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Explicit formulas for effective piezoelectric coefficients of ferroelectric 0-3 composites

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Explicit formulas have been found for the effective piezoelectric coefficients of a 0-3 composite of ferroelectric spherical particles in a ferroelectric matrix. Tensile loading and hydrostatic loading conditions were studied. Assuming that both phases are dielectrically and elastically isotropic, explicit expressions in simple closed form for the effective d_{33}, d_{31} and d_h coefficients were derived in terms of the constituents' piezoelectric coefficients and the dielectric and elastic properties of the composite and constituents. Prediction of the piezoelectric coefficients for specific composite systems was compared with experimental values from published works, and good agreement with data was obtained. Goodness of fit is not limited to low volume fraction of inclusions. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1408595]

I. INTRODUCTION

Piezoelectric material possesses the ability to convert mechanical energy to electrical energy or vice versa. Many transducers, filters and resonators made of piezoelectric materials have been widely used in sonic and ultrasonic applications, electronic instrumentation, biomedical applications, etc. However, most piezoelectric ceramic materials are brittle and may exhibit brittle fracture or unexpected malfunction under mechanical stresses or electric fields. In addition, modern applications desire diverse properties of materials which often cannot be obtained in single phase materials. Piezoelectric composites have therefore attracted strong interest for various device applications, especially biphasic composites where both constituents are ferroelectric, usually involving a piezoelectric ceramic and a vinylidene-trifluoroethylene copolymer.

The piezoelectric properties of ferroelectric 0-3 composites have been studied by many workers theoretically and experimentally. The works of Yamada, Ueda, and Kitayama,[1] Furukawa *et al.*[2,3] and Jayasundere, Smith, and Dunn[4] are examples which give explicit expressions for the effective piezoelectric coefficients of 0-3 composites. However, the result of Yamada *et al.* and co-workers does not seem to be complete since the elastic properties of the constituents are absent from their formulas. They also assume that the piezoelectric particles are ellipsoidal with their long axes perpendicular to the surface of the composite film. In the works of Furukawa *et al.*, the matrix and inclusion particles are taken as incompressible. Also the stress condition under which the piezoelectric formulas are derived is not specified. One is therefore not completely certain that, e.g., their d coefficient formula is meant for d_{33} or d_{31}, or some other d. A similar remark applies to Jayasundere's model. On the other hand, Dunn and Taya[5] and Jiang, Fang, and Hwang[6] have used more rigorous but quite complicated approaches. Complicated formulas for the effective piezoelectric coefficients are obtained and difficult numerical computation schemes must invariably be employed to get predictions of composite properties. In contrast, we aim to obtain simple explicit expressions for some effective piezoelectric coefficients of biphasic ferroelectric 0-3 composites.

Assuming inclusion particles are spherical and that both phases are dielectrically and elastically isotropic, explicit expressions for the effective d_{33}, d_{31} and d_h coefficients have been derived in a previous article[7] for ferroelectric 0-3 composites in the dilute suspension limit. In this article, the dilute suspension results are first reviewed and then generalized to cover the case of nondilute suspension. It is shown that these results compare quite well with several sets of experimental data from published works.

II. THEORY

To find the effective piezoelectric d coefficients of a 0-3 composite, we start from the solution of electro-elasticity equations and boundary conditions of a single inclusion problem.

A. Single inclusion problem

As an approximation, we assume that the equations for mechanical equilibrium are not disrupted by the applied or

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stress-generated electric fields, and hence the stress distribution can be worked out solely from elasticity theory.

Consider an elastic spherical inclusion situated at the origin of coordinates and embedded in an infinitely large matrix. Assume that both inclusion and matrix materials are elastically isotropic and homogeneous, and this assumption is taken to be still valid even when the constituents are polarized. Let there be a uniform tension T acting in the Z direction in the matrix far away from the inclusion. The problem of finding the stress components in the matrix and inclusion is already solved in spherical coordinates by Goodier[8] (summarized in Appendix A).

The volumetric averaging of stresses is defined by

$$\langle \sigma_{kl} \rangle = \frac{1}{V} \int_V \sigma_{kl} dV, \tag{1}$$

where subscripts $k,l = x,y,z$ refer to the three directions and V is volume. The $\langle \sigma_{kli} \rangle$ and $\langle \sigma_{klm} \rangle$ will be used to denote the average over the inclusion volume and the matrix, respectively; in the latter case, the integration is taken over a spherical region from $r=a$ to $r=R$, where a is the inclusion radius and $R>a$. After transforming Goodier's solution to Cartesian coordinates, the volumetric average of each Cartesian stress component is then found for both inclusion and matrix. The nonvanishing components are $\langle \sigma^Z_{xxi} \rangle$, $\langle \sigma^Z_{yyi} \rangle$, $\langle \sigma^Z_{zzi} \rangle$ and $\langle \sigma^Z_{zzm} \rangle$, and obey the following relationships:

$$\begin{cases} \langle \sigma^Z_{xxi} \rangle = \langle \sigma^Z_{yyi} \rangle = (I-J) \langle \sigma^Z_{zzm} \rangle \\ \langle \sigma^Z_{zzi} \rangle = (I+2J) \langle \sigma^Z_{zzm} \rangle \end{cases}, \tag{2}$$

where the superscript Z denotes the direction of the asymptotic uniform tension in the matrix, and

$$I = \frac{1-\upsilon_m}{1+\upsilon_m} \frac{(1+\upsilon_i)\mu_i}{2(1-2\upsilon_i)\mu_m + (1+\upsilon_i)\mu_i}, \tag{3}$$

$$J = \frac{5(1-\upsilon_m)\mu_i}{(7-5\upsilon_m)\mu_m + 2(4-5\upsilon_m)\mu_i}, \tag{4}$$

where μ and ν denote the shear modulus and Poisson's ratio, respectively.

Similarly, for asymptotic uniform tensions in the X and the Y directions

$$\begin{cases} \langle \sigma^X_{yyi} \rangle = \langle \sigma^X_{zzi} \rangle = (I-J) \langle \sigma^X_{xxm} \rangle \\ \langle \sigma^X_{xxi} \rangle = (I+2J) \langle \sigma^X_{xxm} \rangle \end{cases}, \tag{5}$$

$$\begin{cases} \langle \sigma^Y_{xxi} \rangle = \langle \sigma^Y_{zzi} \rangle = (I-J) \langle \sigma^Y_{yym} \rangle \\ \langle \sigma^Y_{yyi} \rangle = (I+2J) \langle \sigma^Y_{yym} \rangle \end{cases}. \tag{6}$$

Now consider a dielectric sphere surrounded by the matrix medium of permittivity ϵ_m, with a uniform electric field applied along the Z direction far away from the inclusion (i.e., the "3" direction). The boundary value problem gives the following equation (Appendix B):

$$\langle D_{3i} \rangle + 2\epsilon_m (\langle E_{3i} \rangle - \langle E_{3m} \rangle) = \langle D_{3m} \rangle. \tag{7}$$

The derivation assumes that the electric displacement D varies linearly as the electric field E. This is valid for small electric field.

B. Composite problem and effective piezoelectric properties

The results of the single inclusion problem are now extended to a composite with a dilute suspension of inclusion particles and then the effective piezoelectric coefficients are solved in terms of the dielectric, elastic and piezoelectric properties of its constituents.

Suppose the composite is subjected to tensile stresses in the X, Y and Z directions simultaneously, and the average electric field acts only in the Z direction, in which case we only need to concern ourselves with the volumetric averages of the electric field and electric displacement in the 3 direction. The following equations can be written for dilute suspension of inclusion particles:[2]

$$\begin{cases} \langle \sigma_{xx} \rangle = \phi \{ \langle \sigma^X_{xxi} \rangle + \langle \sigma^Y_{xxi} \rangle + \langle \sigma^Z_{xxi} \rangle \} + (1-\phi) \langle \sigma^X_{xxm} \rangle \\ \langle \sigma_{yy} \rangle = \phi \{ \langle \sigma^X_{yyi} \rangle + \langle \sigma^Y_{yyi} \rangle + \langle \sigma^Z_{yyi} \rangle \} + (1-\phi) \langle \sigma^Y_{yym} \rangle \\ \langle \sigma_{zz} \rangle = \phi \{ \langle \sigma^X_{zzi} \rangle + \langle \sigma^Y_{zzi} \rangle + \langle \sigma^Z_{zzi} \rangle \} + (1-\phi) \langle \sigma^Z_{zzm} \rangle \\ \langle D_3 \rangle = \phi \langle D_{3i} \rangle + (1-\phi) \langle D_{3m} \rangle \\ \langle E_3 \rangle = \phi \langle E_{3i} \rangle + (1-\phi) \langle E_{3m} \rangle \end{cases}, \tag{8}$$

where $\langle \sigma_{xx} \rangle$, $\langle \sigma_{yy} \rangle$ and $\langle \sigma_{zz} \rangle$ are the volume-averaged stresses in the composite and ϕ is the volume fraction of the inclusion phase.

The constitutive equation for a linear dielectric with piezoelectric effect is, in our case

$$D_3 = \epsilon E_3 + d_{3kl} \sigma_{kl}, \tag{9}$$

where d_{3kl} are the piezoelectric coefficients. Thus the volume-averaged electric displacement in the inclusion phase is

$$\begin{aligned} \langle D_{3i} \rangle = {} & \epsilon_i \langle E_{3i} \rangle + d_{31i} (\langle \sigma^X_{xxi} \rangle + \langle \sigma^Y_{xxi} \rangle + \langle \sigma^Z_{xxi} \rangle) \\ & + d_{32i} (\langle \sigma^X_{yyi} \rangle + \langle \sigma^Y_{yyi} \rangle + \langle \sigma^Z_{yi} \rangle) + d_{33i} (\langle \sigma^X_{zzi} \rangle \\ & + \langle \sigma^Y_{zzi} \rangle + \langle \sigma^Z_{zzi} \rangle) \end{aligned} \tag{10}$$

and the electric displacement in the matrix phase is

$$\begin{aligned} \langle D_{3m} \rangle = {} & \epsilon_m \langle E_{3m} \rangle + d_{31m} \langle \sigma^X_{xxm} \rangle + d_{32m} \langle \sigma^Y_{yym} \rangle \\ & + d_{33m} \langle \sigma^Z_{zzm} \rangle. \end{aligned} \tag{11}$$

We assume that both constituents are piezoelectrically transversely isotropic and that their polar axes are aligned in the 3 direction. That means $d_{31} = d_{32}$ for both inclusion and matrix. The next step is then to solve for $\langle D_3 \rangle$ in terms of $\langle E_3 \rangle$, $\langle \sigma_{xx} \rangle$, $\langle \sigma_{yy} \rangle$ and $\langle \sigma_{zz} \rangle$, using Eqs. (2)–(8), (10) and (11). The result is, after some manipulation

$$\langle D_3 \rangle = \epsilon \langle E_3 \rangle + d_{31} \langle \sigma_{xx} \rangle + d_{32} \langle \sigma_{yy} \rangle + d_{33} \langle \sigma_{zz} \rangle, \tag{12}$$

where

$$\epsilon = \frac{\epsilon_i + 2\epsilon_m + 2\phi(\epsilon_i - \epsilon_m)}{\epsilon_i + 2\epsilon_m - \phi(\epsilon_i - \epsilon_m)} \epsilon_m, \tag{13}$$

$$\begin{aligned} d_{31} = d_{32} = {} & \phi L_E \{ (L^\perp_T + L^\parallel_T) d_{31i} + L^\perp_T d_{33i} \} + (1 \\ & - \phi) \overline{L_E} \{ (\overline{L^\perp_T} + \overline{L^\parallel_T}) d_{31m} + \overline{L^\perp_T} d_{33m} \}, \end{aligned} \tag{14}$$

$$d_{33}=\phi L_E\{2L_T^{\perp}d_{31i}+L_T^{\parallel}d_{33i}\}+(1-\phi)\overline{L}_E\{2\overline{L}_T^{\perp}d_{31m}+\overline{L}_T^{\parallel}d_{33m}\} \tag{15}$$

are the effective permittivity and piezoelectric coefficients of the composite and

$$L_E=\frac{3\epsilon_m}{(1-\phi)\epsilon_i+(2+\phi)\epsilon_m}, \tag{16}$$

$$\overline{L}_E=\frac{1-\phi L_E}{1-\phi}, \tag{17}$$

$$L_T^{\perp}=\frac{I}{1-\phi(1-3I)}-\frac{J}{1-\phi(1-3J)}, \tag{18}$$

$$L_T^{\parallel}=\frac{I}{1-\phi(1-3I)}+\frac{2J}{1-\phi(1-3J)}, \tag{19}$$

$$\overline{L}_T^{\perp}=\frac{-\phi L_T^{\perp}}{1-\phi}, \tag{20}$$

$$\overline{L}_T^{\parallel}=\frac{1-\phi L_T^{\parallel}}{1-\phi}. \tag{21}$$

The effective hydrostatic piezoelectric d_h coefficient (defined by $d_h=d_{33}+2d_{31}$, and similarly for inclusion and matrix) is derived by setting $\langle\sigma_{xx}\rangle=\langle\sigma_{yy}\rangle=\langle\sigma_{zz}\rangle$ in Eq. (12), thus

$$d_h=\phi L_E L_T^h d_{\mathrm{hi}}+(1-\phi)\overline{L}_E\overline{L}_T^h d_{\mathrm{hm}}, \tag{22}$$

where

$$L_T^h=2L_T^{\perp}+L_T^{\parallel}, \tag{23}$$

$$\overline{L}_T^h=2\overline{L}_T^{\perp}+\overline{L}_T^{\parallel}=\frac{1-\phi L_T^h}{1-\phi} \tag{24}$$

or

$$L_T^h=\frac{(3k_m+4\mu_m)k_i}{(3k_m+4\mu_m\phi)k_i+4(1-\phi)\mu_m k_m}, \tag{25}$$

$$\overline{L}_T^h=\frac{(3k_i+4\mu_m)k_m}{(3k_m+4\mu_m\phi)k_i+4(1-\phi)\mu_m k_m}, \tag{26}$$

where k_i and k_m are bulk moduli for inclusion and matrix, respectively.

Equations (13)–(26) are the results based on the foregoing calculation for the dilute suspension regime. The main results are equations for the effective piezoelectric d coefficients given in Eqs. (14), (15) and (22). Note that Eq. (13) is identical to the well-known Maxwell–Wagner formula[9] which is adopted by Furukawa, Fujino, and Fukada in Ref. 2. In the following section, we will show that the L_E's and L_T's [Eqs. (16), (18), (19), (25) and (26)] are electric and stress field factors, respectively. They essentially represent the fractions of applied field distributed to the constituents. This interpretation allows an extension of the main results to higher volume fraction of inclusion.

C. Effective piezoelectric coefficients for concentrated suspension

To generalize the results of the dilute suspension case, the elastic part and the electrostatic part are separately re-expressed in terms of the effective dielectric and elastic properties. Let F_E's be the electric field factors as defined in Eqs. (27) and (28). They can be expressed in terms of the permittivities of the constituents and the effective permittivity of the composite as follows (Appendix C):

$$F_E\equiv\frac{\langle E_{3i}\rangle}{\langle E\rangle}=\frac{1}{\phi}\,\frac{\epsilon-\epsilon_m}{\epsilon_i-\epsilon_m}, \tag{27}$$

$$\overline{F}_E\equiv\frac{\langle E_{3m}\rangle}{\langle E\rangle}=\frac{1}{1-\phi}\,\frac{\epsilon_i-\epsilon}{\epsilon_i-\epsilon_m}, \tag{28}$$

where $\langle E_{3i}\rangle$, $\langle E_{3m}\rangle$ and $\langle E\rangle$ are volume-averaged electric fields for the inclusion phase, matrix and the composite, respectively. The electric field factor F_E has been given by Furukawa, Fujino, and Fukada.[2]

Similarly, let F_T's be the stress field factors as defined in Eqs. (29)–(34). They can be expressed in terms of the elastic properties of the composite and constituents. The stress field factors associated with the hydrostatic loading condition have been derived as (Appendix C):

$$F_T^h\equiv\frac{\langle\sigma_i\rangle}{\langle\sigma\rangle}=\frac{1}{\phi}\,\frac{\dfrac{1}{k}-\dfrac{1}{k_m}}{\dfrac{1}{k_i}-\dfrac{1}{k_m}}, \tag{29}$$

$$\overline{F}_T^h\equiv\frac{\langle\sigma_m\rangle}{\langle\sigma\rangle}=\frac{1}{1-\phi}\,\frac{\dfrac{1}{k_i}-\dfrac{1}{k}}{\dfrac{1}{k_i}-\dfrac{1}{k_m}}, \tag{30}$$

where $\langle\sigma_i\rangle$, $\langle\sigma_m\rangle$ and $\langle\sigma\rangle$ are volume-averaged hydrostatic stresses for the inclusions, matrix and the composite, respectively. Those associated with tensile loading conditions are

$$F_T^{\perp}\equiv\frac{\langle\sigma_{xxi}\rangle}{\langle\sigma_{zz}\rangle}=\frac{1}{\phi}\,\frac{\left(\dfrac{\nu_i}{Y_i}-\dfrac{\nu_m}{Y_m}\right)\left(\dfrac{1}{Y}-\dfrac{1}{Y_m}\right)-\left(\dfrac{1}{Y_i}-\dfrac{1}{Y_m}\right)\left(\dfrac{\nu}{Y}-\dfrac{\nu_m}{Y_m}\right)}{\left(\dfrac{1}{Y_i}-\dfrac{1}{Y_m}\right)\left(\dfrac{1-\nu_i}{Y_i}-\dfrac{1-\nu_m}{Y_m}\right)-2\left(\dfrac{\nu_i}{Y_i}-\dfrac{\nu_m}{Y_m}\right)^2}, \tag{31}$$

$$F_T^{\parallel}\equiv\frac{\langle\sigma_{zzi}\rangle}{\langle\sigma_{zz}\rangle}=\frac{1}{\phi}\frac{\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)\left(\frac{1}{Y}-\frac{1}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\left(\frac{\nu}{Y}-\frac{\nu_m}{Y_m}\right)}{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)^2}, \tag{32}$$

$$\overline{F}_T^{\perp}\equiv\frac{\langle\sigma_{xxm}\rangle}{\langle\sigma_{zz}\rangle}=\frac{1}{1-\phi}\frac{\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\left(\frac{1}{Y_i}-\frac{1}{Y}\right)-\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{\nu_i}{Y_i}-\frac{\nu}{Y}\right)}{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)^2}, \tag{33}$$

$$\overline{F}_T^{\parallel}\equiv\frac{\langle\sigma_{zzm}\rangle}{\langle\sigma_{zz}\rangle}=\frac{1}{1-\phi}\frac{\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)\left(\frac{1}{Y_i}-\frac{1}{Y}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\left(\frac{\nu_i}{Y_i}-\frac{\nu}{Y}\right)}{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)^2}. \tag{34}$$

Y and ν refer to Young's modulus and Poisson's ratio, respectively.

For low volume fraction ϕ, the effective permittivity is given by Eq. (13). Formulas for the effective bulk modulus k and effective shear modulus μ under the dilute limit are (see Appendix D):

$$k=k_m+\frac{\phi(k_i-k_m)}{1+(1-\phi)\frac{k_i-k_m}{k_m+\frac{4}{3}\mu_m}}, \tag{35}$$

$$\mu=\mu_m\left\{1+\frac{15(1-\nu_m)\left(\frac{\mu_i}{\mu_m}-1\right)\phi}{7-5\nu_m+2(4-5\nu_m)\left[\frac{\mu_i}{\mu_m}-\left(\frac{\mu_i}{\mu_m}-1\right)\phi\right]}\right\}. \tag{36}$$

These equations are also reported by Hashin.[10] Substituting Eqs. (13), (35) and (36) into Eqs. (27)–(32) and using the relations

$$Y=2\mu(1+\nu), \tag{37}$$

$$Y=\frac{9k\mu}{3k+\mu}, \tag{38}$$

one can obtain Eqs. (16), (18), (19), (25) and (26) in the previous section. Therefore, the F_E's are identical to L_E's and F_T's to L_T's under dilute conditions. In general, Eqs. (14), (15) and (22) may be rewritten as

$$d_{31}=d_{32}=\phi F_E\{(F_T^{\perp}+F_T^{\parallel})d_{31i}+F_T^{\perp}d_{33i}\}+(1-\phi)\overline{F}_E\{(\overline{F}_T^{\perp}+\overline{F}_T^{\parallel})d_{31m}+\overline{F}_T^{\perp}d_{33m}\}, \tag{39}$$

$$d_{33}=\phi F_E\{2F_T^{\perp}d_{31i}+F_T^{\parallel}d_{33i}\}+(1-\phi)\overline{F}_E\{2\overline{F}_T^{\perp}d_{31m}+\overline{F}_T^{\parallel}d_{33m}\}, \tag{40}$$

$$d_h=\phi F_E F_T^h d_{\rm hi}+(1-\phi)\overline{F}_E\overline{F}_T^h d_{\rm hm}, \tag{41}$$

where the F_E's and F_T's are given by Eqs. (27)–(34), and it is noted that

$$\begin{cases}\phi F_E+(1-\phi)\overline{F}_E=1\\ \phi F_T^{\perp}+(1-\phi)\overline{F}_T^{\perp}=0\\ \phi F_T^{\parallel}+(1-\phi)\overline{F}_T^{\parallel}=1\\ \phi F_T^h+(1-\phi)\overline{F}_T^h=1\end{cases}. \tag{42}$$

For higher volume concentration ϕ, the Bruggeman formula[11]

$$\frac{\epsilon_i-\epsilon}{\epsilon_i-\epsilon_m}=(1-\phi)\left(\frac{\epsilon}{\epsilon_m}\right)^{1/3} \tag{43}$$

may be used to replace the Maxwell–Wagner formula. It is a well-known formula in the literature and has been demonstrated to agree well (up to $\phi\approx0.5$ or 0.6) with measured effective permittivities of many 0–3 ceramic/polymer composite systems that are investigated for their piezoelectric and pyroelectric activities.[12–14] For the effective bulk modulus k, the explicit bounds found by Hashin[10] can be used. There it has been found that the lower bound and upper bound coincide for the effective bulk modulus, and Eq. (35) gives a good approximation for a composite with spherical inclusions. For the effective shear modulus μ, explicit bounds have been given by Hashin[10] and Hashin and Shtrikman[15] for the cases of spherical inclusion and arbitrary phase geometry, respectively. Following Christensen,[16] the lower bound μ_l given by Hashin and Shtrikman[15] for arbitrary phase geometry [which is the same as Eq. (36)] is adopted in our prediction for higher volume fraction ϕ

$$\mu_l=\mu_m\left\{1+\frac{15(1-\nu_m)\left(\frac{\mu_i}{\mu_m}-1\right)\phi}{7-5\nu_m+2(4-5\nu_m)\left[\frac{\mu_i}{\mu_m}-\left(\frac{\mu_i}{\mu_m}-1\right)\phi\right]}\right\}, \tag{44}$$

while for the upper bound μ_u, we adopt the upper bound formula for spherical inclusion geometry of Hashin,[10] which may be rewritten as

$$\mu_u=\mu_m\left[1+\left(\frac{\mu_i}{\mu_m}-1\right)\frac{B}{A+BC}\phi\right], \tag{45}$$

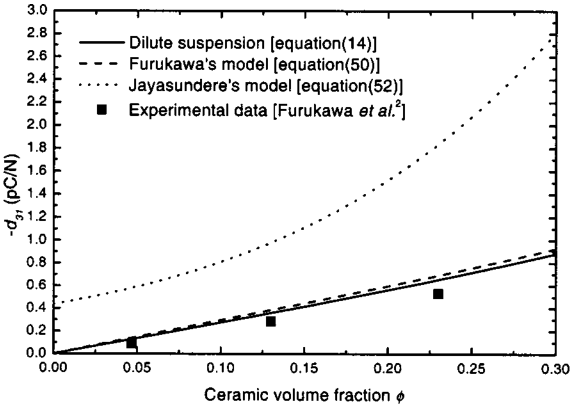

FIG. 1. Comparison with experimental data of Furukawa Fujino, and Fukada (see Ref. 2) for d_{31} of PZT/epoxy composites.

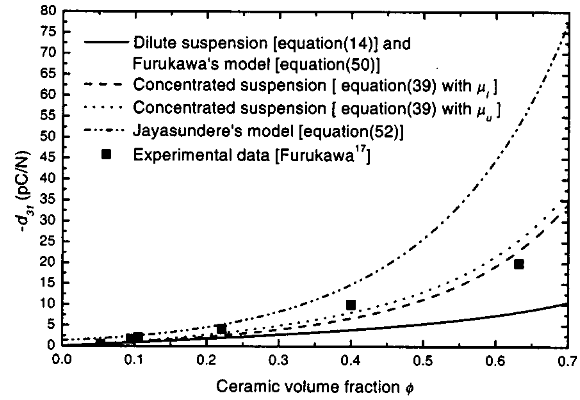

FIG. 2. Comparison with experimental data of Furukawa (see Ref. 17) for d_{31} of PZT/PVDF composites.

where

$$A=\frac{42}{5\mu_m}\frac{\mu_m-\mu_i}{1-\nu_m}\phi(\phi^{2/3}-1)^2\vartheta, \tag{46}$$

$$B=[(7-10\nu_i)-(7-10\nu_m)\vartheta]4\phi^{7/3}+4(7-10\nu_m)\vartheta, \tag{47}$$

$$C=\frac{\mu_i}{\mu_m}+\frac{7-5\nu_m}{15(1-\nu_m)}\left(1-\frac{\mu_i}{\mu_m}\right)+\frac{2(4-5\nu_m)}{15(1-\nu_m)}\times\left(1-\frac{\mu_i}{\mu_m}\right)\phi, \tag{48}$$

$$\vartheta=\frac{(7+5\nu_i)\mu_i+4(7-10\nu_i)\mu_m}{35(1-\nu_m)\mu_m}. \tag{49}$$

In summary, Eqs. (14), (15) and (22) are used for prediction of effective piezoelectric coefficients d_{31}, d_{33} and d_h, respectively, in the dilute suspension limit, with L_E's and L_T's given by Eqs. (16)–(21) and (23)–(26). For higher ceramic volume fractions, Eqs. (39), (40) and (41) are used accordingly for d_{31}, d_{33} and d_h. Electric field factors F_E's are given by Eqs. (27) and (28) with the effective permittivity ϵ given by Eq. (43). Moreover, stress field factors F_T's are given by Eqs. (29)–(34) with the effective bulk modulus k and the effective shear modulus μ (bounded by μ_l and μ_u) given by Eq. (35) and Eqs. (44) and (45), respectively. Equations (37) and (38) may be used to transform between the elastic constants.

III. COMPARISON WITH EXPERIMENTAL DATA

The theoretical predictions for both dilute and concentrated suspensions are compared with experimental data of Furukawa, Fujino and Fukada[2,17] (Figs. 1 and 2), Chan, Chen, and Choy[18] (Fig. 3) and Zou *et al.*[19] (Figs. 4 and 5) for d_{31} of PZT/epoxy composites, d_{31} of PZT/PVDF composites, d_{33} of PZT-P(VDF/TrFE) composites and d_{33}, d_h of $PbTiO_3$-P(VDF/TeFE) composites, respectively. Here, PZT and PVDF denote lead zirconate titanate and polyvinylidene flouride, respectively. Elastic, dielectric and piezoelectric properties of the constituents of these 0–3 composites are listed in Table I.

Figures 1 and 2 give comparisons of experimental data of Furukawa *et al.* with our theory. In addition, the models of Furukawa[2,3] and Jayasundere[4] are also included for comparison. Furukawa's model is

$$d=\phi L_E L_T d_i+\frac{1}{1-\phi}(1-\phi L_E)(1-\phi L_T)d_m \tag{50}$$

with L_E the same as Eq. (16) and

$$L_T=\frac{5c_i}{3c_m+2c_i-3\phi(c_m-c_i)}, \tag{51}$$

where c_i and c_m are the elastic constants (Young's moduli or shear moduli, since the constituents are assumed to be incompressible) for the inclusion and matrix, respectively; and Jayasundere's model is

$$d=d_i\frac{\epsilon}{\epsilon_i}\left(1+\frac{3\phi\epsilon_i}{2\epsilon_m+\epsilon_i}\right), \tag{52}$$

where the effective permittivity ϵ is given by[20]

$$\epsilon=\frac{\epsilon_m(1-\phi)+\epsilon_i\phi[3\epsilon_m/(\epsilon_i+2\epsilon_m)][1+3\phi(\epsilon_i-\epsilon_m)/(\epsilon_i+2\epsilon_m)]}{(1-\phi)+\phi(3\epsilon_m)/(\epsilon_i+2\epsilon_m)[1+3\phi(\epsilon_i-\epsilon_m)/(\epsilon_i+2\epsilon_m)]}. \tag{53}$$

TABLE I. Properties of constituents adopted in our computations for the composites shown in Figs. 1–5. Y_i and Y_m are Young's moduli for the inclusion and matrix, respectively.

Fig.	ϵ_i	ϵ_m	Y_i (GPa)	Y_m (GPa)	ν_i	ν_m	$-d_{31i}$ (pC/N)	d_{31m} (pC/N)	d_{33i} (pC/N)	$-d_{33m}$ (pC/N)
1	1700[a]	4.2[a]	36[a]	1.8[a]	0.3	0.35	177[a]	⋯	400	⋯
2	1900[b]	14[b]	58.7	2.52	0.3	0.4	180[b]	⋯	450	⋯
3	1159[c]	10.7[c]	16.8	2.32	0.35	0.39	127.9[d]	15.3[d]	314.4[c]	38.4[c]
4, 5	150[e]	6[e]	126.7	2.81	0.22	0.4	9.5	⋯	94	⋯

[a]Reference 2.
[b]Reference 17.
[c]Reference 18.
[d]Y. Chen, M. Phil. thesis, The Hong Kong Polytechnic University, 1995.
[e]Reference 19.

Experimental results of the d_{31} of the PZT/epoxy system given by Furukawa and co-workers[2] concern only low ceramic volume fractions, so we have used our dilute suspension formulas for the prediction. The comparison shows that our theory is slightly closer to the experimental data than Furukawa's model. In Furukawa's model, it was assumed that both constituents were incompressible. Nevertheless, our stress field factors L_T for the dilute limit [Eqs. (18) and (19)] cannot be reduced to that of Furukawa's [Eq. (51)] by substituting $v_i = v_m = 0.5$. It is worth noting that the expression for the effective d constant given by Furukawa *et al.*[2,3] [Equation (50)] has the same form as our d_h expression

$$d_h = \phi L_E L_T^h d_{\mathrm{hi}} + \frac{1}{1-\phi}(1-\phi L_E)(1-\phi L_T^h) d_{\mathrm{hm}}, \qquad (54)$$

but not our d_{31} expression

$$d_{31} = \phi L_E\{(L_T^{\perp} + L_T^{\parallel}) d_{31i} + L_T^{\perp} d_{33i}\} + \frac{1-\phi L_E}{1-\phi}\{[1 - \phi(L_T^{\perp} + L_T^{\parallel})] d_{31m} - \phi L_T^{\perp} d_{33m}\}, \qquad (55)$$

while their expressions have been used to predict the effective d_{31} constant. On the other hand, Jayasundere's model does not seem to give good agreement with Furukawa's experimental data, and it does not approach the correct limits at the two extremes. The PZT/PVDF system is another system given by Furukawa.[17] This work reported experimental d_{31} values of PZT/PVDF composites up to 63% ceramic volume fraction. Therefore, we have included both our dilute suspension and the concentrated suspension formulas for comparison. Furukawa's model, shown to be overlapping with our predicted line of dilute suspension in Fig. 2, is only suited for low volume fraction and we therefore would not expect it can predict experimental data at higher volume fractions. This remark also applies to our dilute suspension formulas. However, Jayasundere's model was claimed to work for higher volume fraction of inclusions. It seems that it fails to predict this system at this volume fraction range. Our concentrated suspension formulas look better at higher volume fractions. Concerning the low volume fraction region, Jayasundere's model gives higher $-d_{31}$ values than the experimental results while both Furukawa's model and our model give slightly lower values.

Figure 3 shows the d_{33} experimental data of PZT-P(VDF/TrFE) of Chan, Chen, and Choy.[18] Our prediction shows good agreement with the experimental data in the sense that most data points fall within our predicted lines, especially for the low ceramic volume fraction region. Since both Furukawa's model and Jayasundere's model are thought to describe d_{31} coefficients, we have not included those predictions in this figure. In addition, Jayasundere's model only applies to composites with a single electro-active phase and is therefore not included.

Figures 4 and 5 compare our theory with experimental values of d_{33} and d_h, respectively, of $PbTiO_3$-P(VDF/TeFE) by Zou *et al.*[19] Both figures show that our predictions are in good agreement with experimental values. As experimental data given for this system are restricted to high ceramic volume fractions only, it is not surprising that the dilute suspension predictions fail with both sets of data.

IV. CONCLUSIONS

The effective piezoelectric coefficients d_{33}, d_{31} and d_h for ferroelectric 0–3 composites have been derived in terms of the dielectric, elastic and piezoelectric properties of the constituents for dilute suspension of spherical inclusion particles. To generalize the results for higher volume fractions, all field factors were re-expressed to include the effective dielectric and elastic properties of the composite, which were then evaluated by the Bruggeman formula and Hashin bounds. As the effect of interaction between the randomly

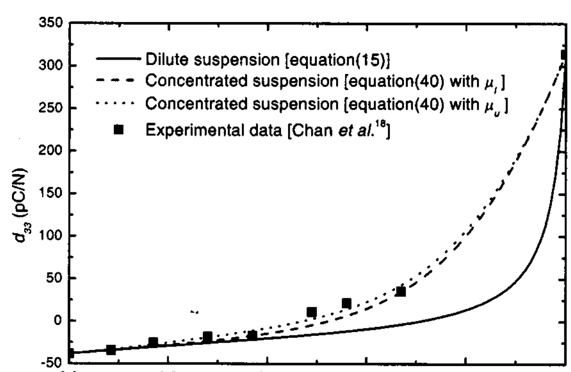

FIG. 3. Comparison with experimental data of Chan, Chen, and Choy (see Ref. 18) for d_{33} of PZT-P(VDF/TrFE) composites.

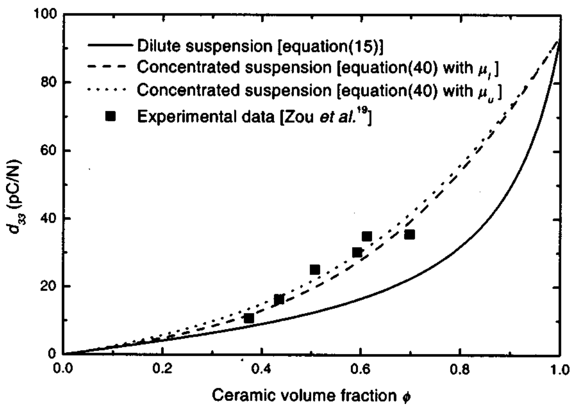

FIG. 4. Comparison with experimental data of Zou *et al.* (see Ref. 19) for d_{33} of $PbTiO_3$-P(VDF/TeFE) composites.

dispersed spherical particles has been to a certain extent implicitly considered in the latter formulas, the final results are expected to be applicable to higher volume fractions of inclusions. Comparison with published experimental data indicates that good agreement has been achieved for various sets of data.

ACKNOWLEDGMENT

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APPENDIX A

A single inclusion is embedded in an infinite matrix medium. A uniform tension T acts in the matrix far away from the inclusion. The stress components expressed in spherical coordinates are given by[8]

$$\sigma_{rri}=2\mu_i T\left\{\frac{1+\upsilon_i}{1-2\upsilon_i}A_3+A_1-\upsilon_i A_2 r^2+[3A_1-3\upsilon_i A_2 r^2]\cos 2\theta\right\}, \tag{A1}$$

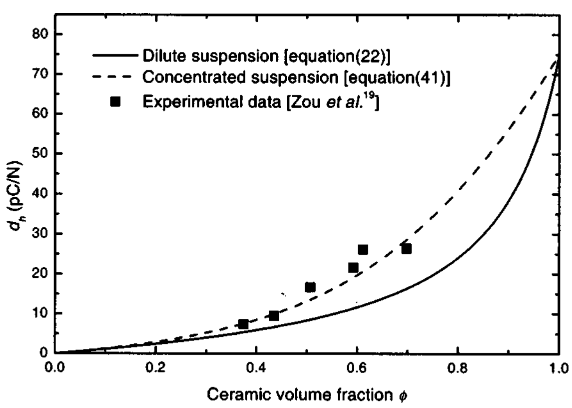

FIG. 5. Comparison with experimental data of Zou *et al.* (see Ref. 19) for d_h of $PbTiO_3$-P(VDF/TeFE) composites.

$$\sigma_{\theta\theta i}=2\mu_i T\left\{\frac{1+\nu_i}{1-2\nu_i}A_3+A_1-5\upsilon_i A_2 r^2-[3A_1+7(2-\upsilon_i)A_2 r^2]\cos 2\theta\right\}, \tag{A2}$$

$$\sigma_{\phi\phi i}=2\mu_i T\left\{\frac{1+\upsilon_i}{1-2\upsilon_i}A-2A_1-(15-7\upsilon_i)A_2 r^2-(7+11\upsilon_i)A_2 r^2\cos 2\theta\right\}, \tag{A3}$$

$$\sigma_{r\theta i}=-2\mu_i T\{3A_1+(7+2\upsilon_i)A_2 r^2\}\sin 2\theta, \tag{A4}$$

$$\sigma_{r\phi i}=\sigma_{\theta\phi i}=0, \tag{A5}$$

$$\sigma_{rrm}=2\mu_m T\left\{\frac{2B_1}{r^3}-\frac{2\upsilon_m}{1-2\upsilon_m}\frac{B_3}{r^3}+\frac{12B_2}{r^5}+\left[-\frac{2(5-\upsilon_m)}{1-2\upsilon_m}\frac{B_3}{r^3}+\frac{36B_2}{r^5}\right]\cos 2\theta\right\}+\frac{T}{2}(1+\cos 2\theta), \tag{A6}$$

$$\sigma_{\theta\theta m}=2\mu_m T\left\{-\frac{B_1}{r^3}-\frac{2\upsilon_m}{1-2\upsilon_m}\frac{B_3}{r^3}-\frac{3B_2}{r^5}+\left[\frac{B_3}{r^3}-\frac{21B_2}{r^5}\right]\cos 2\theta\right\}+\frac{T}{2}(1-\cos 2\theta), \tag{A7}$$

$$\sigma_{\phi\phi m}=2\mu_m T\left\{-\frac{B_1}{r^3}-\frac{2(1-\upsilon_m)}{1-2\upsilon_m}\frac{B_3}{r^3}-\frac{9B_2}{r^5}+\left[\frac{3B_3}{r^3}-\frac{15B_2}{r^5}\right]\cos 2\theta\right\}, \tag{A8}$$

$$\sigma_{r\theta m}=2\mu_m T\left\{-\frac{2(1+\upsilon_m)}{1-2\upsilon_m}\frac{B_3}{r^3}+\frac{24B_2}{r^5}-\frac{1}{2}\right\}\sin 2\theta, \tag{A9}$$

$$\sigma_{r\phi m}=\sigma_{\theta\phi m}=0, \tag{A10}$$

where $A_1, A_2, A_3, B_1, B_2, B_3$ are constants

$$A_1=\frac{1}{4}\frac{5(1-\upsilon_m)}{(7-5\upsilon_m)\mu_m+2(4-5\upsilon_m)\mu_i}, \tag{A11}$$

$$A_2=0, \tag{A12}$$

$$A_3=\frac{1}{2}\frac{1-\upsilon_m}{1+\upsilon_m}\frac{1-2\upsilon_i}{2(1-2\upsilon_i)\mu_m+(1+\upsilon_i)\mu_i}, \tag{A13}$$

$$\frac{B_1}{a^3}=-\frac{1}{8\mu_m}\frac{\mu_m-\mu_i}{(7-5\upsilon_m)\mu_m+2(4-5\upsilon_m)\mu_i}\times\frac{2(1-2\upsilon_i)(6-5\upsilon_m)\mu_m(3+19\upsilon_i-20\upsilon_m\upsilon_i)\mu_i}{2(1-2\upsilon_i)\mu_m+(1+\upsilon_i)\mu_i}+\frac{1}{4\mu_m}\frac{\left[(1-\upsilon_m)\frac{1+\upsilon_i}{1+\upsilon_m}-\upsilon_i\right]\mu_i-(1-2\upsilon_i)\mu_m}{2(1-2\upsilon_i)\mu_m+(1+\upsilon_i)\mu_i}, \tag{A14}$$

$$\frac{B_2}{a^5}=\frac{1}{8\mu_m}\frac{\mu_m-\mu_i}{(7-5\upsilon_m)\mu_m+2(4-5\upsilon_m)\mu_i}, \quad \text{(A15)}$$

$$\frac{B_3}{a^3}=\frac{1}{8\mu_m}\frac{5(1-2\upsilon_m)(\mu_m-\mu_i)}{(7-5\upsilon_m)\mu_m+2(4-5\upsilon_m)\mu_i}. \quad \text{(A16)}$$

Symbols μ,υ denote shear modulus and Poisson's ratio, respectively. Subscripts i and m are used to distinguish inclusion and matrix materials. In the above, Eqs. (A11)–(A13) are not given in the original reference.[8]

APPENDIX B

Consider a dielectric sphere of radius a with permittivity ϵ_i subjected to a uniform electric field $\langle E_m\rangle$ in the Z direction far away from the sphere. The sphere is surrounded by a medium with permittivity ϵ_m. The problem is to solve Laplace equations with azimuthal symmetry

$$\nabla^2\varphi_i=0, \quad \text{(B1)}$$

$$\nabla^2\varphi_m=0, \quad \text{(B2)}$$

where φ_i and φ_m are the electric potential inside and outside the sphere, respectively.

With the boundary condition that φ_i must not have a singularity at the center of sphere $(r=0)$, and the boundary condition at infinity

$$(\varphi_m)_{r\to\infty}=-\langle E_m\rangle z=-\langle E_m\rangle r\cos\theta. \quad \text{(B3)}$$

Solutions of Eqs. (B1) and (B2) give

$$\varphi_i=\sum_{l=0}^{\infty}A_l r^l P_l(\cos\theta), \quad \text{(B4)}$$

$$\varphi_m=-\langle E_m\rangle r\cos\theta+\sum_{l=0}^{\infty}C_l r^{-(l+1)}P_l(\cos\theta). \quad \text{(B5)}$$

$P_l(\cos\theta)$ are the Legendre polynomials.

The boundary condition of the tangential component of electric field is

$$-\frac{1}{r}\frac{\partial\varphi_i}{\partial\theta}\bigg|_{r=a}=-\frac{1}{r}\frac{\partial\varphi_m}{\partial\theta}\bigg|_{r=a} \quad \text{(B6)}$$

and the boundary condition of the normal component of electric displacement is

$$-\epsilon_i\frac{\partial\varphi_i}{\partial r}+d_{3kl}^{(i)}\langle\sigma_{kl}^{(i)}\rangle\cos\theta\bigg|_{r=a}=-\epsilon_m\frac{\partial\varphi_m}{\partial r}+d_{3kl}^{(m)}\langle\sigma_{kl}^{(m)}\rangle\cos\theta\bigg|_{r=a}. \quad \text{(B7)}$$

The piezoelectric terms $d_{3kl}^{(i)}\langle\sigma_{kl}^{(i)}\rangle$ and $d_{3kl}^{(m)}\langle\sigma_{kl}^{(m)}\rangle$ are the contributions of polarization due to stresses in the inclusion (i) and matrix (m), and subscript $k,l=x,y,z$ refer to the three directions. We assume that they are uniform in each of the spherical inclusion and continuous matrix regions, and may be represented by the average in the respective phases. This assumption makes equations (B1) and (B2) plausible.

Applying the boundary conditions to Eqs. (B4) and (B5)

$$\left[-A_1-\langle E_m\rangle+\frac{C_1}{a^3}\right]a\sin\theta+\sum_{l=2}^{\infty}\left(A_l-\frac{C_l}{a^{2l+1}}\right)\times a^l\frac{\partial P_l(\cos\theta)}{\partial\theta}=0, \quad \text{(B8)}$$

$$\left[\left(\frac{\epsilon_i}{\epsilon_m}\right)A_1+\langle E_m\rangle+2\frac{C_1}{a^3}-\frac{d_{3kl}^{(i)}\langle\sigma_{kl}^{(i)}\rangle-d_{3kl}^{(m)}\langle\sigma_{kl}^{(m)}\rangle}{\epsilon_m}\right]\cos\theta+\sum_{l=2}^{\infty}\left[\left(\frac{\epsilon_i}{\epsilon_m}\right)lA_l+(l+1)\frac{C_l}{a^{2l+1}}\right]a^{l-1}P_l(\cos\theta)=0. \quad \text{(B9)}$$

Equations (B8) and (B9) can be satisfied simultaneously only for $A_l=C_l=0$, therefore, they become

$$A_1-\frac{C_1}{a^3}=-\langle E_m\rangle, \quad \text{(B10)}$$

$$\left(\frac{\epsilon_i}{\epsilon_m}\right)A_1+2\frac{C_1}{a^3}=-\langle E_m\rangle+\frac{d_{3kl}^{(i)}\langle\sigma_{kl}^{(i)}\rangle-d_{3kl}^{(m)}\langle\sigma_{kl}^{(m)}\rangle}{\epsilon_m}. \quad \text{(B11)}$$

Eliminating C_1 from Eqs. (B10) and (B11) and then substituting A_1 into Eq. (B4), the electric field inside the sphere (evaluated from the electric potential) is

$$\langle E_i\rangle=\frac{2\epsilon_m\langle E_m\rangle-d_{3kl}^{(i)}\langle\sigma_{kl}^{(i)}\rangle+(\epsilon_m\langle E_m\rangle+d_{3kl}^{(m)}\langle\sigma_{kl}^{(m)}\rangle)}{\epsilon_i+2\epsilon_m}. \quad \text{(B12)}$$

We can finally rewrite this equation in terms of the electric displacements $\langle D_i\rangle=\epsilon_i\langle E_i\rangle+d_{3kl}^{(i)}\langle\sigma_{kl}^{(i)}\rangle$ and $\langle D_m\rangle=\epsilon_m\langle E_m\rangle+d_{3kl}^{(m)}\langle\sigma_{kl}^{(m)}\rangle$ to obtain

$$\langle D_i\rangle+2\epsilon_m(\langle E_i\rangle-\langle E_m\rangle)=\langle D_m\rangle. \quad \text{(B13)}$$

APPENDIX C

1. Derivation of electric field factors F_E and $\bar{F}_E$

Consider the following expression in which $\langle D\rangle$ and $\langle E\rangle$ are volume-averaged electric displacement and volume-averaged electric field, respectively, for the composite

$$\langle D\rangle-\epsilon_m\langle E\rangle=\frac{1}{V}\int_V\{D-\epsilon_m E\}dV=\frac{1}{V}\int_{V_i}\{D-\epsilon_m E\}dV, \quad \text{(C1)}$$

where V, V_i are the volume of the composite and inclusion particles, respectively. Equation (C1) then becomes

$$(\epsilon-\epsilon_m)\langle E\rangle=\phi(\epsilon_i-\epsilon_m)\langle E_i\rangle, \quad \text{(C2)}$$

where ϕ is the volume fraction of the inclusion phase and ϵ is permittivity. From equation (C2),

$$\frac{\langle E_i\rangle}{\langle E\rangle}\equiv F_E=\frac{1}{\phi}\frac{\epsilon-\epsilon_m}{\epsilon_i-\epsilon_m}. \quad \text{(C3)}$$

For the electric field factor $\bar{F}_E$, we follow a similar technique, but this time consider

$$\epsilon_i\langle E\rangle-\langle D\rangle=\frac{1}{V}\int_V\{\epsilon_i E-D\}dV=(1-\phi)(\epsilon_i-\epsilon_m)\times\langle E_m\rangle. \tag{C4}$$

Therefore

$$\frac{\langle E_m\rangle}{\langle E\rangle}\equiv\overline{F}_E=\frac{1}{1-\phi}\,\frac{\epsilon_i-\epsilon}{\epsilon_i-\epsilon_m}. \tag{C5}$$

2. Derivation of stress field factors F_T^h and $\overline{F}_T^h$

The derivation of the stress field factors is similar to the previous case of electric field factors. Consider

$$\langle e\rangle-\frac{\langle\sigma\rangle}{k_m}=\frac{1}{V}\int_V\left\{e-\frac{\sigma}{k_m}\right\}dV=\frac{1}{V}\int_{V_i}\left\{e-\frac{\sigma}{k_m}\right\}dV, \tag{C6}$$

where $\langle\sigma\rangle$ and $\langle e\rangle$ are volume-averaged hydrostatic stress and volume-averaged hydrostatic strain of the composite, respectively, and k is bulk modulus. Equation (C6) then becomes

$$\left(\frac{1}{k}-\frac{1}{k_m}\right)\langle\sigma\rangle=\phi\left(\frac{1}{k_i}-\frac{1}{k_m}\right)\langle\sigma_i\rangle. \tag{C7}$$

Hence,

$$\frac{\langle\sigma_i\rangle}{\langle\sigma\rangle}\equiv F_T^h=\frac{1}{\phi}\,\frac{\frac{1}{k}-\frac{1}{k_i}}{\frac{1}{k_i}-\frac{1}{k_m}}. \tag{C8}$$

The stress field factor $\overline{F}_T^h$ is derived from a similar consideration giving the following expression:

$$\frac{\langle\sigma\rangle}{k_i}-\langle e\rangle=(1-\phi)\left(\frac{1}{k_i}-\frac{1}{k_m}\right)\langle\sigma_m\rangle. \tag{C9}$$

Thus,

$$\frac{\langle\sigma_m\rangle}{\langle\sigma\rangle}\equiv\overline{F}_T^h=\frac{1}{1-\phi}\,\frac{\frac{1}{k_i}-\frac{1}{k}}{\frac{1}{k_i}-\frac{1}{k_m}}. \tag{C10}$$

3. Derivation of stress field factors $F_T^\perp$, $F_T^\parallel$, $\overline{F}_T^\perp$ and $\overline{F}_T^\parallel$

Suppose a composite is subjected to tensile stress of $\langle\sigma_{xx}\rangle$, $\langle\sigma_{yy}\rangle$ and $\langle\sigma_{zz}\rangle$ simultaneously. The stress field factors $F_T^\perp$, $F_T^\parallel$, $\overline{F}_T^\perp$ and $\overline{F}_T^\parallel$ can be derived following the same technique used above

$$\langle e_{zz}\rangle-\left\{\frac{\langle\sigma_{zz}\rangle}{Y_m}-\frac{\nu_m}{Y_m}\langle\sigma_{xx}\rangle-\frac{\nu_m}{Y_m}\langle\sigma_{yy}\rangle\right\}=\frac{1}{V}\int_V\left\{e_{zz}-\frac{\sigma_{zz}}{Y_m}+\frac{\nu_m}{Y_m}\sigma_{xx}+\frac{\nu_m}{Y_m}\sigma_{yy}\right\}dV=\phi\left\{\langle e_{zzi}\rangle-\frac{\langle\sigma_{zzi}\rangle}{Y_m}+\frac{\nu_m}{Y_m}\langle\sigma_{xxi}\rangle+\frac{\nu_m}{Y_m}\langle\sigma_{yyi}\rangle\right\}, \tag{C11}$$

$$\langle e_{xx}\rangle-\left\{\frac{\langle\sigma_{xx}\rangle}{Y_m}-\frac{\nu_m}{Y_m}\langle\sigma_{zz}\rangle-\frac{\nu_m}{Y_m}\langle\sigma_{yy}\rangle\right\}=\phi\left\{\langle e_{xxi}\rangle-\frac{\langle\sigma_{xxi}\rangle}{Y_m}+\frac{\nu_m}{Y_m}\langle\sigma_{zzi}\rangle+\frac{\nu_m}{Y_m}\langle\sigma_{yyi}\rangle\right\}, \tag{C12}$$

where Y and ν are Young's modulus and Poisson's ratio, respectively. Using the relations

$$\langle e_{zz}\rangle=\frac{\langle\sigma_{zz}\rangle}{Y}-\frac{\nu}{Y}\langle\sigma_{xx}\rangle-\frac{\nu}{Y}\langle\sigma_{yy}\rangle, \tag{C13}$$

$$\langle e_{zzi}\rangle=\frac{\langle\sigma_{zzi}\rangle}{Y_i}-\frac{\nu_i}{Y_i}\langle\sigma_{xxi}\rangle-\frac{\nu_i}{Y_i}\langle\sigma_{yyi}\rangle, \tag{C14}$$

$$\langle e_{xx}\rangle=\frac{\langle\sigma_{xx}\rangle}{Y}-\frac{\nu}{Y}\langle\sigma_{zz}\rangle-\frac{\nu}{Y}\langle\sigma_{yy}\rangle, \tag{C15}$$

$$\langle e_{xxi}\rangle=\frac{\langle\sigma_{xxi}\rangle}{Y_i}-\frac{\nu_i}{Y_i}\langle\sigma_{zzi}\rangle-\frac{\nu_i}{Y_i}\langle\sigma_{yyi}\rangle \tag{C16}$$

and considering the case $\langle\sigma_{xx}\rangle=\langle\sigma_{yy}\rangle=0$, equations (C11) and (C12) become

$$\left(\frac{1}{Y}-\frac{1}{Y_m}\right)\langle\sigma_{zz}\rangle=\phi\left\{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\langle\sigma_{zzi}\rangle-\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\times\langle\sigma_{xxi}\rangle-\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\langle\sigma_{yyi}\rangle\right\}. \tag{C17}$$

$$-\left(\frac{\nu}{Y}-\frac{\nu_m}{Y_m}\right)\langle\sigma_{zz}\rangle=\phi\left\{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\langle\sigma_{xxi}\rangle-\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\times\langle\sigma_{zzi}\rangle-\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\langle\sigma_{yyi}\rangle\right\}. \tag{C18}$$

Under this uniaxial tension condition, we may set $\langle\sigma_{xxi}\rangle=\langle\sigma_{yyi}\rangle$, thus

$$\begin{cases}\phi\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\frac{\langle\sigma_{zzi}\rangle}{\langle\sigma_{zz}\rangle}-2\phi\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\frac{\langle\sigma_{xxi}\rangle}{\langle\sigma_{zz}\rangle}=\frac{1}{Y}-\frac{1}{Y_m}\\ \phi\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\frac{\langle\sigma_{zzi}\rangle}{\langle\sigma_{zz}\rangle}-\phi\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)\frac{\langle\sigma_{xxi}\rangle}{\langle\sigma_{zz}\rangle}=\frac{\nu}{Y}-\frac{\nu_m}{Y_m}\end{cases}. \tag{C19}$$

Solving these two equations gives

$$\frac{\langle\sigma_{xxi}\rangle}{\langle\sigma_{zz}\rangle}\equiv F_T^{\perp}=\frac{1}{\phi}\frac{\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\left(\frac{1}{Y}-\frac{1}{Y_m}\right)-\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{\nu}{Y}-\frac{\nu_m}{Y_m}\right)}{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)^2}, \tag{C20}$$

$$\frac{\langle\sigma_{zzi}\rangle}{\langle\sigma_{zz}\rangle}\equiv F_T^{\parallel}=\frac{1}{\phi}\frac{\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)\left(\frac{1}{Y}-\frac{1}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\left(\frac{\nu}{Y}-\frac{\nu_m}{Y_m}\right)}{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)^2}. \tag{C21}$$

For the stress field factors $\overline{F}_T^{\perp}$ and $\overline{F}_T^{\parallel}$, an analogous derivation gives

$$\left\{\frac{\langle\sigma_{zz}\rangle}{Y_i}-\frac{\nu_i}{Y_i}\langle\sigma_{xx}\rangle-\frac{\nu_i}{Y_i}\langle\sigma_{yy}\rangle\right\}-\langle e_{zz}\rangle=(1-\phi)\left\{\frac{\langle\sigma_{zzm}\rangle}{Y_i}+\frac{\nu_i}{Y_i}\langle\sigma_{xxm}\rangle+\frac{\nu_i}{Y_i}\langle\sigma_{yym}\rangle-\langle e_{zzm}\rangle\right\} \tag{C22}$$

and

$$\left\{\frac{\langle\sigma_{xx}\rangle}{Y_i}-\frac{\nu_i}{Y_i}\langle\sigma_{zz}\rangle-\frac{\nu_i}{Y_i}\langle\sigma_{yy}\rangle\right\}-\langle e_{xx}\rangle=(1-\phi)\left\{\frac{\langle\sigma_{xxm}\rangle}{Y_i}-\frac{\nu_i}{Y_i}\langle\sigma_{zzm}\rangle-\frac{\nu_i}{Y_i}\langle\sigma_{yym}\rangle-\langle e_{xxm}\rangle\right\}. \tag{C23}$$

Equation (C13) and the relation

$$\langle e_{zzm}\rangle=\frac{\langle\sigma_{zzm}\rangle}{Y_m}-\frac{\nu_m}{Y_m}\langle\sigma_{xxm}\rangle-\frac{\nu_m}{Y_m}\langle\sigma_{yym}\rangle \tag{C24}$$

are then substituted into Eq. (C22). Also, Eq. (C15) and the relation

$$\langle e_{xxm}\rangle=\frac{\langle\sigma_{xxm}\rangle}{Y_m}-\frac{\nu_m}{Y_m}\langle\sigma_{zzm}\rangle-\frac{\nu_m}{Y_m}\langle\sigma_{yym}\rangle \tag{C25}$$

are substituted into Eq. (C23). When specializing to the condition that $\langle\sigma_{xx}\rangle$ and $\langle\sigma_{yy}\rangle$ vanish, and $\langle\sigma_{xxm}\rangle$ is equal to $\langle\sigma_{yym}\rangle$, we obtain

$$\frac{\langle\sigma_{xxm}\rangle}{\langle\sigma_{zz}\rangle}\equiv \overline{F}_T^{\perp}=\frac{1}{1-\phi}\frac{\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\left(\frac{1}{Y_i}-\frac{1}{Y}\right)-\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{\nu_i}{Y_i}-\frac{\nu}{Y}\right)}{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)^2}, \tag{C26}$$

$$\frac{\langle\sigma_{zzm}\rangle}{\langle\sigma_{zz}\rangle}\equiv \overline{F}_T^{\parallel}=\frac{1}{1-\phi}\frac{\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)\left(\frac{1}{Y_i}-\frac{1}{Y}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)\left(\frac{\nu_i}{Y_i}-\frac{\nu}{Y}\right)}{\left(\frac{1}{Y_i}-\frac{1}{Y_m}\right)\left(\frac{1-\nu_i}{Y_i}-\frac{1-\nu_m}{Y_m}\right)-2\left(\frac{\nu_i}{Y_i}-\frac{\nu_m}{Y_m}\right)^2}. \tag{C27}$$

APPENDIX D

The relations between stresses in the matrix phase and in the composite may be written as follows using Eqs. (2), (5), (6) and the first three equations in Eq. (8)

$$\begin{pmatrix}\langle\sigma_{xxm}^X\rangle\\ \langle\sigma_{yym}^Y\rangle\\ \langle\sigma_{zzm}^Z\rangle\end{pmatrix}=\frac{1}{3}\begin{pmatrix}G^{\parallel} & G^{\perp} & G^{\perp}\\ G^{\perp} & G^{\parallel} & G^{\perp}\\ G^{\perp} & G^{\perp} & G^{\parallel}\end{pmatrix}\begin{pmatrix}\langle\sigma_{xx}\rangle\\ \langle\sigma_{yy}\rangle\\ \langle\sigma_{zz}\rangle\end{pmatrix}, \tag{D1}$$

where

$$G^{\perp}=\frac{1}{1-\phi(1-3I)}-\frac{1}{1-\phi(1-3J)}, \tag{D2}$$

$$G^{\parallel}=\frac{1}{1-\phi(1-3I)}+\frac{2}{1-\phi(1-3J)} \tag{D3}$$

and I, J are given by Eqs. (3) and (4). The superposition of Eqs. (2), (5), and (6) gives

$$\begin{pmatrix}\langle\sigma_{xxi}^X\rangle+\langle\sigma_{xxi}^Y\rangle+\langle\sigma_{xxi}^Z\rangle\\ \langle\sigma_{yyi}^X\rangle+\langle\sigma_{yyi}^Y\rangle+\langle\sigma_{yyi}^Z\rangle\\ \langle\sigma_{zzi}^X\rangle+\langle\sigma_{zzi}^Y\rangle+\langle\sigma_{zzi}^Z\rangle\end{pmatrix}=\begin{pmatrix}I+2J & I-J & I-J\\ I-J & I+2J & I-J\\ I-J & I-J & I+2J\end{pmatrix}\begin{pmatrix}\langle\sigma_{xxm}^X\rangle\\ \langle\sigma_{yym}^Y\rangle\\ \langle\sigma_{zzm}^Z\rangle\end{pmatrix}. \tag{D4}$$

Equation (35) can be obtained by setting $\langle\sigma_{xx}\rangle=\langle\sigma_{yy}\rangle=\langle\sigma_{zz}\rangle\equiv\langle\sigma^k\rangle$. The superscript k is used here to indicate this hydrostatic loading condition. By Eq. (D1), this condition implies $\langle\sigma_{xxm}^X\rangle=\langle\sigma_{yym}^Y\rangle=\langle\sigma_{zzm}^Z\rangle\equiv\langle\sigma_m^k\rangle$ and

$$\langle\sigma_m^k\rangle=\frac{2G^{\perp}+G^{\parallel}}{3}\langle\sigma^k\rangle. \tag{D5}$$

Similarly, Eq. (D4) implies

$$\begin{aligned}\langle\sigma_{xxi}^X\rangle+\langle\sigma_{xxi}^Y\rangle+\langle\sigma_{xxi}^Z\rangle&=\langle\sigma_{yyi}^X\rangle+\langle\sigma_{yyi}^Y\rangle+\langle\sigma_{yyi}^Z\rangle\\&=\langle\sigma_{zzi}^X\rangle+\langle\sigma_{zzi}^Y\rangle+\langle\sigma_{zzi}^Z\rangle\equiv\langle\sigma_i^k\rangle\\&=3I\langle\sigma_m^k\rangle.\end{aligned}\tag{D6}$$

Hooke's law gives

$$\begin{cases}\langle\sigma^k\rangle=k\langle e^k\rangle\\ \langle\sigma_i^k\rangle=k_i\langle e_i^k\rangle\\ \langle\sigma_m^k\rangle=k_m\langle e_m^k\rangle\end{cases},\tag{D7}$$

where k, k_i and k_m are bulk moduli, $\langle e^k\rangle$, $\langle e_i^k\rangle$ and $\langle e_m^k\rangle$ are volume-averaged strains. These strains can also be related by an equation similar to Eq. (8)

$$\langle e^k\rangle=\phi\langle e_i^k\rangle+(1-\phi)\langle e_m^k\rangle.\tag{D8}$$

Using Eqs. (D5)–(D8), k can be expressed, after some manipulation, as

$$k=k_m+\frac{\phi(k_i-k_m)}{1+(1-\phi)\dfrac{k_i-k_m}{k_m+\dfrac{4}{3}\mu_m}},\tag{D9}$$

where μ_m is the shear modulus of the matrix phase.

Equation (36) can be derived using a similar technique. We can follow the same procedures as above but this time set $\langle\sigma_{xx}\rangle=-\langle\sigma_{yy}\rangle\equiv\langle\sigma^\mu\rangle$ and $\langle\sigma_{zz}\rangle=0$. The superscript μ is employed to indicate this shear loading condition. The following equations can be written:

$$\begin{cases}\langle\sigma_{xxm}^X\rangle=-\langle\sigma_{yym}^Y\rangle\equiv\langle\sigma_m^\mu\rangle=\dfrac{G^{\parallel}-G^{\perp}}{3}\langle\sigma^\mu\rangle\\ \langle\sigma_{xxi}^X\rangle+\langle\sigma_{xxi}^Y\rangle+\langle\sigma_{xxi}^Z\rangle=-(\langle\sigma_{yyi}^X\rangle+\langle\sigma_{yyi}^Y\rangle+\langle\sigma_{yyi}^Z\rangle)\equiv\langle\sigma_i^\mu\rangle=3J\langle\sigma_m^\mu\rangle\\ \langle\sigma^\mu\rangle=2\mu\langle e^\mu\rangle\\ \langle\sigma_i^\mu\rangle=2\mu_i\langle e_i^\mu\rangle\\ \langle\sigma_m^\mu\rangle=2\mu_m\langle e_m^\mu\rangle\\ \langle e^\mu\rangle=\phi\langle e_i^\mu\rangle+(1-\phi)\langle e_m^\mu\rangle\end{cases},\tag{D10}$$

where $\langle e^\mu\rangle$, $\langle e_i^\mu\rangle$ and $\langle e_m^\mu\rangle$ are volume-averaged strains under this condition. After some manipulation, the result is

$$\mu=\mu_m\left\{1+\frac{15(1-\nu_m)\left(\dfrac{\mu_i}{\mu_m}-1\right)\phi}{7-5\nu_m+2(4-5\nu_m)\left[\dfrac{\mu_i}{\mu_m}-\left(\dfrac{\mu_i}{\mu_m}-1\right)\phi\right]}\right\},\tag{D11}$$

where ν_m is Poisson's ratio of the matrix phase.

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