Critical radius, size effects and inverse problems for composites with imperfect interface

Robert Lipton and Bogdan Vernescu
Department of Mathematical Sciences, Worcester Polytechnic Institute, 100 Institute Road, Worcester, Massachusetts 06109

(Received 18 July 1995; accepted for publication 12 March 1996)

We provide new bounds on the interfacial barrier conductivity for isotropic particulate composites based on measured values of effective properties, known values of component volume fractions, and the formation factor for the matrix phase. These bounds are found to be sharp. Our tool is a new set of variational principles and bounds on the effective properties of composites with imperfect interface obtained by us [see R. Lipton and B. Vernescu, Proc. R. Soc. London Ser. A **452**, 329 (1996)]. We apply the bounds to solve inverse problems. For isotropic polydisperse suspensions of spheres we are able to characterize the size distribution of the spherical inclusions based on measured values of the effective conductivity. © *1996 American Institute of Physics.* [S0021-8979(96)05212-7]

I. INTRODUCTION

We consider two-phase heat conducting composites with interfacial barrier resistance between phases. Such resistance may arise from the presence of impurities at phase boundaries. At liquid helium temperatures interfacial resistance arises due to acoustic mismatch between component phases as is seen in the work of Garrett and Rosenberg.[1] Starting with the efforts of Maxwell[2] and Rayleigh,[3] a great part of the literature has focused on the idealized case of perfect contact. There one assumes continuity of temperature and heat flux across the phase interface. On the other hand, imperfect interfaces are described by discontinuous temperature fields. We consider a unit cube Q filled with particles of good isotropic conductor of conductivity σ_p, in a matrix of lower conductivity σ_m, (i.e., $\sigma_p > \sigma_m$). We assume that no particles touch the boundary of the cube.

In what follows we make no assumptions about the distribution or shape of the particles. One can think of the cube as representing a (possibly very complicated) period cell for a composite material. Decomposing the temperature field into a periodic fluctuation $\tilde{\phi}$ and a linear part the average intensity measured by an observer outside Q is

$$\overline{\nabla T} = \int_{\partial Q} (\tilde{\phi} + \zeta \cdot \mathbf{r}) \mathbf{n} \, dS = \zeta. \quad (1)$$

Here ∂Q is the boundary of the cube and $\mathbf{n}$ is the outer normal to the boundary. The temperature fluctuation inside the composite satisfies

$$\Delta \tilde{\phi} = 0 \quad \text{inside each phase} \quad (2)$$

and

$$\sigma_p (\nabla \tilde{\phi} + \zeta)_p \cdot \mathbf{n} = \sigma_m (\nabla \tilde{\phi} + \zeta)_m \cdot \mathbf{n} \quad (3)$$

$$\sigma_p (\nabla \tilde{\phi} + \zeta)_p \cdot \mathbf{n} = -\beta (\tilde{\phi}_p - \tilde{\phi}_m) \quad (4)$$

on the two-phase interface. Here $\mathbf{n}$ denotes the normal to the phase boundary pointing into the matrix region, and β is the interfacial barrier conductance. Subscripts p and m denote the side of the interface where field quantities are evaluated. Condition (4) accounts for the interfacial thermal barrier resistance. Here the jump in temperature is proportional to the heat flux across the interface. For some physical situations the interfacial barrier resistance may be thought of as the limiting case of heat transport across bulk phases separated by a thin, poorly conducting interphase region. Denoting the conductivity of the interphase by σ_i and its thickness by l, the conductance β is the finite limit of the ratio σ_i / l as both σ_i and l tend to zero (see Sanchez-Palencia,[4] Dunn, and Taya[5]).

In our previous work[11] new variational principles and bounds on the effective heat conductivity were introduced. These bounds are given in terms of geometric parameters. The lower bound depends on the particle and matrix volume fractions θ_p, θ_m, interfacial surface area S, interfacial barrier conductivity β, and the formation factor of the matrix phase. The upper bound is given in terms of the volume fractions and total moment of inertia of the particle interfaces α. To fix ideas we note that for a monodisperse suspension of spheres of radius a with prescribed volume fraction θ_p, the geometric parameter α is given by $\alpha = 3\theta_p a$ and the total interfacial surface area S is $S = 3\theta_p / a$. For polydisperse suspensions of spheres we have $\alpha = 3\theta_p \langle a \rangle$ and $S = 3\theta_p \langle a^{-1} \rangle$, where $\langle \cdot \rangle$ denotes averaging over all particles in the suspension (see Sec. V).

It is of practical interest to estimate the barrier conductivity and geometric parameters in terms of measured values of effective properties. In Sec. III we apply the monotonicity property to obtain new bounds on the interfacial barrier conductance for isotropic monodisperse suspensions of spheres. The barrier conductivity is bounded above and below by bounds that depend on sphere radius, formation factor, sphere volume fraction, and measured values of the effective conductivity.

The monotonicity property of the bounds in these geometric parameters was also used in Ref. 11 to isolate a distinguished parameter $R_{\text{cr}} = \beta^{-1} / (\sigma_m^{-1} - \sigma_p^{-1})$. This parameter measures the relative importance of the interfacial resistance to the contrast between phase resistances. For isotropic monodisperse suspensions of spheres with radius equal to

 0021-8979/96/79(12)/8964/3/$10.00 © 1996 American Institute of Physics

Downloaded¬16¬Mar¬2005¬to¬128.103.60.225.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright,¬see¬http://jap.aip.org/jap/copyright.jsp

R_{cr}, the effective conductivity is shown to equal that of the matrix, i.e., $\sigma^e = \sigma_m$. We emphasize that this result is obtained for suspensions of spheres at nondilute concentrations. Moreover, we found that $\sigma^e < \sigma_m$ for suspensions of spheres with radii less than R_{cr} and $\sigma^e > \sigma_m$ for spheres with radii greater than R_{cr}. These results extend the work of Chiew and Glandt[8] where the critical radius is observed for dilute suspensions.

In this article we apply a coated sphere construction similar to that of Hashin and Shtrikman[12] to provide an independent proof of the existence of the critical radius, see Sec. IV.

The bounds given in Sec. II can be applied to solve inverse problems. For isotropic particulate suspensions of conductors in a matrix of lesser conductivity, we find that, when the effective conductivity is greater than that of the matrix, then the total moment of inertia of the interface is greater than $d\theta_p R_{cr}$. On the other hand, when the effective property is less than the matrix the ratio of particle volume to interfacial surface $3\theta_p/S$ is less than R_{cr}.

For polydisperse suspensions of spheres, similar observations characterize the size distribution of spheres in terms of measured values of the effective conductivity. Indeed, we obtain the following alternative: if the measured value of the effective conductivity is greater than that of the matrix, then the arithmetic mean of the particle radii lies above R_{cr}, otherwise if the effective conductivity is less than that of the matrix, then the harmonic mean of the particle radii lies below R_{cr}.

II. BOUNDS ON EFFECTIVE PROPERTIES

Writing the local conductivity as $\sigma(\mathbf{r})$ the effective conductivity for the composite is defined by

$$\sigma^e \zeta = \int_Q \sigma(\mathbf{r})(\nabla \tilde{\phi} + \zeta)\, dx. \tag{5}$$

For isotropic suspensions of particles one has the following lower bounds on σ^e, given by (see Ref. 11)

$$LB(m_0, S, \beta) = \sigma_m - \sigma_m[(1-m_0)^{-1} + (\sigma_m \theta_p c)^{-1}]^{-1}, \tag{6}$$

where $c = S/\beta(3\theta_p)^{-1} - (\sigma_p - \sigma_m)(\sigma_m \sigma_p)^{-1}$. Here S is the total surface area of the two-phase interface and m_0 is the effective conductivity of the suspension but with the particles replaced by nonconducting particles of the same shape and a matrix of unit conductivity. The resistivity m_0^{-1} is commonly known as the formation factor, in the porous media literature. The bound is monotone increasing in the arguments m_0 and β. Elementary estimates give $0 \leqslant m_0 \leqslant \theta_m$ and one has

$$\sigma^e \geqslant LB(m_0, S, \beta) \geqslant LB(0, S, \beta)$$
$$= (\theta_m \sigma_m^{-} + \theta_p \sigma_p^{-1} + S(3\beta)^{-1})^{-1}. \tag{7}$$

The upper bound on the effective conductivity for isotropic suspensions as derived in Ref. 11, is given by

$$UB(\alpha,\beta)$$
$$= \left(\sigma_p^{-1} + \frac{\theta_m \beta\alpha/3 + \theta_p^2 \lambda + 2/3\theta_p \sigma_p}{\lambda\beta\alpha/3 + \theta_m \theta_p 2/3 \lambda \sigma_p + 2/9 \theta_p \sigma_p \beta \alpha} \right)^{-1}. \tag{8}$$

Here $\lambda = (\sigma_m^{-1} - \sigma_p^{-1})^{-1}$ and

$$\alpha = \sum_j \int_{\partial Y^j} |\mathbf{r} - \mathbf{r}^j|^2 dS \tag{9}$$

is the sum of the polar moments of inertia of the particle surfaces ∂Y^j. The upper bound is monotone increasing in the parameters β and α. One has $\sigma^e \leqslant UB(\alpha,\beta) \leqslant UB(\alpha,\infty) = HS^+$ where HS^+ is the Hashin–Shtrikman[12] upper bound for isotropic composites with perfectly bonded interfaces.

III. BOUNDS ON INTERFACIAL BARRIER CONDUCTANCE

The upper and lower bounds (6) and (8) are monotonic in the formation factor and in the parameters S, α, and β. We employ this property to obtain bounds on the interfacial conductivity in terms of the measured values of the effective property and the associated geometric parameters.

To fix ideas we consider isotropic monodisperse suspensions of spheres of given radius a, sphere volume fraction θ_p, and formation factor m_0^{-1}. From the monotonicity it is evident that we may invert the bounds to obtain new bounds on the interfacial conductivity. We introduce the intervals I_1, I_2, I_3 defined by

$$I_1 = \{\sigma^e | LB(m_0, 2\theta_p a^{-1}, \infty) \leqslant \sigma^e \leqslant UB(2\theta_p a, \infty)\}, \tag{10}$$

$$I_2 = \{\sigma^e | UB(2\theta_p a, 0) \leqslant \sigma^e < LB(m_0, 2\theta_p a^{-1}, \infty)\}, \tag{11}$$

$$I_3 = \{\sigma^e | LB(m_0, 2\theta_p a^{-1}, 0) \leqslant \sigma^e < UB(2\theta_p a, 0)\}, \tag{12}$$

where

$$LB(m_0, 2\theta_p a^{-1}, \infty) = \sigma_m - \sigma_m\{[(1-m_0)^{-1} - \sigma_p/[\theta_p(\sigma_p - \sigma_m)]\}^{-1}, \tag{13}$$

$$LB(m_0, 2\theta_p a^{-1}, 0) = \sigma_m m_0, \tag{14}$$

$$UB(2\theta_p a, 0) = \theta_m \sigma_m / [2 - (1 - \theta_p \sigma_m/\sigma_p)],$$
$$UB(2\theta_p a, \infty) = HS^+. \tag{15}$$

Here HS^+ is the Hashin–Shtrikman upper bound for perfectly bonded composites.

The bounds on β are given by

$$\underline{\beta} \leqslant \beta < \infty \quad \text{for } \sigma^e \text{ in } I_1, \tag{16}$$

$$\underline{\beta} \leqslant \beta \leqslant \overline{\beta} \quad \text{for } \sigma^e \text{ in } I_2, \tag{17}$$

$$0 \leqslant \beta \leqslant \overline{\beta}, \quad \text{for } \sigma^e \text{ in } I_3, \tag{18}$$

where

$$\underline{\beta} = \frac{\sigma_p[\sigma_p(\sigma^e - \sigma_m) + \theta_p \sigma_m(\sigma_p + \sigma^e)]}{a[2\sigma_p(\sigma_m - \sigma^e) + \theta_p(\sigma_p + \sigma^e)(\sigma_p - \sigma_m)]}, \tag{19}$$

Downloaded¬16¬Mar¬2005¬to¬128.103.60.225.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright,¬see¬http://jap.aip.org/jap/copyright.jsp

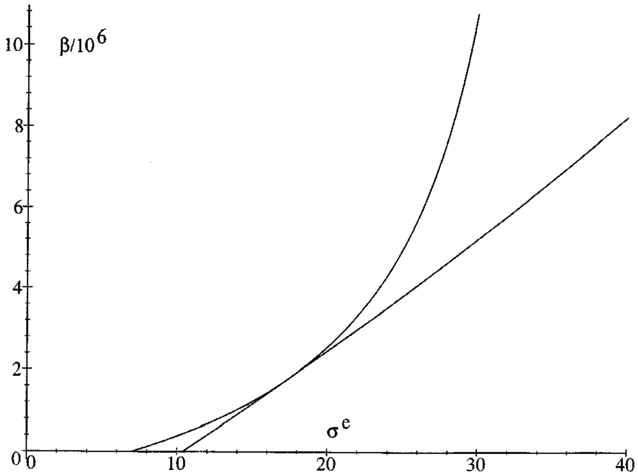

FIG. 1. Bounds on the interfacial barrier conductivity for periodic 3D monodisperse suspensions of diamonds in a ZnS matrix with $\sigma_m = 17.4$ W/(mK), $\sigma_p = 1000$ W/(mK), $\theta_p = 0.4$, and radii $a = 10$ μm. Here the formation factor of the matrix phase is taken to be 0.4.

$$\overline{\beta} = \frac{\theta_p \sigma_m \sigma_p}{a\left[\sigma_p(\sigma_m - \sigma^e)\,\dfrac{1 - m_0}{\sigma^e - \sigma_m m_0} + \theta_p(\sigma_p - \sigma_m)\right]}. \tag{20}$$

Inspection shows that the upper and lower bounds given by (19) and (20) agree when the effective property equals the matrix conductivity. This situation is not uncommon and is seen experimentally in the work in Ref. 9.

IV. MONODISPERSE SUSPENSIONS OF COATED SPHERES

Here we apply the coated spheres construction of Hashin and Shtrikman[12] in the context of imperfect interface to provide another proof of the existence of a critical radius for monodisperse suspensions of spheres.

If one uses the imperfect interface condition (4) and computes the energy of the coated sphere with core σ_p and shell σ_m, then one finds that the energy depends monotonically upon the radius r of the core. The energy is expressed in terms of the effective conductivity of the coated sphere given by

$$\sigma^e = \sigma_m + \frac{\theta_m}{\dfrac{1}{\dfrac{\sigma_p}{f} - \sigma_m} + \dfrac{1 - \theta_m}{3\sigma_m}}, \tag{21}$$

where

$$f = 1 + \frac{\sigma_p}{\beta \tau}. \tag{22}$$

When the core radius equals R_{cr} one sees that the energy dissipated in the coated sphere is equal to that of a coated sphere where both sphere and shell have conductivities equal to σ_m. Thus we can replace matrix material with coated spheres of critical radius without changing the overall conductivity of the sample. We observe that this argument does not depend upon the position of the other coated spheres in the suspension. Thus the result $\sigma^e = \sigma_m$ holds for monodisperse suspensions at critical radius even when the suspensions are anisotropic.

V. INVERSE PROBLEMS

The monotonicity property is also used to gather information on the composite geometry from measured values of the effective conductivity.

We shall assume that the volume fractions θ_p and θ_m are known as well as the values σ_p, σ_m, and β and bound the geometric parameters S and α from measured values of the effective conductivity σ^e. The upper bound (8) is easily seen to be monotonically increasing in α, thus we have the following:

if $\sigma^e > \sigma_m$ then the total moment of inertia of the interface ''α'' satisfies

$$\alpha > 3\theta_p R_{\mathrm{cr}}. \tag{23}$$

On the other hand, the lower bound is monotonically decreasing in the interfacial surface area. Thus it follows that

if $\sigma^e < \sigma_m$ then the particle volume to interfacial surface area ratio satisfies

$$3\theta_p / S < R_{\mathrm{cr}}. \tag{24}$$

For polydisperse suspensions of spheres we introduce the volume averages of the sphere radii, a_i, $i = 1,\ldots,N$, and their reciprocals by

$$\langle a \rangle = \theta_p \sum_{i=1}^{N} a_i \frac{|Y_i|}{\theta_p}, \tag{25}$$

$$\langle a^{-1} \rangle = \theta_p \sum_{i=1}^{N} a_i^{-1} \frac{|Y_i|}{\theta_p}, \tag{26}$$

where $|Y_i|$ is the volume of the ith sphere. For isotropic polydisperse suspensions of spheres we have that $\alpha = 3\theta_p \langle a \rangle$ and $S = 3\theta_p \langle a^{-1} \rangle$ and from (42) and (43) we obtain the characterization of the size distribution of the sphere radii given by

$$\text{if} \quad \sigma^e > \sigma_m \quad \text{then} \quad \langle a \rangle > R_{\mathrm{cr}}, \tag{27}$$

$$\text{and if} \quad \sigma^e < \sigma_m \quad \text{then} \quad \langle a^{-1} \rangle^{-1} < R_{\mathrm{cr}}. \tag{28}$$

ACKNOWLEDGMENT

This work supported in part by NSF Grant No. DMS 9403866 (R.L.).

[1] K. W. Garrett and H. M. Rosenberg, J. Phys. D **7**, 1247 (1974).
[2] J. C. Maxwell (Pergamon, Oxford, 1904), Vol. 1.
[3] Lord Raleigh, Philos. Mag. **34**, 481 (1892).
[4] E. Sanchez-Palencia, *Lecture Notes in Physics* (Springer, Berlin, 1980), p. 127.
[5] M. L. Dunn and M. Taya, J. Appl. Phys. **73**, 1711 (1993).
[6] Y. Benveniste, J. Appl. Phys. **61**, 2840 (1986).
[7] Y. Benveniste and T. Miloh, J. Appl. Phys. **69**, 1337 (1991).
[8] Y. C. Chiew and E. D. Glandt, Chem. Eng. Sci. **42**, 2677 (1987).
[9] A. G. Every, Y. Tzou, D. P. H. Hasselman, and R. Raj, Acta Metall. Mater. **40**, 123 (1992).
[10] D. P. H. Hasselman and L. F. Johnson, J. Compos. Mater. **21**, 508 (1987).
[11] R. Lipton and B. Vernescu, Proc. R. Soc. London Ser. A **452**, 329 (1996).
[12] Z. Hashin and S. Shtrikman, J. Appl. Phys. **33**, 3125 (1962).

Downloaded¬16¬Mar¬2005¬to¬128.103.60.225.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright,¬see¬http://jap.aip.org/jap/copyright.jsp