Effect of the Interface on the Properties of Composite Media

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We develop rigorous bounds on the effective thermal conductivity σ_e of dispersions that are given in terms of the phase contrast between the inclusions and matrix, the interface strength, volume fraction, and higher-order morphological information, including interfacial statistics. The new bounds give remarkably accurate predictions of the thermal conductivity of dispersions of metallic particles in epoxy matrices for various values of the Kapitza resistance. Corresponding results are obtained for the novel situation in which the inclusions possess a superconducting interface.

The preponderance of theoretical predictions of the effective properties of two-phase composites neglect the effect of the interface [1–4]. Interfacial effects are known to be important in a variety of systems and can dramatically alter the effective behavior [5–8]. For example, contact electrical or thermal resistance at the interface (due to roughness) can significantly decrease the effective conductivity and debonding at the interface can erode the effective elastic behavior of the composite. This problem is challenging both experimentally and theoretically. Experimentally it is difficult to measure interfacial properties *in situ* or to construct model systems in which the interfacial properties can be systematically controlled for the examples cited above. Previous rigorous predictions of the effective properties that incorporate the interface are not accurate because they do not account for nontrivial microstructural information.

In this Letter, we present a means to obtain sharp, rigorous bounds on the effective properties of a class of composites in terms of the interfacial strength and crucial microstructural information about the interface. We begin by choosing the problem of determining the effective thermal conductivity σ_e of a dispersion of spheres since there exist accurate experimental measurements of σ_e for such composites in which the interfacial resistance is of the Kapitza type described below. Our bounds give remarkably accurate predictions of the effective thermal conductivity of suspensions of equisized copper spheres in epoxy matrices for various values of the Kapitza resistance. We will also present results for the novel situation in which the spheres possess a *superconducting* interface. Finally, we will discuss how to apply the methodology to study other microgeometries and other effective properties of composites with imperfect interfaces.

We develop rigorous bounds on σ_e by using classical minimum energy principles and by generalizing the cluster-expansion approach of Torquato derived originally for perfect interfaces [9]. Consider an arbitrary random arrangement of equisized spheres of radius a and conductivity σ_2 in a matrix of conductivity σ_1. The interfacial

strength is introduced by first examining a more general *three-phase composite* of a similar dispersion in which the spheres possess a concentric coating of thickness δ and conductivity σ_s. By ultimately passing to the limit that $\delta \rightarrow 0$ and that either $\sigma_s \rightarrow 0$ or $\sigma_s \rightarrow \infty$, we recover the dispersion of interest in which the interfacial property is concentrated on a surface of zero thickness and characterized by the *dimensionless parameters R and C* defined as follows: in the *resistance case*,

$$R \equiv \tilde{R}\sigma_2/a, \quad \text{with } \tilde{R} \equiv \lim_{\substack{\delta \rightarrow 0 \\ \sigma_s \rightarrow 0}} \frac{\delta}{\sigma_s}, \tag{1}$$

and in the *conductance case*

$$C \equiv \tilde{C}/\sigma_1, \quad \text{with } \tilde{C} \equiv \lim_{\substack{\delta \rightarrow 0 \\ \sigma_s \rightarrow \infty}} \sigma_s \delta. \tag{2}$$

In general, $0 \le R \le \infty$ and $0 \le C \le \infty$, with $R = C = 0$ corresponding to the perfect interface, i.e., when there are no jumps in the temperature T and normal component of the heat flux j_n across the sphere-matrix interface. For $R > 0$, T jumps across the interface. By contrast, for $C > 0$, j_n jumps across the interface. To our knowledge, the conductance case has not been studied before in the context of composite materials [10]. The *dimensional* quantities $\tilde{R}$ and $\tilde{C}$ are experimentally measurable as described below. *We show below that there are critical values of both R and C at which the effective conductivity σ_e equals the matrix conductivity σ_1, i.e., the inclusions are effectively hidden.*

At this stage of the analysis, we do not pass to the distinguished limits (1) or (2). Let the aforementioned three-phase composite be exposed to an applied temperature gradient, and let $\sigma(\mathbf{r})$ be the local conductivity at position $\mathbf{r}$, $T(\mathbf{r})$ be the local temperature field, $\mathbf{E}(\mathbf{r}) = -\nabla T(\mathbf{r})$ be the irrotational intensity field, and $\mathbf{J}(\mathbf{r}) = \sigma(\mathbf{r})\mathbf{E}(\mathbf{r})$ be the solenoidal heat flux field. The effective conductivity σ_e of the composite can be defined through the average energy dissipation per unit volume U given by

$$U = \tfrac{1}{2}\sigma_e\langle\mathbf{E}(\mathbf{r})\rangle \cdot \langle\mathbf{E}(\mathbf{r})\rangle = \tfrac{1}{2}\sigma_e^{-1}\langle\mathbf{J}(\mathbf{r})\rangle \cdot \langle\mathbf{J}(\mathbf{r})\rangle, \tag{3}$$

where angular brackets denote an ensemble average. The complexity of the microstructure prohibits one from obtaining the local fields exactly and hence we resort to variational principles. The principle of *minimum potential energy* enables one to bound σ_e from above by constructing irrotational trial fields $\hat{\mathbf{E}}$ with $\langle\hat{\mathbf{E}}\rangle = \langle\mathbf{E}\rangle$, regardless of whether the associated flux is solenoidal. Similarly, the principle of *minimum complementary energy* enables one to bound σ_e from below by constructing solenoidal trial fluxes $\hat{\mathbf{J}}$ with $\langle\hat{\mathbf{J}}\rangle = \langle\mathbf{J}\rangle$, regardless of whether the associated intensity is irrotational.

In order to proceed, one must construct trial fields that account for the complex interactions between the spheres. Following Torquato [9], we base our trial fields on the solutions of the single-inclusion boundary-value problems and find the following *optimized bounds:*

$$\left[\left\langle\frac{1}{\sigma}\right\rangle - \frac{\langle\mathbf{J}^{(1)}/\sigma\rangle \cdot \langle\mathbf{J}^{(1)}/\sigma\rangle}{\langle\mathbf{J}^{(1)} \cdot \mathbf{J}^{(1)}/\sigma\rangle}\right]^{-1}$$

$$\langle\sigma\rangle - \frac{\langle\sigma\mathbf{E}^{(1)}\rangle \cdot \langle\sigma\mathbf{E}^{(1)}\rangle}{\langle\sigma\mathbf{E}^{(1)} \cdot E^{(1)}\rangle}. \quad (4)$$

The trial fields $\mathbf{E}^{(1)}$ and $\mathbf{J}^{(1)}$ are the contributions to the intensity and flux fields (in excess of their average

fields) due to single-body interactions from N coated spheres [11]. Furthermore, for a general property b, $\langle b\rangle = b_1\phi_1 + b_2\phi_2 + b_s\phi_s$, where ϕ_1, ϕ_2, and ϕ_s are the volume fractions of the matrix, inner spheres, and coatings, respectively. The ensemble averages are multidimensional integrals involving two- and three-point spatial correlation functions [9]. Incorporation of such nontrivial microstructural information coupled with the rational-function form of the bounds (4) enables one to obtain sharp estimates of σ_e, even for large inclusion volume fractions and high phase contrast.

We first state and discuss our results for the resistance case and subsequently describe the conductance case. After considerable simplification of the integrals of (4) in the limit (1) (using the same techniques of Ref. [9]), we find the following: *Upper bound in resistance case*:

$$\frac{\sigma_e}{\sigma_1} \leq A_U(R) = 1 + (\alpha - 1)\phi_2 - \frac{B_U}{C_U}, \quad (5)$$

where

$$B_U = \phi_2[-3R\alpha + \phi_1(\alpha - 1 - R)(1 - \alpha)]^2, \quad (6)$$

$$C_U = 9\alpha R + 9R^2 + 3\phi_1[(\alpha - 1)^2 - R^2] + (\alpha - 1)\{[\phi_1(\alpha - 1 - R) + 3R]^2 + 2\zeta_2\phi_1(\alpha - 1 - R)^2\}. \quad (7)$$

Lower bound in resistance case:

$$\frac{\sigma_e}{\sigma_1} \geq A_L(R) = \left\{1 + \frac{1 - \alpha + 3R}{\alpha}\phi_2 - \frac{B_L}{C_L}\right\}^{-1}, \quad (8)$$

where

$$B_L = \phi_2\{2\phi_1[R(4\alpha - 3R - 4) - (\alpha - 1)^2] - 6\alpha R\}^2, \quad (9)$$

$$C_L = \alpha^2(\alpha - 1 - R)^2\left[6\phi_1 + \left(\frac{1}{\alpha} - 1\right)(4\phi_1^2 + 2\zeta_2\phi_1)\right] + 6\alpha R[\alpha^2 + 2(R + 1)^2]$$

$$+ \alpha R\phi_2\left\{(\alpha - 1 - R)^2\left[\frac{16}{9} + 3\phi_2(1 + \phi_2)\right] + 24(\alpha - 1 - R)(R + 1) + 12(\alpha - 1 - R)^2\phi_2\right\}. \quad (10)$$

The dimensionless bounds $A_U(R)$ and $A_L(R)$ depend not only on the dimensionless resistance R defined by (1), but the sphere to matrix conductivity ratio $\alpha \equiv \sigma_2/\sigma_1$, the phase volume fractions ϕ_1 and $\phi_2 = 1 - \phi_1$, and a known microstructural parameter ζ_2 [3,4]. The parameter ζ_2 is a threefold integral over a three-point spatial correlation function and has been computed for a variety of dispersions [4]. In evaluating the integrals of (4) leading to bounds (5) and (8), the one-body contributions to previously studied [12] surface-particle and surface-particle-particle correlation functions also arise *but these integrals can be obtained analytically in terms of volume fractions.* See Ref. [13] for details.

To summarize, the bounds (5) and (8) for nonzero R ultimately can be expressed in terms of the same microstructural information required to compute the perfect-interface case. Indeed, when $R = 0$, the bounds coincide exactly with the perfect-interface bounds of Torquato [9] which are always above the bounds for nonzero R

since they are monotonically decreasing functions of R, i.e., $A_U(R) \leq A_U(0)$ and $A_L(R) \leq A_L(0)$. Hashin's [8] bounding procedure does not incorporate this level of information but instead contains only simple average information; e.g., his procedure yields the lower bound

$$\sigma_e/\sigma_1 \geq \{1 + (1 - \alpha + 3R)\phi_2/\alpha\}^{-1} \quad (11)$$

which is just the harmonic average of the different phases and identical to the first two terms of our lower bound (8). The correction E_L/F_L that incorporates nontrivial microstructural information is significant and serves to tighten the bound. Lipton and Vernescu [14] found an upper bound with the same level of information as contained in (11). They also found a lower bound requiring additional information about the effective conductivity of a similar suspension of insulating spheres in a conducting matrix, which must be experimentally measured or rigorously bounded from below.

Interestingly, the bounds $A_U(R)$ and $A_L(R)$ coincide and equal unity for $\alpha > 1$ when the dimensionless resis-

tance takes on the *critical value* $R_c = \alpha - 1$, i.e., the effective conductivity σ_e exactly equals the matrix conductivity σ_1. When $R = R_c$, the inclusions are effectively hidden. The monotonicity of $A_U(R)$ and $A_L(R)$ ensures that $\sigma_e < \sigma_1$ for $R > R_c$, which implies that the addition of conducting spheres in the matrix ($\alpha > 1$) reduces the conductivity σ_e below that of the matrix conductivity. The critical value R_c is directly related to the notion of a "critical radius" a_c defined to be the radius required to "hide" the particles [5,7,14]. From (1) it is seen that $a_c = \tilde{R}\sigma_2/(\alpha - 1)$.

An interesting situation occurs when the spheres are superconducting relative to the matrix (i.e., $\alpha = \infty$) such that the ratio α/R remains finite. Here we can compare our bounds to the experimental results of de Araujo and Rosenberg [15] who measured the effective thermal conductivity of random dispersions of metallic spheres in epoxy matrices for several values of the interfacial Kapitza resistance at liquid-helium temperatures. Kapitza resistance arises due to the acoustic mismatch at the interface of dissimilar materials that increases dramatically as T^{-3} (where T is temperature) for $T < 20$ K and hence can be conveniently controlled by simply varying T. Values of the Kapitza resistance, exactly equal to the dimensional resistance $\tilde{R}$ defined by (1), were obtained at different temperatures by measuring the ratio of the temperature drop to the heat flux across a thin metal-epoxy sandwich.

Figure 1 compares effective conductivity data of a copper/epoxy composite versus the particle volume fraction ϕ_2 for two different values of temperature (or α/R) to our lower bounds using a Monte Carlo evaluation of ζ_2 for a random array of hard spheres [16]. Our lower bound predictions [17] agree remarkably well with the experimental results. The perfect-interface lower bound is also included to show how dramatically the effective conductivity drops due to interfacial resistance. It is noteworthy that an approximation formula due to Chiew and Glandt [5] also predicts the data well.

Figure 2 compares our bounds for a random dispersion of conducting inclusions with $\sigma_2/\sigma_1 = 10$ and $R = 30$ to corresponding perfect-interface results. The bounds are
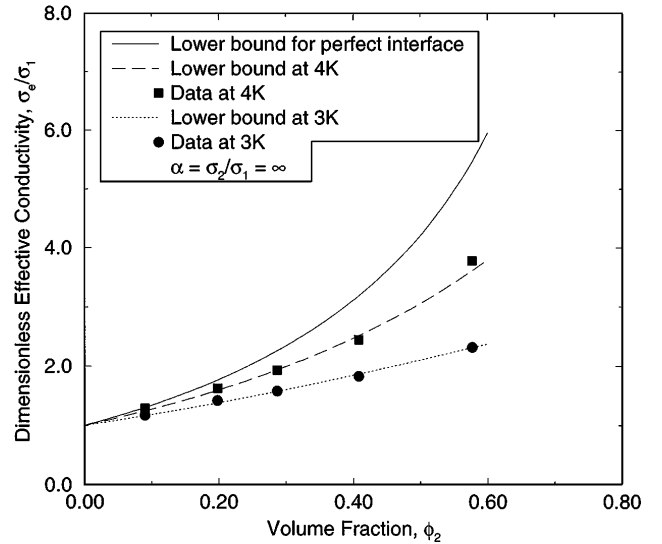

FIG. 1. The scaled effective thermal conductivity σ_e/σ_1 vs the particle volume fraction ϕ_2. Experimental data [15] for copper spheres of radius $a = 50$ μm in epoxy for $T = 4$ K ($\alpha/R = 14.8$) and for $T = 3$ K ($\alpha/R = 4.93$) compared to lower bound (8). Also included is lower bound for perfect interface ($R = 0$). All bounds use ζ_2 from Ref. [14].

rather tight. Note that since $R > R_c = 9$, a thin insulating coating can make relatively conducting inclusions behave effectively as insulating inclusions.

We now state and discuss the bounds in the instance where the spheres possess an infinitesimally thin superconducting coating. Again, after considerable simplification of the integrals of (4) in the limit (2), we find the following: *Upper bound in conductance case*:

$$\frac{\sigma_e}{\sigma_1} \le D_U(C) = 1 + (\alpha + 3C - 1)\phi_2 - \frac{E_U}{F_U}, \quad (12)$$

where

$$E_U = \phi_2\{\phi_1[C(5 - 5\alpha - 6C) - (\alpha - 1)^2] - 3C\}^2, \quad (13)$$

$$F_U = 6C + (\alpha - 1 + 2C)^2[3\phi_1 + (\alpha - 1)(2\zeta_2\phi_1 + \phi_1^2)] + C\phi_2(\alpha - 1 + 2C)^2\left[\frac{16}{9} + 3\phi_2(1 + \phi_2)\right]$$
$$+ 3C[\phi_1(\alpha - 1 + 2C) + 1]^2. \quad (14)$$

Lower bound in conductance case:

$$\frac{\sigma_e}{\sigma_1} \ge D_L(C) = \left\{1 + \left(\frac{1}{\alpha} - 1\right)\phi_2 - \frac{E_L}{F_L}\right\}^{-1}, \quad (15)$$

where

$$E_L = \phi_2[2\phi_1(\alpha - 1 + 2C)(\alpha - 1) + 6C]^2, \quad (16)$$

$$F_L = 6\alpha^2\{3C + 6C^2 + \phi_2[(\alpha - 1)^2 - 4C^2]\} + (\alpha - \alpha^2)\{4[\phi_1(\alpha - C - 1) - 3C\phi_2]^2$$
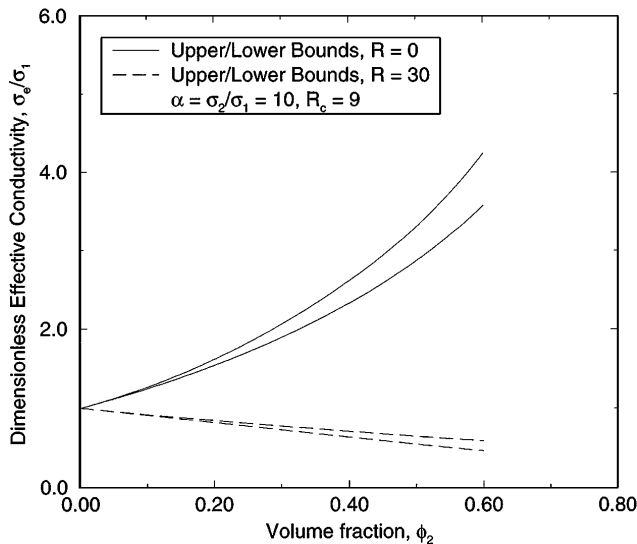$$+ 2\zeta_2\phi_1(\alpha - 1 + 2C)^2\}. \quad (17)$$

FIG. 2. Comparison of the bounds (5) and (8) for two different values of the dimensionless resistance R vs sphere volume fraction ϕ_2 for $\alpha = 10$. All bounds use ζ_2 from Ref. [14]. Here critical value $R_c = 9$.

The dimensionless bounds $D_U(C)$ and $D_L(C)$ depend on C, ϕ_1, ϕ_2 and ζ_2 described earlier. When $C = 0$, we recover the perfect interface bounds of Torquato [9]. The bounds $D_U(C)$ and $D_L(C)$ coincide and equal unity for $\alpha < 1$ when the dimensionless conductivity takes on the *critical value* $C_c = (1 - \alpha)/2$. At this value the spherical inclusions are effectively hidden.

Figure 3 compares our bounds for a random dispersion of insulating inclusions with $\sigma_2/\sigma_1 = 0.1$ and $C = 1$ to corresponding perfect-interface results. It is seen that since $C > C_c = 0.45$, a thin superconducting coating can make relatively insulating inclusions behave effectively as conducting inclusions.

By mathematical analogy, the results obtained here translate immediately into equivalent results for the effective electrical conductivity, dielectric constant, and magnetic permeability. Indeed, the methodology outlined here is general in that it enables one to determine the effect of the interface on any effective property that can be characterized by *minimum energy principles,*, e.g., elastic moduli, thermal expansion coefficient, and thermoelectric moduli. Moreover, *nonspherical inclusions with a size distribution* can be treated analytically provided that the relevant fields are known for a coated inclusion in an infinite matrix. Such solutions are already available for long, oriented cylinders and for arbitrarily shaped ellipsoids in the conduction, elastic, thermoelastic, and thermoelectric problems. An important conclusion is that although the property bounds in the limit that the coating thickness goes to zero depend on, among other quantities, interfacial statistics, they can be written in terms of the same microstructural information as required for the perfect interface.
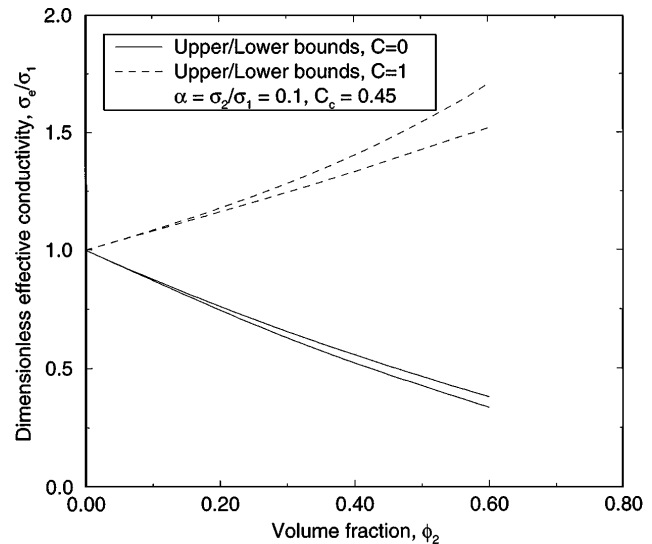
FIG. 3. Comparison of the bounds (12) and (15) for two different values of the dimensionless conductance C vs sphere volume fraction ϕ_2 for $\alpha = 0.1$. All bounds use ζ_2 from Ref. [14]. Here critical value $C_c = 0.45$.

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