NEW THIRD-ORDER BOUNDS ON THE
EFFECTIVE MODULI OF N-PHASE COMPOSITES*

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Summary. We develop some new bounds on the effective moduli of N-phase composites. These new bounds are accurate up to and including terms of third order in $O(|K_i - K_j|, |\mu_i - \mu_j|)$, where K_i and μ_i are the bulk and shear modulus, respectively, of phase i. These bounds use the same statistical information as McCoy's and Beran-Molyneux's bounds but are tighter than, or at worst coincident with, the latter bounds. We also present in the appendix a new perturbation solution for the effective moduli which only requires that $|\delta\mu| = O(|\mu_i - \mu_j|)$ be small.

1. Introduction. We consider the theoretical determination of the effective moduli of a composite material. The composite material in question is comprised of N phases distributed in such a way that the overall material is homogeneous in a statistical sense. Each phase is assumed isotropically elastic and its Lamé moduli are assumed known. The problem has a long history and has been reviewed by Hashin [1], Hale [2], Watt et al. [3] and McCoy [4]. In particular, we are concerned with the problem of determining bounds on the effective shear modulus μ_e and the effective bulk modulus K_e of the composite. These bounds may be conveniently classified by their width. That is, if the upper and lower bounds on K_e, say K_u and K_l, respectively, differ by a term of the order $O(\delta v^{n+1})$, where

$$\delta v = \max_{i,j} (|K_i - K_j|, |\mu_i - \mu_j|,$$

then the bounds are said to be of nth order. In the above K_i and μ_i are the bulk and shear modulus of phase i ($i = 1, 2, \ldots, N$) respectively. An nth-order bound provides an estimate to the effective property accurate up to and including terms of $O(\delta v^n)$. In this sense Reuss' [5] and Voigt's [6] estimates are first-order, Hashin and Shtrikman's [7] and Walpole's [8] bounds are second-order and Beran and Molyneux's [9] and McCoy's [10] bounds are third-order. These third-order bounds for $N = 2$ have been simplified recently by

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Milton [11] who showed that in addition to the volume fractions one needs two geo-metrical parameters which both lie in the interval [0, 1] and are given by some third-order correlation function.

We have recently found some third- and fourth-order bounds on the effective moduli of *two-phase* composites [12] and on the effective thermal conductivity of N-phase com-posites ($N > 2$) [13]. Our new third-order bounds on μ_e for a two-phase composite are tighter than those of McCoy [10], while the third-order bounds on K_e for a two-phase composite are identical to those of Beran and Molyneux [9]. Our third-order bounds on the effective thermal conductivity of N-phase composites ($N > 2$) are tighter than those of Beran [14], although for $N = 2$ they are identical to Beran's bounds. The fourth-order bounds require more information about the microstructure. The extra microstructural parameters are all related to a fourth-order correlation function.

In this communication we derive some new third-order bounds for the effective moduli of N-phase composites. These new bounds are of the same order as McCoy's and Beran and Molyneux's bounds but are tighter than those bounds. Our work is based on a Fourier series representation outlined in [13], the essential features of which are recapitulated below.

2. The phase vector. It suffices for the purposes of the present work to consider the composite as a periodic material in x, y, z, with periods L_x, L_y, L_z. This point of view was mentioned briefly by Brown [15] and is perfectly general as long as the periods L_x, L_y, L_z (the size of the specimen) are much larger than a characteristic length of an inhomoge-neity (grain size). This viewpoint plus the assumption of statistical homogeneity allow us to equate ensemble averages to corresponding volume averages. For further discussion of this point, the reader is referred to McCoy [4, 10].

The detailed microstructure information of the composite is contained in the *phase vector*

$$\Omega_a(\mathbf{x}) = \delta_{ab}, \qquad \text{if } \mathbf{x} \text{ is in phase } b,$$

where δ_{ab} is the Kronecker delta and all Roman subscripts take values from the indexing set $\{1, 2, \ldots, N\}$. The normal summation convention will be used unless stated otherwise. Denoting by the angular brackets the ensemble average, it is clear that

$$\langle \mathbf{\Omega} \rangle = \mathbf{f},$$

where $\mathbf{f} = \{f_1, f_2, \ldots, f_N\}$ is a vector whose component f_i is the volume fraction of phase i. Expressing the fluctuating part of $\mathbf{\Omega}$ by a Fourier series (owing to the periodicity of the composite), we have

$$\mathbf{\Omega} = \mathbf{f} + \mathbf{\Omega}', \qquad \mathbf{\Omega}'(\mathbf{x}) = \sum_{k \neq 0} \omega(\mathbf{k}) \, e^{i\mathbf{k} \cdot \mathbf{x}}, \qquad i^2 = -1 \tag{1}$$

In (1) and elsewhere the prime quantity is a fluctuating component and $\mathbf{k}$, $\mathbf{l}$, $\mathbf{m}$ are wave numbers; they are of the form $\{k_1, k_2, k_3\}$ with k_1, k_2, k_3 being integers varying from $-\infty$ to ∞. Thus complete information about the microstructure is contained in $\omega(\mathbf{k})$. We list below some relations that $\omega(\mathbf{k})$ must satisfy.

First it should be noted that not all of the $\Omega'_a(\mathbf{x})$ are linearly independent. This is because

$$\sum_a \Omega_a(\mathbf{x}) = \sum_a f_a = 1$$

which implies

$$\sum_a \omega_a(\mathbf{k}) = 0.$$

Furthermore, starting from the identities

$$(2\Omega_a(\mathbf{x}) - 1)^2 = 1 \qquad (a \text{ fixed})$$

and

$$\Omega_a(\mathbf{x})\Omega_b(\mathbf{x}) = 0 \qquad (a \neq b),$$

we have

$$\sum_{\mathbf{k} \neq 0} \omega_a(\mathbf{k})\omega_b(-\mathbf{k}) = \Gamma_{ab} \equiv f_a(1 - f_a), \qquad \text{if } a = b$$

$$\equiv -f_a f_b, \qquad \text{if } a \neq b \tag{2}$$

and

$$\sum_{\mathbf{m} \neq 0, \mathbf{k}} \omega_a(\mathbf{k} - \mathbf{m})\omega_b(\mathbf{m}) = (1 - 2f_a)\omega_a(\mathbf{k}), \qquad \text{if } a = b$$

$$= -f_a \omega_b(\mathbf{k}) - f_b \omega_a(\mathbf{k}), \qquad \text{if } a \neq b. \tag{3}$$

We also need the following identity:

$$\sum_{\mathbf{k} \neq 0} \sum_{\mathbf{m} \neq 0, \mathbf{k}} \omega_a(\mathbf{k} - \mathbf{m})\omega_b(\mathbf{m})\omega_c(-\mathbf{k}) = \Delta_{abc} \equiv (1 - 2f_b)\Gamma_{bc}, \qquad \text{if } a = b \text{ (no sum)}$$

$$\equiv -f_a \Gamma_{bc} - f_b \Gamma_{ac}, \qquad \text{if } a \neq b. \tag{4}$$

3. Effective moduli. If the phases are isotropically elastic the local constitutive relation takes the form

$$\sigma(\mathbf{x}) = \lambda \, \mathrm{tr} \, \varepsilon \mathbf{1} + 2\mu\varepsilon, \tag{5}$$

where λ and μ are the Lamé constants at the point $\mathbf{x}$, σ is the stress tensor and ε is the infinitesimal strain tensor which is obtained from the displacement vector $\mathbf{u}$ using

$$\varepsilon = \tfrac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^T),$$

where the superscript T denotes a transpose. With homogeneous boundary conditions, which produce homogeneous stress and strain fields in a homogeneous elastic body, we can decompose the fields into a mean and a fluctuating part:

$$\mathbf{u} = \langle\mathbf{u}\rangle + \mathbf{u}'; \qquad \varepsilon = \langle\varepsilon\rangle + \varepsilon'; \qquad \sigma = \langle\sigma\rangle + \sigma'.$$

The effective Lamé coefficients for the composite, λ_e and μ_e, are then defined by

$$\langle\sigma\rangle = \lambda_e \, \mathrm{tr} \, \langle\varepsilon\rangle\mathbf{1} + 2\mu_e\langle\varepsilon\rangle. \tag{6}$$

This definition is, of course, equivalent to that derived from an energy consideration. Also, instead of λ_e, engineers are more interested in the effective bulk modulus $K_e = \lambda_e + \tfrac{2}{3}\mu_e$. We now derive a third-order perturbation solution for K_e and μ_e. Fourth-order perturbation solutions have been reported [12] for the special case of two-phase composites ($N = 2$).

First, the fluctuating parts of field quantities are expressed as Fourier series in space:

$$\{\mathbf{u}'(\mathbf{x}), \qquad \varepsilon'(\mathbf{x}), \qquad \sigma'(\mathbf{x})\} = \sum_{\mathbf{k} \neq 0} \{\mathbf{U}(\mathbf{k}), \mathbf{E}(\mathbf{k}), \mathbf{S}(\mathbf{k})\}e^{i\mathbf{k}\cdot\mathbf{x}}.$$

Next, for a fixed q, $1 \le q \le N$, we define

$$\delta K_a = K_a - K_q, \qquad \delta \mu_a = \mu_a - \mu_q,$$

where K_a and μ_a are the bulk and shear moduli of phase a, respectively. Noting that

$$K = K_a \Omega_a, \qquad \mu = \mu_a \Omega_a$$

and keeping in mind (1), we obtain

$$K = \langle K \rangle + \delta \mathbf{K} \cdot \mathbf{\Omega}', \qquad \mu = \langle \mu \rangle + \delta \mathbf{\mu} \cdot \mathbf{\Omega}'. \tag{7}$$

When (7) are used in the constitutive relation (5) and the resulting expression averaged, one obtains, using (6),

$$K_e \langle \varepsilon \rangle \mathbf{1} + 2\mu_e \langle \tilde{\boldsymbol{\varepsilon}} \rangle = \left(\langle K \rangle \langle \varepsilon \rangle + \delta K_a \sum_{\mathbf{k} \ne 0} \omega_a(\mathbf{k}) E(-\mathbf{k}) \right) \mathbf{1}$$

$$+ 2 \left(\langle \mu \rangle \langle \tilde{\boldsymbol{\varepsilon}} \rangle + \delta \mu_a \sum_{\mathbf{k} \ne 0} \omega_a(\mathbf{k}) \tilde{\mathbf{E}}(-\mathbf{k}) \right). \tag{8}$$

In (8) and elsewhere any second-order tensor, say $\mathbf{E}$, is expressed as $\frac{1}{3} E \mathbf{1} + \tilde{\mathbf{E}}$, where E is the trace of $\mathbf{E}$ and $\tilde{\mathbf{E}}$ is traceless. From (8) we can find the effective bulk modulus K_e and the effective shear modulus μ_e if we know $\mathbf{E}$. In order to find $\mathbf{E}$ we need the Fourier component $\mathbf{S}(\mathbf{k})$ of $\boldsymbol{\sigma}'$. $\mathbf{S}$ can be found by substituting (7) into the constitutive relation (5), multiplying the resulting expression by $\exp(i\mathbf{k} \cdot \mathbf{x})$ and averaging the final expression. One thus obtains

$$\mathbf{S}(\mathbf{k}) = \left(\langle K \rangle E(\mathbf{k}) + \langle \varepsilon \rangle \, \delta \mathbf{K} \cdot \boldsymbol{\omega}(\mathbf{k}) + \delta \mathbf{K} \cdot \sum_{\mathbf{m} \ne 0, \, \mathbf{k}} \boldsymbol{\omega}(\mathbf{k} - \mathbf{m}) E(\mathbf{m}) \right) \mathbf{1}$$

$$+ 2 \left(\langle \mu \rangle \tilde{\mathbf{E}}(\mathbf{k}) + \langle \tilde{\boldsymbol{\varepsilon}} \rangle \, \delta \boldsymbol{\mu} \cdot \boldsymbol{\omega}(\mathbf{k}) + \delta \boldsymbol{\mu} \cdot \sum_{\mathbf{m} \ne 0} \boldsymbol{\omega}(\mathbf{k} - \mathbf{m}) \tilde{\mathbf{E}}(\mathbf{m}) \right).$$

In a quasi-static deformation state the divergence of $\boldsymbol{\sigma}$ is zero everywhere. This implies $\mathbf{S}(\mathbf{k}) \cdot \mathbf{k}$ is identically zero in Fourier space. This information plus the definition of the strain tensor in Fourier space:

$$\mathbf{E}(\mathbf{k}) = \tfrac{1}{2} i (\mathbf{k} \mathbf{U}(\mathbf{k}) + \mathbf{U}(\mathbf{k}) \mathbf{k})$$

allows us to obtain, after some manipulation,

$$i\mathbf{k} \cdot \mathbf{U}(\mathbf{k}) = - \frac{3 \langle \varepsilon \rangle}{\langle 3K + 4\mu \rangle} \, \delta \mathbf{K} \cdot \boldsymbol{\omega}(\mathbf{k}) - \frac{6 \delta \boldsymbol{\mu} \cdot \boldsymbol{\omega}(\mathbf{k})}{\langle 3K + 4\mu \rangle} \, \langle \tilde{\boldsymbol{\varepsilon}} \rangle : \frac{\mathbf{k}\mathbf{k}}{k^2}$$

$$- i \, \frac{3 \delta K_a - 2 \delta \mu_a}{\langle 3K + 4\mu \rangle} \sum_{\mathbf{m} \ne 0, \, \mathbf{k}} \omega_a(\mathbf{k} - \mathbf{m}) \mathbf{m} \cdot \mathbf{U}(\mathbf{m})$$

$$- i \, \frac{6 \delta \mu_a}{\langle 3K + 4\mu \rangle} \sum_{\mathbf{m} \ne 0, \, \mathbf{k}} \frac{\mathbf{k} \cdot \mathbf{m}}{k^2} \, \mathbf{k} \cdot \mathbf{U}(\mathbf{m}) \omega_a(\mathbf{k} - \mathbf{m}) \tag{9}$$

and

$$i \langle \mu \rangle \mathbf{U}(\mathbf{k}) = - \langle \varepsilon \rangle \, \delta \mathbf{K} \cdot \boldsymbol{\omega}(\mathbf{k}) \frac{\mathbf{k}}{k^2} - 2 \delta \boldsymbol{\mu} \cdot \boldsymbol{\omega}(\mathbf{k}) \langle \tilde{\boldsymbol{\varepsilon}} \rangle \frac{\mathbf{k}}{k^2}$$

$$-\tfrac{1}{3}i\langle 3K + \mu\rangle\mathbf{k}\cdot\mathbf{U}(\mathbf{k})\,\frac{\mathbf{k}}{k^2} - \tfrac{1}{3}i(3\delta K_a - 2\delta\mu_a)\sum_{\mathbf{m}\neq 0,\,\mathbf{k}}\frac{\mathbf{km}\cdot\mathbf{U}(\mathbf{m})}{k^2}\,\omega_a(\mathbf{k}-\mathbf{m})$$

$$-i\delta\mu_a\sum_{\mathbf{m}\neq 0,\,\mathbf{k}}\frac{\mathbf{mU}(\mathbf{m})\cdot\mathbf{k} + \mathbf{U}(\mathbf{m})\mathbf{k}\cdot\mathbf{m}}{k^2}\,\omega_a(\mathbf{k}-\mathbf{m}). \tag{10}$$

Expressions (9) and (10) for $\mathbf{U}(\mathbf{k})$ can, in principle, be solved to any order of accuracy in $\delta v = O(|\delta\mathbf{K}|, |\delta\boldsymbol{\mu}|)$. In the appendix we show how to obtain an equation for $\mathbf{U}(\mathbf{k})$ which can be solved to any order of accuracy in $|\delta\mu|$, without assuming $|\delta\mathbf{K}|$ is small.

3.1 *Effective bulk modulus.* To solve for the effective bulk modulus we let $\langle\varepsilon\rangle = 1$ and $\langle\tilde{\varepsilon}\rangle = 0$. Thence, from (8),

$$K_e = \langle K\rangle + \delta\mathbf{K}\cdot\sum_{\mathbf{k}\neq 0}\boldsymbol{\omega}(\mathbf{k})E(-\mathbf{k}). \tag{11}$$

Now, from (9–10), to second-order in δv we obtain

$$i\langle\mu\rangle\mathbf{U}(\mathbf{k}) = -\frac{3\langle\mu\rangle}{\langle 3K + 4\mu\rangle}\,\delta\mathbf{K}\cdot\boldsymbol{\omega}(\mathbf{k})\,\frac{\mathbf{k}}{k^2}$$

$$+\frac{3\langle\mu\rangle}{\langle 3K + 4\mu\rangle^2}\,(3\delta K_a - 2\delta\mu_a)\delta K_b\sum_{\mathbf{m}\neq 0}\frac{\mathbf{k}}{k^2}\,\omega_a(\mathbf{k}-\mathbf{m})\omega_b(\mathbf{m})$$

$$-\frac{6\langle 3K + \mu\rangle}{\langle 3K + 4\mu\rangle^2}\,\delta\mu_a\,\delta K_b\sum_{\mathbf{m}\neq 0,\,\mathbf{k}}\frac{\mathbf{k}(\mathbf{k}\cdot\mathbf{m})^2}{k^4 m^2}\,\omega_a(\mathbf{k}-\mathbf{m})\omega_b(\mathbf{m})$$

$$+\frac{6\delta\mu_a\,\delta K_b}{\langle 3K + 4\mu\rangle}\sum_{\mathbf{m}=0,\,\mathbf{k}}\frac{\mathbf{m}(\mathbf{k}\cdot\mathbf{m})}{k^2 m^2}\,\omega_a(\mathbf{k}-\mathbf{m})\omega_b(\mathbf{m}). \tag{12}$$

From (12) one can determine $E(\mathbf{k})$ and thus find that the effective bulk modulus is given by using (11):

$$K_e = \langle K\rangle - 3\delta\mathbf{K}\,\delta\mathbf{K}:\Gamma/\langle 3K + 4\mu\rangle$$

$$+ 3\delta\mathbf{K}(3\delta\mathbf{K} - 2\delta\boldsymbol{\mu})\,\delta\mathbf{K}\vdots\Delta/\langle 3K + 4\mu\rangle^2$$

$$+ 18\delta\boldsymbol{\mu}\,\delta\mathbf{K}\,\delta\mathbf{K}\vdots\mathbf{A}/\langle 3K + 4\mu\rangle^2 + O(\delta v^4). \tag{13}$$

In (13) the parameters Γ and Δ are defined in (2) and (4), the double and triple dots denote tensorial contractions and the parameter $\mathbf{A}$ is defined as follows:

$$A_{abc} = \sum_{\mathbf{k}\neq 0,}\sum_{\mathbf{m}\neq 0,\,\mathbf{k}}\frac{(\mathbf{k}\cdot\mathbf{m})^2}{k^2 m^2}\,\omega_a(\mathbf{k}-\mathbf{m})\omega_b(\mathbf{m})\omega_c(-\mathbf{k}). \tag{14}$$

Since A_{abc} is symmetric with respect to the last 2 indices there are at most $\tfrac{1}{2}N(N-1)^2$ parameters contained in $\mathbf{A}$. It is noteworthy that $\mathbf{A}$ also appears in the third-order bounds on the effective thermal conductivity of N-phase materials [13].

3.2 *Effective shear modulus.* To solve for the effective shear modulus μ_e, we let $\langle\varepsilon\rangle = 0$ and $\tilde{\varepsilon}_{ij} = \delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1}$ in (8) from which we obtain

$$\mu_e = \langle\mu\rangle + \delta\boldsymbol{\mu}\cdot\sum_{\mathbf{k}\neq 0}\boldsymbol{\omega}(\mathbf{k})\tilde{E}_{12}(-\mathbf{k}) \tag{15}$$

Proceeding as before, a second-order solution for $\mathbf{U}(\mathbf{k})$ can be found and hence $\tilde{\mathbf{E}}$. From

(15) we find that the effective shear modulus is given by

$$\mu_e = \langle \mu \rangle - \frac{6\langle K + 2\mu \rangle}{5\langle \mu \rangle \langle 3K + 4\mu \rangle} \, \Gamma : \delta\mu \, \delta\mu + \frac{2(3\delta K - 2\delta\mu) \, \delta\mu \, \delta\mu}{5\langle 3K + 4\mu \rangle^2} : (3\mathbf{A} - \Delta)$$

$$+ \frac{\delta\mu \, \delta\mu \, \delta\mu}{15\langle \mu \rangle^2} : (11\mathbf{A} + 3\Delta) - \frac{16\langle 3K + \mu \rangle}{15\langle \mu \rangle^2 \langle 3K + 4\mu \rangle} \, \delta\mu \, \delta\mu \, \delta\mu : \mathbf{A}$$

$$+ \frac{4\langle 3K + \mu \rangle^2}{15\langle \mu \rangle^2 \langle 3K + 4\mu \rangle^2} \, \delta\mu \, \delta\mu \, \delta\mu : (3\mathbf{A}_1 - \mathbf{A}) + O(\delta v^4). \tag{16}$$

In (16) we have appealed to the assumption of statistical isotropy which allows us to evaluate various fourth-order tensors. Furthermore, the new parameter tensor A_1 is given by

$$A_{1abc} = \sum_{\mathbf{k} \neq 0} \sum_{\mathbf{m} \neq 0, \, \mathbf{k}} \frac{(\mathbf{k} \cdot \mathbf{m})^4}{k^4 m^4} \, \omega_a(\mathbf{k} - \mathbf{m}) \omega_b(\mathbf{m}) \omega_c(-\mathbf{k}). \tag{17}$$

Again there are at most $\frac{1}{2}N(N - 1)^2$ parameters contained in $\mathbf{A}_1$. Apart from the obvious need for the expressions (13) and (16) to compare our bounds with, these perturbation results point out the type of statistical information that must be measured to characterize the material. Indeed, by accurately measuring μ_e and K when δv is small, we can partially determine $\mathbf{A}$ and $\mathbf{A}_1$. It is hoped that if this is done for a material with a range of structures, the physical significance of $\mathbf{A}$ and $\mathbf{A}_1$ may become clear.

3.3 *Other forms for* $\mathbf{A}$ *and* $\mathbf{A}_1$. To bring these perturbation results into line with previous findings of Beran and Molyneux [9] and McCoy [10], the method of the Appendix to [12] can be used to show that

$$\mathbf{A} = \frac{1}{16\pi^2} \iint \frac{\mathbf{r} \cdot \mathbf{s}}{r^3 s^3} \frac{\partial^2}{\partial \mathbf{r} \cdot \partial \mathbf{s}} \langle \Omega'(0)\Omega'(r)\Omega'(s) \rangle \, d^3\mathbf{r} \, d^3\mathbf{s}. \tag{18}$$

and

$$\mathbf{A}_1 = \frac{1}{64\pi^2} \iint rs \left(\frac{\partial^2}{\partial \mathbf{r} \cdot \partial \mathbf{s}} \right)^4 \langle \Omega'(0)\Omega'(\mathbf{r})\Omega'(\mathbf{s}) \rangle \, d^3\mathbf{r} \, d^3\mathbf{s}. \tag{19}$$

To make the connection with Miller's [10] symmetric cell materials as described by Brown [17] and Hori [18], we note that

$$\langle \Omega'(0)\Omega'(\mathbf{r})\Omega'(\mathbf{s}) \rangle = \Delta \, g(0, \mathbf{r}, \mathbf{s}),$$

where $g(0, \mathbf{r}, \mathbf{s})$ is the probability of a triangle (whose vertices are at 0, $\mathbf{r}$ and $\mathbf{s}$) having all three vertices lie in one cell when placed randomly in the composite. From (18) and (19) we find

$$\mathbf{A} = 3G \, \Delta, \qquad \mathbf{A}_1 = E^* \, \Delta, \tag{20}$$

where

$$G = \frac{1}{16\pi^2} \iint \frac{\mathbf{r} \cdot \mathbf{s}}{r^3 s^3} \frac{\partial^2}{\partial r_1 \, \partial s_1} \, g(0, \mathbf{r}, \mathbf{s}) \, d^3\mathbf{r} \, d^3\mathbf{s}$$

is the parameter introduced by Miller [16] and

$$E^* = \frac{1}{(8\pi)^2} \iint rs \left(\frac{\partial^2}{\partial \mathbf{r} \cdot \partial \mathbf{s}} \right)^4 g(0, \mathbf{r}, \mathbf{s}) \, d^3\mathbf{r} \, d^3\mathbf{s}$$

is a constant which appears in Silnutzer's bounds [19]. For spherical cells $G = \frac{1}{9}$, $E^* = \frac{1}{5}$; for platelike cells, $G = \frac{1}{3}$, $E^* = 1$ and for needle-like cells $G = \frac{1}{6}$, $E^* = \frac{3}{8}$.

We are now in a position to derive a new set of third-order bounds.

4. Third-order bounds.

4.1 *Upper bounds.* In general, odd-order bounds on the effective thermal conductivity are generated when using classical variational principles whereas even-order bounds on the same are obtained via Hashin and Shtrikman's [1] variational statements. We expect this to be true for the present vector transport problem. To find upper bounds on μ_e and on K_e we resort to the principle of minimum potential energy which states that of the class of strain fields which satisfy compatibility, the field which also satisfies equilibrium is the one which minimizes

$$2W = \langle K(\varepsilon^t)^2 + 2\mu\varepsilon^t : \tilde{\varepsilon}^t \rangle,$$

where

$$\varepsilon^t = \tfrac{1}{3}\varepsilon^t \mathbf{1} + \tilde{\varepsilon}^t$$

is the trial strain field. Expressing

$$\varepsilon^t = \langle \varepsilon \rangle + \sum_{\mathbf{k} \neq 0} \mathbf{e}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{x}},$$

where $\mathbf{e}(\mathbf{k}) = \tfrac{1}{3}e\mathbf{1} + \tilde{\mathbf{e}}$ is the trial Fourier component of ε^t, one has, keeping (7) in mind,

$$\begin{aligned}
2W = &\langle K \rangle \langle \varepsilon \rangle^2 + 2\langle \mu \rangle \langle \tilde{\varepsilon} \rangle : \langle \tilde{\varepsilon} \rangle \\
&+ \langle K \rangle \sum_{\mathbf{k} \neq 0} e(\mathbf{k})e(-\mathbf{k}) + 2\langle \mu \rangle \sum_{\mathbf{k} \neq 0} \tilde{\mathbf{e}}(\mathbf{k}) : \tilde{\mathbf{e}}(-\check{\mathbf{k}}) \\
&+ 2\langle \varepsilon \rangle\, \delta\mathbf{K} \cdot \sum_{\mathbf{k} \neq 0} \omega(\mathbf{k})e(-\mathbf{k}) + 4\delta\boldsymbol{\mu} \cdot \sum_{\mathbf{k} \neq 0} \omega(\mathbf{k})\langle \tilde{\varepsilon} \rangle : \tilde{\mathbf{e}}(-\mathbf{k}) \\
&+ \delta\mathbf{K} \cdot \sum_{\mathbf{k} \neq 0} \sum_{\mathbf{m} \neq 0,\, \mathbf{k}} \omega(\mathbf{m} - \mathbf{k})e(\mathbf{k})e(-\mathbf{m}) \\
&+ 2\delta\boldsymbol{\mu} \cdot \sum_{\mathbf{k} \neq 0} \sum_{\mathbf{m} \neq 0,\, \mathbf{k}} \omega(\mathbf{m} - \mathbf{k})e(\mathbf{k}) : \tilde{\mathbf{e}}(-\mathbf{m}).
\end{aligned}$$

Letting $\langle \tilde{\varepsilon} \rangle = 0$ and $\langle \varepsilon \rangle = 1$, we find the following upper bound on K_e:

$$\begin{aligned}
K_e \leq K_u = &\langle K \rangle + \langle K \rangle \sum_{\mathbf{k} \neq 0} e(k)e(-k) + 2\langle \mu \rangle \sum_{\mathbf{k} \neq 0} \tilde{\mathbf{e}}(\mathbf{k}) : \tilde{\mathbf{e}}(-\mathbf{k}) \\
&+ 2\delta\mathbf{K} \cdot \sum_{\mathbf{k} \neq 0} \omega(\mathbf{k})e(-\mathbf{k}) + \delta\mathbf{K} \cdot \sum_{\mathbf{k} \neq 0} \sum_{\mathbf{m} \neq 0,\, \mathbf{k}} \omega(\mathbf{m} - \mathbf{k})e(\mathbf{k})e(-\mathbf{m}).
\end{aligned} \qquad (21)$$

To find an upper bound on μ_e, we let $\langle \varepsilon \rangle = 0$ and

$$\begin{aligned}
\langle \tilde{\varepsilon}_{ij} \rangle = \delta_{i1}\,\delta_{j2} + \delta_{i2}\,\delta_{j1} : \mu_e &\leq \mu_u \\
= &\langle \mu \rangle + \tfrac{1}{4}\langle K \rangle \sum_{\mathbf{k} \neq 0} e(\mathbf{k})e(-\mathbf{k}) + \tfrac{1}{2}\langle \mu \rangle \sum_{\mathbf{k} \neq 0} \tilde{\mathbf{e}}(\mathbf{k}) : \tilde{\mathbf{e}}(-\mathbf{k}) \\
&+ 2\delta\boldsymbol{\mu} \cdot \sum_{\mathbf{k} \neq 0} \omega(\mathbf{k})\tilde{e}_{12}(-\mathbf{k}) + \tfrac{1}{4}\delta\mathbf{K} \cdot \sum_{\mathbf{k} \neq 0} \sum_{\mathbf{m} \neq 0,\, \mathbf{k}} \omega(\mathbf{m} - \mathbf{k})e(\mathbf{k})e(-\mathbf{m}) \\
&+ \delta\boldsymbol{\mu} \cdot \sum_{\mathbf{k} \neq 0} \sum_{\mathbf{m} \neq 0,\, \mathbf{k}} \omega(\mathbf{m} - \mathbf{k})\tilde{e}_{12}(\mathbf{k})\tilde{e}_{12}(-\mathbf{m}).
\end{aligned} \qquad (22)$$

4.1.1 *Upper bound on K_e.* We note that the strain field in the first-order perturbation

solution for K_e takes the form

$$\delta \mathbf{K} \cdot \omega(\mathbf{k}) \frac{\mathbf{k}}{k^2} \times \text{constant.}$$

Consequently we take for the trial strain field in Fourier space

$$\mathbf{e}(\mathbf{k}) = \alpha \cdot \omega(\mathbf{k}) \frac{\mathbf{k}\mathbf{k}}{k^2},$$

where α is a vector as yet undetermined. We choose $\alpha_q = 0$, without any loss in generality, since the $\omega_a(\mathbf{k})$ are not all independent. The various terms in (21) can be evaluated with the assumption of statistical isotropy and one finally obtains

$$K_u = \langle K \rangle + \tfrac{1}{3}\langle 3K + 4\mu \rangle \Gamma : \alpha\alpha + 2\Gamma : \alpha\delta\mathbf{K}$$

$$+ \Delta \vdots \delta \mathbf{K}\alpha\alpha + \tfrac{2}{3}(3\mathbf{A} - \Delta) \vdots \delta\mu\alpha\alpha. \tag{23}$$

The best upper bound, K_{eu}, is found by setting $\partial K_m / \partial\alpha = 0$ to yield

$$K_{eu} = \langle K \rangle - 3\delta\mathbf{K} \cdot \Gamma[\langle 3K + 4\mu \rangle\Gamma + (3\delta\mathbf{K} - 2\delta\mu) \cdot \Delta + 6\delta\mu \cdot \mathbf{A}]^{-1}\Gamma \cdot \delta\mathbf{K}. \tag{24}$$

In this equation it is implied that the matrices are truncated: each index a runs from $a = 1$ to $a = N$, excluding $a = q$. The order of this upper bound can be found by expanding (24) in powers of $\delta v = O(|\delta K|, |\delta\mu|)$ and one finds that $K_{ub} = K_e + O(\delta v^4)$, where K_e is given by (13). Thus (24) is a third-order bound on K_e.

4.1.2 *Upper bound on μ_e.* To find an upper bound on μ_e one proceeds as in 4.1.1 except that the trial field is now taken from the first-order perturbation solution for μ_e (Sec. 3.2):

$$\mathbf{e}(\mathbf{k}) = \tfrac{1}{2}\alpha \cdot \omega(\mathbf{k}) \left(\frac{\langle\tilde{\varepsilon}\rangle \cdot \mathbf{k}}{k^2}\mathbf{k} + \mathbf{k}\frac{\langle\tilde{\varepsilon}\rangle \cdot \mathbf{k}}{k^2} \right) + 2\beta \cdot \omega(\mathbf{k})\mathbf{k}\mathbf{k} \frac{\langle\tilde{\varepsilon}\rangle : \mathbf{k}\mathbf{k}}{k^4},$$

where $\langle\tilde{\varepsilon}_{ij}\rangle = \delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1}$ and α, β are two vectors, as yet undetermined. Note that we may choose $\alpha_q = \beta_q = 0$ without any loss of generality. The various terms in (22) can be evaluated with the assumption of statistical isotropy and one obtains

$$\mu_u = \langle\mu\rangle + \tfrac{1}{180}(\mathbf{M} : \alpha\alpha + 2\mathbf{N} : \alpha\beta + \mathbf{P} : \beta\beta + 2\mathbf{L}\alpha + \tfrac{4}{5}\mathbf{L}\beta) \tag{25}$$

where

$$\mathbf{M} = 2\langle 6K + 17\mu \rangle\Gamma + 6\delta\mathbf{K} \cdot (3\mathbf{A} - \Delta) + \delta\mu \cdot (21\mathbf{A} + 13\Delta),$$

$$\mathbf{N} = 4\langle 3K + 4\mu \rangle\Gamma + 6\delta\mathbf{K} \cdot (3\mathbf{A} - \Delta) + 4\delta\mu \cdot (3\mathbf{A} + \Delta),$$

$$\mathbf{P} = 4\langle 3K + 4\mu \rangle\Gamma + 6\delta\mathbf{K} \cdot (3\mathbf{A} - \Delta) + 4\delta\mu \cdot (9\mathbf{A}_1 - 6\mathbf{A} + \Delta),$$

and

$$\mathbf{L} = 60\Gamma\delta\mu.$$

The best upper bound on μ_e, μ_{eu}, is found by setting $\partial\mu_u/\partial\alpha = \partial\mu_u/\partial\beta = 0$, and one has

$$\mu_{eu} = \langle\mu\rangle + \tfrac{1}{15}\delta\mu \cdot \Gamma(5[\mathbf{A} + 2[\mathbf{B}]\Gamma \cdot \delta\mu, \tag{26}$$

where

$$\mathscr{A} = 12(\mathbf{P}^{-1}\mathbf{N} - \mathbf{N}^{-1}\mathbf{M})^{-1}(5\mathbf{N}^{-1} - 2\mathbf{P}^{-1}),$$

$$\mathscr{B} = 12(N^{-1}P - M^{-1}N)^{-1}(5M^{-1} - 2N^{-1}).$$

Note that the matrices $\mathbf{M}$, $\mathbf{N}$ and $\mathbf{P}$ are truncated: each index a runs from $a = 1$ to $a = N$, excluding $a = q$. After some lengthy algebra, one can verify that (26) is a third-order bound, viz., $\mu_{eu}\mu_e + O(\delta v^4)$.

4.2 *Lower bounds.* To find lower bounds on K_e and μ_e we start with the principle of minimum complementary potential energy. This principle states that, among the class of trial stress fields $\boldsymbol{\sigma}^t = \tfrac{1}{3}\sigma^t\mathbf{1} + \tilde{\boldsymbol{\sigma}}^t$ that satisfy equilibrium, the one which satisfies compatibility is that which minimizes the integral

$$2W = \langle \tfrac{1}{9}\hat{K}(\sigma^t)^2 + \tfrac{1}{2}\hat{\mu}\boldsymbol{\sigma}^t : \boldsymbol{\sigma}^t \rangle,$$

where we have defined

$$\hat{K} = 1/K, \qquad \hat{\mu} = 1/\mu.$$

For any fixed q, $1 \le q \le N$, define also

$$\delta\hat{K}_a = 1/K_a - 1/K_q, \qquad \delta\hat{\mu}_a = 1/\mu_a - 1/\mu_q;$$

then we have

$$\hat{K} = \langle\hat{K}\rangle + \delta\hat{\mathbf{K}} \cdot \boldsymbol{\Omega}', \qquad \hat{\mu} = \langle\hat{\mu}\rangle + \delta\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\Omega}'.$$

On expressing the trial stress field $\boldsymbol{\sigma}^t$ by

$$\boldsymbol{\sigma}^t = \langle\boldsymbol{\sigma}\rangle + \sum_{\mathbf{k}\neq 0} \mathbf{t}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{x}},$$

where $\mathbf{t}(\mathbf{k}) = \tfrac{1}{3}t(\mathbf{k})\mathbf{1} + \tilde{\mathbf{t}}(\mathbf{k})$ is the trial Fourier stress field, one has

$$2W = \tfrac{1}{9}\langle\hat{K}\rangle\langle\sigma^2\rangle + \tfrac{1}{2}\langle\hat{\mu}\rangle\langle\tilde{\boldsymbol{\sigma}}\rangle : \langle\tilde{\boldsymbol{\sigma}}\rangle$$

$$+ \tfrac{1}{9}\langle\hat{K}\rangle \sum_{\mathbf{k}\neq 0} t(\mathbf{k})t(-\mathbf{k}) + \tfrac{1}{2}\langle\hat{\mu}\rangle \sum_{\mathbf{k}\neq 0} \tilde{\mathbf{t}}(\mathbf{k}) : \tilde{\mathbf{t}}(-\mathbf{k})$$

$$+ \tfrac{2}{9}\langle\sigma\rangle\,\delta\hat{\mathbf{K}} \cdot \sum_{\mathbf{k}\neq 0} \boldsymbol{\omega}(\mathbf{k})t(-\mathbf{k}) + \delta\hat{\boldsymbol{\mu}} \cdot \sum_{\mathbf{k}\neq 0} \boldsymbol{\omega}(\mathbf{k})\langle\tilde{\boldsymbol{\sigma}}\rangle : \tilde{\mathbf{t}}(-\mathbf{k})$$

$$+ \tfrac{1}{9}\delta\hat{\mathbf{K}} \cdot \sum_{\mathbf{k}\neq 0} \sum_{\mathbf{m}\neq 0,\,\mathbf{k}} \boldsymbol{\omega}(\mathbf{m} - \mathbf{k})t(\mathbf{k})t(-\mathbf{m})$$

$$+ \tfrac{1}{2}\delta\hat{\boldsymbol{\mu}} \cdot \sum_{\mathbf{k}\neq 0} \sum_{\mathbf{m}\neq 0,\,\mathbf{k}} \boldsymbol{\omega}(\mathbf{m} - \mathbf{k})\tilde{\mathbf{t}}(\mathbf{k}) : \tilde{\mathbf{t}}(-\mathbf{m}).$$

Putting $\langle\sigma\rangle = 1$ and $\langle\tilde{\sigma}\rangle = 0$ we find the following lower bound on K_e (upper bound on K_e^{-1}):

$$\hat{K}_e \le \hat{K}_l = \langle\hat{K}\rangle + \langle\hat{K}\rangle \sum_{\mathbf{k}\neq 0} t(\mathbf{k})t(-\mathbf{k}) + \tfrac{9}{2}\langle\hat{\mu}\rangle \sum_{\mathbf{k}\neq 0} \tilde{\mathbf{t}}(\mathbf{k}) : \tilde{\mathbf{t}}(-\mathbf{k})$$

$$+ 2\delta\hat{\mathbf{K}} \cdot \sum_{\mathbf{k}\neq 0} \boldsymbol{\omega}(\mathbf{k})t(-\mathbf{k}) + \delta\hat{\mathbf{K}} \cdot \sum_{\mathbf{k}\neq 0} \sum_{\mathbf{m}=0,\,\mathbf{k}} \boldsymbol{\omega}(\mathbf{m} - \mathbf{k})t(\mathbf{k})t(-\mathbf{m})$$

$$+ \tfrac{9}{2}\delta\hat{\boldsymbol{\mu}} \cdot \sum_{\mathbf{k}\neq 0} \sum_{\mathbf{m}\neq 0,\,\mathbf{k}} \boldsymbol{\omega}(\mathbf{m} - \mathbf{k})\tilde{\mathbf{t}}(\mathbf{k}) : \tilde{\mathbf{t}}(-\mathbf{m}). \tag{27}$$

Similarly, by putting $\langle\sigma\rangle = 0$ and $\langle\tilde{\sigma}_{ij}\rangle = \delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1}$, we find the following lower

bound on μ_e:

$$\hat{\mu}_e \leq \hat{\mu}_l = \langle\hat{\mu}\rangle + \tfrac{1}{9}\langle\hat{K}\rangle \sum_{\mathbf{k}\neq 0} t(\mathbf{k})t(-\mathbf{k}) + \tfrac{1}{2}\langle\hat{\mu}\rangle \sum_{\mathbf{k}\neq 0} \tilde{t}(\mathbf{k}) : \tilde{t}(-\mathbf{k})$$

$$+ 2\delta\hat{\mu}\cdot\sum_{\mathbf{k}\neq 0}\omega(\mathbf{k})\tilde{t}_{12}(-\mathbf{k}) + \tfrac{1}{9}\delta\hat{K}\cdot\sum_{\mathbf{k}\neq 0}\sum_{\mathbf{m}\neq 0,\mathbf{k}}\omega(\mathbf{m}-\mathbf{k})t(\mathbf{k})t(-\mathbf{m})$$

$$+ \tfrac{1}{2}\delta\hat{\mu}\cdot\sum_{\mathbf{k}\neq 0}\sum_{\mathbf{m}\neq 0,\mathbf{k}}\omega(\mathbf{m}-\mathbf{k})\tilde{t}(\mathbf{k}) : \tilde{t}(-\mathbf{m}). \tag{28}$$

4.2.1 *Lower bound on K_e.* To proceed further we take the trial Fourier stress field as

$$t(\mathbf{k}) = \tfrac{1}{2}\alpha\cdot\omega(\mathbf{k})\left[1 - \frac{\mathbf{kk}}{k^2}\right],$$

where α is a constant vector to be determined. Without loss of generality we choose $\alpha_q = 0$. Note that this trial field is a generalized form of the first-order Fourier stress field in the perturbation solution for K_e. Various terms in (27) can be evaluated and one obtains

$$\hat{K}_e \leq \hat{K}_l = \langle\hat{K}\rangle + \tfrac{1}{4}\langle 4\hat{K} + 3\hat{\mu}\rangle\Gamma : \alpha\alpha + 2\Gamma : \delta\hat{K}\alpha$$

$$+ (\delta\hat{K}\cdot\Delta + \tfrac{3}{8}\delta\hat{\mu}\cdot(3A - \Delta)) : \alpha\alpha. \tag{29}$$

The best bound is easily found to be K_{el}, where

$$\hat{K}_{el} = \langle\hat{K}\rangle - 8\delta\hat{K}\cdot\Gamma(2\langle 4\hat{K} + 3\hat{\mu}\rangle\Gamma + 8\delta\hat{K}\cdot\Delta$$

$$+ 3\delta\hat{\mu}\cdot(3A - \Delta))^{-1}\Gamma\cdot\delta\hat{K}, \tag{30}$$

in which it is implied that the matrices are truncated. Again, this bound is third-order in δv.

4.2.2 *Lower bound on μ_e.* To find a third-order bound on μ_e we use the trial Fourier stress field

$$t(\mathbf{k}) = \alpha\cdot\omega(\mathbf{k})\langle\tilde{\sigma}\rangle : \frac{\mathbf{kk}}{k^2}\left(\frac{\mathbf{kk}}{k^2} - 1\right)$$

$$+ \beta\cdot\omega(\mathbf{k})\left(\langle\tilde{\sigma}\rangle\frac{\mathbf{kk}}{k^2} + \frac{\mathbf{kk}}{k^2}\langle\tilde{\sigma}\rangle - \langle\tilde{\sigma}\rangle - \langle\tilde{\sigma}\rangle : \frac{\mathbf{kk}}{k^2}1\right)$$

which is a generalized form of the first-order Fourier stress field in the perturbation solution for μ_e. Proceeding as before, we find

$$\hat{\mu}_e \leq \hat{\mu}_l = \langle\hat{\mu}\rangle + \tfrac{1}{135}(\mathbf{M}_1 : \alpha\alpha + 2\mathbf{N}_1 : \alpha\beta + \mathbf{P}_1 : \beta\beta + 2\mathbf{L}_1\cdot\alpha - \tfrac{5}{2}\mathbf{L}_1\cdot\beta), \tag{31}$$

where

$$\mathbf{M}_1 = 4\langle 4\hat{K} + 3\hat{\mu}\rangle\Gamma + 8\delta\hat{K}\cdot(3A - \Delta) + 3\delta\hat{\mu}\cdot(9A_1 - 6A + \Delta),$$

$$\mathbf{N}_1 = 2\langle 4\hat{K} + 3\hat{\mu}\rangle\Gamma + 4\delta\hat{K}\cdot(3A - \Delta) + 6\delta\hat{\mu}\cdot(3A - 2\Delta),$$

$$\mathbf{P}_1 = \langle 4\hat{K} + 57\hat{\mu}\rangle\Gamma + 2\delta\hat{K}\cdot(3A - \Delta) + 3\delta\hat{\mu}\cdot(21A - 2\Delta),$$

$$\mathbf{L}_1 = 18\Gamma\,\delta\hat{\mu}.$$

Again it is implied that the matrices $\mathbf{M}_1$, $\mathbf{N}_1$ and $\mathbf{P}_1$ are truncated. The best lower bound,

μ_e, is found to be

$$\hat{\mu}_{el} = \langle \hat{\mu} \rangle + \tfrac{1}{15}\delta\hat{\mu} \cdot \Gamma(2\mathbb{A} - 5\mathbb{B})\Gamma \cdot \delta\hat{\mu}, \tag{32}$$

where

$$\mathbb{A} = 9(P_1^{-1}N_1 - N_1^{-1}M_1)^{-1}(5P_1^{-1} + 2N_1^{-1}),$$

$$\mathbb{B} = 9(N_1^{-1}P_1 - M_1^{-1}N_1^{-1})^{-1}(5N_1^{-1} + 2M_1^{-1}).$$

4.3 *Two-phase composites.* For $N = 2$, only two microstructural parameters (in addition to volume fractions) are needed in evaluating the bounds: $A = A_{111}$ and $A_1 = A_{1_{111}}$. Specifically, the bounds on K_e and μ_e are, respectively,

$$\langle K \rangle - \frac{3f_1 f_2 \, \delta K^2}{3\langle \tilde{K} \rangle + 4\langle \mu^{-1} \rangle_\zeta^{-1}} \leq K_e \leq \langle K \rangle - \frac{3f_1 f_2 \, \delta K^2}{3\langle \tilde{K} \rangle + 4\langle \mu \rangle_\zeta}, \tag{33}$$

$$\langle \mu \rangle - \frac{6f_1 f_2 \, \delta\mu^2}{6\langle \tilde{\mu} \rangle + \Xi^{-1}} \leq \mu_e \leq \langle \mu \rangle - \frac{6f_1 f_2 \, \delta\mu^2}{6\langle \tilde{\mu} \rangle + \Theta}, \tag{34}$$

where $\delta K = K_1 - K_2$, $\delta\mu = \mu_1$ and we have defined the following:

$$\zeta_1 = \tfrac{1}{2}(3f_1 + 3A/f_1 f_2 - f_2) = 1 - \zeta_2,$$

$$\eta_1 = \tfrac{5}{6}(f_1 + (4A_1 - 3A)/f_1 f_2 + f_2/5) = 1 - \eta_2,$$

$$\Theta = \frac{3\langle \mu \rangle_\eta \langle 6K + 7\mu \rangle_\zeta - 5\langle \mu \rangle_\eta^2}{\langle 2K - \mu \rangle_\zeta + 5\langle \mu \rangle_\eta},$$

$$\Xi = \frac{5\langle \hat{\mu} \rangle_\zeta \langle 6\hat{K} - \hat{\mu} \rangle_\zeta + \langle \hat{\mu} \rangle_\eta \langle \hat{K} + 21\hat{\mu} \rangle_\zeta}{\langle 128\hat{K} + 99\hat{\mu} \rangle_\zeta + 45\langle \hat{\mu} \rangle_\eta},$$

and we also define the following "averages" for ψ ($\psi = K^{\pm 1}$ or $\mu^{\pm 1}$):

$$\langle \tilde{\psi} \rangle = \psi_1 f_2 + \psi_2 f_1, \qquad \langle \psi \rangle_\zeta = \psi_1 \zeta_1 + \psi_2 \zeta_2, \qquad \langle \psi \rangle_\eta = \psi_1 \eta_1 + \psi_2 \eta_2.$$

It is noteworthy that both parameters ζ_1 and η_1 lie in the interval $[0, 1]$. Bounds (33) are precisely those of Beran and Molyneux [9] as simplified by Milton [11]; bounds (34) have been reported in our previous work [12]. In [12] we showed that

$$21\eta_1 - 5\zeta_1 \geq 0, \qquad 21\eta_2 - 5\zeta_2 \geq 0$$

and we constructed second-order bounds on μ_e from (34) which are tighter than Walpole's bounds (when the latter are applicable). The new second-order bounds on μ_e reduce to Hashin and Shtrikman's [7] bounds when $\delta\mu \geq 0$ and

$$\delta K \geq -(3K_1 + 8\mu_1)^2 \, \delta\mu/42\mu_1^2,$$

$$\delta K \geq -(3K_2 + 8\mu_2)^2 K_1 \, \delta\mu/42\mu_1\mu_2 K_2.$$

Here, starting with the bounds (33) on K_e, we show how Hashin and Shtrikman's and Walpole's bounds on the same can be derived. We define

$$\mu_* = \max_{\zeta_1 \in [0, 1]} \langle \mu \rangle_\zeta,$$

$$\hat{\mu}_* = \max_{\zeta_1 \in [0, 1]} \langle \mu^{-1} \rangle_\zeta.$$

Clearly, if $\delta\mu \geq 0$ then $\mu_* = \mu_1$ and $\hat{\mu}_* = \mu_2^{-1}$ and when $\delta\mu \leq 0$ then $\mu_* = \mu_2$ and $\hat{\mu}_* = \mu_1^{-1}$. Because the microstructural parameter ζ_1 lies in $[0, 1]$, we have the following bounds on K_e, from (33):

$$\langle K \rangle - \frac{3f_1 f_2 \, \delta K^2}{3\langle \tilde{K} \rangle + 4\hat{\mu}_*^{-1}} \leq K_e \leq \langle K \rangle - \frac{3f_1 f_2 \, \delta K^2}{3\langle \tilde{K} \rangle + 4\mu_*} . \tag{35}$$

For $\delta\mu \geq 0$ the bounds (35) are equivalent to Hashin and Shtrikman's bounds (see [11]) and when $\delta\mu \leq 0$ they are equivalent to Walpole's bounds. Note that (35) uses only volume fraction information and are second-order in δK, $\delta\mu$. The possibility of using these second-order bounds in bracketing the volume fraction f_1 from experimental data on K_e and μ_e have been discussed elsewhere [20].

5. Comparison with existing bounds. There are two sets of third-order bounds on the effective moduli of composite materials. One set is on K_e and due to Beran and Molyneux [9] and the other is on μ_e and due to McCoy [10].

5.1 *Beran-Molyneux's bounds.* Beran-Molyneux's bounds are given by

$$\left(\langle \hat{K} \rangle - \frac{8\langle K'\hat{K} \rangle^2}{8\langle K'^2\hat{K} \rangle - 3\langle K'^2\hat{\mu} \rangle + 9J'} \right)^{-1} \leq K_e \leq \langle K \rangle$$
$$- \frac{3\langle K'^2 \rangle^2}{\langle 3K + 4\mu \rangle \langle K'^2 \rangle + 3\langle \lambda' K'^2 \rangle + 2J} ,$$

where

$$J = \frac{1}{16\pi^2} \iint \frac{d^3\mathbf{r} \, d^3\mathbf{s}}{rs} \left(\frac{\partial^2}{\partial\mathbf{r} \cdot \partial\mathbf{s}} \right)^2 \langle \mu'(0)K'(\mathbf{r})K'(\mathbf{s}) \rangle,$$

$$J' = \frac{1}{16\pi^2} \iint \frac{d^3\mathbf{r} \, d^3\mathbf{s}}{rs} \left(\frac{\partial^2}{\partial\mathbf{r} \cdot \partial\mathbf{s}} \right)^2 \langle \hat{\mu}(0)K'(\mathbf{r})K'(\mathbf{s}) \rangle.$$

In our notation

$$\langle K'^2 \rangle = \delta\mathbf{K} \, \delta\mathbf{K} : \langle \Omega'\Omega' \rangle = \delta\mathbf{K} \, \delta\mathbf{K} : \Gamma, \qquad \langle \lambda' K'^2 \rangle = \tfrac{1}{3}(3\delta\mathbf{K} - 2\delta\mu) \, \delta\mathbf{K} \, \delta\mathbf{K} \vdots \Delta,$$

$$J = \delta\mu \, \delta\mathbf{K} \, \delta\mathbf{K} \vdots A, \qquad \langle K'\hat{K} \rangle = \delta\mathbf{K} \, \delta\mathbf{K} : \Gamma,$$

$$\langle K'^2\hat{K} \rangle = \langle \hat{K} \rangle \delta\mathbf{K} \, \delta\mathbf{K} : \Gamma + \delta\mathbf{K} \, \delta\mathbf{K} \, \delta\mathbf{K} \vdots \Delta, \qquad J' = \langle \hat{\mu} \rangle \delta\mathbf{K} \, \delta\mathbf{K} : \Gamma + \delta\hat{\mu} \, \delta\mathbf{K} \, \delta\mathbf{K} \vdots A.$$

Thus Beran-Molyneux's upper bound becomes

$$K_\mu^{\text{BM}} = \langle K \rangle - \frac{3(\delta\mathbf{K} \, \delta\mathbf{K} : \Gamma)^2}{\langle 3K + 4\mu \rangle \delta\mathbf{K} \, \delta\mathbf{K} : \Gamma + (3\delta\mathbf{K} - 2\delta\mu)\delta\mathbf{K} \, \delta\mathbf{K} \vdots \Delta + 6\delta\mu \, \delta\mathbf{K} \, \delta\mathbf{K} \vdots A}$$

and their lower bound is

$$K_l^{\text{BM}} = \left(\langle \hat{K} \rangle - \frac{8(\delta\mathbf{K} \, \delta\hat{\mathbf{K}} : \Gamma)^2}{2\langle 4\hat{K} + 3\hat{\mu} \rangle \Gamma : \delta\mu \, \delta\mu + 8\delta\hat{\mathbf{K}} \, \delta\mathbf{K} \, \delta\mathbf{K} \vdots \Delta + 3\delta\hat{\mu} \, \delta\mathbf{K} \, \delta\mathbf{K} \vdots (3A - \Delta)} \right)^{-1} .$$

To show that our bounds on K_e, (24) and (30), are tighter than Beran-Molyneux's bounds, we optimize the expression (23) for the upper bound on K_e subject to the constraint $\alpha = \alpha \, \delta\mathbf{K}$. The resulting best upper bound is identical to Beran-Molyneux's bound.

Similarly, if we optimize the expression for the lower bound on K_e, (29), subject to the same constraint $\alpha = \alpha \, \delta K$, then the resulting best lower bound is identical to Beran-Molyneux's bound. Thus, by construction, our bounds on K_e are always more restrictive than Beran-Molyneux's bounds. For $N = 2$, the two sets of bounds are identical.

5.2 *McCoy's bounds.* McCoy's bounds on μ_e are given in terms of various fourth-order tensors. These can be simplified as in the preceding subsection and one has for McCoy's upper bound

$$\mu_u^M = \langle \mu \rangle - 4\langle 3\lambda + 8\mu \rangle^2 (\mathbf{\Gamma} : \delta\mathbf{\mu} \, \delta\mathbf{\mu})^2/5\phi,$$

and for McCoy's lower bound

$$(\mu_l^M)^{-1} = \langle \hat{\mu} \rangle - 9\langle 9\lambda + 14\mu \rangle^2/15\psi,$$

where

$$\phi = 6\langle \mu \rangle\langle \lambda + 2\mu \rangle\langle 3\lambda + 8\mu \rangle\mathbf{\Gamma} : \delta\mathbf{\mu} \, \delta\mathbf{\mu} + 6\langle \mu \rangle^2 \delta\mathbf{K} \, \delta\mathbf{\mu} \, \delta\mathbf{\mu} \vdots (3\mathbf{A} - \mathbf{\Delta})$$

$$+ \, \delta\mathbf{\mu} \, \delta\mathbf{\mu} \, \delta\mathbf{\mu} \vdots (21\mathbf{A} + 13\mathbf{\Delta})\langle \lambda + 2\mu \rangle^2 - 8\langle \lambda + \mu \rangle\langle \lambda + 2\mu \rangle\delta\mathbf{\mu} \, \delta\mathbf{\mu} \, \delta\mathbf{\mu}$$

$$\vdots (3\mathbf{A} + \mathbf{\Delta}) + 4\langle \lambda + \mu \rangle^2 \delta\mathbf{\mu} \, \delta\mathbf{\mu} \, \delta\mathbf{\mu} \vdots (9\mathbf{A}_1 - 6\mathbf{A} + \mathbf{\Delta})$$

and

$$\psi = \left\{ 4\langle \lambda + \mu \rangle^2 (4\langle 4\hat{K} + 3\hat{\mu} \rangle\mathbf{\Gamma} + 8\delta\hat{\mathbf{K}} \cdot (3\mathbf{A} - \mathbf{\Delta}) + 3\delta\hat{\mathbf{\mu}} \cdot (9\mathbf{A}_1 - 6\mathbf{A} + \mathbf{\Delta})) \right.$$

$$- 4 \, \frac{\langle \lambda + \mu \rangle}{\langle \lambda + 2\mu \rangle} \, (\langle 8\hat{K} + 6\hat{\mu} \rangle\mathbf{\Gamma} + 4\delta\mathbf{K} \cdot (3\mathbf{A} - \mathbf{\Delta}) + 6\delta\hat{\mathbf{\mu}} \cdot (3\mathbf{A} - 2\mathbf{\Delta}))$$

$$\left. + \langle 4\hat{K} + 57\hat{\mu} \rangle\mathbf{\Gamma} + 2\delta\hat{\mathbf{K}} \cdot (3\mathbf{A} - \mathbf{\Delta}) + 3\delta\hat{\mathbf{\mu}} \cdot (21\mathbf{A} - 2\mathbf{\Delta}) \right\} : \delta\mathbf{\mu} \, \delta\mathbf{\mu}.$$

If, in our expression for the upper bound on μ_e, (25), we set

$$\boldsymbol{\alpha} = \alpha \, \delta\mathbf{\mu}, \qquad \boldsymbol{\beta} = -\frac{\langle \lambda + \mu \rangle}{\langle \lambda + 2\mu \rangle} \, \boldsymbol{\alpha},$$

and optimize the resulting expression, then the best upper thus obtained is precisely that of McCoy. Furthermore, if in the expression for the lower bound on μ_e, (31), we set

$$\boldsymbol{\alpha} = -2 \, \frac{\langle \lambda + \mu \rangle}{\langle \lambda + 2\mu \rangle} \, \boldsymbol{\beta}, \qquad \boldsymbol{\beta} = \beta \, \delta\mathbf{\mu}$$

and optimize the resulting expression, then the resulting best lower bound is precisely that of McCoy. Thus our bounds on μ_e are always more restrictive than McCoy's bounds, even when $N = 2$ [12].

In summary, we have presented some third-order bounds on the effective moduli of N-phase composites. These new third-order bounds are tighter, or at worst coincident with, existing third-order bounds due to McCoy and Beran and Molyneux. The main results are given in (24), (26), (30) and (32) and involve an inversion of some second-order tensors of material geometrical parameters. These bounds may be simplified further if one assumes additional information about the composite. For instance, for Miller's symmetric cell materials we have the relations (20) and only two parameters (G and E^*) are required

to evaluate the bounds. Finally the question of attainability of the second-order bounds on the effective properties of N-phase composites ($N \geq 2$) has been discussed in some detail in the recent work of Milton [21] to which the interested reader is referred.

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Appendix: a new perturbation solution for the effective moduli. The perturbation solutions for μ_e and K_e presented in Secs. 3.1 and 3.2 assume that both $|\delta K|$ and $|\delta \mu|$ are small. Here we show how perturbation solutions for μ_e and K_e can be developed which require only that $|\delta \mu|$ be small. For simplicity we will consider only two-phase composites ($N = 2$).

Our aim is to manipulate the expression (10) for $U(k)$ so that the right-hand side does not incorporate U in the terms which are zeroth-order in $\delta \mu$. Operating on both sides of (9) by $\sum_{k \neq 0, n} \omega_1(n - k)$ where $n \neq 0$, we obtain after some manipulation and relabelling

$$
\langle \lambda + 2\mu \rangle k \cdot U(k) = 3i \, \delta K \langle \varepsilon \rangle \omega_1(k) + 2i \, \delta \mu \langle \tilde{\varepsilon}_{ij} \rangle \frac{k_i k_j}{k^2} \omega_1(k)
$$

$$
- \frac{\delta \lambda}{\langle \tilde{\lambda} + 2\mu \rangle} \left[3i \, \delta K \langle \varepsilon \rangle (f_2 - f_1) \omega_1(k) + 2i \, \delta \mu \langle \tilde{\varepsilon}_{ij} \rangle \sum_{m \neq 0, k} \frac{m_i m_j}{m^2} \right.
$$

$$
\cdot \omega_1(k - m) \omega_1(m) + \delta \lambda \omega_1(k) H - \delta \lambda f_1 f_2 \, k \cdot U(k)
$$

$$
\left. - 2 \delta \mu \sum_{n \neq 0, k} \sum_{m \neq 0, n} \omega_1(k - n) \omega_1(n - m) \frac{(m \cdot n) n \cdot U(m)}{n^2} \right]
$$

$$
- 2 \delta \mu \sum_{m \neq 0, k} \omega_1(k - m) \frac{(mk) k \cdot U(m)}{k^2}, \tag{36}
$$

where

$$\lambda = K - \tfrac{2}{3}\mu, \qquad \delta K = K_1 - K_2, \qquad \delta\mu = \mu_1 - \mu_2,$$

$$\langle \tilde{\lambda} + 2\mu \rangle = \langle \tilde{\lambda} \rangle + 2\langle \mu \rangle = f_1 \lambda_2 + f_2 \lambda_1 + 2f_1 \mu_1 + 2f_2 \mu_2,$$

and

$$H = \sum_{\mathbf{k} \neq 0} \mathbf{k} \cdot \mathbf{U}(\mathbf{k})\omega_1(-\mathbf{k}).$$

In obtaining (36) we have taken $N = q = 2$ and used the identities (2) and (3). By multiplying both sides of (9) by $\omega_1(-\mathbf{k})$ and summing over $\mathbf{k} \neq 0$ we find an alternative expression for H:

$$H = \frac{3i\,\delta K f_1 f_2 \langle \varepsilon \rangle}{\langle \tilde{\lambda} + 2\mu \rangle} - \frac{2\,\delta\mu}{\langle \tilde{\lambda} + 2\mu \rangle} \sum_{\mathbf{k} \neq 0} \sum_{\mathbf{m} \neq 0,\,\mathbf{k}} \omega_1(\mathbf{k} - \mathbf{m})\omega_1(-\mathbf{k}) \frac{(\mathbf{m} \cdot \mathbf{k})\mathbf{k} \cdot \mathbf{U}(\mathbf{m})}{k^2}.$$

Substituting this in (36) gives

$$\mathbf{k} \cdot \mathbf{U}(\mathbf{k}) = \frac{3i\,\delta K \langle \varepsilon \rangle\, \omega_1(\mathbf{k})}{\langle \tilde{\lambda} + 2\mu \rangle} - \frac{2\,\delta\mu\langle \tilde{\lambda} + 2\mu \rangle}{(\lambda_1 + 2\langle\mu\rangle)(\lambda_2 + 2\langle\mu\rangle)} \sum_{\mathbf{m} \neq 0,\,\mathbf{k}} \omega_1(\mathbf{k} - \mathbf{m}) \frac{(\mathbf{m} \cdot \mathbf{k})\mathbf{k} \cdot \mathbf{U}(\mathbf{m})}{k^2}$$

$$+ \frac{2i\,\delta\mu\langle \tilde{\varepsilon}_{ij} \rangle}{(\lambda_1 + 2\langle\mu\rangle)(\lambda_2 + 2\langle\mu\rangle)} \left[\frac{k_i k_j}{k^2} \omega_1(\mathbf{k})\langle \tilde{\lambda} + 2\mu \rangle \right.$$

$$- \delta\lambda \sum_{\mathbf{m} \neq 0,\,\mathbf{k}} \frac{m_i m_j}{m^2} \omega_1(\mathbf{k} - \mathbf{m})\omega_1(\mathbf{m}) \Bigg]$$

$$+ \frac{2\,\delta\lambda\,\delta\mu}{(\lambda_1 + 2\langle\mu\rangle)(\lambda_2 + 2\langle\mu\rangle)} \left[\sum_{\mathbf{m} \neq 0,\,\mathbf{k}} \sum_{\mathbf{m} \neq 0,\,\mathbf{n}} \omega_1(\mathbf{k} - \mathbf{n})\omega_1(\mathbf{n} - \mathbf{m}) \frac{(\mathbf{m} \cdot \mathbf{n})\mathbf{n} \cdot \mathbf{U}(\mathbf{m})}{n^2} \right.$$

$$+ \frac{\omega_1(\mathbf{k})\,\delta\lambda}{\langle \tilde{\lambda} + 2\mu \rangle} \sum_{\mathbf{n} \neq 0} \sum_{\mathbf{m} \neq 0,\,\mathbf{n}} \omega_1(\mathbf{n} - \mathbf{m})\omega_1(-\mathbf{n}) \frac{(\mathbf{m} \cdot \mathbf{n})\mathbf{n} \cdot \mathbf{U}(\mathbf{m})}{n^2} \Bigg]. \tag{37}$$

Next by inserting (37) back into (10) we have

$$U_i(\mathbf{k}) = \frac{3i\,\delta K \langle \varepsilon \rangle\, \omega_1(\mathbf{k})k_i}{k^2 \langle \tilde{\lambda} + 2\mu \rangle} + \frac{2i\,\delta\mu\,\omega_1(\mathbf{k})}{\langle \mu \rangle} \left[\frac{k_j}{k^2} \langle \tilde{\varepsilon}_{ij} \rangle - \frac{k_i k_\alpha k_\beta}{k^4} \langle \tilde{\varepsilon}_{\alpha\beta} \rangle \right]$$

$$+ \frac{2i\,\delta\mu\langle \tilde{\varepsilon}_{\alpha\beta} \rangle k_i}{(\lambda_1 + 2\langle\mu\rangle)(\lambda_2 + 2\langle\mu\rangle)k^2} \left[\frac{k_\alpha k_\beta}{k^2} \langle \tilde{\lambda} + 2\mu \rangle\omega_1(\mathbf{k}) \right.$$

$$- \delta\lambda \sum_{\mathbf{m} \neq 0,\,\mathbf{k}} \frac{m_\alpha m_\beta}{m^2} \omega_1(\mathbf{k} - \mathbf{m})\omega_1(\mathbf{m}) \Bigg]$$

$$+ \frac{2\delta\lambda\,\delta\mu k_i}{(\lambda_1 + 2\langle\mu\rangle)(\lambda_2 + 2\langle\mu\rangle)k^2} \left[\sum_{\mathbf{n} \neq 0,\,\mathbf{k}} \sum_{\mathbf{m} \neq 0,\,\mathbf{n}} \omega_1(\mathbf{k} - \mathbf{n})\omega_1(\mathbf{n} - \mathbf{m}) \frac{(\mathbf{m} \cdot \mathbf{n})\mathbf{n} \cdot \mathbf{U}(\mathbf{m})}{n^2} \right.$$

$$+ \frac{\omega_1(\mathbf{k})\,\delta\lambda}{\langle \tilde{\lambda} + 2\mu \rangle} \sum_{\mathbf{n} \neq 0} \sum_{\mathbf{m} \neq 0,\,\mathbf{n}} \omega_1(\mathbf{n} - \mathbf{m})\omega_1(-\mathbf{n}) \frac{(\mathbf{m} \cdot \mathbf{n})\mathbf{n} \cdot U(\mathbf{m})}{n^2} \Bigg]$$

$$- \frac{\delta\mu}{\langle \mu \rangle} \sum_{\mathbf{m} \neq 0,\,\mathbf{k}} \omega_1(\mathbf{k} - \mathbf{m}) \left[\frac{(\mathbf{m} \cdot \mathbf{k})U_i(\mathbf{m}) + m_i \mathbf{k} \cdot \mathbf{U}(\mathbf{m}) - 2(\mathbf{m} \cdot \mathbf{k})\mathbf{k} \cdot \mathbf{U}(\mathbf{m})k_i/k^2}{k^2} \right]$$

$$- \frac{2\,\delta\mu\langle \tilde{\lambda} + 2\mu \rangle k_i}{(\lambda_1 + 2\langle\mu\rangle)(\lambda_2 + 2\langle\mu\rangle)k^2} \sum_{\mathbf{m} \neq 0,\,\mathbf{k}} \frac{(\mathbf{m} \cdot \mathbf{k})\mathbf{k} \cdot U(\mathbf{m})}{k^2}. \tag{38}$$

This achieves our aim: the zeroth-order term in $\delta\mu$ on the right-hand side of (38) does not incorporate U. This equation can in principle be used to solve for $U_i(\mathbf{k})$ to any order in $\delta\mu$, assuming $\delta\mu$ is small. It is not required that $\delta\lambda$ or δK be small. By following the method outlined in Secs. 3.1 and 3.2 we can then obtain expressions for K_e and μ_e correct up to any order in $\delta\mu$. Specifically, we find that to first order in $\delta\mu$,

$$K_e = \langle K \rangle - \frac{3f_1 f_2 \, \delta K^2}{\langle 3\tilde{K} + 4\mu \rangle} + \frac{12 f_1 f_2 \, \delta K^2 \, \delta\mu(\zeta_1 - f_1)}{\langle 3\tilde{K} + 4\mu \rangle^2}, \tag{39}$$

and to second order in $\delta\mu$,

$$\mu_e = \langle \mu \rangle - \frac{6f_1 f_2 \, \delta\mu^2 [\langle K + 2\mu \rangle \langle 3\tilde{K} + 4\mu \rangle - 3f_1 f_2 \, \delta K^2 - 2\langle \mu \rangle(\zeta_1 - f_1) \, \delta K]}{5\langle \mu \rangle (3K_1 + 4\langle \mu \rangle)(3K_2 + 4\langle \mu \rangle)} \tag{40}$$

where

$$\zeta_1 = \tfrac{1}{2}(3f_1 + 3A_{111}/f_1 f_2 - f_2).$$

The expansion (39) is consistent with the bounds (33), which coincide to first order in $\delta\mu$. Similarly the expansion (40) is consistent with the bounds on μ_e, presented in Eq. (47) of [12], which coincide to second order in $\delta\mu$. We remark that there is a typographical error in Eq. (47) of [12]; it should read

$$\mu_{eb}^* = \langle \mu \rangle - \frac{6 \, \delta\mu^2 f_1 f_2}{6\langle \bar{\mu} \rangle + \mu_2 \psi_2}.$$