

Bounds on the thermoelastic properties of suspensions of spheres

S. Torquato

Departments of Mechanical and Aerospace Engineering and of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7910

(Received 14 December 1989; accepted for publication 5 March 1990)

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 α_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 α_e translate immediately into equivalent results for the hygroscopic expansion coefficient β_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 α_e is given by⁵⁻⁹

$$\alpha_e = \langle \alpha \rangle - \frac{K_1 K_2 (\alpha_2 - \alpha_1)}{K_2 - K_1} \left(\frac{1}{K_e} - \left\langle \frac{1}{K} \right\rangle \right), \quad (1)$$

where for some general physical property X

$$\langle X \rangle = X_1 \phi_1 + X_2 \phi_2, \quad (2)$$

ϕ_i is the volume fraction of phase i , α_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 that¹⁰

$$\frac{c_{p,e} - \langle c_p \rangle}{T_0} = 9 \left(\frac{K_1 K_2 (\alpha_2 - \alpha_1)}{K_2 - K_1} \right)^2 \left(\frac{1}{K_e} - \left\langle \frac{1}{K} \right\rangle \right), \quad (3)$$

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

$$c_{P,e} - c_{V,e} = 3T_0 K_e \alpha_e^2. \quad (4)$$

Now since the quantity $K_e \gg \langle K^{-1} \rangle^{-1}$ (as will be shown), then according to Eqs. (3), $c_{P,e} \ll \langle c_P \rangle$.

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

$$\frac{1}{K_e} \approx \left\langle \frac{1}{K} \right\rangle, \quad (5)$$

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_e 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_e translate immediately to bounds on α_e and $c_{P,e}$, 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_e , denoted by $K_e^{(nU)}$ and $K_e^{(nL)}$, then one has from Eq. (1) that

$$\alpha_e^{(nL)} \leq \alpha_e \leq \alpha_e^{(nU)}, \quad (6)$$

where

$$\alpha_e^{(nU)} = \langle \alpha \rangle - \frac{K_1 K_2 (\alpha_2 - \alpha_1)}{K_2 - K_1} \left(\frac{1}{K_e^{(nL)}} - \left\langle \frac{1}{K} \right\rangle \right), \quad (7)$$

$$\alpha_e^{(nL)} = \langle \alpha \rangle - \frac{K_1 K_2 (\alpha_2 - \alpha_1)}{K_2 - K_1} \left(\frac{1}{K_e^{(nU)}} - \left\langle \frac{1}{K} \right\rangle \right), \quad (8)$$

when

$$\frac{\alpha_2 - \alpha_1}{K_2 - K_1} \leq 0, \quad (9)$$

and from Eq. (2) that

$$C_e^{(nL)} \leq C_e \leq C_e^{(nU)}, \quad (10)$$

where

$$C_e \equiv \frac{\langle c_P \rangle - c_{P,e}}{T_0} \quad (11)$$

$$C_e^{(nU)} = 9 \left(\frac{K_1 K_2 (\alpha_2 - \alpha_1)}{K_2 - K_1} \right)^2 \left(\left\langle \frac{1}{K} \right\rangle - \frac{1}{K_e^{(nU)}} \right), \quad (12)$$

$$C_e^{(nL)} = 9 \left(\frac{K_1 K_2 (\alpha_2 - \alpha_1)}{K_2 - K_1} \right)^2 \left(\left\langle \frac{1}{K} \right\rangle - \frac{1}{K_e^{(nL)}} \right). \quad (13)$$

Note that for $(\alpha_2 - \alpha_1)/(K_2 - K_1) \geq 0$ the bounds (7) and

(8) reverse themselves, i.e., the right-hand sides of (7) and (8) become $\alpha_e^{(nL)}$ and $\alpha_e^{(nU)}$, respectively.

One of the simplest bounds on K_e are one-point bounds due to Paul:¹¹

$$K_e^{(1U)} = \langle K \rangle, \quad (14)$$

$$K_e^{(1L)} = \langle K^{-1} \rangle^{-1}, \quad (15)$$

Combination of Eqs. (7), (12), and (15) yields the fact that $\alpha_e \leq \langle \alpha \rangle$ for $(\alpha_2 - \alpha_1)/(K_2 - K_1) \leq 0$, $\alpha_e \geq \langle \alpha \rangle$ for $(\alpha_2 - \alpha_1)/(K_2 - K_1) \geq 0$, and $c_{P,e} \leq \langle c_P \rangle$.

The most restrictive bounds on K_e given the simplest of statistical quantities, the volume fractions ϕ_1 and ϕ_2 , are the two-point bounds obtained by Hashin and Shtrikman¹² and by Walpole:¹³

$$K_e^{(2U)} = K_2 + \frac{\phi_1}{\frac{1}{K_1 - K_2} + \frac{3\phi_2}{3K_2 + 4G_2}}, \quad (16)$$

$$K_e^{(2L)} = K_1 + \frac{\phi_2}{\frac{1}{K_2 - K_1} + \frac{3\phi_1}{3K_1 + 4G_1}}, \quad (17)$$

when

$$(G_2 - G_1)(K_2 - K_1) \geq 0. \quad (18)$$

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

Beran and Molyneux¹⁴ derived three-point bounds on K_e that are narrower than the aforementioned two-point bounds. These bounds were subsequently simplified by Milton¹⁵ and are given by

$$K_e^{(3U)} = \langle K \rangle - \frac{3\phi_1\phi_2(K_2 - K_1)^2}{3\langle \bar{K} \rangle + 4\langle G \rangle_\xi}, \quad (19)$$

$$K_e^{(3L)} = \left(\left\langle \frac{1}{K} \right\rangle - \frac{4\phi_1\phi_2(1/K_1 - 1/K_2)^2}{4\langle 1/\bar{K} \rangle + 3\langle 1/G \rangle_\xi} \right)^{-1}, \quad (20)$$

where, for any property X ,

$$\langle \bar{X} \rangle = X_1\phi_2 + X_2\phi_1, \quad (21)$$

$$\langle X \rangle_\xi = X_1\xi_1 + X_2\xi_2, \quad (22)$$

$$\xi_2 = 1 - \xi_1$$

$$= \frac{9}{2\phi_1\phi_2} \int_0^\infty \frac{dr}{r} \int_0^\infty \frac{ds}{s} \int_{-1}^1 du \hat{S}_3(r,s,t) P_2(u), \quad (23)$$

$$\hat{S}_3(r,s,t) = S_3(r,s,t) - \frac{S_2(r)S_2(s)}{\phi_2}, \quad (24)$$

Here $S_2(r)$ is the probability of finding the end points of a line segment of length r in phase 2 when placed randomly in the composite. $S_3(r,s,t)$ 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 $t^2 = r^2 + s^2 - 2rsu$. $P_2(u)$ is the Legendre polynomial of order two. Note that the three-point microstructural parameter ξ_1 , which lies in the interval $[0,1]$,¹⁵ contains nontrivial spatial information about the composite.

In summary, given the one-, two-, and three-point bounds on K_e described above, one can obtain correspond-

ing bounds on α_e and C_e using relations (7), (8), (12), and (13). In the following section, we will compute three-point bounds on α_e and C_e using Eqs. (19) and (20). Note that corresponding results for the effective hygroscopic expansion coefficient β_e can easily be obtained by replacing $\alpha_e, \alpha_e^{(nL)}, \alpha_e^{(nU)}, \alpha_1,$ and α_2 in the equations above with $\beta_e, \beta_e^{(nL)}, \beta_e^{(nU)}, \beta_1,$ and β_2 .

It is useful at this point to comment on the utility of bounds on effective properties. Besides being useful for testing the merits of theoretical expressions for effective properties, bounds are useful because (1) as successively more microstructural information is included, the bounds become progressively tighter, and (2) one of the bounds can typically provide a good estimate of the effective property, even when the reciprocal bound diverges from it. Calculations of three- and four-point bounds on the effective conductivities and elastic moduli of model suspensions and fiber-reinforced materials has certainly borne out the fact that data lie closer to one of the bounds.¹⁶⁻¹⁹ For example, in the case of the bulk modulus K_e , upper bounds $K_e^{(nU)}$ tend to infinity in the limit $G_2/G_1 \rightarrow \infty$ and $K_2/K_1 \rightarrow \infty$. In the limit $G_2/G_1 \rightarrow \infty$ and $K_2/K_1 \rightarrow \infty$, the lower bound remains finite and, in particular, three-point and higher-order lower bounds give good estimates of K_e/K_1 provided that phase 2 does not possess large *connected* structures. In the case of many random suspensions where the inclusions make up the stronger phase 2, large clusters of inclusions do not form until the random-close-packing density is approached, and hence for such media the lower bound will provide a useful estimate of K_e/K_1 when $G_2 \gg G_1$ and $K_2 \gg K_1$. The model suspension that shall be examined here falls into this class of microstructures, implying that the actual results for α_e will be closer to $\alpha_e^{(3U)}$, Eq. (7), and for C_e will be closer to $C_e^{(3L)}$, Eq. (13).

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 α_e and C_e . In order to compute such bounds, one must first determine the three-point microstructural parameter ζ_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 ζ_2

To date, the three-point parameter ζ_2 has been computed to all orders in the volume fraction ϕ_2 for three model isotropic suspensions: equisized full penetrable spheres,²⁰ multisized fully penetrable spheres,²¹ and an equilibrium ensemble of equisized impenetrable spheres.¹⁶ A hallmark of all of these results is the fact that ζ_2 is nearly linear in the sphere volume fraction ϕ_2 for $\phi_2 \geq 0$ for a wide range of volume fractions and thus, since $\zeta_2(\phi_2 = 0) = 0$ for random distributions of spherical inclusions,²² the slope of ζ_2 at $\phi_2 = 0$ approximately determines the behavior of ζ_2 for a wide range of $\phi_2 \geq 0$. The slope of ζ_2 at $\phi_2 = 0$ is determined by the *zero-density limit* of the radial (pair) distribution

function.²² For example, for equisized impenetrable spheres, through order ϕ_2 , one exactly has²²

$$\zeta_2 = \left(\frac{3}{16} \ln 3 - \frac{5}{12}\right) \phi_2, \approx 0.21068 \phi_2. \quad (25)$$

Thus, in accordance with the discussion above, relation (25) provides a good approximation to ζ_2 for¹⁶ $0 \leq \phi_2 < 0.5$: a very wide range of ϕ_2 considering that the random-close-packing volume fraction is about 0.63 (see Refs. 23 and references therein).

Very recently, Thovert *et al.*²⁴ computed ζ_2 exactly through order ϕ_2 for an equilibrium ensemble of spheres with a continuous distribution in radii a characterized by a density function $n(a)$; they found

$$\zeta_2 = e_1 \phi_2, \quad (26)$$

where

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

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

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

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 , $n(a) = n\delta(a - R)$ [where $\delta(a)$ is the Dirac delta function], and Eq. (27) leads to

$$e_1 = \Delta(1) = \frac{3}{16} \ln 3 - \frac{5}{12}, \quad (31)$$

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

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

Thovert *et al.*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 $N \rightarrow \infty$), and hence substitution of Eq. (33) into Eq. (26) gives the result

$$\zeta_2 = 0.5 \phi_2, \quad (34)$$

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

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

B. Results

The three-point bounds on α_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 polydispersity on bounds on the effective thermoelastic properties. In all

cases, results are reported for the sphere volume fraction range $0 < \phi_2 < 0.5$. For concreteness, we consider the dimensionless material properties $\alpha_1/\alpha_2 = 14$, $K_2/K_1 = 9.1$, $G_2/G_1 = 26$, $G_1/K_1 = 0.21$, and $G_2/K_2 = 0.6$, which corresponds to a composite composed of glass spheres in an epoxy matrix. (Note only three of the ratios K_2/K_1 , G_2/G_1 , G_1/K_1 , and G_2/K_2 are independent.)

In Fig. 1, two- and three-point bounds on the scaled expansion coefficient α_e/α_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 ϕ_2 . 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 α_e/α_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 $\langle \alpha \rangle / \alpha_1$, 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 polydispersity is to decrease α_e/α_1 relative to the monodisperse case. This will be true for any composite in which $(\alpha_2 - \alpha_1)/(K_2 - K_1) < 0$, $G_2 > G_1$, and $K_2 > K_1$. In many applications, it is desired to minimize the thermal expansion coefficient of composites. Thus if minimization of α_e is de-

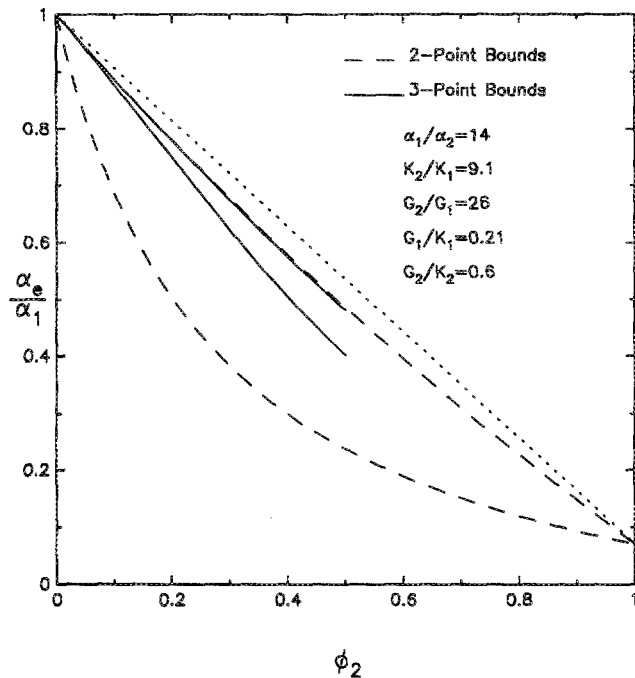


FIG. 1. Upper and lower bounds on the scaled effective thermal expansion coefficient α_e/α_1 for suspensions of monodispersed, impenetrable spheres vs the sphere volume fraction ϕ_2 with $\alpha_1/\alpha_2 = 14$, $K_2/K_1 = 9.1$, $G_2/G_1 = 26$, $G_1/K_1 = 0.21$, and $G_2/K_2 = 0.6$. Two-point bounds 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 $\langle \alpha \rangle / \alpha_1$, which also corresponds to the one-point upper bound.

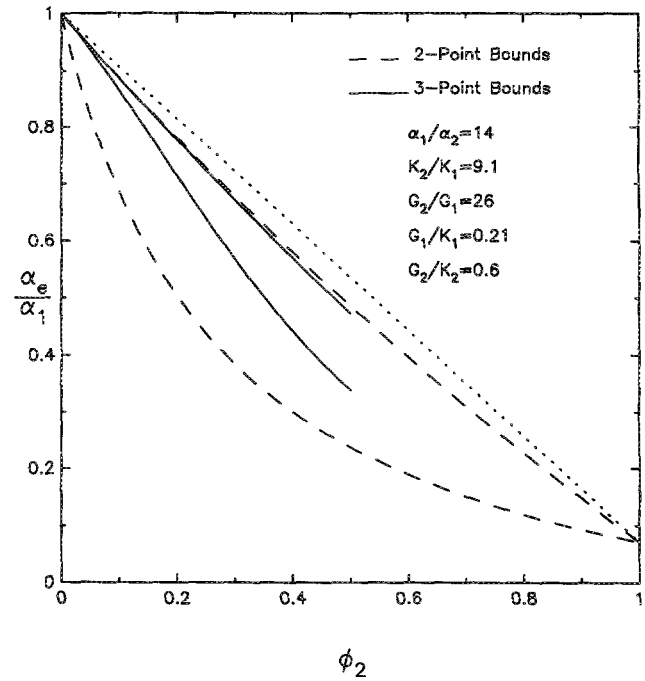


FIG. 2. As in Fig. 1 except for suspensions of polydispersed, impenetrable spheres with the three-point microstructural parameter ζ_2 given by Eq. (34).

sired 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 $C_e/(T_0 K_1 \alpha_1^2)$ are plotted versus ϕ_2 for a

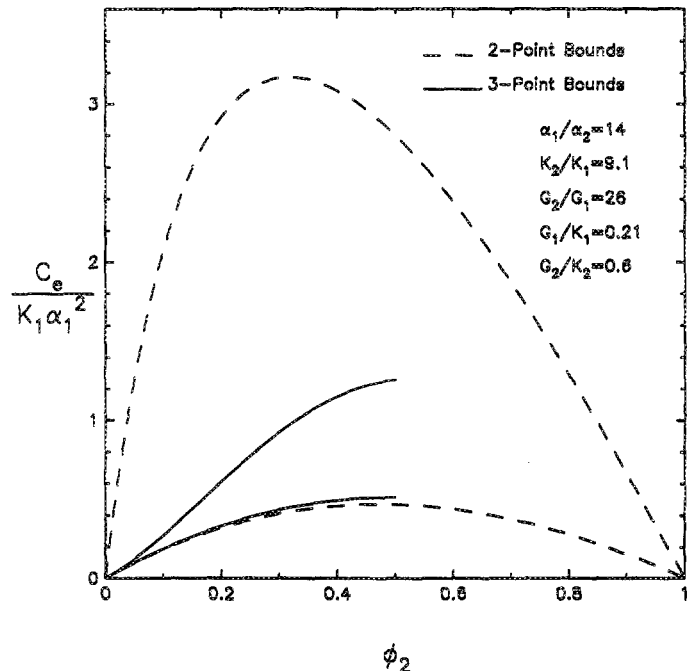


FIG. 3. Upper and lower bounds on the dimensionless quantity $C_e/(T_0 K_1 \alpha_1^2)$ [defined by Eq. (11)] for suspensions of monodispersed, impenetrable spheres vs the sphere volume fraction ϕ_2 with $\alpha_1/\alpha_2 = 14$, $K_2/K_1 = 9.1$, $G_2/G_1 = 26$, $G_1/K_1 = 0.21$, and $G_2/K_2 = 0.6$. 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 $c_{p,c} = \langle c_p \rangle$.

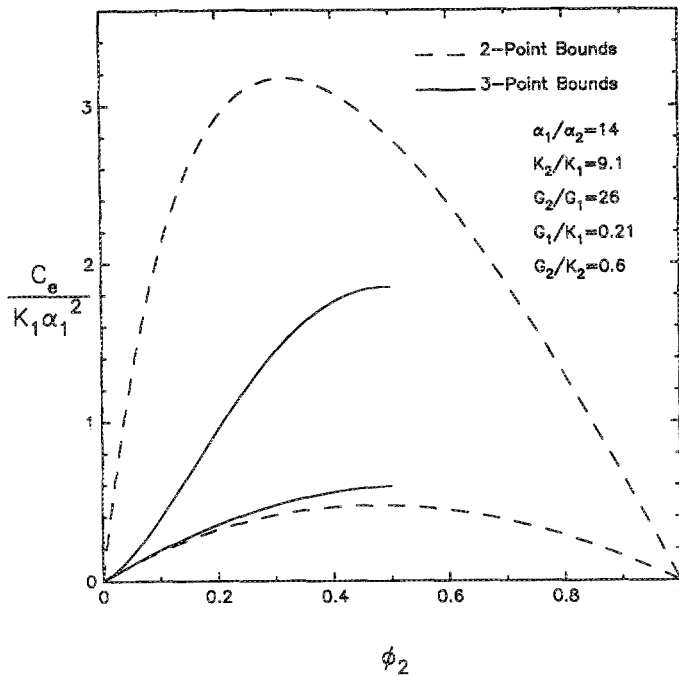


FIG. 4. As in Fig. 3 except for suspensions of polydispersed, impenetrable spheres with the three-point microstructural parameter ξ_2 given by Eq. (34).

monodispersion of impenetrable spheres. Note that the abscissa corresponds to the simple mixture rule $c_{p,e} = \langle c_p \rangle$. The three-point bounds again provide significant improvement over the two-point with the largest improvement coming from the three-point upper bound, as expected.

Figure 4 depicts the bounds on $C_e / (T_0 K_1 \alpha_1^2)$ for the polydispersion of impenetrable spheres corresponding to relation (34). Not surprisingly, the bounds widen (relative to the monodisperse case) and shift upward. Thus, the effect of polydispersivity is to increase C_e or decrease the effective constant-pressure specific heat $c_{p,e}$. Note that corresponding bounds on the constant-volume specific heat $c_{v,e}$ can be simply obtained by employing the results given here and relation 4.

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 polydispersivity (relative to the monodisperse case) is to lower the effective thermal expansion coefficients and specific heats.

ACKNOWLEDGMENT

This research was supported by NASA Grant No. NAGW-1331 to the Mars Mission Research Center, which is a cooperative effort of North Carolina State University and North Carolina A&T State University.

¹Z. Hashin, *J. Appl. Mech.* **50**, 481 (1983).
²G. W. Milton, *Commun. Math. Phys.* **III**, 281 (1987).
³S. Torquato, *Rev. Chem. Eng.* **4**, 151 (1987).
⁴J. Rubinstein and S. Torquato, *J. Fluid Mech.* **206**, 25 (1989).
⁵V. M. Levin, *Mekh. Tverd. Tela* **1**, 88 (1967).
⁶R. A. Schapery, *J. Composite Mater.* **2**, 280 (1968).
⁷B. W. Rosen, Ph.D. dissertation, University of Pennsylvania (1968).
⁸J. L. Cribb, *Nature* **220**, 576 (1968).
⁹T. R. Steel, *Int. J. Solids Struct.* **4**, 1149 (1968).
¹⁰B. W. Rosen and Z. Hashin, *Int. J. Eng. Sci.* **8**, 157 (1970).
¹¹B. Paul, *Trans. Metall. Soc. AIME* **218**, 36 (1960).
¹²Z. Hashin and S. Shtrikman, *J. Mech. Phys. Solids* **11**, 127 (1963).
¹³L. J. Walpole, *J. Mech. Phys. Solids* **14**, 151 (1966).
¹⁴M. Beran and J. Molyneux, *Q. Appl. Math.* **24**, 107 (1965).
¹⁵G. W. Milton, *Phys. Rev. Lett.* **46**, 542 (1981).
¹⁶S. Torquato and F. Lado, *Phys. Rev. B* **33**, 6428 (1986).
¹⁷A. K. Sen, F. Lado, and S. Torquato, *J. Appl. Phys.* **62**, 4135 (1987).
¹⁸S. Torquato and F. Lado, *Proc. R. Soc. London Ser. A* **417**, 59 (1988).
¹⁹S. Torquato and F. Lado, *J. Appl. Mech.* **55**, 347 (1988).
²⁰S. Torquato and G. Stell, *Lett. Appl. Eng. Sci.* **23**, 375 (1985).
²¹G. Stell and P. A. Rikvold, *Int. J. Thermophys.* **7**, 863 (1986).
²²S. Torquato, *J. Chem. Phys.* **83**, 4776 (1985).
²³J. G. Berryman, *Phys. Rev. A* **27**, 1053 (1983).
²⁴J. F. Thovert, I. C. Kim, S. Torquato, and A. Acrivos, *J. Appl. Phys.* **67**, 6088 (1990).