Bounds on the effective properties of polydispersed suspensions of spheres: An evaluation of two relevant morphological parameters

J. F. Thovert
Laboratoire d'Aerothermique du C. N. R. S., 4 ter, route des Gardes, 92190 Meudon, France

I. C. Kim and S. Torquato
Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina 27695-7910

A. Acrivos
The Levich Institute, T202, City College of New York, Convent Avenue at 140 Street, New York, New York 10031

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Expressions for the two microstructural parameters that appear in the variational third-order bounds [G. W. Milton, Phys. Rev. Lett. **46**, 542 (1981)] for the effective conductivity and elastic moduli of composite media are derived analytically to first order in the sphere concentration c for random well-mixed dispersions of impenetrable spheres with an arbitrary size distribution. These relations lead to rigorous bounds on the effective properties which are exactly valid to order c^2 for such models. The apparent *linear* behavior of the microstructural parameters up to moderately high c enables one to apply the bounds beyond second-order in c, however. Employing these results, the effect of polydispersivity on the effective properties is examined. It is worth noting that, under some conditions, polydispersivity can actually lead to a slight decrease of the shear modulus, whereas, for highly conducting particles, polydispersivity always increases the effective conductivity.

I. INTRODUCTION

The problem of determining the effective transport coefficients (conductivity, viscosity, and elastic moduli) of a disordered composite medium from a knowledge of its microstructure has been studied actively for decades.[2–4] However, in view of the complex geometry of even the simplest models, and therefore of real systems, an exact calculation cannot be carried out at present except for very idealized situations.

From the time of Maxwell[5] for the conductivity, Einstein[6] for the viscosity, and Bruggeman[7] and Dewey[8] for the elastic moduli, the method most commonly employed for mixtures containing particles has been the so-called "cluster-expansion" technique in which the effective coefficient is evaluated as a power series in the volume fraction of the dispersed phases, each additional term accounting for the average interaction effects of groups having increasing numbers of particles. For instance, when the particles are randomly distributed, impenetrable, equi-sized spheres of an identical material, the four authors mentioned above derived expressions for the corresponding coefficients that are exact to first order in the particle concentration c, that is, when all interactions between particles are neglected. Their extension to second order requires the evaluation of the pair interaction effects,[3] either by the exact solution of a general two-body problem followed by an appropriate averaging process or by use of an effective medium technique. Similarly, the nth term of the cluster expansion accounts for the interactions of n particles. Although the two-body problems for the various transport processes have been solved exactly for some of the simplest cases (spherical[9–12] or slender particles[13,14] for example), the three-body problems remain mostly intractable, and further improvements of the estimates for the various effective coefficients via the exact cluster-expansion technique are likely to be very limited and costly. Another technique, in which the effective coefficient to be determined is expanded in a power series of the difference between the coefficients of the two components,[2] has even more serious limitations in that its use is restricted to systems having constituents with similar properties.

The use of effective-medium methods is an appealing alternative, owing to their relatively easy implementation, and indeed, these were introduced quite a while back.[7] Here, a many-body problem is replaced by that of a single particle embedded in an effective medium whose macroscopic properties are those of the composite to be determined.[4,15] A self-consistency equation is then used to close the problem. In the most recent models of this kind, the effective continuum surrounding the test particle may have position-dependent characteristics according to the statistics of the microstructure,[10,16–18] and the transport equation may even take a nonlocal form.[14] However, these methods are, as a rule, only approximate, and even though many of them give results to all orders in the concentration, they often fail to give exactly even the $O(c^2)$ term in the corresponding cluster expansion.

The difficulty encountered in the direct evaluation of the effective coefficients of composite materials has given strong impetus for yet another alternative approach, specifically the establishment of rigorous bounds that result from the application of various variational principles using only limited microstructural information. These bounds are derived formally, regardless of the shape of the inclusions, and involve only a few average microstructural parameters. Of course, the bounds become tighter as more morphological information is included in the description of the structure but such information is seldom available. Fortunately, even

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though the bounds generally diverge when the contrast between the materials increases, it turns out that, typically, one of the bounds provides a fairly close approximation to the actual effective coefficient.[19,20]

The purpose of this paper is to analytically derive expressions for the microstructural parameters ζ and η for polydispersed distributions of impenetrable spheres to $O(c)$. Substitution of these analytical expressions into variational third-order bounds[1] on the effective conductivity and elastic moduli leads then to rigorous bounds for such model microstructures which are exactly valid to order c^2. Previous results, however, suggest that the respective slopes of these parameters at $c=0$ determines their behavior for a wide range of c. This therefore implies that the bounds computed here may be applicable beyond second order in c.

This paper is organized as follows. The next section consists of a brief review of the various sets of bounds available for the effective conductivity and elastic moduli of composite materials, and the current knowledge regarding the two microstructural parameters ζ and η appearing in the tighter ones. In Sec. III, an expression correct to $O(c)$ is given for ζ for random dispersions of impenetrable spheres with an arbitrary size distribution by comparing the series expansion, in powers of the concentration c, of the bounds for the effective conductivity with an existing expression for this bulk coefficient. We also evaluate ζ directly thus providing an independent check on our result. The same task is performed in Sec. IV for the parameter η in the same geometry, using an estimate for the effective shear modulus of a dispersion of spheres, both materials being compressible, which is derived here via an effective-medium technique. Again we compute η directly and find agreement with the results of the aforementioned method. Finally, the influence of the polydispersivity is considered in Sec. V, and the results are compared with experimental data.

II. VARIATIONAL BOUNDS FOR THE EFFECTIVE PROPERTIES OF COMPOSITE MATERIALS

We give here a brief review of the variational perturbation bounds for the effective coefficients of composite media, starting with the illustrative case of the thermal conductivity. The bounds for the elastic moduli are then summarized briefly.

A. Bounds on the effective conductivity

Consider a mixture of two homogeneous and isotropic materials, with thermal or electrical conductivities λ_1 and λ_2 and with volume fractions ϕ_1 and ϕ_2. In many instances we shall actually deal with dilute dispersions of particles in a connected matrix, in which case the subscript 1(2) will refer to the connected (dispersed) phase, and ϕ_1 and ϕ_2 will be replaced by $(1-c)$ and c, respectively. Also let

$$\alpha_\lambda = \lambda_2/\lambda_1. \tag{1}$$

All the sets of bounds to be discussed below result from the application, with increasing degree of refinement, of identical extremum principles, which in turn are a consequence of the Laplacian form of the local transport equation. For more details, see for example Torquato's review article.[2] Note that the terminology "perturbation bounds of order n" means that the two bounds are identical to order $(\alpha_\lambda - 1)^n$ and thus give a value for the effective conductivity λ^* exact to this order, contrary to "cluster-bounds" which are identical through given order in c.

The earliest result is due to Wiener,[21]

$$\langle \lambda^{-1}\rangle^{-1} \leqslant \lambda^* \leqslant \langle \lambda \rangle, \tag{2}$$

where the notation $\langle\ \rangle$ denotes the volumetric average

$$\langle X\rangle = \phi_1 X_1 + \phi_2 X_2 = X_1 + \phi_2 (X_2 - X_1). \tag{3a}$$

For later use, let also

$$\langle \widetilde{X}\rangle = X_1 + (1-\phi_2)(X_2 - X_1), \tag{3b}$$

$$\langle X\rangle_\zeta = X_1 + \zeta (X_2 - X_1), \tag{3c}$$

$$\langle X\rangle_\eta = X_1 + \eta (X_2 - X_1). \tag{3d}$$

These first-order bounds are very general, since the volume fraction is the only required morphological information. Thus (2) also applies to anisotropic media such as layered composites (whose effective conductivities in the principal directions actually correspond to the bounds), but is of limited use if the mixture is known to possess a different geometrical property. For example, the second-order bounds for $\alpha_\lambda > 1$ (and conversely for $\alpha_\lambda < 1$) of Hashin and Shtrikman,[22]

$$\lambda_1 \frac{1 + 2\phi_2 \beta_{21}}{1 - \phi_2 \beta_{21}} \leqslant \lambda^* \leqslant \lambda_2 \frac{1 + 2\phi_1 \beta_{12}}{1 - \phi_1 \beta_{12}} \tag{4}$$

with

$$\beta_{ij} = \frac{\lambda_i - \lambda_j}{\lambda_i + 2\lambda_j}, \tag{5}$$

are much tighter than (2), and as a matter of fact, are the best possible set of bounds that can be stated for a mixture, knowing only its composition and the fact that it is macroscopically isotropic. Consequently, any higher-order results have to appeal to a more detailed description of the microstructure. Beran[23] established third-order bounds for the bulk conductivity of an isotropic composite, subsequently simplified independently by Milton[1] and by Torquato,[24] which read

$$\left(\left\langle \frac{1}{\lambda} \right\rangle - \frac{2\phi_1\phi_2[(1/\lambda_1) - (1/\lambda_2)]^2}{2\langle \widetilde{1/\lambda}\rangle + \langle 1/\lambda\rangle_\zeta} \right)^{-1} \leqslant \lambda^* \leqslant \left(\langle\lambda\rangle - \frac{\phi_1\phi_2(\lambda_2 - \lambda_1)^2}{\langle\tilde{\lambda}\rangle + 2\langle\lambda\rangle_\zeta} \right). \tag{6}$$

The structural parameter ζ (commonly called ζ_2 in the literature), which lies between 0 and 1, is defined by

$$\zeta = \frac{9}{2\phi_1\phi_2} \int_0^\infty \frac{dr}{r} \int_0^\infty \frac{ds}{s} \int_{-1}^{1} dx\, P_2(x) \times \left(S_3(r,s,t) - \frac{S_2(r)S_2(s)}{\phi_2} \right), \tag{7}$$

where $S_2(r)$ and $S_3(r,s,t)$ are, respectively, the probability of finding, in phase 2, the end points of a line segment of length r and the vertices of a triangle with sides of length r, s, and t; x is the cosine of the angle opposite the side of length t and so $t^2 = r^2 + s^2 - 2rsx$; and P_2 is the Legendre polynomial of degree 2. The quantity S_n is refered to as the n-point probability function. Milton[25] has given the best lower bound on λ^* for $\alpha_\lambda > 1$, given the same amount of information contained in (6). However, since the latter is identical to Beran's lower bound to $O(c^2)$, which is the order of the forthcoming derivation, we shall employ the lower bound of (6). In fact, Milton's lower bound provides only a small improvement over Beran's bound for higher densities.[2]

Various attempts have been made to derive higher-order bounds on λ^* (see Ref. 2). However, the resulting formal expressions contain microstructural parameters, comparable to ζ, involving high-order correlation functions (4 point or higher) which are beyond practical reach.

The most appealing feature of (6) is the total absence of a hypothesis (except for the isotropy requirement) concerning the structure of the composite, in contrast to the cluster bounds, which are derived using additional information regarding the shape of the particles,[26] and have to be established specifically for any given geometry. Unfortunately, the direct evaluation of ζ is generally so complicated that the list given below appears to contain, to the best of our knowledge, all the three-dimensional problems that have been solved to date.

In the first place, Miller[27] evaluated ζ exactly for a particular model, the so-called "symmetrical-cell materials," using the very specific properties of this structure to avoid a direct calculation. All the subsequent determinations of ζ by use of the n-point probability functions dealt with random dispersons of spheres, and most of them with equi-sized particles. Specifically, Torquato and Stell,[28] and Torquato and Lado,[29] respectively, for fully penetrable and impenetrable spheres, tabulated ζ as a function of the concentration c, over its whole range of admissible values, through use, in the second case, of a superposition approximation to evaluate the three-point probability function. In addition, Torquato[30] gave an exact expression for the two first terms of the expansion

$$\zeta = \sum_{i=0}^{\infty} e_i c^i, \tag{8}$$

for random dispersions of spheres with arbitrary degree of penetrability and showed that e_0 is zero for spheres regardless of whether the system is periodic or random or possesses a size distribution. Felderhof,[31] using the superposition approximation, evaluated the third and fourth terms for impenetrable spheres. Beasley and Torquato[26] calculated (8) exactly up to fourth-order terms. Berryman[32] introduced an experimental procedure, based on image processing techniques, to evaluate ζ on samples of real materials, which was validated when tested against the theoretical expression given by Torquato.[28] Results for polydispersed suspensions are even scarcer. Stell and Rikvold[33] studied dispersions of fully penetrable spheres (i.e., spatially uncorrelated spheres) with a particular type of size-distribution function, and showed that the effective properties of the composite are very weakly influenced by polydispersivity. However, their conclusion cannot be extended to suspensions of impenetrable particles without further analysis. Finally, the value of ζ for some periodic arrays of spheres was deduced by McPhedran and Milton[34] from previous numerical results for λ^*, that is without direct evaluation of the three-point probability function, while the coefficient e_0 was deduced by Torquato[30] for suspensions of ellipsoidal particles by comparing Beran's bounds with the analytical expression of Polder and Van Santen[35] for λ^* to $O(c)$.

It is important to note that in all the cases of random systems of spheres described above, the linear term of (8), $e_1 c$, provides a very good approximation to ζ for a wide range of c. This observation shall be exploited in the ensuing sections.

B. Bounds on the effective elastic moduli

We consider here a mixture of two homogeneous materials having bulk and shear elastic moduli (k_1, k_2) and (μ_1, μ_2), respectively.

Their Poisson ratios are denoted by ν_1 and ν_2, and we define

$$\alpha_k = k_2/k_1, \quad \alpha_\mu = \mu_2/\mu_1. \tag{9}$$

Bounds on the effective elastic moduli k^* and μ^*, corresponding to (4) (Hashin and Shtrikman,[36] Walpole[37]) and (6) are available in the literature. Third-order bounds on k^* are due to Beran and Molyneux[38] (BM). These were later simplified by Milton,[1] and entail the same parameters as in Beran's bounds for λ^*:

$$\left(\left\langle \frac{1}{k} \right\rangle - \frac{4\phi_1\phi_2[(1/k_2) - (1/k_1)]^2}{4\langle \tilde{1}/k \rangle + 3\langle 1/k \rangle_\zeta} \right)^{-1} \leqslant k^* \leqslant \left(\langle k \rangle - \frac{3\phi_1\phi_2(k_2 - k_1)^2}{3\langle \tilde{k} \rangle + 4\langle k \rangle_\zeta} \right). \tag{10}$$

Milton also recast McCoy's[39] third-order bounds on μ^* in the symmetrical form:

$$\left(\left\langle \frac{1}{\mu} \right\rangle - \frac{\phi_1\phi_2(1/\mu_2) - (1/\mu_1)^2}{\langle \tilde{1}/\mu \rangle + 6\Xi} \right)^{-1} \leqslant \mu^* \leqslant \left(\langle \mu \rangle - \frac{6\phi_1\phi_2(\mu_2 - \mu_1)^2}{6\langle \tilde{\mu} \rangle + \Theta} \right), \tag{11}$$

where Ξ and Θ depend on ζ and on a second microstructural parameter η defined as

$$\eta = \frac{5}{21}\zeta + \frac{150}{7\phi_1\phi_2} \int_0^\infty \frac{dr}{r} \int_0^\infty \frac{ds}{s} \int_{-1}^{1} dx\, P_4(x) \times \left(S_3(r,s,t) - \frac{S_2(r)S_2(s)}{\phi_2} \right), \tag{12}$$

where P_4 is the Legendre polynomial of degree 4. Higher-order bounds have also been introduced: Dederichs and Zeller,[40] Kroner[41] for k^*; Milton and Phan-Tien[42] (MPT) for μ^*; but again, high-order morphological information, beyond practical reach, is required here. MPT furthermore improved the third-order McCoy bounds, but these two sets eventually prove to be identical to $O[c^2(\alpha_\mu - 1)^3]$, and hence the forthcoming derivation, exact to the same order, will be carried out starting from (11).

The parameter η has been evaluated in the following cases. It was numerically tabulated for random monodisperse suspensions of impenetrable spheres (Sen, Lado, and Torquato[43]) in the superposition approximation and for fully penetrable (Torquato, Stell, and Beasley[44]) spheres. Torquato, Lado, and Smith[45] gave its $O(c)$ expansion for equisized spherical particles with an arbitrary degree of penetrability. As in the case of ζ, the order c expansion of η provides a good approximation of it for a wide range of c.

Our contribution here is as follows: Through a comparison of (6) and (11) with preexisting (for λ^*) or original (for μ^*) results for the effective conductivity and shear modulus of polydispersed suspensions of impenetrable spheres, we shall derive analytical expressions for ζ and η to $O(c)$ for random dispersions of such particles with arbitrary size distribution (much in the same way as in Torquato's[30] derivation of e_0 for ellipsoids). In other words, via an $O[c^2(\alpha - 1)^3]$ solution of the two easier problems in this geometry (heat conduction and elastic straining with incompressible materials), we provide enough information to state bounds through $O(c^2)$ on λ^*, k^*, and μ^*, for any polydisperse suspension of impenetrable spheres. In order to check our results, we also evaluate ζ and η directly. As discussed below, since ζ and η are known to be approximately linear in c for a relatively wide range of c for $c > 0$, the bounds themselves can be applied to nondilute concentrations.

III. O(c) EXPANSION FOR ζ

We deal in this section with dilute, well-mixed dispersions of impenetrable spheres, having an arbitrary size distribution that is characterized by the density function $n(a)$, the average number of particles with radii lying between a and $a + da$ per unit volume being $n(a)da$. The corresponding partial volume fraction is then

$$c(a) = \tfrac{4}{3}\pi a^3 n(a), \tag{13}$$

and the global concentration is given by

$$c = \frac{4\pi}{3} \int a^3 n(a) da. \tag{14}$$

Aside from an $O(c^2)$ evaluation of λ^*, via the direct exact solution of a general two-body conduction problem, Thovert and Acrivos[10] presented an approximate analytical expression for λ^* in this geometry by use of an effective continuum method. In this approximation, the thermal dipole strength induced within a reference particle in the presence of a macroscopic temperature gradient is estimated via the solution of a single-sphere problem, this particle being embedded in an effective continuum with position-dependent thermal conductivity which is related to the statistics of the microstructure. Chang, Yendler, and Acrivos[17] showed that this method yields estimates of λ^* exact to $O[c^2(\alpha_\lambda - 1)^3]$, and as a matter of fact to $O(c^2\beta_{21}^3)$, even though this refinement is not required here. Finally,

$$\frac{\lambda^*}{\lambda_1} = 1 + 3\beta c + 3\beta^2 \int\int\left[1 + 2\beta\Delta_\zeta\left(\frac{b}{a}\right)\right] \times c(a)c(b)da\,db + O[c^2(\alpha_\lambda - 1)^4], \tag{15}$$

with

$$\beta \equiv \beta_{21} = (\alpha_\lambda - 1)/(\alpha_\lambda + 2). \tag{16}$$

The function Δ_ζ decreases with increasing size ratio (see Fig. 1) and is given by

$$\Delta_\zeta = \frac{3}{16\gamma^3}\left(\frac{(1+2\gamma)^4 - 1}{4(1+2\gamma)^2} - \ln(1+2\gamma)\right), \tag{17}$$

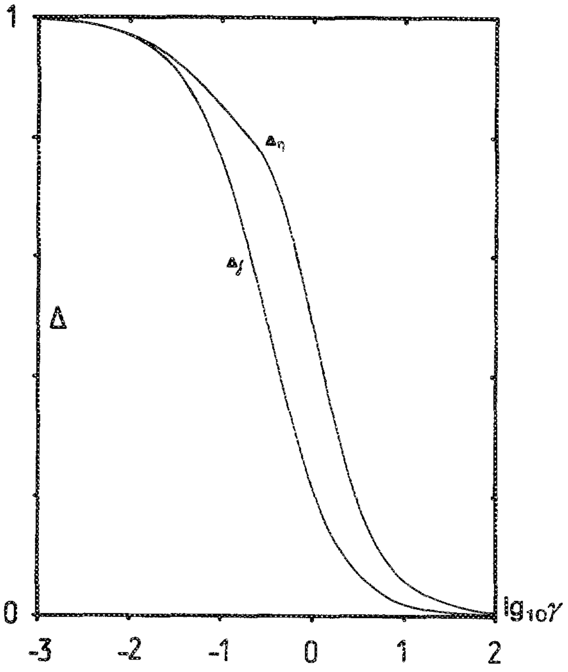

FIG. 1. Functions Δ_ζ (17) and Δ_η (59) vs the size ratio (decimal logarithm).

with the properties

$$\begin{aligned} &\Delta_\zeta(0) = 1, \\ &\Delta_\zeta(1) = \tfrac{5}{12} - \tfrac{3}{16}\ln 3 \cong 0.210\,68, \\ &\Delta_\zeta(\infty) = 0. \end{aligned} \tag{18}$$

On the other hand, using (8), we can expand the third-order bounds (6) in powers of c. It is known[30] that whereas e_1 depends on one- and two-body information, e_0 is uniquely determined by the shape of the particles and vanishes for spheres.

Therefore,

$$1 + 3\beta c + 3\beta^2c^2\left(1 + \tfrac{2}{3}\frac{(\alpha_\lambda - 1)}{\alpha_\lambda}e_1\right) + O(c^3) \leqslant \frac{\lambda^*}{\lambda_1} \leqslant 1 + 3\beta c + 3\beta^2c^2[1 + \tfrac{2}{3}(\alpha_\lambda - 1)e_1] + O(c^3), \tag{19}$$

and thus

$$\lambda^*/\lambda_1 = 1 + 3\beta c + 3\beta^2c^2[1 + 2\beta e_1] + O[c^2(\alpha_\lambda - 1)^4]. \tag{20}$$

Comparison of (15) with (20) yields directly:

$$e_1 = \frac{1}{c^2}\int\int \Delta_\zeta\left(\frac{b}{a}\right)c(a)c(b)da\,db. \tag{21}$$

For a monodisperse composite, (21) gives $e_1 = \Delta_\zeta(1)$, in accordance with Felderhof.[31]

We now evaluate ζ through first order in c using another method and thereby provide an independent check on (21). Specifically, we shall compute the integral (7) directly using the spherical-harmonics-expansion technique of Ref. 29 and the appropriate polydisperse generalizations of the explicit expressions for the S_n developed by Torquato and Stell[46] for monodispersed impenetrable inclusions. Through two-body terms, the S_n depend upon the radial distribution function of the medium. Omitting these details, we find through first order in c that

$$\zeta = \frac{3}{c} \int \int c(a) c(b) da\, db \int_{a+b}^{\infty} \frac{a^3 r^2 dr}{(r^2 - b^2)^3}. \qquad (22)$$

Now, since

$$\Delta_{\zeta} = 3a^3 \int_{a+b}^{\infty} \frac{r^2 dr}{(r^2 - b^2)^3}, \qquad (23)$$

we find that $e_0 = 0$, and e_1 is exactly given by (21). The monodisperse equivalent (22) was given by Torquato[29,30] to be

$$\zeta = 3a^3 c \int_{2a}^{\infty} \frac{r^2 dr}{(r^2 - a^2)^3}. \qquad (24)$$

One sees that there is a simple prescription for mapping the monodisperse result (24) into the polydisperse result (22): on the right-hand side of (24) replace a^2 with b^2 and $2a$ with $a + b$; then weight the right-hand side with the factor $c(a)c(b)/c^2$ and integrate over a and b.

IV. O(c) EXPANSION FOR η

A. Expansion of BM and McCoy's bounds

We shall now apply the same line of reasoning as that of the previous section to the determination of the second microstructural parameter η. To this end, by analogy to (8), we have

$$\eta = \sum_{i=0}^{\infty} f_i c^i, \qquad (25)$$

where, again, f_0 vanishes for spherical particles, and f_1 depends only on one- and two-point geometrical information. The O(c) expansions of BM and McCoy's bounds (10) and (11) were given by Torquato, Lado, and Smith,[45] and may be recast in the form:

$$\frac{k_U^*}{k_1} = 1 + L_{k1} c + L_{k_2} c^2 \times \left(1 + \frac{2}{3} \frac{1 - 2\nu_1}{1 - \nu_1} (\alpha_k - 1) e_1 \right) + O(c^3),$$

$$\frac{k_L^*}{k_1} = 1 + L_{k1} c + L_{k_2} c^2 \times \left[1 + \frac{2}{3} \frac{1 - 2\nu_1}{1 - \nu_1} \left(\frac{\alpha_k - 1}{\alpha_k}\right) e_1 \right] + O(c^3), \qquad (26)$$

and

$$\frac{\mu_U^*}{\mu_1} = 1 + L_{\mu_1} c + L_{\mu_2} c^2 \left(1 + (1 - 2\nu_1) \frac{(13 - 14\nu_1)(\alpha_\mu - 1) + 4(1 + \nu_1)(\alpha_k - 1)}{12(1 - \nu_1)(4 - 5\nu_1)} e_1 + \frac{9(\alpha_\mu - 1) f_1}{20(1 - \nu_1)(4 - 5\nu_1)} \right) + O(c^3),$$

$$\frac{\mu_L^*}{\mu_1} = 1 + L_{\mu_1} c + L_{\mu_2} c^2 \left(1 + (1 - 2\nu_1) \frac{(13 - 14\nu_1)[(\alpha_\mu - 1)/\alpha_\mu] + 4(1 + \nu_1)[(\alpha_k - 1)/\alpha_k]}{12(1 - \nu_1)(4 - 5\nu_1)} e_1 + \frac{9[(\alpha_\mu - 1)/\alpha_\mu] f_1}{20(1 - \nu_1)(4 - 5\nu_1)} \right) + O(c^3). \qquad (27)$$

Here, the subscripts U and L are associated with the upper and lower bounds, and

$$L_{k1} = 3 \frac{(1 - \nu_1)(\alpha_k - 1)}{(1 + \nu_1)\alpha_k + 2(1 - 2\nu_1)},$$

$$L_{k2} = 3 \frac{(1 - \nu_1)(1 + \nu_1)(\alpha_k - 1)^2}{[(1 + \nu_1)\alpha_k + 2(1 - 2\nu_1)]}, \qquad (28)$$

$$L_{\mu 1} = 15 \frac{(1 - \nu_1)(\alpha_\mu - 1)}{2(4 - 5\nu_1)\alpha_\mu + 7 - 5\nu_1},$$

$$L_{\mu 2} = 30 \frac{(1 - \nu_1)(4 - 5\nu_1)(\alpha_\mu - 1)^2}{[2(4 - 5\nu_1)\alpha_\mu + 7 - 5\nu_1]^2}. \qquad (29)$$

When the materials are incompressible, the bounds on μ^* reduce to

$$1 + L_{\mu 1} c + L_{\mu 2} c^2 (1 + \tfrac{3}{5}(\alpha_\mu - 1) f_1) + O(c^3) \leqslant \frac{\mu^*}{\mu_1} \leqslant 1 + L_{\mu 1} c + L_{\mu 2} c^2 \left(1 + \frac{3}{5} \frac{\alpha_\mu - 1}{\alpha_\mu} f_1 \right) + O(c^3). \qquad (30)$$

In view of (30), it is clear that f_1 can be evaluated, provided that μ^* is known independently to O[$c^2(\alpha_\mu - 1)^3$]. But since the equivalent of (15) for μ^* was not available, it had to be derived for the occasion. Although such a derivation is somewhat more cumbersome when the transported quantity is vectorial (displacement) than scalar (heat), the effective-medium method mentioned above can also be applied successfully to the present problem.

B. The shear modulus of a polydisperse, incompressible dispersion of spheres to O[$c^2(\alpha_\mu - 1)^3$]

We consider the polydisperse composite medium described at the beginning of Sec. IV under the action of a macroscopic uniform strain field **E**. Both materials being incompressible ($\nu_1 = \nu_2 = \frac{1}{2}$) the local equations for the problem are

$$\Delta \mathbf{u} = 0,$$

$$\boldsymbol{\sigma} = 2\mu_i\, \mathbf{e}, \qquad (31)$$

with **u**, **σ**, and **e** being the local displacement, stress, and strain tensors, respectively, and μ_i ($i = 1,2$) the local shear modulus of the appropriate material. The constituents and geometry being isotropic, we expect the mixture to have a similarly macroscopic Newtonian behavior:

$$\langle \sigma \rangle = 2\mu^* \langle \mathbf{e} \rangle = 2\mu^* \mathbf{E}. \tag{32}$$

The equations for the average quantities are given by Batchelor[47]:

$$\langle \sigma \rangle = 2\mu_1 \mathbf{E} + \frac{1}{V} \sum \mathbf{S}, \tag{33}$$

where the summation is over all the particles in the macroscopic volume V, and $\mathbf{S}$ is the stresslet within a particle,

$$\mathbf{S} = \int_A \left(\mathbf{n} \cdot \sigma \mathbf{r} - \tfrac{1}{3} (\mathbf{n} \cdot \sigma \cdot \mathbf{r}) \mathbf{I} - \mu_1 (\mathbf{un} + \mathbf{nu}) \right) dA. \tag{34}$$

The integral (34) is over the surface A of the particle, $\mathbf{n}$ is the outward unit normal vector, and $\mathbf{I}$ is the unit second-order tensor. Owing to the linearity and symmetry of the problem, the stresslet has be to proportional to the bulk strain

$$\mathbf{S} = S\mathbf{E}, \tag{35}$$

and upon averaging S over the particles of the same sizes, the combination of (32) and (33) yields

$$\mu^* = \mu_1 + \frac{1}{2} \int n(a)\, \overline{S_a}\, da. \tag{36}$$

To evaluate μ^*, it is sufficient to solve the elasticity problem for a particular bulk strain which for convenience is chosen as the axisymmetric pure straining displacement field (in rectangular coordinates),

$$E_{ij} = \delta_{i1}\delta_{j1} + \delta_{i2}\delta_{j2} - 2\delta_{i3}\delta_{j3}. \tag{37}$$

We apply here the same effective medium method as in Sec. III, which is now described in more detail. The average stresslet within a particle with radius a is evaluated by solving a single-body problem, this particle being embedded in an incompressible continuum with position-dependent shear modulus,

$$\mu(r) = \mu_1 [1 + \epsilon \rho(r)]. \tag{38}$$

The origin is taken at the center of the the particle, and

$$\epsilon \equiv \tfrac{5}{2} \beta_\mu c, \; \beta_\mu = (\alpha_\mu - 1)/(\alpha_\mu + \tfrac{3}{2}). \tag{39}$$

The function $\rho(r)$ is the normalized conditional probability that a point in the composite medium will lie within an inclusion, provided that the center of the reference particle is at the origin. This function vanishes for $r = a$, tends to unity as r tends to infinity, and is actually unity to $O(c^2)$ when r is larger than a plus the diameter of the largest sphere in the dispersion. It can easily be shown, by following reasoning similar to that given in Chang, Yendler, and Acrivos[17] for the conductivity problem, that the value of μ^* resulting from this approximate method is exact through $O[c^2(\alpha_\mu - 1)^3]$.

Chang and Acrivos[48] addressed a problem closely related to that presently being considered, specifically the determination of the effective viscosity of suspensions of equisized hard spheres, and had to solve a less general but comparable single-particle problem with the following minor differences; in the present case, the probability function is affected by the size distribution, while the restriction to rigid particles in their case ($\beta_\mu = 1$), simplified the boundary conditions on the surface of the test sphere as well as the local equation within it (which becomes trivial). Outside the test particle, however, the equations are identical in both cases.

Taking advantage of the incompressibility of the materials and the axial symmetry of the geometry and boundary conditions, we express the displacement field, in spherical coordinates, as

$$u_r = -\frac{1}{r^2 \sin\theta} \frac{\partial \phi}{\partial \theta}, \; u_\theta = \frac{1}{r \sin\theta} \frac{\partial \phi}{\partial r}, \tag{40}$$

with

$$\begin{aligned} &\phi = \cos\theta \sin^2\theta F(r), \quad r \leqslant a, \\ &\phi = \cos\theta \sin^2\theta G(r), \quad r \geqslant a. \end{aligned} \tag{41}$$

Then the second equation in (31) reduces to:

For $r \geqslant a$,

$$\begin{aligned} &\mu'' \left(G'' - \frac{2}{r} G' + \frac{6}{r^2} G \right) + \mu' \left(2G''' - \frac{2}{r} G'' \right. \\ &\quad \left. - \frac{10}{r^2} G' + \frac{24}{r^3} G \right) \\ &\quad + \mu \left(G'''' - \frac{12}{r^2} G'' + \frac{24}{r^3} G' \right) = 0 \end{aligned} \tag{42}$$

and

$$F'''' - \frac{12}{r^2} F'' + \frac{24}{r^3} F' = 0$$

for

$r \leqslant a$,

with the primes denoting derivatives with respect to r. Also $\overline{S_a}$ is given by

$$\begin{aligned} \overline{S_a} = \frac{4\pi}{15} \bigg(&-\frac{a^3}{3} G'''(a) + a^2 G''(a) \\ &+ 2aG'(a) - 10G(a) \bigg) \mu_1. \end{aligned} \tag{43}$$

The boundary condition at infinity is

$$G \to r^3 \quad \text{as } r \to \infty, \tag{44}$$

and the continuity of normal stress and displacement at the interface yields, at $r = a$,

$$\begin{aligned} &F = G, \; F' = G', \\ &\alpha_\mu (a^2 F'' - 2aF' + 6F) = a^2 G'' - 2aG' + 6G, \\ &\alpha_\mu \left(\frac{a^3}{2} F''' - 9aF' + 18F \right) = \frac{a^3}{2} G''' - 9aG' + 18G. \end{aligned} \tag{45}$$

Problems (42)–(45) are solved by expanding all the quantities in powers of the small parameter ϵ according to generic form

$$X = X_0 + \epsilon X_1 + O(\epsilon^2). \tag{46}$$

The solution for the leading terms was given by Batchelor and Green[49] and, translated into our notation, reads

$$\begin{aligned} &F_0 = (1 - \beta_\mu) r^3, \\ &G_0 = \left[1 - \frac{5}{2} \beta_\mu \left(\frac{a}{r} \right)^3 + \frac{3}{2} \beta_\mu \left(\frac{a}{r} \right)^5 \right] r^3. \end{aligned} \tag{47}$$

Thus

$$\overline{S_{a0}} = \frac{20}{3}\pi a^3 \beta_\mu \mu_1, \tag{48}$$

and we obtain, regardless of the size distribution,

$$\mu^* = \mu_1 [1 + \tfrac{5}{2}\beta_\mu c + O(c^2)], \tag{49}$$

in agreement with Dewey's[8] result.

The first-order problem is

$$F_1'''' - \frac{12}{r^2} F_1'' + \frac{24}{r^3} F_1' = 0, \quad r \leqslant a,$$

$$G_1'''' - \frac{12}{r^2} G_1'' + \frac{24}{r^3} G_1' = -\frac{h(r)}{r^4}, \quad r \geqslant a, \tag{50}$$

with the boundary conditions (45) on (F_1, G_1), and

$$G_1 \to 0 \quad \text{as } r \to \infty, \tag{51}$$

where

$$h(r) = r^4 \Big[\rho' \Big(2G_0''' - \frac{2}{r} G_0'' - \frac{10}{r^2} G_0' + \frac{24}{r^3} G_0 \Big) + \rho'' \Big(G_0'' - \frac{2}{r} G_0' + \frac{6}{r^2} G_0 \Big) \Big]. \tag{52}$$

The solution of the first-order problem is somewhat complicated, but by taking advantage of the fact that the r^{-2}, r^3, and r^5 terms of the general solution to (50) do not contribute to the stresslet one can show that

$$\overline{S_{a1}} = \frac{2\pi}{15a} \beta_\mu \mu_1 \int_a^\infty \Big[\Big(\frac{a}{r}\Big)^6 - \frac{5}{3}\Big(\frac{a}{r}\Big)^4 \Big] h(r) dr. \tag{53}$$

When the test particle is surrounded only by a random dispersion of spheres with radius $b = \gamma a$, the function ρ is given (Acrivos and Chang[16]) to $O[c^2(b)]$ by

$$\rho_b(\gamma) = \frac{1}{16\gamma^3} \Big[-\Big(\frac{r}{a}\Big)^3 + 6(2\gamma^2 + 2\gamma + 1)\frac{r}{a} - 8(3\gamma^2 + 3\gamma + 1) + 3(1 + 2\gamma)\frac{a}{r} \Big],$$

for $1 \leqslant \frac{r}{a} \leqslant 1 + 2\gamma$, and

$$\rho_b(\gamma) = 1 \quad \text{for } \frac{r}{a} \geqslant 1 + 2\gamma. \tag{54}$$

Consequently, for a polydisperse composite, to $O(c^2)$,

$$\rho = \frac{1}{c} \int \rho_b c(b) db, \tag{55}$$

and if h_b is related to ρ_b by (52).

$$h = \frac{1}{c} \int h_b c(b) db. \tag{56}$$

Equation (53) then becomes

$$\overline{S_{a1}} = \frac{2\pi}{15} \beta_\mu \mu_1 \frac{1}{c} \int \frac{c(b)}{a} \int_a^{a(1+2\gamma)} \Big[\Big(\frac{a}{r}\Big)^6 - \frac{5}{3}\Big(\frac{a}{r}\Big)^4 \Big] h_b(r) dr\, db, \tag{57}$$

hence (36), (46), and (57) yield

$$\frac{\mu^*}{\mu_1} = 1 + \frac{5}{2}\beta_\mu c + \frac{5}{2}\beta_\mu^2 \times \int\int \Big[1 + \frac{3}{2}\beta_\mu \Delta_\eta\Big(\frac{b}{a}\Big) \Big] c(a)c(b) da\, db, \tag{58}$$

with

$$\Delta_\eta(\gamma) = \frac{1}{16\Gamma^3} \Big(\frac{\Gamma^2 - 1}{4\Gamma^6} (9\Gamma^6 + 29\Gamma^4 - 10\Gamma^2 + 2) - 15 \ln \Gamma \Big), \quad \Gamma \equiv 1 + 2\gamma. \tag{59}$$

Note that Δ_η is a decreasing function of the size ratio (Fig. 1), with

$$\Delta_\eta(0) = 1,$$

$$\Delta_\eta(1) = \frac{4411}{2916} - \frac{15}{16} \ln 3 \cong 0.482\,74,$$

$$\Delta_\eta(\infty) = 0. \tag{60}$$

C. The coefficient f_1

Application of the bounds (30) together with (29) yields

$$\frac{\mu^*}{\mu_1} = 1 + \frac{5}{2}\beta_\mu c + \frac{5}{2}\beta_\mu c^2 \Big(1 + \frac{3}{2}\beta_\mu f_1 \Big) + O[c^2(\alpha_\mu - 1)^4], \tag{61}$$

and since (58) is exact through the same order, we obtain readily that

$$f_1 = \frac{1}{c^2} \int\int \Delta_\eta \Big(\frac{b}{a}\Big) c(a)c(b) da\, db. \tag{62}$$

In the case of a monodisperse composite, (62) agrees with the numerical value for f_1 given by Torquato, Lado, and Smith,[45] and with the result for the c^2 coefficient in (61) of Acrivos and Chang[50] when $\beta_\mu = 1$. Again, we have derived (62) by directly evaluating (12). Specifically, as in the conductivity calculation, we have taken the monodisperse solution given in Refs. 43 and 45 and mapped it into the polydisperse solution in a manner similar to that done at the end of Sec. III.

V. DISCUSSION

A. Effect of the polydispersivity

Since the upper and lower bounds given above for the various transport coefficients are identical to order $(\alpha - 1)^3$, we can recast our results into the unified expression,

$$\frac{K^*}{K_1} = 1 + (p+1)\beta c + (p+1)\beta^2 \times \int\int \Big[1 + p\beta\Delta\Big(\frac{b}{a}\Big) \Big] c(a)c(b) da\, db + O[c^2(\alpha - 1)^4], \tag{63}$$

where the generic transport coefficient K denotes λ, k, or μ (with $\nu_1 = \frac{1}{2}$ in the latter case), and the notation is

$$\begin{bmatrix} K & \alpha & \Delta & p \\ \lambda & \alpha_\lambda & \Delta_\zeta & 2 \\ k & \alpha_k & \Delta_\zeta & 2\dfrac{1-2\nu_1}{1+\nu_1} \\ \mu & \alpha_\mu & \Delta_\eta & \frac{3}{2} \end{bmatrix}.$$

In all cases

$$\beta = (\alpha - 1)/(\alpha + p). \tag{64}$$

In addition, if we let

$$\psi(\gamma) = \psi\left(\frac{1}{\gamma}\right) = \frac{\Delta(\gamma) + \Delta(1/\gamma) - 2\Delta(1)}{\Delta(1)}, \tag{65}$$

(63) rearranges into

$$\frac{K^*}{K_1} = 1 + (p+1)\beta c + (p+1)\beta^2[1 + p\beta\Delta(1)]c^2 + \frac{p(p+1)}{2}\beta^3\Delta(1)\int\int\psi\left(\frac{b}{a}\right) \times c(a)c(b)da\,db + \mathrm{O}[c^2(\alpha-1)^4], \tag{66}$$

where the last term represents the departure of K^* from its value for a monodisperse composite with identical global concentration. The function ψ is depicted in Fig. 2.

The influence of the polydispersivity on λ^* has been studied in Thovert and Acrivos[10] and its effect on k^* is similar since the expressions for both quantities involve the same parameter Δ_ζ. Moreover, since ψ_ζ is always positive, any kind of polydispersivity increases λ^* or k^* (for α_λ or α_k greater than unity). This result holds to $\mathrm{O}[c^2(\alpha-1)^3]$, but the exact solution of the thermal problem (Thovert and Acrivos[10]) showed that (66) is exact to $\mathrm{O}(c^2)$, provided that Δ_ζ is replaced by a function δ of both α_λ and the size ratio, which has, for any value of α_λ, the same qualitative dependence on the size ratio as Δ_ζ. Specifically, the corresponding function ψ_{α_λ} is positive and grows monotonically from 0 to a finite limit when the size ratio is increased from unity to infinity.

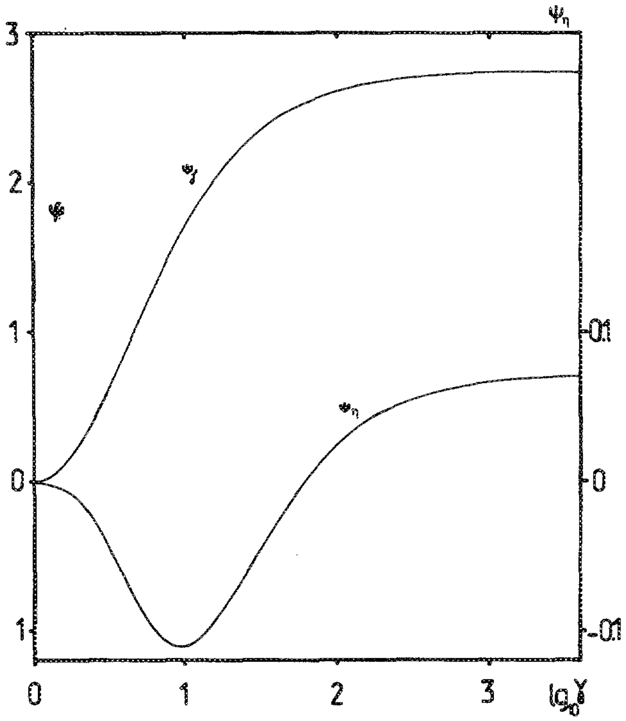

FIG. 2. Functions ψ_ζ and ψ_η defined by (65), plotted against the size ratio.

Whereas the monodisperse configuration corresponds (for a given global concentration) to a minimum of λ^* or k^* (for α_λ or α_k greater than unity), it is easily seen that the maximum value

$$\frac{K^*}{K_1} = 1 + (p+1)\beta c + (p+1)\beta^2\left(1 + \frac{p}{2}\beta\right)c^2 + \mathrm{O}[c^2(\alpha-1)^4], \tag{67}$$

is reached ultimately for a particular type of size-distribution function consisting of a large number of widely separated peaks.

On the other hand, the effective shear modulus of incompressible composities has very different properties. In the first place, it should be noted that the range of variation of ψ_η is much smaller than that of ψ_ζ, and consequently the relative dependence of the value of the c^2 coefficient in (66) on the size distribution is very weak, specifically less than 2% or 3%, which is one order of magnitude smaller than for λ^* or k^*. However, the main feature here is the change of sign of ψ_η.

Thus, whereas (67), corresponding to the size distribution consisting of a large number of widely separated peaks, is still an extremum (a maximum, for $\alpha_\mu > 1$) of μ^*, the shear modulus of a monodisperse composite is no longer the minimum, which is probably close to the shear modulus of a bidisperse mixture with a size ratio $\gamma \equiv 9.12$. In other words, when the contrast between the two phases is small, the polydispersivity may either increase or decrease μ^*. Although the situation is more complicated when the matrix is compressible, the same ambiguity remains.

One might be surprised by this last result, since it is widely believed (Rutgers[51]), that in the mathematically related case of a random dispersion of spherical droplets or solid particles in a viscous liquid, any type of polydispersivity decreases the effective viscosity with respect to a reference monodisperse suspension. However, it should be remembered that (63) is valid only in the limit of small contrast and only for the elasticity problem because, for the case of flow past spherical drops or solid spheres, the normal stress balance in Eq. (45) is discarded and the extra kinematic constraint $G = 0$ at $r = a$ is introduced.

Recall that, as discussed by Thovert and Acrivos,[10] Bruggeman's[52] expression for λ^*, resulting from an effective medium derivation, yields exactly (67) when expanded to $\mathrm{O}(c^2)$. The corresponding expression for μ^* was given erroneously by Bruggeman,[7] but the same effective medium argument applied for any effective transport coefficient, starting from the first-order expansion:

$$K^*/K_1 = 1 + (p+1)\beta c, \tag{68}$$

yields the relation

$$1 - c = \frac{K_2 - K^*}{K_2 - K_1}\left(\frac{K_1}{K^*}\right)^{1/(p+1)}, \tag{69}$$

provided that p does not depend on the characteristics of the constituents. Therefore, (68) is not applicable to k^*, nor to μ^* if the matrix is compressible. However, if $\nu_1 = \frac{1}{2}$, the expansion of (68) to $O(c^2)$ is in full agreement with (67), as expected in view of the approximation underlying Bruggeman's argument.

As noted earlier, evaluation of the microstructural parameters ζ and η to $O(c)$ lead to rigorous bounds on λ^*, k^*, and μ^* which are exact to $O(c^2)$. Such results are not useful for the more practically interesting regimes of moderate to high particle concentrations. The results obtained in the present paper, however, can be used to study the macroscopic behavior of the composite in this more interesting regime if one exploits the observation that ζ and η for the previously studied random systems are exactly linear or nearly linear in c for a wide range of $c>0$ (Torquato and Lado,[29] Torquato,[30] Sen, Lado, and Torquato[43]). For example, for symmetric-cell materials[27] in which the cells are spheres, both ζ and η are exactly linear in c for all c. This model corresponds to a certain polydisperse distribution of spheres. For equisized fully penetrable spheres (i.e., spatially uncorrelated spheres), ζ and η are very nearly linear for almost the entire range of c (Torquato and Lado,[29] Torquato,[30], Sen, Lado, and Torquato[43]). In the case of equisized impenetrable spheres, ζ and η are approximately linear in c for $c \leqslant 4$, where $c = 0.4$ corresponds to about 65% of the random-close-packing volume fraction. (Torquato and Lado,[29] Sen, Lado, and Torquato[43]). Hence, there is strong evidence to suggest that ζ and η for random systems will be nearly linear in c up to moderately high c.

Let us first consider the conductivity problem. The cases of a monodisperse suspension, a bidispersed suspension with widely separated particle sizes, and a polydispersed suspension containing n different and widely separated particle sizes ($n \rightarrow \infty$), (8) and (21), respectively, yield

$$\zeta = 0.210\,68c + O(c^2), \tag{70}$$

$$\zeta = 0.355\,34c + O(c^2), \tag{71}$$

$$\zeta = \tfrac{1}{2}c + O(c^2). \tag{72}$$

Note that the last result could have been obtained from (67) and therefore $\frac{1}{2}$ corresponds to the maximum slope of ζ at $c = 0$, i.e., this is the geometry that gives the largest effect of polydispersivity. Observe further that the bidispersed result (71) lies exactly midway between the monodispersed result (70) and the result (72). A larger value of ζ for conducting particles ($\alpha_\lambda > 1$) implies a larger lower bound on the effective conductivity λ^*. As is well known, the lower bound, in such instances, provides a good estimate of the effective property (even though the reciprocal upper bound may diverge from the lower bound) as long as the system is below the percolation threshold of the conducting or more rigid phase.[19,20] (Note that completely analogous statements apply for the lower bound on the elastic moduli when the particles are more rigid than the matrix.[43]) Finally, it is important to note that in contrast to the geometry of polydispersed, fully penetrable spheres,[33] the linear term of ζ (the quantity e_1) for impenetrable-sphere systems is relatively sensitive to polydispersity in size.

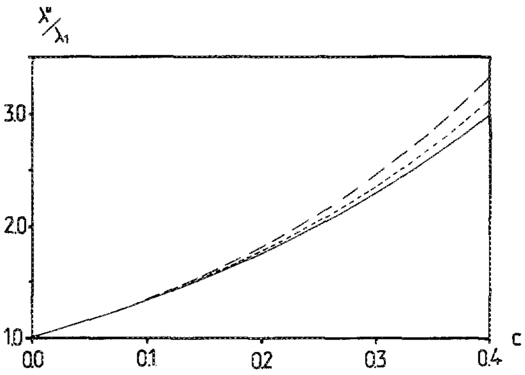

FIG. 3. Beran's third-order lower bound on the effective conductivity when $\alpha_\lambda = \infty$ for: a monodispersion [using (70), short dashes]; a polydispersion [using (72), long dashes]. The second-order lower bound (solid line) of Hashin and Shtrikman.

In Fig. 3 we plot, for the extreme case of $\alpha_\lambda = \infty$, which will show the largest effect of polydispersivity, Beran's lower bounds as obtained from (6) after substituting the monodispersed result (70) and the polydispersed result (72) for $0 \leqslant c \leqslant 0.4$ together with the lower bound of Hashin and Shtrikman. Since the system is well below its percolation threshold, the lower bounds are expected to provide useful estimates of λ^* for the respective models. Clearly then, for the moderate range of c considered in this figure, the effect of polydispersivity on λ^* relative to the monodisperse case is not large, with the largest effect occurring at the highest volume fraction shown. On the other hand, for volume fractions larger than 0.4 and approaching the close-packing fraction, the effect of polydispersivity on λ^* is expected to be significantly larger.

Now let us consider the elasticity problem. For a monodispersion, bidispersion with widely separated particle sizes, and polydispersion containing n different and widely separated particle sizes $n \rightarrow \infty$, (20) and (62), respectively, give

$$\eta = 0.482\,74c + O(c^2), \tag{73}$$

$$\eta = 0.491\,37c + O(c^2), \tag{74}$$

$$\eta = \tfrac{1}{2}c + O(c^2). \tag{75}$$

Again we find that the bidispersed result (74) lies exactly midway between the monodispersed result (73) and result (75). However, we observe that the effect of polydispersivity on η is considerably smaller than the corresponding effect on ζ. Consequently, when the matrix is incompressible ($\nu_1 = \frac{1}{2}$), the effect of polydispersivity on the effective shear modulus μ^* will be very small, since the contribution of η to μ_L in (11) vanishes.

In Fig. 4, we plot the bounds on k^* and μ^* as obtained from (10) and (11) after substituting the monodisperse results (70) and (73) and the polydisperse results (72) and (75), for $0 \leqslant c \leqslant 0.4$, and for

$$\alpha_k = 9.91, \quad \alpha_\eta = 28.6, \quad \nu_1 = 0.394, \tag{76}$$

together with the bounds of Hashin and Shtrikman. As in the conduction case, and even for these compressible materials, the effect of the polydispersivity on the lower bounds for k^* and μ^* is not large for this range of volume fractions.

The available experimental data for the elastic effective moduli of polydisperse composite media are rather rare and

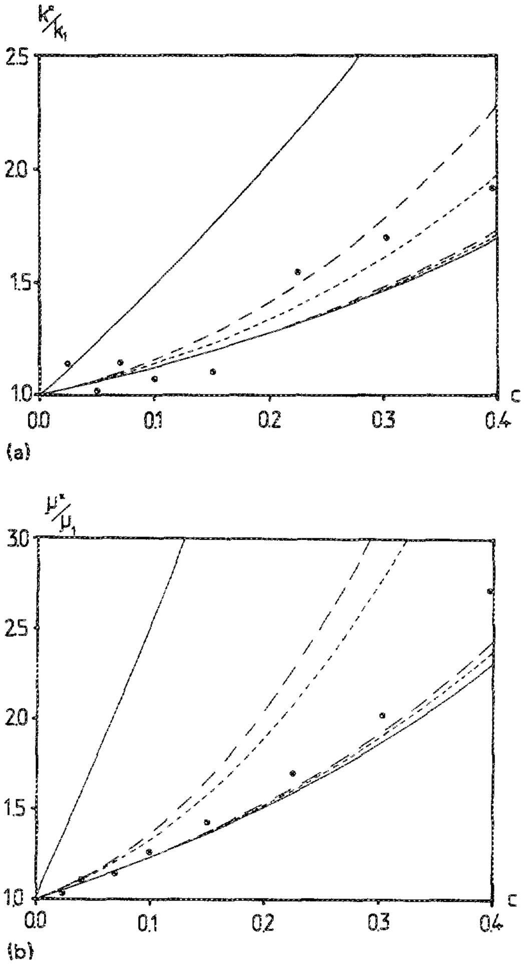

FIG. 4. (a) Beran's third-order bounds on the effective bulk modulus for case (76), for a monodispersion [using (70), short dashes]; a polydispersion [using (72), long dashes]. The bounds of Hashin and Shtrikman (solid line). Smith's (see Ref. 53) data (dots). (b) McCoy's third-order bounds on the effective shear modulus for case (76), and for: a monodispersion [using (70) and (73), short dashes]; a polydispersion [using (72) and (75), long dashes]. The bounds of Hashin and Shtrikman (solid line). Smith's (see Ref. 53) data (dots).

incomplete, because as a rule only one coefficient (generally Young's modulus) was reported. A complete set of data is due to Smith[53] for composites consisting of glass spheres embedded in a glass epoxy matrix, verifying (76). Unfortunately, the size distribution of the inclusions was not fully characterized, and only the range (1–30 μm) was reported. Smith's data are plotted in Fig. 4.

Although the data for μ^* fall between the bounds (11), within the accuracy of measurements, the values for k^* are scattered, and outside the bounds (10) as well as the bounds of Hashin and Shtrikman. The strong aging effect reported by Smith might be partly responsible for these discrepancies (data depicted in Fig. 4 correspond to Table 2 in Smith,[53] i.e., to samples that were 200 days old). In addition, a considerable uncertainty on the reported values of k^* may result from the fact that the measurements were performed on samples undergoing a monoaxial extension in which Young's modulus (related to the axial stress) and Poisson's ratio (ratio of transverse and longitudinal strain) were measured.

Thus, when calculating the bulk and shear moduli,

$$k = E/3(1-2\nu), \quad \mu = E/2(1+\nu), \tag{77}$$

the bulk modulus k, unlike μ, is a very sensitive function of ν (especially when the medium is weakly compressible). Recall, for illustration, that the same flaw appeared in Richard's[54] classical data for a quasi-monodisperse composite. As outlined by Laws,[55] Richard's data for k^* (but not for μ^*), obtained by the same method as Smith's, violate the lower bound of Hashin and Shtrikman. Thus it seems that only triaxial trials are able to provide accurate information on the bulk modulus.

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