\boldsymbol{c}_\mathrm{m} - \boldsymbol{c}_\mathrm{p}) \leqslant \boldsymbol{c}_\mathrm{p}\beta_1(\boldsymbol{c}_\mathrm{p}), \tag{2.7}$$

and the energy dissipation inequality follows. We observe that strict inequality in (2.6) follows from strict inequality in (2.7) provided $\tilde{\varphi}$ is not identically equal to a constant in Σ.

3. The surface to volume dissipation of a sphere and lower bounds on β_1 for starlike particles

We calculate the surface to volume dissipation for a spherical particle of radius a filled with material of unit conductivity. Separation of variables in the eigenvalue problem (1.9) shows that the surface to volume dissipation is given by

$$\beta_1 = 2/a. \tag{3.1}$$

The associated eigenspace is given by the span of the coordinate functions x_1, x_2, x_3 restricted to the surface of the sphere. We remark that separation of variables shows that the set of eigenvalues for the eigenvalue problem (1.9) is given by $n(n+1)/a$ for $n = 1, 2, \ldots$. The associated eigenspace for the nth eigenvalue is the span of the spherical harmonics of order n given by $a^n \mathrm{e}^{\mathrm{i}m\omega} P_n^m(\cos(\theta))$, $m = 1, \ldots, n$ restricted to the surface of the sphere. Here $P_n^m(x)$ are the Legendre functions and ω, θ are polar coordinates on the unit sphere. For a sphere filled with an isotropic conductor of conductivity c_p we easily obtain that $\beta_1 = 2/(c_\mathrm{p} a)$.

Next we consider particles Σ that are starlike with respect to a point $\breve{x}$ inside Σ. We introduce the quantitiy $h_\mathrm{m}(\breve{x}) \equiv \min_{\boldsymbol{x}\in\partial\Sigma}\{(\boldsymbol{x} - \breve{x}) \cdot \boldsymbol{n}\}$. Here $\boldsymbol{n}$ is the unit outward normal to the boundary of Σ. The minimum distance from the point $\breve{x}$ to a tangent plane on the boundary is given by $h_\mathrm{m}(\breve{x})$. Since the domain is starlike with respect to $\breve{x}$ we have $h_\mathrm{m}(\breve{x}) > 0$. The maximum distance from $\breve{x}$ to a point on the boundary is given by $r_\mathrm{M}(\breve{x})$. We denote the largest eigenvalue of the particle conductivity tensor $\boldsymbol{c}_\mathrm{p}$ by γ and state the following inequality.

Theorem 3.1. (A lower bound on the surface to volume dissipation for starlike particles). *If the particle Σ is starlike with respect to the point $\breve{x}$, then*

$$\beta_1(\boldsymbol{c}_\mathrm{p}) \geqslant \frac{1}{r_\mathrm{M}(\breve{x})} \left(\frac{1/\gamma}{3 + r_\mathrm{M}(\breve{x})/h_\mathrm{m}(\breve{x})} \right). \tag{3.2}$$

To establish the lower bound we may assume that the particle Σ is starlike with respect to the origin and appeal to the identity

$$\partial_k\{(x_k(\boldsymbol{c}_\mathrm{p})_{ij} - x_i(\boldsymbol{c}_\mathrm{p})_{kj} - x_j(\boldsymbol{c}_\mathrm{p})_{ik})\partial_i u \partial_j u\} = -2(\boldsymbol{x}\cdot\nabla u)(\mathrm{div}(\boldsymbol{c}_\mathrm{p}\nabla u)) + \boldsymbol{c}_\mathrm{p}\nabla u\cdot\nabla u. \tag{3.3}$$

Here repeated indices are to be summed. Integration over the particle Σ and application the Gauss–Green theorem gives

$$\int_{\partial\Sigma}(\boldsymbol{n}\cdot\boldsymbol{x})\boldsymbol{c}_\mathrm{p}\nabla u\cdot\nabla u - 2(\boldsymbol{x}\cdot\nabla u)(\boldsymbol{n}\cdot\boldsymbol{c}_\mathrm{p}\nabla u)\,\mathrm{d}s = -2\int_\Sigma(\boldsymbol{x}\cdot\nabla u)(\mathrm{div}(\boldsymbol{c}_\mathrm{p}\nabla u))\,\mathrm{d}x + \int_\Sigma \boldsymbol{c}_\mathrm{p}\nabla u\cdot\nabla u\,\mathrm{d}x. \tag{3.4}$$

We consider trial functions u such that $\mathrm{div}(\boldsymbol{c}_\mathrm{p}\nabla) = 0$ inside Σ and we decompose the gradient ∇u on the boundary $\partial\Sigma$ into its normal and tangential parts to obtain

$$\begin{aligned}\int_{\partial\Sigma}(\boldsymbol{n}\cdot\boldsymbol{x})\boldsymbol{c}_\mathrm{p}\nabla_\mathrm{s}u\cdot\nabla_\mathrm{s}u\,\mathrm{d}s &- \int_{\partial\Sigma}(\boldsymbol{c}_\mathrm{p}\boldsymbol{n}\cdot\boldsymbol{n})(\boldsymbol{n}\cdot\boldsymbol{x})(\partial_n u)^2\,\mathrm{d}s - 2\int_{\partial\Sigma}(\boldsymbol{c}_\mathrm{p}\boldsymbol{n}\cdot\boldsymbol{n})(\boldsymbol{x}\cdot\nabla_\mathrm{s}u)(\partial_n u)\,\mathrm{d}s \\ &-2\int_{\partial\Sigma}(\boldsymbol{x}\cdot\nabla_\mathrm{s}u)(\boldsymbol{c}_\mathrm{p}\boldsymbol{n}\cdot\nabla_\mathrm{s}u)\,\mathrm{d}s = \int_\Sigma \boldsymbol{c}_\mathrm{p}\nabla u\cdot\nabla u\,\mathrm{d}x.\end{aligned} \tag{3.5}$$

Here we have written the normal derivitave $\boldsymbol{n}\cdot\nabla u$ as $\partial_n u$. Next we apply Cauchy's inequality to find

$$\left.\begin{aligned}-2(\boldsymbol{c}_\mathrm{p}\boldsymbol{n}\cdot\boldsymbol{n})(\boldsymbol{x}\cdot\nabla_\mathrm{s}u)(\partial_n u) &\leqslant (\boldsymbol{c}_\mathrm{p}\boldsymbol{n}\cdot\boldsymbol{n})(\zeta(\boldsymbol{x}\cdot\nabla_\mathrm{s}u)^2 + \zeta^{-1}(\partial_n u)^2),\\ -2(\boldsymbol{x}\cdot\nabla_\mathrm{s}u)(\boldsymbol{c}_\mathrm{p}\boldsymbol{n}\cdot\nabla_\mathrm{s}u) &\leqslant 2|\boldsymbol{c}_\mathrm{p}\boldsymbol{n}||\boldsymbol{x}||\nabla_\mathrm{s}u|^2,\end{aligned}\right\} \tag{3.6}$$

and

$$(\boldsymbol{x}\cdot\nabla_\mathrm{s}u)^2 \leqslant |\boldsymbol{x}|^2|\nabla_\mathrm{s}u|^2. \tag{3.7}$$

Here ζ is any positive real number. Applying (3.6) and (3.7), noting that $\boldsymbol{c}_\mathrm{p} \leqslant \gamma I$ in the sense of quadratic forms, and $|\boldsymbol{n}| = 1$ we obtain

$$\int_\Sigma \boldsymbol{c}_\mathrm{p}\nabla u\cdot\nabla u dx \leqslant \int_{\partial\Sigma}\gamma(2|\boldsymbol{x}|+\boldsymbol{n}\cdot\boldsymbol{x}+\zeta|\boldsymbol{x}|^2)|\nabla_\mathrm{s}u|^2 - \int_{\partial\Sigma}\gamma(\boldsymbol{n}\cdot\boldsymbol{x}-\zeta^{-1})(\partial_n u)^2\,\mathrm{d}s. \tag{3.8}$$

We have the inequality $h_\mathrm{m}(0) \leqslant \boldsymbol{n}\cdot\boldsymbol{x}$ for $\boldsymbol{x}$ on the boundary of Σ. Thus we set $\zeta^{-1} = h_\mathrm{m}(0)$ to find

$$\int_\Sigma \boldsymbol{c}_\mathrm{p}\nabla u\cdot\nabla u\,\mathrm{d}x \leqslant \int_{\partial\Sigma}\gamma(2|\boldsymbol{x}| + \boldsymbol{n}\cdot\boldsymbol{x} + h_\mathrm{m}(0)^{-1}|\boldsymbol{x}|^2)|\nabla_\mathrm{s}u|^2\,\mathrm{d}s. \tag{3.9}$$

Lastly we note that $\boldsymbol{n}\cdot\boldsymbol{x} \leqslant |\boldsymbol{x}|$, to obtain

$$\int_\Sigma \boldsymbol{c}_\mathrm{p}\nabla u\cdot\nabla u\,\mathrm{d}x \leqslant \gamma\{3r_\mathrm{M}(0) + r_\mathrm{M}(0)^2/h_\mathrm{m}(0)\}\int_{\partial\Sigma}|\nabla_\mathrm{s}u|^2\,\mathrm{d}s. \tag{3.10}$$

The lower bound on β_1 follows noting that (3.10) holds for all functions u such that $\mathrm{div}(\boldsymbol{c}_\mathrm{p}\nabla u) = 0$ on Σ.

4. Novel size effects for particle reinforced composites with interfacial surface conduction

It follows from the energy dissipation inequality and (3.1) that if Σ is a sphere of radius a filled with isotropic conductor $c_{\rm p}$, then the following theorem holds.

Theorem 4.1. (Size effect for spheres).

$$\tilde{\boldsymbol{c}}_{\rm e} \geqslant \boldsymbol{c}_{\rm e}, \tag{4.1}$$

if

$$a\boldsymbol{I} \leqslant 2\alpha(c_{\rm p}\boldsymbol{I} - \boldsymbol{c}_{\rm m})^{-1}. \tag{4.2}$$

This inequality holds in the sense of quadratic forms. (i.e. (4.1) holds if a is less than or equal to the least eigenvalue of the matrix $2\alpha(c_{\rm p}\boldsymbol{I} - \boldsymbol{c}_{\rm m})^{-1}$.)

When both matrix and particles have isotropic conductivities specified by $c_{\rm m}$ and $c_{\rm p}$, respectively, then we have the following.

Theorem 4.2. (Size effect for an isotropically conducting spherical particle in an isotropic matrix).

$$\tilde{\boldsymbol{c}}_{\rm e} \geqslant \boldsymbol{c}_{\rm e}, \tag{4.3}$$

if

$$a \leqslant 2P_{\rm cr} = 2\alpha(c_{\rm m} - c_{\rm p})^{-1}. \tag{4.4}$$

More generally, we consider starlike inclusions Σ. We apply the inequality (3.2) together with the energy dissipation inequality to obtain the following theorem.

Theorem 4.3. (Size effect for starlike particles). *Given that Σ is starlike with respect to a point $\breve{x}$ inside Σ, then*

$$\tilde{\boldsymbol{c}}_{\rm e} \geqslant \boldsymbol{c}_{\rm e}, \tag{4.5}$$

if

$$\{r_{\rm M}(\breve{x})(3 + r_{\rm M}(\breve{x})/h_{\rm m}(\breve{x}))\}\gamma \boldsymbol{c}_{\rm p}^{-1} \leqslant \boldsymbol{P}_{\rm cr}. \tag{4.6}$$

We consider an ellipsoidal particle. Here we suppose that the half lengths of the major and minor axes are specified by a and c, respectively. For this case we choose $\breve{x}$ to be the centre of mass for the ellipse and it follows that $r_{\rm M} = a$, $h_{\rm M} = c$, and we have the following theorem.

Theorem 4.4. (Size effect for ellipsoidal reinforcement). *Given an ellipsoidal reinforcement Σ with major and minor axes specified by a and c, respectively, then*

$$\tilde{\boldsymbol{c}}_{\rm e} \geqslant \boldsymbol{c}_{\rm e}, \tag{4.7}$$

if

$$\{a(3 + a/c)\}\gamma \boldsymbol{c}_{\rm p}^{-1} \leqslant \boldsymbol{P}_{\rm cr}. \tag{4.8}$$

Next we consider cylindrical inclusions of length ℓ and radius R and choose $\breve{x}$ to be the centre of mass of the cylinder. If $\frac{1}{2}\ell \geqslant R$ then $r_{\rm M} = ((\frac{1}{2}\ell)^2 + R^2)^{1/2}$ and $h_{\rm m} = R$. On the other hand if $\frac{1}{2}\ell \leqslant R$, then $h_{\rm m} = \frac{1}{2}\ell$. Such inclusions can be used to model chopped fiber suspensions. We have the following.

Theorem 4.5. (Size effect for a cylindrical inclusion with $\frac{1}{2}\ell \geqslant R$).

$$\tilde{\boldsymbol{c}}_{\rm e} \geqslant \boldsymbol{c}_{\rm e}, \tag{4.9}$$

if

$$\{(3R+\sqrt{(\tfrac{1}{2}\ell)^2+R^2})\sqrt{(\ell/(2R))^2+1}\}\gamma c_{\mathrm{p}}^{-1}\leqslant P_{\mathrm{cr}}. \tag{4.10}$$

Theorem 4.6. (Size effect for a cylindrical inclusion with $\frac{1}{2}\ell \leqslant R$).

$$\tilde{c}_{\mathrm{e}} \geqslant c_{\mathrm{e}}, \tag{4.11}$$

if

$$\{(3\tfrac{1}{2}\ell+\sqrt{(\tfrac{1}{2}\ell)^2+R^2})\sqrt{(2R/\ell)^2+1}\}\gamma c_{\mathrm{p}}^{-1}\leqslant P_{\mathrm{cr}}. \tag{4.12}$$

We remark that these inequalities may be used to select particle dimensions for the design of composites with optimal DC conductivity.

5. Tighter lower bounds on the surface to volume dissipation for isotropically conducting particles

When the particle conductivity is isotropic we obtain lower bounds on the surface to volume dissipation that agree with the actual value when the particle is a sphere. For particle shapes such as chopped fibres and ellipsoids these bounds are not given in terms of explicit formulae, but can be computed numerically. For a particle domain Σ starlike with respect to the point $\breve{x}$ we let $r_{\mathrm{m}}(\breve{x})$ denote the minimum distance from $\breve{x}$ to the boundary. In what follows we drop the explicit reference to the point $\breve{x}$ and simply write r_{m}, r_{M}, and h_{m}. The scalar conductivity of the particle is denoted by c_{p}. The lower bound is given by the following theorem.

Theorem 5.1. (Sharp lower bound on the surface to volume dissipation for isotropically conducting starlike particles). *If the particle Σ is starlike with respect to the point $\breve{x}$, then*

$$\beta_1(c_{\mathrm{p}}) \geqslant \max_{0\leqslant\delta\leqslant h_{\mathrm{m}}} \frac{c_{\mathrm{p}}^{-1}\{(h_{\mathrm{m}}-\delta)r_{\mathrm{m}}^2 h_{\mathrm{m}}/r_{\mathrm{M}}^4+1\}}{\max_{x\in\partial\Sigma}\{(\boldsymbol{n}\cdot\boldsymbol{x}+\delta^{-1}r_{\mathrm{m}}^2|\boldsymbol{x}/r_{\mathrm{m}}-\boldsymbol{n}|^2\}}. \tag{5.1}$$

When the particle is a sphere of radius a and $\breve{x}$ is its centre, then $r_{\mathrm{m}}=r_{\mathrm{M}}=h_{\mathrm{m}}=a$ and the lower bound reduces to

$$\max_{0\leqslant\delta\leqslant a}(c_{\mathrm{p}}^{-1}\{(a-\delta)/a+1\})/a. \tag{5.2}$$

The maximum in (5.2) is obtained for $\delta=0$ and the lower bound is precisely the value of β_1 for a sphere given by $2/(c_{\mathrm{p}}a)$.

Without loss of generality we assume that the particle is starlike with respect to the origin and establish the lower bound. We return to the analysis in § 3 and consider equation (3.5). Since the particle conductivity is isotropic the fourth term in (3.5) drops out and we have

$$\int_{\partial\Sigma}(\boldsymbol{n}\cdot\boldsymbol{x})c_{\mathrm{p}}\nabla_{\mathrm{s}}u\cdot\nabla_{\mathrm{s}}u\,\mathrm{d}s-\int_{\partial\Sigma}c_{\mathrm{p}}(\boldsymbol{n}\cdot\boldsymbol{x})(\partial_n u)^2\,\mathrm{d}s-2\int_{\partial\Sigma}c_{\mathrm{p}}(\boldsymbol{x}\cdot\nabla_{\mathrm{s}}u)(\partial_n u)\,\mathrm{d}s = \int_{\Sigma}c_{\mathrm{p}}\nabla u\cdot\nabla u\,\mathrm{d}x. \tag{5.3}$$

Instead of using the estimate (3.7) we note that $\boldsymbol{n}\cdot\nabla_{\mathrm{s}}u=0$ and write

$$(\boldsymbol{x}\cdot\nabla_{\mathrm{s}}u)^2 = r_{\mathrm{m}}^2((\boldsymbol{x}/r_{\mathrm{m}}-\boldsymbol{n})\cdot\nabla_{\mathrm{s}}u)^2 \leqslant r_{\mathrm{m}}^2|\boldsymbol{x}/r_{\mathrm{m}}-\boldsymbol{n}|^2|\nabla_{\mathrm{s}}u|^2. \tag{5.4}$$

We apply the first inequality given in (3.6) together with (5.4) to find

$$\int_{\Sigma} c_{\mathrm{p}}|\nabla u|^2\,\mathrm{d}x + \int_{\partial\Sigma} c_{\mathrm{p}}(\partial_n u)^2(\boldsymbol{n}\cdot\boldsymbol{x}-\zeta^{-1})\,\mathrm{d}s \leqslant \int_{\partial\Sigma} c_{\mathrm{p}}|\nabla_{\mathrm{s}}u|^2(\boldsymbol{n}\cdot\boldsymbol{x}+\zeta r_{\mathrm{m}}^2|\boldsymbol{x}/r_{\mathrm{m}}-\boldsymbol{n}|^2)\,\mathrm{d}s. \tag{5.5}$$

Noting that $\boldsymbol{n}\cdot\boldsymbol{x}\geqslant h_{\mathrm{m}}$ on the particle boundary it is evident that

$$\int_{\Sigma} c_{\mathrm{p}}|\nabla u|^2\,\mathrm{d}x + (h_{\mathrm{m}}-\zeta^{-1})\int_{\partial\Sigma} c_{\mathrm{p}}(\partial_n u)^2\,\mathrm{d}s \leqslant \int_{\partial\Sigma} c_{\mathrm{p}}|\nabla_{\mathrm{s}}u|^2\,\mathrm{d}s\{\max_{\boldsymbol{x}\in\partial\Sigma}(\boldsymbol{n}\cdot\boldsymbol{x}+\zeta r_{\mathrm{m}}^2|\boldsymbol{x}/r_{\mathrm{m}}-\boldsymbol{n}|^2)\}. \tag{5.6}$$

We apply the estimate of Bramble & Payne (1967) as in Lipton (1996*b*: equations (2.2) and (3.5)) to the second term of (5.6) to find

$$\int_{\partial\Sigma} c_{\mathrm{p}}(\partial_n u)^2\,\mathrm{d}s \geqslant \frac{c_{\mathrm{p}}r_{\mathrm{m}}^2h_{\mathrm{m}}}{r_{\mathrm{M}}^4}\int_{\Sigma}|\nabla u|^2\,\mathrm{d}x. \tag{5.7}$$

We restrict $\zeta^{-1}\leqslant h_{\mathrm{m}}$ and substitution of (5.7) into (5.6) gives the inequality:

$$\left\{(h_{\mathrm{m}}-\zeta^{-1})\frac{c_{\mathrm{p}}r_{\mathrm{m}}^2h_{\mathrm{m}}}{r_{\mathrm{M}}^4}+1\right\}\int_{\Sigma} c_{\mathrm{p}}|\nabla u|^2\,\mathrm{d}x \leqslant \int_{\partial\Sigma} c_{\mathrm{p}}|\nabla_{\mathrm{s}}u|^2\,\mathrm{d}s\{\max_{\boldsymbol{x}\in\partial\Sigma}(\boldsymbol{n}\cdot\boldsymbol{x}+\zeta r_{\mathrm{m}}^2|\boldsymbol{x}/r_{\mathrm{m}}-\boldsymbol{n}|^2)\}. \tag{5.8}$$

The lower bound follows upon setting $\delta=\zeta^{-1}$ and noting that (5.8) holds for all functions u for which $\operatorname{div} c_{\mathrm{p}}(\nabla u)=0$.

6. Size effects based on the statistics of the particle size distribution for anisotropic suspensions of anisotropic conductors

We provide a new criterion on the suspension geometry for which the overall conductivity lies below the conductivity of the matrix material. We consider a suspension of N particles each having a possibly different conductivity. The domain occupied by the ith particle is denoted by B_i and its conductivity by $\boldsymbol{c}_{\mathrm{p}}^i$. The total volume occupied by the particle phase is denoted by $|A_{\mathrm{p}}|$ and the fraction of this occupied by the ith particle is denoted by $\theta_i=|B_i|/|A_{\mathrm{p}}|$ and $\sum_{i=1}^N\theta_i=1$. We write the overall electric energy dissipation due to a prescribed potential $\phi=\boldsymbol{E}\cdot\boldsymbol{x}$ on the boundary $\partial\Omega$ as

$$\boldsymbol{c}_{\mathrm{e}}\boldsymbol{E}\cdot\boldsymbol{E}=\min_{\phi\in V}\{C(A_{\mathrm{p}},\phi)\}, \tag{6.1}$$

where

$$C(A_{\mathrm{p}},\phi)=|\Omega|^{-1}\left(\int_{\Omega}\boldsymbol{c}_{\mathrm{m}}\nabla\phi\cdot\nabla\phi\,\mathrm{d}x-\sum_{i=1}^{N}\int_{B_i}(\boldsymbol{c}_{\mathrm{m}}-\boldsymbol{c}_{\mathrm{p}}^i)\nabla\phi\cdot\nabla\phi\,\mathrm{d}x+\alpha\int_{\Gamma}|\nabla_{\mathrm{s}}\phi|^2\,\mathrm{d}s\right). \tag{6.2}$$

The energy dissipated in the region Ω when filled with pure matrix conductor is simply $\boldsymbol{c}_{\mathrm{m}}\boldsymbol{E}\cdot\boldsymbol{E}$. Thus substitution of $\phi=\boldsymbol{E}\cdot\boldsymbol{x}$ into (6.1) gives the estimate

$$\boldsymbol{c}_{\mathrm{e}}\boldsymbol{E}\cdot\boldsymbol{E}\leqslant\boldsymbol{c}_{\mathrm{m}}\boldsymbol{E}\cdot\boldsymbol{E}+\frac{1}{|\Omega|}T(A_{\mathrm{p}},\boldsymbol{E}), \tag{6.3}$$

where

$$T(A_\mathrm{p}, \boldsymbol{E}) \equiv -\sum_{i=1}^{N} \int_{B_i} (\boldsymbol{c}_\mathrm{m} - \boldsymbol{c}_\mathrm{p}) \boldsymbol{E} \cdot \boldsymbol{E} \, \mathrm{d}x + \alpha \int_{\Gamma} |\nabla_\mathrm{s}(\boldsymbol{E} \cdot \boldsymbol{x})|^2 \, \mathrm{d}s.$$

A straightforward computation shows that

$$T(A_\mathrm{p}, \boldsymbol{E}) = \left\{ \alpha \boldsymbol{M} - |A_\mathrm{p}| \sum_{i=1}^{N} \theta_i (\boldsymbol{c}_\mathrm{m} - \boldsymbol{c}_\mathrm{p}^i) \right\} \boldsymbol{E} \cdot \boldsymbol{E}, \tag{6.4}$$

where

$$\boldsymbol{M} = \int_{\Gamma} \{\boldsymbol{I} - \boldsymbol{n} \otimes \boldsymbol{n}\} \, \mathrm{d}s = -3 \int_{\Gamma} \boldsymbol{x} \otimes \boldsymbol{n} \mathcal{H} \, \mathrm{d}s. \tag{6.5}$$

Here $\mathcal{H}$ is the mean curvature of the interface. It is evident that the inequality (6.3) delivers the following criterion.

Theorem 6.1. (Energy dissipation inequality). *If*

$$\sum_{i=1}^{N} \theta_i (\boldsymbol{c}_\mathrm{m} - \boldsymbol{c}_\mathrm{p}^i) \boldsymbol{E} \cdot \boldsymbol{E} > 0 \quad \textit{and} \quad |A_\mathrm{p}|^{-1} \boldsymbol{M} \boldsymbol{E} \cdot \boldsymbol{E} \leqslant \alpha^{-1} \sum_{i=1}^{N} \theta_i (\boldsymbol{c}_\mathrm{m} - \boldsymbol{c}_\mathrm{p}^i) \boldsymbol{E} \cdot \boldsymbol{E}, \tag{6.6}$$

then

$$\boldsymbol{c}_\mathrm{e} \boldsymbol{E} \cdot \boldsymbol{E} \leqslant \boldsymbol{c}_\mathrm{m} \boldsymbol{E} \cdot \boldsymbol{E}. \tag{6.7}$$

For a polydisperse suspension of N spheres of radii $a_1, a_2, \ldots, a_N$, calculation shows that

$$|A_\mathrm{p}|^{-1} \boldsymbol{M} = 2 \langle a^{-1} \rangle \boldsymbol{I}, \tag{6.8}$$

where $\langle a^{-1} \rangle$ is the volume average of the inverse radii given by

$$\langle a^{-1} \rangle = \sum_{i=1}^{N} \theta_i a_i^{-1}. \tag{6.9}$$

We introduce a similar average for the conductivities given by

$$\langle \boldsymbol{c}_\mathrm{p} \rangle = \sum_{i=1}^{N} \theta_i \boldsymbol{c}_\mathrm{p}^i. \tag{6.10}$$

Thus for polydisperse suspensions of spheres we have the following.

Theorem 6.2. (Energy dissipation inequality based upon the size distribution of multi-phase spheres). *If*

$$(\boldsymbol{c}_\mathrm{m} - \langle \boldsymbol{c}_\mathrm{p} \rangle) \boldsymbol{E} \cdot \boldsymbol{E} > 0 \quad \textit{and} \quad \langle a^{-1} \rangle \leqslant \frac{(2\alpha)^{-1} (\boldsymbol{c}_\mathrm{m} - \langle \boldsymbol{c}_\mathrm{p} \rangle) \boldsymbol{E} \cdot \boldsymbol{E}}{|\boldsymbol{E}|^2}, \tag{6.11}$$

then

$$\boldsymbol{c}_\mathrm{e} \boldsymbol{E} \cdot \boldsymbol{E} \leqslant \boldsymbol{c}_\mathrm{m} \boldsymbol{E} \cdot \boldsymbol{E}. \tag{6.12}$$

When all particles have the same conductivity given by $\boldsymbol{c}_\mathrm{p}$ with $\boldsymbol{c}_\mathrm{m} > \boldsymbol{c}_\mathrm{p}$ the previous result reduces to the following theorem.

Theorem 6.3. (Energy dissipation inequality based upon the size distribution of spheres). *If*

$$\langle a^{-1} \rangle \leqslant \frac{(2\mathrm{P}_\mathrm{cr})^{-1} \boldsymbol{E} \cdot \boldsymbol{E}}{|\boldsymbol{E}|^2}, \tag{6.13}$$

then

$$c_e \boldsymbol{E} \cdot \boldsymbol{E} \leqslant c_m \boldsymbol{E} \cdot \boldsymbol{E}. \tag{6.14}$$

We denote the smallest eigenvalue of the matrix $(2\mathbf{P}_{cr})^{-1}$ by λ_c. It follows immediately from the previous inequality that

$$\text{If } \langle a^{-1} \rangle \leqslant \lambda_c, \quad \text{then } \boldsymbol{c}_e \leqslant \boldsymbol{c}_m \text{ in the sense of quadratic forms.} \tag{6.15}$$

We conclude noting that when both matrix and particle conductors are isotropic that $\lambda_c = (c_m - c_p)/(2\alpha)$ and we have the following.

Theorem 6.4. (Energy dissipation inequality for isotropically conducting spheres in an isotropic matrix).

$$\boldsymbol{c}_e \leqslant \boldsymbol{c}_m \textit{ in the sense of quadratic forms when } \langle a^{-1} \rangle^{-1} \geqslant \frac{2\alpha}{c_m - c_p}. \tag{6.16}$$

We stress that these results hold for anisotropic suspensions.

7. Conclusions and applications

The balance between the effects of a poorly conducting particle and the influence of a conducting interface between particle and matrix phase is examined. The relative influence of these effects is captured by a new quantity that is referred to as the *surface to volume dissipation*. This quantity measures the energy dissipated on the particle surface relative to the energy dissipated inside the particle. When this parameter lies above a critical value, determined by the ratio of the interfacial conductivity to the contrast between particle and matrix conductivities, then the influence of interfacial conductance compensates for the reduced particle conductivity and the overall conductivity of the composite is increased. This holds independently of the conductivities and location of all other particles in the suspension.

The result stated above shows that under the right conditions the presence of interfacial conducting paths will increase the overall conductivity beyond that of the matrix phase even below the interfacial percolation threshold. To see this we consider the conductivity of a container filled with pure matrix material. We compare it to the overall conductivity of a similar container containing a single particle embedded in the matrix. We see that if the surface to volume dissipation of the particle is above the critical value then the overall conductivity of the container filled with matrix and particle is no less than the pure matrix conductivity. For suspensions with several particles, it follows from the results of this paper and similar arguments that if every particle in the suspension has a surface to volume dissipation above the critical value then the overall conductivity is as least as good as the conductivity of the matrix material.

One practical application of the physico-mathematical model treated here is the modelling of ionic diffusion in concrete. This phenomenon is important as ions react with steel reinforcements in the concrete, corroding them and compromising the overall structural properties (Garboczi & Bentz 1996). On the scale of meters concrete may be treated as consisting of a matrix of cement paste with the particle phase being fine aggregates (sand) or coarse aggregates (rocks) (see Garboczi & Bentz 1996). It has been shown that the interfacial transition zone separating the cement paste and the aggregate is a major influence on the overall properties (see Bentz *et* *al.* 1994). The ionic diffusivity in the interface zone is greater than that of the paste and aggregate. Both the cement paste and interface zone conduct electricity. In light of the Nerst–Einstein relation (Atkinson & Nickerson 1984; Garboczi & Bentz 1992) there is a direct relation between the DC electrical conductivity of concrete and the ionic diffusivity. Thus in the applications the overall ionic diffusivity is determined by DC electrical conductivity measurements Garboczi & Bentz (1996). The results given in this paper predict that for sufficiently small aggregates the overall ionic diffusivity of concrete will be greater than that of the cement paste even when the interfacial transition zones do not percolate. On the other hand if the aggregates are modelled as spheres, the results of § 6 give requirements on the aggregate size distribution for which the overall ionic diffusivity of concrete will be less than that of the cement paste. This is desirable if one seeks to mitigate the effects of corrosion in steel reinforced concrete structures.

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