Bounds on the thermoelastic properties of suspensions of spheres

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Three-point upper and lower bounds on the effective thermal expansion coefficient and specific heats of statistically isotropic suspensions of mutually impenetrable spheres are computed for the first time. The three-point bounds depend upon the microstructure via a three-point spatial correlation function of the medium. Both equisized and multisized spheres are considered, and hence the effect of polydispersivity in sphere size on the thermoelastic properties is determined. For reasons of mathematical analogy, the results of this study for the thermal expansion coefficient translate immediately into equivalent results for the hygroscopic expansion coefficient.

I. INTRODUCTION

The problem of theoretically determining the effective transport, electromagnetic, and elastic properties of a composite material of arbitrary microgeometry, given the properties of the constituent materials, has received considerable attention (see Refs. 1–4 and references therein). Comparatively speaking, little effort has been directed toward the prediction of the effective thermoelastic properties, such as the thermal expansion coefficient and the specific heats, of composite materials. The effective thermal expansion coefficients of a composite material are defined as the average strains that result from a unit temperature rise in a traction-free material. The effective specific heat at constant volume and at constant pressure, respectively, are the quantities of heat necessary to produce a uniform unit temperature rise under conditions of constant surface displacements and of constant surface tractions. Thermal expansion behavior can be important when composite materials are used in conjunction with other materials and when it is necessary to match the thermal expansion coefficient of one structural component with another. Knowledge of the specific heats of composites is of obvious importance in determining the thermal transient response of the materials.

Levin5 has shown that a simple relationship exists between the effective expansion coefficients and the effective elastic moduli of two-phase composites. This result was also independently obtained by Schapery,6 Rosen,7 Cribb,8 and Steel.9 The effective specific heats of two-phase composites were shown by Rosen and Hashin10 to be simply related to the effective elastic moduli. Thus, given the effective elastic moduli, one may compute the effective expansion coefficients and specific heats exactly. These relations show that the effective expansion coefficients and specific heats deviate from simple mixture rules as a result of elastic interactions. It also follows from these relations that bounds on the effective elastic moduli lead directly to bounds on the aforementioned effective thermoelastic properties.

In this article, three-point upper and lower bounds on the effective thermal expansion coefficient \( \alpha_e \), effective constant-pressure specific heat \( c_{p,e} \), and effective constant-volume specific heat \( c_{v,e} \) of statistically isotropic suspensions of mutually impenetrable spheres are computed for the first time. These bounds depend upon a three-point spatial correlation function of the medium. The cases of both equisized and multisized spheres are considered, and hence the effect of polydispersivity in sphere size on the thermoelastic properties is studied.

For reasons of mathematical analogy, the results of this study for the thermal expansion coefficient \( \alpha_e \) translate immediately into equivalent results for the hygroscopic expansion coefficient \( \beta_e \).1 In the latter problem, instead of a unit temperature rise, one is concerned with a uniform moisture content or a relative humidity change. The swelling or shrinkage of composites due to hygroscopic effects is a problem of important practical concern.

In Sec. II, basic relations and bounds for the effective thermoelastic properties are given. In Sec. III, the bounds on the effective thermoelastic properties are computed for statistically isotropic composites composed of spheres with a polydispersivity in size distributed throughout a matrix. In Sec. IV, concluding remarks are made.

II. BASIC RELATIONS AND BOUNDS FOR THE THERMOELASTIC PROPERTIES

A. Basic relations

For isotropic two-phase composites, it has been shown that the effective thermal expansion coefficient \( \alpha_e \), is given by\(^{10} \)

\[
\alpha_e = \langle \alpha \rangle - \frac{K_1 K_2}{K_2 - K_1} \left( \frac{1}{K_e} - \frac{1}{K} \right),
\]

where for some general physical property \( X \)

\[
\langle X \rangle = X_1 \phi_i + X_2 \phi_2,
\]

\( \phi_i \) is the volume fraction of phase \( i \), \( \alpha_i \) is the thermal expansion coefficient of phase \( i \), \( K_i \) is the bulk modulus of phase \( i \), and \( K_e \) is the effective bulk modulus of the composite. For such composites, it has been also shown that\(^{10} \)

\[
\frac{c_{p,e} - c_p}{T_0} = \left( \frac{K_1 K_2 (\alpha_2 - \alpha_1)}{K_2 - K_1} \right)^{1/2} \left( \frac{1}{K_e} - \frac{1}{K} \right),
\]

where \( T_0 \) is a base temperature. Given the effective constant-pressure specific heat \( c_{p,e} \), one may obtain the effective constant-volume specific heat \( c_{v,e} \) from the relation
\[ c_{PS} - c_{PS} = 3T_0K_\varepsilon c_{PS}^2. \tag{4} \]

Now since the quantity \( K_\varepsilon \sim (K^{-1})^{-1} \) (as will be shown), then according to Eqs. (3), \( c_{PS} \ll c_{PS} \).

From relations (1), (3), and (4), it is clear that if the effective bulk modulus \( K_\varepsilon \) is known along with the physical properties of the phases at some volume fraction, then one may calculate \( \sigma_\varepsilon \), \( c_{PS} \), and \( c_{PS} \). Equations (1) and (3) show how both \( \sigma_\varepsilon \) and \( c_{PS} \) deviate from simple mixture rules (i.e., \( \sigma_\varepsilon = \langle \sigma \rangle \) and \( c_{PS} = \langle c \rangle \)) as a result of mechanical interactions embodied in the terms involving \( K_\varepsilon^{-1} \sim (K^{-1})^{-1} \). Note that the simple mixture rules approximately apply when

\[ \frac{1}{K_\varepsilon} \sim \left( \frac{1}{K} \right), \tag{5} \]

which corresponds to a composite that has an approximately uniform stress distribution when it is externally pressurized, such as a two-phase material in which the shear modulus of one of the phases is very small compared to the shear modulus of that phase.

### B. Bounds

Except for a few idealized microgeometries, the infinite set of spatial correlation functions required to compute effective properties such as \( K_\varepsilon \) is never available, and hence exact evaluations of effective properties for composites of arbitrary microstructures are generally out of the question. Using limited microstructural information on the composite, however, one can set rigorous bounds on the effective properties. The functional forms of (1) and (3) ensure that bounds on \( K_\varepsilon \) translate immediately to bounds on \( \sigma_\varepsilon \) and \( c_{PS} \), respectively. Specifically, given \( n \)-point bounds (i.e., bounds which depend upon one-point through \( n \)-point spatial correlation functions) on the effective bulk modulus \( K_\varepsilon \), denoted by \( K_\varepsilon^{(n,1)} \) and \( K_\varepsilon^{(n,L)} \), then one has from Eq. (1) that

\[ \sigma_\varepsilon^{(n,1)} \leq \sigma_\varepsilon^{(n,2)} \leq \sigma_\varepsilon^{(n,L)}, \tag{6} \]

where

\[ \sigma_\varepsilon^{(n,1)} = \langle \sigma \rangle - K_\varepsilon K_\varepsilon \left( \frac{\alpha_2 - \alpha_1}{K_\varepsilon - K_1} \right) \left( \frac{1}{K_\varepsilon^{(n,L)}} - 1 \right), \tag{7} \]

\[ \sigma_\varepsilon^{(n,2)} = \langle \sigma \rangle - K_\varepsilon K_\varepsilon \left( \frac{\alpha_2 - \alpha_1}{K_\varepsilon - K_1} \right) \left( \frac{1}{K_\varepsilon^{(n,1)}} - 1 \right). \tag{8} \]

when

\[ \frac{\alpha_2 - \alpha_1}{K_\varepsilon - K_1} < 0, \tag{9} \]

and from Eq. (2) that

\[ C_\varepsilon^{(n,1)} < C_\varepsilon^{(n,2)} < C_\varepsilon^{(n,L)}, \tag{10} \]

where

\[ C_\varepsilon = \frac{c_{PS} - c_{PS}}{T_0} \tag{11} \]

\[ C_\varepsilon^{(n,L)} = \frac{(K_\varepsilon K_\varepsilon) (\alpha_2 - \alpha_1)}{K_\varepsilon - K_1} \left( \frac{1}{K_\varepsilon^{(n,L)}} - 1 \right)^{1/2}, \tag{12} \]

\[ C_\varepsilon^{(n,1)} = \frac{(K_\varepsilon K_\varepsilon) (\alpha_2 - \alpha_1)}{K_\varepsilon - K_1} \left( \frac{1}{K_\varepsilon^{(n,1)}} - 1 \right)^{1/2}. \tag{13} \]

Note that for \( \langle \alpha_2 - \alpha_1 \rangle / (K_\varepsilon - K_1) > 0 \) the bounds (7) and (8) reverse themselves, i.e., the right-hand sides of (7) and (8) become \( \sigma_\varepsilon^{(n,L)} \) and \( \sigma_\varepsilon^{(n,1)} \), respectively.

One of the simplest bounds on \( K_\varepsilon \) are one-point bounds due to Paul:

\[ K_\varepsilon^{(1,U)} = \langle K \rangle, \tag{14} \]

\[ K_\varepsilon^{(1,L)} = \langle K^{-1} \rangle^{-1}. \tag{15} \]

Combination of Eqs. (7), (12), and (15) yields the fact that \( \sigma_\varepsilon \rightarrow (\alpha) \) for \( \langle \alpha_2 - \alpha_1 \rangle / (K_\varepsilon - K_1) < 0 \), \( \alpha \rightarrow (\alpha) \) for \( \langle \alpha_2 - \alpha_1 \rangle / (K_\varepsilon - K_1) > 0 \), and \( c_{PS} \rightarrow (c_{PS}) \).

The most restrictive bounds on \( K_\varepsilon \) given the simplest of statistical quantities, the volume fractions \( \phi_1 \) and \( \phi_2 \), are the two-point bounds obtained by Hashin and Shtrikman and by Walpole:

\[ K_\varepsilon^{(2,U)} = K_1 + \frac{\phi_1}{K_1 - K_2 + 3K_1 + 4G_2}, \tag{16} \]

\[ K_\varepsilon^{(2,L)} = K_1 + \frac{\phi_1}{K_1 - K_2 + 3K_1 + 4G_2}, \tag{17} \]

when

\[ (G_2 - G_1) (K_2 - K_1) > 0. \tag{18} \]

Here \( G_i \) is the shear modulus of phase \( i \). The bounds (16) and (17) are reversed when \( (G_2 - G_1) (K_2 - K_1) < 0 \). Note that the bounds (16) and (17) depend upon two-point correlation functions in a trivial manner.

Beran and Molyneux derived three-point bounds on \( K_\varepsilon \) that are narrower than the aforementioned two-point bounds. These bounds were subsequently simplified by Milton and are given by

\[ K_\varepsilon^{(3,U)} = \langle K \rangle - \frac{3 \phi_1 \phi_2 (K_2 - K_1)}{4 (\langle K \rangle + 4G_\varepsilon)}, \tag{19} \]

\[ K_\varepsilon^{(3,L)} = \left( \frac{1}{K} - \frac{4 \phi_1 \phi_2 (1/K_1 - 1/K_2)^2}{4 (1/K) + 3 (1/G)} \right)^{-1}, \tag{20} \]

where, for any property \( X \),

\[ \langle X \rangle = X_1 \phi_1 + X_2 \phi_1, \tag{21} \]

\[ \langle X \rangle = X_1 \phi_1 + X_2 \phi_2, \tag{22} \]

\[ \xi_2 = 1 - \xi_1 \]

\[ = \frac{9}{2 \phi_1 \phi_2} \int_0^r \int_0^\omega \frac{dr}{2} \int_0^{\omega} \frac{ds}{2} \int_{-1}^{1} du \frac{S_\xi(r,s,t) P_2(u)}{P_2(u)}, \tag{23} \]

\[ S_\xi(r,s,t) = S_\xi(r,s,t) - S_\xi(r,s,t) S_\xi(s) \phi_2, \tag{24} \]

Here \( S_\xi(r,s,t) \) is the probability of finding the end points of a line segment of length \( r \) in phase 2 when placed randomly in the composite. \( S_\xi(r,s,t) \) is the probability of finding the vertices of a triangle of lengths \( r,s \), and \( t \) in phase 2 when placed randomly in the composite, with \( r^2 + s^2 + t^2 = 2rsu \). \( P_2(u) \) is the Legendre polynomial of order two. Note that the three-point microstructural parameter \( \xi \), which lies in the interval \([0,1] \), contains nontrivial spatial information about the composite.

In summary, given the one-, two-, and three-point bounds on \( K_\varepsilon \) described above, one can obtain correspond-
function.\textsuperscript{22} For example, for equisized impenetrable spheres, through order $\phi_2$, one exactly has\textsuperscript{22}

$$\xi^2 = \left( \frac{1}{2} \ln 3 - \frac{1}{2} \right) \phi_2, \quad \approx 0.21068 \phi_2. \quad (25)$$

Thus, in accordance with the discussion above, relation (25) provides a good approximation to $\xi^2_2$ for \textsuperscript{19} $0 < \phi_2 < 0.5$: a very wide range of $\phi_2$ considering that the random-close-packing volume fraction is about 0.63 (see Refs. 23 and references therein).

Very recently, Thovvert \textit{et al.}\textsuperscript{24} computed $\xi^2$ exactly through order $\phi_2$ for an equilibrium ensemble of spheres with a continuous distribution in radii $a$ characterized by a density function $n(a)$, they found

$$\xi^2 = e_1 \phi_2, \quad (26)$$

where

$$e_1 = \frac{1}{\phi_2^2} \int \int \Delta\left( \frac{b}{a} \right) \phi_2(a) \phi_2(b) da db \quad (27)$$

$$\Delta(\gamma) = \frac{3}{16\pi^2} \left( \frac{(1 + 2\gamma)^4 - 1}{4(1 + 2\gamma)^2} - \ln(1 + 2\gamma) \right), \quad (28)$$

$$\phi_2(a) = \frac{4\pi}{3} a^3 n(a), \quad (29)$$

and

$$\phi_2 = \frac{4\pi}{3} \int_0^\infty a^3 n(a) da. \quad (30)$$

Note that for monodispersed spheres of radius $R$ at number density $n, n(a) = n_0 \delta(a - R)$ [where $\delta(a)$ is the Dirac delta function], and Eq. (27) leads to

$$e_1 = \Delta(1) = \frac{1}{3} \ln 3 - \frac{1}{3}, \quad (31)$$

which is in agreement with Eq. (25). For any finite degree of polydispersivity

$$e_1 > \Delta(1). \quad (32)$$

Thovvert \textit{et al.}\textsuperscript{24} determined that $e_1$ achieves a maximum

$$e_1 = 0.5 \quad (33)$$

for a polydispersed suspension of impenetrable spheres containing $N$ different and widely separated particle sizes (in the limit $N \to \infty$), and hence substitution of Eq. (33) into Eq. (26) gives the result

$$\xi^2 = 0.5 \phi_2, \quad (34)$$

which corresponds to the microgeometry that gives the largest effect of polydispersivity.

In light of the above discussion, one can use relation (26) to evaluate three-point bounds on $\alpha_2$ and $C_2$ for polydispersed suspensions of impenetrable spheres for a wide range of sphere volume fractions.

**B. Results**

The three-point bounds on $\alpha_e$, Eqs. (7) and (8), and on $C_e$, Eqs. (12) and (13), are computed for suspensions of monodispersed, impenetrable spheres using relation (25). Such three-point bounds are also evaluated for the polydispersed suspension corresponding to relation (34), thus enabling one to study the maximum effect of polydispersivity on bounds on the effective thermoelastic properties. In all

\[ \text{III. CALCULATIONS OF THREE-POINT BOUNDS ON THERMOELASTIC PROPERTIES} \]

Substitution of the three-point bounds (19) and (20) for $K_e$ into relations (7), (8), (12), and (13) yield three-point bounds on $\alpha_e$ and $C_e$. In order to compute such bounds, one must first determine the three-point microstructural parameter $\xi_2$ for the model of interest. The model microstructures that are considered here are distributions of mutually impenetrable equisized as well as multisized spheres.

**A. Three-point parameter $\xi_2$**

To date, the three-point parameter $\xi_2$ has been computed to all orders in the volume fraction $\phi_2$ for three model isotropic suspensions: equisized full penetrable spheres,$\textsuperscript{20}$ multisized fully penetrable spheres,$\textsuperscript{21}$ and an equilibrium ensemble of equisized impenetrable spheres.$\textsuperscript{15}$ A hallmark of all of these results is the fact that $\xi_2$ is nearly linear in the sphere volume fraction $\phi_2$ for $\phi_2 \geq 0$ for a wide range of volume fractions and thus, for $\xi_2^2(\phi_2 = 0) = 0$ for random distributions of spherical inclusions,$\textsuperscript{22}$ the slope of $\xi_2^2$ at $\phi_2 = 0$ approximately determines the behavior of $\xi_2^2$ for a wide range of $\phi_2 \geq 0$. The slope of $\xi_2^2$ at $\phi_2 = 0$ is determined by the zero-density limit of the radial (pair) distribution function.
cases, results are reported for the sphere volume fraction range $0 < \phi < 0.5$. For concreteness, we consider the dimensionless material properties $\alpha_r/\alpha_1 = 14$, $K_r/K_1 = 9.1$, $G_r/G_1 = 26$, $G_r/K_1 = 0.21$, and $G_r/K_1 = 0.6$, which corresponds to a composite composed of glass spheres in an epoxy matrix. (Note only three of the ratios $K_r/K_1$, $G_r/G_1$, $G_r/K_1$, and $G_r/K_1$ are independent.)

In Fig. 1, two- and three-point bounds on the scaled expansion coefficient $\alpha_r/\alpha_1$ are plotted versus the sphere volume fraction for the monodispersed case. Note that the three-point bounds provide significant improvement over the two-point bounds for a wide range of $\phi$. The greatest improvement occurs in the lower bound, as one would expect based upon the discussion in the preceding section, i.e., the actual value of $\alpha_r/\alpha_1$ will lie closer to the three-point lower bound when the inclusions are stiffer than the matrix. The dotted line in the figure is the simple mixture rule $\langle \alpha_m \rangle / \alpha_1$, which also corresponds to the one-point upper bound.

Bounds for the polydispersed microgeometry corresponding to Eq. (34) are plotted in Fig. 2. Although the three-point bounds improve upon the two-point bounds, the three-point bounds widen (relative to the monodisperse case) and shift downwards. This indicates that the effect of polydispersivity is to decrease $\sigma_r/\alpha_1$ relative to the monodisperse case. This will be true for any composite in which $(\alpha_r - \alpha_1)/(K_r - K_1) < 0$, $G_r > G_1$, and $K_r > K_1$. In many applications, it is desired to minimize the thermal expansion coefficient of composites. Thus, if minimization of $\alpha_r$ is desired for the aforementioned large class of composites, one should manufacture the inclusions with different sizes rather than with the same size.

In Fig. 3, two- and three-point bounds on the dimensionless quantity $C_r/(T_r K_1 \alpha_1^2)$ are plotted versus $\phi_r$ for a

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**FIG. 1.** Upper and lower bounds on the scaled effective thermal expansion coefficient $\alpha_r/\alpha_1$ for suspensions of monodispersed, impenetrable spheres vs the sphere volume fraction $\phi_r$ with $\alpha_r/\alpha_1 = 14$, $K_r/K_1 = 9.1$, $G_r/G_1 = 26$, $G_r/K_1 = 0.21$, and $G_r/K_1 = 0.6$. Two-point bounds are dashed lines as computed from Eqs. (7) and (8) with $n = 2$. Three-point bounds are solid lines as computed from Eqs. (7) and (8) with $n = 3$. The dotted line is the simple mixture rule $\langle \alpha_r/\alpha_1 \rangle$, which also corresponds to the one-point upper bound.

**FIG. 2.** As in Fig. 1 except for suspensions of polydispersed, impenetrable spheres with the three-point microstructural parameter $\xi_3$ given by Eq. (34).

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**FIG. 3.** Upper and lower bounds on the dimensionless quantity $C_r/(T_r K_1 \alpha_1^2)$ [defined by Eq. (11)] for suspensions of monodispersed, impenetrable spheres vs the sphere volume fraction $\phi_r$ with $\alpha_r/\alpha_1 = 14$, $K_r/K_1 = 9.1$, $G_r/G_1 = 26$, $G_r/K_1 = 0.21$, and $G_r/K_1 = 0.6$. Two-point bounds are dashed lines computed from Eqs. (12) and (13) with $n = 2$. Three-point bounds are solid lines as computed from Eqs. (12) and (13) with $n = 3$. The abscissa corresponds to the simple mixture rule $\epsilon_r = \langle \epsilon_r \rangle$. 

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IV. CONCLUSIONS

Bounds on the effective thermal expansion coefficients and specific heats that depend upon the three-point correlation function of the medium have been computed for suspensions of both monodispersed and polydispersed spheres. In all cases, the three-point bounds provide significant improvement over two-point bounds (which contains only volume fraction information) for a wide range of sphere volume fractions. For the large class of particulate composites characterized by $(\alpha_2 - \alpha_1)/(K_2 - K_1) < 0$, $G_2 > G_1$ and $K_2 > K_1$, the effect of polydispersity (relative to the monodisperse case) is to lower the effective thermal expansion coefficients and specific heats.

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