

# Composites with imperfect interface

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New variational principles and bounds are introduced, describing the effective conductivity tensor for anisotropic two-phase heat conducting composites with interfacial surface resistance between phases.

The new upper bound is given in terms of the two-point correlation function, component volume fractions and moment of inertia tensor for the surface of each heterogeneity. The new lower bound is given in terms of the interfacial surface area, component volume fractions and a scale-free matrix of parameters. This matrix corresponds to the effective conductivity associated with the same geometry but with non-conducting inclusions.

The bounds are applied to theoretically predict the occurrence of size effect phenomena. We identify a parameter  $R_{cr}$  that measures the relative importance of interfacial resistance and contrast between phase resistivities. The scale at which size effects occur is determined by this parameter. For isotropic conducting spheres in a less conducting isotropic matrix we show that for monodisperse suspensions of spheres of radius  $R_{cr}$  the effective conductivity equals that of the matrix. For polydisperse suspensions of spheres it is shown that, when the mean radius lies below  $R_{cr}$ , the effective conductivity lies below that of the matrix.

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## 1. Introduction

Composites of technological and physical interest often exhibit imperfect contact between constituent phases. Here we address the problem of estimating the effective thermal conductivity for composites with an interfacial resistance. Such resistance in composite materials may arise from the presence of impurities at phase boundaries. These impurities are due to oxide films or bonding agents at the phase interface. At liquid helium temperatures, interfacial resistance arises due to acoustic mismatch between component phases as seen in experimental work of Garret & Rosenberg (1974).

Starting with the efforts of Maxwell (1904) and Rayleigh (1892) a great part of the literature has focused on the idealized case of perfect contact. Here one assumes the continuity of the temperature and heat flux across the phase interface. On the other hand, imperfect interfaces are described by discontinuous temperature fields. The jump in temperature is assumed to be proportional to the heat flux across the interface.

For composites with perfect contact, the variational description of effective properties have proved successful in the estimation of effective properties. One of the best known are the Hashin–Shtrikman variational principles (1962). These principles yield

the celebrated Hashin–Shtrikman bounds for isotropic heat conducting composites made from two heat conductors specified by the conductivities  $\sigma_2$  and  $\sigma_1$  in proportions  $\theta_2$  and  $\theta_1$ . The Hashin–Shtrikman bounds are the best possible in that they are attainable by special microgeometries (Hashin & Shtrikman 1962). For anisotropic composites the Hashin–Shtrikman variational principle yields bounds in terms of the two point correlation functions (Willis 1982; Avellaneda & Milton 1989).

In this paper we treat two phase composites with interfacial barrier conductivity specified by  $\beta$ . We assume that the composite is made from isotropic conductors specified by  $\sigma_2 > \sigma_1$  in the proportions  $\theta_2, \theta_1$ , respectively. Our tool is a new set of variational principles describing the effective heat conducting properties of anisotropic conductors with barrier resistance, see §2, equations (2.17) and (2.28).

We develop a systematic method that we refer to as the interface comparison method, to obtain the new variational formulation for the effective conductivity. The advantage of the new formulation is that the solution of the associated field equations involves fields that are not coupled at the two-phase boundary. The choice of trials for these principles is a product space of fields, given by the space of periodic square integrable fields over the domain and by the space of square integrable functions defined on the phase boundary. Most importantly the solution operators for these problems have an explicit form or can be written in terms of solution operators for the perfect contact problem (§§2 and 3).

We apply these principles to obtain new upper and lower bounds on the effective conductivity for anisotropic particulate composites with interfacial barrier resistance. These bounds are shown to be optimal for certain parameter values. The lower bounds depend explicitly upon interfacial surface area, interfacial barrier conductivity, component conductivities, and volume fraction. In addition the bound includes a scale-free matrix of parameters. This matrix corresponds to the effective conductivity of a composite with non-conducting inclusions having the same geometry as the original composite. In the porous media literature, this matrix is commonly known as the formation factor tensor (cf. Dullen 1979).

For isotropic particulate mixtures with barrier resistance we can say more. We introduce the effective conductivity function associated with the same inclusion geometry but with perfect contact between phases. The poles and zeros of this function are confined to an interval  $[L_1, L_2]$  on the negative real axis (Bergman 1978; Golden & Papanicolaou 1983). Using the results of Bruno (1991) for the perfect contact case we are able to write lower bounds on the effective conductivity for composites with imperfect contact in terms of the data  $L_1, L_2$ , see equation (3.17).

For isotropic monodisperse suspensions of spheres we show how to apply the estimates of Torquato & Rubinstein (1991) for the perfect contact case to obtain lower bounds for imperfectly bonded conductors in terms of the nearest neighbour distribution function, see equation (3.19).

We present an upper bound for anisotropic composites in terms of volume fraction, the two point correlation function and the moment of inertia tensors of the particle surfaces, see equation (3.59). For the special case of isotropic particulate composites we display upper bounds for particles of conductivity  $\sigma_2$  (or  $\sigma_1$ ) in a matrix of  $\sigma_1$  (or  $\sigma_2$ ). Our bounds are in terms of volume fraction and a parameter  $\alpha$  given by the sum of polar moments of inertia of the surface of each particle, see (3.61). We show that for the same choice of trial fields new bounds are tighter than those derived from simpler variational principles, see (3.70)–(3.72).

We consider the behaviour of the bounds in the surface area  $s$  and total polar

moment of inertia of the interface  $\alpha$ . To fix ideas we note that for a monodisperse suspension of spheres of radius  $r$  with prescribed volume fraction  $\theta_2$ , the geometric parameter  $\alpha$  is given by  $\alpha = 3\theta_2 r$  and the total interfacial surface area  $s$  is  $s = 3\theta_2/r$ . For polydisperse suspensions of spheres we have  $\alpha = 3\theta_2 \langle r \rangle$  where  $\langle r \rangle$  is the average sphere radius appearing in the suspension (see § 4 *d*). We find that in the limits  $s \rightarrow \infty$ ,  $\alpha \rightarrow 0$  these bounds are linked to the effective properties of suspensions of non-conducting inclusions (§ 4 *a*). Here the limit  $\alpha \rightarrow 0$  corresponds to  $s \rightarrow \infty$  (cf. (4.1)). Indeed, as shown in Lipton (1995), we note that the asymptotic behaviour of the bounds is consistent with the effective conductivity for a large class of composites in the high surface area limit. Physically this follows from the behaviour of the effective property under a rescaling of the geometry as shown by Lipton (1995, theorems 3.3 and 3.4). We pursue this topic in § 4 *a*.

We consider monodisperse suspensions of spheres of conductivity  $\sigma_2$  in a matrix of  $\sigma_1$  with  $\sigma_2 > \sigma_1$ . For this case we exhibit a critical radius,  $R_{cr} = \beta^{-1}(\sigma_1^{-1} - \sigma_2^{-1})^{-1}$ , for which the effective conductivity equals that of the matrix (§ 4 *b*). This result follows from a more fundamental interaction between interfacial and phase resistances. We consider a sample of composite containing spheres of critical radius  $R_{cr}$  subjected to a prescribed average heat intensity. We calculate the fields external to the spheres to observe that the temperature gradient is unaffected by the presence of spheres, see (4.6). In this way we see that the mismatch between component resistivities together with the interfacial resistivity conspire to make the spheres undetectable when the composite is subjected to a homogeneous heat intensity.

We show that, for selected values of volume fraction and geometric parameters of the interface, that isotropic monodisperse suspensions of spheres at critical radius provide extreme heat conducting properties (see § 4 *c*).

For polydisperse suspensions of spheres we use the bounds to give new theoretical predictions of size effect phenomena. Indeed, it is shown that if the average sphere radius  $\langle r \rangle$  is less than  $R_{cr}$ , then the effective conductivity lies below the matrix (see theorem 4.2 § 4 *d*).

In § 4 *e* we investigate the general question of optimal design of isotropic particulate suspensions of conducting particles in a matrix of lesser conductivity at fixed volume fraction. In this context we apply the monotonicity of the lower bound to show that the effective conductivity is greater than the matrix provided the interfacial surface area is less than the value  $d\theta_2 R_{cr}^{-1}$  (see theorem 4.3).

Next we consider the problem of the optimal isotropic distribution of conducting spheres of different radii in a matrix of lesser conductivity. For fixed volume fraction of spherical particles, the objective is to find the optimal distribution of spheres that give the best effective heat transport properties in all directions (i.e. maximize the effective conductivity). We use theorems 4.2 and 4.3 to show that any polydisperse distribution with mean radius less than  $R_{cr}$  is suboptimal (see theorem 4.4). Thus we see that the scale of the heterogeneities has an effect on the optimality of a particular design. This is in striking contrast to optimal layout problems with perfect heat transmission between phases where scale plays no role in the optimal design (see Lurie & Cherkhaev 1986; Murat & Tartar 1985).

For isotropic monodisperse suspensions of spheres we can say more. Indeed, collecting our results (see §§ 4 *b*, 4 *d* and 4 *e*) we note that: (1) for spheres of radius less than  $R_{cr}$  the effective property lies below that of the matrix. (2) For spheres of radius greater than  $R_{cr}$  the effective property lies strictly above the matrix, see theorem 4.5. This prediction is rigorous and exact.

Previous size effect predictions have been limited to monodisperse suspensions of spheres based upon approximate phenomenological models and low volume fraction expansions. Indeed, using the approach of Rayleigh and Maxwell, Hasselman & Johnson (1987) develop an effective medium theory. Using this model they are able to give the estimate  $\sigma_1/\beta$  for the critical radius of a monodisperse suspension of spheres. Every *et al.* (1992) also obtained the same estimate for a monodisperse suspension of spheres using a differential effective medium theory. It follows from our result (see (4.5), §4*b*) that their estimate is asymptotically correct in the limit  $\sigma_2 \gg \sigma_1$ . For monodisperse dilute suspensions Chiew & Glandt (1987) show that  $\sigma^e < \sigma_1$  for spherical particles of radius less than  $R_{cr}$  and  $\sigma^e > \sigma_1$  for particle radii greater than  $R_{cr}$ .

The existence of a critical radius has been experimentally observed by Garret & Rosenberg (1974) for composites with epoxy-resin matrix and inclusions of glass spheres, quartz, corundum or diamond. This phenomenon is also seen in the experimental work of Every *et al.* (1992) where it is observed that the thermal conductivity of zinc sulphide is increased by adding large particles of highly conducting diamond, but lowered by the addition of submicron size particles of diamond.

The result given in this paper is, to the best of our knowledge the first theoretical size effect prediction for polydisperse suspensions of spheres at high concentration. Physically all size effects are due to the increase in interfacial surface to volume ratio as the sizes of the inclusions decrease. The scale at which these effects occur is determined by the parameter  $R_{cr}$ . This parameter measures the relative importance of interfacial resistance and contrast between phase resistances.

Lastly we note that the scope of this paper is not limited to the context of heat conductivity. Indeed, this problem is mathematically analogous to the problems of estimating effective diffusivity for multiphase composites separated by permeable membranes (Latour *et al.* 1994) as well as electrostatic problems in composites with interface resistance. We further remark that the techniques introduced here can readily be applied to the context of two-phase elastic mixtures with interfacial slip (see Lipton & Vernescu 1995).

## 2. Variational principles for effective conductivity

### (a) Mathematical and physical background and basic variational principles

For periodic heat conducting composites we may decompose the temperature field  $T$  into two parts, a periodic fluctuation  $\tilde{\phi}$  and a linear part  $\xi \cdot x$  such that  $T = \tilde{\phi} + \xi \cdot x$ . Following Benveniste (1986) the average intensity  $\langle \nabla T \rangle$  seen by an 'outside observer' is

$$\langle \nabla T \rangle = \int_{\partial Q} (\tilde{\phi} + \xi \cdot x) \mathbf{n} \, ds = \xi. \quad (2.1)$$

Here  $Q$  is the unit cell occupied by the composite,  $\partial Q$  is the boundary of the cell and  $\mathbf{n}$  is the outward directed normal.

The cell  $Q$  is composed of two isotropic conducting materials occupying regions  $Y_1$  and  $Y_2$  separated by an interface denoted by  $\Gamma$ . The temperature inside the composite satisfies:

$$\nabla \cdot \{\sigma_i(\nabla \tilde{\phi} + \xi)\} = 0 \quad \text{in } Y_i, \quad i = 1, 2, \quad (2.2)$$

$$[\sigma(x)(\nabla \tilde{\phi} + \xi)] \cdot \mathbf{n} = 0 \quad \text{on } \Gamma, \quad (2.3)$$

$$\sigma_2(\nabla\bar{\phi} + \xi) \cdot \mathbf{n} = -\beta[\bar{\phi}]_1^2 \quad \text{on } \Gamma. \quad (2.4)$$

Here  $\mathbf{n}$  denotes the normal to  $\Gamma$  and points into the interior of phase-1 and (2.3) is the continuity of the normal flux across  $\Gamma$ . Equation (2.4) represents the effect of thermal surface resistance. The quantity  $\sigma_2(\nabla\bar{\phi} + \xi) \cdot \mathbf{n}$  in (2.4) is evaluated on the phase-2 side of  $\Gamma$ . The solution of problem (2.2)–(2.4) is unique up to a constant; this is an application of the Lax–Milgram lemma.

The positive parameter  $\beta^{-1}$  represents the thermal barrier resistance. The  $\beta = \infty$  limit corresponds to the case of perfect contact and condition (2.4) is replaced with  $[\bar{\phi}] = 0$ . The  $\beta = 0$  limit corresponds to a perfectly insulating surface and is usually referred to as the ‘adiabatic’ boundary condition.

The effective conductivity tensor for the composite is defined by

$$\sigma^e \xi = \int_Q \sigma(x)(\nabla\bar{\phi} + \xi) dx. \quad (2.5)$$

The effective conductivity admits two variational formulations analogous to the Dirichlet and Thompson variational principles for the case of perfect contact. The first is

$$\sigma^e \xi \cdot \xi = \min_{\phi \in V} \left\{ \int_Q \sigma(x)(\nabla\phi + \xi)^2 dx + \beta \int_{\Gamma} ([\phi])^2 ds \right\}, \quad (2.6)$$

where the space  $V$  consists of all square integrable,  $Q$ -periodic functions  $\phi$  such that  $\nabla\phi$  is square integrable in each phase. We note that the space  $V$  allows for fields  $\phi$  that are discontinuous across  $\Gamma$ .

The second variational principle is

$$(\sigma^e)^{-1} \bar{\tau} \cdot \bar{\tau} = \min_{\tau \in W} \left\{ \int_Q \sigma^{-1}(x)|(\tau + \bar{\tau})|^2 dx + \frac{1}{\beta} \int_{\Gamma} ((\tau + \bar{\tau}) \cdot \mathbf{n})^2 ds \right\}, \quad (2.7)$$

where the space  $W$  is the infinite-dimensional space of all  $Q$ -periodic square integrable fields  $\tau(x)$  characterized by

$$\nabla \cdot \tau = 0, \quad \int_Q \tau dx = 0, \quad \text{and} \quad [\tau] \cdot \mathbf{n} = 0 \quad \text{on } \Gamma, \quad (2.8)$$

and  $\bar{\tau}$  is any constant vector. For similar variational principles for effective tensors of heterogeneous elastic materials with imperfect interface, see Lene & Leguillon (1982) and Hashin (1992).

### (b) Interface comparison method variational principles

We present two new variational principles describing the effective conductivity tensor.

Before stating the first variational principle we introduce a comparison material with conductivity  $\gamma < \sigma_1$  and formulate two auxiliary conductivity problems. For a square integrable  $Q$ -periodic field  $\mathbf{p}$ , the potential  $\phi^{\mathbf{p}}$  is a solution of

$$\gamma \Delta \phi^{\mathbf{p}} = -\nabla \cdot \mathbf{p} \quad \text{in } Y_i, \quad i = 1, 2, \quad (2.9)$$

$$[\mathbf{p} + \gamma \nabla \phi^{\mathbf{p}}] \cdot \mathbf{n} = 0 \quad \text{on } \Gamma, \quad (2.10)$$

$$(\mathbf{p} + \gamma \nabla \phi^{\mathbf{p}}) \cdot \mathbf{n} = 0 \quad \text{on } \Gamma. \quad (2.11)$$

For a square integrable function  $v$  defined on  $\Gamma$  the potential  $\phi^v$  is a solution of

$$\Delta \phi^v = 0 \quad \text{in } Y_i, \quad i = 1, 2, \quad (2.12)$$

$$[\gamma \nabla \phi^v] \cdot \mathbf{n} = 0, \quad \text{on } \Gamma, \quad (2.13)$$

$$\gamma \nabla \phi^v \cdot \mathbf{n} = -v \quad \text{on } \Gamma. \quad (2.14)$$

We observe that the boundary value problems given by (2.9)–(2.11) and (2.12)–(2.14) can be separately solved in each phase region.

Introducing the linear operators  $M$  and  $R$  given by

$$M\mathbf{p} = \nabla \phi^{\mathbf{p}} \quad \text{in } Y_1 \cup Y_2, \quad (2.15)$$

$$Rv = \nabla \phi^v \quad \text{in } Y_1 \cup Y_2, \quad (2.16)$$

one has the new variational principle given by

$$(P1): \quad \left( \sigma^e - \gamma I + \frac{\gamma^2}{\beta} \int_{\Gamma} \mathbf{n} \otimes \mathbf{n} \right) \boldsymbol{\xi} \cdot \boldsymbol{\xi} = \max_{(\mathbf{p}, v) \in \mathcal{P}} \{2\underline{L}(\boldsymbol{\xi}, \mathbf{p}, v) - \underline{Q}(\mathbf{p}, v)\}, \quad (2.17)$$

where the space  $\mathcal{P}$  defines a couple  $(\mathbf{p}, v)$  of admissible bulk and surface polarizations  $(\mathbf{p}, v)$  where  $\mathbf{p}$  is square integrable and  $Q$ -periodic and  $v$  is square integrable on  $\Gamma$ . The linear form  $\underline{L}(\boldsymbol{\xi}, \mathbf{p}, v)$  is defined by

$$\underline{L}(\boldsymbol{\xi}, \mathbf{p}, v) = \frac{\gamma}{\beta} \int_{\Gamma} v \boldsymbol{\xi} \cdot \mathbf{n} \, ds + \int_Q (\mathbf{p} \cdot \boldsymbol{\xi}) \, dx. \quad (2.18)$$

The quadratic form  $\underline{Q}(\mathbf{p}, v)$  is given by

$$\underline{Q}(\mathbf{p}, v) = \int_Q (\sigma - \gamma)^{-1} |\mathbf{p}|^2 \, dx + \frac{1}{\beta} \int_{\Gamma} v^2 \, ds + \gamma \int_Q |M\mathbf{p} + Rv|^2 \, dx. \quad (2.19)$$

For the second new variational principle we introduce a comparison material with conductivity  $\gamma > \sigma_2$  and formulate two auxiliary conductivity problems. For a square integrable  $Q$ -periodic field  $\mathbf{p}$  the potential  $\psi^{\mathbf{p}}$  is a solution of

$$\Delta \psi^{\mathbf{p}} = \nabla \cdot \mathbf{p} \quad \text{in } Y_1 \cup Y_2, \quad (2.20)$$

$$[\nabla \psi^{\mathbf{p}} - \mathbf{p}] \cdot \mathbf{n} = 0 \quad \text{on } \Gamma, \quad (2.21)$$

$$[\psi^{\mathbf{p}}] = 0 \quad \text{on } \Gamma. \quad (2.22)$$

For a square integrable function  $v$  defined on  $\Gamma$ , the potential  $\psi^v$  is a solution of

$$\Delta \psi^v = 0 \quad \text{in } Y_1 \cup Y_2, \quad (2.23)$$

$$[\partial_n \psi^v] = 0 \quad \text{on } \Gamma, \quad (2.24)$$

$$[\psi^v] = -v \quad \text{on } \Gamma. \quad (2.25)$$

Introducing the linear operators  $N$  and  $S$  defined by

$$N\mathbf{p} = \nabla \psi^{\mathbf{p}} \quad \text{in } Q, \quad (2.26)$$

$$Sv = \nabla \psi^v \quad \text{in } Y_1 \cup Y_2, \quad (2.27)$$

one has

$$(P2): \quad ((\sigma^e)^{-1} - \gamma^{-1} I) \bar{\boldsymbol{\tau}} \cdot \bar{\boldsymbol{\tau}} = \max_{(\mathbf{p}, v) \in \mathcal{P}} \{2\bar{L}(\bar{\boldsymbol{\tau}}, \mathbf{p}, v) - \bar{Q}(\mathbf{p}, v)\}. \quad (2.28)$$

Here the linear form  $\bar{L}(\bar{\boldsymbol{\tau}}, \mathbf{p}, v)$  is defined by

$$\bar{L}(\bar{\boldsymbol{\tau}}, \mathbf{p}, v) = \int_Q \mathbf{p} \cdot \bar{\boldsymbol{\tau}} + \int_{\Gamma} (\bar{\boldsymbol{\tau}} \cdot \mathbf{n}) v \, ds \quad (2.29)$$

and the quadratic form  $\bar{Q}$  is given by

$$\begin{aligned} \bar{Q}(\mathbf{p}, v) = & \int_Q (\sigma^{-1} - \gamma^{-1})^{-1} |\mathbf{p}|^2 dx + \beta \int_{\Gamma} |v|^2 ds \\ & + \gamma^2 \int_Q \left| (N\mathbf{p} + Sv - \mathbf{p}) - \int_Q (N\mathbf{p} + Sv - \mathbf{p}) dy \right|^2 dx. \end{aligned} \quad (2.30)$$

Here we remark that the operator  $N$  can be identified with the projection of square integrable periodic fields onto  $Q$ -periodic curl-free fields.

The right-hand sides of (2.17) and (2.28) can be written alternatively as min max principles for appropriately chosen Lagrangians. Doing so yields the following characterizations of the effective conductivity tensor:

$$\begin{aligned} \left( \sigma^e - \gamma I + \frac{\gamma^2}{\beta} \int_{\Gamma} \mathbf{n} \otimes \mathbf{n} ds \right) \boldsymbol{\xi} \cdot \boldsymbol{\xi} = & \max_{(\mathbf{p}, v) \in \mathcal{P}} \min_{\phi \in V} \underline{\mathcal{L}}(\mathbf{p}, v, \phi) \\ = & \min_{\phi \in V} \max_{(\mathbf{p}, v) \in \mathcal{P}} \underline{\mathcal{L}}(\mathbf{p}, v, \phi), \end{aligned} \quad (2.31)$$

$$\begin{aligned} ((\sigma^e)^{-1} - \gamma^{-1} I) \bar{\boldsymbol{\tau}} \cdot \bar{\boldsymbol{\tau}} = & \max_{(\mathbf{p}, v) \in \mathcal{P}} \min_{\boldsymbol{\tau} \in W} \bar{\mathcal{L}}(\mathbf{p}, v, \boldsymbol{\tau}) \\ = & \min_{\boldsymbol{\tau} \in W} \max_{(\mathbf{p}, v) \in \mathcal{P}} \bar{\mathcal{L}}(\mathbf{p}, v, \boldsymbol{\tau}), \end{aligned} \quad (2.32)$$

where the convex-concave Lagrangians  $\underline{\mathcal{L}}$  and  $\bar{\mathcal{L}}$  are given by

$$\begin{aligned} \underline{\mathcal{L}}(\mathbf{p}, v, \phi) \equiv & 2 \int_Q \mathbf{p} \cdot \boldsymbol{\xi} dx + \frac{2\gamma}{\beta} \int_{\Gamma} v \boldsymbol{\xi} \cdot \mathbf{n} ds - \int_Q (\sigma - \gamma)^{-1} |\mathbf{p}|^2 dx - \frac{1}{\beta} \int v^2 ds \\ & + 2 \int_Q \mathbf{p} \cdot \nabla \phi dx + 2 \int_{\Gamma} v[\phi] ds + \gamma \int_Q |\nabla \phi|^2 dx, \end{aligned} \quad (2.33)$$

$$\begin{aligned} \bar{\mathcal{L}}(\mathbf{p}, v, \boldsymbol{\tau}) = & 2 \int_Q \mathbf{p} \cdot \bar{\boldsymbol{\tau}} dx + 2 \int_{\Gamma} v(\bar{\boldsymbol{\tau}} \cdot \mathbf{n}) ds \\ & - \int_Q (\sigma^{-1} - \gamma^{-1})^{-1} |\mathbf{p}|^2 dx - \beta \int_{\Gamma} v^2 ds \\ & + 2 \int_Q \mathbf{p} \cdot \boldsymbol{\tau} dx + 2 \int_{\Gamma} (\boldsymbol{\tau} \cdot \mathbf{n}) v ds + \gamma^{-1} \int_Q |\boldsymbol{\tau}|^2 dx. \end{aligned} \quad (2.34)$$

We recall that the limit  $\beta \rightarrow \infty$  corresponds physically to the perfect contact case in which there is no surface resistance. For this case the new variational principles (2.17) and (2.28) reduce to the well-known Hashin–Shtrikman variational principles (Hashin & Shtrikman 1962) for conductors with perfect contact.

To show that (2.17) reduces to the lower Hashin–Shtrikman principle as  $\beta \rightarrow \infty$  we appeal to the equivalent saddle formulation (2.31). Passing to the limit  $\beta = \infty$  in (2.31) yields

$$\begin{aligned} (\sigma^e - \gamma I) \boldsymbol{\xi} \cdot \boldsymbol{\xi} = & \min_{\phi \in V} \max_{(\mathbf{p}, v) \in \mathcal{P}} \left\{ 2 \int_Q \mathbf{p} \cdot \boldsymbol{\xi} dx - \int_Q (\sigma - \gamma)^{-1} |\mathbf{p}|^2 dx \right. \\ & \left. + 2 \int_Q \mathbf{p} \cdot \nabla \phi dx + 2 \int_{\Gamma} v[\phi] ds + \gamma \int_Q |\nabla \phi|^2 dx \right\}. \end{aligned} \quad (2.35)$$

We observe from (2.35) that the minimum is obtained for  $[\phi] = 0$ . Switching the order

of max and min leaves the right-hand side of (2.35) unchanged and one obtains

$$(\sigma^e - \gamma I)\xi \cdot \xi = \max_p \left\{ 2 \int_Q p \cdot \xi \, dx - \int_Q (\sigma - \gamma)^{-1} |p|^2 \, dx \right. \\ \left. + \min_{\substack{\phi \in V \\ |\phi|=0}} \left\{ 2 \int_Q p \cdot \nabla \phi \, dx + \gamma \int_Q (\nabla \phi)^2 \, dx \right\} \right\} \quad (2.36)$$

for  $\gamma < \sigma_1$  which is the lower Hashin–Shtrikman variational principle for two-phase conductors with perfect contact. Passing to the  $\beta = \infty$  limit in (2.32) forces  $v = 0$  and we obtain

$$((\sigma^e)^{-1} - \gamma^{-1} I)\bar{\tau} \cdot \bar{\tau} = \max_p \left\{ 2 \int_Q p \cdot \bar{\tau} - \int_Q (\sigma^{-1} - \gamma^{-1})^{-1} |p|^2 \, dx \right. \\ \left. + \gamma^{-1} \int_Q \left| (Np - p) - \int_Q (Np - p) \, dy \right|^2 \, dx \right\} \quad (2.37)$$

for  $\gamma > \sigma_2$  which is the upper Hashin–Shtrikman variational principle for the case of perfect contact. We note that the above statements can be made rigorous by appealing to the theory of epi/hypo-convergence introduced by Attouch & Wets (1983).

(c) *Derivation of the variational principles*

(i) *Lower variational principle by the interface comparison method*

In this section we derive the lower variational principle (P1) for the choice of isotropic comparison material with conductivity  $\gamma < \sigma_1$ . The sequence of steps outlined below comprise the interface comparison method. We begin with the variational principle (2.6). Noting that the solution  $\bar{\phi}$  of (2.2)–(2.4) is the minimizer of (2.6) we write

$$\sigma^e \xi \cdot \xi = \int_Q \sigma(x) |\nabla \bar{\phi} + \xi|^2 \, dx + \beta \int_\Gamma ([\bar{\phi}])^2 \, ds. \quad (2.38)$$

Adding and subtracting the reference energy  $\gamma |\nabla \bar{\phi} + \xi|^2$  to the right-hand side of (2.38) and rearrangement gives

$$(\sigma^e - \gamma)\xi \cdot \xi = \int_Q (\sigma(x) - \gamma) |\nabla \bar{\phi} + \xi|^2 \, dx + \gamma \int_Q |\nabla \bar{\phi}|^2 \, dx \\ + 2\gamma \int_Q \nabla \bar{\phi} \cdot \xi \, dx + \beta \int_\Gamma ([\bar{\phi}])^2 \, ds. \quad (2.39)$$

Integrating by parts, one obtains

$$2\gamma \int_Q \nabla \bar{\phi} \cdot \xi \, dx = 2\gamma \int_\Gamma [\bar{\phi}] \mathbf{n} \cdot \xi \, ds. \quad (2.40)$$

Applying (2.40) and completing the square in the last two terms of (2.39) gives

$$\left( \sigma^e - \gamma I + \frac{\gamma^2}{\beta} \int_\Gamma \mathbf{n} \otimes \mathbf{n} \, ds \right) \xi \cdot \xi = \int_Q (\sigma(x) - \gamma) |\nabla \bar{\phi} + \xi|^2 \, dx + \gamma \int_Q |\nabla \bar{\phi}|^2 \, dx \\ + \beta \int_\Gamma \left( [\bar{\phi}] + \frac{\gamma}{\beta} \xi \cdot \mathbf{n} \right)^2 \, ds. \quad (2.41)$$



Introducing the bulk and surface polarizations  $p$  and  $v$  one has the elementary estimates,

$$\beta \int_{\Gamma} \left( [\bar{\phi}] + \frac{\gamma}{\beta} \xi \cdot n \right)^2 ds \geq \int_{\Gamma} 2v \left( [\bar{\phi}] + \frac{\gamma}{\beta} \xi \cdot n \right) ds - \frac{1}{\beta} \int_{\Gamma} v^2 ds, \quad (2.42)$$

$$\int_Q (\sigma(x) - \gamma) |\nabla \bar{\phi} + \xi|^2 dx \geq 2 \int_Q p \cdot (\nabla \bar{\phi} + \xi) dx - \int_Q (\sigma(x) - \gamma)^{-1} |p|^2 dx, \quad (2.43)$$

for any square integrable and  $Q$ -periodic field  $p$  and any function  $v$  square integrable on  $\Gamma$ . We denote the set of all pairs  $(p, v)$  by  $\mathcal{P}$ . Applying estimates (2.42) and (2.43) to (2.41) we obtain

$$\left( \sigma^e - \gamma I + \frac{\gamma^2}{\beta} \int_{\Gamma} n \otimes n ds \right) \xi \cdot \xi \geq \underline{\mathcal{L}}(p, v, \bar{\phi}), \quad (2.44)$$

where  $\underline{\mathcal{L}}$  is defined by (2.33). Next we observe

$$\left( \sigma^e - \gamma I + \frac{\gamma^2}{\beta} \int_{\Gamma} n \otimes n ds \right) \xi \cdot \xi \geq \underline{\mathcal{L}}(p, v, \bar{\phi}) \geq \inf_{\phi \in V} \underline{\mathcal{L}}(p, v, \phi) = \underline{\mathcal{L}}(p, v, \phi^*), \quad (2.45)$$

where  $\phi^*$  is the minimizer of:

$$\inf_{\phi \in V} \left\{ 2 \int_Q \nabla \phi \cdot p dx + 2 \int_{\Gamma} v[\phi] + \gamma \int_Q |\nabla \phi|^2 dx \right\} \quad (2.46)$$

and satisfies

$$-\gamma \Delta \phi^* = \nabla \cdot p \quad \text{in } Y_1 \cup Y_2, \quad (2.47)$$

$$[\gamma \nabla \phi^* + p] \cdot n = 0 \quad \text{on } \Gamma, \quad (2.48)$$

$$(\gamma \nabla \phi^* + p) \cdot n = -v \quad \text{on } \Gamma. \quad (2.49)$$

Observing that  $\phi^*$  is linear in the data  $(p, v)$  we write  $\phi^* = \phi^p + \phi^v$  where  $\phi^p$  and  $\phi^v$  solve problems (2.9)–(2.11) and (2.12)–(2.14) respectively. Recalling the definitions of the operators  $M$  and  $R$  given by (2.15) and (2.16), inequality (2.45) can be written as the variational inequality:

$$\left( \sigma^e - \gamma I + \frac{\gamma^2}{\beta} \int_{\Gamma} n \otimes n ds \right) \xi \cdot \xi \geq 2\underline{\mathcal{L}}(\xi, p, v) - \underline{\mathcal{Q}}(p, v). \quad (2.50)$$

One observes for the choice of bulk and surface polarizations, consistent with the actual potential inside the composite, i.e.

$$p = (\sigma - \gamma)(\nabla \bar{\phi} + \xi) \quad \text{and} \quad v = \beta \left( [\bar{\phi}] + \frac{\gamma}{\beta} \xi \cdot n \right) \quad (2.51)$$

that (2.50) holds with equality. Thus we have established (P1). Additionally it follows from (2.45) and the previous observation that

$$\left( \sigma^e - \gamma I + \frac{\gamma^2}{\beta} \int_{\Gamma} n \otimes n ds \right) \xi \cdot \xi = \max_{(p,v) \in \mathcal{P}} \min_{\phi \in V} \underline{\mathcal{L}}(p, v, \phi) \quad (2.52)$$

and equation (2.31) follows.

(ii) *Upper variational principle by the interface comparison method*

Here we establish (P2) for the choice of isotropic comparison material with conductivity  $\gamma > \sigma_2$ . We consider the variational principle (2.7) and denote the minimizer by  $\bar{\tau}$ . The effective energy is written:

$$(\sigma^e)^{-1} \bar{\tau} \cdot \bar{\tau} = \int_Q \sigma^{-1}(x) |\bar{\tau} + \bar{\tau}|^2 dx + \frac{1}{\beta} \int_{\Gamma} ((\bar{\tau} + \bar{\tau}) \cdot \mathbf{n})^2 ds. \quad (2.53)$$

Adding and subtracting the reference energy  $\gamma^{-1} |\bar{\tau} + \bar{\tau}|^2$  to the right-hand side of (2.53) yields

$$\begin{aligned} ((\sigma^e)^{-1} - \gamma^{-1}) \bar{\tau} \cdot \bar{\tau} &= \int_Q (\sigma^{-1}(x) - \gamma^{-1}) |\bar{\tau} + \bar{\tau}|^2 dx \\ &\quad + \int_Q \gamma^{-1} |\bar{\tau}|^2 dx + \frac{1}{\beta} \int_{\Gamma} ((\bar{\tau} + \bar{\tau}) \cdot \mathbf{n})^2 ds. \end{aligned} \quad (2.54)$$

One has the elementary estimates,

$$\int_Q (\sigma^{-1}(x) - \gamma^{-1}) |\bar{\tau} + \bar{\tau}|^2 dx \geq 2 \int_Q \mathbf{p} \cdot (\bar{\tau} + \bar{\tau}) dx - \int_Q (\sigma^{-1}(x) - \gamma^{-1})^{-1} |\mathbf{p}|^2 dx, \quad (2.55)$$

$$\frac{1}{\beta} \int_{\Gamma} ((\bar{\tau} + \bar{\tau}) \cdot \mathbf{n})^2 ds \geq 2 \int_{\Gamma} (\bar{\tau} + \bar{\tau}) \cdot \mathbf{n} v ds - \int_{\Gamma} \beta v^2 ds, \quad (2.56)$$

for any square integrable  $Q$ -periodic field  $\mathbf{p}$  and any square integrable function  $v$  on  $\Gamma$ .

Application of the estimates to (2.54) yields

$$((\sigma^e)^{-1} - \gamma^{-1}) \bar{\tau} \cdot \bar{\tau} \geq \bar{L}(\mathbf{p}, v, \bar{\tau}), \quad (2.57)$$

where  $\bar{L}$  is defined by (2.34). Now we observe that

$$((\sigma^e)^{-1} - \gamma^{-1}) \bar{\tau} \cdot \bar{\tau} \geq \bar{L}(\mathbf{p}, v, \bar{\tau}) \geq \inf_{\tau \in W} \bar{L}(\mathbf{p}, v, \tau) = \bar{L}(\mathbf{p}, v, \bar{\tau}^*), \quad (2.58)$$

where  $\bar{\tau}^*$  is the minimizer of

$$\inf_{\tau \in W} \left\{ 2 \int_Q \mathbf{p} \cdot \tau dx + 2 \int_{\Gamma} \tau \cdot \mathbf{n} v ds + \gamma^{-1} \int_Q |\tau|^2 dx \right\}. \quad (2.59)$$

Calculation shows that  $\bar{\tau}^*$  is given by

$$\bar{\tau}^* = \gamma \left\{ \nabla \bar{\psi}^* - \mathbf{p} - \int_Q (\nabla \bar{\psi}^* - \mathbf{p}) dx \right\}, \quad (2.60)$$

where  $\bar{\psi}^*$  is the solution of

$$\Delta \bar{\psi}^* = \nabla \cdot \mathbf{p} \quad \text{in } Y_1 \cup Y_2, \quad (2.61)$$

$$[\nabla \bar{\psi}^* - \mathbf{p}] \cdot \mathbf{n} = 0 \quad \text{on } \Gamma, \quad (2.62)$$

$$[\bar{\psi}^*] = -v \quad \text{on } \Gamma. \quad (2.63)$$

Noting that  $\bar{\psi}^*$  is linear in the data  $(\mathbf{p}, v)$  we write  $\bar{\psi}^* = \bar{\psi}^{\mathbf{p}} + \bar{\psi}^v$  where  $\bar{\psi}^{\mathbf{p}}$  and  $\bar{\psi}^v$  solve problems (2.20)–(2.22) and (2.23)–(2.25) respectively. Recalling the definition

for the operators  $N$  and  $S$  given by (2.26) and (2.27), inequality (2.58) can be written as the variational inequality,

$$((\sigma^e)^{-1} - \gamma^{-1})\bar{\tau} \cdot \bar{\tau} \geq 2\bar{L}(\bar{\tau}, \mathbf{p}, v) - \bar{Q}(\mathbf{p}, v). \quad (2.64)$$

For the choice of bulk and surface polarizations, consistent with the actual heat flux  $\bar{\tau} + \bar{\tau}$  inside the composite, i.e.

$$\mathbf{p} = (\sigma^{-1}(x) - \gamma^{-1})(\bar{\tau} + \bar{\tau}), \quad v = \frac{1}{\beta}(\bar{\tau} + \bar{\tau}) \cdot \mathbf{n} \quad (2.65)$$

one observes that (2.64) holds with equality. In this way we arrive at (P2). Additionally it follows from (2.58) and the previous observation that

$$((\sigma^e)^{-1} - \gamma^{-1})\bar{\tau} \cdot \bar{\tau} = \max_{(\mathbf{p}, v) \in \mathcal{P}} \min_{\tau \in W} \bar{L}(\mathbf{p}, v, \tau), \quad (2.66)$$

and equation (2.32) follows.

### 3. Bounds

Bounds that use reduced microstructural information are easily obtained from the basic variational principles given by equations (2.6) and (2.7). Indeed choosing constant trial fields in (2.6) and (2.7) yields

$$\left( \frac{\theta_1}{\sigma_1} + \frac{\theta_2}{\sigma_2} + \frac{s}{d\beta} \right)^{-1} I \leq \sigma^e \leq (\theta_1\sigma_1 + \theta_2\sigma_2)I. \quad (3.1)$$

Non-constant trial fields that encode microstructural information naturally lead to more refined bounds. For the case of a suspension of particles of conductivity  $\sigma_2$  in a matrix of conductivity  $\sigma_1$ , we choose trial fields of the form:

$$\phi = \begin{cases} 0 & \text{in the matrix,} \\ \mathbf{y}^m \cdot \boldsymbol{\eta} & \text{in the } m\text{th sphere,} \end{cases} \quad (3.2)$$

here  $\mathbf{y}^m$  equals  $\mathbf{x} - \mathbf{r}^m$ , with  $\mathbf{r}^m$  being the centre of the  $m$ th sphere. Restriction of trial fields in (2.6) to the class given above and subsequent optimization over  $\boldsymbol{\eta}$  gives the upper bound,

$$\sigma^e \leq \left[ \theta_1\sigma_1 + \theta_2\sigma_2 \left( 1 - \frac{1}{1 + \beta\alpha/d\theta_2\sigma_2} \right) \right] I. \quad (3.3)$$

Here  $\alpha$  is a geometric parameter of the interface defined by (3.60). For a monodisperse suspension of radius 'a' the parameter reduces to  $a\theta_2d$ . Phase interchange yields the upper bound for suspension of particles of conductivity  $\sigma_1$  in a matrix of  $\sigma_2$ . We remark that trial fields of the type given by (3.2) were previously introduced in the context of two-phase elastic composites with interfacial slip by Hashin (1992).

Here we will present bounds that improve on (3.1) and (3.3). For certain parameter values we show that our bounds are optimal (see §4c).

#### (a) New lower bounds on the effective conductivity

We apply variational principles developed in §2 to obtain lower bounds on the effective conductivity tensor. Here we obtain lower bounds on the effective conductivity for particulate composites in terms of volume fraction, surface area, and a scale-free matrix of parameters. This tensor is the effective conductivity of a composite with the same microgeometry but with non-conducting inclusions.

(i) *Particles of high conductivity in a low conductivity matrix*

We consider particles of phase 2 embedded in a matrix of phase 1 with  $\sigma_2 > \sigma_1$ . We suppose that none of the inclusions intersect the period cell boundary.

To obtain new lower bounds we make the specific choice of surface and bulk polarization fields, in the variational principle (P1) (equation (2.17)) given by

$$p = \chi_2 \mu, \quad v = r \cdot n, \quad (3.4)$$

where  $\mu$ , and  $r$  are vectors in  $\mathbb{R}^d$  and  $n$  is the normal pointing into phase 1. The associated bound is given by

$$\left( \sigma^e - \gamma I + \frac{\gamma^2}{\beta} \int_{\Gamma} n \otimes n \right) \xi \cdot \xi \geq \max_{\substack{\mu \in \mathbb{R}^d \\ r \in \mathbb{R}^d}} \{ 2\underline{L}(\xi, \chi_2 \mu, r \cdot n) - \underline{Q}(\chi_2 \mu, r \cdot n) \}. \quad (3.5)$$

We now set the comparison conductivity  $\gamma$  to  $\sigma_1$  and present the explicit form of  $\underline{L}$  and  $\underline{Q}$ :

$$\underline{L} = \frac{\sigma_1}{\beta} \int_{\Gamma} n \otimes n \, ds \, \xi \cdot r + \theta_2 \xi \cdot \mu, \quad (3.6)$$

$$\begin{aligned} \underline{Q} = & \theta_2 (\sigma_2 - \sigma_1)^{-1} |\mu|^2 + \frac{1}{\beta} \int_{\Gamma} n \otimes n \, ds \, r \cdot r \\ & + \sigma_1^{-1} (\theta_2 |\mu|^2 + 2\theta_2 \mu \cdot r + (I - m_0) r \cdot r). \end{aligned} \quad (3.7)$$

Here the symmetric  $d \times d$  tensor  $m_0$  is the effective conductivity tensor of a composite with non-conducting particles having the same microgeometry as the original composite. The region  $Y_1$  is assumed to be composed of an isotropic conductor with unit conductivity and  $Y_2$  is filled with a perfect insulator. For any constant electric field  $\xi$  the possibly anisotropic effective conductivity is defined by

$$m_0 \xi \cdot \xi = \inf_{\phi \in H_{\text{per}}^1} \int_{Y_1} |\nabla \phi + \xi|^2 \, dx. \quad (3.8)$$

We observe that equation (3.6) for  $\underline{L}$  and the first two terms in (3.7) follow directly upon substitution of the polarizations into (P1). The last three terms in (3.7) follow from solution of the comparison problems (2.9)–(2.11) and (2.12)–(2.14) and evaluation of the non-local term in (2.19). Indeed, we have the following lemma.

**Lemma 3.1.** *For the choice  $p = \chi_2 \mu$  and  $v = r \cdot n$ , the non-local term*

$$\int_Q |Mp + Rv|^2 \, dx$$

in (2.19) is given by

$$\sigma_1^{-2} (\theta_2 |\mu|^2 + 2\theta_2 \mu \cdot r + (I - m_0) r \cdot r).$$

*Proof.* For the choice  $p = \chi_2 \mu$ , solution of (2.9)–(2.11), yields  $M\chi_2 \mu = -\sigma_1^{-1} \chi_2 \mu$ , and therefore:

$$\int_Q |Mp|^2 \, dx = \theta_2 \sigma_1^{-2} |\mu|^2.$$

Solution of (2.12)–(2.14) provides us with the relation  $R(r \cdot n) = -\sigma_1^{-1} r$  in region-2 and so

$$2 \int_Q Mp \cdot Rv \, dx = 2\theta_2 \sigma_1^{-2} r \cdot \mu.$$

Last in region-1 we have that  $R(\mathbf{r} \cdot \mathbf{n})$  is given by

$$\nabla \phi^r \equiv \sum_{i=1}^d r_i \nabla \bar{\phi}^i,$$

where  $\bar{\phi}^i$  is a solution of

$$\Delta \bar{\phi}^i = 0 \quad \text{in } Y_1, \quad (3.9)$$

$$(\nabla \bar{\phi}^i + \sigma_1^{-1} \mathbf{e}^i) \cdot \mathbf{n} = 0 \quad \text{on } \Gamma \quad (3.10)$$

and  $\bar{\phi}^i$  periodic on  $Q$ . In this way we see that  $\bar{\phi}^i$  is the periodic fluctuation in the potential for a composite made from pure insulator in region-2 and an isotropic conductor in region-1. Here the composite is subject to a constant gradient  $\sigma_1^{-1} \mathbf{e}^i$ . The vector  $\mathbf{e}^i$  denotes the unit vector in the  $i$ th coordinate direction. Indeed, integration by parts and application of (3.9) and (3.10) yields

$$\int_{Y_1} |\nabla \phi^r|^2 dx + \sigma_1^{-1} \int_{Y_1} \nabla \phi^r \cdot \mathbf{r} dx = 0.$$

Completing squares gives

$$\sigma_1^{-2} \mathbf{m}_0 \mathbf{r} \cdot \mathbf{r} \equiv \int_{Y_1} |\nabla \phi^r + \sigma_1^{-1} \mathbf{r}|^2 dx = \sigma_1^{-2} \theta_1 |\mathbf{r}|^2 - \int_{Y_1} |\nabla \phi^r|^2 dx. \quad (3.11)$$

We observe for the choice  $v = \mathbf{r} \cdot \mathbf{n}$ , the term  $\int_Q |Rv|^2 dx$  is given by

$$\int_{Y_2} |Rv|^2 dx + \int_{Y_1} |Rv|^2 dx = \theta_2 \sigma_1^{-2} |\mathbf{r}|^2 + \int_{Y_1} |\nabla \phi^r|^2 dx.$$

Finally application of (3.11) gives

$$\int_Q |Rv|^2 dx = \sigma_1^{-2} |\mathbf{r}|^2 - \sigma_1^{-2} \mathbf{m}_0 \mathbf{r} \cdot \mathbf{r}.$$

Now we set

$$\frac{1}{\beta} \int_{\Gamma} \mathbf{n} \otimes \mathbf{n} ds = \mathbf{B}$$

and maximize (3.5) over  $\mu$  and  $\mathbf{r}$  in  $\mathbb{R}^d$  to obtain the lower bound on the effective conductivity given by

$$\begin{aligned} & (\sigma^e - \sigma_1 \mathbf{I} + \sigma_1^2 \mathbf{B}) \boldsymbol{\xi} \cdot \boldsymbol{\xi} \\ & \geq \left( \begin{array}{cc} \theta_2 (\sigma_2 / \sigma_1) (\sigma_2 - \sigma_1)^{-1} \mathbf{I} & \theta_2 \sigma_1^{-1} \mathbf{I} \\ \theta_2 \sigma_1^{-1} \mathbf{I} & \mathbf{B} + \sigma_1^{-1} (\mathbf{I} - \mathbf{m}_0) \end{array} \right)^{-1} \begin{pmatrix} \theta_2 \boldsymbol{\xi} \\ \sigma_1 \mathbf{B} \boldsymbol{\xi} \end{pmatrix} \cdot \begin{pmatrix} \theta_2 \boldsymbol{\xi} \\ \sigma_1 \mathbf{B} \boldsymbol{\xi} \end{pmatrix}. \end{aligned} \quad (3.12)$$

This bound holds for all choices of constant temperature gradients  $\boldsymbol{\xi}$  in  $\mathbb{R}^d$ . For isotropic mixtures the tensor  $\mathbf{B}$  reduces to

$$\mathbf{B} = \frac{s}{d\beta} \mathbf{I}, \quad d = 2, 3,$$

and inequality (3.12) becomes the lower bound on the effective conductivity for isotropic particulate composites given by

$$\sigma^e \geq \sigma_1 - \sigma_1((1 - m_0)^{-1} + (\sigma_1 \theta_2 c)^{-1})^{-1}, \quad (3.13)$$

where  $c$  represents the characteristic combination

$$c = \frac{s}{d\theta_2\beta} - \frac{\sigma_2 - \sigma_1}{\sigma_1\sigma_2}, \quad (3.14)$$

and  $m_0$  is the scalar effective conductivity of a composite with the same geometry but with non-conducting inclusions in a matrix of unit conductivity.

We denote the lower bound on the right-hand side of (3.13) by  $ICL_{12}(m_0, \beta)$ . Elementary Wiener bounds on  $m_0$  show that this parameter is restricted to the interval  $[0, \theta_1]$ . Analysis shows that for  $m_0$  fixed,  $0 < m_0 \leq \theta_1$ , and  $\beta \geq 0$ , one has  $ICL_{12}(m_0, \beta)$  monotone increasing in  $\beta$  and

$$\sigma^e \geq ICL_{12}(m_0, \beta) \geq ICL_{12}(m_0, 0) = \sigma_1 m_0.$$

Here for  $\beta = 0$  the bound reduces to  $\sigma_1 m_0$ . From Bergman (1978) it is known that the effective conductivity is a homogeneous function of the component conductivities and so the quantity  $\sigma_1 m_0$  is precisely the effective conductivity for a matrix of conductivity  $\sigma_1$  with insulating inclusions. On the other hand the bound  $ICL_{12}(m_0, \beta)$  is found to be monotone increasing in  $m_0$  for  $\beta \geq 0$ , and

$$\sigma^e \geq ICL_{12}(m_0, \beta) \geq ICL_{12}(0, \beta) = \left( \frac{\theta_1}{\sigma_1} + \frac{\theta_2}{\sigma_2} + \frac{s}{d\beta} \right)^{-1}.$$

Here  $ICL_{12}(0, \beta)$  is the analogue of the Wiener lower bound for the case of perfect conductivity. The bound  $ICL_{12}(0, \beta)$  may be obtained directly from variational principle (2.7).

The new bound (3.13) provides the means to estimate the effective properties for composites with imperfect interface in terms of the effective conductivity function associated with perfectly bonded composites having no interfacial barrier resistance.

It is shown in the work of Bruno (1991) that effective transport properties for composites with non-conducting inclusions can be characterized in terms of the singularities and zeros of the effective conductivity function for perfectly bonded conductors. These zeros and singularities are known to be confined to an interval on the negative real axis (see Bergman 1978). For composites with singularities and zeros lying inside an interval  $[L_1, L_2]$  on the negative real axis we set

$$s_m = \frac{1}{1 - L_1} \quad \text{and} \quad S_m = \frac{1}{1 - L_2}.$$

From the work of Bruno (1991) it follows that the conductivity  $m_0$  is bounded below by

$$m_0 \geq K(s_m, S_m, \theta_2), \quad (3.15)$$

where

$$K(s_m, S_m, \theta_2) = \frac{1 - S_m}{1 - s_m} \left( 1 + \frac{(1 - \theta_2/\delta)^2}{(1 - \theta_2/\delta)((1 - S_m)/\delta) + (\theta_2/\delta^2)(\theta_1/d - s_m)} \right), \quad (3.16)$$

and  $\delta = S_m - s_m$ . Here equation (3.16) is Bruno's lower bound for insulating inclusions in a matrix of unit conductivity. Collecting our results we display a lower bound

on the effective conductivity of an imperfectly bonded composite that is a function of volume fraction, interfacial surface area, and the spectral parameters  $s_m, S_m$ . The bound is given by

$$\sigma^e \geq \sigma_1 - \sigma_1((1 - K(s_m, S_m, \sigma_2))^{-1} + (\sigma_1 \theta_2 c)^{-1})^{-1}. \quad (3.17)$$

Thus we are able to bound the effective transport properties for composites with imperfect interfaces in terms of the zeros and singularities of the effective conductivity function for composites with perfect contact between phases!

If the composite is made up of spherical inclusions then one can estimate  $s_m$  and  $S_m$  using the procedure of Bruno.

One also can appeal to the work of Torquato & Rubinstein (1991) to bound  $m_0$  below for suspensions of spheres of diameter 'g'. Their lower bound is given by  $m_0 \geq J(\theta_2, H(x))$  where

$$J(\theta_2, H) = 1 + \theta_2 g \int_1^\infty \frac{3}{2} \frac{x^3}{x^3 - 1} H(x) dx. \quad (3.18)$$

Equation (3.18) is the lower bound of Torquato & Rubinstein and  $H$  is the nearest neighbour distribution function for spherical inclusions of diameter  $g$ . The quantity  $H(r) dr$  is the probability that given a sphere of diameter  $g$  at the origin, the centre of the nearest neighbour lies at a distance between  $r$  and  $r + dr$ . In (3.18),  $x = r/g$  represents dimensionless distance. Thus we are able to display an alternative lower bound on the effective conductivity for an imperfectly bonded composite that is determined by volume fraction, interfacial surface area, and nearest neighbour distribution function:

$$\sigma^e \geq \sigma_1 - \sigma_1((1 - J(\theta_2, H))^{-1} + (\sigma_1 \theta_2 c)^{-1})^{-1}. \quad (3.19)$$

We now consider the behaviour of the bounds in the extreme cases  $\beta = \infty$  and  $\beta = 0$ . For  $\beta = \infty$  the lower bound becomes

$$\sigma^e \geq \sigma_1 - \sigma_1((1 - K(s_m, S_m, \theta_2))^{-1} - \sigma_2 \theta_2^{-1} (\sigma_2 - \sigma_1)^{-1})^{-1}. \quad (3.20)$$

From the work of Bruno one has that the parameters  $s_m$  and  $S_m$  satisfy  $s_m \leq \theta_1/d$  and  $S_m \geq \theta_1/d + \theta_2$ . For the choice,  $s_m = \theta_1/d$  and  $S_m = \theta_1/d + \theta_2$  the lower bound (3.20) reduces to the Hashin-Shtrikman lower bound for perfectly conducting isotropic composites in  $d = 2, 3$ .

#### (ii) Particles of low conductivity in a high conductivity matrix

For the case of inclusions of conductivity  $\sigma_1$  embedded in a matrix of conductivity ( $\sigma_2 > \sigma_1$ ), we proceed as in the last section to obtain the lower bound for isotropic suspensions given by

$$\sigma^e \geq ICL_{21}(m_0, \beta), \quad (3.21)$$

where

$$ICL_{21}(m_0, \beta) = \sigma_1 + \sigma_1 \left[ \frac{m_0 \left[ \frac{s}{d\beta} \left( 1 + \frac{\sigma_2 \theta_2}{\sigma_2 - \sigma_1} \right) - \theta_2^2 \sigma_1^{-1} \right] - \frac{s}{d\beta} \frac{\sigma_2 \theta_2}{\sigma_2 - \sigma_1} + \theta_2^2 \sigma_1^{-1}}{m_0 \left[ (\theta_2 - \theta_1) \sigma_1^{-1} - \frac{s}{d\beta} - \frac{\sigma_2 \theta_2}{\sigma_1 (\sigma_2 - \sigma_1)} \right] + \frac{s}{d\beta} \frac{\sigma_2 \theta_2}{\sigma_2 - \sigma_1} + \frac{\sigma_2 \theta_2}{\sigma_1 (\sigma_2 - \sigma_1)} - \theta_2^2 \sigma_1^{-1}} \right]. \quad (3.22)$$

For this geometry elementary Wiener bounds on  $m_0$  give  $0 \leq m_0 \leq \theta_2$ . Analysis shows that for  $0 \leq m_0 \leq \theta_2$  and  $\beta > 0$ , one has  $ICL_{21}(m_0, \beta)$  monotone increasing in  $\beta$  and

$$\sigma^e \geq ICL_{21}(m_0, \beta) \geq ICL_{21}(m_0, 0) = \sigma_1 / (m_0^{-1} - (\sigma_2 - \sigma_1)/(\theta_2 \sigma_2)) \geq \sigma_1 m_0. \quad (3.23)$$

On the other hand  $ICL_{21}(m_0, \beta)$  is found to be monotone increasing in  $m_0$  for  $\beta \geq 0$  and

$$\sigma^e \geq ICL_{21}(m_0, \beta) \geq ICL_{21}(0, \beta) = \left( \frac{s}{d\beta} + \frac{\theta_1}{\sigma_1} + \frac{\theta_2}{\sigma_2} \right)^{-1}. \quad (3.24)$$

In view of the monotonicity of  $ICL_{21}(m_0, \beta)$  in  $m_0$  we are able to use bounds on  $m_0$  for composites with insulating inclusions to obtain bounds on  $\sigma^e$ . Proceeding as before one obtains lower bounds in terms of  $[L_1, L_2]$  or nearest neighbour distribution function.

(b) *New upper bounds on the effective conductivity*

Here we apply the upper variational principle (P2) to obtain an upper bound on the effective conductivity. This bound incorporates partial geometric information on the composite geometry. In addition to volume fraction, the bound contains statistical information in terms of two point correlations and the moment of inertia tensors of the particle surfaces.

(i) *Particles of high conductivity in a low conductivity matrix*

We consider particulate inclusions of conductivity  $\sigma_2$  in a matrix of  $\sigma_1$ . We denote the region occupied by the  $m$ th particle by  $Y_m$  and its boundary by  $\partial Y_m$ . To obtain the upper bound we make a suitable choice of bulk and surface polarization fields in the variational principle (P2). We choose polarizations of the form

$$p(x) = \chi_1 \mu \quad \text{and} \quad v(x) = r \cdot y^m \quad \text{on} \quad \partial Y_m. \quad (3.25)$$

Here  $\mu$  and  $r$  can be any vectors in  $\mathbb{R}^d$ ,  $d = 2, 3$  and  $y^m = x - r^m$  where  $x$  lies on the surface of the  $m$ th particle and  $r^m$  is a reference point inside the particle. Upon substitution into the upper variational principle (P2) and choosing  $\gamma = \sigma_2$ , we obtain the upper bound:

$$((\sigma^e)^{-1} - \sigma_2^{-1}) \bar{\tau} \cdot \bar{\tau} \geq \max_{\mu \in \mathbb{R}^d} \max_{r \in \mathbb{R}^d} \{2\bar{L}(\mu, r) - \bar{Q}(\mu, r)\}, \quad (3.26)$$

where

$$\bar{L}(\mu, r) = \theta_1 \mu \cdot \bar{\tau} + \sum_{m=1}^N \int_{\partial Y_m} n \otimes y^m ds r \cdot \bar{\tau} \quad (3.27)$$

$$\begin{aligned} \bar{Q}(\mu, r) = & \theta_1 \lambda |\mu|^2 + \beta \sum_{m=1}^N \int_{\partial Y_m} y^m \otimes y^m ds \quad r \cdot r \\ & + \sigma_2 (\theta_1 \theta_2 I - T) (\mu - r) \cdot (\mu - r). \end{aligned} \quad (3.28)$$

Here

$$\lambda = (\sigma_1^{-1} - \sigma_2^{-1})^{-1} \quad \text{and} \quad T = \int_Q \chi_1 N \chi_1 dx, \quad (3.29)$$

where  $N$  is the projection onto periodic mean-zero curl-free fields introduced in (2.26). We observe that the equation (3.27) for  $\bar{L}$  and the first two terms in (3.28)



follow directly upon substitution of the polarizations into (P2). The last term appearing in (3.28) follows from substitution in the last term in (2.30). This substitution is nontrivial and requires proof. To facilitate the proof we require explicit formulas for the integral operators  $N$  and  $S$  defined in §2*b*. We provide such formulas in the following theorem.

**Theorem 3.2.** *The operator  $N$  is the projection of any square integrable, periodic bulk polarization  $\mathbf{p}$  onto the space of mean zero gradients of periodic temperature fields and is defined locally in Fourier space by*

$$N\mathbf{p} = \sum_{\mathbf{k} \neq 0} e^{2\pi i \mathbf{k} \cdot \mathbf{x}} \frac{\mathbf{k} \otimes \mathbf{k}}{|\mathbf{k}|^2} \hat{\mathbf{p}}(\mathbf{k}). \quad (3.30)$$

The operator  $S$  transforms square integrable fields  $v$  on  $\Gamma$  into gradients defined on the region  $Y_1 \cup Y_2$  and is represented locally in Fourier space by

$$Sv = \sum_{\mathbf{k} \neq 0} e^{2\pi i \mathbf{k} \cdot \mathbf{x}} \left( \frac{\mathbf{k} \otimes \mathbf{k}}{|\mathbf{k}|^2} - I \right) \int_{\Gamma} e^{-2\pi i \mathbf{k} \cdot \mathbf{y}} v \mathbf{n} ds_{\mathbf{y}} - \int_{\Gamma} v \mathbf{n} ds_{\mathbf{y}}. \quad (3.31)$$

*Proof.* The explicit formulas and properties for the operator  $N$  follows immediately from solution of the comparison problem (2.20)–(2.22) using Fourier expansions. This operator is well-known and forms the basis of the anisotropic Hashin–Shtrikman bounds for composites with perfect interfaces given by Milton & Kohn (1988).

To obtain the representation of the  $S$  operator given by (3.31) we extend the function  $v$  defined on  $\Gamma$  into region-1. Where region-1 has a common boundary with the period cell we require the extension to be periodic there. It may be assumed that the extension of  $v$  has a square integrable gradient in region-1. Denoting the extension of  $v$  also by  $v$  we introduce the auxiliary problem: for a periodic potential  $w$  given by

$$\Delta w = \nabla \cdot (\chi_1 \nabla v) \quad \text{in } Y_1 \cup Y_2, \quad (3.32)$$

$$[\nabla w - \chi_1 \nabla v] \cdot \mathbf{n} = 0 \quad \text{on } \Gamma, \quad (3.33)$$

$$[w] = 0 \quad \text{on } \Gamma. \quad (3.34)$$

It is evident from (3.32)–(3.34), that  $(\nabla w - \chi_1 \nabla v)$  is orthogonal to the subspace of all  $Q$ -periodic polarizations that can be written as gradients of periodic temperature fields, i.e.

$$\int_Q (\nabla w - \chi_1 \nabla v) \cdot \nabla \delta dx = 0. \quad (3.35)$$

Here  $\delta$  is a  $Q$ -periodic vector field. Since  $N$  is the projection onto the subspace of fields that can be written as gradients of potentials we have

$$N(\nabla w - \chi_1 \nabla v) = 0. \quad (3.36)$$

In addition from (3.32)–(3.34) it follows that  $N(\nabla w) = \nabla w$ ; thus we obtain

$$\nabla w = N(\chi_1 \nabla v). \quad (3.37)$$

From (3.32)–(3.34) we observe that the function defined by

$$\phi = w - v, \quad \text{in } Y_1, \quad (3.38)$$

$$\phi = w, \quad \text{in } Y_2, \quad (3.39)$$

is a solution of the comparison problem (2.23)–(2.25). Since the solution  $\phi^v$  of the comparison problem is unique up to a constant we may take  $\phi^v$  to be represented by (3.38) and (3.39). It now follows from (3.37)–(3.39) that

$$Sv = \nabla\phi^v = \nabla w - \chi_1 \nabla v \quad \text{in } Y_1 \cup Y_2. \quad (3.40)$$

Denoting the identity operator by  $I$  we have from (3.37)

$$Sv = (N - I)\chi_1 \nabla v \quad \text{in } Y_1 \cup Y_2. \quad (3.41)$$

In view of (3.30) equation (3.41) can be written as

$$Sv = \sum_{k \neq 0} \left( e^{2\pi i k \cdot x} \left( \frac{k \otimes k}{|k|^2} - I \right) \chi_1 \widehat{\nabla} v(k) \right) - \chi_1 \widehat{\nabla} v(0). \quad (3.42)$$

From the divergence theorem we may write

$$\chi_1 \widehat{\nabla} v(k) = \int_{\Gamma} e^{-2\pi i k \cdot y} v n \, ds_y + (2\pi i) k \int_Q e^{-2\pi i k \cdot y} \chi_1 v \, dy. \quad (3.43)$$

Lastly noting that  $((k \otimes k)/|k|^2 - I)k = 0$  we obtain the desired representation (3.31). ■

The formula for the last term in (3.28) follows from the next theorem.

**Theorem 3.3.** For the choice  $p = \chi_1 \mu$  and  $v = \bar{v}(x)$  where  $\bar{v} = r \cdot y^m$  on  $\partial Y_m$ , the non-local term

$$\int_Q |(Np + Sv - p) - \int_Q (Np + Sv - p) \, dx|^2 \, dx \quad (3.44)$$

in (2.30) is given by

$$(\theta_1 \theta_2 I - T)(\mu - r) \cdot (\mu - r). \quad (3.45)$$

*Proof.* Substitution of  $p = \chi_1 \mu$  and  $v = \bar{v}$  into (3.44) gives the expression

$$\begin{aligned} & \int_Q \chi_1 N \chi_1 \, dx \mu \cdot \mu + \int_Q |S\bar{v}|^2 \, dx + \theta_1 |\mu|^2 \\ & - 2 \left[ \int_Q \chi_1 N \chi_1 \, dx \mu \cdot \mu + \int_Q \chi_1 S\bar{v} \, dx \cdot \mu \right] \\ & - \left[ \left| \int_Q S\bar{v} \, dx \right|^2 + \theta_1^2 |\mu|^2 - 2\theta_1 \int_Q S\bar{v} \, dx \cdot \mu \right]. \end{aligned} \quad (3.46)$$

For the choice  $v = \bar{v}$  we appeal to theorem 3.1 to find formulas for the terms

$$\int_Q |S\bar{v}|^2, \quad \int_Q (S\bar{v}) \cdot \chi_1 \mu \, dx \quad \text{and} \quad \left| \int_Q S\bar{v} \right|^2.$$

Indeed theorem 3.1 equation (3.31) yields

$$\begin{aligned} S\bar{v} = & \sum_{k \neq 0} \left[ e^{2\pi i k \cdot x} \left( \frac{k \otimes k}{|k|^2} - I \right) \left( \sum_m \int_{\partial Y^m} e^{-2\pi i k \cdot y} (r \cdot y^m) n \, ds \right) \right] \\ & - \sum_m \int_{\partial Y^m} (r \cdot y^m) n \, ds. \end{aligned} \quad (3.47)$$

We integrate by parts to find

$$\int_{\partial Y^m} e^{-2\pi i \mathbf{k} \cdot \mathbf{y}} (\mathbf{r} \cdot \mathbf{y}^m) \mathbf{n} \, ds = \left( \int_{Y^m} e^{-2\pi i \mathbf{k} \cdot \mathbf{y}} \, d\mathbf{y} \right) \mathbf{r} - 2\pi i \mathbf{k} \int_{Y^m} e^{-2\pi i \mathbf{k} \cdot \mathbf{y}} \mathbf{r} \cdot \mathbf{y}^m \, d\mathbf{y}. \quad (3.48)$$

Noting that

$$\sum_m \int_{Y^m} e^{-2\pi i \mathbf{k} \cdot \mathbf{y}} \, d\mathbf{y} = \begin{cases} \hat{\chi}_2(\mathbf{k}) = -\hat{\chi}_1(\mathbf{k}), & \mathbf{k} \neq 0, \\ \theta_2, & \mathbf{k} = 0, \end{cases} \quad (3.49)$$

and  $(\mathbf{k} \otimes \mathbf{k} / |\mathbf{k}|^2 - I)\mathbf{k} = 0$  it follows from (3.47), (3.48) and (3.49) that

$$S\bar{v} = - \sum_{\mathbf{k} \neq \mathbf{v}} e^{2\pi i \mathbf{k} \cdot \mathbf{x}} \hat{\chi}_1(\mathbf{k}) \left( \frac{\mathbf{k} \otimes \mathbf{k}}{|\mathbf{k}|^2} - I \right) \mathbf{r} - \theta_2 \mathbf{r}. \quad (3.50)$$

Appealing to the explicit formula for the operator  $N$  given in theorem 3.1 it is evident from (3.50) that

$$S\bar{v} = (T - N)\chi_1 \mathbf{r} - \theta_2 \mathbf{r}, \quad (3.51)$$

where  $T$  is the projection onto periodic square integrable mean-zero vector fields.

Observing that

$$\int_Q \chi_1 T \chi_1 \mathbf{r} \, dx = \int_Q \chi_1 (\chi_1 - \theta_1) \mathbf{r} \, dx = \theta_1 \theta_2 \mathbf{r}, \quad (3.52)$$

it follows from (3.29) and (3.51) that

$$\int_Q |S\bar{v}|^2 \, dx = (\theta_1 \theta_2 I - T) \mathbf{r} \cdot \mathbf{r} + \theta_2^2 |\mathbf{r}|^2, \quad (3.53)$$

$$\int_Q (S\bar{v}) \cdot \chi_1 \boldsymbol{\mu} \, dx = -T \mathbf{r} \cdot \boldsymbol{\mu}, \quad (3.54)$$

$$\left| \int_Q S\bar{v} \, dx \right|^2 = \theta_2 |\mathbf{r}|^2. \quad (3.55)$$

Formula (3.45) follows immediately upon substitution of (3.29) and (3.53) through (3.55) into (3.46). ■

The tensor  $T$  defined by (3.29) is well-known and appears in bounds on the effective conductivity for the perfect contact case (see Kohn & Milton 1988). This tensor  $T$  contains two-point correlation information on the composite microstructure. Indeed  $T$  can be written as

$$T_{i\ell} = \sum_{\mathbf{k} \neq 0} \frac{k_i k_\ell}{|\mathbf{k}|^2} \int_Q e^{2\pi i \mathbf{k} \cdot \mathbf{t}} c_{bb}(\mathbf{t}) \, d\mathbf{t}, \quad (3.56)$$

where  $c_{bb}(\mathbf{t})$  is the two-point correlation,

$$c_{bb}(\mathbf{t}) = \int_Q \chi_1(\mathbf{x} + \mathbf{t}) \chi_1(\mathbf{x}) \, dx. \quad (3.57)$$

This function gives the probability that the ends of a rod of length and orientation described by the vector  $\mathbf{t}$  lies in both phases. This representation for  $T$  is easy to establish. Indeed from (3.29) and the formula for the operator  $N$  given by (3.30) we

can write

$$T_{it} = \sum_{k \neq 0} \frac{k_i k_t}{|k|^2} |\hat{\chi}_1(\mathbf{k})|^2. \quad (3.58)$$

Noting that  $|\hat{\chi}_1(\mathbf{k})|^2 = \chi_1 * \widehat{\chi}_1(\mathbf{k})$  we see that  $|\hat{\chi}_1(\mathbf{k})|^2$  is simply the Fourier transform of  $c_{bb}(t)$  defined by (3.57). The relation between geometric tensors of the type given above and two-point correlations was observed in Willis (1982) and in the works of Avellaneda & Milton (1989).

We are now in a position to display new upper bounds on the effective conductivity for anisotropic composites in terms of second order geometric parameters. We introduce the tensors

$$R = \sum_m \int_{\partial Y^m} \mathbf{n} \otimes \mathbf{y}^m ds, \quad M = \sum_m \int_{\partial Y^m} \mathbf{y}^m \otimes \mathbf{y}^m ds$$

and carry out the optimization implied by (3.26) to obtain the upper bound. For any constant current field  $\bar{\tau}$  one has

$$(\sigma^e - \sigma_2^{-1} I) \bar{\tau} \cdot \bar{\tau} \geq \begin{pmatrix} \theta_1 \lambda I + A & -A \\ -A & \beta M + A \end{pmatrix}^{-1} \begin{pmatrix} \theta_1 \bar{\tau} \\ R \bar{\tau} \end{pmatrix} \cdot \begin{pmatrix} \theta_1 \bar{\tau} \\ R \bar{\tau} \end{pmatrix}, \quad (3.59)$$

with  $A = \sigma_2(\theta_1 \theta_2 I - T)$ .

We note that  $M = \sum_m (\frac{1}{2}(\text{tr } J_m) I - J_m)$  where  $J_m$  is the moment of inertia tensor for the surface of the  $m$ th particle. The two point correlation information enters the bound through the tensor  $T$ . When the composite is statistically isotropic the tensor  $T$  is given by  $T = (\theta_1 \theta_2 / d) I$  ( $d = 2, 3$ ), and the tensor  $M = d^{-1} \alpha I$ , where,  $\alpha = \text{tr } M$ . It follows from the relation

$$\alpha = \text{tr } M = \sum_m \int_{\partial Y^m} |\mathbf{y}^m|^2 ds \quad (3.60)$$

that the parameter  $\alpha$  is equal to the sum of the polar moments of inertia of the surfaces  $\partial Y^m$  with respect to the reference points  $\mathbf{r}^m$ . For this case the bound given by (3.59) reduces to

$$\sigma^e \leq ICU_{12}(\alpha, \beta), \quad (3.61)$$

where

$$ICU_{12}(\alpha, \beta) = \left( \sigma_2^{-1} + \frac{\theta_1 \beta d^{-1} \alpha + \theta_2^2 \lambda + \theta_2 \sigma_2 d^{-1} (d-1)}{\lambda \beta d^{-1} \alpha + \theta_1 \theta_2 d^{-1} (d-1) \lambda \sigma_2 + \theta_2 d^{-2} (d-1) \sigma_2 \beta \alpha} \right)^{-1}. \quad (3.62)$$

It is easily seen that  $ICU_{12}$  is monotone increasing in the variables  $\beta$  and  $\alpha$ . In view of this we may choose the reference points  $\mathbf{r}^m$  so as to minimize  $\alpha$  to obtain the tightest bound. A straightforward calculation shows the best  $\mathbf{r}^m$  is given by

$$\mathbf{r}^m = (|\partial Y^m|)^{-1} \int_{\partial Y^m} \mathbf{y} ds, \quad (3.63)$$

where  $|\partial Y^m|$  is the surface area of the  $m$ th particle. For perfectly bonded conductors  $\beta = \infty$ ; passing to the  $\beta = \infty$  limit in the upper bound (3.62) we recover the Hashin-Shtrikman (1962) upper bound for isotropic two phase composites. Denoting the Hashin-Shtrikman upper bound by  $HS^+$  we have from monotonicity

$$ICU_{12}(\alpha, \beta) \leq HS^+. \quad (3.64)$$

In the limit  $\beta = 0$  the upper bound becomes

$$ICU_{12}(\alpha, 0) = \theta_1 \sigma_1 \left( \frac{1 - d^{-1}}{1 - (1 - \theta_2 \sigma_1 / \sigma_2) d^{-1}} \right). \quad (3.65)$$

Noting that  $\sigma_2 > \sigma_1$  implies  $(1 - \theta_2 \sigma_1 / \sigma_2) > 1 - \theta_2 = \theta_1$  we see that

$$ICU_{12}(\alpha, 0) \geq \theta_1 \sigma_1 \left( \frac{1 - d^{-1}}{1 - \theta_1 d^{-1}} \right). \quad (3.66)$$

Here the right-hand side is the upper bound derived by Bruno (1991) for a composite with a matrix of  $\sigma_1$  in the volume fraction  $\theta_1$  filled with non-conducting material with volume fraction  $\theta_2$ .

(ii) *Particles of low conductivity in a high conductivity matrix*

For the case of inclusions of conductivity  $\sigma_1$  embedded in a matrix of conductivity  $\sigma_2$  we proceed as in the last section to obtain the upper bound for isotropic suspensions given by

$$\sigma^e \leq ICU_{21}(\alpha, \beta), \quad (3.67)$$

where

$$ICU_{21}(\alpha, \beta) = \left( \sigma_2^{-1} + \frac{\theta_1 \beta d^{-1} \alpha + \theta_1^2 \lambda}{\lambda \beta d^{-1} \alpha + \theta_1 \theta_2 d^{-1} (d-1) \lambda \sigma_2 + \theta_2 d^{-2} (d-1) \sigma_2 \beta \alpha} \right)^{-1}. \quad (3.68)$$

This bound is monotone increasing in the parameters  $\alpha$  and  $\beta$  and one has

$$\sigma_2 \left( \frac{1 - d^{-1}}{1 - \theta_2 d^{-1}} \right) = ICU_{21}(\alpha, 0) \leq ICU_{21}(\alpha, \beta) \leq ICU_{21}(\alpha, \infty) = HS^+. \quad (3.69)$$

The left-hand side of the inequality (3.69) is precisely the upper bound derived by Bruno (1991) for a composite with a matrix of  $\sigma_2$  in the volume fraction  $\theta_2$  filled with non-conducting particles in the volume fraction  $\theta_1$ .

(c) *Comparison with elementary bounds*

A straightforward calculation shows that the basic upper bound  $U_{12}(\alpha, \beta)$  given by (3.3) is not as tight as that given by  $ICU_{12}(\alpha, \beta)$  derived in the last section.

We summarize the principal results in the following inequalities.

For isotropic particulate composites with matrix phase conductivity  $\sigma_1$  and particle phase conductivity  $\sigma_2$  in volume fractions  $\theta_1$  and  $\theta_2$  respectively, we have

$$\sigma_1 m_0 \leq ICL_{12}(m_0, \beta) \leq \sigma^e \leq ICU_{12}(\alpha, \beta) \leq U_{12}(\alpha, \beta), \quad (3.70)$$

$$\left( \frac{\theta_1}{\sigma_1} + \frac{\theta_2}{\sigma_2} + \frac{s}{d\beta} \right)^{-1} \leq ICL_{12}(m_0, \beta) \leq \sigma^e \leq ICU_{12}(\alpha, \beta) \leq HS^+. \quad (3.71)$$

When the phases are interchanged we have

$$\left( \frac{\theta_1}{\sigma_1} + \frac{\theta_2}{\sigma_2} + \frac{s}{d\beta} \right)^{-1} \leq ICL_{21}(m_0, \beta) \leq \sigma^e \leq ICU_{21}(\alpha, \beta) \leq HS^+. \quad (3.72)$$

Here  $HS^+$  is the Hashin-Shtrikman upper bound for perfectly bonded isotropic composites.

To fix ideas we plot in figure 1 the interface comparison upper bound (3.62) and

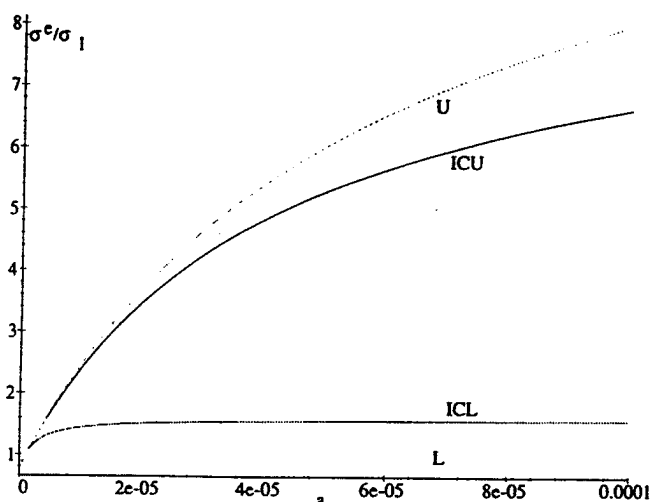


Figure 1. Effective conductivity for ZnS–diamond composites. Interface comparison method upper bound ICU and lower bound ICL compared with the elementary upper bound (3.3) and the lower bound in (3.1) for periodic two-dimensional monodisperse suspensions of diamonds in a ZnS matrix with  $\sigma_1 = 17.4 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\sigma_2 = 1000 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\theta_2 = 0.2$ ,  $\beta = 6 \times 10^{-8} \text{ W m}^{-1} \text{ K}^{-1}$ , and radii  $a \leq 10 \text{ }\mu\text{m}$ . Here  $s_m = (1 - 4\pi/\theta_2)/2$ ,  $S_m = (1 + 4\pi/\theta_2)/2$  and the elementary upper and lower bounds are denoted by U and L respectively.

lower bound (3.17) for periodic monodisperse suspensions of spheres. In the figure these upper and lower bounds are referred to as *ICU* and *ICL*, respectively.

In the next sections we analyse the behaviour of the bounds  $ICL_{12}$ ,  $ICL_{21}$  at fixed volume fraction when the interfacial surface area is allowed to become infinite. We also present inequalities relating the geometric parameter  $\alpha$  to interfacial surface area and analyse the behaviour of  $ICU_{12}$ ,  $ICU_{21}$  in  $\alpha$  for fixed volume fraction.

#### 4. Size effects and extremal microgeometries

The monotonicity of the upper and lower bounds in the geometric parameters of the interface are used to obtain new theoretical predictions of size effect phenomena. We also exhibit microstructures with extremal properties.

For convenience we express a useful inequality between the geometric parameters, that easily follows from two applications of Cauchy's inequality

$$d^2\theta_2(\theta_2/s) \leq \alpha. \quad (4.1)$$

Thus for fixed volume fraction we see that when  $\alpha \rightarrow 0$  we have  $s \rightarrow \infty$ . We note that equality holds in (4.1) for monodisperse suspension of spheres.

##### (a) Asymptotic behaviour of the bounds with interfacial surface area

We consider the behaviour of the bounds as the interfacial surface area is increased for fixed volume fraction. It is interesting to note that all bounds in these limits reduce to bounds on the effective conductivity associated with composites formed from non-conducting inclusions.

For isotropic particulate composites with particles of  $\sigma_2$  in a matrix of lesser con-

ductivity  $\sigma_1$  we have the lower bound as given by equation (3.13). We fix volume fractions and pass to the infinite interfacial surface area limit to find that the lower bound behaves like  $\sigma_1 m_0 + O(s^{-1})$  where  $\sigma_1 m_0$  is the conductivity associated with the same microgeometry but with non-conducting particles and a matrix of conductivity  $\sigma_1$ .

The upper bound for such composites at fixed volume fraction depends upon the  $\alpha$  parameter and is given by (3.62). Passing to the  $\alpha = 0$  limit the bound becomes

$$\theta_1 \sigma_1 \left( \frac{1 - d^{-1}}{1 - (1 - \theta_2 \sigma_1 / \sigma_2) d^{-1}} \right). \quad (4.2)$$

Since  $(1 - \theta_2 \sigma_1 / \sigma_2) > 1 - \theta_2 = \theta_1$  it follows that the above limit is larger than  $\theta_1 \sigma_1 (1 - d^{-1}) / (1 - \theta_1 d^{-1})$  that represents precisely the upper bound on composites of matrix conductivity  $\sigma_1$  with insulating inclusions given by Bruno (1991).

For particulate composites with particles of conductivity  $\sigma_1$  in a matrix of higher conductivity  $\sigma_2$ , the lower bound is given by (3.22). By fixing the volume fractions and considering the limit as the interfacial surface area tends to infinity, the lower bound behaves like

$$\sigma_2 m_0 \left( \frac{m_0}{\theta_2} + \left( 1 - \frac{m_0}{\theta_2} \right) \frac{\sigma_2}{\sigma_1} \right)^{-1} + O(s^{-1}). \quad (4.3)$$

Since  $m_0 < \theta_2$  the first term in (4.3) is less than  $\sigma_2 m_0$ , which represents the effective conductivity of a composite with the same microgeometry but with non-conducting particles in a  $\sigma_2$  conductivity matrix.

Similarly from the upper bound (3.68), when  $\alpha \rightarrow \infty$  we get

$$\sigma_2 \theta_2 \left( \frac{1 - d^{-1}}{1 - \theta_2 d^{-1}} \right), \quad (4.4)$$

which represents the upper bound for composites of conductivity  $\sigma_2$  with insulating inclusions (see Bruno 1991).

The behaviour of these bounds is physically consistent with the behaviour of effective properties for a large class of composites. Indeed, for any periodic particulate composite with fixed proportions  $\theta_1$  and  $\theta_2$ , we rescale the geometry by the factor  $k^{-1}$  where  $k = 1, 2, 3, \dots$ . We then fill the unit cube with a rescaled,  $k^{-1}$  periodic version of the original geometry. Clearly, as  $k$  tends to infinity the volume fraction of the inclusions remain fixed but the distribution of inclusions become increasingly fine and the interfacial surface area tends to infinity. The behaviour of the effective property obtained through rescaling is explained by the following size effect obtained by Lipton (1995, theorem 3.3)

**Theorem 4.1.** *The effective conductivity of the  $k^{-1}$  periodic composite constructed above is identical to that associated with the unrescaled composite with thermal barrier resistance increased by the factor  $k$ .*

*Proof.* We denote the electric potential in the  $k^{-1}$  periodic composite by  $\psi^k$  and we let  $\phi^k$  be the potential in the unrescaled composite with interfacial barrier resistance  $k/\beta$ . Theorem 4.1 follows from the field identity  $\psi^k(\mathbf{x}) = k^{-1} \phi^k(k\mathbf{x})$  and a change of variables in equation (2.5). ■

Next, for a fixed geometry, we observe that if we take the thermal barrier resistance to infinity, then the associated effective conductivity tends to the effective property

for a composite with non-conducting inclusions. Thus from theorem 4.1 we see as in Lipton (1995, theorem 3.4) that the effective conductivity of the  $k^{-1}$  periodic composite tends to that of the unrescaled composite with non-conducting inclusions as  $k$  tends to infinity. In this way we observe that the bounds capture the asymptotics consistent with effective tensors obtained by rescaling.

(b) *Effective behaviour for monodisperse suspensions of spheres at critical particle size*

It is known from experiment that particle size affects the overall thermal transport properties of composites (cf. Garret & Rosenberg 1974; Every *et al.* 1992). In this section we consider a monodisperse suspension of spheres of good conductor  $\sigma_2$  embedded in a matrix of conductivity  $\sigma_1$ . For prescribed barrier resistance  $\beta^{-1}$ , we exhibit a critical particle radius  $R_{cr}$  for which the effective transport properties are identical to the conductivity of the matrix material. At this critical size the effect of the interface resistance is balanced by the higher conductivity of the particles. Denoting the critical radius by  $R_{cr}$  we have

$$R_{cr} = \beta^{-1}(\sigma_1^{-1} - \sigma_2^{-1})^{-1}. \quad (4.5)$$

We begin with the obvious remark that for composites occupying the unit cube we only consider parameter values  $\beta$ ,  $\sigma_2$ ,  $\sigma_1$  for which the right-hand side of (4.5) is less than 1/2.

To establish our formula for the critical radius we consider a dispersion of  $N$  spheres of common radius 'a' with centres denoted by the vectors  $\mathbf{r}^i$ . We assume all spheres are contained in the unit cube and do not touch. We show that for  $a = R_{cr}$  there exists a periodic piecewise affine solution to the problem (2.2)–(2.4) of the form

$$\phi + \xi \cdot \mathbf{x} = \begin{cases} \xi \cdot \mathbf{x} & \text{in the matrix,} \\ \frac{\sigma_1}{\sigma_2} \xi \cdot \mathbf{x} - \left(1 - \frac{\sigma_2}{\sigma_1}\right) \frac{\sigma_1}{\sigma_2} \xi \cdot \mathbf{r}^i, & \text{in the } i\text{th particle.} \end{cases} \quad (4.6)$$

For this choice of temperature field the effective conductivity given by (2.5) reduces to  $\sigma^e = \sigma_1$ .

We start by looking for a solution of the form

$$\phi + \xi \cdot \mathbf{x} = \begin{cases} \xi_A \cdot \mathbf{x} & \text{in the matrix,} \\ \xi_B \cdot \mathbf{x} + c_i & \text{in the } i\text{th particle.} \end{cases} \quad (4.7)$$

From (2.1), (2.3), and (2.4) it follows that

$$\xi + \int_{\Gamma} [\phi] \mathbf{n} \, ds = \theta_1 \xi_A + \theta_2 \xi_B, \quad (4.8)$$

$$\sigma_1 \xi_A \cdot \mathbf{n} = \sigma_2 \xi_B \cdot \mathbf{n}, \quad (4.9)$$

$$\sigma_2 \xi_B \cdot \mathbf{n} = -\beta \{(\xi_B - \xi_A) \cdot \mathbf{x} + c_i\}. \quad (4.10)$$

From (4.9) we may conclude that  $(\sigma_2/\sigma_1)\xi_B = \xi_A$ . On the surface of the  $i$ th sphere the unit normal is written  $\mathbf{n} = (\mathbf{x} - \mathbf{r}_i)/a$ , thus  $\mathbf{x} = a\mathbf{n} + \mathbf{r}^i$  on the surface and (4.10) can be written as

$$\xi_B \cdot \mathbf{n}(\sigma_2 + \beta a(1 - \sigma_2/\sigma_1)) = -\beta((1 - \sigma_2/\sigma_1)\xi_B \cdot \mathbf{r}^i + c_i). \quad (4.11)$$



It is seen from (4.11) that both sides must equal zero thus

$$\xi_B(\sigma_2 + \beta a(1 - \sigma_2/\sigma_1)) = 0, \quad (4.12)$$

$$(1 - \sigma_2/\sigma_1)\xi_B \cdot r^i + c_i = 0. \quad (4.13)$$

We observe from (2.4) that

$$[\phi] = -\frac{\sigma_2}{\beta}\xi_B \cdot n = -\frac{\sigma_2}{\beta}\xi_B \cdot \frac{x - r^i}{a} \quad (4.14)$$

and (4.8) becomes

$$\xi_B = \left( \theta_1 \frac{\sigma_2}{\sigma_1} + \theta_2 + \frac{\theta_2 \sigma_2}{\beta a} \right)^{-1} \xi. \quad (4.15)$$

It is evident from (4.12) that either

$$\xi_B = 0, \quad (4.16)$$

or

$$\sigma_2 + \beta a \left( 1 - \frac{\sigma_2}{\sigma_1} \right) = 0. \quad (4.17)$$

For finite values of  $\beta$ ,  $\sigma_2$ ,  $\sigma_1$  we may rule out the case  $\xi_B = 0$  as this implies  $\xi = 0$  from (4.15).

Equation (4.17) provides the relation defining the critical radius  $R_{cr}$  and is equivalent to (4.5). For the choice of 'a' given by (4.17) we find

$$\xi_B = \frac{\sigma_1}{\sigma_2} \xi. \quad (4.18)$$

Last we deduce from (2.5) that

$$\sigma^e \xi = \theta_1 \sigma_1 \xi_A + \theta_2 \sigma_2 \xi_B \quad (4.19)$$

and from the relation  $\xi_A = (\sigma_2/\sigma_1)\xi_B$  and (4.18) it follows that  $\sigma^e \xi = \sigma_1 \xi$  for any choice of  $\xi$ . Formula (4.6) follows from (4.13) and the above remarks.

The above analysis shows that at the critical radius the overall heat conductance remains that of the matrix irrespective of the location and number of particles.

We point out that the differential effective medium model introduced by Every *et al.* (1992) predicts that  $\sigma^e = \sigma_1$  for spherical particles with radius  $\sigma_1/\beta$ . We remark that in light of our exact calculation their result provides only an estimate of the critical radius. However, for large values of the particle conductivity their estimate approaches the exact value given by (4.5).

### (c) Critical values of the geometric parameters and optimality

We show that monodisperse suspensions of spheres at critical radius, provide extremal conducting properties. Here we consider conducting particles of  $\sigma_2$  in a matrix of  $\sigma_1$ . When the total surface moment of inertia  $\alpha = \theta_2 d R_{cr}$  the upper bound given by (3.62) reduces to

$$ICU_{12}(\theta_2 d R_{cr}, \beta) = \sigma_1. \quad (4.20)$$

Similarly when the surface area  $s = d \theta_2 R_{cr}^{-1}$  then the lower bound given by (3.13) becomes

$$ICL_{12}(m_0, \beta) = \sigma_1. \quad (4.21)$$

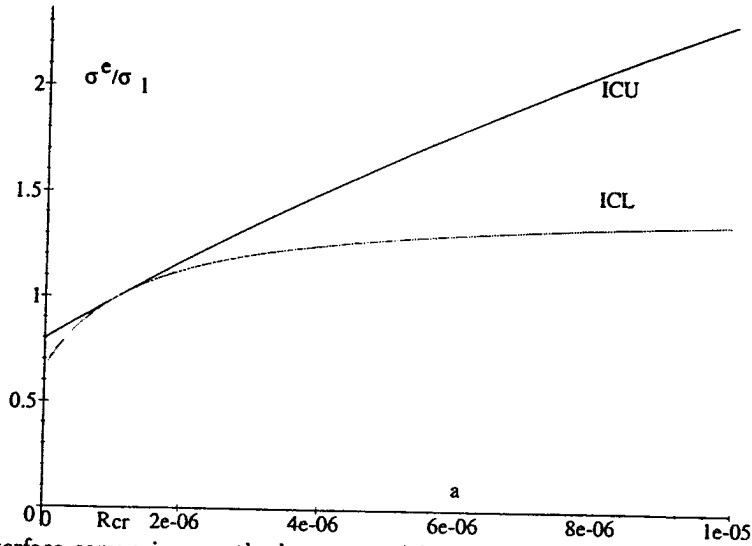


Figure 2. Interface comparison method upper and lower bounds for periodic two-dimensional monodisperse suspensions of diamonds in a ZnS matrix with  $\sigma_1 = 17.4 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\sigma_2 = 1000 \text{ W m}^{-1} \text{ K}^{-1}$ ,  $\theta_2 = 0.2$ ,  $\beta = 6 \times 10^8 \text{ W m}^{-1} \text{ K}^{-1}$ , and radii  $a \leq 10 \text{ }\mu\text{m}$  (here  $s_m = (1 - 4\pi/\theta_2)/2$ ,  $S_m = (1 + 4\pi/\theta_2)/2$ ).

We observe from the results of previous section that for a monodisperse suspension of spheres of critical radius ' $R_{cr}$ ' of conductivity  $\sigma_2$  in a matrix of  $\sigma_1$  that

$$\sigma^e = \sigma_1. \tag{4.22}$$

Moreover, for this suspension the associated geometric parameters  $\alpha$  and  $s$  are given by

$$\alpha = \theta_2 d R_{cr}, \quad s = \theta_2 d R_{cr}^{-1}. \tag{4.23}$$

Thus among all isotropic particulate composites with  $\theta_2$  fixed and  $\alpha$  specified by (4.23) we see that monodisperse suspensions at critical radius give the greatest conductivity. Similarly, among all isotropic particulate composites with  $\theta_2$  fixed and  $s$  specified by (4.23) we see that monodisperse suspensions of spheres of radius  $R_{cr}$  give the lowest conductivity. To fix ideas we plot in figure 2 the upper and lower bounds (3.62) and (3.17) for monodisperse periodic suspensions of spheres in the  $d = 2$  case. For this case the upper and lower bounds touch when the common radius is  $R_{cr}$ .

(d) Size effect phenomena for polydisperse suspensions of spheres

For polydisperse suspensions of spheres the parameter  $\alpha = d\theta_2 \langle r \rangle$ , where  $\langle r \rangle$  is the mean radius of the spherical inclusions given by

$$\langle r \rangle = \sum_{m=1}^N \frac{|Y_m|}{\theta_2} r_m. \tag{4.24}$$

For polydisperse suspensions of spheres of  $\sigma_2$  in a matrix of  $\sigma_1$  with mean radius  $\langle r \rangle$  the upper bound (3.62) becomes

$$ICU_{12}(d\theta_2 \langle r \rangle, \beta) = \left( \sigma_1^{-1} + \frac{\theta_1 \theta_2 \beta \langle r \rangle + \theta_2^2 \lambda + \theta_2 \sigma_2 d^{-1} (d-1)}{\theta_2 \lambda \beta d^{-1} \langle r \rangle + \theta_1 \theta_2 d^{-1} (d-1) \lambda \sigma_2 + \theta_2^2 d (d-1) \sigma_2 \beta \langle r \rangle} \right)^{-1}, \tag{4.25}$$

where  $\lambda = \sigma_1 \sigma_2 (\sigma_2 - \sigma_1)^{-1}$ .

This bound is strictly monotone increasing in  $\langle r \rangle$  and for  $\langle r \rangle = R_{cr}$

$$ICU_{12}(d\theta_2 R_{cr}, \beta) = \sigma_1. \quad (4.26)$$

From monotonicity and (4.26) we have the following theorem.

**Theorem 4.2.** (Size effect theorem). For polydisperse suspensions of spheres of  $\sigma_2$  in a matrix  $\sigma_1$  with  $\sigma_2 > \sigma_1$  and any prescribed volume fraction  $\theta_2$ , if  $\langle r \rangle \leq R_{cr}$  then

$$\sigma^e \leq \sigma_1. \quad (4.27)$$

One has equality in (4.27) only if

$$\langle r \rangle = R_{cr}. \quad (4.28)$$

(e) Necessary conditions of optimal design

We consider suspensions of a  $\sigma_2$  particles in a matrix of  $\sigma_1$  with volume fractions  $\theta_1, \theta_2$  of the constituent materials fixed. We recall the lower bound is given by

$$\sigma^e \geq \left( \frac{\theta_1}{\sigma_1} + \frac{\theta_2}{\sigma_2} + \frac{s}{d\beta} \right)^{-1} \quad (4.29)$$

$$= \sigma_1 \left( 1 - \frac{\sigma_1 \theta_2 \beta^{-1} (s/d\theta_2 - R_{cr}^{-1})}{1 + \sigma_1 \theta_2 \beta^{-1} (s/d\theta_2 - R_{cr}^{-1})} \right). \quad (4.30)$$

From (4.30) we see the lower bound equals  $\sigma_1$  for  $s = d\theta_2 R_{cr}^{-1}$ . It is evident from (4.29) that the lower bound is strictly monotone decreasing in the total interfacial surface area  $s$ . We collect these observations and state the following theorem.

**Theorem 4.3.** For an isotropic suspension of  $\sigma_2$  conducting particles in a matrix of  $\sigma_1$  conductivity with  $\sigma_2 > \sigma_1$  and any prescribed volume fraction  $\theta_2$ , if the total interfacial surface is bounded above by  $d\theta_2 R_{cr}^{-1}$  then

$$\sigma^e > \sigma_1. \quad (4.31)$$

We now consider the problem of the best isotropic distribution of good and bad conductors in the unit cell  $Q$ . Here the best distribution is the one giving the best effective heat transport in all directions (i.e. the largest value of the effective conductivity). It is assumed that the volume fraction of good conductor  $\sigma_2$  is fixed at  $\theta_2$ .

In what follows we investigate the effect of scale in problems of optimal design. To fix ideas we suppose that the volume fraction of the good conductor satisfies the inequality

$$\theta_2 < \frac{2(d-1)}{d} \pi 2^{-d}, \quad d = 2, 3. \quad (4.32)$$

That is the volume fraction is less than that of a sphere (circle) of radius  $1/2$  inscribed within the unit cell. Moreover we restrict the parameters  $\beta, \sigma_1, \sigma_2$  so that the critical radius  $R_{cr}$  satisfies the constraint

$$\frac{2(d-1)}{d} \pi R_{cr}^d < \theta_2, \quad d = 2, 3. \quad (4.33)$$

The above states that we consider only cases where the volume of a single sphere of

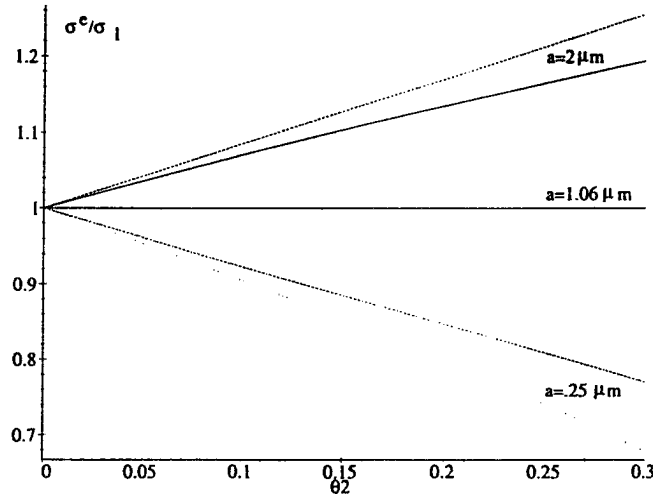


Figure 3. Interface comparison method upper and lower bounds for ZnS–diamond composites as a function of the volume fraction of the diamond, for different diamond particle sizes:  $a = 2 \mu\text{m}$ ,  $a = R_{\text{cr}} = 1.06 \mu\text{m}$ ,  $a = 0.25 \mu\text{m}$ .

critical radius is strictly less than the volume fraction  $\theta_2$  occupied by the polydisperse suspension.

We consider the best distribution of an isotropic, polydisperse, suspension of spheres of good conductor  $\sigma_2$  in a matrix of  $\sigma_1$ , for  $\theta_2$  prescribed and the given constraints (4.32) and (4.33). We have the following theorem characterizing the optimal design.

**Theorem 4.4.** (Optimal design: necessary condition). *The mean radius of the optimal distribution of spheres maximizing the effective conductivity is greater than  $R_{\text{cr}}$ .*

*Proof.* From theorem 4.2 we know that if the mean radius lies below  $R_{\text{cr}}$  then  $\sigma^e \leq \sigma_1$ . So to establish the theorem we construct a polydisperse suspension of spheres with mean radius greater than  $R_{\text{cr}}$  such that the effective conductivity lies above  $\sigma_1$ . The construction is trivial in view of (4.32) and (4.33). Indeed take a suspension consisting of a single sphere of radius  $r$  such that

$$\frac{2(d-1)}{d} \pi r^d = \theta_2. \quad (4.34)$$

Then for this suspension

$$\frac{s}{d\theta_2} = \frac{1}{r}. \quad (4.35)$$

From (4.33) and (4.34) we see that

$$r^{-1} < R_{\text{cr}}^{-1}, \quad (4.36)$$

therefore

$$s < d\theta_2 R_{\text{cr}}^{-1}. \quad (4.37)$$

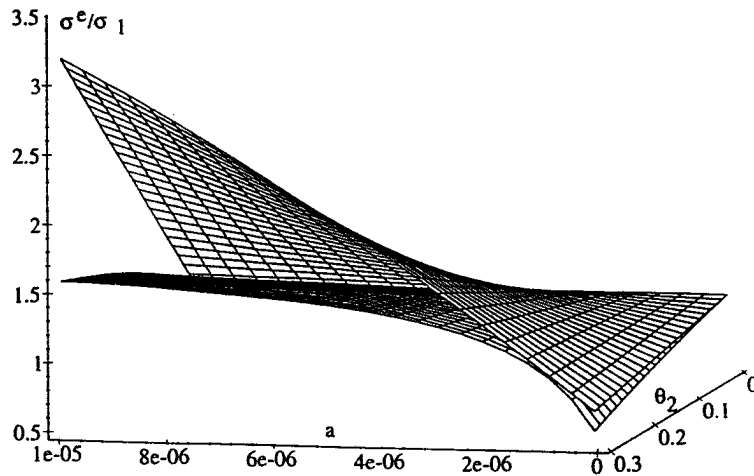


Figure 4. Interface comparison method upper and lower bounds for monodisperse suspensions of diamond in a ZnS matrix as functions of volume fraction  $\theta_2$  and particle radius  $a$ .

We conclude from (4.37) and theorem 4.3 that the effective conductivity for this suspension lies above  $\sigma_1$  and the theorem is established. ■

We conclude this section by making an observation for isotropic monodisperse suspensions of spheres of radius  $r$ . For this case  $\alpha = d\theta_2 r$  and  $s = d\theta_2 r^{-1}$ . Thus we may apply theorems 4.2 and 4.3 to obtain

**Theorem 4.5.** For isotropic monodisperse suspensions of spheres of radius  $r$  at prescribed volume fraction

$$\sigma^e > \sigma_1 \text{ if } r > R_{cr} \quad (4.38)$$

and

$$\sigma^e < \sigma_1 \text{ if } r < R_{cr}.$$

Such a behaviour is illustrated for ZnS–diamond composites in figure 2.

We consider the effect of varying the volume fraction at a fixed particle size for isotropic composites. The bounds on the effective conductivity given by (3.62) and (3.17) are plotted in figure 3 for a periodic suspension of diamonds in a ZnS matrix. We observe that the upper and lower bounds are increasing functions in volume fraction for a particle of size  $2 \mu\text{m}$ , larger than  $R_{cr} = 1.06 \mu\text{m}$ , and that the bounds are decreasing functions in volume fraction for a particle size of  $0.25 \mu\text{m}$ . For  $a = R_{cr} = 1.06 \mu\text{m}$  the upper and lower bound are both equal to  $\sigma_1$ . These bounds predict the same behaviour seen in the experimental results of Every *et al.* (1992).

Lastly we plot the interface comparison method bounds given by (3.62) and (3.17) for a periodic suspension of diamonds in a matrix of ZnS as a function of particle radius and volume fraction in figure 4.

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