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Effect of an inhomogeneous interphase zone on the bulk modulus and conductivity of a particulate composite

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Abstract

A model is presented of a particulate composite containing spherical inclusions, each of which are surrounded by a localized region in which the elastic moduli vary smoothly with radius. This region may represent an interphase zone in a composite, or the transition zone around an aggregate particle in concrete, for example. An exact solution is derived for the displacements and stresses around a single inclusion in an infinite matrix, subjected to a far-field hydrostatic compression, and is then used to derive an approximate expression for the effective bulk modulus of a material containing a random dispersion of these inclusions. The analogous conductivity (thermal, electrical, etc.) problem is then discussed, and it is shown that the expression for the normalized effective conductivity corresponds exactly to that for the normalized effective bulk modulus, if the Poisson ratios of both phases are set to zero.

Keywords: Micromechanics; Effective conductivity; Effective moduli; Composite materials; Functionally graded materials; Interfacial zone; Spherical inclusions

1. Introduction

The behavior of composite materials is greatly influenced by the interface between the matrix and the inclusions. The earliest models for the mechanical behavior of composites assumed that the two components are both homogeneous, and are perfectly bonded across a sharp and distinct interface (Eshelby, 1957; Hashin and Shtrikman, 1961). Later models considered the effect of sliding across the interface (Aboudi, 1989; Jasiuk et al., 1992), debonding between the inclusion and matrix (Benveniste, 1984), and

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other effects. In some materials, the components are well-bonded to each other, but the interface is not sharp. In polymer–fiber composites, for example, as well as in some metal–matrix composites, diffusion of material between the matrix and fiber may create an elastic moduli profile that smoothly varies from that of the fiber to that of the matrix (Theocaris, 1992). In some polymer composites, a binding agent is applied to the fibers to promote adhesion between the fiber and the matrix (Drzal et al., 1983). This binding agent may diffuse into the matrix during the curing process, leading to a gradient in resin concentration. This gradient, in turn, leads to a gradient in the elastic moduli. In other cases, such as the interfacial transition zone around inclusions in mortar or concrete (Lutz et al., 1997), the moduli of the matrix varies as the inclusion particle is approached, but the interface with the inclusion is still distinct, since the inhomogeneous region is restricted to the matrix phase.

Recognition of the importance of modeling the "interphase zone" in composite materials has existed for some time. Hashin and Rosen (1964) developed a model for composites in which a thin layer existed outside of each inclusion. The elastic moduli were uniform within this layer, but different from those in the matrix or inclusions. Herve and Zaoui (1993), Hashin and Monteiro (2002) and others have extended this model by considering a finite number of concentric shells around each inclusion, with the moduli uniform within each shell. Theocaris (1992), Jayaraman and Reifsnider (1992), Jasiuk and Kouider (1993) and others have attempted to account for smooth variation of the moduli, by assuming a power-law variation of moduli with radius, although they still treated the interphase zone as a distinct layer, surrounded by "pure" matrix. Lutz and Zimmerman (1996) modeled the moduli outside of the inclusion with a constant term plus a power-law term, thereby allowing a smooth transition between the interphase layer and the matrix. They used the method of Frobenius series to derive a closed-form solution for a body containing such an inclusion, under hydrostatic far-field loading, and thereby found an expression for the effective elastic moduli of a material that contained a dispersion of such inclusions. The model was successfully used by Lutz et al. (1997) to predict the bulk modulus of concrete. A similar approach can be used for the shear modulus and for thermal/electrical conductivity.

2. Effective bulk modulus

The effective bulk modulus of a composite that has an inhomogeneous interphase zone around each inclusion can be estimated by first solving the problem of a matrix containing a single such inclusion, subjected to a far-field hydrostatic stress. The resulting deformation will have radial symmetry. The only non-zero displacement component will be the radial component, which will vary only with the r co-ordinate; it can therefore be denoted by $u(r)$. The only non-zero components of the strain will be (Sokolnikoff, 1956)

$$\varepsilon_{rr} = \frac{\mathrm{d}u}{\mathrm{d}r}; \quad \varepsilon_{\phi\phi} = \varepsilon_{\theta\theta} = \frac{u}{r}. \tag{1}$$

The only non-trivial equation of stress equilibrium will be

$$\frac{\mathrm{d}\tau_{rr}}{\mathrm{d}r} + \frac{2\tau_{rr} - \tau_{\phi\phi} - \tau_{\theta\theta}}{r} = 0. \tag{2}$$

The stress–strain equations take the usual form for an isotropic material

$$\tau_{rr} = \lambda(\varepsilon_{rr} + \varepsilon_{\phi\phi} + \varepsilon_{\theta\theta}) + 2\mu\varepsilon_{rr} \tag{3}$$

and similarly for the other two normal stresses. (The moduli λ and μ are related to the standard bulk and shear moduli by $K = \lambda + 2\mu/3$, $G = \mu$.) If we combine Eqs. (1)–(3), and allow the moduli to vary with r, we arrive at

$$[\lambda(r) + 2\mu(r)]\left[\frac{d^2u}{dr^2} + \frac{2}{r}\frac{du}{dr} - \frac{2}{r^2}u\;|\right] + [\lambda'(r) + 2\mu'(r)]\frac{du}{dr} + 2\lambda'(r)\frac{u}{r} = 0. \tag{4}$$

We now assume that the moduli in the matrix vary smoothly and monotonically with radius, and approach those of the "pure matrix" component as $r \to \infty$. A convenient algebraic form that satisfies these conditions is the following (Theocaris, 1992; Lutz and Zimmerman, 1996):

$$\lambda(r) = \lambda_m + (\lambda_{if} - \lambda_m)(r/a)^{-\beta}, \quad \mu(r) = \mu_m + (\mu_{if} - \mu_m)(r/a)^{-\beta}, \tag{5}$$

where a is the radius of the inclusion, the subscript 'm' refers to the matrix, and the subscript 'if' refers to the interface with the inclusion (see Fig. 1). The parameter β controls the "thickness" δ of the interphase zones, roughly according to the relationship $\delta \approx 2.3a/\beta$ (Lutz et al., 1997). In order to be able to solve the resulting equations analytically, β must be an integer. Theocaris (1992) fit power-law-type curves to elastic moduli in an interphase zone in a set of E-glass fiber–epoxy resin composites, and found values of β on the order of 100. Lutz et al. (1997) modeled the porosity gradient in the interfacial transition zone of concrete using values of β on the order of 20. Hence, the restriction of β to integral values poses no limitation, in practice.

Substitution of Eq. (5) into Eq. (4) yields an ordinary differential equation that has a regular singular point at infinity, and which can be solved using the method of Frobenius series (Lutz and Ferrari, 1993; Mikata, 1994; Lutz and Zimmerman, 1996). The general solution for the displacements outside of the inclusion is (Lutz and Zimmerman, 1996)

$$u(r) = A_1 r \sum_{n=0}^{\infty} \Gamma_{n\beta}(a/r)^{n\beta} + A_2 r \sum_{n=0}^{\infty} \Gamma_{n\beta+3}(a/r)^{n\beta+3}, \tag{6}$$

where $\{A_1, A_2\}$ are constants, $\Gamma_0 = \Gamma_3 = 1$, and the remaining non-zero Γ_n are found from the following recursion relationship:

$$\Gamma_{n+\beta} = \frac{-\{(M_{if} - M_m)[n^2 - (\beta+3)n - \beta] - 2\beta(\lambda_{if} - \lambda_m)\}}{(n+\beta)(n+\beta-3)(\lambda_m + 2\mu_m)}\Gamma_n, \tag{7}$$

where $M = \lambda + 2\mu$ is the compressional wave modulus. These series will converge if $M_{if} < 2M_m$, i.e., whenever the interphase is softer than the matrix. If $M_{if} > 2M_m$, convergence can be achieved by applying an Euler transformation to the series (Lutz and Ferrari, 1993).

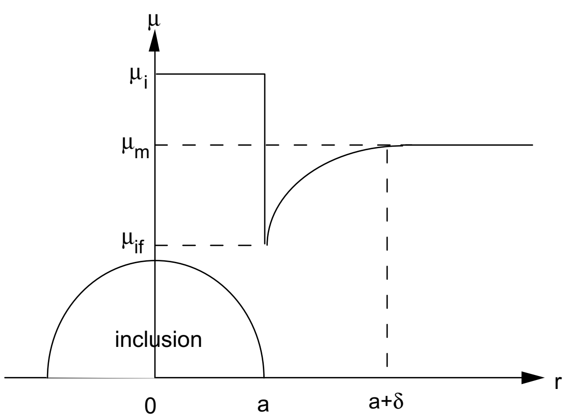

Fig. 1. Schematic diagram of the shear modulus variation described by Eq. (5).

Now consider a homogeneous spherical inclusion of radius a, surrounded by a matrix having an inhomogeneous interphase zone, as described above, subjected to a far-field hydrostatic stress, $-P$. The moduli of the inclusion are denoted by $\{\lambda_i, \mu_i\}$. Outside of the inclusion, in the region $r > a$, the solution will be given by Eq. (6). Inside the inclusion, the solution must have the form appropriate for radially-symmetric deformations of a homogeneous material (Sokolnikoff, 1956)

$$u(r) = B_1 r + B_2 r^{-2}. \tag{8}$$

Four boundary conditions are needed to determine the four constants $\{A_1, A_2, B_1, B_2\}$: $\tau_{rr} \to -P$ as $r \to \infty$, τ_{rr} and u must be continuous at $r = a$, and u must be finite as $r \to 0$. These conditions lead to the following values for the constants:

$$B_1 = A_1 \sum_{n=0}^{\infty} \Gamma_{n\beta} + A_2 \sum_{n=0}^{\infty} \Gamma_{n\beta+3}, \quad B_2 = 0, \quad A_1 = -P/3K_m, \tag{9}$$

$$A_2 = \left(\frac{P}{3K_m}\right) \frac{3(K_i - K_{if}) \sum_{n=0}^{\infty} \Gamma_{n\beta} + (\lambda_{if} + 2\mu_{if}) \sum_{n=0}^{\infty} n\beta \Gamma_{n\beta}}{3(K_i - K_{if}) \sum_{n=0}^{\infty} \Gamma_{n\beta+3} + (\lambda_{if} + 2\mu_{if}) \sum_{n=0}^{\infty} (n\beta + 3) \Gamma_{n\beta+3}}. \tag{10}$$

The solution for the stresses and displacements in and around a single inclusion can be used to estimate the effective bulk modulus of a material that contains a dispersion of such inclusions. In general, the effective bulk modulus K_{eff} of an inhomogeneous body can be found by subjecting the body to hydrostatic stress of magnitude $-P$, and then comparing the strain energy stored in the body to that which would be stored in an identically-shaped homogeneous body (Willis, 1981). Consider a spherical region of radius b, centered on a single inclusion. In the absence of body forces, the strain energy stored in this region can be computed from (Sokolnikoff, 1956)

$$U = \frac{1}{2} \int_{\partial\Omega} \mathbf{T} \cdot \mathbf{u} \, dA, \tag{11}$$

where Ω is the spherical region $r \leqslant b$, $\partial\Omega$ is the boundary $r = b$, $\mathbf{u}$ is the displacement vector, and $\mathbf{T}$ is the traction vector. In the present problem, the only non-zero component of the displacement vector is the radial displacement, u, and the only non-zero component of the traction is τ_{rr}. Hence,

$$U = \frac{1}{2} \int_{\partial\Omega} \tau_{rr}(b) u(b) \, dA = 2\pi b^2 \tau_{rr}(b) u(b). \tag{12}$$

For the hypothetical homogeneous body, the radial displacement would be given by $u(r) = \tau_{rr}(b) r / 3K_{eff}$, so that

$$U = 2\pi b^2 \tau_{rr}(b) \frac{\tau_{rr}(b) b}{3K_{eff}} = \frac{2\pi b^3 [\tau_{rr}(b)]^2}{3K_{eff}}. \tag{13}$$

Equating the strain energy stored in the actual inhomogeneous body, as given by Eq. (12), to that stored in the homogeneous body, as given by Eq. (13), yields

$$K_{eff} = \frac{b \tau_{rr}(b)}{3u(b)} = \frac{\tau_{rr}(b)}{3u(b)/b}. \tag{14}$$

In order to utilize our solution for the single inclusion in an infinite body, we must take the limit as $b \to \infty$. If we were to do this by fixing a, the influence of the inclusion would disappear. Instead, we first put $(a/b)^3 = c$, the volume fraction of inclusions, and then let $b \to \infty$, retaining only terms of order c^0

and c^1. This is justified by noting that these terms will be of the form $c^{1+(\beta/3)}$, $c^{2+(\beta/3)}$, etc., and we expect in practice that $\beta \gg 1$. Moreover, Eq. (7) shows that the coefficient of $c^{1+(\beta/3)}$ will have a factor of β in its denominator, compared to the coefficient of c^1; the higher-order coefficients will have additional factors of β. As an example, for the mortar samples considered by Lutz et al. (1997), which had $\beta = 20$, the relative contribution of the higher order terms would be less than 1%, for inclusion concentrations as high as 60%. (As β is inversely proportional to the interphase thickness, our solution can be thought of as being asymptotically exact in the two limits of small inclusion concentration, and thin interphase.) With this in mind, we find that

$$\frac{K_{\mathrm{eff}}}{K_{\mathrm{m}}} = \frac{1 + (4\mu_{\mathrm{m}}/3K_{\mathrm{m}})fc}{1 - fc}, \tag{15}$$

where

$$f = \frac{-A_2}{A_1} = \frac{3(K_{\mathrm{i}} - K_{\mathrm{if}})\sum_{n=0}^{\infty}\Gamma_{n\beta} + (\lambda_{\mathrm{if}} + 2\mu_{\mathrm{if}})\sum_{n=0}^{\infty} n\beta\Gamma_{n\beta}}{3(K_{\mathrm{i}} - K_{\mathrm{if}})\sum_{n=0}^{\infty}\Gamma_{n\beta+3} + (\lambda_{\mathrm{if}} + 2\mu_{\mathrm{if}})\sum_{n=0}^{\infty}(n\beta + 3)\Gamma_{n\beta+3}}. \tag{16}$$

In the limiting case where the interphase zone is homogeneous, $\Gamma_0 = \Gamma_3 = 1$, all other $\Gamma_n = 0$, $K_{\mathrm{if}} \to K_{\mathrm{m}}$, etc., so $f \to 3(K_{\mathrm{i}} - K_{\mathrm{m}})/(3K_{\mathrm{i}} + 4\mu_{\mathrm{m}})$, and Eq. (15) reduces to the result found by Mori and Tanaka (1973), Christensen (1979), and others.

Fig. 2 shows the effective bulk modulus as a function of the inclusion concentration, for the case where the inclusions are five times stiffer than the pure matrix, $\beta = 10$ (corresponding to an interphase whose thickness is about 1/8th of an inclusion diameter), and several values of the parameter $D = (K_{\mathrm{m}} - K_{\mathrm{if}})/K_{\mathrm{m}}$. The Poisson ratio is taken to be 0.25 throughout the matrix, interphase, and inclusion. The curve for $D = 0$ coincides with the Mori–Tanaka prediction, as well as with the Hashin–Shtrikman lower bound (Hashin and Shtrikman, 1961). Negative values of D correspond to an interphase that is stiffer than the pure matrix; this can occur in a metal–matrix composite, for example, if the inclusion material diffuses into the matrix.

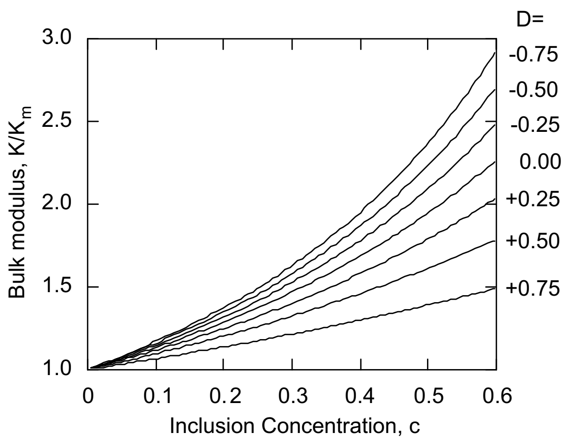

Fig. 2. Effective bulk modulus of a material containing a volume fraction c of inclusions, each surrounded by an interphase zone described by Eq. (5). The inclusion is taken to be five times stiffer than the pure matrix, and the Poisson ratios of all phases are taken to be 0.25.

3. Analogy with conductivity problem

The effective conductivity (thermal, say) is investigated by starting with the basic problem of an inclusion perturbing an otherwise uniform temperature gradient. If the governing equation is expressed in a spherical co-ordinate system centered on the inclusion, with the z-axis aligned with the far-field temperature gradient of magnitude G, the problem is governed by

$$\nabla \cdot [k(r)\nabla T(r,\theta,\phi)] = 0, \tag{17}$$

where T is the temperature and $k(r)$ is the thermal conductivity. Using the standard expressions for the gradient operator in spherical co-ordinates (Arfken, 1985), this equation can be written explicitly as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 k(r)\frac{\partial T}{\partial r}\right] + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{k(r)}{r}\frac{\partial T}{\partial\theta}\right] + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\left[\frac{1}{\sin\theta}\frac{k(r)}{r}\frac{\partial T}{\partial\phi}\right] = 0. \tag{18}$$

The boundary conditions for the temperature are that as

$$r \to \infty, \quad T \approx T_0 + Gz = T_0 + Gr\cos\theta, \tag{19}$$

where θ is the angle of inclination from the z-axis, along with the usual continuity conditions at the inclusion/matrix interface for the temperature and flux. Inserting a temperature field of the form $T(r,\theta,\phi) = T_0 + f(r)\cos\theta$ into Eq. (17) yields the following equation for $f(r)$:

$$k(r)\left[\frac{d^2 f}{dr^2} + \frac{2}{r}\frac{df}{dr} - \frac{2}{r^2}f\right] + k'(r)\frac{df}{dr} = 0. \tag{20}$$

We now note that if we set $\lambda(r) = 0$ in Eq. (4), which corresponds to setting the Poisson ratio equal to zero, we have $2\mu = 3K$ in the elastic problem, and Eq. (4) reduces precisely to Eq. (20), with the correspondence $3K(r) \leftrightarrow k(r)$, $u(r) \leftrightarrow f(r)$. In particular, the analogy holds in regions that are locally homogeneous, such as inside the inclusion, in which case (4) and (20) apply, with $K'(r) = k'(r) = 0$. Hence, the two problems are governed by the same differential equation.

The analogy can be shown to hold all the way through to the calculation of the effective properties. Consider first the four boundary/interface conditions that were imposed in the displacement function. With $\lambda = 0$ in Eq. (3), the radial stress is given by $\tau_{rr} = 2\mu(du/dr) = 3K(du/dr)$. Hence, the far-field boundary condition on the radial displacement is that $du/dr = -P/3K_m$ as $r \to \infty$. Using the already observed correspondences of $3K \leftrightarrow k$ and $u(r) \leftrightarrow f(r)$, this condition transforms into $df/dr = -P/k_m$. From Eq. (18), however, we see that $df/dr \to G$ as $r \to \infty$. Applying Fourier's law to Eq. (18), far from the inclusion, where $k(r) = k_m$, the far-field heat flux, oriented along the z-axis, is found to be given by $q_\infty = -k_m(\partial T/\partial z) = -k_m G$. Hence, $G = -q_\infty/k_m$, which shows that $df/dr \to -q_\infty/k_m$. So, to maintain the analogy, we see that the far-field heat flux, q_∞, plays the role of the far-field hydrostatic pressure, P.

Continuity of the temperature at the outer boundary of the inclusion requires continuity of f at $r = a$. This is directly analogous to the continuity of the radial displacement u at $r = a$. From the discussion in the preceding paragraph, we see that continuity of the radial stress at $r = a$ is equivalent to continuity of the term $3K(du/dr)$. By our analogy, this corresponds to continuity of $k(df/dr)$, which is equivalent to continuity of the heat flux, since $(\partial T/\partial r) = (df/dr)\cos\theta$. Finally, both u and f must be finite at the origin. Thus, both problems are governed by the same differential equation, and the same set of boundary/interface conditions.

Lastly, we must show that the calculation of the effective conductivity follows in analogy with the calculation of the effective bulk modulus. We start with the fact (Christensen, 1979) that the effective conductivity can be defined through the equation $\langle q_z \rangle = -k_{\text{eff}}\langle \partial T/\partial z\rangle$, where the angle brackets denote a volume average over the sphere of radius b. From Gauss' theorem, the volumetric average of the temperature gradient can be expressed as

$$\langle \nabla T \rangle = \frac{1}{V}\int_{\Omega} \nabla T \, dV = \frac{1}{V}\int_{\partial\Omega} T\mathbf{n} \, dA = \frac{1}{V}\int_{\partial\Omega} T\mathbf{e_r} \, dA, \tag{21}$$

where $\mathbf{e_r}$ is the unit vector in the radial direction. Taking the z-component of both sides gives

$$\begin{aligned} \langle \partial T/\partial z \rangle &= \langle \nabla T \cdot \mathbf{e_z} \rangle = \frac{1}{V}\int_{\partial\Omega} T\mathbf{e_r} \cdot \mathbf{e_z} \, dA = \frac{1}{V}\int_{\partial\Omega} T\cos\theta \, dA \\ &= \frac{3}{4\pi b^3}\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} T(b,\phi,\theta)\cos\theta b^2 \sin\theta \, d\theta \, d\phi \\ &= \frac{3}{4\pi b}\int_{\phi=0}^{2\pi} d\phi \int_{\theta=0}^{\pi} T(r,\phi,\theta)\cos\theta\sin\theta \, d\theta \\ &= \frac{3}{2b}\int_{\theta=0}^{\pi} [T_0 + f(b)\cos\theta]\cos\theta\sin\theta \, d\theta \\ &= \frac{3}{2b}\int_{\theta=0}^{\pi} [T_0\cos\theta\sin\theta + f(b)\cos^2\theta\sin\theta] \, d\theta \\ &= \frac{3f(b)}{2b}\int_{\theta=0}^{\pi} \cos^2\theta\sin\theta \, d\theta = \frac{f(b)}{b}. \end{aligned} \tag{22}$$

Again making use of Gauss' theorem, the average heat flux can be expressed as (Markov, 2000)

$$\langle \mathbf{q} \rangle = \frac{-1}{V}\int_{\partial\Omega} k(r)\mathbf{r}(\nabla T \cdot \mathbf{n}) \, dA = \frac{-1}{V}\int_{\partial\Omega} k(r)\frac{\partial T}{\partial r}\mathbf{r} \, dA, \tag{23}$$

where $\mathbf{r}$ is the position vector from the origin. Recalling that $T(r,\theta,\phi) = T_0 + f(r)\cos\theta$, we have $\partial T/\partial r = f'(r)\cos\theta$, so

$$\langle \mathbf{q} \rangle = \frac{-1}{V}\int_{\partial\Omega} k(r)f'(r)\cos\theta\mathbf{r} \, dA. \tag{24}$$

Taking the z-component of both sides, and making use of the fact that $r = b$ and $\mathbf{r} = b\mathbf{e_r}$ on $\partial\Omega$, gives

$$\begin{aligned} \langle q_z \rangle = \langle \mathbf{q} \cdot \mathbf{e_z} \rangle &= \frac{-1}{V}\int_{\partial\Omega} k(b)f'(b)\cos\theta b\mathbf{e_r} \cdot \mathbf{e_z} \, dA = \frac{-1}{V}\int_{\partial\Omega} k(b)f'(b)b\cos^2\theta \, dA \\ &= \frac{-3k(b)f'(b)}{4\pi b^3}\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} b^3\sin\theta\cos^2\theta \, d\theta \, d\phi \\ &= \frac{-3k(b)f'(b)}{2}\int_{\theta=0}^{\pi} \sin\theta\cos^2\theta \, d\theta = -k(b)f'(b). \end{aligned} \tag{25}$$

Using the results (22) and (25), the effective conductivity then follows as:

$$k_{\text{eff}} = \frac{-\langle q_z \rangle}{\langle \partial T/\partial z \rangle} = \frac{k(b)f'(b)}{f(b)/b}. \tag{26}$$

As before, we take b to be large when evaluating (26), in which case $k(b) \to k_{\text{m}}$, and so

$$\frac{k_{\text{eff}}}{k_{\text{m}}} = \lim_{b\to\infty}\left[\frac{bf'(b)}{f(b)}\right]. \tag{27}$$

Now return to expression (14) for the effective bulk modulus. Using Eqs. (1) and (3), and recalling that $3K = 2G$ (because our analogy requires $\nu = 0$!), we see that

$$K_{\text{eff}} = \lim_{b\to\infty} \frac{bK(b)u'(b)}{u(b)}. \tag{28}$$

But as b increases, $K(b) \to K_m$, so we see that

$$\frac{K_{\text{eff}}}{K_m} = \lim_{b\to\infty} \left[\frac{bu'(b)}{u(b)}\right]. \tag{29}$$

Comparison of Eqs. (27) and (29) shows that, since f was the analogue of u, the normalized effective conductive is indeed the analogue of the normalized bulk modulus!

Hence, we conclude that if the conductivity in the interphase zone varies according to an equation such as those given in (5), the normalized effective conductivity, k_{eff}/k_m, will be given by Eqs. (15) and (16), with $(4\mu_m/3K_m) \to 2$ in Eq. (15), and $\{\lambda \to 0, 2\mu, 3K \to k\}$ in Eq. (16). Using this correspondence, the effective conductivity is plotted in Fig. 3, for the case in which the inclusion is five times more conductive than the pure matrix. The parameter D is now defined by $D = (k_m - k_{if})/k_m$. The slight differences between the curves in Figs. 2 and 3 arise solely from the fact that in Fig. 2 the Poisson ratio was taken to be 0.25, whereas Fig. 3 applies to the conductivity problem, and is analogous to the bulk modulus only when $\nu = 0$.

According to the discussion given above, the analogy would hold for *any* radially-symmetric variation of the material properties. Moreover, in any particular material, it seems reasonable to assume that if Eq. (5) provides a good model of the elastic moduli in the interphase zone, the conductivity variations could also be fit with such a power law function, because these property variations would reflect some underlying variation in microporosity or volume fraction. Of course, there would be no reason for *ratios* of the parameters $\{K_m{:}K_i{:}K_{if}\}$ to be precisely the same as the ratios of the conductivity parameters. However, this would not be necessary in order to be able to use the above-derived solution for both properties, with the appropriate numerical values inserted into Eqs. (15) and (16).

The correspondence between the effective bulk modulus and effective conductivity seems to be related to the relationship between the bounds on effective properties discussed by Milton (1984), which involved the assumption that $\lambda \geqslant 0$, which is equivalent to the condition of a non-negative Poisson ratio. As a simple

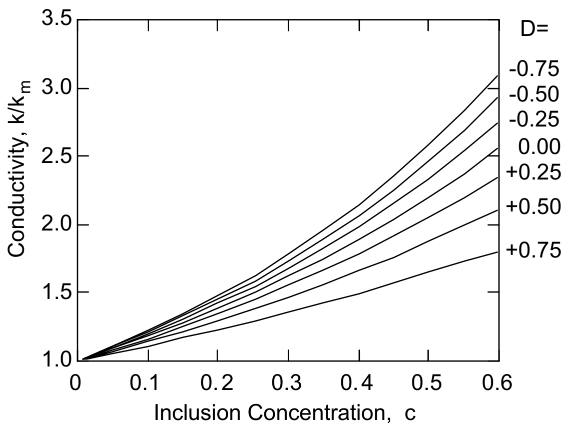

Fig. 3. Effective conductivity of a material containing a volume fraction c of inclusions, each surrounded by an interphase zone whose conductivity is described by an equation of the form of Eq. (5). The inclusions are taken to be five times more conductive than the matrix. In this case the parameter D is defined by $D = (k_m - k_{if})/k_m$.

example, consider the case of spherical inclusions in a homogeneous matrix. For concreteness, assume $K_m > K_i$. When $\lambda_i = \lambda_m = 0$, Eq. (15) reduces to

$$\frac{K_{eff}}{K_m} = \frac{1 - 2[(K_m - K_i)/(K_i + 2K_m)]c}{1 + [(K_m - K_i)/(K_i + 2K_m)]c}, \tag{30}$$

which is the Hashin–Shtrikman upper bound on the bulk modulus, and is also the Hashin–Shtrikman upper bound on the effective conductivity (Christensen, 1979)! Further relationships between effective elastic moduli and effective conductivity are discussed by Kachanov et al. (2001).

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